

Supporting Information

Mechanically Controlled FRET to Achieve Independent Three Colors Switch

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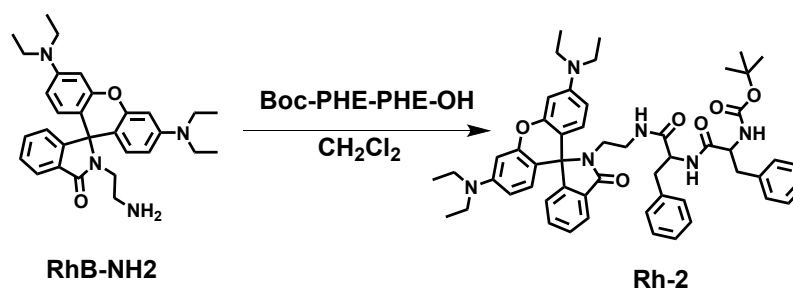
1. Materials and General Methods

All the solvents and reactants were purchased from the commercialized companies and used as received without further purification except for specifying otherwise. ^1H NMR was recorded on the 400 MHz (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/F-920 fluorescence spectrophotometer. The calculation of quantum yield was performed on the Nanolog/FluoroLog-3-2-Ihr320 combined measurement system for infrared fluorescence equipped with an integrating sphere. Fluorescence lifetime were acquired on the Lifespec-Red Picosecond Lifetime Spectrometer ($\lambda_{\text{ex}}=365\text{nm}$). Differential scanning calorimetry (DSC) measurement was carried out by using TA instruments Q100 DSC. Wide angle X-ray diffraction (WAXD) experiments were measured on a Philips X'PertPro diffractometer with a 3 kW ceramic tube as the X-ray source ($\text{Cu K}\alpha$) and an X'celerator detector. Scanning electron microscope (SEM) images were carried out on a Helios NanoLab 600i Dual Beam FIB/FE-SEM (FEI, USA). All the samples were coated with gold before test.

2. Synthesis of Rh-2 and TP-1

Synthesis of Rh-2

Rh-2 was prepared according to the following procedures and reported in our previous paper¹.



Scheme S1. The synthetic route of **Rh-2**.

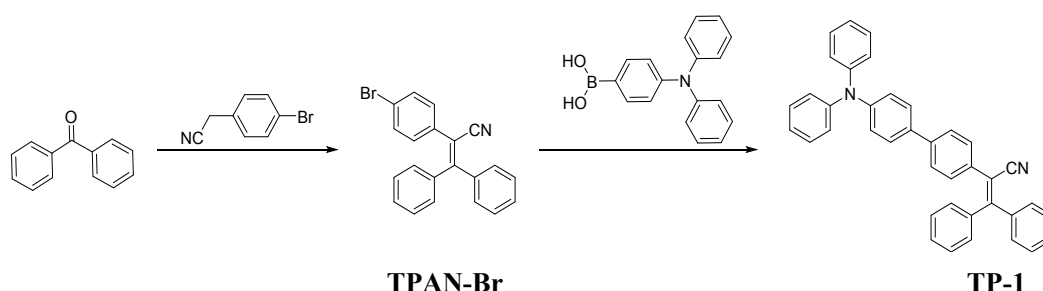
RhB-NH₂ (2.21 g, 4.6 mmol) and Boc-PHE-PHE-OH (2.25 g, 5.5 mmol) were dissolved in dichloromethane (50 mL). After stirring at $-15\text{ }^\circ\text{C}$ (ice-salt bath) for 15 min, a dichloromethane solution containing dicyclohexylcarbodiimide (DCC, 1.12 g, 5.5 mmol) and DMAP (0.10 g, 0.8 mmol) was added dropwise. The solution was kept stirring for 48 h, then the solvent was evaporated. The residue was purified by the column chromatography (dichloromethane/petroleum ether =1/1, v/v) to afford **Rh-2** as a white powder with a yield of 76%.

^1H NMR: (400 MHz, CDCl_3) δ /ppm: 7.87~7.85 (m, 1H, Ar-H), 7.45~7.43 (m, 2H, Ar-H), 7.24~7.23 (m, 1H, Ar-H), 7.21~7.15 (m, 6H, Ar-H), 7.07~7.05 (m, 4H, Ar-H), 6.53~6.51 (d, 1H, NH-), 6.37~6.32 (m, 4H, Ar-H), 6.27~6.24 (m, 2H, Ar-H), 5.05~5.03 (m, 1H, ArCH₂CH-), 4.55~4.50 (m, 1H, ArCH₂CH-), 3.34~3.32 (m, 8H, CH₃CH₂-), 3.21~3.19 (m, 1H, ArCH₂-), 3.16~3.01 (m, 4H, -NCH₂CH₂NH-), 2.99~2.93 (m, 2H, ArCH₂-), 2.83~2.78 (m, 1H, ArCH₂-), 1.37 (s, 9H, (CH₃)₃C-), 1.18~1.15 (t, 12H, CH₃CH₂-).

^{13}C NMR: (125 MHz, CDCl_3) δ /ppm: 170.79, 169.83, 169.71, 153.73, 153.31, 153.24, 148.93, 136.91, 136.68, 132.76, 130.36, 129.43, 129.34, 128.57, 128.52, 128.49, 128.40, 128.11, 126.79, 126.71, 123.84, 122.96, 108.23, 104.70, 97.74, 80.01, 65.60, 55.81, 54.46, 44.37, 40.72, 39.55, 38.21, 28.27, 12.62.

ESI-MS: Calcd. For $C_{53}H_{62}N_6O_6$ $[M+H]^+$: 879.48036. Found: 879.47786.

Synthesis of TP-1



Scheme S2. The synthetic route of TP-1.

Synthesis of TPAN-Br

Benzophenone (4.34 g, 23.8 mmol) and NaH (60%, 1.2 g, 30 mmol) was dissolved in toluene (40 mL), the solution was reflux for 10 min under nitrogen. Then, 4-bromophenylacetonitrile (5 g, 25.5 mmol) in toluene (70 mL) was added dropwise in 1 h by the injection. The solution was kept reflux at 120°C overnight. After cooling to room temperature, 100 mL of water was added to the mixture solution, the organic layer was collected and washed with brine twice. The organic phase was concentrated under vacuum and the crude product was washed with methanol to afford 3.14 g (34 % yield) yellow powder.

¹H NMR (400 MHz, CDCl₃, δ): 7.42~7.45 (m, 5H), 7.33~7.35 (d, 2H), 7.27~7.30 (m, 1H), 7.20~7.23 (t, 2H), 7.11~7.13 (d, 2H), 6.99~7.01 (d, 2H).

Synthesis of TP-1

TP-1 was synthesized according to the literature report². TPAN-Br (868 mg, 2.41 mmol), TPA-B(OH)₂ (766 mg, 2.65 mmol) and Pd(dppf)Cl₂ (20 mg, 0.03 mmol) were added into a Schlenk flask. The flask was evacuated under vacuum and then flushed with dry nitrogen three times. 30 mL anhydrous tetrahydrofuran and 6 mL saturated sodium carbonate solution were added into the flask by the injection. The mixture was refluxed for 24 h. Then, the solvent was evaporated. The residue was purified by the column chromatography (petroleum ether: dichloromethane=3:1, v/v) to afford TP-1 in a yield of 76% (950 mg).

¹H NMR (400 MHz, CDCl₃, δ): 7.42~7.45 (m, 9H), 7.31 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.26~7.27 (d, 2H), 7.25 (s, 2H), 7.19~7.22 (t, 2H), 7.09~7.12 (m, 6H), 7.02~7.07 (m, 4H).

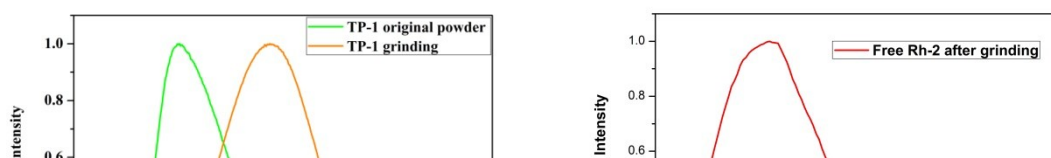
¹³C NMR (125 MHz, CDCl₃) δ/ppm: 157.53, 147.78, 147.69, 140.68, 140.51, 139.38, 133.78, 133.33, 130.94, 130.27, 130.11, 130.00, 129.46, 129.14, 128.60, 128.48, 127.73, 126.52, 124.69, 123.82, 123.26, 120.28, 111.52.

ESI-MS: Calcd. For $C_{39}H_{28}N_2$ $[M+H]^+$: 524.224700. Found: 524.223247

3. The preparation of the blend

The original powder was simply prepared by dissolving TP-1 (5 mg) in a mixed solvent of dichloromethane/petroleum ether (v/v=1:9, 10 mL). The mixed solvent was evaporated at room temperature thoroughly, then a methanol solution (5 mL) of Rh-2 (41 mg) was added and the mixture was kept at room temperature to evaporate the solvent slowly at room temperature for obtaining the original powder.

4. Fluorescent spectra of free TP-1 and Rh-2



(a)

(b)

Figure S1. (a) Fluorescence spectra of free **TP-1**, original sample (green line), the same sample after grinding (yellow line); (b) fluorescence spectra of free **Rh-2** after grinding.

5. NMR spectra and FTMS spectra of Rh-2

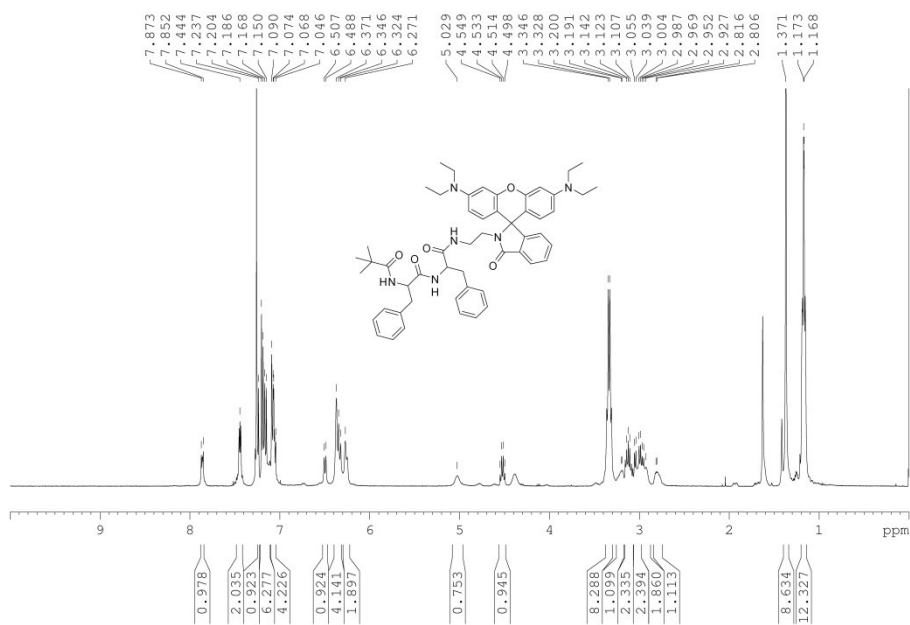


Figure S2. ¹H NMR spectrum of **Rh-2** in CDCl₃.

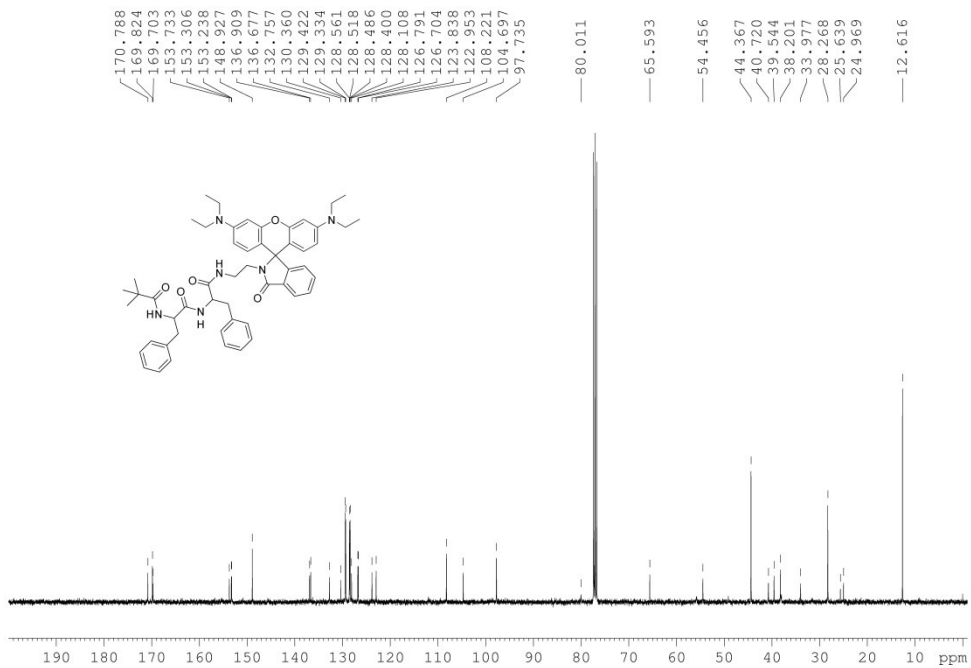


Figure S3. ^{13}C NMR spectrum of Rh-2 in CDCl_3

Analysis Info

Analysis Name 15020134_20150205_000001.d
 Sample RhB-Phe(2)-Boc
 Comment ESI Positive

Acquisition Date 2/5/2015 1:31:49 PM
 Instrument Bruker Apex IV FTMS
 Operator Peking University

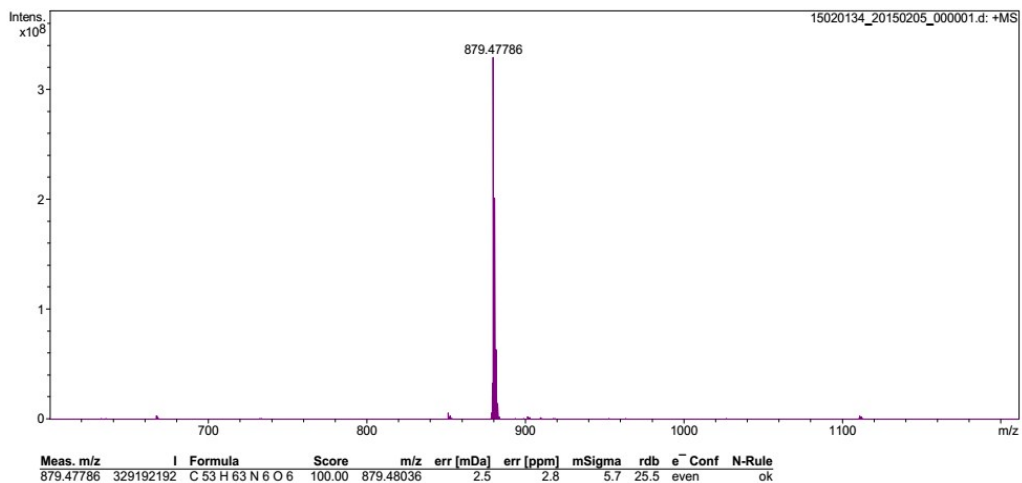


Figure S4. FTMS spectrum of Rh-2.

6. NMR spectra and FTMS spectra of TP-1

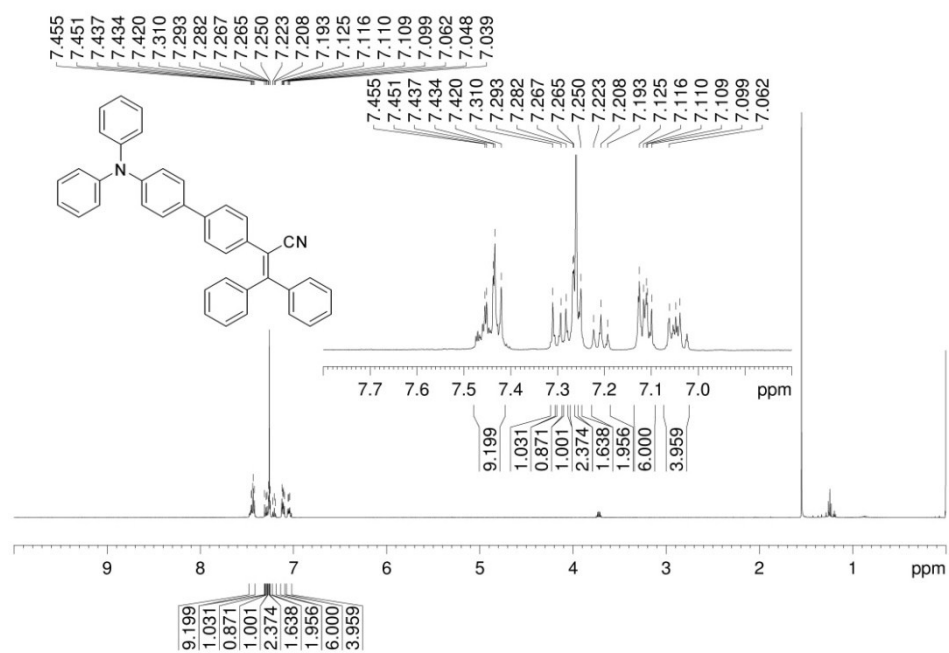


Figure S5. ¹H NMR spectrum of TP-1 in CDCl₃.

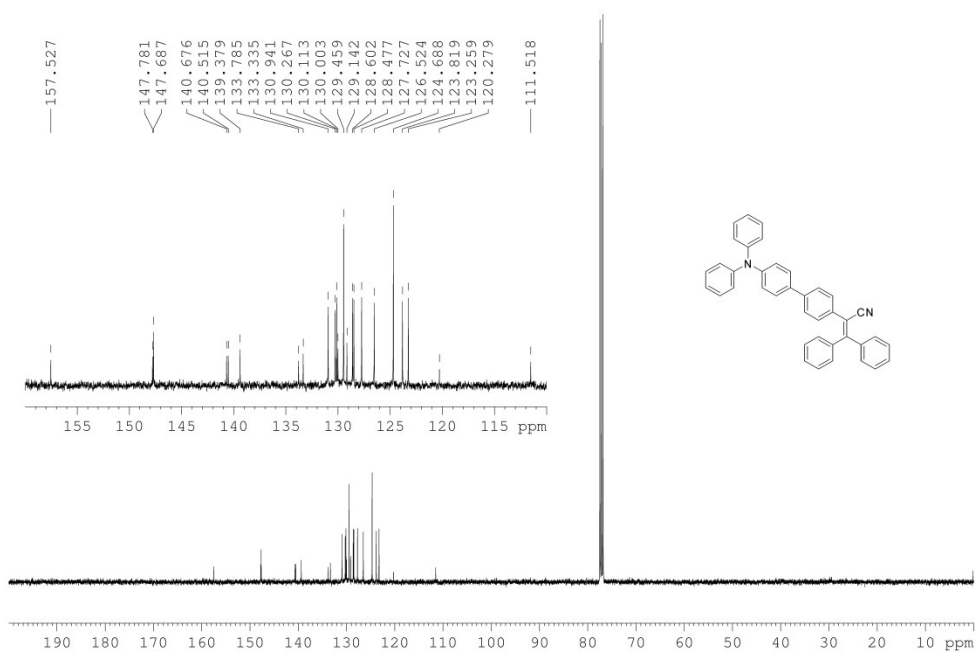


Figure S6. ¹³C NMR spectrum of TP-1 in CDCl₃.

Analysis Info

Analysis Name FTMS-16060294_Pos_20160628_000001.d
Sample TPATPAN
Comment

Acquisition Date 6/28/2016 9:56:09 AM
Instrument Bruker Solarix XR FTMS
Operator Peking University

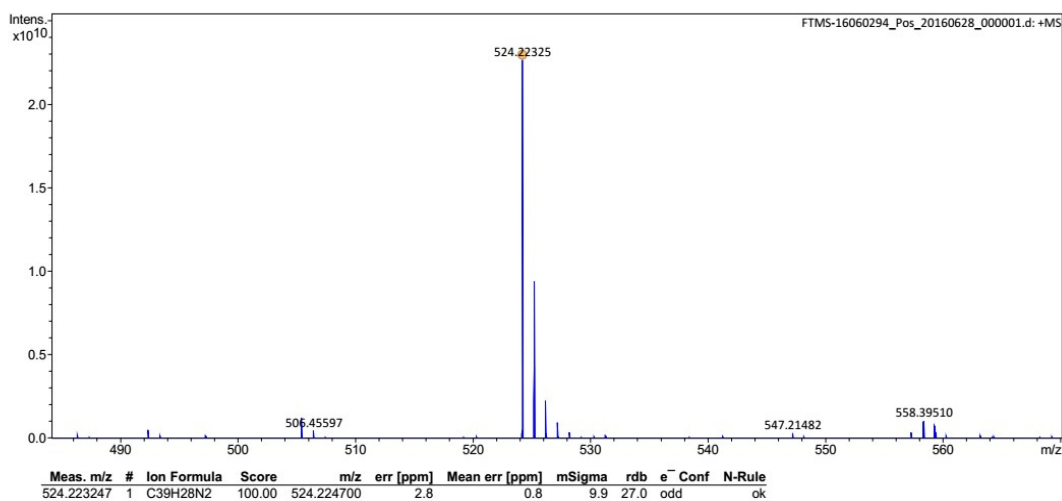


Figure S7. FTMS spectrum of TP-1.

7. The emission of TP-1 and the absorption of Rh-2

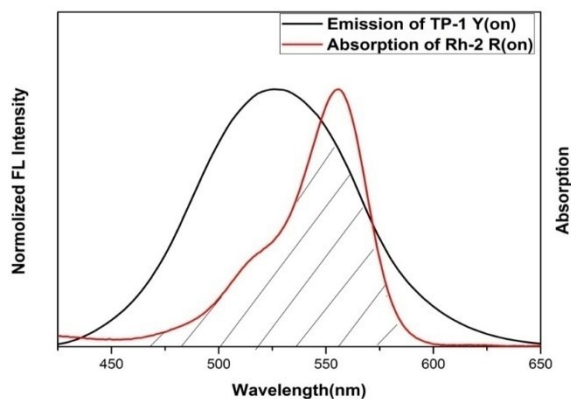


Figure S8. The spectra overlap of the donor's emission (TP-1) and the acceptor's absorption (Rh-2).

8. The fluorescence spectra of the blend with different TP-1 and Rh-2 molar ratio

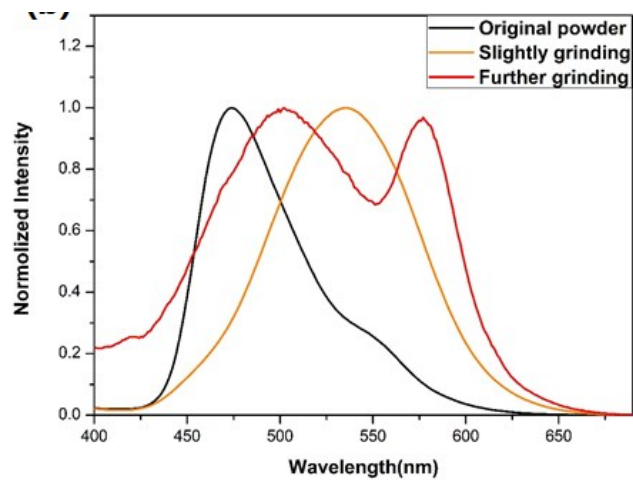


Figure S9. The fluorescence spectra of the TP-1/Rh-2 (the molar ratio of TP-1/Rh-2=1:3), the original powder (black line), the powder after slightly grinding (yellow line), and the same powder after further grinding (red line).

9. Fluorescence spectra and XRD profiles of the recovered powder by heating and solvent treating (methanol)

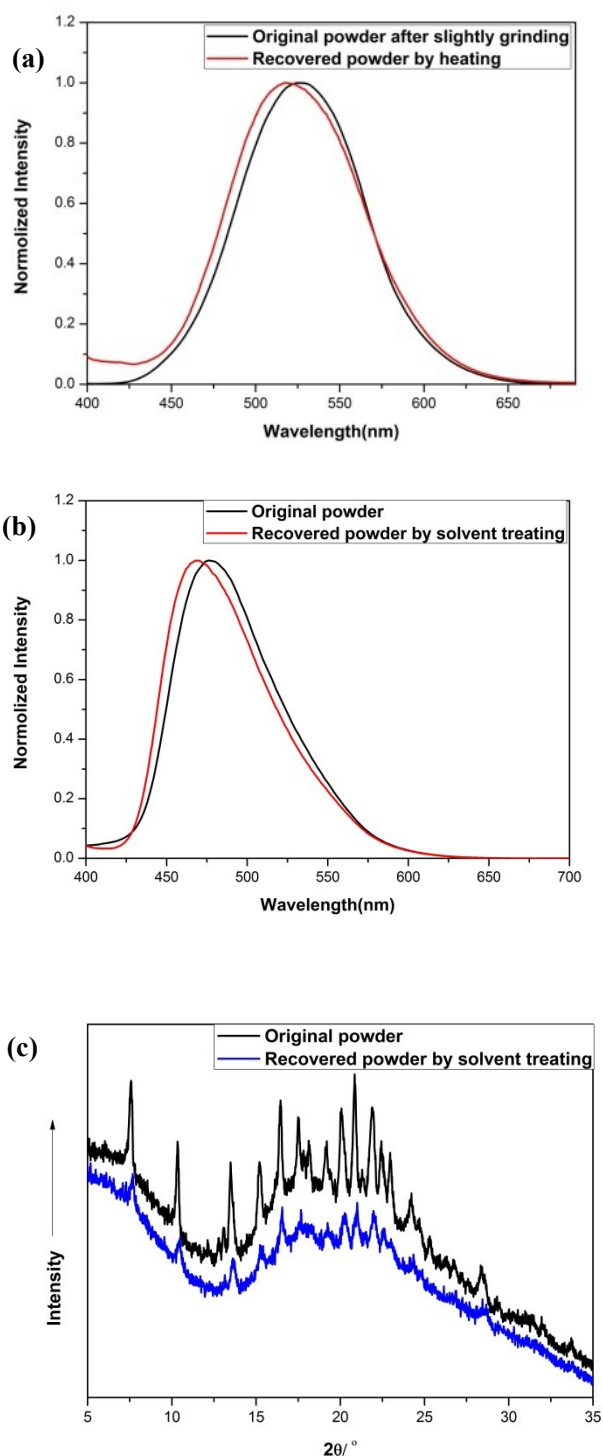


Figure S10. (a) Fluorescence spectra of the original powder after slightly grinding (black line) and the recovered sample by heating the red powder at 150°C for 5 min (red line); (b) fluorescence spectra of the original powder (black line) and the recovered sample treated by methanol (red line); (c) XRD patterns of the original sample (black line) and the recovered sample treated by methanol (blue line).

10. Fluorescent lifetime

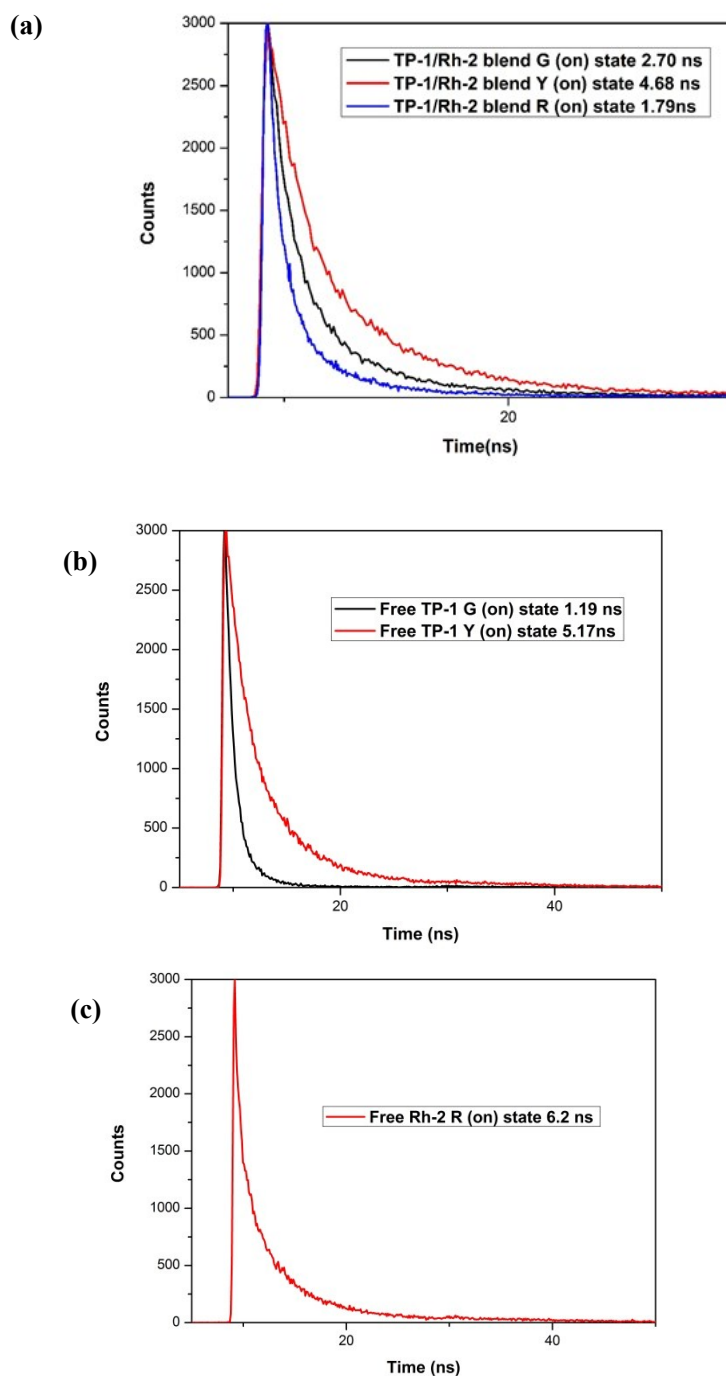


Figure S11. Fluorescent lifetime of (a) the TP-1/Rh-2, G (on) state (green line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=490\text{nm}$), Y (on) state (yellow line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=540\text{nm}$) and R (on) state (red line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=540\text{nm}$); (b) free TP-1 powder, G (on) state (black line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=490\text{nm}$) and Y (on) state (red line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=540\text{nm}$); (c) free Rh-2 powder, R (on) state (red line, $\lambda_{\text{ex}}=365\text{nm}$, $\lambda_{\text{em}}=588\text{nm}$).

11. Time resolved fluorescent spectra

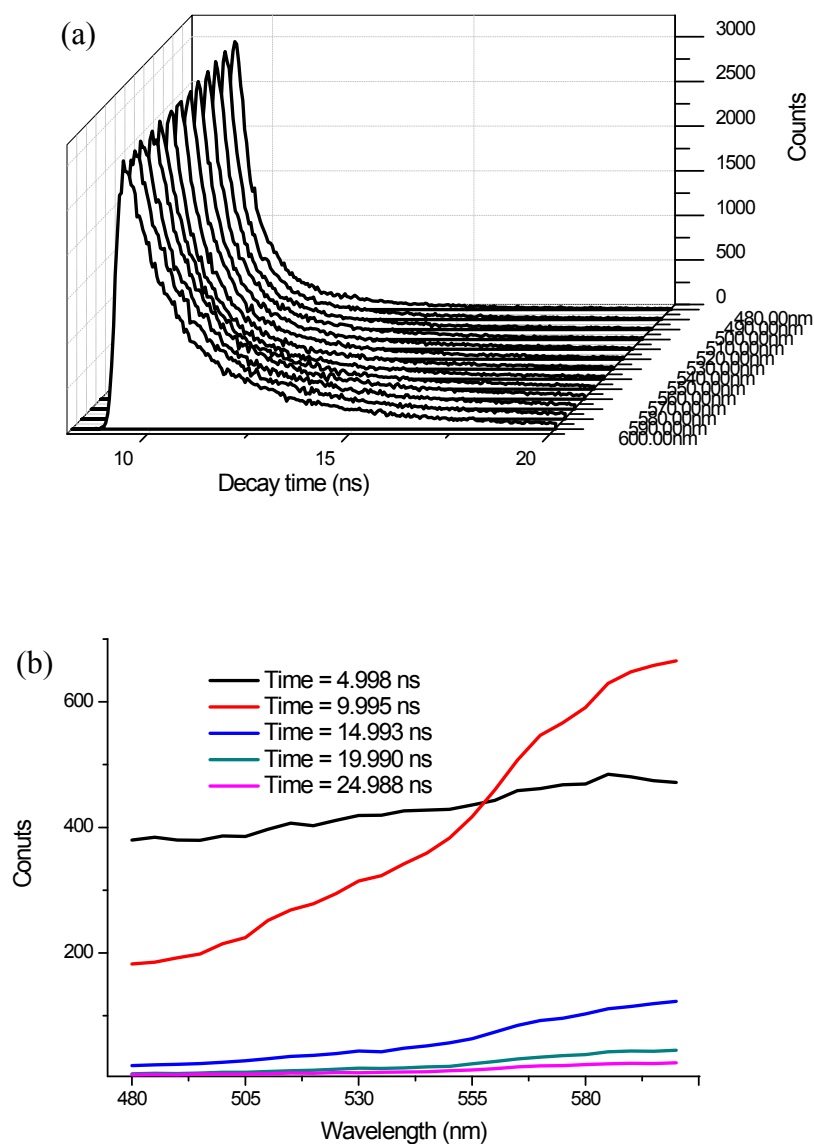


Figure S12. (a) Time-resolved fluorescence decay of the blend in R (on) state. $\lambda_{\text{ex}} = 365$ nm, and $\lambda_{\text{em}} = 480$ nm to 600 nm in 10 nm steps; (b) sliced time-resolved fluorescent spectra of the same R (on) state of the blend.

12. SEM images of the aggregates from free TP-1 and free Rh-2

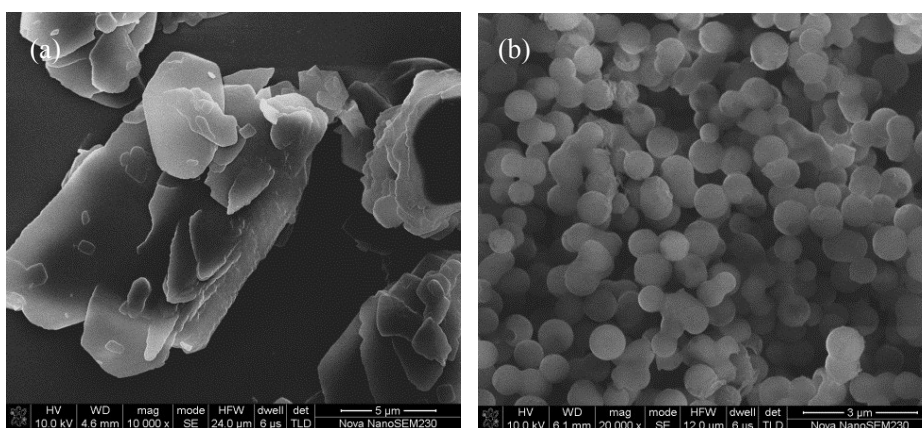


Figure S13. SEM images of (a) TP-1 aggregate from dichloromethane/petroleum; (b) Rh-2 sphere-like aggregates obtained from methanol.

13. DSC Profiles

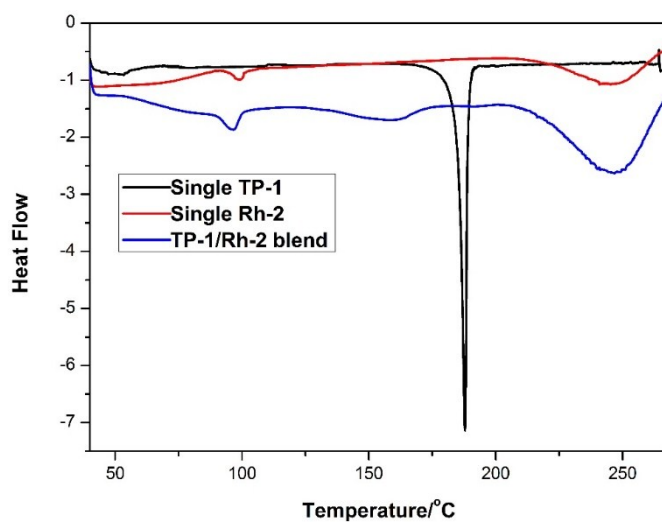


Figure S14. DSC profiles of free TP-1, Rh-2 and the TP-1/Rh-2.

14. Mechanochromic mechanism of the TP-1/Rh-2 blend

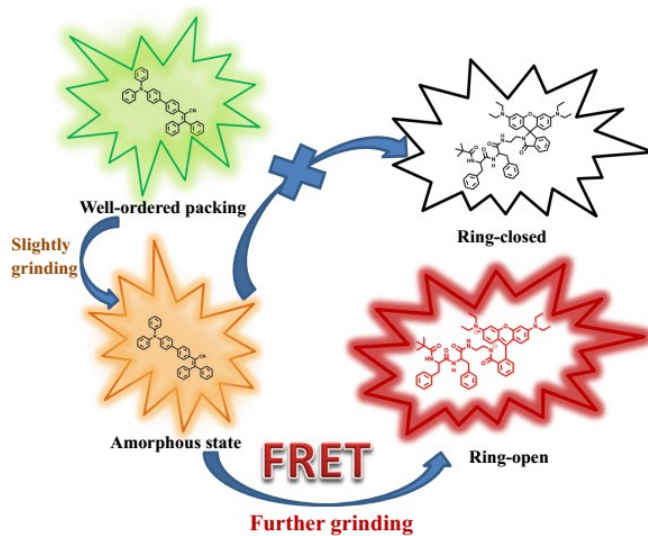


Figure S15. Mechanochromic mechanism of the TP-1/Rh-2 blend.

References

- (1)Ma, Z.; Wang, Z.; Xu, Z.; Jia, X.; Wei, Y. *Journal of Materials Chemistry C* 2015, 3, 3399.
- (2)Yuan, W. Z.; Tan, Y.; Gong, Y.; Lu, P.; Lam, J. W. Y.; Shen, X. Y.; Feng, C.; Sung, H. H. Y.; Lu, Y.; Williams, I. D.; Sun, J. Z.; Zhang, Y.; Tang, B. Z. *Advanced Materials* 2013, 25, 2837.