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Electronic Supplementary Information

Crystal engineering of coordination-polymer-based iodine absorbents using π-electron-rich polycarboxylate aryl ether ligand

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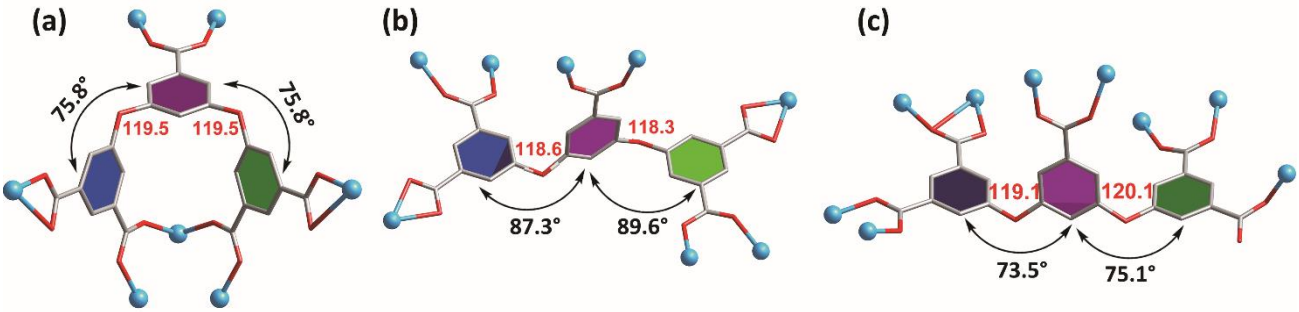
Experimental

Materials and equipments

All reagents and solvents were purchased from commercial sources and used without further purification. Elemental analyses were measured by a Perkin-Elmer 240 elemental analyzer. Fourier transform infrared spectroscopy (FT-IR) were recorded on a Tracer-100 FT-IR spectrometer in the range of 400-4000 cm^{-1}. Thermogravimetric analyses (TGA) were performed on an STA 449 F3 Jupiter thermal analyzer from room temperature (r.t.) to 800 °C at a heating rate of 10 °C min^{-1} under N_2 flow. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE diffractometer with Cu Kα radiation (λ = 1.5418 Å) over the 2ϑ range of 5−50° at 40 kV and 40 mA. The fluorescence measurement was carried out on an F-7000 (HITACHI) Fluorescence spectrophotometer (220−240V) equipped with a 450 W xenon lamp. The absorption spectra were collected with a UV-9000s spectrophotometer. Electrochemical impedance spectroscopy (EIS) measurements were measured on a CHI 660E electrochemical workstation in 1M KOH with a standard three-electrode system from 100000 Hz to 0.01 Hz. A glassy-carbon (GC) electrode with the diameter of 3 mm was employed as the working electrode. A Pt wire was chosen as the counter electrode, and a saturated calomel electrode (SCE) was selected as the reference electrode. 5 mg CP powder was added into 480 μL iso-propanol and 20 μL Nafion. The mixture was ultrasonic to obtain a homogeneous ink.



Scheme S1 Coordination modes of H_5L in CPs (a) **1**, (b) **2** and (c) **3**.

Solid-state fluorescence spectra

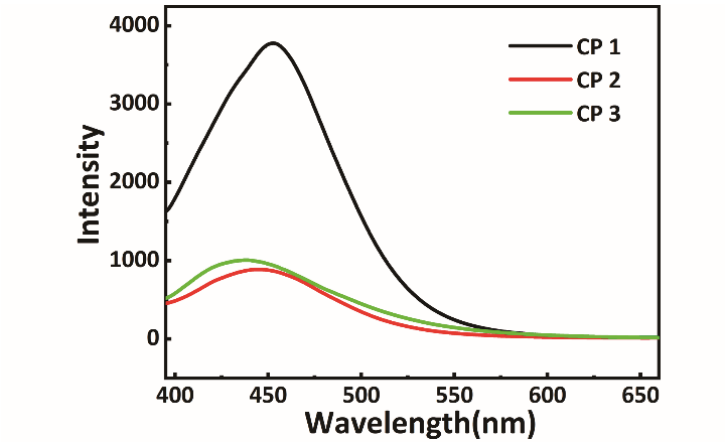


Fig. S1 Solid-state photoluminescent spectra of CPs **1**–**3**.

I_2 absorption/desorption studies

The curve of calibration of I_2 in cyclohexane was achieved by different concentration in cyclohexane solution (0, 0.02, 0.04, 0.06, 0.08, 0.1 mg mL^{-1}) (Fig. S3). Meanwhile, the curve of calibration of I_2 in ethanol was achieved by different concentration in ethanol solution (0.005, 0.01, 0.02, 0.025, 0.04 mg mL^{-1}) (Fig. S4).

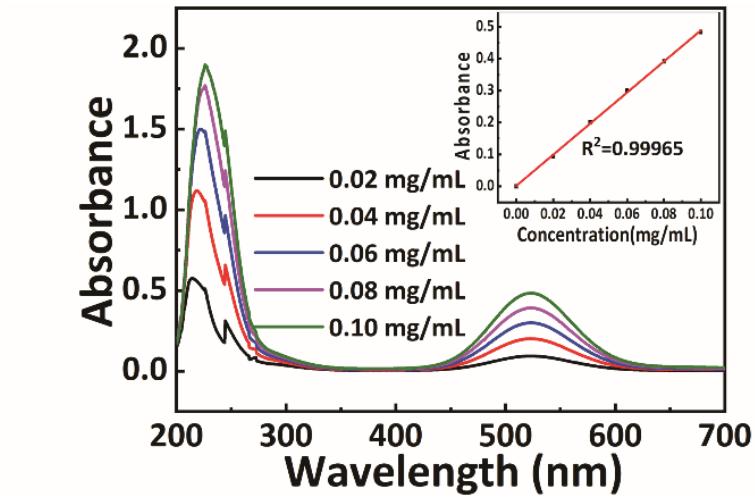


Fig. S2 The curve of calibration in cyclohexane solution.

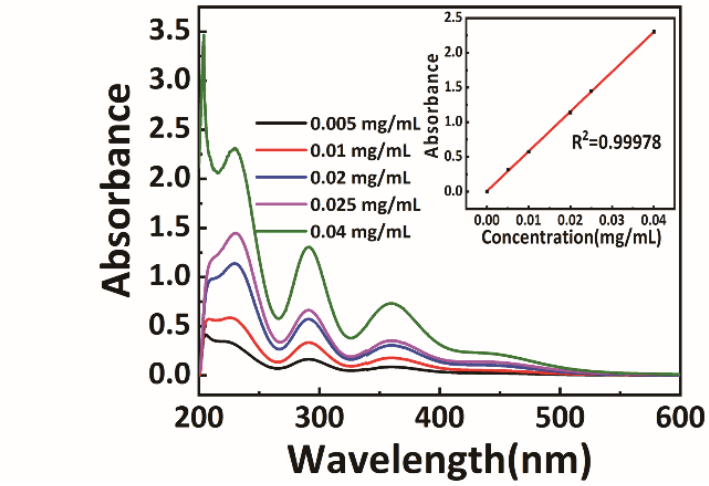


Fig. S3 The curve of calibration in ethanol solution.

Table S1 Selected Bond Lengths (Å) and Angles (°) for CPs **1**–**3** and I_2@**2**.

CP **1**					
Zn(1)-O(1)#1	1.939(3)	Zn(2)-O(4)	2.021(13)	Zn(2)-O(7)	2.185(3)
Zn(1)-O(3)	1.943(3)	Zn(2)-O(4)#3	2.021(13)	Zn(2)-O(8)	2.112(5)
Zn(1)-O(6)#2	1.985(3)	Zn(2)-O(4')#3	2.035(5)	Zn(2)-O(9)	2.079(5)
Zn(1)-O(7)	1.978(2)	Zn(2)-O(4')	2.035(5)	Zn(2)-O(9)#3	2.079(5)
O(1)#1-Zn(1)-O(3)	114.24(14)	O(4)-Zn(2)-O(7)	89.1(4)	O(4')#3-Zn(2)-O(8)	86.3(2)
O(1)#1-Zn(1)-O(6)#2	98.01(14)	O(4)#3-Zn(2)-O(8)	92.8(4)	O(4')-Zn(2)-O(8)	86.3(2)
O(1)#1-Zn(1)-O(7)	120.21(15)	O(4)-Zn(2)-O(8)	92.8(4)	O(4')#3-Zn(2)-O(9)	84.0(3)
O(3)-Zn(1)-O(6)#2	100.59(14)	O(4)-Zn(2)-O(9)#3	109.1(6)	O(4')-Zn(2)-O(9)	169.4(3)
O(3)-Zn(1)-O(7)	112.23(13)	O(4)-Zn(2)-O(9)	163.8(6)	O(8)-Zn(2)-O(7)	177.8(2)
O(7)-Zn(1)-O(6)#2	108.25(11)	O(4)#3-Zn(2)-O(9)#3	163.8(6)	O(9)#3-Zn(2)-O(7)	90.64(14)
O(4)-Zn(2)-O(4)#3	54.7(11)	O(4)#3-Zn(2)-O(9)	109.1(6)	O(9)-Zn(2)-O(7)	90.64(14)
O(4)#3-Zn(2)-O(4')#3	25.8(4)	O(4')#3-Zn(2)-O(4')	104.4(5)	O(9)-Zn(2)-O(8)	87.77(19)
O(4)-Zn(2)-O(4')#3	79.9(7)	O(4')#3-Zn(2)-O(7)	95.04(17)	O(9)#3-Zn(2)-O(8)	87.77(19)
O(4)#3-Zn(2)-O(7)	89.1(4)	O(4')-Zn(2)-O(7)	95.04(17)	O(9)-Zn(2)-O(9)#3	87.0(3)
CP **2**					
Zn(1)-O(3)#1	2.217(3)	Zn(2)-O(2)#3	2.316(3)	Zn(3)-O(9)#5	2.059(5)
Zn(1)-O(6)	1.984(3)	Zn(2)-O(4)#1	1.976(3)	Zn(3)-O(9')#5	1.988(7)
Zn(1)-O(8)#2	2.120(3)	Zn(2)-O(5)	2.034(3)	Zn(3)-O(10)#5	2.442(6)
Zn(1)-O(13)	1.984(3)	Zn(2)-O(13)	1.993(3)	Zn(3)-O(10')#5	2.445(7)

Zn(1)-O(14)	1.878(3)	Zn(2)-C(1)#3	2.514(4)	Zn(3)-O(13)	2.094(3)
Zn(2)-O(1)#3	2.055(3)	Zn(3)-O(7)#4	1.959(3)	Zn(3)-O(14)#6	1.900(3)
O(6)-Zn(1)-O(3)#1	89.98(12)	O(4)#1-Zn(2)-C(1)#3	127.53(13)	O(9)#5-Zn(3)-C(24)#5	23.5(2)
O(6)-Zn(1)-O(8)#2	94.09(13)	O(5)-Zn(2)-O(1)#3	101.57(12)	O(9')#5-Zn(3)-O(13)	98.1(2)
O(6)-Zn(1)-O(13)	106.76(12)	O(5)-Zn(2)-O(2)#3	92.30(11)	O(9')#5-Zn(3)-C(24)#5	21.9(2)
O(8)#2-Zn(1)-O(3)#1	175.91(13)	O(5)-Zn(2)-C(1)#3	98.25(12)	O(10)#5-Zn(3)-O(10')#5	66.04(19)
O(13)-Zn(1)-O(3)#1	87.09(11)	O(13)-Zn(2)-O(1)#3	141.44(12)	O(10)#5-Zn(3)-C(24)#5	33.25(19)
O(13)-Zn(1)-O(8)#2	91.35(12)	O(13)-Zn(2)-O(2)#3	91.81(10)	O(10')#5-Zn(3)-C(24)#5	35.3(2)
O(14)-Zn(1)-O(3)#1	85.66(12)	O(13)-Zn(2)-O(5)	104.64(11)	O(13)-Zn(3)-O(10)#5	82.32(17)
O(14)-Zn(1)-O(6)	115.92(15)	O(13)-Zn(2)-C(1)#3	117.50(13)	O(13)-Zn(3)-O(10')#5	74.0(2)
O(14)-Zn(1)-O(8)#2	92.90(13)	O(7)#4-Zn(3)-O(9)#5	103.1(2)	O(13)-Zn(3)-C(24)#5	85.77(14)
O(14)-Zn(1)-O(13)	136.64(15)	O(7)#4-Zn(3)-O(9')#5	136.7(3)	O(14)#6-Zn(3)-O(7)#4	107.98(13)
O(1)#3-Zn(2)-O(2)#3	59.18(11)	O(7)#4-Zn(3)-O(10)#5	158.16(16)	O(14)#6-Zn(3)-O(9)#5	137.8(2)
O(1)#3-Zn(2)-C(1)#3	29.85(13)	O(7)#4-Zn(3)-O(10')#5	98.12(17)	O(14)#6-Zn(3)-O(9')#5	99.3(2)
O(2)#3-Zn(2)-C(1)#3	29.33(12)	O(7)#4-Zn(3)-O(13)	108.62(11)	O(14)#6-Zn(3)-O(10)#5	87.64(16)
O(4)#1-Zn(2)-O(1)#3	98.07(12)	O(7)#4-Zn(3)-C(24)#5	126.59(17)	O(14)#6-Zn(3)-O(10')#5	153.54(18)
O(4)#1-Zn(2)-O(2)#3	156.11(11)	O(9)#5-Zn(3)-O(10)#5	56.2(2)	O(14)#6-Zn(3)-O(13)	100.93(14)
O(4)#1-Zn(2)-O(5)	100.05(12)	O(9)#5-Zn(3)-O(10')#5	24.5(2)	O(14)#6-Zn(3)-C(24)#5	119.6(2)
O(4)#1-Zn(2)-O(13)	104.55(11)	O(9)#5-Zn(3)-O(13)	95.3(2)		
CP **3**					
Zn(1)-O(1)	1.932(2)	Zn(2)-O(8)#4	2.172(2)	Zn(3)-O(9)	1.943(2)
Zn(1)-O(3)#1	1.950(2)	Zn(2)-O(13)	2.093(2)	Zn(3)-O(13)#2	1.983(2)
Zn(1)-O(10)#2	1.998(2)	Zn(2)-O(14)	2.055(3)		
Zn(1)-O(13)	1.950(2)	Zn(2)-O(15)	2.061(3)	O(1)-Zn(1)-O(3)#1	103.94(11)
Zn(2)-O(4)#1	2.047(2)	Zn(3)-O(6)#5	1.972(2)	O(1)-Zn(1)-O(10)#2	98.17(9)
Zn(2)-O(5)#3	2.064(2)	Zn(3)-O(7)#6	1.956(2)		
O(1)-Zn(1)-O(13)	120.69(10)	O(4)#1-Zn(2)-O(15)	85.27(11)	O(15)-Zn(2)-O(8)#4	91.27(11)
O(3)#1-Zn(1)-O(10)#2	119.10(10)	O(5)#3-Zn(2)-O(8)#4	95.72(10)	O(15)-Zn(2)-O(13)	93.63(11)

O(13)-Zn(1)-O(3)#1	109.23(9)	O(5)#3-Zn(2)-O(13)	93.68(10)	O(6)#5-Zn(3)-O(13)#2	116.90(10)
O(13)-Zn(1)-O(10)#2	106.18(9)	O(13)-Zn(2)-O(8)#4	84.68(8)	O(7)#6-Zn(3)-O(6)#5	105.31(11)
O(4)#1-Zn(2)-O(5)#3	87.93(10)	O(14)-Zn(2)-O(5)#3	86.68(12)	O(7)#6-Zn(3)-O(13)#2	110.95(9)
O(4)#1-Zn(2)-O(8)#4	176.11(10)	O(14)-Zn(2)-O(8)#4	86.27(10)	O(9)-Zn(3)-O(6)#5	102.88(11)
O(4)#1-Zn(2)-O(13)	93.74(9)	O(14)-Zn(2)-O(13)	170.93(10)	O(9)-Zn(3)-O(7)#6	117.81(9)
O(4)#1-Zn(2)-O(14)	95.32(11)	O(14)-Zn(2)-O(15)	87.10(13)	O(9)-Zn(3)-O(13)#2	103.28(10)
O(15)-Zn(2)-O(5)#3	170.32(11)				
CP I_2@**2**					
Zn(2)-O(13)	1.994(3)	Zn(3)-O(7)#3	1.954(3)	Zn(1)-O(6)	1.974(3)
Zn(2)-O(1)#1	1.972(2)	Zn(3)-O(9)#4	1.983(2)	Zn(1)-O(3)#2	2.151(3)
Zn(2)-O(4)#2	1.972(3)	Zn(3)-O(14)#5	1.886(3)	Zn(1)-O(8)#6	2.109(3)
Zn(2)-O(5)	1.966(3)	Zn(1)-O(13)	2.021(2)	Zn(1)-O(14)	1.893(3)
Zn(3)-O(13)	2.034(3)				
O(1)#1-Zn(2)-O(13)	121.49(11)	O(9)#4-Zn(3)-O(13)	97.99(11)	O(6)-Zn(1)-O(3)#2	93.94(12)
O(4)#2-Zn(2)-O(13)	103.86(11)	O(14)#5-Zn(3)-O(13)	111.46(18)	O(6)-Zn(1)-O(8)#6	97.63(13)
O(4)#2-Zn(2)-O(1)#1	104.31(11)	O(14)#5-Zn(3)-O(7)#3	108.02(13)	O(8)#6-Zn(1)-O(3)#2	168.12(13)
O(5)-Zn(2)-O(13)	108.00(11)	O(14)#5-Zn(3)-O(9)#4	124.87(15)	O(14)-Zn(1)-O(13)	141.97(17)
O(5)-Zn(2)-O(1)#1	112.68(11)	O(13)-Zn(1)-O(3)#2	88.36(10)	O(14)-Zn(1)-O(6)	113.36(18)
O(5)-Zn(2)-O(4)#2	104.77(12)	O(13)-Zn(1)-O(8)#6	86.16(10)	O(14)-Zn(1)-O(3)#2	86.66(13)
O(7)#3-Zn(3)-O(13)	104.66(11)	O(6)-Zn(1)-O(13)	104.58(11)	O(14)-Zn(1)-O(8)#6	91.18(13)
O(7)#3-Zn(3)-O(9)#4	107.94(11)				

Symmetry codes: #1 -*x*+1/2, -*y*, *z*+1/2; #2 *x*, *y*-1, *z*; #3 -*x*+1, *y*, *z* for **1**; #1 -*x*+1, -*y*+1, -*z*; #2 -*x*+1, -*y*, -*z*+1; #3 -*x*, -*y*+1, -*z*; #4 *x*, *y*+1, *z*; #5 *x*-1, *y*+1, *z*; #6 -*x*+1, -*y*+1, -*z*+1 for **2**; #1 -*x*+1, -*y*, -*z*+1; #2 -*x*+1, -*y*+1, -*z*+1; #3 -*x*+1, *y*-1/2, -*z*+3/2; #4 *x*-1, -*y*+1/2, *z*+1/2; #5 *x*, -*y*+3/2, *z*-1/2; #6 -*x*+2, *y*+1/2, -*z*+1/2 for **3**; #1 -*x*+2, -*y*+2, -*z*+1; #2 -*x*+1, -*y*+2, -*z*+1; #3 *x*, *y*+1, *z*; #4 *x*+1, *y*+1, *z*; #5 -*x*+1, -*y*+2, -*z*; #6 -*x*+1, -*y*+1, -*z* for I_2@**2**.

Table S2 Comparison of iodine adsorption capacities of CPs.

Entry	Adsorbent	Loading amount (wt%[b])	adsorption amounts q_t	Weak interactions	Soaking method	Reference

			($mg \cdot g^{-1}$)			
1	$\{[Zn_3(\mu_3\text{-}OH)(L)(H_2O)] \cdot 2DMF \cdot 3H_2O\}_n$	13.2 wt %	152.1	C=O···I and π···I interactions	50 mg crystal powders, 3 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	This work
2	CdL_2	15.7 wt %	186.2[a]	$I \cdots OCl_4^-$ and π···I interactions	0.02 mol L^{-1} hexane solutions of I_2	[1]
3	MIL-53-COOH	4.1 wt %	43.1 [a]	C=O···I interactions	100 mg crystal powders, 5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[2]
4	MIL-53-OH	5.5 wt %	58.3 [a]	O–H···I interactions	100 mg crystal powders, 5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[2]
5	MIL-53-Br	5.6 wt %	59.6 [a]	Br···I interactions	100 mg crystal powders,5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[2]
6	MIL-53-NH_2	7.07 wt %	76.1 [a]	N–H···I interactions	100 mg crystal powders, 5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[2]
7	MIL-101-NH_2	23.7 wt % [a]	311	N–H···I interactions	100 mg crystal powders, 5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[2]
10	$\{[Zn_3(DL\text{-}lac)_2(pybz)_2] \cdot 2.5DMF\}_n$	100 wt %	1010	π···I interactions	100 mg crystal powders, 0.1 mol L^{-1} cyclohexane solutions of I_2	[3]
11	[Co-(DpyDtolP)]$_6 \cdot 12H_2O$	29.8 wt %	426.38 [a]	π···I interactions	10 mg crystal powders, 10 ml 2.0 mmol L^{-1} cyclohexane solutions of I_2	[4]
12	$[Cu_2(tpmp)I_2]$	8.4 wt %[a]	92 [a]	Cu–X···I_2 and π···I interactions	50 mg crystal powders, 1.5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[5]
13	$[Cu_2(tpmp)Cl_2]$	9.5 wt %[a]	106 [a]	Cu–X···I_2 and π···I interactions	50 mg crystal powders, 1.5 ml 0.01 mol L^{-1} cyclohexane solutions of I_2	[5]
14	Cd-MOF	23 wt %	298 [a]	N–H···I interactions	100 mg crystal powders, 5 ml 0.1 mol L^{-1} hexane solutions of I_2	[6]
15	EuL	17.4 wt %	210.8 [a]	π···I interactions	200 mg crystal powders, 10 ml 2.0 mol L^{-1} hexane solutions of I_2	[7]
16	$[(CH_3)_2NH_2]_{1.66}$ $[Cd_{1.84}Na_{0.66}$ $(BDC)_3] \cdot DMF \cdot 0.5EtOH$	17.7 wt%	215.06 [a]	π···I interactions	1.02 g crystal powders, 100 ml 0.05 mmol L^{-1} cyclohexane solutions of I_2	[8]
17	$[(In_3O)_2(Cu_2I_2)_3(ina)_{12}$ $(H_2O)_6](NO_3)_2 \cdot 7DMA \cdot 10H_2O$	45 wt %	818.2 [a]	weaker I_{mol}-I_{anion} bond	100 mg crystal powders, 0.01 mol L^{-1} cyclohexane solutions of I_2	[9]
18	IFMC-69	29.4 wt %	418.1 [a]	I_2 and p-electron walls	100 mg crystal powders, 3 ml 0.01 mol L^{-1} hexane solutions of I_2	[10]

19	TMU-16-NH_2	45 wt %	818.2 [a]	weak N–H···I interactions and π···I interactions	100 mg crystal powders, 3 ml 0.005 mol L^{-1} hexane solutions of I_2	[11]
20	{[Cd(bdc)(4-bpmh)]}$_n$·2n(H_2O)	14 wt%	162.7 [a]	π···I interactions	100 mg crystal powders, 3.5 ml 0.1 mol L^{-1} hexane solutions of I_2	[12]
21	{[Cd(2-NH_2bdc)(4-bpmh)]}$_n$·2n(H_2O)	28 wt%	388.9 [a]	weak N–H···I interactions and π···I interactions	100 mg crystal powders, 3.5 ml 0.1 mol L^{-1} hexane solutions of I_2	[12]

% = iodine mass/(adsorbent mass + iodine mass) [a] Caculated

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