

Supporting Information

Single-Crystal-to-Single-Crystal Structural Transformation of a Sandwich-like Copper(II) Pyrazolate Complex and their Excellent Catalytic Performances for MMA Polymerization

Hong-Xi Li,^a Zhi-Gang Ren,^a Dong Liu,^a Yang Chen,^a Jian-Ping Lang,^{*a} Zhen-Ping Cheng,^a Xiu-Lin Zhu,^{*a} and Brendan F. Abrahams^b

^a College of Chemistry, Chemical Engineering and Materials Science, Suzhou University, Suzhou 215123, Jiangsu, P. R. China.

^b School of Chemistry, University of Melbourne, Victoria 3010, Australia

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Experimental Section

General. Solvents like N,N'-dimethylformamide (DMF), MeCN, cyclohexanone (Cy-one) and MMA were dried over CaH₂ and distilled in vacuo. All chemicals and reagents were obtained from commercial sources and used as received. The dmpzH ligand was prepared according to the published procedure.^[1] The elemental analyses for C, H, N were performed on a Carlo-Erba CHNO-S microanalyzer. The IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm⁻¹). Thermal analysis was performed with a Perkin Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C/min and a flow rate of 100 cm³/min (N₂). XRPD were performed using a PANalytical X'Pert PRO MPD system (PW3040/60). Molecular weight and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Waters 1515 apparatus with three HR columns (HR-1, HR-2 and HR-4).

Preparation of [Cu₇(OH)₂(OAc)₆(dmpz)₆(EtOH)₆] (1)

To a stirred solution of dmpzH (282 mg, 2 mmol) in EtOH (5 mL) was added the solution of Cu(OAc)₂·H₂O (400 mg, 2 mmol) in 5 mL EtOH. The resulting blue solution was stirred overnight at room temperature, forming a large number of blue microcrystalline crystals of **1**, which was filtered, washed with EtOH, and briefly dried in air. Yield: 0.546 g (98 % based on CuAc₂·H₂O). IR (KBr, pellet): 3461 (m), 2979 (w), 2936 (w), 1547 (s), 1466 (s), 1417 (s), 1383 (s), 1358 (s), 1178 (s), 1042 (m), 995 (m), 839 (m), 771 (w), 697 (s), 615 (w), 456 (w) cm⁻¹. Anal. Calcd. for C₅₄H₉₂Cu₇N₁₈O₃₂: C, 33.26; H, 4.75; N, 12.93; Found: C, 33.54; H, 4.88; N, 12.68 %.

Preparation of [Cu₇(OH)₂(OAc)₆(dmnpz)₆(MeOH)₆] (2)

Immersing **1** into MeOH for four hours resulted in the formation of **2**, which was collected by filtration, and dried in air. IR (KBr, pellet): 3471 (m), 2977 (w), 2932 (w), 1549 (s), 1464 (m), 1417 (m), 1382 (m), 1358 (m), 1177 (s), 1104 (m), 1020 (m), 993 (m), 838 (m), 769 (w), 691 (s), 615 (w), 598 (w), 446 (w) cm⁻¹. Anal. Calcd. for C₄₈H₈₀Cu₇N₁₈O₃₂: C, 30.89; H, 4.32; N, 13.51; Found: C, 30.66; H, 3.99; N, 13.24 %.

Preparation of [Cu₇(OH)₂(OAc)₆(dmnpz)₆] (3)

Compound **1** was heated at about 140 °C in N₂ for 5 hours to give complex **3**. IR (KBr, pellet): 3490 (m), 2938 (w), 2934 (w), 1548 (s), 1463 (m), 1417 (m), 1381 (m), 1357 (s), 1176 (s), 1102 (w), 1018 (m), 994 (m), 837 (s), 768 (m), 691 (m), 616 (w), 453 (w) cm⁻¹. Anal. Calcd. for C₄₂H₅₆Cu₇N₁₈O₂₆: C, 30.14; H, 3.37; N, 15.06; Found: C, 30.43; H, 3.55; N, 15.45 %.

Preparation of [Cu₇(OH)₂(OAc)₆(dmnpz)₆(MeCN)₄] (4)

The similar work-up to that used in the isolation of **2** afforded blue crystals of **4**. IR (KBr, pellet): 3455 (w), 3003 (w), 2943 (w), 2254 (m), 1548 (s), 1469 (m), 1417 (m), 1382 (m), 1357 (m), 1178 (s), 1041 (w), 994 (w), 836 (m), 769 (w), 697 (s), 618 (w), 455 (w) cm⁻¹. Anal. Calcd. for C₅₀H₆₈Cu₇N₂₂O₂₆: C, 32.67; H, 3.73; N, 16.77; Found: C, 32.54; H, 4.03; N, 16.43 %.

Preparation of [Cu₇(OH)₂(OAc)₆(dmnpz)₆(DMF)₂] (5)

The solution of **1** in DMF and CHCl₃ (v/v = 8:1) was carefully layered by Et₂O and was allowed to stand at ambient temperature. Blue crystals of **5**·2CHCl₃·Et₂O were formed several days later and collected by filtration, washed with CHCl₃, and dried in

air. IR (KBr, pellet): 3456 (w), 2933 (w), 1664 (s), 15458 (s), 1467 (m), 1415 (m), 1385 (m), 1356 (m), 1256 (w), 1177 (s), 1100 (m), 1063 (w), 994 (w), 836 (m), 769 (w), 663 (m), 617 (w), 483 (w) cm^{-1} . Anal. Calcd. for $\text{C}_{50}\text{H}_{68}\text{Cu}_7\text{N}_{22}\text{O}_{26}$: C, 31.68; H, 3.88; N, 15.39; Found: C, 31.63; H, 4.12; N, 15.54 %.

X-ray Crystallographic Study

Single crystals of **1** were obtained directly from the slow diffusion of the EtOH solution of dmpzH into the EtOH solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. Single crystals of **2** or **4** were obtained by immersing **1** in MeOH or MeCN for 30 minutes. Single crystals of $5 \cdot 2\text{CHCl}_3 \cdot \text{Et}_2\text{O}$ were obtained directly from the above preparation. Diffraction intensities of **1**, **2**, **4** and $5 \cdot 2\text{CHCl}_3 \cdot \text{Et}_2\text{O}$ were collected on a Rigaku Mercury CCD X-ray diffractometer (Mo $\text{K}\alpha$, $\lambda = 0.71073 \text{ \AA}$). The crystals of **1**, **2**, **4** and $5 \cdot 2\text{CHCl}_3 \cdot \text{Et}_2\text{O}$ were mounted at the top of a glass fiber with grease at 223 K in a stream of gaseous nitrogen. Cell parameters were refined on all observed reflections by using the program *CrystalClear* (Rigaku and MSc, Ver. 1.3, 2001). The collected data were reduced by the program *CrystalClear*, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1**, **2**, **4** and $5 \cdot 2\text{CHCl}_3 \cdot \text{Et}_2\text{O}$ were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with *SHELXTL-97* program.^[2] All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced at the calculated positions and included in the structure-factor calculations. All the calculations were performed on a Dell workstation using the

CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). Crystal data along with data collection and refinement parameters for **1**, **2**, **4** and **5**·2CHCl₃·Et₂O are summarized in **Table S1**.

MMA Polymerization

The polymerization experiments were performed under an atmosphere of oxygen-free, dry nitrogen. A typical procedure was described as follows. A Schenk tube containing the complex was evacuated and flushed with nitrogen for three times. Deoxygenated solvent and MMA were introduced into the tube. The tube was immersed into an oil bath that was pre-heated to the desired temperature. At different time intervals, each sample was withdrawn with a degassed syringe into MeOH to precipitate the resulting polymer, which was filtered off and washed with MeOH and dried *in vacuo* to a constant weight.

References

- [1] Morgan, G. T.; Ackerman, I. *J. Chem. Soc.*, **1923**, 123, 1308-1318.
- [2] (a) Sheldrick, G. M. *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen, Germany, **1997**. (b) Sheldrick, G. M. *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Table S1. Summary of crystallographic data for **1**, **2**, **4** and **5**·2CHCl₃·Et₂O

Compound	1	2
Empirical Formula	C ₅₄ H ₈₈ Cu ₇ N ₁₈ O ₃₂	C ₄₈ H ₈₀ Cu ₇ N ₁₈ O ₃₂
Formula Weight	1946.27	1866.15
Crystal System	monoclinic	trigonal
Space Group	<i>P2₁/c</i>	<i>R-3c</i>
<i>a</i> (Å)	13.329(2)	18.778(3)
<i>b</i> (Å)	18.527(3)	18.778(3)
<i>c</i> (Å)	16.144(3)	35.187(7)
α (°)		
β (°)	101.400(3)	
γ (°)		120
<i>V</i> (Å ³)	3907.8(11)	10745(3)
<i>Z</i>	2	6
ρ_{calc} (g/cm ³)	1.654	1.730
F(000)	1994	5718
μ (MoK α , cm ⁻¹)	1.962	2.136
<i>R</i> ^{<i>a</i>}	0.0442	0.0944
<i>R</i> _w ^{<i>b</i>}	0.0908	0.1839
<i>GOF</i> ^{<i>c</i>}	1.048	1.183

To be continued Table S1.

Compound	4	5·2CHCl ₃ ·Et ₂ O
Empirical Formula	C ₅₄ H ₇₄ Cu ₇ N ₂₄ O ₂₆	C ₅₅ H ₇₆ Cl ₆ Cu ₇ N ₂₀ O ₂₉
Formula Weight	1920.22	2136.89
Crystal System	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.638(2)	13.717(7)
<i>b</i> (Å)	13.075(3)	14.320(9)
<i>c</i> (Å)	13.262(3)	14.657(3)
α (°)	100.86(3)	62.46(6)
β (°)	93.47(3)	62.25(6)
γ (°)	104.97(3)	80.88(8)
<i>V</i> (Å ³)	1901.8(7)	2253.6(19)
<i>Z</i>	1	1
ρ_{calc} (g/cm ³)	1.677	1.575
<i>F</i> (000)	977	1086
μ (MoK α , cm ⁻¹)	2.011	1.879
<i>R</i> ^{<i>a</i>}	0.0638	0.1357
<i>R</i> _w ^{<i>b</i>}	0.1042	0.1939
<i>GOF</i> ^{<i>c</i>}	1.085	1.192

$$^{[a]} R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^{[b]} R_w = \left\{ \frac{w \sum (|F_o| - |F_c|)^2}{\sum w |F_o|^2} \right\}^{1/2} \quad ^{[c]} \text{GOF} = \left\{ \frac{\sum w (|F_o| - |F_c|)^2}{(M - N)} \right\}^{1/2},$$

where *M* is the number of reflections and *N* is the number of parameters.

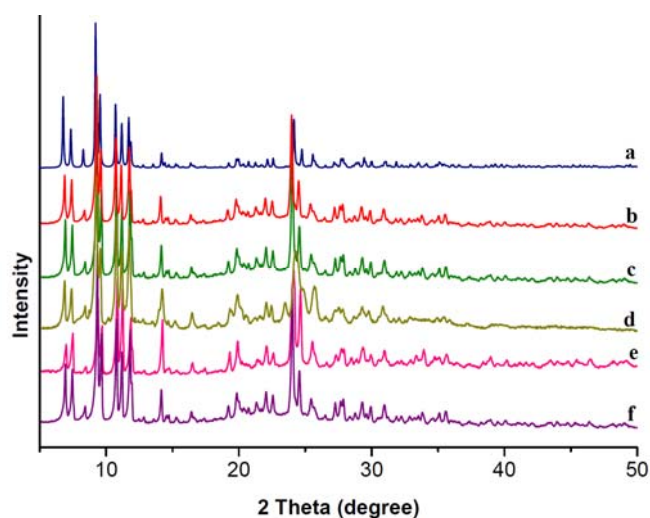


Figure S1. PXRD patterns for **1**. (a) simulated; (b) a single-phase polycrystalline sample of **1**; (c) a sample generated from immersing **2** into EtOH overnight; (d) a sample generated from immersing **3** into EtOH for 4 hours; (e) a sample generated from immersing **4** into EtOH overnight; (f) a sample generated from immersing **5** into EtOH overnight.

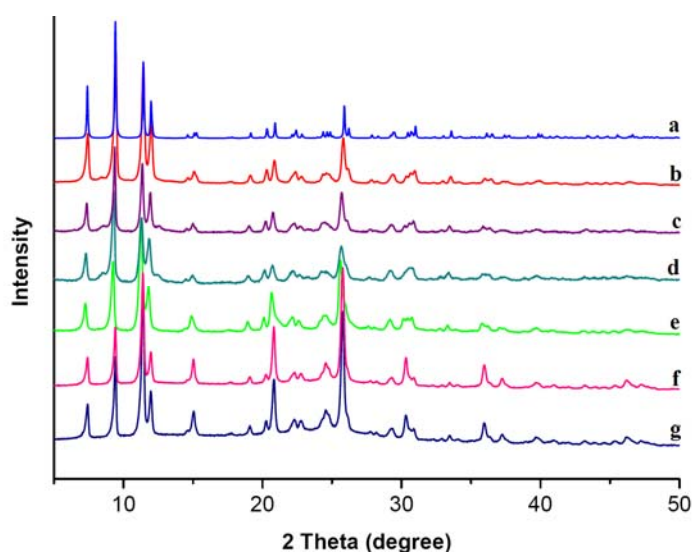


Figure S2. PXRD patterns for **2**. (a) simulated; (b) a sample generated from immersing **1** into MeOH overnight; (c) a sample generated from exposing **1** to a MeOH vapor under pure N₂ for 0.5d; (d) a sample generated from exposing **3** to a MeOH vapor under pure N₂ for 0.5d; (e) a sample generated from immersing **3** into MeOH for 4 hours; (f) a sample generated from immersing **4** into MeOH overnight; (g) a sample generated from immersing **5** into MeOH overnight.

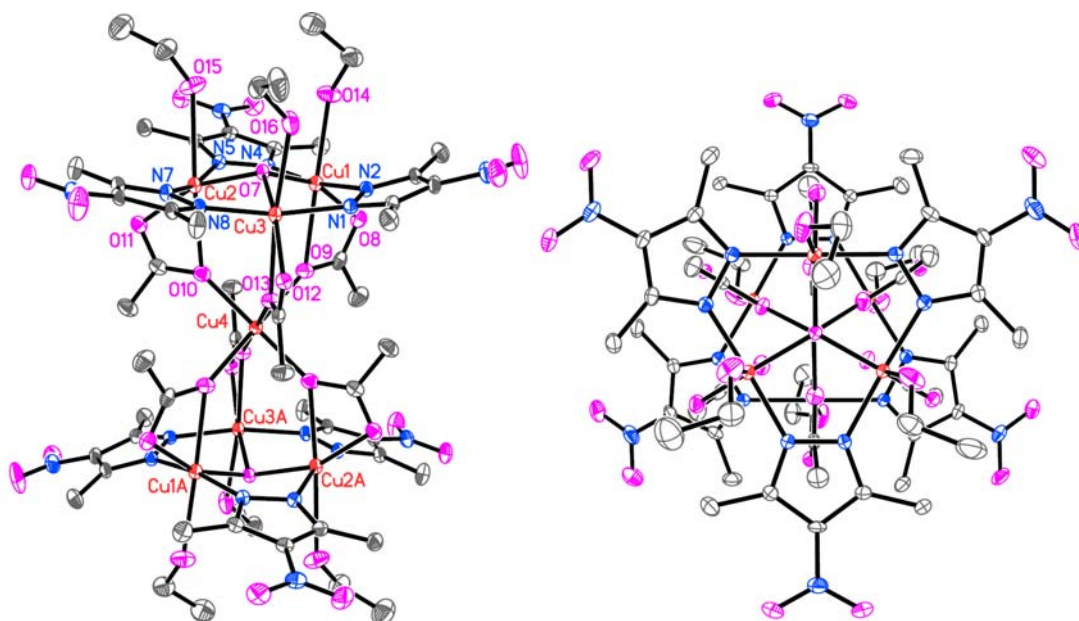


Figure S3. Molecular structure of **1** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry code: A: $-x, -y + 1, -z$.

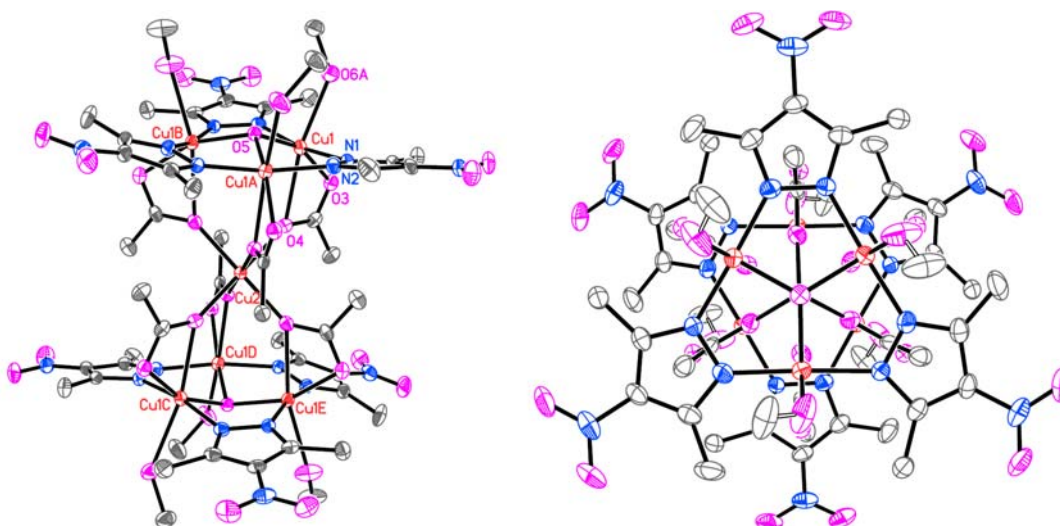


Figure S4. Molecular structure of **2** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry codes: A: $-x + y + 1, -x + 1, z$; B: $y + 1/3, -x + y + 2/3, -z + 2/3$; C: $x - y + 1/3, x - 1/3, -z + 2/3$; D: $-y + 1, x - y, z$; E: $-x + 4/3, -y + 2/3, -z + 2/3$.

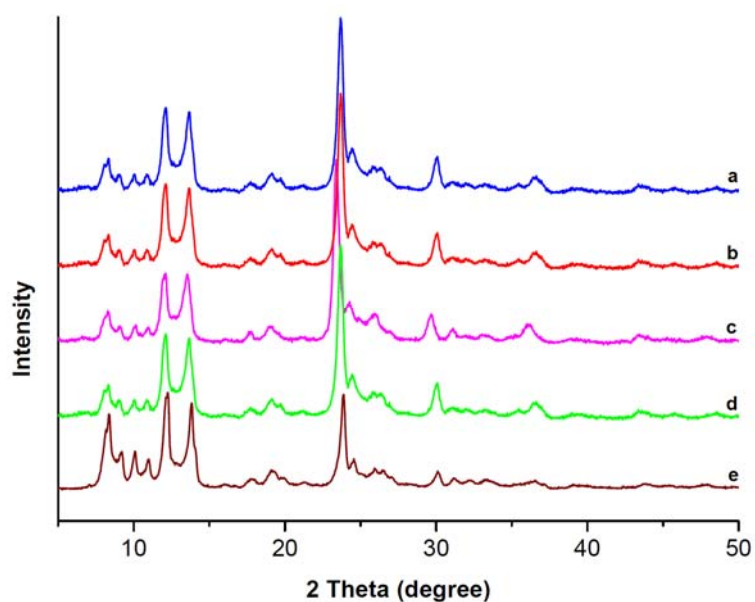


Figure S5. PXRD patterns for **3**. (a) a sample generated from heating **1** at 140 °C for 5 hours; (b) sample generated from heating **2** at 140 °C for 5 hours; (c) a sample generated from heating **4** at 140 °C for 5 hours; (d) a sample generated from heating **5** at 140 °C for 5 hours; (e) a sample generated from immersing **3** into cyclohexanone overnight.

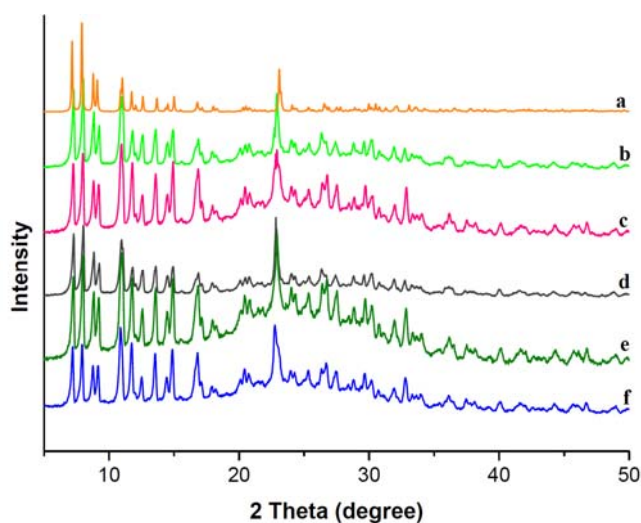


Figure S6. PXRD patterns for **4**. (a) simulated; (b) a single-phase polycrystalline sample of **4**; (c) a sample generated from immersing **1** into MeCN overnight; (d) a sample generated from immersing **2** into MeCN overnight; (e) a sample generated from immersing **3** in MeCN overnight; (f) a sample generated from immersing **5** into MeCN overnight.

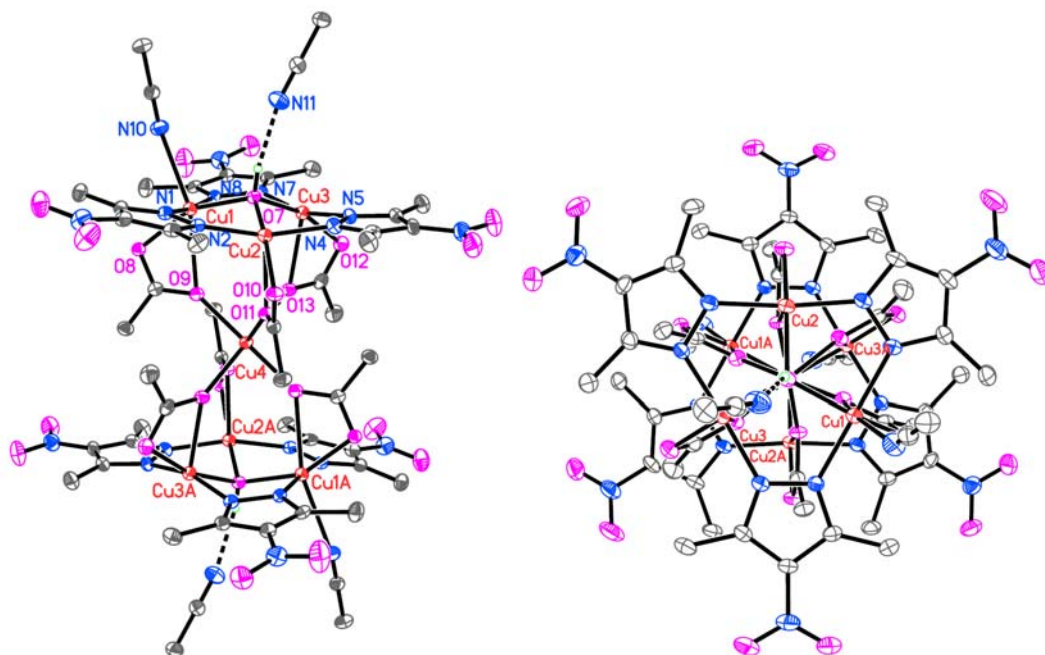


Figure S7. Molecular structure of **4** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry code: A: $-x + 1, -y, -z + 1$.

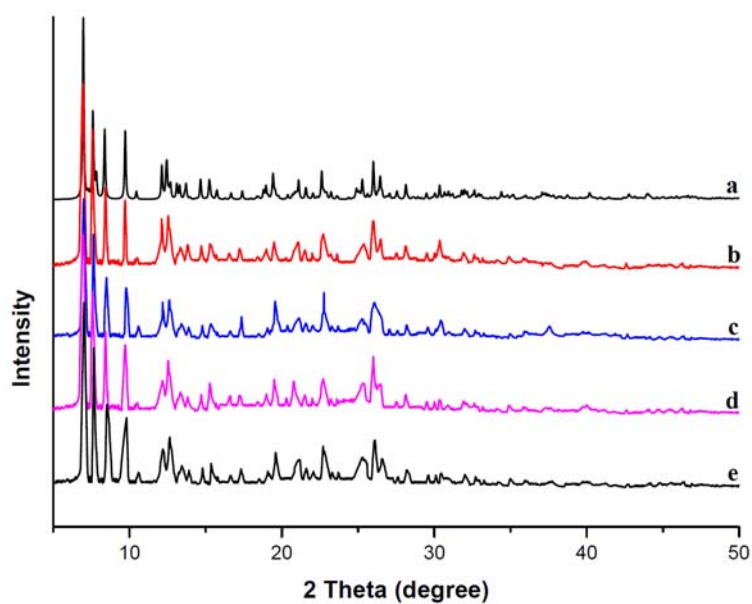


Figure S8. PXRD patterns for **5**. (a) simulated; (b) a sample generated from immersing **1** into DMF/CHCl₃ overnight; (c) a sample generated from immersing **2** into DMF/CHCl₃ overnight; (d) a sample generated from immersing **3** into DMF/CHCl₃ overnight; (e) a sample generated from immersing **4** into DMF/CHCl₃ overnight.

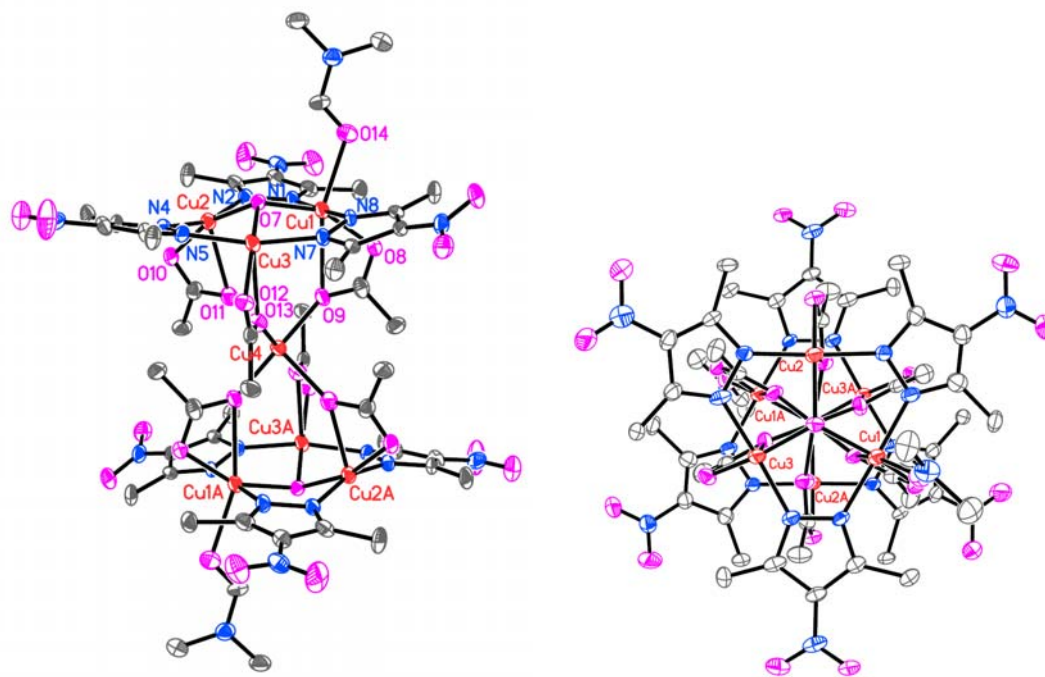
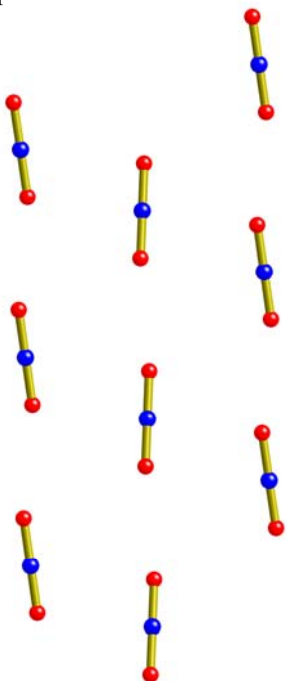
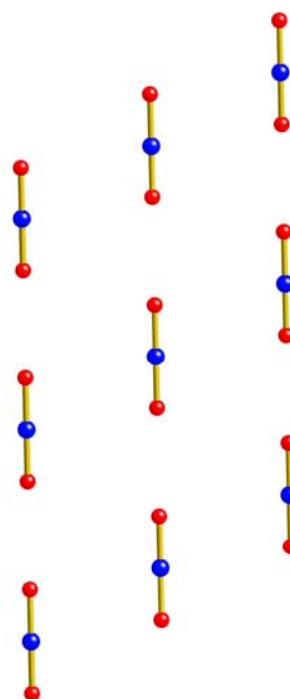


Figure S9. Molecular structure of **5** with 30% thermal ellipsoids. All H atoms are omitted for clarity. Symmetry code: A: $-x, -y + 2, -z + 1$.

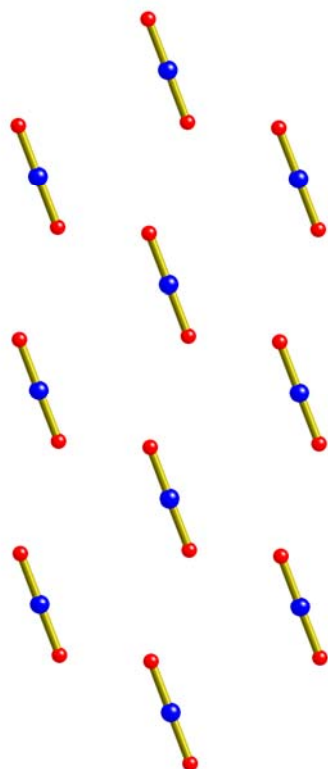
Compound 1



Compound 2



Compound 4



Compound 5

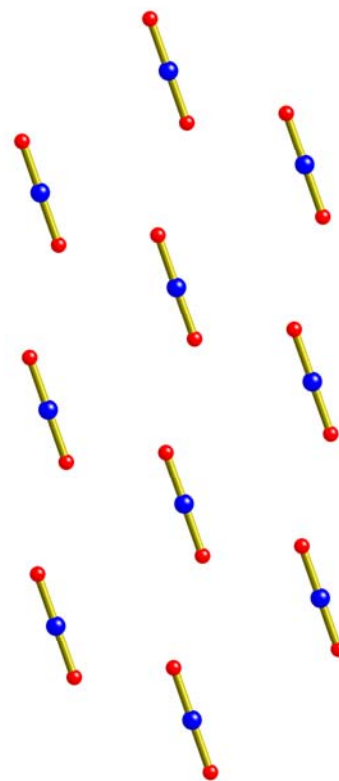


Figure S10. View of the movement of the OH and central Cu centres in complexes **1**, **2**, **4** and **5**.

All other atoms are omitted for clarity.

Table S2. Polymerization of MMA catalyzed by **1**, **2**, **3**, **4**, **5** and Cu(OAc)₂·H₂O

run ^a	catalyst	Time (h)	T (°C)	Solvent	$\frac{MMA}{catalyst}$	Yield ^b (%)	M _n (g/mol)	PDI ^c	Stereochemistry ^d (%)		
									mm	mr	rr
1	1	5	20	EtOH	300	-	-	-			
2	1	5	40	EtOH	300	-	-	-			
3	1	5	40	EtOH	600	-	-	-			
4	1	5	60	EtOH	300	-	-	-			
5	1	5	60	EtOH	600	-	-	-			
6	1	5	80	EtOH	300	-	-	-			
7	1	5	80	EtOH	600	-	-	-			
8	2	5	20	MeOH	300	-	-	-			
9	2	5	40	MeOH	300	-	-	-			
10	2	5	40	MeOH	600	-	-	-			
11	2	5	60	MeOH	300	-	-	-			
12	2	5	60	MeOH	600	-	-	-			
13	2	5	80	MeOH	300	-	-	-			
14	2	5	80	MeOH	600	-	-	-			
15	3	20	R.T.	Cy-one	600	<2	-	-			
16	3	5	40	Cy-one	300	94	22223	1.27	2	31	67
17	3	5	40	Cy-one	400	92	22515	1.29	3	31	66
18	3	5	40	Cy-one	500	88	25835	1.29	2	28	70
19	3	5	40	Cy-one	600	76	41269	1.28	3	30	67
20	3	5	40	Cy-one	900	64	51023	1.28	3	32	65
21	3	5	40	Cy-one	1200	60	36903	1.34	2	30	68
22	3	5	40	Cy-one	2200	54	57443	1.36	2	30	68
23	3	5	40	Cy-one	4000	37	96756	1.51	2	32	66
24	3	5	40	Cy-one	10000	20	120800	1.56	3	33	64
25	3	5	60	Cy-one	300	92	20539	1.15	3	28	69
26	3	5	60	Cy-one	400	90	17947	1.20	2	28	70
27	3	5	60	Cy-one	500	91	19862	1.29	3	32	65
28	3	5	60	Cy-one	600	86	22809	1.23	2	30	68
29	3	5	60	Cy-one	900	74	34576	1.29	3	34	63
30	3	5	60	Cy-one	1200	78	35197	1.38	3	33	64
31	3	5	60	Cy-one	2200	70	47247	1.51	3	34	63
32	3	5	80	Cy-one	300	92	18254	1.34	3	33	64

33	3	5	80	Cy-one	400	90	21602	1.37	3	34	63
34	3	5	80	Cy-one	500	88	22103	1.39	4	34	62
35	3	5	80	Cy-one	600	90	29306	1.40	4	35	61
36	3	5	80	Cy-one	900	79	33797	1.43	3	34	63
37	3	5	80	Cy-one	1200	69	45873	1.65	4	35	61
38	3	5	80	Cy-one	1500	90	42180	1.89	4	36	60
39	4	5	60	MeCN	300	-	-	-			
40	4	5	60	MeCN	400	-	-	-			
41	4	5	60	MeCN	600	-	-	-			
42	4	20	60	MeCN	600	<2	-	-			
43	4	5	80	MeCN	300	25	278636	1.91	3	32	65
44	4	5	80	MeCN	400	29	285480	1.96	4	34	62
45	4	5	80	MeCN	600	41	217830	2.39	4	35	61
46	4	5	80	MeCN	900	77	146145	1.95	4	35	61
47	5	5	60	DMF	300	-	-	-			
48	5	5	60	DMF	400	-	-	-			
49	5	5	60	DMF	500	-	-	-			
50	5	5	80	DMF	300	-	-	-			
51	5	5	80	DMF	400	-	-	-			
52	5	5	80	DMF	500	-	-	-			
53	5	5	120	DMF	300	77	94367	2.32	6	38	56
54	5	5	120	DMF	400	53	88797	2.02	6	39	55
55	5	5	120	DMF	500	38	93149	1.84	5	37	58
56	1^e	5	40	Cy-one	100	32	98545	1.34	3	33	64
57	1'	5	40	Cy-one	300	40	71598	1.68	3	33	64
58	1'	5	40	Cy-one	400	41	82908	1.50	3	31	66
59	1'	5	40	Cy-one	500	39	69854	1.81	4	33	63
60	1'	5	40	Cy-one	600	37	82621	1.65	4	35	61
61	1'	5	60	Cy-one	100	70	39369	1.37	3	31	66
62	1'	5	80	Cy-one	100	62	30395	1.41	4	33	63
62	1'	5	80	Cy-one	200	68	43599	1.46	4	35	61

(a) $V_{\text{MMA}} : V_{\text{solvent}} = 1 : 4$; (b) yield: weight of polymer obtained/weight of monomer used; (c) Determined by GPC analysis in THF, calibrated to a polystyrene standard; (d) stereoregularity is based on ^1H NMR spectroscopic analyses; (e) **1'** = $\text{CuAC}_2\cdot\text{H}_2\text{O}$

Table S3. Polymerization of MMA catalyzed by complexes **1** and **2**

Entry ^a	catalyst	Time (h)	T (°C)	Solvent	$\frac{MMA}{catalyst}$	Yield ^b (%)	M _n (g/mol)	PDI ^c
1	1	5	40	Cy-one	600	67	33657	1.27
2	1	5	40	Cy-one	900	65	47996	1.22
3	1	5	60	Cy-one	600	85	31034	1.20
4	1	5	60	Cy-one	900	69	33709	1.30
5	1	5	80	Cy-one	600	87	39820	1.33
6	1	5	80	Cy-one	900	76	49373	1.37
7	2	5	40	Cy-one	600	71	34573	1.24
8	2	5	40	Cy-one	900	66	46543	1.27
9	2	5	60	Cy-one	600	88	29879	1.28
10	2	5	60	Cy-one	900	74	34576	1.29
11	2	5	80	Cy-one	600	90	39965	1.37
12	2	5	80	Cy-one	900	78	48978	1.41
13	1	5	80	DMF	400	-	-	-
14	1	5	120	DMF	400	55	90021	2.11
15	2	5	40	MeCN	400	-	-	-
16	2	5	60	MeCN	400	-	-	-
17	2	5	80	MeCN	400	27	278970	2.09

(a) $V_{MMA} : V_{solvent} = 1 : 4$; (b) yield: weight of polymer obtained/weight of monomer used; (c) Determined by GPC analysis in THF, calibrated to a polystyrene standard.

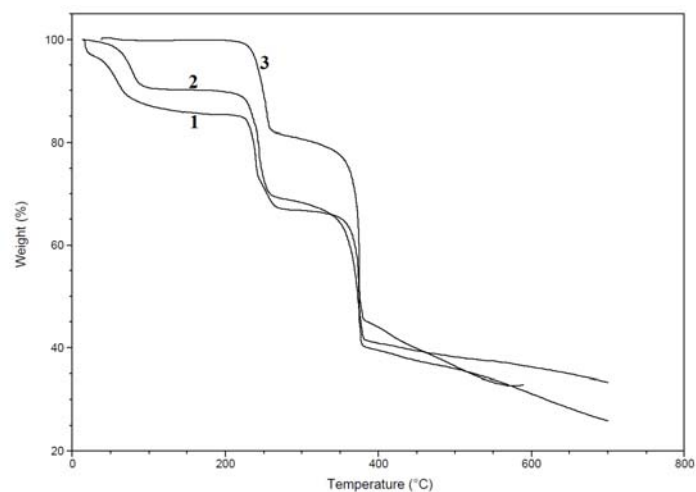


Figure S11. The TGA curves of crystals of **1**, **2** and **3**. All EtOH or MeOH solvent molecules of **1** and **2** were found to be removed below 140 °C.