A highly selective fluorescent sensor for fluoride through ESPT signaling transduction†

Yong-gang Zhao, Bing-guang Zhang, Chun-ying Duan,* Zhi-hua Lin and Qing-jin Meng*

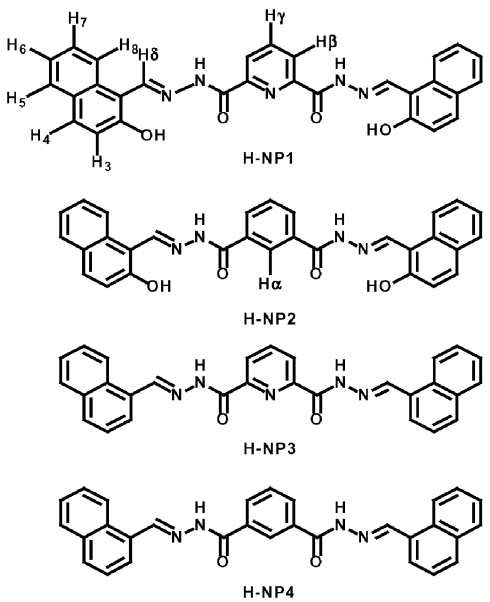
Received (in Durham, UK) 10th April 2006, Accepted 21st June 2006
First published as an Advance Article on the web 13th July 2006
DOI: 10.1039/b605087e

A highly selective fluorescent sensor for fluoride, bis(2-hydroxy-1-naphthaldehyde)-2,6-pyridinedicarboxylic acid hydrazone (H-NP**1**) was synthesized and structurally characterized. UV-Vis and luminescent titrations of H-NP**1** with F^- demonstrated the presence of an H-NP**1**$\cdots F^-$ interaction species with association constant $\log K^{\#} = 5.26 \pm 0.01$. The sensor responded to fluoride ion through an excited-state intermolecular proton transfer (ESPT) mechanism with the emission band red-shifted and enhanced. For further studying the potential mechanism, binding-signaling transduction of related compound H-NP**2**, bis(2-hydroxy-1-naphthaldehyde)-1,3-benzenedicarboxylic acid hydrazone and two control compounds (H-NP**3**) and (H-NP**4**) derived from 1-naphthaldehyde was also investigated for comparison.

Introduction

Selective recognition and sensing of anions species *via* artificial receptors have attracted considerable attention during the past decades, because of their significant importance and potential applications in biological, environmental and supramolecular sciences.[1–3] A coordination chemistry of anions requires that both the energies of non-covalent interactions used to combine an anion guest, and the geometry, basicity of the anion and the nature of the solvent medium to be taken into account.[4] Among these non-covalent interactions, hydrogen-bonding is directional, a feature which allows for the possibility of designing receptors with specific shapes that are capable of differentiating between anionic guests with different geometries.[5,6]

At the same time, not only selectivity should fit the purpose, but also the processes that generate the information and transduce it to the user have to be powerful and unequivocal to fulfill analytical needs with respect to sensitivity and instrumentation.[7] Of particular interest on this regard are fluorescent sensors, as they are both highly sensitive and easy to signal.[8] For this purpose, many fluorescent sensors for anions have been developed on the basis of a variety of signaling mechanisms such as competitive binding,[9] photo-induced electron transfer (PET),[10] metal-to-ligand charge transfer (MLCT),[11] excimer/exciplex,[12] and intramolecular charge transfer.[13] Recently, Choi and Hamilton[14] reported that anion binding close to the fluorophore could lead to the stabilization of positive charge developed in the fluorophore excited state and to opening of another fluorescence emission channel through intermolecular excited state proton transfer (ESPT). To provide a new strategy of linking a fluorophore with emission from an internal charge transfer excited state to an ion-binding domain,[15] we report here the preparation and binding-signaling transduction of the highly selective fluorescent receptor H-NP**1**, bis(2-hydroxy-1-naphthaldehyde)-2,6-pyridinedicarboxylic acid hydrazone (Scheme 1), for fluoride ion, and investigate the potential binding–signalling transduction of H-NP**1** and the related compounds. It is expected that as the anion-binding domain, the two-armed receptor can bind certain anions strongly and selectively through H-bonds by using the amide N–H groups and naphthol groups, from which the acidities of the naphthol OH groups and amide protons were drastically enhanced upon photo-excitation and therefore an ESPT channel was opened.[16]



Scheme 1

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China. E-mail: duancy@nju.edu.cn

† Electronic supplementary information (ESI) available: Color changes, ^{1}H NMR titrations, UV-Vis spectra and emission changes. See DOI: 10.1039/b605087e

Experimental

Materials and measurements

All chemicals used were of reagent grade or better, obtained from commercial sources and used without further purification, except for the solvents for physical measurements which were purified by classical methods. All anions used (F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and $H_2PO_4^-$) were in the form of their tetrabutylammonium salts. The acyl hydrazides (2,6-pyridinedicarboxylic acid hydrazide and 1,3-benzenedicarboxylic acid hydrazide) were obtained according to the published methods.[17] Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 analyzer. UV-Vis spectra were obtained on a Shimmadzu 3100 spectrophotometer in DMSO at room temperature. ^{1}H NMR spectra were measured on a Bruker DRX-500 NMR spectrometer at room temperature. For ^{1}H NMR titrations a solution (5.0×10^{-3} mol L^{-1}) of receptor compound in DMSO-d_6 was prepared. Fluorescence spectra were recorded on an AMINCO Bowman Series 2 Luminescence spectrometer. For fluorometric titration a stock solution of receptor (5.0×10^{-5} mol L^{-1}) and stock solutions (1.0×10^{-2} mol L^{-1}) of the tetrabutylammonium salts of F^-, Cl^-, Br^-, I^- and $H_2PO_4^-$ in DMSO were prepared.

Bis(2-hydroxy-1-naphthaldehyde)-2,6-pyridinedicarbohydrazone (H-NP1)

A mixture of 2,6-pyridinedicarbohydrazide (0.19 g, 1.0 mmol) and 2-hydroxy-1-naphthaldehyde (0.38 g, 2.2 mmol) was refluxed in ethanol for 4 h. The yellow solid formed was filtered off and dried in vacuum. Yield 0.41 g (80%). Anal. Calc. for $C_{29}H_{22}N_5O_4$, C 69.04, H 4.40, N 13.88. Found: C 69.03, H 4.41, N 13.82%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.56 (2H, NH or OH), 12.54 (2H, NH or OH), 9.83 (2H, CH), 8.56–8.54 (2H, d, J = 8.5 Hz, Hβ), 8.44–8.42 (2H, d, J = 7.0 Hz, Np), 8.39–8.37 (H, t, J = 6.5 Hz, Hγ), 8.02–8.00 (2H, d, J = 9.0 Hz, Np), 7.97–7.95 (2H, d, J = 8.0 Hz, Np), 7.71–7.65 (2H, t, J = 7.5 Hz, Np), 7.50–7.47 (2H, t, J = 7.5 Hz, Np), 7.32–7.30 (2H, d, J = 8.5 Hz, Np). Crystals suitable for X-ray structural determination were obtained by evaporation a DMSO solution in air.

Bis(2-hydroxy-1-naphthaldehyde)-1,3-benzenedicarbohydrazone (H-NP2)

A similar procedure to the synthesis of H-NP**1** was carried out using 1,3-benzenedicarbohydrazide in place of 2,6-pyridinedicarbohydrazide. Yield: 0.38 g (75%). Anal. Calc. $C_{30}H_{22}N_4O_4 \cdot H_2O$, C 69.21, H 4.65, N 10.77. Found: C 69.31, H 4.92, N 10.45%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.73 (2H, NH or OH), 12.42 (2H, NH or OH), 9.54 (2H, CH), 8.63 (H, s, H_α), 8.29–8.27 (2H, d, J = 8.5 Hz, H_β), 8.25–8.23 (2H, d, J = 7.5 Hz, Np), 7.97–7.95 (2H, d, J = 9.0 Hz, Np), 7.93–7.91 (2H, d, J = 8.0 Hz, Np), 7.83–7.82 (H, t, J = 7.5 Hz, H_γ), 7.65–7.62 (2H, t, J = 7.5 Hz, Np), 7.45–7.42 (2H, t, J = 7.5 Hz, Np), 7.27–7.25 (2H, d, J = 8.5 Hz, Np). Crystals suitable for X-ray structural determination were obtained by evaporation a DMSO solution in air.

Bis(1-naphthaldehyde)-2,6-pyridinedicarbohydrazone (H-NP3)

A similar procedure to the synthesis of H-NP**1** was carried out using 1-naphthaldehyde in place of 2-hydroxy-1-naphthaldehyde. Yield: 0.38 g (80%). Anal. Calc. for $C_{29}H_{22}N_5O_2$: C 73.70, H 4.70, N 14.83. Found: C 73.59, H 4.75, N 14.86%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.45 (2H, NH), 9.47 (2H, CH), 9.02–9.00 (2H, d, J = 8.5 Hz, Np), 8.44–8.43 (2H, d, J = 7.5 Hz, H_β), 8.37 (H, t, H_γ), 8.11–8.09 (2H, t, J = 4.5 Hz, Np), 8.08–8.06 (4H, d, J = 8.0 Hz, Np), 7.75–7.72 (2H, t, J = 7.5 Hz, Np), 7.70–7.68 (2H, d, J = 7.5 Hz, Np), 7.67–7.66 (2H, t, J = 4 Hz, Np).

Bis(1-naphthaldehyde)-1,3-benzenedicarbohydrazone (H-NP4)

A similar procedure to the synthesis of H-NP**3** was carried out using 1,3-benzenedicarbohydrazide in place of 2,6-pyridinedicarbohydrazide. Yield: 0.39 g (82%). Anal. Calc. for $C_{30}H_{22}N_4O_2$: C 76.58, H 4.71, N 11.91. Found: C 76.59, H 4.71, N 11.82%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.14 (2H, NH), 9.17 (2H, CH), 8.88–8.87 (2H, d, J = 8.5 Hz, Np), 8.58 (H, s, H_α), 8.21–8.20 (2H, d, J = 7.5 Hz, H_β), 8.07–8.03 (4H, d, J = 8.5 Hz, Np), 7.99–7.97 (2H, d, J = 7.0 Hz, Np), 7.78–7.76 (H, t, J = 8.0 Hz, H_γ), 7.72–7.69 (2H, t, J = 7.5 Hz, Np), 7.65–7.62 (4H, t, J = 7.5 Hz, Np).

Crystallography

Parameters for data collection and refinement of the two complexes (H-NP**1** and H-NP**2**) are summarized in Table 1. Intensities of the compounds were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the SMART and SAINT programs.[18] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1.[19] All of the non-hydrogen atoms except the disordered solvent molecules were refined with

Table 1 Crystal data for compounds H-NP**1** and H-NP**2**

	H-NP**1**	H-NP**2**
Formula	$C_{29}H_{21}N_5O_4$	$C_{30}H_{22}N_4O_4$
M_r	503.51	502.52
Color	Deep red	Yellow
Dimensions/mm	2.50 × 1.25 × 0.50	0.25 × 0.15 × 0.70
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	18.720(4)	15.323(3)
b/Å	15.110(3)	9.3464(15)
c/Å	8.5745(18)	17.451(3)
β/°	94.249(4)	104.854(3)
V/Å^3	2418.7(9)	2415.6(7)
Z	4	4
D_c/g cm^{-3}	1.383	1.382
μ(Mo-Kα)/mm^{-1}	0.095	0.094
Measured reflns	5897	11705
Unique reflns	2126	4249
R_{int}	0.1054	0.0611
Strong data [$I_o > 2\sigma(I_o)$]	1782	2314
R_1, wR_2 (observed data)	0.0617, 0.1593	0.0505, 0.0659
R_1, wR_2 (all data)	0.0724, 0.1688	0.1129, 0.0760
GOOF	1.103	0.958
Refined parameters	173	343
Max./min. residuals/e Å^{-3}	0.25, −0.33	0.14, −0.16

anisotropic thermal displacement coefficients. Hydrogen atoms were located geometrically and refined in riding model.

CCDC reference numbers 291364 and 291365.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605087e

Results and discussion

All receptors were prepared *via* two-step simple-controlled reactions from diester to dihydrazide, then to final receptors in good yields. Elemental analyses and spectroscopic characterizations confirm the formation of the two-branched Schiff-base compounds. Crystal structure analysis of compound H-NP**1** exhibits a special configuration with two amide-naphthol arms disposed on the same side (Fig. 1). The two parts of the molecule are symmetrically related with the nitrogen atom N(3) of the pyridine ring lying on the two-fold axis to form a helical species. The dihedral angles between one naphthyl ring and one phenyl ring are about 10.5° on average, with the dihedral angle between two naphthyl rings of 6.4°. Intramolecular hydrogen bonds between the O–H group and imine nitrogen atoms are found with an O···N separation of 2.602(2) Å and O–H···N angle of 147°, respectively. Intermolecular hydrogen bonds are also found between the amide groups and the carboxyl oxygen atoms of neighboring molecules with the N···O separation about 3.103(5) Å and N–H···O angle being 151.9(1)°, respectively.

The crystal structure of H-NP**2** exhibits an asymmetrical open configuration with two amidenaphthol arms deposited on either side of the benzene ring (Fig. 2). The skeleton of the molecule is divided into three planar fragments, one phenyl ring and two naphthyl rings, respectively. The dihedral angles between a naphthyl ring and a phenyl ring are about 11.4° on average, with the dihedral angle between two naphthyl rings *ca.* 6.4°. Bond distances of the two arms are intermediate between formal single bonds and double bonds, indicating extensive delocalization in the whole system.

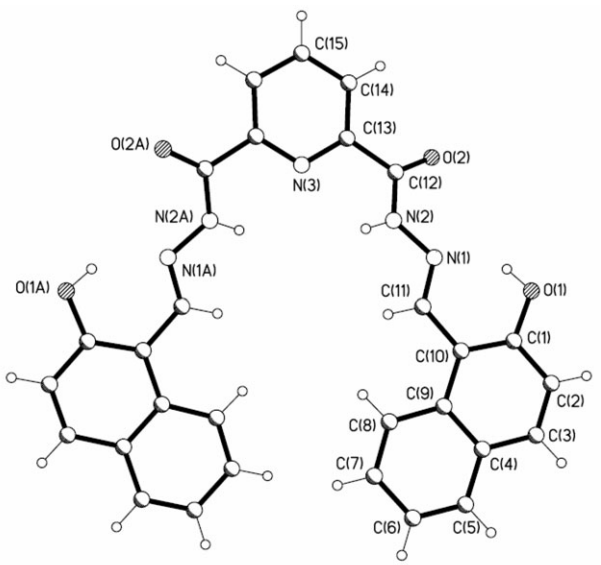


Fig. 1 Molecular structure of compound H-NP**1**.

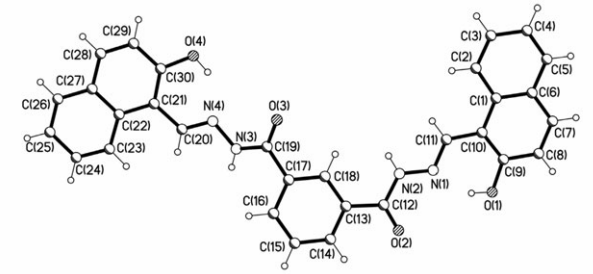


Fig. 2 Molecular structure of compound H-NP**2**.

Compound H-NP**1** exhibits two main bands at about 330 and 370 nm in the UV-Vis spectrum in DMSO solution. While addition of an excess amount (more than 20 times the stoichiometric mole ratio) of Cl^-, Br^-, I^-, NO_3^-, HSO_4^- and even $H_2PO_4^-$ do not induce any detectable changes, the presence of fluoride ion results in the intensities of the absorption bands at 330 and 370 nm decreasing gradually with new bands appearing at 440, 465 and 495 nm (Fig. 3). The presence of several well-defined isosbestic points indicates that only two species coexist in the equilibrium with an association constant log K_{ass} for the 1 : 1 stoichiometry host–guest complex [H-NP**1**···F^-] calculated as 3.78 ± 0.2.

Fig. 4 shows the fluorescence spectrum of H-NP**1** in DMSO solution. Two bands at *ca.* 495 and 520 nm are assigned to the emissions of the substituted naphthalene moieties. After addition of F^-, the bands red-shift and develop with the intensity of the peak at 520 nm enhanced to a limiting value up to *ca.* 250%, indicating a potential excited-state intermolecular excited state proton transfer signaling mechanism.[20] The existence of the ESPT process complicates the determination of the ground-state dissociation constant using fluorescent measurement. The apparent association constant (log $K^{\#}$ = 5.26 ± 0.01), calculated from fluorescence titration with the excitation wavelength at the isosbestic point reflects the contributions of both the ground state association constant K_{ass} and the excited-state association constant K^*.

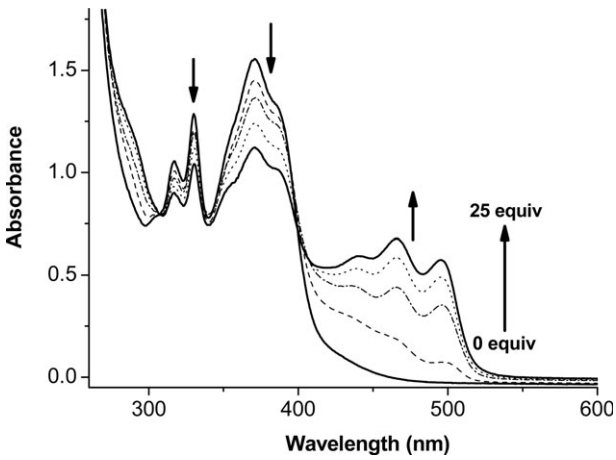


Fig. 3 UV-Vis titrations of H-NP**1** in DMSO (5.0×10^{-5} M) upon addition of F^-.

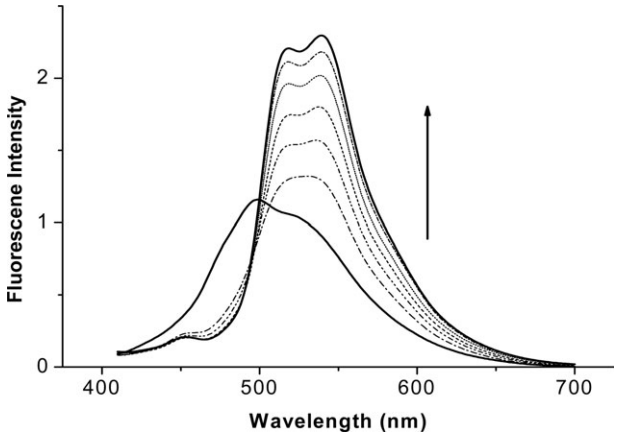


Fig. 4 Changes in emission spectra of H-NP**1** in DMSO (5×10^{-5} M) upon addition of F^-; excitation at 400 nm, the isosbestic point in UV-Vis spectrum.

Upon addition of anions such as Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and even $H_2PO_4^-$, no detectable changes can be observed in the emission spectra. It is suggested that the high selectivity is attributed to the strong intramolecular O–H···N hydrogen bonding of H-NP**1**, from which the hydrogen atoms are fastened, and only the anion showing the most electronegative property has the potential to form additional hydrogen bonding.[21]

Generally, the photoinduced intermolecular proton transfer may proceed in two different ways: binding–excitation–deprotonation and excitation–collision–deprotonation.

Excitation–collision deprotonation mechanism:

$$\text{H-NP} \rightarrow \text{H-NP*} \quad (1)$$

$$\text{H-NP*} + \text{X}^- \rightarrow \text{NP}^{-}\text{*} + \text{HX} \quad (2)$$

Binding–excitation deprotonation mechanism:

$$\text{H-NP} + \text{X}^- \rightarrow [\text{H-NP}\cdots\text{X}^-] \quad (3)$$

$$[\text{H-NP}\cdots\text{X}^-] \rightarrow [\text{H-NP}\cdots\text{X}^-]^* \quad (4)$$

$$[\text{H-NP}\cdots\text{X}^-]^* \rightarrow \text{NP}^{-}\text{*} + \text{HX} \quad (5)$$

Clearly, in the first mechanism, the luminescent intensity (the concentration of the excited species NP^-*) is only dependent on the acid–base property of the anion added, and the selectivity, if present, should be controlled by the acid–base property of the anion itself. In the second mechanism, the luminescent intensity is dependent on the association constants of [H-NP···X^-] both in the ground and excited states, and the selectivity should be controlled by the binding strength of the hydrogen bonding. Consequently, the high selectivity of H-NP**1** for fluoride ion demonstrates that the process represented by eqn (2) does not occur.

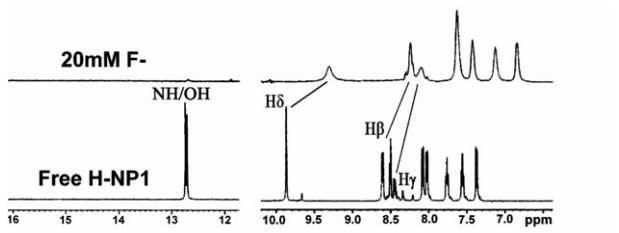


Fig. 5 ^{1}H NMR titrations of H-NP**1** in DMSO-d_6 (5×10^{-3} M) with F^-.

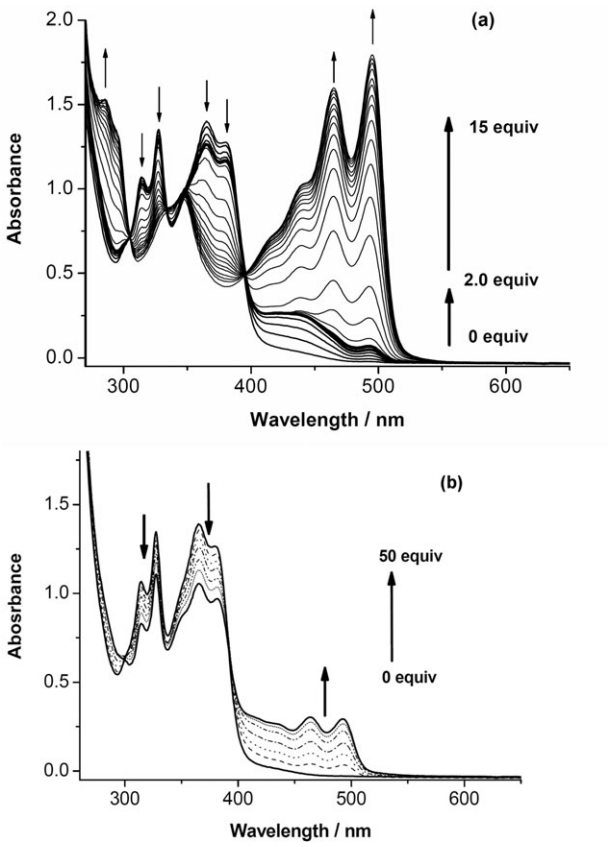


Fig. 6 Family of spectra taken in the course of the titration of H-NP**2** (5×10^{-5}) in DMSO with a standard solution of F^- (a) and $H_2PO_4^-$ (b).

The ^{1}H NMR spectrum of H-NP**1** exhibits two peaks at about 12.71 and 12.74 ppm, which can be assigned to the N–H and O–H protons. Upon addition of F^-, the peaks first shift downfield then broaden and finally disappear, and the other peaks broaden and exhibit significant up-field shifts ($\Delta\delta$ = 0.30–0.57 ppm), indicating the formation of a host–guest hydrogen-bonding complex and the existence of proton exchange between several conformations and an overall change of the electron distribution (Fig. 5).

UV-Vis titrations of H-NP**2** for fluoride ion display a more complex behavior (Fig. 6(a)). The addition of the first stoichiometric ratio of F^- results in the intensities of the absorption bands at 315, 325, 365 and 380 nm decreasing gradually with a new band at 440 nm appearing. In particular, the new band at 440 nm remains present until addition of a second stoichiometric mol ratio of F^-. With a further addition (>2 mol equiv. of F^-), new bands at 465 and 495 nm appear and develop significantly. Meanwhile, another new band forms at 285 nm, which is due to the formation of naphtholate. The titration profiles suggests the presence of two distinct steps: the

formation of the [H-NP**2**···F^-] interaction species through hydrogen-bonding, and the deprotonation of O–H upon further addition of F^- which cause the colorimetric response and visible detection (see ESI†).[4a,22] Fitting the overall titration data by assuming the existence of two equilibria gives the association constants as $\log K_1 = 6.17 \pm 0.02$ and $\log K_2 = 4.54 \pm 0.02$, respectively. Additions of excess amount (more than 20 times stoichiometric ratio) of Cl^-, Br^-, I^-, NO_3^- and HSO_4^- to a DMSO solution of H-NP**2** do not induce any detectable changes. However, the presence of $H_2PO_4^-$ results in significant spectroscopic changes (Fig. 6(b)), indicating the poor selectivity of H-NP**2** for F^- compared to that of H-NP**1**. Detailed spectral analyses reveal that both the absorption shape and intensities of [H-NP**1**···F^-] and [H-NP**2**···$H_2PO_4^-$] species are quite similar.

Fluorescence spectra are also recorded from a solution of the receptor H-NP**2** in the presence of F^-. As shown in Fig. 7(a), the intensity of the peak at 495 nm decreases significantly, while the intensity of the peak at 520 nm remains stable until a second stoichiometric ratio of F^- is added. With the further addition of F^-, the peak at 518 nm red-shifts to 540 nm and increases in intensity to a limiting value up to *ca.* 300%. The association constants for two distinct steps in the luminescent titrations are calculated as $\log K_1 = 6.09 \pm 0.02$ and $\log K_2 = 5.63 \pm 0.02$. The red shift is also presumed as the result of stabilization of the fluorophore excited state relative to the ground state.[14,16,20] The changes found in the fluorescent spectra agree well with the two stepwise processes inferred from the UV-Vis titrations.

The presence of $H_2PO_4^-$ also causes luminescence enhancement with the emission spectrum of the [H-NP**2**···$H_2PO_4^-$] being similar to that of [H-NP**1**···F^-] (Fig. 7(b)). It is reasonable to assume that the response of H-NP**2** towards the $H_2PO_4^-$ anion is due to the cleft-shaped structure of H-NP**2**.

To further study the bonding properties of compound H-NP**2** with anions, ^{1}H NMR titrations were carried out to support the above interpretations. With Cl^-, Br^-, I^-, NO_3^- and HSO_4^-, no chemical shift changes for any protons of H-NP**2** were observed, even up to 10 equiv. of these anions. Upon addition of $H_2PO_4^-$ ion, the NH and OH protons first shift downfield, then broaden and finally disappear with the H_α signal of the phenyl ring downfield shifted about 0.52 ppm (Fig. 8). Meanwhile, the downfield shift ($\Delta\delta = 0.51$) of the CH=N proton H_δ is also observed. The [H-NP**2**···$H_2PO_4^-$] interaction species is thus stabilized by multiple hydrogen bonds.

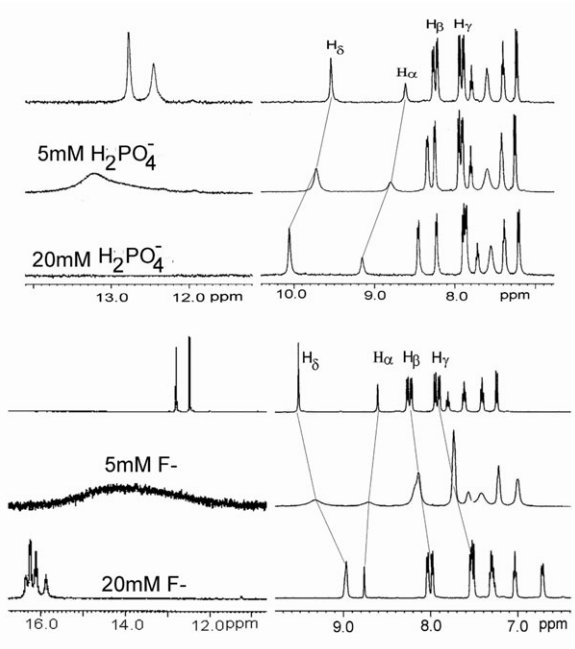


Fig. 8 ^{1}H NMR titrations of H-NP**2** in DMSO-d_6 (5×10^{-3} M) with $H_2PO_4^-$ (top) and F^- (bottom).

Addition of fluoride to a DMSO-d_6 solution of H-NP**2** results in similar downfield shifts, resonance broadening and final disappearance of the O–H and N–H protons. The downfield shift of the H_α proton in the phenyl ring indicates the formation of C–H···F hydrogen bonding.[23] After a fourth stoichiometric mol ratio of F^- was added, low-field signals at 16.25 ppm (triplet), which is assigned to bifluoride ion (FHF^-),[5,24] appeared. At the same time, significant up-field shifts of all the aromatic proton signals ($\Delta\delta = 0.26$–0.57 ppm), except for the H_α proton were found, indicating an overall change of the electron distribution and enhancement of the π localization in the receptor.[4a,25] The downfield shift of H_α suggests that even in the deprotonated species, C–H···F hydrogen bonding still exists, and cooperated with the N–H···F hydrogen bonds.

To further identify the proton transfer sites and signaling transduction, two control compounds H-NP**3**, and H-NP**4**

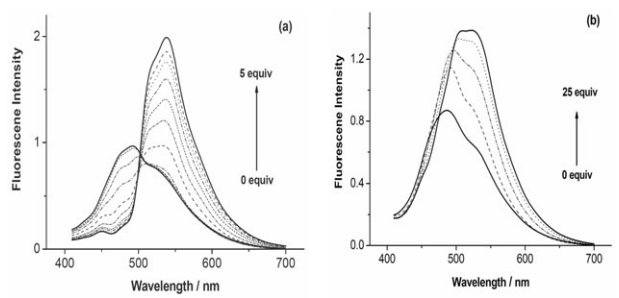


Fig. 7 Changes in emission spectra of H-NP**2** (5×10^{-5} M) in DMSO upon addition of F^- (a) and $H_2PO_4^-$ (b); excitation at 395 nm, the isosbestic point in UV-Vis spectra.

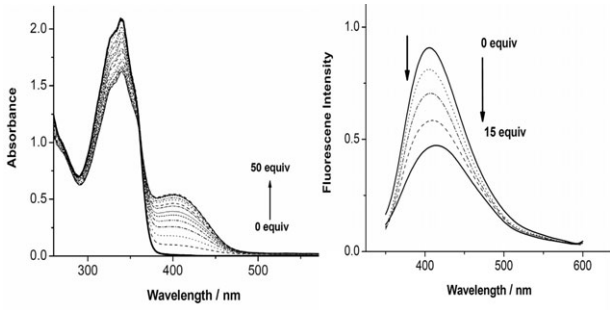


Fig. 9 UV-Vis spectra of H-NP**4** in DMSO (5×10^{-5} M) upon addition of F^- (left). Changes in emission spectra of H-NP**3** in DMSO (5×10^{-5} M) upon addition of fluoride ions. Excited at 362 nm (right).

were prepared. Fig. 9 shows the UV-Vis titrations of receptor H-NP**4**. As can be expected, the absence of O–H groups leads to the spectra being more simple than that of the related compound H-NP**2**. During the titration of F^-, the peak at 340 decreases with a new peak at about 400 nm appearing. Such a spectral change contributes to the formation of a 1 : 1 mol ratio host–guest complex. For compound H-NP**3**, addition of F^- causes obvious spectral changes but no exact isosbestic point is obtained, indicating that the presence of pyridine nitrogen prevents the formation of hydrogen bonding from the N–H groups. The presence of Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, and even $H_2PO_4^-$, lead to no obvious spectroscopic changes being observed even upon addition to 50 equiv. of these anions.

Luminescent titrations of the two receptors H-NP**3** and H-NP**4** exhibit similar spectroscopic changes. For both receptors H-NP**3** and H-NP**4**, fluorescence quenching process occurs upon addition of F^-. The "switch off" behavior demonstrates that the N–H···F hydrogen bonding enhances the PET processes between the fluorophore units and the hydrazone moieties. So it is therefore obvious that proton transfer occurs between the hydroxy groups of the sensor, and the anion induces an efficient luminescent enhancement through ESPT signaling transduction.

Conclusions

A new strategy to achieve highly selective luminescent sensors for fluoride ion was presented. This approach has been utilized to improve selectivity for F^- over $H_2PO_4^-$, NO_3^-, HSO_4^- and other halide anions through excited-state intermolecular proton transfer. The introduction of O–H at the naphthalene fluorophore unit results in a "switch on" ESPT signaling transduction through binding–excitation–deprotonation from which the high selectivity is achieved.

Acknowledgements

This work is supported by the National Natural Science Foundation and the Ministry of Education of China.

References

1 (*a*) A. Bianchi, K. Bowman-James and E. García-España, *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, 1997; (*b*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609; (*c*) T. S. Snowden and E. V. Anslyn, *Curr. Opin. Chem. Biol.*, 1999, **3**, 740.

2 (*a*) A. P. Bisson, V. M. Lynch, M.-K. Monahan and E. V. Anslyn, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2340; (*b*) M. M. G. Antonisse and D. N. Reinhoudt, *Chem. Commun.*, 1998, 443; (*c*) H. Miyaji, P. Anzenbacher, Jr, J. L. Sessler, E. R. Bleasdale and P. A. Gale, *Chem. Commun.*, 1999, 1723; (*d*) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154; (*e*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*f*) M. Takeuchi, T. Shioya and T. M. Swager, *Angew. Chem., Int. Ed.*, 2001, **40**, 3372; (*g*) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2001, **123**, 11372; (*h*) M.-L. Lehaire, R. Scopelliti, H. Piotrowski and K. Severin, *Angew. Chem., Int. Ed.*, 2002, **41**, 1419; (*i*) C. R. Bondy and S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77; (*j*) R. Vilar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1460; (*k*) S. Zhang and L. Echegoyen, *J. Am. Chem. Soc.*, 2005, **127**, 2006.

3 (*a*) L. Fabbrizzi and A. Poggi, *Chem. Soc. Rev.*, 1995, **24**, 197; (*b*) J.-P. Desvergne and A. W. Czarnik, *Chemosensors of Ion and Molecular Recognition*, Kluwer, Dordrecht, 1997, vol. 492; (*c*) K. Fuji, K. Tsubaki, K. Tanaka, N. Hayashi, T. Otsubo and T. Kinoshita, *J. Am. Chem. Soc.*, 1999, **121**, 3807; (*d*) R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419; (*e*) L. S. Evans, P. A. Gale, M. E. Light and R. Quesada, *Chem. Commun.*, 2006, 965.

4 (*a*) M. Vázquez, L. Fabbrizzi, A. Taglietti, R. M. Pedrido, A. M. González-Noya and M. R. Bermejo, *Angew. Chem., Int. Ed.*, 2004, **43**, 1962; (*b*) M. J. Chmielewski and J. Jurczak, *Chem.-Eur. J.*, 2005, **11**, 6080.

5 (*a*) M. Boiocchi, L. Del Boca, D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507; (*b*) T. Gunnlaugsson, P. E. Kruger, P. Jensen, J. Tierney, H. D. P. Ali and G. M. Hussey, *J. Org. Chem.*, 2005, **70**, 10875.

6 (*a*) D. Jiménez, R. Martínez-Mañez, F. Sancenón and J. Soto, *Tetrahedron Lett.*, 2002, **43**, 2823; (*b*) E. J. Cho, J. W. Moon, S. W. Ko, J. Y. Lee, S. K. Kim, J. Yoon and K. C. Nam, *J. Am. Chem. Soc.*, 2003, **125**, 12376.

7 (*a*) C. Suksai and T. Tuntulani, *Chem. Soc. Rev.*, 2003, **32**, 192; (*b*) A. B. Descalzo, K. Rurack, H. Weisshoff, R. Martínez-Máñez, M. Dolores Marcos, P. Amorós, K. Hoffmann and J. Solo, *J. Am. Chem. Soc.*, 2005, **127**, 184; (*c*) E. J. Cho, B. J. Ryu, Y. J. Lee and K. C. Nam, *Org. Lett.*, 2005, **7**, 2607.

8 (*a*) A. W. Czarnik, *Fluorescent chemosensors for Ion and Molecule Recognition*, American Chemical Society, Washington, DC, 1993; (*b*) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (*c*) A. W. Czarnik, *Acc. Chem. Res.*, 1998, **27**, 302; (*d*) M. H. Keefe, K. D. Benkstein and J. T. Hupp, *Coord. Chem. Rev.*, 2000, **205**, 201; (*e*) L. Fabbrizzi, M. Licchelli, G. Rabaioli and A. Taglietti, *Coord. Chem. Rev.*, 2000, **205**, 85; (*f*) P. Anzenbacher, Jr, K. Jursiková and J. L. Sessler, *J. Am. Chem. Soc.*, 2000, **122**, 9350; (*g*) P. E. Kruger, P. R. Mackie and M. Nieuwenhuyzen, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1079; (*h*) L. A. Cabell, M. D. Best, J. J. Lavigne, S. E. Schneider, D. M. Perreault, M. K. Monahan and E. V. Anslyn, *J. Chem. Soc., Perkin Trans. 2*, 2001, 315; (*i*) Y. Kubo, S. Ishihara, M. Tsukahara and S. Tokita, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1455; (*j*) D. H. Lee, J. H. Im, J.-H. Lee and J.-I. Hong, *Tetrahedron Lett.*, 2002, **43**, 9637; (*k*) C. P. Causey and W. E. Allen, *J. Org. Chem.*, 2002, **67**, 5963; (*l*) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi and K. Tamao, *Angew. Chem., Int. Ed.*, 2003, **42**, 2036; (*m*) H. A. Ho and M. Leclerc, *J. Am. Chem. Soc.*, 2003, **125**, 4412; (*n*) V. Amendola, L. Fabbrizzi and E. Monzani, *Chem.-Eur. J.*, 2004, **10**, 76.

9 (*a*) K. Niikura, A. Metzger and E. V. Anslyn, *J. Am. Chem. Soc.*, 1998, **120**, 8533; (*b*) A. Metzger and E. V. Anslyn, *Angew. Chem., Int. Ed.*, 1998, **37**, 649; (*c*) S. L. Wiskur, H. Ait-Haddou, E. V. Anslyn and J. J. Lavigne, *Acc. Chem. Res.*, 2001, **34**, 963; (*d*) L. Fabbrizzi, N. Marcotte, F. Stomeo and A. Taglietti, *Angew. Chem., Int. Ed.*, 2002, **41**, 3811.

10 (*a*) D. H. Vance and A. W. Czarnik, *J. Am. Chem. Soc.*, 1994, **116**, 9397; (*b*) T. Gunnlaugsson, A. P. Davis and M. Glynn, *Chem. Commun.*, 2001, 2556; (*c*) S. K. Kim and J. Yoon, *Chem. Commun.*, 2002, 770; (*d*) T. Gunnlaugsson, A. P. Davis, J. E. O'Brien and M. Glynn, *Org. Lett.*, 2002, **4**, 2449; (*e*) T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer and G. Hussey, *TetrahedronLett.*, 2003, **44**, 6575; (*f*) V. Thiagarajan, P. Ramamurthy, D. Thirumalai and V. T. Ramakrishnan, *Org. Lett.*, 2005, **7**, 657.

11 (*a*) P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71; (*b*) M.-J. Kim, R. Konduri, H. Ye, F. M. MacDonnell, F. Puntoriero, S. Serroni, S. Campagna, T. Holder, G. Kinsel and K. Rajeshwar, *Inorg. Chem.*, 2002, **41**, 2471.

12 (*a*) S. Nishizawa, H. Kaneda, T. Uchida and N. Teramae, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2325; (*b*) S. Nishizawa, Y. Kato and N. Teramae, *J. Am. Chem. Soc.*, 1999, **121**, 9463; (*c*) J. Reichwagen, H. Hopf, A. Del Guerzo, J.-P. Desvergne and H. Bouas-Laurent, *Org. Lett.*, 2004, **6**, 1899; (*d*) J. S. Wu, J. H. Zhou, P. F. Wang, X. H. Zhang and S. K. Wu, *Org. Lett.*, 2005, **7**, 2133.

13 (*a*) F. Y. Wu, Z. Li, Z. C. Wen, N. Zhou, Y. F. Zhao and Y. B. Jiang, *Org. Lett.*, 2002, **4**, 3203; (*b*) F. Y. Wu and Y. B. Jiang, *Chem. Phys. Lett.*, 2002, **355**, 438; (*c*) Z. C. Xu, Y. Xiao, X. H. Qian, J. N. Cui and D. W. Cui, *Org. Lett.*, 2005, **7**, 889.

14 K. Choi and A. D. Hamilton, *Angew. Chem., Int. Ed.*, 2001, **40**, 3912.
15 (*a*) J. Herbich, J. Dobkowski, R. P. Thummel, V. Hegde and J. Waluk, *J. Phys. Chem. A*, 1997, **101**, 5839; (*b*) J. C. Penedo, M. Mosquera and F. Rodríguez-Prieto, *J. Phys. Chem. A*, 2000, **104**, 7429; (*c*) L. M. Tolbert and K. M. Solntsev, *Acc. Chem. Res.*, 2002, **35**, 19; (*d*) J. T. Hynes, T.-H. Tran-Thi and G. Granucci, *J. Photochem. Photobiol., A*, 2002, **154**, 3.
16 X. Zhang, L. Guo, F. Y. Wu and Y. B. Jiang, *Org. Lett.*, 2003, **5**, 2667.
17 (*a*) F. Toda, S. Hyoda, K. Okada and K. Hirotsu, *J. Chem. Soc., Chem. Commun.*, 1995, 1531; (*b*) G. B. Barlin, *Aust. J. Chem.*, 1985, 1491.
18 *MART and SAINT*, Area Detector Control and Integration Software, Siemens Analytical X-ray Systems, Inc., Madison, WI, 1996.
19 G. M. Sheldrick, *SHELXTL V5.1*, Software Reference Manual, Bruker AXS, Inc., Madison, WI, 1997.
20 X. Peng, Y. Wu, J. Fan, M. Tian and K. Han, *J. Org. Chem.*, 2005, **70**, 10524.
21 (*a*) S. K. Kang, J. M. Llinares, D. Powell, D. VanerVelde and K. Bowman-James, *J. Am. Chem. Soc.*, 2003, **125**, 10152; (*b*) M. Shionoya, H. Furuta, V. Lynch, A. Harriman and J. L. Sessler, *J. Am. Chem. Soc.*, 1992, **114**, 5714.
22 (*a*) S. Camiolo, P. A. Gale, M. B. Hursthouse and M. E. Light, *Org. Biomol. Chem.*, 2003, 741; (*b*) T. Gunnlaugsson, P. E. Kruger, P. Jensen, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **44**, 8909.
23 (*a*) J.-L. Thomas, J. Howarth, K. Hanlon and D. McGuirk, *Tetrahedron Lett.*, 2000, **41**, 413; (*b*) K. S. Kim, K. S. Oh and J. Y. Lee, *Proc. Natl. Acad. Sci. USA*, 2000, **97**, 6373; (*c*) P. Tarakeshwar, H. S. Choi and K. S. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 3323; (*d*) C. A. Ilioudis, D. A. Tocher and J. W. Steed, *J. Am. Chem. Soc.*, 2004, **126**, 12395.
24 I. G. Shenderovich, H.-H. Limbach, S. N. Smirnov, P. M. Tolstoy, G. S. Denisov and N. S. Golubev, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5488.
25 C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030.