

Supporting Information

Tunable AIEE fluorescence constructed from a triphenylamine luminogen containing quinoline—application in a reversible and tunable pH sensor

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Experimental section

Materials and instruments

Triphenylamine, 5-Aminoquinoline, POCl_3 , DMF, NaOH, CH_2Cl_2 , THF, MgSO_4 , CH_3COOH , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , CDCl_3 and DMSO were purchased from J&K (CHINA). Melting points were determined on a Kofler melting point apparatus and uncorrected. IR spectra were obtained in KBr discs using a Nicolet 170SX FT-IR spectrometer. Elemental analyses were performed on a Yannaco CHNSO Corder MT-3 analyzer. ^1H NMR and ^{13}C NMR spectra were recorded using an INOVA 400 at 400 and 100 MHz, respectively, with TMS as the internal standard, DMSO-D 6 as the deuterated solvent and chemical shifts reported in ppm. Mass spectra were recorded using a Finnigan MAT95 mass spectrometer. The absorption and fluorescence spectra were obtained on a CARY50 UV-VIS spectrophotometer and an FLS920 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_f) in pure THF and THF/water mixtures were determined with anthracene as the fluorescence reference in ethanol ($\Phi_f = 0.27$). The Quantum Yield (QY) of the as synthesized derivatives was calculated based on the following equation, $\Phi_u = \Phi_s \frac{I_u \text{ As}}{I_s \text{ Au}}^{[56]}$, Φ

was the fluorescence quantum yield, I was the intensity of the fluorescent spectra, A was the optical density at excitation wavelength, and S referred to the standard anthracene with known quantum yield. And the absolute solid fluorescence quantum yields were obtained on a Edinburgh Instruments FS920 integral sphere system. For nanosecond lifetime measurements, the fluorescence decay curve was obtained by using an SPC apparatus (Edinburgh Analytical Instruments, FL-900CDT). Fluorescence microscopy imaging of the nano-aggregations was performed by a Leica DM2500M. SEM images of the aggregations were obtained by Hitachi S4800. All the experiments were carried out at room temperature. The ground and excited states of molecules were optimized with the Becke-3-Lee-Yang-Parr (B3LYP)^[57-59] by density functional theory (DFT) calculations and time-dependent density functional theory (TD-DFT) at the level of 6-31G (d) with Gaussian 09 program^[60]. The vibrational frequencies calculations were also performed to ensure the stability of the calculation result and avoid virtual frequency.

Synthesis and structural characterization

The synthetic route was shown in Scheme 1.

4-(Diphenylamino)benzaldehyde (2). 29.5 mL POCl_3 was added dropwise to 30 mL DMF at 0 °C. After stirring for 40 minutes, 2.5 g of triphenylamine was added. Then, the reaction mixture was heated to 45 °C

and stirred for 14 h. When the reaction was finished, the mixture was cooled to room temperature and poured into ice water. A concentrated solution of sodium hydroxide was slowly added to adjust the pH=7. The product was extracted with dichloromethane. The combined organic layer was dried with magnesium sulfate anhydrous and filtered. With a concentrated organic layer, the white purified compound was obtained by using a column chromatograph of silica gel with ethyl acetate–petroleum ether mixture (1:10 v/v) as the eluent. Yield: 2.5 g (90%). ¹H-NMR (DMSO, 400 MHz) δ (ppm): 9.76 (s, 1H), 7.71 (d, 2H), 7.41 (t, 4H), 7.21 (m, 6H), 6.88 (d, 2H).

Bis(4-benzoyl) aniline (3), tris(4-benzoyl-yl) amine (4). Compound 3 and 4 were prepared according to the general procedure for Compound 2 using 15.5 mL dry DMF, 19 mL POCl₃, 2.0 g triphenylamine or 5.8 mL dry DMF, 7.6 mL POCl₃, and 0.98 g bis(4-benzoyl-yl) aniline. **3:** yield: 2.2 g (90%). ¹H-NMR (DMSO, 400 MHz) δ (ppm) : 9.87 (s, 2H), 7.84 (d, 4H), 7.47 (t, 2H), 7.31 (s, 1H), 7.21 (d, 2H), 7.16 (d, 4H). **4:** yield: 0.86 g (90%). ¹H-NMR (DMSO, 400 MHz) δ (ppm): 9.94 (s, 3H), 7.91 (s, 6H), 7.28 (s, 6H).

Compound 5 (STPAQ). 1 mmol 4-diphenylamino benzaldehyde and 3 mmol 5-Aminoquinoline were added to a flask, and then 6 mL ethanol and 1 to 2 drops of acetic acid were added. The reaction mixture was stirred for 48 h at room temperature. The precipitate was filtered and washed with ethanol, and finally dried under reduced pressure. Yield: 0.30 g (75%). M.p.: 194 °C. Anal. calc. formula: C₂₈H₂₁N₃(%): C: 84.18; H: 5.30; N: 10.52; found: C₂₈H₂₁N₃(%): C: 83.80; H: 5.32; N: 10.46. IR: 1617cm⁻¹ (v_{C=N}) ¹H-NMR (DMSO, 400 MHz) δ (ppm): 8.93 (s, 1H), 8.68 (d, J=8.4, 1H), 8.62 (s, 1H), 7.94 (d, J=8.4, 2H), 7.86 (d, J=8.4, 1H), 7.75 (t, J=7.6, 1H), 7.53 (m, 1H), 7.40 (t, J=7.6, 4H), 7.31(d, J=7.6, 1H), 7.16 (m, 6H), 7.00 (d, J=8.4, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ : 160.2, 151.1, 150.6, 149.5, 148.5, 146.8, 132.8, 130.2, 129.6, 129.5, 129.2, 126.5, 125.6, 124.4, 124.2, 121.2, 120.6, 113.0. HRMS calc. for (M+H⁺)⁺: 399.1735, found: 400.1823.

Compound 6 (DTPAQ) and compound 7 (TTPAQ). DTPAQ and TTPAQ were prepared according to the general procedure for STPAQ by changing the ratio of bis(4-benzoyl)aniline or tris(4-benzoyl-yl) amine and 5-Aminoquinoline. **DTPAQ:** yield: 0.38 g (70%). M.p.: 116 °C. Anal. calc. formula: C₃₈H₂₇N₅ (%): C: 82.44; H: 4.92; N: 12.65; found: C₃₈H₂₇N₅ (%): C: 82.10; H: 5.11; N: 12.74. IR: 1616cm⁻¹ (v_{C=N}) ¹H-NMR (DMSO, 400 MHz) δ (ppm): 8.95 (s, 2H), 8.70 (d, J=6.0, 4H), 8.04 (d, J=8.4, 4H), 7.90 (d, J=8.4, 2H), 7.77 (t, J=7.6, 2H), 7.56 (m, 2H), 7.46 (t, J=7.6, 2H), 7.35 (d, J=7.6, 2H), 7.22 (m, 7H), ¹³C NMR (CDCl₃, 100 MHz) δ : 160.0, 150.6, 150.2, 149.3, 148.4, 146.2, 132.8, 130.8, 130.3, 129.8, 129.6, 126.6, 126.3, 125.2, 124.4, 123.3, 120.7, 113.0. HRMS calc. for (M+H⁺)⁺: 553.2266, found: 554.2416.

TTPAQ: yield: 0.42 g (60%). M.p.: 154 °C. Anal. calc. formula: C₄₈H₃₃N₇(%): C: 81.45; H: 4.70; N: 13.85; found: C₄₈H₃₃N₇ (%): C: 81.04; H: 4.84; N: 14.08. IR: 1616cm⁻¹ (ν_{C=N}) ¹H-NMR (DMSO, 400 MHz) δ (ppm): 8.95 (s, 3H), 8.75 (t, J=12.0, 6H), 8.09 (d, J=8.0, 6H), 7.90 (d, J=8.4, 3H), 7.79 (t, J=7.6, 3H), 7.57 (m, 3H), 7.35 (m, 9H), ¹³C NMR (CDCl₃,100 MHz) δ: 159.8, 150.7, 149.5, 149.1, 148.4, 132.7, 131.9, 130.5, 129.6, 126.9, 124.5, 124.4, 120.7, 113.1. HRMS calc. for (M+H⁺)⁺ : 707.2797, found: 708.2999.

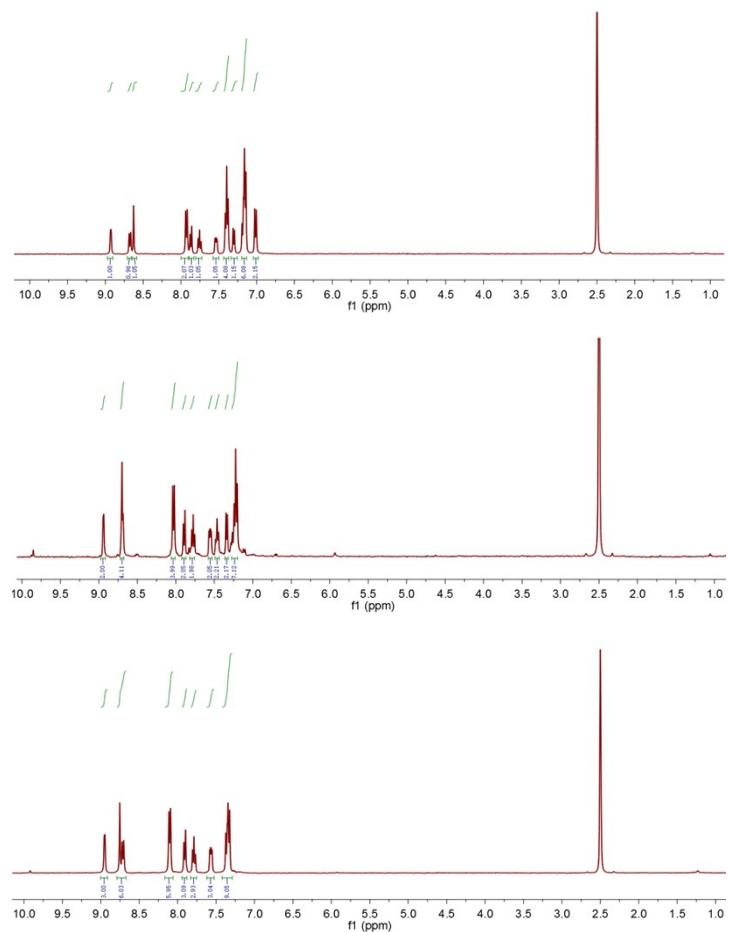


Fig. S1 ¹H NMR spectra of STPAQ, DTPAQ and TTPAQ (from up to down)

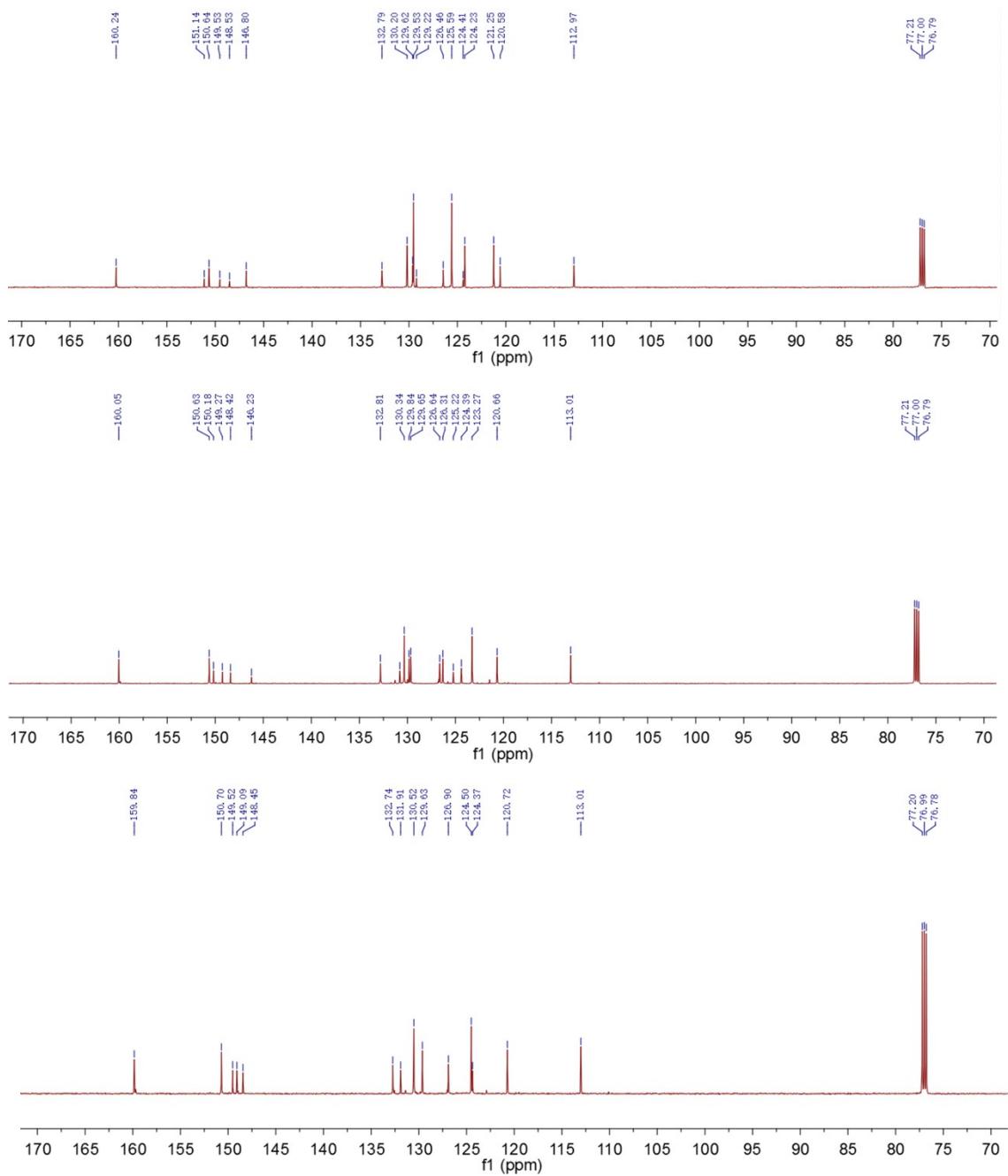




Fig. S3 MS spectra of STPAQ, DTPAQ and TTPAQ (from left to right)

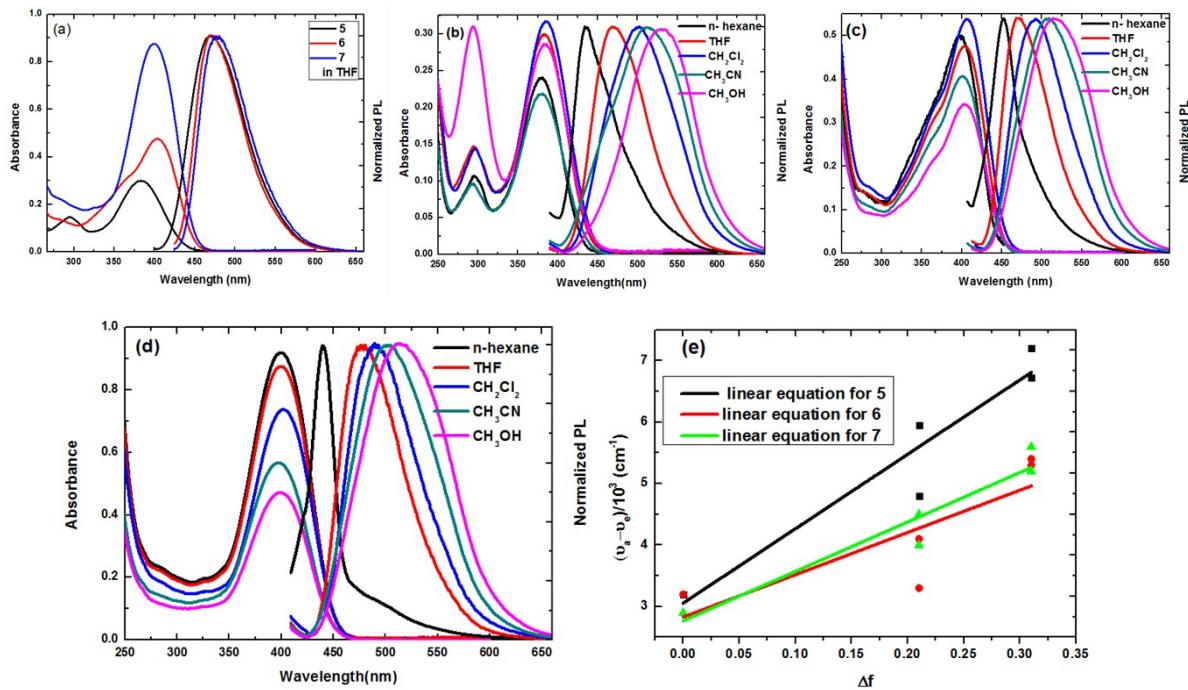


Fig. S4 The absorption and PL spectra of STPAQ, DTPAQ and TTPAQ in THF (a), the absorption and PL spectra of STPAQ (b), DTPAQ (c) and TTPAQ (d) in various solvents(1×10^{-5} mol·L⁻¹), (e) Lippert-Mataga plot of three TPAQs (ν_a = absorption wavenumber, ν_e = emission wavenumber and Δf = orientation polarizability = $(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ε = dielectric constant and n = refractive index)

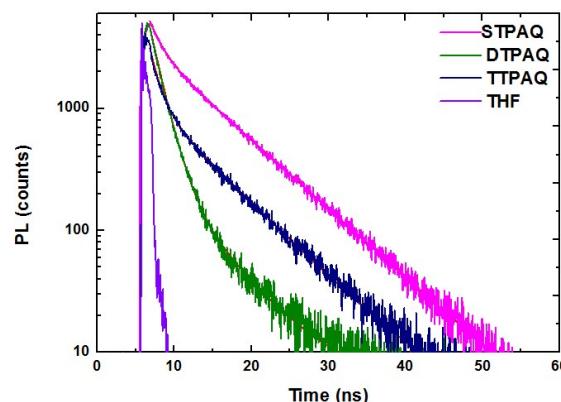


Fig. S5 The fluorescence lifetime of TPAQs

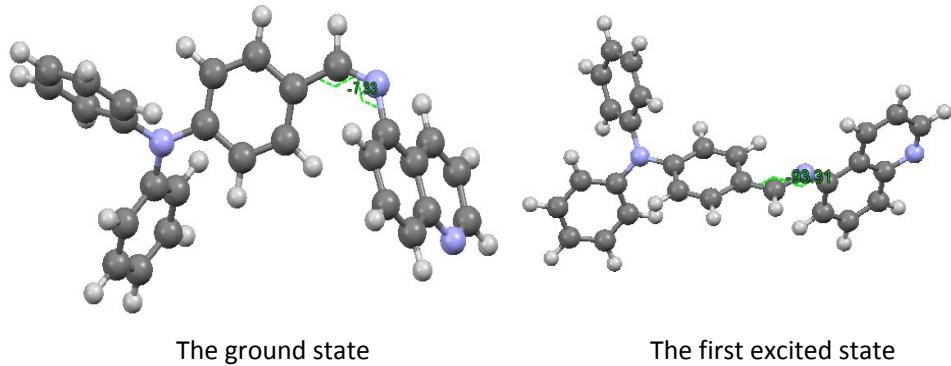


Fig. S6 The configurations of STPAQ in the ground state and the first excited state, obtained by DFT and TD-DFT methods at the level of B3LYP/6-31G(d)

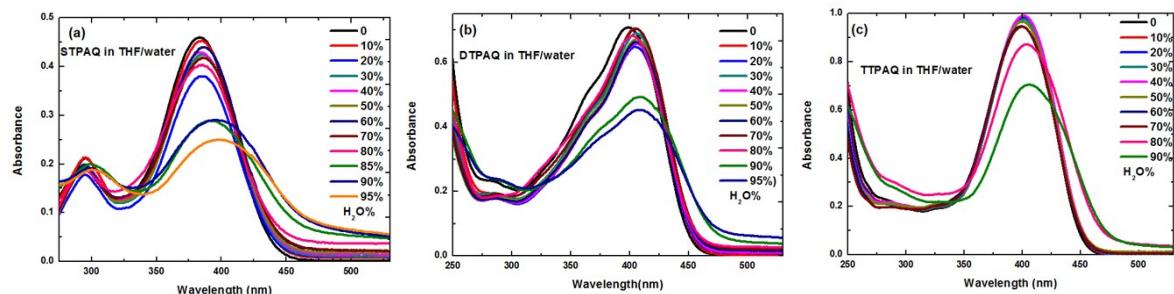


Fig. S7 The UV absorption spectra of STPAQ (a), DTPAQ (b) and TTPAQ (c) in various THF/water solutions (1×10^{-5} mol·L⁻¹)

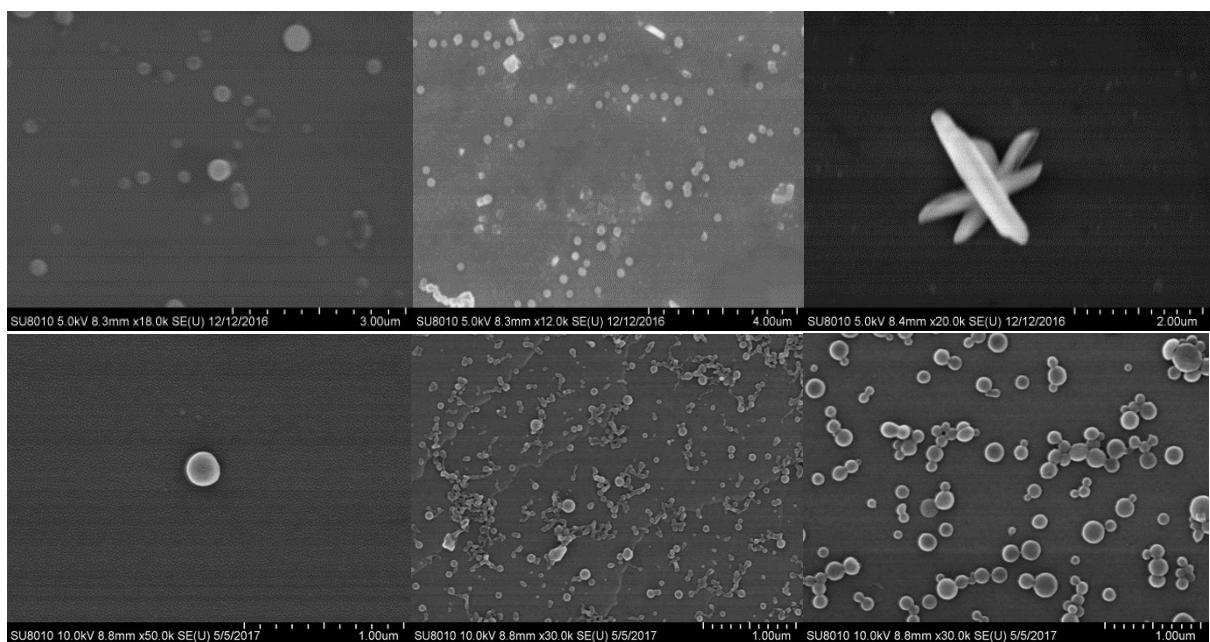
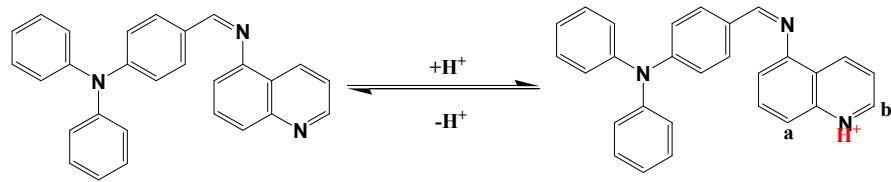


Fig. S8 SEM images in THF/water mixtures of STPAQ (1/9, v/v), DTPAQ (1/9, v/v), TTPAQ (2/8, v/v), STPAQH⁺ (1/9, v/v), DTPAQH₂²⁺ (1/9, v/v) and TTPAQH₃³⁺ (1/9, v/v) at concentrations of 1×10^{-5} mol·L⁻¹ (from left to right, from up to down)



Scheme S1 Reversible transformation between STPAQ and STPAQH⁺ by repeated protonation and deprotonation

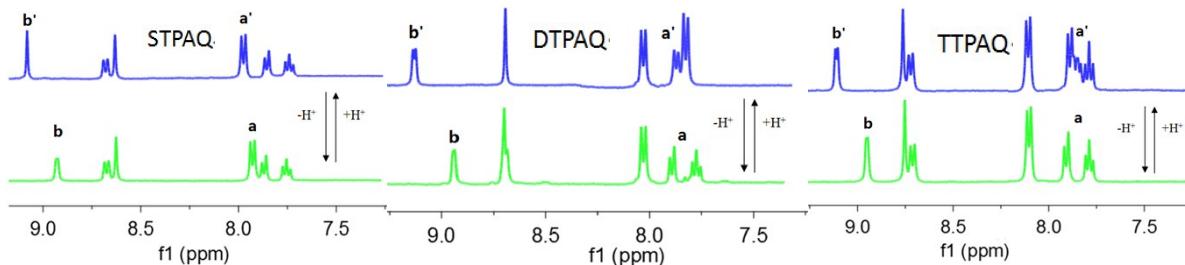


Fig. S9 Chemical shifts changes in reversible transformation between TPAQs and TPAQsH⁺ by repeated protonation and deprotonation

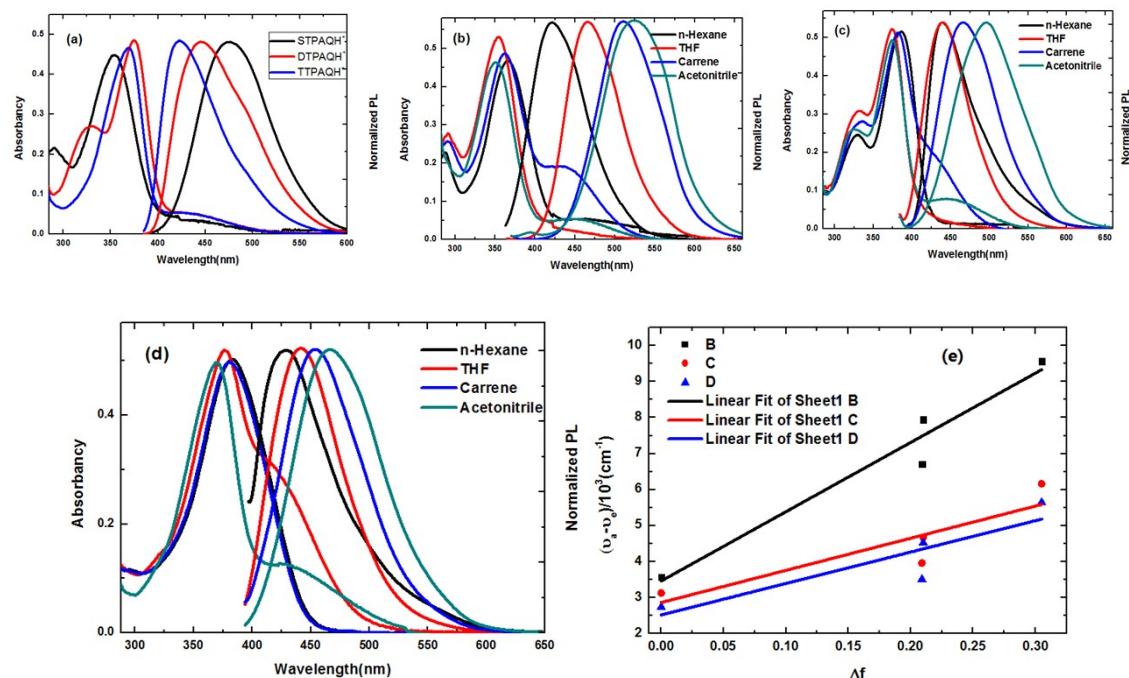


Fig. S10 The absorption and PL spectra of STPAQH⁺, DTPAQH₂²⁺ and TTPAQH₃³⁺ in THF (a), the absorption and PL spectra of STPAQH⁺ (b), DTPAQH₂²⁺ (c) and TTPAQH₃³⁺ (d) in various solvents (1×10^{-5} mol·L⁻¹), (e) Lippert-Mataga plot of three TPAQsH⁺ (v_a = absorption wavenumber, v_e = emission wavenumber and Δf = orientation polarizability = $(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ϵ = dielectric constant and n = refractive index)

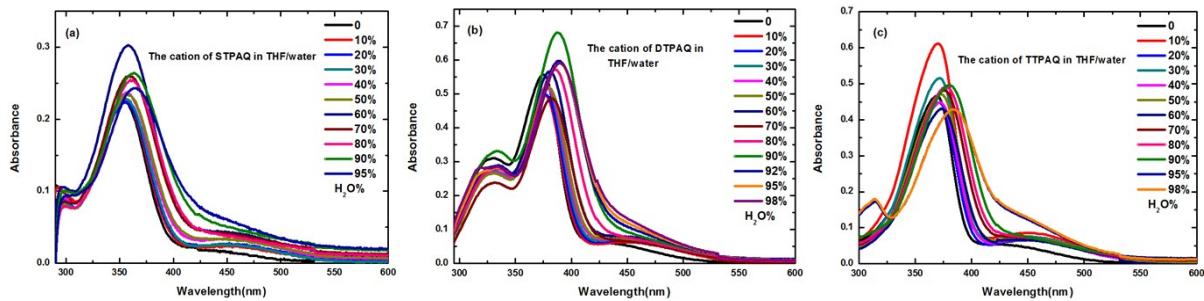


Fig. S11 The UV absorption spectra of STPAQH⁺ (a), DTPAQH₂²⁺ (b) and TTPAQH₃³⁺ (c) in various THF/water solutions (1×10^{-5} mol·L⁻¹)

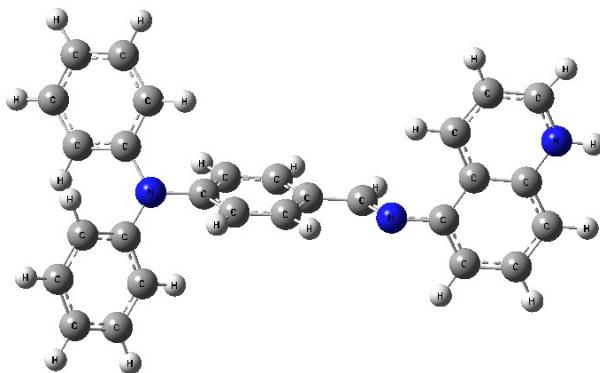


Fig. S12 The structure of STPAQH⁺, obtained by DFT (B3LYP/6-31G(d)) calculation

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