Amylose-wrapped luminescent conjugated polymers†

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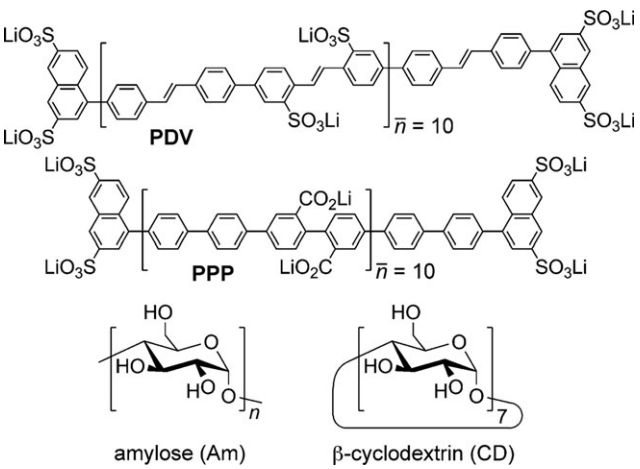
Highly luminescent inclusion complexes consisting of poly(*para*-phenylene) (PPP) or poly(4,4′-diphenylene-vinylene) (PDV) in the helical cavity of amylose have been synthesised, structurally characterised by nuclear Overhauser spectroscopy and used to fabricate electroluminescent light-emitting diodes.

The molecular-scale encapsulation of conjugated polymers can give insulated molecular wires (IMWs)[1] with enhanced stability, photoluminescence[2,3] and electroluminescence efficiency,[1,4] which are promising materials for the fabrication of optoelectronic devices, such as polymer light-emitting diodes (PLEDs).[5] Strategies for the non-covalent encapsulation of conjugated polymers include (i) threading through macrocycles, such as cyclodextrins, to form polyrotaxanes[1–4,6,7] and (ii) wrapping with helical polymers, such as polysaccharides, to form polymer–polymer inclusion complexes.[8–14] Both encapsulation processes are often driven by hydrophobic interactions in aqueous solution. Polyrotaxanes have the obvious advantage of kinetic stability, because the presence of bulky terminal groups can completely prevent the macrocycles from slipping off the polymer backbone.[7] However, polymer–polymer complexes can also have a remarkably high kinetic stability. The wrapping approach has the advantage that the diameter of the one-dimensional cavity of a helical polymer is often much more flexible than that of the corresponding macrocycle. Thus Shinkai's group[8–10] and others[11–14] have shown that the polysaccharides amylose and schizophyllan can accommodate a very wide range of guests. Recently, the polysaccharide complexes of two luminescent conjugated polymers, poly(*para*-phenylene–ethynylene)[10] and poly(*para*-phenylene–vinylene),[12] have been investigated.

Here we present the first investigation of the amylose complexes of luminescent polymers poly(*para*-phenylene) (**PPP**) and poly(4,4′-diphenylenevinylene) (**PDV**), and make a direct comparison of these polymer–polymer complexes with their β-polyrotaxane analogues, **PDV⊂β-CD** and **PPP⊂β-CD**, which are essentially isomers of the amylose complexes.[6] Helical wrapping in previous polymer–polysaccharide complexes has been surmised by circular dichroism and microscopy,[9–12] although neither of these techniques can demonstrate that the polymer guest actually resides inside the one-dimensional cavity of the polysaccharide. Here we report 2D ^{1}H NMR NOE spectra, showing that both conjugated polymers are threaded inside the helical cavity of amylose. Amylose encapsulation enhances the photoluminescence efficiencies of both **PDV** and **PPP** to a greater extent than polyrotaxane formation. Both materials are electroluminescent, but the maximum efficiency and luminescence from the amylose complexes are less than from the corresponding polyrotaxanes.



Polymers **PPP** and **PDV**, and the polyrotaxanes **PDV⊂β-CD** and **PPP⊂β-CD** (all with a number-average degree of polymerisation $\bar{n}$ = 10), were prepared as reported previously.[6] Complexes of both guest polymers with amylose, **PPP⊂Am** and **PDV⊂Am**, were prepared by diluting a solution of the guest and amylose (MW = 15 000) in dimethylsulfoxide with water. As with previously reported polymer–amylose complexes, these complexes were not formed when amylose was added directly to an aqueous solution of **PDV** or **PPP**, even after standing for more than a week at room temperature; the kinetics of formation and dissociation of these polymer–polymer complexes is evidently very slow.

The complexation of amylose with **PPP** and **PDV** was studied in solution by UV-visible spectroscopy and fluorescence titration, as illustrated for **PDV** in Fig. 1(a)–(c). Increasing the amylose concentration led to a shift in the absorption maximum from 400 nm for free **PDV** to 393 nm for **PDV⊂Am** at the end-point (Fig. 1(a)). The UV-visible spectrum of **PPP** was also blue-shifted by 5 nm to 339 nm. The UV-visible spectra were fitted to a simple 1 : 1 binding isotherm, with $K = 2.4 (\pm 0.6) \times 10^7$ M^{-1} for **PPP⊂Am**

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† Electronic supplementary information (ESI) available: Synthesis, UV-visible and fluorescence titration data, time-resolved photoluminescence and details of NMR assignments. See DOI: 10.1039/b803335h/

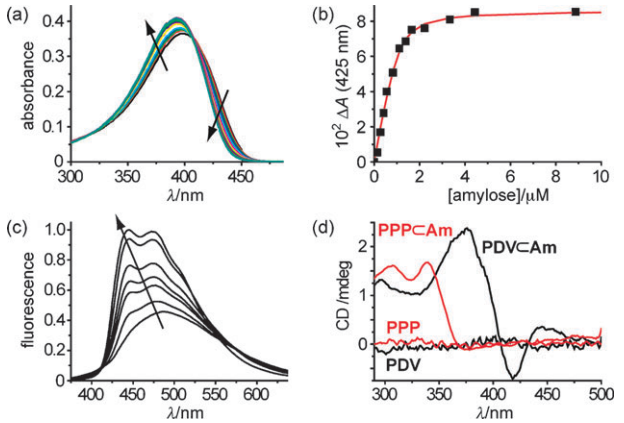

Fig. 1 (a) Effect of increasing amylose concentration on the UV-visible spectrum of **PDV** in 1 : 4 DMSO/water. (b) UV data fitted to a simple 1 : 1 binding isotherm with $K = 8.3 (\pm 2.9)\ \mu M^{-1}$, [**PDV**] = 1.1 μM. (c) Effect of increasing amylose concentration on the fluorescence spectrum of **PDV** in 1 : 9 DMSO/water ($\lambda_{ex} = 348$ nm), [**PDV**] = 0.6 μM. Both (a) and (c) start from [**Am**] = 0. (d) Circular dichroism spectra of **PPP**, **PDV**, **PPP⊂Am** and **PDV⊂Am** in 1 : 9 DMSO/water at 20 °C with a 1 cm path length.

and $K = 8.3 (\pm 2.9) \times 10^6\ M^{-1}$ for **PDV⊂Am**. The similarity in these values suggests that binding is similar in both systems, and that the end-point for the titrations in both cases is consistent with a 1 : 1 stoichiometry.‡ Surprisingly, complex formation was also observed between the polyrotaxane **PDV⊂β-CD** and amylose, with $K = 1.2 (\pm 0.7) \times 10^7\ M^{-1}$, indicating that the presence of threaded cyclodextrins does not block further complexation with amylose. We also tested the complexation of **PDV** with the polysaccharide schizophyllan (**SPG**),[8] but the addition of **SPG** led to no significant change in the absorption and photoluminescence spectra, and there was no evidence of complex formation.

With increasing amylose content, the fluorescence maximum of **PDV** shifted from 487 to 445 nm, with a reversal of the relative intensities of the (0,0) and (0,1) emission peaks and an increase in fluorescence efficiency (Fig. 1(c)). A similar trend was observed for **PPP**, which exhibited a blue-shift upon complexation by 26 nm to 389 nm. The nature of these shifts is in line with the published spectra of polyrotaxanes **PDV⊂β-CD** and **PPP⊂β-CD**, and indicates that aggregation of the conjugated polymer chains was suppressed by amylose complexation.[4] A similar effect was observed upon adding poly(ethylene oxide) to **PDV**.[15] As expected, the fluorescence spectrum changed to that of free **PDV** when a sample of the amylose complex **PDV⊂Am** was treated with salivary amylase, which catalyses hydrolysis of the amylose.[13]

The circular dichroism spectra of **PDV⊂Am** and **PPP⊂Am** (Fig. 1(d)) demonstrate that the conjugated polymers adopt chiral conformations when they associate with amylose. **PDV⊂Am** showed negative and positive Cotton effects at 417 and 375 nm, respectively, while **PPP⊂Am** gave positive Cotton effects, with peaks at 306 and 338 nm. As expected, the conjugated polymers showed no circular dichroism in the absence of amylose, and pure amylose showed no circular dichroism signal in this region.

Molecular mechanics calculations,[16] using the crystallographic coordinates of V-amylose as a starting point,[17] suggest that the amylose helix can easily accommodate **PPP** (Fig. 2). This model is

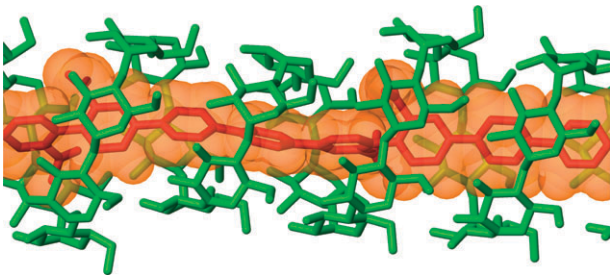

Fig. 2 A fragment taken from a molecular mechanics model of a longer ($n = 10$) **PPP⊂Am** model.[16] Hydrogen atoms are omitted for clarity.

supported by the pattern of ^{1}H NMR NOESY correlations observed in **PDV⊂Am** and **PPP⊂Am**. For example, the NOE spectrum of **PPP⊂Am** (Fig. 3(b)) shows correlations between the **PPP** aromatic backbone protons at 7.2–8.2 ppm, and resonances of the amylose 3-H, 5-H and 6/6′-H C–H protons at 3.9 and 3.6 ppm. These are the protons on the inside of the amylose helix, as illustrated by the cross-section plotted from the crystal coordinates in Fig. 3(a). The observation of these NOEs, and the absence of any NOE between the anomeric 1-H amylose protons at 5.1 ppm

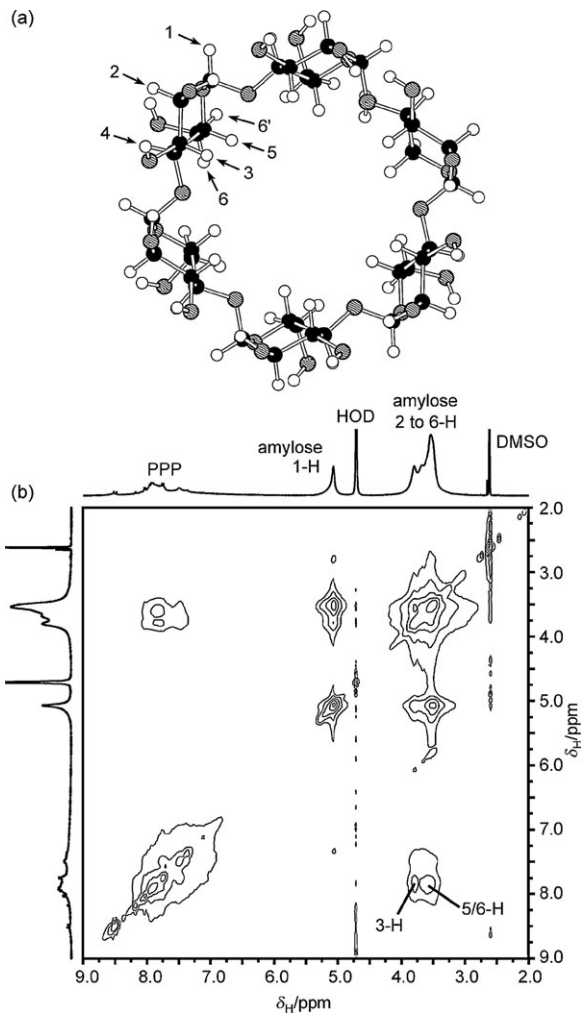

Fig. 3 (a) View down one turn of the V-amylose helix axis in the native crystal.[17] (b) ^{1}H NOESY NMR spectrum of **PPP⊂Am** in d_6-DMSO/D_2O (1 : 4) showing the assignments of the amylose resonances (mixing time 50 ms).

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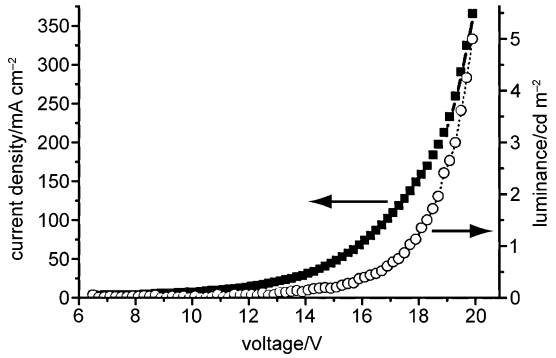

Fig. 4 Current–voltage (■) and luminance–voltage (○) data for a PLED with a device architecture of ITO/**PDV⊂Am**/Ca/Al. The layer of **PDV⊂Am** had a thickness of 80 nm.

and the **PPP** backbone, provides conclusive evidence for the proposed binding mode, with the guest inside the helical cavity of the amylose. Similar correlations were also detected for the **PDV⊂Am** complex; once again, NOEs were only observed between the **PDV** backbone and the amylose 3-H and 5/6-H proton resonances on the internal surface of the helix.

Thin solid films of the polyrotaxane **PDV⊂β-CD** and the wrapped polymer **PDV⊂Am** both displayed blue-shifted fluorescence with respect to the uninsulated **PDV**. The photoluminescence efficiencies (Φ_F) of thin films of **PDV⊂Am** and **PPP⊂Am** (Φ_F = 0.73 and 0.37, respectively) were significantly higher than for thin films of the free polymers (**PDV**: Φ_F = 0.04; **PPP**: Φ_F = 0.10), and also higher than the corresponding values for the polyrotaxanes (**PDV⊂β-CD**: Φ_F = 0.15; **PPP⊂β-CD**: Φ_F = 0.12), probably due to a lower population of non-emissive aggregate states in the amylose complexes and a lower rate of energy migration to any such non-emissive sites. Time-resolved photoluminescence measurements showed that emission from **PDV⊂Am** decayed more slowly than that from **PDV⊂β-CD** or from naked **PDV**, demonstrating that intermolecular excited-state migration to non-luminescent sites was more efficient in the uninsulated species. These results imply that the insulation by amylose wrapping is more effective than cyclodextrin threading, and that gaps between cyclodextrin rings allow closer intermolecular contact than a continuous helical amylose sheath. Simple, single-layer PLED devices were constructed for **PDV**, **PDV⊂Am** and **PDV⊂β-CD** using an identical device fabrication procedure, and electroluminescence was observed from all three materials. Data for an unoptimised device with **PDV⊂Am** are shown in Fig. 4. Initially, the **PDV⊂Am** devices gave anomalously high current densities, but better performances were obtained after preconditioning of the devices for 1 min at 7 V. The external quantum efficiencies (Φ_{EL}) of the **PDV⊂Am** devices ($\Phi_{EL} = 2 \times 10^{-5}$) were comparable to those made from bare **PDV** ($\Phi_{EL} = 7 \times 10^{-5}$), but less than those of polyrotaxane **PDV⊂β-CD** ($\Phi_{EL} = 2.5 \times 10^{-4}$). There is only one previous report of PLEDs fabricated from a conjugated polymer–polysaccharide complex (PPV-amylose);[12b] these extremely thin (10–12 nm) single-layer devices were reported to show a similar luminescence to **PDV⊂Am**, but with a lower turn-on voltage (*ca.* 6 V).

In conclusion, 2D NMR analysis of amylose-wrapped IMWs provides proof that the conjugated polymer resides inside the amylose helix. The photoluminescence efficiencies of these amylose complexes are higher than those of the naked polymers and higher than those of the corresponding polyrotaxanes, demonstrating that encapsulation by amylose is extremely effective in preventing energy transfer and other quenching processes. However, the amylose complexes give less efficient PLEDs than the polyrotaxane, suggesting that the insulation of the amylose hinders charge transport in the thin film. In future, it will be interesting to test blends of conjugated polymers with smaller amounts of amylose to explore whether enhanced luminescence can be achieved without suppressing charge transport.

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Notes and references

‡ The molecular weight of the amylose (15 000 Da) corresponds to a V-amylose helix length of 12.3 nm, which is shorter than the number-average chain length of the **PPP** and **PDV** used here (*ca.* 18 nm and 22 nm, respectively); however, the materials are polydisperse, and there is some uncertainty as to their molecular weights. Further experiments will be required to test whether stable 1 : 1 complexes are only formed when the length of the amylose helix matches that of the conjugated polymer guest.

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