Electronic Supplementary Information (ESI)

Introducing a Flexible Tetracarboxylic Acid Linker into Functional Coordination Polymers: Synthesis, Structural Traits, and Photocatalytic Dye Degradation

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*†Electronic Supplementary Information (ESI) contains: Fig. S1: TGA curves, Fig. S2: PXRD patterns, Fig. S3: diffuse reflectance UV-vis spectra, Figs. S4–S8: absorption spectra of the MB solutions in catalytic tests including kinetic data, Figs. S9–S11: additional topological views of crystal structures, Tables S1 and S2: selected bonding and H-bonding parameters for **1**–**5**.*

Table S1 Selected bond lengths (Å) and bond angles (°) for **1**–**5**[a].

		1			
Mn(1)–O(1)	2.330(2)	Mn(1)–O(2)	2.362(2)	Mn(1)–O(3)i	2.129(2)
Mn(1)–O(8)ii	2.263(2)	Mn(1)–O(9)ii	2.368(2)	Mn(1)–N(1)	2.301(2)
Mn(1)–N(2)	2.285(2)	Mn(2)–O(2)	2.306(2)	Mn(2)–O(4)i	2.106(2)
Mn(2)–O(7)ii	2.090(2)	Mn(2)–O(9)ii	2.216(2)	Mn(2)–N(3)	2.250(2)
Mn(2)–N(4)	2.238(3)				
O(3)i–Mn(1)–O(8)ii	86.42(9)	O(3)i–Mn(1)–N(2)	89.65(9)	N(2)–Mn(1)–O(8)ii	139.37(9)
O(3)i–Mn(1)–N(1)	135.03(9)	N(1)–Mn(1)–O(8)ii	83.15(8)	N(1)–Mn(1)–N(2)	71.50(9)
O(3)i–Mn(1)–O(1)	136.58(8)	O(1)–Mn(1)–O(8)ii	127.40(9)	N(2)–Mn(1)–O(1)	80.33(8)
N(1)–Mn(1)–O(1)	81.34(8)	O(3)i–Mn(1)–O(9)ii	93.32(8)	O(8)ii–Mn(1)–O(9)ii	56.03(7)
N(2)–Mn(1)–O(9)ii	164.55(8)	N(1)–Mn(1)–O(9)ii	115.69(8)	O(1)–Mn(1)–O(9)ii	87.15(7)
O(3)i–Mn(1)–O(2)	82.10(7)	O(8)ii–Mn(1)–O(2)	130.30(7)	N(2)–Mn(1)–O(2)	88.90(8)
N(1)–Mn(1)–O(2)	135.61(8)	O(1)–Mn(1)–O(2)	55.79(7)	O(9)ii–Mn(1)–O(2)	76.52(7)
O(4)i–Mn(2)–O(7)ii	99.73(9)	O(4)i–Mn(2)–O(9)ii	95.65(9)	O(9)ii–Mn(2)–O(7)ii	84.06(8)
O(4)i–Mn(2)–N(4)	92.63(10)	N(4)–Mn(2)–O(7)ii	104.15(9)	N(4)–Mn(2)–O(9)ii	167.21(9)
O(4)i–Mn(2)–N(3)	161.76(9)	O(7)ii–Mn(2)–N(3)	95.59(8)	O(9)ii–Mn(2)–N(3)	95.84(9)
N(4)–Mn(2)–N(3)	73.86(10)	O(4)i–Mn(2)–O(2)	80.88(7)	O(7)ii–Mn(2)–O(2)	164.74(8)
O(9)ii–Mn(2)–O(2)	80.71(7)	N(4)–Mn(2)–O(2)	91.02(8)	N(3)–Mn(2)–O(2)	87.05(8)
Mn(2)–O(2)–Mn(1)	95.87(7)	Mn(2)–O(9)ii–Mn(1)	98.19(8)		
		2			
Cd(1)–O(1)	2.463(3)	Cd(1)–O(2)	2.423(3)	Cd(1)–O(3)i	2.256(3)
Cd(1)–O(6)ii	2.362(3)	Cd(1)–O(7)ii	2.456(4)	Cd(1)–N(1)	2.365(4)
Cd(1)–N(2)	2.356(4)	Cd(2)–O(2)	2.422(3)	Cd(2)–O(4)i	2.204(3)
Cd(2)–O(7)ii	2.363(3)	Cd(2)–O(9)ii	2.217(3)	Cd(2)–N(3)	2.301(4)
Cd(2)–N(4)	2.316(4)				
O(3)i–Cd(1)–N(2)	91.37(14)	O(3)i–Cd(1)–O(6)ii	86.54(13)	O(6)ii–Cd(1)–N(2)	140.51(15)
N(1)–Cd(1)–O(3)i	136.99(15)	N(2)–Cd(1)–N(1)	70.14(14)	O(6)ii–Cd(1)–N(1)	84.89(13)
O(3)i–Cd(1)–O(2)	81.80(12)	O(2)–Cd(1)–N(2)	87.00(13)	O(6)ii–Cd(1)–O(2)	131.41(13)
O(2)–Cd(1)–N(1)	132.87(11)	O(3)i–Cd(1)–O(7)ii	91.94(13)	N(2)–Cd(1)–O(7)ii	164.93(13)
O(6)ii–Cd(1)–O(7)ii	54.41(13)	N(1)–Cd(1)–O(7)ii	116.06(13)	O(2)–Cd(1)–O(7)ii	78.94(11)
O(3)i–Cd(1)–O(1)	134.80(12)	O(1)–Cd(1)–N(2)	79.35(14)	O(6)ii–Cd(1)–O(1)	127.55(13)
N(1)–Cd(1)–O(1)	81.09(13)	O(1)–Cd(1)–O(2)	53.83(10)	O(1)–Cd(1)–O(7)ii	87.92(12)
O(4)i–Cd(2)–O(9)ii	97.36(13)	O(4)i–Cd(2)–N(3)	161.55(14)	N(3)–Cd(2)–O(9)ii	99.18(13)
O(4)i–Cd(2)–N(4)	94.63(15)	O(9)ii–Cd(2)–N(4)	109.05(14)	N(4)–Cd(2)–N(3)	72.24(15)
O(4)i–Cd(2)–O(7)ii	96.22(14)	O(7)ii–Cd(2)–O(9)ii	80.59(12)	N(3)–Cd(2)–O(7)ii	94.51(13)
N(4)–Cd(2)–O(7)ii	164.43(12)	O(2)–Cd(2)–O(4)i	80.13(12)	O(2)–Cd(2)–O(9)ii	160.81(12)
N(3)–Cd(2)–O(2)	86.84(12)	N(4)–Cd(2)–O(2)	90.13(13)	O(2)–Cd(2)–O(7)ii	80.79(11)
Cd(1)–O(2)–Cd(2)	95.61(10)	Cd(1)–O(7)ii–Cd(2)	96.25(12)		
		3			
Mn(1)–O(1)	2.135(2)	Mn(1)–O(3)i	2.354(2)	Mn(1)–O(4)i	2.314(2)
Mn(1)–O(8)ii	2.243(2)	Mn(1)–O(9)ii	2.402(2)	Mn(1)–N(1)	2.299(2)
Mn(1)–N(2)	2.264(2)	Mn(2)–O(2)	2.109(2)	Mn(2)–O(4)i	2.321(2)
Mn(2)–O(6)ii	2.104(2)	Mn(2)–O(9)ii	2.207(2)	Mn(2)–N(3)	2.228(2)
Mn(2)–N(4)	2.249(2)				
O(1)–Mn(1)–O(8)ii	85.89(8)	O(1)–Mn(1)–N(2)	89.75(7)	N(2)–Mn(1)–O(8)ii	141.07(8)
O(1)–Mn(1)–N(1)	133.88(7)	N(1)–Mn(1)–O(8)ii	84.39(7)	N(1)–Mn(1)–N(2)	71.16(7)
O(4)i–Mn(1)–O(1)	81.89(6)	O(8)ii–Mn(1)–O(4)i	129.33(6)	N(2)–Mn(1)–O(4)i	88.01(7)
N(1)–Mn(1)–O(4)i	136.29(6)	O(3)i–Mn(1)–O(1)	137.40(6)	O(8)ii–Mn(1)–O(3)i	125.21(8)
O(3)i–Mn(1)–N(2)	82.00(7)	N(1)–Mn(1)–O(3)i	82.46(6)	O(3)i–Mn(1)–O(4)i	56.24(5)
O(9)ii–Mn(1)–O(1)	91.65(6)	O(8)ii–Mn(1)–O(9)ii	55.82(6)	N(2)–Mn(1)–O(9)ii	163.10(7)
N(1)–Mn(1)–O(9)ii	118.55(7)	O(9)ii–Mn(1)–O(4)i	75.53(5)	O(9)ii–Mn(1)–O(3)i	85.61(6)
O(6)ii–Mn(2)–O(2)	100.31(7)	O(6)ii–Mn(2)–O(9)ii	83.88(6)	O(2)–Mn(2)–O(9)ii	96.47(7)
O(6)ii–Mn(2)–N(3)	103.71(7)	O(2)–Mn(2)–N(3)	91.50(7)	N(3)–Mn(2)–O(9)ii	167.88(7)
O(6)ii–Mn(2)–N(4)	94.10(7)	O(2)–Mn(2)–N(4)	160.98(7)	O(9)ii–Mn(2)–N(4)	97.36(7)
N(3)–Mn(2)–N(4)	72.93(7)	O(6)ii–Mn(2)–O(4)i	163.13(6)	O(4)i–Mn(2)–O(2)	81.91(6)
O(9)ii–Mn(2)–O(4)i	79.25(6)	O(4)i–Mn(2)–N(3)	92.91(6)	O(4)i–Mn(2)–N(4)	87.91(6)
Mn(2)–O(4)i–Mn(1)	97.66(5)	Mn(2)–O(9)ii–Mn(1)	98.30(6)		
		4			
Cd(1)–O(1)	2.416(5)	Cd(1)–O(2)	2.318(5)	Cd(1)–O(4)i	2.209(5)
Cd(1)–O(8)ii	2.334(5)	Cd(1)–O(9)ii	2.339(6)	Cd(1)–N(1)	2.272(6)
Cd(2)–O(6)	2.303(4)	Cd(2)–O(6)iii	2.303(4)	Cd(2)–O(10)	2.300(6)
Cd(2)–O(10)iii	2.300(6)	Cd(2)–N(2)	2.379(6)	Cd(2)–N(2)iii	2.379(6)
Cd(3)–O(3)	2.340(5)	Cd(3)–O(3)iv	2.340(5)	Cd(3)–O(11)	2.329(6)
Cd(3)–O(11)iv	2.329(6)	Cd(3)–N(3)	2.317(8)	Cd(3)–N(3)iv	2.317(8)
O(4)i–Cd(1)–N(1)	123.3(2)	O(4)i–Cd(1)–O(2)	84.07(19)	O(2)–Cd(1)–N(1)	133.9(2)
O(4)i–Cd(1)–O(8)ii	125.7(2)	O(8)ii–Cd(1)–N(1)	96.3(2)	O(8)ii–Cd(1)–O(2)	93.91(18)

O(4)i–Cd(1)–O(9)ii	85.3(2)	O(9)ii–Cd(1)–N(1)	91.9(2)	O(9)ii–Cd(1)–O(2)	129.8(2)
O(8)ii–Cd(1)–O(9)ii	55.31(17)	O(4)i–Cd(1)–O(1)	90.5(2)	N(1)–Cd(1)–O(1)	85.5(2)
O(1)–Cd(1)–O(2)	55.32(17)	O(8)ii–Cd(1)–O(1)	131.62(19)	O(9)ii–Cd(1)–O(1)	172.78(19)
O(6)–Cd(2)–O(10)	92.9(2)	O(6)iii–Cd(2)–O(10)	87.1(2)	O(10)–Cd(2)–N(2)	92.0(2)
O(10)iii–Cd(2)–N(2)	88.0(2)	O(6)–Cd(2)–N(2)	88.61(19)	O(6)iii–Cd(2)–N(2)	91.39(19)
O(11)iv–Cd(3)–N(3)	98.8(3)	O(11)–Cd(3)–N(3)	81.2(3)	O(3)–Cd(3)–N(3)	93.4(2)
O(3)–Cd(3)–N(3)iv	86.6(2)	O(11)iv–Cd(3)–O(3)	101.91(18)	O(11)–Cd(3)–O(3)	78.09(18)
		5			
Cd(1)–O(1)	2.468(3)	Cd(1)–O(4)	2.402(3)	Cd(1)–O(3)i	2.363(3)
Cd(1)–O(4)i	2.402(3)	Cd(1)–O(6)ii	2.264(3)	Cd(1)–O(8)ii	2.341(3)
Cd(1)–O(9)ii	2.387(3)	Cd(2)–O(1)	2.291(3)	Cd(2)–O(2)	2.487(4)
Cd(2)–O(6)iii	2.339(3)	Cd(2)–O(10)	2.221(4)	Cd(2)–O(11)	2.281(3)
Cd(2)–N(1)	2.285(5)				
O(6)iii–Cd(1)–O(8)ii	97.73(12)	O(3)i–Cd(1)–O(6)iii	94.32(12)	O(3)i–Cd(1)–O(8)ii	133.79(11)
O(4)–Cd(1)–O(6)iii	146.01(11)	O(8)ii–Cd(1)–O(4)	88.94(11)	O(3)i–Cd(1)–O(4)	104.94(11)
O(6)iii–Cd(1)–O(9)ii	125.94(11)	O(9)ii–Cd(1)–O(8)ii	55.01(11)	O(9)ii–Cd(1)–O(3)i	82.08(12)
O(9)ii–Cd(1)–O(4)	84.92(12)	O(6)iii–Cd(1)–O(4)i	94.04(12)	O(8)ii–Cd(1)–O(4)i	164.07(10)
O(3)i–Cd(1)–O(4)i	55.33(10)	O(4)i–Cd(1)–O(4)	75.34(12)	O(9)ii–Cd(1)–O(4)i	124.51(11)
O(6)iii–Cd(1)–O(1)	74.03(10)	O(8)ii–Cd(1)–O(1)	85.74(11)	O(3)i–Cd(1)–O(1)	140.38(11)
O(1)–Cd(1)–O(4)	73.29(10)	O(9)ii–Cd(1)–O(1)	135.57(11)	O(4)i–Cd(1)–O(1)	87.23(10)
O(10)–Cd(2)–O(11)	96.08(14)	O(10)–Cd(2)–N(1)	95.54(17)	O(11)–Cd(2)–N(1)	87.77(15)
O(10)–Cd(2)–O(1)	148.10(14)	O(1)–Cd(2)–O(11)	99.65(13)	N(1)–Cd(2)–O(1)	112.58(15)
O(10)–Cd(2)–O(6)iii	87.66(12)	O(11)–Cd(2)–O(6)iii	175.73(13)	N(1)–Cd(2)–O(6)iii	93.95(13)
O(1)–Cd(2)–O(6)iii	76.08(11)	O(10)–Cd(2)–O(2)	100.63(13)	O(11)–Cd(2)–O(2)	82.21(13)
N(1)–Cd(2)–O(2)	161.76(13)	O(1)–Cd(2)–O(2)	54.83(11)	O(6)iii–Cd(2)–O(2)	95.09(12)

[a] Symmetry codes: (**1**) i: $x + 1, y, z$; ii: $x + 1, y + 1, z$; (**2**) i: $x + 1, y, z$; ii: $x + 1, y + 1, z$; (**3**) i: $x - 1, y, z$; ii: $x, y + 1, z$; (**4**) i: $x + 1, y, z$; ii: $x + 1, y + 1, z$; iii: $-x + 1, -y, -z + 1$; iv: $-x + 1, -y + 1, -z + 2$; (**5**) i: $-x + 1, -y + 2, -z + 1$; ii: $-x + 1, -y + 1, -z + 2$; iii: $x, y, z - 1$.

Table S2 Hydrogen bonds in crystal packing [Å, °] for **4** and **5**.

Compound	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry code
4	O(10)–H(1W)···O(7)	0.850	1.866	2.716	179.58	$-x + 1, -y, -z + 1$
	O(10)–H(2W)···O(12)	0.850	2.016	2.866	179.72	$-x + 2, -y + 1, -z + 1$
	O(11)–H(4W)···N(4)	0.850	1.849	2.699	178.08	$x, y - 1, z$
	O(12)–H(5W)···O(6)	0.850	2.049	2.899	179.09	$x, y + 1, z$
	O(12)–H(6W)···O(13)	0.884	1.880	2.752	168.59	$x + 1, y, z$
	O(13)–H(7W)···O(2)	0.850	2.125	2.975	179.60	$x - 1, y, z$
	O(13)–H(8W)···O(7)	0.900	2.490	3.386	174.09	$x, y + 1, z$
5	O(10)–H(1W)···O(8)	0.850	1.872	2.722	179.20	$x + 1, y, z - 1$
	O(11)–H(3W)···O(9)	0.849	1.865	2.693	164.50	$-x + 2, -y + 1, -z + 2$
	O(11)–H(4W)···O(1)	0.829	2.271	3.057	158.49	$-x + 2, -y + 2, -z + 1$

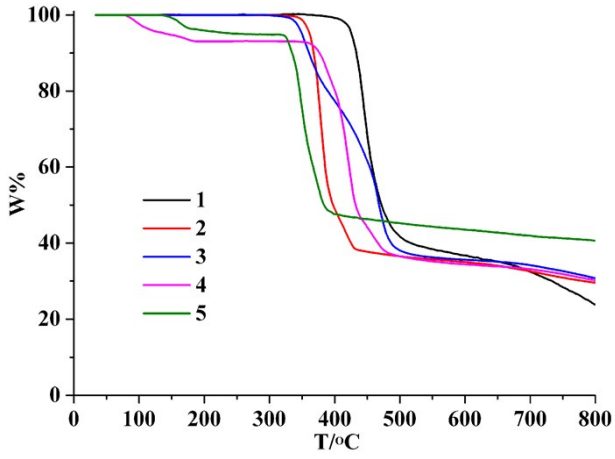

Fig. S1. TGA curves for **1**–**5**.

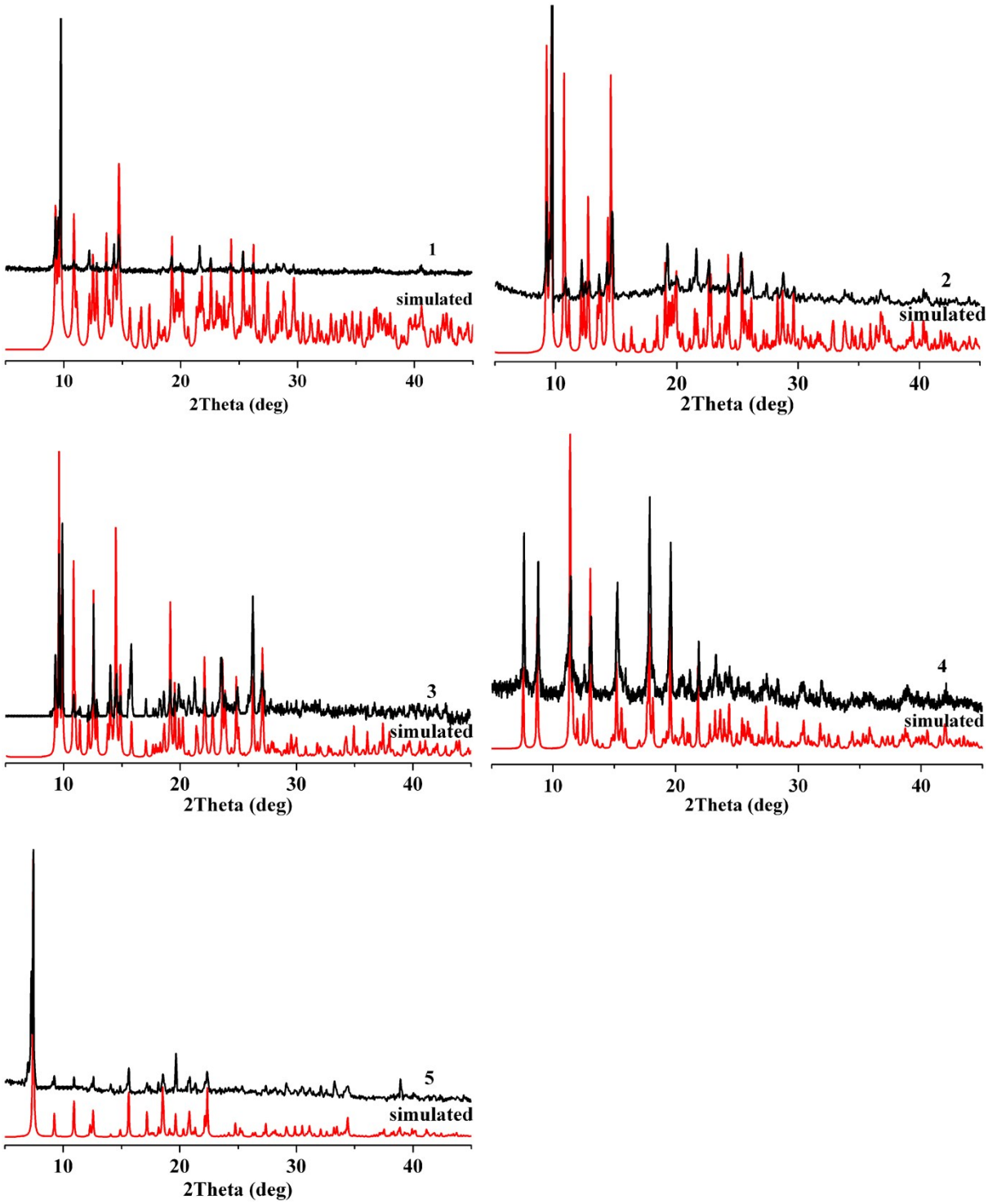

Fig. S2. PXRD patterns of compounds **1**–**5** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

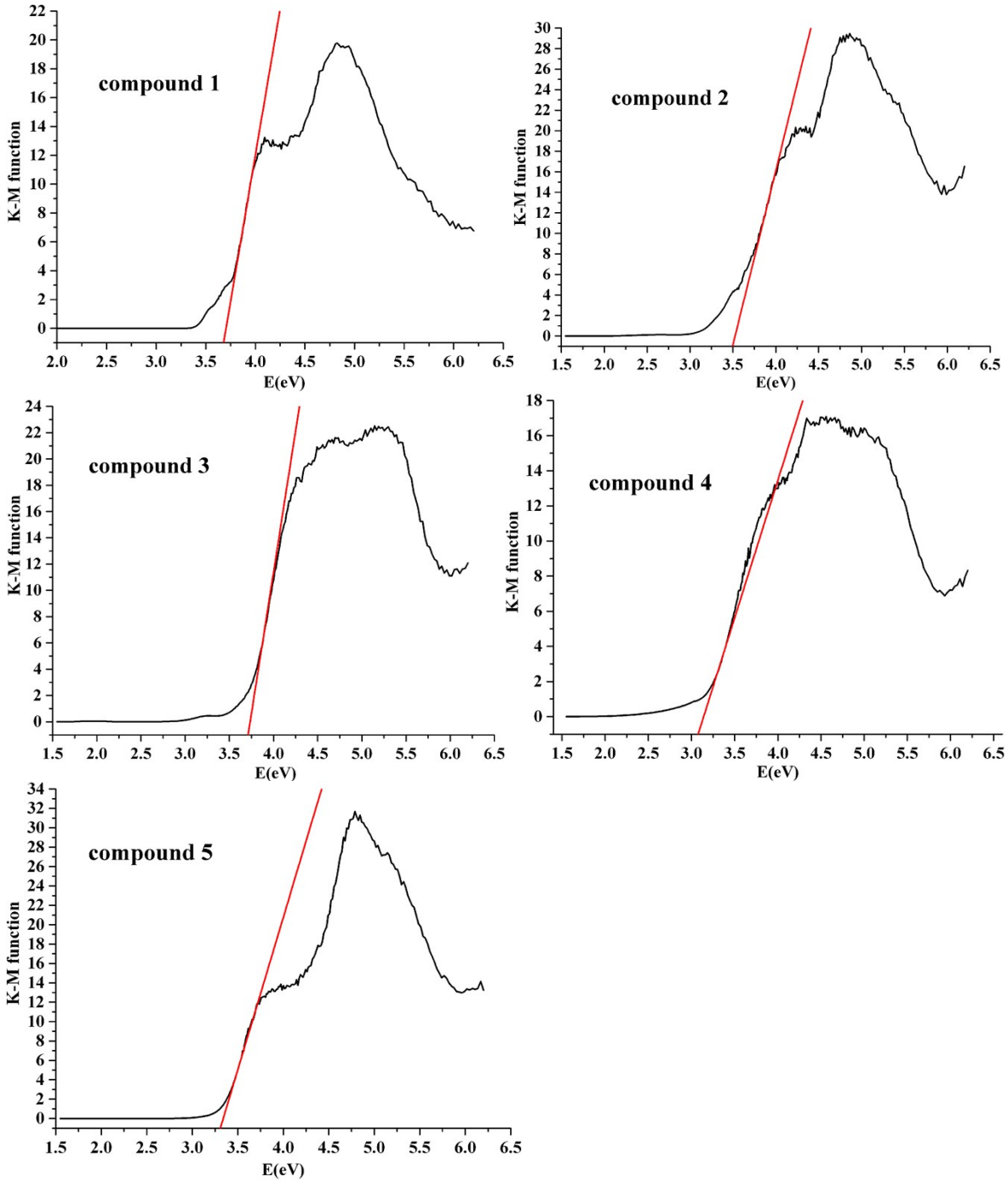

Fig. S3. Kubelka-Munk-transformed diffuse reflectance spectra for **1**–**5**.

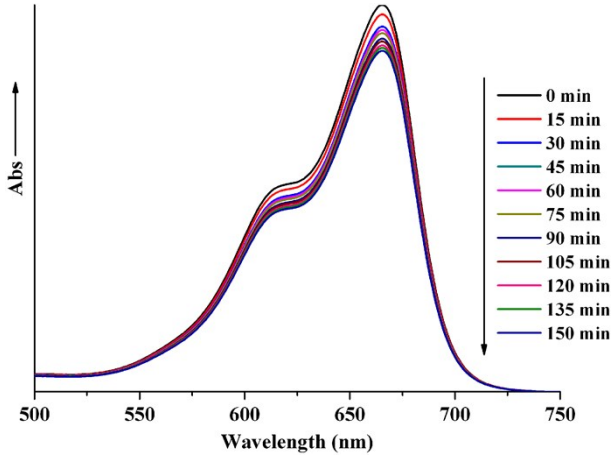

Fig. S4. Time-dependent UV-Vis spectra of the reaction mixture in the course of the MB photodegradation (blank test without catalyst). Reaction conditions: 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

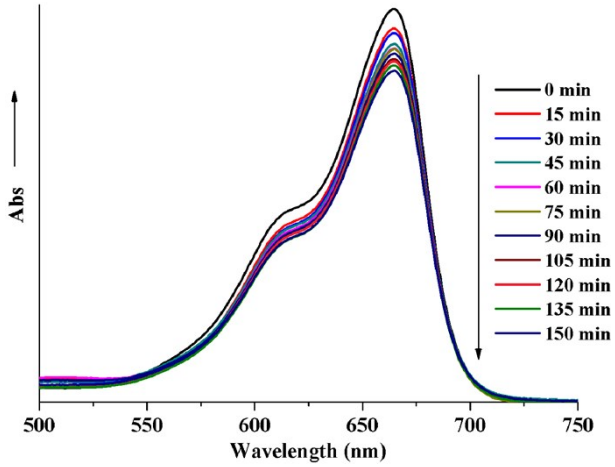

Fig. S5. Time-dependent UV-Vis spectra of the reaction mixture in the course of the MB photodegradation catalyzed by H_4deta (blank test). Reaction conditions: H_4deta (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

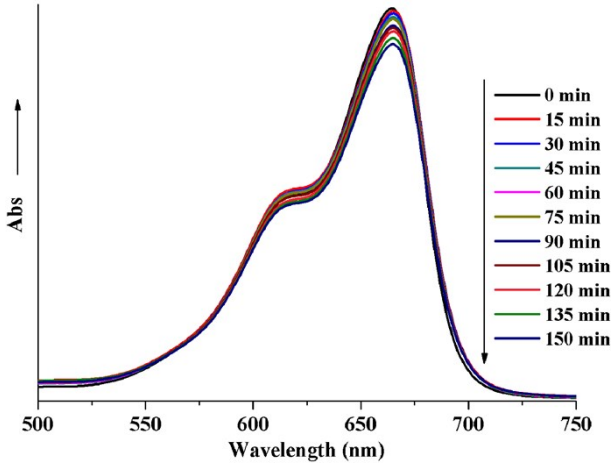

Fig. S6. Time-dependent UV-Vis spectra of the reaction mixtures in the course of the MB photodegradation catalyzed by 4,4′-bipy (blank test). Reaction conditions: 4,4′-bipy (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

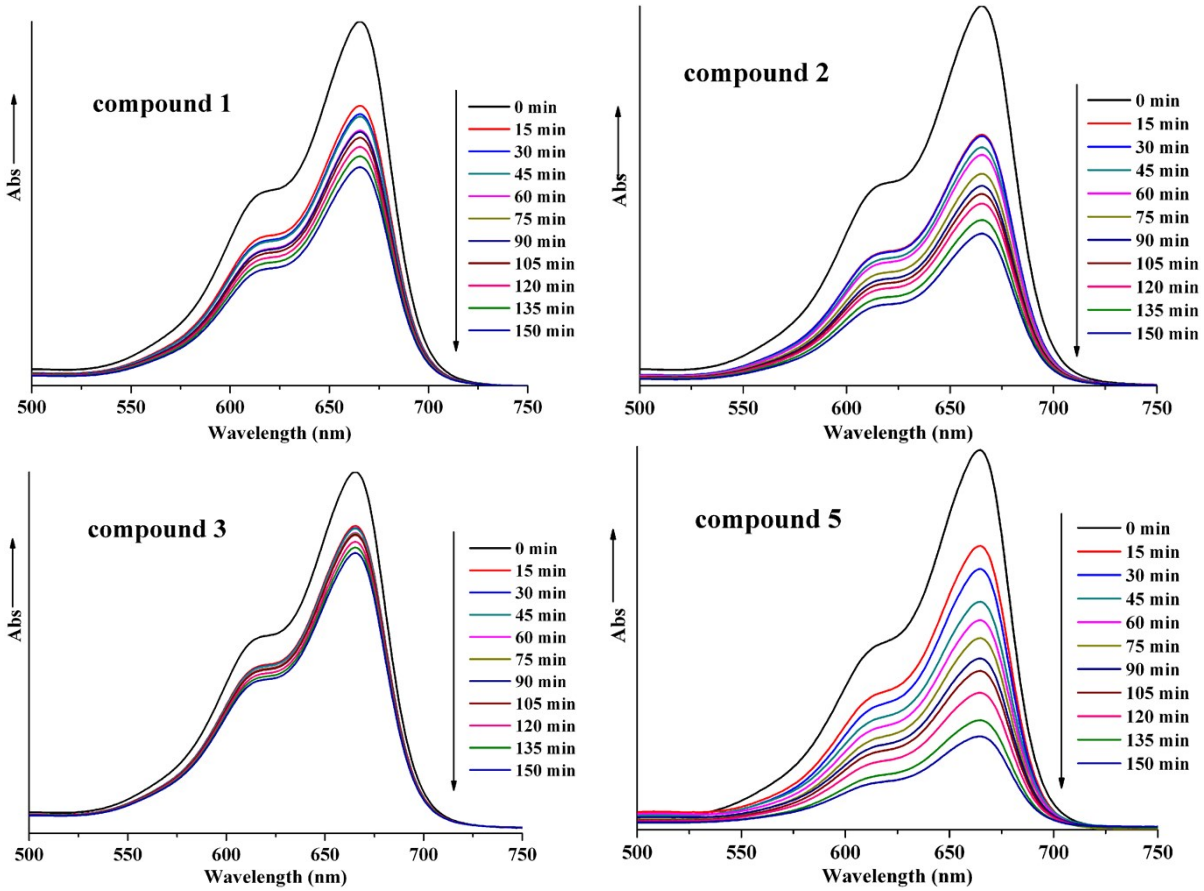

Fig. S7. Time-dependent UV-Vis spectra of the reaction mixtures in the course of the MB photodegradation catalyzed by **1**–**3** and **5**. Reaction conditions: catalyst (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

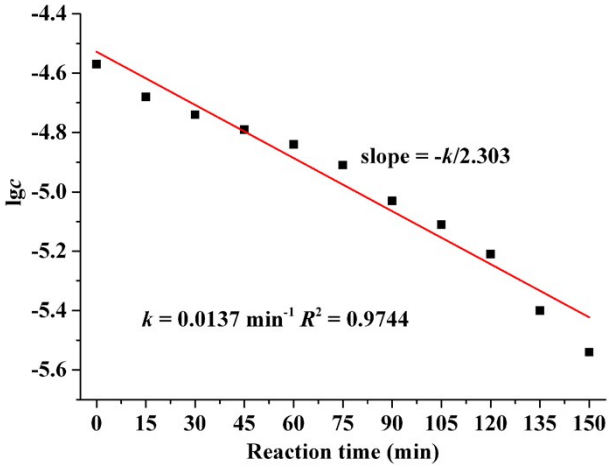

Fig. S8. Relationship between lg[c] and reaction time in the course of the MB photodegradation catalyzed by **4**. The red line corresponds to a linear fit. Reaction conditions: catalyst (50 mg), 100 mL aqueous solution, MB (1 mg), under 125 W Hg lamp irradiation.

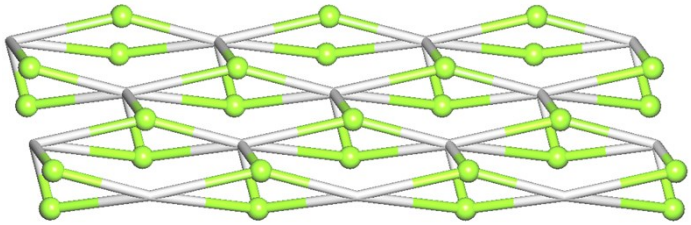

Fig. S9. Alternative topological view of a binodal 3,6-connected 2D layer with a 3,6L66 topology in **1**; rotated view along the *b* axis; 3-connected Mn centers (green balls), centroids of μ_6-deta^{4-} blocks (gray).

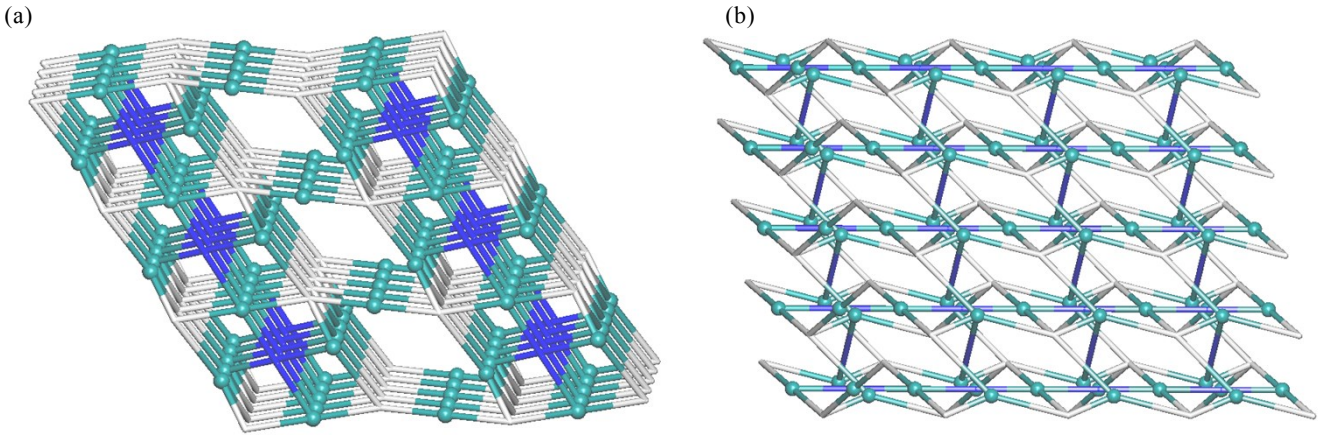

Fig. S10. Alternative topological views of a trinodal 4,4,5-connected 3D net in 4 with a unique topology; representation along the *a* (a) and *c* (b) axis; 2-connected Cd3 and 4-connected Cd1/Cd2 centers (turquoise balls), centroids of 5-connected μ_5-deta^{4-} blocks (gray), centroids of 2-connected μ-4,4′-bipy linkers (blue).

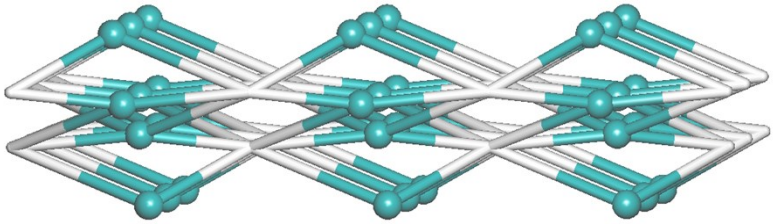

Fig. S11. Alternative topological view of a binodal 4,6-connected layer in 5 with a 4,6L45 topology; rotated view along the *b* axis; 4-connected Cd1 and 2-connected Cd2 centers (turquoise balls), centroids of μ_6-deta^{4-} blocks (gray).