Structure-Property Relationship of Luminescent Ionic Polymers: Towards new Phosphors for Lighting Applications

Dissertation

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I played around with the flowers and the lighting,
so that was a good way to educate myself

Robert Mapplethorpe - Photographer
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Abstract

A series of 1-n-alkyl-3-vinylimidazolium bromide monomers with alkyl chain lengths of C₂-C₆ was synthesized and their photoinduced polymerization behavior investigated. It was found that a radical starter concentration of 2% leads to the maximum conversion rate. Longer alkyl chains lead to faster polymerization and higher conversion rates. It was also shown that the polymerization continues after the irradiation. All prepared polymers are transparent over a wide wavelength range and thermally stable up to 290 °C. Employing the salicylate anion as counter ion for the cationic polymer backbone highly enhances the photoluminescence visible by quantum yields up to 41%. The maximum emission wavelength depends on the chain length in the poly-1-n-alkyl-3-vinylimidazolium salicylates being shorter for intermediate chain lengths. The compounds are thermally stable up to 283 °C. Complexes with the constitution (IL-Cation)[Ln(Sal)₄] (Ln=Tb,La) were synthesized with monomeric and polymeric cations. It was possible to obtain single crystals with sufficient quality for structure determination by X-ray diffraction for (C₂C₁Im)₄[Ln₄Sal₁₂(H₂O)₂] and (C₄C₁Im)₄[Ln₄Sal₁₂(H₂O)₂]. The prepared compounds are excitable over a broad range of wavelengths ranging from 250 to 380 nm. The emission spectra of the lanthanum compounds show the autofluorescence of the salicylate only, while the emission spectra of the terbium compounds show strong green luminescence due to an energy transfer from the salicylate ligand to the optically active terbium center. The terbium compounds were found to show quantum yields ranging from 60% to as high as 92% for the monomeric cations and 41% to 69% for the polymeric cation containing compounds. The quantum yields in the analogue lanthanum compounds were found to range from 7%-28% in case of the monomeric cations and 18% to 47% for those with a cationic polymer backbone. The pure poly-1-n-alkyl-3-vinylimidazolium bromides were also doped with Eu³⁺ and Tb³⁺ to obtain red and green emitters. As expected, characteristic bands from f-f-transitions for both dopants could be observed. In addition a broad band spanning from 280 to 400 nm centered at 315 nm is visible which corresponds to the π→ π* transitions of the polymer. The ratio between the latter and the f-f-transitions decreases with higher doping concentrations. Time delayed luminescence spectroscopy showed that no energy transfer from the polymer backbone takes place for the terbium doped samples, but that it may occur for the europium doped samples. Quantum yields calculated for the europium doped samples were the range of 0.2-1.7% decreasing with higher doping concentration. Furthermore the emission color is tuneable from characteristic green Tb³⁺ or deep red Eu³⁺ emission to pure white emission. In between, several emission colors are realized via superposition of the respective lanthanide and polymer emission.
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1. Introduction and theoretical aspects

Lighting consumes about 20% of the energy produced worldwide.\textsuperscript{[1-3]} Fluorescent lamps and LED lighting with their high efficiency coefficient are major steps to decrease the power consumption. Due to their cost their main market are rich, developed countries while the old incandescent bulb that wastes 95% of its energy on heat and only 5% on actual lighting is still in widespread use. This necessitates further research into energy-efficient, low-cost, alternative light sources. Novel phosphors such as polymer-based functional layers may improve upon the energy requirements, prolong the design life or reduce the production costs.

The aim of this thesis is better to investigate new synthetic approaches towards the luminescent behavior of luminescent (rare-earth) doped ionic polymers. Especially in the field of material science, ionic liquids are established compounds to not only form new materials from them, but also to turn themselves into new functional materials. In this regard, ionic polymers have caught the attention of material scientists during the course of the last years.\textsuperscript{[4-5]} Therefore this thesis aims to design new phosphors for red, green, blue and white emission and reveal correlations between the chemical structure and the luminescent behavior.

Theoretical aspects

From ionic liquids to ionic polymers

Ionic liquids –ILs– are defined as salts with a melting point below 100 °C. In some cases they are apparent as liquids even at room temperature (RTILs).\textsuperscript{[6]} The first IL ever to be synthesized was ethylammonium nitrate in 1914 by Paul Walden, and exhibiting a melting point of 12 °C it was also the first synthesized RTIL.\textsuperscript{[7]} The tremendously growing interest in the research field of ionic liquids can be trailed by the number of scientific articles and patents containing the keyword “ionic liquid”: In 1999 a search in SciFinder resulted in 100 journal articles and 40 patents, while in 2006 these numbers reached 750 journal articles and 150 filed patents.\textsuperscript{[8]} At the present day (31/07/2015) a search request for the keyword “ionic liquids” results in 26851 hits.\textsuperscript{[8]}
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The unique attributes of ionic liquids are reflected in their physico-chemical properties such as an unusually negligible vapor pressure, a high ion conductivity and high chemical stability.[9] These properties can be tuned to derive certain characteristics, which render ILs as perfect candidates in several research fields as well as in industrial applications: The negligible vapor poses the opportunity to employ them as tailor made solvents, with drastically reduced toxicity due to a lower risk of contamination. For that reason, ILs have been discussed as “green solvents”.[10] Due to the research dedicated to ILs, their use already has exceeded the employment as solvent and even in industries, ionic liquids are already in daily use: Their application comprises the use as electrolyte in solar cells[11-12], as media in synthetic and catalytic chemistry[13-14] as well as the first commercial use of methylimidazolium chloride in the BASIL-process[15].

Cations employed in ILs are usually large and asymmetric, while the anions are usually weakly coordinating. The low effective charge, a high degree of charge delocalization, and sterically demanding ions lead to low lattice energies, which already can be thermally overcome at comparably low temperatures.[16] Some ions are depicted in figure 1.

![Figure 1: Typical cations (left) and anions (right) from the “ionic liquid toolbox”: Cations: 1-n-alkyl-3-n-alkylimidazolium-, tris-dimethylaminosulfonium,1-n-alkyl-4-methylpyridinium-, 1-n-alkyl-4-methylpyrrolidinium-, tetra-n-alkylammonium-; anions: -dicynamide, -bis-trifluormethanesulfonamide, hexafluorophosphate, -tetafluoroborate, -trifluormethanesulfonate.](image)

The broad variety of ions employed leads to a theoretical value of over $10^8$ synthesizable ILs[17] and therefore depicts another advantage of using ILs. As the nature of ions employed has a direct impact on the properties of the synthesized IL, these can be tuned to derive so called *tailor made ionic liquids*. These exactly have the desired properties regarding melting point, electric and ion conductivity, electrochemical window and the viscosity or the hydrophobicity/hydrophilicity.[6]

Regarding polymer chemistry, ILs are investigated as (co-)catalysts or initiators for the polymerization reactions, as polymer additives or in the development of functional polymers.[4, ...
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However less focus has been laid on introducing polymerizable groups directly into ionic liquids. Conventional macromolecular polymers (e.g. polyethylene (PE), polypropylene (PP), polystyrole (PS) or polymethylmethacrylate (PMMA)) exhibit excellent mechanical strength and good processability. On the other hand, ILs comprise excellent properties regarding electrochemical applications, as well as their capability to be tuned for a specific task. Therefore, researchers started to combine the advantages of polymers with these of ionic liquids modifying the anion or cation by introducing e.g. unsaturated carbon side chains leading to a new class of compounds: polymerizable ionic liquids. 

Through different polymerization processes these can be turned into ionic polymers (IP) possessing the properties of both substance classes. Chemically, ionic polymers can be seen as polymers, but with a repeating cationic or anionic electrolyte group. The border to known ionic polymers such as Nafion or ion exchange resins, is shallow, and relies of the definitions that common used ions for ILs are altered by the introduction of a polymerizable group. Typically employed anions and cations for synthesizing monomers of IPs are shown in figure 2.

![Typical cations (left) and anions (right) for the monomers of ionic polymers. Cations: terminally acryloylesterificatedimidazolium-, Diallyldimethylanmonium-, 1-n-alkyl-3-vinylimidazolium;anions: -vinylsulfate, -acrylate.](image)

Comparable to ionic liquids the ions for building up the monomers of the IPs can be seen as a toolbox for the synthesis of desired materials. They can be built up using either a polymerizable
anionic or cationic part which after polymerization results in homopolymeric anionic or cationic polymer strains (see scheme 1). They can also consist of a polymerizable anion and cation which either leads to cationic and anionic polymer chains existing beside each other. Depending of their polymerization tendency, they can also form three-dimensional networks with mixed anionic and cationic moieties. The typical polymerization reaction used is the free radical polymerization.\textsuperscript{[25]}\textsuperscript{[26]} A thermal AIBN or photolabile radical initiator leads to the initial formation of radicals, which then start the building up the polymer chains (scheme 1).

![Scheme 1: Free radical polymerization of 1-ethyl-3-vinylimidazoliumbromide using the thermal radical initiator AIBN. After the dissipation of AIBN into the starting radicals, these attack the vinyl double bond to form another radical, which attacks the next vinyl bond. This process leads to a cationic polymer.](image)

Physico-chemical properties of the resulting IPs e.g. solubility can be tuned depending on the cations or anions being employed. This is especially interesting as a lot of functional materials nowadays are processed using different coating techniques such as spin or dip coating, which often recommends the materials to be soluble in a certain solvent.\textsuperscript{[27]} The exchange of e.g. the anion can either be conducted before or after the polymerization which is described in recent literature.\textsuperscript{[28]}

**Luminescence**

Luminescence is defined as the emission of light by returning from an electronic excited state to a state of lower energy.\textsuperscript{[29]} Different types of luminescence are known depending on the question, how the excited electronic state is reached: Examples include chemoluminescence (chemical
energy is used to reach the excited state), triboluminescence which uses the energy of friction, electroluminescence, where the electronic states are excited by electricity or photoluminescence, where a photon of suitable energy excite.\cite{29} Luminescence was first observed in 1602 by the Italian alchemist Vincenzo Casciarolo when he was trying to turn humble materials into gold.\cite{30} He accidentally produced a piece of barite which was observed to “imbibe the sun’s light and emit it afterwards by glowing in the dark”. For organic and closed-shell compounds, the description of the occurring processes can be described using so-called Jablonski diagrams (figure 3)\cite{31}, which however only illustrates the processes of luminescence, rather than to be used for the luminescent behavior of inorganic compounds.

![Jablonski diagram](image)

Figure 3: Jablonski diagram. Radiative processes are designated with straight lines; non-radiative processes are indicated by dashed lines.

After the excitation of an electron, which usually takes about $10^{-15}$ seconds, and always starts from the lowest vibrational energy level of the ground state, different processes (may) take place. The phenomenon of radiative relaxations (luminescence) can be subdivided into two other phenomena which depend on the passed levels while returning to an electronic state of lower
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energy: These can be reached by the transition of a singlet state to another \((S_1 \rightarrow S_0)\). Typically this phenomenon occurs very fast (in the range of nanoseconds) as these transitions do not involve the change of a spin multiplicity – the material only emits light as long as it is excited. These transitions are called fluorescence. In contrary stands the possibility, that the excited electron changes its spin parity into another state \((S_1 \rightarrow T_1)\) and then returns to the ground singlet state. Due to the spin selection rules, these transitions are forbidden and therefore demand time to occur. This leads to the phenomenon of phosphorescence, with emission durations in the range of milliseconds to hours and longer. According to Kasha’s rule\(^{[32]}\), radiative processes always take place from the lowest excited state of a given multiplicity \((S_1, T_1)\). Beside these radiative processes, also non radiative processes occur which are accompanied by the thermal loss of energy. Firstly there is the internal conversion which takes place either in (from a higher vibronic level to a lower one) or in between electronic levels. In contrary to the internal conversion, where the spin multiplicity remains the same, stands the intersystem crossing including the change of the given spin multiplicity e.g. to a triplet state. With some exceptions, that will not be discussed here, the energy of the emitted photons is lower than the energy needed for the excitation. This energy difference is the so called Stokes Shift (figure 4).

For further understanding the mechanism of luminescence, especially of inorganic compounds, configurational coordinate diagrams are used (figure 4). For visual reasons only two vibronic levels are shown. According to the Franck-Condon principle\(^{[33]}\) as well as the Born-Oppenheimer approximation\(^{[34]}\), electrons move much faster than nuclei due to their weight. This is why electronic transitions are to be assigned vertical in these diagrams.

The emission characteristics (e.g. emission bands) strongly depend of the nature of the material excited. These occur from multiple, non resolved vibrational energy bands typically leading to broad emission bands, while the emission from distinct levels leads to sharp emission bands. Transition metal and \(p\)-block element compounds typically show few broad emission bands, while lanthanides show more, but distinct and sharp emission bands.\(^{[35]}\)

For transition metal compounds the appearance of these broad bands can be assigned to the interaction between the \(d\)-orbitals of the optical center and the ligands. Due to the proximity of those to the central atom these can disturb each other (ligand-metal charge transfer (LMCT) or metal-ligand charge transfer (MLCT)) leading to numerous vibronic levels from which emission
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can take place. In the emission spectra of these compounds this overlay of all transitions is visible as broad bands.\textsuperscript{[35]}

Figure 4: Configurational coordinative diagram illustrating the appearance of broad band in the emission and excitation spectra of e.g. transition metal compounds.

Electronic transitions can either be allowed or forbidden. Overall the momentum of the system has to be conserved, which comes down to the following factors:

One of these selection rules is the spin selection rule\textsuperscript{[36]} mentioned above
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\[ \Delta S = 0 \]  \hspace{1cm} (1)

For a single electron, the change of the angular momentum must not change by a value other than 1

\[ \Delta l = \pm 1 \]  \hspace{1cm} (2)

Regarding these transition rules, the electronic dipole-dipole \( ^2F_{5/2} \rightarrow ^2D_{3/2} \) transition in \( \text{Ce}^{3+} \) is allowed, while the transition \( ^7F_0 \rightarrow ^5D_0 \) in \( \text{Eu}^{3+} \) is forbidden.

For more than 1 electron, the spin orbit coupling has to been taken into account resulting in

\[ \Delta J = 0, \pm 1 \text{ (but } J \neq 0 \) \]  \hspace{1cm} (3)

\[ \Delta L = 0, \pm 1 \text{ (but } L \neq 0 \) \]  \hspace{1cm} (4)

Another important selection rule is the La Porte rule\(^{[37]}\): It considers the parity of a given system indicated by the appearance of an inversion center. For allowed transitions, the parity has to change during an electronic transition

Allowed transitions: \( g \rightarrow u, u \rightarrow g \)

Forbidden transitions: \( g \rightarrow g, u \rightarrow u \)

A good example for this selection rule is given by the luminescence of complexes with manganese as the optical active center. For \( \text{Mn}^{2+} \) in a tetrahedral environment, the electronic transitions are allowed as the parity does change; while for octahedral surrounded \( \text{Mn}^{2+} \) (which has an inversion center) the parity does not change. This behavior can easily be observed by the naked eye by comparing samples of both compound classes under broad UV-Irradiation, where the tetrahedral surrounded \( \text{Mn}^{2+} \) exhibits a much brighter green luminescence compared to the red emission of the octahedral coordinated manganese.\(^{[38]}\)

Moving from transition metal- and \( p \)-block compounds to lanthanides emission characteristics change. The diffuse \( f \)-orbitals of the lanthanides are shielded by the outer \( 4d \) and \( 5p \)-levels.\(^{[39]}\) Chemically this induces much less interactions of the \( f \)-orbitals regarding the binding situation and thus also the excitation and emission behavior.\(^{[40]}\) Regarding configurational coordinative diagrams the parabola of the excited state shows a much smaller shift compared to the ground
state. These facts are expressed by rather narrow excitation and emission lines and a much smaller Stokes-Shift. Indeed in some cases even a zero-phonon line becomes visible, where the excitation and emission energies are the same. As $f$-$f$ transitions are parity forbidden, and $f$-$d$ transition are seldom/rarely observed, the cross section of lanthanides for excitation is rather small, and a much weaker emission is observed within these compared to e.g. transition metal compounds. [39] The emission characteristics do not or only slightly change when putting Ln$^{3+}$ ions into different environments. Thus it was possible by Dieke to establish a diagram, where all discrete energy levels could be depicted. [41] It is based on measurements, and comprises the energy levels from the IR to the UV region. Later it was extended for the VUV region by Meijerink et al. (figure 5). [42]

Figure 5: Extended Dieke-diagram. Levels, which are prone for emission, are illustrated in blue. [43]

Despite the observed emission characteristics of the lanthanide ions, sometimes LMCT-lines which are apparent as broad bands can be observed in the emission spectra of e.g. Eu$^{3+}$ compounds. These are especially expressed for Eu$^{3+}$ for example with oxygen ($O^{2-} + Eu^{3+} \rightarrow O^{-}$.
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+ Eu$^{3+}$). Indeed Eu$^{3+}$ is a special case regarding another useful property of the emission characteristics: the intensity ratio of the hypersensitive electric-dipole transition $^5$D$_0$ → $^7$F$_2$ (610 nm) and magnetic dipole $^5$D$_0$ → $^7$F$_1$ transition (590 nm) gives the asymmetry ratio, which can be used to analyze the local environment of the europium ion. E.g. a much more intense $^5$D$_0$ → $^7$F$_2$ emission suggests that the Eu$^{3+}$ ion is in an (highly) asymmetric environment.$^{[44]}$ The answer to the question behind this behavior is again found in the LaPorte$^{[37]}$ selection rule. An inversion center means a much higher symmetry around the optical active center. Thus follows, that the higher the symmetry, the lower is the intensity of the transition.

Anyway the poor absorption cross section of the lanthanides can be overcome by the use of sensitizers: a substance with a high absorption cross-section, which efficiently transfers the absorbed energy to the lanthanide ion for emission.$^{[45]}$ As sensitizers, different lanthanide ions, such as Ce$^{3+}$, broad band semiconductors, organic ligands and dyes can be used. Different types of sensitization have to be distinguished:

![Figure 6: Different mechanisms of sensitisation. Straight lines indicate radiative processes, while dashed lines indicate non-radiative processes. Adapted from$^{[43]}$.](image-url)
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The three latter cases are often observed in inorganic materials, while cross relaxation and phonon assisted transfer usually transfer less energy. The first two mechanisms are also observed when using organic ligands as sensitizers. Non-radiative resonant energy transfer, e.g. the Förster resonance energy transfer (FRET\textsuperscript{46}) occurs when a sensitizer is in suitable proximity to the acceptor, and thus transferring its energy via resonance without the sensitizer emitting. A suitable ligand with a high absorption cross section (e.g. salicylate) is excited and while emitting efficiently transfers the photon energy to the optically active lanthanide ion. The less emission of the sensitizer itself is monitored, the more efficient is the energy transfer.

Energy transfer can not only be beneficial for the emission behavior: It can also decrease the emission intensity - so called quenching occurs.\textsuperscript{47} Different mechanisms for fluorescence quenching are known. One of them is vibrational quenching where the energy of the photons is subsequently absorbed in the infrared of e.g. a host lattice. Especially the $\nu_{\text{OH}}$ vibrations are prone to this behavior due to their relative high vibrational energy. Another quenching mechanism is the above described intersystem crossing, which especially occurs for heavy atoms and oxygen: An excited singlet state becomes an excited triplet state, which is then quenched to the ground state or likely to return to the ground state through a non-radiative decay.\textsuperscript{40} The most important quenching mechanism in lanthanide chemistry is the concentration quenching caused by cross-relaxation. A high concentration of lanthanides in a given host lattice causes a close proximity of Ln\textsuperscript{3+} ions and thus to pronounced cross relaxation. As a non-radiative process, this consumes energy which is not available for photon emission anymore. This is why doping concentrations of lanthanides in phosphors is usually at a level of $\sim$1%.

The efficiency of a given emitting material can be expressed with the so called quantum yield (QY).

\[
\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \tag{5}
\]

Without regard to special effects, such as quantum cutting, which will not be discussed here, the maximum value cannot exceed 1, which equals a quantum yield of 100%.  

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1. Introduction and theoretical aspects

Phosphors and lighting

The task of reducing energy consumption is becoming more and more crucial. Current estimations attribute 15-25% of the energy consumption in the world to lightning devices.\textsuperscript{[1, 3, 48]} Compact fluorescent lamps, CFLs, and light emitting diodes, LEDs, offer energy efficient alternatives to incandescent lamps, which are currently being phased out around the world: The European Union has already banned the production and distribution of these, while the USA and China are both to follow suit by 2014/2016.\textsuperscript{[49–50]} The demand of reducing the energy consumed for lighting results in the need for phosphors with high quantum yields and low production costs. The need for these phosphors not only arises for lighting purposes but also for many electrical devices and medicinal equipment.

![Image of various lighting applications](image)

Figure 7: The need for phosphors ranges from applications in the X-ray region up to the infrared region.
Figure 7 illustrates some of the applications for phosphors. Their use ranges from high energy emitting phosphors e.g. in PET-machines over UV/Vis applications such as solar cells up to IR-applications like bio-imaging.\[^{51}\] Especially interesting with respect to this thesis is the application of phosphors in the UV and Vis range.

Figure 8 shows the scheme of a CFL. Since the phase-out of the traditional light bulb it was the first device to be employed for energy saving. It consists of an evacuated glass container which contains a small amount of mercury (usually ~2 mg per lamp) and grains of different phosphors.

![Schematic of a CFL](image)

**Figure 8: Schematic of a CFL.**\[^{43}\]

After the ignition of the lamp, the mercury evaporates, and can then be excited electrically. Now the typical Hg-emission in the UV region takes place and the phosphor grains on the inner surface of the glass container convert the invisible UV-light into visible light. This happens by additional color mixing of the three basic colors red, green and blue, leading to “white light”. As red phosphors, mainly hexagonal aluminates of the general formula MA\(_{12}\)O\(_{19}\) (M=Ca, Sr, Ba) doped with Eu\(^{2+}\) are used. These are usually modified by the addition of Mg into the host lattice. As the emission of Hg\(^{+}\) with a high intensity at 254 nm overlaps with the 4f-5d transitions of the Eu\(^{2+}\), a broad emission band centered at around 450 nm is observed. Responsible for the green emission is Tb\(^{3+}\), with its most intense \(^5\)D\(_3\) \(\rightarrow\) \(^7\)F\(_1\) emission at around 542 nm. High emission intensities from the \(^5\)D\(_3\) levels (resulting in emissions of 381, 431 and 435 nm) can be overcome by higher doping concentrations of Tb (~35%) thus leading to concentration quenching. The most common employed phosphor is Ce\(_{0.65}\)Mg\(_{0.11}\)Al\(_{11}\)O\(_{19}\):Tb\(_{0.35}\), where Ce\(^{3+}\) serves as a sensitizer.
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with its allowed $4f-5d$ transitions. Red phosphors used in CFLs are based on the characteristic red emission of Eu$^{3+}$ in Y$_2$O$_3$:Eu. Here the mercury emission excites into a CT band of Eu$^{3+}$, followed by a LMCT. These levels are subsequently depopulated by relaxation through various levels until the $^5D_0$ level is reached. This shows the typical Eu$^{3+}$ emissions $^5D_0 \rightarrow ^7F_{0-4}$. Compared to incandescent lamps, CFLs can emit up to 80% of the energy consumed in the form of light. Although being efficient, the toxicity of mercury poses an environmental threat. This concerns not only the manufacturing of the lamp, but also the disposal of them.\textsuperscript{[52]}

Another approach to environmental friendly lighting is the use of LEDs. (O)LEDs are probably the most promising alternative for lighting in the future regarding they are environmental friendly and have a long lifetime (up to 100,000 h). In contrast to other lighting methods, LEDs rely on the recombination in the p-n-junction of a semiconductor (figure 9).

![Figure 9: Schematic of a LED.\textsuperscript{[43]}](image)

When a suitable electric current is applied to the semiconductor, electrons may recombine in the junction and the excess energy is emitted in the form of photons. This phenomenon is a form of electroluminescence. It was first observed by Round in 1907 on a crystal of silicon carbide.\textsuperscript{[53]} The first LED then was reported in 1927 by Oleg Losev.\textsuperscript{[54]} From this point it took more than 30 years until the first practical use for LEDs was investigated by using an IR emitting gallium arsenide LEDs for communication across short distances. From thereon more and more semiconductors were investigated and after bright blue emitting LEDs based on InGaN by Shuji
Nakamura in 1994\textsuperscript{[55]}, research started to focus on LEDs as lighting devices. Again the challenge was to obtain white emission. The most promising approach to this was the idea of mixing blue and yellow light, which as complementary mix up to white emission. The most common employed phosphor in this matter is cerium doped YAG (Y$_3$Al$_5$O$_{12}$:Ce). For his invention, Shuji Nakamura was awarded the millennium technology prize in 2006.\textsuperscript{[56]} Still some problems have to be overcome for the use of LEDs in household lighting. The emission from the downconverted and mixed blue light usually leads to cold white light which is not attributed to be comfortable to the human eye. To overcome this, red LED phosphors such as AlGaAs are added. Another important factor are the costs in producing efficient LEDs. Due to the growing research in this field, this factor could be overcome soon, and therefore rendering LEDs the most suitable lighting devices of the 21\textsuperscript{st} century.

**Luminescent materials from and in ionic liquids and polymers**

Regarding ionic liquid chemistry, luminescent materials can either be obtained from ionic liquids, or the ionic liquid itself can be the material. Our laboratory successfully optimized a method to obtain nanocrystalline luminescent materials: Through a microwave reaction, rare-earth acetates could be decomposed in fluorine rich ionic liquids such as tetrafluoroborates or hexafluorophosphates. This yields in phase pure nanocrystalline rare-earth fluorides with quantum yields up to 193\% (quantum cutting).\textsuperscript{[57-59]} The IL actually acts as a solvent, a reactant and a stabilizer for the nanocrystalline materials formed. Another approach involves subliming rare earth and transition metal compounds directly into an IL via PVD, which is possible due to the negligible vapour pressure of ILs.\textsuperscript{[60-61]} As also shown by our group it is possible to endow ILs with luminescent properties by the inclusion of the lanthanide or transition metal ion in the form of a complex anion, which renders the ionic liquid itself the phosphor.\textsuperscript{[62-66]}

A proof-of-concept has been given for luminescent nanoparticles in PILs: Using the above described microwave reaction in a polymerizable ionic liquid (DADMABF$_4$), europium and terbium acetate were transformed into the respective phase pure rare earth fluorides leading to nanoparticles. In a following reaction step, the ionic liquid was polymerized using a UV lamp, leading to a strong luminescent inorganic-organic composite with strong luminescent properties of the employed rare earth ion.\textsuperscript{[67]}
2. Physicochemical properties of ionic polymers

General aspects

This thesis deals with new rare earth and transition metal doped as well as new ionic polymers based on salicylate anions. Therefore it is crucial to understand the physico-chemical properties of these polymeric compounds. This includes spectroscopic characterization and thermal as well as their polymerization behavior. Especially for the use in lighting devices there are certain requirements to be fulfilled by a compound, such as optical transparency. Two monomer classes for the synthesis of IPs have been the focus of studies over the course of this thesis: diallyldimethylammonium (DADMA) and Vinylimidazolium (Vim) based ones (scheme 3). In contrary to the Vim based monomers, DADMACl is commercially available. The syntheses for C₂⁻ and C₄VimBr are described in literature and have been adapted and refined for the C₃,₅,₆-moieties.

![Scheme 2: General synthesis procedure for the employed monomers.](image)

The reaction is a SN₂ reaction conducted in acetonitrile (scheme 2). C₂VimBr and C₄VimBr were obtained as white crystalline powders after recrystallisation from ethyl acetate in yields of ~60%. C₃,₅,₆VimBr were obtained in lower yields (45-55%) as viscous, pale yellow liquids. Recrystallisation from ethyl acetate has not been successful for these. However, contrary to C₆VimBr, the C₃ and C₅ moieties spontaneously crystallized after being in storage for several weeks. The substances all were fully characterized by means of ¹³C and ¹H-NMR, IR, DSC and thermogravimetric methods. The substances show different hygroscopic behavior, which is being more pronounced for shorter alkyl length than for longer ones: While C₂VimBr tends to stay a crystalline powder only for several minutes and then being liquid, the C₄VimBr remains a solid for up to ~2 hours. All compounds were stored in a glovebox after synthesis and handled under inert atmosphere for following manipulation.
2. Physicochemical properties of ionic polymers

As the Vim based ionic polymers bear an aromatic moiety, which is absent in DADMA, it is possible to gauge this effect on the resulting polymers and or luminescent materials. An overview over the used substances as well as their synthesis procedure is depicted below.

Scheme 3: Different polymer backbones either derived from vinylimidazolium (top) and DADMA based polymers

The polymerization of all vinylimidazolium compounds was conducted in degassed chloroform using AIBN as a thermal radical starter, and successfully repeated several times with yields of ~97% and conversion rates of 96-99% (this point will be further discussed below). After work up and drying all polymers are apparent as a transparent, slightly yellow film. Prolonged heating leads to more yellowish polymers probably due to decomposition of the vinylimidazolium moiety. For DADMACl another polymerization procedure was chosen: K₂S₂O₈ was employed as a thermal radical starter and directly poured into the commercially available aqueous DADMACl solution to obtain conversion rates of 97% after subsequent polymerization, due to the fact that the first one only resulted in a polymer conversation rate of ~87%. As for the monomers, all polymers show distinct hygroscopic behaviour and were stored and handled in inert atmosphere.
2. Physicochemical properties of ionic polymers

Polymerization kinetics of 1-n-alkyl-3vinylimidazolium bromides

A common characteristic for the polymerization behavior is, that the conversion rate can easily be determined by comparing the NMR spectra and integrating specific signals. This shall be discussed on the NMR spectra of the C₂-moieties

![NMR spectra comparison](image)

**Figure 10: Comparison of ¹H-spectra of monomeric and polymeric C₂VimBr.**

Figure 10 shows the typical ¹H-NMR spectra of monomeric and polymeric C₂VimBr. Especially important are the signals between 5 ppm and 7 ppm (two doublets of doublets and a multiplet), arising from the vinyl protons and the triplet at 1.45 ppm arising from the terminal methyl group in the polymer backbone. In a fully polymerized sample, these signals of the vinyl group would no longer be apparent. However as the polymerization reaction rarely reaches completion, the signals from the vinyl group still are apparent even though barely visible. As the hybridization of the vinyl protons changes from \(sp^2\) to \(sp^3\) during the polymerization, the signals of the polymer chain are now upfield shifted.\[^{[68]}\] Due to the different lengths of the polymer chains formed, a lot
2. Physicochemical properties of ionic polymers

of species are apparent which cannot be distinguished anymore in the spectra, and thus the signals of all protons are now broadened.

As the signal intensity of the vinyl protons are directly related to the polymerization degree, it can be calculated

\[
\text{Polymerization degree} = \frac{f_{\text{residual vinyl proton}}}{f_{\text{reference protons}}} \frac{f_{\text{involved protons}}}{f_{\text{involved protons}}} (6)
\]

A polymerization degree of one equals 100%.

However this procedure becomes always more inaccurate the higher the polymerization degree is. The protons, which are directly attached to the imidazolium core are very prone to undergo radical reactions and can therefore not be used as reference protons. As said above, the signals of the former vinyl group are shifted down to lower ppm values to the region of the methylene group(s) and the terminal methyl group. The protons of the latter one are the most acceptable to distinguish the polymerization degree. A higher polymerization degree therefore entails an increasing interference signal from within the methyl group. Thus the measurement error increases proportionally to the polymerization degree. The error value cannot be assigned quantitative, but still, and this is of interest, the polymerization behavior and tendencies can be attributed. As experienced the signals of the vinyl group shift by up to 0.15 ppm in some cases in the course of the reaction. This could be attributed to interactions of the monomers and the polymers, therefore changing the shielding of the protons. This further complicates quantification, due to the fact, that the integrals cannot always be assigned to the same ppm values.

The polymerization behavior of the used monomers is crucial to understand the forming of the matrix used in further doping experiments. It is not the easiest task to determine the ideal concentration of a free radical starter for a polymerization reaction. If not enough of initiator molecules are available, the reaction will be terminated, as an insufficient amount of radicals is available to sustain the polymerization. On the other side, if too many radicals are apparent, the recombination of radicals is dominant and thus the reaction also terminated. Usually the ideal initiator concentration is 1-4% depending on the monomer employed. As with most chemical reactions, also polymerization reactions usually have their highest conversion rates in the
2. *Physicochemical properties of ionic polymers*

beginning of the reaction and then asymptotically converge to the final yield. This also has been reported during the investigation of the polymerization kinetics of tributylammoniumacrylate via UV-Vis spectroscopy.\(^69\) The polymerization of acrylate monomers is achieved easily, as its double bond is activated through the terminal oxygen and the bond delocalization. However this is not the case for the vinylimidazolium monomers, which are therefore harder to polymerize, rendering UV-Vis spectroscopy useless to investigate their polymerization kinetics. Using NMR to understand this for a thermally initiated reaction is also difficult, as the timescale for the polymerization reaction is quite short, especially in the beginning of the reaction. An alternative is to photochemically initiate the reaction, as the light intensity, and thus the speed of the reaction can be adjusted to track it continuously on the one hand, but does not require weeks for the experiments. This also has the advantage that depending on the wavelength, either the monomers double bond (\(\lambda_{\text{abs,max}}=254\text{nm}\)) can be broken, or a photolabile initiator can be employed.

![UV-Vis absorption spectrum of Michler's Keton](image)

**Figure 11:** UV-Vis absorption spectrum of Michler’s Keton.\(^70\)

There are a lot of photolabile radical initiators available, decomposing when irradiated with a certain wavelength. It was decided to use Michler’s Keton with an absorption maximum at 366 nm (figure 11). This led to the employment of UV-B fluorescent lamps, and has the advantage,
2. Physicochemical properties of ionic polymers

that the monomer itself does not absorb (see optical properties (section below)), giving a detailed insight of the polymerization kinetics, which then only depends on the monomer employed and the initiator concentration.

![Figure 12: Michler’s Ketone as a radical starter: After the irradiation the keto-funtion in the excited molecule homolytically dissociates to form the initial radical, which then forms the starting radical in the monomer.]

To examine the polymerization kinetics, different experiments have been conducted. First, the chain length in the monomer was altered from C₂ to C₆ to understand the influence of the side chain. Imidazolium based ILs consist of the positive charged imidazolium core which is quite hydrophilic and an alkyl chain which poses as a hydrophobic part. The hydrophilic/hydrophobic properties of the IL depend on the chain length. On the other hand, a longer side chain possesses a higher sterical demand. Both should have an influence on the polymerization behavior. Secondly, the initiator concentration has been altered: Samples containing no Michler’s Keton have been investigated, and then the concentration has been increased to 1, 2 and finally 3 mol%. This should prove the thesis, that the ideal concentration is about 2%, while higher and lower concentrations should lead to a termination of the reaction at a certain point. The idea that the polymerization reaction should be swift in the beginning, and then slow down led to the following experimental procedure: After dissolving 200 mg of the respective monomers in degassed, deuterated chloroform the samples were irradiated in the UV reactor with a power of ~84 Wm⁻². The degassing of the solvent is crucial not only to prevent side reactions but also highly toxic phosgene is known to originate from dissolved oxygen under UV-irradiation.
2. Physicochemical properties of ionic polymers

Samples without the addition of Michler’s Keton were then investigated by NMR-spectroscopy to determine the polymerization degree after 20, 60, 120 and 240 minutes. For samples containing the radical initiator, NMR spectra were taken after 15, 30, 60, 90, 180, 360 and 720 minutes. Especially in the beginning of the irradiation, it is useless to conduct more measurements, as the polymerization runs faster than measurements can be taken. The amount of the solution was chosen to have a sufficient amount of samples for all NMR analyses. NMR spectra were also taken as fast as possible and off all applicable samples at a time to avoid further error sources, such as autopolymerization due to persistent radicals. From past research it is known, that ILs could have the ability to stabilize radicals.\textsuperscript{[71]} To investigate this, samples were also left in the dark after irradiation and NMR spectra taken again after a longer period of time to investigate the possibility of autopolymerization.

![View inside the employed UV-reactor loaded with samples prior to irradiation.](image)

Figure 13: View inside the employed UV-reactor loaded with samples prior to irradiation.
2. Physicochemical properties of ionic polymers

Influence of the radical starter concentration and the chain length on the polymerization behaviour after a given irradiation time

Before discussing the dependency of the chain length, the polymerization behaviors with different amounts of the radical starter have to be elucidated. Figure 14 shows this for $C_{2-6}$VimBr.

![Figure 14: Influence of the radical starter concentration on the polymerization behavior of $C_{2-6}$VimBr after an irradiation time of 3 hours (4 hours for the 0% samples).](image)

As seen, with no addition of Michler’s ketone, the polymerization degree is very low (<15%) for all samples. A polymerization still occurs, because the lamps employed emit a small amount of light (0.67% of their actual power)\cite{72} in the range of 254 nm, where the double bond absorbs and thus initiates polymerization. The polymerization degree rises with increasing chain length finding its maximum at the $C_6$-moiety (15%). When Employing 1% of Michler’s ketone a significant increased polymerization degree is observed (up to 51% for $C_6$VimBr). However the polymerization degree for the $C_2$ and $C_3$ moiety remains the same if further Michler’s ketone is added, and no trend is visible. This behaves different for the longer chain lengths: The polymerization degree is at its maximum at a concentration of 2% Michler’s ketone and then again decreases when more radical starter is added. The polymerization behavior is also dependent on the irradiation time and the chain length, as seen in figure 14.
2. Physicochemical properties of ionic polymers

Table 1 shows a summary of the obtained values for all samples:

Table 1: Influence of the radical starter concentration on the polymerization degree of C2-VimBr after an irradiation time of 3 hours (4 hours for the 0% samples).

<table>
<thead>
<tr>
<th>Radical starter concentration</th>
<th>C2VimBr</th>
<th>C3VimBr</th>
<th>C4VimBr</th>
<th>C5VimBr</th>
<th>C6VimBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>2</td>
<td>7</td>
<td>6</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>1%</td>
<td>18</td>
<td>19</td>
<td>37</td>
<td>47</td>
<td>51</td>
</tr>
<tr>
<td>2%</td>
<td>8</td>
<td>16</td>
<td>52</td>
<td>58</td>
<td>75</td>
</tr>
<tr>
<td>3%</td>
<td>9</td>
<td>16</td>
<td>36</td>
<td>49</td>
<td>38</td>
</tr>
</tbody>
</table>

These observations are in agreement with the above mentioned thesis: Without the addition of any radical starter, the reaction also occurs as a by-product and in (very) low yields. The addition of 1% Michler’s Ketone generates a sufficient amount of radicals to drastically enhance the reaction, but not enough to completely polymerize the monomers. As soon as 2% of Michler’s ketone are used, the polymerization results in better yields, but an addition of 3% probably generates too much radicals, the recombination of which leads to the termination of the reaction before the polymerization is completed. Hence it can be said, that 2% is the ideal radical starter concentration for this reaction. This is also resembled by the thermally initiated polymerization of these monomers: literature also describes 2% for the ideal radical starter concentration for the polymerization of vinylimidazolium compounds.\(^{[28]}\) As for doping experiments, larger amounts of polymers are needed, these were all synthesized by the employment of 2% AIBN (Azo-bis-isobutyronitrile) in a thermally initiated polymerization.

Reason for the incomplete polymerization will be discussed in a section below.

**Influence of the chain length and the irradiation time on the polymerization behavior**

The second and third factor influencing the polymerization behavior of a given monomer, is the irradiation time and the chain length. As seen in the previous section, 2% of Michler’s Keton is the ideal concentration for these experiments. Thus, only the 2% samples will be discussed here, because the tendencies for the 1% and 3 radical starter containing samples are the same. Graphs for all other samples can be found in the appendix. Figure 15 shows the polymerization degree of C2-C6VimBr until irradiated for 6 hours.
As expected, the reaction occurs fast during the first 30 minutes and continues until irradiation for 3 hours. After this, the reaction runs slower and reaches a plateau approaching a certain degree of polymerization. It can be seen clearly that the chain length and the irradiation time both have a major impact on the polymerization behavior: The first measurement after 15 minutes already shows a clear trend that the polymerization degree is higher, the longer the alkyl chain on the imidazolium backbone is. While the C_2 species shows a polymerization degree of only 2% the other moieties show higher polymerization degrees up to 15% already at C_6. This trend continues until 1.5 hours of irradiation, where the C_2 moiety shows a polymerization degree of 5% and the C_6 moiety reaches 28%. Over the next 1.5 hours, the C_{4-6} species unexpectedly show a much higher polymerization degree (52 - 75%), while not much changes for the shorter alkyl chains (C_2: 8%; C_3 16%). Between this point and the end the of the
irradiation time, not much higher polymerization degrees are observed. All values for the measurement points are shown in table 2.

Table 2: Polymerization degree gain per hour for the different irradiation steps.

<table>
<thead>
<tr>
<th>Irradiation time in h</th>
<th>C₂VimBr</th>
<th>C₃VimBr</th>
<th>C₄VimBr</th>
<th>C₅VimBr</th>
<th>C₆VimBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>8</td>
<td>17</td>
<td>25</td>
<td>36</td>
<td>60</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>28</td>
<td>8</td>
</tr>
<tr>
<td>1.0</td>
<td>5</td>
<td>10</td>
<td>13</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>1</td>
<td>9</td>
<td>11</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>1.5</td>
<td>5</td>
<td>13</td>
<td>17</td>
<td>26</td>
<td>28</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>1</td>
<td>5</td>
<td>7</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>3.0</td>
<td>8</td>
<td>16</td>
<td>52</td>
<td>58</td>
<td>75</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>2</td>
<td>2</td>
<td>23</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>6.0</td>
<td>9</td>
<td>19</td>
<td>53</td>
<td>64</td>
<td>78</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>12.0</td>
<td>48</td>
<td>85</td>
<td>55</td>
<td>85</td>
<td>91</td>
</tr>
<tr>
<td>Polymerization degree gain in Δ%/h</td>
<td>7</td>
<td>11</td>
<td>0</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

In order to react, two radicals have to hit each other to be able to recombine and thus form the polymer chain. This is directly related to the collision cross section of a given molecule, which
2. Physicochemical properties of ionic polymers

itself depends on its size. As shorter alkyl chains have a lower steric demand, the polymerization was expected to proceed much faster with a higher polymerization degree. The obtained results are in contrast to the expected behavior: This can be attributed to two factors: First, a longer side chain induces a bigger inductive effect into the aromatic imidazolium core. The resulting higher effective charge leads to a better stabilization of the radicals, which therefore have a higher chance to react. In order to react, two radicals have to hit each other. A longer alkyl chain length could lead to the formation of micelles or micelle like aggregates, thus restraining the monomers in a way that the distance of the vinyl double bonds decreases, and therefore making it easier to react (figure 16) which has been previously reported in literature.\textsuperscript{73-74} Due to the stronger inductive effect of longer alkyl chains, the positive charge of the imidazolium core is lowered, which makes the polymerization even easier to proceed. Also a longer alkyl chain means a higher degree of hydrophobicity. As known from literature, ILs have the ability to form hydrophilic and hydrophobic domains.\textsuperscript{75-77}

![Figure 16: Proposed arrangement to micelle like aggregates for the longer alkyl chain bearing 1-n-alkyl-vinylimidazolium bromides. As the monomers are restrained through the aggregation, the vinyl bond distances are decreased, and the polymerization processes easier.](image)

**Autopolymerization after irradiation**

From former work in our group\textsuperscript{71} it is indicated, that Ionic liquids could have the ability to stabilize radicals for hours and days. Therefore, measurements were also taken after keeping the
samples in the dark for 15 hours after an irradiation time of 6 hours, followed by another irradiation for 6 hours. For these measurements, only the samples containing 2% Michler’s Ketone were chosen, as it is the ideal concentration for the polymerization of the apparent monomers, as shown above.

![Graph showing polymerization degree of C2-C6VimBr samples containing 2% of Michler’s Ketone after prolonged irradiation and waiting time.](image)

**Figure 17:** Polymerization degree of the C2-C6VimBr samples containing 2% of Michler’s Ketone after prolonged irradiation and waiting time.

Fig. 17 and table 3 summarize the results obtained from this measurement. It can be seen, that all samples show autopolymerization: This is most pronounced for monomers bearing the ethyl- and propyl chain. The polymerization for these continues from 9% to 15% (47%). The intermediate butyl moiety only gains 2% of polymerization degree and exhibits no further polymerization after the subsequent irradiation, while also the C5 and C6- monomers also show a distinct degree of autopolymerization from 64 (78%) to 73% (81%). However the autopolymerization could
also just be due to persistent radicals and not be related to the radical-stabilizing ability of the ionic liquid.

Table 3: Polymerization degree gain per hour for the autopolymerisation experiments.

<table>
<thead>
<tr>
<th></th>
<th>C₂VimBr</th>
<th>C₃VimBr</th>
<th>C₄VimBr</th>
<th>C₅VimBr</th>
<th>C₆VimBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 6 h of irradiation</td>
<td>9</td>
<td>19</td>
<td>53</td>
<td>64</td>
<td>78</td>
</tr>
<tr>
<td>After 15 h without irradiation</td>
<td>15</td>
<td>47</td>
<td>55</td>
<td>73</td>
<td>81</td>
</tr>
<tr>
<td>Polymerization degree gain in %/h</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>After 6 h further irradiation</td>
<td>48</td>
<td>85</td>
<td>55</td>
<td>85</td>
<td>90</td>
</tr>
<tr>
<td>Polymerization degree gain in %/h</td>
<td>6</td>
<td>6</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

IR-spectroscopy

The IR-spectra of all compounds show the expected vibrational bands in both the monomeric and the polymeric moiety. Fig. 18 shows the representative spectra of the monomeric and polymeric C₂-moiety: The hygroscopic behavior of the moieties leads to the appearance of the typical vibrational bands of water ranging from 3590-3290 cm⁻¹ and overlying the ν(N-H) band. The important ν(C=H) band (see below) is visible at 3040 cm⁻¹, while the bands at 2959, 2929 and 2858 cm⁻¹ can be attributed to the ν(CH₃/CH₂) and thus at 1651, 1570 and 1548 cm⁻¹ to the ν(C=N/C=C) stretching bands.
2. Physicochemical properties of ionic polymers

To prove the polymerization of the vinylimidazolium moieties by IR spectroscopy the area of interest within the measured IR-spectra lies around 3040 cm$^{-1}$, where the monomeric IL spectra display a band corresponding to the vibration $\nu$(C-H-sp$^2$) of the vinyl group. The IR-spectra of the polymerized materials show this same absorption band but with a clearly decreased intensity relative to the C=C- and C=N-valence vibrations of the incorporated imidazolium ring. As the $\nu$(C-H-sp$^2$) vibration of the aromatic imidazolium moiety lies in the same region as the $\nu$(C-H-sp$^2$) vibration of the vinyl group, IR-spectroscopy is not an appropriate method of proving the polymerization of the vinyl groups.

**Optical properties**

**UV/Vis spectroscopy**

Materials used in photoluminescent lighting devices, are desired to have a host matrix sporting optical transparency over a wide range of wavelengths. Figure 19 shows the UV-Vis transmission spectra of the prepared monomers and polymers.
2. Physicochemical properties of ionic polymers

Figure 19: UV/Vis transmission spectra of the prepared vinylimidazolium based monomers (left) and their respective polymers (right).

The monomers show a shoulder in the range of 260 to 240 nm which rises from the $\pi$-system of the conjugated vinyl double bond. After polymerization, this shoulder disappears in the polymeric material due to the absence of this double bond. Therefore, all polymers show a high transparency at short wavelengths as well as across the whole range of the visible spectrum.

**Luminescence spectroscopy:**

Upon excitation, which is possible from 270 nm to over 430 nm, all vinylimidazolium bromide polymers show emission in the blue region of the visible spectrum, which is typical for imidazolium containing moieties and thus can be attributed to the allowed $\pi\rightarrow\pi^*$ transitions of the aromatic ring. The luminescence is already visible by the naked eye under a UV-Lamp with broad irradiation centered around 366 nm. They all show a broad emission band ranging from 300 to 600 nm. However, the emission maximum is shifted depending on the aliphatic chain length in the cationic polymer bulk: The hexyl chain containing polymer exhibits the highest $\lambda_{em,\text{max}}$ (445 nm), while the C$_5$ and C$_4$ polymer exhibit the lowest $\lambda_{em,\text{max}}$. The shorter chain lengths lie in the middle of these with $\lambda_{em,\text{max}}$=424 for the C$_2$ and $\lambda_{em,\text{max}}$=416 nm for the C$_3$ polymer (figure 20).
Thermal behavior

Table 4: Decomposition temperatures for the prepared poly 1-n-alkyl-3-vinylimidazolium bromides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{\text{decomp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C$_2$VimBr</td>
<td>289.7</td>
</tr>
<tr>
<td>P-C$_3$VimBr</td>
<td>264.8</td>
</tr>
<tr>
<td>P-C$_4$VimBr</td>
<td>268.3</td>
</tr>
<tr>
<td>P-C$_5$VimBr</td>
<td>260.3</td>
</tr>
<tr>
<td>P-C$_6$VimBr</td>
<td>290.9</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis revealed all compounds to be stable to at least 260 °C for the intermediate chain lengths and up to 290 °C for the longest and shortest alkyl chain. This trend may be due to packing effects in the moieties which will be discussed further below. The thermal stability of these compounds underlines their eligibility as a matrix for designing new phosphors.
2. Physicochemical properties of ionic polymers

Differential scanning calorimetry

Figure 21: DSC thermograph of C$_2$VimBr recorded with a heating and cooling rate of 5K.

DSC thermographs of all monomers and polymers have been recorded. Figure 21 shows the DSC thermograph of C$_2$VimBr representatively. The moieties with an even number of carbon atoms in the aliphatic side chain (C$_6$ excluded) show higher melting temperature than those with an odd number. C$_2$- and C$_4$VimBr were also much easier to recrystallize from ethyl acetate (see above) than the propyl or pentyl chain containing ones.

Table 5: Obtained data from DSC measurements for the 1-alkyl-3vinylimidazolium containing monomers

<table>
<thead>
<tr>
<th>Compound</th>
<th>DSC</th>
<th>T$_g$ Exotherm in °C</th>
<th>T$_g$ Endotherm in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Onset</td>
<td>Offset</td>
</tr>
<tr>
<td>C$_2$VimBr</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>C$_3$VimBr</td>
<td>-40.0</td>
<td>-37.1</td>
<td>-41.6</td>
</tr>
<tr>
<td>C$_4$VimBr</td>
<td>-83.9</td>
<td>-89.3</td>
<td>-46.4</td>
</tr>
<tr>
<td>C$_5$VimBr</td>
<td>-34.0</td>
<td>-30.3</td>
<td>-47.1</td>
</tr>
<tr>
<td>C$_6$VimBr</td>
<td>-62.3</td>
<td>-55.8</td>
<td>-56.6</td>
</tr>
</tbody>
</table>
2. Physicochemical properties of ionic polymers

For the polymer representative measurements of the C\textsubscript{2} and C\textsubscript{4}- moiety showed no appearance of any signals. However also representatively on the C\textsubscript{2}- moiety repeated experiments with a cooling rate of 1K or 10K respectively did not led to the observation of new peaks. DSC thermograms of the investigated compounds can be found in the appendix.

Conclusion

A series of 1-\textit{n}-alkyl-3-vinylimidazolium bromide monomers was synthesized and characterized; starting with the ethyl moiety, the chain length was subsequently extended by one methylene unit up to 1-\textit{n}-hexyl-3-vinylimidazolium bromide; and their polymerization behavior was investigated. Through optimization experiments, it was found that a radical starter concentration of 2\% leads to the maximum conversion rate. Counterintuitively, it was found that a longer alkyl chain in the 1-\textit{n}-alkyl-3-vinylimidazolium backbone leads to faster polymerization and higher conversion rates. One hypothesis to explain this unexpected result is the possible formation of aggregates: In order to react, the vinyl double bonds have to be close enough to each other. A longer alkyl chain length could lead to the formation of micelles or micelle like aggregates, thus restraining the monomers in a way that the distance of the vinyl double bonds decreases, and therefore making it easier to react. Furthermore, it was shown that the polymerization continues after the irradiation by leaving the samples in the dark for 15 h and then taking NMR-spectra again.

UV/Vis-spectroscopy revealed that all prepared polymers are transparent over a wide wavelength range, which is a mandatory factor for the design of efficient phosphors. The fact that all prepared polymers are thermally stable up to 290 °C as shown by TG is another factor that shows the eligibility of these polymers to design new phosphors from them.

Experimental section

1-Bromoethane (99\%), 1-bromopropane (99\%), 1-bromobutane (99\%), 1-bromopentane (99\%), 1-bromohexane (99\%) and azo-bis(isobutyro)nitrile (AIBN) (98\%), 4,4′-Bis(dimethylamino)benzophenone (Michler's ketone) (98\%) were purchased from Sigma-
2. Physicochemical properties of ionic polymers

Aldrich and used as received; potassium persulfate (97%) was purchased from ABCR and used as received; 1-vinylimidazole (98%) was purchased from Alfa Aesar and distilled under reduced pressure prior to use.

Synthesis of Ionic Liquid Monomers

\[
\text{N} \begin{array}{c} \text{N} \\
\text{N} \end{array} \ + \ R \text{Br} \xrightarrow{\text{Reflux, 48 h}} \begin{array}{c} \text{N} \\
\text{N} \end{array} \text{R} \text{Br}^{-}
\]

Scheme 4: Preparation of the 1-\(n\)-alkyl-3-vinylimidazolium bromides.

20 g (19.2 ml, 213 mmol) vinylimidazole was dissolved in acetonitrile. A 1.3 molar excess of the respective alkylbromide was then added drop-wise to the solution, which was then refluxed for 72 h. After cooling to room temperature, activated charcoal was added and the reaction mixture was stirred for an additional 48 h. The mixture was then filtered over neutral alumina. Residual solvent was removed under reduced pressure and the remaining ionic liquid was dried under dynamic vacuum for 48 h. 1-Ethyl-3-vinylimidazolium bromide (C\(_2\)VimBr, yield 73%) and 1-butyl-3-vinylimidazolium bromide (C\(_4\)VimBr, yield 68%) were obtained as white, crystalline powders. 1-Propyl-3-vinylimidazolium bromide (C\(_3\)VimBr, yield 49%), 1-pentyl-3-vinylimidazolium bromide (C\(_5\)VimBr, yield 45%) and 1-hexyl-3-vinylimidazolium bromide (C\(_6\)VimBr, yield 51%) were obtained as pale yellow viscous liquids. In case of C\(_4\)VimBr, the crude product was re-crystallized from ethyl acetate. C\(_2\)VimBr was prepared without any solvent, precipitated during the reaction, filtered off and washed with ethyl acetate and dried in dynamic vacuum for 48 h. All other ionic polymers were washed with ethyl acetate (3 \(\times\) 100 mL) and dried \textit{in vacuo}.

C\(_2\)VimBr

\(^1\)H-NMR (200 MHz, DMSO-\(d_6\)) \(\delta/\text{ppm} = 9.60\) (s, 1H), 8.22(t, 1H), 7.97 (t, 1H), 7.31 (dd, 1H), 5.98 (dd, 1H), 5.42 (dd, 1H), 4.24 (t, 2H), 1.45 (t, 3H)

\(^13\)C-NMR 50 MHz, DMSO-\(d_6\)) \(\delta/\text{ppm} = 135.03, 128.82, 122.08, 119.10, 108.16, 44.56, 14.70\)

IR: 3642-3180 (w), 3134 (m), 3058 (s), 2988 (s), 2909 (m), 2869 (m), 2705 (m), 1656 (s), 1579 (s), 1543 (s), 1459 (s), 1417 (s), 1379 (s), 1328 (s), 1303 (s)

\(T_m = 84.5^{\circ}\text{C}\)
2. Physicochemical properties of ionic polymers

$C_3$VimBr

$^1$H-NMR (200 MHz, DMSO-$d_6$) δ /ppm = 9.77 (s, 1H), 8.29 (t, 1H), 8.02 (t, 1H), 7.36 (dd, 1H), 6.02 (dd, 1H), 5.41 (dd, 1H), 4.20 (t, 2H), 1.85 (m, 2H), 0.86 (t, 3H)

$^{13}$C-NMR 50 MHz, DMSO-$d_6$ δ/ppm = 135.25, 128.77, 122.18, 119.17, 108.60, 50.57, 22.51, 10.34

IR: 3601-3249 (w), 3126 (m), 3052 (s), 2979 (s), 2959 (s), 2933 (m), 2876 (m), 1647 (s), 1569 (s), 1550 (s), 1405 (s), 1384 (s), 1347 (s), 1316 (s)

$T_m = 59.3^\circ C$

$C_4$VimBr

$^1$H-NMR (200 MHz, DMSO-$d_6$) δ/ppm = 9.61 (s, 1H), 8.23 (t, 1H), 7.96 (t, 1H), 7.31 (dd, 1H), 5.98 (dd, 1H), 5.42 (dd, 1H), 4.22 (t, 2H), 1.82 (m, 2H), 1.29 (m, 2H), 0.90 (t, 3H)

$^{13}$C-NMR 50 MHz, DMSO-$d_6$ δ/ppm = 135.27, 128.84, 123.21, 119.15, 108.61, 48.89, 31.00, 18.74, 13.23

IR: 3582-3252 (w), 3108 (m), 3090 (m) 2980 (s), 2979 (s), 2968 (s), 2953 (s), 2926 (s), 2869 (m), 2846 (m), 2692 (m), 1650 (s), 1564 (s), 1539 (s), 1457 (s), 1433 (s), 1412 (s), 1366 (s), 1337 (m)

$T_m = 83.9^\circ C$

$C_5$VimBr

$^1$H-NMR (200 MHz, DMSO-$d_6$) δ/ppm = 9.55 (s, 1H), 8.16 (t, 1H), 7.90 (t, 1H), 7.28 (dd, 1H), 5.94 (dd, 1H), 5.39 (dd, 1H), 4.19 (t, 2H), 1.69-1.64 (m, 2H), 1.38-1.10 (m, 4H), 0.83 (t, 3H)

$^{13}$C-NMR 50 MHz, DMSO-$d_6$ δ/ppm = 134.98, 128.64, 123.14, 119.12, 108.74, 49.20, 28.72, 27.53, 21.42, 13.65

IR: 3590–3290 (w), 3121 (m), 3040 (m), 2959 (s), 2929 (s), 2858 (s), 1651 (s), 1570 (s), 1548 (s), 1458 (m), 1373 (s), 1318 (s)

$T_m = 83.9^\circ C$
2. Physicochemical properties of ionic polymers

$C_6$VimBr

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 9.88 (s, 1H), 8.33 (t, 1H), 8.04 (t, 1H), 7.38 (dd, 1H), 6.05 (dd, 1H), 5.41 (dd, 1H), 4.24 (t, 2H), 1.84 (q, 2H), 1.24 (m, 6H), 0.82 (t, 3H)

$^{13}$C-NMR (50 MHz, DMSO-$d_6$) $\delta$/ppm = 135.24, 128.89, 123.44, 119.43, 109.01, 49.48, 30.70, 29.29, 25.30, 22.03, 12.97

IR: 3573-3285 (w), 3120 (m), 3045 (m), 2955 (s), 2928 (s), 2858 (s), 2727 (w), 1650 (s), 1569 (s), 1546 (s), 1457 (s), 1377 (s), 1311 (s)

Polymerization of Ionic Liquid Monomers

![Scheme 5: Polymerization of n-alkyl-3-vinylimidazolium bromides.](image)

In a typical polymerization reaction, 3 g of the respective monomer were dissolved in 25 ml of chloroform. 2 mol% AIBN (azo-$bis$(isobutyro)nitrile) were added and the reaction mixture refluxed at 80 °C for 24 h. In the case of poly-C$_2$VimBr the polymer precipitated during the reaction, the precipitate was subsequently washed with chloroform and dried in vacuo for 24 h. For all other polymers, the solvents were evaporated under reduced pressure, and the remaining transparent polymers were dried for 24 h in vacuo. In all cases yields >96% were obtained.
2. Physicochemical properties of ionic polymers

P-C$_2$VimBr
$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 10.06-9.03 (s, 1H), 8.16-7.32 (s, 2H), 4.97-3.65 (m, 4H), 1.49 (d, 2H) (1.06, t, 3H)

IR: 3566–3220 (w), 3120 (s), 3041(s), 2972(s), 2935(s), 2884(s), 2865(s), 1635 (w), 1569(s), 1548(s), 1435(m), 1386(m), 1339(m), 1312 (w)

P-C$_3$VimBr
$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 10.10-9.13 (s, 1H), 8.33-7.23 (s, 2H), 4.94-3.37 (m, 2H), 4.15 (dd, 2H), 2.08 – 1.74 (m, 2H), 1.05 – 0.71 (s, 3H).

IR: 3550–3262(w), 3130 (m), 3044 (s), 2964 (s), 2937 (s), 2874 (m), 1655 (w), 1638 (s), 1568 (s), 1546 (s), 1452 (m), 1379 (w), 1343 (w), 1309 (w)

P-C$_4$VimBr
$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 10.54-9.36 (s, 1H), 8.88-7.38 (s, 3H), 4.57 – 3.69 (m, 3H), 2.17 – 1.79 (m, 2H), 1.41 – 1.09 (m, 2H), 1.08 – 0.74 (s, 3H).

IR: 3600–3215 (m), 3124 (m), 3050 (s), 2958 (s), 2932 (s), 2869 (s), 1625 (w), 1569 (s), 1548 (s), 1459 (m), 1438 (m), 1376 (w), 1340 (w), 1313 (w)

P-C$_5$VimBr
$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 10.22 – 8.99 (s,1H), 8.37-7.00 (s, 2H), 5.02-3.65 (m,2H), 1.08-1.49 (m, 4H), 0.12-1.06 (s, 3H).

IR: 3580–3265 (m), 3122 (m), 3047 (s), 2954 (s), 2929 (s), 2859 (s), 1619 (w), 1568 (s), 1549 (s), 1459 (m), 1438 (s), 1378 (w), 1310 (w)

P-C$_6$VimBr
$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 10.28-9.39 (m, 1H) 7.06 –8.11(m, 2H), 3.16 – 4.90 (m, 2H) 1.33 – 1.81 (m, 2H), 1.30 – 0.85 (m, 6H), 0.65 (s, 3H)
2. **Physicochemical properties of ionic polymers**

IR: 3560–3265 (w), 3122 (w), 3050 (m), 2955 (s), 2927 (s), 2857 (s), 1625 (w), 1568 (s), 1549 (s), 1456 (s), 1438 (s), 1378 (w), 1310 (w)

$^1$H-NMR spectroscopy: Some polymer signals are always underlying solvent or other peaks.

**Preparation of the samples for irradiation experiments**

200 mg of the respective monomer were dissolved in 4 ml of degassed, deuterated chloroform. The respective amount of radical starter was then dissolved in the monomer solution under vigorous stirring, and the vials irradiated for the respective times.
3. From halide to salicylate anions in ionic polymers

General aspects

The decreasing availability of lanthanides and their increasing price gives rise in the demand for alternative luminescent materials without the employment of lanthanides. One option is to use organic phosphors. In contrary to lanthanides, luminescent organic materials are readily available, do mostly not suffer the problem of a complex processing (such as inert handling), and their sourcing is independent of mineral deposits. Regarding their luminescent properties, their electronic transitions are formally allowed leading to a high absorption and thus excitation cross section with a strong emission. This arises from the π-system which is moreover conjugated over the carboxylate and hydroxyl function in the salicylate anion. Organic phosphors are already in use in OLEDs, dye lasers and can even be used as a sensitizer for lanthanides. The salicylate (2-hydroxybenzoate) anion is an interesting candidate for such applications: Determining the quantum yield of solid materials, sodium salicylate has been used for many years as a standard. After excitation a broad emission band from 360 to 540 nm centered at 410 nm is monitored, which is visible as strong blue luminescence, with a quantum yield of ~60%. Moreover it can be excited over a large region of wavelengths.

Salicylate compounds usually are nontoxic and some choline compounds (choline magnesium salicylate and choline salicylate) are used as nonsteroidal, anti-inflammatory drug which are effective in treating fever, pain and inflammation in the body. Strong luminescence and nontoxicity makes the salicylate anion an ideal candidate to be used in lighting devices as an efficient blue emitter. Previous work also showed, that salicylate based ionic liquids possess a color tuneability depending on the cation employed.

Ionic liquids based on aromatic cations and their polymers, especially these based on imidazolium, possess intrinsic, but weak luminescent properties. This arises from low lying π→π* transitions and usually are situated at a maximum emission wavelength at about 420 nm. As mentioned above, ionic polymers offer the opportunity to vary their properties by anion exchange either before or after the polymerization. To enhance the emission of these ionic
liquids and their polymers, it is an obvious option to use the salicylate anion as a counter anion for the vinylimidazolium and DADMA polymer backbone.

**Results and discussion**

**General discussion**

The chemistry of polymers is completely different from monomer chemistry and therefore demands a different approach in synthesis and analytics. Previous work in our group described the synthesis of salicylate ionic liquids bearing different cations and thus exhibiting greatly varying emission characteristics. However a similar approach was chosen for the synthesis of the polymers described in this chapter.

The easiest way to synthesize these polymers would be to first conduct the anion exchange on the monomer and then polymerize it. It was found, however that the polymerization does not take place after replacing the bromide anion with salicylate. This effect was observed for thermal radical starters such as AIBN or potassium persulfate as well as for the photoinitiated polymerization with and without the addition of Michler’s ketone as an additional radical starter.

Therefore the anion exchange had to take place after the polymerization of the vinylimidazolium-bromides.

This proved to be rather complicated. By trying to extract the polymer salicylates with an organic solvent, it seemed that the cationic polymer chains in combination with the bromide/salicylate anion mixture acted like a surfactant. Depending on the length of the side chain in the employed vinylimidazolium polymer the phase separation of these reaction mixtures took days to weeks. This behavior demanded the optimization of the synthesis which resulted in a repeated washing/drying process at cost of the yields, but resulting in more pure products.

Polymer chains have the ability to entangle other molecules and especially the intermolecular cation-anion interaction of common salts with ionic polymer-chains is poorly understood and described. Thus it is not surprising, that an anion exchange conducted on ionic polymer
3. From halide to salicylate anions in ionic polymers

chains leads to a higher amount of impurities in the resulting material. Therefore it is important to have a close look on these impurities and their impact on the final luminescent material.

Elemental analysis was conducted on all polymer salicylates and revealed impurities in the substances. NMR-spectroscopy helped to prove, that the differing values of the elemental analysis do not rise from salicylate impurities

Table 6: Measured and calculated values of the CHNS-elemental analysis

<table>
<thead>
<tr>
<th>Polymer</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C₂Vim(Sal)</td>
<td>10.77</td>
<td>64.61</td>
<td>6.15</td>
<td>10.95/10.90</td>
<td>52.64/52.84</td>
<td>6.32/6.37</td>
</tr>
<tr>
<td>P-C₃Vim(Sal)</td>
<td>10.22</td>
<td>65.69</td>
<td>6.57</td>
<td>6.26/6.18</td>
<td>48.84/48.53</td>
<td>5.56/5.49</td>
</tr>
<tr>
<td>P-C₄Vim(Sal)</td>
<td>9.72</td>
<td>66.67</td>
<td>6.94</td>
<td>6.16/6.29</td>
<td>47.02/47.03</td>
<td>5.62/5.82</td>
</tr>
<tr>
<td>P-C₅Vim(Sal)</td>
<td>9.27</td>
<td>67.55</td>
<td>7.28</td>
<td>7.07/7.07</td>
<td>48.26/48.14</td>
<td>4.96/4.92</td>
</tr>
<tr>
<td>P-C₆Vim(Sal)</td>
<td>8.86</td>
<td>68.35</td>
<td>7.59</td>
<td>6.58/6.65</td>
<td>50.72/50.82</td>
<td>6.88/6.84</td>
</tr>
</tbody>
</table>

For monomer chemistry, ion chromatography is the ideal analytic technique to quantify inorganic impurities, such as sodium or bromide ions. The columns employed in this technique are not suited for polymers, as they would stick to the resins. However the content of sodium can be quantified by atom absorption spectroscopy (AAS). Assuming, that the impurities do only rise from sodium bromide, and then extrapolating the measured values of the elemental analysis gives the opportunity to validate this thesis.

Table 7: Measured CHNS and AAS values and total product mass extrapolated with the assumption, that NaBr ist the only impurity. (1st measurement/2nd measurement)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
<th>AAS :Na(%)</th>
<th>Total mass including NaBr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC₂Vim(Sal)</td>
<td>10.95/10.90</td>
<td>52.64/52.84</td>
<td>6.32/6.37</td>
<td>3.2/3.19</td>
<td>102%</td>
</tr>
<tr>
<td>PC₃Vim(Sal)</td>
<td>6.26/6.18</td>
<td>48.84/48.53</td>
<td>5.56/5.49</td>
<td>7.12/7.50</td>
<td>105%</td>
</tr>
<tr>
<td>PC₄Vim(Sal)</td>
<td>6.16/6.29</td>
<td>47.02/47.03</td>
<td>5.62/5.82</td>
<td>6.06/5.95</td>
<td>98%</td>
</tr>
<tr>
<td>PC₅Vim(Sal)</td>
<td>7.07/7.07</td>
<td>48.26/48.14</td>
<td>4.96/4.92</td>
<td>5.72/6.54</td>
<td>97%</td>
</tr>
<tr>
<td>PC₆Vim(Sal)</td>
<td>6.58/6.65</td>
<td>50.72/50.82</td>
<td>6.88/6.84</td>
<td>5.41/5.08</td>
<td>101%</td>
</tr>
</tbody>
</table>
Table 7 shows that the impurities only arise from sodium bromide. However, as sodium bromide is not interfering with the optical properties of the resulting salicylate polymers, it can be neglected regarding UV-Vis and luminescence spectroscopy.

**Optical properties**

![UV-Vis spectra](image)

**Figure 22**: UV-Vis spectra of the prepared P-C<sub>n</sub>-Vim salicylates from 200 to 400 nm (left) and the segment from 200 -350 nm (right) recorded at room temperature with a concentration of 10<sup>-4</sup> mol/l in ethanol.

The UV-Vis spectra of the prepared polymers are depicted in figure 22 and have a similar appearance with a pronounced band at 205 nm (ε ≈ 25000-40000), followed by a shoulder at 230 nm (ε ≈ 10000) and another less pronounced band at 300 nm (ε ≈ 5000). These can be attributed to allowed π → π* transitions within the salicylate anion. When compared to the UV-Vis spectrum of free salicylic acid, the absorption is increased in the range from 200 to 250 nm, which arises from the presence of the imidazolium π system with its π → π* transitions. Interestingly, the absorption band at around 300 nm is slightly bathochromic shifted for the ethyl chain bearing polymer. This can be attributed to a smaller π- π* interaction in this moiety which will be discussed below.
3. From halide to salicylate anions in ionic polymers

Luminescence spectroscopy

![Excitation spectra of the prepared polymers from 250 to 380 nm. Sodium salicylate is added in a dotted line for comparison reasons.](image)

All synthesized compounds show a similar excitation spectrum: They all are excitable over a broad wavelength range from 250 to 280 nm which corresponds to the $\pi\rightarrow\pi^*$ transitions of the salicylate anion. Compared to sodium salicylate, the excitation is more pronounced for all polymers, especially in the range of 250 to 340 nm which is due to the addition $\pi$-system of the aromatic imidazolium unit apparent. The different excitation characteristics could arise from traces of residual water within these compounds. This could lead to equilibrium between the salicylate anion and salicylic acid, which then leads to the formation of different domains which involves a change of the $\pi$-$\pi$ interaction and thus the excitation behavior.
3. From halide to salicylate anions in ionic polymers

Figure 24: Emission spectra of the prepared polymers from 340 to 540 nm recorded with an excitation wavelength of 315 nm. Sodium salicylate is added in a dotted line for comparison reasons (left). Dependence of the maximum emission energy of the polymer cation (right).

As expected, the emission spectra of the prepared polymers (figure 24) show a broad band spanning from 360 to 550 nm centered at around 410 nm. This results in a bright blue luminescence upon UV-irradiation. The emission maxima, which were taken from a gaussian fitting of the experimental data, show a hypsochromic shift regarding the emission characteristica of the sodium salt ($\lambda_{em,max}= 418$ nm). The shortest and longest alkyl chain show the smallest shift with their emission maxima at 414 nm (P-C$_6$Vim(Sal)) and 411 nm for the C$_2$ moiety. The intermediate chain lengths show a bigger hypsochromic shift with their emission maxima at 408 nm for the propyl chain bearing polymer, 407 nm for the butyl moiety and 406 nm for P-C$_5$-Vim(Sal). P-DADMA(Sal) shows a similar $\lambda_{em,max}$ at 405 nm. The nature of the anion is the same in all cases, and can thus be excluded from discussing this change, and as the nature of the cation is similar in all cases, the change of the maximum emission wavelength cannot be solely attributed to cation-anion interaction and has to be further discussed. One possibility could be seen in the increasing inductive effect of the side chain. As the longest and shortest alkyl chain have the smallest hypsochromic shift, and the intermediate chain lengths show bigger emission gaps, it can be said that no dependence of the emission maxima from the electron donating effect of the side chain can be observed. The same argumentation can be
3. From halide to salicylate anions in ionic polymers

followed by taking steric demands in consideration. Another explanation for the rather small shift in the maximum emission wavelength may lay in a type of solvatochromism: As the polarity of the surrounding area of a given ion changes with its alkyl chain length, the emission maxima are shifted.

As stated above, also a change in the π-π interaction can lead to a change of the emission characteristics and especially the strongest emission wavelength. Ionic liquids are known for forming hydrophobic and hydrophilic domains: Tails of alkyl chains form micelle-like aggregates (see above), and charged head groups (imidazolium in this case) form polar channels which leads to a close distance to their salicylate counter anion.\textsuperscript{75-77} A change in the length of the alkyl chains leads to a change of the distance between the polar head-groups and thus a change in the π-π interactions responsible for the shift of the maximum emission wavelength. A short alkyl chain such as C\textsubscript{2} may act in a similar way like the C\textsubscript{6} chain. While in the C\textsubscript{2} moiety the π-π interaction is very pronounced due to the close proximity of the anion-cation pairs, the C\textsubscript{6} chain could lead to big hydrophobic domains and thus provide enough space for the anions and cations to slip in between these domains being close to each other again. The intermediate chain lengths on the other hand have a well suitable size to separate the anions and cations and thus reducing the π-π interactions in these moieties. The resulting reduced π-π interactions lead to a lower orbital energy inducing a hypsochromic shift in the emission wavelength. The fact, that sodium salicylate shows the highest $\lambda_{\text{em, max}}$ supports this thesis: The sodium salicylate crystal lattice leads to a very close proximity of the ions, and therefore pronounced π-π interactions resulting in its $\lambda_{\text{em, max}}$. Another explanation for the shift of the emission maxima could be that the C\textsubscript{2,3} moieties possess a consistently high polarity while the intermediate chain lengths a consistently low polarity. The C\textsubscript{6}-moiety is able to form hydrophobic domains. The salicylate counter anion should always be located in domains or spaces with a high polarity, which attributes to the emission behavior. A further technique to investigate the proximity of the π-systems in these compounds would be the employment of ROESY (rotating frame-NOE) NMR-spectroscopy. In contrary to their monomeric counterparts, the bulk polymer structure is too complex to resolve signals which render this technique useless.
3. *From halide to salicylate anions in ionic polymers*

![Image](image.png)

**Figure 25**: A sample of P-C_{2}Vim(Sal) under broad UV irradiation centered around 366 nm.

It is expected, that the quantum yields of these new ionic polymer salicylates suffer from excessive vibrational quenching of the cationic polymer bulk. Interestingly, the measured quantum yields lay in the same order of magnitude as sodium salicylate:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantum Yield in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C_{2}Vim( Sal)</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>P-C_{3}Vim( Sal)</td>
<td>34 ± 2</td>
</tr>
<tr>
<td>P-C_{4}Vim( Sal)</td>
<td>41 ± 1</td>
</tr>
<tr>
<td>P-C_{5}Vim( Sal)</td>
<td>41 ± 2</td>
</tr>
<tr>
<td>P-C_{6}Vim( Sal)</td>
<td>35 ± 1</td>
</tr>
<tr>
<td>P-DADMA(Sal)</td>
<td>36 ± 2</td>
</tr>
</tbody>
</table>

Table 8: Calculated quantum yields for the prepared poly 1-n-alkyl-3vinylimidazolium salicylates.

For the vinylimidazolium based polymers, the quantum yields show similar values around 35%, with the C_{4} and C_{5} moieties exhibiting slightly higher values. The trend of the quantum yield values, is the same as observed for the maximum emission wavelengths in the emission spectra of these compounds. The butyl and pentyl bearing polymers show the biggest hypsochromic shift, slightly higher quantum yields than the compounds with shorter and longer alkyl chains. Again, this could be attributed to the proximity of the anion-cation pairs and the forming of polar/apolar domains\cite{75-77} and clusters in the material and thus a more efficient
absorption/emission behavior of these compounds. However P-DADMA(Sal) exhibits a quantum yield of 36% and thus close to these of the C_{2,3,6} moieties, which indicates a similar cation-anion interaction and supports the thesis of forming polar and apolar pockets and channels as stated above. However its maximum emission wavelength is some more hypsochromic shifted. This can be attributed to the lack of the π-system in this compound.

The lifetimes of all these compounds is too short to be measured on the employed fluorescence measurement device, and therefore cannot be compared and related to the $\lambda_{\text{em,max}}$ or the calculated quantum yields.

**Thermal analysis**

The vinylimidazolium based compounds were thermally investigated using DSC and TG techniques.

![Thermogravimetric results for P-C_{2}Vim(Sal) starting at 30 °C to 1000 °C with a heating rate of 10 K/min.](image)

Figure 26: Thermogravimetric results for P-C_{2}Vim(Sal) starting at 30 °C to 1000 °C with a heating rate of 10 K/min.

All prepared compounds show a minor mass los starting at 100 °C, which is probably due to traces of residual water which was also found by the investigation of these compounds via IR-spectroscopy. Despite the C_{2} moiety, all polymers show their first major mass loss between 260 and 270 °C. Also the mass losses of all these compounds lie in the same percentage range. The
mass losses of the compounds probably rise from the decomposition of both, the salicylate ion and the poly-cation backbone, as especially the first mass loss should be much smaller if it could be attributed to only either the salicylate anion or the polymer-backbone.

Table 9: Measured decomposition temperatures and residual masses of the P-C_{2-6}Vim based salicylate polymers.

<table>
<thead>
<tr>
<th></th>
<th>T_{decomp} in °C</th>
<th>Residual mass in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C_{2}Vim(Sal)</td>
<td>283</td>
<td>2.57</td>
</tr>
<tr>
<td>P-C_{3}Vim(Sal)</td>
<td>263</td>
<td>1.20</td>
</tr>
<tr>
<td>P-C_{4}Vim(Sal)</td>
<td>277</td>
<td>3.18</td>
</tr>
<tr>
<td>P-C_{5}Vim(Sal)</td>
<td>260</td>
<td>1.58</td>
</tr>
<tr>
<td>P-C_{6}Vim(Sal)</td>
<td>263</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Figure 26 shows the thermogram of P-C_{2}Vim(Sal). This gives evidence, that the anion exchange does not have any impact on the thermal behavior in this temperature range and therefore is only depending of the cationic polymer backbone. DSC measurements have also been conducted for the C_{2},C_{4} and C_{6} species representatively and showed no appearance of any signals. However, polymers usually exhibit at least a glass transition in this region, which was not observed for any of the prepared materials. This can either rise from a T_g lying much higher than the examined temperature range, or the applied cooling/heating rate was too high or low to detect these.

**Conclusion**

A set of salicylate containing ionic polymers based on vinylimidazolium and DADMA cationic polymer backbones have successfully been synthesized. The synthesis procedure could be optimized within regard to simple extraction by an organic solvent. Residual inorganic impurities could be identified and quantified by a combination of AAS and EA. The compounds were fully characterized by NMR, and IR techniques and investigated by optical and thermal means. The prepared polymers showed to exhibit strong thermal stability up to 260 °C. All polymers show strong luminescence in the blue region of the visible spectrum. Their emission maxima are shifted depending on the nature of the polymer backbone employed and the aliphatic chain attached to the imidazolium core for the vinylimidazolium polymers from 404 to 414 nm. High
3. From halide to salicylate anions in ionic polymers

quantum yields (35-40%) and a broad region for excitation shows the eligibility for these materials as efficient blue emitters for lighting applications.

Experimental section

Materials and methods

DADMACl (60wt% aqueous solution) was purchased by ABCR and used as received. All other chemicals used in this chapter are enumerated in the chapter above.

Synthesis

Synthesis of poly-1-R-3-Vinyl-Imidazolium salicylates

![Scheme 6: Synthesis of the salicylate polymers based on poly-C_2,6-vinylimidazolium backbones.](image)

1 Equivalent of the respective 1-\(n\)-alkyl-3-vinylimidazolium polymer was dissolved in 90 ml of ethanol in a 250 ml Schlenk-flask. 1 Equivalent of sodium salicylate was then added to the reaction mixture which was then stirred for 24 hours (exact masses are shown in table 10). The reaction mixture was filtrated. The solvent was removed under reduced pressure and the colorless residuals quickly washed with 2x1 ml water and 4x2 ml acetone to remove residual NaBr. The colorless products were then dried for 48 h in a dynamic vacuum and stored under inert atmosphere.
3.2 Synthesis of poly-dimethyldiallylammonium salicylate (DADMA(Sal))

Scheme 7: Synthesis of the salicylate polymers based on poly-diallyldimethylammonium backbone.

6 g of dimethyldiallylammonium chloride polymer were dissolved in 90 ml of ethanol in a 250 ml Schlenk-flask. The reaction mixture was stirred for three days to fully dissolve the reactant. 1 Equivalent of sodium salicylate (37 mmol, 9.8 g) was added to the reaction mixture and stirred for another 24 hours. The suspension was filtered and the solvent was removed under reduced pressure. The colorless residuals were washed with 2x1 ml of water and 4x2 ml of acetone to remove residual sodium bromide and salicylate. The residuals were then dissolved in ethanol again, remaining impurities filtered off, and the solvent was removed under reduced pressure. The colorless powder was then dried in a dynamic vacuum for 48 hours, and the colorless product was stored under inert atmosphere.

Table 10: Summary of the masses and yields for the synthesis of the alicylate polymers based on P-C2-4-vinylimidazolium and P-DADMA backbones.

<table>
<thead>
<tr>
<th>Starting polymer</th>
<th>Molar mass (g/mol)</th>
<th>Added weight (g)</th>
<th>Added weight Na(Sal) (g)</th>
<th>Product</th>
<th>Molar mass (g/mol)</th>
<th>Yield (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C2VimBr</td>
<td>203.08</td>
<td>0.52</td>
<td>0.41</td>
<td>P-C2Vim(Sal)</td>
<td>260.29</td>
<td>0.50</td>
<td>75</td>
</tr>
<tr>
<td>P-C3VimBr</td>
<td>217.08</td>
<td>0.25</td>
<td>0.18</td>
<td>P-C3Vim(Sal)</td>
<td>274.29</td>
<td>0.26</td>
<td>81</td>
</tr>
<tr>
<td>P-C4VimBr</td>
<td>231.08</td>
<td>0.51</td>
<td>0.35</td>
<td>P-C4Vim(Sal)</td>
<td>288.29</td>
<td>0.51</td>
<td>80</td>
</tr>
<tr>
<td>P-C5VimBr</td>
<td>245.08</td>
<td>0.53</td>
<td>0.34</td>
<td>P-C5Vim(Sal)</td>
<td>302.29</td>
<td>0.55</td>
<td>84</td>
</tr>
<tr>
<td>P-C6VimBr</td>
<td>259.08</td>
<td>0.58</td>
<td>0.36</td>
<td>P-C6Vim(Sal)</td>
<td>316.29</td>
<td>0.21</td>
<td>30</td>
</tr>
<tr>
<td>P-DADMACl</td>
<td>160.50</td>
<td>6.00</td>
<td>6.00</td>
<td>P-DADMA(Sal)</td>
<td>262.16</td>
<td>7.12</td>
<td>73</td>
</tr>
</tbody>
</table>
3. From halide to salicylate anions in ionic polymers

P-C₂Vim(Sal):

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 15.87 (s, 1H), 9.62 (s, 1H), 8.21 (s, 1H), 7.97 (s, 1H), 7.67 (d, 1H), 7.14 (d, 1H), 6.64 (dd, 2H), 4.24 (q, 1H), 4.22 (m, 1H), 3.53 (s, 3H), 1.43 (d, 3H).

IR: 3450 (s), 3192 (m), 3075 (m), 2977 (w), 1628 (m), 1564 (m), 1437 (m) 1382 (m), 1154 (s), 1127 (w), 1036 (w).

EA (calculated N%,C%,H%/measured N%,C%,H%): 10.77, 64.61, 6.15 / 10.93, 52.74, 6.35

P-C₃Vim(Sal):

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 16.07 (s, 1H), 9.83 (s, 1H), 7.99 (s, 2H), 7.66 (d, 1H), 7.13 (d, 1H), 6.63 (d, 2H), 3.94 (m, 3H), 1.68 (s, 2H), 0.77 (s, 3H).

IR: 3415 (m), 3036 (m), 2958 (m), 2922 (m), 2849 (w), 1628 (m), 1564 (s), 1491 (s), 1464 (s), 1364 (s), 1291 (m), 1154 (s).

EA (calculated N%,C%,H%/measured N%,C%,H%): 10.22, 65.69, 6.57 / 6.22, 48.69, 5.53

P-C₄Vim(Sal):

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 15.89 (s, 1H), 9.60 (s, 1H), 8.23 (s, 1H), 7.96 (s, 1H), 7.67 (d, 1H), 7.15 (t, 1H), 6.62 (t, 2H), 4.21 (m, 1H), 3.89 (m, 1H), 3.36 (s, 3H), 1.68 (s, 2H), 1.19 (s, 2H), 0.87 (d, 3H).

IR: 3396 (m), 3120 (w), 3073 (m), 2968 (m), 2864 (w), 1628 (m), 1571 (s), 1485 (s), 1473 (s), 1381 (s), 1324 (s), 1162 (s).

EA (calculated N%,C%,H%/measured N%,C%,H%): 9.72, 66.67, 6.94 / 6.23, 47.03, 5.72
3. From halide to salicylate anions in ionic polymers

P-C₅Vim(Sal):

¹H-NMR (200 MHz, DMSO-d₆) δ/ppm = δ = 16.04 (s, 1 H), 9.71(s,1 H), 7.79 (d,1 H), 7.64 (d,1 H), 7.14(t, 1H), 6.62 (d, 2 H), 3.92 (s, 2H), 3.33 (s, 3H), 1.67 (s, 2H), 1.16 (s, 4H), 0.83 (t, 3H).

IR: 3405 (m), 3139 (w), 3069 (w), 2935 (m), 2872 (w), 1624 (s), 1576 (m), 1483 (s), 1386 (s), 1331 (s), 1257 (s), 1163 (s).

EA (calculated N%,C%,H%/measured N%,C%,H%): 9.27, 67.55, 7.28 / 7.07, 48.20, 4.94

P-C₆Vim(Sal):

¹H-NMR (200 MHz, DMSO-d₆) δ/ppm = 15.61 (s, 1H), 9.71 (s, 1H), 8.07 (s, 1H), 7.87 (s, 1H), 7.67 (d, 1H), 7.13 (d, 1H), 6.64 (d, 2H), 3.96 (s, 2H), 3.38 (s, 3H), 1.73 (s, 2H), 1.18 (s, 6H), 0.81 (s, 3H).

IR: 3405 (m), 3135 (w), 3069 (w), 2936 (w), 2862 (w), 1629 (m), 1581 (s), 1481 (s), 1456 (s), 1385 (s), 1331 (m), 1254 (m), 1161 (s).

EA (calculated N%,C%,H%/measured N%,C%,H%): 8.86, 68.35, 7.59 / 6.62, 50.77, 6.86

P-DADMA(Sal)

¹H-NMR (200 MHz, DMSO-d₆) δ/ppm = 7.69 (d, 4H), 7.31 (t, J = 7.9, 1.7 Hz, 4H), 6.82 (t, 8H), 3.72 (q, 3H), 3.52 (s, 6H), 1.07 (t, 3H).

IR: 3686-3100 (w), 3019 (w), 2936 (w), 2855 (w), 2703 (w), 1631 (s), 1574 (s), 1481 (s), 1386 (s), 1320 (s), 1293 (m)

EA (calculated N%,C%,H%/measured N%,C%,H%): 8.04, 68.42, 5.32 / 7.97, 53.09, 6.67
4. From salicylate ionic liquids to salicylate containing rare earth complexes

Figure 27: Photograph of (choline)[La(Sal)₄] (left) and (choline)[Tb(Sal)₄] (right) under broad UV-irradiation ($\lambda_{\text{exc. max}}=366$ nm).

General aspects

As stated in the introduction, a lot of lighting and active display devices contain lanthanide ions as a primary emitter. For an efficient emission, phosphors also have to efficiently absorb. Lanthanides however, suffer from a poor absorption cross section, which can be overcome by the introduction of a sensitizer: a substance with a high absorption cross-section, which efficiently transfers the absorbed energy to the lanthanide ion for emission. As sensitziers, different lanthanide ions, such as Ce$^{3+}$, broad band semiconductors, organic ligands and dyes can be used.$^{[85-86]}$ A drawback with organic fluorophores is their lack of photostability.$^{[87]}$ However, it has already been reported that incorporating such dyes into ionic liquids can enhance their photostability.$^{[71]}$ Highly luminescent and color-tunable salicylate ionic liquids have recently been made by our group.$^{[83]}$ Adding optically active transition metal or $f$-element ions to ionic liquids has let to highly luminescent ionic liquids.$^{[62, 66, 88-90]}$ In case of a combination of an imidazolium based ionic liquid cation and Eu$^{3+}$ it was found that the ionic liquid cation can act as an antenna and enhance the emission.$^{[91]}$ However, the IL cation is not in close proximity to the lanthanide cation compared to the IL anion which can act as a direct ligand.$^{[90]}$ The salicylate anion should be the right anion to sensitize Tb$^{3+}$. For that reason, the combination of complex terbium salicylato anions with common ionic liquid cations was investigated, where the cheap, readily available and non-toxic salicylate acts as a sensitizer for the terbium emission.
establish that indeed an efficient energy transfer from the salicylate ligand to the terbium cation takes place the isostructural lanthanum complexes were synthesized for comparison reasons.

**Results and discussion**

**Structural aspects**

![Diagram](image)

Scheme 8: Preparation of (Cat)[M(Sal)_4](M=La,Tb).

The set of ionic lanthanum and terbium complexes bearing the salicylate ligand were synthesized by addition of lanthanide (III) salicylate (Ln(III)Sal, Ln = La, Tb) to an equimolar amount of a salicylate ionic liquid ((Cat)Sal) in ethanol, leading to the immediate precipitation of the products as colorless powders. Several different ionic liquid cations (Cat) were used to investigate the influence on the resulting optical properties: these can be classified into non-aromatic (choline, diallyldimethylammonium (DADMA)) and aromatic 1-ethyl-3-methylimidazolium (C2C1Im), 1-butyl-3-methylimidazolium (C4C1Im), 1-ethyl-3-vinylimidazolium (C2Vim)) (Scheme 8). Among these, DADMA and C2Vim are polymerizable and therefore can be compared to their polymeric counterparts (chapter 6).
4. From salicylate ionic liquids to salicylate containing rare earth complexes

All compounds were found to contain the tetrakissalicylatolanthanoate anion, Ln[Sal]₄⁻, as confirmed by electrospray ionization (ESI) mass spectrometry in the negative mode, showing peaks at m/z = 686.77 for [La(Sal)₄]⁻ and m/z= 706.76 [Tb(Sal)₄]⁻. The crystal structures of the C₂C₁im compounds could be obtained from single crystals of sufficient quality for structure determination by X-ray diffraction. The crystals could be obtained by combining the respective lanthanide salicylate and C₂C₁im(Sal) in a glass ampoule, which was sealed under vacuum and heated to 150 °C for 24 hours, before cooling slowly over 72 hours to room temperature. Crystallographic data and details of the structure refinement of the isotypic compounds can be found in Table 11.

Table 11: Crystallographic data and details of the structure refinement for (C₂C₁Im)₄[La₄Sal₁₂(H₂O)₂] and (C₂C₁Im)₄[Tb₄Sal₁₂(H₂O)₂].

<table>
<thead>
<tr>
<th></th>
<th>(C₂C₁Im)₄[La₄Sal₁₂(H₂O)₂]</th>
<th>(C₂C₁Im)₄[Tb₄Sal₁₂(H₂O)₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>La₄ C₁36 H₁28 N₈ O₅₀</td>
<td>Tb₄ C₁36 H₁28 N₈ O₅₀</td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>3230.12</td>
<td>3310.10</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>170(2)</td>
<td>170(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₁ (no. 2)</td>
<td>P₁ (no. 2)</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>13.1800(19)</td>
<td>13.1364(19)</td>
</tr>
<tr>
<td>b</td>
<td>13.2503(20)</td>
<td>13.2532(24)</td>
</tr>
<tr>
<td>c</td>
<td>20.8341(28)</td>
<td>20.6358(33)</td>
</tr>
<tr>
<td>Unit cell angles (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>82.308(17)</td>
<td>82.716(21)</td>
</tr>
<tr>
<td>β</td>
<td>78.580(16)</td>
<td>78.223(18)</td>
</tr>
<tr>
<td>γ</td>
<td>71.504(17)</td>
<td>72.150(15)</td>
</tr>
<tr>
<td>Volume</td>
<td>3372.30(322)</td>
<td>3339.79(233)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated, g/cm³)</td>
<td>1.58</td>
<td>1.63</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>1.333</td>
<td>2.186</td>
</tr>
<tr>
<td>F(000)</td>
<td>1615.7</td>
<td>1647.7</td>
</tr>
<tr>
<td>θ-range for data collection</td>
<td>2.4 - 25</td>
<td>2.5 - 25</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-15 ≤ h ≤ 15</td>
<td>-15 ≤ h ≤ 15</td>
</tr>
</tbody>
</table>
4. From salicylate ionic liquids to salicylate containing rare earth complexes

<table>
<thead>
<tr>
<th></th>
<th>-15 ≤ k ≤ 15</th>
<th>-15 ≤ k ≤ 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflection collected</td>
<td>22392</td>
<td>27027</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6304</td>
<td>4772</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full matrix least-squares on $F^2$</td>
<td></td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>9879/33/904</td>
<td>10908/33/767</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>0.973</td>
<td>1.027</td>
</tr>
<tr>
<td>Final $R$ indices [I&gt;2σ(I)]</td>
<td>$R_1 = 0.065$</td>
<td>$R_1 = 0.102$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.170$</td>
<td>$wR_2 = 0.291$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.101$</td>
<td>$R_1 = 0.189$</td>
</tr>
<tr>
<td></td>
<td>$wR_2 = 0.192$</td>
<td>$wR_2 = 0.324$</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.043</td>
<td>0.118</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>+6.00/-1.19</td>
<td>+1.723/-1.787</td>
</tr>
</tbody>
</table>

Structure analysis reveals for both the solid lanthanum(III) and the terbium(III) compound a composition of $(C_2C_1Im)_4[Ln_4Sal_{12}(H_2O)_2]$. The compounds crystallize isotypic $(C_2C_1Im)_4[Ln_4Sal_{16}(H_2O)_2]$ in the triclinic space group P\(\overline{1}\) (no. 2) with one formula unit in the unit cell. The most distinct feature is a linear tetrameric polyanion, $[Ln_4Sal_{16}(H_2O)_2]^{4+}$, Figure 28, in which both the two crystallographically independent lanthanide ions are coordinated by a distorted square antiprism of oxygen atoms. The middle lanthanide ions are coordinated eight salicylate ligands which bridge in a \(\mu_2\)-bidentate-fashinon via the carboxylate group to the neighboring lanthanide. The terminal lanthanides are coordinated by four \(\mu_2\)-bidentate salicylate ligand and their coordination sphere is saturated by three monodentatelly terminal salicylate ligands and one water molecule (figure 29). The distance between the lanthanum atoms in these anionic components is about 4.5 Å and the lanthanum oxygen distance is found in the typical range from 2.40 to 2.65 Å. Also all other interatomic distances are in the expected range. The $C_2C_1Im$ cations are located between these linear $[La_4Sal_{16}(H_2O)_2]^{4+}$ tetrameric units in the direction of the $a$ and $b$-axes, where the shortest distance between the lanthanum ions of neighbouring anionic units is equal to the lengths of the unit cell dimensions, being 13.18 Å and 13.25 Å, respectively. Along the $c$-axis, no cations are located between these units, therefore the shortest La-La distance is 8.44 Å (figure 29).
4. From salicylate ionic liquids to salicylate containing rare earth complexes

Figure 28. Anionic unit $[\text{La}_4\text{Sal}_{16}(\text{H}_2\text{O})_2]^\text{+}$. 

Figure 29. Packing diagram of $(\text{C}_2\text{C}_1\text{Im})_4[\text{La}_4\text{Sal}_{16}(\text{H}_2\text{O})_2]$. View along the crystallographic c-axis. $(\text{C}_1\text{C}_2\text{Im})$cations are red colored.

Figure 30 shows the comparison between the experimental PXRD pattern from the samples synthesized without inert condition with the theoretical pattern from the single crystals obtained through the synthesis in glass ampoules. These show some differences against each other due to
4. From salicylate ionic liquids to salicylate containing rare earth complexes

the fact that the SXRD analysis was taken at 77K and the PXRD pattern at room temperature.

![Graph showing PXRD data comparison](image)

**Figure 30: Comparison of the simulated and measured PXRD pattern of (C2C1Im)4[LaSal4]**

Only suitable crystals of (C2C1Im)4[LaSal16(H2O)2] and (C2C1Im)4[TbSal16(H2O)2] for SXRD analysis could be obtained.

Onto determine the water content of the other compounds thermogravimetric measurements have been performed. To determine the water content, the region up to 160 °C in the thermographs was examined and the mass loss in this region was used to calculate the amount of water molecules per Ln3+ ion. The region below 160 °C was chosen, as some of the water evaporates before reaching 100 °C, and as the heating rate in these experiments was 10K/min, to allow all the water to evaporate.

From the mass loss in the TG it can be seen, that all compounds besides the choline derivatives contain 1.2 to 3.09 mass% of water, which corresponds to semi-hydrates with 0.5 to 1 water molecules per lanthanide ion. Water content derived from thermogravimetric analysis is in a good agreement with the values determined from single crystal analysis for (C2C1Im)4[LaSal16(H2O)2] and (C2C1Im)4[TbSal16(H2O)2]. The excess amount of the calculated water content can be attributed to remaining residual solvent (table 12).
4. From salicylate ionic liquids to salicylate containing rare earth complexes

Table 12: Water content and decomposition temperatures of the prepared tetrakis salicylatolanthanate and -terbate compounds derived from thermogravimetric analysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water content from TG in %</th>
<th>Water molecules/Ln³⁺</th>
<th>T_{decomp} in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₂C₁Im)[La(Sal)₄]</td>
<td>1.64</td>
<td>0.7</td>
<td>218</td>
</tr>
<tr>
<td>(C₂C₁Im)[Tb(Sal)₄]</td>
<td>1.20</td>
<td>0.6</td>
<td>214</td>
</tr>
<tr>
<td>(C₄C₁Im)[La(Sal)₄]</td>
<td>3.09</td>
<td>1.5</td>
<td>226</td>
</tr>
<tr>
<td>(C₄C₁Im)[Tb(Sal)₄]</td>
<td>2.16</td>
<td>1.0</td>
<td>258</td>
</tr>
<tr>
<td>(C₂Vim)[La(Sal)₄]</td>
<td>2.89</td>
<td>1.3</td>
<td>228</td>
</tr>
<tr>
<td>(C₂Vim)[Tb(Sal)₄]</td>
<td>1.32</td>
<td>0.6</td>
<td>232</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)₄]</td>
<td>2.53</td>
<td>1.2</td>
<td>226</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)₄]</td>
<td>1.36</td>
<td>0.6</td>
<td>263</td>
</tr>
<tr>
<td>(choline)[La(Sal)₄]</td>
<td>0.00</td>
<td>0.0</td>
<td>266</td>
</tr>
<tr>
<td>(choline)[Tb(Sal)₄]</td>
<td>0.78</td>
<td>0.3</td>
<td>235</td>
</tr>
<tr>
<td>La(Sal)₃</td>
<td>7.45</td>
<td>2.4</td>
<td>218</td>
</tr>
<tr>
<td>Tb(Sal)₃</td>
<td>4.18</td>
<td>1.4</td>
<td>233</td>
</tr>
</tbody>
</table>

The fact that the choline derivatives contain little to no water indicates, that these compounds exist not as (semi-) hydrates, which nicely corresponds with the fact that these samples show the highest quantum yield of the terbium compounds (see section below).

However, this difference in the decomposition temperatures when comparing the terbium to the lanthanum compounds could rise from minor impurities, which influence the decomposition process in the thermogravimetric analysis.

For all samples, no melting point could be assigned, due to the decomposition of the samples. Thermogravimetric analysis reveal the compounds to be stable up to over 200 °C, ranging from 218.2 °C for (C₂C₁Im)[La(Sal)₄] to 266.4 °C for (choline)[La(Sal)₄]. The decomposition is probably due to thermal instability of the salicylate ligand which is in agreement with the decomposition temperature of the sole lanthanide- and terbium salicylate (T_{onset}= 218.0 °C, 233.3°C respectively).
Elemental analysis has also been performed and shows lower values for the C, H and N contents. These tendencies are in agreement with those described in chapters 2 and 4. However, no AAS analysis could be performed on these compounds to validate that NaBr is the only impurity.

**Optical properties**

![Normalized emission spectra of the lanthanum compounds recorded at room temperature from 350 to 580 nm (right). Dependence of the maximum emission energy from the employed cation (right).](image)

Under broad UV-Irradiation (254 or 366 nm), the as-prepared samples exhibit intense emission (fig. 27) which can easily be observed by the naked eye. For all compounds, emission spectra were recorded by exciting into the absorption band of the salicylate ligand at 310 nm to make sure all compounds were excited under the same conditions. Even though a higher absorption is possible at longer wavelengths, a shorter excitation wavelength has also been chosen to collect the whole emission range of the compounds.

The lanthanum compounds show a broad emission in the range of 360 - 540 nm with a maximum at 400 nm. The C\textsubscript{2}C\textsubscript{1}Im compound shows a bathochromic shift of the emission band center to 430 nm. This may be due to packing effects, since the C\textsubscript{2}C\textsubscript{1}Im cation bears two short alkyl chains, leading to closer packing in the crystal structure of the compounds. This would lead to a
closer proximity of the salicylate moieties, increasing the likelihood of energy-lowering $\pi-\pi$-interactions. On average, the emission spectra are very similar to those of sodium salicylate (NaSal), also given in figure 31 for comparison. This indicates that the broad band emission in the lanthanum compounds is due to the auto-fluorescence of the salicylate anion.

4. From salicylate ionic liquids to salicylate containing rare earth complexes

Figure 32: Normalized emission spectra of terbium compounds recorded with an excitation wavelength of 315 nm at room temperature.

Under similar condition the terbium compounds exhibit strong green emission with the typical $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3 f-f$-transitions (figure 32). No broad band emission due to salicylate fluorescence could be observed. This may arise from efficient energy transfer from the salicylate ligand to the terbium cation. To further investigate this, excitation spectra were recorded (figure 33). The excitation spectra of the terbium compounds monitored at the most intense emission at 542 nm ($^5D_4 \rightarrow ^7F_5$ transition) show broad bands extending throughout the measured region, instead of the typical narrow f-f-excitation bands. This corroborates a very efficient energy transfer between the salicylate ligand and the Tb$^{3+}$ ion. To establish the relative position of the salicylate states with respect to the terbium levels, the excitation spectra of the analogue lanthanum compounds were recorded monitoring emission of the salicylate ligand around 420 nm (figure 33). These spectra were seen to be very similar to their terbium counterparts, with broad bands observed, which can be attributed to the $\pi \rightarrow \pi^*$ transitions.
4. From salicylate ionic liquids to salicylate containing rare earth complexes

Figure 33: Normalized excitation spectra of the prepared lanthanum compounds from 280 to 410 nm (left) and the analogous terbium compounds from 280 to 470 nm (right) recorded at room temperature. Spectra of sodium salicylate and the respective lanthanide salicylate are added for comparison reasons.

Scheme 9: Proposed energy scheme for the photonic processes including the energy transfer to the active terbium center in the lanthanum- and terbium tetrakis(salicylato) containing complexes.

Using the fluorescence spectra of the lanthanum compounds it is possible to establish an energy diagram for the photonic processes probably occurring in this materials: The zero phonon energy (ground vibrational state) of the salicylate ligand in rare earth compounds can be estimated from the overlap point between the excitation and emission spectra and the $S_1$-state can be estimated from the point where the emission of the compounds is negligible. The proposed mechanism can
Figure 34: Dependancy of the quantum yield (left) and lifetime of the water content for the terbium containing samples.

be seen from scheme 9: After populating the excited state of the salicylate ligand, the energy is transferred into the $^5D_{4.3}$ levels around 21000 and 27000 cm$^{-1}$ of terbium through dipole-dipole interactions. The ground state of the lanthanum and terbium ions is the same, with the latter one not being dependant on $f$-electrons thus giving the opportunity to estimate the energy of the ground state in the analogous of the terbium compounds. An energy transfer from the $^5D_{4.3}$ level should therefore be possible as the emitting terbium levels lie in the same energetic region $^5D_3$ or below $^5D_2$. This requires a very short distance between the sensitizer and activator species, as is guaranteed through ligation of the salicylate to the Tb, previously shown in the crystal structure. Radiative emission then occurs from this state into the $^7F_{5.3}$ levels.

Quantum yields of all terbium and lanthanum compounds were measured using an integration sphere, and are given in Table 13 alongside those of NaSal and Tb(III)Sal. The quantum yields were observed to be significantly lower for the lanthanum compounds compared to terbium counterparts. Furthermore, the salicylate emission from all lanthanum compounds reported herein presents poorer efficiency than that observed in the sodium salt (60%). This could stem from the heavy atom effect, whereby the presence of a heavy atom such as lanthanum increases the probability of inter-system crossing of the excited state, leading to non-emitting or poorly emitting species. In the case of terbium, quantum efficiencies higher than 60% and as high as 92% have been observed, some of them being significantly higher than the quantum yield of the simple Tb(III)Sal (65%). An explanation of this improved quantum yield may be found by
examining the environment of the activator ion. Water is well known to be responsible for vibrational quenching of luminescence due to its high energy OH stretching vibrations. The crystal structure of Tb(III)Sal is unknown and no crystals of sufficient quality for X-ray structural determination could be produced during this study. However, the crystal structure of the samarium counterpart (Sm(III)(Sal)₃) has been previously reported, [⁹²] showing that each Sm bears one water ligand in its coordination sphere. TG measurements of Tb(III)Sal showed 1.4 H₂O per Tb centre, although some may be physisorbed rather than coordinating. In contrast, as seen in the crystal structures of the C₂C₁im compounds, only 2 water ligands exist per 4 Tb centres. Therefore reduction of the amount of water present leads to a more efficient luminescence: 65% vs. 83%, Tb(III)Sal vs. (C₂C₁Im)[TbSal₄]. The trend of measured luminescence lifetimes agrees with the trend observed in the quantum yields, where a higher level of quenching lead to a shorter luminescence lifetime. These tendencies are depicted in figure 34. The differences between photophysical properties of the different compounds may be due to differences in the crystal structures imposed by the different cations employed and further structural analysis is needed to confirm or reject this hypothesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantum Yield [%]</th>
<th>Lifetime [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₂C₁Im)[La(Sal)₄]</td>
<td>17 ± 4</td>
<td>*</td>
</tr>
<tr>
<td>(C₂C₁Im)[Tb(Sal)₄]</td>
<td>83 ± 4</td>
<td>1.07 ± 0.02</td>
</tr>
<tr>
<td>(C₄C₁Im)[La(Sal)₄]</td>
<td>28 ± 2</td>
<td>*</td>
</tr>
<tr>
<td>(C₄C₁Im)[Tb(Sal)₄]</td>
<td>64 ± 2</td>
<td>0.95 ± 0.01</td>
</tr>
<tr>
<td>(C₂Vim)[La(Sal)₄]</td>
<td>14 ± 2</td>
<td>*</td>
</tr>
<tr>
<td>(C₂Vim)[Tb(Sal)₄]</td>
<td>74 ± 3</td>
<td>1.19 ± 0.00</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)₄]</td>
<td>7 ± 0²</td>
<td>*</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)₄]</td>
<td>60 ± 7</td>
<td>1.27 ± 0.03</td>
</tr>
<tr>
<td>(Choline)[La(Sal)₄]</td>
<td>7 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(Choline)[Tb(Sal)₄]</td>
<td>92 ± 2</td>
<td>1.45 ± 0.04</td>
</tr>
<tr>
<td>NaSal</td>
<td>56</td>
<td>*</td>
</tr>
<tr>
<td>La(Sal)₃</td>
<td>42 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>Tb(Sal)₃</td>
<td>55 ± 2</td>
<td>1.17 ± 0.07</td>
</tr>
</tbody>
</table>

Table 13: Lifetimes and quantum yields of the terbium compounds. (*: Lifetime to short to measure with the equipment used. ² Error smaller than significant value (0,41)
Finally, in addition to the high intensity photoluminescence observed, the electroluminescent behavior was tested qualitatively by applying a high voltage to the terbium containing samples. This was done using a teslator to the samples in a Schlenk tube, which was evacuated prior to the measurement. The spectrum was recorded using a CCD-detector. All prepared terbium compounds show intense electroluminescence (figure 36).

![Electroluminescence spectrum](image)

Figure 35: Electroluminescence spectrum of $C_4C_1\text{Im}[\text{Tb(Sal)}_4]$ recorded at room temperature.

**Conclusion:**

A set of ionic lanthanum- and terbium complexes has been synthesized from salicylate based ionic liquids and was fully characterized using NMR, mass spectrometry and optical spectroscopy. The lanthanum compounds show auto-fluorescence of the salicylate ligand only, whereas the terbium compounds show intense green photoluminescence when excited over a broad range of wavelengths, thanks to very efficient energy transfer from the salicylate ligand to the terbium ion. Highly efficient materials result, with quantum yields measured to be as high as 92%. The superior photoluminescence efficiency of these compounds compared to simple Tb(III) salicylate can be explained by the reduced vibrational quenching due to fewer water molecules in the coordination sphere of Tb, as seen in the crystal structure. Furthermore, the terbium
containing samples exhibit high intensity electroluminescence, which renders these compounds good candidates for future lighting applications.

**Experimental section**

**Materials**

Lanthanum(III)-chloride heptahydrate was purchased from ABCR. Terbium(III,IV)oxide (99.99%) was purchased from SmartElements. Choline chloride (99%) was purchased from Acros Organics, 1-chlorobutane and 1-methylimidazole were purchased from SigmaAldrich. Ethanol (99.9% over molecular sieve) was purchased from Acros Organics.

**Synthesis**

In a typical reaction to prepare (Cat)Sal, stoichiometric amounts of ethanolic solutions of NaSal and the corresponding (Cat)Cl were combined. The precipitated NaCl was filtered off and washed with ethanol. The filtrates were concentrated under reduced pressure, and the remains were dried at 60 °C in a dynamic vacuum for at least 24 h. In all cases pale yellow, viscous liquids were obtained.

To obtain the complexes (Cat)[M(Sal)₄] the rare earth(III)salicylates were dissolved in anhydrous ethanol. An at least 1.5 molar excess of the corresponding ionic liquid was poured into the solution. This lead to the precipitation of (Cat)[M(Sal)₄] which was filtered off, washed with ethanol and then dried at 80 °C for at least 12 h. Colorless powders were isolated with yields of 80 to 85%.

In a typical reaction the Tb₄O₇ was dissolved in the respective mineral acid (HCl/HBr) by heating to 100 °C and a minimum 12-fold excess of the ammonium halide was added. The water and acid were boiled off, until an almost dry, pale yellow solid remained.

For the rare-earth(III)salicylates, the corresponding rare earth chloride hydrates and NaSal in a ratio of 1:3 were combined in acetone. The precipitated NaCl was filtered off and washed with acetone. Acetone was evaporated under reduced pressure, and the remains were dried at 60 °C in
4. From salicylate ionic liquids to salicylate containing rare earth complexes

a dynamic vacuum for at least 24 h. Colorless powders were obtained in yields of 80% Tb(Sal)$_3$ and 84% La(Sal)$_3$.

1-Ethyl-3-methylimidazoliumtetrakisalicylatolanthanate(C$_2$C$_1$Im)[La(Sal)$_4$]

MS: ESI$: m/z = 686.77 ([La(Sal)]$_4^-$)

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 14.53 (s, 1H), 9.23 (s, 1H), 8.07 – 7.66 (m, 6H), 7.31 (t, 4H), 6.78 (d, 8H), 4.26 (q, 2H), 3.91 (s, 3H), 1.48 (t, 3H).

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.51, 51.14, 3.91 / 2.49, 54.69, 3.43

IR: 3151 (w), 3100 (w), 3004 (w), 2370 (w), 2341 (w), 1623 (m), 1592 (s), 1545 (s), 1482 (s) 1459 (s), 1383 (s), 1342 (s), 1308 (m), 1246 (s), 1160 (s), 1143 (s), 1097 (m), 1032 (m) 956 (m), 864 (m), 816 (m), 755 (s), 703 (s), 663 (s), 620 (m), 570 (m), 532 (s), 493 (m), 459 (m), 391 (s)

1-Ethyl-3-methylimidazoliumtetrakisalicylatoterbate(C$_2$C$_1$Im)[Tb(Sal)$_4$]

MS: ESI$: m/z = 706.76 [Tb(Sal)$_4$]

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.42, 49.89, 3.82 / 2.32, 44.14, 3.06

IR: 3145 (w), 3118 (w), 2356 (w), 2343 (w), 1623 (m), 1599 (m), 1560 (s), 1459 (s), 1384 (s), 1337 (m), 1246 (m), 1143 (m), 1030 (m), 887 (m), 863 (m) 817 (m), 754 (s), 703 (s), 663 (s), 618 (m), 584 (s), 533 (m), 465 (m), 397 (s)

1-Butyl-3-methylimidazoliumtetrakisalicylatolanthanate(C$_4$C$_1$Im)[La(Sal)$_4$]

MS: ESI$: m/z = 686.77 ([La(Sal)]$_4^-$)

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 9.06 (s, 1H), 7.80 – 7.60 (m, 6H), 7.16 (s, 4H), 6.63 (s, 8H), 4.16 (t, 3H), 3.85 (s, 3H) 1.78 (q, 3H), 1.28 (dt, 2H), 0.91 (t, 3H).

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.39, 52.31, 4.27 / 2.61, 45.11, 3.55
4. From salicylate ionic liquids to salicylate containing rare earth complexes

IR: 3623 (w), 3529-3327 (w), 3158 (w), 3120 (w), 3042 (w), 2869 (w), 1569 (s), 1579 (s), 1541 (s), 1492 (s), 1454 (s), 1385 (s), 1333 (s), 1254 (s), 1159 (s), 1136 (s), 1030 (s), 885 (s), 863 (s), 830 (s), 755 (s), 701 (s), 658 (s), 617 (s), 585 (s), 574 (s), 533 (s), 457 (s), 394 (s)

1-Butyl-3-methylimidazoliumtetrakis salicylatoterbate(C₄C₁Im)[Tb(Sal)₄]

MS: ES⁺ m/z = 706.76 [Tb(Sal)₄]

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.31, 51.07, 4.17 / 2.85, 43.62, 3.47

IR: 3152 (w), 3048 (w), 2963 (w), 2870 (w), 2357 (w), 1626 (m), 1599 (s), 1549 (s), 1459 (s), 1383 (s), 1333 (s), 1248 (s), 1138 (s), 1031 (m), 885 (s), 860 (s), 830 (s), 757 (s), 711 (s), 663 (s), 580 (s), 534 (s), 468 (s), 408 (s),

1-Ethyl-3-vinylimidazoliumtetrakis salicylatolanthanate(C₂Vim)[La(Sal)₄]

MS: ES⁺ m/z = 686.77 ([La(Sal)]₄⁻)

¹H-NMR (200 MHz, DMSO-d₆) δ/ppm = 14.84 (s, 4H), 9.54 (s, 1H), 8.21 (t, 1H), 7.96 (t, 1H), 7.72 (d, 4H), 7.32 (dd, 1H), 7.18 (t, 4H), 6.61 (s, 8H), 5.98 (dd, 1H), 5.45 (dd, 1H), 1.48 (t, 3H).

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.46, 51.86, 3.86 / 2.81, 45.73, 3.72

IR: 3572-3268 (w), 3219-2938 (w), 2358 (m), 2332 (w), 1624 (m), 2569 (s), 1544 (m), 1493 (s), 1454 (s), 1384 (s), 1331 (s), 1251 (s), 1137 (m), 1030 (m), 884 (m), 863 (s), 827 (m), 815 (m), 755 (s), 701 (s), 660 (s), 585 (s), 533 (s), 457 (s), 390 (s)

1-Ethyl-3-vinylimidazoliumtetrakis salicylatoterbate(C₂Vim)[Tb(Sal)₄]

MS: ES⁺ m/z = 706.76 [Tb(Sal)₄]

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.37, 50.61, 3.76 / 2.56, 44.09, 3.22
4. From salicylate ionic liquids to salicylate containing rare earth complexes

IR: 3612-3272 (w), 3200-2879 (w), 3139 (w), 3052 (w), 2369 (w), 2342 (w), 1624 (m), 1597 (s), 1563 (s), 1501 (m), 1457 (s), 1386 (s), 1336 (m), 1250 (s), 1160 (m), 1140 (m), 1030 (m), 956 (w), 888 (m), 863 (m), 813 (m), 755 (s), 701 (s), 663 (s), 578 (m), 578 (m), 533 (m), 462 (s), 398 (s)

Diallyldimethylammoniumtrakisalicylatolanthanate (DADMA)[La(Sal)$_4$]

MS: ESI$: m/z = 686.77 ([La(Sal)]$_4$$^{-}$)

$^1$H-NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 15.08 (s, 4H), 7.70 (s, 4H), 7.14 (t, 4H), 6.58 (s, 8H), 6.10 (m, 2H), 5.62 (d, 4H), 3.94 (d, 4H), 2.98 (s, 6H).

EA (calculated N%,C%,H%/measured N%,C%,H%): 1.72, 53.15, 4.46 / 1.30, 46.04, 3.76

IR: 3676-3542 (w), 3506-3308 (w), 1624 (w), 1597 (s), 1560 (m), 1543 (s), 1493 (s), 1459 (s), 1384 (s), 1334 (s), 1308 (m), 1251 (s), 1137 (m), 1031 (m), 958 (m), 887 (s), 861 (m), 831 (m), 757 (s), 700 (s), 661 (s), 584 (s), 534 (s), 455 (s), 392 (s)

Diallyldimethylammoniumtrakisalicylatoerbate(DADMA)[Tb(Sal)$_4$]

MS: ESI$: m/z = 706.76 [Tb(Sal)]$_4$$^{-}$

EA (calculated N%,C%,H%/measured N%,C%,H%): 1.68, 51.87, 4.35 / 1.59, 46.04, 3.74

IR: 3575 (w), 3379 (w), 3088 (w), 3045 (w), 1626 (m), 1579 (s), 1553 (s), 1496 (s), 1460 (s), 1384 (s), 1333 (s), 1248 (s), 1138 (m), 1033 (m), 958 (m), 890 (s), 861 (s), 834 (m), 817 (m), 753 (s), 700 (s), 664 (s), 580 (s), 533 (s), 460 (s), 404 (s)

Trimethyl-(2-hydroxyethyl)ammoniumtrakisalicylatolanthanate (Chol)[La(Sal)$_4$]

MS: ESI$: m/z = 686.77 ([La(Sal)]$_4$$^{-}$)
4. From salicylate ionic liquids to salicylate containing rare earth complexes

$^1$H NMR (200 MHz, DMSO) $\delta$/ppm=14.98 (s, 4H), 7.72 (d, 4H), 7.18 (t, 4H), 6.62 (s, 8H), 5.41 (s, 1H), 3.86 (t, 2H), 3.51 – 3.36 (t, 2H), 3.14 (s, 9H).

EA (calculated N%, C%, H% / measured N%, C%, H%): 1.77, 50.07, 4.33 / 1.87, 47.21, 3.41

IR: 3570-3126 (w), 3053 (w), 2835 (w), 2369 (w), 2340 (w), 1591 (m), 1560 (m), 1377 (s), 1341 (s), 1306 (s), 1246 (s), 1141 (s), 1088 (m), 1030 (m), 950 (m), 863 (s), 818 (s), 754 (s), 660 (s), 565 (m), 535 (s), 455 (s), 392 (s)

Trimethyl-(2-hydroxyethyl)ammoniumtetrakisalicylatoterbate (Chol)[Tb(Sal)$_4$]

MS: ESI$: m/z = 706.76$ [Tb(Sal)$_4$]$^-$

EA (calculated N%, C%, H% / measured N%, C%, H%): 1.73, 48.84, 4.22 / 1.36, 45.15, 3.41

IR: 3126-2913 (w), 2372 (w), 2332 (w), 1624 (w), 1593 (s), 1557 (s), 1460 (s), 1384 (s), 1246 (s), 1144 (s), 1090 (m), 1031 (m), 953 (m), 865 (m), 811 (m), 755 (s), 703 (s), 661 (s), 534 (m), 462 (m), 397 (s)

Lanthanum(III)salicylate La(Sal)$_3$

$^1$H NMR (200 MHz, DMSO) $\delta$/ppm =14.44 (s, 1H), 7.78 (dd, 1H), 7.51 – 7.03 (td, 1H), 6.70 (t, 2H).

MS: ESI$: m/z = 548.88$ La(Sal)$_3^-$

EA (calculated C%, H% / measured C%, H%): 45.82, 2.72 / 46.84, 3.97

Terbium(III)salicylate Tb(Sal)$_3$

MS: ESI$: m/z = 566.88$ Tb(Sal)$_3^-$

EA (calculated C%, H% / measured C%, H%): 44.21, 2.63 / 42.22, 3.39
5. From salicylate containing rare earth complexes to their polymers

General aspects

As discussed in previous chapters, the aim of this thesis is to combine the physicochemical properties of ionic liquids with those of polymers especially with respect to new luminescent materials. As the formation and the properties of tetrakis(salicylatolanthanoidate) complexes of ionic liquids have been investigated, the next step will be to synthesize and investigate such compounds with a cationic polymer backbone bulk. This is especially interesting regarding the difference between the monomeric cation and its polymeric counterpart for the C$_2$Vim- and DADMA species and also regarding the lack of aromaticity in the DADMA polymer. Furthermore it should again be possible to gauge the impact of altering the aliphatic chain length in the cationic polymer bulk on the physicochemical properties.

Results and discussion

General discussion

With regard to previous experiments it was chosen to synthesize the polymeric complexes with a strategy combined from the experiences with the compounds described in chapter 2 and 3: First polymerize the vinylimidazolium and DADMA halides, conduct the anion metathesis yielding in the salicylate polymer and fuse these with the already synthesized lanthanoid salicylates. Attention has to be paid for sodium bromide impurities which have been found in the salicylate polymers even though they do not have any impact on the optical properties. As we saw with sole vinylimidazolium based polymers, the element analysis showed differences between the calculated and measured values (table 14). Again, AAS has been conducted to distinguish the sodium content of the samples and to extrapolate the elemental analysis data (table 15). In contrast to the sole poly-vinylimidazolium salicylates the values differ more. It has also be taken into account that some of the mass in the compounds is due to physisorbed or coordinated water,
what is indicated by the amount of water derived from TG data of these compounds (table 16), and the measurement error. However, taking the water content into consideration when calculating the theoretical EA-data does not or only slightly (1-2%) changes the values for the extrapolated total mass. As no NMR spectra could be recorded for the terbium compounds, due to their paramagnetism, it cannot be excluded, that this was caused from residual sodium or unreacted terbium salicylate entangled and retained by the polymer chains. The same argumentation can be used for (P-C₆Vim)[Tb(Sal)₄]. However, as expected with such complex compounds in polymer chemistry and an additional synthesis step, always residuals of the starting materials are retained in the compounds.

Table 14: Calculated and measured CHNS values of the prepared polymer tetrakissalicylatolanthanate and tetrakissalicylatoteterbate compounds.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(P-C₂Vim)[La(Sal)₄]</td>
<td>3.46</td>
<td>51.90</td>
<td>3.80</td>
<td>3.66/3.58</td>
<td>46.92/46.92</td>
<td>3.92/3.87</td>
</tr>
<tr>
<td>(P-C₂Vim)[Tb(Sal)₄]</td>
<td>3.37</td>
<td>50.60</td>
<td>3.76</td>
<td>0.40/0.46</td>
<td>45.56/45.55</td>
<td>3.47/3.35</td>
</tr>
<tr>
<td>(P-C₃Vim)[La(Sal)₄]</td>
<td>3.36</td>
<td>52.41</td>
<td>4.00</td>
<td>3.31/3.39</td>
<td>46.39/46.46</td>
<td>4.19/4.19</td>
</tr>
<tr>
<td>(P-C₃Vim)[Tb(Sal)₄]</td>
<td>3.31</td>
<td>51.19</td>
<td>3.94</td>
<td>3.22/3.17</td>
<td>44.96/44.89</td>
<td>3.83/3.92</td>
</tr>
<tr>
<td>(P-C₄Vim)[La(Sal)₄]</td>
<td>3.34</td>
<td>53.00</td>
<td>4.20</td>
<td>2.55/2.52</td>
<td>42.00/41.71</td>
<td>3.84/3.60</td>
</tr>
<tr>
<td>(P-C₄Vim)[Tb(Sal)₄]</td>
<td>3.26</td>
<td>51.76</td>
<td>4.10</td>
<td>0.12/0.13</td>
<td>45.82/45.82</td>
<td>3.12/3.20</td>
</tr>
<tr>
<td>(P-C₅Vim)[La(Sal)₄]</td>
<td>3.29</td>
<td>53.50</td>
<td>4.30</td>
<td>1.08/1.08</td>
<td>47.66/47.65</td>
<td>3.36/3.44</td>
</tr>
<tr>
<td>(P-C₅Vim)[Tb(Sal)₄]</td>
<td>3.21</td>
<td>52.30</td>
<td>4.27</td>
<td>1.95</td>
<td>45.52</td>
<td>3.62</td>
</tr>
<tr>
<td>(P-C₆Vim)[La(Sal)₄]</td>
<td>3.23</td>
<td>54.00</td>
<td>4.50</td>
<td>5.86</td>
<td>55.13</td>
<td>5.68</td>
</tr>
<tr>
<td>(P-C₆Vim)[Tb(Sal)₄]</td>
<td>3.16</td>
<td>52.83</td>
<td>4.43</td>
<td>3.71</td>
<td>48.10</td>
<td>5.00</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)₄]</td>
<td>1.70</td>
<td>53.14</td>
<td>4.46</td>
<td>1.42/1.39</td>
<td>49.79/49.79</td>
<td>4.30/4.44</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)₄]</td>
<td>1.70</td>
<td>51.87</td>
<td>4.35</td>
<td>1.33/1.37</td>
<td>47.25/47.46</td>
<td>4.13/4.25</td>
</tr>
</tbody>
</table>
Table 15: Measured CHNS and AAS values of the prepared polymer tetrakisalicylatolanthanate and tetrakisalicylatoterbiate compounds and total product mass extrapolated with the assumption, that NaBr/NaCl is the only impurity. (1st measurement/2nd measurement)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>N(%)</th>
<th>C(%)</th>
<th>H(%)</th>
<th>AAS :Na(%)</th>
<th>Total mass including NaBr/NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P-C\textsubscript{4}Vim)[La(Sal)]</td>
<td>3.66/3.58</td>
<td>46.92/46.92</td>
<td>3.92/3.87</td>
<td>0.73/0.98</td>
<td>98%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[Tb(Sal)]</td>
<td>0.40/0.46</td>
<td>45.56/45.55</td>
<td>3.47/3.35</td>
<td>7.39/7.34</td>
<td>110%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[La(Sal)]</td>
<td>3.31/3.39</td>
<td>46.39/46.46</td>
<td>4.19/4.19</td>
<td>2.66/2.31</td>
<td>105%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[Tb(Sal)]</td>
<td>3.22/3.17</td>
<td>44.96/44.89</td>
<td>3.83/3.92</td>
<td>2.44/2.54</td>
<td>102%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[La(Sal)]</td>
<td>2.55/2.52</td>
<td>42.0/41.71</td>
<td>3.84/3.6</td>
<td>1.11/0.98</td>
<td>85%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[Tb(Sal)]</td>
<td>0.12/0.13</td>
<td>45.82/45.82</td>
<td>3.12/3.2</td>
<td>3.45/3.78</td>
<td>106%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[La(Sal)]</td>
<td>1.08/1.08</td>
<td>47.66/47.65</td>
<td>3.36/3.44</td>
<td>2.58/2.99</td>
<td>90%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[Tb(Sal)]</td>
<td>1.95</td>
<td>45.52</td>
<td>3.62</td>
<td>1.62/1.88</td>
<td>81%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[La(Sal)]</td>
<td>1.6/1.49</td>
<td>45.03/44.18</td>
<td>6.4/5.06</td>
<td>3.63/3.07</td>
<td>101%</td>
</tr>
<tr>
<td>(P-C\textsubscript{4}Vim)[Tb(Sal)]</td>
<td>3.71</td>
<td>48.10</td>
<td>5.00</td>
<td>5.76</td>
<td>110%</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)]</td>
<td>1.42/1.39</td>
<td>49.79/49.79</td>
<td>4.3/4.44</td>
<td>4.54/4.51</td>
<td>104%</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)]</td>
<td>1.33/1.37</td>
<td>47.25/47.46</td>
<td>4.13/4.25</td>
<td>2.07/2.26</td>
<td>95%</td>
</tr>
</tbody>
</table>

**Thermal analysis**

Due to the fact that neither the sole vinylimidazolium salicylate polymers, nor the monomeric forms of the tetrakisalicylatolanthanates and -terbates showed any glass transition or melting/crystallization point, no DSC measurements have been conducted for the compounds described in this chapter. To determine the water content and the thermal stability of the compounds however, thermogravimetric measurements have been conducted. Water contents range from 0.9 to 2.37 water molecules per lanthanide atom. Some of the water may be coordinated and some physiosorbed to the compounds. The measured decomposition temperatures lie in the range of 210 °C - 230 °C and are pretty similar to those of the monomeric tetrakisalicylato complexes described in chapter 3. However, with regard to whether the terbium
or the lanthanum compound is decomposing first, no trend is observable. The considerable high thermal stability of these compounds supports their suitability for the desired application as phosphors.

Table 16: Water content and decomposition temperatures of the prepared tetrakissalicylatolanthanate and -terbate compounds derived from thermogravimetric analysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water content from TG in %</th>
<th>Water molecules/Ln$^{3+}$</th>
<th>$T_{\text{decomp}}$ in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P-C$_2$Vim)[La(Sal)$_4$]</td>
<td>2.48</td>
<td>1.1</td>
<td>216</td>
</tr>
<tr>
<td>(P-C$_2$Vim)[Tb(Sal)$_4$]</td>
<td>1.92</td>
<td>0.9</td>
<td>226</td>
</tr>
<tr>
<td>(P-C$_3$Vim)[La(Sal)$_4$]</td>
<td>2.92</td>
<td>1.4</td>
<td>212</td>
</tr>
<tr>
<td>(P-C$_3$Vim)[Tb(Sal)$_4$]</td>
<td>2.76</td>
<td>1.3</td>
<td>230</td>
</tr>
<tr>
<td>(P-C$_4$Vim)[La(Sal)$_4$]</td>
<td>3.54</td>
<td>1.7</td>
<td>232</td>
</tr>
<tr>
<td>(P-C$_4$Vim)[Tb(Sal)$_4$]</td>
<td>2.60</td>
<td>1.3</td>
<td>214</td>
</tr>
<tr>
<td>(P-C$_5$Vim)[La(Sal)$_4$]</td>
<td>5.37</td>
<td>2.7</td>
<td>220</td>
</tr>
<tr>
<td>(P-C$_5$Vim)[Tb(Sal)$_4$]</td>
<td>4.22</td>
<td>2.1</td>
<td>212</td>
</tr>
<tr>
<td>(P-C$_6$Vim)[La(Sal)$_4$]</td>
<td>3.26</td>
<td>1.6</td>
<td>212</td>
</tr>
<tr>
<td>(P-C$_6$Vim)[Tb(Sal)$_4$]</td>
<td>1.71</td>
<td>0.9</td>
<td>215</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)$_4$]</td>
<td>3.12</td>
<td>1.5</td>
<td>233</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)$_4$]</td>
<td>3.02</td>
<td>1.4</td>
<td>219</td>
</tr>
<tr>
<td>La(Sal)$_3$</td>
<td>7.45</td>
<td>2.4</td>
<td>218</td>
</tr>
<tr>
<td>Tb(Sal)$_3$</td>
<td>4.18</td>
<td>1.4</td>
<td>233</td>
</tr>
</tbody>
</table>
Optical properties

Luminescence spectroscopy

The excitation of the lanthanum compounds was recorded monitoring the emission of the salicylate ligand at 420 nm. For terbium compounds, the emission of the most intense $f-f$ $^{5}D_{4}→^{7}F_{5}$ transition was located at 542 nm. The excitation spectra show a broad band spanning from the deep UV region up to 400 nm, corresponding to the $\pi→\pi^*$ transitions of the salicylate ligand. For the terbium compounds, no typical sharp $f-f$-excitation bands could be monitored, which, as for the monomers described above corroborates to an energy transfer from the salicylate ligand to the optically active Tb$^{3+}$ center, which will be discussed below taking the emission spectra into account.

Figure 36: Excitation spectra of the prepared polymer tetrakis(salicylatolanthanate) and tetrakis(salicylatoterbiate) compounds recorded at room temperature with an emission wavelength of 420 nm for the lanthanum compounds and 542 nm for the terbium compounds.

All compounds show a higher absorption than their respective sole rare-earth salicylate. For the vinylimidazolium compounds this is due to the additional aromatic system apparent, and the forming of polar and apolar pockets due to the now complex anion. This argumentation can also be used for the appearance of the excitation spectrum of the DADMA moiety, which shows a similar excitation behavior (fig. 36).
5. From salicylate containing rare earth complexes to their polymers

![Emission spectra of the prepared polymeric tetrakis(salicylatolanthanate) compounds from 340 to 580 nm (left) recorded with an excitation wavelength of 311 nm. Dependence of the maximum emission energy of employed cation. Lanthanum salicylate is added for comparison reasons. *: Sole La(Sal)₃.](image)

Under broad UV irradiation (λₓₑₓₘₐₓ=366 nm) all lanthanum compounds exhibit bright blue luminescence easily observed by the naked eye. Emission spectra of the lanthanum compounds were recorded while exciting the samples at 310 nm (figure 37). The wavelength has been chosen to monitor the whole emission bands of the compounds ranging from 340 to 540 nm. As for the lanthanum compounds, no excitable f-electrons are apparent, it is expected, that only the auto fluorescence of the salicylate ligand can be monitored in these samples. Indeed, the emission spectra are very similar to these of the sole poly-vinylimidazolium based salicylates described in chapter 2 and those of sodium salicylate. The bands are centered in the blue region of the visible spectrum and centered at around 415 nm. The emission maxima of the compounds are also shifted depending on the aliphatic chain length attached to the imidazolium core in the polymeric cation backbone. The P-DADMA containing species shows a λₑₓₘₐₓ of 419 nm and is most bathochromically shifted. The compounds bearing the shortest and longest alkyl chain show the highest a λₑₓₘₐₓ with 417 nm for the ethyl bearing and 416 nm for the hexyl chain bearing polymer. The intermediate chain lengths show a more hypsochromic shift, most pronounced for the butyl chain carrying polymer (410 nm), and less pronounced for the C₅ (411 nm) and C₃ moiety (413 nm). Interestingly, this is the same trend as observed for the sole polyvinylimidazolium based salicylates (figure 39). As the anion is the same in all cases, this can solely be attributed to the length of the aliphatic side chain. The trend can be attributed to the formation of polar domains, cation-anion interactions, and steric demands of the aliphatic side...
chain of the imidazolium core. A detailed analysis of this behavior has been given in chapter 2 and can be transferred to these compounds. The absolute emission maxima however are all more bathochromically shifted compared to the compounds not bearing the lanthanum ion (figure 38). This indicates fewer energy lowering \( \pi-\pi \) interactions, due to the salicylate ligands being restrained by their attachment to the lanthanum ion leading to a bigger steric bulk and therefore a greater separation of the salicylates. Another explanation can be that four salicylate ligands are apparent per lanthanum unit. This leads to an overall charge of this complex anion distributed over a much bigger surface area compared to the sole poly-vinylimidazolium based salicylates, which contributes to less \( \pi-\pi \) interactions.

![Figure 38: Comparison of the emission maxima observed for the sole poly-vinylimidazolium based salicylates and the tetrakissalicylatolanthanate based polymers. Line is only added to guide the eye.](image-url)
5. From salicylate containing rare earth complexes to their polymers

![Emission spectra](image)

Figure 39: Emission spectra of the prepared polymer tetrakisalicylate terbiumates recorded at room temperature with an excitation wavelength of 310 nm.

The terbium compounds exhibit bright green luminescence under broad UV-irradiation ($\lambda_{\text{ex, max}}=366$ nm). This is also resembled by their emission spectra exhibiting the typical sharp $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions (figure 39). However as in the case of the monomeric complexes described in chapter 3, no broad band arising from the luminescence of the salicylate ligand could be observed. This also gives evidence of an efficient energy transfer from the salicylate ligand to the optically active Tb$^{3+}$ center. The proposed mechanism of the photonic processes in these materials can be seen in chapter 3 (scheme 9).

The quantum yields of the prepared compounds range from 18% ((P-C$_4$Vim)[LaSal$_4$]) to 69% ((P-C$_3$Vim)[TbSal$_4$]) and are always lower for the lanthanum containing samples than for the terbium ones. This is expected due to the salicylate ligand acting as an antenna, and thus enhancing the emission of the rare earth ion, which for the lanthanum compounds, only the autofluorescence of the ligand is responsible for the emission.
5. From salicylate containing rare earth complexes to their polymers

Table 17: Calculated quantum yields for the tetrakisalicylatotertbiate compounds. (*: Lifetime to short to measure with the equipment used. *^2: error smaller than significant value.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantum Yield in %</th>
<th>Life Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSal</td>
<td>56[^1]</td>
<td>*</td>
</tr>
<tr>
<td>La(Sal)$_3$</td>
<td>42 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>Tb(Sal)$_3$</td>
<td>55 ± 2</td>
<td>1.17 ± 0.07</td>
</tr>
<tr>
<td>(P-C$_2$Vim)[LaSal$_4$]</td>
<td>47 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(P-C$_2$Vim)[TbSal$_4$]</td>
<td>50 ± 2</td>
<td>9.44 ± 0.57</td>
</tr>
<tr>
<td>(P-C$_3$Vim)[LaSal$_4$]</td>
<td>30 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(P-C$_3$Vim)[TbSal$_4$]</td>
<td>69 ± 0</td>
<td>8.60 ± 0.41</td>
</tr>
<tr>
<td>(P-C$_4$Vim)[LaSal$_4$]</td>
<td>18 ± 0</td>
<td>*</td>
</tr>
<tr>
<td>(P-C$_4$Vim)[TbSal$_4$]</td>
<td>49 ± 1</td>
<td>10.14 ± 0.39</td>
</tr>
<tr>
<td>(P-C$_5$Vim)[LaSal$_4$]</td>
<td>39 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(P-C$_5$Vim)[TbSal$_4$]</td>
<td>41 ± 0 *^2</td>
<td>8.90 ± 0.89</td>
</tr>
<tr>
<td>(P-C$_6$Vim)[LaSal$_4$]</td>
<td>24 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(P-C$_6$Vim)[TbSal$_4$]</td>
<td>47 ± 1</td>
<td>8.97 ± 0.50</td>
</tr>
<tr>
<td>(P-DADMA)[LaSal$_4$]</td>
<td>40 ± 1</td>
<td>*</td>
</tr>
<tr>
<td>(P-DADMA)[TbSal$_4$]</td>
<td>64 ± 2</td>
<td>5.00 ± 0.01</td>
</tr>
</tbody>
</table>

However, no correlation between the chain lengths and the quantum yield has been observed. The only moiety containing no π-system in the cationic polymer backbone shows no really differing quantum yields in the cases of both, the lanthanum and terbium containing compounds.

However the quantum yields all lie in the same order of magnitude as sodium salicylate. This underlines the possibility for the use of these materials as phosphors for lighting applications.
Conclusion

A set of tetrakissalicylato lanthanate and terbate complexes bearing a polycationic diallyldimethylammonium backbone and vinylimidazolium backbones with subsequently prolonged aliphatic chain lengths from C₂ to C₆ has successfully been synthesized and characterized by NMR (for the lanthanum compounds only), IR spectroscopy, thermogravimetric analysis, elemental analysis and AAS. All compounds were optically investigated regarding their excitation and emission characteristics as well as their quantum yields. The lanthanum compounds show autofluorescence from the salicylate ligand only, with their emission maxima being hypsochromically shifted compared to sodium salicylate. The shift directly depends on the length of the aliphatic chain length attached to the imidazolium core. The terbium compounds only show the typical sharp f-f-transitions of terbium which indicates an efficient energy transfer from the close salicylate ligand to the optically active center. The high quantum yield of the compounds, as well as their thermal stability shows the eligibility of the prepared compounds for the desired application as phosphors.

Experimental section

The synthesis of the starting materials has been discussed in the chapters above.

Synthesis of the 1-n-alkyl-3vinylimidazolium tetrakissalicylatolanthoanate polymers:

In a typical reaction the polymer salicylate and the respective rare earth salicylate were both separately dissolved in a small amount of anhydrous ethanol. Combining both solutions led to the precipitation of a white solid. The reaction mixture was then stirred for 24 hours at room temperature. The white precipitates were filtered off and dried in vacuo for 48 hours at room temperature.

Exact masses and yields can be seen in table 18
Table 18: Utilised masses of the starting material and yields of the synthesis for the 1-n-alkyl-3-vinylimidazolium tetrakisalicylatolanthanate polymers.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Molar mass (g/mol)</th>
<th>Employed mass (g)</th>
<th>Product</th>
<th>Molar mass (g/mol)</th>
<th>Yield (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-C₃Vim(Sal)</td>
<td>260.30</td>
<td>0.19</td>
<td>(P-C₃Vim)[La(Sal)₄]</td>
<td>810.54</td>
<td>0.14</td>
<td>24.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00</td>
<td>(P-C₃Vim)[Tb(Sal)₄]</td>
<td>830.56</td>
<td>0.33</td>
<td>10.38</td>
</tr>
<tr>
<td>P-C₅Vim(Sal)</td>
<td>274.30</td>
<td>0.13</td>
<td>(P-C₅Vim)[La(Sal)₄]</td>
<td>824.57</td>
<td>0.17</td>
<td>45.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>(P-C₅Vim)[Tb(Sal)₄]</td>
<td>844.58</td>
<td>0.20</td>
<td>50.70</td>
</tr>
<tr>
<td>P-C₄Vim(Sal)</td>
<td>288.30</td>
<td>0.07</td>
<td>(P-C₄Vim)[La(Sal)₄]</td>
<td>838.57</td>
<td>0.10</td>
<td>53.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>(P-C₄Vim)[Tb(Sal)₄]</td>
<td>858.62</td>
<td>0.40</td>
<td>44.96</td>
</tr>
<tr>
<td>P-C₆Vim(Sal)</td>
<td>302.30</td>
<td>0.21</td>
<td>(P-C₆Vim)[La(Sal)₄]</td>
<td>852.62</td>
<td>0.30</td>
<td>51.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>(P-C₆Vim)[Tb(Sal)₄]</td>
<td>872.64</td>
<td>0.43</td>
<td>72.93</td>
</tr>
<tr>
<td>P-ClVim(Sal)</td>
<td>316.30</td>
<td>0.19</td>
<td>(P-ClVim)[La(Sal)₄]</td>
<td>866.57</td>
<td>0.47</td>
<td>89.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>(P-ClVim)[Tb(Sal)₄]</td>
<td>886.67</td>
<td>0.23</td>
<td>39.66</td>
</tr>
<tr>
<td>P-DADMA(Sal)</td>
<td>262.17</td>
<td>0.40</td>
<td>(P-DADMA)[La(Sal)₄]</td>
<td>813.58</td>
<td>0.96</td>
<td>76.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>(P-DADMA)[Tb(Sal)₄]</td>
<td>833.6</td>
<td>0.92</td>
<td>72.65</td>
</tr>
</tbody>
</table>

Poly-1-ethyl-3-vinylimidazoliumtetrakisalicylatolanthanate (P-C₂Vim)[La(Sal)₄]:

¹H NMR (200 MHz, DMSO-d₆) δ/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H), 7.20 (t, 4H), 6.66 (t, 8H), 4.23 (q, 2H), 3.42 (m, 5H), 1.45 (m, 3H).

MS: ESI⁺: m/z = 686.74 [La(Sal)₄]⁺, m/z = 548.89 [La(Sal)₃]⁺, m/z = 411.06 [La(Sal)₂]⁺
5. From salicylate containing rare earth complexes to their polymers

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.46, 51.90, 3.80 / 3.62, 46.92, 3.90

Poly-1-propyl-3-vinylimidazoliumtetrakis salicylatolanthanate (P-C3Vim)[La(Sal)4]:

1H NMR (200 MHz, DMSO-d6) δ/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H) = 14.97 (s, 1H), 9.73 (m, 1H), 8.15 (s, 1H), 7.94 (s, 1H), 7.72 (d, 4H), 7.20 (t, 4H), 6.67 (t, 8H), 3.89 (m, 2H), 3.39 (s, 6H), 1.65 (m, 2H), 0.74 (s, 3H).

MS: ESI: m/z = 686.74 [La(Sal)4]−, m/z = 548.88 [La(Sal)3]−, m/z = 411.03 [La(Sal)2]−

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.36, 52.41, 4.00 / 3.35, 46.43, 4.19

Poly-1-butyl-3-vinylimidazoliumtetrakis salicylatolanthanate (P-C4Vim)[La(Sal)4]:

1H NMR (200 MHz, DMSO-d6) δ/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H) = 9.60 (s, 1H), 8.23 (s, 1H), 7.96 (s, 1H), 7.72 (d, 4H), 7.23 (t, 4H), 6.69 (t, 8H), 4.19 (s, 2H), 3.37 (s, 7H), 2.12 (s, 2H), 1.24 (s, 2H), 0.9 (s, 3H).

MS: ESI: m/z = 686.75 [La(Sal)4]−, m/z = 548.89 [La(Sal)3]−, m/z = 411.02 [La(Sal)2]−

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.34, 53.00, 4.20 / 2.54, 41.86, 3.72

Poly-1-pentyl-3-vinylimidazoliumtetrakis salicylatolanthanate (P-C5Vim)[La(Sal)4]:

1H NMR (200 MHz, DMSO-d6) δ/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H), δ = 15.21 (s, 1H), 9.67 (s, 1H), 7.96 (d, 2H), 7.69 (d, 4H), 7.20 (t, 4H), 6.65 (t, 8H), 3.92 (s, 3H), 3.34 (s, 3H), 1.69 (d, 2H), 1.23 (s, 1H), 0.74 (s, 5H).

MS: ESI: m/z = 686.75 [La(Sal)4]−, m/z = 548.90 [La(Sal)3]−, m/z = 411.02 [La(Sal)2]−

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.29, 53.50, 4.30 / 1.08, 47.66, 3.40
5. From salicylate containing rare earth complexes to their polymers

Poly-1-hexyl-3-vinylimidazoliumtetakisalicylatolanthanate (P-C$_6$Vim)[La(Sal)$_4$]:

$^1$H NMR (200 MHz, DMSO-$d_6$) $\delta$/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H), = 15.03 (s, 1H), 9.77 (s, 1H), 7.95 (s, 2H), 7.71 (s, 4H), 7.20 (s, 4H), 6.68 (d, 8H), 3.88 (s, 2H), 3.36 (s, 8H), 1.66 (s, 2H), 1.07 (d, 6H), 0.78 (s, 3H).

MS: ESI: m/z = 686.75 [La(Sal)$_4$]$^-$ m/z = 548.91 [La(Sal)$_3$]$^-$ m/z = 411.03 [La(Sal)$_2$]$^-$

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.23, 54.00, 4.50 / 5.86, 55.13, 5.68

Poly-diallyldimethylammoniumtetakisalicylatolanthanate (P-DADMA)[La(Sal)$_4$]:

$^1$H NMR (200 MHz, DMF-$d_6$) $\delta$/ppm = 9.58 (s, 1H), 8.21 (s, 1H), 7.95 (s, 1H), 7.72 (d, 4H), 7.92 (s, 4H), 7.22 (s, 4H), 6.73 (s, 8H), 3.58 (q, 2H), 1.17 (t, 3H)

MS: ESI: Not measurable

EA (calculated N%, C%, H%/measured N%, C%, H%): 1.70, 53.14, 4.46 / 1.41, 49.79, 4.36

Poly-1-ethyl-3-vinylimidazoliumtetakisalicylatoterbate (P-C$_2$Vim)[Tb(Sal)$_4$]:

MS: ESI: m/z = 706.74 [Tb(Sal)$_4$]$^-$ m/z = 568.92 [Tb(Sal)$_3$]$^-$ m/z = 431.06 [Tb(Sal)$_2$]$^-$

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.37, 50.60, 3.76 / 0.45, 45.56, 3.41

Poly-1-propyl-3-vinylimidazoliumtetakisalicylatoterbate (P-C$_3$Vim)[Tb(Sal)$_4$]:

MS: ESI: m/z = 706.76 [Tb(Sal)$_4$]$^-$ m/z = 568.93 [Tb(Sal)$_3$]$^-$ m/z = 431.04 [Tb(Sal)$_2$]$^-$

EA (calculated N%, C%, H%/measured N%, C%, H%): 3.31, 51.19, 3.94 / 3.20, 44.93, 3.88
5. From salicylate containing rare earth complexes to their polymers

Poly-1-butyl-3-vinylimidazoliumtetrakis salicylatoterbate (P-C_4Vim)[Tb(Sal)_4]:

MS: ESI: m/z = 706.66 [Tb(Sal)_4]^−, m/z = 568.92 [Tb(Sal)_3]^−, m/z = 431.06 [Tb(Sal)_2]^−

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.26, 51.76, 4.10 / 0.13, 45.82, 3.16

Poly-1-pentyl-3-vinylimidazoliumtetrakis salicylatoterbate (P-C_5Vim)[Tb(Sal)_4]:

MS: ESI: m/z = 706.72 [Tb(Sal)_4]^−, m/z = 568.91 [Tb(Sal)_3]^−, m/z = 431.06 [Tb(Sal)_2]^−

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.21, 52.30, 4.27 / 1.95, 45.52, 3.62

Poly-1-hexyl-3-vinylimidazoliumtetrakis salicylatoterbate (P-C_6Vim)[Tb(Sal)_4]:

MS: ESI: m/z = 706.70 [Tb(Sal)_4]^−, m/z = 568.85 [Tb(Sal)_3]^−, m/z = 431.03 [Tb(Sal)_2]^−

EA (calculated N%,C%,H%/measured N%,C%,H%): 3.16, 52.83, 4.43 / 3.71, 48.10, 5.00

(P-DADMA)[Tb(Sal)_4]:

MS: ESI: Not measurable

EA (calculated N%,C%,H%/measured N%,C%,H%): 1.70, 51.87, 4.35 / 1.35, 47.36, 4.16
6. Comparison of the tetrakissalicylatolanthanate and -terbate containing monomers and polymers

6. Comparison of the tetrakissalicylatolanthanate and -terbate containing monomers and polymers

For the C₂Vim and the DADMA cation containing tetrakissalicylatolanthanate and -terbate compounds both the monomeric and the polymeric form has been synthesized and investigated. This offers the opportunity to compare the thermic and luminescent behaviour to gauge the effect of the polymerization on the resulting material.

Thermal analysis:

The obtained decomposition temperatures from thermogravimetric analysis all are accumulated in a region between 214°C and 232°C (table 19). The only exception is (DADMA)[Tb(Sal)₄] with a decomposition temperature of 263°C. This can either arise from minor impurities in the material or more probable from π-π interactions of the two allyl groups apparent in this monomer, which could result in a more stable compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_{decomp} (TG_{onset}) in °C</th>
<th>Residual mass in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₂Vim)[La(Sal)₄]</td>
<td>228</td>
<td>27.0</td>
</tr>
<tr>
<td>(P-C₂Vim)[La(Sal)₄]</td>
<td>216</td>
<td>24.3</td>
</tr>
<tr>
<td>(C₂Vim)[Tb(Sal)₄]</td>
<td>232</td>
<td>43.0</td>
</tr>
<tr>
<td>(P-C₂Vim)[Tb(Sal)₄]</td>
<td>220</td>
<td>25.9</td>
</tr>
<tr>
<td>(DADMA)[La(Sal)₄]</td>
<td>226</td>
<td>30.2</td>
</tr>
<tr>
<td>(P-DADMA)[La(Sal)₄]</td>
<td>214</td>
<td>19.3</td>
</tr>
<tr>
<td>(DADMA)[Tb(Sal)₄]</td>
<td>263</td>
<td>32.0</td>
</tr>
<tr>
<td>(P-DADMA)[Tb(Sal)₄]</td>
<td>220</td>
<td>29.0</td>
</tr>
</tbody>
</table>
6. Comparison of the tetrakissalicylatolanthanate and -terbate containing monomers and polymers

Luminescence spectroscopy

Figure 40: Comparison of the excitation spectra for the monomeric and polymeric forms of the C$_2$Vim (top left) and DADMA (top right) cation based tetrakissalicylatolanthanates, and the monomeric and polymeric forms of the C$_2$Vim (bottom left) and DADMA (bottom right) cation based tetrakissalicylatoterbates. Spectra were recorded at room temperature with an emission wavelength of 420/430 nm for the lanthanum compounds and 542 nm for the terbium compounds respectively.

Figure 40 shows the comparative excitation spectra of the prepared monomers and polymers. For the terbium containing samples, the polymerization has only a minor influence on the excitation
6. Comparison of the tetrakisalicylatolanthanate and -terbate containing monomers and polymers

spectra. The C$_2$-Vim polymer shows only a slightly lower excitation from 350 to 400 nm. This arises from the absence of the conjugated vinyl double bond apparent in the monomer. For the DADMA compounds, the excitation behavior is nearly the same for the monomer and the polymer. This indicates that isolated double bonds do not contribute to the luminescent behavior.

As the excitation behavior in the lanthanum compounds only relies on the luminescent properties of the salicylate ligand, it can be used as a probe to investigate the $\pi$-$\pi$ interactions in between the salicylate ligands and the monomeric cation or the polymeric cation backbone. For these compounds, the change in the appearance of the excitation spectra is more pronounced: The band at 362 nm decreases in the case of the vinylimidazolium species and completely vanishes in case of the DADMA moiety. This can be discussed properly taking the emission spectra of the lanthanum compounds into account:

![Emission Spectra](image)

Figure 41: Comparison of the emission spectra for the monomeric and polymeric forms of the C$_2$Vim (left) and DADMA (right) cation based tetrakisalicylatolanthanates. Spectra were recorded at room temperature with an excitation wavelength of 310 nm.

The appearance of the emission spectra of the vinylimidazolium monomer and polymer do not differ much, while the DADMA containing monomer shows an additional band at 350 nm and a more pronounced emission up to its maximum at 403 nm probably arising from the allylic double bonds interfering with the tetrakisalicylato anion, as this band cannot be observed for the
6. Comparison of the tetrakisalicylatolanthanate and -terbate containing monomers and polymers

sole DADMA(Sal) polymer (see chapter 3). As seen in figure 41, The emission maxima of the polymers are hypsochromic shifted compared to the monomers. With a value of 16 nm this is more pronounced for the vinylimidazolium polymer than for the DADMA polymer, which shows a shift of 11 nm. This indicates a decrease in the π-π interactions and therefore a closer proximity of the tetrakisalicylated anion and the respective cation. This leads to less quenching and better emission as seen in the quantum yields of these compounds (discussion below). The fact, that the shift is more pronounced for the C2-Vim species also indicates, that the imidazolium core of the cationic polymer bulk is decreased due to the polymerization and therefore closer to the luminescent salicylate ligand, contributes to these emission characteristics e.g. due to an energy transfer from the imidazolium core to the salicylate. This fact however cannot be investigated by means of luminescence spectroscopy as the excitation characteristics of the imidazolium core (chaper 1) and these of the salicylate ligand are too similar to only excite the imidazolium cationic polymer backbone only.

![Figure 42: Comparison of the emission spectra for the monomeric and polymeric forms of the DADMA and C2Vim cation based tetrakisalicylatoterbates. Spectra were recorded at room temperature with an emission wavelength of 542 nm.](image)

As seen in figure 42, the emission characteristics of the terbium compounds do not change. This is expected, as in these compounds the f-electrons solely are responsible for their emission. The salicylate emission is completely supressed due to the efficient energy transfer to the optically
6. Comparison of the tetrakissalicylatolanthanate and -terbate containing monomers and polymers

active terbium center. Its emission characteristics are defined by the shielded $f$-electrons, and therefore the typical $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3 f.f$-transitions are clearly visible in the emission spectra of these compounds.

![Figure 43](image_url)

**Figure 43:** Comparison of the quantum yields for the monomeric and polymeric forms of the DADMA and C$_2$Vim cation based tetrakissalicylatoterbates. Spectra were recorded exciting the salicylate ligand at 310 nm and the respective emission wavelength of the compound (420/430 nm for lanthanum and 542 for the strongest $^5D_4 \rightarrow {}^7F_5 f.f$ transition in the terbium compounds).

Figure 43 shows the quantum yields of each the polymeric and monomeric forms of the respective lanthanum and terbium compounds. First off, it is clearly visible that the polymerization has a greater influence on the quantum yields of the lanthanum compounds than on those of the terbium compounds. This can be rationalized, as the lanthanum compound lacks $f$-electrons, which are primarily responsible for the emission behaviour of terbium. Thus the emission characteristics are solely depending on the salicylate ligand. For the terbium C$_2$Vim-moiety the quantum yield decreases by 24%, while for the respective DADMA-moiety, the change is negligible due to the error of the measurement. This indicates that the conjugated vinyl bond apparent in the C$_2$Vim species, together with the imidazolium core contributes to the antenna effect of the salicylate ligand due to anion-cation interaction. The allylic double bonds of
6. Comparison of the tetrakis(salicylato)lanthanate and -terbato containing monomers and polymers

the DADMA species are isolated and lack an aromatic π-system, which lowers their contribution to the emission behavior and quantum yields of these compounds. Interestingly, the impact of the polymerization has a pronounced effect on the quantum yield of the lanthanum containing compounds. For the C₂Vim containing compound, the quantum yield increases by a factor of 3.4 and for the DADMA containing species by a factor of 5.7. This trend is in accordance with the hypsochromic shift observed in the emission spectra of the respective monomers and polymers:

The C₂Vim species shows a shift of 11 nm and the DADMA compound a shift of 16 nm. The hypsochromic shift indicates an increase in the π-π interaction in these compounds which results in a significantly higher quantum yield.
7. Luminescent Organic-Inorganic Hybrid Materials based on Lanthanide-doped Ionic Polymers with color tuneability

Figure 44: Photograph of two of the prepared organic-inorganic hybrid materials: 5 mol% TbCl$_3$ in P-C$_3$VimBr (top); 5 mol% EuCl$_3$ in P-C$_3$VimBr (bottom).

General aspects

In the previous chapters it was shown, that the luminescent properties of vinylimidazolium based ionic polymers can be enhanced and tuned depending on either another anion, or the inclusion of complex terbium anions containing the salicylate ligand. However, previous work in our group showed, that the reaction of anhydrous lanthanide halides into the corresponding halide ionic liquid leads to compounds with the general composition [Cat]$_n$[Ln$^{n+}$X$_6$] such as [C$_{12}$mim]$_4$[EuBr$_6$], [bpytr]$_4$[LnI$_6$][Tf$_2$N], (Ln = La, Er) or [C$_{12}$mim]$_3$[TbBr$_6$]. Especially for the
terbium and europium based complexes the ionic liquid cation enhances their luminescent properties, either by an energy transfer from the ionic liquid cation to the optically active rare-earth ion or the compounds obtain the ability to be by color tunable. As seen above, the insertion of rare earth compounds is also possible for vinylimidazolium polymers, where the salicylate ligand acts as an efficient antenna. The next step thus is to introduce the trivalent bromide of europium and the trivalent chlorides and bromides of terbium into these ionic liquids to form poly-(1-vinyl-3-n-alkyl-imidazolium) cations with a mixture of halide (X') and halolanthanate counterions, [Ln₃X₃]^{3x-y}. If this is done in different doping concentrations the effect of multiphonon quenching as well as the color tuneability of these compounds can be studied.

**Results and discussion**

1-n-Alkyl-3-vinylimidazolium bromide ILs, prepared by quaternization of 1-vinylimidazole, bearing different alkyl chain lengths (C₂-C₆) were first polymerized via free radical polymerization using AIBN in CHCl₃ chapter 2.

The synthesized poly(1-vinyl-3-n-alkyl-imidazolium bromides) were doped with trivalent lanthanide halides by combining their ethanolic solutions followed by evaporation of the solvent (Scheme2). Different molar ratios of dopant lanthanide halide (1, 5, 10, 20 mol% with respect to the number of imidazolium units) were explored in order to study the influence of the
concentration on the photophysical properties. Tb$^{3+}$ and Eu$^{3+}$ were chosen, not only because they are widely used as green and red emitters but also because, especially in the case of Eu$^{3+}$, the optical properties depend strongly on the local coordination environment of the lanthanide ion, which is resembled by the ratio of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transition intensities. Thus, the lanthanide ion may serve as a probe for the local environment in the polymer.$^{[93]}$ In order to gauge the effect of the halide ion, both terbium chloride and bromide where tested. Chloride is a stronger ligand compared to bromide, whereas bromide has a higher mass. For europium, it was only possible to study the chloride, due to the tendency of the bromide to form Eu$^{2+}$. In contrast to their chloride analogues, bromide polymers bear the advantage of an easy and clean synthesis. The resulting materials could be described chemically as poly-((1-vinyl-3-n-alkyl-imidazolium) cations with a mixture of halide (X') and halolanthanate counterions, [Ln$_x$X$_y$]$^{3+}$.$^{[94]}$

**Luminescence spectroscopy**

Photoluminescence spectroscopy was performed to investigate the photophysical properties of the as-prepared doped polymer materials. The steady state emission spectra were recorded under excitation of the most intense $f-f$ transitions of the respective lanthanide ion, namely $^5L_6 \leftarrow ^7F_0$ at 393 nm for Eu$^{3+}$ and $^5D_6 \leftarrow ^7F_6$ at 377 nm for Tb$^{3+}$. As can be seen in Figures 45 and 46 for the propyl polymers (P-C$_3$VimBr) with different lanthanide doping concentrations, the characteristic emission bands caused by the typical $f-f$ transitions of Eu$^{3+}$ or Tb$^{3+}$ are present. In addition, a broad underlying band with a maximum in the blue-green region is visible, particularly for low doping concentrations. This band can also be observed in the undoped polymers and arises from $\pi^* \rightarrow \pi$ transitions in the imidazolium head groups.$^{[95]}$ This can be further confirmed by time-delayed emission spectroscopy (see SI). As expected in the spectra recorded with a delay of 0.05 ms, the broad band is no longer visible due to the relatively short lived luminescence of $\pi^* \rightarrow \pi$ transitions.$^{[95]}$

For Eu$^{3+}$-containing samples, calculating the ratio of the intensities of the hypersensitive electric-dipole transition $^5D_0 \rightarrow ^7F_2$ (610 nm) and magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition (590 nm) gives the asymmetry ratio, which can be used to analyze the local environment of the lanthanide ion in the polymer.$^{[96]}$ The intensity of the hypersensitive electric-dipole transition depends strongly on the site symmetry of the Eu$^{3+}$ ion, whilst the magnetic dipole transition is insensitive to
environmental differences. For the doped PIL samples, this asymmetry ratio \( (\frac{\langle 5 \text{D}_0 \rightarrow 7 \text{F}_1 \rangle}{\langle 5 \text{D}_0 \rightarrow 7 \text{F}_2 \rangle}) \) is found to vary only slightly from one sample to another, calculated close to 0.25. The fact that the \( 5 \text{D}_0 \rightarrow 7 \text{F}_2 \) emission is much more intense suggests that the Eu\(^{3+}\) ion is in an asymmetric environment, which points to a mixed chloride/bromide ligand sphere.\[^{97}\] Typically upon reacting lanthanide trihalides with organic halides octahedral hexahalogenido complex anions are obtained.\[^{98-100}\] If the ligand sphere would contain the same halide, a much higher asymmetry ratio would be expected than found. E.g. in \([\text{C}_{12}\text{mim}]_4\text{EuBr}_6\text{Br} \) a value of 1.26 is found,\[^{101}\] similar values have been found for \([\text{pyH}]_3\text{EuX}_3\) (\(\text{pyH} = \text{pyridinium}, \text{X} = \text{Cl, Br} \)).\[^{102}\]

In the elpasolite \(\text{Cs}_2\text{NaEuCl}_6\)\[^{103-104}\] where Eu\(^{3+}\) is coordinated by a slightly distorted octahedron of chloride anions the value is 1.4. The characteristics of the Eu\(^{3+}\) emission does not vary greatly for different doping concentrations of EuCl\(_3\) in P-C\(_3\)VimBr. However, the lower the dopant ion concentration, the more intense is the emission from \(\pi \rightarrow \pi^*\) transitions from the imidazolium group relative to the emission of Eu\(^{3+}\) (figure 45).

![Figure 45: Emission spectra of P-C\(_3\)VimBr doped with different concentrations of EuCl\(_3\).](image)

By comparing the emission spectra of the same doping concentration in polymers bearing different chain lengths no distinct changes can be observed.
7. Luminescent Organic-Inorganic Hybrid Materials based on Lanthanide-doped Ionic Polymers

Similar to observations made for the Eu$^{3+}$ containing samples, the emission spectra of the Tb$^{3+}$ containing samples show that the intensities of the emission caused by the Tb$^{3+}$ fluorescence transitions increases with increasing Tb$^{3+}$ concentration, relative to the emission intensity originating from $\pi\rightarrow\pi^*$ transitions (Fig. 46). Tb$^{3+}$ is known to be an efficient emitter of green light originating from electronic transitions from the electronically excited $^5$D$_4$ level to the $^7$F$_3$ multiplet of the ground state. Corresponding emission bands are apparent in the measured emission spectra (figure 46). A notable difference in the emission spectra of the same polymer but doped with TbCl$_3$ and TbBr$_3$ can be observed, which can be best seen in the line shape of the most intense $^5$D$_4\rightarrow^7$F$_5$ emission for the highest (20%) doping concentration, as the intensity for this transition is slightly decreasing (figure 46). This is probably due to the different coordination environments of the Tb$^{3+}$ ion in these samples, which is expected as one bears a mixed chloride-bromide ligand sphere, and the other only bromide. Indeed, this is a common observation for trivalent terbium in different environments.

![Emission Spectra](image)

Figure 46: Left: emission spectrum of TbBr$_3$ in P-C$_3$VimBr ; right: emission spectrum for TbCl$_3$ in P-C$_3$VimBr.

Excitation spectra were also recorded and are given in figure 47 for the propyl bearing polymer samples. In the case of Eu-containing samples, the emission was monitored at the most intense $^7$F$_0\rightarrow^5$D$_2$ transition (610 nm); while for Tb-containing samples the $^5$D$_4\rightarrow^7$F$_5$ emission was monitored (547 nm). As expected, a series of absorption lines are apparent corresponding to the characteristic f-f transitions of the respective lanthanide ion. For both, Tb$^{3+}$ and Eu$^{3+}$ doped
samples broad bands originating from the polymer with a maximum around 315 nm were observed, which decrease in relative intensity with increasing doping concentration. For the Tb\(^{3+}\) doped samples, an additional broad band is observed, centered around 280 nm corresponding to allowed \(f-d\) electronic transitions (\(^7F_0 \rightarrow ^9D\)).\(^{[105]}\)

![Figure 47: Excitation spectra of EuCl\(_3\) in P-C\(_3\)VimBr (left); excitation spectra of TbCl\(_3\) in P-C\(_3\)VimBr (middle); excitation spectra of TbBr\(_3\) in P-C\(_3\)VimBr (right).](image)

The excitation band at 315 nm corresponds to an absorption of the polymers due to \(\pi \rightarrow \pi^*\) transitions. Exciting directly into this band gives a noticeably brighter lanthanide emission, and better resolved spectra could be recorded (figure 48).

![Figure 48: Emission spectra of EuCl\(_3\) in P-C\(_3\)VimBr (left); excitation spectra of TbCl\(_3\) in P-C\(_3\)VimBr (middle); excitation spectra of TbBr\(_3\) in P-C\(_3\)VimBr (right).](image)

This may suggest that an energy transfer process takes place in these samples, whereby energy initially absorbed by the organic polymer is transferred to the lanthanide ions, which then subsequently emit. This process is illustrated in Scheme 11. This would explain the visibly much brighter emission, as the formally allowed \(\pi \rightarrow \pi^*\) transitions in the polymer would absorb much more strongly than the parity forbidden \(f-f\) transitions. Sensitization of lanthanide ions using
organic molecules is widely reported\textsuperscript{106-107} and finds use in different applications such as biolabelling, solar cells, organic electroluminescent devices and light emitting diodes.\textsuperscript{108-111} Imidazolium cation to lanthanide energy transfer has already been reported for ionic liquid crystals.\textsuperscript{97} To further corroborate this hypothesis, time-delayed excitation spectra were recorded using a delay of 0.5 ms, thereby eliminating any effect from short-lived organic luminescence, which spans the entire visible spectrum (figure 49). It can be seen in the example spectrum of a Tb\textsuperscript{3+} doped polymer that the broad band, situated at 315 nm in the steady state spectra is no longer prominent, however, the strong band with a maximum at around 280 nm due to the $^7F_6 \rightarrow ^9D_{f-d}$ transition is clearly visible and unperturbed by any signal resulting from the polymer. In contrast, in the spectrum of the Eu\textsuperscript{3+} doped propyl bearing polymer $f-f$ absorption and short waved UV-absorption lines are apparent\textsuperscript{112}. Although the given resolution is low and does not allow a clear distinction of the observed short waved UV $f-f$ absorption lines, the apparent broad absorption band may be assigned to originate from an energy transfer from the polymer to the luminescent Eu\textsuperscript{3+} species (figure 49).

Figure 49: Time resolved (with delay 0.05 ms) vs. steady state excitation spectra of P-C\textsubscript{3}VimBr doped with 5% TbBr\textsubscript{3} (left) and P-C\textsubscript{3}VimBr doped with 5% EuCl\textsubscript{3} (right).
7. Luminescent Organic-Inorganic Hybrid Materials based on Lanthanide-doped Ionic Polymers

Scheme 11: Proposed energy level diagram for the energy transfer from the polymeric ionic media to the trivalent lanthanide ion.

Emission lifetimes have also been calculated from the measurement of photoluminescence decay curves of all polymers. Double exponentials were needed to fit all decay curves, indicating activator ions present in different environments within the same material. Average lifetimes were therefore calculated (figure 50). Eu$^{3+}$-doped polymers possess systematically shorter lifetimes than their Tb$^{3+}$ counterparts. This may be due to the smaller energy gap between the lowest excited state and the ground state, which is easier to bridge via vibrational relaxation. Furthermore, a trend is observable in the Eu$^{3+}$ doped series, where the average lifetime decreases with increasing concentration of dopant (1% gives 0.75 ms, 20% gives 0.35 ms in the case of P-C$_3$VimBr). This is a typical effect in inorganic materials, often referred to as concentration quenching.[113] They are significantly longer for the C$_4$ and C$_3$ polymers, than for all others. For P-C$_2$VimBr, the lanthanide-lanthanide distance is supposed to be the shortest making concentration quenching more likely than in polymers bearing sterically more demanding cation units. Increasing the steric bulk by increasing the chain length helps to increase the lanthanide-lanthanide distance and therefore minimizes concentration quenching. As a counter effect, vibrational quenching due to the presence of more C-H bonds is augmented. At intermediate chain lengths (C$_3$ and C$_4$), an optimal balance between these two effects is realized.
Quantum yields for the europium containing samples were also calculated and range from 0.03 to about 1.2% (figure 52). The Quantum yield decreases with higher doping concentrations. The trend is in good agreement with the lifetimes observed for all samples, giving proof of enhanced quenching with growing doping concentration, corresponding to the described effect of concentration quenching.

Figure 51: Calculated quantum yields for the Eu$^{3+}$ doped polymers taken with an excitation wavelength of 393 nm and an emission wavelength of 610 nm.
The prepared Eu\(^{3+}\) and Tb\(^{3+}\) doped materials exhibit a photoluminescence emission-color which was proven to be tunable by variation of the applied excitation wavelength\(^{[89]}\). As the dopant lanthanide species, as well as the ionic polymer host material emit light upon photo-excitation, the superposition of both, the dopant and the polymer emission generates an overall emission with different color impression in dependence with the respective excitation wavelength. CIE-color coordinates were calculated from emission spectra, monitored at different excitation wavelength (figure 53). The respective color coordinates demonstrate that the emission color is tunable from pure and characteristic green Tb\(^{3+}\) or deep red Eu\(^{3+}\) emission to pure white bluish emission resulting from the ionic polymer. In between, several emission colors are realized via superposition of the respective lanthanide and polymer emission.
Conclusion

A simple route to luminescent polymer composite materials has been established by dispersing lanthanide halides into ionic polymers based on 1-vinyl-3-alkylimidazolium bromides. As expected, characteristic absorption lines are visible rising from the typical \( f-f \)-transitions. In addition a broad band spanning from 280 to 400 nm centered at 315 nm is visible which corresponds to the \( \pi \rightarrow \pi^* \) transitions of the polymer. The ratio between the latter and the \( f-f \)-transitions decreases with higher doping concentrations. After excitation of the \( f-f \)-transitions at 393 nm for Eu\(^{3+} \) and 377 nm for Tb\(^{3+} \) respectively, the Eu\(^{3+} \) doped samples showed to exhibit the typical \( ^5D_0 \rightarrow ^7F_0, \ ^5D_0 \rightarrow ^7F_1, \ ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_3 \ ^5D_0 \rightarrow ^7F_4 \ f-f\)-transitions and thus emitting in the red region of the visible spectrum, while the Tb\(^{3+} \) doped samples exhibited green emission due to the \( ^5D_4 \rightarrow ^7F_6, \ ^5D_4 \rightarrow ^7F_5, \ ^5D_4 \rightarrow ^7F_4 \) and \( ^5D_4 \rightarrow ^7F_3 \ f-f\)-transitions. After excitation into the above mentioned broad band of the polymer at 315 nm the emission spectra recorded showed the same appearance as those directly exciting into the \( f-f \)-transitions but with higher intensities. This indicates that an energy transfer from the polymer backbone to the lanthanide ion may be possible. Time delayed luminescence spectroscopy which eliminates the appearance of the short living emission of the polymers revealed that this is not the case for the terbium doped samples, but however that an energy transfer may take place for the europium doped samples. Quantum yields calculated for the europium doped samples showed to rather low in the range of 0.2-1.7\% decreasing with higher doping concentration due to concentration quenching. Regarding the length of the alkyl chain in the polymer backbone, no trend could be observed. The respective color coordinates demonstrate that the emission color is tunable from pure and characteristic green Tb\(^{3+} \) or deep red Eu\(^{3+} \) emission to pure white bluish emission resulting from the ionic polymer. In between, several emission colors are realized via superposition of the respective lanthanide and polymer emission.
Experimental Section

Materials and Methods

Tb$_4$O$_7$ (99.99%) was purchased from SmartElements, EuCl$_3$ (anhydrous, 99.9%) and hydrobromic acid (48%) were purchased from ABCR; hydrochloric acid (37%), NH$_4$Cl and NH$_4$Br were purchased from J. T. Baker; ethanol (99.9%, extra dry) was purchased from AcrosOrganics. All other chemicals are enumerated in the chapters above.

Preparation of terbium halides

For the preparation of terbium halides, the ammonium halide route was employed. In a typical reaction Tb$_4$O$_7$ was dissolved in the respective mineral acid (HCl/HBr) by heating to 100 °C and a minimum 12-fold excess of the ammonium halide was added. The water and acid were boiled off, until an almost dry, pale yellow solid remained. The decomposition of the respective ammonium hexahalogenidoterbate was achieved by heating to 450 °C under dynamic vacuum for 24 h. For further purification, terbium chloride was sublimed at 700 °C under 10$^{-6}$ mbar. The purity of the rare-earth halides was proven by PXRD and showed minor residuals of NH$_4$Br for TbBr$_3$.

Preparation of the Luminescent Organic-Inorganic Hybrid Materials

All manipulations were conducted under inert conditions either in a glovebox or using common Schlenk-techniques.

200 mg of the respective 1-$n$-alkyl-3-vinylimidazoliumbromide polymer (alkyl chain length: C$_2$-C$_8$)) was dissolved in 10 ml ethanol (p.a., dry) under vigorous stirring. The lanthanide halide to be used was either dissolved/dispersed in 10 ml ethanol (p.a., dry). Following this, the homogeneous polymer solution was split into four fractions of 2.5 ml, and each fraction was charged with the required volume of lanthanide halide solution or dispersion to produce a lanthanide halide dopant concentration of either 1, 5, 10, 20 mol% with respect to one imidazolium equivalent in the polymer. After 2 hours of intense stirring at room temperature the solvent was removed and the samples were dried under dynamic vacuum for additional 48 h. Exact masses can be found in the appendix.
The aim of this thesis was to design new phosphors for lighting based on 1-\textit{n}-alkyl-3-vinylimidazolium and diallydimethylammonium salts. In the course of this the following questions have been raised:

- How does the length of the alkyl chain influence the formation of the polymer and thus the matrix for the new phosphors?
- Is it possible to design efficient blue, green and red emitters from these matrices?
  - If so, how does the kind of the cationic polymer backbone influence the luminescent and physicochemical properties?
- Is it possible to design a white emitter?

To answer these questions, firstly a series of 1-\textit{n}-alkyl-3-vinylimidazolium bromide monomers was synthesized; starting with the ethyl moiety, the chain length was subsequently extended by one methylene unit up to 1-\textit{n}-hexyl-3-vinylimidazolium bromide; and their polymerization behavior was investigated. Through optimization experiments, it was found that a radical starter concentration of 2\% leads to the maximum conversion rate of monomer to polymer. Counterintuitively, it was found that a longer alkyl chain in the 1-\textit{n}-alkyl-3-vinylimidazolium backbone leads to faster polymerization and higher conversion rates. One hypothesis to explain this unexpected result is the possible formation of aggregates: In order to react, the vinyl double bonds have to be close enough to each other. A longer alkyl chain length could lead to the formation of micelles or micelle-like aggregates, thus restraining the monomers in a way that the distance of the vinyl double bonds decreases, and therefore making it easier to react. Furthermore, it was shown that the polymerization continues after the irradiation by leaving the samples in the dark for 15 h and then taking NMR-spectra again. UV/Vis-spectroscopy revealed that all prepared polymers all are transparent over a wide wavelength range, which is a mandatory factor for the design of efficient phosphors. The fact that all prepared polymers are
thermally stable up to 290 °C as shown by TG is another factor that shows the eligibility of these polymers to design new phosphors from them.

The formation of aggregates could be further examined with DLS or even better SANS experiments. For the polymerization kinetics it would be interesting to conduct CIDNP-NMR experiments to further investigate the polymerization tendencies under irradiation during the measurement and to get a deeper insight into radical reaction. Regarding the radical stability it would be interesting to conduct EPR experiments during and after the irradiation.

Imidazolium ionic liquids possess intrinsic but weak emission in the blue region of the visual spectrum, when excited at 270 to 430 nm. Employing the salicylate ligand as the counter anion for the cationic polymer backbone through an anion metathesis highly enhanced the photoluminescence of all prepared polymers. Imidazolium compounds usually cannot be excited below 270 nm and show poor excitation behavior up to 330 nm. The excitation for the salicylate containing polymers is easily possible in the range of 250 to 380 nm being even higher for shorter wavelengths. To investigate the influence of an apparent π-system poly-diallyldimethylammonium salicylate synthesize and characterize poly-diallyldimethylammonium salicylate, which lacks this π-system, was also synthesized and characterized: Upon excitation the prepared poly-1-n-alkyl-3-vinylimidazolium salicylates as well as the poly-diallyldimethylammonium salicylate show broad emission bands spanning 350 to 540 nm. The maximum emission wavelength $\lambda_{em,max}$ however depends on the chain length in the poly-1-n-alkyl-3-vinylimidazolium: The C$_2$ moiety shows the longest $\lambda_{em,max}$, which subsequently decreases with extending the alkyl chain until it rises from the C$_5$ ($\lambda_{em,max}= 406$ nm) to the C$_6$ moiety ($\lambda_{em,max}= 414$ nm). This indicates a change in the π-π interactions: Stronger π-π interactions involve lower orbital energies, what results in lower emission energies and thus longer $\lambda_{em,max}$. From the C$_2$ to the C$_5$ moieties the steric bulk subsequently increases and thus the π-π interactions are lowered. The C$_6$ moiety poses a special case with the longest $\lambda_{em,max}$. This can be attributed to the forming of polar and apolar domains and hydrophilic/hydrophobic pockets. This leads to an inversion regarding π-π interactions which are now very strong through the new alignment of ion pairs in the compound. The fact that poly-diallyldimethylammonium salicylate shows a shorter $\lambda_{em,max}$ than any of the vinylimidazolium polymers (405 nm) supports the thesis of the correlation between the π-π interactions and the $\lambda_{em,max}$. Quantum yields as high
as 41% were achieved and it was shown that the variation of the alkyl chain length in the 1-\(n\)-alkyl-3-vinylimidazolium based samples as well the employment of the poly-diallyldimethylammonium cation does not have a major impact on the quantum yield. The thermal stability of these compounds measured by TG is very similar to those of the bromide counterparts ranging from 260 °C up to 283 °C. This indicates that the thermal stability of the polymer does not significantly vary by changing the anion. The high quantum yields and the thermal stability compounds shows the success of designing an efficient blue emitter based on poly-1-\(n\)-alkyl-3-vinylimidazolium as well as the poly-diallyldimethylammonium backbones.

To design an efficient green emitter it was chosen to exploit the ability of the salicylate ion to act as a sensitizer for Tb\(^{3+}\) which is known for its bright green, but rather weak luminescence. To investigate this and to establish a successful synthesis route, first monomeric cations were employed to form complexes with the constitution (IL-Cation)[Ln(Sal)\(_4\)] (Ln=Tb,La). The synthesis proved to be successful and for (C\(_2\)C\(_1\)Im)\(_4\)[Ln\(_4\)Sal\(_{12}\)(H\(_2\)O)\(_2\)] and (C\(_4\)C\(_1\)Im)\(_4\)[Ln\(_4\)Sal\(_{12}\)(H\(_2\)O)\(_2\)] it was possible to obtain single crystals with sufficient quality for structure determination by X-ray diffraction. The prepared compounds are excitable over a broad range of wavelengths ranging from 250 to 380 nm. The emission spectra of the lanthanum compounds show the autofluorescence of the salicylate only, while the emission spectra of the terbium compounds show strong green emission with the typical \(5\)D\(_4\)→\(7\)F\(_6\), \(5\)D\(_4\)→\(7\)F\(_5\), \(5\)D\(_4\)→\(7\)F\(_4\) and \(5\)D\(_4\)→\(7\)F\(_3\) \(f\)-\(f\)-transitions but no emission of the salicylate ligand, which indicates an energy transfer from the salicylate ligand to the terbium center. The comparison of the emission spectra of the lanthanum and terbium compounds made it possible to establish an absolute energy diagram for the photonic processes in these compounds as in the lanthanum compounds no excitable \(f\)-electrons are apparent and indeed it was found that an efficient energy transfer from the salicylate ligand to the optically active terbium center takes place:
General Conclusion and Outlook

Scheme 12: Proposed energy scheme for the photonic processes including the energy transfer to the optically active terbium center in the lanthanum- and terbium tetrakissalicylato containing complexes.

The quantum yield of the terbium compounds were found to range from 60% to as high as 92% and thus even higher of the simple Tb(Sal)₃. Water is known to quench the emission of rare earth compounds due to its high energy OH stretching vibrations. Thus, the water content of the samples has been extracted from the measured thermograms and a correlation between the observed lifetimes and the calculated quantum yields was found: The compounds with the lowest water content show the highest quantum yield. As expected the quantum yields of the lanthanum compounds were lower than these of the terbium compounds (7%-28%), as no energy transfer can take place due to the absence of excitable f-electrons. In addition to the high achieved quantum yields, all terbium samples show intense electroluminescence measured with a CCD camera upon excitation using a teslator which adds to their eligibility to be used as efficient green emitters for lighting applications.

The established synthesis route was then successfully transferred to the poly-1-n-alkyl-3-vinylimidazolium as well as the poly-diallyldimethylammonium backbones. As well as the monomers, excitation for these compounds is also possible from 250 – 380 nm showing strong absorption in the region below 280 nm. As with their monomeric counterparts, the lanthanum compounds only show autofluorescence of the salicylate ligand. The emission maxima of these compounds are shifted depending on the alkyl chain present in the poly-1-n-alkyl-3-
vinylimidazolium very similar to the pure poly-1-n-alkyl-3-vinylimidazolium all being bathocromically shifted by around 4 nm. This showed that the lowering of π-π interactions primarily is depending of the nature of the cation and not on the anion.

![Diagram](image.png)

Figure 53: Comparison of the emission maxima observed for the sole poly-vinylimidazolium based salicylates and the tetrakissalicylatolanthanate based polymers. Line is only added to guide the eye.

The prepared terbium compounds all show the typical $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ $ff$-transitions and as well as the prepared monomers no emission of the salicylate indicating that the energy transfer process described for the monomers also can be transferred to the polymeric species. The quantum yields of the prepared terbium compounds range from 41% to 69%, these of the lanthanum compounds from 18% to 47% thus being significantly higher for the polymeric form than for the complexes of the monomeric IL-cations. Figure 54 illustrates this for the direct comparable monomeric and polymeric forms of the 1-n-ethyl-3-vinylimidazolium and the diallyldimethylammonium based terbium and lanthanum compounds, which illustrates the successful improvement of the quantum yields through the employment of ionic polymers especially for the lanthanum compounds. This underlines the success of designing efficient green emitters based on the employed cationic polymer backbones.
General Conclusion and Outlook

Figure 54: Comparison of the quantum yields for the monomeric and polymeric forms of the DADMA and C2Vim cation based tetrakis(salicylato)terbates and tetrakis(salicylato)lanthanates. Spectra were recorded exciting the salicylate ligand at 310 nm and the respective emission wavelength of the compound (420/430 nm for lanthanum and 542 for the strongest $^5D_4 \rightarrow ^7F_5, 6 f-f$ transition in the terbium compounds).

Also, the pure poly-1-$n$-alkyl-3-vinylimidazolium bromides were doped with Eu$^{3+}$ and Tb$^{3+}$ to obtain red and green emitters based on rare-earth ions without the employment of the salicylate ligand. As expected, characteristic absorption lines are visible rising from the typical $f-f$ transitions. In addition a broad band spanning from 280 to 400 nm centered at 315 nm is visible which corresponds to the $\pi \rightarrow \pi^*$ transitions of the polymer. The ratio between the latter and the $f-f$-transitions decreases with higher doping concentrations. After excitation of the $f-f$-transitions at 393 nm for Eu$^{3+}$ and 377 nm for Tb$^{3+}$ respectively, the Eu$^{3+}$ doped samples showed to exhibit the typical $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4 f-f$-transitions and thus emitting in the red region of the visible spectrum, while the Tb$^{3+}$ doped samples exhibited green emission due to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3 f-f$-transitions. After excitation into the above mentioned broad band of the polymer at 315 nm the emission spectra recorded showed the same appearance as those directly exciting into the $f-f$-transitions but with higher intensities. This indicates that an energy transfer from the polymer backbone to the lanthanide ion may be possible. Time delayed luminescence spectroscopy which eliminates the appearance of the short living emission of the polymers revealed that this is not the case for the terbium doped samples,
but however that an energy transfer may take place for the europium doped samples. Quantum yields calculated for the europium doped samples showed to rather low in the range of 0.2-1.7% decreasing with higher doping concentration due to concentration quenching. Regarding the length of the alkyl chain in the polymer backbone no trend could be observed. The respective color coordinates demonstrate that the emission color is tunable from pure and characteristic green Tb$^{3+}$ or deep red Eu$^{3+}$ emission to pure white bluish emission resulting from the ionic polymer. In between, several emission colors are realized via superposition of the respective lanthanide and polymer emission.

In summary it can be said that

- A radical starter concentration of 2% shows the best conversion rates and the alkyl chain length in the 1-\(n\)-alkyl-3-vinylimidazolium bromides significantly influences the polymerization behavior of monomers. The longer the alkyl chain, the higher the polymerization degree after a given time.
- Emitters of all colors can be designed:
  - Efficient blue emitters are accessible by replacing the bromide anion with salicylate.
  - Efficient green emitters are accessible through incorporating terbium into complex anions of the poly-1-\(n\)-alkyl-3-vinylimidazolium salicylates.
  - Red emitters can be designed by doping the 1-\(n\)-alkyl-3-vinylimidazolium bromides with EuCl$_3$. 
- A white emitter can be obtained with Eu$^{3+}$ and Tb$^{3+}$ doped 1-\(n\)-alkyl-3-vinylimidazolium bromides by carefully choosing the right excitation wavelength, through the superposition of the polymer and lanthanide emission.
- The length of the alkyl chain influences the emission behavior and the physicochemical properties.
Bibliography

[40] A. A. Kaplyanskii, R. M. McFarlane, *Spectroscopy of Crystals Containing Rare Earth Ions*, Elsevier Science, **2012**.
[43] C. P. Lorbeer, Ruhr-Universität Bochum (Bochum), **2012**.
Bibliography


[116] Stoe&Cie, Darmstadt, Germany, **2002**.

[117] Stoe&Cie, Darmstadt, Germany, **2002**.


# Appendix

## List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAS</td>
<td>atom absorption spectroscopy</td>
</tr>
<tr>
<td>a. u.</td>
<td>arbitrary unit</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2'-Azobis(2-methylpropionitrile)</td>
</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
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<tr>
<td>Cat</td>
<td>placeholder for a specific cation</td>
</tr>
<tr>
<td>CIDNP</td>
<td>Chemically Induced Dynamic Nuclear Polarization of Radical Pairs (NMR technique)</td>
</tr>
<tr>
<td>CFL</td>
<td>compact fluorescent lamp</td>
</tr>
<tr>
<td>C&lt;sub&gt;n&lt;/sub&gt;</td>
<td>aliphatic alkyl chain consisting of n carbon atoms</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DADMA</td>
<td>diallyldimethylammonium-</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>EA</td>
<td>elemental analysis</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Im</td>
<td>imidazolium-</td>
</tr>
<tr>
<td>K</td>
<td>degree Kelvin</td>
</tr>
<tr>
<td>Ln</td>
<td>placeholder for a specific lanthante</td>
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m  multiple
MALDI-TOF-MS matrix assisted LASER desorption ionisation- time of flight mass spectrometry
MeCN methyl cyanide (acetonitrile)
MS mass spectrometry
NMR nuclear magnetic resonance
NOE Nuclear overhauser effect
NP nanoparticle(s)
(O)LED (organic) light emitting diode
PET positron emission tomography
P- poly-
ppm parts per million
q quintet
ROE rotating frame nuclear overhauser effect
s singlet
Sal salicylate (ligand)
SANS small angle neutron scattering
t triplet
TG thermogravimetry
$T_{\text{decomp}}$ decomposition temperature
Vim vinylimidazolium-
XRD X-Ray diffraction
Appendix

Instrumentation

Irradiation experiments for polymerization kinetics have been conducted using a CCP-ICH2 photoreactor with UV-A lamps employed (Luzchem, Ottawa, Canada).

Photoluminescence (fluorescence and phosphorescence) measurements were carried out on a Fluorolog FL 3-22 spectrometer at room temperature (Horiba JobinYvon, Unterhachingen, Germany). A continuous xenon lamp (450 W) is used for steady state measurements, whereas a pulsed xenon lamp is used for lifetime measurements. Prior to measurements the samples were filled into silica tubes and positioned in the sample chamber to ensure proper alignment with the beam.

UV/Vis spectra were recorded on a Cary5000 UV/Vis spectrometer in silica-cuvettes with a path length of 2 mm.

Thermogravimetric measurements have been conducted using a Netzsch STA 449 F3 DSC-TG.

DSC measurements have been conducted on a computer-controlled Phoenix DSC 204 F1 thermal analyzer (Netzsch, Selb, Germany) under a constant flow of argon gas with a heating/cooling rate of 10 K min$^{-1}$. Samples of ~ 5 mg were cold-sealed in aluminium crucibles.

NMR Spectra were recorded on a BRUKER DPX 200 MHz spectrometer (BRUKER, Billerica, USA). Chemical shifts are given in ppm against TMS. Spectra were calibrated with respect to the peak of the corresponding solvent.

Mass spectra were recorded with a LCQ Classic mass spectrometer Finnigan MAT (San Jose, USA) equipped with a Nano-ESI ionizator and an iontrap detector.

IR spectra were recorded on a BRUKER alpha IR-spectrometer (BRUKER, Billerica, USA) in ATR modeequipped with a diamond cell.

EA measurements were taken on an Elementar Analysysystem (Hanau, GER) varioEl CHNSO analysis system using helium as a carrier gas and a thermal conductivity detector.
Powder X-ray diffraction (PXRD) patterns were recorded on a Huber G670 Guinier camera system (Huber, Rimsting, Germany) equipped with an image plate detector using monochromated Mo Kα X-ray radiation with a wavelength of 0.70173 Å.

Crystal structure determination: Suitable crystals of \((\text{C}_1\text{C}_2\text{Im})_4[\text{Ln}_4\text{Sal}_{16}(\text{H}_2\text{O})_2]\) (Ln = La, Tb) were mounted on a cryoloop (Hampton Research, Aliso Viejo, United States). The most suitable crystal for every compound was then used to collect a complete intensity data set on a STOE IPDS I single crystal X-ray diffractometer using Mo Kα X-ray radiation with a wavelength of 0.70173 Å which was monochromated through a graphite monochromator. Data reduction was conducted using X-Red\(^{[116]}\) and included Lorentz corrections, as corrections for background and polarization effects. After optimization of the crystals shape with X-Shape\(^{[117]}\) an absorption correction was undertaken using X-Red. SIR92\(^{[118]}\) and SHELXL-97\(^{[119]}\) was used to solve the crystal structures by direct methods and to refine atoms against \(F^2\) by a full-matrix least-squares procedure. Whereas hydrogen atoms were constrained to match their respective bonded atom, all non-hydrogen atoms were anisotropically refined. Structure factors were taken from International Tables for Crystallography.\(^{[120]}\) Diamond\(^{[121]}\) was used to draw the crystal structure.
Appendix

DSC-Thermograms

A1 1: DSC thermogram of C₃VimBr (left) and C₄VimBr (right)

A1 2: DSC thermogram of C₅VimBr (left) and C₆VimBr (right)

A1 3: DSC thermogram of P-C₂VimBr (left) and P-C₄VimBr (right)
Appendix

A1 4: DSC thermogram of P-C4VimBr with a cooling rate of 10 K min\textsuperscript{-1} (left) and P-C6VimBr (right)

A1 5: DSC thermogram of P-C2Vim(Sal) (left) and P-C4Vim(Sal) (right)

A1 6: DSC thermogram of P-C2Vim(Sal)

NMR-spectra from the irradiation experiments
Appendix

A2 1: NMR-spectra of C$_2$VimBr with the addition of 0% Michler’s Ketone.

A2 2: NMR-spectra of C$_2$VimBr with the addition of 1% Michler’s Ketone.
Appendix

A2 3: NMR-spectra of C2VimBr with the addition of 2% Michler’s Ketone.

A2 4: NMR-spectra of C2VimBr with the addition of 3% Michler’s Ketone.
Appendix

A2 5: NMR-spectra of C3VimBr with the addition of 0% Michler’s Ketone.

A2 6: NMR-spectra of C3VimBr with the addition of 2% Michler’s Ketone.
Appendix

A2 7: NMR-spectra of C3VimBr with the addition of 3% Michler's Ketone.

A2 8: NMR-spectra of C4VimBr with the addition of 0% Michler's Ketone.
Appendix

A2.9: NMR-spectra of C₄VimBr with the addition of 1% Michler’s Ketone.

A2.10: NMR-spectra of C₄VimBr with the addition of 2% Michler’s Ketone.
Appendix

A2 11: NMR-spectra of C4VimBr with the addition of 3% Michler's Ketone.

A2 12: NMR-spectra of C4VimBr with the addition of 0% Michler's Ketone.
Appendix

A2 13: NMR-spectra of C5VimBr with the addition of 0% Michler’s Ketone.

A2 14: NMR-spectra of C6VimBr with the addition of 2% Michler’s Ketone.
Appendix

A2 15: NMR-spectra of C$_5$VimBr with the addition of 1% Michler’s Ketone.

A2 16: NMR-spectra of C$_5$VimBr with the addition of 3% Michler’s Ketone.
Appendix

A2 17: NMR-spectra of C₆VimBr with the addition of 0% Michler’s Ketone.

A2 18: NMR-spectra of C₆VimBr with the addition of 2% Michler’s Ketone.
Appendix

A2 19: NMR-spectra of C₆VimBr with the addition of 1% Michler’s Ketone.

A2 20: NMR-spectra of C₆VimBr with the addition of 3% Michler’s Ketone.
Appendix

PXRD patterns

A3 1: Measured PXRD pattern for TbCl$_3$ in comparison with literature data.
Appendix

A3 2: A3 3: Measured PXRD pattern for TbBr$_3$ in comparison with literature data.

A3 4: A3 5: Measured PXRD pattern for EuCl$_3$ in comparison with literature data.
Appendix

Plots for the polymerization degrees:

A4 1: Polymerization degree of the prepared 1-n-alkyl-3vinylimidazolium bromides with the addition of 1% Michler’s Ketone.

A4 2: Polymerization degree of the prepared 1-n-alkyl-3vinylimidazolium bromides with the addition of 3% Michler’s Ketone.
A4 3: Polymerization degree of C3VimBr with the addition of 0%, 1%, 2% and 3% Michler's Ketone (MK).

A4 4: Polymerization degree of C4VimBr with the addition of 0%, 1%, 2% and 3% Michler’s Ketone (MK).
Appendix

A4 5: Polymerization degree of C<sub>3</sub>VimBr with the addition of 0%, 1%, 2% and 3% Michler’s Ketone (MK).
Appendix

Luminescence spectra

A5 1: Photoluminescence emission Spectra of PC3VimBr:EuCl3; Excitation wavelength = 315 nm.

A5 2: Photoluminescence emission Spectra of PC3VimBr:EuCl3; Excitation wavelength = 393 nm.
Appendix

A5.3: Photoluminescence emission Spectra of different polymers doped with EuCl₃ (20%); Excitation wavelength = 393 nm.

A5.4: Photoluminescence emission Spectra of PC3VimBr:TbBr₃; Excitation wavelength = 315 nm.
Appendix

A5 5: Photoluminescence emission Spectra of PC3VimBr:TbBr3; Excitation wavelength = 377 nm.

A5 6: Photoluminescence emission Spectra of PC3VimBr:TbCl3; Excitation wavelength = 315 nm.
Appendix

A5 7: Photoluminescence emission spectra of PC3VimBr:TbCl₃; Excitation wavelength = 377 nm.

A5 8: Photoluminescence emission spectra of different polymers doped with TbCl₃(20%); Excitation wavelength = 377 nm.
Appendix

A5 9: Photoluminescence excitation spectra of PC3VimBr:EuCl3; Emission wavelength = 610 nm.

A5 10: Photoluminescence excitation spectra of PC3VimBr:TbBr3; Emission wavelength = 547 nm.
Appendix

A5 11: Photoluminescence excitation spectra of PC3WimBr: TbCl₃; Emission wavelength = 547 nm.
### Tables

Table 20: Respective amounts of dopants in different polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molar ratio of LnX₃</th>
<th>m (polymer)/mg</th>
<th>n (polymer)/mmol</th>
<th>n (LnX₃)/mmol</th>
<th>m (EuCl₃)/mg</th>
<th>m (TbCl₃)/mg</th>
<th>m (TbBr₃)/mg</th>
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</thead>
<tbody>
<tr>
<td>P-C₂VimBr</td>
<td>1%</td>
<td>200</td>
<td>0.99</td>
<td>0.01</td>
<td>2.54</td>
<td>2.61</td>
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<td>12.70</td>
<td>13.06</td>
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<td>11.87</td>
<td>12.22</td>
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<tr>
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