Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Schiff Base-bridged TPE-Rhodamine Dyad: Facile Synthesis, Distinct Response to Shearing and Hydrostatic Pressure, Sequential Multicolored Acidichromism

Xuedan Liu,[ad] **Chunran Ma,**[ad] **Aisen Li,**[b] **Weiqing Xu,**[b] **Zhiyong Ma,***[a] **and Xinru Jia**[c]

[a] *Beijing State Key Laboratory of Organic-Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: mazhy@mail.buct.edu.cn*
[b] *State Key Laboratory for Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun 130012, China.*
[c] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.*
[d] *These authors contributed equally to this work.*

1. Materials and General Methods

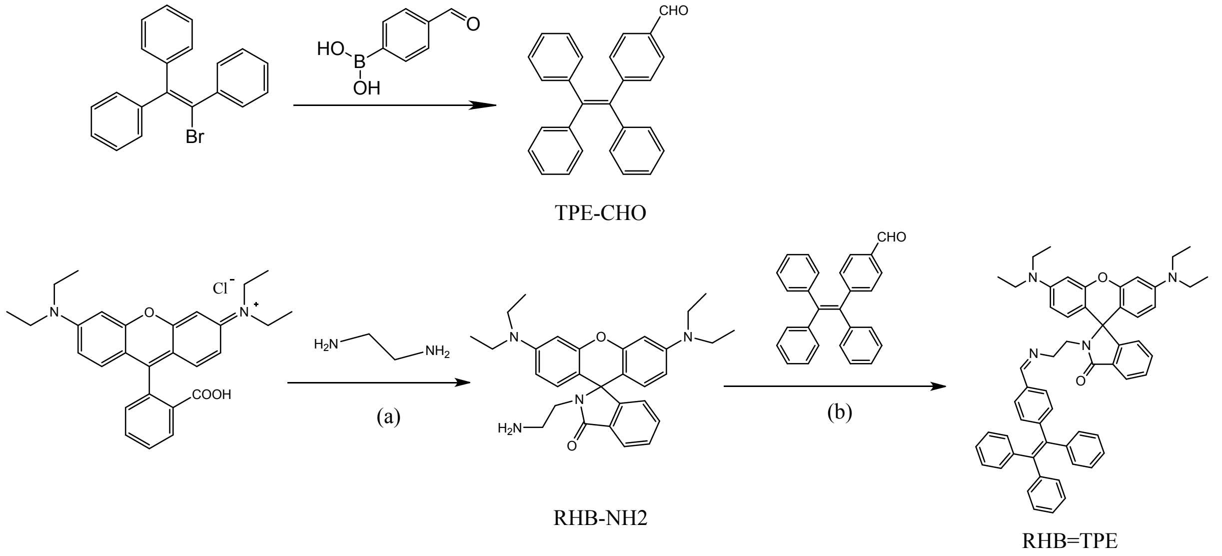
All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

^{1}H NMR was recorded on the 400 MHz spectrometer (Bruker ARX400) and ^{13}C NMR spectra were recorded on the Bruker 125 MHz spectrometer at room temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. UV-vis spectra were acquired on the Hitachi U-4100 UV-vis spectrophotometer. Steady fluorescence spectra were performed on the Hitachi F-7000 or Edinburgh Instruments FLS920 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) measurement was carried out by using TA instruments Q100 DSC. Wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X'PertPro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu Kα) and an X'celerator detector. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer with graphite monochromator and Mo Kα radiation [λ (MoKα) = 0.71073 Å]. Structures were solved by direct methods with SHELXS-97 and refined against F2 with SHELXS-97.

Molecular simulation was according to the density functional method at the B3LYP/6-31*G(d) level based on the single crystal data.

Hydrostatic pressure experiments were carried out using BGI-type diamond anvil cell (DAC) equipment with silicon oil as pressure-transmitting medium. The diameter of diamond anvils was 0.3 mm. T301 stainless steel gaskets with thickness of 0.25 mm and center hole of 0.1 mm were preinstalled. The pressure determination was conducted on a Horiba Jobin Yvon JY-T64000 spectrometer using a pre-implanted ruby chip according to the R1 fluorescence technique. The excitation wavelength was 514.5 nm and the output power was 7 mW. The in situ PL spectra measurements were performed on a Jobin Yvon iHR320 spectrometer equipped with a fluorescent microscope in the reflection mode. Mercury lamp was used as the excitation source and 365 nm was selected as excitation wavelength. The fluorescent images was snapshot by putting the DAC containing the ruby and single crystal on the fluorescent microscope (IX71, Dlympus, 20×, nemerical aperture=0.4). All experiments were carried out at room temperature.

2. Synthesis of targeted molecule



Scheme S1. Syntheses of **RhB=TPE**. Reagents and conditions: (a) Ethylenediamine, Ethanol, reflux 12 h; (b) Ethanol, reflux 6 h.

Compound TPE-CHO was synthesized according to literature report [1].

(1) RhB-NH2

Add RHB（5g, 10.44mmol） and ethylenediamine （5mL, 74.9mmol）to the round-bottomed flask. Ethanol (50 mL, HPLC grade) was then added and the solution was kept refluxing for 12h. After cooling to room temperature, the resulting solution was evaporated in vacuo and the residue was dissolved in water (50mL). Extracting the mixture solution with dichloromethane (30 mL×2) , and the organic phases were combined and washed with water (50 mL×3). The organic phase is dried over anhydrous sodium sulfate and evaporated in vacuo to give a pure product RhB-NH2. Yield:86.6%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 5.4, 3.1 Hz, 1H), 7.43 (dt, J = 7.1, 3.6 Hz, 2H), 7.09 (dd, J = 5.3, 3.1 Hz, 1H), 6.43 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.1 Hz, 2H), 6.27 (dd, J = 8.8, 2.2 Hz, 2H), 3.33 (q, J = 7.1 Hz, 8H), 3.17 (d, J = 6.6 Hz, 2H), 2.40 (t, J = 6.6 Hz, 2H), 1.16 (t, J = 7.0 Hz, 12H).

(2) RhB=TPE

Add RHB-NH2 (201.8mg, 0.416mmol) and TPE-CHO (150mg, 0.416mmol) to a 50 mL round-bottomed flask. Ethanol (15 mL, HPLC grade) was then added and the solution was kept refluxing for 6h. The precipitate was filtered and dried to give pure product RHB=TPE. Yield: 95%.

^{1}H NMR (400 MHz, CDCl3) δ 7.98 (s, 1H), 7.90 (dd, J = 5.5, 3.1 Hz, 1H), 7.42 (dd, J = 5.6, 3.0 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.10 – 7.05 (m, 10H), 7.00 (d, J = 8.1 Hz, 8H), 6.44 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.3 Hz, 2H), 6.24 (dd, J = 8.9, 2.4 Hz, 2H), 3.39 (s, 4H), 3.32 (d, J = 7.1 Hz, 8H), 1.16 (t, J = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, CDCl3) δ 162.36 (s), 153.88 (s), 153.32 (s), 148.76 (s), 146.28 (s), 143.66 – 143.25 (m), 140.36 (s), 134.17 (s), 132.33 (s), 131.69 – 131.04 (m), 128.91 (s), 127.77 (dd, J = 17.3, 10.2 Hz), 127.43 (s), 126.61 (d, J = 12.9 Hz), 123.79 (s), 122.74 (s), 108.05 (s), 105.59 (s), 97.87 (s), 64.93 (s), 58.99 (s), 44.36 (s), 41.29 (s), 12.64 (s).

HR-ESI-MS Calcd. For $C_{57}H_{54}N_4O_2$ $[M+H]^+$: 827.43195. Found: 827.43099.

3. NMR spectra and HR-MS of RhB=TPE

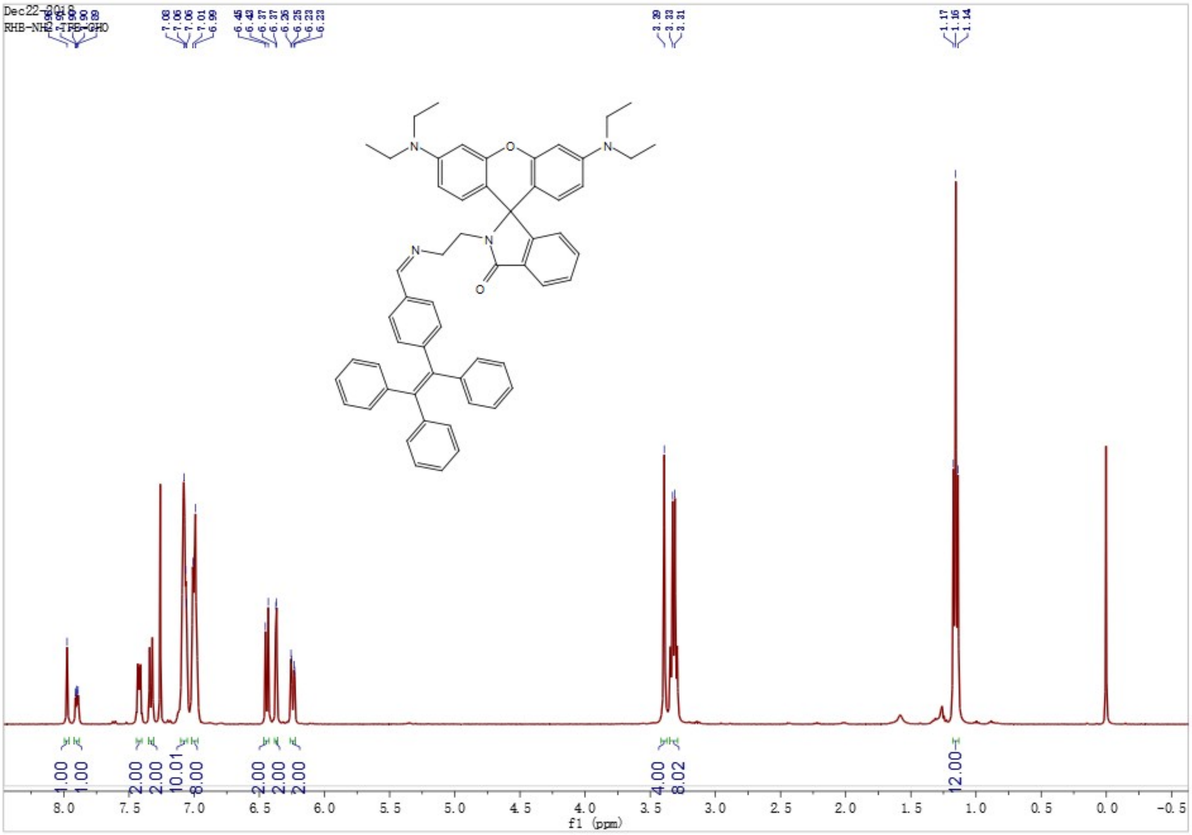


Figure S1. ^{1}H NMR spectrum of **RhB=TPE** in $CDCl_3$

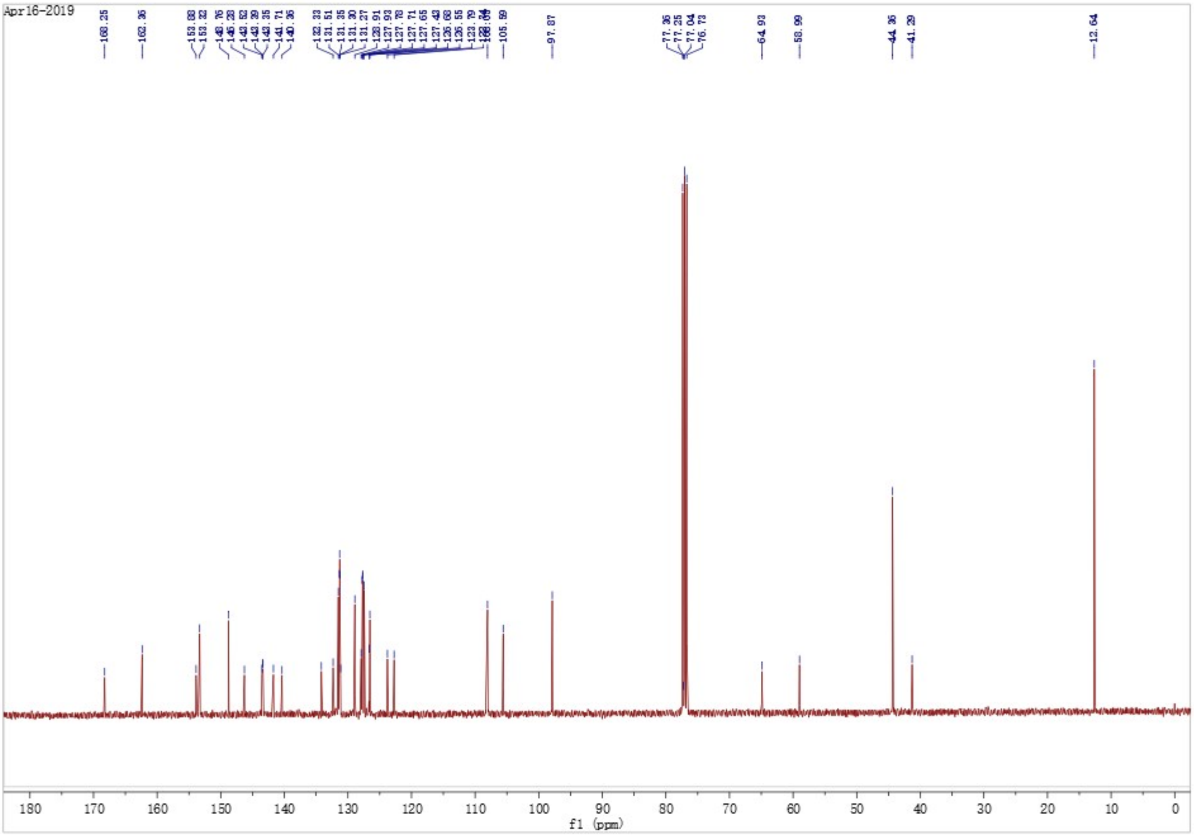
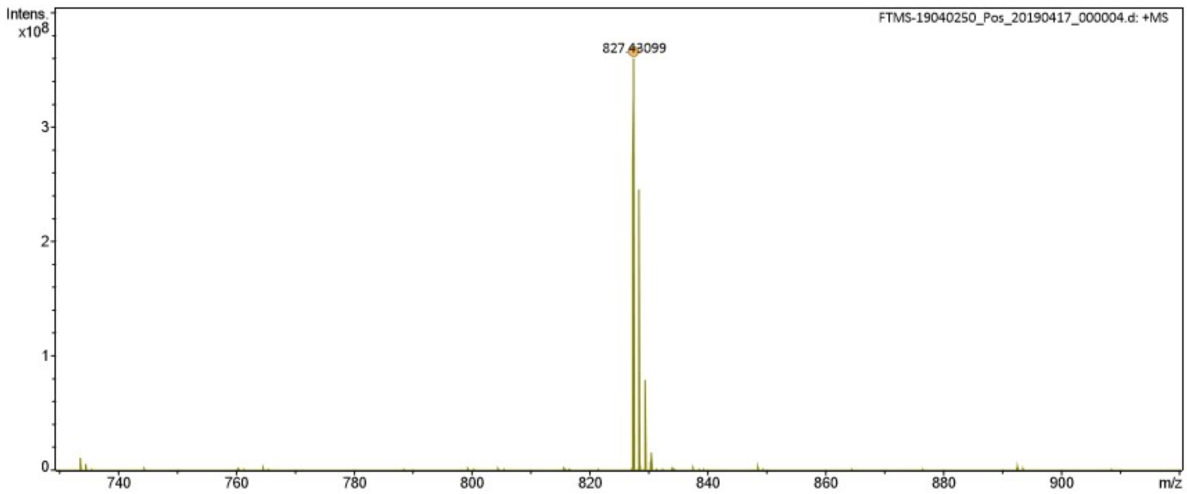


Figure S2. ^{13}C NMR spectrum of **RhB=TPE** in $CDCl_3$.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
827.430988	1	C57H55N4O2	100.00	827.431953	1.2	2.0	24.8	33.0	even	ok

Figure S3. HR-MS spectrum of **RhB=TPE**.

4. Decay curves of LE emission and HLCT emission

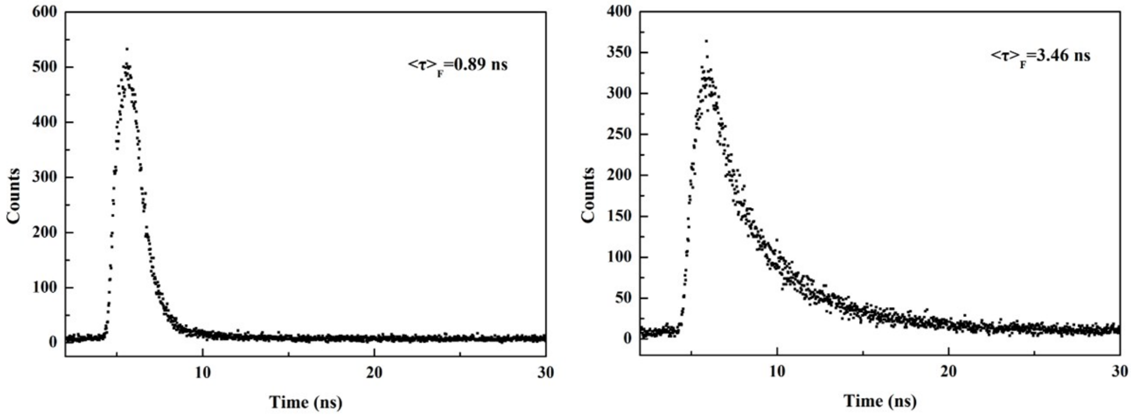


Figure S4. Decay curves of emissions at 440 nm (left) and 475 nm (right).

5. Thermal recovery of RhB=TPE

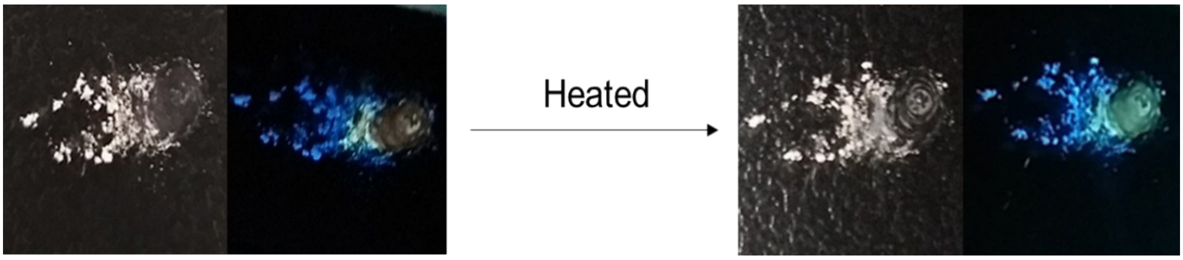


Figure S5. After annealing at 180 °C for 5 minutes, the reddish powder returned to green.

6. Molecular simulation based on DFT calculation

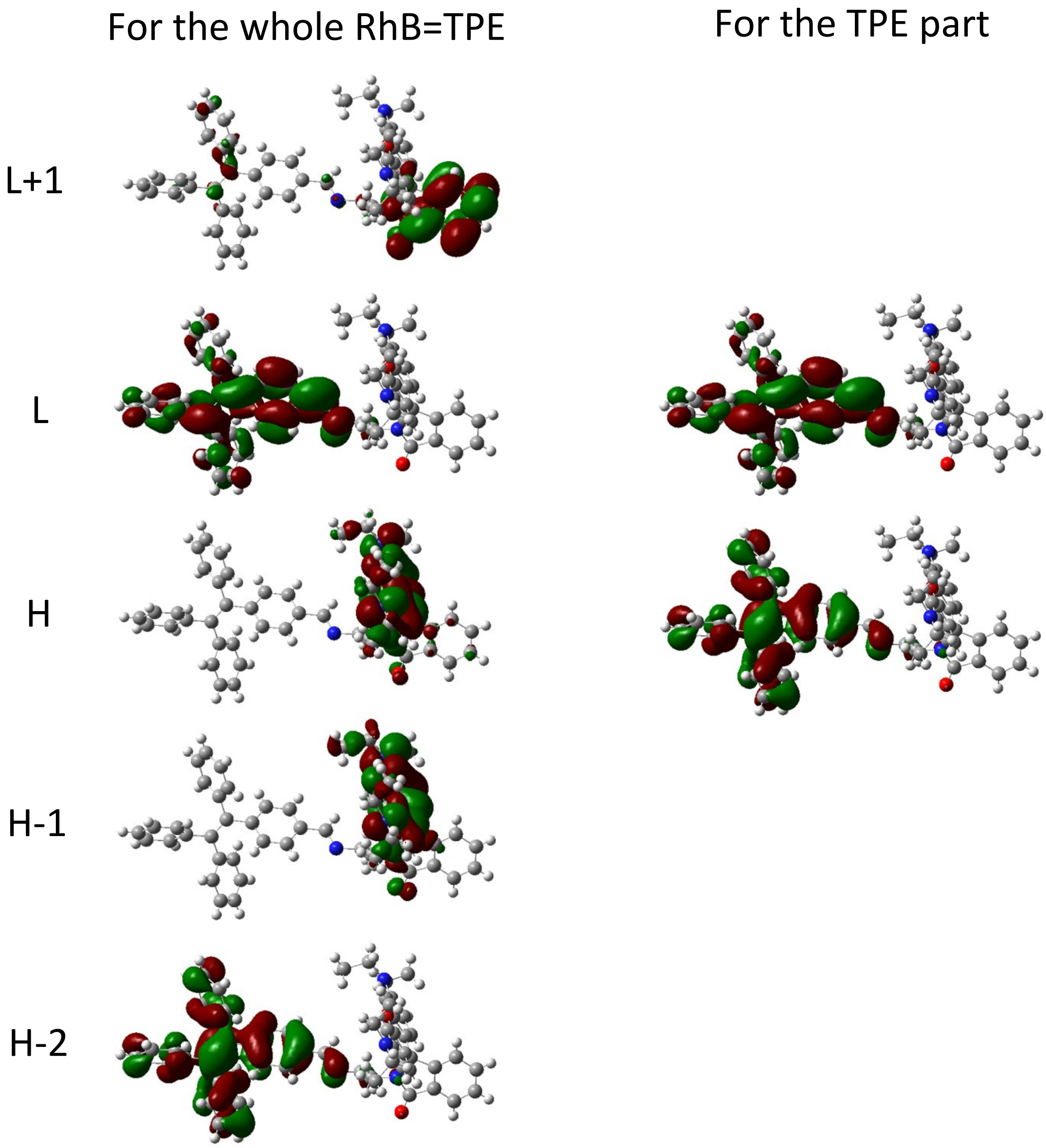


Figure S6. Molecular obitals for the whole **RhB=TPE** and the HOMO and LUMO for the TPE part.

7. Fluorescent images of RhB=TPE in different solvent

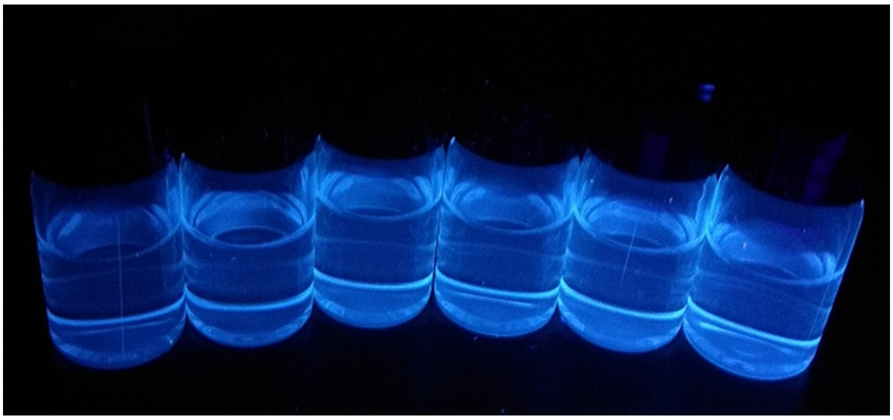


Figure S7. Fluorescent images of RhB=TPE in different solvent. (From left to right, n-hexane, toluene, THE, ethanol, DMF and MeCN).

8. Single crystal of RhB=TPE

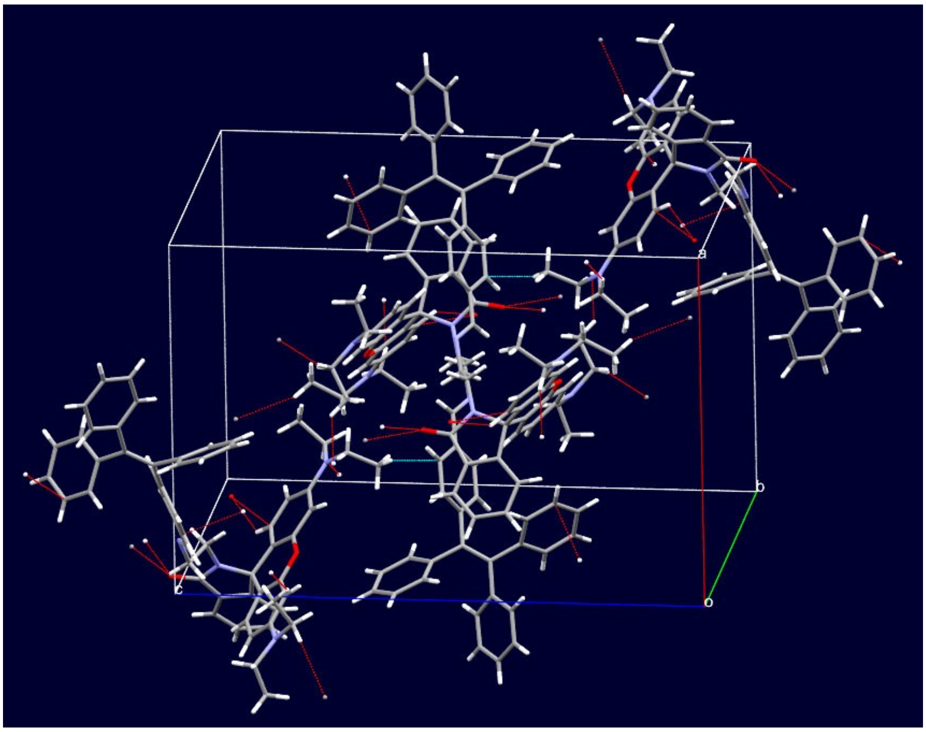


Figure S8. Unit cell in the single crystal of **RhB=TPE**.

Table S1. Detailed data of the single crystal of **RhB=TPE**.

Identification code	**RhB=TPE**
CCDC Number	1911107
Empirical formula	$C_{57}H_{54}N_4O_2$
Formula weight	827.04
Temperature	285 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 21/n
Unit cell dimensions	a = 16.0797(12) Å, α= 90.00°.
	b = 13.1053(11) Å, β= 91.561(3).
	c = 22.9527(19) Å, γ= 90.00°.
Volume	4835.0(7) Å^3
Z	4
Density (calculated)	1.136 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	1760
Crystal size	0.25 x 0.18 x 0.15 mm^3
Theta range for data collection	2.70 to 28.27°.
Index ranges	-20<=h<=21, -17<=k<=17, -30<=l<=30
Reflections collected	11994
Final R indices [I>2sigma(I)]	R1 =0.0750, wR2 = 0.1705
R indices (all data)	R1 = 0.1916, wR2 = 0.2298

9. DSC

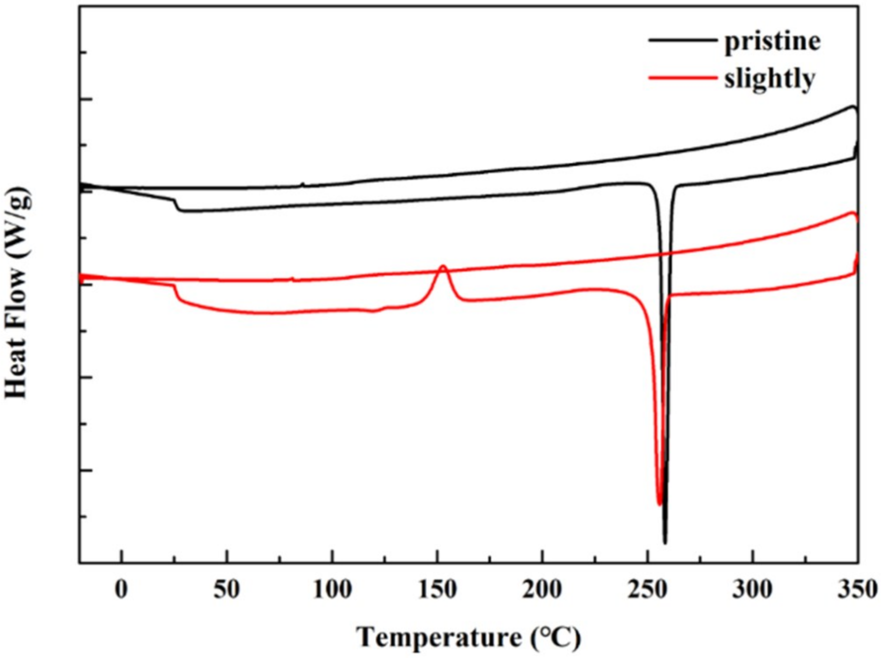
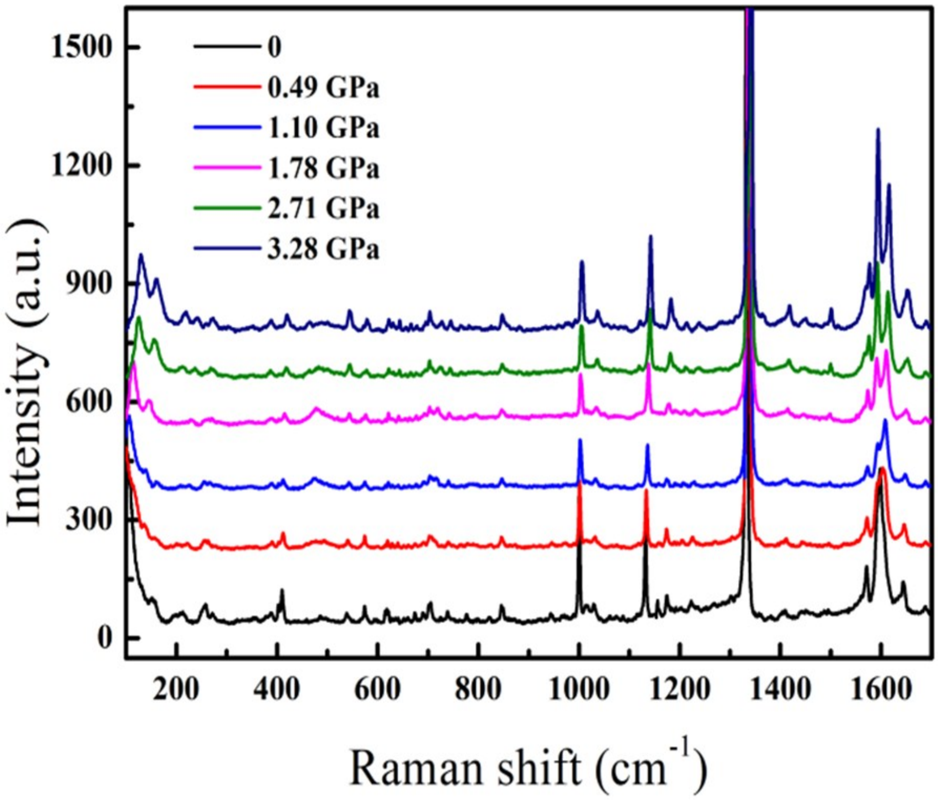


Figure S9. DSC curves of the pristine and slightly grinding powder**.**

10. Raman spectra of the RhB=TPE single crystal



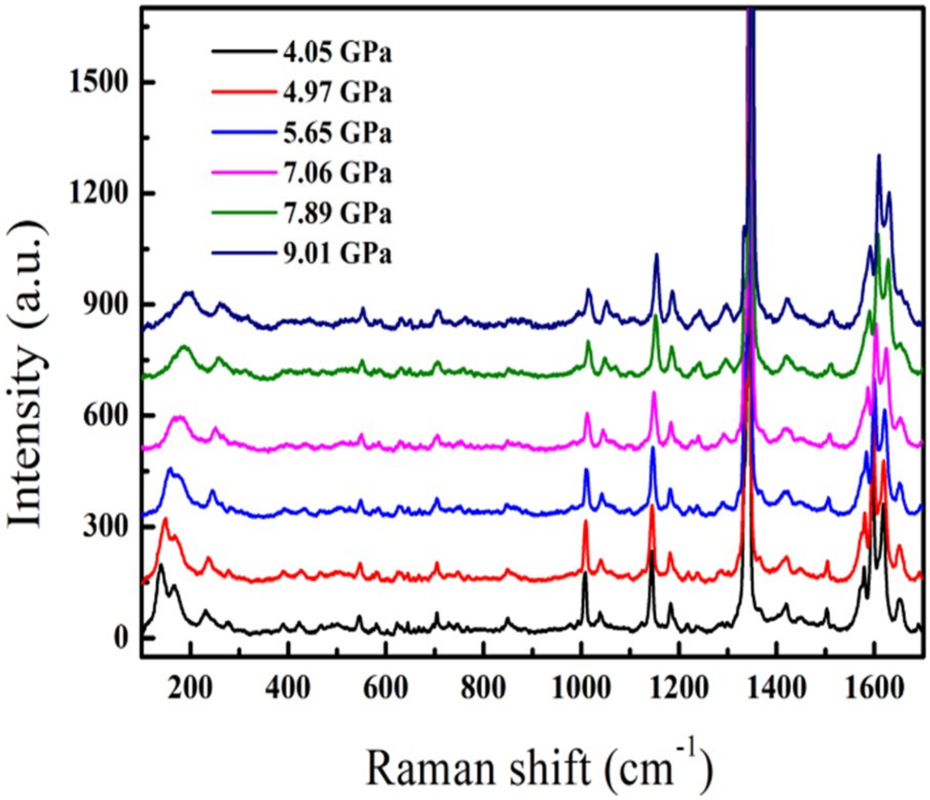


Figure S10. Raman spectra of the **RhB=TP**E single crystal during the process of decompression in the pressure range of 0~9.01 GPa.

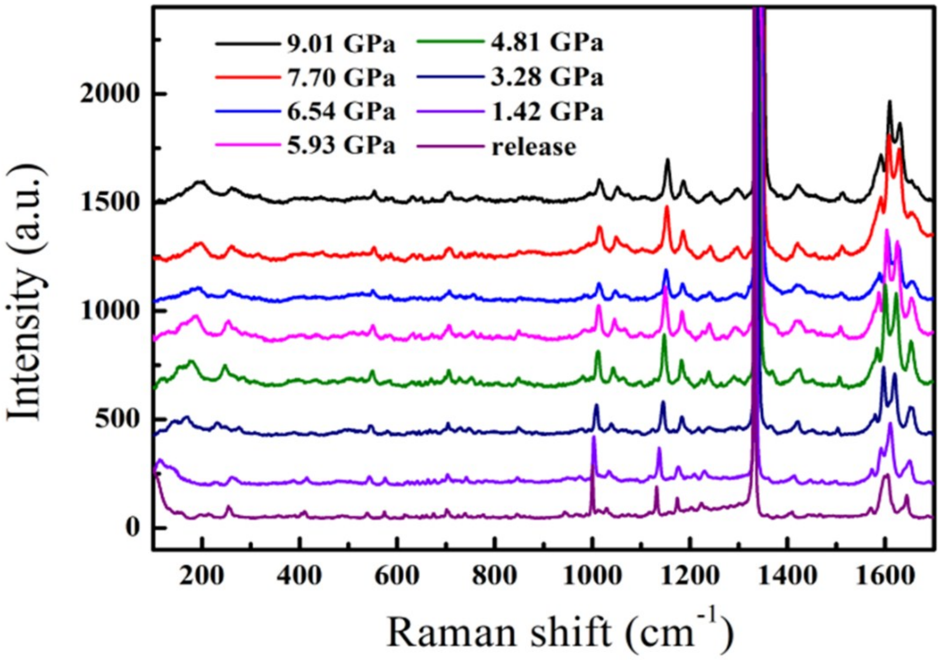


Figure S11. Raman spectra of the **RhB=TPE** single crystal when releasing the pressure.

11. Decay curves of the yellow and reddish emissions

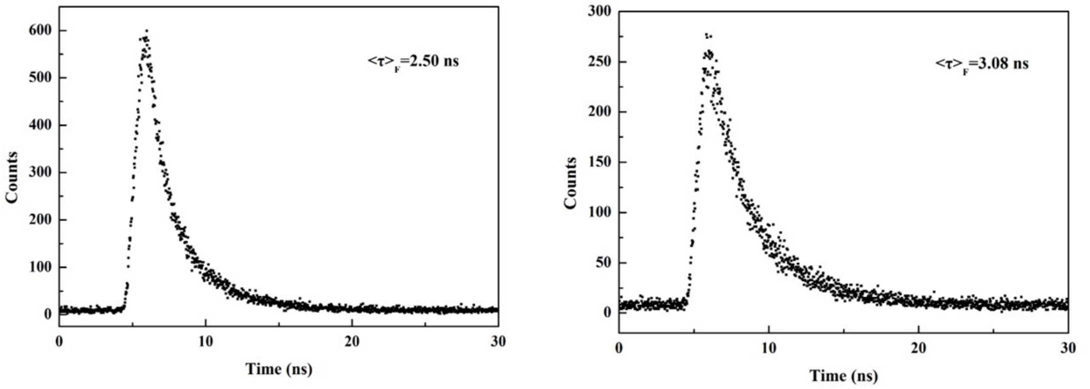


Figure S12. Decay curves of the 550 nm emission (left) and the 590 nm emission (right).

12. The color change of TPE=C4 powder after fuming with TFA

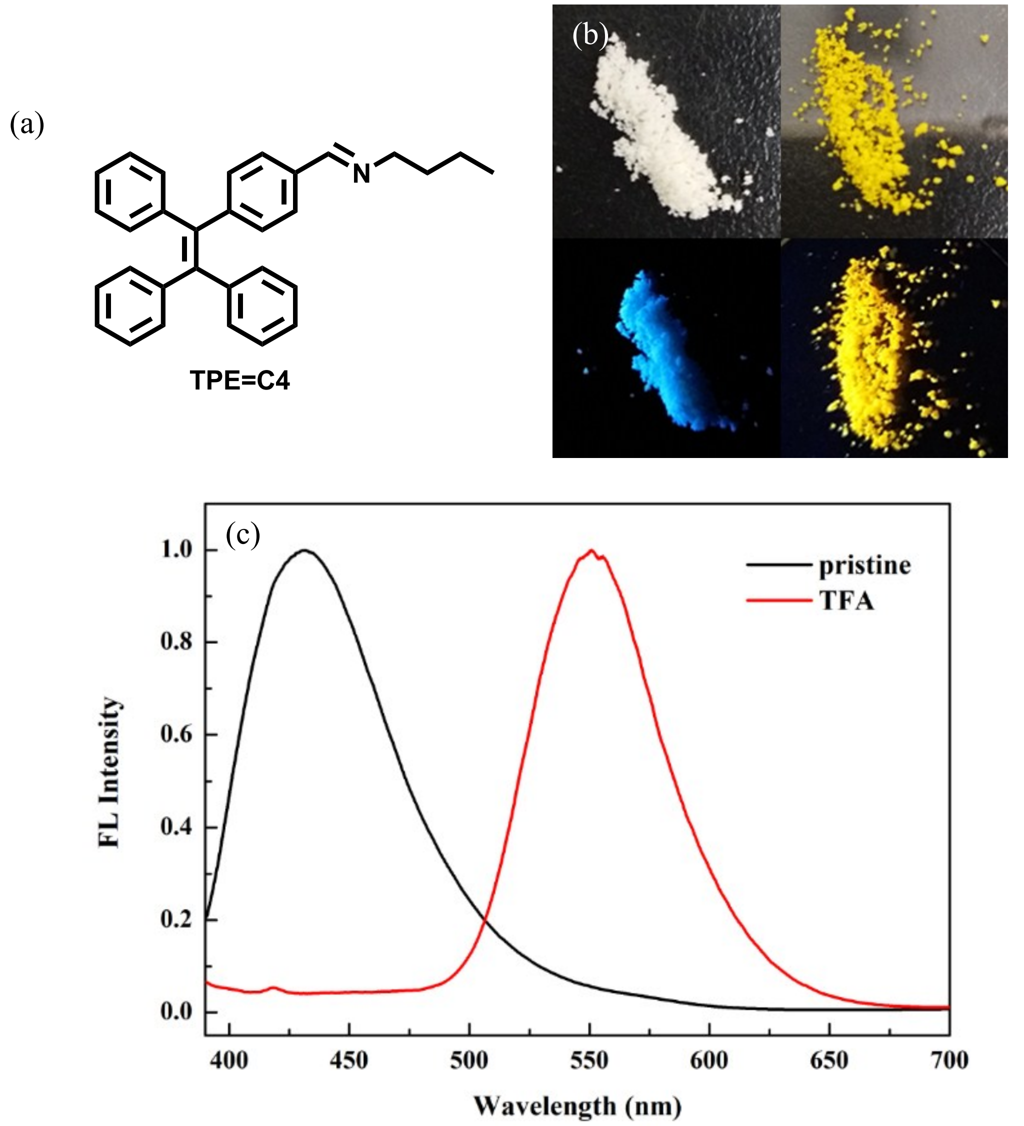


Figure S13. (a) Molecular structure of **TPE=C4**. The color change of (b) the **TPE=C4** powder after fuming with TFA and (c) the corresponding fluorescence spectra.

13. Reversible color change between the treatments of TFA and TEA

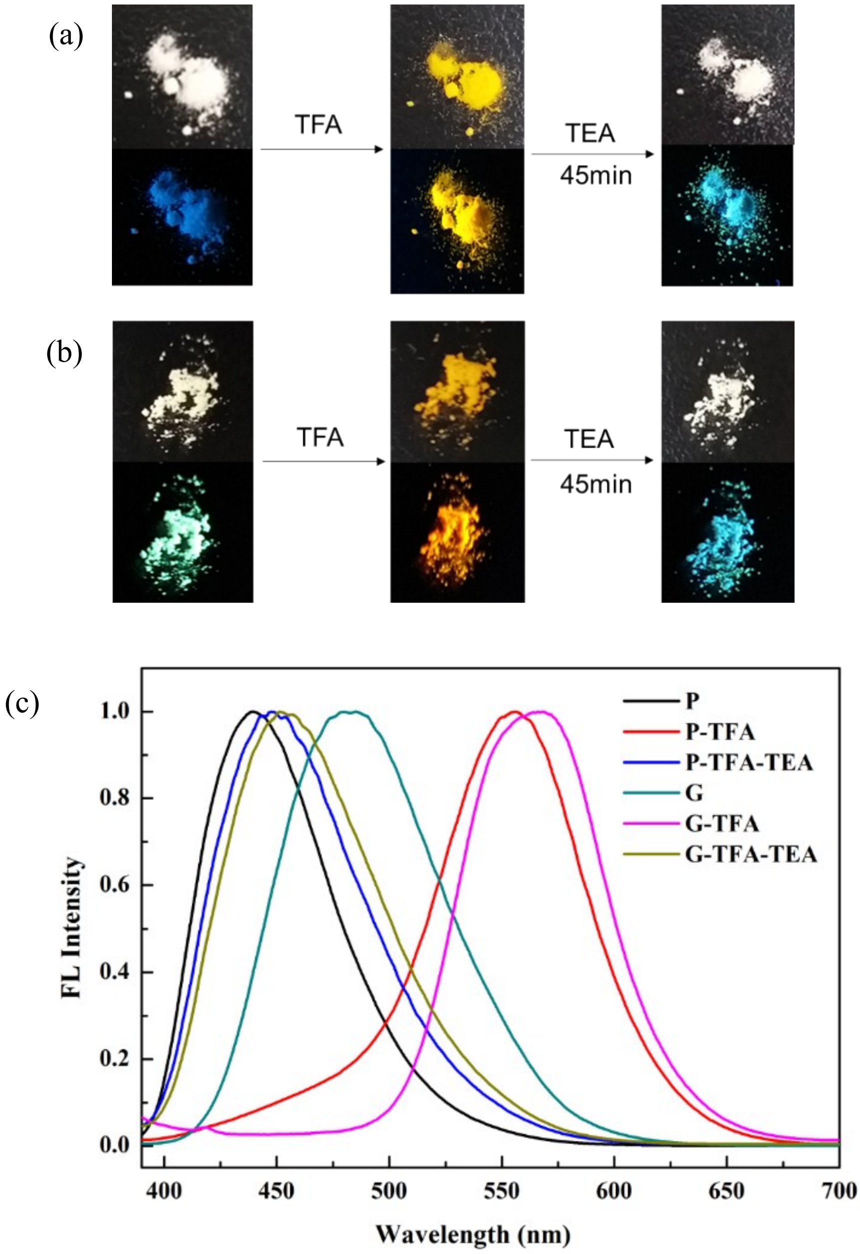


Figure S14. The color change of (a) the TFA-treated pristine powder (P) and (b) the TFA-treated ground powder (G) recovered with TEA and (c) the corresponding fluorescence

References

[1] C. Ma, B. Xu, G. Xie, J. He, X. Zhou, B. Peng, L. Jiang, B. Xu, W. Tian, Z. Chi, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2014, 50, 7374-7377.