Electronic Supporting Information

Kinetic analysis of the mechanochemical syntheses of dialkyl 2,2'-bipyridyl-4,4'-dicarboxylate complexes of palladium

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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. The CDCl₃ was stored over activated alumina to remove trace HCl in the solution. Trace acid can result in protonation of the complexes below. Elemental analyses were performed at Atlantic Microlabs, Norcross VA. The lack of liquid crystalline behavior for these complexes was determined via polarized optical microscopy 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. Various alcohols, PdI₂, and PdCl₂ were obtained from Sigma-Aldrich. Ark Pharm was the source of 2,2'-bipyridine-4,4'-dicarboxylic acid, which was also utilized without further purification. PtCl₂ was obtained from Stem Chemical or Sigma-Aldrich. All reagents were utilized without further purification. Dialkyl 2,2'-bipyridine-4,4'-dicarboxylate (Lⁿ) complexes 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 all ligands has been reported previously [1-3]. Mechanochemical reactions were performed in a Spex 5100 Mixer Miller at 3000 cycles per minute (back-and-forth motions of the sample vial) using a 2.5 mL stainless steel grinding jar with a 6.35 mm diameter stainless steel ball. The mechanochemical syntheses discussed below are quantitative as determined by ¹H NMR spectroscopy.

ESI 1.2.1 PdL^{β10}I₂. In a steel vial, PdI₂ (174.0 mg, 0.4830 mmol) and L^{β10} (204.6 mg, 0.3898 mmol) were premixed before milling for 60 min. The reaction was dissolved in 5 mL of chloroform and filtered to remove excess PdI₂. The solvent was then evaporated to yield a dark red, paste-like in quantitative yield. The material is hygroscopic, but water is readily lost upon drying under vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 10.19 (d, *J* = 6.0 Hz, 2H, ArH^{6,6'}), 8.65 (s, 2H, ArH^{3,3'}), 8.11 (dd, *J* = 0.8, 5.6 Hz, 2H, ArH^{5,5'}), 5.26 (sex, *J* = 6.0 Hz, 2H, β-H), 1.80 (m, 2H, γ-Ha), 1.68 (m, 2H, γ-Hb), 1.41 (d, *J* = 6.4 Hz, 6H, α-H), 1.4-1.2 (br m, 24H, -OCHCH₂C₆H₁₂CH₃), 0.85 (t, *J* = 6.0 Hz, 6H, -CH₃). ¹³C NMR (CDCl₃, δ): 162.56 (C=O),

156.29 (ArC^{2,2'}), 155.01 (ArC^{6,6'}), 140.85 (ArC^{4,4'}), 126.84 (ArC^{5,5'}), 122.68 (ArC^{3,3'}), 74.94 (β -C), 35.80 (γ -CH₂), 31.81 (CH₂), 29.45 (CH₂), 29.38 (CH₂), 29.21 (CH₂), 25.45 (CH₂), 22.63 (CH₂), 19.95 (α -C), 14.09 (CH₃). Anal. Calcd. for C₃₂H₄₈N₂O₄PdI₂: C, 43.42; H, 5.48; N, 3.17. Found: C, 43.61; H, 5.55; N, 3.23.

ESI 1.2.2 PdL ^{β 16}I₂. In a steel vial, PdI₂ (205.1 mg, 0.5694 mmol) and L ^{β 16} (171.9 mg, 0.2480 mmol) were premixed before milling for 3 minutes. The reaction was dissolved in 5 mL of chloroform and filtered to remove excess PdI₂. The solvent was then evaporated to yield a voluminous dark red powder in quantitative yield. The material is hygroscopic, but water is readily lost upon drying under vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 10.15 (d, J = 5.2 Hz, 2H, ArH^{6,6'}), 8.65 (s, 2H, ArH^{3,3'}), 8.10 (dd, J = 2.0, 6.0 Hz, 2H, ArH^{5,5'}), 5.26 (sex, J = 6.8 Hz, 2H, β -H), 1.80 (m, 2H, γ -Ha), 1.67 (m, 2H, γ -Hb), 1.41 (d, J = 6.4 Hz, 6H, α -H), 1.4-1.2 (br m, 48H, -OCHCH₂C₁₂H₂₄CH₃), 0.85 (t, J = 7.2 Hz, 6H, -CH₃). ¹³C NMR (CDCl₃, δ): 162.79 (C=O), 156.29 (ArC^{2,2'}), 155.30 (ArC^{6,6'}), 141.08 (ArC^{4,4'}), 127.08 (ArC^{5,5'}), 122.84 (ArC^{3,3'}), 75.19 (β -C), 36.04 (γ -CH₂), 32.14 (CH₂), 29.91 (CH₂), 29.89 (CH₂), 29.81 (CH₂), 29.79 (CH₂), 29.64 (CH₂), 29.59 (CH₂), 25.70 (CH₂), 22.91 (CH₂), 20.18 (α -C), 14.36 (CH₃). Anal. Calcd. for C₄₄H₇₂N₂O₄PdI₂: C, 50.17; H, 6.90; N, 2.66. Found: C, 50.45; H, 6.77; N, 2.62.

ESI 1.3 Kinetic Sampling. Reaction mixtures were prepared similar to those discussed above in PdI₂:Lⁿ ratios appropriate to the experiment. The reaction mixture was typically sampled at 1, 2, 3, 5, and 10 minute intervals and then every 10 minutes thereafter. Samples were dissolved in CDCl₃ that had been treated to remove trace acid (see above) and filtered to remove unreacted PdI₂ prior to ¹H NMR spectroscopic analysis.

References

- [1] Pucci D, Barberio G, Crispini A, Ghedini M, Francescangeli O. Induction of mesomorphism through supramolecular association in Coordination Pd(II) compounds of dialkyl 2,2'-bipyridine-4,4'-dicarboxylates. *Mol. Cryst. Liq. Cryst.* 2003;395:325-335.
- [2] Hyatt MG, Allenbaugh RJ. Mechanochemical synthesis and thermal property investigation of metallomesogens and transition metal complexes. *Liq. Cryst.* 2015;42(1):113-118.
- [3] Allenbaugh RJ, Aoyama Y, Hyatt MG, Reynolds TH, Morgan ML, Adler AM, et al. Dialkyl 2,2'-bipyridine-4,4'-dicarboxylate complexes of Pt^{II}, Cd^{II} and Re^I: the effects of metal centre geometry and ligand substitution on phase behaviour. *Liq. Cryst.* 2013;40(6):783-786.

ESI 2. Differential Scanning Calorimetry.

ESI Figure 1. DSC trace for $\text{PdL}^{\beta 10}\text{I}_2$ over two cycles with initial heating from the as purified product.

ESI Figure 2. DSC trace for $\text{PdL}^{\beta 16}\text{I}_2$ over two cycles with initial heating from the as purified product.

ESI 3. ^1H NMR spectroscopy

ESI Figure 3. Aromatic region of the ^1H NMR spectra for the synthesis of $\text{PdL}^{\beta 10}\text{I}_2$. The resonances at ~ 8.1 and ~ 7.9 ppm correspond to the 5,5' aromatic protons of the complex and free ligand, respectively, and were utilized to determine relative concentrations of the two species. These data correspond to the plots for $\text{PdL}^{\beta 10}\text{I}_2$ shown in Figures 2 and 3 of the main text, and correspond to 1, 3, 5, 10, 15, 20, 30, 40, 50, 60, 70, and 80 minutes of reaction time (beginning with the bottom trace).

ESI 4. Rate related parameters (k).

ESI Table 1. Rate related parameters (k) values for fitting of linear models to kinetic data. The data from individual reactions was fitted to each model. Over all the resulting fits, the minimum and maximum k values for each model were determined to give the range of R^2 values presented here. Model fittings designated with * include a point at $t=0$, where defined.

Model	$\text{PdL}^{\beta^{10}}\text{I}_2$	$\text{PdL}^{\alpha^{16}}\text{I}_2$	$\text{PdL}^{\beta^{16}}\text{I}_2$
P2	0.0033-0.0105	0.0027-0.0065	0.0031-0.0032
P3	0.0023-0.0077	0.0039-0.0054	0.0025-0.0026
P4	0.0018-0.0060	0.0037-0.0050	0.0021-0.0022
A2	0.0142-0.0327	0.0040-0.0185	0.0044-0.0044
A3	0.0086-0.0216	0.0028-0.0121	0.0034-0.0035
A4	0.0062-0.0162	0.0048-0.0093	0.0027-0.0028
B1	0.0475-0.1131	0.0174-0.0697	0.0167-0.0178
R2	0.0073-0.0194	0.0005-0.0074	0.0023-0.0023
R3	0.0073-0.0202	0.0003-0.0071	0.0016-0.0017
D1	0.0077-0.0216	0.0001-0.0081	0.0025-0.0027
D2	0.0096-0.0223	0.0001-0.0087	0.0016-0.0017
D3	0.0070-0.0194	0.0005-0.0074	0.0023-0.0023
D4	0.0030-0.0076	0.00001-0.0026	0.0004-0.0004
F0/R1	0.0051-0.0162	0.0009-0.0078	0.0036-0.0036
F1	0.0387-0.0803	0.0010-0.0625	0.0057-0.0059
F2	0.3375-1.2832	0.0010-0.7392	0.0092-0.0100
F3	2.0300-53.2030	0.0011-33.5830	0.0153-0.0175
P2*	0.0060-0.0177	0.0027-0.0072	0.0040-0.0041
P3*	0.0054-0.0160	0.0039-0.0057	0.0037-0.0038
P4*	0.0050-0.0150	0.0035-0.0048	0.0034-0.0053
A2*	0.0169-0.0442	0.0028-0.0225	0.0053-0.0055
A3*	0.0121-0.0347	0.0040-0.0141	0.0046-0.0047
A4*	0.0099-0.0301	0.0048-0.0105	0.0041-0.0042
B1*	0.0475-0.1131	0.0174-0.0889	0.0167-0.0178
R2*	0.0080-0.0217	0.0005-0.0093	0.0025-0.0026
R3*	0.0076-0.0212	0.0003-0.0085	0.0018-0.0018
D1*	0.0084-0.0239	0.0001-0.0106	0.0026-0.0028
D2*	0.0097-0.0237	0.0001-0.0102	0.0016-0.0018
D3*	0.0077-0.0217	0.0005-0.0093	0.0025-0.0026
D4*	0.0029-0.0076	0.00001-0.0032	0.0004-0.0004
F0/R1*	0.0067-0.0211	0.0009-0.0096	0.0040-0.0041
F1*	0.0385-0.0801	0.0001-0.0646	0.0061-0.0065
F2*	0.3303-1.2314	0.0001-0.7766	0.0097-0.0106
F3*	1.8772-50.7320	0.0011-35.4480	0.0158-0.0181