Supramolecular cruciforms†

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By self-assembling fluorescent pyridyl cruciforms with bis-Pd-pincer complexes, supramolecular assemblies with attractive optical properties were synthesized; these assemblies show potential as electro-optical materials.

Conjugated materials have important electrical, optical and redox properties that make them outstanding candidates for integration into electro-optical and light-emitting devices (LEDs). Such functional materials can be based on either small molecules, oligomers, or polymers, each with distinct advantages.[1,2] Small molecules are monodisperse and are easier to purify and characterize. Polymers and oligomers, on the other hand, are polydisperse. However, in contrast to their small molecule analogues, polymers are amenable to solution processing techniques such as ink-jet printing and spin casting. Naturally, it would be attractive to merge the advantages of small molecules, such as easy characterization and purification, with the solution processibility of oligomers and polymers.

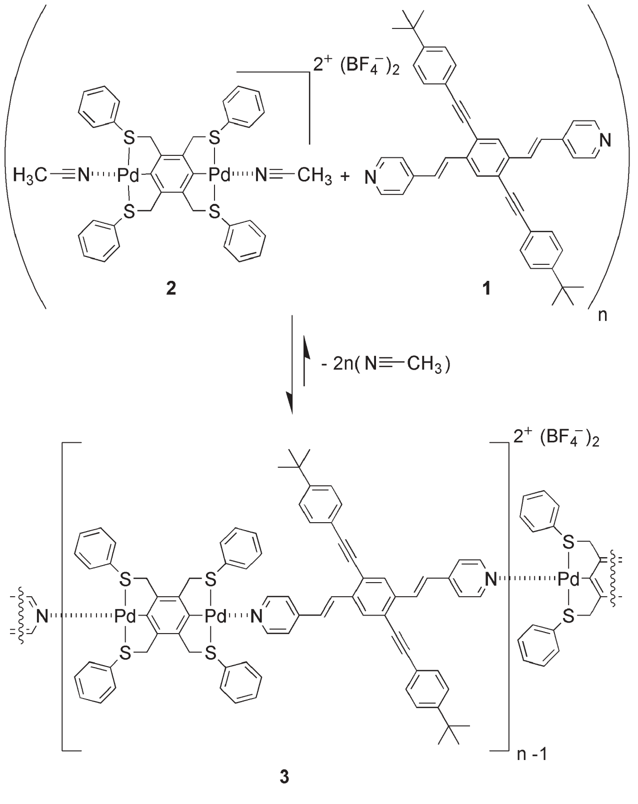
In this contribution, we incorporate a fluorescent cruciform[3] into self-assembled supramolecular aggregates. Cruciform **1**[4] was self-assembled through its pyridyl termini with the bis-Pd-pincer complex **2**,[5] creating fluorescent supramolecule **3** with tunable emission and molecular weight (Scheme 1). The self-assembly occurs readily under ambient conditions by employing the well-studied pyridine-pincer coordination.[6,7] The resulting supramolecular material combines the advantages of small molecules and polymers—a well-defined yet easily processable system.

Cruciforms are fluorescent cross-conjugated 1,4-distyryl-2,5-bis(arylethynyl)benzenes with unusual optical, electronic and redox properties that can be readily tuned by varying the donor–acceptor substituents at any terminus.[1] These cruciforms exhibit a spatially-orthogonal HOMO–LUMO arrangement; the HOMO is localized along the axis featuring electron releasing substituents and the LUMO is aligned along the axis featuring electron deficient substituents making cruciforms unusual materials.[4,8]

We rationalized that pyridyl cruciforms could be assembled into supramolecular aggregates[9] using metal coordination *via* Pd-pincer complexes. Metallated pincer complexes are employed in metal coordination owing to their chemo-activated coordination that is fast and quantitative.[6,7] This coordination strength can also be varied by exploiting several common classes of ligands (nitriles < pyridines < thioureas < phosphines).[7] Bis-pincer complex **2** has previously been used to generate pyrazine and pyridyl coordination polymers[2,6d] and is ideally suited for the main-chain assembly of **1**. Pyridyl cruciform **1** contains two terminal pyridine moieties, *i.e.* it serves as a bifunctional ligand that can easily displace the acetonitrile-coordinated bis-pincer complex **2**, generating supramolecular complex **3** in one simple step.

Charged supramolecular complex **3** is soluble in organic solvents such as CH_2Cl_2 and $CHCl_3$ at dilute concentrations, and readily soluble in DMF or DMSO at higher concentrations. DMF was chosen as the solvent for characterization of the physical properties because it is a less competitive/coordinating solvent than DMSO, permitting higher association constants (K_a), resulting in a stronger supramolecular complex.

Using ^1H NMR spectroscopy, the self-assembly event between **1** and **2** in d_7-DMF could be monitored by diagnostic signals indicative of a pincer–pyridine complex. A 0.1 ppm upfield shift of



Scheme 1 Supramolecular complex **3**, based on cruciform **1**, self-assembled with bis-pincer complex **2** in a 1 : 1 molar ratio.

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the ±-pyridyl proton signal and a 0.15 ppm downfield shift of the pincer methylene proton signal were observed upon the addition of 0.75 equivalents of **2**. The resulting spectrum remained constant with the addition of as much as three equivalents of **2**, except for a slight further upfield shift of the α-pyridyl proton signal of **1** and a slight upfield shift of the methylene proton signal of **2**, settling directly between the signals of the fully coordinated and uncoordinated species (see ESI†). These observations can be explained by an equilibrium faster than the NMR time scale, leading to peak broadening and the averaging of signals.[7] Nevertheless, these results prove that coordination took place and that the self-assembled complex forms reversibly.

A primary goal of the study was to establish a highly controlled polymeric system, where molecular weights of the oligomers and polymers can be manipulated by controlling the feed ratio of **1** to **2**. The association constant for the formation of supramolecular complex **3** can be used to estimate, as a first approximation, the expected degree of polymerization (DP) at different monomer concentrations.[10] Using isothermal titration calorimetry (ITC), we measured the association constant of the coordination complex of **1** and **2** to be 5 700 M^{-1} (295 K, DMF).‡ This measured association constant should allow for the formation of oligomers and polymers.

To demonstrate the control over molecular weight when forming supramolecular complex **3**, viscosimetry was employed. A 1 : 1 mixture of **1** to **2** is expected to result in high molecular weight polymers, while non-stoichiometric equivalents of the two components, such as ratios of 1 : 2 of **1** (**2**) or **2** (**1**) should yield lower molecular weight terminated oligomers **2**–**1**–**2** (**1**–**2**–**1**). These changes in molecular weight, resulting from the different monomer feed ratios, can be qualitatively detected by viscosimetry. We determined that the relative viscosity reaches a maximum as the concentration of bis-pincer complex **2** approaches a 1 : 1 stoichiometry with cruciform **1**, resulting in the formation of 14-mers.[10] Upon an increase in the ratio of either **1** or **2**, the solution viscosity descends towards the viscosity of pure DMF as the molecular weight decreases from a polymer towards smaller and smaller oligomers (Table 1).

Having investigated the metal coordination of **1** and **2** and the formation of their supramolecular complex **3**, we then characterized its optical properties. Previously, we have demonstrated that dramatic emission shifts result when cruciform molecules are exposed to various metal cations.[4c] Here, emission shifts accompany the polymer formation observed upon the addition of bis-pincer complex **2** to cruciform **1**. Spectroscopic studies in DMF proved difficult as self-assembly was not readily observed at the very low concentrations needed for fluorescence spectroscopy.

Table 1 Relative viscosities of varying ratios of **1** to **2**

Ratio of **1** : **2**[a]	Relative viscosity[b]
0 : 0	1
0 : 1	insoluble
1 : 2	1.25
1 : 1	2.83
2 : 1	1.33
5 : 1	1.19
1 : 0	1.09

[a] Total concentration is 0.033 M in 1 mL DMF. [b] Standardized to 1 mL DMF in an Ubbelohde semi-micro viscometer.

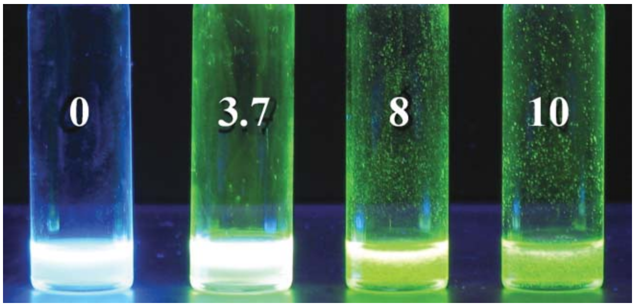


Fig. 1 Change in emission upon the addition of bis-pincer complex **2** (0, 3.7, 8 and 10 equivalents) to cruciform **1** in $CHCl_3$. The photograph is taken under illumination at 365 nm.

As a result, all spectroscopic measurements were performed in $CHCl_3$. It is important to note that the K_a value is expected to be significantly higher in this less polar and non-coordinating environment. When carrying out the emission experiments in $CHCl_3$, a bathochromic shift (445–515 nm) was observed upon the addition of 4.5 equivalents of **2** to **1** (Fig. 1 and Fig. 2). This shift can be reversed by the addition of a more competitive ligand such as PPh_3; upon addition of PPh_3, the blue fluorescence of the small molecule cruciform is restored as the phosphine ligand initiates decomplexation (see ESI†).

We next examined the change in the emission upon addition of mono-Pd-pincer complex **4** to cruciform **1**.§ This was done as a control to characterize the changes in the emission of the coordinated species in more detail. In this model system, we also observed a bathochromic shift (445–491 nm) (Fig. 3). We rationalize that these shifts are the result of the spatially-orthogonal HOMO–LUMO arrangement present in **1**. Upon complexation, the LUMO, localized on the styryl axis, is stabilized while the HOMO remains relatively unaffected. As a consequence, the HOMO–LUMO gap shrinks and the emission is significantly red-shifted. This shift is not observed at the expected molar ratio of 1 : 1, which correlates to the highest DP at the concentrations used for viscosimetry, because of the relatively low concentrations of the solutions used for the optical measurements. In the case of bis-pincer complex **2**, the slightly larger shift (λ_{max}em = 515 *vs.*

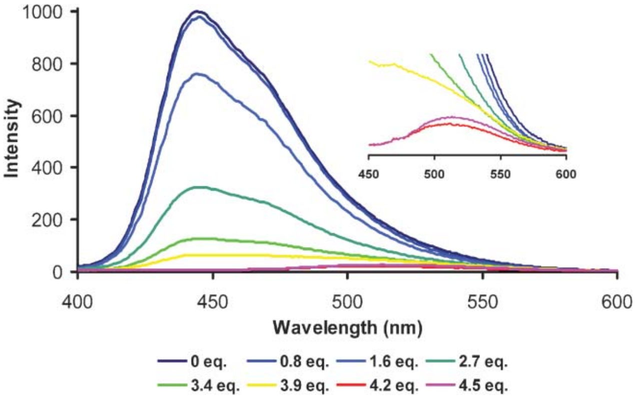
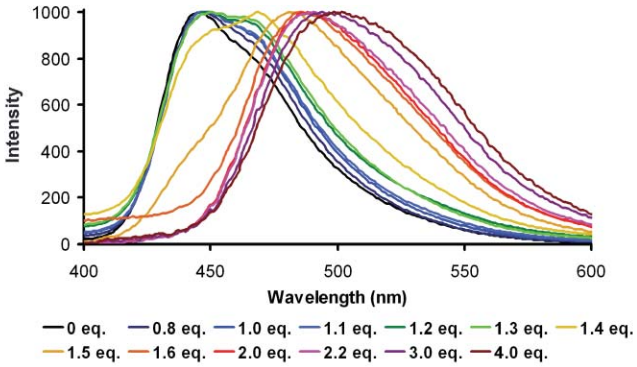


Fig. 2 Changes in emission in $CHCl_3$ upon the titration of bis-pincer complex **2** into cruciform **1**. The concentration of **1** in the samples was 0.081 mM; equivalents (eq.) in the legend refer to the added amount of bis-pincer complex **2**.



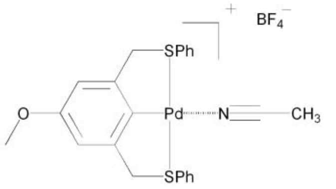


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Fig. 3 Normalized emission upon addition of mono-pincer complex **4** to cruciform **1** in $CHCl_3$.¶ Due to solubility and signal/noise issues, the concentration of **1** ranges from 0.154 mM (0 eq.) to 0.146 mM (4.0 eq.). Equivalents (eq.) in the legend refer to the equivalents of **4** added.

491 nm) is probably the result of aggregation of the coordination complex **3** in $CHCl_3$. These spectroscopic results demonstrate that the fluorescent properties of **1** are retained in the coordination aggregates **3**.

In conclusion, we have demonstrated the self-assembly of cruciform **1** with the bis-Pd-pincer complex **2** to create the new fluorescent supramolecular material **3**. The metal coordination event was characterized by ^1H NMR spectroscopy and ITC. Results from these experiments indicate that the polymer properties, resulting from changes in the degree of polymerization, can be tailored by altering the ratios of **1** to **2**. The direct dependence of the molecular weight of the supramolecular aggregate on the monomer feed ratio was proven by viscosimetry. These results prove a high degree of control over the materials properties. We also examined the optical properties of the resulting material. In all cases, red shifts in the emission spectra were observed upon coordination.

Current efforts are targeted towards the manipulation of the optical properties of these materials. Previous efforts in our group have demonstrated that donor/acceptor substitutions of the aryleneethynylene axis of the cruciform ligand permit facile modification of their optical properties.[1] Therefore, by combining this degree of control over the optical properties with aggregate formation, a wide variety of assemblies with tunable polymer and optical properties are envisaged.

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Notes and references

‡ The reported association constant represents an average binding affinity for each assembly event leading to supramolecular complex **3**.

§ Schemes and experimental details for mono-Pd-pincer complex **4** can be found in the ESI.†

¶ Spectra were normalized to an intensity of 1000 to highlight the resulting shift upon the addition of **4** as well as to eliminate concentration effects. Details and raw spectral data prior to normalization can be found in the ESI.†

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