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Supramolecular Device for Artificial Photosynthetic Mimics As Helix-Mediated Antenna/Reaction Center Ensemble

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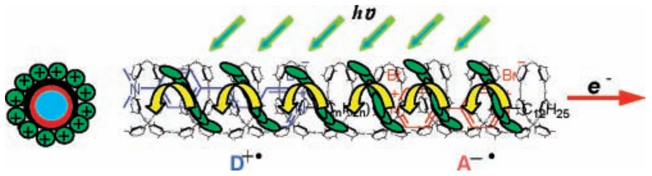
ABSTRACT



We have developed a novel integrated supramolecular device for a photosynthetic antenna/reaction center (RC) model based on a helical amylose, which plays an important role as the host for cyanine dye J-aggregation onto the helical surface and also for inclusion of a D–A chain chromophore inside the helical cavity, where the J-aggregates function as an array of photoreceptor antenna that funnel excitation across the helix to the chromophore.

In nature, photosynthetic bacteria have evolved intricate self-assemblies of chlorophyll and carotenoid aggregates onto proteins as scaffolds. Most chlorophylls serve as light-harvesting antenna (LH-I and LH-II) that capture the sunlight and funnel the electronic excitation cascading into the photosynthetic reaction center (RC),[1] where the photon energy is converted into electronic energy.

The light-harvesting complexes are circularly arranged as such that LH-I complexes surround the RC and are surrounded in turn by LH-II antenna complexes. It is assumed that the excitation energy is delocalized over the aggregates and excitation transfer takes place effectively between inter- as well as intracomplexes, achieving the quantum yield of near unity at RC.[1]

There have been various types of covalently linked, multichromophoric systems reported[2] for artificial photosynthetic mimics, but little is known for a supramolecularly integrated device as an antenna/RC ensemble. We were interested in developing a helical supramolecular device mimicking a photosynthetic antenna. We envisioned J-aggregates of a cyanine dye can play an important role as an antenna array due to the very large absorption cross-section and efficient exciton migration over many molecular aggregates.[3] Interestingly, when they are bound to a rigid helical surface, and an acceptor is incorporated inside the helix, the device configuration (see the Abstract graphic)

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uniquely resembles the circular arrangement of a photosynthetic antennas, such that the photoexcited energy of the J-aggregates (antennas) in the periphery is directed onto the acceptor (RC) in the center, thereby amplifying the energy-transfer quenching (Figure 1).

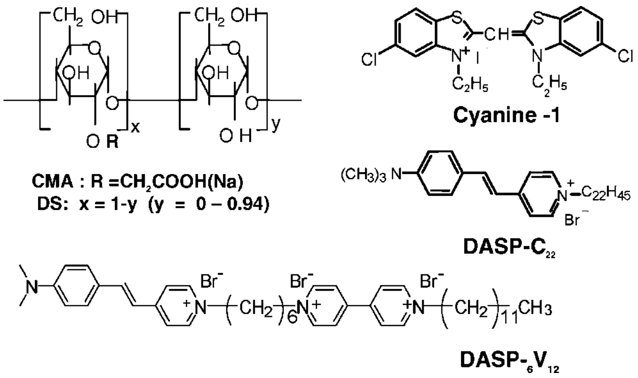

Figure 1. Chemical structures of the supramolecular device components: carboxymethyl amylose (CMA) and cyanine dyes.

First, we have investigated the possible J-aggregation formation of a cyanine dye (cyanine-1) in the presence of carboxymethyl amylose (CMA) and found that the cyanine J-aggregation occurs onto the CMA at various degrees of carboxymethylation (DS), forming a CMA/cyanine-1 super-helix,[4] while CMA itself is a random-coil in solution due to the electrostatic repulsion. The super-helix formation was proven by an extraordinarily large induced circular dichroism (CD) and a large enhancement ($> \times 10^2$) of fluorescence intensity ($\Phi_f = 0.43$) of the cyanine dye J-aggregates.[4]

From the distance effect consideration[5] on the excitation transfer (from the antenna to an energy/electron-acceptor), the inside of the super-helix is the best accessible site for an acceptor, which is therein circularly surrounded by the J-aggregate antenna array.

Not only that, under this circumstance the chromophore takes advantage[6] of the helical host, benefiting from aggregation-free, single molecular confinement within the helix, which gives a longer excited-state lifetime.[7] In a recent communication, we reported that when a flexible-chain, electron donor−acceptor (D−A) chromophore is helically encapsulated, the electron transfer (eT) prevails along the helical axis with a clear distance dependence. By contrast, the eT of the encapsulation-free counterpart exhibits no distant dependence and a very poor efficiency due to a self-quenching resulting mainly from aggregation and/or solvent deactivation of chromophores.[7] In addition, it is worth noting that the helical encapsulation of a chromophore is an effective means to develop one-dimensional self-assembly,[8] since no self-assembly occurs with the encapsulation-free counterpart, suggesting that lateral interactions of helices including H-bonding promote the surface binding.

In this paper, we report a unique supramolecular nanodevice for an artificial photosynthetic antenna/RC ensemble based on CMA and two-component dyes (cyanine dye and D−A chromophore), where CMA is indispensable not only for imparting the functional role to the antenna but also accommodating a chromophore (DASP-C_{22} or DASP-$_6V_{12}$)[6,7] into the cavity of the super-helix (Figure 2). The device is prepared by integration of two competitive (**A**, **B**) but sequentially controlled self-organization processes (**B**), namely, J-aggregation of a cyanine dye onto CMA surface, forming super-helix, and the subsequent treatment of DASP-chromophore for encapsulation with the super-helix. This procedure is critical for the completion of the device (see the Supporting Information, S-1), particularly with CMA of a high DS (> 0.1). The occurrence of the processes was verified by UV/vis and CD spectra of individual chromophores[4,6,7] and their fluorescence intensity changes due to excitation transfer (from the antenna) to DASP-C_{22} (energy-acceptor), along with the concomitant increase in the DASP-C_{22} emission due to energy-transfer (ET). The transfer efficiency is assessed by changes in the fluorescence intensity in the presence and in the absence of the encapsulated DASP-C_{22} or DASP-$_6V_{12}$. Also, the time-resolved fluorescence lifetimes of the J-aggregates and the DASP chromophores are measured (see the Supporting Information, S-1) and correlated.

For CMA, it is almost impossible to assume a helical conformation by itself, and even with an extremely low degree (e.g., DS = 0.06) of carboxymethylation, the helical encapsulation of DASP, for example, is significantly decreased compared to that of neutral amylose, such that at a higher DS (> 0.1), CMA loses the inclusion capability completely (see the Supporting Information, S-2). However, surprisingly enough, when the higher DS, random-coil CMA is transformed into a super-helix by cyanine J-aggregation, it turns out perfectly capable of encapsulating DASP-C_{22} and even DASP-$_6V_{12}$; the latter reveals a particularly strong affinity (Figure 2, route **B**) for the highest DS (1.53) CMA super-helix, thereby rendering a remarkable stability,[9] while for the lowest DS (0.06) CMA super-helix, its charge interaction with DASP-$_6V_{12}$ is destructive, rendering the encapsulation detrimental.[10] Accordingly, for a low DS (< 0.1) CMA, the alternative route **A** is preferred. The helical

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(8) Remarkably, this supramolecule forms self-assembly thin films on various substrates. This will be published elsewhere in detail.

(9) The supramolecular device prepared using the high DS (1.53) CMA super-helix are very stablesuch that their UV/vis and CD spectra in aqueous solution exhibit no significant changes at least for 1 month.

(10) DASP- $_6V_{12}$ is very cooperative with the high DS (1.53) CMA super-helix for encapsulation. This may be associated with the tight super-helix structure (see the Supporting Information, S-3).

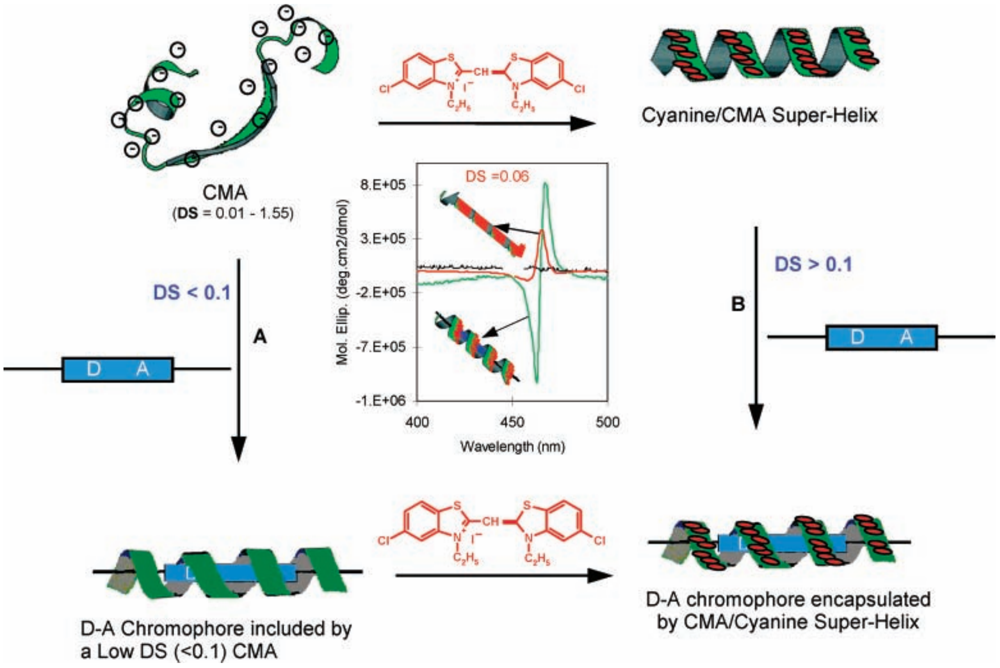

Figure 2. Pictorial representation of supramolecular architecture for the photosynthetic antenna/RC ensemble, where the DASP-viologen (D−A) chain chromophore is encapsulated by the super-helix of CMA/cyanine J-aggregates as antenna. Inset shows a different CD intensity in the cyanine J-aggregates, reflecting the state of the super-helix with CMA (DS* = 0.06).

cyanine/CMA super-structure is already heavily twisted,[4] but it becomes even more pronounced, as shown in Figure 2 (inset), upon encapsulating a chromophore (DASP-C_{22}).

Figure 3 (left) shows a strong absorption band at 460 nm (a, b, c) due to the cyanine J-aggregation of the super-helix (with 1.53 DS CMA), which is unaffected by the presence (encapsulation) of DASP-C_{22} or DASP-$_6V_{12}$, and a weak and broad absorption band around 480 nm (d) for the free DASP-$_6V_{12}$ in a random-coil CMA (1.53 DS) solution. The peak position of DASP-C_{22} is commonly red-shifted[6] when encapsulated with amylose. By the same token, with the super-helix encapsulation the absorption band of DASP-$_6V_{12}$ (c) is red-shifted to 500 nm from 475 nm of the encapsulation-free counterpart (d). This is reflected in the fluorescence emission bands (see Figure 4 inset and Supporting Information, S-4). The strong J-band as a proof of the super-helix encapsulation (b, c) is manifested by CD spectra (right),[11] in that the induced CD (of the J-aggregates) remains mostly unchanged by treating (encapsulating) DASP-C_{22} (b) and DASP-$_6V_{12}$ (c). By contrast, the super-helix based on the lowest DS (0.06) CMA is disrupted (see the Supporting Information, S-3) by the presence of DASP-$_6V_{12}$ to monomeric cyanine,[12] losing the CD signal of the helical J-band.

The fluorescence spectra (Figure 4, left) provide conclusive evidence for the super-helical inclusion of DASP-C_{22}, which brings about a sharp fluorescence quenching (ca. 90%) of the J-aggregates at 475 nm, accompanying the concomitant enhancement (> × 20)[7a] of DASP fluorescence (at 605 nm) due to ET (details in inset). A similar red-shift (15 nm) is observed for DASP-$_6V_{12}$ in the emission band due to the encapsulation (see Supporting Information, S-4 and Note). When DASP-$_6V_{12}$ (instead of DASP-C_{22}) is encapsulated by the super-helix, the excited-state of the DASP moiety is almost completely quenched by eT of the viologen subunit ($_6V_{12}$) to a charge-separated state. The overall quenching efficiency along the pathways, from photoinduced ET from

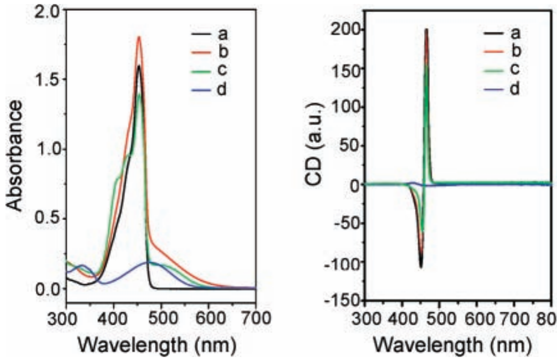

Figure 3. Absorption (left) and CD (right) spectra of cyanine J-aggregates/CMA (1.53 DS) super-helix: (a) super-helix alone (with no chromophore encapsulated), (b) DASP-C_{22} encapsulating super-helix, (c) DASP-$_6V_{12}$ encapsulating super-helix, and (d) CMA (1.53 DS)/DASP-$_6V_{12}$ mixture; [cyanine] = 2.3×10^{-5} M, [CMA (1.53 DS)] = 0.9×10^{-3} M, and [DASP-C_{22}] = [DASP-$_6V_{12}$] = 1.7×10^{-5} M in H_2O.

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(11) There is a close correlation between the absorption and CD spectra (Figure 2) of DASP-$_6V_{12}$ in the presence and absence of the super-helix (based on the cyanine J-aggregation with a high DS (1.53) CMA).

(12) It is likely that the multiple-charges of DASP-$_6V_{12}$ override a relatively weak cyanine J-aggregation with the low DS (0.06) CMA.

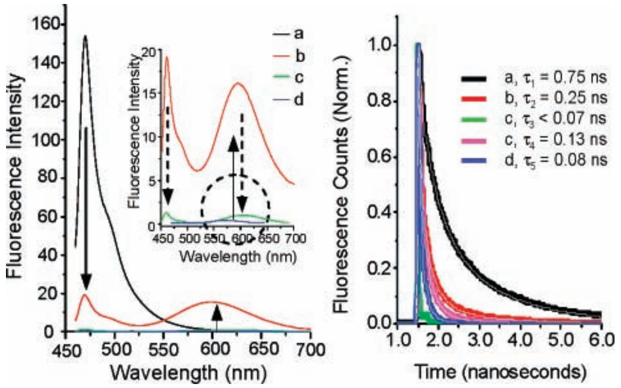
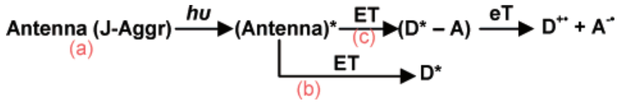


Figure 4. (Left) Changes in the fluorescence intensity (at 475 nm, ex at 457 nm) (a) of cyanine J-aggregates/CMA (1.53 DS) super-helix, (b) upon encapsulation of DASP-C_{22} by the super-helix, accompanied by an enhancement at 605 nm (upward arrow), (c) upon encapsulation of DASP−DASP-$_6V_{12}$ by the super-helix, accompanied by decreased intensity (downward broken arrows), and (d) of the CMA (1.53 DS)/DASP-$_6V_{12}$ mixture; [cyanine] =2.3 × 10^{-5} M, [CMA (1.53 DS)] = 0.9 × 10^{-3} M, and [DASP-C_{22}] = [DASP-$_6V_{12}$] =1.7 × 10^{-5} M in H_2O. (Right) Time-resolved fluorescence lifetimes of the photoexcited species; the lifetimes were detected at 475 nm for τ_1, τ_2, andτ_3 and at 605 nm for τ_4 and τ_5 (τ values are shown as an average).

the antenna and the subsequent eT to DASP-$_6V_{12}$ is >90% (Scheme 1).

Scheme 1



A time-resolved fluorescence decay profile of the excited-state species along the transport pathways (above) is illustrated in Figure 4 (right). This demonstrates that when detected at 475 nm, the fluorescence lifetime (τ_1) of the J-aggregates (of the super-helix) is decreased by a factor of 5 due to ET quenching (τ_2) by DASP-C_{22}, and the subsequent eT quenching by the $_6V_{12}$ subunit further decreases the lifetime (τ_3) by at least another factor of 3. Such a dramatic shortening of J-aggregates lifetime is a clear indication of ET/eT along the pathways. Separately, when the decay was detected (for eT) at 605 nm (for τ_4 or τ_5), the τ_4 is longer compared to the τ_3. This is unclear but can be explained by that the DASP excited-state is interfered by a concomitant deactivation process[13] involving a direct eT to the $_6V_{12}$ subunit (in encapsulation) from the excited J-aggregates. Nonetheless, the eT rate is still very fast: $k_e = 1/\tau_{D-A} - 1/\tau_D = 1.3 \times 10^{10}\ s^{-1}$. However, compared to $\tau_{4,}$ the unusually shortened τ_5 (due to the free DASP-$_6V_{12}$ dissolved in the random-coil CMA solution) is not due to the efficient eT but is attributed to self-quenching[7b] resulting from aggregations, particularly due to CMA-mediated electrostatic binding of the free DASP-$_6V_{12}$ and/or nonradiative deactivation of the polar solvent (Supporting Information, S-4 note).[14]

In conclusion, we have constructed a unique supramolecular device for an artificial photosynthetic mimic by integration of a functional amylose (a high DS CMA) with two interactive dye molecules; one on the helical surface and the other inside the helix. Cyanine dye J-aggregates complexed with CMA (super-helix) function as an array of photoreceptor antennas, and a donor−acceptor (D−A) chromophore encapsulated by the super-helix functions as reaction center (RC). Steady-state energy/electron transfer (ET/eT) was investigated throughout the excitation transfer pathways and correlated to their time-resolved lifetimes. From the high transfer efficiency and the stability, we believe that the supramolecular device as an antenna/RC ensemble can be a viable model for artificial photosynthesis.

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Supporting Information Available: Additional spectral data are available. This material is available free of charge via the internet at http://pubs.acs.org.

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[13] The $_6V_{12}$ subunit (inside the super-helix) in proximity to the J-aggregates (on the super-helix surface) can also quench the excitation of the J-aggregates directly, not through DASP subunit, such that τ_4 (involvingDASP to $_6V_{12}$ eT process) becomes longer compared to τ_3 (involving the J-aggregate quenching by DASP subunit).

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