## **Supporting Information**

#### Novel self-assembled 2D networks based on zinc metal ion co-ordination: Synthesis and

#### comparative study with 3D networks

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Fig S1. <sup>1</sup>H NMR spectrum of 5 (400 MHz, CDCl<sub>3</sub>).







Fig S3. <sup>1</sup>H NMR spectrum of compound 1 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>).



Fig S4. <sup>13</sup>C NMR spectrum of compound 1 (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>).

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Fig. S5. High Resolution Mass spectra 1.



Fig. S6 Cyclic voltammogram of 1 on a platinum electrode (wire) in 0.1 M  $Bu_4NPF_6$ , DCM solution with a sweep rate of 100 mV/s.



Fig. S7. TGA scans of 2D metal-ion co-ordinated self-assembled supramolecular networks N1–3.



Fig. S8. DSC scans of 2D metal-ion co-ordinated self-assembled supramolecular networks N1-3.



Dark yellow fluorescent yellow insoluble solid

8 PF<sub>6</sub><sup>-</sup>



Light yellow fluorescent yellow insoluble solid



**Fig. S9.** Molecular structure of tetragonal molecule **10**. b) Formation of 3D Zn(II)-co-ordinated self-assembled supramolecular network **S1**. c) Formation of 3D Zn(II)-co-ordinated self-assembled supramolecular networks **S3** and **S4**.



Fig. S10 Time -resolved fluorescence decay profile of 3D self-assembled networks S1, S3 and S4 in solid state.

**Table S1:** Lifetimes and pre-exponential factors from the fitting. An average lifetime,  $\tau_a$ , was also calculated using  $\tau_a = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$  for comparison.

Compound	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_1$ (ns)	$\tau_{average} (ns)$
S1	0.45	$0.47 \pm 0.01$	0.55	$3.85 \pm 0.02$	3.54±0.06
S3	0.62	$0.26 \pm 0.01$	0.38	$2.18{\pm}0.02$	1.87±0.06
S4	0.40	0.31±0.01	0.27	$1.55 \pm 0.02$	1.27±0.06



**Fig. S11.** (a) Fragment A (generated from 1) (b) Fragment B (the common tpy end groups coordinated with the  $Zn^{2+}$  and the associated  $PF_6^-$  counter ions), and (c) Fragment C (generated from 3). Grey – carbon, red – oxygen, blue – nitrogen, purple – Zn, pink – P, pale blue – F, and white – hydrogen. For Fragment A and C the full library of structures are shown in (d) and (e) respectively. Each conformer is coloured differently and the bonding atoms are represented as spheres.



Fig. S12 Idealised cluster networks of (a) N1 and (b) N3 generated through an automated network-building process.



Fig S13 Cluster networks of (a) N1 and (b) N3 generated through an automated networkbuilding process.



**Fig S14** TEM images of network N1 on carbon coated copper grids. TEM images with 50 nm and 20 nm scalebars were obtained for low and high resolution respectively.