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A new fluorescent as well as chromogenic chemosensor for anions based on an anthracene carbamate derivative

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Abstract—A new fluorescent as well as chromogenic anion sensor, 1,8-anthradiol bis(*N*-phenylcarbamate) **2**, was synthesized. It exhibits new selective red-shifted absorption and fluorescence bands with F^- and AcO^-, which could be attributed to the anthracene moiety directly involved in the bonding interaction with the anions.

Anion recognition and sensing via synthetic receptors are of current interest in supramolecular chemistry[1] because of the important roles of anions in a wide range of chemical, biological, and environmental processes. Of particular interest in this regard are fluorescent sensors due to the high sensitivity and simplicity of fluorescence.[2,3] In recent years, the development of colorimetric anion sensing is also particularly challenging.[4,5]

Synthetic anion receptors[6] are generally composed of binding sites and co-valently linked signaling subunit. Anion binding sites include not only positively charged guanidinium or ammonium based on electrostatic interactions, but also neutral H-bonding donor groups such as (thio)ureas, calix[4]pyrroles, porphyrins, or activated amides by formation of hydrogen bonds.[7] In particular, amide NH groups are well-known to be involved in the anion binding of proteins[8] and they have been widely used in developing anion receptors and sensors.

Since the first designed anion receptor containing anthracene was reported by Czarnik and co-workers[9a] in 1989, fluorescent chemosensors for anions based on anthracene derivatives have attracted considerable attention.[2] In particular, anthrylpolyamines were used as photoinduced electron transfer (PET) sensors for phosphate and pyrophosphate in aqueous solution.[9] Some anthracene-linked calix[4]pyrroles were designed and synthesized as new fluorescent sensors for anions.[3a] Furthermore, Gunnlaugsson et al. reported for the first time the charge neutral anthracene based fluorescent PET sensors for anions in 2001.[10] Recently, Kim and Yoon reported a fluorescent PET chemosensor for fluoride ions based on a bis-urea anthracene derivative.[3d] Here, we report a new fluorescent as well as chromogenic anion sensor, 1,8-anthradiol bis(*N*-phenylcarbamate) **2**, which exhibits red-shifted fluorescent and absorption bands in the presence of F^- and AcO^-. Although this unique fluorescent and absorption behavior was recently found in a naphthalene urea system used as a fluoride selective chemosensor,[3e] to the best of our knowledge, it has not been reported in the designed fluorescent chemosensors for anions based on the anthracene. Moreover, our system also displays a high selective recognition with F^- and AcO^- over other anions examined as $H_2PO_4^-$, Cl^-, Br^-, I^-, and HSO_4^-.

The chemosensor **2** was readily synthesized from the 1,8-dimethoxylanthracene **1a**.[11] Thus, **1a** was treated with BBr_3 in CH_2Cl_2 to give 1,8-anthradiol **1b**, which was reacted with phenyl isocyanate in the presence of dibutyl tin diacetate (DBTDA) to afford the product **2** in 81% yield (Scheme 1).[12]

As shown in Figure 1, the characteristic absorption bands of **2** due to the anthracene moiety considerably decrease while a new red-shifted band around 406 nm appears in the presence of fluoride ion. This indicates the complex formation. AcO^- induced almost same spectral changes of **2** as F^- did. In the case of

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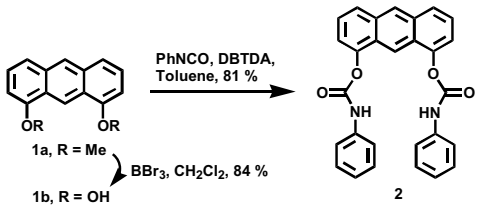


Scheme 1. Synthesis of compound **2**.

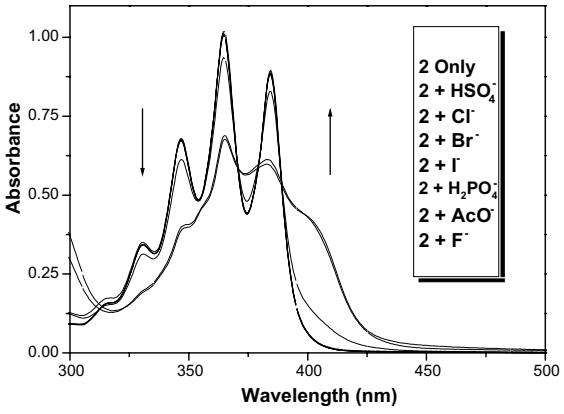


Figure 1. Absorption changes of **2** (100 μM) upon the addition of tetrabutylammonium anion salts (0.6 equiv) in MeCN/DMSO (98:2, v/v).

$H_2PO_4^-$, however, only little changes in the absorption spectrum of **2** took place. Furthermore, no obvious spectral changes were observed even in the presence of 100 equiv of Cl^-, Br^-, I^-, and HSO_4^-. It was noteworthy that F^-, AcO^-, and $H_2PO_4^-$ of 10 equiv each could induce significant color changes of the solutions of **2** (100 μM) in MeCN/DMSO (98:2, v/v) from deep yellow to yellow to light yellow, respectively. Meanwhile, other anions including Cl^-, Br^-, I^-, and HSO_4^- caused no color changes in the same conditions. Thus, **2** could be considered as a potential 'naked-eye' chemosensor for F^-, AcO^-, and also $H_2PO_4^-$.

Same tendency was observed in the fluorescence spectra of **2**. As shown in Figure 2, receptor **2** displayed a typical anthracenic emission in the absence of fluoride ion, which gradually decreased as the concentration of fluoride ion increased. Particularly, a new red-shifted band yielding the composite spectrum with λ_{max} at ~445 nm was observed upon addition of the fluoride. This unique fluorescence behavior[13] implied that anthracene moiety could be directly involved in the bonding interaction with the fluoride ion along with the formation of fluorescing complex. In the case of AcO^-, similar spectral changes were observed (Fig. 3). However, when the concentration of AcO^- increased to about 2.5 equiv, further addition of AcO^- induced only a nominal change in the fluorescence intensity. From the fluorescence titration experiments, the association constants[14] for the fluoride and acetate were calculated to be 1.55×10^5 and $3.6\times10^5\ M^{-1}$, respectively.

In the other anions examined, $H_2PO_4^-$ was found to induce smaller spectral changes[15] than those for F^- and

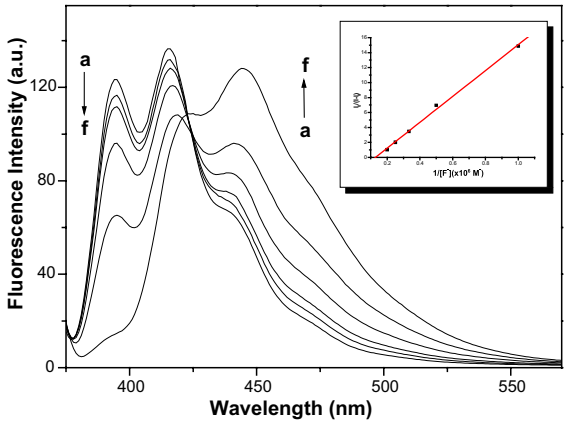


Figure 2. Fluorescent titrations of **2** (1 μM) with $Bu_4N^+F^-$ in MeCN/DMSO (98:2, v/v), λ_{ex} = 364 nm. From a to f, [F^-]: 0, 1, 2, 3, 4, 5 μM; Inset: the plot of $I_0/(I-I_0)$ versus 1/[F^-].

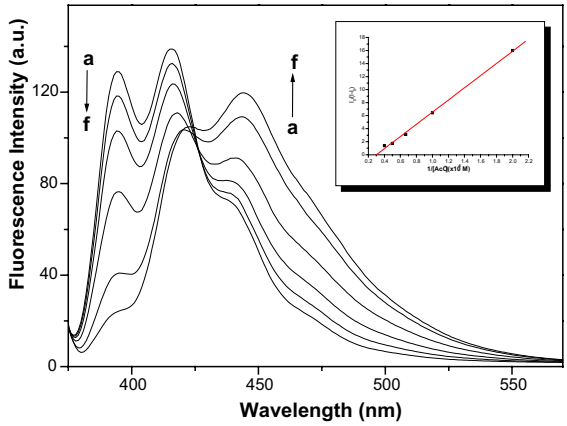


Figure 3. Fluorescent titrations of **2** (1 μM) with $Bu_4N^+AcO^-$ in MeCN/DMSO (98:2, v/v), λ_{ex} = 364 nm. From a to f, [AcO^-]: 0, 0.5, 1, 1.5, 2, 2.5 μM. Inset: the plot of $I_0/(I-I_0)$ versus 1/[AcO^-].

AcO^-. In the cases of Cl^-, Br^-, I^-, and HSO_4^-, no obvious spectral changes of **2** were observed. Even in the presence of large excess of the anions (up to 1000 equiv each), only very little fluorescence quenching of **2** observed. Although no obvious selectivity between F^- and AcO^- was found, **2** showed very high sensitivity and selectivity toward F^- and AcO^- over other anions examined. This selectivity may be due to high charge density and small size of F^- and AcO^-, which enables them to be strong hydrogen binding acceptor to interact with the receptor **2**.

To look into the anion binding properties of receptor **2**, NMR experiments in DMSO-d_6 were performed. Figure 4 shows a partial ^1H NMR spectrum of **2**, each peak was assigned according to its ^1H–^1H COSY spectrum. Upon the addition of 1 equiv F^-, dramatic changes occurred in the ^1H NMR spectrum of **2**. Firstly, the NH protons broadened and shifted downfield signal to ~11.2 ppm. Upon the addition of 2 equiv F^-, the NH signal was not observed (Fig. 4c). Meanwhile, the H_h proton signal at the 9-position of anthracene moiety shifted downfield ($\Delta\delta$ = +0.25 ppm), which indicated that the fluoride ion

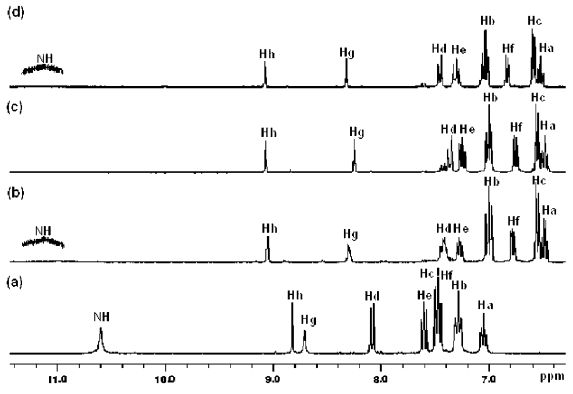
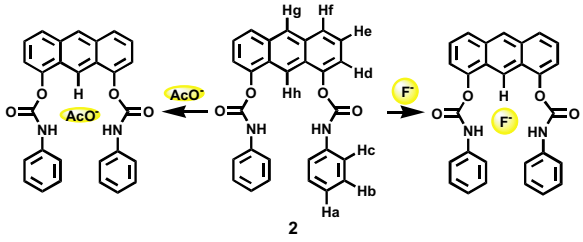


Figure 4. Partial ^{1}H NMR (300 MHz) of **2** (1 mM) in DMSO-d_6. (a) Compound **2** only; (b) **2** + 1 equiv of n-$Bu_4N^+F^-$; (c) **2** + 2 equiv of n-$Bu_4N^+F^-$; (d) **2** + 1 equiv of n-$Bu_4N^+AcO^-$. The numbering of protons is given in Scheme 2.



Scheme 2. Proposed binding mode of **2** with F^- and AcO^-.

has a strong hydrogen bonding interaction not only with the protons of the amide, but also with the H_h proton (Scheme 2). The interaction between H_h and the fluoride ion may also be an example of $C_{aromatic}$–H hydrogen bonding. On the other hand, H_c and H_d protons at the *ortho* position to carbamate group showed a significant upfield shift ($\Delta\delta = -0.95$ and -0.71 ppm, respectively) upon the addition of F^-. It implied that there is no hydrogen bonding interaction between H_c/H_d and the oxygen in the carbonyl groups, which would induce the H_c/H_d proton signals to shift downfield. Moreover, the other aromatic proton signals shifted moderate upfield ($\Delta\delta = -0.30$ to -0.70 ppm). These facts could be the result of the enhanced resonance of anthracene and phenyl electrons from anionic character of carbamate nitrogen and oxygen.[3f] In the case of the acetate, the spectral changes of **2** and binding mode of **2** with AcO^- were similar to those for the fluoride, which is consistent with the results of the above fluorescent and chromogenic methods.

In summary, we have presented a new fluorescent as well as chromogenic anion chemosensor **2**, which showed high sensitivity and selectivity toward F^- and AcO^- over other anions including $H_2PO_4^-$, Cl^-, Br^-, I^-, and HSO_4^-. In particular, the appearance of new red-shifted fluorescence and absorption bands in the presence of F^- and AcO^-, which could be attributed to the anthracene moiety directly involved in the hydrogen bonding interaction with the anions, providing a great advantage for the detect of those anions.

Acknowledgements

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12. Compound **2**: ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 10.62 (s, 2H, N*H*), 8.82 (s, 1H), 8.71 (s, 1H), 8.09 (d, $J = 8.5$ Hz, 2H), 7.61 (dd, $J = 7.4$, 8.5 Hz, 2H), 7.45–7.50 (m, 6H), 7.29 (dd, $J = 7.4$, 7.6 Hz, 4H), 7.06 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 151.8, 146.1,

138.4, 132.3, 128.9, 128.8, 127.2, 126.0, 125.7, 123.1, 118.7, 118.4, 113.3; MALDI-TOF MS (*m*/*z*): 471 $[M+Na]^+$; Anal. Calcd for $C_{28}H_{20}O_4N_2 \cdot 1/3H_2O$: C, 74.00; H, 4.58; N, 6.16. Found: C, 73.86; H, 4.51; N, 6.04.

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15. Because the complex stoichiometry between **2** and $H_2PO_4^-$ could not be determined, the association constant for dihydrogen phosphate was not available.