

Supporting Information

Multiple stimulus responsive behavior of a triphenylamine-substituted acylhydrazone derivative

Hongyang Qi ^a, Binglian Bai ^{a*}, Haitao Wang ^b, Jue Wei ^{a*}, Min Li ^{b*}, Hong Xin ^c

^a College of Physics, Jilin University, Changchun 130012, PR China. E-mail:

baibinglian@jlu.edu.cn, weijue@jlu.edu.cn; ^b Key Laboratory for Automobile Materials, Ministry of Education, Institute of Materials Science and Engineering, Jilin University, Changchun 130012, PR China. E-mail: minli@jlu.edu.cn; ^c College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, PR China.

Experimental Section

Measurements

¹H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer, using dimethyl sulfoxide-*d* and chloroform-*d* as solvent and tetramethylsilane (TMS) as an internal standard ($\delta=0.00$). Field emission scanning electron microscopy (FE-SEM) images were taken with a JSM-6700F apparatus. X-ray diffraction (XRD) experiments were performed on a Bruker Avance D8 X-ray diffractometer. FT-IR spectra were recorded with a Perkin-Elmer spectrometer (Spectrum One B). The xerogels were obtained by freezing and pumping the partial organogel of TBHM for 8 h, and then the xerogels were pressed into a tablet with KBr for FT-IR measurement. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer, and photoluminescence was measured on a Perkin-Elmer LS 55 spectrometer, and the excitation wavelength is 365nm. The HR-MS spectra were recorded on a Autoflex speed TOF/TOF spectrometer. The room-temperature PL quantum yields in solutions of varying polarities were measured using sulfuric acid aqueous solution ($\Phi=0.546$) as the standard.

TBHM: ¹H NMR (300 MHz, DMSO-*d*₆): ppm 11.57(s, 1H), 8.36(s, 1H), 7.88(d, 2H), 7.59(d, 2H), 7.35 (t, 4H), 7.16-6.92 (m, 10H), 4.03 (t, 2H), 1.72 (m, 2H), 1.49-1.17 (m, 18H), 0.85 (t, 3H).

FT-IR (KBr, cm^{-1}): 3179, 3031, 3005, 2920, 2850, 1647, 1591, 1565, 1508, 1489, 1421, 1381, 1317, 1278, 1263, 1174, 1146, 1103, 1071, 1028.

^{13}C NMR (300 MHz, $\text{DMSO-}d_6$): ppm 160.92, 148.60, 146.24, 129.37, 127.64, 125.21, 124.58, 123.40, 121.28, 113.51, 67.59.

Elemental analysis: calculated for $\text{C}_{38}\text{H}_{45}\text{N}_3\text{O}_2$, C, 79.27; H, 7.88; N, 7.30. Found: C, 79.10; H, 7.75; N, 7.33.

MS: m/z: calculated for: 575.35, found: 575.52.

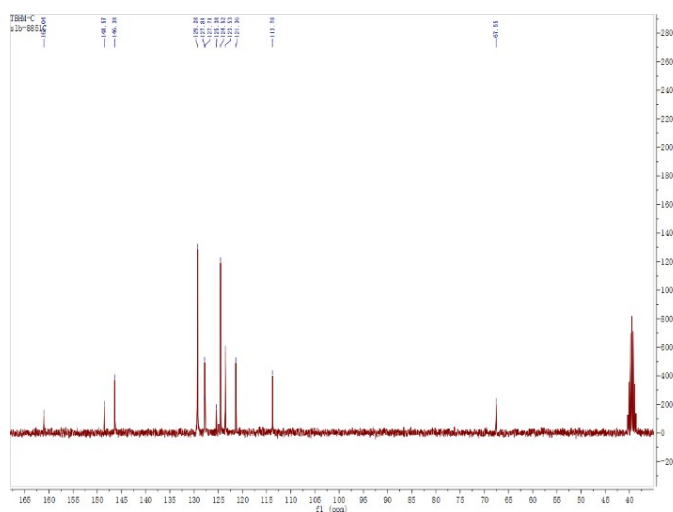


Fig. S1 ^{13}C NMR spectrum of TBHM in $\text{DMSO-}d_6$.

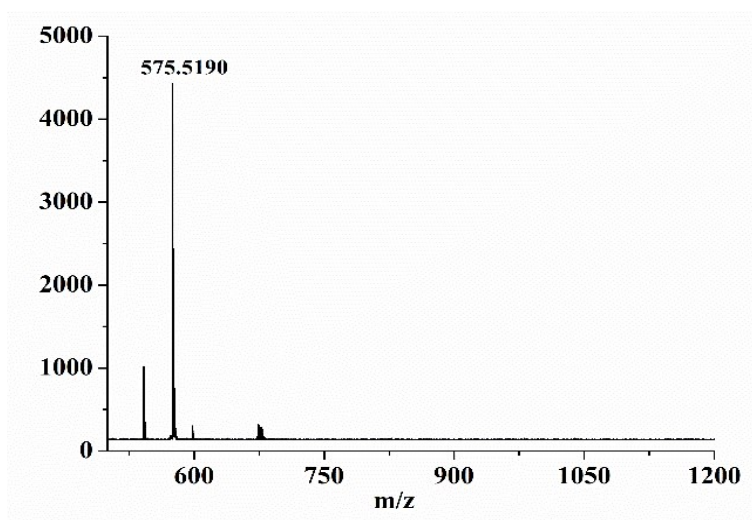


Fig. S2 HR-MS spectrum of TBHM.

Table. S1 Physical properties of TBHM($1 \times 10^{-5} \text{M}$) in different solvents.

Solvent	Cyclohexane	toluene	THF	EA	DMF	DMSO
$\lambda_{(ab)}$ ^a	362	367	365	363	368	369
$\lambda_{(em)}$ ^b	400	419	431	433	456	462
$\Delta\nu$ ^d	2624	3386	4202	4431	5239	5465
Φ_f (%)	3.26%	9.06%	15.87%	11.88%	23.87%	27.25%

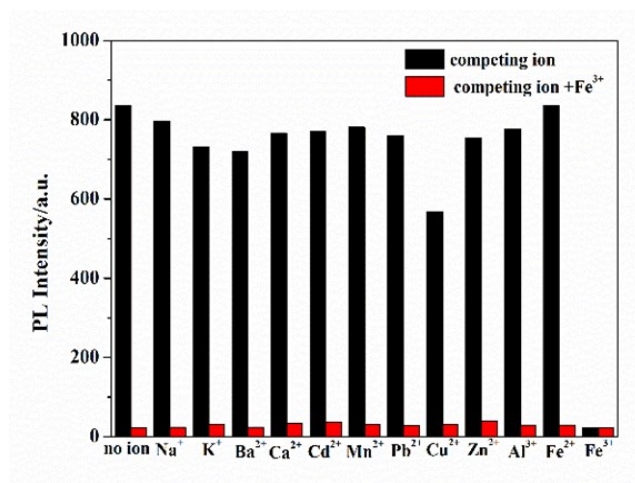


Fig. S3 Fluorescence intensity changes of TBHM ($5 \times 10^{-5} \text{M}$) upon addition of Fe³⁺ in the presence of other interfered metal ions in DMSO/H₂O (9:1).

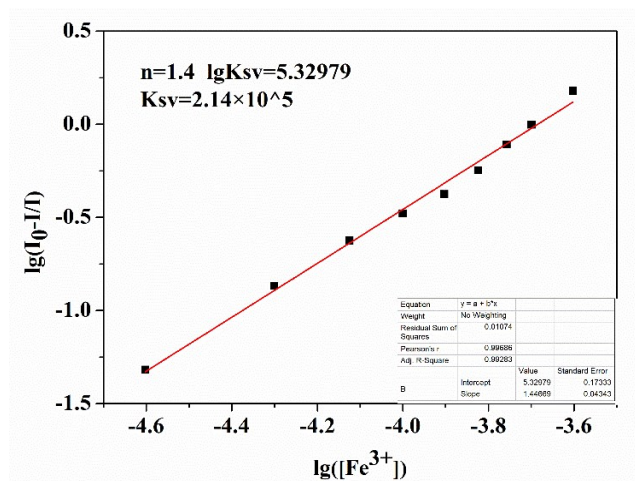


Fig. S4 The titration curves of TBHM (5×10^{-5} M) when the concentration range of 2.5×10^{-5} M to 2.5×10^{-4} M.

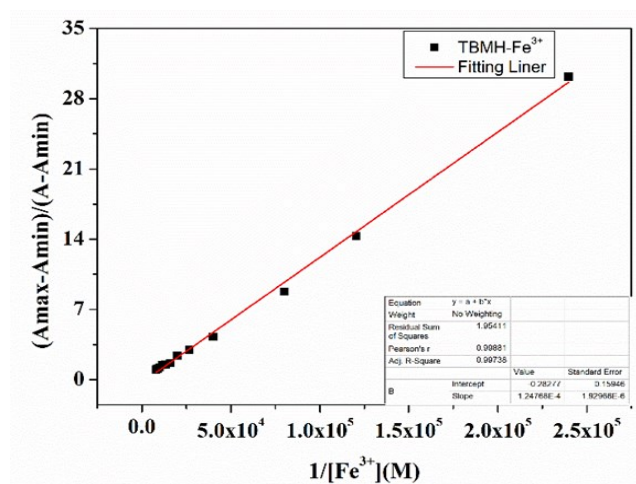


Fig. S5 Benesi-Hildebrand plot of TBHM with Fe^{3+} .

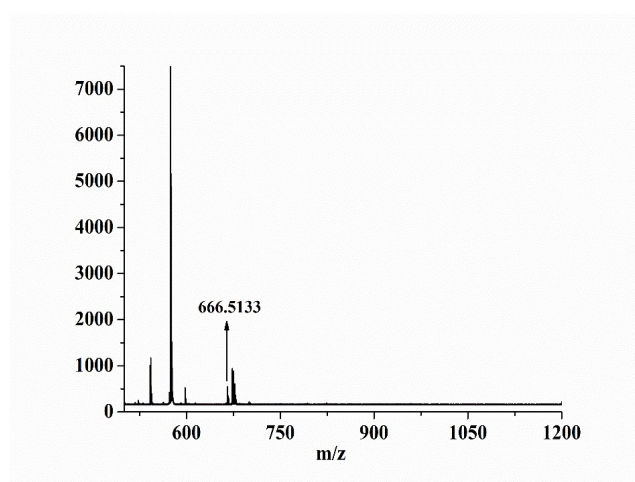


Fig. S6 HR-MS spectrum of **TBHM+Fe³⁺** complex in tetrahydrofuran (0.1mg/ml, Fe^{3+} is introduced in the form of $FeCl_3 \cdot 6H_2O$, and a chloride ion was complexed). It may be due to the concentration of the solution is high in the MS spectrum (0.1mg/ml), the intermolecular hydrogen bond interactions between C=O and N-H groups in compound TBHM cause the molecules to aggregate themselves, which hinder the interaction between TBHM and Fe^{3+} , therefore, the mass spectrum of TBHM- Fe^{3+} complex is relatively weak.

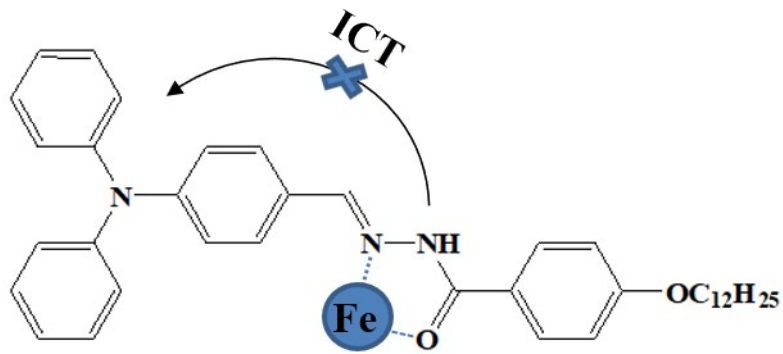


Fig. S7 The possible binding mode for the TBHM with Fe³⁺.

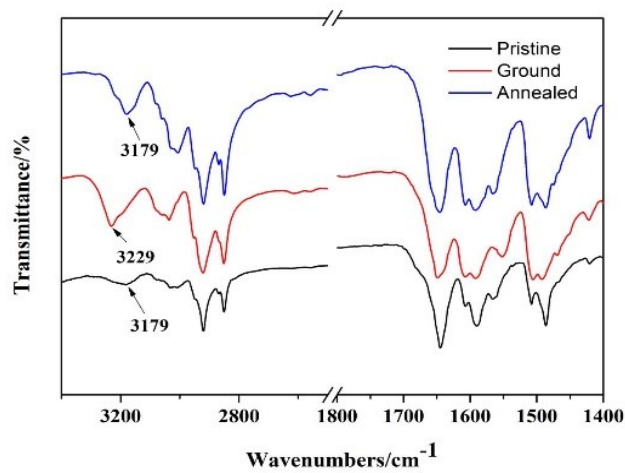


Fig. S8 The FT-IR images of TBHM (a) pristine and (b) ground and (c) annealed.

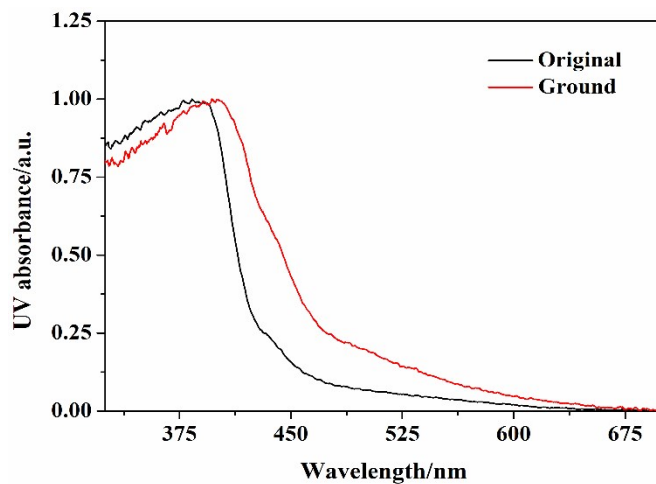


Fig. S9 Normalized UV-vis absorption spectra of as-prepared and ground samples of TBHM.

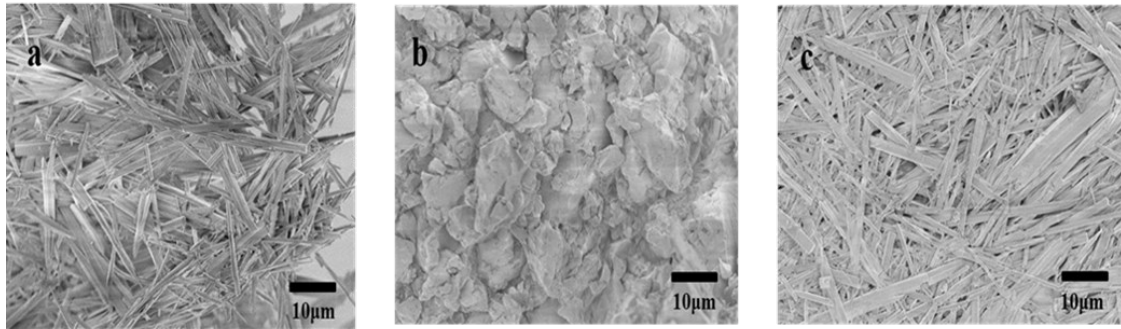
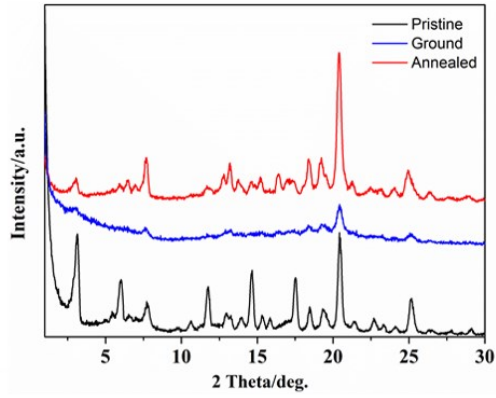


Fig. S10 The XRD and SEM images of TBHM (a) pristine and (b) ground and (c) annealed.

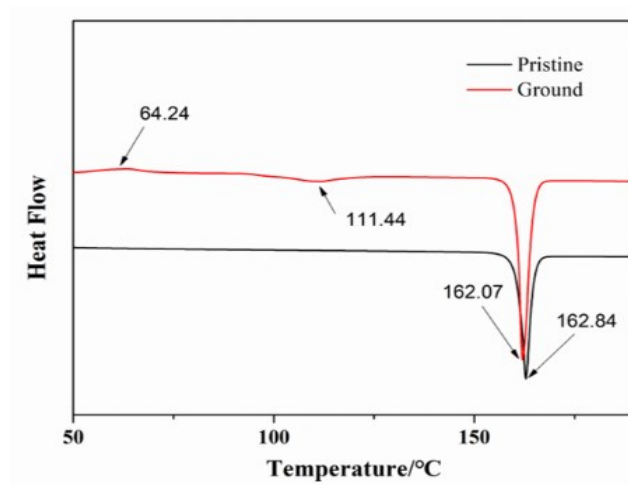


Fig. S11 DSC curve of TBHM before and after grinding on first heating run.

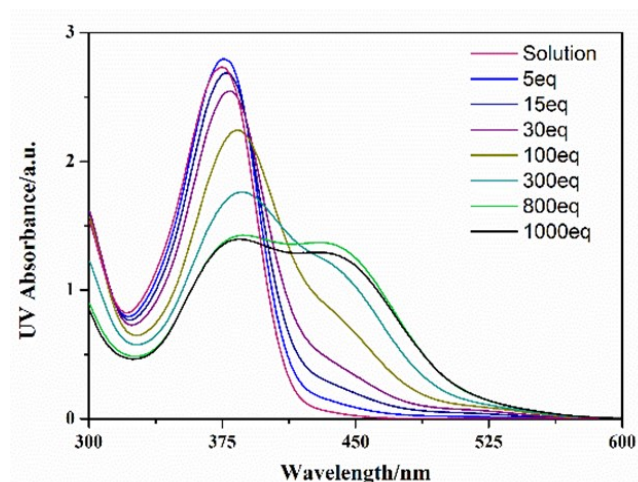


Fig. S12 UV-vis absorption spectral changes of TBHM with the addition of different equivalents of TFA in chloroform solutions.

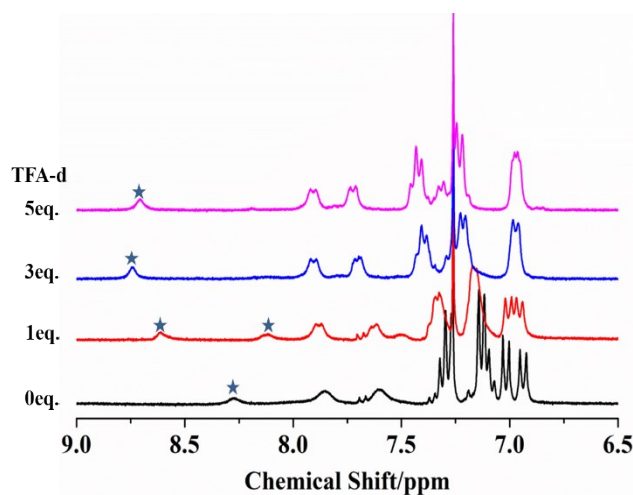


Fig. S13 Partial ^1H NMR spectra of TBHM upon addition of TFA-*d* (0-5eq) in CDCl_3 .

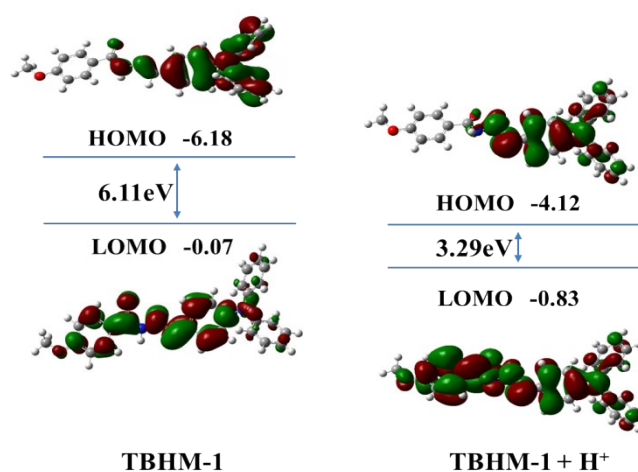


Fig. S14 The molecular frontier orbital contributions calculated from theory for TBHM-1 and its protonated form.

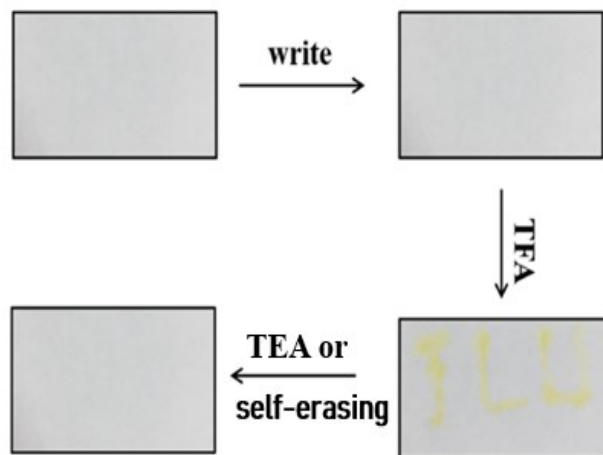


Fig. S15 Photographic images of information encryption and decryption under daylight.