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SUPPLEMENTARY INFORMATION

Lamellar columnar liquid-crystalline mesophases as a 2D platform for anhydrous proton conduction

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Structural characterisation of Pd(II) compounds

Compounds [$PdBr_2(Hpz^{R(n,n)py})$] 9-13

[$PdBr_2(Hpz^{R(6,6)py})$] (9): orange solid (44%). Found: C, 44.8; H, 5.0; N, 6.2. $PdC_{26}H_{35}N_3O_2Br_2 \cdot 0.1CH_2Cl_2$ requires C, 45.0; H, 5.1; N, 6.0%. ν_{max}/cm^{-1}: 3263m ν(N–H), 2926 – 2857s $\nu(C–H)_{aliph}$, 1597s ν(C=C + C=N), 778m $\gamma(C–H)_{py.}$ δ_H (300.16 MHz; $CDCl_3$; TMS): 0.92 (6H, t, ^3J 6.9, CH_3), 1.35 (12H, m, CH_2), 1.80 (4H, qt, ^3J 6.6, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 5.30 (s, CH_2Cl_2), 6.53 (1H, t, ^4J 2.1, Hp), 6.63 (2H, d, ^4J 2.1, Ho), 7.06 (1H, d, ^4J 2.0, H4'), 7.39 (1H, ddd, ^3J 7.3, 5.8, ^4J 1.3, H5), 7.92 (1H, d, ^3J 7.3, H3), 8.09 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.20 (1H, d, ^3J 5.7, H6), 11.00 (1H, br, NH).

[$PdBr_2(Hpz^{R(12,12)py})$] (10): orange solid (58%). Found: C, 54.0; H, 6.8; N, 5.1. $PdC_{38}H_{59}N_3O_2Br_2 \cdot 0.3CH_3CN$ requires C, 53.4; H, 7.0; N, 5.3%. ν_{max}/cm^{-1}: 3260m ν(N–H), 2921 – 2851s $\nu(C–H)_{aliph}$, 1597s ν(C=C + C=N), 779m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.27 (36H, m, CH_2), 1.80 (4H, qt, ^3J 6.7, CH_2), 2.10 (s, CH_3CN), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 2.0, Hp), 6.63 (2H, d, ^4J 2.1, Ho), 7.04 (1H, s, H4'), 7.41 (1H, ddd, ^3J 7.3, 5.7, ^4J 1.3, H5), 7.90 (1H, d, ^3J 7.4, H3), 8.08 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.25 (1H, d, ^3J 5.7, H6), 11.00 (1H, s, NH). δ_C (75.48 MHz; $CDCl_3$; TMS): 14.1 (CH_3), 22.7 – 31.9 (CH_2), 68.5 (OCH_2), 102.4 (C4'), 103.4 (Cp), 104.0 (Co), 123.1 (C3), 125.2 (C5), 127.2 (Ci), 140.6 (C4), 145.5 (C3'), 150.1 (C2), 151.7 (C6), 152.1 (C5'), 161.0 (Cm).

[$PdBr_2(Hpz^{R(14,14)py})$] (11): orange solid (61%). Found: C, 55.2; H, 7.2; N, 4.8. $PdC_{42}H_{67}N_3O_2Br_2$ requires C, 55.3; H, 7.4; N, 4.6%. ν_{max}/cm^{-1}: 3290m ν(N–H), 2920 – 2851s $\nu(C–H)_{aliph}$, 1598s ν(C=C + C=N), 779m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.26 (44H, m, CH_2), 1.80 (4H, qt, ^3J 6.6, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 2.0, Hp), 6.64 (2H, d, ^4J 2.0, Ho), 7.04 (1H, s, H4'), 7.41 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.1, H5), 7.89 (1H, d, ^3J 7.5, H3), 8.09 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.2, H4), 9.25 (1H, d, ^3J 5.6, H6), 11.05 (1H, s, NH).

[$PdBr_2(Hpz^{R(16,16)py})$] (12): orange solid (64%). Found: C, 56.6; H, 7.5; N, 4.4. $PdC_{46}H_{75}N_3O_2Br_2$ requires C, 57.0; H, 7.8; N, 4.3%. ν_{max}/cm^{-1}: 3278w ν(N–H), 2919 – 2850s $\nu(C–H)_{aliph}$, 1600m ν(C=C + C=N), 779w $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.26 (52H, m, CH_2), 1.80 (4H, qt, ^3J 6.5, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.54 (1H, t, ^4J 2.0, Hp), 6.64 (2H, d, ^4J 2.1, Ho), 7.02 (1H, d, ^4J

1.8, H4'), 7.43 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.1, H5), 7.87 (1H, d, ^3J 7.5, H3), 8.08 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.3, H4), 9.29 (1H, d, ^3J 5.8, H6), 11.08 (1H, br, NH).

[$PdBr_2(Hpz^{R(18,18)py})$] (13): orange solid (64%). Found: C, 59.0; H, 7.8; N, 4.0. $PdC_{50}H_{83}N_3O_2Br_2$ requires C, 58.6; H, 8.2; N, 4.1%. ν_{max}/cm^{-1}: 3267w ν(N–H), 2919 – 2850s $\nu(C–H)_{aliph}$, 1597m ν(C=C + C=N), 779w $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.25 (60H, m, CH_2), 1.80 (4H, qt, ^3J 6.8, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.54 (1H, t, ^4J 2.0, Hp), 6.65 (2H, d, ^4J 2.1, Ho), 7.01 (1H, d, ^4J 1.7, H4'), 7.44 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.3, H5), 7.86 (1H, d, ^3J 7.6, H3), 8.06 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.30 (1H, d, ^3J 5.7, H6), 11.07 (1H, d, ^4J 1.5, NH).

Compounds [$PdI_2(Hpz^{R(n,n)py})$] 14-18

[$PdI_2(Hpz^{R(6,6)py})$] (14): red solid (53%). Found: C, 39.7; H, 4.4; N, 5.4. $PdC_{26}H_{35}N_3O_2I_2$ requires C, 39.9; H, 4.5; N, 5.4%. ν_{max}/cm^{-1}: 3311m ν(N–H), 2926 – 2855m $\nu(C–H)_{aliph}$, 1595s ν(C=C + C=N), 778m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.93 (6H, t, ^3J 6.9, CH_3), 1.36 (12H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.99 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 2.1, Hp), 6.64 (2H, d, ^4J 2.1, Ho), 7.01 (1H, d, ^4J 1.7, H4'), 7.38 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.3, H5), 7.91 (1H, d, ^3J 7.4, H3), 8.09 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.45 (1H, d, ^3J 5.6, H6), 11.00 (1H, d, ^4J 1.4, NH).

[$PdI_2(Hpz^{R(12,12)py})$] (15): red solid (67%). Found: C, 48.0; H, 6.1; N, 4.5. $PdC_{38}H_{59}N_3O_2I_2$ requires C, 48.0; H, 6.3; N, 4.4%. ν_{max}/cm^{-1}: 3308m ν(N–H), 2920 – 2850s $\nu(C–H)_{aliph}$, 1595m ν(C=C + C=N), 778m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.27 (36H, m, CH_2), 1.81 (4H, qt, ^3J 6.6, CH_2), 3.99 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 2.0, Hp), 6.64 (2H, d, ^4J 1.9, Ho), 6.98 (1H, d, ^4J 1.9, H4'), 7.41 (1H, ddd, ^3J 7.5, 5.8, ^4J 1.2, H5), 7.87 (1H, d, ^3J 7.5, H3), 8.08 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.51 (1H, d, ^3J 5.8, H6), 11.03 (1H, d, ^4J 1.4, NH). δ_C (75.48 MHz; $CDCl_3$; TMS): 14.1 (CH_3), 22.7 – 31.9 (CH_2), 68.5 (OCH_2), 102.6 (C4'), 103.1 (Cp), 104.0 (Co), 123.2 (C3), 125.5 (C5), 127.2 (Ci), 140.3 (C4), 145.2 (C3'), 150.1 (C2), 152.5 (C5'), 153.1 (C6), 161.0 (Cm).

[$PdI_2(Hpz^{R(14,14)py})$] (16): red solid (61%). Found: C, 50.2; H, 6.6; N, 4.3. $PdC_{42}H_{67}N_3O_2I_2$ requires C, 50.1; H, 6.7; N, 4.2%. ν_{max}/cm^{-1}: 3308m ν(N–H), 2917 – 2849s $\nu(C–H)_{aliph}$, 1595m ν(C=C + C=N), 778m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$;

TMS): 0.88 (6H, t, ^3J 6.8, CH_3), 1.26 (44H, m, CH_2), 1.81 (4H, qt, ^3J 6.6, CH_2), 3.99 (4H, t, ^3J 6.4, OCH_2), 6.54 (1H, t, ^4J 2.0, Hp), 6.65 (2H, d, ^4J 1.9, Ho), 6.98 (1H, d, ^4J 1.7, H4'), 7.41 (1H, ddd, ^3J 7.7, 5.5, ^4J 1.1, H5), 7.87 (1H, d, ^3J 7.6, H3), 8.08 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.2, H4), 9.52 (1H, d, ^3J 5.4, H6), 11.04 (1H, br, NH).

[$PdI_2(Hpz^{R(16,16)py})$] (17): red solid (72%). Found: C, 52.5; H, 7.0; N, 4.0. $PdC_{46}H_{75}N_3O_2I_2$ requires C, 52.0; H, 7.1; N, 4.0%. ν_{max}/cm^{-1}: 3309m ν(N–H), 2919 – 2850s $\nu(C–H)_{aliph}$, 1597m ν(C=C + C=N), 779w $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.26 (52H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.99 (4H, t, ^3J 6.5, OCH_2), 6.55 (1H, t, ^4J 2.0, Hp), 6.66 (2H, d, ^4J 2.1, Ho), 6.96 (1H, d, ^4J 2.0, H4'), 7.43 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.2, H5), 7.85 (1H, d, ^3J 7.5, H3), 8.07 (1H, ddd, ^3J 7.7, 7.7, ^4J 1.3, H4), 9.57 (1H, d, ^3J 5.8, H6), 11.10 (1H, br, NH).

[$PdI_2(Hpz^{R(18,18)py})$] (18): red solid (72%). Found: C, 53.7; H, 7.3; N, 3.9. $PdC_{50}H_{83}N_3O_2I_2$ requires C, 53.7; H, 7.5; N, 3.8%. ν_{max}/cm^{-1}: 3306m ν(N–H), 2917 – 2849s $\nu(C–H)_{aliph}$, 1595m ν(C=C + C=N), 778m $\gamma(C–H)_{py}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.26 (60H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.99 (4H, t, ^3J 6.5, OCH_2), 6.55 (1H, t, ^4J 2.2, Hp), 6.66 (2H, d, ^4J 2.0, Ho), 6.96 (1H, d, ^4J 2.0, H4'), 7.43 (1H, ddd, ^3J 7.4, 5.7, ^4J 1.4, H5), 7.84 (1H, d, ^3J 7.8, H3), 8.08 (1H, dd, ^3J 7.7, 7.7, ^4J 1.4, H4), 9.58 (1H, d, ^3J 5.9, H6), 11.09 (1H, br, NH).

Compounds [$PdCl_2(Hpz^{R(n,n)iq})$] 19-26

[$PdCl_2(Hpz^{R(4,4)iq})$] (19): pale orange solid (60%). Found: C, 52.0; H, 4.8; N, 7.0. $PdC_{26}H_{29}N_3O_2Cl_2 \cdot 0.1CH_2Cl_2$ requires C, 52.1; H, 4.9; N, 7.0%. ν_{max}/cm^{-1}: 3296w ν(N–H), 2919 – 2851s $\nu(C–H)_{aliph}$, 1636 – 1595s ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 1.02 (6H, t, ^3J 7.3, CH_3), 1.53 (4H, m, CH_2), 1.80 (4H, qt, ^3J 6.7, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 5.30 (s, CH_2Cl_2), 6.53 (1H, t, ^4J 2.0, Hp), 6.60 (2H, d, ^4J 1.9, Ho), 7.24 (1H, s, H4'), 7.69 (2H, m, H7, H8), 7.95 (1H, pt, ^3J 8.1, H6), 8.07 (1H, d, ^3J 8.3, H5), 8.35 (1H, s, H4), 9.33 (1H, s, H1), 10.73 (1H, s, NH).

[$PdCl_2(Hpz^{R(6,6)iq})$] (20): pale orange solid (70%). Found: C, 56.1; H, 5.7; N, 6.7. $PdC_{30}H_{37}N_3O_2Cl_2$ requires C, 55.5; H, 5.8; N, 6.5%. ν_{max}/cm^{-1}: 3274w ν(N–H), 2915 – 2849s $\nu(C–H)_{aliph}$, 1636 – 1596s ν(C=C + C=N), 754 – 716m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.94 (6H, t, ^3J 7.0, CH_3), 1.37 (12H, m, CH_2), 1.81 (4H, qt, ^3J 6.7,

CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.50 (1H, t, ^4J 2.0, Hp), 6.58 (2H, d, ^4J 2.1, Ho), 7.26 (1H, m, H4'), 7.64 (2H, m, H7, H8), 7.93 (1H, ddd, ^3J 8.1, 6.3, ^4J 1.7, H6), 8.07 (1H, d, ^3J 8.2, H5), 8.37 (1H, s, H4), 9.25 (1H, s, H1), 10.74 (1H, s, NH).

[$PdCl_2(Hpz^{R(8,8)iq})$] (21): pale orange solid (60%). Found: C, 57.8; H, 6.3; N, 6.1. $PdC_{34}H_{45}N_3O_2Cl_2$ requires C, 57.9; H, 6.4; N, 6.0%. ν_{max}/cm^{-1}: 3270w ν(N–H), 2919 – 2851s $\nu(C–H)_{aliph}$, 1637 – 1596s ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.90 (6H, t, ^3J 6.9, CH_3), 1.31 (20H, m, CH_2), 1.81 (4H, qt, ^3J 6.7, CH_2), 3.98 (4H, t, ^3J 6.3, OCH_2), 6.51 (1H, br, Hp), 6.57 (2H, br, Ho), 7.29 (1H, br, H4'), 7.65 (2H, m, H7, H8), 7.93 (1H, pt, ^3J 7.2, H6), 8.09 (1H, d, ^3J 7.8, H5), 8.40 (1H, s, H4), 9.20 (1H, s, H1), 10.59 (1H, br, NH).

[$PdCl_2(Hpz^{R(10,10)iq})$] (22): pale orange solid (63%). Found: C, 60.1; H, 6.9; N, 5.6. $PdC_{38}H_{53}N_3O_2Cl_2$ requires C, 60.0; H, 7.0; N, 5.5%. ν_{max}/cm^{-1}: 3272w ν(N–H), 2921 – 2852s $\nu(C–H)_{aliph}$, 1636 – 1596s ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.89 (6H, t, ^3J 6.6, CH_3), 1.29 (28H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.51 (1H, t, ^4J 1.9, Hp), 6.57 (2H, d, ^4J 1.9, Ho), 7.29 (1H, d, ^4J 1.5, H4'), 7.64 (2H, m, H7, H8), 7.94 (1H, ddd, ^3J 7.9, 6.4, ^4J 1.0, H6), 8.09 (1H, d, ^3J 8.2, H5), 8.40 (1H, s, H4), 9.22 (1H, s, H1), 10.55 (1H, br, NH).

[$PdCl_2(Hpz^{R(12,12)iq})$] (23): pale orange solid (67%). Found: C, 62.1; H, 7.3; N, 5.1. $PdC_{42}H_{61}N_3O_2Cl_2$ requires C, 61.7; H, 7.5; N, 5.1%. ν_{max}/cm^{-1}: 3272w ν(N–H), 2921 – 2852s $\nu(C–H)_{aliph}$, 1637 – 1595s ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.27 (36H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.98 (4H, t, ^3J 6.3, OCH_2), 6.50 (1H, t, ^4J 1.9, Hp), 6.56 (2H, d, ^4J 2.0, Ho), 7.29 (1H, d, ^4J 1.6, H4'), 7.65 (2H, m, H7, H8), 7.94 (1H, pt, ^3J 7.1, H6), 8.09 (1H, d, ^3J 7.9, H5), 8.40 (1H, s, H4), 9.19 (1H, s, H1), 10.58 (1H, br, NH). δ_C (75.48 MHz; $CDCl_3$; TMS): 14.1 (CH_3), 22.6 – 31.9 (CH_2), 68.5 (OCH_2), 101.4 (C4'), 103.2 (Co), 103.9 (Cp), 120.8 (C4), 126.6 (Ci), 126.9 (C10), 128.0 (C5), 128.7 (C8), 129.7 (C7), 134.0 (C6), 135.2 (C9), 141.9 (C3), 145.0 (C3'), 151.7 (C5'), 154.1 (C1), 160.9 (Cm).

[$PdCl_2(Hpz^{R(14,14)iq})$] (24): pale orange solid (45%). Found: C, 63.8; H, 7.8; N, 4.6. $PdC_{46}H_{69}N_3O_2Cl_2$ requires C, 63.3; H, 8.0; N, 4.8%. ν_{max}/cm^{-1}: 3271w ν(N–H), 2921 – 2851s $\nu(C–H)_{aliph}$, 1637 – 1596s ν(C=C + C=N), 754 – 718m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.8, CH_3), 1.26 (44H, m, CH_2), 1.81 (4H, qt, ^3J 6.9, CH_2), 3.99 (4H, t, ^3J 6.4, OCH_2), 6.53 (1H, t, ^4J 1.7, Hp), 6.63 (2H, d, ^4J 1.6, Ho), 7.20

(1H, d, ^4J 1.3, H4'), 7.71 (1H, pt, ^3J 7.2, H7), 7.79 (1H, d, ^3J 7.5, H8), 7.95 (1H, pt, ^3J 7.4, H6), 8.06 (1H, d, ^3J 8.1, H5), 8.31 (1H, s, H4), 9.43 (1H, s, H1), 10.88 (1H, br, NH).

[$PdCl_2(Hpz^{R(16,16)iq})$] (25): pale orange solid (53%). Found: C, 65.1; H, 8.1; N, 4.4. $PdC_{50}H_{77}N_3O_2Cl_2$ requires C, 64.6; H, 8.3; N, 4.5%. ν_{max}/cm^{-1}: 3262w ν(N–H), 2920 – 2851s $\nu(C–H)_{aliph}$, 1637 – 1596s ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.26 (52H, m, CH_2), 1.81 (4H, qt, ^3J 6.7, CH_2), 3.98 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 1.9, Hp), 6.63 (2H, d, ^4J 2.0, Ho), 7.18 (1H, d, ^4J 1.3, H4'), 7.71 (1H, pt, ^3J 7.1, H7), 7.81 (1H, d, ^3J 8.3, H8), 7.95 (1H, pt, ^3J 7.5, H6), 8.05 (1H, d, ^3J 8.3, H5), 8.29 (1H, s, H4), 9.45 (1H, s, H1), 10.95 (1H, br, NH).

[$PdCl_2(Hpz^{R(18,18)iq})$] (26): pale orange solid (44%). Found: C, 65.4; H, 8.5; N, 3.9. $PdC_{54}H_{85}N_3O_2Cl_2 \cdot 0.1CH_2Cl_2$ requires C, 65.4; H, 8.6; N, 4.2%. ν_{max}/cm^{-1}: 3247w ν(N–H), 2917 – 2850s $\nu(C–H)_{aliph}$, 1637 – 1597m ν(C=C + C=N), 752 – 719m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.25 (60H, m, CH_2), 1.81 (4H, qt, ^3J 6.6, CH_2), 3.98 (4H, t, ^3J 6.4, OCH_2), 5.30 (s, CH_2Cl_2), 6.51 (1H, t, ^4J 2.2, Hp), 6.59 (2H, d, ^4J 2.2, Ho), 7.26 (1H, m, H4'), 7.65 (2H, m, H7, H8), 7.94 (1H, ddd, ^3J 7.9, 5.9, ^4J 2.2, H6), 8.08 (1H, d, ^3J 8.2, H5), 8.37 (1H, s, H4), 9.27 (1H, s, H1), 10.73 (1H, s, NH).

Compounds [$PdBr_2(Hpz^{R(n,n)iq})$] 27-30

[$PdBr_2(Hpz^{R(12,12)iq})$] (27): orange solid (62%). Found: C, 55.7; H, 6.6; N, 4.7. $PdC_{42}H_{61}N_3O_2Br_2$ requires C, 55.7; H, 6.8; N, 4.6%. ν_{max}/cm^{-1}: 3325w ν(N–H), 2917 – 2850s $\nu(C–H)_{aliph}$, 1635 – 1595m ν(C=C + C=N), 754 – 717m $\gamma(C–H)_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 7.0, CH_3), 1.27 (36H, m, CH_2), 1.82 (4H, qt, ^3J 6.6, CH_2), 3.99 (4H, t, ^3J 6.5, OCH_2), 6.52 (1H, t, ^4J 2.0, Hp), 6.57 (2H, d, ^4J 2.0, Ho), 7.23 (1H, d, ^4J 1.9, H4'), 7.65 (2H, m, H7, H8), 7.94 (1H, ddd, ^3J 8.1, 5.7, ^4J 1.4, H6), 8.09 (1H, d, ^3J 8.2, H5), 8.38 (1H, s, H4), 9.46 (1H, s, H1), 10.64 (1H, d, ^4J 1.6, NH). δ_C (75.48 MHz; $CDCl_3$; TMS): 14.1 (CH_3), 22.7 – 31.9 (CH_2), 68.5 (OCH_2), 101.4 (C4'), 103.3 (Co), 103.7 (Cp), 120.8 (C4), 126.9 (Ci), 127.0 (C10), 128.0 (C5), 128.7 (C8), 129.6 (C7), 133.9 (C6), 135.1 (C9), 141.9 (C3), 144.8 (C3'), 151.9 (C5'), 155.2 (C1), 160.8 (Cm).

[$PdBr_2(Hpz^{R(14,14)iq})$] (28): orange solid (58%). Found: C, 57.7; H, 7.1; N, 4.5. $PdC_{46}H_{69}N_3O_2Br_2$ requires C, 57.4; H, 7.2; N, 4.4%. ν_{max}/cm^{-1}: 3291w ν(N–H), 2919 – 2851s ν(C–H)$_{aliph}$, 1635 – 1596m ν(C=C + C=N), 755 – 716m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.6, CH_3), 1.27 (44H, m, CH_2), 1.82 (4H, qt, ^3J 6.7, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 1.9, Hp), 6.59 (2H, d, ^4J 2.0, Ho), 7.20 (1H, d, ^4J 1.8, H4'), 7.71 (2H, m, H7, H8), 7.95 (1H, ddd, ^3J 8.0, 5.8, ^4J 1.6, H6), 8.08 (1H, d, ^3J 8.1, H5), 8.35 (1H, s, H4), 9.54 (1H, s, H1), 10.72 (1H, br, NH).

[$PdBr_2(Hpz^{R(16,16)iq})$] (29): orange solid (68%). Found: C, 59.5; H, 7.5; N, 4.1. $PdC_{50}H_{77}N_3O_2Br_2$ requires C, 59.0; H, 7.6; N, 4.1%. ν_{max}/cm^{-1}: 3291w ν(N–H), 2919 – 2851s ν(C–H)$_{aliph}$, 1635 – 1596m ν(C=C + C=N), 755 – 717m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.8, CH_3), 1.26 (52H, m, CH_2), 1.82 (4H, qt, ^3J 6.9, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.52 (1H, t, ^4J 1.9, Hp), 6.59 (2H, d, ^4J 1.9, Ho), 7.21 (1H, d, ^4J 1.8, H4'), 7.69 (2H, m, H7, H8), 7.95 (1H, ddd, ^3J 8.1, 6.0, ^4J 2.0, H6), 8.09 (1H, d, ^3J 8.2, H5), 8.36 (1H, s, H4), 9.52 (1H, s, H1), 10.70 (1H, br, NH).

[$PdBr_2(Hpz^{R(18,18)iq})$] (30): orange solid (61%). Found: C, 60.0; H, 7.6; N, 3.9. $PdC_{54}H_{85}N_3O_2Br_2$ requires C, 60.4; H, 7.0; N, 3.9%. ν_{max}/cm^{-1}: 3276w ν(N–H), 2918 – 2850s ν(C–H)$_{aliph}$, 1635 – 1596m ν(C=C + C=N), 755 – 716m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.25 (60H, m, CH_2), 1.81 (4H, qt, ^3J 6.8, CH_2), 3.99 (4H, t, ^3J 6.6, OCH_2), 6.52 (1H, t, ^4J 1.9, Hp), 6.59 (2H, d, ^4J 1.9, Ho), 7.20 (1H, d, ^4J 1.8, H4'), 7.72 (2H, m, H7, H8), 7.95 (1H, ddd, ^3J 7.9, 6.6, ^4J 1.5, H6), 8.08 (1H, d, ^3J 8.2, H5), 8.34 (1H, s, H4), 9.55 (1H, s, H1), 10.77 (1H, br, NH).

Compounds [$PdI_2(Hpz^{R(n,n)iq})$] 31-34

[$PdI_2(Hpz^{R(12,12)iq})$] (31): red solid (55%). Found: C, 50.7; H, 6.1; N, 4.3. $PdC_{42}H_{61}N_3O_2I_2$ requires C, 50.4; H, 6.2; N, 4.2%. ν_{max}/cm^{-1}: 3381w ν(N–H), 2924 – 2855m ν(C–H)$_{aliph}$, 1597s ν(C=C + C=N), 770 – 725m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.27 (36H, m, CH_2), 1.82 (4H, qt, ^3J 6.8, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.52 (1H, t, ^4J 1.9, Hp), 6.58 (2H, d, ^4J 2.0, Ho), 7.11 (1H, d, ^4J 1.8, H4'), 7.66 (1H, pt, ^3J 7.3, H7), 7.76 (1H, d, ^3J 8.0, H8), 7.93 (1H, ddd, ^3J 7.8, 6.7, ^4J 1.0, H6), 8.08 (1H, d, ^3J 8.1, H5), 8.28 (1H, s, H4), 9.81 (1H, s, H1), 10.73 (1H, br, NH). δ_C (75.48 MHz; $CDCl_3$; TMS): 14.1 (CH_3), 22.7 – 31.9 (CH_2), 68.5 (OCH_2), 101.6

(C4'), 103.3 (Cp), 103.6 (Co), 120.6 (C4), 127.0 (Ci), 127.7 (C10), 128.2 (C5), 128.7 (C8), 129.5 (C7), 133.7 (C6), 135.0 (C9), 142.2 (C3), 144.5 (C3'), 152.4 (C5'), 156.8 (C1), 160.9 (Cm).

[$PdI_2(Hpz^{R(14,14)iq})$] (32): red solid (63%). Found: C, 52.8; H, 6.5; N, 4.1. $PdC_{46}H_{69}N_3O_2I_2$ requires C, 52.3; H, 6.6; N, 4.0%. ν_{max}/cm^{-1}: 3330w ν(N–H), 2918 – 2849s ν(C–H)$_{aliph}$, 1632 – 1596m ν(C=C + C=N), 794 – 715m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.88 (6H, t, ^3J 6.9, CH_3), 1.27 (44H, m, CH_2), 1.82 (4H, qt, ^3J 6.7, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.52 (1H, t, ^4J 2.0, Hp), 6.58 (2H, d, ^4J 2.0, Ho), 7.11 (1H, d, ^4J 1.9, H4'), 7.65 (1H, pt, ^3J 7.2, H7), 7.75 (1H, d, ^3J 8.0, H8), 7.93 (1H, ddd, ^3J 8.0, 6.7, ^4J 1.0, H6), 8.08 (1H, d, ^3J 8.1, H5), 8.28 (1H, s, H4), 9.81 (1H, s, H1), 10.72 (1H, d, ^4J 1.6, NH).

[$PdI_2(Hpz^{R(16,16)iq})$] (33): red solid (72%). Found: C, 54.4; H, 7.0; N, 3.8. $PdC_{50}H_{77}N_3O_2I_2$ requires C, 54.0; H, 7.0; N, 3.8%. ν_{max}/cm^{-1}: 3325w ν(N–H), 2916 – 2850s ν(C–H)$_{aliph}$, 1634 – 1596m ν(C=C + C=N), 794 – 715m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.26 (52H, m, CH_2), 1.82 (4H, qt, ^3J 6.7, CH_2), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.53 (1H, t, ^4J 1.9, Hp), 6.61 (2H, d, ^4J 1.9, Ho), 7.09 (1H, d, ^4J 1.7, H4'), 7.68 (1H, pt, ^3J 7.4, H7), 7.83 (1H, d, ^3J 8.2, H8), 7.93 (1H, pt, ^3J 7.2, H6), 8.07 (1H, d, ^3J 8.2, H5), 8.25 (1H, s, H4), 9.89 (1H, s, H1), 10.81 (1H, br, NH).

[$PdI_2(Hpz^{R(18,18)iq})$] (34): red solid (66%). Found: C, 54.9; H, 7.1; N, 4.2. $PdC_{54}H_{85}N_3O_2I_2 \cdot 0.4CH_3CN$ requires C, 55.5; H, 7.3; N, 4.0%. ν_{max}/cm^{-1}: 3325w ν(N–H), 2916 – 2849s ν(C–H)$_{aliph}$, 1636 – 1595m ν(C=C + C=N), 796 – 717m γ(C–H)$_{iq}$. δ_H (300.16 MHz; $CDCl_3$; TMS): 0.87 (6H, t, ^3J 6.9, CH_3), 1.25 (60H, m, CH_2), 1.82 (4H, qt, ^3J 6.6, CH_2), 2.10 (s, CH_3CN), 4.00 (4H, t, ^3J 6.5, OCH_2), 6.52 (1H, t, ^4J 2.2, Hp), 6.57 (2H, d, ^4J 1.9, Ho), 7.12 (1H, d, ^4J 1.7, H4'), 7.64 (1H, pt, ^3J 7.0, H7), 7.72 (1H, d, ^3J 8.0, H8), 7.93 (1H, pt, ^3J 7.4, H6), 8.09 (1H, d, ^3J 8.3, H5), 8.29 (1H, s, H4), 9.77 (1H, s, H1), 10.69 (1H, br, NH).

Table S1 Selected bond distances and angles for $[PdBr_2(Hpz^{R(6,6)py})]\cdot CH_3CN$, **9**$\cdot CH_3CN$.

Bond distances /Å		Bond angles /º	
Pd–N1	1.998(5)	N1–Pd–N3	79.3(3)
Pd–N3	2.082(5)	N1–Pd–Br2	174.6(2)
Pd–Br1	2.408(1)	N1–Pd–Br1	92.5(2)
Pd–Br2	2.394(1)	N3–Pd–Br2	95.6(2)
		N3–Pd–Br1	171.8(2)
		Br2–Pd–Br1	92.5(1)

Table S2 Selected bond distances and angles for $[PdCl_2(Hpz^{R(4,4)iq})]$ **19**

Bond distances /Å		Bond angles /º	
Pd–N1	1.999(6)	N1–Pd–N3	79.7(2)
Pd–N3	2.041(5)	N1–Pd–Cl2	171.9(3)
Pd–Cl1	2.268(2)	N1–Pd–Cl1	93.2(3)
Pd–Cl2	2.294(3)	N3–Pd–Cl2	95.0(3)
		N3–Pd–Cl1	172.7(3)
		Cl1–Pd–Cl2	92.3(2)

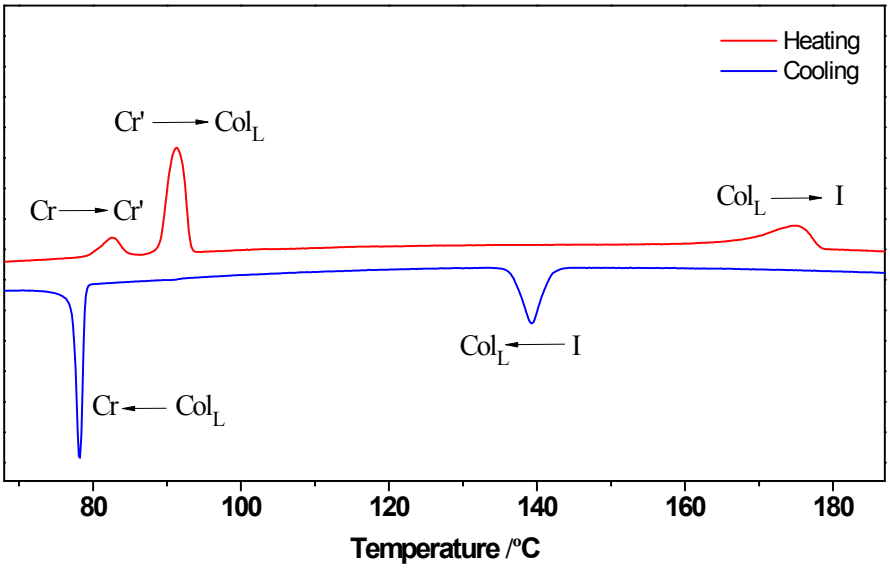

Figure S1 DSC thermogram for $[PdBr_2(Hpz^{R(12,12)py})]$ **10** after the first heating-cooling cycle.

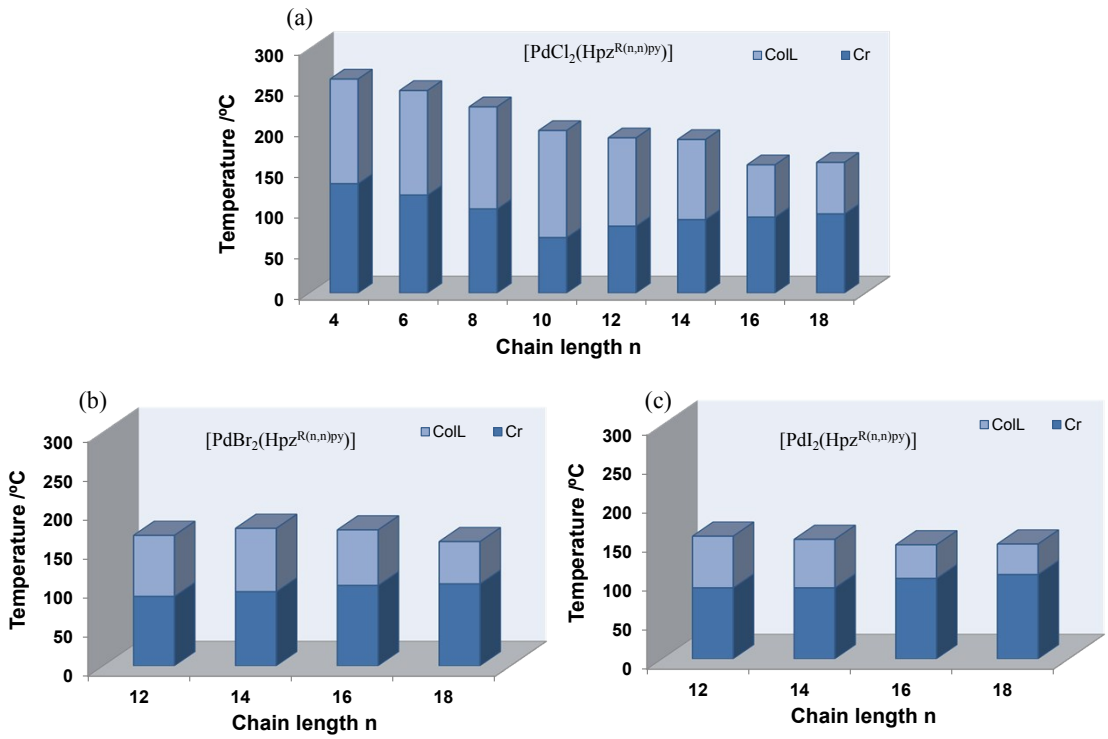

Figure S2 Bar diagram showing the range of existence of solid and liquid crystal phases for the dihalide pyridylpyrazole Pd(II) compounds. Data for the chloride compounds are taken from ref. 1.

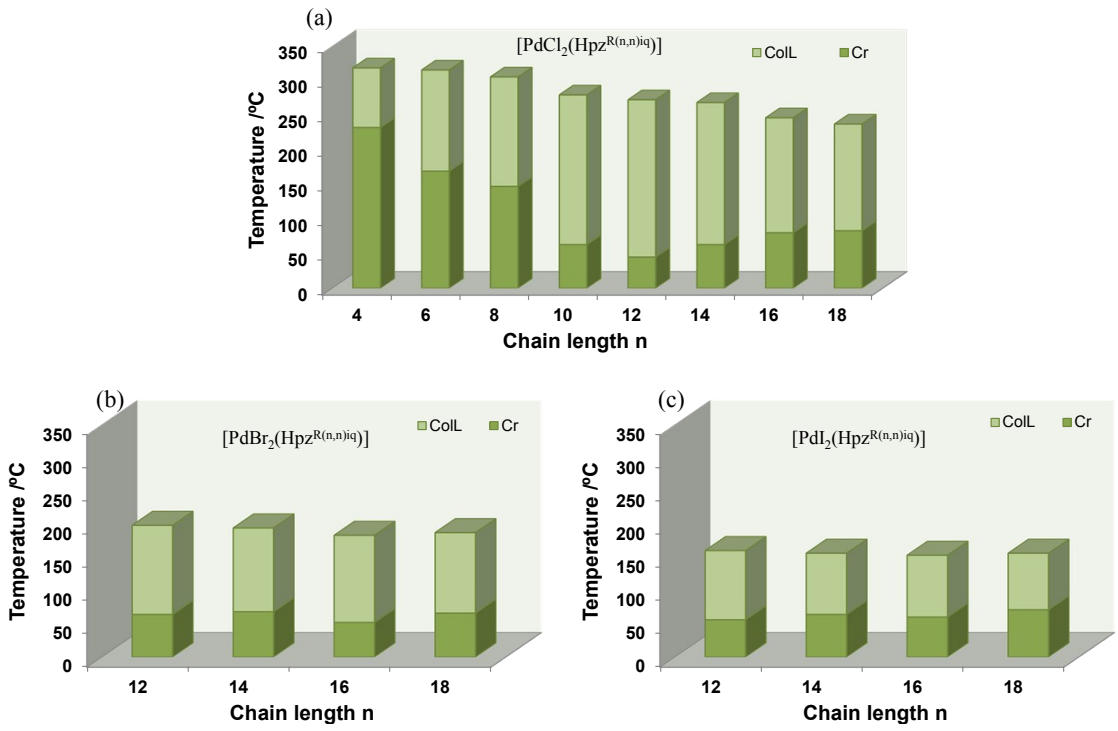

Figure S3 Bar diagram showing the range of existence of solid and liquid crystal phases for the dihalide isoquinolinylpyrazole Pd(II) compounds.

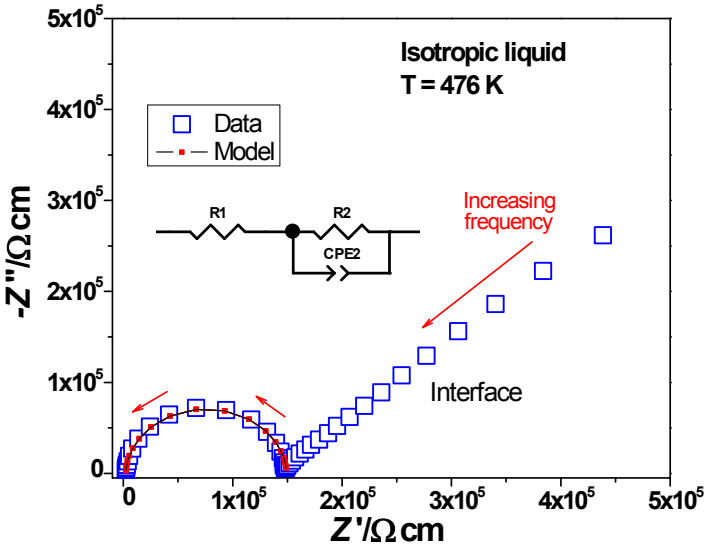

Figure S4 *Z*'' vs. *Z*' plots for the dibromide Pd(II) compound [$PdBr_2(Hpz^{R(12,12)iq})$] **27** in the isotropic liquid phase at 476 K.

References

[1] C. Cuerva, J. A. Campo, P. Ovejero, M. R. Torres and M. Cano, *Dalton Trans.*, 2014, **43**, 8849.