

Electronic Supplementary Information (ESI) for

## A Pillar-layered Binuclear 3D Cobalt(II) Coordination Polymer as Electrocatalyst for Overall Water Splitting and Chemosensor for Cr(VI) Anions Detection

Dongsheng Zhao<sup>a</sup>, Junqi Song<sup>a</sup>, Xiutang Zhang<sup>\*a</sup>, Feng Wang<sup>a</sup>, Bei Li<sup>a</sup>, Lulu Yang<sup>a</sup>, Yuxin Deng<sup>a</sup>, Qingbo Li<sup>\*b</sup>,  
Liming Fan<sup>\*a</sup>

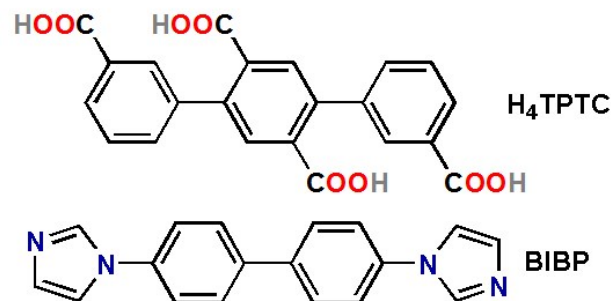
<sup>a</sup>Department of Chemistry, College of Science, North University of China, Taiyuan, P. R. China.

<sup>b</sup>Center for Optics Research and Engineering, Shandong University, Qingdao, Shandong, P. R. China.

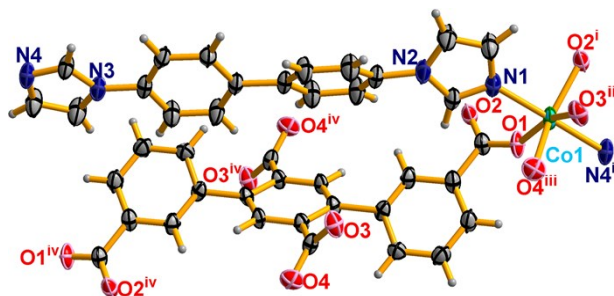
E-mail: limingfan@nuc.edu.cn; xiutangzhang@163.com; liqingbo2016@sdu.edu.cn.

### Table of Contents

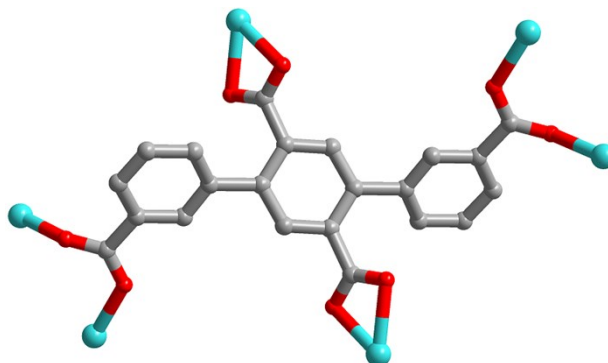
10	<b>Fig. S1</b> Selected H <sub>4</sub> TPTC and BIBP organic ligands in the assembly of <b>1</b> .....	2
	<b>Fig. S2</b> The asymmetry unit of <b>1</b> with 50% probability (Symmetry codes: i 1-x, 2-y, -z; ii 1-x, 1-y, 1-z; iii x, 1+y, -1+z; iv -x, 1-y, 1-z.).....	2
	<b>Fig. S3</b> The coordination mode of TPTC <sup>4-</sup> ligand in <b>1</b> .....	2
	<b>Fig. S4</b> The binuclear {Co <sub>2</sub> (COO) <sub>2</sub> } SBU in <b>1</b> .....	2
15	<b>Fig. S5</b> The BIBP as pillars to connect the binuclear {Co <sub>2</sub> (COO) <sub>2</sub> } SBUs in <b>1</b> .....	3
	<b>Fig. S6</b> PXRD patterns of <b>1</b> under different conditions.....	3
	<b>Fig. S7</b> TGA curve for <b>1</b> .....	3
	<b>Fig. S8</b> The $\chi_m$ versus T of <b>1</b> .....	3
	<b>Fig. S9</b> Relative cyclic voltammogram profile of NF.....	4
20	<b>Fig. S10</b> Lines fitting plots between $v^{1/2}$ and i of NF.....	4
	<b>Fig. S11</b> PXRD patterns of <b>1</b> after electrochemical testing.....	4
	<b>Fig. S12</b> The fluorescence spectra of free H <sub>4</sub> TPTC, BIBP and <b>1</b> in solid state at room temperature.....	5
	<b>Fig. S13</b> The luminescence intensities of CP <b>1</b> which were dispersed in the aqueous solution of different anions.....	5
	<b>Fig. S14</b> The changes of emission spectra of <b>1</b> in aqueous solutions with incremental addition of CrO <sub>4</sub> <sup>2-</sup> anion.....	5
25	<b>Fig. S15</b> The changes of emission spectra of <b>1</b> in aqueous solutions with incremental addition of Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> anion.....	6
	<b>Fig. S16</b> The recycled tests for <b>1</b> to detect the (a) CrO <sub>4</sub> <sup>2-</sup> anion and (b) Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> anion for 5 times.....	6
	<b>Table S1</b> Crystal data for <b>1</b> .....	7
	<b>Table S2</b> Selected bond lengths (Å) and angles (°) for <b>1</b> .....	7
	<b>Table S3</b> Comparison of electrocatalytic performances of MOFs based materials for OER.....	7
30	<b>Table S4</b> Comparison of electrocatalytic performances of MOFs based materials for HER.....	7
	<b>Table S5</b> Comparison of various MOFs based chemosensors for the detection of Cr(VI) anions.....	7



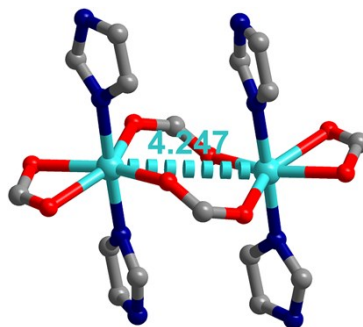
**Fig. S1** Selected  $\text{H}_4\text{TPTC}$  and  $\text{BIBP}$  organic ligands in the assembly of **1**.



**Fig. S2** The asymmetry unit of **1** with 50% probability (Symmetry codes: i  $1-x, 2-y, -z$ ; ii  $1-x, 1-y, 1-z$ ; iii  $x, 1+y, -1+z$ ; iv  $-x, 1-y, 1-z$ ).



**Fig. S3** The coordination mode of  $\text{TPTC}^{4-}$  ligand in **1**.



**Fig. S4** The binuclear  $\{\text{Co}_2(\text{COO})_2\}$  SBU in **1**.

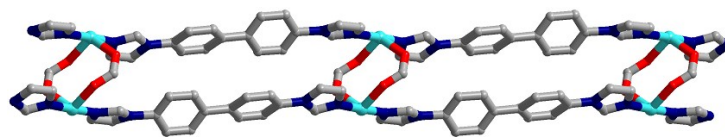
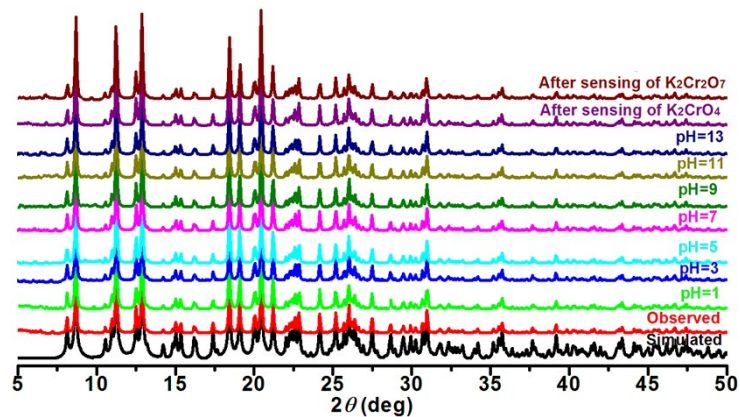


Fig. S5 The BIBP as pillars to connect the binuclear  $\{\text{Co}_2(\text{COO})_2\}$  SBUs in **1**.



5

Fig. S6 PXRD patterns of **1** under different conditions.

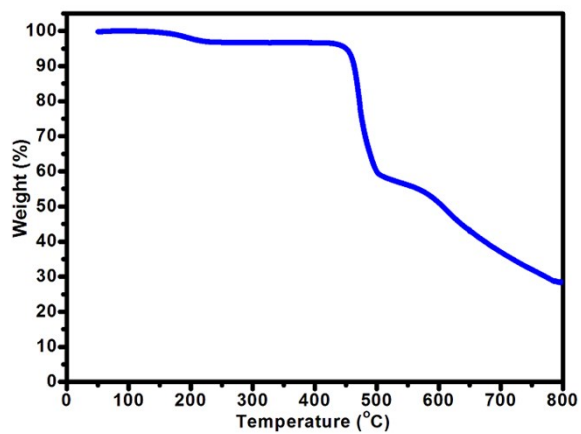


Fig. S7 TGA curve for **1**.

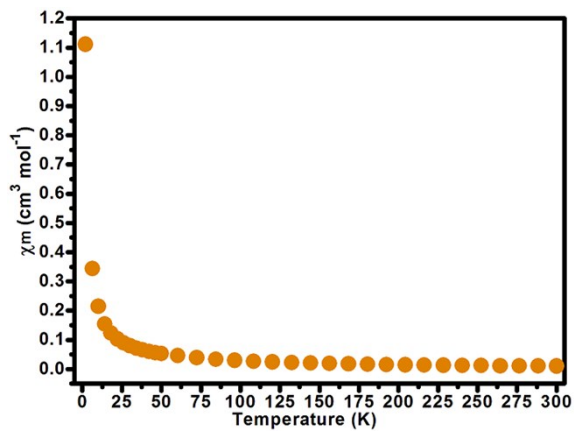


Fig. S8 The  $\chi_m$  versus T of **1**.

10

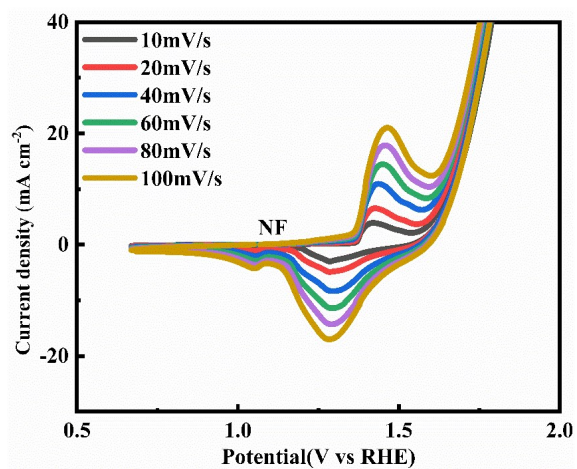


Fig. S9 Relative cyclic voltammogram profile of NF.

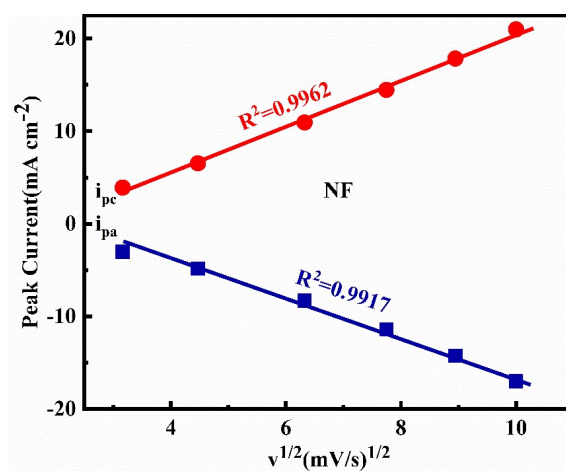


Fig. S10 Lines fitting plots between  $v^{1/2}$  and  $i$  of NF.

5

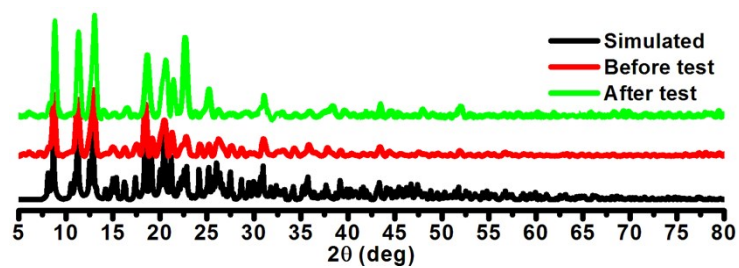


Fig. S11 PXRD patterns of 1 after electrochemical testing.

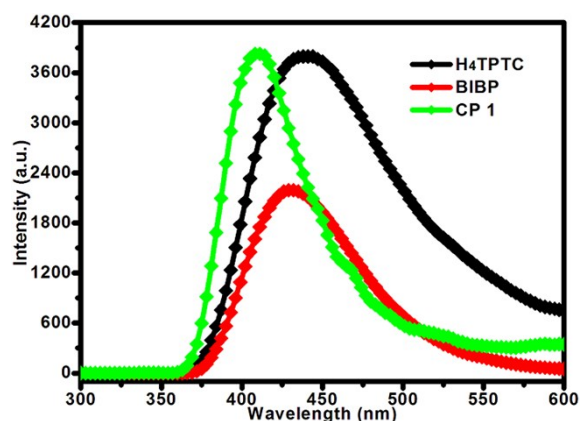
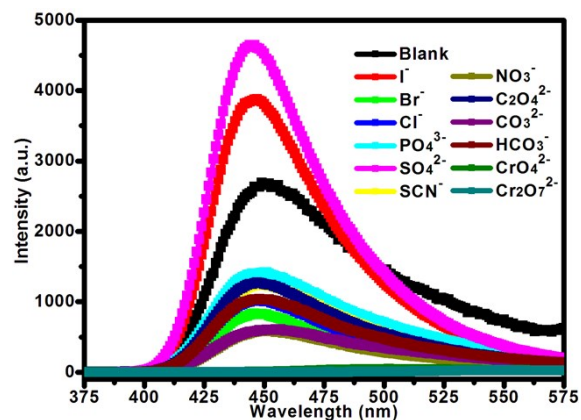


Fig. S12 The fluorescence spectra of free H<sub>4</sub>TPTC, BIBP and **1** in solid state at room temperature.



5 Fig. S13 The luminescence intensities of **1** which were dispersed in the aqueous solution of different anions.

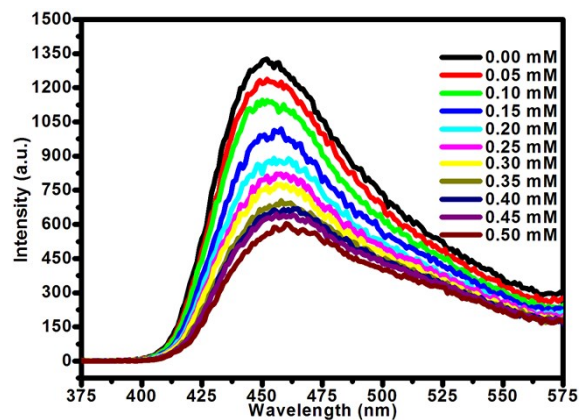
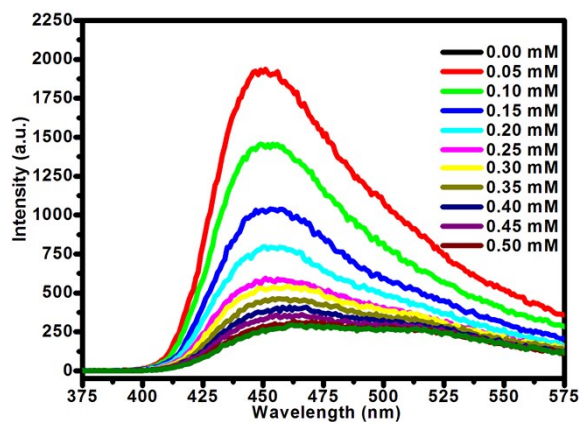
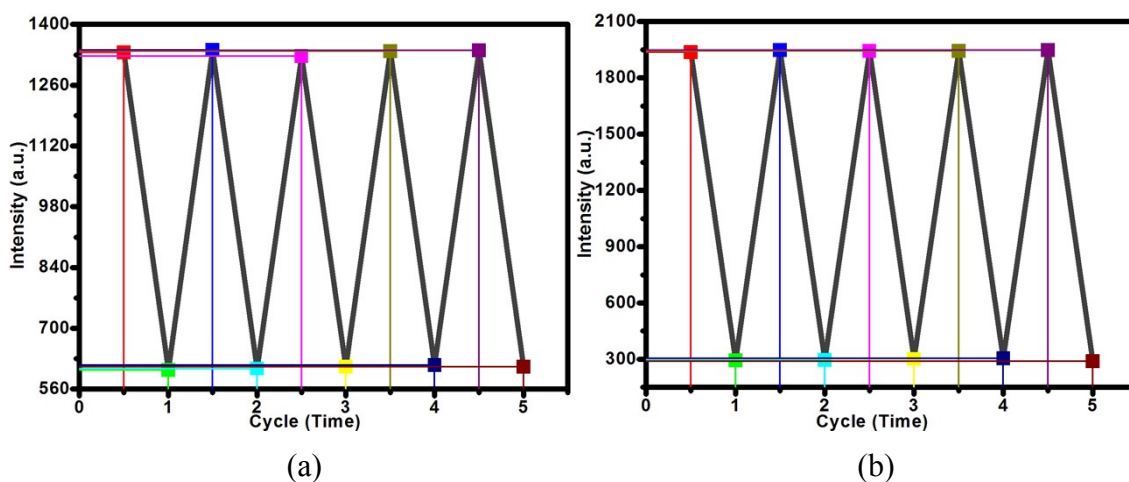


Fig. S14 The changes of emission spectra of **1** in aqueous solutions with incremental addition of CrO<sub>4</sub><sup>2-</sup> anion.



**Fig. S15** The changes of emission spectra of **1** in aqueous solutions with incremental addition of  $\text{Cr}_2\text{O}_7^{2-}$  anion.



**Fig. S16** The recycled tests for **1** to detect the (a)  $\text{CrO}_4^{2-}$  anion and (b)  $\text{Cr}_2\text{O}_7^{2-}$  anion for 5 times.

5

**Table S1** Crystal data for **1**.

Formula	C <sub>29</sub> H <sub>21</sub> CoN <sub>4</sub> O <sub>5</sub>
Formula weight	564.43
Crystal system	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	10.3161(3)
<i>b</i> (Å)	14.7176(4)
<i>c</i> (Å)	16.3208(4)
$\alpha$ (°)	90
$\beta$ (°)	98.968(3)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	2447.67(12)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.532
$\mu$ (mm <sup>-1</sup> )	0.751
Temperature (K)	295(2)
<i>F</i> (000)	1160
<i>R</i> <sub>int</sub>	0.0521
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0465
w <i>R</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1172
Gof	1.044

**Table S2** Selected bond lengths (Å) and angles (°) for **1**.

Co(1)-O(1)	2.036(2)	O(2) <sup>#1</sup> -Co(1)-O(4) <sup>#3</sup>	149.54(8)	N(1)-Co(1)-N(4) <sup>#2</sup>	178.24(9)	O(1)-Co(1)-O(4) <sup>#3</sup>	99.40(8)
Co(1)-O(2) <sup>#1</sup>	2.0704(2)	N(4) <sup>#2</sup> -Co(1)-O(4) <sup>#3</sup>	95.39(9)	O(1)-Co(1)-O(3) <sup>#3</sup>	158.38(8)	O(1)-Co(1)-N(4) <sup>#2</sup>	86.09(9)
Co(1)-N(1)	2.118(2)	O(2) <sup>#1</sup> -Co(1)-N(1)	93.31(9)	O(2) <sup>#1</sup> -Co(1)-O(3) <sup>#3</sup>	90.43(8)	N(1)-Co(1)-O(4) <sup>#3</sup>	85.32(9)
Co(1)-N(4) <sup>#2</sup>	2.132(2)	O(3) <sup>#3</sup> -Co(1)-O(4) <sup>#3</sup>	59.14(7)	N(1)-Co(1)-O(3) <sup>#3</sup>	88.76(9)	O(1)-Co(1)-O(2) <sup>#1</sup>	111.06(9)
Co(1)-O(3) <sup>#3</sup>	2.208(2)	O(2) <sup>#1</sup> -Co(1)-N(4) <sup>#2</sup>	86.90(9)	N(4) <sup>#2</sup> -Co(1)-O(3) <sup>#3</sup>	92.99(8)	O(1)-Co(1)-N(1)	92.20(9)
Co(1)-O(4) <sup>#3</sup>	2.224(2)						

Symmetry codes: #1 -x+1, -y+1, -z+2; #2 x+1, y, z+1; #3 x, -y+1/2, z+1/2.

**Table S3** Comparison of electrocatalytic performances of MOFs based materials for OER.

Catalyst	Substrate	Electrolyte	$\eta_{10}$	Reference
Co-BPDC/Co-BDC <sub>3</sub>	GCE	1 M KOH	335 mV	47
UTSA-16	GCE	1 M KOH	408 mV	48
Co-ZIF-9(III)	GCE	1 M KOH	380 mV	49
Unsaturated ZIF-67	GCE	1 M KOH	410 mV	50
CTGU-14	GCE	1 M KOH	454 mV	51
<b>1</b> @NF	NF	1 M KOH	377 mV	<b>this work</b>

**Table S4** Comparison of electrocatalytic performances of MOFs based materials for HER.

Catalyst	Substrate	Electrolyte	$\eta_{10}$	Reference
Ni-ZIF	GCE	1 M KOH	218 mV	52
Fe <sub>2</sub> Co-MOF	GCE	1 M KOH	221 mV	53
NiFe-MOF	NF	1 M KOH	255 mV	54
Co/Cu-MOF	GCE	1 M KOH	391 mV	55
Ni-CP	GCE	1 M KOH	422 mV	56
<b>1</b> @NF	NF	1 M KOH	242 mV	<b>this work</b>

**Table S5** Comparison of various MOFs based chemosensors for the detection of Cr(VI) anions.

Analyte	MOFs based Fluorescent Materials	Quenching constant (K <sub>SV</sub> , M <sup>-1</sup> )	Detection Limits	Media	Ref
CrO <sub>4</sub> <sup>2-</sup>	[Cd <sub>2</sub> (HDDDB)(bib) <sub>1.5</sub> (H <sub>2</sub> O)]	4.7 × 10 <sup>3</sup>	N/A	H <sub>2</sub> O	61
	[Cd <sub>2</sub> (HDDDB)( <i>m</i> -bimb)]	2.5 × 10 <sup>3</sup>	N/A	H <sub>2</sub> O	
	[Cd <sub>2</sub> (DDB)( <i>p</i> -bimb)]	6.0 × 10 <sup>3</sup>	N/A	H <sub>2</sub> O	
	[Tb(Hbptc)(H <sub>2</sub> O) <sub>4</sub> ]	1.27 × 10 <sup>4</sup>	2.36 × 10 <sup>-6</sup> M	H <sub>2</sub> O	62
	[Ni <sub>1.5</sub> (H <sub>2</sub> L)(bib) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3.0 × 10 <sup>3</sup>	N/A	H <sub>2</sub> O	63
	[Pb <sub>2</sub> (HL)(bib) <sub>1.5</sub> (H <sub>2</sub> O)]	7.4 × 10 <sup>3</sup>	N/A	H <sub>2</sub> O	
	{[Co(TPTC) <sub>0.5</sub> (BIBP)]·H <sub>2</sub> O} <sub>n</sub>	2.5 × 10 <sup>3</sup>	3.42 × 10 <sup>-6</sup> M	H <sub>2</sub> O	<b>this work</b>
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	[Cd <sub>2</sub> (HDDDB)(bib) <sub>1.5</sub> (H <sub>2</sub> O)]	2.7 × 10 <sup>4</sup>	N/A	H <sub>2</sub> O	61
	[Cd <sub>2</sub> (HDDDB)( <i>m</i> -bimb)]	1.8 × 10 <sup>4</sup>	N/A	H <sub>2</sub> O	
	[Cd <sub>2</sub> (DDB)( <i>p</i> -bimb)]	2.8 × 10 <sup>4</sup>	N/A	H <sub>2</sub> O	
	[Cd(TIPA) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ]	7.15 × 10 <sup>4</sup>	8 ppb	H <sub>2</sub> O	62
	[Tb(Hbptc)(H <sub>2</sub> O) <sub>4</sub> ]	1.04 × 10 <sup>5</sup>	2.88 × 10 <sup>-7</sup> M	H <sub>2</sub> O	63
	[Cd <sub>3</sub> {Ir(ppy-COO) <sub>3</sub> } <sub>2</sub> ]	3.475 × 10 <sup>4</sup>	145.1 ppb	H <sub>2</sub> O	64
	[Ni <sub>1.5</sub> (H <sub>2</sub> L)(bib) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> ]	2.9 × 10 <sup>4</sup>	N/A	H <sub>2</sub> O	65
	[Pb <sub>2</sub> (HL)(bib) <sub>1.5</sub> (H <sub>2</sub> O)]	2.8 × 10 <sup>4</sup>	N/A	H <sub>2</sub> O	
	{[Co(TPTC) <sub>0.5</sub> (BIBP)]·H <sub>2</sub> O} <sub>n</sub>	1.15 × 10 <sup>4</sup>	2.96 × 10 <sup>-7</sup> M	H <sub>2</sub> O	<b>this work</b>