Supporting Information

Molecular packing, crystal to crystal transformation, electron transfer behaviour, photochromic and fluorescent property of three hydrogen-bonded supramolecular complexes containing benzenecarboxylate donors and viologen acceptors

Hengjun Chen,[a] Min Li,[a] Guiming Zheng,[a] YiFang Wang,[a] Yang Song,[a] Conghui Han,[a] Zhiyong Fu*[a] Shijun Liao,[a] and Jingcao Dai[b]

General methods and materials

All the reagents were purchased from commercial sources and used without further purification; N-(3-carboxyphenyl)-4,4'-bipyridinium chloride was synthesized according to a reported method.[S1] ATA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N2 at a rate of 10 ºC min-1. The X-ray powder diffraction (XRD) data were collected with a Bruker D8 Advance X-ray diffractometer using CuKα radiation (λ = 1.5406 Å). UV-Visible diffuse-reflectance spectral measurements were carried out using a HITACHI U-3010 spectrometer. Fluorescence spectra were obtained using a F-4500 FL Spectrophotometer. The excitation wavelength used for emission spectra are 245 nm, 250 nm and 430 nm for compound **1-3** respectively. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm-1 using a KBr tablet. The ESR spectra were recorded at room temperature with a Bruker EMX-10/12 Electron Spin Resonance Spectrometer, with 1,1-diphenyl-2-picrylhydrazyl as reference. The C, H and N microanalyses were carried out with a Vario EL III elemental analyzer. A 150 W xenon lamp was used as light source.

Single Crystal Data

The measurements were taken on a Rigaku R-AXIS SPIDER CCD diffractometer with graphite-Monochromated Mo/Kα radiation. Data were collected at 298K, using the ω- and φ-scans to a maximum θ value of 25.03º. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-97.[S2] And the structures were solved by direct methods SHELXS-97.[S3]All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the oxygen atoms of the carboxyl groups and the nitrogen atoms of the CPBPY molecules are located from difference Fourier mapping. Other hydrogen atoms were included at geometrically idealized positions. CCDC 958696, 958697 and 1009254 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.ukf/data_request/cif.

Table S1. Crystal data for compound 1, 2 and 3.

	1	**2**	**3**
Formula	$C_{27}H_{18}N_2O_{10}$	$C_{44}H_{40}N_4O_{17}$	$C_{22}H_{15}N_2O_6$
Formula weight	530.43 g/mol	896.80 g/mol	403.36g/mol
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	P-1	$P2_1/c$
a (Å)	26.032(7)	7.3700(15)	8.9819(18)
b (Å)	8.8150(15)	9.5200(19)	12.923(3)
c (Å)	21.444(8)	15.776(3)	15.042(3)
α (°)	90.00	90.26(3)	90.00
β (°)	110.25(3)	102.68(3)	97.40(3)
γ (°)	90.00	106.00(3)	90.00
Volume ($Å^3$)	4617(2)	1035.6(4)	1731.4(6)
Z	8	1	4
Crystal density (g/cm^3)	1.526	1.433	1.548
F (000)	2192	465	836
Goodness-of-fit on F^2	1.079	1.071	1.025
Final R indices [I >2σ (I)][a]	R_1=0.471 wR_2=0.1289	R_1=0.0422 wR_2=0.0976	R_1=0.0441 wR_2=0.1008
R indices (all data)	R_1=0.0653 wR_2=0.1454	R_1=0.0764 wR_2=0.1114	R_1=0.1180 wR_2=0.1483

[a] $R_1=\sum\|F_0\| - \|F_c\|/\sum\|F_0\|$. $wR_2=[\sum[w(F_0^2-F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$.

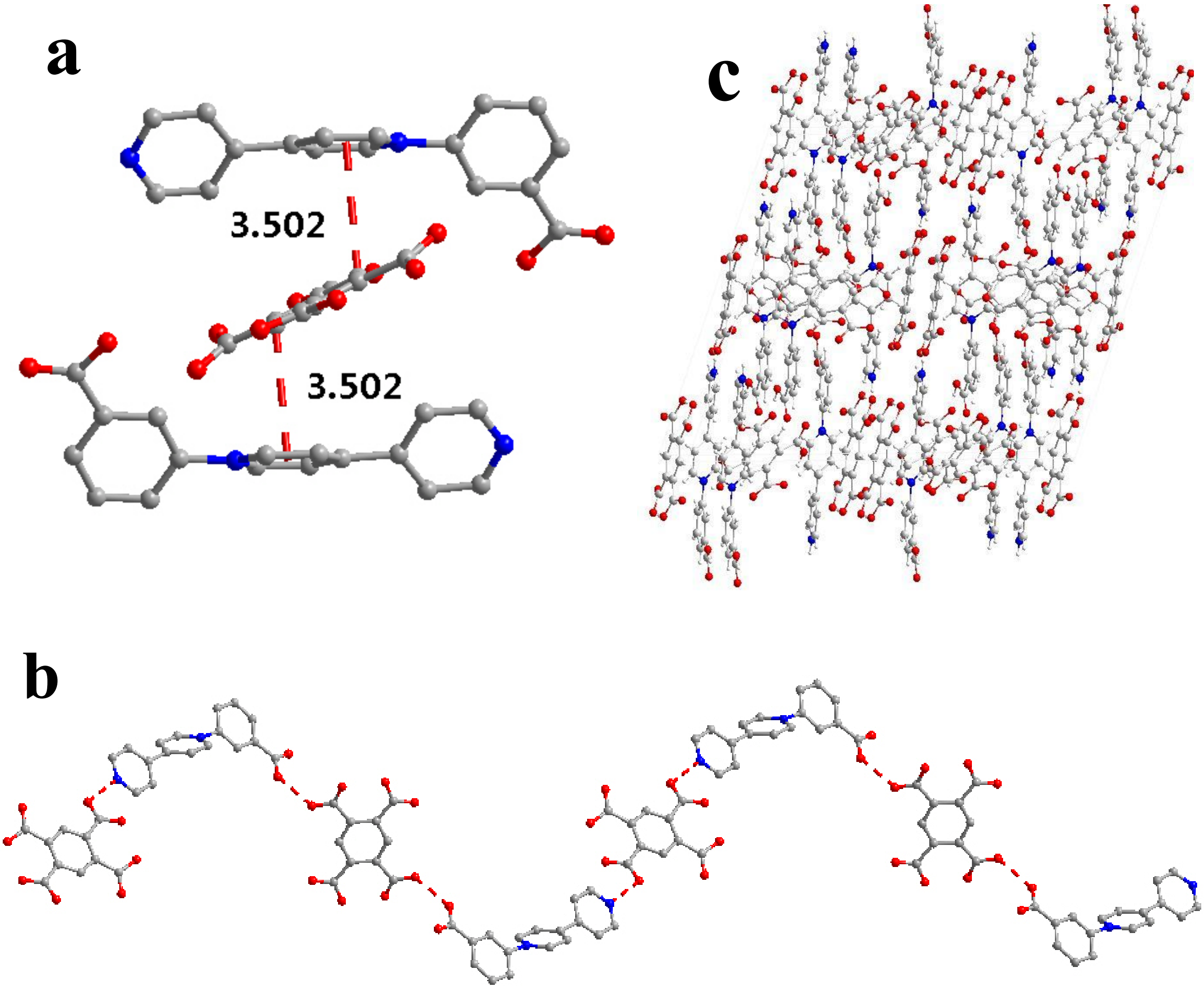


Fig. S1 **(a)** The **π–π** interactions in compound **1** with the $[H_2CPBPY]^{2+}$ and the $[H_2BTEC]^{2-}$ units; **(b)** The Donor-Acceptor supramolecular chain in a ···DADADA··· order; **(c)** Packing diagrams of the unit cell of **1** viewed along the *b* axis;

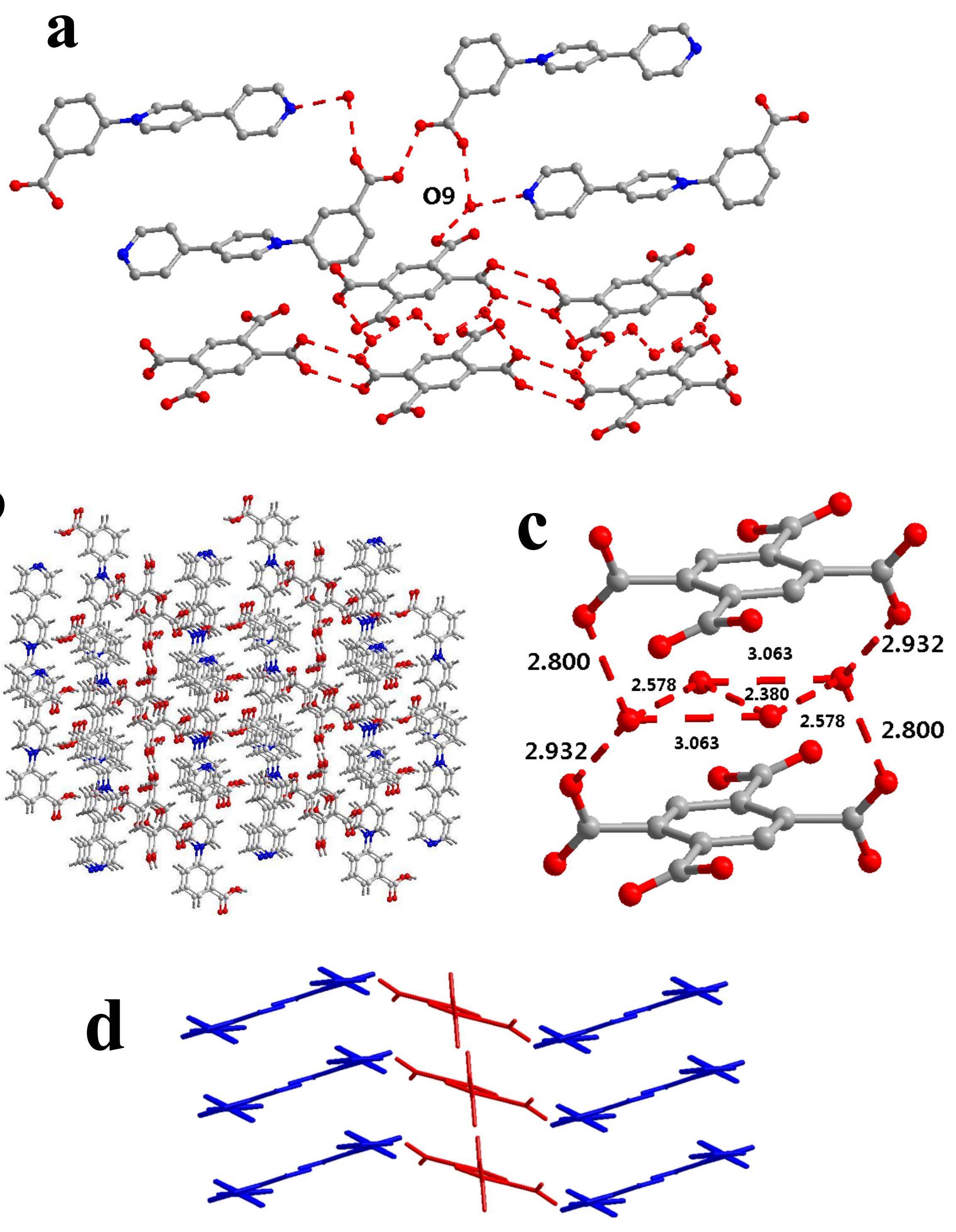


Fig S2 **(a)** The supramolecular HCPBPY chains and ···H_2BTEC-$(H_2O)_4$-H_2BTEC··· network in compound **2**; **(b)** Packing diagrams of the unit cell of **2** viewed along the *a* axis; **(c)** Diagram to show the distances of the oxygen atoms in the ···H_2BTEC-$(H_2O)_4$-H_2BTEC··· network; **(d)** Simplified packing diagram. Blue: HCPBPY chains; red: H_2BTEC network.

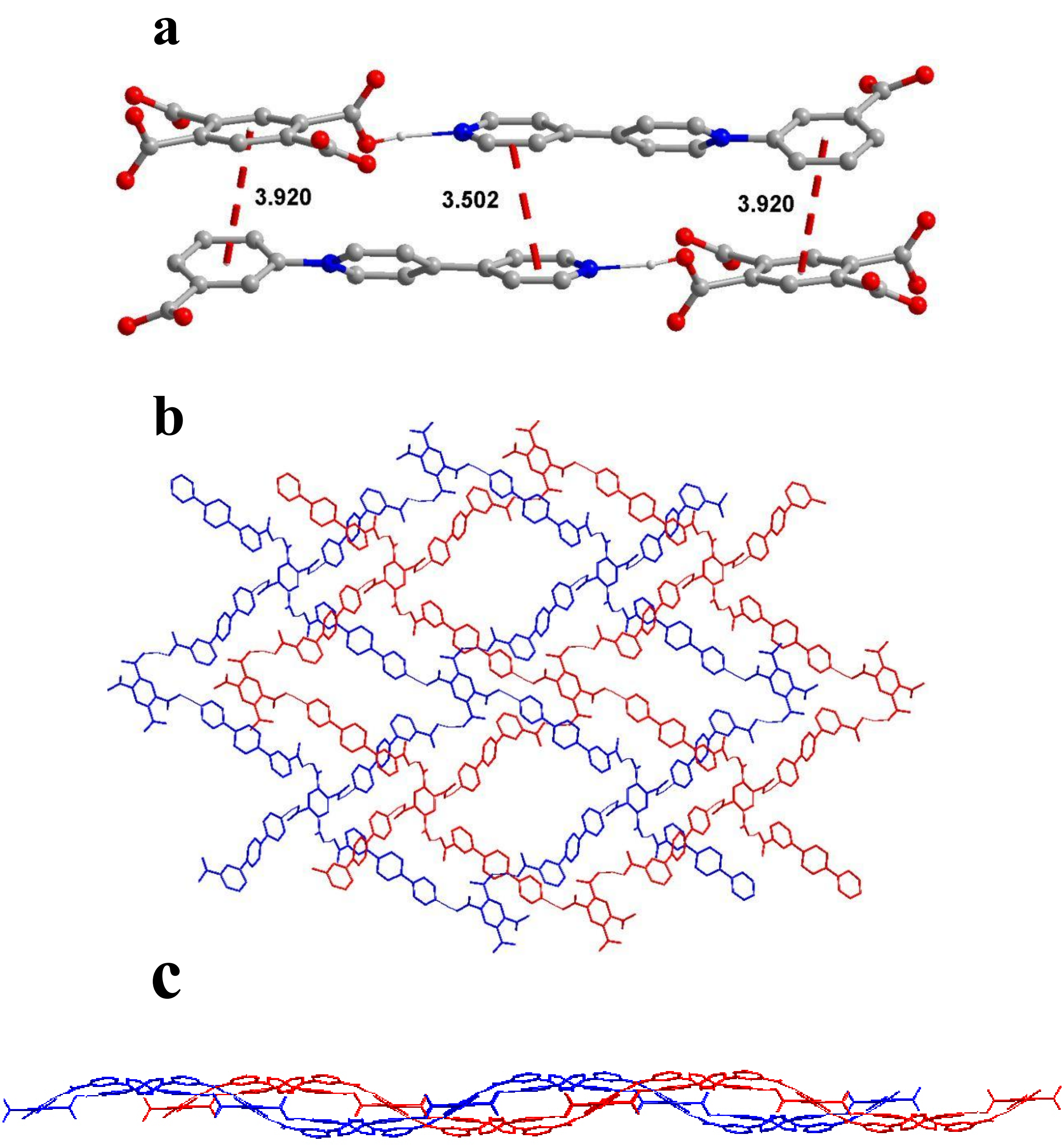
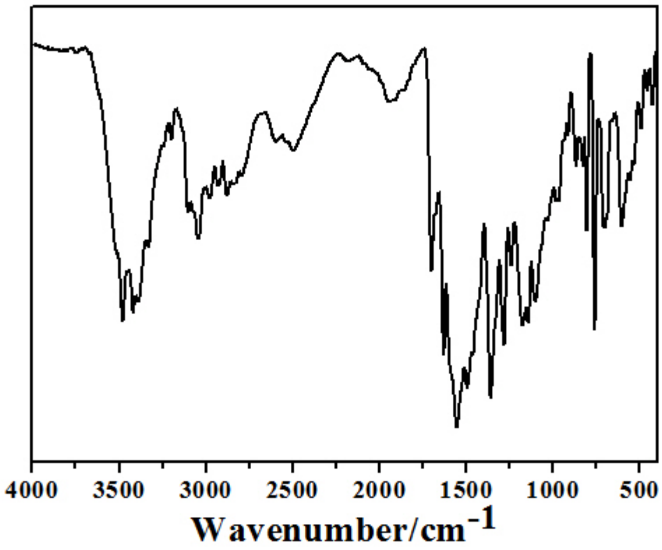


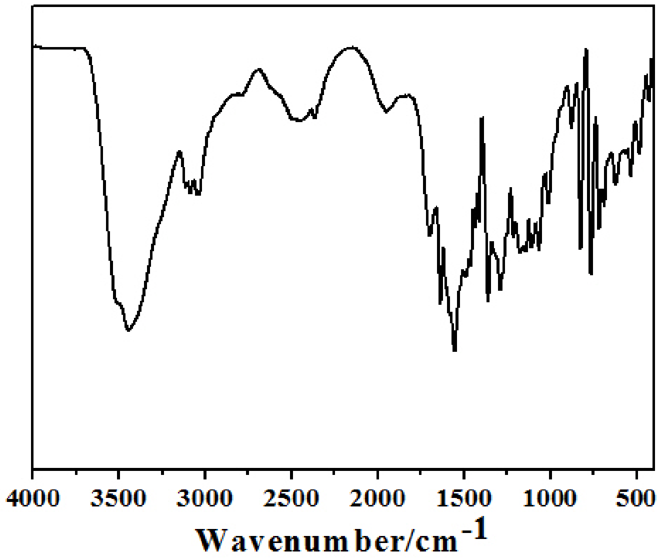
Fig S3 (a) The π–π interactions between the $[HCPBPY]^{+}$ and the $[H_2BTEC]^{2-}$ units in compound **3; (b)** The arrangement of the interpenetrating structure of **3**; **(c)** Diagram to show the interpenetrating mode of the supramolecular networks.

IR Spectra

a



b



c

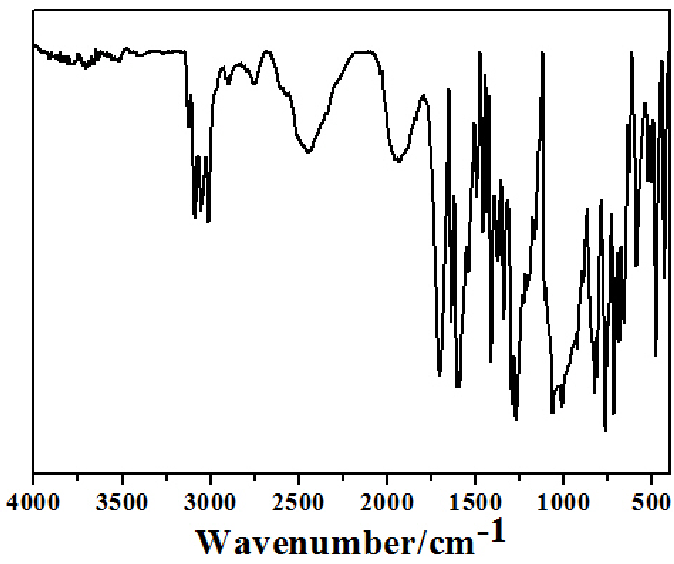


Fig. S4. IR spectrum of (a) compound **1**; (b) compound **2;** (c) compound **3**.

PXRD Data

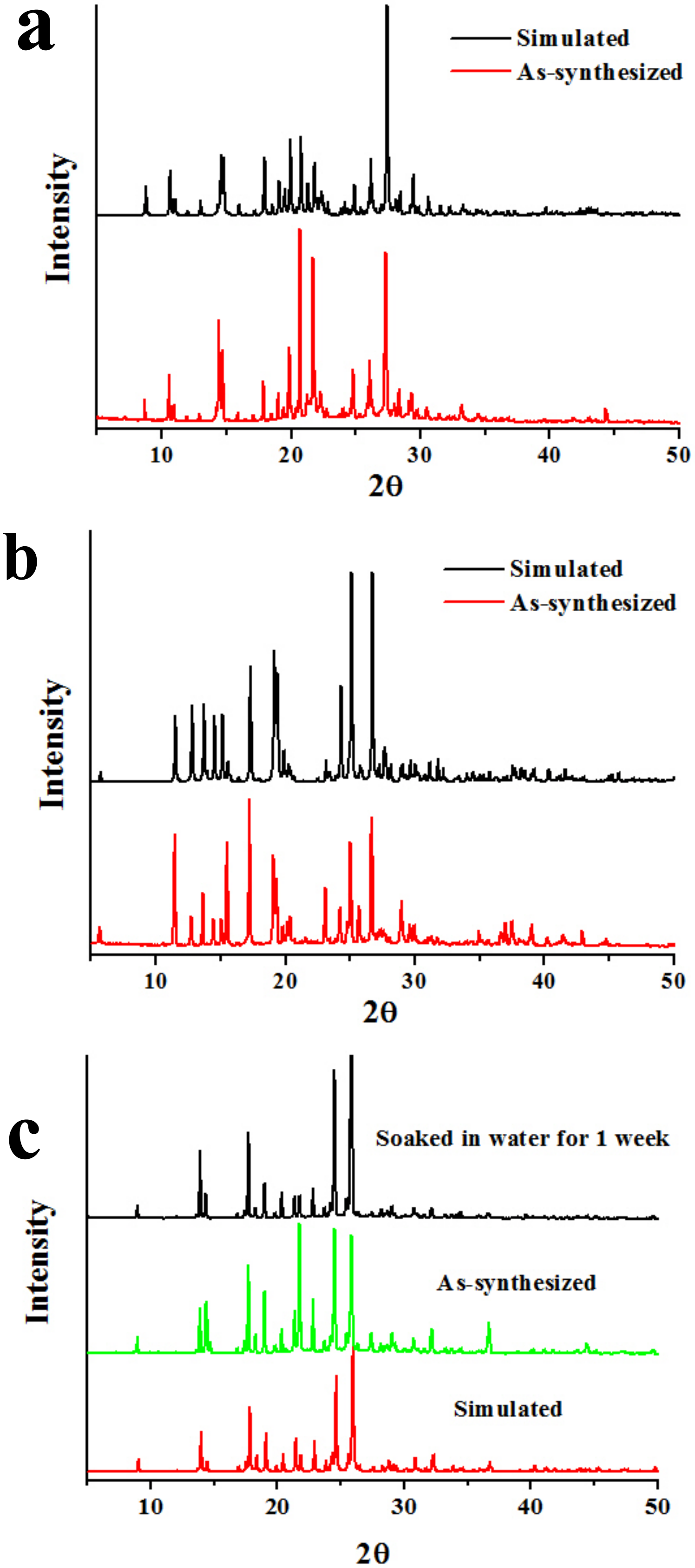


Fig. S5. Experimental and simulated powder X-ray diffraction patterns of: (a) compound **1**; (b) compound **2**; (c) compound **3**.

ESR Spectra

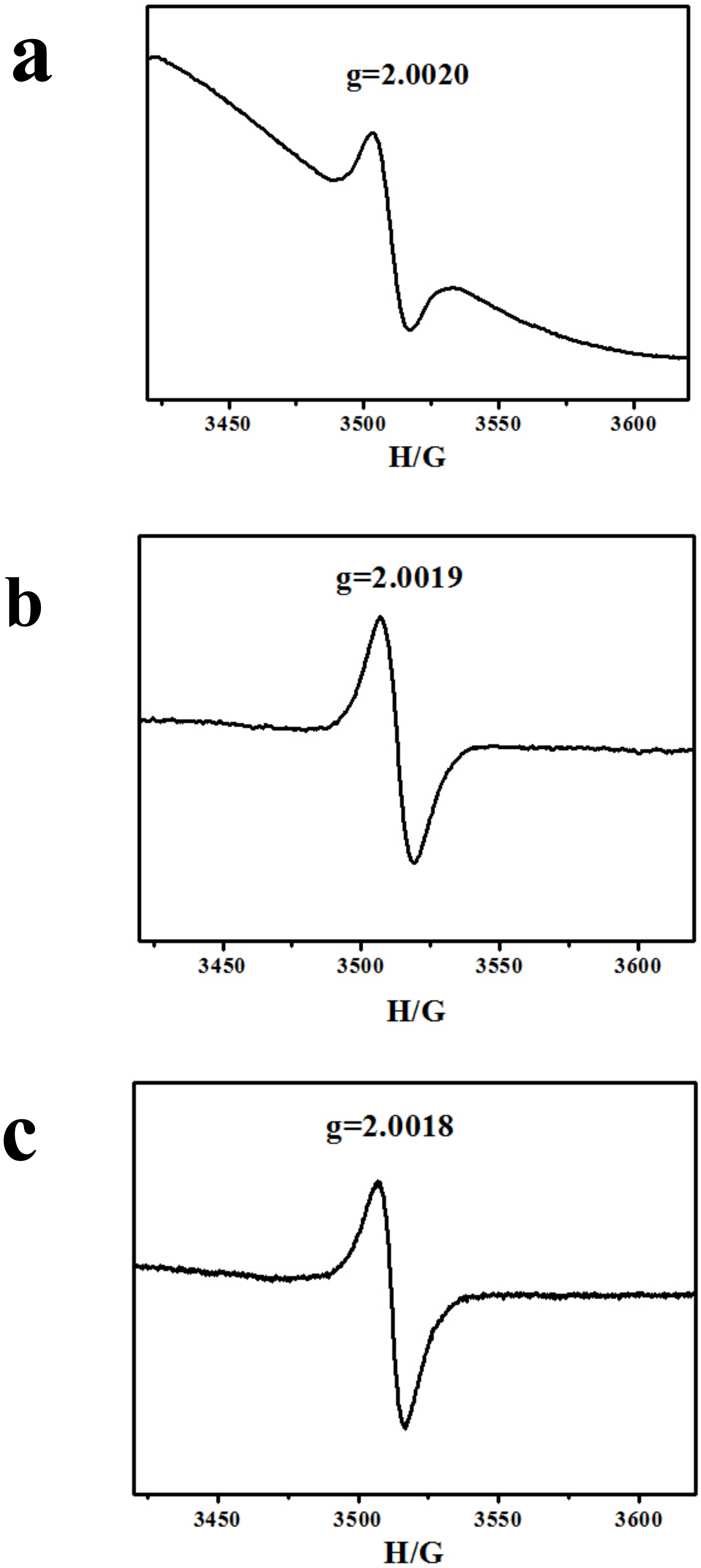


Fig. S6 ESR spectrum of (a) compound **1,** g = 2.0020; (b) compound **2,** g = 2.0019; (c) compound **3,** g = 2.001.

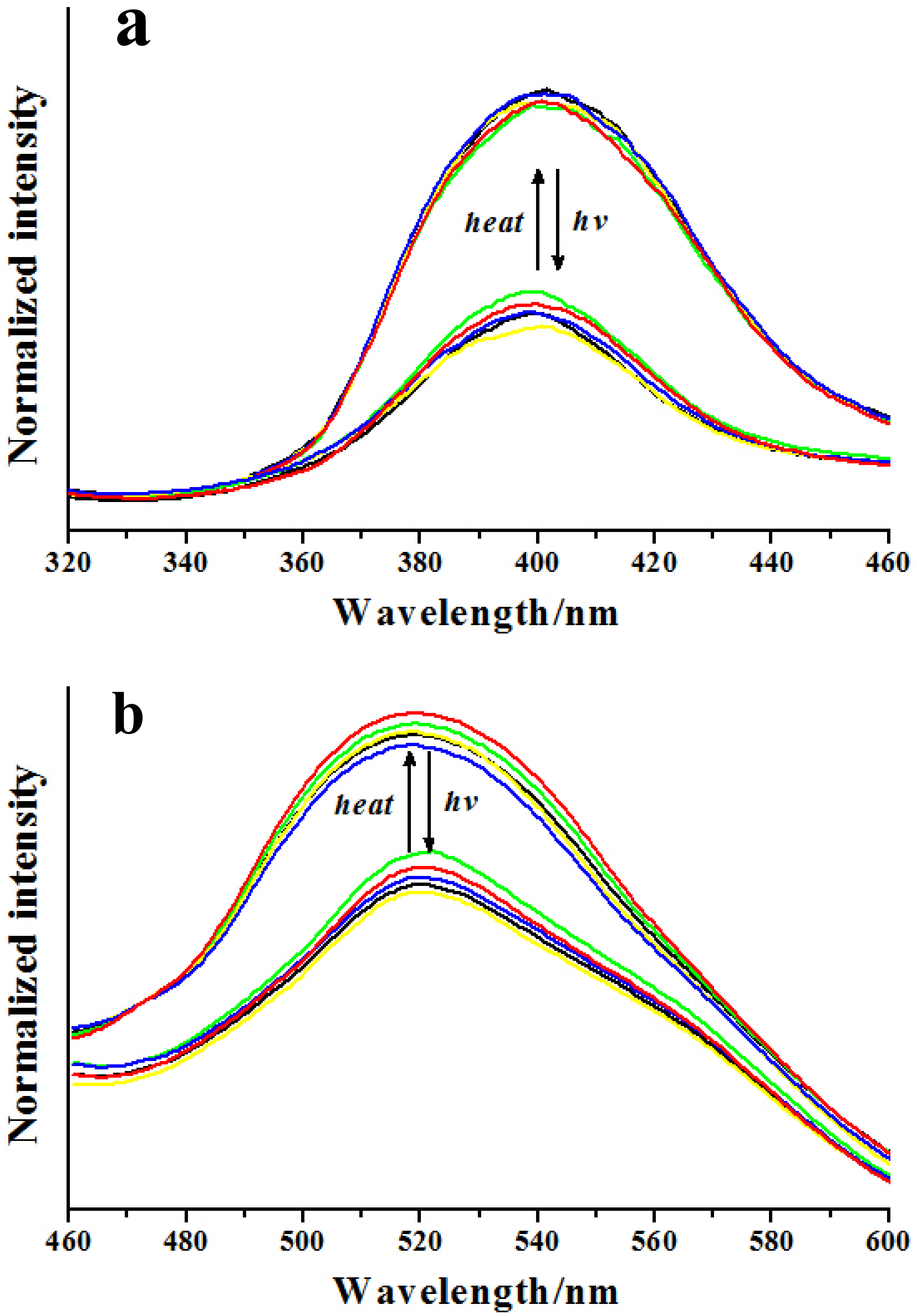


Fig S7. Fluorescence spectral changes on alternate excitation by photoirradiation and heating over five cycles in air: (a) compound **1**; (b) compound **3**.

The calculation of kinetic rate constants

After irradiation UV-Vis spectra are recorded and the calculations of kinetics of light reversion based on the intensity values of the wavelength at 666 nm, 674 nm and 657 nm for compound **1**, **2** and **3** respectively. The kinetic rate constants are determined by the literature calculation method.[S4] The following equation is used for data treatment:

$$In\frac{A_\infty - A_0}{A_\infty - A_t} = kt$$

where A_0, A_t, A_∞ are the observed absorption data at the beginning, versus time, and at the end of the reaction, respectively

[S1] D. Bongard, M. Moller, S. N. Rao, D. Corr and L. Walder, *Helv. Chim. Acta*, 2005, **88**, 3200.

[S2] G.M. Sheldrick, SHELXTL, version 5.1; Bruker Analytical X-ray Instruments Inc ., Madison, Wisconsin, 1998.

[S3] G. M. Sheldrick, SHELXS-97, PC version; University of Göttingen, Göttingen, Germany, 1997.

[S4] T. Kawato, H. Koyama, H. Kanatomi and M. Isshiki, *J. Photochem.*, 1985, **28**, 103.