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Fluoride Ion-Triggered Dual Fluorescence Switch Based on Naphthalimides Winged Zinc Porphyrin

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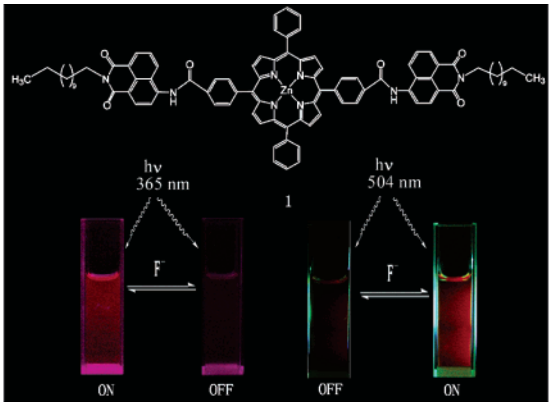

A novel fluoride ion-triggered dual fluorescence molecular switch based on naphthalimides winged zinc porphyrin (**1**) was designed and prepared. The fluorescence of the zinc porphyrin unit could be regulated "ON−OFF" on the excitation of 365 nm and "OFF−ON" on the excitation of 504 nm, respectively, in the presence of fluoride ion. The obvious color changes induced by the intermolecular proton transfer on N−H fragments are clearly visible to the naked eye.

Electron- and energy-transfer processes in porphyrin-based donor−acceptor systems are receiving considerable attention because of their importance in photosynthetic research and molecular photo/electro-active devices.[1] The controlling of these processes at molecular level using external stimuli is an interesting scientific challenge. Recently, much effort has been devoted to this area.[2] Another dramatic area is the recognition and sensing of anions.[3] In particular, the sensing of fluoride ion has attracted growing attention due to its great potential for biological and industrial applications, and the unique properties of fluorine as compared to its congeners as a result of relative size and electronegativity.[4] Derivatives of 1,8-naphthalimide are frequently used as fluorophores in probe pH, cation, and anion,[5] and we recently demonstrated that 4-benzoylamido-*N*-butyl-1,8-naphthalimide could be used as both a colorimetric and a fluorescent selective chemosensor for fluoride ion[6] because of the unique intermolecular proton-transfer (IPT) signaling mechanism.[7]

With regard to these two areas, photoinduced electron transfer (PET) and excitation energy transfer (EET) are two significant processes. PET signaling systems are of natural "all or none" switch ability: guest-induced "off−on" and "on−off" fluorescence are both designable.[8] Also, the importance of EET within the photosynthetic reaction center has prompted its mimicry within supramolecules.[9] Moreover, the excited states of mol-

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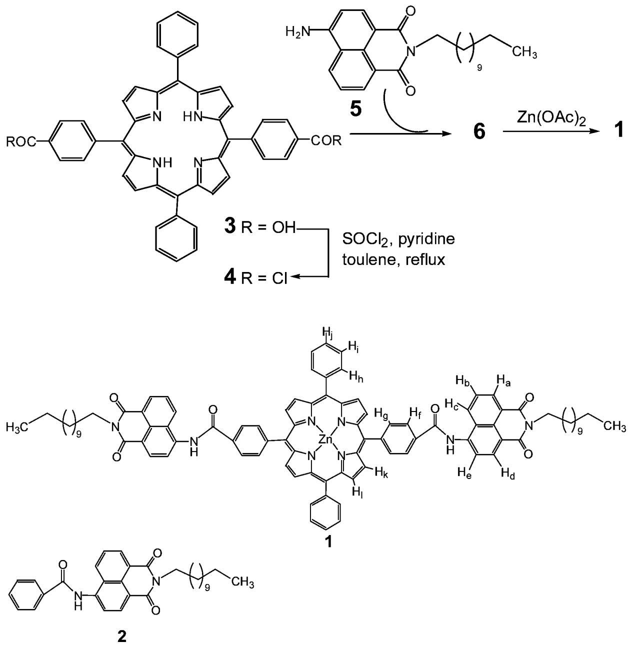
ecules can fluoresce and undergo electron and energy transfer.[10] Each of these processes can be used for switching and storing data.[11] As is scarcely studied, opposite switching actions can be displayed by one molecular system observed at two different wavelengths.[12] Here, we present a new fluoride ion-triggered dual fluorescence molecular switch based on naphthalimide−zinc porphyrin−naphthalimide triad **1**. Porphyrin, being smaller and less basic, is expected to remain uncharged under the condition of anion. However, a variety of known anion binding motifs appended to the porphyrin core to effectively anion binding have been employed.[12b,13]

The two naphthalimide chromophores (as energy donor: D) and the zinc porphyrin core (an energy acceptor: A) in **1** share amide junctions, which can take intermolecular proton transfer between the hydrogen of amide and fluoride ion. This situation could lead to changes in the UV−vis spectra, and EET plays a key role at different excitation wavelengths in the presence or absence of fluoride ion. It could serve as both the fluorescent "on−off" switch and the "off−on" switch with fluoride ion on the given adequate excitation control, and thus could actualize the opposite fluorescence switch in one molecule.

Compound **1** was prepared according to Scheme 1. Also, 4-benzoylamido-*N*-dodecyl-1,8-naphthalimide **2**[6,14] and zinc tetraphenylporphyrin[15] (**ZnTPP**) were synthesized for reference experiments.

The spectroscopy investigation was first carried out in THF. **1** has almost the same absorption spectrum as that of **ZnTPP**, in which the Soret band is observed at 417 nm, while the Q-bands are observed around 550 and 590 nm (Figure 1a). The similarity between the UV−vis spectrum of **1** and the additive sum of **2** and **ZnTPP** indicates that the electronic coupling between the two chromophores in the ground state is negligibly small.

SCHEME 1. Synthetic Routes and the Structures of Compounds 1 and 2



When Bu$_4$NF (TBAF) as a fluoride source is added to THF solution of **1**, a dramatic color change is observed from pale to dark orange (see Figure 1b and Figure 2). As compared to compound **2** (Figure S1[16]), where the maximum of absorption shifts from 368 to 504 nm, we also find that the new band with the peak around 500 nm forms and increases along with the absorption decreasing at 360 nm for **1**. This result supports the view that the two chromophores, the naphthalimide and the zinc porphyrin, generate their absorption bands independently in the presence of fluoride ions. It apparently depends on the extent of the IPT in the amido nitrogen near the naphthalimide, which causes the significant increase in the charge density on the nitrogen with associated enhancement in the push−pull effect of the ICT transition.[4a,17] As a result, the band at 500 nm, pertinent to the deprotonated receptor and responsible for the dark orange color, forms with the addition of fluoride ion.

Porphyrin emits strongly from the first singlet-excited state, and the naphthalimide is also emissive but exhibits distinctly different spectra. Excitation at 365 nm leads to an enhanced emission at 608 (655) nm as compared to **ZnTPP** (Figure S2[16]), and the emission of naphthalimides is almost quenched amounting to excitation energy transfer from naphthalimide chromophore to the zinc porphyrin core for the sake of the overlaps between the emission spectrum of the isolated naphthalimide moiety and the absorption of **ZnTPP** via the Förster mechanism.[18]

Interestingly, at different excitation wavelengths, **1** shows different change trends in its fluorescence spectra. Upon the addition of TBAF to **1**, the fluorescence intensity over 608 nm decreases at the excitation of 365 nm (Figure 3a). On the contrary, a remarkable enhancement of the feature **ZnTPP** fluorescence intensity is observed by adding fluoride ion to a THF solution of **1** under the excitation of 504 nm (Figure 3b).

There exist two competitive processes (PET and EET), but the changes in EET should take responsibility for these dual changes in fluorescence spectra. When **1** is excited by 365 nm, EET gets weaker featured with the decreasing absorption at 365 nm in the presence of F$^-$. Furthermore, with associated enhancement in the push−pull effect of the ICT transition, the photoinduced electron transfer from negatively charged naphthalimide ([Naph]$^-$) to the zinc porphyrin is also enhanced.[19]

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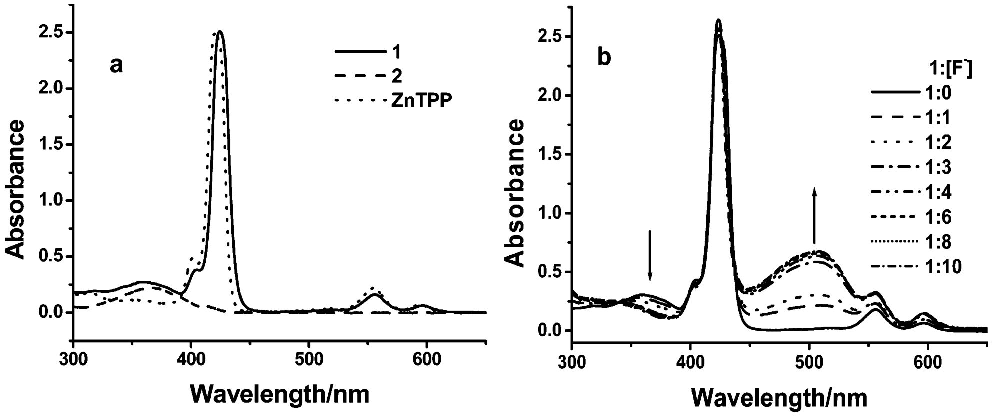

FIGURE 1. (a) Absorption spectra of **1**, **2**, and **ZnTPP** (1.0×10^{-5} M in THF); (b) absorption titration spectra of **1** (1.0×10^{-5} M in THF) with TBAF.

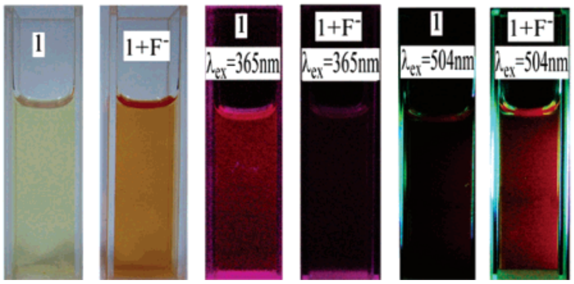

FIGURE 2. Color changes observed for samples in THF. Left: **1** and **1**·TBAF. Middle: visible emission under the excitation of 365 nm, **1** and **1**·TBAF. Right: visible emission under the excitation of 504 nm, **1** and **1**·TBAF.

It causes much lower fluorescence intensity relative to **ZnTPP** at the excitation of 365 nm (Figure S2[16]). Also, EET turns over under the excitation of 504 nm (Figure 4). At this wavelength, zinc porphyrin core could obtain more energy from the excited $[Naph]^-$ moieties. Furthermore, it is almost transparent in the absorption of 504 nm before the addition of F^- due to the enhancement of symmetry for the zinc complex for **1**, and thus the emission here is very weak, and development of a large new absorption band around 504 nm results from the formation of $[Naph]^-$ on the effect of F^-. These courses were easily observed by the naked eye (using the excitations of 365 and 504 nm, respectively, shown in Figure 2).

Fluorescence excitation spectra provide a better overall view of energy transfer in donor–acceptor systems.[20] Close matching of the fluorescence excitation spectrum and absorption spectrum together with the decrease at 365 nm and increase at 504 nm is observed for **1** and **1**·TBAF (Figure S3[16]). These results indicate a high yield of energy transfer, as absorption by the $[Naph]^-$, which contributes to the enhanced emission of the **ZnTPP** in the presence of fluoride ion at the excitation of 504 nm. Fluorescence quantum yields (Φ_F) and lifetimes were determined for the clarification of the PET and EET in these systems (Table S1[16]). We found that the Φ_F value of **1**·TBAF significantly undershot the parent quantum yield (from 0.037 to 0.026) because of the existence of PET.

It is thus demonstrated that the "on–off" and "off–on" behavior of the zinc porphyrin fluorophore can be controlled on the basis of different excitation wavelength with the cooperation of fluoride ion. With the addition of F^-, the EET entrance at $\lambda_{ex} = 504$ nm is opened, and the EET entrance at $\lambda_{ex} = 365$ nm gets closed simultaneously. On the other hand, PET is also enhanced in the presence of fluoride ions, but EET is dominant over PET. Also, the reversible chemical switch could be obtained by proton stimuli (Figure S4[16]). The process is fully reversible by the addition of water; the dark orange THF solution of **1**·TBAF turns pale. Upon the addition of other halide anions such as Cl^-, Br^-, and I^-, no significant changes in the absorption and the fluorescence spectra are observed, excluding quenching by the heavy atom effect at the excitation of 365 nm (Figure S5[16]). When less basic anion (CH_3COO^-) is specifically employed, similar results are obtained except for relatively lower affinity as compared to that of the fluoride ion (Figures S6 and S7[16]).

The interaction of receptor **1** with fluoride ion (used as tetrabutylammonium salt) was further investigated by ^1H NMR spectroscopy (see Figure S8[16]). Because of the paramagnetic effect of the porphyrin cycle, the signals of amide NH shift upfield and partially superpose the signals of β-pyrrole. Accordingly, it is hard to observe the trend of change of the amide NH with the titration of F^-. However, it is found that the amide NH proton signals in the downfield part of the spectrum disappeared with an increase in the concentration of F^-. In the spectra in Figure S8, very obvious downfield shifts are observed for H_c and H_e, which are close to the negatively charged nitrogen atom because of a through-space effect. Also, the other protons of naphthalimides are upshifted due to the through-bond effects.[5c,6,7a] Upon the addition of fluoride ions, the downfield shift of protons H_f is also observed, which is ascribed to the through-space effects, the polarization C–H bond in proximity to the hydrogen bond. The H_g of the phenyl rings linked to the amide NH upshifts because of the through-bond effects. These observations clearly support the theory that the proton-transfer interaction between compound **1** and F^- involves the amide NH group.[4a]

In summary, we have presented here a rational strategy for the development of a new colorimetric (pale to dark orange) fluoride ion sensor **1**, which operates by an intermolecular

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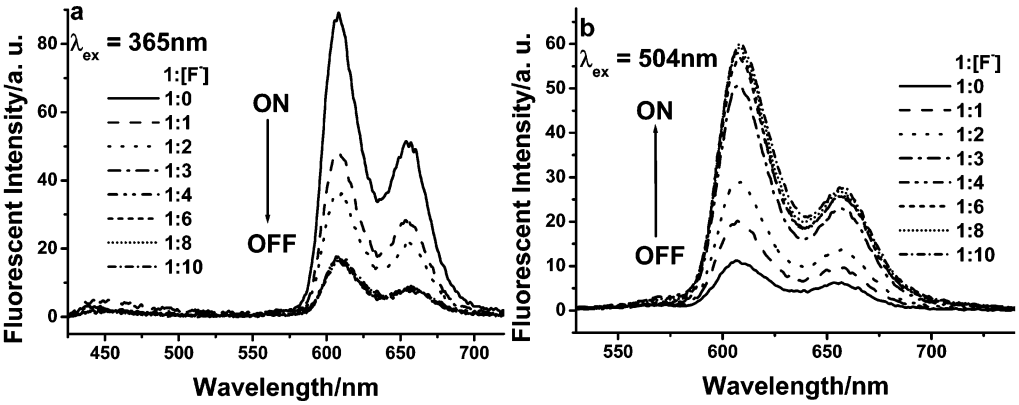

FIGURE 3. Fluorescence titration spectra of **1** (1.0×10^{-5} M in THF) with TBAF: (a) excitation wavelength, 365 nm (ON−OFF); (b) excitation wavelength, 504 nm (OFF−ON).

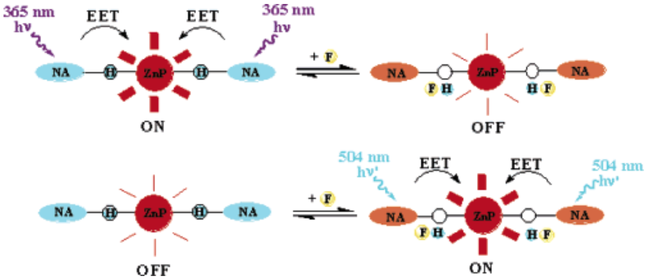

FIGURE 4. Schematic representation of the different emission for **1** in the presence of fluoride ion.

proton-transfer signaling mechanism. It exhibits opposite changes of fluorescence with fluoride ion at λ_{ex} = 365 nm and λ_{ex} = 504 nm because of the changes in the energy pathway. This behavior of wavelength-dependent dual fluorescent switch is easily observed by the naked eye. It provides a feasible way to construct a switching system that would be operated by appending zinc porphyrin with suitable chromophores, which has anion bonding affinity.

Experimental Section

Compound 6. A solution of **3**[21] (270 mg, 384.6 μmol), thionyl chloride (0.5 mL, 6.85 mmol), and pyridine (0.50 mL) in toluene (30.0 mL) was refluxed for 3 h under argon atmosphere. The excess reagent and solvents were removed under reduced pressure; the residue was redissolved in a mixture of THF (50 mL) and pyridine (1.0 mL). To the reaction mixture was added 4-amino-*N*-dodecyl-1,8-naphthalimide **5**[6,14] (600 mg, 1.57 mmol), and the solution was allowed to stir overnight at reflux under argon atmosphere. Solvents were removed in vacuo, and the crude product was purified by silica gel column chromatography (CH_2Cl_2/acetone 20:1). Further purification was done by recrystallization from chloroform/methanol, producing **6** as purple microcrystalline (205 mg, 37% yield): mp 222−225 °C. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.92 (d, 4H, J = 4.3), 8.86 (d, 4H, J = 4.4), 8.80 (s, 2H), 8.70 (m, 6H), 8.45 (d, 4H, J = 8.0), 8.41 (m, 6H), 8.24 (d, 4H, J = 6.4), 7.80 (m, 8H), 4.21 (t, 4H, J = 7.6), 1.77 (m, 4H), 1.44 (m, 8H), 1.29 (m, 28H), 0.89 (t, 6H, J = 6.9), −2.82 (s, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 165.9, 164.0, 163.5, 146.8, 141.8, 138.4, 135.2, 134.6, 133.6, 132.2, 131.2, 128.9, 128.0, 126.9, 126.8, 125.7, 124.2, 123.6, 120.9, 119.8, 119.4, 118.5, 40.6, 31.9, 29.7, 29.6, 29.4, 29.3, 28.2, 27.2, 22.7, 14.1. MALDI-TOF: m/z (%) 1428.4(100) $[M^+ + 1]$.

Compound 1. The free-base porphyrin **6** (20 mg, 14 μmol) was taken up in dichloromethane (5 mL) followed by the addition of a solution of zinc(II) acetate dihydrate (60 mg, 273 μmol) dissolved in methanol (2 mL). The resulting solution was stirred under argon for 24 h. Solvents were removed in vacuo, leaving a red residue. Water (10 mL) was added, and the mixture was stirred for 30 min and then filtered. The crude red solid was extracted with CH_2Cl_2, washed with water, saturated aqueous $NaHCO_3$ solution, followed by saturated NaCl solution, and dried over anhydrous Na_2SO_4. The solution was removed under vacuo, leaving a red powder. Further recrystallization from CH_2Cl_2/hexane gave the product (20 mg, 96%): mp 190−193 °C. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.01 (d, 4H, J = 4.5), 8.97 (d, 4H, J = 4.6), 8.71 (s, 2H), 8.58 (m, 6H), 8.45 (d, 4H, J = 7.7), 8.38 (d, 4H, J = 7.9), 8.31 (d, 2H, J = 9.9), 8.26 (d, 4H, J = 6.8), 7.80 (m, 8H), 4.13 (t, 4H, J = 7.4), 1.73 (m, 4H), 1.55 (m, 8H), 1.26 (m, 28H), 0.90 (t, 6H, J = 6.9). ^{13}C NMR ($CDCl_3$) δ (ppm): 165.8, 163.9, 162.1, 150.4, 149.6, 147.7, 142.4, 135.1, 134.4, 133.3, 132.7, 131.9, 131.6, 130.9, 126.7, 125.6, 123.8, 123.2, 121.8, 119.4, 40.5, 36.5, 31.9, 29.6, 29.4, 28.1, 27.2, 22.7, 14.1. MALDI-TOF: m/z (%) 1490.6(100) $[M^+ + 1]$.

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Supporting Information Available: ^1H NMR spectra and MALDI-TOF spectra of **6** and **1**; absorption spectra and fluorescence spectra of **2** and **2**·TBAF; fluorescence spectra of **1**, **1**·TBAF, and **ZnTPP**; excitation spectra of **1** and **1**·TBAF; fluorescence spectra of **1**·TBAF and **1**·TBAF+H^+; fluorescence spectra of **1** in the presence of chloride, bromide, and iodide; absorption titration spectra of **1** with $[Bu_4N]CH_3COO$; titration profiles on the band at 504 nm for F^- and CH_3COO^-; partial ^1H NMR spectra of **1** in DMSO-d_6 in the presence of F^-; fluorescence quantum yields (Φ_F); and decay lifetimes of **1**, **1**·TBAF, and **ZnTPP**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Compound **3** was synthesized following the literature method. (a) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872. (b) Schmidt, I.; Jiao, J.; Thamyongkit, P.; Sharada, D. S.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2006**, *71*, 3033−3050. (c) Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6535−6551.