Electronic Supporting Information

Mechanochemical synthesis and thermal property investigation of metallomesogens and transition metal complexes

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ESI 1. Experimental Details

ESI 1.1 General Procedures. Proton and carbon-13 NMR spectra were recorded on a JEOL-ECS 400 MHz spectrometer at room temperature in CDCl₃ solution. IR spectra were taken neat using a Nicolet IR200, spectrophotometer with an ATR sample stage. Only the most intense bands are reported. Elemental analyses were performed at Atlantic Microlabs, Norcross VA. Optical micrographs were obtained at room temperature using a model A1530 USB camera and Scope Image Plus image capture. Differential Scanning Calorimetry (DSC) measurements using a TA Instruments DSC Q200 were performed with a ramp rate of 10 °C min⁻¹. Two heating/cooling cycles were performed for each sample. Data discussed in this article is taken from the second heating/cooling cycle. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q500 at a ramp rate of 10 °C min⁻¹ using a platinum pan. Decomposition temperatures are reported for the inflection of the first mass loss.

ESI 1.2 Synthetic Procedures. CdCl₂, 4,4'-dimethyl-2,2'-bipyridine, 2,2'-bipyridine-4,4'-dicarboxylic acid, and various alcohols were obtained from Sigma-Aldrich and used without further purification. PtCl₂ was obtained from Stem Chemical and also used without further purification. (2-decyl) 2,2'-bipyridine-4,4'-dicarboxylate (L^{β10}) and (2-hexadecyl) 2,2'-bipyridine-4,4'-dicarboxylate (L^{β16}) were synthesized according to the general synthetic method of Pucci et al. [1] and were purified by triple recrystallization from hot ethanol. Characterization information for L^{β16} has been provided previously [2]. Silver dodecylsulfate (AgDOS) was synthesized according to literature procedure [3]. The solvent synthesis of PtL^{β16}Cl₂ has been previously reported [2]. Mechanochemical reactions were performed in a Spex 5100 Mixer Miller at 50 Hz using a 2.5 mL stainless steel grinding jar with a 6.35 mm diameter stainless steel ball or a 12 mL polystyrene grinding jar with a 9.5 mm diameter methacrylate ball. Yields reported herein are isolated recoveries. All mechanochemical reactions are quantitative as determined by ¹H NMR spectroscopy.

ESI 1.2.1 L^{β10} characterization. Yield: 53.1 %. IR (neat) $\tilde{\nu}_{\text{max}}$: cm⁻¹ 2862, 2797, 1689, 1262, 1218, 1112, 747. ¹H NMR (400 MHz, CDCl₃, δ): 8.90 (d, *J* = 1.6 Hz, 2H, ArH^{3,3'}), 8.85 (d, *J* = 4.6 Hz, 2H, ArH^{6,6'}), 7.88 (dd, *J* = 1.2, 4.5 Hz, 2H, ArH^{5,5'}), 5.20 (sex, *J* = 7.6 Hz, 2H, β-H), 1.77 (m, 2H, γ-Ha), 1.62 (m, 2H, γ-Hb), 1.36 (d, *J* = 6.0 Hz, 6H, α-H), 1.24 (br m, 24H, -OCHCH₂C₆H₁₂CH₃), 0.84 (t, *J* = 7.2 Hz, 6H, -CH₃). ¹³C NMR (CDCl₃, δ): 164.79 (C=O), 156.57 (ArC^{2,2'}), 150.02 (ArC^{6,6'}), 139.39 (ArC^{4,4'}), 123.22 (ArC^{5,5'}), 120.54 (ArC^{3,3'}), 73.08 (β-C), 35.90 (CH₂), 31.83 (CH₂), 29.45 (CH₂), 29.42 (CH₂), 29.20 (CH₂), 25.45 (CH₂), 22.63 (CH₂),

20.00 (α -C), 14.08 (CH₃). Anal. Calcd. for C₃₂H₄₈N₂O₄: C, 73.25; H, 9.22; N, 5.34. Found: C, 72.98; H, 9.09; N, 5.42.

ESI 1.2.3 CdL ^{β 16}Cl₂. In a steel vial, CdCl₂ (15.2 mg, 0.0829 mmol) and L ^{β 16} (56.3 mg, 0.0812 mmol) were premixed and then milled for 2 hours. The resulting product was dissolved in 10 mL of chloroform, and the mixture was filtered to remove excess CdCl₂. Chloroform was removed from the filtrate to yield the desired product as a pale brown to off-white solid. Yield (69.6 mg, 0.0794 mmol) 97.8%. IR (neat) $\tilde{\nu}_{\text{max}}$: cm⁻¹ 2866, 2799, 1692, 1245, 1222, 1101, 750, 709, 681. ¹H NMR (400 MHz, CDCl₃, δ) 9.36 (d, J = 4.4 Hz, 2H, ArH^{6,6'}), 8.79 (s, 2H, ArH^{3,3'}), 8.15 (d, J =4.8 Hz, 2H, ArH^{5,5'}), 5.25 (sex, J =6.4, 2H, β -H), 1.80 (m, 2H, γ -Ha), 1.65 (m, 2H, γ -Hb), 1.40 (d, J =5.6, 6H, α -H), 1.25 (br m, 48H, -OCHCH₂C₁₂H₂₄CH₃), 0.85 (t, J =6.8 Hz, 6H, -OCHCH₂C₁₂H₂₄CH₃). ¹³C NMR (CDCl₃, δ): 163.25 (C=O), 151.77 (ArC^{6,6'}), 149.36 (ArC^{2,2'}), 141.85 (ArC^{4,4'}), 125.76 (ArC^{5,5'}), 121.24 (ArC^{3,3'}), 74.31 (β -C), 35.84 (CH₂), 31.90 (CH₂), 29.68 (CH₂), 29.64 (CH₂), 29.52 (CH₂), 29.44 (CH₂), 29.35 (CH₂), 25.49 (CH₂), 22.67 (CH₂), 19.93 (α -C), 14.11 (CH₃). Anal. Calcd. for C₄₄H₇₂N₂O₄CdCl₂: C, 60.30; H, 8.28; N, 3.20. Found: C, 60.49; H, 8.24; N, 3.33.

ESI 1.2.5 PtL ^{β 16}Cl₂· x H₂O. In a steel vial, PtCl₂ (11.55 mg, 0.0432 mmol) and L ^{β 16} (19.5 mg, 0.0281 mmol) were premixed before milling for two hours. The reaction was dissolved in 5 mL of chloroform, transferred to a centrifuge tube and centrifuged, to remove excess PtCl₂. The solvent was then evaporated to yield a thick orange oily solid in quantitative yield, x =3.5, (28.9 mg, 0.028 mmol). The material is hygroscopic, but water is readily lost upon drying under vacuum. TGA, DSC, IR and ¹H NMR data are consistent with the literature [2].

ESI 1.2.6 [AgL ^{β 10}₂(DOS)]·H₂O. In a polystyrene vial, Ag(DOS) (25.8 mg, 0.0691 mmol) and L ^{β 10} (64.2 mg, 0.122 mmol) were premixed and ball milled for three hours. The obtained product was dissolved using 10 mL of hexanes to more easily remove it from the milling vial, pipet filtered and evaporated to dryness. The material was dissolved in 10 mL of chloroform, transferred to a centrifuge tube and centrifuged to remove excess silver salt. The solvent was evaporated off to give a yellow oily solid. Yield (85.5 mg, 0.0593 mmol) 97.0%. IR (neat) $\tilde{\nu}_{\text{max}}$: cm⁻¹ 2869, 2801, 1692, 1244, 1209, 1096, 748, 709. ¹H NMR (400 MHz, CDCl₃, δ) 8.95 (d, J =5.2 Hz, 4H, ArH^{6,6'}), 8.74 (s, 4H, ArH^{3,3'}), 8.00 (dd, J =1.2 Hz, J =4.8 Hz, 4H, ArH^{5,5'}), 5.22 (sex, J =6.4, 4H, β -H), 4.00 (t, J =6.6 Hz, 2H, -SOCH₂), 1.79 (m, 4H, γ -Ha), 1.6-1.5 (br m, 6H, γ -Hb and -SOCH₂CH₂), 1.39 (d, J =6.4, 12H, α -H), 1.3-1.2 (br m, 66H, -OCHCH₂C₆H₁₂CH₃ and -SO(CH₂)₂(CH₂)₉CH₃), 0.85 (t, J =6.8 Hz, 15H, -OCHCH₂C₆H₁₂CH₃ and -SO(CH₂)₂(CH₂)₈CH₃). ¹³C NMR (CDCl₃, δ): 163.90 (C=O), 153.27 (ArC^{6,6'}), 151.81 (ArC^{2,2'}), 140.42 (ArC^{4,4'}), 124.53 (ArC^{5,5'}), 121.36 (ArC^{3,3'}), 73.85 (β -C), 68.52 (-SOCH₂), 35.85 (CH₂), 31.89 (CH₂), 31.82 (CH₂), 30.93 (CH₂), 29.64 (CH₂), 29.62 (CH₂), 29.59 (CH₂), 29.57 (CH₂), 29.45 (CH₂), 29.41 (CH₂), 29.34 (CH₂), 29.21 (CH₂), 25.80 (CH₂), 25.45 (CH₂), 22.67 (CH₂), 22.63 (CH₂), 19.96 (α -C), 14.08 (CH₃). Anal. Calcd. for C₇₆H₁₂₃N₄SO₁₃Ag: C, 63.36; H, 8.61; N, 3.89. Found: C, 63.25; H, 8.59; N, 3.85.

ESI 1.2.7 AgL^{β16}₂(DOS). In a polystyrene vial, Ag(DOS) (157.4 mg, 0.423 mmol) and L^{β16} (580.9 mg, 0.838 mmol) were premixed and ball milled for three hours. After the first hour of milling, a second ball was added to the mill to help minimize the ball sticking due to the relatively large amount of reagents for the size of the vial. The obtained product was washed out of the vial using 10 ml of hexanes, evaporated to dryness, dissolved in 10 mL of chloroform, centrifuged and evaporated to dryness to give a yellow oily solid. Yield (700.8 mg, 0.398 mmol) 95.0%. IR (neat) $\tilde{\nu}_{\max}$: cm⁻¹ 2867, 2799, 1692, 1221, 1101, 748, 708. ¹H NMR (400 MHz, CDCl₃, δ) 8.94 (d, *J*=5.6 Hz, 4H, ArH^{6,6'}), 8.76 (s, 4H, ArH^{3,3'}), 8.00 (dd, *J*=1.2 Hz, *J*=4.8 Hz, 4H, ArH^{5,5'}), 5.22 (sex, *J*=6.4 Hz, 4H, β-H), 4.05 (t, *J*=6.9 Hz, 2H, -SOCH₂C₁₀H₂₀CH₃), 1.77 (m, 4H, γ-Ha), 1.62 (br m, H, 6H, γ-Hb and -SOCH₂CH₂C₉H₁₈CH₃), 1.38 (d, *J*=6.0 Hz, 12H, α-H), 1.32 (br m, 114H, -OCHCH₂C₁₂H₂₄CH₃, -SOCH₂CH₂C₉H₁₈CH₃), 0.85 (t, *J*=6.9 Hz, 15H, -OCHCH₂C₁₂H₂₄CH₃, -SOCH₂C₁₀H₂₀CH₃). ¹³C NMR (CDCl₃, δ): 164.13 (C=O), 153.82 (ArC^{2,2'}), 151.52 (ArC^{6,6'}), 140.40 (ArC^{4,4'}), 124.43 (ArC^{5,5'}), 121.34 (ArC^{3,3'}), 73.84 (β-C), 68.61 (-SOCH₂), 35.97 (CH₂), 32.00 (CH₂), 29.77 (CH₂), 29.67 (CH₂), 29.62 (CH₂), 29.53 (CH₂), 29.44 (CH₂), 29.34 (CH₂), 25.92 (CH₂), 25.56 (CH₂), 22.77 (CH₂), 20.06 (α-C), 14.21 (CH₃). Anal. Calcd. for C₁₀₀H₁₆₉N₄SO₁₂Ag: C, 68.27; H, 9.68; N, 3.18. Found: C, 68.32; H 9.65; N, 3.24.

ESI 1.2.8 [AgL^{β10}NO₃]. In a polystyrene vial, AgNO₃ (73.6 mg, 0.433 mmol) and L^{β10} (69.9 mg, 0.133 mmol) were premixed and ball milled for three hours. The obtained product and excess silver salt were washed out of the vial using 5 mL of hexanes and evaporated to dryness. The product was then dissolved in 10 mL of chloroform, transferred to a centrifuge tube and centrifuged to remove excess silver salt. The solvent was then evaporated off to give a yellow solid. Yield (83.1 mg, 0.120 mmol) 89.8%. IR (neat) $\tilde{\nu}_{\max}$: cm⁻¹ 2870, 2802, 1690, 1245, 1221, 1096, 748, 709. ¹H NMR (400 MHz, CDCl₃, δ) 8.95 (d, *J*=5.2 Hz, 2H, ArH^{6,6'}), 8.76 (s, 2H, ArH^{3,3'}), 8.07 (dd, *J*=1.2 Hz, *J*=4.8 Hz, 2H, ArH^{5,5'}), 5.24 (sex, *J*=6.4, 2H, β-H), 1.79 (m, 2H, γ-Ha), 1.65 (m, 2H, γ-Hb), 1.40 (d, *J*=6.4, 6H, α-H), 1.4-1.2 (br m, 24H, -OCHCH₂C₆H₁₂CH₃), 0.85 (t, *J*=7.2 Hz, 6H, -OCHCH₂C₆H₁₂CH₃). ¹³C NMR (CDCl₃, δ): 163.66 (C=O), 152.56 (ArC^{6,6'}), 151.94 (ArC^{2,2'}), 141.05 (ArC^{4,4'}), 125.06 (ArC^{5,5'}), 121.79 (ArC^{3,3'}), 74.26 (β-C), 35.94 (CH₂), 31.91 (CH₂), 29.55 (CH₂), 29.49 (CH₂), 29.30 (CH₂), 25.54 (CH₂), 22.73 (CH₂), 20.06 (α-C), 14.18 (CH₃). Anal. Calcd. for C₃₂H₄₈N₃O₇Ag: C, 55.33; H, 6.97; N, 6.05. Found: C, 55.37; H, 6.81; N, 6.08.

ESI 1.2.9 [AgL^{β16}NO₃]. In a polystyrene vial, AgNO₃ (37.0 mg, 0.218 mmol) and L^{β16} (77.9 mg, 0.112 mmol) were premixed and ball milled for three hours. After the first hour of milling, a second ball was added to the mill to reduce ball-sticking due to the relatively large reaction volume relative to the size of the vial. The obtained product and excess salt were washed out of the vial using 10 mL of hexanes and evaporated to dryness. The product will incorporate hexanes, which can be removed by drying under vacuum, either before or after removal of the excess silver salt. To remove the excess silver salt, the product was dissolved in chloroform and the mixture was centrifuged. The decantate solution was then evaporated to give a yellow liquid. Yield (93.6 mg, 0.108 mmol) 96.5%. IR (neat) $\tilde{\nu}_{\max}$: cm⁻¹ 2867, 2800, 1691, 1246, 1223, 1101, 748, 708. ¹H NMR (400 MHz, CDCl₃, δ) 8.98 (d, *J*=4.8 Hz, 2H, ArH^{6,6'}),

8.73 (s, 2H, ArH^{3,3'}), 8.09 (dd, $J=1.2$ Hz, $J=4.8$ Hz, 2H, ArH^{5,5'}), 5.24 (sex, $J=6.4$, 2H, β -H), 1.79 (m, 2H, γ -Ha), 1.65 (m, 2H, γ -Hb), 1.40 (d, $J=6.4$, 6H, α -H), 1.2-1.4 (br m, 48H, -OCHCH₂C₁₂H₂₄CH₃), 0.85 (t, $J=6.8$ Hz, 6H, -OCHCH₂C₁₂H₂₄CH₃). ¹³C NMR (CDCl₃, δ): 163.37 (C=O), 152.21 (ArC^{6,6'}), 151.85 (ArC^{2,2'}), 141.20 (ArC^{4,4'}), 125.23 (ArC^{5,5'}), 121.85 (ArC^{3,3'}), 74.32 (β -C), 35.84 (CH₂), 31.90 (CH₂), 29.67 (CH₂), 29.64 (CH₂), 29.57 (CH₂), 29.51 (CH₂), 29.41 (CH₂), 29.34 (CH₂), 25.46 (CH₂), 22.67 (CH₂), 19.95 (α -C), 14.11 (CH₃). Anal. Calcd. for C₄₄H₇₂N₃O₇Ag: C, 61.24; H, 8.41; N, 4.87. Found: C, 61.01; H, 8.34; N, 4.85.

References

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ESI 2. Differential Scanning Calorimetry.

ESI Figure 1. DSC trace for $\text{CdL}^{\beta 16}\text{Cl}_2$ over two cycles with initial heating from the as purified product.

ESI Figure 2. DSC trace for $[\text{AgL}^{\beta 16}\text{NO}_3]$ over two cycles with initial heating from the as purified product.

ESI Figure 3. DSC trace for [AgL^{β16}₂](DOS) over two cycles with initial heating from the as purified product. Sample was dried in a vacuum oven prior to analysis.

ESI Figure 4. DSC trace for [AgL^{β10}₂](DOS) over two cycles with initial heating from the as purified product.

ESI Figure 5. DSC trace for $[\text{AgL}^{\beta 10}\text{NO}_3]$ over two cycles with initial heating from the as purified product.