Electronic Supporting Information

Materials and Physical Measurements

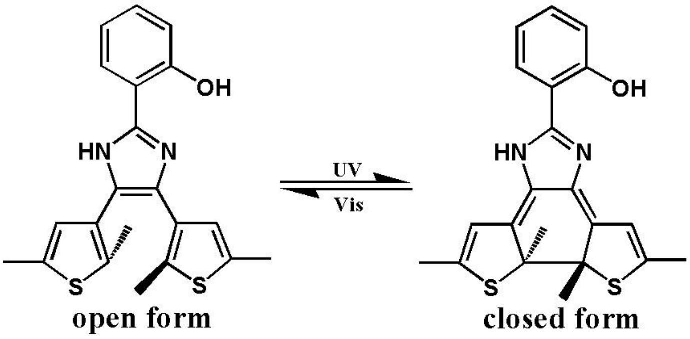
Compound 2-(2-hydroxyphenyl)-4,5-bis(2,5-dimethyl(3-thienyl))-1*H*-imidazole (hpbdtiH) was prepared according to the literature.[S1] All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. The powder XRD patterns were recorded on a BRUKER D8 ADVANCE X-ray diffractometer. Thermal analyses were measured from room temperature to 800 ^{o}C under N_2 gas flow using a Mettler-Toloedo TGA/DSC instrument. The heating rate was 10 ^{o}C/min. Magnetic susceptibility data of **1** were obtained on microcrystalline samples (7.65 mg), using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants.[S2] The UV−vis absorption spectra were carried out on PerkinElmer Lambda950 UV-visible spectrophotometer. Photoirradiation was carried out using a 500 W Xe lamp, and monochromatic light was obtained by passing the light through a monochromator. The ^{1}H NMR spectra were recorded at room temperature with a 500 MHz BRUKER AM-500 spectrometer. The irradiation of ^{1}H NMR sample was carried out using 6 W lamp with light of 365 nm.

Synthesis of $Co(hpbdti)_2 \cdot 3CH_3OH$ (**1**)

To the solution of hpbdtiH (0.2 mmol, 0.0761 g) and $CoCl_2 \cdot 6H_2O$ (0.2 mmol, 0.0476 g) in methanol (5 mL) and acetonitrile (5 mL) was added triethylamine (0.1 mL). The mixture was stirred at room temperature for two days. The resultant solid was filtrated, washed with acetonitrile, and dried in air, obtaining brick red powder (0.0840 g). The solution of such powder in the mixture of CH_3OH (10 mL) and $CHCl_3$ (10 mL) was allowed to evaporate at room temperature, resulting in brick red blocky crystals after one week. These crystals were obtained as a monophasic material based on the powder XRD patterns (Fig. S1). Yield: 49 mg (54% based on hpbdtiH). Anal. found (calcd) for $C_{45}H_{50}O_5N_4S_4Co$: C, 59.31 (59.13); H, 5.20 (5.51), N, 6.37 (6.13). IR (KBr, cm^{-1}): 3620(w), 3201-2854(w), 1601(m), 1553(m), 1533(w), 1477(s), 1454(s), 1311(s), 1261(w), 1244(w), 1310(m), 1215(w), 1139(s), 1041(w), 856(m), 830(m), 766(s), 750(s), 706(m), 501(m), 472(w). Thermal analysis revealed a weight loss of 10.6% in 35-155 ^{o}C, agreeing with the theoretical value 10.5% for three lattice methanol molecules (Fig. S2).

X-Ray crystallographic studies

The colorless needlelike single crystal of hpbdtiH was obtained through the evaporation of its solution of petroleum ether and ethyl acetate. Single crystals of dimensions 0.20 × 0.08 × 0.06 mm^3 for hpbdtiH, and 0.23 × 0.20 × 0.18 mm^3 for **1** were used for structural determination on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at room temperature. A hemisphere of data were collected in the θ range 2.04 to 25.00^{o} for hpbdtiH, and 1.53 to 25.00^{o} for **1** using a narrow-frame method with scan widths of 0.30^{o} in ω and an exposure time of 10 s per frame. Numbers of observed and unique reflections are 10349 and 3344 (R_{int} = 0.1014) for hpbdtiH, and 25715 and 8190 (R_{int} = 0.0397) for **1**, respectively. The data were integrated using the Siemens *SAINT* program,[S3] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full matrix least squares using *SHELXTL*.[S4] All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. The crystallographic data for compound **1** are listed in Table S1, and selected bond lengths and angles are given in Tables S2. CCDC 937485 contains the supplementary crystallographic data of **1**, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme S1

The χ”-frequency equations 1 and 2

Equation 1: for single-step relaxation

$$\chi''(\omega) = \chi_s + \frac{(\chi_T - \chi_s)[(\omega\tau)^{1-\alpha} cos(\alpha\pi/2)]}{1+(\omega\tau)^{2-2\alpha} + 2(\omega\tau)^{1-\alpha} sin(\alpha\pi/2)}$$

Equation 2: for two-step relaxation (P is percent of one of two relaxations)

$$\chi''(\omega) = \chi_s + \frac{P(\chi_T - \chi_s)[(\omega\tau_1)^{1-\alpha_1} cos(\alpha_1\pi/2)]}{1+(\omega\tau_1)^{2-2\alpha_1} + 2(\omega\tau_1)^{1-\alpha_1} sin(\alpha_1\pi/2)} + \frac{(1-P)(\chi_T - \chi_s)[(\omega\tau_2)^{1-\alpha_2} cos(\alpha_2\pi/2)]}{1+(\omega\tau_2)^{2-2\alpha_2} + 2(\omega\tau_2)^{1-\alpha_2} sin(\alpha_2\pi/2)}$$

Table S1 Crystallographic data for **1**.

	1
Formula	$C_{45}H_{50}O_5N_4S_4Co$
M	914.06
Crystal system	Monoclinic
Space group	$P2_1/c$
T/K	173
a/Å	12.4660(12)
b/Å	26.573(2)
c/Å	14.9037(14)
β / °	109.321(2)
V/Å^3	4659.0(7)
Z	4
D_c (g cm^{-3})	1.303
F(000)	1916
GooF on F^2	1.028
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0449, 0.1248
R_1, wR_2 (all data)^a	0.0682, 0.1406
$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$/e Å^{-3}	0.316, -0.262

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (^{o}) for **1**

Co1-O1	1.9283(19)	Co1-N1	1.968(2)
Co1-O2	1.908(2)	Co1-N3	1.983(2)
O1-C21	1.334(3)	N2-C15	1.346(3)
O2-C42	1.329(3)	N3-C35	1.389(4)
N1-C15	1.339(3)	N3-C36	1.341(3)
N1-C14	1.385(3)	N4-C34	1.375(4)
N2-C13	1.378(3)	N4-C36	1.350(3)
O(2)-Co(1)-O(1)	99.72(9)	O(2)-Co(1)-N(3)	93.43(9)
O(2)-Co(1)-N(1)	133.73(9)	O(1)-Co(1)-N(3)	121.76(9)
O(1)-Co(1)-N(1)	94.56(8)	N(1)-Co(1)-N(3)	115.56(9)

Table S3 Relaxation times (s) and α values for process A for **1**.

T (K)	τ(A)	α(A)
5.4	4.12211E-4	0.32442
5.6	3.27859E-4	0.25366
5.8	2.24408E-4	0.22669
6.0	1.71887E-4	0.19073
6.2	1.19919E-4	0.18252
6.4	1.13781E-4	0.10968
6.6	6.47226E-5	0.15365

Table S4 Relaxation times (s) and α values of processes B and C for **1**.

T (K)	τ(B)	α(B)	τ(C)	α(C)
2.0	0.19525	0.20621	0.00402	0.14564
2.2	0.18617	0.24811	0.00321	0.14
2.4	0.13806	0.1549	0.00264	0.13779
2.6	0.10744	0.17986	0.00204	0.11491
2.8	0.08878	0.13092	0.00173	0.12093
3.0	0.06876	0.09671	0.00144	0.10154
3.2	0.05265	0.06127	0.0012	0.12325
3.4	0.03984	0.03863	0.00102	0.12425
3.6	0.02981	0.03954	8.46704E-4	0.13943
3.8	0.02161	0.00616	7.1938E-4	0.10304
4.0	0.01648	0.03592	5.95239E-4	0.13559
4.2	0.01122	0.11745	4.98155E-4	0.07135
4.4	0.00867	0.00595	4.37676E-4	0.16697
4.6	0.00565	0.05037	3.42183E-4	0.06912
4.8	0.00424	0.0254	3.29451E-4	0.12837
5.0	0.00287	0.00562	2.56239E-4	0.07915
5.2	0.00187	0.04118	2.40324E-4	0.02883

Table S5 The structural comparison of Co(II) tetrahedron between **1** and $(PhP_4)_2[Co(SPh)_4]$.[S5]

	1	$(PhP_4)_2)[Co(SPh)_4]$
Coordination atoms	Two O and two N atoms	Four S atoms
Range of bond lengths (Å)	1.908(2)-1.983(2)	2.316(4)-2.342(4)
Range of bond angles (°)	93.43(9)-133.73(9)	95.6 (2)-121.3(2)
Dihedral angles (°)	(O1,Co,O2) vs (N1,Co,N2) = 66.1(1)	(S1,Co,S3) vs (S2,Co,S4) = 81.3
	(O1,Co,N1) vs (O2,Co,N3) = 72.9(1)	(S1,Co,S4) vs (S2,Co,S3) = 102.4
	(O1,Co,N3) vs (O2,Co,N1) = 83.6(1)	(S1,Co,S2) vs (S3,Co,S4) = 93.8

Table S6 Peak assignment for ^{1}H NMR spectra of hpbdtiH (500 MHz, CD_3CN) before and after irradiation (λ = 365 nm).

	Before irradiation (ppm)	After irradiation (ppm)
4 H, $C_6H_4(OH)$	m, 6.93 – 7.71	m, 6.93 – 7.71
12 H, 2 $C_4SH(CH_3)_2$	4 s, 2.14, 2.20, 2.35, 2.43	2 s, 2.14, 2.39
2 H, 2 $C_4SH(CH_3)_2$	2 s, 6.58, 6.72	1 s, 6.64

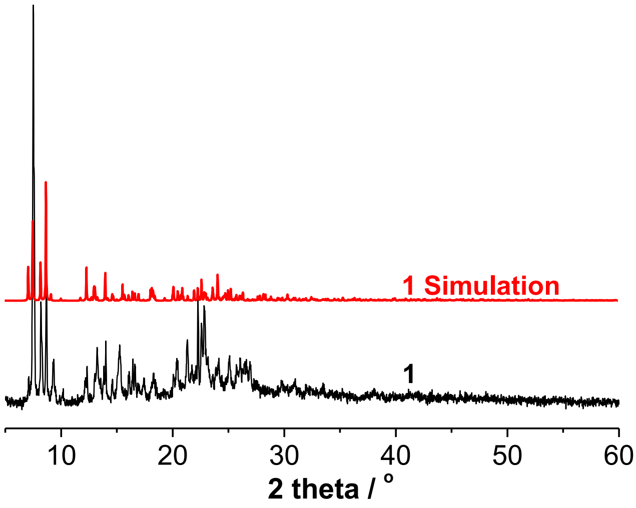


Fig. S1 Experimental and simulated XRD patterns of **1**.

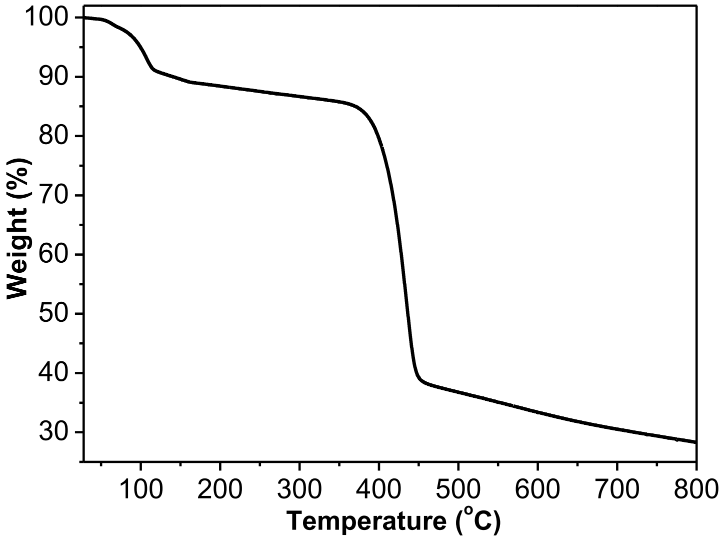


Fig. S2 TG curve of compound **1**.

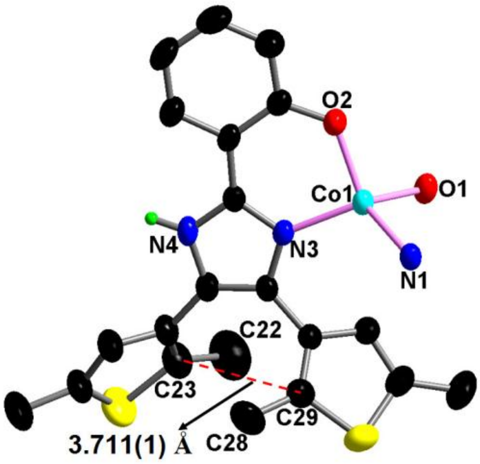


Fig. S3 The C23···C29 distance in the antiparallel-conformation hpbdti$^-$ ligand from **1**.

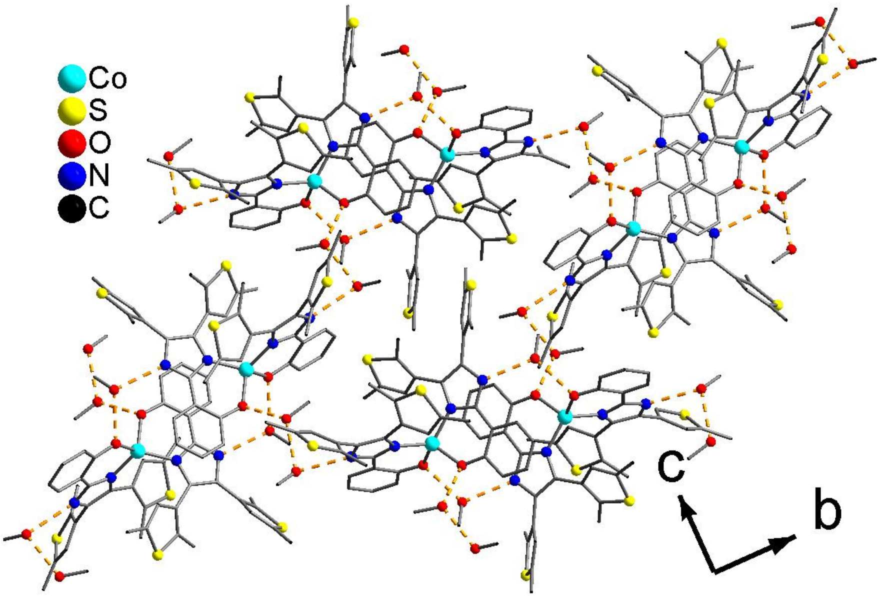


Fig. S4 Supramolecular layer structure of **1**.

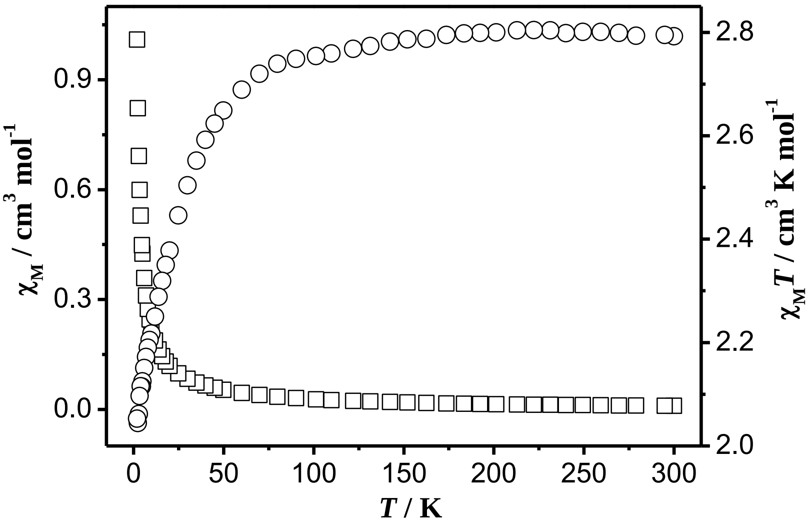


Fig. S5 The χ_M and $\chi_M T$ vs T plots for **1**.

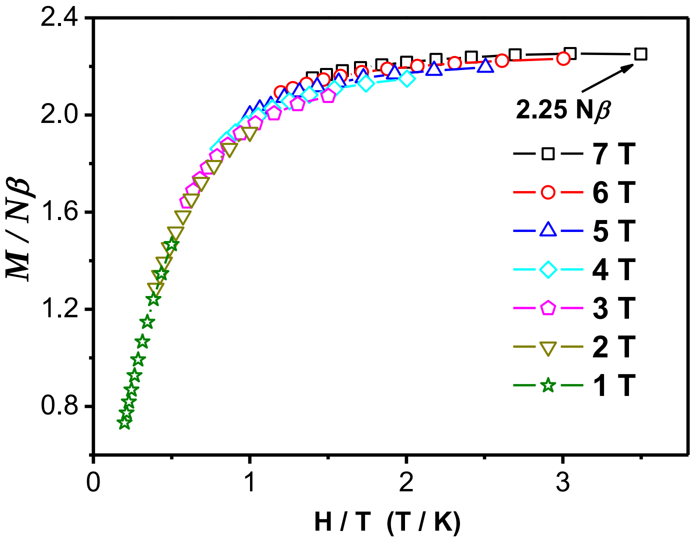


Fig. S6 Low-temperature magnetization data for **1** collected under various applied dc fields. The solid lines are for eye guide.

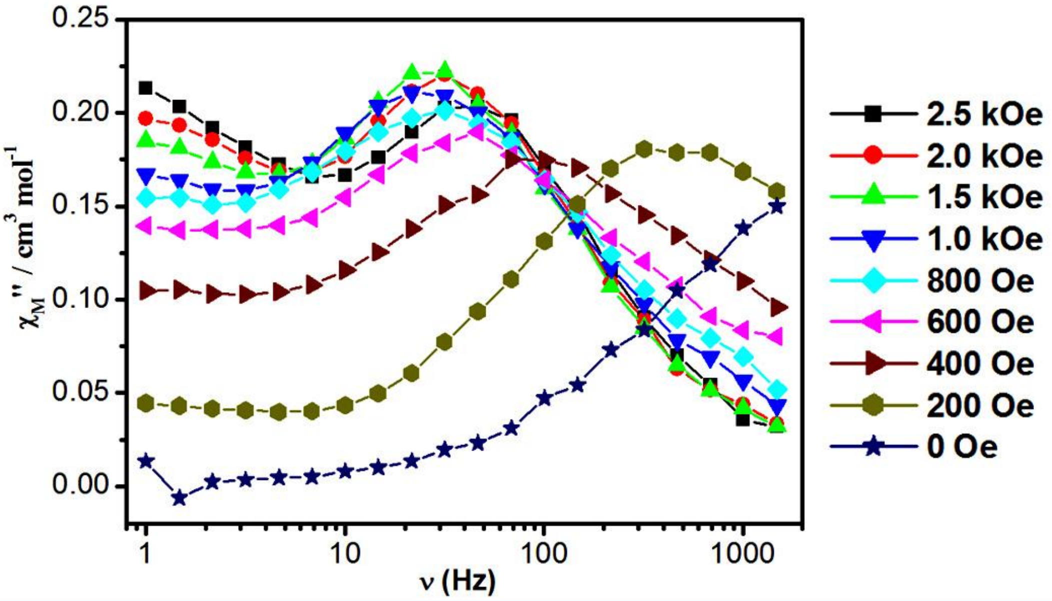


Fig. S7 Frequency dependence of the out-of-phase (χ_M'') ac susceptibility at 2 K under the applied static field from 0 to 2500 Oe. The solid lines are for eye guide.

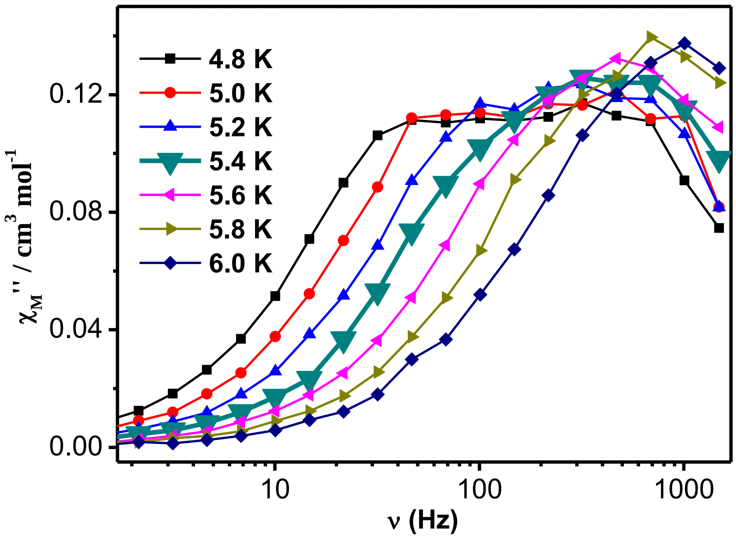


Fig. S8 Frequency dependence of the out-of-phase (χ_M'') ac susceptibility in the temperature ranges of 4.8-6.0 K under applied static field of 2000 Oe (solid lines are guides for the eye.). The curve at 5.4 K was highlighted, indicating the transition from one-step relaxation to two-step relaxation.

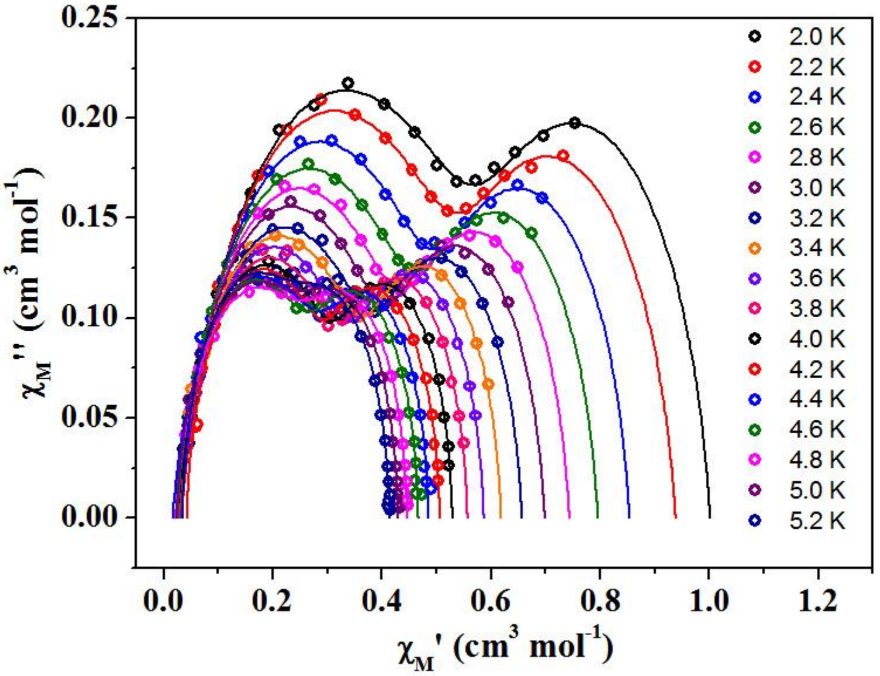


Fig. S9 Cole-Cole plots of **1** in the temperature range of 2.0-5.2 K under applied static field of 2000 Oe.

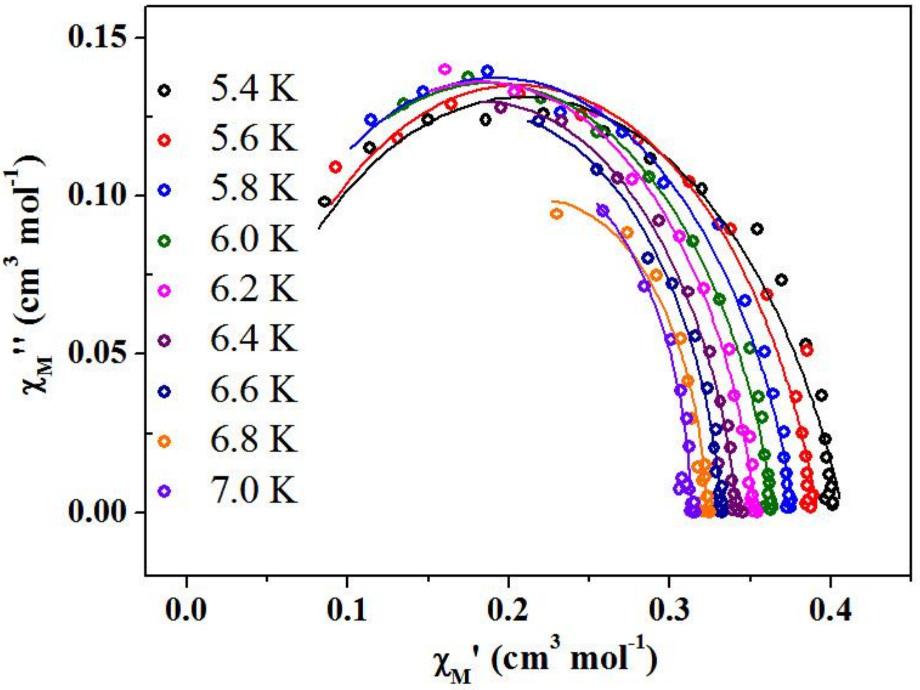


Fig. S10 Cole-Cole plots of **1** in the temperature range of 5.4-7.0 K under applied static field of 2000 Oe.

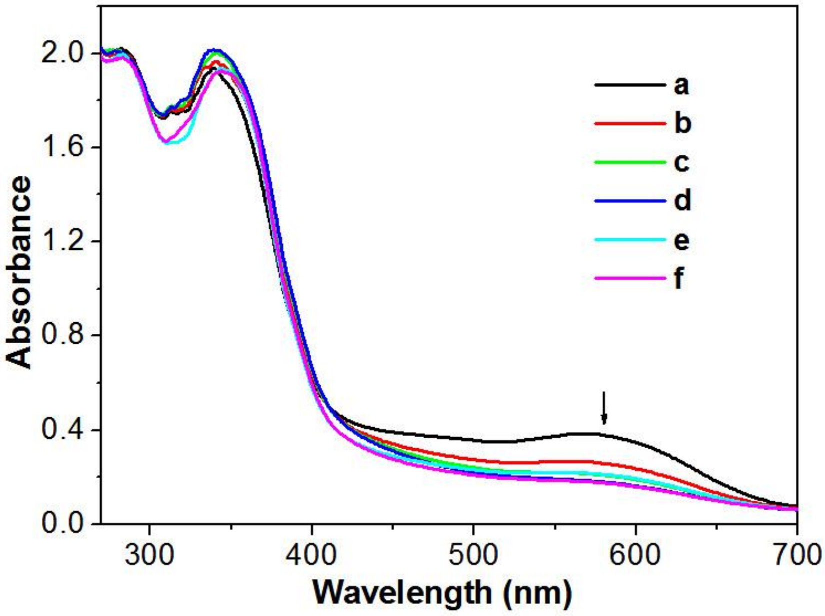


Fig. S11 Plot a: irradiating (λ = 350 nm) the solution of **1** for 20 minutes; plots b-d: irradiating (λ = 575 nm) the solution corresponding to plot a for 5, 10, 15 minutes, respectively; plots d and e: placing the solution corresponding to plot a in the dark for 20, 30 minutes, respectively.

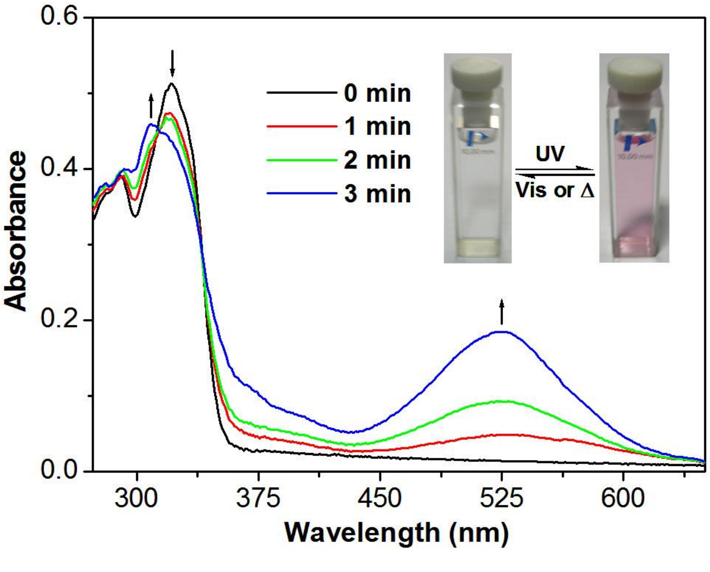


Fig. S12 Absorption-spectra changes of hpbdtiH in CH_2Cl_2-CH_3CN (v/v = 1/4) solution ($c = 2.5 \times 10^{-5}$ M) upon UV irradiation (λ = 321 nm) for 0 - 3 minutes.

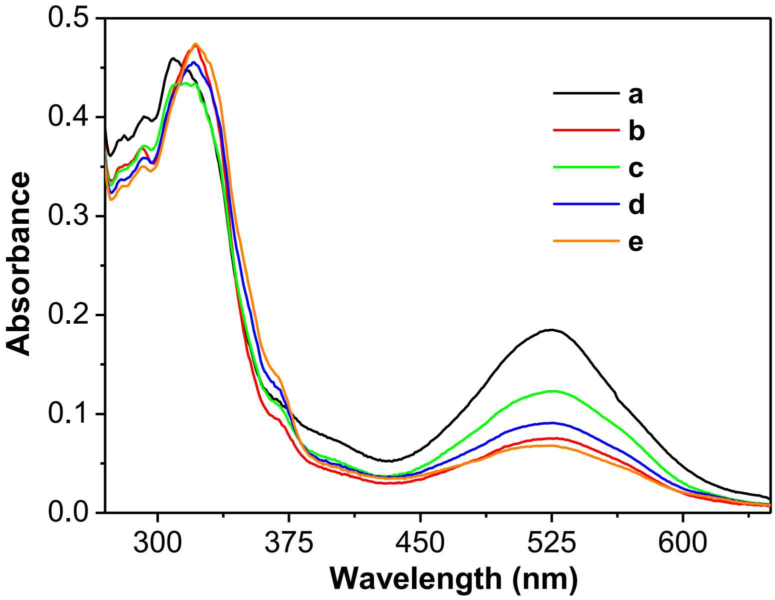


Fig. S13 Plot a: irradiating (λ = 321 nm) hpbdtiH solution for 3 minutes; plot b: irradiating (λ = 524 nm) the solution corresponding to plot a for 5 minutes; plots c-e: placing the solution corresponding to plot a in the dark for 10, 20, 30 minutes, respectively.

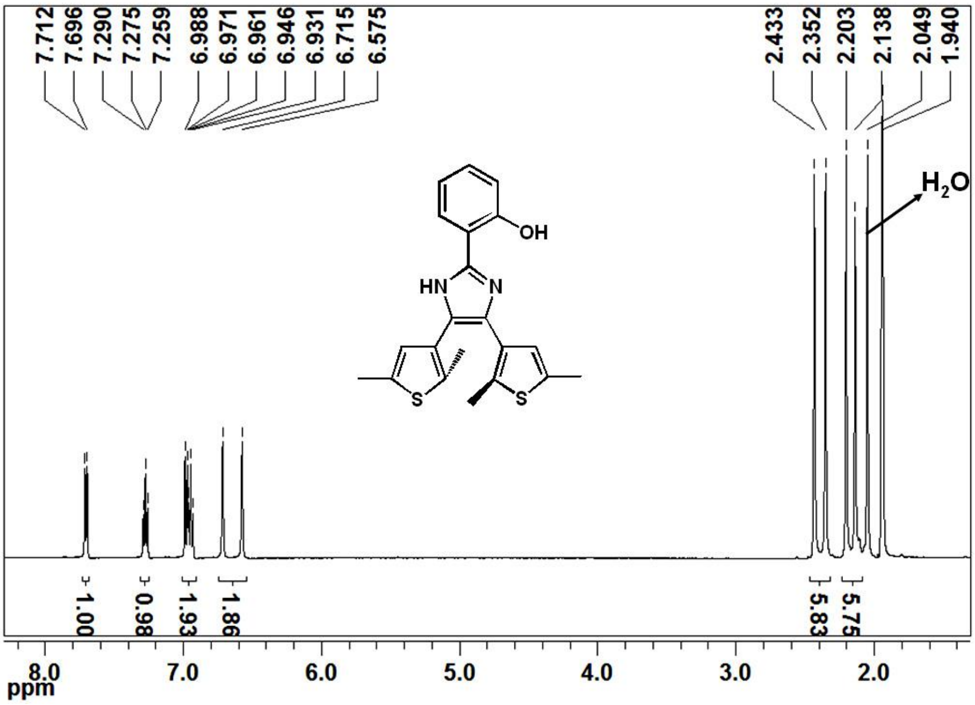


Fig. S14 ^{1}H NMR spectrum of hpbdtiH (500 MHz, CD_3CN) before irradiation.

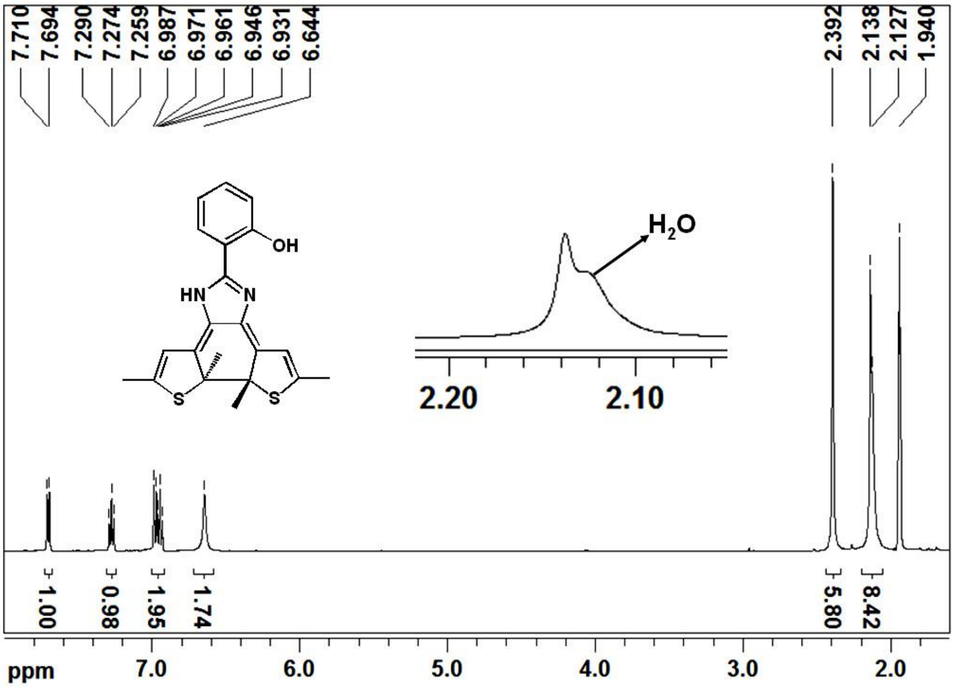


Fig. S15 ^{1}H NMR spectrum of hpbdtiH (500 MHz, CD_3CN) after irradiation for 30 minutes (λ = 365 nm).

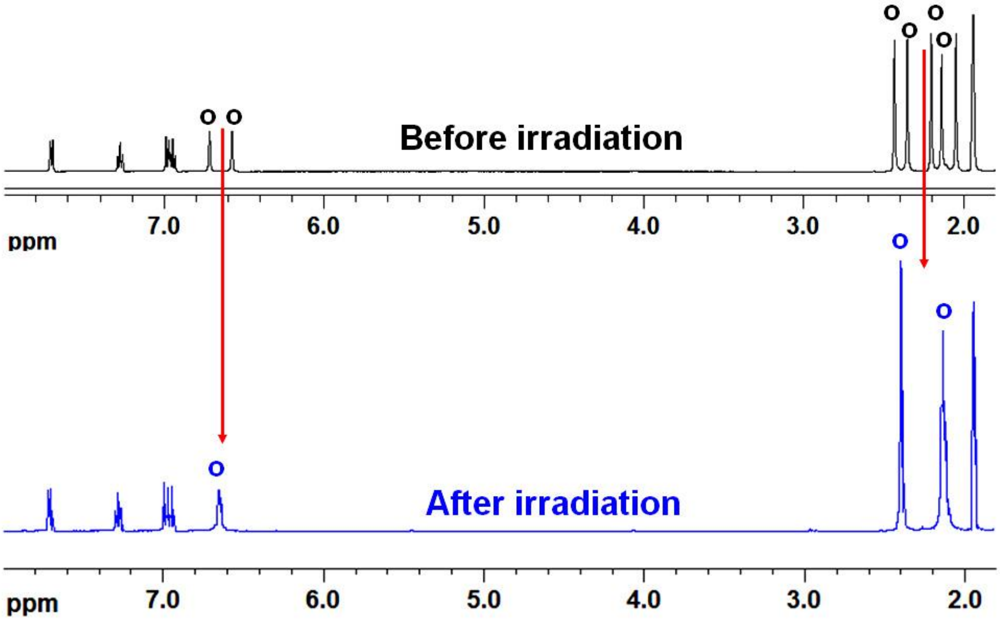


Fig. S16 The comparison of hpbdtiH ^{1}H NMR before and after irradiation. o = selected peaks indicating the conversion from open form (before irradiation) to closed form (after irradiation).

References

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