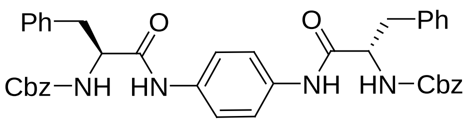
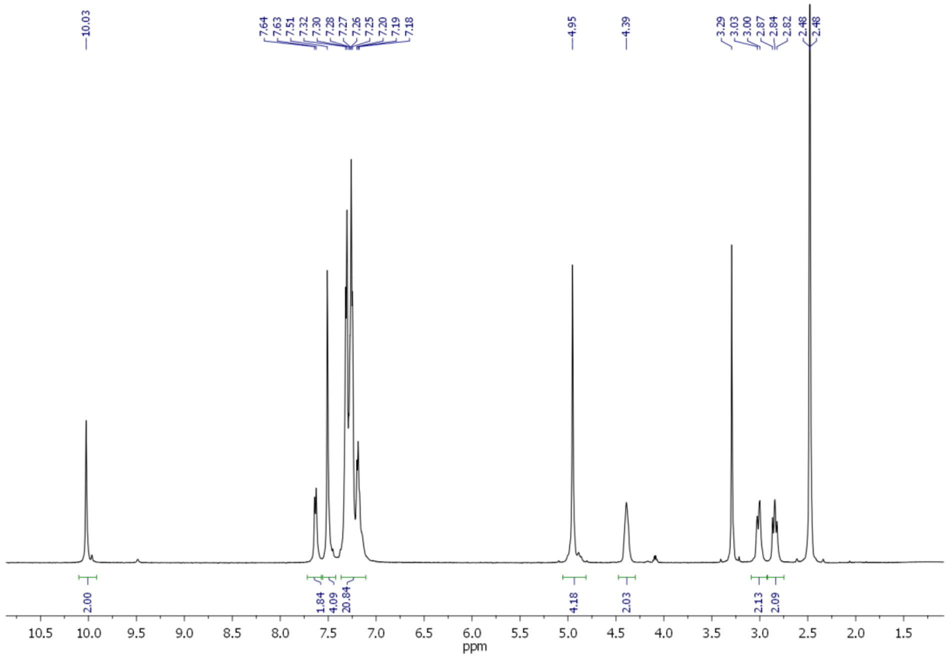
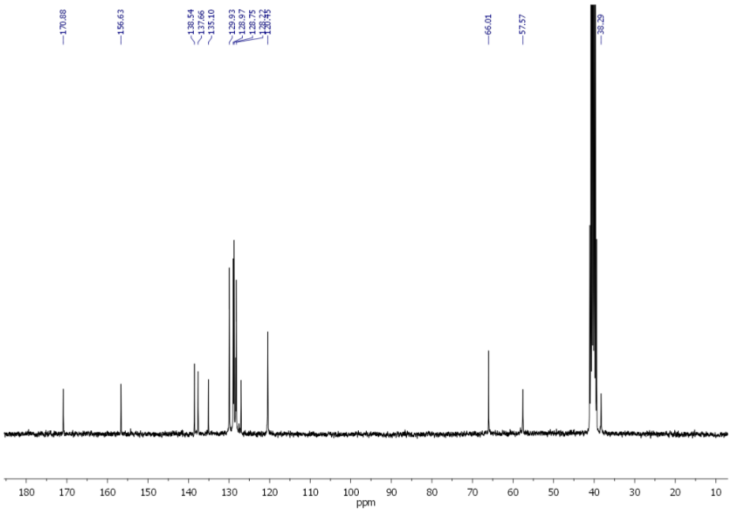
Zinc(II) coordination polymers with pseudopeptidic ligands

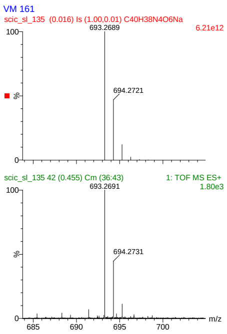
Vicente Martí-Centelles[1,2], D. Krishna Kumar[1], Andrew J.P. White[1], Santiago V. Luis*[2] and Ramon Vilar*[1]

1. Selected spectroscopic data for 2-Cbz.

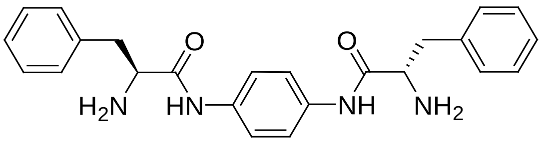


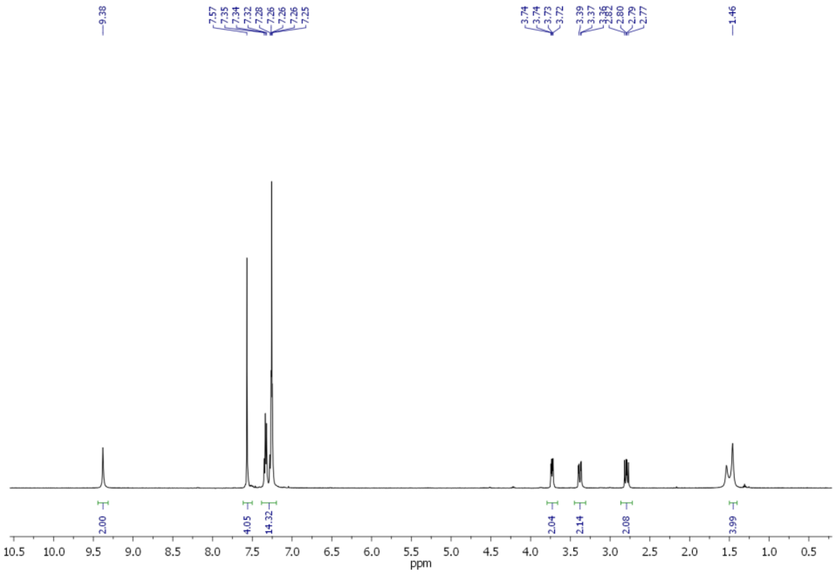


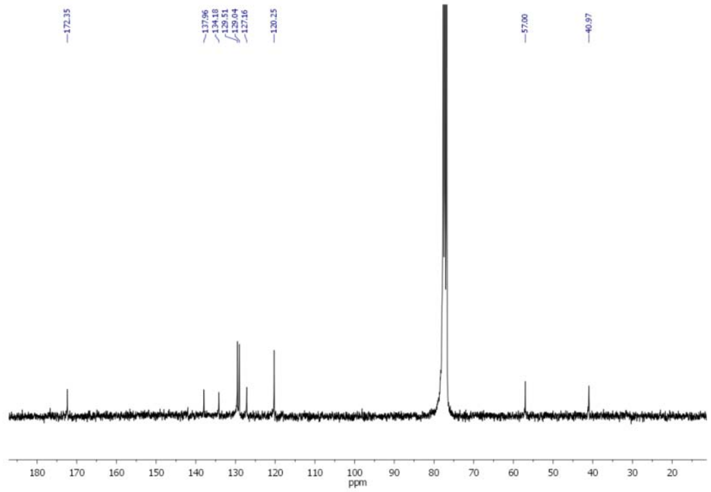


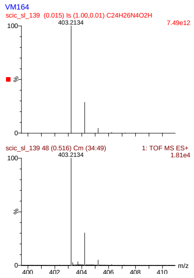


2. Selected spectroscopic data for ligand 2.

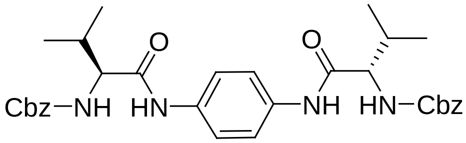


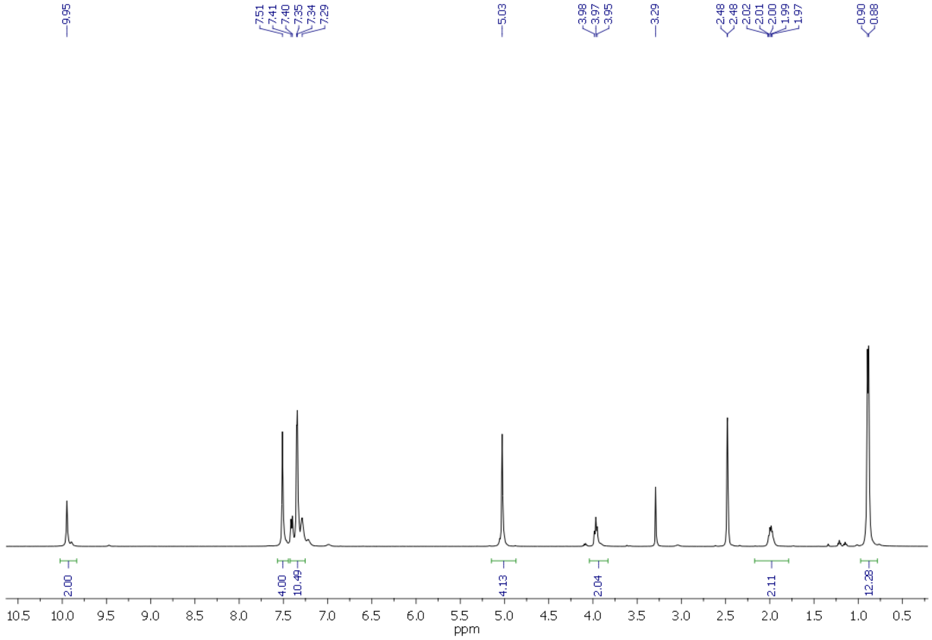


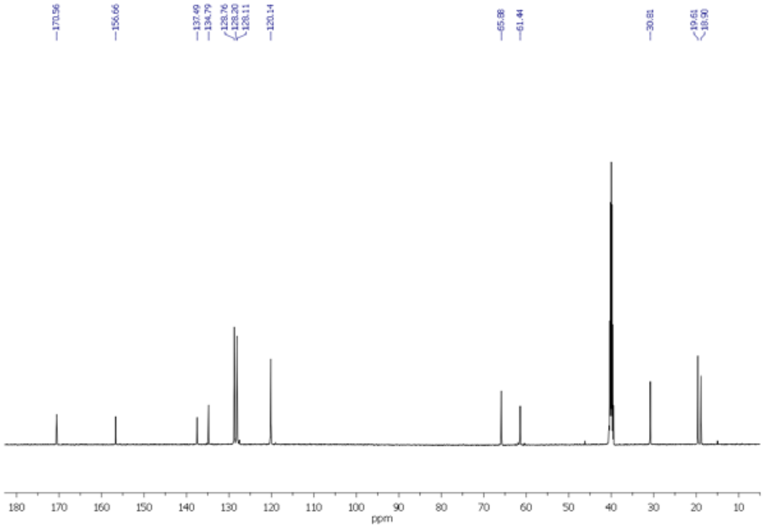


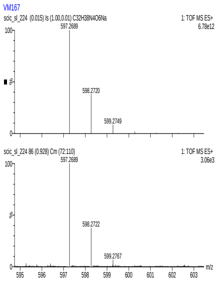


3. Selected spectroscopic data for 3-Cbz.

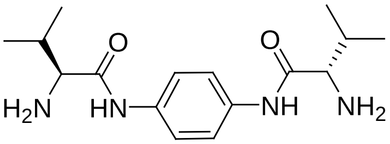


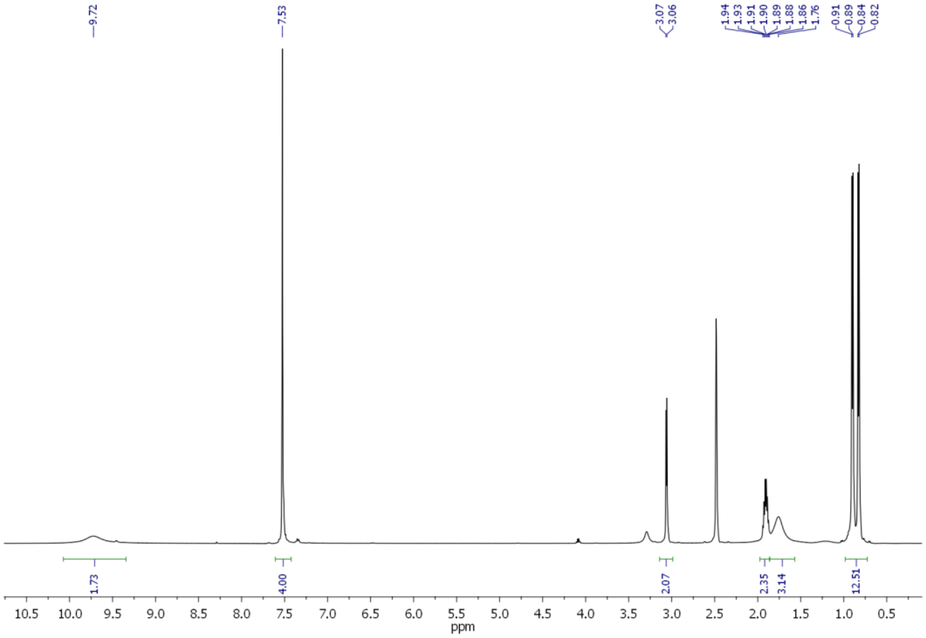


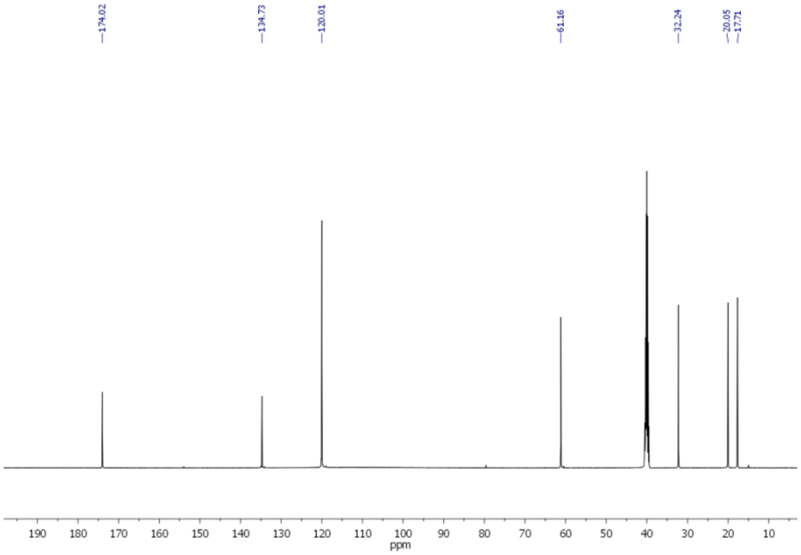


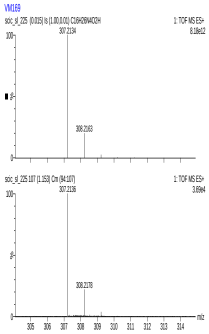


4. Selected spectroscopic data for ligand 3.

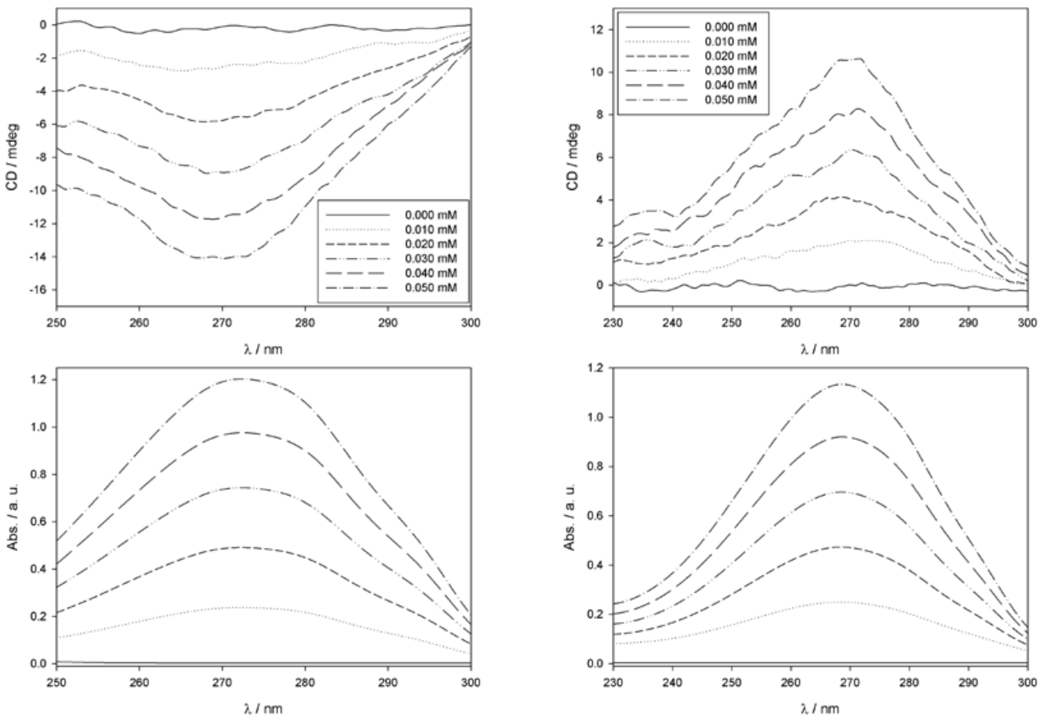




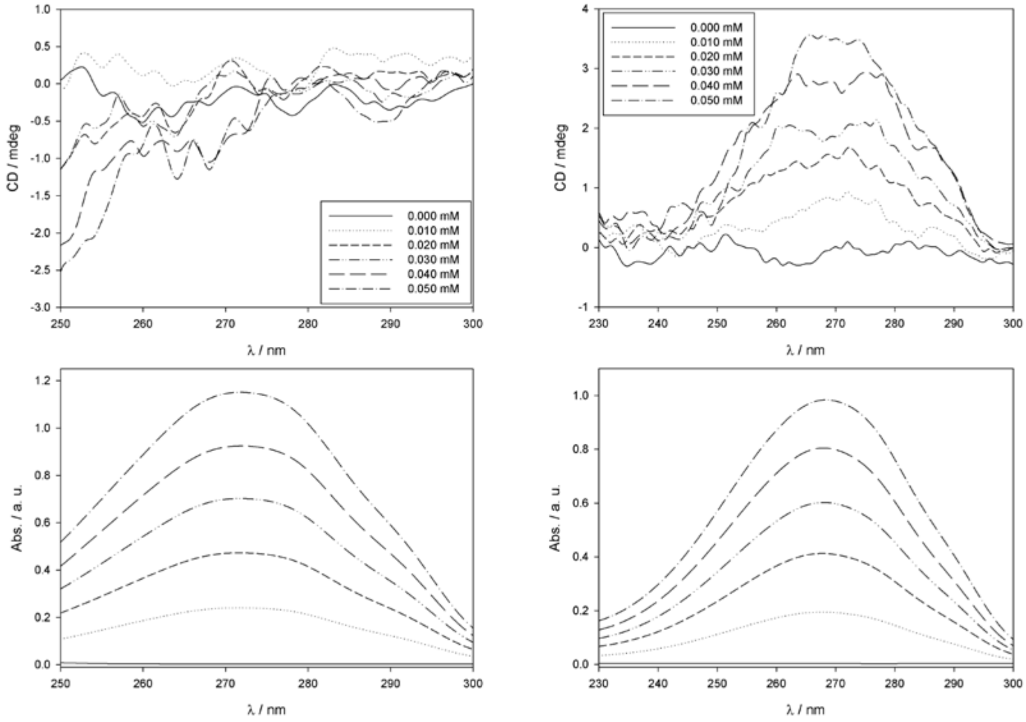




5. Circular Dichroism Spectroscopy for Ligands 2 and 3



Absorption and circular dichroism (CD) spectra of compound **2** in: $CHCl_3$ (left hand side spectra) and MeOH (right hand side spectra).



Absorption and circular dichroism (CD) spectra of compound **3** in: $CHCl_3$ (left hand side spectra) and MeOH (right hand side spectra).

6. X-ray crystallography – supplementary data

The X-ray crystal structure of 2

All twelve of the N–H hydrogen atoms in the structure of **2** were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of 3

All six of the N–H hydrogen atoms in the structure of **3** were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of 4

The S(50)-based sulphate anion in the structure of **4** was found to be disordered. Two orientations of ca. 81 and 19% partial occupancy were identified, their geometries optimised (with all 8 S–O distances, and all 12 O–S–O angles, restrained to be similar), the thermal parameters of adjacent atoms restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically. The oxygen atoms of five water molecule sites were clearly identified, with one of them [O(65)] being assigned as only 50% occupancy on the basis of its thermal parameter. (This 50% occupancy water molecule is *ca*. 2.36 Å away from one of the major occupancy oxygen atoms of the disordered S(50) sulphate anion; this implausible separation is clearly an artefact of the disorder.) The rest of the solvent was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.[1] This suggested a total of 244 electrons per unit cell, equivalent to 30.5 electrons per asymmetric unit. The crystal was grown from an ethanol/water mixture, and the shape of the residual electron density peaks observed in the disordered solvent region before the use of SQUEEZE, and the already identified water molecule sites, suggested that the unassigned solvent was probably ethanol [C_2H_6O, 26 electrons]. 30.5 Electrons equates to *ca*. 1.17 ethanol molecules (30.4 electrons). This was rounded down to 1, and this interpretation of the included solvent was used for the calculations of the contents of the asymmetric unit.

The N–H and O–H hydrogen atoms of the cationic chains and the included water molecules could not be reliably located, and so the asymmetric unit is low by 29 hydrogen atoms. Combined with the atoms "removed" by the use of SQUEEZE, the atom list for the asymmetric unit is low by $C_2H_{35}O$ (and that for the unit cell by $C_8H_{140}O_4$) compared to what is actually presumed to be present.

The X-ray crystal structure of 5

The O(70)-based included ethanol solvent molecule in the structure of **5** was found to be disordered and adjacent to a 2-fold axis. Two unique orientations of *ca*. 35 and 15% partial occupancy were identified, with two others of the same occupancies being generated by action of the C_2 axis. The geometries of the two unique orientations were optimized (with the 2 O-C distances, the 2 C-C distances, and the 2 O-C-C angles, restrained to be similar), the thermal parameters of adjacent atoms restrained to be similar, and all of the atoms refined isotropically. The nine unique N–H hydrogen atoms of the cationic chain were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å. The O–H hydrogen atoms of the included water and ethanol solvent molecules could not be reliably located, so the unit cell is low by 27 hydrogen atoms.

The X-ray crystal structure of 6

The C(5)-based C_6H_4 ring in the structure of **6** is disordered across a 2-fold axis, the ring being inclined by *ca*. 40° to the C_2 axis. This was modelled by using one complete, idealised, 50% occupancy ring (treated as a regular hexagon of side length 1.39 Å), the non-hydrogen atoms of which were refined anisotropically, with a second 50% occupancy orientation being generated by action of the C_2 symmetry. The two N–C(Ar) bonds were restrained to be similar, and the N–C_6–N atoms were restrained to be coplanar. The O(30)-based included water molecule was also found to be disordered across a 2-fold axis. This was modelled by using one 50% position with a second 50% occupancy position being generated by action of the C_2 symmetry. The three N–H hydrogen atoms were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å. The O–H hydrogen atoms of the O(30) and O(40)-based water molecules were not located, so the unit cell is low by 19 hydrogen atoms.

The X-ray crystal structure of 7

The coordinated bromine atom Br(1) in the structure of 7 was found to be disordered. Two sites of ca. 78 and 22% partial occupancy were identified, their thermal parameters restrained to be similar, and both were refined anisotropically. Part of one of the N,O chelate rings bound to the same metal atom was also found to be disordered. Two orientations of ca. 61 and 39% partial occupancy were identified for N(41), C(42) and the C(55)-based isopropyl group, their geometries optimized (with the 6 bond lengths and 9 bond angles involving the split atoms restrained to be similar to their counterparts in the other orientation), the thermal parameters of adjacent atoms restrained to be similar, and only the major occupancy non-hydrogen atoms were refined anisotropically.

Initially the Br(6) and Br(7) atoms were treated as full occupancy bromide anions. However, their internuclear separation of ca. 3.1 Å is unrealistic, their thermal parameters were too large, and to achieve charge balance with the assumed protonation of the nitrogen atoms (see below) only an overall –1 charge was required. As there did not seem to be anything other than bromide ions that they could sensibly be, they were both refined anisotropically as 50% occupancy bromine atoms.

The included solvent was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.[1] This suggested a total of 891 electrons per unit cell, equivalent to ca. 223 electrons per asymmetric unit. The crystal was grown from an ethanol/water mixture, and ΔF maps before the use of SQUEEZE showed a mixture of isolated residual electron density peaks and small chains of peaks in a roughly 1:1 ratio. This suggested an approximately equal amount of water [H_2O, 10 electrons] and ethanol [C_2H_6O, 26 electrons]. Seven water molecules and six ethanol molecules equates to 226 electrons, and this interpretation of the included solvent was used for the calculations of the contents of the asymmetric unit.

The N–H hydrogen atoms of the cationic chains could not be reliably located, and so the asymmetric unit is low by 24 hydrogen atoms. Combined with the atoms “removed” by the use of SQUEEZE, the atom list for the asymmetric unit is low by $C_{12}H_{74}O_{13}$ (and that for the unit cell by $C_{48}H_{296}O_{52}$) compared to what is actually presumed to be present.

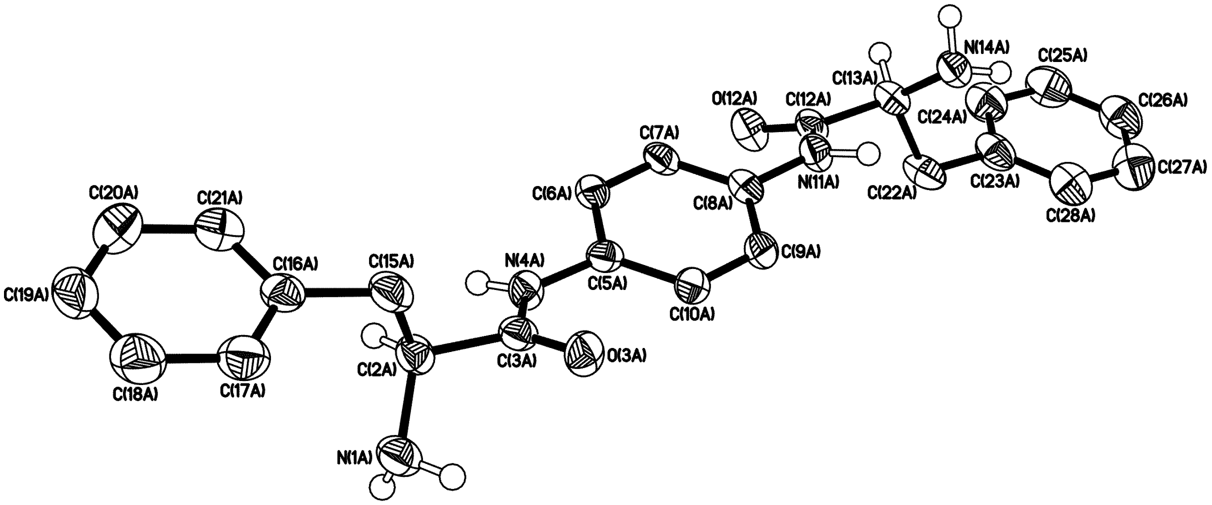


Fig. S1 The molecular structure of one (**2-A**) of the two crystallographically independent molecules present in the structure of **2** (50% probability ellipsoids).

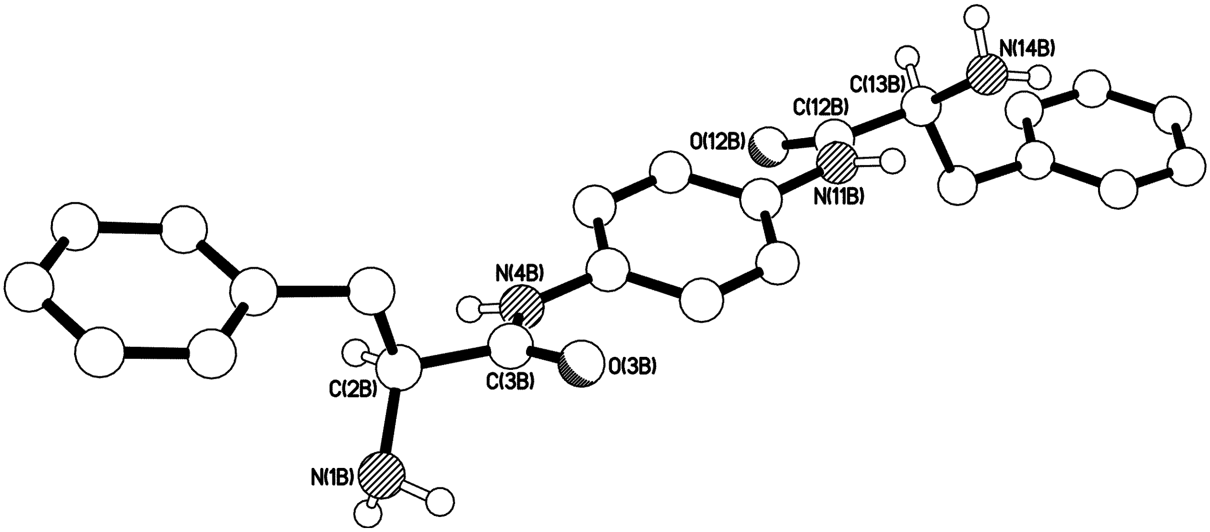


Fig. S2 The molecular structure of one (**2-B**) of the two crystallographically independent molecules present in the structure of **2**.

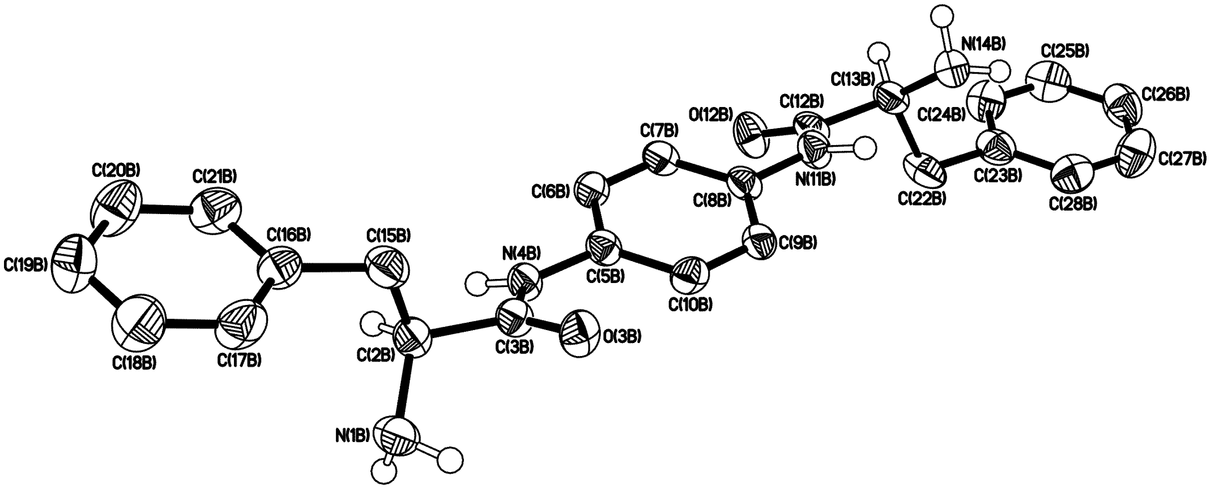


Fig. S3 The molecular structure of one (**2-B**) of the two crystallographically independent molecules present in the structure of **2** (50% probability ellipsoids).

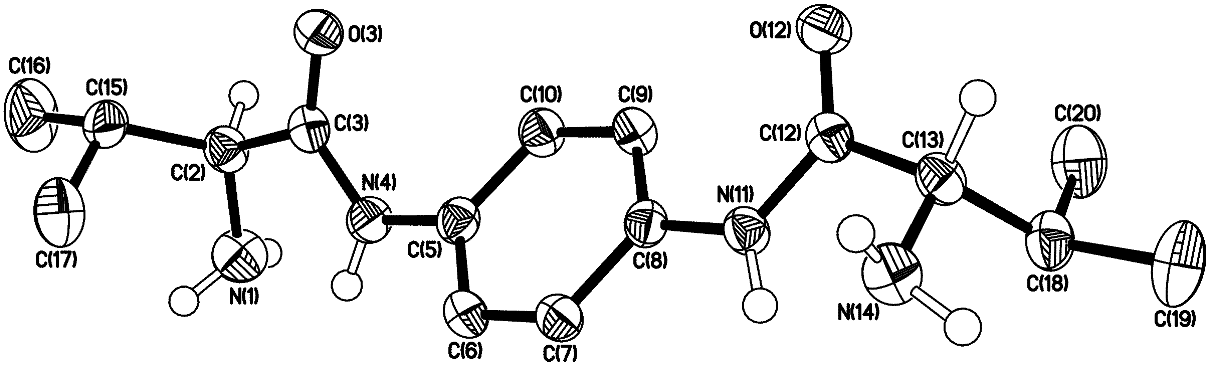


Fig. S4 The molecular structure of **3** (50% probability ellipsoids).

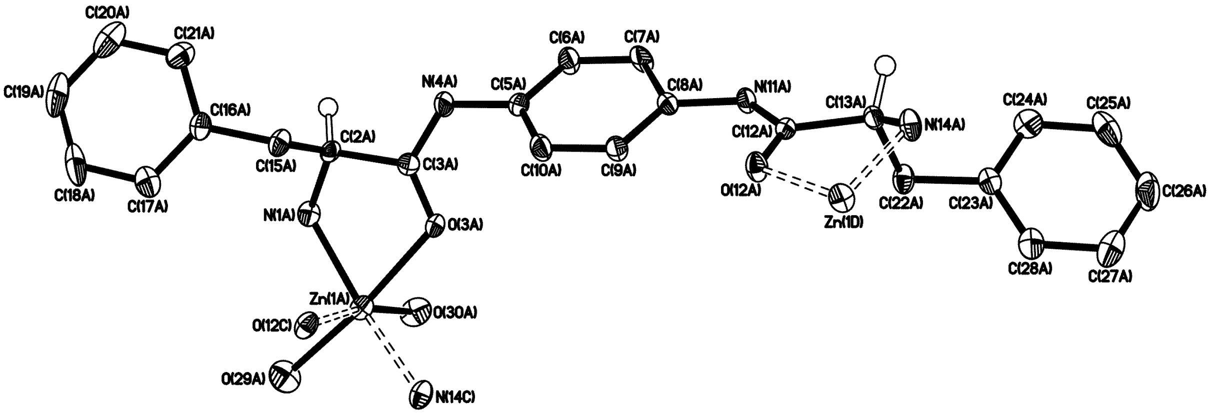


Fig. S5 The unique portion of one (**4-A**) of the two crystallographically independent cationic chains present in the structure of **4** (50% probability ellipsoids).

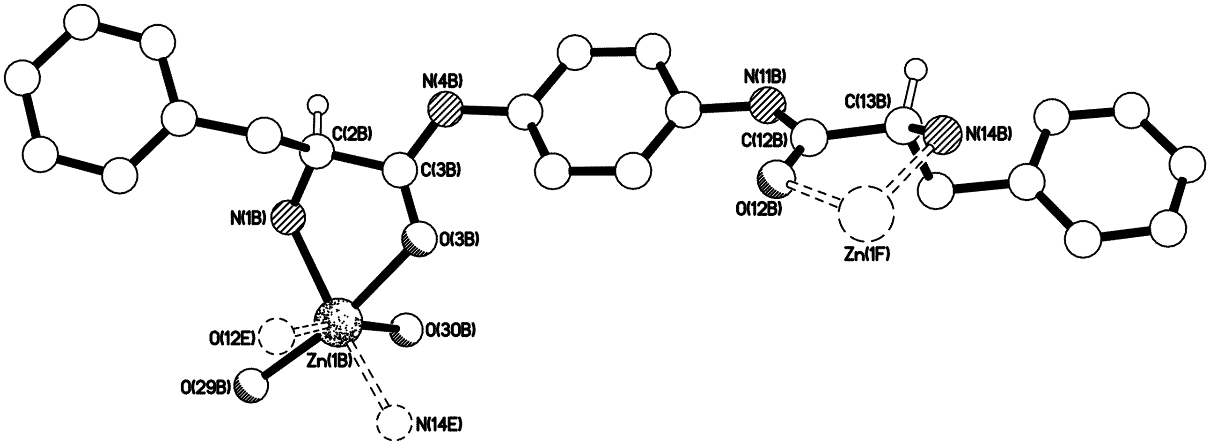


Fig. S6 The unique portion of one (**4-B**) of the two crystallographically independent cationic chains present in the structure of **4**.

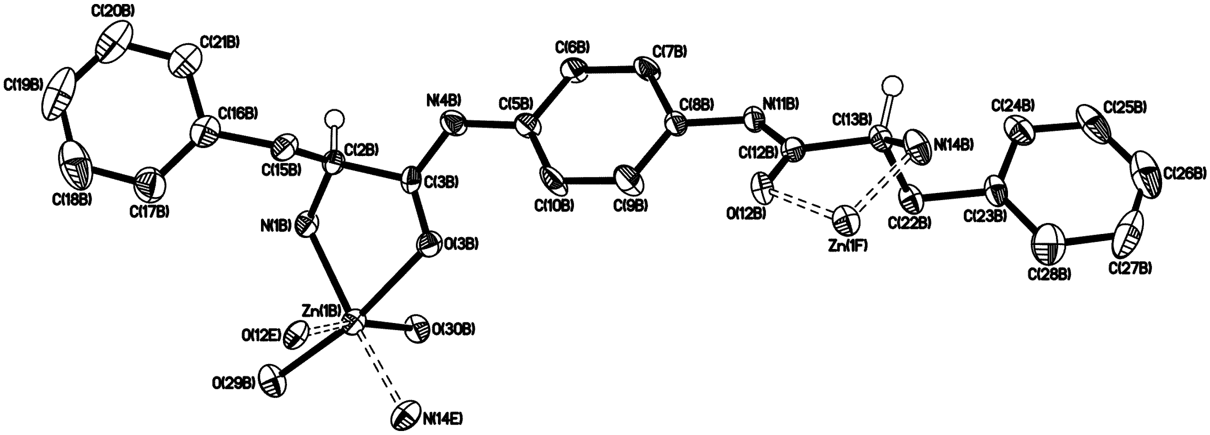


Fig. S7 The unique portion of one (**4-B**) of the two crystallographically independent cationic chains present in the structure of **4** (50% probability ellipsoids).

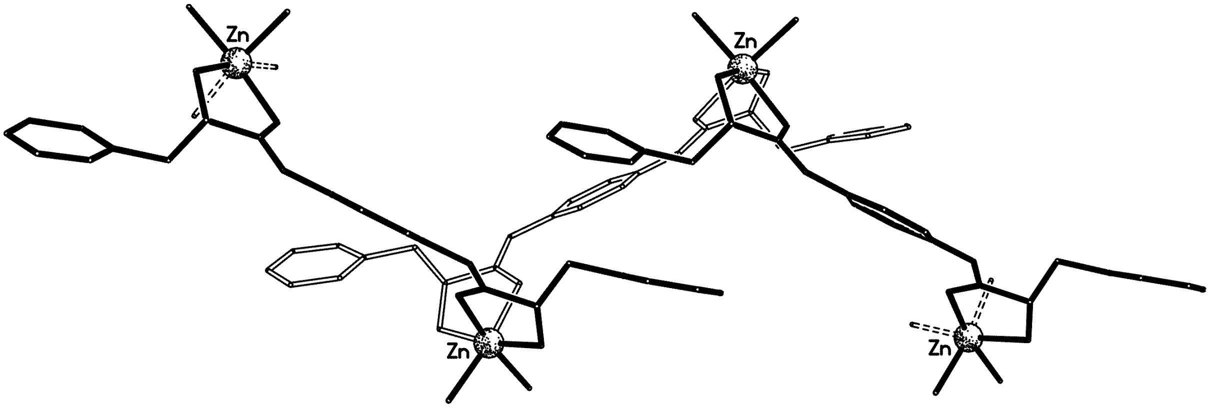


Fig. S8 Part of one (**4-B**) of the two crystallographically independent cationic chains present in the structure of **4**.

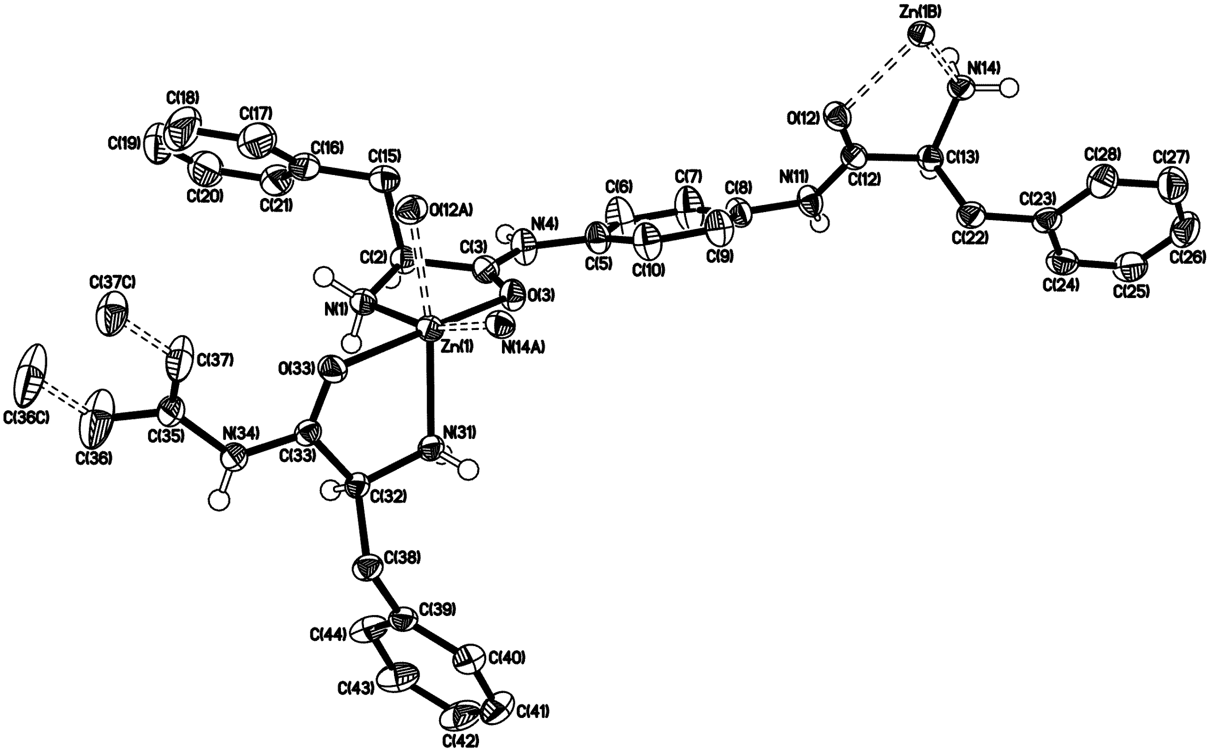


Fig. S9 The unique portion of the cationic network in the structure of **5** (50% probability ellipsoids).

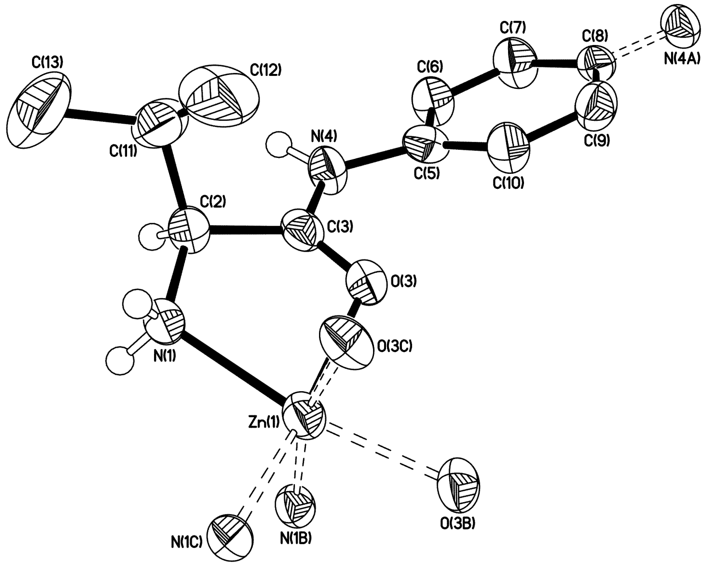


Fig. S10 The unique portion of the cationic network in the structure of **6**. The zinc atom sits on a 3-fold axis, and a 2-fold axis passes through the centre of the aryl ring (50% probability ellipsoids).

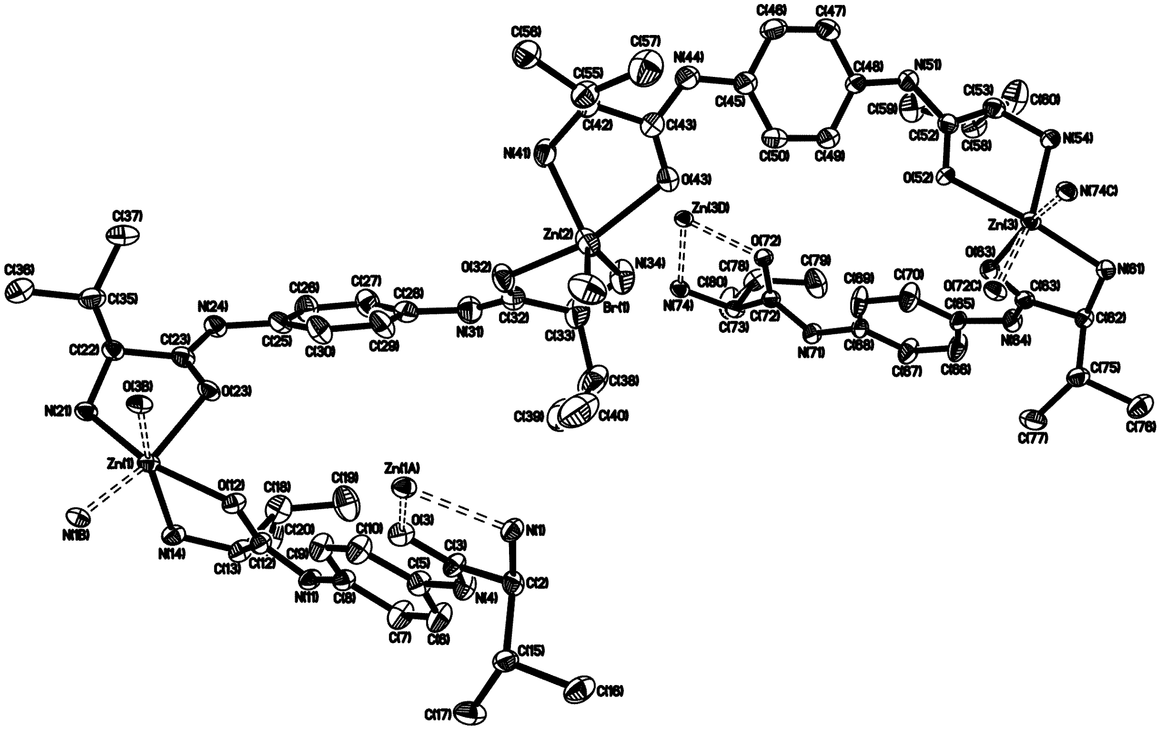


Fig. S11 The unique portion of the cationic sheets in the structure of 7 (30% probability ellipsoids).

7. Thermogravimetric Analyses (TGA)

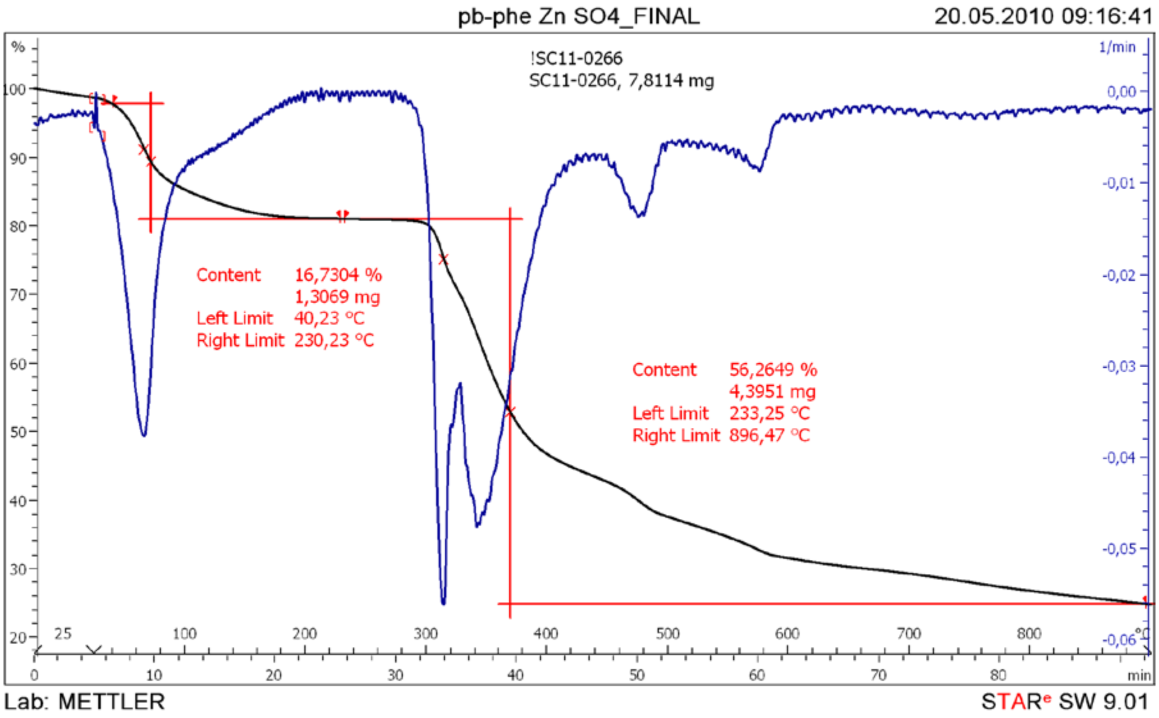


Fig. S12 TGA plot of **4.** Wt Loss for solvents (5 H_2O + 0.5 EtOH) = (113.11/677.04)*100 = 16.7% [40 °C to 230 °C]; observed 16.7%. Wt Loss for Ligand: (402.4/677.04)*100 = 59.4% [233 °C to 896 °C]; observed 56.3%

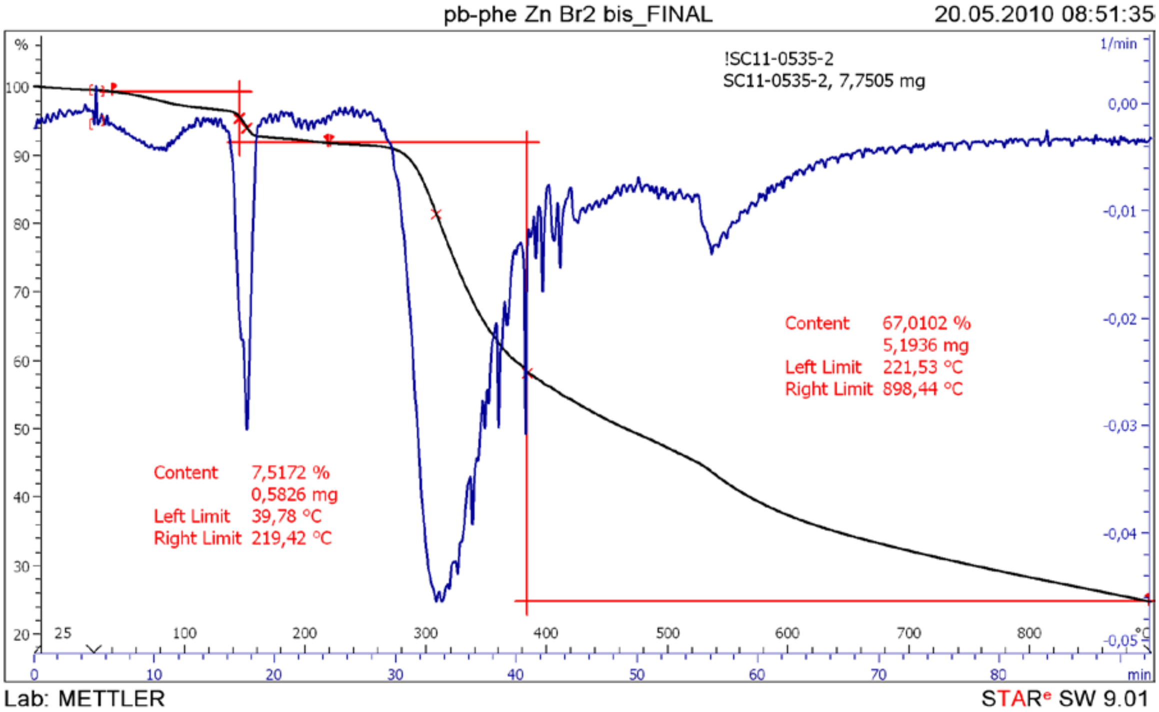


Fig. S13 TGA plot of **5**. Wt Loss for solvents (4 H_2O +1 EtOH) = (118.3/1775.9)*100 = 6.7% [40 °C to 219 °C]; observed: 7.5%. Wt Loss for Ligand: (1207/1775.97)*100 = 67.9% [222 °C to 898 °C]; observed: 67.0%

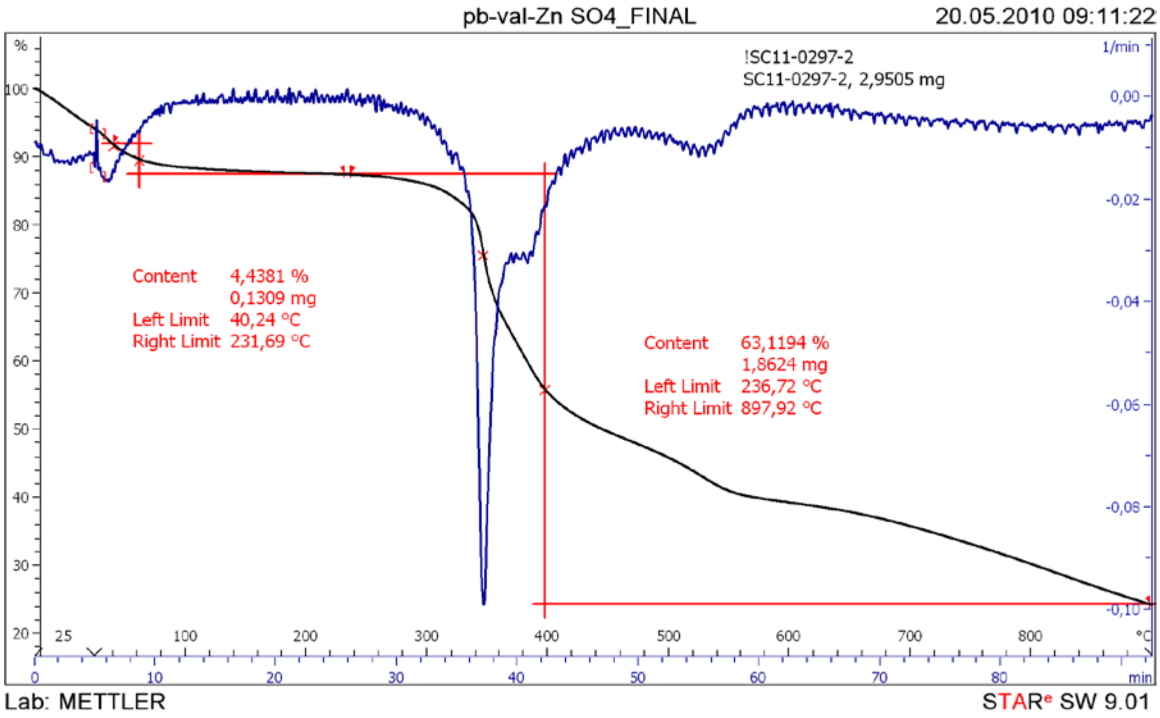


Fig. S14 TGA plot of **6**. Wt Loss for solvents (3 H_2O) = (54/13501)*100 = 4.0% [40 °C to 232 °C]; observed 4.4%. Wt Loss for Ligand: (919.2/1350)*100 = 68.1% [236 °C to 898 °C]; observed: 63.1%

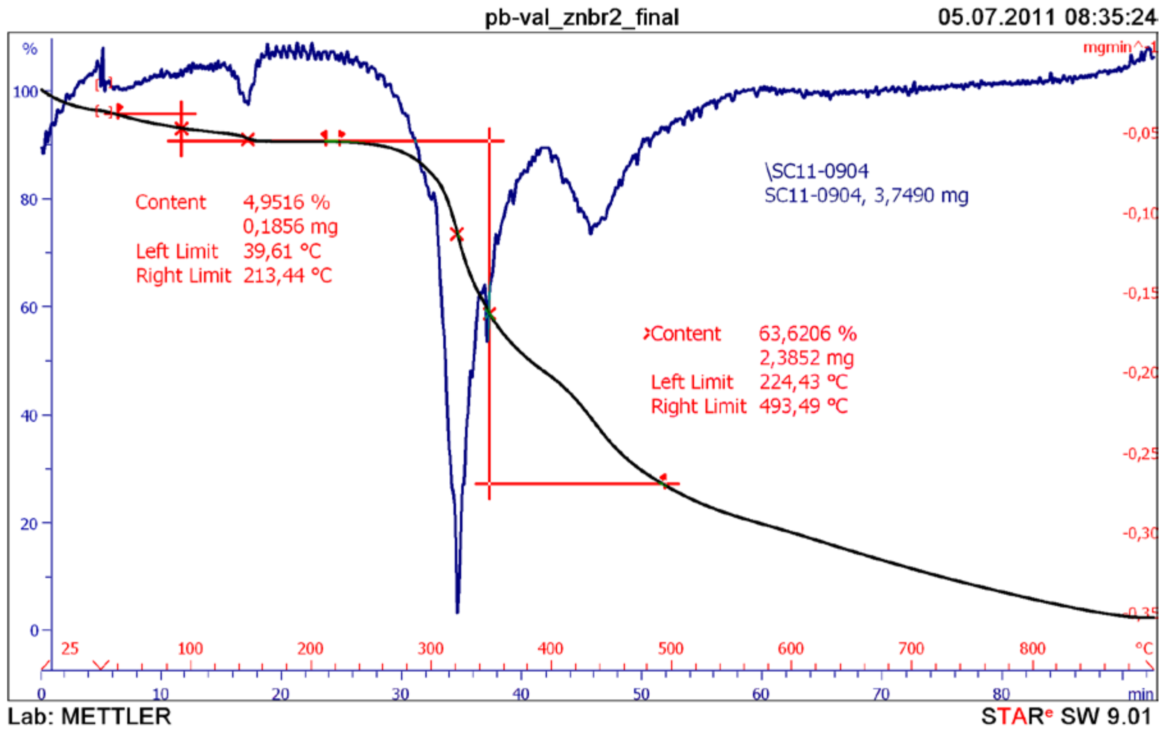


Fig. S15 TGA plot of **7**. Wt Loss for solvents (3 H_2O + 1 EtOH) = (82.10/2001.32)*100=5.0% [40 ºC to 213 ºC]; observed 4.9%. Wt Loss for Ligand: (1225.61/2001.32)*100=61.2% [224 ºC to 493 ºC]; observed: 63.6%

8. X-ray powder diffraction pattern for 5

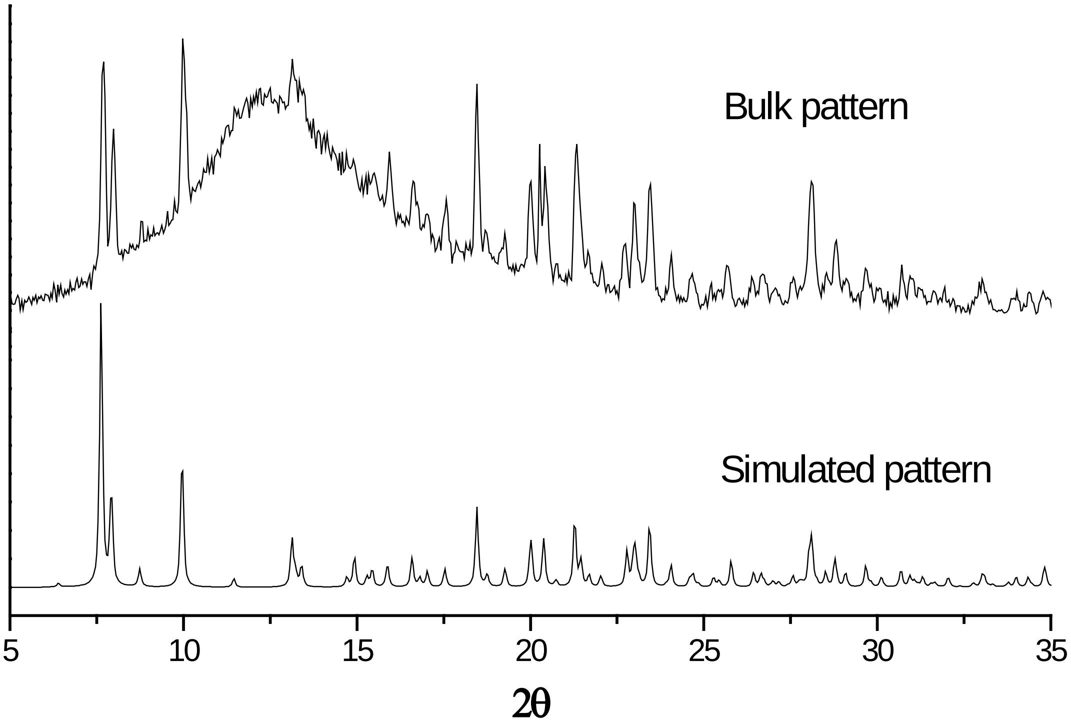


Fig. S16. Comparison of the X-ray powder diffraction of **5** with the simulated patter from the single crystal X-ray structure of **5**.

References.

1 A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.