

COMMUNICATION

Cite this: *RSC Adv.*, 2015, 5, 31479Received 18th November 2014
Accepted 24th March 2015

DOI: 10.1039/c4ra14765k

www.rsc.org/advances

Amine functionalized tetraphenylethylene: a novel aggregation-induced emission based fluorescent chemodosimeter for nitrite and nitrate ions†

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A novel AIE-based fluorescent probe for the detection of trace amounts of nitrite and nitrate ions in water has been developed. The probe, a monoamine of tetraphenylethylene, spontaneously detects nitrites (or nitrates) by a fluorescence “turn-off” method via diazotization followed by formation of a non fluorescent TPE-azodye. The salient features of this method are high sensitivity and selectivity, cost effective synthesis, fast detection process and low detection limit.

The dramatic increase in the concentration of nitrite and nitrate ions in groundwater, rivers and lakes from chemical fertilizers, livestock waste, *etc.* is a growing threat to public health and the environment.¹ Nitrite is well-known to have key physiological roles in blood flow regulation, signaling and hypoxic nitric oxide homeostasis.² It reacts with dietary components in the stomach to generate carcinogenic nitrosamine.³ Another latent hazard with nitrite ions is their capability to change oxyhemoglobin into methemoglobin when present in the bloodstream, thereby interfering with oxygen transport in the blood.⁴ Nitrate, though less toxic, is converted to nitrite by microbial reduction under physiological conditions.⁴ High concentrations of nitrate and nitrite ions in drinking water results in a number of medical issues, such as premature birth, intrauterine growth restriction and birth defects of the central nervous system.⁴ Therefore, the monitoring of nitrite (and nitrate) levels in drinking water and food stuffs is of great importance.

To date, a large number of techniques have been developed for the detection of nitrite ions, based on organic

chromophores,⁵ electrochemical detection,⁶ ion chromatography,⁷ and others.⁸ Many of these available methods require the use of sophisticated instruments and thus are not cost-effective. In addition, some of these are not sufficiently sensitive or selective for the determination of trace amounts of nitrite ions, and hence cannot be used for real-time applications. Recently, a few sensitive chromogenic sensors have been reported for nitrite ions.⁹ However, over the last decade, fluorimetric probes have brought about a revolution in sensing technology because of their operational simplicity and cost-effectiveness, in addition to high sensitivity and selectivity.¹⁰ Surprisingly, molecular probes for nitrite ions based on the fluorimetric technique are rare.¹¹ Therefore, it is highly desirable to develop new and sensitive methods for the determination of trace levels of nitrite ions in water and other substances. However, conventional organic fluorophores have a major inadequacy, despite several advantages. Although they are highly emissive in dilute solutions, the aggregation-caused quenching effect (ACQ) in the condensed phase restricts their real world applications.¹² Recently, the advancement of luminogen molecules, which emit more effectively in the aggregated form than in the solution due to the aggregation-induced emission (AIE) mechanism, has stimulated great research interest for various applications.^{13–17} Using this novel phenomenon, a great variety of AIE active molecules have been designed for cell imaging,^{16a,d,e,17i} optical devices,^{17h,j} electroluminescent materials,^{15f,16e} chemo/biosensors,^{13,15,17a,b,d,g,k} *etc.* Tetraphenylethylene (TPE), due to its easy synthesis and simple functionalization strategies, is one of the most studied luminophores and the demonstration of its practical applications for the detection of analytes¹⁵ and for other purposes¹⁶ has been investigated in recent times. However, to the best of our knowledge, the aggregation-induced emission property has not been exploited to develop a sensor for the detection of nitrite ions to date. In this regard, we envisioned that a TPE-amine may serve as an efficient sensor for nitrite ions by making use of a simple “diazotization” reaction. As a part of our continued effort for the development of fluorescent sensors for

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† Electronic supplementary information (ESI) available: General information, synthetic procedures, experimental procedures, pH study, limit of detection, details of theoretical calculations and spectral data; spectra of probe 1 and azo dye 2. See DOI: 10.1039/c4ra14765k

biologically/environmentally important analytes,^{11a,15f,m,18} we report, herein, an AIE-active TPE-based fluorescent chemodosimeter for selective and sensitive detection of nitrite (and nitrate) ions in contaminated water.

For this sensing purpose, probe **1** (Fig. 1) was synthesized using a McMurry cross-coupling reaction, from benzophenone and 4-aminobenzophenone in a single-step, adopting a reported procedure (see ESI† for details).¹⁹ The probe readily undergoes “diazotization” by the reaction with nitrite ions in acidic water at 0–5 °C. Upon addition of an alkaline β -naphthol solution, a TPE-azodye congener (**2**) is formed, which is non-fluorescent in either the solid state or in solution (Fig. 1).

As anticipated, probe **1** was non-emissive in THF solution, and since its solubility is very poor in water the addition of a large volume of water or mild acid (*viz.* 0.1 N HCl) preserves an intense fluorescence response under identical conditions, manifesting the AIE behaviour. As the diazotization process requires acidic conditions, the solvent dependent AIE behaviour of the probe was examined in THF and aqueous HCl. The fluorescence signal from the solution of probe **1** started to appear once the volume of THF in 0.1 N aqueous HCl (pH 1) was reduced to only 10% and approached a maximum at and below 3% THF in 0.1 N aqueous HCl (Fig. 2). As a preliminary study, we checked the ability of probe **1** to detect nitrite ions in 20% THF in water at pH 1. We expected a turn-on type fluorescence response from the probe in the presence of nitrite ions due to the anticipated poor solubility of the resultant azo-dye (**2**) in the same solvent system. To our surprise, a non-fluorescent solution of **1** did not show any fluorescence response even with the addition of one equiv. of nitrite. Moreover, the solid dye settled down to the bottom, and as an added surprise, the dye was found to be non-fluorescent in the solid state as well. This unexpected outcome prompted us to carry out a thorough investigation of the theoretical aspects of the electronic ground and excited states of both **1** and **2**. We also established the optimum conditions for the diazotization reaction by measuring the fluorescence intensity of various solutions at different pH values, containing 1 equiv. of nitrite ions at 0–5 °C. A pH range of 1–7 was studied and pH 1 was found to be most suitable in terms of the time required for completion of the reaction (Fig. S1 of ESI†). The rate of diazotization becomes slower and slower up to pH 4.

As expected, the probe does not work at or near neutral pH. Low temperature, a requirement of conventional diazotization

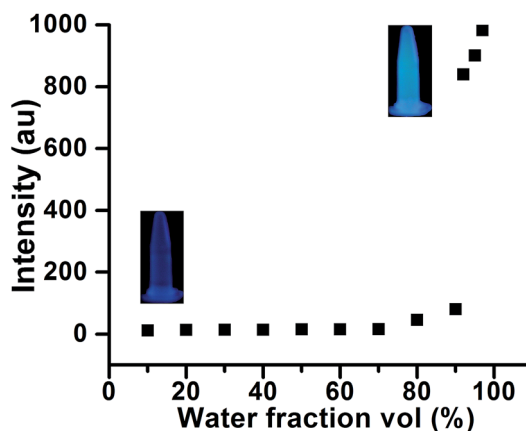


Fig. 2 Plot of fluorescence intensity of probe **1** (30 μ M) against various proportions of a 0.1 N HCl–THF mixture (λ_{ex} 345 nm, λ_{em} 447 nm).

reactions, was maintained for all fluorimetric studies to avoid any side reactions.

To understand the ground and excited state behaviours, quantum mechanical studies were carried out at the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) levels using the Gaussian 09 program (see ESI† for details). The optimized structures showed that the ethylenic C=C bond (1.37 Å) of probe **1** almost became a single bond (1.48 Å) in the photo-excited singlet state, while the adjacent C–C single bond lengths were found to decrease by 0.02 to 0.05 Å. The S_0 – S_1 transition arises due to the HOMO \rightarrow LUMO excitation and this was characterized by a movement of the π -cloud from the aniline moiety towards the central ethylenic part (Fig. S3 of ESI†). However, the non-coplanarity of the phenyl rings and the central C–C bond are likely to hinder the extensive π -delocalization in both the ground and excited states. A better co-planarity, resulting in improved delocalization, can be expected in the aggregated form and might be the reason behind the fluorescent nature of TPE-amine **1** in this state. However, the azo dye **2** was found to be non-fluorescent in nature, both in the solution and in the solid state. A major fraction of the π -cloud from its HOMO was found to be shifted away from the TPE-moiety and resided close to the azo bond and naphthalene moiety in the LUMO. The π electronic cloud was found to disappear from the three phenyl rings and the central ethylene part of the TPE moiety on HOMO \rightarrow LUMO excitation (Fig. 3). The phenyl ring of the TPE moiety connected

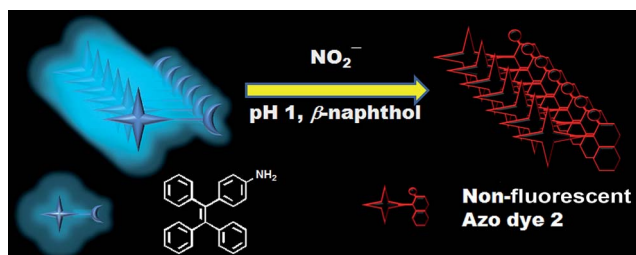


Fig. 1 The sensing mechanism for the detection of nitrite ions.

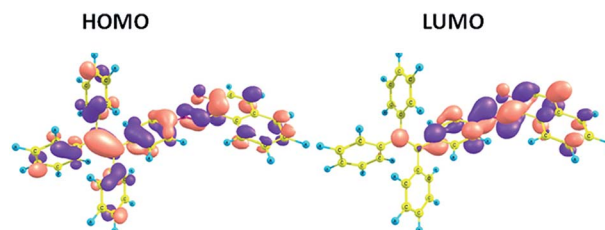


Fig. 3 Frontier molecular orbital diagrams of HOMO and LUMO of azo-dye **2** at optimized ground state geometry.

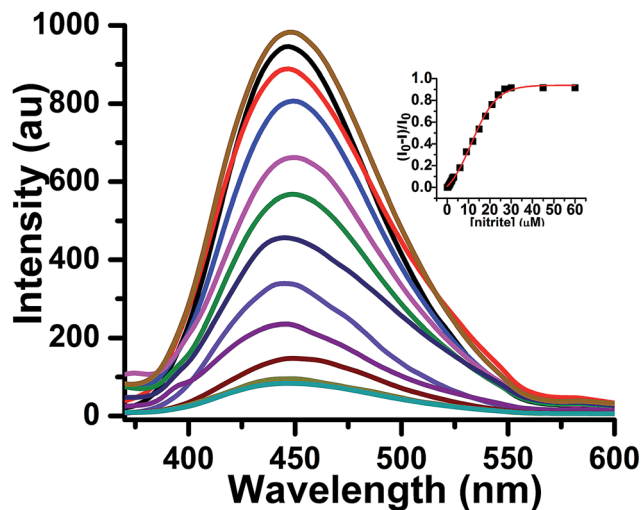


Fig. 4 Fluorescence response of probe 1 (30 μM) upon addition of different concentrations of nitrite (0–60 μM) and alkaline β -naphthol solution [solvent system: 3% THF in 0.1 N aqueous HCl; λ_{ex} 345 nm]. Inset: plot of relative emission intensity against no. of equiv. of nitrite ions.

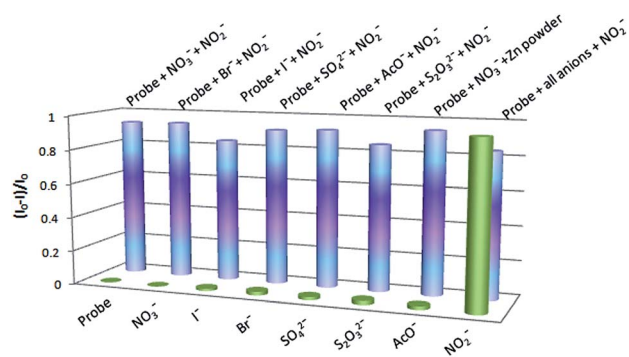


Fig. 5 Maximum fluorescence response of probe 1 (30 μM) upon addition of different anions (30 μM) in 3% THF–0.1 N aqueous HCl.

to the electron withdrawing azo bond and the naphthalene moiety situated on the other side of this bond are co-planar, and create a channel for shifting the π -cloud from TPE to this part during the S_0 – S_1 transition. The disappearance of the π electron cloud on the major portion of the TPE moiety during the $\text{HOMO} \rightarrow \text{LUMO}$ excitation is probably related to the observed nonfluorescent nature of the azo-dye (2). This photo-induced intramolecular charge transfer process is subsequently followed by a non-radiative decay path from the charge separated excited state. The energy gap between the excited state at its optimized geometry and the ground state at this geometry was found to be negligibly small, which indicates a possibility of strong vibronic coupling between the states, leading to a non-radiative decay of the singlet excited state (see ESI†). Moreover, neither is the aggregated state expected to have better π -delocalization (even if it becomes completely planar) as the electron withdrawing part of the dye will still inhibit any π -electronic cloud over the TPE part.

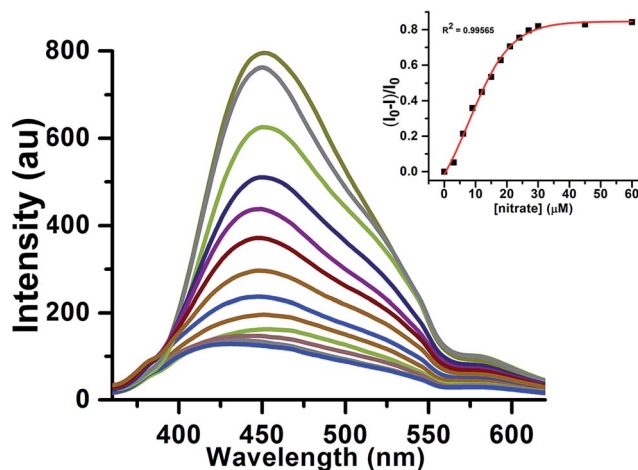


Fig. 6 Fluorescence response of probe 1 (30 μM) upon addition of different concentration of nitrate (0–60 μM) and a small amount of Zn powder, followed by alkaline β -naphthol solution [solvent system: 3% THF in 0.1 N aqueous HCl; λ_{ex} 345 nm]. Inset: plot of relative emission intensity against no. of equiv. of nitrate ions.

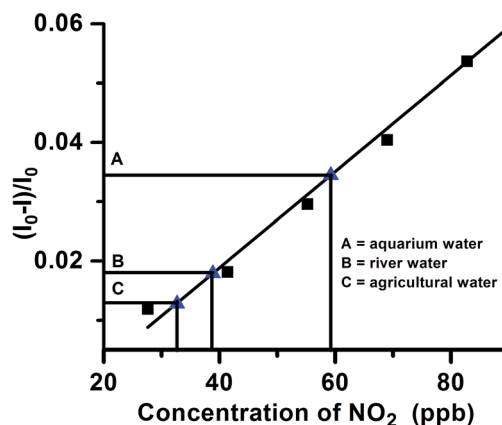


Fig. 7 A plot of the relative intensities of different real samples on a standard fluorescence curve to quantify the levels of nitrite ions in those samples.

For the sensing study, we selected 3% THF in 0.1 N HCl as the most suitable solvent system in which probe 1 fluoresces with the highest intensity. In a typical experiment, the fluorescence response of the highly fluorescent TPE-amine 1 gradually turned off upon addition of 0–2 equiv. of nitrite ions, followed by the addition of alkaline β -naphthol after an interval of 5 min at 0–5 $^{\circ}\text{C}$ and incubation of the resultant mixture for a further 5 min (Fig. 4). Initially, the solution showed an intense blue fluorescence at λ_{max} 447 nm and upon the addition of nitrite the fluorescence intensity decreased slowly, with almost no change in the absorption maxima. It is expected that probe 1 would be quickly diazotized in the presence of nitrite ions under acidic conditions at low temperature and would react with alkaline β -naphthol to form the corresponding azo-dye 2. Since the dye is non-fluorescent in solution as well as in the solid state, the fluorescence response decreases gradually. A drop in the

fluorescence intensity of about 15-fold was observed, indicating that the probe could efficiently detect trace levels of nitrite ions in solution. The azo-dye **2** was subsequently isolated in good quantity by carrying out a relatively large scale reaction and its structure was confirmed using ^1H NMR, ^{13}C NMR and ESI-MS spectra (see ESI† for details). In a separate experiment, the non-fluorescent nature of azo-dye **2** in solution was verified by measuring its fluorescence response in various proportions of THF in water (Fig. S6 of ESI†).

The selectivity of probe **1** was assessed by challenging it with several other environmentally relevant anions, such as I^- , Br^- , CH_3COO^- , N_3^- , SO_4^{2-} , NO_3^- , which do not induce any change in fluorescence intensity relative to the blank, even at relatively high concentrations, providing evidence for its high selectivity to nitrite ions (Fig. 5).

The specificity is an outcome of the fact that diazotization of the amine group of probe **1** is only possible when nitrite ions are present in the system. However, the expected drop in the fluorescence intensity was not observed in the case of oxidizable anions like I^- , $\text{S}_2\text{O}_3^{2-}$ and Br^- . Oxidizable anions, mainly iodide, are expected to impede the detection of nitrite ions by reacting with them under acidic conditions to produce NO gas.²⁰ However, as a reactive radical species, NO does not last long in aqueous solution but undergoes oxidation to generate mainly nitrite ions.²¹ Making an allowance for these facts, we presume that both the reactions take place in a successive manner, to different extents depending on the kind of oxidizable anion present in the solution for the competition experiments, maintaining a similar level of nitrite ions in solution and rendering a minor drop in the fluorescence intensity. Our conjecture was supported by the fact that the fluorescence emission of probe **1** is negligible in the presence of NO under the established diazotization conditions at pH 1 (Fig. S7 of ESI†).

Our sensing system is able to detect nitrite ions well below 1 ppm, the MCL set by the EPA for drinking water. Probe **1** responds to NO_2^- ions linearly below the micro molar concentration range and from that the detection limit of probe **1** was estimated to be 6×10^{-7} M or 27.6 ppb of NaNO_2 (Fig. S8 of ESI†).

Notably, we extended the capability of this probe to the detection of nitrate ions by performing an *in situ* Zn powder-facilitated reduction step. The reduction was carried out by adding a small amount of zinc (a toothpick full), which spontaneously catalyzes the reduction of nitrate to nitrite ions in a short amount of time. Therefore, a similar fluorimetric response was obtained to that of nitrite ions when 0–2 equiv. of nitrate ions was added to probe **1** in 3% THF in 0.1 N HCl at 0–5 °C, adding a toothpick full of Zn-dust and shaking the resultant mixture for 5 min followed by addition of alkaline β -naphthol solution and incubation of the resultant mixture for a further 5 min (Fig. 6).

The applicability of probe **1** was verified by detecting the nitrite levels in several real samples. The samples were collected from various sources, such as river, paddy field, and aquarium water. For the determination of nitrite levels in each real sample, it was made appropriately acidic by addition of conc.

HCl, then probe **1** was added at 0–5 °C followed by the addition of β -naphthol, and the fluorescence intensity was measured. The levels of nitrite in the real samples were obtained by plotting the intensity values on a standard fluorescence intensity curve and were found to be in the range of 30–60 ppb (Fig. 7).

Conclusions

In conclusion, we have developed a novel AIE-based fluorescent probe for the detection of trace amounts of nitrite ions in water. The function of probe **1**, which is an amine derivative of tetraphenylethylene, depends on diazotization of its amino group in the presence of dissolved nitrite followed by coupling with β -naphthol to produce an azo-dye (**2**). Although the probe is highly fluorescent in 3% THF–0.1 N HCl solution, the resultant azo-dye is non-fluorescent in solution as well as in the solid state and thereby, the probe acts as a turn-off type molecular sensor for nitrite ions in the presence of many other interfering anionic species. The probe works equally well for the detection of nitrate ions under reducing conditions (in the presence of Zn-dust). High sensitivity and selectivity, low detection limit, and fast reaction coupled with cost effective synthesis make this probe highly promising for practical purposes.

Acknowledgements

A.C. thanks DST (India) (project no. SR/FT/CS-092/2009) for financial support. M.B. is also thankful to CSIR (India) (project no. 02(0075)/2012/EMR-II) for research funding. D.G.K. is thankful to DST (India) for research fellowships. The authors sincerely thank Dr Supriya Tilvi of NIO, Goa, India for timely help with some spectral data.

Notes and references

- 1 C. J. Johnson and C. K. Burton, *Am. J. Ind. Med.*, 1990, **18**, 449.
- 2 M. T. Gladwin, A. N. Schechter, D. B. Kim-Shapiro, R. P. Patel, N. Hogg, S. Shiva, R. O. Cannon III, M. Kelm, D. A. Wink, M. G. Espey, E. H. Oldfield, R. M. Pluta, B. A. Freeman, J. R. Lancaster Jr, M. Feelisch and J. O. Lundberg, *Nat. Chem. Biol.*, 2005, **1**, 308.
- 3 I. A. Wolff and A. E. Wasserman, *Science*, 1972, **177**, 15.
- 4 J. O. Lundberg, E. Weitzberg and M. T. Gladwin, *Nat. Rev. Drug Discovery*, 2008, **7**, 156.
- 5 (a) G. J. Mohr and O. S. Wolfbeis, *Analyst*, 1996, **121**, 1489; (b) M. Bru, M. I. Burguete, F. Galindo, S. V. Luis, M. J. Marin and L. Vilara, *Tetrahedron Lett.*, 2006, **47**, 1787.
- 6 (a) P. Wang, X. Wang, L. Bi and G. Zhu, *Analyst*, 2000, **125**, 1291; (b) A. Rahim, L. S. S. Santos, S. B. A. Barros, L. T. Kubota, R. Landers and Y. Gushikem, *Electroanalysis*, 2014, **26**, 541.
- 7 J. M. Doyle, M. L. Miller, B. R. McCord, D. A. McCollam and G. W. Mushrush, *Anal. Chem.*, 2000, **72**, 2302.
- 8 (a) X. Chen, F. Wang and Z. Chen, *Anal. Chim. Acta*, 2008, **623**, 213; (b) Y. Qiu, H. Deng, J. Mou, S. Yang, M. Zeller, S. R. Batten, H. Wu and J. Li, *Chem. Commun.*, 2009, 5415; (c) P. Li, Y. Ding, A. Wang, L. Zhou, S. Wei, Y. Zhou,

- Y. Tang, Y. Chen, C. Cai and T. Lu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 2255.
- 9 (a) W. L. Daniel, M. S. Han, J.-S. Lee and C. A. Mirkin, *J. Am. Chem. Soc.*, 2009, **131**, 6362; (b) N. Adarsh, M. Shanmugasundaram and D. Ramaiah, *Anal. Chem.*, 2013, **85**, 10008; (c) N. Xiao and C. Yu, *Anal. Chem.*, 2010, **82**, 3659.
- 10 (a) Y. Yang, Q. Zhao, W. Feng and F. Li, *Chem. Rev.*, 2013, **113**, 192; (b) R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3936; (c) M. J. Culzoni, A. M. de la Pena, A. Machuca, H. C. Goicoechea and R. Babiano, *Anal. Methods*, 2013, **5**, 30 and references cited therein (d) H. N. Kim, W. X. Ren, J. S. Kim and J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 3210; (e) M. E. Jun, B. Roy and K. H. Ahn, *Chem. Commun.*, 2011, **47**, 7583; (f) F. Long, A. Zhu, H. Shi, H. Wang and J. Liu, *Sci. Rep.*, 2013, **3**, 2308; (g) M. Li, H. Gou, I. Al-Ogaidi and N. Wu, *ACS Sustainable Chem. Eng.*, 2013, **1**, 713; (h) J. Chan, S. C. Dodanil and C. J. Chang, *Nat. Chem.*, 2012, **4**, 973; (i) X. Chen, G. Zhou, X. Peng and J. Yoon, *Chem. Soc. Rev.*, 2012, **41**, 4610.
- 11 (a) V. Kumar, M. Banerjee and A. Chatterjee, *Talanta*, 2012, **99**, 610; (b) A. Büldt and U. Karst, *Anal. Chem.*, 1999, **71**, 3003; (c) M. Strianese, S. Milione, V. Bertolasi and C. Pellecchia, *Inorg. Chem.*, 2013, **52**, 11778.
- 12 (a) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970; (b) H. Tong, Y. Hong, Y. Dong, M. Haubler, J. W. Y. Lam, Z. Li, Z. Guo, Z. Guo and B. Z. Tang, *Chem. Commun.*, 2006, 3705.
- 13 B. Z. Tang and A. Qin, *Aggregation-Induced Emission: Fundamentals and Applications*, Wiley, New York, 2013, vol. 1 and 2.
- 14 For selected recent reviews on AIE-active materials and their applications, see: (a) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429; (b) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878; (c) Y. Hong, J. W. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (d) H. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (e) R. T. K. Kwok, C. W. T. Leung, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2015, DOI: 10.1039/c4cs00325j.
- 15 For some recent examples on TPE-based chemosensors/bioprobes, see: (a) H.-T. Feng, S. Song, Y.-C. Chen, C.-H. Shen and Y.-S. Zheng, *J. Mater. Chem. C*, 2014, **2**, 2353; (b) J. Zhang, Q. Yang, Y. Zhu, H. Liu, Z. Chi and C.-Y. Su, *Dalton Trans.*, 2014, **43**, 15785; (c) N. Zhao, J. W. Y. Lam, H. H. Y. Sung, H. M. Su, I. D. Williams, K. S. Wong and B. Z. Tang, *Chem.-Eur. J.*, 2014, **20**, 133; (d) X. Wang, J. Hu, G. Zhang and S. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 9890; (e) H.-T. Feng and Y.-S. Zheng, *Chem.-Eur. J.*, 2014, **20**, 195; (f) X. Lou, C. W. T. Leung, C. Dong, Y. Hong, S. Chen, E. Zhao, J. W. Y. Lam and B. Z. Tang, *RSC Adv.*, 2014, **4**, 33307; (g) X. Wang, H. Liu, J. Li, K. Ding, Z. Lv, Y. Yang, H. Chen and X. Li, *Chem.-Asian J.*, 2014, **9**, 784; (h) C. J. Kassl and F. C. Pigge, *Tetrahedron Lett.*, 2014, **55**, 4810; (i) J.-H. Ye, J. Liu, Z. Wang, Y. Bai, W. Zhang and W. He, *Tetrahedron Lett.*, 2014, **55**, 3688; (j) F. Hu, Y. Huang, G. Zhang, R. Zhao and D. Zhang, *Tetrahedron Lett.*, 2014, **55**, 1471; (k) T. Noguchi, B. Roy, D. Yoshihara, Y. Tsuchiya, T. Yamamoto and S. Shinkai, *Chem.-Eur. J.*, 2014, **20**, 381; (l) D. G. Khandare, V. Kumar, A. Chattopadhyay, M. Banerjee and A. Chatterjee, *RSC Adv.*, 2013, **3**, 16981; (m) D. G. Khandare, H. Joshi, M. Banerjee, M. S. Majik and A. Chatterjee, *RSC Adv.*, 2014, **4**, 47076; (n) J. Mei, Y. Wang, J. Tong, J. Wang, A. Qin, J. Z. Sun and B. Z. Tang, *Chem.-Eur. J.*, 2013, **19**, 613; (o) J. Li, J. Liu, J. W. Y. Lam and B. Z. Tang, *RSC Adv.*, 2013, **3**, 8193; (p) J. Liang, R. T. K. Kwok, H. Shi, B. Z. Tang and B. Liu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8784; (q) C. Yu, Y. Wu, F. Zeng, X. Li, J. Shi and S. Wu, *Biomacromolecules*, 2013, **14**, 4507; (r) H. Liu, Z. Lv, K. Ding, X. Liu, L. Yuan, H. Chen and X. Li, *J. Mater. Chem. B*, 2013, **1**, 5550; (s) Y. Yan, Z. Che, X. Yu, X. Zhi, J. Wang and H. Xu, *Bioorg. Med. Chem.*, 2013, **21**, 508; (t) T. Han, X. Feng, B. Tong, J. Shi, L. Chen, J. Zhi and Y. Dong, *Chem. Commun.*, 2012, **48**, 416; (u) G. Huang, G. Zhang and D. Zhang, *Chem. Commun.*, 2012, **48**, 7504; (v) X. Wang, J. Hu, T. Liu, G. Zhang and S. Liu, *J. Mater. Chem.*, 2012, **22**, 8622; (w) Y. Liu, Z. Wang, G. Zhang, W. Zhang, D. Zhang and X. Jiang, *Analyst*, 2012, **137**, 4654.
- 16 For some recent examples of TPE-based molecules for various other applications, see: (a) Y. Chen, M. Li, Y. Hong, J. W. Y. Lam, Q. Zheng and B. Z. Tang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10783; (b) C. Zhang, S. Jin, S. Li, X. Xue, J. Liu, Y. Huang, Y. Jiang, W.-Q. Chen, G. Zou and X.-J. Liang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5212; (c) S. Yao, X. Yang, M. Yu, Y. Zhang and J.-X. Jiang, *J. Mater. Chem. A*, 2014, **2**, 8054; (d) W. Qin, K. Li, G. Feng, M. Li, Z. Yang, B. Liu and B. Z. Tang, *Adv. Funct. Mater.*, 2014, **24**, 635; (e) C. W. T. Leung, Y. Hong, S. Chen, E. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Am. Chem. Soc.*, 2013, **135**, 62; (f) Z. Zhao, C. Y. K. Chan, S. Chen, C. Deng, J. W. Y. Lam, C. K. W. Jim, Y. Hong, P. Lu, Z. Chang, X. Chen, P. Lu, H. S. Kwok, H. Qiu and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 4527; (g) J.-P. Xu, Y. Fang, Z.-G. Song, J. Mei, L. Jia, A. Qin, J. Z. Sun, J. Ji and B. Z. Tang, *Analyst*, 2011, **136**, 2315.
- 17 For selected recent examples of various AIE-active materials other than TPE and their applications, see: (a) N. Na, F. Wang, J. Huang, C. Niu, C. Yang, Z. Shang, F. Han and J. Ouyang, *RSC Adv.*, 2014, **4**, 35459; (b) L. Wang, D. Wang, H. Lu, H. Wang, L. Xue and S. Feng, *Appl. Organomet. Chem.*, 2013, **27**, 529; (c) O. Simalou, R. Lu, P. Xue, P. Gong and T. Zhang, *Eur. J. Org. Chem.*, 2014, **2014**, 2907; (d) G. Zhang, A. Ding, Y. Zhang, L. Yang, L. Kong, X. Zhang, X. Tao, Y. Tian and J. Yang, *Sens. Actuators, B*, 2014, **202**, 209; (e) C. Y. K. Chan, J. W. Y. Lam, Z. Zhao, S. Chen, P. Lu, H. H. Y. Sung, H. S. Kwok, Y. Ma, I. D. Williams and B. Z. Tang, *J. Mater. Chem. C*, 2014, **2**, 4320; (f) X. Tang, L. Yao, H. Liu, F. Shen, S. Zhang, H. Zhang, P. Lu and Y. Ma, *Chem.-Eur. J.*, 2014, **20**, 7589; (g) H. Zhang, Y. Qu, Y. Gao, J. Hua, J. Li and B. Li, *Tetrahedron Lett.*, 2013, **54**, 909; (h) W. Z. Yuan, Y. Gong, S. Chen, X. Y. Shen,

- J. W. Y. Lam, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H. S. Kwok, Y. Zhang, J. Z. Sun and B. Z. Tang, *Chem. Mater.*, 2012, **24**, 1518; (i) X. Zhang, X. Zhang, S. Wang, M. Liu, L. Tao and Y. Wei, *Nanoscale*, 2013, **5**, 147; (j) J. Mei, J. Wang, J. Z. Sun, H. Zhao, W. Yuan, C. Deng, S. Chen, H. H. Y. Sung, P. Lu, A. Qin, H. S. Kwok, Y. Ma, I. D. Williams and B. Z. Tang, *Chem. Sci.*, 2012, **3**, 549; (k) Y. Liu, Y. Tang, N. N. Barashkov, I. S. Irgibaeva, J. W. Y. Lam, R. Hu, D. Birimzhanova, Y. Yu and B. Z. Tang, *J. Am. Chem. Soc.*, 2010, **132**, 13951; (l) L. Xu, Y. Li, S. Li, R. Hu, A. Qin, B. Z. Tang and B. Su, *Analyst*, 2014, **139**, 2332.
- 18 S. Hazra, S. Balaji, M. Banerjee, A. Ganguly, N. N. Ghosh and A. Chatterjee, *Anal. Methods*, 2014, **6**, 3784.
- 19 X. F. Duan, J. Zeng, J. W. Lu and Z. B Zhang, *J. Org. Chem.*, 2006, **71**, 9873.
- 20 C. A. Abeledo and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1931, **53**, 2893.
- 21 L. J. Ignarro, J. M. Fukuto, J. M. Griscavage, N. E. Rogers and R. E. Byrns, *Proc. Natl. Acad. Sci. U. S. A.*, 1993, **90**, 8103.