Supplementary Material (ESI) for Chemical Communications

Diffusion-based studies on the self-stacking and nanorod formation of platinum(II) intercalators

Supplementary information

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Materials and methods

Materials Wilmad 507-PP-7 5mm NMR tubes were purchased from Sigma Aldrich. K_2PtCl_4 was purchased from Precious Metals Online. Deuterium oxide (99.9%) was purchased from Cambridge Isotope Laboratories. 1,5-Cyclooctadiene, 2,2':6',2''-terpyridine, (1*S*,2*S*)-diaminocyclohexane and 5,6-dimethyl-1,10-phenanthroline were purchased from Sigma-Aldrich. All other solvents were of analytical grade or higher and used as received.

Inorganic synthesis [Pt(terpy)Cl]Cl was synthesized in a two step processed using previously published methods.[1, 2] In brief, K_2PtCl_4 was coordinated with 1,5-cyclooctadiene, which was then displaced with the coordination of 2,2':6',2''-terpyridine. The final product was obtained by recrystallisation from H_2O/EtOH. ^1H NMR (400 MHz, D_2O, 20 mM, 25 °C) δ 8.09 (m, 2H); 7.86 (2H, d, J = 8.0 Hz); 7.80 (1H, d, J = 5.0 Hz); 7.37 (1H, t, J = 6.4 Hz). ^{195}Pt NMR (86 MHz, D_2O): -2838 ppm (bs).

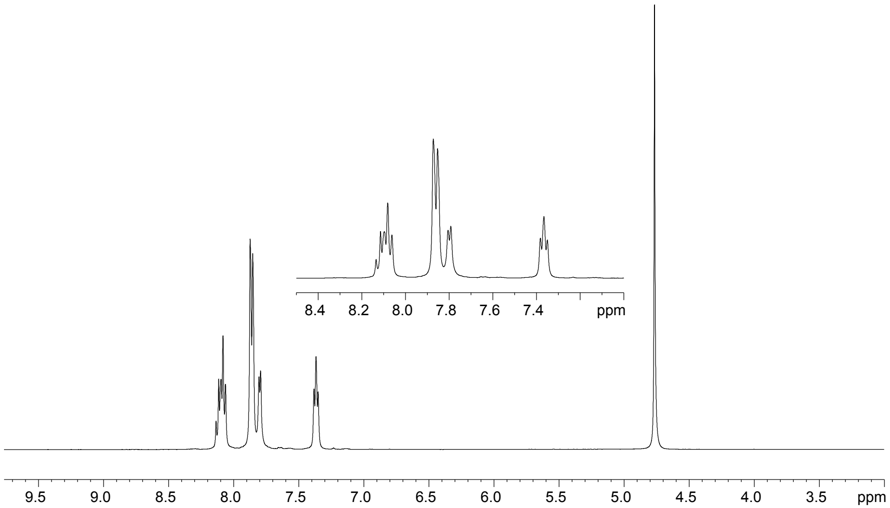


Fig. S1 The ^1H NMR spectrum of $[Pt(terpy)Cl]^+$ (400 MHz, 20 mM, D_2O).

56MESS was synthesised using a previously published method.[3] In brief, K_2PtCl_4 was coordinated with 1*S*,2*S*-diaminocyclohexane, followed by 5,6-dimethyl-1,10-phenanthroline. Excess 5,6-Me_2-phen was removed using a Waters Sep-pak® reverse phase C-18 column. ^1H NMR (400 MHz, D_2O, 20 mM, 25 °C) δ 8.86 (d, 2H, J = 8.9 Hz); 8.83 (d, 2H, J = 5.5 Hz); 8.02 (dd, 2H, J_1 = 8.9 Hz, J_2 = 5.5 Hz); 2.78 (m); 2.55 (s, 3H); 2.30 (m, 1H); 1.73 (m, 1H); 1.56 (m, 1H); 1.31 (m, 1H). ^{195}Pt NMR (86 MHz, D_2O): -2720 ppm (bs).

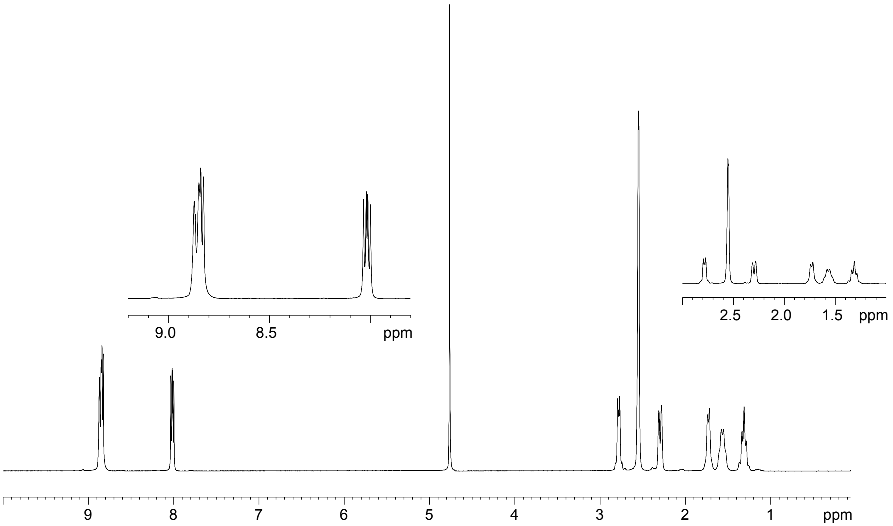


Fig. S2 The ^{1}H NMR spectrum of **56MESS** (400 MHz, 20 mM, D_2O).

Sample preparation Stock solutions of ~ 30-40 mM metal complex and 20 and 200 mM NaCl were prepared in D_2O. Samples containing varying concentration of metal complex were prepared by mixing the stock solution with appropriate amounts of D_2O in 5 mm Wilmad NMR tubes. The volume of metal complex stock was varied to yield solutions of 1-25 mM in a final volume of 600 μL. The volume of NaCl stock was also varied to yield solutions of desired concentration.

PGSE diffusion measurements ^{1}H NMR spectra were recorded out on a Bruker Avance 400 spectrometer, operating at a ^{1}H resonance frequency of 400.13 MHz. Spectra were obtained with a 5-mm BBO probe using a sweep width of 2,400 Hz, an acquisition time of 0.7-1.0 s, a 90° pulse width of 15 μs and a recycle delay of 4 s. A line broadening of 0.5 Hz was applied prior to Fourier transformation. Measurements were performed at either 298 or 310 K. Spectra were internally referenced to the residual HDO peak at 4.77 ppm. More scans were used on samples of low concentration in order to obtain a sufficient signal-to-noise ratio. Diffusion measurements were performed using a modified Hahn spin-echo–based PGSE pulse sequence, optimised to reduce signal loss due to spin–spin relaxation.[4, 5] The separation between the leading edges of the gradient pulses, Δ, which defines the time scale of the diffusion measurement, was set to 10-25 ms. The gradient pulse width, δ, was set to 5-7.5 ms. Echo attenuation of the H5 resonance of $[Pt(terpy)Cl]^+$ and the methyl of **56MESS** (Fig. S3) was measured at 16 different gradient amplitudes (g, between 0-0.41 $T.m^{-1}$) in each diffusion measurement. For a single species undergoing free isotropic diffusion the attenuation (E) of the spin–echo signal is given by:[6]

$$E = e^{-\gamma^2 g^2 \delta^2 D\left(\Delta - \delta/3\right)} \tag{1.1}$$

where γ is the gyromagnetic ratio of the observed nucleus. The diffusion coefficient and the associated error were determined using a nonlinear least squares (NLLS) fit of (1.1) onto the PGSE data using OriginPro 8 (Fig. S4) (OriginLab, MA). In all cases the errors in the diffusion coefficients were less than 1%. The literature states that once gradient calibration errors and temperature fluctuations are taken into account, the true errors are approximately 1%.[7]

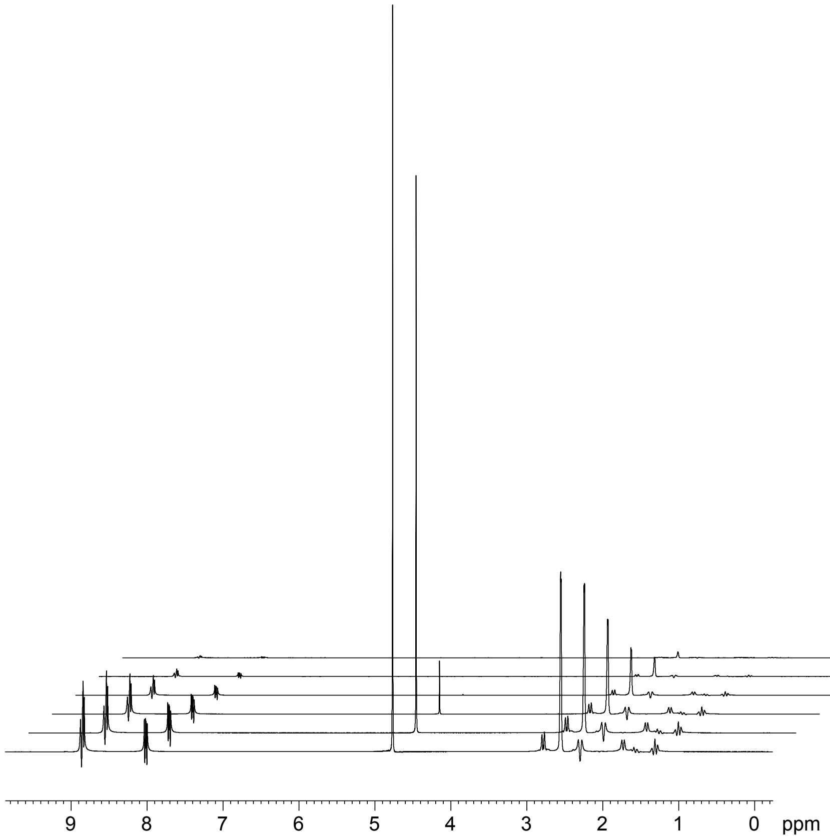


Fig. S3 A Waterfall plot of the ^{1}H NMR signal attenuation of the **56MESS** resonances with increasing gradient strength.

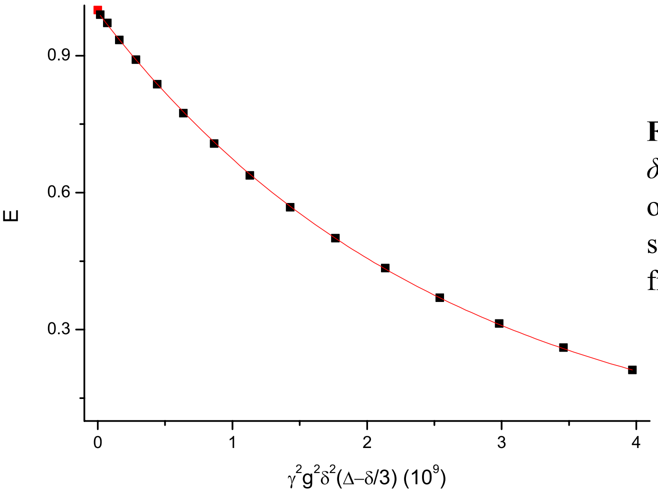


Fig. S4 The signal attenuation *vs.* $\gamma^2 g^2 \delta^2 (\Delta-\delta/3)$ for [Pt(terpy)Cl]$^+$ (2 mM, 25 ºC). The fit of the experimental data to the equation is shown in red. The first point was excluded from all calculations.

Calculation of ellipsoid length

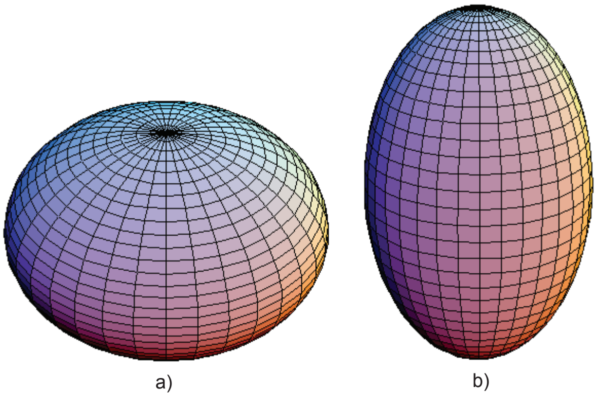


Fig. S5 A three dimensional model of an a) oblate and b) prolate ellipsoid.

The Stokes-Einstein equation relates the diffusion coefficient to the radius and friction coefficient of the molecule

$$D = \frac{kT}{6\pi\eta Rf} \tag{1.2}$$

where k is Boltzmann's constant, T is temperature (K), η is the viscosity of the solvent, R is the radius of a sphere of equal volume, and f is the friction coefficient.

For an oblate ellipsoid the friction coefficient is given by

$$f = \frac{\sqrt{1-p^2}}{p^{1/3}\tan^{-1}(\sqrt{1-p^2}/p)} \tag{1.3}$$

Where $p = b/c < 1$ and $R = (b^2c)^{1/3}$, where b is the semi major axis and c is the semi minor axis.

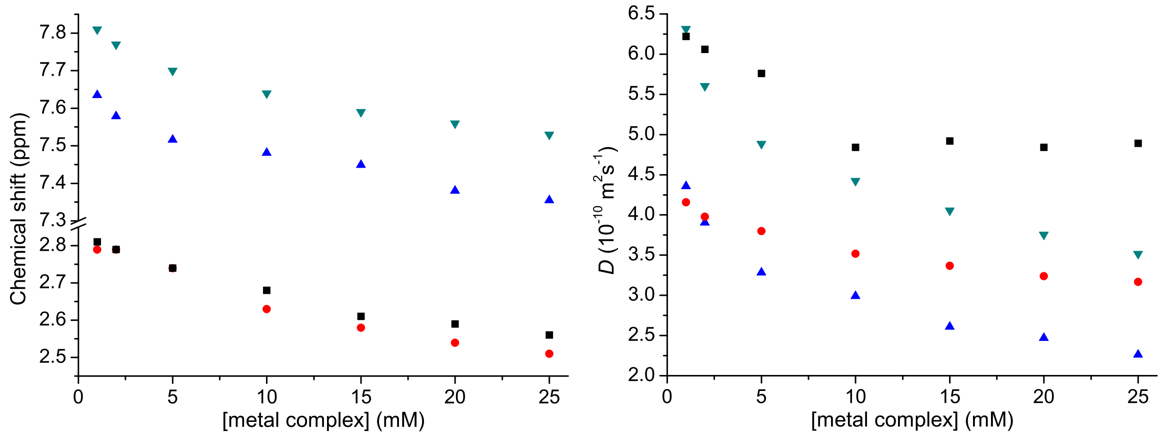
For a prolate ellipsoid the friction coefficient is given by

$$f = \frac{\sqrt{p^2-1}}{p^{1/3}\tanh^{-1}(\sqrt{p^2-1}/p)} \tag{1.4}$$

Where $p = b/c > 1$ and $R = (c^2b)^{1/3}$, where b is the semi major axis and c is the semi minor axis.

The value of c was estimated as 0.75 nm (radial diameter ~ 1.5 nm) for **56MESS** and 0.50 nm (radial diameter ~ 1.0 nm) for $[Pt(terpy)Cl]^+$ based on measurements from X-ray crystal data. Fitting of the data was first attempted using the oblate model. The values of b were then modified (using MathCad 14) until the calculated and experimental diffusion coefficients were in agreement. If the calculated diffusion coefficient could not be reduced to that of the experimental value with $b < c$, the prolate model was used.

The number of molecules in the aggregate was estimated assuming a standard π-π stacking distance of 0.34 nm. The oblate model was used for all calculations of **56MESS** nanorod dimensions. The prolate model was used for the majority of calculations of $[Pt(terpy)Cl]^+$ nanorod dimensions at 25 °C (except 1 and 2 mM). The oblate model was used for the majority of calculations at 37 °C (except 25 mM).



a)

b)

Fig. S6 The a) chemical shift change and b) the diffusion coefficient of the methyl resonance of **56MESS** (■ 37 ºC, ● 25 ºC) and the H5 resonance of [Pt(terpy)Cl]$^+$ (▼ 37 ºC, ▲ 25 ºC) with increasing concentration.

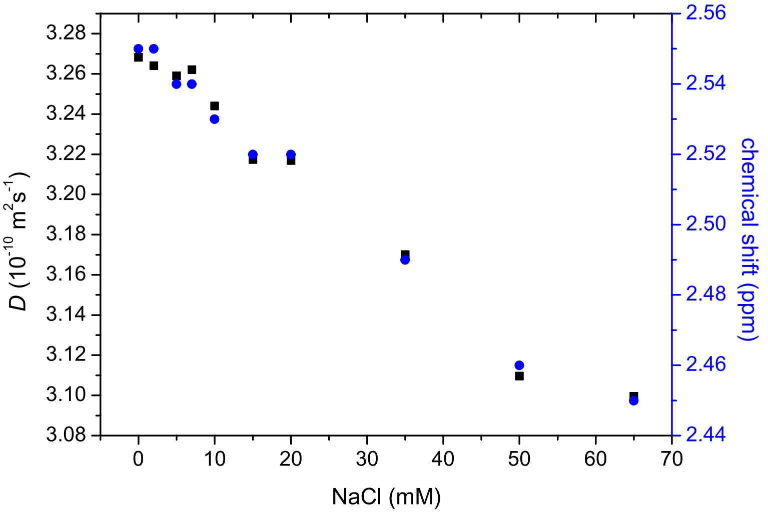


Fig. S7 The diffusion coefficient of 20 mM **56MESS** (■) decreases with increased NaCl concentration. The decrease in chemical shift of the methyl resonance (●) follows a similar trend.

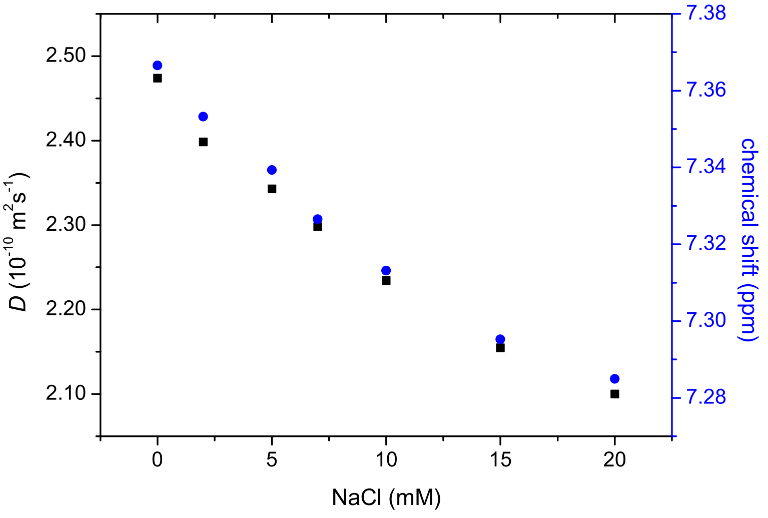


Fig. S8 The diffusion coefficient of 20 mM [Pt(terpy)Cl]$^+$ (■) decreases with increased NaCl concentration. The decrease in chemical shift of the H5 resonance (●) follows a similar trend.

References

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