Supplementary Material (ESI) for Chemical Communications

Solid-state single-crystal-to-single-crystal transformation from a 2D layer to a 3D framework mediated by lattice iodine release

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Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. The C, H and N elemental analysis were conducted on a Perkin–Elmer 2400CHN elemental analyzer. IR-spectra were measured on a Mattson Alpha-Centauri spectrometer at the range of 4000–400 cm^{-1}. X-ray powder diffractions were carried out on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu K_α radiation (λ = 0.154 nm) and 2θ ranging from 5 to 50°. All UV/vis spectra were recorded on a Cary 500 UV–VIS–NIR spectrophotometer from 200 nm to 600 nm using the same solvent in the examined solution as a blank.

Impedance test

The pellet of sample **1** with 1.57 cm in diameter and 0.19 cm in thickness was prepared by first grinding the samples into a homogeneous powder with a mortar and pestle. The powders were then added to a die, sandwiched between two stainless steel electrodes and pressed.

The electrochemical impedance spectroscopy (EIS) was performed with an advanced electrochemical system (PARSTAT 2273, Ametek, USA) at room temperature. An ac voltage of 50 mV in amplitude with a frequency range from 50 Hz to 600 kHz was superimposed on the dc potential and applied to the material. The experimental data of the electrochemical impedance plot were analyzed by applying the nonlinear least squares fitting to the theoretical model represented by a Randles equivalent electrical circuit attached by PARSTAT 2273.

The constant phase element (CPE) was introduced to account for the non-ideality of the interface between the electrode and electrolyte in the practical impedance spectrum. Every conductivity can be calculated by following equation.

$$\sigma = \frac{l}{R_s S}$$

where l and S are the thickness (cm) and cross-sectional area (cm^2) of the pellet respectively, and R_s, which was extracted directly from the impedance plots, is the bulk resistance of the sample (Ω).

X-ray crystallography

Single-crystal X-ray diffraction data for **1** and **2** were recorded at a temperature of 293 (2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program.[2] Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups.

References

1 G. M. Sheldrick, SHELXS-97, *Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

2 G. M. Sheldrick, SHELXL-97, *Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table S1. Crystal data and structure refinements for compounds **1** and **2.**

	1	**2**
Formula	$C_6H_4Cu_{0.5}INO_2$	$C_{24}H_{16}Cu_2N_4O_8$
Fw	280.77	615.49
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc
a /Å	5.8382(3)	4.9737(17)
b /Å	12.5979(6)	25.022(3)
c /Å	10.8127(5)	11.0111(16)
α / °	90	90
β / °	91.121(4)	98.48(2)
γ / °	90	90
V /Å^3	795.11(7)	1355.4(5)
Z	4	2
D_c/ g cm^{-3}	2.345	1.508
F(000)	522	620
R(int)	0.0282	0.0467
GOF on F^2	1.055	1.022
R_1 [$I > 2\sigma(I)$]	0.0408	0.0746
wR_2 (all data)	0.0943	0.1927

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

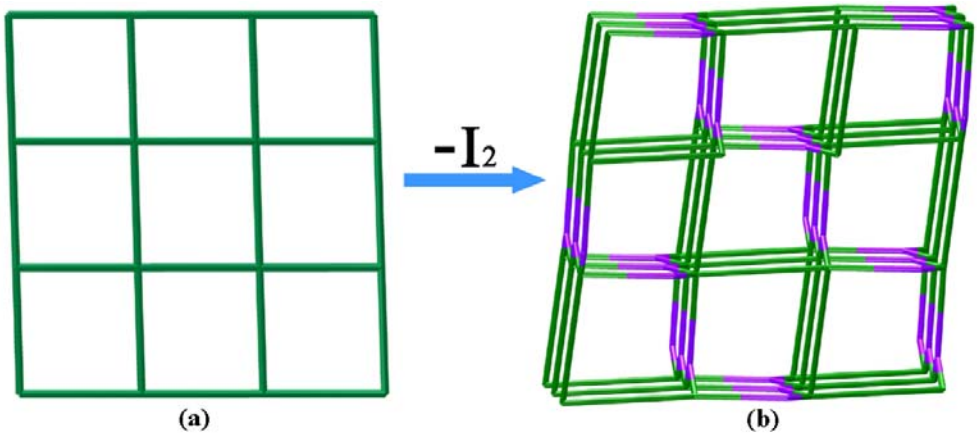
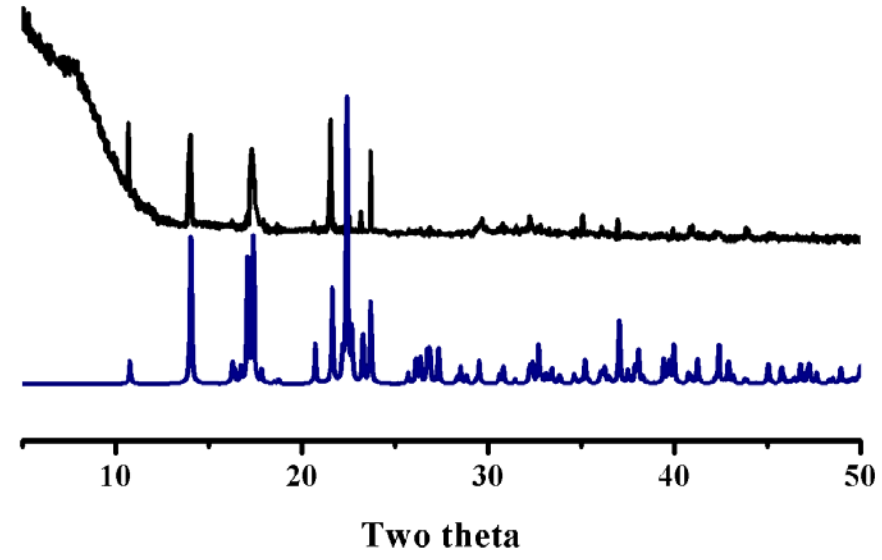
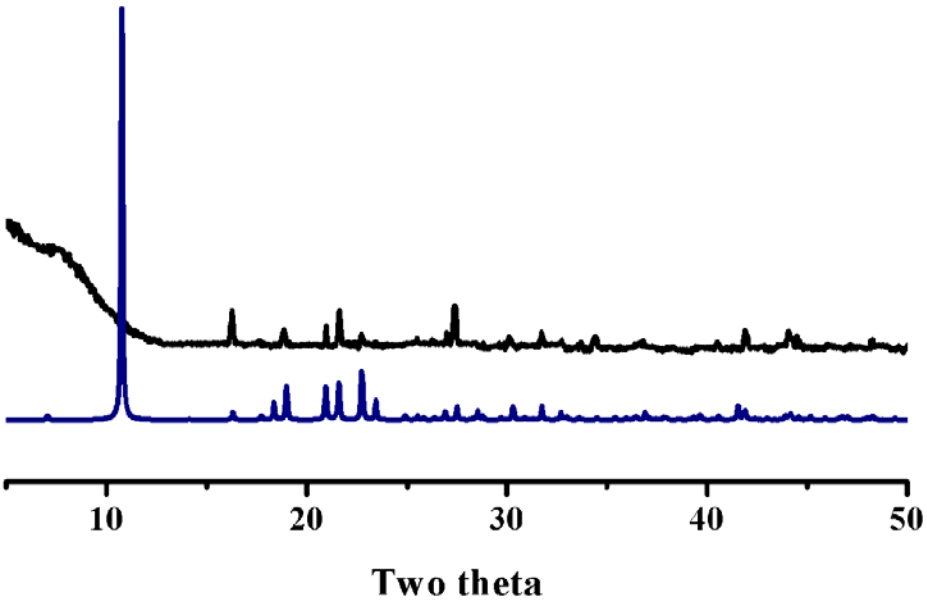


Fig. S1. (a) Schematic representation of the 2D (4,4) network of 1 and (b) view of the 3D (3,5)-connected net of 2.

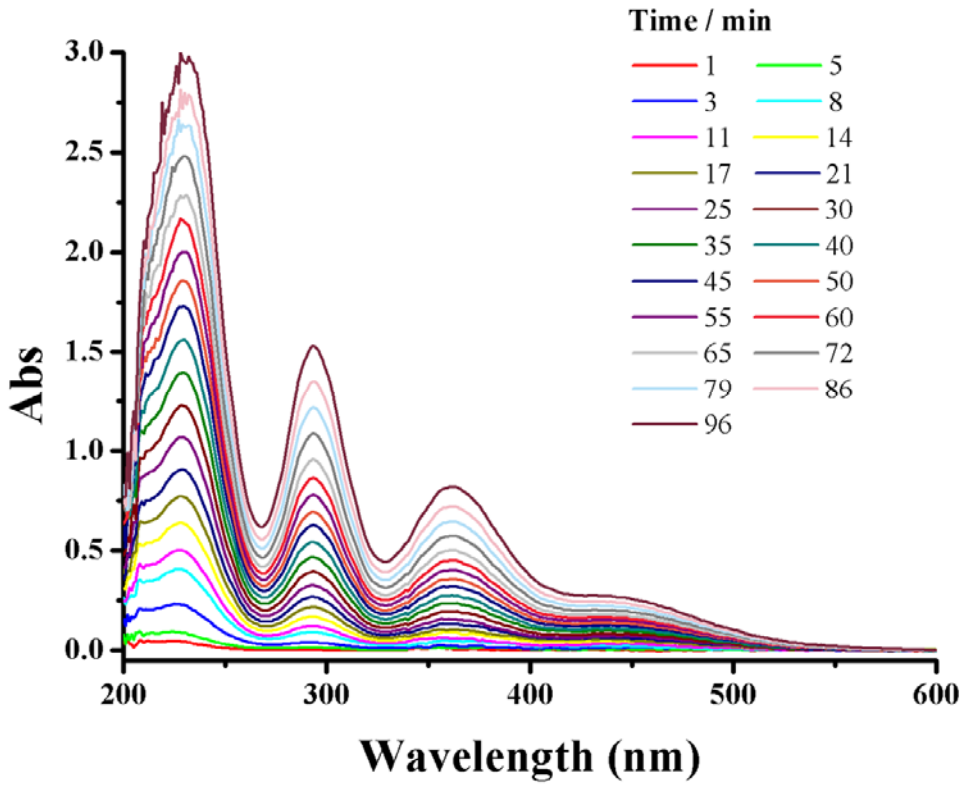


(a)

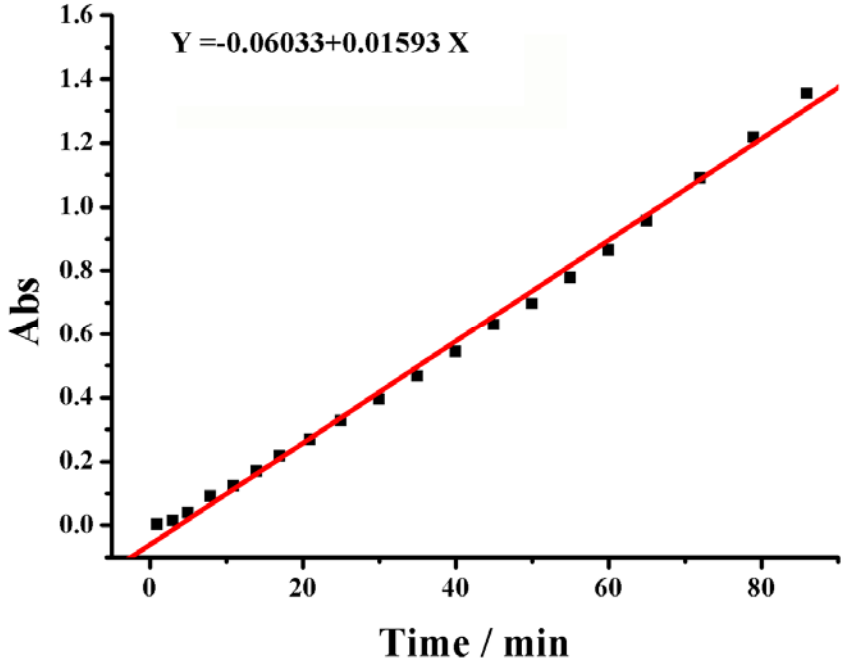


(b)

Fig. S2. The simulated (blue) and experimental (black) PXRD patterns for compounds **1** (a) and **2** (b).

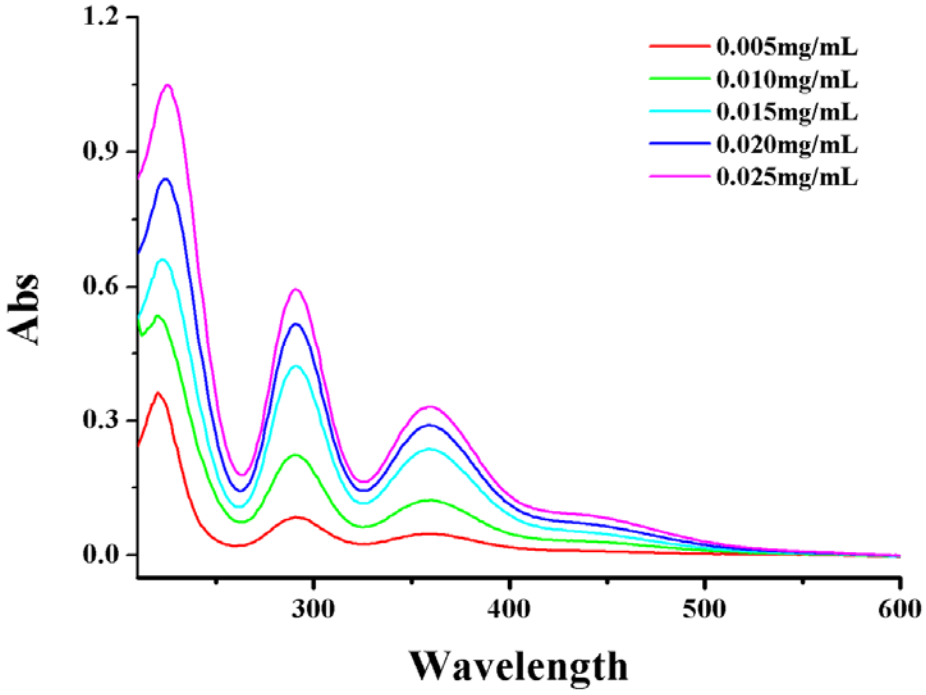


(a)

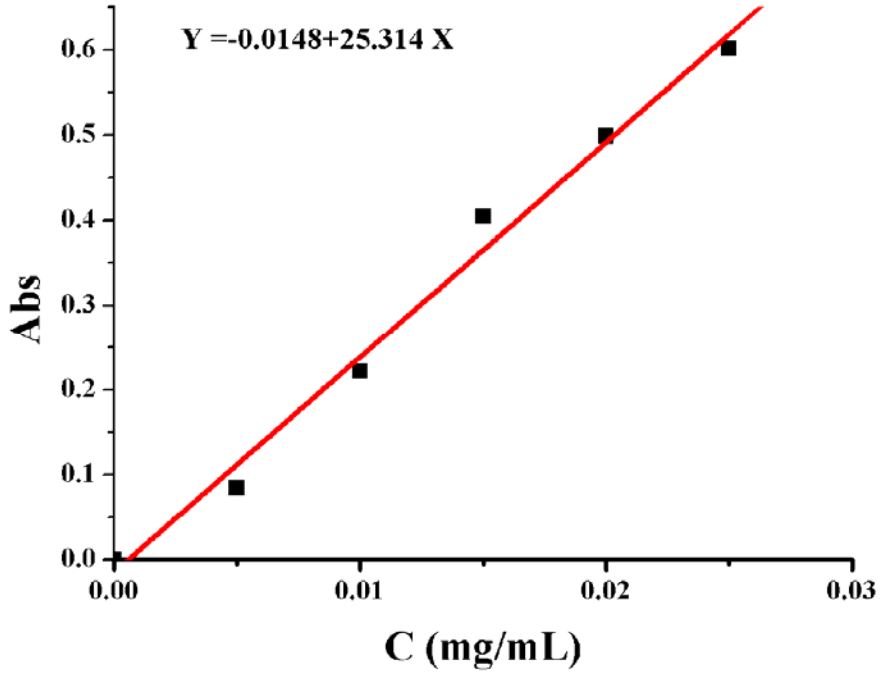


(b)

Fig. S3. (a) Temporal evolution of UV/vis absorption spectra for the I_2 delivery from three single crystals of **1** in 3 mL of MeOH and (b) the controlled delivery of I_2 ([I_2] = Kt) in the first 96 min.

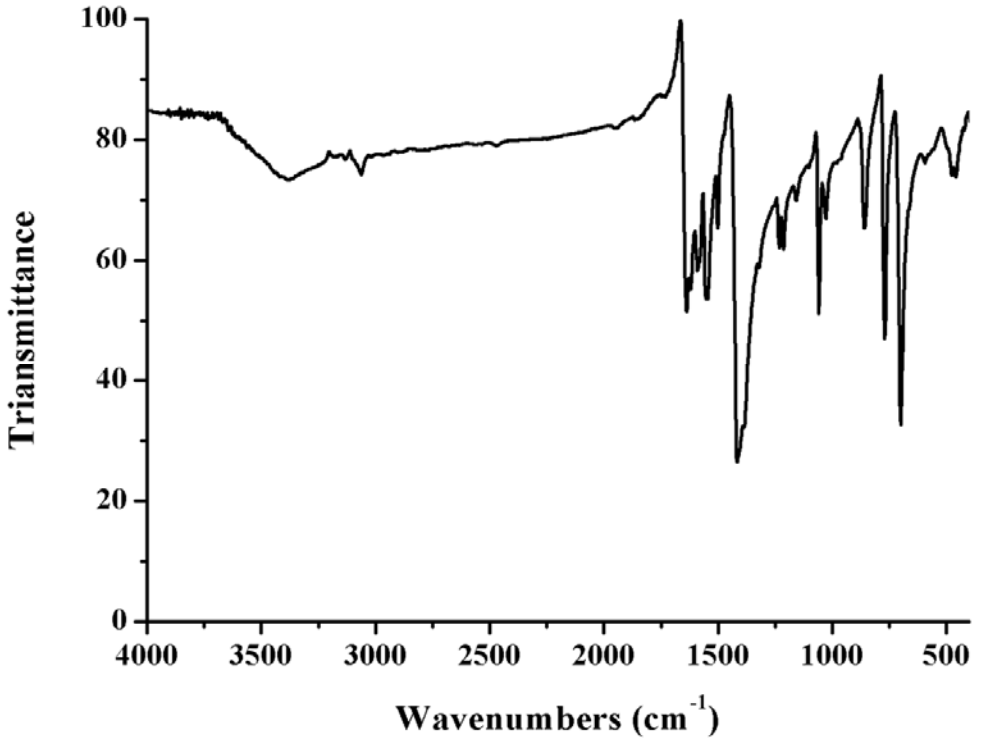


(a)

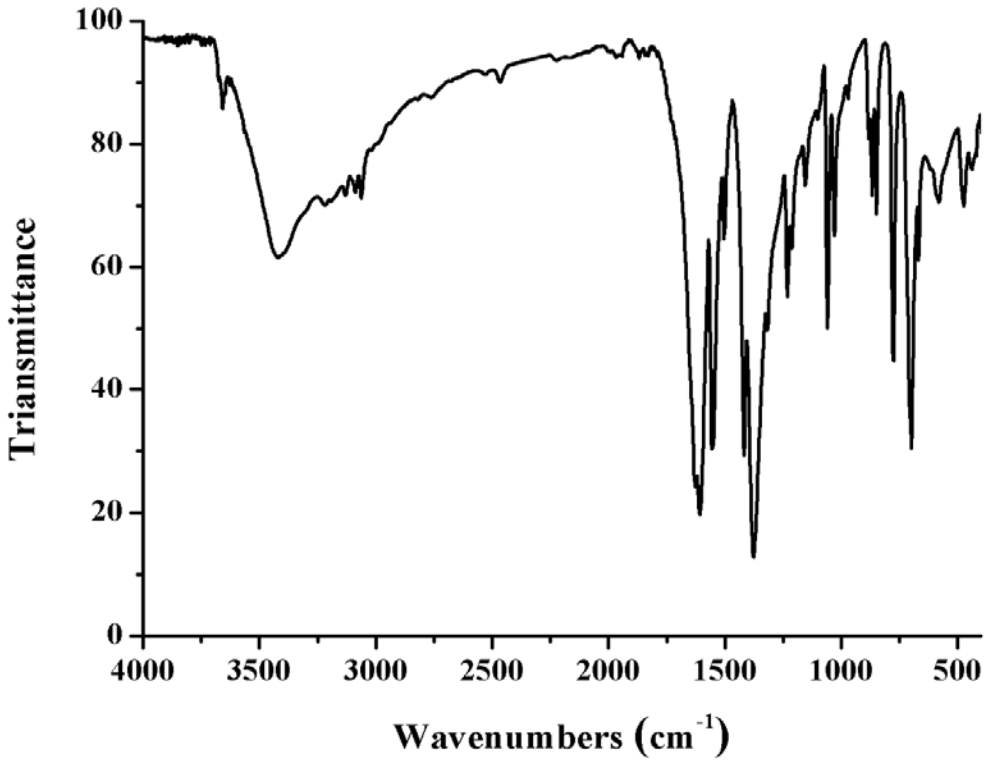


(b)

Fig. S4. (a) Calibration plot of standard iodine by UV/vis spectra in methanol solution and (b) he fitting of Abs value *vs* concentration of I_2, the relatively good linearity satisfies Lambert-Beer Law.



(a)



(b)

Fig. S5. IR spectra of compounds **1** and **2**.