

Supporting Information

Fluorescence-Responsive Detection of Ag(I), Al(III), and Cr(III) Ions Using Cd(II)-Based Pillared-Layer Frameworks

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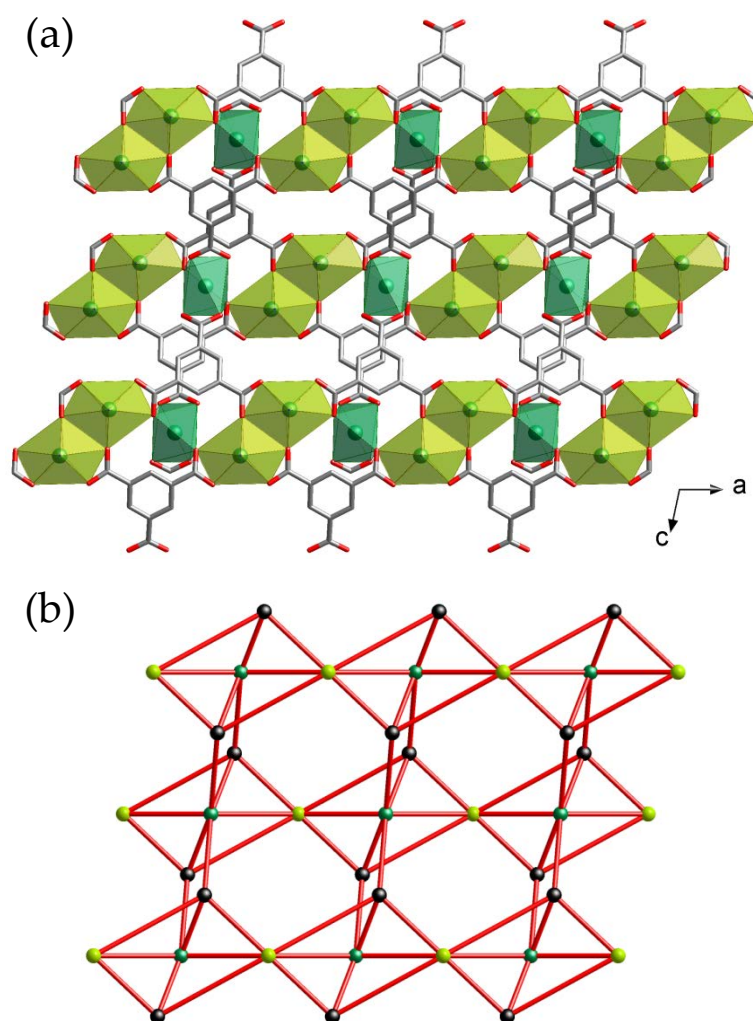


Figure S1. (a) Polyhedral and (b) schematic representations of the two-dimensional $[\text{Cd}_2(\text{btc})_3]_n$ bilayer structure of **1** showing the (4,6,6)-connected net topology.

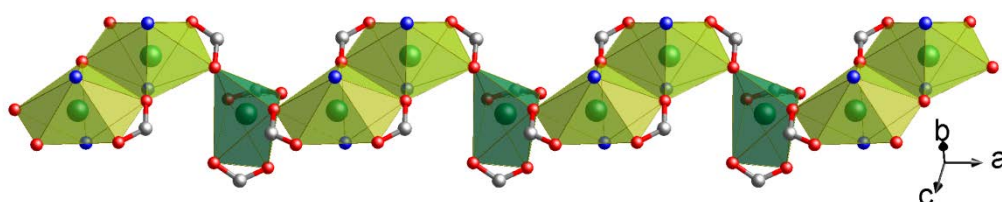


Figure S2. The one-dimensional $\{\text{Cd}_3(\text{CO}_2)_6\}_n$ chains running along the $[100]$ direction in **1**.

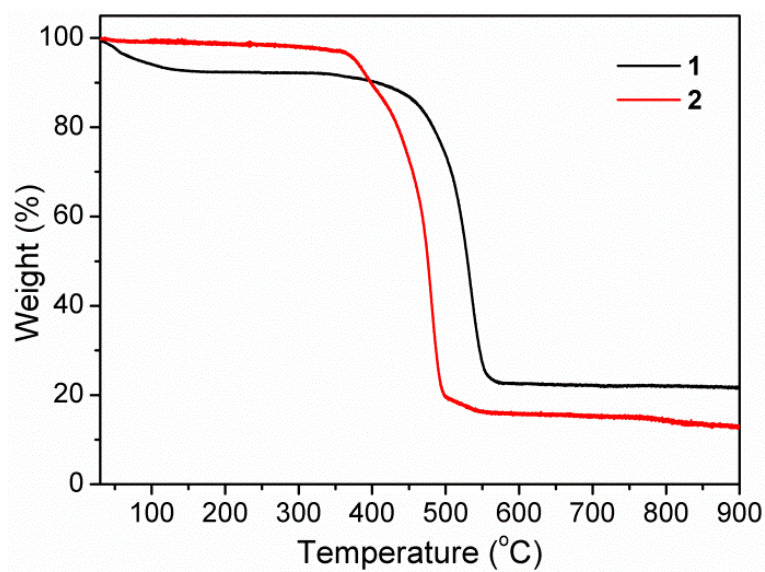


Figure S3. TG curves of **1** and **2**.

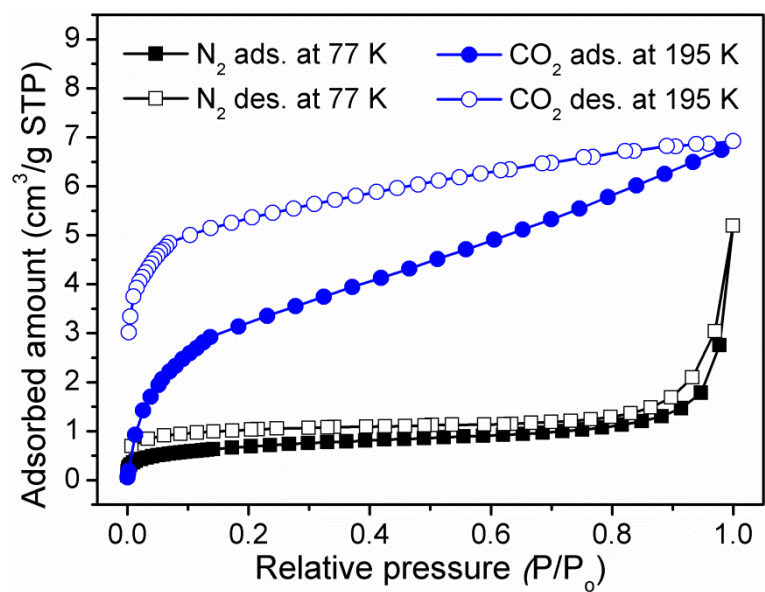


Figure S4. N_2 and CO_2 adsorption isotherms of thermally activated **1**.

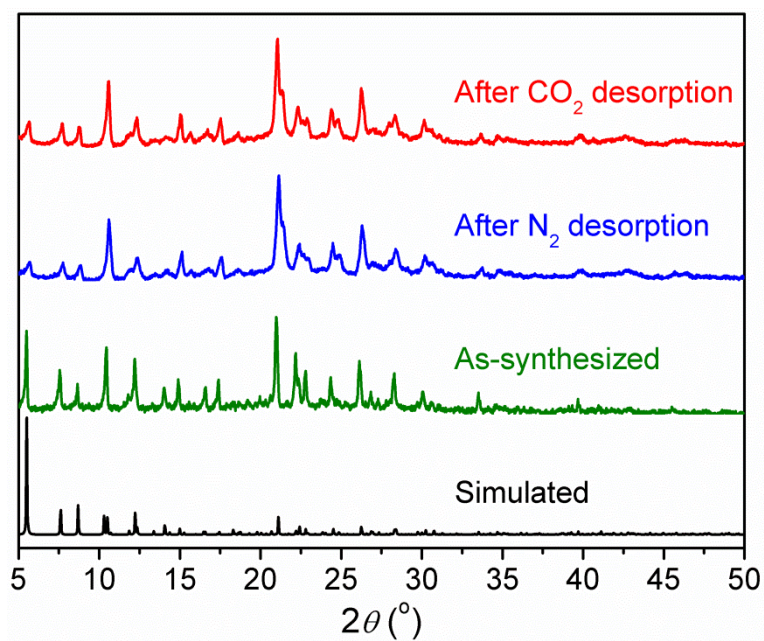


Figure S5. XRPD patterns of **1** before and after N₂ and CO₂ adsorption–desorption.

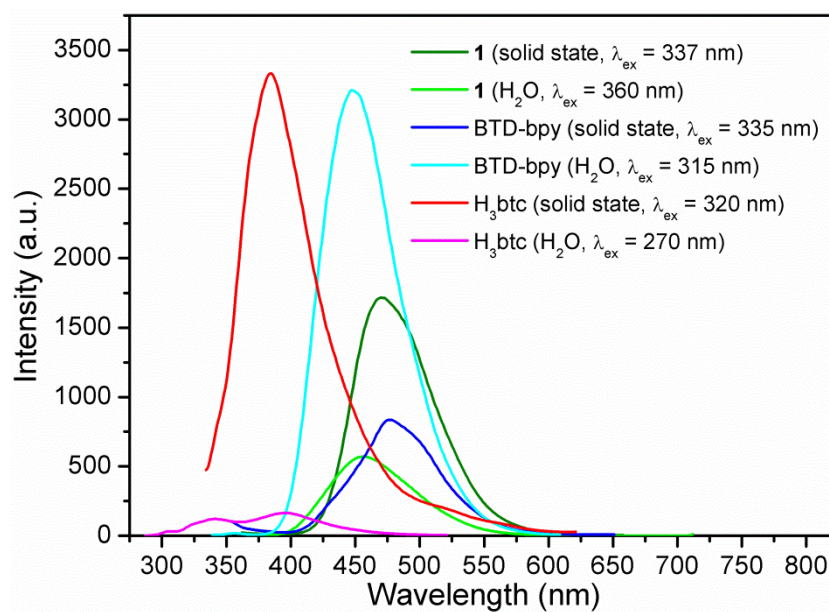


Figure S6. Emission spectra of **1**, BTDBpy and H₃btc in solid-state and in H₂O at room temperature.

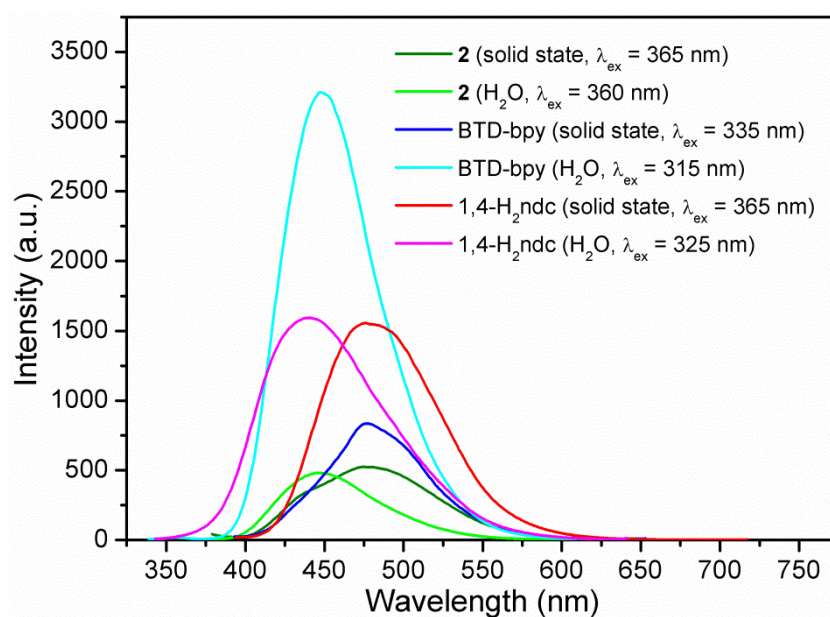
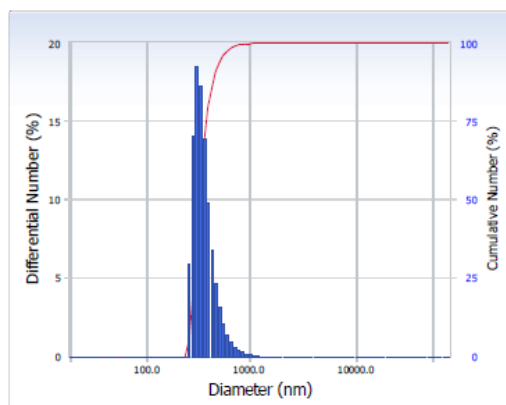


Figure S7. Emission spectra of **2**, BTD-bpy and 1,4-H₂ndc in solid-state and in H₂O at room temperature.

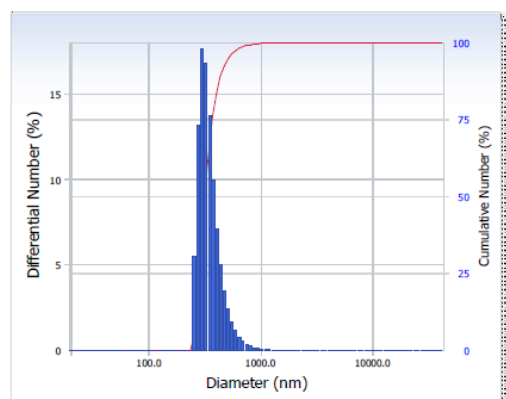
(a)



Distribution Results (Contin)

Peak	Diameter (nm)	Std. Dev.
1	372.3	102.9
2	0.0	0.0
3	0.0	0.0
4	0.0	0.0
5	0.0	0.0
Average	372.3	102.9

(b)



Distribution Results (Contin)

Peak	Diameter (nm)	Std. Dev.
1	362.2	100.2
2	0.0	0.0
3	0.0	0.0
4	0.0	0.0
5	0.0	0.0
Average	362.2	100.2

Figure S8. Particle size distributions of (a) 1 and (b) 2.

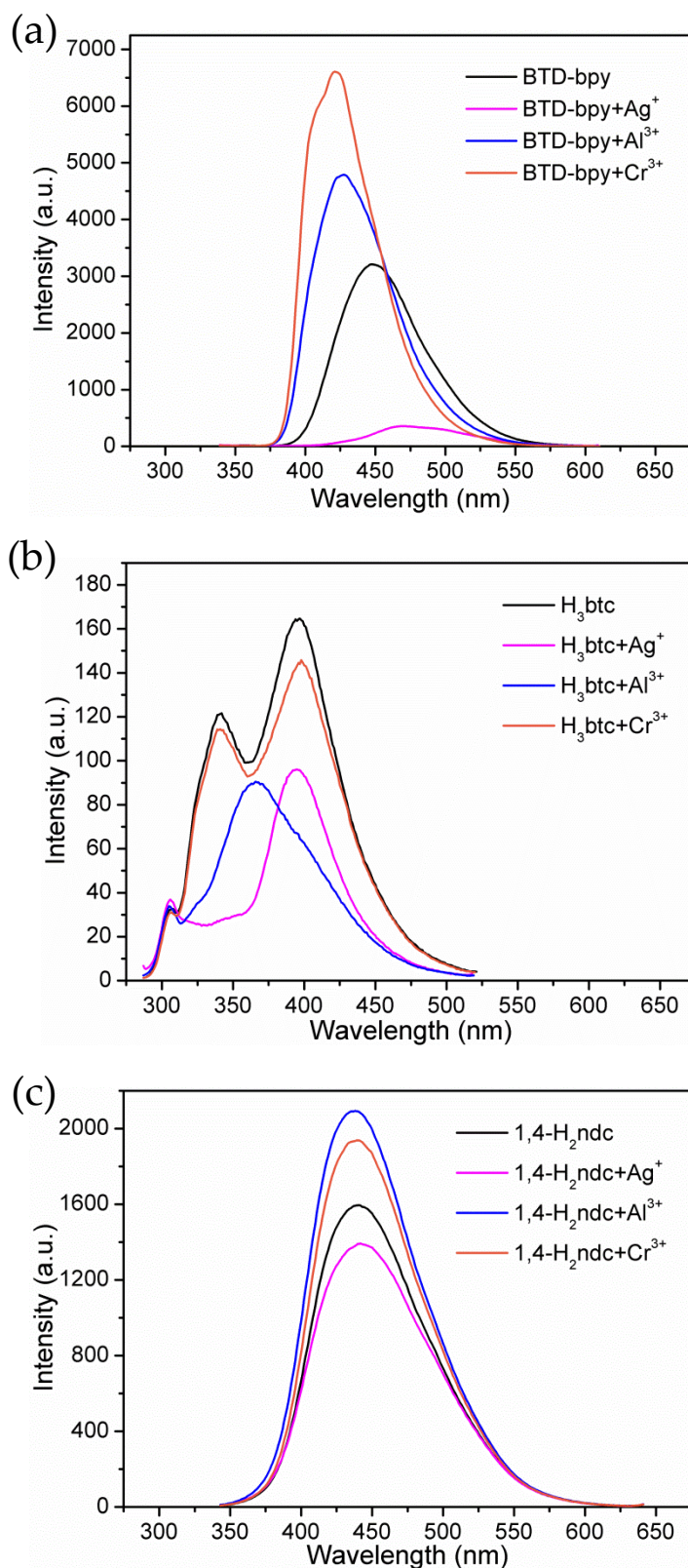


Figure S9. Emission spectra of (a) BTD-bpy, (b) H₃btc, and (c) 1,4-H₂ndc in H₂O (1 mg/3 mL) before and after addition of Ag⁺, Al³⁺, and Cr³⁺ ions (1.0 mM).

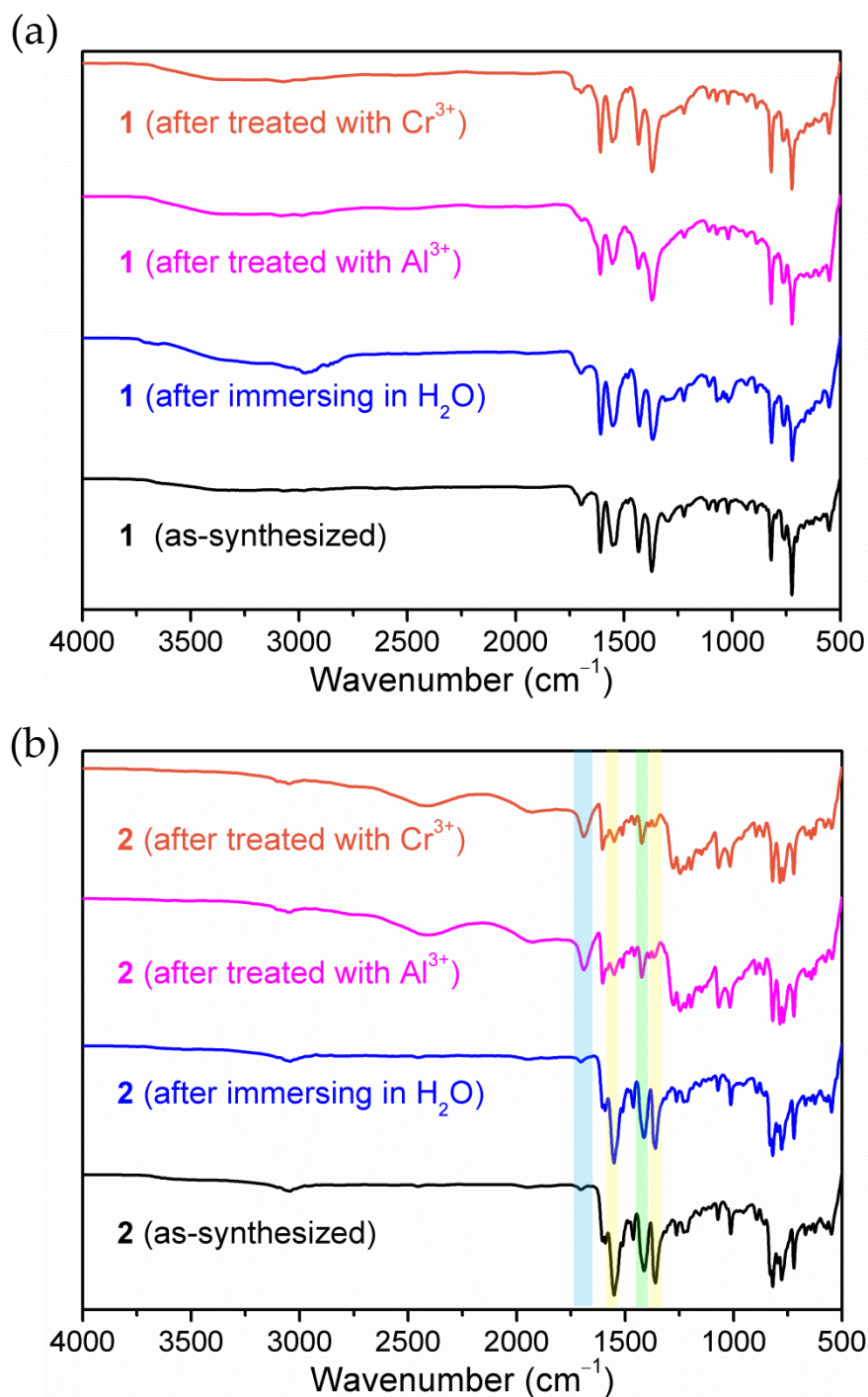


Figure S10. (a) IR spectra of **1**: as-synthesized, after immersion in H_2O for 1 day, after treated with Al^{3+} and Cr^{3+} in H_2O for 1 day. (b) IR spectra of **2**: as-synthesized, after immersion in H_2O for 1 day, after treated with Al^{3+} and Cr^{3+} in H_2O for 1 day.

Table S1. Comparison of literature reports for Ag⁺ detection using CP/MOF-based luminescence chemosensors.

Luminescence chemosensors	Analyte	Solvent	Mechanism	DL, μM	Ref.
Sm ₃ (HDBA) ₆ ·H ₂ O (Sm-MOF)	Ag ⁺	H ₂ O	Turn-on	3.95	S1
Eu ³⁺ @Ga(OH)(btec)·0.5H ₂ O (Eu-MIL-61)	Ag ⁺	H ₂ O	Turn-on	0.23	S2
Sm ³⁺ /(Ga(OH)(btec)·0.5H ₂ O (Sm-MIL-61)	Ag ⁺	H ₂ O	Turn-on	0.03	S3
Eu ³⁺ @Al(OH)(H ₂ btec)·H ₂ O (Eu ³⁺ @MIL-121)	Ag ⁺	H ₂ O	Turn-on	0.1	S4
Sm ³⁺ @Al(OH)(H ₂ btec)·H ₂ O (Sm ³⁺ @MIL-121)	Ag ⁺	H ₂ O	Turn-on	0.09	S5
Eu ³⁺ @C ₁₂ H ₆ N ₂ O _{5.33} Zr (Eu ³⁺ @UiO-67)	Ag ⁺	H ₂ O	Turn-off	0.049	S6
[Co(DCTP)(L ¹)(H ₂ O) ₂] _n (NCST-1)	Ag ⁺	H ₂ O	Turn-off	1.33	S7
{[Mn ₂ (Hbtc) ₂ (L ²) ₂ (H ₂ O) ₂]·2H ₂ O} _n (NCST-4)	Ag ⁺	EtOH	Turn-off	0.67	S8
{Cd ₃ (btc) ₂ (BTD-bpy) ₂]·1.5MeOH·4H ₂ O} _n (1)	Ag ⁺	H ₂ O	Turn-off	0.56	This work
[Cd ₂ (1,4-ndc) ₂ (BTD-bpy) ₂] _n (2)	Ag ⁺	H ₂ O	Turn-off	1.47	This work

Abbreviations: H₅DBA = 3,5-di(2',4'-dicarboxylphenyl)benzoic acid; H₄btec = pyromellitic acid; H₂DCTP = 2,5-dichloroterephthalic acid; L¹ = 1,4-bis(benzimidazol-1-ylmethyl)benzene; H₃btc = benzene-1,3,5-tricarboxylic acid; L² = 1,4-bis(5,6-dimethylbenzimidazole)butane; BTD-bpy = bis(pyridin-4-yl)benzothiadiazole; 1,4-H₂ndc = naphthalene-1,4-dicarboxylic acid.

Table S2. Comparison of literature reports for Al³⁺ detection using CP/MOF-based fluorescence chemosensors in water.

Fluorescence chemosensors	Analyte	Mechanism	DL, μM	Ref.
$\{[\text{Ba}_3\text{La}_{0.5}(\text{L}^3)_{2.5}(\text{H}_2\text{O})_3(\text{DMF})]\}_n$	Al ³⁺	Turn-off	1.11	S9
$[\text{Cd}(\text{PAM})(4\text{-bpdb})_{1.5}] \cdot \text{DMF}$	Al ³⁺	Turn-off	0.56	S10
$[\text{Zn}(5\text{-NH}_2\text{-1,3-bdc})(\text{H}_2\text{O})]$	Al ³⁺	Turn-off	2.44	S11
$[\text{Zn}_2(5\text{-NH}_2\text{-1,3-bdc})_2(\text{NI-bpy-44})] \cdot \text{DMF}$	Al ³⁺	Turn-off	5.59	S11
$[\text{Eu}_2(\text{ppda})_2(\text{npdc})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	Al ³⁺	Turn-off	109	S12
$[\text{Zn}_2(\text{OH})(1,4\text{-ndc})_{1.5}(\text{Cz-3,6-bpy})] \cdot 2\text{H}_2\text{O}$	Al ³⁺	Ratiometric	9.97	S13
$\{[\text{Zn}_2(\text{OH})(\text{Br-1,4-bdc})_{1.5}(\text{Cz-3,6-bpy})] \cdot \text{H}_2\text{O}\}_n$	Al ³⁺	Ratiometric turn-off	0.59	S14
$\{[\text{Zn}_2(\text{OH})(\text{Br-1,4-bdc})_{1.5}(\text{Cz-Pr-3,6-bpy})] \cdot 0.5\text{H}_2\text{O}\}_n$	Al ³⁺	Ratiometric turn-off	1.89	S14
$\{[\text{Zn}_2(\text{OH})(\text{NO}_2\text{-1,4-bdc})_{1.5}(\text{Cz-3,6-bpy})] \cdot 2\text{H}_2\text{O}\}_n$	Al ³⁺	Ratiometric turn-on	4.74	S14
$\{[\text{Zn}_2(\text{OH})(\text{NO}_2\text{-1,4-bdc})_{1.5}(\text{Cz-Pr-3,6-bpy})] \cdot 0.5\text{H}_2\text{O}\}_n$	Al ³⁺	Ratiometric turn-on	5.90	S14
$[\text{Co}(\text{OBA})(\text{DATZ})_{0.5}(\text{H}_2\text{O})]$	Al ³⁺	Turn-on	2.5	S15
$[\text{Co}(\text{H}_2\text{L})(\text{TPY})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	Al ³⁺	Turn-on	1.67	S16
$\text{Zn}(\text{DMA})(\text{TBA})$	Al ³⁺	Turn-on	1.97	S17
$[\text{Zn}(\text{H}_2\text{dhbdc})(\text{Cz-3,6-bpy})]_n$	Al ³⁺	Turn-on	0.62	S18
$[\text{Cd}(\text{H}_2\text{dhbdc})(\text{NI-mbpy-34})_2]_n$	Al ³⁺	Turn-on	0.34	S19
$\{[\text{Cd}(\text{Br-1,3-bdc})(\text{NI-mbpy-34})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$	Al ³⁺	Turn-on	3.37	S20
$\{\text{Cd}_3(\text{btc})_2(\text{BTD-bpy})_2\} \cdot 1.5\text{MeOH} \cdot 4\text{H}_2\text{O}\}_n$ (1)	Al ³⁺	Turn-on	4.97	This work
$[\text{Cd}_2(1,4\text{-ndc})_2(\text{BTD-bpy})_2]_n$ (2)	Al ³⁺	Turn-on	0.25	This work

Abbreviations: H₃L³ = p-terphenyl-3,4'',5-tricarboxylic acid; DMF = N,N'-dimethylformamide; PAM = 4,4'-methylenebis(3-hydroxy-2-naphthalene-carboxylic acid; 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene; 5-NH₂-1,3-H₂bdc = 5-amino-1,3-benzenedicarboxylic acid; NI-bpy-44 = N-(pyridin-4-yl)-4-(pyridin-4-yl)-1,8-naphthalimide; H₂ppda = 4-(pyridine-3-yloxy)phthalic acid; H₂npdc = naphthalene-1,4-dicarboxylic acid; 1,4-H₂ndc = naphthalene-1,4-dicarboxylic acid; Cz-3,6-bpy = 3,6-bis(pyridin-4-yl)-9H-carbazole; Br-1,4-H₂bdc = 2-bromobenzene-1,4-dicarboxylic acid; Cz-Pr-3,6-bpy = 3,6-bis(pyridin-4-yl)-9-n-propyl-9H-carbazole; NO₂-1,4-H₂bdc = 2-nitrobenzene-1,4-dicarboxylic acid; DMA = N,N'-dimethylacetamide; H₂TBA = 4-(1H-tetrazol-5-yl)-benzoic acid; H₂OBA = 4,4'-oxybis(benzoic acid); DATZ = 3,5-diamino-1,2,4-triazole; H₄L = [1,1':4',1''-terphenyl]-2',4,4'',5'-tetracarboxylic acid; TPY = 4,3':5',4''-terpyridine; H₄dhbdc = 2,5-dihydroxyterephthalic acid; NI-mbpy-34 = N-(pyridin-3-ylmethyl)-4-(pyridin-4-yl)-1,8-naphthalimide; Br-1,3-H₂bdc = 5-bromobenzene-1,3-dicarboxylic acid; H₃btc = benzene-1,3,5-tricarboxylic acid; BTD-bpy = bis(pyridin-4-yl)benzothiadiazole.

Table S3. Comparison of literature reports for Cr³⁺ detection using CP/MOF-based fluorescence chemosensors in water.

Fluorescence Chemosensors	Analyte	Mechanism	DL, μM	Ref.
[Zn(5-NH ₂ -1,3-bdc)(H ₂ O)]	Cr ³⁺	Turn-off	13.9	S11
[Zn ₂ (5-NH ₂ -1,3-bdc) ₂ (NI-bpy-44)]·DMF	Cr ³⁺	Turn-off	7.87	S11
[Zn(L ⁴)(H ₂ O)]·H ₂ O	Cr ³⁺	Turn-off	2.44	S21
[Eu ₂ (ppda) ₂ (npdc)(H ₂ O)]·H ₂ O	Cr ³⁺	Turn-off	61.7	S12
{[Eu ₃ (bpydb) ₃ (HCOO)(OH) ₂ (DMF)]·3DMF·2H ₂ O} _n	Cr ³⁺	Turn-off	1.0	S22
[Zn ₂ (OH)(1,4-ndc) _{1.5} (Cz-3,6-bpy)]·2H ₂ O	Cr ³⁺	Ratiometric	8.61	S13
{[Zn ₂ (OH)(Br-1,4-bdc) _{1.5} (Cz-3,6-bpy)]·H ₂ O} _n	Cr ³⁺	Ratiometric turn-off	0.49	S14
{[Zn ₂ (OH)(Br-1,4-bdc) _{1.5} (Cz-Pr-3,6-bpy)]·0.5H ₂ O} _n	Cr ³⁺	Ratiometric turn-off	2.18	S14
{[Zn ₂ (OH)(NO ₂ -1,4-bdc) _{1.5} (Cz-3,6-bpy)]·2H ₂ O} _n	Cr ³⁺	Ratiometric turn-on	3.03	S14
{[Zn ₂ (OH)(NO ₂ -1,4-bdc) _{1.5} (Cz-Pr-3,6-bpy)]·0.5H ₂ O} _n	Cr ³⁺	Ratiometric turn-on	3.22	S14
[Cd(H ₂ dhbdc)(NI-mbpy-34) ₂] _n	Cr ³⁺	Turn-on	1.47	S19
{[Cd(Br-1,3-bdc)(NI-mbpy-34)(H ₂ O)]·2H ₂ O} _n	Cr ³⁺	Turn-on	2.81	S20
[Zn(Br-1,3-bdc)(NI-mbpy-34)] _n	Cr ³⁺	Turn-on	3.13	S23
{[Cd ₂ (adc) ₂ (4-nvp) ₆](MeOH)·(H ₂ O)] _n	Cr ³⁺	Turn-on	0.31	S24
{Cd ₃ (btc) ₂ (BTD-bpy) ₂]·1.5MeOH·4H ₂ O} _n (1)	Cr ³⁺	Turn-on	3.03	This work
[Cd ₂ (1,4-ndc) ₂ (BTD-bpy) ₂] _n (2)	Cr ³⁺	Turn-on	0.79	This work

Abbreviations: 5-NH₂-1,3-H₂bdc = 5-amino-1,3-benzenedicarboxylic acid; NI-bpy-44 = N-(pyridin-4-yl)-4-(pyridin-4-yl)-1,8-naphthalimide; DMF = N,N'-dimethylformamide; H₂L⁴ = 5-(2-methylpyridin-4-yl)isophthalic acid; H₂ppda = 4-(pyridine-3-yloxy)phthalic acid; H₂npdc = naphthalene-1,4-dicarboxylic acid; bpydbH₂ = 4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoic acid; 1,4-H₂ndc = naphthalene-1,4-dicarboxylic acid; Cz-3,6-bpy = 3,6-bis(pyridin-4-yl)-9H-carbazole; Br-1,4-H₂bdc = 2-bromobenzene-1,4-dicarboxylic acid; Cz-Pr-3,6-bpy = 3,6-bis(pyridin-4-yl)-9-n-propyl-9H-carbazole; NO₂-1,4-H₂bdc = 2-nitrobenzene-1,4-dicarboxylic acid; H₄dhbdc = 2,5-dihydroxyterephthalic acid; NI-mbpy-34 = N-(pyridin-3-ylmethyl)-4-(pyridin-4-yl)-1,8-naphthalimide; Br-1,3-H₂bdc = 5-bromobenzene-1,3-dicarboxylic acid; H₂adc = 9,10-anthracenedicarboxylic acid; 4-nvp = 4-(1-naphthylvinyl)pyridine; H₃btc = benzene-1,3,5-tricarboxylic acid; BTD-bpy = bis(pyridin-4-yl)benzothiadiazole.

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