

Light-Harvesting and Energy-Transfer System Based on Self-Assembling Perylene Diimide-Appended Hexaazatriphenylene

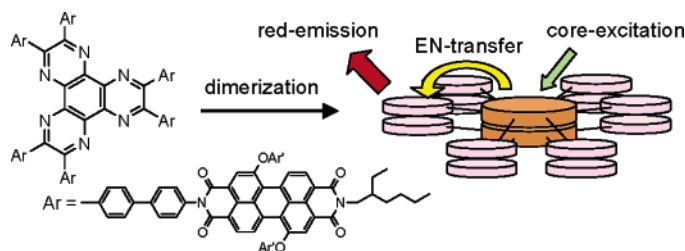
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ABSTRACT



Six perylene diimide-appended hexaazatriphenylene, HAT-PDI₆, was self-assembled in both solution and film state to form a highly stabilized dimer aggregate, in which an efficient energy transfer occurs from the hexaazatriphenylene core to the perylene-diimide moiety.

Energy transfer in a donor–acceptor system is an important process in a natural photo synthetic system,¹ as well as an artificial photovoltaic.² In the natural system, antenna chlorophyll moieties are arranged in a highly ordered self-assembling manner to achieve light harvesting and energy transfer with extremely high efficiency.³ Recently, artificial energy-transfer systems were created by using long-range ordering in well-defined supramolecular aggregates com-

posed of π -conjugated components.^{4,5} In the self-assembled systems, the acceptor molecules, which possess structural similarity with the donor molecules, such as perylene diimides with different substituents⁴ and oligo(*p*-phenylenevinylene)s with different repeating units,⁵ are efficiently incorporated in the well-defined columnar-type aggregates composed of donor molecules without destabilization of self-assembled ordering. However, quantitative analysis of the energy transfer in the systems was difficult due to significant overlap between donor and acceptor emissions.

Recently, we reported that fluorescent hexaazatriphenylenes (HATs) can be self-assembled in both solution and bulk state to form one-dimensional columnar-type ag-

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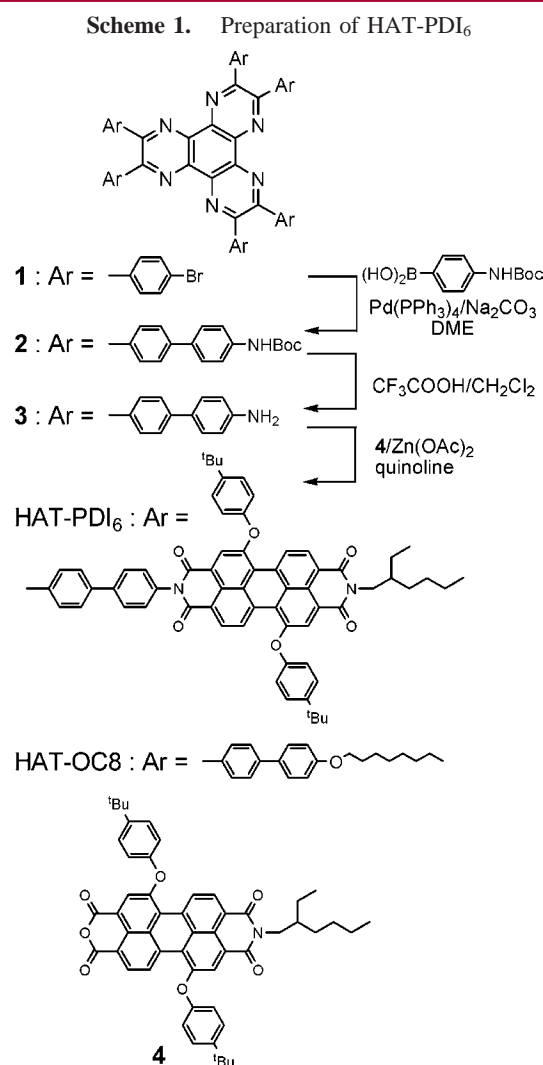
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gregates.⁶ This finding led us to design and prepare a new type of energy transfer system based on the incorporation of HAT possessing an acceptor moiety into HAT-based columnar-type aggregate. In this strategy, we have selected perylene diimide as the acceptor moiety⁷ because of its strong accepting nature,⁸ suitable overlap of its absorption spectrum with the fluorescence spectrum of the HAT chromophore used as donor moiety,⁹ and good separation between the fluorescence spectra of the HAT and PDI chromophores.⁹ In this Letter, we report the preparation of a six perylene diimide-appended HAT derivative (HAT-PDI₆) and its self-assembling nature in both solution and film state. Finally, the energy transfer in the HAT-based aggregate system incorporating HAT-PDI₆ is discussed.

Six perylene diimide-appended hexaazatriphenylene HAT-PDI₆ was prepared according to Scheme 1. Perylene monoim-



ide **4** was derived from perylene dicarboxylic acid anhydride in three steps via bromination,¹⁰ aryloxylation,¹¹ and imidation.¹¹ In the final imidation step, the desired 1,7-diaryloxy isomer **4** was isolated from the reaction mixture including other isomers.^{10b} HAT with six amino-containing biphenyl

groups **3** was obtained by deprotection of the corresponding *N*-Boc derivative **2**, which was derived from HAT having six bromophenyl groups **1**⁶ by coupling reaction with *N*-Boc-4-aminophenylboronic acid in the presence of a palladium-(0) catalyst. Finally, HAT-PDI₆ was obtained by condensation reaction of **3** with six molecules of **4** in quinoline in the presence of zinc acetate.¹² Identification of HAT-PDI₆ was performed by means of spectroscopic methods and MALDI-TOF mass spectrometry. HAT-PDI₆ can dissolve in various solvents from polar to nonpolar ones such as toluene, dichloromethane, chloroform, 1,1,2,2-tetrachloroethane, and THF. A stable film of HAT-PDI₆ was prepared by conventional spin-coating technique.

A direct evidence for the aggregation of HAT-PDI₆ is provided from the MALDI-TOF mass spectrometry^{13,14} and gel permeation chromatography (GPC).^{11,15} In the MALDI-TOF mass spectrum, a multiple of the parent ion of HAT-PDI₆ (*m/z* 5929) is seen at *m/z* 11,858, which is assigned to a dimer aggregate of HAT-PDI₆ molecules (S-Figure 2 in Supporting Information). The molecular weight of 10,100 for the aggregate in THF solution, which was estimated from GPC analysis using polystyrene references, is very similar to that (11,858) of the dimer species of HAT-PDI₆ (S-Figure 3 in Supporting Information).

The UV-vis spectrum of HAT-PDI₆ in toluene shows two bands at 511 and 544 nm arising from PDI chromophores and a band around 390 nm from the HAT chromophore (Figure 1). The former two bands are assigned to the

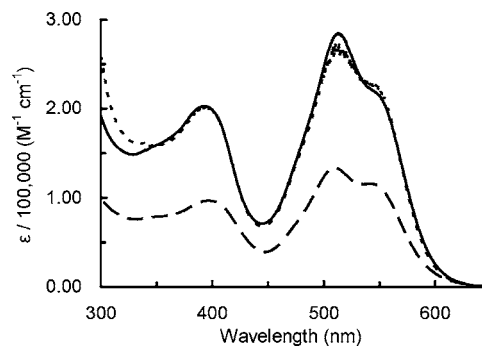


Figure 1. UV-vis spectra of HAT-PDI₆ at 20 °C in toluene [1.0 mM (solid line) and 0.001 mM (dotted line)] and at the spin-coating film (dashed line, a.u. unit).

transition from the ground state to the $\nu = 0$ level of the lowest excited state (0-0 vibronic transition) and to the $\nu = 1$ level (0-1 vibronic transition), respectively.^{13,17,18} The

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spectral pattern with intense PDI 0-1 vibronic transition and a shoulderlike 0-0 one is very similar to those of perylene diimide based aggregates with H-type stacking mode, which is rationalized by the molecular exciton model.^{13,14,17,18} Characterization in the absorption band of the HAT chromophore is difficult because of overlap with the weak band of PDI chromophores. The UV-vis spectra in toluene and THF changed slightly depending on concentration (0.001–1.0 mM) and temperature (20–75 °C), indicating high stability of the dimer aggregate in the solution (Figure 1 and S-Figure 4 in Supporting Information). The spectrum of the spin-coating film is very similar to those of the solution (Figure 1). The results show that in the film state the HAT-PDI₆ molecules are self-assembled with similar H-aggregation mode created in the solution state.

Concentration- and temperature-dependent UV-vis spectral change was observable in 1,1,2,2-tetrachloroethane. The absorbance of the PDI 0-0 vibronic transition at 553 nm increased with lowering concentration and increasing temperature, whereas the PDI 0-1 vibronic transition at 514 nm weakened (S-Figure 5 in Supporting Information). The phenomena are attributed to the dynamic exchange between the monomer and dimer species.

In the ¹H NMR spectra of HAT-PDI₆, a line-broadening effect arising from the π -stacked aggregation was observed in chloroform-*d*₁ and 1,1,2,2-tetrachloroethane-*d*₂. The chemical shifts and the shape of the broad resonances are independent of concentration in the range of 0.01–1.0 mM, indicating the dominance of a single aggregate species (S-Figure 6 in Supporting Information).^{15,16} At dilute concentration and high temperature, a set of sharp resonances is newly generated in addition to the broad ones in 1,1,2,2-tetrachloroethane-*d*₂ (S-Figures 6 and 7 in Supporting Information). The results indicate that the dynamic exchange between the monomer and dimer species is slow in the NMR time scale.

The aggregation of HAT-PDI₆ is reflected in fluorescence spectra. In toluene solution, a broad emission around 660 nm arising from the PDI chromophore is seen in the whole

range of 0.001–1.0 mM concentration, which is assigned to emission from the dimer aggregate (Figure 2a).^{17,19} The

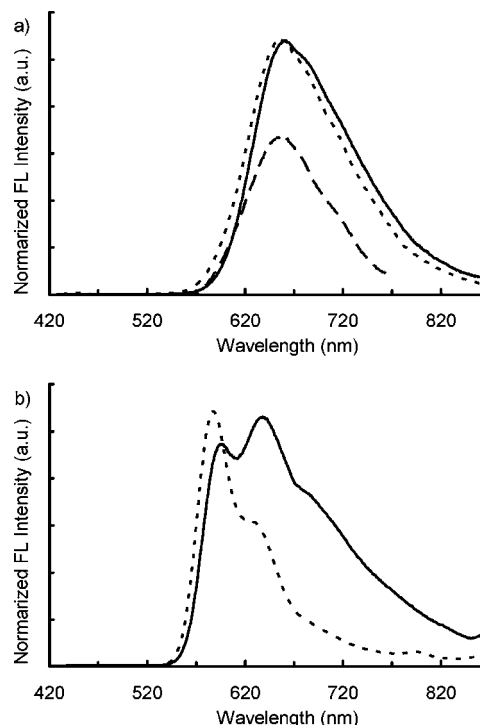


Figure 2. Fluorescence spectra of HAT-PDI₆ at 20 °C (a) in toluene [0.1 mM (solid line), 0.001 mM (dotted line)], and at the spin-coating film (dashed line), and (b) in 1,1,2,2-tetrachloroethane [0.1 mM (solid line), 0.001 mM (dotted line)]. Excited at 394 nm in toluene, at 403 nm in 1,1,2,2-tetrachloroethane, and at 400 nm in the film.

dimer emission is supported by time-resolved fluorescence spectra, from which a long-lived species with a lifetime of 18.5 ns was detected in toluene at 0.001 mM (S-Figure 10 in Supporting Information). The value is as large as those of perylene diimide based H-aggregates reported so far.¹⁹ Similarly, the THF solution also provides the dimer emission (S-Figure 8 in Supporting Information). In contrast, in the dilute 1,1,2,2-tetrachloroethane solution (0.001 mM), monomer emission is observable around 590–630 nm in addition to the weak dimer emission around 690 nm as a shoulder (Figure 2b). With increasing concentration (0.1 mM), the intensity of the monomer emission decreased whereas the dimer emission was enhanced, indicating again the dynamic exchange between the monomer and dimer species. The broad emission around 650 nm found in the film state indicates once again that in the film state the HAT-PDI₆ molecule is self-assembled with H-aggregation mode (Figure 2a).

Interestingly, red PDI emission is provided upon direct excitation of the PDI chromophore as well as upon indirect

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excitation of the HAT chromophore (S-Figure 9 in Supporting Information). Upon excitation of the HAT chromophore, no emission from the HAT core was seen in either the monomer or dimer species, indicating the energy transfer from the HAT core to the PDI moiety. The energy transfer was supported also by a good agreement between UV-vis and excitation spectra (S-Figures 11 and 12 in Supporting Information). These results provide the valuable information that an efficient light-harvesting and energy-transfer system can be created if HAT-PDI₆ is incorporated in HAT-based columnar-type aggregate.

As a preliminary test, a film of HAT derivative with six octyloxy-containing biphenyl groups (HAT-OC8 in Scheme 1)²⁰ doped with 5 mol % HAT-PDI₆ was prepared by spin coating from cyclohexane solution, and the energy transfer from the HAT-OC8-based medium to the HAT-PDI₆ incorporated in the medium was examined. The spin-coating samples provide a clear overlap of the fluorescence spectrum of HAT-OC8 and the absorption spectrum of HAT-PDI₆ (S-Figure 13 in Supporting Information). In the presence of HAT-PDI₆, the emission from HAT-OC8 around 510 nm was quenched significantly even upon excitation of the HAT chromophore (Figure 3). In addition, the PDI emission around 650 nm upon indirect excitation of the HAT chromophore is enhanced by a factor of 4 times compared to that observed upon direct excitation of the PDI chromophore, indicating the light-harvesting effect of the HAT-OC8-based medium (Figure 3).²¹ The energy-transfer phenomenon was easily visualized by change in the emission color from green HAT emission to red PDI emission (Figure 3).

In conclusion, we have shown that six perylene diimide-appended hexaazatriphenylene can be self-assembled to form a stable dimer aggregate in both solution and film state. In the aggregate structure, an efficient energy transfer from the HAT core to the peripheral PDI moiety proceeds. We believe

(20) Both in film state and in nonpolar solution such as cyclohexane, HAT-OC8 forms stable columnar-type aggregate. In contrast, HAT-OC8 dissolved molecularly in polar solvents such as dichloromethane and chloroform. The details for preparation and aggregation property of HAT-OC8 will be published elsewhere, and the selected spectral data are shown in Figures 15 and 16 in Supporting Information.

(21) When the spin-coating film was prepared from polar dichloromethane and chloroform solutions including molecularly dissolved HAT-OC8, the energy-transfer efficiency was reduced significantly, suggesting an importance of the HAT-OC8-based columnar-type aggregate as a good light-harvesting antenna as well as an energy-transfer reagent.

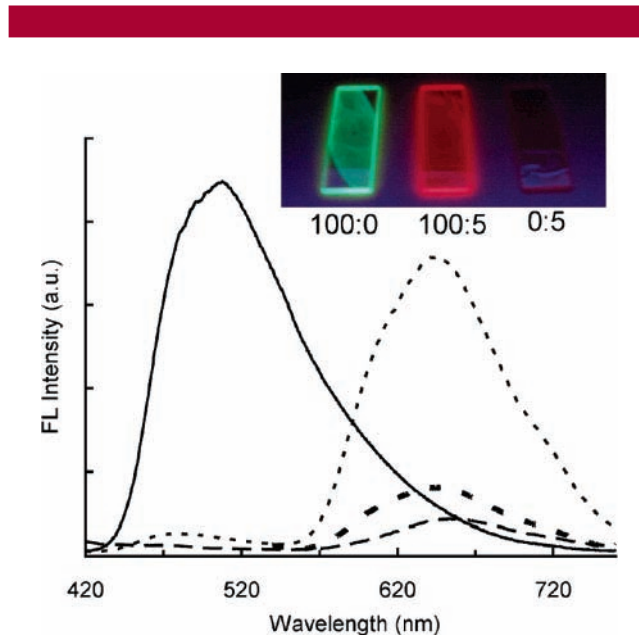


Figure 3. Fluorescent images under UV light (365 nm) and fluorescence spectra excited at the HAT chromophore (395 nm) of HAT-OC8/HAT-PDI₆ mixtures with 100:0 (solid line), 100:5 (dotted line), and 0:5 (dashed line) molar ratio in the spin-coating film at 20 °C. The fluorescence spectrum of the 100:5 mixture excited at the PDI chromophore (at 517 nm) is indicated by the wide dotted line.

that the present system will be developed to provide self-assembled light harvesting and energy transfer systems.

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Supporting Information Available: Experimental procedure, GPC trace, and MALDI-TOF-MS, ¹H NMR, UV-vis, and fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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