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pH-Responsive dye with dual-state emission in both visible and near infrared regions

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A new dual-state emission (DSE) dye comprised of tetraphenylethene (TPE), triphenylamine (TPA), and indoline groups has been synthesized, which showed efficient fluorescence in both solution and solid. The dye is comprised of three parts and these parts show different fluorescence properties which can be very useful in some applications since the dye can produce information-rich responses. For example, the dye is pH-sensitive in both solution and solid states, and it emits yellow fluorescence in normal pH and red/NIR fluorescence in acidic condition. Cytotoxicity of the dye is low at concentration of 3 μM which was confirmed by a methyl thiazolyl tetrazolium (MTT) experiment, and *in vitro* experiments revealed that the pH responsive performance can be used in bioimaging. It provides a novel pH-sensitive DSE dye ever reported, which has potential application in many fields.

dual-state emission, fluorescence, near infrared, pH-responsive, dye

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1 Introduction

Organic fluorescent dyes have attracted much attention for their applications in a wide range of bio-imaging, chem/biosensors, and optoelectronic materials, etc. [1], and the mechanism of luminescence is complex and mystic. Traditional organic luminophores are mainly composed of planar aromatic rings and emit efficiently in dilute solutions [2,3]. But the emission is weak or quenched in concentrated solution or in the aggregated state, as the aggregation-caused quenching (ACQ) [4]. Tang *et al*. [2] developed aggregation-induced emission (AIE or AIEE) fluorescent dyes which show quenching or weakened emission in solution, but exhibit strong fluorescence upon aggregation [5]. Recently, thousands of AIE dyes were prepared and well-studied [6]. However, AIE/ACQ can only work for the state of aggregation or solution. AIE materials were active in only aggregation state, strongly decided by the intermolecular interaction. When it has strong interaction with other molecules, AIE materials might be disaggregated and exhibit no or weak fluorescence. The quenching of ACQ materials in solid or high concentration also limited the application of the traditional dyes. Thus, incorporating the merits of ACQ and AIE dyes to create efficient dyes in both solution and solid states are attractive [7].

Recently, a new concept called dual-state emission (DSE) appeared, and the dye exhibit highly efficient luminescence in both solution and the solid state [8–13], and some interesting works have been reported by filling the gap between ACQ and AIE [3,5,9,10,14–16], Xu *et al.* [5] reported a deep-blue luminescent compound that emits efficiently both in solution and solid state. An arch-bridge-type fluorophore

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also exhibits dual photoluminescence [10]. However, as the contradiction of ACQ and AIE, dyes featuring DSE is hard to design and synthesis. In addition, DSE with intelligent performance, such as stimulation-responsive emission, have not been reported by now. Stimulation-responsive emission dyes are thus of great importance essentially and arrest much attention [17,18].

Tetraphenylethene (TPE) is the most widely used unit in AIE as it is convenient for the preparation and high fluorescence quantum yield in solid or aggregation state [19]. In solution, the propeller shape of TPE consume the energy of luminophores, result in non-emission (AIE) or very low quantum yield (AIEE) [20,21]. For ACQ dyes, substantial rigidity with limited intramolecular motions is necessary in solution [9]. Indoline group is the basic unit of cyanine dyes, featuring rigidity and large π plane. Triphenylamine (TPA) also enjoys rigidity and large π plane. TPE-TPA has been reported by Tang *et al.* [22], which is AIE. Here, while indoline was conjugated to TPE-TPA, a new dye (TTIN) was synthesized (Scheme 1 and Figure S1, Supporting Information online) and it exhibits dual photoluminescence in both solution and solid. Moreover, the dye was pH sensitive, it emits yellow light in the normal pH range while it shows emission in far red and NIR region in acidic conditions, both in solution and solid states. So, a pH-responsive dye which emitting in both solution and solid states was synthesized and its photoluminescence performance was studied (Figure 1).

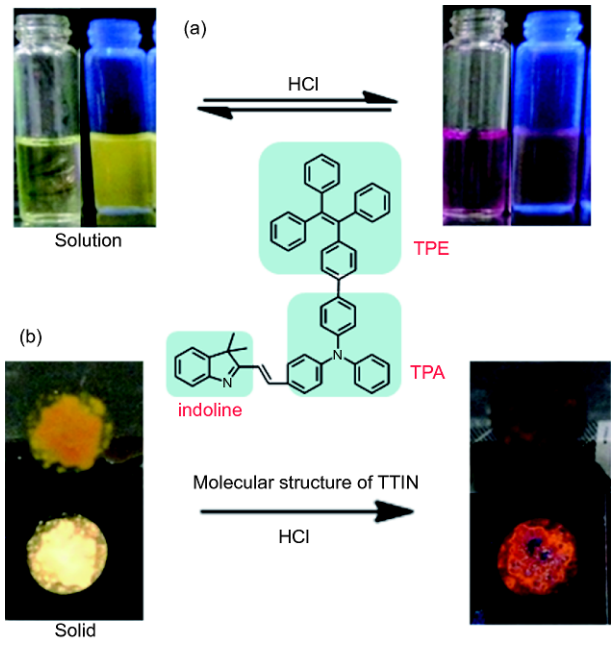


Figure 1 DSE of TTIN dye with pH sensitivity. (a) Solution state which dissolved in tetrahydrofuran (THF):water=2:1. (left: photo image, right: fluorescence image). (b) Solid state (up: photo image, down: fluorescence image) (color online).

2 Experimental

2.1 Materials

THF, *n*-hexaneand other organic solvent were purchased from Sinoreagent Corporation (China). Diphenylmethane, 4-bromobenzophenone, 2,3,3-trimethylindolenine, and 4-(*N*, *N*-Diphenylamino) benzaldehyde were obtained from Aladdin Corporation (China) and used without further purification.

2.2 Characterization

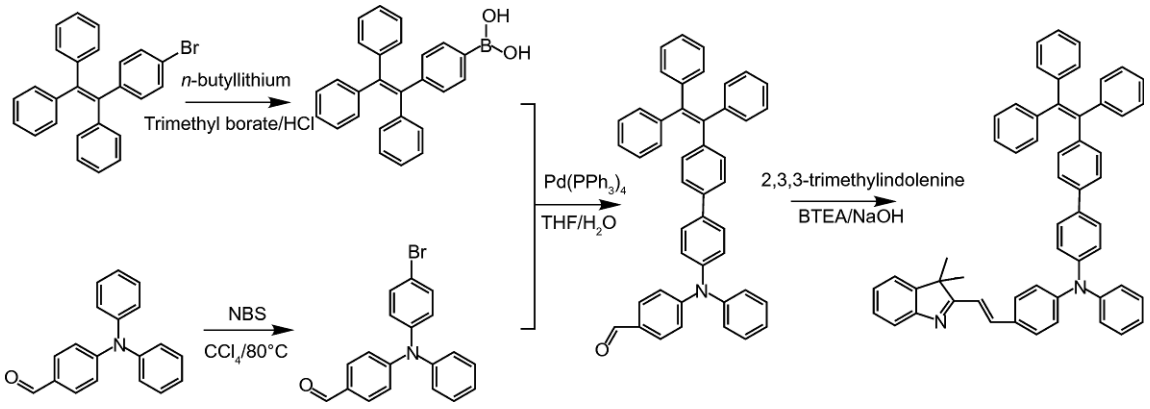
Bruker AC 300 spectrometer was applied to obtain ^{1}H-NMR spectra of compounds (Germany). Size and size distribution of the aggregates were determined by dynamic light scattering (DLS) carried out on a Malvern Zetasizer Nano ZS90 with a He-Ne laser (633 nm). F97pro fluorescence spectrophotometer (Shanghai Lengguang industrial Co. Ltd., China) used to carry out fluorescence measurements. All excitation and emission slit width was 10 nm, but photomultiplier tube (PMT) sensitivity was adjusted as requirement. UV-Vis spectra were obtained on an UV1700pc (Shanghai AuCy Scientific Instrument Co. Ltd., China) Ultraviolet spectrophotometer. TEM: JEOL-2010 (Japan).

2.3 Synthesis of TPE-B(OH)$_2$

As shown in Scheme 1 [23], in a flame dried Schlenk flask, 1.2 g TPE-Br was dissolved in 30 mL anhydrous THF followed by evacuating under vacuum and flush with nitrogen for five times. The solution was cooled down to −78 °C with liquid nitrogen-ethanol bath, and then 2.5 mL *n*-butyllithium hexanes solution (2.5 M) was injected under N_2. The reaction maintained for 5 h, and the color of the system turned to brownish dark and 1.8 mL trimethyl borate was injected under the protection by N_2 gas. The solution was heated to room temperature and stirred for 4 h. HCl (2 M, 10 mL) aqueous solution was added and the mixture was stirred overnight. Finally, the mixture was extracted with 50 mL dichloromethane (DCM) three times and then the organic solvent dried over anhydrous sodium sulfate. After DCM was evaporated, and the crude product was purified on a column chromatography with petroleum ether/ethylacetate (EA)=5:1 eluted. 0.7 g, 63%. ^{1}H-NMR (300 MHz, DMSO-d_6) δppm: 7.96 (s, 1H), 7.57–7.50 (m, 2H), 7.15–7.05(m, 9H), 7.01–6.90 (m, 8H).

2.4 Synthesis of TPA-CHO-Br

In a 50 mL round-bottom flask which equipped with condenser, 4-(*N*,*N*-Diphenylamino)benzaldehyde (0.54 g) and *N*-bromosuccinimide (NBS) (0.35 g) were refluxed in 10 mL CCl_4 for 6 h, and the reaction was then cooled to room temperature and 10 mL water was added. The crude product



Scheme 1 Synthesis of TTIN.

was extracted with 20 mL DCM three times and the dried. 3 mL ethanol was added and the product was purified by recrystallization. 0.5 g. 71%. ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 9.84 (s, 1H), 7.73 (d, J=9 Hz, 2H), 7.47 (d, J=9 Hz, 2H), 7.39–7.34 (m, 2H), 7.21–7.15 (m, 3H), 7.7–7.03(m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δppm: 189, 131.78, 130.35, 128.87, 128.73, 126.42, 125.29, 118.91. MS (ESI^+) m/z: 352.0326 ($M+H^+$), $C_{19}H_{15}ONBr$.

2.5 Synthesis of TPE-TPA-CHO

TPA-CHO-Br (0.4 g) and TPE-$B(OH)_2$ (0.35 g) were dissolved in 20 mL THF. 2 mL Na_2CO_3 aqueous solution (2 M) and $Pd(PPH_3)_4$ (10 mg) were then added. The mixture was evacuated under vacuum and backfilled with N_2 three times. The reaction was refluxed at 80 °C overnight, which bubbled with N_2 gas [23]. After cooling down to room temperature, 10 mL brine was poured to quench the reaction. The product was extracted with 20 mL DCM three times and then was evaporated to remove DCM. TPE-TPA-CHO was purified on a column chromatography with petroleum ether/EA=4:1 eluted. Obtain 320 mg product in yield of 60%. ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 9.83 (s, 1H), 7.72 (d, J=9 Hz, 2H), 7.54 (d, J=9 Hz, 2H), 7.36 (d, J=6 Hz, 2H), 7.21 (d, J=9 Hz, 2H), 7.14–7.01 (m, 24H); ^{13}C-NMR (75 MHz, DMSO-d_6) δppm: 190.62, 152.50, 145.54, 145.90, 142.23, 140.76, 140.07, 137.03, 135.92, 132.78, 130.61, 130.01, 128.86, 127.77, 126.39, 125.64, 125.52, 125.45, 119.00, 118.77, 118.11. MS (ESI^+) m/z: 604.26398 ($M+H^+$), $C_{45}H_{34}ON$.

2.6 Synthesis of TPE-TPA-indolenine (TTIN)

TPE-TPA-CHO (82 mg), 2,3,3-trimethylindolenine (62 mg), and benzyltriethylammonium (BTEA) (14 mg) were added in a tube. 2 mL 50% NaOH aqueous solution was added by ten portions in 20 min. Under vigorous stirring, the reaction mixture was performed at 50 °C overnight [24]. NaOH aqueous solution was removed by suction and the solid was then washed by deionization (DI) water five times followed by 1 mL ethanol twice. The mixture was then purified by preparation thin liquid chromatography (PTLC) and 70 mg TTIN was obtained, yield 71%. ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 7.70 (d, J=9 Hz, 1H), 7.52–7.49 (m, 4H), 7.37–7.33 (m, 6H), 7.20–7.00 (m, 27H), 1.57 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δppm: 183.54, 148.98, 146.91, 146.34, 146.23, 143.75, 143.71, 142.56, 141.08, 140.53, 138.04, 135.76, 131.82, 131.41, 131.25, 129.54, 129.48, 128.72, 127.87, 127.63, 116.47, 125.02, 123.92, 122.54, 121.09, 120.26, 60.39, 52.55, 24.04. MS (ESI^+) m/z: 745.35706 ($M+H^+$), $C_{56}H_{45}N_2$.

2.7 Cell imaging and MTT

HepG2 (liver hepatocellular cells) cells were seeded at a density of 3×10^5 in a plate incubated for 16 h. Afterwards, the original medium was replaced with 3 μM of TTIN in culture medium and incubated for another 4 h. Then the medium was removed and washed twice with various pH values PBS buffer from 4.0 to 7.4. Next, the cell was maintained in phosphate buffer saline (PBS) buffer with various pH for 10 min before took photos [25]. In a 96-well plate, HepG2 cells were seed at a density of 5000 cells per well and incubated for 24 h. Culture medium was replaced with 100 μL of medium containing TTIN at various concentrations or complete DMSO (control). After 24 h of incubation, the cells were washed with PBS, the viability was then evaluated by MTT assay.

3 Results and discussion

At first, DSE behaviors of the as-prepared TTIN dye were studied in THF-hexane mixture as shown in Figure 2(a). TTIN can be well dissolved in THF but not in hexane. In THF, the dye shows emission at 508 nm, yellow, with about 19% quantum yield. When fraction of hexane was increased

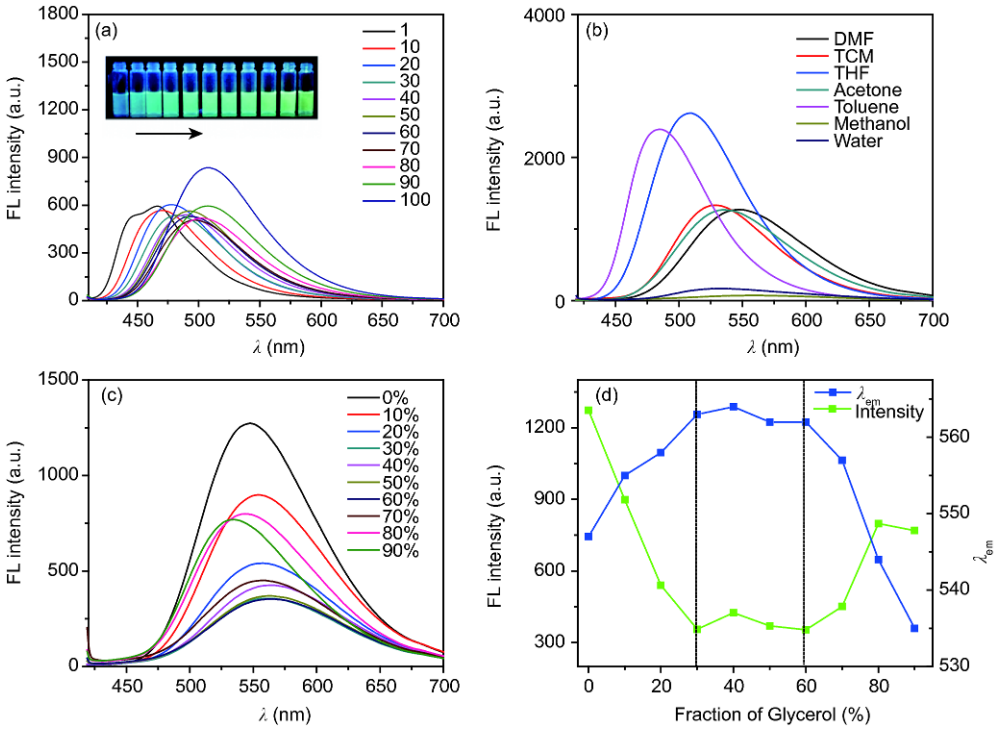


Figure 2 (a) Fluorescence spectra of TTIN in various THF-hexane mixture with changing content of THF, (b) in different solvents, (c) in DMF-glycerol mixture with changing content of glycerol, (d) fluorescence intensity and emission peak in different DMF-glycerol mixture. All the concentration is 25 μM (color online).

up to 10%, the quantum yield swiftly decreased to 13% with emission at 508 nm. No aggregation formed with low concentration of hexane. The change of quantum yield might be due to the solvent effect (Figure S2). When the concentration of THF was progressively decreased to 1%, the quantum yield maintained at around 11%. Different to the stable quantum yield, the emission peak shifted to the blue region gradually. In 99% hexane solvent, two emission peaks were observed at both 467 and 446 nm, respectively. As shown in Figure 1 and Scheme 1, TTIN molecule could be divided into three parts: TPE, TPA and indoline. TPE is an AIE unit, while indoline is ACQ, and the contradictive parts occupied both the ends of TTIN, conjugated by a dual photoluminescence unit TPA [9]. Some reports showed that TPA is adaptive to modify group, or TPE-TPA is AIE [22] while TPA-indoline have strong fluorescence in solution [26]. The two totally different effects of the two TTIN ends were harmonized by the TPA unit, and none of them was in dominant. In solution, substantial rigid TPA-indoline part is photoluminescence, and the intramolecular rotations of TPE do not consume the whole energy. While in aggregation or solid, considering the remote distance between TPE and indoline, the indoline part of TTIN might be quenched, as the propeller shape of TPE might have little influence on stopping the aggregation of indoline. However, the restriction of intramolecular rotations in TPE-TPA unit induces the photoluminescence. The harmony of AIE an ACQ thus might features DSE of TTIN. The fluorescence spectra in different solvents also were tested, as shown in Figure 2(b). In THF and toluene, middle polarity solvent, the fluorescence intensity is strong and the emission peak is less than 510 nm. Upon increasing polarity of solvent (TCM, DMF, methanol), emission peak shifts to long wavelength companied with attenuating of fluorescence intensity, which is consistent with the TICT mechanism [9,17,27,28]. While in water, a poor solvent for the dye, TTIN was in aggregation state. The fluorescence intensity was recovered and the emission peak blue-shifted to 533 nm compared to that in methanol.

To better understand the TICT and AIE behavior of the TTIN dye and exclude the effect of hydrogen bond, the fluorescence spectra of TTIN in different alcohols with changing of the lengths of alkyl groups has also been investigated, as shown in Figure 3. While the molecular length of alcohols was extended, the polarity of solvent decreased, resulting in weak TICT effect. The fluorescence is gradually intensified along with blueshift of the emission peak. Except the TICT, the solubility of TTIN dye in long chain alcohol is poor, and the aggregation might also contribute to the fluorescence enhancement and blueshift. The counteractive effect of TICT and AIE has also been tested in DMF-glycerol mixed solution, as glycerol is more polar than that of DMF, along with high viscosity. At first, the decrease in fluorescence intensity and the redshift of the emission peak was observed by the increasing the content of glycerol, indicating

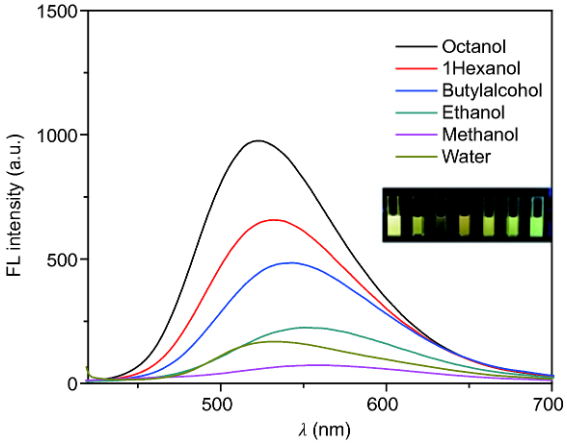


Figure 3 Fluorescence spectra of the TTIN dye in different alcohols with changing molecular lengths (E_x=400 nm). The insert picture is the photograph which exposed to 365 nm UV lamp. The first in the left is THF which was a reference, followed by water, methanol, ethanol, butylalcohol, 1-hexanol, and octanol (color online).

TICT dominates. When the content of glycerol is over 30%, the polarity of the mixture increased which induced TICT. But the viscosity also increased to suppress the intramolecular rotations [20], which is counterproductive to TICT, and the fluorescence intensity and emission peak became stable. When the glycerol fraction is more than 60%, aggregation take control, combined assistance of viscosity to restrict the intramolecular rotations, and the fluorescence intensity was recovered with a blueshift of the emission peak.

Interestingly, the TTIN dye is pH sensitive, and the pH sensitivity is not only in solution but also in solid or nanoaggregative states, which make it outstanding from the pH sensitive dyes for only AIE or ACQ. The indoline group of TTIN could be protonation, which turned into an electron-withdrawing group. The strong electron-withdrawing thus induce TICT, which make it a potential pH probe. TTIN dye can be dissolved in THF and the mixture of THF and water, and the pH sensitivity of the solution state was studied in its THF-H_2O (2:1) mixture, as shown in Figure 4(a–d). Interestingly, only one emission peak 566 nm was found in

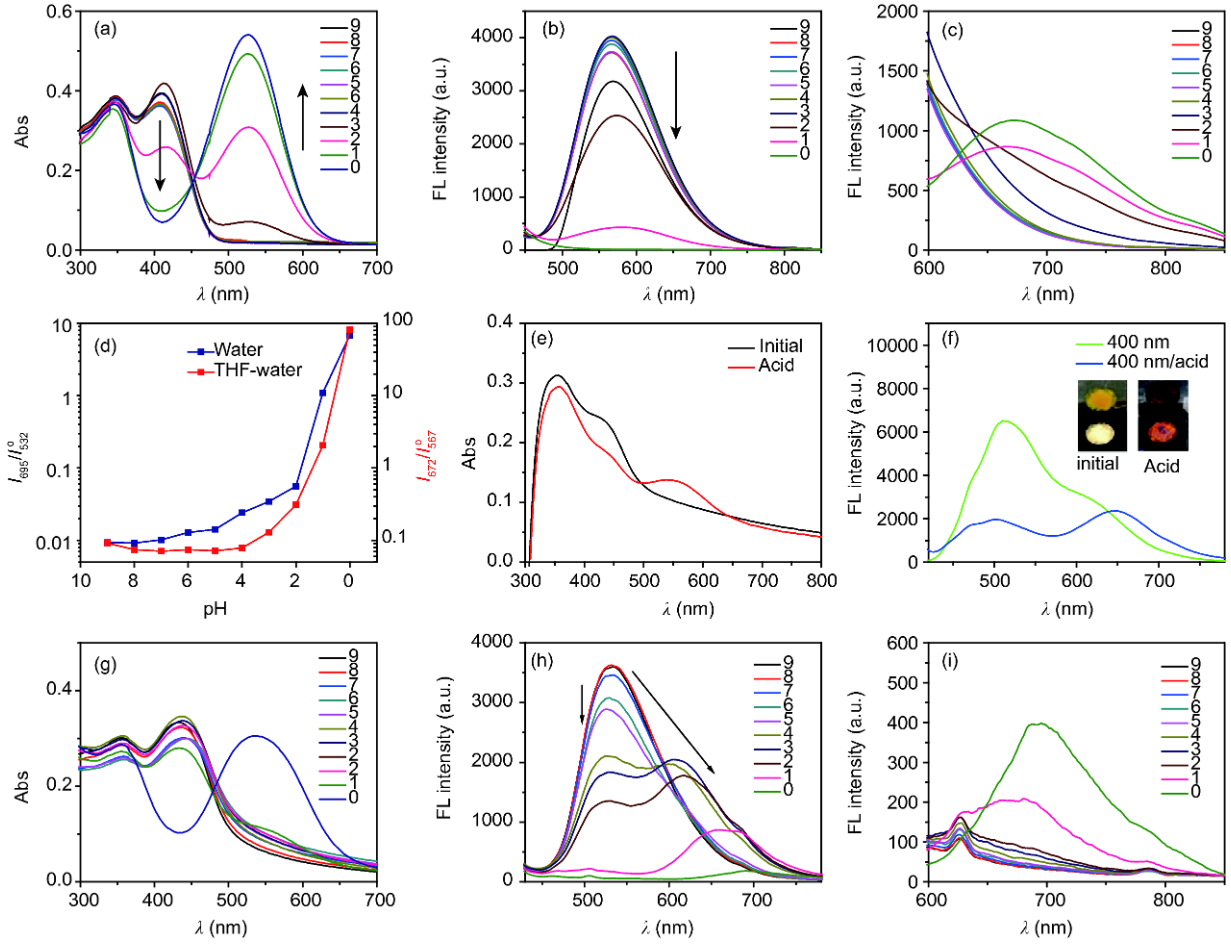


Figure 4 Absorption and fluorescence spectra of TTIN in different solvents (25 μM) or solid state at various pHs. (a–d) in THF/H_2O (2:1): (a) absorption, (b) excited by 400 nm, (c) excited by 520 nm, and (d) ratiometric fluorescence responses to pHs; (e) absorption and (f) fluorescence spectra of solid TTIN, inset shows the photo and fluorescence images of the solid at normal and acidic condition; (g–i) in pure water: (g) absorption, (h) excited by 400 nm, (i) excited by 520 nm (color online).

fluorescence spectra. With gradually increasing acidity, the emission is continually weakened, in consistence with the colour changes of the photo images (Figure S3). At solution state in THF-H_2O solution, the new absorption peak 527 nm emerged at pH 3, and the colour change could be observed by naked eyes at pH 2.

Solid of the TTIN dye also shows pH sensitive behavior, as shown in Figure 4(e, f). The solid was prepared by volatilizing from TTIN ethyl acetate solution, which emits in the yellow region normally. However, when the film was immersed in pH 0 solution for 30 min, colour changes to red and the emission redshifted to red and NIR region, indicating that TTIN is pH sensitive in solid. pH sensitivity of TTIN in nano-aggregative states in water (or 10% FBS solution, Figure S4) was also investigated, as shown in Figure 4(d, g–i). At pH 9, 8 and 7, the fluorescence intensity is stable and emission peak is 532 nm, located in the yellow region. However, when the pH decreased gradually, the intensity of 532 nm becomes weak as the TICT effect. Meanwhile, a new emission peak in the red region emerges from fluorescence spectra when pH below 5.0. The new emission peak exhibits redshift and attenuation of intensity with the enhancement of acidity. When the pH below 1.0, the new emission peak moved to the near infrared (NIR) region. The dual emission peaks of TTIN enable it a ratiometric fluorescent probe as shown in Figure 4(d), and a near 1000 fold enhancement of fluorescence ratio of I_{695}/I_{532} can be found [29,30]. The absorption spectra also showed pH sensitivity (Figure 4(g, i)), which is colorimetric. The color of the TTIN aqueous solution is yellow at high pH solution. When pH decreased to 0, it turned into red. The reversibility has also been tested, as shown in Figure 5(d). After 3 times cycles, TTIN still be reversible to acidic environment. The decrease of basic environment may due to the aggregation state of the TTIN molecules, which make OH^- hard to get inside of nanoaggregations.

Another interesting phenomenon is the morphology of nano-aggregates which was observed by TEM (Figure 5). In DI water, the TTIN aggregate is sphere, but it displays regular triangle morphology when it was protonated by HCl aqueous solution (pH 0). The protonated TTIN is positive charge, and the intermolecular interaction might different from normal TTIN molecules, results in the interesting morphology. In addition, for aggregative state in water, when pH below 1, the new absorption peak emerged at 538 nm, and only at pH 0 red colour could be observed by naked eyes. The difference might due to the steric hindrance in aggregation or solid state. Proton must overcome the hindrance to touch the inner TTIN molecules and make it hard protonation. When in solution state, proton in solution contact easily with TTIN molecules. Furthermore, a newly TICT state might form in the aggregation or the solid state as the crowded molecules were forced by twisting. That induces dual emission peaks of TTIN when excited by 400 nm.

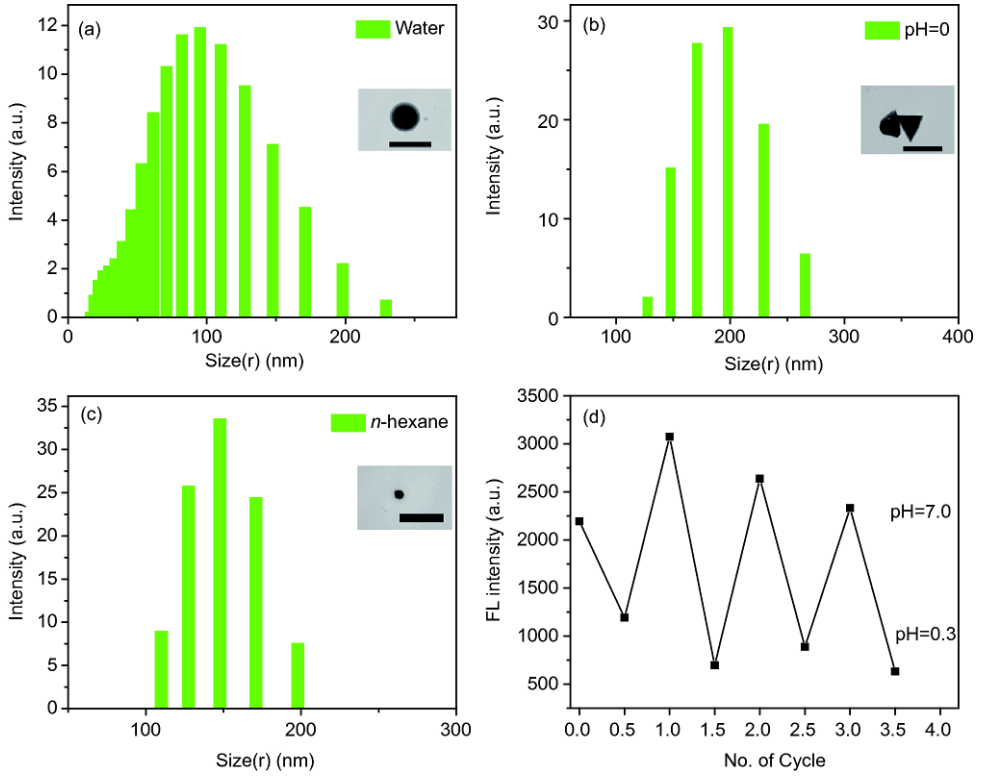


Figure 5 DLS (radius) and TEM of TTIN in different solvent. (a) DI water; (b) pH 0 HCl aqueous solution; (c) *n*-hexane. All three scale bar were 600 nm. (d) Reversible switching of the emission TTIN by repeated adjustment of its aqueous solution to acidic or neutral environments (color online).

While in solution, the molecules did not twist by the interaction, inducing a longer wavelength emission peak in far red and NIR region by the TICT effect.

Comparison test was also carried out and the results were shown in Figure 6 to demonstrate the advantage of TTIN. AIE dye TPE-Br, ACQ dye rhodamine B (RB) and TTIN were papered in solution and aggregate states. As shown in Figure 6, TPE was emitted blue fluorescence in aggregation state but non-emission in solution state. The orange fluorescence of RB is strong in solution state but quenched in aggregation states. That is a non-emission state would exist, no matter ACQ or AIE dyes. The non-emission state limited its application. However, the fluorescence of TTIN could be observed in both states, endows it a wide potential application.

The pH responsive performance can be used in bioimaging. As the pH sensitivity and multi-emission fluorescence of TTIN, particularly in the far red and NIR regions, it is a good probe for bioimaging [31–33]. As shown in Figure 7 HepG2 cells were incubated with TTIN for 4 h in plate and the intracellular pH of the cells was adjusted using PBS buffer from 7.4 to 5.0. When excited by light in blue channel, cells could be observed and the visible fluorescence is dominating, which have little difference for acidic environment. While excited by light in the green channel, far red and NIR fluorescence take as control, and the pH sensitivity becomes obvious. In normal pH 7.4, the fluorescence is weak and cells were hard to be recognized. While in acidic environment pH 5.0, the fluorescence is much stronger than that of normal pH. For visible fluorescence, it is hard to penetrate deep into tissues but can be visible without

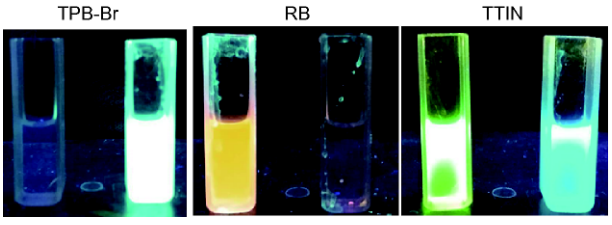


Figure 6 Photo images of TPE-Br, RB, and TTIN. The left side was in solution state and right side was in aggregative state. For the solution, all three dyes were dissolved in THF. For aggregation, TPE-Br was dispersed in water while RB and TTIN were dispersed in hexane (color online).

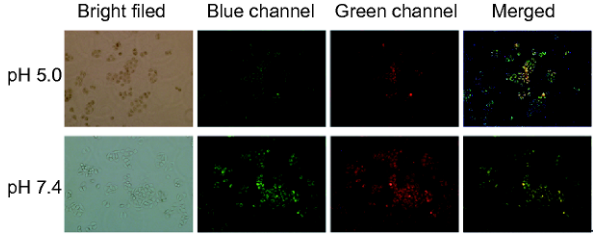


Figure 7 The HepG2 tumor cells fluorescence images after treatment by TTIN (concentration: 3 μM, incubation time: 4 h) (color online).

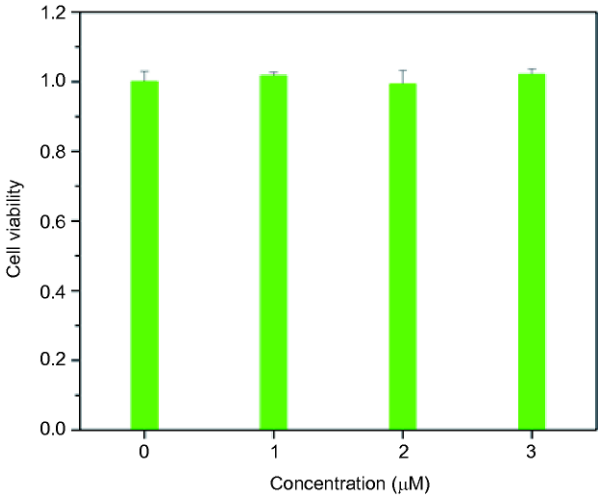


Figure 8 MTT assay of the TTIN molecules over HepG2 cells (color online).

equipment. For NIR emission, it can penetrate deep into tissues and provide useful diagnostic information [34], but not visible for naked eyes. TTIN featuring multi-emission, including in visible and NIR region, is definitely much promising in the application of bio-imaging. The pH sensitivity of TTIN also makes it a potential pH probe *in vitro* and *in vivo* such as lysosome and tumour. The MTT assay also shows the noninvasive of TTIN in the concentration 3 μM (Figure 8).

4 Conclusions

In summary, a DSE dye TTIN has been synthesized, which emits yellow or red/NIR fluorescence in both solution and solid states. The photoluminescence is efficient without intramolecular rotation consuming and it filled the gap of AIE and ACQ. Moreover, the dye is pH sensitive, both in solid and solution states. When the solution or solid is in acidic condition, both of them emit red/NIR fluorescence, makes it a potential material in bioimaging, chem/bio-sensors, and optoelectronic materials.

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Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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