Synthesis and optical properties of metallo-supramolecular polymers†

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Metal–ligand interactions between metal ions, such as Zn^{2+}, and ditopic low-molecular weight conjugated monomers, which utilize the 2,6-bis(1′-methylbenzimidazolyl)pyridine ligand, lead to the formation of supramolecular conjugated polymers with interesting optical properties.

In our quest to develop organic/inorganic hybrid polymers, which are stable at high temperatures yet readily processible, we have embarked on the exploration of a new class of metallo-supramolecular polymers. The general molecular design attempts to merge the structure of thermally stable poly(arylene alkylene)s,[1] which can be easily accessed by the reduction of poly(phenylene ethynylene)s,[2] with the advantages of a dynamic (reversible) polymerization process,[3] to allow access to materials that are otherwise difficult to process.[4] Certain metal–ligand interactions offer this dynamic behaviour, in conjunction with large equilibrium constants, which provide the thermodynamic driving force required for polymer formation.[5] As a first step we herein report on the synthesis of a new conjugated ditopic monomer **1** (Fig. 1) and the formation and initial characterization of metallo-supramolecular polymers based on this monomer and Zn^{2+}. The new monomer utilizes the 2,6-bis(1′-methylbenzimidazolyl)pyridine (BIP) ligand[6] as the binding unit and 1,4-diethynylbenzene as the core moiety. In particular the electronic spectra of the conjugated systems comprising **1** and Zn^{2+} nicely reflect the presence of various species upon metal-induced polymerization and allow for a unique elucidation of the different stages of the self-assembly process. These data also illustrate the potential of tailoring the electronic properties of ligand-containing conjugated molecules through their interaction with metals.[7]

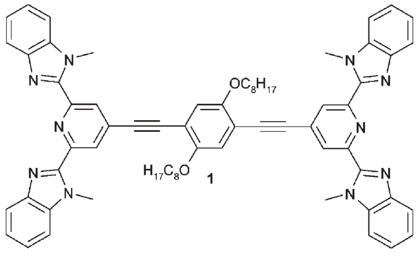

Fig. 1 Chemical structure of the ditopic monomer **1** based on the 2,6-bis(1′-methylbenzimidazolyl)pyridine (BIP) ligand.

The key step in the synthesis of ditopic monomer **1** is the Sonogashira coupling of 2,5-dioctyloxy-1,4-diiodobenzene[8] with 2,6-bis(1′-methylbenzimidazolyl)-4-ethynylpyridine (prepared *via* the Pd-catalyzed coupling of 2,6-bis(1′-methylbenzimidazolyl)-4-bromopyridine[9] and trimethylsilylacetylene followed by removal of the TMS protecting group under basic conditions), which affords **1** in good yield.

Monomer **1** exhibits electronic properties that are significantly different from those of similar BIP ligands, which are not further conjugated.[6] The UV-vis absorption spectrum of **1** (Fig. 2(a)) shows a band associated with the BIP moiety (λ^{abs}_{max} = 321 nm), and additionally displays transitions with λ^{abs}_{max} of 352 and 390 nm that appear to originate from the chromophore constituted by the BIP ligands and the 1,4-diethynylphenylene (DPE) bridge.[7,10] **1** is much more emissive than similar BIP ligands, which are not further conjugated. The emission associated with the isolated BIP moieties (around 368 nm) is virtually absent; instead, an emission band at 448 nm is observed, which on account of an excitation scan allowed us to link this band with the electronic

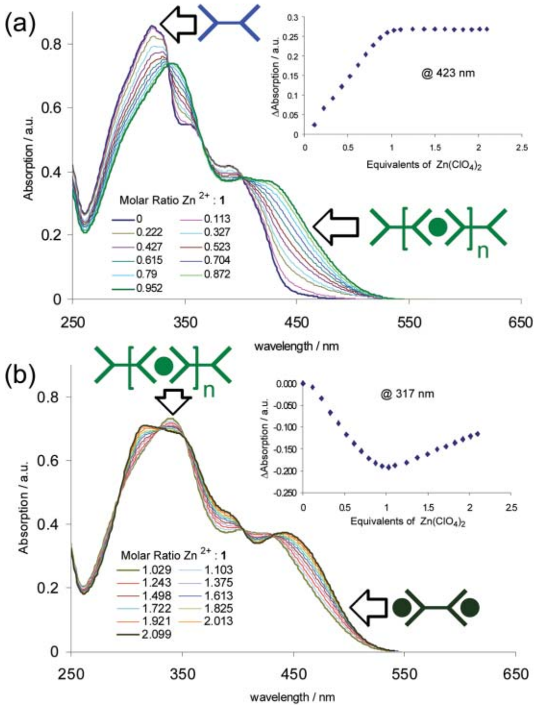

Fig. 2 UV-vis spectra acquired upon titration of **1** (10 μM) in $CH_3CN/CHCl_3$ (1/9 v/v) with $Zn(ClO_4)_2$. Shown are spectra at selected Zn^{2+}:**1**: ratios ranging from 0 to 1 (a) and from 1 to 2 (b). The insets show the normalized absorption at 423 nm (a) and 317 nm (b) as function of Zn^{2+}:**1** ratio.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of **1**, details of complexation studies and spectroscopic experiments. See http://www.rsc.org/suppdata/cc/b4/b410734a/

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transition (presumably π–π^*) that is also responsible for the lowest-energy absorption of **1**.

With the goal of attaining insight into the mechanism of the metal-ion-mediated self-assembly processes of these ditopic ligands, we titrated $Zn(ClO_4)_2$ into solutions of **1** and examined the resulting products by means of UV-vis absorption and PL spectroscopy. At a concentration of 10 μM the titration of **1** with up to 1 eq. of Zn^{2+} rendered the originally colorless solution orange. Concomitantly, the lowest-energy absorption of the monomer is red-shifted to *ca*. 421 nm (Fig. 2(a)), presumably as a result of a charge transfer occurring within the monomer between the electron rich central aryl component and the metal-coordinated, electron-deficient BIP moiety.[11] The spectra further reveal a shift of the two other absorption bands to 404 and 339 nm. This series of spectra displays three isosbestic points, suggesting equilibria between a finite number of spectroscopically distinct species. Upon addition of Zn^{2+}, the intensities of the new peaks increase in linear fashion, until a metal-to-monomer ratio of 1:1 is reached. Beyond this point, the subsequent addition of Zn^{2+} causes new spectral changes (Fig. 2(b)). The lowest-energy absorption is further red-shifted to 441 nm, while the 404 peak shifts to *ca*. 390 nm and the 339 nm peak appears to split into two bands at *ca*. 345 and 317 nm. The spectral changes level off at a metal-to-monomer ratio of 2:1. Isosbestic points are again observed, but they occur at different wavelengths than seen for the previously mentioned titration data (metal-to-monomer ratios of below 1:1), indicating equilibration between a different set of spectroscopically distinct species. Thus, these data are consistent with the fact that at a 1:1 Zn^{2+}-to-monomer ratio a metallo-supramolecular complex has formed, in which each Zn^{2+} is complexed with two monomers, and the resulting (monomer–Zn^{2+}–) repeat unit is the origin of the observed dominating electronic transitions. At metal-to-monomer ratios of above 1:1, depolymerization occurs, driven by the formation of the chain-terminating monomer–Zn^{2+}–solvent complexes. Insets in Fig. 2(a) and (b) show the change in absorption at two selected wavelengths, highlighting the different nature of the predominant species involved in the self-assembly process at Zn^{2+}-to-monomer ratios of below and above 1:1. It should be noted that the high extinction coefficient of **1** dictated rather low concentrations (10 μM) for the above discussed optical experiments. As a result,[6] these conditions clearly favour the formation of oligomeric species, as opposed to high-molecular weight macromolecules. In fact, as discussed above, the UV data nicely reflect a linear combination of absorption spectra associated with three distinctly different chromophores that we assign as free ligand, 1:1 Zn^{2+} to ligand and 1:2 Zn^{2+} to ligand complex. As discussed above, the relative contribution of these species was found to depend on the concentration of Zn^{2+} in the expected manner.

Evidence for the formation of metallo-supramolecular polymers at higher concentrations comes from viscosity data (Fig. 3) for a series of solutions with different $Zn(ClO_4)_2$:**1** ratios. Keeping the total solute concentration constant, the data show a steady increase of the reduced viscosity up to a Zn^{2+}:**1** ratio of 1. Beyond this point a decrease in the reduced viscosity is observed, confirming the depolymerization of the supramolecular polymer.

Metal-binding also exerts a pronounced influence on the emission characteristics of **1** as is evident from the PL spectra observed upon titration of $Zn(ClO_4)_2$ into a solution of **1** (Fig. 4). The emission maximum is strongly red-shifted from 448 nm to *ca*. 594 nm and experiences significant broadening. Similar to the absorption titration experiment for the same system, the emission spectra gradually change as the metal-to-monomer ratio is increased. At a ratio of 1:1 the emission of the uncomplexed monomer has completely disappeared. Interestingly, in contrast to the absorption data, subsequent addition of Zn^{2+} results in no further spectral changes. This behaviour is consistent with the fact that essentially irrespective of the relative amount of Zn^{2+}, emission occurs always from the same low-energy electronic states, presumably the monomer–Zn^{2+}–solvent complexes referred to above. We are currently studying the nature of this in more detail.

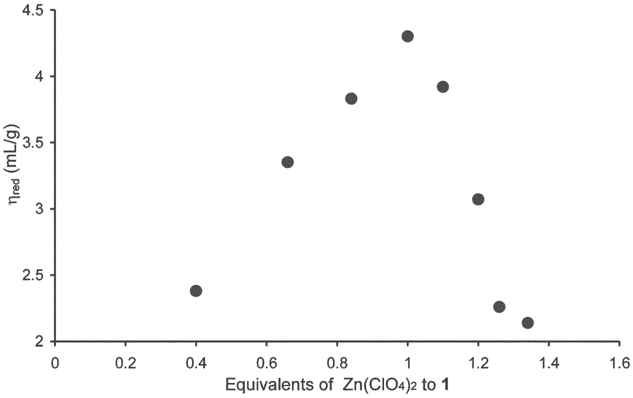

Fig. 3 Reduced viscosities of a series of dimethylacetamide solutions comprising $Zn(ClO_4)_2$ and **1** at different molar ratios. The total concentration of solute was kept constant at 35 mg mL^{-1}.

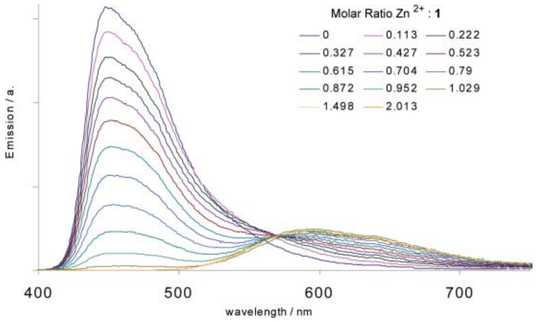

Fig. 4 PL spectra acquired upon titration of **1** (10 μM) in CH_3CN–$CHCl_3$ (1:9 v/v) $Zn(ClO_4)_2$. Shown are spectra at selected Zn^{2+}:**1** ratios of 0–2:1.

In conclusion, a new ditopic conjugated monomer featuring BIP ligands was synthesized and polymerized *via* coordination with Zn^{2+}. The electronic spectra of samples with different metal-to-monomer ratios reflect the presence of various species and allow for a unique elucidation of the different stages of the self-assembly process. Complexation studies with other metals and reduction of **1** to yield the more flexible monomer with a 1,4-diethylbenzene core are currently in progress.

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