

Non-linear Properties in Coordination Copolymers

Derived from Randomly Mixed Ligands

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1. Synthesis

General Methods

Phenanthrenequinone, *N*-bromosuccinimide, 2-bromomesitylene (Sigma-Aldrich), *tert*-butyllithium solution (Acros), sulfuric acid, trifluoroacetic acid (Fisher), and triisopropylchlorosilane (GFS Chemicals) were purchased from commercial vendors and used as obtained. 2,2',6,6'-Tetramethylbiphenyl-4,4'-dicarboxylic acid (H₂Me₄BPDC) was prepared from 2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl according to a published procedure.¹

2,7-Dibromophenanthrenequinone (1). Phenanthrenequinone (6.00 g, 28.8 mmol) was suspended in trifluoroacetic acid (60 mL) in a 500 mL flask, followed by the slow addition of sulfuric acid (45 mL) at 0 °C. *N*-bromosuccinimide (15.5 g, 87.1 mmol) was slowly added to the mixture at 0 °C, then the reaction mixture heated at 60 °C for 48 h. After cooling to room temperature, the orange suspension was poured into ice water (~300 mL). The brown solid was collected by filtration and washed with copious amounts of water followed by ethanol until colored impurities were thoroughly removed from the solid to afford **1** as an orange solid (6.54 g 49.7 % yield). The obtained solid was used for the next reaction without further purification. mp: 320-322 (lit. 323 °C)²; ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.26 (2H, d, *J* = 8.9 Hz), 8.08 (2H, d, *J* = 2.4 Hz), and 7.96 (2H, dd, *J* = 8.9 and 2.4 Hz) ppm.

2,7-Dibromo-9,10-bis(triisopropylsilyloxy)phenanthrene (2). Compound **1** (3.00 g, 8.20 mmol) was suspended in CH₂Cl₂ (250 mL). Zinc powder (8.00 g, 122 mmol),

tetramethylethylenediamine (4.89 mL, 32.8 mmol), and triisopropylchlorosilane (7.00 mL, 32.8 mmol) were added in succession. The mixture was heated to reflux overnight and then filtered through a plug of celite. The solid was further washed with CH₂Cl₂ and the combined filtrate was evaporated. The crude product was purified by a flash chromatography on silica gel eluting with 3% CH₂Cl₂ in hexanes. The off-white solid was further purified by recrystallization in CH₂Cl₂/MeOH to afford **2** as a white solid (2.75 g, 49.2% yield). ¹H NMR (300 MHz, CDCl₃): δ 8.37 (2H, d, J = 1.9 Hz), 8.35 (2H, d, J = 10.5 Hz), 7.62 (2H, dd, J = 8.8 and 2.2 Hz), 1.37 (6H, m), and 1.05 (36H, d, J = 7.8 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 138.5, 132.2, 128.3, 125.6, 125.4, 124.4, 121.0, 18.2, and 14.3 ppm; Anal. Calcd for C₃₂H₄₈Br₂O₂Si₂: C, 56.46; H, 7.11. Found C, 56.76; H, 7.12.

9,10-bis(triisopropylsilyloxy)phenanthrene-2,7-dicarboxylic acid (H₂TPDC).

Compound **2** (2.00 g, 2.94 mmol) was dissolved in a THF (50 mL) and diethyl ether (30 mL) mixture. 1.5 M *t*-BuLi (in pentane, 7.84 mL, 11.8 mmol) was added slowly at -78°C. After 10 min, CO₂ was purged into the solution to quench the anion and the mixture was allowed to warm with continuous CO₂ purging. After 30 min, water (50 mL) and 1 M HCl (50 mL) were added and the organic layer was separated. The organic layer was extracted with 1 M NaOH (50 mL) three times and the combined aqueous layers were acidified with 4 M HCl to precipitate a yellow powder that was collected by filtration and washed with water. The yellow powder was dissolved in 0.5 M NaOH and filtered to remove insoluble solid. The filtrate was acidified with 1 M HCl and the yellow solid was collected by filtration and washed with water to afford H₂TPDC as a yellow powder (1.35

g, 75.2% yield). ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 8.91 (2H, d, $J = 9.4$ Hz), 8.89 (2H, s), 8.11 (2H, d, $J = 9.0$ Hz), 1.37 (6H, m), and 1.00 (36H, d, $J = 7.2$ Hz) ppm; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 167.2, 138.4, 130.3, 129.4, 128.9, 125.2, 124.2, 124.1, 17.7, and 13.4 ppm; FT-IR (KBr): 3091, 2964, 2947, 2891, 2868, 1691, 1614, 1591, 1578, 1531, 1439, 1412, 1363, 1290, 1256, 1175, 1136, 1063, 1016, 1001, 918, 885, 827, 758, 685, 601, 505, and 455 cm^{-1} ; Anal. Calcd for $\text{C}_{34}\text{H}_{50}\text{O}_6\text{Si}_2$: C, 66.84; H, 8.25. Found C, 66.64, H, 8.27.

$\text{Zn}_4\text{O}(\text{TPDC})_3$. H_2TPDC (50.0 mg, 0.0818 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (74.4 mg, 0.250 mmol) were dissolved in DEF (5 mL) and heated at $100\text{ }^\circ\text{C}$ for 12 h. The hot mother liquor was decanted. The yellow cubic crystals were washed with DMF (15 mL) twice then CH_2Cl_2 (15 mL) twice, and immersed in CH_2Cl_2 for 24 h. The crystals were dried under vacuum at room temperature (23.3 mg, 40.7% yield based on H_2TPDC). FT-IR (KBr): 3093, 2945, 2891, 2868, 1687, 1604, 1525, 1437, 1394, 1309, 1261, 1224, 1178, 1144, 1117, 1061, 1016, 1001, 984, 916, 883, 849, 773, 743, 703, 685, 654, and 459 cm^{-1} ; PXRD (Cu $\text{K}\alpha$ 1.5418 \AA) $2\theta(I/I_0, \%)$: 5.14 (100), 7.28 (39.8), 8.87 (4.0), 10.3 (15.4), 11.5 (23.6), 12.6 (5.9), 13.4 (1.2), 14.6 (4.8), 15.5 (2.4), 16.3 (2.9), 18.6 (7.1), 19.9 (3.3), 22.4 (2.6), 23.7 (3.9), 25.8 (3.3), 26.8 (1.3), 29.8 (1.2), 32.5 (1.4), and $42.6 (2.0)$.

$\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$. $\text{H}_2\text{Me}_4\text{BPDC}$ (24.0 mg, 0.0805 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (74.4 mg, 0.250 mmol) were dissolved in DEF (4 mL) and heated at $100\text{ }^\circ\text{C}$ for 12 h. The hot mother liquor was decanted. The colorless parallelepiped crystals were washed with DMF (15 mL) twice then CH_2Cl_2 (15 mL) twice, and immersed in CH_2Cl_2 for 24 h. The

crystals were dried under vacuum at room temperature (23.1 mg, 74% yield based on H₂Me₄BPDC). FT-IR (KBr): 3053, 2970, 2947, 2920, 2858, 1792, 1603, 1549, 1429, 1398, 1373, 1265, 1038, 1003, 932, 905, 789, and 762 cm⁻¹; PXRD (Cu Kα 1.5418 Å) 2θ (*I*/*I*₀, %): 5.18 (100), 7.06 (12.8), 7.58 (67.6), 8.28 (6.3), 9.19 (3.6), 10.4 (8.1), 11.3 (33.8), 11.9 (8.3), 13.2 (1.7), 14.1 (9.9), 15.6 (37.9), 16.7 (2.9), 17.4 (4.3), 17.8 (2.4), 19.3 (0.9), 20.0 (3.5), 21.3 (3.5), 21.9 (2.3), 22.5 (9.8), 23.5 (4.0), 25.1 (7.2), 26.3 (1.8), 27.4 (2.9), 28.4 (2.8), 29.4 (1.0), 31.3 (1.3), 33.3 (1.2), 35.1 (1.8), 37.6 (1.5), 42.3 (3.1), 43.0 (2.8), 43.9 (0.9), and 44.5 (1.3); Anal. Calcd for C₅₄H₄₈O₁₃Zn₄: C, 55.60; H 4.15. Found: C, 55.48; H, 4.02.

BDC-ABDC random mixed linker coordination copolymer. Zn(NO₃)₂·6H₂O (0.224 g, 7.69 mmol) was dissolved in 10 mL of DMF. A mixture of 2-amino-1,4-benzenedicarboxylic acid (H₂ABDC) and 1,4-benzenedicarboxylic acid (H₂BDC) was added to the solution (total moles of organic linkers ~2.56 mmol). The mixture was sonicated for 30 min and heated to 100 °C. After 1 day, cubic-shaped crystals were obtained. After cooling to room temperature the product was isolated by decanting the hot mother liquor and washing with DMF (10 mL) three times. The resulting solid was then immersed in 10 mL CH₂Cl₂ for 2 days, during which time the CH₂Cl₂ was replaced three times.

TPDC-Me₄BPDC random mixed linker coordination copolymer. A mixture of Zn(NO₃)₂·6H₂O (0.0744 g, 0.250 mmol) and the appropriate amount of 9,10-bis(triisopropylsilyloxy)phenanthrene-2,7-dicarboxylic acid (H₂TPDC) with 3,3',5,5'-

tetramethyl-4,4'-biphenyldicarboxylic acid (H₂Me₄BPDC) (total ~0.08 mmol, Table S1) was dissolved in DEF (5 mL). The solution was heated at 100 °C for 12 h. The hot mother liquor was decanted and the crystals were washed with DMF (15 mL) twice then CH₂Cl₂ (15 mL) twice, and immersed in CH₂Cl₂ for 24 h. The crystals were then dried under vacuum for 12 h at room temperature.

2. Characterization of TPDC-Me₄BPDC random mixed linker coordination copolymers

The ratio of the components in the coordination copolymer was determined by ¹H NMR spectroscopy after the crystals were digested in DMSO-*d*₆ containing HCl.

Table S1. The composition of random mixed linker coordination copolymers of Zn₄O(Me₄BPDC)_{3-x}(TPDC)_x (0 ≤ x ≤ 3) and BET surface areas

Feed (H ₂ Me ₄ BPDC: H ₂ TPDC)	mole fraction (y = x/3) of TPDC (x) in copolymer ^a	BET surface area (m ² /g) ^b
10:0	0 (0)	1700
9:1	0.09 (0.27)	1580
8:2	0.17 (0.51)	1923
7:3	0.33 (0.99)	2676
6:4	0.40 (1.2)	3055
5:5	0.48 (1.4)	2965
4:6	0.50 (1.5)	2850
3:7	0.60 (1.8)	2645
2:8	0.67 (2.0)	2380
1:9	0.81 ((2.4)	2155
0:10	1.0 (3.0)	1990

^a Determined by ¹H NMR. ^b Determined from N₂ isotherm at 77 K

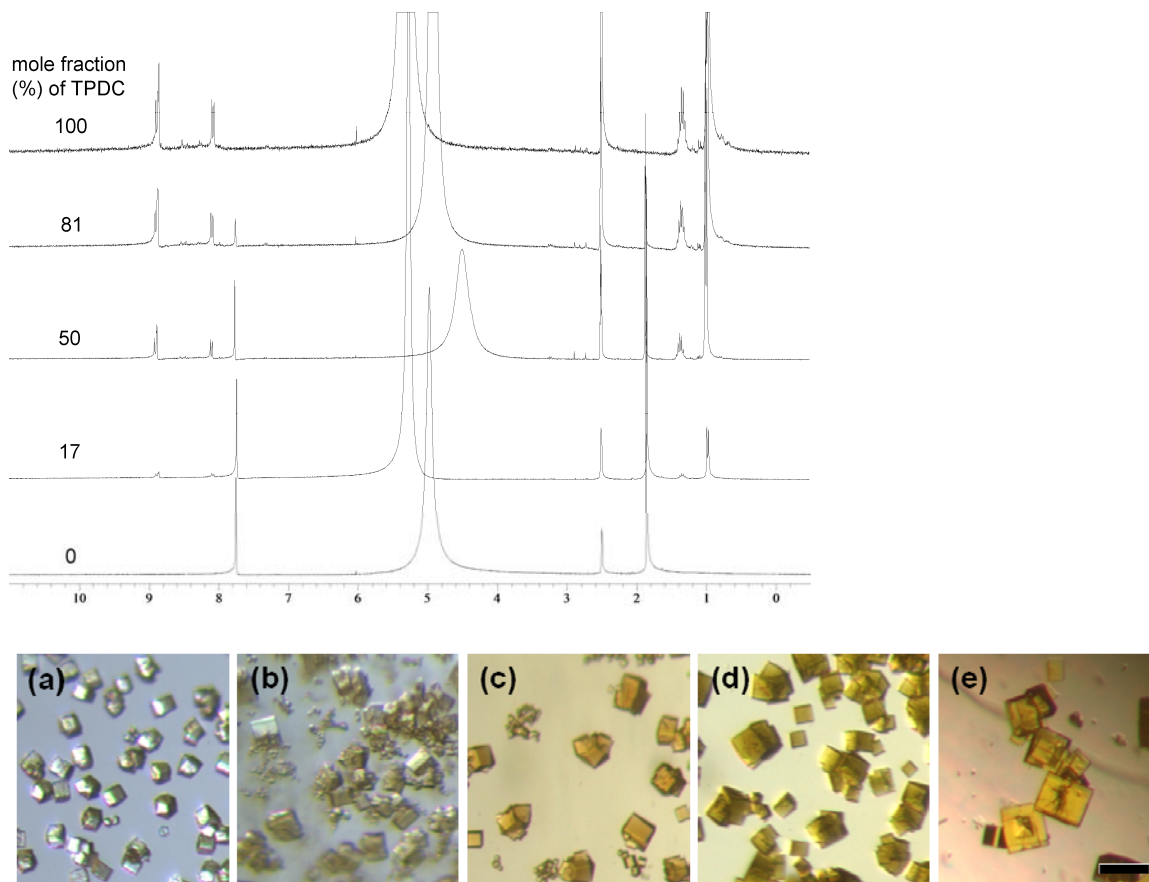


Figure S1. Top: ^1H NMR spectra on $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_{3-x}(\text{TPDC})_x$ copolymer digested solutions in $\text{DMSO}-d_6$ containing HCl Bottom: Optical images of crystals of $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_{3-x}(\text{TPDC})_x$ copolymers. The mole fraction (%) of TPDC in the copolymer is (a) 0, (b) 9, (c) 50, (d) 81, and (e) 100. The scale bar is 200 μm . Pure $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})$ exhibits colorless parallelepiped crystals. As the composition of TPDC increases, yellow colored cubic crystals were gradually appeared.

Physical mixing of $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$ and $\text{Zn}_4\text{O}(\text{TPDC})_3$. The dried MCPs were physically mixed and the surface area was measured. The composition of the mixture was determined by the weight of two MCPs.

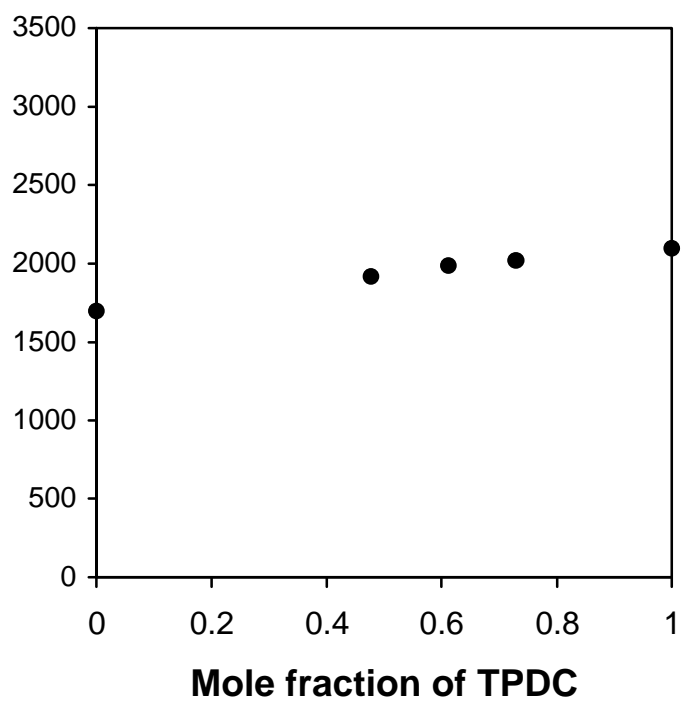


Figure S2. Surface area of MCP mixtures as function of TPDC mole fraction in the MCP mixture.

3. X-ray crystallography

Crystals of $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$ exchanged in CH_2Cl_2 were coated in Paratone N oil. A clear block crystal ($0.11 \times 0.11 \times 0.12 \text{ mm}^3$) was mounted on a MitiGen MicroMounts tip. X-ray diffraction data were collected on a Rigaku R-Axis Spider diffractometer (460 mm \times 256 mm curved imaging plate detector, graphite monochromated Cu $K\alpha$ radiation operating at 2 kW power) at 293 K. Data were collected using the d*TREK package in the CrystalClear software suite (v. 2.0, Rigaku 2009) to obtain overlapping ϕ and ω scans. A total of 110 oscillation images were collected from 20.0 to 185° using widths of 1.5° in ω , at $\chi=0.0^\circ$ and $\phi = 180.0^\circ$. Using the FS_PROCESS package in CrystalClear, the raw intensity data were then reduced to F^2 values with corrections for Lorentz, and polarization effects. Decay of the crystal during data collection was negligible. An empirical absorption correction was applied as implemented by FS_PROCESS. The structure was solved by direct methods and refined against all data using the CrystalStructure (v. 4.0) software package in the trigonal space group $R\bar{3}2/c$ (#167), $Z = 12$ using direct methods.³ Hydrogen atoms were placed at calculated positions (C-H = 0.93 Å) using a riding model with isotropic thermal parameters 1.2 times that of the attached carbon atom. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore the SQUEEZE routine of PLATON⁴ was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.

Table S2. Crystal data and structure refinement for Zn₄O(Me₄BPDC)₃.

Empirical formula	C ₅₄ H ₄₈ O ₁₃ Zn ₄	
Formula weight	1166.49	
Temperature	293 K	
Wavelength	1.54180	
Crystal System	Trigonal	
Space Group	<i>R</i> $\bar{3}$ /c (#167)	
Unit Cell Dimensions	a = 22.6523(6) Å	$\alpha = 90^\circ$
	b = 22.6523(6) Å	$\beta = 90^\circ$
	c = 65.9502(16) Å	$\gamma = 120^\circ$
Volume	29307.0(13) Å ³	
Z	12	
Density (calculated)	0.793 g/cm ³	
Absorption coefficient	1.392 mm ⁻¹	
F(000)	7152	
Crystal Size	0.11 × 0.11 × 0.12 mm ³	
Theta range for data collection	6.54 to 65.44	
Index ranges	-16 ≤ h ≤ 26, -22 ≤ k ≤ 20, -67 ≤ l ≤ 41	
Reflections collected	19777	
Independent reflections	5305 [R(int) = 0.0315]	
Completeness to theta = 66.63	91.9 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9627 and 0.9020	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5305 / 0 / 214	
GOF on F ²	1.381 (2.191 before SQUEEZE)	
Final R indices [I > 2σ(I)]	R1 = 0.0824 (0.1200 before SQUEEZE), wR2 = 0.2275 (0.3518 before SQUEEZE)	
R indices (all data)	R1 = 0.1042 (0.1490 before SQUEEZE), wR2 = 0.2391 (0.3644 before SQUEEZE)	
Largest diff. peak and hole	0.751 and -1.032 e ⁻ /Å ³	

4. N₂ isotherm measurements

N₂ adsorption isotherms were measured by a volumetric method at 77 K in the range $1.00 \times 10^{-3} \leq P/P_0 \leq 1.00$ on a NOVA 4200 by Quantachrome Instruments (Boynton Beach, Florida, USA). The quantity for the measurement is 20-30 mg for each sample. All BET analysis is performed by plotting $x/v(1-x)$ vs x , where x is an adsorption points over the range $P/P_0 < 0.06$ ($P_0 = 1$ bar) and v is the volume of nitrogen adsorbed per gram of MOF at STP. Ultra-high purity N₂ (99.999%) was purchased from Cryogenic Gasses and used as received.

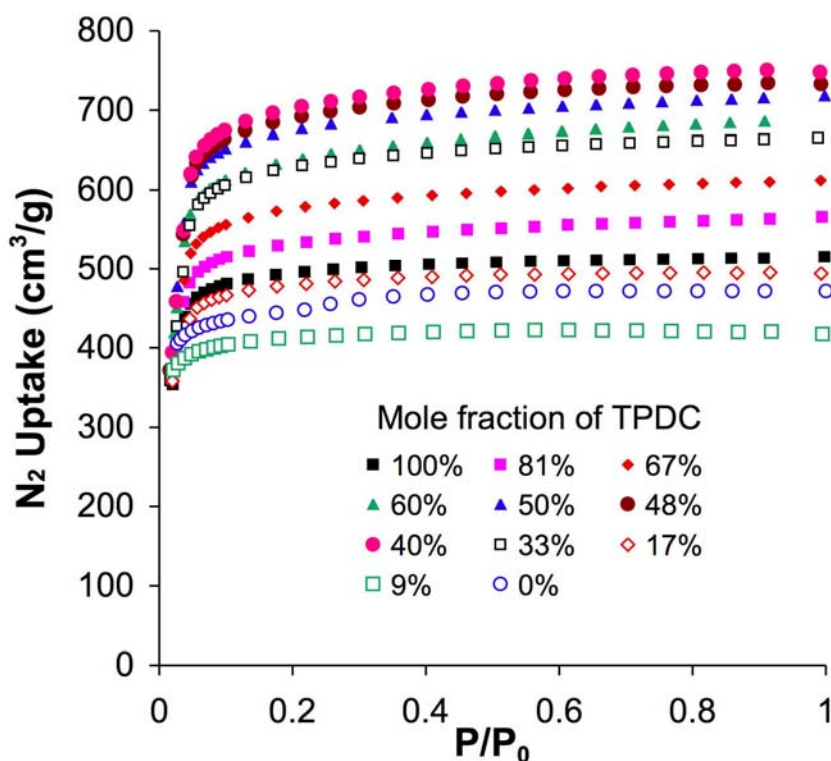


Figure S3. N₂ adsorption isotherms of random mixed linker coordination copolymers of Zn₄O(Me₄BPDC)_{3-x}(TPDC)_x as function of TPDC mole fraction in the copolymer.

5. References

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6. Acknowledgment and Disclaimer

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