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# Unique solvent-dependent fluorescence of nitro-group-containing naphthalene derivatives with weak donor-strong acceptor system

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### ABSTRACT

We synthesized nitro-group-containing  $\pi$ -conjugated naphthalene derivatives with a weak donor–strong acceptor system and investigated their photophysical properties. The nitro group was introduced into naphthalene through the phenyl or phenylethynyl moiety at the C2 and C7 positions as the strong acceptor moiety, and a methoxy group was introduced into naphthalene directly at the position opposite to the nitro group, as a weak donor moiety. While 2-(4-nitrophenyl)naphthalene did not show fluorescence in various solvents, 2-methoxy-6-(4-nitrophenyl)naphthalene showed fluorescence in weakly polar solvents ( $\Phi_F = 0.11$  in CH<sub>2</sub>Cl<sub>2</sub>), with a large Stokes shift ( $\Delta v = 12,000$  cm<sup>-1</sup>). Additionally, 2-methoxy-6-(4-nitrophenyl)naphthalene did not show fluorescence is remarkable for environmental fluorescence sensor applications.

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Recently, fluorescent probes showing fluorescence solvatochromism or on/off switching as environment-sensitive sensors or reporters are investigated.<sup>1</sup> In many cases, these probes have a fluorophore moiety, which has a donor-acceptor system in the  $\pi$ -conjugated system.<sup>2,3</sup> While many fluorescent dyes with various functional groups as the donor and acceptor moieties have been reported, very few Letters focus on nitro-group-containing fluorescent dyes.<sup>4</sup> Generally,  $\pi$ -extended compounds in which the nitro group is introduced directly into the fluorophore show very weak fluorescence as compared to unsubstituted compounds, since the nitro group elongates the path for internal conversion immediately after intersystem crossing.<sup>5</sup> Nevertheless, in our previous study, we found that a fluorene in which the nitro group is introduced through a phenyl moiety shows specific solvent-dependent fluorescence.<sup>6</sup> Interestingly, the fluorescence properties of nitrogroup-containing compounds depend on the manner in which the nitro group is introduced into the fluorophore. Introduction of a nitro group into a fluorophore through a  $\pi$ -conjugated linker moiety such as a phenyl group is an effective method to induce fluorescence in a nitro-group-containing dye. On the other hand, the reported dyes having donor-acceptor systems have been synthesized with a strong donor such as an amino group and a nitro group. These dyes show fluorescence properties similar to those of dyes with other strong acceptors such as a cyano group. Hence, we believe that it is possible to synthesize a novel dye showing environmental fluorescence by introducing a nitro group through a  $\pi$ -conjugated linker moiety for constructing a donor-acceptor system and by using a weak donor group.

In this study, we synthesized naphthalene derivatives in which a nitro group was introduced through a phenyl or phenylethynyl moiety as the acceptor moiety and a methoxy group as the weak donor group and found that the resulting compounds show unique solvent-dependent fluorescence. Naphthalene was used as the core structure to construct simple nitro-group-containing donor–acceptor systems. Nitro group was introduced through phenyl moiety or phenylethynyl moiety to naphthalene at the C2 and C7 positions (**1a–4a**). In the previous study, phenyl group was an effective linker to induce unique fluorescence and ethynyl moiety was used as an additional linker because that is a famous moiety to expand  $\pi$ -conjugation. Additionally, a methoxy group was introduced to naphthalene at the C3 and C6 positions (**1b–4b**) to construct a donor–acceptor system as shown in Scheme 1. Their photophysical properties were evaluated in various solvents.

The naphthalene derivatives were synthesized from corresponding bromonaphthalenes using transmetal catalyzed Suzuki–Miyaura<sup>7</sup> and Sonogashira<sup>8</sup> cross coupling reactions, respectively.

UV-vis absorption and fluorescence spectra of **1–4** were measured in toluene, dichloromethane, tetrahydrofuran, chloroform, acetonitrile, and methanol. Figure 1 shows the representative UV-vis absorption and fluorescence spectra of all the compounds in dichloromethane. Table 1 summarizes the photophysical properties of the compounds which showed fluorescence in various solvents. The lowest-energy absorption band of **1a** was observed

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Scheme 1. Synthesis of nitrophenyl naphthalene 1 and 3, and nitrophenylethynyl 2 and 4.



**Figure 1.** UV-vis absorption (solid line) and fluorescence (dashed line) spectra of **1a-4b** in CH<sub>2</sub>Cl<sub>2</sub>. The compounds **1a** and **3a** did not show fluorescence. Excitation wavelength for fluorescence measurements was absorption maxima.

at around 320 nm in various solvents. The absorption maxima of **1b** and **2a** were redshifted about 20 nm as compared to that of **1a**, indicating extension of the  $\pi$ -electronic conjugation by the

Table 1								
Photophysical	properties	of	1b-4b	in	various	solvents	at	25 °

methoxy or ethynyl group. While the lowest absorption maxima of **3** and **4** were almost the same as those of **1** and **2**, the extinction coefficients of the lowest-energy absorption bands of **3** and **4** were greater than those of **1** and **2**. These results indicated that the donor-acceptor systems at the C2–C6 and C3–C7 positions are separated by the  $\pi$ -electronic conjugation system.

In the case of **2a** and **4a**, fluorescence could be observed only in dichloromethane or chloroform, and the fluorescence quantum yield, too, was very low ( $\Phi_{\rm F}$  <0.01). The weak fluorescence of **1a**– **4a** could be attributed to the nitrophenyl-group-induced rapid intersystem crossing from a singlet excited state to a triplet excited state.<sup>5</sup> Therefore, the linker strategy was an effective method to induce fluorescence of nitronaphthalene derivatives because 1-nitronaphthalene showed no fluorescence under normal condition. The Stokes shift of almost nitronaphthalene derivatives over  $10.000 \text{ cm}^{-1}$ . This is because the rapid distortion of nitro group by photoexcitation caused dramatic change in their structure. The solvent-dependent fluorescence properties were unique to the nitrophenyl-substituted naphthalene derivatives. Upon the introduction of donor groups at the C2 and C6 positions of the nitrophenyl naphthalene derivatives, the fluorescence spectra showed a redshift and  $\Phi_{\rm F}$  increased. The maximum fluorescence quantum yield of **1b**  $(\Phi_{\rm F} = 0.11)$  was obtained in dichloromethane. The fluorescence intensity decay followed single-exponential kinetics. The fluorescence lifetime  $(\tau)$  increased with an increase in  $\Phi_{\rm F}$ . The fluorescence rate constant  $k_{\rm f}$  and nonradiative relaxation constant  $k_{\rm nr}$  were calculated from  $\Phi_{\rm F}$  and  $\tau$ .<sup>9</sup> The main factor that contributed to the fluorescence enhancement was the decrease in  $k_{\rm nr}$ . In particular, in the case of **1b** in dichloromethane and chloroform,  $k_{nr}$  was one order of magnitude smaller than that in the other cases. These results indicated that the donor-acceptor system served to decrease  $k_{nr}$ , thereby increasing  $\Phi_{\rm F}$ . However, in our previous study, <sup>6a</sup> 2,7-bis(4-nitrophenyl)fluorene derivative exhibited the highest  $\Phi_{\rm F}$  in DMF, not in chloroform. As a result, there is no specific interaction for suppressing  $k_{\rm nr}$  between nitro group and halogen solvent in the excited state. It is difficult to classify the fluorescence properties of nitrophenylgroup-containing chromophores in the present stage.

Figure 2 shows the UV–vis absorption and fluorescence spectra of **1b** in various solvents. While the absorption spectra did not show any obvious dependence on the solvent, solvatochromic fluorescence spectra, which showed strong dependence on the solvent polarity, were observed. The Stokes shift of **1b** in various solvents was very large, with the maximum value approaching 306 nm (13,870 cm<sup>-1</sup>) in CH<sub>3</sub>CN. This value of Stokes shift was larger than

Compound	Solvent	$\lambda_{abs}$ (nm)	$\lambda_{em}^{a}(nm)$	$\Delta v (\text{cm}^{-1})$	${\Phi_{ m F}}^{ m a,b}$	$\tau^{a}(ns)$	$k_{\rm f}  (10^8  { m s}^{-1})$	$k_{\rm nr}  (10^8  {\rm s}^{-1})$
1b	THF	344	534	10,340	0.006	0.33	0.18	30.1
	CHCl <sub>3</sub>	346	573	11,450	0.055	1.87	0.29	5.05
	CH <sub>2</sub> Cl <sub>2</sub>	345	591	12,070	0.11	2.04	0.54	4.36
	CH <sub>3</sub> CN	341	647	13,870	0.006	0.22	0.27	45.2
2a	CHCl <sub>3</sub>	338	536	10,500	0.005	0.25	0.20	39.8
	$CH_2Cl_2$	339	546	11,180	0.006	0.35	0.17	20.8
2b	THF	356	533	9330	0.025	0.57	0.44	17.1
	CHCl <sub>3</sub>	360	592	10,890	0.030	0.77	0.39	12.6
	$CH_2Cl_2$	356	635	12,340	0.015	0.32	0.47	30.8
3b	CHCl <sub>3</sub>	336	544	9270	0.010	0.62	0.16	16.0
	$CH_2Cl_2$	337	578	10,050	0.009	0.53	0.17	18.7
4a	$CH_2Cl_2$	347	527	9840	0.007	0.27	0.26	37.8
4b	THF	361	514	8250	0.009	0.25	0.36	39.6
	CHCl₃	362	577	10,290	0.053	0.90	0.59	10.5
	$CH_2Cl_2$	360	593	10,910	0.019	0.38	0.50	25.8

Data corresponding to no-fluorescence cases have been omitted.

<sup>a</sup> The solutions were prepared with 0.1 absorption at  $\lambda_{abs}$ .  $\lambda_{ex} = \lambda_{abs}$ .

<sup>b</sup> Measured as absolute quantum yield.



Figure 2. UV-vis absorption (solid line) and fluorescence (dashed line) spectra of 1b in various solvents. Excitation wavelength for fluorescence measurements was absorption maxima.

no substituted nitronaphthalene derivatives. These results indicated that the introduction of methoxy groups at the C2 position induced internal charge transfer (ICT) character. Such solvatochromic fluorescence spectra and large Stokes shift were also observed in the case of 2b and 4b. To analyze the ICT character in further detail, we investigated the correlation between the energy of the fluorescence emission maximum,  $E_{\rm F}$ , and the Dimroth-Reichardt solvent parameter  $E_{T}(30)$ , shown in Figure 3.<sup>10</sup> A linear correlation between  $E_{\rm F}$  and  $E_{\rm T}(30)$  was observed for **1b**. This result suggested that the solvatochromic fluorescence resulting from the donor groups at the C2 position of **1b** induced ICT. In general, the  $\Phi_{\rm F}$  value of a fluorescent dye showing ICT character increases with decreasing solvent polarity. The maximum  $\Phi_{\rm F}$  of **1b** ( $\Phi_{\rm F}$  = 0.11) was observed in chloroform, which is a weakly polar solvent, and **1b** showed very weak fluorescence quantum yields ( $\Phi_{\rm F}$  <0.01) in other polar (acetonitrile) or non-polar (toluene) solvents. Thus, the unique fluorescence properties of nitrophenyl-substituted naphthalene derivatives could be explained by the solvent dependence of the fluorescence quantum yield induced by the nitrophenyl groups and ICT character.

In conclusion, we successfully synthesized nitro-group-containing naphthalene derivatives that showed unique solvent-dependent fluorescence. In particular, compound 1b showed fluorescence with a large Stokes shift in weakly polar solvents but no fluorescence in polar and non-polar solvents. The compound showing fluorescence in weakly polar solvent only with a large Stokes shift is remarkable, and it is expected that abovementioned compounds applied fluorophore of high resolution fluorescence sensor with a small signal noise ratio because of their large Stokes shift. Our results suggested that the combination of nitro group with linker method and donor moiety has a potential to develop novel high resolution and desirable environmentally-responsive fluorescence sensor<sup>6a</sup> which was a useful tool for in vivo imaging. Further investigations of the fluorescence properties of nitrophenyl-substituted naphthalene derivatives, in addition to quantum chemical calculations and transient absorption studies, are in progress.

# Supplementary data

Supplementary data (experimental details, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, UV–vis absorption and fluorescence spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.096.

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