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Heterobimetallic Eu(III)/Pt(II) single-chain nanoparticles: a path to enlighten catalytic reactions
Heterobimetallic Eu(III)/Pt(II) single-chain nanoparticles: a path to enlighten catalytic reactions †

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We introduce the formation and characterization of heterometallic single-chain nanoparticles entailing both catalytic and luminescent properties. A terpolymer containing two divergent ligand moieties, phosphines and phosphine oxides, is synthesized and intramolecularly folded into nanoparticles via a selective metal complexation of Pt(ii) and Eu(III). The formation of heterometallic Eu(III)/Pt(II) nanoparticles is evidenced by size exclusion chromatography, multinuclear NMR (1H, 31P(2H), 19F, 195Pt) as well as diffusion-ordered NMR and IR spectroscopy. Critically, we demonstrate the activity of the SCNPs as a homogeneous and luminescent catalytic system in the amination reaction of allyl alcohol.

As a rare example, Lemco and colleagues designed heterobimetallic single-chain nanoparticles via the introduction of catalytically active Ir(i) and Rh(i) ions into a diene-functionalized polymer chain.13 However, no targeted metal placement was carried out, as merely one type of ligand moiety was present, suitable for both metal species. Thus, the introduction of orthogonal linker moieties into the polymer chain is mandatory for a selective and controlled incorporation of different metal ions. To form heterometallic SCNPS structures, at least one of the metal precursors needs to induce the chain collapse, whereas a second metal species coordinating to an orthogonal ligand system can add additional functionality. Striving for a SCNP system, which exhibits both luminescent and catalytic properties, we herein report the synthesis and in-depth characterization of a bifunctional terpolymer, featuring both phosphine and phosphine oxide ligand moieties. The terpolymer enables SCNP formation via orthogonal complexation of platinum(ii) and europium(ii), providing novel catalytic material (Fig. 1). The combinatorial design of catalytic and luminescent properties within a SCNP system allows i.e. the visualization and tracking of the polymer nanoparticles during catalysis and helps to monitor a successful catalyst separation.

Results and discussion

Polymer synthesis and characterization

Ligand systems applied in metal–SCNP chemistry, mostly containing oxygen- and nitrogen-donor functionalities,9,17–19 tend to coordinate non-selectively to metal ions. In recent studies, our teams investigated the introduction of phosphine moieties into polymer chains, which enabled subsequent SCNP formation via the addition of Pd(ii) as well as Pt(ii) ions.8,20 Advantageously, phosphines can readily be oxidized, thereby changing their...
coordination behavior significantly due to the ionic character of the P=O bond.\(^{21}\) In a terpolymer exhibiting both phosphine and phosphine oxide moieties, the soft phosphine ligands can selectively coordinate to Pt(II) centers, inducing the single chain collapse, whereas the phosphine oxide functionalities act as a hard acid counterpart for the complexation of luminescent Eu(III). For the synthesis of a suitable bifunctional terpolymer, the monomers 4-(diphenyl-phosphino)styrene, 4-(diphenyl-phosphino oxide)styrene and styrene, working as a spacer monomer, were copolymerized via nitroxide mediated polymerization (NMP),\(^{22}\) yielding \(\text{PP/Oxide}\) (Scheme 1). Hereby, the phosphine and phosphine oxide functionalities are statistically distributed along the chain. The monomer composition of terpolymer \(\text{PP/Oxide}\) was determined by 1H and 31P{1H} NMR spectroscopy (in CDCl\(_3\)), comparing the resonance integrals of the respective monomer species (ESI, Fig. S2 and S3†). Analysis resulted in a monomer ratio of approx. 3.5 mol% phosphine and 1.7 mol% phosphine oxide functionalities in the terpolymer, in agreement with the feed ratio. The given values are – within the margin of error of NMR spectroscopy – estimates which are additionally hampered by the solvent resonance in the \(^1\)H NMR spectrum. Therefore, \(^{31}\)P{\(^1\)H} NMR experiments, applying bis(diphenyl-phosphino)methane (DPPPM) as an external standard, were additionally performed and resulted in 0.17 mmol phosphine oxide and 0.35 mmol phosphine species per 1 g of terpolymer \(\text{PP/Oxide}\) (Fig. S21†), which is in agreement with the priorly determined values. Accordingly, two resonances, in a ratio of 2 : 1, are observed at \(\delta = -6.2\) ppm and \(\delta = 29.2\) ppm in the \(^{31}\)P{\(^1\)H} NMR spectrum of \(\text{PP/Oxide}\), attributed to the implemented triarylphosphine and triarylphosphine oxide species (Fig. 4A). The characterization of \(\text{PP/Oxide}\) via SEC (THF, RI) resulted in \(M_p = 41\) 400 g mol\(^{-1}\) (average molecular weight 25 300 g mol\(^{-1}\)) with a dispersity of \(D = 1.4\) (Fig. 3, top). Combining the results of the SEC and NMR analysis, approx. 8–9 phosphine and 4 phosphine oxide moieties are estimated per chain. In addition, \(\text{PP/Oxide}\) was analyzed by IR spectroscopy (ESI, Fig. S22†). Among others, characteristic bands at \(v = 1202\) and \(v = 1118\) cm\(^{-1}\) are attributed to the P=O vibrational stretching and C–H deformation mode of the triarylphosphine oxide units.\(^{23,24}\)

SCNPs formation and characterization

As phosphate ligands are capable of forming stable 2 : 1 complexes with Pt(II)-ions via coordinative bond formation, the intramolecular collapse of terpolymer \(\text{PP/Oxide}\) into SCNPs was induced by addition to the platinum complex \([\text{PtCl}_2(\text{cod})]\), (cod = cyclooctadiene) in high dilution (Scheme 2).

Herein, cod is readily substituted by two phosphate ligands of \(\text{PP/Oxide}\), as already established in previous studies on Pt(II)-linked SCNPs.\(^{8}\) The orthogonal properties of the phosphate
oxide ligands, which do not coordinate to Pt(II), allow for the simultaneous complexation of a second suitable metal species. Thus, the europium precursor [Eu(dbm)\(_3\)(H\(_2\)O)\(_2\)] (dbm = dibenzoyl-methanide) was employed, coordinating exclusively to the phosphine oxides, via release of H\(_2\)O, yielding Eu(dbm)\(_3\)(n)/Pt(n)–SCNPs. Hereby, the phosphine oxide Eu(n) coordination can be realized either prior or subsequent to the Pt induced chain folding, resulting in an analogue Eu(n)–Pt(n)–SCNP system. Thus, the nanoparticle formation is independent from the sequence of metal ion addition, allowing dual functionalization and single-chain collapse in one step. Additional experiments, investigating stepwise metal addition and selective coordination behavior of platinum and europium towards the disparate ligand systems, are presented in the ESI (Schemes S4 and S5†).

In theory, the attachment of either one or two phosphine oxides to a [Eu[\(\beta\)-diketonate]\(_3\)] species is possible.\(^{35,36}\) However, the small number of approx. four phosphine oxide units per chain, combined with a high steric demand of the rigid polymer backbone suggests a 1 : 1 coordination ratio. In addition, the coordination of [Eu(dbm)\(_3\)] to a sole triarylphosphine oxide functionalized copolymer (stylene based) was investigated at high concentrations. Yet, no network formation was observed, as it is expected in case of a 2 : 1 ligand to Eu(n) coordination. For this reason, an Eu(n) coordination ratio of 1 : 1 is presumed. This assumption was further confirmed by DOSY NMR measurements (see below).

Following an analogous reaction procedure, different Eu(n) complexes can be applied, emphasizing the versatile applicability of the bifunctional polymer system. In case of the precursor [Eu(tta)\(_3\)(H\(_2\)O)] (tta = thenoyltrifluoroacetionate) heterometallic Eu(tta)(n)/Pt(n)–SCNPs were obtained, exhibiting e.g. a convenient \(^{19}\)F NMR sensor (Fig. 2 and ESI, Scheme S3†).

To confirm the assumption of an orthogonal metal complexation and verify the metal-induced chain compaction, the obtained particles were thoroughly investigated (for detailed analysis of the Eu(tta)(n)/Pt(n)–SCNPs refer to ESI†). The expected collapse into a more compact structure was verified by SEC analysis (THF, RI).\(^{27}\) In comparison to the terpolymer P\(_{\text{PP/Oxide}}\), the SEC trace for the Eu(dbm)(n)/Pt(n)–SCNPs is shifted towards longer retention times (Fig. 3, top), indicating a smaller hydrodynamic radius and thus pointing to the formation of nanoparticles without intermolecular side reactions. Further, the curve indicates the existence of a small molecular species (not shown in the spectrum), which most likely originates from unbound europium(n) complexes. To some extent the phosphine oxide coordination is apparently not sufficiently strong to withstand SEC measurement conditions. Consequently, the depicted SEC elugram rather represents a trace of Pt(n)-linked SCNPs. Furthermore, the transition of the linear terpolymer into a more compact nanoparticle was demonstrated by diffusion ordered spectroscopy (DOSY).\(^{28,29}\) Based on the obtained diffusion coefficients, the hydrodynamic radii of the particles were calculated, applying the Stokes–Einstein equation (see ESI†). The mean hydrodynamic radius of P\(_{\text{PP/Oxide}}\) resulted in \(r_1 = 8.0\) nm, whereas a radius of \(r_2 = 1.9\) nm was determined for the Eu(dbm)(n)/Pt(n)–SCNP. Interestingly, sole addition of [Eu(dbm)\(_3\)(H\(_2\)O)\(_2\)] to P\(_{\text{PP/Oxide}}\), resulting in the intermediate metallopolymer ‘P\(_{\text{PP/Oxide}}\)–Eu(dbm)’, affording a slightly larger hydrodynamic radius of \(r_2 = 11.2\) nm. Hence, the addition of an Eu species to P\(_{\text{PP/Oxide}}\) does not seem to induce chain compaction. The results are in line with a 1 : 1 coordination ratio of Eu(n) to the phosphine oxide ligands of P\(_{\text{PP/Oxide}}\), confirming the orthogonal behavior of the two ligand moieties.

To determine the photophysical properties, photoluminescent emission (PL) spectra of the Eu(dbm)(n)/Pt(n)–SCNPs were measured using a FTIR spectrometer. The spectra were recorded in solution at room temperature and normalized to a constant molar concentration of Eu(n). The spectra show a broad emission band at \(\lambda_{\text{em}} = 580\) nm for the Eu(dbm)(n)/Pt(n)–SCNP, whereas the Eu(dbm)(n)/Pt(n)–SCNP exhibit a distinct peak at \(\lambda_{\text{em}} = 610\) nm. This difference is attributed to the different coordination environments of the Eu(n) ions in the two systems. The PL spectra were recorded in a concentration range of 10 to 1000 \(\text{ppm}\) Eu(n) in THF, and the emission intensities were normalized to the absorbance at the excitation wavelength of \(\lambda_{\text{exc}} = 350\) nm. The results indicate that the Eu(n) ions are coordinated in different environments, leading to distinct emission behaviors.

**Fig. 2** \(^{19}\)F NMR spectrum of Eu(tta)(n)/Pt(n)–SCNPs in CDCl\(_3\). The tta moiety of the Eu(n) moiety allows tracking of the SCNPs in solution via \(^{19}\)F NMR spectroscopy.

**Fig. 3** SEC traces (THF, RI) of P\(_{\text{PP/Oxide}}\) and the Eu(dbm)(n)/Pt(n)–SCNPs (top). Photoluminescence emission (PL) spectrum of Eu(dbm)(n)/Pt(n)–SCNPs (298 K) in the solid state, after excitation at \(\lambda = 350\) nm (bottom).
SCNPs were recorded in the solid state (Fig. 3, bottom). After excitation at $\lambda = 350$ nm, the spectrum features characteristic bands resulting from 4f-4f transitions ($^5D_0 \rightarrow ^5F_J$) and is dominated by a band at $\lambda = 612$ nm ($^3D_0 \rightarrow ^3F_2$ transition). The resulting bright red luminescence is typical for europium(III) compounds. The coordination of phosphine oxide moieties to Eu(III)-diketonates is reported to further enhance the luminescence, working as an antenna ligand. As 4f-4f transitions are virtually unaffected by the surrounding ligands of Eu(III), an almost identical emission spectrum is observed for the Eu(tta)(III)/Pt(II) and analogous model complexes.

Furthermore, the $\text{Eu}_{(dmb)3}[/itex]/\text{Pt}(n)$-SCNPs were characterized by multinuclear NMR spectroscopy, primarily to gain closer insights into the metal coordinated folding units. In the $^{31}$P$[itex]^{1}H$ NMR spectrum (CDCl$_3$) of the SCNPs, the resonance of the tris-arylphtoshine and tris-arylphosphine oxide species in a ratio of approximately 2:1 is observed, accompanied by platinum(II) satellites $\delta \approx -4420$ ppm ($t$, $J_{Pt,P} = 3715$ Hz), confirming the obtained $^{31}$P$[itex]^{1}H$ NMR data (ESI, Fig. S6†). The coordination of $\text{[Eu(dmb)3]}$ to the phosphine oxide moieties of PP/Oxide is additionally evidenced by $^{1}H$ NMR spectroscopy. In the corresponding spectrum a characteristic high field resonance at $\delta = 16.9$ ppm is attributed to the methine group of the dbm ligands (ESI, Fig. S4†). Further information was obtained by IR spectroscopy. In the IR spectrum of the $\text{Eu}_{(dmb)3}$/$\text{Pt}(n)$-SCNPs bands for the dbm ligands are detected at $\bar{v} = 1519$ cm$^{-1}$, 1549 cm$^{-1}$ and 1600 cm$^{-1}$ (ESI, Fig. S23†), pointing towards its successful encapsulation in PP/Oxide-SCNPs.

### Catalytic application

As a proof-of-principle, both synthesized heterometalic Eu(III)/Pt(II)-SCNPs were subsequently investigated as homogeneous catalytic systems in the amination reaction of allyl alcohol (for details refer to ESI†). A similar catalytic study has previously been reported for sole Pt(II)-SCNPs, which proved to be an active and recyclable system for this reaction. Yet in the current approach, the additional Eu(III) functionalities of the heterometallic SCNPs enable a photophysical detection of the catalyst via illumination with UV-light. This allows e.g. a facile verification of catalyst separation. As mentioned before, the nanoparticles featuring the tta modified Eu(III) complexes exhibited a visibly more intense luminescence, thus being more suitable as a luminescent sensor for the catalytic reaction. Aniline and allyl alcohol were employed as starting material, using 4 mol% of catalyst (equals 2 mol% of Eu species) and ferrocene as an internal standard (Fig. 5, top). These comparatively high catalytic loadings were applied mainly with regards to the amount of Eu(III) species, as the luminescence is partially quenched by the catalyst loadings. The reaction was performed in an NMR Young tube and the respective conversion was determined by $^{1}H$ NMR spectroscopy (ESI, Fig. S28–S32†). A temperature of approx. 100 °C led to a near quantitative allyl alcohol conversion within less than 48 h, whereat merely small differences were observed for the $\text{Eu(tta)3}$ and $\text{Eu(dmb)3}$ modified SCNPs. In each case, the mono allyl-substituted amine was predominantly generated (>80%).

The results are similar to the data obtained for the literature-known Pt(II)-SCNPs as well as the mononuclear platinum complex cis-$\text{[PtCl(PPh$_3$)$_2$]}$, yet a different reaction procedure and catalyst loading need to be considered when compared in detail. After the catalytic reaction, the SCNPs were easily isolated by precipitation in methanol, or subsequent column
SCNPs, nations, is feasible. centers, as well as the implementation of other metal combinations, was synthesized via NMP, giving way to the facile formation of heterometallic Eu(III)/Pt(II) SCNPs. The SCNP synthesis proved to be selective in metal coordination and independent from the sequence of metal addition. In addition, featuring catalytic and luminescent centers, the SCNPs were employed as a homogeneous catalytic system. The selective coordination of two metal species exhibiting different functionalities represents, to this date, an unprecedented concept in the realm of single-chain nanoparticles. The combinatorial design of catalytically active and luminescent properties within a SCNP system may not only allow the visualization of the catalyst (and its separation), yet tracking for specific systems seems practicable.

Conflicts of interest

There are no conflicts to declare.

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