Block modification of rod-shaped π conjugated carbon frameworks with donor and acceptor groups toward highly fluorescent molecules: synthesis and emission characteristics†

Takanori Ochi, Yoshihiro Yamaguchi,* Tateaki Wakamiya, Yoshio Matsubara and Zen-ichi Yoshida*

Received 19th November 2007, Accepted 17th January 2008
First published as an Advance Article on the web 27th February 2008
DOI: 10.1039/b717832h

To create organic molecules that are highly fluorescent at a longer wavelength region, we investigated the synthesis (using Pd-catalyzed cross-coupling) and photophysical properties (Φ_f, λ_{em}, τ, λ_{abs}, and ε) of the following π conjugated molecular rods consisting of *p*-phenyleneethynylene units modified by donor (OMe) and/or acceptor (CN) groups: (1) side-donor modification systems (SD systems), (2) side-acceptor modification systems (SA systems), and (3) systems consisting of a donor block and an acceptor block (BL systems). As a consequence, very high Φ_f values (>0.95) were obtained for BL systems. Bathochromic shifts of λ_{em} for the same π conjugation length were largest for BL systems. Thus we succeeded in creating highly efficient light emitters at a longer wavelength region by block modification (*e.g.*, $\Phi_f = 0.97$, $\lambda_{em} = 464$ nm for **BL-9**). Considerably intense solid emission ($\Phi_f \sim 0.5$) at a longer wavelength region (500–560 nm) was also found for BL systems. It has been found that **BL-6** and **BL-8** exhibit interesting two photon absorption characteristics.

Introduction

Recent progress in biological,[1] chemical,[2] and materials[3] science utilizing organic fluorescent materials has resulted in a great need for highly efficient fluorophores. However, general concepts or methods for the creation of highly fluorescent materials at the desired wavelength regions have not yet been established, even though various attempts at achieving this goal have been made.[4] Thus the development of methods for the creation of highly fluorescent materials should be an urgent and significant subject. For this purpose we considered π conjugated molecular rods consisting of *p*-phenyleneethynylene units, because a marked increase in both the emission efficiency and emission wavelength should be expected by side modification with appropriate groups. Here, we report the synthesis and fluorescence emission characteristics of the following rod-shaped π conjugated carbon frameworks modified by donor and acceptor groups: (1) side-donor modification systems (**SD** systems),[5] (2) side-acceptor modification systems (**SA** systems),[4a] and (3) side-donor and acceptor modification systems of block type (**BL** systems),[6] which are outlined in Chart 1.

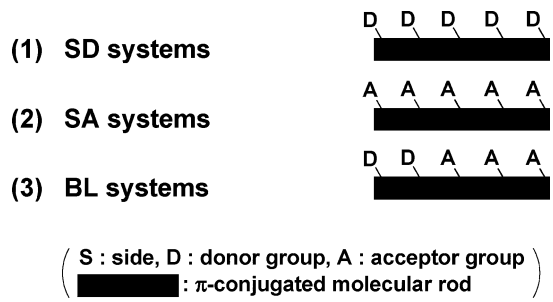


Chart 1

Results and discussion

Molecular design and synthesis

With regard to the π-conjugated backbone of **SD**, **SA**, and **BL** systems, we considered oligophenyleneethynylenes that contain two to six benzene rings respectively, as shown in Fig. 1. As for the side modification groups, a methoxy (MeO) group was selected as an electron donating group, and a cyano (CN) group as an electron withdrawing group, because of their stability to the various synthetic processes employed and the photostability of the final products.

The synthesis of the oligophenyleneethynylenes was carried out by repeating the Sonogashira cross-coupling reaction,[7] in which the reactivity difference between iodine and bromine on the same benzene ring is key to obtaining the desired arrangement of the donor and acceptor units. The combination of $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N–THF was appropriate as the catalytic system for synthesis of the **SD**, **SA**, and **BL** systems.

The synthesis of **SD** systems is shown in Scheme 1. Firstly, five kinds of donor units (**1–5**) were prepared. **SD-1** and **SD-2**, containing two and three benzene rings, were synthesized by the cross-coupling of 2-iodoanisole with donor units **2** and **4**, respectively. **SD-3**, containing four benzene rings, was obtained in good yields by the same procedure using **5** as a donor unit. Donor unit **5** was reacted at the more reactive iodo-substituted position of 5-bromo-2-iodoanisole to give **6**, followed by a second

Department of Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan. E-mail: yamaguch@chem.kindai.ac.jp, yoshida@chem.kindai.ac.jp; Fax: +81 6 6723 2721; Tel: +81 6 6721 2332

† Electronic Supplementary Information (ESI) available: Synthetic routes to donor units (**1–3** and **9–11**) and acceptor units (**4**, **5**, and **13**), UV–vis and fluorescence spectra for **BL** systems, and typical Z-scan traces of **BL-6** and **BL-8**. See DOI: 10.1039/b717832h

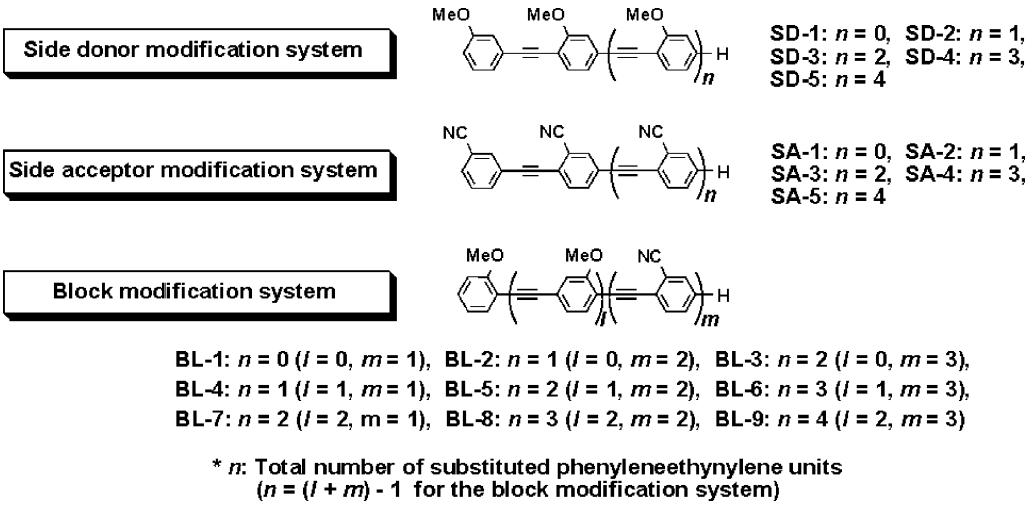
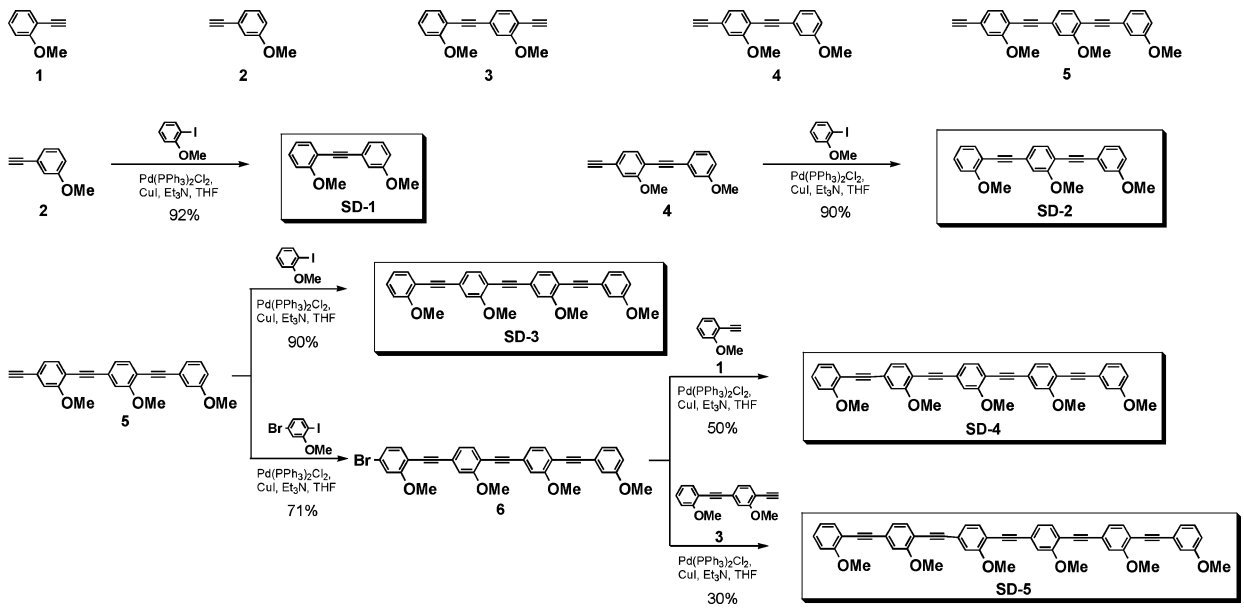


Fig. 1 Structures of side-donor- and/or acceptor-modified phenyleneethynylene molecular rods.



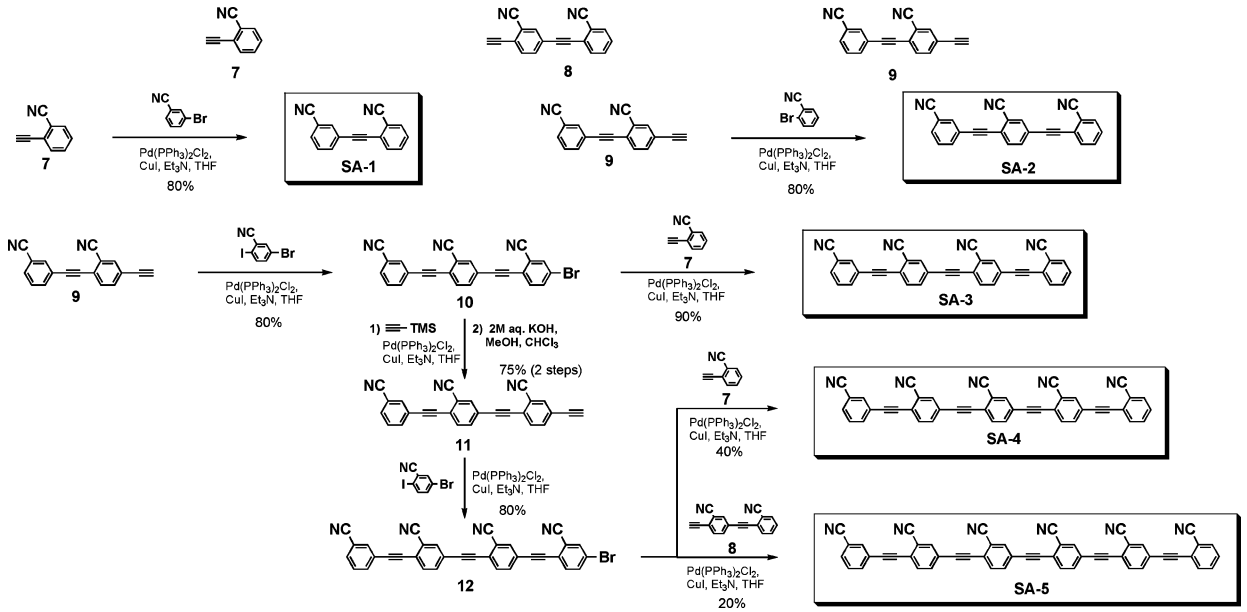
Scheme 1 Synthesis of **SD** systems.

cross-coupling with donor units **1** and **3** at the remaining bromo-substituted position, providing **SD-4** and **SD-5**, respectively.

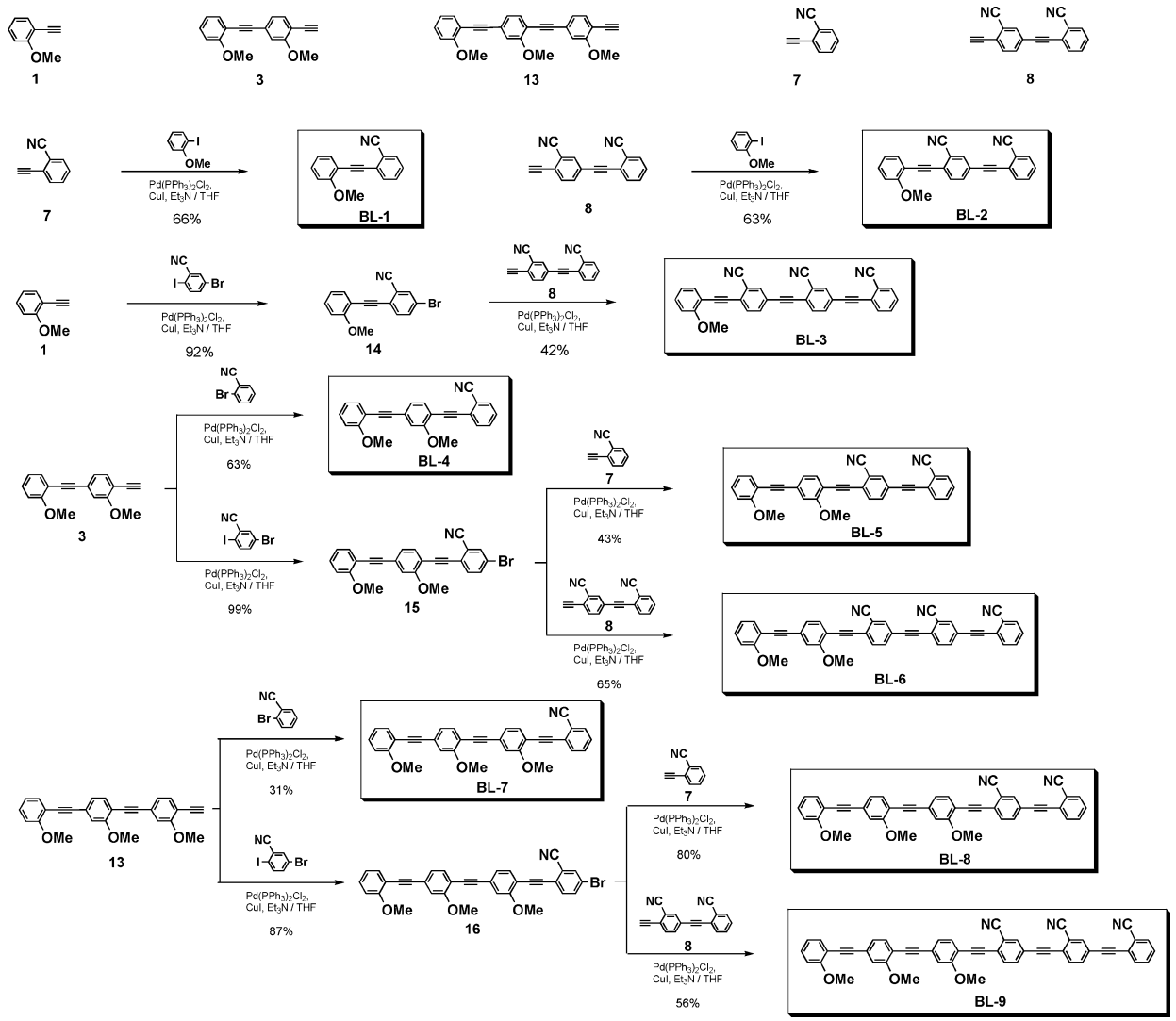
The synthesis of **SA** systems is shown in Scheme 2. **SA-1**, containing two benzene rings, was synthesized by the cross-coupling of acceptor unit **7** with 3-bromobenzonitrile. Synthesis of **SA-2**, containing three benzene rings, was realized by the cross-coupling of acceptor unit **9** with 2-bromobenzonitrile. Acceptor unit **9** was first reacted at the more reactive iodo-substituted position of 5-bromo-2-iodobenzonitrile to give **10**, followed by a second cross-coupling with acceptor unit **7** at the remaining bromo-substituted position, providing **SA-3**. The bromo-derivative **10** was converted into the new acceptor unit **11** by cross-coupling with trimethylsilylacetylene, followed by alkaline hydrolysis. Then **11** was coupled at the more reactive iodo-substituted position of 5-bromo-2-iodobenzonitrile to give **12**, followed by a second cross-coupling with acceptor units **7** and **8** at the remaining bromo-substituted position, providing **SA-4** and **SA-5**, respectively.

Block modification systems (**BL-1**–**BL-9**) were synthesized by way of (1) preparation of donor units (**1**, **3**, and **13**), (2) preparation of acceptor units (**7** and **8**), and (3) cross-coupling between donor units and acceptor units, utilizing the reactivity difference between aryl iodides and aryl bromides as shown in Scheme 3. **BL-1** and **BL-2**, containing two and three benzene rings, were synthesized by the cross-coupling of acceptor units **7** and **8** with 2-iodoanisole, respectively. **BL-4** and **BL-7**, containing three and four benzene rings, were synthesized by the cross-coupling of 2-bromobenzonitrile with donor units **3** and **13**, respectively. Donor units **1**, **3**, and **13** were reacted at the more reactive iodo-substituted position of 5-bromo-2-iodobenzonitrile to give **14**, **15**, and **16**, followed by a second cross-coupling with acceptor units **7** and **8** at the remaining bromo-substituted position, providing **BL-3**, **BL-5**, **BL-6**, **BL-8**, and **BL-9**, respectively.

The structures of **SD**, **SA**, and **BL** systems were confirmed by spectral data (^{1}H and ^{13}C NMR spectroscopy and HR-FAB MS).[8]



Scheme 2 Synthesis of **SA** systems.



Scheme 3 Synthesis of **BL** systems.

Photophysical properties

The photophysical properties of **SD**, **SA**, and **BL** systems and the parent systems (**PR**)[9] are summarized in Table 1. So far we have reported[4a–e] the fluorescence quantum yield values using quinine sulfate as the fluorescence standard and the lifetime (τ) values obtained from the absorption spectra (ε). Strictly speaking, the emission characteristics should be discussed on the basis of the absolute quantum yield (Φ_f) values and the directly measured lifetime (τ) values, which are shown in Table 1.

Measurement of τ values was made for the efficiently fluorescent compounds (n: 2–4, $\Phi_f > ca.$ 0.9) in each system. This is because our particular attention is focused on the emission characteristics of highly efficient fluorophores at longer wavelength regions. From τ values and Φ_f values in Table 1, it is shown that the emission is typical fluorescence, and the intersystem crossing (ISC) to the triplet state is negligible for the compounds ($n \geq 2$). It is worth noting that the emission characteristics, in particular the quantum yield of **SD**, **SA**, **BL** and **PR**, change strikingly between the $n = 0$ and $n = 1$ systems, suggesting that diphenylacetylenes ($n = 0$) have different π systems from oligophenyleneethynylenes ($n \geq 1$) with respect to emission characteristics. A similar phenomenon is observed for *trans*-stilbene (Φ_f 0.04, $n = 0$) and *p*-distyrylbenzene (Φ_f 0.87, $n = 1$) by Saltiel *et al.*[10] and Sandros *et al.*[11] Interestingly, while Φ_f values essentially increase with the π conjugation length of the parent systems, donor/acceptor modification also effectively increases the Φ_f values. Thus very high Φ_f values (>0.95) are observed for donor/acceptor modification systems such as **SD-4** ($n = 3$), **SD-5** ($n = 4$), **SA-5** ($n = 4$), **BL-3** ($n = 2$), **BL-7** ($n = 2$), **BL-8** ($n = 3$), and **BL-9** ($n = 4$).

Although the parent systems (**PR-1**–**PR-4**) only emit in the UV region, this problem was overcome by donor and/or acceptor modification. Among them, the block modification was most effective for the bathochromic shift of the fluorescence maximum (λ_{em}) for the same π conjugation length (for example, in the case of $n = 2$: **BL-5** (434 nm) > **BL-3** (419 nm) > **BL-7** (407 nm) > **SD-3** (397 nm) > **PR-3** (389 nm) > **SA-3** (388 nm)). Thus we succeeded in the creation of highly efficient light-emitters in a longer wavelength region, by the block modification of the longer π conjugated backbones (*e.g.*, $\Phi_f = 0.97$, $\lambda_{em} = 464$ nm for **BL-9** ($n = 4$) and $\Phi_f = 0.94$, $\lambda_{em} = 455$ nm for **BL-6** ($n = 3$), see Fig. 2). The superiority in emission wavelength of **BL-9** and **BL-6** over others can be explained by the smallest HOMO–LUMO gap (Table 2) and the biggest Stokes shift (Table 1). It should be noted that **BL-9** and **BL-6** have such high Φ_f values (close to unity) despite having possible decreases in Φ_f values due to the twisted intramolecular charge transfer (TICT), which is well known for donor/acceptor-substituted π conjugated systems.[12]

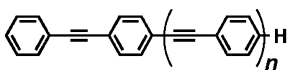
We examined the solvent effect on the photophysical properties of **BL-6** and **BL-8**. The results are summarized in Table 3. It is noted that an increase in solvent polarity does not appreciably affect λ_{abs}, but considerably affects λ_{em} (increases) and Φ_f (decreases) for **BL-6** and **BL-8**.

Interestingly λ_{em} for **BL** systems in the solid state was remarkably shifted to longer wavelengths. On the other hand, the Φ_f value

Table 1 The photophysical properties of **SD**, **SA**, and **BL** systems and the parent systems (**PR**) in chloroform[a]

Compound	n	Φ_f [b]	τ/ns	λ_{em}/nm	logε	λ_{abs}/nm	Stokes shift/nm
SD-1	0	0.23		331	4.31	311	20
SD-2	1	0.83		371	4.65	344	27
SD-3	2	0.94	4.14	397	4.75	360	37
SD-4	3	0.96	5.43	412	4.95	371	41
SD-5	4	0.97	4.55	420	5.13	380	40
SA-1	0	0.35		328	4.32	317	11
SA-2	1	0.83		363	4.69	339	24
SA-3	2	0.88	5.70	388	4.89	354	34
SA-4	3	0.90	4.59	402	4.94	371	31
SA-5	4	0.95	6.17	410	5.14	373	37
BL-1	0	0.44		374	4.40	326	47
BL-2	1	0.86		403	4.61	358	45
BL-3	2	0.95	4.93	419	4.87	370	49
BL-4	1	0.84		392	4.66	352	40
BL-5	2	0.93	5.36	434	4.81	380	54
BL-6	3	0.94	5.02	455	4.92	386	69
BL-7	2	0.95	4.73	407	4.90	365	42
BL-8	3	0.95	5.51	443	4.96	387	56
BL-9	4	0.97	5.31	464	4.99	392	72
PR-1	0	0.01		320	4.41	299	21
PR-2	1	0.83		348	4.59	328	20
PR-3	2	0.87	6.01	389	4.77	343	46
PR-4	3	0.93	6.29	389	5.13	354	35

[a] All spectra were measured at 295 K. [b] Absolute quantum yield (Φ_f) values were determined with a Hamamatsu C9920-01 calibrated integrating sphere system. [c] Parent systems (**PR**):



PR-1: *n* = 0, PR-3: *n* = 2
PR-2: *n* = 1, PR-4: *n* = 3

Table 2 HOMO–LUMO gaps of **BL** systems calculated by the DFT method

		Calcd (DFT and TD-DFT)		
Compound	*n*	HOMO/eV	LUMO/eV	HOMO–LUMO gap/eV
BL-1	0	−6.79	−0.75	6.04
BL-2	1	−6.73	−1.44	5.30
BL-3	2	−6.72	−1.80	4.92
BL-4	1	−6.36	−0.98	5.38
BL-5	2	−6.37	−1.49	4.88
BL-6	3	−6.37	−1.81	4.56
BL-7	2	−6.17	−1.09	5.08
BL-8	3	−6.18	−1.51	4.67
BL-9	4	−6.19	−1.80	4.38

[a] Functional: BHandHLYP. Basis set: cc-pVDZ.

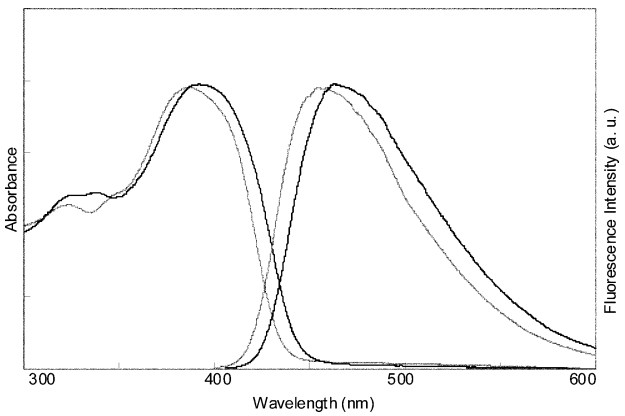


Fig. 2 Absorption (left) and fluorescence (right) spectra of **BL-6** (grey) and **BL-9** (black) in chloroform.

Table 3 Effect of solvent on absorption and fluorescence spectra of **BL-6** and **BL-8**[a]

Compound	Solvent	Φ_f [b]	λ_{em}/nm	logε	λ_{abs}/nm
BL-6	Benzene	0.99	437	4.86	388
	THF	0.88	459	4.90	383
	CH_3CN	0.67	482	4.91	375
	DMF	0.61	493	4.85	379
BL-8	Benzene	0.99	432	4.89	387
	THF	0.95	446	4.92	385
	CH_3CN	0.83	464	4.91	384
	DMF	0.72	468	4.85	379

[a] All spectra were measured at 295 K. [b] For examination of solvent effect on quantum yield, we calculated the quantum yield relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4)

tends to decrease compared with that for systems in solution. However, it is noted that **BL-3**, **BL-4**, **BL-6** and **BL-8** are still intense ($\Phi_f > 0.5$) fluorophores even in the solid state (Table 4). The design and synthesis of highly emissive organic materials that can fluoresce even in the solid state is a fundamental and important requirement for various optoelectronic applications, such as two photon absorption (TPA), two photon fluorescence, blue-emitting electroluminescence, and organic thin film transistor (TFT).[13] In particular, with respect to the TPA of π conjugated molecular rods consisting of *p*-phenyleneethynylene units, only a few papers appear in the literature[14] in contrast with that of

Table 4 The photophysical properties of BL systems in chloroform solution and in the solid state[a]

Compound		Φ_f [b]	λ_{em}/nm	$\Delta\lambda_{em}$/nm [c]
BL-1	$CHCl_3$	0.44	374	4
	Solid	0.02	378	
BL-2	$CHCl_3$	0.86	403	74
	Solid	0.02	477	
BL-3	$CHCl_3$	0.95	419	80
	Solid	0.51	499	
BL-4	$CHCl_3$	0.84	392	123
	Solid	0.49	515	
BL-5	$CHCl_3$	0.93	434	93
	Solid	0.16	527	
BL-6	$CHCl_3$	0.94	455	107
	Solid	0.48	562	
BL-7	$CHCl_3$	0.95	407	105
	Solid	0.33	512	
BL-8	$CHCl_3$	0.95	443	89
	Solid	0.46	532	
BL-9	$CHCl_3$	0.97	464	121
	Solid	0.11	585	

[a] All spectra were measured at 295 K. [b] Absolute quantum yield (Φ_f) values were determined with a Hamamatsu C9920-01 calibrated integrating sphere system. [c] $\Delta\lambda_{em}$/nm = λ_{em} (Solid) − λ_{em} ($CHCl_3$).

p-phenylenevinylene units.[15] Thus we have investigated the TPA for **BL-6** and **BL-8**.

As shown in Fig. 3, we have found that **BL-6** and **BL-8** exhibit an interesting two photon absorption. The real TPA maximum peak for **BL-6** and **BL-8** appeared at 760 nm (13 157 cm^{-1}) with values

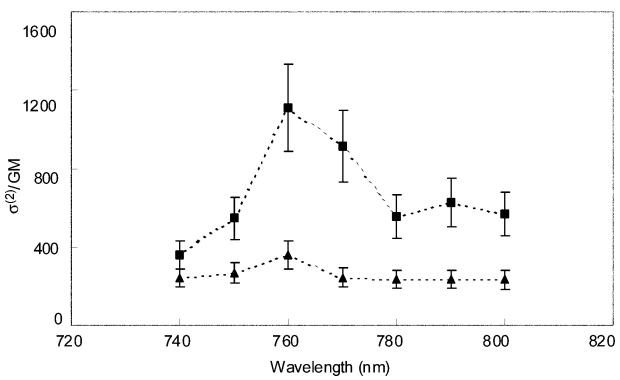


Fig. 3 Two photon absorption spectra of **BL-6** (squares) and **BL-8** (triangles) in pyridine (7 mM).

of 1108 ± 222 GM and 357 ± 71 GM respectively. The effective $\sigma^{(2)}$ values obtained herein are clearly large compared with those of other donor/acceptor π conjugated systems (1.3–116 GM)[16] and *meso*-tetraphenylporphyrin (H_2TPP) (29 GM)[17] obtained by using the same nanosecond pulses. Therefore, **BL** systems could also be valuable for wavelength convertors.

Conclusions

In conclusion, we synthesized many novel π conjugated molecular rods modified by donor and/or acceptor groups (**SD-1–SD-5**, **SA-1–SA-5**, and **BL-1–BL-9**) by devising reaction conditions, and disclosed their fluorescence emission characteristics in solution and in solid form. Consequently, it has been demonstrated that the block modification is most effective for the enhancement of fluorescence emission characteristics (increases in Φ_f, and the bathochromic shift of λ_{em}) of rod-shaped π conjugated carbon frameworks. Considerably intense emissions ($\Phi_f \sim 0.5$) in a longer wavelength region (500–560 nm) were observed from solids. It is worth noting that very interesting two photon absorption characteristics have been found for **BL** systems.

Experimental

General

UV–vis absorption spectra and fluorescence spectra measurements in spectral grade solvents were performed with a Shimadzu UV-3100PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Absolute quantum yields (Φ_f) were determined by the Hamamatsu C9920-01 calibrated integrating sphere system. Time-resolved fluorescence spectra were measured by a Photon Technology International GL-3300 with a Photon Technology International GL-302 and a nitrogen laser–pumped dye laser system equipped with a four-channel digital delay–pulse generator (Stanford Research Systems Inc. DG535) and a motor driver (Photon Technology International MD-5020). The excitation wavelength was 337 nm from a nitrogen laser without laser dye. The fluorescence lifetimes τ were fitted by a single-exponential curve using a microcomputer. 10-Methylacridinium perchlorate, newly prepared, was used to check the reliability of the measured τ value.[18] To avoid oxygen quenching, the bubbling of argon in the solution and/or the freeze–pump–thaw were performed immediately before the measurement of Φ_f and τ. The effective TPA cross sections $\sigma^{(2)}$ of 7.0 mM solutions of **BL-6** and **BL-8** in pyridine were determined by single-beam, open-aperture Z-scan measurements, conducted by using an optical parametric oscillator (Continuum Surelight OPO) pumped with a Q-switched Nd:YAG laser (Continuum Surelight I-10), frequency tripled ($\lambda = 355$ nm) from the fundamental wavelength of 1064 nm to give 5 ns pulses (FWHM) with a repetition rate of 10 Hz. The laser intensities were attenuated with a filter to give a peak power of 24 GW cm^{-2}. The laser beam was focused by using a plano-convex lens with a focal length of 100 nm. The samples were placed in a 2 mm quartz cuvette and scanned at a range of 60 mm around the focal point. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer in $CDCl_3$ (300 MHz for ^1H, 75 MHz for ^{13}C). The method for the determination of the molecular formula from a HR MS spectrum is described in the literature.[19] Needless to say, our HR MS data are based on the results obtained by the analysis of molecular ion peaks observed in the LR MS spectra. Thin layer chromatography (TLC) was performed on aluminium plates precoated with 0.25 mm thick silica-gel 60 F_{254} (Merck). Column chromatography was performed using silica gel (PSQ 100B, Fuji Silysia).

Synthetic procedures

General procedure for the Sonogashira cross-coupling reaction. A Schlenk flask charged with the halogen-derivative (1.0 equiv.), $Pd(Ph_3P)_2Cl_2$ (0.1 equiv.) and CuI (0.05 equiv.) was evacuated and back-filled with Ar three times. Then dry Et_3N and THF (2 : 1, v/v) was added to the flask. The mixture was stirred under an Ar atmosphere at ambient temperature, then a solution of the acetylene-derivative (1.2 equiv.) in dry THF was added slowly. The reaction mixtures were stirred or refluxed under an Ar atmosphere. The reaction was monitored by TLC. After the reaction was complete, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography followed by recrystallization.

2-Methoxy-1-[(3-methoxyphenyl)-ethynyl]-benzene (SD-1). By the general procedure the reaction of **2** (243 mg, 1.84 mmol) with 2-iodoanisole (358 mg, 1.53 mmol) was completed after 0.5 h at ambient temperature. The crude product was purified by column chromatography (hexane–benzene, 2 : 1) followed by recrystallization from hexane to provide **SD-1** (335 mg, 92%) as colorless crystals. M.p. 39–40 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.92 (s, 3H), 6.88 (ddd, $J = 1.2$, 2.7, 7.8 Hz, 1H), 6.90 (dd, $J = 1.2$, 8.1 Hz, 1H), 6.95 (dd, $J = 1.5$, 7.5 Hz, 1H), 7.09 (dd, $J = 1.5$, 2.4 Hz, 1H), 7.16 (ddd, $J = 2.4$, 2.7, 7.8 Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.31 (ddd, $J = 1.8$, 7.2, 8.4 Hz, 1H), 7.50 (dd, $J = 1.8$, 7.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.26, 55.80, 85.48, 93.30, 110.63, 114.84, 114.84, 116.23, 120.44, 124.24, 124.47, 129.24, 129.78, 133.56, 159.21, 159.87. HR MS (FAB, positive ion mode) calcd for $C_{16}H_{14}O_2$ 238.0994, found 238.0988.

2-Methoxy-4- [(2-methoxyphenyl)-ethynyl]-1- [(3-methoxyphenyl)ethynyl]-benzene (SD-2). By the general procedure the reaction of **4** (245 mg, 0.93 mmol) with 2-iodoanisole (183 mg, 0.78 mmol) was completed after 1 h at ambient temperature. The crude product was purified by column chromatography (hexane–benzene, 1 : 1) to provide **SD-2** (258 mg, 90%) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 6.89 (dd, $J = 1.2$, 2.7, 8.1 Hz, 1H), 6.91 (d, $J = 8.7$ Hz, 1H), 6.95 (ddd, $J = 1.2$, 7.2, 7.2 Hz, 1H), 7.09 (m, 2H), 7.16 (ddd, $J = 1.5$, 2.4, 7.2 Hz, 2H), 7.25 (dd, $J = 7.5$, 7.8 Hz, 1H), 7.33 (ddd, $J = 1.8$, 7.5, 8.4 Hz, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.51 (dd, $J = 1.5$, 7.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.28, 55.82, 55.94, 85.39, 87.39, 93.21, 94.85, 110.65, 112.03, 112.47, 113.58, 115.02, 116.24, 120.51, 124.09, 124.26, 124.31, 124.69, 129.30, 130.05, 133.27, 133.60, 159.25, 159.51, 159.92. HR MS (FAB, positive ion mode) calcd for $C_{25}H_{20}O_3$ 368.1412, found 368.1421.

2-Methoxy-4- [[2-methoxy-4- [(2-methoxyphenyl)-ethynyl]-phenyl]-ethynyl]-1-[(3-methoxyphenyl)-ethynyl]-benzene (SD-3). By the general procedure the reaction of **5** (478 mg, 1.22 mmol) with 2-iodoanisole (236 mg, 1.01 mmol) was completed after 1 h at ambient temperature. The crude product was purified by column chromatography (hexane–benzene, 1 : 2) followed by recrystalliza-

tion from hexane–benzene to provide **SD-3** (455 mg, 90%) as pale yellow crystals. M.p. 151–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 3.96 (s, 3H), 6.89 (ddd, J = 1.2, 2.7, 8.1 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.96 (ddd, J = 1.2, 7.5, 7.5 Hz, 1H), 7.08 (d, J = 1.5 Hz, 1H), 7.09 (d, J = 1.5 Hz, 2H), 7.16 (dd, J = 1.5, 8.1 Hz, 1H), 7.16 (ddd, J = 1.5, 1.5, 7.8 Hz, 1H), 7.26 (dd, J = 7.8, 7.8 Hz, 2H), 7.34 (ddd, J = 1.8, 7.5, 8.1 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.51 (dd, J = 1.8, 7.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.29, 55.83, 55.96, 55.96, 85.37, 87.28, 87.61, 93.15, 94.74, 94.98, 110.65, 111.98, 112.17, 112.66, 113.55, 114.19, 115.05, 116.24, 120.52, 124.09, 124.13, 124.28, 124.47, 124.98, 129.31, 130.11, 133.30, 133.45, 133.61, 133.61, 159.25, 159.51, 159.51, 159.93. HR MS (FAB, positive ion mode) calcd for $C_{34}H_{26}O_4$ 498.1831, found 498.1826.

2-Methoxy-4-[[2-methoxy-4-[[2-methoxy-4-[(2-methoxyphenyl)-ethynyl]- phenyl]-ethynyl]- phenyl]-ethynyl]-1- [(3-methoxyphenyl)-ethynyl]-benzene (SD-4). The reaction of **5** (825 mg, 2.10 mmol) with 5-bromo-2-iodoanisole (543 mg, 1.74 mmol) for 1 h at ambient temperature provided bromide **6** (711 mg, 1.23 mmol, 71%). By the general procedure the reaction of **1** (65 mg, 0.49 mmol) with the obtained bromide **6** (237 mg, 0.41 mmol) was completed after 12 h under reflux. The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **SD-4** (128 mg, 50%) as yellow crystals. M.p. 212–213 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 3.96 (s, 6H), 6.89 (ddd, J = 1.2, 2.4, 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.96 (ddd, J = 1.2, 7.8, 7.8 Hz, 1H), 7.08 (d, J = 1.5 Hz, 1H), 7.09 (d, J = 1.5 Hz, 1H), 7.10 (d, J = 1.8 Hz, 2H), 7.16 (dd, J = 1.5, 7.8 Hz, 1H), 7.15–7.19 (m, 3H), 7.26 (dd, J = 7.8, 7.8 Hz, 1H), 7.34 (ddd, J = 1.8, 7.8, 8.4 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.51 (dd, J = 1.8, 7.8 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.30, 55.84, 55.98, 55.98, 55.98, 85.37, 87.26, 87.51, 87.66, 93.15, 94.68, 94.87, 95.00, 110.66, 111.98, 112.12, 112.36, 112.69, 113.56, 113.56, 113.56, 115.07, 116.26, 120.53, 124.11, 124.15, 124.15, 124.28, 124.28, 124.46, 124.78, 125.05, 129.31, 130.13, 133.32, 133.32, 133.62, 133.62, 159.26, 159.54, 159.54, 159.54, 159.94. HR MS (FAB, positive ion mode) calcd for $C_{43}H_{32}O_5$ 628.2250, found 628.2246.

2-Methoxy-4-[[2-methoxy-4-[[2-methoxy-4- [[2-methoxy-4-[(2-methoxyphenyl)- ethynyl]-phenyl]- ethynyl]-phenyl]- ethynyl]-phenyl]-ethynyl]-1-[(3-methoxyphenyl)-ethynyl]-benzene (SD-5). By the general procedure the reaction of **3** (210 mg, 0.80 mmol) with bromide **6** (386 mg, 0.67 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene–EtOAc, 9 : 1) followed by recrystallization from benzene–chloroform to provide **SD-5** (152 mg, 30%) as yellow crystals. M.p. 257–258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 3.96 (s, 9H), 6.90 (ddd, J = 1.2, 2.7, 8.1 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.96 (ddd, J = 1.2, 7.8, 7.8 Hz, 1H), 7.08 (d, J = 1.2 Hz, 1H), 7.10 (bs, 4H), 7.16 (dd, J = 1.2, 7.8 Hz, 1H), 7.15–7.20 (m, 4H), 7.26 (dd, J = 7.8, 7.8 Hz, 1H), 7.34 (ddd, J = 2.1, 7.8, 8.4 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.51 (dd, J = 1.5, 7.5 Hz, 1H), 7.55 (dd, J = 2.1, 5.7 Hz, 1H). HR MS (FAB, positive ion mode) calcd for $C_{52}H_{38}O_6$ 758.2668, found 758.2676.

2-[(3-Cyanophenyl)-ethynyl]-benzonitrile (SA-1). By the general procedure the reaction of **7** (219 mg, 1.72 mmol) with 3-bromobenzonitrile (260 mg, 1.43 mmol) was completed after 12 h under reflux. The crude product was purified by column chromatography (benzene) followed by recrystallization from hexane–benzene to provide **SA-1** (261 mg, 80%) as colorless crystals. M.p. 117–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (ddd, J = 1.5, 6.9, 7.5 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.62 (dd, J = 1.2, 7.5 Hz, 1H), 7.65 (s, 1H), 7.67 (m, 1H), 7.73 (bd, J = 7.5 Hz, 1H), 7.84 (ddd, J = 1.5, 1.5, 7.8 Hz, 1H), 7.88 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 87.61, 93.02, 113.04, 117.30, 117.82, 123.63, 126.14, 129.01, 129.44, 132.25, 132.33, 132.53, 132.74, 133.68, 135.07, 136.04. HR MS (FAB, positive ion mode) calcd for $C_{16}H_8N_2$ 228.0687, found 228.0665.

5-[(2-Cyanophenyl)-ethynyl]-2-[(3-cyanophenyl)-ethynyl]-benzonitrile (SA-2). By the general procedure the reaction of **9** (359 mg, 1.42 mmol) with 2-bromobenzonitrile (215 mg, 1.18 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **SA-2** (335 mg, 80%) as colorless crystals. M.p. 196–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (ddd, J = 1.5, 6.9, 7.8 Hz, 1H), 7.53 (dd, J = 7.8, 7.8 Hz, 1H), 7.62 (dd, J = 1.2, 7.8 Hz, 1H), 7.65 (s, 1H), 7.67 (s, 1H), 7.69 (ddd, J = 1.5, 1.5, 8.1 Hz, 1H), 7.73 (bd, J = 8.1 Hz, 1H), 7.83 (dd, J = 1.8, 8.4 Hz, 1H), 7.84 (m, 1H), 7.88 (ddd, J = 1.5, 1.5, 8.4 Hz, 1H), 7.92 (bd, J = 1.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 87.40, 89.51, 92.73, 95.20, 113.15, 115.62, 116.09, 116.41, 117.25, 117.75, 123.32, 123.37, 125.90, 126.22, 129.25, 129.52, 132.29, 132.36, 132.59, 132.59, 132.80, 135.15, 135.60, 135.64, 136.11. HR MS (FAB, positive ion mode) calcd for $C_{25}H_{11}N_3$ 353.0953, found 353.0942.

5-[[2-Cyano-4- [(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-2- [(3-cyanophenyl)-ethynyl]-benzonitrile (SA-3). The reaction of **9** (820 mg, 3.25 mmol) with 5-bromo-2-iodobenzonitrile (832 mg, 2.40 mmol) for 1 h at ambient temperature provided bromide **10** (933 mg, 2.16 mmol, 80%). By the general procedure described the reaction of **7** (83 mg, 0.65 mmol) with bromide **10** (233 mg, 0.54 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene–chloroform to provide **SA-3** (233 mg, 90%) as pale yellow crystals. M.p. 284–285 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (ddd, J = 1.5, 6.3, 7.2 Hz, 1H), 7.53 (dd, J = 7.5, 7.5 Hz, 1H), 7.61 (dd, J = 1.5, 7.8 Hz, 1H), 7.66 (m, 2H), 7.68 (m, 1H), 7.69 (ddd, J = 1.5, 1.5, 7.2 Hz, 1H), 7.73 (bd, J = 7.5 Hz, 1H), 7.83 (dd, J = 1.5, 8.4 Hz, 2H), 7.88 (ddd, J = 1.5, 1.5, 8.4 Hz, 1H), 7.90 (bs, 1H), 7.92 (bd, J = 1.5 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 87.38, 89.28, 89.71, 92.69, 94.88, 95.43, 113.17, 115.65, 116.14, 116.37, 117.24, 117.74, 123.01, 123.34, 123.58, 125.86, 125.93, 126.51, 129.29, 129.52, 132.29, 132.39, 132.42, 132.59, 132.59, 132.63, 132.81, 135.16, 135.63, 135.63, 135.68, 135.68, 135.68, 136.13. HR MS (FAB, positive ion mode) calcd for $C_{34}H_{14}N_4$ 478.1219, found 478.1224.

5-[[2-Cyano-4-[[2-cyano-4-[(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-phenyl]-ethynyl]-2-[(3-cyanophenyl)-ethynyl]-benzonitrile (SA-4). The reaction of trimethylsilylacetylene (191 mg, 1.94 mmol) with bromide **10** (700 mg, 1.62 mmol) for 12 h under reflux, followed by alkaline hydrolysis (2 M aq. KOH 2 ml,

MeOH 3 ml, $CHCl_3$ 5 ml) for 1 h at ambient temperature provided **11** (460 mg, 1.22 mmol, 75%). The reaction of **11** with 5-bromo-2-iodobenzonitrile (314 mg, 1.02 mmol) for 1 h at ambient temperature provided bromide **12** (457 mg, 0.82 mmol, 80%). By the general procedure described the reaction of **7** (70 mg, 0.55 mmol) with bromide **12** (256 mg, 0.46 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (chloroform) followed by recrystallization from chloroform to provide **SA-4** (110 mg, 40%) as yellow crystals. M.p. >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (ddd, J = 1.5, 6.3, 7.5 Hz, 1H), 7.53 (dd, J = 7.5, 7.5 Hz, 1H), 7.58–7.63 (m, 1H), 7.66 (bs, 2H), 7.68 (bs, 1H), 7.68 (ddd, J = 1.2, 1.5, 7.5 Hz, 1H), 7.74 (bd, J = 7.2 Hz, 1H), 7.78 (dd, J = 1.5, 7.5 Hz, 1H), 7.82–7.86 (m, 1H), 7.83 (dd, J = 1.2, 8.4 Hz, 2H), 7.89 (ddd, J = 1.2, 1.2, 8.4 Hz, 1H), 7.90 (bs, 1H), 7.93 (bs, 3H). HR MS (FAB, positive ion mode) calcd for $C_{43}H_{17}N_5$ 603.1484, found 603.1489.

5-[[2-Cyano-4-[[2-cyano-4-[[2-cyano-4-[(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-phenyl]-ethynyl]-phenyl]-ethynyl]-2-[(3-cyanophenyl)-ethynyl]-benzonitrile (SA-5). By the general procedure the reaction of **8** (87 mg, 0.35 mmol) with bromide **12** (162 mg, 0.29 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (chloroform) to provide **SA-5** (42 mg, 20%) as a yellow solid. M.p. >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (ddd, J = 1.5, 6.9, 7.5 Hz, 1H), 7.53 (dd, J = 7.5, 7.5 Hz, 1H), 7.58–7.63 (m, 2H), 7.66 (bs, 2H), 7.68 (bs, 1H), 7.68 (ddd, J = 1.5, 1.5, 7.5 Hz, 1H), 7.75 (bd, J = 7.5 Hz, 1H), 7.78 (dd, J = 1.5, 7.5 Hz, 1H), 7.82–7.88 (m, 2H), 7.83 (dd, J = 1.5, 8.4 Hz, 2H), 7.89 (ddd, J = 1.2, 1.2, 8.4 Hz, 1H), 7.90 (bs, 1H), 7.93 (bs, 4H). HR MS (FAB, positive ion mode) calcd for $C_{52}H_{20}N_6$ 728.1749, found 728.1755.

2-[(2-Methoxyphenyl)-ethynyl]-benzonitrile (BL-1). By the general procedure the reaction of **7** (261 mg, 2.05 mmol) with 2-iodoanisole (400 mg, 1.71 mmol) was completed after 0.5 h at ambient temperature. The crude product was purified by column chromatography (hexane–benzene, 2 : 1) followed by recrystallization from EtOH to provide **BL-1** (263 mg, 66%) as colorless crystals. M.p. 82–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 6.92 (d, J = 8.1 Hz, 1H), 6.97 (ddd, J = 1.5, 7.5, 7.5 Hz, 1H), 7.34 (dd, J = 1.8, 7.8 Hz, 1H), 7.38 (ddd, J = 1.5, 7.8, 7.8 Hz, 1H), 7.54 (dd, J = 1.5, 8.1 Hz, 1H), 7.58 (ddd, J = 1.8, 7.5, 7.5 Hz, 1H), 7.65 (ddd, J = 0.9, 1.5, 8.1 Hz, 1H), 7.67 (ddd, J = 0.9, 1.5, 7.8 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.83, 89.51, 92.63, 110.73, 111.32, 115.15, 117.62, 120.52, 127.55, 127.95, 130.79, 132.11, 132.23, 132.62, 133.95, 160.32. HR MS (FAB, positive ion mode) calcd for $C_{16}H_{11}NO$ 233.0841, found 233.0858.

5-[(2-Cyanophenyl)-ethynyl]-2-[(2-methoxyphenyl)-ethynyl]-benzonitrile (BL-2). By the general procedure the reaction of **8** (433 mg, 1.72 mmol) with 2-iodoanisole (335 mg, 1.43 mmol) was completed after 1 h at ambient temperature. The crude product was purified by column chromatography (hexane–benzene, 1 : 1) followed by recrystallization from hexane–benzene (1 : 1) to provide **BL-2** (322 mg, 63%) as colorless crystals. M.p. 168–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 3H), 6.93 (d, J = 8.1 Hz, 1H), 6.98 (ddd, J = 1.2, 7.5, 7.5 Hz, 1H), 7.38 (ddd, J = 1.8, 7.5, 7.5 Hz, 1H), 7.48 (ddd, J = 1.8, 7.2, 7.5 Hz, 1H), 7.59 (dd, J = 1.8, 7.5 Hz, 1H), 7.61 (ddd, J = 0.9, 7.5, 7.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.71 (ddd, J = 0.9, 1.8, 7.5 Hz, 1H), 7.77 (dd, J = 1.5, 8.1 Hz, 1H), 7.88 (d, J = 1.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.82, 88.84, 89.49, 93.21, 95.22, 110.70, 110.77, 111.07, 115.66, 116.73, 117.31, 120.62, 122.09, 126.15, 127.87, 131.30, 131.80, 132.07, 133.21, 133.77, 134.56, 135.00, 136.38, 136.63, 160.49. HR MS (FAB, positive ion mode) calcd for $C_{25}H_{14}N_2O$ 358.1106, found 358.1140.

5-[[2-Cyano-4-[(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-2-[(2-methoxyphenyl)-ethynyl]-benzonitrile (BL-3). The reaction of **1** (141 mg, 1.07 mmol) with 5-bromo-2-iodobenzonitrile (274 mg, 0.89 mmol) for 1 h at ambient temperature provided bromide **14** (256 mg, 0.82 mmol, 92%). By the general procedure the reaction of **8** (227 mg, 0.90 mmol) with bromide **14** (234 mg, 0.75 mmol) was completed after 12 h under reflux. The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **BL-3** (153 mg, 42%) as pale yellow crystals. M.p. 218–219 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 3H), 6.94 (d, J = 8.1 Hz, 1H), 6.98 (ddd, J = 1.2, 7.5, 7.5 Hz, 1H), 7.30–7.38 (m, 1H), 7.38 (ddd, J = 1.8, 7.5, 7.8 Hz, 1H), 7.49 (ddd, J = 1.8, 7.5, 7.8 Hz, 1H), 7.59 (dd, J = 1.8, 7.5 Hz, 1H), 7.62–7.67 (m, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.72 (m, 1H), 7.78 (dd, J = 1.8, 7.8 Hz, 1H), 7.81 (dd, J = 1.8, 8.1 Hz, 1H), 7.89 (d, J = 1.2 Hz, 1H), 7.91 (d, J = 1.2 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.82, 88.64, 89.50, 89.50, 92.76, 95.38, 95.50, 110.76, 111.03, 112.16, 115.72, 116.02, 116.44, 116.66, 117.24, 120.62, 121.75, 123.34, 125.90, 126.25, 128.15, 128.58, 130.27, 131.32, 131.79, 132.16, 133.29, 133.78, 134.62, 135.01, 136.10, 136.48, 136.68, 160.50. HR MS (FAB, positive ion mode) calcd for $C_{34}H_{17}N_3O$ 483.1372, found 483.1367.

2-[[2-Methoxy-4-[(2-methoxyphenyl)-ethynyl]-phenyl]-ethynyl]-benzonitrile (BL-4). By the general procedure the reaction of **3** (500 mg, 1.91 mmol) with 2-bromobenzonitrile (290 mg, 1.59 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (hexane–benzene, 1 : 2) followed by recrystallization from hexane–benzene to provide **BL-4** (365 mg, 63%) as yellow crystals. M.p. 109–110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.97 (s, 3H), 6.92 (d, J = 8.1 Hz, 1H), 6.97 (ddd, J = 0.9, 7.5, 7.5 Hz, 1H), 7.10 (d, J = 1.5 Hz, 1H), 7.17 (dd, J = 1.5, 8.1 Hz, 1H), 7.34 (ddd, J = 1.5, 7.5, 8.1 Hz, 1H), 7.40 (ddd, J = 1.2, 7.5, 7.5 Hz, 1H), 7.51 (dd, J = 1.8, 7.5 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.56 (ddd, J = 1.2, 7.5, 8.1 Hz, 1H), 7.65 (ddd, J = 0.9, 1.2, 6.0 Hz, 1H), 7.67 (ddd, J = 0.9, 1.5, 6.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.80, 55.97, 87.89, 90.91, 92.41, 93.12, 110.58, 110.64, 111.43, 111.93, 113.90, 115.18, 117.59, 120.53, 124.50, 125.75, 125.83, 127.41, 131.35, 132.66, 133.21, 133.60, 134.58, 159.91, 159.96. HR MS (FAB, positive ion mode) calcd for $C_{25}H_{17}NO_2$ 363.1259, found 363.1267.

5-[(2-Cyanophenyl)-ethynyl]-2-[[2-methoxy-4-[(2-methoxyphenyl)-ethynyl]-phenyl]-ethynyl]-benzonitrile (BL-5). The reaction of **3** (627 mg, 2.39 mmol) with 5-bromo-2-iodobenzonitrile (613 mg, 1.99 mmol) for 1 h at ambient temperature provided bromide **15** (871 mg, 1.97 mmol, 99%). By the general procedure the reaction of **7** (153 mg, 1.20 mmol) with bromide **15** (442 mg, 1.00 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (hexane–benzene, 1 : 2) followed by recrystallization from benzene to provide **BL-5** (210 mg, 43%) as deep yellow crystals. M.p. 186–187 °C. ^{1}H NMR

(300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.97 (s, 3H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.96 (ddd, $J = 1.2$, 7.5, 7.5 Hz, 1H), 7.10 (d, $J = 1.2$ Hz, 1H), 7.17 (dd, $J = 1.2$, 7.8 Hz, 1H), 7.33 (ddd, $J = 1.8$, 7.8, 8.1 Hz, 1H), 7.47 (ddd, $J = 1.5$, 7.2, 7.5 Hz, 1H), 7.51 (dd, $J = 1.2$, 7.2 Hz, 1H) 7.54 (d, $J = 8.1$ Hz, 1H), 7.61 (ddd, $J = 1.2$, 7.8, 7.8 Hz, 1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.65 (dd, $J = 0.3$, 8.4 Hz, 1H), 7.71 (ddd, $J = 0.3$, 1.5, 7.8 Hz, 1H), 7.77 (dd, $J = 1.5$, 8.4 Hz, 1H), 7.88 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.95, 56.11, 88.20, 88.95, 90.89, 93.09, 93.15, 95.01, 110.58, 110.73, 111.09, 111.89, 113.86, 113.88, 115.50, 115.54, 115.61, 116.66, 116.69, 117.29, 122.21, 126.12, 126.17, 126.22, 127.60, 127.63, 132.13, 132.74, 133.18, 133.46, 134.60, 135.89, 159.96, 160.06. HR MS (FAB, positive ion mode) calcd for $C_{34}H_{20}N_2O_2$ 488.1525, found 488.1520.

5-[[2-Cyano-4- [(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-2-[[2-methoxy-4- [(2-methoxyphenyl)-ethynyl]-phenyl]-ethynyl]-benzonitrile (BL-6). By the general procedure the reaction of **8** (293 mg, 1.16 mmol) with bromide **15** (429 mg, 0.97 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **BL-6** (386 mg, 65%) as yellow crystals. M.p. 221–222 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.98 (s, 3H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.96 (ddd, $J = 1.2$, 7.5, 7.5 Hz, 1H), 7.10 (d, $J = 1.2$ Hz, 1H), 7.17 (dd, $J = 1.2$, 7.5 Hz, 1H), 7.34 (ddd, $J = 1.8$, 7.8, 8.4 Hz, 1H), 7.49 (ddd, $J = 1.5$, 7.2, 7.5 Hz, 1H), 7.51 (dd, $J = 1.2$, 7.2 Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.62 (ddd, $J = 1.2$, 7.8, 7.8 Hz, 1H), 7.65 (dd, $J = 1.2$, 8.1 Hz, 1H), 7.66 (dd, $J = 0.9$, 8.4, Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.72 (ddd, $J = 0.9$, 1.5, 7.2 Hz, 1H), 7.77 (dd, $J = 1.5$, 8.1 Hz, 1H), 7.81 (dd, $J = 1.5$, 8.4 Hz, 1H), 7.88 (d, $J = 1.5$ Hz, 1H), 7.90 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.83, 56.12, 88.26, 88.76, 89.57, 90.91, 92.77, 93.09, 95.31, 95.36, 110.79, 111.04, 111.89, 113.44, 113.87, 115.67, 115.67, 116.02, 116.43, 116.63, 117.25, 120.65, 121.87, 123.32, 123.90, 125.91, 126.23, 126.27, 127.92, 131.36, 132.20, 132.27, 132.45, 132.81, 133.26, 133.53, 133.93, 134.67, 135.58, 135.95, 136.70, 159.96, 160.13. HR MS (FAB, positive ion mode) calcd for $C_{43}H_{23}N_3O_2$ 613.1790, found 613.1783.

2-[[2-Methoxy-4- [[2-methoxy-4- [(2-methoxyphenyl)-ethynyl]-phenyl]-ethynyl]-phenyl]-ethynyl]-benzonitrile (BL-7). By the general procedure the reaction of **13** (372 mg, 0.95 mmol) with 2-bromobenzonitrile (144 mg, 0.79 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **BL-7** (121 mg, 31%) as yellow crystals. M.p. 127–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 3.96 (s, 3H), 3.97 (s, 3H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.96 (ddd, $J = 1.2$, 7.5, 7.5 Hz, 1H), 7.09 (d, $J = 1.2$ Hz, 2H), 7.16 (dd, $J = 1.5$, 8.1 Hz, 2H), 7.34 (ddd, $J = 1.5$, 7.8, 8.1 Hz, 1H), 7.40 (ddd, $J = 1.5$, 7.8, 7.8 Hz, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.51 (dd, $J = 1.5$, 7.5 Hz, 1H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.56 (ddd, $J = 1.2$, 7.2, 7.2 Hz, 1H), 7.65 (ddd, $J = 0.9$, 1.2, 6.0 Hz, 1H), 7.68 (ddd, $J = 0.9$, 1.5, 6.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.85, 55.96, 56.12, 87.69, 87.81, 91.04, 92.41, 93.15, 94.62, 110.73, 111.57, 111.97, 112.06, 113.38, 113.81, 113.81, 115.14, 115.18, 117.59, 120.65, 123.87, 124.40, 125.07, 125.12, 125.56, 127.36, 132.08, 132.70, 133.06, 133.59, 133.87, 159.94, 159.94, 159.97. HR MS (FAB, positive ion mode) calcd for $C_{34}H_{23}NO_3$ 493.1678, found 493.1682.

5-[(2-Cyanophenyl)-ethynyl]-2- [[2-methoxy-4- [[2-methoxy-4- [(2-methoxyphenyl)-ethynyl]- phenyl]-ethynyl]- phenyl]- ethynyl]-benzonitrile (BL-8). The reaction of **13** (797 mg, 2.03 mmol) with 5-bromo-2-iodobenzonitrile (520 mg, 1.69 mmol) for 1 h at ambient temperature provided bromide **16** (842 mg, 1.47 mmol, 87%). By the general procedure the reaction of **7** (140 mg, 1.10 mmol) with bromide **16** (527 mg, 0.92 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene) followed by recrystallization from benzene to provide **BL-8** (455 mg, 80%) as yellow crystals. M.p. 194–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.96 (s, 3H), 3.98 (s, 3H), 6.92 (d, $J = 7.5$ Hz, 1H), 6.96 (ddd, $J = 1.2$, 7.8, 7.8 Hz, 1H), 7.10 (bs, 2H), 7.17 (ddd, $J = 1.5$, 1.5, 7.8 Hz, 2H), 7.34 (ddd, $J = 1.8$, 7.2, 7.5 Hz, 1H), 7.46 (dd, $J = 1.8$, 7.2 Hz, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.50 (ddd, $J = 1.8$, 7.2, 7.2 Hz, 1H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.61 (ddd, $J = 1.5$, 8.1, 8.1 Hz, 1H), 7.65 (ddd, $J = 0.9$, 1.2, 8.1 Hz, 1H), 7.66 (d, $J = 8.1$ Hz, 1H), 7.72 (ddd, $J = 0.9$, 1.5, 7.2 Hz, 1H), 7.77 (dd, $J = 1.8$, 8.1 Hz, 1H), 7.88 (d, $J = 1.2$ Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.85, 56.13, 56.13, 87.71, 88.08, 88.97, 91.00, 93.15, 93.15, 94.59, 94.98, 110.54, 111.24, 111.96, 113.37, 113.81, 113.81, 113.81, 115.50, 115.63, 116.69, 117.30, 120.63, 122.24, 123.90, 124.43, 125.16, 125.99, 126.12, 127.60, 131.32, 132.17, 132.41, 132.78, 133.59, 134.42, 134.60, 135.54, 135.88, 136.64, 159.59, 159.93, 160.07. HR MS (FAB, positive ion mode) calcd for $C_{43}H_{26}N_2O_3$ 618.1943, found 618.1941.

5-[[2-Cyano-4- [(2-cyanophenyl)-ethynyl]-phenyl]-ethynyl]-2-[[2-methoxy-4- [[2-methoxy-4- [(2-methoxyphenyl)- ethynyl]-phenyl]-ethynyl]-phenyl]-ethynyl]-benzonitrile (BL-9). By the general procedure the reaction of **8** (166 mg, 0.66 mmol) with bromide **16** (315 mg, 0.55 mmol) was completed after 12 h (reflux). The crude product was purified by column chromatography (benzene–EtOAc, 9 : 1) followed by recrystallization from benzene to provide **BL-9** (229 mg, 56%) as yellowish orange crystals. M.p. 270–271 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H), 3.96 (s, 3H), 3.98 (s, 3H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.96 (ddd, $J = 1.2$, 7.2, 7.8 Hz, 1H), 7.10 (bs, 2H), 7.17 (ddd, $J = 1.5$, 1.5, 7.5 Hz, 2H), 7.34 (ddd, $J = 1.5$, 7.2, 7.5 Hz, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.51 (ddd, $J = 1.8$, 1.8, 7.5 Hz, 1H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.62 (ddd, $J = 1.5$, 8.1, 8.1 Hz, 1H), 7.65 (dd, $J = 0.9$, 8.1 Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 2H), 7.73 (ddd, $J = 0.9$, 1.5, 7.5 Hz, 1H), 7.78 (dd, $J = 1.8$, 8.1 Hz, 1H), 7.82 (dd, $J = 1.5$, 8.1 Hz, 1H), 7.90 (d, $J = 1.8$ Hz, 1H), 7.91 (d, $J = 1.2$ Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.85, 56.13, 56.13, 87.70, 88.11, 88.76, 89.56, 91.01, 91.01, 92.76, 93.14, 94.60, 95.25, 110.51, 111.24, 111.93, 111.96, 113.35, 113.37, 113.79, 113.81, 115.50, 115.63, 115.67, 115.67, 115.99, 116.00, 116.03, 116.61, 117.27, 120.64, 121.90, 122.00, 122.24, 123.32, 123.90, 124.41, 125.15, 125.89, 126.12, 127.60, 131.32, 132.23, 133.94, 134.42, 134.60, 134.66, 135.93, 136.72, 159.57, 160.07, 160.07. HR MS (FAB, positive ion mode) calcd for $C_{52}H_{29}N_3O_3$ 743.2209, found 743.2215.

Acknowledgements

We thank Dr Yukihiro Shimoi (National Institute of Advanced Industrial Science and Technology (AIST)) for the DFT and TD-DFT calculations, and Dr Kazuya Ogawa (Nara Institute

of Science and Technology (NAIST)) for the measurement of TPA. This work was supported by Grants-in-Aid for Creative Scientific Research (No. 16GS0209) and Scientific Research (No. 16550131) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

1 (*a*) R. B. Thompson, *Fluorescence Sensors and Biosensors*, CRC Press LLC, Boca Raton, FL, 2006; (*b*) T. Nishioka, J. Yuan, Y. Yamamoto, K. Sumitomo, Z. Wang, K. Hashino, C. Hosoya, K. Ikawa, G. Wang and K. Matsumoto, *Inorg. Chem.*, 2006, **45**, 4088–4096; (*c*) K. Yoshimoto, S. Nishizawa, M. Minagawa and N. Teramae, *J. Am. Chem. Soc.*, 2003, **125**, 8982–8983; (*d*) X. Song, J. Nolan and B. I. Swanson, *J. Am. Chem. Soc.*, 1998, **120**, 11514–11515; (*e*) N. H. Norton, *Biomedical Sensors, Fundamentals, and Applications*, Noys Publications, Park Ridge, NJ, 1982.

2 (*a*) J. Shi, E. Forsythe, D. C. Morton and B. M. Bolotin, *Organic Luminescent Materials*, U.S. Pat. Appl. Publ., 2005; (*b*) B. M. Krasovitskii and B. M. Bolotin, *Organic Luminescent Materials*, VCH, Weinheim, Germany, 1988.

3 (*a*) J. Shinar, *Organic Light-Emitting Devices*, Springer, New York, 2004; (*b*) K. Müllen and U. Scherf, *Organic Light Emitting Devices*, Wiley-VCH, Weinheim, 2006.

4 For example, see: (*a*) Y. Yamaguchi, T. Ochi, T. Wakamiya, Y. Matsubara and Z. Yoshida, *Org. Lett.*, 2006, **8**, 717–720; (*b*) Y. Yamaguchi, S. Kobayashi, T. Wakamiya, Y. Matsubara and Z. Yoshida, *Angew. Chem., Int. Ed.*, 2005, **44**, 7040–7044; (*c*) Y. Yamaguchi, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara and Z. Yoshida, *J. Am. Chem. Soc.*, 2005, **127**, 9332–9333; (*d*) Y. Yamaguchi, T. Ochi, S. Miyamura, T. Tanaka, S. Kobayashi, T. Wakamiya, Y. Matsubara and Z. Yoshida, *J. Am. Chem. Soc.*, 2006, **128**, 4504–4505; (*e*) T. Ochi, Y. Yamaguchi, S. Kobayashi, T. Wakamiya, Y. Matsubara and Z. Yoshida, *Chem. Lett.*, 2007, **36**, 794–795.

5 U. H. F. Bunz, *Chem. Rev.*, 2000, **100**, 1605–1644.

6 Fluorescent non-block type donor/acceptor oligo(phenyleneethynylene)s (OPEs), see: (*a*) J. N. Wilson and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2005, **127**, 4124–4125; (*b*) J. A. Marsden, J. J. Miller, L. D. Shircliff and M. M. Haley, *J. Am. Chem. Soc.*, 2005, **127**, 2464–2476; (*c*) J. N. Wilson, P. M. Windscherf, U. Evans and U. H. F. Bunz, *Macromolecules*, 2002, **35**, 8681–8683; (*d*) P. Nguyen, Z. Yuan, L. Agocs and T. B. Marder, *Inorg. Chim. Acta*, 1994, **220**, 289–296.

7 K. Sonogashira, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991. vol. 3, pp. 521–549.

8 The compounds were thoroughly purified by repeated column chromatography followed by recrystallization.

9 **PR-1**, see: (*a*) A. Beeby, K. S. Findlay, P. J. Low and T. B. Marder, *J. Am. Chem. Soc.*, 2002, **124**, 8280–8284; (*b*) K. S. Findlay, P. J. Low and T. B. Marder, *Chem. Commun.*, 2003, 2406–2407.

10 J. Saltiel, A. S. Waller, D. F. Sears Jr. and C. Z. Garrett, *J. Phys. Chem.*, 1993, **97**, 2516–2522.

11 K. Sandros, M. Sundahl, O. Wennerstrom and U. Norinder, *J. Am. Chem. Soc.*, 1990, **112**, 3082–3086.

12 B. Valeur, *Molecular Fluorescence*, Wiley-VCH, Weinheim, 2005.

13 For example, see: (*a*) H. Langhals, O. Krotz, K. Polborn and P. Mayer, *Angew. Chem., Int. Ed.*, 2005, **44**, 2427–2428; (*b*) S. H. Lee, B.-B. Jang and Z. H. Kafali, *J. Am. Chem. Soc.*, 2005, **127**, 9071–9078; (*c*) Y. Kim, J. Bouffard, S. E. Kooi and T. M. Swager, *J. Am. Chem. Soc.*, 2005, **127**, 13726–13731.

14 (*a*) Y. Zhao, Y. Shirai, A. D. Slepkov, L. Cheg, L. B. Alemany, T. Sasaki, F. A. Hegmann and J. M. Tour, *Chem.–Eur. J.*, 2005, **11**, 3643–3658; (*b*) R. Schroeder, J. N. Wilson, U. H. F. Bunz and B. Ullrich, *J. Phys. Chem. B*, 2003, **107**, 11604–11607.

15 S. Barlow and S. R. Marder, in *Functional Organic Materials*, ed. T. J. J. Müller and U. H. F. Bunz, Wiley-VCH, Weinheim, 2007, pp. 418–437.

16 B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.*, 1998, **10**, 1863–1874.

17 J. T. Dy, K. Ogawa, A. Satake, A. Ishizumi and Y. Kobuke, *Chem.–Eur. J.*, 2007, **13**, 3491–3500.

18 S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 8459–8467.

19 Y.-C. Ning, *Structural Identification of Organic Compounds with Spectroscopic Techniques*, Wiley-VCH, Weinheim, 2005.