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N-rich porous polymer with isolated Tb³⁺-ions displays unique temperature dependent behavior through the absence of thermal quenching

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Abstract: The challenge of measuring fast moving or small scale samples is based on the absence of contact between sample and sensor. Grafting lanthanides onto hybrid materials arises as one of the most promising accurate techniques to obtain noninvasive thermometers. In this work, a novel bipyridine based Porous Organic Polymer (bpyDAT POP) was investigated as temperature sensor after grafting with Eu(acac)₃ and Tb(acac)₃ complexes. The bpyDAT POP successfully showed temperature dependent behavior in the 10 - 310 K range, proving the potential of amorphous, porous organic frameworks. More intriguingly, we observed unique temperature dependent behavior; instead of the standard observed change in emission as a result of a change in temperature for both Eu³⁺ and Tb³⁺, the emission spectrum of Tb³⁺ remained constant. This work provides framework- and energy-based explanations for the observed phenomenon. The conjugation in the bpyDAT POP framework is interrupted, creating energetically isolated Tb³⁺ environments. Energy transfer from Tb³⁺ to Eu³⁺ is therefore absent, nor energy back transfer from Tb³⁺ to bpyDAT POP ligand (i.e. no thermal quenching) is detected.

Introduction

Given that temperature is a fundamental parameter that affects the kinetics of virtually every process, temperature sensors are ubiquitous and indispensable for correct processing, storage and use of materials and products.¹⁻³ They are applied for scientific research as well as in the industry. The market is expected to

grow considerably thanks to device miniaturization and fast technological advancements. The need for reliable and precise temperature sensors is therefore very high. Noninvasive temperature sensors - sensors which do not disrupt the medium of interest, are indispensable for fast-moving or small scale samples.⁴⁻⁵ Areas of interest are for example microelectronics, microfluids and nanomedicine. Luminescent based noninvasive sensors are one of the most promising accurate thermometers, since their luminescence can depend on the temperature.⁶⁻⁷ These materials consist of trivalent lanthanide ions (Ln³⁺) which possess following unique and beneficial luminescence properties: (i) narrow emission peaks ranging from the ultraviolet-visible to near-infrared region (ii) relatively long decay times (iii) high quantum yields and (iv) high photostability.⁸⁻⁹ The major downside of these ions is low absorption coefficients, as a result of parity-forbidden 4f-4f transitions. To improve their light absorption, Ln³⁺ ions are grafted onto organic-inorganic hybrid materials.¹⁰⁻¹¹ These so called 'antenna' absorb the light and subsequently transfer excitation to the metal ions, thereby improving their light absorption. Various hybrid materials have been developed, among them Metal Organic Frameworks (MOFs) and coordination polymers are most extensively studied.¹²⁻¹⁵ The presence of multiple luminescent centers in lanthanide-based materials allows their use as ratiometric temperature sensor. These reliable sensors are independent of the concentration and inhomogeneity of the luminescent centers in the material and of fluctuations in the excitation source or detector. To elucidate and discover interesting luminescent and sensing properties, the

FULL PAPER

study of novel classes of lanthanide-based materials is essential and ongoing. Based on the success of organic-inorganic hybrid antennas, purely organic substances have recently been investigated as potential antenna for luminescence-based temperature sensing. In 2020, some of us (A. M. Kaczmarek *et al.*) were the first to successfully use a crystalline, porous organic antenna (bipyridine-based Covalent Organic Framework (TpBpy COF)), as a temperature sensor, in which the nitrogen rich building blocks create an ideal complexation environment for lanthanide ions.¹⁶ This material showed unique and unusual temperature dependent behavior where no thermal quenching was observed for the terbium (Tb^{3+}) ions as a result of the absence of energy transfer from terbium (Tb^{3+}) to europium (Eu^{3+}). Inspired by this result, we developed a novel 6,6'-(2,2'-bipyridine-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) (bpyDAT) based Porous Organic Polymer (POP) and investigated the luminescent and potential unique temperature dependent behavior after grafting of the bpyPOP with $\text{Eu}(\text{acac})_3$ and $\text{Tb}(\text{acac})_3$ complexes. POPs are renowned for their lightweight, high surface areas, excellent stability and tunability. These features paved the way towards very diverse application fields (gas storage/separation, heterogeneous catalysis, chemical and bio-sensing, energy storage and conversion).¹⁷⁻²³ POPs differ from the crystalline COFs in their amorphous nature. In this work, we determine whether porous, amorphous materials are potential noninvasive thermometers. Remarkably, we also observe the peculiar temperature dependent behavior (no thermal quenching) and provide framework- and energy-based explanations.

Results and Discussion

The development of a novel temperature sensor involves three main steps. First the required antenna, in which appropriate lanthanide coordination pockets are present, is assembled and characterized. Secondly, the lanthanide ions are grafted onto the framework. Lastly, the luminescent and temperature dependent properties are investigated. We selected 6,6'-(2,2'-bipyridine-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) (bpyDAT) and terephthalaldehyde as starting materials to synthesize a novel bipyridine-triazine-based POP (bpyDAT POP). The porous

polymer is formed via Schiff base condensation reaction in DMSO, and subsequent attack of the imine double bond by primary amines, resulting in the generation of an amina (Figure 1).^{26, 27} The bpyDAT POP contains numerous N-moieties which form excellent anchoring points for grafting of lanthanide complexes. The chemical connectivity between the building blocks was investigated by FTIR spectroscopy (Figure S2). Bands for NH_2 -stretching and deformation (1633 cm^{-1}) of the primary amine groups in bpyDAT clearly disappeared in the spectrum of bpyDAT POP. This indicates that all amine functionalities within the framework have reacted. The broad band at 3381 cm^{-1} corresponds to N-H amina stretching vibrations of secondary amines. The presence of a sharp band around 1570 cm^{-1} in both linker and POP, indicates the triazine quadrant stretch.²⁸ The corresponding band at 1658 cm^{-1} indicates C=N stretching in the bipyridine ring. The band at 1525 cm^{-1} demonstrates stretching vibration of C=C bonds. Elemental analysis reveals C, H, N content of 46.2, 3.6 and 28.9 % respectively. The calculated experimental ratio ($\text{N/C} = 0.63$) is in agreement with the theoretical content ($\text{N/C} = 0.64$), and demonstrates that the composition of the precursors is preserved during the polymerization reaction. As expected, the bpyDAT POP is very rich in nitrogen. The different binding states of nitrogen functionalities are further verified via curve fitting of the high-resolution XPS N1s spectrum (Figure 2). The peak at 399.55 eV corresponds to NH linkages and the peak at 398.55 eV to the imine groups of the triazine and bipyridine moieties. The PXRD pattern shows a broad peak between 2θ values of 15 to 30° , consistent with the amorphous nature of the material (Figure S3). The surface area was investigated via nitrogen sorption measurement at 77 K (Figure 3). The isotherm shows reversible type IV adsorption. A steep increase at a relative pressure of $P/P_0 < 0.1$, suggests a permanent microporous material. The presence of hysteresis in the desorption at $P/P_0 > 0.9$, can probably be ascribed to adsorbate condensation within interparticle voids, since this is observed in POPs with a similar structure.^{20-21, 23} The fact that the isotherm does not close at the cavitation point of $P/P_0 = 0.42$ is indicative for a slight swelling of the polymer in liquid nitrogen, a typical feature of some polymers and POPs. The Brunauer-Emmett-Teller (BET) surface area is $505\text{ m}^2\text{ g}^{-1}$. The thermal stability of the bpyDAT POP was investigated via thermal

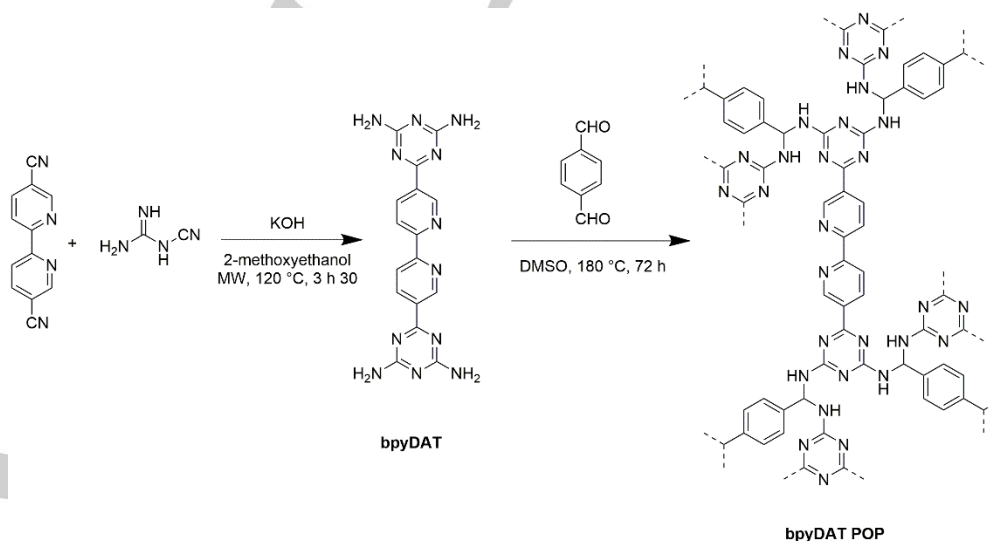


Figure 1. Synthesis of 6,6'-(2,2'-bipyridine-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) (bpyDAT) and bpyDAT POP.

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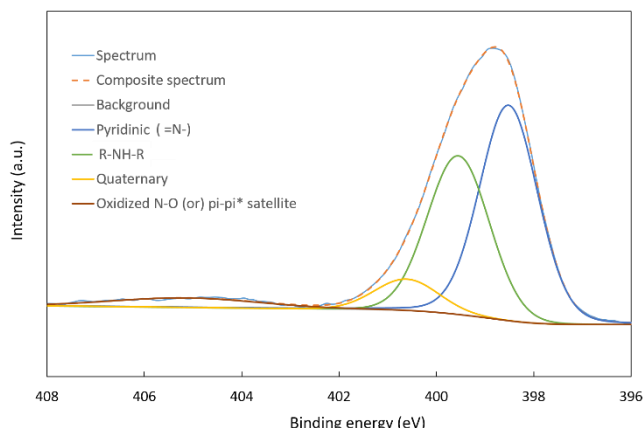


Figure 2. XPS (N1s) spectrum of bpyDAT POP showing the presence of NH and C=N nitrogen binding states.

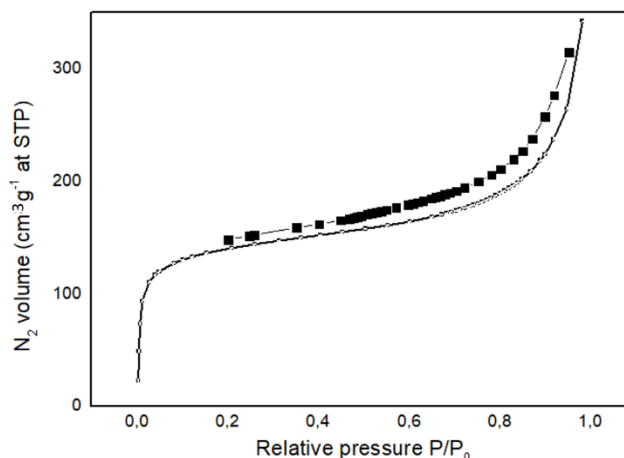


Figure 3. Nitrogen (N_2) adsorption/desorption isotherm of bpyDAT POP

gravimetric analysis (Figure S4). The bpyDAT POP is stable up to 400 °C, implying its high thermal stability. Lanthanide complexes ($Eu(acac)_3$ and $Tb(acac)_3$) were successfully grafted onto the framework through post-synthetic modification, using an excess of lanthanide complexes (Figure 4). The acac-ligand serves as a second antenna for the absorption of light and it protects the lanthanides from quenching by H_2O . First, the bpyDAT POP grafted with only Eu^{3+} or Tb^{3+} complexes were studied and after elucidating the luminescent properties of the separate lanthanide ions onto bpyDAT POP, mixtures of Eu^{3+}/Tb^{3+} were grafted onto the POP. The grafting of the $Eu^{3+}(acac)_3$ complex was proven by TEM-EDX S5. The ultrasound-assisted sample preparation causes the presence of limited amount of dots outside the sample. A homogeneous distribution of nitrogen and europium throughout the sample is observed. A similar distribution behavior is expected for Tb^{3+} and mixed complex grafting. The successful grafting is further proven by XRF (Figure S6) and FTIR spectroscopy (Figure S7). The lanthanides are most probably grafted onto different bipyridine units in the framework, observed by the appearance of peaks in the FTIR spectra related to the acac-ligand (1400 cm^{-1} , $\nu(C-H)$) and a small shift in the imine stretching band (1680 cm^{-1}). Bipyridine units are well known in thermometry-based literature as excellent ligands for anchoring of Eu^{3+} and Tb^{3+} complexes.^{16, 29} The oxidation states of the grafted Tb and Eu complexes were determined via XPS. In the 3d spectrum of the $Eu_{acac}@bpyDAT$ POP sample (Figure S8), the observed peaks at 1164.67 eV and 1134.97 eV are characteristic of $Eu(III)$ $3d_{3/2}$ and $Eu(III)$ $3d_{5/2}$ binding energies, confirming the 3+

oxidation state of Eu cations. Furthermore, the peaks at 1154.87 eV and 1125.27 eV indicate the binding energies $Eu(II)$ $3d_{3/2}$ and $Eu(II)$ $3d_{5/2}$ of the Eu^{2+} ions. The reduction of Eu^{3+} to Eu^{2+} probably occurred during the measurement. In the Eu4d spectrum shown in Figure S9, the same oxidation states are observed. The characteristic peaks of $Eu(III)$ $3d_{3/2}$ (142.47 eV) and $Eu(III)$ $3d_{5/2}$ (136.67 eV) correspond to the multiplet structure of trivalent $4d_{4f}^6$ configuration of Eu^{3+} , the characteristic peaks of $Eu(II)$ $3d_{3/2}$ (131.67 eV) and $Eu(II)$ $3d_{5/2}$ (129.07 eV) to the divalent $4d_{4f}^7$ configuration of Eu^{2+} .³⁰ In the Tb3d spectrum (Figure S10) of $Tb_{acac}@bpyDAT$ POP, the peaks at 1277.25 eV and 1242.55 eV correspond to $Tb(III)$ $3d_{3/2}$ and $Tb(III)$ $3d_{5/2}$ of Tb^{3+} . In the 4d spectrum (Figure S11), the peaks in the range of 147 - 152 eV correspond to Tb^{3+} . The presence of multiple energy bindings is explained by multiplet effects. The multiplicity of final states results from coupling a 4d core hole with an incomplete outer 4f shell (4d-4f excitations) in low-energy excited emission spectra.³¹ The lanthanide content of the samples is determined using ICP-OES (Table S1).

Luminescence study

The luminescent properties of the different materials were investigated. First, the excitation-emission spectrum of the pristine (ungrafted) bpyDAT POP was recorded at room temperature to get insight into the luminescent behavior of the antenna (Figure S12). The excitation spectrum consisted of a broad band from 250-425 nm, with a maximum at 372 nm. The emission band is obtained when excited in this peak maximum. A broad band is observed from 400-550 nm, with a maximum at 438 nm. Next, the room temperature photoluminescence study of the $Eu(acac)_3$ grafted bpyDAT POP ($Eu_{acac}@bpyDAT$ POP) revealed a broad band, originating from bpyDAT POP, in the excitation spectrum from 275 nm to 425 nm, with a maximum at 347 nm (Figure 5). Due to grafting, the maximum has shifted towards a lower wavelength. Upon excitation in this maximum, the emission spectrum showed the characteristic $^5D_0 \rightarrow ^7F_{0-4}$ transition peaks of Eu^{3+} . The transitions have been assigned to the appropriate peaks in Table S2. The weak broad band in the emission spectrum (450-520 nm) resulted from incomplete energy transfer from the POP ligand to the Eu^{3+} ions. The luminescence decay time of $Eu_{acac}@bpyDAT$ POP was determined by fitting a biexponential function to the curve, resulting in two decay times, $t_1 = 362\text{ }\mu\text{s}$ and $t_2 = 66\text{ }\mu\text{s}$ (Figure S13). The presence of two decay times indicated two different

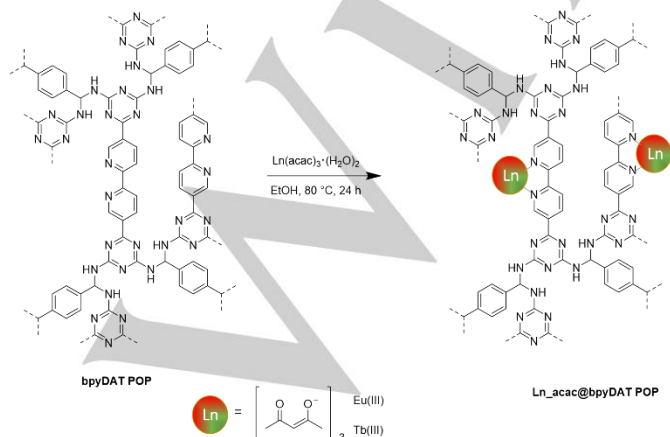


Figure 4. Synthesis of the $Ln_{acac}@bpyDAT$ POP materials.

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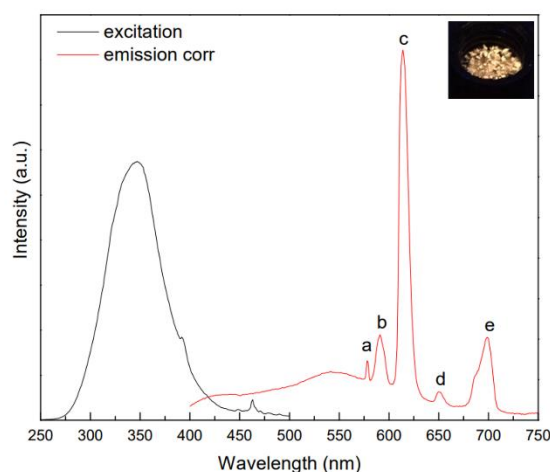


Figure 5. Excitation-emission spectrum of Eu_acac@bpyDAT POP (excited at 347 nm, observed at 614 nm) at room temperature. Picture in the upper right corner of the sample when placed under UV lamp (at 302 nm excitation wavelength).

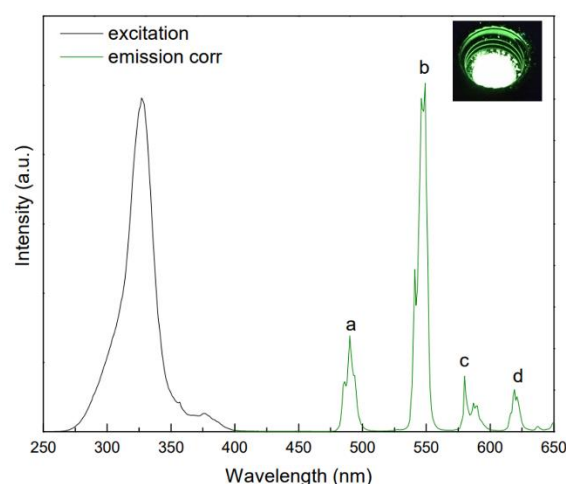


Figure 6. Excitation-emission spectrum of Tb_acac@bpyDAT POP (excited at 326 nm, observed at 549 nm) at room temperature. Picture in the upper right corner of the sample when placed under UV lamp (at 302 nm excitation wavelength).

coordination environments of the Eu^{3+} ions grafted to the POP. As one decay time (t_2) is significantly shorter, it must be present in an unfavorable environment (e.g. in the presence of several water molecules in its first coordination sphere). Subsequently, the room temperature excitation-emission spectrum for Tb^{3+} grafted bpyDAT POP (Tb_acac@bpyDAT POP) was recorded (Figure 6) and showed a moderate broad ligand band from 275–350 nm, with a maximum at 326 nm. After excitation in this maximum, the emission spectrum revealed the characteristic $^5\text{D}_4 \rightarrow ^7\text{F}_{6-3}$ transition peaks of Tb^{3+} . The absence of a broad band in the emission spectrum, suggested efficient energy transfer from the ligand to the Tb^{3+} -ions. This indicated the close existence of the triplet energy levels of the POP and the accepting levels of the Tb^{3+} -ions. Table S3 connected the observed peaks with the corresponding transitions. The decay time of this material was determined by plotting a single exponential function, resulting in $t_1 = 941 \mu\text{s}$ (Figure S14). The Eu_acac@bpyDAT POP material yielded red emission, whereas the Tb_acac@bpyDAT POP material yielded green emission under UV excitation (302 nm). After elucidating the luminescent properties of the separate lanthanide ions onto the bpyDAT POP, we grafted different ratios of Eu^{3+} - and Tb^{3+} -ions simultaneously onto the porous material to investigate their potential use as a ratiometric temperature sensor. This type of sensor relies on two discriminable transition peaks,

thereby eliminating variations in the sample and equipment. The different ratios, determined via ICP-OES, of $\text{Eu}(\text{acac})_3$ and $\text{Tb}(\text{acac})_3$ are: 50 % Eu, 50 % Tb (1); 34 % Eu, 66 % Tb (2); 25 % Eu, 75 % Tb (3). The resulting excitation-emission spectra are presented in Figure 7 and their corresponding peak-transition assignments are found in Table S4-6. Each graph depicts a picture with the observed emission color under UV radiation (302 nm) in the upper right corner. The more Tb^{3+} present in the material, the more the emission wavelengths fall in the green region. The emission spectrum of 1 shows a higher Eu-to-Tb ratio, resulting in incomplete energy transfer from the POP material to the lanthanide ions. This is suggested by the weak broad band in the emission spectrum, and the presence of a sharp f-f Eu^{3+} transition peak in the excitation spectrum, like in the pure Eu_acac@bpyDAT POP grafted sample. The two other grafted materials show a strong Tb^{3+} peak (549 nm) and a weaker Eu^{3+} peak (611 nm), whereby efficient and complete energy transfer from the ligand to the lanthanide ions is observed.

The decay times of the different samples are shown in Table S7; the corresponding decay profiles are presented in Figures S15–20. Standard luminescent behavior of Eu/Tb grafted materials is mostly characterized by energy transfer of the ligand to Tb^{3+} and subsequently to Eu^{3+} ions. This is caused by the proximity of the triplet and accepting levels of the ligand and the ions. As a result

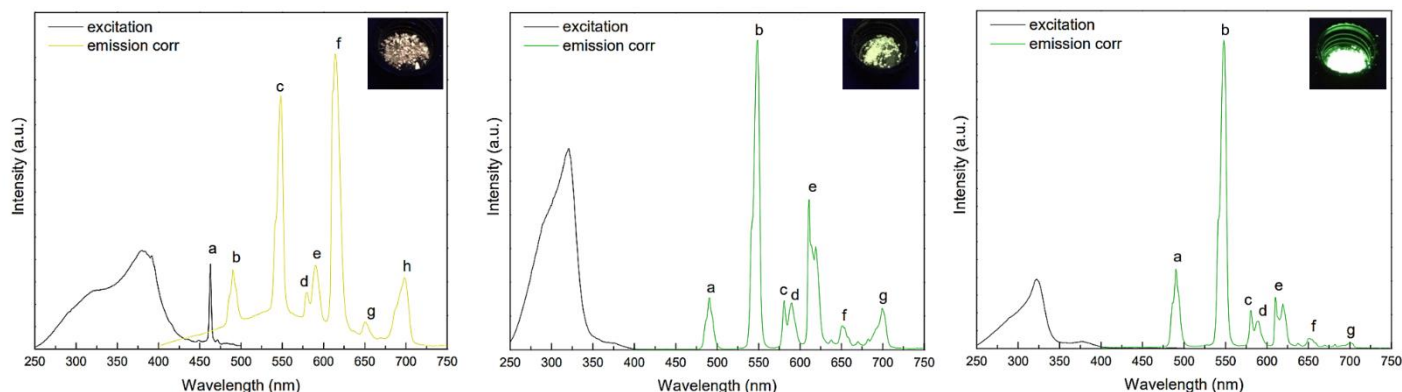


Figure 7. Room temperature emission-excitation spectra of the samples 1 (excited at 380 nm, observed at 614 nm), 2 (excited at 321 nm, observed at 549 nm) and 3 (excited at 322 nm, observed at 548 nm) respectively.

FULL PAPER

of the energy transfer, the decay time of Tb^{3+} -ions in mixed Eu/Tb samples will decrease in comparison to the pure Tb_acac@bpyDAT POP sample and the decay time of Eu^{3+} -ions will increase since they receive energy.³²⁻³³ Remarkably, in our samples the decay time of Tb^{3+} remains constant, while the decay time of Eu^{3+} increases. The Tb^{3+} decay time is not decreasing, suggesting the absence of energy transfer of Tb^{3+} to Eu^{3+} or implying a long distance between the Eu^{3+} and Tb^{3+} ions. The different decay times for Eu^{3+} arise from different coordination environments. When looking at the bpyDAT POP structure, it can be observed that the material is not fully conjugated, the conjugation is interrupted at the aminal nodes. As a result, electronic communication, and thus through-bond energy transfer is rather limited, thereby explaining the observed phenomenon.

Materials **1** and **2** were further investigated for their temperature-dependent luminescence properties. Since the Eu^{3+} peak in material **3** is very weak, it was excluded from the temperature study. Temperature dependent emission spectra were recorded in the temperature range of 10 - 310 K for both samples (Figure 8). The corresponding integrated areas under the 614 nm (Eu) and 548 nm (Tb) (**1**) and 612 nm and 549 nm (**2**) peaks as a function of the temperature are shown in Figure S22. Intriguingly, the intensity of the Tb^{3+} peak (548-549 nm) shows nearly no fluctuations throughout the whole temperature profile whilst the intensity of the Eu^{3+} peak (614-612 nm) clearly decreases upon temperature increase (i.e. temperature dependent). This peculiar temperature behavior was observed only once before.¹⁶ To explain this unique behavior, we hypothesized the absence of Tb-to-ligand energy back transfer, resulting in no temperature quenching of Tb^{3+} . This is possible if the energy of the ligand's

lowest triplet level is well above the $^5\text{D}_4$ accepting level of Tb^{3+} . To prove our hypothesis and to gain insight in the energy transfer mechanism, we unraveled the lowest triplet level of bpyDAT POP ligand. Therefore, the emission spectrum of bpyDAT POP grafted with GdCl_3 at 77 K in ethanol/methanol mixture (4:1) was recorded. The analysis is depicted in Figure S21. In gadolinium complexes, the energy at the triplet level of the ligand is not transferred to the Gd^{3+} metal, as the resonance level of Gd^{3+} lies far above the triplet level.³⁴ Subsequently, we have recorded the decay time at its maximum and observed microsecond range lifetimes, confirming the band belongs to the triplet level of the material (Figure S22). The triplet level of bpyDAT POP corresponds to the high-energy edge of this band, the lowest triplet level is therefore located at 416 nm (24,040 cm^{-1}). The triplet level lies well above the energy level of the $^5\text{D}_4$ accepting level of Tb^{3+} , energy back transfer from Tb^{3+} to the ligand is therefore absent. On the other hand, the high-excited levels of Eu^{3+} (400 nm, 25,000 cm^{-1}) are closer to the ligand triplet level and allow energy back transfer, as can be seen by the decrease in intensity as temperature increases. The intensity decrease can therefore be attributed to thermal quenching of the Eu^{3+} ions via the lowest triplet level of the ligand. This states the importance of appropriate ligand environment for the luminescent temperature behavior.

Even with stable emission of Tb^{3+} upon changing the temperature, the material can be investigated as temperature sensor. For a ratiometric temperature sensor, the ratio of the peak intensities ($I_{\text{Eu}}/I_{\text{Tb}}$) is determinative. Since the intensities of europium do

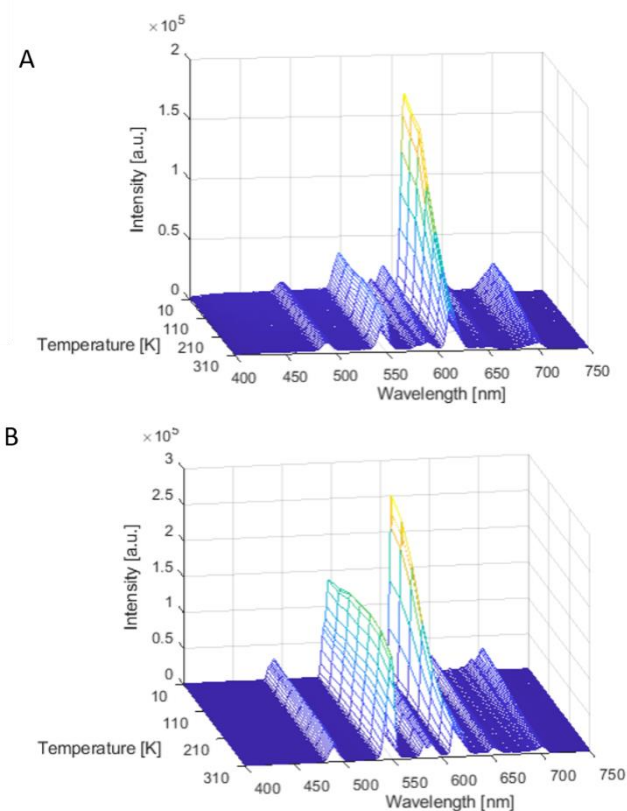


Figure 8. Emission maps recorded between 10 - 310 K for A. sample **1** and B. sample **2**.

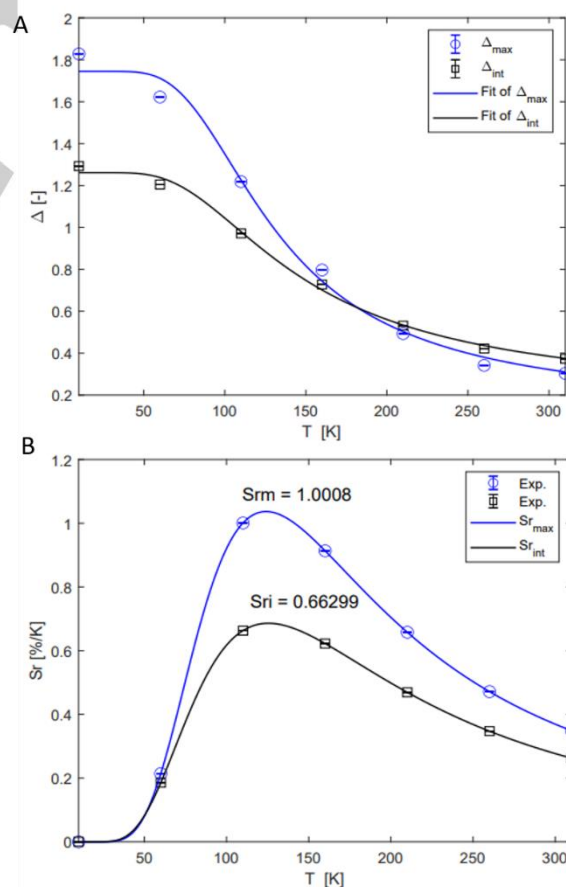


Figure 9. A. Plot representing Δ as a function of temperature (equation 3) for **2**. The points show the experimental delta values. The solid line corresponds to the best fit of the experimental values. B. Relative thermal sensitivity as a function of temperature (10 - 310 K). The solid line is a guide for the eyes.

FULL PAPER

decrease, we were able to calculate the ratio of the integrated areas under the peaks (I_{614}/I_{548}). All calculations were performed using the TeSen software tool.²⁵ The data points could be well fitted ($R^2 = 0.99637$) using equation (3) (Experimental section) for sample **2** yielding $\Delta_0 = 1.2615 \pm 0.0002$, $\alpha = 7.5203 \pm 0.0052$, $\Delta E = 248 \pm 0.160 \text{ cm}^{-1}$. The fitting of equation (3) when calculated from the maxima of the peaks ($R^2 = 0.9916$) yielded $\Delta_0 = 1.7448 \pm 0.0003$, $\alpha = 17,192 \pm 0.009$, $\Delta E = 282 \pm 0.121 \text{ cm}^{-1}$ (Figure 9A). Applying equation (4), the relative sensitivity was represented as a function of temperature (Figure 9B). The maximum relative sensitivity was calculated to be $1 \% \text{ K}^{-1}$ (125 K), when using the data from the maxima of the peaks. Furthermore, the temperature uncertainty was calculated using equation (5), $\delta T < 0.25 \text{ K}$ in the temperature range 60 - 310 K confirming good temperature sensor behavior (Figure 10A). The repeatability of the thermometer was determined using equation (6), revealing an excellent repeatability of 98.5 % (Figure 10B). The temperature dependent luminescent properties of **1** are presented and analyzed in the Supporting Information (Figure S24-25). The sensor operates with moderate sensitivity in a similar temperature range, as expected since the ratio I_{614}/I_{548} only varies in the numerator.

In Table 1, we compared the maximum relative sensitivity of our temperature sensor with Eu/Tb grafted materials that operate in a similar temperature range and can conclude our sensor shows comparable sensitivity with most of the reported temperature sensors. Our maximum sensitivity can however not compete with the highest reported sensitivity, obtained in organic-inorganic MOF-based antenna.

Conclusion

In an effort to develop a temperature sensor, based on a novel bpyDAT POP material, we discovered peculiar luminescent temperature behavior when anchoring a mixture of 33% Eu^{3+} and 67% Tb^{3+} onto the bpyDAT POP material. The material can be used as temperature sensor in the range of 10 to 310 K with moderate sensitivity ($S_r = 1.00 \% \text{ K}^{-1}$). After demonstrating the potential of crystalline porous organic frameworks (COFs) in temperature sensing, we now prove amorphous porous organic polymers (POPs) are potential thermometers. More intriguingly, the unique temperature dependent behavior observed in the TpBpy COF, recently investigated by our group, was also detected in the bpyDAT POP, thereby becoming the second material with this peculiar feature. This work provides framework- and energy-based explanations for the observed phenomenon. The conjugation in the framework is interrupted at the animal nodes, creating energetically isolated Tb^{3+} environments. Energy transfer from Tb^{3+} to Eu^{3+} is therefore absent, nor energy back transfer from Tb^{3+} to bpyDAT POP ligand (i.e. no thermal quenching) is detected due to the large energy gap between the lowest triplet level of the bpyDAT POP ligand and the $^5\text{D}_4$ energy level (Tb^{3+}). The interruption of the conjugation and the bpy units are present in both TpBPyCOF and bpyDAT POP. In this way, an 'energy island' is obtained, resulting in a unique temperature dependent luminescent emission behavior when the energy is released through luminescence. The Tb^{3+} emission spectrum remains stable throughout the investigated temperature range, while the emission spectrum of Eu^{3+} does show temperature dependency. For future research, it is recommended to explore fully conjugated porous organic frameworks (POPs – amorphous), or covalent organic frameworks (COFs – crystalline) as potential, organic temperature sensors when aiming at high thermal sensitivity.

Table 1. Comparison of the relative sensitivity S_r (S_m) for various reported Eu/Tb materials operating in a similar temperature regime.

Material	Range (K)	S_m (% K^{-1})	Ref
cyEu-phTb	10 - 200	1.85	35
$\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{L})_1\text{@PMMA}$	77 - 297	0.46	36
$\text{Tb}_{0.95}\text{Eu}_{0.05}\text{HL}$	1 - 290	31 (4 K)	15
$\text{Tb}_{0.95}\text{Eu}_{0.05}(\text{btb})$	10 - 320	2.85 (14 K)	37
$[(\text{Tb}_{0.914}\text{Eu}_{0.086})_2(\text{pda})_3(\text{H}_2\text{O})](\text{H}_2\text{O})_2$	10 - 325	5.96 (25 K)	12
Eu, TbPOM@MOF	60 - 360	0.71 (60 K)	14
$[\text{Tb}_{0.5}\text{Eu}_{0.7}(\text{d-cam})(\text{Himdc})_2 \cdot (\text{H}_2\text{O})_2]_3$	100 - 450	0.11 (450 K)	38
$\text{Tb}_{0.7}\text{Eu}_{0.3}\text{L MOF}$	40 - 300	0.17 (300 K)	39
$\text{Tb}_{0.4}\text{Eu}_{0.6}\text{TpBpy COF}$	10 - 360	1.02 (110 K)	16
$\text{Tb}_{0.05}\text{Eu}_{0.95}\text{TpBpy COF}$	10 - 360	1.40 (160 K)	16
$\text{Eu}_{0.34}\text{Tb}_{0.66}\text{-acac@bpy DAT POP (2)}$	10 - 310	1.00 (125 K)	This work

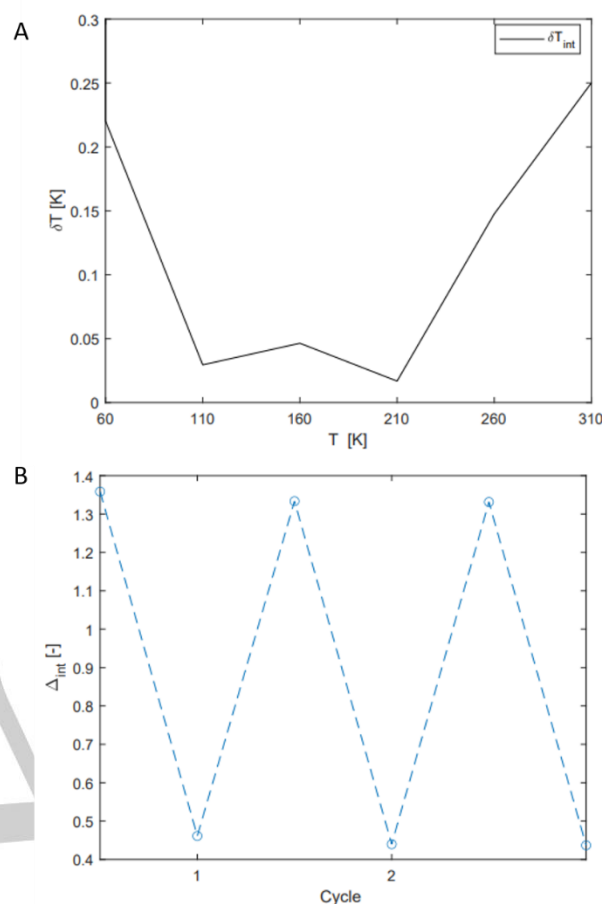


Figure 10. A. Calculated temperature uncertainty δT in the range 60 - 310 K (the values below 60 K were high and are therefore omitted for clarity), and B. repeatability for sample **2**.

quenching) is detected due to the large energy gap between the lowest triplet level of the bpyDAT POP ligand and the $^5\text{D}_4$ energy level (Tb^{3+}). The interruption of the conjugation and the bpy units are present in both TpBPyCOF and bpyDAT POP. In this way, an 'energy island' is obtained, resulting in a unique temperature dependent luminescent emission behavior when the energy is released through luminescence. The Tb^{3+} emission spectrum remains stable throughout the investigated temperature range, while the emission spectrum of Eu^{3+} does show temperature dependency. For future research, it is recommended to explore fully conjugated porous organic frameworks (POPs – amorphous), or covalent organic frameworks (COFs – crystalline) as potential, organic temperature sensors when aiming at high thermal sensitivity.

FULL PAPER

Experimental Section

Materials All chemicals were purchased from Merck and TCI Europe, and were used as received. The solvents used during preparation were reagent grade and were not purified further.

Synthesis and characterization of the bpyDAT POP

The bpyDAT POP was obtained in a one-step synthesis procedure. The monomer 6,6'-(2,2'-bipyridine-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) was prepared according to an optimized literature procedure.²⁴ The synthesis and characterization can be found in the ESI. The polymerization reaction was performed in dry glassware. In a 50 mL flask, 0.8 mmol 6,6'-(2,2'-bipyridine-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) and 1.6 mmol terephthalaldehyde were dissolved under stirring in 15 mL anhydrous DMSO. The temperature was slowly increased towards 160 °C under an argon atmosphere, and the reaction mixture was refluxed for 72 h. A grey precipitation is observed. After cooling down, the precipitate was filtered off and rinsed with 50 mL water. To fully remove the unreacted monomer, the collected grey powder was further washed with a MeOH/THF (1:1) mixture using a Soxhlet apparatus. The resulting off-white powder was collected by filtration and washed with acetone. The final product was dried under vacuum for 48 h at 150 °C, to afford bpyDAT POP in 67 % yield. The porous polymer was characterized using multiple techniques, including Fourier Transform Infrared Spectrophotometer (FTIR) spectroscopy, thermogravimetric analysis (TGA), elemental analysis, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD) analysis, Brunauer-Emmett-Teller (BET) surface area and transmission electron microscopy-energy-dispersive X-ray spectroscopy (TEM/EDX). IR spectra with a S/N-ratio of 30,000:1 were obtained from samples in neat form with a Qest ATR (Attenuated Total Reflectance) accessory with diamond crystal puck using a Shimadzu IRAFFINITY-1S Fourier Transform Infrared Spectrophotometer (FTIR). A TA Netzsch Model STA 449 F3 Jupiter system was used to perform a thermogravimetric analysis (TGA) under air flow (100 mL/min). For CHNS elemental analysis a Thermo Flash 2000 thermal analyzer (Thermo Scientific) is used with V₂O₅ as catalyst and methionine as standard. XPS measurements were performed using a PHI Versaprobe II spectrometer equipped with a monochromatic Al K_α X-ray source (hν = 1486.6 eV) operating with a beam size of 100 μm and a power of 25.8 W. All measurements were conducted at a pressure of at least 10⁻⁶ Pa and photoelectrons were detected by a hemispherical analyzer positioned at an angle of 45° with respect to the normal of the sample surface. Individual high-resolution C1s, N1s, Eu3d, Eu4d, Tb3d and Tb4d spectra were recorded with a pass energy of 23.5 eV (step size = 0.1 eV). Binding energies were calibrated with respect to the C-C/C-H peak of the C1s spectrum at 285.0 eV. Deconvolution of the high-resolution N1s, Eu4d and Tb4d spectra were carried out using Gaussian-Lorentzian peak shapes (80–100% Gaussian). PXRD pattern was collected on a Thermo Scientific ARL X'Tra diffractometer, operated at 40 kV, 30 mA using Cu K_α radiation (λ = 1.5406 Å). The specific BET surface area was measured on a Belsorp Mini II apparatus at 77 K. Prior to analysis, the sample was dried at 100 °C under vacuum for 24 h. HAADF-STEM and the EDX mapping analysis was performed using JEOL JEM-2200FS High-Resolution STEM equipped with an EDX spectrometer with a spatial resolution of 0.13 nm, image lens spherical aberration corrector, electron energy loss spectrometer (filter) and an emission field gun (FEG) operating at 200 keV. X-ray fluorescence (XRF) was measured on Rigaku Nex CG. The metal loading was determined using an ICP-OES Optima 8000 atomic emission spectrometer.

Synthesis and characterization of the lanthanide bpyPOP DAT temperature sensor

Synthesis of the lanthanide bpyPOP DAT. The Ln-grafted samples were prepared by weighing 2 mg of the bpyPOP DAT sample. Next, 10 times molar amounts (based on the theoretical number of coordination sites) of the lanthanide acetylacetonate complexes, in appropriate ratios (Ln = Eu, Tb), were weighed. All products were placed in a Pyrex tube and 5 mL of ethanol was added. The tube was sealed well and placed on a heating block set at 80 °C for 24 h. The next day the samples were cooled to room temperature, collected by centrifugation and washed several times with ethanol before drying at 80 °C in air.

Luminescence and temperature sensor study. The luminescence of solid POP samples was studied. Solid powdered samples were put between quartz plates (Starna cuvettes for powdered samples, type 20/C/Q/0.2). Luminescence measurements were performed on an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup. A 450 W xenon lamp was used as the steady state excitation source. Luminescence decay times were recorded using a 60 W pulsed Xe lamp, operating at a frequency of 100 Hz. A Hamamatsu R928P photomultiplier tube was used to detect the emission signals in the near UV to visible range. All of the luminescence measurements were recorded at room temperature unless indicated otherwise. In order to compare the measurements, the same amounts of powders were used as well as the same settings for each measurement (same slit size, step, and dwell time). All emission spectra in the manuscript have been corrected for detector response. The luminescence decay curves of the samples were measured when excited into the maximum of the broad ligand band and monitored at the appropriate wavelength (strongest peak of the given lanthanide). All of the decay curves could be well fitted using either a single exponential function or a biexponential function.

$$I = A \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (2)$$

Where I represents the luminescence intensity of a transition and A , A_1 and A_2 are constants, t is time and τ , τ_1 and τ_2 are the luminescence lifetimes.

The temperature measurements were performed using an ARS closed cycle cryostat at a temperature range between 10 - 310 K. For the conversion of the intensity into the temperature, the thermometric parameter Δ was employed. Here, $\alpha = W_0/W_R$ is the ratio between the nonradiative (W_0 at $T = 0$ K) and radiative (W_R) rate, ΔE is the activation energy for the nonradiative channel, and Δ_0 is the thermometric parameter at $T = 0$ K.^{2-3, 25}

$$\Delta = \frac{I_1}{I_2} = \frac{\Delta_0}{1 + \alpha \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (3)$$

The relative temperature sensitivity S_r was calculated using the following equation:

$$S_r = 100\% \times \left| \frac{1}{\Delta} \frac{\partial \Delta}{\partial T} \right| \quad (4)$$

S_r indicates the relative change of the thermometric parameter per degree of temperature change (% K⁻¹). Compared with S_a , S_r has the important advantage of being independent of the nature of the thermometer and allows direct and quantitative comparison of different materials.

Another important parameter when assessing the performance of a thermometer is the temperature uncertainty δT . It can be determined using the following equation²³:

$$\delta T = \frac{1}{S_r} \frac{\delta \Delta}{\Delta} \quad (5)$$

FULL PAPER

where $\frac{\Delta\lambda}{\lambda}$ is the relative error in the determination of the thermometric parameter. The repeatability of the thermometer was calculated employing the equation²⁻³:

$$R = 1 - \frac{\max|\Delta c - \Delta i|}{\Delta c} \quad (6)$$

where Δc is the mean thermometric parameter and Δi is the value of each measurement of thermometric parameter.

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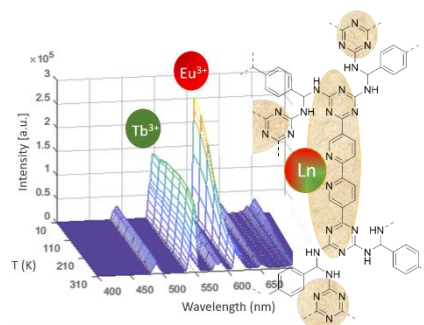
Keywords: Porous Organic Polymer • Lanthanides • Ratiometric thermometer • Thermal quenching • Sensor

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FULL PAPER

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Entry for the Table of Contents



A novel bipyridine-based Porous Organic Polymer (bpyDAT POP) is investigated as temperature sensor after grafting with $\text{Eu}(\text{acac})_3$ and $\text{Tb}(\text{acac})_3$ complexes. The material successfully demonstrates the potential of amorphous, porous polymers in temperature sensing. Furthermore, peculiar temperature dependent behavior is observed through the interruption of conjugation in the framework and the absence of thermal quenching.