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Synthesis and Characterization of Donor−Acceptor Chromophores for Unidirectional Electron Transfer

M. F. Pepitone,[†] G. G. Jernigan,[‡] J. S. Melinger,[‡] and O.-K. Kim*[,†]

Chemistry Division, Electronics Science & Technology Division and Institute for Nanoscience, Naval Research Laboratory, Washington, DC 20375-5342

oh.kim@nrl.navy.mil

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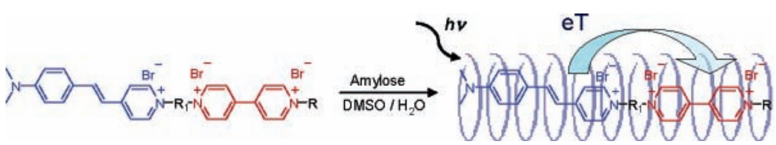
ABSTRACT



A series of electron-transfer chromophores containing a donor and acceptor linked by an alkyl spacer were synthesized, and their electronic spectra were investigated. By inclusion with amylose, the supramolecularly encapsulated chromophores exhibit enhanced fluorescence quenching with discrete distance dependence and acquire the ability to sustain self-assemblies of a densely packed supramolecular array on a SiOH/Si substrate.

The key process in photosynthesis is a cascade of energy transfer (ET) with directionality between arrays of photoreceptor pigments (bound to a protein matrix) and a subsequent electron transfer (eT) to a reaction center at a remote distance.[1] A variety of molecular architectures have been devised to mimic the photosynthetic process, and these include molecular wires and arrays,[2] dendrimers,[3] and supramolecular assemblies.[4] Through the investigation of model donor−acceptor (D−A) chromophores, it has been recognized that D−A distance is an important parameter for a long-lived charge-separated state.[5] However, due to conformational flexibility, the geometrical distance alone cannot be an effective measure for control of the forward and backward process. Research efforts have been made to overcome this problem by rigidifying the chromophore by incorporating a stiff linker between D−A units.[6]

This distance-related chain flexibility problem can be addressed by a supramolecular architecture, which employs a host polymer such as amylose[7] capable of encapsulating chromophores. Earlier, we developed a supramolecular technique to align dipoles of nonlinear optical chromophores[8] by helical encapsulation with amylose. This supramolecular assembly provides the chromophores with many functional

† Chemistry Division.
‡ Electronics Science & Technology Division.

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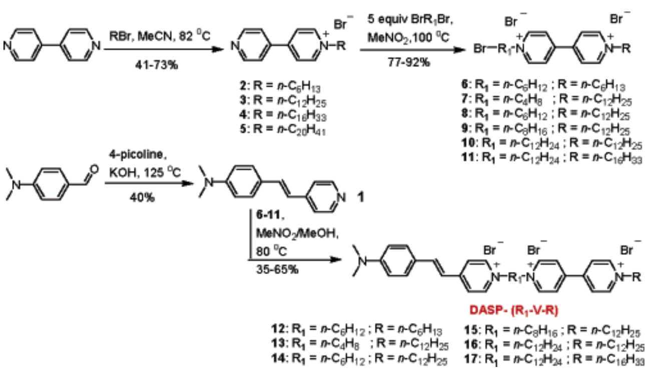
advantages such as the suppression of intermolecular interactions by the confinement of single molecules in a rigid environment, which yields a large (orders of magnitude) increase in the fluorescence quantum yield.[9]

Herein, we report the synthesis and photophysical properties of a series of 4-[4-(dimethylamino)styryl]pyridine (DASP)-based chromophores with various D−A distances. The DASP-based chromophores are studied in solution in an encapsulation with helical amylose or in the nonencapsulated (free) state. A combination of absorption, fluorescence, and time-resolved fluorescence spectroscopy is used to study the state of the encapsulation relative to the free state in solution and to characterize the distance dependence of the electron transfer. We also compare the fluorescence properties of the chromophores in solution with that of a thin film, which was made by casting an aqueous solution of the chromophores onto a silicon substrate. Finally, we describe the film morphology by atomic force microscopy (AFM).

Scheme 1. Synthesis of DASP-(R_1-V-R) **12−17**



Scheme 1 depicts the synthesis of the D−A chromophores [DASP-(R_1-V-R)] utilizing a 4-[4-(dimethylamino)styryl]-pyridine moiety as the donor (D) and a 4,4′-dipyridyl moiety as the acceptor (A). A simple synthetic approach has been designed on the basis of quaternizing the pyridines in a specific order. The first step was the synthesis of 4-[4-(dimethylamino)styryl]pyridine **1** from literature procedures.[10] 4,4′-Dipyridyl was then N-alkylated using a modification of the literature procedures,[11] and the resulting 1-*n*-alkyl-4-(4-pyridyl)pyridinium bromides **2−5** were reacted with an excess (5 equiv) of dibromoalkanes in nitromethane to afford 1-(bromoalkyl)-1′-alkyl-4,4′-bipyridinium dibromides **6−11**. Synthesis of DASP-(R_1-V-R) was completed by refluxing **6−11** with an excess (5 equiv) of DASP **1** in a 4:1 (v/v) $MeNO_2$/MeOH solvent system. After removal of solvent, the unreacted DASP was removed by washing a 1:1 (v/v) H_2O/MeOH solution of the crude product with $MeCl_2$, followed by recrystallization (see Supporting Information) to afford **12−17**. An initial attempt to synthesize **12−17** involved the formation of an α-bromo-*n*-alkyl-DASP moiety, by refluxing DASP with an excess of α,ω-dibromoalkane in acetonitrile, which was then reacted with a 1-alkyl-4-(4-pyridyl)pyridinium bromide in a variety of solvent systems. Unfortunately, isolation and purification of the product was not achieved via this route. Appending a 4,4′-dipyridyl to the α-bromo-*n*-alkyl-DASP moiety was achieved, but the final N-alkylation was sluggish under a variety of conditions.

Encapsulation of the chromophores was achieved[9] by dilution of DMSO stock solutions of the chromophore (1×10^{-3} M) and amylose (1×10^{-1} M) with DMSO, followed by a dropwise addition of H_2O with continuous stirring for 14 h at room temperature. A helical encapsulation with amylose is evidenced by enhanced fluorescence[8,9] of the chromophore (vide infra).

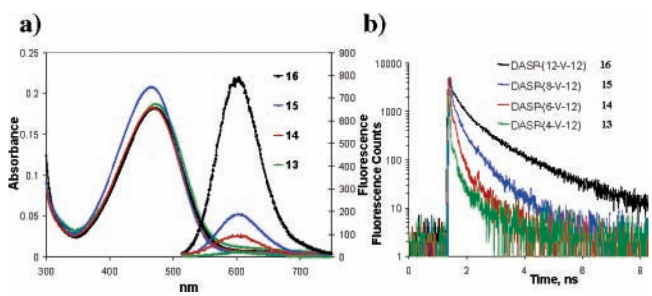


Figure 1. Absorption and fluorescence spectra (a) and excited-state lifetimes (b) of amylose-encapsulated **13−16** in 10% DMSO. [**13−16**] = 1×10^{-5} M and [amylose] = 1×10^{-3} M.

Figure 1a shows absorbance and fluorescence measurements for the series of encapsulated DASP-(R_1-V-12) **13−16** in 10% DMSO/H_2O. Each of the fluorescence signals has been scaled to the absorbance at the excitation wavelength of 500 nm. We note that the fluorescence intensity of **16** is comparable to that of DASP-C_{22}[9a] (see Figures S1 and S2, Supporting Information), which has no acceptor. This suggests that there is a high energy-barrier for eT of **16** over the longest C_{12} spacer resulting in a negligible eT. After the large gap of the fluorescence intensity between the spacer lengths (R_1) C_{12} and C_8, a consistent decrease in the intensity of DASP-(R_1-V-12) persists between the bridge lengths C_8 and C_4. This is indicative of the distance dependency of photoinduced eT between D−A (based on the fluorescence quenching) between C_8 and C_4.

The same trend is also reflected in the fluorescence lifetimes of the encapsulated **13−16**, which show a consistent

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decrease of the fluorescence lifetime with decreasing D−A distances (Figure 1b). We note that the nonlinear decay profiles indicate a somewhat inhomogeneous distribution of chromophore emitters, perhaps reflecting various encapsulation states in solution. We also observed that in the presence of amylose the fluorescence intensity of **16** peaks near 10% DMSO and attenuates with increasing DMSO volume fractions (Figure S3, Supporting Information). This means that the degree of the helical encapsulation depends strongly on the DMSO/H_2O mixture ratios and attains the maximum under the present experimental condition (10% DMSO). A similar observation was made in our previous work[8,9] where the fluorescence intensity of a nonpolar (OPV) chromophore increased sharply in a water-rich DMSO mixture. However, the difference observed between the polar and the nonpolar chromophores is that the emission band of the polar DASP-based chromophore, **16**, tends to shift more to the blue with increasing water fraction, whereas that of the nonpolar counterpart is little affected by the solvent polarity changes. This is probably due to the environmental sensitivity of the polar chromophore (see Figure S4 and Note, Supporting Information).

On the other hand, the emission properties of the free DASP-(R_1-V-12) exhibit a markedly different pattern relative to their encapsulated counterparts (Figure 2a). First, the fluorescence intensities of the free DASP-(R_1-V-12) are all significantly smaller (than the encapsulated counterparts), as if a larger eT quenching took place. Second, the differences in the fluorescence quenching among different bridge lengths of the free chromophores are noticeably smaller, particularly in the bridge lengths between C_6 and C_{12}. Finally, the fluorescence lifetimes (Figure 2b) are nearly as short as the instrumental response time (∼40 ps) and virtually indistinguishable from each other. These observations suggest the presence of an additional quenching process that competes with eT. One possibility is self-quenching due to aggregation of the free chromophores in the water-rich DMSO mixture. This is manifested by a measureable blue-shift (up to 15 nm) of the absorption maximum and a steady and concomitant decrease in the fluorescence intensity of **16** with increasing water content in DMSO/H_2O mixtures (Figure S5, Supporting Information), relative to 100% DMSO where the aggregation is almost free. In light of the fact that band broadening around 400 nm (aggregation band) is not significant, it is more likely that the unusually large quenching observed (Figure 2a) is largely associated with nonradiative deactivation by increasingly polar solvents.[12]

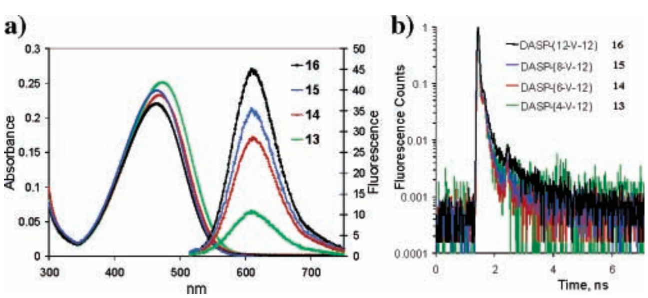
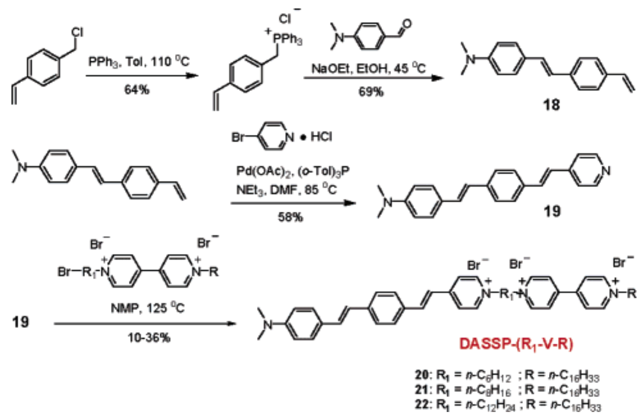


Figure 2. Absorbance and fluorescence spectra (a) and excited-state lifetimes (b) of free **13**−**16** in 10% DMSO. [**13**−**16**] = 1 × 10^{-5} M and [amylose] = 0 M.

A preliminary electrochemical study[13a] shows helical encapsulation brings about a pronounced effect on the voltammetric behavior.[13b] The half-wave potentials ($E_{1/2}$) and the peak-to-peak potential gap (ΔE_p) for **16** with and without encapsulation are $E_{1/2} = 0.135$ and 0.215 V and $\Delta E_p = 70$ and 90 mV, respectively. We interpret that these potential waves are attributable to oxidation of the D-subunit, and such a fast redox reaction by the encapsulation is associated with binding of the D-head, the *N*,*N*-dimethylamino group, to a gold electrode. This is supported by an AFM image showing a bundle of the encapsulated chromophore onto a gold substrate while the free counterpart has no features.

In an attempt to modify the photophysical properties of the donor, an extension of the DASP chromophore was synthesized by reacting commercially available 4-vinylbenzyl chloride with triphenylphosphine to yield 4-vinylbenzyl-triphenylphosphonium chloride following literature procedures.[14] A Wittig reaction using NaOEt in EtOH afforded the *E* precursor **18** that was subsequently used in a Heck reaction with 4-bromopyridine hydrochloride to afford DASSP **19**. DASSP was N-alkylated with 1-(α-bromoalkyl)-1′-hexadecyl-4,4′-bipyridinium dibromides by heating in NMP to yield a series of DASSP-(R_1-V-16) **20**−**22** (Scheme 2) (see Supporting Information). Full spectroscopic characterization will be reported in a timely manner.

Scheme 2. Synthesis of DASSP-(R_1-V-R) **20**−**22**



We have also characterized the encapsulated chromophore, **16**, in a solid thin film. Self-assembled films on a hydroxylated silicon substrate were prepared by wetting the substrate with a dilute solution of the encapsulated **16**. Fluorescence spectra taken of these thin films reveal the characteristic line shape of individual chromophores in solution and thus

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suggest that the chromophores remain inside the amylose helix after film formation (Figure 3).

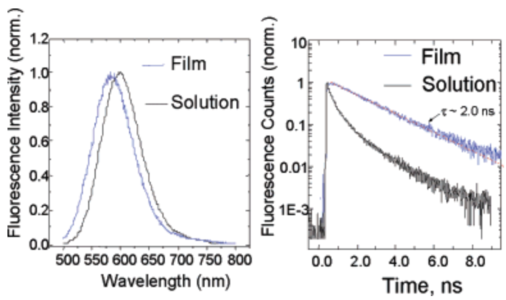

Figure 3. Fluorescence spectra (left) and excited-state fluorescence lifetime (right) of amylose-encapsulated **16**: 10% DMSO solution ([**16**] = 1×10^{-5} M and [amylose] = 1×10^{-3} M) and solution-cast supramolecular thin film on a SiOH/Si surface.

Remarkably, there is an order of magnitude increase in the excited-state lifetimes of the thin-film chromophores on the silicon substrate (Figure 3), relative to that in solution. Further, the fluorescence decay from the film is nearly described by a single exponential, which suggests there is a more homogeneous encapsulation of chromophores in the film than in the solutions. If the chromophores were to release out of the helix upon film formation, then it is expected that their aggregation would significantly quench the emission and produce much shorter fluorescence decay times.

Atomic force microscopy (AFM) images of the thin-film chromophores (Figure 4) reveal a high packing density, whose geometric configuration is about 14 nm tall and 50 nm wide. Given that the length scale of the amylose helix is about 5 nm, the film shown most likely contains more than one layer. We suggest that the first layer of the film in contact with the surface is oriented with the terminal dimethylamine binding to the surface. We believe that for the amylose-based supramolecular system to self-assemble into a film with directional order, at least three important criteria must be met: (1) rigidified helices by inclusion of a guest dye, (2) substrate-specific functionality (e.g., *N*,*N*-dimethylamino group) at the chromophore terminus for interface binding, and (3) intermolecular hydrogen-bonding capability of the host helix.

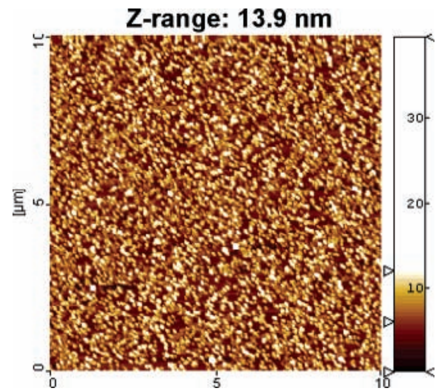

Figure 4. Tapping mode AFM image of encapsulated supramolecular assembly **16** on a SiOH/Si surface.

In conclusion, we have synthesized a series of D−A pair chromophores, and the chromophores were encapsulated with helical amylose. Photoinduced electron transfer (eT) of the chromophores was investigated based on the fluorescence quenching with respect to the encapsulation. For the encapsulated chromophores, the eT quenching shows a clear dependence on the D−A distance along the helical axis. For the free chromophores, the fluorescence quenching has a mixed contribution both from eT and self-quenching due to aggregation and/or solvent deactivation. The AFM image of the supramolecules as a self-assembled thin film reveals densely packed crystalline bundles. This occurs only when the amylose is included with a guest dye, and no features appear with the guest or host by itself.

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Supporting Information Available: Experimental details for synthetic procedures, NMR spectra of **1**, **3**−**18**, and **20**−**22**, and spectroscopic (absorption and emission) data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Cyclic voltammetry of **16** with and without amylose in 25% DMSO: 300 μL of sample + 100 μL of $NaClO_4$ (0.100 M); potential range −1.0 to +0.40 V vs Ag/AgCl, 3 M KCl; scan rate, 5 mV s^{-1}. (b) However, two reduction waves ($E_{1/2}$) of the A-subunit (viologen), which are supposed to appear around −0.3 and −0.7 V, respectively, were not observed upon sweeping the potential down to −1.0 V, regardless of encapsulation of the chromophore. At present, it is not clear whether it is due to a high polar aq solution (25% DMSO), low concentration, or the orientation of the D-head to the electrode surface (bringing the A-subunit far away).

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