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New Fluorophores with Rod-Shaped Polycyano π-Conjugated Structures: Synthesis and Photophysical Properties

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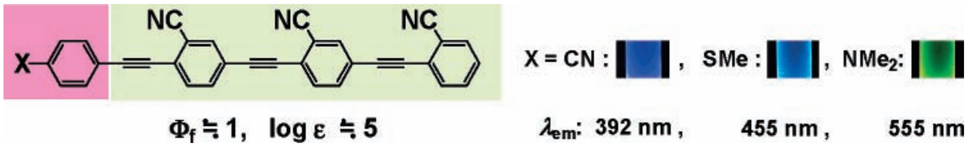
ABSTRACT



Novel rod-shaped polycyano-oligo(phenyleneethynylene)s were synthesized by Pd cross-coupling reaction. Polycyano groups were found to greatly improve the emission efficiency (Φ_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 ϵ 4.89, λ_{em} 455 nm) and very intense yellow light-emitting fluorophore with the NMe$_2$ group ($\Phi_f = 0.999$, log ϵ 4.75, λ_{em} 555 nm). Contrasting Φ_f solvent dependency of 6 and 7 and a linear relationship between Φ_f and σ_p-X over the whole region of σ_p-X were also found.

Polycyano π-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[1] and ferromagnets.[2] However, to the best of our knowledge, fluorescence characteristics of polycyano π-systems have not been reported so far, even though electroluminescent polyphenylenevinylenes with cyano groups have been reported.[3] In view of the increasing importance of strongly light-emitting fluorophores ($\Phi_f \approx 1.0$, log $\epsilon \approx 5$)[4] in biological, chemical, and materials science, we report here the synthesis and excellent light-emitting properties of polycyano-oligo(phenyleneethynylene)s (polycyano OPEs, **1**−**3**) and polycyano-tetrameric PEs (**4**−**7**) with a donor group substituting the end cyano group of **3** (Figure 1) together with the parent OPEs (**8**, dimeric PE; **9**, trimeric PE; **10**, tetrameric PE) as the reference systems (synthesis of **9** and **10**, see Supporting Information).

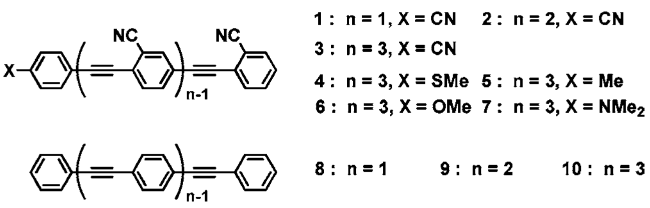


Figure 1. Structure of polycyano OPEs (**1**−**3**), donor-substituted polycyano-tetrameric PEs (**4**−**7**), and parent OPEs (**8**−**10**).

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[1] (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.

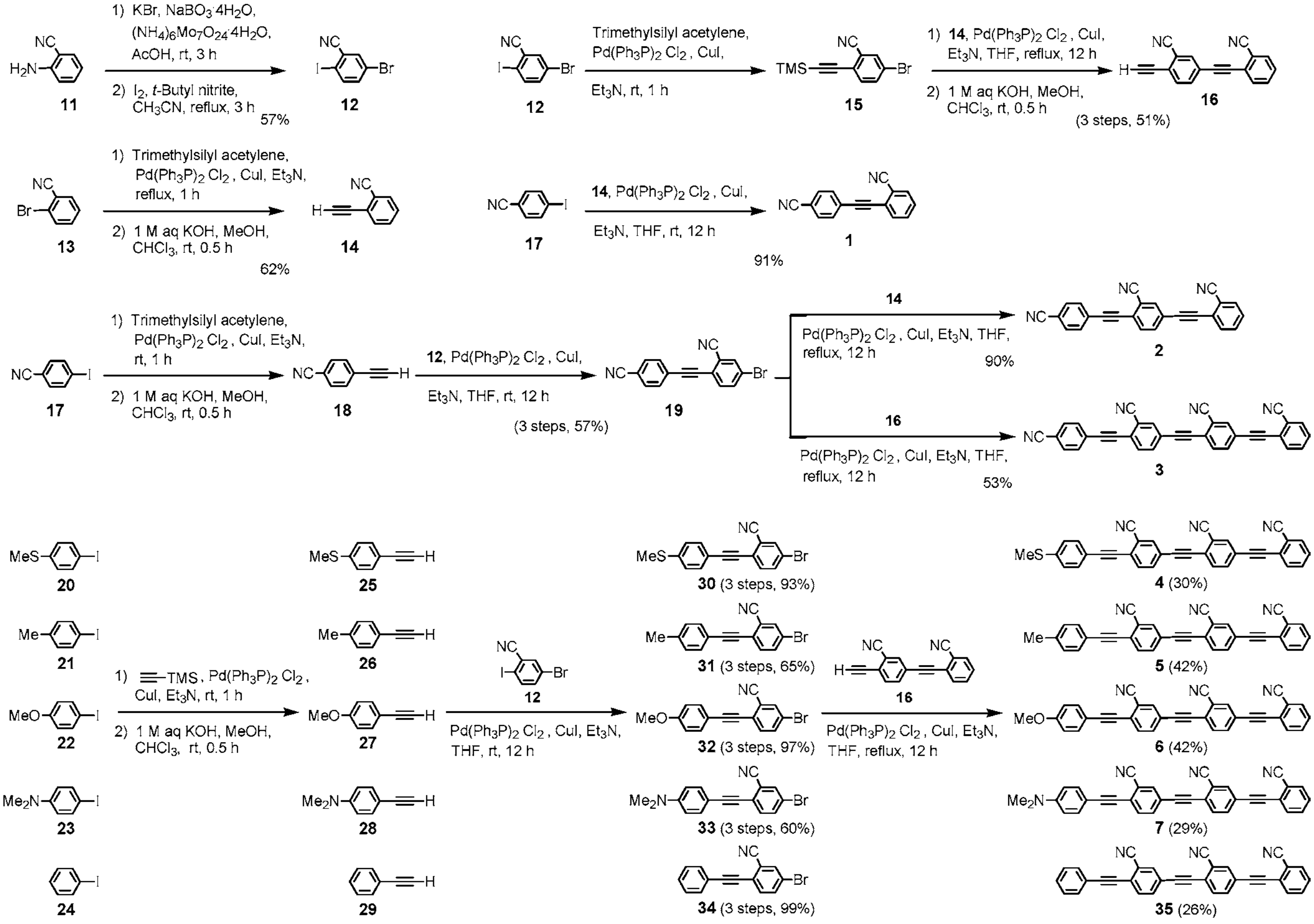
[2] (a) Sugimoto, T.; Murahashi, E.; Ikeda, K.; Yoshida, Z.; Nakatsuji, H.; Yamaguchi, J.; Kai, Y.; Kasai, N. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 417. (b) Sugimoto, T. *New Funct. Mater.* **1993**, *C*, 369.

[3] For example, see: (a) Krasoviskii, B. M.; Bolotin, B. M. *Organic Luminescent 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.

[4] (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.

10.1021/ol0528991 CCC: \$33.50

Scheme 1. Synthesis of Polycyano OPEs (**1**−**3**), Polycyano-tetrameric PEs (**4**−**7**) and **35** (X = H)



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

Emission and absorption characteristics[5] 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 (τ) are shown in Table 1.

Table 1. Photophysical Properties of Polycyano OPEs (**1**−**3**) and the Corresponding Parent OPEs (**8**−**10**) (in CHCl$_3$)[a]

comp	Φ_f[b]	λ_{em} (nm)	log ϵ	λ_{abs} (nm)	τ (ns)	k_r (s^{-1})	k_d (s^{-1})	k_r/k_d
1	0.452	332	4.58	297	2.64	1.71×10^8	2.08×10^8	0.83
2	0.783	370	4.74	340	1.83	4.29×10^8	1.19×10^8	3.61
3	0.858	392	4.94	357	1.14	7.51×10^8	1.24×10^8	6.04
8	0.003	320	4.41	299	3.89	8.74×10^5	2.56×10^8	0.003
9	0.500	348	4.59	328	2.57	1.95×10^8	1.95×10^8	1.00
10	0.610	387	4.77	345	1.70	3.59×10^8	2.30×10^8	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$_2$SO$_4$).

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.[6]

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 Φ_f and λ_{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 (Φ_f 0.86, λ_{em} 392 nm).

It is worth noting that polycyano groups play an important role for improvement of the emission characteristics (in particular, of Φ_f and λ_{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-cyanophenylene-ethynylene units) for **1**−**3** (2.90×10^8) and for **8**−**10** (1.79

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(5) 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 (λ_{em}) (10^{-6}−10^{-7} impurity).

(6) (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.

× 10^8) and the slopes for linear plots of k_d versus n for **1−3** (−0.42 × 10^8) and for **8−10** (−0.13 × 10^8). This linear relatiohship could be explained by movability of the dipolar unit (exciton) (see Supporting Information).

Further search was made for the more intense fluorophores ($\Phi_f \approx 1.0$, 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_2) in place of the end cyano group[4a,7] and synthesized them by the reactions shown in Scheme 1.

Emission and absorption characteristics of polycyano-tetrameric PEs (**4−7**) modified by the end donor group together with the τ, 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 group to tricyano-tetrameric PE significantly improves the Φ_f, λ_{em}, and k_r/k_d values compared with those of tetracyano-tetrameric PE **3**. Thus we achieved the creation of a very intense blue fluorophore with the SMe group (Φ_f 0.972, log ϵ 4.89, λ_{em} 455 nm) and very intense yellow fluorophore with the NMe_2 group (Φ_f 0.999, log ϵ 4.75, λ_{em} 555 nm). Fluorescence spectra and colors of **3**, **4**, and **7** are shown in Figure 2.

Table 2. Emission and Absorption Characteristics of Donor-Substituted Polycyano-tetrameric PEs (**4−7**) (in $CHCl_3$)[a]

comp	Φ_f[b]	λ_{em} (nm)	log ϵ	λ_{abs} (nm)	τ (ns)	k_r (s^{-1})	k_d (s^{-1})	k_r/k_d
4	0.972	455	4.89	375	1.29	7.54×10^8	2.17×10^7	34.71
5	0.960	403	4.91	360	1.23	7.78×10^8	3.24×10^7	24.00
6	0.982	434	4.87	371	1.36	7.22×10^8	1.32×10^7	54.56
7	0.999	555	4.75	425	1.78	5.61×10^8	5.62×10^5	999.0

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

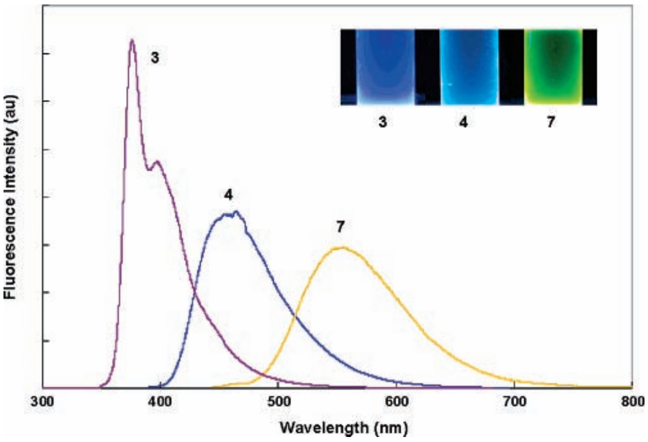

Figure 2. Fluorescence spectra and colors of **3**, **4**, and **7** in $CHCl_3$.

This sort of end-donor modification of polycyano OPEs is superior to the end-acceptor modification of polymethoxy OPEs[4a] 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.

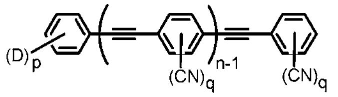

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Figure 3. Molecular design for the strongly fluorescent materials.

In regard to structure-emissivity relationship, we found out that the quantum yield (Φ_f) linearly increases with an increase in electron-donating ability of end-substituent X as shown in Figure 4 where the linear relationship between Φ_f and the Hammett substituent constants (σ_p-X)[8] is kept over the whole region of σ_p-X values including a cyano group.

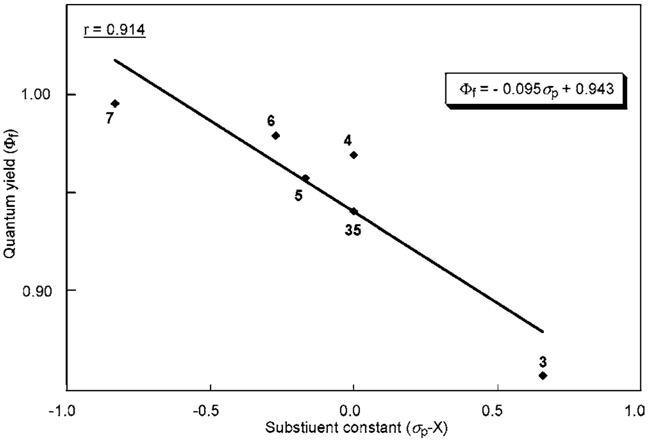

Figure 4. The relationship between quantum yield (Φ_f) and substiuent constant (σ_p-X) for the substiuent X of terminal benzene ring of the donor-substituted polycyano-tetrameric PEs (**4−7**) and **35** (X = H), and tetracyano-tetrameric PE **3** (X = CN). Hammett substituent constants (σ_p-X):[8] 0.66 (**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_2).

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 (Φ_f) of **6** (X = OMe) and **7** (X = NMe_2) is quite contrasting. Almost no solvent effect is observed for the absorption spectra of both **6** and **7**,

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(7) 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.

(8) 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	Φ_f	λ_{em} (nm)	log ϵ	λ_{abs} (nm)	k_r (s^{-1})	k_d (s^{-1})	k_r/k_d
6	benzene	0.972	420	4.84	371	6.72×10^8	1.94×10^7	34.71
	$CHCl_3$	0.982	434	4.87	371	7.22×10^8	1.32×10^7	54.56
	THF	0.972	460	4.89	369	7.55×10^8	2.17×10^7	34.71
	CH_3CN	0.973	490	4.89	364	7.55×10^8	2.10×10^7	36.04
	DMF	0.949	513	4.86	369	6.87×10^8	3.69×10^7	18.61
7	benzene	0.999	519	4.76	426	5.75×10^8	5.75×10^5	999
	$CHCl_3$	0.999	555	4.75	425	5.61×10^8	5.62×10^5	999
	THF	0.084	621	4.77	422	4.96×10^7	5.39×10^8	0.092
	CH_3CN	0.002	682	4.78	413	9.04×10^5	6.02×10^8	0.002
	DMF	0.002	699	4.73	423	1.16×10^6	5.36×10^8	0.002

[a] All spectra were measured at 295 K.

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 Φ_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 Φ_f, λ_{em}, k_r, and k_d could be explained by a difference in the dipole moment in the excited state (μ_e) and in the ground state (μ_g) of **6** ($\mu_e = 10.74$ D $< \mu_g = 11.52$ D) and **7** ($\mu_e = 12.89$ D $> \mu_g = 12.75$ D) (see Supporting Information).

In conclusion, we succeeded in the creation of a highly efficient violet fluorophore (**3**, Φ_f 0.86, λ_{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**, λ_{em} 455 nm) and yellow (**7**, λ_{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 (Φ_f) of **6** and **7** and a linear relationship between Φ_f and σ_p-X over the whole region of σ_p-X are other interesting findings.

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Supporting Information Available: Synthesis, spectral data, solvent dependency, plots of λ_{em} and Φ_f versus σ, 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.

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