

Detection of zinc ions under aqueous conditions using chirality assisted solid-state fluorescence of a bipyridyl based fluorophore†

Sivaramapanicker Sreejith, Kizhumuri P. Divya and Ayyappanpillai Ajayaghosh*

Received (in Cambridge, UK) 20th February 2008, Accepted 27th March 2008

First published as an Advance Article on the web 23rd April 2008

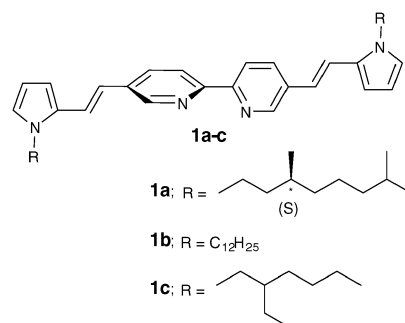
DOI: 10.1039/b802958j

A pyrrole end-capped bipyridyl ligand **1a** incorporating a chiral handle exhibited high solid-state emission when compared to the achiral analogue **1b** and to the racemic molecule **1c** which allowed the design of a reusable fluorescent probe for the selective detection of Zn^{2+} under aqueous conditions.

Zinc is the second most abundant transition metal in the human body, and plays a vital role in biological functions such as gene expression, apoptosis, enzyme regulation and neurotransmission.¹ In recent years a variety of molecular probes for the detection of Zn^{2+} ions in aqueous or nonaqueous solutions have been reported.^{2,3} In most of these cases, due to high sensitivity, fluorescence technique has been widely used for the detection of analytes.⁴ However, development of solid-state fluorescence sensors, for the detection of Zn^{2+} under aqueous conditions has been limited due to the strong quenching of the luminescence of organic fluorophores in the solid state.⁵ In this context, molecules that exhibit enhanced luminescence in the solid state are of great importance.^{6,7}

Enhanced solid-state fluorescence has been reported in some *p*-phenylenevinylene derivatives.⁸ Adjustment of the tilt angle between the long axes of the transition dipole of adjacent molecules in the solid-state is responsible for the enhanced emission in these molecules.⁹ In view of this observation, we anticipated that incorporation of a chiral handle to a fluorescent molecule may improve the solid-state emission due to the asymmetric carbon induced helical twist, resulting in emissive aggregates which may allow the fabrication of a solid-state sensor for Zn^{2+} . As a proof-of-principle to our hypothesis, we demonstrate here the enhanced solid-state emission and fabrication of a reusable dipstick probe for Zn^{2+} using a chiral ligand **1a** when compared to that of analogous achiral **1b** and racemic **1c** ligands. Earlier, we reported the use of the fluorescent probes **1b** and **1c** for the ratiometric detection of Zn^{2+} in solutions.¹⁰ However, due to the weak fluorescence of the molecules in the solid state (Fig. 1), attempts to design a practical device for the detection of Zn^{2+} were not successful. In this context, we prepared the chiral molecule **1a**, by the Wittig–Horner coupling of (*S*)-1-(3,7-dimethyloctyl)-1*H*-pyrrole-2-carbaldehyde with 2,2'-bipyridyl phosphonate (yield 40–45%). In acetonitrile, **1a** (6×10^{-6} M) showed an absorption maximum at 408 nm

with strong fluorescence at 537 nm ($\lambda_{\text{ex}} = 440$ nm, $\Phi_{\text{f}} = 0.51$). More interestingly, in contrast to **1b** and **1c**, **1a** showed strong emission in the solid state (Table 1).



The enhanced solid-state emission of **1a** could be due to the helical twist in the aggregates which may weaken the π -interaction between the molecules. In order to prove this, we conducted circular dichroism (CD) measurements of **1a** in solution as well as in solid-state (Fig. 2). In acetonitrile solution, **1a** (6×10^{-6} M) is CD silent. However, in the solid state, significant CD response was obtained. Ignoring the marginal contribution from the linear dichroic response, the observed CD spectrum indicates a helical twist in the molecular aggregates. Furthermore, the CD spectrum is weak and nonbisignate, indicating a weak exciton coupling, probably due to the disorganized aggregation process, which prevent fluorescence quenching in **1a** in the solid-state.

The solid-state emission¹¹ of **1a** after dispersing in a poly(methylmethacrylate) (PMMA) film is shown in Fig. 3(a). As expected, **1a** exhibited an emission maximum at 535 nm with a high quantum yield ($\Phi_{\text{f}} = 0.46$) which is *ca.* 25 times higher than that of **1b** in PMMA matrix ($\Phi_{\text{f}} = 0.018$). When the **1a** dispersed PMMA film was immersed in a solution of

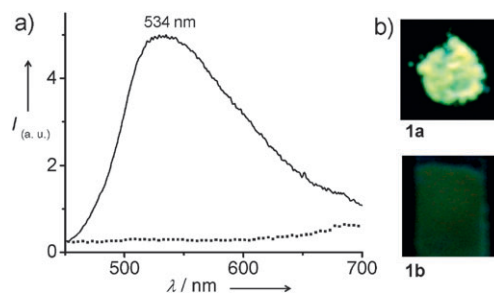


Fig. 1 (a) Solid-state emission spectra of **1a** (—) and **1b** (···) ($\lambda_{\text{ex}} = 400$ nm). (b) Photographs showing solid-state fluorescence of **1a** and **1b**.

Photosciences and Photonics Group, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), CSIR, Trivandrum, 695019, India.
 E-mail: ajayaghosh62@gmail.com; Fax: +91-471-2490186;
 Tel: +91-471-2515306

† Electronic supplementary information (ESI) available: Experimental section. See DOI: 10.1039/b802958j

Table 1 Photophysical parameters of **1a**, **1b** and **1c** in acetonitrile solution and in the solid state

Compound	Acetonitrile				Solid state	
	$\lambda_{\text{abs}}^a/\text{nm}$	$\log \epsilon$	$\lambda_{\text{em}}^a/\text{nm}$	Φ_f^b	$\lambda_{\text{em}}^c/\text{nm}$	Φ_f^d
1a	408	4.74	537	0.51	534	0.460
1b	406	4.20	537	0.43	NE ^e	NE ^e
1c	407	4.52	537	0.46	NE ^e	NE ^e

^a Determined in spectroscopic grade acetonitrile. ^b Fluorescence quantum yields ($\pm 5\%$ error) were determined using quinine sulfate as the standard ($\Phi_f = 0.546$ in $0.05 \text{ M H}_2\text{SO}_4$). ^c Solid-state emission ($\pm 2\%$ error) was recorded using a combination of spectrofluorimeter and integrated sphere. ^d Quantum yield measured using eqn (2) (ESI[†]). ^e No detectable emission.

$\text{Zn}(\text{ClO}_4)_2$ ($3 \times 10^{-4} \text{ M}$) in acetonitrile–water (50% v/v), the absorption peak at 400 nm was red-shifted to 484 nm. Similarly, Cu^{2+} , Hg^{2+} , Ag^+ and Fe^{2+} showed significant red-shift to the absorption spectra revealing that these changes are not specific to Zn^{2+} ions. However, the fluorescence response was specific for Zn^{2+} ions. The fluorescence of **1a** was significantly quenched with cations such as Cu^{2+} , Hg^{2+} , Ag^+ and Fe^{2+} but not Zn^{2+} . In the case of Zn^{2+} , the emission maximum was shifted to 640 nm with significant visual color change from green to red, thus allowing the specific visual detection (Fig. 3(b)).

The selectivity of the probe towards Zn^{2+} was tested by preparing a **1a** coated plate which exhibited a bright greenish yellow fluorescence (Fig. 4). Aqueous solutions of different metal salts ($5 \times 10^{-4} \text{ M}$) were spotted on the plate, individually and as mixtures. Analysis of this plate reveals that the fluorescence of **1a** changes from greenish-yellow to red in selective response to Zn^{2+} ions (spots 1–4). Promisingly, in a mixture of alkali, alkaline earth and transition metal cations that are mixed with Zn^{2+} showed the red emission of the $\text{Zn}^{2+} \cdot \mathbf{1a}$ complex, revealing the high selectivity of the probe. On the other hand, individually Ag^+ , Cu^{2+} , Fe^{2+} and Hg^{2+} salts resulted in dark spots (spots 5–8) due to fluorescence quenching whereas Na^+ , K^+ , Ca^{2+} and Mg^{2+} salts did not change the fluorescence of **1a** much. A quantitative analysis of the specificity of Zn^{2+} sensing in the solid-state was carried out by measuring the relative fluorescence intensity of **1a** in the absence and presence of cations. Plots of the relative fluorescence intensities against the corresponding cations indicate that Zn^{2+} , in the absence and presence of other cations, exhibits maximum relative fluorescence intensity (Fig. 4(b)). Thus a selective screening of Zn^{2+} is possible by monitoring the emission color under illumination.

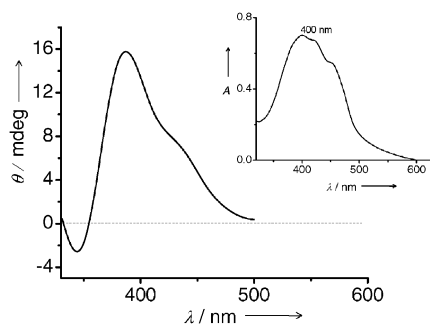


Fig. 2 Circular dichroism spectra of **1a** in the solid-state (—) and in acetonitrile (···) ($6 \times 10^{-6} \text{ M}$). The inset shows the corresponding solid-state absorption spectrum of **1a**.

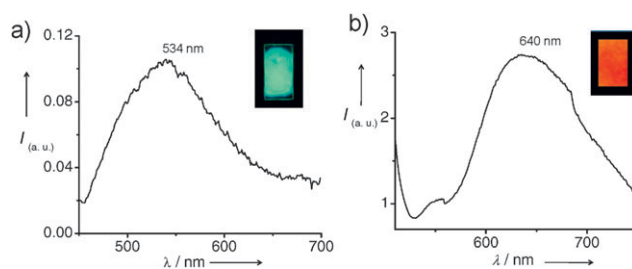


Fig. 3 Solid-state emission spectra of **1a** in PMMA matrix (a) in the absence and (b) in the presence of Zn^{2+} ions. Insets show emission colors of **1a** and the **1a**- Zn^{2+} complex in PMMA matrix when illuminated using 365 nm UV light.

The above results encouraged us to develop a dipstick probe for the detection of Zn^{2+} in water, completely avoiding organic solvents.¹² For this purpose, **1a** was adsorbed on alumina, a slurry of which was coated on a thermoplastic stick as support (Fig. 5). The prepared stick as such was used for the detection. The performance of the stick was tested by dipping it into a $\text{Zn}(\text{ClO}_4)_2$ solution ($5 \times 10^{-4} \text{ M}$, 15 mL) in water under neutral pH. The color of the stick wherever in contact with Zn^{2+} was changed from greenish-yellow to orange which was accompanied by a fluorescence change from greenish yellow to deep red (Fig. 5(c) and (d)), upon illumination with 365 nm UV light. The detection limit of **1a** to Zn^{2+} in solution is of the order of 10^{-6} M whereas in the solid-state the visible detection limit is in the range of 10^{-4} M .

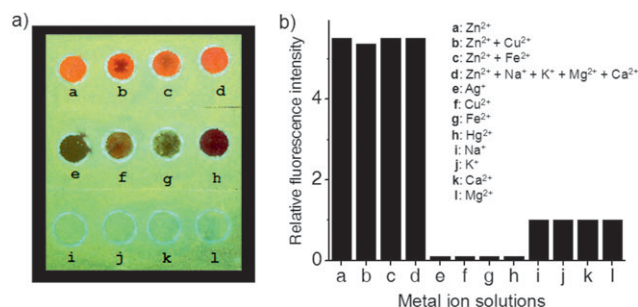


Fig. 4 (a) Screening of various metal ion solutions in water under neutral pH on a **1a** coated plate under 365 nm UV illumination. (b) Plot of fluorescence intensity of **1a** in the presence of (a) Zn^{2+} , (b) $\text{Zn}^{2+} + \text{Cu}^{2+}$ (1 : 1), (c) $\text{Zn}^{2+} + \text{Fe}^{2+}$ (1 : 1), (d) $\text{Zn}^{2+} + \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+}$ (1 : 1 : 1 : 1 : 1), (e) Ag^+ , (f) Cu^{2+} , (g) Fe^{2+} , (h) Hg^{2+} , (i) Na^+ , (j) K^+ , (k) Ca^{2+} and (l) Mg^{2+} [metal ion concentration ($5 \times 10^{-4} \text{ M}$)]. The relative fluorescence intensity of **1a** in the presence of Na^+ was taken as unity for normalization.

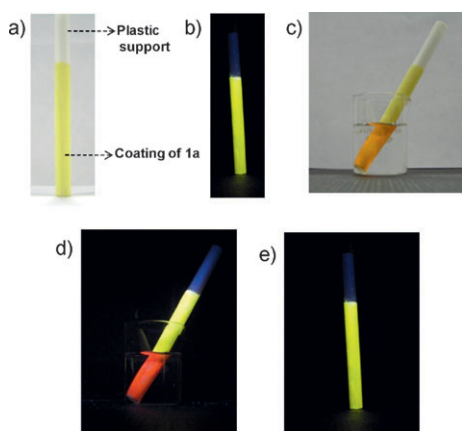


Fig. 5 Photographs of (a) a dipstick, coated with **1a** in alumina matrix; (b) after illumination by 365 nm UV light. (c) After immersing in aqueous medium (pH, 7.2) containing Zn^{2+} ions (5×10^{-4} M) in daylight and (d) after illumination by 365 nm UV light in the presence of Zn^{2+} . (e) Photograph of the dipstick used in (c) after washing with EDTA solution followed by illumination.

The important criteria for the successful use of a practical sensor are its reusability and ability to detect a specific cation in the vicinity of other competing ions. In the present case, the reusability of the dip-stick for the detection of Zn^{2+} was tested after washing the used stick with EDTA solution. Since EDTA is a good Zn^{2+} chelator, decomplexation occurs upon washing with EDTA solution. After washing and drying, the initial greenish yellow fluorescence of the stick was regained and it was ready for another trial (Fig. 5(e)). The regenerated stick upon immersion in an aqueous solution of Zn^{2+} exhibited the bright red emission when illuminated. This processes were repeated 10 times without loss of the emission intensity to any considerable extent, indicating the reusability of the probe a large number of times.

In conclusion, a chiral bipyridyl ligand exhibited 25 times the fluorescence in PMMA matrix when compared to an analogous achiral derivative and was even more fluorescent in the native powder form. This phenomenon has been exploited in the fabrication of a reusable solid-state fluorescent device which selectively detects Zn^{2+} in presence of other competing cations in water. The present strategy which uses the property of enhanced solid-state emission of a chiral organic fluorophore for the visual detection of a biologically relevant cation in water is a novel approach when compared to other known methods. Moreover, this method allows the imaging of Zn^{2+} in analytical samples, which expands the future scope of this strategy.

We thank Department of Science and Technology (DST), New Delhi, Government of India for financial support. A. A. is grateful to the DST for a Ramanna Fellowship. S. S. and K. P. D. thank Council of Scientific and Industrial Research (CSIR), Government of India for research fellowships. This work is contribution No. NIIST-PPG-262.

Notes and references

1. J. M. Berg and Y. Shi, *Science*, 1996, **271**, 1081–1085; C. E. Outten and T. V. O'Halloran, *Science*, 2001, **292**, 2488–2492; P. Jiang and Z. Guo, *Coord. Chem. Rev.*, 2004, **248**, 205–229.

2. For recent reviews, see: E. Kimura and T. Koike, *Chem. Soc. Rev.*, 1998, **27**, 179–184; N. C. Lim, H. C. Freake and C. Brückner, *Chem.–Eur. J.*, 2005, **11**, 38–49; Z. Dai and J. W. Canary, *New J. Chem.*, 2007, **31**, 1708–1718.
3. W. Jiang, Q. Fu, H. Fan and W. Wang, *Chem. Commun.*, 2008, 259–261; K. Komatsu, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc.*, 2007, **129**, 13447–13454; H.-H. Wang, Q. Gan, X.-J. Wang, L. Xue and S.-H. Liu, *Org. Lett.*, 2007, **9**, 4995–4998; X.-a. Zhang, K. S. Lovejoy, A. Jasanoff and S. J. Lippard, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 10780–10785; A. E. Dennis and R. C. Smith, *Chem. Commun.*, 2007, 4641–4643; Y. Mei and P. A. Bentley, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 3131–3134; K. Kiyose, H. Kojima, Y. Urano and T. Nagano, *J. Am. Chem. Soc.*, 2006, **128**, 6548–6549; C. R. Goldsmith and S. J. Lippard, *Inorg. Chem.*, 2006, **45**, 555–561; B. Tang, H. Huang, K. Xu, L. Tong, G. Yang, X. Liu and L. An, *Chem. Commun.*, 2006, 3609–3611; E. Kawabata, K. Kikuchi, Y. Urano, H. Kojima, A. Odani and T. Nagano, *J. Am. Chem. Soc.*, 2005, **127**, 818–819; M. Taki, J. L. Wolford and T. V. O'Halloran, *J. Am. Chem. Soc.*, 2004, **126**, 712–713; S. C. Brudette, C. J. Frederickson, W. Bu and S. J. Lippard, *J. Am. Chem. Soc.*, 2003, **125**, 1778–1787; K. R. Gee, Z.-L. Zhou, W.-J. Qian and R. Kennedy, *J. Am. Chem. Soc.*, 2002, **124**, 776–778; B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1997, **119**, 12–21.
4. R. A. Bissell, A. P. de Silva, H. Q. Gunaratne, P. L. M. Lynch, G. E. M. Maguire and K. R. A. S. Sandanayake, *Chem. Soc. Rev.*, 1992, **21**, 187–195; A. P. de Silva, H. Q. Gunaratne, T. Gunluggsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566; J.-P. Desvergne and A. W. Czarnik, *Chemosensors for Ion and Molecular Recognition. NATO ASI Series*, Kluwer Academic, Dordrecht, The Netherlands, 1997, vol. 492; D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574; J. F. Callan, A. P. de Silva and D. C. Magri, *Tetrahedron*, 2005, **61**, 8551–8588; G. V. Zyryanov, M. A. Palacios and P. Anzenbacher, Jr, *Angew. Chem., Int. Ed.*, 2007, **46**, 7849–7852.
5. T. Mayr, G. Liebsch, I. Klimant and O. S. Wolfbeis, *Analyst*, 2002, **127**, 201–203; T. Mayr, I. Klimant, O. S. Wolfbeis and T. Werner, *Anal. Chim. Acta*, 2002, **462**, 1–10; O. S. Wolfbeis, *J. Mater. Chem.*, 2005, **15**, 2657–2669.
6. For enhanced solid-state fluorescence in conjugated molecules, see: S. Özçelik and D. L. Akins, *J. Phys. Chem. B*, 1999, **103**, 8926–8929; R. Deans, J. Kim, M. R. Machacek and T. M. Swager, *J. Am. Chem. Soc.*, 2000, **122**, 8565–8566; M. Levitus, K. Schmieder, H. Ricks, K. D. Shimizu, U. H. F. Bunz and M. A. Gracia-Garibay, *J. Am. Chem. Soc.*, 2001, **123**, 4259–4265; B.-K. An, S.-K. Kwan, S.-D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410–14415; Z. Xie, B. Yang, G. Cheng, L. Liu, F. He, F. Shen, Y. Ma and S. Liu, *Chem. Mater.*, 2005, **17**, 1287–1289; F. He, H. Xu, B. Yang, Y. Duan, L. Tian, K. Huang, Y. Ma, S. Liu, S. Feng and J. Shan, *Adv. Mater.*, 2005, **17**, 2710–2714.
7. For enhanced solid state fluorescence in small molecules, see: S. Jayanty and T. P. Radhakrishnan, *Chem.–Eur. J.*, 2004, **10**, 791–797; C. T. Chen, *Chem. Mater.*, 2004, **16**, 4389–4400; C.-L. Chiang, M.-F. Wu, D.-C. Dai, Y.-S. Wen, J.-K. Wang and C.-T. Chen, *Adv. Funct. Mater.*, 2005, **15**, 231–238; H. Langhals, O. Krotz, K. Polborn and P. Meyer, *Angew. Chem., Int. Ed.*, 2005, **44**, 2427–2428; Y. Liu, Y. Nishiura, Y. Wang and Z. Hou, *J. Am. Chem. Soc.*, 2006, **128**, 5592–5593; Y. Mizobe, H. Ito, I. Hisaki, M. Miyata, Y. Hasegawa and N. Tohnai, *Chem. Commun.*, 2006, 2126–2128.
8. Z. Xie, B. Yang, G. Cheng, L. Liu, G. Yang, H. Xu, L. Ye, M. Hanif, S. Liu, D. Ma and Y. Ma, *J. Am. Chem. Soc.*, 2005, **127**, 14152–14153.
9. J. Cornil, D. A. dos Santos, X. Crispin, R. Sibey and J. L. Brédas, *J. Am. Chem. Soc.*, 1998, **120**, 1289–1299; J. Cornil, D. Beljonne, J. P. Calbert and J. L. Brédas, *Adv. Mater.*, 2001, **13**, 1053–1067; S. Siddiqui and F. C. Spano, *Chem. Phys. Lett.*, 1999, **308**, 99–105.
10. A. Ajayaghosh, P. Carol and S. Sreejith, *J. Am. Chem. Soc.*, 2005, **127**, 14962–14963; P. Carol, S. Sreejith and A. Ajayaghosh, *Chem.–Asian J.*, 2007, **2**, 338–348.
11. L.-O. Pålsson and A. P. Monkman, *Adv. Mater.*, 2002, **14**, 757–758; J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230–232.
12. A. Ajayaghosh and S. Sreejith, *Indian Pat. Appl.*, 0105NF 2007/IN, 2007.