

检测钠离子的荧光探针:含稠合外环的硼-二吡咯亚甲基染料的合成与光物理性质研究

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摘要: 本文报道了两种中位为苯并冠醚亚单元取代的含稠合外环的硼-二吡咯亚甲基染料的合成、光谱和电化学性质。研究结果表明:在荧光团中引入吸电子的酯基使化合物 **2** 成为一种高灵敏性的检测钠离子的荧光探针。

关键词: 硼-二吡咯亚甲基染料; 稠合外环; 电子转移; 荧光探针

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Fluorescent Probe for Na⁺: Synthesis and Spectroscopic Studies of Exocyclic Ring-Fused Boron Dipyrromethene Dyes

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Abstract: Two new exocyclic ring-fused boron-dipyrromethene (BDP) dyes with benzo crown ether subunit at *meso*-position were prepared. Their spectroscopic and electrochemical properties were investigated. The introduction of the electron withdrawing ester groups to the chromophore makes compound **2** to be a very sensitive fluorescent probe for Na⁺ analysis.

Key words: boron-dipyrromethene (BDP) dyes; fused exocyclic rings; electron transfer; fluorescent sensor

0 Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BDP) dyes are both rigid cyanine-type dyes with a fixed planarity of the chromophoric π -electron system and extremely fluorescent materials^[1] and have found various applications in many different areas, for example,

as laser dyes^[2], as molecular probes for biochemical researches, especially in tagging proteins and DNA sequencing^[3], fluorescent sensors^[4], optical devices^[4,5] and dopants in liquid crystals^[6]. In recent years, an increasing number of publications have reported the synthesis^[3a,3b,7] of BDP-based fluorescent probes and their applications as selective and efficient sensors for

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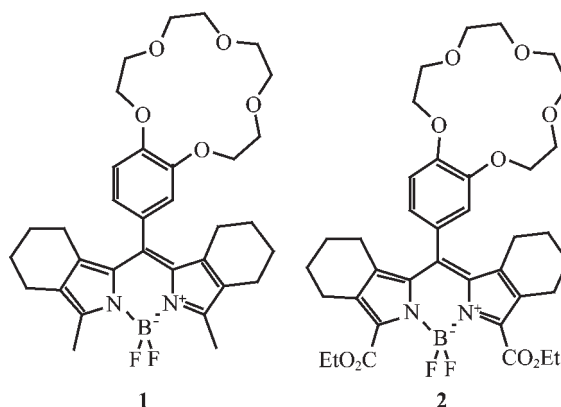
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ionic species^[8]. One important reason is that BDP dyes have many advantageous photophysical and chemical characteristics, such as high fluorescence quantum yields, high absorption coefficients, high stability against light and chemical reactions^[9], and these dyes are readily soluble in a large variety of solvents of different polarity^[1c]. In addition, their absorption and emission wavelengths can be tuned by a variety of different substituents not only on the *meso*-position of the indacene core but also on the pyrrole side, and the structural modifications of these compounds are known to generate dyes with emission peaks ranging from green to the NIR region^[3a,3b,5,9b]. Recently, Burgess et al and we have reported a series of BDP derivatives with 3,5-diaryl groups or restricted ring-fused systems which devote extensively to the engineering of BDP structures as well as examination of their salient physical and spectroscopic properties^[3a,3b].

It is well demonstrated that different substitutions such as 4'-azacrown ether^[4c,4e,10] and 4'-azathiacycrown ether^[4a] at *meso* position showed interesting photoinduced electron transfer (PET) mediated fluorescence off/on switch, thus acting as sensors for alkaline-earth-metal ions and soft transition metal cations, respectively. More importantly, a variety of BDP derivatives with selective fluoroionophore for sodium ion have been extensively developed to monitor this vital and widespread cation in nature^[4c,4e]. Among the reported fluorescent indicators for Na⁺, all-oxygen containing benzo crown ether that forms a rigid cavity around Na⁺ has been used as a receptor. However, the sensitivity of Na⁺ fluoroionophore with the receptor linked to a BDP chromophore is very poor due to the silent fluorescent switching resulting from the weak electron-donating ability of the benzo crown ether moiety. In order to compensate for the weaker donor strength, we attempted to increase the electron affinity of the BDP chromophore by introducing the electron-withdrawing ester group (**2**), and hence improving the sensitivity to Na⁺ while keeping its selectivity. In addition, to the best of our knowledge, examples of boron-dipyrromethene analogous fused with exocyclic rings, especially at positions 1, 2, 6, 7 are very rare^[4e]. Herein, we present the

synthesis, spectroscopic and electrochemical properties of **2** and its analogue **1** carrying BDP chromophore with fused exocyclic rings. Furthermore, their complexation properties with Na⁺ have been investigated.



1 Experimental

1.1 Instruments

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. Melting points were determined with a Reichert Thermo-mover apparatus without correction. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX500 spectrometer at ambient temperature. NMR chemical shifts are expressed in ppm relative to TMS as the internal standard. The MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager De pro spectrometer. IR spectra were recorded on Bruker Vector 22 spectrometer with KBr pellets in the 4 000 ~400 cm⁻¹ region. UV-Visible spectra were carried out on a UV-3100 spectrophotometer. Fluorescence spectra were measured on an Aminco Bowman 2 Luminescence spectrophotometer with a xenon arc lamp as the light source. The fluorescence quantum yields (Φ_f) were determined relative to rhodamine B in ethanol. The complex stability constants were determined from fluorescence measurements. The complex stability constants *K* were determined by titrating a dilute solution (typically 10⁻⁵ mol · L⁻¹) of ligand by adding aliquots of metal ion solution. The titration data were fitted according to the procedure described in the reference^[11]. Cyclic voltammetry were carried out in 0.1 mol · L⁻¹ TBAP (tetra-*n*-butylammonium perchlorate) in

acetonitrile on a Perkin-Elmer electrochemical analysis system model 283 with a platinum disk as the working electrode, Ag/AgCl as the quasi-reference electrode, and a platinum wire as the counterelectrode. Redox potentials were referenced internally against ferrocenium/ferrocene (Fc^+/Fc). All measurements were performed under an inert atmosphere with a scan rate of $250 \text{ mV} \cdot \text{s}^{-1}$ at room temperature.

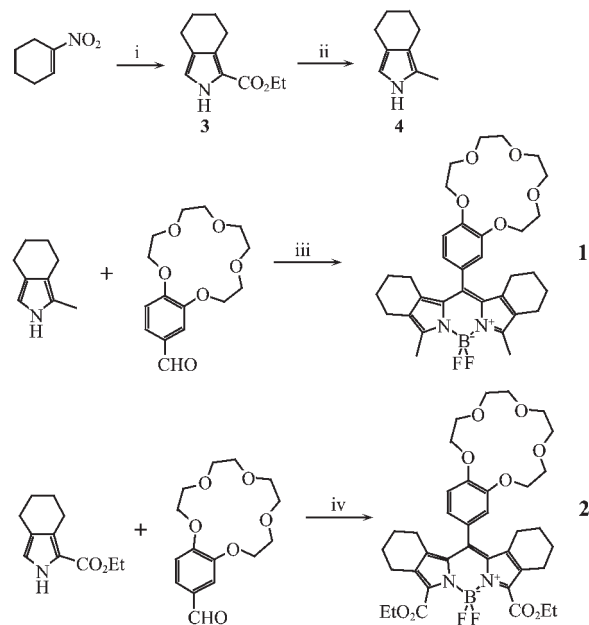
1.2 Reagents and materials

All syntheses were carried out under an atmosphere of nitrogen. Unless otherwise noted, all reagents or solvents were of analytical grade and were used as received. Dry CH_2Cl_2 was obtained by refluxing and distilling over CaH_2 under an inert atmosphere. Dry tetrahydrofuran (THF) was distilled from sodium/benzophenone. The solvents used for photophysical measurement were of spectroscopic grade and used without further purification. 4-formyl-benzo-15-crown-5 was prepared according to the procedure described in the literature^[12]. 2-Ethoxycarbonyl-4,5,6,7-tetrahydroisindole was synthesized according to the literature^[13].

1.3 Synthesis

The synthetic procedures for the preparation of **1** and **2** are given in Scheme 1. 2-methyl-4,5,6,7-tetrahydro-2H-isindole (**4**) was obtained as pale red liquid by refluxing 2-ethoxycarbonyl-4,5,6,7-tetrahydroisindole (**3**) with excess of LiAlH_4 in dry THF and purified by silica gel column chromatography. BDP **1** was prepared according to a published procedure^[4c] by acid-catalyzed condensation of **4** with 4-formyl benzo crown-5 and oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by treatment with Et_3N and $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The crude product was purified by column chromatography on silica gel elution with 50% EtOAc /petroleum ether and recrystallized from CHCl_3 /hexane to give **1** as red solid in 40% yield. m. p. 170°C ; ^1H NMR (500 MHz, CDCl_3): $\delta=6.93$ (d, 1H, $J=8.1$ Hz), 6.78 (d, 1H, $J=8.1$ Hz), 6.76 (s, 1H), 3.82~4.21 (m, 16H), 2.49 (s, 6H), 2.35 (t, 4H), 1.69 (t, 4H), 1.62 (m, 4H), 1.44 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): 152.42, 150.1, 148.98, 140.46, 138.65, 129.70, 127.86, 127.66, 120.52, 113.01, 112.93, 70.61, 70.44,

69.76, 69.52, 68.96, 68.89, 68.29, 68.02, 23.69, 22.72, 22.18, 20.94, 12.08. IR (neat): $\nu=1549$, 1480 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1202 cm^{-1} (B-F); MALDI-TOF MS: m/z 595.32 $[\text{M}+\text{H}^+]$; elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{41}\text{BF}_2\text{N}_2\text{O}_5$: C 66.67, H 6.95, N 4.71; found: C 66.74, H 6.92, N, 4.75.



Reaction conditions: (i) $\text{CNCH}_2\text{CO}_2\text{Et}$, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) in dry THF at r.t.; (ii) LiAlH_4 in dry THF, reflux; (iii) TFA, DDQ, $(\text{Et})_3\text{N}$, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, in dry CH_2Cl_2 at r.t.; (iv) TFA, DDQ, $(\text{Et})_3\text{N}$, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, reflux in dry CH_2Cl_2

Scheme 1 Synthetic route for the preparation of **1** and **2**

Compound **2** was synthesized by refluxing **3** with 4-formyl-benzo-15-crown-5 in CH_2Cl_2 in the presence of catalytic amount of trifluoroacetic acid (TFA) under nitrogen, followed by oxidation with DDQ, and subsequently treatment with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in the presence of Et_3N at room temperature. The crude product was purified by silica gel flash column chromatography using ethyl acetate-petroleum ether (6:4, V/V) as eluent and recrystallized from CHCl_3 /hexane to yield compound **2** as red solid in 25% yield. m.p. 138°C ; ^1H NMR (500 MHz, CDCl_3): $\delta=6.97$ (d, 1H, $J=8.1$ Hz), 6.77 (d, 1H, $J=8.2$ Hz), 6.72 (s, 1H), 4.45 (q, 4H), 3.81~4.22 (m, 16H), 2.59 (t, 4H), 1.73 (t, 4H), 1.58 (m, 8H), 1.43 (t, 6H); IR (neat): $\nu=1544$, 1484 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1204 cm^{-1} (B-F), $1720 (\text{C}=\text{O})$; MALDI-TOF MS: m/z 692.07 $[\text{M}^+ + \text{H-F}]$; elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{45}\text{BF}_2\text{N}_2\text{O}_9$:

C 62.54, H 6.38, N 3.94; found C 62.40, H 6.44, N 3.88.

2 Results and discussion

2.1 Spectroscopic properties

The absorption and emission spectra of **1** and **2** in nonpolar and polar solvents are listed in Table 1.

As shown in Fig.1, the absorption spectrum of **1** exhibits a strong narrowed band centered at 525 nm and a shoulder on the high-energy side centered at about 496 nm. In addition, a considerably weaker and broad absorption band is found at about 400 nm, which can be attributed to the S_0 - S_2 transition involved with the exocyclic ring skeleton. The absorption maximum of **1** was red shifted for 10~20 nm relative to those of the classic BDP dyes carrying only alkyl substituents on the indacene core^[14] due to the introduction of the fused exocyclic rings on the pyrrole side. The absorption bands are slightly shifted hypsochromically with the increase of the solvent polarity. The similarity of **1** to classic BDP dyes in the absorption spectrum indicates the absence of donor-acceptor interaction in the ground state due to the decoupled structure between the indacene plane and *meso* subunit. Excitation of **1** yields the typical fluorescence spectra of the classic BDP, with a narrow and slightly Stokes-shifted band of mirror image. The intensity and position of the fluorescent spectra are almost independent of the solvent polarity, indicating that emission occurs from the weakly polar, relaxed Franck-Condon excited state. The fluorescence maximum of **1** is observed at 543 ± 2 nm in hexane, which is comparable to that of the tetramethyl diethyl-(8-phenyl)-substituted derivatives^[15]. The Stokes-shift between the absorption and emission maxima of **1** is smaller than those of the other reported BDP dyes^[2a]. This may be due to

the fused exocyclic rings, which block a non-radiative deactivation of the excited states by controlling the rate of internal conversion. In addition, the almost independence of the solvent polarity for Stokes shift suggests that there is no difference in the permanent dipole moments between the ground and the excited state^[16]. Surprisingly, compound **1** that carries the electron-donating benzo crown moiety still displays a strong emission originated from the BDP locally excited (LE) state in CH_3CN , indicating that there is virtually no photo-induced electron transfer from the weak benzo crown donor to the dipyrromethene chromophore.

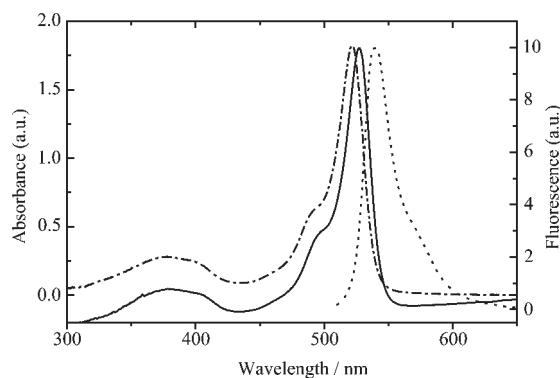


Fig.1 Absorption spectra of **1** in hexane (solid line) and CH_3CN (dash-dotted line) and the emission spectra of **1** in CH_3CN (dotted line). The emission spectra of **1** in hexane is identical in shape and position with that in CH_3CN , and is omitted for clarity

The absorption and emission spectra of **2** in hexane are similar to those of **1**, showing the typical spectroscopic features for BDP chromophore (Fig.2). However, the introduction of the ester groups in **2** gives rise to about 20 nm red-shift in both the emission and absorption maxima with decreased molar extinction coefficients compared to **1**. In contrast to **1**, compound **2** displays very weak residual fluorescence near 560

Table 1 Absorption and emission properties of **3** and **4** in hexane and acetonitrile

Compound	Solvent	$\varepsilon_{\text{max}}(\text{abs}) / (\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1})$	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}$	Φ_{f}	Stokes shift / nm
1	Hexane	91 700	525	544	0.92	19
	CH_3CN	91 600	522	539	0.89	17
2	Hexane	51 000	543	567	0.34	24
	CH_3CN	19 000	532	562	0.004	30

nm in acetonitrile (Fig.3). The electron withdrawing ester groups decreases HOMO level of the BDP chromophore in compound **2**, which activates the electron transfer from the relatively weak benzo crown donor to the chromophore.

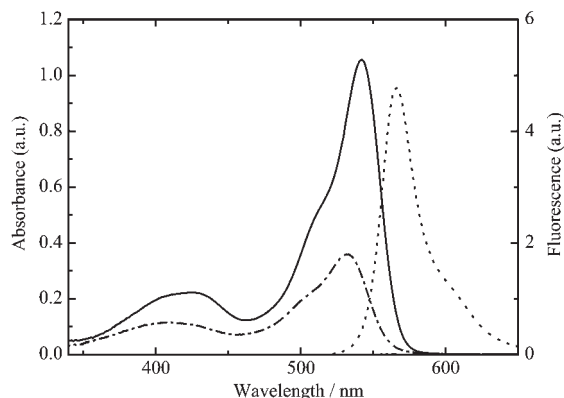


Fig.2 Absorption (solid line) and emission (dotted line) spectra of **2** in hexane and CH₃CN (dash-dotted line) (λ_{ex} =490 nm)

2.2 Fluorimetric Titrations of **1** and **2** with Na⁺

In polar solvent such as acetonitrile, all the features (position, shape and height) of the absorption spectra for **1** and **2** are essentially Na⁺ independent, indicating that the effect of binding Na⁺ with **1** and **2** can not be differentiated by absorption behavior. The emission spectrum of **1** shows only a slight bathochromic shift in the presence of Na⁺ (Fig.3). This poor response behavior of **1** to Na⁺ is due to the weak electron donating ability of the benzo crown ether moiety which is insufficient to quench the emission of BDP chromophore even in polar solvents, and therefore it is difficult to accurately assess its binding constant with Na⁺.

Therefore, it is necessary to modify the BDP chromophore to restore its sensitivity to Na⁺ while keeping excellent selectivity. The free energy change of the PET process is determined not only by the electron-donating ability of the receptor, but also by the oxidation potential and the excitation energy of the fluorophore^[17]. Based on the previously reported design concept^[4c], in order to compensate for the considerably weaker donor strength of the benzo crown moiety, an electron withdrawing ester group was incorporated to the BDP chromophore in this work to increase the

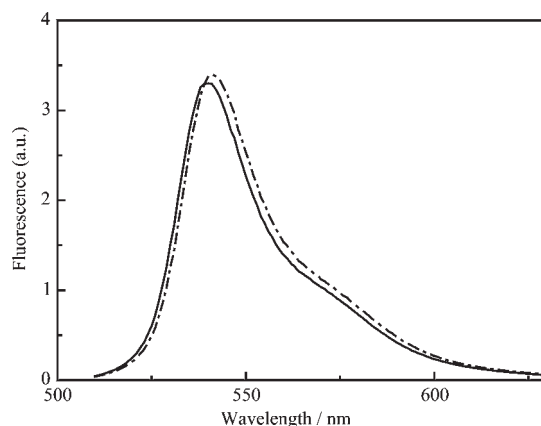


Fig.3 Fluorescence spectra of **1** (solid line) and in the presence of 70 equiv of Na⁺ ion (dash-dotted line) ($c_1=2.02 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in CH₃CN)

BDP's electron affinity and favor the photoinduced electron transfer thermodynamically. The emission spectrum of compound **2** in response to the addition of Na⁺ ion using the corresponding perchlorate is shown in Fig.4a. Increasing the concentration of the Na⁺ causes a significant fluorescence enhancement from the BDP-localized emission in acetonitrile. Moreover, the fluorescence band at ca. 560 nm can be attributed to no pronounced changes in shape or position for the BDP-localized LE emission in the presence of the Na⁺ with respect to the unbound state. This indicates that binding of Na⁺ to the benzo crown ether unit in **2** drastically reduces the electron-donating ability of the receptor and hence leads to a suppression of the PET process due to coordination effect (essentially, electrostatic interaction or electric field effect at the simplest level) between the positively charged cation and the all-oxygen containing benzo crown ether. The association constant K_s for the interaction of **2** with Na⁺ in acetonitrile is estimated by the nonlinear curve-fitting analysis of the fluorescence titration data (Fig.4b) according to equation 1, where the fluorescence signals F_{min} is the initial fluorescence value of **2**, and F_{max} is the maximum fluorescence value in the presence of Na⁺ (F_{max} can not be accurately determined, it can be left as a floating parameter in the analysis).

$$F=(F_{\text{max}}c_{\text{Na}}K_s+F_{\text{min}})/(1+K_sc_{\text{Na}}) \quad (1)$$

The $\lg K_s$ value of a well-defined 1:1 complex stoichiometry formation between **2** and Na⁺ was found to

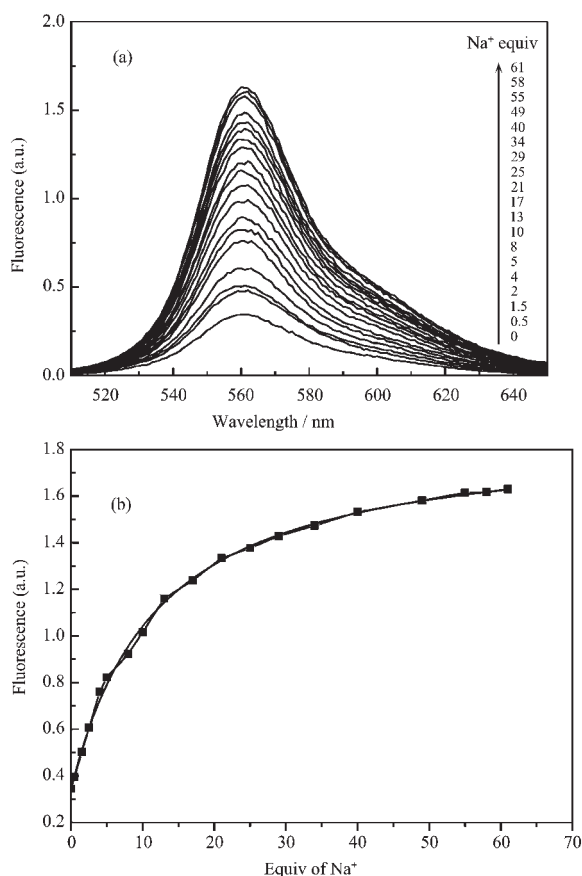


Fig.4 (a) Changes in fluorescence intensity of **2** as a function of c_{Na^+} ($c_2=2.11 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in CH_3CN); (b) The best fit to the fluorimetric titration data of **2** ($\lambda_{\text{ex}}=490 \text{ nm}$, $\lambda_{\text{em}}=560 \text{ nm}$)

be 3.15. The considerably high cation-induced fluorescence enhancement $F_{\text{max}}/F_{\text{min}}$ compared to the unbound state makes **2** to be a very sensitive fluorescent probe for Na^+ analysis.

2.3 Electrochemical properties

The redox properties of **1** and **2** were examined

Table 2 Redox potentials and electron-transfer parameters of **1** and **2** in acetonitrile (potentials in mV vs Fc^+/Fc)

	$E_{1/2}^{(\text{red})} / \text{mV}$	$E_{1/2}^{(\text{ox})} / \text{mV}$	$E_{1/2}^{(\text{ox})} / \text{mV}$	E_{00} / eV	E_c / eV	$\Delta G_{\text{ET}}^a / \text{eV}^b$
1	-1 696	565	1 150 ^b	2.36	0.1	0.39
2	-968	n.m. ^c	1 150 ^b	2.30	0.1	-0.28

^a According to Eq. (2); ^b Value of dimethoxybenzene; ^c Electrochemical wave could not be detected.

3 Conclusion

Two exocyclic ring-fused boron-dipyrromethene dyes with benzo crown ether subunits on *meso*-position were synthesized by a one-pot, three-step proce-

by cyclic voltammetry in $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP in acetonitrile. Compound **1** displays a reversible reduction wave at $-1 696 \text{ mV}$ (vs Fc^+/Fc) and a reversible oxidation wave at 565 mV , which are close to those of the conventional BDP dyes. Whereas compound **2** shows a considerably less negative reduction potential at -968 mV owing to the incorporation of electron withdrawing ester group.

The thermodynamic driving force (ΔG_{ET}) for the excited state electron transfer in polar media can be described by the Rehm-Weller equation^[17] (equation 2) where $E_{1/2}(\text{D}^+/\text{D})$ and $E_{1/2}(\text{A}/\text{A}^-)$ are the ground-state oxidation potential of the receptor and the reduction potential of the electron-deficient fluorophore, respectively. E_{00} is the zero-zero transition energy of the excited state donor-acceptor pair (D-A^*). E_c is the Coulomb stabilization energy of the radical ion pair $\text{D}^+\text{-A}^-$.

$$\Delta G_{\text{ET}} = E_{1/2}(\text{D}^+/\text{D}) - E_{1/2}(\text{A}/\text{A}^-) - E_{00} - E_c \quad (2)$$

The oxidation potential of the benzo crown moiety can not be obtained under the present experimental conditions. To assess the feasibility of PET within the dyes, we took the value of dimethoxybenzene ($1 150 \text{ mV}$ vs Fc^+/Fc) as a model for **1** and **2**. E_c is taken as 0.1 eV ^[4c]. As can be seen from the calculated values of ΔG_{ET} for two compounds summarized in Table 2, light-induced electron transfer within **2** is thermodynamically favorable while the opposite result is obtained for **1**. All these findings are in good agreement with the experimental observations that only compound **2** shows a significant PET induced fluorescence quenching.

and their spectroscopic and electrochemical properties were investigated. The longest wavelength absorption band is red shifted $15 \sim 20 \text{ nm}$ for **1** and $20 \sim 40 \text{ nm}$ for **2** compared to those of the classic BDP dyes. Dye **1** displays a strong fluorescence emission

with poor response to Na^+ , irrespective of the solvent polarity. Whereas dye **2** containing electron withdrawing ester group exhibits very weak residual fluorescence in CH_3CN solution, and its fluorescence intensity considerably enhanced upon adding of Na^+ . Dye **2** can be used as fluorescent probe for Na^+ in the visible region.

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