

Supramolecular Nanodevice Based on Helical Encapsulation of Photo-/Electroactive Oligomers

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Introduction

There have been made numerous types of molecular devices to develop enhanced sensitivity and efficiency in sensing/monitoring, switching/processing and energy/electron-transport systems. They are architected either by covalent bonding or noncovalent bonding/bindings through H-bonding, electrostatic-, dipolar-, pi-pi- or/and steric interactions in a systematic and controlled manner. The non-covalent means are the basic elements for constructing supramolecular devices, so that diverse applications are possible for integrating structures and thus, versatile new functional properties.

We have developed a unique supramolecular nanodevice to develop high efficiency energy/electron-transfer (ET/eT) properties mimicking the photosynthetic reaction center by encapsulating a donor-acceptor (D-A) chain chromophore with a helix-forming polymer, amylose.

It has been known that ET/eT is D-A distance dependent while a long-lived charge-separated state requires a remote separation of D-A moieties. Such a conflicting molecular situation has to be resolved by a new device concept. The key is to make the ET/eT rates very fast over a long distance at a minimal energy loss. Nonetheless, the geometrical distance of D-A does not have much meaning as long as the chain has a conformational flexibility. An elegant solution was found, that is, to rigidify the chromophor using rigid linkers between the chromophoric units. This has shown a significant effect. However, still the missing part is the energy loss in transport of energy/electrons, occurring due to unwanted excited-state quenchings such as by aggregation and environmental deactivation.

All these problems can be resolved simultaneously by a supramolecular architecture that is based on a helical encapsulation of chromophores that we have developed.^{1,2} Of the advantages gained by encapsulation of the chromophores, the most notable one is the large enhancement of the fluorescence quantum yield, which results from single molecular confinement in the rigid and quenching-free environment. A particularly distinctive feature of the supramolecular system is the formation of oriented self-assembly thin films upon casting a solution since amylose alone is unable to do it.

Herein, we discuss highly efficient, one-dimensional ET/eT properties of amylose-encapsulated D-A chromophores along the helical channel.

Results and discussion

A series of bidirectional and unidirectional D-A chain chromophores based on OPV (D) with various acceptors (As) and alkyl-spacer lengths have been synthesized (Structures below). Helical encapsulation of the chromophores with amylose is evidenced by the red-shift of absorption maximum, enhanced fluorescence intensity and marked circular dichroism spectra. The extent of ET/eT, which depends on the encapsulation, D-A distance, D/A strength and local environment, was determined based on the degree of the fluorescence quenching of D due to the presence of A in aq solutions.

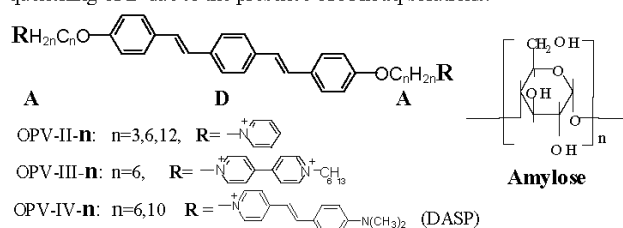


Figure 1- (left) shows photo-induced eT of OPV-III-6, confined in an amylose helix, was determined based on the fluorescence quenching of the OPV unit (D) by the viologen residue (A), where the blue emission of OPV at 432 nm is almost completely quenched (>95%). The initial fluorescence intensity of the OPV unit (without A) is represented by OPV-II-12 and thus, extrapolated as the control.

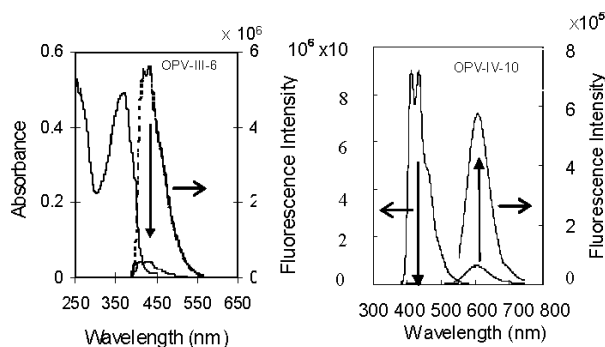


Figure 1. Electron- and energy-transfer in helically encapsulated OPV-based chromophores by excitation of OPV unit (D) at 375 nm: (left); Decrease in fluorescence intensity of OPV unit in OPV-III-6 due to eT to viologen moiety (A). (right); Fluorescence quenching of OPV and concomitant enhanced fluorescence intensity of DASP unit (A) in OPV-IV-10 due to ET.

Figure 1-(right) shows through-space ET between OPV- and DASP (A) units in OPV-IV-10 with the helical encapsulation. For this molecule the emission band of OPV and the absorption band of DASP are well overlapped. For OPV-IV-10, the initial OPV fluorescence is nearly completely quenched (>99%) by the DASP unit (A) upon excitation of the OPV unit, and the subsequent ET excitation of the DASP unit brings about a large enhancement (> x10) in DASP fluorescence ($\lambda_{em} = 620$ nm). A Förster-type calculation using a dyad model confirms the efficient ET observed experimentally.

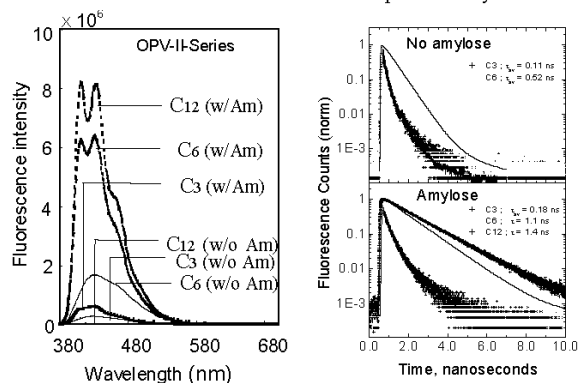


Figure 2. Dependence of fluorescence intensity (left) and fluorescence decay rate (right) of OPV-II (with and without amylose) on D-A distance (Cn).

On the basis of fluorescence quenching and lifetime data (Figure 2, right), eT rates of encapsulated C₃ and C₆ chromophores are estimated to be 6.8×10^9 s⁻¹ and 0.21×10^9 s⁻¹, respectively. It was further confirmed that the eT in the encapsulated chromophores depends explicitly on the A strength; ammonium < pyridinium, < viologen. In contrast, the eT quenching for the encapsulation-free counterparts has mixed contributions from both the distance effect and non-radiative deactivation by aggregation and/or collisional quenching. These are closely related to the environmental sensitivity of the free chromophores and are reflected in their low fluorescence quantum yields and very short lifetimes, particularly for the encapsulation-free OPV-II-12 due to a strong aggregation (Fig.2-left). On the contrary, the electronic coupling of the D-A chromophores confined in the amylose helix is little affected by local environment, so that one-dimensional event of transport prevails.

Conclusion

Fluorescence quenching of the helically-encapsulated D-A chromophores is dominated by photo-induced eT/ET with a well-defined distance effect and A strength, whereas the free chromophores have mixed contributions from some eT but largely from self-quenching due to aggregation and/or conformational flexibility

References

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- [2] Kim, O.-K.; Je, J.-T.; Melinger, J.S. *J. Am. Chem. Soc.* **2006**, *128*, 4532.