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Supplementary Materials: Metal(II) Coordination Polymers from Tetracarboxylate Linkers: Synthesis, Structures, and Catalytic Cyanosilylation of Benzaldehydes

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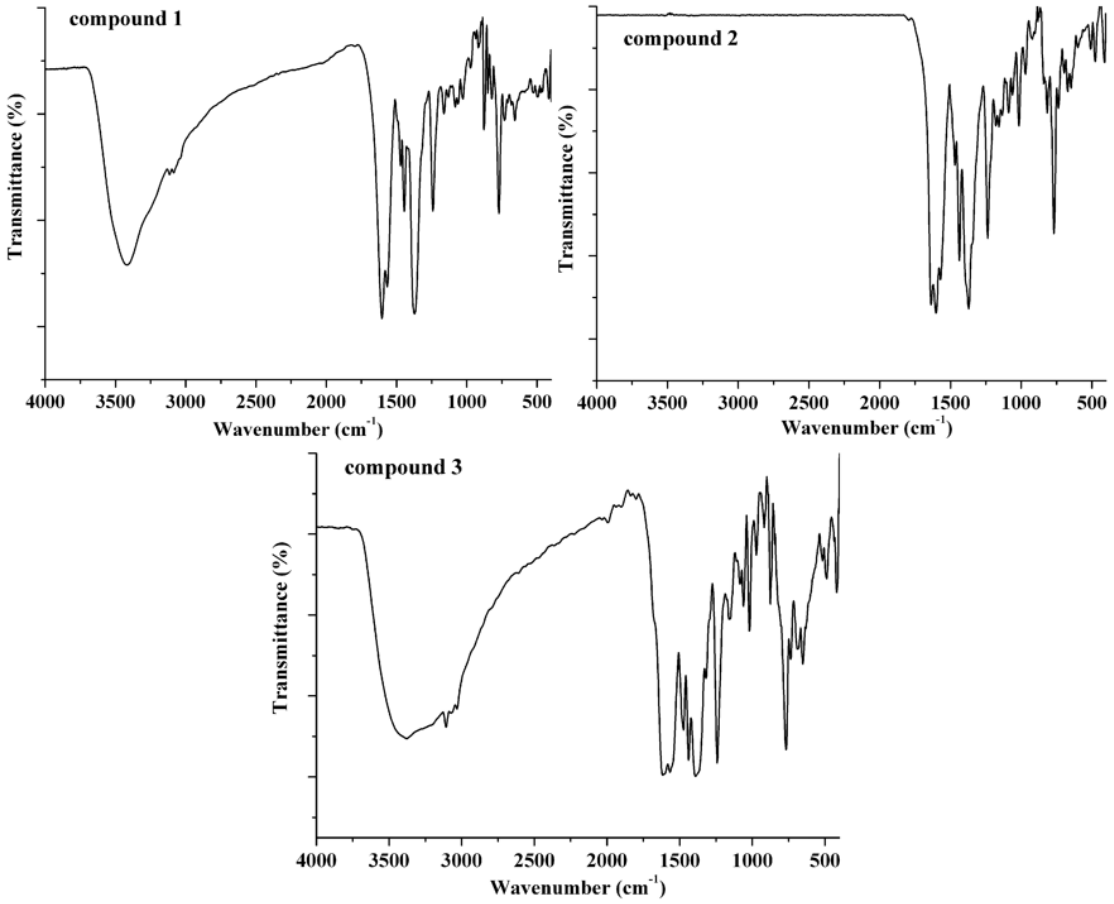

Figure S1. IR spectra of compounds **1–3**.

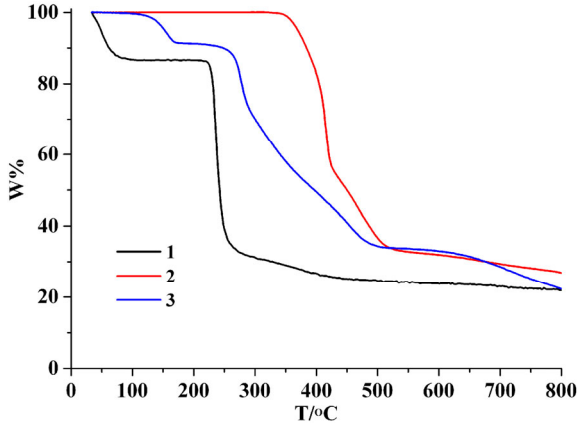

Figure S2. TGA curves of **1**–**3**.

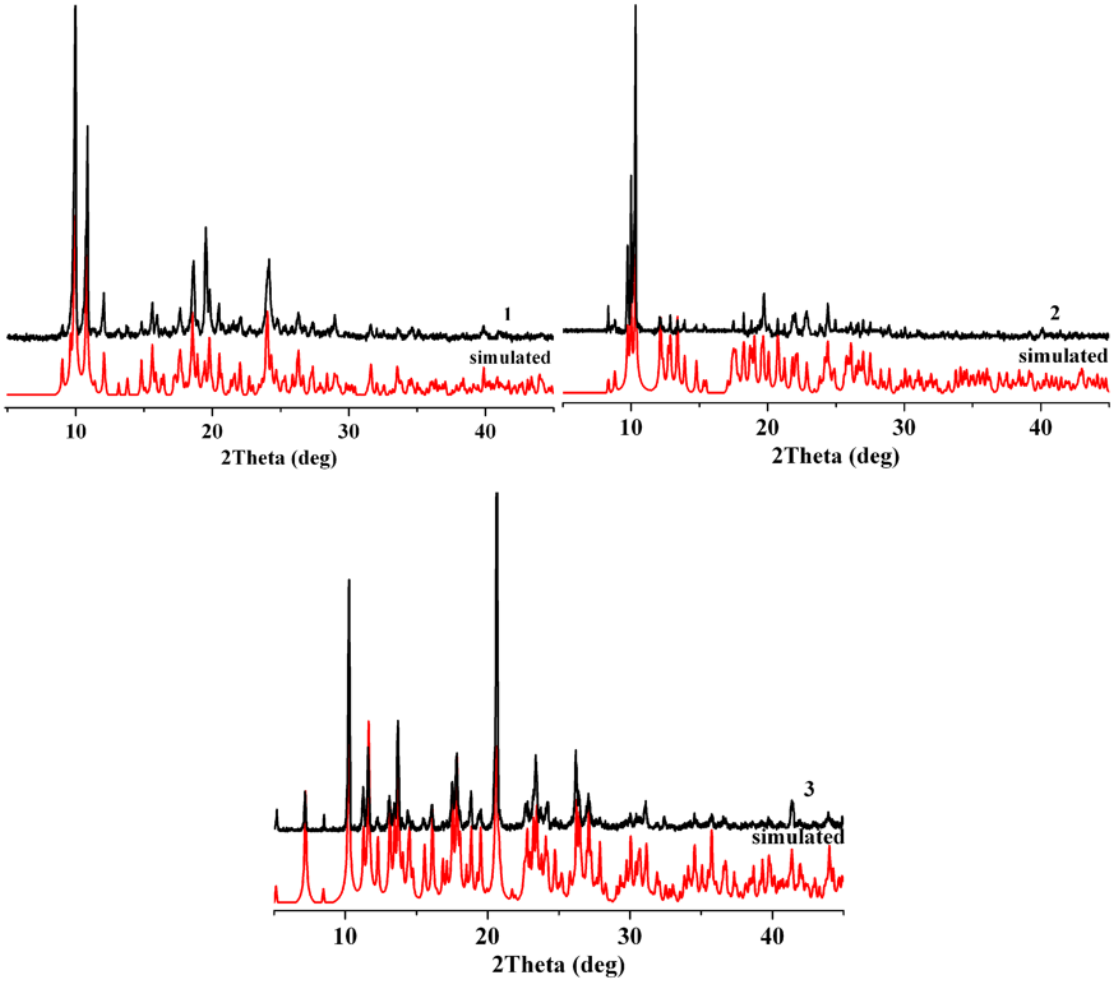

Figure S3. PXRD patterns of **1**–**3** at room temperature.

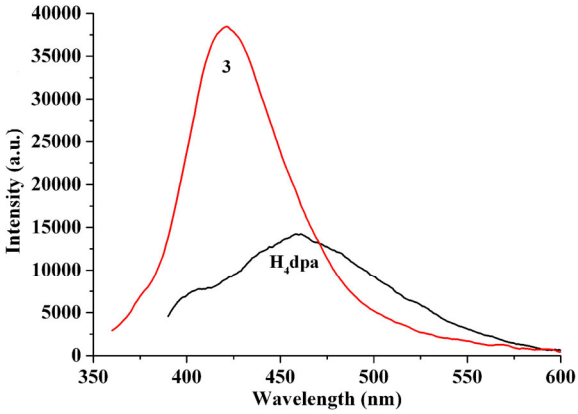

Figure S4. Solid-state emission spectra of H_4dpa and **3** at room temperature.

The emission spectra of CP **3** and H_4dpa were recorded at room temperature (Figure S3). Excitation of **3** and H_4dpa at 360 nm results in the emission peaks and 421 and 460 nm, respectively. Comparison of these emissions suggests a ligand-based nature of the observed luminescence in **3**. Hence, the emission band in **3** can be assigned to the intraligand π–π* or n–π* transition of H_4dpa. An enhancement of the luminescence in the CP **3** can be explained by a binding of ligands to zinc(II) centers.

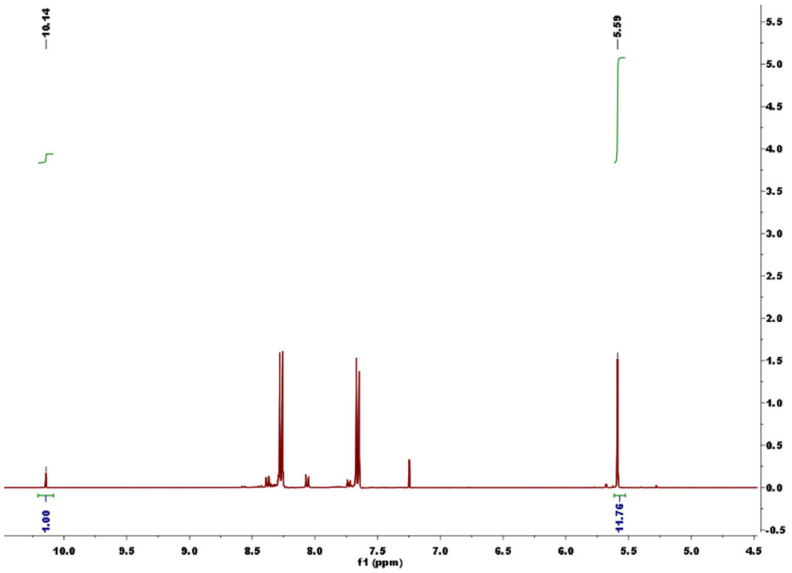

Figure S5. Example of the integration in the ^{1}H-NMR spectrum for determining yields of cyanosilylation reaction products (reaction conditions of Table 1, entry 6).

Calculation of the product yield in the cyanosilylation of benzaldehydes

The –CH signal of 4-nitrobenzaldehyde (substrate) is observed at 10.14 ppm (Figure S5), while that signal of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (product) is detected at 5.59 ppm.

Total of –CH signals in the reaction mixture: unreacted 4-nitrobenzaldehyde + 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 1+11.76 = 12.76

Percentage of the unreacted benzaldehyde: 100/12.76 = 7.84%

Conversion of 4-nitrobenzaldehyde = yield of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 100−7.84 = 92.2%.

The precision of this procedure was confirmed by repeating a number of the ^{1}H-NMR analyses in the presence of internal standard (1,2-dimethoxyethane) which was added to

the $CDCl_3$ solution; this procedure led to product yields similar to those obtained by the above method. For example, for conditions of entry 6 (Table 1), 91.9% product yield was obtained with internal standard (Figure S6) vs. 92.2% yield without standard (Figure S5).

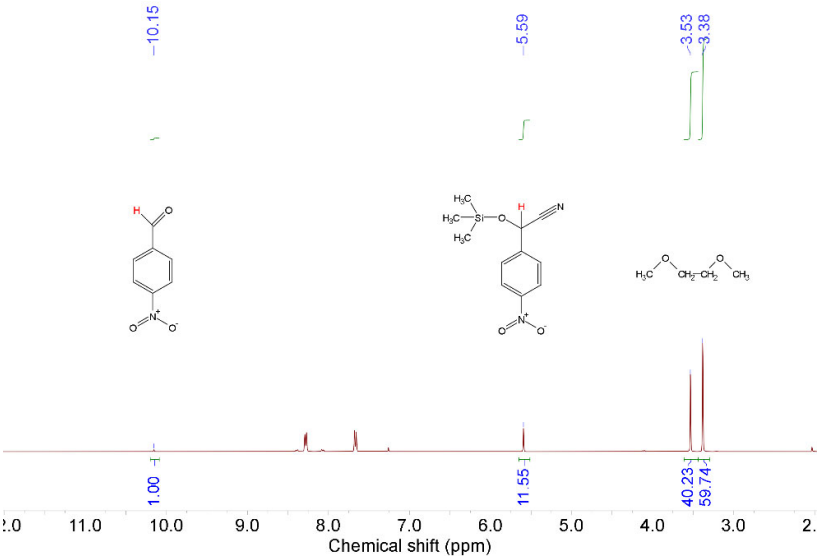

Figure S6. Example of the integration in the ^{1}H-NMR spectrum for determining yields of cyanosilylation reaction products (reaction conditions of Table 1, entry 6) in the presence of an internal standard (1,2-dimethoxyethane, 0.150 M in $CDCl_3$ solution).

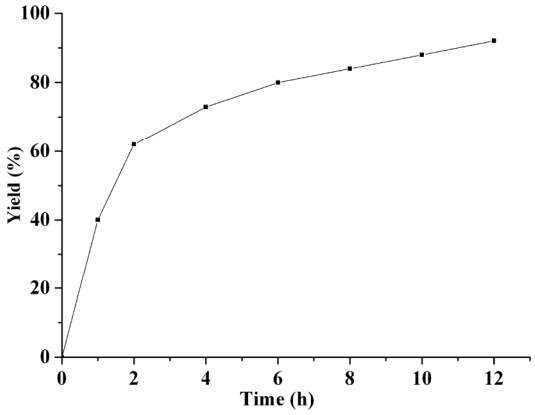

Figure S7. Accumulation of 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile vs. time in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN catalyzed by **3**. Reaction conditions are those of Table 1, entries 1–7.

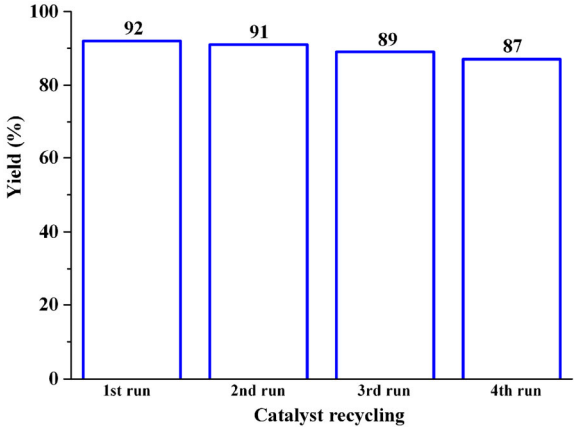

Figure S8. Catalyst recycling experiments in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN and catalyst **3**.

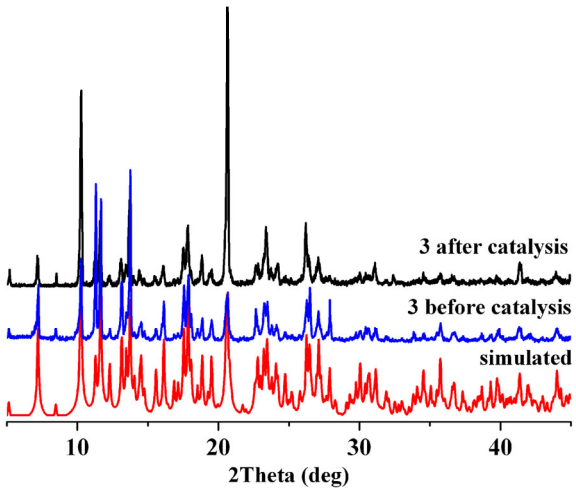

Figure S9. PXRD patterns for **3**: simulated (red), before (blue) and after (black) catalysis.

Table S1. Selected bond lengths (Å) and bond angles (°) for compounds **1**–**3**.

		1			
Cu(1)–O(2)	1.942(2)	Cu(1)–O(9)i	1.991(3)	Cu(1)–N(1)	1.998(3)
Cu(1)–N(2)	1.992(3)	Cu(2)–O(4)	1.949(2)	Cu(2)–O(6)ii	1.968(2)
Cu(2)–O(10)	2.345(3)	Cu(2)–N(3)	2.004(3)	Cu(2)–N(4)	2.058(3)
O(2)–Cu(1)–O(9)i	91.28(11)	O(2)–Cu(1)–N(2)	170.95(13)	N(2)–Cu(1)–O(9)i	92.96(13)
O(2)–Cu(1)–N(1)	97.52(13)	N(1)–Cu(1)–O(9)i	157.29(13)	N(1)–Cu(1)–N(2)	81.48(15)
O(4)–Cu(2)–O(6)ii	95.85(11)	O(4)–Cu(2)–N(3)	170.59(11)	N(3)–Cu(2)–O(6)ii	91.74(11)
O(4)–Cu(2)–N(4)	91.35(12)	N(4)–Cu(2)–O(6)ii	164.50(12)	N(4)–Cu(2)–N(3)	79.97(12)
O(4)–Cu(2)–O(10)	93.12(11)	O(10)–Cu(2)–O(6)ii	100.49(12)	O(10)–Cu(2)–N(3)	90.95(12)
O(10)–Cu(2)–N(4)	92.78(12)				
		2			
Mn(1)–O(2)	2.120(3)	Mn(1)–O(6)i	2.087(3)	Mn(1)–O(9)ii	2.109(3)
Mn(1)–N(1)	2.238(4)	Mn(1)–N(2)	2.227(4)	Mn(2)–O(2)	2.192(3)
Mn(2)–O(4)	2.111(4)	Mn(2)–O(7)i	2.217(4)	Mn(2)–O(8)ii	2.147(3)
Mn(2)–N(3)	2.277(4)	Mn(2)–N(4)	2.226(4)		
O(6)i–Mn(1)–O(9)ii	94.22(14)	O(6)i–Mn(1)–O(2)	96.73(14)	O(2)–Mn(1)–O(9)ii	105.87(14)
O(6)i–Mn(1)–N(2)	164.71(15)	N(2)–Mn(1)–O(9)ii	92.65(16)	O(2)–Mn(1)–N(2)	94.50(15)
O(6)i–Mn(1)–N(1)	91.14(14)	O(9)ii–Mn(1)–N(1)	122.30(15)	O(2)–Mn(1)–N(1)	130.43(14)
N(2)–Mn(1)–N(1)	73.66(16)	O(4)–Mn(2)–O(8)ii	92.91(15)	O(4)–Mn(2)–O(2)	85.86(13)
O(8)ii–Mn(2)–O(2)	90.96(14)	O(4)–Mn(2)–O(7)i	174.64(13)	O(8)ii–Mn(2)–O(7)i	89.71(15)
O(2)–Mn(2)–O(7)i	89.43(13)	O(4)–Mn(2)–N(4)	95.47(14)	O(8)ii–Mn(2)–N(4)	92.76(15)
O(2)–Mn(2)–N(4)	175.97(14)	O(7)i–Mn(2)–N(4)	89.07(14)	O(4)–Mn(2)–N(3)	96.60(15)
O(8)ii–Mn(2)–N(3)	163.30(15)	O(2)–Mn(2)–N(3)	103.36(13)	O(7)i–Mn(2)–N(3)	82.01(15)
N(4)–Mn(2)–N(3)	72.72(14)				
		3			
Zn(1)–O(2)	1.973(2)	Zn(1)–O(3)i	1.988(2)	Zn(1)–O(10)	2.093(3)
Zn(1)–N(1)	2.181(3)	Zn(1)–N(2)	2.119(3)	Zn(2)–O(6)	2.062(3)
Zn(2)–O(9)ii	2.019(3)	Zn(2)–O(11)	2.043(3)	Zn(2)–N(3)	2.122(3)
Zn(2)–N(4)	2.157(3)				
O(2)–Zn(1)–O(3)i	105.83(11)	O(2)–Zn(1)–O(10)	95.86(11)	O(10)–Zn(1)–O(3)i	97.97(11)
O(2)–Zn(1)–N(2)	102.32(11)	O(3)i–Zn(1)–N(2)	149.75(12)	O(10)–Zn(1)–N(2)	89.91(11)
O(2)–Zn(1)–N(1)	99.26(10)	N(1)–Zn(1)–O(3)i	88.95(12)	O(10)–Zn(1)–N(1)	160.99(11)
N(1)–Zn(1)–N(2)	75.69(11)	O(9)ii–Zn(2)–O(11)	99.86(13)	O(6)–Zn(2)–O(9)ii	96.37(12)
O(6)–Zn(2)–O(11)	93.08(12)	N(3)–Zn(2)–O(9)ii	154.43(12)	O(11)–Zn(2)–N(3)	104.73(13)
O(6)–Zn(2)–N(3)	89.25(12)	N(4)–Zn(2)–O(9)ii	92.64(12)	O(11)–Zn(2)–N(4)	99.58(12)
O(6)–Zn(2)–N(4)	162.99(12)	N(3)–Zn(2)–N(4)	76.61(12)		

Symmetry codes: (**1**) i: $x + 1, y, z + 1$; ii: $x + 1, y, z$; (**2**) i: $x + 1, y, z$; ii: $x + 1, -y + 3/2, z + 1/2$; (**3**) i: $-x, -y + 1, -z$; ii: $-x + 1/2, y - 1/2, -z + 1/2$.

Table S2. Hydrogen bonds in crystal packing (Å, °) for compounds **1** and **3**.

Compound	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry code
1	O(10)–H(1W)···O(7)	0.850	2.118	2.968	179.59	$x + 1, y, z$
	O(10)–H(2W)···O(12)	0.820	2.008	2.826	174.64	$x + 1, y, z + 1$
3	O(10)–H(1W)···O(12)	0.728	1.944	2.665	170.78	$x - 1, y, z$
	O(10)–H(2W)···O(1)	0.837	1.871	2.678	161.60	
	O(11)–H(3W)···O(7)	0.820	1.922	2.664	150.13	
	O(11)–H(4W)···O(13)	0.753	1.882	2.613	163.40	$x - 1, y, z$
	O(12)–H(5W)···O(2)	0.850	1.941	2.790	178.89	
	O(12)–H(6W)···O(4)	0.872	1.939	2.793	166.26	$-x + 1, -y + 1, -z$
	O(13)–H(7W)···O(6)	0.848	1.985	2.791	158.34	
	O(13)–H(8W)···O(8)	0.864	2.066	2.750	135.58	$-x + 1/2, y - 1/2, -z + 1/2$