Electronic Supplementary Information

Reinvestigating 2,5-di(pyridine-2-yl)pyrazine ruthenium complexes: selective deuteriation and Raman spectroscopy as tools to probe ground and excited-state electronic structure in homo- and heterobimetallic complexes

Martin Schulz, Johannes Hirschmann, Apparao Draksharapu, Gurmeet Singh Bindra, Suraj Soman, Avishek Paul, Robert Groarke, Mary T. Pryce, Sven Rau, Wesley R. Browne,* and Johannes G. Vos*

Synthesis and Characterisation of 2,5-dpp and d_{10}-2,5-dpp

2,5-di(pyridin-2-yl)pyrazine ^{1}H NMR ($CDCl_3$): δ 9.59 (s, 2H, 3-H, 6-H), 8.68 (d, 2H, J = 4.7 Hz, 9-H, 15-H), 8.38 (d, 2H, J = 7.8 Hz, 12-H, 18-H), 7.91 (t, 2H, J = 7.6 Hz, 11-H, 17-H), 7.80 (t, 2H, J = 5.0 Hz, 10-H, 16-H).

(d_{10})-2,5-di(pyridin-2-yl)pyrazine Sodium (460 mg, 20,01 mmol) was added slowly to 20 cm^3 of D_2O cooled with an ice bath. 2,5-di(2-pyridin-2-yl)pyrazine (150 mg, 0.64 mmol) was added and heated under pressure for 6 days in a teflon lined steel dissolution bomb. The mixture was subsequently cooled to r.t. and neutralized with aqueous HCl. The aqueous phase was extracted with dichloromethane and the combined organic phases were dried over magnesium sulphate. Evaporation of the solvent yielded the deuteriated product as a white solid (0.066 g, 42%). The degree of deuteriation was determined by ^{1}H NMR spectroscopy to be >98%. Yield 66 mg. ^{1}H NMR ($CDCl_3$): δ = 9.59 (s, 3-H, 6-H), 8.68 (s, 2H, 9, 15), 8.38 (s, 2H, 12, 18), 7.80 (s, 2H, 11, 17), 7.31 (s, 2H, 10, 16).

Synthesis of mononuclear ruthenium(II) complexes 1a-d

2,5-di(pyridin-2-yl)pyrazine (0.21 mmol) were dissolved in 5 cm^3 of an ethanol/water (3:1 v/v) and heated at reflux. Subsequently, [Ru(2,2'-bipyridine)$_2$Cl$_2$].2H$_2$O (0.14 mmol) dissolved in 20 cm^3 of an ethanol/water mixture was added slowly over a period of 1 h. The brown solution was heated at reflux for 6 h. After cooling to r.t. ethanol was removed in vacuo and non-reacted starting material was removed by filtration. 2 cm^3 of saturated $NH_4PF_{6(aq)}$ was added to the filtrate, yielding a brown precipitate. The crude product was collected and washed with small amounts of water and diethyl ether. Recrystallization from acetone/water (2:1 v/v) afforded brown crystalline solids.

[*bis*-(2,2'-bipyridine)(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)] $(PF_6)_2.H_2O$ (**1a**)
Yield 71%. ^{1}H NMR (DMSO-d_6): δ = 10.04 (s, 1H, 3-H), 9.04 (d, 1H, 12-H), 8.90-8.51 (m, 4H, bipy), 8.59 (s, 1H, 6-H), 8.53 (d, 1H, 15-H), 8.42 (d, 1H, 18-H), 8.28-8.19 (m, 5H, bipy, 11-H), 8.08 (d, 1H, bipy), 8.03 (t, 1H, 17-H), 7.83 (d, 1H, bipy), 7.80 (d, 1H, 9-H), 7.72 (d, 2H, bipy), 7.63-7.57 (m, 4H, bipy, 10-H), 7.52 (m, 1H, 16-H), 7.48 (m, 1H, bipy). $C_{34}H_{26}F_{12}N_8P_2Ru.H_2O$ (955.64): calcd. C 42.73, H 2.95, N 11.73; found C 43.11, H 2.94, N 11.46.

[*bis*-(d_8-2,2'-bipyridine)(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)]$(PF_6)_2.H_2O$ (**1b**)
Yield 48%. ^{1}H NMR (DMSO-d_6): δ = 10.04 (s, 1H, 3-H), 9.04 (d, 1H, 12-H), 8.90 (s, bipy), 8.89 (s, bipy), 8.86 (s, bipy), 8.85 (s, bipy), 8.59 (s, 1H, 6-H), 8.53 (d, 1H, 15-H), 8.42 (d, 1H, 18-H), 8.28 (s, bipy), 8.25 (t, 1H, 11-H), 8.23 (s, bipy), 8.20 (s, bipy), 8.19 (s, bipy), 8.08 (s, bipy), 8.03 (t, 1H, 17-H), 7.83 (s, bipy), 7.80 (d, 1H, 9-H), 7.74 (s, bipy), 7.72 (s, bipy), 7.63 (s, bipy), 7.60 (t, 1H, 10-H), 7.59 (s, bipy), 7.57 (s, bipy), 7.52 (t, 1H, 16-H), 7.48 (s, bipy). $C_{34}H_{10}D_{16}F_{12}N_8P_2Ru.H_2O$ (971.74): calcd. C 42.02, H 2.90, N 11.53; found C 42.14, H 2.94, N 11.63.

[*bis*-(2,2'-bipyridine)(d_{10}-2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)]$(PF_6)_2.H_2O$ (**1c**)
Yield 67%. ^{1}H NMR (DMSO-d_6): δ = 10.04 (s, 3-H), 9.04 (s, 12-H), 8.90-8.85 (m, 4H, bipy), 8.59 (s, 6-H), 8.53 (s, 15-H), 8.42 (s, 18-H), 8.28-8.19 (m, 4H, bipy, 11-H), 8.08 (d, 1H, bipy), 8.03 (s, 17-H), 7.83 (d, 1H, bipy), 7.80 (s, 9-H), 7.72 (d, 2H, bipy), 7.63-7.57 (m, 3H, bipy, 10-H), 7.52 (s, 16-H), 7.48 (t, 1H, bipy). $C_{34}H_{16}D_{10}F_{12}N_8P_2Ru.H_2O$ (965.70): calcd. C 42.29, H 2.93, N 11.60; found C 42.33, H 3.05, N 11.41.

[*bis*-(d_8-2,2'-bipyridine)(d_{10}-2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)]$(PF_6)_2.H_2O$ (**1d**)
Yield 61%. $C_{34}D_{26}F_{12}N_8P_2Ru.H_2O$ (981.80): calcd. C 41.59, H 2.88, N 11.41; found C 41.83, H 2.82, N 11.29.

Synthesis of dinuclear ruthenium(II) complexes 2a-d.

2,5-di(pyridin-2-yl)pyrazine (0.21 mmol) and [Ru(2,2'-bipyridine)$_2$Cl$_2$].2H$_2$O (0.47 mmol) were dissolved in 20 cm^3 of ethanol/water (3:1 v/v) and heated at reflux for 6 h. After cooling to r.t. ethanol was removed in vacuo and non-reacted starting material was removed by filtration. 2 cm^3 of saturated $NH_4PF_{6(aq)}$ were added to the filtrate, yielding a dark precipitate. The crude precipitate was collected and washed with small amounts of water and diethyl ether. Recrystallization from acetone/water (2:1 v/v) afforded dark crystalline solids. The complexes are obtained as diastereomeric mixtures (ΔΛ and ΛΛ/ΔΔ isomers).

[μ-(2,5-di(pyridin-2-yl)pyrazine)*bis*-{*bis*-2,2'-bipyridine)ruthenium(II)}](PF$_6$)$_4$.(CH$_3$)$_2$CO (**2a**)
Yield 69%. ^{1}H NMR (DMSO-D$_6$): δ = 8.91-8.80 (m, 8H, bipy), 8.68 (s, 1H, dpp), 8.59 (s, 1H, dpp), 8.33-8.11 (m, 11H, dpp, bipy), 8.05-8.02 (m, 3H, dpp, bipy), 7.83-7.80 (m, 2H, bipy), 7.77-7.71 (m, 2H, dpp), 7.68-7.64 (m, 2H, bipy), 7.47-7.43 (m, 2H, bipy), 7.30-7.27 (m, 2H, bipy). $C_{54}H_{42}F_{24}N_{12}P_4Ru_2.(CH_3)_2CO$ (1699.07): calcd. C 40.29, H 2.85, N 9.89; found; C 40.17, H 3.35, N 10.02.

[μ-(2,5-di(pyridin-2-yl)pyrazine)*bis*-(*bis*-(d$_8$-2,2'-bipyridine) ruthenium(II)}](PF$_6$)$_4$0.5(CH$_3$)$_2$CO (**2b**)
Yield 75%. ^{1}H NMR (DMSO-D$_6$): δ = 8.68 (s, 1H, dpp), 8.61 (s, 1H, dpp), 8.18-8.11 (m, 3H, dpp), 8.05-8.02 (m, 1H, dpp), 7.77-7.71 (m, 2H, dpp), 7.61-7.56 (m, 2H, dpp). $C_{54}H_{10}D_{32}F_{24}N_{12}P_4Ru_2.0.5(CH_3)_2CO$ (1702.25): calcd. C 39.16, H 2.66, N 9.87; found C 39.09, H 2.98, N 9.70.

[μ-(d$_{10}$-2,5-di(pyridin-2-yl)pyrazine)*bis*-{*bis*-(2,2'-bipyridine) ruthenium(II)}](PF$_6$)$_4$.0.5(CH$_3$)$_2$CO.H$_2$O (2c)
Yield 32%. ^{1}H NMR (DMSO-D$_6$): δ = 8.91-8.80 (m, 8H, bipy), 8.33-8.20 (m, 8H, bipy), 8.05-8.04 (m, 2H, bipy), 7.68-7.64 (m, 2H, bipy), 7.62-7.50 (m, 6H, bipy), 7.47-7.43 (m, 2H, bipy), 7.30-7.27 (m, 2H, bipy). $C_{54}H_{32}D_{10}F_{24}N_{12}P_4Ru_2.0.5(CH_3)_2CO.H_2O$ (1727.14): calcd. C 39.63, H 2.89, N 9.73; found C 39.39, H 3.21, N 10.04.

[μ-(d$_{10}$-2,5-di(pyridin-2-yl)pyrazine)*bis*-{(*bis*-(d$_8$-2,2'-bipyridine ruthenium(II)) (PF$_6$)$_4$ • (CH$_3$)$_2$CO • 2 H$_2$O (**2d**)
Yield 75%. ^{1}H NMR (DMSO-D$_6$): no signals. $C_{54}D_{42}F_{24}N_{12}P_4Ru_2.(CH_3)_2CO.2H_2O$ (1777.35): calcd. C 38.52, H 2.93, N 9.46; found C 38.82, H 3.29, N 9.88.

[Ruthenium(II)(2,2'-bipyridine)$_2$(μ-2,5-di(pyridin-2-yl)pyrazine)PdCl$_2$] (PF$_6$)$_2$·2 H$_2$O (3)
1a (0.100 mg, 0.10 mmol) was dissolved in 5 ml of dichloromethane and added drop wise to a solution of [Pd(acetonitrile)$_2$Cl$_2$] (0.026 g, 0.10 mmol) in 5 ml of dichloromethane. The reaction mixture was heated at reflux for 24 h. Subsequently, the mixture was cooled to room temperature and the product was precipitated by addition of 10 ml of n-hexane. After filtration and washing with 10 ml of diethyl ether a reddish purple solid was obtained. Yield: 0.107 g (0.09 mmol, 90%). Anal. Calcd for $C_{34}H_{26}Cl_2F_{12}N_8P_2PdRu \cdot 2\ H_2O$ (1150.98): C, 35.48; H, 2.63; N, 9.74%. Found: C, 35.30; H, 2.22; N, 9.31%. ^{1}H-NMR (Acetonitrile-d$_3$, 400MHz): δ = 10.05 (s, 1H, 3-H), 8.91 (d, *J* = 4.8 Hz, 1H, 15-H), 8.62 (d, *J* = 8.4 Hz, 1H, 12-H), 8.57 – 8.52 (m, 4H, bpy), 8.42 (s, 1H, 6-H), 8.15 (ddd, *J* = 6.0 Hz, *J* = 1.8 Hz, 1H, 11-H), 8.19-8.08 (m, 4H, bpy), 8.10 (ddd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H, 17-H), 7.81 (d, *J* = 8.0 Hz, 1H, 9-H), 7.82-7.75 (m, 4H, bpy), 7.66 (d, *J* = 7.6 Hz, 1H, 18-H), 7.59 (m, 1H, 10-H), 7.61 (m, 1H, 16-H), 7.50-7.44 (m, 4H, bpy).

[Ruthenium(II)(2,2'-bipyridine)$_2$(μ-2,5-di(pyridin-2-yl)pyrazine)PtCl$_2$] (PF$_6$)$_2$·2 H$_2$O (4)
1a (0.100 mg, 0.10 mmol) was dissolved in 5 ml of dichloromethane and added drop wise to a solution of [Pt(DMSO)$_2$Cl$_2$] (0.042 g, 0.10 mmol) in 5 ml of dichloromethane. The reaction mixture was heated at reflux for 24 h. The mixture was allowed to cool to room temperature and the product precipitated by addition of 10 ml of n-hexane. After filtration and washing with 10 ml of diethyl ether a reddish purple solid was obtained. Yield: 0.115 g (0.09 mmol, 90%). Anal. Calcd for $C_{34}H_{26}Cl_2F_{12}N_8P_2PtRu \cdot 2\ H_2O$ (1239.64): C, 32.94; H, 2.44; N, 9.04%. Found: C, 32.93; H, 2.07; N, 8.67%. ^{1}H-NMR (Acetonitrile-d$_3$, 400MHz): δ = 10.48 (s, 1H, 3-H), 9.46 (d, *J* = 4.8 Hz, 1H, 15-H), 8.63 (d, *J* = 8.4 Hz, 1H, 12-H), 8.57 – 8.48 (m, 4H, bpy), 8.55 (d, *J* = 8.0 Hz, 1H, 18-H), 8.32 (s, 1H, 6-H), 8.19-8.05 (m, 4H, bpy), 8.19 (ddd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H, 11-H), 8.07-7.55 (m, 4H, bpy), 8.05 (ddd, *J* = 8.0 Hz, *J* = 1.8 Hz, 1H, 17-H), 7.81 (d, *J* = 5.6 Hz, 1H, 9-H), 7.67-7.42 (m, 4H, bpy), 7.48 (m, 1H, 10-H), 7.42 (m, 1H, 16-H).

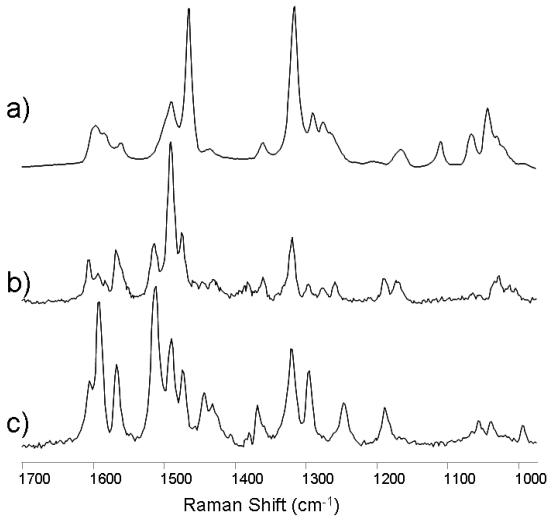

Fig. S1 rR spectra of **1a** at λ_{exc} (a) 785 nm (SERS) and (b) 450 nm and (c) 355 nm in CH_3CN (solvent subtracted)

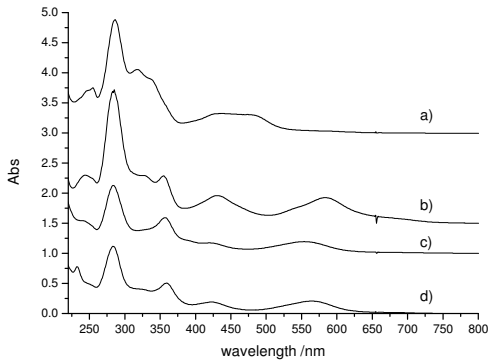

Fig. S2 UV/Vis absorption spectra of a) **1a**, b) **2a**, c) **3** and d) **4** in CH_3CN