# Supporting Information for

# Metallo-supramolecular squares with aminoacid-decorated bipyridines: Heterochiral self-sorting through self-assembly

Alexander Rang, Martin Nieger, Marianne Engeser, Arne Lützen, and Christoph A. Schalley\*

# 1. Syntheses and Analytical Data

**Synthesis and analytical data of 2.** Acid chloride **1** (470 mg, 354.0 g/mol, 1.3 mmol) and (S)-methyl 2-aminopropanoate (3 equivalents, 4.0 mmol, 139.6 g/mol, 556 mg) are suspended in 15 ml THF and triethylamine (8 equivalents, 10.6 mmol, 101.2 g/mol, 0.73 g/ml, 1.5 ml) is added. The suspension is stirred for 5 hours and all volatile compounds are removed *in vacuo*. The resulting residue is resolved in dichloromethane and washed with a dilute aqueous sodium carbonate solution. Again, all volatile compounds are removed *in vacuo* and the resulting residue is purified by column chromatography (374 mg, 0.90 mmol, 68 %).

m.p.: 146 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.80 (s, 2H, H-2 and H-2'), 8.67 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, 2H, H-6 and H-6'), 7.92 (s, 2H, H<sub>amide</sub>), 7.16 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, 2H, H-5 and H-5'), 4.53 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H, H<sub>CH</sub>), 3.63 (s, 6H, H<sub>COOCH3</sub>), 1.31 (d, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 6H, H<sub>CH3</sub>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 174.0 (quaternary carbon, Cq), 166.7 (Cq), 150.7 (CH), 147.9 (CH), 144.3 (Cq), 131.1 (Cq), 123.7 (CH), 52.7 (CH), 48.5 (CH<sub>3</sub>), 17.8 (CH<sub>3</sub>).

MS (EI, high resolution) 414.1537 calc. for C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub> 414.1539 (0.5 ppm).

**Synthesis of 3a,b.** For square formation, equimolar amounts of organic ligand **2** and metal precursor complexes  $(dpppM(OTf)_2(H_2O)_2 \text{ with } M = Pd [a] \text{ or } Pt [b])$  are mixed in acetone (for MS studies,  $4 \cdot 10^{-4}$  M) or  $[D_6]$ -acetone (for NMR experiments,  $9 \cdot 10^{-3}$  M) and stirred for one hour before the measurements to avoid kinetically controlled product formation. For CD-spectroscopy, the acetone is removed in vacuo and the resulting residues are dissolved in methanol. Note, that <sup>195</sup>Pt (natural abundance 34 %) is the only NMR active Pt isotope. Thus, phosphorous atoms in **3b** are seen as one singlet (<sup>190</sup>Pt -<sup>194</sup>Pt and <sup>196</sup>Pt - <sup>198</sup>Pt, 66 %) and one doublet (<sup>195</sup>Pt, 34 %) at the same chemical shift.

# Analytical data of 3a.

 $m.p. > 250^{\circ}C$ 

<sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]-acetone):  $\delta$  9.44 (d, <sup>3</sup>J<sub>HH</sub>= 4 Hz, 4H, H<sup>2</sup><sub>out</sub>), 9.20 (d, <sup>3</sup>J<sub>HH</sub>= 4 Hz, 4H, H<sup>2</sup><sub>in</sub>), 8.54 (d, <sup>3</sup>J<sub>HH</sub>= 2 Hz, 4H, H<sup>6</sup><sub>in</sub>), 8.41 (d, <sup>3</sup>J<sub>HH</sub>= 2 Hz, 4H, H<sup>6</sup><sub>out</sub>), 8.40 (m, 16H, H<sub>dppp</sub>), 7.34 (m, 4+4+32+32+4+4H, H<sub>amide</sub>, H<sub>amide</sub>, H<sub>dppp</sub>, H<sub>dppp</sub>, H<sup>5</sup><sub>in</sub>, H<sup>5</sup><sub>out</sub>), 4.08 (dq, <sup>3</sup>J<sub>HH</sub>= 7 Hz and 6 Hz, 4H, H<sub>CH</sub>), 3.99 (dq, <sup>3</sup>J<sub>HH</sub>= 7 Hz and 6 Hz, 4H, H<sub>CH</sub>), 3.54 (s, 12H, H<sub>OCH3</sub>), 3.41 (br, 8H, H<sub>dppp</sub>), 3.24 (s, 12H, H<sub>OCH3</sub>), 3.09 (br, 8H, H<sub>dppp</sub>), 1.46 (d, <sup>3</sup>J<sub>HH</sub>= 7 Hz, 24H, H<sub>CH3</sub>), 1.28 (m, 8H, H<sub>dppp</sub>)

<sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]-acetone): δ 172.6 (CO), 171.5 (CO), 162.6 (CO), 162.1 (CO), 150.6 (C2), 150.4 (C2), 149.3 (C6), 148.8 (C6), 147.4 (C4), 145.2 (C4), 135.4, 135.3, 134.6, 133.4, 133.3, 133.3, 132.6, 132.4, 130.7, 130.6, 130.4, 130.4, 130.2, 130.2, 129.7, 129.6, 129.6, 128.6, 128.6 (C3), 127.9 (C3), 125.3, 125.2, 124.8, 124.7, 124.5, 124.2, 123.9, 123.7, 122.3 (C5), 119.8 (C5), 51.6 (OCH<sub>3</sub>), 51.4 (OCH<sub>3</sub>), 49.8 (CH), 49.6 (CH), 28.8, 22.4, 22.1, 17.2, 16.5, 16.3, 15.6 (CH<sub>3</sub>), 15.3 (CH<sub>3</sub>)

<sup>31</sup>P NMR (202 MHz, [D<sub>6</sub>]-acetone):  $\delta$  6.2 (d, <sup>2</sup>J<sub>PP</sub>= 31 Hz, 4P), 4.4 (d, <sup>2</sup>J<sub>PP</sub>= 31 Hz, 4P) ESI-MS (FTICR, 4·10<sup>-4</sup> M, acetone): m/z 2313.3 Da (M-2OTf).

# Analytical data of 3b.

m.p. > 250°C

<sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]-acetone):  $\delta$  9.43 (dd, <sup>3</sup>J<sub>HH</sub>= 6 Hz and 2 Hz, 4H, H<sup>2</sup><sub>out</sub>), 9.21 (dd, <sup>3</sup>J<sub>HH</sub>= 6 Hz and 2 Hz, 4H, H<sup>2</sup><sub>in</sub>), 8.63 (d, <sup>3</sup>J<sub>HH</sub>= 3 Hz, 4H, H<sup>6</sup><sub>in</sub>), 8.57 (d, <sup>3</sup>J<sub>HH</sub>= 3 Hz, 4H, H<sup>6</sup><sub>out</sub>), 8.40 (m, 16H, H<sub>dppp</sub>), 7.40 (m, 4+4+32+32+4+4H, H<sub>amide</sub>, H<sub>amide</sub>, H<sub>dppp</sub>, H<sub>dppp</sub>, H<sup>5</sup><sub>in</sub>, H<sup>5</sup><sub>out</sub>), 4.09 (dq, <sup>3</sup>J<sub>HH</sub>= 7 Hz and 6 Hz, 4H, H<sub>CH</sub>), 3.96 (dq, <sup>3</sup>J<sub>HH</sub>= 7 Hz and 6 Hz, 4H, H<sub>CH</sub>), 3.50 (br, 12+8H, H<sub>OCH3</sub> and H<sub>dppp</sub>), 1.47 (d, <sup>3</sup>J<sub>HH</sub>= 7 Hz, 24H, H<sub>CH3</sub>), 1.29 (m, 8H, H<sub>dppp</sub>)

<sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]-acetone): δ 172.4 (CO), 171.3 (CO), 162.4 (CO), 161.9 (CO), 150.4 (C2), 150.3 (C2), 149.1 (C6), 148.6 (C6), 147.2 (C4), 145.0 (C4), 135.2, 134.4, 133.2, 133.1, 132.4, 132.2, 130.5, 130.4, 130.3, 130.2, 130.1, 130.0, 129.6, 129.5, 129.4, 128.4 (C3), 127.7 (C3), 125.1, 125.0, 124.6, 124.5, 124.3, 124.0, 123.8, 123.5, 122.1 (C5), 119.6 (C5), 51.4 (OCH<sub>3</sub>), 51.3 (OCH<sub>3</sub>), 49.6 (CH), 49.4 (CH), 22.1, 21.9, 17.0, 15.5 (CH<sub>3</sub>), 15.1(CH<sub>3</sub>) <sup>31</sup>P NMR (202 MHz, [D<sub>6</sub>]-acetone): δ -12.7 (d, <sup>2</sup>J<sub>PP</sub>= 30 Hz, 4P) and -13.7 (d, <sup>2</sup>J<sub>PP</sub>= 30 Hz, 4P), <sup>1</sup>J<sub>195PLP</sub> = 3057 Hz (as typically observed, the Pt satellites are somewhat broadened)

ESI-MS (FTICR, 4·10<sup>-4</sup> M, acetone): m/z 1611.0 Da (M-3OTf); 2490.5 Da (M-2OTf).

### Variable-temperature <sup>1</sup>H NMR spectra of 2.



*Figure S1:* Variable-temperature  ${}^{1}HNMR$  spectra of 2 in  $CDCl_{3}(*)$ .

Not unexpectedly, the signals for the amino acid residues are sharp in the <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub> while the signals for the bipyridine backbone are broad. Broadened signals are also observed in the room-temperature <sup>1</sup>H NMR spectrum (see Figure S1). Low-temperature measurements (<sup>1</sup>H) reveal the coexistence of two species in an almost temperature independent 3:1 ratio. The activation barrier can be estimated to amount to ca.  $\Delta G^{\ddagger} = 60$  kJ mol<sup>-1</sup>. In [D<sub>6</sub>]-acetone, sharp signals are found in the room temperature <sup>1</sup>H NMR spectrum as well as the <sup>13</sup>C NMR spectrum. Thus, the interconversion of the two isomers is faster in acetone than in CDCl<sub>3</sub>. Low-temperature measurements show again two sets of signals, now in a 3:2 ratio. Together with the crystal structure analysis (see below) of the ligands, these results point to the existence of an intramolecular hydrogen bond in chloroform which needs to be broken during the interconversion of diastereomers. Acetone weakens this hydrogen bond and thus, the interconversion is faster.

#### ESI-FTICR-MS spectra of 3a,b.



Figure S2: FTICR-MS spectra of a) 3a and b) 3b (both: acetone, 4•10<sup>-4</sup> M, labels represent the composition as [metal:ligand:OTf]<sup>n+</sup>); insets: experimental and calculated isotope patterns. Note that for 3a the signals for [4:4:6]<sup>2+</sup> overlap with minor signals for [2:2:3]<sup>+</sup> (< 5% intensity).

<sup>1</sup>H and <sup>31</sup>P NMR spectra of 3b.



*Figure S3:* <sup>1</sup>*H* and <sup>31</sup>*P* NMR spectra of a) **2** and b) **3b** (all: acetone (\*), rt, residual water marked with circles). The spectra are comparable to the results for **3a** discussed in the main text. Signal integration for the two doublets in the <sup>31</sup>*P* NMR is again exactly 1:1.





*Figure S4:* HH-COSY of *3b*: *a*) 7.0 to 9.6 ppm and *b*) 0.5 to 4.5 ppm. Please note that two signals at 3.5 ppm overlap; A/B assignment for  $H_{CH}$  and  $H_{CH3}$  not possible. Asterisks indicate amide signals.



*Figure S5:* HMQC of **3b** (acetone, rt, aromatic region): Asterisks indicate amide signals, unassigned peaks belong to dppp's phenyl groups.

#### Crystal structure data for both enantiomers of 2.

**Crystal data for** (*S*,*S*)-2: C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>, M = 414.42, space group  $P2_12_12_1$  (No. 19), orthorhombic, a = 8.709(1), b = 11.104(1), c = 21.032(3) Å, V = 2033.9(4) Å<sup>3</sup>; Z = 4;  $\rho_{\text{ber.}} = 1.353$  g cm<sup>-3</sup>;  $\mu$  (Mo<sub>Ka</sub>)= 0.102 mm<sup>-1</sup>, F(000) = 872, 33705 reflections ( $2\theta_{\text{max}} = 55^{\circ}$ ) measured (4640 unique, R<sub>int</sub> = 0.045),  $R(\text{for I} > 2\sigma(I))= 0.0298$ , wR2(all data) = 0.0752, GOF = 1.053 for 279 parameters and 2 restraints, largest diff. peak and hole 0.261 eÅ<sup>-3</sup>/-0.185 eÅ<sup>-3</sup>. H atoms were localized by difference electron density determination and those bonded to nitrogen were refined freely while the rest were refined using a riding model. The absolute structure cannot be determined reliably, but is known from the stereochemistry of the sidechains (Flack's x-parameter -0.1(7); see Ref. 15b in the main text).



Figure S6: ORTEP plot (50% probability level) of the crystal structure of (S,S)-2.

**Crystal data for** (*R*,*R*)-2: C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>, M = 414.42, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), orthorhombic, a = 8.732(1), b = 11.123(1), c = 21.076(2) Å, V = 2047.0(4) Å<sup>3</sup>; Z = 4;  $\rho_{\text{ber.}} = 1.345$  g cm<sup>-3</sup>;  $\mu$  (Mo<sub>Ka</sub>)= 0.101 mm<sup>-1</sup>, *F*(000) = 872, 29007 reflections ( $2\theta_{\text{max}} = 55^{\circ}$ ) measured (4671 unique, R<sub>int</sub> = 0.067), *R*(for I >  $2\sigma$ (I))= 0.0414, *wR2*(all data) = 0.0991, GOF = 1.088 for 279 parameters and 2 restraints, largest diff. peak and hole 0.254 eÅ<sup>-3</sup>/-0.243 eÅ<sup>-3</sup>. H atoms were localized by difference electron density determination and those bonded to nitrogen were refined freely while the rest were refined using a riding model. The absolute structure cannot be determined reliably, but is known from the stereochemistry of the sidechains (Flack's x-parameter -0.7(9) ; see Ref. 15b in the main text).



Figure S7: ORTEP plot (50% probability level) of the crystal structure of (R,R)-2.

Both enantiomers crystallize in enantiomorphous crystals. Therefore, we show the packing pattern in the following only for (S,S)-2. The packing for the (R,R)-2 enantiomer is mirror symmetrical to the one shown.



*Figure S8:* View of the unit cell of (*S*,*S*)-2, the packing pattern and the hydrogen bonding connecting the individual molecules in the crystal.

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*Figure S9:* View of the helical pattern of alternating intramolecular and intermolecular hydrogen bonds in structure of (*S*,*S*)-2.

**Crystal data for 3b:**  $[C_{188}H_{192}N_{16}O_{24}P_8Pt_4]^{8+} - 8 [CF_3SO_3]^- - 7 C_3H_6O, <math>M = 5686.80$ , space group  $P2_1$  (No. 4), monoclinic, a = 14.955(1), b = 27.472(1), c = 31.536(3) Å,  $\beta = 100.57(1)^\circ$ , V = 12737(2) Å<sup>3</sup>; Z = 2;  $\rho_{\text{ber.}} = 1.483$  g cm<sup>-3</sup>;  $\mu$  (Mo<sub>K $\alpha$ </sub>)= 2.398 mm<sup>-1</sup>, F(000) = 5728, 113953 reflections ( $2\theta_{\text{max}} = 50^\circ$ ) measured (42874 unique,  $R_{\text{int}} = 0.027$ ),  $R(\text{for I} > 2\sigma(I)) = 0.0760$ , wR2(all data) = 0.2060, GOF = 1.074 for 1241 parameters and 3078 restraints, largest diff. peak and hole 2.854 eÅ<sup>-3</sup> (triflate) / -1.555 eÅ<sup>-3</sup>; a semi-empirical absorption correction was applied, max./min. transmission 0.4305/0.3258, absolute structure parameter x = 0.06(1) (see Ref. 15b in the main text).

The structure shows unequivocally the constitution, conformation and configuration of the cation, with probably disorder in the side chains, the phenyl groups, the anions and the solvent and a large void (>1200 Å<sup>3</sup>, but without, even heavily disordered, unidentifiable, solvent).

Due to the bad quality of the data, caused by this disorder, only the Pt, P and six of the eight Satoms were refined anisotropically. Restraints for geometry and displacement parameters were used to refine the sidechains, the anions and the solvent molecules. The phenyl groups were refined as a rigid group using a constrained model (AFIX 66). The disorder of the anions, side chains, phenyl groups, and solvent molecules could not be resolved. Due to these problems, there are a also number of short intermolecular H -H, but also X - Y contacts, and NH-groups without acceptor.



*Figure S10:* View of the metallo-supramolecular square **3b** together with counterions and solvent molecules.



*Figure S11:* Side view of the metallo-supramolecular square **3b** (counterions and solvent molecules omitted).



*Figure S12:* Packing pattern of *3b* (view along the crystallographic *a*-axis; counterions and solvent molecules omitted for clarity).



*Figure S12:* Packing pattern of **3b** (view along the crystallographic b-axis; counterions and solvent molecules omitted for clarity).