Supporting Information

Diamond-like Cuprous Coordination Polymer Based on $[Cu_8I_6]^{2+}$ Cluster with Multistimuli-responsive Luminescence and Iodine Adsorption Behavior

Han-Wen Zheng, Dong-Dong Yang, Qiong-Fang Liang, Yan-Ping Liu, Jia-Hui Shan, Qian-Qian Liu, Hong-Wei Tan, Ling Chen, and Xiang-Jun Zheng*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing, 100875, China.

Corresponding author:

Tel.: +86-10-58805522; fax: +86-10-58802075.

E-mail address: xjzheng@bnu.edu.cn (X. -J. Zheng)

Contents

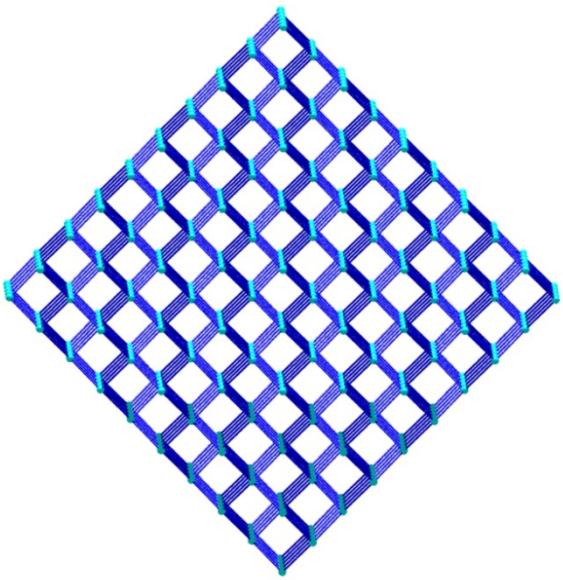


Fig. S1 The topological feature of complex **1**. Cyan spheres represent the $[Cu_8I_6]^{2+}$ clusters, and blue lines represent the CN groups.

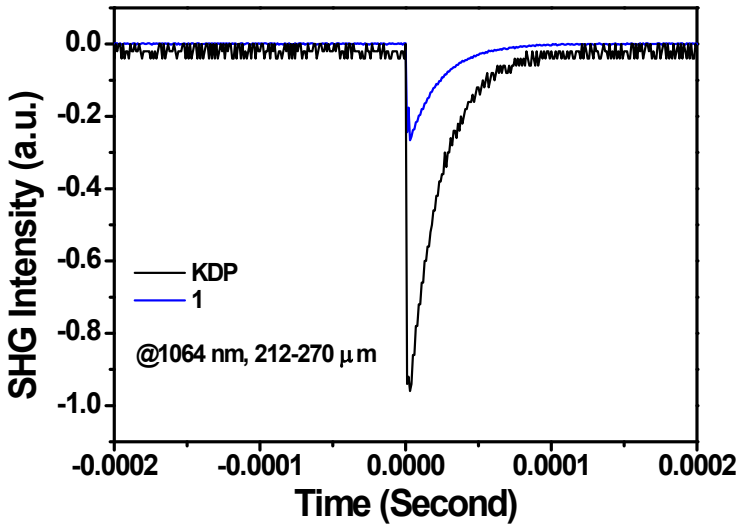


Fig. S2 Oscilloscope traces of SHG signals of KDP and **1**.

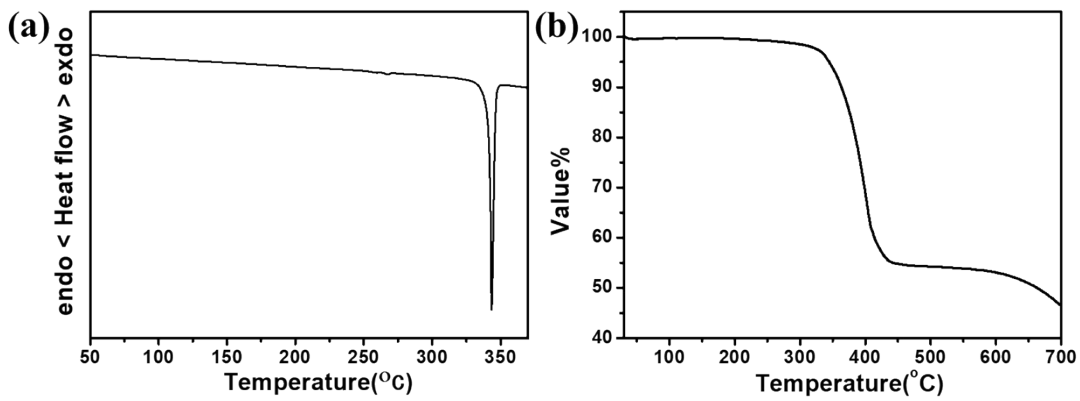


Fig. S3 (a) Differential scanning calorimetry (DSC) and (b) thermogravimetric analysis (TGA) of complex **1**.

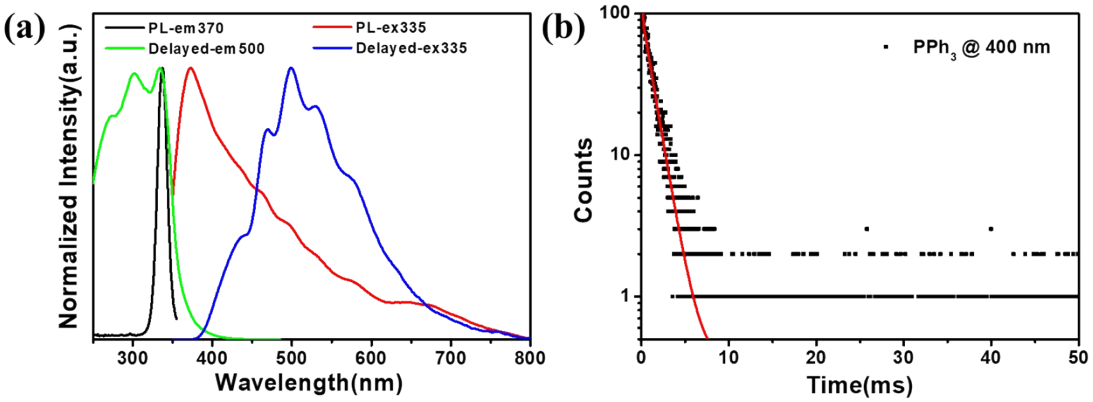


Fig. S4 (a) PL and delayed (1 ms) excitation and emission spectra and (b) PL decay curve at 400 nm of ligand PPh_3 at 77 K.

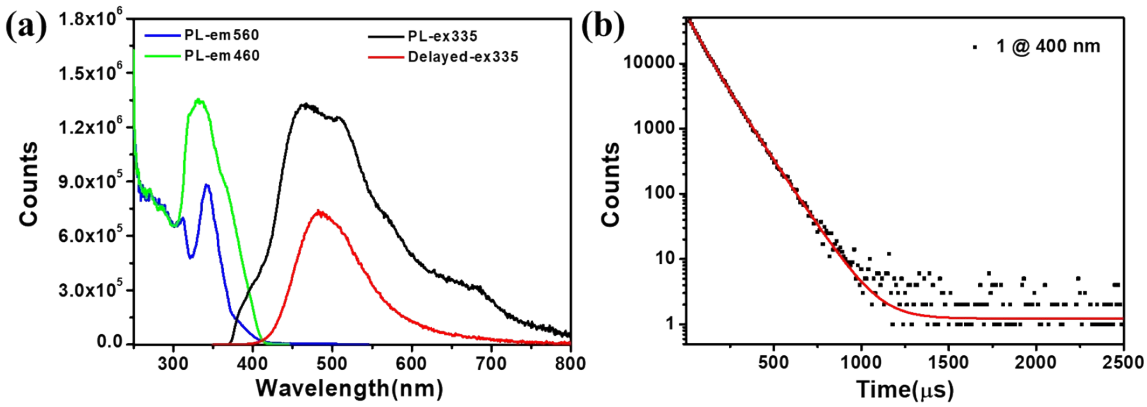


Fig. S5 (a) PL and delayed (1 ms) excitation and emission spectra and (b) PL decay curve at 400 nm of **1** at 77 K.

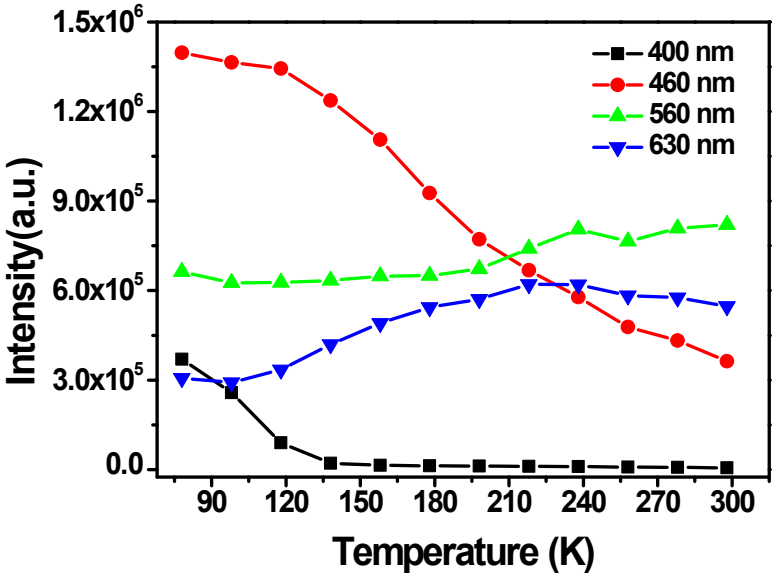


Fig. S6 The intensity at 400 nm, 460 nm, 560 nm and 615 nm in the temperature range of 77-297 K.

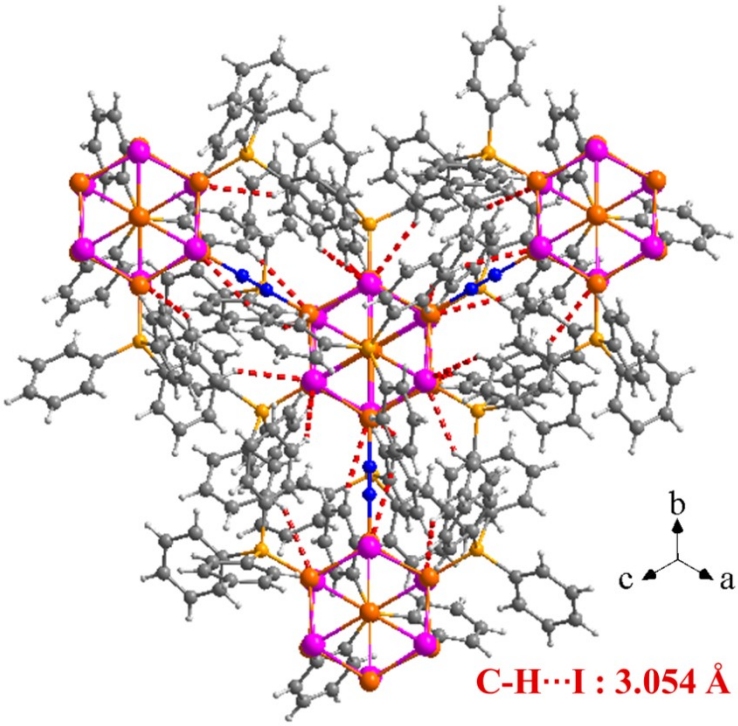


Fig. S7 The halogen bonds in **1**.

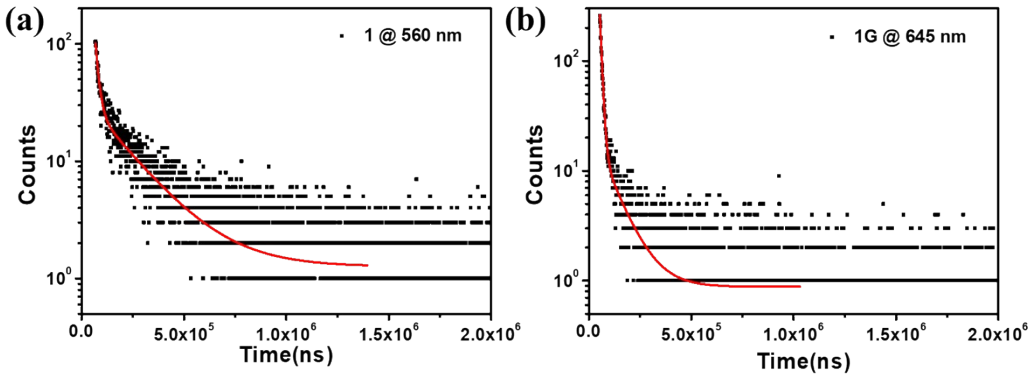


Fig. S8 PL decay curves at room temperature (297 K) of (a) **1** at 560 nm and **1G** at 645 nm.

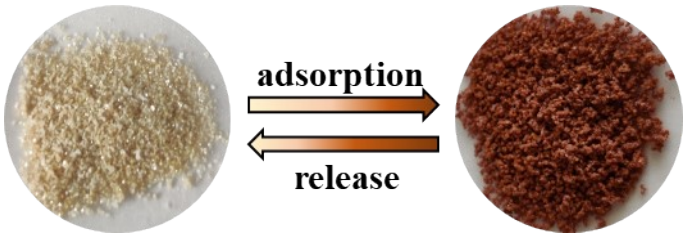


Fig. S9 Photographs of samples before and after adsorption and release process.

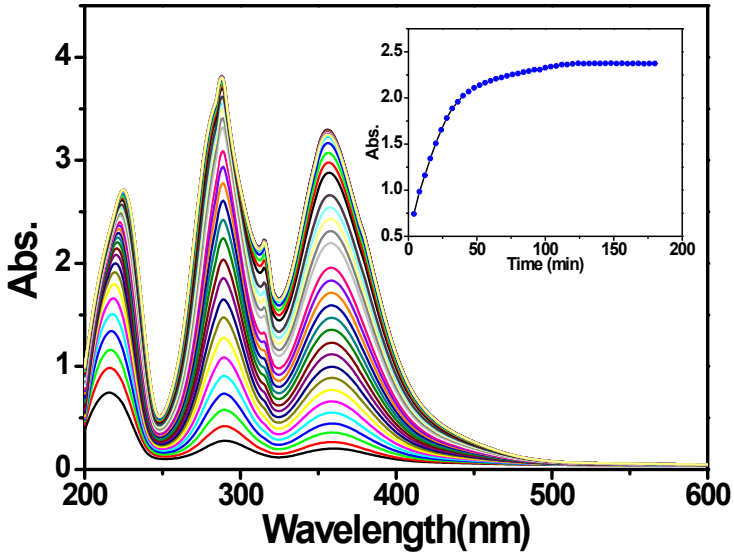


Fig. S10 The I_2 release UV-vis spectra of complex **1** (1 mg) in ethanol (3 mL), the insets of figures are dynamic intensity plots (monitored at 217 nm) over time.

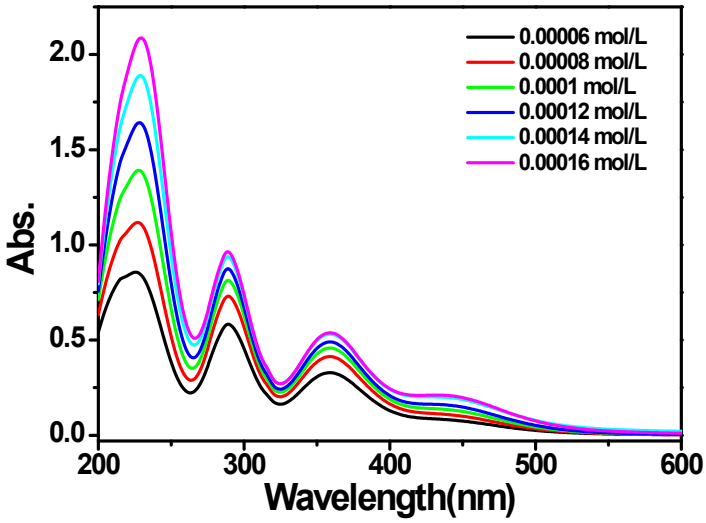


Fig. S11 UV-vis spectra of iodine in ethanol at different concentrations.

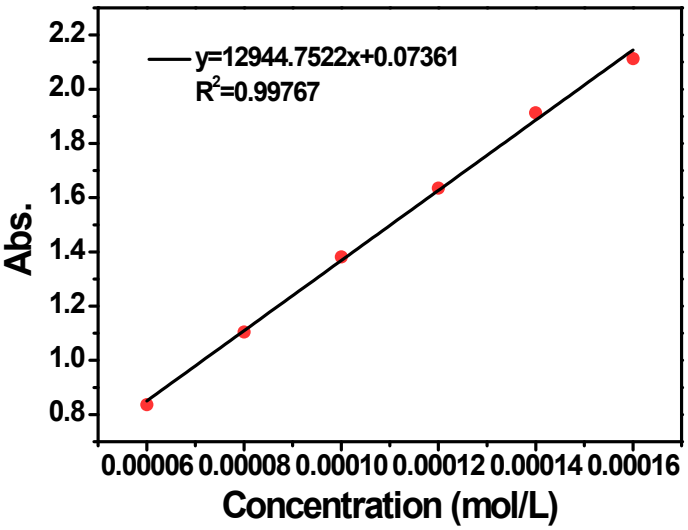


Fig. S12 Calibration plot of standard iodine by UV-vis spectra.

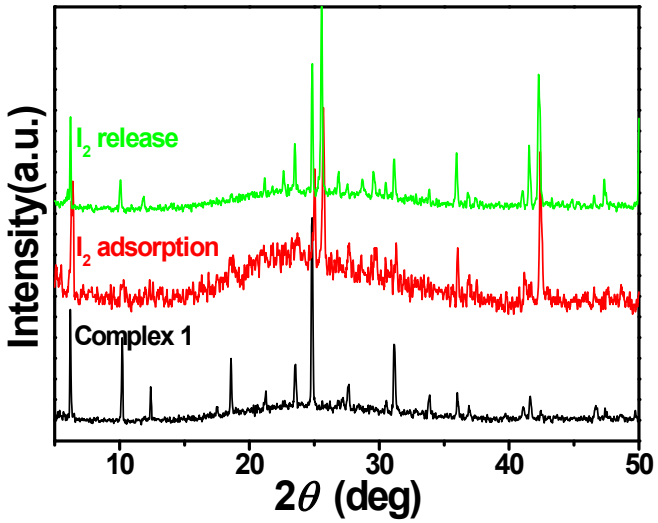


Fig. S13 PXRD patterns of samples before and after adsorption and release process.

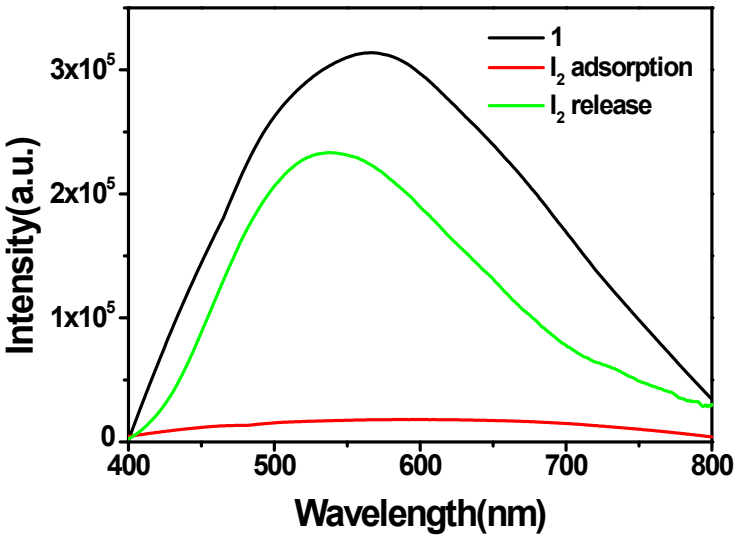
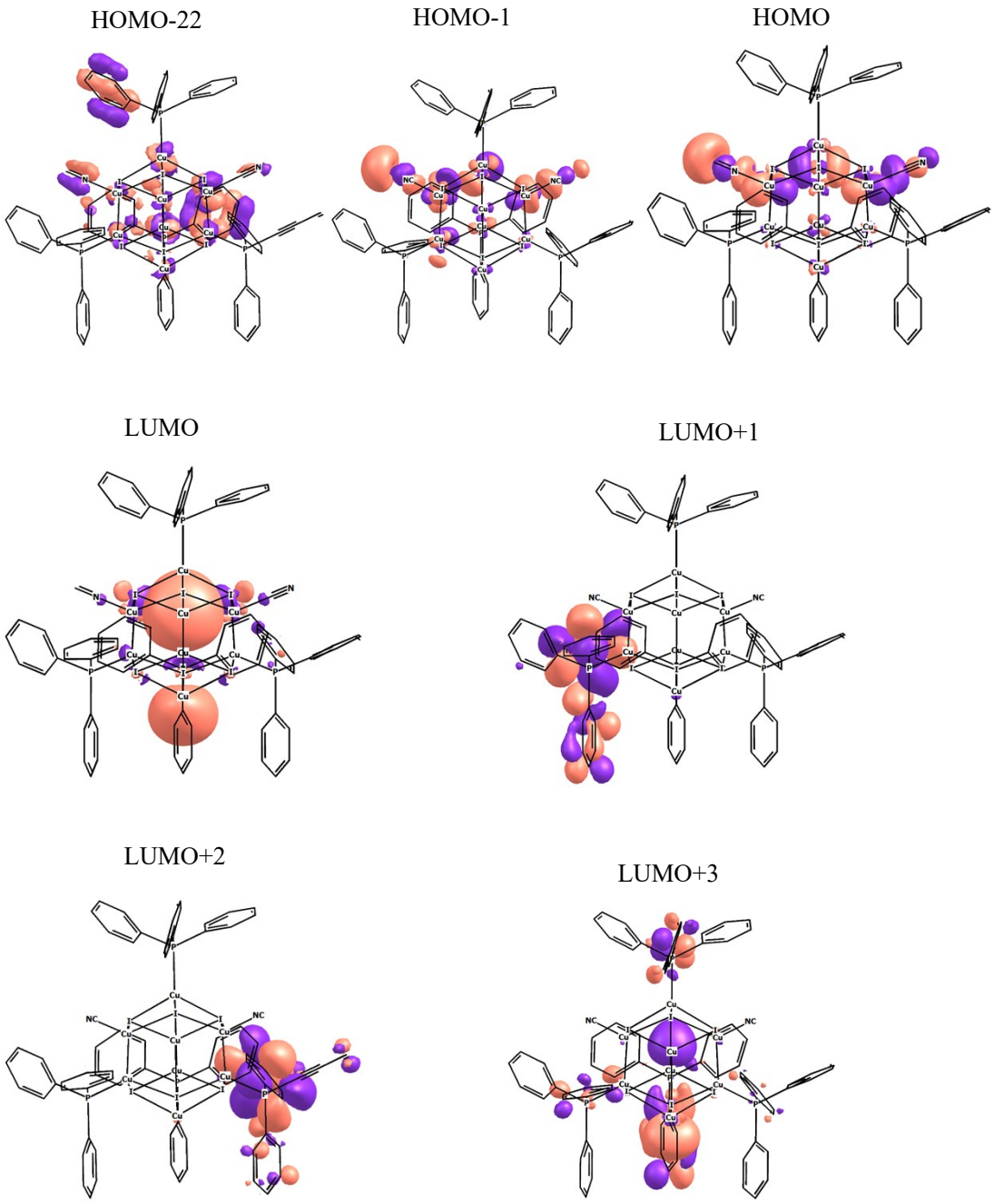
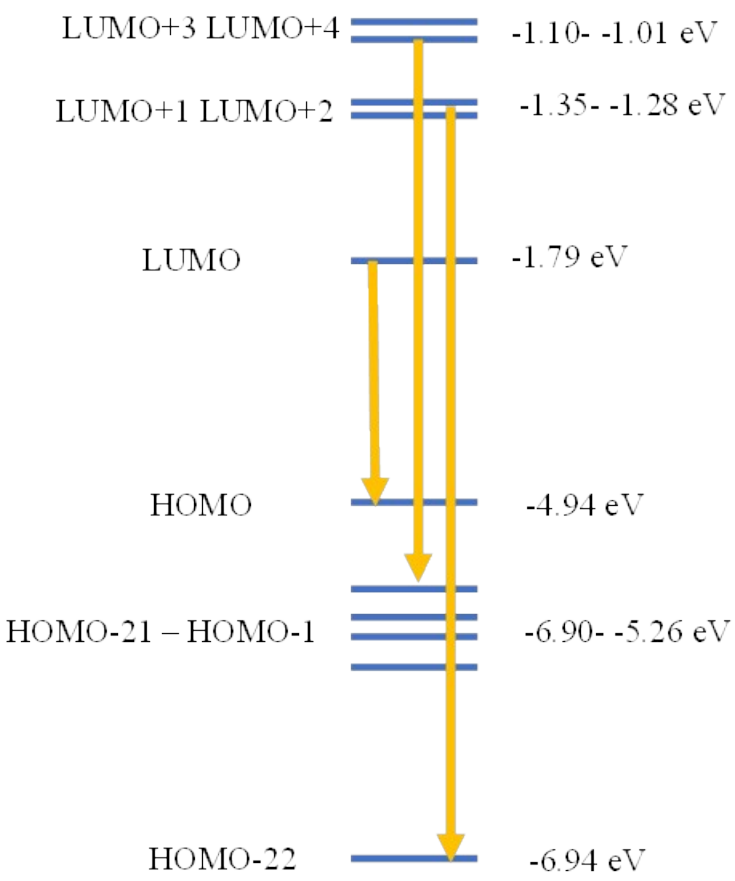


Fig. S14 Emission spectra of crystalline sample (**1**) before and after adsorption and release process (λ_{ex} = 365 nm).



Scheme S1 Calculated frontier orbitals for $[Cu_8I_6(CN)_2(PPh_3)_4]$ unit.



Scheme S2 Possible luminescence energy transition diagram for complex **1**.

Table S1 Crystal data and structure refinement parameters of complex **1** and **1a**.

Compound	**1**	**1a**
Empirical formula	$C_{74}H_{60}Cu_8I_6N_2P_4$	$C_{74}H_{60}Cu_8I_6N_2P_4$
Formula weight	2370.84	2370.71
Temperature/K	100.00(10)	272.5(5)
Crystal system	Cubic	Cubic
Space group	$Fd\bar{3}$	$Fd\bar{3}m$
a/Å	24.6471(5)	24.91275(9)
b/Å	24.6471(5)	24.91275(9)
c/Å	24.6471(5)	24.91275(9)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	14972.6(9)	15461.98(17)
Z	8	8
ρ_{calc} g/cm^3	2.104	2.037
μ/mm^{-1}	23.003	22.275
F(000)	9024.0	9024.0
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/°	10.152 to 132.904	11.782 to 152.906
Index ranges	-28 ≤ h ≤ 23, -18 ≤ k ≤ 11, -29 ≤ l ≤ 13	-31 ≤ h ≤ 31, -31 ≤ k ≤ 31, -30 ≤ l ≤ 30
Reflections collected	3841	44589
Independent reflections	1077 [R_{int} = 0.0561, R_{sigma} = 0.0288]	821 [R_{int} = 0.1138, R_{sigma} = 0.0145]
Data/restraints/parameters	1077/0/72	821/0/71
Goodness-of-fit on F^2	1.119	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0958	R_1 = 0.0417, wR_2 = 0.1069
R indices (all data)	R_1 = 0.0377, wR_2 = 0.0964	R_1 = 0.0437, wR_2 = 0.1080
Largest diff. peak/hole (e Å^{-3})	0.89/-1.48	0.87/-1.20
CCDC number	2127744	2132839

Table S2 Selected Bond Lengths (Å) and Angles (deg) of complex **1**.

I1—Cu1^{i}	2.6731 (5)	Cu1—I1^{iii}	2.6731 (5)
I1—Cu1	2.6731 (5)	Cu1—P1	2.241 (2)

I1—Cu2	2.6894 (6)	Cu2—I1^{ii}	2.6894 (6)
I1—Cu2^{i}	2.6894 (6)	Cu2—I1^{iv}	2.6894 (6)
Cu1—I1^{ii}	2.6731 (5)	Cu2—N7	1.943 (9)
Cu1^{i}—I1—Cu1	117.02 (4)	C2^{v}—P1—Cu1	114.40 (13)
Cu1^{i}—I1—Cu2	74.535 (19)	C2^{iii}—P1—Cu1	114.40 (13)
Cu1—I1—Cu2^{i}	74.536 (19)	C2—P1—Cu1	114.40 (13)
Cu1—I1—Cu2	74.535 (19)	I1^{iv}—Cu2—I1^{ii}	104.54 (3)
Cu1^{i}—I1—Cu2^{i}	74.536 (19)	I1^{iv}—Cu2—I1	104.54 (3)
Cu2—I1—Cu2^{i}	118.61 (6)	I1^{ii}—Cu2—I1	104.54 (3)
I1^{ii}—Cu1—I1	105.45 (3)	N7—Cu2—I1	114.04 (3)
I1^{iii}—Cu1—I1	105.45 (3)	N7—Cu2—I1^{iv}	114.04 (3)
I1^{iii}—Cu1—I1^{ii}	105.45 (3)	N7—Cu2—I1^{ii}	114.04 (3)
P1—Cu1—I1^{ii}	113.25 (2)	N7^{vi}—N7—Cu2	180.0 (16)
P1—Cu1—I1	113.25 (2)	C7^{vi}—N7—Cu2	180.0 (16)
P1—Cu1—I1^{iii}	113.25 (2)		

Symmetry codes: (i) *x*, -*y*+1/4, -*z*+1/4; (ii) *y*+1/2, *z*, *x*-1/2; (iii) *z*+1/2, -*x*+3/4, -*y*+1/4; (iv) *z*+1/2, *x*-1/2, *y*; (v) -*y*+3/4, -*z*+1/4, *x*-1/2; (vi) -*x*+1, -*y*, -*z*.

Table S3 Selected Bond Lengths (Å) and Angles (deg) of complex **1a**.

I1—Cu1^{i}	2.6880 (9)	Cu1—I1^{iii}	2.6880 (9)
I1—Cu1	2.6880 (9)	Cu1—P1	2.248 (4)
I1—Cu2^{ii}	2.7233 (12)	Cu2—I1^{iii}	2.7232 (12)
I1—Cu2	2.7232 (12)	Cu2—I1^{i}	2.7232 (12)
Cu1—I1^{ii}	2.6880 (9)	Cu2—N7	2.085 (15)
Cu1—I1—Cu1^{i}	117.33 (8)	I1^{i}—Cu2—I1	103.35 (6)
Cu1^{i}—I1—Cu2	75.08 (3)	I1^{iii}—Cu2—I1	103.35 (6)
Cu1—I1—Cu2	75.08 (3)	I1^{iii}—Cu2—I1^{i}	103.35 (6)
Cu1^{i}—I1—Cu2^{ii}	75.08 (3)	N7—Cu2—I1^{i}	115.06 (5)
Cu1—I1—Cu2^{ii}	75.08 (3)	N7—Cu2—I1	115.06 (5)
Cu2—I1—Cu2^{ii}	120.65 (11)	N7—Cu2—I1^{iii}	115.06 (5)
I1^{iii}—Cu1—I1	105.27 (5)	C7—Cu2—I1^{i}	115.06 (5)
I1^{ii}—Cu1—I1	105.27 (5)	C7—Cu2—I1	115.06 (5)
I1^{ii}—Cu1—I1^{iii}	105.27 (5)	C7—Cu2—I1^{iii}	115.06 (5)
P1—Cu1—I1^{ii}	113.40 (4)	C2—P1—Cu1	114.2 (3)
P1—Cu1—I1	113.40 (4)	C2^{vii}—P1—Cu1	114.2 (3)
P1—Cu1—I1^{iii}	113.40 (4)	C2^{iv}—P1—Cu1	114.2 (3)
C2^{vi}—P1—Cu1	114.2 (3)	C2^{viii}—P1—Cu1	114.2 (3)
C2^{v}—P1—Cu1	114.2 (3)		

Symmetry codes: (i) -*y*+3/4, *x*-1/2, -*z*+1/4; (ii) *y*+1/2, -*x*+3/4, -*z*+1/4; (iii) -*z*+3/4, -*y*+1/4, *x*-1/2; (iv) *z*+1/2, *y*, *x*-1/2; (v) *x*, -*z*+1/4, -*y*+1/4; (vi) *z*+1/2, -*x*+3/4, -*y*+1/4; (vii) -*y*+3/4, -*x*+3/4, *z*; (viii) -*y*+3/4, -*z*+1/4, *x*-1/2.