Electronic Supplementary Information

One 1D anionic coordination polymer showing superior Congo Red sorption and its dye composite exhibiting remarkably enhanced photocurrent response

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Contents

Experimental Section

General. The ligand N,N'-di(3-pyridyl)succinamide (L) was synthesized according to the literature procedures.[1] All other chemicals and reagents were obtained from commercial sources and used as received. The elemental analyses for C, H, N, S were performed on Elementar vario MICRO cube elemental analyzer. The IR spectra were recorded on a Bruker VERTEX70 spectrometer in the range of 500 − 4000 cm^{-1}. The TGA were performed using a Mettler TGA/SDTA851 thermal analyzer under an air atmosphere with a heating rate of 10 $°C \cdot min^{-1}$ in the temperature region of 20 − 800 °C. Powder X-ray diffraction (PXRD) patterns were collected using a PANalytical X'Pert Pro MPD diffractometer 40 kV, 40 mA with Cu Kα (λ = 1.5406 Å) radiation. The emission spectra were measured on a Varian Cary Eclipse fluorescence spectrophotometer. The concentrations of zinc ions were determined by inductive coupled plasma optical emission spectrometry (ICP-OES) on a Varian 710-ES ICP optical emission spectrometer. The UV-Vis absorption spectra were measured on a Varian Cary-50 UV-visible spectrophotometer. BET surface areas measurement was conducted on an ASAP2020 M+C instrument. The UPS measurements were carried out in a ThermFish Scientific ESCALAB 250Xi using a He I (21.22 eV) discharged lamp. The samples were prepared by spin coating the solution on the pre-cleaned glass/Au surfaced and sputter cleaned with 2 keV Ar ion beam for 20 s in the analysis chamber. A bias of –5 eV was applied to the samples for separation of the sample and the secondary edge for the analyzer.

Synthesis of $[Zn(1,2,3\text{-}BTA)(H_2O)]\cdot(H_2L)_{0.5}\cdot 2H_2O$ ($1\cdot 2H_2O$). A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (44 mg, 0.2 mmol), N,N'-bis(3-pyridyl)succinamide (L) (27 mg, 0.1 mmol), 1,2,3-$H_3BTA \cdot 2H_2O$ (42 mg, 0.2 mmol) and 10 mL NaOH (0.01 M) was stirred for 10 min in a 25 mL Teflon reactor and then sealed and heated at 120 °C for 48 h. After cooling to r.t. at the rate of 5 °C/h, colourless needles of **1**$\cdot 2H_2O$ were formed and collected by filtration, washed with H_2O and dried under vacuum. Yield: 55 mg (60% based on Zn). Anal. Calcd. for $C_{16}H_{17}N_2O_{10}Zn$ (462.69): C 41.53, H 3.70, N 6.05; found: C 41.65, H 3.81, N 5.84. IR (KBr pellets, cm^{-1}) 3357(w), 3078(w), 1684(m), 1609(s), 1586(s), 1559(s), 1484(s), 1449(s), 1369(s), 1340(m), 1282(m), 1256(m), 1199(m),1179(m), 879(m), 833(m), 797(s), 781(s), 703(s), 666(m), 623(w).

Synthesis of 1·0.75CR·6H$_2$O. Compound **1**·2H_2O (40 mg, 0.086 mmol) was well grounded at ambient temperature for *ca*. 60 min and then added to an aqueous Congo Red (CR) solution (50 mL, 1 $g{\cdot}L^{-1}$, 0.072 mmol CR). The dye solution containing **1**·2H_2O was mixed well with magnetic stirring and maintained for a fixed time of 2 h. The precipitation was separated by centrifugation, rinsed with water repeatedly, and then dried in vacuum at 50 °C. The final sample was then labelled as **1**·0.75CR·6H_2O. Yield: 77 mg (85% based on Zn). Anal. Calcd. for $C_{40}H_{41.5}N_{6.5}Na_{1.5}O_{18.5}S_{1.5}Zn$ (1057.25): C 45.44, H 3.96, N 8.61, S 4.55, Zn 6.18; found: C 45.14, H 4.17, N 9.06, S 4.01, Zn 6.50. IR (KBr pellets, cm^{-1}): 3605(w), 3185(w), 3069(w), 1690(m), 1554(s), 1470(s), 1421(m), 1391(m), 1369(s), 1350(m), 1326(s), 1218(s), 1197(s), 1171(s), 1077(s), 1040(m), 938(m), 913(m), 880(m), 834(m), 796(m), 782(m), 755(m), 716(m), 698(m), 666(m), 633(m).

X-ray Structure Determinations. Diffraction intensities of **1**·2H_2O was collected on an Agilent Gemini Atlas with Mo Kα ($\lambda = 0.71073$ Å) by ω scan mode. Single crystals of **1**·2H_2O was mounted at the top of a glass fibre with grease at r.t. Cell parameters of **1**·2H_2O were refined on all observed reflections by using the program *CrysAlisPro* (Agilent Technologies, Version 1.171.36.32, 2013). The collected data were reduced by the program *CrysAlisPro*, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structure of **1**·2H_2O was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with *SHELXTL-97* program.[2] All non-hydrogen atoms in **1**·2H_2O were refined anisotropically. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. All the calculations were performed on a Dell workstation using the *Olex2* crystallographic software package.[3]

Photocurrent response measurement. The photocurrent experiments were performed using a quartz cell equipped with the sample coated ITO glass working electrode, a Pt plate auxiliary electrode and a SCE reference electrode. An aqueous solution of Na_2SO_4 (100 mL, 0.1 mol·L^{-1}) was used as the medium in a quartz cell. The photoelectrodes of the compounds were prepared by powder coating method. As a typical procedure, all samples were grounded and pressed uniformly on an ITO glass (100 Ω/□) with 0.785 cm^2 effective area (Φ 1.0 cm). A 150 W high pressure xenon lamp, positioned 15 cm away the surface of the ITO electrode to the light. The electrode was typically irradiated over 0 – 400 s with interval 20 s. The applied voltages were 0.5 V for **1**·$2H_2O$, and −0.5 V for **1**·0.75CR·$6H_2O$ for photocurrent measurements.

References

1. M. Sarkar, K. Biraha, *Cryst. Growth Des.* 2006, **6**, 202.

2. (a) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997. (b) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339.

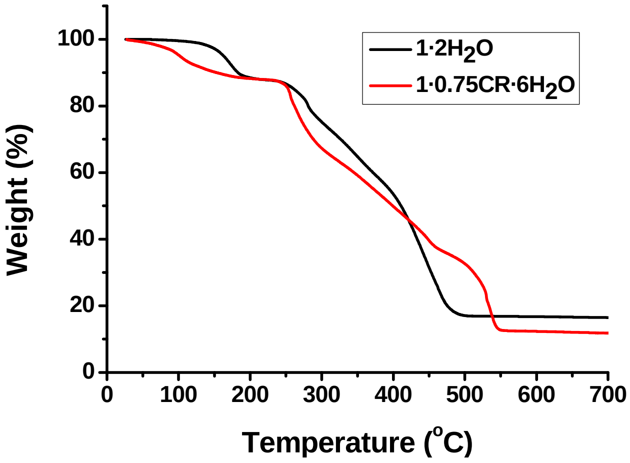


Fig. S1. The TGA curves for **1**·$2H_2O$ and **1**·0.75CR·$6H_2O$.

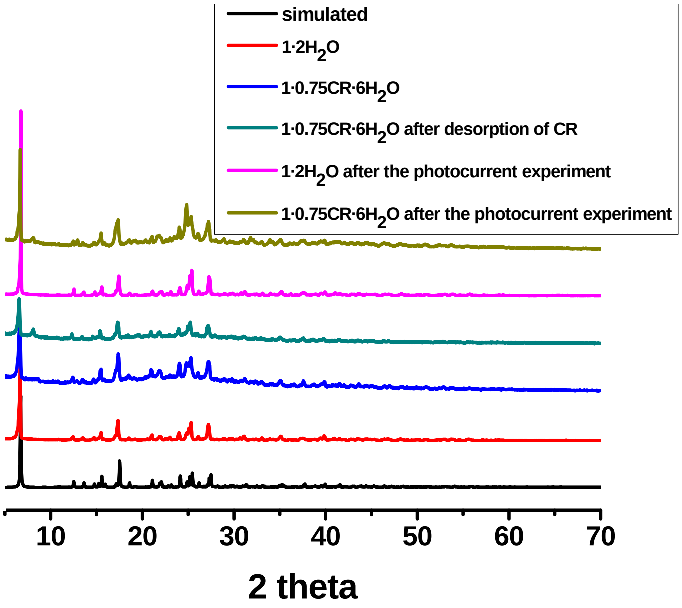


Fig. S2. The simulated and observed PXRD patterns of **1**·$2H_2O$, the observed patterns of **1**·0.75CR·$6H_2O$ before and after adsorption and desorption, the observed patterns of **1**·$2H_2O$ and **1**·0.75CR·$6H_2O$ after the photocurrent experiment.

Table S1. Summary of crystallographic data for **1**·$2H_2O$.

Compound	**1**·$2H_2O$
Empirical Formula	$C_{16}H_{17}N_2O_{10}Zn$
Formula Weight	462.69
Crystal System	triclinic
Space Group	$P\bar{1}$
a (Å)	7.1095(2)
b (Å)	9.5924(4)
c (Å)	13.2708(4)
α(°)	83.938(3)
β (°)	84.247(3)
γ(°)	86.754(3)
V (Å^3)	894.46(5)
Z	2
ρ_{calc} (g cm^{-3})	1.718
F(000)	474.0
μ (MoKα, mm^{-1})	1.435
Total reflections	10401
Unique reflection	4090 (R_{int} = 0.0236)
No. Observations	3847 ($I > 2.00\sigma(I)$)
No. Parameters	281
R^a	0.0268
$R_w{}^b$	0.0677
GOF^c	1.079

a) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; b) $R_w = [\Sigma w(F_o{}^2-F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; c) $GOF = \{\Sigma w[(F_o{}^2-F_c{}^2)^2]/(n-p)\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**·2H_2O.

Compound **1**·2H_2O

Zn(1)-O(1)	1.9562(12)	Zn(1)-O(4A)	1.9552(13)
Zn(1)-O(5B)	1.9913(12)	Zn(1)-O(5)	1.9832(13)
O(1)-Zn(1)-O(5B)	112.26(5)	O(1)-Zn(1)-O(8)	88.94(6)
O(4A)-Zn(1)-O(1)	115.24(6)	O(4A)-Zn(1)-O(5B)	108.24(5)
O(4A)-Zn(1)-O(8)	126.67(6)	O(8)-Zn(1)-O(5B)	104.08(6)

Symmetry Codes: A : 2-*x*, 1-*y*, 1-*z*; B: 2-*x*, -*y*, 1-*z*; C : 1-*x*, 1-*y*, 1-*z*; D: 1-*x*, 1-*y*, 2-*z*.

Table S3. Hydrogen bond lengths (Å) and angles (°) for **1**·2H_2O.

Hydrogen bond D-H···A	D-H	H···A	D···A	D-H···A	Sym. op. for A
O(9)-H(9A)···O(5)	0.80(3)	2.07(3)	2.845(2)	165(3)	-1+*x*, 1+*y*, *z*
O(9)-H(9B)···O(6)	0.78(3)	2.00(3)	2.760(2)	162(3)	*x*, 1+*y*, *z*
O(10)-H(10A)···O(6)	0.86 (1)	2.26(3)	3.000(3)	144(4)	*x*, 1+*y*, *z*
O(10)-H(10B)···O(7)	0.87(1)	2.09(2)	2.906(3)	158(5)	1-*x*, 1-*y*, 2-*z*
N(1) -H(1)···O(3)	0.85(3)	1.92(3)	2.723(2)	158(2)	1-*x*,1-*y*, 1-*z*
N(2) -H(2)···O(9)	0.86	2.00	2.850(2)	171.2	*x*, -1+*y*, *z*

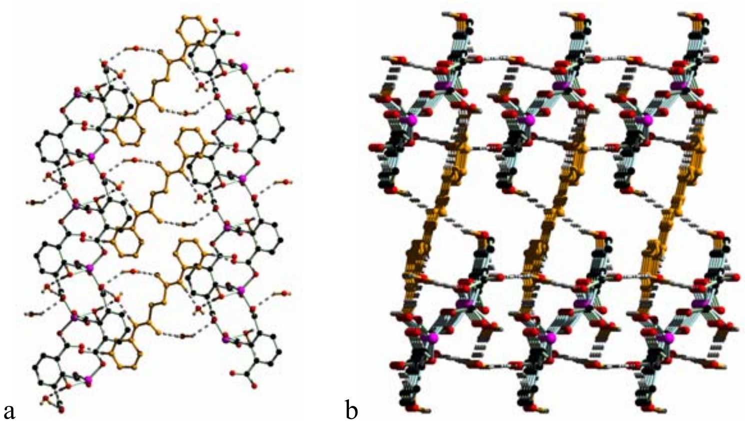
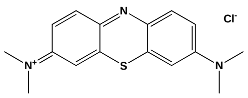


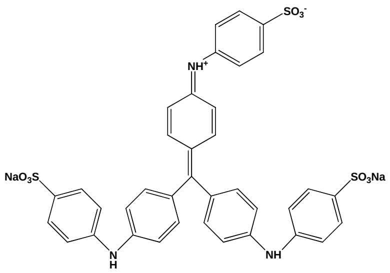
Fig. S3. (a) The 2D supermolercular network of **1**·2H_2O formed through H-bonds interactions (O8-H8A···O9, N1-H1···O3, N2-H2···O9, O9-H9···O5, O10-H10B···O7, O10-H10A···O6 N1-H1···O3) viewed along the *a* axis. hydrogen bonds are shown as gray dotted lines; (b) The 3D supramolecular network of **1**·2H_2O formed by H-bonds (O9-H9B···O6) viewed along the *b* axis.

Chart S1. A list of dyes tested for absorption.

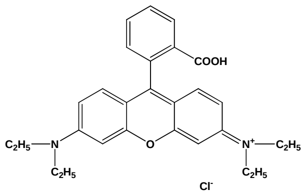
(a) positively charged:



Methylene Blue

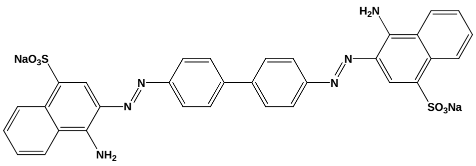


Methyl Blue

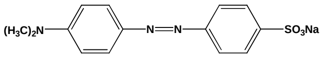


Rhodamine B

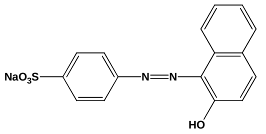
(b) negatively charged:



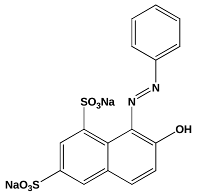
Congo Red



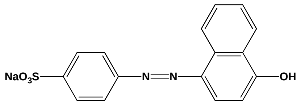
Methyl Orange



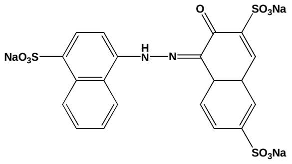
Orange II



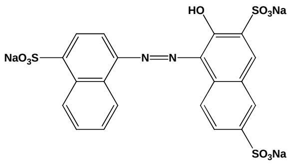
Orange G



Orange I



Amaranth



Sunset Yellow

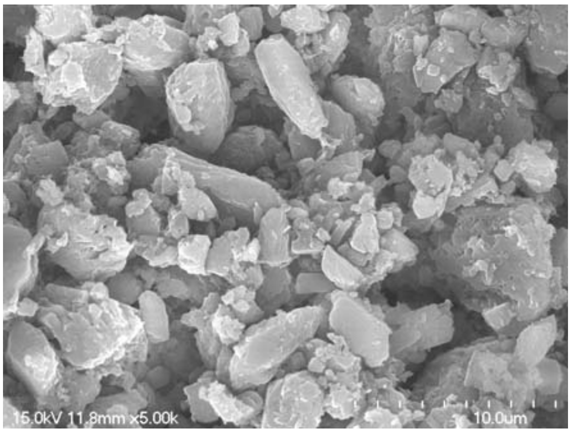


Fig. S4. The scanning electron microscopy (SEM) image of **1**·0.75CR·6H_2O.

Fig. S5. (a) The picture of the crystals of the dye-absorbed sample **1**·0.75CR·6H_2O obtained from immersing the crystals into the aqueous solution of CR for 2h; (b) One piece obtained from cutting one CR-absorbed crystal that was took out of the solution. The shining part shows that CR molecules do not go into the interior part of the crystal and are absorbed on the very surface of the crystal.

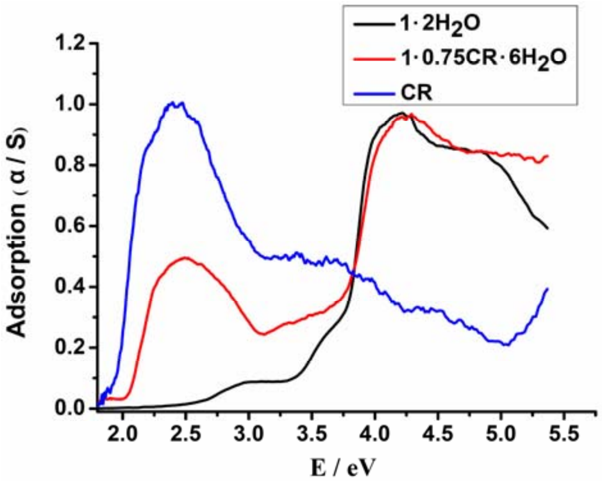
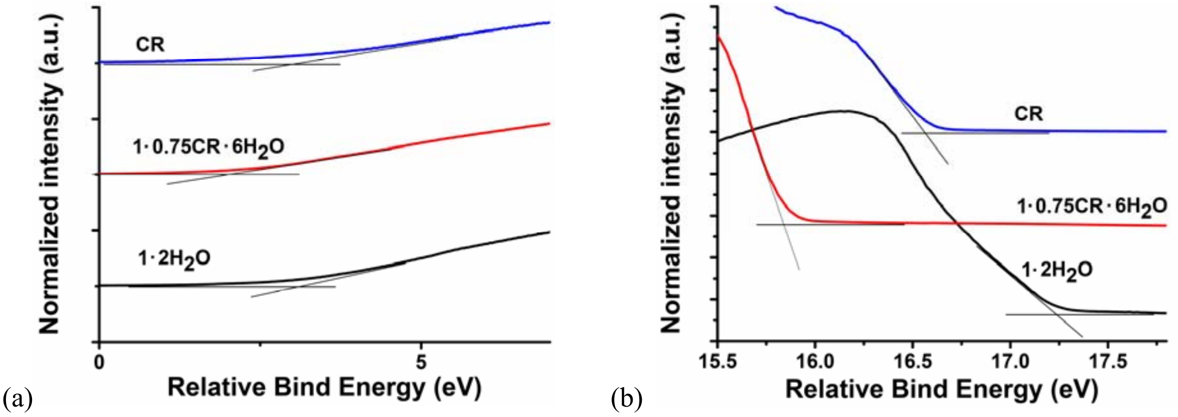


Fig. S6 The solid-state optical diffuse-reflection spectra of **1**·$2H_2O$, **1**·0.75CR·$6H_2O$, and CR derived from diffuse reflectance data at ambient temperature.



(a) (b)

Fig. S7 Ultraviolet photoelectron spectroscopy (UPS) spectra. (*a*) The HOMO region of **1**·$2H_2O$, **1**·0.75CR·$6H_2O$ and CR. (*b*) The inelastic cut-off region of **1**·$2H_2O$, **1**·0.75CR·$6H_2O$ and CR.

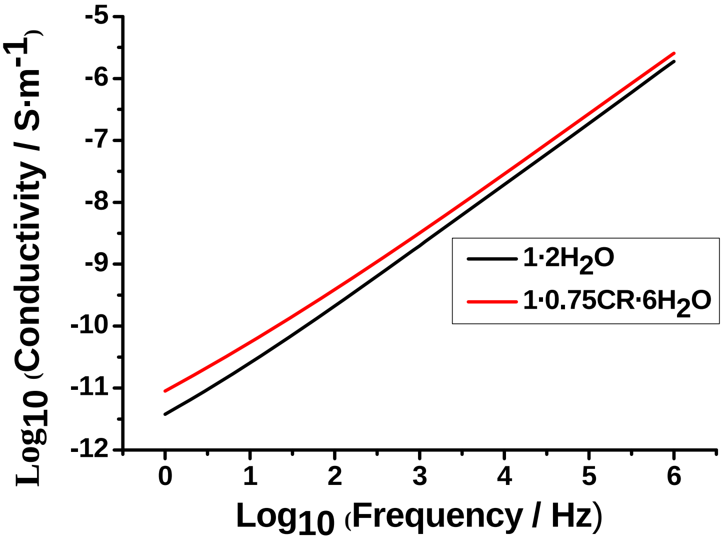


Fig. S8 Frequency dependence of the electrical conductivity of **1**·2H_2O and **1**·0.75CR·6H_2O at room temperature.

We carried out the conducting property tests on **1**·2H_2O and **1**·0.75CR·6H_2O by measuring their electrical conductivities of the powders in variable frequencies at 298 K. As shown in Fig. S7, the conductivities of **1**·2H_2O and **1**·0.75CR·6H_2O increased almost linearly from 1 Hz to 10^6 Hz upon the increase of frequency, with the magnitude ranging from *ca.* 10^{-11} S·cm^{-1} to *ca.* 10^{-6} S·cm^{-1}. The conductivity of **1**·0.75CR·6H_2O was better than **1**·2H_2O, presumably due to the presence of a large amount of conjugated ingredients (CR). In general, the conducting behaviour of **1**·0.75CR·6H_2O was better than that of **1**·2H_2O.