## New Fluorophores with Rod-Shaped Polycyano $\pi$ -Conjugated Structures: Synthesis and Photophysical Properties

LETTERS 2006 Vol. 8, No. 4 717-720

ORGANIC

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

Department of Chemistry, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

yamaguch@chem.kindai.ac.jp; yoshida@chem.kindai.ac.jp

## Received November 30, 2005



Novel rod-shaped polycyano-oligo(phenyleneethynylene)s were synthesized by Pd cross-coupling reaction. Polycyano groups were found to greatly improve the emission efficiency ( $\Phi_f$ ) of OPEs. By the end donor modification, we achieved the creation of very intense blue light-emitting fluorophore with the SMe group ( $\Phi_f = 0.972$ , log  $\epsilon$  4.89,  $\lambda_{em}$  455 nm) and very intense yellow light-emitting fluorophore with the NMe<sub>2</sub> group ( $\Phi_f = 0.999$ , log  $\epsilon$  4.75,  $\lambda_{em}$  555 nm). Contrasting  $\Phi_f$  solvent dependency of 6 and 7 and a linear relationship between  $\Phi_f$  and  $\sigma_p$ -X over the whole region of  $\sigma_p$ -X were also found.

Polycyano  $\pi$ -conjugated systems represented by tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-quinodimethane (TCNQ) continue to attract great interest as strong electron acceptors, in particular in the fields of organic conductors<sup>1</sup> and ferromagnets.<sup>2</sup> However, to the best of our knowledge, fluorescence characteristics of polycyano  $\pi$ -systems have not been reported so far, even though electroluminescent polyphenylenevinylenes with cyano groups have been reported.<sup>3</sup> In view of the increasing importance of strongly light-emitting fluorophores ( $\Phi_f \approx 1.0$ , log  $\epsilon \approx 5$ )<sup>4</sup> in biological, chemical, and materials science, we report here the synthesis and excellent light-emitting properties of polycyano-oligo(phen-

10.1021/ol0528991 CCC: \$33.50 © 2006 American Chemical Society Published on Web 01/28/2006 yleneethynylene)s (polycyano OPEs, 1-3) and polycyanotetrameric PEs (4-7) with a donor group substituting the end cyano group of 3 (Figure 1) together with the parent



Figure 1. Structure of polycyano OPEs (1-3), donor-substituted polycyano-tetrameric PEs (4-7), and parent OPEs (8-10).

OPEs (8, dimeric PE; 9, trimeric PE; 10, tetrameric PE) as the reference systems (synthesis of 9 and 10, see Supporting Information).

 <sup>(1) (</sup>a) Ferraris, J.; Cowan, D. O.; Walatka, V. V., Jr.; Perlstein, J. H. J. Am. Chem. Soc. **1973**, 95, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. Solid State Commun. **1973**, 12, 1125. (c) Nakasuji, K.; Sasaki, M.; Kotani, T.; Murata, I.; Enoki, T.; Imaeda, K.; Inokuchi, H.; Kawamoto, A.; Tanaka, J. J. Am. Chem. Soc. **1987**, 109, 6970.

<sup>(2) (</sup>a) Sugimoto, T.; Murahashi, E.; Ikeda, K.; Yoshida, Z.; Nakatsuji, H.; Yamaguchi, J.; Kai, Y.; Kasai, N. *Mater. Res. Soc. Symp. Proc.* **1992**, 247, 417. (b) Sugimoto, T. *New Funct. Mater.* **1993**, *C*, 369.

<sup>(3)</sup> For example, see: (a) Krasoviskii, B. M.; Bolotin, B. M. Organic Luminescenct Materials; VCH: Weinheim, Germany, 1988; pp 23–29. (b) Fahlman, M.; Salaneck, W. R.; Morakt, S. C.; Holmes, A. B.; Bredas, J. L. Chem. Eur. J. **1997**, *3*, 286. (c) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Angew. Chem., Int. Ed. **1998**, *37*, 402.

<sup>(4) (</sup>a) Yamaguchi, Y.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. J. Am. Chem. Soc. **2005**, *127*, 9332 and references therein. (b) Bunz, U. H. F. Chem. Rev. **2000**, *100*, 1605.



The synthesis of polycyano OPEs (1-3) was effectively accomplished by Pd cross-coupling reaction as shown in Scheme 1.

Emission and absorption characteristics<sup>5</sup> of **1**–**3** and the parent OPEs (**8**–**10**) together with radiative rate constant ( $k_r$ ), radiationless rate constant ( $k_d$ ),  $k_r/k_d$  (our measure for emissivity), and emission lifetime ( $\tau$ ) are shown in Table 1.

Table 1.	Photophysical Properties of Polycyano OPEs (1-3)
and the Co	prresponding Parent OPEs (8–10) (in $CHCl_3$ ) <sup><i>a</i></sup>

comp	$\Phi_{\mathrm{f}}{}^{b}$	$_{(nm)}^{\lambda_{em}}$	$\log \epsilon$	$_{(nm)}^{\lambda_{abs}}$	$\tau$ (ns)	$k_{\rm r}({\rm s}^{-1})$	$k_{ m d}({ m s}^{-1})$	$k_{ m r}/k_{ m d}$
1	0.452	332	4.58	297	2.64	$1.71  imes 10^8$	$2.08  imes 10^8$	0.83
2	0.783	370	4.74	340	1.83	$4.29 imes10^8$	$1.19 imes10^8$	3.61
3	0.858	392	4.94	357	1.14	$7.51  imes 10^8$	$1.24 imes10^8$	6.04
8	0.003	320	4.41	299	3.89	$8.74 imes10^5$	$2.56 imes10^8$	0.003
9	0.500	348	4.59	328	2.57	$1.95  imes 10^8$	$1.95  imes 10^8$	1.00
10	0.610	387	4.77	345	1.70	$3.59 imes10^8$	$2.30  imes 10^8$	1.56

 $^a$  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).

Since  $k_r$  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.<sup>6</sup> As seen in Table 1, it is evident that the introduction of cyano groups at the side and end of rod-shaped OPEs increases the  $\Phi_{\rm f}$  and  $\lambda_{\rm em}$  values compared with those of the parent OPEs (8–10). In particular, tetracyano-tetrameric OPE 3 exhibits a red shift of the fluorescence emission maximum and a significant increase in the quantum yield, thus providing the highly efficient violet fluorophore ( $\Phi_{\rm f}$  0.86,  $\lambda_{\rm em}$  392 nm).

It is worth noting that polycyano groups play an important role for improvement of the emission characteristics (in particular, of  $\Phi_f$  and  $\lambda_{em}$ ). The superior emissive properties of **1–3** relative to **8–10** is ascribed to the increase in their  $k_r$  values and the decrease in their  $k_d$  values compared with those for **8–10**, which seems to be explained by easier formation of a dipolar unit (exciton) by CN groups (see Supporting Information). This is obvious from the slopes for linear plots of  $k_r$  versus *n* (number of 2-cyanophenyleneethynylene units) for **1–3** (2.90 × 10<sup>8</sup>) and for **8–10** (1.79

<sup>(5)</sup> 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), purity of organic fluorescent compounds was checked by constancy of the fluorescence intensity at the maximum ( $\lambda_{em}$ ) ( $10^{-6}-10^{-7}$  impurity).

<sup>(6) (</sup>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.

× 10<sup>8</sup>) and the slopes for linear plots of  $k_d$  versus *n* for **1–3** (-0.42 × 10<sup>8</sup>) and for **8–10** (-0.13 × 10<sup>8</sup>). This linear relationship could be explained by movability of the dipolar unit (exciton) (see Supporting Information).

Further search was made for the more intense fluorophores ( $\Phi_{\rm f} \approx 1.0$ , log  $\epsilon \approx 5$ ) at the desired wavelength region, for example, at blue (around 460 nm) and yellow (around 550 nm) regions. For this purpose we considered the end modification of **3** with a donor group (**4**, SMe; **5**, Me; **6**, OMe; **7**, NMe<sub>2</sub>) in place of the end cyano group<sup>4a,7</sup> and synthesized them by the reactions shown in Scheme 1.

Emission and absorption characteristics of polycyanotetrameric PEs (4–7) modified by the end donor group together with the  $\tau$ ,  $k_r$ ,  $k_d$ , and  $k_r/k_d$  values are summarized in Table 2. As seen in Table 2, the introduction of end-donor

**Table 2.** Emission and Absorption Characteristics of Donor-Substituted Polycyano-tetrameric PEs (4-7) (in CHCl<sub>3</sub>)<sup>*a*</sup>

comp	$\Phi_{\mathrm{f}}{}^{b}$	$_{(nm)}^{\lambda_{em}}$	$\log \epsilon$	$_{(nm)}^{\lambda_{abs}}$	$\tau$ (ns)	$k_{\rm r}({\rm s}^{-1})$	$k_{\rm d}({ m s}^{-1})$	$k_{ m r}/k_{ m d}$
4 5 6 7	0.972 0.960 0.982 0.999	$455 \\ 403 \\ 434 \\ 555$	4.89 4.91 4.87 4.75	$375 \\ 360 \\ 371 \\ 425$	1.29 1.23 1.36 1.78	$\begin{array}{l} 7.54\times 10^8 \\ 7.78\times 10^8 \\ 7.22\times 10^8 \\ 5.61\times 10^8 \end{array}$	$\begin{array}{c} 2.17 \times 10^{7} \\ 3.24 \times 10^{7} \\ 1.32 \times 10^{7} \\ 5.62 \times 10^{5} \end{array}$	$34.71 \\ 24.00 \\ 54.56 \\ 999.0$

 $^a$  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).

group to tricyano-tetrameric PE significantly improves the  $\Phi_{\rm f}$ ,  $\lambda_{\rm em}$ , and  $k_{\rm r}/k_{\rm d}$  values compared with those of tetracyanotetrameric PE **3**. Thus we achieved the creation of a very intense blue fluorophore with the SMe group ( $\Phi_{\rm f}$  0.972, log  $\epsilon$  4.89,  $\lambda_{\rm em}$  455 nm) and very intense yellow fluorophore with the NMe<sub>2</sub> group ( $\Phi_{\rm f}$  0.999, log  $\epsilon$  4.75,  $\lambda_{\rm em}$  555 nm). Fluorescence spectra and colors of **3**, **4**, and **7** are shown in Figure 2.



Figure 2. Fluorescence spectra and colors of 3, 4, and 7 in CHCl<sub>3</sub>.

This sort of end-donor modification of polycyano OPEs is superior to the end-acceptor modification of polymethoxy

OPEs<sup>4a</sup> with respect to the emission characteristics. From the obtained results, it is suggested that strongly fluorescent materials at a desired wavelength region could be created by (1) selection of number and position of the appropriate donor groups (D) at the terminal benzene ring of **36**, (2) selection of number and position of cyano groups in **36**, and (3) selection of number of phenyleneethynylene unit.



Figure 3. Molecular design for the strongly fluorescent materials.

In regard to structure-emissivity relationship, we found out that the quantum yield  $(\Phi_f)$  linearly increases with an increase in electron-donating ability of end-substituent X as shown in Figure 4 where the linear relationship between  $\Phi_f$ 



**Figure 4.** The relationship between quantum yield ( $\Phi_f$ ) and substituent constant ( $\sigma_p$ -X) for the substituent X of terminal benzene ring of the donor-substituted polycyano-tetrameric PEs (4–7) and **35** (X = H), and tetracyano-tetrameric PE **3** (X = CN). Hammett substituent constants ( $\sigma_p$ -X):<sup>8</sup> 0.66 (**3**, X = CN), 0.00 (**4**, X = SMe), 0.00 (**35**, X = H), -0.17 (**5**, X = Me), -0.27 (**6**, X = OMe), -0.83 (**7**, X = NMe<sub>2</sub>).

and the Hammett substituent constants  $(\sigma_p - X)^8$  is kept over the whole region of  $\sigma_p - X$  values including a cyano group.

The effect of solvent on the photophysical properties of **6** and **7** is shown in Table 3. As shown in this table, the solvent effect on emission efficiency ( $\Phi_f$ ) of **6** (X = OMe) and **7** (X = NMe<sub>2</sub>) is quite contrasting. Almost no solvent effect is observed for the absorption spectra of both **6** and **7**,

<sup>(7)</sup> Other examples of the donor-acceptor substituted OPEs: (a) Marsden, J. A.; Miller, J. J.; Shircliff, L. D.; Haley M. M. J. Am. Chem. Soc. **2005**, *127*, 2464. (b) Wilson, J. N.; Bunz, H. F. J. Am. Chem. Soc. **2005**, *127*, 4124.

<sup>(8)</sup> Hansch, C.; Leo, A.; Taft, W. Chem. Rev. 1991, 91, 165.

**Table 3.** Effect of Solvent on Absorption and Fluorescence Characteristics of **6** and  $7^a$ 

comp	solvent	$\Phi_{\mathrm{f}}$	$_{(nm)}^{\lambda_{em}}$	$\log \epsilon$	$_{(nm)}^{\lambda_{abs}}$	$k_{\rm r}({\rm s}^{-1})$	$k_{\rm d}({\rm s}^{-1})$	$k_{ m r}/k_{ m d}$
6	benzene CHCl <sub>3</sub> THF CH <sub>3</sub> CN	0.972 0.982 0.972 0.973	420 434 460 490	4.84 4.87 4.89 4.89	371 371 369 364	$\begin{array}{c} 6.72 \times 10^8 \\ 7.22 \times 10^8 \\ 7.55 \times 10^8 \\ 7.55 \times 10^8 \end{array}$	$\begin{array}{c} 1.94 \times 10^{7} \\ 1.32 \times 10^{7} \\ 2.17 \times 10^{7} \\ 2.10 \times 10^{7} \end{array}$	$34.71 \\ 54.56 \\ 34.71 \\ 36.04$
7	DMF benzene CHCl <sub>3</sub> THF CH <sub>2</sub> CN	0.949 0.999 0.999 0.084 0.002	513 519 555 621 682	4.86 4.76 4.75 4.77 4.78	369 426 425 422 413	$6.87 \times 10^{8}$ $5.75 \times 10^{8}$ $5.61 \times 10^{8}$ $4.96 \times 10^{7}$ $9.04 \times 10^{5}$	$3.69 \times 10^{7}$ $5.75 \times 10^{5}$ $5.62 \times 10^{5}$ $5.39 \times 10^{8}$ $6.02 \times 10^{8}$	18.61 999 999 0.092 0.002
<sup>a</sup> A	DMF ll spectra	0.002 0.002 were m	699 easure	4.73 d at 2	423 95 K.	$1.16 \times 10^6$	$5.36 \times 10^8$	0.002

whereas the fluorescence maximum of **6** and **7** are shifted to longer wavelengths as solvent polarity increase. Although the quantum yield of **6** is not altered with a change in the solvent polarity, that of **7** remarkably decreases with an increase in the solvent polarity. The observed effect of the solvent on the  $\Phi_f$  values of **6** and **7** can be interpreted by a change in the  $k_r$  and  $k_d$  values of **6** and **7** with a change in the solvent polarity. The  $k_r$  and  $k_d$  values of **6** are not so altered by solvent polarity. On the contrary the  $k_r$  values decrease and the  $k_d$  values increase for **7** with an increase in solvent polarity. The contrasting solvent polarity effect on  $\Phi_{\rm f}$ ,  $\lambda_{\rm em}$ ,  $k_{\rm r}$ , and  $k_{\rm d}$  could be explained by a difference in the dipole moment in the excited state ( $\mu_{\rm e}$ ) and in the ground state ( $\mu_{\rm g}$ ) of **6** ( $\mu_{\rm e} = 10.74 \text{ D} < \mu_{\rm g} = 11.52 \text{ D}$ ) and **7** ( $\mu_{\rm e} = 12.89 \text{ D} > \mu_{\rm g} = 12.75 \text{ D}$ ) (see Supporting Information).

In conclusion, we succeeded in the creation of a highly efficient violet fluorophore (**3**,  $\Phi_f$  0.86,  $\lambda_{em}$  392 nm) of polycyano OPE type, in contrast to TCNE and TCNQ, which scarcely fluoresce ( $\Phi_f < 10^{-4}$ ). Furthermore, we created very intense blue (**4**,  $\lambda_{em}$  455 nm) and yellow (**7**,  $\lambda_{em}$  555 nm) fluorophores ( $\Phi_f \approx 1.0$ , log  $\epsilon \approx 5$ ) by an introduction of the appropriate end-donor group. In addition, contrasting solvent dependency of the emission efficiency ( $\Phi_f$ ) of **6** and **7** and a linear relationship between  $\Phi_f$  and  $\sigma_p$ -X over the whole region of  $\sigma_p$ -X are other interesting findings.

Acknowledgment. This work was supported by Grantin-Aid for Creative Scientific Research (no. 16GS0209) and Scientific Research (no. 16550131) from the Ministry of Education, Science, Sport, and Culture of Japan.

**Supporting Information Available:** Synthesis, spectral data, solvent dependency, plots of  $\lambda_{em}$  and  $\Phi_f$  versus  $\sigma$ , plots of  $k_r$  and  $k_d$  versus n, and MO calculation for polycyano OPEs modified by donor and acceptor groups. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0528991