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PAPER

Selective sensing of $H_2PO_4^-$ (Pi) driven by the assembly of anthryl pyridinium ligands†

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Synthesis of a simple amidopyridinium-based sensor (**F1**) and its fluorescence behavior toward $H_2PO_4^-$ (Pi) were investigated. The anthryl group in **F1** exhibited a strong excimer emission *via* Pi-directed assembly of **F1**; other anions showed a negligible effect. The Pi-induced assembly of **F1** was rationalized by photophysical experiments and DFT calculation.

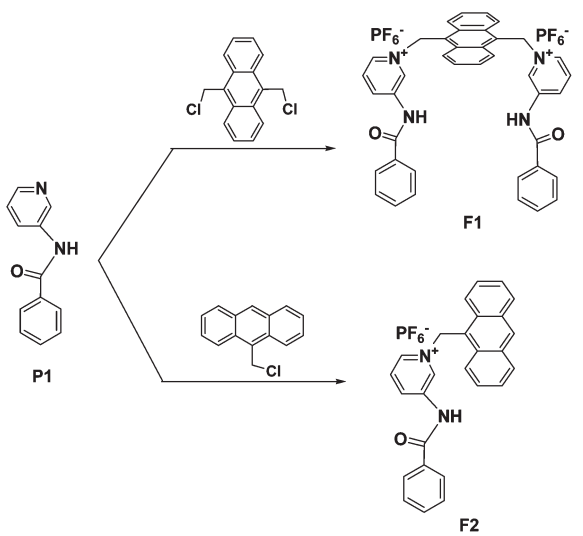
Introduction

Anions play significant roles in various chemical, biological, medical and environmental processes. In particular, organic or inorganic phosphates are not only biologically important compounds because of their pivotal roles in signal transduction and energy storage in biological systems, but also because they are responsible for the eutrophication of waterways.[1] Accordingly, the selective detection of phosphates in the form of dihydrogen phosphate, phosphate or pyrophosphate has been a major research focus. In order to achieve this, fluorescent chemosensors attract particular attention due to their high selectivity, sensitivity and simplicity.[2]

Although many highly sensitive and selective receptors are currently available for pyrophosphate (PPi) determination, only a few have been reported for Pi.[3] In addition, from the viewpoint of sensing mechanism, most of the chemosensors for Pi did not go beyond the traditional mechanisms of emission processes, such as intramolecular charge transfer processes (ICT),[4] photoinduced electron transfer processes (PET),[5] metal-to-ligand charge transfer processes (MLCT),[6] and excimer formation intramolecularly.[7] Recently, anion directed assembly has drawn considerable attention.[8,2a] One purpose is to elucidate the parallels between anion coordination chemistry and traditional metal coordination chemistry.[9] Another purpose is to construct multidimensional architectures to realize anion recognition and develop novel functional materials.[10] However, fluorescence sensing of anions *via* anion directed assembly is rare[11] and to the best of our knowledge, no report on the fluorescence sensing for Pi *via* an assembly mechanism has been published.

The anthracene fluorophore has often been used in the design of effective chemosensors for anions because the relative proximity between anthracene moieties induces monomer and excimer emissions at considerably different wavelengths.[12] The positive effect of the amidopyridinium framework as an anion binding motif has been identified by the authors and others.[13] In addition, an effective Pi sensor bearing an anthryl pyridinium ligand by formation of excimer emission intramolecularly as well as the development of new anion fluorescent sensors have also been reported by the authors.[13c]

In this paper, a new strategy for selective fluorescent sensing of Pi is presented. The selectivity originated from the Pi directed assembly of anthryl pyridinium-based ligand **F1**. For the purpose of comparison, **F2** bearing one arm of the anthryl pyridinium motif was also designed as a control molecule (Scheme 1).



Scheme 1 Synthesis and structures of **F1** and **F2**.

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†Electronic supplementary information (ESI) available: $^1H/^{13}C$ NMR spectra and HRMS for **F1** and **F2**, UV-vis absorption spectra and the fluorescence spectra of **F2** upon addition of various anions details. See DOI: 10.1039/c2ob26135a

Results and discussion

Synthesis of F1 and F2

The synthesis of **F1** and **F2** was achieved readily by treatment of intermediate **P1** with 9,10-bis(chloromethyl)anthracene and 9-(chloromethyl)anthracene respectively in dry $CHCl_3$ followed by anion exchange with KPF_6 in DMF. The structures of **F1** and **F2** were confirmed by using ^1H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

Photophysical properties in solution

In order to elucidate the status of **F1** in solution, the concentration-dependent experiment was firstly investigated. Fig. 1 shows that at the range of low concentration from 10^{-7} to 5.0×10^{-6} M, **F1** displayed only typical monomer emission of anthracene fluorescence consisting of three bands centered at 407 nm, 429 nm and 460 nm. The relatively low fluorescence intensity of **F1** was ascribed to the quenching effect of a PET process from the anthracene moieties to the charged pyridinium ring.[14] With the concentration of **F1** solution increasing from 10^{-5} to 10^{-4} M, a new obvious emission peak centered at a longer wavelength was observed, which might be due to the relative proximity of the anthracene moiety at a higher concentration. This result indicated that **F1** has a tendency to aggregate to some extent at high concentration.

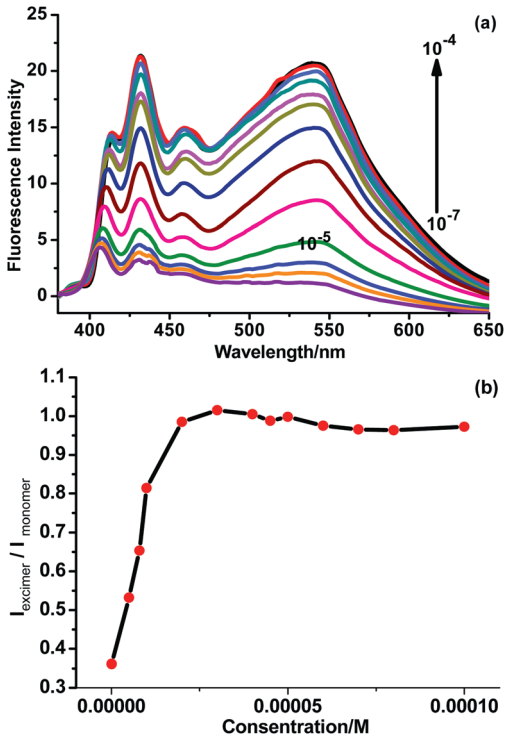

Fig. 1 Fluorescence spectra of various concentrations of **F1** in CH_3CN (a) and fluorescence ratio ($I_{excimer}/I_{monomer}$) of receptor **F1** centered at 431 nm and 539 nm respectively (b).

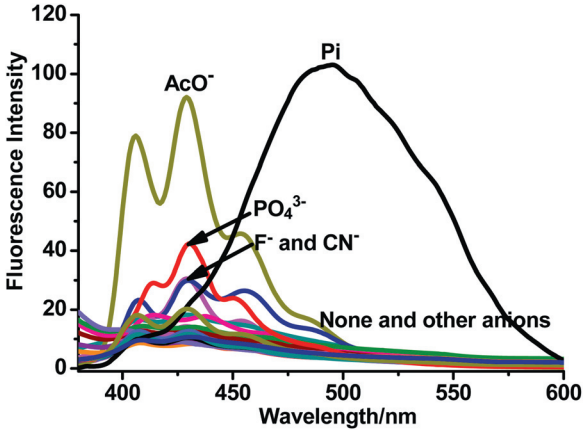

Fig. 2 Fluorescence spectra of receptor **F1** (5.0 μM) upon addition of 5 equiv. of various anions at an excitation of 360 nm in CH_3CN.

Anion binding studies

With the purpose to exclude the influence of self-aggregation of **F1** on anion sensing, the concentration of **F1** was chosen as 5.0×10^{-6} M for the measurements (Fig. 1). Fig. 2 shows the fluorescence change of **F1** upon addition of various inorganic anions (F^-, Cl^-, Br^-, I^-, Pi, NO_3^-, AcO^-, CN^-, ADP, AMP, ATP, CDP, CTP, GTP, UTP, HSO_4^-, PO_4^{3-}, HPO_4^{2-}, SO_4^{2-}, $P_4O_7^{4-}$ (PPi) and Pi as their tetra-*n*-butylammonium salts). It was found that upon addition of F^-, CN^-, PO_4^{3-} and especially AcO^-, a clear "turn-on" fluorescence of monomer emission of anthracene was observed due to the inhibition of the PET process from the anthracene fluorophore to the pyridinium moiety.[15] Furthermore, it is worth noting from Fig. 2 that, compared to other anions, only Pi induced an apparent bathochromic shift of fluorescence emission with increasing intensity and gave rise to a strong green fluorescence. This broad emission band induced by addition of Pi might be ascribed to the excimer emission between the anthracene fluorophore, and this phenomena has been well-documented by the authors[13c] and other groups.[14,16] Considering only one anthracene fluorophore in **F1**, the excimer emission should originate from the Pi-directed assembly of **F1** in this circumstance. As far as we are aware, **F1** is the first fluorescent sensor selective for Pi by an assembly mechanism and interestingly, it has the potential to act as dual-channel fluorescent sensor for Pi and AcO^- simultaneously. As a contrast, the control molecule **F2** did not show any anion-directed assembly phenomena under the same conditions. Introduction of Pi, F^-, CN^-, AcO^- and PO_4^{3-} all induced fluorescence from increased monomer emission resulting in no discrimination ability towards them (See ESI, Fig. S9†).

Furthermore, a competition experiment was also performed to validate the selectivity of chemosensor **F1** in practice. Fig. 3 shows the response of **F1** to Pi in the presence of other anions. The presence of other background anions did not show obvious disturbance of the fluorescence response induced by the **F1**–Pi system in CH_3CN. Therefore **F1** shows a selective detection for Pi even in the presence of competing anions.

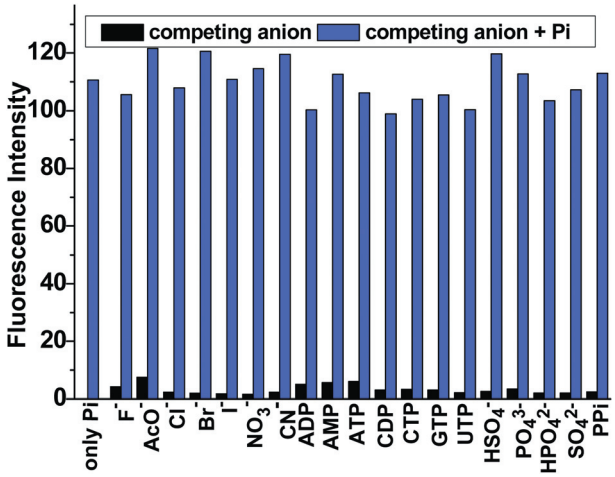

Fig. 3 The fluorescence responses of **F1** (5.0 μM) upon addition of various anions (25 μM) and Pi (25 μM) in CH_3CN.

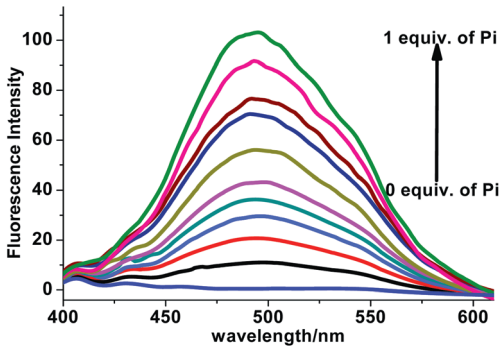

Fig. 4 Fluorescence titration spectra of **F1** (5 μM) upon addition of various amounts of Pi (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 equiv.) at an excitation of 360 nm in CH_3CN.

Potential binding mode

In order to know more about the binding mode between Pi and **F1**, the corresponding titration experiment was done (Fig. 4). The liner dependence of the intensity ratio within 1 equiv. range of Pi testified that **F1** forms a 1 : 1 complex with Pi, whose binding constant was determined to be about $(3.0 \pm 0.1) \times 10^6$ M^{-1}. And by fluorescence titration, the detection limit of **F1** toward Pi was obtained as 3.62×10^{-7} mol L^{-1}, which is sufficiently low for the detection of the concentration of Pi found in many chemical systems (Fig. 5). Moreover, the Job plot (Fig. 6) and elemental analysis both confirm the 1 : 1 stoichiometry for the **F1**–Pi complex. Considering there is only one anthracene fluorophore in the **F1** structure and the appearance of the excimer emission between anthracene fluorophores upon addition of Pi, a 2 : 2 stoichiometry ratio between **F1** and Pi was proposed. Absorption experiments were also performed to provide more evidence to support Pi-directed assembly of **F1** (Fig. 7). As shown in Fig. 7, only Pi induced the apparent red-shift of the absorption bands of anthracene indicating the formation of some interaction and association between anthracenes in the ground state.[17]

To further understand the fluorescence changes of **F1** upon addition of the Pi anion, a density functional theory (DFT) calculation was executed for Pi complexation to **F1**. Due to the 2 : 2 stoichiometry between **F1** and Pi, the lowest-energy conformation for the Pi complex of **F1** was located and represented in Fig. 8. As shown in Fig. 8, the average distance of hydrogen bond between Pi and **F1** was 1.99 Å, which indicates that **F1** can assemble directed by Pi through the effective hydrogen bond. The theoretical DFT calculation results are in excellent agreement with the observed experimental observation that the distinct fluorescence excimer emission upon addition of Pi is associated with the anthryl–anthryl* interaction in the **F1**–Pi complex.

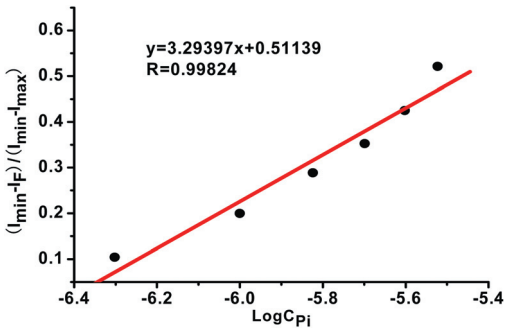

Fig. 5 Normalized response of fluorescence signal to changing Pi concentrations in CH_3CN (5 μM).

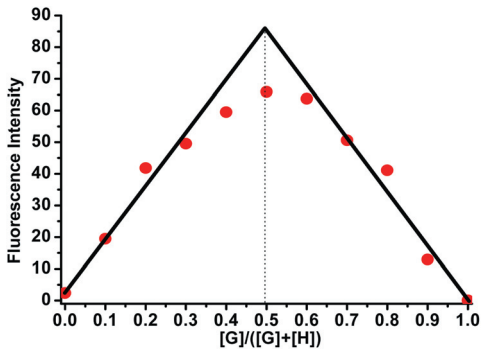

Fig. 6 Job plot of a 1 : 1 complex of **F1** and Pi in CH_3CN (total concentration = 20 μM).

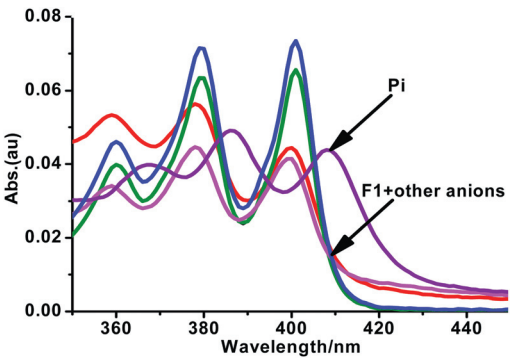

Fig. 7 UV-vis spectra of **F1** (5.0 μM) upon addition of 5 equiv. of various anions in CH_3CN.

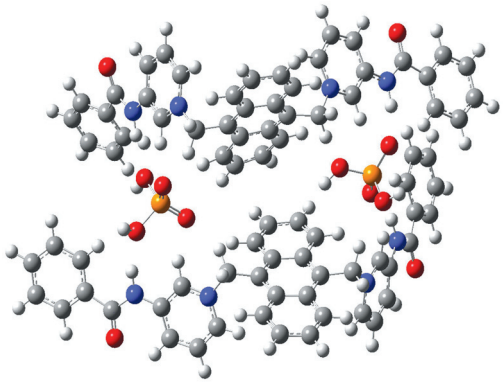

Fig. 8 Lowest energy structure for the Pi–**F1** complex.

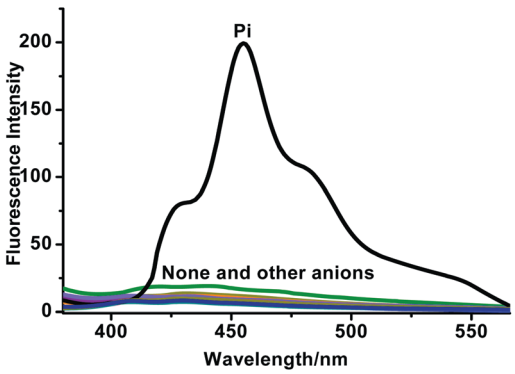

Fig. 9 Fluorescence spectra of receptor **F1** (5.0 μM) in CH_3CN with 5% H_2O upon addition of 5 equiv. of various anions.

The application of F1 in aqueous solution

To validate the selectivity of chemosensor **F1** in aqueous solution, the fluorescence spectral changes of **F1** upon addition of various anions in CH_3CN with 5% H_2O were measured. As shown in Fig. 9, upon addition of various anions mentioned above to CH_3CN with 5% H_2O solution of **F1**, only Pi induced a dramatic fluorescence enhancement. However, quite different emission spectra compared with that in CH_3CN were observed. It might be that the presence of water affects the conformation of **F1** and the complex between **F1** and Pi, which needs further exploration. Although **F1** could not be used to detect Pi in 100% H_2O, the possibility of using **F1** in CH_3CN with 5% H_2O implies that **F1** is strong enough to use the sensing mechanism to detect Pi also in more polar environments.

Conclusions

In conclusion, a new strategy for selective Pi sensing driven by assembly of **F1** exhibiting a turn-on and bathochromic shift of fluorescence has been presented in this paper. Plausible 2 : 2 stoichiometry between **F1** and Pi was deduced from the fluorescence titration, Job plot, absorption spectra, elemental analysis and DFT calculation, providing a novel sensing mechanism for Pi. It was found that **F1** kept the high selectivity for Pi even in aqueous solution. Further work will be focused on the exploration of the detailed structure–property relationship and the design of new sensors on the basis of the anion-directed assembly mechanism. We also think the results are instructive for the construction of new supramolecular architectures.

Experimental section

General

All chemical reagents and solvents for synthesis were purchased from commercial suppliers and were used without further purification. Elemental analysis was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mass spectra were measured on a Agilent 6310 MS spectrometer and a Q-TOF MS spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE-400 spectrometer. The photoluminescence (PL) studies were conducted with a JASCO FP-6300 spectrofluorimeter. A U-4100 Spectrophotometer was used for UV-vis measurements.

Computation methods

The calculation was conducted by using the Gaussian 2009 series of programs. The Pi–**F1** complex was fully optimized using the hybrid density functional B3LYP level of theory with the 6-31G basis set.

Synthesis

Synthesis of 3-(benzoylamino)pyridine (P1). 3-(Benzoylamino)pyridine (**P1**) was synthesized according to reference 18. ^1H NMR (400 MHz, DMSO-d_6) δ[ppm]: 10.45 (s, 1H), 8.94 (d, J = 2.0 Hz, 1H), 8.31 (d, J = 4.8 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 6.8 Hz, 2H), 7.64–7.60 (m, 3H), 7.41 (dd, J = 4.4 Hz, J = 12.8 Hz).

Preparation of F1. A mixture of compound **P1** (0.594 g, 3 mmol) and 9,10-bis(chloromethyl)anthracene (0.412 g, 1.5 mmol) in dry $CHCl_3$ (15 mL) was refluxed for 48 h, and gradually a yellow precipitate was formed. After cooling to room temperature, the precipitate was filtered off and washed several times with cold $CHCl_3$ to give pure **F1** as chloride salts in 56% yield. Then, the chloride salt (100 mg) was dissolved in DMF. During dropwise addition of saturated aqueous KPF_6 solution, a light yellow precipitate was formed. After washing the precipitate several times with distilled water, the desired chemosensor **F1** was obtained in 87% yield. ^1H NMR (400 MHz, DMSO-d_6) δ[ppm]: 11.15 (s, 2H), 9.56 (s, 2H), 8.71 (d, J = 8.0 Hz, 2H), 8.62 (d, J = 8.0 Hz), 8.61 (m, 4H), 8.10 (t, J = 7.2 Hz, 2H), 7.90 (d, J = 7.6 Hz, 4H), 7.80 (m, 4H), 7.65 (m, 2H), 7.56 (m, 4H), 7.14 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ[ppm]: 166.93, 140.09, 139.15, 135.85, 135.21, 133.42, 133.29, 131.92, 129.19, 129.86, 128.80, 128.39, 126.69, 125.14, 56.76; HRMS: calcd for $C_{40}H_{32}N_4O_{22}^+$, 600.2525; Found 600.2522. Anal. calcd for $C_{40}H_{32}F_{12}N_4O_2P_2$: C, 53.94; H, 3.62; N, 6.29; Found: C, 53.75; H, 3.68; N, 6.17. M.P.: 279–280 °C.

Preparation of F2. A mixture of compound **P1** (0.099 g, 0.5 mmol) and 9-(chloromethyl) anthracene (0.114 g, 0.5 mmol)

in dry $CHCl_3$ (20 mL) was refluxed for 50 h, and gradually a yellow precipitate was formed. After cooling to room temperature, the precipitate was filtered off and washed several times with cold $CHCl_3$ to give pure **F2** as the chloride salt in 67% yield. Then, the chloride salt (100 mg) was dissolved in DMF. During dropwise addition of saturated aqueous KPF_6 solution, a light yellow precipitate was formed. After washing the precipitate several times with distilled water and ether, the desired **F2** was obtained in 82% yield. ^{1}H NMR (400 MHz, CD_3CN-d_3) δ[ppm]: 9.31 (s, H), 9.23 (s, H), 8.89 (s, H), 8.60 (d, J = 7.2 Hz, H), 8.48 (m, H), 8.25 (m, 4H), 7.92 (m, H), 7.82 (m, 2H), 7.68 (m, 5H), 7.53 (m, 2H), 6.78 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN-d_3) δ[ppm]: 166.41, 140.17, 138.74, 135.18, 134.21, 133.08, 132.95, 132.74, 131.81, 131.54, 129.75, 128.88, 128.80, 128.65, 128.55, 128.40, 127.99, 127.88, 127.67, 125.90, 124.49, 122.72, 121.04, 120.41, 57.32; HRMS: calcd for $C_{27}H_{21}N_2O^+$, 389.1668; Found 389.1654. Anal. calcd for $C_{27}H_{21}F_6N_2OP$: C, 60.68; H, 3.96; N, 5.24; Found: C, 60.80; H, 3.91; N, 5.27. M.P.: 138–140 °C.

Preparation of F1–Pi complex. Upon addition of 1 equiv. of Pi to the solution of **F1** (10^{-4} M, 50 mL) in CH_3CN, a light yellow precipitate was formed. After washing the precipitate several times with CH_3CN, the desired **F1**–Pi complex was dried under the vacuum conditions and used for elemental analysis. Anal. calcd for **F1** + $H_2PO_4^-$ – PF_6^-: C, 57.01; H, 4.07; N, 6.65; Found: C, 56.43; H, 3.98; N, 6.77.

Measurement of fluorescence spectra and UV-vis spectra

The fluorescence spectra and UV-vis spectra were all measured at room temperature. Stock solutions of the receptors (5.0 μM) were prepared in CH_3CN or in CH_3CN with 5% H_2O and the fluorescence spectra or UV-vis spectra were recorded immediately when 5 equiv. of stock solutions of guests (as the corresponding TBA salts) were added.

General procedure for fluorescence titrations

In this fluorescence titration experiment, the concentration of the receptor **F1** was fixed at (5.0 μM) in CH_3CN. A 3 mL mixture solution of the **F1** and Pi was used for the fluorescence measurement every time. Stock solutions of Pi (as the corresponding TBA salt) in the concentration range 10^{-3} M in CH_3CN were individually added in different amounts to the receptor solution until the fluorescence spectra did not change.

Calculation of detection limit

The fluorescence titration data was used to calculate the detection limit based on a reported method.[19] According to the result of the titration experiment, the fluorescent intensity data at 500 nm were normalized between the minimum intensity and the maximum intensity. A linear regression curve of $I_{min} - I_F/I_{min} - I_{max}$ against log[Pi] was created based on the titration experiment date (Fig. 5), and the point at which this line crossed the horizontal axis was taken as the detection limit (3.62×10^{-7} M).

Measurement of stability constant

The stability constant of the receptor toward Pi reported herein was determined from a nonlinear least-square curve fitting method based on the fluorescence titration data. In this method, the concentration of the receptor **F1** was fixed at 5.0 μM in CH_3CN and the molar ratios of the guest to host were changed by the addition of Pi. Fluorescence spectra were monitored immediately after each addition. The stability constant (K) of the receptor **F1** toward Pi were evaluated using twelve fluorescence titration data points by an iterative nonlinear least squares curve-fitting program.[20]

Job plots

The continuous variation method (Job plot)[20,21] was used for determining the stoichiometric ratio between **F1** and Pi. In this method, solutions of **F1** and Pi of the same concentrations were prepared in CH_3CN to be used for the experiment. Then **F1** and Pi solutions were mixed in different proportions maintaining a total volume of 4 mL and a total concentration of 20 μM of the mixture. Then the emission spectra of the solutions of different compositions were recorded immediately when **F1** and Pi solutions were mixed.

Acknowledgements

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Notes and references

1 (*a*) Z. Szijgyarto, A. Garedew, C. Azevedo and A. Saiardi, *Science*, 2011, **334**, 802; (*b*) V. Ramalingam, M. E. Domaradzki, S. Jang and R. S. Muthyala, *Org. Lett.*, 2008, **10**, 3315; (*c*) J. Yoon, S. K. Kim, N. J. Singh and K. S. Kim, *Chem. Soc. Rev.*, 2006, **35**, 355; (*d*) D. H. Lee, S. Y. Kim and J. I. Hong, *Angew. Chem., Int. Ed.*, 2004, **43**, 4777.

2 (*a*) B. Schazmann, N. Alhashimy and D. Diamond, *J. Am. Chem. Soc.*, 2006, **128**, 8607; (*b*) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 1; (*c*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486.

3 (*a*) N. Ahmed, V. Suresh, B. Shirinfar, I. Geronimo, A. Bist, I.-C. Hwang and K. S. Kim, *Org. Biomol. Chem.*, 2012, **10**, 2094; (*b*) J. Yoon, S. K. Kim, N. J. Singh and K. S. Kim, *Chem. Soc. Rev.*, 2006, **35**, 355; (*c*) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465; (*d*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.

4 (*a*) X. Qian, Y. Xiao, Y. Xu, X. Guo, J. Qian and W. Zhu, *Chem. Commun.*, 2010, **46**, 6418; (*b*) F. Y. Wu, Z. Li, L. Guo, X. Wang, M. H. Lin, Y. F. Zhao and Y. B. Jiang, *Org. Biomol. Chem.*, 2006, **4**, 624.

5 K. Ghosh, A. R. Sarkar and A. Patra, *Tetrahedron Lett.*, 2009, **50**, 6557.

6 (*a*) X. L. Ni, X. Zeng, C. Redshaw and T. Yamato, *J. Org. Chem.*, 2011, **76**, 5696; (*b*) C. He, W. Zhu, Y. Xu, Y. Zhong, J. Zhou and X. Qian, *J. Mater. Chem.*, 2010, **20**, 10755.

7 (*a*) J. S. Wu, J. H. Zhou, P. F. Wang, X. H. Zhang and S. K. Wu, *Org. Lett.*, 2005, **7**, 2133; (*b*) S. K. Kim, J. H. Bok, R. A. Bartsch, J. Y. Lee and J. S. Kim, *Org. Lett.*, 2005, **7**, 4839.

8 (*a*) C. J. Serpell, J. Cookson, A. L. Thompsona and P. D. Beer, *Chem. Sci.*, 2011, **2**, 494; (*b*) A. J. McConnell and P. D. Beer, *Chem.–Eur. J.*, 2011, **17**, 2724; (*c*) A. J. McConnell, C. J. Serpell, A. L. Thompson, D. R. Allan and P. D. Beer, *Chem.–Eur. J.*, 2010, **16**, 1256; (*d*) T. Wang and X. P. Yan, *Chem.–Eur. J.*, 2010, **16**, 4639; (*e*) C. J. Serpell, N. L. Kilah, P. J. Costa, V. Félix and P. D. Beer, *Angew. Chem., Int. Ed.*, 2010, **49**, 5322; (*f*) S. Nishizawa, Y. Kato and N. Teramae, *J. Am. Chem. Soc.*, 1999, **121**, 9463.

9 (*a*) K. Užarević, I. Đilović, D. Matković-Čalogović, D. Šišak and M. Cindrić, *Angew. Chem., Int. Ed.*, 2008, **47**, 7022; (*b*) P. A. Gale and R. Quesada, *Coord. Chem. Rev.*, 2006, **250**, 3219.

10 (*a*) R. Vilar, *Eur. J. Inorg. Chem.*, 2008, 357; (*b*) M. S. Vickers and P. D. Beer, *Chem. Soc. Rev.*, 2007, **36**, 211.

11 (*a*) S. G. Li, C. D. Jia, B. Wu, Q. Luo, X. J. Huang, Z. W. Yang, Q. S. Li and X. J. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 5721; (*b*) S. J. Coles, J. G. Frey, P. A. Gale, M. B. Hursthouse, M. E. Light, K. Navakhun and G. L. Thomas, *Chem. Commun.*, 2003, 568; (*c*) J. Keegan, P. E. Kruger, M. Nieuwenhuyzen, J. O. Brienb and N. Martin, *Chem. Commun.*, 2001, 2192.

12 (*a*) K. Ghosh, A. R. Sarkar and A. Patra, *Tetrahedron Lett.*, 2009, **50**, 6557; (*b*) K. Ghosh and G. Masanta, *Tetrahedron Lett.*, 2008, **49**, 2592.

13 (*a*) W. T. Gong, S. Bao, F. R. Wang, J. W. Ye, G. L. Ning and K. Hiratani, *Tetrahedron Lett.*, 2011, **52**, 630; (*b*) G. Li, W. T. Gong, J. W. Ye, Y. Lin and G. L. Ning, *Tetrahedron Lett.*, 2011, **52**, 1313; (*c*) K. Ghosh, A. R. Sarkar and A. P. Chattopadhyay, *Eur. J. Org. Chem.*, 2009, 4515; (*d*) W. T. Gong, U. Harigae, J. Seo, S. S. Lee and K. Hiratani, *Tetrahedron Lett.*, 2008, **49**, 2268; (*e*) W. T. Gong and K. Hiratani, *Tetrahedron Lett.*, 2008, **49**, 5655; (*f*) W. T. Gong, K. Hiratani and S. S. Lee, *Tetrahedron*, 2008, **64**, 11007.

14 (*a*) M. H. Filby, S. J. Dickson, N. Zaccheroni, L. Prodi, S. Bonacchi, M. Montalti, M. J. Paterson, T. D. Humphries, C. Chiorboli and J. W. Steed, *J. Am. Chem. Soc.*, 2008, **130**, 4105; (*b*) A. Yamauchi, T. Hayashita, S. Nishizawa, M. Watanabe and N. Teramae, *J. Am. Chem. Soc.*, 1999, **121**, 2319.

15 K. Ghosh, A. R. Sarkar, A. Ghoraib and U. Ghosh, *New J. Chem.*, 2012, **36**, 1231.

16 (*a*) K. Ghosh and I. Saha, *New J. Chem.*, 2011, **35**, 1397; (*b*) H. S. Jung, M. Park, D. Y. Han, E. Kim, C. Lee, S. Ham and J. S. Kim, *Org. Lett.*, 2009, **11**, 3378.

17 (*a*) Y. Molard, D. M. Bassani, J. P. Desvergne, P. N. Horton, M. B. Hursthouse and J. H. R. Tucker, *Angew. Chem., Int. Ed.*, 2005, **44**, 1072; (*b*) H. K. Cho, D. H. Lee and J.-In. Hong, *Chem. Commun.*, 2005, 1690; (*c*) F. Fages, J.-P. Desvergne and H. B. Laurent, *J. Org. Chem.*, 1994, **59**, 5264.

18 S. Ueda and H. Nagasawa, *J. Org. Chem.*, 2009, **74**, 4272.

19 (*a*) W. Lin, L. Yuan, Z. Cao, Y. Feng and L. Long, *Chem.–Eur. J.*, 2009, **15**, 5096; (*b*) A. Caballero, R. Martmez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina and J. Veciana, *J. Am. Chem. Soc.*, 2005, **127**, 15666; (*c*) M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414.

20 (*a*) Y. Nakahara, T. Kida, Y. Nakatsuji and M. Akashi, *Org. Biomol. Chem.*, 2005, **3**, 1787; (*b*) K. A. Conners, *Binding Constants, the Measurement of Molecular Complex Stability*, John Wiley & Sons, New York, 1987, p. 147.

21 P. Job, *Ann. Chim.*, 1928, **9**, 113.