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Photoluminescent supramolecular polymers: metal-ion directed polymerization of terpyridine-functionalized perylene bisimide dyes

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Perylene bisimide dyes bearing one and two 2,2′:6′,2″-terpyridine receptor groups were prepared and the structural and optical properties of their Zn^{2+} complexes were investigated by ^{1}H NMR and fluorescence experiments.

Photoluminescent polymers have received significant interest in the last decade especially in the fields of organic light emitting diodes[1] and plastic solar cells.[2] Introduction of metal ions into conjugated polymers has been investigated with regard to higher electroluminescence quantum yields by harvesting triplet state emission.[3] However the purification and processing of such polymers is a difficult task. Therefore new concepts such as supramolecular polymerization[4] of photoactive building blocks might be of interest. Here we report on the metal-directed polymerization of highly fluorescent perylene bisimide dyes provided with terpyridine receptor units and a dimeric assembly which proved to be useful to elucidate the impact of the metal ion on the photophysical properties of the perylene dye.

The highly soluble bis-2,2′:6′,2″-terpyridine (tpy)-functionalized perylene bisimide dye **3** was synthesized by condensation of 4′-aminophenyl-tpy[5] and tetra(*p-tert*-butylphenoxy)perylene bisanhydride in quinoline with zinc acetate as catalyst in 50% yield (Scheme 1). The monotopic compound **1** is available under the same conditions in 40% yield using the corresponding perylene imide anhydride.[6] Both dyes exhibit strong absorption in the red region ($\lambda_{\max}$ = 583 nm, ε = 55000 dm^3 mol^{-1} cm^{-1} in CH_2Cl_2) and intense fluorescence ($\lambda_{\max}$ = 620 nm, Φ_{fl} = 0.92 in CH_2Cl_2).†

The complexation of the monotopic dye **1** with an octahedrally coordinating metal ion yields a dimeric complex which can be seen as a model reaction for the formation of the coordination polymer. Complexation can be achieved with zinc(II) trifluoromethanesulfonate (triflate) in a mixture of chloroform and acetonitrile and can be easily followed in an ^{1}H NMR titration experiment from the characteristic change of the chemical shift values δ of the tpy-signals upon complexation.[7] The spectra clearly show the formation of the dimeric complex **2** and the disappearance of the uncomplexed ligand at a dye : Zn^{2+} ratio of 2 : 1. As illustrated in Fig. 1 no dynamical processes appear but all species can be distinguished and their concentrations can be quantified by integration of the NMR signals. The titration curve in Fig. 2 shows the concentrations of the different species during the titration experiment. Interestingly, the addition of an excess amount of zinc triflate gives rise to a second process in which complex **2** is dissociated again in favour of an open form with the zinc ion only attached to one tpy-unit and its other coordination sites are presumably saturated by solvent molecules. Both processes, the formation of complex **2** and its decomposition, are therefore slow on the NMR timescale but fast on the laboratory timescale and fully reversible.

The same NMR titration studies were carried out with the ditopic ligand **3**. The spectra show analogous changes of the chemical shifts upon complexation and the disappearance of ligand signals exactly at a 1 : 1 stoichiometry. In addition, line broadening is observed as is expected for NMR signals of polymers (Fig. 1). From these data the formation of coordina-

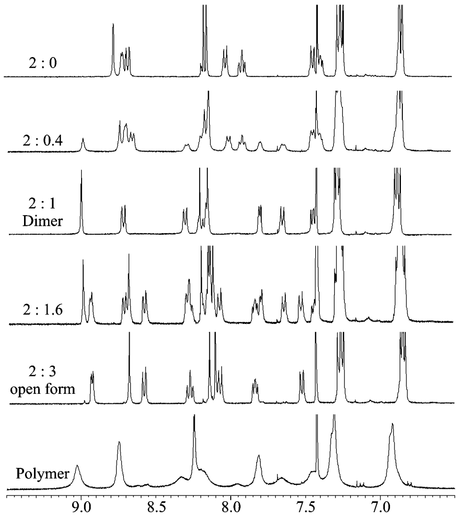
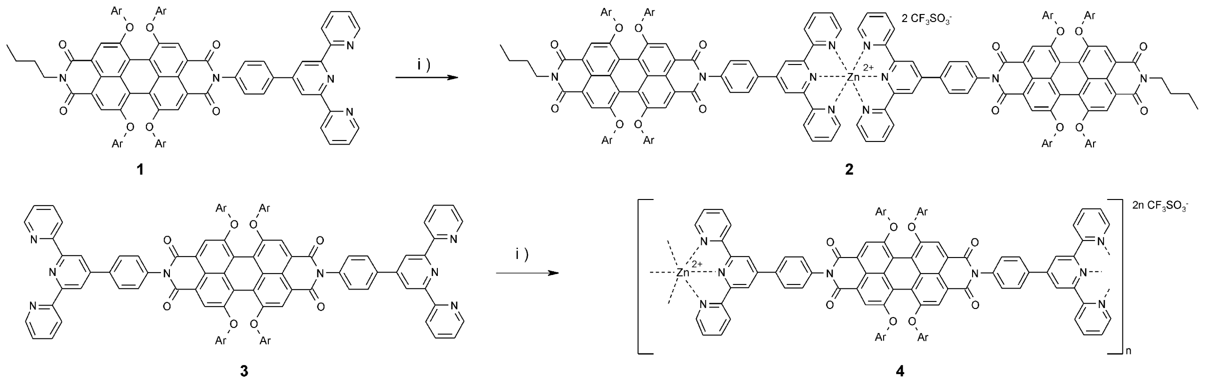


Fig. 1 NMR titration of dye **1** with zinc triflate in $CDCl_3$–CD_3CN (80 : 20) with the corresponding dye : Zn^{2+} ratios; bottom spectrum: NMR spectrum of polymer **4** showing analogous chemical shifts δ as the dimer.



Scheme 1 Complexation of terpyridine functionalized perylene bisimide dyes. *Reagents*: i) $Zn(CF_3SO_3)_2$, $CHCl_3$–CH_3CN (80 : 20), Ar = *p-tert*-butylphenyl.

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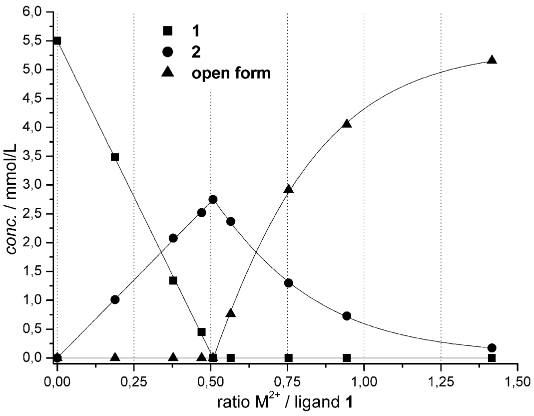

Fig. 2 Concentration of uncomplexed ligand **1** (■), dimer **2** (●) and the open form (▲) upon addition of Zn(CF$_3$SO$_3$)$_2$ to a 5.5 mM solution of **1** in CDCl$_3$–CD$_3$CN (80:20) calculated from integrated ^{1}H NMR signals.

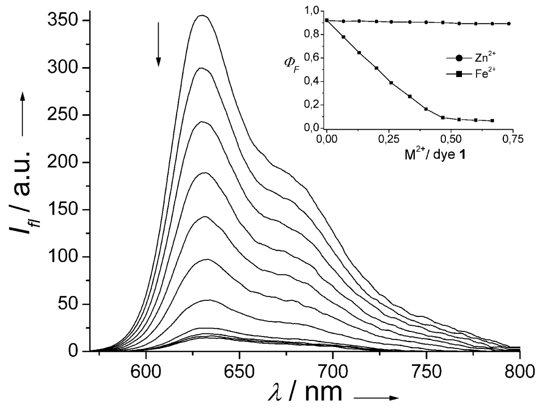

Fig. 3 Fluorescence titration experiment of **1** (10^{-5} M in CHCl$_3$–CH$_3$OH (60:40), λ_{exc} = 550 nm) with iron(II) perchlorate; inset: fluorescence quantum yields upon addition of zinc(II) triflate (●) and iron(II) perchlorate (■) calculated from the integrated fluorescence spectra.

tion polymer **4** can be concluded. Owing to the extremely rigid structure of both the perylene bisimide and the metal–tpy-complex unit a rigid rod-like structure is expected for polymer **4**. After precipitation from CHCl$_3$–CH$_3$CN the polymer can only be redissolved in DMF. Nevertheless, ^{1}H NMR spectra recorded in deuterated DMF prove that the polymeric structure remains intact also in polar solvents. As for the dimer, evidence for the reversibility of the tpy-complexation by Zn^{2+} ions is given for the polymer, since exceeding the 1:1 stoichiometry of zinc ions leads to the formation of the open zinc complex and results in a degradation of the polymeric strands into small monomeric and oligomeric fragments.

Although the coordination of zinc(II) metal ions to the tpy-units of **1** and **3** is strong there is little electronic interaction between the Zn(tpy)$_2^{2+}$ unit and the perylene bisimide chromophore according to UV/Vis and fluorescence spectroscopy. Thus the UV/Vis spectra show almost unchanged absorption properties of the chromophore upon dimerization (**2**) and polymerization (**4**) at wavelengths λ > 350 nm. At shorter wavelengths, *i.e.* 250–350 nm, a small increase in the absorption attributed to tpy-complexation can be observed. Table 1 shows the fluorescence quantum yields determined in chloroform and DMF. The intense fluorescence of the ligand is preserved in the dimer and only decreased by 20% for the polymer (which could only be investigated in DMF for solubility reasons).

Additional functional possibilities for such photoluminescent supramolecular polymers are exemplified by an experiment in which the zinc(II) metal salt is replaced by iron(II) perchlorate hexahydrate. Here NMR titrations indicate that the complex formation is not reversible at r.t. so that no decomposition of the respective Fe(tpy)$_2^{2+}$ complexes takes place in the presence of excess iron(II). Even more importantly, the perylene bisimide fluorescence is drastically quenched to a fluorescence quantum yield of only 0.04 in CHCl$_3$. The complexation can be followed by a fluorescence titration experiment which shows only a marginal change in the case of zinc(II) but a significant decrease for iron(II) (Fig. 3). This result shows that by application of different metal ions the M(tpy)$_2$-unit can be changed from a purely structural to a functional unit which opens up interesting possibilities with regard to the investigation of directional electron or energy transfer processes within the rigid-rod polymers. Incorporation of functional metals such as Ru^{2+} and Os^{2+} might be especially appealing.[8]

Table 1 Fluorescence quantum yields of ligand **1**, dimer **2** and polymer **4**

Φ_{fl}	CHCl$_3$	DMF
Ligand **1**	0.92	0.75
Dimer **2**	0.90	0.74
Polymer **4**	—	0.61

In summary, two new perylene bisimide dyes bearing terpyridine receptor units have been synthesized and assembled to fluorescent and non-fluorescent dimeric and polymeric structures by metal ion coordination. It is anticipated that incorporation of other metal ions in these polymers will lead to interesting multinuclear assemblies with new photophysical properties.

Notes and references

† The synthesis of these compounds will be published elsewhere. All compounds have been characterized by ^{1}H NMR, mass spectrometry and elemental analysis.

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