Dynamic Formation of Self-Organized Corner-Connected Square Metallocycles by Stoichiometric Control

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General Methods

Ligand 1, (en)Pd(OTf)$_2$, and (en)Pt(OTf)$_2$ were prepared according to published procedures. All other reagents used were commercial grade chemicals from freshly opened containers. Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F$_{254}$ foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. Proton and carbon nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 or Bruker Avance 500 equipped with a dual cryoprobe for $^1$H and $^{13}$C, using the deuterated solvent as lock and the residual protiated solvent as internal standard. DOSY experiments were referenced using the value 1.92 x $10^{-9}$ m$^2$s$^{-1}$ for the DHO signal in D$_2$O at 298 K and the value 2.18 x $10^{-9}$ m$^2$s$^{-1}$ for the CHD$_2$CN signal in CD$_3$CN at 298 K. Mass spectrometry experiments were carried out in a LC-Q-q-TOF Applied Biosystems QSTAR Elite spectrometer for low- and high-resolution ESI.

Metallocycle 5a·2BF$_4$·12NO$_3$

To a solution of Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ (2.2 mg, 5.0 x $10^{-3}$ mmol) in D$_2$O (2.0 mL), ligand 1·2NO$_3$ (9.0 mg, 0.020 mmol) and (en)Pd(NO$_3$)$_2$ (2.9 mg, 0.010 mmol) were added. $^1$H NMR (500 MHz, D$_2$O) δ: 2.93 (8H, s); 7.48 (8H, m); 8.00 (8H, d, $J = 6.9$ Hz); 8.04 (8H, d, $J = 6.9$ Hz); 8.52 (16H, m); 8.95 (8H, d, $J = 6.9$ Hz); 9.14 (8H, d, $J = 5.5$ Hz); 9.40 (16H, m); $^{13}$C NMR (125 MHz, D$_2$O) δ: 48.8 (CH$_2$); 77.7 (CH$_2$); 125.2 (CH); 125.8 (CH); 127.4 (CH); 127.5 (CH); 144.2 (C); 144.9 (C); 145.8 (CH); 152.1 (CH); 152.3 (CH); 154.6 (C); 154.9 (C).

Metallocycle 6a·4BF$_4$·16NO$_3$

To a solution of Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ (3.0 mg, 6.7 x $10^{-3}$ mmol) in D$_2$O (2.0 mL), ligand (9.0 mg, 0.020 mmol) and (en)Pd(NO$_3$)$_2$ (1.5 mg, 5.0 x $10^{-3}$ mmol) were added. 1·2NO$_3$ NMR (500 MHz, D$_2$O) δ: 2.92 (8H, s); 7.48 (12H, m); 8.00 (8H, d, $J = 7.0$ Hz); 8.04 (16H, d, $J = 4.9$ Hz); 8.52 (24H, m); 8.95 (8H, d, $J = 6.8$ Hz); 9.14 (16H, d, $J = 6.4$ Hz); 9.40 (24H, m); $^{13}$C NMR (125 MHz, D$_2$O) δ: 46.8 (CH$_2$); 77.7 (CH$_2$); 125.3 (CH); 125.8 (CH); 127.4 (CH); 127.5 (CH); 144.2 (C); 144.9 (C); 145.8 (CH); 152.1 (CH); 152.3 (CH); 154.6 (C); 154.9 (C).

Metallocycle 7a·6BF$_4$·20NO$_3$

To a solution of Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ (3.3 mg, 7.5 x $10^{-3}$ mmol) in D$_2$O (2.0 mL), ligand 1·2NO$_3$ (9.0 mg, 0.020 mmol) and (en)Pd(NO$_3$)$_2$ (1.5 mg, 5.0 x $10^{-3}$ mmol) were added. $^1$H NMR (500 MHz, D$_2$O) δ: 2.93 (8H, s); 7.48 (16H, m); 8.00 (8H, d, $J = 6.9$ Hz); 8.04 (24H, d, $J = 5.2$ Hz); 8.52 (32H, m); 8.96 (8H, d, $J = 6.8$ Hz); 9.14 (24H, d, $J = 6.1$ Hz); 9.40 (32H, m); $^{13}$C NMR (125 MHz, D$_2$O) δ: 46.8 (CH$_2$); 77.7 (CH$_2$); 125.3 (CH); 125.8 (CH); 127.4 (CH); 127.5 (CH); 144.2 (C); 144.9 (C); 145.8 (CH); 152.1 (CH); 152.3 (CH); 154.6 (C); 154.9 (C).

**Metallocycle 5a·2BF₄·4OTf·8PF₆**

To a solution of Pd(CH₂CN)₂(BF₄)₂ (2.2 mg, 5.0×10⁻³ mmol) in CD₂CN (2.0 mL), ligand 1·2PF₆ (12.5 mg, 0.020 mmol) and (en)Pd(OTh)₂ (5.6 mg, 0.010 mmol) were added. ¹H NMR (500 MHz, CD₂CN): δ: 2.90 (8H, s); 4.36 (8H, s); 6.12 (12H, s); 7.12 (16H, m); 8.42 (16H, m); 8.99 (8H, m); 9.13 (16H, m); 9.20 (8H, m); ¹³C NMR (125 MHz, CD₂CN): δ: 47.9 (CH₂); 78.3 (CH₂); 126.2 (CH); 127.0 (CH); 128.5 (CH); 128.7 (CH); 145.0 (C); 145.7 (C); 147.1 (CH); 147.1 (CH); 153.5 (CH); 154.0 (CH); 155.6 (C); 155.8 (C).

**Metallocycle 6a·4BF₄·4OTf·12PF₆**

To a solution of Pd(CH₂CN)₄(BF₄)₂ (3.0 mg, 6.7×10⁻³ mmol) in CD₂CN (2.0 mL), ligand 1·2PF₆ (12.5 mg, 0.020 mmol) and (en)Pd(OTh)₂ (3.7 mg, 6.7×10⁻³ mmol) were added. ¹H NMR (500 MHz, CD₂CN): δ: 2.90 (8H, s); 4.36 (8H, s); 6.12 (12H, s); 7.12 (12H, s); 7.98 (24H, m); 8.41 (24H, m); 8.98 (8H, m); 9.12 (24H, m); 9.18 (16H, m); ¹³C NMR (125 MHz, CD₂CN): δ: 47.9 (CH₂); 78.4 (CH₂); 126.2 (CH); 127.0 (CH); 128.5 (CH); 128.7 (CH); 145.0 (C); 145.7 (C); 147.0 (CH); 147.0 (CH); 153.5 (CH); 154.0 (CH); 155.6 (C); 155.8 (C).

**Metallocycle 7a·6BF₄·4OTf·16PF₆**

To a solution of Pd(CH₂CN)₆(BF₄)₂ (3.3 mg, 7.5×10⁻³ mmol) in CD₂CN (2.0 mL), ligand 1·2PF₆ (12.5 mg, 0.020 mmol) and (en)Pd(OTh)₂ (2.8 mg, 5.0×10⁻³ mmol) were added. ¹H NMR (500 MHz, CD₂CN): δ: 2.90 (8H, s); 4.36 (8H, s); 6.12 (12H, s); 7.12 (16H, s); 7.97 (32H, m); 8.41 (32H, m); 8.98 (8H, m); 9.11 (32H, m); 9.18 (24H, m); ¹³C NMR (125 MHz, CD₂CN): δ: 47.9 (CH₂); 78.4 (CH₂); 126.2 (CH); 127.0 (CH); 128.5 (CH); 128.7 (CH); 145.1 (C); 145.8 (C); 147.0 (CH); 147.1 (CH); 153.5 (CH); 154.0 (CH); 155.6 (C); 155.8 (C).

**Metallocycle 5b·14PF₆**

A solution of Pt(CH₂CN)₂Cl₂ (2.9 mg, 8.4×10⁻³ mmol), AgOTf (4.3 mg, 16.7×10⁻³ mmol), ligand 1·2PF₆ (20.6 mg, 0.033 mmol) and (en)Pt(OTh)₂ (10.7 mg, 16.7×10⁻³ mmol) in CH₂CN (3.0 mL) was heated protected from light for 8d at 55°C. The suspension was filtered over a cap of Celite to remove AgCl and the solvent was removed under reduced pressure without heating. The crude product was suspended in water (17 mL) and ion exchange resin (Amberlite IRA-402, 0.50 g) was added. The mixture was stirred at room temperature for 24 h. The resin was removed by filtration and an excess of KPF₆ is added to the filtrate until no further precipitation was observed. The solid was filtered and washed with water to yield 5b·14PF₆ as a grey solid (14.0 mg, 41 %). ¹H NMR (500 MHz, CD₂CN): δ: 2.83 (8H, s); 5.05 (8H, s); 7.16 (8H, s); 7.96 (8H, m); 8.01 (8H, m); 8.45 (16H, m); 9.01 (8H, m); 9.15 (16H, m); 9.22 (8H, m); ¹³C NMR (125 MHz, CD₂CN): δ: 48.7 (CH₂); 78.4 (CH₂); 126.7 (CH); 127.4 (CH); 128.5 (CH); 128.7 (CH); 144.9 (C); 145.8 (C); 147.1 (CH); 147.2 (CH); 154.3 (CH); 154.8 (CH); 155.3 (C); 155.5 (C). HRMS-ESI (m/z): calcd for [M–5PF₆]⁺: 662.8638, found 662.8639; calcd for [M–6PF₆]⁺: 528.2258, found 528.2255; calcd for [M–8PF₆]⁺: 359.9281, found 359.9284; calcd for [M–9PF₆]⁺: 303.8289, found 303.8289.

**Metallocycle 6b·20PF₆**

A solution of Pt(CH₂CN)₂Cl₂ (12.0 mg, 34.5×10⁻³ mmol), AgOTf (17.7 mg, 68.9×10⁻³ mmol), ligand 1·2PF₆ (63.7 mg, 0.103 mmol) and (en)Pt(OTh)₂ (23.0 mg, 34.5×10⁻³ mmol) in CH₂CN (11.0 mL) was heated protected from light for 8d at 55°C. The suspension was filtered over a cap of Celite to remove AgCl and the solvent was removed under reduced pressure without heating. The crude product was suspended in water (25 mL) and ion exchange resin (Amberlite IRA-402, 1.00 g) was added. The mixture was stirred at room temperature for 24 h. The resin was removed by filtration and an excess of KPF₆ is added to
the filtrate until no further precipitation was observed. The solid was filtered and washed with water to yield 6b·20PF₆ as a brown solid (60.9 mg, 61%). ¹H NMR (500 MHz, CD₃CN) δ: 2.83 (8H, s); 5.05 (8H, s); 7.16 (12H, s); 7.96 (24H, m); 8.42 (24H, m); 8.97 (8H, m); 9.07 (24H, m); 9.11 (16H, m); ¹³C NMR (125 MHz, CD₃CN) δ: 48.7 (CH₃); 78.4 (CH₃); 123.5 (CH); 126.7 (CH); 128.2 (CH); 127.4 (CH); 128.5 (CH); 128.7 (CH); 144.9 (C); 145.8 (C); 146.8 (CH); 147.1 (CH); 147.2 (CH); 151.6 (CH); 154.2 (CH); 154.8 (CH); 155.5 (C). HRMS-ESI (m/z): calcd for [M–6PF₆]⁺ 814.4018, found 814.4044.
**Figure S1:** $^1$H NMR (D$_2$O, 500 MHz) spectrum of 5a·2BF$_4$·12NO$_3$

**Figure S2:** $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of 5a·2BF$_4$·12NO$_3$
Figure S3: HSQC (D$_2$O, 500 MHz and 125 MHz) spectrum of 5a·2BF$_4$·12NO$_3$

Figure S4: HMBC (D$_2$O, 500 MHz and 125 MHz) spectrum of 5a·2BF$_4$·12NO$_3$
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Figure S7: $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of 6a·4BF$_4$·16NO$_3$
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Figure S9: $^{13}$C NMR (D$_2$O, 125 MHz) spectrum of 7a·6BF$_4$·20NO$_3$
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Figure S11: $^1$H NMR (CD$_3$CN, 500 MHz) spectrum of 5a·2BF$_4$·4OTf·8PF$_6$

Figure S12: $^{13}$C NMR (CD$_3$CN, 125 MHz) spectrum of 5a·2BF$_4$·4OTf·8PF$_6$
Figure S13: HSQC (CD$_3$CN, 500 and 125 MHz) spectrum of 5a·2BF$_4$·4OTf·8PF$_6$

Figure S14: HMBC (CD$_3$CN, 500 and 125 MHz) spectrum of 5a·2BF$_4$·4OTf·8PF$_6$
Figure S15: COSY (CD$_3$CN, 500 MHz) spectrum of 5a·2BF$_4$·4OTf·8PF$_6$
**Figure S16:** DOSY (CD$_3$CN, 500 MHz) spectrum of $5a\cdot2$BF$_4$$\cdot$4OTf$\cdot$8PF$_6$

**Figure S17:** Fitting of $I/I_0$ for some $^1$H signals of compound $5a\cdot2$BF$_4$$\cdot$4OTf$\cdot$8PF$_6$ to a simple one-component exponential.
Figure S18: $^1$H NMR (CD$_3$CN, 500 MHz) spectrum of $6a \cdot 4$BF$_4 \cdot 4$OTf $\cdot 12$PF$_6$

Figure S19: $^{13}$C NMR (CD$_3$CN, 125 MHz) spectrum of $6a \cdot 4$BF$_4 \cdot 4$OTf $\cdot 12$PF$_6$
Figure S20: DOSY (CD$_3$CN, 500 MHz) spectrum of 6a·4BF$_4$·4OTf·12PF$_6$

Figure S21: Fitting of $I/I_o$ for some $^1$H signals of compound 6a·4BF$_4$·4OTf·12PF$_6$ to a simple one-component exponential.
Figure S22: $^1$H NMR (CD$_3$CN, 500 MHz) spectrum of 7a·6BF$_4$·4OTf·16PF$_6$

Figure S23: $^{13}$C NMR (CD$_3$CN, 125 MHz) spectrum of 7a·6BF$_4$·4OTf·16PF$_6$
Figure S24: DOSY (CD$_3$CN, 500 MHz) spectrum of 7a·6BF$_4$·4OTf·16PF$_6$.

Figure S25: Fitting of $I/I_0$ for some $^1$H signals of compound 7a·6BF$_4$·4OTf·16PF$_6$ to a simple one-component exponential.
**Figure S26**: Partial $^1$H NMR (CD$_3$CN, 500 MHz) spectra of: a) 4a·4OTf·4PF$_6$, b) 5a·2BF$_4$·4OTf·8PF$_6$, c) 6a·4BF$_4$·4OTf·12PF$_6$, d) 7a·6BF$_4$·4OTf·16PF$_6$
Figure S27: $^1$H NMR (CD$_3$CN, 500 MHz) spectrum of 5b·14PF$_6$

Figure S28: $^{13}$C NMR (CD$_3$CN, 125 MHz) spectrum of 5b·14PF$_6$
Figure S29: ESI-MS of 5b·14PF$_6$.

Figure S30: Observed (top) and theoretical (bottom) isotopic distribution for the fragment [5b·6PF$_6$]$^+$.
**Figura S31:** $^1$H NMR (CD$_3$CN, 500 MHz) spectrum of $6b$·20PF$_6$

**Figure S32:** $^{13}$C NMR (CD$_3$CN, 125 MHz) spectrum of $6b$·20PF$_6$
**Figure 33**: ESI-MS of $6b \cdot 20PF_6$.

**Figure 34**: Observed (top) and theoretical (bottom) isotopic distribution for the fragment $[6b \cdot 14PF_6]^+$. 
Dynamic formation of dimer, trimer, and tetramer in D$_2$O.

Three stock solutions were prepared: solution A: 20 mM of 1·2NO$_3$, solution B: 20 mM of 2a, solution C: 10 mM of 3a·2BF$_4$

0.3 mL of solution A were mixed with 0.3 mM of solution B. To this solution were added 0.3 mL of A and 0.30 mL of C. This addition was repeated twice. To the resulting solution of tetramer 0.15 mL of solution A and 0.15 mL of solution B were added, and finally 0.45 mL of A and 0.45 mL of B were added. Upon each addition an aliquot was extracted and a $^1$H NMR spectrum was recorded, which were identical to those obtained and reported above.
Diffusion coefficients were calculated according to three models: prolate ellipsoid (left), oblate ellipsoid (center) and cylindrical (right).

\[ D = \frac{k_B T}{6\pi\mu R f} \]

\( k_B \), Boltzmann constant, \( T \), temperature, \( R \), hydrodynamic radius, \( f \) correction factor of each model, and \( \mu \) viscosity (D$_2$O, 1.232x10$^{-3}$ Pa s at 298 K)$^5$

**Model: Prolate ellipsoid**

\[ R = \sqrt[3]{ab^2} \]

\[ f = \frac{P^{-1/3}\sqrt{P^2 - 1}}{\ln (P + \sqrt{P^2 - 1})} \]

Where \( P = a/b \)

---

### Model: Oblate ellipsoid

\[ R = \frac{\sqrt{a^2}}{b} \]

\[ f = \frac{P^{-2/3}\sqrt{P^2 - 1}}{\arctan(\sqrt{P^2 - 1})} \]

\[ P = \frac{a}{b} \]

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### Model: Cylinder

\[ R = \sqrt[3]{3ab^2} \]

\[ f = \frac{(2/3)^{1/3}p^{2/3}}{\ln(2p) - 0.3} \]

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<td>1.97E-10</td>
<td>9.36532E-10</td>
<td>10.329957</td>
<td>1.470748218</td>
<td>1.28625E-10</td>
<td>9.89067299</td>
</tr>
<tr>
<td>6a</td>
<td>3.00E-09</td>
<td>1.97E-10</td>
<td>1.21109E-09</td>
<td>15.1906812</td>
<td>1.642112597</td>
<td>9.90861E-11</td>
<td>10.0501901</td>
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<tr>
<td>7a</td>
<td>3.98E-09</td>
<td>1.97E-10</td>
<td>1.46166E-09</td>
<td>20.1410484</td>
<td>1.78645823</td>
<td>6.785E-11</td>
<td>10.1684499</td>
</tr>
</tbody>
</table>

### Table S1. Diffusion coefficients and dimensions of metallocycles

<table>
<thead>
<tr>
<th>Compound</th>
<th>-logD (m·s⁻¹)</th>
<th>Calculated dimensions A × B</th>
<th>Calculated -logD (m·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>9.64</td>
<td>2.22 × 1.38°</td>
<td>9.64°</td>
</tr>
<tr>
<td>5a</td>
<td>9.8</td>
<td>4.08 × 1.25°</td>
<td>9.86°</td>
</tr>
<tr>
<td>6a</td>
<td>9.9</td>
<td>6.00 × 1.22°</td>
<td>9.93°</td>
</tr>
<tr>
<td>7a</td>
<td>10.0</td>
<td>7.95 × 1.20°</td>
<td>9.99°</td>
</tr>
</tbody>
</table>

| * | A is the distance between the diagonally opposite methylene carbons of the ethylenediamine ligands in the modeled structures. B is the larger distance between opposite methylene groups of the bipyridinium ligands. * Distances measured in the Pd analog. * Value fitted according to oblate ellipsoidal model. * Value fitted according to cylindrical model. |
Computational Methods

Full geometry optimizations of the 4a-7a systems were performed at the HF level by using the Gaussian 03 program package (Revision C.01). In these calculations we used the standard 3-21G basis set for C, H and N atoms, while for Pd the LanL2DZ valence and effective core potential functions were used. The stationary points found on the potential energy surfaces as a result of the geometry optimizations on the 4a and 5a systems have been tested to represent energy minima rather than saddle points via frequency analysis. Due to the considerable effort involved in the calculation of second derivatives, the optimized geometries of 6a and 7a were not characterized through frequency calculations.

Figure 35: Calculated structures of 4a-7a.

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