Supporting Information

Novel self-assembled 2D networks based on zinc metal ion co-ordination: Synthesis and comparative study with 3D networks

Deepa Rajwar,a Xinfeng Liu,b Zheng Bang Lim,a Sung Ju Cho,a Shi Chen,b Yeng Ming Lam,a Abbie Trewin,c Jens M.H. Thomas,d Tze Chien Sum,b* Andrew C. Grimsdalea*

aSchool of Materials Science and Engineering, Nanyang Technological University, Singapore. Fax: +65-6790 9081; Tel: +65-6790 6728; bDivision of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore. 637371 (Singapore) Fax: +65-6316 2971; Tel: +65-6795 7981; cDepartment of Chemistry, Lancaster University, Bailrigg, Lancaster, LA1 4YB, UK.; dInstitute of Integrative Biology, University of Liverpool, Liverpool, L69 7ZB, UK. E-mail: jens.thomas@liverpool.ac.uk

Corresponding authors. E-mail address: tzechien@ntu.edu.sg (Sum Tze Chien) and ACGrimsdale@ntu.edu.sg (A. C. Grimsdale)

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Fig S1. $^1$H NMR spectrum of 5 (400 MHz, CDCl$_3$).

Fig S2. $^1$H NMR spectrum of 9 (400 MHz, CDCl$_3$).
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Fig. S8. DSC scans of 2D metal-ion co-ordinated self-assembled supramolecular networks N1-3.
Zn(OAc)$_2$, NMP excess NH$_4$PF$_6$  
92 %  

Dark blue fluorescent colourless soluble solid  

Dark 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 \( \tau_a = \left( A_1 \tau_1^2 + A_2 \tau_2^2 \right) / \left( A_1 \tau_1 + A_2 \tau_2 \right) \) for comparison.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( A_1 )</th>
<th>( \tau_1 ) (ns)</th>
<th>( A_2 )</th>
<th>( \tau_2 ) (ns)</th>
<th>( \tau_{ave} ) (ns)</th>
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<tbody>
<tr>
<td>S1</td>
<td>0.45</td>
<td>0.47±0.01</td>
<td>0.55</td>
<td>3.85±0.02</td>
<td>3.54±0.06</td>
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<tr>
<td>S3</td>
<td>0.62</td>
<td>0.26±0.01</td>
<td>0.38</td>
<td>2.18±0.02</td>
<td>1.87±0.06</td>
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<tr>
<td>S4</td>
<td>0.40</td>
<td>0.31±0.01</td>
<td>0.27</td>
<td>1.55±0.02</td>
<td>1.27±0.06</td>
</tr>
</tbody>
</table>
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 network-building 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.