



Environment-responsive multicolor fluorescent dyes based on nitrophenyl or nitrophenylethynyl oligothiophene derivatives: correlation between fluorescence and π -conjugation length

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ABSTRACT

We report the unique environment-responsive fluorescence of nitrophenyl or nitrophenylethynyl oligothiophene derivatives with different numbers of thiophene rings. With an increase in the number of thiophene rings, the maximum fluorescence quantum yield (Φ_F) was obtained even in low-polarity solvents. For 5,5'-bis(4-nitrophenyl)-2,2'-bithiophene (**BNP2T**), a nitro-group-containing fluorescent dye without a strong donor moiety, the maximum Φ_F of 0.43 was observed in CHCl_3 , which is a large value, and multicolor fluorescence with a moderate quantum yield was observed in various solvents. Thus, we can design functional nitrophenyl-based fluorescent dyes that would find applications as bioimaging probes, polarity sensors, etc.

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Environment-responsive fluorescent dyes have received considerable attention as they find potential applications as fluorescence sensors and in vivo imaging probes.¹ Fluorescence solvatochromism is an environment-sensitive phenomenon. Because of their large transition moment, dyes showing strong fluorescent solvatochromism have both donor and acceptor moieties in the same π -conjugated system.^{2,3} While many dyes bearing various substituents have been reported, there are very few reports on dyes with a nitro group as the acceptor moiety.⁴ This is because the nitro group is a very strong electron-withdrawing (deactivating) group, which can cause a dramatic change in the photophysical properties when introduced into a π -extended system, such as marked fluorescence suppression or redshift of the absorption spectra.⁵ Extensive studies have been carried out to understand the unique effect of the nitro substituent on the photophysical properties of π -extended compounds, including electron absorption,⁶ excited-state dynamics,⁷ and phosphorescence.⁸ In these compounds, the main mode of relaxation from an excited state to the ground state is internal conversion (IC), which immediately follows intersystem crossing (ISC); hence, other modes of relaxation such as fluorescence are not usually observed.⁹ However, in our previous study, we observed strong and specific solvent-dependent fluorescence when a nitro group was introduced into the phenyl moiety of a π -conjugated system with a weak donor-strong acceptor system.¹⁰ In this case, the

fluorescence depended strongly on the solvent polarity, because of the strong electron-withdrawing nature of the nitro group. Introduction of a nitro group via a linker moiety such as a phenyl group is an effective means of inducing fluorescence in nitro-group-containing compounds. Interestingly, the optimal solvent in which fluorescence was induced from nitro-group-containing compounds changed depending on the chromophore. Thus, it is possible to develop novel environment-responsive dyes based on the specific fluorescence of the nitro group.

Oligothiophene is a suitable core structure that can be used to develop the abovementioned class of dyes because they show strong fluorescence with various substituents and exhibit weak donor capacity.^{4c,11} Additionally, the π -conjugation length of oligothiophene can be easily tuned by modifying the number of thiophene rings, which means that it is possible to change the chromophore systematically.

In this study, we synthesized oligothiophenes with different numbers of thiophene rings and introduced a nitrophenyl moiety at both ends of the molecules directly (**BNPnT**) or through an ethynyl linker moiety (**BNPEnT**). Then, we investigated the influence of π -conjugation length on the fluorescence properties. We succeeded in the development of an environment-responsive multicolor fluorescence dye with a moderate quantum yield in various solvents, **BNP2T**, which showed strong fluorescence in weak polar solvents.

BNPnT was synthesized from the corresponding dibromothiophene and *p*-nitrophenyl boronic acid by Pd-catalyzed Suzuki–Miyaura cross coupling.^{12,13} For additional π -extension, we

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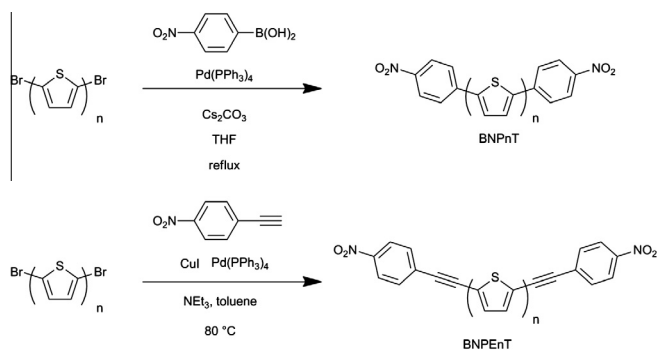
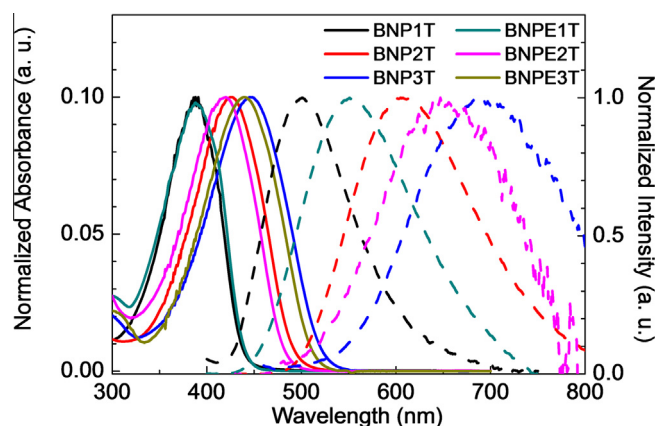
Scheme 1. Synthesis of **BNPnT** and **BNPEnT**.

Figure 1. UV-vis absorption and fluorescence spectra of **BNPnT** and **BNPEnT** in CH_2Cl_2 . **BNPE3T** did not show fluorescence. Excitation wavelength for fluorescence measurements was the absorption maxima.

Table 1
Photophysical properties of **BNPnT** and **BNPEnT** in various solvents

Compound	Solvent	λ_{abs} (nm)	$\lambda_{\text{em}}^{\text{a}}$ (nm)	$\Delta\nu$ (cm^{-1})	$\Phi_{\text{F}}^{\text{a,b}}$	$\tau^{\text{c,d}}$ (ns)	k_{f} (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
BNP1T	THF	387	485	5220	0.01	--	--	--
	CHCl_3	386	498	5830	0.03	0.26	1.2	37.3
	CH_2Cl_2	388	501	5810	0.06	0.24	2.4	39.3
	DMF	393	528	6510	0.26	0.98	2.7	7.5
	DMSO	396	549	7040	0.40	1.44	2.8	4.2
BNP2T	PhCH_3	420	497, 523	3690	0.22	0.51	4.2	15.3
	THF	423	543	5220	0.29	0.85	3.4	8.4
	CHCl_3	424	598	6860	0.43	1.57	2.8	3.6
	CH_2Cl_2	425	605	7000	0.40	1.64	2.5	3.6
	DMF	431	635	7450	0.11	0.61	1.8	14.6
BNP3T	DMSO	436	667	7940	0.09	0.52	1.7	17.6
	PhCH_3	442	528, 559	3690	0.39	0.86	4.5	7.1
	THF	443	587	5540	0.25	0.86	2.9	8.8
	CHCl_3	444	667	7530	0.08	0.41	1.8	22.6
	CH_2Cl_2	446	684	7940	0.04	0.34	1.1	28.3
BNPE1T	THF	383	493	5830	0.01	0.28	0.4	35.3
	CHCl_3	390	538	7050	0.12	0.69	1.7	12.8
	CH_2Cl_2	389	553	7620	0.16	0.78	2.1	10.7
	DMF	386	578	8610	0.03	0.29	1.0	33.5
BNPE2T	DMSO	388	619	9620	0.02	0.21	0.9	46.8
	PhCH_3	413	486, 514	3640	0.34	0.33	10.2	20.2
	THF	411	556	6350	0.19	0.62	3.1	13.0
BNPE3T	CHCl_3	412	634	8500	0.04	0.18	2.4	50.3
	CH_2Cl_2	420	647	8350	0.01	0.22	0.4	45.1
	PhCH_3	436	518, 547	3630	0.44	0.33	13.4	16.9
	THF	436	609	6520	0.05	0.80	0.6	11.9

Data corresponding to no-fluorescence cases have been omitted.

^a The solutions were prepared with 0.1 absorbance at λ_{abs} . $\lambda_{\text{ex}} = \lambda_{\text{abs}}$.

^b Measured as absolute quantum yield.

^c Detection fluorescence wavelength is λ_{em} .

^d Excitation wavelength is 355 nm.

inserted an ethynyl moiety between the oligothiophene and nitrophenyl moieties to obtain **BNPEnT** by Pd- and Cu-catalyzed Sonogashira cross coupling of the corresponding dibromothiophene and 1-ethynyl-4-nitrobenzene.^{14,15} The number of thiophene rings was varied ($n = 1-3$), and the photophysical properties of the resulting compounds were evaluated (Scheme 1).

Figure 1 shows the UV-vis absorption and fluorescence spectra of **BNPnT** and **BNPEnT** in CH_2Cl_2 , and Table 1 summarizes the photophysical data in various solvents. Unfortunately, the photophysical measurements were not too accurate because of the poor solubility of these compounds in polar solvents such as acetonitrile and methanol and in non-polar solvents such as hexane. Extension of π -conjugation is clearly indicated by the redshift of the spectra with an increase in the number of thiophene rings. While the UV-vis spectra showed a slight shift upon the introduction of an ethynyl moiety, the fluorescence spectra showed a much larger shift. This result indicated that the excited state of **BNPEnT** is more polarized as compared to that of **BNPnT**, thus facilitating the introduction of an ethynyl moiety, which resulted in a large Stokes shift. In the case of **BNPE1T**, the maximum Stokes shift was about 9620 cm^{-1} in DMSO.

While the UV-vis absorption of **BNPnT** and **BNPEnT** showed only slight differences in various solvents, the fluorescence spectra varied greatly depending on the solvent. The spectra of all compounds were redshifted with increasing solvent polarity, indicating internal charge transfer (ICT) from the thiophene moiety to the nitrophenyl moiety, because the nitro group is a strong acceptor and thiophene is a weak donor. This ICT character was confirmed by Lippert-Mataga equation and $E_{\text{T}}(30)$ increasing number of thiophene rings (see supporting information). The fluorescence quantum yield (Φ_{F}) also depended on the solvent polarity. In the case of **BNPnT**, solvent-polarity-dependent maximum Φ_{F} of **BNPnT** decreased with an increase in the number of thiophene rings. The maximum Φ_{F} of **BNP1T**, **BNP2T**, and **BNP3T** was 0.396 in DMSO, 0.434 in CHCl_3 , and 0.387 in PhCH_3 , respectively. This solvent dependence was also

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