

# Structural and magnetic properties of novel dinuclear Cu(II) complexes featuring triazolyl-naphthalimide ligands

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## Abstract

Naphthalimide based ligands have received significant attention for their ability to act as secondary building units (SBUs) for metal-containing network structures. The potentially bridging 1,2,4-triazole containing *N*-(1,2,4-triazolyl)-1,8-naphthalimide (**L**<sub>1</sub>) and *N*-(1,2,4-triazolyl)-4-dimethylamino-1,8-naphthalimide (**L**<sub>2</sub>) were prepared, characterized and complexed with Cu(II) salts. **L**<sub>1</sub> resulted in crystallographically characterized dinuclear complexes, [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>] and [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>(OAc)<sub>4</sub>] when reacted with Cu(NO<sub>3</sub>)<sub>2</sub> and Cu<sub>2</sub>(OAc)<sub>4</sub> respectively. Packing interactions are dominated by  $\pi \cdots \pi$  and anion  $\cdots \pi$  interactions and gave rise to structure extension through weak supramolecular interactions. Solid state EPR and magnetism measurements on [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>] revealed the expected values for a non-magnetically coupled square based pyramidal dimer structure, while [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>(OAc)<sub>4</sub>] showed strong anti-ferromagnetic coupling ( $J_{\text{Cu-Cu}} = -185.6 \text{ cm}^{-1}$ ).

**Key Words:** Naphthalimide, Cu(II), Magnetism, Triazole, Supramolecular

## 1. Introduction

*N*-Substituted-1,8,-naphthalimide derivatives have been utilised in a range of applications from fluorescent dyes through to their more recent use in magnetically interesting, metal-containing extended network structures.[1-4] In this, their  $\pi$ -deficient character has been exploited giving rise to systems where the extension of structure arises through  $\pi$ -based ( $\pi \cdots \pi$  stacking, anion  $\cdots \pi$  interactions and C=O  $\cdots \pi$  interactions) contacts and results in frameworks constructed from less traditional weak non-covalent supramolecular interactions rather than the more typical charge assisted coordination bonds observed in coordination polymers and metal-organic frameworks (MOFs). Reger and co-workers have been instrumental in this field and have developed many 1,8-naphthalimide transition metal conjugates with a range of coordinating groups [4-21] whose structures were extended in the solid state by means of the naphthalimide groups acting as secondary building units through  $\pi$ -based interactions. Such self-assembled systems have applications in areas including molecular electronics, porous materials for sensing and gas storage, supramolecular spintronics and crystal engineering development.[22, 23] Given our interests in the development of magnetically interesting transition metal systems [24-31] and our interests in the development of naphthalimide containing systems [32-34] we have combined 1,2,4-triazole coordination chemistry with 1,8-naphthalimide chemistry to generate two new ligands (**L**<sub>1</sub> and **L**<sub>2</sub>, scheme 1) that show excellent structure extension through  $\pi$ -based interactions as well as interesting coordination chemistry. These naphthalimide-triazolyl systems are also ideal for the generation of multi-functional architectures as the ligand strands also

show excellent fluorescent properties (*i.e.*  $L_2$  is highly emissive) therefore emissive framework materials, ideal for sensors, can potentially be generated.

Herein we describe the synthesis, characterisation, coordination chemistry and structural analysis of two novel naphthalimide based ligands  $L_1$  and  $L_2$ . In line with our previous studies [35] our primary aim was to probe the ability of  $L_1$  and  $L_2$  to develop higher order supramolecular architectures in combination with metal salts and here we have employed Cu(II) for this purpose.. In doing so we have shown that these simple ligands generate systems where structure extension occurs through  $\pi \cdots \pi$  and anion  $\cdots \pi$  interactions.

## 2. Experimental

### 2.1 Materials and Instrumentation

All chemicals were purchased from commercial sources and used as received. Solvents were HPLC grade and were used without further purification. 4-(Dimethylamino)-1,8-naphthalic anhydride was prepared from the reaction of 4-bromo-1,8-naphthalic anhydride with dimethylamine using published procedures.[33] Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer with Smart ITR accessory between 400-4000  $\text{cm}^{-1}$ . NMR spectra were recorded on a Bruker DPX400 NMR spectrometer at 300 K. Chemical shifts are reported in parts per million and referenced to the residual solvent peak ( $(\text{CD}_3)_2\text{SO}$ :  $^1\text{H}$   $\delta$  2.50 ppm,  $^{13}\text{C}$   $\delta$  39.52 ppm). Standard conventions indicating multiplicity were used: m = multiplet, t = triplet, d = doublet, s = singlet. Mass spectrometry samples were analysed using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser. Samples were introduced to the mass spectrometer via a Dionex Ultimate 3000 autosampler and uHPLC pump [Gradient 20% acetonitrile (0.2% formic acid) to 100% acetonitrile (0.2% formic acid) in five minutes at 0.6 mL min. Column: Acquity UPLC BEH C18 (Waters) 1.7 micron 50 x 2.1mm]. High-resolution mass spectra were recorded using positive/negative ion electrospray ionisation. UV-Vis absorption spectra were recorded on an Agilent Technologies Cary100 Spectrometer between 200 and 800 nm. Fluorescence measurements were carried out using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer. Variable temperature magnetic susceptibility for poly-crystalline powder samples were recorded on a Quantum Design MPMS® XL-7 SQUID magnetometer at 0.1 T. Magnetic susceptibility was recorded in the range of 300-4 K cooling at 3 K/min. The diamagnetism of the sample and sample holder were accounted for using Pascal constants and by measurement, respectively. The EPR spectra were collected at 77 K using a Magnetech ms200 X-band EPR working at 9.381 GHz with magnetic field centred at 300 mT and a field sweep of 400 mT. A modulation amplitude of 0.5 mT was used in conjunction with a microwave power of 0.1 mW and a gain of 10. Single-crystal X-ray diffraction data was either collected at 100 K on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn 724+ detector mounted at the window of an FR-E+ Superbright Mo- $K_\alpha$  rotating anode generator ( $\lambda = 0.71075 \text{ \AA}$ ) with HF or VHF varimax optics, or a Rigaku 007 HF diffractometer equipped with an enhanced sensitivity Saturn 944+ detector with a Cu- $K_\alpha$  rotating anode generator ( $\lambda = 1.5418 \text{ \AA}$ ) with HF varimax optics.[36] Unit cell parameters were refined against all data and an **empirical** absorption correction applied in either CrystalClear [37] or CrysAlisPro.[38] All structures were solved by direct methods using SHELXS-2013[39] and refined on  $F_o^2$  by SHELXL-2013[39] Using Olex2.[40] All H-atoms were positioned geometrically and refined using a riding model with  $d(\text{CH}) = 0.95 \text{ \AA}$ ,  $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$  for aromatic protons. The crystallographic data are summarised below. CCDC entries 1451355-1451358 contain the crystallographic data for the structures reported in this article.

## 2.2 Synthesis of $L_1$

1,8-Naphthalic anhydride (1.570 g, 8.0 mmol) and 4-amino-4*H*-1,2,4-triazole (0.706 g, 8.0 mmol) were added to DMF (16 mL) to give a suspension. The off-white reaction mixture was stirred at 160°C under nitrogen for 8h. The resulting reaction mixture was then cooled and distilled water (20 mL) was added giving a voluminous white precipitate. The resulting solid was isolated by filtration and washed by distilled water (2 x 50 mL). The solid was recrystallized from hot methanol and dried to give an off-white solid, 0.9 g (43%). Mass Spec. (HR, ESI<sup>+</sup>) *m/z*: 265.0715 ([ $L_1$ +H]<sup>+</sup>, C<sub>14</sub>H<sub>9</sub>N<sub>4</sub>O<sub>2</sub> requires 265.0720), 287.0532 ([ $L_1$ +Na]<sup>+</sup>, C<sub>14</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>Na requires 287.0539). IR(neat):  $\nu$  (cm<sup>-1</sup>): 3134.3, 3059.7, 1719.9 (C=O), 1674.4 (C=O), 1580.1, 1574.8, 1440.2 (C=N), 1390.1 (C=N), 1061.6 (C-N), 1116.3 (C-N), 1175.8 (C-N), 1026.6. UV/vis  $\lambda_{\max}$  (MeCN) 340 nm;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 334 nm <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  ppm: 7.98 (dd, 2H, Naphth-H), 8.62 (d, 4H, 2xNaphth-H), 8.82 (s, 2H, Triazole-H). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 101 MHz)  $\delta$  ppm: 122.0, 127.9, 128.0, 132.0, 132.3, 136.3, 143.7, 161.7.

X-ray quality colourless plate like single crystals (0.12 x 0.07 x 0.04 mm) of  $L_1$  were grown by slow evaporation of DMF. **Crystal Data:** C<sub>14</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub> (*M*=264.25 g/mol): monoclinic, space group *P2<sub>1</sub>/c* (no. 14), *a* = 11.406(2) Å, *b* = 15.520(3) Å, *c* = 6.8292(14) Å,  $\beta$  = 103.97(3)°, *V* = 1173.2(4) Å<sup>3</sup>, *Z* = 4, *T* = 100 K,  $\mu$ (Mo K $\alpha$ ) = 0.105 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.4960 g/cm<sup>3</sup>, 8158 reflections measured (5.24° ≤ 2 $\theta$  ≤ 50°), 2056 unique (*R*<sub>int</sub> = 0.1530, *R*<sub>sigma</sub> = 0.2543) which were used in all calculations. The final *R*<sub>1</sub> was 0.0584 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1331 (all data).

## 2.3 Synthesis of $L_2$

4-Dimethylamino-1,8-naphthalic anhydride (1.442 g, 6.0 mmol) and 4-amino-4*H*-1,2,4-triazole (0.520 g, 6.0 mmol) were added to DMF (16 mL) to give a suspension. The orange-brown reaction mixture was stirred at 160°C under nitrogen for 8h. The resulting reaction mixture was then cooled and distilled water (20 mL) was added. The solid was isolated by filtration and purified by column chromatography using silica and an acetone-hexane (1:4) solvent mixture to elute the anhydride starting material and then pure acetone to elute  $L_1$ . Removal of solvent *in vacuo* gave pure  $L_1$  as an orange solid, 0.500 g (30%). Mass Spec. (HR, ESI<sup>+</sup>) *m/z*: 308.1148 ([ $L_2$ +H]<sup>+</sup>, C<sub>16</sub>H<sub>14</sub>N<sub>5</sub>O<sub>2</sub> requires 308.1142). IR:  $\nu$  (cm<sup>-1</sup>): 3122.9, 2979.2, 2803.2, 1702.9 (C=O), 1657.3 (C=O), 1582.8, 1498.7, 1451.2, 1390.9, 1340.6 (C=N), 1316.7 (C=N), 1242.0 (C-N), 1213.7, 1176.7, 1138.3, 1129.3, 1070.3, 1063.4, 1019.5. UV/vis  $\lambda_{\max}$  (MeCN) 447 nm;  $\lambda_{\max}$  (CHCl<sub>3</sub>) 443 nm <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  ppm: 3.19 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 7.27 (br d, 1H, Naphth-H), 7.82 (br dd, 1H, Naphth-H), 8.41 (br d, 1H, Naphth-H), 8.55 (br d, 1H, Naphth-H), 8.65 (br d, 1H, Naphth-H), 8.80 (s, 2H, triazole-H). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 101 MHz)  $\delta$  ppm: 44.9, 111.8, 113.2, 122.1, 124.4, 125.4, 130.6, 132.2, 133.7, 133.9, 158.1, 161.0, 161.9.

Orange plate like crystals (0.4 x 0.3 x 0.1 mm) of  $L_2$  were grown by vapour diffusion of diethylether into a DMF solution of  $L_2$ . The crystal contained non-merohedral twinning [twinned data refinement scales: 0.6741(12) 0.3259(12) where component 2 rotated by 179.9712° around [1.00 -0.00 -0.00] (reciprocal) or [0.98 -0.00 0.18] (direct)]. **Crystal Data:** C<sub>16</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub> (*M*=307.31 g/mol): monoclinic, space group *P2<sub>1</sub>/c* (no. 14), *a* = 12.0954(4) Å, *b* = 15.9987(4) Å, *c* = 7.0636(2) Å,  $\beta$  = 96.094(3)°, *V* = 1359.16(7) Å<sup>3</sup>, *Z* = 4, *T* = 100 K,  $\mu$ (CuK $\alpha$ ) = 0.859 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.502 g/cm<sup>3</sup>, 4481 reflections measured (13.292° ≤ 2 $\theta$  ≤ 133.984°), 4481 unique (*R*<sub>int</sub> = 0.0397, *R*<sub>sigma</sub> = 0.0203) which were used in all calculations. The final *R*<sub>1</sub> was 0.0380 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.1099 (all data).

## 2.4 Synthesis of [Cu<sub>2</sub>( $L_1$ )<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>]

Copper(II) nitrate trihydrate (0.024 g, 0.1 mmol) and  $L_1$  (0.053 g, 0.2 mmol) were dissolved in CH<sub>3</sub>CN-MeOH (1:1 - 10 mL) and heated at 60°C with stirring for 6 h. The resulting blue solution was divided into 4 equal portions and subjected to vapour diffusion of diethyl ether at room temperature.

After 3 days blue crystals were obtained (0.021 g, 27%). IR:  $\nu$  (cm<sup>-1</sup>): 1704, 1590, 1536, 1470, 1397, 1308, 1291, 1230, 1173, 1140, 1118, 1077, 1016, 891, 846, 771, 726, 627, 533. **Crystal Data** for [Cu<sub>2</sub>(L<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>]: C<sub>56</sub>H<sub>32</sub>Cu<sub>2</sub>N<sub>20</sub>O<sub>20</sub> (*M*=1432.09 g/mol): triclinic, space group *P* $\bar{1}$  (no. 2), *a* = 8.3676(12) Å, *b* = 13.0331(18) Å, *c* = 13.773(2) Å,  $\alpha$  = 72.508(8)°,  $\beta$  = 80.202(11)°,  $\gamma$  = 79.362(10)°, *V* = 1397.4(4) Å<sup>3</sup>, *Z* = 1, *T* = 100(2) K,  $\mu$ (MoK $\alpha$ ) = 0.863 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.702 g/cm<sup>3</sup>, 15625 reflections measured (5.146° ≤ 2 $\theta$  ≤ 49.998°), 4904 unique (*R*<sub>int</sub> = 0.0261, *R*<sub>sigma</sub> = 0.0296) which were used in all calculations. The final *R*<sub>1</sub> was 0.0307 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.0796 (all data).

### 2.5 Synthesis of [Cu<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>(OAc)<sub>4</sub>]

Copper(II) acetate monohydrate (0.041 g, 0.2 mmol) and L<sub>1</sub> (0.054 g, 0.2 mmol) were dissolved in CH<sub>3</sub>CN-MeOH (1:1 - 10 mL) and heated at 60°C with stirring for 8 h. The resulting blue solution was divided into 4 equal portions and subjected to vapour diffusion of diethyl ether resulting in the formation of blue-green crystals (0.012 g, 14%). IR:  $\nu$  (cm<sup>-1</sup>): 3472, 3369, 3266, 1707, 1600, 1435, 1420, 1354, 1326, 1233, 1222, 1172, 1138, 1114, 1051, 1032, 892, 850, 802, 776, 686, 626, 533. **Crystal Data**: C<sub>36</sub>H<sub>28</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>12</sub> (*M*=891.74 g/mol): monoclinic, space group *C*2/*c* (no. 15), *a* = 29.020(6) Å, *b* = 8.1450(16) Å, *c* = 18.711(4) Å,  $\beta$  = 108.42(3)°, *V* = 4196.1(16) Å<sup>3</sup>, *Z* = 4, *T* = 100 K,  $\mu$ (MoK $\alpha$ ) = 1.081 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.412 g/cm<sup>3</sup>, 11880 reflections measured (5.506° ≤ 2 $\theta$  ≤ 49.996°), 3673 unique (*R*<sub>int</sub> = 0.0252, *R*<sub>sigma</sub> = 0.0401) which were used in all calculations. The final *R*<sub>1</sub> was 0.0379 (*I* > 2 $\sigma$ (*I*)) and *wR*<sub>2</sub> was 0.0991 (all data).

## 3. Results and discussion

### 3.1 Ligand Synthesis

The ligands, 1,8-naphthalimide-1,2,4-triazole (L<sub>1</sub>) and 4-(dimethylamino)-1,8-naphthalimide-1,2,4-triazole (L<sub>2</sub>) were synthesised as shown in Scheme 1. The reaction of one equivalent of 1,8-naphthalic anhydride or 4-dimethylamino-1,8-naphthalic anhydride with one equivalent of 4-amino-4*H*-1,2,4-triazole in DMF at 160°C under N<sub>2</sub> gave L<sub>1</sub> as a pure off white solid (43%) and L<sub>2</sub> as a crude brown solid on addition of distilled water to the reaction mixtures. L<sub>2</sub> required chromatographic purification to give the pure product as an orange powder (30%). Both ligands were fully characterised using NMR spectroscopy, IR spectroscopy, UV/vis spectroscopy and mass spectrometry.

<sup>1</sup>H-NMR spectra showed the expected aromatic naphthalimide protons for L<sub>1</sub> and L<sub>2</sub> (these were significantly shifted from the corresponding peaks of the starting naphthalic anhydrides) and the characteristic triazole protons at around 8.8 ppm. Mass spectrometry confirmed the successful formation of L<sub>1</sub> and L<sub>2</sub> with peaks at 265.0715, *m/z* and 308.1148 *m/z* corresponding to the [M+H]<sup>+</sup> ions for L<sub>1</sub> and L<sub>2</sub> respectively. Additionally a peak was observed for the [M+Na]<sup>+</sup> species of L<sub>1</sub> (287.0532 *m/z*) species.

Colourless crystals of L<sub>1</sub> were grown from slow evaporation of a DMF solution and the low temperature (100 K) X-ray structure determined. L<sub>1</sub> crystallised in the monoclinic space group *P*2<sub>1</sub>/*c* and contained one molecule in the asymmetric unit (Figure 1A). The triazole ring is orthogonal to the naphthalimide ring, a feature commonly observed in such ligand species, with an angle of 79° between the mean planes of the two rings. Packing interactions are dominated by  $\pi$ ··· $\pi$  stacking interactions between neighbouring naphthalimide rings (Figure 1B) as well as weaker non-classical CH hydrogen bonding from the triazole CH groups (Figure 2A). Neighbouring molecules of L<sub>1</sub> are arranged into alternating stacks through strong  $\pi$ ··· $\pi$  stacking interactions [centroid···centroid = 3.632 Å and centroid···central naphtha-C = 3.414 Å]. These alternating stacks are then linked to neighbouring stacks through weaker CH···O and CH···N hydrogen bonding.

Small orange crystals of L<sub>2</sub> were grown from slow evaporation of a DMF solution and the low temperature (100 K) X-ray structure determined. The crystal contained non-merohedral twinning

where one component was rotated by *ca.* 180°. **L**<sub>2</sub> crystallised in the monoclinic space group *P*2<sub>1</sub>/*c* with one molecule in the asymmetric unit (Figure 3A). The triazole ring in **L**<sub>2</sub> is perpendicular to the naphthalimide ring plane, (81°) and the packing interactions are again dominated by  $\pi\cdots\pi$  stacking interactions between neighbouring naphthalimide rings [centroid $\cdots$ centroid = 3.601 Å, Figure 3B] as well as weaker non-classical CH hydrogen bonding from the triazole CH groups (Figure 4A).

The solid state packing interactions present in both **L**<sub>1</sub> and **L**<sub>2</sub> involve  $\pi\cdots\pi$  stacking between neighbouring naphthalimide units, and with these being the dominant interaction we expect this same interaction to be present in subsequent coordination complexes. Therefore, these ligand species should be ideal for the preparation of new metal-based supramolecular architectures where the structure-directing properties of the ligands might influence the physical properties (*e.g.* magnetism or photophysical properties) of the metal centres.

The absorption and the emission properties of **L**<sub>1</sub> and **L**<sub>2</sub> were briefly investigated and were typical for 1,8-naphthalimide based compounds.[1] Both **L**<sub>1</sub> and **L**<sub>2</sub> displayed high-energy absorptions in the 200-250 nm range, typical for such organic species. **L**<sub>1</sub> displayed a broad absorption band with  $\lambda_{\text{max}}$  at 340 nm whilst for **L**<sub>2</sub> this broad absorption had  $\lambda_{\text{max}}$  at 440 nm (attributed to an ICT band) when recorded in CHCl<sub>3</sub> and MeCN. Upon excitation at  $\lambda_{\text{max}}$ , both **L**<sub>1</sub> and **L**<sub>2</sub> show broad fluorescence emission (Figure 5). **L**<sub>1</sub> displayed emission with  $\lambda_{\text{max}}$  at 380 nm when excited at 340 nm in both CHCl<sub>3</sub> and MeCN whereas **L**<sub>2</sub> displayed broad emission at 511 and 532 nm when excited at 440 nm in CHCl<sub>3</sub> and MeCN respectively.

### 3.2 Coordination chemistry of **L**<sub>1</sub> and **L**<sub>2</sub>

**L**<sub>1</sub> and **L**<sub>2</sub> were reacted with Cu(II) salts [Cu(NO<sub>3</sub>)<sub>2</sub>, Cu(OAc)<sub>2</sub>, CuSO<sub>4</sub>] in a range of solvents and with a range of M:L ratios in order to assess their coordination ability and determine the effect that the naphthalimide group has on the packing in the solid state structures. Despite many attempts the only sets of reaction conditions that gave bulk samples of single crystals were Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O with **L**<sub>1</sub> in a 1:2 ratio in MeCN/MeOH (1:1) and Cu(OAc)<sub>2</sub> with **L**<sub>1</sub> in a 1:1 ratio in MeCN/MeOH (1:1). The reaction of two equivalents of **L**<sub>1</sub> and one equivalent of Cu(NO<sub>3</sub>)<sub>2</sub> at 60°C in MeCN/MeOH (1:1) for 1 hour gave a clear blue solution that on cooling to room temperature was subjected to vapour diffusion of diethyl ether. After 3 days a number of blue crystals of [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>] were obtained (27%). Reaction of Cu(OAc)<sub>2</sub> with **L**<sub>1</sub> gave a very small number of blue single crystals suitable for diffraction studies. The resulting molecular structure was found to be a paddlewheel Cu(II) dimer of [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>(OAc)<sub>4</sub>]. To date, reactions involving either CuSO<sub>4</sub> or **L**<sub>2</sub> have not resulted in any crystalline samples.

### 3.3 Crystallographic analysis of [Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>]

[Cu<sub>2</sub>(**L**<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>] crystallised in the triclinic space group *P***T** and contained half of a molecule in the asymmetric unit with the other half generated by a centre of inversion (Figure 6).

The result is a dimeric complex where each copper(II) is coordinated to two nitrogen atoms from different triazole groups, two nitrate oxygen atoms and one naphthalimide carbonyl oxygen atom from a symmetry generated naphthalimide to give an overall N<sub>2</sub>O<sub>4</sub> coordination sphere (Figure 6). Analysis of the coordination geometry around Cu(II) reveals the degree of trigonality ( $\tau$ ) to be 0.06, which is consistent with a slightly distorted square-pyramidal coordination environment. Bond lengths and angles are consistent with other axially elongated square-based pyramidal structures where the equatorial (square base) bond lengths average 1.985(2) Å whilst the axial bond to the carbonyl oxygen atom is 2.307(2) Å. The coordination of the carbonyl oxygen atoms in naphthalimides to transition metals is not a commonly observed occurrence and only three structures are reported in the CSD[19, 41, 42]. The naphthalimide ligand that bridges the two copper(II) centres

gives rise to a 14 membered ring involving the two copper(II) centres and shows strong  $\pi \cdots \pi$  stacking between the neighbouring triazole rings [centroid $\cdots$ centroid = 3.517 Å].

Packing interactions in  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  are dominated by strong anion $\cdots\pi$  and face-to-face  $\pi \cdots \pi$  stacking interactions. Anion $\cdots\pi$  interactions exist between two neighbouring dimers where the distal oxygen atoms of the coordinated nitrate anions are involved in anion $\cdots\pi$  interactions to the imide rings of neighbouring dimers (Figure 7) with O $\cdots$ centroid distances of 2.881 Å and 2.852 Å for the two different interactions. The interactions are self-complementary so there are 4 interactions in total between two dimers and this extends them into chains of dimers in the direction of the crystallographic a-axis (Figure 8). These anion $\cdots\pi$  linked chains are linked to neighbouring chains via offset face-to-face  $\pi \cdots \pi$  stacking between naphthalene rings where all four naphthalimide ligands are involved in stacking interactions to link the chains [centroid $\cdots$ centroid distances = 3.718 Å].

### 3.4 Crystallographic analysis of $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$

$[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  crystallised in the monoclinic space group  $C2/c$  and contained half of one molecule in the asymmetric unit with the other half generated by a centre of inversion (Figure 9).

The resulting paddlewheel dimer consists of two Cu(II) centres bridged by four acetate molecules and capped with two  $\text{L}_1$  molecules to give  $\text{O}_4\text{N}$  coordination environments around each copper atom. The Cu(II) ions are 2.651(2) Å apart, similar to other copper paddlewheel complexes.[35] The copper ions adopt a near perfect square-based pyramidal geometry with the degree of trigonality ( $\tau$ ) being 0.[43] Bond lengths and angles are also consistent with other axially elongated square-based pyramidal structures where the equatorial acetate oxygen Cu-O bond lengths average 1.968(2) Å whilst the axial triazole nitrogen atom Cu-N bond length is 2.180(2) Å (Table 2).

Packing interactions in  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  also involve the naphthalimide  $\pi$ -system, as well as CH hydrogen bonding involving the somewhat acidic triazole CH moiety (a commonly observed packing interaction in such structures).[44] Paddlewheel dimer units are packed into *pseudo* 1D chains through face-to-face  $\pi \cdots \pi$  stacking between neighbouring naphthalimide moieties [centroid $\cdots$ centroid = 3.806 Å] (Figure 10). These chains are then linked to neighbouring chains through weak CH hydrogen bonding between triazole CH and naphthalimide C=O groups [C $\cdots$ O = 3.458 Å and  $\angle(\text{CH}\cdots\text{O}) = 147^\circ$ ] (Figure 11).

### 3.5 Magnetism and EPR studies

Variable temperature magnetic susceptibility measurements were obtained for poly-crystalline powder samples of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  and  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  and are shown in Figures 12 and 13 respectively. The  $\chi_{\text{M}}T$  value of just below 0.8  $\text{cm}^3\text{mol}^{-1}\text{K}$  for  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  across the entire temperature range is representative of a Cu(II) dimer with negligible magnetic interaction between the Cu(II) centres. In the plot for  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  the  $\chi_{\text{M}}T$  value decreases on cooling from 0.8  $\text{cm}^3\text{mol}^{-1}\text{K}$  to 0  $\text{cm}^3\text{mol}^{-1}\text{K}$  indicative of antiferromagnetic coupling.

The solid state X-band EPR spectrum of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$ , measured at 77 K, also showed negligible interaction between the Cu(II) ions (Figure 14). The g factor derived from the data is 2.07 and is in line with square-pyramidal geometry. There are no obvious hyperfine interactions from the triazole  $^{14}\text{N}$  nuclei. There was no EPR signal at 77 K at X-band for  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$ , presumably due to the large antiferromagnetic coupling between the Cu(II) ions coupled with the sensitivity of the X-band EPR used.

Both the magnetic and EPR data for  $[\text{Cu}_2(\mathbf{L}_1)_4(\text{NO}_3)_4]$  and the magnetic data for  $[\text{Cu}_2(\mathbf{L}_1)_2(\text{OAc})_4]$  were fitted using the program PHI[45] utilising the Hamiltonian:

$$\hat{H} = -2 \sum_{\substack{ij \in N \\ i < j}} \vec{\hat{S}}_i \cdot \vec{J}_{ij} \cdot \vec{\hat{S}}_j - g\mu_B \sum_i \vec{B} \cdot \vec{\hat{S}}_i$$

The resulting fit gave a  $g_{\text{iso}}$  of 2.067 and a  $J_{\text{Cu-Cu}} = -0.05 \text{ cm}^{-1}$ , this correlates well with the very weakly interacting Cu(II) ion model. This is not unexpected as the Cu(II) centres were shown to be  $\sim 6.5 \text{ \AA}$  apart (see above).

Conversely, for  $[\text{Cu}_2(\mathbf{L}_1)_2(\text{OAc})_4]$  the fit gave  $g_{\text{iso}}$  of 2.07 and  $J_{\text{Cu-Cu}} = -185.6 \text{ cm}^{-1}$  consistent with a strongly anti-ferromagnetic interaction between the Cu(II) centres.  $[\text{Cu}_2(\mathbf{L}_1)_2(\text{OAc})_4]$  was EPR silent, further emphasising the strong anti-ferromagnetic coupling between the metal centres.

## 4. Conclusion

The synthesis of two new 1,8-naphthalimide-1,2,4-triazolyl based ligands,  $\mathbf{L}_1$  and  $\mathbf{L}_2$  was achieved and the solid state packing revealed significant  $\pi$ -based interactions. Coordination chemistry was attempted using Cu(II) salts in the hope that the  $\pi$ -based interactions would be the dominant intermolecular interaction and allow for functional metal-organic networks to be constructed using supramolecular self-assembly.  $\text{Cu}(\text{NO}_3)_2$  when reacted with  $\mathbf{L}_1$  gave single crystals of a dimeric complex  $[\text{Cu}_2(\mathbf{L}_1)_4(\text{NO}_3)_4]$  whilst reaction of  $\mathbf{L}_1$  with  $\text{Cu}_2(\text{OAc})_4$  gave the paddlewheel dimer  $[\text{Cu}_2(\mathbf{L}_1)_2(\text{OAc})_4]$ . The expected  $\pi$ -based interactions were also present in the complex and resulted in the extension of the structure into a supramolecular metal-organic network. EPR and magnetism measurements of  $[\text{Cu}_2(\mathbf{L}_1)_4(\text{NO}_3)_4]$  showed very little coupling between the square based pyramidal Cu(II) centres, however the interaction between the Cu(II) centres in  $[\text{Cu}_2(\mathbf{L}_1)_2(\text{OAc})_4]$  was found to be strongly anti-ferromagnetic. The use of naphthalimide based ligands and triazole coordination sites has resulted in metal-organic supramolecular networks where interesting dimer complexes were assembled into extended networks through non-covalent  $\pi \cdots \pi$  and anion  $\cdots \pi$  interactions. These initial results suggest that  $\mathbf{L}_1$  and  $\mathbf{L}_2$  (and subsequent derivatives) could be ideal for developing magnetically interesting self-assembled systems, a rapidly expanding area in molecular electronics research and multi-functional devices. Such research requires modular ligand design so that a range of functional groups to fine-tune the system or allow for immobilisation of assemblies can be readily incorporated and so that predictable intermolecular interactions can be generated, all properties that these triazole-naphthalimide systems possess.

## 5. Supplementary Information

Supporting information is available for this article. CCDC entries 1451355-1451358 contain the crystallographic data for the structures reported in this article. All data supporting this study are openly available from the University of Southampton repository at <http://dx.doi.org/10.5258/SOTON/390630>

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## 7. References

- [1] S. Banerjee, E. B. Veale, C. M. Phelan, S. A. Murphy, G. M. Tocci, L. J. Gillespie, D. O. Frimannsson, J. M. Kelly and T. Gunnlaugsson, *Chem. Soc. Rev.*, **42**, 1601, (2013).
- [2] C. J. McAdam, B. H. Robinson and J. Simpson, *Organometallics*, **19**, 3644, (2000).
- [3] R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, **39**, 3936, (2010).
- [4] D. L. Reger, A. Leitner and M. D. Smith, *Cryst. Growth Des.*, **15**, 5637, (2015).
- [5] D. L. Reger, J. D. Elgin, R. F. Semeniuc, P. J. Pellechia and M. D. Smith, *Chem. Commun.*, 4068, (2005).
- [6] D. L. Reger, A. Debreczeni, M. D. Smith, J. Jezierska and A. Ozarowski, *Inorg. Chem.*, **51**, 1068, (2012).
- [7] D. L. Reger, R. F. Semeniuc, J. D. Elgin, V. Rassolov and M. D. Smith, *Cryst. Growth Des.*, **6**, 2758, (2006).
- [8] D. L. Reger, E. Sirianni, J. J. Horger, M. D. Smith and R. F. Semeniuc, *Cryst. Growth Des.*, **10**, 386, (2010).
- [9] D. L. Reger, A. Debreczeni, B. Reinecke, V. Rassolov and M. D. Smith, *Inorg. Chem.*, **48**, 8911, (2009).
- [10] D. L. Reger, B. Reinecke, M. D. Smith and R. F. Semeniuc, *Inorg. Chim. Acta*, **362**, 4377, (2009).
- [11] D. L. Reger, J. D. Elgin, P. J. Pellechia, M. D. Smith and B. K. Simpson, *Polyhedron*, **28**, 1469, (2009).
- [12] D. L. Reger, A. Debreczeni and M. D. Smith, *Inorg. Chim. Acta*, **364**, 10, (2010).
- [13] D. L. Reger, J. J. Horger and M. D. Smith, *Chem. Commun.*, **47**, 2805, (2011).
- [14] D. L. Reger, J. Horger, M. D. Smith and G. J. Long, *Chem. Commun.*, 6219, (2009).
- [15] D. L. Reger, J. J. Horger, M. D. Smith, G. J. Long and F. Grandjean, *Inorg. Chem.*, **50**, 686, (2011).
- [16] D. L. Reger, A. Debreczeni, J. J. Horger and M. D. Smith, *Cryst. Growth Des.*, **11**, 4068, (2011).
- [17] D. L. Reger, A. Debreczeni and M. D. Smith, *Eur. J. Inorg. Chem.*, **2012**, 712, (2012).
- [18] D. L. Reger, A. Debreczeni and M. D. Smith, *Inorg. Chim. Acta*, **378**, 42, (2011).
- [19] D. L. Reger, J. J. Horger, A. Debreczeni and M. D. Smith, *Inorg. Chem.*, **50**, 10225, (2011).
- [20] D. L. Reger, A. Debreczeni and M. D. Smith, *Inorg. Chem.*, **50**, 11754, (2011).
- [21] D. L. Reger, A. P. Leitner and M. D. Smith, *Cryst. Growth Des.*, (2015).
- [22] T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, **113**, 734, (2013).
- [23] G. Seeber, G. J. T. Cooper, G. N. Newton, M. H. Rosnes, D.-L. Long, B. M. Kariuki, P. Kogerler and L. Cronin, *Chem. Sci.*, **1**, 62, (2010).
- [24] A. Bhattacharjee, V. Ksenofontov, J. A. Kitchen, N. G. White, S. Brooker and P. Gütllich, *Appl. Phys. Lett.*, **92**, (2008).
- [25] G. N. L. Jameson, F. Werner, M. Bartel, A. Absmeier, M. Reissner, J. A. Kitchen, S. Brooker, A. Caneschi, C. Carbonera, J.-F. Letard and W. Linert, *Eur. J. Inorg. Chem.*, 3948, (2009).
- [26] J. A. Kitchen and S. Brooker, *Dalton Trans.*, **39**, 3358, (2010).
- [27] J. A. Kitchen, G. N. L. Jameson, V. A. Milway, J. L. Tallon and S. Brooker, *Dalton Trans.*, **39**, 7637, (2010).
- [28] J. A. Kitchen, N. G. White, G. N. L. Jameson, J. L. Tallon and S. Brooker, *Inorg. Chem.*, **50**, 4586, (2011).
- [29] J. A. Kitchen, J. Olguin, R. Kulmaczewski, N. G. White, V. A. Milway, G. N. L. Jameson, J. L. Tallon and S. Brooker, *Inorg. Chem.*, **52**, 11185, (2013).
- [30] J. P. Byrne, J. A. Kitchen, O. Kotova, V. Leigh, A. P. Bell, J. J. Boland, M. Albrecht and T. Gunnlaugsson, *Dalton Trans.*, **43**, 196, (2014).



- [31] R. Kulmaczewski, J. Olguin, J. A. Kitchen, H. L. C. Feltham, G. N. L. Jameson, J. L. Tallon and S. Brooker, *J. Am. Chem. Soc.*, **136**, 878, (2014).
- [32] S. Banerjee, J. A. Kitchen, S. A. Bright, J. E. O'Brien, D. C. Williams, J. M. Kelly and T. Gunnlaugsson, *Chem. Commun.*, **49**, 8522, (2013).
- [33] S. Banerjee, J. A. Kitchen, T. Gunnlaugsson and J. M. Kelly, *Org. Biomol. Chem.*, (2013).
- [34] E. B. Veale, J. A. Kitchen and T. Gunnlaugsson, *Supramol. Chem.*, **25**, 101, (2013).
- [35] J. A. Kitchen, P. N. Martinho, G. G. Morgan and T. Gunnlaugsson, *Dalton Trans.*, **43**, 6468, (2014).
- [36] S. J. Coles and P. A. Gale, *Chem. Sci.*, **3**, 683, (2012).
- [37] CrystalClear-SM Expert 3.1, (Rigaku, 2012).
- [38] CrysAlisPro 38.41, (Rigaku Oxford Diffraction, 2015).
- [39] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **A64**, 112, (2008).
- [40] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, **42**, 339, (2009).
- [41] R. Garcia-Bueno, M. D. Santana, G. Sanchez, J. Garcia, G. Garcia, J. Perez and L. Garcia, *Dalton Trans.*, **39**, 5728, (2010).
- [42] B. K. Nicholson, P. M. Crosby, K. R. Maunsell and M. J. Wyllie, *J. Organomet. Chem.*, **716**, 49, (2012).
- [43] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1349, (1984).
- [44] R. M. Hellyer, J. A. Joule, D. S. Larsen and S. Brooker, *Acta Crystallogr. Sect. C*, **C63**, 358, (2007).
- [45] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, **34**, 1164, (2013).

## Tables:

Table 1: Selected bond lengths [Å] and angles [°] for [Cu<sub>2</sub>(L<sub>1</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>]

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Cu(1)-O(201)	1.9724(15)
Cu(1)-O(101)	1.9866(15)
Cu(1)-N(3)	1.9891(16)
Cu(1)-N(24) <sup>a</sup>	1.9906(16)
Cu(1)-O(22)	2.3068(15)
Cu(1)-Cu(1) <sup>a</sup>	6.4799 (11)
O(201)-Cu(1)-O(101)	169.93(6)
O(201)-Cu(1)-N(3)	87.88(7)
O(101)-Cu(1)-N(3)	90.41(6)
O(201)-Cu(1)-N(24) <sup>a</sup>	93.28(6)
O(101)-Cu(1)-N(24) <sup>a</sup>	90.70(6)
N(3)-Cu(1)-N(24) <sup>a</sup>	166.46(7)
O(201)-Cu(1)-O(22)	82.07(6)
O(101)-Cu(1)-O(22)	88.03(6)
N(3)-Cu(1)-O(22)	90.59(6)
N(24) <sup>a</sup> -Cu(1)-O(22)	102.94(6)

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<sup>a</sup> -x+1,-y+2,-z

**Table 2: Selected bond lengths [Å] and angles [°] for [Cu<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>(OAc)<sub>4</sub>]**

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<b>Cu(1)-O(3)</b>	1.9758(18)
<b>Cu(1)-O(4)</b>	1.9648(18)
<b>Cu(1)-O(5)</b>	1.9657(19)
<b>Cu(1)-O(6)</b>	1.9638(19)
<b>Cu(1)-N(4)</b>	2.181(2)
<b>Cu(1)-Cu(1)<sup>b</sup></b>	2.6511(11)
<b>O(3)-Cu(1)-N(4)</b>	90.95(8)
<b>O(4)<sup>b</sup>-Cu(1)-O(3)</b>	168.32(8)
<b>O(4)<sup>b</sup>-Cu(1)-O(5)</b>	90.35(8)
<b>O(4)<sup>b</sup>-Cu(1)-N(4)</b>	100.72(8)
<b>O(5)-Cu(1)-O(3)</b>	89.21(8)
<b>O(5)-Cu(1)-N(4)</b>	93.98(8)
<b>O(6)-Cu(1)-O(3)</b>	88.76(8)
<b>O(6)-Cu(1)-O(4)<sup>b</sup></b>	89.31(8)
<b>O(6)-Cu(1)-O(5)</b>	168.30(8)
<b>O(6)-Cu(1)-N(4)</b>	97.58(8)

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<sup>b</sup><sub>1-X,-Y,1-Z</sub>

## Figure Captions

**Scheme 1:** Synthetic protocol for ligands  $L_1$  and  $L_2$

**Figure 1:** Molecular structure of  $L_1$  with thermal ellipsoids at 50% probability (A). Packing of  $L_1$  showing  $\pi \cdots \pi$  stacking between molecules (B)

**Figure 2:** View of C-H based hydrogen-bonding interactions in  $L_1$  (A). Packing of  $L_1$  showing  $\pi$ -stacked chains in the crystallographic b direction (B)

**Figure 3:** Molecular structure of  $L_2$  with thermal ellipsoids at 50% probability (A). Packing of  $L_2$  showing  $\pi \cdots \pi$  stacking between molecules (B)

**Figure 4:** View of C-H based hydrogen-bonding interactions in  $L_2$  (A). Packing of  $L_2$  showing  $\pi$  stacked chains in the crystallographic b direction (B)

**Figure 5:** Emission spectra of  $L_1$  (left) and  $L_2$  (right) in  $\text{CHCl}_3$  (blue) and MeCN (red).

**Figure 6:** Molecular structure of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  with thermal ellipsoids set at 50%.

**Figure 7:** Packing interactions of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  showing  $\pi \cdots \pi$  stacking and non-classical interaction between molecules.

**Figure 8:** Long range order of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  showing the chains of dimers along the crystallographic a axis.

**Figure 9:** Molecular structure of  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  with thermal ellipsoids set at 50%.

**Figure 10:** Packing of  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  showing  $\pi \cdots \pi$  stacking between molecules.

**Figure 11:** Packing of  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  showing non-classical interaction between molecules.

**Figure 12:** Plot of  $\chi_m T$  versus T for  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  between 4-300 K.

**Figure 13:** Plot of  $\chi_m T$  versus T for  $[\text{Cu}_2(\text{L}_1)_2(\text{OAc})_4]$  between 4-300 K.

**Figure 14:** Solid state X-band EPR spectrum of  $[\text{Cu}_2(\text{L}_1)_4(\text{NO}_3)_4]$  measured at 77 K (black) and the calculated fit (red).