

Polycatenar pyrazole and pyrazolate ligands as building blocks of new columnar Pd(II) metallomesogens

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Characterisation of 3-(3,5-bis(alkyloxy)phenyl)-5-(2-pyridin-2-yl)pyrazole [Hpz^{R(n,n)}py] (R(n,n) = C₆H₃(OC_nH_{2n+1})₂; n = 4, 8, 10, 14, 16, 18) (1-8)

[Hpz^{R(4,4)}py] (1): colourless solid (71%). Found: C, 72.3; H, 7.4; N, 11.5. C₂₂N₃H₂₇O₂ requires C, 72.1 H, 7.3; N, 11.5%. $\nu_{\max}/\text{cm}^{-1}$ 3144, 3104w $\nu(\text{N-H})$, 1595s $\nu(\text{C=C} + \text{C=N})$, 779m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.98 (6H, t, ³J 7.4, CH₃), 1.51 (4H, m, CH₂), 1.76 (4H, qt, ³J 6.6, CH₂), 4.02 (4H, t, ³J 6.6, OCH₂), 6.46 (1H, t, ⁴J 2.3, H_p), 6.99 (2H, d, ⁴J 2.2, H_o), 7.03 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.77 (1H, m, 3-H), 7.77 (1H, m, 4-H), 8.65 (1H, d, ³J 4.7, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 13.8 (CH₃), 19.2 (CH₂), 31.3 (CH₂), 67.8 (OCH₂), 100.7 (C-4'), 101.4 (C_p), 104.2 (C_o), 120.1 (C-3), 122.8 (C-5), 134.2 (C_i), 137.0 (C-4), 144.8 (C-3'), 148.7 (C-2), 149.4 (C-6), 151.4 (C-5'), 160.6 (C_m).

[Hpz^{R(8,8)}py] (3): colourless solid (68%). Found: C, 75.4; H, 9.0; N, 8.8. C₃₀N₃H₄₃O₂ requires C, 75.1 H, 8.7; N, 8.8%. $\nu_{\max}/\text{cm}^{-1}$ 3212w $\nu(\text{N-H})$, 1589s $\nu(\text{C=C} + \text{C=N})$, 791m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (6H, t, ³J 7.0, CH₃), 1.30 (16H, m, CH₂), 1.47 (4H, m, CH₂), 1.79 (4H, m, CH₂), 4.00 (4H, t, ³J 6.6, OCH₂), 6.46 (1H, t, ⁴J 2.1, H_p), 6.99 (2H, d, ⁴J 2.2, H_o), 7.03 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.77 (1H, m, 3-H), 7.77 (1H, m, 4-H), 8.63 (1H, d, ³J 4.6, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 14.0 (CH₃), 22.6 (CH₂), 25.0 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.3 (CH₂), 31.8 (CH₂), 68.1 (OCH₂), 100.7 (C-4'), 101.4 (C_p), 104.1 (C_o), 120.1 (C-3), 122.7 (C-5), 134.2 (C_i), 136.9 (C-4), 144.9 (C-3'), 148.8 (C-2), 149.4 (C-6), 151.1 (C-5'), 160.6 (C_m).

[Hpz^{R(10,10)}py] (4): colourless solid (66%). Found: C, 75.9; H, 9.7; N, 7.6. C₃₄N₃H₅₁O₂·0.3EtOH requires C, 76.1 H, 9.4; N, 7.0%. $\nu_{\max}/\text{cm}^{-1}$ 3245w $\nu(\text{N-H})$, 1597s $\nu(\text{C=C} + \text{C=N})$, 778m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.89 (6H, t, ³J 7.0, CH₃), 1.24 (t, ³J 7.0, EtOH), 1.27 (28H, m, CH₂), 1.79 (4H, qt, ³J 6.6, CH₂), 3.72 (q, ³J 7.0, EtOH), 4.00 (4H, t, ³J 6.3, OCH₂), 6.46 (1H, t, ⁴J 2.2, H_p), 6.99 (2H, d, ⁴J 2.1, H_o), 7.03 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.77 (1H, m, 3-H), 7.77 (1H, m, 4-H), 8.65 (1H, d, ³J 4.7, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 14.1 (CH₃), 22.6-31.9 (CH₂), 68.0 (OCH₂), 100.7 (C-4'), 101.3 (C_p), 104.0 (C_o), 120.1 (C-3), 122.7 (C-5), 134.0 (C_i), 137.0 (C-4), 145.0 (C-3'), 148.8 (C-2), 149.3 (C-6), 151.0 (C-5'), 160.5 (C_m).

[Hpz^{R(14,14)}py] (6): colourless solid (78%). Found: C, 77.5; H, 10.5; N, 6.4. C₄₂N₃H₆₇O₂·0.3EtOH requires C, 77.3 H, 10.0; N, 6.2%. $\nu_{\max}/\text{cm}^{-1}$ 3218w $\nu(\text{N-H})$, 1594s $\nu(\text{C=C} + \text{C=N})$, 779m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (6H, t, ³J 6.9, CH₃), 1.26 (44H, m, CH₂), 1.26 (m, EtOH) 1.79 (4H, qt, ³J 6.4, CH₂), 3.73 (q, ³J 7.0, EtOH), 4.00 (4H, t, ³J 6.4, OCH₂), 6.46 (1H, t, ⁴J 2.1, H_p), 6.98 (2H, d, ⁴J 2.1, H_o), 7.02 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.73 (1H, d, ³J 7.7, 3-H), 7.77 (1H, ddd, ³J 7.9, 7.7, ⁴J 1.6, 4-H), 8.64 (1H, d, ³J 4.6, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 14.1 (CH₃), 22.7-31.9 (CH₂), 68.0 (OCH₂), 100.7 (C-4'), 101.3 (C_p), 104.0 (C_o), 120.0 (C-3), 122.7 (C-5), 134.1 (C_i), 136.9 (C-4), 144.8 (C-3'), 148.7 (C-2), 149.4 (C-6), 151.2 (C-5'), 160.5 (C_m).

[Hpz^{R(16,16)}py] (7): colourless solid (63%). Found: C, 78.0; H, 10.8; N, 5.8. C₄₆N₃H₇₅O₂·0.4EtOH requires C, 78.2 H, 10.4; N, 5.5%. $\nu_{\max}/\text{cm}^{-1}$ 3219w $\nu(\text{N-H})$, 1596s $\nu(\text{C=C} + \text{C=N})$, 776m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (6H, t, ³J 6.9, CH₃), 1.26 (52H, m, CH₂), 1.26 (m, EtOH) 1.79 (4H, qt, ³J 6.2, CH₂), 3.73 (q, ³J 7.0, EtOH), 4.00 (4H, t, ³J 6.5, OCH₂), 6.46 (1H, t, ⁴J 2.2, H_p), 6.98 (2H, d, ⁴J 2.2, H_o), 7.03 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.73 (1H, d, ³J 7.7, 3-H), 7.77 (1H, ddd, ³J 7.9, 7.7, ⁴J 1.6, 4-H), 8.65 (1H, d, ³J 4.6, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 14.1 (CH₃), 22.7-31.9 (CH₂), 68.1 (OCH₂), 100.6 (C-4'), 101.3 (C_p), 104.1 (C_o), 120.1 (C-3), 123.0 (C-5), 134.2 (C_i), 137.0 (C-4), 144.5 (C-3'), 148.5 (C-2), 149.4 (C-6), 151.6 (C-5'), 160.6 (C_m).

[Hpz^{R(18,18)py}] (8): colourless solid (71%). Found: C, 77.9; H, 11.1; N, 5.2. C₅₀N₃H₈₃O₂·0.8EtOH requires C, 78.2; H, 10.5; N, 4.9%. $\nu_{\max}/\text{cm}^{-1}$ 3147, 3100w $\nu(\text{N-H})$, 1594s $\nu(\text{C=C} + \text{C=N})$, 778m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (6H, t, ³J 6.8, CH₃), 1.23 (t, ³J 7.0, EtOH), 1.26 (60H, m, CH₂), 1.78 (4H, m, CH₂), 3.72 (q, ³J 7.0 EtOH), 4.00 (4H, t, ³J 6.4, OCH₂), 6.44 (1H, t, ⁴J 2.1, H_p), 6.97 (2H, d, ⁴J 2.1, H_o), 7.01 (1H, s, 4'-H), 7.26 (1H, m, 5-H), 7.71 (1H, d, ³J 7.8, 3-H), 7.76 (1H, ddd, ³J 7.9, 7.8, ⁴J 1.6, 4-H), 8.61 (1H, d, ³J 4.6, 6-H). δ_{C} (75.48 MHz; CDCl₃; Me₄Si): 14.2 (CH₃), 22.7-31.9 (CH₂), 68.1 (OCH₂), 100.7 (C-4'), 101.4 (C_p), 104.0 (C_o), 120.1 (C-3), 123.0 (C-5), 134.0 (C_i), 137.1 (C-4), 144.5 (C-3'), 148.5 (C-2), 149.4 (C-6), 151.4 (C-5'), 160.6 (C_m).

Characterisation of the complexes [Pd(pz^{R(n,n)py})₂] (R(n,n) = C₆H₃(OC_nH_{2n+1})₂; n = 4, 8, 10, 14, 16, 18) (9-16)

[Pd(pz^{R(4,4)py})₂] (9): yellow solid (56%). Found: C, 63.3; H, 6.3; N, 10.1. PdC₄₄N₆H₅₂O₄ requires C, 63.0; H, 6.3; N, 10.1%. $\nu_{\max}/\text{cm}^{-1}$ 1591s $\nu(\text{C=C} + \text{C=N})$, 752m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 1.00 (12H, t, ³J 7.4, CH₃), 1.57 (8H, m, CH₂), 1.83 (8H, qt, ³J 6.7, CH₂), 4.06 (8H, t, ³J 6.6, OCH₂), 6.42 (2H, t, ⁴J 2.2, H_p), 6.80 (2H, s, 4'-H), 7.05 (4H, d, ⁴J 2.3, H_o), 7.13 (2H, ddd, ³J 7.6, 5.6, ⁴J 1.2, 5-H), 7.45 (2H, d, ³J 7.8, 3-H), 7.70 (2H, ddd, ³J 7.6, 7.8, ⁴J 1.3, 4-H), 10.24 (2H, d, ³J 5.6, 6-H).

[Pd(pz^{R(8,8)py})₂] (11): yellow solid (62%). Found: C, 68.0; H, 8.0; N, 7.9. PdC₆₀N₆H₈₄O₄ requires C, 67.9; H, 7.9; N, 8.0%. $\nu_{\max}/\text{cm}^{-1}$ 1590s $\nu(\text{C=C} + \text{C=N})$, 755m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.90 (12H, t, ³J 6.6, CH₃), 1.31 (32H, m, CH₂), 1.52 (8H, m, CH₂), 1.85 (8H, qt, ³J 6.9, CH₂), 4.05 (8H, t, ³J 6.8, OCH₂), 6.42 (2H, t, ⁴J 2.2, H_p), 6.84 (2H, s, 4'-H), 7.05 (4H, d, ⁴J 2.3, H_o), 7.15 (2H, ddd, ³J 7.3, 5.7, ⁴J 1.2, 5-H), 7.54 (2H, d, ³J 7.7, 3-H), 7.77 (2H, ddd, ³J 7.3, 7.7, ⁴J 1.3, 4-H), 10.34 (2H, d, ³J 5.7, 6-H).

[Pd(pz^{R(10,10)py})₂] (12): yellow solid (57%). Found: C, 69.7; H, 8.6; N, 7.2. PdC₆₈N₆H₁₀₀O₄ requires C, 69.5; H, 8.3; N, 7.2%. $\nu_{\max}/\text{cm}^{-1}$ 1596s $\nu(\text{C=C} + \text{C=N})$, 766m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (12H, t, ³J 6.9, CH₃), 1.28 (56H, m, CH₂), 1.84 (8H, qt, ³J 6.7, CH₂), 4.05 (8H, t, ³J 6.6, OCH₂), 6.42 (2H, t, ⁴J 2.2, H_p), 6.87 (2H, s, 4'-H), 7.07 (4H, d, ⁴J 2.2, H_o), 7.21 (2H, ddd, ³J 7.8, 5.5, ⁴J 1.3, 5-H), 7.55 (2H, d, ³J 7.7, 3-H), 7.79 (2H, ddd, ³J 7.8, 7.7, ⁴J 1.2, 4-H), 10.35 (2H, d, ³J 5.5, 6-H).

[Pd(pz^{R(14,14)py})₂] (14): yellow solid (66%). Found: C, 72.2; H, 9.5; N, 6.0. PdC₈₄N₆H₁₃₂O₄ requires C, 71.8; H, 9.2; N, 6.0%. $\nu_{\max}/\text{cm}^{-1}$ 1598s $\nu(\text{C=C} + \text{C=N})$, 767m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (12H, t, ³J 6.9, CH₃), 1.26 (88H, m, CH₂), 1.84 (8H, qt, ³J 6.6, CH₂), 4.05 (8H, t, ³J 6.5, OCH₂), 6.42 (2H, t, ⁴J 2.2, H_p), 6.87 (2H, s, 4'-H), 7.07 (4H, d, ⁴J 2.2, H_o), 7.20 (2H, ddd, ³J 7.8, 5.4, ⁴J 1.3, 5-H), 7.55 (2H, d, ³J 7.6, 3-H), 7.79 (2H, ddd, ³J 7.8, 7.6, ⁴J 1.2, 4-H), 10.34 (2H, d, ³J 5.4, 6-H).

[Pd(pz^{R(16,16)py})₂] (15): yellow solid (60%). Found: C, 73.2; H, 9.8; N, 5.6. PdC₉₂N₆H₁₄₈O₄ requires C, 73.0; H, 9.4; N, 5.6%. $\nu_{\max}/\text{cm}^{-1}$ 1597s $\nu(\text{C=C} + \text{C=N})$, 766m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (12H, t, ³J 6.9, CH₃), 1.25 (104H, m, CH₂), 1.83 (8H, qt, ³J 6.7, CH₂), 4.05 (8H, t, ³J 6.5, OCH₂), 6.42 (2H, t, ⁴J 2.2, H_p), 6.90 (2H, s, 4'-H), 7.08 (4H, d, ⁴J 2.2, H_o), 7.23 (2H, ddd, ³J 7.8, 5.6, ⁴J 1.3, 5-H), 7.59 (2H, d, ³J 7.6, 3-H), 7.84 (2H, ddd, ³J 7.8, 7.6, ⁴J 1.2, 4-H), 10.40 (2H, d, ³J 5.6, 6-H).

[Pd(pz^{R(18,18)py})₂] (16): yellow solid (54%). Found: C, 74.1; H, 10.2; N, 5.2. PdC₁₀₀N₆H₁₆₄O₄ requires C, 73.6; H, 9.6; N, 5.2%. $\nu_{\max}/\text{cm}^{-1}$ 1596s $\nu(\text{C=C} + \text{C=N})$, 764m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (12H, t, ³J 6.8, CH₃), 1.25 (120H, m, CH₂), 1.83 (8H, qt, ³J 6.7, CH₂), 4.05 (8H, t, ³J 6.5, OCH₂), 6.43 (2H, t, ⁴J 2.2, H_p), 6.94 (2H, s, 4'-H), 7.10 (4H, d, ⁴J 2.2, H_o), 7.29 (2H, ddd, ³J 7.8, 5.5, ⁴J 1.3, 5-H), 7.64 (2H, d, ³J 7.6, 3-H), 7.87 (2H, ddd, ³J 7.8, 7.6, ⁴J 1.2, 4-H), 10.45 (2H, d, ³J 5.5, 6-H).

Characterisation of the complexes [PdCl₂(Hpz^{R(n,n)py})] (R(n,n) = C₆H₃(OC_nH_{2n+1})₂; n = 4, 8, 10, 14, 16, 18) (17-24)

[PdCl₂(Hpz^{R(4,4)py})] (17): pale orange solid (60%). Found: C, 47.6; H, 4.9; N, 7.5. PdC₂₂N₃H₂₇O₂Cl₂·0.2CH₂Cl₂ requires C, 47.8; H, 4.8; N, 7.7%. $\nu_{\max}/\text{cm}^{-1}$ 3187w $\nu(\text{N-H})$, 1596s $\nu(\text{C=C} + \text{C=N})$, 771m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃): 1.00 (6H, t, ³J 7.0, CH₃), 1.52 (4H, m, CH₂), 1.77 (4H, qt, ³J 6.7, CH₂), 3.99 (4H, t, ³J 6.4, OCH₂), 5.30 (s, CH₂Cl₂), 6.52 (1H, t, ⁴J 2.2, H_p), 6.65 (2H, d, ⁴J 2.2, H_o), 7.07 (1H, s, 4'-H), 7.41 (1H, ddd, ³J 7.7, 5.5, ⁴J 1.3, 5-H), 7.89 (1H, d, ³J 7.6, 3-H), 8.08 (1H, ddd, ³J 7.7, 7.6, ⁴J 1.4, 4-H), 9.01 (1H, d, ³J 5.5, 6-H), 11.29 (1H, s, NH).

[PdCl₂(Hpz^{R(8,8)py})] (19): pale orange solid (66%). Found: C, 54.0; H, 6.5; N, 6.3. PdC₃₀N₃H₄₃O₂Cl₂·0.2CH₂Cl₂ requires C, 53.6; H, 6.5; N, 6.4%. $\nu_{\max}/\text{cm}^{-1}$ 3191w $\nu(\text{N-H})$, 1600s $\nu(\text{C=C} + \text{C=N})$, 770m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (6H, t, ³J 6.7, CH₃), 1.33 (16H, m, CH₂), 1.46 (4H, m, CH₂), 1.80 (4H, m, CH₂), 3.97 (4H, t, ³J 6.4, OCH₂), 5.30 (s, CH₂Cl₂), 6.51 (1H, t, ⁴J 2.1, H_p), 6.65 (2H, d, ⁴J 2.1, H_o), 7.09 (1H, s, 4'-H), 7.40 (1H, ddd, ³J 7.8, 5.6, ⁴J 1.3, 5-H), 7.91 (1H, d, ³J 7.8, 3-H), 8.07 (1H, ddd, ³J 7.8, 7.6, ⁴J 1.2, 4-H), 8.97 (1H, d, ³J 5.6, 6-H), 11.34 (1H, s, NH).

[PdCl₂(Hpz^{R(10,10)}py)] (20): pale orange solid (66%). Found: C, 57.4; H, 7.2; N, 5.9. PdC₃₄N₃H₅₁O₂Cl₂ requires C, 57.6; H, 7.0; N, 6.0%. $\nu_{\max}/\text{cm}^{-1}$ 3188w $\nu(\text{N-H})$, 1596s $\nu(\text{C=C} + \text{C=N})$, 772m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.88 (6H, t, ³J 6.5, CH₃), 1.27 (24H, m, CH₂), 1.46 (4H, m, CH₂), 1.79 (4H, m, CH₂), 3.96 (4H, t, ³J 6.7, OCH₂), 6.53 (1H, t, ⁴J 2.1, H_p), 6.65 (2H, d, ⁴J 2.1, H_o), 7.06 (1H, s, 4'-H), 7.41 (1H, ddd, ³J 7.8, 5.4, ⁴J 1.3, 5-H), 7.89 (1H, d, ³J 7.8, 3-H), 8.07 (1H, ddd, ³J 7.8, 7.6, ⁴J 1.3, 4-H), 9.02 (1H, d, ³J 5.4, 6-H), 11.22 (1H, s, NH).

[PdCl₂(Hpz^{R(14,14)}py)] (22): pale orange solid (67%). Found: C, 61.3; H, 8.2; N, 5.1. PdC₄₂N₃H₆₇O₂Cl₂ requires C, 61.3; H, 7.9; N, 5.2%. $\nu_{\max}/\text{cm}^{-1}$ 3185w $\nu(\text{N-H})$, 1596s $\nu(\text{C=C} + \text{C=N})$, 772m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (6H, t, ³J 6.5, CH₃), 1.26 (40H, m, CH₂), 1.44 (4H, m, CH₂), 1.79 (4H, qt, ³J 6.7, CH₂), 3.97 (4H, t, ³J 6.8, OCH₂), 6.53 (1H, t, ⁴J 2.1, H_p), 6.64 (2H, d, ⁴J 2.1, H_o), 7.06 (1H, s, 4'-H), 7.43 (1H, ddd, ³J 7.7, 5.7, ⁴J 1.3, 5-H), 7.88 (1H, d, ³J 7.7, 3-H), 8.08 (1H, ddd, ³J 7.7, 7.6, ⁴J 1.2, 4-H), 9.03 (1H, d, ³J 5.7, 6-H), 11.11 (1H, s, NH).

[PdCl₂(Hpz^{R(16,16)}py)] (23): pale orange solid (73%). Found: C, 62.8; H, 8.6; N, 4.8. PdC₄₆N₃H₇₅O₂Cl₂ requires C, 63.2; H, 8.4; N, 4.5%. $\nu_{\max}/\text{cm}^{-1}$ 3195w $\nu(\text{N-H})$, 1597s $\nu(\text{C=C} + \text{C=N})$, 773m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (6H, t, ³J 6.7, CH₃), 1.25 (48H, m, CH₂), 1.46 (4H, m, CH₂), 1.78 (4H, m, CH₂), 3.97 (4H, t, ³J 6.7, OCH₂), 6.53 (1H, t, ⁴J 2.2, H_p), 6.65 (2H, d, ⁴J 2.2, H_o), 7.05 (1H, s, 4'-H), 7.43 (1H, ddd, ³J 7.7, 5.6, ⁴J 1.3, 5-H), 7.86 (1H, d, ³J 7.7, 3-H), 8.07 (1H, ddd, ³J 7.7, 7.7, ⁴J 1.3, 4-H), 9.06 (1H, d, ³J 5.6, 6-H), 11.19 (1H, s, NH).

[PdCl₂(Hpz^{R(18,18)}py)] (24): pale orange solid (52%). Found: C, 64.2; H, 8.9; N, 4.5. PdC₅₀N₃H₈₃O₂Cl₂ requires C, 64.1; H, 8.7; N, 4.2%. $\nu_{\max}/\text{cm}^{-1}$ 3188w $\nu(\text{N-H})$, 1598s $\nu(\text{C=C} + \text{C=N})$, 772m $\gamma(\text{C-H})_{\text{py}}$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 0.87 (6H, t, ³J 6.6, CH₃), 1.25 (56H, m, CH₂), 1.46 (4H, m, CH₂), 1.80 (4H, m, CH₂), 3.95 (4H, t, ³J 6.6, OCH₂), 6.54 (1H, t, ⁴J 2.1, H_p), 6.67 (2H, d, ⁴J 2.1, H_o), 7.00 (1H, s, 4'-H), 7.45 (1H, ddd, ³J 7.7, 5.4, ⁴J 1.2, 5-H), 7.83 (1H, d, ³J 7.7, 3-H), 8.06 (1H, ddd, ³J 7.7, 7.8, ⁴J 1.3, 4-H), 9.12 (1H, d, ³J 5.4, 6-H), 11.34 (1H, s, NH).

Table S1. Selected bond distances (Å) and angles (°) for [Hpz^{R(4,4)}py]₂ **1**

N1 – N2	1.351(2)	N1 – N2 – C3	104.5(2)
N1 – C5	1.337(3)	N2 – C3 – C4	110.0(2)
N2 – C3	1.334(3)	C3 – C4 – C5	106.7(2)
C3 – C4	1.345(3)	N1 – C5 – C4	105.7(2)
C4 – C5	1.357(3)	N2 – N1 – C5	113.1(2)
C5 – C6	1.468(3)	C4 – C5 – C6	134.0(2)
C6 – C7	1.372(3)	N1 – C5 – C6	120.2(2)
C7 – C8	1.372(3)	C4 – C3 – C11	129.8(3)
C8 – C9	1.360(4)	N2 – C3 – C11	120.2(2)
C9 – C10	1.367(4)		
N3 – C10	1.329(3)		
C3 – C11	1.470(3)		

Table S2. Selected bond distances (Å) and angles (°) for [Pd(pz^{R(10,10)}py)₂] **12**

Pd – N1	1.929(7)	N1 – Pd – N3	78.5(4)
Pd – N3	2.041(7)	N1 – Pd – N3' ^a	101.5(4)
N1 – N2	1.361(8)		
N2 – C3	1.374(8)		
C3 – C4	1.370(9)		
C4 – C5	1.36(2)		
N1 – C5	1.366(9)		

^a $-x + 1, -y + 1, -z + 1$

Fig. S1. DSC deconvolution of the pyrazole ligand [Hpz^{R(16,16)py}] **7** showing the temperatures of the solid-mesophase (84.4 °C) and mesophase-isotrope (87.4 °C).

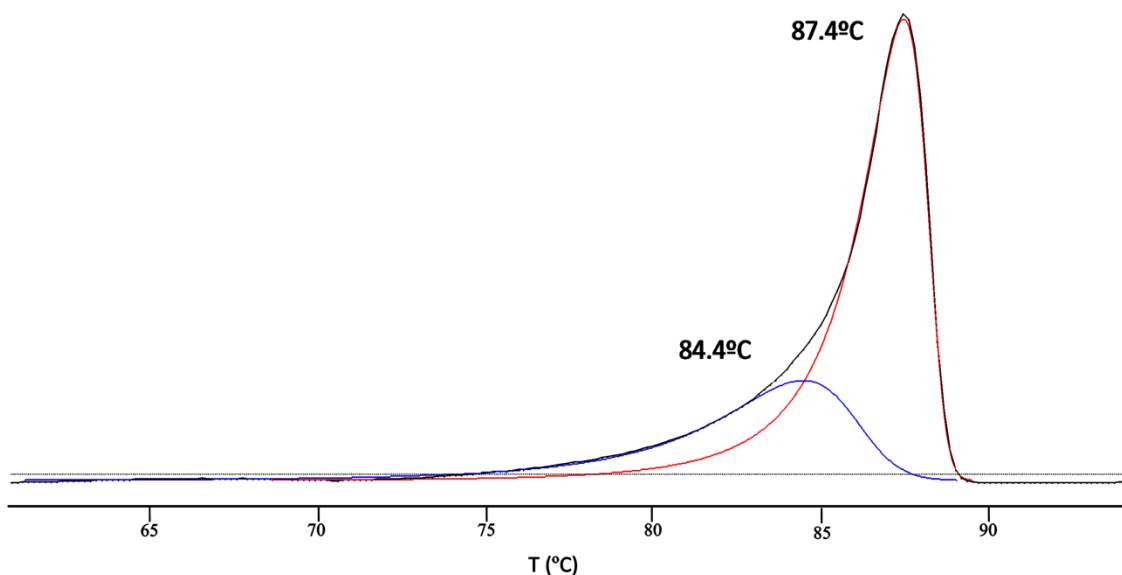


Fig. S2. PLUTO plot for [PdCl₂(Hpz^{R(4,4)py})] **17**. Hydrogen atoms have been omitted for clarity. Unit cell dimensions (distances in Å and angles in degrees): $a = 8.7556(4)$; $b = 15.2818(15)$; $c = 17.4874(17)$; $\alpha = 95.186(8)$; $\beta = 90.035(6)$; $\gamma = 95.510(6)$.

