

## Supporting Information

# **A multi-responsive Indium-viologen hybrid with ultrafast-response photochromism and electrochromism**

Qiu-Yue Pan,<sup>a</sup> Meng-En Sun,<sup>a</sup> Chong Zhang,<sup>a</sup> Lin-Ke Li,<sup>a</sup> Hua-Li Liu,<sup>a</sup> Kai-Jie Li,<sup>a</sup> Hai-Yang Li<sup>\*a</sup>  
and Shuang-Quan Zang<sup>\*a</sup>

*<sup>a</sup> Henan Key Laboratory of Crystalline Molecular Functional Materials, Henan International Joint Laboratory of Tumor Theranostical Cluster Materials, Green Catalysis Center, and College of Chemistry, Zhengzhou University, Zhengzhou 450001, China*

E-mail: [zangsqzg@zzu.edu.cn](mailto:zangsqzg@zzu.edu.cn); [lihaiyang@zzu.edu.cn](mailto:lihaiyang@zzu.edu.cn)

## Experimental section

### Materials and reagents.

All reagents and solvents, including  $\text{InCl}_3$ , 4,4'-dipyridine, S-3-chloro-1,2-propanediol, HCl aqueous solution (37%, 0.5 mL), acetonitrile ( $\text{CH}_3\text{CN}$ ), Ethanol (EtOH) and acetone were commercially available and used without further purification.

### Characterization.

Single-crystal X-ray diffraction (SCXRD) data were collected on a Bruker APEX-II CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 300 K. The structure was assessed with direct methods (SHELXS) and refined by full-matrix least squares in F2 using OLEX2, which utilizes the SHELXL-2015 module. The crystal structure was visualized in DIAMOND 3.2. Powder X-ray Diffraction (PXRD) patterns of the samples were recorded on a D/MAX-3D diffractometer (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ). Simulated powder patterns were obtained with Mercury software and crystallographic information file (CIF) from a single-crystal X-ray experiment. The Fourier transform infrared (FT-IR) spectra were performed on ALPHA II spectrometer with KBr pellets. TGA were performed on a TA Q50 thermal analyzer from RT to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (flow rate = 60 mL/min). Elemental analyses (EA) for C, H and N were collected on a Perkin-Elmer 240 elemental analyzer. A high-speed camera operating at 1000 frames per second was used to capture the color transitions process. Solid-state UV-vis diffuse reflectance spectra were recorded using a Hitachi UH4150 UV-vis spectrophotometer. ESR for solid state were recorded on Bruker A300. Cyclic voltammetry was carried out on an electrochemical working station CHI 660E (Shanghai) in 0.5 M acetonitrile solution. Electronic absorption spectra measurements were performed on America PINE spectroelectrochemical. A typical three-electrode system was employed, using compound **1** in ITO glass as working electrode, a platinum sheet as counter electrode, and an Ag/AgCl electrode as reference electrode.

### Synthesis of {1-(S-2,3-dihydroxypropyl)-4,4'-bipyridinium chloride}.

1-(S-2,3-dihydroxy-propyl)-4,4'-bipyridinium chloride was synthesized according to previously reported procedure in the literature.<sup>1</sup>

### Synthesis of compound **1**.

InCl<sub>3</sub> (22.1 mg, 0.1 mmol), 1-(S-2,3-dihydroxypropyl)-4,4'- bipyridinium chloride (26.7 mg, 0.1 mmol), HCl aqueous solution (37%, 0.5 mL) were dissolved in 3 mL CH<sub>3</sub>CN and 3 mL CH<sub>3</sub>CH<sub>2</sub>OH at room temperature. The resulted clear solution was allowed to evaporate at room temperature for several days, then the light yellow bulk crystals were obtained in a yield of 52% based on InCl<sub>3</sub>. Elemental analysis, calcd (%) for (C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>InCl<sub>6</sub>·Cl (**1**): C, 37.71; N, 6.77; H, 3.86. Found C, 37.28; N, 6.43; H, 3.81.

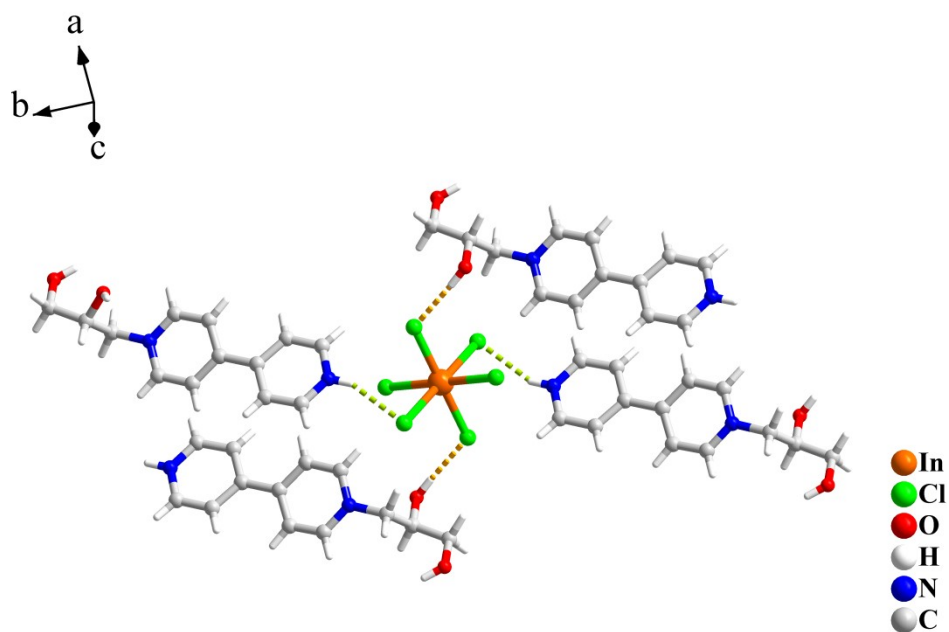
#### **The preparation of compound 1 working electrode**

Clean and dry the ITO glass with water, ethanol and acetone in turn. 20 mg compound crystal, 0.5 mL methanol and 20 μL 5% Nafion were added to the bottle and the mixture was ultrasonic for 30 min. The solution was dispersed to ITO glass by Pipetting gun and let it dry overnight at room temperature to obtain the compound working electrode.

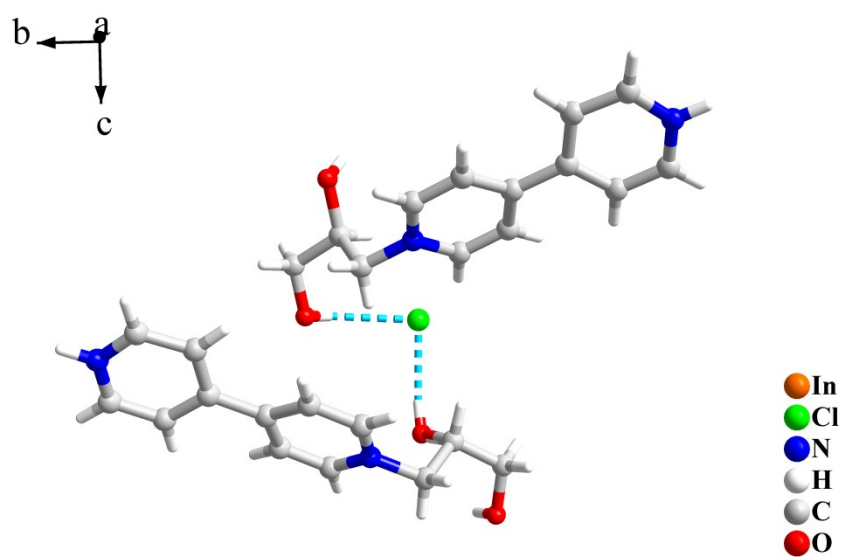
#### **The preparation of compound 1 suspension.**

1 mg crystals were dispersed in 0.5 M LiClO<sub>4</sub> aqueous solution and dispersed uniformly in the solution by ball mill.

## Supporting Figures



**Figure S1.** View of  $\text{N-H}\cdots\text{Cl}$  (green dashed line) and  $\text{O-H}\cdots\text{Cl}$  (orange dashed line) hydrogen bonding interactions between an individual  $[\text{InCl}_6]^{3-}$  and  $[\text{HL}]^{2+}$  at RT.



**Figure S2.** View of  $\text{O-H}\cdots\text{Cl}$  (blue dashed line) hydrogen bonding interactions between the free  $\text{Cl}^-$  ion and the neighboring  $[\text{HL}]^{2+}$  at RT.

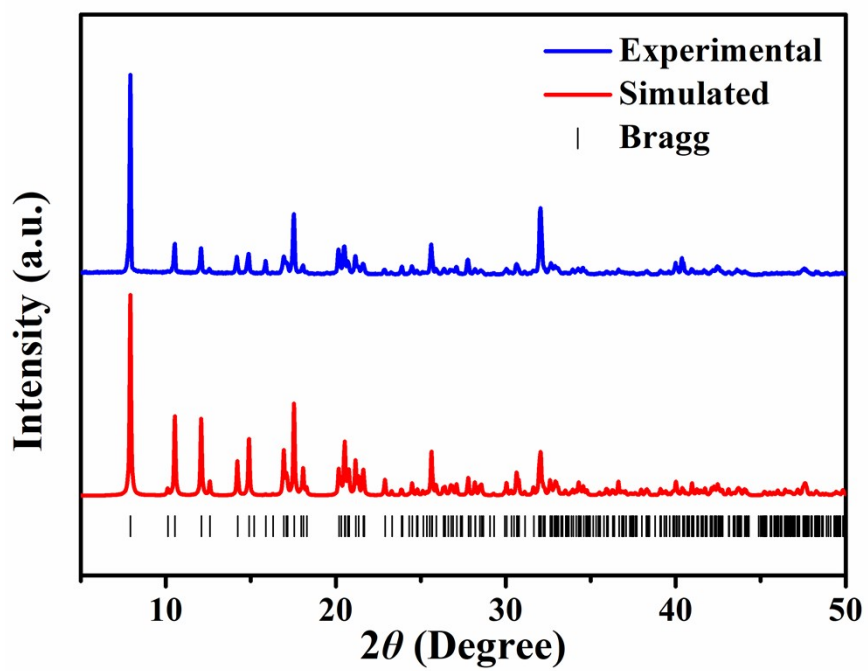


Figure S3. PXRD patterns of compound 1.

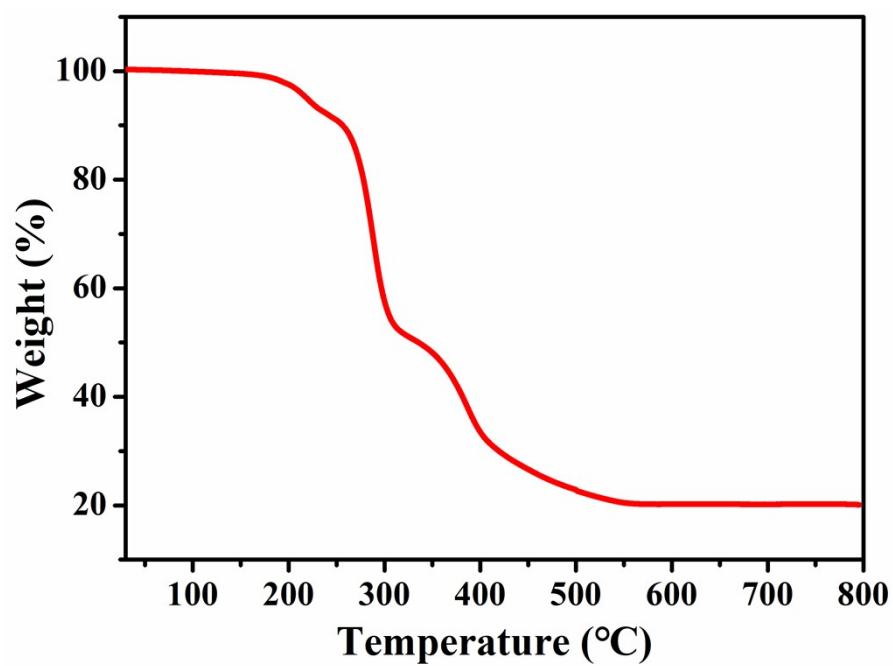
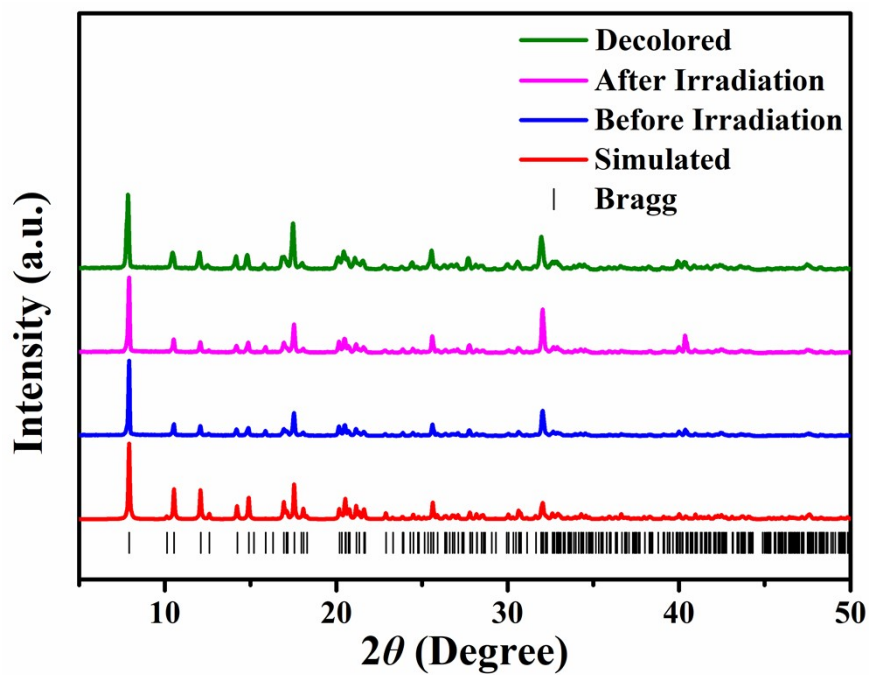
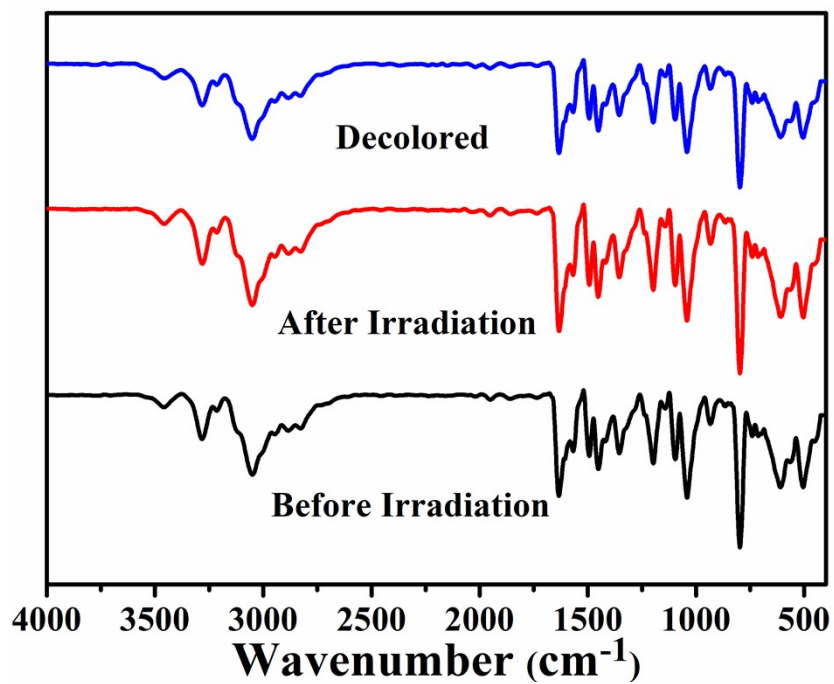


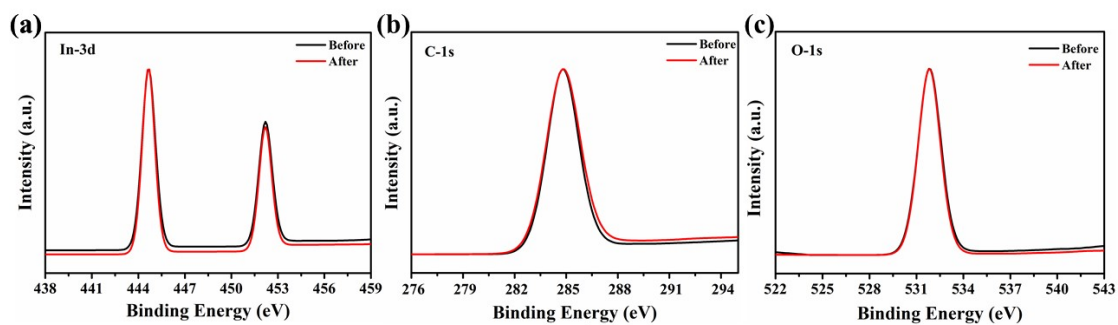
Figure S4. TGA plot of compound 1.



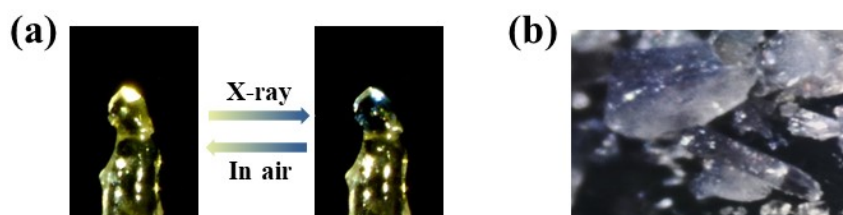
**Figure S5.** Powder X-ray diffraction (PXRD) patterns of compound 1 before irradiation (blue), after irradiation (magenta) and decolored (olive).



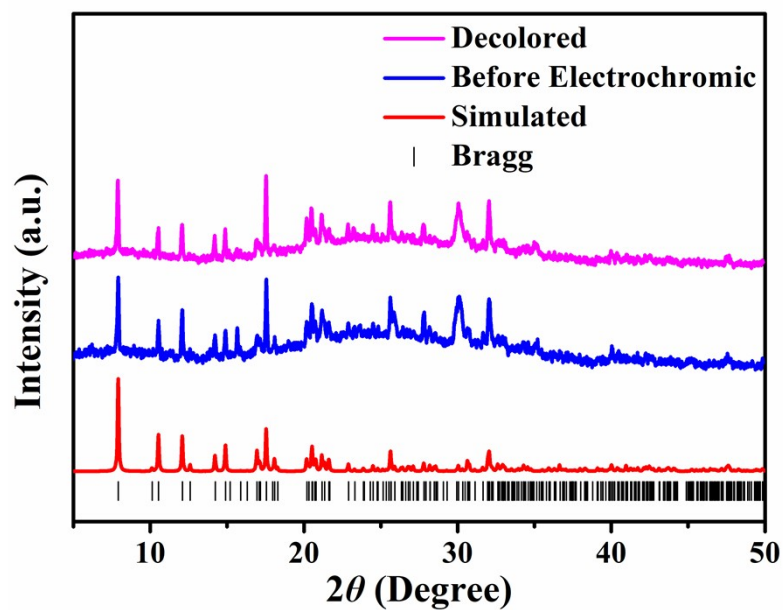
**Figure S6.** FT-IR spectra of compound 1 at different conditions.



**Figure S7.** In 3d (a), C 1s (b), and O 1s (c) XPS core-level spectra of **1** before and after UV irradiation.



**Figure S8.** (a) X-ray (Cu-K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ; irradiation time: 5 min)-induced photochromic process of the single-crystal **1**. (b) The X-ray-induced color change was captured using an X-ray photoelectron spectrometer (Al-K $\alpha$ ,  $\lambda = 8.357 \text{ \AA}$ ; powered at 120W) after illumination.



**Figure S9.** Powder X-ray diffraction (PXRD) spectra of compound **1** before electrochromic (blue) and decolored (magenta).

## Supporting Tables

**Table S1.** Photoresponsive time of some viologen-based photochromic hybrids.

Compound	Photoresponsive time	Ref.
[PV][Zn <sub>3</sub> (m-BDC) <sub>4</sub> ]·H <sub>2</sub> O	1 s	[38]
(BzV) <sub>5</sub> [Bi <sub>3</sub> Cl <sub>14</sub> ] <sub>2</sub> ·(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> O	10 s	[35]
(BzV) <sub>2</sub> [Bi <sub>2</sub> Cl <sub>10</sub> ]	30 s	[35]
Zn(CPBPY)(HBTC)·H <sub>2</sub> O	2 min	[40]
{[Eu(μ <sub>2</sub> -OH)(L)(H <sub>2</sub> O)]·NO <sub>3</sub> ·H <sub>2</sub> O} <sub>n</sub>	3 min	[39]
(BuV) <sub>2</sub> [Bi <sub>2</sub> Cl <sub>10</sub> ]	15 min	[33]
Cd-MOF	20 min	[41]
(C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> InCl <sub>6</sub> ·Cl	0.1 s	this work

**Table S2.** Crystal data and structure refinement for compound **1**

Empirical formula	C <sub>26</sub> H <sub>32</sub> Cl <sub>7</sub> InN <sub>4</sub> O <sub>4</sub>
Formula weight	827.52
Temperature / K	300.0
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / Å	11.4085(4)
<i>b</i> / Å	14.0475(6)
<i>c</i> / Å	10.6955(4)
<i>α</i> / °	90
<i>β</i> / °	102.008(2)
<i>γ</i> / °	90
Volume / Å <sup>3</sup>	1676.56(11)
<i>Z</i>	2
ρ <sub>calc</sub> / g cm <sup>-3</sup>	1.639
μ / mm <sup>-1</sup>	1.301
F(000)	832.0
Radiation	Mo Kα (λ = 0.71073)



2 $\theta$ range for data collection / °	4.662 to 55
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -13 ≤ l ≤ 13
Reflections collected	75367
Independent reflections	3838 [R <sub>int</sub> = 0.0413, R <sub>sigma</sub> = 0.0126]
Data / restraints / parameters	3838 / 0 / 208
Goodness-of-fit on F <sup>2</sup>	1.308
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0720, wR <sub>2</sub> = 0.1887
Final R indexes [all data]	R <sub>1</sub> = 0.0757, wR <sub>2</sub> = 0.1901
Largest diff. peak/hole / e Å <sup>-3</sup>	1.30 / -1.09
CCDC number	2108103

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{[\sum w(F_o^2)^2]}$$

**Table S3.** Selected bond lengths (Å) and bond angles (°) for compound **1**

Bond length (Å)		Bond angles (°)	
In1-C11	2.5048 (18)	C11-In1-C11 <sup>1</sup>	180.0
In1-C11 <sup>1</sup>	2.5048 (18)	C11 <sup>1</sup> -In1-C12 <sup>1</sup>	92.09 (6)
In1-C12 <sup>1</sup>	2.556 (2)	C11 <sup>1</sup> -In1-C12	87.91 (6)
In1-C12	2.556 (2)	C11-In1-C12 <sup>1</sup>	87.91 (6)
In1-C13 <sup>1</sup>	2.504 (2)	C11-In1-C12	92.09 (6)
In1-C13	2.503 (2)	C12-In1-C12 <sup>1</sup>	180.0
		C13 <sup>1</sup> -In1-C11 <sup>1</sup>	89.22 (7)
		C13-In1-C11	89.22 (7)
		C13-In1-C11 <sup>1</sup>	90.78 (7)
		C13 <sup>1</sup> -In1-C11	90.78 (7)
		C13 <sup>1</sup> -In1-C12 <sup>1</sup>	89.52 (8)
		C13 <sup>1</sup> -In1-C12	90.47 (8)
		C13-In1-C12	89.52 (8)
		C13-In1-C12 <sup>1</sup>	90.48 (8)
		C13-In1-C13 <sup>1</sup>	180.0

**Table S4.** Parameters of the hydrogen bonds in compound 1

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1	0.860	2.438	154.67	3.236	Cl2
C8-H8	0.930	2.630	148.22	3.456	Cl1
C2-H2	0.930	2.865	155.04	3.729	Cl2
C10-H10	0.930	2.554	150.75	3.396	O2
C4-H4	0.930	2.815	128.68	3.473	Cl4a
C12-H12a	0.980	2.988	112.84	3.487	Cl4a
C11-H11B	0.970	2.926	160.96	3.856	Cl2
C9-H9	0.930	2.785	154.55	3.647	Cl4a
C5-H5	0.930	2.648	135.10	3.371	Cl3
C1-H1A	0.930	2.545	164.91	3.451	Cl1
O1Ba-H1Ba	0.820	2.186	166.47	2.989	Cl4a
O2-H2A	0.820	2.394	145.71	3.106	Cl4a

Symmetry codes: <sup>1</sup>  $x, y+1, z$ ; <sup>2</sup>  $-x+2, y+1/2, -z+1/2$ ; <sup>3</sup>  $-x+1, y+1/2, -z+3/2$ ; <sup>4</sup>  $-x+1, y+1/2, -z+3/2$ ;  
<sup>5</sup>  $x, -y+1/2, z-1/2$ ; <sup>6</sup>  $-x+2, -y, -z+1$ ; <sup>7</sup>  $x, y+1, z$ ; <sup>8</sup>  $-x+2, y+1/2, -z+1/2$ ; <sup>9</sup>  $x, -y+1/2, z-1/2$ .

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### Supplementary Reference.

1. T. Fu, Y. L. Wei, C. Zhang, L. K. Li, X. F. Liu, H. Y. Li and S. Q. Zang, *Chem. Commun.*, 2020, **56**, 13093-13096.