Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Understanding the role of the flexible linker through kinetics and mechanistic study of Pt(II) amphiphiles derived from a bis(2-pyridylmethyl)amine chelate headgroup.

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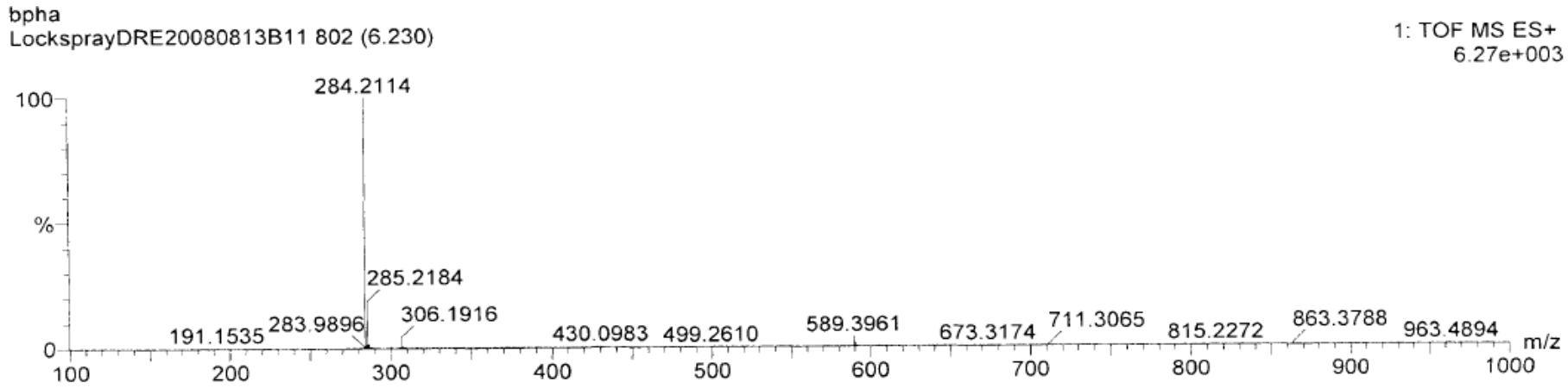
Table SI 1 Summary of the wavelengths (nm) used for monitoring the reactions between a series of Pt(II) mononulcear complexes with bis(2-pyridylmethyl) chelates and thiourea nucleophiles.

Complex	nu	Wavelength (λ), nm
bpma	tu dmtu tmtu	276 276 300
bpea	tu dmtu tmtu	276 276 330
bppa	tu dmtu tmtu	276 276 326
bpba	tu dmtu tmtu	283 286 325
bpbta	tu dmtu tmtu	288 286 320
bpha	tu dmtu tmtu	308 307 336
bpda	tu dmtu tmtu	300 305 300



Minimum:				-1.5			
Maximum:		5.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
284.2114	284.2127	-1.3	-4.6	7.5	181.8	3.8	C18 H26 N3

Figure SI 1a Low resolution ES^+ mass spectrum of *N,N*-bis(2-pyridylmethyl)hexylamine (**L5**).

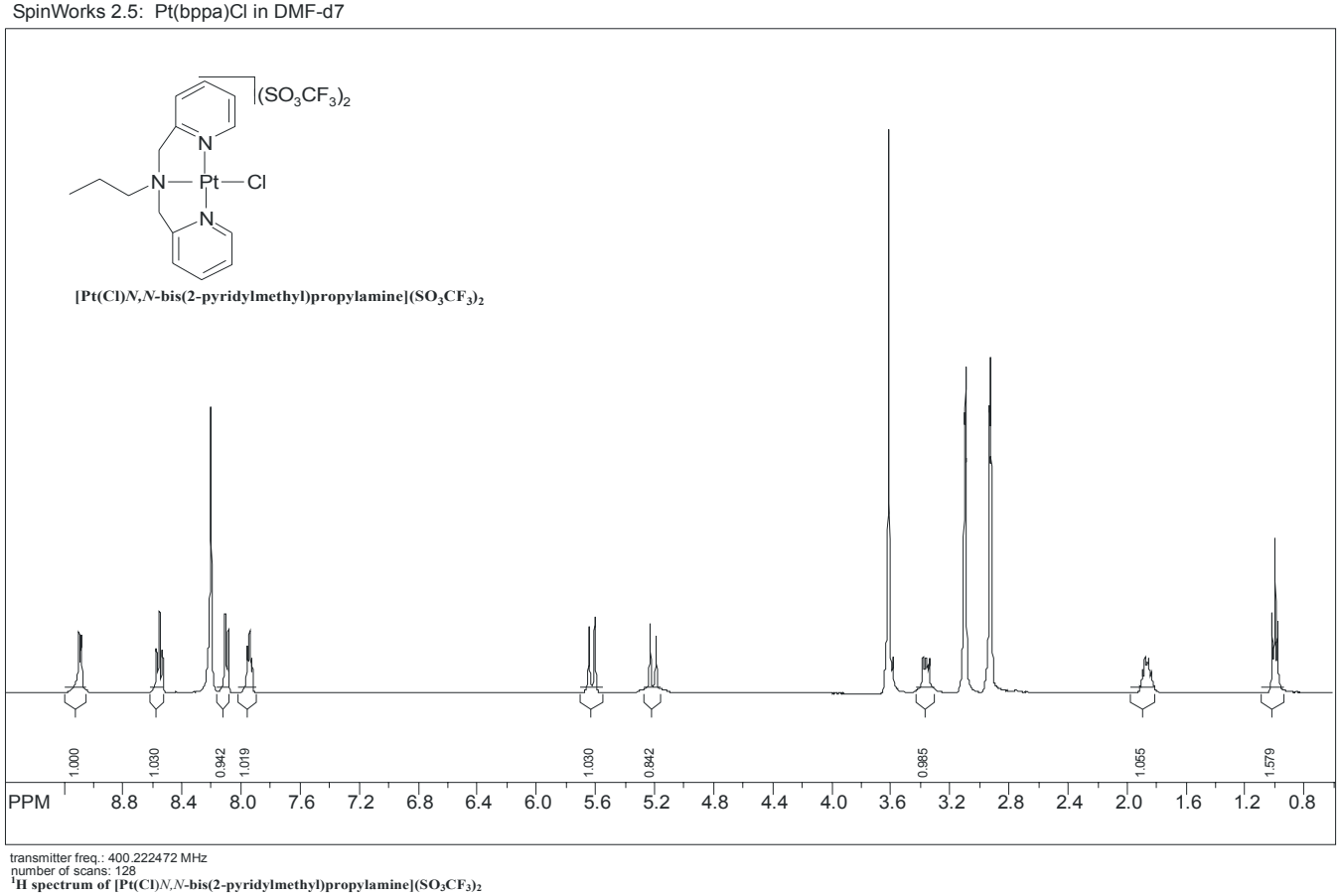


Figure SI 1b ^{1}H Spectrum of [Pt(Cl)*N,N*-bis(2-pyridylmethyl)propylamine]$(SO_3CF_3)_2$.

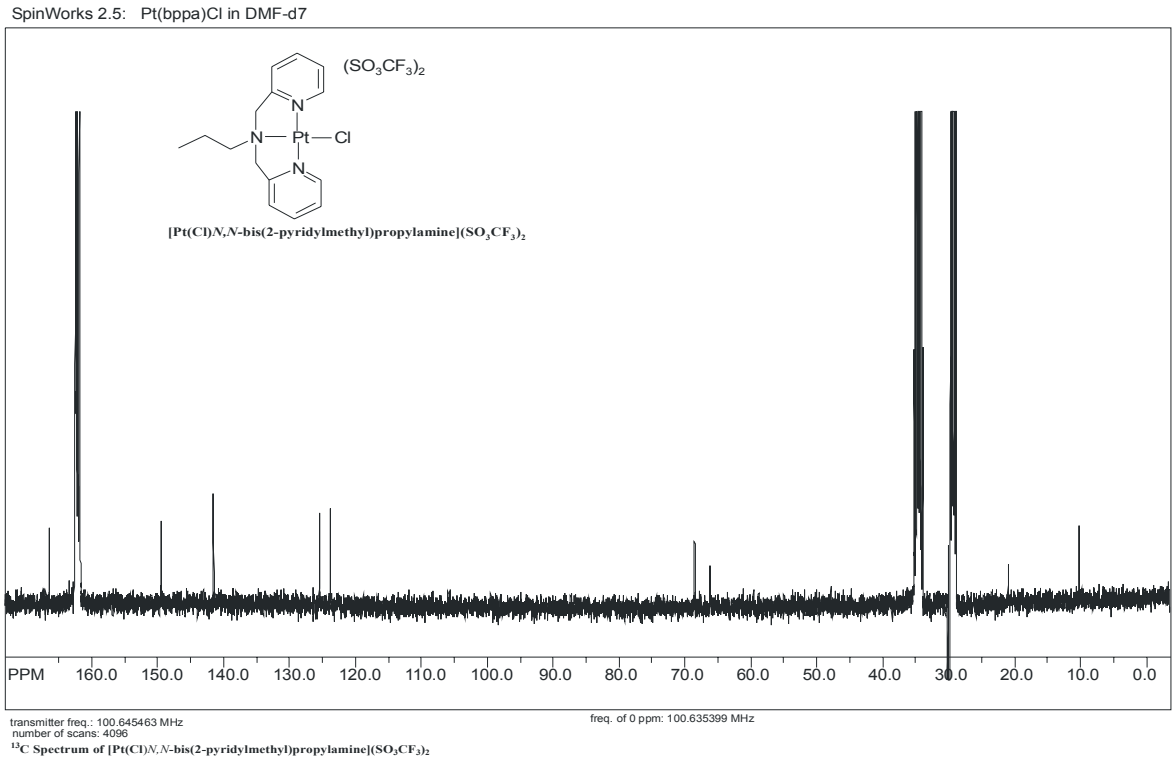


Figure SI 1c ^{13}C Spectrum of [Pt(Cl)*N,N*-bis(2-pyridylmethyl)propylamine]$(SO_3CF_3)_2$.

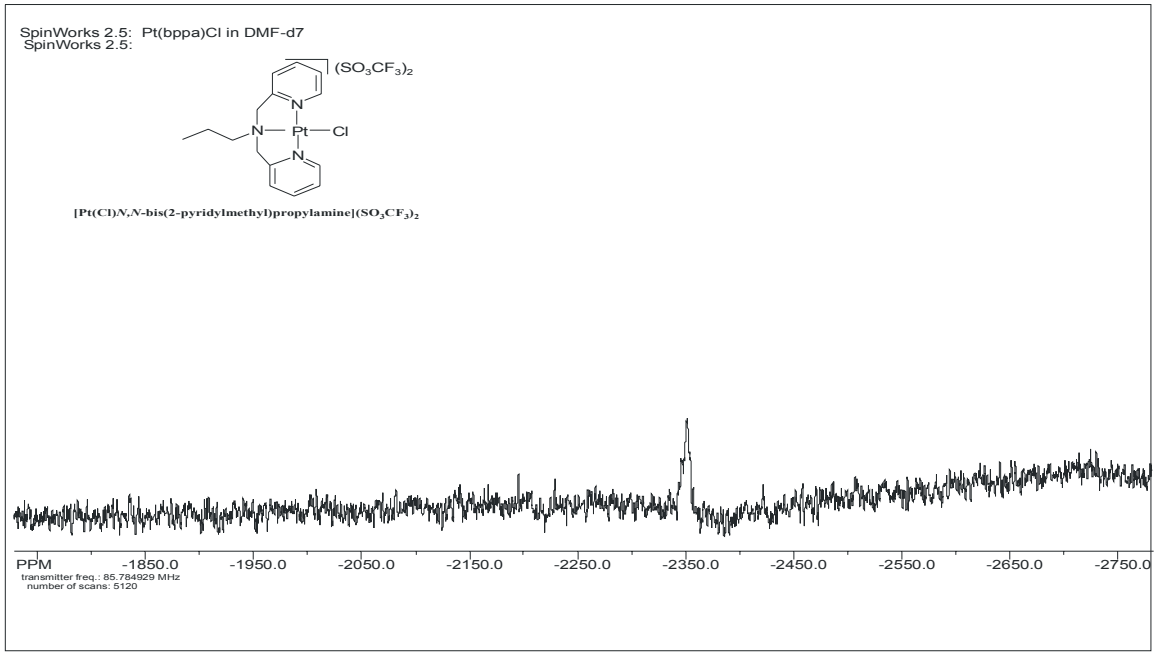


Figure SI 1d ^{195Pt} Spectrum of [Pt(Cl)*N,N*-bis(2-pyridylmethyl)propylamine]$(SO_3CF_3)_2$.

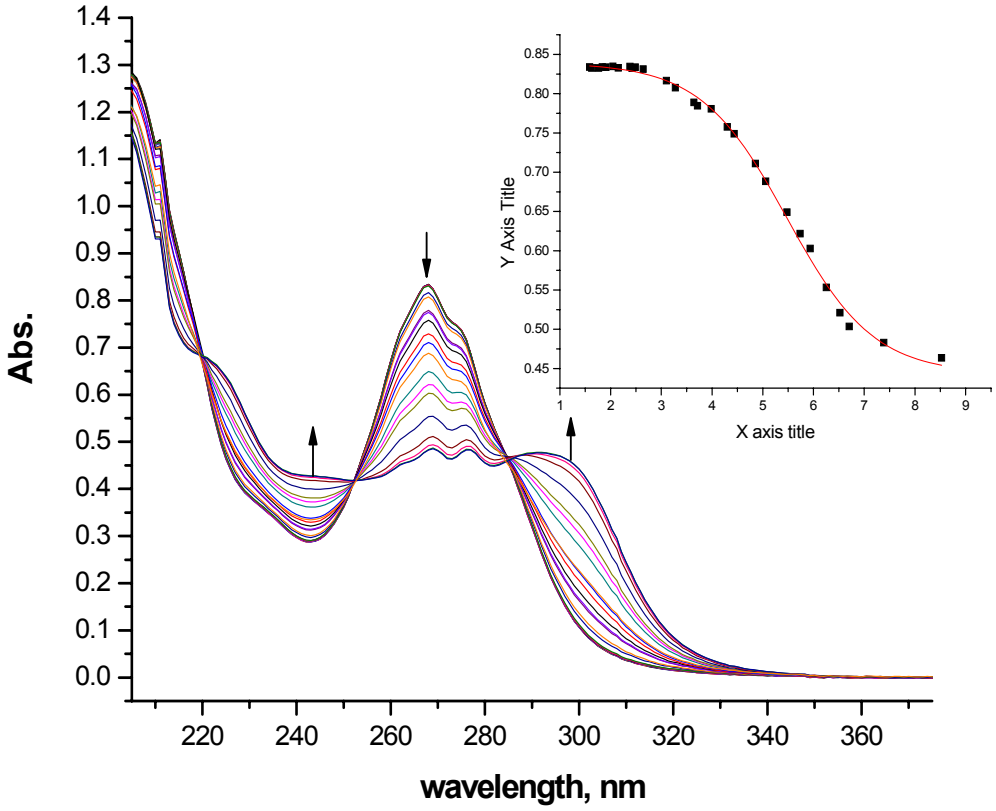


Figure SI 2 UV-visible spectra for the titration of 0.1 mM **bpea** with NaOH, pH range 2- 9, T = 298 K. Inset is the titration curve at 267 nm.

Table SI 2a Average observed rate constants, $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **bptba** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	**[dmtu], M**	$k_{obs\ 1}$, s^{-1}	**[tmtu], M**	$k_{obs\ 1}$, s^{-1}
5.3366E-4	0.562	5.36E-4	0.5645	5.36E-4	0.1517
0.00107	1.117	0.00107	1.135	0.00107	0.3012
0.0016	1.619	0.00161	1.572	0.00161	0.4554
0.00213	2.166	0.00214	2.153	0.00214	0.6032
0.00267	2.633	0.00268	2.608	0.00268	0.7561

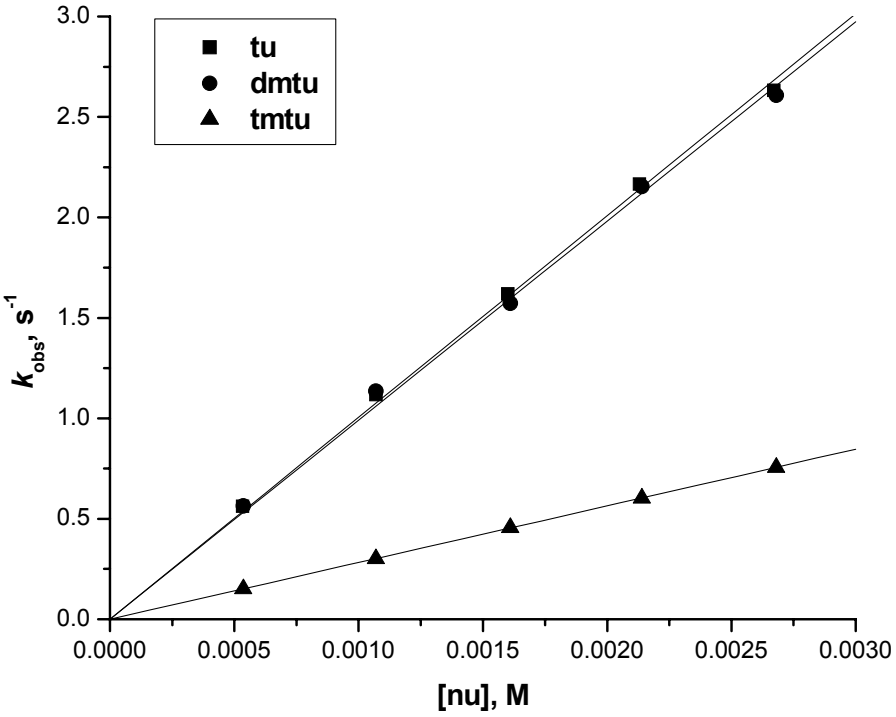


Figure SI 3a Concentration dependence of $k_{obs.(1^{st})}$, s^{-1}, for the substitution of the aqua ligand in **bptba** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

Table SI 2b Average observed rate constants, $k_{obs.(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **bptba** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	**[dmtu], M**	$k_{obs\ 1}$, s^{-1}	**[tmtu], M**	$k_{obs\ 1}$, s^{-1}
5.346E-4	0.00612	5.33E-4	0.00578	5.33E-4	0.0018
0.00107	0.0121	0.00107	0.0116	0.00107	0.00406
0.0016	0.01834	0.0016	0.0174	0.0016	0.00595
0.00214	0.02424	0.00213	0.02314	0.00213	0.00801
0.00267	0.0306	0.00267	0.0288	0.00267	0.00998

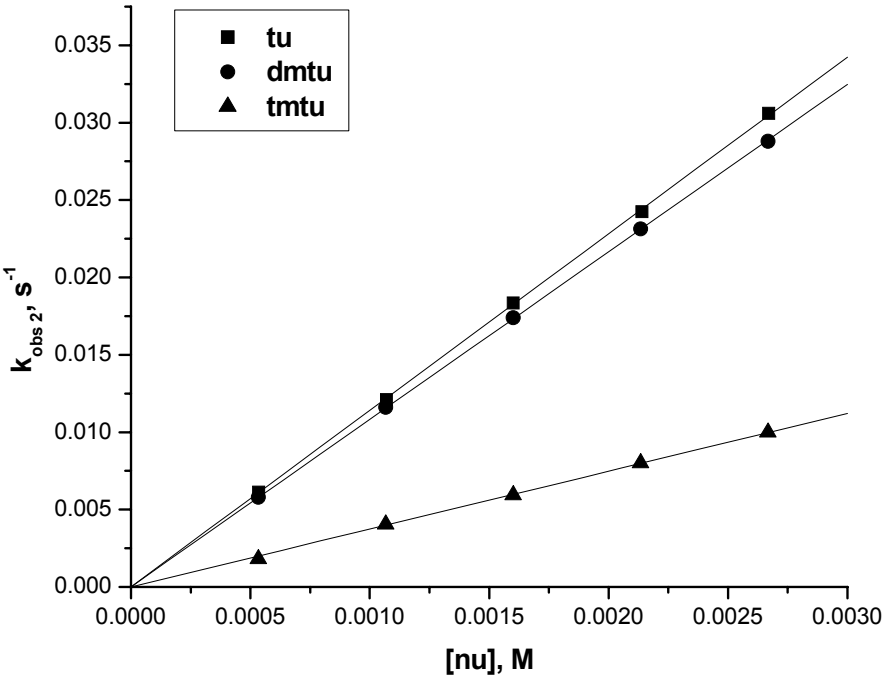


Figure SI 3b Concentration dependence of $k_{obs.(1^{st})}$, s^{-1}, for the substitution of the aqua ligand in **bptba** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

Table SI 2c Temperature dependence of $k_{2(1^{st}),}$ M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **bptba** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	**ln(*k*/T)**	**1/T, K^{-1}**	**ln(*k*/T)**	**ln(*k*/T)**	**ln(*k*/T)**
0.00325	1.541	0.00325	1.613	0.00325	0.2078
0.0033	1.337	0.0033	1.412	0.0033	-0.1072
0.00335	1.067	0.00335	1.1829	0.00335	-0.4222
0.00341	0.7764	0.00341	0.919	0.00341	-0.7307
0.00347	0.5587	0.00347	0.7219	0.00347	-1.035

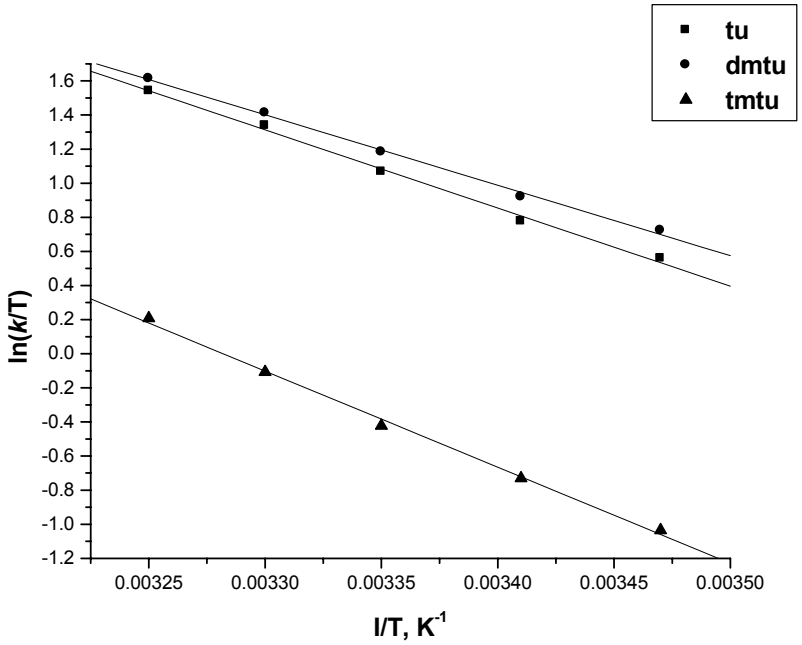


Figure SI 3d Temperature dependence of $k_{2(1^{st})}$, M^{-1} s^{-1}, for the simultaneous displacement of the first aqua ligand in **bptba** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

Table SI 2d Temperature dependence of $k_{2(2^{nd})}$, M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bptba** by thiourea, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	-2.33	0.00325	-2.63	0.00325	-3.79
0.0033	-2.594	0.0033	-2.924	0.0033	-4.072
0.00335	-2.896	0.00335	-3.226	0.00335	-4.382
0.00341	-3.281	0.00341	-3.581	0.00341	-4.74
0.00347	-3.62	0.00347	-3.92	0.00347	-5.09

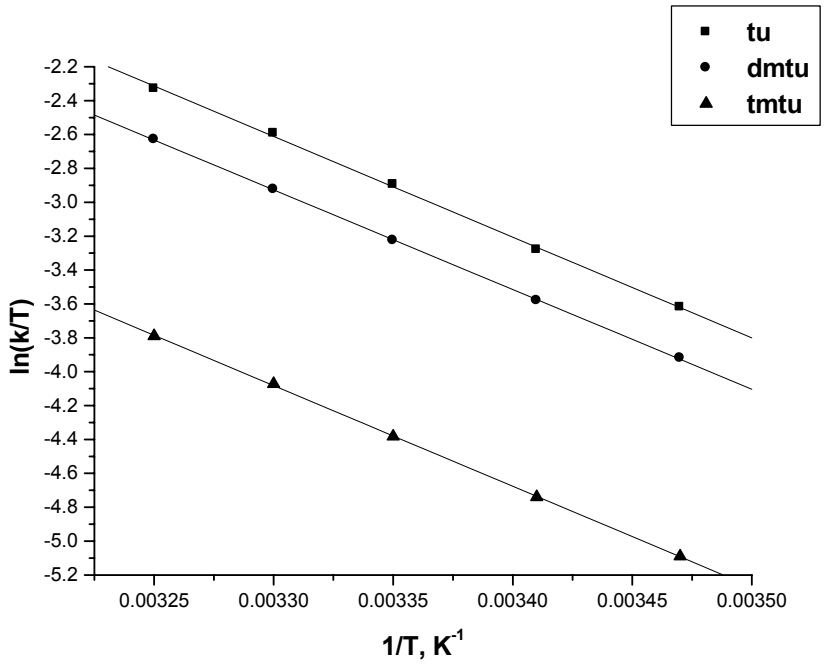


Figure SI 3e Temperature dependence of $k_{2\ (2^{nd}),}$ M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bptba** by thiourea, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

Table SI 3a Average observed rate constants, $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **bpea** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	**[dmtu], M**	$k_{obs\ 1}$, s^{-1}	**[tmtu], M**	$k_{obs\ 1}$, s^{-1}
5.346E-4	0.2719	5.346E-4	0.3313	5.336E-4	0.1169
0.00107	0.5449	0.00107	0.6673	0.00107	0.2323
0.0016	0.8151	0.0016	0.9914	0.0016	0.3477
0.00214	1.048	0.00214	1.318	0.00213	0.4615
0.00267	1.347	0.00267	1.638	0.00267	0.5792

Table SI 3b Average observed rate constants, $k_{obs.(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **bpea** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	**[dmtu], M**	$k_{obs\ 1}$, s^{-1}	**[tmtu], M**	$k_{obs\ 1}$, s^{-1}
5.333E-4	0.00254	5.334E-4	0.00303	5.334E-4	0.00144
0.00107	0.00514	0.00107	0.00638	0.00107	0.00273
0.0016	0.00758	0.0016	0.0091	0.0016	0.00399
0.00213	0.01054	0.00213	0.01242	0.00213	0.00551
0.00266	0.01357	0.00267	0.0153	0.00267	0.00687

Table SI 3c Temperature dependence of $k_{2(1^{st}),}$ M^{-1} s^{-1}, for the simultaneous

displacement of the aqua ligands in **bpea** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	0.9559	0.00325	1.155	0.00325	0.2492
0.0033	0.755	0.0033	0.9367	0.0033	-0.0284
0.00335	0.5278	0.00335	0.7203	0.00335	-0.3174
0.00341	0.2808	0.00341	0.4787	0.00341	-0.6556
0.00347	0.036	0.00347	0.2091	0.00347	-0.9644

Table SI 3d Temperature dependence of $k_{2(2^{nd})}$, M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bpea** by thiourea, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)	1/T, K^{-1}	ln(*k*/T)
0.00325	-3.447	0.00325	-3.351	0.00325	-4.163
0.0033	-3.775	0.0033	-3.648	0.0033	-4.46
0.00335	-4.054	0.00335	-3.913	0.00335	-4.763
0.00341	-4.45	0.00341	-4.244	0.00341	-5.14
0.00347	-4.761	0.00347	-4.563	0.00347	-5.489

Table SI 4a Average observed rate constants, $k_{obs.(1^{st})}$, s^{-1}, for the simultaneous displacement of the aqua ligands in **bppa** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	[dmtu], M	$k_{obs\ 1}$, s^{-1}	[tmtu], M	$k_{obs\ 1}$, s^{-1}
5.333E-4	0.2732	5.3369E-4	0.3549	5.3519E-4	0.1052
0.00107	0.5463	0.00107	0.7126	0.00107	0.209
0.0016	0.8153	0.0016	1.08	0.00161	0.3105
0.00213	1.134	0.00213	1.426	0.00214	0.4222
0.00266	1.418	0.00267	1.799	0.00268	0.526

Table SI 4b Average observed rate constants, $k_{obs.(2^{nd})}$, s^{-1}, for the dechelation of the pyridyl units in **bppa** by thiourea nucleophiles, pH = 2.0, T = 298 K, I = 0.02 M {0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$}.

[tu], M	$k_{obs\ 1}$, s^{-1}	[dmtu], M	$k_{obs\ 1}$, s^{-1}	[tmtu], M	$k_{obs\ 1}$, s^{-1}
5.333E-4	0.00254	5.333E-4	0.00306	5.3519E-4	0.00137
0.00107	0.00514	0.00107	0.00638	0.00107	0.00258
0.0016	0.00758	0.0016	0.00922	0.00161	0.0039
0.00213	0.01054	0.00213	0.0124	0.00214	0.00532
0.00266	0.01337	0.00266	0.0155	0.00268	0.00659

Table SI 4c Temperature dependence of $k_{2(1^{st})}$, M^{-1} s^{-1}, for the simultaneous displacement of the aqua ligands in **bppa** by thiourea nucleophiles, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	**ln(*k*/T)**	**1/T, K^{-1}**	**ln(*k*/T)**	**1/T, K^{-1}**	**ln(*k*/T)**
0.00325	0.9706	0.00325	1.155	0.00325	0.2078
0.0033	0.771	0.0033	0.9367	0.0033	-0.1072
0.00335	0.5761	0.00335	0.7203	0.00335	-0.4222
0.00341	0.3109	0.00341	0.4787	0.00341	-0.7307
0.00347	0.0109	0.00347	0.2091	0.00347	-1.035

Table SI 4d Temperature dependence of $k_{2(2^{nd})}$, M^{-1} s^{-1}, for the dechelation of the pyridyl units in **bppa** by thiourea, pH = 2.0, I = 0.02 M (0.01 M CF_3SO_3H, adjusted with $Li(SO_3CF_3)$).

1/T, K^{-1}	**ln(*k*/T)**	**1/T, K^{-1}**	**ln(*k*/T)**	**1/T, K^{-1}**	**ln(*k*/T)**
0.00325	-3.531	0.00325	-3.321	0.00325	-4.062
0.0033	-3.835	0.0033	-3.633	0.0033	-4.39
0.00335	-4.143	0.00335	-3.948	0.00335	-4.73
0.00341	-4.53	0.00341	-4.318	0.00341	-5.109
0.00347	-4.836	0.00347	-4.658	0.00347	-5.497

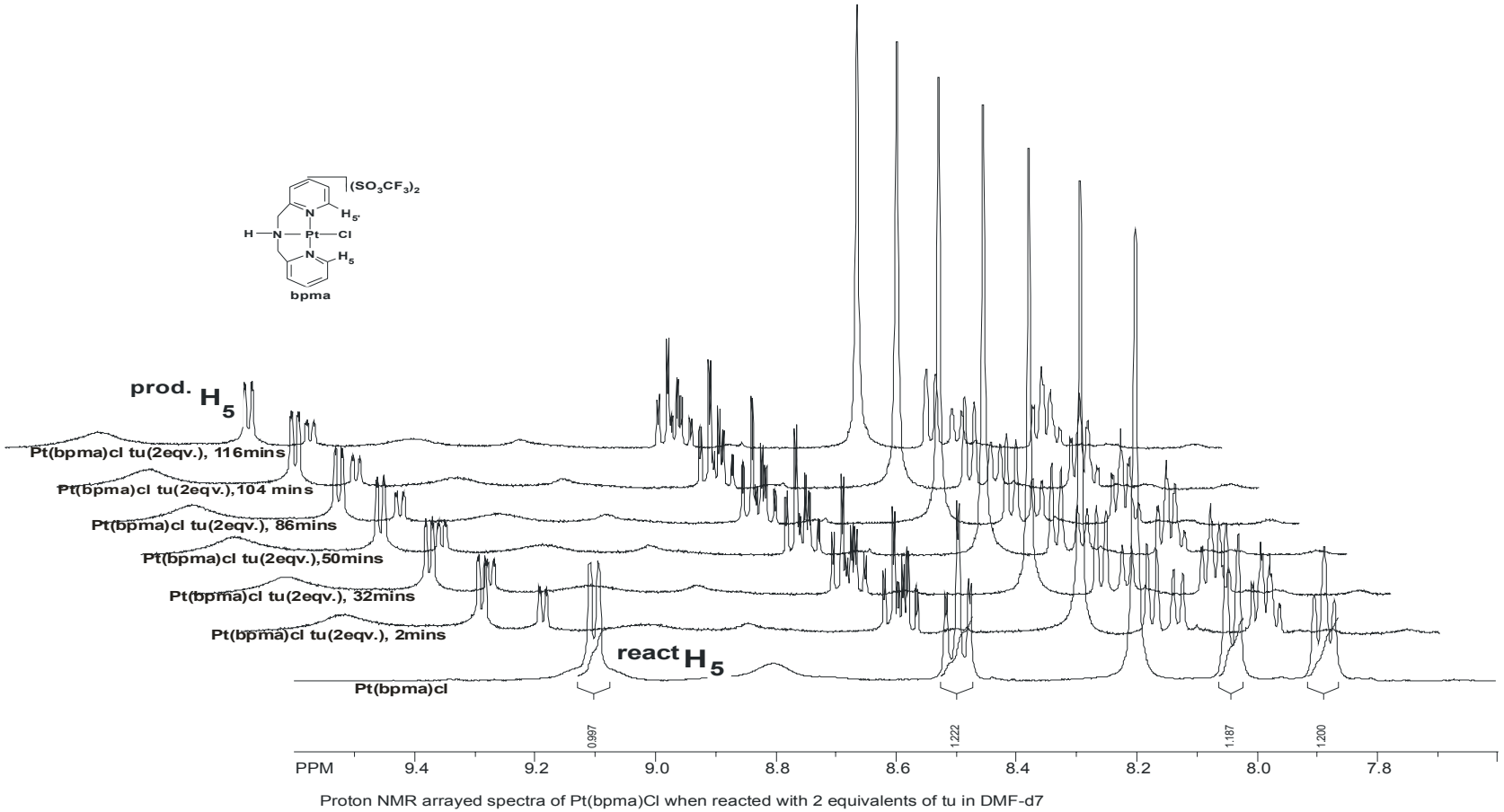
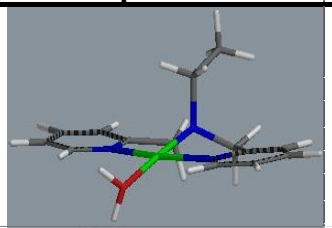
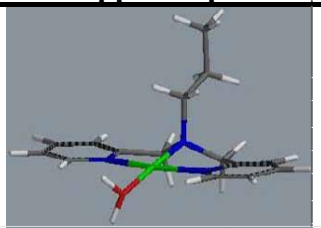
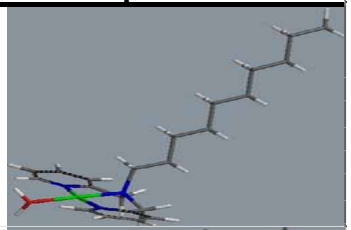


Figure SI 4 NMR (500 MHz) spectra array of **bpma-Cl** (showing only the aromatic region) acquired during its reaction with two equivalents of thiourea (tu) in DMF-*d*7 at 298 K. The doublet at δ = 9.12 ppm corresponds to substituted product.

Table SI 5 A comparative depiction of the DFT-calculated minimum energy structures of Pt(II) amphiphiles and their analogous dinuclears.

	bpea/En	**bppa/Prop**	**bpda/Dec**
Monomeric complex			
Dinuclear complex