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Supporting Information

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Strong Means Slow: Dynamic Contributions to the Bulk Mechanical Properties of Supramolecular Networks

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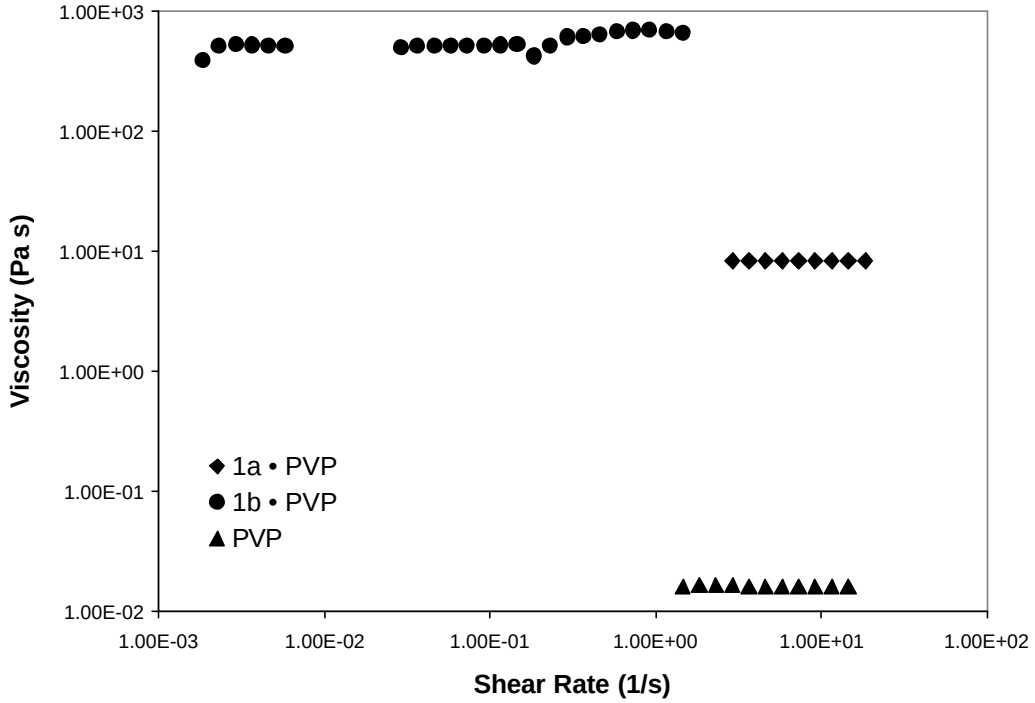


Figure 1. Viscosity vs. steady shear rate for 1·PVP DMSO solutions (5% functional group equivalence, 100 mg ml^{-1}). Gaps in the data reflect the limits of the range accessible in the rheometer.

NMR Kinetic Studies EXSY data was acquired using a 500 MHz Varian NMR for **2b** and **2c**. The following equation[1] was used to calculate *k* (I_{AA} and I_{AB} are the volume integrals of the diagonal and cross peaks, respectively):

$$I_{AA}/I_{AB} = [\ 1 + \exp(-2kt_m)]/[\ 1 - \exp(-2kt_m)].$$

For **2b** (20mM **2b**, 43mM **3**), the intensity exchange of the bound and free pincer methylene peaks at 4.17 and 4.03 ppm, respectively, were monitored. For **2c** (20mM **2c**, 43mM **3**), the intensity exchange of the bound and free pyridine peak at 8.55 and 8.97 ppm, respectively, were monitored. The exchange rate for **2d** was acquired by monitoring by ^{1}H NMR (10mM **2d,** 20mM **3)** the replacement of bound pyridine by excess pyridine-d_5 (5μL). The decay of the protonated signal was then fit to the following equation[2]:

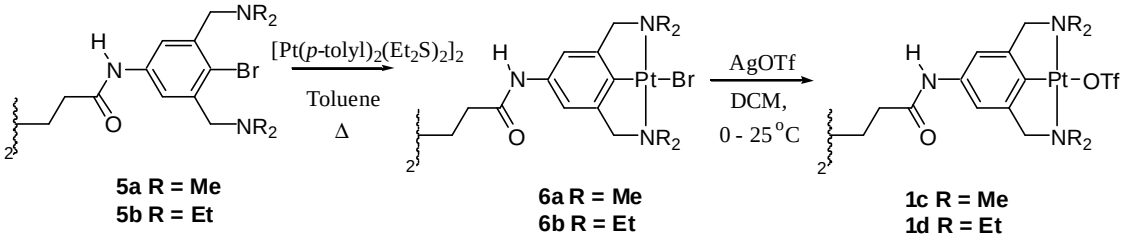
$$\ln[(R_t - R_{inf})/(R_t + 1)] = -k\ t$$

where R_t represents the ratio of bound to free peak areas (8.86 and 8.56 respectively) of pyridine at time t and R_{inf} represents the same ratio of peak areas at infinite time.

Representative sample preparation. 5% **1a**·PVP. Poly-4-vinylpyridine, (MW 60,000, 200mg, 3.3 μmol) was dissolved in 2 mL of DMSO. To this mixture was added 480 μL of a 100 mg mL^{-1} solution of **1a** in DMSO. The mixture was then heated to 80 ^{o}C and cooled, 3 times.

Rheological Measurements. All rheological data were obtained using a Bohlin VOR Rheometer with a concentric cylinder geometry C-14 (fixed bob and rotating cup). Sample (~2 mL) was loaded into the cup, with heating when necessary to allow flow, and the bob was lowered into the cup. The sample was allowed to equilibrate to 20^o C. Oscillatory data were obtained at an amplitude of 50%.

Materials. All starting metal complexes were purchased from Strem. Poly(4-vinylpyridine) and silver triflate were purchased from Aldrich. All other starting materials were purchased from Acros and used without further purification. ^{1}H NMR spectra were acquired using a Varian 400 MHz NMR. ^{13}C NMR were taken at 75 MHz. Mass spectra were acquired by George Dubay at Duke University.



Scheme 1. Synthesis of Pt-Pincer Monomers

Synthesis. Compounds **5a** and **5b** were synthesized according to literature procedures.[3] Compounds **1a** and **1b** were synthesized as previously reported.[4] $[Pt(p\text{-tolyl})_2(Et_2S)_2]_2$ was synthesized according to literature procedures.[5]

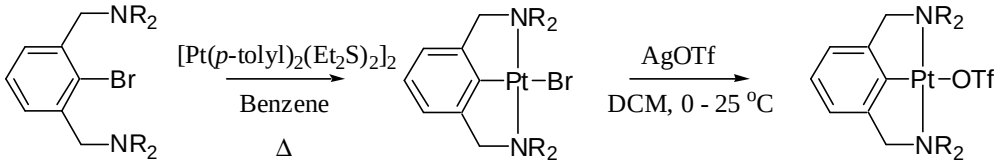
Pt-Me-Br Monomer (6a).[6] 0.500g of **5a** was dissolved in 50 mL of Benzene. 0.400g of $[Pt(p\text{-tolyl})_2(Et_2S)_2]_2$ was added and the solution was stirred and heated to 80° C overnight. The solution was then filtered through celite and washed with benzez until yellow color on celite was washed through. The celite was then washed with chloroform into a clean flask. The chloroform solution was then reduced to volume under vacuum and the product was purified using flash chromatography with chloroform and 4% methanol. Yield 10%. ^{1}H NMR ($CDCl_3$) δ 7.54 (s, 2H), 7.03 (s, 4H), 3.94 (s, 8H), 3.02 (s, 24H), 2.36 (s, 4H), 1.77 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 171, 144, 134, 113, 55, 37, 25.

MS (FAB) *m/z* 992.2 (M-Br $^{+}$, $C_{30}H_{46}N_6O_2BrPt_2$, calcd. 992.02). HRMS could not be obtained.

Pt-Et-Br Monomer (6b).[6] Compound was synthesized according to the procedure for **6a**. Yield 12%. ^{1}H NMR ($CDCl_3$) δ 7.65 (s, 2H), 6.93 (s, 4H), 3.96 (s, 8H), 3.46 (m, 8H), 2.81 (m, 8H), 2.34 (s, 4H), 1.74 (s,4H), 1.46 (t, J=7.2, 24H). ^{13}C NMR ($CDCl_3$) δ 171, 145, 140, 133, 111, 69, 60, 37, 25, 13. HRMS (FAB) *m/z* 1101.3373 (M-Br $^{+}$, $C_{38}H_{62}N_6O_2BrPt_2$, calcd. 1101.3371).

Pt-Me-OTf Monomer (1c).[7] 0.071g of **6a** was dissolved in DCM and placed in an ice bath and stirred. 0.034g of AgOTf was added and the solution was allowed to warm to room temperature overnight. The solution was filtered and reduced to volume under vacuum. Yield 90%. ^{1}H NMR (*d*-DMSO) δ 9.71 (s, 2H), 7.16 (s, 4H), 4.15 (s, 8H), 2.93 (s, 24H), 2.27 (s, 4H), 1.58 (s, 4H). ^{13}C NMR (*d*-DMSO) δ 171, 144, 122, 119, 111, 76, 54, 36, 25. MS (FAB) *m/z* 1061.2 (M-OTf^{+}, $C_{31}H_{46}N_6O_5F_3SPt_2$, calcd. 1062.1). HRMS could not be obtained.

Pt-Et-OTf Monomer (1d).[7] Compound was synthesized according to the procedure for **1c**. Yield 90%. ^{1}H NMR (*d*-DMSO) δ 9.61 (s, 2H), 6.99 (s, 4H), 4.06 (s, 8H), 3.03 (m, 8H), 2.86 (m, 8H), 2.24 (s, 4H), 1.56 (s,4H), 1.41 (t, J=7.2, 24H). ^{13}C NMR (*d*-DMSO) δ 170, 145, 136, 110, 69, 58, 36, 25, 13. MS (FAB) *m/z* 1173.3 (M-OTf^{+}, $C_{39}H_{64}N_6O_5F_3SPt_2$, calcd. 1176.32). HRMS could not be obtained.



7a R = Me **8a R = Me** **2c R = Me**
7b R = Et **8b R = Et** **2d R = Et**

Scheme 2. Synthesis of functional groups for kinetic and thermodynamic studies

Compounds **7a** and **7b** were synthesized according to literature procedures.[8]

Pt-Methyl-Br Pincer Complex (8a).[8] 0.110g of **7a** was dissolved in 20 ml of benzene. 0.212g of [Pt(*p*-tolyl)$_2$(Et$_2$S)$_2$]$_2$ was added to the solution and the mixture was stirred and heated to 70ºC overnight. The solution was then filtered through celite and reduced to volume under vacuum. Product was then purified using flash chromatography with CH_3Cl/5%MeOH as the solvent. Yield 53%. ^{1}H NMR ($CDCl_3$) δ 6.98 (t, J=7.60, 1H), 6.79 (d, J=7.20, 2H), 3.99 (s, 4H), 3.08 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 147, 143, 124, 119, 55. HRMS (FAB) *m/z* 464.0359 (M^+, $C_{12}H_{19}N_2BrPt$, calcd. 464.0358).

Pt-Ethyl-Br Pincer Complex (8b).[8] Compound was synthesized according to the procedure for **8a**. Yield 46%. ^{1}H NMR ($CDCl_3$) δ 6.93 (t, J=7.60, 1H), 6.71 (d, J=7.60, 2H), 4.03 (s, 4H), 3.51 (m, 4H), 2.87 (m, 4H), 1.50 (t, J=7.20, 12H). ^{13}C NMR ($CDCl_3$) δ 145, 144, 123, 118, 70, 60, 13. HRMS (FAB) *m/z* 521.1004 (M^+, $C_{16}H_{27}N_2BrPt$, calcd. 521.1007).

Pt-Methyl-OTf Pincer Complex (2c).[7] 0.101g of **8a** was dissolved in 20 mL of dry DCM and placed into an ice bath. While stirring, 0.060g of AgOTf was added to the solution. The solution was removed from the ice bath and warmed to room temperature overnight. The solution was then filtered and reduced to volume under vacuum. Yield 85%. ^{1}H NMR ($CDCl_3$) δ 6.99 (t, J=7.20, 1H), 6.78 (d, J=7.60, 2H,), 4.00 (s, 4H), 3.02 (t, J=6.8, 12H). ^{13}C NMR ($CDCl_3$) δ144, 125, 120, 76, 54. HRMS (FAB) *m/z* 385.1164 (M-OTf $^{+}$, $C_{12}H_{19}N_2Pt$, calcd. 385.1175).

Pt-Ethyl-OTf Pincer Complex (2d).[7] Compound was synthesized according to the procedure for **2c**. Yield 87%. ^{1}H NMR ($CDCl_3$) δ 6.94 (t, J=7.60, 1H), 6.71 (d, J=7.20, 2H), 4.038 (s, 4H), 3.33 (m, 4H), 2.91 (m, 4H), 1.51 (t, J=7.20, 12H). ^{13}C NMR ($CDCl_3$) δ 145, 124, 119, 69, 59, 13. HRMS (FAB) *m/z* 592.1428 (M^+, $C_{17}H_{29}N_2O_3F_3SPt$, calcd. 592.1422).

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