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ARTICLE

Multiple stimuli-responsive and reversible fluorescence switches based on a diethylamino-functionalized tetraphenylethene

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Tetra(4-(diethylamino)phenyl)ethene (TPE-4N), a new derivative of tetraphenylethene (TPE), is facilely prepared by one step from bis(4-(diethylamino)phenyl)methanone in a good yield of 85%. TPE-4N shows aggregation-induced emission (AIE) feature with high solid-state fluorescence quantum yields up to 63.5%. It is of strong proton capture capability, allowing for reversible fluorescence switching in acid and basic solutions. A good linear relationship between the emission intensity and the pH value ranging from 4.4 to 6.0 is established. By exposing in hydrochloride vapor, the color of TPE-4N powder is changed from yellow-green to white, accompanied with fluorescence color tuning from green to sky-blue. The resulting protonated luminogen (*p*-TPE-4N) can be readily reverted to TPE-4N by fuming with hot triethylamine vapor. The protonation and deprotonation progresses are reversible and can be repeated for many times without fatigue in solid state. In addition, *p*-TPE-4N exhibits reversible thermochromism between 80–120 °C, and reverts to TPE-4N by heating up to 120 °C. The multiple stimuli-responsive and reversible fluorescence indicates TPE-4N is a promising candidate for chemical sensing and environmental monitoring.

Introduction

Stimuli-responsive luminescent materials attract more and more attention because of their promising practical applications, such as pH indicators,¹ temperature monitors,² pressure sensors,³ solvent vapor detectors,⁴ viscosity probes,⁵ mechanochromic materials,⁶ photo switches,⁷ and so on. A great many luminescent materials that can alter their fluorescence signals towards various external stimuli have been extensively studied. The underlying mechanisms adopted in the design of these materials can be excimer/excimer formation,⁸ fluorescence resonance energy transfer (FRET),⁹ charge transfer,¹⁰ excited-state intramolecular proton transfer (ESIPT) and so forth.¹¹ In design of stimuli-responsive materials, some additional principles are also crucial to achieve good performance. Firstly, the materials with a simple structure are preferred, for complex structures usually require complicated and multiple synthetic procedures, with a very low comprehensive yield, in order to integrate the stimuli-response groups (signals collectors) and chromophores (reporters) into one molecule. Secondly, compared

to the conventional single reporter for stimulation, the reversible and multiple stimuli responses show merits of providing more valuable information and higher commercial potentiality. Thirdly, the quantitative relationship between the output signals and stimuli-source or intensity is necessary and important in many conditions. Lastly and importantly, for real-world detection applications, the favorable working conditions are in aqueous media or solid state, but most organic chromophores are hydrophobic aromatic compounds, and exist as aggregates in these systems. Their emission generally weakens greatly, owing to the aggregation-caused quenching (ACQ) effect.¹²

An exciting breakthrough appeared in 2001, when some propeller-like molecules, which were almost nonfluorescent in solutions, were found to be strong emitters in the aggregated form.¹³ The phenomenon named as aggregation-induced emission (AIE) is exactly the opposite of the ACQ effect, and the restriction of intramolecular rotations (RIR) is considered to be the main cause.¹⁴ From then on, more and more AIE-active luminogens (AIEgens) are developed and studied in diverse research frontiers, such as organic light-emitting diodes (OLEDs),¹⁵ chemosensors,¹⁶ bioprobes,¹⁷ bioimaging,¹⁸ and so forth. Among the reported AIE fluorophores, tetraphenylethene (TPE) is a prototypical molecule because of its facile synthesis and splendid AIE effect.¹⁹ By using TPE as a key building block, a lot of efficient stimuli-responsive AIEgens are constructed, and exhibit various responses to pH, light, temperature, viscosity, pressure, mechanical force, and so on.²⁰ However, the molecular structures of these AIEgens are usually complicated, and their syntheses could be trivial and troublesome.

N,N-diethylbenzamine (DEA) is a well-known derivative from aniline, and exhibits strong proton capture ability. It is widely used

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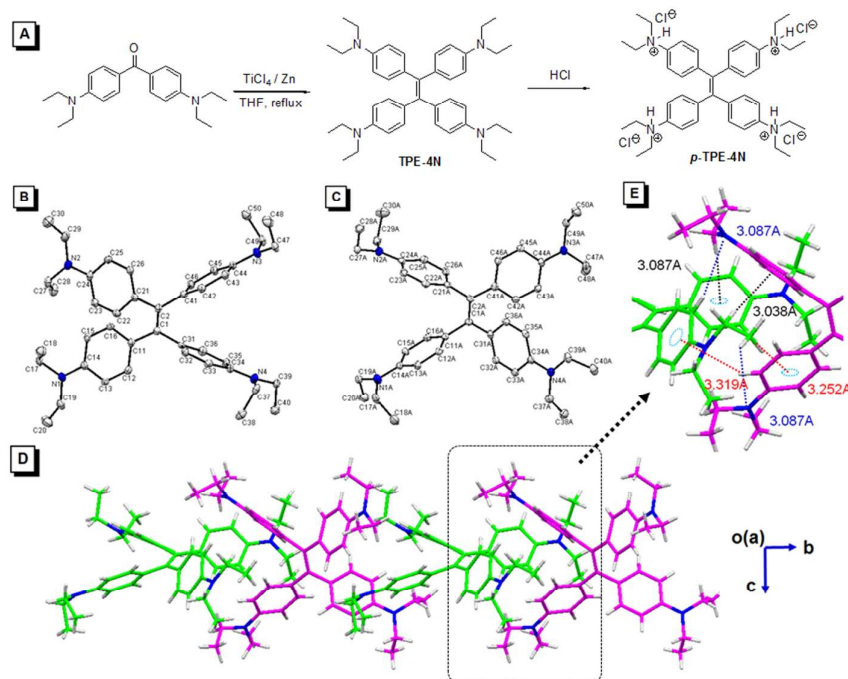
as an important building block for pH sensors.²¹ The protonation and deprotonation processes of DEA moiety usually give rise to obvious changes in fluorescence intensity and wavelength, which can even be recognised by naked eyes.²² In this work, we prepared a novel TPE derivative, tetra(4-(diethylamino)phenyl)ethene (TPE-4N), where four DEA groups were used to replace the phenyl rings in TPE. TPE-4N showed AIE feature and multiple stimuli-responsive ability. Due to the presence of DEA group, TPE-4N had strong proton capture capability, allowing for reversible fluorescent switching in acidic and basic solutions. After fuming with hydrochloride vapor, the yellow-green powder of TPE-4N was turned to white one, accompanied with a fluorescence color change from green to sky-blue. The protonated luminogen (*p*-TPE-4N) could be readily reverted to TPE-4N by fuming with hot triethylamine vapor. The protonated and deprotonated progresses could be repeated by many times without fatigue in solid state. In addition, reversible and irreversible thermochromism was also observed for *p*-TPE-4N at different temperatures. Herein, we would like to present the synthesis, characterization, photophysical property and multiple stimuli-responsive performance of such a simple TPE-based probe.

TPE-4N was prepared from 4,4'-diethylaminobenzophenone by one-pot McMurry reaction in the presence of TiCl₄ and zinc dust (**Scheme 1A**). The product was purified by column chromatography, and the isolated yield reached 85 %. The structure of TPE-4N was spectroscopically characterized by NMR and high resolution mass spectra (HRMS), together with X-ray crystallography, and satisfactory data were obtained (Experimental section and **Fig. S1 and S2**).

Single crystals of TPE-4N were grown from petroleum ether and dichloromethane mixture (1 : 1, v/v). Two similar propeller-like conformations were observed for TPE-4N molecules (**Scheme 1B and 1C**), with close dihedral angles of about 40° between the phenyl ring and central ethene group, and slight difference in the arrangement of peripheral ethyl chains. The two molecules with different conformations were aligned in a cross-staggered manner along one-dimensional (1-D) direction (**Scheme 1E**), which was different from TPE packing mode (**Fig. S3**). In two neighbouring molecules, multiple C-H...π and C-H...N interaction were formed as illustrated in the **Scheme 1E**. These multiple weak interactions provide sufficient driving force to make every TPE-4N molecule accumulate along this direction. Some of the C-H...π and C-H...H-C bond were observed in 2-D and 3-D direction as shown in **Fig. S4**.²³ All of these interactions made every atom fixed at given position, and the intramolecular rotation was restricted greatly, leading to a larger AIE factor as discussed below.²⁴

Results and discussion

Synthesis and characterization



Scheme 1. Synthetic route to TPE-4N and *p*-TPE-4N (A) and its ORTEP drawing of single crystal structure with two conformations (B shown as a pink one and C shown as a green one in D or E); In bottom are the interaction of the two conformation along one-dimensional direction in crystal (D), and the inserted image is the details (E): C-H...π of methylene (black line), C-H...N (blue line) and C-H...π of phenyl group (red line).

Aggregation-induced emission (AIE)

Like most TPE-based materials, TPE-4N was soluble in common organic solvents such as chloroform, tetrahydrofuran (THF),

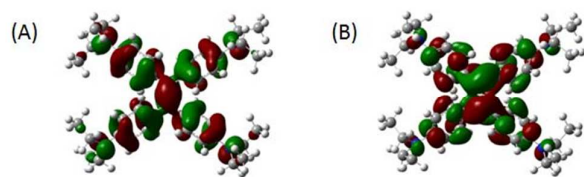


Fig. 1 The HOMO (A) and LUMO (B) orbital distribution of TPE-4N calculated by B3LYP/6-31G(d).

methanol, ethanol, and so on. TPE-4N showed similar absorption spectral profiles in solvents with different polarity (Fig. S5A). Two obvious absorption bands were found in the absorption spectra. The major one was located at about 305 nm, being close to the absorption of bare TPE (309 nm), revealing that this band was associated with the π - π^* transition of TPE core. An absorption shoulder appeared at \sim 400 nm, which was possibly caused by the novel n - π^* transition between the lone-pair electrons on nitrogen atom and the new conjugated system. TPE-4N showed a stable emission peak at 544 nm in different solvents (Fig. S5B), suggesting that TPE-4N lacked obvious D-A interaction, and the emission was from the radiative decay of the localized excited state.²⁵ The result was consistent with the electron-density distribution of the HOMO

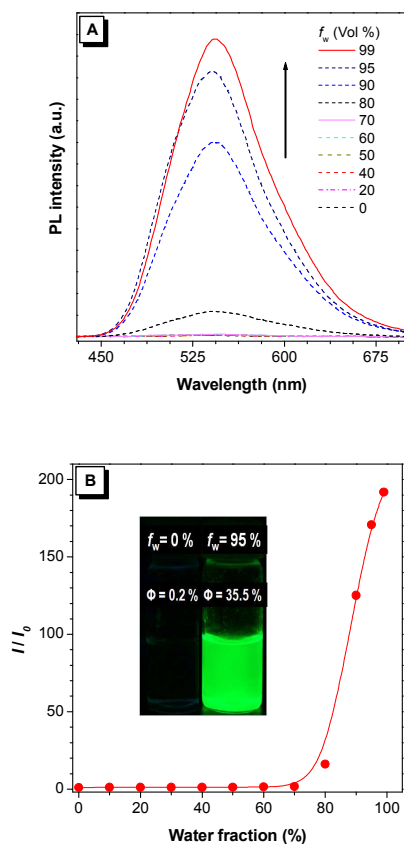


Fig. 2. (A) The PL spectra of TPE-4N in THF-water mixtures with different water fractions (f_w); (B) A plot of I/I_0 versus water fractions

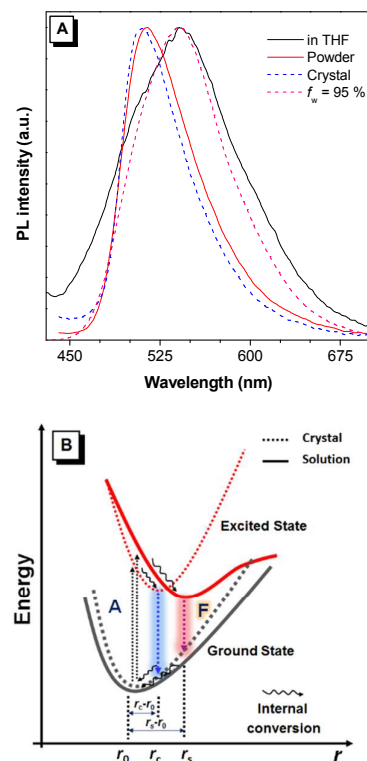


Fig. 3 (A) The fluorescence in THF, powder, crystal and THF-water mixtures ($f_w = 95\%$) of TPE-4N; (B) the diagrammatic presentation of blue-shifted emission in the aggregated state. (r , molecular geometry)

in THF-water mixtures, where I_0 is the PL intensity in pure THF solution (Inserted: fluorescent images of f_w 0% and 95%). and LUMO (Fig. 1), calculated by B3LYP/6-31G(d) set. The fluorescence quantum yields (Φ) of TPE-4N in various solutions were very low (less than 0.3%), because the multi-intramolecular rotations of the phenyl rotors against the ethene stator drastically dissipated the excited state energy in a nonradiative pathway.²⁷

The AIE property of TPE-4N was further investigated. Since THF was a good solvent for TPE-4N, but water was a poor one, the fluorescence of TPE-4N was gradually intensified when water was progressively added into its THF solution. When the volume fraction of water (f_w) reached 80%, the luminogenic molecules were aggregated into nanoparticles, and started to emit bright green light with maximum at 541 nm. PL intensity was increased by up to about 200 times (I/I_0) at $f_w = 99\%$ in comparison with that at $f_w = 0\%$. Quantitative data showed that, from THF solution to nanoparticles, the Φ value was increased from 0.2% to 35.5% ($f_w = 95\%$), equal to a 178-fold enhancement, indicating the excellent AIE property.

In the solid state, TPE-4N became highly emissive. The powders and crystals of TPE-4N showed emission peaks at 513 and 509 nm, respectively, being greatly blue-shifted in comparison with that in solution (Fig. 3A), and the Φ values were enhanced to 63.5% in powder and 68.9% in crystal. Meanwhile, the emission spectra

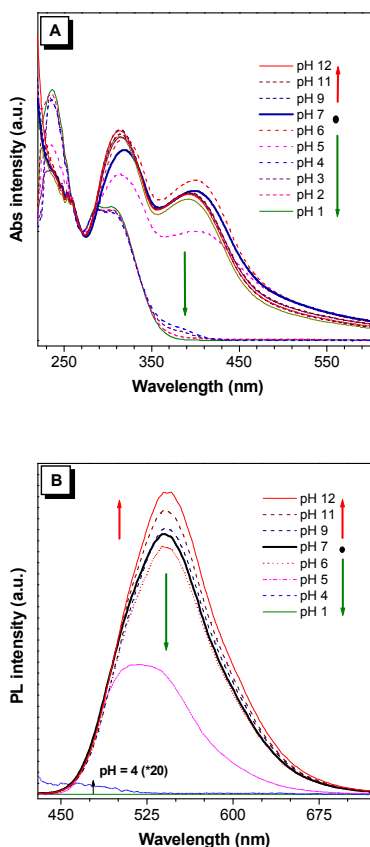


Fig. 4 The absorption (A) and fluorescence (B) of TPE-4N in buffers with different pH values.

became narrow as the aggregate formation. For example, the full width at half-maximum of the emission spectrum in THF was 120 nm, while that was decreased to 90 nm in particles, to 70 nm in powder, and to 60 nm in crystal, further validating the RIR mechanism for the AIE phenomenon.

To this blue-shifted emission of TPE-based materials from the solution to crystal, the Fig. 3B gave a good diagrammatic explanation.²⁶ In solution, the configuration of the molecule in the excited state had large freedom degree to tuning conformation by intramolecular twisting or stretching motion (internal conversion), and the long-wavelength emission was observed in this state. While in crystal, the excited state configuration had little tuning space, and a bluer emission was generated. The amorphous state was somewhere in between.

pH response

Owing to the intrinsic electron-rich nature of DEA group, the TPE-4N was of high electron density, and thus, exhibited a stronger proton capture capability. In different buffers with in a wide pH range (pH = 1.0–12.0), TPE-4N showed apparent changes in absorption and emission spectra (Fig. 4). In neutral buffer solution (pH = 7.0), the TPE-4N exhibited two absorption peaks at about 400 nm and 320 nm, which were similar to those in THF except for a

minor red-shift caused by aggregation effect in aqueous system. At pH > 6.0, there was only a slight change in absorption spectrum of TPE-4N (Fig. 4A). However, when the buffer became more acidic, the absorption peak at 400 nm dramatically decreased (pH = 5.0), and even disappeared (pH < 4.0), while the absorption band around 320 nm moderately decreased and slightly blue-shifted. These results implied that the main conjugation from TPE changed little, but the molecule underwent a protonation process at pH < 6.0, in which the lone-pair electrons on nitrogen atoms were occupied by protons and the n- π^* transition was impaired.

The photoluminescence (PL) spectra of TPE-4N in buffers also changed obviously. As displayed in Fig. 4B, the PL intensity enhanced slowly as the increase of pH from 7.0 to 12.0, but decreased quickly at pH < 6.0. In acidic condition, TPE-4N was protonated to form quaternary ammonium salt and its solubility in water was improved. With the increase of proton concentration, TPE-4N was fully protonated by 4 equivalent protons, generating a highly water-soluble salt (*p*-TPE-4N) as illustrated in Scheme 1A. The aggregates of neutral TPE-4N were thus dissolved in acidic buffer, where the free rotation of phenyl rings was activated, and the emission was quenched. Consequently, as shown in Fig. 5, TPE-4N showed neutral and protonated states in basic and acidic buffers, corresponding to

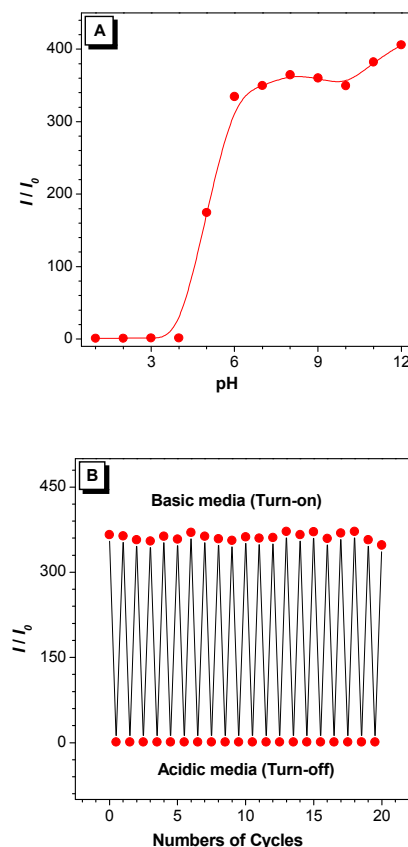


Fig. 5 (A) The plot of I/I_0 versus pH value, where I_0 is the PL intensity in pH = 1.0; (B) The reversible transformation in acidic medium (pH = 4.0, turn-off) and basic medium (pH = 10.0, turn-on), where I_0 is the PL intensity in pH = 4.0.

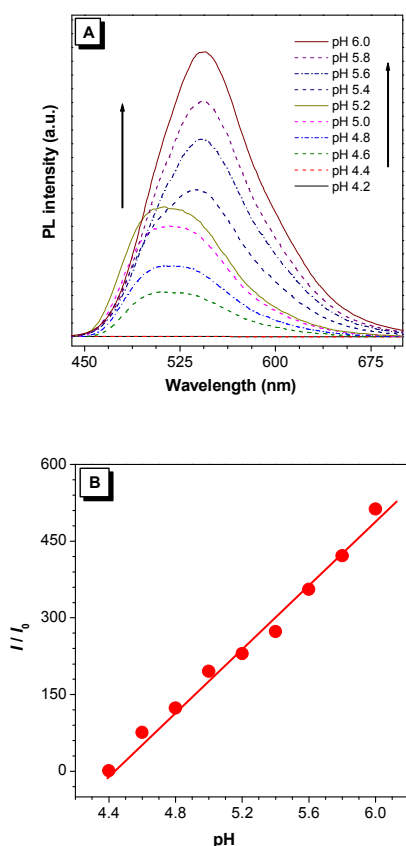


Fig. 6 (A) The PL spectra of TPE-4N in different buffers with pH values ranging from 4.2 to 6.0; (B) The plot of I/I_0 versus pH value, where I_0 is the PL intensity in pH = 4.4.

fluorescence “turn-on” and “turn-off” states, respectively, which could be easily modulated by alternative additions of NaOH and HCl to the buffers. From the acidic (pH = 4.0) to basic (pH = 10.0) conditions, the emission of the buffers was altered apparently from weak blue at 480 nm ($\Phi_{\text{PL}} \approx 0.01\%$) and bright yellow-blue at 544 nm ($\Phi_{\text{PL}} \approx 38.5\%$). The switching was very fast, and could be repeated for many cycles (20 cycles tested) without any changes in the spectral profiles in Fig. 5B. Meantime, an obvious jump in emission intensity was recorded in the pH range of 4.0–6.0, implying that there might be a quantitative relationship between the emission intensity and the pH value. In detailed buffer solutions with a fine change in pH value ($\Delta\text{pH} = 0.2$), the absorption and PL spectra showed the regular changes as displayed in Fig. 5B and Fig. 6A. Slight red-shifts in PL spectra were observed, which were attributed to the partial deprotonation of p-TPE-4N as the increase of pH value. Luckily, a clearer increase in emission intensity was observed from pH = 4.4 to pH = 6.0, with a good linear response ($r^2 = 0.9210$) (Fig. 6B). This range was an important scale for environmental and life science, such as the physiological process of lysosomes (pH = 5),²⁶ acid rain detection (pH = 5.6–4.6)²⁷ and so on, revealing TPE-4N had the great potential as a fluorescent pH probe.

Besides the reversible fluorescence switching associated with pH value in solution, the solid of TPE-4N also shown responses to acidic and basic vapors. The yellow powder of TPE-4N with yellow-green emission (510 nm) became white one with sky-blue emission (458 nm), by exposed in HCl for 5 min (Fig. 7A). The blue emission was very similar to the emission of naked TPE in solid state, which was attributed to that the protonation of TPE-4N by HCl blocked the electron-donating process, resulting in a similar electronic structure to that of naked TPE. The subsequent treatment with hot triethylamine (TEA) vapor returned the emission color of the powder to yellow-green immediately, because of the deprotonation process.

To examine the potential in real-world application, test strip was prepared by depositing TPE-4N on a filter paper. The obtained test strip was yellow under the daylight, and shown yellow-green emission at about 540 nm under illumination of UV light. After exposed to HCl vapor for 5 seconds, it became colorless observed by naked eyes, and the emission was changed to sky-blue (460 nm). The strip was then converted back to original color after fuming with hot TEA vapors for another 5 seconds. The switch between the yellow-green and sky-blue emissions could be repeated for many times without fatigue (Fig. 7B), for the alternate treatments with HCl and hot TEA vapors did not cause destructive effects on the molecules.

Thermochromism

After fuming in HCl vapor for 10 min, the pristine yellow-green powder of TPE-4N was turned to white powder of p-TPE-4N as

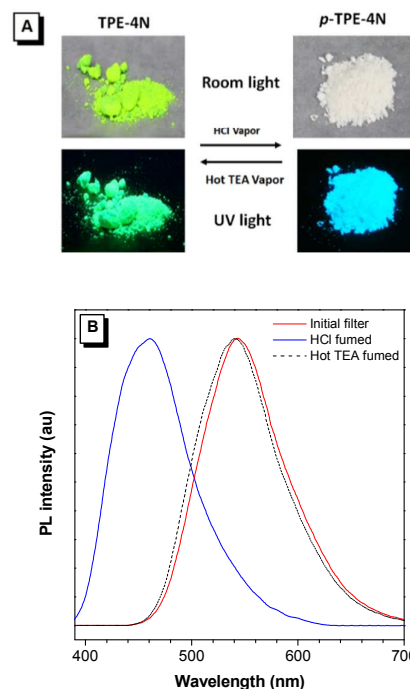


Fig. 7 (A) The photographs of TPE-4N and p-TPE-4N in powder under room and UV light; (B) Reversible switches of the filter emission of TPE-4N by the HCl/hot TEA fuming.

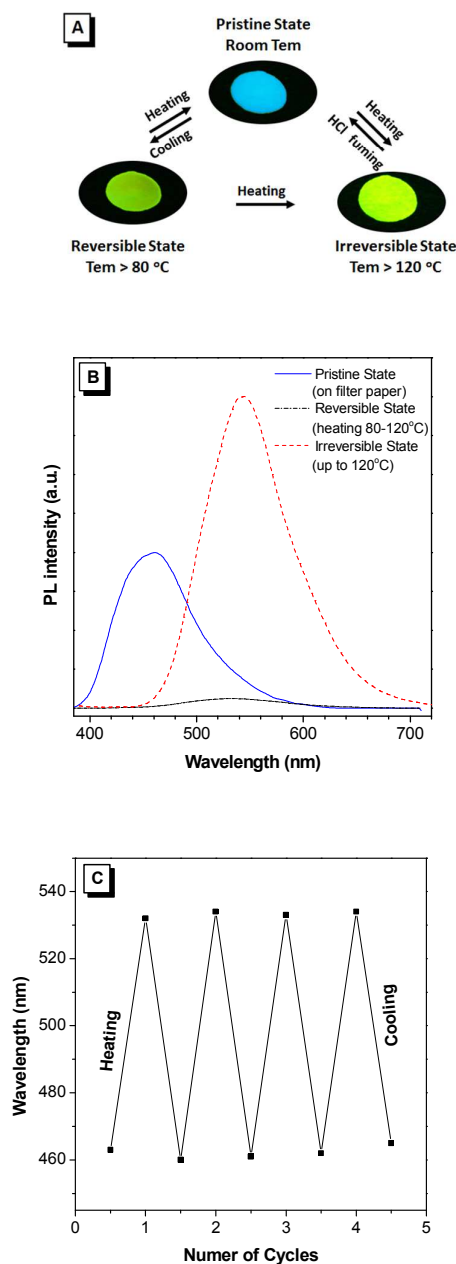


Fig. 8 (A) The thermodynamic reversible and irreversible fluorescence spectra of *p*-TPE-4N in filter; (B) the fluorescence switches in acidic and basic solutions were realized, and a good linear relationship between the emission intensity and the pH value ranging from 4.4 to 6.0 was established as well. Its yellow-green powder could turn to white one, accompanied with a fluorescence color change from green to sky-blue after fuming with HCl vapor, and then, its protonated luminogen (*p*-TPE-4N) could be readily reverted by fuming with hot TEA vapor. The switching could be repeated by many times without fatigue in solid state. In addition, *p*-TPE-4N could be prepared with large quantities by fuming with HCl vapor, which exhibited reversible thermochromism between strong sky-blue emission and weak yellow-green one. Such a simple

in Fig. 7A, which did not dissolve in most organic solvents, but its solubility in water could reach 40 mg mL⁻¹, presenting a typical salt behaviour. The ¹H NMR spectrum in D₂O (Fig. S7) showed that there was only one signal assigned to the protons on the phenyl rings, further validating that all the amino groups in TPE-4N had been protonated. The *p*-TPE-4N powder exhibited blue emission at 458 nm with a good Φ of 25.5%, but its solution in water gave weak sky-

blue emission located at 480 nm with a low Φ value of 1.0%. The filter paper deposited with *p*-TPE-4N from its aqueous solution had a fluorescence peak at 465 nm and a Φ value of 12.5%. The fluorescence efficiency increased from solution, to amorphous film (on filter paper), and to powder, implying that the *p*-TPE-4N was a novel salt with AIE character.

To test the thermochromic property, the filter paper of *p*-TPE-4N was heated using a hot-blower. When the temperature was lower than 80 °C, the color and fluorescence of the filter paper had no obvious change (colorless by naked eye and sky-blue emission under UV-lamp, about 465 nm). When the temperature was higher than 80 °C, the filter paper became yellow slowly, and the emission changed to very weak yellow-green (about 532 nm). When the temperature got higher than 120 °C, the filter paper also became yellow, but with bright yellow-green emission, which was easily recognized as the emission of TPE-4N in amorphous state (about 544 nm), suggesting that TPE-4N was recovered. Hence, this obvious emission change was considered to be caused by the thermal transition from *p*-TPE-4N to TPE-4N (and HCl) at high temperatures.

Interestingly, the weak yellow-green emission from the filter paper by heating at 80–120 °C could return to sky-blue one after slow cooling in ambient condition. And then, we alternately conducted the heating (below 120 °C) and cooling treatments for many times, and found that the emission switching between sky-blue and weak yellow-green could be repeated without apparent changes in emission color and intensity as shown in Fig. 8B and 8C. To this reversible fluorescence switch, a reasonable working mechanism was described as follows. When heating up to 80 °C, the whole molecular energy increased, and the molecules had enough freedom degree to tune the excited-state conformation (Fig. 3B). In this process, the excited-state energy was consumed, leading to redder and weaker emission, similar to that in solution state. After cooling in nature, the motional freedom degree was decreased, and the excited state of the molecule mainly relaxed in a radiative manner. Therefore, the bluer and stronger emission recovered, like in crystal state.

Conclusions

In this work, we prepared a simple TPE-based fluorophore (TPE-4N) with AIE feature and multiple stimuli-responsive ability. Due to the presence of electron rich group, TPE-4N had strong proton capture capability, giving fluorescence responses to pH change via protonation and deprotonation processes. Reversible fluorescence switches in acidic and basic solutions were realized, and a good linear relationship between the emission intensity and the pH value ranging from 4.4 to 6.0 was established as well. Its yellow-green powder could turn to white one, accompanied with a fluorescence color change from green to sky-blue after fuming with HCl vapor, and then, its protonated luminogen (*p*-TPE-4N) could be readily reverted by fuming with hot TEA vapor. The switching could be repeated by many times without fatigue in solid state. In addition, *p*-TPE-4N could be prepared with large quantities by fuming with HCl vapor, which exhibited reversible thermochromism between strong sky-blue emission and weak yellow-green one. Such a simple

fluorescent probe with a multiple stimuli-responsive ability (pH-response, vapor-chromism and thermochromism) could find an array of high-tech applications.

Experimental section

Materials and instrumentation

All reagents were purchased from commercial suppliers and used as received without further purification. The absorption spectra were recorded using a UV-2600 spectrophotometer (Shimadzu) with quartz cuvettes of 1 cm pathlength. Fluorescence spectra were obtained using an LS-55 Fluorescence spectrophotometer (PerkinElmer) at room temperature. X-ray diffraction (XRD) intensity data were collected on a Bruker-Nonices Apex CCD diffractometer with graphite monochromated MoK α radiation. Processing of the intensity data was conducted using the SAINT and SADABS routines, and the structure and refinement was carried out using the SHELTL suits of X-ray programs (version 6.10). The ORTEP drawing of TPE-4N is given in Scheme 1 and its crystal data are summarised in Table S1. High-resolution mass spectra (HRMS) were obtained on a GCT Premier CAB 048 mass spectrometer operated in MALDI-TOF mode.

Measurement of fluorescence quantum yield (Φ)

Φ was measured by the optical dilute method with a standard of quinine sulfate ($\Phi_r = 0.55$, quinine in 0.05 mol L⁻¹ sulfuric acid) calculated by: $\Phi_s = \Phi_r(A_r/A_s)(n_s/n_r)^2(D_s/D_r)$, where the subscripts **s** and **r** refer to the sample and reference standard solution respectively; **n** is the refractive index of the solvents; **D** is the integrated intensity. The value of **A** is absorption intensity at 365 nm. The refractive indices of the solvents at room temperature are taken from a standard source. Errors for Φ values ($\pm 10\%$) are estimated. The solid-state (powder, crystal and deposited point on filter) emission efficiency was measured by absolute photoluminescence quantum yield measurement system (C11347-11 Quantaurus-QY, HAMAMARSU).

Measurement of AIE and pH sensing

For AIE property measurement, 0.05 mL stock solution was added to a 10.0 mL flask with different amount of water and THF. After well mixed, the solution was allowed to stand at room temperature for 2 min. The pH responses were measured in the mixed solvents of THF-aqueous ($v : v = 5 : 95$). B-R buffer solution (a mixture of 0.04 mol L⁻¹ H₃BO₃, H₃PO₄ and CH₃COOH in water) following the operation above. The buffer solutions at pH = 1 and 2 were prepared by HCl and KCl mixture. All of these solutions were detected by Sartorius PB-10 pH meter, and standardized by standard buffer solutions (4.01, 6.86 and 9.18). All of the measured concentration of TPE-4N is 1.0×10^{-5} mol L⁻¹.

Synthesis

Tetra(4-(diethylamino)phenyl)ethene (TPE-4N): Into a 250 mL two necked round-bottom flask with a reflux condenser were placed 3.9

g (60 mmol) of zinc dust and 6.48 g (20 mmol) of bis(4-(diethylamino)phenyl)methanone. The flask was evacuated under vacuum and flushed with dry nitrogen by three times. 150 mL of THF was then added. The mixture was cooled to $-78\text{ }^\circ\text{C}$ and 2.2 mL (20 mmol) of TiCl₄ was added dropwise. The mixture was slowly warmed to room temperature, stirred for 0.5 h, and then refluxed overnight. The reaction was quenched with 10% aqueous K₂CO₃ solution, and was poured in water. The mixture was extracted with CH₂Cl₂ by three times. The combined organic layers were washed with brine twice. After solvent evaporation, the crude product was purified on a silica-gel column using petroleum ether as eluent. A green-yellow solid was obtained in 85% yield. ¹H NMR (400 MHz, CDCl₃), δ (CDCl₃, ppm): 6.89 (s, 8H), 6.41 (s, 8H), 3.78-2.92 (m, 16H), 1.05-0.95 (m, 24H). ¹³C NMR (125 MHz, CDCl₃), δ (CDCl₃, ppm): 145.36, 133.23, 131.45, 110.20, 109.68, 44.25, 12.75. HRMS (C₄₂H₅₆N₄): m/z 616.4509 (M⁺, calcd 615.4505).

Tetra(4-(diethylamino)phenyl)ethene hydrochloride (p-TPE-4N): 2g TPE-4N was placed in a 20 mL weighing bottle without a cap and sealed in a 200 mL weighing bottle with 30 mL concentrated hydrochloric acid (37%) for 10 min. The green-yellow powder of TPE-4N was tuned to white powder in 100% yield. ¹H NMR (400 MHz, D₂O), δ (TMS, ppm): 7.31-7.25 (m, 16H), 3.65-3.35 (m, 16H), 1.07-0.97 (m, 24H). ¹³C NMR (125 MHz, D₂O), δ (TMS, ppm): 143.56, 141.43, 135.67, 133.52, 122.89, 53.56, 9.78.

Crystal data for TPE-4N (CCDC 1061949): C₄₂H₅₆N₄; $M_w = 616.91$; triclinic; $P1$; $a = 10.9822(9)$, $b = 17.3332(9)$, $c = 19.1196(8)$ Å; $\alpha = 88.643(4)$, $\beta = 86.828(5)$, $\gamma = 81.890(5)^\circ$; $V = 3597.2(4)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.139$ g cm⁻³; $\mu = 0.501$ mm⁻¹ ($\lambda(\text{MoK}\alpha) = 1.5418$); $F(000) = 1344$; $T = 99.9(4)$ K; $2\theta_{\text{max}} = 66.5$ (98.66) $^\circ$; 20202 measured reflections; 12722 independent reflections ($R_{\text{int}} = 0.0539$); GOF on $F^2 = 1.002$; $R_1 = 0.0475$; $wR_2 = 0.0829$ (all data); Δe 0.233 and -0.204 e Å⁻³.

Acknowledgements

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Graphical Abstract

Multiple stimuli-responsive and reversible fluorescence switches based on a diethylamino-functionalized tetraphenylethene

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A simple fluorescent probe exhibits an AIE character and multiple stimuli-responsive ability (pH-response, vapor-chromism and thermochromism).