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PAPER

A specific chemodosimeter for fluoride ion based on a pyrene derivative with trimethylsilylethynyl groups†

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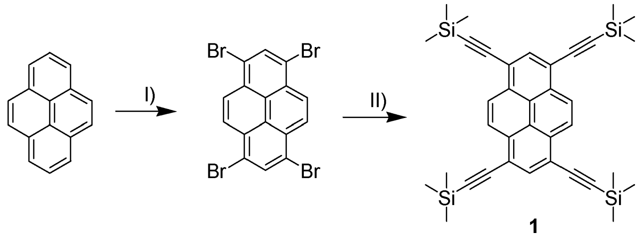
Pyrene derivative **1** containing four trimethylsilylethynyl substituents was synthesized and investigated as a chromogenic and fluorescent chemodosimeter sensor for fluoride ions. **1** showed a high sensitivity and specific selectivity over a rapid response time toward fluoride anions compared to other anions, such as Cl^-, Br^-, ClO_4^-, $H_2PO_4^-$ and HPO_4^{2-}. TD-DFT calculations showed that the delocalization of the σ-electrons of the silicon destabilized the HOMO energy level of **1**, thus red shifting both its absorption and emission spectrum. The addition of F^- removed the trimethylsilyl substituents and resulted in a blue shift of both the absorption and fluorescent spectra of **1**, which could be monitored by the color change with the naked-eye. Moreover, an easy to prepare test paper, which was obtained by immersing a filter paper into a THF solution of **1**, could be utilized to detect and estimate the concentration of fluoride anions in water.

Introduction

The development of fluorescent chemosensors for sensing and reporting biologically important anions has received considerable attention in recent years because of their significant role in the continuation of all biological and psychological processes in the body.[1] Among various anions, excess fluoride anion released from a variety of sources is a pollutant with considerable potential for producing ecological damage.[2] Therefore, it is very important to develop sensitive and selective sensors for fluoride anions. Remarkable progress in the design, synthesis and characterization of fluoride anion-responsive sensors has been made over the past few years.[3] To date, most of them are based on hydrogen bonding or Lewis acid coordination; thus, fluoride sensing or signaling has proved very difficult in aqueous solution. Only a few sensors can reversibly sense fluoride anions in aqueous systems.[4] These sensing systems suffer from some drawbacks, such as the need for high fluoride concentrations, signal generation or the dependence on ternary systems with complex equilibria.[5] The chemodosimeter approach based on the extraordinary affinity between fluoride and silicon, however, which shows high selectivity and sensitivity, has received comparatively much less attention.[6] Recently, a few chromogenic and fluorescence chemodosimeters for fluoride anions have been reported.[5–7] Interestingly, as a popular fluorophore, pyrene, which is a commercial dye and a polycyclic aromatic hydrocarbon (PAH) consisting of four fused benzene rings,[8] has never been reported as a probe for fluoride anion detection based on the chemodosimeter approach. In this paper, we report an easily synthesized pyrene derivative that exhibits a specific response, high sensitivity and a rapid response time toward fluoride anions. Moreover, an easy to prepare test paper can be utilized to detect and estimate the concentration of fluoride anions in water.

Results and discussion

Sensor **1** was prepared according to a published procedure.[9] 1,3,6,8-Tetrabromopyrene was obtained in 92% yield *via* an exhaustive bromination of pyrene. Following a Sonogashira ethynylation reaction with trimethylacetylene, 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**1**) was formed (Scheme 1). Mishra *et al.* have reported the spectroscopic properties of **1** in detail. In light of this, herein, we focus on its optical and sensing aspects for anions.[10]



Scheme 1 (I) Br_2 (4.4 equiv.), nitrobenzene, 120 °C, 4 h, 92%. (II) $(CH_3)_3SiC{\equiv}CH$ (6 equiv.), $N(Et)_3$, toluene, $[Pd^{II}(PPh_3)_2Cl_2]$ (5.0 mol%), CuI (5.0 mol%), PPh_3 (10.0 mol%), 80 °C.

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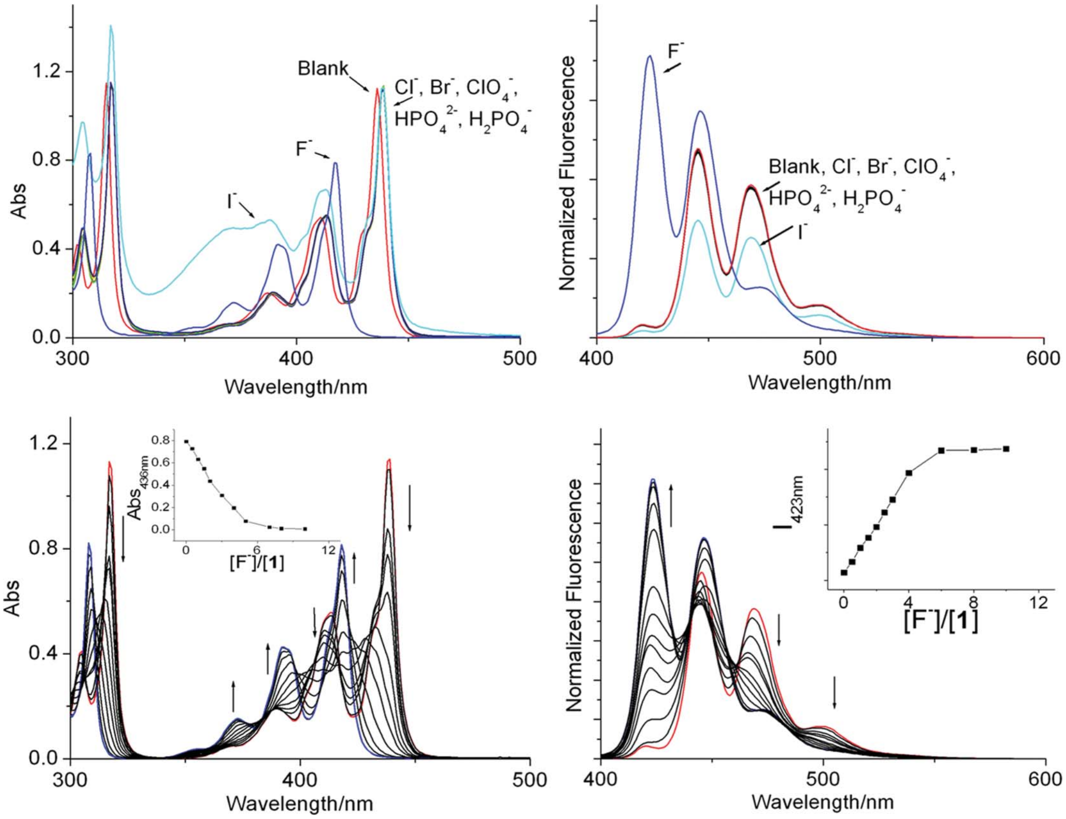
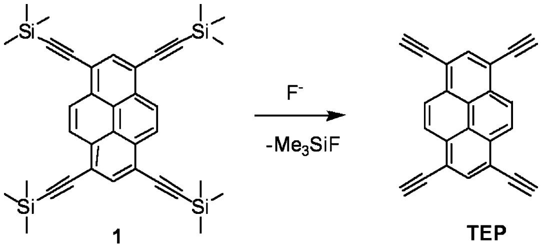


Fig. 1 Top: absorption and fluorescence response of 10 μM **1** in THF (red line) after the addition of 10 equiv. F^- (blue line); Cl^-, Br^-, ClO_4^-, HPO_4^{2-} and $H_2PO_4^-$ (black line); I^- (cyan line). Bottom: absorption and fluorescent titration spectra of 10 μM **1** in THF upon the addition of F^- (0 – 10 equiv.), $\lambda_{ex} = 385$ nm.

To obtain an excellent chemosensor, a high selectivity is a matter of necessity. We first evaluated the selective properties of **1** towards various anions in THF solution. Fig. 1 shows the absorption and fluorescence spectra changes of **1** in the presence of various anions. It is evident that the addition of F^- and I^- resulted in significant spectral changes to **1**. Upon the addition of F^-, the absorption bands at 436 and 410 nm corresponding to the S_0–S_1 transition of **1** were blue-shifted to 417 and 392 nm, respectively, while the intensities of the absorption bands in the region 300–410 nm increased in the presence of I^-. The fluorescence spectra of **1** in the presence of various anions when excited at 385 nm showed that the addition of F^- resulted in a blue shift of the emission maximum with a slightly increased intensity, whereas the fluorescent quantum yield of **1** decreased from 0.66 to 0.14 in the presence of I^-.

The titration experiments showed that both the absorption and fluorescent spectra of **1** gradually blue-shifted upon the addition of F^-. This might be due to the elimination of trimethylsilyl (TMS) substituents to form 1,3,5,7-tetraethynylpyrene (**TEP**) (Scheme 2), since the absorption and emission spectra of **TEP** match well with those of **1** in the presence of F^-. Furthermore, the interaction of **1** with fluoride anion was completed within a few seconds (Fig. 2). Therefore, **1** could be used for the real-time and real-space analysis of F^- in environmental pollution monitoring.



Scheme 2 Proposed sensing mechanism for the interaction of **1** with fluoride anions.

The photograph in Fig. 3 shows the color change after the addition of various anions to THF solutions of **1**. Halide anions such as Cl^- and Br^-, and more complicated anions such as ClO_4^-, $H_2PO_4^-$ and HPO_4^{2-} failed to cause any obvious color or fluorescence changes. In the presence of F^-, a significant colour change from light green to colourless and an emission change from blue to purple were obvious. Meanwhile, a colour change from light green to yellowish green and a fluorescence change from a strong blue emission to a weak emission was also observed in the presence of excess I^- (Fig. 3). On the addition of Cl^-, Br^-, ClO_4^-, $H_2PO_4^-$ and HPO_4^{2-}, the absorption bands at 436 and 410 nm corresponding to the S_0–S_1 transition of **1** slightly red-shifted by about 3 nm, while the emission bands did not show any notable shift compared to that of **1**, which might be due to the very weak interaction between the anions and **1** in the ground state. The relatively more strong interaction between **1** and I^- caused the absorption bands in the 350–400 nm region to increase and the emission intensity to decrease.[11] To confirm our speculation,

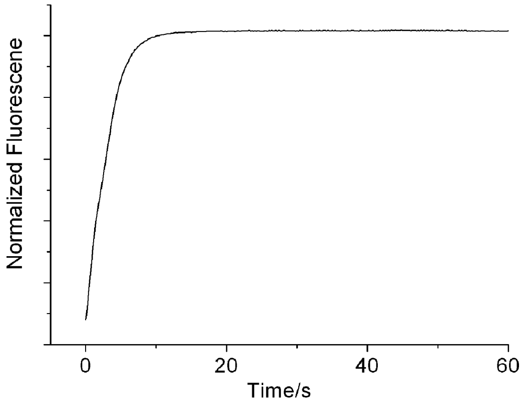


Fig. 2 The response time of **1** (10 μM) in THF by the addition of 10 equiv. of fluoride ion.

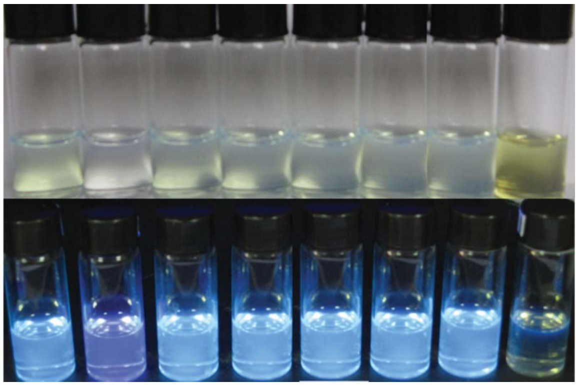


Fig. 3 A picture of the colour and fluorescence changes of **1** in THF (5×10^{-5}M) in the presence of 10 equiv. of anions (excited at 365 nm using a UV lamp).

we measured the ^{1}H NMR spectrum of **1** in the presence of iodide anions in $CDCl_3$ (10% DMSO-d_6) (Fig. S1, ESI†). After the addition of I^-, the protons from the pyrene ring significantly broadened while the chemical shifts were unchanged, whereas both the chemical shift and the peak shape of the protons from TMS were unchanged, suggesting that iodide anions only interact with the pyrene ring. Our investigation clearly demonstrates the possibility of designing and preparing host–guest systems for anion recognition on the basis of aromatic receptors. Actually, the complexes of aromatic rings with anions also present interesting features, that is, the presence of ethynyl groups attached to benzene favors the anion-π interaction, which has been reported recently.[12]

TD-DFT calculations were carried out to understand the observed spectroscopic properties in detail. Fig. 4 shows the partial MO energy diagram and frontier orbitals at the B3LYP/6-31G(d) level. The lowest energy excitation of **1** is predicted to lie at 468 nm ($f = 1.04$) and to arise primarily from the HOMO → LUMO one-electron transition (Table. S1, ESI†).

The energies of the HOMO and LUMO of **1** were both destabilized relative to those of TEP due to the electron-donating properties of the TMS substituents. Since the destabilization of the HOMO is greater than that of the LUMO, the absorption and emission bands of **1** were red-shifted by 19 nm compared with those of TEP. From the MO distribution, we can observe that the MO distribution of the HOMO is composed of the σ-electrons of the silicons and the π orbitals of the aromatic rings (Fig. S2, ESI†).

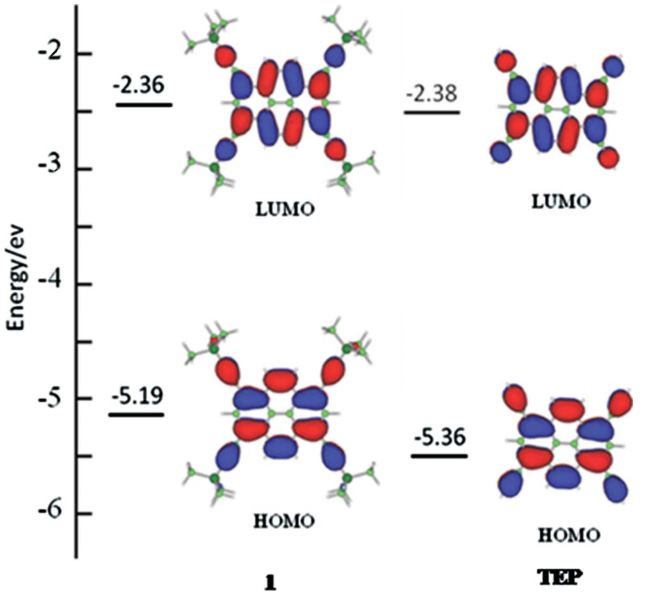


Fig. 4 Energy level diagram for the frontier π-MOs of dyes **1** (left) and **TEP** (right) at an isosurface value of 0.02.

In a previous paper, its authors speculated that the red-shift of the lowest energy transition was due to the stabilization of the LUMO by a σ*–π* interaction;[10] however, according to our calculations, the red-shift of the lowest energy transition is attributed to the narrowing of the energy gap between the HOMO and the LUMO due to a σ–π interaction.

Most literature on fluoride anion sensors has focused on the design of selective fluorescent probes used in aqueous or polar organic solvents, which is inconvenient for achieving real-time monitoring.[13] In terms of convenient and practical solid-state sensors, we prepared a portable chemosensor test paper by placing a filter paper into a THF solution of **1** (1 mM) and then drying it in air. The fluorescence image changes of the test paper in various concentrations of F^- could be easily observed with the naked eye (Fig. 5). The detection limit was approximately 1 ppm, which reaches the range of standard drinking water concentration.[14] Consequently, the easy to prepare test paper could be utilized to detect and estimate the concentration of fluoride ions in water.

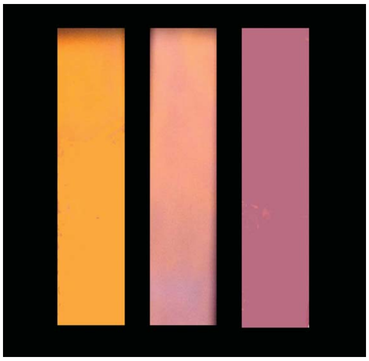


Fig. 5 Fluorescence images of test papers after immersing them in aqueous solutions containing fluoride anions of different concentration. From left to right: 0, 1 and 10 ppm (excited at 365 nm using a UV lamp).

Conclusions

In conclusion, we have demonstrated pyrene derivative **1** with four TMS substituents as a colorimetric and fluorescence chemodosimeter sensor for fluoride anions. This chemosensor shows a very high sensitivity, a rapid response time and a high selectivity for F^-. Such significant spectroscopic changes in **1** upon the addition of fluoride anions is attributed to the elimination of the TMS substituents through a strong interaction between the fluoride anion and the silicon atoms, which increases the energy gap between the HOMO and LUMO due to the lack of σ–π interactions between the silicons and the pyrene. Moreover, test papers have established the utility of **1** in monitoring fluoride anions in water, indicating its potential application to detect and estimate the concentration of fluoride anions in real-time.

Experimental section

Reagents and instruments

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. Triethylamine was distilled over calcium hydride. Toluene was dried over sodium metal and distilled. ^1H NMR spectra were recorded on a Bruker DPX400 spectrometer and referenced to the residual proton signals of the solvent. Mass spectra were measured on an Ion-Soec 4.7 T HiRes MALDI instrument. UV-vis absorption spectra were acquired on a scinco S-3150 UV-vis spectrophotometer. Fluorescence spectra were measured on an Edinburgh LFS920 luminescence spectrophotometer (the pathlength of the quartz cell was 1 cm) with a xenon arc lamp as the light source.

Procedure for anion sensing

Stock solutions of the anions (2 mM) were prepared with the corresponding salts (tetrabutylammonium fluoride for F^-) in deionized water. A stock solution of **1** (1 mM) was prepared in THF. The solution of **1** was then diluted to 10 μM with THF. In titration experiments, each time a 2 mL solution of **1** (10 μM) was filled into a quartz optical cell of 1 cm optical path length, the fluoride ion stock solution was added into the quartz optical cell gradually using a micropipette. In selectivity experiments, the test samples were prepared by placing appropriate amounts of each anion stock solution into a 2 mL solution of **1** (10 μM). During fluorescence measurements, the excitation wavelength was 385 nm, and emission spectra were collected between 400–650 nm. Quantum yields were determined relative to anthracene in ethanol ($\Phi_F = 0.27$ at 25 °C)[15]

Synthesis

1,3,6,8-Tetrabromopyrene [9]**.** Bromine (16.0 g, 0.11 mol) was added dropwise with vigorous stirring to a solution of pyrene (5.0 g, 0.025 mol) in nitrobenzene (100 mL) at 120 °C. The mixture was kept at 120 °C for 4 h and then cooled to room temperature to yield a pale green precipitate. This was filtered, washed with ethanol (100 mL) and dried under vacuum. The solid product was obtained with 92% yield.

1,3,6,8-Tetrakis(trimethylsilanylethynyl)pyrene (1) [9]**.** 1,3,6,8-Tetrabromopyrene (0.25 g, 0.48 mmol) was suspended in triethylamine (10 mL) and toluene (3 mL), and bis(triphenylphosphine)palladium(II) dichloride (68 mg, 0.10 mmol), copper(I) iodide (36 mg, 0.19 mmol) and triphenylphosphine (50 mg, 0.19 mmol) were added under an argon atmosphere. While stirring, the reaction mixture was heated to 60 °C and trimethylsilylethyne (0.28 g, 2.88 mmol) injected. After 10 min, the reaction was heated to 80 °C and stirred overnight. The cooled reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane) to afford **1** as an orange solid (229 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.61$ (m, 4 H, 4,5,9,10-pyrene-H), 8.32 (s, 2 H, 2,7-pyrene-H), 0.38 (s, 36 H, CH_3); MS: m/z (%): 587.25 $[M]^+$.

DFT calculations

The G03W software package[16] was used to carry out a DFT geometry optimisation using the B3LYP functional with 6-31G(d) basis sets. TD-DFT calculations were then carried out using the same approach.

Acknowledgements

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References

1 (*a*) E. Kimura and T. Koike, *Chem. Soc. Rev.*, 1998, **27**, 179; (*b*) C. Mcdonagh, C. S. Burke and B. D. MacCraith, *Chem. Rev.*, 2008, **108**, 400; (*c*) E. Galbraith and T. D. James, *Chem. Soc. Rev.*, 2010, **39**, 3831; (*d*) P. A. Gale, *Chem. Commun.*, 2011, **47**, 82–86; (*e*) Z. Xu, X. Chen, H. N. Kim and J. Yoon, *Chem. Soc. Rev.*, 2010, **39**, 127.

2 (*a*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*b*) K. Bowman-James, *Acc. Chem. Res.*, 2005, **38**, 671; (*c*) P. A. Gale, *Acc. Chem. Res.*, 2006, **39**, 465; (*d*) M. Cametti and K. Rissanen, *Chem. Commun.*, 2009, 2809; (*e*) *Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine*, Agency for Toxic Substances and Disease Registry (ATSDR), US Department of Health and Human Services, Atlanta, USA, 2003; (*f*) J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell and Y. Magara, Fluoride in Drinking Water, *WHO Drinking-Water Quality Series*, IWA Publishing, London, UK and Seattle, USA, 2006.

3 (*a*) M. R. Martínez and F. Sancenón, *Coord. Chem. Rev.*, 2006, **250**, 3081; (*b*) M. Cametti and K. Rissanen, *Chem. Commun.*, 2009, 2809; (*c*) K. Chellappan, N. J. Singh, I. C. Hwang, J. W. Lee and K. S. Kim, *Angew. Chem.*, 2005, **117**, 2959, (*Angew. Chem., Int. Ed.*, 2005, **44**, 2899); (*d*) H. S. Jung, H. J. Kim, J. Vicens and J. S. Kim, *Tetrahedron Lett.*, 2009, **50**, 983; (*e*) C. W. Chiu and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2006, **128**, 14248; (*f*) T. W. Hudnall, M. Melaimi and F. P. Gabbaï, *Org. Lett.*, 2006, **8**, 2747; (*g*) X. Y. Liu, D. R. Bai and S. N. Wang, *Angew. Chem.*, 2006, **118**, 5601, (*Angew. Chem., Int. Ed.*, 2006, **45**, 5475); (*h*) Z. Q. Liu, M. Shi, F. Y. Li, Q. Fang, Z. H. Chen, T. Yi and C. H. Huang, *Org. Lett.*, 2005, **7**, 5481; (*i*) E. Quinlan, S. E. Matthews and T. Gunnlaugsson, *J. Org. Chem.*, 2007, **72**, 7497; (*j*) M. H. Lee and F. P. Gabbaï, *Inorg. Chem.*, 2007, **46**, 8132; (*k*) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962; (*l*) H. M. Chawla, R. Shrivastava and S. N. Sahu, *New J. Chem.*, 2008, **32**, 1999; (*m*) A. Mallick, T. Katayama, Y. Ishibasi, M. Yasuda and H. Miyasaka, *Analyst*, 2011, **136**, 275; (*n*) R. Pérez-Ruiz, Y. Díaz, B. Goldfuss, D. Hertel, K. Meerholz and A. G. Griesbeck, *Org. Biomol. Chem.*, 2009, **7**, 3499; (*o*) Q. Wang, C. Tan, H. Tamiaki and H. Chen, *Photochem. Photobiol. Sci.*, 2010, **9**, 791; (*p*) C. Liu, X. Qian, G. Sun, L. Zhao and Z. Li, *New J. Chem.*, 2008, **32**, 472;

(*q*) Y. Shiraishi, H. Maehara and T. Hirai, *Org. Biomol. Chem.*, 2009, **7**, 2072; (*r*) A. Lascaux, S. Le Gac, J. Wouters, M. Luhmer and I. Jabin, *Org. Biomol. Chem.*, 2010, **8**, 4607; (*s*) T. Wang, Y. Bai, L. Ma and X. P. Yan, *Org. Biomol. Chem.*, 2008, **6**, 1751; (*t*) S. C. Jha, M. Lorch, R. A. Lewis, S. J. Archibald and R. W. Boyle, *Org. Biomol. Chem.*, 2007, **5**, 1970.

4 (*a*) C. R. Cooper, N. Spencer and T. D. James, *Chem. Commun.*, 1998, 1365; (*b*) T. W. Hudnall and F. P. Gabbai, *J. Am. Chem. Soc.*, 2007, **129**, 11978.

5 (*a*) A. Bozdemir, F. Sozmen, O. Buyukcakir, R. Guliyev, Y. Cakmak and E. U. Akkaya, *Org. Lett.*, 2010, **12**, 1400; (*b*) R. Hu, J. Feng, D. Hu, S. Wang, S. Li, Y. Li and G. Yang, *Angew. Chem.*, 2010, **122**, 5035.

6 M. R. Raoa, S. M. Mobina and M. Ravikanth, *Tetrahedron*, 2010, **66**, 1728.

7 (*a*) T. H. Kim and T. M. Swager, *Angew. Chem.*, 2003, **115**, 4951, (*Angew. Chem., Int. Ed.*, 2003, **42**, 4803); (*b*) S. Y. Kim and J. I. Hong, *Org. Lett.*, 2007, **9**, 3109; (*c*) X. F. Yang, *Spectrochim. Acta, Part A*, 2007, **67**, 321; (*d*) S. Y. Kim, J. Park, M. Koh, S. B. Park and J. I. Hong, *Chem. Commun.*, 2009, 4735; (*e*) X. F. Yang, H. P. Qi, L. P. Wang, Z. Su and G. Wang, *Talanta*, 2009, **80**, 92; (*f*) X. F. Yang, S. J. Ye, Q. Bai and X. Q. Wang, *J. Fluoresc.*, 2007, **17**, 81; (*g*) C. Q. Zhu, J. L. Chen, H. Zheng, Y. Q. Wu and J. G. Xu, *Anal. Chim. Acta*, 2005, **539**, 311.

8 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1969.

9 S. Bernhardt, M. Kastler, V. Enkelmann, M. Baumgarten and K. Müllen, *Chem.–Eur. J.*, 2006, **12**, 6117.

10 T. Shysmala, S. Sankararaman and A. K. Mishra, *Chem. Phys.*, 2006, **330**, 469.

11 P. Gamez, T. J. Mooibroek, S. J. Teat and J. Reedijk, *Acc. Chem. Res.*, 2007, **40**, 435.

12 X. Lucas, A. Frontera, D. Quiñonero and P. M. Deyà, *J. Phys. Chem. A*, 2010, **114**, 1926.

13 Z. H. Lin, Y. G. Zhao, C. Y. Duan, B. G. Zhang and Z. P. Bai, *Dalton Trans.*, 2006, 3678.

14 M. A. Lennon, *Bull. W. H. O.*, 2006, **84**, 759.

15 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **72**, 3251.

16 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. 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. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision B.03)*, Gaussian, Inc., Wallingford, CT, 2004.