

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# A novel triple-mode fluorescent pH probe from monomer emission to aggregation-induced emission

Zhenghua Wang,<sup>a</sup> Jia-Hai Ye,<sup>\*a</sup> Jing Li,<sup>a</sup> Yang Bai,<sup>b</sup> Wenchao Zhang,<sup>a</sup> and Weijiang He<sup>\*b</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

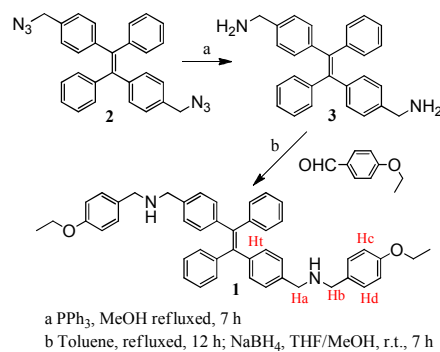
A tetraphenylene (TPE)-based pH fluorescent probe was synthesised which could selectively monitor pH variation in THF/H<sub>2</sub>O (2:8, v/v) solution in wide-range pH (1.99-11.64) values. It displayed a monomer emission under acidic condition, but exhibited ratiometric fluorescence under neutral condition and aggregation-induced emission (AIE) under basic condition subsequently.

The measurement of pH plays an important role in a variety of system, especially in living organization such as cell growth, cell adhesion, chemo taxis and ionic transition, *et al.*<sup>1,2</sup> Many methods in detecting pH value have been applied so far, for instance, potentiometric,<sup>3</sup> nuclear magnetic resonance (NMR),<sup>4</sup> absorbance spectroscopy and acid-base indicator titration *etc.* Among the fluorophores developed, the utilization of fluorescence probe to detect pH attracts increasing attention due to its excellent properties compared to the traditional measurements like well sensitive and selective, noninvasiveness and high signal-to-noise ratio, *etc.*<sup>5,6</sup> Fluorescence-based techniques like BODIPY,<sup>7</sup> chromenoquinoline,<sup>8</sup> rhodamine,<sup>6,9</sup> transition metal complex<sup>10</sup> fluorescein,<sup>11</sup> naphthalimide<sup>12</sup> and quantum dots<sup>13</sup> is becoming more and more popular for the measurement of intracellular pH and cell imaging.<sup>2,14</sup> What is more, sol-gel<sup>15</sup> and nanoparticles<sup>16</sup> based pH probes have also been developed.

By contrast to those fluorescent probes with absolute intensity at only one peak, the fluorescence intensity at two wavelengths (ratiometric fluorescent probes)<sup>17</sup> and calculation of their ratio gives more inspiration of the design of pH probes. The normal organic dyes experience small Stokes shifts, which may lead to self-quenching and the excitation backscattering effects may cause detection errors. Because of these disadvantages, the designing of ratiometric fluorescent probes are utilized to reduce these bad influence of such factors.<sup>18</sup>

Most traditional fluorophores are usually constructed based on aromatic molecular motifs, which may experience strong molecular interaction in concentrated solutions and solid aggregates, resulting in fluorescence intensity decreasing. In order to avoid the aggregation-caused quenching (ACQ) effect in practical applications, aggregation-induced emission (AIE) based system was reported by Tang and co-workers in 2001.<sup>19</sup> AIE effect is general property which is caused by restriction of intramolecular rotation (RIR) in the aggregates. The development of fluorescence probes, solid-state emitters and other functional materials based on AIE effect has encouraged many researchers

these years.<sup>20</sup> With an excellent AIE effect, tetraphenylethylene (TPE)-based fluorescence probes have been widely designed and synthesized.<sup>21,22</sup> Moreover, most of the fluorescent probes for pH detection were based on the mechanism of protonation and deprotonation of molecules. The working principle of AIE-based pH sensing process is the dissolution (disaggregation) and aggregation of an AIE luminogen in different pH environment.<sup>22,23</sup> Inspired by this mechanism, fluorescent pH probes based on AIEE can be readily designed. AIE systems with monomer emission cannot be widely observed. As reported, bridged TPE units with phenyl rings locked display monomer emission in both solution and crystalline states as a result of the RIR mechanism.<sup>24</sup> With the change of the degree of polarity of solvent, molecules consisted by hydrophilic and hydrophobic moieties also exhibit monomer emission and AIE at the same time.<sup>25</sup> Recently, Zheng *et al.* reported the TPE derivatives with hydrophilic and flexible chains around the TPE core or bridged TPE structure to reduce its hydrophobic force as it can made the compound more compatible with water and restricted the rotation of the phenyl rings to display the enhancement of monomer emission and decrease of aggregate-induced due to the encapsulation in the cavity of  $\gamma$ -cyclodextrin or the bridged TPE unit.<sup>26</sup>

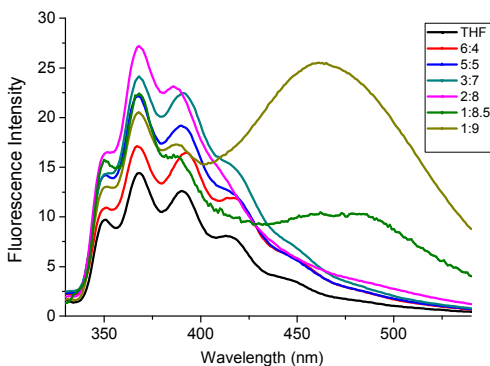


Scheme 1 Synthesis of probe 1

Herein, we reported a new amphiphilic molecule fluorescent probe **1** constructed on TPE, which act as a hydrophobic moiety, linked with two potential hydrophilic moieties, secondary amines for wide-range pH detection. The probe **1** showed triple-mode fluorescent responses from monomer emission to aggregation-induced emission over the pH range 1.99 to 11.64 in THF/H<sub>2</sub>O (2:8, v/v) solution based on the solvation and AIEE mechanisms.

The selectivity experiment over metal cations showed that the TPE-based pH probe exhibited a highly selectivity under complex conditions.

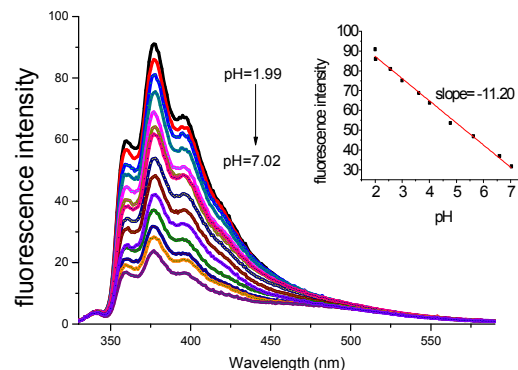
The target probe molecule **1** and intermediary compound **3** were synthesized in a facile route as shown in Scheme 1. Compound **3** was reduced from **2**<sup>21a</sup> under reflux in methanol with the presence of triphenylphosphine (PPh<sub>3</sub>). Compound **1** was obtained from **3** and *p*-ethoxybenzaldehyde in toluene under reflux and then reduced by sodium borohydride (NaBH<sub>4</sub>) under room temperature in THF/methanol. The chemical structures of new compounds were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR FT-IR and MS.



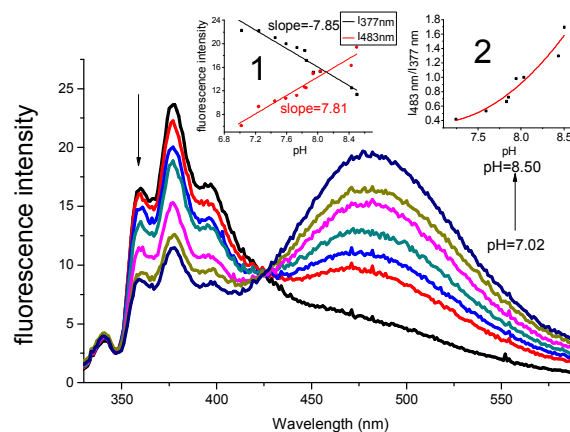
**Fig. 1** Fluorescence spectra ( $\lambda_{\text{exc}} = 305 \text{ nm}$ ) of probe **1** ( $10 \mu\text{M}$ ) in a THF/H<sub>2</sub>O binary solvent mixture.

Probe **1**, as a potential AIE-active compound, was soluble in some common organic solvents, such as chloroform, acetonitrile, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF), but undissolved in water. Herein, the AIE behavior of probe **1** was investigated in aqueous THF solution ( $10 \mu\text{M}$ ) with different THF/water ratios. As shown in Fig. 1, when the water fraction in dilute THF solution was increased from 0 to 80%, probe **1** indeed showed as a weak fluorescence emitter, only with the monomer emission at 377 nm. And what was more that the fluorescence intensity increased as the water fraction ratio increasing. When it is molecularly dissolved in a good solvent almost no fluorescence as expected. As the water fraction increased to 1:8.5, a new band at 483 nm was expected to be observed for probe **1** as a result of the aggregation at a high water fraction solution. When the water fraction was reached to 90%, a strong AIE band was found. The fluorescence changes of probe **1** in aqueous THF solution ( $10 \mu\text{M}$ ) with different THF/water ration under UV light (365 nm) were also carried out (Fig. S2, ESI<sup>†</sup>). When the water fraction in dilute THF solution increased from 0% to 70%, probe **1** showed almost no fluorescence as expected. An enhancement of fluorescent of probe **1** can be observed as the water fraction in THF/water mixture exceeded 80%. The fluorescence enhancement of probe **1** was attributed to the formation of nanoaggregates suggesting the probe **1** was AIE-active. As a conclusion, based on above AIE behavior of probe **1**, the UV-vis and fluorescence experiments were carried out in THF/H<sub>2</sub>O (2:8, v/v) aqueous solution. The UV-vis absorption titration spectral of probe **1** ( $10 \mu\text{M}$ ) to pH was carried out in a solution of THF/H<sub>2</sub>O (2:8, v/v) as shown in Fig. S14-16 (ESI<sup>†</sup>). When pH value changed from 2.08 to 8.09, there were minimal changes at two wavelengths of 277 nm and

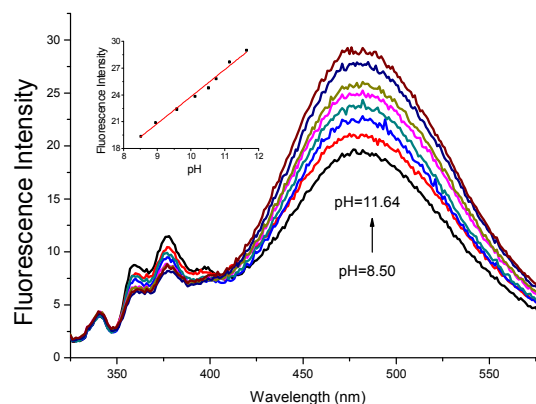
328 nm, respectively. But in the strong alkaline condition (pH = 9.94-11.84), there was no change at 328 nm while with a clearly enhancement at 277 nm.



**Fig. 2** Fluorescence responses to the probe **1** ( $10 \mu\text{M}$ ) to different pH: 1.99, 2.01, 2.55, 2.98, 3.60, 4.00, 4.77, 5.08, 5.62, 6.58 and 7.02 in THF/H<sub>2</sub>O (2:8, v/v) ( $\lambda_{\text{exc}} = 305 \text{ nm}$ ). Inset: linear relationship of fluorescence intensity at 377 nm and varying pH values from 1.99 to 7.02.



**Fig. 3** Fluorescence responses to the probe **1** ( $10 \mu\text{M}$ ) to different pH: 7.02, 7.24, 7.59, 7.85, 8.03, 8.43 and 8.50 in THF/H<sub>2</sub>O (2:8, v/v) ( $\lambda_{\text{exc}} = 305 \text{ nm}$ ). Inset 1: linear relationship of fluorescence intensity at 377 nm (black line) and 483 nm (red line) to pH; Inset 2: Ratio metric calibration curve of  $I_{483 \text{ nm}}/I_{377 \text{ nm}}$  (intensity at 483 nm vs intensity at 377 nm)



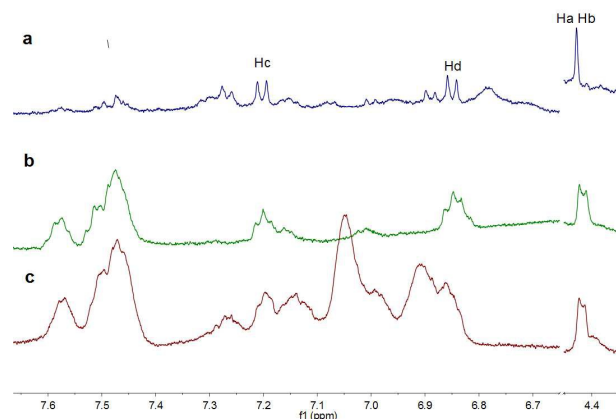
**Fig. 4** Fluorescence responses to the probe **1** ( $10 \mu\text{M}$ ) to different pH: 8.50, 8.94, 9.57, 10.11, 10.51, 10.74, 11.13 and 11.64 in THF/H<sub>2</sub>O (2:8, v/v) ( $\lambda_{\text{exc}} = 305 \text{ nm}$ ). Inset: linear relationship of fluorescence intensity at 483 nm to pH

Next, the fluorescence properties of probe **1** (10  $\mu\text{M}$ ) were investigated as it displayed a strong fluorescence at 377 nm when excited at 305 nm in THF/H<sub>2</sub>O (2:8, v/v). The standard pH titrations on probe **1** were obtained in a solution of THF/H<sub>2</sub>O (2:8, v/v). In the fluorescence spectrum (Fig. 2), probe **1** exhibited an emission band at 377 nm under an acidic condition. As the pH value increased from 1.99 to 7.02, the fluorescence intensity of probe **1** at 377 nm linearly decreased. And the fluorescence quantum yield of probe **1** under acidic condition was 10.9%. Upon addition of base to the solution of probe **1** (10  $\mu\text{M}$ ) in THF/H<sub>2</sub>O (2:8, v/v), varying the pH of the media from 7.02 to 8.50, a gradual decrease in intensity of emission band at 377 nm was observed along with the appearance of a new band at 483 nm in a ratiometric manner (Fig. 3). The calculations of fluorescence intensity ration of the two emission band at 483 nm and 377 nm ( $I_{483\text{ nm}}/I_{377\text{ nm}}$ ) within the range of pH from 7.02 to 8.50 (Fig. S6 and S7, ESI†) established that aggregates of probe **1** served as dual-emission ratiometric probe for pH detection. Actually, this ratiometric taking place allowed us to correct the pH sensitivity. As the pH continuously changed from 8.50 to 11.64, the fluorescence intensity was increased at 483 nm (Fig. 4) as a result of aggregation of probe **1** under alkaline condition and the fluorescence quantum yield was calculated to be 6.7%. These fluorescence changes also can be observed with naked eyes easily upon the addition of both acid and base into the solution of probe **1** (10  $\mu\text{M}$ ) in THF/H<sub>2</sub>O (2:8, v/v) under UV light (365 nm) (Fig. S13, ESI†). A strong fluorescence emission can be observed of probe **1** in an alkaline solution while fluorescence quenched in an acidic solution. In other words, according to fluorescence emission measurements, probe **1** behaved as a typical pH-induced “off-on” type fluorescence molecular switch for base.

As it was known that TPE-based fluorescent with monomer emission cannot be widely observed. Bridged TPE and TPE core with hydrophilic moieties could exhibit monomer emission with the appearance of AIE at the same time. Probe **1** showed monomer emission under acidic condition and exhibited dual-emission wavelength both monomer emission and AIE under neutral condition. In order to have a better understanding of the mechanism of probe **1**, the fluorescence tests were investigated in water and THF solutions. There were no changes of fluorescence spectrum both intensity and wavelength in a solution of THF was found with the addition of both acid and base (Fig. S17, ESI†). And what was more, only a weak monomer emission at 377 nm exhibited. Meanwhile, when probe **1** was dissolved in water, only AIE can be obtained. It exhibited fluorescence quenching with the addition of acid but there was no changes under alkaline condition (Fig. S18 and S19, ESI†). It means that both THF and water fraction played important roles to the dual-emission properties of probe **1**. Probe **1** contains a hydrophobic moiety and two potential hydrophilic moieties as an amphiphilic molecule. With the hydrophobic part forming the inner core, while the hydrophilic chains interacted with the surrounding water medium. With the hydrophobic alkyl chains avoiding the solvent and the THF fraction, which acted as a cave for TPE core staying without assembled, the hydrophobic moiety, TPE stayed in the cave with the water fraction surrounded and the hydrophilic moieties can stretched into the water fraction, resulting in restriction of the phenyl rings rotated freely. As a conclusion, due to the two

chains stretched into water and TPE moiety restricted in the THF, the phenyl rings also could not rotate freely, which resulted in the appearance of monomer emission at 377 nm. The molecular arrangement became more defined at higher water content. When the probe **1** was dissolved in a low water fraction ratio medium (<80%), monomer emission was enhanced as water ration increasing. This was caused by decrease of the cave, provided by the THF. But when the water fraction ratio was reached to 85% and more, the cave was not enough for TPE core stay, resulting in an aggregated emission at 483 nm. And what was more, as the water fraction ratio was increased the aggregated-induced emission enhanced and the monomer emission quenched meanwhile.

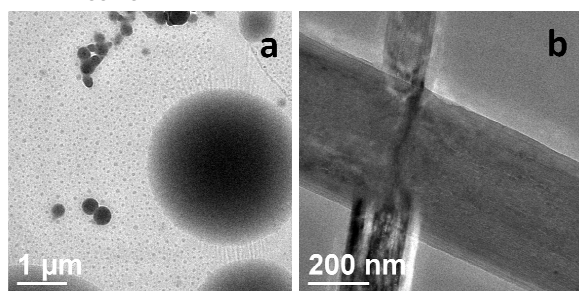
In order to get more evidence for the mechanism, the <sup>1</sup>H NMR spectra changes of probe **1** in *d*<sub>8</sub>-THF/D<sub>2</sub>O to acid and base were given (Fig. 5). When probe **1** was dissolved in neutral and base condition, because of the aggregation formatted by N-H...N hydrogen bonding, the H<sub>a</sub> and H<sub>b</sub> were under different chemical environment, resulting in a doublet at 4.23 ppm. As the base was added into the mixture, the hydrophilicity decreased and the compound **1** aggregated and stacked. The probe **1** cannot be well dissolved in the high D<sub>2</sub>O solution, which resulting in the losing of the signal of H<sub>i</sub>, the protons of TPE core, H<sub>a</sub> and H<sub>b</sub>. But when acid was added into the solution of probe **1**, the amino parts transferred into salts and it can be well dissolved in D<sub>2</sub>O, the doublet was changed into singlet and shifted to 4.28 ppm due to the breakup of intermolecular hydrogen bond. The protons of phenyl rings in the chain moieties was stretched into D<sub>2</sub>O without stacked with TPE core, which caused the signal appearance of H<sub>c</sub> and H<sub>d</sub> as two doublet (7.21, 7.19 and 6.86, 6.84 ppm).



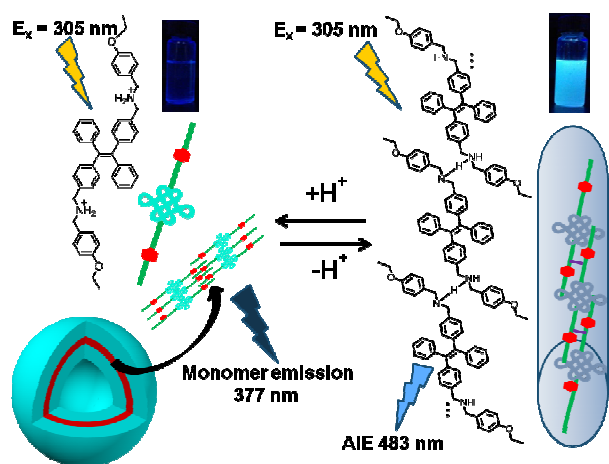
**Fig. 5** Changes of <sup>1</sup>H NMR spectra of probe **1** in *d*<sub>8</sub>-THF/D<sub>2</sub>O. (a) with the addition of 4 equiv. CF<sub>3</sub>COOH; (b) with the addition of 4 equiv. NaOH; (c) without any addition

The size and morphology of the microstructure formed by compound **1** under different condition in THF aqueous solution were shown in Fig. 6 by TEM. When probe **1** was under acidic condition, the TEM images indicated that the spherical morphology with a diameter about 2  $\mu\text{m}$ , convincingly indicating that caused by the amphiphile and the solvent effect. When base was added into to solution of probe **1**, the TEM image confirmed the formation of large size self-assembled lineally crystalline TPE nanowires with a diameter about 200-450 nm due to the hydrogen bonding induced J-aggregation. This resulted in enhancement and red-shift photoluminescence in comparison with those of TPE

spherical aggregates.



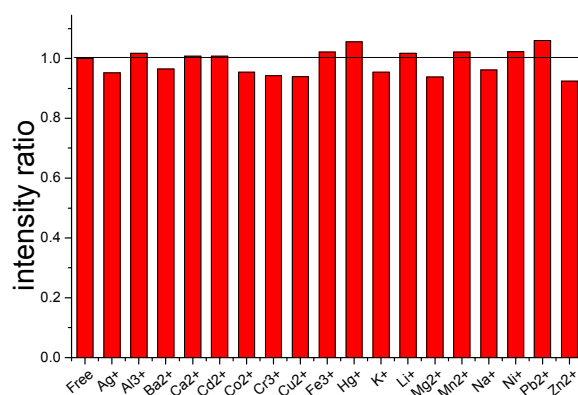
**Fig. 6** TEM image of compound **1** with the addition of (a) acid; (b) base in THF/H<sub>2</sub>O mixture.



**Fig. 7** Mechanism of pH response of probe **1**

A sensing mechanisms based on the transformation from vesicles to aggregation which lead to the triple-mode fluorescence behaviors with the responding from acid to base conditions was proposed as shown in Fig. 7. When probe **1** was under an acidic condition, its amine groups were transformed to ammonium salts, which could be well dissolved in a high water fraction solution. As a result, no emission of aggregated states at 483 nm can be observed. These ammonium salts states of probe **1** could be well dissolved in a high water fraction solution. The two potential hydrophilic moieties became more resolvable in the mixture solvent and most water was around the two chains. But the TPE core was hydrophobic moiety, the THF molecules will surrounded the TPE core. This hydrophobic solvophobic interaction caused monomer emission. A spherical core formatted by the amphiphile and solvophobic interaction. The probe **1** with chains stretched into water fraction and the TPE was stayed in the THF fraction, resulting in restriction of the phenyl rings rotating freely which is similar to the encapsulation in the cavity of  $\gamma$ -cyclodextrin.<sup>26a</sup> This fraction of THF acted as a cave for TPE core staying without assembled. And what was more, the N-atoms were positive charged, the atoms with the same charge would repel between two molecules. Additionally, attributed to the deprotonation of amine groups, the electron-donating ability of N-atoms were recovered, and the photoinduced electron transfer (PET) process would be more efficient, which resulted in fluorescence quenching at the band 377 nm of monomer emission

of probe **1** as the pH value decreased from 1.99 to 7.02. But when base was added into the solution of probe **1** in THF/H<sub>2</sub>O media, the molecules of probe **1** were transformed back to the amine form. The decrease in the hydrophilicity induced the molecules to aggregate in the aqueous medium, resulting in TPE core assembled and staked with a new emission band at 483 nm. The deprotonation of probe **1** induced the intermolecular hydrogen bonding, resulting in the formation of J-aggregation of probe **1**. The fluorescence wave shifted from 377 nm to 483 nm. This 106 nm red-shift caused from monomer emission to AIE. When the pH changed from 7.02 to 8.50, the monomer emission quenched, meanwhile, AIEE in a ratiometric manner. It played as a ratiometric fluorescent probe for pH. As the base was continuously added, and the pH vale changed from 8.50 to 11.64, a significant AIEE exhibited. But there were no significant changes of monomer emission at 377 nm.



**Fig. 8** Ratios of fluorescence intensity at 377 nm of probe **1** (10  $\mu$ M) in the presence of various metal ions (4 equiv.) in aqueous solution of THF/H<sub>2</sub>O (2:8, v/v)

On account of that the amine groups can bind with many metal ions in solution, the selectivity experiments of probe **1** to H<sup>+</sup> over metal ions, including Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Li<sup>+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup> and Cr<sup>3+</sup> were also further investigated in THF aqueous (THF/H<sub>2</sub>O = 2:8, v/v). As shown in Fig. 8 and Fig. S11 (ESI<sup>†</sup>), no changes of the fluorescence properties were observed for probe **1** upon addition of all of the metal ions both the fluorescence emission intensity and wavelengths. Upon on that, with a highly selectivity to proton, the pH-responsive behavior of probe **1** could not be interfered by metal ions in a complex environment.

In summary, we have described the synthesis and photophysical properties of a novel TPE-based triple-mode fluorescent probe for pH **1** detection in a wide range of pH value from 1.99 to 11.64 in a high water fraction solution of THF/H<sub>2</sub>O (2:8, v/v) media. When probe **1** was dissolved in acidic condition (pH value changed from 1.99 to 7.02), only fluorescence quenching of monomer emission at 377 nm. But when the probe **1** was under an alkaline condition, it exhibited a new fluorescence band at 483 nm due to AIE effect. As the pH value increased from 7.02 to 8.50, the fluorescence intensity was decreased at 377 nm and increased at 483 nm in a ratiometric manner. As the pH value continuously increased from 8.50 to 11.64, a significant AIEE at band of 483 nm displayed. Moreover, it also displayed

an excellent selectivity to various metal cations. This new finding provided a new method to the utilization of fluorescence with AIE effect to detect pH as expected. All the results demonstrate the TPE-based pH fluorescent probe has great potential in practical application and it also gives an excellent model for pH fluorescent probe designing. What is the most important; a new fluorescence sensing mechanism for pH was proposed a the transformation from vesicles to aggregation.

## Acknowledgements

This project was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

## Notes and references

<sup>a</sup> School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, P. R. China; Fax: (86) 25 8431 5857; Tel: (86) 25 8430 3116;; E-mail: yejihai@nju.edu.cn

<sup>b</sup> State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China, Fax: (86) 25 8331 4502; Tel: (86) 25 8359 7066; E-mail: hewej69@nju.edu.cn

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- (a) H. R. Kermis, Y. Kostov, P. Harms, G. Rao *Biotechnol. Prog.*, 2002, **18**, 1047; (b) B. Tang, F. Yu, P. Li, L. Tong, X. Duan, T. Xie, X. Wang *J. Am. Chem. Soc.*, 2009, **131**, 3016; (c) M. Tantama, Y. P. Hung, G. Yellen *J. Am. Chem. Soc.*, 2011, **133**, 10034; (d) X. Chen, T. Pradhan, F. Wang, J. S. Kim, J. Yoon *Chem Rev*, 2012, **112**, 1910; (e) G. T. Hanson, T. B. McAnaney, E. S. Park, M. E. P. Rendell, D. K. Yarbrough, S. Chu, L. Xi, S. G. Boxer, M. H. Montrose, S. J. Remington *Biochemistry*, 2002, **41**, 15477; (f) D. G. Pijanowska, A. Baraniecka, R. Wiater, G. Ginalska, J. Lobarzewski, W. Torbic *Sensors and Actuators B: Chemical*, 2001, **78**, 263; (g) P. Vermathen, A. A. Capizzano, A. A. Maudsley *Magnetic Resonance in Medicine*, 2000, **43**, 665.
- (a) Y. Urano, D. Asanuma, Y. Hama, Y. Koyama, T. Barrett, M. Kamiya, T. Nagano, T. Watanabe, A. Hasegawa, P. L. Choyke, H. Kobayashi *Nat. Med.*, 2009, **15**, 104; (b) P. Li, H. Xiao, Y. Cheng, W. Zhang, F. Huang, W. Zhang, H. Wang, B. Tang *Chem. Commun.*, 2014, **50**, 7184.
- E. G. Webb, R. C. Alkire *Journal of The Electrochemical Society*, 2002, **149**, B280.
- A. A. Sehgal, L. Duma, G. Bodenhausen, P. Pelupessy *Chemistry – A European Journal*, 2014, **20**, 6332.
- (a) S. Brasselet, W. E. Moerner *Single Mol.*, 2000, **1**, 17; (b) C. Sun, P. Wang, L. Li, G. Zhou, X. Zong, B. Hu, R. Zhang, J. Cai, J. Chen, M. Ji *Appl Biochem Biotechnol*, 2014, **172**, 1036.
- W. L. Czaplyski, G. E. Purnell, C. A. Roberts, R. M. Allred, E. J. Harbron *Org. Biomol. Chem.*, 2014, **12**, 526.
- (a) J. Han, A. Loudet, R. Barhoumi, R. C. Burghardt, K. Burgess *J. Am. Chem. Soc.*, 2009, **131**, 1642; (b) N. Boens, V. Leen, W. Dehaen *Chem. Soc. Rev.*, 2012, **41**, 1130.
- W. Huang, W. Lin, X. Guan *Tetrahedron Letters*, 2014, **55**, 116.
- (a) N. I. Georgiev, A. M. Asiri, K. A. Alamry, A. Y. Obaid, V. B. Bojinov *Journal of Photochemistry and Photobiology A: Chemistry*, 2014, **277**, 62; (b) L. Liu, P. Guo, L. Chai, Q. Shi, B. Xu, J. Yuan, X. Wang, X. Shi, W. Zhang *Sensors and Actuators B: Chemical*, 2014, **194**, 498.
- S. Z. Topal, E. Onal, A. G. Gurek, C. Hirel *Dalton. Trans.*, 2013, **42**, 11528.
- (a) X. L. Guan, Z. X. Su *Polymers for Advanced Technologies*, 2008, **19**, 385; (b) M. J. Doughty *Ophthalmic and Physiological Optics*, 2010, **30**, 167; (c) G. Ghini, C. Trono, A. Giannetti, G. L. Puleo, L. Luconi, J. Amadou, G. Giambastiani, F. Baldini *Sensors and Actuators B-Chemical*, 2013, **179**, 163.
- N. V. Marinova, N. I. Georgiev, V. B. Bojinov *Journal of Photochemistry and Photobiology A: Chemistry*, 2011, **222**, 132.
- T. Kurabayashi, N. Funaki, T. Fukuda, S. Akiyama, M. Suzuki *Analytical Sciences*, 2014, **30**, 545.
- (a) D. K. Rana, S. Dhar, S. C. Bhattacharya *Phys. Chem. Chem. Phys.*, 2014, **16**, 5933; (b) H. S. Lv, S. Y. Huang, Y. Xu, X. Dai, J. Y. Miao, B. X. Zhao *Bioorg. Med. Chem. Lett.*, 2014, **24**, 535; (c) R. Sanders, A. Draaijer, H. C. Gerritsem, P. M. Houpt, Y. K. Levine *Analytical Biochemistry*, 1995, **227**, 302.
- (a) S. A. Grant, R. S. Glass *Sensors and Actuators B*, 1997, **45**, 35; (b) D. Wencel, B. D. MacCraith, C. McDonagh *Sensors and Actuators B: Chemical*, 2009, **139**, 208.
- B. Korzeniowska, R. Woolley, J. DeCoursey, D. Wencel, C. E. Loscher, C. McDonagh *Journal of Biomedical Nanotechnology*, 2014, **10**, 1336.
- (a) J. Fan, C. Lin, H. Li, P. Zhan, J. Wang, S. Cui, M. Hu, G. Cheng, X. Peng *Dyes and Pigments*, 2013, **99**, 620; (b) C. G. Niu, X. Q. Gui, G. M. Zeng, X. Z. Yuan *Analyst*, 2005, **130**, 1551; (c) H. Sun, A. M. Scharff-Poulsen, H. Gu, K. Almdal *Chem. Mater.*, 2006, **18**, 3381.
- J. Fan, M. Hu, P. Zhan, X. Peng *Chem. Soc. Rev.*, 2013, **42**, 29.
- (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang *Chem. Commun.*, 2001, 1740; (b) Y. Hong, J. W. Lam, B. Z. Tang *Chem. Soc. Rev.*, 2011, **40**, 5361.
- (a) C. Gao, G. Gao, J. Lan, J. You *Chem. Commun.*, 2014, **50**, 5623; (b) X. G. Hou, Y. Wu, H. T. Cao, H. Z. Sun, H. B. Li, G. G. Shan, Z. M. Su *Chem. Commun.*, 2014, **50**, 6031; (c) P. Wang, X. Yan, F. Huang *Chem. Commun.*, 2014, **50**, 5017; (d) K. Li, Z. Zhu, P. Cai, R. Liu, N. Tomczak, D. Ding, J. Liu, W. Qin, Z. Zhao, Y. Hu, X. Chen, B. Z. Tang, B. Liu *Chemistry of Materials*, 2013, **25**, 4181; (e) G.-L. Fu, C.-H. Zhao *Tetrahedron*, 2013, **69**, 1700; (f) D. Ding, K. Li, B. Liu, B. Z. Tang *Accounts Of Chemical Rsfeatch*, 2013, **46**, 2441; (g) Z. Zhao, B. Chen, J. Geng, Z. Chang, L. Aparicio-Ixta, H. Nie, C. C. Goh, L. G. Ng, A. Qin, G. Ramos-Ortiz, B. Liu, B. Z. Tang *Particle & Particle Systems Characterization*, 2014, **31**, 481.
- (a) J.-H. Ye, L. Duan, C. Yan, W. Zhang, W. He *Tetrahedron Letters*, 2012, **53**, 593; (b) J.-H. Ye, J. Liu, Z. Wang, Y. Bai, W. Zhang, W. He *Tetrahedron Letters*, 2014, **55**, 3688; (c) S. Zhang, J. Yan, A. Qin, J. Sun, B. Z. Tang *Science China Chemistry*, 2013, **56**, 1253; (d) S. Chen, J. Liu, Y. Liu, H. Su, Y. Hong, C. K. W. Jim, R. T. K. Kwok, N. Zhao, W. Qin, J. W. Y. Lam, K. S. Wong, B. Z. Tang *Chemical Science*, 2012, **3**, 1804; (e) S. Chen, Y. Hong, Y. Liu, J. Liu, C. W. Leung, M. Li, R. T. Kwok, E. Zhao, J. W. Lam, Y. Yu, B. Z. Tang *J. Am. Chem. Soc.*, 2013, **135**, 4926.
- Y. Dong, J. W. Y. Lam, A. Qin, Z. Li, J. Liu, J. Sun, Y. Dong, B. Z. Tang *Chemical Physics Letters*, 2007, **446**, 124.
- Y. Hong, J. W. Lam, B. Z. Tang *Chem. Commun.*, 2009, 4332.
- (a) B.-P. Jiang, D.-S. Guo, Y.-C. Liu, K.-P. Wang, Y. Liu *ACS Nano*, 2014, **8**, 1609; (b) J. Shi, N. Chang, C. Li, J. Mei, C. Deng, X. Luo, Z. Liu, Z. Bo, Y. Q. Dong, B. Z. Tang *Chem. Commun.*, 2012, **48**, 10675.
- S. Kohmoto, R. Tsuyuki, Y. Hara, A. Kaji, M. Takahashi, K. Kishikawa *Chem. Commun.*, 2011, **47**, 9158.
- (a) S. Song, H. -F. Zheng, D. -M. Li, J. -H. Wang, H. -T. Feng, Z. -H. Zhu, Y. -C. Chen, Y. -S. Zheng *Org. Lett.*, 2014, **16**, 2170; (b) J. -H. Wang, H. -T. Feng, J. Luo, and Y. -S. Zheng *J. Org. Chem.* 2014, **79**, 5746.

---

### A novel triple-mode fluorescent pH probe from monomer emission to aggregation-induced emission

Zhenghua Wang, Jia-Hai Ye,\* Jing Li, Yang Bai, Wenchao Zhang and Weijiang He\*

A tetraphenylene(TPE)-based pH fluorescent probe could selectively monitor pH variation in THF/H<sub>2</sub>O (2:8, v/v) solution in wide-range pH (1.99-11.61). From acidic to basic conditions, It displayed monomer emission, ratiometric fluorescence and aggregation-induced emission successively.

---

