Electronic Supplementary Material (ESI) for CrystEngComm.

Cyclometallated Platinum(II) and Palladium(II) Complexes Containing 1,5-Diarylbiguanides: Synthesis, Characterisation and Hydrogen Bond-directed Assembly

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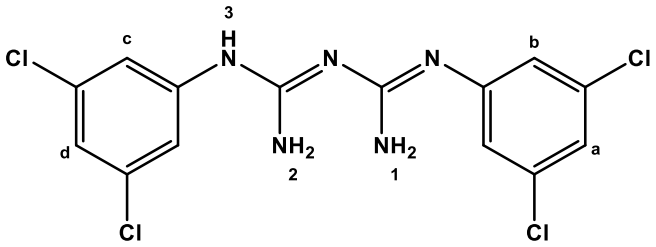
Supplementary Information

Contents:

1. Experimental Details.

1.1. Ligands

1,5-Bis(3,5-dichlorophenyl)biguanide, (HL4)



Purple-grey solid, **HL4** (1.16 g, 66%). Anal. Calc. for $C_{14}H_{11}N_5Cl_4$: C, 43.00; H, 2.84; N, 19.90; Found: C, 43.23; H, 3.05; N, 18.06. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 1.9 Hz, 2H, Ha, Hd), 7.09 (t, *J* = 1.8 Hz, 2H, Hb, Hc). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.77, 124.21, 124.03, 122.05. IR u_{max}/cm^{-1} 3500, 3438, 3396, 3288, 3150, 3074, 1600, 1531, 1413, 1381, 1259, 1138, 1106, 1039, 993, 923, 896, 846, 797, 763, 674, 566, 510, 469, 458, 443, 428. ESI-MS (*m/z*) (MeOH): $[C_{14}H_{12}N_5Cl_4]^+$ expected 374.1823, found 374.1818.

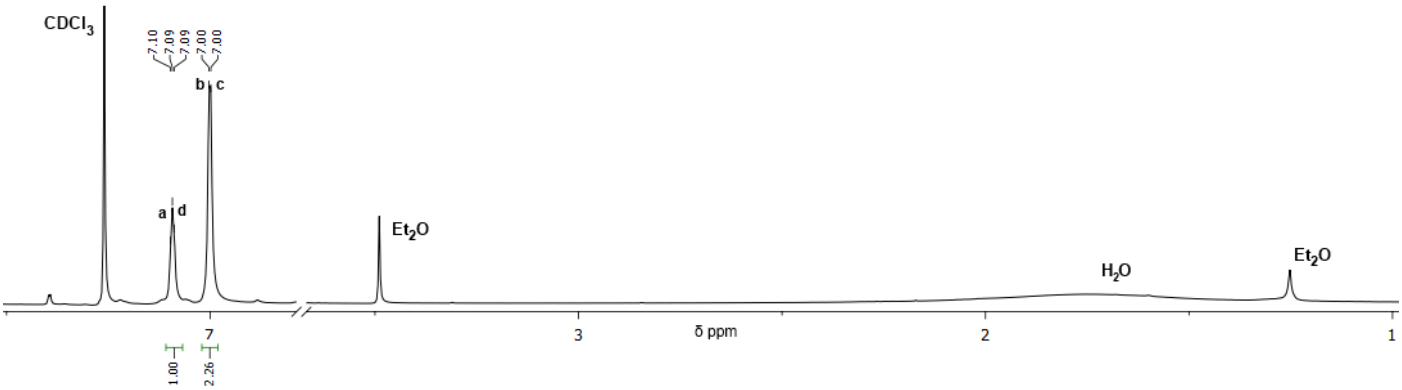
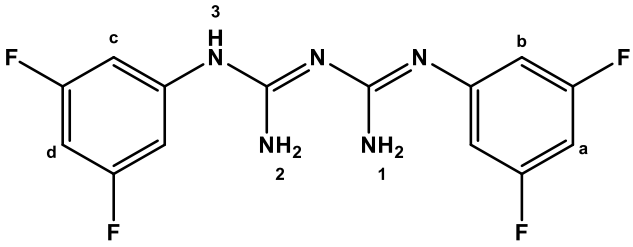


Fig. S1. ^{1}H NMR of **HL4** in $CDCl_3$ at 400 MHz.

1,5-Bis(3,5-difluorophenyl)biguanide, (HL5)



White solid, **HL5** (0.819 g, 56%). Anal. Calc. for $C_{14}H_{11}N_5F_4.0.2(C_2N_3H)$: C, 51.07; H, 3.33; N, 23.16; Found: C, 50.96 H, 3.16; N, 23.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 – 6.60 (m, 4H, Hb, Hc), 6.54 (tt, *J* = 9.1, 2.4 Hz, 2H, Ha, Hd). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.12, 164.97, 162.65, 162.50, 106.49, 106.38. IR u_{max}/cm^{-1} 3502, 3467, .406, 3322, 3114, 2977, 2176, 1651, 1590, 1560, 1448, 1417, 1357, 1321, 1194, 1159, 1112, 986, 963, 870, 855, 825, 780, 743, 708, 671, 650, 628, 586, 543, 507, 482, 437, 408. ESI-MS (*m/z*) (MeOH): $[C_{14}H_{12}N_5F_4]^+$ expected 326.1023, found 326.1039.

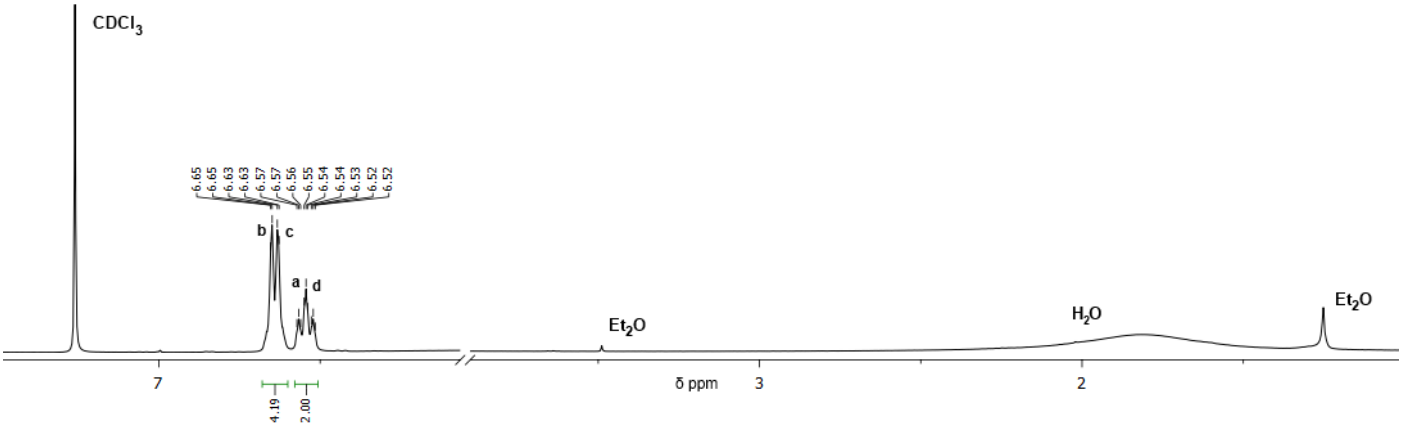


Fig. S2. ^{1}H NMR of **HL5** in $CDCl_3$ at 400 MHz.

1.2. Platinum(II) Complexes

Neutral 1,5-diarylbiguanido 2-phenylpyridine platinum(II) complexes were prepared through the following general method using the appropriately substituted 1,5-diarylbiguanide: A solution of $[Pt(ppy)\mu^2\text{-}Cl]_2$ (76.8 mg, 0.10 mmol), 1,5-diarylbiguanide ligand (0.20 mmol), and sodium carbonate (42.4 mg, 0.40 mmol) in dry N,N-dimethylformamide, was stirred for 48 hours at room temperature under an argon atmosphere. The resulting solution was dissolved into a mixture of chloroform (30 mL) and water (80 mL) which was separated and an extraction of chloroform (30 mL) performed on the aqueous phase. The combined organic phases were then washed with water (5 x 80 mL) before being dried over magnesium sulfate* before filtration and reduction of the solvent to ~10 mL on a rotary evaporator not exceeding 40°C. Immediate addition of excess petroleum ether precipitated the complex which was then collected *via* filtration after cooling to room temperature and washed with petroleum ether before being dried *in vacuo* to give the corresponding complex.**

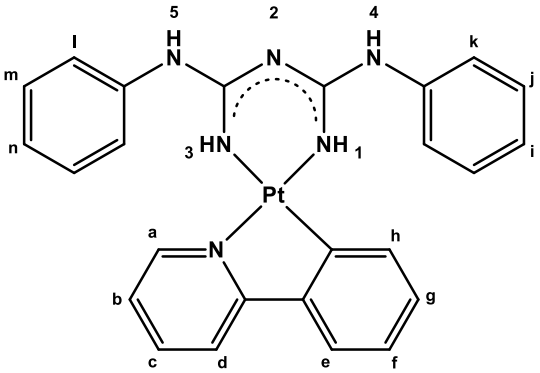
* Due to much lower chloroform solubility the complex [Pt(ppy)(**L4**)] began to precipitate during the washing of the organic phase so the undried chloroform solution was reduced in volume and the precipitate directly collected *via* filtration and washed with a minimum of cold chloroform then petroleum ether before drying *in vacuo*.

** The complex [Pt(ppy)(**L3**)] required additional purification *via* column chromatography on silica eluting with a 5:1 mixture of ethyl acetate and 40-60 petroleum ether to obtain the pure complex.

NMR Assignment

NMR in dmso-d_6 of M(ppy)(**L**) complexes gave spectra with sharp and well resolved signals including those of the NH protons. Determination of the solution state structure was done through a series of NMR experiments including ^{1}H, and ^{13}C 1D spectra and COSY, NOSEY, HSQCAD, and HMBCAD 2D spectra. COSY signals allowed the identification of the groups of peaks for the phenyl, and pyridine, of the phenylpyridine ligand, and the two aryl groups of the biguanide. Peaks of the ^{13}C spectra which did not show signals associated with protons in the HSQCAD lead to identification of the ^{13}C signals of various carbons, in combination with the HMBCAD, the carbons of the aryl rings where they join the biguanide and have the methoxy groups substituted are identifiable from their signals corresponding to the methoxy protons and NH and aryl group protons. One of the carbon signals of the phenylpyridine had a HMBCAD signal related to the NH proton of one of the coordinated N atoms, therefore this carbon was assigned as the metallated carbon and from there final assignment of the phenylpyridine signals could be made with the NOSEY confirming the ordering of the assignment with a interaction shown between protons Hd and He, and assignments of NH signals could also be made using the HMBCAD signals with the aryl rings separating NH1 and NH3 from NH4 and NH5, and the interaction between the metallated C and NH1 allowing assignment of NH1 from NH3 and NH4 from NH5. Typically the proton signals of the aryl rings would overlap into a multiplet so the assignments of protons Hi – Hl (or in the case of [Pt(ppy)(**L1**)] and [Pd(ppy)(**L1**)] Hi – Hn) are usually grouped, always in the case of symmetrically related protons, such as Hi and Hl.

[Pt(ppy)(L1)]



Bright yellow solid, [Pt(ppy)(**L1**)] (91.4 mg, 76%). Anal. Calc. for $C_{25}H_{22}N_6Pt.0.5H_2O$: C, 49.18; H, 3.80; N, 13.76; Found: C, 48.93; H, 3.75; N, 13.67. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 – 8.72 (m, 2H, Ha, NH4), 8.36 (s, 1H, NH5), 8.05 – 7.99 (m, 2H, Hc, Hd), 7.72 (d, 1H, He), 7.52 (d, J = 7.5 Hz, 1H, Hh), 7.44 – 7.37 (m, 4H, Hl, Hk), 7.35 (td, J = 6.0, 2.6 Hz, 1H, Hb), 7.24 – 7.10 (m, 5H, Hg, Hm, Hj), 7.05 (t, J = 7.4 Hz, 1H, Hf), 6.98 – 6.89 (m, 2H, Hn, Hi), 6.85 (s, 1H, NH3), 6.39 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.19, 155.05, 153.48, 151.28, 146.11, 144.75, 140.98, 140.82, 137.87, 129.45, 128.69, 128.47, 124.06, 124.02, 122.16, 122.11, 121.87, 121.33, 121.04, 120.69, 120.27, 119.37. IR υ_{max}/cm^{-1} 3358, 3039, 1607, 1582, 1522, 1480, 1453, 1425, 1305, 1235, 1178, 1158, 1065, 1032, 746, 728, 696, 667, 630, 584, 473, 449, 414. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 398 (8200) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{23}N_6Pt]^+$ expected 602.1628, found 602.1675.

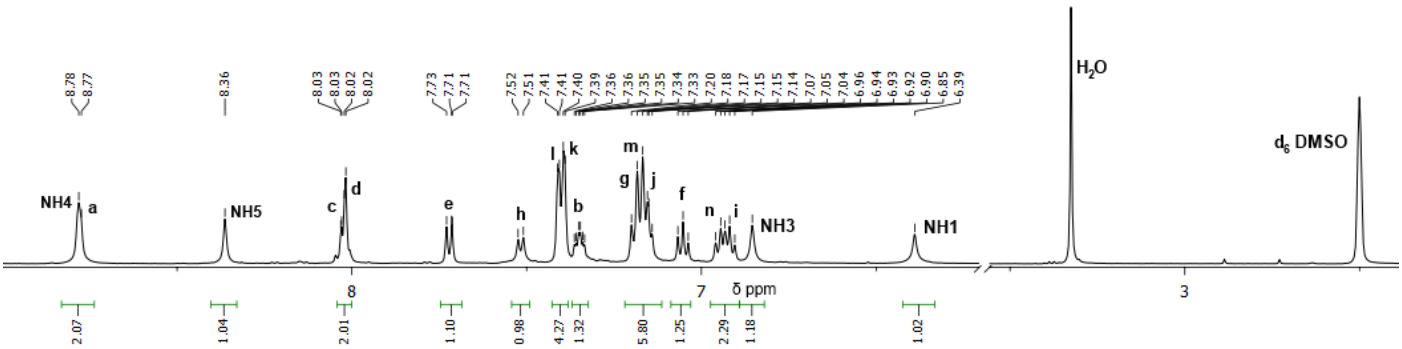


Fig. S3. ^{1}H NMR of [Pt(ppy)(**L1**)] in DMSO-d_6 at 500 MHz.

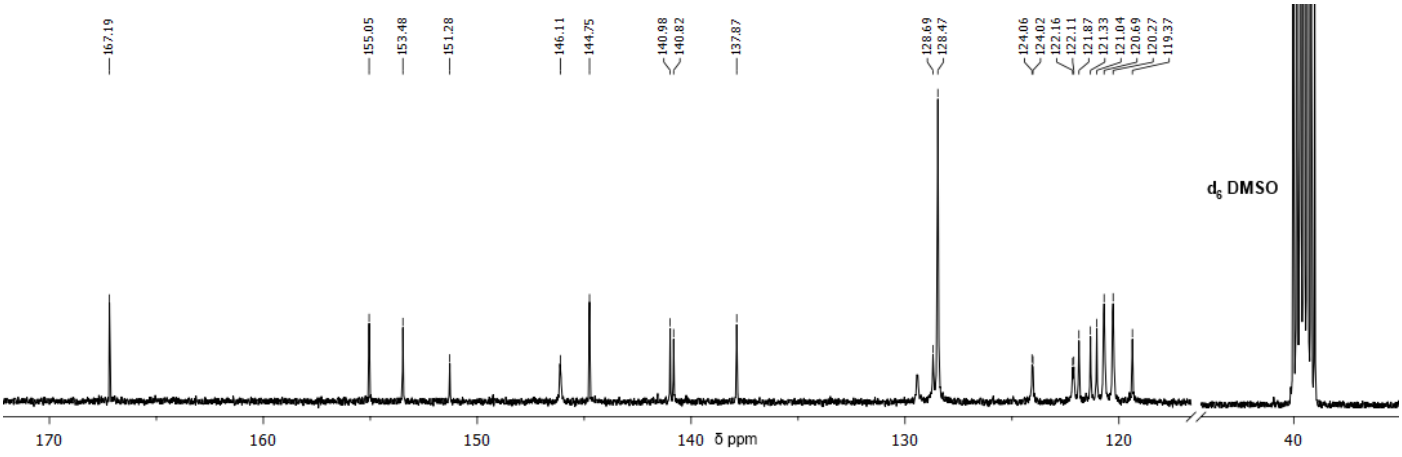
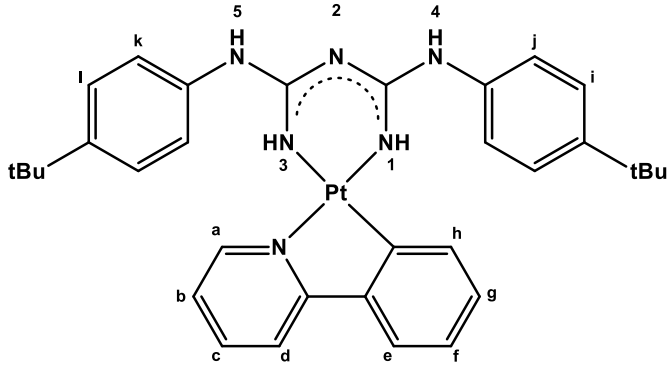


Fig. S4. ^{13}C NMR of [Pt(ppy)(**L1**)] in DMSO-d_6 at 126 MHz.

[Pt(ppy)(L2)]



Bright yellow solid, [Pt(ppy)(**L2**)] (108.5 mg, 76%). Anal. Calc. for $C_{33}H_{38}N_6Pt$: C, 55.53; H, 5.37; N, 11.77; Found: C, 55.53; H, 5.49; N, 11.68. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (d, J = 5.9 Hz, 1H, Ha), 8.68 (s, 1H, NH4), 8.26 (s, 1H, NH5), 8.06 – 7.98 (m, 2H, Hc, Hd), 7.71 (dd, 1H, He), 7.53 (d, J = 7.7 Hz, 1H, Hh), 7.36 – 7.27 (m, 5H, Hb, Hj, Hk), 7.22 – 7.11 (m, 5H, Hi, Hl, Hg), 7.05 (t, J = 7.4 Hz, 1H, Hf), 6.79 (s, 1H, NH3), 6.31 (s, 1H, NH1), 1.30 – 1.26 (m, 18H, tBu). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.24, 155.26, 153.70, 146.15, 144.76, 143.56, 143.23, 138.41, 138.26, 137.80, 129.50, 128.67, 124.97, 124.04, 122.10, 121.80, 120.85, 120.40, 119.36, 33.88, 33.85, 31.35, 31.33, 31.32. IR u_{max}/cm^{-1} 3421, 3039, 2955, 2902, 2866, 1607, 1507, 1480, 1426, 1392, 1362, 1306, 1264, 1238, 1190, 1112, 1063, 1014, 823, 811, 743, 727, 658, 415. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 400 (10000) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{33}H_{39}N_6Pt]^+$ expected 714.2881, found 714.2827.

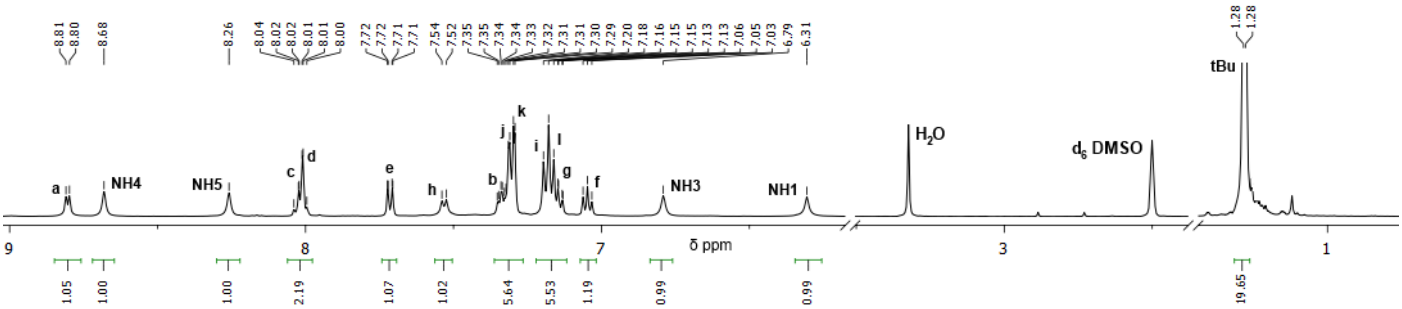


Fig. S5. ^{1}H NMR of [Pt(ppy)(**L2**)] in DMSO-d_6 at 500 MHz. tBu peak clipped for clarity.

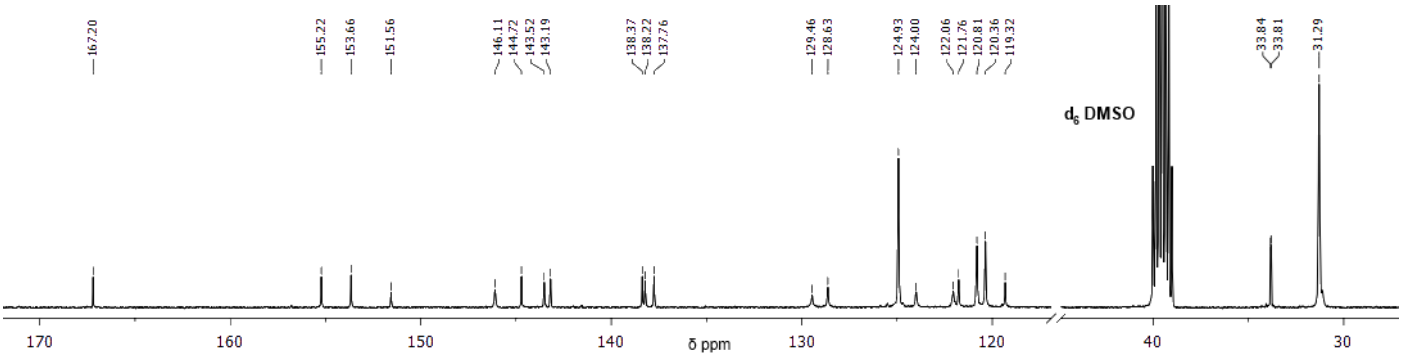
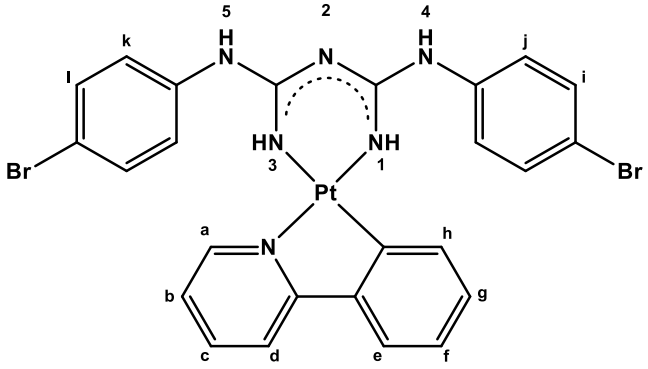


Fig. S6. ^{13}C NMR of [Pt(ppy)(**L2**)] in DMSO-d_6 at 126 MHz.

[Pt(ppy)(L3)]



Yellow solid, [Pt(ppy)(**L3**)] (27.3 mg, 18%). Anal. Calc. for $C_{25}H_{20}N_6Br_2Pt.0.5EtOAc.0.3NaCl$: C, 39.50; H, 2.95; N, 10.24; Found: C, 39.46; H, 2.51; N, 10.36. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 1H, NH4), 8.77 (dd, J = 5.7, 1.2 Hz, 1H, Ha), 8.46 (s, 1H, NH5), 8.05 – 7.99 (m, 2H, Hc, Hd), 7.72 (dd, J = 7.8, 1.3 Hz, 1H, He), 7.53 (dd, J = 7.6, 1.1 Hz, 1H, Hh), 7.38 – 7.25 (m, 9H, Hb, Hi, Hj, Hk, Hl), 7.17 (td, J = 7.3, 1.3 Hz, 1H, Hg), 7.10 – 7.02 (m, 1H, Hf), 6.93 (s, 1H, NH3), 6.44 (s, 1H, NH1). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.16, 154.72, 153.18, 146.20, 144.76, 140.32, 140.23, 137.96, 131.10, 131.07, 129.45, 128.69, 122.66, 122.52, 122.17, 121.97, 112.80, 112.67. IR υ_{max}/cm^{-1} 3357, 3271, 3058, 2964, 1607, 1575, 1477, 1419, 1389, 1304, 1284, 1233, 1066, 1006, 810, 745, 727, 657, 487, 451, 438, 411. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 390 (6500) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{21}N_6Br_2Pt]^+$ expected 760.9816, found 760.9845.

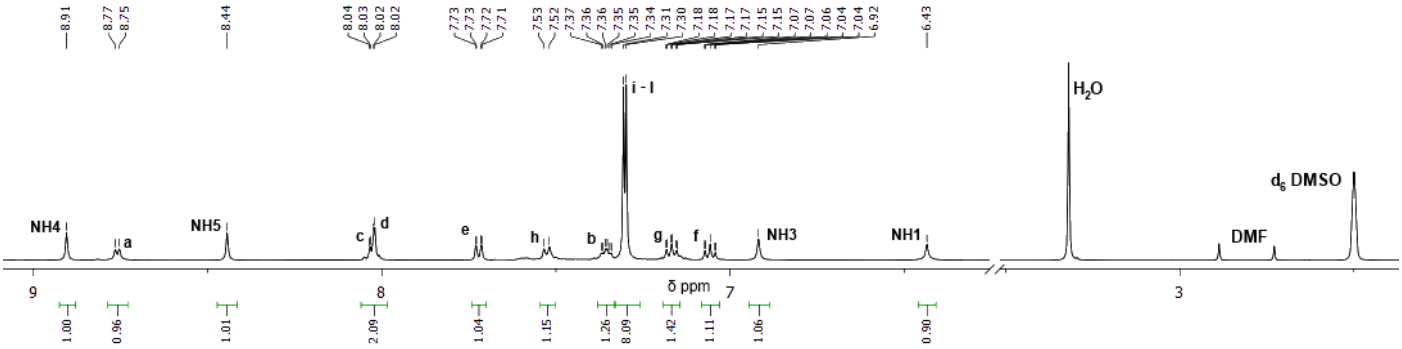


Fig. S7. ^{1}H NMR of [Pt(ppy)(**L3**)] in DMSO-d_6 at 500 MHz.

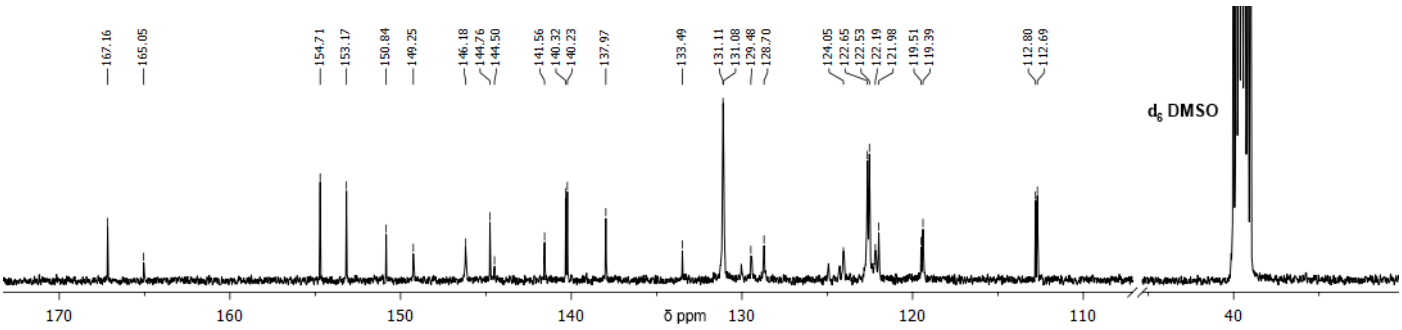
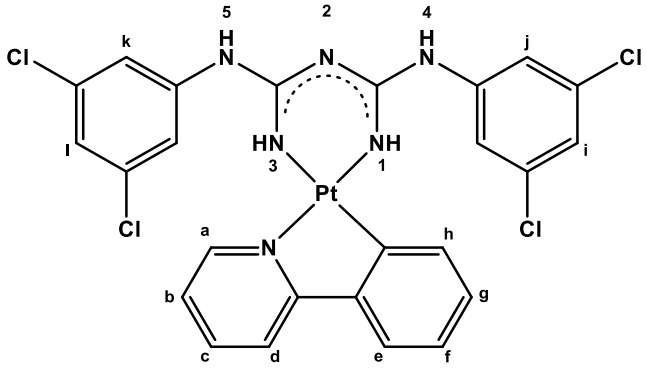


Fig. S8. ^{13}C NMR of [Pt(ppy)(**L3**)] in DMSO-d_6 at 126 MHz.

[Pt(ppy)(L4)]



Bright yellow solid, [Pt(ppy)(**L4**)] (44.1 mg, 30%). Anal. Calc. for $C_{25}H_{18}N_6Cl_4Pt.1.5H_2O$: C, 39.18; H, 2.76; N, 10.97. Found: C, 39.15; H, 2.64; N, 10.82. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.27 (s, 1H, NH4), 8.82 – 8.72 (m, 2H, NH5, Ha), 8.08 – 8.00 (m, 2H, Hc, Hd), 7.74 (dd, J = 7.8, 1.3 Hz, 1H, He), 7.54 (d, J = 7.4 Hz, 1H, Hh), 7.45 – 7.34 (m, 5H, Hb, Hj, Hk), 7.23 – 7.15 (m, 2H, Hg, Hi/Hl), 7.07 (td, J = 7.4, 1.1 Hz, 1H, Hf), 7.04 – 7.00 (m, 2H, NH3, Hi/Hl), 6.65 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.16, 153.66, 152.20, 146.31, 143.13, 143.02, 138.23, 133.96, 133.93, 129.48, 128.73, 124.11, 122.24, 119.79, 119.76, 119.74, 119.47, 117.42, 117.41, 117.39, 117.36, 117.32. IR υ_{max}/cm^{-1} 3413, 3391, 3378, 3334, 3046, 1625, 1583, 1573, 1547, 1523, 1495, 1475, 1441, 1421, 1389, 1303, 1250, 1236, 1114, 1097, 1071, 991, 938, 849, 827, 800, 742, 727, 688, 658, 627, 569, 556, 529, 488, 412. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 391 (11800) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{19}N_6Cl_4Pt]^+$ expected

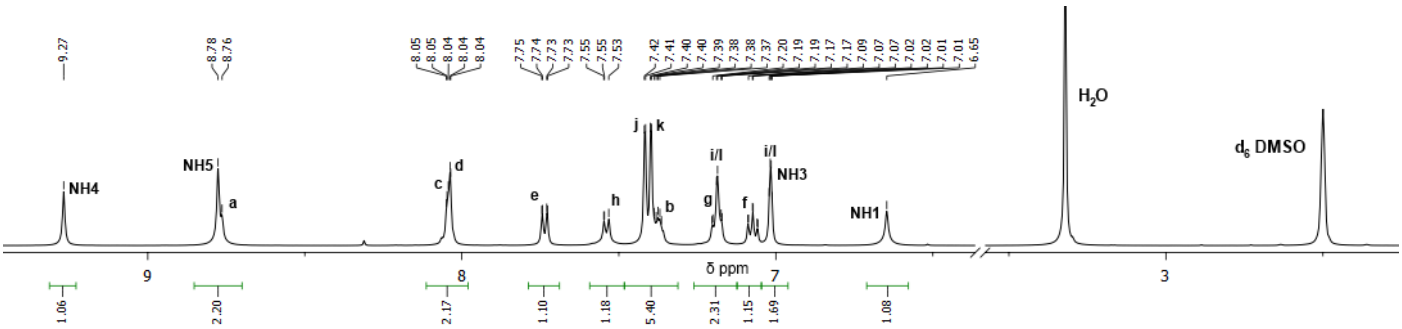


Fig. S9. ^{1}H NMR of [Pt(ppy)(**L4**)] in DMSO-d_6 at 500 MHz.

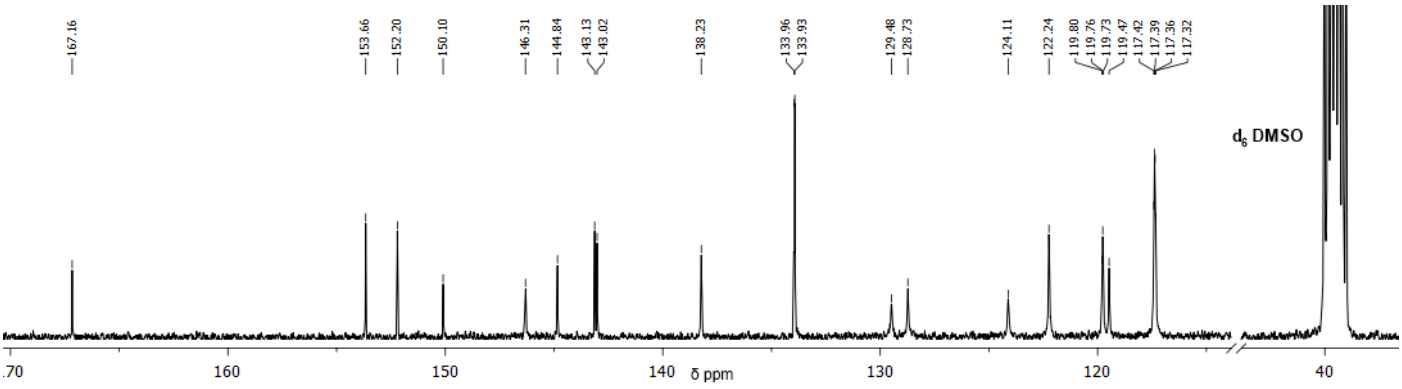
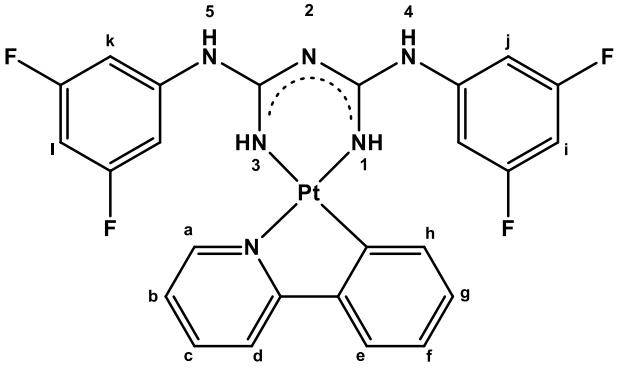


Fig. S10. ^{13}C NMR of [Pt(ppy)(**L4**)] in DMSO-d_6 at 126 MHz.

[Pt(ppy)(L5)]



Dark yellow solid, [Pt(ppy)(**L5**)] (75.6 mg, 56%). Anal. Calc. for $C_{25}H_{18}N_6F_4Pt.0.2NaCl$: C, 43.82; H, 2.65; N, 11.09; Found: C, 43.66; H, 2.85; N, 11.46. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H, NH4), 8.78 (d, J = 10.2 Hz, 2H, NH5, Ha), 8.08 – 8.00 (m, 2H, Hc, Hd), 7.74 (dd, 1H, He), 7.55 (d, J = 7.5 Hz, 1H, Hh), 7.37 (td, J = 5.6, 3.1 Hz, 1H, Hb), 7.22 – 7.02 (m, 7H, NH3, Hi, Hj, Hk, Hl), 6.69 – 6.56 (m, 3H, NH1, Hf, Hg). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.83, 161.49, 161.42, 161.33, 161.27, 153.87, 152.40, 150.26, 146.31, 143.37, 138.20, 129.51, 128.72, 124.09, 122.21, 119.46, 102.33, 102.06, 95.63. IR u_{max}/cm^{-1} 3053, 2185, 1587, 1456, 1424, 1256, 1168, 1115, 982, 830, 750, 729, 651, 593, 508, 415. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 389 (11400) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{23}H_{19}N_6F_4Pt]^+$ expected 674.1252, found 674.1307.

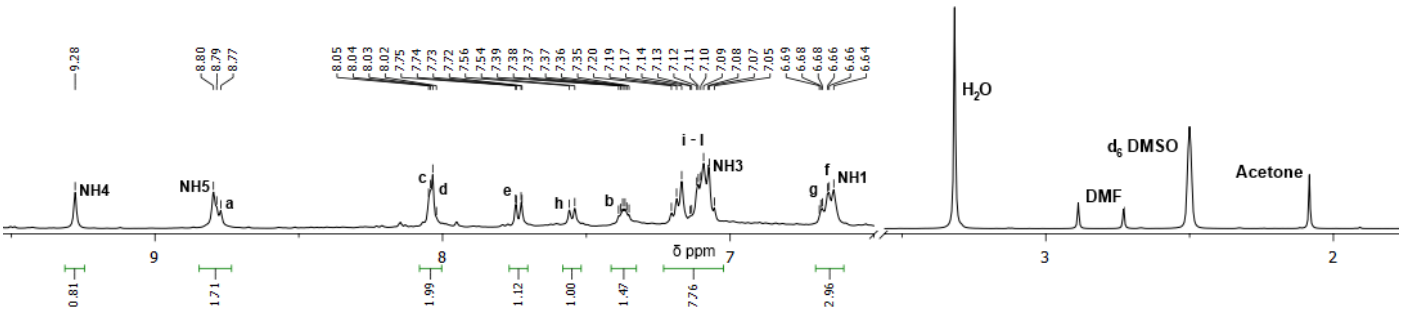


Fig. S11. ^{1}H NMR of [Pt(ppy)(**L5**)] in DMSO-d_6 at 400 MHz.

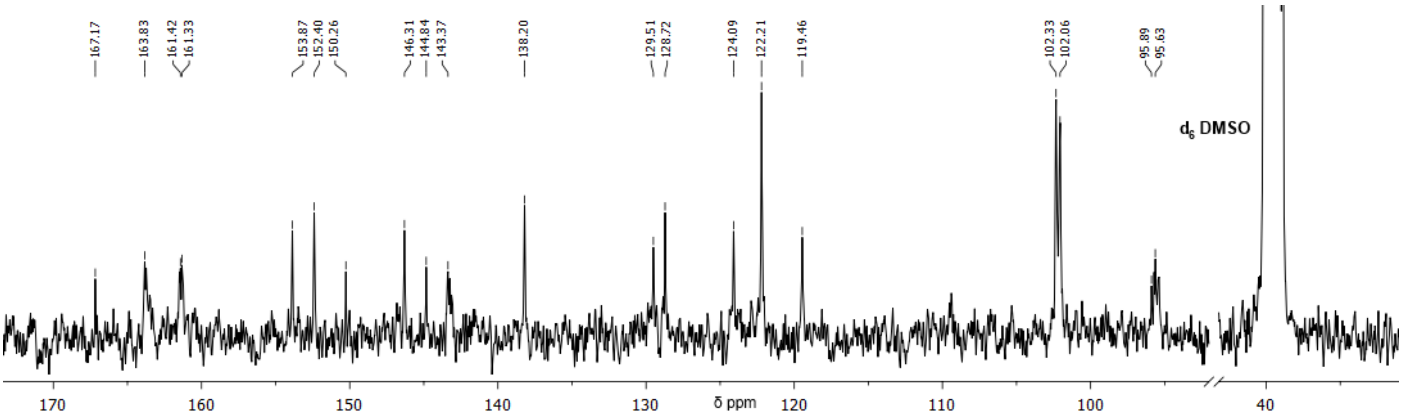
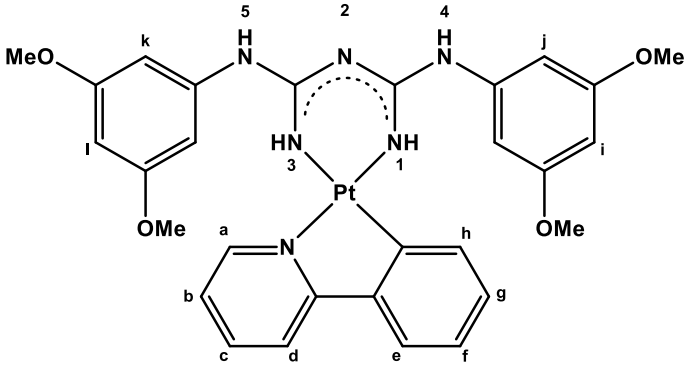


Fig. S12. ^{13}C NMR of [Pt(ppy)(**L5**)] in DMSO-d_6 at 101 MHz.

[Pt(ppy)(L6)]



Bright yellow solid, [Pt(ppy)(**L6**)] (73.6mg, 51%). Anal. Calc. for $C_{28}H_{30}N_6O_4Pt.0.2NaCl$: C, 47.50; H, 4.12; N, 11.46; Found: C, 47.73; H, 4.04; N, 11.36. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (s, 1H, NH4), 8.76 (d, J = 5.9 Hz, 1H, Ha), 8.38 (s, 1H, NH5), 8.07 – 7.99 (m, 2H, Hc, Hd), 7.72 (dd, J = 7.8, 1.4 Hz, 1H, He), 7.51 (d, J = 7.5 Hz, 1H, Hh), 7.35 (td, J = 5.9, 2.8 Hz, 1H, Hb), 7.15 (td, 1H, Hf), 7.06 (t, J = 7.4 Hz, 1H, Hg), 6.92 (s, 1H, NH3), 6.70 – 6.62 (m, 4H, Hj, Hk), 6.48 (s, 1H, NH1), 6.05 (t, J = 2.2 Hz, 1H, Hl/Hi), 6.02 (t, J = 2.2 Hz, 1H, Hl/Hi), 3.56 – 3.52 (m, 12H, OMe). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.20, 160.48, 154.56, 152.98, 151.04, 146.08, 144.77, 142.76, 142.58, 137.97, 129.39, 128.69, 124.06, 122.17, 121.96, 119.42, 97.79, 97.76, 97.42, 97.39, 93.91, 93.84, 93.61, 93.54, 54.67, 54.62. IR u_{max}/cm^{-1} 3406, 3305, 3181, 2933, 1666, 1598, 1580, 1547, 1495, 1481, 1450, 1414, 1374, 1349, 1302, 1231, 1205, 1192, 1176, 1161, 1122, 1096, 1047, 1032, 982, 944, 829, 816, 761, 739, 660, 629, 439, 418. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 396 (10500) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{28}H_{31}N_6O_4Pt]^+$ expected 722.2051, found 722.2087.

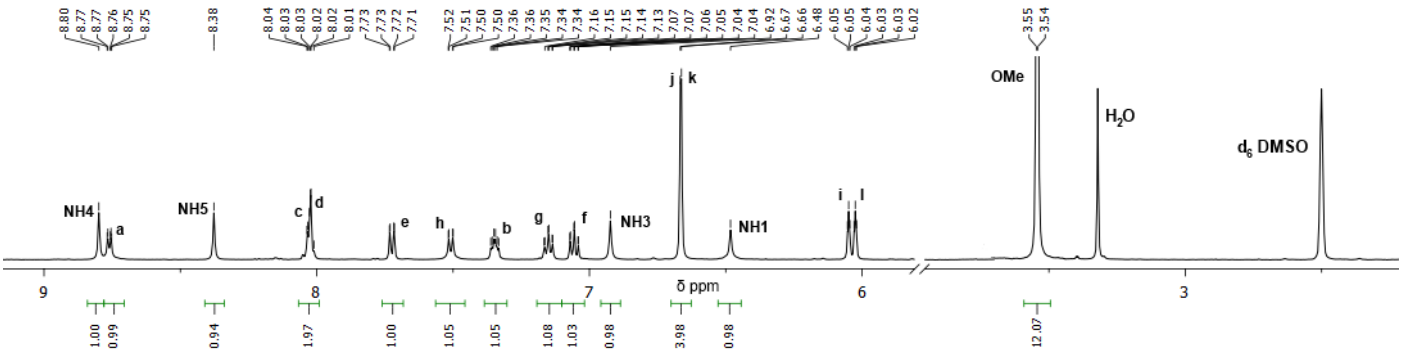


Fig. S13. ^{1}H NMR of [Pt(ppy)(**L6**)] in DMSO-d_6 at 500 MHz. OMe peak clipped for clarity.

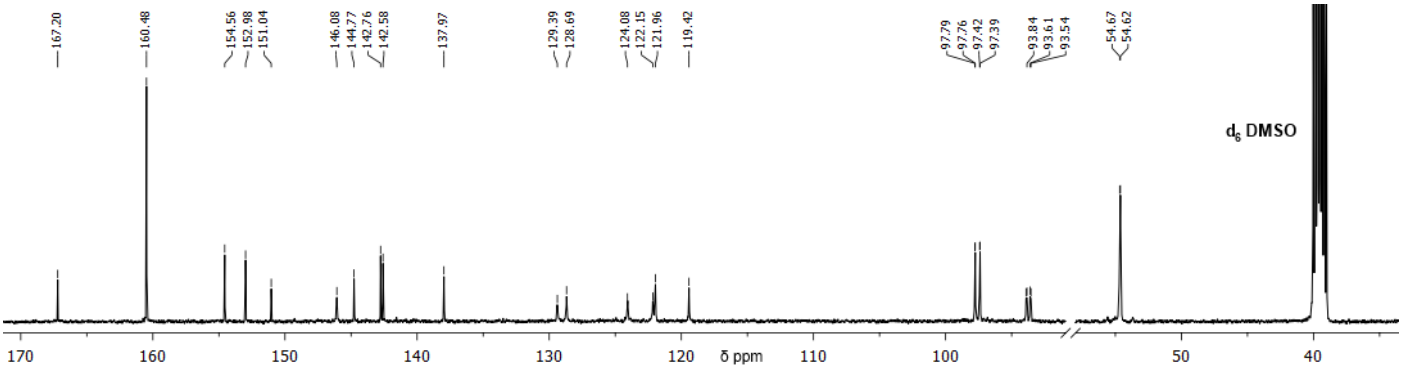


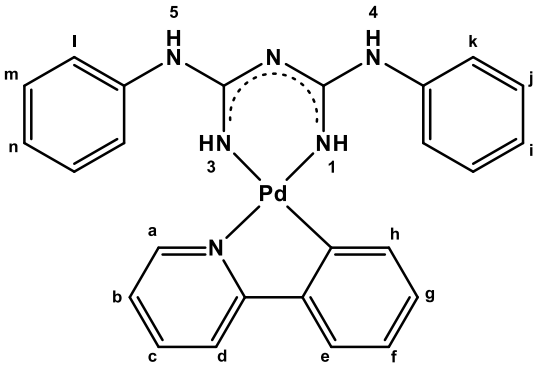
Fig. S14. ^{13}C NMR of [Pt(ppy)(**L6**)] in DMSO-d_6 at 126 MHz.

1.3. Palladium(II) Complexes

Charged 1,5-diarylbiguanide 2-phenylpyridine palladium(II) acetate complexes were prepared through the following general method using the appropriately substituted 1,5-diarylbiguanide: To a solution of $[Pd(ppy)\mu^2\text{-}OAc]_2$ (64.1 mg, 0.10 mmol) in dichloromethane (15 mL), two equivalents of the ligand (0.20 mmol) was added and the resulting solution stirred at room temperature overnight, during which time a pale yellow or cream precipitate formed. The solution was poured into an excess of diethylether (80 mL) and stirred for a further 10 min. The resulting yellow or cream precipitates were filtered and washed with diethylether before being dried *in vacuo* to give the corresponding complex.

Neutral 1,5-diarylbiguanido 2-phenylpyridine palladium(II) complexes were prepared from the corresponding acetate complex through the following general method: To a suspension of the charged palladium(II) complex (0.075 mmol) in acetone (10 mL), a solution of sodium methoxide (17 μL, 25 wt%) was added and the resulting solution was stirred at room temperature overnight. Reduction of the solvent and addition of diethylether gave pale yellow solids which were collected via filtration and washed with diethylether before being dried *in vacuo* to give the corresponding neutral complex.

[Pd(ppy)(L1)]



Pale yellow solid, [Pd(ppy)(**L1**)] (38.5 mg, 74%). Anal. Calc. for $C_{25}H_{22}N_6Pd$: C, 58.54; H, 4.32; N, 16.39; Found: C, 58.60; H, 5.26; N, 16.37. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (s, 1H, NH4), 8.49 (d, J = 5.6 Hz, 1H, Ha), 8.20 (s, 1H, NH5), 8.10 – 8.01 (m, 2H, Hc, Hd), 7.74 (dd, J = 7.7, 1.4 Hz, 1H, He), 7.44 – 7.36 (m, 6H, Hh, Hk, Hl, Hm/Hn), 7.23 – 7.12 (m, 5H, Hi, Hj, Hm/Hn), 7.09 (t, J = 7.4 Hz, 1H, Hb), 6.96 – 6.86 (m, 2H, Hf, Hg), 5.88 (s, 1H, NH3), 5.38 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.57, 160.14, 157.52, 156.71, 147.29, 145.53, 141.17, 141.07, 138.81, 130.97, 128.41, 123.74, 123.48, 122.34, 121.15, 120.82, 120.62, 120.13, 119.35, 79.16. IR υ max/cm^{-1} 3420, 3395, 3356, 3173, 3039, 1612, 1601, 1580, 1514, 1498, 1478, 1448, 1423, 1229, 1194, 1178, 1057, 1025, 1001, 979, 899, 837, 788, 744, 727, 670, 628, 585, 490, 469, 446, 410. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 384 (4200) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{23}N_6Pd]^+$ expected 513.1023, found 513.1015.

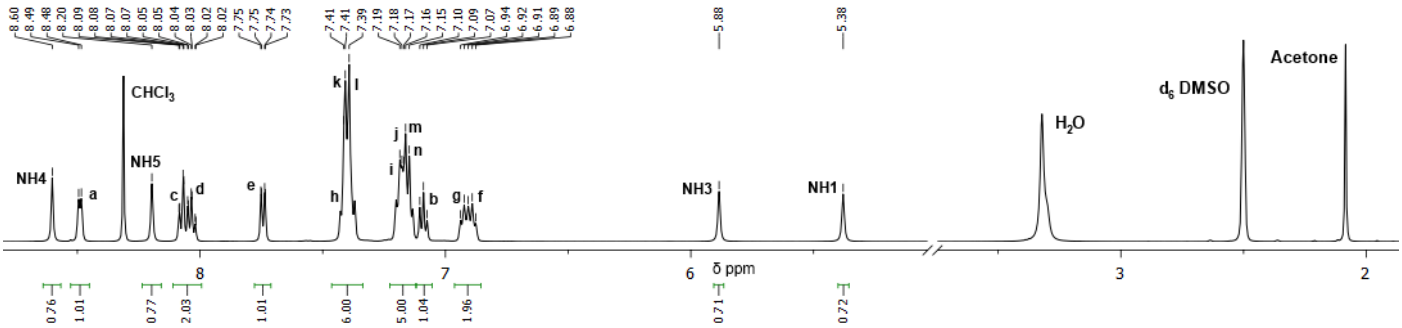


Fig. S15. ^{1}H NMR of [Pd(ppy)(**L1**)] in DMSO-d_6 at 500 MHz.

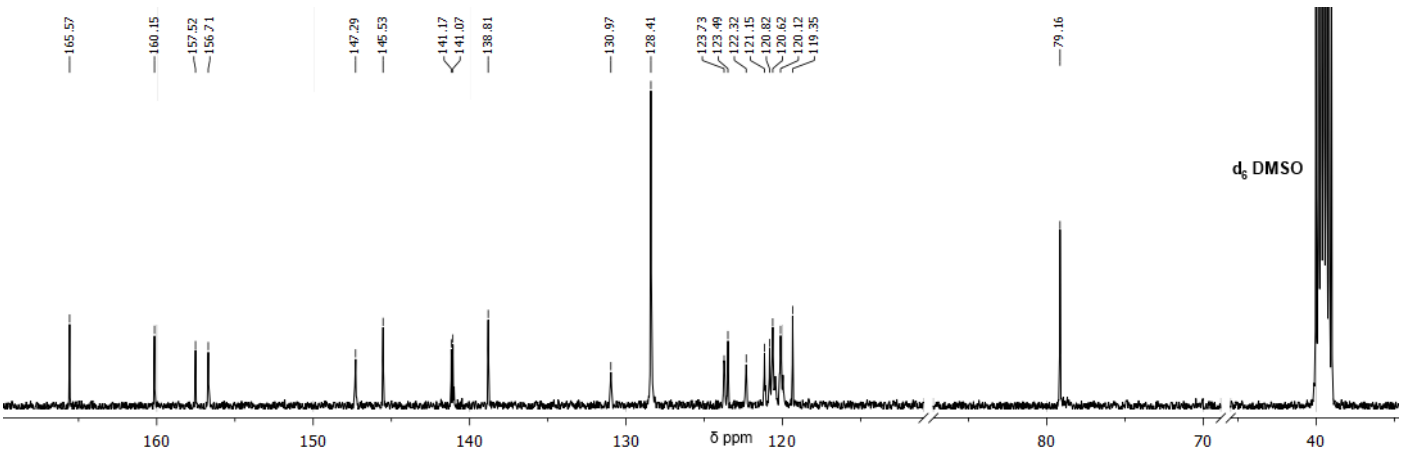
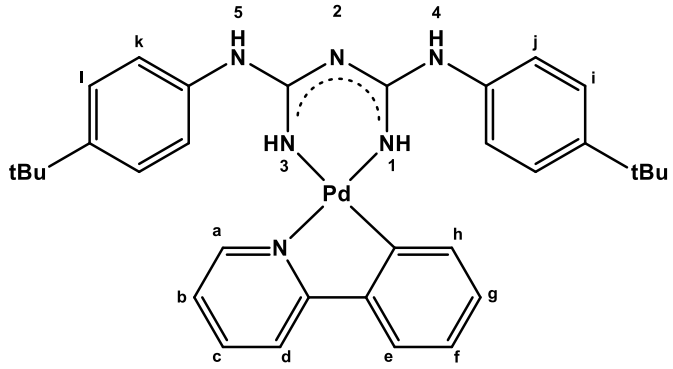


Fig. S16. ^{13}C NMR of [Pd(ppy)(**L1**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(L2)]



Yellow crystalline solid, [Pd(ppy)(**L2**)] (28.2 mg, 48%). Anal. Calc. for $C_{33}H_{38}N_6Pd{\cdot}0.5H_2O$: C, 62.50; H, 6.20; N, 13.25. Found: C, 62.55; H, 6.16; N, 13.34. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 – 8.44 (m, 2H, Ha, NH4), 8.10 – 7.99 (m, 3H, Hc, Hd, NH5), 7.74 (d, J = 7.5 Hz, 1H, He), 7.45 – 7.36 (m, 2H, Hb, Hh), 7.33 – 7.25 (m, 4H, Hk, Hj), 7.22 – 7.11 (m, 5H, Hg, Hi, Hl), 7.09 (t, J = 7.3 Hz, 1H, Hf), 5.79 (s, 1H, NH3), 5.28 (s, 1H, NH1), 1.27 (d, J = 4.4 Hz, 18H, tBu). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.38, 157.65, 156.88, 147.25, 143.36, 142.98, 138.76, 138.55, 138.46, 131.03, 128.28, 124.89, 124.87, 123.69, 123.42, 122.28, 120.78, 120.22, 119.33, 33.82, 33.78, 31.31. IR umax/cm-1 3427, 2959, 2865, 1602, 1506, 1471, 1431, 1233, 743, 722, 570. UV-vis (DMSO): λ_{max} (ε/$M^{-1}cm^{-1}$) = 384 (3800) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{33}H_{39}N_6Pd]^+$ expected 625.2266, found 625.2211.

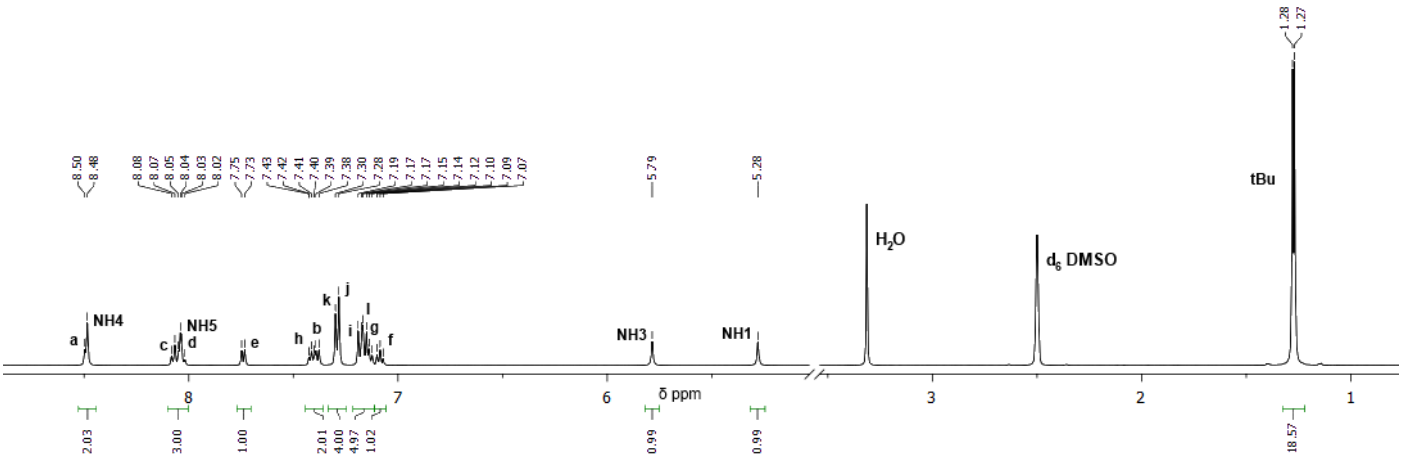


Fig. S17. ^{1}H NMR of [Pd(ppy)(**L2**)] in DMSO-d_6 at 500 MHz.

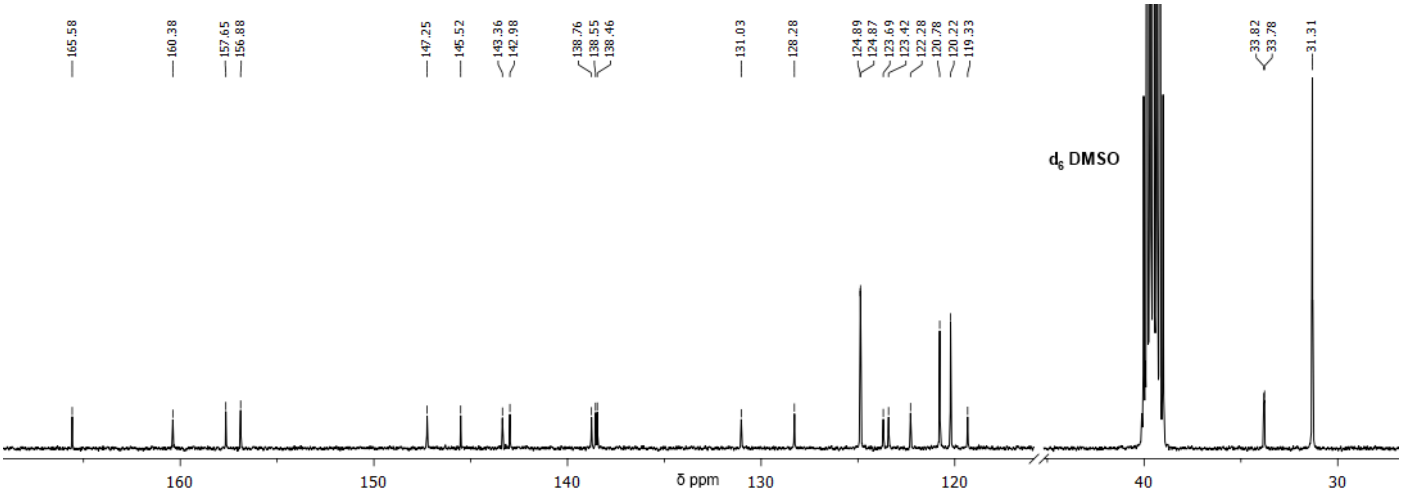
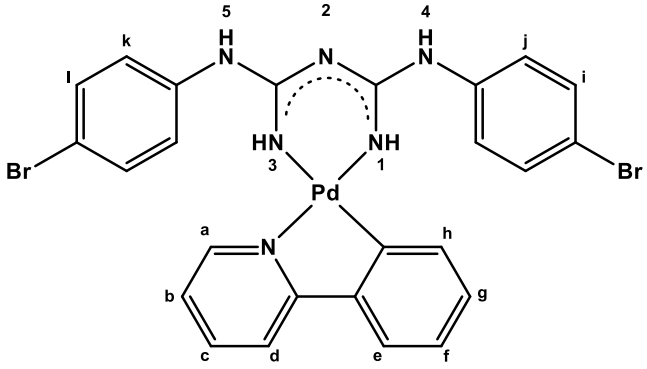


Fig. S18. ^{13}C NMR of [Pd(ppy)(**L2**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(L3)]



Cream solid, [Pd(ppy)(**L3**)] (39.7 mg, 79%) Anal. Calc. for $C_{25}H_{20}Br_2N_6Pd{\cdot}NaOAc$: C, 43.08; H, 3.08; N, 11.16. Found: C, 42.64; H, 3.06; N, 10.58. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.81 (s, 1H, NH4), 8.56 (d, J = 5.2 Hz, 2H, NH5, Ha), 8.08 – 8.01 (m, 2H, Hc, Hd), 7.74 (d, J = 7.6 Hz, 1H, He), 7.43 – 7.39 (m, 2H, Hb, Hh), 7.37 – 7.21 (m, 8H, Hi-l), 7.16 (t, J = 7.3 Hz, 1H, Hg), 7.09 (t, J = 7.4 Hz, 1H, Hf), 6.11 (s, 1H, NH3), 5.43 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.52, 159.88, 157.24, 156.40, 147.64, 145.56, 140.65, 140.55, 138.84, 131.03, 131.00, 130.97, 128.37, 123.73, 123.55, 122.51, 122.39, 122.29, 119.31. IR u_{max}/cm^{-1} 3400, 3275, 1685, 1627, 1604, 1585, 1555, 1487, 1399, 1220, 1068, 1007, 837, 750, 729, 644. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 386 (2400) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{21}Br_2N_6Pd]^+$ expected 670.9215, found 670.9164.

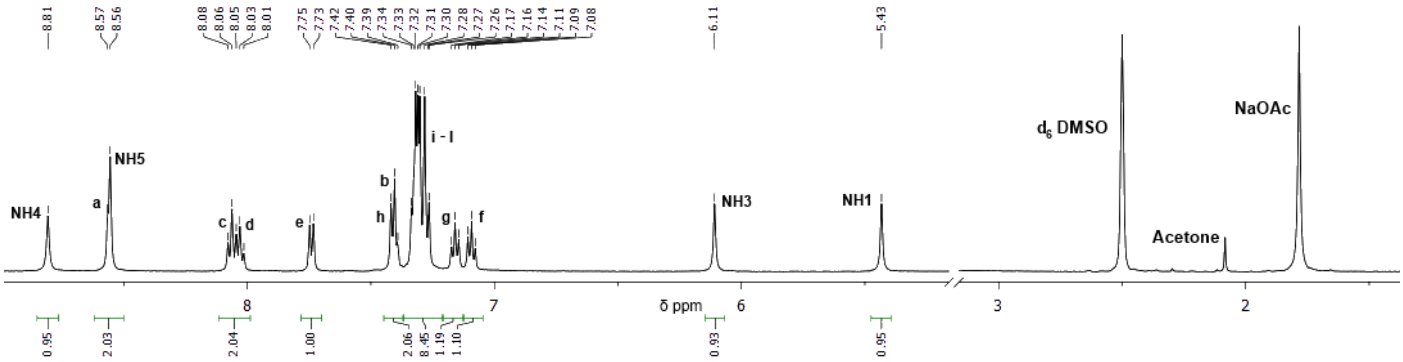


Fig. S19. ^{1}H NMR of [Pd(ppy)(**L3**)] in DMSO-d_6 at 500 MHz.

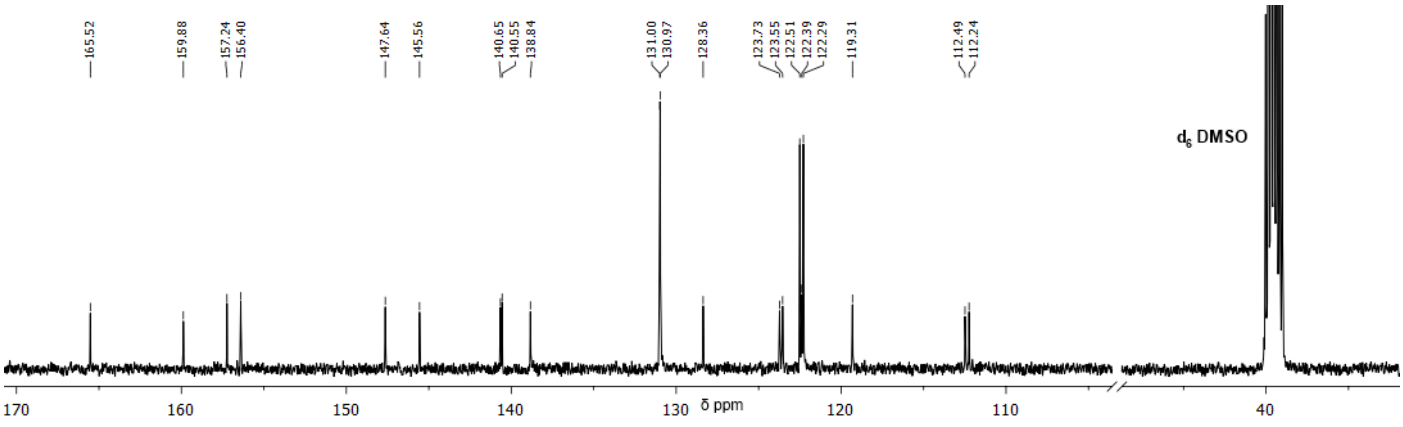
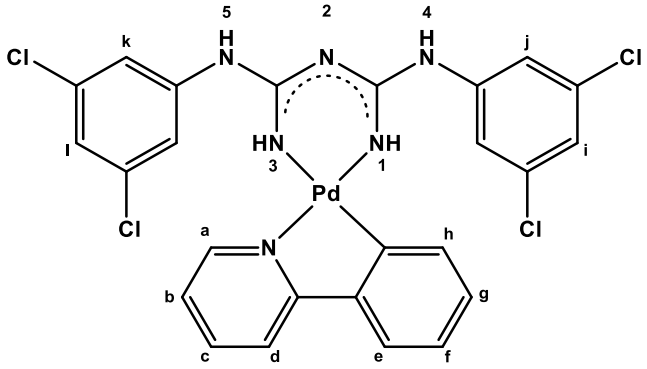


Fig. S20. ^{13}C NMR of [Pd(ppy)(**L3**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(L4)]



Pale yellow solid, [Pd(ppy)(**L4**)] (18.5 mg, 38%). Anal. Calc. for $C_{25}H_{18}Cl_4N_6Pd.H_2O$: C, 44.77; H, 3.31; N, 12.53. Found C, 44.96; H, 3.24; N, 12.31. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.12 (s, 1H, NH4), 8.63 (s, 1H, NH5), 8.50 (d, J = 5.6 Hz, 1H, Ha), 8.08 (dd, J = 15.9, 7.7 Hz, 2H, Hc, Hd), 7.76 (d, J = 7.6 Hz, 1H, He), 7.49 – 7.36 (m, 6H, Hb, Hh, Hj, Hk), 7.19 (t, J = 7.4 Hz, 1H, Hf), 7.12 (t, J = 7.4 Hz, 1H, Hg), 6.98 (dt, J = 3.2, 1.6 Hz, 2H, Hi, Hl), 6.21 (s, 1H, NH3), 5.62 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.55, 159.22, 156.35, 155.60, 147.45, 145.58, 143.33, 143.29, 139.08, 133.85, 133.84, 130.96, 128.44, 123.86, 123.77, 122.45, 119.55, 119.49, 119.48, 117.24. IR υ_{max}/cm^{-1} 3413, 3050, 1629, 1572, 1544, 1518, 1492, 1469, 1437, 1419, 1301, 1234, 1113, 1067, 827, 796, 743, 727, 656. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 384 (2300) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{19}Cl_4N_6Pd]^+$ expected 650.9441, found 650.9438.

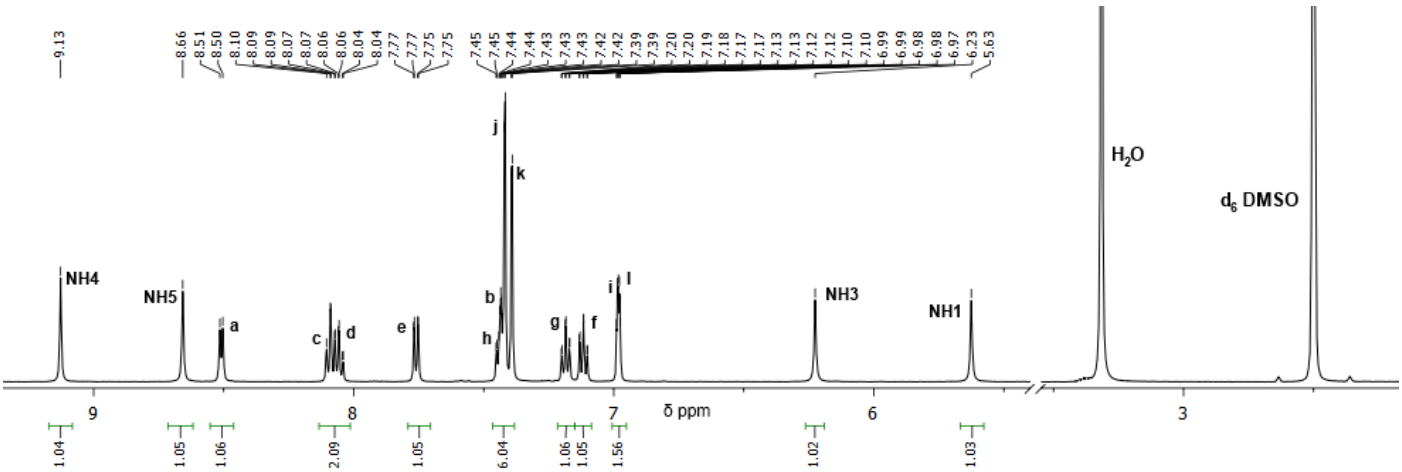


Fig. S21. ^{1}H NMR of [Pd(ppy)(**L4**)] in DMSO-d_6 at 500 MHz.

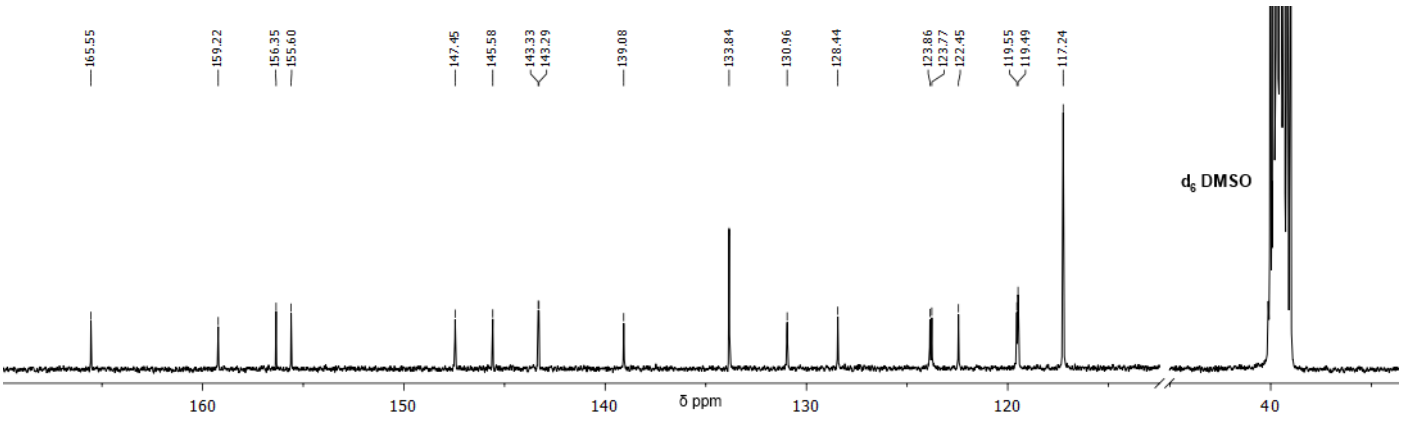
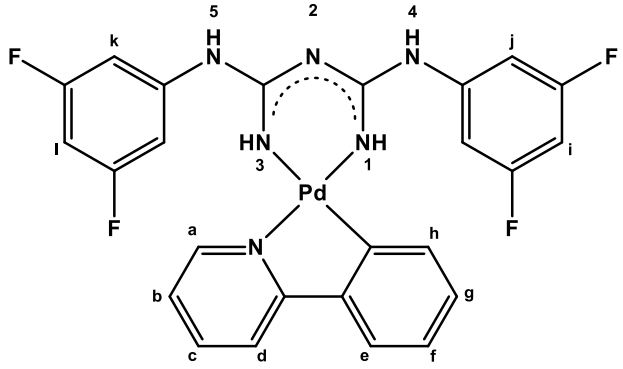


Fig. S22. ^{13}C NMR of [Pd(ppy)(**L4**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(L5)]



Pale yellow solid, [Pd(ppy)(**L5**)] (28.5 mg, 74%). Anal. Calc. for $C_{25}H_{18}F_4N_6Pd.H_2O.0.5CH_3OH$: C, 49.49; H, 3.58; N, 13.58. Found C, 49.71; H, 3.21; N, 13.23. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.33 (s, 1H, NH4), 9.29 (s, 1H, NH5), 8.70 (d, J = 5.6 Hz, 1H, Ha), 8.12 – 7.94 (m, 2H, Hc, Hd), 7.75 (d, J = 7.6 Hz, 1H, He), 7.46 (d, J = 7.5 Hz, 1H, Hh), 7.39 (t, J = 6.5 Hz, 1H, Hb), 7.22 – 7.03 (m, 6H, Hg, Hf, Hj, Hk), 6.65 – 6.47 (m, 3H, Hi, Hl, NH3), 5.64 (s, 1H, NH1). ^{13}C NMR (126 MHz, DMSO-d_6) δ 173.32, 165.49, 163.53, 163.40, 161.48, 156.63, 155.74, 148.09, 145.62, 143.83, 138.91, 131.08, 128.36, 123.75, 123.66, 122.41, 119.28, 102.09, 101.98, 101.89, 101.75, 95.25, 95.15, 95.04, 94.93. IR υ max/cm^{-1} 3419, 3394, 3376, 3219, 3057, 1625, 1599, 1580, 1556, 1532, 1510, 1453, 1424, 1408, 1304, 1249, 1214, 1169, 1155, 1115, 1076, 1006, 995, 978, 826, 808, 744, 731, 714, 700, 670, 647, 590, 561, 551, 526, 506, 478, 412. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 384 (2800) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{19}F_4N_6Pd]^+$ expected 585.0646, found 585.0612.

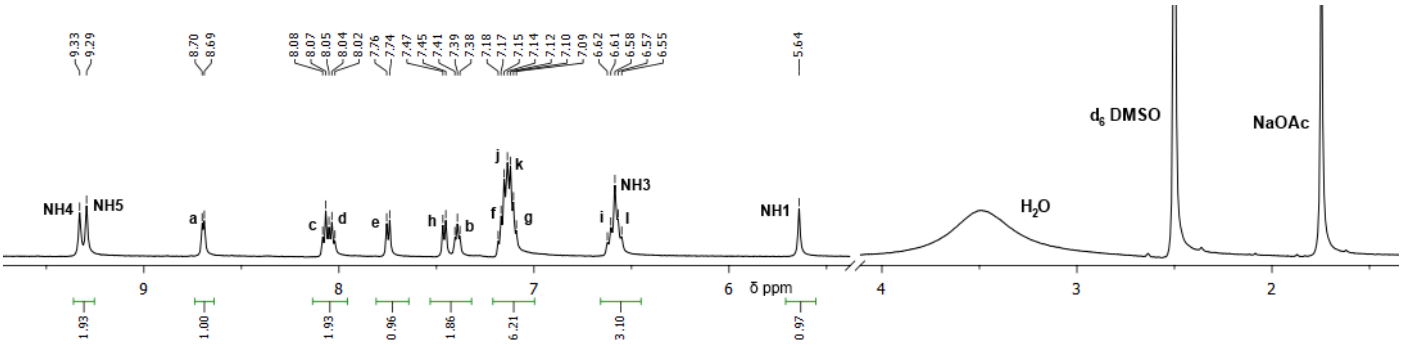


Fig. S23. ^{1}H NMR of [Pd(ppy)(**L5**)] in DMSO-d_6 at 500 MHz.

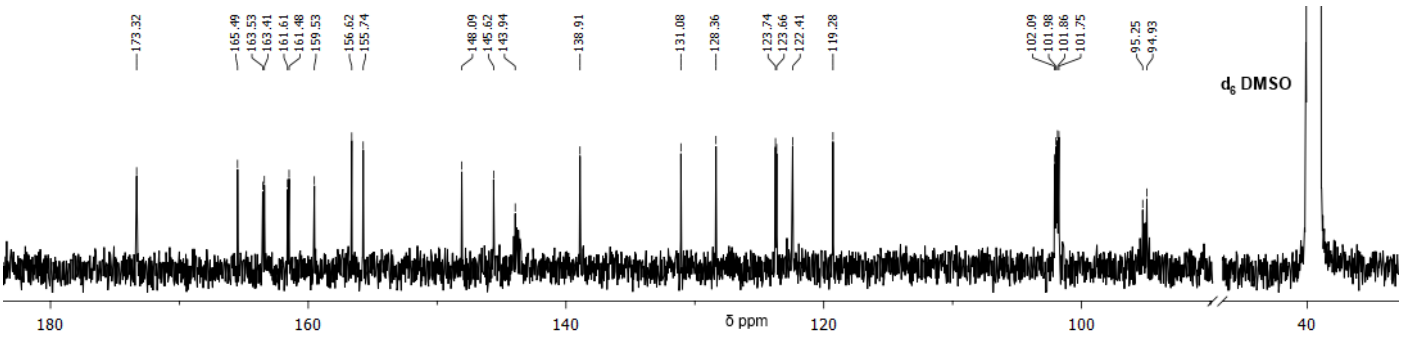
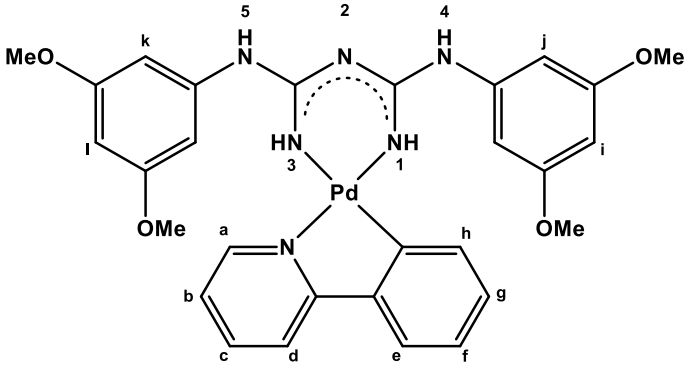


Fig. **S24**. ^{13}C NMR of [Pd(ppy)(**L5**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(L6)]



Pale yellow solid, [Pd(ppy)(**L6**)] (47.5 mg, 34%). Anal. Calc. for $C_{29}H_{30}N_6O_4Pd{\cdot}0.5NaOAc$: C, 53.46; H, 4.71; N, 12.47. Found C, 53.42; H, 4.66; N, 12.13. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.67 (s, 1H, NH4), 8.56 (d, J = 5.6 Hz, 1H, Ha), 8.46 (s, 1H, NH5), 8.11 – 7.98 (m, 2H, Hc, Hd), 7.74 (d, J = 7.5 Hz, 1H, He), 7.45 – 7.34 (m, 2H, Hb, Hh), 7.19 – 7.05 (m, 2H, Hf, Hg), 6.68 (dd, J = 6.7, 2.2 Hz, 4H, Hj, Hk), 6.11 (s, 1H, NH3), 6.00 (dt, J = 19.0, 2.3 Hz, 2H, Hi, Hl), 5.48 (s, 1H, NH1), 3.55 (d, J = 4.8 Hz, 12H, OMe). ^{13}C NMR (126 MHz, DMSO-d_6) δ 173.45, 160.43, 160.40, 157.17, 156.28, 147.45, 145.57, 143.08, 142.90, 138.86, 128.34, 123.54, 122.35, 97.73, 97.31, 93.71, 93.35, 54.65, 54.63. IR υ max/cm^{-1} 3361, 2931, 2836, 1716, 1682, 1591, 1527, 1447, 1421, 1305, 1236, 1193, 1148, 1061, 927, 816, 745, 727, 660, 605, 536, 460, 444, 410. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 378 (29100) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{29}H_{31}O_4N_6Pd]^+$ expected 633.1436, found 633.1396.

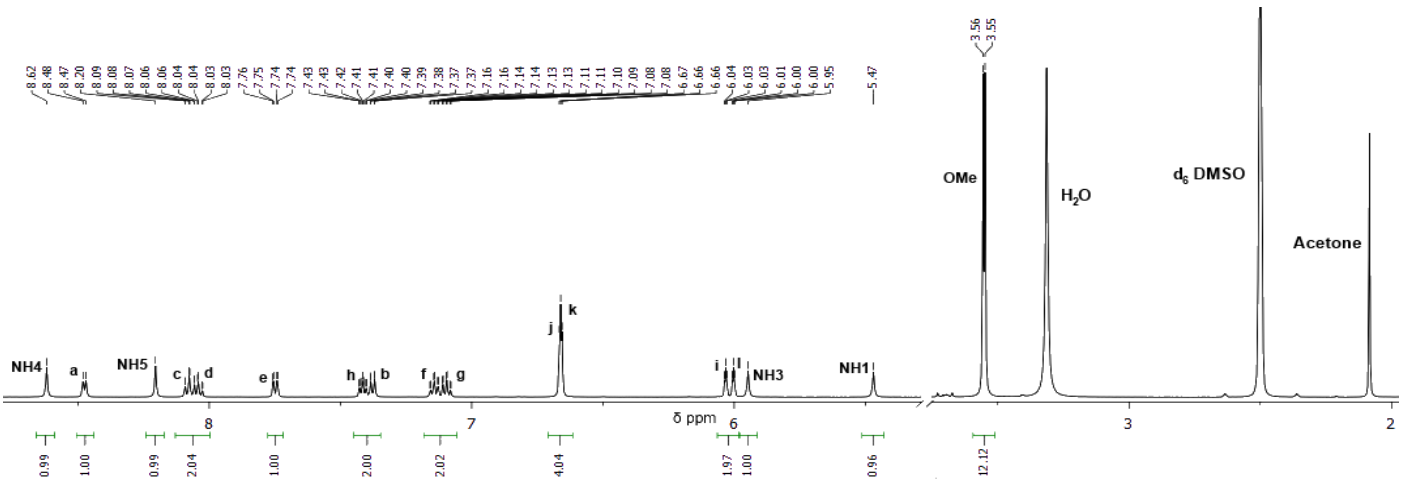


Fig. S25. ^{1}H NMR of [Pd(ppy)(**L6**)] in DMSO-d_6 at 500 MHz.

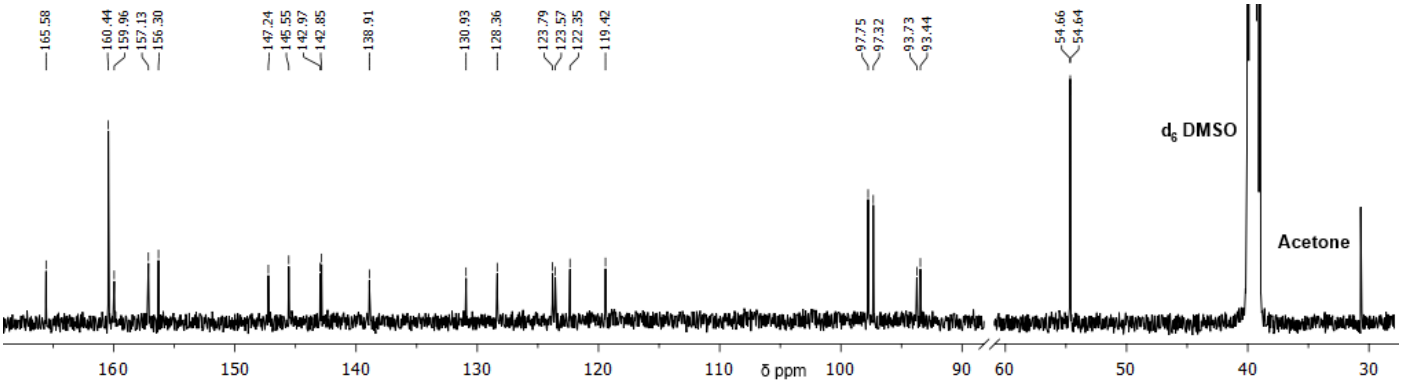
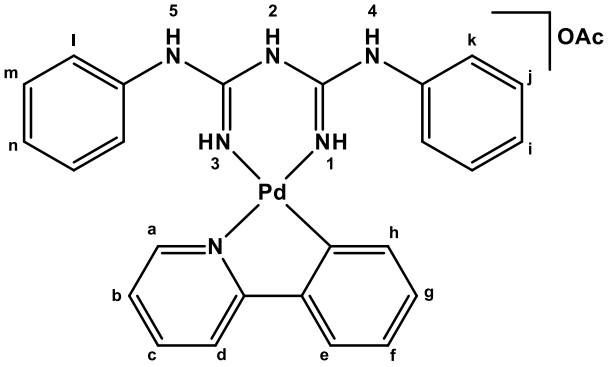


Fig. S26. ^{13}C NMR of [Pd(ppy)(**L6**)] in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL1)]OAc



Pale cream product, [Pd(ppy)(**HL1**)]OAc (92.8 mg, 81%). Anal. Calc. for $C_{27}H_{26}N_6O_2Pd$: C, 56.60; H, 4.57; N, 14.67; Found: C, 56.76;H, 4.69; N, 14.81. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.95 (s, 1H, NH2), 8.60 (s, 1H, NH5), 8.48 (d, J = 5.6 Hz, 1H, Ha), 8.18 (s, 1H, NH4), 8.12 – 8.01 (m, 2H, Hc, Hd), 7.75 (dd, J = 7.7, 1.4 Hz, 1H, He), 7.45 – 7.35 (m, 6H, Hb, Hh, Hk, Hl), 7.22 – 7.12 (m, 5H, Hf, Hj, Hm), 7.09 (t, J = 7.3 Hz, 1H, Hg), 6.95 – 6.86 (m, 2H, Hi, Hn), 5.87 (s, 1H, NH3), 5.37 (s, 1H, NH1), 1.91 (s, 3H, OAc). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.99, 165.57, 160.13, 157.50, 156.70, 147.26, 145.53, 141.15, 141.06, 138.83, 130.96, 128.42, 123.75, 123.50, 122.33, 121.17, 120.85, 120.63, 120.13, 119.37, 21.08. IR υ max/cm^{-1} 3401, 3362, 3273, 3056, 2981, 2673, 1683, 1630, 1596, 1562, 1493, 1483, 1449, 1397, 1303, 1262, 1219, 1200, 1004, 857, 747, 728, 711, 695, 671, 643, 595, 519, 491, 472, 416. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 380 (3700) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{23}N_6Pd]^+$ expected 513.1023, found 513.1015.

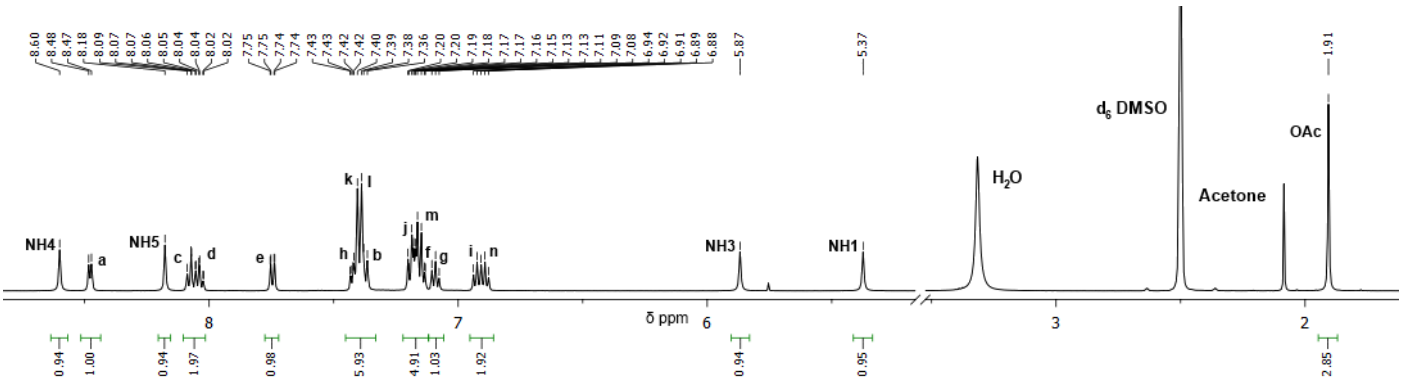


Fig. S27. ^{1}H NMR of [Pd(ppy)(**HL1**)]OAc in DMSO-d_6 at 500 MHz. NH2 peak appears as a short and broad singlet and is omitted for clarity of the other peaks in the Fig..

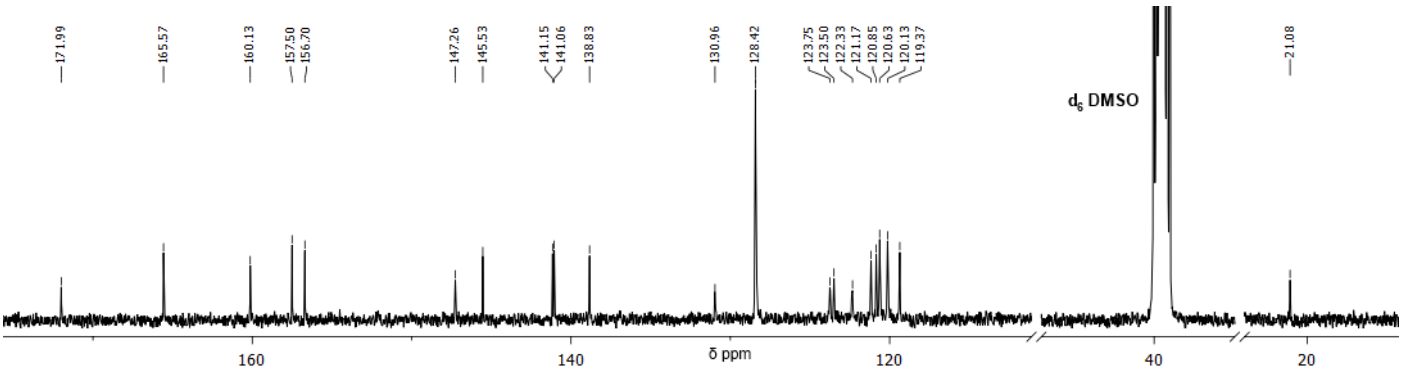
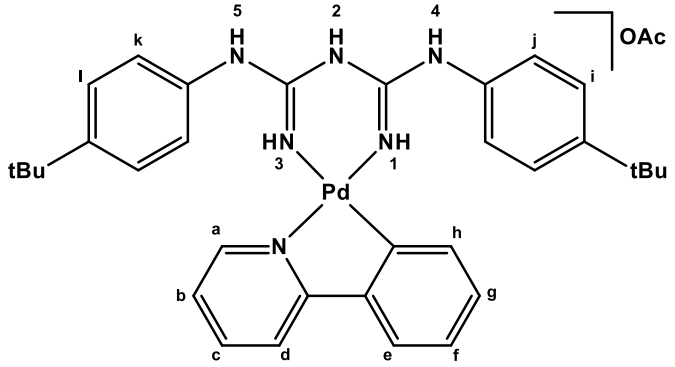


Fig. S28. ^{13}C NMR of [Pd(ppy)(**HL1**)]OAc in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL2)]OAc



Cream solid, [Pd(ppy)(**HL2**)]OAc (86.3 mg, 63%). Anal. Calc for $C_{35}H_{42}N_6O_2Pd{\cdot}0.5H_2O$: C, 60.56; H, 6.24; N, 12.11. found C, 60.55; H,6.39; N, 12.20. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 – 8.47 (m, 2H, Ha, NH4), 8.10 – 8.01 (m, 3H, Hc, Hd, NH5), 7.74 (dd, J = 7.7, 1.5 Hz, 1H, He), 7.44 – 7.35 (m, 2H, Hh, Hb), 7.32 – 7.26 (m, 4H, Hi, Hl), 7.21 – 7.06 (m, 6H, Hf, Hg, Hj, Hk), 5.79 (s, 1H, NH3), 5.28 (s, 1H, NH1), 1.91 (s, 3H, OAc), 1.27 (d, J = 4.5 Hz, 18H, tBu). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.58, 160.37, 157.63, 156.87, 147.26, 145.52, 143.38, 142.99, 138.77, 138.54, 138.45, 131.03, 128.29, 124.90, 124.88, 123.70, 123.43, 122.29, 120.79, 120.23, 119.34, 33.83, 33.78, 31.31. IR υ max/cm^{-1} 3382, 2961, 2866, 1671, 1622, 1600, 1577, 1556, 1511, 1402, 1360, 1267, 1224, 848, 748, 748, 727, 645. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 364 (3600) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{33}H_{39}N_6Pd]^+$ expected 625.2266, found 625.2217. $[C_{33}H_{38}N_6NaPd]^+$ expected 647.2085, found 647.2036.

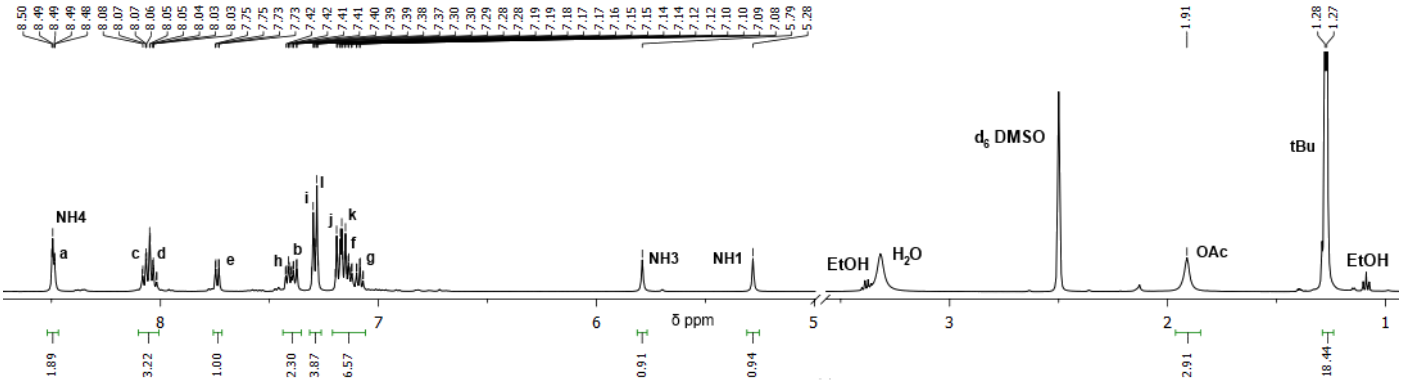


Fig. S29. ^{1}H NMR of [Pd(ppy)(**HL2**)]OAc in DMSO-d_6 at 500 MHz. tBu peak clipped for clarity.

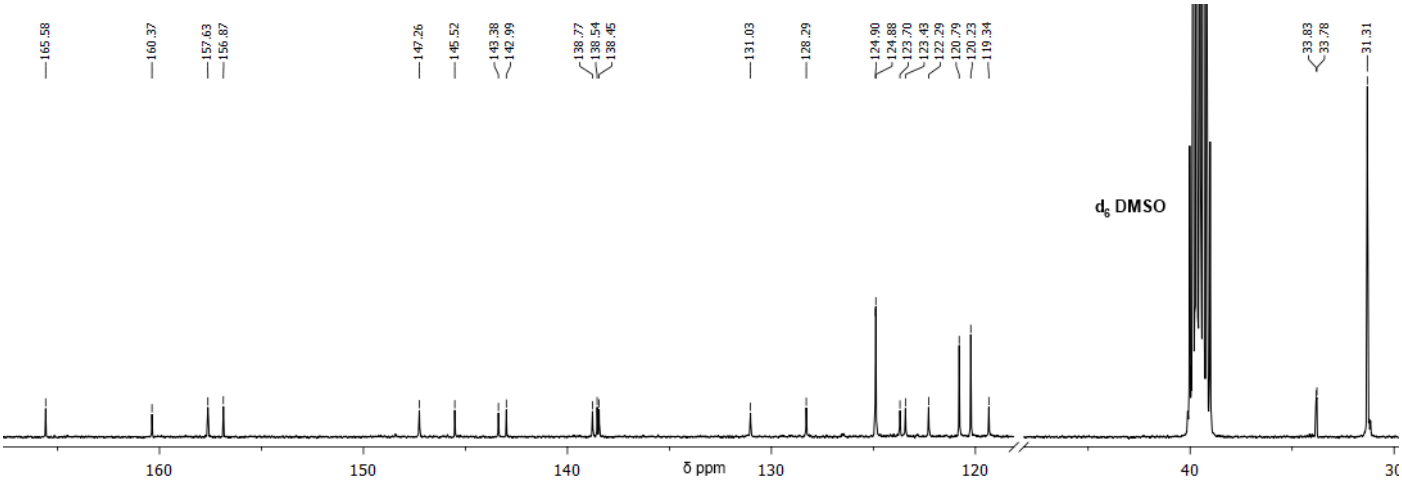
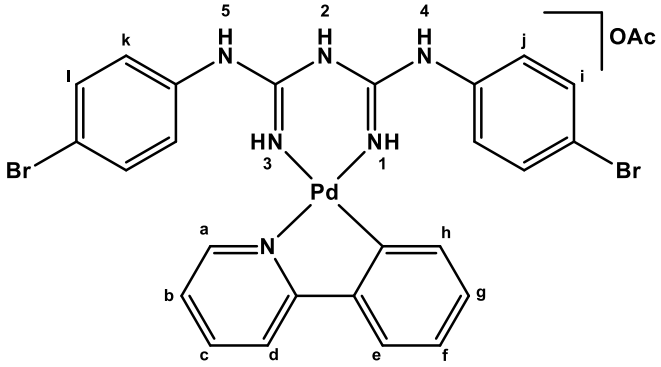


Fig. S30. ^{13}C NMR of [Pd(ppy)(**HL2**)]OAc in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL3)]OAc



Cream solid, [Pd(ppy)(**HL3**)]OAc (81.8 mg, 56%). Anal. Calc. for $C_{27}H_{24}Br_2N_6O_2Pd{\cdot}0.5H_2O$: C, 43.84; H, 3.41; N, 11.36. Found: C, 43.72; H, 3.08; N, 11.24. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (s, 1H, NH4), 8.48 (d, J = 5.7 Hz, 1H, Ha), 8.30 (s, 1H, NH5), 8.11 – 8.00 (m, 2H, Hc, Hd), 7.74 (d, J = 7.5 Hz, 1H, He), 7.44 – 7.37 (m, 2H, Hb, Hh), 7.33 – 7.25 (m, 8H, Hi-l), 7.16 (t, J = 7.3 Hz, 1H, Hf), 7.10 (t, J = 7.5 Hz, 1H, Hg), 5.95 (s, 1H, NH3), 5.42 (s, 1H, NH1), 1.90 (s, 3H, OAc). ^{13}C NMR (126 MHz, DMSO-d_6) δ 175.13 , 168.68 , 162.92 , 160.33 , 159.54, 150.49, 148.67, 143.62, 142.03, 134.18, 134.15, 134.11, 131.52, 126.90, 126.71, 125.65, 125.52, 125.46, 122.51, 115.69. IR υ_{max}/cm^{-1} 3277, 2622, 1723, 1684, 1626, 1585, 1555, 1486, 1199, 1068, 1007, 857, 750, 729, 644. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 385 (3200) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{21}Br_2N_6Pd]^+$ expected 670.9215, found 670.9193.

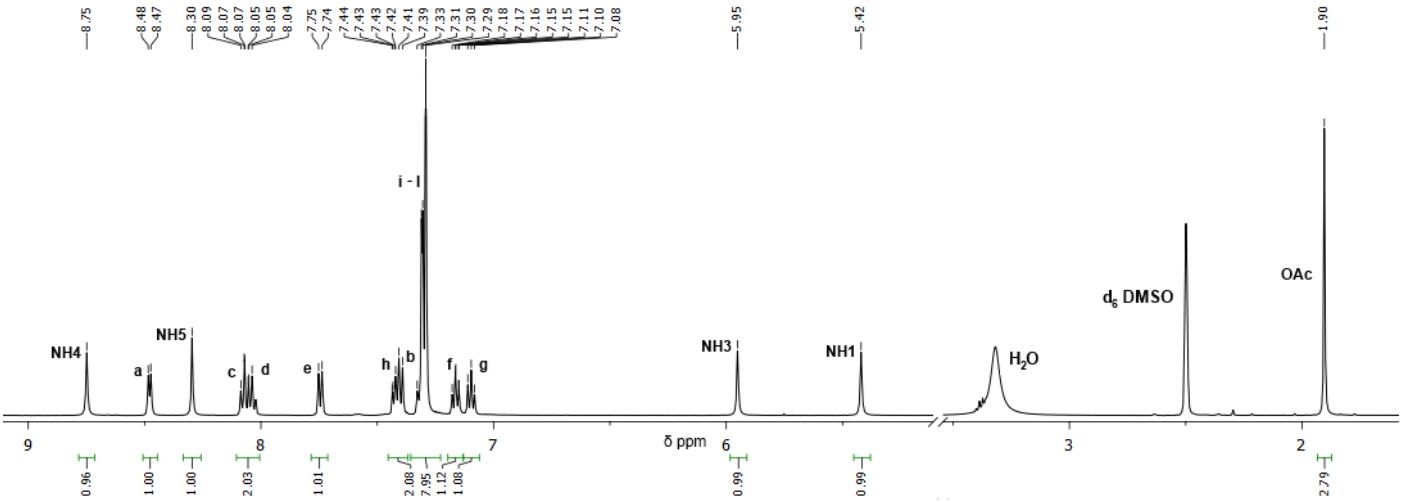


Fig. S31. ^{1}H NMR of [Pd(ppy)(**HL3**)]OAc in DMSO-d_6 at 500 MHz.

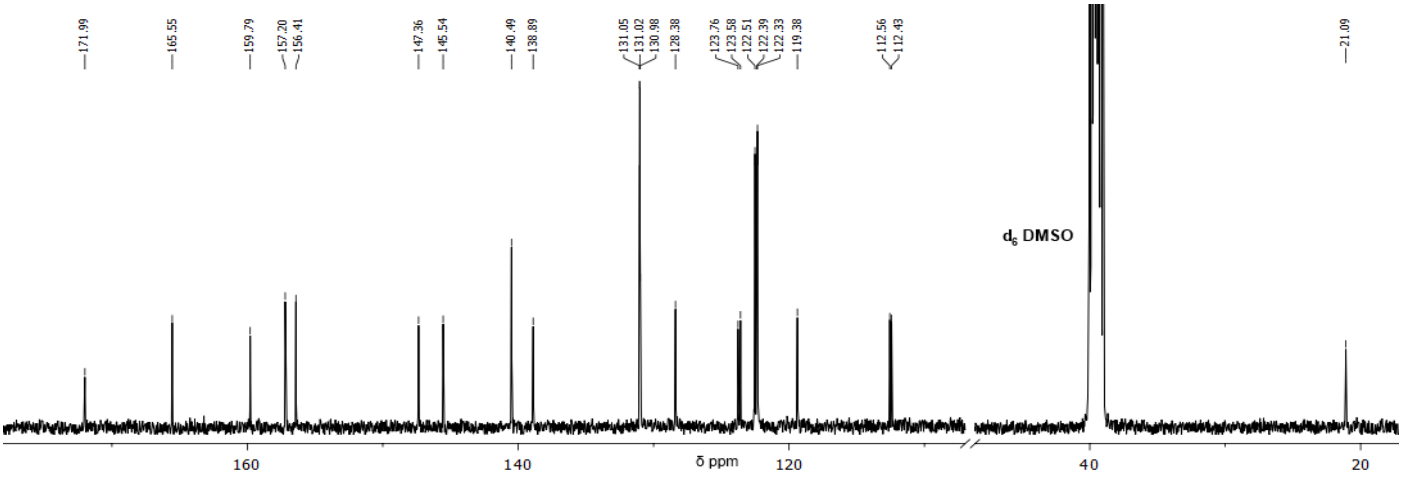
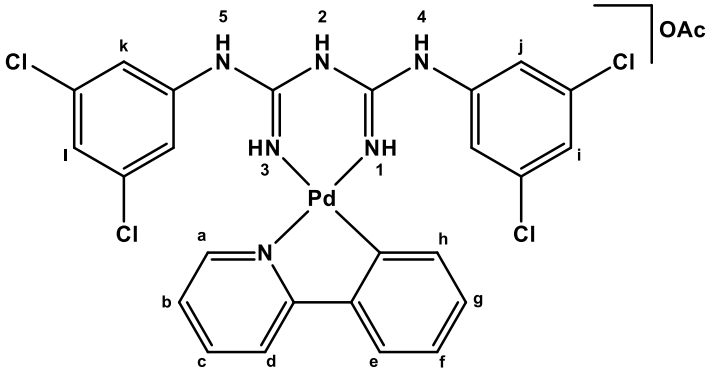


Fig. S32. ^{13}C NMR of [Pd(ppy)(**HL3**)]OAc in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL4)]OAc



Cream product, [Pd(ppy)(**HL4**)]OAc (96.7 mg, 68%). Anal. Calc. for $C_{27}H_{22}N_6O_2Cl_4Pd{\cdot}0.5H_2O$: C, 45.06; H, 3.22; N, 11.68. Found: C, 45.22; H, 3.17; N, 11.73. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.94 (s, 1H, NH2), 9.12 (s, 1H, NH4), 8.62 (s, 1H, NH5), 8.50 (d, J = 5.7 Hz, 1H, Ha), 8.15 – 8.01 (m, 2H, Hc, Hd), 7.76 (dd, J = 7.8, 1.4 Hz, 1H, He), 7.47 – 7.37 (m, 6H, Hb, Hh, Hj, Hk), 7.19 (td, J = 7.3, 1.4 Hz, 1H, Hf), 7.13 (t, J = 7.4, 1H, Hg), 6.98 (dt, J = 3.5, 1.9 Hz, 2H, Hi, Hl), 6.21 (s, 1H, NH3), 5.63 (s, 1H, NH1), 1.91 (s, 3H, OAc). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.55, 159.22, 156.34, 155.61, 147.42, 145.58, 143.31, 143.28, 139.08, 133.85, 133.84, 130.95, 128.44, 123.86, 123.77, 122.44, 119.56, 119.51, 119.48, 117.25, 21.05. IR u max/cm^{-1} 3390, 3375, 3326, 3063, 2626, 1720, 1679, 1627, 1607, 1580, 1524, 1485, 1439, 1410, 1330, 1315, 1302, 1223, 1114, 1093, 997, 866, 835, 811, 742, 724, 689, 665, 650, 611, 576, 474, 433, 410. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 385 (2100) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{19}Cl_4N_6Pd]^+$ expected 650.9441, found 650.9440.

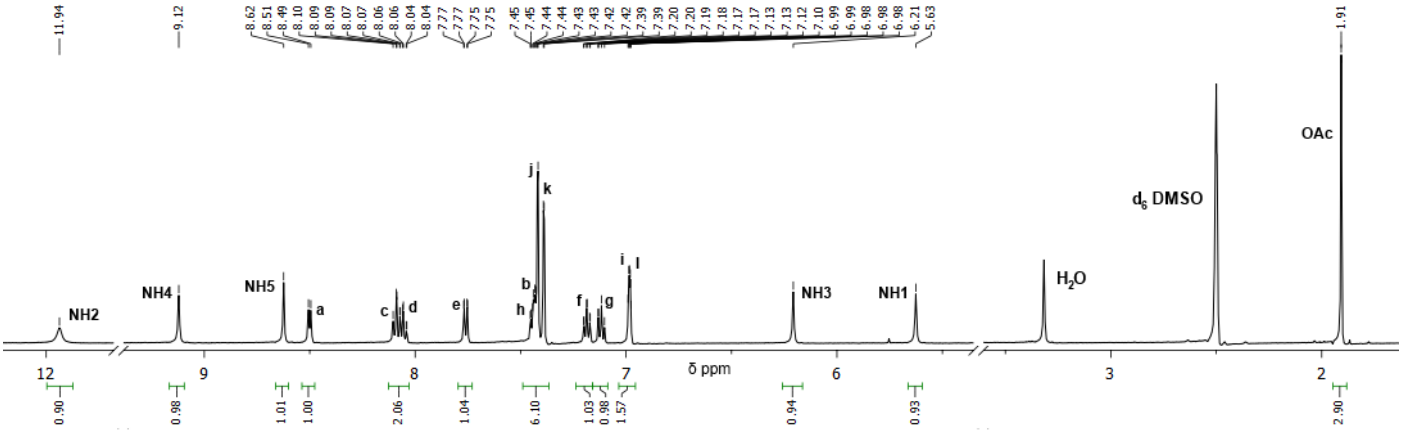


Fig. S33. ^{1}H NMR of [Pd(ppy)(**HL4**)]OAc in DMSO-d_6 at 500 MHz.

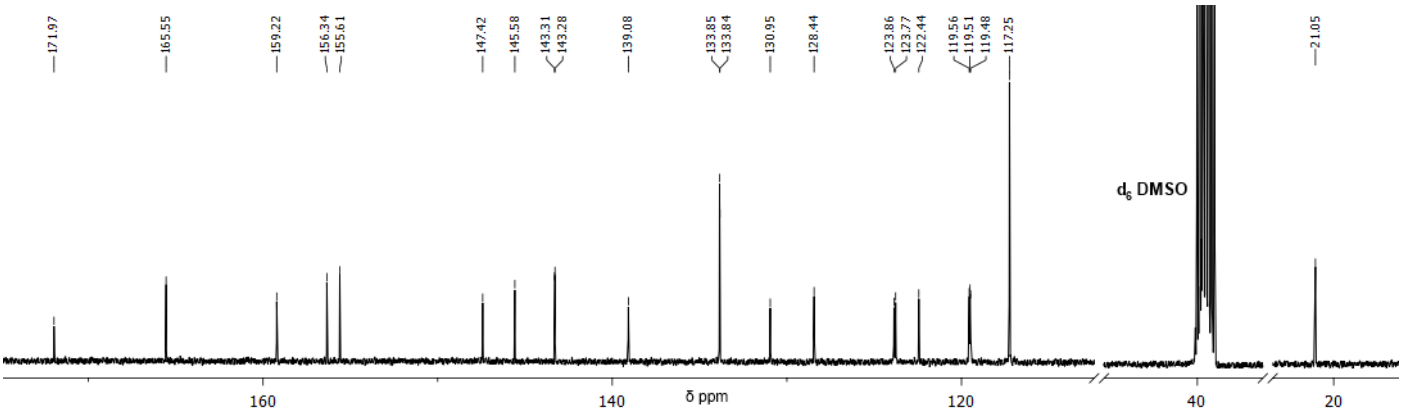
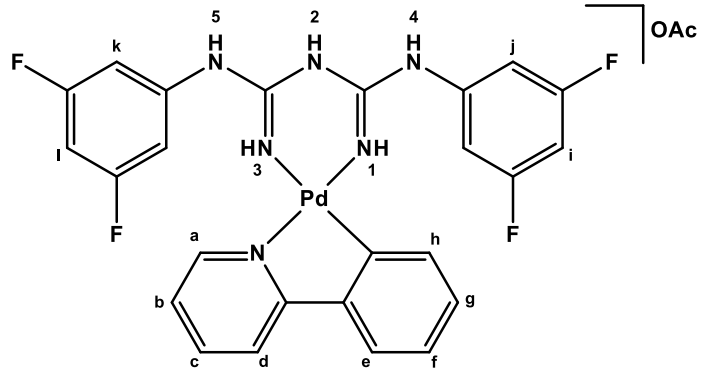


Fig. S34. ^{13}C NMR of [Pd(ppy)(**HL4**)]OAc in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL5)]OAc



Pale cream solid, [Pd(ppy)(**HL5**)]OAc (98.0 mg, 76%). Anal. Calc. for $C_{27}H_{23}F_4N_6O_2Pd.H_2O$: C, 48.92; H, 3.65; N, 12.68. Found: C, 48.84; H, 3.60; N, 12.80. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.94 (s, 1H, NH2), 9.13 (s, 1H, NH4), 8.64 (s, 1H, NH5), 8.50 (d, J = 5.6 Hz, 1H, Ha), 8.12 – 8.01 (m, 2H, Hc, Hd), 7.76 (d, J = 7.5 Hz, 1H, He), 7.46 – 7.42 (m, 2H, Hh, Hb), 7.21 – 7.02 (m, 6H, Hi, Hj, Hk, Hl), 6.67 – 6.57 (m, 2H, Hf, Hg), 6.19 (s, 1H, NH3), 5.62 (s, 1H, NH1), 1.91 (s, 3H, OAc). ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.02, 165.56, 163.56 (d, J = 5.2 Hz), 163.43 (d, J = 5.6 Hz), 161.64 (d, J = 5.5 Hz), 161.51 (d, J = 5.3 Hz), 159.33, 159.25, 145.57, 143.55 (td, J = 13.9, 3.5 Hz), 139.06, 131.00, 128.42, 123.82, 123.75, 122.46, 122.40, 119.47, 116.45, 103.57, 103.37, 102.13, 101.92. IR υ_{max}/cm^{-1} 3391, 3357, 3084, 2652, 1682, 1647, 1607, 1589, 1564, 1482, 1458, 1411, 1220, 1182, 1120, 981, 856, 747, 729, 653. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 384 (3900) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{25}H_{19}F_4N_6Pd]^+$ expected 585.0637, found 585.0631.

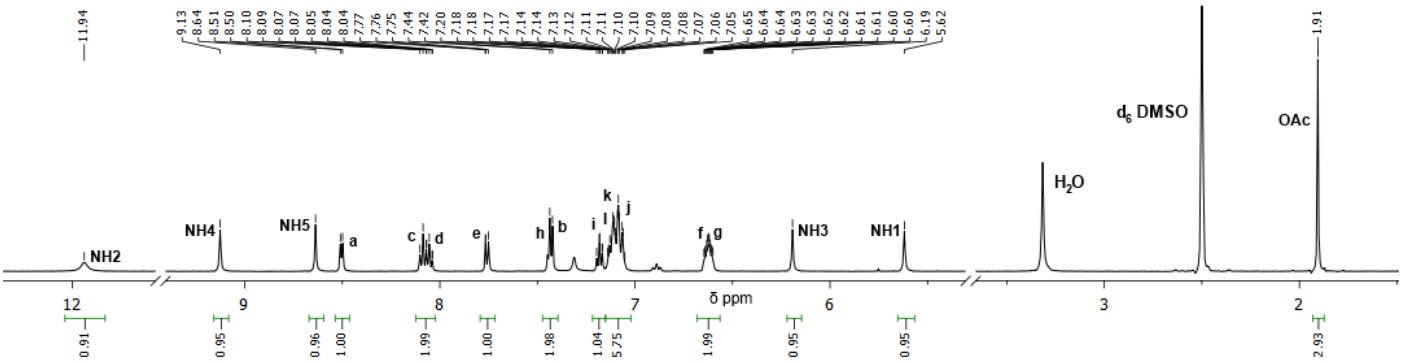


Fig. S35. ^{1}H NMR of [Pd(ppy)(**HL5**)]OAc in DMSO-d_6 at 500 MHz.

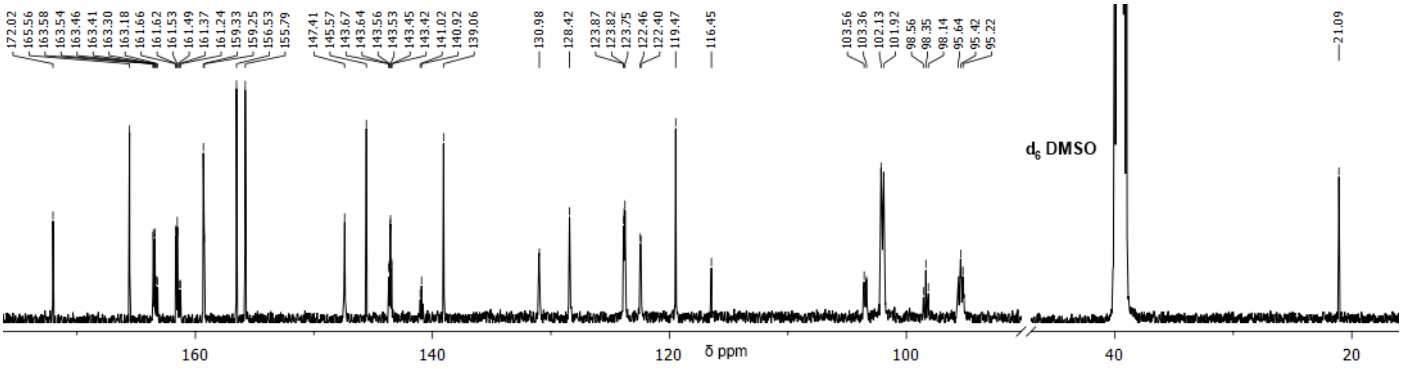
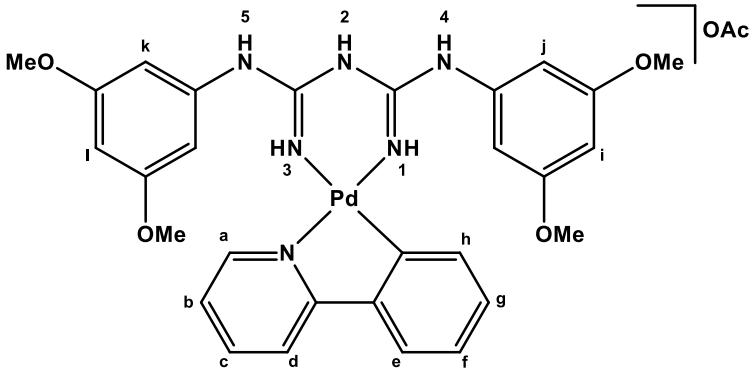


Fig. S36. ^{13}C NMR of [Pd(ppy)(**HL5**)]OAc in DMSO-d_6 at 126 MHz.

[Pd(ppy)(HL6)]OAc



Pale cream solid, [Pd(ppy)(**HL6**)]OAc (101.2 mg, 73%). Anal. Calc. for $C_{31}H_{34}N_6O_6Pd$: C, 53.72; H, 4.94; N, 12.13. Found: C, 53.59; H, 4.82; N, 12.05. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.63 (s, 1H, NH4), 8.48 (d, J = 5.6 Hz, 1H, Ha), 8.22 (s, 1H, NH5), 8.12 – 8.01 (m, 2H, Hc, Hd), 7.75 (dd, J = 7.7, 1.5 Hz, 1H, He), 7.46 – 7.34 (m, 2H, Hh, Hb), 7.18 – 7.06 (m, 2H, Hf, Hg), 6.72 – 6.62 (m, 4H, Hj, Hk), 6.03 (t, J = 2.2 Hz, 1H, Hi/l), 6.00 (t, J = 2.3 Hz, 1H, Hi/l), 5.96 (s, 1H, NH3), 5.47 (s, 1H, NH1), 3.59 – 3.52 (m, 12H, OMe), 1.90 (s, 3H, OAc). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.58, 160.45, 159.96, 157.13, 156.30, 147.26, 145.56, 142.97, 142.85, 138.91, 130.93, 128.36, 123.80, 123.57, 122.35, 119.42, 97.76, 97.33, 93.74, 93.44, 54.67, 54.65, 21.11. IR υ max/cm^{-1} 3360, 2940, 2841, 1718, 1683, 1587, 1475, 1424, 1407, 1362, 1205, 1181, 1158, 1070, 1051, 929, 811, 739, 724, 709, 649, 608, 539, 510, 461, 407. UV-vis (DMSO): λ_{max} (ε/M^{-1}cm^{-1}) = 374 (5400) nm. ESI-MS (*m/z*) (DMSO/MeOH): $[C_{29}H_{31}O_4N_6Pd]^+$ expected 633.1442, found 633.1357.

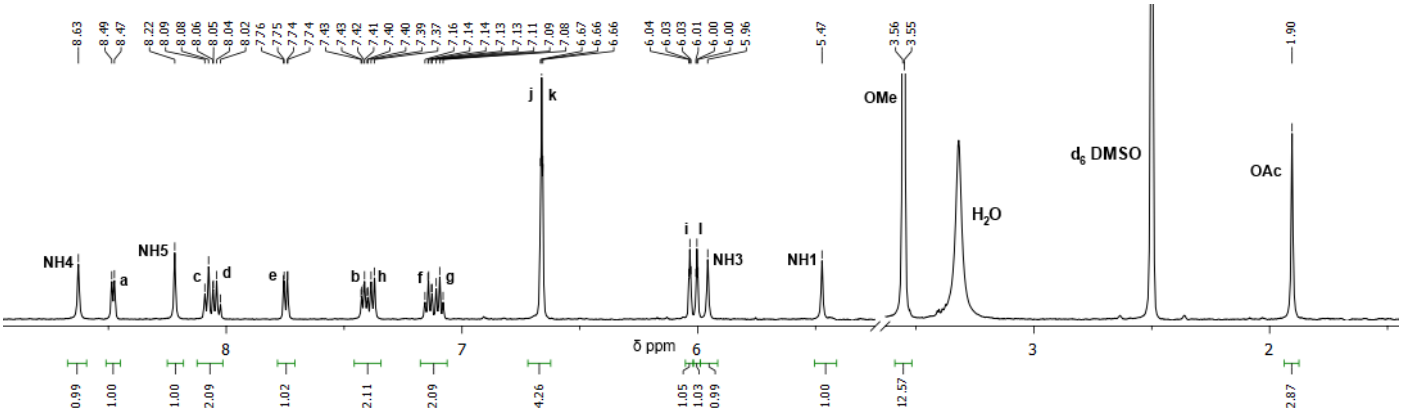


Fig. S37. ^{1}H NMR of [Pd(ppy)(**HL6**)]OAc in DMSO-d_6 at 500 MHz. OMe peak clipped for clarity.

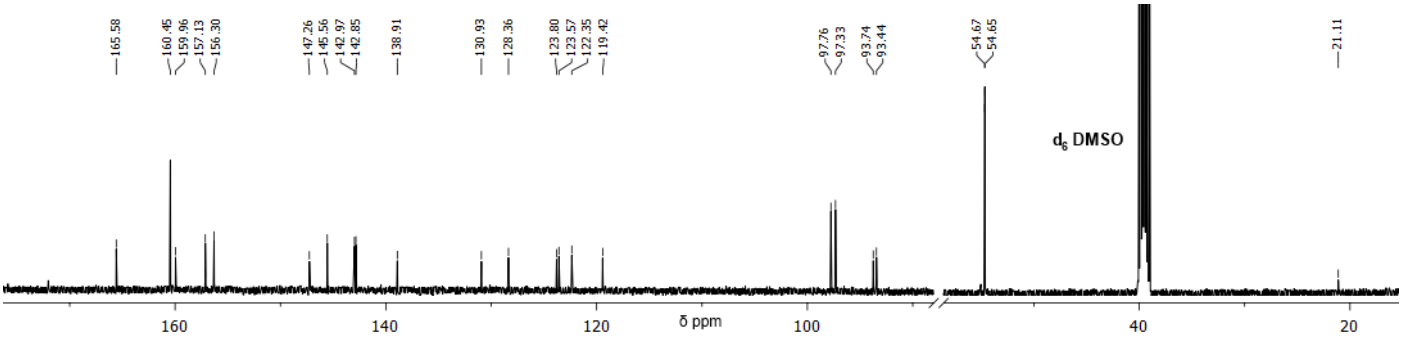


Fig. S38. ^{13}C NMR of [Pd(ppy)(**HL6**)]OAc in DMSO-d_6 at 126 MHz.

2. Crystallography

Yellow/green crystals of [Pt(ppy)(**L5**)]·2DMF were grown from the partial evaporation of a DMF solution. Orange crystals of [(Pt(ppy)(**L2**)(dmaNaph)]·0.3$CHCl_3$, were grown from the diffusion of petroleum ether into a 2:3 chloroform solution of [Pt(ppy)(**L2**)] and 4-dimethylaminonaphthalimide. Yellow crystals of [(Pt(ppy)(**L6**))(dmaNaph)] were grown from the diffusion of diethylether into a 2:3 chloroform solution of [Pt(ppy)(**L6**)] and 4-dimethylaminonaphthalimde. Yellow crystals of [(Pt(ppy)(**HL1**))(barb)] were grown from the diffusion of diisopropylether into a 2:1 chloroform solution of [Pt(ppy)(**L1**)] and barbital. X-ray data for these complexes were collected at 100 K on an Agilent Technologies Supernova system using Cu Kα radiation with exposures over 1.0°, and data were treated using CrysAlisPro[1] software. The structures were solved using SHELXT[2] and weighted full-matrix refinement on F^2 was carried out using SHELXL-2014[2] running within the WinGX[3] package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model, excepting those on the nitrogen atoms of the biguanide of **5**·2DMF, on N4 and N5 of **2**:naphth, and on N1, N3-5, and N7 of **6**:naphth which were assigned from electron density maps. The SQUEEZE methodology was applied during the refinement of [(Pt(ppy)(**L2**)(dmaNaph)]·0.3$CHCl_3$ - electron density corresponding to 118 electrons was removed, which approximates to 2.5 hexane molecules.

Colourless crystals of **HL4** and **HL5** were grown from cooling of hot aqueous ethanol solutions of **HL4** and **HL5**, respectively. Yellow crystals of [Pd(ppy)(**HL2**)]OAc were grown from diffusion of diethylether into an acetonitrile solution of [Pd(ppy)(**L2**)]OAc. Yellow crystals of [Pd(ppy)(**L2**)]·2DMF were grown from the partial evaporation of a DMF solution of [Pd(ppy)(**L2**)]. Yellow/green crystals of [Pd(ppy)(**L4**)]·2DMF were grown from the diffusion of diethylether into a DMF solution of [Pd(ppy)(**L4**)]OAc. Yellow/green crystals of [Pd(ppy)(**L5**)]·2DMF were grown from the partial evaporation of a DMF solution of [Pd(ppy)(**L5**)]OAc. X-ray data for these complexes were collected at 100 K on an Agilent Technologies Supernova system using Cu Kα radiation with exposures over 1.0°, and data were treated using CrysAlisPro[1] software. The structures were solved using SIR-97[4] and weighted full-matrix refinement on F^2 was carried out using SHELXL-2014[2] running within the WinGX[3] package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model, excepting those on N1, N2, N4, and N5 of **8H**, on the nitrogen atoms of the biguanide of **10**·2DMF, and N1, N4, and N5 of **11**·2DMF, which were assigned from electron density maps.

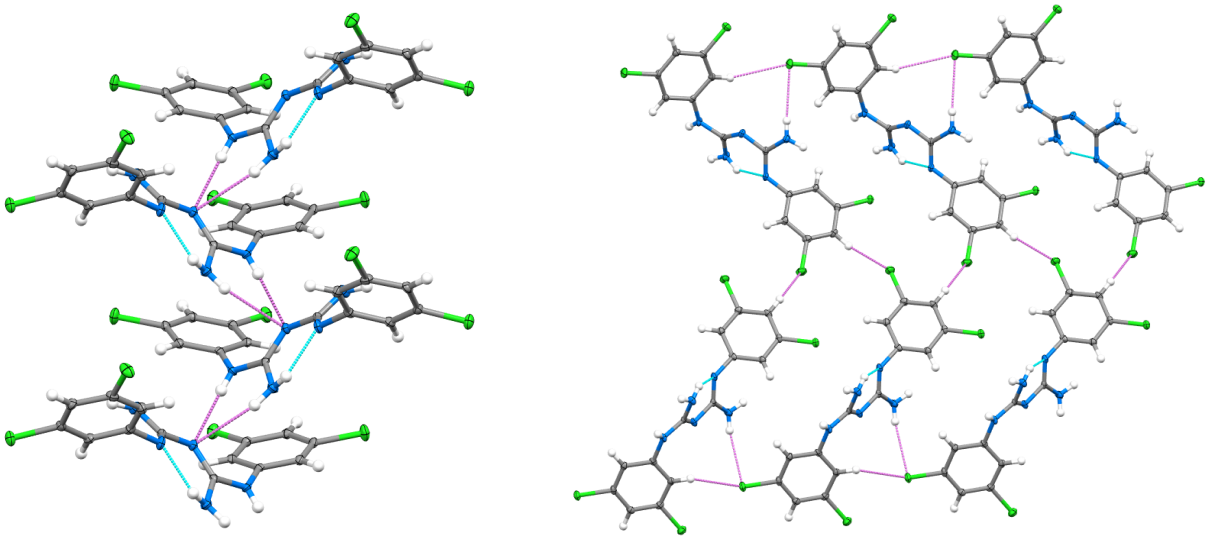


Fig. S39. Packing of **HL4**. Left: View down the *a* axis, showing chains of molecules assembled by NH···N hydrogen bonding. Right: View down *c* axis showing CH···Cl hydrogen bonding which assembles the chains into the overall 3-D structure.

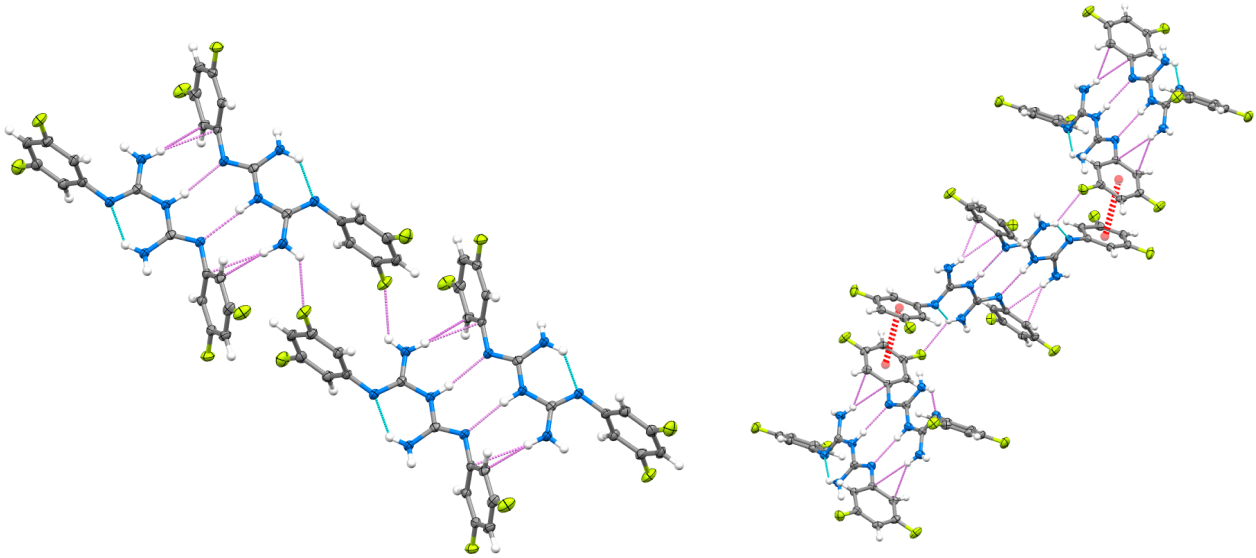


Fig. S40. Packing of **HL5**. Left: View down the *c* axis showing the combination of NH···N, NH···Cl and NH···π hydrogen bonding, generating chains. Right: View down the *a* axis showing assembly of chains via NH···Cl hydrogen bonds and π-π stacking interactions into the overall 3-D structure.

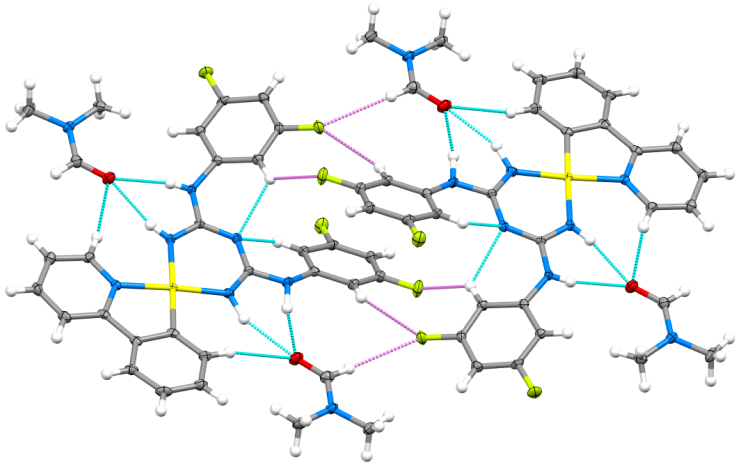


Fig. S41. Packing of [Pt(ppy)(**L5**)].2dmf.

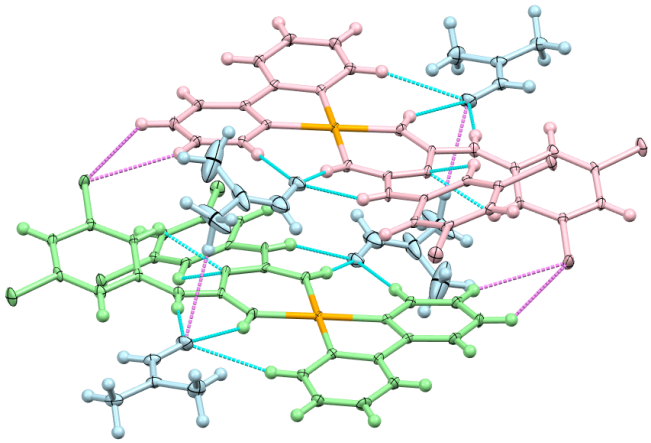


Fig. S42. Packing of [Pd(ppy)(**L4**)].2dmf.

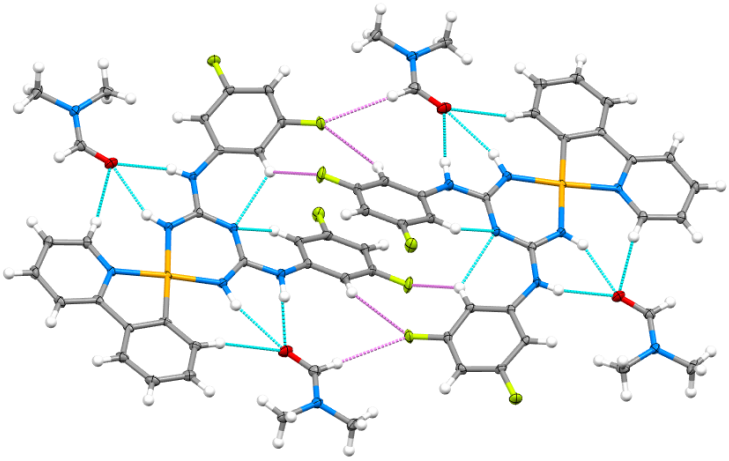


Fig. S43. Packing of [Pd(ppy)(**L5**)].2dmf.

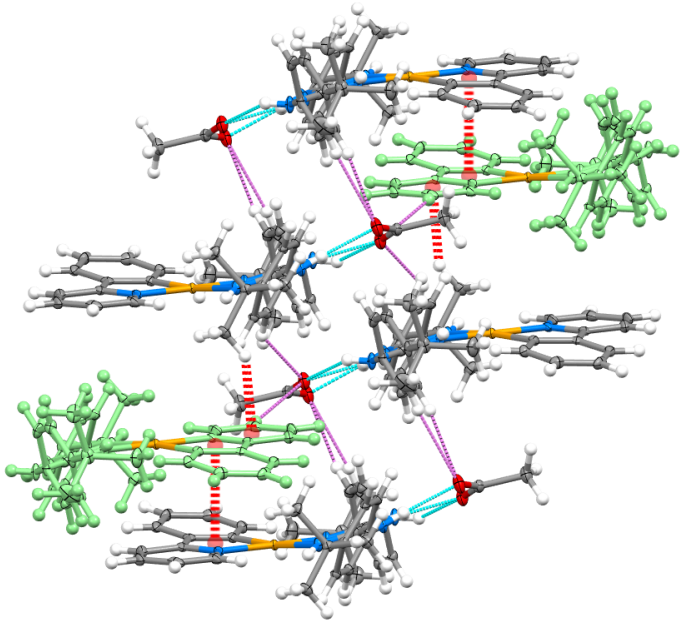


Fig. S44. Packing of [Pd(ppy)(**HL2**)]OAc

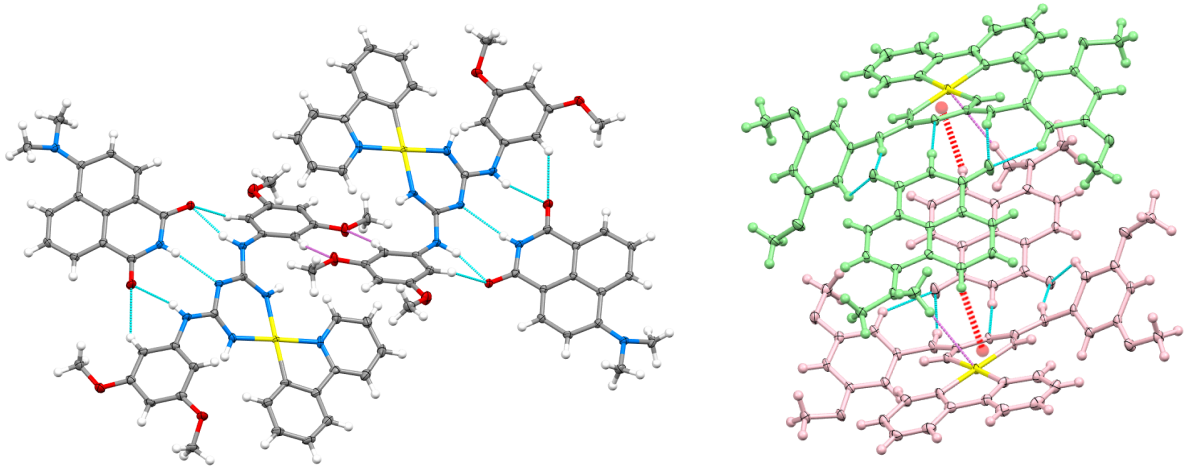


Fig. S45. Packing of [Pt(ppy)(**L6**).dmaNaph]

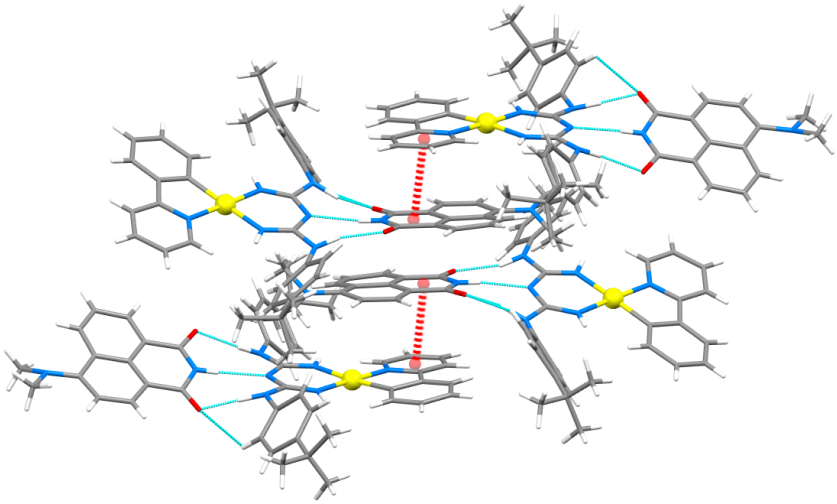


Fig. S46. Packing of [Pt(ppy)(**L2**).dmaNaph]

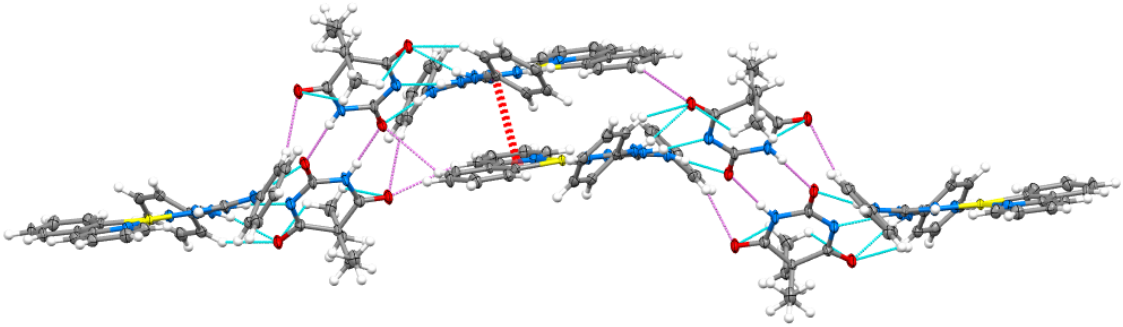


Fig. S47. Packing of [Pt(ppy)(**HL1**).barb].$CHCl_3$

4. Transient Absorption Spectrum of [Pt(ppy)(L2)]

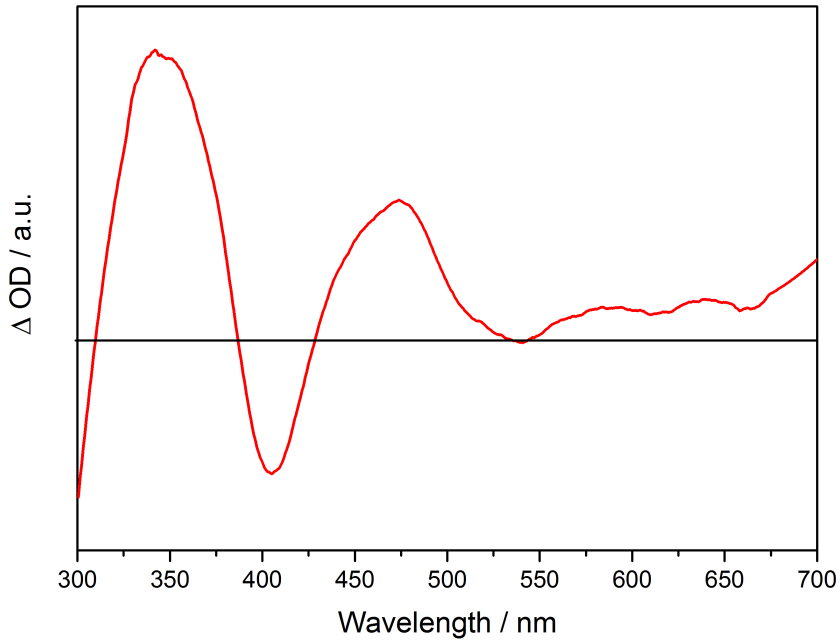


Fig. S48. A representative transient absorption spectrum of [Pt(ppy)(**L2**)] in DMF taken with 355 nm excitation with a 100 ns gate width.

4. Hirshfeld Surface Analysis

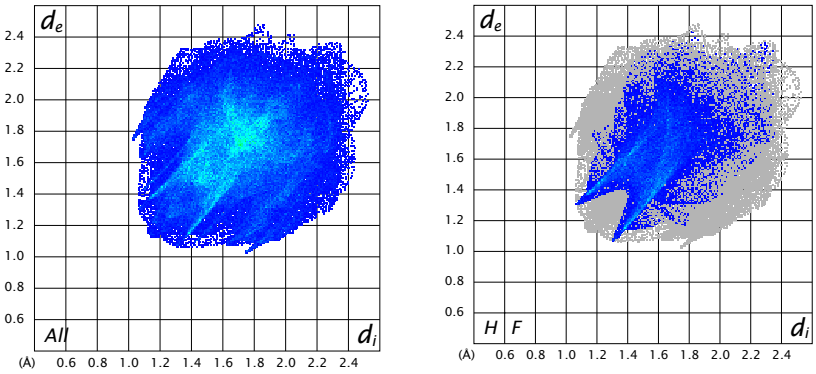


Fig. S49. Fingerprint plots of intermolecular interactions in [Pt(ppy)(**L5**)].2DMF: (left) all interactions, (right) H-F interactions, which constitute 19.1% of the total.

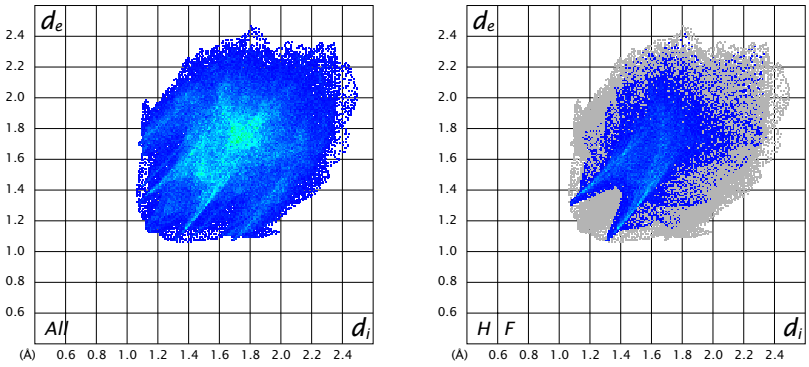


Fig. S50. Fingerprint plots of intermolecular interactions in [Pd(ppy)(**L5**)].2DMF: (left) all interactions, (right) H-F interactions, which constitute 19.0% of the total.

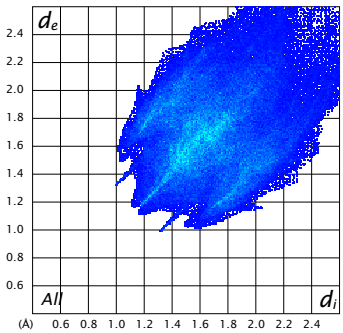


Fig. S51. Fingerprint plots of all intermolecular interactions in [Pd(ppy)(**L2**)].2DMF.

5. Quantificantion of non-planarity of triple hydrogen bonded assemblies

The spatial orientation between two, reasonably planar, triply hydrogen bonded molecules can be broken down into two components. First of these is the twist or torsion, τ, between the planes of the two molecules which can be imagined as around an axis running through both molecules. Second is the bending out of plane, θ, which can be imagined as around an axis running parallel with the hydrogen bonding surfaces. These two values give a better quantitate analysis to the arrangement of the two molecules with respect to each other than simply stating the overall angle between the planes of the two molecules, especially since inorganic triple hydrogen bonding systems, unlike their typically planar counterparts, are often in non-planar arrangements. To calculate τ and θ a series of distances need to be measured from the crystal structure of the hydrogen bonded system. For simplicity the molecules are named 1 and 2 and each of the hydrogen bonding pairs A, B, and C as shown in Fig. 1. A centroid behind B_1 (where the $Centroid_1$-B_1 line is perpendicular to the A_1-C_1) and a plane generated from A_2, B_2, and C_2 also need to be generated.

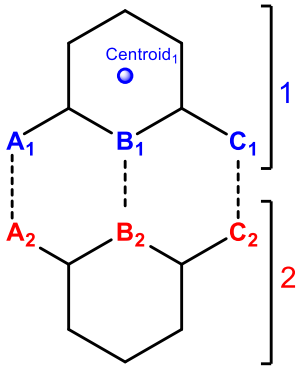


Fig. S52. Example of naming atoms on a generic structure.

The calculation for the torsion uses the difference of A_1 and C_2 in their separation from the plane of molecule 2 (note if they are opposite sides of this plane one of the distances should be negative) against their distance apart which in **Equation 1** can be converted to an angle using an inverse sine function.

Equation 1

$$\tau = \sin^{-1}\left(\frac{|(A_1\cdots plane_2)-(C_1\cdots plane_2)|}{(A_1\cdots C_1)}\right)$$

Calculating the bend between the molecules is done in much the same way utilising the differing separation of B_1 and $centroid_1$ from the plane of molecule 2, in **Equation 2** which once again is an inverse sine function.

Equation 2

$$\theta = \sin^{-1}\left(\frac{|(centroid_1\cdots plane_2)-(B_1\cdots plane_2)|}{(B_1\cdots centroid_1)}\right)$$

Table S1. Calculated angles for co-crystallised complexes [Pt(ppy)(**HL1**):barb], [Pt(ppy)(**L2**):dmaNaph], and [Pt(ppy)(**L6**):dmaNaph]

Complex	**τ** (°)	**θ** (°)
[Pt(ppy)(**HL1**):barb]	37.00	10.78
[Pt(ppy)(**L2**):dmaNaph]	23.78	6.32
[Pt(ppy)(**L6**):dmaNaph]	10.03	29.59

6. References

(1) CrysAlisPro; Agilent Technologies: Yarton, Oxfordshire, England, 2012.
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