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** ($\Phi_{\rm f} = 0.96$, $\lambda_{\rm em} = 455 \,\rm nm$ in CHCl₃) and **BL-8** ($\Phi_{\rm f} = 0.98$, $\lambda_{\rm em} = 464 \,\rm nm$ in CHCl₃) are created by block modification of oligophenylene ethynylenes with donor and acceptor groups. A linear relationship with positive slope between $\Phi_{\rm f}$ 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 exciton²) 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 reaction³ 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 ¹³C 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



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).

emission lifetime (τ) are summarized in Table 1. The k_r and k_d were calculated from τ and Φ_f .⁴

As shown in Table 1, it is demonstrated that the $\Phi_{\rm f}$ and $\lambda_{\rm em}$ values increase effectively by the block modification, though $\Phi_{\rm f}$ values increase essentially with the π -conjugation length even for the parent system. Thus, very high $\Phi_{\rm f}$ 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

Com- pound	n	${\pmb{\varPhi}_{\mathrm{f}}}^{\mathrm{b}}$	$\lambda_{\rm em}$ /nm	Stokes shift/nm	$\log \mathcal{E}$	λ_{abs} /nm	τ /ns	$k_{\rm r}$ $/{ m s}^{-1}$	$k_{\rm d}$ $/{ m s}^{-1}$
BL-1	1	0.82	403	45	4.61	358	2.45	$3.34 imes 10^8$	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

^aAll spectra were measured at 295 K. ^bQuantum yield is calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H₂SO₄).



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 $\lambda_{\rm em}$, 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., $\Phi_{\rm f} = 0.98$, $\lambda_{\rm em} = 464$ nm for **BL-8**, $\Phi_{\rm f} = 0.96$, $\lambda_{\rm em} =$ 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 found⁵ 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 migration⁶ 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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- 7 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.