Electronic Supporting Information (ESI) for manuscript:

Coordination assemblies of Cd^{II} with 2,2′:6′,2″-terpyridine (*terpy*), 2,3,5,6-tetra-(2-pyridyl)pyrazine (*tppz*) and pseudohalide ions – structural diversification and luminescent properties

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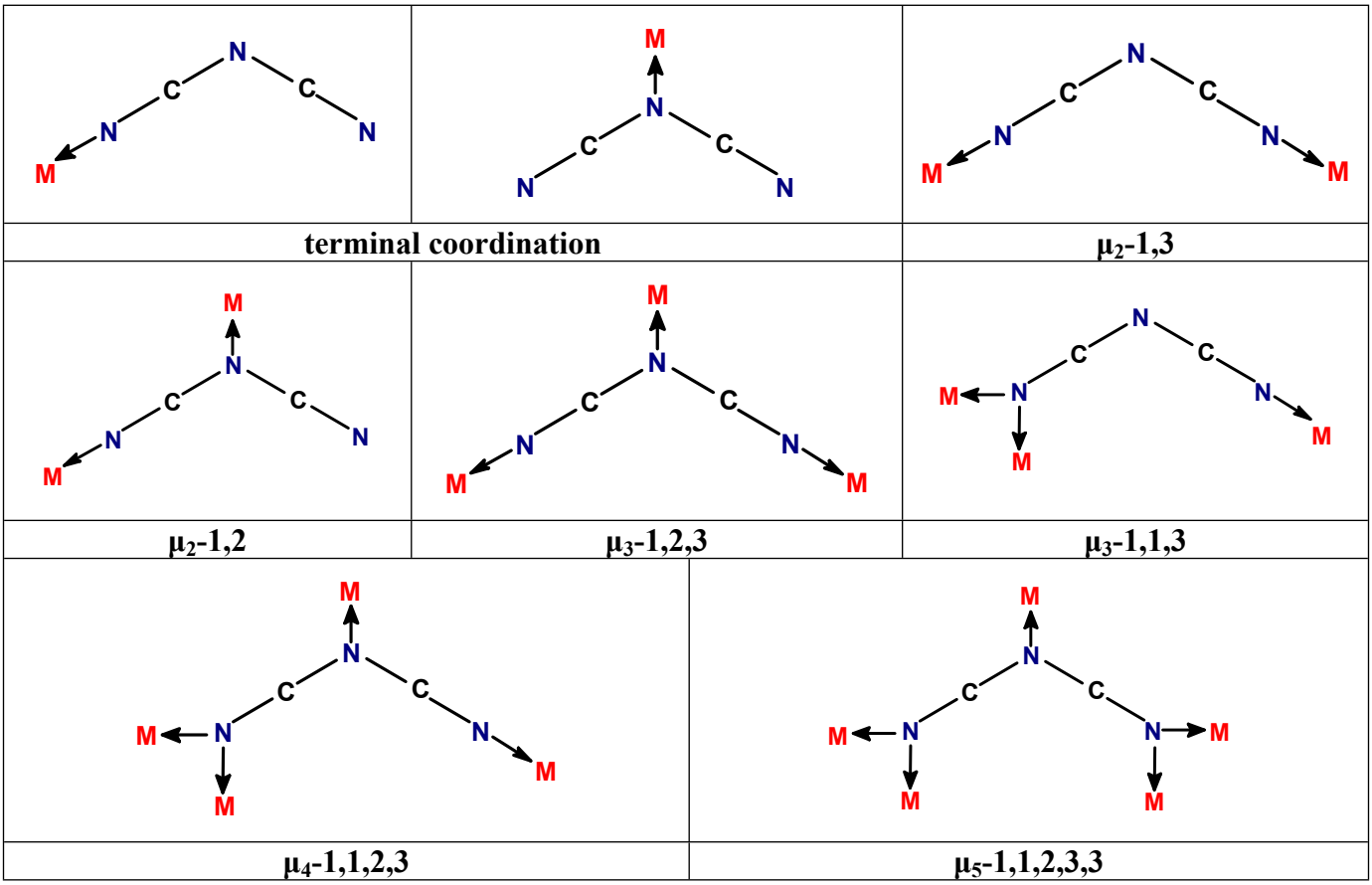
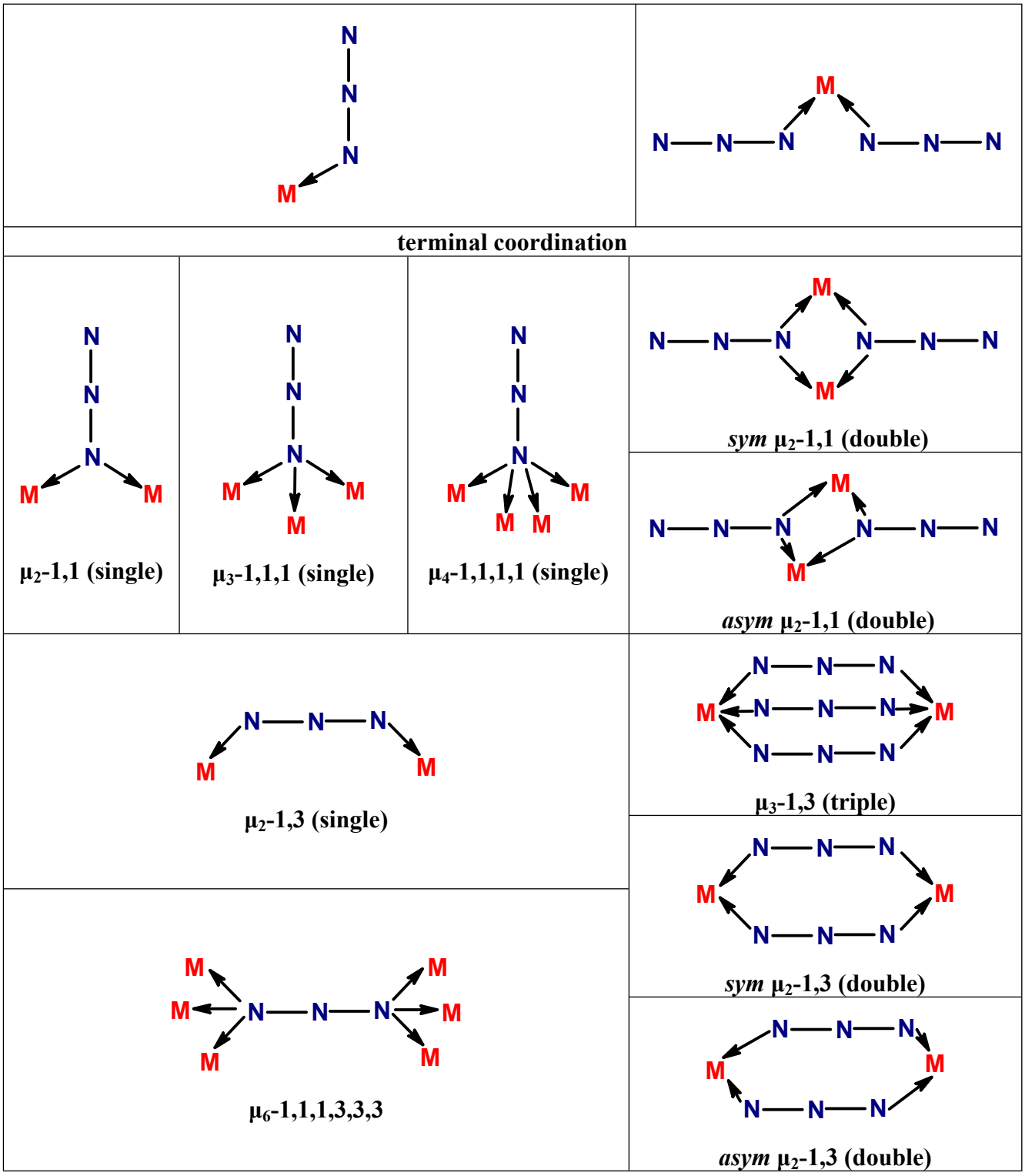


Scheme S1. Possible coordination modes of dicyanamide ligands.



Scheme S2. Possible coordination modes of dicyanamide ligands.

$[Cd(terpy)(dca)(H_2O)]_n$ • n(dca)
│ Stage I m.l. 3.87% / 3.63%
↓ v.p.: H_2O (357-408 K) endo
$[Cd(terpy)(dca)]_n$ • n(dca)
│ Stage II m.l. 11.46% / 11.68%
│ Stage IIa v.p.: CN^+, CO, NO, N^+, $-O_2$; m.l. 3.68% / — (629-730 K) exo
↓ Stage IIb v.p.: CN^+, CO^+, CO_2^+, NO, NO_2, $-O_2$; m.l. 7.78% / — (730-751 K) exo
$[CdO_{0.5}(terpy)(dca)]_n$
│ Stage III m.l. 11.30% / 11.68%
│ Stage IIIa v.p.: CO, CO_2, NO, NO_2, $-O_2$; m.l. 5.35% / — (751-760 K) exo
↓ Stage IIIb v.p.: CO_2, NO_2, $-O_2$; m.l. 5.85% / — (760-767 K) exo
nCdO*•n(terpy)
│ Stage IV m.l. 47.43% / 47.16%
↓ v.p.: CO, CO_2, NO, NO_2, H_2O, $-O_2$ (757-890 K) exo
nCdO*

$[Cd(tppz)(dca)(NO_3)]_n$
│ Stage I m.l. 17.51% / 17.82%
│ v.p.: CO, CO_2, NO, NO_2, $-O_2$ (536-637 K) exo
nCdO* • n(tppz)
│ Stage III m.l. 61.50% / 61.76%
↓ v.p.: CO, CO_2, NO, NO_2, H_2O, $-O_2$ (637-807 K) exo
nCdO*

$[Cd(tppz)(dca)(NO_3)(H_2O)]$
│ Stage I m.l. 2.80% / 2.78%
↓ v.p.: H_2O (374-425 K) endo
$[Cd(tppz)(dca)(NO_3)]$
│ Stage II m.l. 17.51% / 17.32%
│ v.p.: CO, CO_2, NO, NO_2, $-O_2$ (543-651 K) exo
CdO* • (tppz)
│ Stage III m.l. 59.86% / 60.04%
│ Stage IIIa v.p.: CO, CO_2, NO, NO_2, H_2O, $-O_2$; m.l. 17.02% / — (651-738 K) exo
↓ Stage IIIb v.p.: CO, CO_2^+, $-O_2$; m.l. 42.84% / — (738-854 K) exo
CdO*

Scheme 3. Stages of the thermal decomposition of the studied compounds (v.p. – main volatile products (including fragmentation ones) and oxygen uptake ($-O_2$) according to mass spectrometry, m.l. - experimental mass loss / theoretical mass loss, * - product was confirmed by XRPD)

Table S1. Crystal data and structure refinement for compounds **1-5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{17}H_{11}Cd\,N_7O_3$	$C_{19}H_{13}Cd\,N_9O$	$C_{15}H_{11}Cd\,N_7O_3$	$C_{15}H_{13}Cd\,N_7O_4$	$C_{30}H_{18}Cd_2N_{18}$
Formula weight	473.73	495.78	449.71	467.72	855.42
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$	P-1
Unit cell dimensions [Å °]	a = 8.5178(3)	a = 7.6683(3)	a = 8.15961(1)	a= 9.3280(5)	a= 7.7803(4)
	b = 14.4262(6)	b = 8.8264(4)	b = 11.21043(1)	b= 13.9183(5)	b= 10.2661(4)
	c = 14.9256(5)	c = 14.996(7)	c = 17.04066(1)	c= 13.8508(6)	c= 10.7220(5)
		α= 78.424(4)			α= 81.920(4)
	β = 100.234(3)	β = 79.894(4	β = 94.4222(3)	β = 109.222(5)	β = 79.820(4)
		γ= 81.624(4)			γ= 75.630(4)
Volume [$Å^3$]	1804.86(12)	972.45(7)	1554.116(1)	1698.00(13)	812.34(6)
Z	4	2	4	4	1
Density (calc.) [Mg/m^3]	1.743	1.693	1.922	1.830	1.749
Absorption coefficient [mm^{-1}]	1.245	1.155	1.440	1.326	1.363
F(000)	936	492	888	928	420
Crystal size [mm]	0.158x0.141x0.119	0.112x0.105x0.045	0.170x0.094x0.060	0.054x0.035x0.034	0.204x0.111x0.079
θ range for data collection [°]	3.32 to 25.05	3.34 to 25.04	3.39 to 25.04	3.44 to 25.05	3.58 to 25.05
Index ranges	-10≤ h ≤ 10	-9 ≤ h ≤ 9	8 ≤ h ≤ 8	-11≤ h≤ 11	-9 ≤ h ≤ 9
	-17≤ k ≤ 14	-10 ≤ k ≤ 10	-13 ≤ k ≤ 13	-16 ≤ k ≤ 16	-12 ≤ k ≤ 12
	-17≤ l ≤ 16	-17≤ l ≤ 17	-20≤ l ≤ 20	-16≤ l≤ 16	-12≤ l ≤ 12
Reflections collected	10263	8682	10245	19921	7622
Independent reflections	3180 ($R_{(int)}$ = 0.0348)	3428 ($R_{(int)}$ =0.0364)	2753 ($R_{(int)}$ =0.0363)	2999 ($R_{(int)}$ = 0.0374)	2876 ($R_{(int)}$ = 0.0396)
Completeness to 2theta [%]	99.7%	99.7%	99.7%	99.7%	99.7
Max. and min. transmiss.	1.000 and 0.768	1.000 and 0.934	1.000 and0.844	1.000 and 0.789	1.000 and 0.733
Data / restraints / parameters	3180 / 0 / 264	3428 / 0 / 271	2753 / 0 / 235	2999 / 0 / 245	2876 / 0 / 226
Goodness-of-fit on F^2	1.029	1.036	1.043	1.053	0.994
Final R indices [I>2σ(I)]	R1 = 0.0340	R1 = 0.0279	R1 = 0.0262	R1 = 0.0247	R1 = 0.0320
	wR2 = 0.0716	wR2 = 0.0611	wR2 = 0.0547	wR2 = 0.0592	wR2 = 0.0690
R indices (all data)	R1 = 0.0504	R1 = 0.0339	R1 = 0.0330	R1 = 0.0339	R1 = 0.0384
	wR2 = 0.0759	wR2 = 0.0634	wR2 = 0.0568	wR2 =0.0619	wR2 = 0.0728
Largest diff. peak and hole [$e\,Å^{-3}$]	0.569 and -0.483	0.355 and -0.500	0.359 and -0.499	0.492 and -0.463	0.406 and -0.524

Table S2. Crystal data and structure refinement for compounds **6-9**.

	6	**7**	**8**	**9**
Empirical formula	$C_{26}H_{16}CdN_{10}O_3$	$C_{26}H_{18}Cd\ N_{10}O_4$	$C_{13}H_{12}CdN_7O_4$	$C_{12}H_8CdN_9$
Formula weight	628.89	646.90	442.70	390.67
Temperature [K]	293.0(2)	293.0(2)	293.0(2)	293.0(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	P-1
Unit cell dimensions [Å, °]	a = 9.2897(4)	a = 14.204(5)	a = 9.4767(3)	a = 7.9227(7)
	b = 8.9304(3)	b = 9.8521(4)	b = 12.5129(4)	b = 8.9657(9)
	c = 31.2856(11)	c = 18.7354(6)	c = 14.3126(5)	c = 10.1460(10)
				α= 74.850(8)
	β = 97.826	β = 94.64(3)	β = 106.191(4)	β = 74.240(8)
				γ= 83.61(3)
Volume [$Å^3$]	2571.30(17)	2613.2(9)	1629.89(9)	668.87(11)
Z	4	4	4	2
Density (calc.) [Mg/m^3]	1.625	1.644	1.804	1.940
Absorption coefficient [mm^{-1}]	0.900	0.890	1.375	1.644
F(000)	1256	1296	876	382
Crystal size [mm]	0.157x0.070x0.044	0.182x0.047x0.038	0.192x0.086x0.053	0.492x0.147x0.087
θ range for data collection [°]	3.32 to 25.05	3.41 to 25.05	3.38 to 25.05	3.49 to 25.05
Index ranges	$-10 \le h \le 11$	$-16 \le h \le 16$	$-11 \le h \le 11$	$-9 \le h \le 9$
	$-10 \le k \le 10$	$-10 \le k \le 11$	$-14 \le k \le 14$	$-10 \le k \le 10$
	$-37 \le l \le 36$	$-22 \le l \le 22$	$-17 \le l \le 16$	$-12 \le l \le 12$
Reflections collected	12531	13616	17079	6136
Independent reflections	4541 ($R_{(int)}$ = 0.0464)	4617 ($R_{(int)}$ = 0.0417)	14956 ($R_{(int)}$ =0.0325)	2363 ($R_{(int)}$ =0.0392]
Completeness to 2theta [%]	99.7%	99.8%	99.8%	99.7%
Max. and min. transmiss.	1.000 and 0.550	1.000 and 0.713	1.000 and 0.766	1.000 and 0.667
Data / restraints / parameters	4541 / 0 / 361	4617 / 0 / 370	2881 / 0 / 228	2363 / 0 / 199
Goodness-of-fit on F^2	1.211	1.021	1.057	1.078
Final R indices [I>2σ(I)]	R1 = 0.0468	R1 = 0.0334	R1 = 0.0280	R1 = 0.0282
	wR2 = 0.0948	wR2 = 0.0784	wR2 = 0.0681	wR2 = 0.0640
R indices (all data)	R1 = 0.0746	R1 = 0.0489	R1 = 0.0341	R1 = 0.0304
	wR2 = 0.0980	wR2 = 0.0840	wR2 = 0.0707	wR2 = 0.0652
Largest diff. peak and hole [e $Å^{-3}$]	0.649 and -0.705	0.576 and -0.452	0.649 and -0.583	0.530 and -0.587

Table S3. Short intra- and intermolecular contacts detected in the structures **1-9**.

D—H•••A	D—H [Å]	H•••A [Å]	D•••A [Å]	D—H•••A [°]
		1		
C(1)—H(1)•••O(2)	0.93	2.52	3.213(4)	131.9
C(13)—H(13)•••O(3)_# 1	0.93	2.45	3.279(5)	147.8
C(15) —H(15)•••O(1)	0.93	2.58	3.236(5)	127.6
		2		
O(99)—H(1[a])•••N(96)# 2	0.79	2.03	2.820(4)	178.4
O(99)—H(1B)•••N(94)# 3	1.02	1.85	2.840(4)	165.0
C3— H3•••N96#4	0.93	2.61	3.534(5)	171.7
C9—H9•••N95# 5	0.93	2.61	3.412(4)	144.8
C14—H14•••O99#6	0.93	2.59	3.508 (4)	167.7
		3		
C4—H4•••N99_#7	0.93	2.52	3.408(4)	160.0
C15– H15•••O2	0.93	2.53	3.151(4)	124.5
		4		
O99—H99A•••O3_# 8	0.86	1.97	2.788(3)	156.6
C1—H1•••O2	0.93	2.57	3.259(4)	131.2
C2—H2•••N99_#9	0.93	2.56	3.484(4)	173.5
C4—H4•••O3_#7	0.93	2.24	3.141(4)	162.2
C15—H15•••O1	0.93	2.44	3.106(4)	128.1
		5		
C1—H1•••N94_#10	0.93	2.55	3.274(5)	135.1
C3—H3•••N96_#11	0.93	2.57	3.270(6)	132.3
C7—H7•••N95_#12	0.93	2.53	3.361(4)	148.1
C9—H9•••N99_#5	0.93	2.54	3.457(5)	169.3
		6		
C1—H1•••O1	0.93	2.51	3.143(8)	125.8
C11—H11••• N98 _#13	0.93	2.62	3.404(9)	142.6
		7		
O99—H99A •••N6_#14	0.75	2.05	2.793(4)	175.3
O99—H99B•••N97 _#14	0.66	2.37	3.005(4)	162.7
C4—H4•••N4	0.93	2.61	2.959(5)	102.6
C17—H17•••O3_#15	0.93	2.60	3.288(5)	131.3
		8		
O99—H99•••O2 _# 16	0.82	1.99	2.736(5)	151.6
C9—H9•••O99 _# 17	0.93	2.33	3.222(7)	159.4
C12—H12•••O2	0.93	2.46	3.121(4)	128.3
		9		
C1—H1•••N95_#18	0.93	2.57	3.357(5)	143.0
C2—H2•••N97_#3	0.93	2.60	3.476(5)	157.7
C9 —H9•••N97	0.93	2.60	3.274(4)	130.2
C11—H11•••N95_#19	0.93	2.58	3.375(4)	144.1

Symmetry transformations used to generate equivalent atoms:
#1= -1/2-x,-1/2+y,1/2-z; #2: 1+x,y-1,z; #3: 1+x,y,z; #4: 1-x,2-y,-z; #5= x,y-1,z; #6:= 2-x,-y,1-z; #7=1/2+x,3/2-y,-1/2+z; #8=-x,1-y,1-z; #9=-1/2-x,1/2+y; #10=1-x,1-y,2-z #11 =x,y,1+z; #12=1-x,-y,2-z #13=1/2-x,-1/2+y,3/2-z; #14=3/2-x,-1/2+y,3/2-z; #15=-1+x,y,z; #16= -x,1-y,-z; #17= 1-x,1-y,-z #18= 1-x,2-y,1-z #19-1+x,-1+y,1+z

Table S4. The selected bond lengths [Å] and angles[°] for **1**

Bond lengths		Bond angels	
Cd(1)–N(1)	2.381(3)	N(2)–Cd(1)–N(1)	69.45(10)
Cd(1)–N(2)	2.338(3)	N(2)–Cd(1)–N(3)	69.23(9)
Cd(1)–N(3)	2.374(3)	N(3)–Cd(1)–O(1)	86.17(9)
Cd(1)–N(99)	2.293(3)	O(2)–Cd(1)–N(1)	84.74(9)
Cd(1)–N(97)	2.266(4)	O(2)–Cd(1)–O(1)	50.88(9)
Cd(1)–O(1)	2.556(3)	N(99)–Cd(1)–N(1)	85.92(11)
Cd(1)–O(2)	2.420(3)	N(99)–Cd(1)–O(1)	81.21(11)
C(98)–N(97)#1	1.107(5)	N(99)–Cd(1)–O(2)	82.23(11)
N(98)–C(98)	1.284(6)	N(99)–Cd(1)–N(2)	95.49(10)
N(98)–C(99)	1.284(6)	N(99)–Cd(1)–N(3)	99.13(10)
N(99)–C(99)	1.132(5)	N(97)–Cd(1)–N(1)	92.93(14)
		N(97)–Cd(1)–N(2)	99.58(13)
		N(97)–Cd(1)–N(3)	92.64(14)
		N(97)–Cd(1)–O(1)	88.04(14)
		N(97)–Cd(1)–O(2)	81.22(13)
		N(97)–Cd(1)–N(99)	163.44(14)
		N(97)#2–C(98)–N(98)	173.1(5)
		N(99)–C(99)–N(98)	172.9(4)
		C(99)–N(98)–C(98)	120.6(4)
		C(99)–N(99)–Cd(1)	141.2(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y+1/2; #2 -x+1/2,y-1/2,-z+1/2

Table S5. The selected bond lengths [Å] and angles[°] for **2**

Bond lengths		Bond angels	
Cd(1)–N(1)	2.371(2)	N(2)–Cd(1)–N(1)	69.42(8)
Cd(1)–N(2)	2.322(2)	N(2)–Cd(1)–N(3)	70.29(8)
Cd(1)–N(3)	2.354(2)	N(97)–Cd(1)–N(1)	95.02(10)
Cd(1)–N(97)	2.229(3)	N(99)–Cd(1)–N(1)	93.44(9)
Cd(1)–N(99)	2.283(3)	N(97)–Cd(1)–N(2)	159.69(9)
Cd(1)–O(99)	2.387(2)	N(99)–Cd(1)–N(2)	99.35(8)
N(99)–C(99)	1.143(4)	N(97)–Cd(1)–N(3)	123.81(10)
C(99)–N(98)	1.295(4)	N(99)–Cd(1)–N(3)	93.82(9)
N(98)–C(98)	1.299(4)	N(97)–Cd(1)–N(99)	94.40(9)
C(98)–N(97)#1	1.136(4)	N(1)–Cd(1)–O(99)	92.73(8)
C(97)–N(96)	1.141(5)	N(2)–Cd(1)–O(99)	87.35(8)
N(95)–C(97)	1.292(5)	N(3)–Cd(1)–O(99)	84.57(8)
C(96)–N(95)	1.302(5)	N(97)–Cd(1)–O(99)	80.24(8)
C(96)–N(94)	1.145(4)	N(99)–Cd(1)–O(99)	172.16(8)
		C(99)–N(98)–C(98)	121.3(3)
		N(99)–C(99)–N(98)	173.3(3)
		N(97)#1–C(98)–N(98)	173.7(3)
		C(97)–N(95)–C(96)	121.5(3)
		N(94)–C(96)–N(95)	174.3(4)
		N(96)–C(97)–N(95)	173.2(4)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z.

Table S6. The selected bond lengths [Å] and angles[°] for **3**

Bond lengths		Bond angles	
Cd(1)–N(1)	2.361(2)	N(2)–Cd(1)–N(1)	69.34(8)
Cd(1)–N(2)	2.348(2)	N(2)–Cd(1)–N(3)	68.83(8)
Cd(1)–N(3)	2.392(2)	N(1)–Cd(1)–O(1)	88.67(8)
Cd(1)–N(97)	2.319(3)	N(2)–Cd(1)–O(2)	149.44(8)
Cd(1)–N(99)#1	2.439(3)	N(3)–Cd(1)–O(2)	83.48(8)
Cd(1)–O(1)	2.646(2)	N(97)–Cd(1)–N(1)	89.40(9)
Cd(1)–O(2)	2.363(2)	N(97)–Cd(1)–N(2)	103.59(9)
N(98)–N(99)	1.175(3)	N(97)–Cd(1)–N(3)	96.91(9)
N(98)–N(97)	1.173(4)	N(97)–Cd(1)–O(1)	78.92(9)
		N(97)–Cd(1)–O(2)	92.00(9)
		O(2)–Cd(1)–O(1)	50.63(7)
		O(2)–Cd(1)–N(99)#2	81.14(9)
		N(1)–Cd(1)–N(99)#2	81.35(9)
		N(2)–Cd(1)–N(99)#2	93.01(8)
		N(3)–Cd(1)–N(99)#2	104.20(9)
		N(98)–N(97)–Cd(1)	133.3(2)
		N(98)–N(99)–Cd(1)#1	122.0(2)
		N(97)–Cd(1)–N(99)#2	156.82(10)
		N(99)#2–Cd(1)–O(1)	79.65(8)
		N(97)–N(98)–N(99)	175.6(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y+1/2,-z+1/2; #2 -x+3/2,y-1/2,-z+1/2

Table S7. The selected bond lengths [Å] and angles[°] for **4**.

Bond lengths	Experimental	Bond angels	Experimental
Cd(1)–N(1)	2.359(2)	N(2)–Cd(1)–N(1)	69.69(8)
Cd(1)–N(2)	2.332(2)	N(2)–Cd(1)–N(3)	69.42(8)
Cd(1)–N(3)	2.368(2)	N(99)–Cd(1)–N(1)	90.89(9)
Cd(1)–N(99)	2.293(3)	N(99)–Cd(1)–N(2)	99.42(9)
Cd(1)–O(1)	2.407(2)	N(99)–Cd(1)–N(3)	97.47(9)
Cd(1)–O(2)	2.530(2)	N(99)–Cd(1)–O(1)	91.34(9)
Cd(1)–O(99)	2.369(2)	N(99)–Cd(1)–O(2)	84.23(10)
N(98)–N(97)	1.151(4)	N(99)–Cd(1)–O(99)	163.47(10)
N(98)–N(99)	1.166(4)	N(1)–Cd(1)–O(99)	84.27(8)
		N(2)–Cd(1)–O(99)	93.72(8)
		N(3)–Cd(1)–O(99)	96.52(8)
		N(1)–Cd(1)–O(1)	136.82(8)
		N(3)–Cd(1)–O(1)	83.18(7)
		N(1)–Cd(1)–O(2)	86.25(8)
		O(99)–Cd(1)–O(1)	81.61(8)
		O(99)–Cd(1)–O(2)	79.70(8)
		O(2)–Cd(1)–O(1)	51.16(8)
		N(97)–N(98)–N(99)	177.9(4)
		N(98)–N(99)–Cd(1)	119.0(2)

Table S8. The selected bond lengths [Å] and angles[°] for **5**.

Bond lengths		Bond angles	
Cd(1)–N(1)	2.366(3)	N(2)–Cd(1)–N(1)	69.88(9)
Cd(1)–N(2)	2.330(3)	N(2)–Cd(1)–N(3)	68.81(9)
Cd(1)–N(3)	2.398(3)	N(1)–Cd(1)–N(97)#1	83.81(10)
Cd(1)–N(94)	2.257(3)	N(2)–Cd(1)–N(97)#1	90.43(9)
Cd(1)–N(97)	2.274(3)	N(3)–Cd(1)–N(97)#1	95.25(10)
Cd(1)–N(97)#1	2.436(3)	N(94)–Cd(1)–N(1)	99.06(11)
N(94)–N(95)	1.190(5)	N(94)–Cd(1)–N(2)	101.85(10)
N(95)–N(96)	1.156(5)	N(94)–Cd(1)–N(3)	90.49(11)
N(97)–N(98)	1.204(4)	N(94)–Cd(1)–N(97)	93.23(11)
N(98)–N(99)	1.155(4)	N(97)–Cd(1)–N(1)	116.02(10)
		N(97)–Cd(1)–N(2)	162.87(11)
		N(97)–Cd(1)–N(3)	103.34(10)
		N(94)–Cd(1)–N(97)#1	167.65(10
		N(97)–Cd(1)–N(97)#1	74.82(11)
		N(95)–N(94)–Cd(1)	119.0(3)
		N(98)–N(97)–Cd(1)	121.0(2)
		N(98)–N(97)–Cd(1)#1	121.4(2)
		Cd(1)–N(97)–Cd(1)#1	105.18(11)
		N(96)–N(95)–N(94)	175.9(4)
		N(99)–N(98)–N(97)	177.8(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2.

Table S9. The selected bond lengths [Å] and angles[°] for **6**.

Bond lengths		Bond angles	
Cd(1)–N(1)	2.377(4)	N(2)–Cd(1)–N(1)	67.67(14)
Cd(1)–N(2)	2.391(4)	N(2)–Cd(1)–N(3)	68.69(14)
Cd(1)–N(3)	2.325(4)	N(99)–Cd(1)–N(1)	87.20(19)
Cd(1)–N(97)	2.351(6)	N(99)–Cd(1)–N(2)	100.3(2)
Cd(1)–N(99)	2.307(6)	N(99)–Cd(1)–N(3)	90.9(2)
Cd(1)–O(1)	2.363(4)	N(97)–Cd(1)–N(1)	94.56(16)
Cd(1)–O(2)	2.459(5)	N(97)–Cd(1)–N(2)	81.95(17)
N(97)–C(98)	1.130(7)	N(97)–Cd(1)– N(3)	88.97(17)
C(98)–N(98)	1.275(9)	N(99)–Cd(1)–N(97)	177.6(2)
N(99)–C(99)	1.119(9)	C(98)–N(97)–Cd(1)	156.1(5)
C(99)–N(98)#1	1.303(10)	C(99)–N(99)–Cd(1)	146.5(6)
N(98)–C(99)#2	1.303(10)	N(1)–Cd(1)–O(1)	83.96(16)
		N(3)–Cd(1)–O(2)	88.73(16)
		N(99)–Cd(1)–O(1)	92.1(2)
		N(99)–Cd(1)–O(2)	88.9(2)
		N(97)–Cd(1)–O(1)	86.42(19)
		N(97)–Cd(1)–O(2)	88.7(2)
		N(7)–O(1)–Cd(1)	96.9(3)
		N(7)–O(2)–Cd(1)	92.2(3)
		O(1)–Cd(1)–O(2)	52.32(16)
		N(99)–C(99)–N(98)#1	173.4(8)
		N(97)–C(98)–N(98)	172.1(7)
		C(98)–N(98)–C(99)#2	126.3(6)

Symmetry transformations used to generate equivalent atoms: #1 x,y-1,z; #2 x,y+1,z

Table S10. The selected bond lengths [Å] and angles[°] for **7**.

Bond lengths		Bond angles	
Cd(1)–N(1)	2.386(3)	N(2)–Cd(1)–N(1)	68.54(9)
Cd(1)–N(2)	2.362(2)	N(3)–Cd(1)–N(2)	69.34(9)
Cd(1)–N(3)	2.355(3)	N(97)–Cd(1)–N(1)	87.49(10)
Cd(1)–N(97)	2.365(3)	N(97)–Cd(1)–N(2)	79.70(10)
Cd(1)–O(1)	2.358(3)	N(97)–Cd(1)–N(3)	93.73(10)
Cd(1)–O(2)	2.468(3)	O(99)–Cd(1)–N(1)	95.63(9)
Cd(1)–O(99)	2.272(2)	O(99)–Cd(1)–N(2)	102.90(9)
N(97)–C(98)	1.142(5)	O(99)–Cd(1)–N(3)	85.07(9)
N(98)–C(98)	1.283(5)	O(99)–Cd(1)–O(1)	88.70(9)
N(98)–C(99)	1.287(6)	O(99)–Cd(1)–O(2)	91.12(9)
N(99)–C(99)	1.116(6)	O(99)–Cd(1)–N(97)	176.50(10)
		N(97)–Cd(1)–O(1)	89.92(11)
		N(97)–Cd(1)–O(2)	85.49(10)
		N(1)–Cd(1)–O(1)	86.20(9)
		N(3)–Cd(1)–O(2)	84.65(8)
		O(1)–Cd(1)–O(2)	52.76(9)
		C(98)–N(97)–Cd(1)	131.3(3)
		C(98)–N(98)–C(99)	122.2(4)
		N(97)–C(98)–N(98)	172.3(4)
		N(99)–C(99)–N(98)	173.7(6)

Table S11. The selected bond lengths [Å] and angles[°] for **8**.

Bond lengths		Bond angles	
Cd(1)–N(1)	2.401(3)	N(2)–Cd(1)–N(1)	65.81(8)
Cd(1)–N(2)	2.519(3)	N(2)–Cd(1)–N(3)	64.59(8)
Cd(1)–N(3)	2.476(3)	N(97)#1–Cd(1)–N(1)	103.21(10)
Cd(1)–N(97)#1	2.283(3)	N(97)#1–Cd(1)–N(2)	88.08(9)
Cd(1)–N(97)	2.442(3)	N(97)#1–Cd(1)–N(3)	90.16(9)
Cd(1)–O(1)	2.324(3)	N(97)–Cd(1)–N(1)	86.23(9)
Cd(1)–O(2)	2.474(3)	N(97)–Cd(1)–N(2)	142.99(9)
N(97)–N(98)	1.194(4)	N(97)–Cd(1)–N(3)	145.44(10)
N(98)–N(99)	1.148(4)	N(98)–N(97)–Cd(1)#1	122.8(2)
		N(98)–N(97)–Cd(1)	125.6(2)
		Cd(1)#1–N(97)–Cd(1)	105.31(11)
		N(97)#1–Cd(1)–N(97)	74.69(11)
		N(1)–Cd(1)–O(1)	84.27(9)
		N(2)–Cd(1)–O(1)	100.42(9)
		N(3)–Cd(1)–O(1)	89.73(9)
		N(1)–Cd(1)–O(2)	130.33(9)
		N(2)–Cd(1)–O(2)	139.13(9)
		N(3)–Cd(1)–O(2)	82.28(9)
		N(97)#1–Cd(1)–O(1)	170.51(10)
		N(97)–Cd(1)–O(1)	100.31(10)
		N(97)#1–Cd(1)–O(2)	116.56(10)
		N(97)–Cd(1)–O(2)	77.43(9)
		N(4)–O(1)–Cd(1)	95.6(2)
		N(4)–O(2)–Cd(1)	88.7(2)
		O(1)–Cd(1)–O(2)	54.05(9)
		N(99)–N(98)–N(97)	178.9(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z.

Table S12. The selected bond lengths [Å] and angles[°] for **9**.

Bond lengths	Experimental	Bond angels	Experimental
Cd(1)–N(1)	2.497(3)	N(1)–Cd(1)–N(2)	63.31(8)
Cd(1)–N(2)	2.564(2)	N(3)#1–Cd(1)–N(1)	121.19(8)
Cd(1)–N(3)#1	2.424(3)	N(3)#1–Cd(1)–N(2)	63.77(8)
Cd(1)–N(94)	2.576(3)	N(1)–Cd(1)–N(94)	82.57(10)
Cd(1)–N(96)	2.246(3)	N(2)–Cd(1)–N(94)	142.40(10)
Cd(1)–N(99)	2.279(3)	N(3)#1–Cd(1)–N(94)	153.83(11)
Cd(1)–N(99)#2	2.454(3)	N(3)#1–Cd(1)–N(99)#2	82.83(9)
N(99)–N(98)	1.186(4)	N(99)–Cd(1)–N(1)	90.76(9)
N(97)–N(98)	1.155(4)	N(99)–Cd(1)–N(2)	81.55(9)
N(96)–N(95)	1.170(4)	N(99)#2–Cd(1)–N(1)	155.35(9)
N(95)–N(94)#3	1.151(4)	N(99)#2–Cd(1)–N(2)	133.17(9)
		N(99)–Cd(1)–N(3)#1	105.07(9)
		N(99)–Cd(1)–N(94)	83.72(11)
		N(99)#2–Cd(1)–N(94)	75.26(11)
		N(99)–Cd(1)–N(99)#2	76.39(11)
		N(98)–N(99)–Cd(1)	121.3(2)
		N(98)–N(99)–Cd(1)#2	130.5(2)
		N(97)–N(98)–N(99)	179.3(4)
		N(96)–Cd(1)–N(1)	94.15(11)
		N(96)–Cd(1)–N(2)	111.68(10)
		N(96)–Cd(1)–N(3)#1	82.88(10)
		N(96)–Cd(1)–N(99)	166.71(10)
		N(96)–Cd(1)–N(99)#2	94.38(11)
		N(96)–Cd(1)–N(94)	84.68(11)
		N(95)#3–N(94)–Cd(1)	130.8(3)
		N(95)–N(96)–Cd(1)	130.6(3)
		N(94)#3–N(95)–N(96)	175.4(4)
		Cd(1)–N(99)–Cd(1)#2	103.61(11)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1; #2 -x,-y+2,-z+1; #3 -x+1,-y+2,-z+1

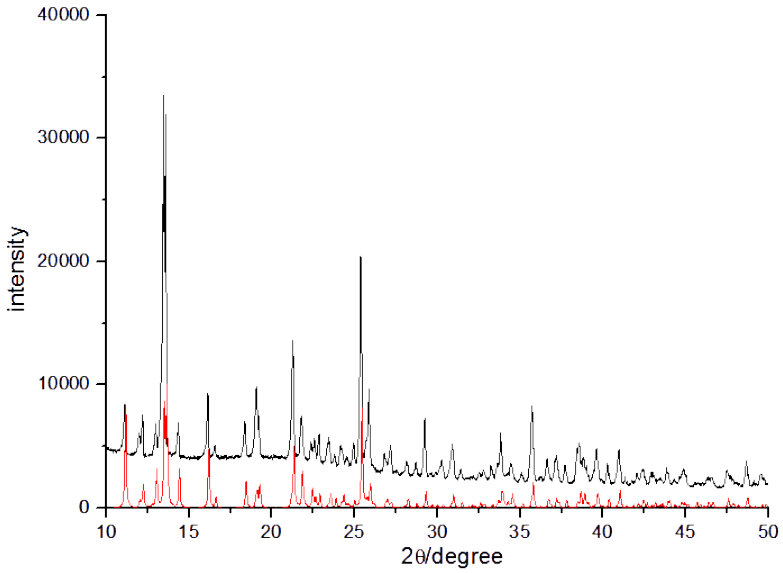


Figure S1. The powder XRD pattern of compound **1** (experimental - black) and the simulation of the powder pattern of **1** from the crystal structure (red).

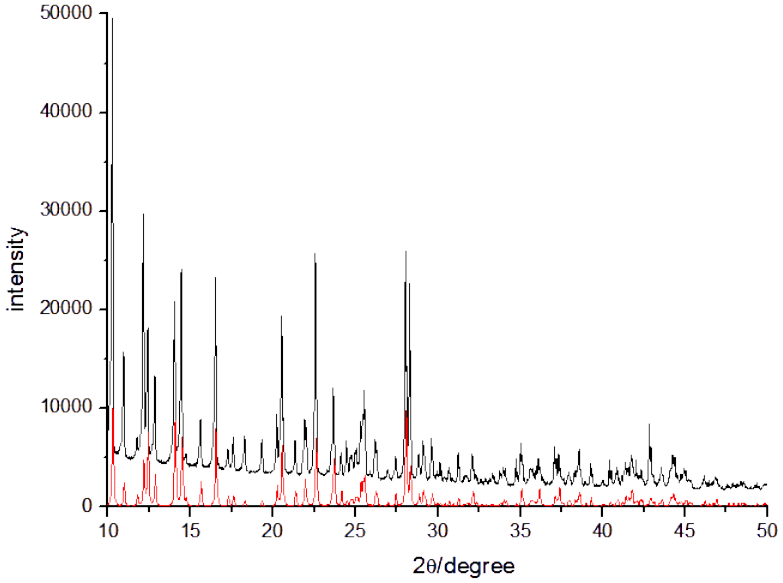


Figure S2. The powder XRD pattern of compound **2** (experimental - black) and the simulation of the powder pattern of **2** from the crystal structure (red).

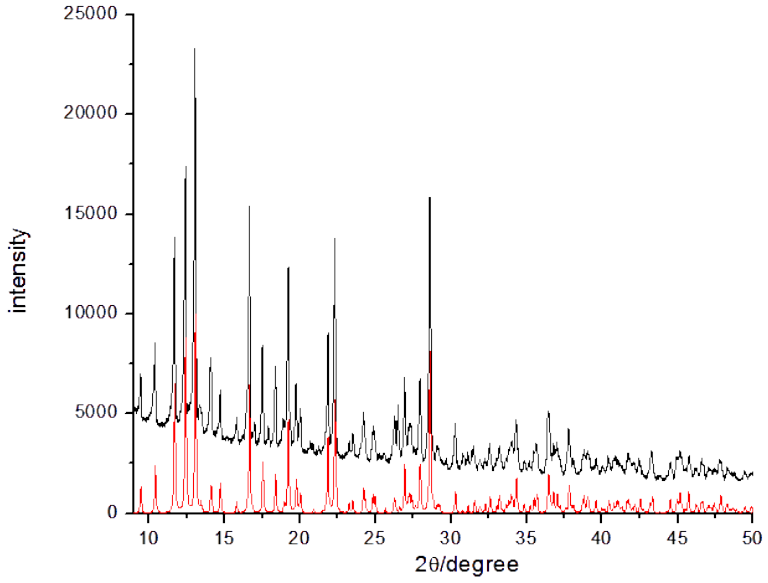


Figure S3. The powder XRD pattern of compound **3** (experimental - black) and the simulation of the powder pattern of **2** from the crystal structure (red).

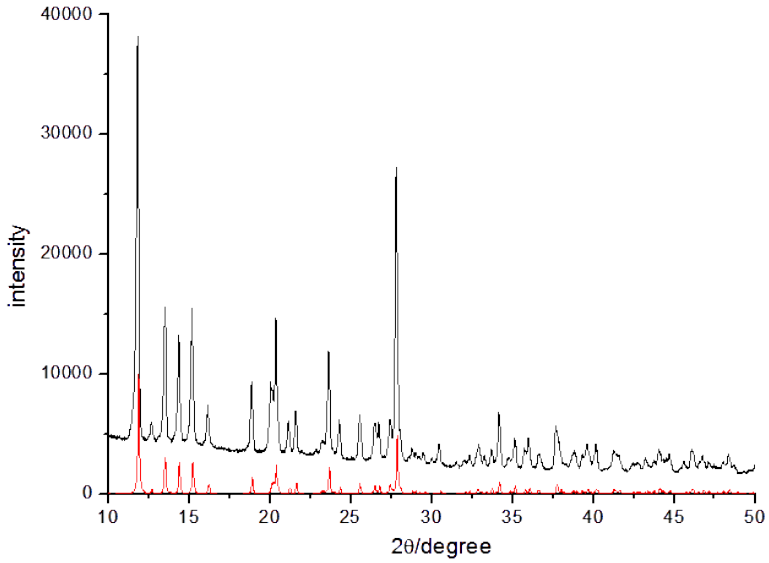


Figure S4. The powder XRD pattern of compound **4** (experimental - black) and the simulation of the powder pattern of **1** from the crystal structure (red).

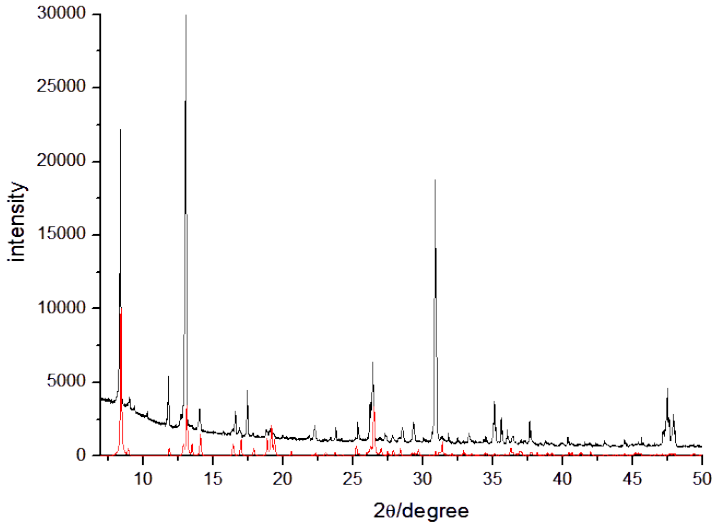


Figure S5. The powder XRD pattern of compound **5** (experimental - black) and the simulation of the powder pattern of **5** from the crystal structure (red).

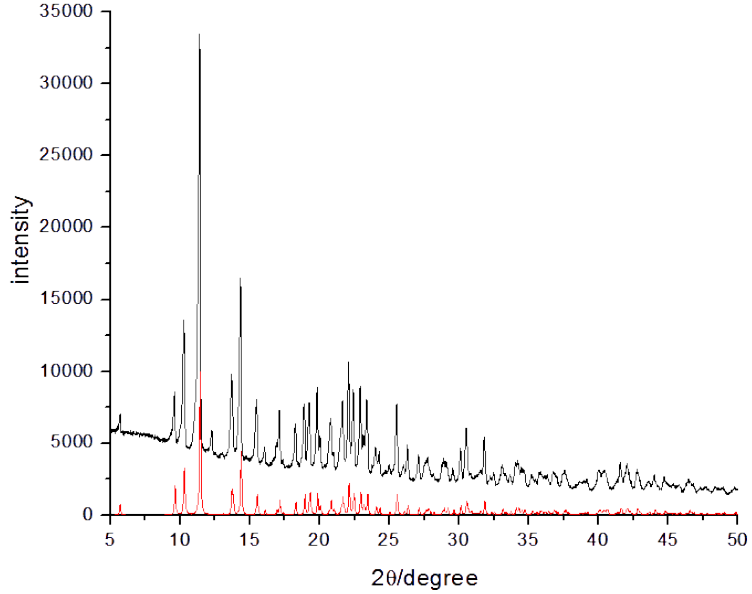


Figure S6. The powder XRD pattern of compound **6** (experimental - black) and the simulation of the powder pattern of **6** from the crystal structure (red).

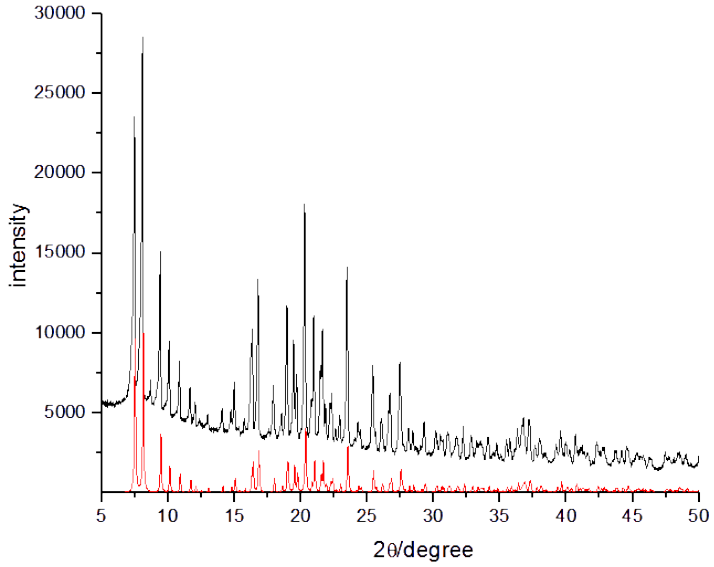


Figure S7. The powder XRD pattern of compound **7** (experimental - black) and the simulation of the powder pattern of **7** from the crystal structure (red).

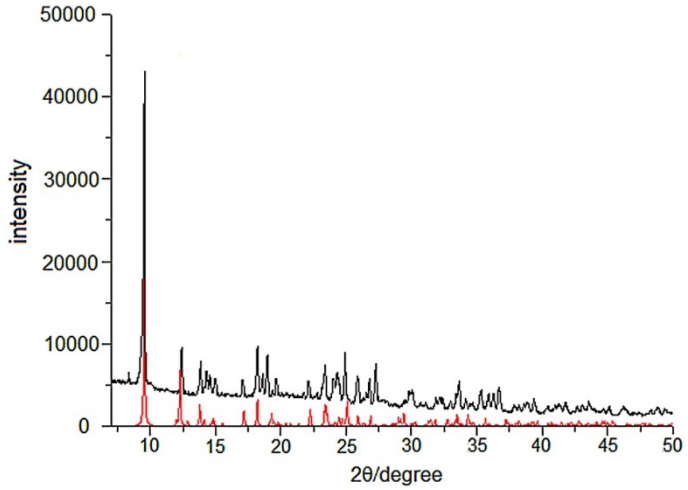


Figure S7. The powder XRD pattern of compound **8** (experimental - black) and the simulation of the powder pattern of **8** from the crystal structure (red).

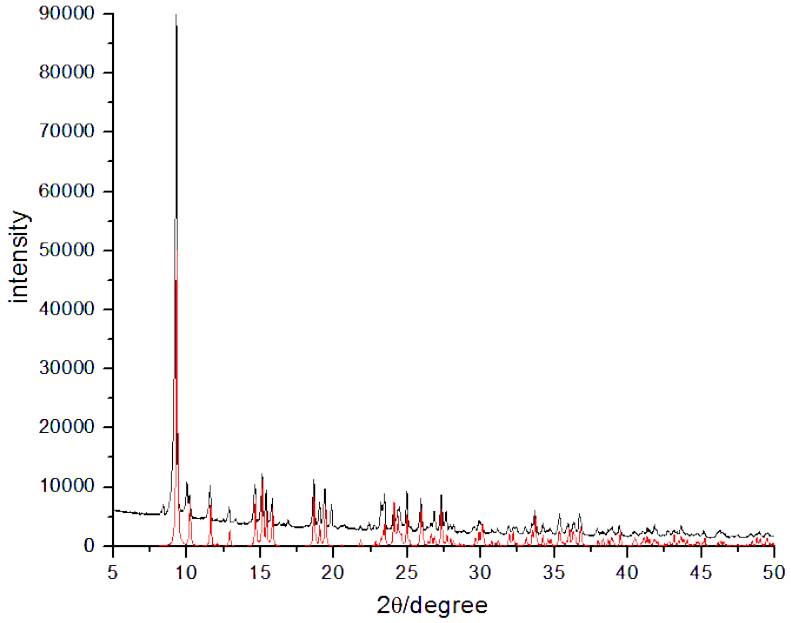


Figure S9. The powder XRD pattern of compound **9** (experimental - black) and the simulation of the powder pattern of **7** from the crystal structure (red).

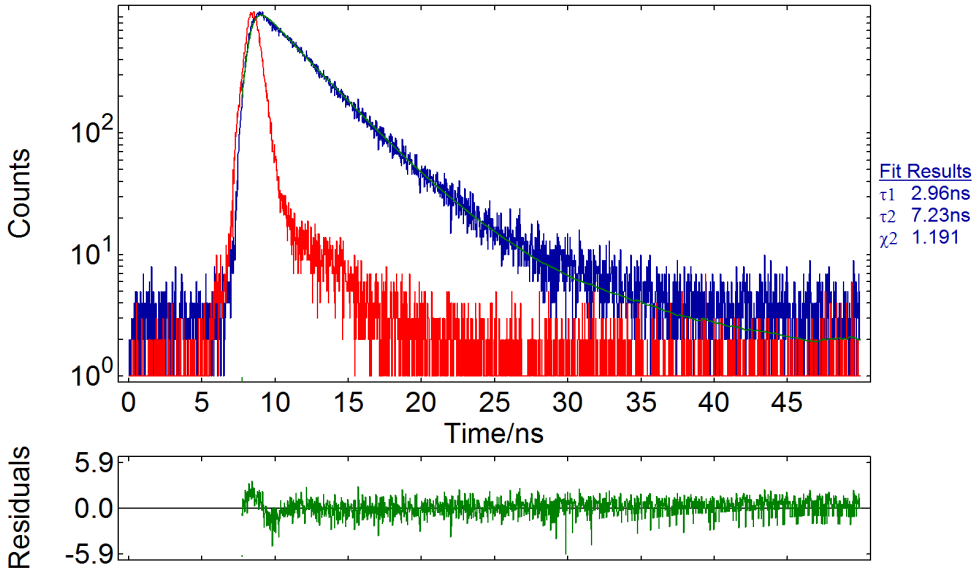


Figure S10. The solid state luminescent decay curve of **terpy**.

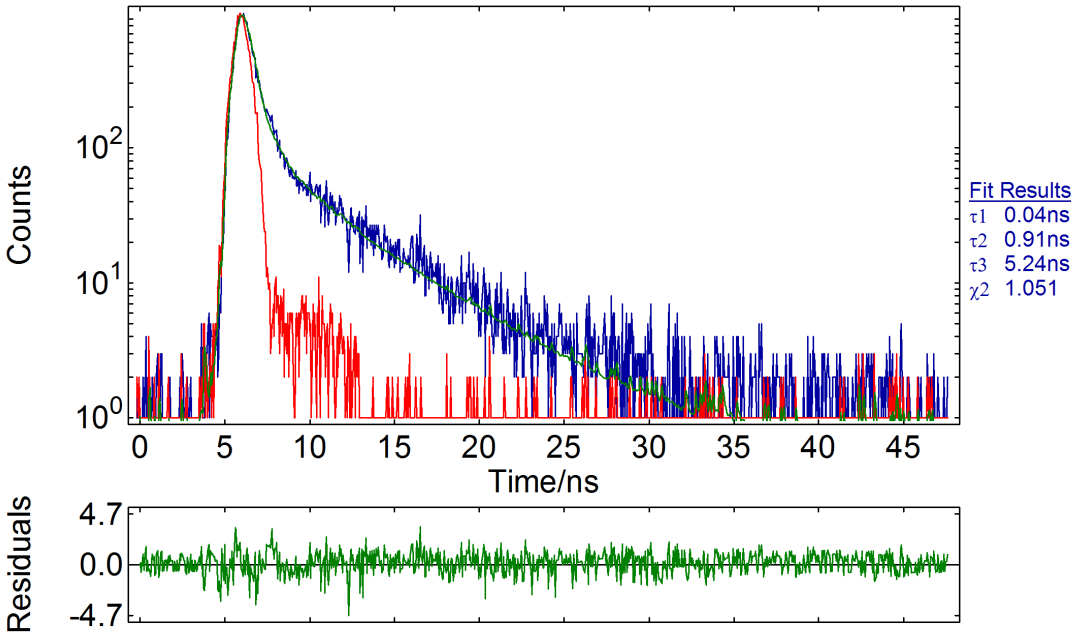


Figure S11. The solid state luminescent decay curve of **tppz**.

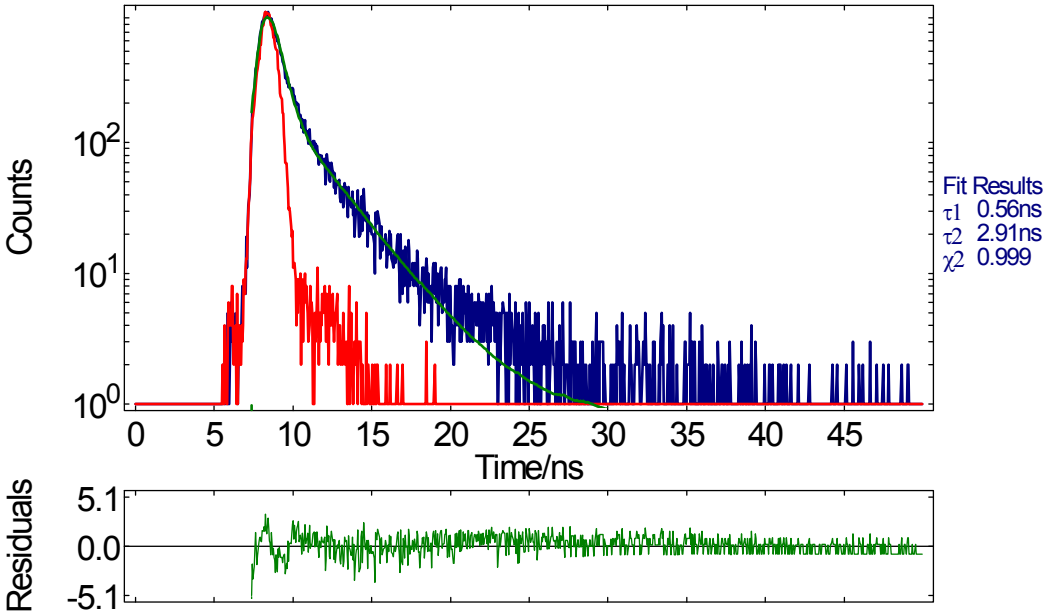


Figure S12. The solid state luminescent decay curve of **1**.

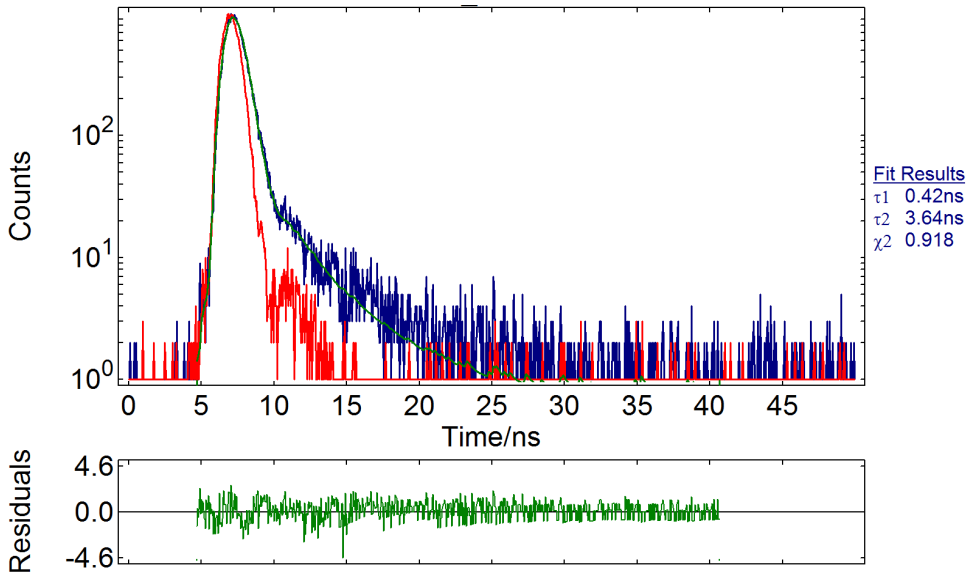


Figure S13. The solid state luminescent decay curve of **2**.

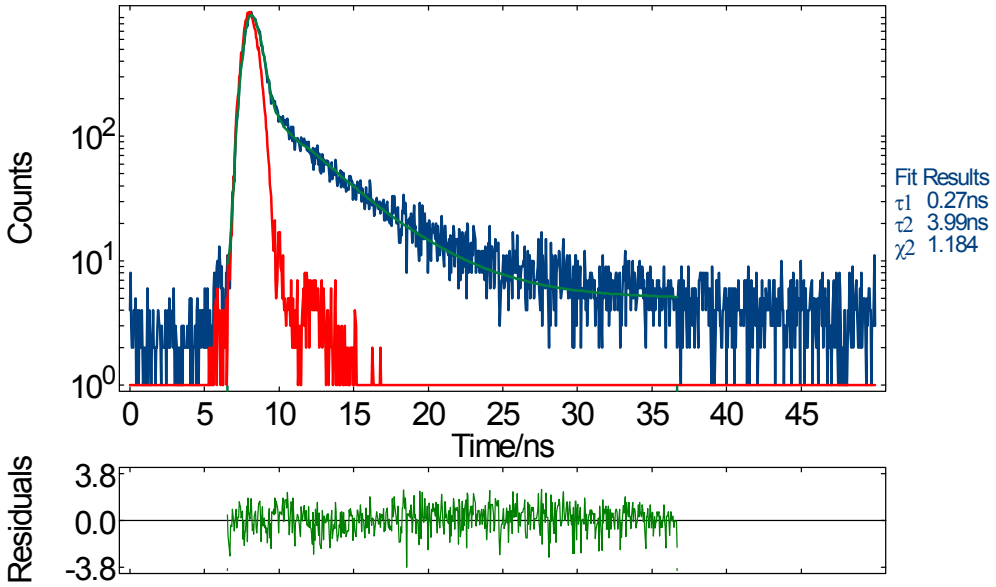


Figure S14. The solid state luminescent decay curve of **3**.

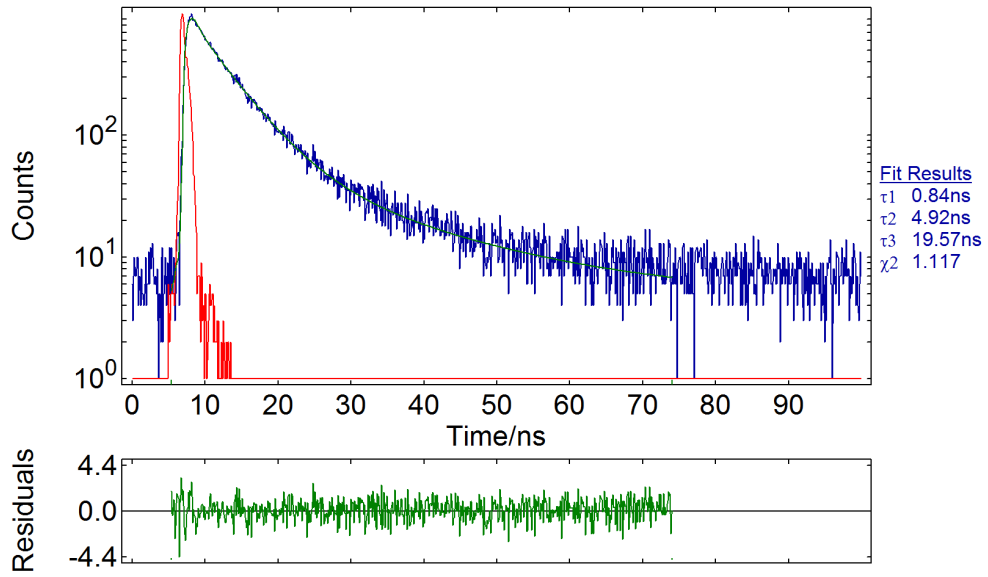


Figure S15. The solid state luminescent decay curve of **4**.

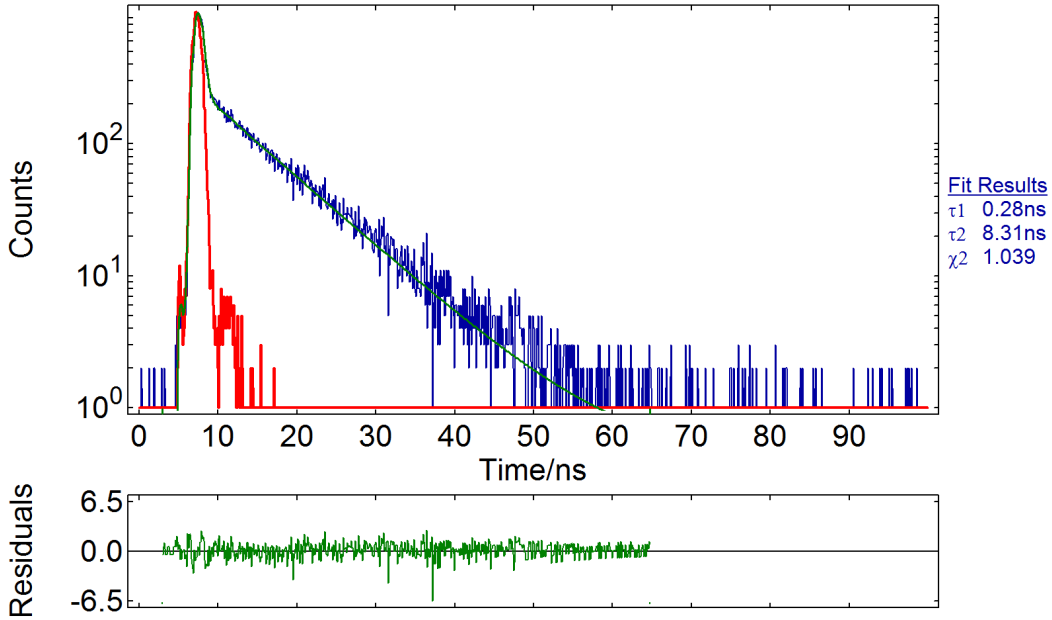


Figure S16. The solid state luminescent decay curve of **5**.

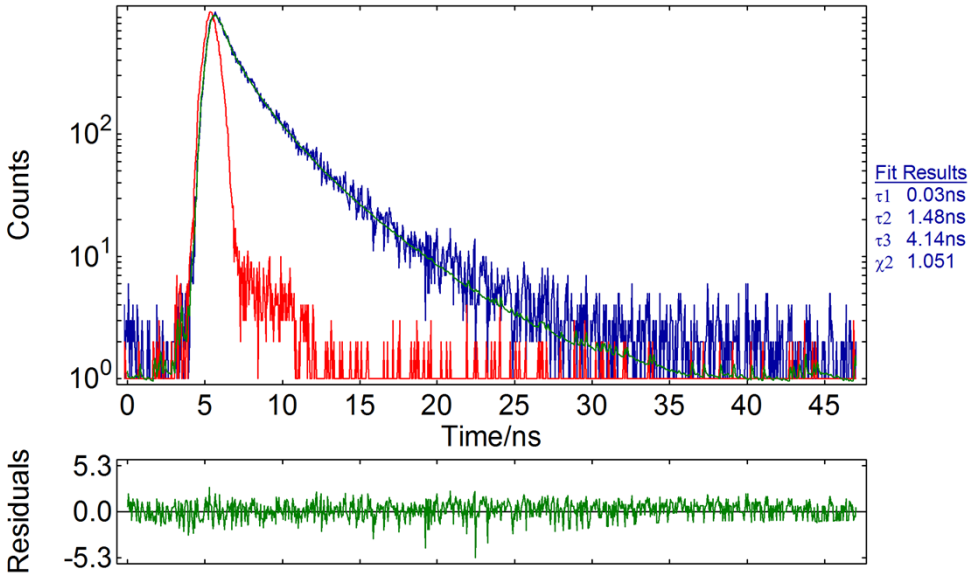


Figure S17. The solid state luminescent decay curve of **6**.

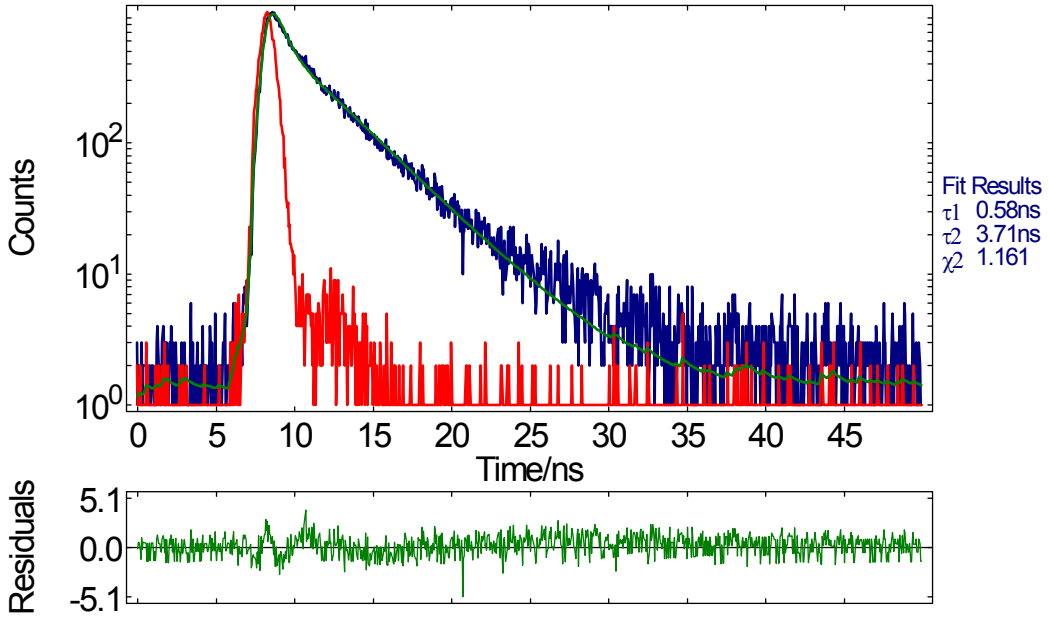


Figure S18. The solid state luminescent decay curve of **7**.

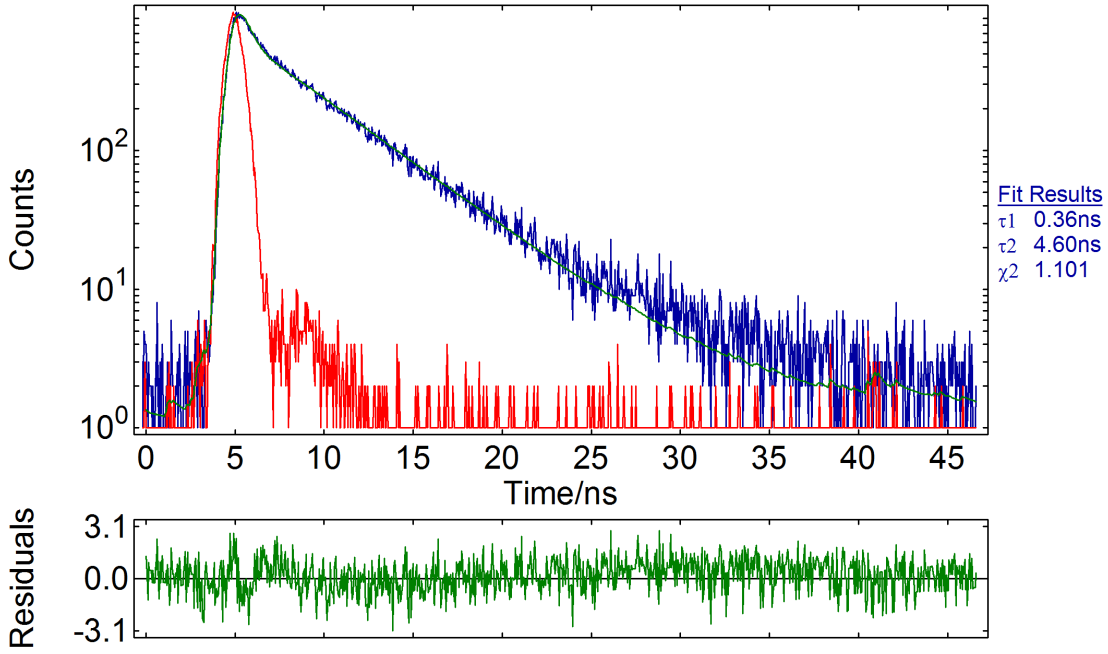


Figure S19. The solid state luminescent decay curve of **8**.

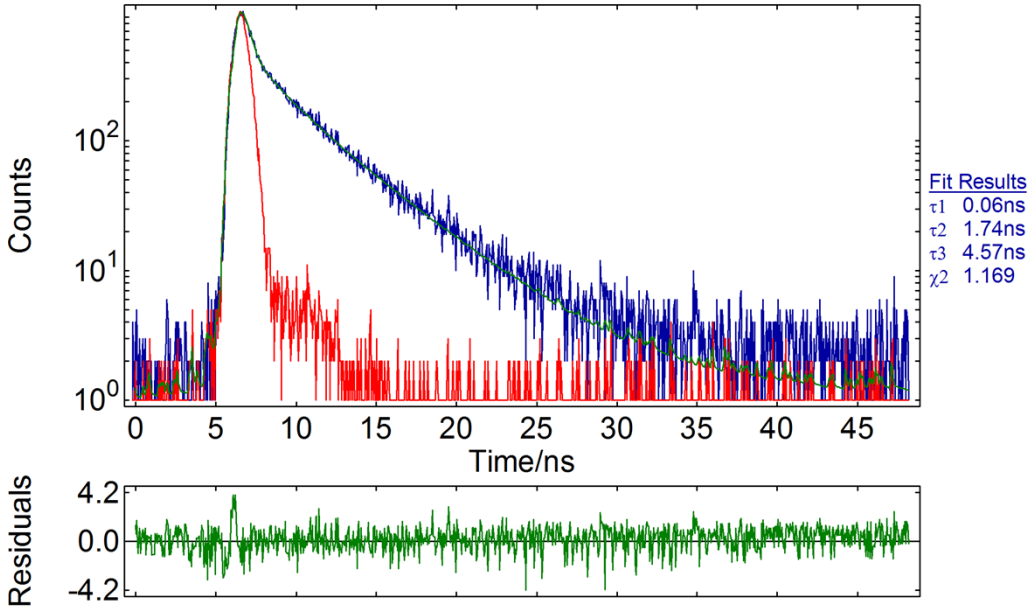


Figure S20. The solid state luminescent decay curve of **9**.

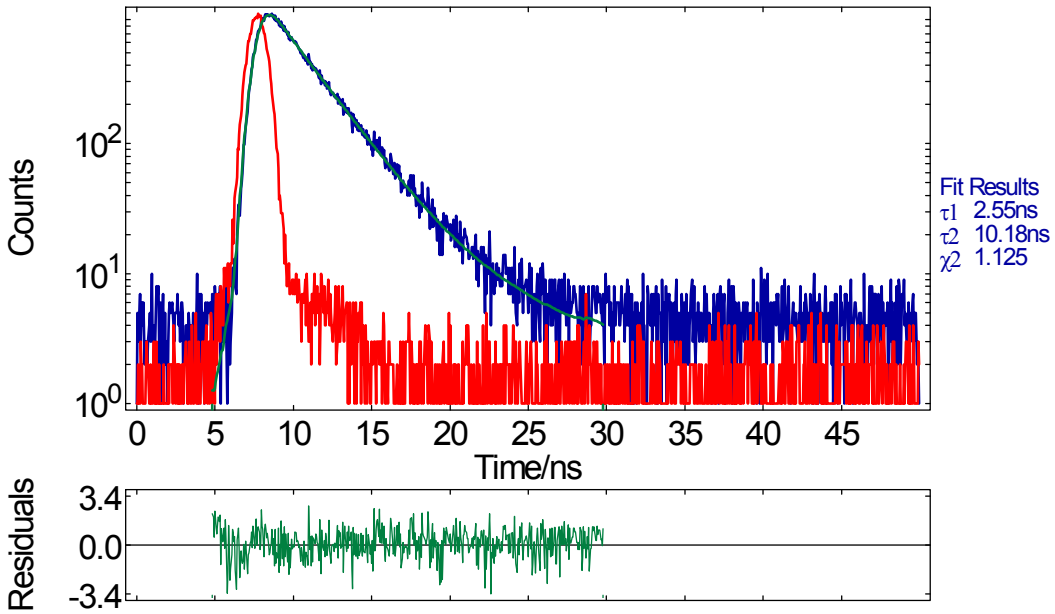


Figure S21. The luminescent decay curve of **terpy** in acetonitrile solution (10^{-4} M).

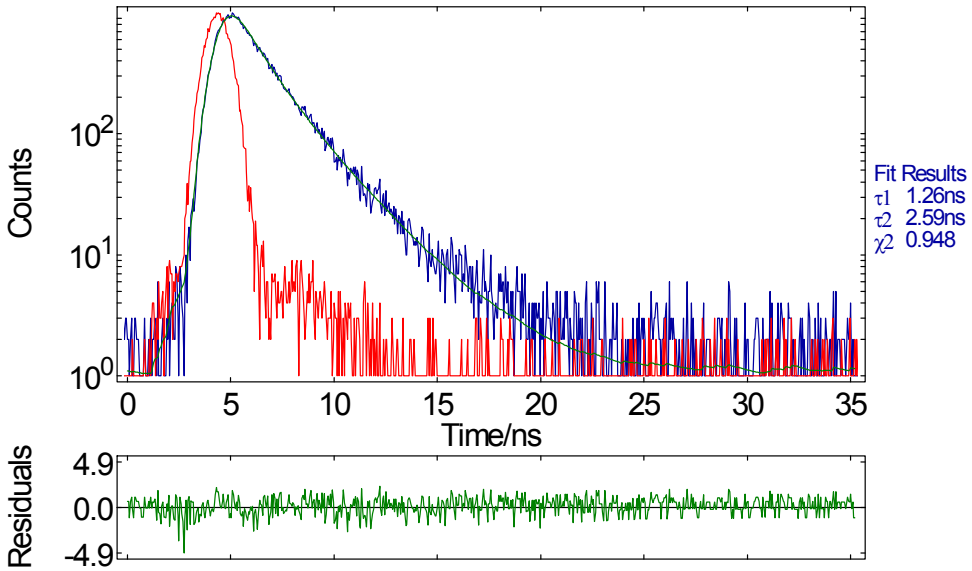


Figure S22. The luminescent decay curve of **tppz** in acetonitrile solution (10^{-4} M).

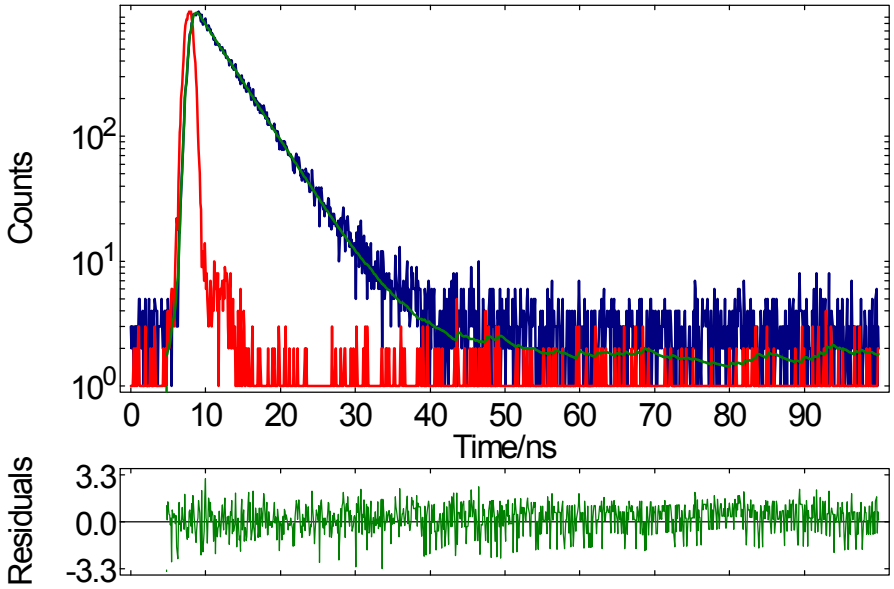


Figure S23. The luminescent decay curve of **4** in acetonitrile solution (10^{-4} M).

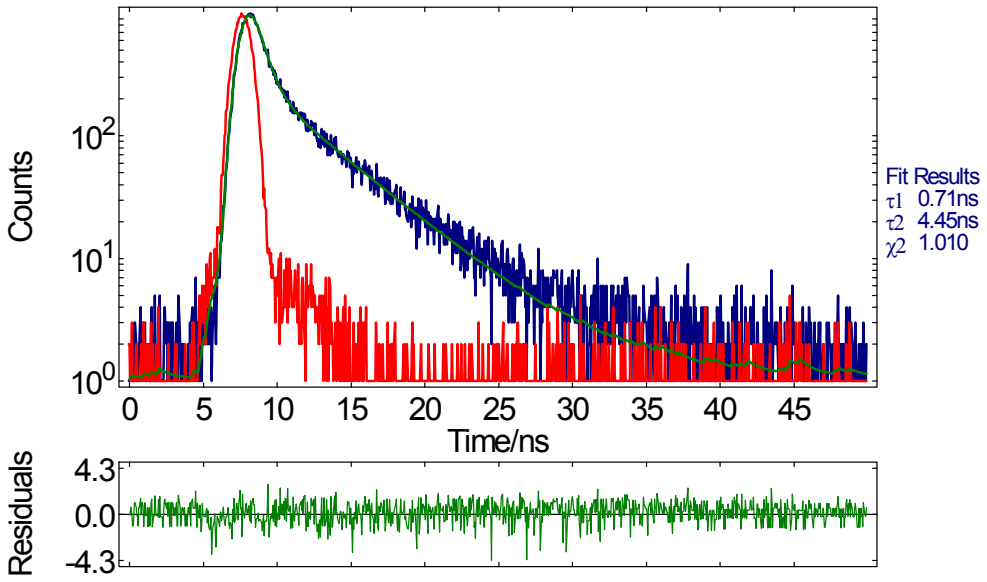


Figure S24. The luminescent decay curve of **5** in acetonitrile solution (10^{-4} M).

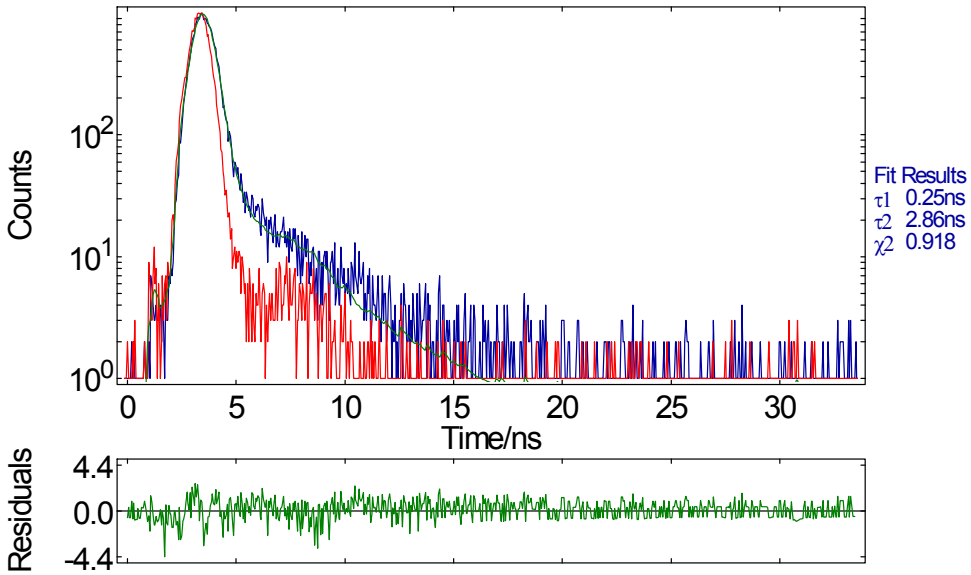


Figure S25. The luminescent decay curve of **7** in acetonitrile solution (10^{-4} M).

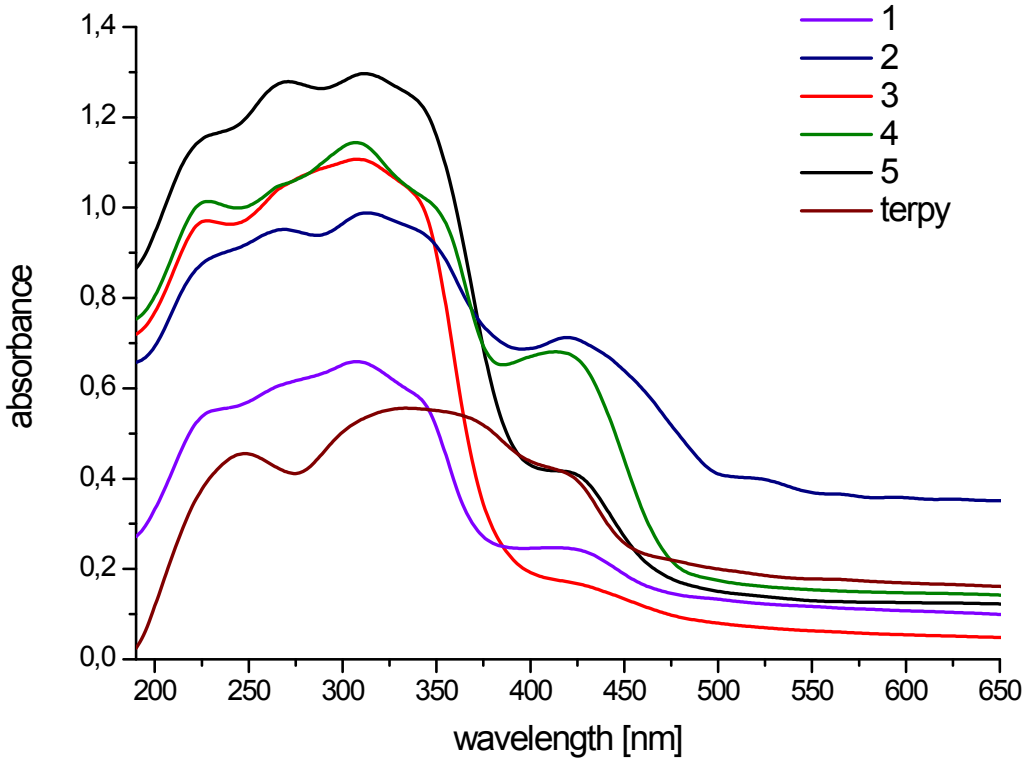


Figure S26. The reflectance spectra of the solid *terpy* and its cadmium complexes **1-5**

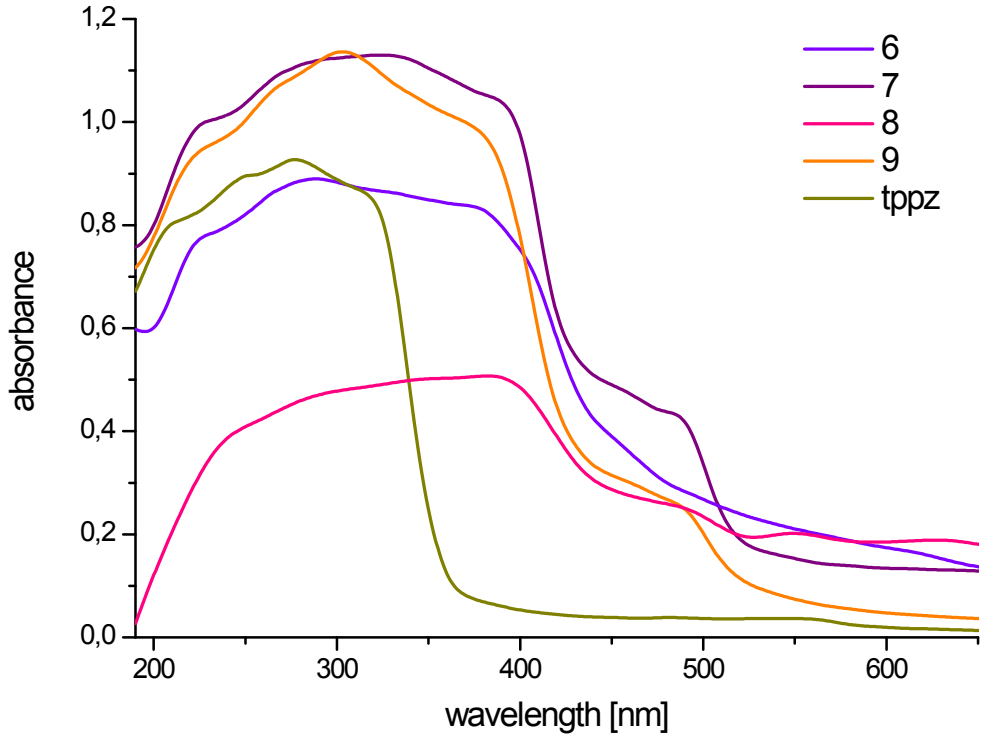


Figure S27. The reflectance spectra of the solid *tppz* and its cadmium complexes **6-9**

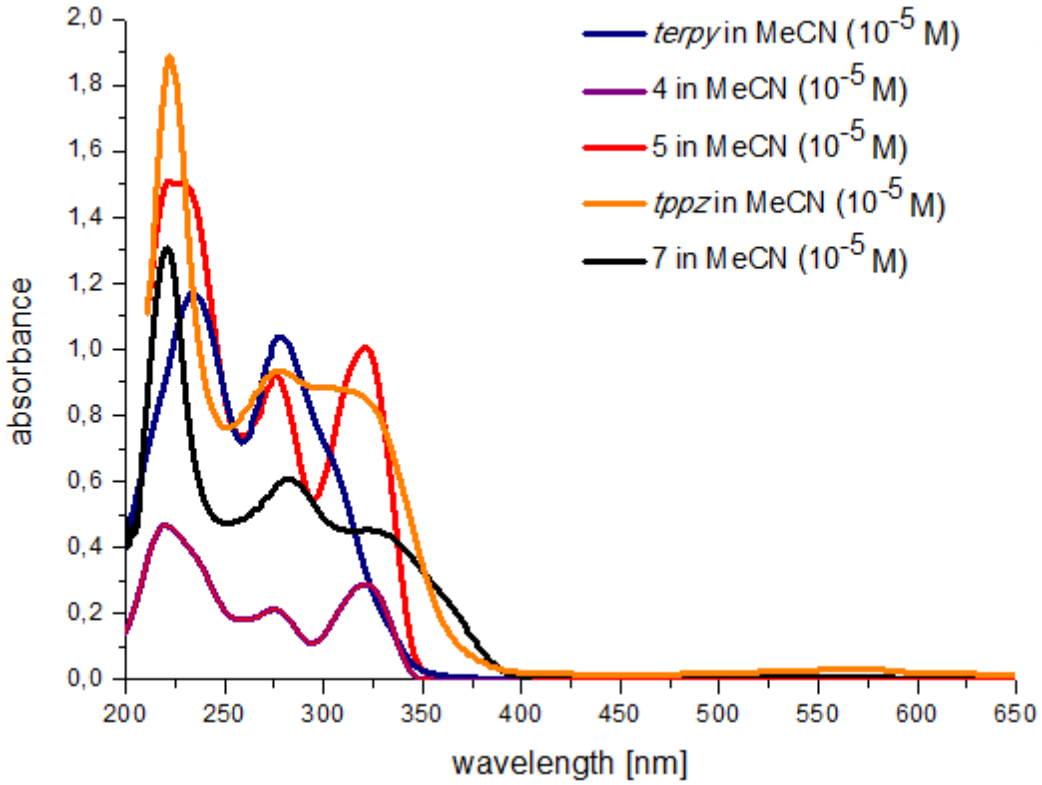


Figure S28. The absorption spectra of the free ligands and cadmium(II) complexes **4**, **5** and **7** in acetonitrile.