Supporting Information

Development of chiral N,N-ditopic metalloligands based on *Cinchona* alkaloids' backbone for constructing homochiral coordination polymers

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Experimental Section

General Remarks: General experimental procedure: All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. Commercial cinchonine was purfied by column chromatography using Merck silica gel 60 (230-400 mesh) and 2-metoxyethanol as eluent; column output was monitored on TLC plates (0.25 mm, Merck silica gel 60 F254 on aluminium). Pure cinchonine (R_f = 0.47 in methoxyethanol) was recrystallized with toluene and dried in the vacum dessicator. Compound **1a** was prepared by a previously published method.[1] NMR spectra were recorded on a Varian Mercury 400 Spectrometer.

Synthesis and characterization

Synthesis of 1b: Compound **1b** was prepared similarly to a previously published method.[2] A slurry of cinchonine (0.30 g, 1.02 mmol) in THF (10 mL) was cooled to -78°C, and Et_3Al (0.68 mL of a 1.5 M solution in THF, 0.51 mmol) was added dropwise. Then the reaction mixture was warmed to room temperature and stirred for 4h. Compound **1b** was obtained as polycrystalline solid from THF solution at 4°C, isolated yield ca. 89%. Elemental analysis (%) calcd for $C_{46}H_{62}N_4O_2Al_2$: C 72.99, H 8.26, N 7.40; found: C 72.83, H 8.32, N 7.26; ^1H NMR ($CDCl_3$, 400 MHz), qn = quinuclidine moiety: δ = 9.01 (d, 2H, Ar-*H*), 8.19 (d, 2H, Ar-*H*), 8.04 (d, 2H, Ar-*H*), 7.87 (d, 2H, Ar-*H*), 7.72 (m, 2H, Ar-*H*), 7.56 (m, 2H, Ar-*H*), 6.03 (d, 2H, O-C-*H*), 4.80-4.55 (m, 2H, =C(R)-*H*), 4.52 (d, 2H, =CH_2), 4.43 (d, 2H, =CH_2), 3.70 (m, 2H, qn-*H*), 3.27 (m, 2H, qn-*H*), 2.85 (m, 4H, qn-*H*), 2.67 (m, 2H, qn-*H*), 2.11 (m, 2H, qn-*H*), 1.66 (m, 2H, qn-*H*), 1.56 (m, 4H, qn-*H*), 1.04 (m, 4H, qn-*H*), 1.01 (t, 12H, Al-CH_2CH_3), 0.15--0.30 (overlapping q, 8H, Al-CH_2CH_3).

Synthesis of 2a: Into 0.500 g of **1a** (0.71 mmol) dissolved in toluene (10 mL), Me_2Zn (0.36 mL of a 2 M solution in toluene, 0.72 mmol) was syringed dropwise in 20 ^oC. The reaction mixture remained colourless and was stirred for 2h. Compound **2a** was isolated as colourless crystals after crystallization from toluene/hexane solution at -10 ^oC. Yield 89%. Elemental analysis (%) calcd for $C_{44}H_{60}N_4O_2Al_2Zn$: C 66.35, H 7.60, N 7.04; found: C 67.83, H 7.85, N 6.78; ^1H NMR (C_6D_6 , 400 MHz), qn = quinuclidine moiety: δ = 9.16 (d, 2H, Ar-*H*), 8.72 (d, 2H, Ar-*H*), 8.18 (d, 2H, Ar-*H*), 7.57 (d, 2H, Ar-*H*), 7.27 (m, 2H, Ar-*H*), 7.12 (m, 2H, Ar-*H*), 6.05 (d, 2H, O-C-*H*), 4.38 (m, 4H, vinyl-*H*), 4.14 (d, 2H, vinyl-*H*), 3.25 (m, 2H, qn-*H*), 2.92 (m, 2H, qn-*H*), 2.52 (m, 4H, qn-*H*), 2.06 (m, 2H, qn-*H*), 1.36 (m, 2H, qn-*H*), 1.13-0.59 (overlapping m, br, 10H, qn-*H*), 0.01 (s, 6H, Zn-CH_3), -0.28 (s, 6H, Al-CH_3), -1.03 (s, 6H, Al-CH_3).

Synthesis of 2b: Into 0.500 g of **1b** (0.66 mmol) dissolved in toluene (10 mL), Et_2Zn (0.44 mL of a 1.5 M solution in toluene, 0.66 mmol) was syringed dropwise in 20^oC. The reaction mixture turned immediately to pale yellow and was stirred for 2h. Compound **2** was isolated as orange pillar-shaped crystals after crystallization from toluene solution at 20 ^oC. Yield 83%. Elemental analysis (%) calcd for $C_{50}H_{72}N_4O_2Al_2Zn{\cdot}C_7H_8$: C 70.38, H 8.29, N 5.76; found: C 69.72, H 8.36, N 5.93; ^1H NMR ($CDCl_3$, 400 MHz), qn = quinuclidine moiety: δ = 9.01 (d, 2H, Ar-*H*), 8.19 (d, 2H, Ar-*H*), 8.04 (d, 2H, Ar-*H*), 7.87 (d, 2H, Ar-*H*), 7.72 (m, 2H, Ar-*H*), 7.56 (m, 2H, Ar-*H*), 6.03 (d, 2H, O-C-*H*), 4.80-4.55 (m, 2H, vinyl-*H*), 4.52 (d, 2H, vinyl-*H*), 4.43 (d, 2H, vinyl-*H*), 3.27 (m, 2H, qn-*H*), 2.85 (m, 4H, qn-*H*), 2.67 (m, 2H, qn-*H*), 2.11 (m, 2H, qn-*H*), 1.90-0.80 (overlapping m and t, 24H, qn-*H* and Al-CH_2CH_3), 1.11 (t, 6H, Zn-CH_2CH_3), 0.70--0.20 (overlapping m, br, 8H, Al-CH_2-CH_3), 0.35-0.20 (overlapping q, 4H, Zn-CH_2CH_3).

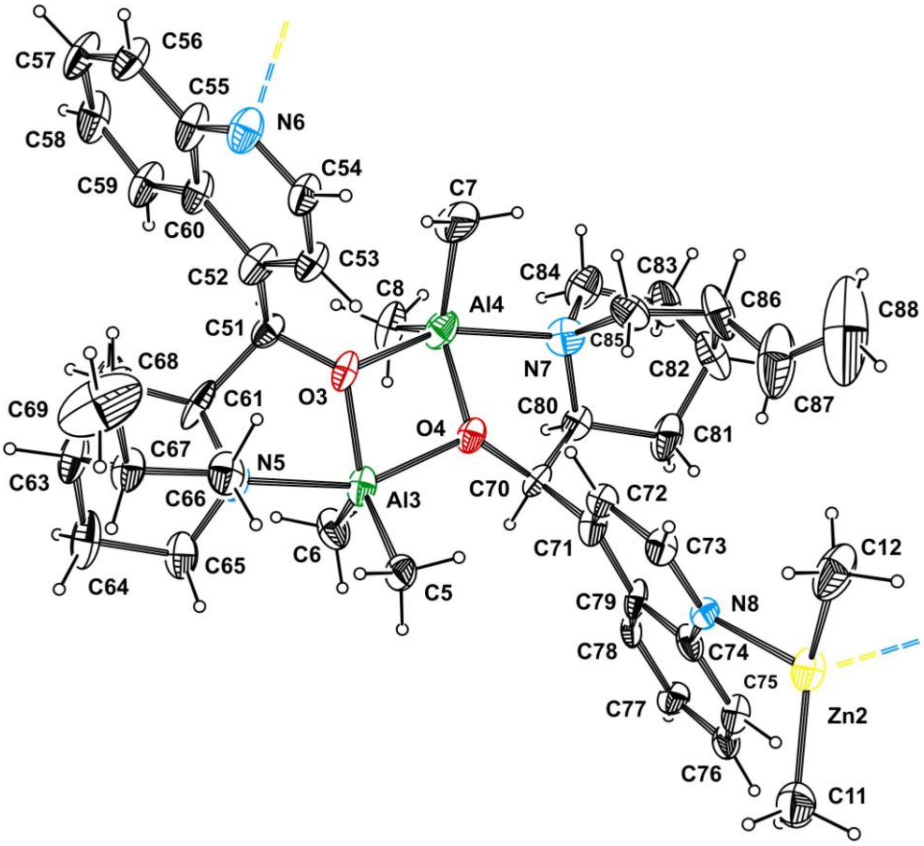
X-ray Structure Determination

Crystal data for **2a**, $C_{88}H_{120}N_8O_4Al_4Zn2$: M = 1592.63, crystal dimensions 0.46 × 0.34 × 0.22 mm^3, orthorhombic, space group $P\ 2_12_12$ (no. 18), a = 25.1451(4) Å, b = 31.1622(7) Å c = 14.4981(7) Å, U = 11360.4(6) $Å^3$, Z = 4, F(000) = 3392, D_c = 0.931 g m^3, T = 100(2)K, μ(Mo-Kα) = 0.493 mm^{-1}, Flack parameter = 0.00(22) ,Nonius Kappa-CCD diffractometer, θ_{max} = 21.26 °, 12368 unique reflections. The structure was solved by direct methods using the SHELXS97 [3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97 [4]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R1 = 0.0955$, $wR2 = 0.1894$ for all data and 956 parameters ($R1 = 0.0736$, $wR2 = 0.1797$ for 10415 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.136. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.37/- 0.39 eÅ^{-3}. The structure contained molecules of toluene. The toluene molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data.

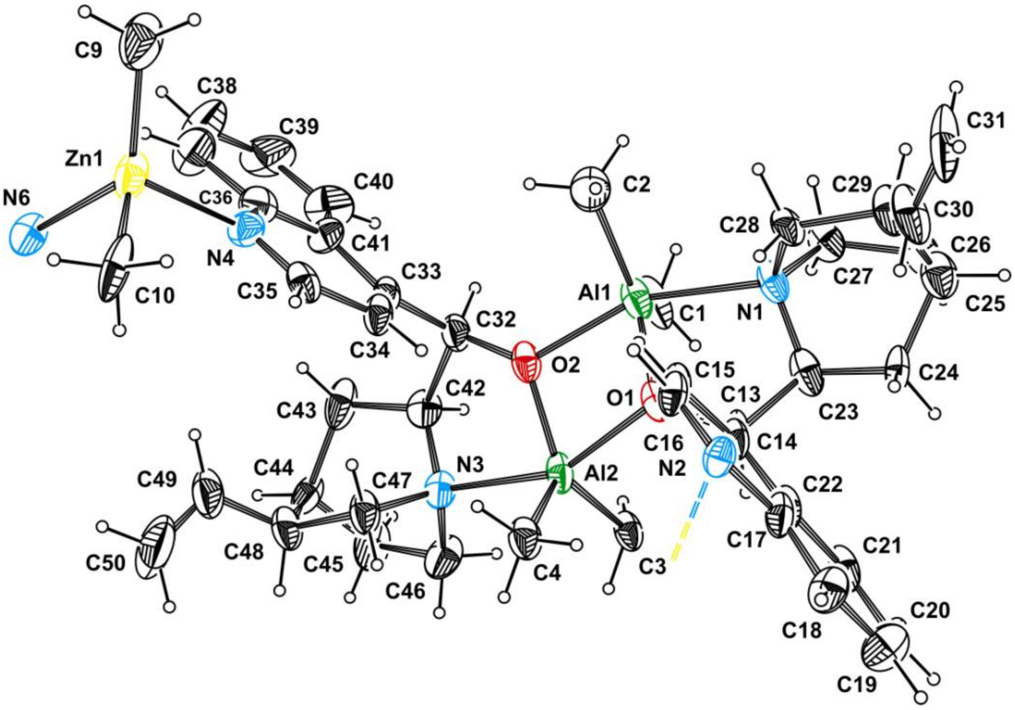
Crystal data for **2b**·toluene, $C_{50}H_{72}N_4O_2Al_2Zn$·toluene: $M = 972.60$, crystal dimensions 0.54 × 0.28 × 0.16 mm^3, orthorhombic, space group $P\ 2_12_12_1$ (no. 19), $a = 9.5132(10)$ Å, $b = 18.4101(16)$ Å, $c = 30.0492(19)$ Å, $U = 5262.6(8)$ Å^3, $Z = 4$, $F(000) = 2088$, $D_c = 1.228$ g m^3, $T = 100(2)$K, μ(Mo-Kα) = 0.545 mm^{-1}, Flack parameter = 0.12(21), Nonius Kappa-CCD diffractometer, $\theta_{max} = 21.97$ °, 6380 unique reflections. The structure was solved by direct methods using the SHELXS97 [3] program and was refined by full matrix least–squares on F^2 using the program SHELXL97 [4]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2 or 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. Refinement converged at $R1 = 0.0943$, $wR2 = 0.1642$ for all data and 595 parameters ($R1 = 0.0706$, $wR2 = 0.1496$ for 4311 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 0.999. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.84/-0.57 eÅ^{-3}. The structure contained additional molecules of toluene. The toluene molecules appear to be highly disordered and it was difficult to model their positions and distribution reliably. Therefore, the SQUEEZE function of PLATON (van der Sluis & Spek, 1990; Spek, 2001) was used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the model with one toluene molecule was employed for the final refinement.

(a)

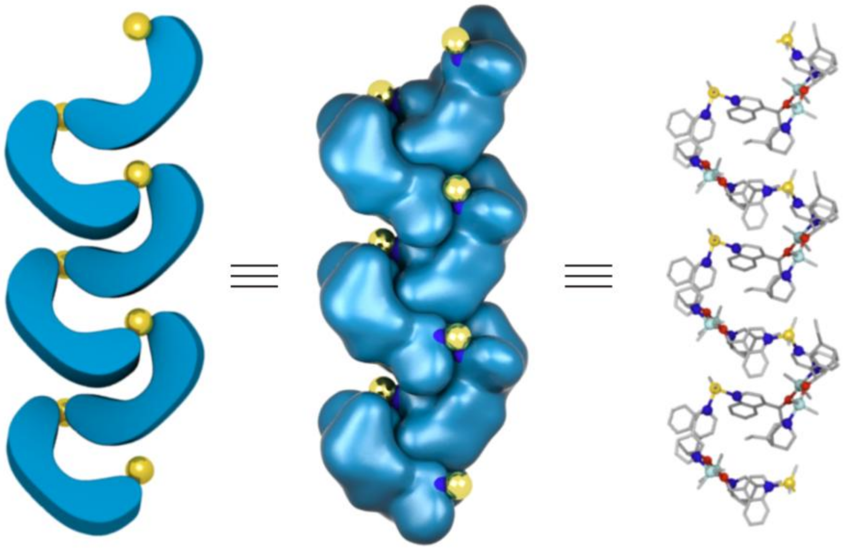
unit **A**



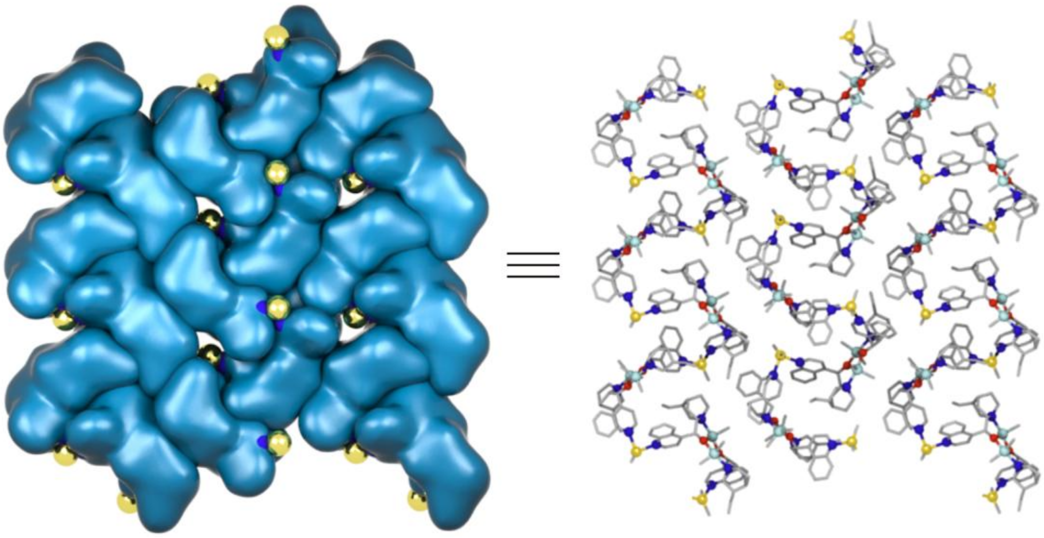
unit **B**



(b)



(c)



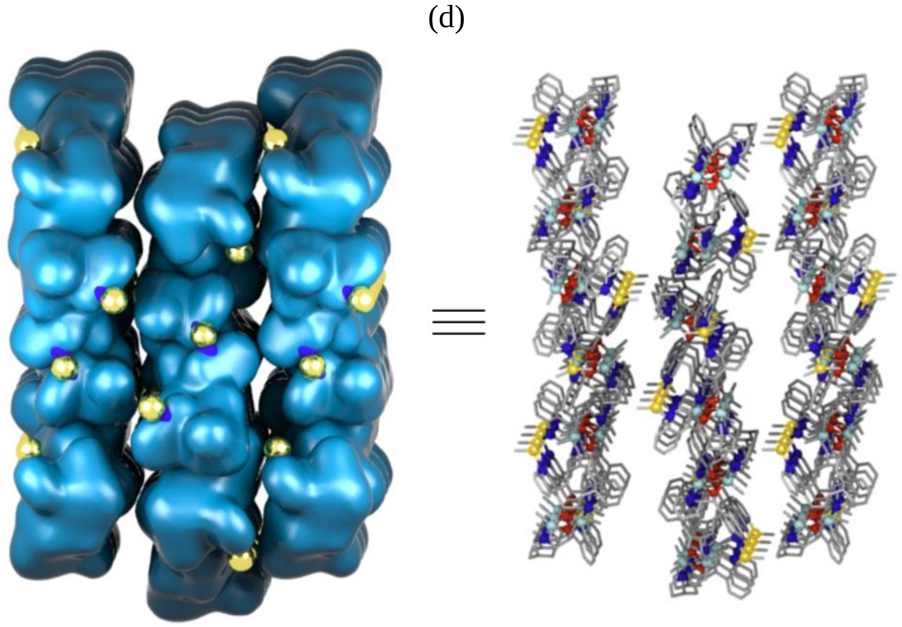


Fig. S1 (a) ORTEP diagrams of molecular structures of two independent units of **2a** (in main text of the manuscript these molecules are designed as **A** and **B**, respectively) with thermal ellipsoids set at 30% probability; (b) side view of a single zig-zag chain of **2a**; the middle picture shows the zig-zag architecture being expressed by the metalloligand's shape; (c) view along *a* axis on the crystal structure of **2a** showing a single 2D layer formed by the metalloligand's shape-driven assembling of single zig-zag chains; (d) view along *c* axis showing the loose stacking of 2D layers. Gold, cyan, blue and red balls represent Zn, Al, N and O atoms, respectively.

Table S1 Selected bond lengths (Å) and angles (deg) for compound **2a**.

Al1 – O1	1.845(8)
Al1 – O2	1.997(7)
Al2 – O1	1.981(6)
Al2 – O2	1.825(8)
Al3 – O3	1.848(7)
Al3 – O4	1.974(7)
Al4 – O3	1.980(7)
Al4 – O4	1.868(7)
Al1 – N1	2.210(9)
Al2 – N3	2.242(8)
Al3 – N5	2.146(8)

Al4 – N7	2.137(9)
Al1 – C1	2.007(11)
Al1 – C2	1.990(12)
Al2 – C3	1.964(9)
Al2 – C4	1.989(11)
Al3 – C5	2.019(11)
Al3 – C6	2.005(11)
Al4 – C7	1.956(14)
Al4 – C8	1.983(12)
Zn1 – N4	2.339(9)
Zn1 – N6	2.276(8)
Zn1 – C9	1.943(15)
Zn1 – C10	1.969(16)
Zn2 – C11	2.021(12)
Zn2 – C12	1.977(13)
Zn2 – N2	2.298(8)
Zn2 – N8	2.257(7)

N1 – Al1 – O2	153.3(4)
O1 – Al1 – C1	116.3(5)
O1 – Al1 – C2	126.0(5)
O2 – Al1 – C1	96.0(4)
O2 – Al1 – C2	96.5(4)
N3 – Al2 – O1	153.0(4)
N1 – Al1 – C1	97.1(4)
N1 – Al1 – C2	98.0(4)
O1 – Al2 – N3	153.0(4)
O2 – Al2 – C3	121.6(4)
O2 – Al2 – C4	120.0(4)
N3 – Al2 – C3	94.3(4)
N3 – Al2 – C4	97.7(4)
O3 – Al3 – C5	132.7(4)
O3 – Al3 – C6	109.8(4)
O4 – Al3 – C5	98.8(4)
O4 – Al3 – C6	99.2(4)
O3 – Al4 – C7	97.8(4)
O3 – Al4 – C8	99.9(4)
O4 – Al4 – C7	127.4(6)
O4 – Al4 – C8	115.1(5)
N5 – Al3 – O4	152.0(3)
N7 – Al4 – O3	151.5(4)
N5 – Al3 – O3	79.2(3)
N7 – Al4 – O4	78.6(3)
N4 – Zn1 – N6	90.1(3)
N2 – Zn2 – N8	91.1(3)

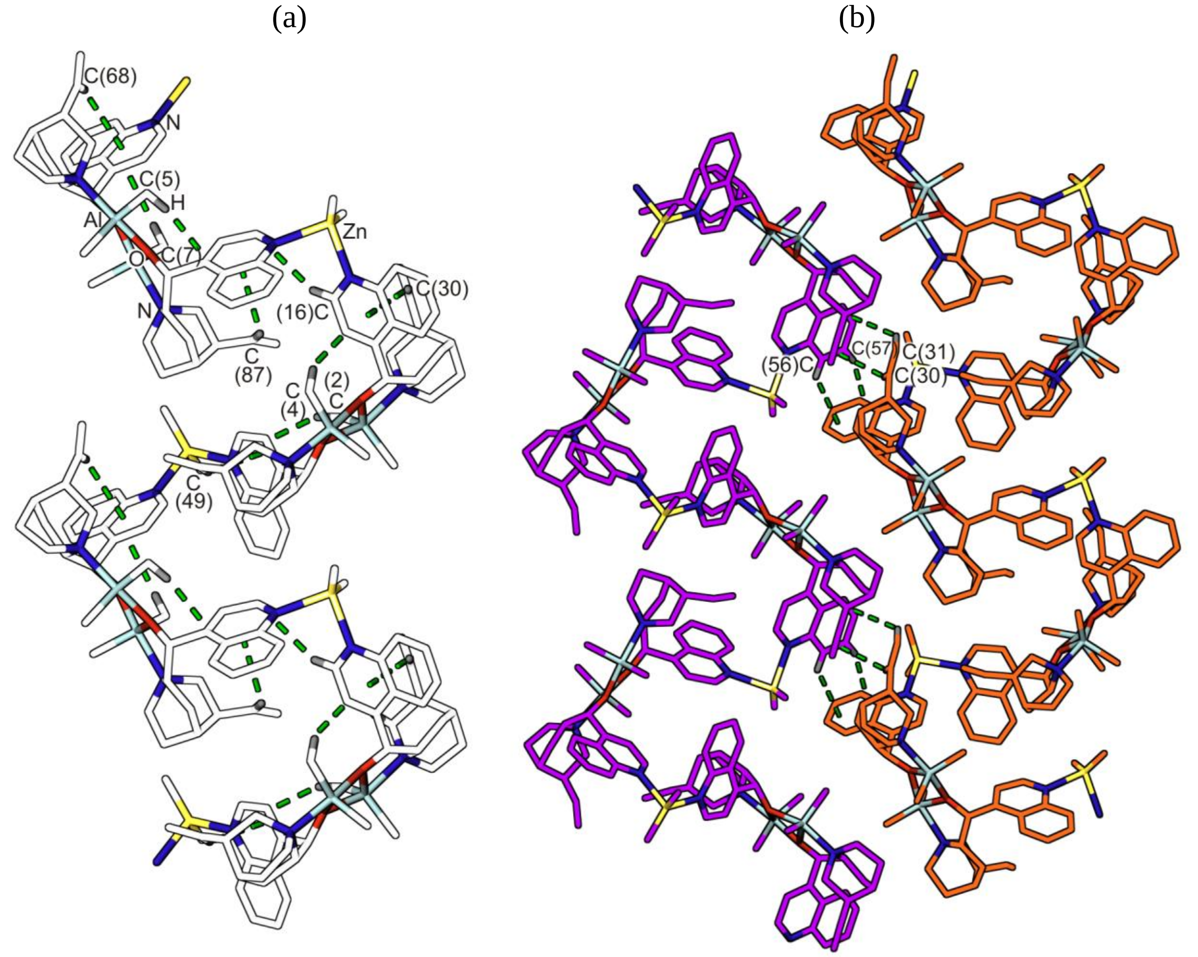
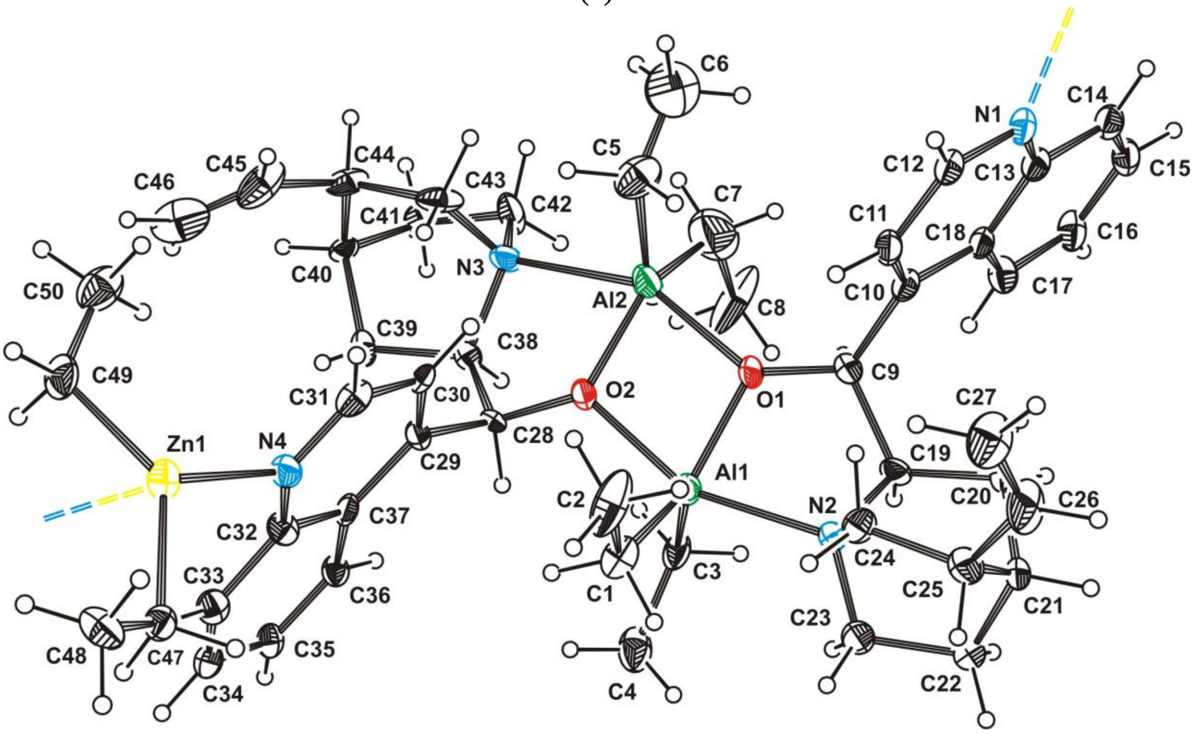


Fig. S2 C-H···π interactions (green dashed lines) within a single zig-zag chain (a) and between neighbouring chains (b) of **2a**. Hydrogen π-acceptor atoms are shown on the picture.

Table S2 Selected C-H···π distances (Å) for compound **2a**.[5]

C(2)-H···π	2.5
C(4)-H···π	2.5
C(5)-H···π	2.9
C(7)-H···π	2.9
C(16)-H···π	2.7
C(30)-H···π	3.2
C(30)-H···π (interchain)	3.0
C(31)-H···π	3.1
C(49)-H···π	3.0
C(56)-H···π	3.5
C(57)-H···π	3.0
C(68)-H···π	3.5
C(87)-H···π	3.5

(a)


C6
N1
C14
C12
C13
C15
C5
C44
C43
C42
C46
C45
C7
C41
C11
C18
C16
C50
C40
N3
C10
C17
Al2
C8
C39
C38
C49
C31
C30
O2
O1
C9
C27
C28
C19
Zn1
N4
C29
Al1
C20
C26
C2
N2
C32
C37
C24
C25
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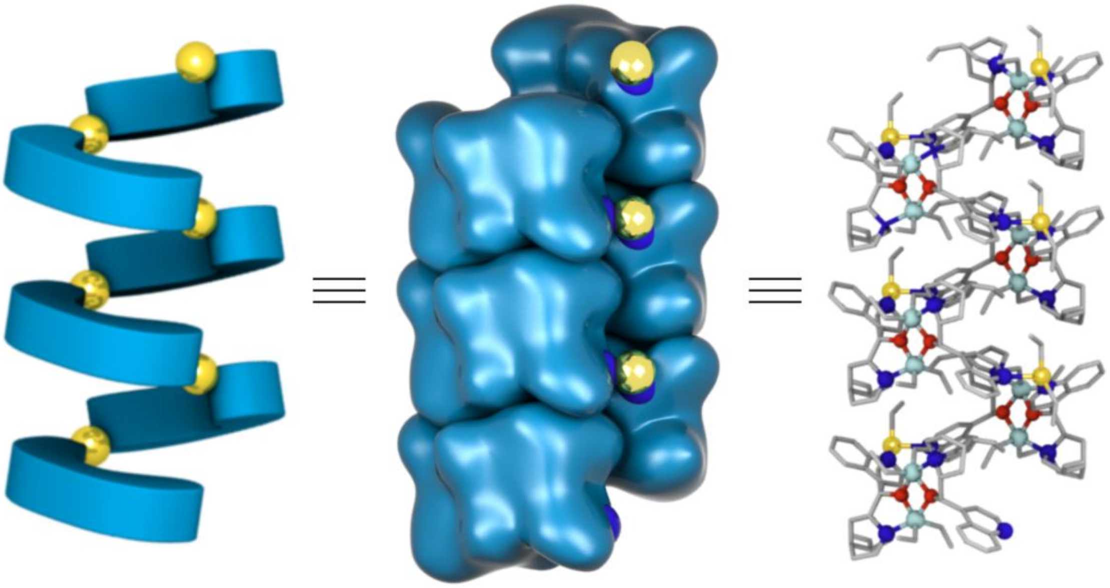
C36
C23
C48
C47
C35
C22
C34
C4

(b)



(c)

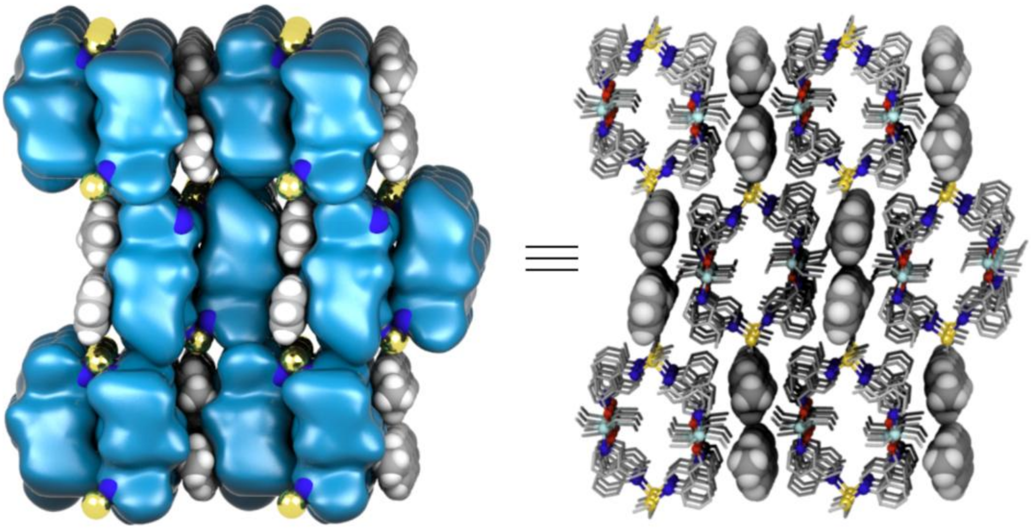


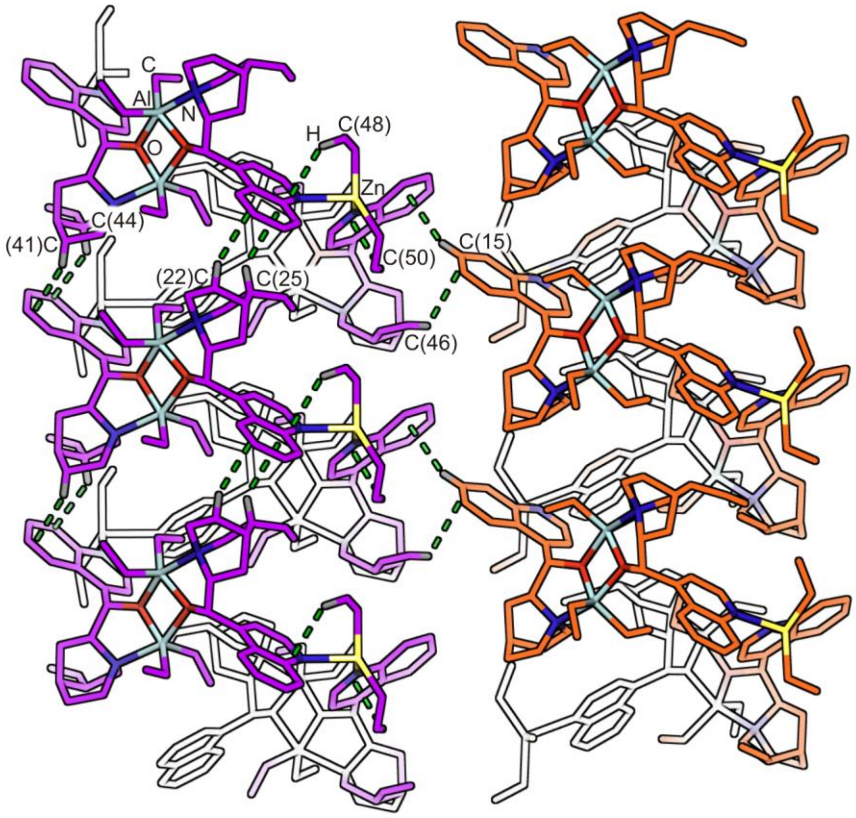
Fig. S3 (a) ORTEP diagram of molecular structure of **2b** with thermal ellipsoids set at 30% probability; (b) side view of a single helical nanotube of **2b**; the middle picture shows the helical architecture being expressed by the metalloligand's shape; (c) view along *a* axis on the crystal structure of **2b** showing the arrangement of helices with entrapped toluene molecules (shown in space-filling mode). Gold, cyan, blue and red balls represent Zn, Al, N and O atoms, respectively.

Table S3 Selected bond lengths (Å) and angles (deg) for compound **2b**.

Al1 – O1	1.847(5)
Al1 – O2	1.975(5)
Al2 – O1	2.027(6)
Al2 – O2	1.822(6)
Al1 – N2	2.142(6)
Al2 – N3	2.263(7)
Al1 – C1	1.974(9)
Al1 – C3	1.993(8)
Al2 – C5	2.242(10)
Al2 – C7	1.844(13)
Zn1 – N4	2.264(7)
Zn1 – C47	1.990(8)
Zn1 – C49	2.029(9)

N2 – Al1 – O2	155.4(2)
O1 – Al1 – C1	128.9(3)
O1 – Al1 – C3	114.6(3)
O2 – Al1 – C1	96.2(3)
O2 – Al1 – C3	95.2(3)
O2 – Al1 – N2	155.4(2)
N2 – Al1 – C1	97.2(3)
N2 – Al1 – C3	97.2(3)
O1 – Al2 – N3	152.8(3)
O2 – Al2 – C5	108.9(4)
O2 – Al2 – C7	140.1(6)
N3 – Al2 – C5	99.1(4)
N3 – Al2 – C7	93.9(5)
O1 – Al2 – C5	97.8(3)
O1 – Al2 – C7	99.8(5)
N4 – Zn1 – C47	111.4(3)
N4 – Zn1 – C49	98.6(3)

(a)



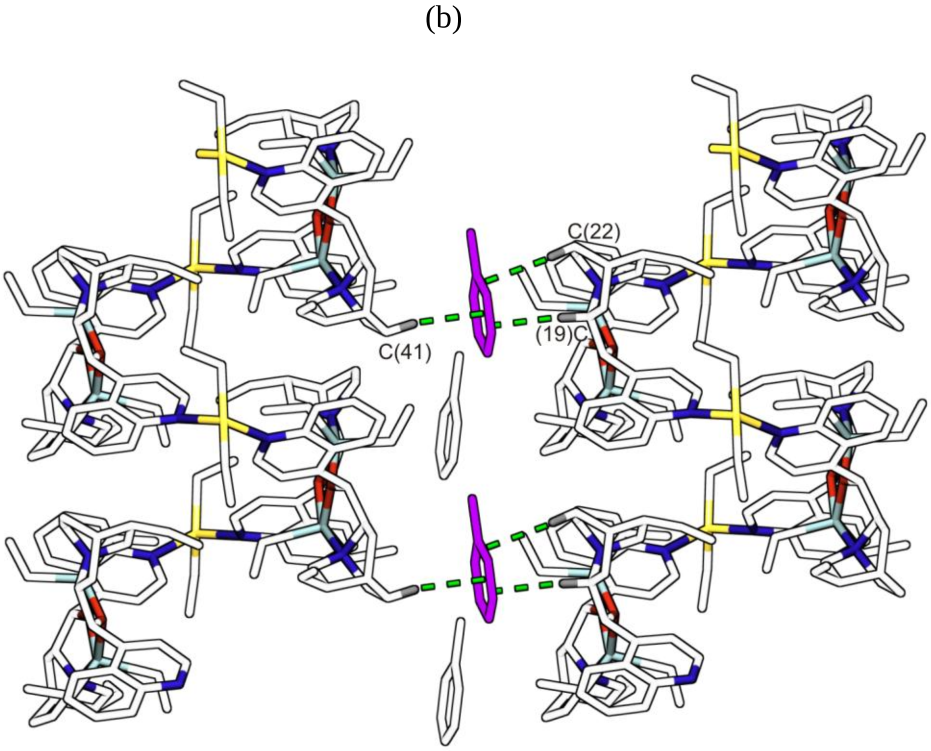


Fig. S4 (a) C-H···π interactions (green dashed lines) within a single helical chain and between neighbouring helices of **2b**; C-H···π interactions between the coordination polymer **2b** and the encapsulated toluene molecules. Hydrogen π-acceptor atoms are shown on the picture.

Table S4 Selected C-H···π distances (Å) for compound **2b**.[5]

C(15)-H···π	2.7
C(19)-H···π (toluene)	3.0
C(22)-H···π	2.9
C(22)-H···π (toluene)	2.7
C(25)-H···π	3.3
C(41)-H···π	2.9
C(41)-H···π (toluene)	2.6
C(44)-H···π	2.8
C(46)-H···π	3.2
C(48)-H···π	2.8
C(50)-H···π	2.9

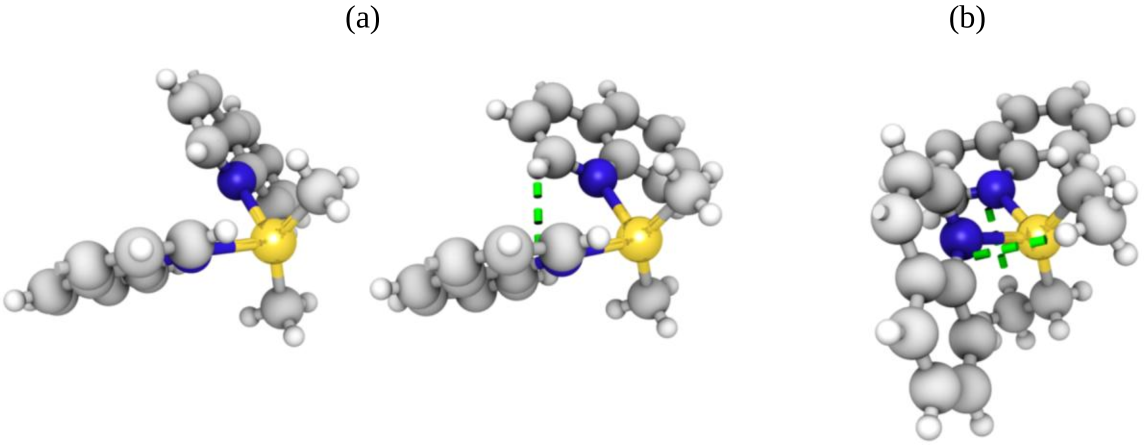


Fig. S5 Relative orientations of the neighbouring quinoline planes connected by ZnR_2 unit in the structure of **2a** (a) and **2b** (b). Two independent such groups exist in the structure of **2a**, where in **2b** only one can be distinguished. C-H··π interactions are shown as green dashed lines.

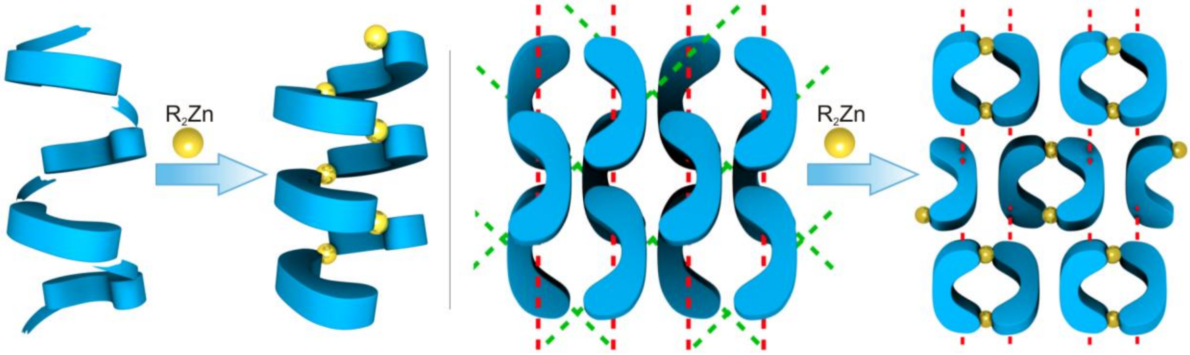


Fig. S6 From "virtual helix" to "real helix" - an illustration of the concept. The picture on the right side shows the top view of the arrangement of helices; a single non-covalent bilayer of the free metalloligand (the "tongue-to-groove" structure) forms a "virtual bilayer" () upon connecting by ZnR_2 units. C-H··N and C-H··π interactions are shown as green and red dashed lines, respectively.

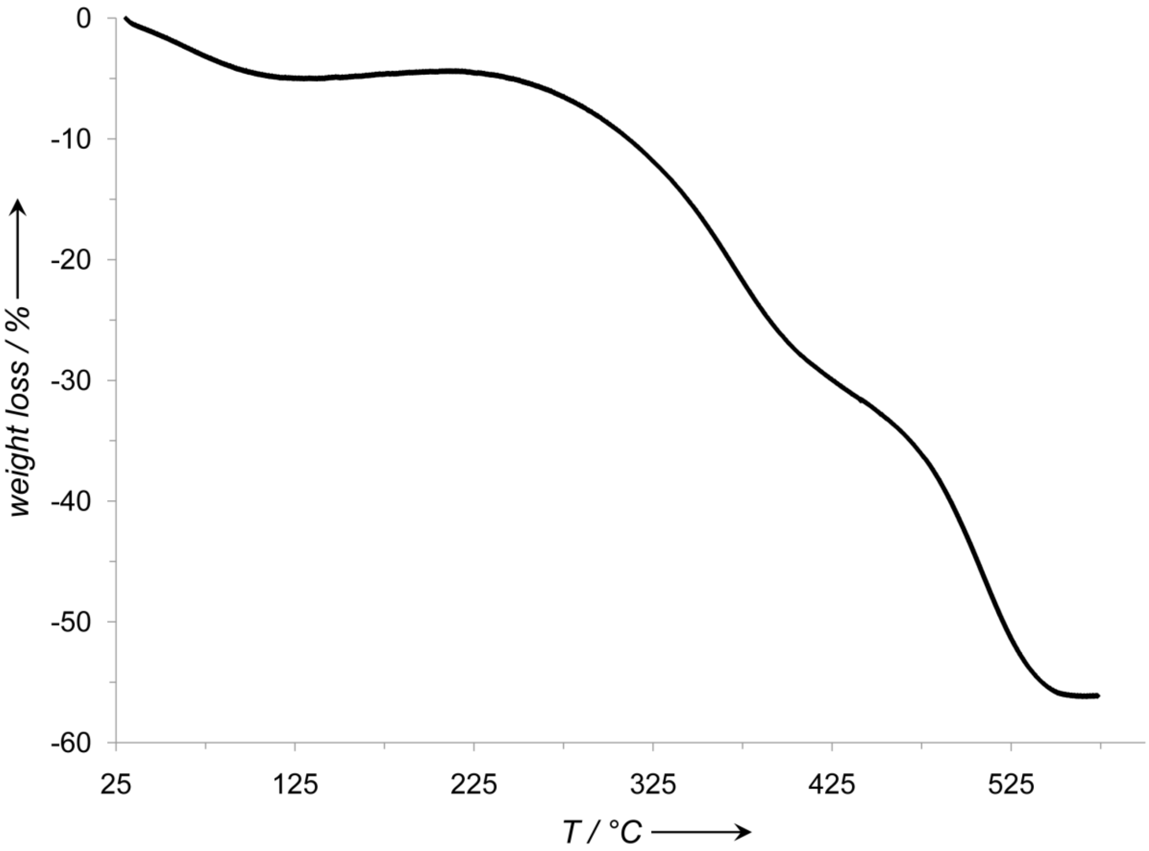


Fig. S7 The TGA curve of **2b**.

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[1] J. Lewiński, T. Kaczorowski, D. Prochowicz, T. Lipińska, I. Justyniak, Z. Kaszkur, J. Lipkowski, *Angew. Chem. Int. Ed.*, 2010, DOI: 10.1002/anie.201002925.

[2] R. Kumar, M. L. Sierra, J. P. Oliver, *Organometallics*, 1994, **13**, 4285.

[3] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.

[4] G. M. Sheldrick, SHELXL-97, Program for Structure Refinement, Universität Göttingen, 1997.

[5] The C-H···π interaction lenghts were estimated measuring the distance between a hydrogen π-acceptor atom and the closest point on the appropriate quinoline plane.