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Supporting Information

Luminescent Anion Sensing by Transition-Metal Dipyridylbenzene Complexes Incorporated into Acyclic, Macro cyclic and Interlocked Hosts

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Contents

1. Experimental and $^1$H, $^{13}$C NMR and HRMS spectra ........................................................................................................................................2

   1. General Considerations .........................................................................................................................................................2

   1.1 Synthesis of 2,4-dibromo-isophthalic acid 2 ..........................................................................................................................2

   1.2 Synthesis of dimethyl-2,4-dibromo-isophthalate ester 3 .......................................................................................................3

   1.3 Synthesis of dimethyl-2,4-di-2-pyridyl-isophthalate ester (dpb-ester) 4 ..................................................................................4

   1.4 Synthesis of (dimethyl-2,4-di-2-pyridyl-isophthalate ester) platinum(II) chloride ([Pt$(^{1}$dpbester)Cl]) 5-Pt .......................6

   1.5 Synthesis of (dimethyl-2,4-di-2-pyridyl-isophthalate ester)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru$(^{1}$dpb-acid)(tppy)PF$_6$]) 5-Ru-PF$_6$ .........................................................................................................................7

   1.6 Synthesis of (2,4-di-2-pyridyl-isophthalic acid) platinum(II) chloride ([Pt$(^{1}$dpbacid)Cl]) 6-Pt .............................................8

   1.7 Synthesis of (2,4-di-2-pyridyl-isophthamic acid)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru$(^{1}$dpb-acid)(tppy)PF$_6$]) 6-Ru-PF$_6$ .........................................................................................................................9

   1.8 Synthesis of (dihexyl-2,4-di-2-pyridyl-isophthalamide) platinum(II) chloride ([Pt$(^{1}$dpb-hexyl)Cl]) 7-Pt ............................10

   1.9 Synthesis of (dihexyl 2,4-di-2-pyridyl-isophthalamide)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru$(^{1}$dpb-hexyl)(tppy)PF$_6$]) 7-Ru-PF$_6$ ..............................................................................................................11

   1.10 Synthesis of (2,4-di-2-pyridyl-isophthalamide macrocycle) platinum(II) chloride ([Pt$(^{1}$dpb-macrocycle)Cl]) 10-Pt ...........12

   1.11 Synthesis of (2,4-di-2-pyridyl-isophthalamide macrocycle)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru$(^{1}$dpb-macrocycle)(tppy)PF$_6$]) 10-Ru-PF$_6$ ............................................................................................................15

   1.12 Synthesis of [2]rotaxane (2,4-di-2-pyridyl-isophthalamide macrocycle) platinum(II) chloride ([Pt$(^{1}$dpb-macrocycle)Cl]) [2]rotaxane 12-Pt-Cl .................................................................................................................................17

   1.13 Synthesis of [2]rotaxane (2,4-di-2-pyridyl-isophthalamide)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru$(^{1}$dpb-macrocycle)(tppy)PF$_6$][2]rotaxane) 12-Ru-(PF$_6$)$_2$ .........................................................................................19

2. UV-vis and luminescence data ..............................................................................................................................................22

   2.1 Absorption, Emission and Excitation profiles for novel receptors ..........................................................................................22

   2.2 Luminescent Anion binding titrations .....................................................................................................................................25

   2.2.1 Anion titrations with [Pt$(^{1}$dpb-hexyl)Cl] 7-Pt ..................................................................................................................25

   2.2.2 Anion titrations with [Pt$(^{1}$dpb-macrocycle)Cl] 10-Pt ......................................................................................................28

   2.2.3 Anion titrations with [Ru$(^{1}$dpb-hexyl)(tppy)PF$_6$] 7-Ru-PF$_6$ ............................................................................................31

   2.2.4 Anion titrations with [Ru$(^{1}$dpb-macrocycle)(tppy)PF$_6$] 10-Ru-PF$_6$ ..................................................................................34

   2.2.5 Anion titrations with [2]rotaxane [Ru$(^{1}$dpb-macrocycle)(tppy)PF$_6$][2]rotaxane) 12-Ru-(PF$_6$)$_2$ ................................................37

3. $^1$H NMR anion titration data ....................................................................................................................................................38
4. Single crystal X-ray crystallography .................................................................................................................. 38

dimethyl-2,4-di-2-pyridyl-isophthalate ester 4 (CCDC 1978092) ........................................................................... 39

[Ru\textsuperscript{II}(dpb-hexyl)(tpy)]Cl \textit{7-Ru-PF}_6 (CCDC 1978093) ........................................................................... 40

syn-[Ru\textsuperscript{II}(dpb-macrocycle)(tpy)]PF\textit{6 10-Ru-PF}_6 (CCDC 1978096) ...................................................... 42

anti-[Ru\textsuperscript{II}(dpb-macrocycle)(tpy)]PF\textit{6 10-Ru-PF}_6 (CCDC 1978101) ...................................................... 44

5. References .................................................................................................................................................. 46

1. Experimental and \textsuperscript{1}H, \textsuperscript{13}C NMR and HRMS spectra

General Considerations

Commercial grade chemicals and solvents were used without further purification. Where anhydrous solvents were used, they were degassed with \textit{N}_2 and passed through an MBraun MPSP-800 column. Where degassed solvents were used, they were degassed via bubbling of \textit{N}_2 gas through the solution unless stated otherwise. Triethylamine was distilled from and stored over potassium hydroxide. De-ionised water dispensed from a Millipore Milli-Q purification system was used in all cases. Tetrabutylammonium (TBA) salts were stored under vacuum in a desiccator. Microwave reactions were carried out using a Biotage Initiator 2.0 microwave. All synthetic procedures have been reliably repeated multiple times. Routine 300 MHz NMR spectra were recorded on a Varian Mercury 300 spectrometer, \textit{1}H NMR operating at 300 MHz, \textit{13}C\textit{1}H at 76 MHz, \textit{19}F at 283 MHz and \textit{31}P at 121 MHz. Where the solubility of the compounds were too low, or not enough compound existed, a Bruker AVII500 with \textit{13}C Cryoprobe spectrometer was used for obtaining \textit{13}C\textit{1}H at 126 MHz, however in some cases a compete \textit{13}C\textit{1}H spectrum could not be obtained. All 500 MHz \textit{1}H Spectra and all \textit{1}H NMR titrations were recorded on a Varian Unity Plus 500 spectrometer. All chemical shift (\textit{\delta}) values are given in parts per million and are referenced to the solvent. In cases where solvent mixtures are used, the main solvent is used as the reference. Where an apparent multiplet (\textit{e.g.} app. t.) is quoted, \textit{J}_{app} is given. Low resolution ESI mass spectra were recorded on a Micromass LCT Premier XE spectrometer. Accurate masses were determined to four decimal places using Bruker \mu\textsc{TOF} and Micromass GCT spectrometers. UV/visible experiments were carried out on a PG instruments T60U spectrometer at 293 K. Steady-state fluorescence spectra were recorded on JobinYvon-Horiba Fluorolog-3 spectrophotometer or a Varian Cary-Eclipse spectrometer.

2,4-dibromo-1,5-dimethylbenzene \textit{1}, \textit{2}-tributylstannylpyridine\textsuperscript{2}, 4-tolyl-2,2′:6′,2″-terpyridine\textsuperscript{3}, 4-tolyl-2,2′:6′,2″-terpyridine ruthenium trichloride\textsuperscript{4}, diamine \textit{8},\textsuperscript{5} 3,5-bis-hexylamide pyridinium chloride \textit{9-Cl}\textsuperscript{6} and pyridinium axle-Cl \textit{11-Cl}\textsuperscript{7} were synthesised as previously described.

Synthesis of 2,4-dibromo-isophthalic acid 2

\[
\begin{align*}
\text{HO} & \quad \text{Br} \\
\text{Br} & \quad \text{OH}
\end{align*}
\]
This compound is known and has been previously synthesised via a different procedure.\(^8\)

KOH (3.20 g, 58.1 mmol) was added to a solution of 1,5-dibromo-2,4-dimethylbenzene 1 (15.0 g, 56.8 mmol) in water (300 mL). The resulting solution was diluted with pyridine (150 mL) and heated to 70 °C. 5.00 g portions of KMnO\(_4\) were added in 12 hour intervals until no further decolourisation of the solution was observed upon its addition (ca. 2 weeks). The resulting solution was filtered through Celite and the solution concentrated to 150 mL in vacuo. This solution was acidified to pH = 5 with conc. HCl(aq). The precipitate was collected via filtration, washed with water (3 × 200 mL) and hexane (2 × 100 mL) and dried in vacuo to give a white solid (16.5 g, 89%, 50.9 mmol).\(^1\) H NMR (300 MHz, CD\(_3\)OD) \(\delta\) 8.27 (1H, s, ArH), 8.10 (1H, s, ArH); \(^{13}\)C NMR (76 MHz, CD\(_3\)OD) \(\delta\) 167.9, 140.8, 134.9, 133.6, 126.2; ESI-HRMS m/z calcd. for [C\(_8\)H\(_4\)Br\(_2\)O\(_4\) – H]\(^+\) 322.8384, found 322.8376.

\(^1\)H NMR spectrum (400 MHz, CDCl\(_3\), 298 K)

\(^{13}\)C NMR spectrum (76 MHz, CDCl\(_3\), 298 K)

Synthesis of dimethyl-2,4-dibromo-isophthalate ester 3

This compound is known and has been previously synthesised via a different procedure.\(^9\)

5 drops of conc. H\(_2\)SO\(_4\)(aq) were added to a solution of 4,6-dibromoisophthalic acid 2 (1.00 g, 3.11 mmol) in MeOH (15 mL) in a 20 mL microwave vial. The reaction mixture was subjected to microwave irradiation at 100 °C for 20 minutes. This was repeated four times and the reaction mixtures combined upon completion. The resulting solution was poured onto ice water, basified with 25 % NH\(_4\)OH(aq) and extracted with Et\(_2\)O (3 ×
100 mL). The combined organic layers were dried over anhydrous MgSO$_4$ and the solvent removed in vacuo to give a white solid (3.86 g, 89%, 10.9 mmol). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.29 (1H, s, ArH), 8.02 (1H, s, ArH), 3.94 (6H, s, C$_2$H$_6$); $^{13}$C NMR (76 MHz, CDCl$_3$) δc 165.0, 140.0, 134.2, 130.8, 126.1, 53.0; FI-HRMS m/z calcd. for [C$_{10}$H$_8$Br$_2$O$_4$]$^+$ 351.8768, found 351.8769.

$^1$H NMR spectrum (400 MHz, CD$_3$OD, 298 K)

$^{13}$C NMR spectrum (76 MHz, CD$_3$OD, 298 K)

Synthesis of dimethyl-2,4-di-2-pyridyl-isophthalate ester (dpb-ester) 4

Dimethyl 2,4-dibromoisophthalate 3 (2.10 g, 5.96 mmol), 2-(tributylstannyl)pyridine (6.00 mL, 18.0 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.20 g, 0.285 mmol) and LiCl (2.00 g, 47.2mmol) were dissolved in anhydrous toluene (100 mL), degassed via 3 freeze-pump-thaw cycles, and placed under N$_2$. The reaction mixture was then heated under reflux for 48 hours under N$_2$. The resulting solution was cooled, sat. KF$_{aq}$ (10 mL) was added and the solution stirred for 30 minutes. The solution was filtered through Celite, washed with water (50 mL) and toluene (50 mL) and extracted with CH$_2$Cl$_2$ after adding sat. NaHCO$_3$$_{aq}$ (10 mL). Purification by column chromatography (SiO$_2$; hexane/Et$_2$O; 100:0→10:90) gave the product as an off-white solid (1.21 g, 58%, 3.47 mmol). $^1$H NMR
(300 MHz, CDCl₃) δH 8.66 (2H, d, JHH = 5.3, ArH), 8.32 (1H, s, ArH), 7.78 – 7.68 (3H, m, ArH), 7.49 (2H, d, JHH = 7.6, ArH), 7.26 (2H, app. t, Japp = 6.5, ArH), 3.74 (6H, s, CH₃); ¹³C NMR (76 MHz, CDCl₃) δC 167.9, 157.2, 149.1, 143.4, 136.3, 131.5, 131.5, 131.0, 122.9, 122.6, 52.2; ESI-HRMS m/z calcd. for [C₂₀H₁₆N₂O₄]⁺ 371.1002, found 371.1006.

¹H NMR spectrum (400 MHz, CDCl₃, 298 K)

¹³C NMR spectrum (76 MHz, CDCl₃, 298 K)

HRMS spectrum (ESI)
Synthesis of (dimethyl-2,4-di-2-pyridyl-isophthalate ester) platinum(II) chloride ([PtII(dpbeste)Cl]) 5-Pt

K₂PtCl₄ (50 mg, 0.1200 mmol) dissolved in H₂O (10 mL) was added to dimethyl 4,6-di(pyridin-2-yl)isophthalate 4 (42 mg, 0.120 mmol) in acetonitrile (30 mL). The reaction mixture was heated under vigorous reflux for 72 hours. The resulting solution was cooled, filtered and washed with H₂O (10 mL), EtOH (10 mL), acetonitrile (10 mL) and Et₂O (10 mL). The solvent was removed in vacuo and subsequent drying under high vacuum gave a yellow solid (45 mg, 64%, 78 µmol). ¹H NMR (500 MHz, d₆-DMSO) δ H 9.38 (2H, d, JHH = 6.3, ArH), 8.31 (2H, d, app. t, Japp = 7.5, ArH), 8.12 (2H, d, JHH = 7.8, ArH), 7.69 (2H, app. t, Japp = 7.2, ArH), 7.56 (1H, s, ArH); ¹³C NMR (126 MHz, d₆-DMSO) δC 167.1, 163.3, 151.7, 140.6, 139.0, 129.5, 125.7, 124.4, 123.8, 123.6, 53.3; El-HRMS m/z calcd. for [C₂₀H₁₅ClN₂O₄Pt·Cl]⁺ 542.0680, found 542.0695.

¹H NMR spectrum (400 MHz, d₆-DMSO, 298 K)

¹³C NMR spectrum (76 MHz, d₆-DMSO, 298 K) CH₂Cl₂ indicated by *

HRMS spectrum (El)
Synthesis of (dimethyl-2,4-di-2-pyridyl-isophthalate ester)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru\textsuperscript{II}(dpb-ester)(ttpy)PF\textsubscript{6}]) 5-Ru·PF\textsubscript{6}

RuCl\textsubscript{3}(ttpy) (0.200 g, 0.377 mmol) was added to a solution of AgBF\textsubscript{4} (0.265 g, 1.36 mmol) in acetone (40 mL) in the dark. The reaction mixture was heated under reflux for two hours. The resulting solution was cooled and filtered through Celite. The solvent was removed in vacuo and the solid dissolved in n-butanol (40 mL). Dimethyl 2,4-di(pyridin-2-yl)isophthalate 4 (0.210 g, 0.602 mmol) was added and heated to reflux for 18 hours under N\textsubscript{2}. The solution was cooled and concentrated to 10 mL in vacuo. Sat. NH\textsubscript{4}PF\textsubscript{6}(aq) (2 mL) was added and the solution filtered. The resulting solid was purified by column chromatography (SiO\textsubscript{2}; CH\textsubscript{2}Cl\textsubscript{2}/MeOH; 98:2) to give the product as a purple solid (0.220 g, 76%, 0.24 mmol). \textsuperscript{1}H NMR (300 MHz, (CD\textsubscript{3})\textsubscript{2}CO) δ H 10.16 (2H, s, ArH), 9.72 (2H, d, $^3$J\textsubscript{HH} = 8.2, ArH), 9.01 (4 H, app. dd, $J_{app}$ = 17.7, 8.2, ArH), 8.72 – 8.62 (2H, m, ArH), 8.58 – 8.45 (3H, m, ArH), 8.32 (4H, app. dd, $J_{app}$ = 17.7, 6.8, ArH), 8.05 – 7.84 (4H, m, ArH), 7.67 (2H, t, $^3$J\textsubscript{HH} = 6.5, ArH), 4.92 (6H, s, CO\textsubscript{2}CH\textsubscript{3}), 3.31 (3H, s, ArCH\textsubscript{3}); \textsuperscript{13}C NMR (76 MHz, (CD\textsubscript{3})\textsubscript{2}CO) δ C 170.8, 167.0, 160.0, 155.5, 154.1, 152.5, 136.5, 136.1, 131.0, 130.0, 129.1, 128.3, 127.6, 124.9, 124.3, 123.7, 121.0, 53.2, 21.3, remaining quaternary carbons not detected; \textsuperscript{19}F NMR (283 MHz, CDCl\textsubscript{3}) δ F -73.0 (d, $^1$J\textsubscript{PF} = 713 Hz, PF\textsubscript{6}); \textsuperscript{31}P NMR (121 MHz, CDCl\textsubscript{3}) δ P -144.32 (sept., $^3$J\textsubscript{PF} = 714 Hz, PF\textsubscript{6}); ESI-HRMS m/z calcd. for [C\textsubscript{42}H\textsubscript{32}F\textsubscript{6}N\textsubscript{5}O\textsubscript{4}PRu–PF\textsubscript{6}]\textsuperscript{+} 772.1504, found 772.1502.

\textsuperscript{1}H NMR spectrum (300 MHz, (CD\textsubscript{3})\textsubscript{2}CO, 298 K)
Synthesis of (2,4-di-2-pyridyl-isophthalic acid) platinum(II) chloride ([Pt\(^2\)(dpbacid)Cl] \(6\)-Pt)
[Pt(II)(dpbester)Cl] \textbf{5-Pt} (0.200 g, 0.344 mmol) was suspended in a solution of KOH (1.93 g, 34.0 mmol) dissolved in MeOH (5 mL). The reaction mixture was stirred at 40 °C for 18 hours. H₂O (2 mL) was added and the MeOH was removed \textit{in vacuo}. The resulting solution was neutralised with conc. HCl\textsubscript{(aq)}, filtered and washed with H₂O (2 × 5 mL) and MeOH (2 × 5 mL). The yellow precipitate was dried \textit{in vacuo} to give a yellow solid, the platinum bis-acid intermediate (186 mg, 99%, 0.339 mmol). This was used in the next step without characterisation due to extremely low solubility.

**Synthesis of (2,4-di-2-pyridyl-isophthic acid)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru(II)(dpb-acid)(ttpy)PF₆]) 6-Ru-PF₆**

10 % w/w NaOH\textsubscript{(aq)} (0.9 mL) was added to a solution of [Ru(II)(dpb-ester)(ttpy)PF₆] \textbf{5-Ru-PF₆} (10 mg, 12 µmol) dissolved in dioxane (6.7 mL) and MeOH (2.4 mL). The reaction mixture was stirred at ambient temperature for 18 hours. H₂O (0.5 mL) was added and MeOH and dioxane were removed \textit{in vacuo}. The resulting solution was then neutralised with conc. HCl\textsubscript{(aq)}, cooled for 30 minutes at 4 °C and filtered, and washed with H₂O (2 × 2 mL) and Et₂O (2 × 2 mL). The solvent was removed \textit{in vacuo} and subsequent drying under high vacuum gave the compounds as a purple solid (5.1 mg, 52%). Due to solubility issues, this was not characterised and used in the next step without further purification. ¹H NMR (500 MHz, CD₃CN) \(\delta_H\) 8.99 (2H, s, ArH), 8.57 (2H, d, \(^3J_{HH} = 7.0, \) ArH), 8.31 (2H, d, \(^3J_{HH} = 7.8, \) ArH), 8.11 (2H, d, \(^3J_{HH} = 7.8, \) ArH), 7.76 (1H, s, ArH), 7.73 (2H, app. t, \(J_{app} = 7.8, \) ArH), 7.64 (2H, app. t, \(J_{app} = 7.3, \) ArH), 7.56 (2H, d, \(^3J_{HH} = 6.7, \) ArH) 7.28 (2H, d, \(^3J_{HH} = 4.9, \) ArH), 7.04 (2H, d, \(^3J_{HH} = 6.1, \) ArH), 6.97 (2H, app. t, \(J_{app} = 5.8, \) ArH), 6.77 (2H, app. t, \(J_{app} = 5.8, \) ArH), 2.52 (3H, s, CH₃); ESI-LRMS m/z calcd. for \([C₄₀H₂₈F₆N₅O₄PRu–PF₆]^+\) 744.1, found 744.1.

¹H NMR spectrum (400 MHz, CD₂OD, 298 K) Et₂O indicated by *
Oxalyl chloride (0.110 mL, 1.37 mmol) was added dropwise to a suspension of Pt(dpb-acid)Cl 6-Pt (0.189 g, 0.343 mmol) in anhydrous CH₂Cl₂ (100 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N₂ at ambient temperature until homogenous (ca. 6 hours). The solvent was removed in vacuo and dried under high vacuum. Anhydrous, distilled Et₃N (0.384 mL, 2.75 mmol) and hexylamine (0.270 mL, 2.06 mmol) were added to the acid chloride intermediate dissolved in CH₂Cl₂ (100 mL) at 0 °C. The reaction mixture was stirred for two hours at ambient temperature. The resulting solution was washed with sat. NaHCO₃(aq) (50 mL), 10 % w/w citric acid (50 mL) and sat. brine (50 mL) and dried over anhydrous MgSO₄. The solvent was removed in vacuo. Purification by preparative thin-layer chromatography (SiO₂; CH₂Cl₂/Methanol 90:10) gave a yellow solid (15.2 mg, 6%, 22 µmol). ¹H NMR (500 MHz, CDCl₃) δH 9.55 (2H, d, 4JHH = 5.8, ArH), 9.13 (2H, t, 3JHH = 5.6, NH), 8.47 (2H, app. t, Japp = 8.0, ArH), 8.10 (2H, d, 3JHH = 8.3, ArH), 7.87 (2H, app. t, Japp = 6.6, ArH), 1.45 – 1.56 (4H, m, NHCH₂), 1.20 – 1.38 (16H, m, CH₃), 0.69 – 0.86 (6H, m, CH₃); ¹³C NMR (76 MHz, CDCl₃) δC 168.6, 164.3, 151.3, 137.7, 136.8, 134.2, 123.7, 122.4, 122.0, 40.1, 31.7, 29.6, 27.0, 22.8, 14.3; EI-HRMS m/z calcd. for [C₃₀H₃₇ClN₄O₄Pt - Cl]⁺ 680.2564, found 680.2791; UV-Vis λ max(CH₂Cl₂)/nm; ε/dm³ mol⁻¹ cm⁻¹: 251 (48,100) 295 (29,700) 364 (5,800) 379 (8,600) 416 (9,000).

¹H NMR spectrum (500 MHz, CDCl₃, 298 K)

¹³C NMR spectrum (76 MHz, CDCl₃, 298 K)
Synthesis of (dihexyl 2,4-di-2-pyridyl-isophthalamide)(4-tolyterpyridine) ruthenium(II) hexafluorophosphate ([Ru\textsuperscript{II}(dpb-hexyl)(ttpy)PF\textsubscript{6}]) 7·Ru·PF\textsubscript{6}

Oxalyl chloride (0.00400 mL, 0.0520 mmol) was added dropwise to a solution of [Ru\textsuperscript{II}(dpb-acid)(ttpy)PF\textsubscript{6}] 6·Ru·PF\textsubscript{6} (9.6 mg, 0.0130 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (50 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N\textsubscript{2} at ambient temperature until homogenous. The solvent was removed in vacuo and dried under high vacuum. Anhydrous, distilled Et\textsubscript{3}N (0.0140 mL, 0.104 mmol) and hexylamine (0.0100 mL, 0.0780 mmol) were added to the acid chloride intermediate dissolved in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (50 mL) at 0 °C. The reaction mixture was stirred for two hours at ambient temperature under N\textsubscript{2}. The solvent was then removed in vacuo and the solid was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (15 mL) and washed with 0.1 M NH\textsubscript{4}PF\textsubscript{6(aq)} (10 × 10 mL) and H\textsubscript{2}O (2 × 10 mL). The organic layer was dried over MgSO\textsubscript{4}, and the solvent removed in vacuo. Purification by preparative thin-layer chromatography (SiO\textsubscript{2}; CH\textsubscript{2}Cl\textsubscript{2}/MeOH; 90:10) gave a purple solid (9.24 mg, 81 %). \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ\textsubscript{H} 8.77 (2H, s, Ar\textsubscript{H}), 8.35 (2H, app. dt, J=8.1, 1.2, Ar\textsubscript{H}), 8.28 (2H, app. dd, J=8.4, 1.1, Ar\textsubscript{H}), 8.01 – 7.93 (2H, m, Ar\textsubscript{H}), 7.65 (2H, app. td, J=7.8, 1.5, Ar\textsubscript{H}), 7.58 – 7.47 (4H, m, Ar\textsubscript{H}), 7.29 (1H, s, Ar\textsubscript{H}), 7.28 – 7.23 (2H, m, Ar\textsubscript{H}), 7.09 – 7.05 (2H, m, Ar\textsubscript{H}), 6.99 (2H, app. ddd, J=7.3, 5.6, 1.4, Ar\textsubscript{H}),
6.83 (2H, \( t=5.8\), ArH), 6.63 (2H, app. ddd, \( J=7.2\), 5.7, 1.4, ArH), 3.58 (4H, app. td, \( J=7.3\), 5.8, NCH\(_2\)), 2.54 (3H, s, CH\(_3\)), 1.77 – 1.68 (4H, m, CH\(_2\)), 1.52 – 1.43 (4H, m, CH\(_2\)), 1.33 – 1.39 (8H, m, CH\(_2\)), 0.92 – 0.88 (6H, m, CH\(_3\)); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \): 171.6, 167.6, 157.9, 156.6, 153.1, 150.2, 135.2, 134.5, 130.7, 127.2, 123.6, 122.5, 121.6, 119.2, 53.6, 46.0, 40.5, 31.7, 29.9, 29.4, 26.9, 22.8, 21.6, 15.4, 14.2, remaining quaternary carbons undetected; \(^{19}\)F NMR (283 MHz, CDCl\(_3\)) \( \delta \): -72.5 (d, \( J \approx 713 \) Hz, PF\(_3\)); \(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \( \delta \): -144.53 (sept., \( J \approx 713 \) Hz, PF\(_3\)); ESI-HRMS m/z calcd. for [C\(_{52}\)H\(_{47}\)Cl\(_{2}\)N\(_2\)O\(_2\)Pt‰PF\(_3\)]\(^+\) 910.3391, found 910.3390; UV-Vis \( \lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}; \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1} \): 241 (39,900) 289 (64,800) 374 (9,600) 616 (14,200) 549 (12,800)

**Synthesis of (2,4-di-2-pyridyl-isophthalamide macrocycle) platinum(II) chloride ([Pt\(^{II}\)(dpb-macrocycle)Cl]) 10-Pt**

Oxalyl chloride (11 \( \mu \)L, 0.138 mmol) was added dropwise to a solution of Pt\(^{II}\)(dpbacid)Cl \( 6\text{-Pt} \) (19.0 mg, 0.0346 mmol) in anhydrous CH\(_2\)Cl\(_2\) (100 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N\(_2\) at ambient temperature until homogenous (ca. 6 hours). The solvent was removed in vacuo and dried under high vacuum. Bis-amine (0.0160 g, 0.0346 mmol), pyridinium thread \( 9\text{-Cl} \) (0.0130 g, 0.0346 mmol) and anhydrous, distilled Et\(_3\)N (0.0120 mL, 0.0865 mmol) were dissolved in anhydrous CH\(_2\)Cl\(_2\) (100 mL) and stirred until homogenous. The acid chloride in anhydrous CH\(_2\)Cl\(_2\) (100 mL) was added dropwise, and the reaction mixture stirred for three hours at ambient temperature under N\(_2\). The solvent was removed in vacuo and the resulting solid was purified by preparative thin-layer chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH; 98:2) to give a yellow solid (8.1 mg, 24%, 8.2 \( \mu \)mol). \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \( \delta \): 9.35 (2H, d, \( J_{\text{HH}} = 5.6\), ArH), 9.17 (2H, t, \( J_{\text{HH}} = 5.6\) Hz, NH), 8.28 (2H, app. t, \( J_{\text{app}} = 7.6\), ArH), 7.95 (2H, d, \( J_{\text{HH}} = 7.4\), ArH), 7.67 (2H, app. t, \( J_{\text{app}} = 7.5\), ArH), 7.12 (1H, s, ArH), 6.91 (4H, d, \( J_{\text{HH}} = 9.0\), ArH), 6.84 (4H, d, \( J_{\text{HH}} = 9.0\), ArH), 4.11 (4H, d, \( J_{\text{HH}} = 5.4\), CH\(_3\)), 3.97 (4H, t, \( J_{\text{HH}} = 4.8\), CH\(_2\)), 3.65 — 3.75 (8H, m, CH\(_2\)), 3.48 — 3.59 (8H, m, CH\(_2\)); \(^{13}\)C NMR (126 MHz, DMSO-d\(_6\)) \( \delta \): 167.9, 164.4, 152.8, 152.4, 140.6, 136.7, 135.3, 124.9, 123.1, 122.5, 115.6, 115.3, 70.0, 69.0, 69.0, 67.7, 66.5, 30.7; MALDI-TOF MS m/z calcd. for [C\(_{52}\)H\(_{47}\)Cl\(_{2}\)N\(_2\)O\(_2\)Pt - Cl]\(^+\) 942.27, found 942.02; UV-Vis \( \lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm} \): 234 (69,000) 253 (60,600), 295 (49,600) 361 (8,400) 380 (9,000) 419 (10,000).

\(^1\)H NMR spectrum (400 MHz, DMSO-d\(_6\), 298 K)
\(^{13}\)C NMR spectrum (76 MHz, DMSO-\(d_6\), 298 K)

MS spectrum (MALDI-TOF)

\(^1\)H NMR spectrum (500 MHz, CD\(_2\)Cl\(_2\), 298 K)
$^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 298 K)

HRMS spectrum (ESI)
Synthesis of (2,4-di-2-pyridyl-isophthalamidemacrocycle)(4-tolylterpyridine)ruthenium(II) hexafluorophosphate ([Ru\(^{11}\)(dpb-macrocycle)(tppy)PF\(_6\)]) 10-Ru·PF\(_6\)

Oxalyl chloride (0.0400 mL, 0.450 mmol) was added dropwise to a solution of [Ru\(^{11}\)(dpb-acid)(tppy)PF\(_6\)] 6-Ru·PF\(_6\) (0.100 g, 0.112 mmol) in anhydrous CH\(_2\)Cl\(_2\) (100 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N\(_2\) at ambient temperature until homogenous (ca. 6 hours). The solvent was removed in vacuo and dried under high vacuum. Bis-amine 8 (0.0521 g, 0.112 mmol), pyridinium thread 9-Cl (0.0430 g, 0.112 mmol) and anhydrous, distilled Et\(_2\)N (0.0400 mL, 0.281 mmol) were dissolved in anhydrous CH\(_2\)Cl\(_2\) (100 mL) and stirred until homogenous. The acid chloride in anhydrous CH\(_2\)Cl\(_2\) (100 mL) was added dropwise, and the reaction mixture stirred for three hours at ambient temperature under N\(_2\). The solvent was removed in vacuo. The resulting solid was dissolved in CH\(_2\)Cl\(_2\) (15 mL) and washed with 0.1 M NH\(_4\)PF\(_6\)(aq) (10 × 10 mL) and H\(_2\)O (2 × 10 mL). The organic layer was dried over MgSO\(_4\), and the solvent removed in vacuo. The resulting solid was purified by column chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH; 96:4) and preparative thin-layer chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH; 98:2) to give a purple solid (71.5 mg, 48%, 54.2 µmol). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ\(_H\) 9.47 (2H, t, \(^3\)\(^i\)J\(_HH\) = 5.6, Ar\(\text{H}\)), 8.76 (2H, s, Ar\(\text{H}\)), 8.55 (2H, d, \(^3\)\(^i\)J\(_HH\) = 8.5, Ar\(\text{H}\)), 8.35 (2H, d, \(^3\)\(^i\)J\(_HH\) = 8.1, Ar\(\text{H}\)), 7.97 (2H, d, \(^3\)\(^i\)J\(_HH\) = 7.8, Ar\(\text{H}\)), 7.59 (1H, s, Ar\(\text{H}\)), 7.55 (2H, t, \(^3\)\(^i\)J\(_HH\) = 7.9, Ar\(\text{H}\)), 7.50 (2H, d, \(^3\)\(^i\)J\(_HH\) = 7.9, Ar\(\text{H}\)), 7.44 (2H, d, \(^3\)\(^i\)J\(_HH\) = 5.5, Ar\(\text{H}\)), 7.37 (2H, t, \(^3\)\(^i\)J\(_HH\) = 8.0, Ar\(\text{H}\)), 7.00 (2H, t, \(^3\)\(^i\)J\(_HH\) = 6.7, Ar\(\text{H}\)), 6.91 – 6.84 (6H, m, Ar\(\text{H}\)), 6.62 (4H, d, \(^3\)\(^i\)J\(_HH\) = 8.6, Ar\(\text{H}\)), 6.50 (2H, t, \(^3\)\(^i\)J\(_HH\) = 6.6, Ar\(\text{H}\)), 4.27 (4H, t, \(^3\)\(^i\)J\(_HH\) = 6.1, CH\(_2\)), 3.94 (4H, app. q, J\(_app\) = 6.0, CH\(_2\)), 3.84 (4H, t, \(^3\)\(^i\)J\(_HH\) = 5.0, CH\(_2\)), 3.77 (4H, t, \(^3\)\(^i\)J\(_HH\) = 4.9, CH\(_2\)), 3.71 (8H s, CH\(_3\)), 2.50 (3H, s, CH\(_3\)); \(^13\)C NMR (126 MHz, CDCl\(_3\)) δ\(_C\) 165.52, 158.31, 153.86, 151.94, 148.64, 147.04, 145.48, 145.03, 143.62, 136.70, 135.15, 134.87, 133.85, 131.99, 131.22, 130.77, 127.52, 125.96, 124.45, 120.58, 116.30, 115.01, 114.87, 70.90, 70.74, 70.23, 68.50, 65.86, 63.97, 34.48, 31.55; \(^19\)F NMR (283 MHz, CDCl\(_3\)) δ\(_F\) -71.96 (d, \(^1\)J = 713 Hz, PF\(_6\)); \(^31\)P NMR (121 MHz, CDCl\(_3\)) δ\(_P\) -144.31 (sept., \(^3\)\(^i\)J\(_PP\) = 714 Hz, PF\(_6\)); ESI-HRMS m/z calc. for [C\(_{60}\)H\(_{50}\)F\(_{6}\)N\(_{6}\)O\(_{3}\)Ru – PF\(_6\)]\(^+\) 1172.3508, found 1172.3528; UV-Vis \(\lambda_{max}(CH\(_2\)Cl\(_2\))/nm; \(\varepsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}\): 233 (40,400) 288 (64,300) 373 (9,300) 516 (12,900) 554 (11,700)

\(^1\)H NMR spectrum (400 MHz, CD\(_3\)OD, 298 K)
$^{13}$C NMR spectrum (76 MHz, CD$_3$OD, 298 K)

HRMS spectrum (ESI)
Synthesis of [2]rotaxane (2,4-di-2-pyridyl-isophthalamide macrocycle) platinum(II) chloride ([Pt^II(dpb-macrocycle)Cl] [2]rotaxane) 12-Pt-Cl

Oxalyl chloride (0.0400 mL, 0.496 mmol) was added dropwise to a solution of Pt^II(dpβ-acid)Cl 6-Pt (0.0682 g, 0.124 mmol) in anhydrous CH₂Cl₂ (100 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N₂ at 40 °C until homogenous (ca. 6 hours). The solvent was removed in vacuo and dried under high vacuum. Bis-amine 8 (0.0576 g, 0.124 mmol), pyridinium axle 11-Cl (0.133 g, 0.124 mmol) and anhydrous, distilled Et₃N (0.043 mL, 0.310 mmol) were dissolved in anhydrous CH₂Cl₂ (100 mL) and stirred until homogenous. The acid chloride in anhydrous CH₂Cl₂ (100 mL) was added dropwise, and the reaction mixture stirred for three hours at ambient temperature under N₂. The solvent was removed in vacuo. Purification by column chromatography (SiO₂; CH₂Cl₂/MeOH 99:1→95:5), preparative thin-layer chromatography (SiO₂; CH₂Cl₂/MeOH 99:1→95:5) and size-exclusion chromatography (Bio-Beads S-X1/ CHCl₃) gave the compound as a yellow solid (7.6 mg, 3 %, 3.7 µmol). ¹H NMR (500 MHz, CDCl₃/CD₃OD 9:1) 9.58 (1H, s, PyH), 9.32 (2H, d, ³JHH = 5.8, ArH), 9.13 (1H, s, ArH), 8.75 (2H, s, PyH), 8.04 (1H, s, ArH), 7.79 (2H, d, ³JHH = 8.3, ArH), 7.67 (6H, app. dd, J_app = 20.6, 8.3, ArH + StH), 6.64 (4H, d, ³JHH = 8.5, HQH), 6.28 (4H, d, ³JHH = 8.6, HQH), 4.09 (4H, s, OCH₂), 3.92 (4H, s, OCH₂), 3.75 (4H, s, OCH₂), 3.65 – 3.56 (8H, m, OCH₂), 3.48 – 3.42 (4H, m, NCH₃), 3.30 (3H, s, NCH₃), 1.22 (36H, s, C(CH₃)₃); ¹³C NMR (126 MHz, CDCl₃/CD₃OD 9:1) δ: 169.1, 164.7, 158.7, 152.9, 151.9, 148.7, 146.9, 144.8, 143.5, 139.3, 134.9, 133.9, 133.6, 131.9, 131.0, 130.6, 128.8, 127.4, 125.9, 124.3, 123.6, 123.1, 119.6, 115.6, 115.0, 70.7, 70.6, 70.2, 68.3, 67.5, 66.2, 63.9, 57.8, 40.2, 38.7, 34.3, 31.3, 30.4, 29.7, 28.9, 23.7, 23.0, 22.7, 17.9, 14.0, 10.9; MALDI-TOF MS m/z calcd. for [C₁₁₆H₁₂₁Cl₂N₁₀O₁₁Pt – Cl]⁺ 2018.32, found 2018.89.
$^1$H NMR spectrum (500 MHz, CDCl$_3$/CD$_3$OD 9:1, 298 K)

$^{13}$C NMR spectrum (126 MHz, CDCl$_3$/CD$_3$OD 9:1, 298 K)
Synthesis of [2]rotaxane \((2,4\text{-di-2-pyridyl-isophthalamide})\)(4-tolylterpyridine) ruthenium(II) hexafluorophosphate \((\text{[Ru}^1\text{(dpb-macrocycle)(ttpy)PF}_6\text{] [2]rotaxane})\) 12-Ru\((\text{PF}_6)_2\)
Oxalyl chloride (0.08 mL, 0.1 mmol) was added dropwise to a solution of [Ru⁴(dpbb-acid)(tppy)PF₆]⁶-Ru·PF₆ (0.023 g, 0.025 mmol) in anhydrous CH₂Cl₂ (10 mL) and anhydrous degassed catalytic DMF (1 drop). The reaction mixture was stirred under N₂ at 40°C until homogenous (ca. 6 hours). The solvent was removed in vacuo and dried under high vacuum. Bis-amine 8 (0.012 g, 0.025 mmol), pyridinium axle 11-Cl (0.027 g, 0.025 mmol) and anhydrous, distilled Et₃N (0.008 mL, 0.0625 mmol) were dissolved in anhydrous CH₂Cl₂ (10 mL) and stirred until homogenous. The acid chloride in anhydrous CH₂Cl₂ (10 mL) was added dropwise, and the reaction mixture stirred for three hours at ambient temperature under N₂. The solvent was removed in vacuo. Purification by column chromatography (SiO₂; CH₂Cl₂/MeOH; 95:5) and by preparative thin-layer chromatography (SiO₂; EtOAc/MeOH; 100:0→98:2). This was dissolved in CH₂Cl₂ (15 mL) and washed with 0.1 M NH₄PF₆(aq) (10 × 10 mL) and H₂O (2 × 10 mL). The organic layer was dried over MgSO₄, and the solvent removed in vacuo to give the compound as a purple solid (4.9 mg, 6% over two-steps, 1.95 µmol); ¹H NMR (500 MHz, CD₂Cl₂) δ H 9.47 (1H, br.s, ArH), 9.37 (1H, br.s, ArH), 8.78 (2H, s, ArH), 8.67 (1H, s, ArH+StH), 8.32 (4H, d, ⁽³J_HH⁾ = 8.2, ArH+StH), 8.00 (4H, d, ⁽³J_HH⁾ = 7.9, ArH+StH), 7.79 (4H, s, ArH), 7.55 (5H, app. dd, ⁽J_app⁾ = 15.0, 8.2, ArH), 7.38 (4H, d, ⁽³J_HH⁾ = 8.5, StH), 7.30 (11H, d, ⁽³J_HH⁾ = 7.5, ArH+StH), 7.23 – 7.20 (9H, m, ArH+StH), 7.06 (4H, d, ⁽³J_HH⁾ = 5.9, StH), 6.79 (4H, d, ⁽³J_HH⁾ = 8.0, HQH), 6.62 (2H, t, ⁽³J_HH⁾ = 6.6, ArH), 6.33 (4H, d, ⁽³J_HH⁾ = 8.6, HQH), 4.10 (4H, s, OCH₂), 3.93 (4H, s, OCH₃), 3.77 (4H, s, OCH₂), 3.70 (4H, s, OCH₃), 3.63 (4H, s, OCH₂), 3.44 (4H, s, NCH₂), 2.53 (3H, s, ArCH₃), 1.24 (36H, s, C(CH₃)₃); ¹³C NMR (126 MHz, CDCl₃/CD₂OD 9:1) δ C 165.2, 165.1, 164.5, 164.4, 158.4, 158.3, 153.2, 152.2, 152.1, 148.7, 147.0, 146.0, 144.6, 144.5, 143.6, 143.5, 138.0, 136.6, 135.5, 134.8, 133.4, 131.8, 131.0, 130.6, 129.3, 128.9, 127.4, 127.3, 127.0, 125.8, 125.8, 124.4, 124.3, 123.8, 121.6, 120.6, 120.4, 114.9, 70.7, 70.6, 70.0, 68.3, 65.5, 63.8, 41.1, 41.0, 39.2, 34.3, 31.3, 29.7; ³¹F NMR (472 MHz, CD₂Cl₂) δ F -70.9 (d, ⁽³J = 742 Hz, PF₆⁻); ³¹P NMR (121 MHz, CDCl₃) δ P -144.35 (sept., ⁽³J_HH⁾ = 714 Hz, PF₆⁻); ESI-HRMS m/z calcd. for [C₁₃₈H₁₃₈F₆N₁₀O₁₄]⁺PRu – 2PF₆⁻: 1106.4793, found 1106.4795; UV-Vis λ_max(CH₂Cl₂)/nm; e/dm³ mol⁻¹ cm⁻¹: 251 (96,300) 289 (64,000) 371 (9,800) 516 (14,200) 557 (12,100).

¹H NMR spectrum (500 MHz, CD₂Cl₂, 298 K)

¹³C NMR spectrum (126 MHz, CDCl₃/CD₂OD 9:1, 298 K)
$^1$H-^1$H ROESY 2D Correlation NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298 K)

HRMS spectrum (ESI)
2. UV-vis and luminescence data

2.1 Absorption, Emission and Excitation profiles for novel receptors

Photophysical properties of $[\text{Pt}^{II}(\text{dpb-hexyl})\text{Cl}]$ in CH$_2$Cl$_2$ (Absorption = blue, emission = red and excitation = dashed)

Photophysical properties of $[\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]$ in CH$_2$Cl$_2$ (Absorption = blue, emission = red and excitation = dashed)
Photophysical properties of $[\text{Ru}^{II}(\text{dpb-hexyl})(\text{ttpy})]\text{PF}_6$ in CH$_2$Cl$_2$/MeOH 95:5 (Absorption = blue, emission = red and excitation = dashed)

Photophysical properties of $[\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6$ in CH$_2$Cl$_2$/MeOH 95:5 (Absorption = blue, emission = red and excitation = dashed)
Photophysical properties of [Ru(II)(dpb-macrocycle)(ttpy)]PF$_6$ in CH$_2$Cl$_2$/MeOH 95:5 (Absorption = blue, emission = red and excitation = dashed)

Emissive properties of [Pt(II)(dpb-macrocycle)Cl] emission as a function of excitation wavelength

Emissive properties of [Pt(II)(dpb-macrocycle)Cl] in CH$_2$Cl$_2$ as a function of changing excitation wavelength
2.2 Luminescent Anion binding titrations

Luminescence experiments were carried out on a Varian Cary-Eclipse spectrometer for the platinum (II) receptors using an excitation wavelength of 320 nm at 293 K. To a 2.5 mL, $1 \times 10^{-5}$ M solution of each receptor was added aliquots of the tetrabutylammonium salts dissolved in a stock solution made up with the receptor, such that the same concentration of the host was maintained throughout the titration experiments. Luminescence experiments were carried out on a Horiba Fluorolog spectrometer for the ruthenium (II) receptors using an excitation wavelength of 530 nm at 293 K. To a 1 mL, $1 \times 10^{-4}$ M solution of each receptor was added aliquots of the tetrabutylammonium salts dissolved in a stock solution made up with the receptor, such that the same concentration of the host was maintained throughout the titration experiments. In both cases the titration data was analysed and association constants determined using the SPECFIT program.$^{10,11}$

2.2.1 Anion titrations with [PtII(dpb-hexyl)Cl] 7-Pt

Emission spectra of [PtII(dpb-hexyl)Cl] in the presence of increasing amounts of chloride ($\text{CH}_2\text{Cl}_2$, 293 K; $\lambda_{\text{ex}}=320\text{ nm}$)
Emission spectra of \([\text{Pt}^{II}(dpb\text{-hexyl})\text{Cl}]\) in the presence of increasing amounts of bromide (\(\text{CH}_2\text{Cl}_2, 293 \text{ K}; \lambda_{\text{ex}} = 320 \text{ nm}\))

Emission spectra of \([\text{Pt}^{II}(dpb\text{-hexyl})\text{Cl}]\) in the presence of increasing amounts of iodide (\(\text{CH}_2\text{Cl}_2, 293 \text{ K}; \lambda_{\text{ex}} = 320 \text{ nm}\))
Emission spectra of [Pt(dpb-hexyl)Cl] in the presence of increasing amounts of acetate (CH₂Cl₂, 293 K; λ₂₃ = 320 nm)

Emission spectra of [Pt(dpb-hexyl)Cl] in the presence of increasing amounts of dihydrogenphosphate (CH₂Cl₂, 293 K; λ₂₃ = 320 nm)
Emission spectra of [Pt\textsuperscript{II}(dpb-hexyl)Cl] in the presence of increasing amounts of sulphate (CH\textsubscript{2}Cl\textsubscript{2}, 293 K; \(\lambda_{\text{ex}} = 320\) nm)

2.2.2 Anion titrations with [Pt\textsuperscript{II}(dpb-macrocycle)Cl] 10-Pt

Emission spectra of [Pt\textsuperscript{II}(dpb-macrocycle)Cl] in the presence of increasing amounts of chloride (CH\textsubscript{2}Cl\textsubscript{2}, 293 K; \(\lambda_{\text{ex}} = 320\) nm)
Emission spectra of $[\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]$ in the presence of increasing amounts of bromide (CH$_2$Cl$_2$, 293 K; $\lambda_{ex} = 320$ nm)

Emission spectra of $[\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]$ in the presence of increasing amounts of iodide (CH$_2$Cl$_2$, 293 K; $\lambda_{ex} = 320$ nm)
Emission spectra of \([\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]\) in the presence of increasing amounts of acetate (\(\text{CH}_2\text{Cl}_2, 293 \text{ K}; \lambda_{\text{ex}} = 320 \text{ nm}\))

Emission spectra of \([\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]\) in the presence of increasing amounts of dihydrogenphosphate (\(\text{CH}_2\text{Cl}_2, 293 \text{ K}; \lambda_{\text{ex}} = 320 \text{ nm}\))
Emission spectra of $[\text{Pt}^{II}(\text{dpb-macrocycle})\text{Cl}]$ in the presence of increasing amounts of sulphate ($\text{CH}_2\text{Cl}_2$, 293 K; $\lambda_{\text{ex}} = 320$ nm)

2.2.3 Anion titrations with $[\text{Ru}^{II}(\text{dpb-hexyl})(\text{ttpty})]\text{PF}_6$ 7-Ru-PF6

Emission spectra of $[\text{Ru}^{II}(\text{dpb-hexyl})(\text{ttpty})]\text{PF}_6$ in the presence of increasing amounts of chloride ($\text{CH}_2\text{Cl}_2$/MeOH 95:5, 293 K; $\lambda_{\text{ex}} = 530$ nm)
Emission spectra of [RuII(dp-b-hexyl)(tppy)]PF₆ in the presence of increasing amounts of bromide
(CH₂Cl₂/MeOH 95:5, 293 K; λₑₓ = 530 nm)

Emission spectra of [RuII(dp-b-hexyl)(tppy)]PF₆ in the presence of increasing amounts of iodide (CH₂Cl₂/MeOH 95:5, 293 K; λₑₓ = 530 nm)
Emission spectra of [Ru\textsuperscript{II}(dpb-hexyl)(ttpy)]PF\textsubscript{6} in the presence of increasing amounts of acetate (CH\textsubscript{2}Cl\textsubscript{2}/MeOH 95:5, 293 K; $\lambda_{\text{ex}} = 530$ nm)

Emission spectra of [Ru\textsuperscript{II}(dpb-hexyl)(ttpy)]PF\textsubscript{6} in the presence of increasing amounts of dihydrogenphosphate (CH\textsubscript{2}Cl\textsubscript{2}/MeOH 95:5, 293 K; $\lambda_{\text{ex}} = 530$ nm)
Emission spectra of [Ru$^{II}$](dpb-hexyl)(ttpy)]PF$_6$ in the presence of increasing amounts of sulphate
(CH$_2$Cl$_2$/MeOH 95:5, 293 K; $\lambda_{ex}$ = 530 nm)

2.2.4 Anion titrations with [Ru$^{II}$](dpb-macrocycle)(ttpy)]PF$_6$ 10-Ru-PF$_6$

Emission spectra of [Ru$^{II}$](dpb-macrocycle)(ttpy)]PF$_6$ in the presence of increasing amounts of chloride
(CH$_2$Cl$_2$/MeOH 95:5, 293 K; $\lambda_{ex}$ = 530 nm)
Emission spectra of $[\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6$ in the presence of increasing amounts of bromide

$(\text{CH}_2\text{Cl}_2/\text{MeOH} \ 95:5, \ 293 \ K; \ \lambda_\text{ex} = 530 \ nm)$

Emission spectra of $[\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6$ in the presence of increasing amounts of iodide

$(\text{CH}_2\text{Cl}_2/\text{MeOH} \ 95:5, \ 293 \ K; \ \lambda_\text{ex} = 530 \ nm)$
Emission spectra of [Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} in the presence of increasing amounts of acetate 
(CH\textsubscript{2}Cl\textsubscript{2}/MeOH 95:5, 293 K; \(\lambda_{\text{ex}} = 530\) nm)

Emission spectra of [Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} in the presence of increasing amounts of hydrogenphosphate 
(CH\textsubscript{2}Cl\textsubscript{2}/MeOH 95:5, 293 K; \(\lambda_{\text{ex}} = 530\) nm)
Emission spectra of \([\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6\) in the presence of increasing amounts of sulphate (\(\text{CH}_2\text{Cl}_2/\text{MeOH} 95:5, 293 \text{ K}; \lambda_{\text{ex}} = 530 \text{ nm}\))

### 2.2.5 Anion titrations with [2]rotaxane \([\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6\) 12-Ru-(PF\(_6\))

Emission spectra of [2]rotaxane \([\text{Ru}^{II}(\text{dpb-macrocycle})(\text{ttpy})]\text{PF}_6\) in the presence of increasing amounts of chloride (\(\text{CH}_2\text{Cl}_2/\text{MeOH} 95:5, 293 \text{ K}; \lambda_{\text{ex}} = 530 \text{ nm}\))
3. H NMR anion titration data

Initial NMR sample volumes and concentrations were 500 μL and 2.0 mM respectively. Solutions (100 mM) of anion were added as their tetrabutylammonium salts. Spectra were recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10 equivalents. In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale. Association constants were obtained by analysis of the resulting data using the WinEQNMR2 computer program. Binding stoichiometry was investigated by visual analysis of the titration data, and using approximations of Job plots. Estimates for the association constant and the limiting chemical shifts were added to the program’s input file. The parameters were refined by non-linear least-squares analysis using WINEQNMR2 to achieve the best fit between observed and calculated chemical shifts. The input parameters for the final chemical shift and association constant were adjusted based on the program output until convergence was reached. Comparison of the calculated and experimental binding isotherms demonstrated that an appropriate model with an appropriate stoichiometry were used.

4. Single crystal X-ray crystallography

Data was collected at 150(2) K using either graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer in the case of dimethyl-2,4-di-2-pyridyl-isophthalate ester 4. For [Ru11(dpbb-hexyl)(tppy)]Cl and anti- and syn-[Ru11(dpb-macrocycle)(tppy)]PF6 10-Ru-PF6, data were collected using silicon double crystal monochromated synchrotron radiation (λ = 0.66890 Å) at Diamond Light Source, Beamline I19 on a custom built Rigaku diffractometer.

When using the Nonius machine, a series of ω-scans were typically performed in such a way as to collect every independent reflection to a maximum resolution of 0.77 Å, aiming for 99.5% completeness. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package. When using synchrotron radiation, ω-scans were performed such that a half-sphere of data was collected to a maximum resolution of 0.77 Å. Cell refinement, data reduction and scaling were performed using the CrystalClear package.

The structures were solved by direct methods using the SIR92 software or by charge flipping using Superflip. Structures were refined using full-matrix least-squares on F2 within the CRYSTALS suite. All non-hydrogen atoms were refined with anisotropic displacement parameters unless specified otherwise. Disordered portions were modelled using refined partial occupancies. Geometric and vibrational restraints were applied where appropriate to ensure physically reasonable models.

In some cases, the molecular structure within solvent voids could not be resolved in the difference map and PLATON SQUEEZE was therefore used to account for the residual electron density in the refinement.

After the construction of a stable, physically reasonable and complete model, the weights were optimised, analogous reflections were omitted and absent high-angle data (in the case of poorly diffracting samples) were pruned using the Wilson plot. This generally led to convergence of the refinement, giving the final structure.
For the more challenging structures, in which the refinement did not converge immediately, initially half-shifts, then restraints and finally rigid body refinement were used to overcome the problem. IUCr CheckCIF/PLATON was used to validate the structures and warnings were dealt with as appropriate or justified using validation reply forms.

**dimethyl-2,4-di-2-pyridyl-isophthalate ester 4 (CCDC 1978092)**

![Single crystal X-ray structure of dimethyl-2,4-di-2-pyridyl-isophthalate ester (ellipsoids are plotted at the 50% probability level)](image1)

![Single crystal X-ray structure of dimethyl-2,4-di-2-pyridyl-isophthalate ester (ellipsoids are plotted at the 50% probability level; hydrogen atoms omitted for clarity)](image2)

![Single crystal X-ray structure of dimethyl-2,4-di-2-pyridyl-isophthalate ester (ellipsoids are plotted at the 50% probability level; hydrogen atoms omitted for clarity)](image3)
**CCDC 1978092** contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Single crystals of were grown from vapour diffusion of methanol into a chloroform solution of the compound over several days.

| Compound reference | dimethyl-2,4-di-2-pyridyl-isophthalate ester |
|--------------------|---------------------------------------------|
| Chemical formula   | C$_{20}$H$_{16}$N$_2$O$_4$                     |
| Formula Mass       | 348.36                                      |
| Crystal system     | Monoclinic                                   |
| a/Å                | 7.0471(3)                                   |
| b/Å                | 10.9564(4)                                  |
| c/Å                | 11.2964(5)                                  |
| α/°                | 73.2309(16)                                 |
| β/°                | 89.9992(15)                                 |
| γ/°                | 90.0079(19)                                 |
| Unit cell volume/Å$^3$ | 835.11(6)                           |
| Temperature/K      | 150                                         |
| Space group        | $P2_111$                                    |
| No. of formula units per unit cell, Z | 2                                           |
| No. of reflections measured | 6494                                        |
| No. of independent reflections | 3704                                      |
| $R_{int}$          | 0.027                                       |
| Final $R_1$ values ($I > 2σ(I)$) | 0.0670                                    |
| Final wR($F^2$) values ($I > 2σ(I)$) | 0.1723                                    |
| Final $R_1$ values (all data) | 0.0744                                    |
| Final wR($F^2$) values (all data) | 0.1835                                    |

[Ru$^{II}$(dpb-hexyl)(ttppy)]Cl $\cdot$ Ru$\cdot$PF$_6$ (CCDC 1978093)

Single crystal X-ray structure of [Ru$^{II}$(dpb-hexyl)(ttppy)]Cl (ellipsoids are plotted at the 50% probability level)
Single crystal X-ray structure of [Ru(II)(dpb-hexyl)(tpy)]Cl (ellipsoids are plotted at the 50% probability level; hydrogen atoms omitted for clarity)

CCDC 1978093 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single crystals of were grown from vapour diffusion of diisopropyl ether into an acetonitrile solution of the compound in the presence of excess tetra-n-butyl ammonium chloride over several days.
syn-[Ru\textsuperscript{II}(dpb-macrocycle)(tppy)]PF\textsubscript{6}\ ·\ Ru\cdot PF\textsubscript{6} (CCDC 1978096)

Single crystal X-ray structure of syn-[Ru\textsuperscript{II}(dpb-macrocycle)(tppy)]PF\textsubscript{6} (ellipsoids are plotted at the 50% probability level; disorder omitted for clarity)
Single crystal X-ray structure of syn-[Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} (ellipsoids are plotted at the 50% probability level; disorder, solvent and hydrogen atoms omitted for clarity)

CCDC 1978096 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Single crystals of were grown from vapour diffusion of diisopropyl ether into a chloroform solution of the compound over several days.
| Compound reference | syn-[Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} |
|--------------------|---------------------------------------------------------------|
| Chemical formula   | C\textsubscript{64}H\textsubscript{60}N\textsubscript{7}O\textsubscript{9}Ru·PF\textsubscript{6}·CHCl\textsubscript{3} |
| Formula Mass       | 1436.6                                                        |
| Crystal system     | Triclinic                                                     |
| a/Å                | 11.6196(4)                                                   |
| b/Å                | 15.1032(6)                                                   |
| c/Å                | 19.5089(9)                                                   |
| α/°                | 95.892(3)                                                    |
| β/°                | 96.002(3)                                                    |
| γ/°                | 90.684(3)                                                    |
| Unit cell volume/Å\textsuperscript{3} | 3386.0(2)                                                      |
| Temperature/K      | 100                                                          |
| Space group        | P\textsubscript{1}−                                          |
| No. of formula units per unit cell, Z | 2                                                             |
| No. of reflections measured | 11024                                                         |
| No. of independent reflections | 10271                                                        |
| \(R_\text{int}\)  | 0.079                                                        |
| Final \(R_1\) values \((I > 2σ(I))\) | 0.0758                                                        |
| Final \(wR(F^2)\) values \((I > 2σ(I))\) | 0.1902                                                        |
| Final \(R_1\) values (all data) | 0.0913                                                        |
| Final \(wR(F^2)\) values (all data) | 0.1859                                                        |

\textit{anti-}[Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} 10·Ru·PF\textsubscript{6} (CCDC 1978101)

![Single crystal X-ray structure of \textit{anti-}[Ru\textsuperscript{II}(dpb-macrocycle)(ttpy)]PF\textsubscript{6} (ellipsoids are plotted at the 50% probability level; disorder omitted for clarity)](image-url)
Single crystal X-ray structure of *anti*-\([\text{Ru}^{II}\text{(dpb-macrocycle)}(\text{ttpy})]\)PF₆ (ellipsoids are plotted at the 50% probability level; disorder, solvent and hydrogen atoms omitted for clarity)

**CCDC 1978101** contains the supplementary crystallographic data for this paper. These can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Single crystals of were grown from vapour diffusion of diisopropyl ether into an acetone/H₂O (9:1) solution of the compound over several days.
| Compound reference | anti-[Ru^II(dpbb-macrocycle)(ttpy)]PF_6 |
|----------------------|---------------------------------------|
| Chemical formula     | C_{64}H_{56}N_{7}O_{9}Ru·F_{6}P·C_{3}H_{6}O |
| Formula Mass         | 1373.30                                |
| Crystal system       | Triclinic                              |
| a/Å                  | 10.4341(5)                             |
| b/Å                  | 12.3603(5)                             |
| c/Å                  | 24.9734(12)                            |
| a/°                  | 80.884(4)                              |
| β/°                  | 84.607(4)                              |
| γ/°                  | 76.012(4)                              |
| Unit cell volume/Å^3 | 3080.6(3)                              |
| Temperature/K        | 100                                    |
| Space group          | P1_1                                    |
| No. of formula units per unit cell, Z | 2                                      |
| No. of reflections measured | 25967                                |
| No. of independent reflections | 17475                          |
| R_int                | 0.041                                  |
| Final R_1 values (I > 2σ(I)) | 0.0491              |
| Final wR(F^2) values (I > 2σ(I)) | 0.0915                    |
| Final R_1 values (all data) | 0.0660                         |
| Final wR(F^2) values (all data) | 0.1029                      |

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