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Rigid Molecular Architectures That Comprise a 1,3,5-Trisubstituted Benzene Core and Three Oligoaryleneethynylene Arms: Light-Emitting Characteristics and π Conjugation between the Arms

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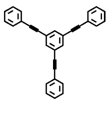
Rigid molecular architectures which consist of a trivalent core and three π extended arms (so-called star-shaped molecules) are currently attracting considerable attention because of potential application as devices,[1] such as light-emitting diodes (LEDs), field effect transistors (FETs), and nonlinear optics (NLO). However, with respect to the light-emitting characteristics associated with LEDs, only a few papers (dealing with the light-emitters with $\Phi_f < 0.86$) appear in the literature.[2] Apart from this, it should be interesting to examine if π conjugation occurs between the arms across the 1,3,5-trisubstituted benzene core of star-shaped molecules, though such an interaction is reported for condensed polycyclic systems.[3] Thus we have investigated the light-emitting characteristics and occurrence of π conjugation between the arms of star-shaped rigid molecules that comprise a 1,3,5-triethynylbenzene core and methoxy group-substituted oligo(*p*-phenyleneethynylene) arms. Consequently, we achieved the ultimate goal ($\Phi_f \approx 1.0$, $\log \epsilon > 5$) for organic molecules with respect to light-emitting ability by integrating the dimethoxyphenylacetylene unit with low Φ_f (0.29 in cyclohexane), not the fluorene unit with high Φ_f (0.74 in cyclohexane). Furthermore, we have found that π conjugation occurs between the arms.



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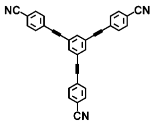

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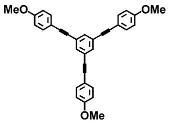

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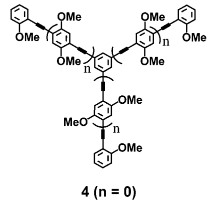
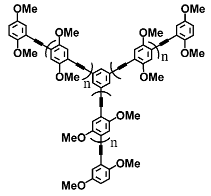


4 (n = 0)
6 (n = 1)
8 (n = 2)



5 (n = 0)
7 (n = 1)
9 (n = 2)

In regard to the star-shaped molecules, we considered **1** (the simplest star-shaped hydrocarbon system), **2** (cyano-substituted **1** at each terminal), **3** (methoxy-substituted **1** at each terminal), **4**, **6**, and **8** (homologues containing zero, one, and two dimethoxyphenyleneethynylene units and a monomethoxyphenyl terminal at each arm) (abbreviated as MMPT homologues), and **5**, **7**, and **9** (homologues containing zero, one, and two dimethoxyphenyleneethynylene units and dimethoxyphenyl terminal at each arm) (abbreviated as DMPT homologues). Synthesis of **1**−**10** was achieved by a Pd C−C cross-coupling reaction (see Supporting Information).

Table 1. Photophysical Data of Star-Shaped Molecules **1**−**9** in $CHCl_3$[a]

compound	Φ_f[b]	λ_{em} (nm)	$\log \epsilon$	λ_{abs} (nm)	τ (ns)	k_r (s^{-1})	k_d (s^{-1})	k_r/k_d
1	0.15	353	4.93	305	1.17	1.28×10^8	7.23×10^8	0.18
2	0.14	357	5.11	320	0.78	1.80×10^8	1.11×10^9	0.16
3	0.23	360	4.93	316	1.17	1.96×10^8	6.55×10^8	0.30
4	0.24	359	4.77	314	1.70	1.41×10^8	4.48×10^8	0.32
5	0.46	384	4.81	334	1.55	2.97×10^8	3.49×10^8	0.85
6	0.83	406	5.02	377	0.95	8.69×10^8	1.78×10^8	4.88
7	0.85	409	5.11	380	0.78	1.10×10^9	1.93×10^8	5.67
8	0.97	433	5.11	405	0.78	1.25×10^9	3.86×10^7	32.33
9	0.98	464	5.29	426	0.51	1.93×10^9	3.93×10^7	49.00

[a] All spectra were measured for 10^{-7} M solution at 295 K. [b] Quantum yield is calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4).

The photophysical data[4] of star-shaped molecules **1**−**9** together with radiative rate constant (k_r), radiationless rate constant (k_d), k_r/k_d (a measure for emissivity) and emission lifetime (τ) are summarized in Table 1. Since the k_r and k_d are related to the corresponding emission quantum yields and lifetimes by $\Phi_f = k_r \times \tau$ and $k_r + k_d = \tau^{-1}$, it is possible to calculate the values of k_r and k_d wherever quantum yield and lifetime data are available.[5]

As demonstrated in Table 1, the introduction of a methoxy (donor) group into the benzene rings of each arm of the simplest star-shaped hydrocarbon system **1** brings about a slight red shift of the fluorescence emission maximum (λ_{em}) and an increase in quantum yield (Φ_f) (**3**, **4**), though the introduction of a cyano (acceptor) group does not improve the Φ_f value (**2**). Although the emission efficiency (Φ_f) increases with increasing dimethoxyphenyleneethynylene unit in each arm, the light-emitting characteristics of star-shaped molecules (**4**−**9**) can be better understood by dividing into two homologous series, MMPT (**4**, **6**, and **8**) and DMPT (**5**, **7**, and **9**). For both series, the values of Φ_f, λ_{em}, $\log \epsilon$, and λ_{abs} increase regularly with a number of dimethoxyphenyleneethynylene units. Thus we succeeded in creating very intense violet-blue (**8**, $\Phi_f = 0.97$, $\log \epsilon = 5.11$) and blue (**9**, $\Phi_f = 0.98$, $\log \epsilon = 5.29$) bright light-emitters, and thereby we achieved the ultimate goal ($\Phi_f \approx 1.0$, $\log \epsilon > 5$) for organic molecules with respect to light-emitting ability.

We examined the relations of k_r and of k_d with the number of dimethoxyphenyleneethynylene units excluding the terminal aryleneethynylene groups (**3n**, a measure for π extension). Consequently, as seen in Figure 1, we found[6] linear relationships between k_r and **3n** (slope $= 1.85 \times 10^8$, $r^2 = 0.9684$) and k_d and **3n** (slope $= -0.68 \times 10^8$, $r^2 = 0.9672$) in the MMPT series, as well as between k_r and **3n** (slope $= 2.79 \times 10^8$, $r^2 = 0.9995$) and k_d and **3n** (slope $= -0.51 \times 10^8$, $r^2 = 1.0000$) in the DMPT series. For both series, k_r values increase and k_d values decrease with **3n**, indicating that emission efficiency of the homologues in both series increases with the number of dimethoxyphenyleneethynylene units. However, from slopes for plots of k_r versus **3n** and k_d versus **3n**, the DMPT

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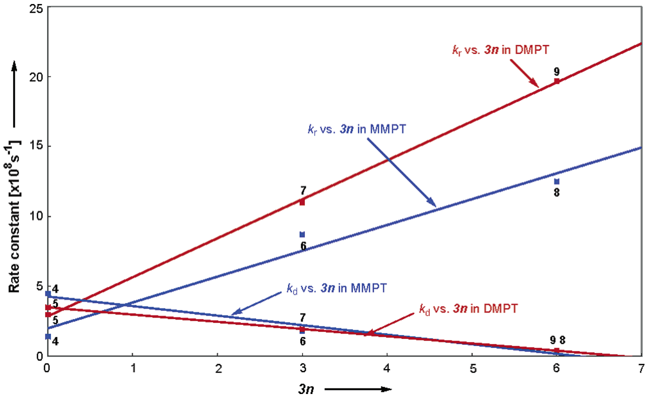
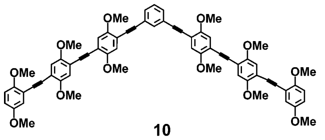


Figure 1. The relationship of k_r and k_d to **3n** in MMPT and DMPT homologues (blue line for MMPT homologues, red line for DMPT homologues).

Table 2. Photophysical Data of Star-Shaped System (**9**), Banana-Shaped System (**10**), and Rod-Shaped System (**11**) in $CHCl_3$[a]

compound	Φ_f[b]	λ_{em} (nm)	log ϵ	λ_{abs} (nm)	$\Delta\lambda_{abs}$ (nm)	ϵ/ϵ_{11}	k_r (s^{-1})	k_d (s^{-1})
9	0.98	464	5.29	426	36	3.50	1.93×10^9	3.93×10^7
10	0.90	432	4.96	402	12	1.59	8.02×10^8	8.92×10^7
11	0.81	430	4.75	390	0	1.00	4.55×10^8	1.07×10^8

[a] All spectra were measured for 10^{-7} M solution at 295 K. [b] Quantum yield is calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4).



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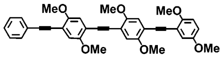

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homologues are favored over the MMPT homologues with respect to the emission characteristics. The emissive superiority of the DMPT homologues to the MMPT homologues might be explained by movability (number) of the dipolar dimethoxyphenylacetylene unit (donor, OMe; acceptor, C≡C) in the excited singlet state as suggested in the previous paper.[7]

To know if any π conjugation occurs between the arms of star-shaped molecules, we have examined the $\Delta\lambda_{abs}$ and ϵ/ϵ_{11} values for 1,3,5-trisubstituted benzene (**9**, star shape), 1,3-disubstituted benzene (**10**, banana shape), and monosubstituted benzene (**11**, rod shape)[8] with the trimeric(dimethoxyphenyleneethynylene) group. The results are summarized in Table 2.

As seen in Table 2, the values of $\Delta\lambda_{abs}$ and ϵ/ϵ_{11} evidently increase in the order of **9** (star shape) > **10** (banana shape) > **11** (rod shape). Difference in λ_{abs} between **9** and **11** becomes 36 nm, and ϵ_9/ϵ_{11} becomes 3.50. These data clearly indicate an extension of the π conjugation between the arms. Although an increase in $\Delta\lambda_{abs}$ is reported for condensed polycyclic systems,[3] the star-shape molecule (**9**) seems to be a more straightforward example for meta conjugation.

The solvent dependency on the emission characteristics of **8** and **9** is contrasting (see Supporting Information). The Φ_f and λ_{em} values of **9** are remarkably altered with a change in solvent polarity, while little solvent dependency on Φ_f and λ_{em} values of **8** is observed,[9] which seems to be explained in terms of a marked disparity between difference density distribution in the excited singlet and the ground state (see Supporting Information).

In conclusion, we have synthesized the star-shaped architectures that comprise a 1,3,5-triethynylbenzene core and methoxy group-substituted oligo(*p*-phenyleneethynylene) arms. We achieved the ultimate goal ($\Phi_f \approx 1.0$, log $\epsilon > 5$) for organic molecules with respect to light-emitting ability by creating very intense violet-blue (**8**, $\Phi_f = 0.97$, log $\epsilon = 5.11$) and blue (**9**, $\Phi_f = 0.98$, log $\epsilon = 5.29$) bright light-emitters. We have found that π conjugation occurs between the arms of **9** despite the *meta*-substituted system. A linear relationship of k_r (with positive slope) and of k_d (with negative slope) to the number of dimethoxyphenyleneethynylene units (**3n**) for MMPT (**4**, **6**, and **8**) and DMPT (**5**, **7**, and **9**) homologues and the contrasting solvent effect on λ_{em} of **8** and **9** are also interesting findings. It is noted that Φ_f, λ_{em}, λ_{abs}, k_r, k_d, and solvent effect are controlled by the number (one or two) of the methoxy groups on the terminal benzene rings.

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Supporting Information Available: Synthesis, NMR data, HR MS data, fluorescence spectra for **6**, **7**, **8**, and **9**, solvent effect on spectra of **8** and **9**, and MO and MM2 calculation for **8** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) For example, see: (a) Kreger, K.; Jandke, M.; Strohriegl, P. *J. Synth. Met.* **2001**, *119*, 163. (b) Ponomarenko, S. A.; Kirchneyer, S.; Elschner, A.; Huisman, B.-H.; Karbach, A.; Drechsler, D. *Adv. Funct. Mater.* **2003**, *13*, 591. (c) Kannan, K.; He, G. S.; Lin, T.-C.; Prasad, P. N.; Vaia, R. A.; Tan, L.-S. *Chem. Mater.* **2004**, *16*, 185.

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(4) The compounds were purified by repeated column chromatography followed by recrystallization. Quite different from the usual case (purity checked by NMR, elemental analysis, etc., 10^{-2}—10^{-3} impurity), purification of light-emitting materials was checked by constancy of the fluorescence intensity at the maximum (λ_{em}) (10^{-6}—10^{-7} impurity).

(5) (a) Barltrop, J. A.; Coyle, J. D. *Principles of Photochemistry*; Wiley: New York, 1978; p 68. (b) Leventis, N.; Rawashdeh, A.-M. M.; Elder, I. A.; Yang, J.; Dass, A.; Sotiriou-Leventis, C. *Chem. Mater.* **2004**, *16*, 1493.

(6) A similar relation is found for the donor/acceptor rod-shaped light-emitting materials.[7]

(7) Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7040.

(8) Yamaguchi, Y.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2005**, *127*, 9332.

(9) We have confirmed that the Φ_f and λ_{em} values of **8** and **9** in polar solvents are not so altered with change in concentration from 10^{-6} to 10^{-8} M.

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