Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Self-assembly of two supramolecular indium(III) metal-organic frameworks for reversible iodine capture and large band gap change semiconductor behavior

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Table S1 Selected bond lengths (Å) and bond angles (°) for **1** and **2**

		1	
In(1)-O(4)	2.263(4)	In(1)-Cl(1)	2.457(1)
In(1)-O(2)	2.266(4)	In(1)-Cl(3)	2.476(1)
In(1)-O(3)	2.435(4)	In(1)-Cl(2)	2.475(1)
In(1)-O(1)	2.438(4)	O(4)-In(1)-Cl(2)	90.01(16)
O(4)-In(1)-O(2)	175.58(13)	O(2)-In(1)-Cl(2)	90.67(16)
O(4)-In(1)-O(3)	55.61(12)	O(3)-In(1)-Cl(2)	82.51(12)
O(2)-In(1)-O(3)	128.81(13)	O(1)-In(1)-Cl(2)	89.56(12)
O(4)-In(1)-O(1)	129.09(13)	Cl(1)-In(1)-Cl(2)	94.89(9)
O(2)-In(1)-O(1)	55.29(12)	O(4)-In(1)-Cl(3)	90.38(16)
O(3)-In(1)-O(1)	73.90(11)	O(2)-In(1)-Cl(3)	89.72(16)
O(4)-In(1)-Cl(1)	87.67(10)	O(3)-In(1)-Cl(3)	89.45(12)
O(2)-In(1)-Cl(1)	87.92(9)	O(1)-In(1)-Cl(3)	82.42(12)
O(3)-In(1)-Cl(1)	143.07(9)	Cl(1)-In(1)-Cl(3)	95.15(9)
O(1)-In(1)-Cl(1)	143.03(9)	Cl(2)-In(1)-Cl(3)	169.96(5)
		2	
In(1)-O(1)	2.157(6)	O(1)-In(1)-N(1)	74.6(2)
In(1)-N(2)	2.206(6)	N(2)-In(1)-N(1)	71.3(2)
In(1)-N(4)	2.314(6)	N(4)-In(1)-N(1)	100.3(2)
In(1)-Cl(2)	2.406(2)	Cl(2)-In(1)-N(1)	85.20(16)
In(1)-Cl(1)	2.418(2)	Cl(1)-In(1)-N(1)	166.97(17)
In(1)-N(1)	2.461(6)	O(3)-In(2)-N(5)	85.4(2)
In(2)-O(3)	2.183(6)	O(3)-In(2)-N(8)	73.3(2)
In(2)-N(5)	2.203(6)	N(5)-In(2)-N(8)	158.1(2)
In(2)-N(8)	2.301(6)	O(3)-In(2)-Cl(4)	100.69(16)
In(2)-Cl(4)	2.412(2)	N(5)-In(2)-Cl(4)	96.95(18)
In(2)-Cl(3)	2.418(2)	N(8)-In(2)-Cl(4)	91.84(17)
In(2)-N(7)	2.427(6)	O(3)-In(2)-Cl(3)	157.20(16)
O(1)-In(1)-N(2)	86.1(2)	N(5)-In(2)-Cl(3)	97.89(18)
O(1)-In(1)-N(4)	73.4(2)	N(8)-In(2)-Cl(3)	100.01(19)
N(2)-In(1)-N(4)	159.4(2)	Cl(4)-In(2)-Cl(3)	101.29(8)
O(1)-In(1)-Cl(2)	156.03(16)	O(3)-In(2)-N(7)	74.8(2)
N(2)-In(1)-Cl(2)	99.69(17)	N(5)-In(2)-N(7)	72.9(2)
N(4)-In(1)-Cl(2)	98.23(17)	N(8)-In(2)-N(7)	96.3(2)
O(1)-In(1)-Cl(1)	99.96(16)	Cl(4)-In(2)-N(7)	169.00(16)
N(2)-In(1)-Cl(1)	96.79(18)	Cl(3)-In(2)-N(7)	84.56(16)
N(4)-In(1)-Cl(1)	89.22(17)	Cl(2)-In(1)-Cl(1)	102.39(9)

Table S2 Important hydrogen bond and π···π stacking interactions for **1** and **2**

	Coordination number	D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°	structure
1	7	C8–H8A···O2	0.930	2.718	3.564	151.676(1)	3D
		C18–H18A···O4	0.929	2.731	3.591	151.133(1)	
2	6	C35–H35A···O3	0.950	2.230	3.199	157.153(3)	3D
		C8–H8A···O1	0.950	2.504	3.411	159.580(2)	
		C16–H16A···O2	0.950	2.554	3.216	126.921(1)	
		C49–H49A···Cl1	0.951	2.692	3.611	162.739(1)	
		C41–H41A···Cl3	0.949	2.820	3.629	143.757(2)	
		π_{Cg1}–π_{Cg1}			3.629		
		π_{Cg2}–π_{Cg2}			3.672		

C_{g1} = benzene ring

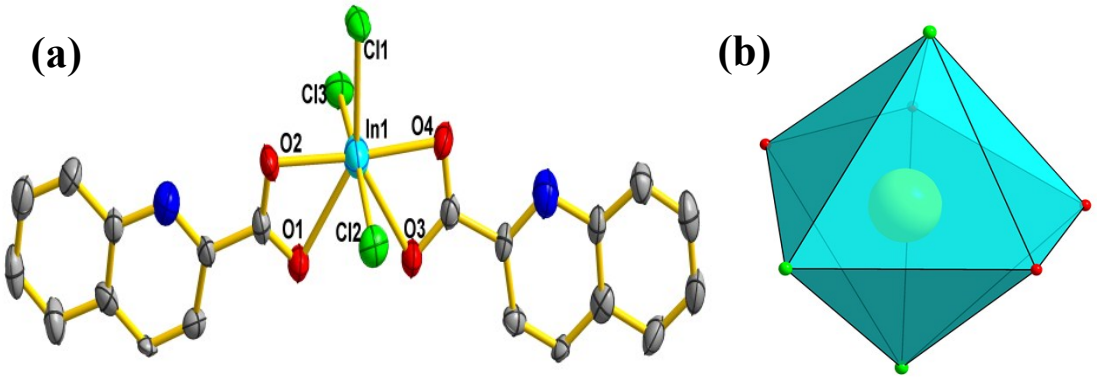

Fig. S1 (a) X-ray structure of compound **1**, H atoms for clarity. Thermal ellipsoid is drawn at 50% probability. (b) Polyhedral of the In(III) centre in **1**.

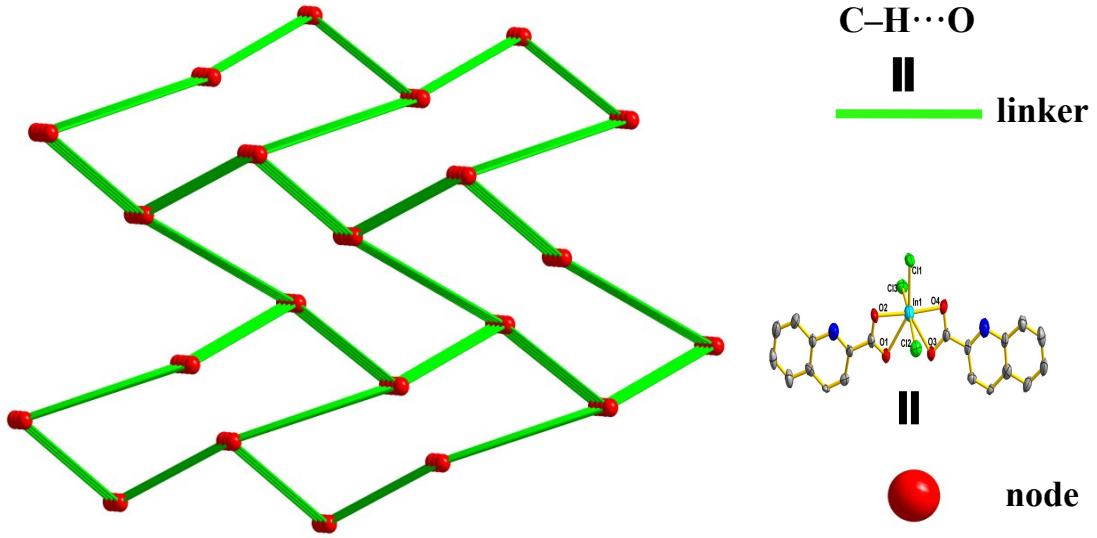

Fig. S2 Topological view of the three-dimensional structure of compound **1**.

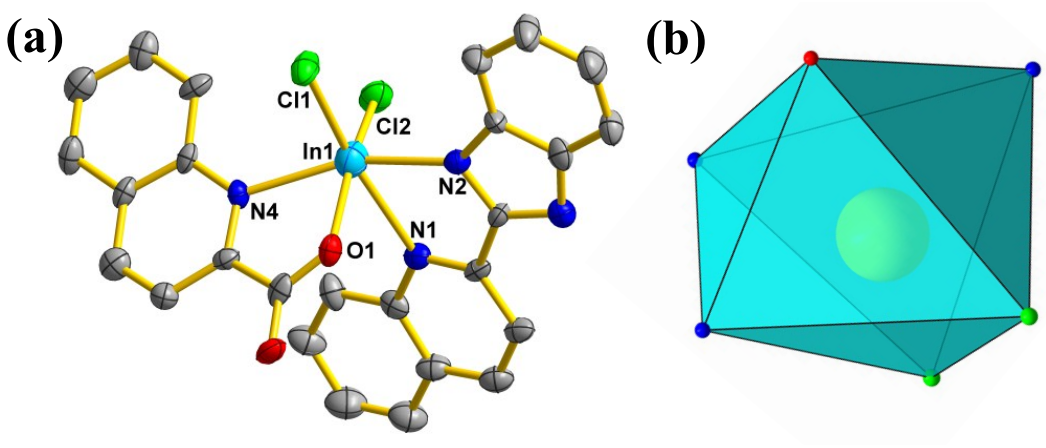

Fig. S3 (a) X-ray structure of compound **2**, H atoms for clarity. Thermal ellipsoid is drawn at 50% probability. (b) Polyhedral of the In(III) centre in **2**.

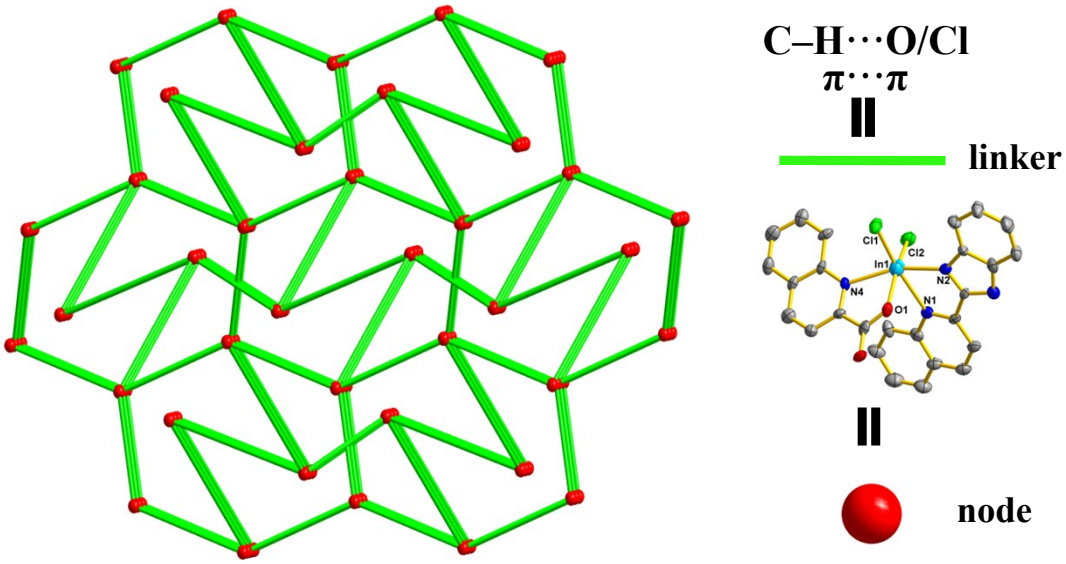

Fig. S4 Topological view of the three-dimensional structure of compound **2**.

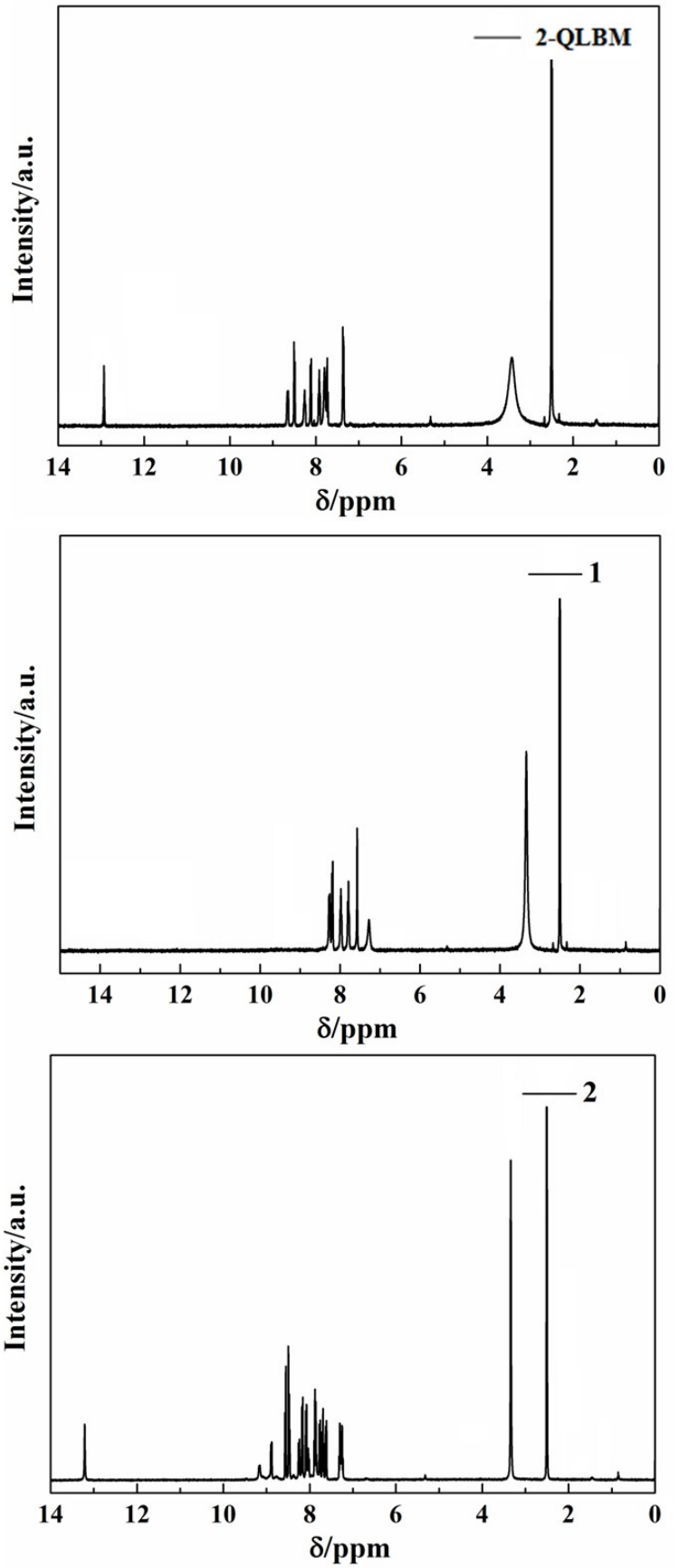

Fig. S5 ^{1}H NMR spectra of **2-QLBM**, **1** and **2**.

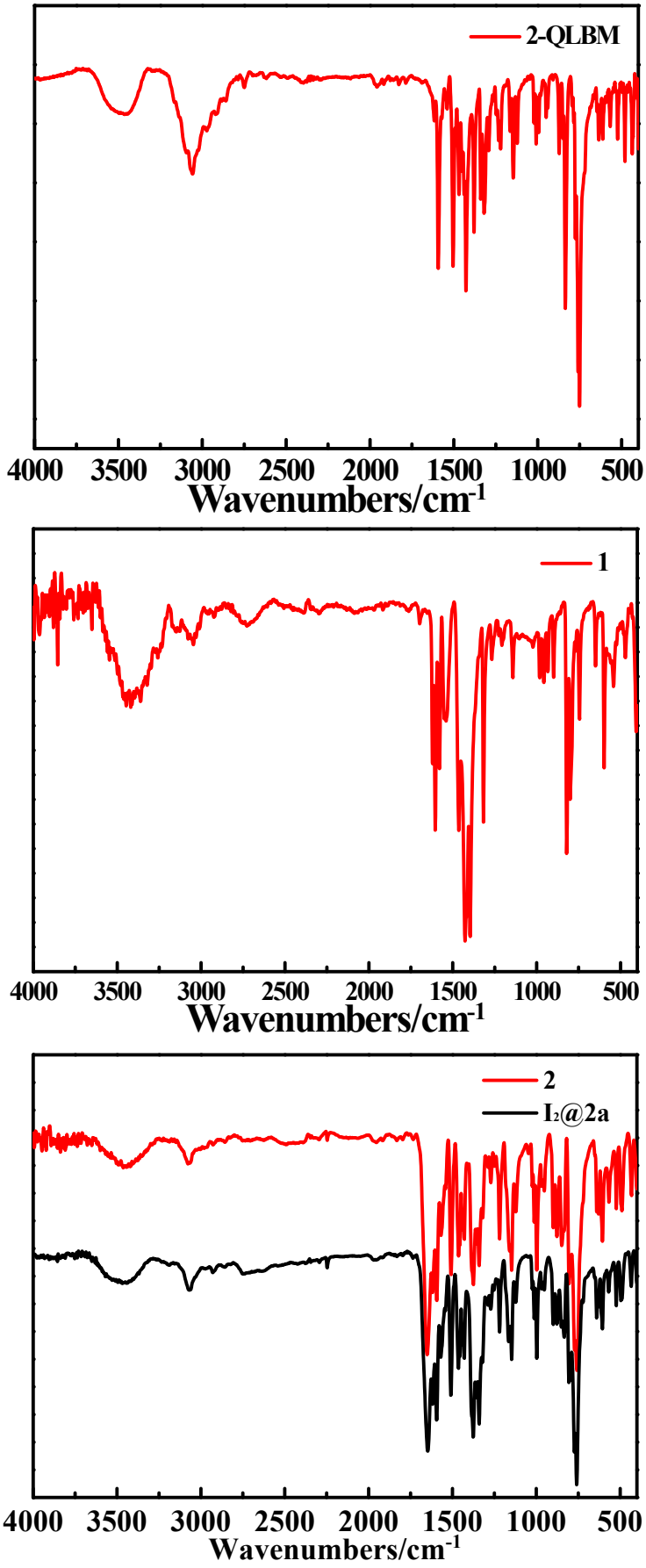

Fig. S6 IR spectra of **2-QLBM**, **1**, **2** and **I_2@2.**

Table S3 Elemental analysis results of activated compounds[a] and after iodine uptake in solvent[a]

Compoud	C%	H%	N%
1a	42.35 (42.33)	2.48 (2.49)	4.91 (4.94)
2a	51.13 (51.10)	2.81 (2.80)	9.15 (9.17)
I_2@2a	40.69 (40.66)	2.57 (2.56)	7.91 (7.93)

[a]Theoretical results are given in parentheses

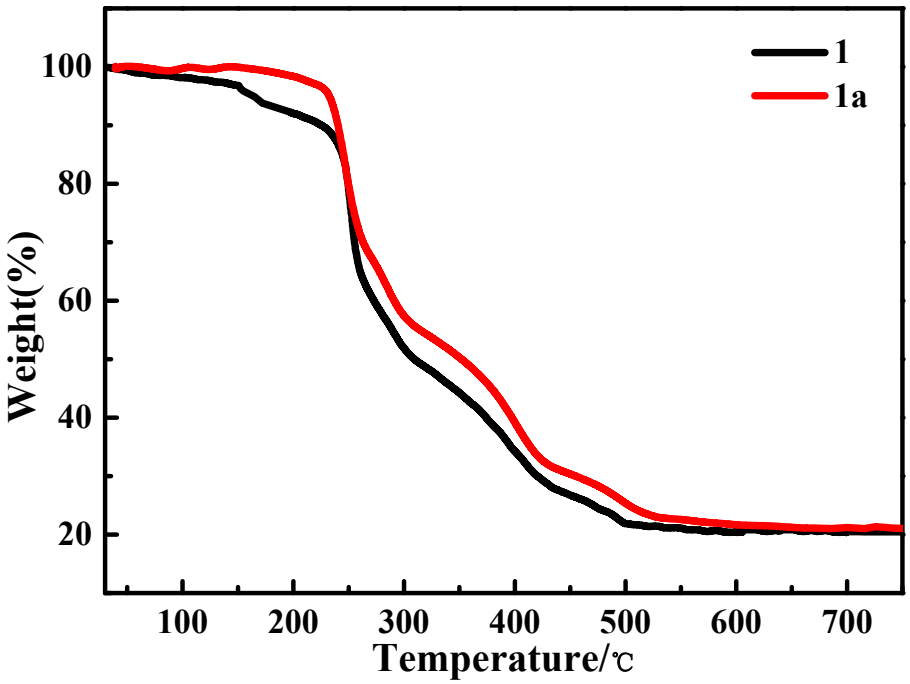

Fig. S7 Thermal gravimetric curves for **1** and **1a.**

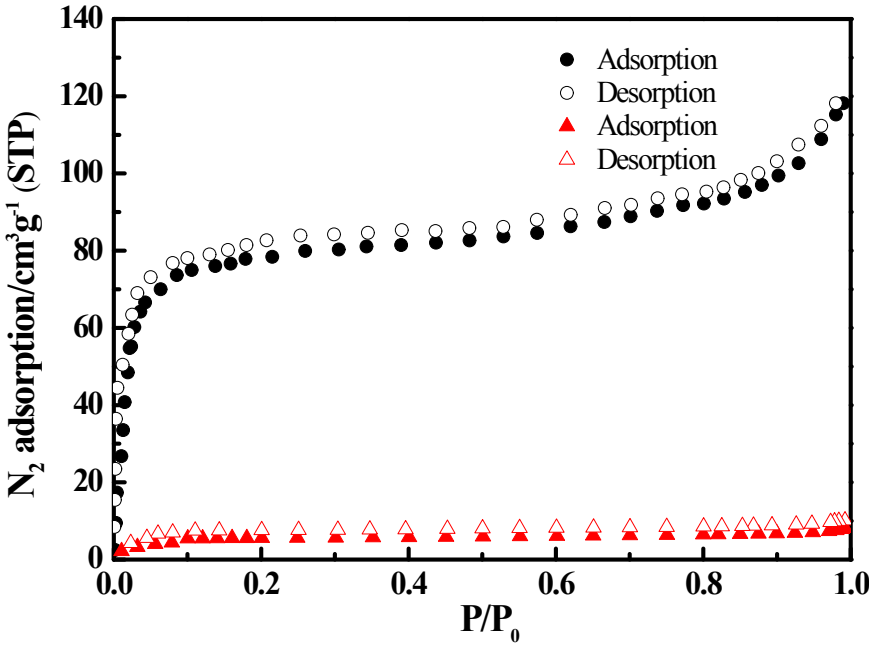

Fig. S8 Nitrogen adsorption isotherms of **1a** (red) and **2a** (black) at 77 K.

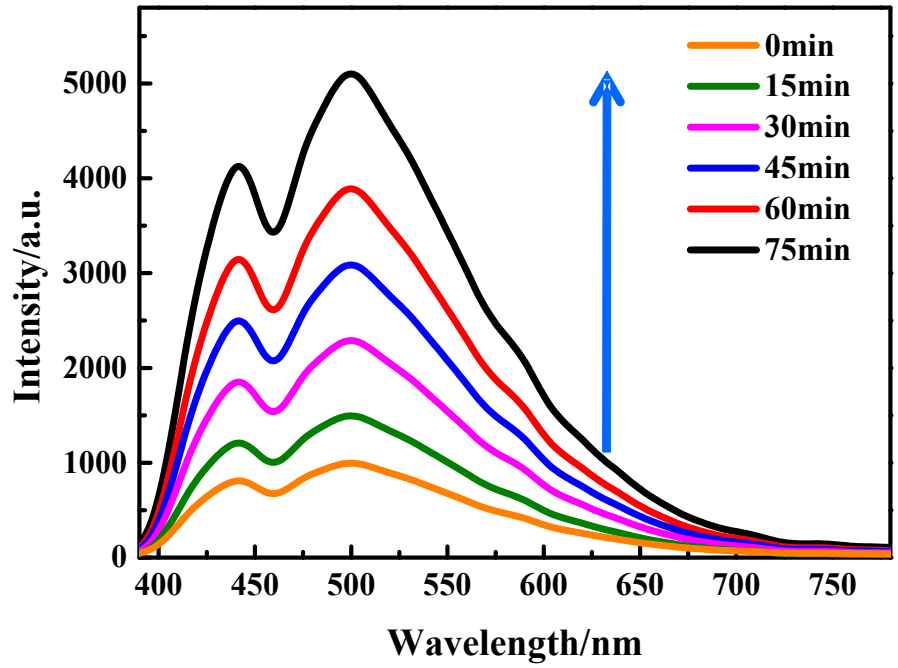

Fig. S9 After immersed in ethanol for 0~75 min, the luminescence intensity of **I_2@2a** was gradually recovered.

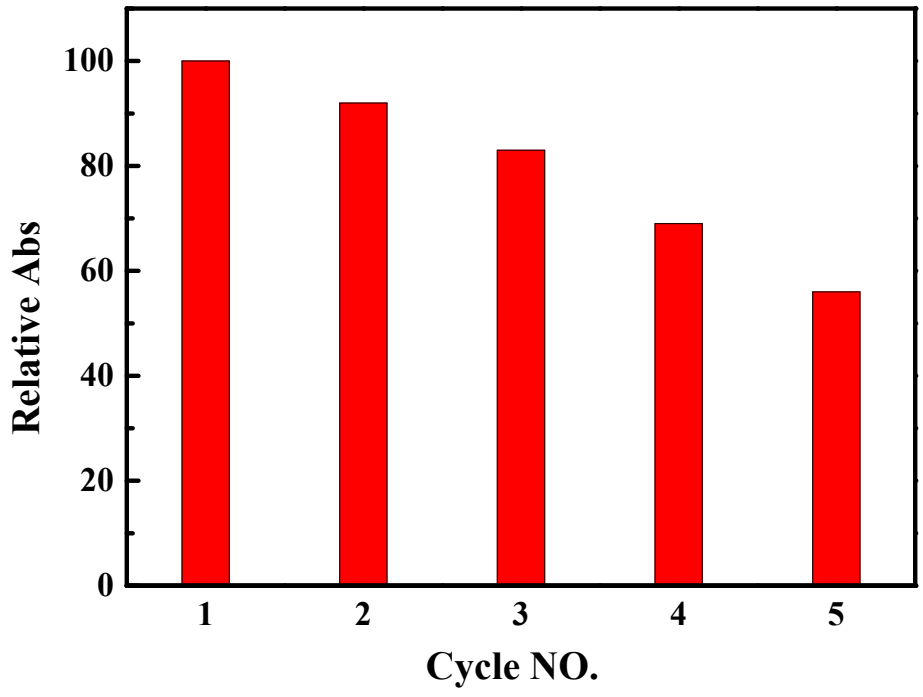

Fig. S10 Desorption efficiency of **I_2@2a** in serial recycle tests.

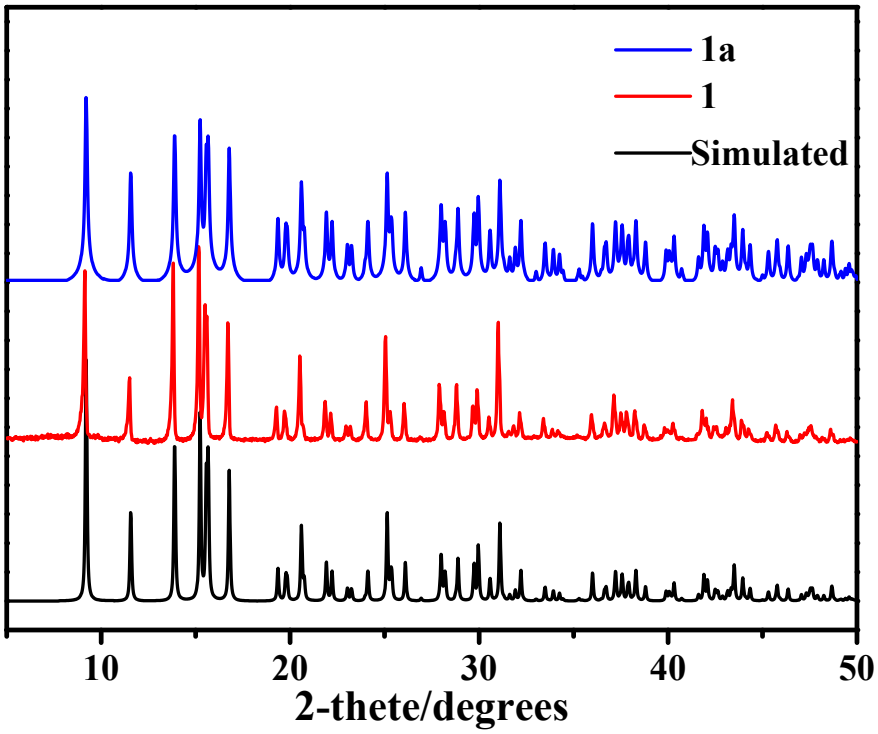

Fig. S11 PXRD patterns of **1** and **1a** with the relevant simulated pattern.

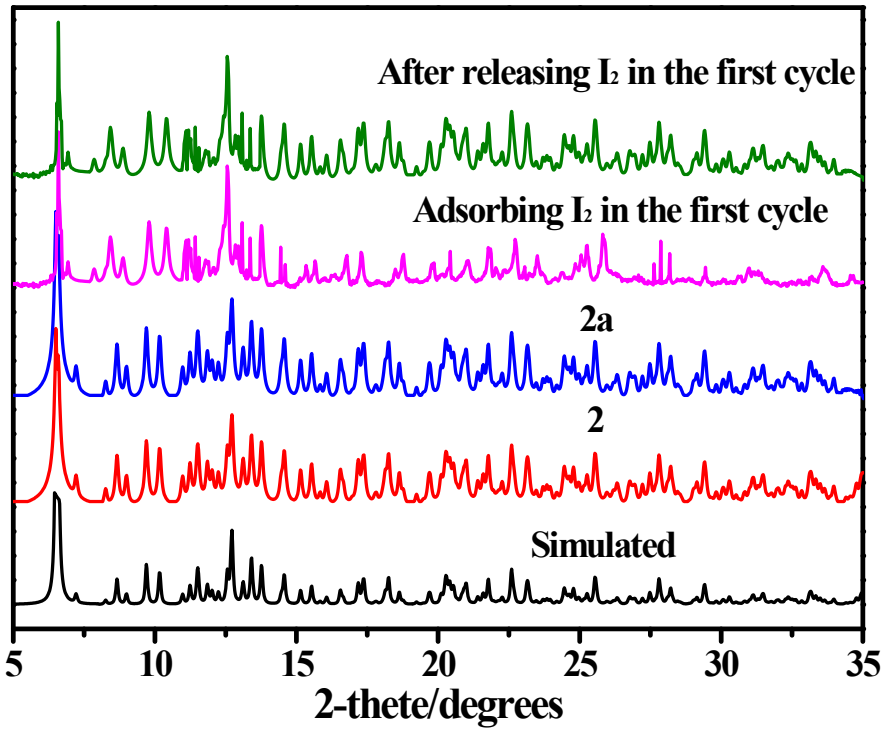

Fig. S12 PXRD patterns of **2**, **2a**, **2a** after adsorbing I_2 in the first cycle and **2a** after releasing I_2 in the first cycle with the relevant simulated pattern.

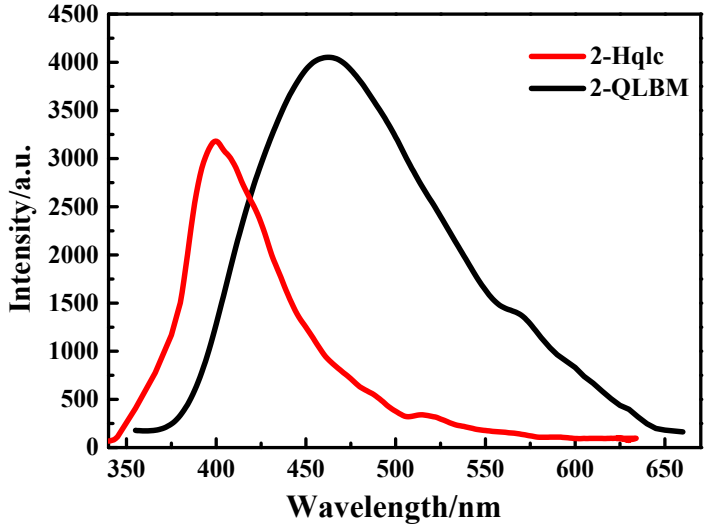

Fig. S13 Emission spectra of free 2-Hqlc and **2-QLBM** ligands in the solid state at 298 K.

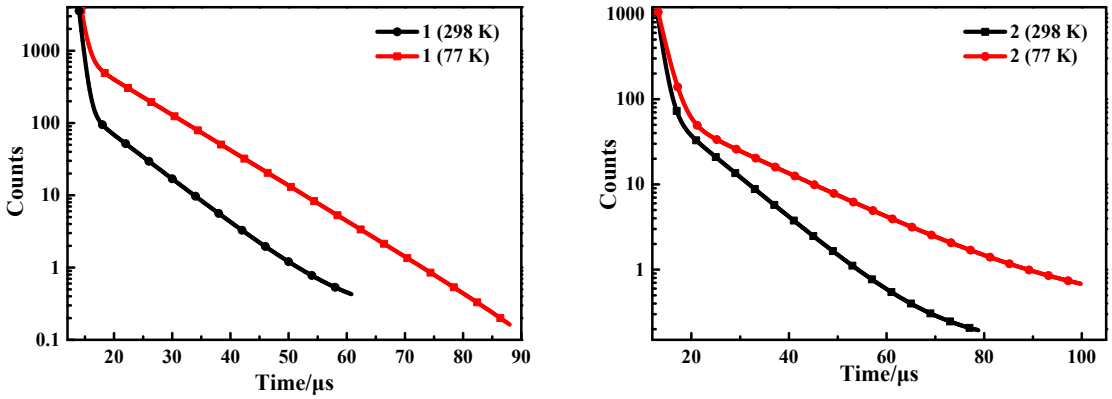

Fig. S14 Luminescence decay curves of **1** and **2** in the solid state at 298 and 77K.

Table S4 Luminescent data for **1** and **2**

Compoud	Excitation (λ, nm)	Emission (λ_{max}, nm)	CIE (x, y)	Lifetime (μs)		<τ>(μs)	Conditions[a]
				τ_1	τ_2		
1	390	426	0.18, 0.08	0.60	7.09	5.98	Solid, 298 K
	390	475	0.25, 0.33	0.75	8.89	8.61	Solid, 77 K
2	390	443^{sh}, 498	0.16, 0.18	1.07	9.16	7.81	Solid, 298 K
	390	529^{sh}, 605	0.43, 0.50	1.64	16.32	14.26	Solid, 77 K

[a]Concentration in DMSO, CH_3CN, CH_3OH and $CHCl_3$ solution: $c = 1 \times 10^{-6}$ M.

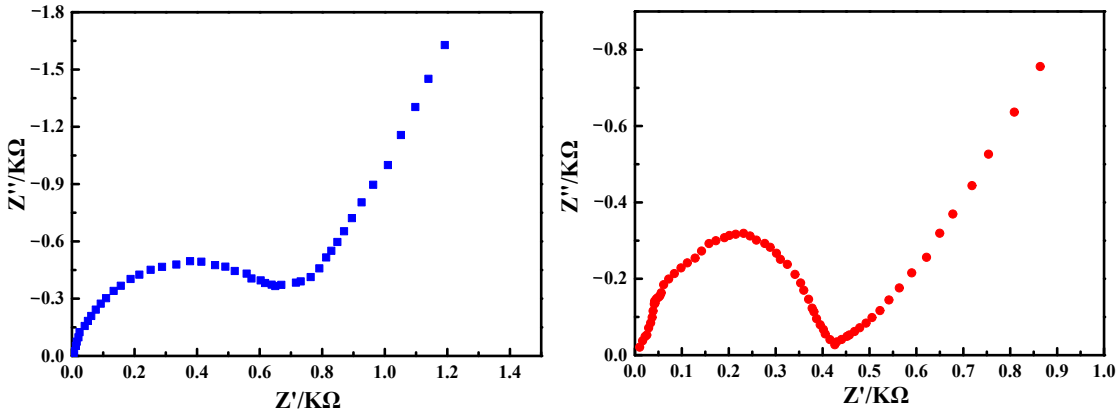

Fig. S15 Nyquist plots of the pellet sample (a) compound **1** at 25 °C and 98% RH, S = 1.135 cm^2, L = 0.125 cm. (b) compound **2** at 25 °C and 98% RH, S = 1.135 cm^2, L = 0.098 cm.