## **Supporting information**

For

# A fluorescence turn-on probe for selective detection of nitrogen dioxide

Biplab Mondal<sup>\*</sup> and Vikash Kumar

Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati, Assam 781039, India

E-mail: <u>biplab@iitg.ac.in</u>

Phone: 91-361-258-2317. Fax: 91-361-258-2339

### **Table of Contents**

| Sl. | Description  | Page |
|-----|--|------|
| No. |  | No.  |
|     |  |      |
| 1   | Experimental Section   | 3    |
| 2   | Figure S1: FT-IR spectrum of ligand $L_1$ in KBr pellet.   | 8    |
| 3   | Figure S2: <sup>1</sup> H-NMR spectrum of ligand L1 in CDCl <sub>3</sub> .                                   | 8    |
| 4   | <b>Figure S3:</b> $^{13}$ C-NMR spectrum of ligand L1 in CDCl <sub>3</sub> .                                 | 9    |
| 5   | Figure S4: ESI mass spectrum of ligand L1 in methanol.   | 9    |
| 6   | Figure S5: UV-Visible spectrum of ligand L1 in methanol.   | 10   |
| 7   | Figure S6: FT-IR spectrum of complex 1 in KBr pellet.  | 10   |
| 8   | Figure S7: UV-Visible spectrum of complex 1in methanol.  | 11   |
| 9   | Figure S8: X-Band EPR spectrum of complex 1 in methanol at room temperature.                                 | 11   |
| 10  | Figure S9: ESI mass spectrum of complex 1 in methanol.   | 12   |
| 11  | Figure S10: UV-visible spectra of complex 1 before (black trace) and after (red trace)                       | 12   |
|     | purging nitric oxide in methanol.  |      |
| 12  | Figure S11: UV-visible spectra of complex 1 before (black trace) and after (blue trace)                      | 13   |
|     | purging nitrogen dioxide in methanol.  |      |
| 13  | Figure S12: X-Band EPR spectra of complex 1 after purging nitrogen dioxide (blue                             | 13   |
|     | line) in methanol at room temperature.   |      |
| 14  | <b>Figure S13</b> : FT-IR spectrum of modified ligand $L1'$ in KBr pellet.                                   | 14   |
| 15  | <b>Figure S14:</b> <sup>1</sup> H-NMR spectrum of modified ligand $L1'$ in CDCl <sub>3</sub> .               | 14   |
| 16  | <b>Figure S15:</b> <sup>13</sup> C-NMR spectrum of modified ligand L1 <sup>/</sup> in CDCl <sub>3</sub> .    | 15   |
| 17  | <b>Figure S16:</b> ESI mass spectrum of modified ligand $L1'$ in methanol.                                   | 15   |
| 18  | <b>Figure S17:</b> Fluorescence responses ( $\lambda_{ex}$ , 350 nm) for 40 $\mu$ M solution of free ligand, | 16   |
|     | L1 (dashed line) and after addition of one equivalent of $[Cu(CH_3COO)_2.2H_2O]$ in                          |      |
|     | methanol (solid line).   |      |
| 19  | <b>Figure S18:</b> Fluorescence responses ( $\lambda_{ex}$ , 350 nm) of deoxygenated methanol solution       | 16   |

|    | (40 µM) of complex 1 before (solid line) and after (dashed line) purging of 5   |    |  |  |  |
|----|---|----|--|--|--|
|    | equivalent of NO at 298 K.  |    |  |  |  |
| 20 | Figure S19: FT-IR spectrum of ligand L2 in KBr pellet.  |    |  |  |  |
| 21 | Figure S20: <sup>1</sup> H-NMR spectrum of ligand L2 in CDCl <sub>3</sub> .   |    |  |  |  |
| 22 | <b>Figure S21:</b> ${}^{13}$ C-NMR spectrum of ligand L <sub>2</sub> in CDCl <sub>3</sub> .                           | 18 |  |  |  |
| 23 | Figure S22: ESI mass spectrum of ligand $L_2$ in methanol.  | 18 |  |  |  |
| 24 | Figure S23: UV-visible spectrum of ligand $L_2$ in methanol.  | 19 |  |  |  |
| 25 | Figure S24: FT-IR spectrum of complex 2 in KBr pellet.  | 19 |  |  |  |
| 26 | Figure S25: UV-visible spectrum of complex 2 in methanol.   | 20 |  |  |  |
| 27 | Figure S26: X-Band EPR spectrum of complex 2 in methanol at room temperature.   | 20 |  |  |  |
| 28 | Figure S27: ESI mass spectrum of complex 2 in methanol.   | 21 |  |  |  |
| 29 | Figure S28: UV-visible spectra of complex 2 before (black trace) and after (red trace)                                | 21 |  |  |  |
|    | purging nitric oxide in methanol.   |    |  |  |  |
| 30 | Figure S29: UV-visible spectra of complex 2 before (black trace) and after (green                                     | 22 |  |  |  |
|    | trace) purging nitrogen dioxide in methanol.  |    |  |  |  |
| 31 | Figure S30: X-Band EPR spectrum of complex 2 after purging nitrogen dioxide   | 22 |  |  |  |
|    | (green dotted line) in methanol at room temperature.  |    |  |  |  |
| 32 | Figure S31: FT-IR spectrum of modified ligand $L2'$ in KBr pellet.  | 23 |  |  |  |
| 33 | <b>Figure S32:</b> <sup>1</sup> H-NMR spectrum of ligand $L2'$ in CDCl <sub>3</sub> .                                 | 23 |  |  |  |
| 34 | <b>Figure S33:</b> $^{13}$ C-NMR spectrum of ligand L2' in CDCl <sub>3</sub> .  | 24 |  |  |  |
| 35 | <b>Figure S34:</b> ESI mass spectrum of ligand $L2'$ in methanol.   | 24 |  |  |  |
| 36 | <b>Figure S35:</b> Fluorescence responses ( $\lambda_{ex}$ , 354 nm) for 20 $\mu$ M solution of free ligand,          | 25 |  |  |  |
|    | L2 (dashed line) and after addition of one equivalent of [Cu(CH <sub>3</sub> COO) <sub>2</sub> .2H <sub>2</sub> O] in |    |  |  |  |
|    | methanol(solid line).   |    |  |  |  |
| 37 | <b>Figure S36:</b> Fluorescence responses ( $\lambda_{ex}$ , 354 nm) of deoxygenated methanol solution                | 25 |  |  |  |
|    | $(20 \ \mu M)$ of complex <b>2</b> before (solid line) and after (dashed line) purging of 5                           |    |  |  |  |
|    | equivalent of NO at 298 K.  |    |  |  |  |
| 38 | Table S1: Crystallographic table for ligand L1.   | 26 |  |  |  |
| 39 | Table S2:       Selected bond angles (°) of ligand L1   | 26 |  |  |  |
| 40 | Table S3:         Selected bond lengths of ligand L1  | 27 |  |  |  |
| 41 | Table S4: Crystallographic table for complex 1  | 27 |  |  |  |
| 42 | Table S5:       Selected bond angles (°) of complex 1   | 28 |  |  |  |
| 43 | Table S6:         Selected bond lengths of complex 1  | 28 |  |  |  |

#### **Experimental Section**

#### Materials and methods

All reagents and solvents of reagent grade were purchased from commercial sources and used as received except specified. Methanol was dried by heating over iodine activated magnesium with a magnesium loading of 5 gm/lit. Then the dried methanol was kept over 20% m/v 3Å molecular sieves for 4-5 days before using. Deoxygenation of the solvent and solutions was effected either by repeated vacuum/purge cycles or bubbling with argon for 30 minutes or using freeze-pump-thaw cycles. NO<sub>2</sub> gas was prepared by the reaction of purified NO with  $O_2$  followed by passing through an oxygen trap to remove extra oxygen, if any. UV-visible spectra were recorded on a Perkin Elmer Lambda 25 UV visible spectrophotometer. FT-IR spectra of the solid samples were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was measured using a Systronic 305 conductivity bridge. 1H-NMR spectra were recorded in a 400 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced either with an internal standard (Me4Si) or to the residual solvent peaks. The X-band Electron Paramagnetic Resonance (EPR) spectra were recorded on a JES-FA200 ESR spectrometer, at room temperature and 77 K with microwave power, 0.998 mW; microwave frequency, 9.14 GHz and modulation amplitude, 2. Elemental analyses were obtained from a Perkin Elmer Series II Analyzer. The magnetic moment of complexes was measured on a Cambridge Magnetic Balance.

Single crystals were grown by slow diffusion followed by slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube MoKa radiation (l = 0.71073 Å) at 273(3) K, with increasing w (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software. Structures were solved by direct methods using SHELXS-97 and

refined with full-matrix least squares on F2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Structural illustrations have been drawn with ORTEP-3 for Windows.

#### Syntheses

#### Ligand L1:

*N*, *N*-dimethylethylenediamine (880 mg, 0.01 mol) and anthracene-10-carbaldehyde (2.06 g, 0.01 mol) were added in 20 ml of distilled ethanol in a round bottom flask fitted with a stir bar. The mixture was stirred for 12 h at room temperature to result corresponding Schiff's base. Then the imine was reduced by slow addition of 2.1 equivalent of NaBH<sub>4</sub>. After removal of methanol under reduced pressure, the crude product was dissolved in water and neutralized with dilute acetic acid. The corresponding amine was extracted from the aqueous solution by dichloromethane ( $4 \times 50$  ml portions). The organic layer was dried over rotary evaporator to get the amine. The amine thus obtained was then purified by column chromatography using neutral aluminum oxide. Then the purified amine (2.5 g, 0.009 mol), 2,4-di-*tert*-butylphenol (1.85 g, 0.009 mol) and formalin (1.09 g of 37% solution, 0.0135 mol) were taken in 50 mol of methanol and the mixture was stirred for 8 h. The solution was removed under reduced pressure to get the crude product. The compound was purified by column chromatography to get ligand L1. Yield: ~75%.

Elemental analyses: calcd.(%): C, 82.21; H, 8.93; N, 5.64 ; found(%): C, 82.26; H, 8.94; N, 5.71. FT-IR (in KBr): 3183, 2959, 1479, 1361, 1223, 729 cm<sup>-1</sup>. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta_{ppm}$ : 8.38 (1H, s), 8.34 (2H, d), 7.97 (1H, s), 7.95 (1H, d), 7.48 (4H, m), 7.29 (1H, d), 7.06 (1H, d), 4.55 (2H,s), 3.78 (2H, s), 2.53 (2H, t), 2.39 (2H, t), 1.86 (6H, s), 1.53 (9H, s), 1.30 (9H, s). <sup>13</sup>C-NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta_{ppm}$ : 154.0, 140.1, 136.0, 131.7, 131.5, 129.5, 129.0,

127.8, 125.9, 125.3, 125.2, 125.0, 123.3, 122.7, 57.3, 55.9, 50.9, 49.4, 44.5, 35.4, 34.3, 31.9,
30.0. Mass (M+H<sup>+</sup>)/z: calcd: 497.345; found: 497.366.

#### Ligand L2:

*N*, *N*-dimethylethylenediamine (440 mg, 5 mmol) and dansyl chloride (1.35 g, 5 mmol) was added in 20 ml of acetonitrile. The mixture was stirred for 1 h at room temperature to give corresponding sulphonamide. To the reaction mixture, 100 ml water was added. Then the sulphonamide was extracted with dichloromethane (50 ml  $\times$  3 portions) and dried under vacuum. The solid thus obtained was dissolved in 20 ml of methanol and to this 2,4-di-*tert*-butyl-6-chloromethylphenol (1.27 g, 5 mmol), equivalent amount of triethylamine was added and the reaction mixture was refluxed for 24 h. After removal of methanol under reduced pressure, the crude product was dissolved in water and neutralized with dilute acetic acid and was extracted from the aqueous solution by dichloromethane (50 ml  $\times$  3 portions). The organic layer was dried over rotary evaporator to get the crude mass. The ligand L2 thus obtained was then purified by column chromatography using neutral aluminum oxide. Yield: ~60%.

Elemental analyses: calcd.(%): C, 68.98; H, 8.40; N, 7.78; found(%): C, 68.94; H, 8.40; N, 7.89. FT-IR (in KBr): 3417, 2955, 1611, 1482, 1434, 1140, 790 cm<sup>-1</sup>. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta_{ppm}$ : 8.57 (1H, d), 8.26 (2H, t), 7.54 (2H, m), 7.27 (1H, d), 7.13 (1H, d), 6.31 (1H, d), 4.38 (2H, s), 3.47 (2H, t), 2.89 (6H, s), 2.67 (2H, t), 2.26 (6H, s), 1.28 (9H, s), 0.98 (9H, s). <sup>13</sup>C-NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta_{ppm}$ : 152.7, 152.0, 141.7, 137.9, 134.4, 130.8, 130.6, 130.3, 130.1, 128.4, 125.7, 124.1, 123.2, 121.3, 119.8, 115.5, 60.1, 47.4, 45.9, 45.5, 44.0, 35.3, 34.0, 31.5, 29.9. Mass (M+H<sup>+</sup>)/z: calcd: 540.35; found: 540.351.

#### Complex 1:

To a stirred solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.398 g, 2 mmol) in 15 ml methanol was added a solution of ligand L<sub>1</sub> (0.992 g, 2 mmol) in 50 ml methanol. The reaction mixture was stirred for 2 h. Then solvent was reduced to 5 ml under vacuum and 20 ml of diethyl ether was added. Then it was kept in freezer for 12 h to obtain the complex **1** as a dark brown precipitate. Yield: 0.97 g (~80%). Elemental analyses: calcd.(%): C, 69.93; H, 7.50; N, 4.53; found(%): C, 69.99; H, 7.52; N, 4.61. UV-vis. (methanol):  $\lambda_{max}$ , 665 nm. FT-IR (KBr pellet): 2954, 1576, 1467, 1441, 735 cm<sup>-1</sup>. The complex **1** behaves as 1:1 electrolyte in methanol solution [AM (S cm-1), 151]. The observed magnetic moment is found to be 1.58 BM.

#### **Complex 2:**

To a stirred solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.398 g, 2 mmol) in 10 ml methanol was added a solution of ligand L2 (1.080 g, 2 mmol) in 50 ml methanol. The reaction mixture was stirred for 2 h. The solvent was reduced under vacuum to 5 ml and 20 ml of diethylether was added to this. The mixture was kept in freezer for 12 h to obtain the complex 2 as a brown precipitate. Yield: 1.20 g (~70%). Elemental analyses: calcd.(%): C, 59.94; H, 7.16; N, 6.35; found(%): C, 59.98; H, 7.16; N, 6.42. UV-vis. (methanol):  $\lambda_{max}$ , 685 nm. FT-IR (KBr pellet): 2954, 1480, 1460, 1140, 791 cm<sup>-1</sup>. The complex 2 behaves as 1:1 electrolyte in methanol solution [AM (S cm-1), 148]. The observed magnetic moment is found to be 1.56 BM.

#### Isolation of modified ligand L1':

To 30 ml of methanol solution of complex 1 (620 mg), nitrogen dioxide was bubbled till the brown color of the solution becomes colorless. This solution was allowed to stir for 10 minutes at room temperature. The excess NO<sub>2</sub> was removed by application several cycles of vacuum and argon purging. Then the solvent was reduced to 5 ml under vacuum using rotavapour. Then equivalent amount of aqueous solution of Na<sub>2</sub>S was added to the solution remove copper ion as its sulphide. The precipitate was filtered off and from the filtrate, the modified ligand L1<sup>*I*</sup> was extracted with dichloromethane (4 × 50 ml portions) and purified using column chromatography. Yield: 350 mg. (~70%). Elemental analyses: calcd.(%): C, 74.20; H, 7.26; N, 8.65 ; found(%): C, 74.26; H, 7.25; N, 8.74. FT-IR (in KBr): 2964, 1589, 1466, 1333, 1167 cm<sup>-1</sup>. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta_{ppm}$ : 8.35 (1H, s), 8.22 (2H, d), 8.11 (3H, m), 7.94(1H, d), 7.91 (1H, s), 7.40 (4H, m), 4.51 (2H,s), 3.75 (2H, s), 2.50 (4H, s), 1.87 (6H, s), 1.51 (9H, s). <sup>13</sup>C-NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta_{ppm}$ : 165.0, 138.3, 134.3, 131.7, 131.5, 129.2, 127.4, 126.1, 125.3, 125.1, 124.7, 124.26, 123.4, 55.4, 54.9, 50.6, 48.0, 43.8, 35.6, 29.6. Mass (M+H<sup>+</sup>)/z: calcd: 486.27; found: 486.278.

#### **Isolation of modified ligand L2':**

Similar procedure applied as in case of L1'. Yield: 200 mg (~70%).

Elemental analyses: calcd.(%): C, 61.34; H, 6.86; N, 10.60; found(%):C, 61.39; H, 6.87; N, 10.71. FT-IR (in KBr): 3444, 2955, 1642, 1460, 1315, 1140, 733 cm<sup>-1</sup>. <sup>1</sup>H-NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta_{ppm}$ : 8.5 (1H, d), 8.2 (2H, t), 8.0 (1H, d), 7.8 (1H, d), 7.5 (2H, m), 7.1 (1H, d), 4.0 (2H, s), 2.8 (6H, s), 2.7 (2H, t), 2.5 (2H, t), 2.2 (6H, s), 1.3 (9H, s). <sup>13</sup>C-NMR: (100 MHz, CDCl<sub>3</sub>)  $\delta_{ppm}$ : 164.5, 151.9, 141.6, 138.6, 137.8, 137.4, 134.3, 130.7, 130.6, 130.2, 128.3, 125.7, 124.0, 123.2, 123.0, 122.4, 122.3. Mass (M+H<sup>+</sup>)/z: calcd: 529.40; found: 529.27.



Figure S1: FT-IR spectrum of ligand L1 in KBr pellet.



Figure S2: <sup>1</sup>H-NMR spectrum of ligand L1 in CDCl<sub>3</sub>.



Figure S3: <sup>13</sup>C-NMR spectrum of ligand L1 in CDCl<sub>3</sub>.



Figure S4: ESI mass spectrum of ligand L1 in methanol.



Figure S5: UV-Visible spectrum of ligand L1 in methanol.



Figure S6: FT-IR spectrum of complex 1 in KBr pellet.



Figure S7: UV-Visible spectrum of complex 1in methanol.



Figure S8: X-Band EPR spectrum of complex 1 in methanol at room temperature.



Figure S9: ESI mass spectrum of complex 1 in methanol.



Figure S10: UV-visible spectra of complex 1 before (black trace) and after (red trace) purging nitric oxide in methanol.



**Figure S11**: UV-visible spectra of complex **1** before (black trace) and after (blue trace) purging nitrogen dioxide in methanol.



**Figure S12**: X-Band EPR spectra of complex **1** after purging nitrogen dioxide (blue line) in methanol at room temperature.



Figure S13: FT-IR spectrum of modified ligand L1' in KBr pellet.



Figure S14: <sup>1</sup>H-NMR spectrum of modified ligand L1<sup>/</sup> in CDCl<sub>3</sub>.



Figure S15: <sup>13</sup>C-NMR spectrum of modified ligand L1<sup>/</sup> in CDCl<sub>3</sub>.



Figure S16: ESI mass spectrum of modified ligand L1' in methanol.



**Figure S17:** Fluorescence responses ( $\lambda_{ex}$ , 350 nm) for 40  $\mu$ M solution of free ligand, L1 (dashed line) and after addition of one equivalent of [Cu(CH<sub>3</sub>COO) <sub>2</sub>.2H<sub>2</sub>O] in methanol (solid line).



**Figure S18:** Fluorescence responses ( $\lambda_{ex}$ , 350 nm) of deoxygenated methanol solution (40  $\mu$ M) of complex 1 before (**solid line**) and after (**dashed line**) purging of 5 equivalent of NO at 298 K.



Figure S19: FT-IR spectrum of ligand L2 in KBr pellet.



Figure S20: <sup>1</sup>H-NMR spectrum of ligand L2 in CDCl<sub>3</sub>.



Figure S21: <sup>13</sup>C-NMR spectrum of ligand L<sub>2</sub> in CDCl<sub>3</sub>.



Figure S22: ESI mass spectrum of ligand L<sub>2</sub> in methanol.



Figure S23: UV-visible spectrum of ligand  $L_2$  in methanol.



Figure S24: FT-IR spectrum of complex 2 in KBr pellet.



Figure S25: UV-visible spectrum of complex 2 in methanol.



Figure S26: X-Band EPR spectrum of complex 2 in methanol at room temperature.



Figure S27: ESI mass spectrum of complex 2 in methanol.



Figure S28: UV-visible spectra of complex 2 before (black trace) and after (red trace) purging nitric oxide in methanol.



Figure S29: UV-visible spectra of complex 2 before (black trace) and after (green trace) purging nitrogen dioxide in methanol.



**Figure S30**: X-Band EPR spectrum of complex **2** after purging nitrogen dioxide (green dotted line) in methanol at room temperature.



Figure S31: FT-IR spectrum of modified ligand L2' in KBr pellet.



Figure S32: <sup>1</sup>H-NMR spectrum of ligand L2' in CDCl<sub>3</sub>.



Figure S33: <sup>13</sup>C-NMR spectrum of ligand L2' in CDCl<sub>3</sub>.



Figure S34: ESI mass spectrum of ligand L2' in methanol.



**Figure S35:** Fluorescence responses ( $\lambda_{ex}$ , 354 nm) for 20  $\mu$ M solution of free ligand, L2 (dashed line) and after addition of one equivalent of [Cu(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O] in methanol(solid line).



**Figure S36:** Fluorescence responses ( $\lambda_{ex}$ , 354 nm) of deoxygenated methanol solution (20  $\mu$ M) of complex **2** before (**solid line**) and after (**dashed line**) purging of 5 equivalent of NO at 298 K.

| Table S1: | Crystallogra | phic table for | ligand L1. |
|-----------|--------------|----------------|------------|
|-----------|--------------|----------------|------------|

|                                | L1   |
|--------------------------------|--|
| Formulae                       | C <sub>34</sub> H <sub>44</sub> N <sub>2</sub> O |
| Mol. wt.                       | 496.71   |
| Crystal system                 | Monoclinic                                       |
| Space group                    | P2(1)/c  |
| Temperature /K                 | 293(2)   |
| Wavelength /Å                  | 0.71073  |
| a /Å                           | 11.4955(11)                                      |
| b /Å                           | 10.9564(13)                                      |
| c /Å                           | 23.216(2)  |
| α/°                            | 90.00  |
| β/°                            | 95.880(9)  |
| ٧/°                            | 90.00  |
| $V/Å^3$                        | 2908.7(5)  |
| Ζ                              | 4  |
| Density/Mgm <sup>-3</sup>      | 1.134  |
| Abs. co-eff. /mm <sup>-1</sup> | 0.067  |
| Abs. correction                | multi-scan                                       |
| F(000)                         | 1080   |
| Total no. of reflections       | 5110   |
| Reflections, $I > 2\sigma(I)$  | 2500   |
| Max. 20/°                      | 25.00  |
| Ranges (h, k, l)               | -13≤h ≤13  |
|                                | -13≤ k ≤9  |
|                                | $-27 \le 1 \le 24$                               |
| Complete to $2\theta$ (%)      | 99.8   |
| Refinement method              | Full-matrix least-                               |
|                                | squares on $F^2$                                 |
| $\operatorname{Goof}(F^2)$     | 1.174  |
| R indices $[I > 2\sigma(I)]$   | 0.0701   |
| R indices (all data)           | 0.1488   |

Table S2: Selected bond angles (°) of ligand L1

| Atoms           | Angles (°) | Atoms           | Angles (°) |
|-----------------|------------|-----------------|------------|
| C2 - N1 - C1    | 110.9(3)   | C8 - C9 - C10   | 123.7(3)   |
| C1 - N1 - C3    | 111.8(3)   | C21 - C22 - C23 | 123.5(3)   |
| C4 - N2 - C20   | 112.4(2)   | C25 - C24 - C23 | 120.9(3)   |
| C4 - N2 - C5    | 112.1(2)   | C24 - C25 - C26 | 120.2(4)   |
| O1 - C11 - C10  | 118.5(3)   | C25 - C26 - C27 | 120.8(3)   |
| C11 - C10 - C16 | 122.1(3)   | C26 - C27 - C28 | 120.2(3)   |
| C17 - C16 - C18 | 107.2(3)   | C29 - C28 - C27 | 121.6(3)   |

| N2 - C20 - C21 | 115.2(2) | C29 - C34 - C21 | 119.7(3) |
|----------------|----------|-----------------|----------|

| Atoms     | Distances (Å) | Atoms     | Distances (Å) |
|-----------|---------------|-----------|---------------|
| N1 - C1   | 1.461(5)      | C27 - C22 | 1.427(5)      |
| N1 - C2   | 1.467(4)      | 01 - C11  | 1.375(4)      |
| N1 - C3   | 1.464(4)      | C31 - C32 | 1.418(6)      |
| N2 - C4   | 1.463(4)      | C29 - C28 | 1.389(5)      |
| N2 - C20  | 1.470(4)      | C6 - C11  | 1.400(5)      |
| N2 - C5   | 1.470(4)      | C8 - C7   | 1.376(4)      |
| C21 - C22 | 1.414(4)      | C8 - C12  | 1.540(5)      |
| C23 - C22 | 1.437(5)      | C12 - C14 | 1.524(5)      |

Table S3: Selected bond distances (Å) of ligand L1

 Table S4: Crystallographic table for complex 1.

|                                | Complex 1  |
|--------------------------------|--|
| Formulae                       | C <sub>36</sub> H <sub>46</sub> N <sub>2</sub> O <sub>3</sub> Cu |
| Mol. wt.                       | 618.29   |
| Crystal system                 | Monoclinic   |
| Space group                    | C2/c   |
| Temperature /K                 | 296(2)   |
| Wavelength /Å                  | 0.71073  |
| a /Å                           | 28.2038(9)   |
| b /Å                           | 12.6258(4)   |
| c /Å                           | 22.7579(8)   |
| α/°                            | 90.00  |
| β/°                            | 128.0360(10)   |
| V/°                            | 90.00  |
| $V/Å^3$                        | 6382.9(4)  |
| Ζ                              | 8  |
| Density/Mgm <sup>-3</sup>      | 1.287  |
| Abs. co-eff. /mm <sup>-1</sup> | 0.722  |
| Abs. correction                | none   |
| F(000)                         | 2632   |
| Total no. of reflections       | 5622   |
| Reflections, $I > 2\sigma(I)$  | 4006   |
| Max. 20/°                      | 25.00  |
| Ranges (h, k, l)               | -32≤h ≤33  |
|                                | $-12 \le k \le 15$   |
|                                | $-26 \le 1 \le 27$   |
| Complete to $2\theta$ (%)      | 100  |
| Refinement method              | Full-matrix least-   |
|                                | squares on $F^2$   |

| $Goof(F^2)$                  | 1.473  |
|------------------------------|--------|
| R indices $[I > 2\sigma(I)]$ | 0.0410 |
| R indices (all data)         | 0.0596 |

 Table S5:
 Complex 1 selected bond angles (°).

| Atoms         | Angles (°) | Atoms          | Angles (°) |
|---------------|------------|----------------|------------|
| N2 - Cu1 - N1 | 86.41(9)   | N2 - Cu1 - O2  | 165.15(9)  |
| N2 - Cu1 - O1 | 94.16(9)   | N1 - Cu1 - O2  | 94.52(9)   |
| N1 - Cu1 - O1 | 159.58(9)  | O2 - Cu1 - O1  | 90.11(9)   |
| Cu1 - N1 - C2 | 113.1(2)   | Cu1 - N1 - C1  | 106.4(2)   |
| Cu1 - N1 - C3 | 108.2(2)   | Cu1 - O1 - C11 | 125.6(2)   |
| N1 - C3 - C4  | 109.7(2)   | N2 - C4 - C3   | 110.3(2)   |
| O1 - C11 - C6 | 120.1(3)   | Cu1 - N2 - C5  | 106.2(2)   |
| Cu1 - N2 - C4 | 104.6(2)   | Cu1 - O2 - C35 | 119.0(2)   |

| Tabla S6. | Complex | 1 salacted | bond | distances | (Å)  |
|-----------|---------|------------|------|-----------|------|
| Table So: | Complex | I selected | bona | distances | (A). |

| Atoms    | Distances (Å) | Atoms     | Distances (Å) |
|----------|---------------|-----------|---------------|
| Cu1 - N2 | 2.079(3)      | Cu1 - N1  | 2.044(2)      |
| Cu1 - O2 | 1.935(2)      | Cu1 - O1  | 1.888(2)      |
| N2 - C5  | 1.511(3)      | N2 - C4   | 1.492(3)      |
| N2 - C20 | 1.510(4)      | N1 - C3   | 1.485(5)      |
| C4 - C3  | 1.530(4)      | C5-C6     | 1.491(3)      |
| C11 - C6 | 1.399(5)      | C11 - C10 | 1.423(3)      |
| O2 - C35 | 1.231(6)      | N1 - C1   | 1.488(4)      |
| N1 - C2  | 1.494(3)      | 01 - C11  | 1.334(4)      |