# Aggregation-Induced Emission Enhancement of Polycyclic Aromatic Alkaloids Derivatives and the Crucial Role of excited-state proton- transfer

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## Experimental Section

**General Information.** All reagents and starting materials are commercially available and were used as received. Scheme 1 shows the synthesis routes and molecular structures of the two polycyclic aromatic alkaloids derivatives, TBBH and TBBF. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Avance 400 spectrometer. Mass spectrum was determined with an AXIMA-CFR plus MALDI-TOF mass spectrograph. Absorption measurements were carried out on a TU-1800 spectrophotometer. Photoluminescence (**PL**) measurements were recorded using a Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp. **IR** spectra were obtained on a VERTEX-70 spectrometer. The X-ray diffraction intensity data were collected at 293 K on a Bruker Smart Apex2 CCD area-detector diffractometer with graphite-monochromated Mo Ka radiation ($\lambda$=0.71069 Å ). Data were corrected for absorption. Processing the intensity data was carried out using the Bruker SMART routine, and the structures were solved by direct methods and refined by a full-matrix least-squares technique on $F^2$ using SIR-97 programs. Crystallographic data and refinement parameters are given in Table S3

## Synthesis of N-Trifluoracetyltryptamin

Under an argon atmosphere, Tryptamine (8.0 g, 50.0 mmol) in 300 mL

Dichloromethane was stirred at 0 °C. Then **TFAA** (8.5ml, 60.0 mmol) was slowly added, after 5h reacted at 0 °C, water was added to terminate the reaction. The mixture was extracted, dried over with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography over silica gel with petroleum ether / dichloromethane (2:1) as a eluate, a product of a yellow solid 10.28g, Yield of 80.30%.$^{1}$H NMR ($CDCl_3$, 300 MHz, ppm) δ: 3.04 (t, *J* = 7.2Hz, 2H), 3.68 (dd, *J* = 6.6Hz, *J* = 6.6Hz, 2H), 6.40 (s, 1H), 7.03 (s, 1H), 7.12-7.26 (m, 2H), 7.37 (d, *J* = 8.1Hz, 1H), 7.57-7.60 (d, *J* = 7.2Hz, 1H) ,8.13 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 24.71, 40.10, 111.44, 111.47, 118.46, 119.78, 122.25, 122.52, 126.95, 136.49; MALDI/TOF MS calcd for $C_{12}H_{11}F_3N_2O$ 256.08, found 255.98.

**Synthesis of N-Formyl -2-(3-trifluoracetylaminopropionyl)aniline**

$NaIO_4$ (6.84 g, 32.0 mmol) was dissolved in 160 mL of water and then stirred for 30 minutes at 0 °C. N-Trifluoracetyltryptamin (2.05 g, 8.0 mmol) in 160 mL methanol was dropped. After removing the ice bath, the reaction was stirred at room temperature for 20 hours. The mixture was poured into 150 mL of water and extracted with dichloromethane (3 × 150 mL). The crude product was purified by flash column chromatography (petroleum ether/$CH_2Cl_2$ = 1:1) to give 1.98g as white solid (86.08% yield). $^{1}$H NMR ($CDCl_3$, 300 MHz, ppm) δ: 3.38 (t, *J* = 5.7Hz, 2H), 3.76-3.83 (m, 2H), 6.91 (s, 1H), 7.17 (m, 1H), 7.61 (t, *J* = 7.8Hz, 1H), 7.85 (d, *J* = 8.4Hz, 1H), 8.52 (s, 1H), 8.76 (d, *J* = 8.4Hz, 1H), 11.43 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 34.79, 38.59, 113.87, 117.69, 121.11, 121.85, 123.36, 130.80, 135.92, 140.06, 159.82, 202.84; MALDI/TOF MS calcd for $C_{12}H_{11}F_3N_2O_3$ 288.07, found 287.86.

**Synthesis of 2-(3-trifluoracetylaminopropionyl)aniline**

N-Formyl-2-(3-trifluoracetylaminopropionyl)aniline (1.45 g, 5.0 mmol) was dissolved in 100 mL Methanol solution, conc. HCl (0.62 mL, 7.5 mmol) was dropped into the reaction mixture, refluxed for 1 hour. After cooling to room temperature, the reaction solution is neutralized with 1 M potassium carbonate solution to PH=6. The yellow residue was poured into 25 mL water and extracted with $CH_2Cl_2$ (3 × 75 mL). The organic phase was dried with sodium sulfate and the solvent removed under vacuum.

The crude product was purified by flash column chromatography (petroleum ether/$CH_2Cl_2$ = 1:1) to give 1.02g as yellow crystal (78.46% yield). $^1$H NMR ($CDCl_3$, 300 MHz, ppm) δ: 3.24 (t, *J* = 5.7Hz, 2H), 3.77 (dd, *J* = 6.0Hz, *J* = 6.0Hz, 2H), 6.29 (s, 2H), 6.65 (m, 2H), 7.28 (m, 2H), 7.63 (d, *J* = 8.4Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 34.98, 37.60, 113.96, 116.14, 117.16, 117.52, 117.77, 130.90, 135.11, 150.57, 200.55; MALDI/TOF MS calcd for $C_{11}H_{11}F_3N_2O_2$ 260.08, found 259.93.

**Synthesis of 4-(2-(3-trifluoroacetylamino)propionylphenylamino)-9 -(2-trifluoroacetylamino )ethylacridine-1,2-dione (TBBF)**

2-(3-trifluoracetylaminopropionyl)aniline (1.3g, 5mmol) was reacted with catechol (0.24g, 2.2mmol) in aq. EtOH in the presence of (5.0g, 25mmol) $NaIO_3$ at room temperature for 30 hours. Then 30mL water was added to terminate the reaction. The mixture was extracted with $CH_2Cl_2$, dried over with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography over silica gel with ethanol / dichloromethane (1 : 30) as a eluate, a product of a orange solid 0.53g, Yield of 17.5%.$^1$H NMR ($CDCl_3$, 300 MHz, ppm) δ: 3.42 (m, 2H), 3.62 (m, 4H), 3.88 (t, *J* = 6.9Hz, 2H), 6.48 (s, 1H), 7.40 (t, *J* = 7.8Hz, 1H), 7.82 (m, 2H), 7.89 (t, *J* = 8.4Hz, 1H), 8.06 (t, *J* = 8.4Hz, 1H) ,8.13 (d, *J* = 7.8Hz, 1H), 8.24(d, *J* = 7.8Hz, 1H), 8.54(d, *J* = 8.4Hz, 1H), 9.45 (t, *J* = 8.4Hz, 1H), 9.68 (t, *J* = 8.4Hz, 1H), 11.86 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 27.85, 29.77, 35.52, 37.41, 103.68, 123.42, 123.98, 125.21, 126.36, 128.57, 128.61, 129.77, 130.57, 132.01, 133.67, 134.46, 138.42, 146.72, 150.36, 151.55, 156.47, 156.72, 156.95, 157.20, 178.14, 182.79, 201.24; MALDI/TOF MS calcd for $C_{28}H_{20}F_6N_2O_5$ 606.13, found 605.84.

**Synthesis of 4-(2-acetylphenylamino)-9-methylacridine-1,2-dione (TBBH)**

**TBBH** was prepared according to the same procedure as that of **TBBF** from1-(2-aminophenyl)ethanone (2.97g, 22mmol) and catechol (1.1g, 10mmol). Column chromatography(ethanol / dichloromethane =1:30 as a eluate, a product of a orange solid 1.16g, Yield of 32.58%.$^1$H NMR ($CDCl_3$, 300 MHz, ppm) δ: 2.72 (d, 3H), 3.19 (s, 3H), 6.91 (s, 1H), 7.25 (m, 1H), 7.25(t, *J* = 8.4Hz, 1H), 7.58 (d, *J* = 8.4Hz,

1H), 7.74(m, 2H), 7.87 (t, $J$ = 7.2Hz, 1H), 8.27(m, 2H), 12.31 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100.61 MHz, ppm) δ: 15.55, 28.17, 103.29, 122.20, 122.57, 123.67, 125.11, 127.10, 128.41, 130.48, 131.42, 133.27, 138.40, 146.23, 146.80, 149.97, 151.67, 178.45, 182.58, 200.47; MALDI/TOF MS calcd for $C_{22}H_{16}N_2O_3$ 356.12, found 357.0.

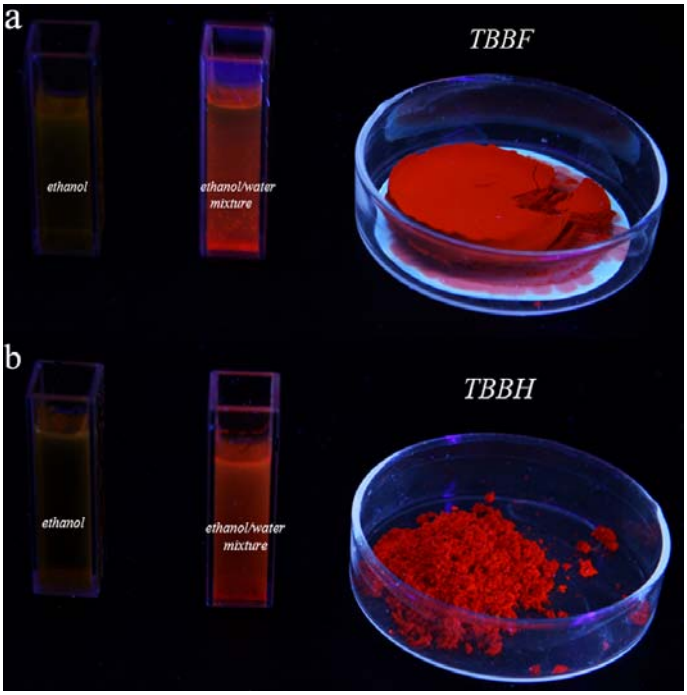


**Fig. S1** (a) The fluorescence of **TBBF** in ethanol (left), ethanol/water = 1:9 (middle) and solid of **TBBF** under illumination with a 365.0nm lamp (right). (b) The fluorescence of **TBBH** in ethanol (left), ethanol/water = 1:9 (middle) and solid of **TBBH** under illumination with a 365.0nm lamp (right).

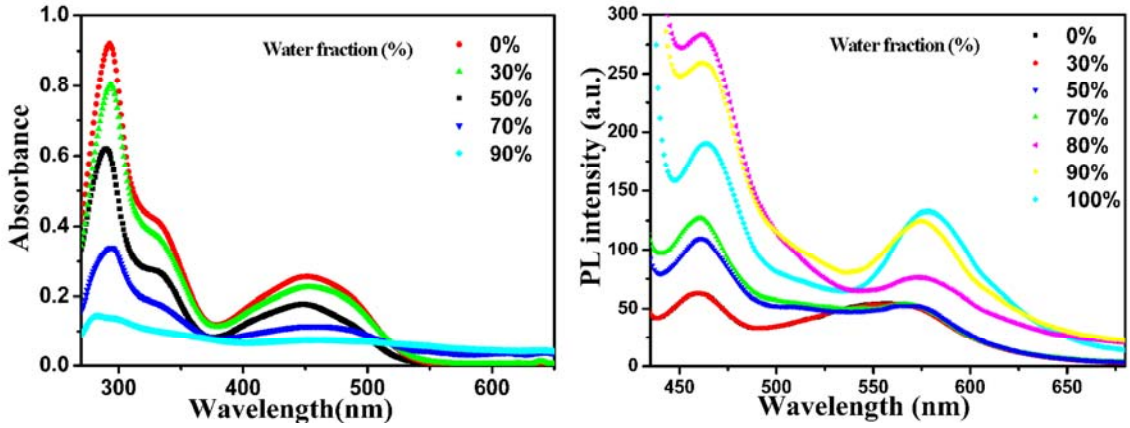


**Fig. S2** Absorption and **PL** spectra of **TBBH** in ethanol-water mixtures with different fractions of water; c = 5μM.

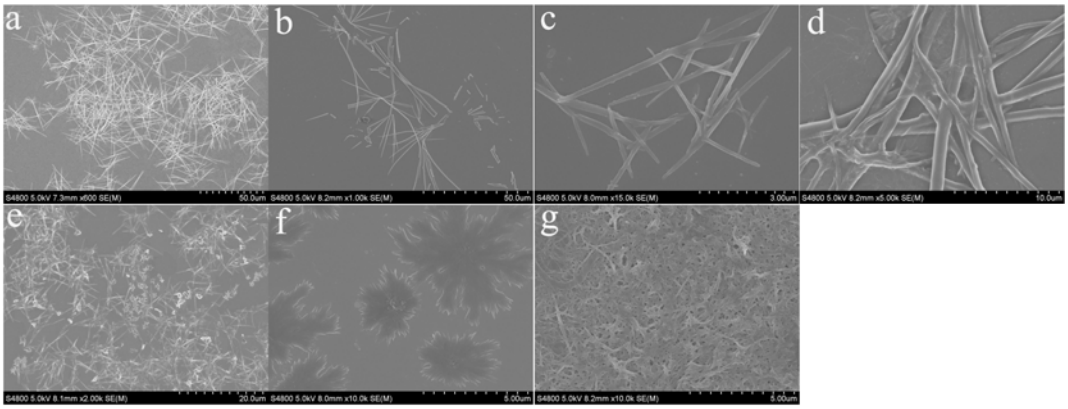


**Fig. S3 SEM** images of **TBBH** (The volume of water: a. 0%; b. 30%; c. 50%; d. 70%; e. 80%; f. 90%; g. 100%)

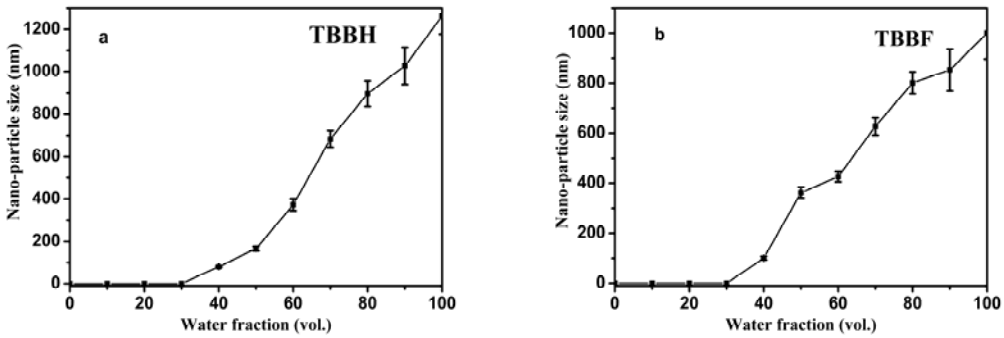


**Fig. S4** The nano-particle size of **TBBH** (a) and **TBBF** (b) in ethanol/water solution.

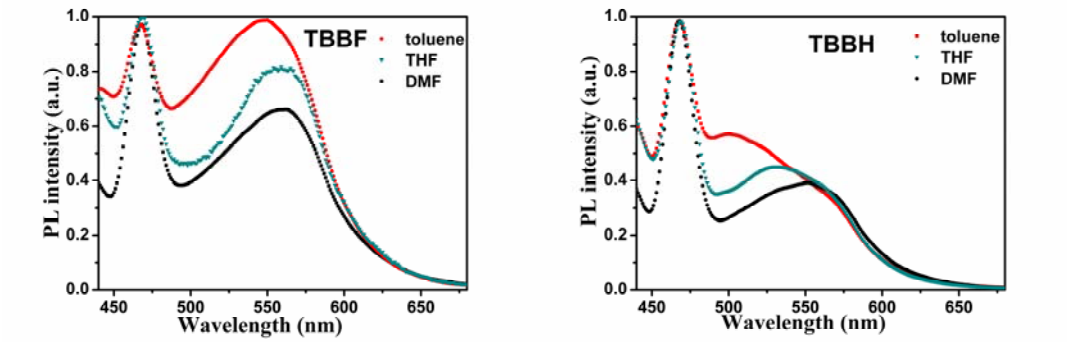


**Fig. S5** Emission spectra of **TBBF** (left) and **TBBH** (right) in toluene, **THF**, **DMF**. Excitation wavelength, 400nm; c = 20μM

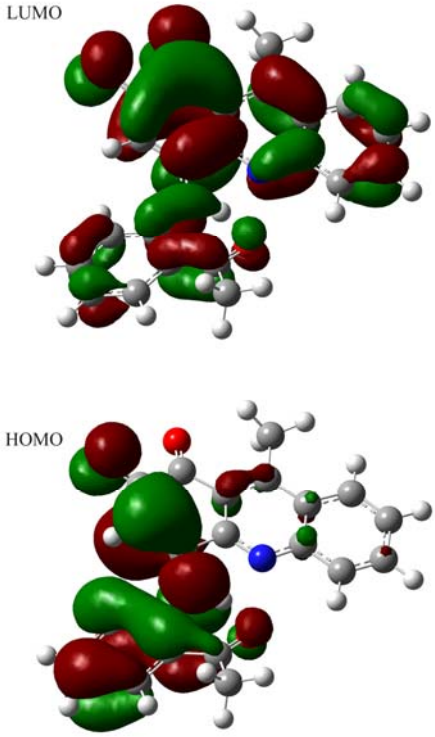


**Fig. S6** The **HOMO** and **LUMO** of **TBBH** are obtained by calculation.

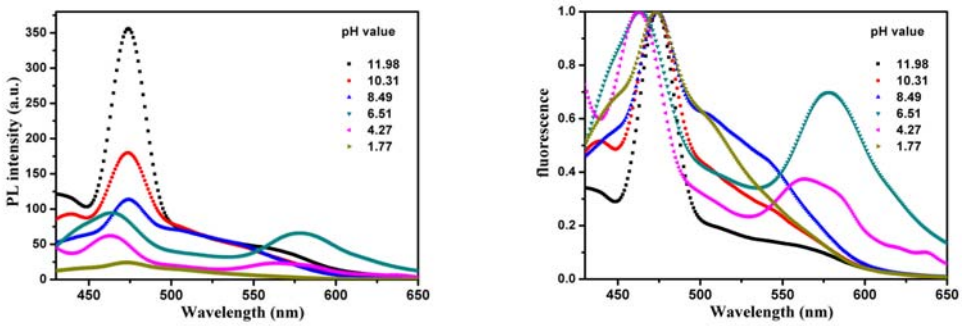


**Fig. S7 PL** spectra and normalized fluorescence emission spectra of **TBBH** in different **pH**.

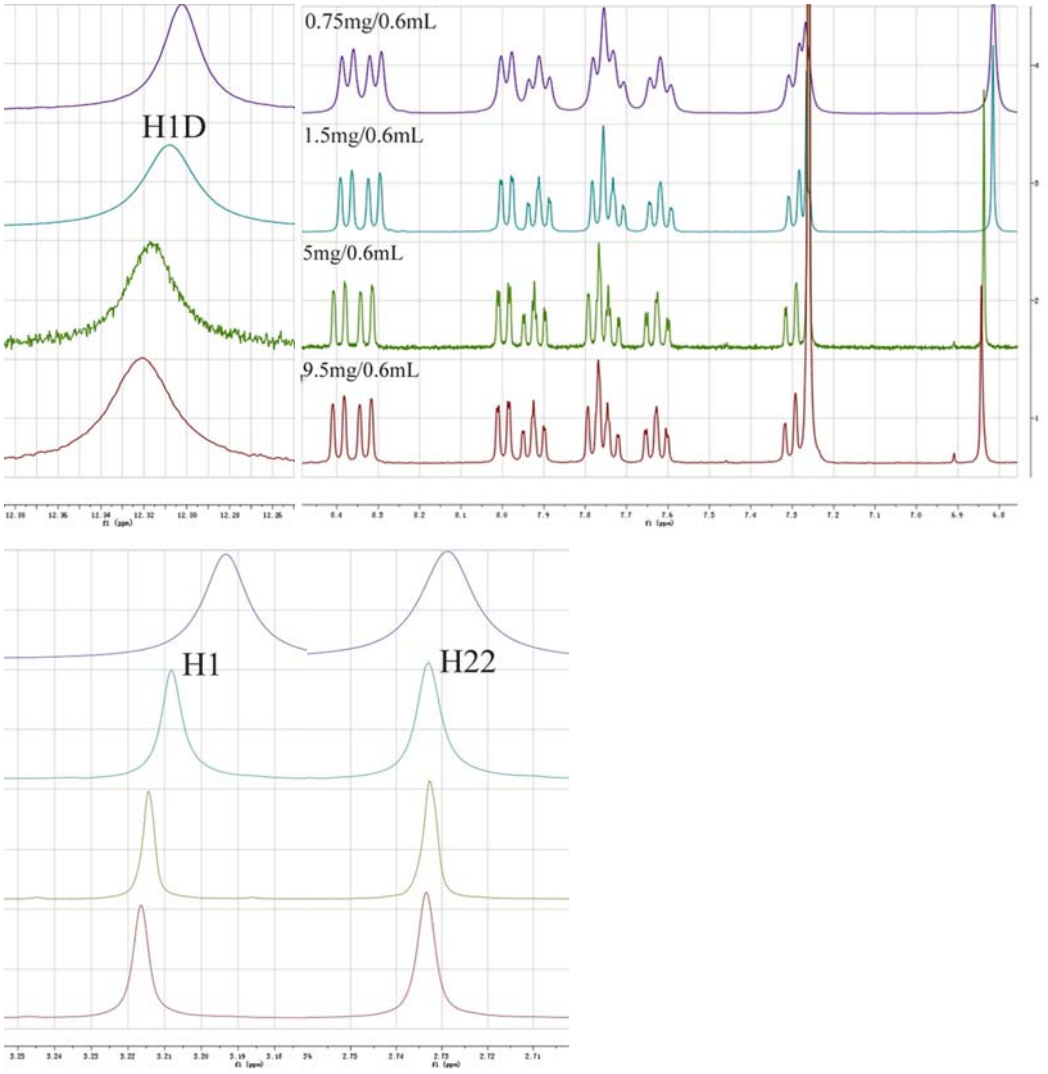


**Fig. S8 NMR** spectra of **TBBH** taken in $CDCl_3$ at room temperature with various concentrations.

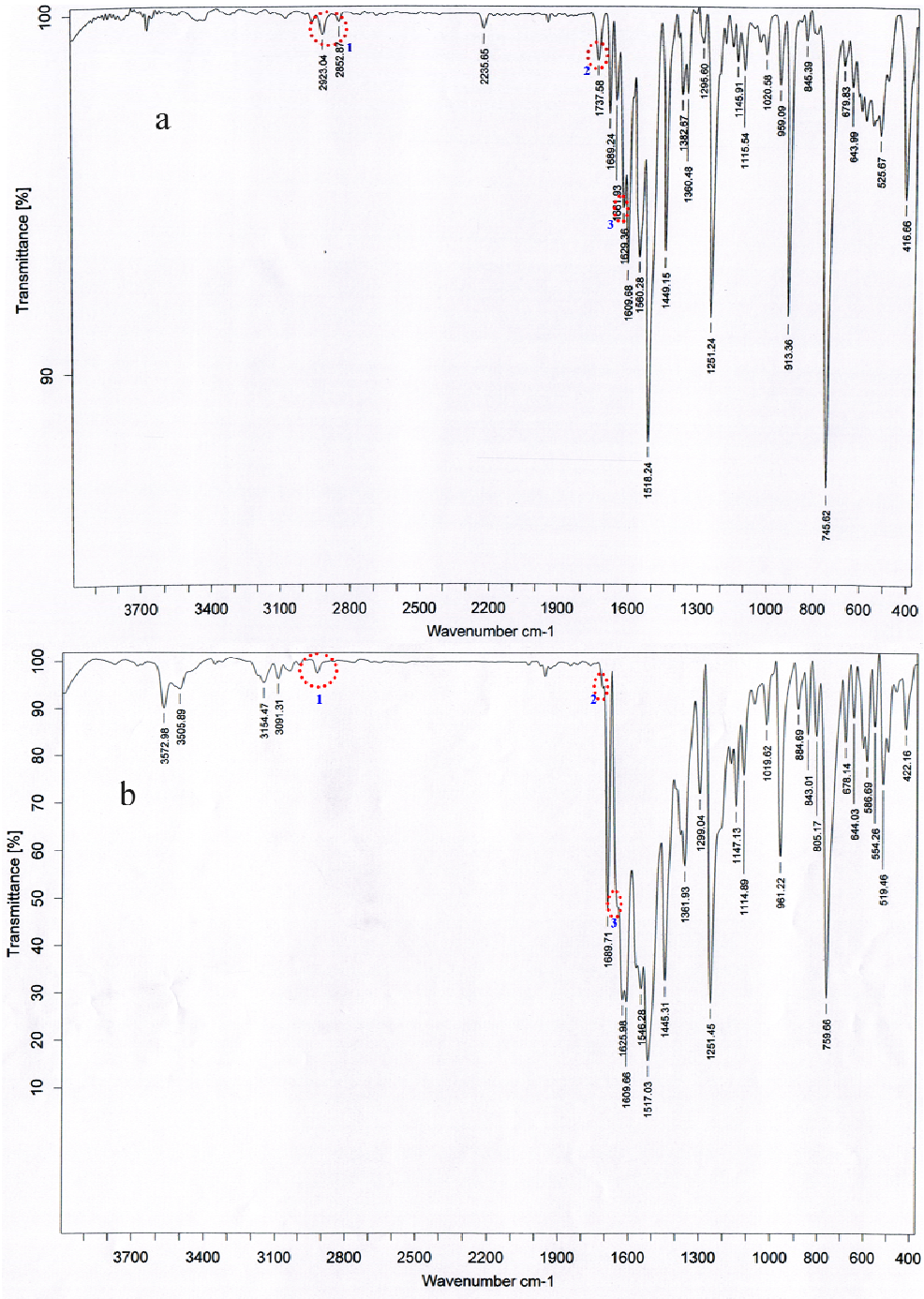


**Fig. S9 IR** spectra of **TBBH** (a) in solution ($CDCl_3$) and (b) solid state.

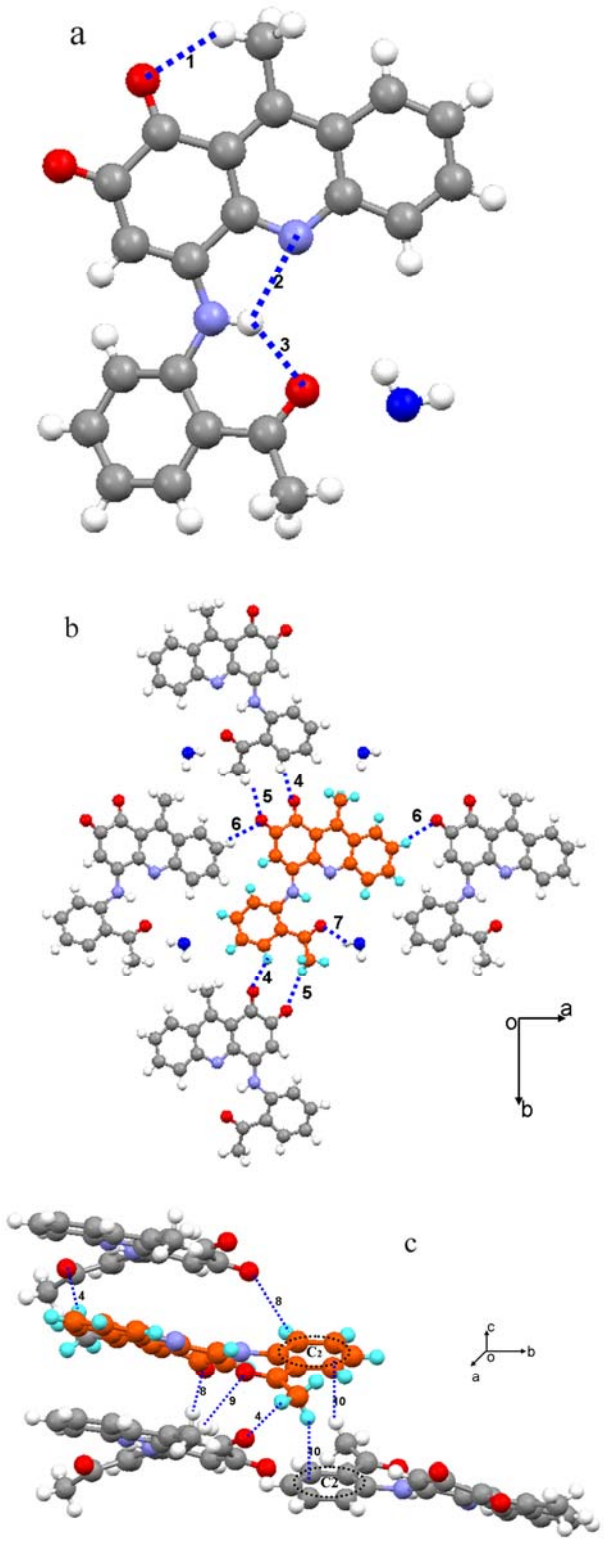


**Fig. S10** (a) Intramolecular interactions in the single molecule; (b) Intermolecular interactions within the crystal structure of **TBBH** projected onto the *ab* plane; (c) Intermolecular interactions within the crystal structure of **TBBH** projected onto the *bc* plane.

**Table S1** : Optical Properties of **TBBF** and **TBBH** in Ethanol/Water Mixtures

| Compound | $f_w$(vol %) [a] | $\lambda_{ab}$ [b] (nm) | $\lambda_{em}$ [c] (nm) | $\Phi_F$ [d] (%) | $\tau$ [e] (ns) | | |
|---|---|---|---|---|---|---|---|
| | | | | | $A_1/A_2$ | $\tau_1$ | $\tau_2$ |
| TBBF | 0% | 294, 455 | 443, 470, 509 | 6.5 | 1/0 | 0.072 | |
| | 30% | 295, 455 | 450, 476, 510 | 24.5 | 1/0 | 0.087 | |
| | 50% | 295, 457 | 452, 479, 511, 565 | 30.9 | 0.70/0.30 | 0.096 | 4.457 |
| | 70% | 296, 460 | 455, 481, 570 | 65.0 | 0.45/0.55 | 0.984 | 6.452 |
| | 90% | 296, 460 | 481, 571 | 71.9 | 0.39/0.61 | 1.127 | 5.545 |
| TBBH | 0% | 293, 451 | 460, 560 | 5.5 | 1/0 | 0.045 | |
| | 30% | 294, 454 | 460, 561 | 6.3 | 0.96/0.04 | 0.054 | 5.090 |
| | 50% | 293, 452 | 461, 567 | 10.7 | 0.71/0.29 | 0.171 | 5.124 |
| | 70% | 294, 457 | 461, 570 | 15.1 | 0.59/0.41 | 0.627 | 5.273 |
| | 90% | 289, | 462, 575 | 61.1 | 0.43/0.57 | 0.756 | 5.542 |

[a] $f_w$ = water fraction, solution concentration: 5μM.; [b] $\lambda_{ab}$ = absorption maximum; [c] $\lambda_{em}$ = emission maximum, excitation wavelength: 400nm; [d] Quantum yields were calculated on the basis of coumarin as standard ($\Phi$ = 0.56 in ethanol); [e] Dynamic parameters determined from $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$, where $A_1/A_2$ are the fractions (A) and lifetimes ($\tau$) of shorter (1) and longer (2) lived species. Solution concentration: 5μM. Excitation wavelength: 400nm.

**Table S2** Prominent molecular forces for structure of **TBBH**

| Type | No | Orientation of interaction | | Distance (Å) | Angle (deg) |
|---|---|---|---|---|---|
| intra | 1 | N(1) --H(1D) | ....O(1) | 2.03 | 129 |
| | 2 | N(1) --H(1D) | ....N(2) | 2.12 | 112 |
| | 3 | C(22) --H(22C) | ....O(2) | 2.12 | 127 |
| inter | 4 | C(4) --H(4A) | ....O(2) | 2.37 | 146 |
| | 5 | C(1) --H(1B) | ....O(3) | 2.59 | 140 |
| | 6 | C(17) --H(17A) | ....O(3) | 2.61 | 113 |
| | 7 | C(7) --H(7A) | ....O(3) | 2.66 | 138 |
| | 8 | O(4) --H(10) | ....O(1) | 2.16 | |
| | 9 | C(1) --H(22B) | ....O(1) | 2.60 | 126 |
| | 10 | C(1) --H(1C) | .... Cg(2) | 2.82 | 17.89 |

**Table S3** Crystal data and structure refinement parameters for **TBBH**

| | |
|---|---|
| Compound reference | TBBH |
| Chemical formula | $C_{22}H_{16}N_2O_3 \quad H_2O$ |
| Formula Mass | 374.38 |
| Crystal system | Monoclinic |
| $a$/Å | 10.898(3) |
| $b$/Å | 22.742(7) |
| $c$/Å | 7.482(2) |
| $\alpha$/° | 90.00 |
| $\beta$/° | 106.178(4) |
| $\gamma$/° | 90.00 |
| Unit cell volume/Å$^3$ | 1780.8(9) |
| Temperature/K | 273(2) |
| Space group | *P21/c* |
| No. of formula units per unit cell, $Z$ | 4 |
| No. of reflections measured | 19956 |
| No. of independent reflections | 3798 |
| $R_{int}$ | 0.1114 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0775 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.2049 |
| Final $R_1$ values (all data) | 0.1930 |
| Final $wR(F^2)$ values (all data) | 0.2729 |
| Goodness of fit on $F^2$ | 1.000 |