

Electronic Supplementary Information for

Unsuspected mesomorphism in “tail-free” cyclopalladated 3,5-disubstituted-2,2'-pyridylpyrroles

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General Methods

¹H NMR spectra were acquired on a Bruker Avance DRX-300 spectrometer in CDCl₃ solution, with TMS as internal standard. Infrared spectra were recorded with a Spectrum One FT-IR Perkin-Elmer spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer by the Microanalytical Laboratory at University of Calabria. The thermal behaviour of all samples was studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam CO 600 heating stage. The transition temperatures and enthalpies were measured on a Perkin-Elmer Pyris1 Differential Scanning Calorimeter with a heating and cooling rate of 10 °C/min. The apparatus was calibrated with indium. Three heating/cooling cycles were performed on each sample. The powder X-ray diffraction patterns of **5** and **6** at variable temperature were obtained using a Bruker AXS General Area Detector Diffraction System (D8 Discover with GADDS) with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). Measurements were performed by placing samples in Lindemann capillary tubes with an inner diameter of 0.5 mm. The highly sensitive area detector was placed at a distance of 20 cm from the sample (2θ detector placed at 14°) and equipped with a CalCTec (Italy) heating stage. The samples were heated at a rate of $5.0 \text{ }^\circ\text{C min}^{-1}$ to the appropriate temperature, and then cooled down at the same rate lowering the temperature step by step. XRD spectra in the mesophase were recorded with an exposure time of 2 hours.

All commercially available starting materials (Sigma-Aldrich Chemical Co) 1,1,1,5,5,5-hexafluoropentane-2,4-dione (98 %), 2-(aminomethyl)pyridine (99 %), tosic acid (98.5 %), palladium(II) acetate (99.98 %) were used as received without further purification.

Syntheses and Analytical Data

The 3,5-dimethyl-2-(2'-pyridyl)pyrrole (**HL**¹) has been prepared as reported in the literature (ref.7).

The 3,5-bis(trifluoromethyl)-2-(2'-pyridyl)pyrrole (**HL**²) has been prepared as follow: 1,1,1,5,5,5-hexafluoropentane-2,4-dione (0.80 g, 3.85 mmol) and 2-(aminomethyl)pyridine (0.42 g, 3.85 mmol) along with a catalytic amount of tosic acid (0.11 g, 0.60 mmol) were added to xylenes (20 mL). The reaction flask was fitted with a Dean-Stark trap (xylenes, 20 mL) and a reflux condenser. The apparatus was flushed with nitrogen and stirred at room temperature for 30 min. The mixture was then heated to reflux (170 °C) for 72 h with progressive additions of sulfuric acid (0.22 mL, 4.10 mmol). The reaction was monitored by GC/MS to monitor product formation. The mixture was extracted with a saturated solution of ammonium chloride and, following removal of solvent, the product was obtained as a green solid in a 48% yield (0.52 g.). M.p. 90°C.

¹H NMR (CDCl₃, ppm) δ 10.60 (1H, br s, H¹), 8.60 (1H, d, H⁶), 7.84 (2H, m, H⁵H³), 7.30 (1H, t, H⁴), 6.89 (1H, s, H⁴).

¹⁹F NMR (CDCl₃, ppm) δ 57.79 (s), 62.00 (s).

FT-IR (KBr, cm⁻¹): 3139, 2315, 1605.

Anal. Calc. for C₁₁H₆N₂F₆: C, 47.14; H, 2.14; N, 10.00 %. Found: C, 47.48; H, 2.34; N, 10.38 %.

Complex 1. To a stirred solution of Palladium(II) acetate (0.20 g, 0.89 mmol) in 15 mL of dichloromethane was added the stoichiometric amount of **HL**¹ (0.15 g, 0.89 mmol), the resulting red solution was stirred at room temperature for 2 h. The dark solution formed was evaporated under reduced pressure adding cyclohexane and methanol for eliminating the acetic acid formed.

The dark purple product was recrystallized from chloroform and ethyl acetate. The solid was collected by filtration and dried under vacuum. Yield 0.17 g, 55%. M.p. 214° C.

¹H NMR (CDCl₃, ppm) δ 7.36 (1H, d, H⁶), 7.28 (1H, t, H⁵), 6.82 (1H, d, H³), 6.30 (1H, t, H⁴), 5.15 (1H, s, H⁴), 2.12 (3H, s, CH₃), 2.06 (3H, s, CH₃), 1.85 (3H, s, CH₃).

FT IR (KBr, cm⁻¹) 1608, 1564, 1490, 1417, 1355, 769.

Anal. Calc. for C₂₆H₂₈N₄O₄Pd₂: C, 46.36; H, 4.16; N, 8.32 %. Found: C, 46.57; H, 4.38; N, 8.72 %.

Complex 2. To a stirred solution of Palladium(II) acetate (0.20 g, 0.89 mmol) in 15 mL of dichloromethane was added the stoichiometric amount of **HL**² (0.25 g, 0.89 mmol), the resulting green solution was stirred at room temperature for 2 h. The brown-green solution formed was evaporated under reduced pressure adding cyclohexane and methanol to eliminate the acetic acid

formed. The greenish product was recrystallized from chloroform and ethyl acetate. The solid was collected by filtration and dried under vacuum. Yield 0.24 g, 30%. M.p. 265° C.

^1H NMR (CDCl_3 , ppm) δ 7.73 (1H, d, H^6), 7.62 (1H, t, H^5), 7.46 (1H, d, H^3), 6.75 (1H, t, H^4), 6.38 (1H, s, H^4), 2.18 (3H, s, CH_3).

^{19}F NMR (CDCl_3 , ppm) δ 58.92 (s), 61.90 (s).

FT IR: (KBr, cm^{-1}) 1610, 1566, 1470, 1296, 1233, 1142, 1107, 995, 774, 730.

Anal.Calc. for $\text{C}_{26}\text{H}_{16}\text{N}_4\text{O}_4\text{F}_{12}\text{Pd}_2$: C, 35.13; H, 1.80; N, 6.31 %. Found: C, 35.44; H, 1.91; N, 6.67 %.

Complex 3. To a suspension of complex **1** (0.10 g, 0.15 mmol) in ethanol was added K(acac) (0.06 g, 0.44 mmol), the resulting red solution was stirred at room temperature for 6 h. The orange solid formed was collected by filtration and then recrystallized from chloroform and ethanol. Yield 0.06 g, 54%.

M.p. 176 °C.

^1H NMR (CDCl_3 , ppm) δ 8.08 (1H, d, H^6), 7.52 (1H, t, H^5), 7.21 (1H, d, H^3), 6.66 (1H, t, H^4), 5.68 (1H, s, H^4), 5.45 (1H, s, H^a), 2.33 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.07 (3H, s, CH_3), 2.04 (3H, s, CH_3).

FT IR: (KBr, cm^{-1}) 1605, 1581, 1521, 1491, 1358, 1272, 1154, 764, 736.

Anal.Calc. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2\text{Pd}$ C, 51.03; H, 4.78; N, 7.45 %. Found: C, 51.35; H, 4.55; N, 7.38 %.

Complex 4. Yield 44%. M.p. 236° C (dec.).

^1H NMR (CDCl_3 , ppm) δ 8.35 (1H, d, H^6), 7.78 (2H, m, H^5H^3), 7.11 (1H, t, H^5), 6.79 (1H, s, H^4), 5.52 (1H, s, H^a), 2.18 (6H, sb, CH_3).

^{19}F NMR (CDCl_3 , ppm) δ 58.20 (s), 62.14 (s).

FT IR: (KBr, cm^{-1}) 3598, 1610, 1234, 711.

Anal.Calc. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{F}_6\text{Pd}$ C, 39.40; H, 2.48; N, 5.74 %. Found: C, 39.70; H, 2.85; N, 5.63 %.

Complex 5. To a suspension of complex **1** (0.10 g, 0.15 mmol) in methanol was added the 1,1,1,5,5,5-hexafluoropentane-2,4-dione (0.15 g, 0.74 mmol), the mixture was stirred at room temperature for 24h. The brown solid formed was collected by filtration and then recrystallized from chloroform and methanol. Yield 0.14 g 97%.

^1H NMR (CDCl_3 , ppm) δ 7.81 (1H, d, H^6), 7.55 (1H, t, H^5), 7.20 (1H, d, H^3), 6.67 (1H, t, H^4), 6.29 (H, s, H^a), 5.65 (1H, s, H^4), 2.31 (3H, s, CH_3), 2.26 (3H, s, CH_3).

^{19}F NMR (CDCl_3 , ppm) δ 43.43 (s), 44.24 (s).

FT IR: (KBr, cm^{-1}) 1629, 1608, 1548, 1493, 1261, 1147, 1104, 764, 733.

Anal.Calc. for $C_{16}H_{12}N_2O_2F_6Pd$: C, 39.67; H, 2.48; N, 5.78 %. Found: C, 40.06; H, 2.11; N, 5.73 %.

Complex 6.

Yield 63%. 1H NMR ($CDCl_3$, ppm) δ 8.15 (1H, d, H^6), 7.92 (1H, t, H^5), 7.84 (1H, d, H^3), 7.19 (1H, t, H^4), 6.78 (1H, s, H^a), 6.43 (1H, s, H^4).

^{19}F NMR ($CDCl_3$, ppm) δ 43.89 (s), 44.37 (s), 58.20 (s), 62.14 (s).

FT IR: (KBr, cm^{-1}) 1630, 1569, 1532, 1472, 1260, 1226, 1150, 1108, 997, 775, 743.

Anal.Calc. for $C_{16}H_{12}N_2O_2F_{12}Pd$. C, 32.43; H, 1.01; N, 4.73 %. Found: C, 32.53; H, 0.94; N, 5.01 %.

DSC Measurements

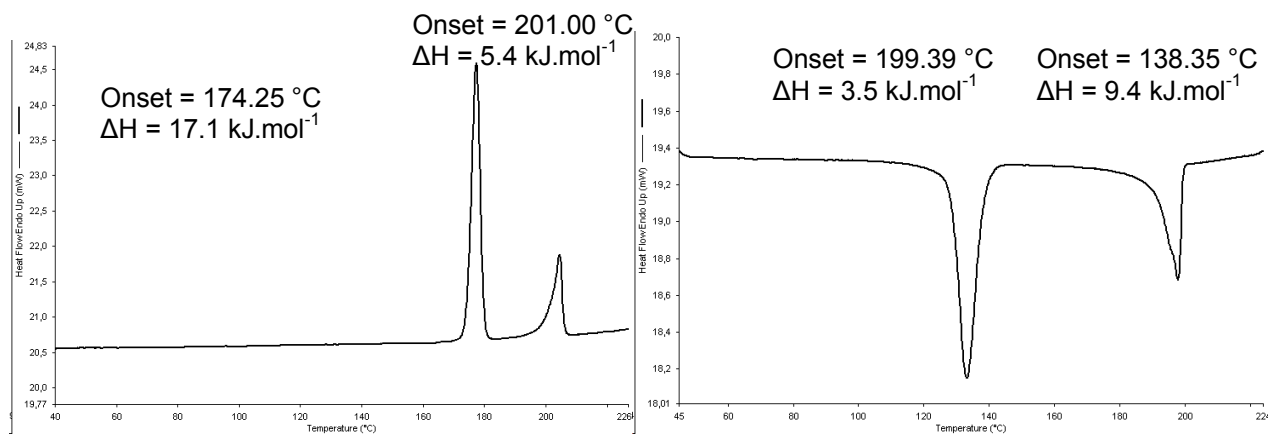


Figure S1. DSC thermograms for complex 5 a) second heating and b) second cooling scan.

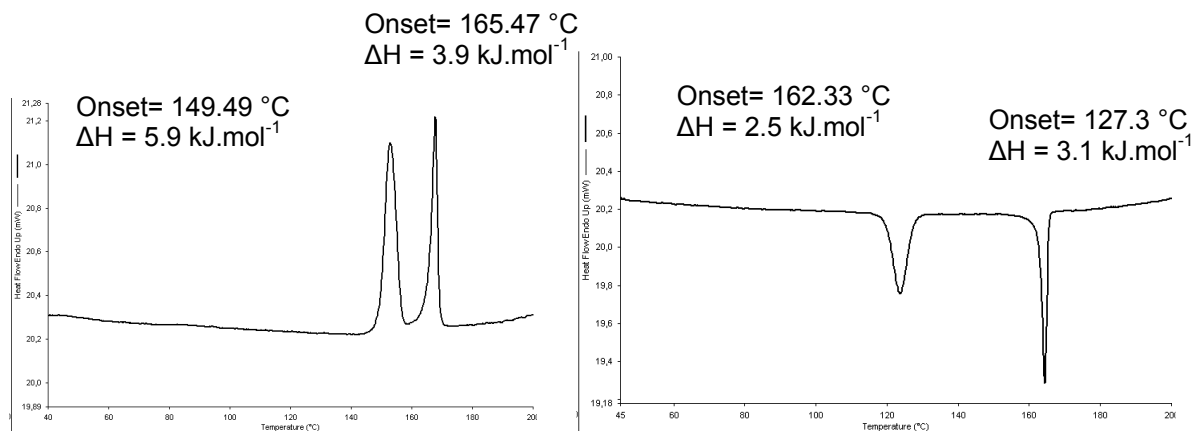


Figure S2. DSC thermograms for complex 6 a) second heating and b) second cooling scan.

Powdered X-ray diffraction

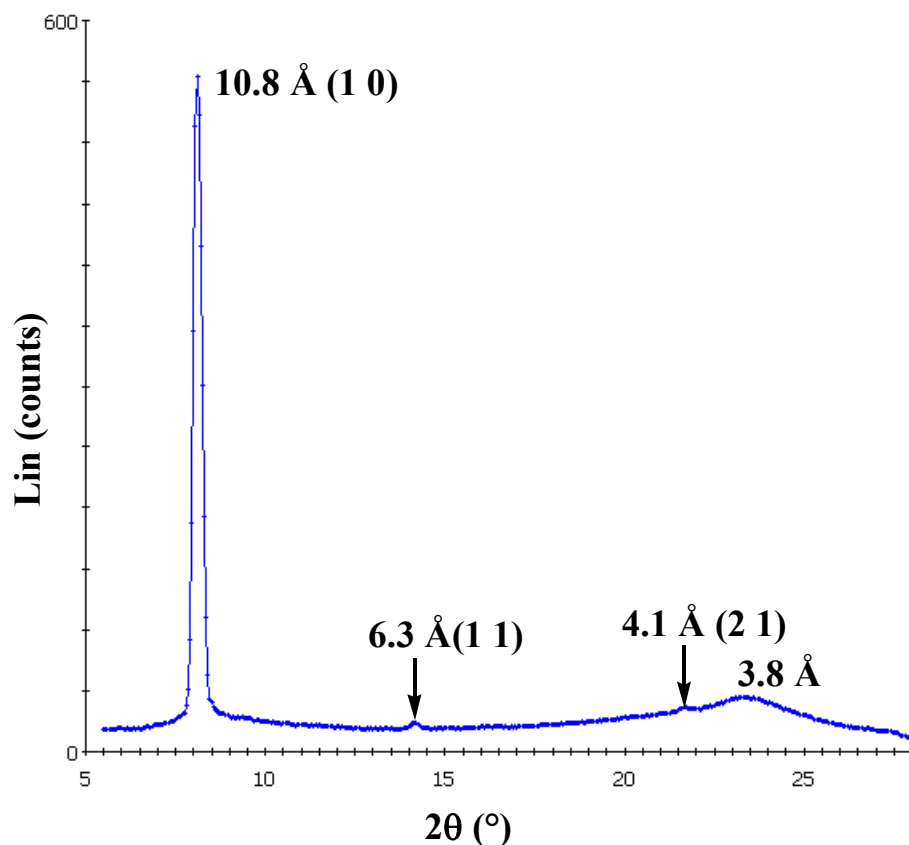


Figure S3. X-Ray diffraction pattern of complex 6 (140 °C on cooling).

X-RAY DIFFRACTION DATA DETAILS

X-ray Crystallography.

Suitable crystals for the X-ray analysis for complexes **3-6** were obtained by layering ethylic ether on dichloromethane solutions. The intensity data were collected at room temperature on a Bruker-Nonius X8 Apex CCD area detector single crystal diffractometers both equipped with graphite monochromator and MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were processed through the *SAINT*^{S1} reduction and *SADABS*^{S2} absorption software. The structures were solved by direct methods through the *SHELXTL-NT*^{S3} structure determination package and refined by full-matrix least-squares based on F^2 . Generally, all non-hydrogen atoms were refined anisotropically and hydrogen

atoms were included as idealized atoms riding on the respective carbon atoms with C-H bond lengths appropriate to the carbon atom hybridization. In the case of complex **5**, the fluorine atoms of one the CF₃ group of the hexafluoroacetylacetonate ligand are disordered in two sets A and B with group occupancy of about 0.5 and therefore introduced in the refinement isotropically.

References to Supplementary Information

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- S1 *SAINTE*, Version 6.45 Copyright (c) 2003, Bruker Analytical X-ray Systems Inc.
- S2 G.M. Sheldrick, *SADABS*. Version 2.10, Bruker AXS Inc., Madison, WI, USA, 2003
- S3 *SHELXTL-NT*, Version 5.1 Copyright (c) 1999, Bruker Analytical X-ray Systems Inc.