

ESI to accompany

Greasy tails switch 1D-coordination [$\{Zn_2(OAc)_4(4'-(4-RO C_6H_4)-4,2':6',4''-$ tpy) $\}_n$] polymers to discrete [$Zn_2(OAc)_4(4'-(4-RO C_6H_4)-4,2':6',4''-$ tpy) $_2$] complexes

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Experimental details

4-Hydroxybenzaldehyde (Sigma-Aldrich), 4-methoxybenzaldehyde (Sigma-Aldrich), 4-ethoxybenzaldehyde (Sigma-Aldrich), 4-ⁿpropoxybenzaldehyde (Sigma-Aldrich), 4-ⁿbutoxybenzaldehyde (Sigma-Aldrich) and 4-ⁿheptoxybenzaldehyde (Sigma-Aldrich), 1-bromopentane (Fluka), 1-bromohexane (Acros), 1-bromooctane (Fluka), 1-bromononane (Apollo), 1-bromodecane (Fluka) and Zn(OAc)₂·2H₂O (Sigma-Aldrich) were used as received from the suppliers. 4-ⁿHexoxybenzaldehyde was prepared as previously described.¹

4-ⁿPentoxybenzaldehyde

The following method gives a higher yield than that reported.² 4-Hydroxybenzaldehyde (1.00 g, 8.11 mmol) and anhydrous potassium carbonate (2.76 g, 20 mmol) were dissolved in acetonitrile (100 mL). The reaction mixture was stirred and refluxed for 15 min. 1-Bromopentane (1.39 g, 1.14 mL, 9 mmol) was added and the reaction mixture refluxed for 12h. The mixture was cooled to room temperature, water (500 mL) was added and the product extracted from petroleum ether (200 mL). The organic layer was washed with NaOH (aq)

solution (10%, 2 × 50 mL) and water (2 × 50 mL). The organic layer was dried over MgSO₄ and concentrated on a rotary evaporator. 4-Pentoxybenzaldehyde (1.40 g, 7.29 mmol, 90%) was obtained as a pale yellow oil and used in the next reaction step without further purification. ¹H NMR (400 MHz, CDCl₃) δ / ppm 9.88 (s, 1H, H^{Ald}), 7.82 (m, 2H, H^{Ar2}), 6.99 (m, 2H, H^{Ar3}), 4.04 (t, J = 6.5 Hz, 2H, H^{OCH2}), 1.84 (m, 2H, H^{CH2}), 1.55–1.25 (m, 4H, H^{CH2}), 0.95 (m, 3H, H^{Me}). Data match those reported.¹

4-ⁿOctoxybenzaldehyde

4-Hydroxybenzaldehyde (1.00 g, 8.11 mmol) and anhydrous potassium carbonate (2.76 g, 20 mmol) were dissolved in acetonitrile (100 mL). The reaction mixture was stirred and refluxed for 15 min. 1-Bromooctane (1.74 g, 1.57 mL, 9 mmol) was added and the reaction mixture refluxed for 12h. The mixture was cooled to room temperature, water (500 mL) was added and it was extracted from petroleum ether (200 mL). The organic layer was washed with NaOH (aq.) solution (10%, 2 × 50 mL) and water (2 × 50mL). The organic layer was dried over MgSO₄ and concentrated at low pressure at a rotation evaporator. 4-Octoxybenzaldehyde (1.41 g, 6 mmol, 74 %) was obtained as a pale yellow oil and used in the next reaction step without further purification. ¹H NMR (400 MHz, CDCl₃) δ / ppm 9.88 (s, 1H, H^{Ald}), 7.82 (m, 2H, H^{Ar2}), 6.97 (m, 2H, H^{Ar3}), 4.04 (t, J = 6.5 Hz, 2H, H^{OCH2}), 1.84 (m, 2H, H^{CH2}), 1.55–1.15 (m, 10H, H^{CH2}), 0.87 (m, 3H, H^{Me}). The data are consistent with those reported.³

4-ⁿNonoxybenzaldehyde

4-Hydroxybenzaldehyde (1.00 g, 8.11 mmol) and anhydrous potassium carbonate (2.76 g, 20 mmol) were dissolved in acetonitrile (100 mL). The reaction mixture was stirred and refluxed for 15 min. 1-Bromononane (1.86 g, 1.72 mL, 9 mmol) was added and the reaction mixture refluxed for 12h. The mixture was cooled to RT, water (500 mL) was added and it was extracted from petroleum ether (200 mL). The organic layer was washed with NaOH (aq.) solution (10%, 2 × 50 mL) and water (2 × 50mL). The organic layer was dried over MgSO₄ and concentrated at low pressure at a rotation evaporator. 4-ⁿNonoxybenzaldehyde (1.62 g, 6.52 mmol, 80%) was obtained as a pale yellow

oil and used in the next reaction step without further purification. ^1H NMR (400 MHz, CDCl_3) δ / ppm 9.88 (s, 1H, H^{Ald}), 7.80 (m, 2H, H^{Ar2}), 6.98 (m, 2H, H^{Ar3}), 4.04 (t, $J = 6.5$ Hz, 2H, H^{OCH_2}), 1.81 (m, 2H, H^{CH_2}), 1.47 (m, 2H, H^{CH_2}), 1.40 – 1.20 (m, 10H, H^{CH_2}), 0.87 (m, 3H, H^{Me}). The data are consistent with those reported.³

4-([4,2':6',4''-Terpyridin]-4'-yl)phenol

Compound **1** (1.00 g, 2.95 mmol) was placed in a microwave vial (10 mL) with pyridinium chloride (1.04 g, 9.00 mmol). The solid mixture was heated in the microwave reactor at 200 °C for 1 h. The reaction mixture was then cooled to room temperature and was washed multiple times with water (≈ 100 mL total). The combined washings and residue was filtered and the product collected. 4-([4,2':6',4''-Terpyridin]-4'-yl)phenol was isolated as a yellow solid (0.46 g, 1.42 mmol, 48%) and was used without further purification. M.p. decomposition > 280 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ / ppm 10.01 (s, 1H, H^{OH}), 8.86 (m, 4H, H^{A2}), 8.53-8.52 (m, 6H, $\text{H}^{\text{B3}}/\text{H}^{\text{A3}}$), 8.03 (m, 2H, H^{C2}), 6.97 (m, 2H, H^{C3}); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ / ppm 159.4 (C^{C4}), 153.5 (C^{A4}), 150.4 (C^{B4}), 148.3 (C^{A2}), 147.5 (C^{B2}), 128.77 (C^{C2}), 127.0 (C^{C1}), 121.7 (C^{A3}), 118.7 (C^{B3}), 116.0 (C^{C3}). IR (solid, ν / cm^{-1}) 3378 (w), 3090 (w), 3029 (w), 2899 (w), 2756 (w), 2683 (w), 2589 (w), 2492 (w), 2079 (w), 1631 (w), 1588 (s), 1565 (m), 1519 (m), 1463 (m), 1398 (m), 1360 (m), 1291 (m), 1239 (m), 1215 (m), 1173 (m), 1109 (w), 1060 (m), 1012 (m), 882 (w), 815 (s), 737 (m), 673 (m), 633 (m), 618 (m), 566 (s), 517 (s). ESI-MS m/z 326.3 $[\text{M}+\text{H}]^+$ (calc. 326.1).

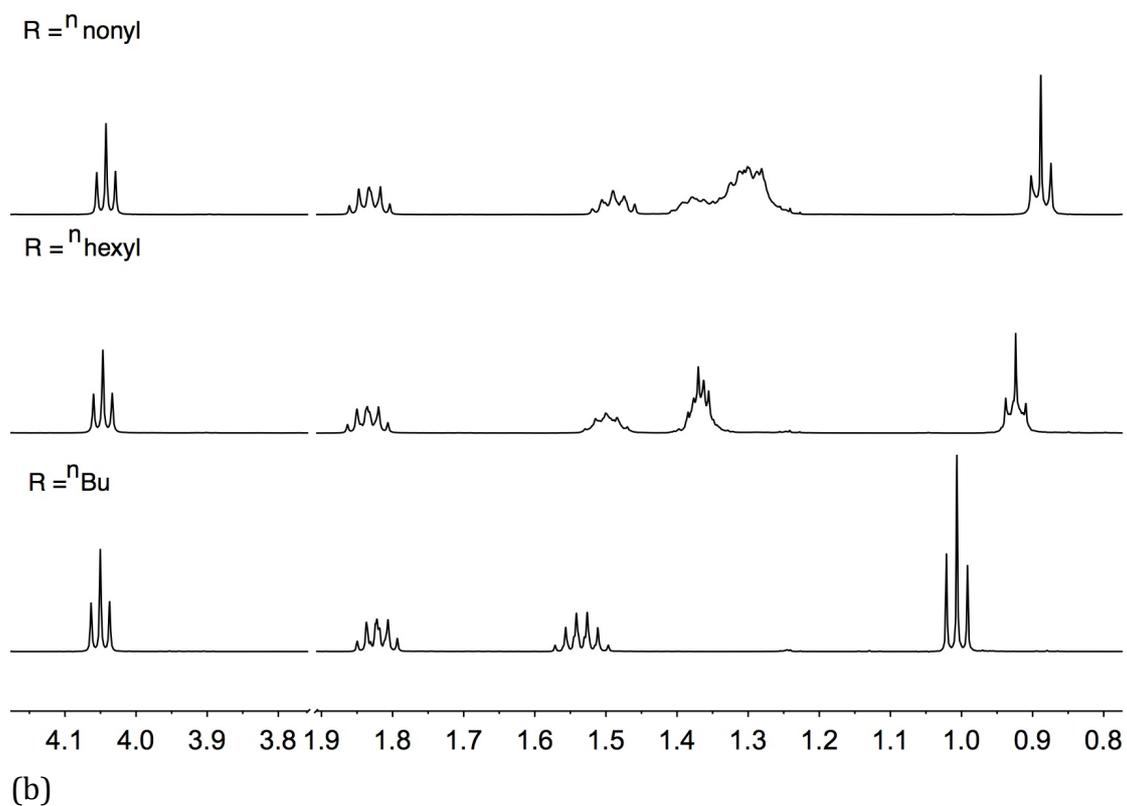
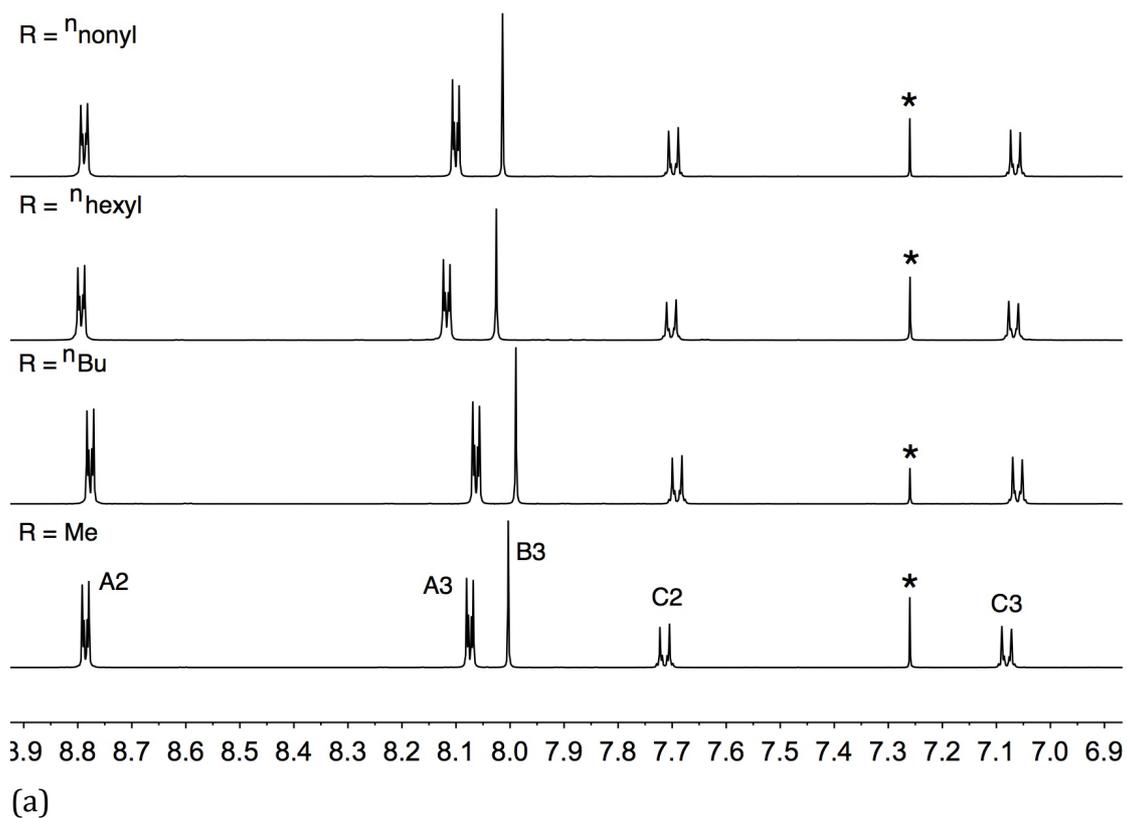


Fig. S1. 500 MHz ${}^1\text{H}$ NMR spectra of **1**, **4**, **6** and **9** (295 K, CDCl_3): (a) aromatic region (* = residual CHCl_3) for **1**, **4**, **6** and **9**, and (b) alkyl region for **4**, **6** and **9**.

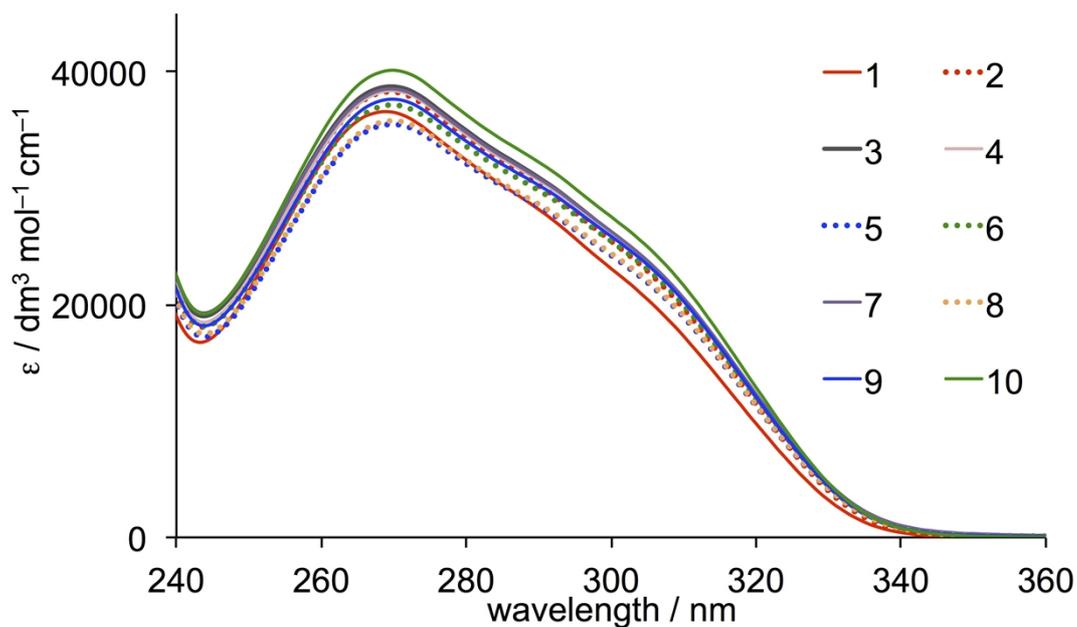


Fig. S2. Solution absorption spectra of ligands **1-10** (MeCN, 2.5×10^{-5} M).

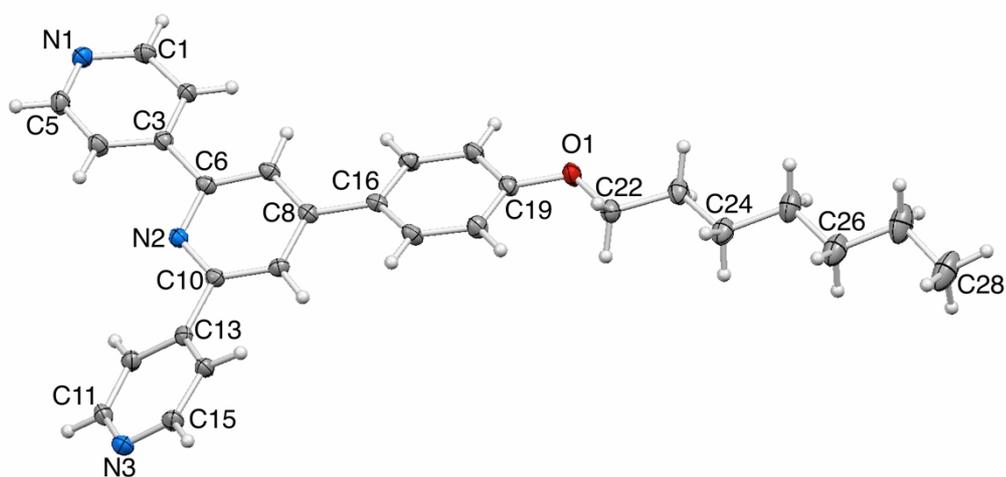


Fig. S3. Structure of **7** with ellipsoids plotted at 40% probability level. Selected bond parameters: N1-C1 = 1.327(4), N1-C5 = 1.331(4), N2-C10 = 1.339(3), N2-C6 = 1.339(4), N3-C11 = 1.337(4), N3-C15 = 1.340(4), C19-O1 = 1.361(3), O1-C22 = 1.435(3) Å; C1-N1-C5 = 115.8(2), C10-N2-C6 = 117.3(2), C11-N3-C15 = 115.8(3), C19-O1-C22 = 117.6(2)°.

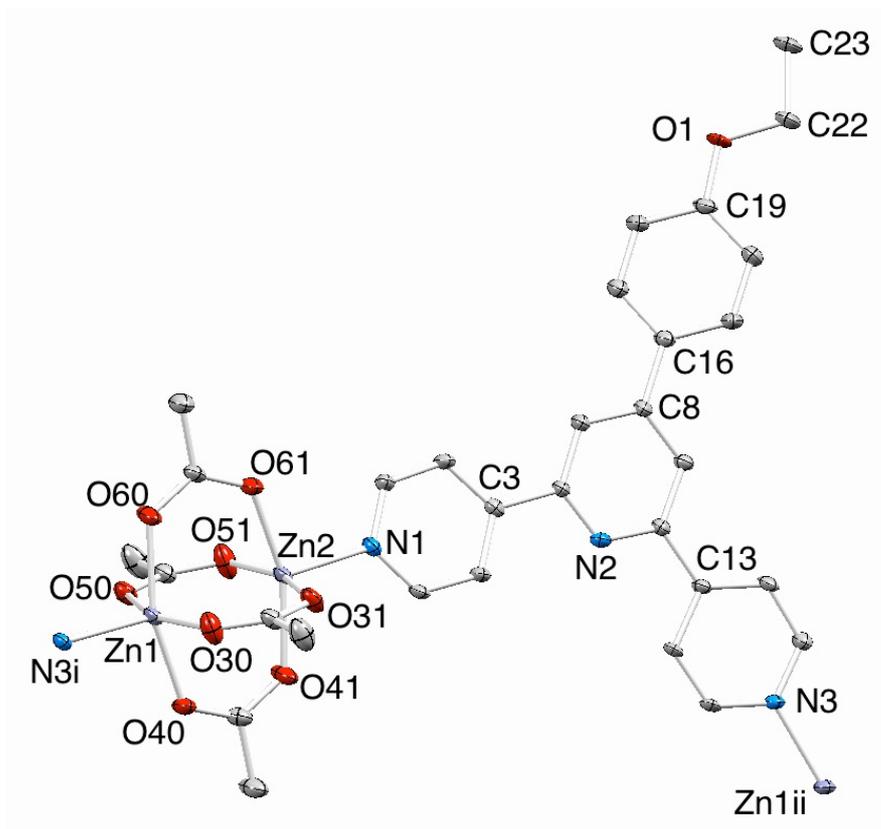


Fig. S4. Repeat unit in $[\{Zn_2(OAc)_4(\mathbf{2})\}_n]$ with ellipsoids plotted at 40% probability level. Symmetry codes: $i = 1+x, 1/2-y, 1/2+z$; $ii = -1+x, 1/2-y, -1/2+z$. Selected bond distances: $Zn1-N3^i = 2.029(4)$, $Zn1-O30 = 2.034(4)$, $Zn1-O40 = 2.035(3)$, $Zn1-O60 = 2.059(3)$, $Zn1-O50 = 2.059(3)$, $Zn2-O61 = 2.029(3)$, $Zn2-O51 = 2.032(4)$, $Zn2-N1 = 2.033(4)$, $Zn2-O41 = 2.043(3)$, $Zn2-O31 = 2.059(3)$, $Zn1\dots Zn2 = 2.8959(9)$ Å.

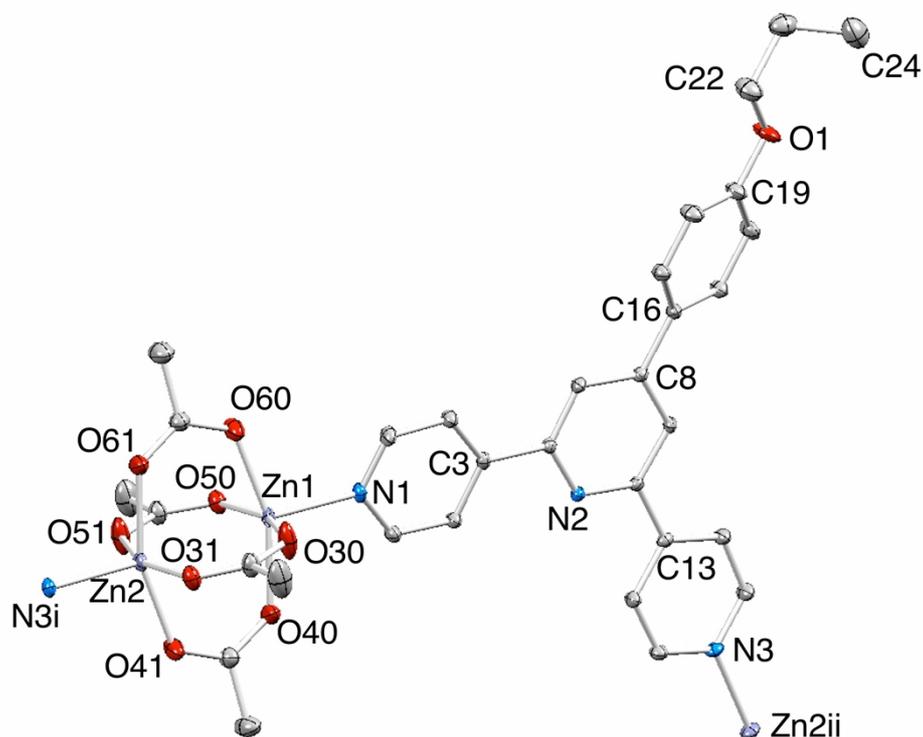


Fig. S5. Repeat unit in $[\{Zn_2(OAc)_4(\mathbf{3})\}_n]$ with ellipsoids plotted at 40% probability level. Symmetry codes: $i = -1+x, \frac{3}{2}-y, -\frac{1}{2}+z$; $ii = 1+x, \frac{3}{2}-y, \frac{1}{2}+z$. Selected bond distances: Zn1–O30 = 2.0310(17), Zn1–O60 = 2.0368(16), Zn1–N1 = 2.0373(16), Zn1–O50 = 2.0558(15), Zn1–O40 = 2.0628(16), Zn2–O51 = 2.0265(17), Zn2–N3ⁱ = 2.0339(16), Zn2–O41 = 2.0345(16), Zn2–O31 = 2.0562(15), Zn2–O61 = 2.0608(16), Zn1...Zn2 = 2.9078(4) Å.

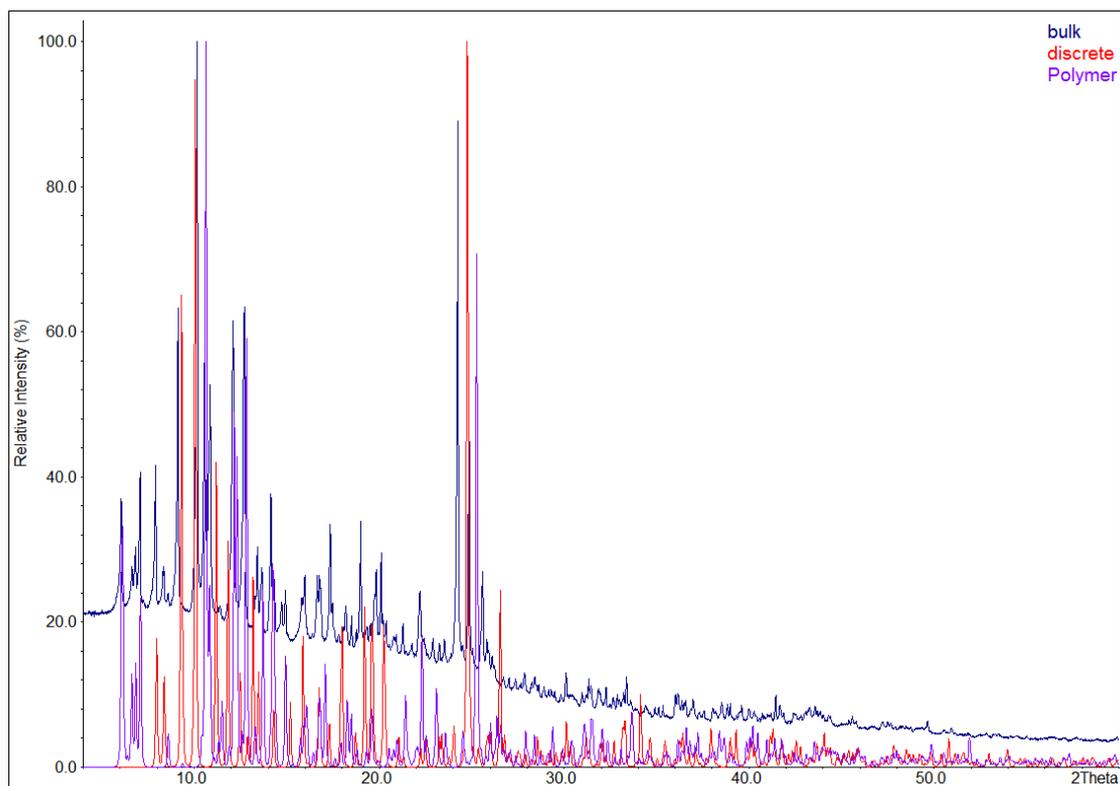


Fig. S6. Experimental powder diffraction pattern for the bulk sample of polymer $[\{2\text{Zn}_2(\text{OAc})_4(\mathbf{5})\cdot 2\text{H}_2\text{O}\}_n]$ and discrete complex $[\text{Zn}_2(\text{OAc})_4(\mathbf{5})_2]$ compared to the calculated powder patterns from single crystal data for the two components. Shifts in observed and theoretical peaks are due to the difference between the temperatures of the measurement (room temperature powder and single crystal structures at 123 K).

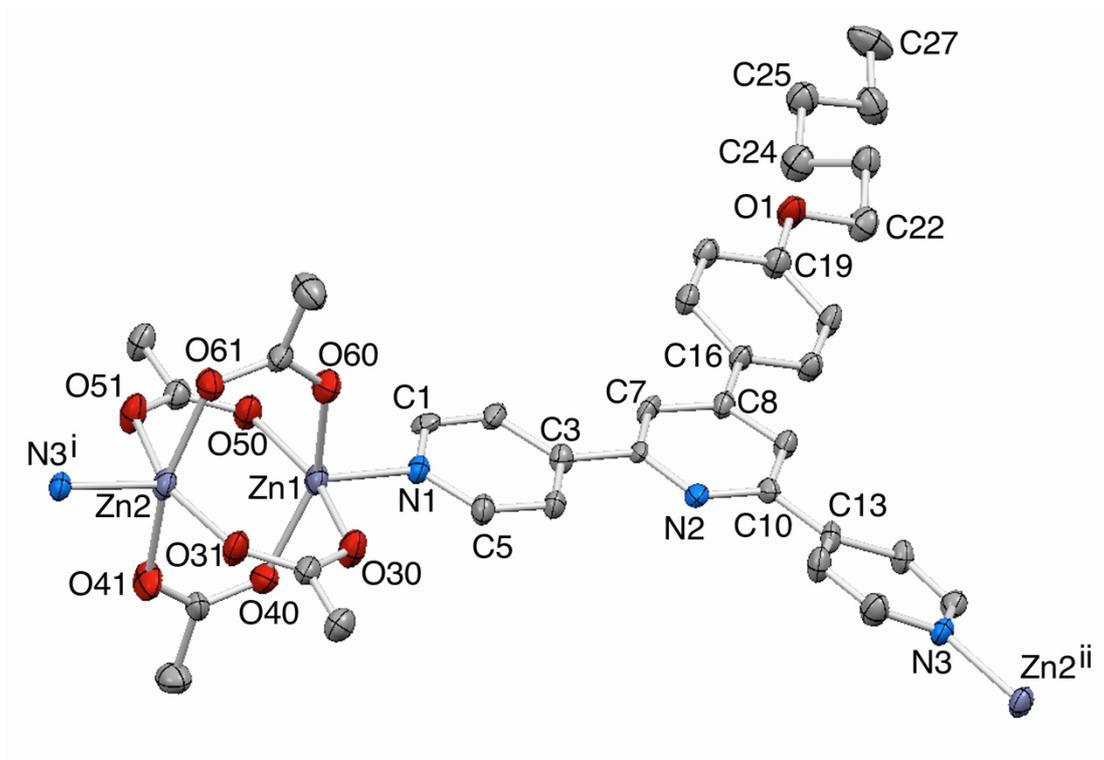


Fig. S7. Repeat unit in $[\{Zn_2(OAc)_4(\mathbf{6}) \cdot MeCO_2H\}_n]$ with ellipsoids plotted at 40% probability level and H atoms omitted. Symmetry codes: $i = -x, 1/2+y, 3/2-z$; $ii = -x, -1/2+y, 3/2-z$. Selected bond distances: Zn1–N1 = 2.024(7), Zn1–O30 = 2.031(7), Zn1–O50 = 2.042(7), Zn1–O60 = 2.053(8), Zn1–O40 = 2.062(7), Zn2–O31 = 2.013(7), Zn2–N3ⁱ = 2.026(7), Zn2–O41 = 2.035(8), Zn2–O51 = 2.048(7), Zn2–O61 = 2.078(7), Zn1...Zn2 = 2.9311(17) Å.

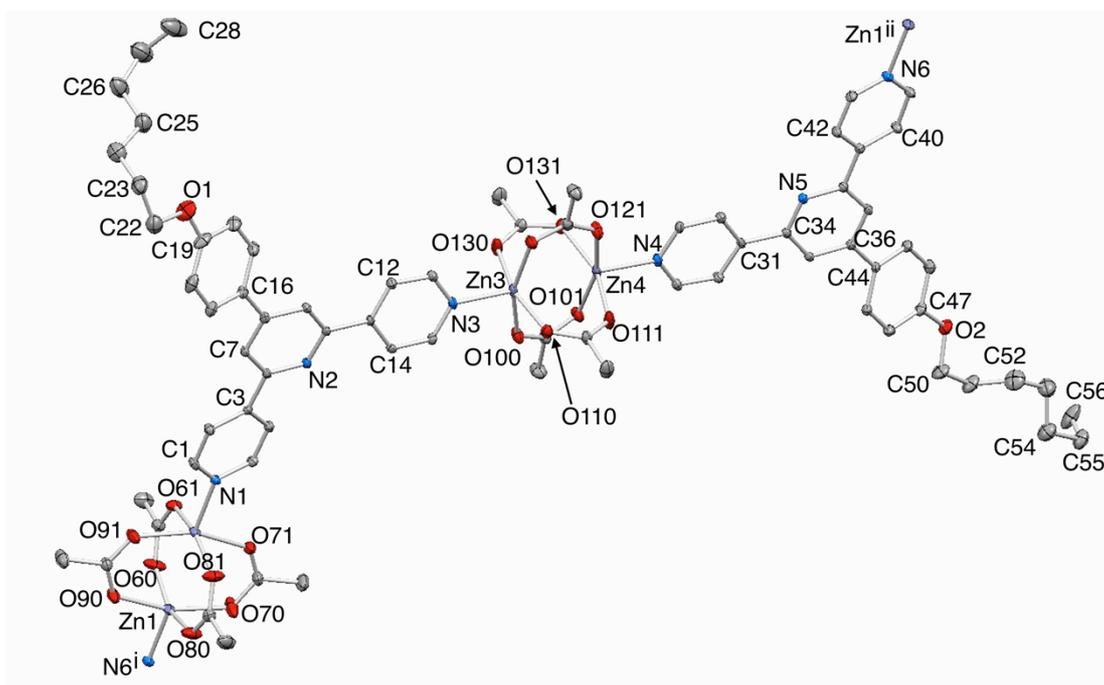


Fig. S8. Repeat unit in $[\{4\text{Zn}_2(\text{OAc})_4(\mathbf{7})\cdot 3\text{H}_2\text{O}\}_n]$ with ellipsoids plotted at 30% probability level and H atoms omitted. Symmetry codes: $i = 2+x, 1+y, z$; $ii = -2+x, -1+y, z$. Important bond distances: $\text{Zn1}-\text{O60} = 2.015(4)$, $\text{Zn1}-\text{N6}^i = 2.031(3)$, $\text{Zn1}-\text{O90} = 2.037(3)$, $\text{Zn1}-\text{O80} = 2.048(4)$, $\text{Zn1}-\text{O70} = 2.050(4)$, $\text{Zn2}-\text{O91} = 2.018(3)$, $\text{Zn2}-\text{N1} = 2.028(3)$, $\text{Zn2}-\text{O71} = 2.046(3)$, $\text{Zn2}-\text{O61} = 2.056(3)$, $\text{Zn2}-\text{O81} = 2.063(3)$, $\text{Zn3}-\text{O130} = 2.032(3)$, $\text{Zn3}-\text{N3} = 2.035(3)$, $\text{Zn3}-\text{O110} = 2.047(3)$, $\text{Zn3}-\text{O120} = 2.048(3)$, $\text{Zn3}-\text{O100} = 2.054(3)$, $\text{Zn4}-\text{O101} = 2.031(3)$, $\text{Zn4}-\text{O111} = 2.038(3)$, $\text{Zn4}-\text{N4} = 2.042(3)$, $\text{Zn4}-\text{O121} = 2.051(3)$, $\text{Zn4}-\text{O131} = 2.061(3)$, $\text{Zn1}\dots\text{Zn2} = 2.9144(8)$, $\text{Zn3}\dots\text{Zn4} = 2.8995(7)$ Å.

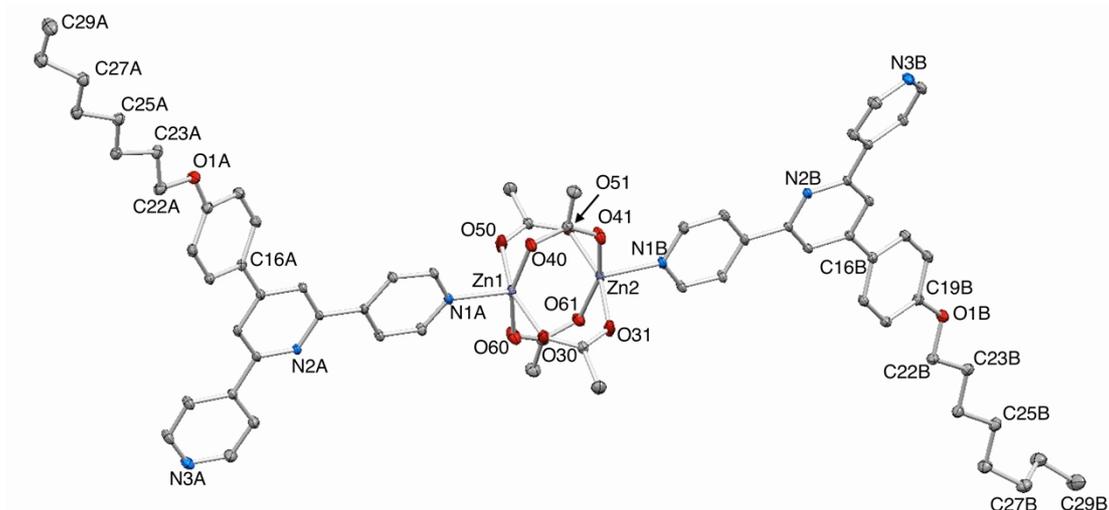


Fig. S9. Molecular structure of $[\text{Zn}_2(\text{OAc})_4(\mathbf{8})_2]$ with H atoms omitted for clarity and ellipsoids plotted at 40% probability level. Selected bond lengths: Zn1–O50 = 2.0212(18), Zn1–O40 = 2.0382(17), Zn1–N1A = 2.0404(17), Zn1–O60 = 2.0458(18), Zn1–O30 = 2.0546(17), Zn2–O31 = 2.0322(17), Zn2–O51 = 2.0378(16), Zn2–O41 = 2.0409(18), Zn2–N1B = 2.0482(18), Zn2–O61 = 2.0546(17), Zn1...Zn2 = 2.9071(4) Å.

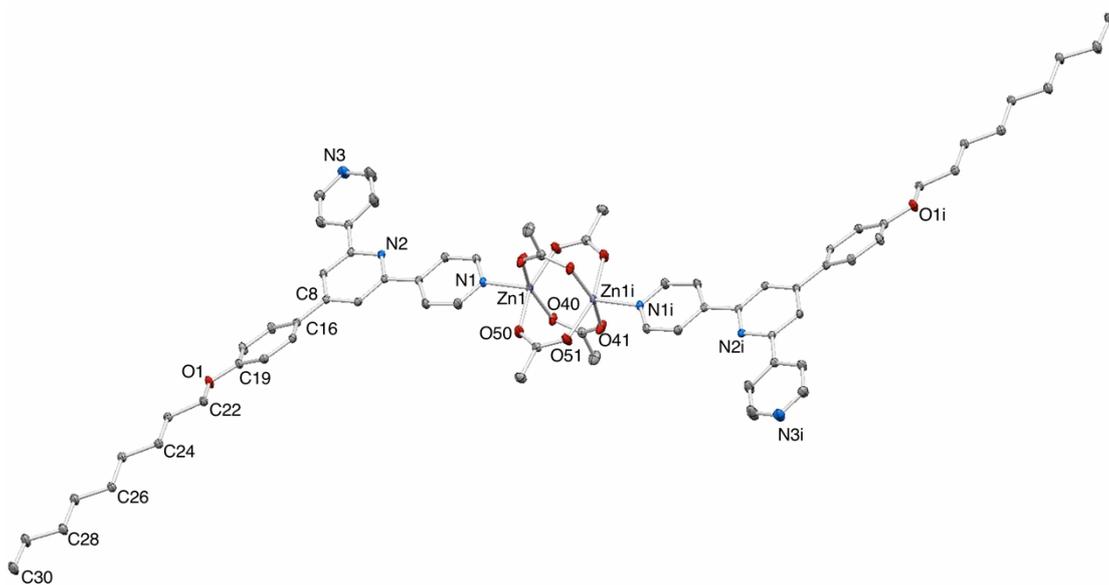


Fig. S10. Molecular structure of $[\text{Zn}_2(\text{OAc})_4(\mathbf{9})_2]$ with H atoms omitted for clarity and ellipsoids plotted at 40% probability level. Selected bond distances: Zn1–N1 = 2.0334(15), Zn1–O40 = 2.0390(15), Zn1–O50 = 2.0707(14), Zn1ⁱ–O41 = 2.0244(16), Zn1ⁱ–O51 = 2.0259(15), Zn1...Zn1ⁱ = 2.9116(5) Å; symmetry code $i = 1-x, 1-y, 1-z$.

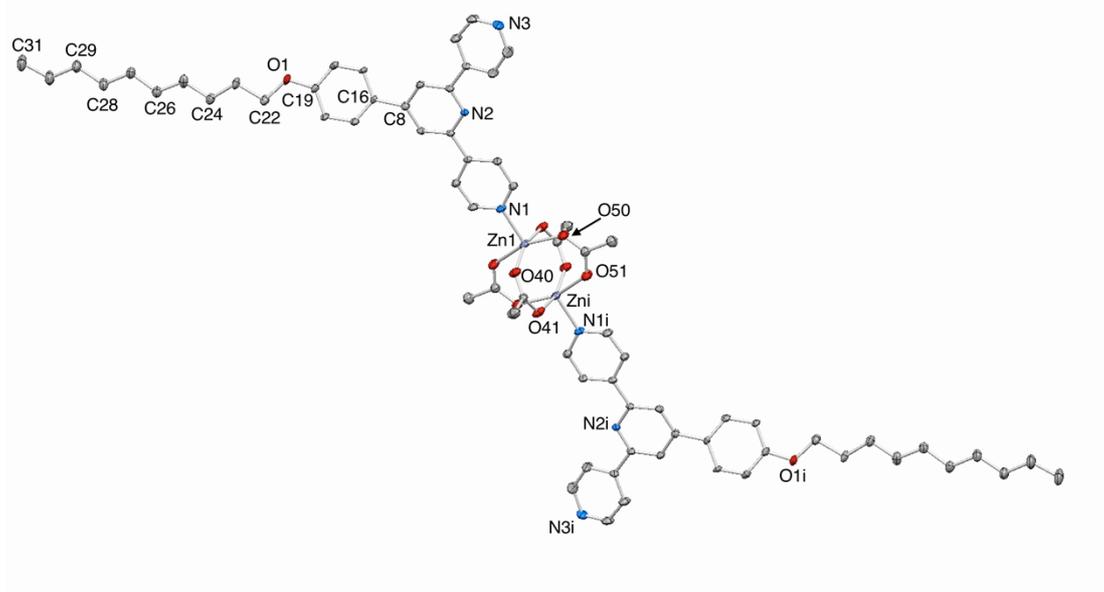


Fig. S11. Molecular structure of $[\text{Zn}_2(\text{OAc})_4(\mathbf{10})_2]$ with H atoms omitted and ellipsoids plotted at 40% probability level. The ligand is disordered and only one site (49% occupancy) is shown. Selected bond distances: $\text{Zn1}-\text{O50} = 2.0203(19)$, $\text{Zn1}-\text{O40} = 2.027(2)$, $\text{Zn1}-\text{N1} = 2.0389(19)$, $\text{Zn1}^i-\text{O41} = 2.047(2)$, $\text{Zn1}^i-\text{O51} = 2.0687(19)$, $\text{Zn1}-\text{Zn1}^i = 2.8984(6)$ Å; symmetry code $i = 1-x, 1-y, 1-z$.

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 - 2 Y. Kim, J. Kim, K. Oh, D.-S. Lee and S. B. Park, *Med. Chem. Lett.*, 2012, **3**, 151.
 - 3 A. Tavares, P. H. Schneider and A. A. Merlo, *Eur. J. Org. Chem.*, 2009, 889.