A Luminescent Oligo(*p*-phenylenevinylene) Wrapped with Amylose

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When wrapped with amylose, oligo(*p*-phenylenevinylene) exists in a state that is isolated from the external environment, thereby hampering the π–π interactions and displaying an intense blue emission arising from the chiral conformation of the main chain.

In the design of advanced conjugated molecules, the encapsulation of π-conjugated polymers and oligomers at the molecular-scale level, often termed "insulated molecular wires (IMWs)," is particularly interesting.[1] This is because IMWs show high environmental stability, high luminescence efficiency arising from the reduced π–π interactions within the confined systems, and/or separation from the external environment, which makes them promising materials for optoelectronics such as organic light-emitting diodes (OLEDs). There are usually two strategies for the noncovalent encapsulating of conjugated polymers, i.e., (i) threading through macrocycles such as cyclodextrins to form (pseudo)-polyrotaxanes, and (ii) wrapping with helical polymers such as amylose to form polymer–inclusion complexes. Whereas a number of rotaxane-type IMWs have been prepared,[2,3] IMWs based on the wrapping approach are still limited.[4] Recently, we[5] and others[6–9] have reported supramolecular complexes of conjugated polymers wrapped with the polysaccharides amylose and schizophyllan (SPG). Interestingly, the conjugated polymers within the helical channel of the polysaccharides were found to be optically active. The advantage of the wrapping approach lies in the flexibility of the polysaccharide host and hence the helical dimension of the host is adjusted to match the size of guests.

Here, we report the photophysical properties of amylose-wrapped oligo(*p*-phenylenevinylene) (N$^+$OPV) (Chart 1). When wrapped with amylose, N$^+$OPV adopts a chiral conformation to display optical activity within the helical cavity of amylose. The remarkable feature in the present work is that the amylose-wrapped N$^+$OPV exhibits an intense blue emission arising from the chiral conformation of the main chain.

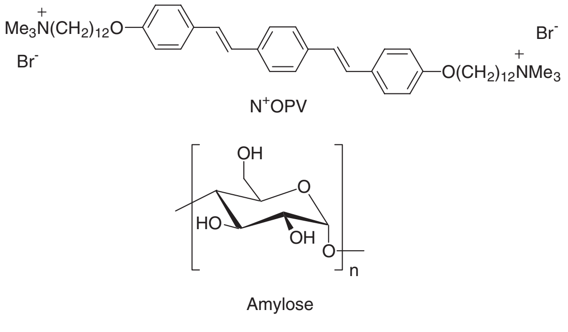

Chart 1. Chemical structures of N$^+$OPV and amylose.

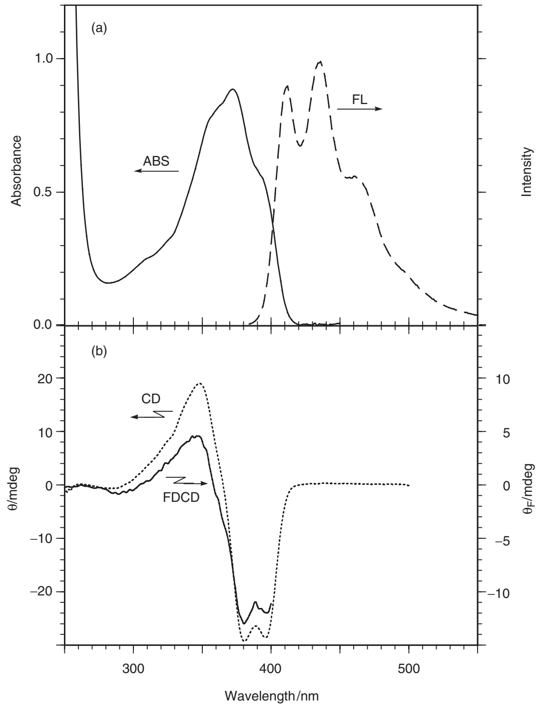

Figure 1. (a) Absorption, fluorescence (excited at 385 nm), (b) circular dichroism (CD), and fluorescence-detected circular dichroism (FDCD, monitored at 435 nm) spectra of the N$^+$OPV/amylose complex in a 30% aqueous DMSO solution. [N$^+$OPV] $= 2.00 \times 10^{-6}$ M, [Amylose per glucose unit] $= 2.00 \times 10^{-4}$ M.

A water-soluble oligo(*p*-phenylenevinylene) was our choice as the guest molecule, because poly- and oligo(*p*-phenylenevinylene)s are among the most extensively studied families of molecular electronic materials resulting from their interesting photophysical properties, including photo- and electroluminescence. N$^+$OPV was synthesized as described in Scheme S1.[10] In a typical preparation of the complex, a mixture of N$^+$OPV and amylose in DMSO was dispersed ultrasonically, and then water was added to the mixture (H_2O/DMSO $= 7/3$ v/v). The complexation of N$^+$OPV and amylose was studied by absorption, fluorescence, circular dichroism (CD), and fluorescence-detected circular dichroism (FDCD)[11] spectroscopies. Figure 1a shows the absorption and fluorescence spectra of a mixture of N$^+$OPV and amylose in a 30% aqueous DMSO solution. With an increase in amylose content, the absorption maximum gradually red shifted from 321 nm ($\varepsilon = 22500\,\mathrm{M^{-1}\,cm^{-1}}$) to 373 nm ($\varepsilon = 44300\,\mathrm{M^{-1}\,cm^{-1}}$). This observed shift means that the N$^+$OPV backbone adopts a more conjugated conformation of the N$^+$OPV main chain by complexation with amylose. In the fluorescence spectrum, N$^+$OPV in the presence of amylose showed intense fluorescence at the emission maximum of 437 nm with a fluorescence quantum yield of 98%. The absorption and fluorescence intensities as a function of the concentration of amylose allowed the determination of the binding constant (K_a) to be $9.3 \times 10^4\,M^{-1}$ (Figure S1).[10] The mole ratio of N^+OPV to the glucose residues along the amylose chain was estimated to be 1:36, which is consisted with the model based on the calculated molecular length of N^+OPV and 6/1 helical amylose.[12] In the CD spectrum, as shown in Figure 1b, negative and positive Cotton effects appeared at 400 and 350 nm, respectively, in the same wavelength range as the absorption, which are characteristic of a π–π^* transition of the N^+OPV main chain. On the other hand, N^+OPV in the absence of amylose showed no Cotton signal, and amylose itself did not show any absorption in this wavelength region. Thus, the observed CD spectral feature indicates that a supramolecular complex between N^+OPV and amylose is formed, and that the N^+OPV main chain residing in the left-handed helical channel of amylose adopts a chiral left-handed conformation.[13,14] Further, the FDCD spectrum monitored at 435 nm displayed a bisignate signal in the π–π^* transition region of N^+OPV, which was also in good agreement with that of the observed CD spectrum. This apparently implies that the observed intense fluorescence is attributed to the emission from the chiral N^+OPV main chain.

To demonstrate the stability of the amylose-wrapped N^+OPV, a fluorescence quenching experiment of N^+OPV in the absence and presence of amylose using $Fe(CN)_6{}^{4-}$ as a quencher[15] was examined. Upon addition of $K_4Fe(CN)_6$ to free N^+OPV in a 30% aqueous DMSO solution, the observed fluorescence was instantly quenched (Figure S2).[10] The first linear part of the Stern–Volmer plot gave a quenching constant (K_{SV}) of $2.1 \times 10^6\,M^{-1}$. On the other hand, when the amylose-wrapped N^+OPV was used, fluorescence quenching was also observed, but the quenching constant was much smaller ($K_{SV} = 5.4 \times 10^4\,M^{-1}$), indicating that the amylose-wrapped N^+OPV has acquired deterrence against the fluorescence quenching.

A remarkable spectral feature of the amylose-wrapped conjugated molecule was also observed in the solid state. While a film of N^+OPV showed a blue-green emission at around 480 nm, the amylose-wrapped N^+OPV in the solid state exhibited an intense blue emission at around 440 nm (Figure 2). In addition, the solid-state fluorescence of the amylose-wrapped N^+OPV showed no significant difference in terms of the shape and wavelength of the peaks from that observed in aqueous solution (Figure 1a, see also Figure S3[10]), indicating that the situation of the N^+OPV main chain is actually the same. This is because N^+OPV is insulated by wrapping with amylose at the molecular-scale level to reduce the π–π interactions.

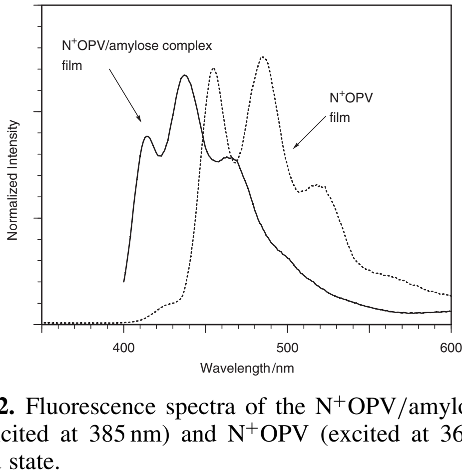

Figure 2. Fluorescence spectra of the N^+OPV/amylose complex (excited at 385 nm) and N^+OPV (excited at 365 nm) in the solid state.

In summary, we have demonstrated that N^+OPV wrapped with amylose exhibits an intense blue emission arising from the chiral conformation of the main chain in the left-handed helical channel of amylose, and here the conjugated molecule is isolated from the external environment to reduce the π–π interactions even in the solid state. This finding provides a good illustration of how to control the photophysical properties of conjugated molecules for application to optoelectronic devices.

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