Supporting Information

N-donor ligands enhancing luminescence properties of seven Zn/Cd

(II) MOFs based on a large rigid π-conjugated carboxylate ligand

Run-Ping Ye,[ab] Xin Zhang,[a] Ji-Quan Zhai,[a] Ye-Yan Qin,[a] Lei Zhang,[a] Yuan-Gen Yao*[a] and Jian Zhang[a]

[a]Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China
E-mail: yyg@fjirsm.ac.cn; Fax: +86-591-8371-4946; Tel: +86-591-8371-1523
[b]University of Chinese Academy of Sciences, Beijing, 100049, China.

Table S1. Selected bond distances (Å) and bond angles (°).

Compound **1**			
Zn(1)-O(1)	1.9537(19)	Zn(1)-O(3)#1	1.955(2)
Zn(1)-O(2)#2	1.979(2)	Zn(1)-O(1W)	1.987(2)
O(2)-Zn(1)#2	1.979(2)	O(3)-Zn(1)#3	1.955(2)
Zn(1)-O(4)#1	2.5339(26)		
O(1)-Zn(1)-O(3)#1	132.31(9)	O(1)-Zn(1)-O(2)#2	107.02(8)
O(3)#1-Zn(1)-O(2)#2	98.14(9)	O(1)-Zn(1)-O(1W)	106.36(9)
O(3)#1-Zn(1)-O(1W)	104.25(10)	O(2)#2-Zn(1)-O(1W)	106.46(9)
Compound **2**			
Cd(1)-O(1)	2.240(4)	Cd(1)-N(2)	2.266(4)
Cd(1)-O(3)#1	2.367(3)	Cd(1)-N(3)#2	2.407(4)
Cd(1)-O(4)#1	2.446(4)	Cd(1)-O(3)#3	2.509(4)
Cd(1)-O(2)	2.638(4)	O(3)-Cd(1)#3	2.509(4)
O(3)-Cd(1)#4	2.367(3)	O(4)-Cd(1)#4	2.446(4)
N(3)-Cd(1)#5	2.407(4)		
O(1)-Cd(1)-N(2)	137.82(15)	O(1)-Cd(1)-O(3)#1	86.64(13)
O(1)-Cd(1)-N(3)#2	87.53(15)	N(2)-Cd(1)-O(3)#1	130.41(14)
O(3)#1-Cd(1)-N(3)#2	100.75(14)	N(2)-Cd(1)-N(3)#2	101.60(15)
N(2)-Cd(1)-O(4)#1	85.23(14)	O(1)-Cd(1)-O(4)#1	136.93(13)
N(3)#2-Cd(1)-O(4)#1	83.23(14)	O(3)#1-Cd(1)-O(4)#1	54.41(12)
N(2)-Cd(1)-O(3)#3	86.64(13)	O(1)-Cd(1)-O(3)#3	83.63(13)
N(3)#2-Cd(1)-O(3)#3	170.83(12)	O(3)#1-Cd(1)-O(3)#3	76.38(13)
O(1)-Cd(1)-O(2)	52.92(13)	O(4)#1-Cd(1)-O(3)#3	101.64(12)
O(3)#1-Cd(1)-O(2)	139.06(12)	N(2)-Cd(1)-O(2)	86.52(14)

O(4)#1-Cd(1)-O(2)	164.22(12)	N(3)#2-Cd(1)-O(2)	85.29(14)
O(3)#3-Cd(1)-O(2)	91.27(12)		

Compound **3**

Cd(1)-N(2)	2.237(3)	Cd(1)-O(1)#1	2.269(2)
Cd(1)-O(4)#2	2.325(3)	Cd(1)-O(5)	2.412(3)
Cd(1)-O(4)#3	2.472(3)	Cd(1)-O(2)#1	2.477(3)
Cd(1)-O(3)#2	2.533(3)	Cd(1)-C(1)#1	2.692(4)
O(1)-C(1)	1.248(4)	O(1)-Cd(1)#4	2.269(2)
O(2)-C(1)	1.250(4)	O(2)-Cd(1)#4	2.477(3)
O(3)-Cd(1)#5	2.533(3)	O(4)-Cd(1)#5	2.325(3)
O(4)-Cd(1)#6	2.472(3)		

N(2)-Cd(1)-O(1)#1	144.48(10)	N(2)-Cd(1)-O(4)#2	126.37(10)
O(1)#1-Cd(1)-O(4)#2	84.14(9)	N(2)-Cd(1)-O(5)	88.94(10)
O(1)#1-Cd(1)-O(5)	98.19(9)	O(4)#2-Cd(1)-O(5)	108.91(9)
N(2)-Cd(1)-O(4)#3	79.60(10)	O(1)#1-Cd(1)-O(4)#3	87.29(9)
O(4)#2-Cd(1)-O(4)#3	83.86(9)	O(5)-Cd(1)-O(4)#3	166.48(9)
N(2)-Cd(1)-O(2)#1	91.17(10)	O(1)#1-Cd(1)-O(2)#1	54.70(9)
O(4)#2-Cd(1)-O(2)#1	137.86(9)	O(5)-Cd(1)-O(2)#1	87.72(9)
O(4)#3-Cd(1)-O(2)#1	85.39(9)	N(2)-Cd(1)-O(3)#2	85.35(10)
O(1)#1-Cd(1)-O(3)#2	130.17(9)	O(4)#2-Cd(1)-O(3)#2	53.15(9)
O(5)-Cd(1)-O(3)#2	76.67(9)	O(4)#3-Cd(1)-O(3)#2	109.17(9)
O(2)#1-Cd(1)-O(3)#2	164.05(10)		

Compound **4**

Zn(1)-O(4)#1	1.9754(19)	Zn(1)-O(1)	2.0035(18)
Zn(1)-O(2)#2	2.0043(18)	Zn(1)-N(1)	2.077(2)
Zn(1)-O(3)#1	2.538(2)	O(2)-Zn(1)#3	2.0043(18)
O(3)-Zn(1)#1	2.538(2)	O(4)-Zn(1)#1	1.9754(19)

O(4)#1-Zn(1)-O(1)	104.74(8)	O(4)#1-Zn(1)-O(2)#2	100.11(8)
O(1)-Zn(1)-O(2)#2	95.51(7)	O(4)#1-Zn(1)-N(1)	130.61(8)
O(1)-Zn(1)-N(1)	107.87(8)	O(2)#2-Zn(1)-N(1)	112.36(8)
O(4)#1-Zn(1)-O(3)#1	56.57(7)	O(1)-Zn(1)-O(3)#1	102.55(7)
O(2)#2-Zn(1)-O(3)#1	153.38(7)	N(1)-Zn(1)-O(3)#1	80.61(8)

Compound **5**

Zn(1)-O(6)	1.923(4)	Zn(1)-O(4)	1.926(4)
Zn(1)-O(13)#1	1.930(4)	Zn(1)-O(2)#2	1.960(4)
Zn(2)-O(8)	1.969(4)	Zn(2)-O(19)#3	1.983(4)
Zn(2)-O(11)	2.039(4)	Zn(2)-N(6)	2.117(5)
Zn(2)-N(5)	2.162(5)	Zn(3)-O(16)	1.959(4)
Zn(3)-O(9)	1.967(4)	Zn(3)-O(12)	1.973(4)

Zn(3)-O(18)#3	2.037(4)	Zn(3)-O(1W)	2.164(5)
Zn(4)-O(1)#2	2.019(4)	Zn(4)-O(7)	2.057(4)
Zn(4)-O(14)#1	2.065(4)	Zn(4)-N(7)	2.164(5)
Zn(4)-N(8)	2.164(5)	Zn(4)-O(2W)	2.189(6)
O(13)-Zn(1)#4	1.930(4)	O(19)-Zn(2)#3	1.983(4)
O(18)-Zn(3)#3	2.037(4)	O(1)-Zn(4)#2	2.019(4)
O(14)-Zn(4)#4	2.065(4)		

O(6)-Zn(1)-O(4)	117.43(17)	O(6)-Zn(1)-O(13)#1	119.46(18)
O(4)-Zn(1)-O(13)#1	103.80(18)	O(6)-Zn(1)-O(2)#2	102.87(18)
O(4)-Zn(1)-O(2)#2	97.10(17)	O(13)#1-Zn(1)-O(2)#2	114.28(18)
O(8)-Zn(2)-O(19)#3	105.15(19)	O(8)-Zn(2)-O(11)	112.83(18)
O(19)#3-Zn(2)-O(11)	96.94(17)	O(8)-Zn(2)-N(6)	101.0(2)
O(19)#3-Zn(2)-N(6)	149.3(2)	O(11)-Zn(2)-N(6)	87.37(17)
O(8)-Zn(2)-N(5)	92.66(18)	O(19)#3-Zn(2)-N(5)	86.21(18)
O(11)-Zn(2)-N(5)	152.24(18)	O(16)-Zn(3)-O(9)	101.06(18)
N(6)-Zn(2)-N(5)	76.7(2)	O(9)-Zn(3)-O(12)	147.78(18)
O(16)-Zn(3)-O(12)	110.76(18)	O(9)-Zn(3)-O(18)#3	95.8(2)
O(16)-Zn(3)-O(18)#3	92.85(16)	O(12)-Zn(3)-O(18)#3	87.8(2)
O(16)-Zn(3)-O(1W)	96.52(19)	O(9)-Zn(3)-O(1W)	87.9(2)
O(12)-Zn(3)-O(1W)	83.7(3)	O(18)#3-Zn(3)-O(1W)	169.1(2)
O(1)#2-Zn(4)-O(7)	103.33(17)	O(1)#2-Zn(4)-O(14)#1	101.37(19)
O(7)-Zn(4)-O(14)#1	95.95(18)	O(1)#2-Zn(4)-N(7)	87.11(18)
O(7)-Zn(4)-N(7)	166.06(18)	O(14)#1-Zn(4)-N(7)	90.9(2)
O(1)#2-Zn(4)-N(8)	160.96(17)	O(7)-Zn(4)-N(8)	91.57(17)
O(14)#1-Zn(4)-N(8)	88.60(19)	N(7)-Zn(4)-N(8)	76.44(18)
O(1)#2-Zn(4)-O(2W)	83.5(2)	O(7)-Zn(4)-O(2W)	84.7(2)
O(14)#1-Zn(4)-O(2W)	174.7(2)	N(7)-Zn(4)-O(2W)	87.4(3)
N(8)-Zn(4)-O(2W)	86.2(2)		

Compound **6**

Zn(1)-O(1)	1.9385(15)	Zn(1)-O(4)#1	1.9898(14)
Zn(1)-O(2W)	2.1066(16)	Zn(1)-N(2)	2.1109(18)
Zn(1)-N(3)	2.2457(17)	O(4)-Zn(1)#2	1.9898(14)

O(1)-Zn(1)-O(4)#1	134.86(7)	O(1)-Zn(1)-O(2W)	99.61(7)
O(4)#1-Zn(1)-O(2W)	88.18(6)	O(1)-Zn(1)-N(2)	117.11(7)
O(4)#1-Zn(1)-N(2)	106.61(7)	O(2W)-Zn(1)-N(2)	93.22(7)
O(1)-Zn(1)-N(3)	88.07(7)	O(4)#1-Zn(1)-N(3)	91.58(6)
O(2W)-Zn(1)-N(3)	169.38(7)	N(2)-Zn(1)-N(3)	76.67(7)

Compound **7**

Zn(1)-O(1)	1.9372(18)	Zn(1)-O(4)#1	
Zn(1)-O(1W)	2.0999(18)	Zn(1)-N(3)	1.9763(19)

Zn(1)-N(2)	2.204(2)	O(4)-Zn(1)#2	2.114(2)
			1.9763(19)
O(1)-Zn(1)-O(4)#1	125.94(8)	O(1)-Zn(1)-O(1W)	
O(4)#1-Zn(1)-O(1W)	89.61(8)	O(1)-Zn(1)-N(3)	101.78(8)
O(4)#1-Zn(1)-N(3)	110.49(8)	O(1)-Zn(1)-N(2)	121.75(9)
O(1W)-Zn(1)-N(3)	91.02(8)	O(4)#1-Zn(1)-N(2)	89.73(9)
O(1W)-Zn(1)-N(2)	165.74(7)	N(3)-Zn(1)-N(2)	90.38(8)
			75.65(8)

Symmetry codes for compounds **1-7**. For **1**, #1 x, y+1, z; #2 -x+1, -y, -z+2; #3 x, y-1, z. For **2**, #1 x-1,y,z; #2 x,y,z-1; #3 -x+2,-y+1,-z+1; #4 x+1,y,z. For **3**, #1 -x+3/2,y-1/2,-z+1/2; #2 -x+1/2,y-1/2,-z+1/2; #3 x+1/2,-y+1/2,z-1/2; #4 x+3/2,y+1/2,-z+1/2; #5 -x+1/2,y+1/2,-z+1/2; #6 x-1/2,-y+1/2,z+1/2. For **4**, #1 -x+1/2,-y-1/2,-z+1; #2 -x+1/2,y-1/2,-z+1/2; #3 -x+1/2,y+1/2,-z+1/2. For **5**, #1 x,y-1,z; #2 -x,-y,-z+1; #3 -x+1,-y+1,-z+1; #4 x,y+1,z. For **6**, #1 -x+1,y+1/2,-z+3/2; #2 -x+1,y-1/2,-z+3/2. For **7**, #1 -x+1,y-1/2,-z+3/2; #2 -x+1,y+1/2,-z+3/2.

Table S2. Intermolecular π-π interaction distances (Å).

π-π interactions	**Plane A**	**Plane B**	**Distance**
Compound **1**			
Cg(A)•••Cg(B)	C2···C3···C4···C6···C7··· C8	C2···C3···C4···C6···C7··· C8	3.603(19)
Compound **2**			
Cg(A)•••Cg(B)	N1···C9···C12···C11···C10	N1···C9···C12···C11···C10	3.629(4)
Cg(A)•••Cg(B)	C2···C3···C4···C6···C7··· C8	C11···C12···C13···C14···C15··· C16	3.625(3)
Compound **4**			
Cg(A)•••Cg(B)	N1···C9···C12···C11···C10	C11···C12···C13···C14···C15··· C16	3.629(2)
Compound **5**			
Cg(A)•••Cg(B)	N1···C9···C11···C16···C10	C51···C52···C53···C54···C55··· C56	3.609(3)
Cg(A)•••Cg(B)	N2···C25···C28···C27···C26	N5···C73···C72···C74···C75···C76	3.887(5)
Cg(A)•••Cg(B)	N4···C57···C60···C59···C58	C2···C3···C4···C6···C7··· C8	3.600(4)
Cg(A)•••Cg(B)	C2···C3···C4···C6···C7··· C8	C59···C60···C61···C62···C63··· C64	3.735(3)
Compound **6**			
Cg(A)•••Cg(B)	N1···C9···C10···C11···C12	C2···C3···C5···C6···C7··· C8	3.8520(12)
Compound **7**			
Cg(A)•••Cg(B)	N1···C9···C12···C11···C10	C2···C3···C4···C6···C7··· C8	3.5336(16)

Table S3. Hydrogen bond distances (Å) and bond angles (°).

Donor---H···Acceptor	d(D---H)	d(H···A)	d(D···A)	∠D---H···A
Compound **1**				
O1W---H1WA···O2W	0.87	1.81	2.672(5)	170
O1W---H1WB···O4	0.87	1.79	2.654(3)	170
O2W---H2WB···O1	0.85	2.32	2.960(4)	133
C6---H6···O5 (intra)	0.93	2.30	2.852(5)	118
Compound **5**	0.86	2.48	3.295(16)	159
O1W---H1WB···O3W	0.85	2.08	2.635(16)	122
O2W---H2WB···O3W	0.93	2.21	2.849(7)	126
C6---H6···O5	0.93	2.27	2.873(11)	122
C39---H39···O15	0.93	2.18	2.819(7)	126
C54---H54···O20	0.93	2.29	3.122(9)	149
C75---H75···O3	0.93	2.49	3.177(10)	131
C88---H88···O20				
Compound **6**				
O2W---H2WA···O2	0.87	2.47	3.048(2)	125
O2W---H2WB···O1W	0.87	1.85	2.709(2)	166
O1W---H1WA···O3	0.85	1.92	2.772(3)	178
O1W---H1WB···O5	0.85	2.12	2.914(2)	156
C8---H8···O5	0.93	2.27	2.898(3)	124
C26---H26···O2	0.93	2.42	3.281(3)	154
Compound **7**				
O1W---H1WA···O2	0.87	2.58	3.167(3)	126
O1W---H1WB···O2W	0.86	1.85	2.702(3)	169
O2W---H2WB···O5	0.85	2.06	2.889(3)	164
C8---H8···O5	0.93	2.27	2.894(3)	124
C24---H24···O2	0.93	2.53	3.223(5)	132
C26---H26···O1W	0.93	2.50	3.080(3)	121

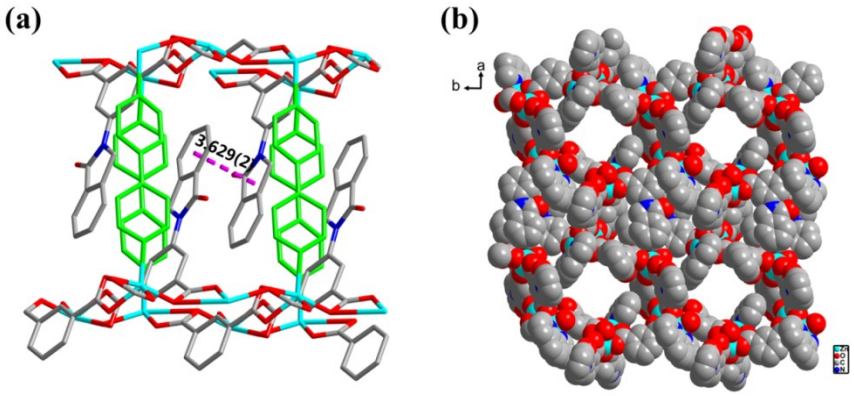

Fig. S1. (a) Intramolecular π-π interactions in complex **4**. (b) pace-filling model of complex **5**.

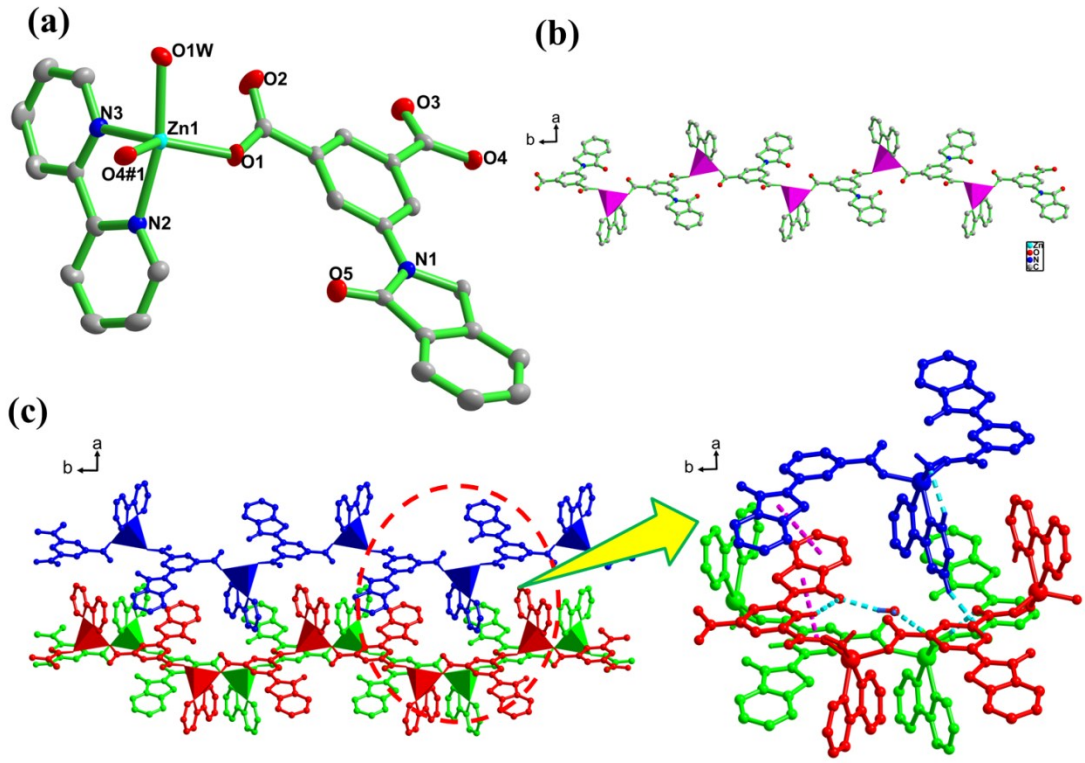

Fig. S2. (a) Coordination environments of Zn (II) ion with 40% thermal ellipsoids. (b) An infinite 1D chain of **7** viewed along the crystallographic *c*-axis. (c) 2D supramolecular network via intermolecular π-π interactions and hydrogen bonds. (Symmetry codes: #1 -x+1, y-1/2, -z+3/2).

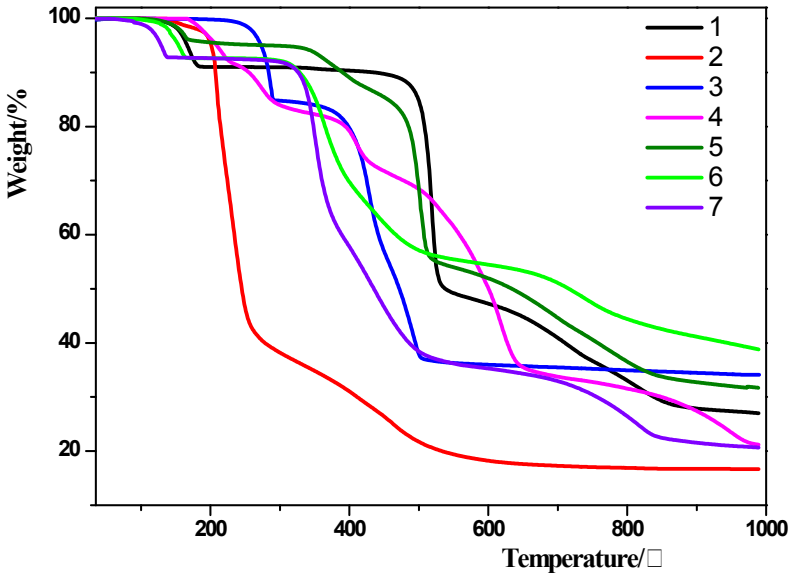

Fig. S3. The TGA curves for complexes **1**–**7**.

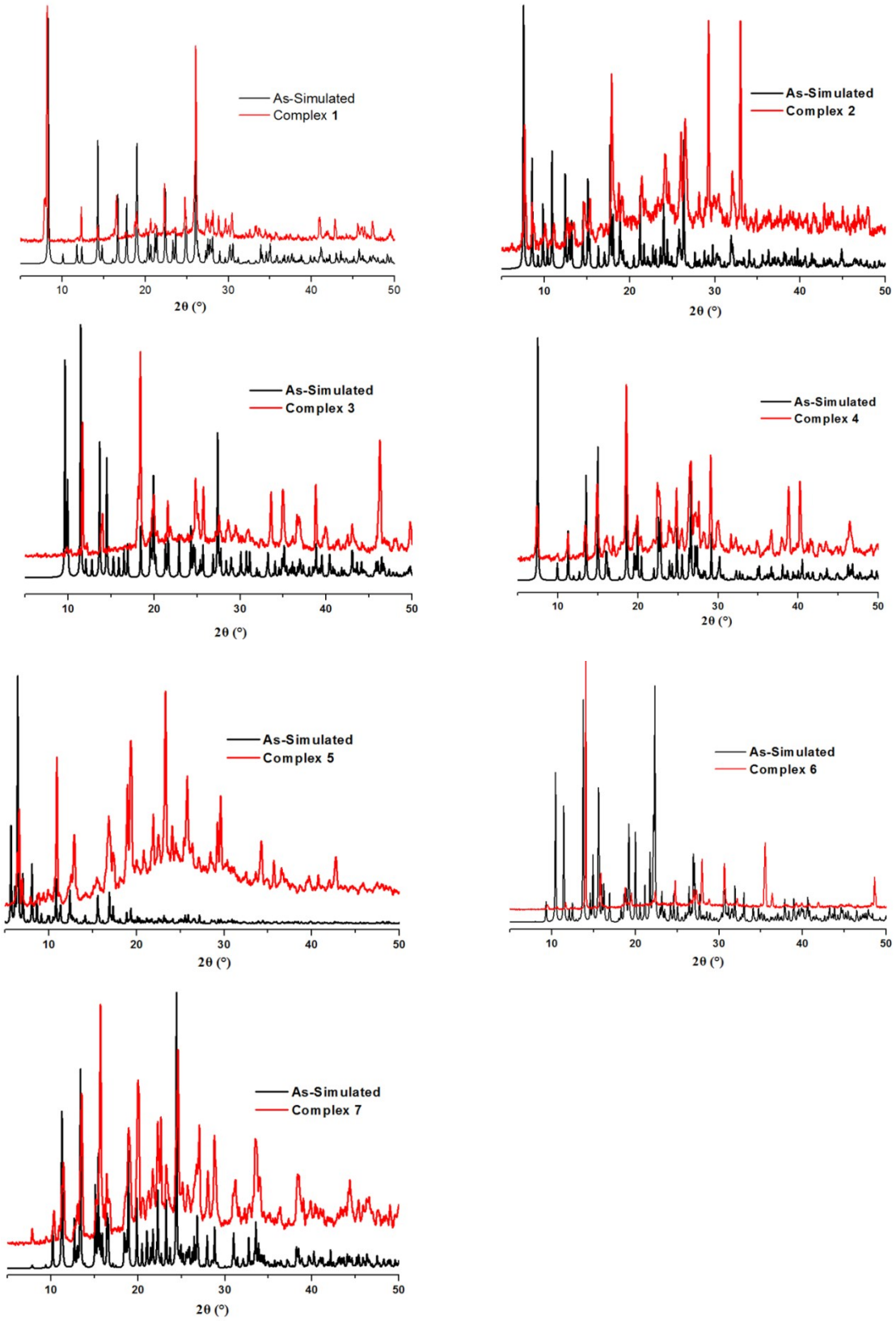

Fig. S4. The Powder X-ray diffraction (PXRD) patterns of **1-7**.

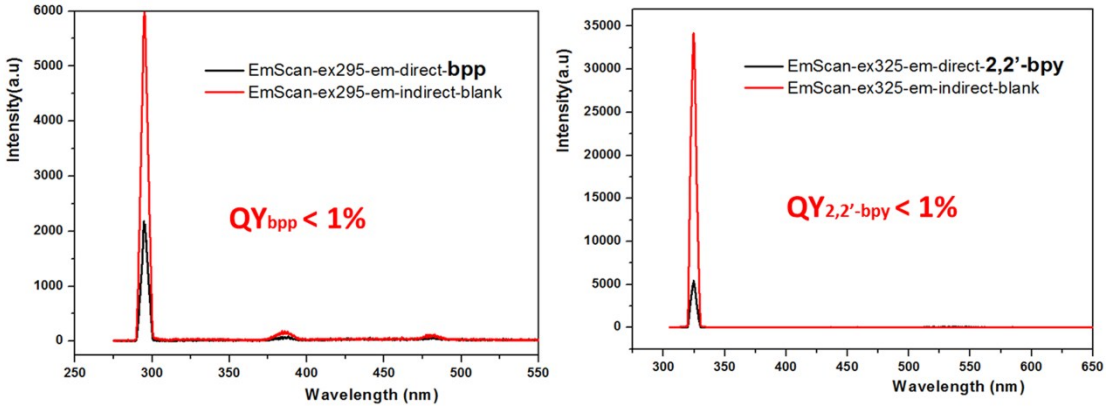

Fig. S5. The QY curves of free bpp and 2,2'-bpy ligands.

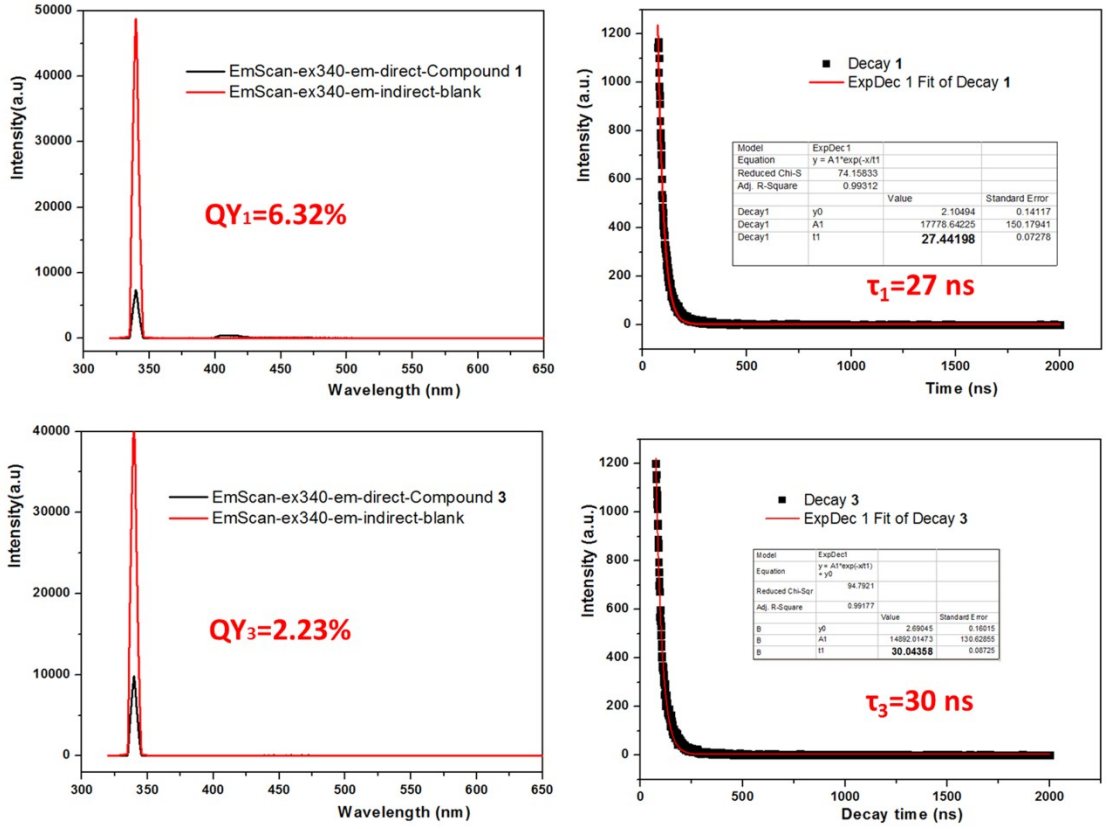

Fig. S6. The QY and Decay curves of compounds **1** and **3**.

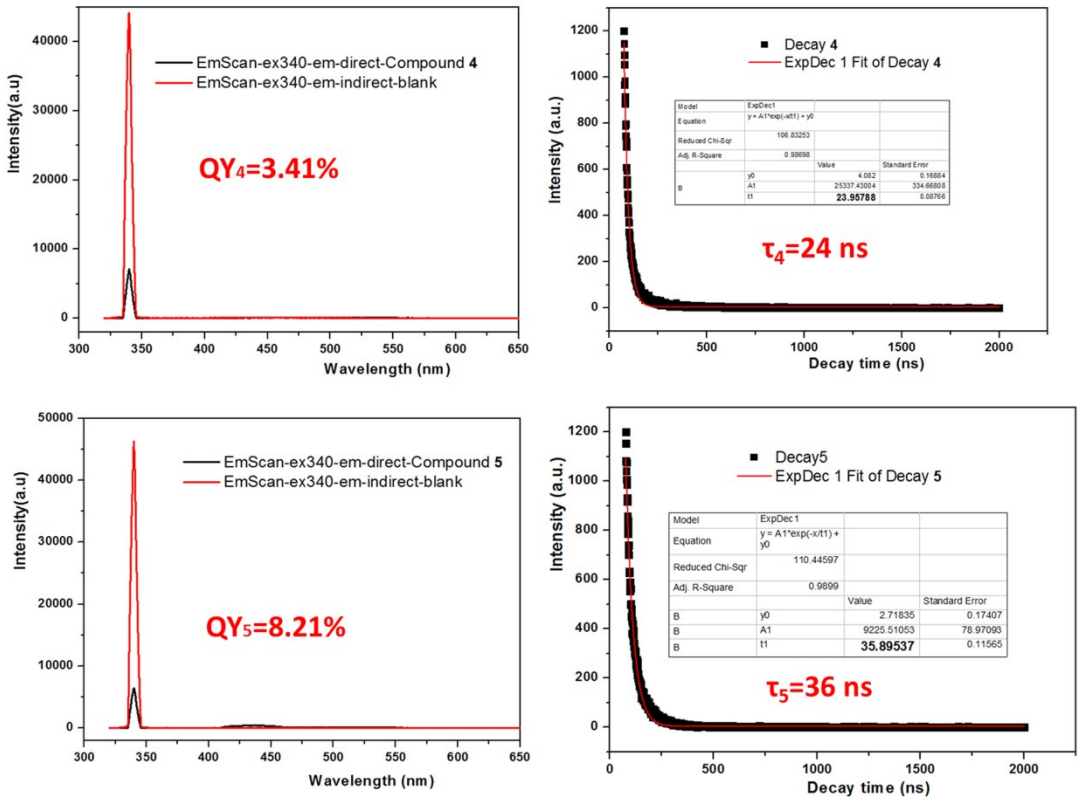

Fig. S7. The QY and Decay curves of compounds **4** and **5**.

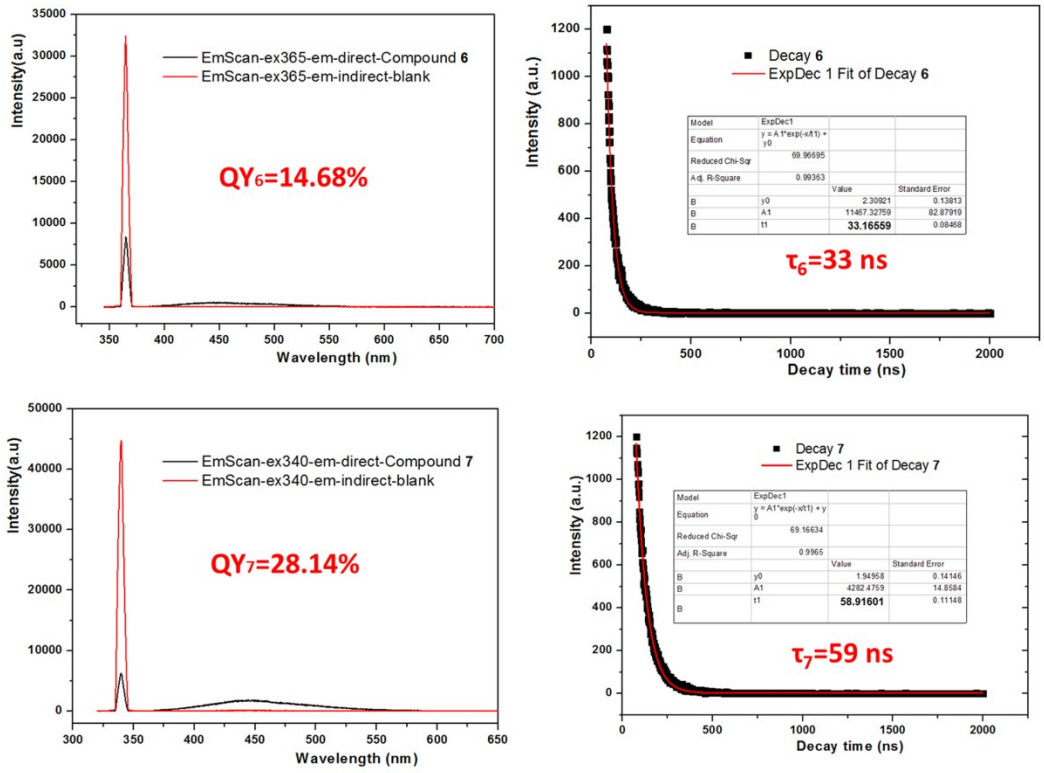

Fig. S8. The QY and Decay curves of compounds **6** and **7**.