Supporting Information

Water-stable Cd(II)/Zn(II) coordination polymers as recyclable luminescent sensors for detecting hippuric acid in simulated urine for indexing toluene exposure with high selectivity, sensitivity and fast response

Jiao-Jiao Zhao, Lei Zhang, Peng-Yu Liu, Wei-Zhe Chen, Zhi-Liang Liu and Yan-Qin Wang*

Table S1. Crystallographic data and structure refinements for CPs **1-3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{29}H_{21}CdN_7O_{3.5}$	$C_{58}H_{40}Zn_2N_{14}O_6$	$C_{31}H_{25}Cd_2N_7O_{10}$
Formula weight	635.93	1159.78	880.38
Temperature/K	296.15	296.15	296.15
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.0248(8)	12.8324(9)	9.5327(6)
b/Å	13.2191(10)	14.0562(9)	10.2308(7)
c/Å	14.1609(11)	16.8239(12)	18.6797(12)
α/°	117.1500(10)	97.0300(10)	82.8490(10)
β/°	102.4070(10)	101.5180(10)	76.5790(10)
γ/°	100.6180(10)	114.7100(10)	73.1260(10)
Volume/Å^3	1696.2(2)	2628.0(3)	1692.54(19)
Z	2	2	2
ρ_{calcd}/g cm^{-3}	1.245	1.466	1.727
μ/mm^{-1}	0.681	0.980	1.323
F(000)	640.0	1188.0	872.0
Reflections collected	10372	16053	10263
Independent reflections	7438	11504	7394
R_{int}	0.0216	0.0186	0.0114
Goodness-of-fit on F^2	0.980	1.040	1.043
R_1, wR_2 [I > 2σ(I)]	R_1 = 0.0387	R_1 = 0.0400	R_1 = 0.0262
	wR_2 = 0.0886	wR_2 = 0.0937	wR_2 = 0.0642
R_1, wR_2 (all data)	R_1 = 0.0550	R_1 = 0.0658	R_1 = 0.0318
	wR_2 = 0.0952	wR_2 = 0.1033	wR_2 = 0.0666

Table S2. The selected bond lengths (Å) and angles (◦) for CPs **1-3**.

		1	
Cd1-O1	2.398(2)	Cd1-O2	2.320(2)
Cd1-O3	2.347(2)	Cd1-N1	2.281(2)
Cd1-N3C	2.330(2)	Cd1-N4B	2.318(3)
O2-Cd1-O1	55.13(7)	O3-Cd1-O1	87.17(8)
O2-Cd1-O3	94.56(9)	N1-Cd1-N3C	111.34(9)
N1-Cd1-N4B	86.21(9)	N4B-Cd1-N3C	92.02(9)
N1-Cd1-O1	105.21(8)	N3C-Cd1-O1	141.57(8)
N4B-Cd1-O1	101.99(8)	N1-Cd1-O2	160.34(8)
O2-Cd1-N3C	87.95(8)	O2-Cd1-N4B	97.25(9)
N1-Cd1-O3	83.64(9)	N3C-Cd1-O3	85.47(9)
N4B-Cd1-O3	167.83(8)		
Symmetry transformations used to generate equivalent atoms: A: -x, 1-y, -1-z; B: +x, +y, -1+z; C: +x, 1+y, +z.			
		2	
Zn2-O4	2.001(2)	Zn2-N8	2.017(2)
Zn2-N12A	2.058(2)	Zn2-N14B	2.082(2)
Zn2-O3	2.401(2)	Zn1-O2	1.9249(18)
Zn1-N4B	2.029(2)	Zn1-N7	2.027(2)
Zn1-N5C	2.047(2)	O4-Zn2-N8	128.08(8)
O4-Zn2-N12A	118.70(9)	N8-Zn2-N12A	102.88(8)
O4-Zn2-N14B	95.18(8)	N8-Zn2-N14B	99.41(8)
N12A-Zn2-N14B	109.03(8)	O4-Zn2-O3	58.59(8)
N8-Zn2-O3	94.93(8)	N12A-Zn2-O3	89.15(8)
N14B-Zn2-O3	153.47(8)	O2-Zn1-N4B	112.53(8)
O2-Zn1-N7	119.09(9)	N4B-Zn1-N7	103.07(8)
O2-Zn1-N5C	108.45(9)	N4B-Zn1-N5C	100.12(8)
N7-Zn1-N5C	111.89(8)		
Symmetry transformations used to generate equivalent atoms: A: +x, -1+y, +z; B: -1+x, -1+y, +z; C: -1+x, +y, +Z.			
		3	
Cd1-O4	2.1870(18)	Cd1-O2A	2.2458(19)
Cd1-N7B	2.321(2)	Cd1-N3C	2.335(2)
Cd1-O5D	2.3782(18)	Cd2-N1	2.256(2)
Cd1-O1A	2.5285(19)	Cd2-O6	2.2811(18)
Cd2-O7	2.258(3)	Cd2-O3D	2.425(2)
Cd2-N6E	2.306(2)	Cd2-O5	2.5252(18)
O4-Cd1-N7B	122.70(8)	O4-Cd1-O2A	139.95(7)
O4-Cd1-N3C	90.34(8)	O2A-Cd1-N7B	94.89(8)
N7B-Cd1-N3C	85.43(8)	O2A-Cd1-N3C	107.37(8)
O4-Cd1-O5D	82.01(7)	O2A-Cd1-O5D	88.75(7)
N7B-Cd1-O5D	84.96(7)	N3C-Cd1-O5D	161.87(7)

O4-Cd1-O1A	91.50(7)	O2A-Cd1-O1A	54.32(7)
N7B-Cd1-O1A	145.33(7)	N3C-Cd1-O1A	89.21(8)
O5D-Cd1-O1A	107.31(7)	N1-Cd2-O7	97.56(10)
N1-Cd2-O6	126.57(8)	O7-Cd2-O6	86.74(10)
N1-Cd2-N6E	94.17(8)	O7-Cd2-N6E	102.66(13)
O6-Cd2-N6E	136.94(7)	N1-Cd2-O3D	91.59(8)
O7-Cd2-O3D	166.62(9)	O6-Cd2-O3D	79.96(7)
N6E-Cd2-O3D	86.31(8)	N1-Cd2-O5	176.69(7)
O7-Cd2-O5	85.61(9)	O6-Cd2-O5	54.37(6)
N6E-Cd2-O5	84.17(7)	O3D-Cd2-O5	85.45(6)

Symmetry transformations used to generate equivalent atoms: A: 1+x, 1+y, +Z; B: 1-x, 2-y, 2-z; C: -1+x, +y, 1+z; D: -x, 1-y, 2-z; E: -1+x, -1+y, +z.

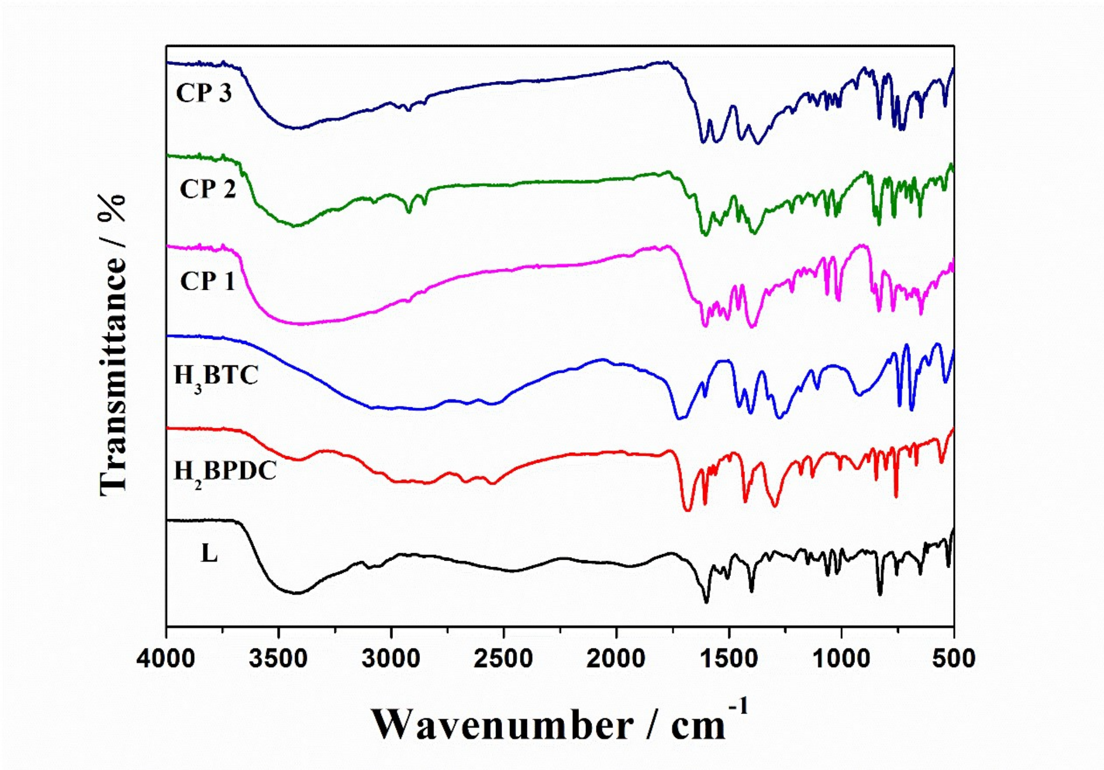

Fig. S1 The IR spectra of three ligands and CPs **1-3**.

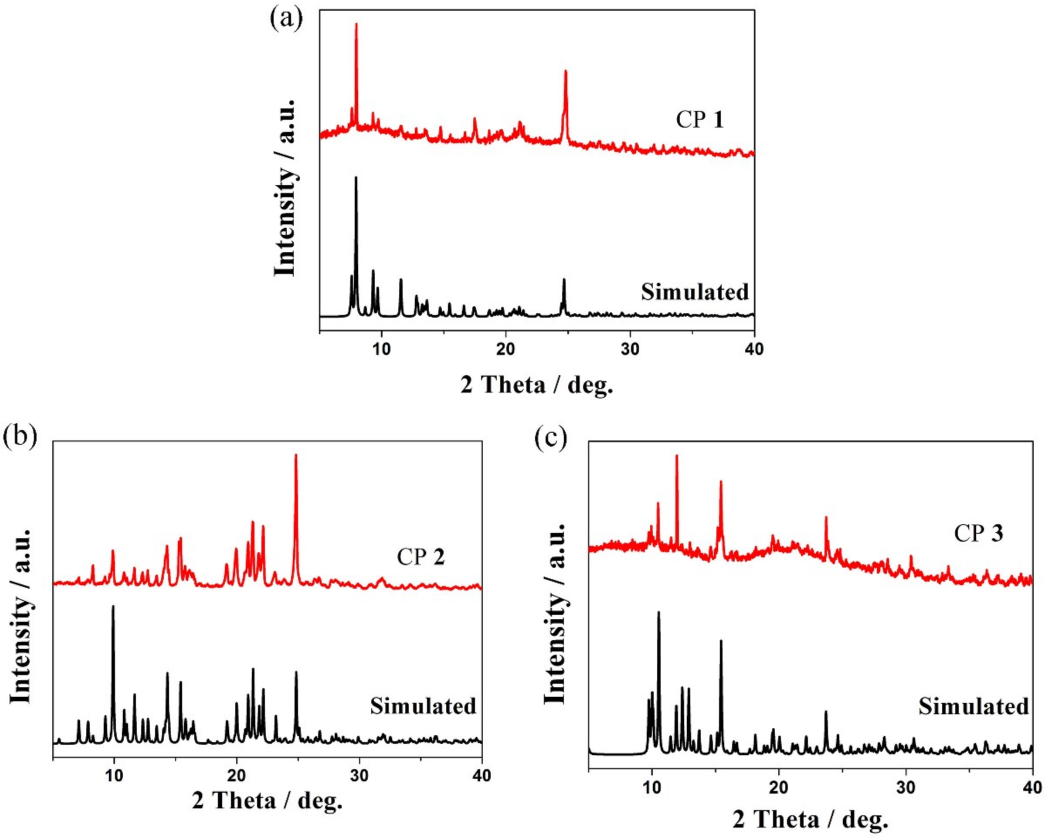

Fig. S2 The PXRD patterns for CPs **1-3**.

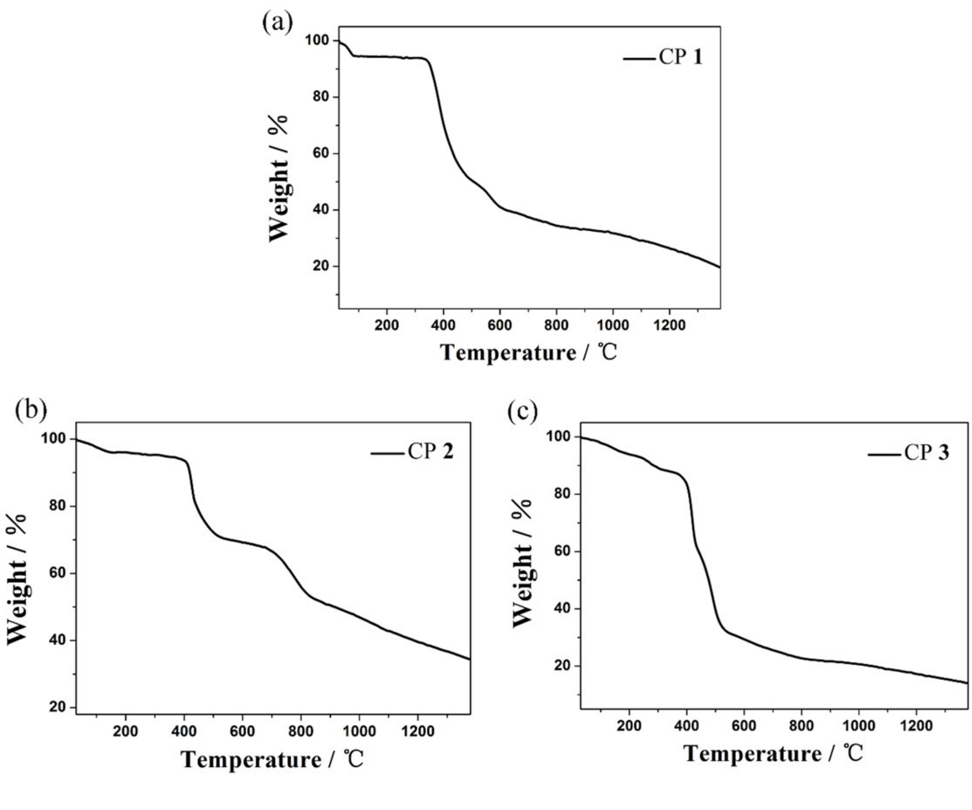

Fig. S3 The TGA curves for CPs **1-3**.

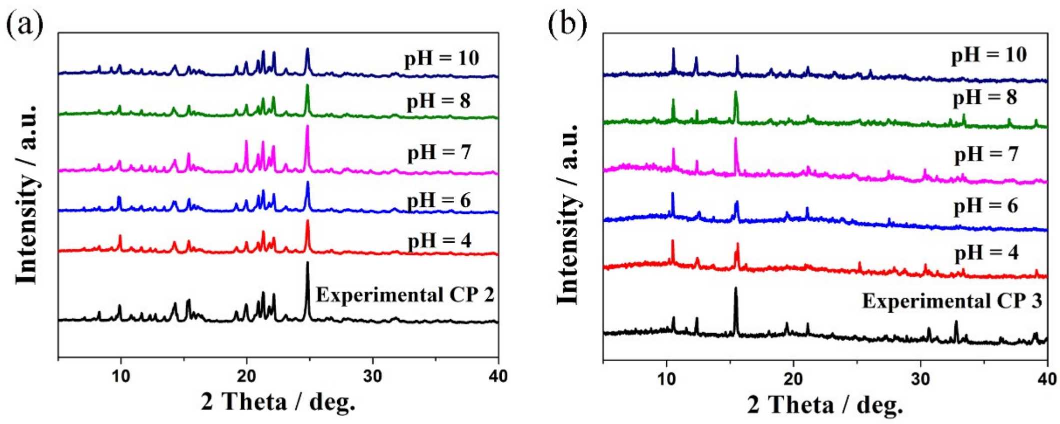

Fig. S4 PXRD patterns of ground samples of CP **2** and CP **3** under different pH conditions for 24 h.

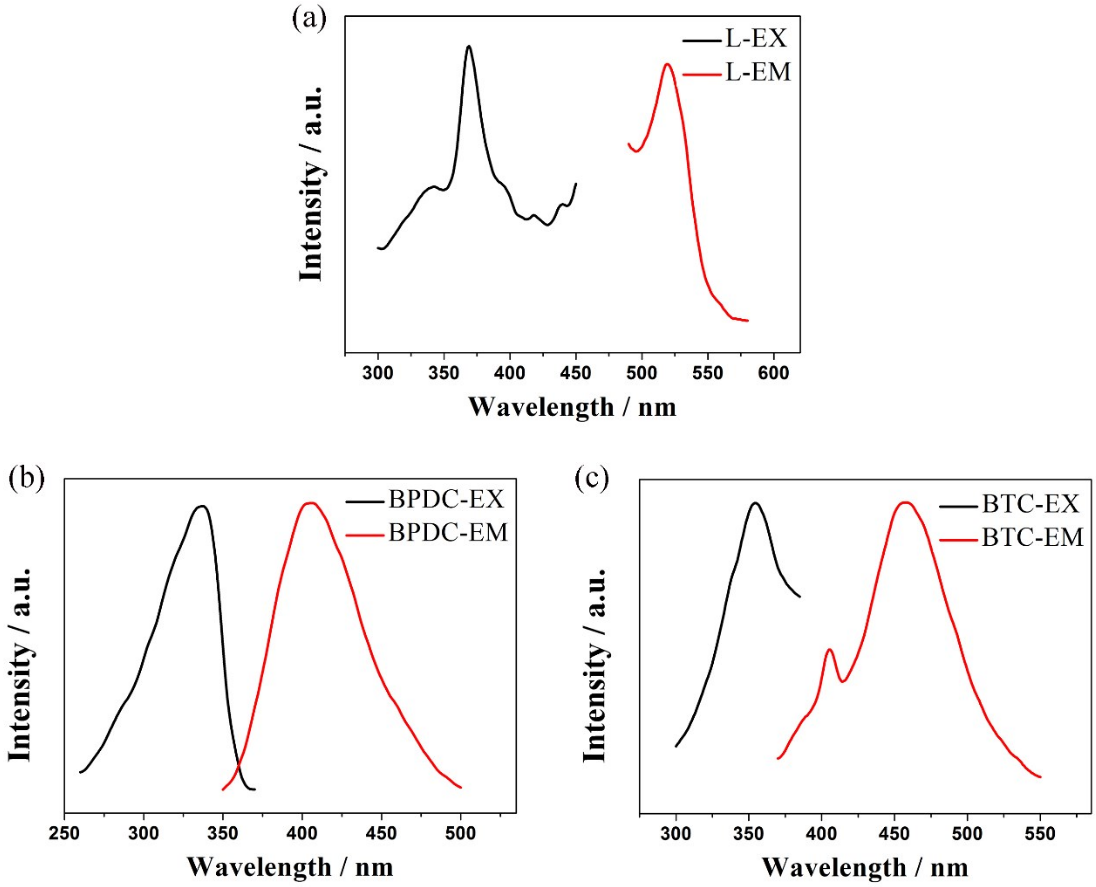

Fig. S5 The solid-state excitation and emission spectra of free L, BPDC and BTC ligands at room temperature.

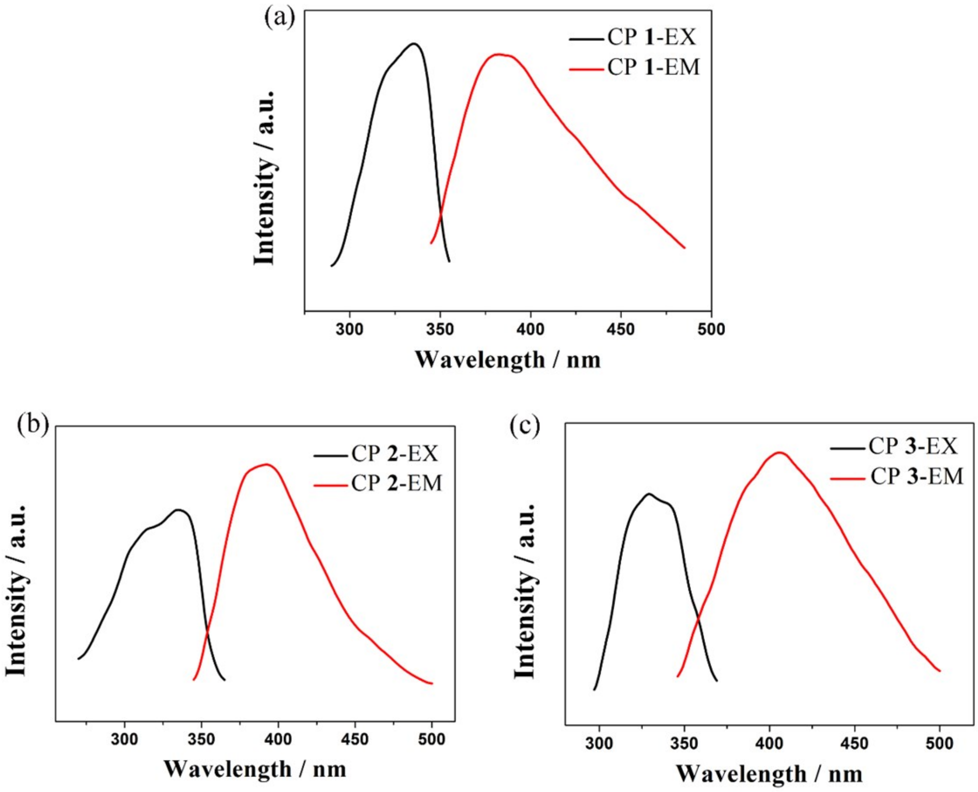

Fig. S6 The solid-state excitation and emission spectra of CPs **1-3** at room temperature.

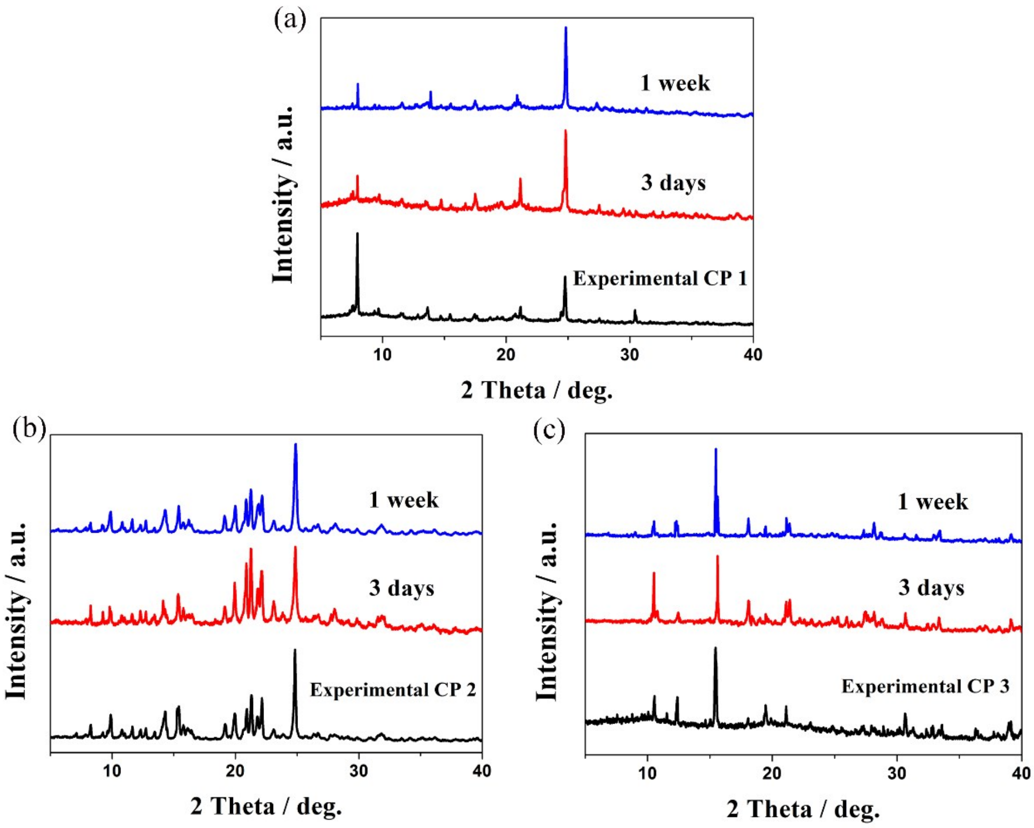

Fig. S7 PXRD patterns of CPs **1-3** after immersing in water for three days and one week.

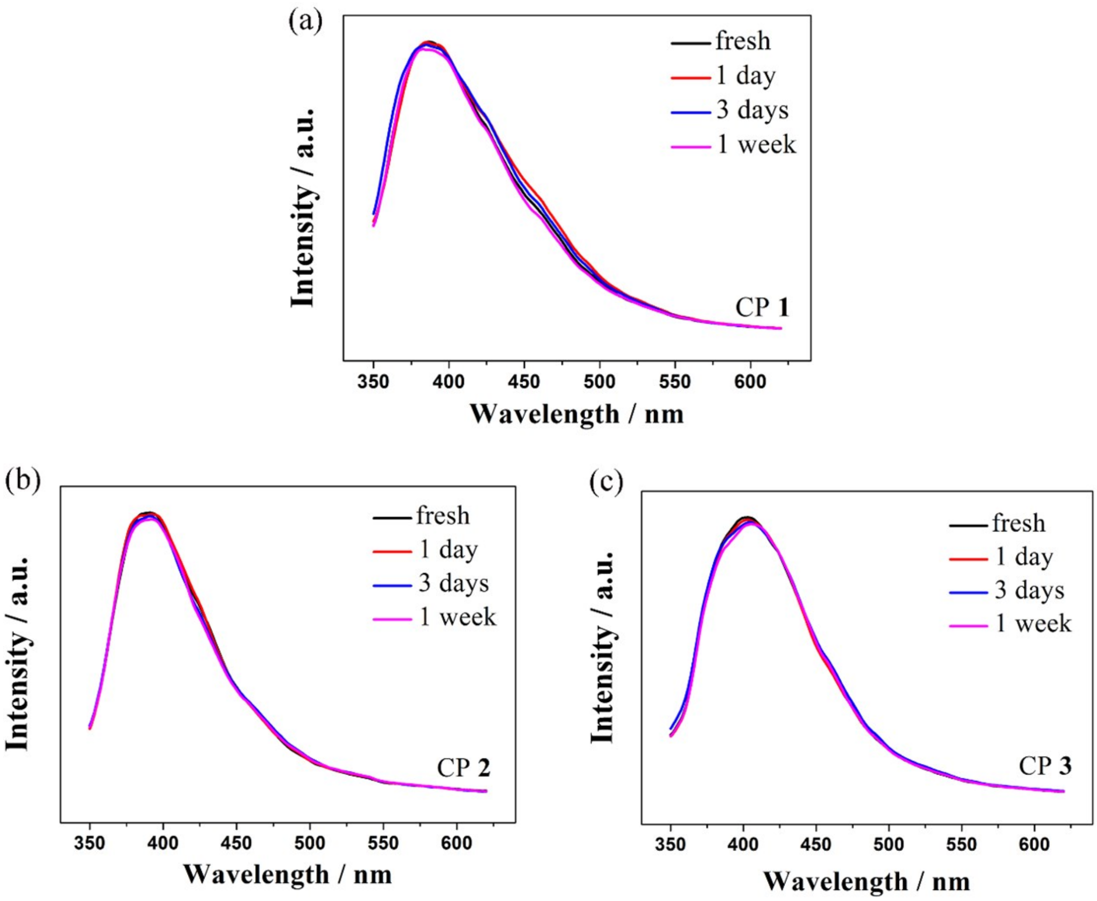

Fig. S8 Day-to-day fluorescence stability of CPs **1-3**.

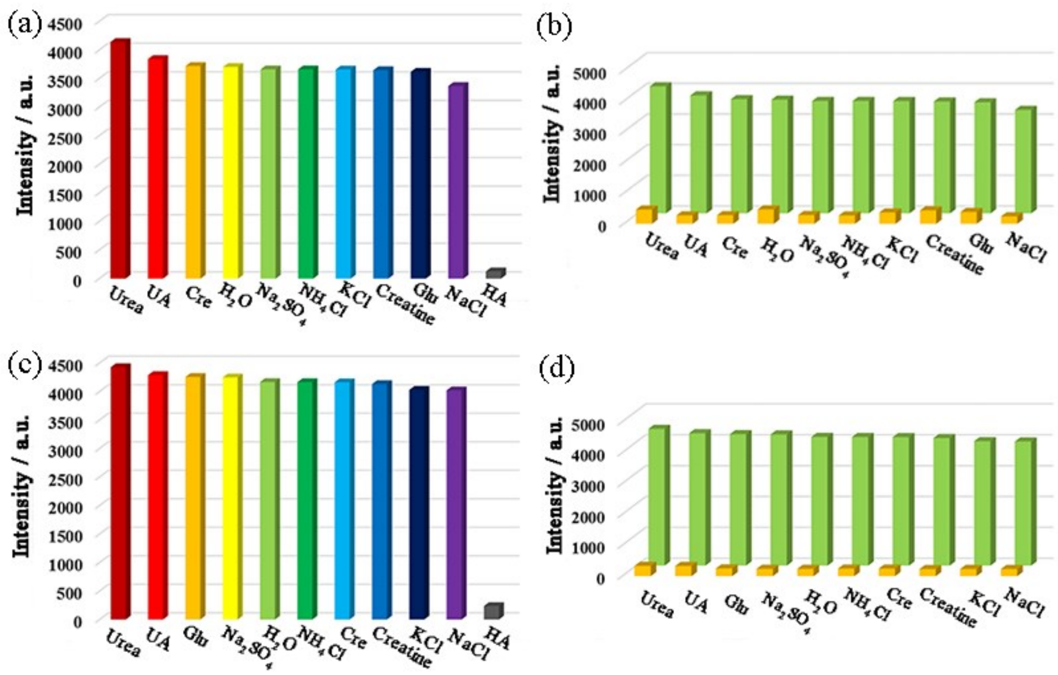

Fig. S9 Luminescence intensities of CP **2** (a) and CP **3** (c) dispersed in the routine urine chemicals upon excitation at 335 and 330 nm, respectively. Luminescence intensities of CP **2** (b) and CP **3** (d) upon the addition of HA (orange) in the background of other interferences (green).

Table S3. Comparison of the analytical parameters of previously reported sensors with CPs **1-3**.

Material	Method	LOD (μg mL^{-1})	Reusability	Ref
Diflunisal electrode	Potentiometric ion sensor	63	-	1
Capillary column	Gas Chromatography	4.6	+	2
MIL-121@Eu^{3+}	Fluorescent sensor	9	+	3
MIL-124@Eu^{3+}	Fluorescent sensor	8.1	+	4
CC[4]A@MIL-53-NH_2(Al)	Fluorescent sensor	3.7	+	5
CP **1**	Fluorescent sensor	3.2	+	This work
CP **2**	Fluorescent sensor	4	+	This work
CP **3**	Fluorescent sensor	5	+	This work

H_4btec = 1,2,4,5-benzenetetracarboxylic acid;[3] 1,2,4-H_3btc = 1,2,4-benzenetricarboxylate;[4] NH_2-BDC = 2-Amino-1,4-benzenedicarboxylic acid.[5]

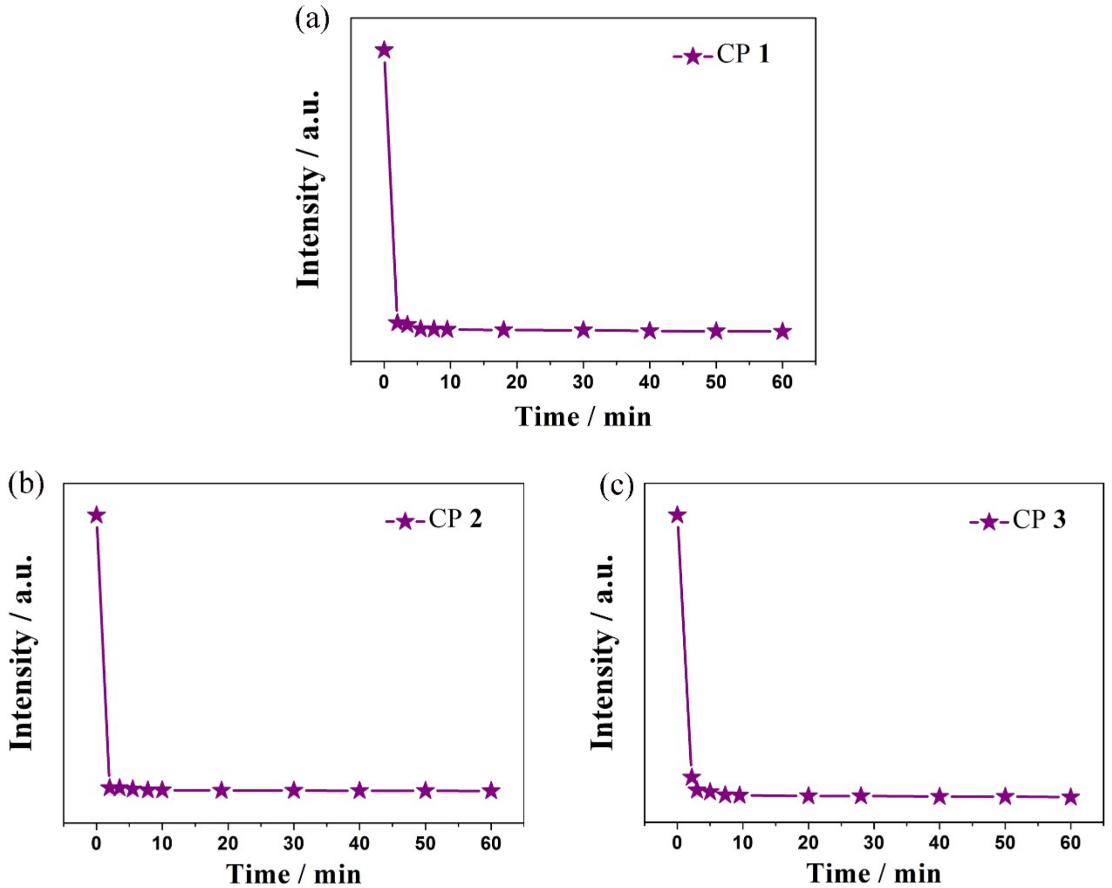

Fig. S10 Time-dependent fluorescence intensities of CPs **1-3** upon addition of HA aqueous solution.

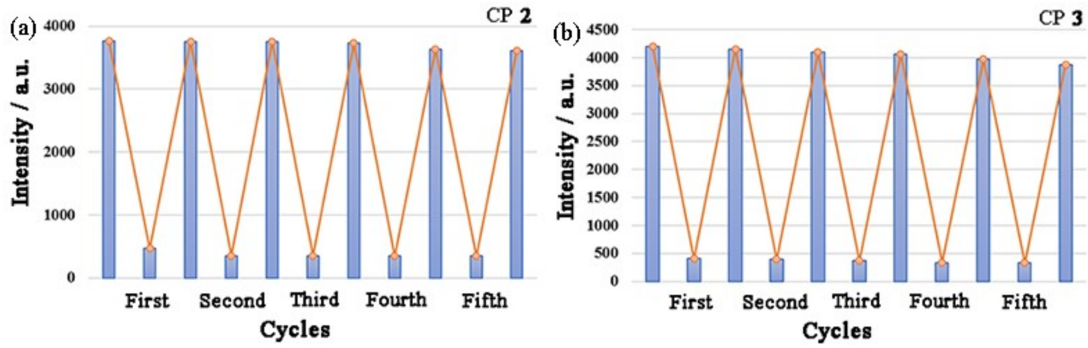

Fig. S11 Five cycles test of CP **2** and CP **3** towards sensing HA.

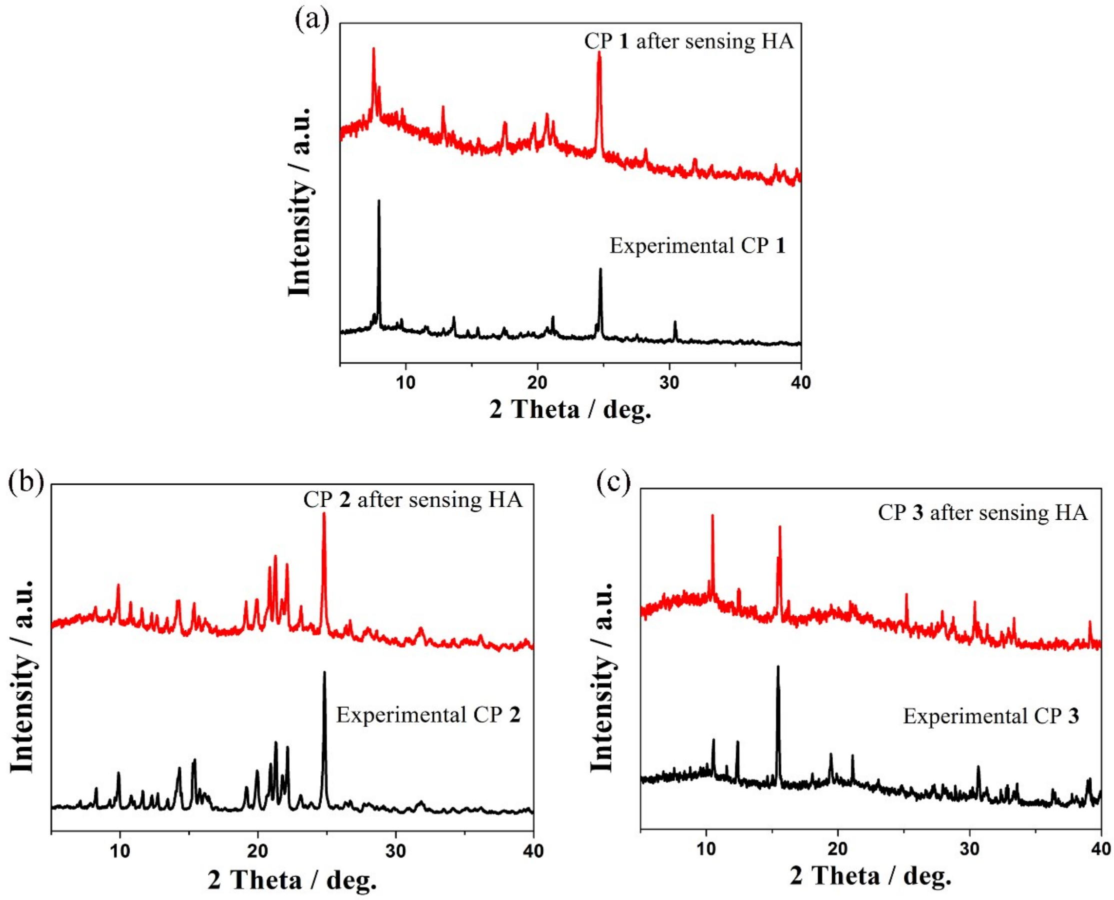

Fig. S12 PXRD patterns of CP**s 1-3** and CP**s 1-3** immersed in HA aqueous solution.

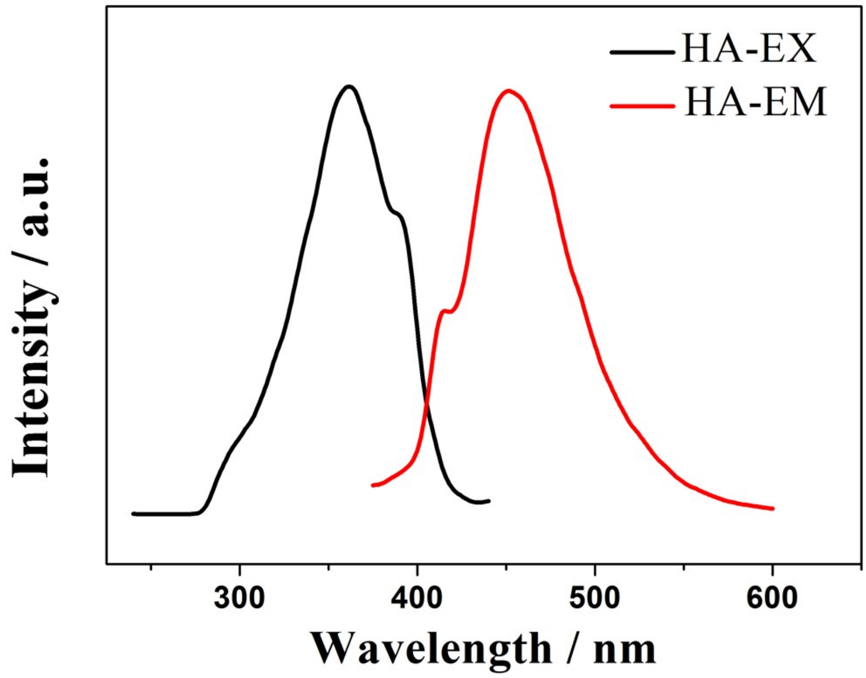

Fig. S13 Excitation (black line) and emission spectra (red line) of HA.

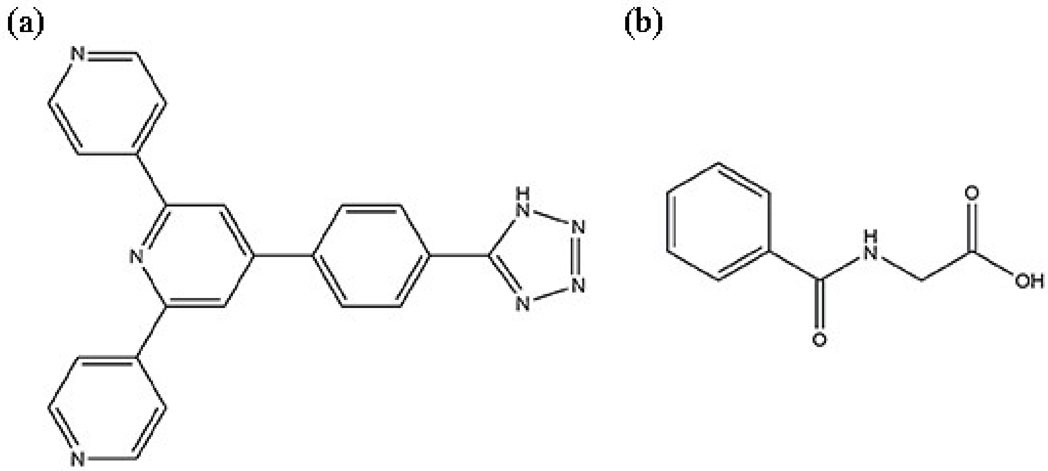

Fig. S14 The structural formulas of ligand and hippuric acid.

1 A. Davilas, M. Koupparis, P. Macheras and G. Valsami, In-vitro study on the competitive binding of diflunisal and uraemic toxins to serum albumin and human plasma using a potentiometric ion-probe technique, *J. Pharm. Pharmacol.,* 2006, **58**, 1467.
2 F. Cosnier, H. Nunge, B. Cossec and L. Gate, Simultaneous Determination of Aromatic Acid Metabolites of Styrene and Styrene-Oxide in Rat Urine by Gas Chromatography–Flame Ionization Detection, *J. Anal. Toxicol.,* 2012, **36**, 312.
3 J. N. Hao and B. Yan, Recyclable lanthanide-functionalized MOF hybrids to determine hippuric acid in urine as a biological index of toluene exposure, *Chem. Commun.,* 2015, **51**,

14509.

4 S. J. Qin, J. N. Hao, X. Y. Xu, X. Lian and B. Yan, Highly sensing probe for biological metabolite of benzene series pollutants based on recyclable Eu^{3+} functionalized metal-organic frameworks hybrids, *Sens. Actuators, B*, 2017, **253**, 852.

5 Y. Du, X. Li, H. Zheng, X. Lv and Q. Jia, Design of a calix[4]arene-functionalized metal-organic framework probe for highly sensitive and selective monitor of hippuric acid for indexing toluene exposure, *Anal. Chim. Acta.,* 2018, **1001**, 134.