Electronic Supplementary Information for Dalton Transactions

Mesomorphism of ionic allylpalladium(II) complexes containing pzR2py as ligands and $[BF_4]^-$, $[PF_6]^-$ or $[CF_3SO_3]^-$ as counteranions (pzR2py = 2-[3,5-bis(4-alkyloxyphenyl)pyrazol-1-yl]pyridine)

Mari Carmen Torralba[a], José Antonio Campo[a], José Vicente Heras[a], Duncan W. Bruce[b] and Mercedes Cano[a,*]

[a] *Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 MADRID, Spain*

[b] *Department of Chemistry, University of York, Heslington, YORK YO10 5DD, UK*

SUPPLEMENTARY INFORMATION

Spectroscopic data of the compounds studied:

• *2-[3,5-bis(4-decyloxyphenyl)pyrazol-1-yl]pyridine ($pz^{dp2}py$)*

$pz^{dp2}py$:. IR (KBr, cm^{-1}): ν(CN) 1614 (vs), $\gamma(CH)_{py}$ 792 (m). ^{1}H-NMR ($CDCl_3$, *δ*, *J* in Hz): 8.42 (ddd, ^3J = 4.9, ^4J = 2.0, ^5J = 0.8, 1H, H6), 7.85 (d, ^3J = 9.0, 2H, H*o*), 7.74 (ddd, ^3J = 8.1, ^3J = 7.3, ^4J = 2.0, 1H, H4), 7.49 (ddd, ^3J = 8.1, ^4J = ^5J = 1.0, 1H, H3), 7.22 (d, ^3J = 8.8, 2H, H*o*), 7.20 (ddd, ^3J = 7.2, ^3J = 4.8, ^4J = 1.0, 1H, H5), 6.95 (d, ^3J = 9.0, 2H, H*m*), 6.84 (d, ^3J = 9.0, 2H, H*m*), 6.71 (s, 1H, H4'), 4.00 (t, ^3J = 6.8, 2H, OCH_2), 3.96 (t, ^3J = 6.6, 2H, OCH_2), 1.79 (m, 4H, CH_2), 1.5-1.2 (m, 28H, CH_2), 0.88 (t, ^3J = 6.8, 6H, CH_3).

• *[Pd(η^3-C_3H_5)($pz^{R2}py$)][BF_4] (R = $C_6H_4OC_nH_{2n+1}$; n = 10* (**I_{10}**)*, 12* (**I_{12}**)*, 14* (**I_{14}**)*, 16* (**I_{16}**)*, 18* (**I_{18}**)*)*

Spectroscopic data are given for **I_{10}**. Data for the other homologues are essentially identical, varying only in the integration of the signal at *δ* 1.5-1.2.

[Pd(η^3-C_3H_5)($pz^{dp2}py$)][BF_4] (**I_{10}**): IR (KBr, cm^{-1}): ν(CN) 1610 (vs), $\gamma(CH)_{py}$ 772 (s), ν(BF) 1053 (vs), δ(FBF) 518 (w).^{1}H-NMR ($CDCl_3$; *δ*, *J*, in Hz): 8.87 (d, ^3J = 4.0, 1H, H6), 7.80 (ddd, ^3J = 8.7, ^3J = 7.3, ^4J = 1.7, 1H, H4), 7.58 (d, ^3J = 8.8, 2H, H*o*), 7.56 (1H, H5, masked by the H*o* protons), 7.39 (d, ^3J = 8.8, 2H, H*o*), 7.06 (d, ^3J = 8.6, 2H, H*m*), 7.04 (d, ^3J = 8.6, 2H, H*m*), 6.97 (d, ^3J = 8.8, 1H, H3), 6.70 (s, 1H, H4'), 5.68 (m, ^3J_a = 12.7, ^3J_s = 6.3, 1H, H*meso*(C_3H_5)), 4.57 (br, 1H, H*s*(C_3H_5)), 4.04 (t, ^3J = 6.6, 4H, OCH_2), 3.59 (br, 1H, H*a*(C_3H_5)), 3.39 (br, 1H, H*s*(C_3H_5)), 3.05 (br, 1H, H*a*(C_3H_5)), 1.83 (m, 4H, CH_2), 1.5-1.2 (m, 28H, CH_2), 0.88 (t, ^3J = 6.8, 6H, CH_3).

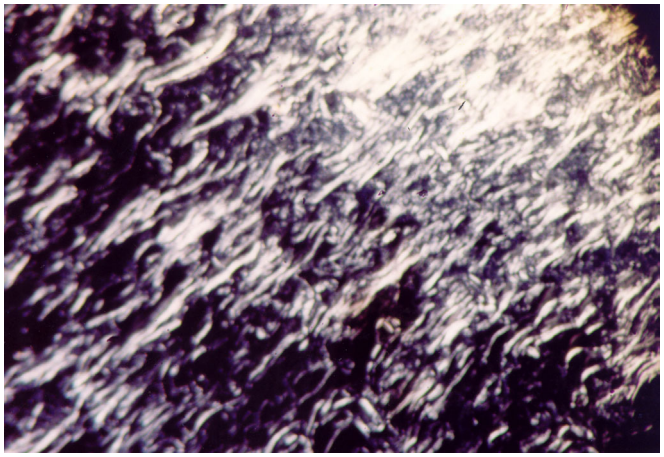
• *[Pd(η^3-C_3H_5)($pz^{R2}py$)][X] (X = PF_6^-, R = $C_6H_4OC_nH_{2n+1}$; n = 12* (**II_{12}**)*, 14* (**II_{14}**)*, 16* (**II_{16}**)*, 18* (**II_{18}**); *X = $CF_3SO_3^-$, R = $C_6H_4OC_nH_{2n+1}$; n = 12* (**III_{12}**)*, 14* (**III_{14}**)*, 16* (**III_{16}**)*, 18* (**III_{18}**)*)*

Spectroscopic data are given for **II_{12}** and **III_{12}**. Data for the other homologues are essentially identical, varying only in the integration of the signal at *δ* 1.5-1.2.

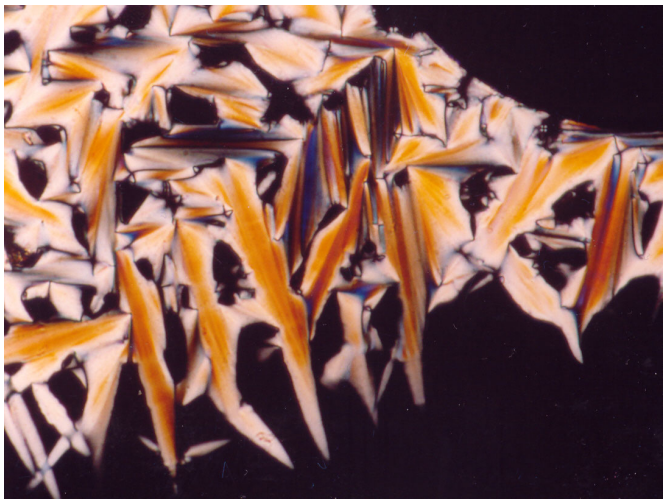
[Pd(η^3-C_3H_5)($pz^{ddp2}py$)][PF_6] (**II_{12}**): IR (KBr, cm^{-1}): ν(CN) 1611 (s), $\gamma(CH)_{py}$ 776 (m), ν(PF) 839 (vs), δ(FPF) 557 (m).^{1}H-NMR ($CDCl_3$; *δ*, *J*, in Hz): 8.73 (d, ^3J = 4.4, 1H, H6), 7.80 (ddd, ^3J = 8.8, ^3J = 7.3, ^4J = 1.5, 1H, H4), 7.58 (d, ^3J = 8.8, 2H, H*o*), 7.47

(1H, H5, masked by the H*o* protons), 7.40 (d, ^3J = 8.6, 2H, H*o*), 7.06 (d, ^3J = 8.8, 2H, H*m*), 7.04 (d, ^3J = 8.8, 2H, H*m*), 6.99 (d, ^3J = 8.8, 1H, H3), 6.70 (s, 1H, H4'), 5.67 (m, ^3J_a = 12.4, ^3J_s = 6.8, 1H, H*meso*(C_3H_5)), 4.3 (br, 1H, H*s*(C_3H_5)), 4.04 (t, ^3J = 6.4, 4H, OCH_2), 3.7-3.0 (br, 3H, H*s* + H*a*(C_3H_5)), 1.83 (m, 4H, CH_2), 1.5-1.2 (m, 36H, CH_2), 0.88 (t, ^3J = 6.5, 6H, CH_3).

[Pd(η^3-C_3H_5)(pz^{ddp2}py)][CF_3SO_3] (**III$_{12}$**): IR (KBr, cm^{-1}): ν(CN) 1610 (s), $\gamma(CH)_{py}$ 769 (m), $\nu_d(SO_3)$ + $\nu(CF_3)$ 1256 (vs), $\nu_s(SO_3)$ 1029 (s).^{1}H-NMR ($CDCl_3$; δ; *J*, in Hz): 8.89 (d, ^3J = 4.4, 1H, H6), 7.81 (dd, ^3J = 7.8, 1H, H4), 7.59 (d, ^3J = 8.6, 2H, H*o*), 7.54 (1H, H5, masked by the H*o* protons), 7.40 (d, ^3J = 8.9, 2H, H*o*), 7.06 (d, ^3J = 8.8, 2H, H*m*), 7.04 (d, ^3J = 8.8, 2H, H*m*), 6.97 (d, ^3J = 8.3, 1H, H3), 6.70 (s, 1H, H4'), 5.69 (m, ^3J_a = 12.4, ^3J_s = 6.8, 1H, H*meso*(C_3H_5)), 4.04 (t, ^3J = 6.1, 5H, OCH_2 + H*s*(C_3H_5)), 3.7-3.2 (br, 3H, H*s* + H*a*(C_3H_5)), 1.84 (m, 4H, CH_2), 1.5-1.2 (m, 36H, CH_2), 0.88 (t, ^3J = 6.6, 6H, CH_3).



(a)



(b)

Figure S1: Other optical textures observed for the SmA phase of these complexes: (a) $\mathbf{I_{16}}$ at 117 ºC; (b) $\mathbf{II_{18}}$ at 120 ºC.

All DSC data below were obtained at a scan rate of 5 K min^{-1}.

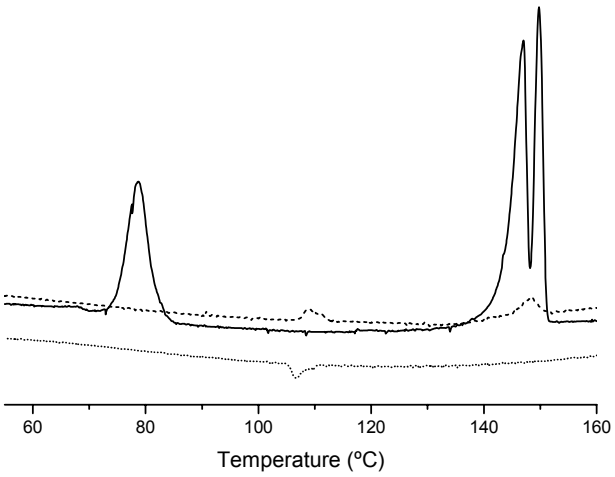


Figure S2: DSC trace of $\mathbf{I_{12}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

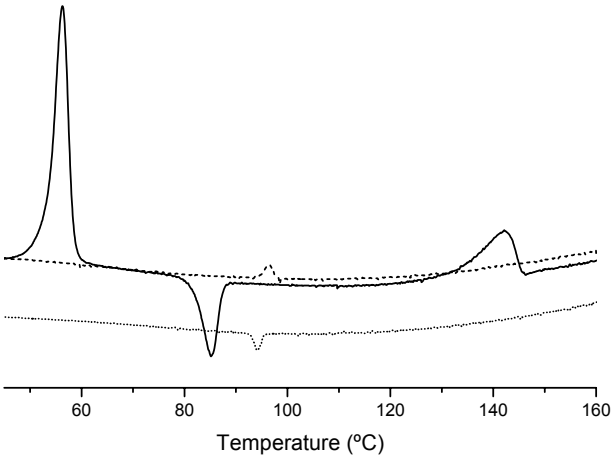


Figure S3: DSC trace of $\mathbf{II_{14}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

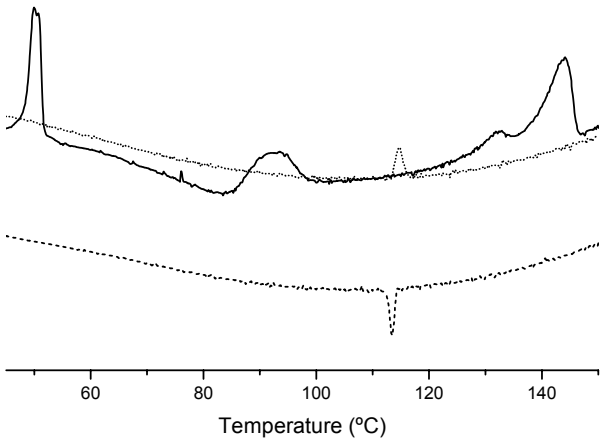


Figure S4: DSC trace of $\mathbf{II_{16}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

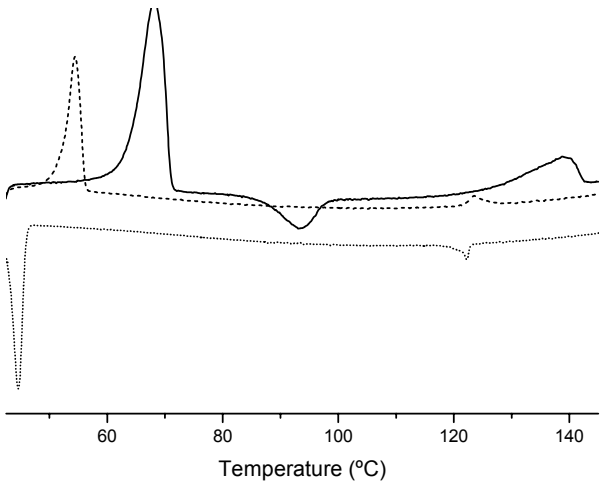


Figure S5: DSC trace of $\mathbf{II_{18}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

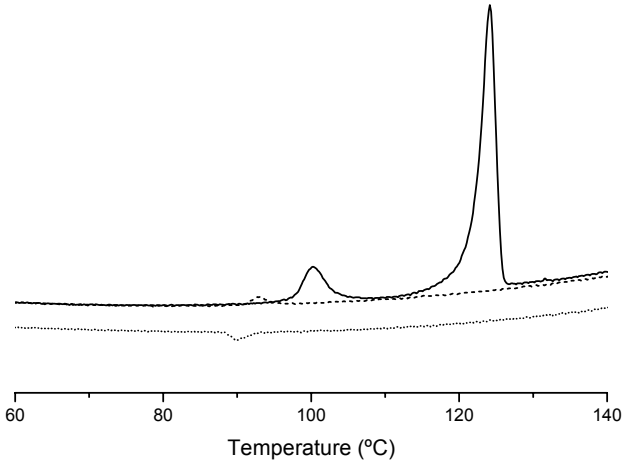


Figure S6: DSC trace of $\mathbf{III_{14}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

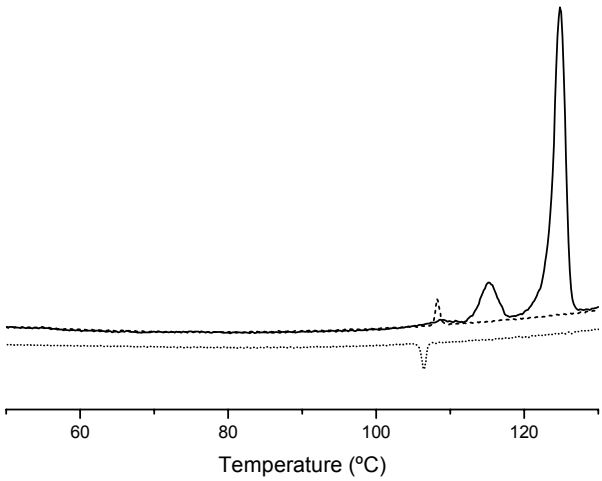


Figure S7: DSC trace of $\mathbf{III_{16}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).

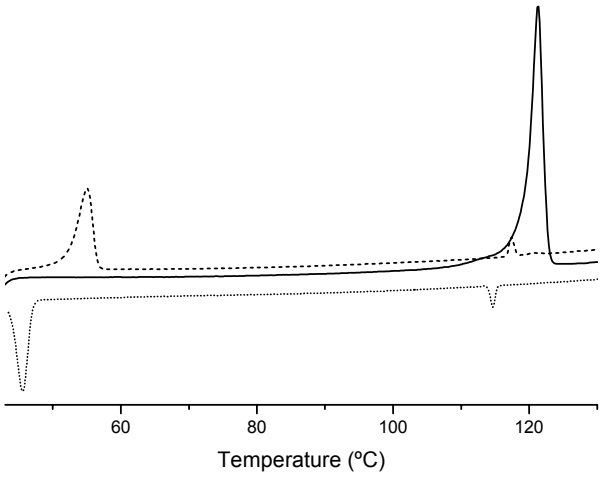


Figure S8: DSC trace of $\mathbf{III_{18}}$: first heating (solid line), first cooling (dotted line), second heating (dashed line).