An Efficient Energy Transfer Found in Triphenylene/Hexaazatriphenylene System with Electronic Complimentarity and Structural Similarity

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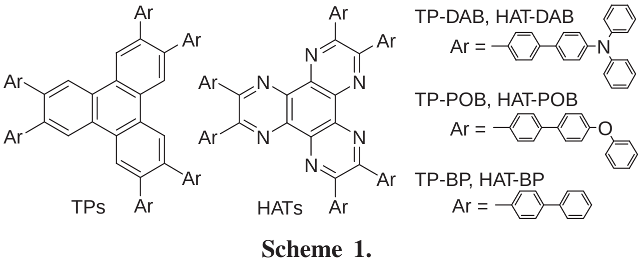
In a donor–acceptor system with structural similarity and electronic complimentarity, an efficient energy transfer was observed from energy-donor triphenylenes to energy-acceptor hexaazatriphenylenes in a film state.

Energy transfer in a donor–acceptor system is an important process in a natural photosynthetic system.[1] In an artificial system such as OLED and photovoltaic devices, low-molecular-weight donor and acceptor organic molecules have been used to fabricate devices by conventional spin-coating and vacuum-deposition techniques. In terms of morphological stability, the donor and acceptor molecules should have similar structure to each other to avoid device destabilization.[2] In addition, when the donor and acceptor molecules have electronic complimentarity to each other, an efficient energy transfer would be expected. To the best of our knowledge, there are no reports on the energy transfer in a donor–acceptor system with structural similarity and electronic complimentarity. Triphenylene (TP)[3] and hexaazatriphenylene (HAT)[4] have completely similar structure to each other except for the presence and absence of the nitrogen atoms. The former acts as donor whereas the latter as acceptor.[3,4] Bushby's group reported that a donor–acceptor alternative stacking can be created in a TP–HAT system without any comments on the energy transfer from TP to HAT.[5] Recently, we reported that HATs with six peripheral aromatic groups show self-assembling ability as well as light-emitting performance both in bulk and solution states.[6,7] Interestingly, the HAT derivative with six diphenylaminobiphenyl groups forms an amorphous-type solid preserving the one-dimensional ordering in a cooling process from the discotic liquid crystalline phase.[6] This finding led us to design and prepare a new-type energy-transfer system based on the combination of donor TP and acceptor HAT with structural similarity in a film state (Scheme 1).

Triphenylene derivatives, TP-DAB, TP-POB, and TP-BP with (diphenylamino)biphenyl, phenoxybiphenyl, and biphenyl groups, respectively, were prepared by coupling reactions of hexabromotriphenylene[8] with the corresponding arylboronic acids in the presence of palladium(0) catalyst. Hexaazatriphenylene derivatives HAT-DAB, HAT-POB, and HAT-BP were obtained from condensation reactions of hexaaminobenzene with the corresponding diarylethanediones, according to methods reported previously.[6]



Scheme 1.

Film samples were prepared from spin-coating of the benzene solutions of TPs, HATs, and TP/HAT mixtures on a quartz glass plate. The TP/HAT ratio (mol/mol) changed in the range from 100:0, 100:1, 100:10, 100:100, to 0:100. Transparent amorphous films can be obtained from the TP-DAB/HAT-DAB system, whereas turbid crystalline films were given from the TP-POB/HAT-POB and TP-BP/HAT-BP systems. In each DAB, POB, and BP system, an efficient energy transfer can be predicted from the overlap between the fluorescence spectrum of the donor TP and the UV–vis spectrum of the acceptor HAT (Figure 1 and Supporting Information).

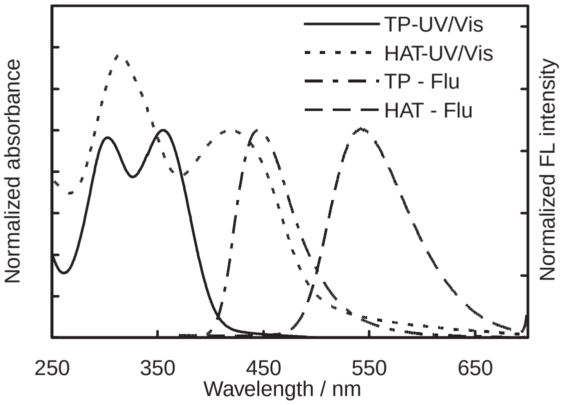


Figure 1. UV–vis and fluorescence spectra of TP-DAB and HAT-DAB in the spin-coated film.

In the DAB system, strong blue emission at 445 nm is observable in the donor TP-DAB whereas green emission at 543 nm in the acceptor HAT-DAB (Figure 2). In the 100:100 mixture of TP-DAB/HAT-DAB, the blue emission from TP-DAB was completely quenched and only the green emission from HAT-DAB was detected, indicating an energy transfer from TP-DAB to HAT-DAB. The energy transfer is also supported by evidence of the overlap between the UV–vis and excitation spectra (Supporting Information). Even in the presence of 10 equivalents of HAT-DAB, the quenching of TP-DAB emission occurred significantly. The blue TP-DAB emission remained slightly in the presence of 1 equivalent of HAT-DAB. The emission band of HAT-DAB shifts hypsochromically from 543 to 500 nm by changing the TP-DAB/HAT-DAB ratio from 0:100, 100:100, 100:10, to 100:1 (Figure 2). The result suggests that with decreasing the concentration the HAT-DAB molecules

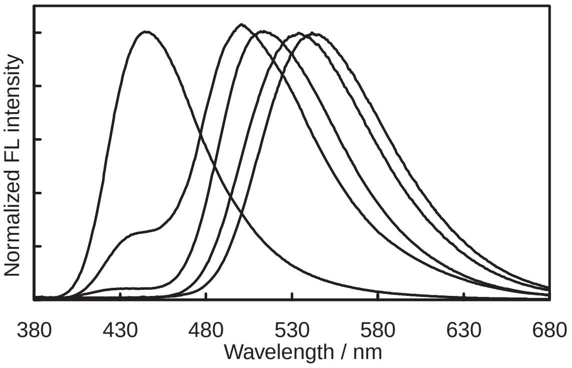


Figure 2. Fluorescence spectra of the TP-DAB/HAT-DAB mixtures (100:0, 100:1, 100:10, 100:100, and 0:100 (mol/mol), from left to right) in the spin-coated film.

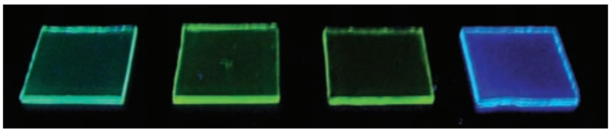


Figure 3. Fluorescent images of the TP-DAB/HAT-DAB mixtures (100:10, 100:100, 0:100, and 100:0 (mol/mol), from left to right).

tend to be incorporated molecularly in the host TP-DAB medium through complimentary polytopic interactions between TP and HAT molecules.[5] Similar energy-transfer phenomena along with the hypsochromic shifts were observable in the POB and PB systems (Supporting Information).

The energy-transfer phenomena can be visualized as shown in Figure 3. The green emission color found in the 100:100 mixture of TP-DAB/HAT-DAB is very similar to that of the acceptor HAT-DAB but not to the blue emission of the donor TP-DAB. The bluish-green emission color found in the 100:10 mixture of TP-DAB/HAT-DAB is attributed to the hypsochromic shift of the emission band, as described above. In the BP and POB systems, clear pictures could not be obtained because of their inferior film-forming nature.

A rapid energy-transfer rate can be estimated from the time-resolved fluorescence spectroscopy. In the parent TP-DAB and HAT-DAB, the dimension decays are multiexponential and the fluorescent lifetime was estimated roughly to be several ns. In the 100:10 mixture of TP-DAB/HAT-DAB, the decay of the donor TP-DAB emissions is accelerated significantly within 25 ps under the measurement conditions of 25 ps pulse-width, indicating a resonance energy transfer.

Morphology for the spin-coated films of the TP/HAT mixtures was observed by atomic force microscopy (Figure 4). In the DAB system, all the films of TP-DAB, HAT-DAB, and TP-DAB/HAT-DAB (100:100) were extremely flat with the difference between the highest and the deepest part of the film being roughly <1.0 nm, indicating the formation of glassy amorphous films.[6] Thus, the excellent amorphous film-forming ability can be preserved in the TP-DAB/HAT-DAB two-component system. In contrast, the BP and POB systems showed the formation of crystalline solids.[9]

In conclusion, we have demonstrated that an energy-transfer system can be created by combination of energy-donor triphenylenes and energy-acceptor hexaazatriphenylenes with structural similarity and electronic complimentarity. The glassy amorphous film ability in each triphenylene and hexaazatriphenylene molecule with (diphenylamino)biphenyl aromatic groups is preserved in the mixed two-component system where an efficient energy transfer is achieved under the optimized conditions.

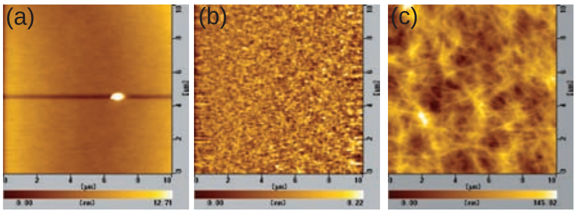


Figure 4. AFM images and the height profiles of the 100:100 (mol/mol) mixtures of (a) TP-DAB/HAT-DAB, (b) TP-POB/HAT-POB, and (c) TP-BP/HAT-BP.

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References and Notes

1 a) W. Kühlbrandt, D. N. Wang, Y. Fujiyoshi, *Nature* **1994**, *367*, 614. b) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdel, N. W. Isaacs, *Nature* **1995**, *374*, 517.

2 Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fuka, Y. Inoue, F. Sato, S. Tokito, *J. Am. Chem. Soc.* **2004**, *126*, 8138.

3 a) M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky, R. H. Grubbs, *Angew. Chem., Int. Ed.* **1999**, *38*, 2741. b) L. Y. Park, D. G. Hamilton, E. A. McGehee, K. A. McMenimen, *J. Am. Chem. Soc.* **2003**, *125*, 10586. c) H. Ringsdorf, R. Wüstefeld, E. Zerta, M. Ebert, J. H. Wendorff, *Angew. Chem., Int. Ed.* **1989**, *28*, 914.

4 a) R. I. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barberà, M. G. Debije, J. Piris, Y. H. Geerts, *Adv. Mater.* **2003**, *15*, 1614. b) K. Pieterse, P. A. van Hal, R. Kleppinger, J. A. J. M. Vekemans, R. A. J. Janssen, E. W. Meijer, *Chem. Mater.* **2001**, *13*, 2675. c) A. Okabe, T. Fukushima, K. Ariga, T. Aida, *Angew. Chem., Int. Ed.* **2002**, *41*, 3414.

5 a) E. O. Arikainen, N. Boden, R. J. Bushby, O. R. Lozman, J. G. Vinter, A. Wood, *Angew. Chem., Int. Ed.* **2000**, *39*, 2333. b) O. R. Lozman, R. J. Bushby, J. G. Vinter, *J. Chem. Soc., Perkin Trans. 2* **2001**, 1446.

6 a) T. Ishi-i, T. Hirayama, K. Murakami, H. Tashiro, T. Thiemann, K. Kubo, A. Mori, S. Yamasaki, T. Akao, A. Tsuboyama, T. Mukaide, K. Ueno, S. Mataka, *Langmuir* **2005**, *21*, 1261. b) T. Hirayama, S. Yamasaki, H. Ameku, T. Ishi-i, T. Thiemann, S. Mataka, *Dyes Pigm.* **2005**, *67*, 105.

7 T. Ishi-i, K. Murakami, Y. Imai, S. Mataka, *Org. Lett.* **2005**, *7*, 3175.

8 R. Breslow, B. Jaun, R. Q. Kluttz, C. Xia, *Tetrahedron* **1982**, *38*, 683.

9 In the TP-BP/HAT-BP system, needle-like one-dimensional aggregates (length of 5–10 µm and wide of 200–400 nm) can be observed. The long-range ordering would be ascribed to alternative layered arrangement of TP-BP and HAT-BP molecules with highly-ordered manner.[5] The details will be reported elsewhere.

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