Electronic Supplementary Material (ESI) for Dalton Transactions.


# Electronic supplementary information

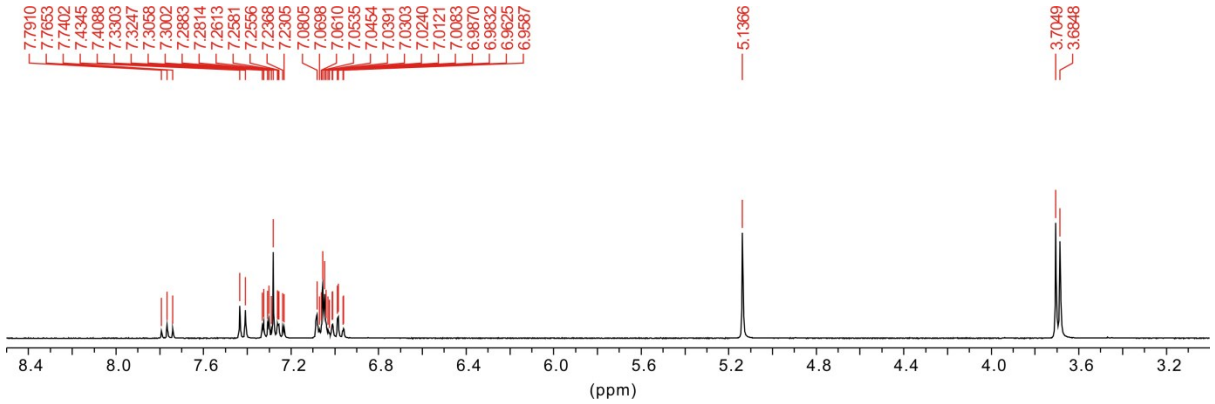
## A double decker type complex: copper(I) iodide complexation with mixed donor macrocycles via [1:1] and [2:2] cyclisations

Yunji Kang,[a] In-Hyeok Park,*[a] Mari Ikeda,[b] Yoichi Habata[c] and Shim Sung Lee*[a]

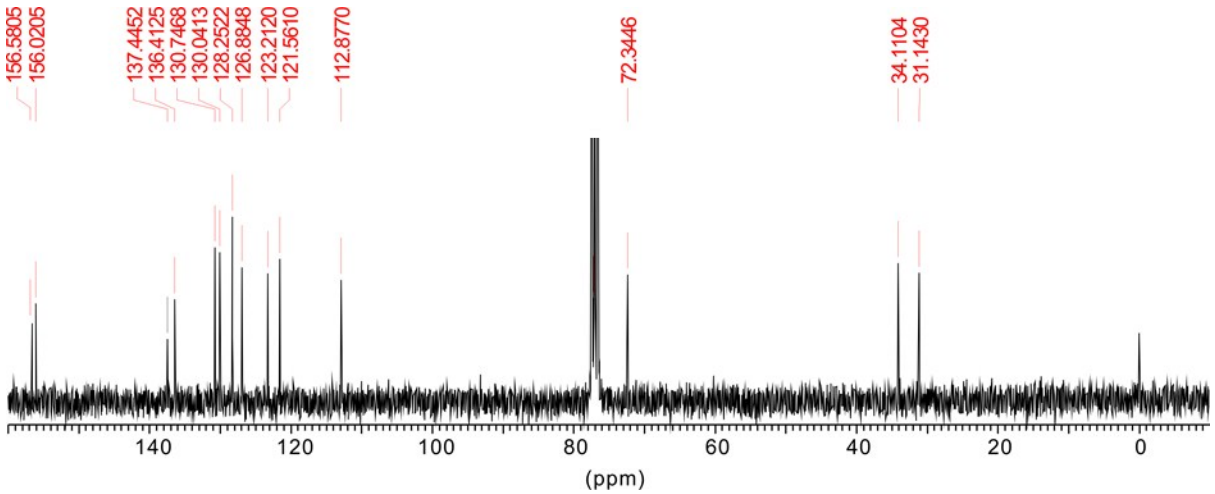
[a.] Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea

[b.] Education Center, Faculty of Engineering, Chiba Institute of Technology, 2-1-1 Shibazono, Narashino, Chiba 275-0023, Japan

[c.] Department of Chemistry, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan




(a)




(b)

**Fig. S1** (a) $^{1}H$ and (b) $^{13}C$ NMR spectra of **L**$^{1}$ in $CDCl_3$.

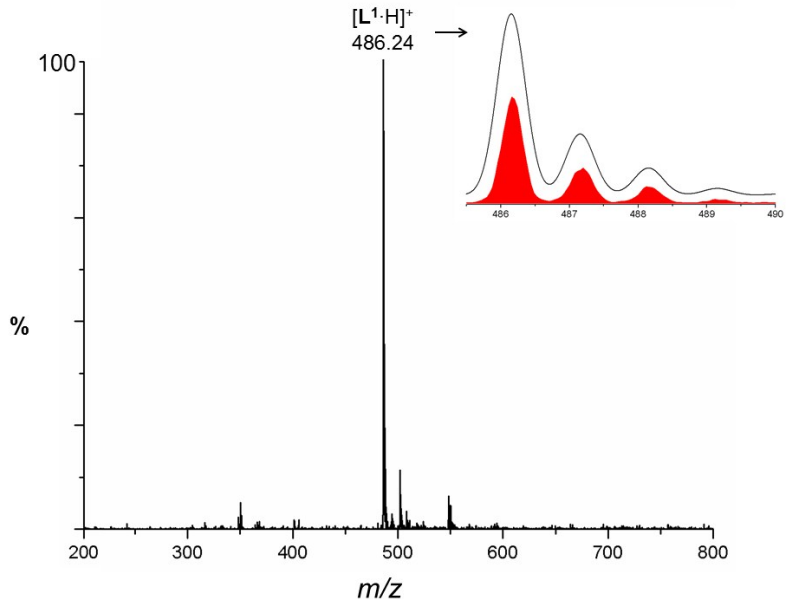
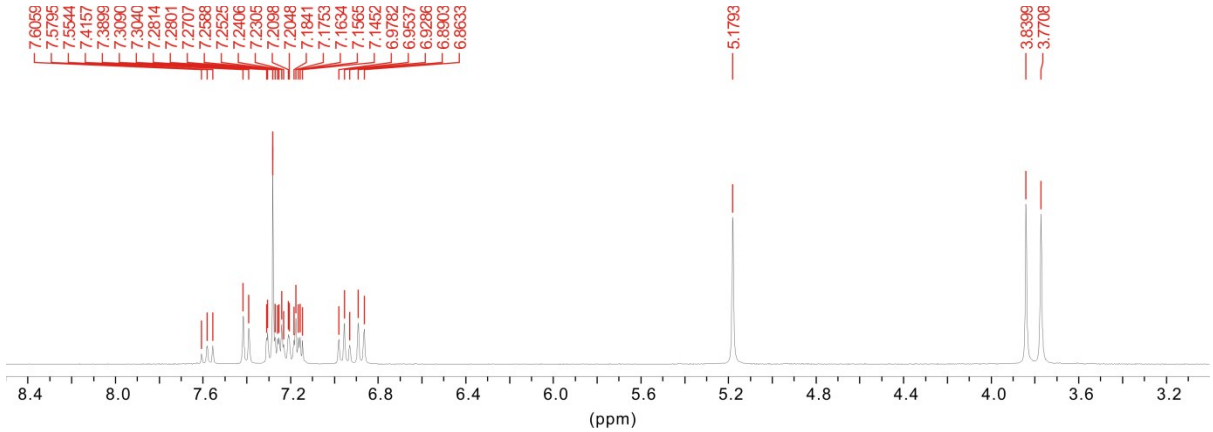
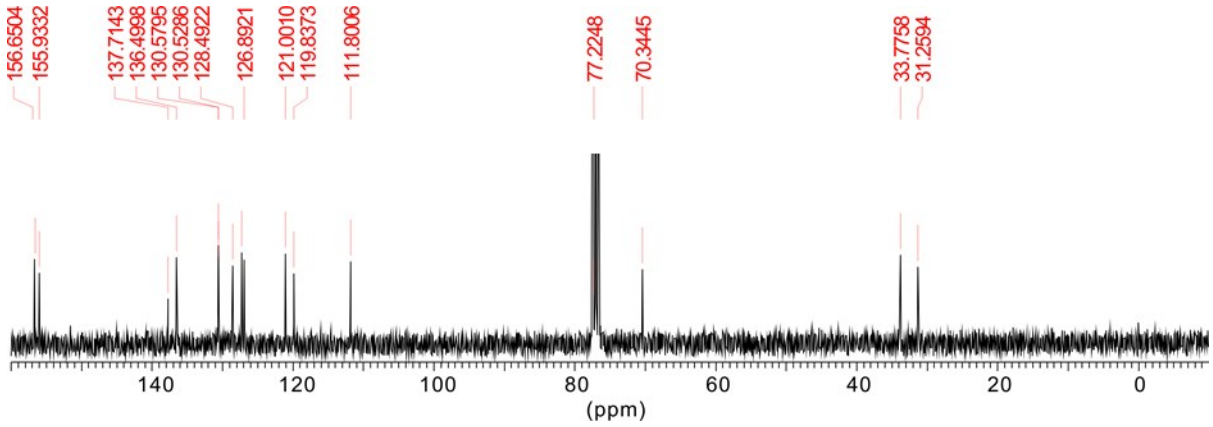



**Fig. S2** ESI-mass spectrum of **L**$^{1}$.




(a)




(b)

**Fig. S3** (a) $^{1}H$ and (b) $^{13}C$ NMR spectra of $\mathbf{L^2}$ in $CDCl_3$.

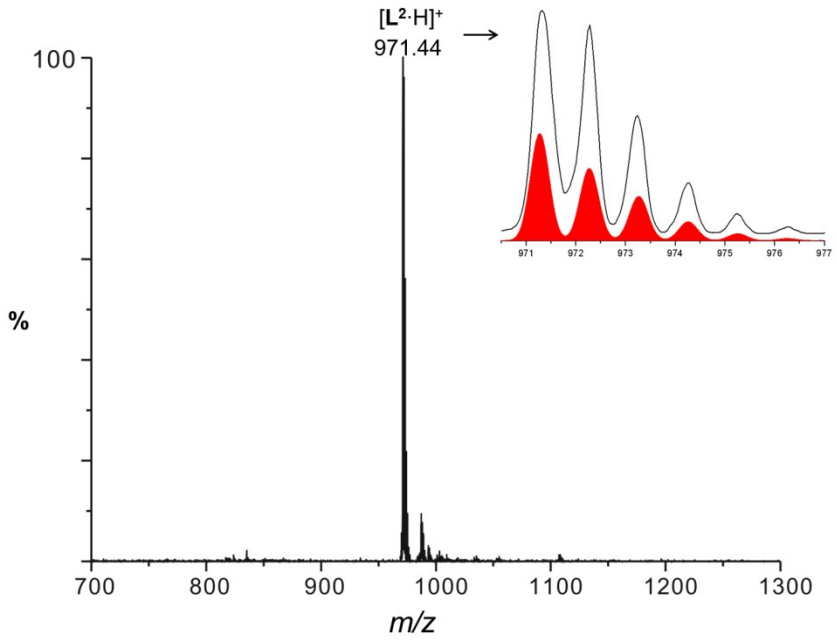



**Fig. 4** ESI-mass spectrum of $\mathbf{L^2}$.

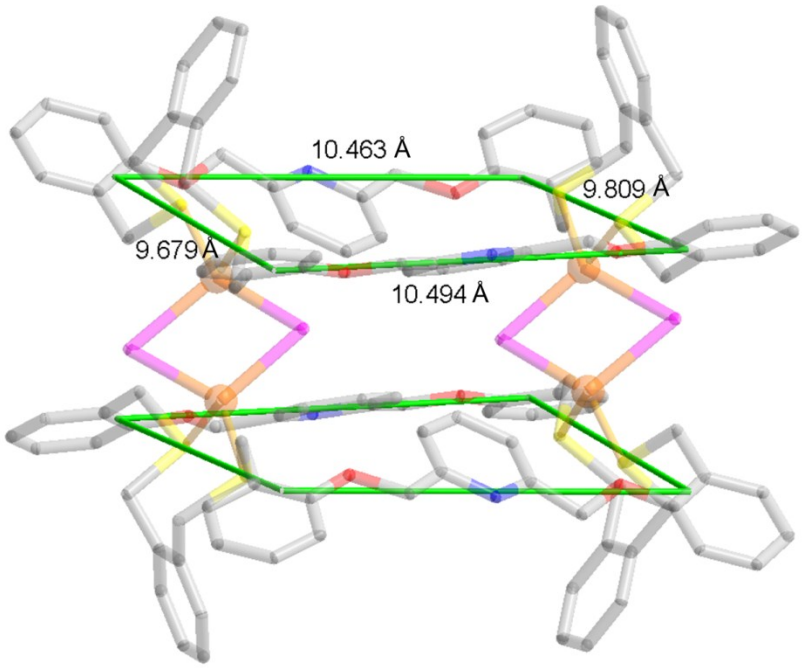



**Fig. S5** The rectangular configuration of $\mathbf{L^2}$ with one nanometer square area in **2a**.

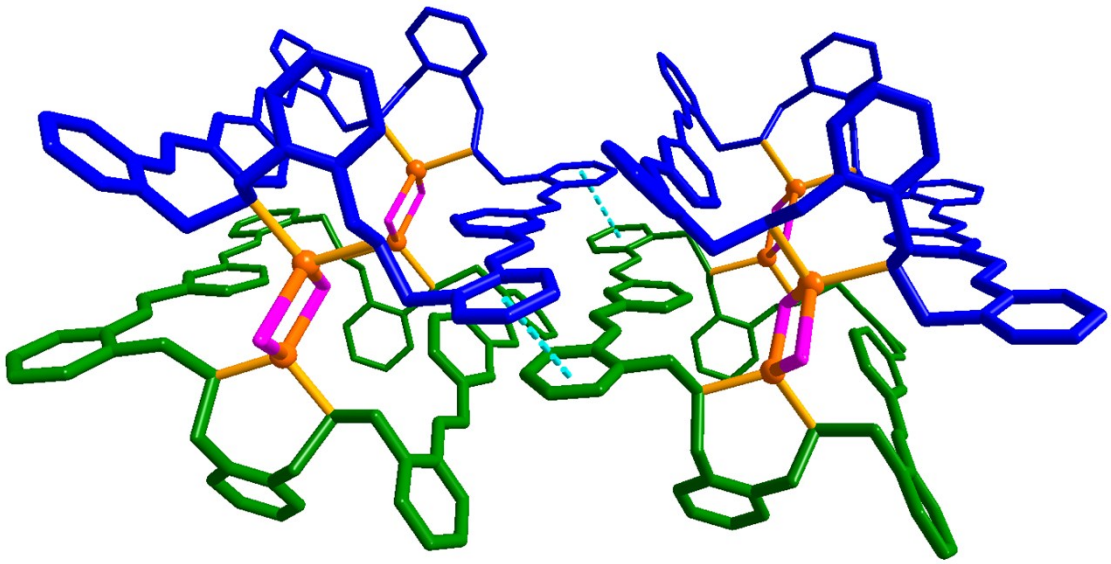
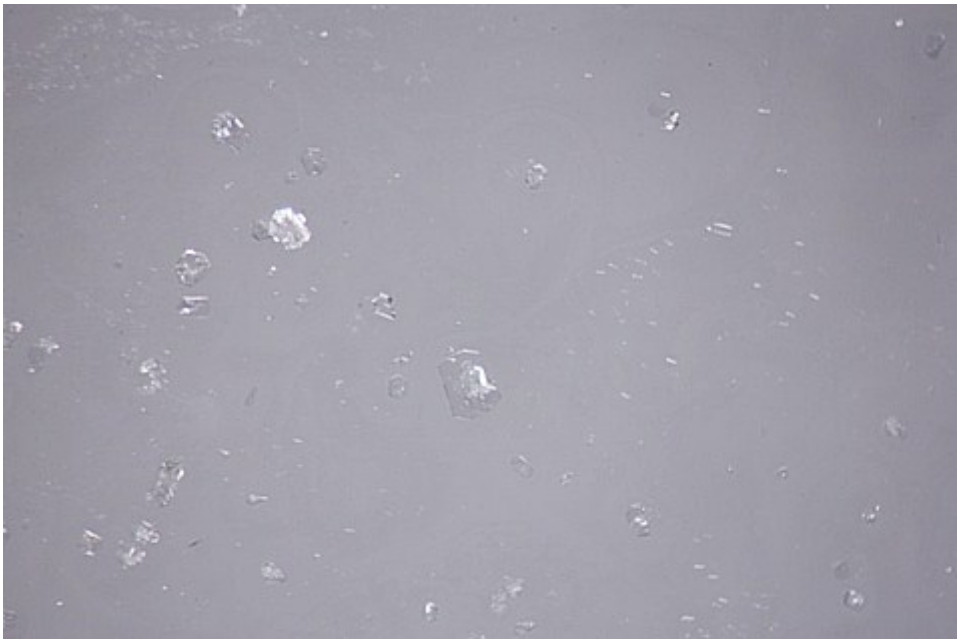


**Fig. S6** Intermolecular π-π stacking interaction (centroid-centroid distance 4.47 Å, dotted lines) in the packing structure of **2a**.



(a)

(b)

**Fig. S7** Photographs of (a) **2a** (colourless, fresh crystals) and (b) **2b** (pale yellow, the same crystals of **2a** but after 3 days).

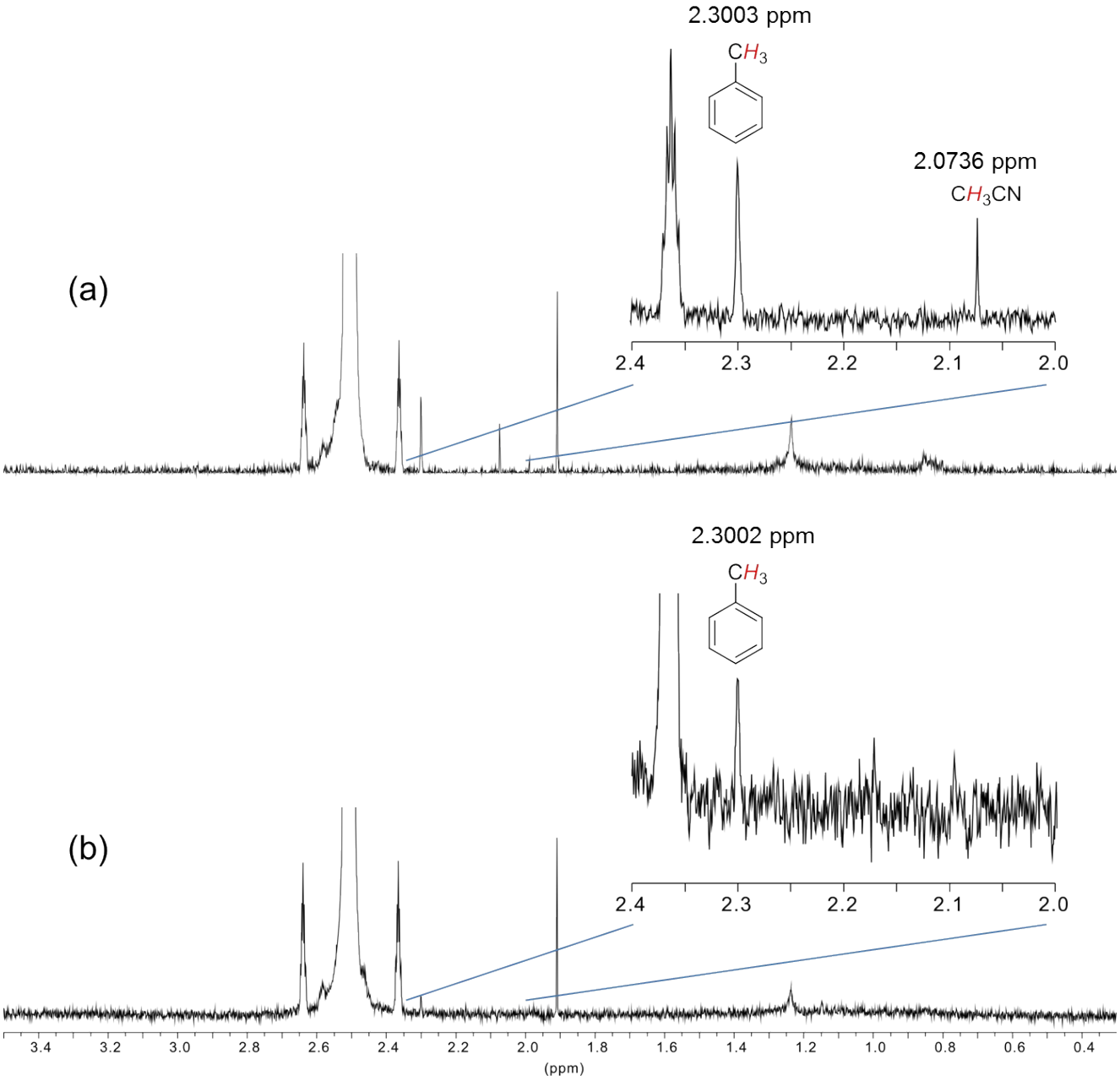



**Fig. S8** $^{1}$H NMR (500 MHz) spectra of (a) **2a** and (b) **2b** in DMSO-$d_6$ with small drops of $HNO_3$ to dissolve each crystalline sample. From the comparison of the two spectra, it was confirmed that the acetonitrile molecules in **2a** (singlet at 2.0736 ppm) were removed in **2b**.

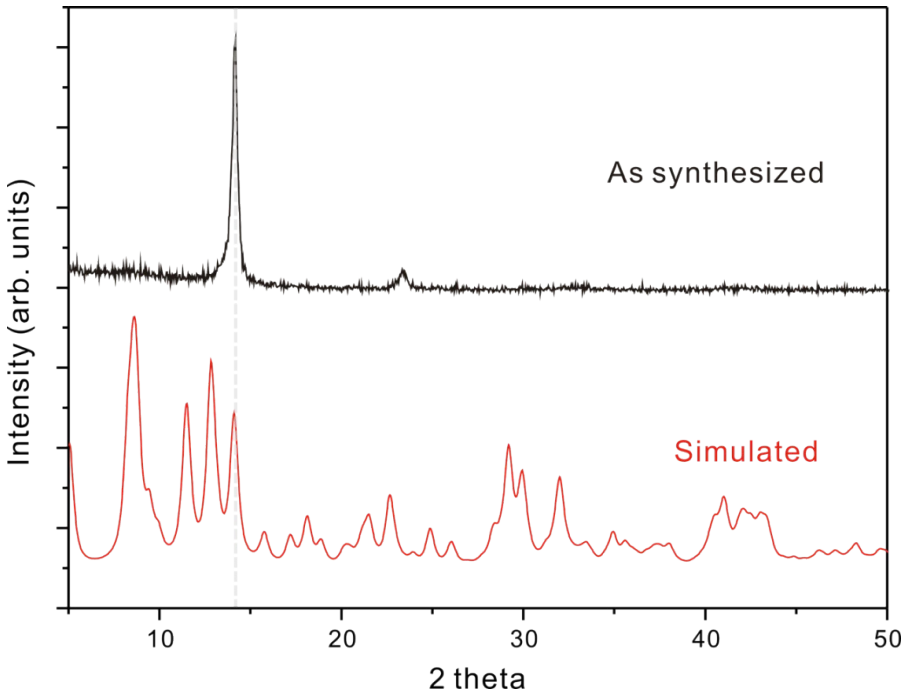



**Fig. S9** PXRD patterns for **2a**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The simple patterns and intensity variations for the synthesized sample compared to the simulated one are mainly due to the flexible nature of the product.[S1-S3]

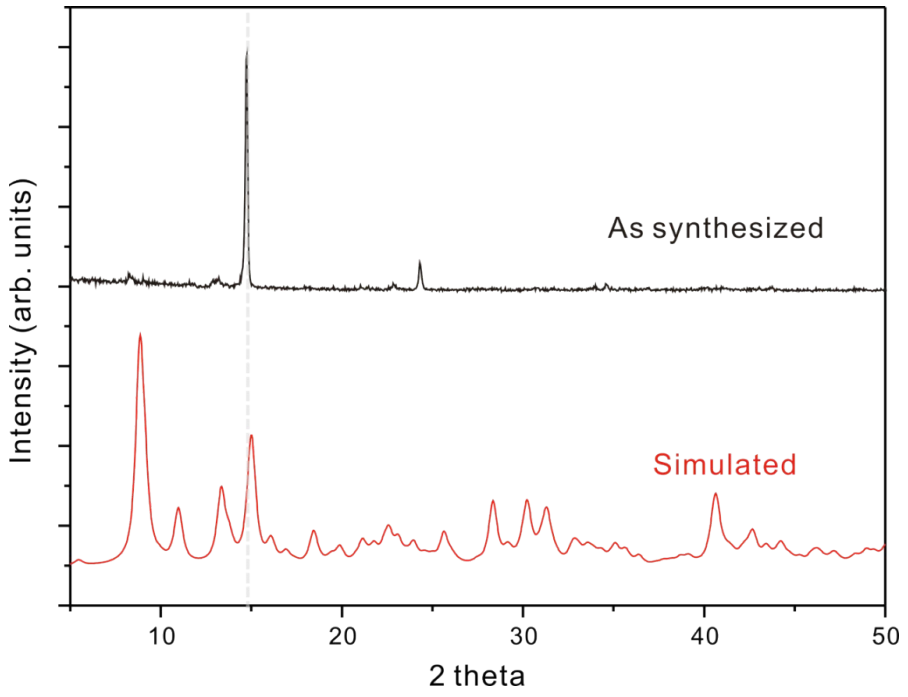



**Fig. S10** PXRD patterns for **2b**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The simple patterns and intensity variations for the synthesized sample compared to the simulated one are mainly due to the flexible nature of the product.[S1-S3]

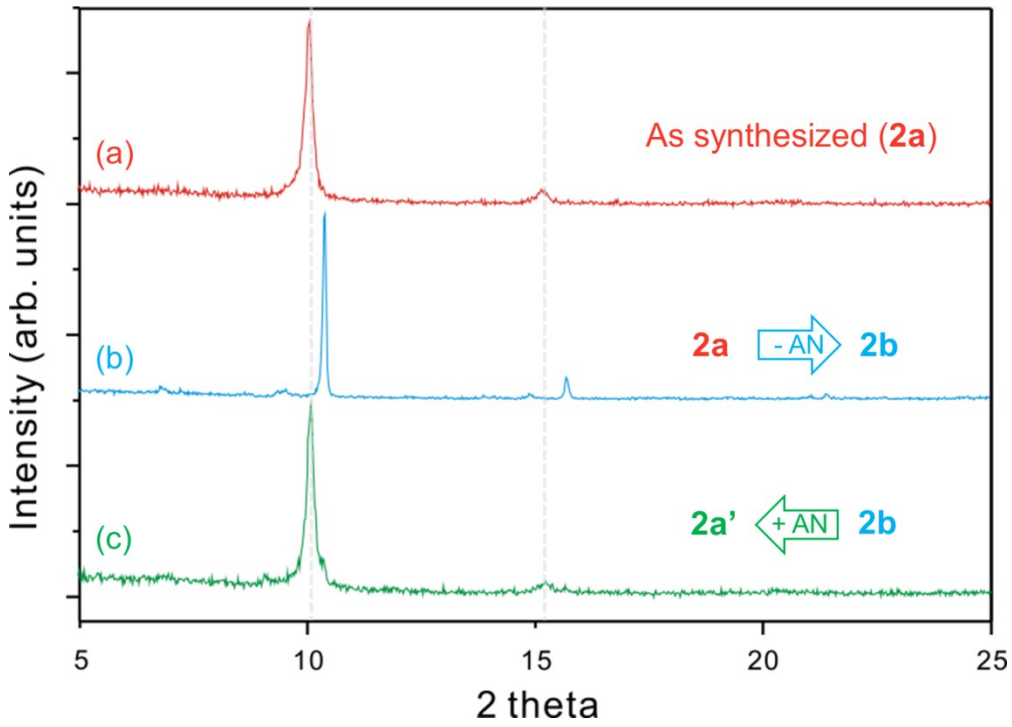



**Fig. 11** PXRD patterns for (a) **2a** (fresh crystals), (b) **2b** (acetonitrile-free crystals of **2a**) and (c) **2a'** (crystals of **2b** exposed to acetonitrile).

**References:**

S1. J. Duan, M. Higuchi, M. L. Foo, S. Horike, K. P. Rao and S. Kitagawa, *Inorg. Chem.*, 2013, **52**, 8244.

S2. S. Henke, R. Schmid, J.-D. Grunwaldt and R. A. Fischer, *Chem. Eur. J.*, 2010, **16**, 14296.

S3. W. Kaneko, M. Ohba and S. Kitagawa, *J. Am. Chem. Soc.,* 2007, **129**, 13706.

**Table S1** Crystallographic data and refinement parameters

| | **1** | **2a** | **2b** |
|---|---|---|---|
| formula | $C_{33}H_{37}CuI_3NO_3S_2$ | $C_{116}H_{108}Cu_4I_4N_4O_8S_8$ | $C_{116}H_{108}Cu_4I_4N_4O_8S_8$ |
| formula weight | 1004.00 | 2704.30 | 2704.30 |
| crystal system | Monoclinic | Triclinic | Triclinic |
| space group | $P2_1/n$ | $P$-1 | $P$-1 |
| $a$ (Å) | 8.7764(2) | 14.5063(18) | 14.275(3) |
| $b$ (Å) | 13.5763(3) | 15.144(2) | 14.778(3) |
| $c$ (Å) | 30.1113(6) | 18.221(3) | 18.504(3) |
| $\alpha$ (°) | 90 | 98.408(10) | 109.751(11) |
| $\beta$ (°) | 98.3400(10) | 96.873(9) | 93.682(11) |
| $\gamma$ (°) | 90 | 118.076(8) | 116.299(10) |
| $V$ (Å$^3$) | 3549.85 | 3411.4(8) | 3186.1(10) |
| $Z$ | 4 | 1 | 1 |
| $D_{calc}$(g/cm$^3$) | 1.879 | 1.316 | 1.409 |
| $\mu$ (mm$^{-1}$) | 3.375 | 1.690 | 1.814 |
| $2\theta_{max}$ (°) | 52.00 | 52.00 | 52.00 |
| reflections collected | 53917 | 40212 | 69740 |
| independent reflections | 6946 [$R_{int}$ = 0.0299] | 13118 [$R_{int}$ = 0.1230] | 12323 [$R_{int}$ = 0.0773] |
| goodness-of-fit on $F^2$ | 1.162 | 1.126 | 1.148 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0251, 0.0448 | 0.1437, 0.3599 | 0.1099, 0.3211 |
| $R_1$, $wR_2$ (all data) | 0.0331, 0.0470 | 0.2566, 0.3946 | 0.2027, 0.3614 |

**Table S2** Selected bond distances (Å) and bond angles (°) for **1**

| | | | |
|---|---|---|---|
| Cu1-N1 | 2.038(2) | Cu1-S1 | 2.2660(8) |
| Cu1-S2 | 2.2997(8) | Cu1-O1 | 2.610(2) |
| Cu1-O2 | 2.726(2) | | |
| I1-I2-I3 | 177.089(10) | S1-Cu1-S2 | 115.31(3) |
| S1-Cu1- N1 | 122.56(7) | S2-Cu1- N1 | 122.03(7) |

**Table S3** Selected bond distances (Å) and bond angles (°) for **2a** and **2b**[a]

| | **2a** | **2b** |
|---|---|---|
| Cu1-Cu2 | 2.965(3) | 2.902(3) |
| Cu1-I1 | 2.586(2) | 2.680(2) |
| Cu1-I2 | 2.698(3) | 2.5724(18) |
| Cu1-S1 | 2.345(4) | 2.301(4) |
| Cu1-S2 | 2.333(4) | 2.317(3) |
| Cu2-I1 | 2.621(2) | 2.598(2) |
| Cu2-I2 | 2.685(3) | 2.762(2) |
| Cu2-S3A | 2.337(5) | 2.335(4) |
| Cu2-S4A | 2.311(5) | 2.317(4) |
| | | |
| Cu1-I1-Cu2 | 69.41(8) | 68.29(7) |
| Cu1-I2-Cu2 | 66.84(7) | 64.42(6) |
| Cu2-Cu1-S1 | 126.97(13) | 127.78(11) |
| Cu2-Cu1-S2 | 125.95(13) | 123.34(11) |
| Cu2-Cu1-I1 | 55.86(7) | 56.28(5) |
| Cu2-Cu1- I2 | 56.38(7) | 56.42(6) |
| I1-Cu1-S1 | 114.31(14) | 114.66(10) |
| I1-Cu1-S2 | 113.14(13) | 111.18(10) |
| I2-Cu1-S1 | 105.03(14) | 105.20(10) |
| I2-Cu1-S2 | 105.10(13) | 104.32(10) |
| I1-Cu1-I2 | 112.23(9) | 112.69(7) |
| Cu1-Cu2-S4A | 124.73(14) | 128.57(12) |
| Cu1-Cu2- S3A | 127.90(14) | 127.57(12) |
| Cu1-Cu2- I1 | 54.73(6) | 55.44(5) |
| Cu1-Cu2- I2 | 56.78(7) | 59.16(6) |
| I1-Cu2-S4A | 109.56(14) | 110.52(12) |
| I1-Cu2-S3A | 111.91(15) | 109.97(11) |
| I2-Cu2-S4A | 106.72(15) | 108.81(13) |
| I2-Cu2-S3A | 109.61(15) | 108.52(12) |
| I1-Cu2-I2 | 111.49(9) | 114.60(8) |
| S1-Cu1-S2 | 106.25(17) | 108.09(13) |
| S3A-Cu2-S4A | 107.34(18) | 103.86(15) |

[a]symmetry operation: A) -x+1,-y,-z+1.