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New imidazolium systems bearing two pyrene groups as fluorescent chemosensors for anions and anion induced logic gates

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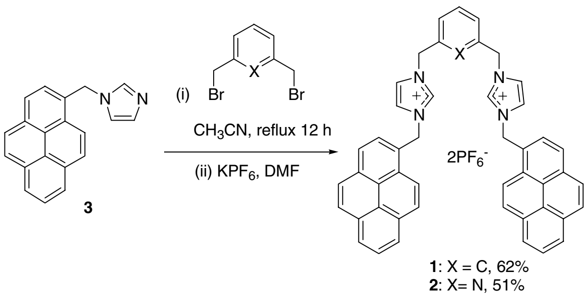
Abstract—Two new imidazolium systems bearing two pyrene groups have been synthesized and the binding properties of these hosts were examined via fluorescent changes. The fluorescent changes of host **2** upon the addition of anions were also utilized as a NOR logic gate and an INH logic gate.

Anions play an important role in a wide range of chemical and biological processes, and numerous efforts have been devoted to the development of abiotic receptors for anionic species.[1] Sensors based on anion-induced changes in fluorescence appear to be particularly attractive due to the simplicity and high detection limit of fluorescence.[1a,d,2] In contrast to the well-known type of hydrogen bonding for the anion binding such as amide, pyrrole, urea etc., various types of receptors containing imidazolium moieties have been reported.[1a] Especially, we have recently reported few fluorescent anthracene derivatives bearing imidazolium moieties, which show selective binding for $H_2PO_4^-$, pyrophosphate or GTP over other anions.[3] Herein, we report two new fluorescent anion receptors (**1** and **2**) bearing two imidazolium groups as well as two pyrene groups. The binding affinities of these hosts could be easily monitored via the changes of pyrene eximer peaks. The fluorescent changes of host **2** upon the addition of anions were utilized as a NOR logic gate and an INH logic gate.



Scheme 1. Syntheses of compound **1** and **2**.

The synthetic procedures of compounds **1** and **2** are summarized in Scheme 1. 1-Imidazolylmethylpyrene **3** was synthesized by the published procedure.[3b] This intermediate was then reacted with either α,α′-dibromo-*m*-xylene or 2,6-bis(bromomethyl)pyridine in acetonitrile refluxing for 12 h followed by anion exchange with NH_4PF_6, which gave the compounds **1**[4] and **2**[5] in 62% and 51% yield, respectively.

Figures 1 and 2 explain the fluorescent emission changes of **1** (3 μM) and **2** (3 μM) upon the addition of $H_2PO_4^-$, HSO_4^-, $CH_3CO_2^-$, I^-, Br^-, Cl^-, and F^- (30 μM) in acetonitrile. As expected, compounds **1** and **2** bearing two pyrene groups as well as two imidazolium groups displayed distinct eximer peaks around 475 nm. As shown in Figure 1, the intensities of monomer peak as well as eximer peak of **1** were quenched significantly

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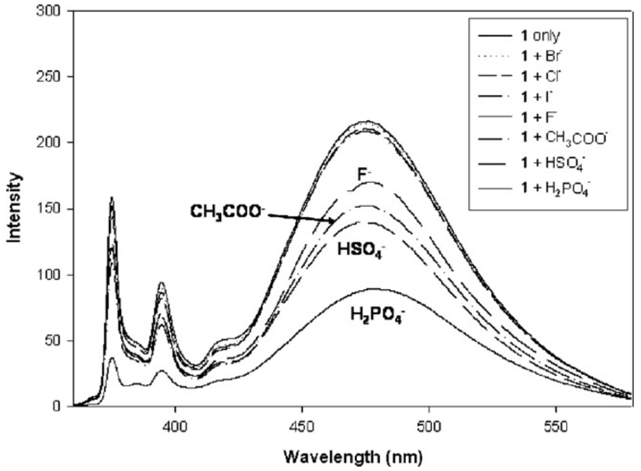


Figure 1. Fluorescent emission changes of **1** (3 μM) upon the addition of tetrabutylammonium salt of HSO_4^-, $CH_3CO_2^-$, I^-, Br^-, Cl^-, F^- and $H_2PO_4^-$ (10 equiv) in acetonitrile (excitation at 343 nm) (excitation and emission slit: 5 nm).

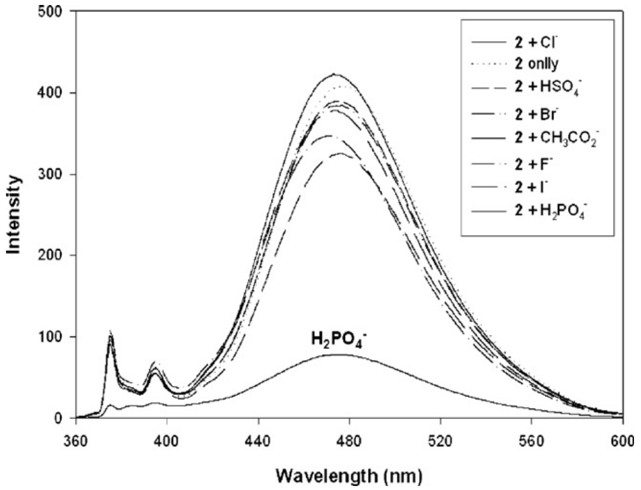


Figure 2. Fluorescent emission changes of **2** (3 μM) upon the addition of tetrabutylammonium salt of HSO_4^-, $CH_3CO_2^-$, I^-, Br^-, Cl^-, F^- and $H_2PO_4^-$ (10 equiv) in acetonitrile (excitation at 343 nm) (excitation and emission slit: 5 nm).

upon the addition of $H_2PO_4^-$. There were relatively small quenching effects with HSO_4^-, $CH_3CO_2^-$ and F^-. On the other hand, compound **2** displayed a quite selective fluorescent quenching effect with $H_2PO_4^-$ among the anions examined. The fluorescent quenching effect was induced possibly due to the photo-induced electron transfer (PET) process.[3e] From the fluorescence titration experiments (Fig. 3 and S-Fig. 1), the association constants of **1** with $H_2PO_4^-$ and I^- were calculated as 246,000 and 1260 M^{-1} (error < 15%).[6] The association constants of **2** with $H_2PO_4^-$ and I^- were calculated as 194,400 and 1500 M^{-1} (error <15%) (Fig. 4 and S-Fig. 2).[6] However, when more than 1000 equiv of HSO_4^- or $H_2PO_4^-$ were added, a new blue-shifted peak was observed (Fig. 5). The blue-shifted excimer emission can be attributed to a pyrene dimer formed in the ground state, a so-called static excimer. Depending on the origin of the pyrene dimer, there are two kinds of

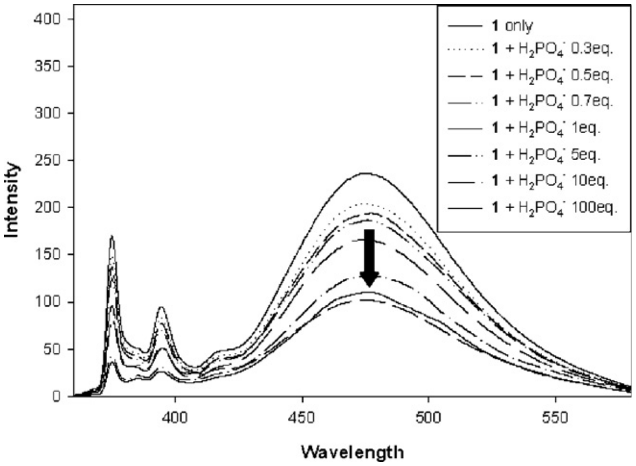


Figure 3. Fluorescent titrations of compound **1** (3 μM) with $H_2PO_4^-$ in acetonitrile (excitation at 343 nm) (excitation and emission slit: 5 nm).

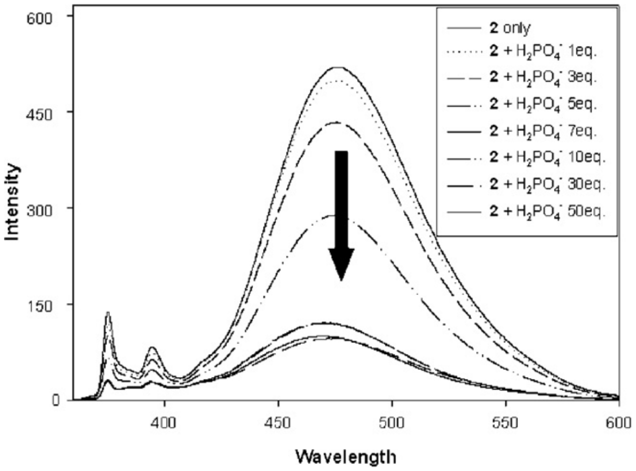


Figure 4. Fluorescent titrations of compound **2** (3 μM) with $H_2PO_4^-$ in acetonitrile (excitation at 343 nm) (excitation and emission slit: 5 nm).

excimers, such as a dynamic eximer and a static eximer. The former is emitted from a pyrene dimer formed in the excited state, and, the latter is emitted from a pyrene formed in the ground state.[7] Recently, Kim et al. reported a fluoride-selective fluorescent chemosensor based on the formation of a static eximer.[8] On the other hand, Yang et al. [9] and our group[10] recently reported a static eximer formation in the presence of Cu^{2+} ion.

Recently, remarkable progress has been achieved in the development of molecular logic gates based on the fluorescent sensors. However, most of these examples utilized fluorescent changes, which were induced by pH changes or addition of metal ions.[11] Only a paucity of fluorescent logic gates utilizing both cation and anion as inputs are available.[12] Since there has not been any report in which imidazolium receptor was used as a molecular logic gate or two different anions were used as inputs, we utilized our system as a NOR logic gate and an INH logic gate.

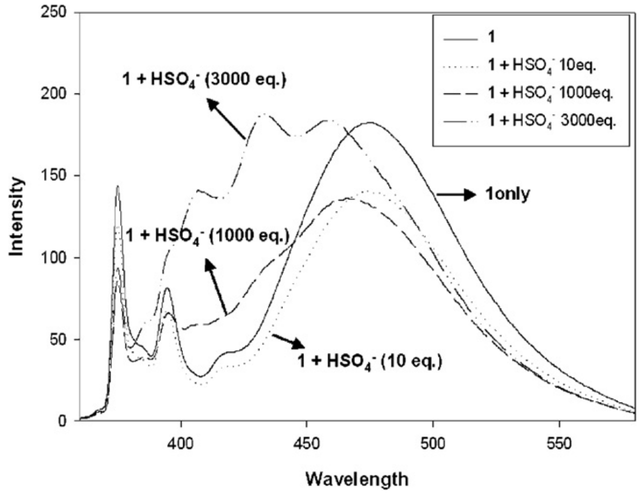
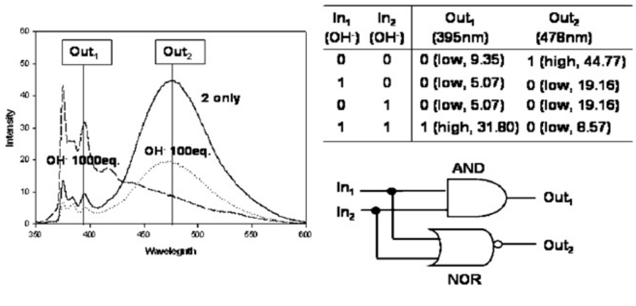


Figure 5. Fluorescent emission changes of **1** (3 μM) upon the addition of tetrabutylammonium salt of HSO_4^- (10, 1000 and 3000 equiv) in acetonitrile (excitation at 343 nm) (excitation and emission slit: 5 nm).

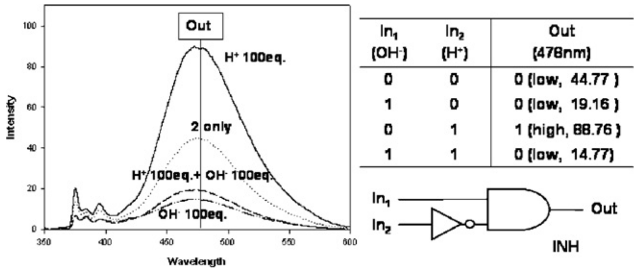
As shown in Figure 6, compound **2** displayed a large fluorescent quenching effect upon the addition of OH^- (100 equiv) in acetonitrile. On the other hand, the addition of excess OH^- (1000 equiv) induced a similar fluorescent quenching effect of the eximer peak, but the fluorescent intensity due to the monomer emission was increased significantly. Accordingly, operation by amounts of OH^- expresses AND (Out_1) and NOR (Out_2) functions (Fig. 6). As shown in Figure 7, compound **2** displayed fluorescent enhancements upon the addition of trifluoroacetic acid (TFA). This can be attributed to the protonation of nitrogen in the pyridine ring, which can block the partial PET (photo-induced electron transfer) mechanism from pyridine moiety (or which can induce a conformation change). On the other hand, compound **1** did not show any fluorescent changes upon the addition of TFA. The addition of OH^- to compound **2** induced a fluorescent quenching effect as described. Also, a similar quenching effect was observed upon the addition of both OH^- and TFA. This quenching effect is due to the binding with either trifluoroacetate or OH^-, which was confirmed by the addition of tetrabutylammonium trifluoroacetate. Operation by TFA and OH^- shows an INH gate as shown in Figure 7.

To have a structural insight, we performed density functional tight binding[13] (DFTB with dispersion consideration) calculations in gas phase. The stack conformation of **2** is ~15 kcal/mol more stable than the open form, where the two pyrene rings do not interact with each other. However, if we consider the interaction of the OH^- with either of the stack and open conformers, the **2**-OH^- complex in open form is ~10 kcal/mol more stable than the stack form (Fig. 8). It shows that the presence of OH^- in the solution would definitely affect the π–π interaction of the two pyrene rings not only in the ground state but also in the excited state. On the other hand, if we consider the conformer of **2** with the protonation at pyridine, we observed that the stack conformer is ~11 kcal/mol more stable than that of the open conformer in the ground state. Based on the experimental observation of the enhancement of the eximer peak upon mixing with TFA, we assume that the stack conformer of the protonated **2** will be much more stablized in the excited state as compared to the neutral counterpart. This in conjunction with the blockage of the partial PET, would give rise to the enhancement of the eximer peak of **2** upon adding TFA.



In1 (OH-)	In2 (OH-)	Out1 (395nm)	Out2 (478nm)
0	0	0 (low, 9.35)	1 (high, 44.77)
1	0	0 (low, 5.07)	0 (low, 19.16)
0	1	0 (low, 5.07)	0 (low, 19.16)
1	1	1 (high, 31.80)	0 (low, 8.57)

Figure 6. Fluorescence spectra of **2** (1 μM) in the absence and presence of tetrabutylammonium hydroxide in acetonitrile, truth table, and logic scheme.



In1 (OH-)	In2 (H+)	Out (478nm)
0	0	0 (low, 44.77)
1	0	0 (low, 19.16)
0	1	1 (high, 88.76)
1	1	0 (low, 14.77)

Figure 7. Fluorescence spectra of **2** (1 μM) in the absence and presence of tetrabutylammonium hydroxide and TFA in acetonitrile, truth table, and logic scheme.

In conclusion, we report two new fluorescent anion receptors (**1** and **2**) bearing two imidazolium groups as well as two pyrene groups. The binding affinities of these

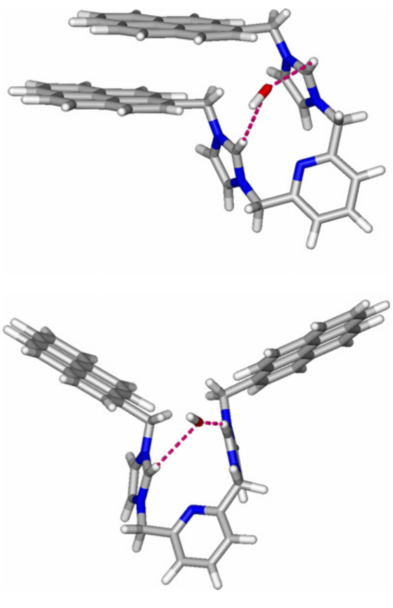


Figure 8. DFTB optimized geometry of the stack and the open conformers of **2**-OH^- complex.

hosts could be easily monitored via the changes of pyrene eximer peaks. For example, the association constants of **2** with $H_2PO_4^-$ and I^- were calculated as 194,400 and 1500 M^{-1}. The fluorescent changes of host **2** upon the addition of anions were utilized as a NOR logic gate and an INH logic gate. This is the first example of fluorescent logic gate, which utilized two different anions as inputs.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.161.

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4. Compound **1**. Procedure A. A mixture of **3** (348 mg, 1.23 mmol) and α,α′-dibromo-*m*-xylene (135 mg, 0.51 mmol) in acetonitrile (20 mL) was refluxed for 24 h under N_2. After cooling to the room temperature, the precipitate was filtered and washed with cold CH_2Cl_2. The bromide salt was dissolved in 3.5 mL DMF. During the dropwise addition of saturated aqueous NH_4PF_6 solution (1.5 mL), light yellow precipitate was formed. After washing the precipitate several times with water, desired product was obtained as a light yellow solid (729 mg, 62%); mp 138–141 °C; ^1H NMR (CD_3CN, 250 MHz) δ 8.46 (s, 2H), 8.27 (dd, 6H, $J = 7.68$, 375 Hz), 8.20 (m, 4H), 8.06 (dd, 4H, $J = 16.63$, 7.16 Hz), 7.41 (m, 4H), 7.27 (t, 2H, $J = 1.76$ Hz) 7.35 (d, 1H, $J = 1.49$) 7.20 (s, 1H), 6.02 (s, 4H), 5.18 (s, 4H); ^{13}C NMR (CD_3CN, 125 MHz) δ 136.09, 134.99, 132.77, 131.45, 130.79, 130.38, 129.61, 129.43, 128.93, 128.89, 128.80, 127.57, 127.12, 126.61, 126.35, 125.81, 125.56, 125.10, 124.41, 123.56, 122.91, 122.19, 52.78, 51.50; HRMS (FAB) $m/z = 813.2592$ $(M-PF_6)^+$, calcd for $[C_{48}H_{36}F_{12}N_4P_2–PF_6] = 813.2582$.
5. Compound **2**. Application of procedure A to **3** (348 mg, 1.23 mmol) and 2,6-bis(bromomethyl)pyridine (136 mg, 0.51 mmol) gave 600 mg of compound **2** (51%); mp 120–122 °C; ^1H NMR (CD_3CN, 250 MHz) δ 8.36 (s, 2H), 8.36–8.20 (m, 6H), 8.11–8.05 (m, 6H), 7.93 (d, 4H, $J = 7.81$ Hz), 7.78 (t, 2H, $J = 7.69$ Hz), 7.30 (d, 3H, $J = 7.79$ Hz), 7.16 (t, 2H, $J = 1.84$ Hz), 7.08 (t, 2H, $J = 1.78$ Hz), 5.89 (s, 4H), 5.13 (s, 4H); ^{13}C NMR (CD_3CN, 125 MHz) δ 162.6, 153.2, 139.3, 136.4, 132.7, 131.4, 130.7, 129.4, 128.8, 128.6, 127.5, 127.1, 126.6, 126.3, 125.9, 125.6, 125.0, 123.5, 122.9, 122.5, 122.0, 53.5, 51.3; HRMS (FAB) $m/z = 814.2527$ $(M-PF_6)^+$, calcd for $[C_{47}H_{36}F_{12}N_5P_2–PF_6] = 814.2534$.
6. (a) Association constants were obtained using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, United Kingdom; (b) Conners, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*; Wiley: New York, 1987.
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