Indole-azadiene conjugate as a colorimetric and fluorometric probe for selective fluoride ion sensing†

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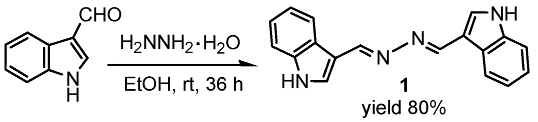
An indole-azadiene conjugate (**1**), synthesized by facile one-step condensation, behaves as a highly selective probe for detection of fluoride ion both in colorimetric and fluorometric analyses. The probe **1** shows F^--selective color change from colorless to yellow and appearance of green fluorescence. ^1H NMR analysis and *ab initio* calculation reveal that the F^--induced colorimetric and fluorometric responses of **1** are simply driven by hydrogen bonding interaction between the indolic NH protons and F^-.

Introduction

Anions play a fundamental and important role in a wide range of chemical, biological, medical, and environmental processes. Design and development of efficient anion probes, capable of sensing the targeted anion highly selectively, has therefore attracted a great deal of attention.[1] Of particular interest is the design of probes for selective fluoride ion (F^-) detection due to pivotal roles of F^- in dental care[2] and in the treatment of osteoporosis.[3] Various kinds of colorimetric[4] or fluorometric[5] probes for selective F^- detection have been synthesized so far. For practical application, probes that can detect F^- by both colorimetric and fluorometric analyses are favorable due to their ease of use. Several dual mode F^- probes have been proposed;[6] however, all of these probes require complicated synthesis steps (at least two steps). Easily preparable dual mode F^- probes are therefore necessary for practical application.

Herein, we report that a simple-structured molecule (**1**), 1,4-bis(3-indolyl)-2,3-diaza-1,3-buthadiene, synthesized by facile one-step condensation (Scheme 1), behaves as a highly selective F^- probe in both colorimetric and fluorometric analyses. The probe **1** shows F^--induced color change from colorless to yellow and appearance of green fluorescence. We describe that the F^--induced colorimetric and fluorometric responses of **1** are simply driven by hydrogen bonding interaction between indolic NH protons and F^-.



Scheme 1 Synthesis of the probe, **1**.

Results and discussion

The symmetrical probe **1** is easily obtained by stirring an ethanol solution containing indole-3-carbaldehyde and hydrazine monohydrate at room temperature for 36 h,[7] as a yellow-white powder, with 80% yield (Scheme 1). The purity of **1** was fully confirmed by ^1H and ^{13}C NMR and EI-MS analyzes (see ESI†, Fig. S2–S4).

Fig. 1 shows changes in absorption and fluorescence spectra of **1** (25 μM) measured in DMSO upon addition of 50 equiv of respective anions (F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, $H_2PO_4^-$, HSO_4^-, NO_3^-, and SCN^-) as a *n*-tetrabutylammonium (*n*-bu_4N^+) salt. As shown in Fig. 1a, without anions, **1** exhibits a characteristic absorption band centered at 352 nm. F^- addition leads to a decrease in this absorption, along with an appearance of red-shifted absorption centered at 409 nm. As shown in Fig. 2, the

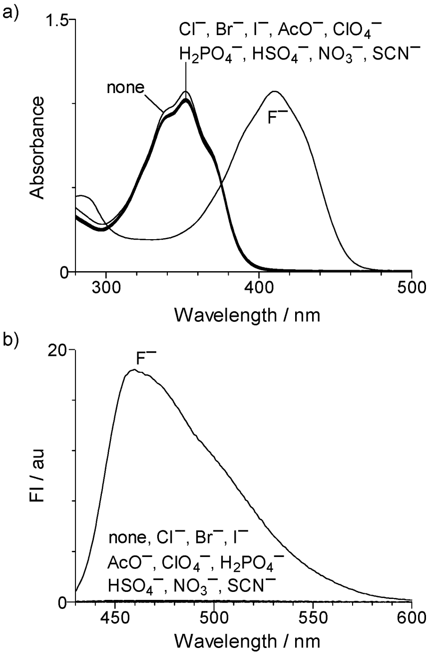


Fig. 1 Changes in (a) absorption and (b) fluorescence (λ_{ex} = 420 nm) spectra of **1** (25 μM) measured in DMSO upon addition of 50 equiv of respective anions (as a *n*-bu_4N^+ salt).

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† Electronic supplementary information (ESI) available: Evidence for no FHF^- dimer formation, supplementary data (Fig. S1–S9 and Table S1), and Cartesian coordinates for **1** and **1**–F^- and **1**–$2F^-$ complexes. See DOI: 10.1039/b821466b

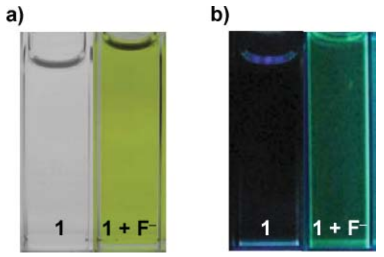

Fig. 2 Change in (a) color and (b) fluorescence color of **1** upon addition of F^- (as a n-bu$_4$N$^+$ salt) in DMSO.

solution color changes from colorless to yellow upon addition of F^-. In contrast, addition of other anions does not show any spectral change. As shown in Fig. 1b, without anions, **1** does not show any fluorescence (λ_{ex} = 420 nm). F^- addition, however, leads to an appearance of fluorescence at 420–600 nm. As shown in Fig. 2, bright green fluorescence is observed upon addition of F^-. In contrast, addition of other anions does not show any fluorescence. These data clearly suggest that the probe **1** behaves as a colorimetric and fluorometric probe for selective F^- sensing. It must be noted that the F^--induced changes in absorption and fluorescence spectra are unaffected by other anions (see ESI†, Fig. S5), indicating that the simple probe **1** can detect F^- selectively even in the presence of other anions. It must also be noted that indole itself shows F^--selective fluorescence enhancement, but the absorption spectrum scarcely changes. In contrast, indole-3-carbardehyde, the starting material, shows F^--selective red-shift of the absorption band, but does not show fluorescence enhancement (see ESI†, Fig. S6 and S7).

Fig. 3 shows the results of absorption titration of **1** with F^-. The F^- addition leads to a decrease in 352 nm absorption, along with an increase in the 409 nm band. The spectral change almost stops upon addition of 30 equiv of F^-. The clear isosbestic points at 304 and 376 nm indicate that a single component is produced in response to the interaction between **1** and F^-. Fig. 4 shows the results of fluorescence titration (λ_{ex} = 420 nm) of **1** with F^-. Addition of F^- leads to continuous increase in the 420–600 nm fluorescence. The intensity increase is saturated upon addition of 30 equiv of F^-, which is similar to the results of absorption titration (Fig. 3). Although the fluorescence quantum yield of **1** is low (ϕ_F = 0.0017 with 30 equiv of F^-),[8] the fluorescence enhancement upon F^- addition is much higher than that of early-reported fluorescent F^- probes.[6,9]

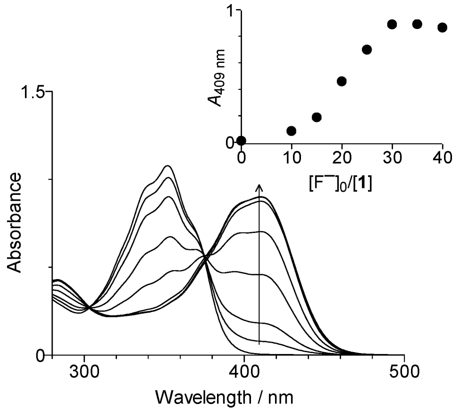

Fig. 3 Absorption titration of **1** (25 μM) with F^- (as a n-bu$_4$N$^+$ salt) in DMSO. Inset: change in absorbance monitored at 409 nm.

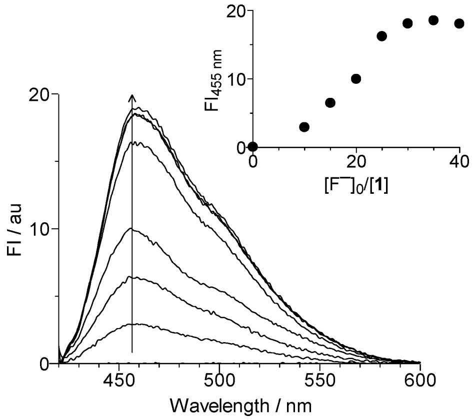

Fig. 4 Fluorescence (λ_{ex} = 420 nm) titration of **1** (25 μM) with F^- (as a n-bu$_4$N$^+$ salt) in DMSO. Inset: change in fluorescence intensity monitored at 455 nm.

The probe **1** associates with F^- in a 1:2 stoichiometry. This is confirmed by the Benesi-Hildebrand analysis.[10] When assuming a 1:2 association between **1** and F^-, the Benesi-Hildebrand equation is given as follows:

$$\frac{1}{FI - FI_0} = \frac{1}{FI_\infty - FI_0}\left[\frac{1}{K[F^-]_0^2} + 1\right] \qquad (1)$$

FI_0 is the fluorescence intensity of **1**, FI_∞ is the intensity measured with excess amount of F^-, FI is the intensity measured with F^-, K is the association constant (M^{-2}), and $[F^-]_0$ is the concentration of F^- added (M). As shown in Fig. 5, plot of $1/(FI - FI_0)$ against $1/[F^-]_0^2$ shows a liner relationship, indicating that **1** actually associates with F^- in a 1:2 stoichiometry. The association constant, K, between **1** and two F^-, is determined from the ratio of intercept/slope to be 1.1×10^6 M^{-2}.

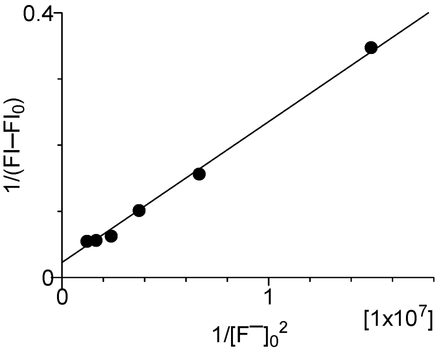

Fig. 5 Benesi-Hildebrand plots (λ_{em} = 455 nm) of **1** using eqn 1, assuming 1:2 stoichiometry for association between **1** and F^-. The plots assuming 1:1 association is shown in Fig. S8 (ESI†).

The association of **1** and F^- occurs through a hydrogen bonding interaction between the NH protons of **1** and F^-. Several F^- probes driven by F^--induced removal of NH protons have been proposed.[11] In these cases, ^{1}H NMR titration with F^- detects a formation of FHF^- dimer at *ca.* 15–17 ppm.[11a–c] However, in the present case, ^{1}H NMR titration of **1** with F^- (DMSO-d_6, 303 K) reveals that FHF^- dimer does not form by the reaction of **1** with

F$^-$ (see ESI†, evidence for no FHF$^-$ dimer formation), indicating that removal of NH protons does not occur. The interaction between the NH protons of **1** and F$^-$ is confirmed by ^{1}H NMR analysis. As shown in Fig. 6, the indolic NH protons of **1** (δ = 11.7 ppm) disappear completely upon F$^-$ addition, indicating that F$^-$ indeed interacts with indolic NH protons.[4e,f] In this case, other protons of **1** shift upfield, suggesting that this interaction affects π-electrons of **1** and, hence, may lead to the change in absorption and fluorescence spectra.

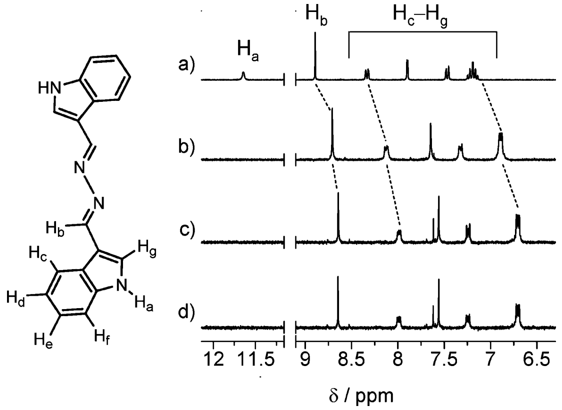

Fig. 6 Change in partial ^{1}H NMR spectra of **1** in DMSO-d_6 upon addition of (a) 0, (b) 5, (c) 30, and (d) 50 equiv of F$^-$ (as a n-bu$_4$N$^+$ salt).

To clarify the mechanism for the changes in absorption and fluorescence spectra of **1**, electronic properties of ground state and excited state of **1** and **1**–2F$^-$ complex were studied by *ab initio* molecular orbital calculation. The calculation was performed on the time-dependent density functional theory (TDDFT) using a B3LYP/6-31G* basis set within the Gaussian 03 programs. As shown in Table S1 (see ESI†), the lowest singlet electronic transition for both **1** and **1**–2F$^-$ complex is HOMO-LUMO transition. The lowest singlet transition energy of **1** is determined to be 374 nm, which is similar to that of the observed absorption maximum of **1** (352 nm, Fig. 3). In contrast, the transition energy of the **1**–2F$^-$ complex (414 nm) is much lower than that of **1** (374 nm) and is similar to the absorption maximum of **1** obtained with F$^-$ (409 nm).

Fig. 7 shows the HOMO and LUMO orbitals of **1** and **1**–2F$^-$ complex, respectively. Electronic transition of both compounds has a π,π^* character; however, the LUMO orbital of each compound is different. The π-electrons of LUMO orbital of **1** are localized on the azadiene moiety and the electron density on the indole moieties is poor. This is probably due to the inherent electron donating property of the indole moieties.[12] The less populated π-electron density on the indole moieties of **1**, therefore, results in no fluorescence of **1** (Fig. 4). In contrast, as shown in Fig. 7, π-electrons of LUMO orbital of the **1**–2F$^-$ complex are extended to the indole moieties (see red circle). This is because the hydrogen bonding interaction between the indolic NH protons and F$^-$ promotes a negative charge transfer from the azadiene moiety to the indole moieties.[13] The population of π-electrons on the indole moieties, therefore, probably allows an appearance of 420–600 nm fluorescence (Fig. 4).

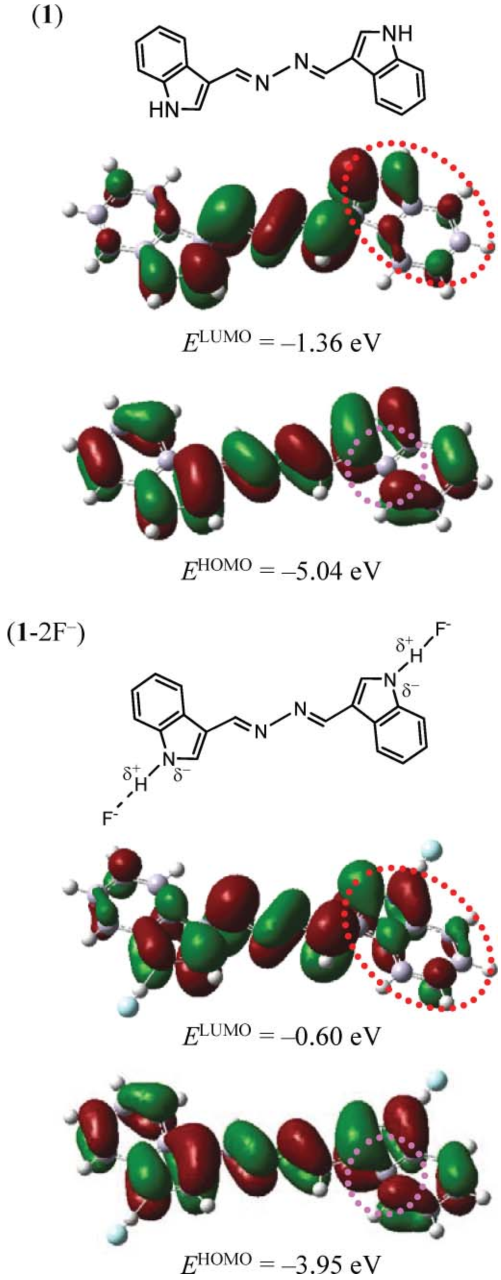

Fig. 7 HOMO and LUMO orbitals of **1** and **1**–2F$^-$ complex calculated on the DFT level using a B3LYP/6-31G* basis set.

The **1**–2F$^-$ complex formation generates a dipolar situation, with a partial negative charge on the indole nitrogen and a partial positive charge on the indolic NH proton interacting with F$^-$ (Fig. 7). Therefore, solvents with higher dielectric constants would stabilize the dipole and, hence, cause a red-shift of the charge-transfer transition. As shown in Fig. S9 (ESI†), a roughly linear relationship exists between the $\lambda_{\max}$ of the absorption band of the **1**–2F$^-$ complex and the dielectric constant of the medium. The data clearly indicates that the **1**–2F$^-$ complex has a charge-transferred electronic configuration, as shown in Fig. 7.

The interaction between the indolic NH protons and F$^-$ also affects the electronic configuration of HOMO orbitals. As shown in Fig. 7, upon F$^-$ interaction, π-electrons of the HOMO orbitals of **1** are extended to the indole moieties (see pink circle) due to the negative charge transfer.[13] As summarized in Fig. 8, upon F$^-$ interaction, the HOMO energy level increases significantly

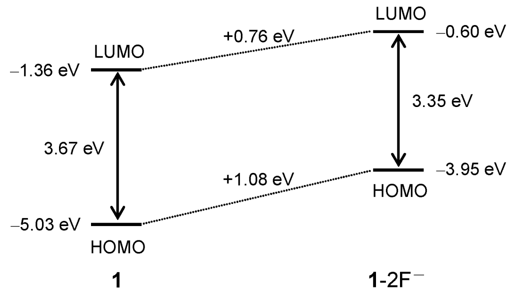

Fig. 8 Energy diagrams of HOMO and LUMO orbitals of **1** and **1**–2F⁻ complex calculated on the DFT level using a B3LYP/6-31G* basis set.

(Δ1.08 eV), although the increase in LUMO energy level is not so large (Δ0.76 eV). As a result of this, the HOMO-LUMO gap decreases (3.67 → 3.35 eV). This may therefore lead to red shift of the absorption spectrum (Fig. 3). The above DFT calculation results fully support the change in absorption spectra upon association of the indolic NH protons of **1** with two F^-.[14]

Several colorimetric and fluorometric cation probes with azadiene moiety have been proposed,[15] where the azadiene moiety behaves as a cation binding site. In the present case, π-electrons on HOMO and LUMO orbitals of **1** are localized on the azadiene moiety and the electron density on the indole moieties is poor. However, upon interaction with F^-, π-electrons are extended to the indole moieties, leading to dynamic changes in absorption and fluorescence spectra. This suggests that the azadiene moiety of **1** acts as a "controller" that tunes π-electron population on the indole moieties upon interaction with F^-.

Conclusions

We found that an indole-azadiene conjugate, **1**, synthesized by one-step facile condensation, behaves as a highly sensitive F^- probe in both colorimetric and fluorometric analyses. The changes in absorption and fluorescence spectra are simply driven by interaction between indolic NH protons and F^-. The simple probe design presented here may contribute to the development of more efficient and more useful dual mode anion probes.

Experimental

All of the reagents used were of the highest commercial quality and used without further purification. Fluorescence spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer (λ_{ex} = 420 nm).[16] Absorption spectra were measured on an UV-vis photodiode-array spectrophotometer (Shimadzu; Multispec-1500). All of the spectroscopic measurements were carried out at 298 ± 0.1 K under dry N_2. ^1H and ^{13}C NMR spectra were recorded by a JEOL JNM-GSX270 Excalibur. EI-MS chart was obtained by a JEOL JMS 700 mass spectrometer.

Synthesis of probe 1

Indole-3-carbaldehyde (0.20 g, 1.35 mmol) and hydrazine monohydrate (0.03 g, 0.67 mmol) were dissolved in ethanol (15 mL) and stirred at room temperature for 36 h under dry N_2. The precipitate formed was recovered by filtration, washed thoroughly with ethanol, and dried in vacuo, affording **1** as a yellow-white powder (0.153 g, 0.53 mol, yield 79.6%). ^1H NMR (270 MHz, DMSO-d_6, TMS): δ (ppm) = 7.14–7.24 (m, 4H, Ar*H*), 7.45–7.48 (d, 2H, Ar*H*), 7.89–7.90 (d, 2H, Ar*H*), 8.32–8.35 (d, 2H, Ar*H*), 8.89 (s, 2H, -C*H*=N-), 11.64 (s, 2H, -N*H*-). ^{13}C NMR (68 MHz, DMSO-d_6, TMS): δ (ppm) = 111.6, 111.9, 120.2, 121.8, 122.3, 124.5, 131.4, 136.9, 154.6. EI-MS: Calcd for $C_{18}H_{14}N_4$: 286.1, found: *m*/*z* 286.2 (M). Elemental Anal.: Calcd: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.28; H, 4.58; N, 19.46.

Computational details

Preliminary geometry optimizations were performed using the WinMOPAC version 3.0 software (Fujitsu Inc.) at the semiempirical PM3 level,[17] where the optimization of **1**–F^- and **1**–2F^- complexes was done using a bound structure, in which F atoms are directly bound to the NH protons. The obtained structures were fully refined in the gas-phase with tight convergence criteria at the DFT level with the Gaussian 03 package,[18] using the B3LYP/6-31G* basis set for all atoms. The excitation energies and the oscillator strengths of the compounds were calculated with the TD-DFT calculation.

Acknowledgements

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Notes and references

1 (*a*) For reviews: R. Martínez-Manêz and F. Sancenón, *Coord. Chem. Rev.*, 2006, **250**, 3081; (*b*) R. Martínez-Manêz and F. Sancenón, *J. Fluoresc.*, 2005, **15**, 267; (*c*) C. Suksai and T. Tuntulani, *Chem. Soc. Rev.*, 2003, **32**, 192; (*d*) R. Martínez-Manêz and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419; (*e*) C. R. Bondy and S. J. Loeb, *Coord. Chem. Rev.*, 2003, **240**, 77; (*f*) P. A. Gale, Ed. Special issue: 35 Years of Synthetic Anion Receptor Chemistry. *Coord. Chem. Rev.*, 2003, **240**, 191; (*g*) P. D. Beer and P. A. Gale, P. A., *Angew. Chem. Int. Ed.*, 2001, **40**, 486; (*h*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.

2 (*a*) K. L. Kirk, *Biochemistry of the Halogens and Inorganic Halides*, Plenum Pless, New York, 1991, p 58; (*b*) P. E. Rakita, *J. Chem. Educ.*, 2004, **81**, 677.

3 (*a*) M. Kleerekoper, *Endocdinol. Metab. Clin. North Am.*, 1998, **27**, 441; (*b*) D. Briancon, *Rev. Rhum.*, 1997, **64**, 78; (*c*) E. Kissa, *Clin. Chem.*, 1987, **33**, 253.

4 (*a*) For example: X. He, S. Hu, K. Liu, Y. Guo, J. Xu and S. Shao, *Org. Lett.*, 2006, **8**, 333; (*b*) E. J. Cho, B. J. Ryu, Y. J. Lee and K. C. Nam, *Org. Lett.*, 2005, **7**, 2607; (*c*) D. Esteban-Gómez, L. Fabbrizzi and M. Licchelli, *J. Org. Chem.*, 2005, **70**, 5717; (*d*) M. Vázquez, L. Fabbrizzi, A. Taglietti, R. M. Pedrido, A. M. González-Noya and M. R. Bermejo, *Angew. Chem. Int. Ed.*, 2004, **43**, 1962; (*e*) D. A. Jose, D. K. Kumar, B. Ganguly and A. Das, *Org. Lett.*, 2004, **6**, 3445; (*f*) J. Y. Lee, E. J. Cho, S. Mukamel and K. C. Nam, *J. Org. Chem.*, 2004, **69**, 943; (*g*) M. H. Lee and F. P. Gabbaï, *Inorg. Chem.*, 2007, **46**, 8132.

5 (*a*) For example: K. M. K. Swamy, Y. J. Lee, H. N. Lee, J. Chun, Y. Kim, S.-J. Kim and J. Yoon, *J. Org. Chem.*, 2006, **71**, 8626; (*b*) X. Y. Liu, D. R. Bai and S. Wang, *Angew. Chem. Int. Ed.*, 2006, **45**, 5475; (*c*) J.-S. Wu, J.-H. Zhou, P.-F. Wang, X.-H. Zhang and S.-K. Wu, *Org. Lett.*, 2005, **7**, 2133; (*d*) G. Xu and M. A. Tarr, *Chem. Commun.*, 2004, 1050; (*e*) 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; (*f*) X. Jiang, M. C. Vieweger, J. C. Bollinger, B. Dragnea and D. Lee, *Org. Lett.*, 2007, **9**, 3579.

6 (*a*) R. M. F. Batista, E. Oliveira, S. P. G. Costa, C. Loderio and M. M. M. Raposo, *Org. Lett.*, 2007, **9**, 3201; (*b*) C.-I. Lin, S. Selvi, J.-M. Fang, P.-T. Chou, C.-H. Lai and Y.-M. Cheng, *J. Org. Chem.*, 2007, **72**, 3537; (*c*) V. Luxami and S. Kumar, *Tetrahedron Lett.*, 2007, **48**, 3083; (*d*) Z. Lin, S. Ou, C. Duan, B. Zhang and Z. Bai, *Chem. Commun.*, 2006, 624; (*e*) Y. Zhao, Z. Lin, S. Ou, C. Duan, H. Liao and Z. Bai, *Inorg. Chem.*

Commun., 2006, **9**, 802; (*f*) S. K. Kim, J. H. Bok, R. A. Bartsch, J. Y. Lee and J. S. Kim, *Org. Lett.*, 2005, **7**, 4839; (*g*) Z.-Q. Liu, M. Shi, F.-Y. Li, Q. Fang, Z.-H. Chen, T. Yi and C.-H. Huang, *Org. Lett.*, 2005, **7**, 5481; (*h*) Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi and K. Tamao, *Angew. Chem. Int. Ed.*, 2003, **42**, 2036; (*i*) S. Yamaguchi, S. Akiyama and K. Tamao, *J. Am. Chem. Soc.*, 2000, **122**, 6793; (*j*) T. W. Hudnall and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2007, **129**, 11978; (*k*) M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima and F. P. Gabbaï, *Chem. Commun.*, 2007, 1133; (*l*) T. H. Kim, M. S. Choi, B.-H. Sohn, S.-Y. Park, W. S. Lyoo and T. S. Lee, *Chem. Commun.*, 2008, 2364; (*m*) W. Tan, D. Zhang, Z. Wang, C. Liu and D. Zhu, *J. Mater. Chem.*, 2007, **17**, 1964; (*n*) M. Zhang, M. Li, F. Li, Y. Cheng, J. Zhang, T. Yi and C. Huang, *Dyes Pig.*, 2008, **77**, 408.

7 N. R. El-Rayyes and A. H. Katrib, *J. Chem. Eng. Data*, 1983, **28**, 132.

8 Fluorescent quantum yield of **1** was determined using fluorescein as a standard (in 0.1 M aqueous NaOH solution, $\phi_F = 0.85 \pm 0.01$): C. A. Parker and W. T. Rees, *Analyst*, 1960, **85**, 587.

9 The detection limit of **1** for F^- is determined to be 222 μM: M. Shortreed, R. Kopelman and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414.

10 (*a*) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703; (*b*) J. J. B. Nevado, J. A. M. Pulgarin and M. A. G. Laguna, *Talanta*, 2001, **53**, 951; (*c*) M. Maffi, J.-J. Aaron and C. Lion, *J. Incl. Phenom.*, 1998, **30**, 227.

11 (*a*) F. Han, Y. Bao, Z. Yang, T. M. Fyles, J. Zhao, X. Peng, J. Fan, Y. Wu and S. Sun, *Chem. Eur. J.*, 2007, **13**, 2880; (*b*) X. Peng, Y. Wu, J. Fan, M. Tian and K. Han, *J. Org. Chem.*, 2005, **70**, 10524; (*c*) A. B. Descalzo, K. Rurack, H. Weisshoff, R. Martínez-Mánez, M. D. Marcos, P. Amorós, K. Hoffmann and J. Soto, *J. Am. Chem. Soc.*, 2005, **127**, 184; (*d*) Y. Wu, X. Peng, J. Fan, S. Gao, M. Tian, J. Zhao and S. Sun, *J. Org. Chem.*, 2007, **72**, 62; (*e*) M. Boiocchi, L. Del Boca, D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507.

12 (*a*) B. K. Kaletaş, H. C. Joshi, G. von der Zwan, M. Fanti, F. Zerbetto, K. Goubitz, L. De Cola, B. König and R. M. Williams, *J. Phys. Chem. A.*, 2005, **109**, 9443; (*b*) B. K. Kaletaş, C. Mandle, G. von der Zwan, M. Fanti, F. Zerbetto, L. De Cola, B. König and R. M. Williams, *J. Phys. Chem. A.*, 2005, **109**, 6440; (*c*) S. Kim, H. Moon, J. Hwang, J. Sohn, J. Seo, S. Y. Park, T. I. Kang and B. R. Cho, *Chem. Phys.*, 2000, **256**, 289.

13 (*a*) H. Miyaji and J. L. Sessler, *Angew. Chem. Int. Ed.*, 2001, **40**, 154; (*b*) P. Anzenbacher, Jr., M. A. Palacios, K. Jursíková and M. Marquez, *Org. Lett.*, 2005, **7**, 5027.

14 The probe **1** has two NH protons; therefore, **1**–F^- 1:1 complex may form. As shown in Table S1 (ESI†), E^{LUMO} and E^{HOMO} values for the 1:1 complex are determined by DFT calculation to be −0.98 eV and −4.38 eV ($\Delta E = 3.40$ eV), respectively. The ΔE values are similar to that of the 1:2 complex (Fig. 8). However, the isosbestic points in the absorption spectrum (Fig. 3) and the linear relationship in the Benesi-Hildebrand plot (Fig. 5) indicate the formation of only 1:2 complex. As shown in Table S1 (ESI†), heat of formation (ΔH_f°; 1 atm, 298.15 K) for free **1** and 1:1 and 1:2 complexes is determined by DFT calculation to be −4083, −5066, and −5634 kJ mol^{-1}, respectively. This suggests that the 1:2 complex is more stable than the 1:1 complex. This is probably the reason for almost no formation of 1:1 complex.

15 P. Molina, A. Tárraga and A. Cabollero, *Eur. J. Inorg. Chem.*, 2008, 3401.

16 (*a*) G. Nishimura, H. Maehara, Y. Shiraishi and T. Hirai, *Chem. Eur. J.*, 2008, **14**, 259; (*b*) X. Zhang, Y. Shiraishi and T. Hirai, *Org. Lett.*, 2007, **9**, 5039; (*c*) Y. Shiraishi, R. Miyamoto, X. Zhang and T. Hirai, *Org. Lett.*, 2007, **9**, 3921; (*d*) Y. Shiraishi, R. Miyamoto and T. Hirai, *Langmuir*, 2008, **24**, 4273.

17 (*a*) Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 8304; (*b*) Y. Shiraishi, H. Maehara, K. Ishizumi and T. Hirai, *Org. Lett.*, 2007, **9**, 3125.

18 *Gaussian 03*, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.