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Effectively selective fluorescent chemosensor for terephthalate

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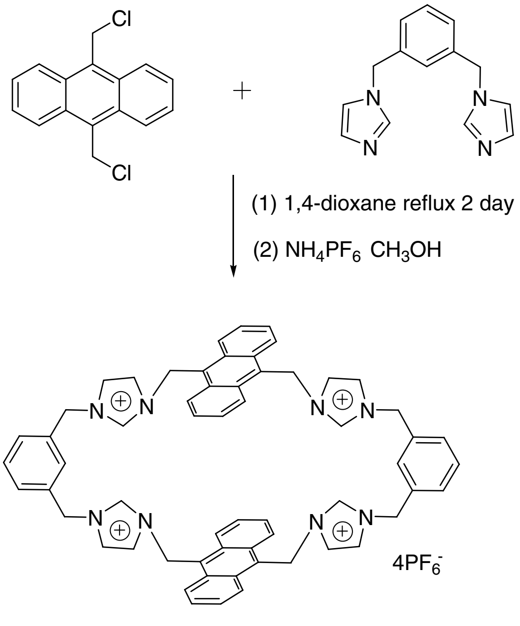
Abstract—A novel fluorescent calix[8]arene-like chemosensor **1** was designed and synthesized for effectively selective recognition of terephthalate. The receptor enclosed and acted on the special guest by synergistic effects of cavity size, π–π stacking and hydrogen bonding interaction.

Selective bindings of anions through synthetic receptors have received a significant amount of attention and a variety of novel binding strategies have emerged due to their important roles in chemistry, biology and environmental science.[1] However, design and construction of anion receptors still remains a huge challenging problem compared to more extensively studied recognition of cations. In contrast to the well known type of hydrogen bonding in neutral receptors for anion binding such as amide, pyrrole, urea, etc., recently Yoon, Kim and others have reported that imidazolium linked benzene, anthracene and cavitand derivatives have been utilized for halides, dihydrogen phosphate and dicarboxylates recognition by the strong $(C–H)^{+}\cdots X^{-}$ hydrogen binding between imidazolium moieties and these anions.[2] In contrast to some known receptors for dicarboxylate recognition,[2a,3] herein we present the first fluorescent photoinduced electron transfer (PET) chemosensor **1** for the effectively selective recognition of terephthalate **2a**. The receptor is a calix[8]arene-like imidazolium linked cyclophane, which may recognize the guest molecule through synergistic effects of cavity size, π–π stacking and hydrogen bonding interaction.

The synthesis of the receptor **1**[4] was accomplished by reaction of α,α′-bis(imidazol-1-yl)-*m*-xylene[5] with 9,10-bis(chloromethyl)anthracene in dioxane and anion exchange with NH_4PF_6 in methanol (Scheme 1).



1

Scheme 1.

The calculation[6] shows that the receptor **1** has large calix[8]arene-like cavity and possesses an appreciable amount of rigidity due to the presence of methylene group spacer between the aromatic units (Fig. 1).

In the ^{1}H NMR spectrum, the addition of bis(tetrabutylammonium) terephthalate[3b] to a solution of receptor **1** (8:1) in DMSO-d_6 resulted in a large downfield shift

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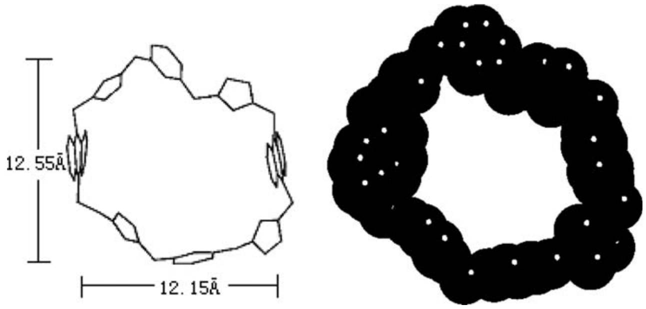

Figure 1. Calculated minimum energy conformer of receptor **1** and space filling view.

($\Delta\delta = 0.92$ ppm) of the C(2)–H of the imdazolium ring owing to the formation of receptor **1**-anion complexation by CH^+-anion charged hydrogen bonds.[3d] In the electron impact (EI) mass spectrum, a peak at *m*/*z* 1483 that is corresponding to [1-PF_6+2a] was observed. These observations indicated that the strong hydrogen bondings between the receptor **1** and the guest **2a** were formed.

The changes in absorption spectrum of receptor **1** in the presence of different concentrations of **2a** were shown in Figure 2. With increasing concentrations of **2a**, **1** showed a decreased absorption and an increased bathochromic shift (maximum value 4 nm) corresponding to the anthracene unit. Meanwhile, three isosbestic points at 359.9, 379.1 and 399.9 nm were observed, which clearly indicated that a kinetic balance presented in the solution and a new complex was formed between **1** and **2a**. Using the Job plot,[7] the formation of 1:1 complex between **1** and **2a** was further confirmed.

Similarly, malonate (**2b**), succinate (**2c**), adipate (**2d**) and tartrate (**2e**) with **1** formed 1:1 complexes. On the other hand, acetate, Cl^-, Br^- and I^- with **1** gave 2:1 complexes (Supplementary data).

The changes in fluorescence spectrum of **1** in the resence of various dicarboxylates (**2a**–**e**), acetate, Cl^-, Br^- and I^- (equiv ratio = 1:6) were shown in Figure 3. It exhibited the decrease in fluorescence intensity, which can attribute to the promotion of PET process from the N atom of the imidazolium unit to the anthracene unit owing to the formation of the $(C–H)^+\cdots X^-$ hydrogen bond between the receptor **1** and anions. Also as displayed in Figure 3, the receptor **1** showed selective recognition for **2a** effectively over **2b**–**e**, acetate, Cl^-, Br^- and I^-.

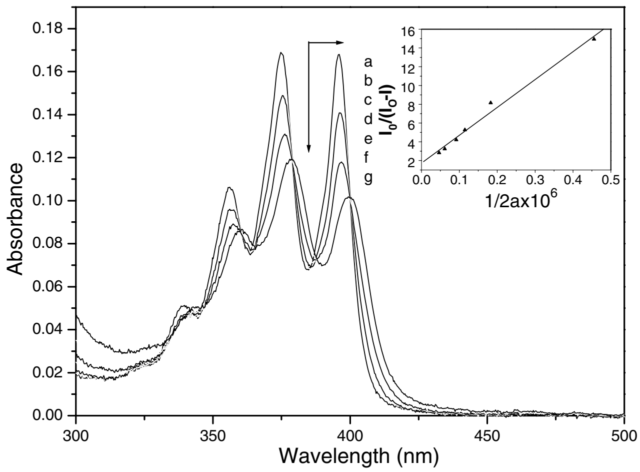

Figure 2. Absorption spectra of receptor **1** (11 μM) with **2a** in the order of increasing **2a** at 0.0, 0.2, 0.5, 0.8, 1.0, 1.5 and 2.0 equiv. Insert shows the Benesi–Hilderbrand analysis.

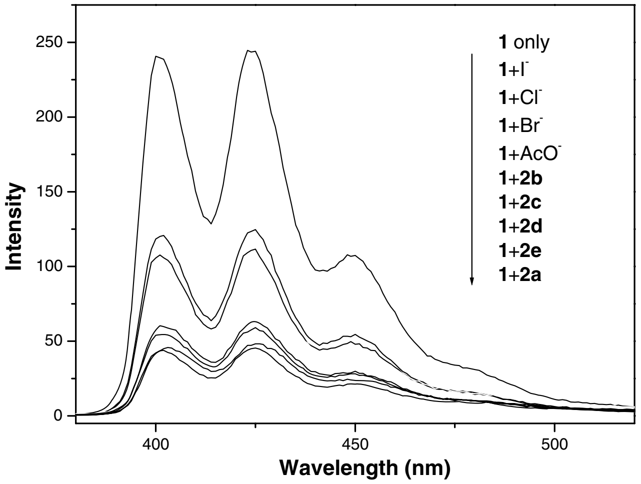

Figure 3. Fluorescent emission spectra of receptor **1** (11 μM) with tetrabutylammonium salt of **2a**–**e** AcO^-, Cl^-, Br^- and I^- (equivalent ratio 1:6) in CH_3CN.

The association constants[7] and binding free energies for **2a**–**e**, acetate, Cl^-, Br^- and I^- were calculated from fluorescence titrations in CH_3CN (Table 1), in which there was a maximum value for **2a** ($5.40 \times 10^5\ M^{-1}$). The selectivity for **2a** was more than 10–30 times of that for **2b**–**e** and more than 60–70 times of that for acetate, Cl^-, Br^- and I^-.

The receptor **1** binded **2a** exceptionally strongly and selectively to form an inclusion complex. This complex presented high degree of structure (shape and size) and interaction site complementarity between **1** and **2a**. The **2a** (anion size ~ 7.5 A) was fitted into the cavity of the receptor **1** and was held by four $(C–H)^+\cdots O^-$ hydrogen bonds and π–π interaction. The strong and

Table 1. Association constants and free energy change for the **1**-anion complex

Anion	K_a (M^{-1})[a]	ΔG (kcal/mol)
Cl^-	9.23×10^3	−5.33
Br^-	7.36×10^3	−5.21
I^-	9.83×10^3	−5.36
ACO^-	9.08×10^3	−5.32
Terephthalate (**2a**)	5.40×10^5	−7.71
Malonate (**2b**)	3.18×10^4	−6.05
Succinate (**2c**)	5.45×10^4	−6.36
Adipate (**2d**)	1.60×10^4	−5.65
Tartrate (**2e**)	1.45×10^4	−5.60

[a] In CH_3CN. Error are estimated to be <10%.

multiple binding interactions resulted in the high stability for the [**2a** ⊂ **1**] complex.

In conclusion, we have designed and synthesized an effectively selective fluorescence photoinduced electron transfer chemosensor **1** for terephthalate. The novel anion recognition depends on synergistic effects of cavity size, π–π stacking and hydrogen bonding interactions in the receptor **1**.

Acknowledgements

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Supplementary data

Spectroscopic data for the receptor **1**. Figures showing the change in absorption and fluorescence spectra and the job plots of receptor **1** in the presence of various given anions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.06.030.

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4. Receptor **1**: A solution of $\alpha\alpha'$-bis(imidazol-1-yl)-*m*-xylene (2.40 g, 10 mmol) and 9,10-bis(chloromethyl)-anthracene (2.80 g, 10 mmol) in 1,4-dioxane (60 mL) was refluxed for 48 h under N_2. And then, cooled to room temperature. The yellow precipitate was collected and dissolved in CH_3OH and the anion exchange was carried out by NH_4PF_6. The desired product was yielded as a yellow powder (2.61 g, 36%). Anal Found: C, 49.38; H, 3.62; N, 7.72. $C_{60}H_{52}N_8F_{24}P_4$ require C, 49.19; H, 3.58; N, 7.65. Mp >270 °C; ^{1}H NMR (300 MHz, DMSO-d_6) 5.35 (8H, s), 6.59 (8H, s), 7.17 (4H, s), 7.25 (4H, d, $J = 7.4$ Hz), 7.58 (4H, s), 7.69 (4H, s), 7.76–7.79 (8H, m), 8.59–8.61 (8H, m), 9.22 (4H, s); ^{13}C NMR (75 MHz, DMSO-d_6) 45.35, 51.86, 122.26, 122.26, 124.30, 127.36, 128.23, 129.13, 129.70, 134.72, 135.52; EIMS *m*/*z* calcd for $C_{60}H_{52}F_{24}N_8P_4$ ($M-1\text{-}PF_6$) 1319.25, found 1319.15 $[M-1\text{-}PF_6]^+$.
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