Supporting Informatin

An ultrastable zinc(II)-organic framework as a recyclable multi-responsive luminescent sensor for Cr(III), Cr(VI), and 4-NP in the aqueous phase with high selectivity and sensitivity

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Table S1. Crystallographic data and structure refinements for Zn-MOF-**1**

Zn-MOF -1	
Formula	$C_{14}H_{13}ZnNO_6$
Mr	356.62
Crystal system	Triclinic
space group	$P\bar{1}$
a, Å	8.2143(5)
b, Å	9.7414(6)
c, Å	10.4899(6)
α, deg	107.352(2)
β, deg	101.099(2)
γ , deg	111.798(2)
V, Å^3	699.00(7)
Z	2
D_c, g cm^{-3}	1.694
μ, mm^{-1}	1.786
Unique.reflns/R_{int}	2499 / 0.0168
R_1 [I>2σ(I)]	0.0253
wR_2(All data)	0.0698
GOF	0.971

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

Zn1-O2C	**1.9608(15)**	**Zn-O5**	**1.9803(15)**
Zn1-N1A	**2.0447(18)**	**Zn1-O6**	**2.0866(18)**
Zn1-O5B	**2.4510(16)**	**O2C-Zn1-O5**	**123.16(7)**
O5-Zn1-N1A	**118.83(7)**	**O2C-Zn1-N1A**	**113.99(7)**
O5-Zn1-O6	**97.38(7)**	**O2C-Zn1-O6**	**95.98(7)**
O2C-Zn1-O5B	**86.31(6)**	**N1A-Zn1-O6**	**96.65(7)**
N1A-Zn1-O5B	**89.20(6)**	**O5-Zn1-O5B**	**75.19(6)**
Zn1-O5-Zn1B	**104.81(6)**	**O6-Zn1-O5B**	**172.18(6)**

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

Table S3. Hydrogen bond lengths (Å) and angles (◦) for Zn-MOF-**1**

D-H	A	d(D-H)	d(H..A)	<DHA	d(D..A)
O1	O3 [x, y+1, z]	0.850	1.913	157.23	2.717
O6	O1	0.960	1.822	173.01	2.778
O6	O4 [-x+2, -y+1, -z+1]	0.960	1.834	146.21	2.686

D : Donor; A: Acceptor

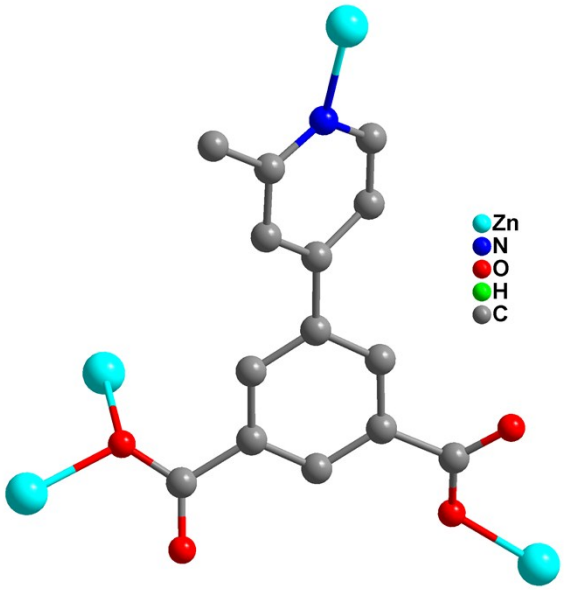

Fig. S1 The coordination environment of the uique L^{2-} in the asymmetric unit.

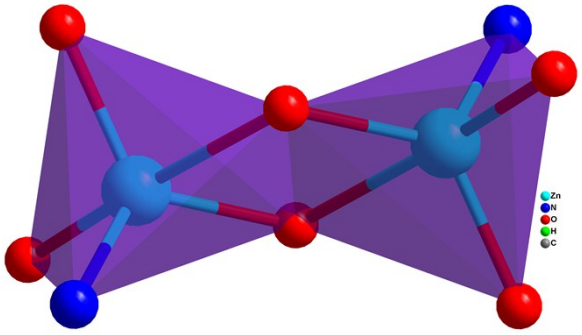

Fig. S2 The dinuclear Zn_2 unit in the structure of Zn-MOF-**1**

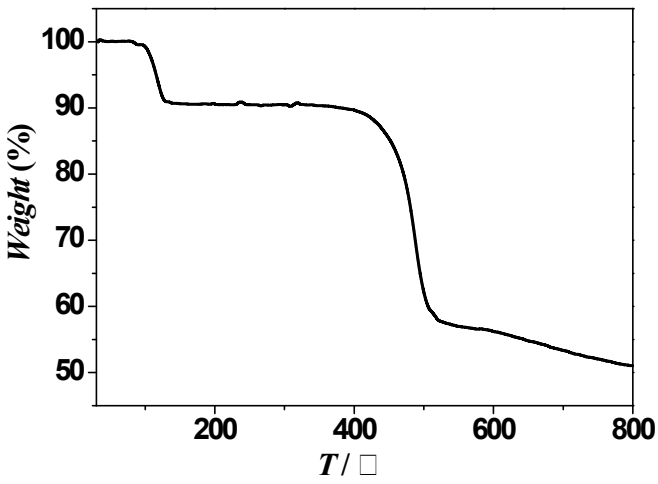

Fig. S3 The TGA curve for Zn-MOF-**1**

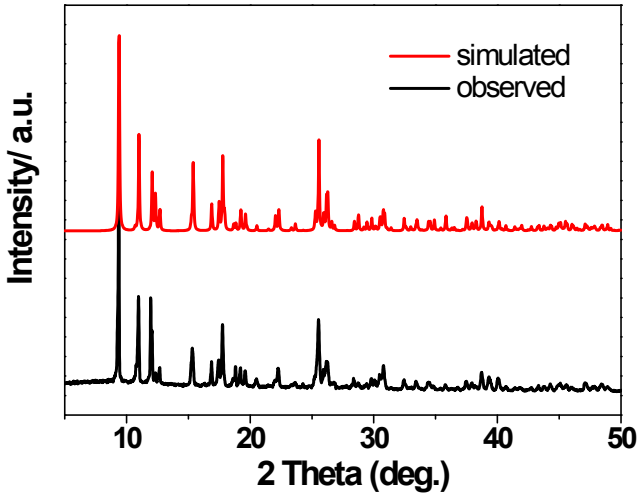

Fig. S4. PXRD patterns for Zn-MOF-**1**.

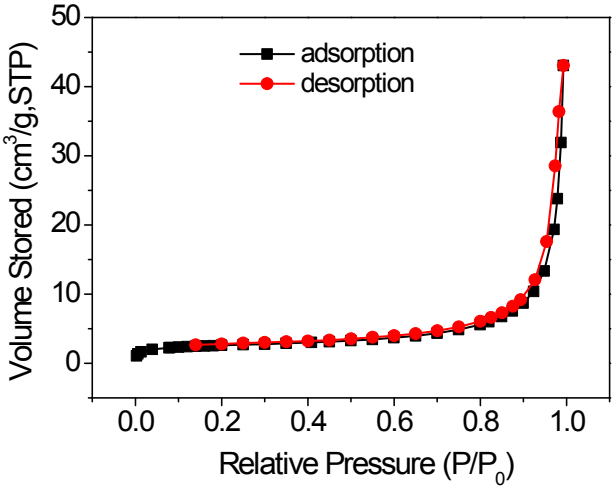

Fig. S5. N_2 sorption isotherm measured at 77 K of Zn-MOF-**1**.

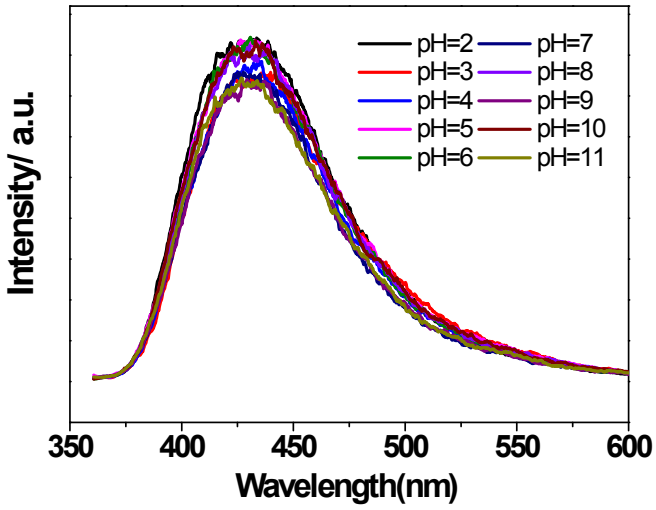

Fig. S6. The emission spectra of Zn-MOF-**1** in different pH values in the range of 2-11.

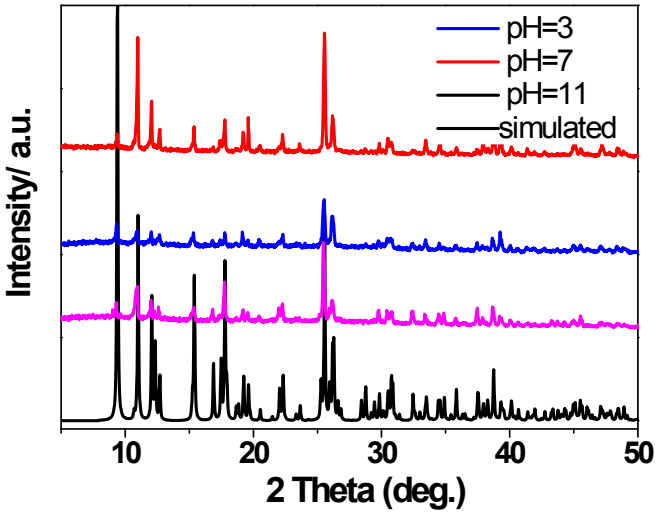

Fig. S7. PXRD patterns of Zn-MOF-**1** in different pH values in the range of 2-11.

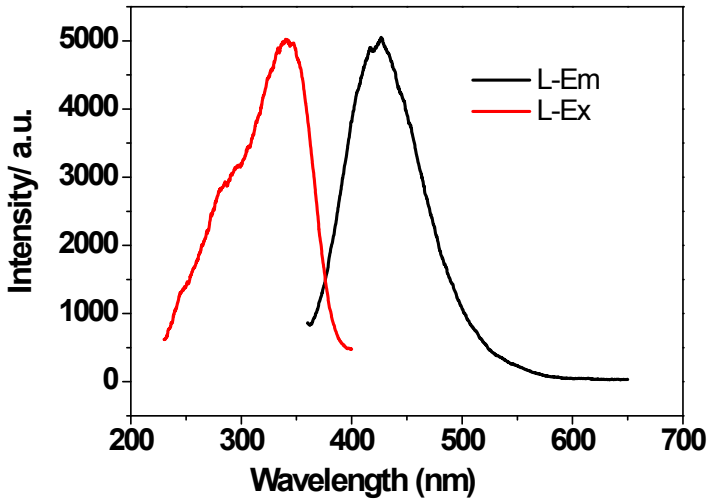

Fig. S8 The solid-state excitation (λ_{em} = 346 nm) and emission spectra (λ_{ex} = 426 nm) of free H_2L ligands at room temperature.

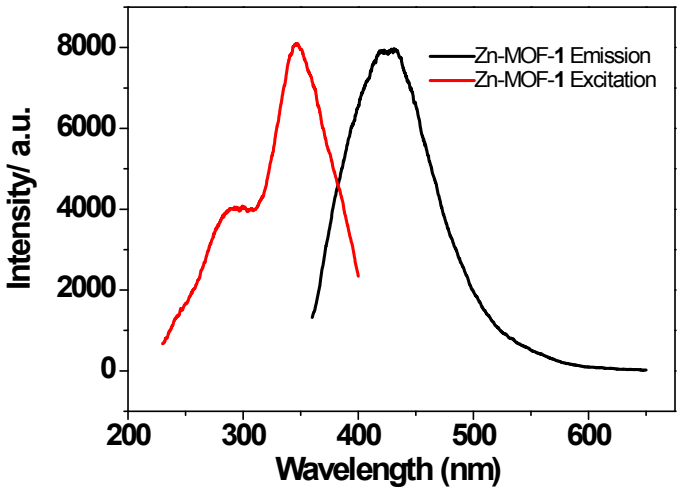

Fig. S9 The solid-state excitation spectra (λ_{em} = 346 nm) and emission spectra (λ_{ex} = 426 nm) of Zn-MOF-**1** at room temperature.

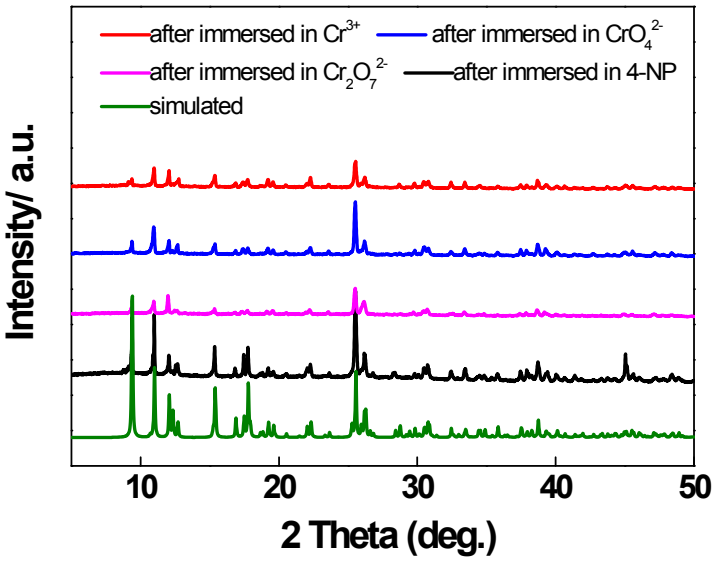

Fig. S10 The powder X-ray diffraction (PXRD) patterns for Zn-MOF-**1** and Zn-MOF-**1** immersed in 0.01 M aqueous solutions of Cr^{3+}, CrO_4^{2-}, $Cr_2O_7^{2-}$ ions and 4-NP.

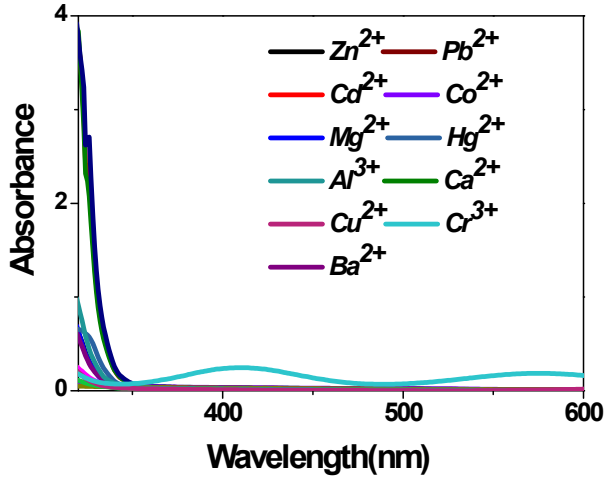

Fig. S11 UV-Vis spectra of different metal ions in aqueous solutions.

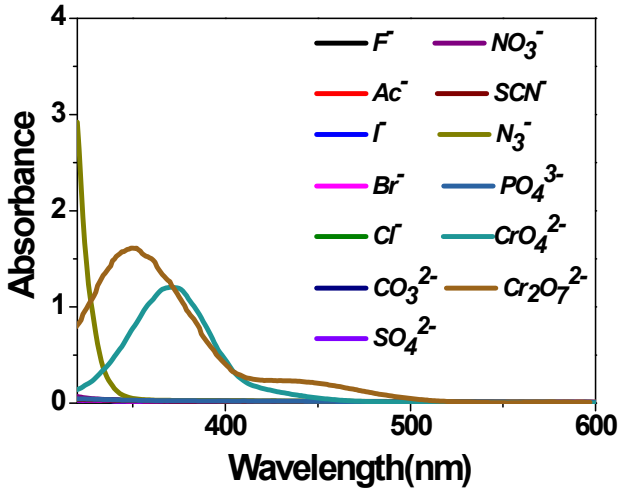

Fig. S12 UV-Vis spectra of different anions in aqueous solutions.

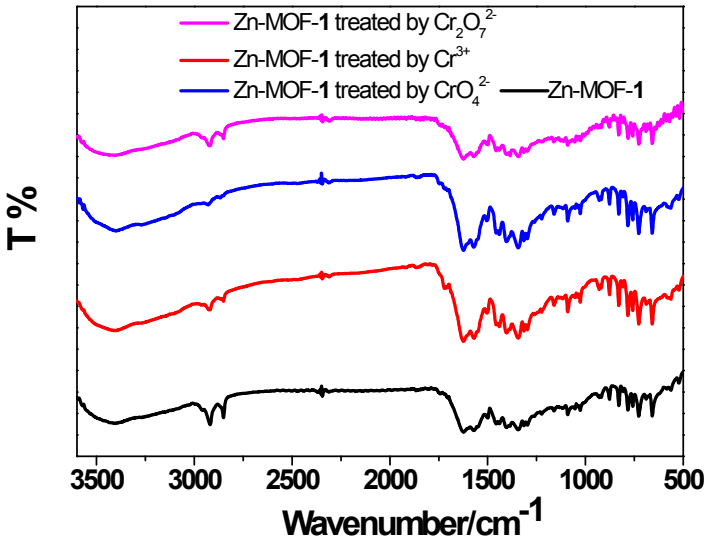

Fig. S13. IR characterization of as-synthesized Zn-MOF-**1,** Zn-MOF-**1** treated by Cr^{3+}, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions.

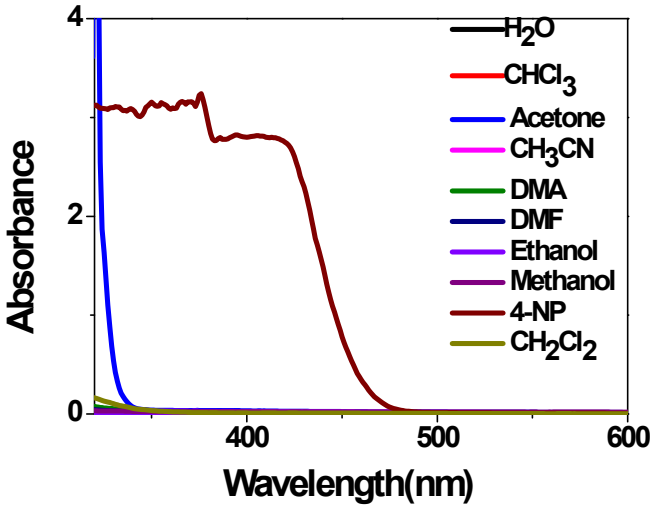

Fig. S14 UV-Vis spectra of different small organic molecules in aqueous solutions.

Table S4. Sensing performance comparision between other MOF-based fluorescent sensors with Zn-MOF-**1** for Cr(III) and Cr(VI) ions

MOF-based fluorescent materials	**analyte**	**detection limits**	**responsive time**	**quenching constant**	**recyclability**	**solvent**	**Ref**
Zn-MOF-**1**	Cr^{3+}	2.44 μM	Seconds	$2.03X10^4$	YES	Water	This
	CrO_4^{2-}	4.8 μM		$1.02X10^4$			work
	$Cr_2O_7^{2-}$	3.53 μM		$2.07X10^4$			
$[Zn_2(TPOM)(BDC)_2] \cdot 4H_2O$	Cr^{3+}	4.9 μM	Seconds		YES	DMF	[1]
	CrO_4^{2-}	4.8 μM		$4.45X10^3$			
	$Cr_2O_7^{2-}$	3.9 μM		$7.59X10^3$			
$[Zn(L)(BBI)\cdot(H_2O)_2]$	$Cr_2O_7^{2-}$	–	–		YES	Water	[2]
Eu_4L_3	$Cr_2O_7^{2-}$	10 μM	24 h	$1.526X10^3$	YES	DMF	[3]
$[Cd(TPTZ)(H_2O)_2(HCOOH)(IPA)_2]_n$	$Cr_2O_7^{2-}$	–	12 h		NO	Water	[4]
$[Cd_6(L)_2(bib)_2(DMA)_4]$	CrO_4^{2-}	–	5 min		NO	Water	[5]
$[Cd_3(L)(tib)(DMF)_2]$	$Cr_2O_7^{2-}$						
$[Zn_5(Htrb)_2(H_2O)_2(V_5O_{15})_2]\cdot 11H_2O$	Cr^{3+}	–	–		NO	Water	[6]
$[Ag_3(Htrb)(H_4V_5O_{16})]\cdot H_2O$							
$[Zn(2\text{-}NH_2bdc)(bibp)]_n$	$Cr_2O_7^{2-}$	–	–		NO	Water	[7]
1-Eu	$Cr_2O_7^{2-}$	22 μM	–		NO	Ethanol	[8]
$[Zn_2(tpeb)_2(2,3\text{-}ndc)_2]\cdot H_2O\}_n$	Cr^{3+}	0.88 ppb	–		YES	Water	[9]
	CrO_4^{2-}	1.734 ppb					
	$Cr_2O_7^{2-}$	2.623 ppb					
$[EuL(H_2O)_3]\cdot 3H_2O\cdot 0.75DMF$	$Cr_2O_7^{2-}$	–	–		YES	DMF	[10]
$[Eu_2(tpbpc)_4\cdot CO_3\cdot H_2O]\cdot DMF\cdot solvent$	Cr^{3+}	3.64 ppm	Seconds	$5.14X10^2$	YES	Water	[11]
	CrO_4^{2-}	0.33 ppm		$4.85X10^3$			
	$Cr_2O_7^{2-}$	1.07 ppm		$1.04X10^4$			
$[Me_2NH_2]_4[Zn_6(qptc)_3(trz)_4]\cdot 6H_2O$	Cr^{3+}	–	–		NO	Water	[12]
$[Tb(TATAB)(H_2O)_2]\cdot NMP\cdot H_2O\}_n$	$Cr_2O_7^{2-}$	1 μM	–	$1.11X10^4$	NO	Water	[13]
Eu^{3+}@MIL-121	$Cr_2O_7^{2-}$	0.054 μM	–	$4.34X10^3$	NO	Water	[14]
$[Zn(btz)]_n$	CrO_4^{2-}	10 μM	–	$3.19X10^3$	YES	Water	[15]
	$Cr_2O_7^{2-}$	20 μM		$4.23X10^3$			
$[Zn_2(ttz)H_2O]_n$	CrO_4^{2-}	2 μM		$2.35X10^3$	YES	Water	[15]
	$Cr_2O_7^{2-}$	20 μM		$2.19X10^3$			
$[Zn_{2.5}(cpbda)(OH)_2]\cdot DMF$	CrO_4^{2-}	–	–		NO	Water	[16]
	$Cr_2O_7^{2-}$						
$\{[Cu(butylmalonate)_2(H_2O)](2\text{-}APH)_2\cdot H_2O$	$Cr_2O_7^{2-}$	–	–		NO	Water	[17]

$[Eu_7(mtb)_5(H_2O)_{16}]\cdot NO_3\cdot 8DMA\cdot 18H_2O$	CrO_4^{2-}	0.56 ppb	–	–	NO	deionized water	[18]

TPOM= tetrakis(4-pyridyloxymethylene)methane, BDC= 2-aminoterephthalic acid;[1] L=benzo-(1,2;4,5)-bis(thiophene-2′-carboxylic acid, BBI=1,1′-(1,4-butanediyl)bis(imidazole;[2] L= 5,5′-(carbonylbis(azanediyl))diisophthalic acid;[3] TPTZ =4-[4-(1H-1,2,4-triazol-1-yl)phenyl]phenyl}-1H-1,2,4-triazole, IPA=isophthalic acid;[4] L= 4-(carboxyphenyl)oxamethyl]-3-oxapentane acid, bib = 4,4′-di(1H-imidazol-1-yl)-1,1′-biphenyl, tib= 1,3,5-tri(1H-imidazol-1-yl)benzene;[5] Htrb= hexakis (1,2,4-triazol-ylmethy1)-benzene;[6] bibp = 4,4′-bis(imidazol-1-ylmethyl)-biphenyl;[7] 1= 3-(1H-pyrazol-3-yl) benzoic acid;[8] tpeb = 1,3,5-tri-4-pyridyl-1,2-ethenylbenzene, 2,3-ndc = 2,3-naphthalenedicarboxylic acid;[9] L = biphenyl-3′-nitro-3,4′,5-tricarboxylic acid;[10] tpbpc =4′-[4,2′;6′,4″]-terpyridin-4′-yl-biphenyl -4-carboxylic acid;[11] qptc = terphenyl-2,5,2′5′-tetracarboxylic acid, trz = 1,2,4-triazole;[12] TATAB = 4,4′,4″-s-triazine-1,3,5-triyltri-m-aminobenzoic acid, NMP = N-methyl-2-pyrrolidone;[13] btec =pyromellitic acid;[14] btz =1,5-bis(5-tetrazolo)-3-oxapentane, ttz= 1,2,3-tris-[2-(5-tetrazolo)-ethoxy] propane;[15] cpbda =3,5-bis(4-carboxyphenoxy)benzoic acid;[16] 2-APH= protonated 2-aminopyridine;[17] 4mtb = 4-[tris(4-carboxyphenyl) methyl]benzoic acid.[18]

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