Supporting Information

Equipping metallosupramolecular macrocycles with functional groups: Assemblies of pyridine-substituted urea ligands

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1. Experimental Section

Molecular modeling

The calculated structures were optimized with the MM2 force field implemented in the CAChe WorkSystem Pro program package for Windows (version 6.1.12.33; Fujitsu Ltd., Krakow/Poland, 2000-2004).

Melting points

Melting points were measured with a Büchi 510 Melting Point apparatus and are not corrected. Due to the properties of the silicon oil used in this apparatus, only melting points up to 250 °C could be measured.

NMR spectroscopy

^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{1}H,^{1}H NOESY NMR, ^{1}H 2D DOSY NMR spectra were recorded on Joel ECX 400 MHz, Joel ECP 500 MHz, Bruker AC 250 MHz, Bruker AC 500 MHz, Bruker AM 300, Bruker DMX 500 MHz, and Bruker DRX 500 MHz NMR spectrometers. Chemical shifts are reported in ppm. In ^{1}H and ^{13}C NMR spectra, the residual solvents were used as internal standards. For ^{31}P NMR spectra 85% phosphoric acid was used as external standard. ^{13}C and ^{31}P NMR spectra were recorded with broadband decoupling for ^{1}H. Coupling constants (*J*) are given in Hz. The abbreviations used for the signal multiplicities are: s = singlet; d = doublet; t = triplet; m = multiplet and br for broad signals.

Mass spectrometry

EI mass spectra were measured with a MAT 711 EI mass spectrometer from Varian MAT (Bremen, Germany) or with a HP 5989 A EI mass spectrometer from HEWLETT-PACKARD in Palo Alto (CA, USA). Standard ionization energies of 70 and 80 eV were used. HRMS ESI spectra were recorded using an Agilent 6210 ESI TOF mass spectrometer from Agilent Technologies in Santa Clara (CA, USA). The flow rate was set to 4 µL/min and the spray voltage was adjusted to 4 kV. The desolvation gas was used with a pressure of 15 psi (1 bar). All other parameters were optimized to get the maximal abundance for the respective $[M+H]^{+}$. ESI-TOF and ESI FTICR mass spectrometer were used to analyze the complexes under study. The experiments measured from pure DMF were performed with a QSTAR Elite mass spectrometer equipped with an API 200 TurboIonSpray ESI source from AB Sciex (former MDS Sciex) in Concord, Ontario (Canada). The samples were injected into the ESI source with a flow rate of 5 µL/min. The electric potential of the ESI capillary was set to 4.5

kV. All other parameters were optimized to get maximum abundance of the ions under study. ESI FTICR mass spectrometric experiments were performed on an Ionspec QFT-7 ESI FTICR mass spectrometer from Agilent Technologies (formerly Varian Inc., Walnut Creek, USA). The ESI FTICR mass spectrometer is equipped with a 7 T superconducting magnet and a Micromass Z-spray ESI source from Waters Co. (Saint-Quentin, France) which had a stainless steel capillary with an inner diameter of 0.65 mm. In regular experiments, the solvent flow rate of the integrated syringe pump was set to 4 μL/min and the spray voltage was 3.8 kV. All other parameters were optimized for maximum abundances of the desired ions. Both, the temperatures of the ESI source and the steel needle, were set to 40 °C. No nebulizer gas was used throughout the experiments.

Starting materials

The starting materials for the syntheses were used as purchased. Metal complexes **17** and **18** were prepared according to literature procedures.[1]

1.1 Ligand syntheses

General procedure for urea ligand synthesis[2]

500 mg of the aminopyridine or (aminomethyl)pyridine and 0.6 eq. of *N*,*N*′-carbonyldiimidazole were dissolved in 80 mL of dry toluene. The solution was heated to 80 °C for 3.5 h. A second portion of 0.1 eq. of *N*, *N*′-carbonyl-diimidazole was added to the hot solution. After 30 min. of heating, the mixture was cooled to r.t. and stirred for 15 h at r.t. The resulting precipitate was collected by filtration and washed with toluene and diethyl ether.

1,3-di(pyridin-3-yl)urea 9 ($C_{11}H_{10}N_4O$; 214.22 g/mol): Using the general synthetic procedure 1 546.93 mg (2.55 mmol, 85 % c.y.) of **9** were obtained as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 8.77 (s, 2 H, NH), 8.55 (d, 2 H, $^4J_{HH}$ = 2.4 Hz, $H_{o\text{-py}}$), 8.14 (dd, 2 H, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz, $H_{o\text{-py}}$), 7.93 (ddd, 2 H, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 1.5 Hz, $H_{p\text{-py}}$), 7.20 (dd, 2 H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 4.7 Hz, $H_{m\text{-py}}$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ = 151.7 (CO), 142.1 ($C_{o\text{-py}}$), 39.3 ($C_{o\text{-py}}$), 135.3 ($C_{p\text{-py}}$), 124.4 ($C_{m\text{-py}}$), 122.4 ($C_{m\text{-py}}$) ppm. ESI MS (HRMS): calculated: 215.0933 amu ($[M+H]^+$); found: 215.0931 amu ($[M+H]^+$). EI MS (EI^+, 70 eV): m/z (%) = 214.1 ($[M]^{+\cdot}$, 100), 121.1 ([M

– $PyNH]^{+\cdot}$, 25), 120.1 ($[M - PyNH_2]^{+\cdot}$, 14), 94.1 ($[PyNH_2]^{+\cdot}$, 78), 78.1 ($[Py - H]^{+\cdot}$, 14), 67.1 ($[C_4H_5N]^{+\cdot}$, 15). m.p. > 250 °C.

1,3-bis(2-methylpyridin-3-yl)urea 10 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 336.06 mg (1.39 mmol, 60 % c.y.) of **10** could be obtained as a white powder. ^{1}H NMR (250 MHz, DMSO-d_6, 303 K): δ = 8.59 (s, 2 H, NH), 8.18 (d, 2 H, $^3J_{HH}$ = 8.3 Hz, $H_{o\text{-py}}$), 8.13 (d, 2 H, $^3J_{HH}$ = 4.7 Hz, $H_{p\text{-py}}$), 7.23 (dd, 2 H, $^3J_{HH}$ = 8.3 Hz and $^3J_{HH}$ = 4.7 Hz, $H_{m\text{-py}}$), 2.50 (s, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, DMSO-d_6, 303 K): δ = 153.0 (CO), 148.2 ($C_{o\text{-py}}$), 142.8 ($C_{o\text{-py}}$), 133.6 ($C_{m\text{-py}}$), 127.9 ($C_{p\text{-py}}$) 121.4 ($C_{m\text{-py}}$), 21.2 (CH_3) ppm. ESI MS (HRMS): calculated: 243.1246 amu ($[M+H]^+$); found: 243.1239 amu ($[M+H]^+$). EI MS (EI^+, 80 eV): m/z (%) = 241.9 ($[M]^{+\cdot}$, 40), 134.7 ($[M + H - C_6H_8N_2]^{+\cdot}$, 16), 133.7 ($[M - C_6H_8N_2]^{+\cdot}$, 22), 108.0 ($[C_6H_8N_2]^{+\cdot}$, 100), 92.2 ($[C_6H_6N]^{+\cdot}$, 8), 80.2 ($[Py + H]^{+\cdot}$, 20). m.p. > 250 °C.

1,3-bis(4-methylpyridin-3-yl)urea 11 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 347.18 mg (1.43 mmol, 62 % c.y.) of **11** were obtained as a white powder. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ = 8.88 (s, 2 H, NH), 8.45 (s, 2 H, $H_{o\text{-py}}$), 8.15 (d, 2 H, $^3J_{HH}$ = 4.9 Hz, $H_{o\text{-py}}$), 7.23 (d, 2 H, $^3J_{HH}$ = 4.9 Hz, $H_{m\text{-py}}$), 2.28 (s, 6 H, CH_3) ppm. ^{13}C NMR (75.5 MHz, DMSO-d_6, 298 K): δ = 152.8 (CO), 144.0 ($C_{o\text{-py}}$), 143.5 ($C_{o\text{-py}}$), 137.4 ($C_{m\text{-py}}$), 134.4 ($C_{p\text{-py}}$) 125.1 ($C_{m\text{-py}}$), 7.3 (CH_3) ppm. ESI MS (HRMS): calculated: 243.1246 amu ($[M+H]^+$); found: 243.1247 amu ($[M+H]^+$). EI MS (EI^+, 70 eV): m/z (%) = 243.1 ($[M + H]^{+\cdot}$, 8), 242.1 ($[M]^{+\cdot}$, 48), 135.1 ($[M + H - C_6H_8N_2]^{+\cdot}$, 30), 134.1 ($[M - C_6H_8N_2]^{+\cdot}$, 26), 108.1 ($[C_6H_8N_2]^{+\cdot}$, 100), 92.1 ($[C_6H_6N]^{+\cdot}$, 7), 80.1 ($[Py + H]^{+\cdot}$, 12). m.p. > 250 °C.

1,3-bis(5-methylpyridin-3-yl)urea 12 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 419.84 mg (1.73 mmol, 75 % c.y.) of **12** were obtained as a white powder. ^{1}H NMR (250 MHz, DMSO-d_6, 303 K): δ = 8.91 (s, 2 H, NH), 8.41 (s, 2 H, $H_{o\text{-py}}$), 8.05 (s, 2 H, $H_{o\text{-py}}$), 7.79 (s, 2 H, $H_{p\text{-py}}$), 2.28 (s, 6 H, CH_3) ppm. ^{13}C NMR (63 MHz, DMSO-d_6, 303 K): δ = 152.6 (CO), 143.39 ($C_{o\text{-py}}$), 137.4 ($C_{o\text{-py}}$), 135.8 ($C_{m\text{-py}}$), 132.8 ($C_{p\text{-py}}$) 125.7 ($C_{m\text{-py}}$), 17.9 (CH_3) ppm. ESI MS (HRMS): calculated: 243.1245 amu ($[M+H]^+$); found: 243.1247 amu ($[M+H]^+$). EI MS (EI^+, 80 eV): m/z (%) = 241.9 ($[M]^{+\cdot}$, 16), 134.9 ($[M + H - C_6H_8N_2]^{+\cdot}$, 14), 133.8 ($[M - C_6H_8N_2]^{+\cdot}$, 61), 108.0 ($[C_6H_8N_2]^{+\cdot}$, 100), 92.2 ($[C_6H_6N]^{+\cdot}$, 5), 80.2 ($[Py + H]^{+\cdot}$, 27). m.p. > 250 °C.

1,3-bis(6-methylpyridin-3-yl)urea 13 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 520.43 mg (2.15 mmol, 93 % c.y.) of **13** were obtained as a white powder. ^{1}H NMR (500 MHz, DMSO-d_6, 303 K): δ = 8.61 (s, 2 H, NH), 8.47 (d, 2 H, $^4J_{HH}$ = 2.6 Hz, $H_{o\text{-py}}$), 7.78 (dd, 2 H, $^3J_{HH}$ = 8.4 Hz and $^4J_{HH}$ = 2.6 Hz, $H_{p\text{-py}}$), 7.15 (d, 2 H, $^3J_{HH}$ = 8.4 Hz, $H_{m\text{-py}}$), 2.41 (s, 6 H, CH_3) ppm. ^{13}C NMR (126 MHz, DMSO-d_6, 303 K): δ = 152.5 (CO), 150.9 ($C_{o\text{-py}}$), 139.4 ($C_{o\text{-py}}$), 133.3 ($C_{m\text{-py}}$), 126.0 ($C_{p\text{-py}}$) 122.2 ($C_{m\text{-py}}$), 22.7 (CH_3) ppm. ESI MS (HRMS): calculated: 243.1246 amu ($[M+H]^+$); found: 243.1242 amu ($[M+H]^+$). EI MS (EI^+, 80 eV): m/z (%) = 242.1($[M]^{+\cdot}$, 17), 134.9 ($[M + H - C_6H_8N_2]^{+\cdot}$, 13), 133.8 ($[M - C_6H_8N_2]^{+\cdot}$, 76), 108.0 ($[C_6H_8N_2]^{+\cdot}$, 100), 92.2 ($[C_6H_6N]^{+\cdot}$, 4), 80.2 ($[Py + H]^{+\cdot}$, 38). m.p. > 250 °C.

1,3-bis((pyridin-3-yl)methyl)urea 14 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 503.64 mg (2.08 mmol, 90 % c.y.) of **14** were obtained as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ = 8.47 (s, 2 H, $H_{o\text{-py}}$), 8.42 (d, 2 H, $^3J_{HH}$ = 4.8, $H_{o\text{-py}}$), 7.63 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, $H_{p\text{-py}}$), 7.32 (dd, 2 H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.8 Hz, $H_{m\text{-py}}$), 6.63 (t, 2 H, $^3J_{HH}$ = 6.0 Hz, NH), 4.24 (d, 4 H, $^3J_{HH}$ = 6.0 Hz, CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ = 158.1 (CO), 148.6 ($C_{o\text{-py}}$), 147.9 ($C_{o\text{-py}}$), 136.3 ($C_{m\text{-py}}$), 134.9 ($C_{p\text{-py}}$), 123.4 ($C_{m\text{-py}}$), 40.7 (CH_2) ppm. ESI MS (HRMS): calculated: 243.1246 amu ($[M+H]^+$); found: 243.1241 amu ($[M+H]^+$). EI MS (EI^+, 70 eV): m/z (%) = 243.2 ($[M + H]^{+\cdot}$, 16), 242.1 ($[M]^{+\cdot}$, 100), 150.1 ($[M - C_6H_6N]^{+\cdot}$, 10), 135.0 ($[M + H - C_6H_8N_2]^{+\cdot}$, 13), 134.0 ($[M - C_6H_8N_2]^{+\cdot}$, 7), 107.0 ($[C_6H_7N_2]^{+\cdot}$, 59), 93.0 ($[C_6H_7N]^{+\cdot}$, 24), 92.0 ($[C_6H_6N]^{+\cdot}$, 27), 80.0 ($[Py + H]^{+\cdot}$, 16), 79.0 ($[Py]^{+\cdot}$, 9), 65.0 ($[C_5H_5]^{+\cdot}$, 11). m.p. > 250 °C.

1,3-bis((pyridin-4-yl)methyl)urea 15 ($C_{13}H_{14}N_4O$; 242.28 g/mol): Using the general synthetic procedure 1 307.52 mg (1.27 mmol, 55 % c.y.) **15** were obtained as a white powder. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ = 8.49 (d, 4 H, $^3J_{HH}$ = 5.7 Hz, $H_{o\text{-py}}$), 7.24 (d, 4 H, $^3J_{HH}$ = 5.7 Hz, $H_{m\text{-py}}$), 6.73 (t, 2 H, $^3J_{HH}$ = 6.1 Hz, NH), 4.26 (d, 4 H, $^3J_{HH}$ = 6.1 Hz, CH_2) ppm. ^{13}C NMR (76 MHz, DMSO-d_6, 298 K): δ = 158.1 (CO), 150.0 ($C_{p\text{-py}}$), 149.4 ($C_{o\text{-py}}$), 121.9 ($C_{m\text{-py}}$), 42.1 (CH_2) ppm. ESI MS (HRMS): calculated: 243.1246 amu ($[M+H]^+$); found: 243.1248 amu ($[M+H]^+$). EI MS (EI^+, 70 eV): m/z (%) = 243.2 ($[M + H]^{+\cdot}$, 16), 242.1 ($[M]^{+\cdot}$, 100), 150.1 ($[M - C_6H_6N]^{+\cdot}$, 3), 135.0 ($[M + H - C_6H_8N_2]^{+\cdot}$, 12), 134.0 ($[M - C_6H_8N_2]^{+\cdot}$, 12), 107.0 ($[C_6H_7N_2]^{+\cdot}$, 35), 93.0 ($[C_6H_7N]^{+\cdot}$, 13), 92.0 ($[C_6H_6N]^{+\cdot}$, 15), 80.0 ($[Py + H]^{+\cdot}$, 15), 79.0 ($[Py]^{+\cdot}$, 12), 65.0 ($[C_5H_5]^{+\cdot}$, 6). m.p. > 250 °C.

1.2 Self-assembly of metallo-supramolecular complexes

General procedure for the synthesis of water-soluble complexes with (en)Pd(NO_3)$_2$:

2 mg of the ligands **9** - **15**, respectively, were mixed with an equimolar amount of (en)Pd(NO_3)$_2$ **16**. These mixtures were dissolved in H_2O, D_2O, DMSO or DMSO-d_6, respectively, and stirred for one hour at r.t. The solutions were then used without workup to examine the systems under study. No discrete complexes were observed with ligands **10** and **13**.

Numbers given in parenthesis for the signals of the ESI mass spectra refer to [number of metal centers including the cis-coordinated chelating ligand : number of dipyrdiylurea ligands : number of counterions].

[(Pd(en))$_2$(9)$_2$](NO$_3$)$_4$ 19a ($C_{26}H_{36}N_{16}O_{14}Pd_2$; 1008.07 g/mol): ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ = 9.82 (s, 4 H, $H_{o\text{-pyridine}}$), 9.61 (s, 4 H, NH_{urea}), 8.61 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.8 Hz, 4 H, $H_{o\text{-pyridine}}$), 7.58 (m, 8 H, $H_{m\text{-pyridine}}$ and $H_{p\text{-pyridine}}$), 5.59 (s, 8 H, $(NH_2)_{en}$), 2.69 (s, 8 H, $(CH_2)_{en}$) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 948 ([2:2:3]$^+$), 443 ([2:2:2]$^{2+}$).

[(Pd(en))$_2$(11)$_2$](NO$_3$)$_4$ 20 ($C_{30}H_{44}N_{16}O_{14}Pd_2$; 1064.13 g/mol): ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ = 9.58 (s, $H_{o\text{-pyridine}}$), 8.92 (s, NH_{urea}), 8.48 (d, $^3J_{HH}$ = 5.8 Hz, $H_{o\text{-pyridine}}$), 7. (d, $^3J_{HH}$ = 5.8 Hz, $H_{m\text{-pyridine}}$), 5.57 (s, $(NH_2)_{en}$); 2.89 (s, $(CH_2)_{en}$), 2.33 (s, CH_3) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 1004 ([2:2:3]$^+$ and [4:4:6]$^{2+}$), 972 ([(4:4:6) – HNO_3]$^{2+}$), 472 ([2:2:2]$^{2+}$).

[(Pd(en))$_2$(12)$_2$](NO$_3$)$_4$ 21a ($C_{30}H_{44}N_{16}O_{14}Pd_2$; 1064.13 g/mol): ^{1}H NMR (DMSO-d_6, 250 MHz, 303 K): δ = 9.65 (d, $^4J_{HH}$ = 2.0 Hz, $H_{o\text{-pyridine}}$), 9.53 (s, NH_{urea}), 8.49 (d, $^4J_{HH}$ = 1.0 Hz, $H_{o\text{-pyridine}}$), 7.36 (m, $H_{p\text{-pyridine}}$), 5.55 (br, $(NH_2)_{en}$), 2.68 (br, $(CH_2)_{en}$), 2.31 (s, CH_3) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 1004 ([2:2:3]$^+$ and [4:4:6]$^{2+}$), 972 ([(4:4:6) – HNO_3]$^{2+}$), 941 ([(4:4:6) – 2 HNO_3]$^{2+}$), 648 ([4:4:5]$^{3+}$), 472 ([1:1:1]$^+$ and [2:2:2]$^{2+}$).

[(Pd(en))$_2$(14)$_2$](NO$_3$)$_4$ 22a ($C_{30}H_{44}N_{16}O_{14}Pd_2$; 1064.13 g/mol): ^{1}H NMR (DMSO-d_7, 500 MHz, 298 K): δ = 8.65 (d, $^3J_{HH}$ = 5.5 Hz, $H_{o\text{-pyridine}}$), 8.56 (s, $H_{o\text{-pyridine}}$), 7.86 (d, $^3J_{HH}$ = 7.8 Hz, $H_{p\text{-pyridine}}$), 7.86 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 5.5 Hz, $H_{m\text{-pyridine}}$), (t, $^3J_{HH}$ = 5.9 Hz, NH_{urea}), 5.58

(s, $(NH_2)_{en}$), 4.19 (d, $^3J_{HH}$ = 5.9 Hz, $(CH_2)_{urea}$), 2.67 (s, $(CH_2)_{en}$) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 1004 ($[2:2:3]^+$), 761 ($[2:1:3]^+$), 472 ($[1:1:1]^+$ and $[2:2:2]^{2+}$).

$[(Pd(en))_2(15)_2](NO_3)_4$ 23a ($C_{30}H_{44}N_{16}O_{14}Pd_2$; 1064.13 g/mol): ^{1}H NMR (DMSO-d_7, 500 MHz, 298 K): δ = 8.77 (d, $^3J_{HH}$ = 6.0 Hz, $H_{o\text{-pyridine}}$), 7.42 (d, $^3J_{HH}$ = 6.0 Hz, $H_{m\text{-pyridine}}$), 6.90 (t, $^3J_{HH}$ = 5.5 Hz, NH_{urea}), 5.56 (s, $(NH_2)_{en}$), 4.29 (d, $^3J_{HH}$ = 5.5 Hz, $(CH_2)_{urea}$), 2.67 (s, $(CH_2)_{en}$) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 1004 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 882 ($[4:3:6]^{2+}$), 761 ($[2:1:3]^+$), 472 ($[1:1:1]^+$ and $[2:2:2]^{2+}$).

General procedure for the synthesis of complexes containing (dppp)M(OTf)$_2$ (M = Pd^{2+} 17 or M = Pt^{2+} 18):

2 mg of the ligands **9 - 15** were mixed with an equimolar amount of (dppp)Pd(OTf)$_2$ (**17**) or (dppp)Pt(OTf)$_2$ (**18**), respectively. These mixtures were dissolved in DMSO, DMSO-d_6, DMF or DMF-d_7, respectively, and stirred for one hour (mixtures containing **17**) or one day (mixtures containing **18**) at r.t. The solutions were then used without workup to examine the systems under study. No discrete complexes were observed using ligands **10** and **13**.

$[(Pd(dppp))_2(9)_2](OTf)_4$ 24a ($C_{80}H_{72}F_{12}N_8O_{14}P_4Pd_2S_4$; 2062.45 g/mol; M_2L_2) and **$[(Pd(dppp))_3(9)_3](OTf)_6$ 24b** ($C_{120}H_{108}F_{18}N_{12}O_{21}P_6Pd_3S_6$; 3093.67 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 273 K): δ = 9.81 (s, $H_{o\text{-pyridine}}$, M_2L_2); 9.43 (s, $H_{o\text{-pyridine}}$, M_3L_3); 9.17 (s, NH_{urea}, M_2L_2); 9.11 (d, $^3J_{HH}$ = 4.7 Hz, $H_{o\text{-pyridine}}$, M_2L_2), 9.07 (d, $^3J_{HH}$ = 4.6 Hz, $H_{o\text{-pyridine}}$, M_3L_3), 8.68 (s, NH_{urea}, M_3L_3), 8.53 (m, $H_{m\text{-pyridine}}$, M_2L_2), 8.22 (m, $H_{m\text{-pyridine}}$ (M_3L_3) and $H_{p\text{-pyridine}}$ (M_2L_2)), 7.15-8.26 (m, $H_{p\text{-pyridine}}$ (M_3L_3) and $H_{dppp\text{-phenyl}}$, M_2L_2 and M_3L_3), 3.28 (m, $(PC\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3); 1.72 (m, $(PCH_2C\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 303 K): δ = 9.8 (s, P_{dppp}, M_3L_3), 9.3 (s, P_{dppp}, M_2L_2) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 1913 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1226 ($[4:4:5]^{3+}$), 1095 ($[1:2:1]^+$), 882 ($[1:1:1]^+$ and $[2:2:2]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 2944 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2730 ($[3:2:5]^+$), 1913 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1504 ($[3:4:4]^{2+}$), 1398 ($[3:3:4]^{2+}$), 1095 ($[1:2:1]^+$), 882 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$).

$[(Pd(dppp))_2(11)_2](OTf)_4$ 25a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pd_2S_4$; 2116.62 g/mol; M_2L_2) and **$[(Pd(dppp))_3(11)_3](OTf)_6$ 25b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pd_3S_6$; 3141.55 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 298 K): δ = 9.70 (s, $H_{o\text{-pyridine}}$, M_2L_2), 9.17 (s, $H_{o\text{-pyridine}}$, M_3L_3), 8.96 (s,

NH_{urea}, M_2L_2), 8.81 (m, $H_{o\text{-pyridine}}$ (M_2L_2) and NH (M_3L_3)), 8.63 (s $H_{o\text{-pyridine}}$, M_3L_3), 8.41(m, $H_{dppp\text{-phenyl}}$, M_2L_2), 7.93 (m, $H_{dppp\text{-phenyl}}$, M_3L_3), 7.84-7.27 (m, $H_{p\text{-pyridine}}$ (M_3L_3) and $H_{dppp\text{-phenyl}}$, M_2L_2 and M_3L_3), 7.03 (s, $H_{p\text{-pyridine}}$, M_2L_2); 3.32 (m, $(PC\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3); 2.29 (m, $(PCH_2C\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3); 2.17 (br., CH_3, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298 K): δ = 10.1 (s, P_{dppp}, M_3L_3), 9.7 (s, P_{dppp}, M_2L_2) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 1969 ($[2:2:3]^+$), 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 3028 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2211 ($[2:3:3]^+$), 1969 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1559 ($[3:4:4]^{2+}$), 1439 ($[3:3:4]^{2+}$), 1151 ($[1:2:1]^+$), 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$).

$[(Pd(dppp))_2(12)_2](OTf)_4$ 26a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pd_2S_4$; 2116.62 g/mol; M_2L_2) and **$[(Pd(dppp))_3(12)_3](OTf)_6$ 26b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pd_3S_6$; 3141.55 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 298 K): δ = 9.70 (s, $H_{o\text{-pyridine}}$, M_2L_2), 9.17 (s, $H_{o\text{-pyridine}}$, M_3L_3), 8.97 (s, $H_{o\text{-pyridine}}$, M_2L_2), 8.81 (m, NH_{urea} (M_2L_2) and $H_{o\text{-pyridine}}$ (M_3L_3)), 8.63 (s, $H_{p\text{-pyridine}}$, M_3L_3), 8.41 (br., NH_{urea}, M_3L_3), 8.00-7.30 (m, $H_{dppp\text{-phenyl}}$), 7.03 (s, $H_{p\text{-pyridine}}$, M_2L_2), 3.40-3.20 (m, $(PC\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3); 2.42-1.92 (m, CH_3 and $(PCH_2C\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298 K): δ = 6.3 (s, P_{dppp}, M_3L_3), 6.0 (s, P_{dppp}, M_2L_2) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$), 557 ($[2:2:1]^{3+}$), 501 ($[1:2:0]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 3028 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2211 ($[2:3:3]^+$), 1969 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1559 ($[3:4:4]^{2+}$), 1439 ($[3:3:4]^{2+}$), 1151 ($[1:2:1]^+$), 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$).

$[(Pd(dppp))_2(14)_2](OTf)_4$ 27a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pd_2S_4$; 2116.62 g/mol; M_2L_2) and **$[(Pd(dppp))_3(14)_3](OTf)_6$ 27b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pd_3S_6$; 3141.55 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 273K): δ = 9.09 (m, $H_{o\text{-pyridine}}$), 8.53 (s, $H_{o\text{-pyridine}}$), 8.33 (m, $H_{dppp\text{-phenyl}}$), 8.00-7.15 (m, $H_{dppp\text{-phenyl}}$ and NH_{urea}), 6.78 (m, $H_{m\text{-pyridine}}$), 4.12 (m, NCH_2), 3.76 (m, NCH_2), 3.36 (m, $(PC\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3), 1.79 (m, $(PCH_2C\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 233 K): δ = 10.7 (s, P_{dppp}, M_3L_3), 10.5 (s, P_{dppp}, M_2L_2) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$), 557 ($[2:2:1]^{3+}$), 501 ($[1:2:0]^{2+}$), 380 ($[1:1:0]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 3028 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2211 ($[2:3:3]^+$), 1969 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1439 ($[3:3:4]^{2+}$), 1151 ($[1:2:1]^+$), 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$).

$[(Pd(dppp))_2(15)_2](OTf)_4$ 28a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pd_2S_4$; 2116.62 g/mol; M_2L_2): ^{1}H NMR (DMF-d_7, 500 MHz, 303 K): δ = 8.81 (d, $^3J_{HH}$ = 4.9 Hz, $H_{o\text{-pyridine}}$), 7.77 (m, $H_{dppp\text{-phenyl}}$), 7.60

(m, $H_{dppp\text{-}phenyl}$), 7.50 (m, $H_{dppp\text{-}phenyl}$), 7.07 (d, $^3J_{HH}$ = 4.9 Hz, $H_{m\text{-}pyridine}$), 6.88 (m, NH_{urea}), 4.18 (d, $^3J_{HH}$ = 5.50 Hz, CH_2), 3.37 (m, $(PC\underline{H_2})_{dppp}$), 1.72 (m, (m, $PCH_2C\underline{H_2})_{dppp}$) ppm. ^{31}P NMR (DMF-$d_7$; 202 MHz; 303 K): δ = 9.2 (s, P_{dppp}) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$), 557 ($[2:2:1]^{3+}$), 501 ($[1:2:0]^{2+}$), 380 ($[1:1:0]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 1969 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1151 ($[1:2:1]^+$), 910 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 667 ($[1:0:1]^+$).

$[(Pt(dppp))_2(9)_2](OTf)_4$ 29a ($C_{80}H_{72}F_{12}N_8O_{14}P_4Pt_2S_4$; 2239.76 g/mol; M_2L_2) and **$[(Pt(dppp))_3(9)_3](OTf)_6$ 29b** ($C_{120}H_{108}F_{18}N_{12}O_{21}P_6Pt_3S_6$; 3359.65 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 298 K): δ = 9.71 (m, NH_{urea}, M_2L_2), 9.38 (s, $H_{o\text{-}pyridine}$, M_3L_3), 9.18 (s, $H_{o\text{-}pyridine}$, M_2L_2), 9.13 (d, $^3J_{HH}$ = 4.89 Hz, $H_{o\text{-}pyridine}$, M_2L_2), 9.07 (d, $^3J_{HH}$ = 4.89 Hz, $H_{o\text{-}pyridine}$ M_3L_3), 8.72 (m, NH_{urea}, M_3L_3), 8.54 (m, $H_{dppp\text{-}phenyl}$, M_2L_2), 8.20 (m, $H_{dppp\text{-}phenyl}$, M_3L_3), 7.76-7.26 (m, $H_{dppp\text{-}phenyl}$ and $H_{m\text{-}pyridine}$ and $H_{p\text{-}pyridine}$, M_2L_2 and M_3L_3), 3.71 (m, $(PC\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3), 3.37 (m, $PC\underline{H_2}$, M_2L_2 and M_3L_3), 2.95 (m, $(PCH_2C\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298K): δ = -15.81 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3000 Hz, M_3L_3), -16.13 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3000 Hz, M_3L_3) ppm. ESI MS (ESI^+, DMSO/acetonitrile): *m/z* = 2090 ($[2:2:3]^+$), 1344 ($[4:4:5]^{3+}$), 970 ($[2:2:2]^{2+}$). ESI MS (ESI^+, DMF): *m/z* = 3210 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2090 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1637 ($[3:4:4]^{2+}$), 1530 ($[3:3:4]^{2+}$), 1344 ($[4:4:5]^{3+}$), 1184 ($[1:2:1]^+$), 970 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 756 ($[1:0:1]^+$).

$[(Pt(dppp))_2(11)_2](OTf)_4$ 30a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pt_2S_4$; 2295.87 g/mol; M_2L_2) and **$[(Pt(dppp))_3(11)_3](OTf)_6$ 30b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pt_3S_6$; 3407.52 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 298 K): δ = 9.58 (s, $H_{o\text{-}pyridine}$, M_2L_2), 9.07 (d, $^3J_{HH}$ = 5.9 Hz, $H_{o\text{-}pyridine}$, M_3L_3), 9.02 (d, $^3J_{HH}$ = 4.7 Hz, $H_{o\text{-}pyridine}$, M_2L_2), 8.56 (s, NH_{urea}, M_3L_3), 8.49 (m, $H_{dppp\text{-}phenyl}$, M_2L_2), 8.41 (m, NH_{urea}, M_2L_2), 8.24 (m, $H_{dppp\text{-}phenyl}$, M_3L_3), 8.22 (m, $H_{o\text{-}pyridine}$, M_3L_3), 7.76-7.12 (m, $H_{dppp\text{-}phenyl}$ and $H_{m\text{-}pyridine}$, M_2L_2 and M_3L_3), 3.27 (m, $(PC\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3), 2.62 (m, $(PCH_2C\underline{H_2})_{dppp}$, M_2L_2 and M_3L_3), 2.29 (s, CH_3, M_3L_3), 2.08 (s, CH_3, M_2L_2) ppm. ^{31}P NMR (DMF-d_7, 121 MHz, 298K): δ = -12.6 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3021 Hz, M_2L_2), -12.6 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3021 Hz, M_2L_2) ppm. ESI MS (ESI^+, DMSO/acetone): *m/z* = 2146 ($[2:2:3]^+$), 1381 ($[4:4:5]^{3+}$), 998 ($[2:2:2]^{2+}$), 616 ($[2:2:1]^{3+}$). ESI MS (ESI^+, DMF): *m/z* = 3291 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2144 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1692 ($[3:4:4]^{2+}$), 1570 ($[3:3:4]^{2+}$), 1238 ($[1:2:1]^+$), 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 756 ($[1:0:1]^+$), 616 ($[2:2:1]^{3+}$).

[(Pt(dppp))$_2$(12)$_2$](OTf)$_4$ 31a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pt_2S_4$; 2295.87 g/mol; M_2L_2) and **[(Pt(dppp))$_3$(12)$_3$](OTf)$_6$ 31b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pt_3S_6$; 3407.52 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 298K): δ = 9.56 (s, $H_{o\text{-pyridine}}$, M_2L_2), 9.27 (s, $H_{o\text{-pyridine}}$, M_3L_3), 9.05 (s, $H_{o\text{-pyridine}}$, M_2L_2), 8.90 (s, NH_{urea}, M_2L_2), 8.80 (s, NH_{urea}, M_3L_3), 8.66 (s, $H_{o\text{-pyridine}}$, M_3L_3), 8.50 (m, $H_{dppp\text{-phenyl}}$, M_2L_2), 7.94 (m, $H_{dppp\text{-phenyl}}$, M_3L_3), 7.77-7.33 (m, $H_{dppp\text{-phenyl}}$ (M_2L_2 and M_3L_3) and $H_{p\text{-pyridine}}$, M_3L_3), 7.07 (s, $H_{p\text{-pyridine}}$, M_2L_2), 3.71 (m, $(PC\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3), 2.16 (br., CH_3), 2.08 (m, $(PCH_2C\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298 K): δ = -11.8 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3020 Hz, M_3L_3), -12.0 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3020 Hz, M_2L_2) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 1381 ($[4:4:5]^{3+}$), 1120 ($[2:3:2]^{2+}$), 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 616 ($[2:2:1]^{3+}$), 566 ($[(2:2:1) - HOTf]^{3+}$), 546 ($[1:2:0]^{2+}$). ESI MS (ESI$^+$, DMF): *m/z* = 3291 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2144 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1692 ($[3:4:4]^{2+}$), 1570 ($[3:3:4]^{2+}$), 1238 ($[1:2:1]^+$), 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 756 ($[1:0:1]^+$) 616 ($[2:2:1]^{3+}$).

[(Pt(dppp))$_2$(14)$_2$](OTf)$_4$ 32a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pt_2S_4$; 2295.87 g/mol; M_2L_2) and **[(Pt(dppp))$_3$(14)$_3$](OTf)$_6$ 32b** ($C_{126}H_{84}F_{18}N_{12}O_{21}P_6Pt_3S_6$; 3407.52 g/mol; M_3L_3): ^{1}H NMR (DMF-d_7, 500 MHz, 273K): δ = 9.09 (s, $H_{o\text{-pyridine}}$, M_2L_2), 8.84 (s, $H_{o\text{-pyridine}}$, M_3L_3), 8.51 (s, $H_{o\text{-pyridine}}$ M_2L_2), 8.00-7.15 (m, NH_{urea} (M_3L_3), $H_{dppp\text{-phenyl}}$, $H_{o\text{-pyridine}}$, and $H_{o\text{-pyridine}}$, M_2L_2 and M_3L_3), 6.67 (t, NH_{urea}, M_2L_2), 4.13 and 3.77 (m, NCH_2, M_2L_2 and M_3L_3), 3.41 (m, $(PC\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3), 1.77 (m, $(PCH_2C\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298K): -14.6 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3025 Hz, M_3L_3), -15.1 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3025 Hz, M_3L_3) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 696 ($[2:3:1]^{3+}$), 616 ($[2:2:1]^{3+}$), 546 ($[1:2:0]^{2+}$). ESI MS (ESI$^+$, DMF): *m/z* = 3291 ($[3:3:5]^+$ and $[6:6:10]^{2+}$), 2144 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1238 ($[1:2:1]^+$), 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 756 ($[1:0:1]^+$).

[(Pt(dppp))$_2$(15)$_2$](OTf)$_4$ 33a ($C_{84}H_{80}F_{12}N_8O_{14}P_4Pt_2S_4$; 2295.87 g/mol; M_2L_2): ^{1}H NMR (DMF-d_7, 500 MHz, 303 K): δ = 8.81 (d, $^3J_{HH}$ = 4.9 Hz, $H_{o\text{-pyridine}}$), 7.80 (m, $H_{dppp\text{-phenyl}}$), 7.61 (m, $H_{dppp\text{-phenyl}}$), 7.51 (m, $H_{dppp\text{-phenyl}}$), 7.09 (d, $^3J_{HH}$ = 4.9 Hz, $H_{m\text{-pyridine}}$), 6.95 (t, $^3J_{HH}$ = 5.7 Hz, NH_{urea}), 4.19 (d, $^3J_{HH}$ = 5.7 Hz, CH_2), 3.46 (m, $(PC\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3), 1.72 (m, $^3J_{P\text{-}H}$ = 24.20 Hz, $PCH_2C\underline{H}_2)_{dppp}$, M_2L_2 and M_3L_3) ppm. ^{31}P NMR (DMF-d_7, 202 MHz, 298K): -15.5 (s, P_{dppp}, $^1J_{Pt\text{-}P}$ = 3036 Hz) ppm. ESI MS (ESI$^+$, DMSO/acetonitrile): *m/z* = 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 696 ($[2:3:1]^{3+}$), 616 ($[2:2:1]^{3+}$), 546 ($[1:2:0]^{2+}$). ESI MS (ESI$^+$, DMF): *m/z* = 2144 ($[2:2:3]^+$ and $[4:4:6]^{2+}$), 1238 ($[1:2:1]^+$), 998 ($[1:1:1]^+$ and $[2:2:2]^{2+}$), 756 ($[1:0:1]^+$) 616 ($[2:2:1]^{3+}$).

1.3 Crystal structure data

Data were collected on a Bruker-Nonius Kappa Apex II diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 123 K for **12** and **24a**, and 173 K for **10**, **11**, **13**, **23a**, **25a,** and **28a**. *COLLECT*[3] software was used for the data collection and *DENZOSMN*[4] for the data processing. The intensities were corrected for absorption using the multi-scan absorption correction method (*SADABS2008*[5]). The crystal structures were solved by direct methods by *SIR97*[6] (**12**, **13**, **23a**, **24a**, **25a**, and **28a**) and *SHELXS97*[7] (**10** and **11**), and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations[7] based on F^2 using the programs integrated in the *WinGX*[8] program package. The hydrogen atoms of the water molecules in the crystal of **11** have been found in a difference Fourier map and their coordinates and thermal parameters are refined freely. All other hydrogen atoms in **11** and in other structures were included in calculated positions as riding atoms, with *SHELXL97*[7] defaults. In the absence of significant anomalous scattering, the Flack parameter for compound **12** was inconclusive, and the Friedel equivalents were therefore merged prior to the final refinement. Restraints on anisotropic displacement parameters and on geometrical parameters on the heavily disordered triflate anions in **24a**, **25a** and **28a** were applied, as well as one constraint on anisotropic displacement parameters for atoms of one triflate in **25a**. The sulphur and carbon atoms of this triflate in **25a** were refined with fixed occupancy ratio of 0.60/0.40, while some of them in **28a** are refined with fixed occupancy ratio of 0.50/0.50 and 0.60/0.40, respectively. Restraints on anisotropic displacement parameters were also applied during the refinement of some atoms of *N*,*N*-dimethylformamide molecules, and some geometrical restraints were used in the refinement of one *N*,*N*-dimethylformamide and one diethylether molecule in **25a** and on the heavily disordered nitrate anion in **23a** were applied. The nitrogen N4N and oxygen O12 atoms in this nitrate is refined with fixed occupancy ratio of 0.60/0.40. The positions of water hydrogen atoms are determined by best hydrogen bond that can be created and coordinates are kept fixed during refinement for **23a**. In **25a** and **28a** the positions of water hydrogen atoms are determined by best hydrogen bond that can be created and are refined with O-H distance restraint of 0.84 Å for **25a** and 1.00 Å for **28a**. The positions of hydrogen atoms in two water molecules in **28a** could not be calculated nor determined and were thus not included in the model. The structures of compounds **24a, 25a** and **28a** contain solvent accessible voids with small amount of solvent molecule(s) used for re-crystallization. As they could not be modeled satisfactorily, the data were treated with the *SQUEEZE* routine in *PLATON*.[9] Unusually high

residual electron density was observed for **24a** (4.215 eÅ^{-3}, 1.14 Å from S18), but could not be modeled, in **23a** the residual electron density of 4.419 eÅ^{-3} was found 1.25 Å from O12' and is a consequence of a disordered nitrate anion present in this structure. Details of crystal data, data collection and refinement parameters are given in Table S1. *PLATON*[9] and *Mercury*[10] programs were used for structure analysis and the preparation of drawings. CCDC 864202 - 864209 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-ray crystallographic data for ligands **10**, **11**, **12**, **13** and complexes **23a**, **24a**, **25a**, and **28a**.

	10	**11**	**12**	**13**	**23a**	**24a**	**25a**	**28a**
Formula	$C_{13}H_{14}N_4O$	$C_{16}H_{20}N_6O_2$	$C_{13}H_{14}N_4O$	$C_{13}H_{14}N_4O$	$C_{30}H_{52}N_{16}O_{18}Pd_2$	$C_{80}H_{72}F_{12}N_8O_{14}P_4Pd_2S_4$	$C_{95}H_{108}F_{12}N_{11}O_{18.50}P_4Pd_2S_4$	$C_{85.50}H_{85}Cl_3F_{12}N_8O_{16}P_4Pd_2S_4$
Formula weight	242.28	328.38	242.28	242.28	1137.68	2062.38	2392.84	2275.85
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,c\,2_1\,b$	$P\,2_1/c$	$P\,2_1/c$	$P\,\bar{1}$	$P\,\bar{1}$	$P\,2_1/n$
a / Å	12.0896(2)	8.4693(4)	8.3851(7)	7.3327(3)	13.577(4)	15.7089(3)	16.3896(2)	23.0442(5)
b / Å	4.5931(1)	13.3280(6)	11.5345(6)	8.3914(3)	15.891(5)	16.7004(3)	18.3213(2)	19.7734(4)
c / Å	21.5276(5)	15.0145(8)	12.4214(10)	19.4356(9)	20.526(6)	34.7739(6)	21.5285(3)	25.6540(5)
α / °	90	90	90	90	90	85.194(1)	87.680(1)	90
β / °	96.920(1)	103.537(4)	90	91.255(2)	91.995(7)	82.836(1)	78.927(1)	106.841(1)
γ / °	90	90	90	90	90	88.750(1)	71.110(1)	90
V / Å^3	1186.69(4)	1647.7(1)	1201.4(1)	1195.6(1)	4426 (2)	9019.1(3)	6000.9(1)	11188.2(4)
Z	4	4	4	4	4	4	2	4
$D_{calc.}$ / g cm^{-3}	1.356	1.324	1.34	1.346	1.695	1.519	1.324	1.351
μ /mm^{-1}	0.091	0.092	0.090	0.090	0.903	0.651	0.503	0.602
θ range / °	3.40 - 25.00	2.47 - 24.99	2.93 - 25.00	3.21 - 24.98	1.62 - 30.05	0.59 - 25.00	2.67 - 25.00	1.94 - 25.00
Coll. Refl. no.	3886	21314	7448	15175	65917	75806	71355	77842
Indpt. refl. No./$R_{Int.}$	2093/0.0244	2890/0.1406	1112/0.0869	2094/0.0725	12812/0.0388	31694/0.0543	21076/0.050	19696/0.058
Refl. No. $I \geq 2\sigma(I)$	1769	1808	950	1568	10995	19752	16013	13377
Data/Restr/Param	2093/0/165	2890/2/227	1112/1/165	2094/0/165	12812/555/0	31694/269/2233	21076/107/1317	19696/1256/124
S	1.100	1.017	1.068	1.056	1.169	1.175	1.115	1.097
R [$I \geq 2\sigma(I)$] R [all data]	0.0357/0.0452	0.0566/0.1087	0.0444/0.0568	0.0516/0.0763	0.0631/0.0725	0.1103/0.1532	0.0780/0.1000	0.1129/0.1470
wR [$I \geq 2\sigma(I)$] wR [all data]	0.0871/0.0930	0.1085/0.1278	0.0880/0.0929	0.1163/0.1288	0.1356/0.1385	0.3137/0.3438	0.2499/0.2707	0.3102/0.3338
Res. el. dens./e Å^{-3}	0.152/-0.198	0.262/-0.205	0.176/-0.180	0.206/-0.218	1.705/-1.745	4.215/-2.411	2.761/-2.813	3.039/-2.629

2. Additional data on the di-pyridylurea ligands

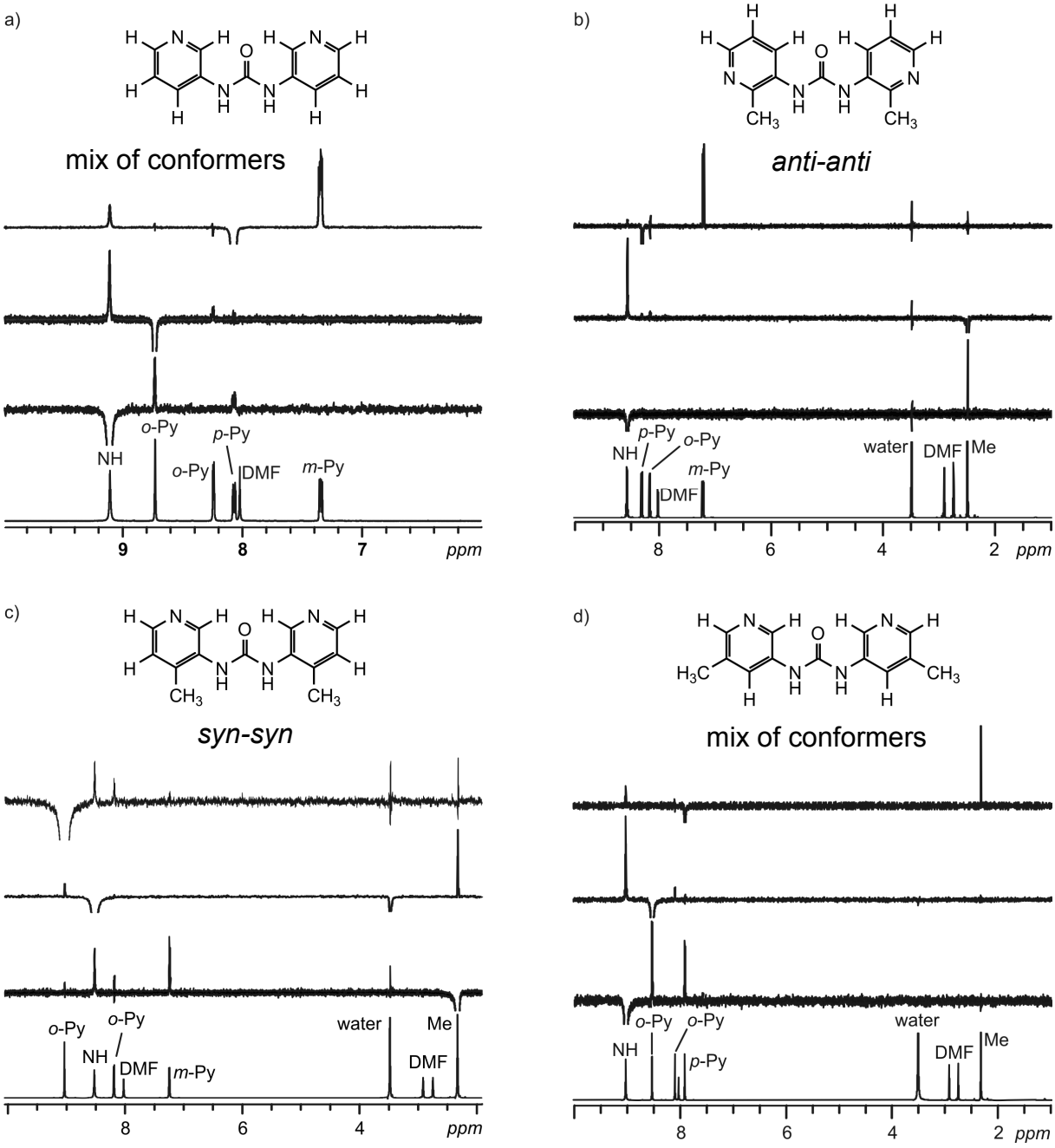

Figure S1. The 1D ^{1}H NOESY NMR spectra of ligands a) **9**, b) **10**, c) **11**, and d) **12**. All spectra were recorded in DMF-d_7 at 298 K. Due to its low solubility, no NOESY NMR spectra of ligand **13** could be recorded.

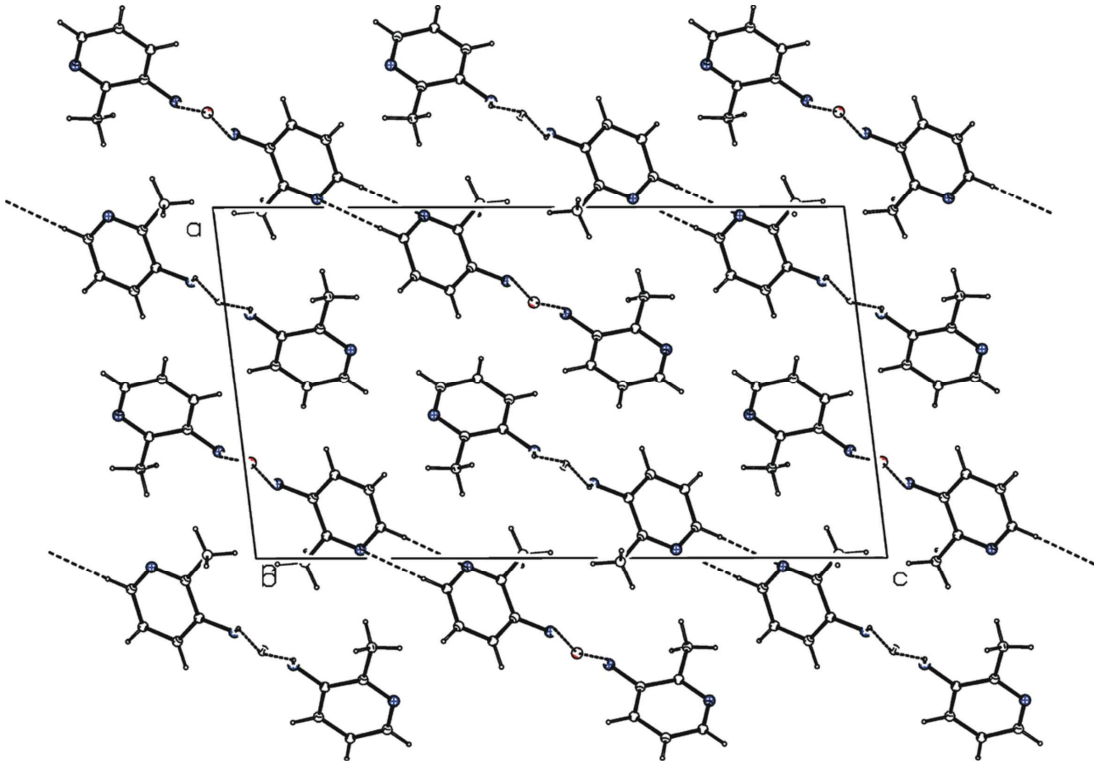

Figure S2. A crystal packing diagram of **10**, viewed along the crystallographic *b* axis, showing hydrogen-bonded sheets. Hydrogen bonds are indicated by dashed lines.

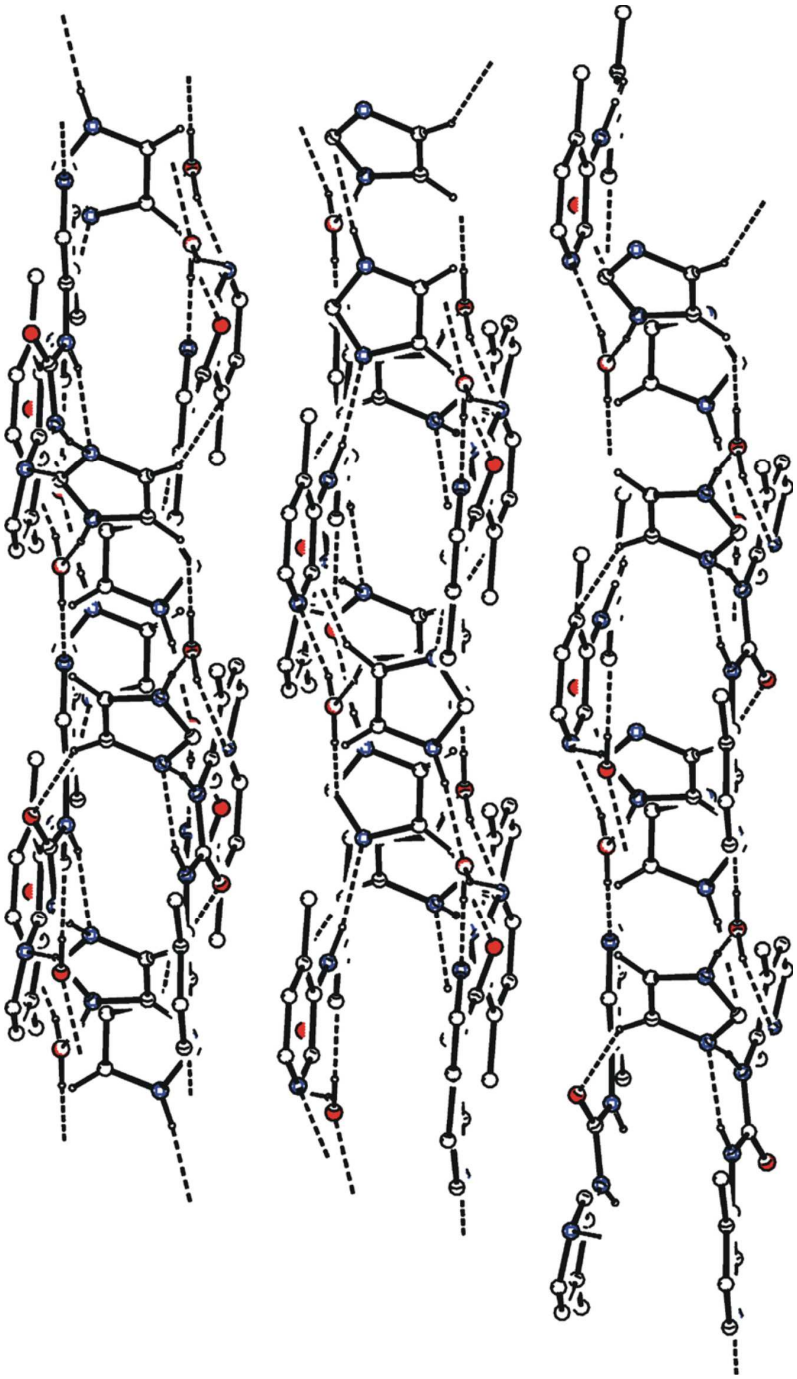

Figure S3. A part of the crystal structure of **11**, showing a two-dimensional network and imidazole hydrogen atoms pointing to the pyridine rings of the neighbouring molecules. Hydrogen bonds are indicated by dashed lines, and hydrogen atoms not involved in intermolecular interactions have been omitted for clarity.

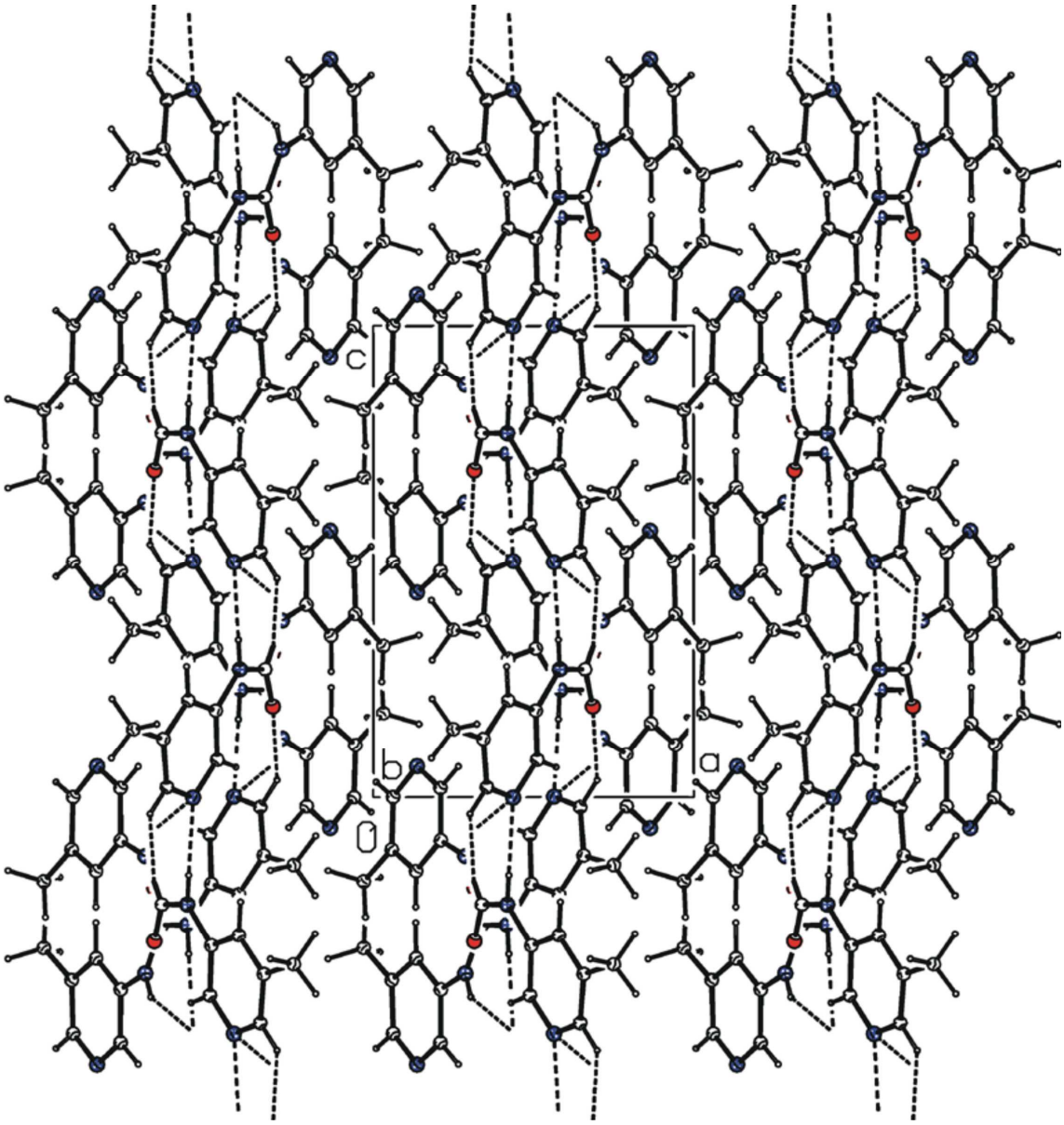

Figure S4. A crystal packing diagram of **12**, viewed along the crystallographic *b* axis, showing a two-dimensional network formed by N–H···N and C–H···O hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

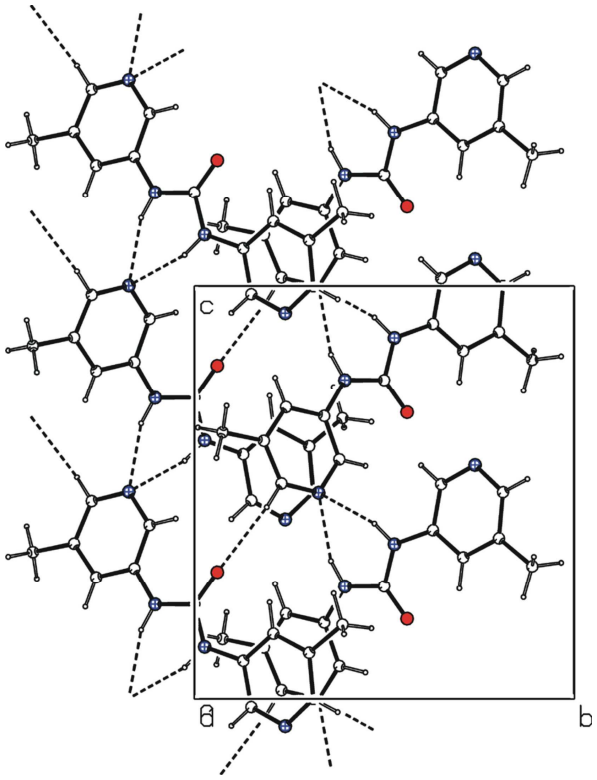

Figure S5. A crystal packing diagram of **12**, viewed along the crystallographic *a* axis, showing stacking of the molecules and π···π interactions.

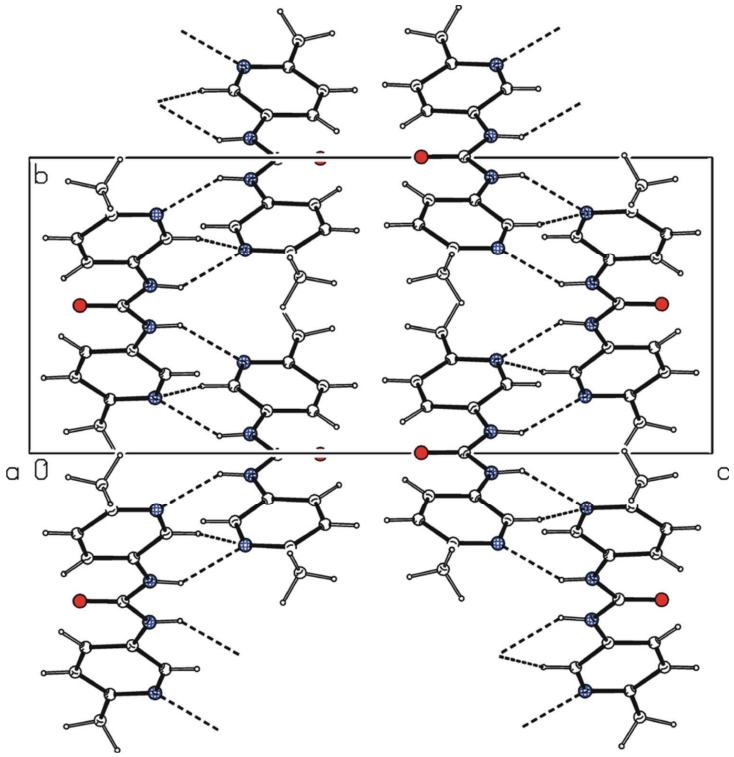

Figure S6. A crystal packing diagram of **13**, viewed along the crystallographic *a* axis, showing a two-dimensional network formed by N–H···N and C–H···N hydrogen bonds. Hydrogen bonds are indicated by dashed lines.

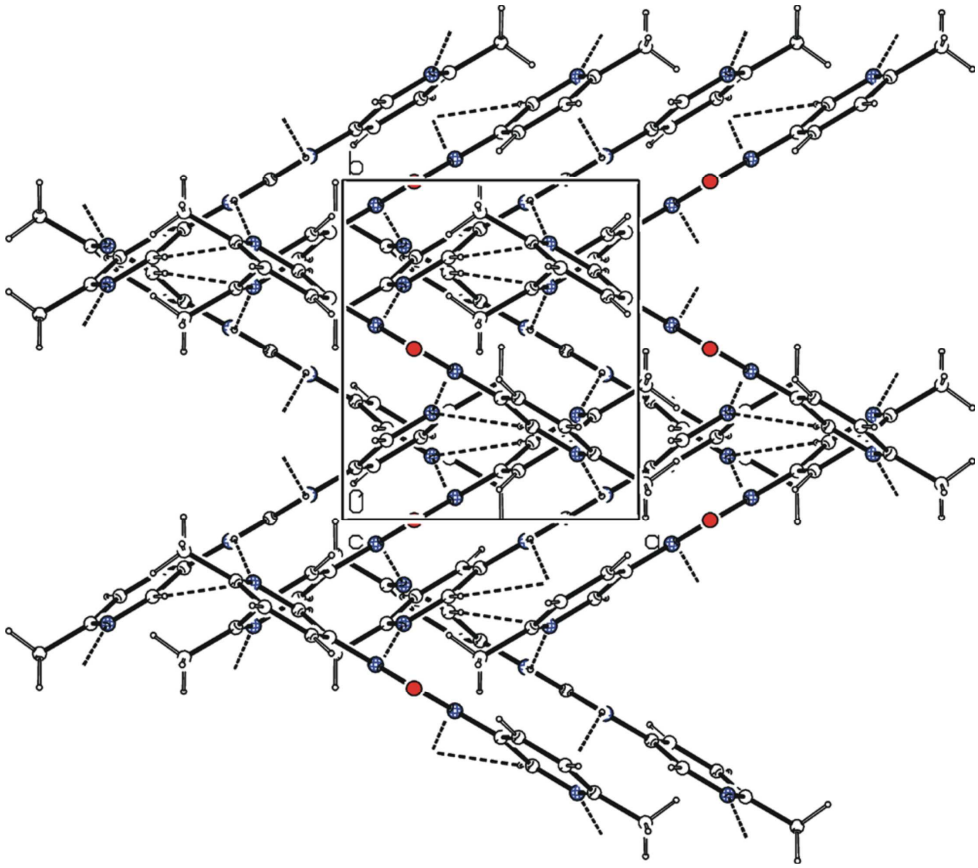

Figure S7. A crystal packing diagram of **13**, viewed along the crystallographic *c* axis, showing hydrogen-bonded molecules disposed in herringbone fashion. Hydrogen bonds are indicated by dashed lines.

Table S2. Dihedral angle analysis of ligands **10 - 13**.

	10	**11**	**12**	**13**
Py (N1-C6)/ Py' (N1'-C6')	26.95(7)^{o}	12.86(15)^{o}	14.3(2)^{o}	18.91(12)^{o}
N7/C8/O8/N7' / Py	44.86(8)^{o}	21.91(17)^{o}	4.3(2)^{o}	8.26(14)^{o}
N7/C8/O8/N7' / Py'	49.20(8)^{o}	16.20(17)^{o}	14.8(2)^{o}	11.19(14)^{o}

Table S3. Hydrogen-bonding geometry for ligands **10 - 13**.

	D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (°)	Symmetry codes
10	C4–H4•••O8	0.95	2.58	2.9409(18)	103	
	C4'–H4'•••O8	0.95	2.64	2.9452(18)	99	
	N7–H7•••O8	0.88	2.08	2.8638(16)	148	x, -1+y, z
	N7'–H7'•••O8	0.88	2.11	2.8793(17)	145	x, -1+y, z
	C6'–H6'•••N1'	0.95	2.61	3.556(2)	178	2-x, 1/2+y, 1/2-z
11	C2–H2•••O8	0.95	2.27	2.845(4)	118	
	C2'–H2'•••O8	0.95	2.22	2.834(4)	122	
	N7–H7•••N10	0.88	2.18	3.011(4)	157	
	N7'–H7'•••N10	0.88	2.18	3.010(4)	158	
	N12–H12•••O15	0.88	1.96	2.802(4)	159	
	O15–H15A•••N1'	0.96(2)	1.84(2)	2.784(3)	169(4)	x, -1+y, z
	O15–H15B•••N1	0.95(3)	1.99(3)	2.898(4)	158(3)	1+x, -1/2-y, 1/2+z
	C14–H14•••O8	0.95	2.53	3.376(4)	149	-x, -y, 1-z
12	C2–H2•••O8	0.95	2.26	2.890(5)	123	
	C4'–H4'•••O8	0.95	2.39	2.948(5)	117	
	N7–H7•••N1	0.88	2.09	2.936(5)	162	1-x, y, 1/2+z
	N7'–H7'•••N1	0.88	2.23	3.044(5)	154	1-x, y, 1/2+z
	C6–H6•••O8	0.95	2.47	3.318(5)	149	1-x,-1/2+y,1-z
13	C4–H4•••O8	0.95	2.30	2.864(3)	117	
	C4'–H4'•••O8	0.95	2.28	2.872(3)	120	
	N7–H7•••N1'	0.88	2.19	2.965(3)	147	1-x, -1/2+y, 1/2-z
	N7'–H7'•••N1	0.88	2.17	2.944(3)	146	-x, 1/2+y, 1/2-z
	C2'–H2'•••N1	0.95	2.57	3.342(4)	139	-x, 1/2+y, 1/2-z

Table S4. The geometry of C–H•••π interactions for **10 - 13**.

	D–H•••Cg	D–H (Å)	H•••Cg (Å)	D•••Cg (Å)	D–H•••Cg (°)	Symmetry codes
10	C9–H9C•••Py[a]	0.98	2.73	3.4593(16)	132	x, -1+y, z
	C9'–H91'•••Py'	0.98	2.71	3.5799(18)	148	x, -1+y, z
11	C13–H13•••Py	0.95	2.80	3.554(4)	137	x, -1/2-y, 1/2+z
12	C9'–H92'•••Py	0.98	2.80	3.683(5)	150	-1+x, 1/2+y, 3/2-z
13	C9–H9C•••Py'	0.98	2.82	3.582(3)	135	-1+x, -1+y, z
	C9'–H93'•••Py	0.98	2.82	3.552(3)	132	1+x, 1+y, z

[a] Py denotes the N1/C2/C3/C4/C5/C6 ring, and Py' the N1'/C2'/C3'/C4'/C5'/C6' pyridine ring

Table S5. The geometry of π•••π interactions for ligand **13**.

	Cg•••Cg	Cg•••Cg (Å)	α (°)	CgI•••Perp (Å)	Slippage (Å)	Symmetry codes
13	Py•••Py'[a]	3.795(2)	5.3(2)	3.5084(17)	*ca*. 1.45	x, -1/2+y, 3/2-z
	Py'•••Py	3.795(2)	5.3(2)	3.5061(17)	*ca*. 1.45	x, 1/2+y, 3/2-z

[a] Py denotes the N1/C2/C3/C4/C5/C6 ring, and Py' the N1'/C2'/C3'/C4'/C5'/C6' pyridine ring

3. Additional data on the metallo-supramolecular complexes

Table S6. Selected bond lengths and angles of the crystal structures of complexes **23a**, **24a**, **25a** and **28**.

length / angle	**23a**	**24a**	**25a**	**28**
Pd1-N11 (Å)	2.036(4)	2.106(7)	2.100(4)	2.087(6)
Pd1-N12 (Å)	2.032(4)	2.100(7)	2.107(4)	2.099(6)
Pd2-N11' (Å)	2.047(4)	2.078(9)	2.095(5)	2.087(7)
Pd2-N12' (Å)	2.038(4)	2.113(9)	2.106(4)	2.103(6)
Pd3-N13 (Å)		2.106(3)		
Pd3-N14 (Å)		2.102(7)		
Pd4-N13' (Å)		2.088(10)		
Pd4-N14' (Å)		2.119(9)		
N11-Pd1-N12 (°)	90.99(15)	85.7(3)	86.22(16)	86.0(2)
N11'-Pd1-N12' (°)	91.56(16)	86.3(4)	88.59(17)	85.8(3)
N13-Pd1-N14 (°)		85.7(3)		
N13'-Pd1-N14' (°)		86.2(4)		
Pd1-N1 (Å)	2.036(4)			
Pd1-N2 (Å)	2.034(4)			
Pd2-N3 (Å)	2.028(4)			
Pd2-N4 (Å)	2.025(4)			
N1-Pd1-N2 (°)	84.63(17)			
N3-Pd2-N4 (°)	84.22(17)			
Pd1-P1 (Å)		2.275(2)	2.2745(14)	2.275(2)
Pd1-P2 (Å)		2.281(2)	2.2787(14)	2.275(2)
Pd2-P3 (Å)		2.274(3)	2.2818(14)	2.273(2)
Pd2-P4 (Å)		2.262(3)	2.2714(15)	2.281(2)
Pd3-P5 (Å)		2.263(3)		
Pd3-P6 (Å)		2.277(3)		
Pd4-P7 (Å)		2.269(4)		
Pd4-P8 (Å)		2.273(3)		
P1-Pd1-P2 (°)		90.54(9)	89.36(5)	90.36(8)
P3-Pd2-P4 (°)		89.97(12)	92.28(5)	90.55(8)
P5-Pd3-P6 (°)		90.49(9)		
P7-Pd4-P8 (°)		89.62(13)		

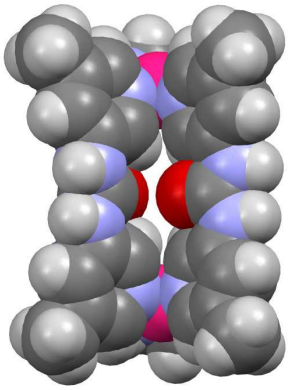

Figure S8. Spacefilling model of the cation of complex **23a**, showing the space between the two bispyridylurea ligands which are too small for counter-anion encapsulation. Counter-anions and solvent molecules have been omitted for clarity.

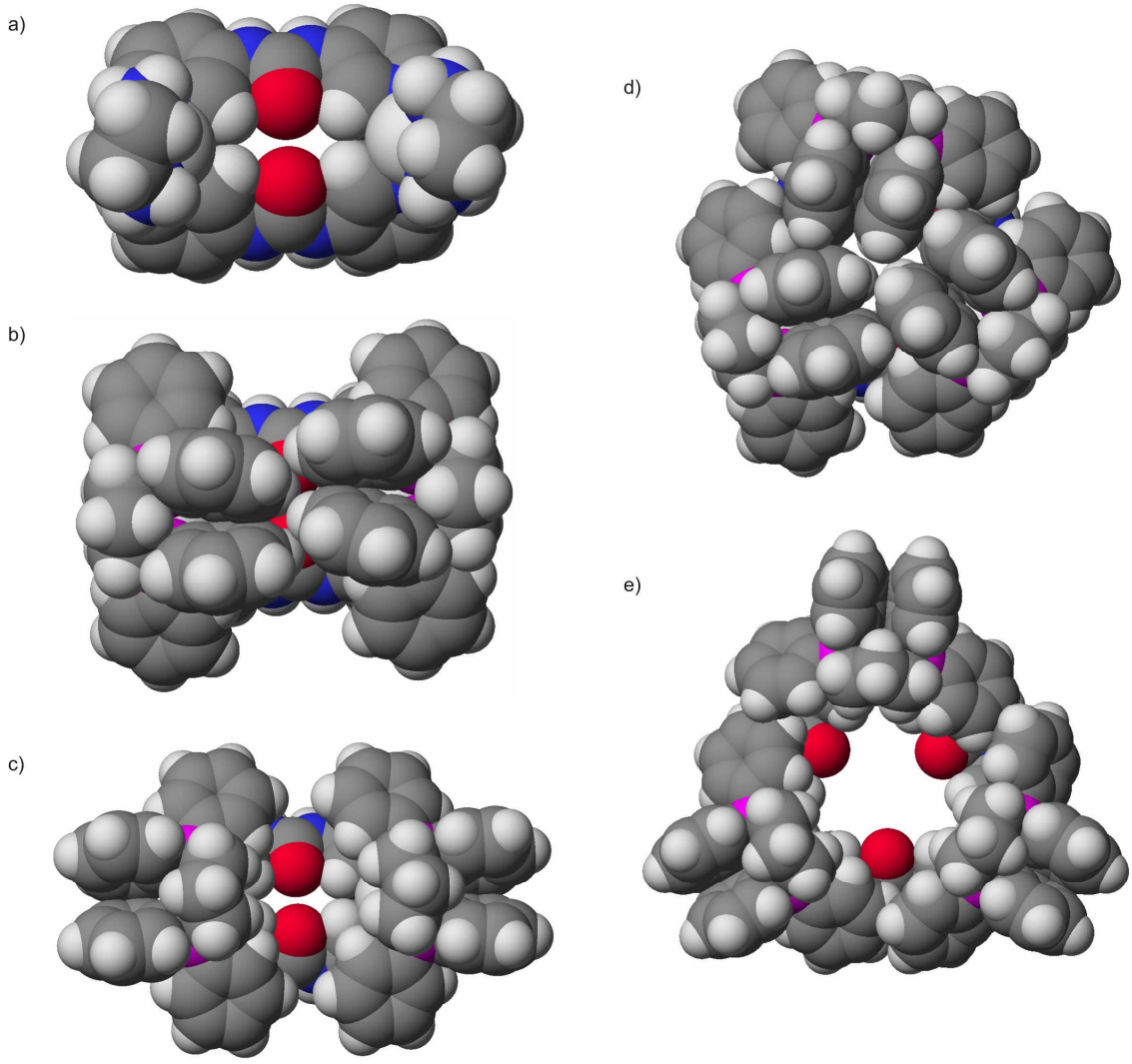

Figure S9. MM2 force-field-optimized structures of a) **19a**, b) the small isomer of **22a**, c) the large isomer of **22a**, d) the small isomer of **22b** and e) the large isomer of **22b** in space-filling representation.

Table S7. The experimental data of the ^{1}H NMR DOSY experiments compared to the calculated radii of the complexes under study. The radii were obtained from calculated structures which were geometry-optimized using the MM2 force field.

Compound	solvent	T [K]	D [m^2s^{-1}]	$r_{exp.}$ [nm]	$r_{cal.}$ [nm]
19a	DMSO	298	$1.41 \cdot 10^{-10}$	0.778	0.879
20a	DMSO	298	$1.30 \cdot 10^{-10}$	0.840	0.905
21a	DMSO	298	$1.32 \cdot 10^{-10}$	0.829	0.992
22a	DMSO	298	$1.21 \cdot 10^{-10}$	0.907	0.967
23a	DMSO	298	$1.32 \cdot 10^{-10}$	0.831	1.045
24a	DMF	243	$1.19 \cdot 10^{-10}$	0.759	1.048
24b	DMF	243	$8.43 \cdot 10^{-11}$	1.188	1.098
25a	DMF	273	$2.10 \cdot 10^{-10}$	0.826	1.066
25b	DMF	273	$1.84 \cdot 10^{-10}$	0.942	1.093
26a	DMF	243	$8.88 \cdot 10^{-11}$	1.013	1.065
26b	DMF	243	$8.43 \cdot 10^{-11}$	1.066	1.100
27a	DMF	233	$7.03 \cdot 10^{-11}$	1.002	1.190
27b	DMF	233	$6.69 \cdot 10^{-11}$	1.053	1.307
28a	DMF	243	$7.83 \cdot 10^{-11}$	1.149	1.271
29a	DMF	298	$2.93 \cdot 10^{-10}$	0.918	1.052
29b	DMF	298	$2.64 \cdot 10^{-10}$	1.019	1.102
30a	DMF	298	$2.71 \cdot 10^{-10}$	0.992	1.075
30b	DMF	298	$2.54 \cdot 10^{-10}$	1.060	1.097
31a	DMF	298	$2.81 \cdot 10^{-10}$	0.958	1.068
31b	DMF	298	$2.59 \cdot 10^{-10}$	1.038	1.104
32a	DMF	298	$2.92 \cdot 10^{-10}$	0.921	1.193
32b	DMF	298	$2.47 \cdot 10^{-10}$	1.089	1.317
33a	DMF	298	$2.65 \cdot 10^{-10}$	1.014	1.276

Viscosity coefficients used for DMF at different temperatures: $\eta_{233\ K} = 2.420$ g $m^{-1}s^{-1}$ $\eta_{243\ K} = 1.979$ g $m^{-1}s^{-1}$, $\eta_{273\ K} = 1.154$ g $m^{-1}s^{-1}$, $\eta_{298\ K} = 0.811$ g $m^{-1}s^{-1}$. The viscosities for 233 K and 243 K were extrapolated from literature data.[11] The viscosity coefficient for DMSO at 298 K is: $\eta_{298\ K} = 1.996$ g $m^{-1}s^{-1}$

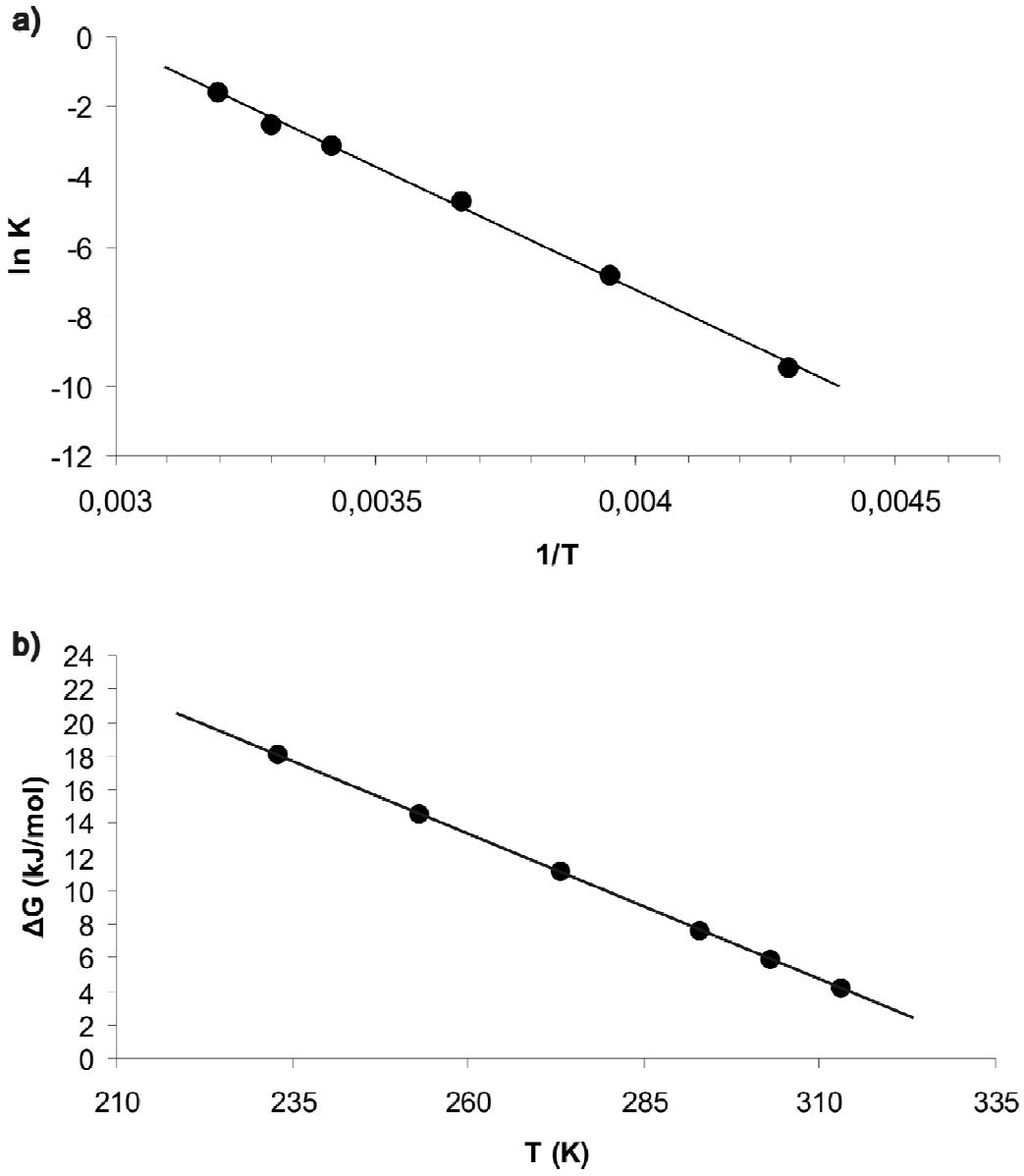

Figure S10. a) Van't Hoff plot of ln *K* over *1/T* for the equilibrium of **24a/b** and b) plot of free enthalpy ΔG_{eq} over temperature *T*.

4. Titration of 24a/b with $NBu_4H_2PO_4$ in DMF-d_7

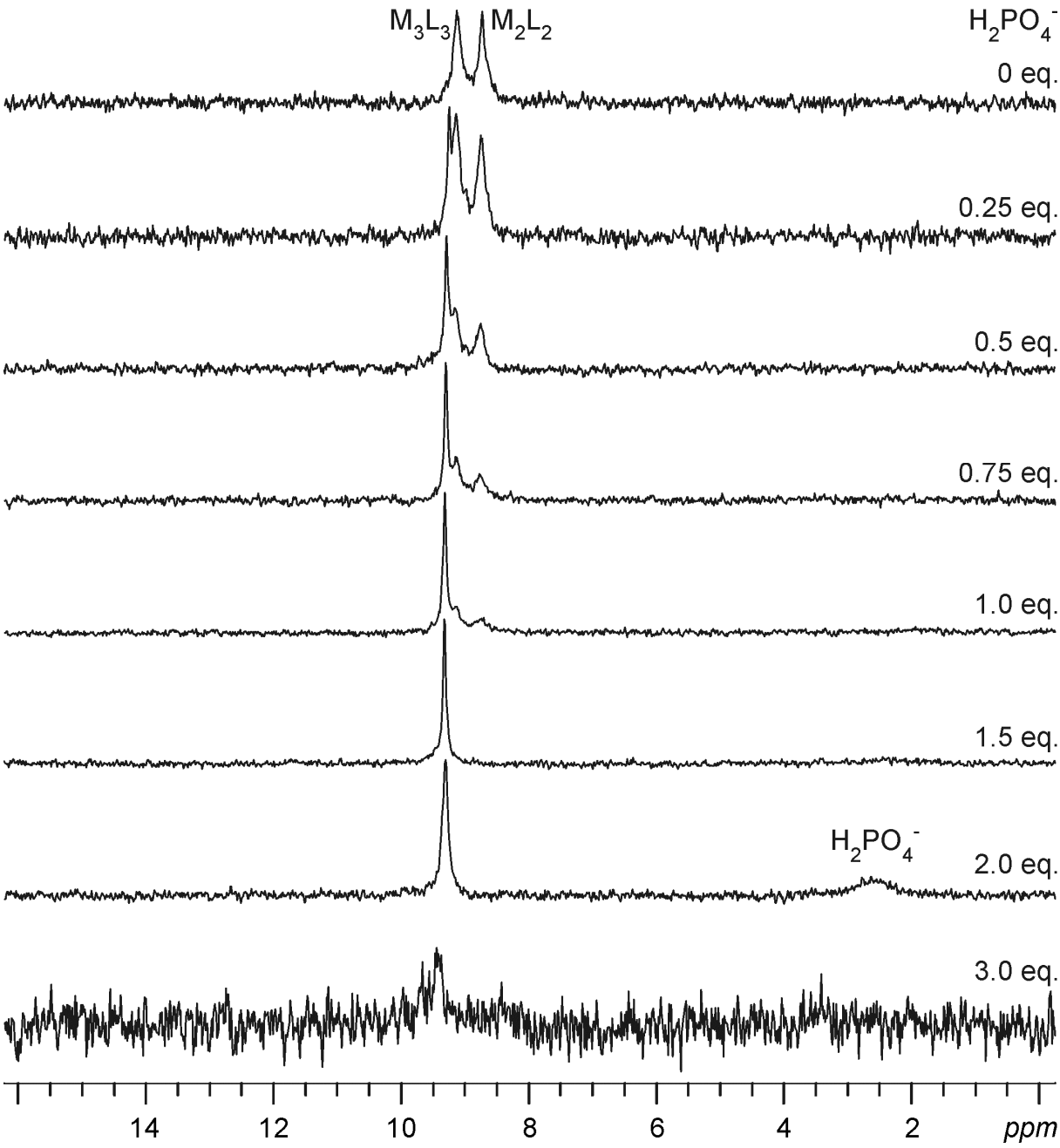

Figure S11. ^{31}P NMR titration of **24a/b** with $NBu_4H_2PO_4$ in DMF-d_7. Clearly, the behaviour is similar to the titration with NBu_4HSO_4 as shown in the main text: The initially formed M_3L_3 and M_2L_2 complexes converge into one new species upon addition of 1 eq. of the guest salt.

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