Rod-shaped Oligophenyleneethynylenes Modified by Donor and Acceptor Groups in a Block Manner: Synthesis and Light-emitting Characteristics

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Highly efficient blue light emmitters represented by **BL-5** ($\Phi_f = 0.96$, $\lambda_{em} = 455\,nm$ in $CHCl_3$) and **BL-8** ($\Phi_f = 0.98$, $\lambda_{em} = 464\,nm$ in $CHCl_3$) are created by block modification of oligophenylene ethynylenes with donor and acceptor groups. A linear relationship with positive slope between Φ_f and the movability of the energetically equivalent dipolar structure unit is found for the first time.

The importance of organic light-emitting materials with high emission efficiency in biological, chemical, and materials science has been greatly increasing. However, a general concept or a method for creation of highly fluorescent molecules in a desired wavelength region has not been established yet, though various attempts to achieve this goal have been made.[1] Thus, the development of method for creation of highly fluorescent molecules should be an urgent subject. Here, we report synthesis and light-emitting characteristics of oligophenyleneethynylenes modified by donor and acceptor groups in a block manner (**BL-1**–**BL-8**, see Figure 1) together with a relationship between quantum yield (Φ_f) and the movability of the energetically equivalent dipolar structure unit (so-called intramolecular exciton[2]) in the excited singlet state.

Synthesis of block modification system (**BL-1**–**BL-8**) was made in the following order using the Pd C–C coupling reaction[3] as the key step: (1) preparation of acceptor blocks (**1** and **2**), (2) preparation of donor blocks (**3**, **4**, and **5**), and (3) cross-coupling reaction between donor blocks and acceptor blocks (Figure 2, further detail, see the Electronic Supporting Information).[7] The structures of **BLs** were confirmed by spectral data (^1H and ^{13}C NMR spectroscopy and HR-FAB MS, see the Electronic Supporting Information).[7]

The photophysical data of block modification system (**BL-1**–**BL-8**), and parent system (**PR-1**–**PR-3**)[1c] together with radiative rate constant (k_r), radiationless rate constant (k_d), and emission lifetime (τ) are summarized in Table 1. The k_r and k_d were calculated from τ and Φ_f.[4]

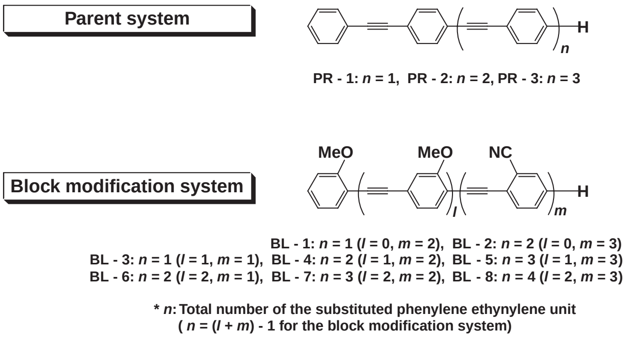

Figure 1. Structures of the parent (**PR**) system and the block modification (**BL**) system.

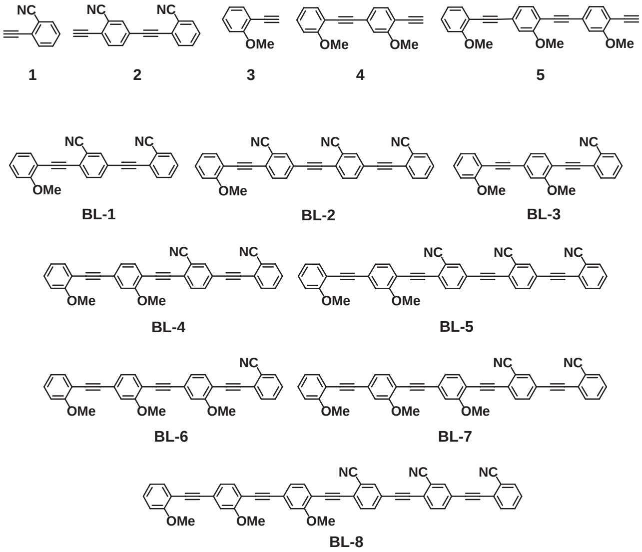

Figure 2. Structures of donor blocks, acceptor blocks, and block modification system (**BL-1**–**BL-8**).

As shown in Table 1, it is demonstrated that the Φ_f and λ_{em} values increase effectively by the block modification, though Φ_f values increase essentially with the π-conjugation length even for the parent system. Thus, very high Φ_f values (>0.95) and emission at longer wavelength (>430 nm) are observed for the block modification system such as **BL-4** ($n = (l + m) - 1 = 2$), **BL-5** ($n = (l + m) - 1 = 3$), **BL-7** ($n = (l + m) - 1 = 3$),

Table 1. Photophysical data of block modification system and parent system in chloroform[a]

Compound	n	Φ_f[b]	λ_{em} /nm	Stokes shift/nm	log ε	λ_{abs} /nm	τ /ns	k_r /s^{-1}	k_d /s^{-1}
BL-1	1	0.82	403	45	4.61	358	2.45	3.34×10^8	7.33×10^7
BL-2	2	0.93	419	49	4.87	370	1.35	6.89×10^8	5.19×10^7
BL-3	1	0.84	392	40	4.66	352	2.19	3.84×10^8	7.31×10^7
BL-4	2	0.95	434	54	4.81	380	1.55	6.13×10^8	3.23×10^7
BL-5	3	0.96	455	69	4.92	386	1.20	7.98×10^8	3.33×10^7
BL-6	2	0.95	407	42	4.90	365	1.25	7.57×10^8	3.99×10^7
BL-7	3	0.98	443	56	4.96	387	1.10	8.94×10^8	1.82×10^7
BL-8	4	0.98	464	72	4.99	392	1.02	9.58×10^8	1.95×10^7
PR-1	1	0.50	348	20	4.59	328	2.57	1.95×10^8	1.95×10^8
PR-2	2	0.61	387	42	4.77	345	1.70	3.59×10^8	2.30×10^8
PR-3	3	0.83	388	38	4.80	350	1.58	5.24×10^8	1.07×10^8

[a] All spectra were measured at 295 K. [b] Quantum yield is calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4).

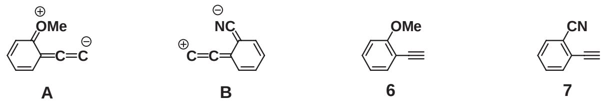

Chart 1.

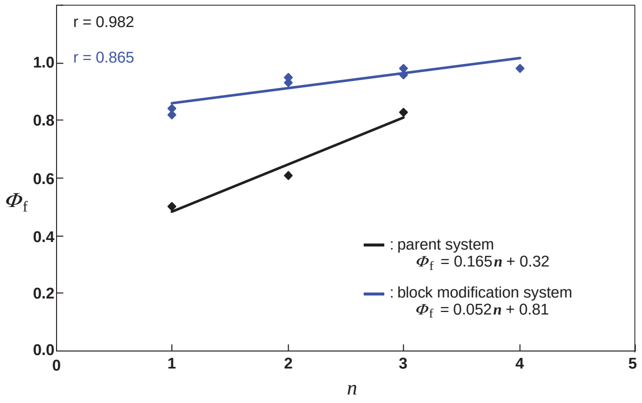

Figure 3. The relationship between quantum yield (Φ_f) and the movability (number, *n*) of the dipolar structure unit.

and **BL-8** ($n = (l + m) - 1 = 4$). This is ascribable to the increase in k_r value and decrease in k_d value as shown in Table 1. The Stokes shift also increases by the block modification.

Although the parent system (**PR-1**–**PR-3**) only emits in the UV region, this disadvantage was surmounted by the block modification. Thus, the block modification is highly effective not only for the bathochromic shift of λ_{em}, but also for the increase in the emission efficiency, leading to creation of the highly efficient light-emitters in the longer wavelength region (e.g., $\Phi_f = 0.98$, $\lambda_{em} = 464$ nm for **BL-8**, $\Phi_f = 0.96$, $\lambda_{em} = 455$ nm for **BL-5**) (see the Electronic Supporting Information).[7]

In regard to the relation between Φ_f and intramolecular exciton, we previously proposed a concept[1b] that the emission efficiency (Φ_f) depends on the movability of the energetically equivalent dipolar structure unit (so-called intramolecular exciton) in the excited singlet state shown by **A** and **B** in the present case (Chart 1).

To establish this concept, we examined the relationship between the light-emitting efficiency (Φ_f) and the movability of the dipolar structures (**A** and **B**). Consequently, we found[5] that Φ_f values linearly increase with an increase in n as shown in Figure 3. It is worth noting that a linear correlation is seen between Φ_f and n, because this is a first successful example of the quantification of contribution of intramolecular exciton to Φ_f.

The energy migration[6] between different excitons (**A** and **B**) in the block modification system is ascribed to their energetic equivalence as indicated by the overlap of fluorescence and absorption spectra of **6** and **7** (see the Electronic Supporting Information).[7] The high intercept values (0.81) for the block modification system imply that the block modification is effective for creation of light-emitters with high emission efficiency even if n is small. A linear relationship was also found between λ_{em} (or λ_{abs}) and n as expected (see the Electronic Supporting Information).[7]

In conclusion, we synthesized novel rod-shaped oligophenylene ethynylenes modified by donor and acceptor groups in a block manner (**BL-1**–**BL-8**), and disclosed their light-emitting characteristics. It is worth noting that the quantum yield (Φ_f) increases linearly with the movability of the energetically equivalent dipolar structure unit (intramolecular exciton). Furthermore, it is demonstrated that the block modification is highly effective for the improvement of light-emitting characteristics (increase in Φ_f and the bathochromic shift of λ_{em} and λ_{abs}).

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References and Notes

1 a) Y. Yamaguchi, T. Ochi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *Org. Lett.* **2006**, *8*, 717. b) Y. Yamaguchi, S. Kobayashi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *Angew. Chem., Int. Ed.* **2005**, *44*, 7040. c) Y. Yamaguchi, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara, Z. Yoshida, *J. Am. Chem. Soc.* **2005**, *127*, 9332. d) J. N. Wilson, U. H. F. Bunz, *J. Am. Chem. Soc.* **2005**, *127*, 4124. e) J. A. Marsden, J. J. Miller, L. D. Shircliff, M. M. Haley, *J. Am. Chem. Soc.* **2005**, *127*, 2464. f) J. N. Wilson, P. M. Windscherf, U. Evans, M. L. Myrick, U. H. F. Bunz, *Macromolecules* **2002**, *35*, 8681. g) K. Koishi, T. Ikeda, K. Kondo, T. Sakaguchi, K. Kamada, K. Tawa, K. Ohta, *Macromol. Chem. Phys.* **2000**, *201*, 525. h) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791. i) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321. j) M. Biswas, P. Nguyen, T. B. Marder, L. R. Khundkar, *J. Phys. Chem. A* **1997**, *101*, 1689.

2 a) E. E. Nesterov, Z. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **2005**, *127*, 10083. b) J. G. Müller, J. M. Lupton, J. Feldmann, U. Lemmer, U. Scherf, *Appl. Phys. Lett.* **2004**, *84*, 1183. c) J. G. Müller, U. Lemmer, G. Raschke, M. Anni, U. Scherf, J. M. Lupton, J. Feldmann, *Phys. Rev. Lett.* **2003**, *91*, 267403. d) Q. Zhou, T. M. Swager, *J. Am. Chem. Soc.* **1995**, *117*, 12593.

3 K. Sonogashira, *Comprehensive Organic Synthesis*, ed. by B. M. Trost, I. Fleming, Pergamon, Oxford, **1991**, Vol. 3, p. 521.

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

5 The lower ($\Phi_f = 0$) and upper ($\Phi_f = 1$) limit of quantum yield should be taken into consideration for the application of linear relationship between Φ_f and *n*.

6 a) M. I. Sluch, A. Godt, U. H. F. Bunz, M. A. Berg, *J. Am. Chem. Soc.* **2001**, *123*, 6447. b) N. P. Balsara, L. J. Fetters, N. Hadjichristidis, D. J. Lohse, C. C. Han, W. W. Graessley, R. Krishnamoorti, *Bull. Chem. Soc. Jpn.* **1999**, *32*, 6137.

7 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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