Communication

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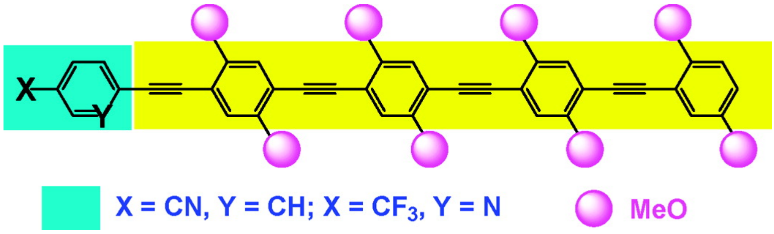

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Light-Emitting Efficiency Tuning of Rod-Shaped π Conjugated Systems by Donor and Acceptor Groups

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To date, research on light-emitting materials has been animated not only in chemistry[1] (e.g., molecular materials, probes, sensors, and tracers) but also in biological science (e.g., biosensing[2]) and materials science (e.g., optoelectronics[3]). For further development of these fields, creation of highly efficient light-emitting materials at the desired wavelength region should be indispensable, though other factors should also be taken into consideration. Since no general concept or method for this purpose has been established yet, first we have chosen oligo(*p*-phenylene ethynylene)s (OPEs, trimeric to pentameric systems) as the rod-shaped π systems and tried to tune their electronic structures by donor and acceptor groups, so that they emit very intense fluorescence ($\Phi_f \approx 1.0$, $\log \epsilon > 4.5$) at 460 nm as an example of the desired wavelength region. In connection with this trial, we examined whether any relationship would be found between the structure and fluorescence quantum yield (Φ_f) of OPEs modified by donor and acceptor groups, for the first time. Marder,[4] Bunz,[5] and others[6] have reported the relation of the spectra (λ_{abs} and λ_{em}) to the structure of donor−acceptor oligo- and poly(*p*-arylene ethynylene)s (OAEs and PAEs).

After various trials, we achieved our goal by a combination of side modification by MeO (donor) groups and end modification by a CN-substituted benzene ring or a CF_3-substituted pyridine ring (acceptor) of OPE rod-shaped molecules.[7] Herein we wish to report the results.

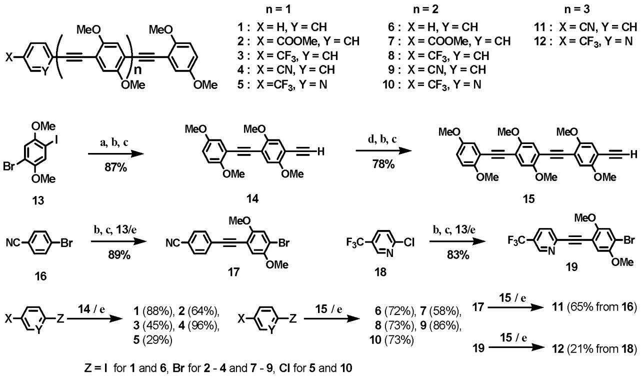
General synthesis of trimeric, tetrameric, and pentameric PE modified by EWG (X) at the end and by EDGs (2,5-dimethoxy groups at each benzene ring) at the side (abbreviated as E (EWG)/S (EDG) PEs) was effectively accomplished by a repeating Sonogashira Pd-coupling reaction,[8] as shown in Scheme 1 (for details, see Supporting Information).

Emission and absorption characteristics of the parent and the modified PEs together with emission lifetime (τ), radiative rate constant (k_r), and radiationless rate constant (k_d) are demonstrated in Table 1.

As seen in Table 1, the E (EWG)/S (EDG) modification evidently increases Φ_f and λ_{em} compared with those of the parent PEs (TriPE and TetraPE).[9] This tendency is bigger for the tetrameric system ($n = 2$) than for the trimeric system ($n = 1$). In particular, E (CN/Ph)/S (MeO) (**9**) and E (CF_3/Py)/S (MeO) (**10**) modifications are remarkable and effective to provide the highly efficient blue light emitters. We tried to examine the relation of Φ_f to the Hammett substituent constant (σ_p−X).[10]

The result is worth noting because the quantum yield (Φ_f) linearly increases with an increase in the electron-withdrawing ability of X, as shown in Figure 1 (correlation factor: $r = 0.986$ for $n = 1$, $r = 0.943$ for $n = 2$; slope: $\rho = 0.0431$ for $n = 1$, $\rho = 0.121$ for $n = 2$). To our knowledge, the finding of the linear relationship between Φ_f and σ values is unprecedented. An approximately linear relation for the plot of λ_{em} versus σ was also found as expected (see Supporting Information).

Scheme 1 [a]



[a] Reagents and conditions: (a) 2,5-dimethoxy phenylacetylene, $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, THF, rt, 7 h; (b) trimethylsilyl acetylene, $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, THF, rt, 7 h; (c) 1 M aq. KOH, MeOH, $CHCl_3$, rt, 0.5 h; (d) **13**, $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, THF, rt, 7 h; (e) $Pd(Ph_3P)_2Cl_2$, CuI, Et_3N, THF, reflux.

Table 1. Emission and Absorption Characteristics of Parent and Modified PEs (trimeric, tetrameric, and pentameric systems) by EWG at the End and by EDGs (MeOs) at the Side (in $CHCl_3$)

compound	Φ_f[a]	λ_{em} (nm)	$\log \epsilon$	λ_{abs} (nm)	τ (ns)	k_r (s^{-1})	k_d (s^{-1})
TriPE	0.50	348	4.59	328	2.57	1.95×10^8	1.95×10^8
1	0.76	401	4.58	370	2.63	2.89×10^8	9.12×10^7
2	0.78	428	4.70	376	2.00	3.91×10^8	1.10×10^8
3	0.78	411	4.56	376	2.75	2.83×10^8	7.99×10^7
4	0.79	434	4.80	381	1.58	4.98×10^8	1.33×10^8
5	0.76	436	4.66	383	2.19	3.47×10^8	1.10×10^8
TetraPE	0.61	387	4.77	345	1.70	3.59×10^8	2.30×10^8
6	0.81	430	4.74	390	1.82	4.45×10^8	1.04×10^8
7	0.85	441	4.84	395	1.45	5.88×10^8	1.04×10^8
8	0.86	435	4.71	395	1.95	4.41×10^8	7.18×10^7
9	0.91	447	4.71	398	1.95	4.67×10^8	4.62×10^7
10	0.82	455	4.71	401	1.95	4.21×10^8	9.23×10^7
PentaPE	0.83	388	4.80	350	1.58	5.24×10^8	1.07×10^8
11	0.96	458	4.96	414	1.10	8.76×10^8	3.65×10^7
12	0.99	459	4.92	415	1.20	8.23×10^8	8.32×10^6

[a] Quantum yield is calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4).

It was found that k_d rather than k_r[11] (see Supporting Information) varies with σ_p−X, as seen in Table 1. Thus, E (EWG)/S (EDG) modification of tetrameric PE was shown to bring about the significant improvement of light-emitting efficiency in the trimeric and tetrameric systems.

Figure 1 and Table 1 suggest a possibility that E (CN/Ph)/S (MeO) and E (CF_3/Py)/S (MeO) modification of tetrameric PE may provide the very intense blue light emitter ($\Phi_f \approx 1.0$, $\lambda_{em} = 460$ nm, $\log \epsilon \approx 5$), which is our final goal in the present investigation. This possibility was realized by preparing the pentameric systems **11** and **12** (see Scheme 1 and Table 1). The absorption

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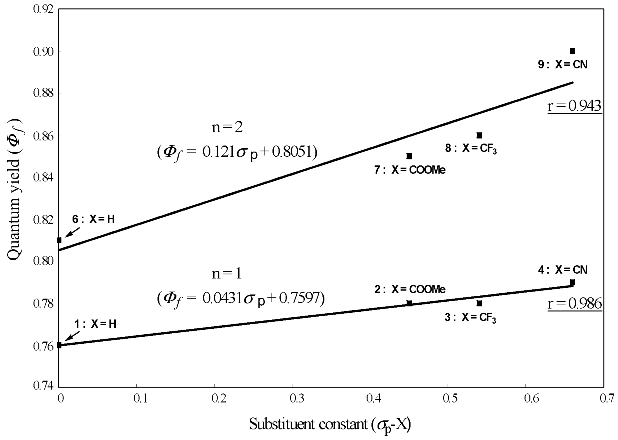

Figure 1. The relationship between quantum yield (Φ_f) and substituent constant for the electron-withdrawing substituent X (σ_p-X) for E (EWG)/S (EDG) PEs.

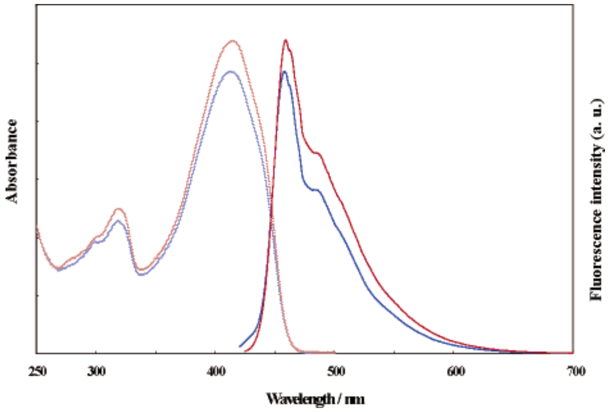

Figure 2. Absorption (left) and fluorescence (right) spectra of **11** (blue) and **12** (red) in CHCl$_3$.

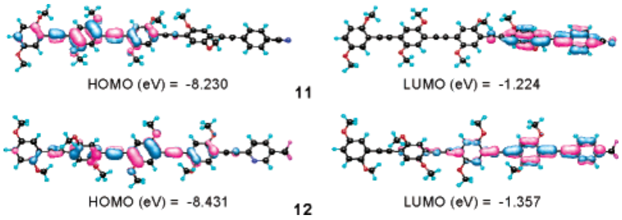

Figure 3. AM1 HOMO and LUMO diagrams for **11** and **12**.

and (sharp) fluorescence spectra of **11** and **12** are shown in Figure 2. The high Φ_f ($\approx$1.0) values for **11** and **12** are due to a marked decrease in their k_d value and to a substantial increase in their k_r values (see Table 1).

It is to be noted that contrary to the reported cases,[4b,d,12] Φ_f, λ_{em}, λ_{abs}, and log ϵ values for **11** and **12** are not so altered with benzene, CHCl$_3$, THF, CH$_3$CN, and DMF (change in solvent polarity) (see Supporting Information). Judging from the result, it is not likely to form much of a charge transfer excited state as expected from the HOMO/LUMO diagrams (Figure 3 and Supporting Information). INDO/S calculation indicates that the dipole moment of PentaPE in the excited state (μ_e = 0.57 D) is larger than that in the ground state (μ_g = 0.09 D), as expected. On the other hand, calculated dipole moments of E (EWG)/S (EDG) PEs in the excited state do not exceed those in the ground state (for example, μ_e = 0.66 D and μ_g = 1.99 D for **11**; see Supporting Information for others).

Such a dipole moment change in the excited and ground states of E (EWG)/S (EDG) PEs appears to be responsible for little solvent dependency to the spectra of **11** and **12**. From these arguments, it is inferred that the acetylenic structure of E (EWG)/S (EDG) PEs in the ground state (see Supporting Information) may also be held in the excited state as reported for TriPE.[13]

In conclusion, we succeeded in the creation of highly efficient light emitters by E (EWG)/S (EDG) modification of rod-shaped OPEs. We also made very interesting findings on the relationships between (1) Φ_f and Hammett σ constant, and (2) light-emitting characteristics (λ_{em}, Φ_f) and solvent polarity. These should be valuable for the molecular design of highly efficient light emitters.

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Supporting Information Available: Synthesis, NMR data, HR MS data, absorption and fluorescence spectra, plot of λ_{em} versus σ and Φ_f versus σ, and MO calculation for oligo-PEs 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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