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Electronic Supporting Information for:

Chemoresponsive Viscosity Switching of a Metallo-Supramolecular Polymer Network Near the Percolation Threshold

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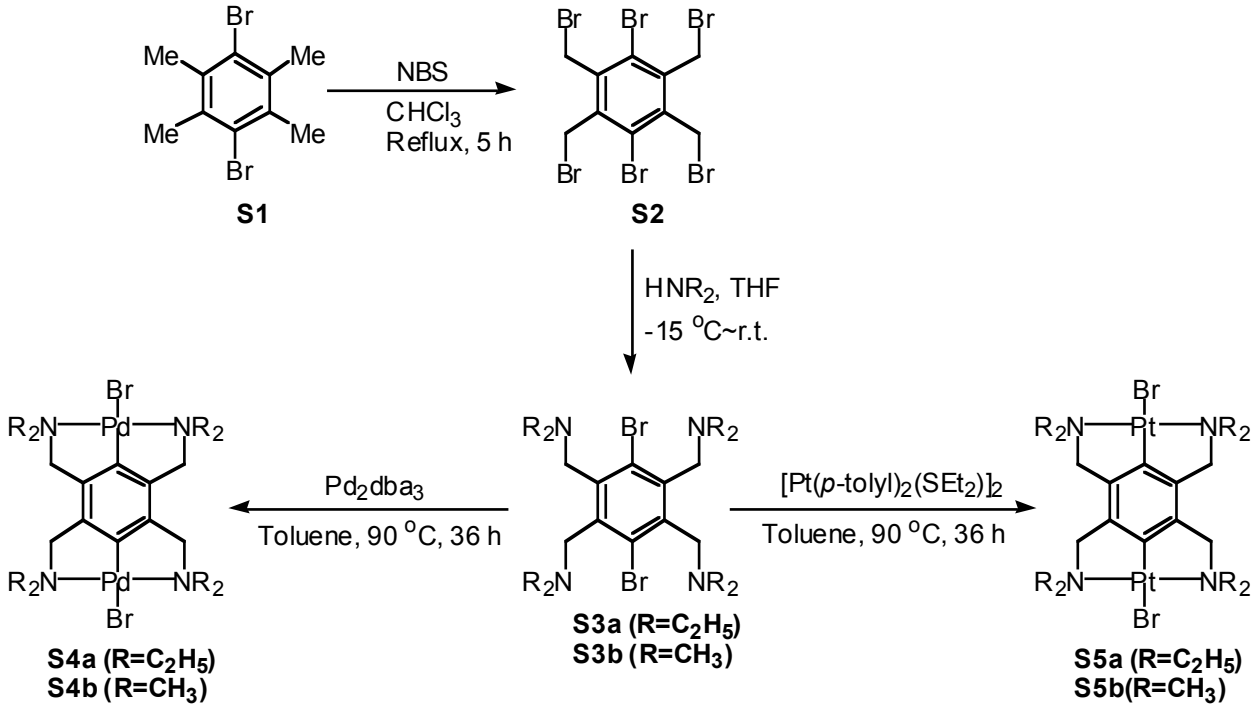
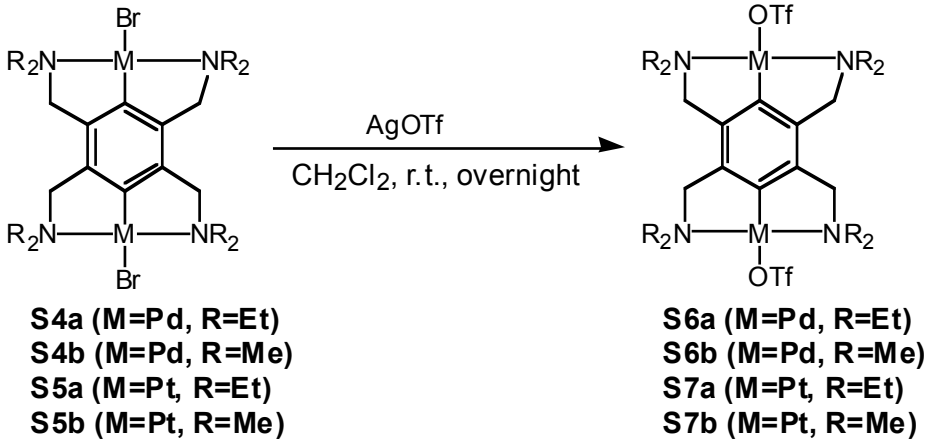
Synthesis and characterization. The detailed synthesis and characterization of 1,4-phenylene bridged bimetallic complexes **S6-S7** are reported elsewhere,[1] but they are reviewed here for convenience.

Materials and Methods. Dimethyl sulfoxide (DMSO) (Acros) and dichloromethane (Acros) were used as received. Solvents were dried and stored under nitrogen. Deuterated solvents, DMSO-d_6 and $CDCl_3$, were purchased from Cambridge Isotope Laboratories, Inc. ^{1}H NMR spectra were acquired using a Varian 400 MHz spectrometer. ^{13}C NMR spectra were acquired at 100 MHz. Mass spectra were acquired by Georgy Dubay at Duke University. Elemental analysis data were obtained from M-H-W laboratories, Phoenix, AZ.

Synthesis. Compounds **S1**[2], $[PtCl_2(SEt_2)_2]$[3] and $[Pt(p\text{-tolyl})_2(SEt_2)]_2$[4] were synthesized according to literature procedure.



Scheme S1. Synthesis of dibromo bimetallic pincer complexes **S4** and **S5.**



Scheme S2. Conversion of dibromo pincer complexes in corresponding triflate salts.

1,4-Dibromo-{2,3,5,6-tetrakis(bromomethyl)}benzene, 1,4-$C_6Br_2(CH_2Br)_4$-2,3,5,6 (S2). Compound **S2**[5a] was generated by a previously published process[5b] used to make the 1,2,4,5-tetrakis-(bromomethyl)benzene. *N*-bromosuccinimide (12.816 g, 0.072 mol) was added to a stirred solution of **S1** (2.920 g, 0.01 mol) in $CHCl_3$ (150 mL) at room temperature. The reaction mixture was heated to reflux and stirred for 5 hrs, at which time the product had precipitated. The reaction mixture was

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allowed to cool to room temperature, and the product was filtered and washed with cold dichloromethane (5 x 100 mL). The white solid was dried under vacuum. Yield 75% (4.560 g). ^{1}H NMR ($CDCl_3$) δ 4.84 (s, 8H, $PhCH_2$). ^{13}C NMR ($CDCl_3$) δ 153.1, 128.4, 30.7. HRMS (FAB) *m/z* 607.5659 (M^+, $C_{10}H_8Br_6$, calcd. 607.5665). The resulting white solid was used in the subsequent amination without further purification.

1,4-Dibromo-[2,3,5,6-tetrakis{(diethylamino)methy}]benzene, 1,4-$C_6Br_2(CH_2NEt_2)_4$-2,3,5,6 (S3a). Compounds **S3a** was generated using a related, previously reported procedure.[6] Compound **S2** (6.080 g, 0.01 mol) was added to a stirred solution of diethylamine (21.942 g, 0.30 mol) in THF (60 mL) at –10 ºC. The reaction mixture was allowed to warm to room temperature over a period of 1h and then heated to 55 ºC for 5 min. The reaction mixture was allowed to cool to room temperature, and all volatiles were removed under vacuum to leave a white solid residue. This residue was suspended in aqueous NaOH (100 mL, 2 M) and with vigorous stirring of the mixture Et_2O (300 mL) was added. Stirring was stopped, and from the resulting two-layer system the organic layer was collected and the water layer extracted with Et_2O (200 mL). The combined organic layer and extracts were washed with saturated aqueous NaCl (100 mL) and dried with $MgSO_4$. The solution was filtered and reduced to volume under vacuum. The resulting white solid was dried under vacuum. Yield 91% (5.246 g). ^{1}H NMR ($CDCl_3$) δ 4.11 (s, 8H, $PhCH_2$), 2.52 (q, *J*=7.1 Hz, 16H, NCH_2), 0.94 (t, *J* = 7.1 Hz, 24H, CH_3). ^{13}C NMR ($CDCl_3$) δ 140.1, 132.6, 55.7, 45.8, 11.8. HRMS (FAB) *m/z* 577.2308 ($[M+H]^+$, $C_{26}H_{49}N_4Br_2$, calcd. 577.2304). The product was carried on to subsequent metallation products without further purification.

1,4-Dibromo-[2,3,5,6-tetrakis{methylpiperidyl}]benzene, 1,4-C_6Br_2-$[CH_2N(\text{-}CH_2)_5]_4$-2,3,5,6 (S3b). Compound **S3b** was synthesized according to the procedure for **S3a**. The resulting white solid was dried under vacuum. Yield 92% (5.746 g). ^{1}H NMR ($CDCl_3$) δ 4.07 (s, 8H, $PhCH_2$), 2.40 (s, 16H, NCH_2), 1.46-1.39 (m, 24H, CH_2). ^{13}C NMR ($CDCl_3$) δ 139.3, 132.8, 59.6, 54.7, 26.4, 24.7. HRMS (FAB) *m/z* 625.2305 ($[M+H]^+$, $C_{30}H_{49}N_4Br_2$, calcd. 625.2295). The product was used in the synthesis of the

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metallated products without further purification.

[2,3,5,6-Tetrakis{(diethylamino)methy}phenylene-1,4-bis{bromopalladium(II)}], [$(PdBr)_2$-1,4-{$C_6(CH_2NEt_2)_4$-2,3,5,6}] (S4a). Compound **S3a** (1.441 g, 2.50 mmol) was dissolved in dry toluene (50 mL). $Pd_2(dba)_3$ (2.562 g, 2.80 mmol) was added, and the solution was stirred and heated to 90 ºC for 36 hrs. The solution was then filtered through celite and washed with toluene until the yellow color on celite was washed through. The celite was then washed with hot chloroform (1 L) into a clean flask. The chloroform solution was reduced to volume under vacuum, and the product (yellow solid) was purified using flash chromatography (SiO_2, $CHCl_3$:CH_3OH = 97:3). The resulting yellow solid was dried under vacuum. Yield 94% (1.855 g). ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 8H, $PhCH_2$), 3.45(dq, *J* = 12.0 Hz, 7.0 Hz, 8H, NCH_2), 2.62 (dq, *J* = 12.0 Hz, 7.0 Hz, 8H, NCH_2), 1.57 (t, *J* = 7.0 Hz, 24H, CH_3). ^{13}C NMR (CD_2Cl_2) δ 151.0, 138.3, 65.7, 59.2, 14.5. Anal. Calcd for $C_{26}H_{48}Br_2N_4Pt_2$: C, 39.56; H, 6.13; N, 7.10. Found; C, 39.73; H, 6.11; N, 7.11. HRMS (FAB) *m/z* 706.1153 ([M-Br] $^+$, $C_{26}H_{48}N_4BrPd_2$, calcd. 706.1148).

[2,3,5,6-Tetrakis{(dimethylamino)methy}phenylene-1,4-bis{bromopalladium(II)}], [$(PdBr)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (S4b). Compound **S4b** was synthesized according to the procedure for **S4a**. The resulting white solid was dried under vacuum. Yield 83% (1.405 g). ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 8H, $PhCH_2$), 2.92 (s, 24H, NCH_3). ^{13}C NMR and mass spectra could not be obtained due to poor solubility, but the structure was confirmed from its subsequent conversion to **S6b**. The product was converted directly into the triflated product, **S6b**, without further purification.

[2,3,5,6-Tetrakis{(diethylamino)methy}phenylene-1,4-bis{bromoplatinum(II)}], [$(PtBr)_2$-1,4-{$C_6(CH_2NEt_2)_4$-2,3,5,6}] (S5a). Compound **S3a** (2.000 g, 3.47 mmol) was dissolved in dry toluene (75 mL). [Pt(*p*-tolyl)$_2$(SEt_2)]$_2$ (4.541 g, 4.82 mmol) was added and the solution was stirred and heated to 90 ºC for 36 hrs. The solution was then filtered through celite and washed with toluene until the yellow color on celite was washed through. The celite was then washed with dichloromethane (1 L) into a clean flask, and the dichloromethane solution was reduced to volume under vacuum. The product was purified

using flash chromatography (SiO_2, $CHCl_3$:CH_3OH = 97:3). The resulting yellow solid was dried under vacuum. Yield 72% (2.415 g). ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 8H, $^3J_{Pt-H}$ = 32.8 Hz, $PhCH_2$), 3.51 (dq, *J* = 12.1 Hz, 7.1 Hz, 8H, NCH_2), 2.84 (dq, *J* = 12. 1 Hz, 7.1 Hz, 8H, NCH_2), 1.49 (t, *J* = 7.1 Hz, 24H, CH_3). ^{13}C NMR ($CDCl_3$) δ 133.2, 68.7, 60.6, 13.7. Anal. Calcd for $C_{26}H_{48}Br_2N_4Pt_2$: C, 32.31; H, 5.01; N, 5.80. Found; C, 32.26; H, 4.93; N, 5.74. HRMS (FAB) *m/z* 884.2305 ([M-Br] $^+$, $C_{26}H_{48}N_4BrPt_2$, calcd. 884.2337).

[2,3,5,6-Tetrakis{(dimethylamino)methy}phenylene-1,4-bis{bromoplatinum(II)}], [$(PtBr)_2$-1,4-{$C_6(CH_2NMe_2)_4$-2,3,5,6}] (S5b). Compound **S5b** was synthesized according to the procedure for **S5a**. The resulting white solid was dried under vacuum. Yield 81% (2.401 g). ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 8H, $PhCH_2$, $^3J_{Pt-H}$ not observed due to very poor S/N ratio), 3.07 (s, 24H, NCH_3, $^3J_{Pt-H}$ not observed due to very poor S/N ratio). ^{13}C NMR and mass spectra could not be obtained due to poor solubility, but the structure was confirmed from its subsequent conversion to **S7b**. The product was converted directly into the triflated product, **S7b**, without further purification.

[2,3,5,6-Tetrakis{(diethylamino)methy}phenylene-1,4-bis(palladiumtrifluoromethanesulfonate)], [$(PdOTf)_2$-1,4-{$C_6(CH_2NEt_2)_4$-2,3,5,6}] (S6a). Compound **S4a** (0.553 g, 0.70 mmol) was dissolved in dichloromethane (75 mL), and the reaction flask was wrapped by aluminum foil. AgOTf (0.389 g, 1.50 mmol) was added to the reaction mixture at 0 ºC. The solution was stirred for 24 hrs at room temperature and, after removing the aluminum foil, stirred for an additional 4 hrs. The reaction mixture was filtered, and the solid washed with dichloromethane (3 x 100 mL), and the solvent was evaporated. The resulting yellow solid was dried under vacuum. Yield 96% (0.623 g). ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 8H, $PhCH_2$), 3.22 (dq, *J* = 12.6 Hz, 7.1 Hz, 8H, NCH_2), 2.65 (dq, *J*= 12.6 Hz, 7.1 Hz, 8H, NCH_2), 1.57 (t, *J* = 7.1 Hz, 24H, CH_3). ^{1}H NMR (CD_3OD) δ 3.90 (s, 8H, $PhCH_2$), 3.00 (dq, *J* = 12.8 Hz, 7.0 Hz, 8H, NCH_2), 2.74 (dq, *J*= 12.8 Hz, 7.0 Hz, 8H, NCH_2), 1.54 (t, *J* = 7.0 Hz, 24H, CH_3). ^{13}C NMR ($CDCl_3$) δ 144.9, 137.8, 64.6, 57.4, 14.0. ^{13}C NMR (CD_3OD) δ 146.3, 139.4, 65.4, 58.4, 14.4. MS (FAB) *m/z* 928 ([M+1]$^+$, 3), 926 ([M-1]$^+$, 3), 779 (100), 777 (80), 630 (6), 524 (6). HRMS (FAB) *m/z* 777.1405 ([M-

$CF_3SO_3]^+$, $C_{27}H_{48}O_3N_4F_3SPd_2$, calcd. 777.1411). Anal. Calcd for $C_{28}H_{48}O_6N_4F_6S_2Pd_2$: C, 36.25; H, 5.22; N, 6.04. Found; C, 36.36; H, 5.28; N, 5.95.

[2,3,5,6-Tetrakis{(dimethylamino)methy}phenylene-1,4-bis(palladiumtrifluoromethane-sulfonate)], [(PdOTf)$_2$-1,4-{C$_6$(CH$_2$NMe$_2$)$_4$-2,3,5,6}] (S6b). Compound **S6b** was synthesized according to the procedure for **S6a**. The resulting white solid was dried under vacuum. Yield 97% (0.554 g). ^{1}H NMR (CD_3OD) δ 3.86 (s, 8H, $PhCH_2$), 2.74 (s, 24H, NCH_3). ^{13}C NMR (CD_3OD) δ148.8, 138.9, 72.6, 52.6. MS (FAB) *m/z* 816 ([M+1]$^+$, 3), 814 ([M-1]$^+$, 1), 667 (100), 665 (90), 613 (24), 518 (21). HRMS (FAB) *m/z* 665.0221 ([M-CF_3SO_3]$^+$, $C_{19}H_{32}F_3N_4O_3Pd_2S$, calcd. 665.0216). Anal. Calcd for $C_{20}H_{32}F_6N_4O_6Pd_2S_2$: C, 29.46; H, 3.96; N, 6.87. Found; C, 29.36; H, 4.04; N, 6.73.

[2,3,5,6-Tetrakis{(diethylamino)methy}phenylene-1,4-bis(platinumtrifluoro-methanesulfonate)], [(PtOTf)$_2$-1,4-{C$_6$(CH$_2$NEt$_2$)$_4$-2,3,5,6}] (S7a). Compound **S7a** was synthesized according to the procedure for **S6a**. The resulting yellow solid was dried under vacuum. Yield 95 % (0.735 g). ^{1}H NMR (CD_3OD) δ 3.95 (s, 8H, $^3J_{Pt\text{-}H}$ = 46.4 Hz, $PhCH_2$), 3.06 (dq, *J* = 12.5 Hz, 7.1 Hz, 8H, NCH_2), 2.90 (dq, *J*= 12.5 Hz, 7.1 Hz, 8H, NCH_2), 1.42 (t, *J* = 7.1 Hz, 24H, CH_3). ^{13}C NMR (CD_3OD) δ 149.7, 137.3, 68.4, 60.4, 13.8. MS (FAB) *m/z* 1104 (M$^+$, 3), 955 (100), 847 (17), 806 (8), 775 (8). HRMS (FAB) *m/z* 954.2678 ([M-CF_3SO_3]$^+$, $C_{27}H_{48}F_3N_4O_3Pt_2S$, calcd. 954.2674). Anal. Calcd for $C_{28}H_{48}F_6N_4O_6Pt_2S$: C, 30.43; H, 4.38; N, 5.07. Found; C, 30.36; H, 4.39; N, 4.99.

[2,3,5,6-Tetrakis{(dimethylamino)methy}phenylene-1,4-bis(platinumtrifluoromethane-sulfonate)], [(PtOTf)$_2$-1,4-{C$_6$(CH$_2$NMe$_2$)$_4$-2,3,5,6}] (S7b). Compound **S7b** was synthesized according to the procedure for **S7a**. The resulting yellow solid was dried under vacuum. Yield 97% (0.554 g). ^{1}H NMR (CD_3OD) δ 3.86 (s, 8H, $^3J_{Pt\text{-}H}$ = 44.4 Hz, $PhCH_2$), 2.74 (s, 24H, $^3J_{Pt\text{-}H}$ = 32.0 Hz, NCH_3). ^{13}C NMR (CD_3OD) δ138.9, 137.3, 75.1, 54.2. MS (FAB) *m/z* 992 (M$^+$, 1), 843 (100), 734 (19), 694 (26), 613 (55). HRMS (FAB) *m/z* 841.1390 ([M-CF_3SO_3]$^+$, $C_{19}H_{32}O_3N_4F_3Pt_2S$, calcd. 841.1401). Anal. Calcd for $C_{20}H_{32}O_6N_4F_6Pt_2S_2$: C, 24.20; H, 3.25; N, 5.64. Found; C, 24.40; H, 3.50; N, 5.39.

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