CrystEngComm



View Article Online

PAPER



Cite this: *CrystEngComm*, 2014, **16**, 9915

Received 9th July 2014, Accepted 14th September 2014

DOI: 10.1039/c4ce01422g

www.rsc.org/crystengcomm

Greasy tails switch 1D-coordination [$\{Zn_2(OAc)_4(4'-(4-ROC_6H_4)-4,2':6',4''-tpy)\}_n$] polymers to discrete [$Zn_2(OAc)_4(4'-(4-ROC_6H_4)-4,2':6',4''-tpy)_2$] complexes[†]

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The homologous series of 4'-(4-ROC₆H₄)-4,2':6',4"-tpy ligands with R = Me, Et, "Pr, "Bu, "pentyl, "hexyl, ⁿheptyl, ⁿoctyl, ⁿnonyl and ⁿdecyl (1-10, respectively) are reported, including single crystal structures of 6 and 7. Reactions of zinc(11) acetate with 1-10 have been investigated using room temperature crystallization methods (diffusion or layering). For ligands with the shortest alkoxy substituents, 1-dimensional coordination polymers $[{Zn_2(OAc)_4(L)}_n]$ (L = 1, 2 or 3) are formed. In each polymer, the $4'-(4-ROC_6H_4)-4.2':6'.4''$ -tpy ligands bind zinc through the two outer pyridine donors. The polymer structures are similar with the *n*-propyl chain adopting a folded conformation in $[{Zn_2(OAc)_4(3)}_n]$ which allows it to fit in the cavity occupied by methyl or ethyl groups in $[{Zn_2(OAc)_4(1)_n}]$ and $[{Zn_2(OAc)_4(2)_n}]$. Reaction between 5 and $Zn(OAc)_2 \cdot 2H_2O$ gives both the coordination polymer [$\{2Zn_2(OAc)_4(5) \cdot 2H_2O\}_n$] and the discrete complex $[Zn_2(OAc)_4(5)_2]$. Although the zig-zag form of the polymer chain in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ mimics those in $[\{Zn_2(OAc)_4(L)\}_n]$ (L = 1, 2 or 3), packing interactions differ and the wider separation of the chains in a sheet results in the incorporation of water molecules in the lattice. π -Stacking between pyridine rings in $[{Zn_2(OAc)_4(L)}_n]$ (L = 1, 2 or 3) produces infinite assemblies in contrast to isolated tetradecker π -stacks in [$\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n$]. This assembly is replicated in $[{4Zn_2(OAc)_4(7)} \cdot 3H_2O_n]$ (*n*-heptoxy substituents). In contrast, the *n*-hexoxy-containing coordination polymer crystallizes with acetic acid in the lattice; $[{Zn_2(OAc)_4(6)} \cdot MeCO_2H]_n]$ consists of zig-zag polymer chains which π -stack in a manner which is unique among the other polymers. Further lengthening of the alkoxy chain favours the formation of $[Zn_2(OAc)_4(L)_2]$ (L = 8, 9 or 10) which are analogues of $[Zn_2(OAc)_4(5)_2]$. In each, the 4'-(4-ROC₆H₄)-4,2':6',4''-tpy ligand is monodentate. The alkoxy chains are in extended (or close to extended) conformations and pack into planar sheets with interdigitated chains. Pockets in the sheets are occupied by methyl groups of $\{Zn_2(OAc)_4\}$ units in the adjacent sheet in a balland-socket assembly motif. The study shows that coordination polymers $[{Zn_2(OAc)_4(L)}_n]$ in which π -stacking are the dominant interactions are favoured for small alkoxy substituents (ligands 1–3); for ligands 8–10, discrete complexes $[Zn_2(OAc)_4(L)_2]$ in which van der Waals interactions dominate are observed. In the intermediate range (ligands 5-7), the preference between the two structure types appears to be marginal

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Introduction

4,2':6',4"-Terpyridine (4,2':6',4"-tpy) ligands are readily accessible building blocks for the assembly of coordination polymers and networks.¹ In contrast to the bis(chelating) mode of 2,2':6',2"-terpyridine (the most commonly encountered terpyridine isomer), 4,2':6',4"-tpy offers a V-shaped building block with a fixed internal angle of 120°. Despite possessing three N-donors, 4,2':6',4"-tpy typically coordinates through only the outer pyridine domains. This preference was

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[†] Electronic supplementary information (ESI) available: Synthesis and characterization of precursors. Fig. S1–S11: ¹H NMR and electronic spectra of ligands, structural figures and powder diffraction data. See DOI: 10.1039/ c4ce01422g

initially demonstrated in the 1-dimensional coordination polymer [{ $ZnCl_2(4,2':6',4''-tpy)$ }_n],² and has now been observed in a wide range of [{ $ZnX_2(4'-R-4,2':6',4''-tpy)$ }_n] (X = Cl, Br) and [{ $Zn_2(OAc)_4(4'-R-4,2':6',4''-tpy)$ }_n] complexes.¹ Recently, there has been interest in the incorporation of coordinatively non-innocent carboxylate groups (*e.g.* 4-carboxyphenyl, 2-carboxyphenyl) in the 4'-position of the 4,2':6',4''-tpy domain.³⁻⁷ The introduction of heterocyclic substituents (pyridine,⁸⁻¹⁷ imidazole¹⁸ and pyrimidine¹⁹) in the 4'-position of 4,2':6',4''-tpy is a simple means of increasing structural diversity and enhancing the dimensionality. Ditopic bis(4,2':6',4''-terpyridine) ligands remain underexplored,^{20,21} and open further routes to developing 2- and 3-dimensional assemblies containing 4,2':6',4''-tpy metal-binding domains.

In 2002, Cave and Raston reported the synthesis and structure of the helical coordination polymer $[{ZnCl_2L}_n]$ in which L is 4'-(4-octoxyphenyl)-4,2':6',4"-terpyridine.²² Despite incorporating long alkyl chains, the polymer is structurally similar to others in the $[{ZnX_2(4'-R-4,2':6',4''-tpy)}_n]$ family.¹ In contrast, we have observed that the reaction of 4'-(4-dodecoxyphenyl)-4,2':6',4"-terpyridine with zinc(II) acetate leads to a discrete molecule containing a $\{Zn_2(OAc)_4\}$ paddle wheel unit with monodentate 4'-(4-dodecoxyphenyl)-4,2':6',4"-tpy ligands in the axial sites.²³ This breaks the common pattern of reactions of $Zn(OAc)_2 \cdot 2H_2O$ with 4'-X-4,2':6',4"-tpy ligands leading to zigzag chains with the tpy domain bridging between $\{Zn_2(OAc)_4\}$ units.¹ We now present a systematic study of the reactions of Zn(OAc)2.2H2O with a homologous series of $4'-(4-ROC_6H_4)-4,2':6',4''-tpy ligands (1-10, Scheme 1) in which$ R is an alkyl substituent, and we illustrate the competition between π -stacking interactions of aromatic domains and van der Waals interactions between alkoxy chains as a function of chain length in determining the structure type.

Experimental

Electrospray mass spectra were measured on a Bruker Esquire 3000 instrument using MeCN solutions of samples. Absorption spectra were recorded on Varian Carry 5000 spectrometer, and IR spectra on a Shimadzu FTIR-8400S or Perkin Elmer UATR Two spectrophotometer. ¹H and ¹³C NMR spectra were recorded using a Bruker Avance III-500 or 400 NMR



Scheme 1 Structures of the ligands and numbering scheme for NMR spectroscopic assignments.

spectrometers at 295 K; chemical shifts were referenced to residual solvent peaks with respect to δ (TMS) = 0 ppm.

Commercial sources or synthetic and characterization details for precursors, as well as IR spectroscopic data for the ligands are given in the ESI.[†]

4'-(4-Methoxyphenyl)-4,2':6',4"-terpyridine (1)

p-Anisaldehyde (1.21 mL, 1.36 g, 10.0 mmol) was dissolved in EtOH (60 mL). 4-Acetylpyridine (2.27 mL, 2.47 g, 20.0 mmol) was added, followed by crushed KOH (1.12 g, 20.0 mmol). The mixture changed from colourless to yellow, to red. Aqueous NH₃ (25%, 49.3 mL, 44.9 g, 320 mmol) was added dropwise and the mixture was stirred at room temperature overnight. The white precipitate that formed was collected by filtration, washed with water $(3 \times 10 \text{ mL})$ and EtOH $(3 \times 10 \text{ mL})$ and was recrystallized from EtOH. Compound 1 was obtained as a white solid (1.61 g, 4.73 mmol, 47.3%). M.p. 203.5 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.78 (m, 4H, H^{A2}), 8.07 (m, 4H, H^{A3}), 8.00 (s, 2H, H^{B3}), 7.71 (m, 2H, H^{C2}), 7.08 (m, 2H, H^{C3}), 3.91 (s, 3H, H^{Me}); ¹³C{¹H}NMR (126 MHz, CDCl₃) δ/ppm 161.1 (C^{C4}), 155.3 (C^{A4}), 150.8 (C^{B4}), 150.7 (C^{A2}), 146.3 (C^{B2}), 130.2 (C^{C1}), 128.5 (C^{C2}), 121.3 (C^{A3}), 118.6 (C^{B3}), 114.9 (C^{C3}), 55.6 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ mol dm⁻³) λ/nm (ε/dm^3 mol⁻¹ cm⁻¹) 269 (36600). ESI-MS m/z 340.3 $[M + H]^+$ (calc. 340.1). Found C 77.19, H 5.08, N 12.36; required for C₂₂H₁₇N₃O C 77.86, H 5.05, N 12.38.

4'-(4-Ethoxyphenyl)-4,2':6',4"-terpyridine (2)

4-Ethoxybenzaldehyde (1.50 g, 10.0 mmol) was dissolved in EtOH (60 mL), then 4-acetylpyridine (2.27 mL, 2.47 g, 20.0 mmol) was added, followed by crushed KOH (1.12 g, 20.0 mmol). Colour changes, addition of aqueous NH₃ (25%, 49.3 mL, 44.9 g, 320 mmol), work up and recrystallization were as for the preparation of 1. Compound 2 was obtained as a white solid (2.23 g, 6.31 mmol, 63.1%). M.p. 211.7 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.78 (m, 4H, H^{A2}), 8.07 (m, 4H, H^{A3}), 8.00 (s, 2H, H^{B3}), 7.70 (m Hz, 2H, H^{C2}), 7.06 (m, 2H, H^{C3}), 4.13 (q, J = 7.0 Hz, 2H, H^{OCH_2}), 1.48 (t, J = 7.0 Hz, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.5 (C^{C4}) , 155.3 (C^{A4}) , 150.8 (C^{B4}) , 150.6 (C^{A2}) , 146.3 (C^{B2}) , 130.0 (C^{C1}), 128.5 (C^{C2}), 121.34 (C^{A3}), 118.5 (C^{B3}), 115.4 (C^{C3}), 63.9 (C^{OCH₂}), 14.9 (C^{Me}). UV-VIS (MeCN, 2.5×10^{-5} M) λ/nm $(\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ 269 (38 300). ESI-MS m/z 354.3 $[M + H]^+$ (calc. 354.2). Found C 76.59, H 5.64, N 11.35; required for C₂₃H₁₉N₃O·0.5H₂O C 76.22, H 5.56, N 11.59.

4'-(4-^{*n*}Propoxyphenyl)-4,2':6',4"-terpyridine (3)

4-Propoxybenzaldehyde (1.63 mL, 1.69 g, 10.0 mmol) was dissolved in EtOH (60 mL); 4-acetylpyridine (2.27 mL, 2.47 g, 20.0 mmol) was added followed by crushed KOH (1.12 g, 20.0 mmol). Colour changes, addition of aqueous NH₃ (25%, 49.3 mL, 44.9 g, 320 mmol), work up and recrystallization were as for the preparation of 1. Compound 3 was obtained as a white solid (2.21 g, 6.01 mmol, 60.1%). M.p. 195.8 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.77 (m, 4H, H^{A2}), 8.05

(m, 4H, H^{A3}), 7.98 (s, 2H, H^{B3}), 7.68 (m, 2H, H^{C2}), 7.06 (m, 2H, H^{C3}), 4.00 (t, J = 6.5 Hz, 2H, H^{OCH₂}), 1.86 (m, 2H, H^{CH₂Me}), 1.08 (t, J = 7.4 Hz, 3H, H^{Me}); ¹³C{¹H} MMR (126 MHz, CDCl₃) δ /ppm 160.7 (C^{C4}), 155.2 (C^{A4}), 150.7 (C^{B4}), 150.6 (C^{A2}), 146.3 (C^{B2}), 129.87 (C^{C1}), 128.4 (C^{C2}), 121.3 (C^{A3}), 118.4 (C^{B3}), 115.4 (C^{C3}), 69.9 (C^{OCH₂}), 22.7 (C^{CH₂Me}), 10.7 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ M) λ /nm (ε /dm³ mol⁻¹ cm⁻¹) 270 (38 700). ESI-MS m/z 368.3 [M + H]⁺ (calc. 368.2). Found C 77.82, H 5.79, N 11.60; required for C₂₄H₂₁N₃O C 78.45, H 5.76, N 11.44.

4'-(4-ⁿButoxyphenyl)-4,2':6',4"-terpyridine (4)

Compound 4 has previously been prepared by a grinding method,²⁴ but we find the following more convenient; NMR spectra were not previously assigned.

4-Butoxybenzaldehyde (1.76 mL, 1.82 g, 10.0 mmol) was dissolved in EtOH (60 mL), then 4-acetylpyridine (2.27 mL, 2.47 g, 20.0 mmol) was added to the solution and crushed KOH (1.12 g, 20.0 mmol) was added in one portion. Colour changes, addition of aqueous NH₃ (25%, 49.3 mL, 44.9 g, 320 mmol), work up and recrystallization were as for the preparation of 1. Compound 4 was obtained as a white solid (2.15 g, 5.63 mmol, 56.3%). M.p. 188.9 °C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 8.78 (m, 4H, H^{A2}), 8.06 (m, 4H, H^{A3}), 7.99 (s, 2H, H^{B3}), 7.69 (m, 2H, H^{C2}), 7.13-7.02 (m, 2H, H^{C3}), 4.06 (t, J = 6.5 Hz, 2H, H^{OCH_2}), 1.82 (m, 2H, $H^{OCH_2CH_2}$), 1.53 (m, 2H, H^{CH_2Me}), 1.01 (t, J = 7.4 Hz, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ/ppm 160.7 (C^{C4}), 155.3 (C^{A4}), 150.8 (C^{B4}), 150.6 (C^{A2}), 146.3 (C^{B2}), 129.9 (C^{C1}), 128.4 (C^{C2}), 121.3 (C^{A3}), 118.5 (C^{B3}), 115.4 (C^{C3}), 68.1 (C^{OCH₂}), 31.4 (C^{OCH₂CH₂}), 19.4 (C^{CH_2Me}), 14.0 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ M) λ/nm $(\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ 270 (38400). ESI-MS m/z 382.3 [M + H]⁺ (calc. 382.2). Found C 78.12, H 6.18, N 11.17; required for C₂₅H₂₃N₃O C 78.71, H 6.08, N 11.02.

4'-(4-^{*n*}Pentoxyphenyl)-4,2':6',4"-terpyridine (5)

4-Pentoxybenzaldehyde (1.40 g, 7.29 mmol) was dissolved in EtOH (30 mL), then 4-acetylpyridine (1.70 mL, 1.85 g, 15.0 mmol) was added to the solution and crushed KOH (0.84 g, 15.0 mmol) was added in one portion. Colour changes, addition of aqueous NH₃ (25%, 49.3 mL, 32.4 mL, 29.4 g, 210 mmol), work up and recrystallization were as for the preparation of 1. Compound 5 was obtained as a white solid (1.74 g, 4.40 mmol, 60.3%). M.p. 172.3 °C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 8.79 (m, 4H, H^{A2}), 8.12 (m, 4H, H^{A3}), 8.02 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.07 (m, 2H, H^{C3}), 4.05 (t, J = 6.6 Hz, 2H, H^{OCH₂}), 1.84 (m, 2H, H^{OCH₂CH₂}), 1.48 (m, 2H, $H^{CH_2CH_2Me}$), 1.41 (m, 2H, H^{CH_2Me}), 0.96 (t, J = 7.2 Hz, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.8 (C^{C4}), 155.1 (C^{A4}), 150.9 (C^{B4}), 150.0 (C^{A2}), 146.9 (C^{B2}), 129.8 (C^{C1}), 128.5 (C^{C2}), 121.5 (C^{A3}), 118.7 (C^{B3}), 115.5 (C^{C3}), 68.4 (C^{OCH₂}), 29.0 (C^{OCH₂CH₂}), 28.3 (C^{CH₂CH₂Me), 22.6 (C^{CH₂Me)}, 14.2 (C^{Me}).} UV-VIS (MeCN, 2.5 × 10^{-5} M) λ/nm (ϵ/dm^3 mol⁻¹ cm⁻¹) 270 (35 500). ESI-MS m/z 396.4 $[M + H]^+$ (calc. 396.2). Found C 78.12, H 6.44, N 10.43; required for C₂₆H₂₅N₃O C 78.96, H 6.37, N 10.62.

4'-(4-^{*n*}Hexoxyphenyl)-4,2':6',4"-terpyridine (6)

4-Hexoxybenzaldehyde (0.62 g, 2.99 mmol) was dissolved in EtOH (20 mL), then 4-acetylpyridine (0.79 mL, 0.87 g, 7.00 mmol) was added to the solution and crushed KOH (0.39 g, 7.00 mmol) was added in one portion. Colour changes, addition of aqueous NH₃ (25%, 27.7 mL, 25.2 g, 180 mmol), work up and recrystallization were as for the preparation of 1. Compound 6 was obtained as a white solid (0.76 g, 1.86 mmol, 62.1%). M.p. 183.4 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.79 (m, 4H, H^{A2}), 8.12 (m, 4H, H^{A3}), 8.03 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.07 (m, 2H, H^{C3}), 4.05 (t, J = 6.6 Hz, 2H, H^{OCH_2}), 1.83 (m, 2H, $H^{OCH_2CH_2}$), 1.50 (m, 2H, H^{OCH₂CH₂CH₂), 1.37 (m, 4H, H^{CH₂}), 0.92 (m, 3H,} H^{Me} ; ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.8 (C^{C4}), 155.07 (C^{A4}), 150.9 (C^{B4}), 150.0 (C^{A2}), 146.9 (C^{B2}), 129.8 (C^{C1}), 128.5 (C^{C2}), 121.5 (C^{A3}), 118.8 (C^{B3}), 115.5 (C^{C3}), 68.4 (C^{OCH_2}), 31.7 ($C^{CH_2CH_2Me}$), 29.3 ($C^{OCH_2CH_2}$), 25.9 ($C^{OCH_2CH_2CH_2CH_2}$), 22.7 (C^{CH_2Me}), 14.2 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ M) λ/nm $(\varepsilon/dm^3 mol^{-1} cm^{-1})$ 270 (37100). ESI-MS m/z 410.4 $[M + H]^+$ (calc. 410.2). Found C 78.60, H 6.63, N 10.25; required for C₂₇H₂₇N₃O C 79.19, H 6.65, N 10.26.

4'-(4-^{*n*}Heptoxyphenyl)-4,2':6',4"-terpyridine (7)

4-Heptoxybenzaldehyde (0.95 mL, 0.94 g, 4.27 mmol) was dissolved in EtOH (40 mL), then 4-acetylpyridine (0.97 mL, 1.06 g, 8.54 mmol) was added to the solution and crushed KOH (0.48 g, 8.54 mmol) was added in one portion. Colour changes, addition of aqueous NH₃ (25%, 21.1 mL, 19.2 g, 137 mmol), work up (but using 5 mL H₂O and EtOH instead of 10 mL) and recrystallization were as for the preparation of 1. Compound 7 was obtained as a white solid (1.15 g, 2.72 mmol, 63.8%). M.p. 188.1 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.79 (m, 4H, H^{A2}), 8.07 (m, 4H, H^{A3}), 8.00 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.06 (m, 2H, H^{C3}), 4.04 (t, J = 6.6 Hz, 2H, H^{OCH₂}), 1.84 (m, 2H, H^{OCH₂CH₂}), 1.49 (m, 2H, H^{OCH₂CH₂CH₂),} 1.38 (m, 2H, H^{OCH₂CH₂CH₂CH₂), 1.33 (m, 4H, H^{CH₂}), 0.91} (m, 3H, H^{Me}); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ /ppm 160.7 (C^{C4}), 155.3 (C^{A4}), 150.8 (C^{B4}), 150.7 (C^{A2}), 146.3 (C^{B2}), 129.8 (C^{C1}), 128.5 (C^{C2}), 121.3 (C^{A3}), 118.5 (C^{B3}), 115.4 (C^{C3}), 68.4 (C^{OCH_2}), 31.9 ($C^{CH_2CH_2Me}$), 29.4 ($C^{OCH_2CH_2}$), 29.2 ($C^{OCH_2CH_2CH_2CH_2}$), 26.2 (C^{OCH2CH2CH2}), 22.8 (C^{CH2Me}), 14.3 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ M) λ/nm (ε/dm^3 mol⁻¹ cm⁻¹) 270 (38500). ESI-MS m/z 424.5 $[M + H]^+$ (calc. 424.2). Found C 78.82, H 6.96, N 10.00; required for C₂₈H₂₉N₃O C 79.40, H 6.90, N 9.92.

4'-(4-ⁿOctoxyphenyl)-4,2':6',4"-terpyridine (8)

Compound 8 has previously been prepared by a grinding method,²⁴ but we find the following more convenient; NMR spectra were not previously assigned.

4-Octoxybenzaldehyde (1.41 g, 6 mmol) was dissolved in EtOH (50 mL), then 4-acetylpyridine (1.36 mL, 1.48 g, 12 mmol) was added to the solution and crushed KOH (0.67 g, 12 mmol) was added in one portion. Colour changes, addition of aqueous NH_3 (25%, 30.8 mL, 28 g, 200 mmol),

work up (but using 5 mL H₂O and EtOH instead of 10 mL) and recrystallization were as for the preparation of 1. Compound 8 was obtained as a white solid (1.54 g, 3.52 mmol, 58.7%). M.p. 189.8 °C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 8.80 (m, 4H, H^{A2}), 8.14 (m, 4H, H^{A3}), 8.04 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.07 (m, 2H, H^{C3}), 4.05 (t, J = 6.6 Hz, 2H, H^{OCH_2}), 1.83 (m, 2H, H^{OCH₂CH₂}), 1.49 (m, 2H, H^{OCH₂CH₂CH₂}), 1.33 (overlapping m, 8H, H^{CH₂}), 0.90 (m, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.8 (C^{C4}), 155.0 (C^{A4}), 151.0 (C^{B4}), 149.7 (C^{A2}), 147.1 (C^{B2}), 129.7 (C^{C1}), 128.5 (C^{C2}), 121.6 (C^{A3}), 118.9 (C^{B3}), 115.5 (C^{C3}), 68.4 (C^{OCH₂}), 32.0 (C^{CH₂CH₂Me), 29.5 (C^{CH₂}), 29.4} (C^{CH₂}), 29.3 (C^{OCH₂CH₂}), 26.2 (C^{OCH₂CH₂CH₂}), 22.8 (C^{CH₂Me}), 14.3 (C^{Me}). UV-VIS (MeCN, 2.5×10^{-5} M) $\lambda/\text{nm} (\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ 270 (35 800). ESI-MS m/z 438.5 $[M + H]^+$ (calc. 438.3). Found C 79.14, H 7.11, N 9.59; required for C₂₉H₃₁N₃O C 79.60, H 7.14, N 9.60.

4'-(4-ⁿNonoxyphenyl)-4,2':6',4"-terpyridine (9)

4-Nonoxybenzaldehyde (1.62 g, 6.52 mmol) was dissolved in EtOH (50 mL), then 4-acetylpyridine (1.81 mL, 1.98 g, 16 mmol) was added to the solution and crushed KOH (0.90 g, 16 mmol) was added in one portion. Colour changes, addition of aqueous NH₃ (25%, 38.5 mL, 35.1 g, 300 mmol), work up (but using 7 mL H₂O and EtOH instead of 10 mL) and recrystallization were as for the preparation of 1. Compound 9 was obtained as a white solid (1.83 g, 4.05 mmol, 62.1%). M.p. 167.7 °C. ¹H NMR (500 MHz, CDCl₃) δ/ppm 8.79 (m, 4H, H^{A2}), 8.10 (m, 4H, H^{A3}), 8.01 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.06 (m, 2H, H^{C3}), 4.04 (t, J = 6.6 Hz, 2H, H^{OCH_2}), 1.83 (m, 2H, $H^{OCH_2CH_2}$, 1.48 (m, 2H, $H^{OCH_2CH_2CH_2}$), 1.37 (m, 2H, H^{OCH₂CH₂CH₂CH₂), 1.35–1.23 (overlapping m, 8H, H^{CH₂}), 0.88} (m, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.8 (C^{C4}), 155.1 (C^{A4}), 150.9 (C^{B4}), 150.2 (C^{A2}), 146.7 (C^{B2}), 129.8 (C^{C1}) , 128.5 (C^{C2}) , 121.5 (C^{A3}) , 118.7 (C^{B3}) , 115.4 (C^{C3}) , 68.4 (C^{OCH_2}) , 32.0 $(C^{CH_2CH_2CH_2Me})$, 29.7 $(C^{CH_2CH_2CH_2CH_2CH_2Me})$, 29.5 $(C^{OCH_2CH_2CH_2CH_2})$, 29.4 $(C^{CH_2CH_2CH_2Me})$, 29.3 $(H^{OCH_2CH_2})$, 26.2 $(C^{OCH_2CH_2CH_2})$, 22.8 (C^{CH_2Me}) , 14.3 (C^{Me}) . UV-VIS (MeCN, 2.5 × 10^{-5} M) λ/nm (ε/dm^3 mol⁻¹ cm⁻¹) 270 (37600). ESI-MS m/z452.5 [M + H]⁺ (calc. 452.3). Found C 80.09, H 7.33, N 9.37; required for C₃₀H₃₃N₃O C 79.79, H 7.37, N 9.30.

4'-(4-ⁿDecoxyphenyl)-4,2':6',4"-terpyridine (10)

4-([4,2':6',4"-Terpyridin]-4'-yl)phenol (see ESI†) (0.35 g, 1.00 mmol) was dissolved in acetone (40 mL), K₂CO₃ (0.27 g, 2.00 mmol) was added to the solution and the reaction mixture was refluxed for 15 min. 1-Bromodecane was added and the reaction mixture was refluxed overnight. The brown precipitate was filtered, dissolved in chloroform and washed with aq. K₂CO₃ solution. The organic layers were dried over MgSO₄ and the solvent removed. The off-white solid so obtained was purified by column chromatography (SiO₂, ethylacetate: cyclohexane 1:1, $R_f = 0.6$). Compound 10 was obtained as a white solid (0.11 g, 0.24 mmol, 23.6%). M.p. 153.8 °C. ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.80 (m, 4H, H^{A2}), 8.13 (m, 4H, H^{A3}), 8.03 (s, 2H, H^{B3}), 7.70 (m, 2H, H^{C2}), 7.07 (m, 2H, H^{C3}), 4.05 (t, J = 6.6 Hz, 2H, H^{OCH₂}), 1.83 (m, 2H, H^{OCH₂CH₂), 1.49 (m, 2H, H^{OCH₂CH₂CH₂), 1.42–1.12 (overlapping m, 12H, H^{CH₂}), 0.88 (m, 3H, H^{Me}); ¹³C{¹H} NMR (126 MHz, CDCl₃) δ /ppm 160.8 (C^{C4}), 155.0 (C^{A4}), 151.0 (C^{B4}), 149.8 (C^{A2}), 147.1 (C^{B2}), 129.7 (C^{C1}), 128.5 (C^{C2}), 121.6 (C^{A3}), 118.8 (C^{B3}), 115.5 (C^{C3}), 68.4 (C^{OCH₂}), 32.0 (C^{CH₂}), 29.7 (C^{CH₂}), 29.71 (C^{CH₂}), 29.5 (C^{CH₂}), 29.5 (C^{CH₂}), 29.3 (C^{OCH₂CH₂}), 26.2 (C^{CH₂}), 22.8 (C^{OCH₂CH₂CH₂), 14.3 (C^{Me}). UV-VIS (MeCN, 2.5 × 10⁻⁵ M) λ /nm (ε /dm³ mol⁻¹ cm⁻¹) 270 (40132). ESI-MS *m*/*z* 466.6 [M + H]⁺ (calc. 466.3). Found C 80.04, H 7.54, N 9.29; required for C₃₁H₃₅N₃O C 79.96, H 7.58, N 9.02.}}}

$[\{\operatorname{Zn}_2(\operatorname{OAc})_4(1)\}_n]$

An MeOH solution of 1 (17.0 mg, 0.05 mmol) was placed in a vial inside a vial containing an MeOH solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol); the total volume of solvent was 20 mL. Colourless crystals of $[{Zn_2(OAc)_4(1)}_n]$ (5.6 mg, 0.008 mmol, 16%) grew within 2 weeks. IR (solid, ν/cm^{-1}) 3074 (w), 2986 (w), 2930 (w), 2833 (w), 2051 (w), 1635 (s), 1617 (s), 1598 (s), 1539 (m), 1519 (m), 1423 (s), 1347 (m), 1327 (m), 1297 (m), 1259 (m), 1243 (m), 1222 (m), 1180 (m), 1120 (w), 1067 (m), 1051 (w), 1036 (m), 1025 (m), 993 (m), 936 (w), 897 (w), 850 (m), 832 (s), 813 (m), 774 (w), 747 (w), 733 (w), 685 (m), 666 (s), 652 (m), 641 (m), 619 (s), 568 (m), 526 (m), 497 (m). Found C 47.51, H 4.02, N 5.78; required for $C_{30}H_{29}N_3O_9Zn_2\cdot3H_2O$ C 47.39, H 4.64, N 5.53.

$[{Zn_2(OAc)_4(2)}_n]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 2 (17.7 mg, 0.05 mmol) in CHCl₃ (5 mL). Colourless crystals of $[{Zn_2(OAc)_4(2)}_n]$ (3.1 mg, 0.008 mmol, 9%) were obtained after 2 weeks. IR (solid, ν/cm^{-1}) 2972 (w), 1637 (s), 1617 (s), 1604 (s), 1539 (m), 1520 (m), 1506 (m), 1469 (m), 1422 (s), 1326 (m), 1297 (m), 1270 (m), 1245 (s), 1221 (m), 1184 (m), 1124 (w), 1068 (m), 1047 (w), 1029 (m), 981 (m), 935 (w), 897 (w), 851 (m), 835 (s), 817 (m), 751 (w), 732 (w), 688 (w), 666 (s), 652 (s), 642 (m), 620 (s), 604 (m), 529 (m), 497 (w). Found C 51.31, H 4.55, N 5.63; required for $C_{31}H_{31}N_3O_9Zn_2C$ 51.69, H 4.34, N 5.83.

$[\{\operatorname{Zn}_2(\operatorname{OAc})_4(3)\}_n]$

A solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 3 (18.4 mg, 0.05 mmol) in CHCl₃ (5 mL). Colourless crystals of $[\{\text{Zn}_2(\text{OAc})_4(3)\}_n]$ (19.7 mg, 0.027 mmol, 54%) grew within 2 weeks. IR (solid, ν/cm^{-1}) 2975 (w), 1635 (s), 1617 (s), 1604 (s), 1539 (m), 1520 (m), 1506 (m), 1469 (m), 1424 (s), 1345 (m), 1326 (m), 1298 (m), 1271 (m), 1245 (s), 1220 (m), 1184 (m), 1124 (w), 1068 (m), 1047 (w), 1029 (m), 981 (m), 935 (w), 897 (w), 851 (m), 835 (s), 817 (m), 749 (w), 733 (w), 688 (m), 666 (s), 653 (s), 642 (m), 620 (s), 605 (m), 529 (s), 497 (m). Found C 53.03, H 4.64, N 6.17; required for $C_{32}H_{33}N_3O_9Zn_2$ C 52.34, H 4.53, N 5.72.

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$[\{\operatorname{Zn}_2(\operatorname{OAc})_4(4)\}_n]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 4 (19.1 mg, 0.05 mmol) in CHCl₃ (5 mL). Colourless crystals of $[{Zn_2(OAc)_4(4)}_n]$ (16.36 mg, 0.014 mmol, 28%) grew within 2 weeks, but were not of X-ray quality. For the bulk sample: found C 51.74, H 4.87, N 5.57; required for $C_{33}H_{35}N_3O_9Zn_2 \cdot H_2O$ C 51.72, H 4.87, N 5.48.

$[\{2Zn_2(OAc)_4(5){\cdot}2H_2O\}_n]$ and $[Zn_2(OAc)_4(5)_2]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 5 (19.8 mg, 0.05 mmol) in CHCl₃ (5 mL). Colourless blocks of $[Zn_2(OAc)_4(5)_2]$ mixed with crystals of $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ were obtained. The bulk sample was characterized by powder X-ray diffraction (see text).

$[{\rm Zn}_2({\rm OAc})_4(6)\cdot{\rm MeCO}_2{\rm H}_n]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (44.0 mg, 0.20 mmol) in MeOH (8 mL) was layered over a solution of 6 (41.0 mg, 0.1 mmol) in CHCl₃ (5 mL) as solvents. Colourless crystals of [$Zn_2(OAc)_4(6) \cdot MeCO_2H$ }_n] (30 mg, 0.136 mmol, 68%) were obtained. IR (solid, ν/cm^{-1}) 2929 (w), 1636 (s), 1616 (s), 1519 (m), 1425 (s), 1293 (w), 1240 (m), 1182 (m), 1068 (w), 1031 (m), 850 (m), 834 (s), 731 (w), 666 (s), 653 (s), 621 (s), 603 (m), 528 (m). Found C 53.02, H 5.31, N 5.42; required for C₃₅H₃₉N₃O₉Zn₂·H₂O·MeCO₂H C 52.91, H 5.20, N 5.29.

$[{4Zn_2(OAc)_4(7)} \cdot 3H_2O]_n]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 7 (21.2 mg, 0.05 mmol) in CHCl₃ (5 mL). After 2 weeks, colourless crystals of $\{2[Zn_2(OAc)_4(7)]\cdot 3H_2O\}$ (4.8 mg, 0.004 mmol, 6%) had grown. Found C 53.48, H 5.50, N 5.26; required for $C_{144}H_{158}N_{12}O_{36}Zn_8 \cdot 3H_2O$ C 53.88, H 5.15, N 5.24.

$[\operatorname{Zn}_2(\operatorname{OAc})_4(8)_2]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of 8 (21.9 mg, 0.05 mmol) in CHCl₃ (5 mL). Colourless crystals of $[Zn_2(OAc)_4(8)_2]$ (19.4 mg, 0.016 mmol, 31%) were obtained after 2 weeks. IR (solid, ν/cm^{-1}) 2923 (w), 1639 (s), 1597 (s), 1516 (m), 1422 (s), 1296 (w), 1243 (m), 1179 (m), 1065 (w), 1029 (w), 997 (w), 849 (w), 828 (s), 804 (w), 680 (w), 664 (m), 637 (m), 620 (m), 604 (m), 523 (m). Satisfactory analysis for the bulk sample could not be obtained.

$[Zn_2(OAc)_4(9)_2]$

A solution of $Zn(OAC)_2 \cdot 2H_2O$ (44.0 mg, 0.20 mmol) in MeOH (8 mL) was layered over a solution of 9 (22.6 mg, 0.05 mmol) in CHCl₃ (5 mL). After 2 weeks, colourless crystals of $[Zn_2(OAC)_4(9)_2]$ (58 mg, 0.046 mmol, 91%) had grown. IR (solid, ν/cm^{-1}) 2951 (w), 2924 (w), 2851 (w), 1639 (s), 1619 (s), 1595 (s), 1539 (s), 1519 (s), 1481 (m), 1463 (m), 1424 (s), 1399 (s),

1298 (m), 1242 (m), 1178 (m), 1118 (w), 1073 (w), 1064 (m), 1030 (m), 1011 (m), 998 (m), 956 (w), 895 (w), 852 (m), 831 (s), 807 (m), 725 (w), 692 (w), 681 (m), 665 (s), 644 (m), 637 (m), 620 (s), 604 (s), 524 (m), 497 (w). Found C 62.33, H 6.08, N 6.46; required for $C_{68}H_{78}N_6O_{10}Zn_2 \cdot 2H_2O$ C 62.53, H 6.33, N 6.43.

$[Zn_2(OAc)_4(10)_2]$

A solution of $Zn(OAc)_2 \cdot 2H_2O$ (21.9 mg, 0.100 mmol) in MeOH (8 mL) was layered over a solution of **10** (23.3 mg, 0.05 mmol) in CHCl₃ (5 mL). After 2 weeks, colourless crystals of [$Zn_2(OAc)_4(10)_2$] (13.5 mg, 0.010 mmol, 21%) had grown. IR (solid, ν/cm^{-1}) 2923 (m), 2851 (w), 1638 (s), 1619 (s), 1597 (s), 1560 (m), 1539 (m), 1519 (s), 1462 (w), 1424 (s), 1399 (s), 1343 (w), 1297 (m), 1242 (s), 1179 (m), 1118 (w), 1073 (m), 1064 (m), 1030 (m), 1017 (m), 997 (m), 897 (w), 849 (m), 830 (s), 808 (m), 735 (w), 724 (w), 680 (m), 664 (s), 644 (m), 637 (s), 620 (s), 603 (s), 524 (s). Found C 64.49, H 6.40, N 6.56; required for $C_{70}H_{82}N_6O_{10}Zn_2 C$ 64.76, H 6.37, N 6.47.

Crystallography

Single crystal data were collected on a Bruker APEX-II diffractometer with data reduction, solution and refinement using the programs APEX²⁵ and SHELXL97 or SHELX-13.²⁶ ORTEP diagrams and structure analysis used Mercury v. 3.0.1 or 3.3.^{27,28} Crystallographic data for all structures are given in Table 1. Powder diffractograms were measured on a STOE STADI P diffractometer equipped with a Cu K α_1 radiation ($\lambda = 1.540598$ Å) and a Mythen1K detector.

Results and discussion

Ligand synthesis and characterization

Compounds 1-9 were prepared using the one pot method of Wang and Hanan²⁹ summarized in Scheme 2, and were isolated in yields ranging from 47.3 to 63.1%. A convenient route to compound 10 proved to be the reaction of nucleophilic 4-([4,2':6',4"-terpyridin]-4'-yl)phenol (formed by deprotection of 1 with pyridinium chloride) with 1-bromodecane (Scheme 3); this strategy is analogous to that used for the preparation of polyethyleneoxy-functionalized tpy derivatives.³⁰ The electrospray mass spectrum of each compound exhibited a base peak corresponding to $[M + H]^+$. The ¹H and $^{13}C{^{1}H}$ NMR spectra of 1–10 were assigned using COSY, NOESY, HMQC and HMBC methods, and representative ¹H NMR spectra are shown in Fig. S1.[†] The NOESY spectrum of 1 is shown in Fig. 1 and illustrates that crosspeaks between protons HA3/HB3, HB3/HC2 and HC3/HOMe (see Scheme 1 for labelling) allow unambiguous assignments of the aromatic protons in the A and C rings. The appearance of a triplet or multiplet around ∂ 4 ppm in the ¹H NMR spectrum of each compound along with an HMQC associated signal in the ¹³C NMR spectrum at ∂ 55.6 ppm in 1 or in the range 2 64-69 ppm for 2-10 was consistent with the presence of the alkoxy substituent. Fig. S2[†] shows the solution

Table 1	Crystallographic data for ligands	6 and 7, and the zinc(II) complex	tes. $T = 123$ K and threshold $I > 2\sigma(I)$ for all structures
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$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			7	6	Compound
Formula weight 409.52 423.54 703.4 720.37 Crystal colur and habit Colourless block Colourless block Colourless plate Monoclinic <	$C_{30}H_{29}N_3O_9Zn_2$ $C_{31}H_{31}N_3O_9Zn_2$	C ₃₀ H ₂₉ N ₃	C ₂₈ H ₂₉ N ₃ O	C ₂₇ H ₂₇ N ₃ O	Formula
	06.34 720.37	706.34	423.54	409.52	Formula weight
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Colourless block Colourless plate	Colourles	Colourless plate	Colourless block	Crystal colour and habit
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Aonoclinic Monoclinic	Monoclin	Monoclinic	Triclinic	Crystal system
$a, b, c A$ 10.0691(8), 10.7273(9), 10.3470(19), 11.0840(13), 7.972(6), 15.2139(11), 7.9713(10), 15.403 a, β, γ^0 93.200(3), 106.786(3), 90, 92.930(7), 90 90, 90.666(5), 90 90, 90.562(10), 90 $U A^3$ 1067.91(15) 2314.5(4) 3022.6(4) 3075.1(6) $D_s/Mg m^{-3}$ 1.274 1.215 1.552 1.556 Z 4 4 4 4 μ (Cu-Ka)/mm ⁻¹ 0.612 0.581 2.455 2.425 Refin. collected (R _{im}) 20505 (0.0288) 8976 (0.0456) 25 658 (0.0579) 27 516 (0.0831) Unique refin. 3824 2852 5339 5485 Refin. collected (R _{im}) 0.0334 (0.0357) 0.0349 (0.0417) 0.0528 (0.0620) 0.0574 (0.0782) Parameters 281 0.0916 (0.0937) 0.08455 (0.0893) 0.1428 (0.1487) 0.1438 (0.1550) Goodness of fit 1.044 1.035 1.097 1.073 1.073 CCD deposition 1002439 1002432 1002429 1002430 1002430 Compound [[Zn_2(OAc)_i(5)]-R] [Zn_2(OAc)_i(6)-MeCC Colourless block Colourless block Colourless bl	P_{2_1}/c P_{2_1}/c	$P2_1/c$	Cc	$P\bar{1}$	Space group
$\begin{array}{cccccccccccccccccccccccccccccccccccc$.9572(6), 15.2139(11), $7.9713(10), 15.4036(16),$	7.9572(6)	19.3470(19), 11.0840(1	10.0691(8), 10.7273(9),	a, b, c/A
a_{i} β_{i} γ^{0} 93, 200(3), 106.786(3), 90, 92.930(7), 90 90, 90.666(5), 90 90, 90.562(10), 90 U/h^{3} 1067.91(15) 2314.5(4) 3022.6(4) 3075.1(6) D_{q} /Mg m ⁻³ 1.274 1.215 1.552 1.556 Z 4 4 4 4 4 μ (Cu-Ka)/mm ⁻¹ 0.612 0.581 2.455 2.425 5359 5485 Refln, collected (R_{int}) 20 505 (0.0288) 8976 (0.0456) 25 653 (0.0579) 27 516 (0.0831) 0.14159 Parameters 281 291 402 411 4119 90, 90.762 (0.0782) 0.0574 (0.0782) W_{R} (W_{R} all data) 0.0334 (0.0357) 0.0349 (0.0417) 0.0528 (0.0620) 0.0574 (0.0782) 0.0732 Goodness of fit 1.044 1.035 1.097 1.073 1.073 CCDC deposition 1002439 1002432 1002430 1002430 1002430 Compound [{Zn_2(OAc)_4(3)}_n] [Zn_2(OAc)_4(5)-2H_2O_{1/2}] [Zn_2(OAc)_4(6)-MeCC 1.073 Formula C_{32}H_{33}N_{30}G_{2}T_2 C_{60}H_{20}N_{6}G_{10}G_{2}D_2 Clourless block </td <td>4.9697(17) 25.046(3)</td> <td>24.9697(1</td> <td>10.8074(10)</td> <td>11.9802(9)</td> <td></td>	4.9697(17) 25.046(3)	24.9697(1	10.8074(10)	11.9802(9)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0, 90.666(5), 90 90, 90.562(10), 90	90, 90.66	90, 92.930(7), 90	93.200(3), 106.786(3),	$\alpha, \beta, \gamma/^{\circ}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2022 6(4) $2075 1(6)$	2022 6(4)	2214 5(4)	117.792(3) 1067 01(15)	T7/Å3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	552 1 556	1 552	1 215	1 274	$D/Mg m^{-3}$
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4	4	4	2	<i>Z</i>
Refln. collected (R_{int})20 505 (0.0288)8976 (0.0456)25 658 (0.0579)27 516 (0.0831)Unique refln.3824285253595485Befln. for refinement3549256245364159Parameters281291402411 R_1 (R_1 all data)0.0334 (0.0357)0.0349 (0.0417)0.0528 (0.0620)0.0574 (0.0782)We ₂ (we ₂ all data)0.0937)0.0855 (0.0893)0.1428 (0.1487)0.1438 (0.1550)Goodness of fit1.0441.0351.0971.073CCDC deposition1002439100243210024291002430Compound[{Zn ₂ (OAc) ₄ (3) _P][{Zn ₂ (OAc) ₄ (5)·2H ₂ O) _R][Zn ₂ (OAc) ₄ (5)·2][{Zn ₂ (OAc) ₄ (6)·MeCCFormulaC _{32H₃₃N₃O₃Zn₂C_{68H₇₈N₆O₂₀Zn₂C_{60H₆₂N₆O₁₀Zn₂C_{37H₄₃N₃O₁₇Zn₂Formula weight734.391560.941157.94836.52Crystal colour and habitColourless blockColourless blockColourless blockColourless blockColourless blockS1511(6), 16.0769(12),15.1794(6), 17.1547(7),10.8959(6), 11.2529(7),8.0908(9), 29.735(3), 24.7374(18)$\alpha, \beta, \gamma'^{o}$90, 90.796(3), 90115.890(2), 100.999(2),1109.804(2), 102.546(2),90, 90.76(9), 90U/Å³3241.4(4)3554.1(3)1358.81(14)3952.3(7)$D_d/Mg m^{-3}$1.5051.4551.4151.406Z4214$\mu(Ck-Ka)/mm^{-1}$2.3122.631.6262.0}}}}	.455 2.425	2.455	0.581	0.612	μ (Cu-K α)/mm ⁻¹
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	5 658 (0.0579) 27 516 (0.0831)	25 658 (0.	8976 (0.0456)	20 505 (0.0288)	Refln. collected (R_{int})
Refin. for refinement 3549 2562 4536 4159 Parameters 281 291 402 411 R1, R, all data) 0.0334 (0.0357) 0.0349 (0.0417) 0.0528 (0.0620) 0.0574 (0.0782) wR2, (wR2, all data) 0.0916 (0.0937) 0.0855 (0.0893) 0.1428 (0.1487) 0.1438 (0.1550) Goodness of fit 1.044 1.035 1.097 1.073 CCDC deposition 1002439 1002432 1002429 1002430 Compound [{Zn2(OAc)_4(3)} _n] [{2Zn2(OAc)_4(5)-2H_2O} _n] [Zn2(OAc)_4(5)_2] [{Zn2(OAc)_4(6)·MeCC Formula weight 734.39 1560.94 1157.94 836.52 Crystal colour and Colourless block Colourless block Colourless block Colourless block Crystal system Monoclinic Triclinic Triclinic Monoclinic Space group $P_{2_1/c}$ P_1 $P_{2_1/c}$ P_1 $P_{2_1/c}$ $a, b, c/Å$ 8.1511(6), 16.0769(12), 15.1794(6), 17.1547(7), 10.9850(6), 11.2529(7), 8.0908(9), 29.735(3), $24.7374(18)$ $72.9227(7)$ 12.1372(7) 16.6368(18) a, f	359 5485	5359	2852	3824	Unique refln.
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	536 4159	4536	2562	3549	Refln. for refinement
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$.02 411	402	291	281	Parameters
wR2 (wR2 all data)0.0916 (0.0937)0.0855 (0.0893)0.1428 (0.1487)0.1438 (0.1550)Goodness of fit1.0441.0351.0971.073CCDC deposition1002439100243210024291002430Compound $[{Zn_2(OAc)_4(3)}_n]$ $[{ZZn_2(OAc)_4(5)·2H_2O}_n]$ $[Zn_2(OAc)_4(5)_2]$ $[{Zn_2(OAc)_4(6)·MeCC}_{37H_43N_5O_9Zn_2}$ Formula weight734.391560.941157.94836.52Crystal colour andColourless blockColourless blockColourless blockColourless blockControls blockColourless blockColourless blockColourless blockColourless blockCystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P_{1/c}$ P_1 P_1 $P_{21/c}$ $a, b, clÅ$ 8.1511(6), 16.0769(12),15.1794(6), 17.1547(7),10.8959(6), 11.2529(7),8.0908(9), 29.735(3), u, β, γ'^o 90, 90.796(3), 90115.890(2), 100.999(2),109.804(2), 102.546(2),90, 99.076(9), 90 $U/Å^3$ 3241.4(4)3554.1(3)1358.81(14)3952.3(7) $D_c/Mg m^{-3}$ 1.5051.4551.4151.406Z4214 $u(Cu-K\alpha)/mm^{-1}$ 2.3122.1631.6262.004Refln. collected77.184 (0.0382)65.543 (0.0533)21.259 (0.0274)25.130 (0.1318) (R_{inh}) T10.00545684459Unique refln.586112.84248757029Refln. for553110.005<	0.0528 (0.0620) 0.0574 (0.0782)	0.0528 (0	0.0349(0.0417)	0.0334(0.0357)	R_1 (R_1 all data)
Goodness of fit1.0441.0351.0971.073CCDC deposition1002439100243210024291002430CCDC deposition1002439100243210024291002430Compound $[{2n_2(OAc)_4(3)}_n]$ $[{2n_2(OAc)_4(5) \cdot 2H_2O}_n]$ $[Zn_2(OAc)_4(5)_2]$ $[{2n_2(OAc)_4(6) \cdot MeCC}_1/2n_2 - C_{37}H_{43}N_3O_{12}n_2 - C_{66}H_{78}N_6O_{20}Zn_2 - C_{66}H_{62}N_6O_{10}Zn_2 - C_{37}H_{43}N_3O_{11}Zn_2 - C_{97}H_{43}N_3O_{11}Zn_2 - C_{97}H_{43}N_3O_{12}N_2 - C_{97}H_{43}N_2 $.1428 (0.1487) 0.1438 (0.1550)	0.1428(0	0.0855(0.0893)	0.0916(0.0937)	wR_2 (wR_2 all data)
CCDC deposition1002439100243210024291002430Compound $[[Zn_2(OAc)_4(3)]_n]$ $[[Zn_2(OAc)_4(5):2H_2O]_n]$ $[Zn_2(OAc)_4(5):2]$ $[[Zn_2(OAc)_4(6):MeCC]$ Formula $C_{32H_{33}N_3O_2D_2$ $C_{68H_{78}N_6O_{20}Zn_2$ $C_{60}H_{62}N_6O_{10}Zn_2$ $C_{37H_{43}N_3O_{11}Zn_2$ Formula weight734.391560.941157.94836.52Crystal colour andColourless blockColourless blockColourless blockColourless blockCitystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P_{2_1/c}$ P_1 P_1 $P_2_{1/c}$ $a, b, c/A$ $8.1511(6), 16.0769(12),$ $15.1794(6), 17.1547(7),$ $10.8959(6), 11.2529(7),$ $8.0908(9), 29.735(3),$ $24.7374(18)$ $17.2922(7)$ $12.1372(7)$ $16.6368(18)$ $\alpha, \beta, \gamma l^{\circ}$ 90, 90.796(3), 90115.890(2), 100.999(2), $109.804(2), 102.546(2),$ $90, 99.076(9), 90$ $U/Å^3$ $3241.4(4)$ $3554.1(3)$ 1358.81(14) $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 4214 μ (Cu-K α)/mm^{-1} 2.312 2.163 1.626 2.004 Refln. collected $77.184 (0.0382)$ $65.543 (0.0533)$ $21.259 (0.0274)$ $25.130 (0.1318)$ (R_{int})Unique refln. 5531 10.005 4568 4459 refinement P_1 2.842 4875 7029 Refln. for 5531 $0.00516 (0.0685)$ 0.0324	.097 1.073	1.097	1.035	1.044	Goodness of fit
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	002429 1002430	1002429	1002432	1002439	CCDC deposition
Formula $C_{32}H_{33}N_3O_9Zn_2$ $C_{68}H_{78}N_6O_{20}Zn_2$ $C_{60}H_{62}N_6O_{10}Zn_2$ $C_{37}H_{43}N_3O_{11}Zn_2$ Formula weight734.391560.941157.94836.52Crystal colour andColourless blockColourless blockColourless blockColourless blockColourless blockhabitCrystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P_{2_1/c}$ P_1 P_1 $P_2_{1/c}$ a, b, c/Å8.1511(6), 16.0769(12),15.1794(6), 17.1547(7),10.8959(6), 11.2529(7),8.0908(9), 29.735(3),24.7374(18)17.2922(7)12.1372(7)16.6368(18) $a, \beta, \gamma/^o$ 90, 90.796(3), 90115.890(2), 100.999(2),109.804(2), 102.546(2),90, 99.90.76(9), 90U/Å ³ 3241.4(4)3554.1(3)1358.81(14)3952.3(7) D_c/Mg m ⁻³ 1.5051.4551.4151.406Z4214 $\mu(Cu-K\alpha)/mm^{-1}$ 2.3122.1631.6262.004Refln. collected77 184 (0.0382)65 543 (0.0533)21 259 (0.0274)25 130 (0.1318)(R _{int})Unique refln.586112 84248757029Refln. for553110 00545684459refinement7029910355485Refln. for53140.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)	$(OAc)_4(5)_2] \qquad [{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$	$[Zn_2(OAc)_4(5)]$	$[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$	$[\{\operatorname{Zn}_2(\operatorname{OAc})_4(3)\}_n]$	Compound
Formula weight734.391560.941157.94836.52Crystal colour and habitColourless blockColourless blockColourless blockColourless blockColourless blockCrystal systemMonoclinicTriclinicTriclinicMonoclinicSecondar Secondar S	$H_{62}N_6O_{10}Zn_2$ $C_{37}H_{43}N_3O_{11}Zn_2$	C60H62N6O10	C68H78N6O20Zn2	$C_{32}H_{33}N_3O_9Zn_2$	Formula
Crystal colour and habitColourless blockColourless blockColourless blockColourless blockColourless blockCrystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P_{2_1/c}$ $P\bar{1}$ $P\bar{1}$ $P_{2_1/c}$ $a, b, c/Å$ $8.1511(6), 16.0769(12),$ $15.1794(6), 17.1547(7),$ $10.8959(6), 11.2529(7),$ $8.0908(9), 29.735(3),$ $a, f, \gamma/^o$ $90, 90.796(3), 90$ $115.890(2), 100.999(2),$ $109.804(2), 102.546(2),$ $90, 99.076(9), 90$ $a, \beta, \gamma/^o$ $90, 90.796(3), 90$ $115.890(2), 100.999(2),$ $109.804(2), 102.546(2),$ $90, 99.076(9), 90$ $u/Å^3$ $3241.4(4)$ $3554.1(3)$ $1358.81(14)$ $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 421 4 $\mu(Cu-K\alpha)/mm^{-1}$ 2.312 2.163 1.626 2.004 (R_{int}) Unique refln. 5861 12.842 4875 7029 Unique refln. 5861 12.842 4875 7029 Refln. for 5531 10.005 4568 4459 refinement -10005 4568 4459 Parameters 420 910 355 485	.94 836.52	1157.94	1560.94	734.39	Formula weight
habitCrystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P2_1/c$ $P\overline{1}$ $P\overline{1}$ $P\overline{1}$ $P2_1/c$ $a, b, c/\overline{A}$ $8.1511(6), 16.0769(12),$ $15.1794(6), 17.1547(7),$ $10.8959(6), 11.2529(7),$ $8.0908(9), 29.735(3),$ $24.7374(18)$ $17.2922(7)$ $12.1372(7)$ $16.6368(18)$ $\alpha, \beta, \gamma/^{\circ}$ 90, 90.796(3), 90 $115.890(2), 100.999(2),$ $109.804(2), 102.546(2),$ $90, 90.076(9), 90$ $u^{1}A^{3}$ $3241.4(4)$ $3554.1(3)$ $1358.81(14)$ $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 42 1 4 $\mu(Cu-K\alpha)/mm^{-1}$ 2.312 2.163 1.626 2.004 Refln. collected $77.184(0.0382)$ $65.543(0.0533)$ $21.259(0.0274)$ $25.130(0.1318)$ (R_{int}) $Refln. for$ 5861 12.842 4875 7029 Refln. for 5314 10005 4568 4459 refinement $R_1(R_i all data)$ $0.0331(0.0348)$ $0.0516(0.0685)$ $0.0324(0.0344)$ $0.1061(0.1554)$	urless block Colourless block	Colourless b	Colourless block	Colourless block	Crystal colour and
Crystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $P_{2_1/c}$ $P\bar{1}$ $P\bar{1}$ $P\bar{1}$ $P_{2_1/c}$ $a, b, c/Å$ $8.1511(6), 16.0769(12),$ $15.1794(6), 17.1547(7),$ $10.8959(6), 11.2529(7),$ $8.0908(9), 29.735(3),$ $24.7374(18)$ $17.2922(7)$ $12.1372(7)$ $16.6368(18)$ $\alpha, \beta, \gamma/^{\circ}$ 90.0796(3), 90 $115.890(2), 100.999(2),$ $109.804(2), 102.546(2),$ $90, 99.076(9), 90$ $u/Å^3$ $3241.4(4)$ $3554.1(3)$ $1358.81(14)$ $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 421 4 $\mu(Cu-K\alpha)/mm^{-1}$ 2.312 2.163 1.626 2.004 Refln. collected 77184 (0.0382) 65543 (0.0533) 21259 (0.0274) 25130 (0.1318) (R_{int}) $Refln.$ for 5861 12842 4875 7029 Refln. for 5331 10005 4568 4459 refinement R_1 (R_1 all data) 0.0331 (0.0348) 0.0516 (0.0685) 0.0324 (0.0344) 0.1061 (0.1554)					habit
Space group P_{2_1}/c P_1 P_{2_1}/c $a, b, c/Å$ $8.1511(6), 16.0769(12), 24.7374(18)$ $15.1794(6), 17.1547(7), 10.8959(6), 11.2529(7), 8.0908(9), 29.735(3), 24.7374(18)$ $17.2922(7)$ $12.1372(7)$ $16.6368(18)$ $\alpha, \beta, \gamma/^{0}$ 90, 90.796(3), 90 $115.890(2), 100.999(2), 109.804(2), 102.546(2), 90, 99.076(9), 90$ $108.227(2)$ $91.431(2)$ $U/Å^{3}$ $3241.4(4)$ $3554.1(3)$ $1358.81(14)$ $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 4 2 1 4 $\mu(Cu-K\alpha)/mm^{-1}$ 2.312 2.163 1.626 2.004 Refln. collected 7184 (0.0382) 6543 (0.0533) 21259 (0.0274) 25130 (0.1318) (R_{int}) $Refln. for$ 5531 10005 4568 4459 refinement $Parameters$ 420 910 355 485 R_1 (R_1 all data) 0.0331 (0.0348) 0.0516 (0.0685) 0.0324 (0.0344) 0.1061 (0.1554)	inic Monoclinic	Triclinic	Triclinic	Monoclinic	Crystal system
a, b, c/A8.1511(6), 16.0769(12), 24.7374(18)15.1794(6), 17.1547(7), 17.2922(7)10.8959(6), 11.2529(7), 12.1372(7)8.0908(9), 29.735(3), 16.6368(18) $\alpha, \beta, \gamma'^{0}$ 90, 90.796(3), 90115.890(2), 100.999(2), 108.227(2)109.804(2), 102.546(2), 91.431(2)90, 99.076(9), 90 $U^{1}A^{3}$ 3241.4(4)3554.1(3)1358.81(14)3952.3(7) $D_{c}/Mg m^{-3}$ 1.5051.4551.4151.406Z4214 $\mu(Cu-K\alpha)/mm^{-1}$ 2.3122.1631.6262.004Refln. collected7184 (0.0382)6543 (0.0533)21 259 (0.0274)25 130 (0.1318) (R_{int}) $Refln. for$ 55311000545684459refinement $Parameters$ 420910355485 $R_1(R_1 all data)$ 0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)	$P2_1/c$	<i>P</i> 1	<i>P</i> 1	$P2_1/c$	Space group
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	959(6), 11.2529(7), 8.0908(9), 29.735(3),	10.8959(6), 1	15.1794(6), 17.1547(7),	8.1511(6), 16.0769(12),	<i>a</i> , <i>b</i> , <i>c</i> /A
$\alpha, \rho, \gamma/^{5}$ $90, 90, 796(3), 90$ $115, 890(2), 100, 999(2), 100, 999(2), 102, 546(2), 102, 546(2), 90, 99, 076(9), 90108, 227(2)91.431(2)U/Å^{3}3241.4(4)3554.1(3)1358.81(14)3952.3(7)D_{c}/Mg m^{-3}1.5051.4551.4151.406Z4214\mu(Cu-K\alpha)/mm^{-1}2.3122.1631.6262.004Refln. collected7184 (0.0382)6543 (0.0533)21259 (0.0274)25130 (0.1318)(R_{int})Refln. for55311000545684459refinementParameters420910355485R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)$	3/2(7) 16.6368(18)	12.1372(7)	17.2922(7)	24./3/4(18)	<i>0</i> 10
$108.22/(2)$ $91.431(2)$ $U/Å^3$ $3241.4(4)$ $3554.1(3)$ $1358.81(14)$ $3952.3(7)$ $D_c/Mg m^{-3}$ 1.505 1.455 1.415 1.406 Z 4214 $\mu(Cu-K\alpha)/mm^{-1}$ 2.312 2.163 1.626 2.004 Refln. collected $77184 (0.0382)$ $65543 (0.0533)$ $21259 (0.0274)$ $25130 (0.1318)$ (R_{int}) $Refln. for586112.84248757029Refln. for553110.005545684459refinementParameters420910355485R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)$	304(2), 102.546(2), 90, 99.076(9), 90	109.804(2), 1	115.890(2), 100.999(2),	90, 90./96(3), 90	$\alpha, \beta, \gamma/2$
D_A 5241.4(4)5354.1(5)1536.8(14)5952.3(7) $D_c/Mg m^{-3}$ 1.5051.4551.4151.406 Z 4214 $\mu(Cu-K\alpha)/mm^{-1}$ 2.3122.1631.6262.004Refln. collected7184 (0.0382)65 543 (0.0533)21 259 (0.0274)25 130 (0.1318) (R_{int}) $Refln. for586112 84248757029Refln. for553110 00545684459refinementParameters420910355485R_1(R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)$	31(2) 91(14) 2052 2(7)	91.431(2)	108.22/(2)	2241.4(4)	TT/ Å 3
$D_c/Mg III$ 1.3051.4351.4151.406 Z 4214 μ (Cu-K α)/mm ⁻¹ 2.3122.1631.6262.004Refln. collected77 184 (0.0382)65 543 (0.0533)21 259 (0.0274)25 130 (0.1318) (R_{int}) Unique refln.586112 84248757029Refln. for553110 00545684459refinementParameters420910355485 R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)	5 1 406	1 415	1 455	5241.4(4) 1 505	$D/Mg m^{-3}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	A	1,415	1.455	1.505	7
Refl. collected77 184 (0.0382)65 543 (0.0533)21 259 (0.0274)25 130 (0.1318) (R_{int}) $Refl. collected586112 84248757029Unique refl.553110 00545684459refinementParameters420910355485R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)$	6 2.004	1.626	2.163	2.312	μ (Cu-Ka)/mm ⁻¹
(R_{int}) 12842 4875 7029 Refln. for553110 00545684459refinement $Parameters$ 420910355485 R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)	59 (0.0274) 25 130 (0.1318)	21 259 (0.027	65 543 (0.0533)	77 184 (0.0382)	Refln. collected
Unique refln.586112 84248757029Refln. for553110 00545684459refinementParameters420910355485 R_1 (R_1 all data)0.0331 (0.0348)0.0516 (0.0685)0.0324 (0.0344)0.1061 (0.1554)		((R_{int})
Refl. for 5531 10 005 4568 4459 refinement	7029	4875	12842	5861	Unique refln.
refinement 910 355 485 Parameters 420 910 0.0324 (0.0344) 0.1061 (0.1554) R1 (R1 all data) 0.0331 (0.0348) 0.0516 (0.0685) 0.0324 (0.0344) 0.1061 (0.1554)	4459	4568	10 005	5531	Refln. for
Parameters 420 910 355 485 R1 (R1 all data) 0.0331 (0.0348) 0.0516 (0.0685) 0.0324 (0.0344) 0.1061 (0.1554)					refinement
R_1 (R_1 all data) 0.0331 (0.0348) 0.0516 (0.0685) 0.0324 (0.0344) 0.1061 (0.1554)	485	355	910	420	Parameters
	24 (0.0344) 0.1061 (0.1554)	0.0324 (0.034	0.0516(0.0685)	0.0331(0.0348)	R_1 (R_1 all data)
$wR_2 (wR_2 all data) 0.0981 (0.1007) 0.1364 (0.1490) 0.0845 (0.0863) 0.2826 (0.3108)$	45 (0.0863) 0.2826 (0.3108)	0.0845 (0.086	0.1364(0.1490)	0.0981(0.1007)	wR_2 (wR_2 all data)
Goodness of fit 1.062 1.043 1.051 1.136	1 1.136	1.051	1.043	1.062	Goodness of fit
CCDC deposition 1002431 1002437 1002436 1002440	436 1002440	1002436	1002437	1002431	CCDC deposition
Compound $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n] [Zn_2(OAc)_4(8)_2] [Zn_2(OAc)_4(9)_2] [Zn_2(OAc)_4(10)_2]$	$n_2(OAc)_4(9)_2$ [Zn ₂ (OAc) ₄ (10) ₂]	[Zn ₂ (OAc) ₄	$[Zn_2(OAc)_4(8)_2]$	$[{4Zn_2(OAc)_4(7)\cdot 3H_2O}_n]$	Compound
Formula $C_{144}H_{164}N_{12}O_{39}Zn_8$ $C_{66}H_{74}N_6O_{10}Zn_2$ $C_{68}H_{78}N_6O_{10}Zn_2$ $C_{70}H_{02}N_6O_{10}Zn_2$	$C_{70}H_{82}N_6O_{10}Zn_2$	C68H78N2C	C66H74N6O10Zn2	$C_{144}H_{164}N_{12}O_{39}Zn_8$	Formula
Formula weight 3216.06 1242.10 1270.14 1298.20	270.14 1298.20	1270.14	1242.10	3216.06	Formula weight
Crystal colour and Colourless block Colourless block Colourless block Colourless plate	olourless block Colourless plate	Colourless	Colourless block	Colourless block	Crystal colour and
habit	-				habit
Crystal system Triclinic Triclinic Triclinic Triclinic	riclinic Triclinic	Triclinic	Triclinic	Triclinic	Crystal system
Space groupP1P1P1P1P1P1	$P\bar{1}$	$P\bar{1}$	PĪ	P1	Space group
<i>a, b, c</i> /A 15.1693(8), 17.4457(10), 14.2398(7), 14.7602(7), 10.9315(7), 11.2063(8), 10.7384(5), 11.18	1.9315(7), 11.2063(8), 10.7384(5), 11.1810(6), 12.7384(5), 11.1810(6), 12.7384(5), 13.1810(6), 13.1800(6), 13.18	10.9315(7)	14.2398(7), 14.7602(7),	15.1693(8), 17.4457(10),	<i>a</i> , <i>b</i> , <i>c</i> /A
17.6212(16) 15.7924(8) 13.3817(9) 13.7983(7) 104.114(4) 110 (07(4) 00 079(6) (6.140(6) 00 079(6) 00 000 000 000 000 000 000 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	13.3817(9)	15.7924(8)	1/.6212(16)	<i>R</i> /0
α, p, γ^{*} 104.114(4), 112.007(4), 89.058(2), 66.110(2), 96.615(3), 102.460(3), 91.221(3), 103.62	9.013(3), 102.400(3), 91.221(3), 103.627(3), 04.4(2) 04.927(2)	96.615(3),	89.058(2), 66.110(2),	104.114(4), 112.60/(4), 100.122(2)	$\alpha, \rho, \gamma/\sim$
$\frac{109.132(3)}{108^3} \qquad \qquad$	9.344(5) $94.82/(3)$	99.944(3)	87.738(Z) 2022 5(2)	109.132(3) 2692 4(5)	17/Å3
U/A 3083.4(3) 3032.5(3) 1556.69(18) 1602.91(14) D/Mg m ⁻³ 1.447 1.402 1.255 1.245	255 1002.91(14)	1 255.69(18	3U32.5(3) 1 402	3083.4(3) 1 447	U/A
$ \nu_{C}$ mg m 1.44/ 1.455 1.555 1.545 7 1 0 1 1 1	1.343 1	1.000	1.495	1.447	$D_{c/W}$ m
L I I I $\mu(Cu-K\alpha)/mm^{-1}$ 2.000 1.402 1.466 1.425	466 1 425	1 166	4 1 493	1 2 099	$\mu(Cu-K\alpha)/mm^{-1}$
$\mu_{1,455}$ 1.455 1.455 1.455 Refln. collected 43.849 (0.0505) 42.825 (0.0365) 28.581 (0.0345) 30.682 (0.0438)	30 683 (0.0345) 30 683 (0.0438)	28 581 (0 0	42,825 (0,0365)	43 849 (0.0505)	Refln, collected
(R _{int})		20001 (0.0			(R_{int})
Unique refln. 12 927 10 870 5584 5791	i84 5791	5584	10 870	12 927	Unique refln.

(cc) BY

$[Zn_2(OAc)_4(10)_2]$
4752
518
0.0444 (0.0567)
0.1151 (0.1241)
1.023
1002434

absorption spectra of the ten 4'-(4-ROC₆H₄)-4,2':6',4"-tpy ligands. Each exhibits an intense absorption band around 270 nm with a shoulder at 305 nm. Dominant contributions to these bands come from $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions.

Single crystals of 6 and 7 suitable for X-ray analysis were serendipitously obtained from layer diffusion of solutions of 6 in CHCl₃ and Zn(OAc)₂·2H₂O in MeOH, or by slow evaporation of the solvent from a MeOH solution of 7, respectively. Fig. 2 and S3[†] show the structures of these compounds and important bond parameters are given in the figure captions. All bond lengths and angles are as expected. At the molecular level, the two structures are similar with the alkyl chain in an extended conformation and the phenyltpy domain twisted. The angles between the rings containing atoms N1/N2, N2/N3 and N2/C16 are 17.6, 22.7 and 14.3° in 6, and 16.9, 27.9 and 20.0° in 7. Compounds 6 and 7 crystallize in the triclinic $P\bar{1}$ and monoclinic Cc space groups, respectively, and the packing of molecules of 6 and 7 necessarily differs. In both structures, the primary assembly motif is a ribbon built up by translation (Fig. 3a) with CH…N short contacts (in 6, C14H14a…N1ⁱ = 2.57 Å, symmetry code i = x, 1 + y, z; in 7, C2H2a...N3ⁱ = 2.67 Å, symmetry code i = x, y, 2 + z). In 6, adjacent ribbons are related by inversion leading to interdigitation of hexoxy chains and the assembly of planar sheets (Fig. 3b). The packing, dictated by $P\bar{1}$ symmetry, resembles that observed in 4'-(4-"butoxyphenyl)-4,2':6',4"-terpyridine (CSD³¹ code ACUKAK),³² 4'-(4-dodecoxyphenyl)-4,2':6',4"-terpyridine



Scheme 2 Synthetic approach to compounds 1-9.

(QATQEJ),²³ and 4'-(4-ⁿoctadecoxyphenyl)-2,2':6',2"-terpyridine $(\text{IERNUQ})^{33}$ and $4'-(4-^n \text{octoxyphenyl})-2,2':6',2''-\text{terpyridine}$ (JERPAY).³³ A similar layer arrangement is also observed in 4'-(4-octoxyphenyl)-4,2':6',4"-terpyridine³⁴ (XAYPOC); each sheet is built up from centrosymmetric pairs of molecules but in this case, additional symmetry in the space group C2/c, affects the relationship between molecules in adjacent sheets. In 7, neighbouring ribbons are related by a glide plane giving rise to an off-axis interdigitation of heptoxy chains, all of which point in the same direction (Fig. 3c). The overall packing in 7 (Fig. 3d) involves a combination of π -stacking of aromatic rings, CH $\cdots\pi$ contacts and inter-chain van der Waals interactions, with no one type apparently predominant. It is likely that the energy difference between the two different molecular arrangements in the lattices of 6 and 7 is small, and that environmental effects influence the observed packing.

Coordination polymers formed between $Zn(OAc)_2 \cdot 2H_2O$ and ligands 1–3

Layer diffusion of solutions of 1–3 with $Zn(OAc)_2 \cdot 2H_2O$ yielded single crystals suitable for X-ray diffraction. Structure determination confirmed the formation of the onedimensional coordination polymers $[{Zn_2(OAc)_4(1)}_n]$, $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$. Elemental analytical data and solid state IR spectra were recorded for the bulk materials. All three compounds crystallize in the space group $P2_1/c$ with unit cell dimensions that are similar (Table 1) and related to the cell parameters of a family of $[{Zn_2(OAc)_4(4'-X-4,2':6',4''-tpy)}_n]$ polymers¹ where X = Ph,³⁵ 4-BrC₆H₄,³⁶ 4-MeSC₆H₄,³⁶ biphenyl-4-yl,³⁷ pentafluorobiphenyl-4-yl³⁷ and ^tBu.³⁸ Because of the similarity in the structures of $[{Zn_2(OAc)_4(1)}_n]$, $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$, we



Scheme 3 Synthetic route to 10.

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Fig. 1 500 MHz NOESY spectrum of compound 1 in $CDCl_3$ (295 K). The signal marked * is residual $CHCl_3$.

discuss only $[\{Zn_2(OAC)_4(1)\}_n]$ in detail, and then present a comparison of the three compounds. Fig. 4 shows the repeat unit in $[\{Zn_2(OAC)_4(1)\}_n]$. The polymer chain comprises paddle-wheel $\{Zn_2(OAC)_4\}$ units interconnected by 1 which coordinates through the two outer N-donors. The bond parameters of the $\{Zn_2(OAC)_4\}$ entity (Fig. 4 caption) are typical. The 4,2':6',4"-tpy is virtually planar (angles between the rings containing atoms N1/N2 and N2/N3 = 4.6 and 4.0°, respectively) and the phenyl substituent is twisted 28.6° out of the plane of the pyridine ring to which it is bonded. The methoxy group lies in the plane of the phenyl ring. This, along with the C19–O1–C22 bond angle of 117.2(4)° and the difference in C19–O1 (1.370(5) Å) and O1–C22 (1.432(6) Å) bond lengths, is consistent with extension of the π -delocalization from the phenyl ring to atom O1.

Each polymer chain in $[{Zn_2(OAc)_4(1)}_n]$ has a zigzag form and chains assemble into sheets with the 4-methoxyphenyl group pointing into a V-shaped cavity in an adjacent chain (red or blue chains in Fig. 5a). This assembly replicates that observed in related complexes, and detailed discussion here



Fig. 2 Structure of compound 6 with ellipsoids plotted at 40% probability level. Selected bond metrics: N1-C1 = 1.3375(14), N1-C5 = 1.3393(14), N2-C10 = 1.3449(14), N2-C6 = 1.3428(13), N3-C11 = 1.3397(15), N3-C15 = 1.3379(15), C19-O1 = 1.3601(13), O1-C22 = 1.4361(13) Å; C1-N1-C5 = 115.75(9), C10-N2-C6 = 117.28(9), C11-N3-C15 = 116.00(9), C19-O1-C22 = $117.75(8)^{\circ}$.



Fig. 3 (a) Assembly of molecules of 6 into ribbons; molecules are related by translation and an analogous motif occurs in 7. (b) Part of one planar sheet in 6 showing interdigitation of chains. (c) Oblique interdigitation of heptoxy chains in adjacent ribbons of molecules of 7; magenta ribbon is related to the pale grey one by a glide plane. (d) Packing of molecules of 7 with heptoxy chains oriented in the same direction.

is unnecessary.¹ Of relevance to the present study is the packing of the sheets. Fig. 5a shows that the chains in adjacent sheets are arranged so that the 4,2':6',4"-tpy domains are offset from one another, facilitating face-to-face π -interactions between the pyridine rings containing N2 and N3 and those with N2ⁱ and N3ⁱ (symmetry code i = -1 - x, 1 - y, 1 - z). The interplane and centroid…centroid distances are 3.32 and 3.68 Å, respectively. As Fig. 5b shows, the π -interactions extend to form a tetradecker stack involving symmetry related pyridine rings containing atoms N1ⁱⁱ and N1ⁱⁱⁱ (symmetry code ii = -1 + x, y, z); the distance from



Fig. 4 Repeat unit in $[\{Zn_2(OAC)_4(1)\}_n]$ 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-N1 = 2.028(3), Zn2-N3ⁱ = 2.034(3), Zn1-O5 = 2.032(3), Zn1-O7 = 2.037(3), Zn1-O9 = 2.039(3), Zn1-O3 = 2.061(3), Zn2-O4 = 2.032(3), Zn2-O2 = 2.038(3), Zn2-O8 = 2.046(3), Zn2-O6 = 2.069(3), Zn1...Zn2 = 2.9058(7) Å.



Fig. 5 (a) Packing of zigzag chains in $[{\text{Zn}_2(\text{OAc})_4(1)}_n]$; chains coloured blue lie in one sheet, interacting through π -stacking of tpy domains with chains in the adjacent sheet (red); a representative π -interaction is shown in space-filling representation. (b) Infinite column of face-to-face interactions between slipped tpy domains can be described in terms of repeating tetradecker π -stacked py/bpy/py assembly motifs (top left).

the centroid of the N1-containing ring to the least squares planes through the N2/N3 bipyridine domain is 3.35 Å. The tetradecker π -stack is the repeat assembly motif which results in efficient interactions between slipped 4,2':6',4"-tpy units of adjacent sheets to give infinite π -stacked oblique columns running through the lattice.

The repeat units in the polymers of $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$ (Fig. S4 and S5[†]) are structurally analogous to that in $[{Zn_2(OAc)_4(1)}_n]$, and bond parameters (see respective figure captions) are comparable. As in $[{Zn_2(OAc)_4(1)}_n]$, the 4,2':6',4"-tpy units in $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$ are close to planar (angles between the rings containing N1/N2 and N2/N3 are both 6.4° in $[{Zn_2(OAc)_4(2)}_n]$, and are 6.2 and 7.6° in $[{Zn_2(OAc)_4(3)}_n]$). The phenyl substituent is twisted through 27.3° with respect to the plane of the central pyridine ring in $[{Zn_2(OAc)_4(2)}_n]$ compared to 28.2° in $[{Zn_2(OAc)_4(3)}_n]$, and 28.6° in $[{Zn_2(OAc)_4(1)}_n]$. The polymer chains in $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$ adopt the same zigzag configuration as in $[{Zn_2(OAc)_4(1)}_n]$, and the packing of the chains into sheets and stacking interactions between the sheets follow the same assembly principles in all three compounds. In $[{Zn_2(OAc)_4(2)}_n]$, the parameters that define the tetradecker π -stack assembly motif (see the description of $[{Zn_2(OAc)_4(1)}_n]$ and Fig. 5b) are interplane and centroid ... centroid distances of 3.32 and 3.70 Å for the central bpy/bpy domain and a centroid-to-plane distance of 3.38 Å for the py/bpy stacking interaction. These distances are close to the corresponding values of 3.32, 3.68 and 3.35 Å in $[{Zn_2(OAc)_4(1)}_n]$, but increase to 3.39, 3.75 and 3.41 Å on going to $[{Zn_2(OAc)_4(3)}_n]$. An associated parameter that increases is the distance between adjacent chains in one sheet, and this is assessed from the distance d defined in Fig. 6a. This dimension has been used in an overview of related $[{Zn_2(OAc)_4(4'-X-4,2':6',4''-tpy)}_n]$ structures in which d varies from 12.088 Å (X = ${}^{t}Bu$) to 13.347 Å (X = biphenyl-4-yl).¹ In $[{Zn_2(OAc)_4(1)}_n]$, $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$, d = 12.417(6), 12.601(6) and 13.277(3) Å, respectively, and the trend is consistent with the accommodation of the increasingly bulkier alkyl group in the V-shaped cavity of an adjacent chain (Fig. 6b-d). It is significant that the n-propyl chain is not in an extended conformation (Fig. S5[†]). Folding of the chain allows accommodation in the pocket (Fig. 6d) without the need for the chains to move further apart. Such lateral movement would be detrimental to the π -stacking interactions between chains in adjacent sheets.



Fig. 6 (a) Distance *d* measures the separation of central pyridine rings of 4,2':6',4"-tpy units in adjacent chains in the same sheet. Accommodation of the alkoxy substituent in the V-shaped pocket of an 4,2':6',4"-tpy unit in an adjacent chain: (b) methoxy, (c) ethoxy, (d) *n*-propoxy.

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Reaction between $Zn(OAc)_2 \cdot 2H_2O$ and 4 (the *n*-butoxy-tailed ligand) under the same layering conditions as for reactions between $Zn(OAc)_2 \cdot 2H_2O$ and 2 or 3 led to the formation of crystals, but none was suitable for structural determination. However, elemental analysis of the bulk sample was consistent with the formulation $[{Zn_2(OAc)_4(4)}_n \cdot H_2O]$ and the inclusion of H_2O in the lattice is consistent with that observed in $[{2Zn_2(OAc)_4(5)} \cdot 2H_2O]_n]$ (see below) as the alkoxy chain lengthens.

A frustrated system: $[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$ and $[Zn_2(OAc)_4(5)_2]$

Room temperature layering of an MeOH solution of $Zn(OAc)_2 \cdot 2H_2O$ over a $CHCl_3$ solution of 5 with a molar ratio $Zn(OAc)_2$ to 5 of 2 : 1 resulted in the formation of colourless blocks. Elemental analysis of the bulk sample was not definitive in terms of the product, and single crystal X-ray diffraction confirmed the presence of two materials: the 1D-coordination polymer [$\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n$] and the discrete complex [$Zn_2(OAc)_4(5)_2$].

The compound $[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$ crystallizes in the triclinic space group P1, with two independent $\{Zn_2(OAc)_4\}$ and two independent ligands 5 in the asymmetric unit (Fig. 7). This contrasts with $[{Zn_2(OAc)_4(1)}_n]$, $[\{\operatorname{Zn}_2(\operatorname{OAc})_4(2)\}_n]$ and $[\{\operatorname{Zn}_2(\operatorname{OAc})_4(3)\}_n]$ (monoclinic, $P2_1/c$ and one independent $[{Zn_2(OAc)_4}(L)]$ unit). The second feature that distinguishes the polymer containing the pentoxy-tailed ligand 5 from those of containing the methoxy, ethoxy and *n*-propoxy-substituted ligands is the presence of solvent in the lattice (see later). As Fig. 7 shows, the 1D-chain in $[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$ mimics that in the earlier polymers in the series and the bond parameters for the $\{Zn_2(OAc)_4\}$ units are unexceptional. The tpy domains of the two independent ligands are more slightly twisted than in the complexes with shorter alkoxy chains; in $[{2Zn_2(OAc)_4(5) \cdot 2H_2O_{ln}}]$ the angles between the planes of the



Fig. 7 Repeat unit in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ with ellipsoids plotted at 40% probability level; water molecules are omitted. Symmetry codes: i = -2 + x, -1 + y, z; ii = 2 + x, 1 + y, z. Selected bond distances: Zn1-O70 = 2.027(3), Zn1-N1 = 2.029(3), Zn1-O90 = 2.043(3), Zn1-O60 = 2.046(3), Zn1-O80 = 2.050(3), Zn2-O81 = 2.011(3), Zn2-O71 = 2.032(3), Zn2-O61 = 2.034(4), Zn2-N6ⁱⁱ = 2.036(3), Zn2-O91 = 2.050(3), Zn3-O100 = 2.024(3), Zn3-N3 = 2.030(3), Zn3-O130 = 2.035(3), Zn3-O120 = 2.042(3), Zn3-O110 = 2.047(3), Zn3-Zn4 = 2.8967(6), Zn4-O111 = 2.015(3), Zn4-O131 = 2.032(3), Zn4-N4 = 2.045(3), Zn4-O121 = 2.054(3), Zn4-O101 = 2.066(3), Zn1\cdotsZn2 = 2.9048(6) Å.

rings containing N1/N2 and N2/N3 are 4.5 and 9.1°, and between those with N4/N5 and N5/N6 are 5.5 and 10.4°. The phenyl rings in the two 4,2':6',4"-tpy ligands are twisted 26.3 and 27.4° with respect to each central pyridine ring. The most noticeable difference between the two independent ligands is the conformation of the pentoxy chain. The chain containing atom O2 is in an approximately extended conformation, and the maximum deviation of an alkyl C atom from the plane through the phenyl ring to which the chain is attached is 1.17 Å for C50; the terminal atom C52 lies 0.77 Å out of this plane. In contrast, the chain containing O1 is twisted out of the plane of the phenyl ring containing C16 (Fig. 7); the terminal atom C26 lies 3.02 Å away from the plane of the phenyl ring containing C16.

At first glance, the packing of the chains in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ appears the same as in $[\{Zn_2(OAc)_4(1)\}_n]$ (compare Fig. 8a with Fig. 5a). However, adjacent chains in the same sheet (*e.g.* blue in Fig. 8a) are not equally separated. The distance *d* defined in Fig. 6a has alternating values of 12.521(6) and 15.719(6) Å within a sheet in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$. The smaller and larger separations correspond, respectively, to accommodation of folded or extended pentoxy chains (Fig. 8a). The slippage of the chains affects the π -stacking interactions. In contrast to the infinite



(b)

Fig. 8 (a) Packing of zigzag chains in $[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$; chains coloured blue and red lie in adjacent sheets. (b) Discrete tetradecker π -stack; pyridine rings coloured green or yellow (space-filling representation) are, respectively, attached to *n*-pentoxyphenyl domains with extended or folded chains.

 π -stacked assemblies in [{Zn₂(OAc)₄(1)}_n], [{Zn₂(OAc)₄(2)}_n] and [{Zn₂(OAc)₄(3)}_n] (Fig. 5b), 4,2':6',4"-tpy domains in [{ZZn₂(OAc)₄(5)·2H₂O}_n] assemble in discrete tetradecker π -stacks (Fig. 8b) made up of three pairs of bpy/bpy interactions. For the central bpy/bpy domain of the stack (yellow space-filling representation in Fig. 8b), the interplane and centroid…centroid distances are 3.31 and 3.65 Å; for the outer bpy/bpy stacking interaction (green to yellow in Fig. 8b), the angle between the least squares planes through the bpy units is 6.3° and the centroid…plane separation is 3.34 Å.

In contrast to $[{Zn_2(OAc)_4(1)}_n]$, $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$, the change in packing associated with the longer alkyl chains in $[{Zn_2(OAc)_4(5)}_n]$ gives rise to cavities in the lattice that are occupied by H_2O molecules (modelled as one full, one half and two quarter occupancies). The partial occupancies mean that detailed discussion of interactions involving these molecules is not meaning-ful. Solvent inclusion indicates that the packing of the 1-dimensional polymer chains is less efficient with *n*-pentoxy-substituted ligands than with the methoxy, ethoxy and *n*-propoxy-substituted ligands. Note that the elemental analytical data for the bulk material containing the *n*-butoxy-substituted ligand 4 are also consistent with the presence of water in the lattice.

The colourless blocks of the polymer $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ were accompanied in the same crystallization tube by colourless crystals of the discrete complex $[Zn_2(OAc)_4(5)_2]$. The Zn: ligand ratio of 1:1 in $[Zn_2(OAc)_4(5)_2]$ differs from the 2:1 ratio observed in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$, and the discrete molecular structure is described in detail in a later section along with the structures of $[Zn_2(OAc)_4(8)_2]$, $[Zn_2(OAc)_4(9)_2]$ and $[Zn_2(OAc)_4(10)_2]$.

The bulk sample containing ligand 5 was characterized by powder X-ray diffraction and the data in Fig. S6[†] confirm the presence of both components.

$[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$ and $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$

Crystallization experiments combining zinc(II) acetate with either ligand 6 or 7 resulted in colourless blocks, single crystal X-ray structure determinations of which confirmed 1-dimensional coordination polymers $[{Zn_2(OAc)_4(6) \cdot MeCO_2H_{in}}]$ and $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$. Elemental analysis for the bulk samples was consistent with formulations of $[{Zn_2(OAc)_4(6) \cdot H_2O \cdot MeCO_2H}_n]$ and $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$. The coordination modes of ligands 6 and 7 mimic those of 1-3 and 5 in the respective polymers. Fig. S7 and S8⁺ show the structures of the repeat units in $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$ and $[{4Zn_2(OAc)_4(7) \cdot 3H_2O_n}]$, the asymmetric units in which contain one and two independent ligands, respectively. In $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$, the 4,2':6',4"-tpy domain is slightly twisted (angles between the least squares planes of the rings containing N1/N2 and N2/N3 = 3.5 and 17.6°) and the phenyl ring deviates 15.4° from the plane of the pyridine ring containing N2 (see Fig. S7† for atom numbering). In $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$, the corresponding angles are 9.4,

11.6 and 29.7° for one independent ligand, and 0.5, 11.8 and 26.1° for the second.

In $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$, the *n*-hexoxy chain is in an approximately extended conformation and adjacent chains pack into sheets in an analogous manner to those in $[{Zn_2(OAc)_4(1)}_n], [{Zn_2(OAc)_4(2)}_n] \text{ and } [{Zn_2(OAc)_4(3)}_n].$ However, comparison of Fig. 9a with Fig. 6b-d illustrates that the increased chain length forces the chains much further apart, while retaining a similar overall packing regime; the distance d (defined in Fig. 6a) is 16.78(1) Å. The voids between adjacent chains in a sheet (Fig. 9a) are partially occupied by acetate groups from $\{Zn_2(OAc)_4\}$ in adjacent sheet and the remaining cavities are filled by acetic acid molecules (Fig. 9b). Supporting evidence for $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$ rather than a salt containing protonated 6 and acetate ions is two-fold. First, acetate oxygen atom O100 is 2.69(1) Å distant from atom $O61^{iii}$ of an $\{Zn_2(OAc)_4\}$ unit (symmetry code iii = -1 - x, -1/2 + y, 3/2 - z) consistent with a hydrogen bond (H100···O61ⁱⁱⁱ = 1.85 Å; O100-H100···O61ⁱⁱⁱ = 171°). Secondly, the planarity of the 4,2':6',4"-tpy is inconsistent with protonation of atom N2 (the non-coordinated nitrogen atom). To the best of our knowledge, the pK_a values of the conjugate acids of 4,2':6',4"-tpy have not been determined. For [Hpy]⁺ (py = pyridine), $pK_a = 5.14^{39}$ but this is highly dependent upon solvent.⁴⁰ Tocher and coworkers have shown that crystallizations of pyridine with a number of simple organic acids lead to either salts or co-crystals, and if the difference between pK_a values of acid and $[Hpy]^+$ is small, predictions of salt formation are ambiguous.³⁹ For the bidentate ligand 6, the only site available for protonation is the central pyridine nitrogen, and therefore 2,4,6-triphenylpyridine is a more appropriate model than pyridine. The pK_a of [H(2,4,6-triphenylpyridine)]⁺ (determined in 70% EtOH solution) is 1.82,⁴¹ and the pK_a of coordinated $[H6]^+$ should be closer to this value than to that of [Hpy]⁺. This is consistent



Fig. 9 $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$: (a) accommodation of the *n*-hexoxy chain in the V-shaped pocket of an 4,2':6',4"-tpy unit in an adjacent chain forces the chains apart (compare Fig. 6). (b) Packing of sheets (green, red, blue) and inclusion of MeCO_2H molecules (yellow).

with the observation of acetic acid (rather than acetate and protonated 4,2':6',4"-tpy) in the lattice of $[{Zn_2(OAc)_4(6) \cdot MeCO_2H_{n}}]$ $(pK_a \text{ of } MeCO_2H = 4.75).$

The π -stacking motifs which define the interactions between the sheets in $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$ do not replicate those in the polymers discussed above. Centrosymmetric pairs of ligands 6 stack with π -interactions between phenyl and pyridine (with N1) rings (Fig. 10a); the angle between the ring planes = 11.9° and centroid_{Ph}…plane_{py} distance = 3.36 Å. These interactions are augmented by pyridine ... pyridine (N1/N2^{iv} rings, symmetry code iv = -x, 1 – y, (2 - z) interactions at an intercentroid separation of 3.57 Å, which result in an infinite stack of ligands (Fig. 10b).

In $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$, the *n*-heptoxy chains in the two independent ligands adopt a folded and nearextended conformation, respectively. This is reminiscent of $[{2Zn_2(OAc)_4(5) \cdot 2H_2O}_n]$ and, as in the latter, the zigzag chains in $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$ assemble into sheets with two characteristic inter-chain separations (d = 12.579(7) and 16.869(7) Å; d is defined in Fig. 6a). The shorter and longer separations are, respectively, associated with accommodation of the folded and extended chains (as shown in Fig. 8a for $[{2Zn_2(OAc)_4(5) \cdot 2H_2O_n}]$ in which values of d are 12.521(6) and 15.719(6) Å. The differences between the separation of the chains in the two structures has little effect on the overall packing. This involves discrete tetradecker π -stacks comprising three pairs of bpy/bpy interactions, each stack being terminated by two $\{Zn_2(OAc)_4\}$ units (Fig. 11). A comparison of Fig. 8b and 11 shows the similarity of the packing in $[{2Zn_2(OAc)_4(5) \cdot 2H_2O_n}]$ and $[{4Zn_2(OAc)_4(7) \cdot 3H_2O_n}]$. For the central bpy/bpy interaction (Fig. 11, yellow space-filling representations), the interplane separation is 3.35 Å, while for the outer bpy/bpy interaction (Fig. 11, green to yellow), the angle between the least squares planes through the bpy units is 7.5° and the centroid…plane distance is 3.26 Å.

Discrete complexes formed between Zn(OAc)₂·2H₂O and ligands 5 and 8-10

The molecular structure of $[Zn_2(OAc)_4(5)_2]$ (Fig. 12) resembles that reported for $[Zn_2(OAc)_4(L)_2]$ where L = 4'-(4-dodecoxyphenyl)-4,2':6',4"-tpy.²³ [Zn₂(OAc)₄(5)₂] crystallizes in the $P\bar{1}$ space group with half of the molecule in



Fig. 11 Discrete tetradecker π -stack in [{4Zn₂(OAc)₄(7)·3H₂O}_n]; pyridine rings (space-filling representation) coloured green or yellow are attached, respectively, to *n*-heptoxyphenyl units containing extended or folded chains

the asymmetric unit; all bond metrics (Fig. 12 caption) are unexceptional. Each ligand 5 is monodentate and binds through atom N1 to an axial site of the paddlewheel $\{Zn_2(OAc)_4\}$ unit. The *n*-pentoxy group adopts an extended conformation (Fig. 12). The 4,2':6',4"-tpy domain is virtually planar (the angles between the planes of the rings containing N1/N2 an N2/N3 are 1.3 and 6.5°). The phenyl ring is twisted 25.0° out of the plane of the central pyridine ring, consistent with minimizing H...H interactions. The molecules pack into sheets (Fig. 13a) with the pendant pyridine ring containing N3 directed into the V-shaped cavity defined by the pyridine rings containing N1ⁱⁱ and N2ⁱⁱ and the phenyl ring with C16ⁱⁱ (symmetry code ii = 1 + x, y, z) of an adjacent ligand 5; the shortest N…HC contact is 2.47 Å. Fig. 13a shows the interdigitation of the n-pentoxy chains, and also illustrates that the sheets contain voids between phenyl units of adjacent chains. These pockets accommodate the methyl groups of two of the four acetato-ligands from the next sheet (Fig. 13b).

For ligands 8-10 with the longest alkoxy chains, single crystals of discrete complexes were obtained from reactions



Fig. 10 π -Stacking of centrosymmetric pairs of ligands in [{Zn₂(OAc)₄(6)·MeCO₂H}] involving pyridine (with N1) and phenyl rings and (b) additional pyridine ... pyridine (N1/N2) interactions.



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Fig. 13 (a) Packing of molecules of $[Zn_2(OAc)_4(5)_2]$ into a sheet, and (b) filling of the cavities in each sheet with methyl residues (space-filling representation) of $\{Zn_2(OAc)_4\}$ units from adjacent sheets.

with zinc(II) acetate. The structures of $[Zn_2(OAc)_4(8)_2]$, $[Zn_2(OAc)_4(9)_2]$ and $[Zn_2(OAc)_4(10)_2]$ are analogous to that of $[Zn_2(OAc)_4(5)_2]$ and are shown in Fig. S9–S11.[†] Each complex crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of $[Zn_2(OAc)_4(8)_2]$ contains a whole molecule and the independent ligands differ in the conformations of the *n*-octoxy chains (Fig. S9[†]). Molecules of $[Zn_2(OAc)_4(9)_2]$ and $[Zn_2(OAc)_4(10)_2]$ are centrosymmetric and both contain chains in fully extended conformations. The ligand in $[Zn_2(OAc)_4(10)_2]$ is disordered and the 4-decoxyphenyl units were modelled over two sites of occupancies 49 and 51%. Bond parameters for the three complexes are as expected (see captions to Fig. S9-S11[†]). In the three complexes, the deviation from planarity of the 4,2':6',4"-tpy units vary with angles between the planes of adjacent pyridine rings lying in the range 0.5 to 20.4°; the phenyl substituents are twisted with respect to the central pyridine ring by between 24.3 and 26.4°. The molecular packing in each of $[Zn_2(OAc)_4(8)_2]$, $[Zn_2(OAc)_4(9)_2]$ and $[Zn_2(OAc)_4(10)_2]$ replicates that in $[Zn_2(OAc)_4(5)_2]$ (Fig. 13). Scheme 4 defines a parameter x which can be used to quantify the effect of increasing the length of the alkoxy chain. The $Zn \cdots Zn$ separation, x, varies from 34.802(2) Å in [Zn₂(OAc)₄(5)₂], 39.089(2) Å in $[Zn_2(OAc)_4(8)_2]$, 39.005(3) Å in $[Zn_2(OAc)_4(9)_2]$ to 41.285(2) Å in $[Zn_2(OAc)_4(10)_2]$; the latter value is not affected by the disorder in the structure. In each compound, packing of sheets involves the accommodation of methyl residues of $\{Zn_2(OAc)_4\}$ units from adjacent sheets into the hollows in each sheet, as shown in Fig. 13b.

Conclusions

The synthesis and characterization of $4'-(4-ROC_6H_4)-4,2':6',4''-tpy$ ligands 1–10 (Scheme 1) have been described. The results of crystallization experiments combining zinc(π) acetate with ligands



Scheme 4 Defined here for $[Zn_2(OAc)_4(5)_2]$, the Zn…Zn separation, *x*, quantifies the effect of increasing the alkoxy chain (see text) within a sheet.

(L) 1–10 reveal that coordination polymers $[{Zn_2(OAc)_4(L)}_n]$ or complexes $[Zn_2(OAc)_4(L)_2]$ are formed (Scheme 5). Polymers containing bidentate 4,2':6',4"-tpy domains bridging $\{Zn_2(OAc)_4\}$ paddle-wheel units are favoured for short alkoxy chains and discrete complexes $[Zn_2(OAc)_4(L)_2]$ containing monodentate 4,2':6',4"-tpy domains are favoured for the longest chains. In the polymers, π -stacking interactions between aromatic (pyridine and/or phenyl) rings are dominant while packing of the discrete complexes features dominant van der Waals interactions between interdigitated chains.

Each polymer has a zigzag backbone and the chains nest together to generate planar sheets. The increasing length of the alkoxy substituent forces the polymer chains further apart



Scheme 5 Overview of the formation of crystallographically proven coordination polymers and discrete complexes as a function of alkoxy chain length.

within each sheet. In $[{Zn_2(OAc)_4(3)}_n]$ (*n*-propoxy group), the substituent adopts a folded conformation to compensate for its increased length and this permits the packing in $[{Zn_2(OAc)_4(3)}_n]$ to be essentially the same as in $[{Zn_2(OAc)_4(1)}_n]$ and $[{Zn_2(OAc)_4(2)}_n]$ (methoxy and ethoxy). Although the zigzag form of the polymer chain in $[\{2Zn_2(OAc)_4(5)\cdot 2H_2O\}_n]$ replicates those in $[\{Zn_2(OAc)_4(1)\}_n]$ $[{Zn_2(OAc)_4(2)}_n]$ and $[{Zn_2(OAc)_4(3)}_n]$, lattice packing interactions are significantly different (isolated tetradecker π -stacks *versus* infinite π -stacked assemblies) and the wider separation of the polymer chains in a sheet results in the incorporation of water molecules. The assembly in $[{2Zn_2(OAc)_4(5) \cdot 2H_2O_n}]$ (in which there are two independent ligands with different conformations) is also observed in $[{4Zn_2(OAc)_4(7) \cdot 3H_2O}_n]$. In contrast, the *n*-hexoxy-containing coordination polymer crystallizes with acetic acid in the lattice, and the zigzag polymer chains in $[{Zn_2(OAc)_4(6) \cdot MeCO_2H}_n]$ pack in a manner that is unique among the other polymers.

In conclusion, we have shown that the backbones chains formed between of the zigzag polymer 4'-(4-ROC₆H₄)-4,2':6',4"-tpy ligands and $\{Zn_2(OAc)_4\}$ units are structurally invariant, and that changes in the length of the alkoxy substituents can be accommodated up to a certain point by a combination of conformational changes of the alkyl groups, π -stacking interactions between arene rings and incorporation of H2O or MeCO2H molecules into the lattice. Once the alkoxy substituents reach a length of eight or more C atoms, the formation of discrete complexes appears to be preferred, presumably driven by favourable van der Waals interactions between interdigitated alkoxy groups. Although we do not have crystallographic support for the formation of $[Zn_2(OAc)_4(6)_2]$ and $[Zn_2(OAc)_4(7)_2]$, it is reasonable to conclude that the range between the n-pentoxy and n-heptoxy substituents represents an intermediate zone where the preference between the two structure types is marginal.

Acknowledgements

We thank the Swiss National Science Foundation, the European Research Council (Advanced Grant 267816 LiLo) and the University of Basel for financial support. Srboljub Vujovic is thanked for laboratory support.

Notes and references

- 1 C. E. Housecroft, Dalton Trans., 2014, 43, 6594.
- 2 M. Barquín, J. Cancela, M. J. González Garmendia, J. Quintanilla and U. Amador, *Polyhedron*, 1998, 17, 2373.
- 3 F. Yuan, Q.-E. Zhu, H.-M. Hu, J. Xie, B. Xu, C.-M. Yuan, M.-L. Yang, F.-X. Dong and G.-L. Xue, *Inorg. Chim. Acta*, 2013, 397, 117.
- 4 H.-N. Zhang, F. Yuan, H.-M. Hu, S.-S. Shen and G.-L. Xue, *Inorg. Chem. Commun.*, 2013, 34, 51.
- 5 Y.-L. Gai, F.-L. Jiang, L. Chen, Y. Bu, M.-Y. Wu, K. Zhou, J. Pan and M.-C. Hong, *Dalton Trans.*, 2013, 42, 9954.

- 6 B. Xu, J. Xie, H.-M. Hu, X.-L. Yang, F.-X. Dong, M.-L. Yang and G.-L. Xue, *Cryst. Growth Des.*, 2014, 14, 1629.
- 7 M.-S. Wang, M.-X. Li, X. He, M. Shao and Z.-X. Wang, *Inorg. Chem. Commun.*, 2014, 42, 38.
- 8 C. Liu, Y.-B. Ding, X.-H. Shi, D. Zhang, M.-H. Hu, Y.-G. Yin and D. Li, *Cryst. Growth Des.*, 2009, **9**, 1275.
- 9 B.-C. Wang, Q.-R. Wu, H.-M. Hu, X.-L. Chen, Z.-H. Yang, Y.-Q. Shangguan, M.-L. Yang and G.-L. Xue, *CrystEngComm*, 2010, 12, 485.
- 10 J. Song, B.-C. Wang, H.-M. Hu, L. Gou, Q.-R. Wu, X.-L. Yang, Y.-Q. Shangguan, F.-X. Dong and G.-L. Xue, *Inorg. Chim. Acta*, 2011, 366, 134.
- 11 Y.-Q. Chen, S.-J. Liu, Y.-W. Li, G.-R. Li, K.-H. He, Y.-K. Qu, T.-L. Hu and X.-H. Bu, *Cryst. Growth Des.*, 2012, 12, 5426.
- 12 Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang and X.-H. Bu, *Chem. Sci.*, 2013, 4, 3678.
- 13 J. Heine, J. Schmedt auf der Günne and S. Dehnen, *J. Am. Chem. Soc.*, 2011, 133, 10018.
- 14 E. C. Constable, G. Zhang, C. E. Housecroft and J. A. Zampese, *CrystEngComm*, 2011, 13, 6864.
- V. N. Dorofeeva, S. V. Kolotilov, M. A. Kiskin, R. A. Polunin,
 Z. V. Dobrokhotova, O. Cador, S. Golhan, L. Ouahab,
 I. L. Eremenko and V. M. Novotortsev, *Chem. Eur. J.*, 2012,
 18, 5006.
- 16 D.-Y. Ma, D.-E. Sun and G.-Q. Li, Acta Crystallogr., Sect. E: Struct. Rep. Online, 2011, 67, m913.
- 17 Y.-Q. Chen, G.-R. Li, Y.-K. Qu, Y.-H. Zhang, K.-H. He, Q. Gao and X.-H. Bu, *Cryst. Growth Des.*, 2013, 13, 901.
- 18 E. C. Constable, C. E. Housecroft, M. Neuburger, S. Vujovic, J. A. Zampese and G. Zhang, *CrystEngComm*, 2012, 14, 3554.
- 19 J. Granifo, R. Gaviño, E. Freire and R. Baggio, J. Mol. Struct., 2014, 1063, 102.
- 20 E. C. Constable, C. E. Housecroft, S. Vujovic and J. A. Zampese, *CrystEngComm*, 2014, **16**, 3494.
- 21 J. Yoshida, S.-I. Nishikiori and H. Yuge, J. Coord. Chem., 2013, 66, 2191.
- 22 G. W. V. Cave and C. L. Raston, J. Supramol. Chem., 2002, 2, 317.
- 23 E. C. Constable, G. Zhang, C. E. Housecroft and J. A. Zampese, *Inorg. Chem. Commun.*, 2012, 15, 113.
- 24 G. W. V. Cave and C. L. Raston, *J. Chem. Soc., Perkin Trans.* 1, 2001, 3258.
- 25 Bruker Analytical X-ray Systems, Inc., APEX2, version 2 User Manual, M86-E01078, Madison, WI, 2006.
- 26 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
- I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 2002, 58, 389.
- 28 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, 41, 466.
- 29 J. Wang and G. S. Hanan, Synlett, 2005, 1251.
- 30 H. S. Chow, E. C. Constable, C. E. Housecroft, M. Neuburger and S. Schaffner, *Dalton Trans.*, 2006, 2881.

- 31 F. H. Allen, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 2002, 58, 380.
- 32 G. W. V. Cave and C. L. Raston, *J. Chem. Soc., Perkin Trans.* 1, 2001, 3258.
- 33 E. C. Constable, H.-J. Guntherodt, C. E. Housecroft, L. Merz, M. Neuburger, S. Schaffner and Y. Tao, *New J. Chem.*, 2006, 30, 1470.
- 34 G. W. V. Cave and C. L. Raston, Chem. Commun., 2000, 2199.
- 35 E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuburger and J. A. Zampese, *CrystEngComm*, 2010, 12, 2146.
- 36 E. C. Constable, G. Zhang, E. Coronado, C. E. Housecroft and M. Neuburger, *CrystEngComm*, 2010, 12, 2139.
- 37 E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle,S. Vujovic and J. A. Zampese, *Polyhedron*, 2013, 62, 120.
- 38 E. C. Constable, C. E. Housecroft, P. Kopecky, M. Neuburger, J. A. Zampese and G. Zhang, *CrystEngComm*, 2012, 14, 446.
- 39 S. Mohamed, D. A. Tocher, M. Vickers, P. G. Karamertzanis and S. L. Price, *Cryst. Growth Des.*, 2009, 9, 2881.
- 40 L. Chmurzyński, J. Heterocycl. Chem., 2000, 37, 71.
- 41 A. R. Katritzky and D. E. Leahy, J. Chem. Res., 1985, 28.