2206 *J. Phys. Chem. A* **2008,** *112,* 2206−2210

Photoinduced Electron Transfer in Coaggregates of Dicyanonaphthalene and Pyrazoline

Fugang Shen,[†,‡] Aidong Peng,[†] Yu Chen,[†] Yang Dong,[†,‡] Ziwen Jiang,[†,‡] Yaobing Wang,[†,‡] Hongbing Fu,[†] and Jiannian Yao*,[†]

Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China, and Graduate School, Chinese Academy of Sciences, Beijing 100039, P.R. China

Received: August 2, 2007; In Final Form: November 20, 2007

The photophysical properties of mixed coaggregates containing 1,4-dicyanonaphthalene (DCN) and 1,3,5-triphenyl-2-pyrazoline (TPP) have been studied. The absorption spectra of mixed coaggregates indicate that a charge-transfer complex is not formed in the ground state between DCN and TPP. The fluorescence of TPP in the mixed coaggregates is quenched by DCN, accompanied with a broad and structureless emission at about 560 nm from an exciplex between DCN and TPP. The color of the emission from mixed coaggregates is tunable by changing the DCN content. The excited-state properties of the TPP−DCN molecule pair are investigated theoretically with a quantum chemistry method. The theoretical results have also confirmed that the broad emission at about 560 nm in the mixed coaggregates originates from the exciplex rather than from the charge-transfer complex.

Introduction

Photoinduced electron transfer (PET) is one of the fundamental processes of natural photosynthetic systems and has been well understood for covalently linked donor−acceptor molecules in solution.[1−4] In recent years, the PET in self-assembled aggregates of covalently linked or hydrogen-bonded donor−acceptor molecules in organic solvents has also been studied extensively.[5−10] However, photoinduced intermolecular electron transfer in mixed coaggregates that consist of electron-rich and electron-deficient components has been reported just occasionally by Janssen and co-workers, who investigated charge transfer in supramolecular coaggregates of oligo(*p*-phenylene vinylene) and perylene bisimide in water.[11]

In this paper, we study the PET in mixed coaggregates that consist of electron-donor and electron-acceptor molecules. In our previous work, we have found that pyrazolines are good electron donors.[12−14] Here we choose 1,3,5-triphenyl-2-pyrazoline (TPP) as the electron donor for the mixed assemblies and 1,4-dicyanonaphthalene (DCN) as the electron acceptor (Figure 1). The planar and hydrophobic π systems of TPP and DCN enable π−π stacking interactions that facilitate the formation of coaggregates in polar solvents. It has been found that in the coaggregates, TPP and DCN do not form an intermolecular charge-transfer complex in the ground state, but they form an exciplex in the excited state. The fluorescence of TPP in the mixed coaggregates is quenched by DCN via the formation of an exciplex. The color of the emission from the mixed coaggregates can be tuned by changing the DCN content. The calculations of excited states confirm that the electron transfer takes place through an electron transition from the lowest unoccupied molecular orbital (LUMO) of the excited TPP to that of the ground-state DCN.

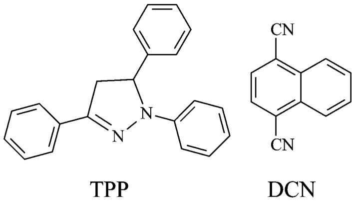

Figure 1. Structures of TPP and DCN molecules.

Experimental Section

Materials. 1,3,5-Triphenyl-2-pyrazoline was synthesized as previously described[15] and was purified by repeated recrystallization before use. DCN was purchased from Lancaster and used without further treatment.

Methods. All the aggregates, including coaggregates of TPP and DCN and pure TPP or DCN aggregates, were prepared through the reprecipitation method.[16,17] In a typical preparation, a stock solution (100 μL) of a TPP and DCN mixture (or TPP and DCN individually) in ethanol was rapidly injected into 3 mL of ultrapure water at room temperature with vigorous stirring. The concentration of TPP in the injected stock solutions was constant at 1×10^{-3} M. Mixing of ethanol with the water phase rapidly changes the character of the solvent, and the planar and hydrophobic π systems of TPP and DCN enable π−π stacking interactions which result in the formation of coaggregates in water.

The UV−vis absorption spectra and steady-state fluorescence spectra of aggregates in water were measured using a Shimadzu UV-1601 PC double-beam spectrophotometer and a Hitachi F-4500 fluorospectrometer, respectively. Time-resolved fluorescence measurements were carried out on a Horiba NAES-1100 time-resolved spectrofluorometer with a single-photon counting system.

The emission images of the aggregates were acquired on a fluorescence microscope (Lecia DMRBE) with a spot-enhanced charge-coupled device (CCD, Diagnostic Instruments, Inc.). The samples were prepared by placing a drop of the dispersion of aggregates onto a freshly cleaned glass slide.

---

* Author to whom correspondence should be addressed. Phone/Fax: +86-10-82616517. E-mail: jnyao@iccas.ac.cn.

[†] Institute of Chemistry, Chinese Academy of Sciences.

[‡] Graduate School, Chinese Academy of Sciences.

10.1021/jp076207x CCC: $40.75

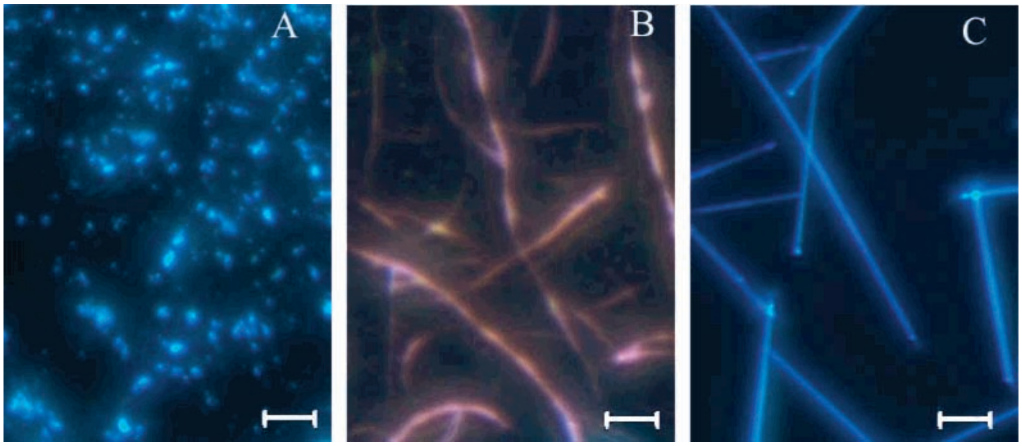

Figure 2. Fluorescence microscopy images of the as-prepared aggregates that were deposited onto glass slides and excited using a UV light with a wavelength range from 330 to 380 nm. (A) aggregates of pure TPP, (B) 1:1 molar mixed coaggregates of TPP and DCN, and (C) aggregates of pure DCN. All scale bars correspond to 10 μm.

Cyclic voltammetric measurements were carried out on a CHI660 electrochemical workstation using a conventional three-electrode cell consisting of a working electrode: platinum disk; a counter electrode: platinum wire; and a reference electrode: SCE. Solutions of TPP and DCN (1×10^{-3} M) in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte were deaerated before use.

The ground-state geometry optimizations of TPP, DCN, and the TPP−DCN molecule pair were performed using density functional theory with Becke's three-parameter hybrid exchange functional (B3LYP functional) at the 6-31G basis level. The excited-state electronic structures were calculated using time-dependent density functional theory (TD-DFT) with the B3LYP/6-31G method. All of the above quantum-chemical calculations were performed with the Gaussian 03 suite of programs.[18]

Results and Discussion

Fluorescence Microscopy Images. After being dropped on a glass slide, the as-prepared aggregates were observed by a fluorescence microscope and all the samples were excited using a UV light (330−380 nm). Representative images of the aggregates are shown in Figure 2. The pure TPP aggregates are blue amorphous particles, and the pure DCN aggregates are blue rods that have uniform diameter all through the entire length, while the 1:1 molar mixed coaggregates are reddish amorphous rods with a nonuniform appearance. The reddish emission color from the amorphous rods indicates that TPP and DCN form coaggregates accompanied by a new excited state that is different from the excited states of TPP and DCN.

UV−Vis Absorption Spectra. The UV−vis absorption spectrum of the 1:1 molar mixed coaggregate of TPP and DCN in water is shown in Figure 3, together with the absorption spectra of pure TPP and DCN in water at the same concentration. The absorption peaks of DCN appear at 321 and 335 nm, while the TPP absorption peak appears at 365 nm. The absorption spectra reveal that the singlet excited-state energy level of TPP lies below that of DCN. As a result, in the coaggregates, excitation of TPP cannot result in the singlet energy transfer from TPP to DCN.

The absorption spectrum is well-known to be very sensitive to the existence of the ground-state complex. As can be seen in Figure 3, the spectrum of the 1:1 mixed coaggregates is almost identical to the linear superposition of the spectrum of pure DCN and TPP aggregates in water at the same concentration, and no new absorption band is observed. This result suggests that there are no prominent electronic interactions between the TPP and DCN components in the ground state; in other words, TPP and DCN do not form an intermolecular charge-transfer complex in the mixed coaggregates.

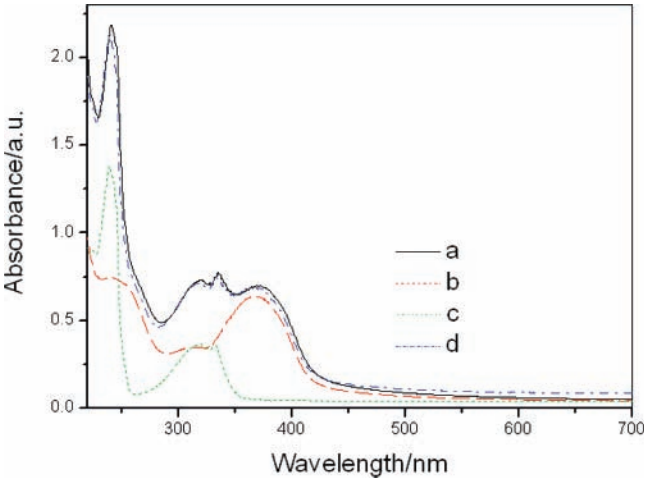

Figure 3. Absorption spectra of aggregates: (a) 1:1 molar mixed coaggregates of DCN and TPP in water, (b) pure TPP aggregates in water, (c) pure DCN aggregates in water, and (d) linear superposition of (b) and (c).

Fluorescence Spectra. To investigate the PET reactions of the mixed coaggregates, the fluorescence spectra of coaggregates were studied. In the experiments, the amounts of TPP were kept constant while those of DCN increased in the mixed coaggregates. The coaggregates were excited at 365 nm to ensure the selective excitation of the TPP component. It can be observed that the fluorescence intensity of the TPP emission at 456 nm decreases considerably with increasing amounts of DCN molecules in the coaggregates (Figure 4A). The increased fluorescence quenching implies that the contacts of TPP and DCN molecules rise in number with increasing DCN content in the coaggregates and PET takes place. We also observe a broad, structureless, and red-shifted emission at about 560 nm in the mixed coaggregates, and the emission intensity at 560 nm increases considerably with increasing amounts of DCN molecules in the coaggregates. From Figure 4A, it can also be found that DCN can hardly be excited at 365 nm, which excludes the fact that the emission at 560 nm is from DCN. Figure 4B shows the fluorescence excitation spectra of pure TPP aggregates and 1:1 molar mixed coaggregates monitored at 456 and 560 nm, respectively. The excitation spectra are

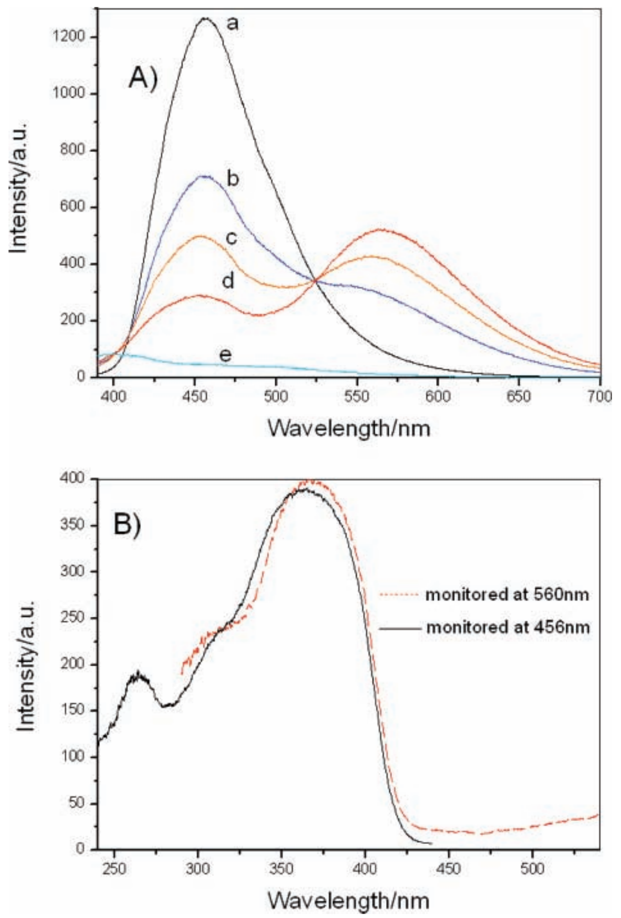

Figure 4. (A) Fluorescence emission spectra of suspensions of coaggregates of TPP and DCN with different molar ratios in water: (a) pure TPP; (b) TPP/DCN = 4:1; (c) TPP/DCN = 2:1; (d) TPP/DCN = 1:1; and (e) pure DCN. The excitation wavelength is 365 nm. (B) Fluorescence excitation spectra of the pure TPP aggregates emission at 456 nm, and the 1:1 molar mixed coaggregates emission at 560 nm.

almost identical, which excludes the possibility that the emission at about 560 nm is from the ground-state charge-transfer complex.[19,20] As a comparison, the emission spectra of TPP (10^{-3} M) with different amounts of DCN in anhydrous ethanol have also been studied (see Supporting Information, Figure S1). In the presence of DCN, no quenching of the emission from TPP and no new emission at about 560 nm have been observed for the mixed solutions of TPP and DCN with the same compositions as the coaggregates. The difference is attributed to the fact that the TPP and DCN molecules are freely mobile in the mixed solution and their approach to a close distance within the lifetime of the excited TPP is difficult.

More interesting, the emission colors of the mixed coaggregates vary with the content of DCN in coaggregates. Figure 5 depicts the photographs taken under a UV lamp (355 nm). It is clearly seen that the 1:1 molar mixed coaggregates are reddish, while the emission of TPP is at 456 nm and the emission of DCN is at 396 nm (see Supporting Information, Figure S2), the blending of TPP and DCN solution is blue, so it is concluded that the emission color change of mixed coaggregates can be attributed to the occurrence of a broad emission band at 500 to 650 nm.

Time-Resolved Fluorescence Study on the 1:1 Mixed Coaggregates of TPP and DCN. It has been observed from the steady-state emission measurements that in the coaggregates the emission from TPP gets quenched and a new emission appears at about 560 nm. To confirm that the new emission is

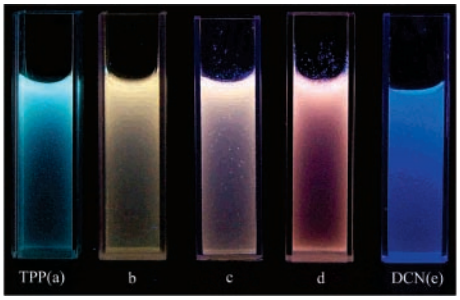

Figure 5. Photographs of the suspensions of mixed coaggregates with different TPP/DCN molar ratios taken under a UV lamp (355 nm): (a) pure TPP aggregates; (b) TPP/DCN = 4:1; (c) TPP/DCN = 2:1; (d) TPP/DCN = 1:1; and (e) pure DCN aggregates.

the exciplex fluorescence and the PET takes place in the coaggregates, time-resolved fluorescence measurements were carried out for the pure TPP aggregates and the 1:1 molar mixed coaggregates excited at 365 nm. The fluorescence decay profiles were monitored at 456 nm for pure TPP aggregates and 1:1 mixed coaggregates and at 560 nm for 1:1 mixed coaggregates. Figure 6 shows the typical fluorescence decay profiles. The fluorescence decay curve of pure TPP aggregates monitored at 456 nm is monoexponential, with a lifetime of 3.73 ns, while the lifetime of TPP emission (monitored at 456 nm) in 1:1 molar mixed coaggregates is 0.41 ns. Such a drastic reduction in the fluorescence lifetimes should be attributed to the intermolecular electron transfer from the excited TPP to DCN. The emission decay profiles monitored at 560 nm can be well-fitted to a dual exponential function with lifetimes of 0.41 ns (8.9%) and 40.18 ns (91.1%). It can be observed from the fluorescence emission spectra that the emission of TPP is a broad band and has a trailing edge at 560 nm. So the short lifetime component (0.41 ns) is for the emission from TPP. And also, in organic molecules, the complex state generally exhibits a long decay time as compared to that of the initial excited state.[21] Thus the long lifetime component (40.18 ns) confirms the existence of the complex state. The complex is an exciplex, that is, the excited-state complex. This inference is in accordance with the absence of absorption character of an intermolecular charge-transfer complex in the longer-wavelength region.

An exciplex is conventionally treated as a mixing of a contact ion-pair state and a local excited state.[22,23] The research group of Gould has shown that an exciplex can be considered to be essentially a pure ion pair when its emission maximum is lower in energy than the 0,0 transition of the acceptor excited singlet state by 5000 cm^{-1}.[24,25] In our case, the emission maximum of the TPP−DCN exciplex is lower in energy than the 0,0 transition of the DCN excited singlet state by 12251 cm^{-1}, so the TPP−DCN exciplex can be considered to be a pure ion pair.

Theoretical Modeling of Electron Transfer. Before further addressing the PET in the coaggregates of TPP and DCN, it is instructive to consider the thermodynamics of such a process. In general, the Gibbs free energy changes of PET can be estimated from the Weller equation:[26]

$$\Delta G = E(D/D^{+}) - E(A/A^{-}) - E_{0-0} - e^{2}/\alpha\epsilon$$

here, $E(\mathrm{D/D^+})$, $E(\mathrm{A/A^-})$, and E_{0-0} represent the oxidation of donor (TPP), the reduction potential of acceptor (DCN), and the lowest excited-state energy of TPP. $e^2/\alpha\epsilon$ is the columbic term. The excitation energy E_{0-0} for TPP is 3.40 eV, the reduction potential of DCN is −0.92 eV, and the oxidation potential of TPP is 0.59 eV. Thus we can estimate that the ΔG

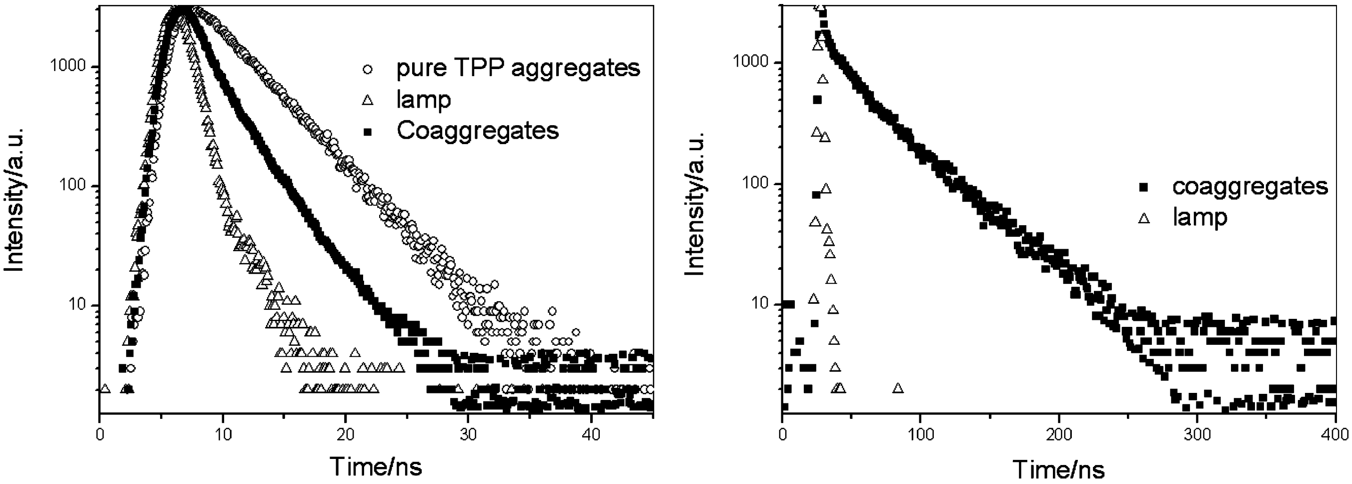

Figure 6. Fluorescence decay profiles of pure TPP aggregates monitored at 450 nm (left) and 1:1 molar mixed coaggregates of TPP and DCN monitored at 450 and 560 nm (right).

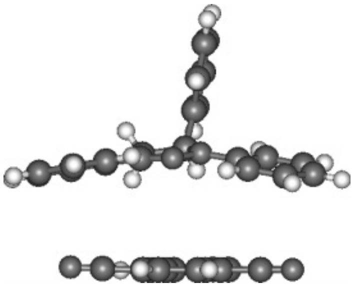

Figure 7. Optimized structure of the TPP−DCN molecule pair in the mixed coaggregates.

for the PET is −1.49 eV. Due to the fact that ΔG is negative, the PET between TPP and DCN is permitted in thermodynamics.

In the mixed coaggregates of TPP and DCN, there are two possible pathways for the electron transfer when the TPP is excited at 365 nm. One pathway is via the intermolecular charge-transfer (ICT) state by a transition of an electron from the HOMO of TPP to the LUMO of DCN;[27] the other pathway is via the transition of an electron from the LUMO of TPP to the LUMO of DCN, in other words, a transition of an electron from the excited-state TPP to the ground-state DCN. Quantum-chemical calculations have been performed to gain a deeper insight into the electron-transfer process between TPP and DCN in the mixed coaggregates.

Figure 7 displays the optimized ground-state geometry of the TPP−DCN molecule pair in the mixed coaggregates. We can see that the naphthalene ring of DCN and the pyrazoline ring of TPP are in a face-to-face stacking mode. The distance between the naphthalene ring and the pyrazoline ring is 3.9 Å. This distance fulfills the criteria of exciplex formation.[28]

The frontier molecular orbitals and the absorption and corresponding oscillator strength of the TPP and DCN molecule pair are calculated, as shown in Figure 8 and Table 1. The HOMO is found to be strictly located on the TPP moiety, while the LUMO is strictly located on the DCN moiety. The first excited state which corresponds to a pure transition of the HOMO of TPP to the LUMO of DCN is an intermolecular charge-transfer (ICT) state, but the oscillator strength is so small that the transition for the first excited state is a forbidden transition. This is in accordance with the UV−vis absorption spectra that have no absorption peak at 627 nm. The fourth excited state has strong oscillator strength, and the calculated molecular orbitals show that the fourth excited state is almost a TPP HOMO−LUMO transition.

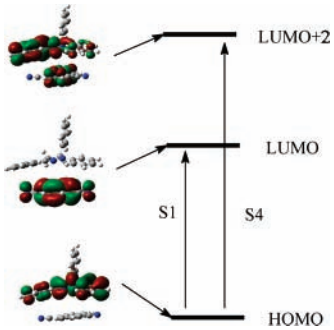

Figure 8. Calculated frontier molecular orbitals of TPP−DCN molecule pair.

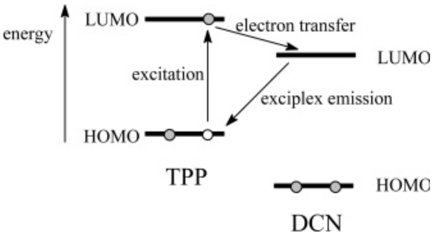

Figure 9. Energy diagram representing the photophysical events that can take place in coaggregates of TPP and DCN.

TABLE 1: Calculated Absorption Wavelengths (nm) and Each Corresponding Oscillator Strength for the TPP−DCN Molecule Pair

excited state	absorption (nm)	oscillator strength
S1	627	0.0086
S2	375	0.0033
S3	357	0.0559
S4	355	0.2609
S5	333	0.0103

From the above results, we conclude that the PET in the coaggregates does not take place through ICT. The whole PET process is summarized in Figure 9. After the excitation of TPP, an electron is promoted to the LUMO level of the excited TPP, it is then transferred to the lower-lying LUMO level of the DCN, and a hole remains on the HOMO level of the TPP; thereby an exciplex comes into being. When the electron comes back to the HOMO of the TPP, the exciplex fluorescence emission is observed at about 560 nm.

Conclusion

The photophysical properties of the mixed π-conjugated TPP−DCN coaggregates in water were investigated. TPP and DCN do not form an intermolecular charge-transfer complex in the ground state, whereas they form an exciplex in the excited state. The fluorescence of TPP in the mixed coaggregates was quenched by DCN via exciplex formation. Interestingly, the exciplex formation changes the emission color of the mixed aggregates. Quantum-chemical calculations show that DCN and TPP are in a face-to-face stacking mode (in the mixed coaggregates, optimized ground-state geometry of the TPP−DCN molecule pair favors a face-to-face stacking mode), which benefits the formation of an exciplex. The calculations of excited states confirm that the electron transfer takes place through an electron transition from the LUMO of excited TPP to the LUMO of the DCN.

Acknowledgment. This work was supported by the National Science Foundation of China (No. 502 21201,90301010,-20471062,508730842), the Chinese Academy of Sciences and the National Research Fund for Fundamental Key Projects No. 973. (2006 CB 806200)

Supporting Information Available: Fluorescence emission spectra of TPP in ethanol incorporating increasing amounts of DCN, and fluorescence emission spectrum of pure DCN aggregates in water. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(2) Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C. *J. Phys. Chem. B* **2003**, *107*, 6668.

(3) Brédas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971.

(4) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(5) Becker, E. H. A.; Meskers, S. C. J.; Schenning, A. P. H. J.; Chen, Z. J; Würthner, F.; Marsal, P.; Beljonne, D.; Cornil, J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2006**, *128*, 649.

(6) Schenning, A. P. H. J.; Herrikhuyzen, J. V.; Jonkheijim, P.; Chen, Z. J.; Würther, F.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 10252.

(7) Würthner, F.; Chen, Z. J.; Hoeben, F. J. M.; Osswald, P.; You, C. C.; Jonkheijm, P.; Herrikhuyzen, J. V.; Schenning, A. P. H. J.; Van der Schoot, P. P. A.; Meijer, E. W.; Becker, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611.

(8) Neuteboom, E. E.; Van Hal, P. A.; Janssen, R. A. J. *Chem. Eur. J.* **2004**, *10*, 3907.

(9) Rybtchinski, B.; Sinks, L. E.; Wasielewski, M. R. *J. Phys. Chem. A* **2004**, *108*, 7497.

(10) Prasad, E.; Copids, K. R. *J. Am. Chem. Soc.* **2000**, *122*, 3191.

(11) Bekers, E. H. A.; Jonkheijm, P.; Schenning, A. P. H. J.; Meskers, S. C. J.; Janssen, R. A. J. *Chem. Phys. Chem.* **2005**, *6*, 2029.

(12) Fu, H. B.; Yao, J. N. *J. Am. Chem. Soc.* **2001**, *123*, 1434.

(13) Fu, H. B.; Loo, B. H.; Xiao, D. B.; Xie, R. M.; Ji, X. H.; Yao, J. N.; Zhang, B. W.; Zhang, L. Q. *Angew. Chem., Int. Ed.* **2002**, *41*, 962.

(14) Xiao, D. B.; Xi, L.; Yang, W. S.; Fu, H. B.; Shuai, Z. G.; Fang, Y.; Yao, J. N. *J. Am. Chem. Soc.* **2003**, *125*, 6740.

(15) Sandler, S. R.; Tsou, K. C. *J. Chem. Phys.* **1963**, *39*, 1062.

(16) Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys., Part 2* **1992**, *31*, L1132.

(17) Peng, A. D.; Xiao, D. B.; Ma, Y.; Yang, W. S.; Yao, J. N. *Adv. Mater.* **2005**, *17*, 2070.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, rev. B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(19) Zhu, W. Q.; Zheng, X. Y.; Jiang, X. Y.; Zhang, Z. L.; Xu, S. H.; Zhang, B. W. *Acta Chim. Sinica* **2005**, *6*, 1182.

(20) Abad, S.; Vayá, L.; Jiménez, M. C.; Pischel, U.; Miranda, M. A. *Chem. Phys. Chem.* **2006**, *7*, 2175−2183.

(21) Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer, Part A*; Elsevier: New York, 1988.

(22) Zhang, G. H.; Thomas, J. K. *J. Phys. Chem. B* **1997**, *110*, 8569.

(23) Mulliken, R. S.; Person, W. B. *Molecular Complex*; Wiley-Interscience: New York, 1969.

(24) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176.

(25) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.

(26) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.

(27) Sun, M. T.; Pullerits, T.; Kjellberg, P.; Beenken, W. J. D.; Han, K. L. *J. Phys. Chem. A* **2006**, *110*, 6324.

(28) Valeur, B. *Molecular Fluorescence Principles and Applications*; Wiley-VCH: Weinheim, 2002.