Anion- and temperature-dependent assembly, crystal structures and luminescent properties of six new Cd(II) coordination polymers based on 2,3,5,6-tetrakis(2-pyridyl)pyrazine

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Supporting information

Table S**1** Selected bond lengths [Å] and angles[°] for the compounds **1**-**6**.[a]

Compound **1**			
Cd(1)-N(4)	2.314(3)	Cd(1)-N(2)	2.426(3)
Cd(1)-N(3)	2.390(3)	Cd(1)-N(4)#1	2.443(3)
Cd(1)-N(1)	2.403(3)	Cd(1)-Cl(1)	2.4834(11)
N(4)-Cd(1)-N(3)	96.56(12)	N(1)-Cd(1)-N(4)#1	85.26(11)
N(4)-Cd(1)-N(1)	124.95(12)	N(2)-Cd(1)-N(4)#1	78.92(10)
N(3)-Cd(1)-N(1)	136.05(10)	N(4)-Cd(1)-Cl(1)	96.20(8)
N(4)-Cd(1)-N(2)	151.06(11)	N(3)-Cd(1)-Cl(1)	99.66(9)
N(3)-Cd(1)-N(2)	67.99(9)	N(1)-Cd(1)-Cl(1)	90.36(8)
N(1)-Cd(1)-N(2)	68.37(9)	N(2)-Cd(1)-Cl(1)	110.12(7)
N(4)-Cd(1)-N(4)#1	77.11(12)	N(4)#1-Cd(1)-Cl(1)	167.70(9)
N(3)-Cd(1)-N(4)#1	91.42(12)		
Compound **2**			
Cd(1)-N(5)	2.367(3)	Cd(1)-O(1)	2.399(3)
Cd(1)-N(3)	2.367(3)	Cd(1)-N(2)	2.411(2)
Cd(1)-N(1)	2.376(3)	Cd(1)-O(2)	2.431(3)
Cd(1)-N(7)#1	2.357(3)		

N(7)#1-Cd(1)-N(5)	173.88(10)	N(5)-Cd(1)-N(2)	80.76(10)
N(7)#1-Cd(1)-N(3)	92.18(10)	N(3)-Cd(1)-N(2)	68.18(9)
N(5)-Cd(1)-N(3)	87.52(10)	N(1)-Cd(1)-N(2)	69.28(9)
N(7)#1-Cd(1)-N(1)	84.60(11)	O(1)-Cd(1)-N(2)	151.52(9)
N(5)-Cd(1)-N(1)	91.46(10)	N(7)#1-Cd(1)-O(2)	88.49(11)
N(3)-Cd(1)-N(1)	137.04(9)	N(5)-Cd(1)-O(2)	95.97(11)
N(7)#1-Cd(1)-O(1)	92.80(11)	N(3)-Cd(1)-O(2)	136.14(10)
N(5)-Cd(1)-O(1)	93.25(11)	N(1)-Cd(1)-O(2)	86.70(10)
N(3)-Cd(1)-O(1)	83.84(9)	O(1)-Cd(1)-O(2)	52.34(10)
N(1)-Cd(1)-O(1)	139.03(9)	N(2)-Cd(1)-O(2)	155.57(10)
N(7)#1-Cd(1)-N(2)	93.44(10)		

Compound **3**

Cd(1)-N(4)	2.348(4)	Cd(1)-N(6)#1	2.407(4)
Cd(1)-O(1)	2.354(3)	Cd(1)-N(3)	2.415(3)
Cd(1)-O(2)	2.403(3)	Cd(1)-N(2)	2.455(3)
Cd(1)-N(1)	2.405(3)		
N(4)-Cd(1)-O(1)	97.50(12)	O(1)-Cd(1)-N(3)	139.56(10)
N(4)-Cd(1)-O(2)	104.78(12)	O(2)-Cd(1)-N(3)	85.47(9)
O(1)-Cd(1)-O(2)	54.53(9)	N(1)-Cd(1)-N(3)	134.80(9)
N(4)-Cd(1)-N(1)	93.25(12)	N(6)#1-Cd(1)-N(3)	90.65(10)
O(1)-Cd(1)-N(1)	85.37(10)	N(4)-Cd(1)-N(2)	82.25(11)
O(2)-Cd(1)-N(1)	137.34(9)	O(1)-Cd(1)-N(2)	152.46(10)
N(4)-Cd(1)-N(6)#1	168.84(12)	O(2)-Cd(1)-N(2)	152.24(10)
O(1)-Cd(1)-N(6)#1	91.79(11)	N(1)-Cd(1)-N(2)	67.20(9)
O(2)-Cd(1)-N(6)#1	85.64(11)	N(6)#1-Cd(1)-N(2)	86.66(10)
N(1)-Cd(1)-N(6)#1	81.31(11)	N(3)-Cd(1)-N(2)	67.98(9)
N(4)-Cd(1)-N(3)	86.29(11)		

Compound **4**

Cd(1)-N(7)	2.323(5)	Cd(2)-N(4)	2.312(4)
Cd(1)-N(10)	2.363(5)	Cd(2)-N(2)	2.422(4)
Cd(1)-N(4)	2.366(4)	Cd(2)-N(1)	2.422(4)
Cd(2)-N(12)	2.261(5)	Cd(2)-N(3)	2.449(5)
Cd(2)-N(7)	2.300(5)		
N(7)#1-Cd(1)-N(7)	101.2(3)	N(12)-Cd(2)-N(7)	90.41(19)
N(7)#1-Cd(1)-N(10)#1	87.79(18)	N(12)-Cd(2)-N(4)	167.17(18)
N(7)-Cd(1)-N(10)#1	169.26(17)	N(7)-Cd(2)-N(4)	78.04(16)
N(7)#1-Cd(1)-N(10)	169.26(17)	N(12)-Cd(2)-N(2)	104.44(17)
N(7)-Cd(1)-N(10)	87.79(18)	N(7)-Cd(2)-N(2)	152.55(16)
N(10)#1-Cd(1)-N(10)	84.0(3)	N(4)-Cd(2)-N(2)	88.39(15)
N(7)#1-Cd(1)-N(4)	95.67(16)	N(12)-Cd(2)-N(1)	84.39(19)
N(7)-Cd(1)-N(4)	76.51(16)	N(7)-Cd(2)-N(1)	137.29(16)
N(10)#1-Cd(1)-N(4)	96.86(16)	N(4)-Cd(2)-N(1)	100.24(16)
N(10)-Cd(1)-N(4)	92.18(17)	N(2)-Cd(2)-N(1)	68.24(14)

N(7)#1-Cd(1)-N(4)#1	76.50(16)	N(12)-Cd(2)-N(3)	88.85(18)
N(7)-Cd(1)-N(4)#1	95.67(16)	N(7)-Cd(2)-N(3)	92.53(16)
N(10)#1-Cd(1)-N(4)#1	92.18(17)	N(4)-Cd(2)-N(3)	97.14(16)
N(10)-Cd(1)-N(4)#1	96.86(16)	N(2)-Cd(2)-N(3)	65.35(14)
N(4)-Cd(1)-N(4)#1	167.8(2)	N(1)-Cd(2)-N(3)	129.56(15)
Compound **5**			
Cd(1)-N(8)	2.290(4)	Cd(2)-N(10)	2.306(4)
Cd(1)-N(4)	2.313(4)	Cd(2)-N(4)#1	2.338(3)
Cd(1)-N(1)	2.386(3)	Cd(2)-N(13)	2.369(3)
Cd(1)-O(2)	2.404(3)	Cd(2)-O(5)	2.370(3)
Cd(1)-N(2)	2.436(3)	Cd(2)-O(4)	2.432(3)
Cd(1)-N(3)	2.447(3)	Cd(2)-N(11)	2.435(3)
Cd(1)-O(1)	2.464(3)	Cd(2)-N(12)	2.435(3)
N(8)-Cd(1)-N(4)	173.02(14)	N(10)-Cd(2)-N(4)#1	173.85(13)
N(8)-Cd(1)-N(1)	89.96(14)	N(10)-Cd(2)-N(13)	89.16(14)
N(4)-Cd(1)-N(1)	95.62(13)	N(4)#1-Cd(2)-N(13)	93.80(13)
N(8)-Cd(1)-O(2)	83.09(13)	N(10)-Cd(2)-O(5)	87.83(14)
N(4)-Cd(1)-O(2)	92.96(12)	N(4)#1-Cd(2)-O(5)	97.54(13)
N(1)-Cd(1)-O(2)	87.35(12)	N(13)-Cd(2)-O(5)	90.16(12)
N(8)-Cd(1)-N(2)	100.49(13)	N(10)-Cd(2)-O(4)	94.84(14)
N(4)-Cd(1)-N(2)	85.55(12)	N(4)#1-Cd(2)-O(4)	86.07(13)
N(1)-Cd(1)-N(2)	67.71(11)	N(13)-Cd(2)-O(4)	142.65(11)
O(2)-Cd(1)-N(2)	154.69(12)	O(5)-Cd(2)-O(4)	53.03(11)
N(8)-Cd(1)-N(3)	88.76(14)	N(10)-Cd(2)-N(11)	83.60(13)
N(4)-Cd(1)-N(3)	90.34(12)	N(4)#1-Cd(2)-N(11)	90.48(12)
N(1)-Cd(1)-N(3)	134.20(11)	N(13)-Cd(2)-N(11)	134.30(11)
O(2)-Cd(1)-N(3)	137.75(12)	O(5)-Cd(2)-N(11)	134.28(12)
N(2)-Cd(1)-N(3)	67.56(11)	O(4)-Cd(2)-N(11)	83.03(11)
N(8)-Cd(1)-O(1)	83.75(14)	N(10)-Cd(2)-N(12)	93.40(13)
N(4)-Cd(1)-O(1)	89.28(13)	N(4)#1-Cd(2)-N(12)	82.73(12)
N(1)-Cd(1)-O(1)	139.71(12)	N(13)-Cd(2)-N(12)	68.18(11)
O(2)-Cd(1)-O(1)	52.42(12)	O(5)-Cd(2)-N(12)	158.27(12)
N(2)-Cd(1)-O(1)	152.55(11)	O(4)-Cd(2)-N(12)	148.06(11)
N(3)-Cd(1)-O(1)	85.56(12)	N(11)-Cd(2)-N(12)	67.31(11)
Compound **6**			
Cd(1)-N(7)#1	2.299(5)	Cd(2)-N(4)	2.225(4)
Cd(1)-N(4)	2.318(4)	Cd(2)-N(10)	2.239(5)
Cd(1)-N(1)	2.372(4)	Cd(2)-N(7)	2.301(5)
Cd(1)-N(3)	2.375(4)	Cd(2)-N(12)#2	2.352(5)
Cd(1)-N(2)	2.448(4)	Cd(2)-O(2)#3	2.395(4)
Cd(1)-O(2)	2.466(4)	Cd(2)-O(1)	2.474(4)
Cd(1)-O(1)	2.480(4)		
N(7)#1-Cd(1)-N(4)	174.80(17)	N(3)-Cd(1)-O(1)	128.34(13)

N(7)#1-Cd(1)-N(1)	86.88(16)	N(2)-Cd(1)-O(1)	155.25(14)
N(4)-Cd(1)-N(1)	90.26(16)	O(2)-Cd(1)-O(1)	52.54(13)
N(7)#1-Cd(1)-N(3)	100.06(16)	N(4)-Cd(2)-N(10)	160.87(19)
N(4)-Cd(1)-N(3)	85.04(15)	N(4)-Cd(2)-N(7)	93.09(17)
N(1)-Cd(1)-N(3)	134.54(13)	N(10)-Cd(2)-N(7)	102.7(2)
N(7)#1-Cd(1)-N(2)	89.59(16)	N(4)-Cd(2)-N(12)#2	95.00(17)
N(4)-Cd(1)-N(2)	93.30(14)	N(10)-Cd(2)-N(12)#2	96.00(18)
N(1)-Cd(1)-N(2)	67.21(13)	N(7)-Cd(2)-N(12)#2	88.88(18)
N(3)-Cd(1)-N(2)	67.97(14)	N(4)-Cd(2)-O(2)#3	86.98(15)
N(7)#1-Cd(1)-O(2)	75.41(15)	N(10)-Cd(2)-O(2)#3	86.24(17)
N(4)-Cd(1)-O(2)	103.62(14)	N(7)-Cd(2)-O(2)#3	76.79(15)
N(1)-Cd(1)-O(2)	133.37(13)	N(12)#2-Cd(2)-O(2)#3	165.63(16)
N(3)-Cd(1)-O(2)	91.39(14)	N(4)-Cd(2)-O(1)	73.91(14)
N(2)-Cd(1)-O(2)	152.21(14)	N(10)-Cd(2)-O(1)	90.55(19)
N(7)#1-Cd(1)-O(1)	103.50(16)	N(7)-Cd(2)-O(1)	166.73(15)
N(4)-Cd(1)-O(1)	72.26(14)	N(12)#2-Cd(2)-O(1)	89.59(17)
N(1)-Cd(1)-O(1)	92.28(13)	O(2)#3-Cd(2)-O(1)	104.61(14)

[a]Symmetry transformations used to generate equivalentatoms: #1 -x+1,-y+1,-z+1 for compound **1**; #1 x-1,y,z for compound **2**; #1 -x+1/2,y+1/2,-z+3/2 for compound **3**; #1 -x+1,y,-z+5/2 for compound **4**; #1 x,-y+1,z+1/2 for compound **5**; #1 x,-y+1/2,z+1/2 #2 -x+2,-y+1,-z+1 #3 x,-y+1/2,z-1/2 for compound **6**.

Table S**2** Selected details of the hydrogen bonds in compounds **2**-**3**.

	symmetry code	*d*(D–H)/ Å	*d*(H⋯A)/ Å	*d*(D⋯A)/ Å	∠D–H⋯A/ °
Compound **2**					
C(9)–H(9)⋯O(3)	x,y-1,z	0.93	2.53	3.161(5)	125
C(10)–H(10) ⋯O(3)	x,y-1,z	0.93	2.66	3.221(5)	119
Compound **3**					
O(3)–H(3A)⋯O(2)	x, y, z	0.85	2.00	2.844(4)	178.5
O(3)–H(3B)⋯N(4)	-x,-y+1,-z+1	0.85	2.16	3.007(5)	175.7

Table **S3**. Structural comparison of the reported Cd-tppz compounds.[b]

Compound	$[Cd_2(tppz)Cl_4]$[11h]	$[Cd_2(tppz)(NO_3)_4(MeOH)_2]$[11f]	$\{[Cd_2(tppz)Cl_4]\cdot EG\}_n$[11g]	$\{[Cd_2(N_3)_2(tppz)(NO_3)_2]\cdot 2MeOH\}_n$[11b]	$\{[Cd_2(N_3)_4(tppz)]\}_n$[11b]	$\{[Cd_2(tppz)(pic)Cl_3]\}_n$[11h]
Cd(II) salt used for synthesis	$CdCl_2$	$Cd(NO_3)_2$	$CdCl_2$	$Cd(NO_3)_2$	$Cd(NO_3)_2$	$CdCl_2$
Main ligand used for synthesis	pmpc	tppz	tppz	tppz	tppz	pmpc
Coordination mode of the tppz ligand	bis-tridentate μ_2-bridge	bis-tridentate μ_2-bridge	bis-tridentate μ_2-bridge	bis-tridentate μ_2-bridge	bis-tridentate μ_2-bridge	bis-tridentate μ_2-bridge
Coordination number of Cd(II) ions	5-coordinated	7-coordinated	6-coordinated	7-coordinated	7-coordinated	6- and 7-coordinated
Anion of the Cd(II) salt remained in the structure	Cl^-	NO_3^-	Cl^-	NO_3^-	None	Cl^-
Coordination mode of the anion of the Cd(II) salt	μ_1	μ_1	μ_1 and μ_2	μ_1	None	μ_2 and μ_3
Coordination mode of the azide co-ligand	None	None	None	$\mu_{1,1}$-N_3^-	$\mu_{1,1}$-N_3^- and $\mu_{1,3}$-N_3^-	None
Dimensionality / topology of the structure	0D dinuclear cluster	0D dinuclear cluster	1D chain with loops and rods topology	1D chain with loops and rods topology	2D (6,3) network	2D (4,4) network

[b] EG = ethylene glycol; pic = picolinate; pmpc = *N*-(2-pyridyl-methyl) pyridine-2-carbaldimine.

References 11b and 11f – 11h are provided in the main text.

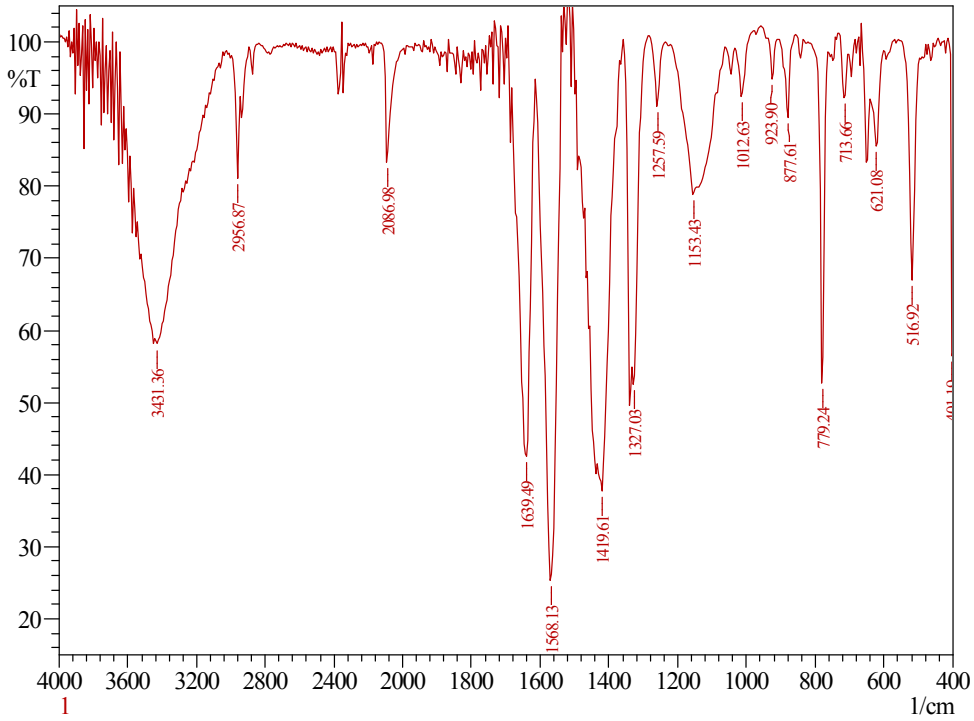

Figure S**1**. FT-IR spectrum of compound **1**.

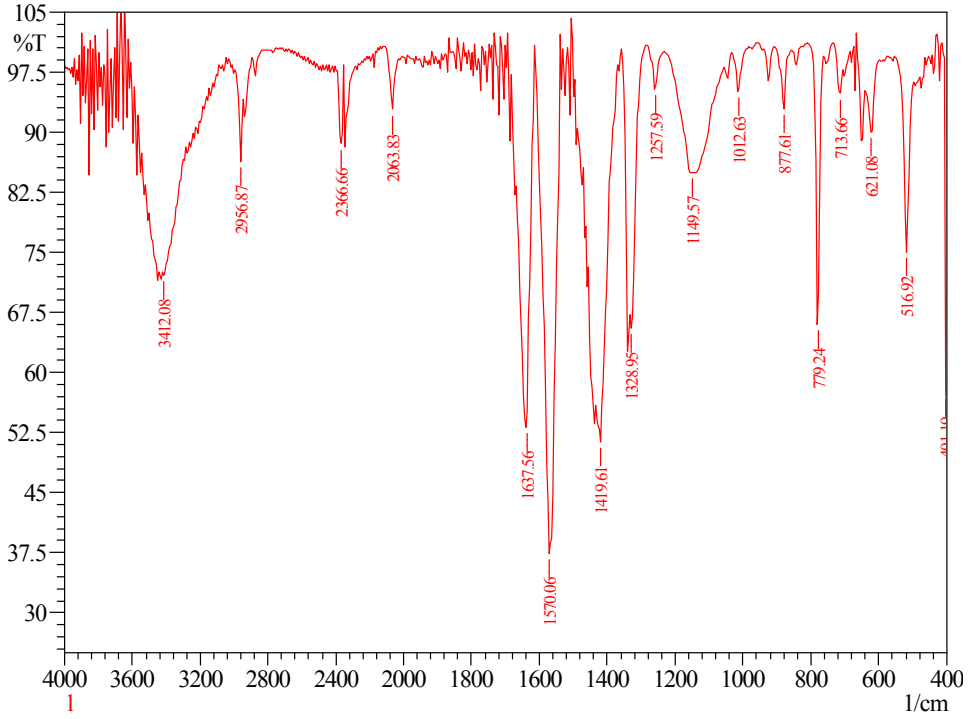

Figure S**2**. FT-IR spectrum of compound **2**.

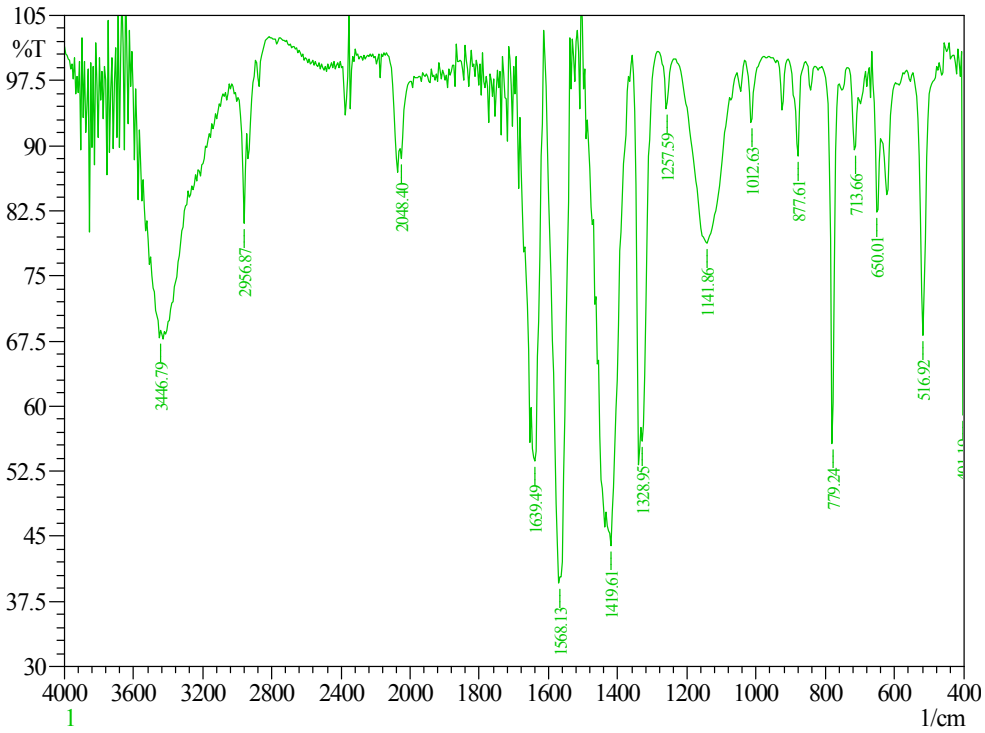

Figure S**3**. FT-IR spectrum of compound **3**.

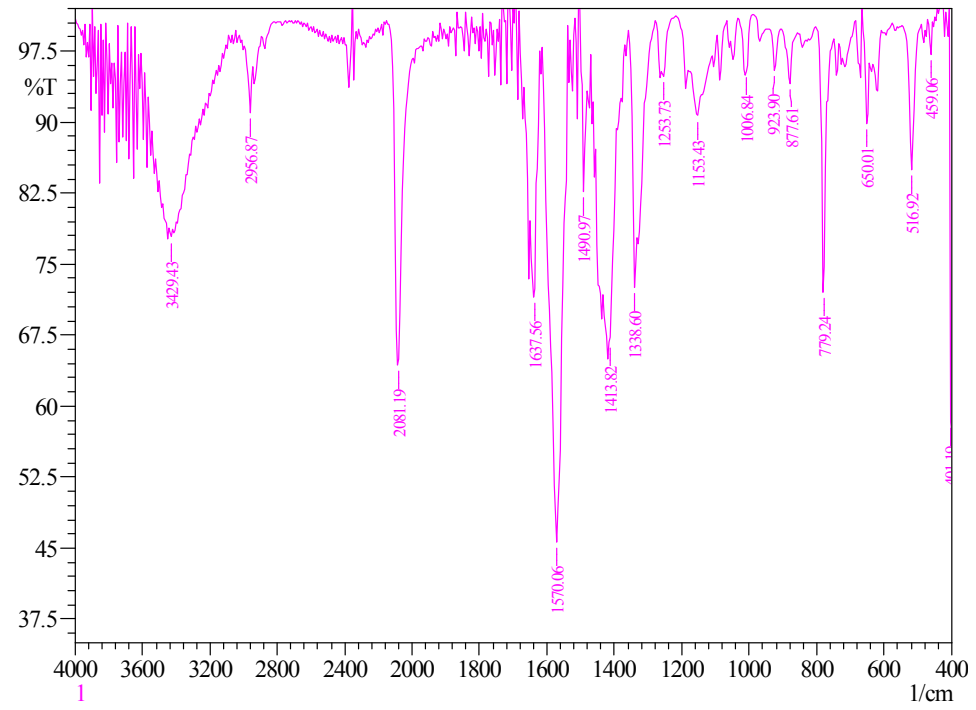

Figure S**4**. FT-IR spectrum of compound **4**.

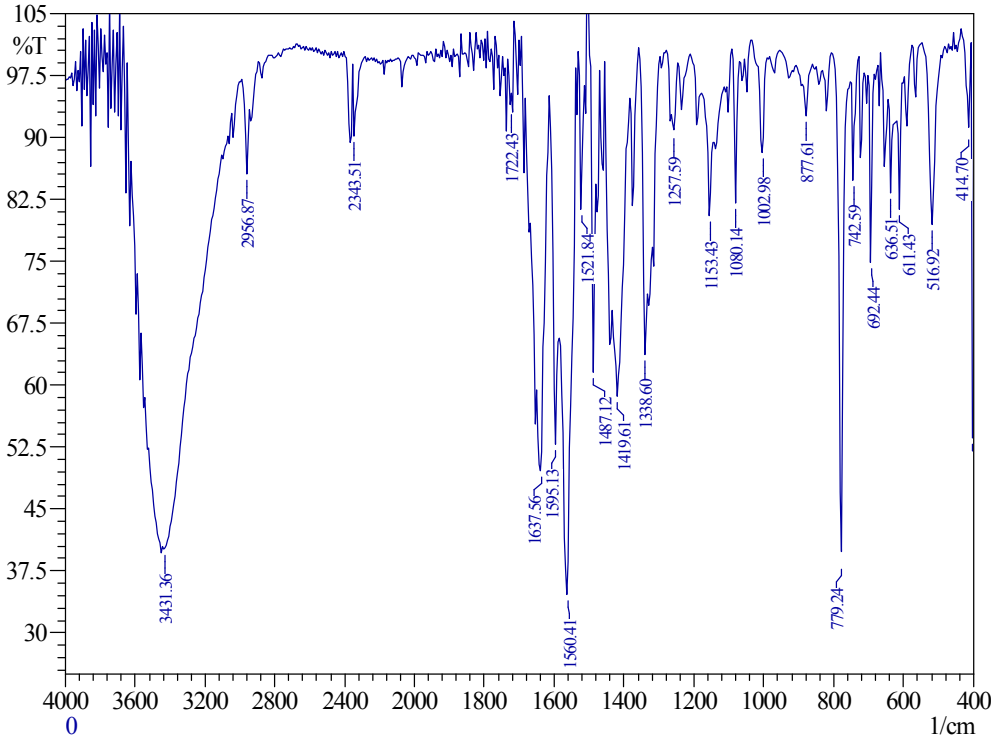

Figure S**5**. FT-IR spectrum of compound **5**.

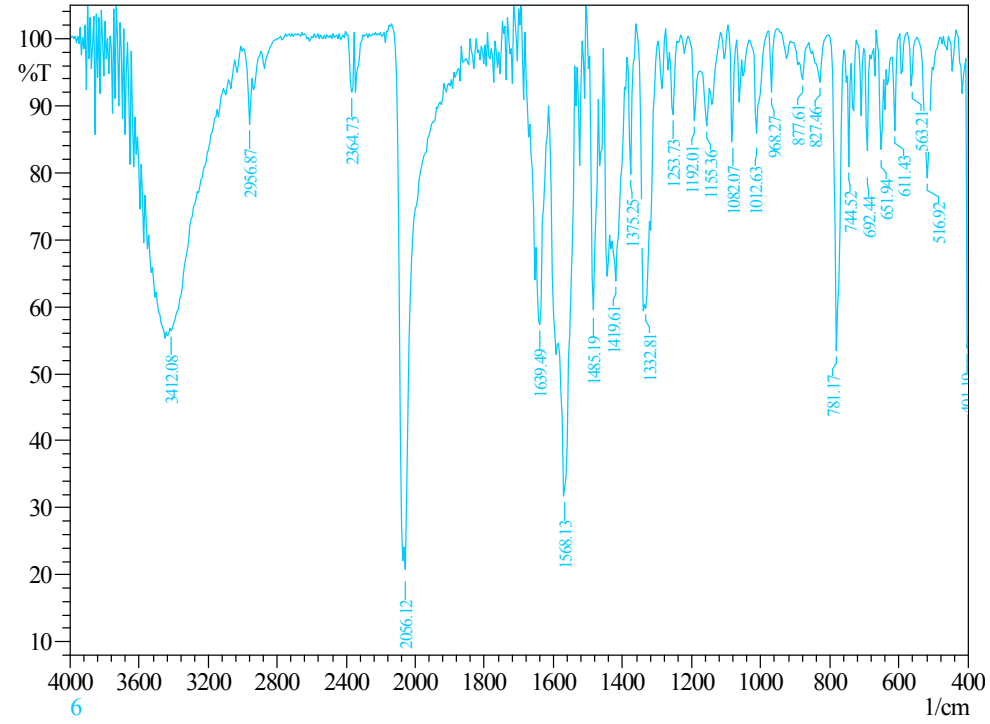

Figure S**6**. FT-IR spectrum of compound **6**.

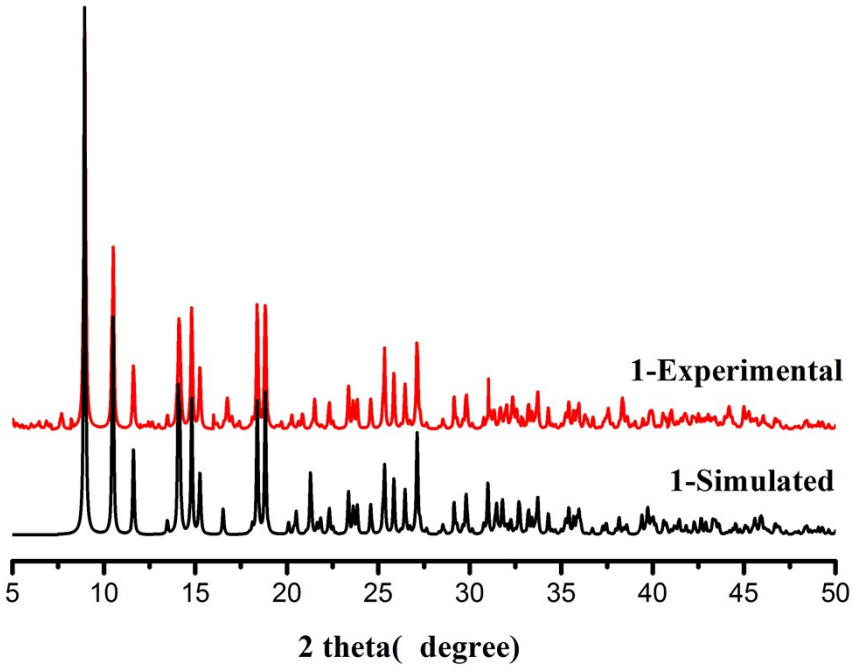

Figure S**7** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **1**.

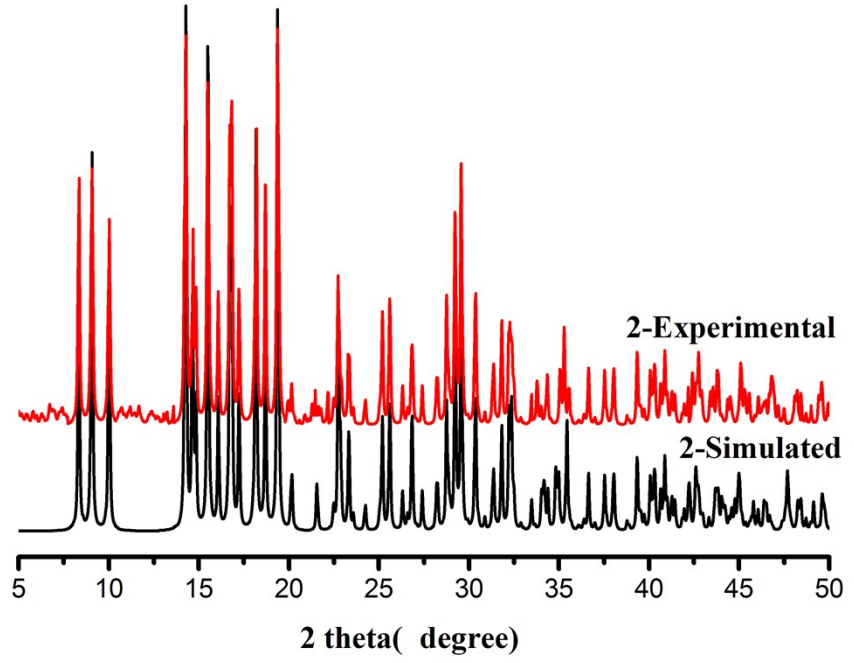

Figure S**8** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **2**.

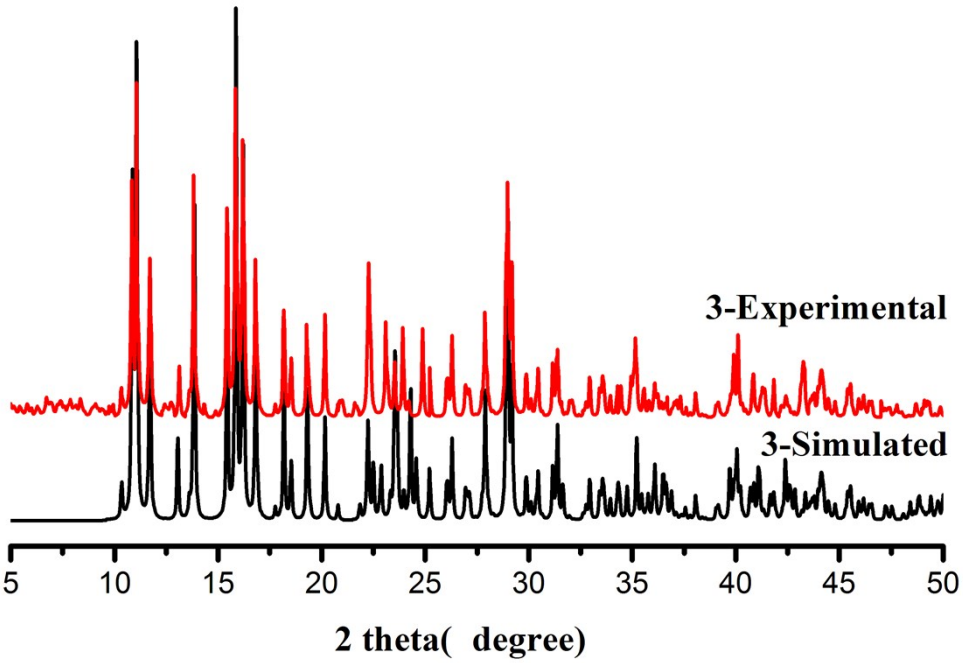

Figure S**9** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **3**.

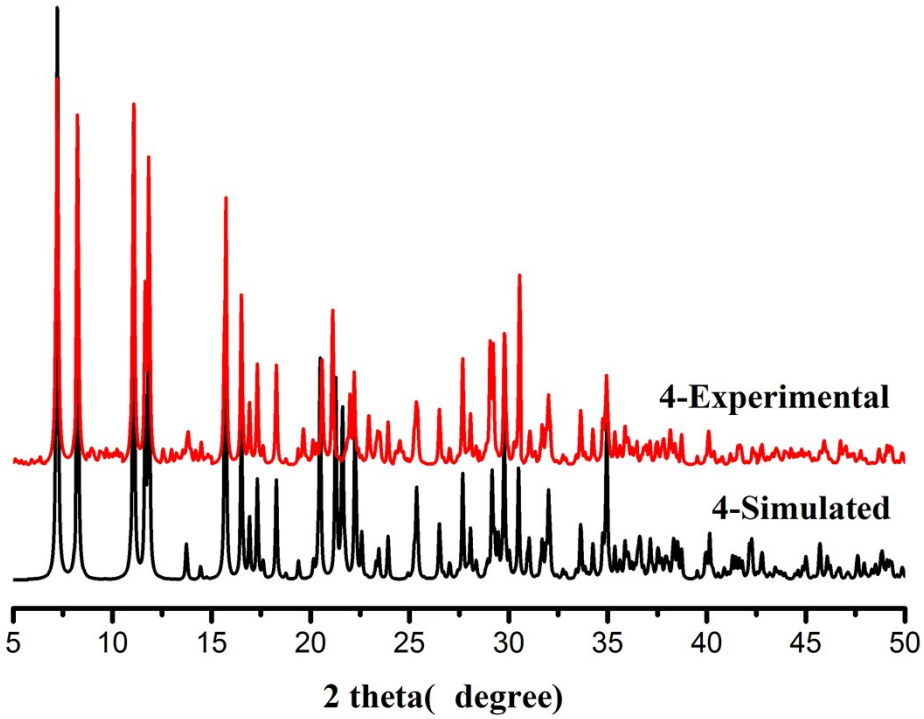

Figure S**10** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **4**.

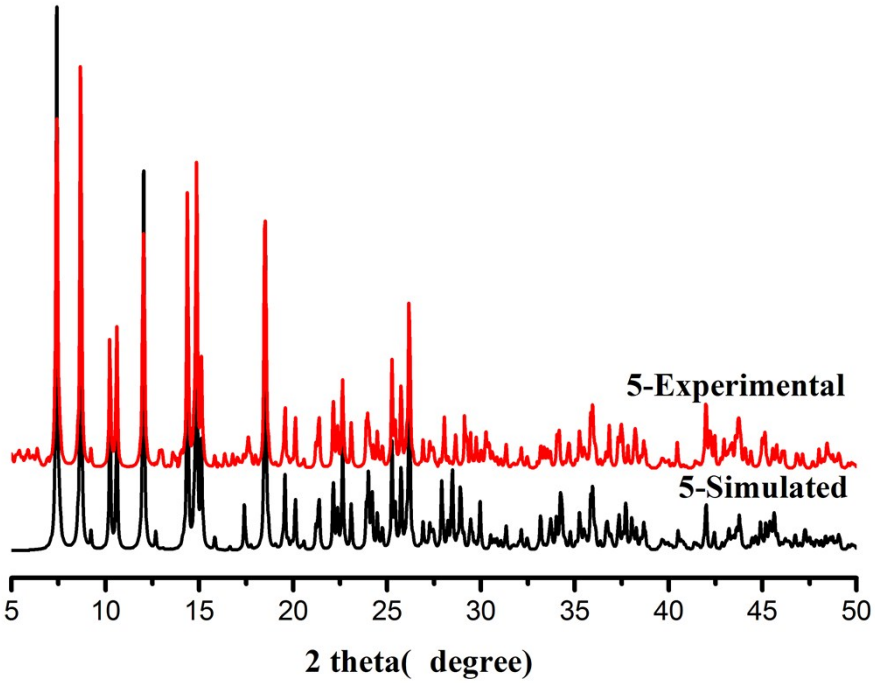

Figure S**11** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **5**.

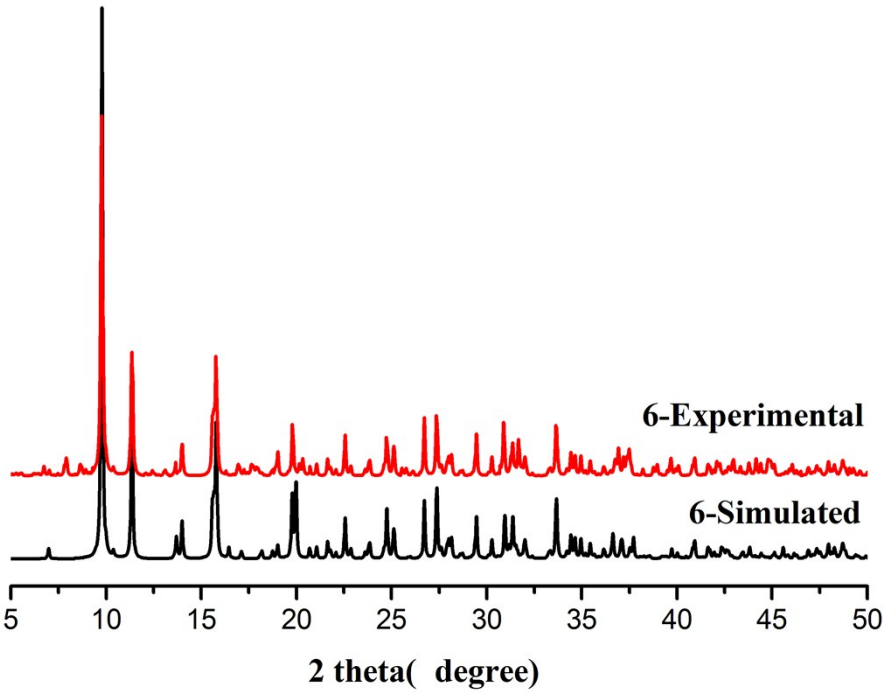

Figure S**12** The simulated X-ray powder diffraction patterns (black) and the experimental one (red) of compound **6**.