Supplementary Information

Mixed matrix membranes based on fluorescent coordination polymers for detecting Cr2O72- in water

Yu-Kang Teng,[a] Qian Wu,[a] Yao Sun,[a] Chen Wang,[a] Rui Zhang,[b*] Zhen-Zhong Lu[a*]

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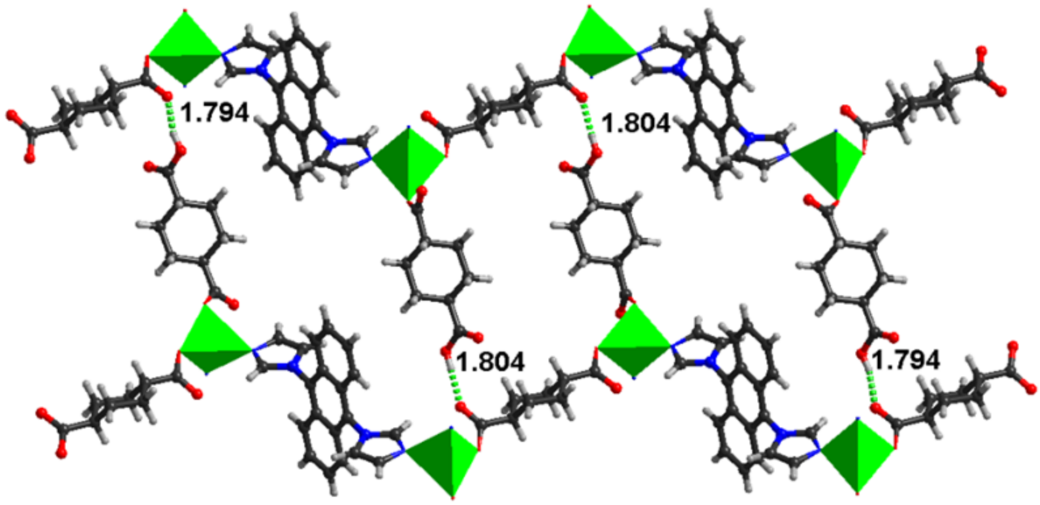

Figure S1. The O-H···O hydrogen bonds formed between adjacent layers in **1**.

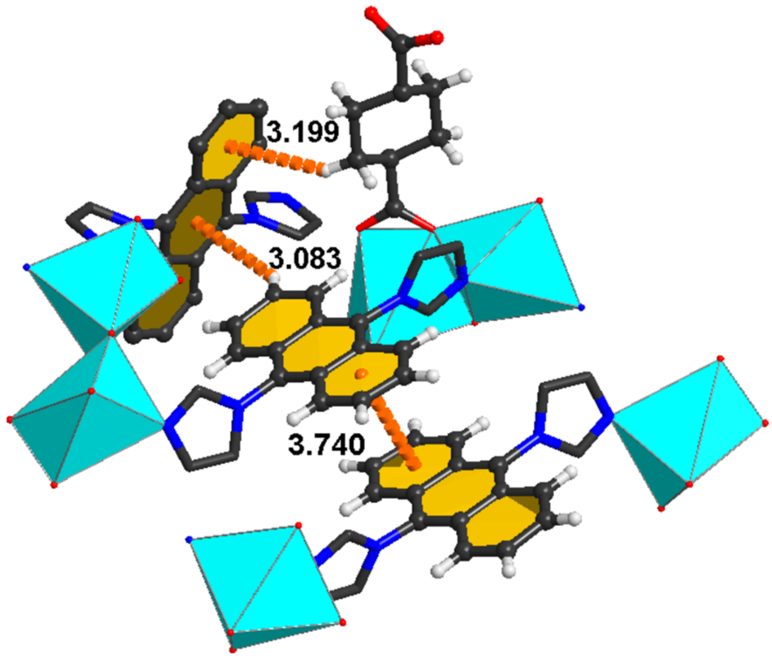

Figure S2. The π-π interactions between the anthranene groups and C-H···π interactions between *dia* and *cda* ligands in **3**.

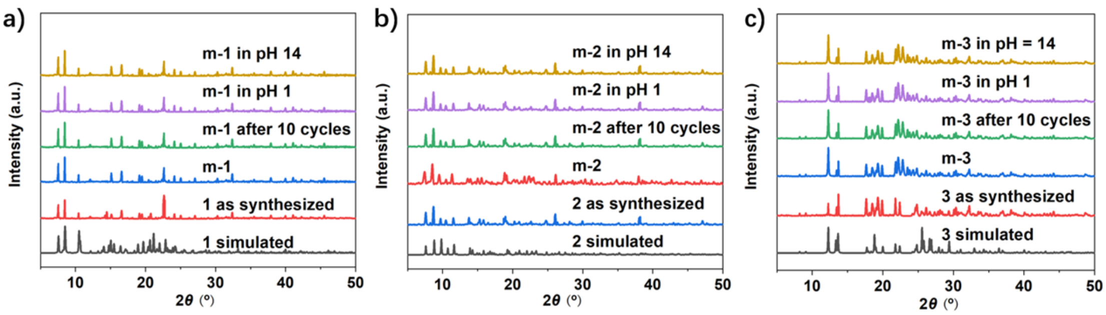

Figure S3. a) Powder XRD of **1**, **m-1** and **m-1** in aqueous solutions at pH 1, 14 for 24 hours and after 10 cycles detecting tests. b) Powder XRD of **2**, **m-2** and **m-2** in aqueous solutions at pH 1 or 14 for 24 hours and after 10 cycles detecting tests. c) Powder XRD of **3**, **m-3** and **m-3** in aqueous solutions at pH 1 or 14 for 24 hours and after 10 cycles detecting tests.

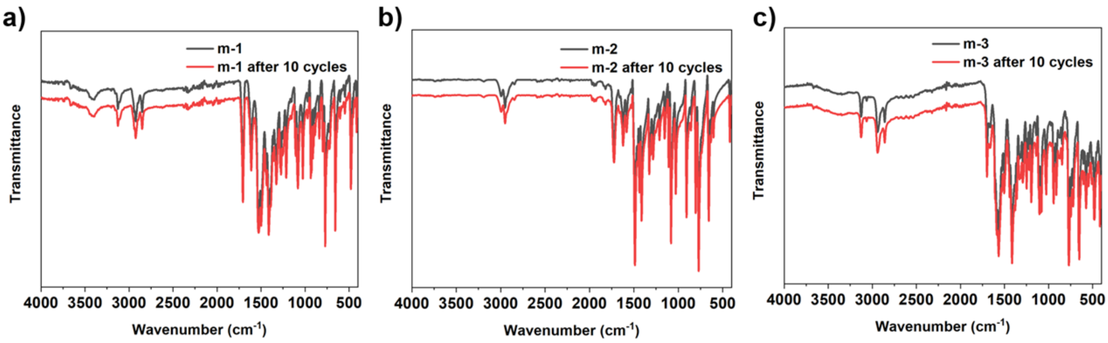

Figure S4. The FT-IR spectra for **m-1**, **m-2** and **m-3**.

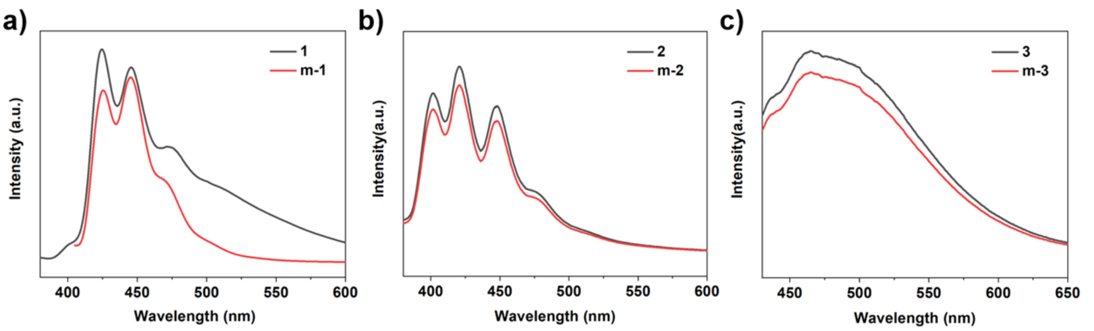

Figure S5. The emission spectra of **1-3** and **m-1, m-2** and **m-3** (excited at 365 nm).

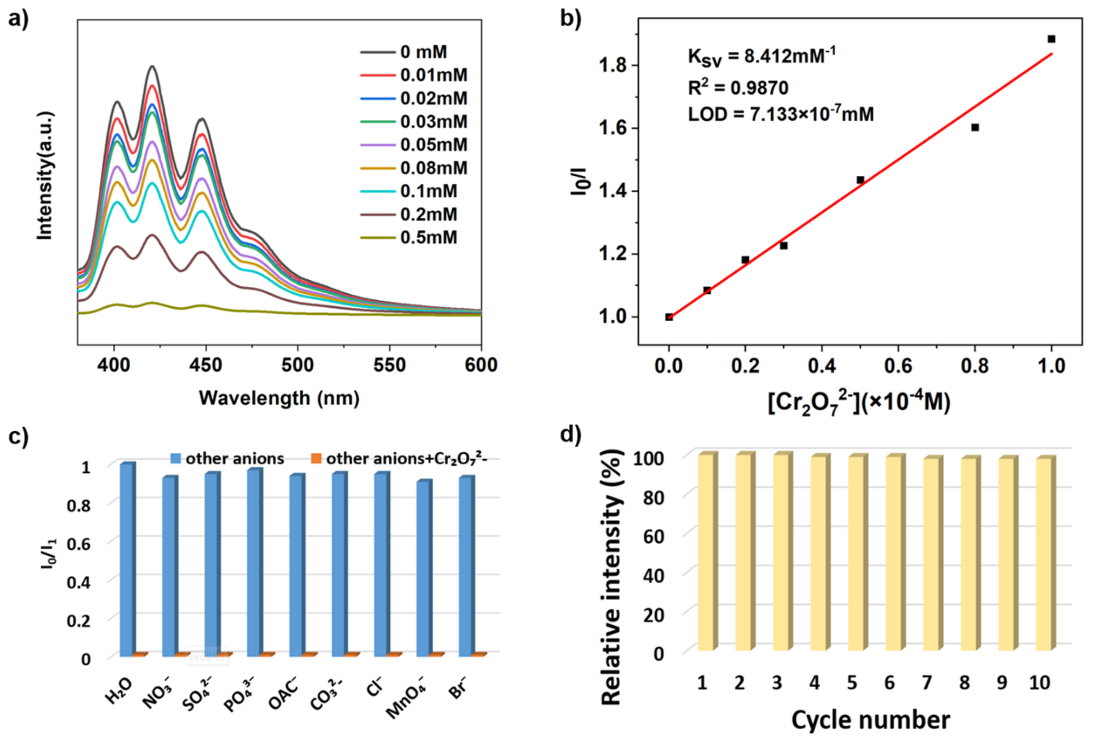

Figure S6. a) Fluorescence quenching of **m-2** towards different concentrations of $Cr_2O_7^{2-}$ solution (0 - 1.0 × 10^{-4} mol·L^{-1}, λ_{ex} = 350 nm). **b)** Stern-Volmer plot of I_0/I_1 *vs*. concentration of $Cr_2O_7^{2-}$ solution for **m-2**. c) Relative fluorescence intensity of **m-2** dispersed in aqueous solutions of interfering anions (blue) and subsequent addition of $Cr_2O_7^{2-}$ (orange). d) The variations of relative fluorescence intensity of **m-2** for detecting $Cr_2O_7^{2-}$ under 10 cycles.

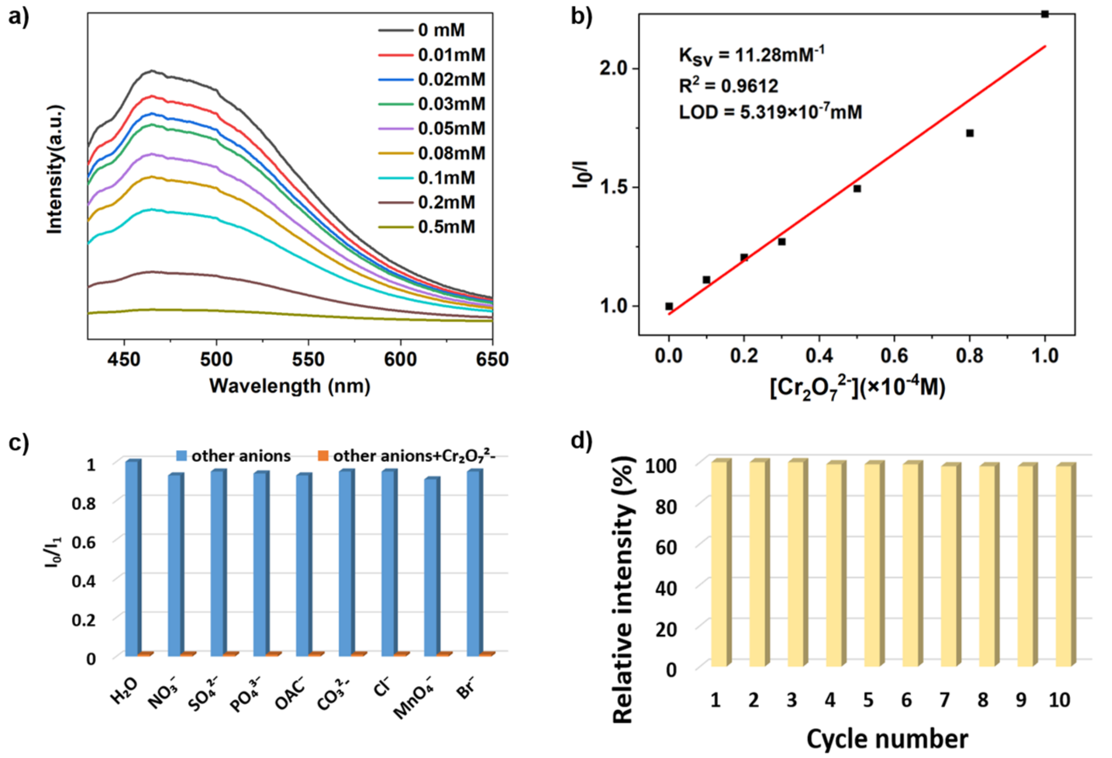

Figure S7. a) Fluorescence quenching of **m-3** towards different concentrations of $Cr_2O_7^{2-}$ solution (0 - 1.0 × 10^{-4} mol·L^{-1}, λ_{ex} = 350 nm). **b)** Stern-Volmer plot of I_0/I_1 *vs*. concentration of $Cr_2O_7^{2-}$ solution for **m-3**. c) Relative fluorescence intensity of **m-3** dispersed in aqueous solutions of interfering anions (blue) and subsequent addition of $Cr_2O_7{}^{2-}$ (orange). d) The variations of relative fluorescence intensity of **m-3** for detecting $Cr_2O_7^{2-}$ under 10 cycles.

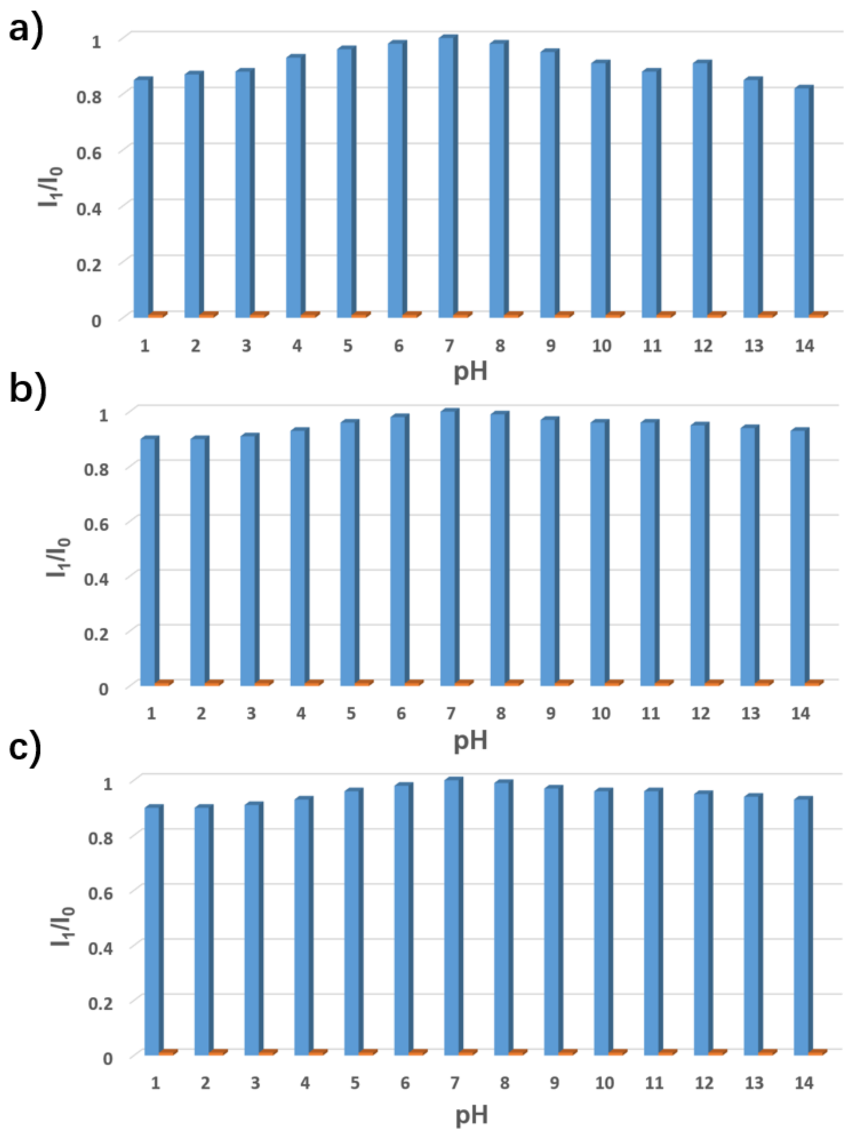

Figure S8. Relative fluorescence intensity of **m-1** (a), **m-2** (b) and **m-3** (c) in different pH aqueous solutions (blue) and subsequent addition of $Cr_2O_7^{2-}$ (1 × 10^{-3} mol·L^{-1}, red).

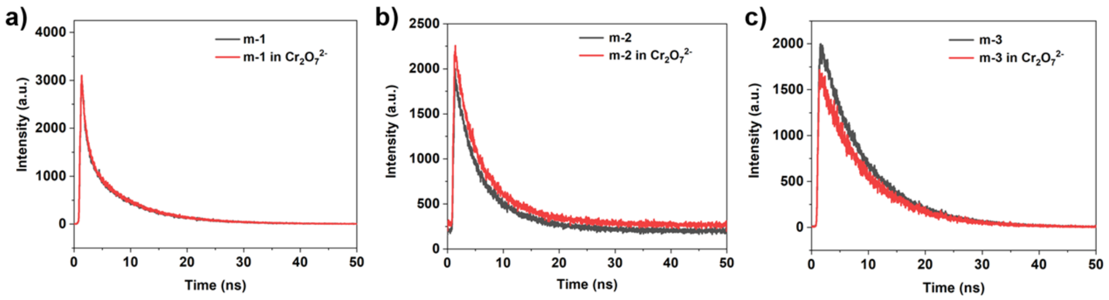

Figure S9. Time-resolved fluorescence decay curves of **m-1**, (a) and **m-2**, (b) and **m-3**,(c) before and after the addition of $Cr_2O_7^{2-}$.

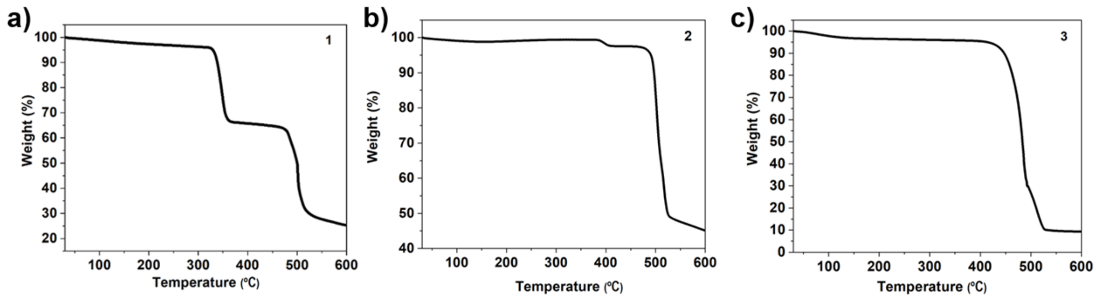

Figure S10. TG profile of **1, 2** and **3**.

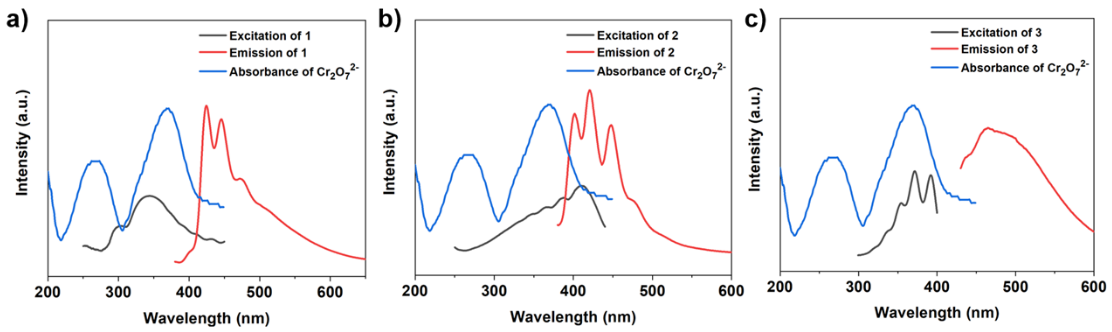

Figure S11. The excitation and emission spectra of **1**, **2** and **3**, and UV–Vis absorption spectra of $Cr_2O_7^{2-}$solution.

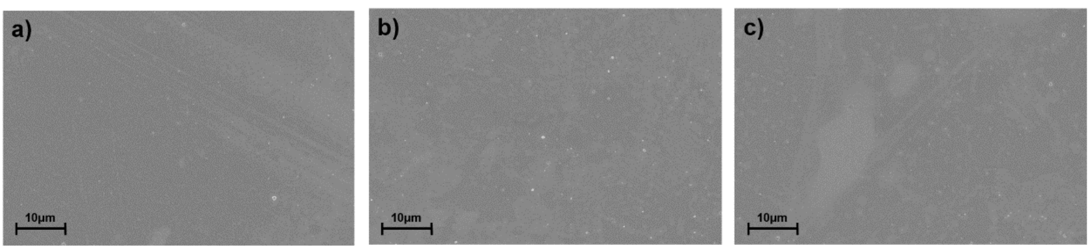

Figure S12. The SEM images for **m-1, m-2** and **m-3**.

Table S1. Crystal data and structure refinement details for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{56}H_{49}ZnN_8O_8$	$C_{56}H_{48}Zn_2N_8O_8$	$C_{46}H_{45}Cd_2N_6O_8$
Molecular weight	1027.43	1091.81	1034.71
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$
a (Å)	12.3978(6)	11.9919(7)	13.1661(2)
b(Å)	13.1970(7)	16.8356(10)	20.0691(4)
c(Å)	21.5304(11)	17.1730(9)	17.0366(3)
α (°)	76.780(2)	64.117(3)	90
β (°)	75.297(2)	79.161(3)	104.9600(10)
γ (°)	62.998(2)	77.410(4)	90
V (Å^3)	3009.5(3)	3027.2(3)	4349.03(13)
Z	2	2	4
F(000)	1332	1128	2156
μ (mm^{-1})	0.710	0.710	1.541
D_c (g/cm^3)	1.415	1.198	1.629
R(int)	0.0867	0.1667	0.0346
GOF on F^2	1.049	0.990	1.044
R_1^a [I>2σ(I)]	0.0688	0.0904	0.0312
wR_2^b [I>2σ(I)]	0.1784	0.1967	0.1025

Table S2. Performance of fluorescent CPs for $Cr_2O_7^{2-}$ detection.

CPs	LOD(μM)	Linear range (mM)	$K_{SV}(M^{-1})$	Response time	ref
$[\{Zn_2(5N_3\text{-}IPA)_2(4,4'\text{-}azp)_2\}(H_2O)_8]_n$	0.004	-	5.87×10^4	-	1
Eu-mtb MMM (70 wt%)	0.005			seconds	2
$Zn(NIPH)_2(HPF)_2]$	0.02	-	1.3×10^4	-	3
RhB-Zn-MOF	0.02		1.57×10^4		4
$Zn(tpbpc)_2]$	0.047	0-250	1.65×10^5	10 min	5
SQDs@UiO-66-NH_2	0.16	0-200	2.9×10^4	10 s	6
$[Cd_{1.5}(L)_2(\mathit{bpy})(NO_3)]\cdot 2DMF\cdot 2H_2O$	0.422	-	5.42×10^4	-	7
3	**0.5**	**0-100**	$\mathbf{1.28\times 10^4}$	**Seconds**	**This work**
$[Al(OH)(IPA\text{-}CHO)]\cdot 0.5H_2O\cdot 0.4DMF$	0.69	-	1.43×10^4	seconds	8
2	**0.7**	**0-100**	$\mathbf{8.41\times 10^3}$	**Seconds**	**This work**
1	**0.8**	**0-100**	$\mathbf{6.79\times 10^3}$	**Seconds**	**This work**
MOF-Cel-Nap	1.07			seconds	9
[Zn(LBIX)(HEA)]n	1.53	10–60	1.15×10^4		10
NU-100	1.8	-	1.34×10^4	-	11
$[Ag(btx)_{0.5}(DCTP)_{0.5}]_n$	2.04	5-50	1.92×10^4	-	12
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	2.35	0-120	9.31×10^3	seconds	13
$[Cd(IPA)(3\text{-}PN)]_n$	2.52	0-400	2.91×10^3	-	14
$\{[Zn_2(TPOM)(NH_2\text{-}BDC)2]\cdot 4H_2O\}_n$	3.9	-	$7{,}59 \times 10^3$	-	15
[Zn3(OH)2(btca)2·2DMF]·H2O	9.31	5-30	2.0×10^4		16
$[Zn(IPA)(3\text{-}PN)]_n$	12.02	-	1.37×10^3	-	13

Table S3 Selected bond lengths (Å) and angles (º) for **1**, **2** and **3**.

1						
	Zn1-O1	1.946(3)	O1-Zn1-O2	105.92(1)		
	Zn1-O2	1.944(4)	O1-Zn1-N1	105.52(1)		
	Zn1-N1	2.036(4)	O2-Zn1-N2	100.00(1)		
	Zn1-N2	1.998(3)	N1-Zn1-N2	104.26(1)		
2						
	Zn1-O1	1.917(6)	O1-Zn1-O2	100.5(2)		
	Zn1-O2	1.9413(5)	O1-Zn1-N1	113.6(3)		
	Zn1-N1	2.0218(6)	O2-Zn1-N2	114.6(3)		
	Zn1-N2	1.9963(6)	N1-Zn1-N2	99.5(3)		
3						
	Cd1-O1	2.3440(2)	O1-Cd1-O2	56.57(8)	O3-Cd1-O4	54.55(9)
	Cd1-O2	2.2912(2)	O2-Cd1-O4	116.29(1)	O3-Cd1-N1	103.83(1)
	Cd1-O3	2.3085(3)	O4-Cd1-N1	92.78(1)	O6-Cd1-O1	118.38(8)
	Cd1-O4	2.3388(2)	O1-Cd1-N1	100.89(8)	O6-Cd1-O2	84.80(8)
	Cd1-O6	2.3190(2)	O3-Cd1-O1	104.67(9)	O6-Cd1-O4	79.15(8)
	Cd1-N1	2.2383(2)	O3-Cd1-O2	103.87(1)	O6-Cd1-N1	88.30(9)
	Cd2-O4	2.6008(3)	O4-Cd2-O6	75.58(8)	N3-Cd2-N2	114.91(1)
	Cd2-O6	2.2170(9)	O4-Cd2-O7	87.97(8)	N3-Cd2-O6	99.78(9)
	Cd2-O7	2.3310(1)	O4-Cd2-O8	77.94(1)	O7-Cd2-O8	56.42(7)
	Cd2-O8	2.3503(2)	O4-Cd2-N2	81.10(1)	O6-Cd2-O8	97.22(8)
	Cd2-N2	2.2277(2)	N3-Cd2-O7	89.73(1)	N2-Cd2-O6	105.48(9)
	Cd2-N3	2.2893(3)	N3-Cd2-O8	87.57(9)	O7-Cd2-N2	94.14(8)

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