# **Electronic Supporting Information (ESI):**

# Isoreticular Synthesis of 2D MOFs with Rotating Aryl Rings

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**Inorganic Chemistry Frontiers** 

#### **EXPERIMENTAL SECTION**

The compound 1,2,4-triazole-1-propanenitrile, and 4,4'-(1,4-(xylene)diyl)bis(1,2,4-triazole) (**di-MTZ**<sup>Ph</sup>) were prepared as described previously.<sup>1</sup> All other reagents were purchased from commercial vendors and used without purification. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or a Varian VNMRS 500 MHz narrow-bore broadband system. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to the residual solvent. Solid <sup>13</sup>C CP-MAS NMR samples were recorded on a Varian Inova 400 MHz spectrometer and referenced to an external adamantane sample. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. Thermogravimetric analysis data were collected on a TA Instruments TGA Q50 under N<sub>2</sub>. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

4,4'-[naphthalene-2,6-diylbis(methylene)]bis-(1-(2-cyanoethyl)-1,2,4-**Synthesis** of triazolium) dibromide, 1. 2,6-bis(bromomethyl)naphthalene (2.00 g, 0.00635 mol) and 1,2,4triazole-1-propanenitrile (1.56 g, 0.0128 mol) were added to a 100 mL round bottom flask and diluted with acetonitrile (40 mL). The reaction was subsequently heated to reflux for 24 h. The reaction was cooled to rt and the crude solid product was washed with acetonitrile (3 x 30 mL) and dried under reduced pressure. The crude product was again added to a 100 mL round bottom flask along with an additional quantity of 1,2,4-triazole-1-propanenitrile (1.56 g, 0.0128 mol) and diluted with 40 mL of acetonitrile. The reaction was again heated to reflux for 24 h, and this process of reflux followed by washing was repeated an additional third time to ensure completion of the reaction. After the third reflux, the reaction was cooled to rt and diethyl ether (35 mL) was added to the reaction mixture, followed by drying under reduced pressure. The crude solid product was washed with acetonitrile (3 x 30 mL) and dried under reduced pressure to yield the pure product (2.51 g, 70.2% yield). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 499.72 MHz): δ 10.44 (s, 2H), 9.52 (s, 2H), 8.08 (s, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 5.80 (s, 4H), 4.75 (t, J = 6.3 Hz, 4H), 3.25 (t, J = 6.3 Hz, 4H).  ${}^{13}C{}^{1}H$  NMR (DMSO-d<sub>6</sub>, 125.66 MHz):  $\delta$  145.08, 143.50, 132.55, 131.98, 129.00, 127.93, 126.73, 117.70, 50.63, 47.26, 17.34. IR (neat): 3097, 3018, 2977, 2256, 1822, 1580, 1518, 1441, 1419, 1381, 1339, 1317, 1290, 1258, 1230, 1182, 1166, 1139, 1067, 1043, 1023, 979, 918, 840, 766, 718, 676 cm<sup>-1</sup>. ESI/MS (m/z): [M<sup>-</sup>Br]<sup>+</sup> 477.11, [M<sup>-2</sup>Br]<sup>2+</sup> 199.10. Anal. Calcd. for C<sub>22</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>8</sub>: C, 47.33; H, 3.97; N, 20.07. Found: C, 47.36; H, 3.92; N, 19.97.

Synthesis of 4,4'-[naphthalene-2,6-diylbis(methylene)]bis(1,2,4-triazole), 2 (di-MTZ<sup>Nap</sup>). Potassium hydroxide (1.01 g, 0.0179 mol) and 1 (2.50 g, 0.00448 mol) were added to a 50 mL Erlenmeyer flask containing 25 mL of water. The product precipitated from solution as a white powder, and the crude product was filtered after stirring for 24 h and washed with water (3 x 50 mL), acetonitrile (3 x 50 mL), and tetrahydrofuran (3 x 50 mL). The pure product was dried under reduced pressure to yield 1.22 g (94.1 % yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 499.72 MHz):  $\delta$  8.66 (s, 4H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.79 (s, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 5.45 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 125.66 MHz):  $\delta$  143.33, 134.67, 132.24, 128.62, 126.28, 126.14, 47.63. IR (neat): 3102, 3037, 2941, 1648, 1608, 1529, 1465, 1448, 1387, 1351, 1338, 1276, 1255, 1192, 1178, 1129,

1076, 974, 951, 918, 903, 881, 828, 762, 694 cm<sup>-1</sup>. Anal. Calcd. for  $C_{16}H_{14}N_6$ : C, 66.19; H, 4.86; N, 28.95. Found: C, 65.69; H, 5.00; N, 28.24.

**Synthesis of 4,4'-[4,4'-bitolyl]bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, 3.** 4,4'bis(bromomethyl)-1,1'-biphenyl (2.00 g, 0.00588 mol) was added to a 100 mL round bottom flask which had 1,2,4-triazole-1-propanenitrile (1.437 g, 0.0118 mol) and the mixture was diluted with acetonitrile (40 mL). The reaction was heated to reflux for 24 h, followed by cooling the reaction to rt and washing the precipitate with diethyl ether (30 mL), and then dried under reduced pressure. The crude white solid was then washed with acetonitrile (3 x 30 mL) and dried under reduced pressure to yield the pure product (2.75 g, 84.1 % yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 499.72 MHz)  $\delta$ 10.40 (s, 2H), 9.51 (s, 2H), 7.78 (d, *J* = 8.3 Hz, 4H), 7.63 (d, *J* = 8.2 Hz, 4H), 5.65 (s, 4H), 4.74 (t, *J* = 6.3 Hz, 4H), 3.25 (t, *J* = 6.3 Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 125.66 MHz):  $\delta$  144.97, 143.38, 139.92, 133.01, 129.56, 127.32, 117.71, 50.21, 47.25, 17.31. IR (neat): 3101, 3032, 3018, 2982, 2254, 1820, 1584, 1519, 1500, 1439, 1419, 1393, 1381, 1367, 1341, 1297, 1215, 1182, 1143, 1068, 1043, 1024, 1005, 980, 965, 916, 849, 833, 816, 787, 756, 708 cm<sup>-1</sup>. ESI/MS (*m/z*): [M-Br]<sup>+</sup> 503.11, [M-2Br]<sup>2+</sup> 212.14. Anal. Calcd. for C<sub>24</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>8</sub>: C, 49.33; H, 4.14; N, 19.18. Found: C, 49.31; H, 4.08; N, 18.90.

**Synthesis of 4,4'-(4,4'-bitolyl)bis(1,2,4-triazole), 4 (di-MTZ<sup>Biph</sup>).** Potassium hydroxide (1.17 g, 0.0208 mol) and **3** (2.90 g, 0.00521 mol) were added to a 50 mL Erlenmeyer flask containing 25 mL of water. After 24 h, the product precipitated from solution as a white powder and was filtered and washed with water (3 x 50 mL), acetonitrile (3 x 50 mL), and tetrahydrofuran (3 x 50 mL). The pure product was dried under reduced pressure to yield 1.40 g (85.2 % yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 499.72 MHz)  $\delta$  8.65 (s, 4H), 7.66 (d, *J* = 7.7 Hz, 4H), 7.38 (d, *J* = 7.8 Hz, 4H), 5.32 (s, 4H). <sup>13</sup>C{<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 125.66 MHz):  $\delta$  143.27, 139.25, 136.05, 128.29, 127.12, 47.21. IR (neat): 3089, 3029, 2962, 1664, 1613, 1522, 1500, 1458, 1439, 1403, 1378, 1361, 1336, 1316, 1207, 1179, 1169, 1074, 1006, 976, 967, 950, 889, 854, 833, 796, 755, 746, 712, 693 cm<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>6</sub>: C, 68.34; H, 5.10; N, 26.56. Found: C, 67.80; H, 5.18; N, 25.77.

Synthesis of  $[Ag(di-MTZ^{Ph})(ClO_4)] \cdot NMP \cdot H_2O$ , 5. Silver(I) perchlorate monohydrate (0.0331 g, 0.0147 mmol) and di-MTZ^{Ph} (0.0177 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved in 1 mL of water and 2 mL of NMP, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block, followed by mixing of the solutions and additional heating. After heating for 3 h, colorless needles formed and were isolated and washed with water and acetone to yield the pure product (35.2 mg, 84.8 % yield). IR (neat): 3587, 3115, 1678, 1622, 1540, 1501, 1453, 1423, 1404, 1337, 1295, 1210, 1194, 1168, 1089, 1014, 984, 960, 928, 892, 832, 811, 748, 715, 678, 653 cm<sup>-1</sup>. Anal. Calcd. for C<sub>12</sub>H<sub>14</sub>ClAgN<sub>6</sub>O4•DMA: C, 36.16; H, 4.11; N, 17.36. Found: C, 36.36; H, 4.12; N, 17.34.

Synthesis of  $[Cu(di-MTZ^{Nap})(ClO_4)] \cdot DMA \cdot H_2O$ , 6. Copper(II) perchlorate hexahydrate (0.0136 g, 0.0367 mmol) and di-MTZ^{Nap} (0.0213 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved in 1 mL of water and 2 mL of DMA, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block, followed by mixing of the solutions and additional heating. After heating for 24 h, colorless needles formed and were isolated and washed with water and acetone to yield the pure product (7.10 mg, 42.8 % yield). IR (neat): 3371, 3114,

1633, 1586, 1551, 1446, 1395, 1377, 1340, 1214, 1194, 1091, 1071, 1001, 968, 942, 907, 874, 818, 802, 767, 750, 732, 697 cm<sup>-1</sup>. Anal. Calcd. for  $C_{16}H_{14}ClCuN_6O_4 \bullet DMA \bullet H_2O$ : C, 43.01; H, 4.51; N, 17.56. Found: C, 42.99; H, 3.76; N, 17.35.

Synthesis of [Cu(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • DEF, 7. Copper(II) perchlorate hexahydrate (0.0136 g, 0.0367 mmol) and di-MTZ<sup>Biph</sup> (0.0232 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved in 1 mL of water and 2 mL of DEF, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block, followed by mixing of the solutions and additional heating. After heating for 24 h, colorless needles formed and were isolated and washed with water and acetone to yield the pure product (2.40 mg, 13.1 % yield). IR (neat): 3618, 3133, 2968, 2917, 2870, 2838, 1661, 1605, 1545, 1503, 1455, 1432, 1396, 1380, 1355, 1336, 1307, 1262, 1210, 1189, 1085, 1008, 973, 942, 859, 819, 754, 703, 684 cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>ClCuN<sub>6</sub>O<sub>4</sub>•DEF: C, 47.59; H, 4.69; N, 16.89. Found: C, 47.59; H, 4.63; N, 16.84.

**Synthesis of [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] · 3DMA, 8.** Silver(I) perchlorate monohydrate (0.0331 g, 0.0147 mmol) and **di-MTZ<sup>Biph</sup>** (0.0232 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved in 1 mL of DMA and 2 mL of DMA, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block, followed by mixing of the solutions and additional heating. After heating for 24 h, the solution was pipetted to another 4 mL scintillation vial and allowed to cool to rt. Colorless needles formed after cooling and were isolated and washed with acetone to yield the pure product (23.0 mg, 59.7 % yield). IR (neat): 3123, 1703, 1542, 1501, 1444, 1389, 1356, 1185, 1083, 1006, 864, 803, 751, 693 cm<sup>-1</sup>. Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>ClAgN<sub>6</sub>O<sub>4</sub>: C, 41.28; H, 3.08; N, 16.05. Found: C, 41.16; H, 3.23; N, 15.76.

**Synthesis of [Ag(di-MTZ<sup>Biph</sup>)(CIO<sub>4</sub>)] • NMP, 9.** Silver(I) perchlorate monohydrate (0.0331 g, 0.0147 mmol) and **di-MTZ<sup>Biph</sup>** (0.0232 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved in 1 mL of DMA and 2 mL of DMA, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block, followed by mixing of the solutions and additional heating. After heating for 24 h, the solution was pipetted to a 20 mL vial and 2 mL of heated (85 °C) NMP was added while solution was still hot, and allowed to cool to rt. Colorless needles formed after cooling. IR (neat): 3109, 2932, 1673, 1629, 1537, 1501, 1443, 1392, 1356, 1296, 1263, 1189, 1088, 1062, 1009, 982, 932, 890, 850, 807, 751, 704 cm<sup>-1</sup>.

**X-ray Structure Determinations.** Data was collected on a Bruker SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1,800 W power (45 kV, 40 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur focusing optics. Single crystals were mounted on nylon CryoLoops (Hampton Research) with Paratone-N (Hampton Research) and frozen at -100 °C and -173 °C, respectively. Initial scans of each specimen were taken to obtain preliminary unit cell parameters and to assess the mosaicity (i.e. breadth of spots between frames) of the crystal to select the required frame width for data collection. For all cases frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker APEX2* software suite to carry out overlapping  $\phi$  and  $\omega$  scans at detector setting of 2 $\theta = 28^{\circ}$ . Following data collection, reflections were sampled from all regions of the Ewald sphere to re-determine unit cell parameters for data integration. Following exhaustive review of collected frames the resolution of the dataset was judged, and, if necessary, regions of the frames where no coherent scattering was observed

were removed from consideration for data integration using the *Bruker SAINTplus* program.<sup>2</sup> Data was integrated using a narrow frame algorithm and was subsequently corrected for absorption. Absorption corrections were performed for both samples using the SADABS program.<sup>2</sup> Space group determination and tests for merohedral twinning were carried out using *XPREP*.<sup>2</sup> In all cases, the highest possible space group was chosen. Final models were refined anisotropically (with the exception of H atoms).

Final models were refined anisotropically (with the exception of H atoms). Disorder in 5 led to refinement of the oxygen atom from water as the oxygen was disordered over two positions. Reducing the occupancies accordingly led to satisfactory refinement. Disorder in 6 led to squeezing of the structure, which led to the copper, sulfate anion, as well as one nitrogen on the triazole linker to be anisotropic. This structure was solved in the C2 space group due to disorder in the naphthyl moiety of the framework. Disorder in 7 led to squeezing the solvent within the pore from the structure. This led to satisfactory refinement of the crystal. Disorder in 9 led to squeezing of the solvent from the structure. This led to satisfactory refinement of the crystal.

**Powder X-ray experiments.** Powder X-ray diffraction (PXRD) data was collected using a Panalytical Empyrean  $\theta$ -2 $\theta$  diffractometer in reflectance Bragg-Brentano geometry. Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å; 1,800 W, 45 kV, 40 mA) was focused using a planar Gobel Mirror riding the K $\alpha$  line. A 0.25 mm divergence slit was used for all measurements. Diffracted radiation was detected using a PIXcel<sup>3d</sup> detector [( $6^{\circ}$  2 $\theta$  sampling width) equipped with a Ni monochrometer]. All samples were mounted onto a zero background quartz plate fixed on a sample holder by dropping powders and then leveling the sample surface. The best counting statistics were achieved by using a 0.0394° 2 $\theta$  step scan from 3 – 50° with an exposure time of 119.85 s per step and a revolution spin rate of 4 s.

### NMR Figures for compounds 1-4.

**Figure S1.** <sup>1</sup>H NMR for 4,4'-[naphthalene-2,6-diylbis(methylene)]bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, **1**.



**Figure S2.** <sup>13</sup>C NMR for 4,4'-[naphthalene-2,6-diylbis(methylene)]bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, **1**.



Figure S3. <sup>1</sup>H NMR for 4,4'-[naphthalene-2,6-diylbis(methylene)]bis(1,2,4-triazole), 2.



**Figure S4.** <sup>13</sup>C NMR for 4,4'-[naphthalene-2,6-diylbis(methylene)]bis(1,2,4-triazole), **2**.



Figure S5. <sup>1</sup>H NMR for 4,4'-[4,4'-bitolyl]bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, **3**.



Figure S6. <sup>13</sup>C NMR for 4,4'-[4,4'-bitolyl]bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, **3**.



**Figure S7.** <sup>1</sup>H NMR for 4,4'-(4,4'-bitolyl)bis(1,2,4-triazole), 4.



**Figure S8.** <sup>13</sup>C NMR for 4,4'-(4,4'-bitolyl)bis(1,2,4-triazole), 4.



# IR Figures for MOFs 5-9.

Figure S9. IR for [Ag(di-MTZ<sup>Ph</sup>)(ClO<sub>4</sub>)] • NMP • H<sub>2</sub>O, 5.



Figure S10. IR for [Cu(di-MTZ<sup>Nap</sup>)(ClO<sub>4</sub>)] • DMA • H<sub>2</sub>O, 6.



Figure S11. IR for [Cu(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • DEF, 7.



Figure S12. IR for [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • 3DMA, 8.





Figure S13. IR for [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • NMP, 9.

# TGA data for MOFs 5-8.

Figure S1: TGA for [Ag(di-MTZ<sup>Ph</sup>)(ClO<sub>4</sub>)] • NMP • H<sub>2</sub>O, 5.



Figure S2: TGA for [Cu(di-MTZ<sup>Nap</sup>)(ClO<sub>4</sub>)] • DMA • H<sub>2</sub>O, 6.





Figure S3: TGA for [Cu(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • DEF, 7.

Figure S4: TGA for [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • 3DMA, 8.



## PXRD patterns for frameworks 6-9.

Figure S5: PXRD pattern for [Cu(di-MTZ<sup>Nap</sup>)(ClO4)] • DMA • H2O, 6.



Figure S6: PXRD pattern for [Cu(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • DEF, 7: experimental (red) and simulated (black).



Figure S7: PXRD pattern for [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • 3DMA, 8: experimental (red) and simulated (black).



Figure S8: PXRD pattern for [Ag(di-MTZ<sup>Biph</sup>)(ClO<sub>4</sub>)] • NMP, 9: experimental (red) and simulated (black).



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