Supporting Information

On the importance of the amide configuration on the gelation process and topochemical polymerization of phenylacetylene macrocycles

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1. General

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co., TCI America Co. or Oakwood Products Inc. and were used as received. Solvents used for organic synthesis were obtained from Fisher Scientific (except THF from Sigma- Aldrich Co. Canada) and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). Other solvents were obtained from Fisher Scientific and were used as received. Tetrahydrofuran (THF) and triethylamine (Et₃N) used for Sonogashira reactions were degassed 30 minutes prior to use. All anhydrous and air sensitive reactions were performed in oven-dried glassware under positive argon pressure. Analytical thin-layer chromatographies were performed with silica gel 60 F254, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Compounds were visualized using 254 nm and/or 365 nm UV wavelength and/or aqueous sulfuric acid solution of ammonium heptamolybdate tetrahydrate (10 g/100 mL H_2SO_4 + 900 mL H_2O). Flash column chromatographies were performed on 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada).

Apparatus

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) operating at 400 MHz (¹H) and 100 MHz (¹³C). High resolution mass spectra (HRMS) were recorded with an Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with an ESI or APPI ion source (Agilent Technologies, Toronto, Canada). MALDI-TOF measurements were performed on a Bruker Biflex IV equipped with nitrogen laser. FT-IR was recorded in ATR mode on

Infrared spectrometer (Thermo-Nicolet Magne 850) equipped with Golden Gate. UVvisible absorption spectra were recorded on a Varian diode-array spectrophotometer (model Cary 500) using 3-mm path length quartz cells. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6360 LV. X-ray diffraction was recorded on Siemens X-rays diffractometer (Model S3 D5000).

Gelation test

To test the gelation properties of PAMs in a given solvent, we proceeded as follow: in a vial, a PAMs was dissolved in a solvent. After dissolution by sonication, the vial was sealed and heated until a clear solution was obtained. The clear solution was allowed to slowly cool down at room temperature. The stability of the gel was confirmed by tube inversion.

SEM imaging

Organogel obtained in ethyl acetate was deposited on a stainless steel substrate and allowed to dry for 3-4 days. Then, gold particles were sputtered on dried gel prior to imaging.

Computation

All calculations were realized with the Gaussian 09 package.¹ The equilibrium geometries were computed using the density functional theory (DFT). The 6-31G(d,p) basis set was employed with the hybrid M05-2X exchange-correlation functional.² This functional was recommended for systems with weak dispersion interactions, such as hydrogen bonding.³

2. Synthetic procedure



Compound 3a. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 3,5-diiodoaniline (2.50 g, 7.25 mmol) and Et₃N (3.03 mL, 21.7 mmol) in CH₂Cl₂ (18 mL) under N₂ atmosphere. In another round bottom flask equipped with a magnetic stir bar, a solution of lauroyl chloride (2.51 mL, 10.8 mmol) in CH₂Cl₂ (18 mL) under N₂ atmosphere was prepared. The first solution was added dropwise to the other and the resulting solution was stirred overnight. The reaction mixture was diluted with CH₂Cl₂, washed with water (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 20% EtOAC/hexanes as eluents to afford compound **3a** (3.16 g, 83% yield) as a white amorphous powder. m.p: 105-109°C; ¹H NMR (CDCl₃, 400 MHz): 7.89 (s, 2H), 7.76 (s, 1H), 7.22 (s, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.69 (m, 2H), 1.26 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 171.8, 140.9, 140.0, 135.1, 127.8, 123.2, 94.7, 37.9, 32.1, 29.8, 29.7, 29.6, 29.4, 25.7, 22.9, 14.4. HRMS (APPI-TOF) *m*/*z* calcd for C₁₈H₂₇I₂NO[M+H]⁺: 528.0255, found 528.0259; FTIR (ATR): 3275m, 2916m, 2850m, 1656m, 1558m.



Compound 4a. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with **3a** (3.00 g, 3.02 mmol), degassed THF (56 mL), degassed TEA (3.13 mL, 22.8 mmol), PdCl₂(PPh₃)₂ (160 mg, 0.23 mmol), CuI (43 mg, 0.23 mmol) and trimethylsilylacetylene (3.21 mL, 22.8 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted with CH₂Cl₂, washed with NH₄Cl (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using 5% EtOAc/hexanes to 7% EtOAc/hexanes as eluents to afford compound **4a** (2.62 g, 98% yield) as a dark orange oil. ¹H NMR (CDCl₃, 400 MHz): 7.59 (s, 2H), 7.56 (s, 1H), 7.29 (s, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.67 (m, 2H), 1.24 (m, 16H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.21 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz): 172.1, 138.2, 131.3, 124.4, 123.2, 103.9, 95.3, 37.9, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 25.8, 22.9, 14.4, 0.1. HRMS (APPI-TOF) *m*/*z* calcd for C₂₈H₄₅NOSi₂[M+H]⁺: 468.3112, found 468.3125; FTIR (ATR): 3295w, 2923m, 1663m, 1431m, 1248m, 830m.



Compound 5a. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with **4a** (2.60 g, 5.56 mmol), KOH (936 mg, 16.7 mmol), THF (14 mL), MeOH (13 mL) and water (1.0 mL). The reaction mixture was stirred for 15 minutes, diluted with CH_2Cl_2 , washed with 10% aqueous HCl (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting product was directly charged without further purification in a 100 mL round bottom flask equipped with a magnetic stir bar charged with 3,5-diiodo-1-octylbenzene (4.10 g, 9.27 mmol), degassed

THF (30 mL), degassed diisopropylethylamine (4.31 mL, 24.7 mmol), PdCl₂(PPh₃)₂ (87 mg, 0.12 mmol) and CuI (24 mg, 0.12 mmol) under nitrogen atmosphere. The mixture was stirred overnight at room temperature, diluted with CH₂Cl₂, washed with NH₄Cl (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to 5% EtOAc/hexanes as eluents to afford compound **5a** (840 mg, 29% yield) as a white amorphous powder: m.p: 86-95°C; ¹H NMR (CDCl₃, 400 MHz): 7.66 (br s, 4H), 7.49 (s, 2H), 7.38 (s, 1H), 7.31 (s, 1H), 7.27 (s, 2H), 2.53 (t, *J* = 7.7 Hz, 4H), 2.37 (t, *J* = 7.7 Hz, 2H), 1.72 (m, 2H), 1.59 (m, 4H), 1.25 (m, 36H), 0.88 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz): 145.4, 138.4, 137.9, 137.7, 137.6, 131.2, 130.5, 124.8, 124.2, 122.8, 93.9, 89.9, 88.0, 81.9, 38.1, 35.6, 32.2, 32.1, 31.3, 29.8 (2C), 29.7, 29.6 (2C), 29.5, 29.4 (2C), 25.8, 22.9 (2C), 21.6, 14.4. HRMS (APPI-TOF) *m*/*z* calcd for C₅₀H₆₇I₂NO[M+H]⁺: 952.3385, found 952.3412; FTIR (ATR): 3279w, 2915m, 2848m, 1657m, 1536m, 866m.



Compound 6a. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **5a** (1.00 g, 1.05 mmol), degassed THF (10 mL), degassed Et₃N (0.58 mL, 4.20 mmol), PdCl₂(PPh₃)₂ (37 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) and triisopropylsilyl acetylene (0.94 mL, 4.20 mmol). The reaction mixture was stirred overnight, diluted with CH₂Cl₂, washed with NH₄Cl and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to 5 % EtOAc/hexanes as eluents to afford

compound **6a** (1.09 g, 98% yield) as an orange oil. ¹H NMR (CDCl₃, 400 MHz): 7.70 (s, 2H), 7.50 (s, 1H), 7.45 (s, 2H), 7.42 (s, 1H), 7.27 (s, 2H), 7.25 (s, 2H), 2.56 (t, J = 7.7 Hz, 4H), 2.35 (t, J = 7.5 Hz, 2H), 1.71 (m, 2H), 1.60 (m, 4H), 1.25 (m, 36H), 1.14 (s, 42H), 0.88 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz): 172.0, 143.5, 138.5, 132.8, 132.3, 131.8, 124.4, 123.9, 123.1, 122.7, 106.7, 91.0, 89.9, 88.6, 81.8, 37.9, 35.8, 32.2 (2C), 31.5, 29.9 (2C), 29.8, 29.7 (2C), 29.6 (2C), 29.5 (2C), 25.8, 22.9 (2C), 18.9, 18.8, 14.4, 11.5; HRMS (APPI-TOF) *m*/*z* calcd for C₇₂H₁₀₉NOSi₂[M+H]⁺: 1060.8120, found 1060.8158; FTIR (ATR): 3294w, 2923m, 2863m, 1663m, 881m.



PAM 1a. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **6a** (1.00 g, 0.94 mmol), THF (19 mL) and TBAF 1.0M solution in THF (2.83 mL, 2.83 mmol). The reaction mixture was stirred until complete disappearance of the starting product by TLC, diluted with CH_2Cl_2 , washed with water (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was charged without further purification in a 100 mL round bottom flask charged with

degassed pyridine (28 mL). Another 500 mL round bottom flask equipped with a magnetic stir bar was charged with CuCl (6.58 g, 66.4 mmol), CuCl₂ (1.38 g, 10.3 mmol) and degassed pyridine (133.7 mL) under N₂ atmosphere. The substrate solution was added dropwise to the catalyst solution over 4 days and the reaction mixture was stirred for an additional 7 days. The reaction mixture was diluted with CHCl₃ and poured in water. The organic phase was extracted successively with water, 25% aqueous NH₄OH, water, 10% aqueous CH₃COOH, water, 10% aqueous NaOH and brine. The organic layer was dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using 30% hexanes/CHCl₃ to CHCl₃ as eluent to afford PAM **1a** (140 mg, 20%) as a white amorphous powder. m.p: >150°C; ¹H NMR (CDCl₃, 400 MHz): 7.58 (s, 4H), 7.49 (s, 4H), 7.39 (s, 2H), 7.24 (s, 4H), 7.20 (s, 4H), 7.10 (s, 2H), 2.50 (t, *J* = 7.6 Hz, 8H), 2.31 (t, J = 7.2 Hz, 4H), 1.67 (m, 4H), 1.54 (m, 8H), 1.19 (m, 72H), 0.80 (m, 18H); ¹³C NMR (CDCl₃, 100 MHz): 171.7, 143.8, 138.3, 133.8, 133.7, 132.5, 132.4, 124.3, 123.4, 122.4, 121.2, 89.7, 88.9, 81.2, 74.3, 38.0, 35.7, 32.2, 32.1, 31.2, 29.9 (2C), 29.8 (2C), 29.7, 29.6 (2C), 29.5 (2C), 29.4 (2C), 25.7, 22.9, 14.4; MS (MALDI-TOF): m/z calcd for C₁₀₈H₁₃₄N₂O₂[M+H]⁺: 1492.1, found 1492.1; FTIR (ATR): 3271w, 2920m, 2849m, 1657m, 1536m, 1435m.



Compound 3b. A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 3,5-diiodoaniline (2.50 g, 7.25 mmol), pentacosadiynoïc acid (4.07 g, 10.9 mmol), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (2.084 g, 10.9 mmol), 4-

(dimethylamino)pyridine (443 mg, 3.62 mmol) and CH₂Cl₂ (36 mL). The reaction mixture was stirred overnight and diluted with CH₂Cl₂. The organic layer was washed with water (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using 10% acetone/hexanes to 20% acetone/hexanes as eluents to afford compound **3b** (3.59 g, 71% yield) as a white viscous solid. ¹H NMR (CDCl₃, 400 MHz): 7.89 (s, 2H), 7.77 (s, 1H), 7.01 (s, 1H), 2.33 (t, J = 7.4 Hz, 2H), 2.24 (t, J = 6.3 Hz, 4H), 1.69 (m, 2H), 1.51 (m, 6H), 1.37 (m, 22H), 0.88 (t, J = 6.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 171.4, 140.7, 139.8, 127.6, 94.5, 77.7, 77.5, 65.3, 65.2, 37.6, 31.9, 29.6 (3C), 29.5, 29.4, 29.1 (3C), 28.9, 28.8, 28.7, 28.4, 28.3, 25.3, 22.7, 19.2, 19.1, 14.4; HRMS (APPI-TOF) *m*/*z* calcd for C₃₁H₄₅I₂NO[M+H]⁺: 702.1663, found 702.1662; FTIR (ATR): 3298w, 2922m, 2848m, 1670m, 1572m.



Compound 4b. A 250 mL round bottom flask equipped with a magnetic stir bar was charged with **3b** (3.60 g, 5.13 mmol), degassed THF (51 mL), degassed TEA (2.82 mL, 20.5 mmol), PdCl₂(PPh₃)₂ (144 mg, 0.21 mmol), CuI (39 mg, 0.21 mmol) and trimethylsilylacetylene (2.89 mL, 20.5 mmol) under argon atmosphere. The reaction mixture was stirred overnight at room temperature, diluted with CH₂Cl₂, washed with NH₄Cl (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using 5% acetone/hexanes as eluent to afford compound **4b** (3.03 g, 92% yield) as a dark orange oil. ¹H NMR (CDCl₃, 400 MHz): 7.60 (s, 2H), 7.43 (s, 1H), 7.29 (s, 1H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 4H), 1.67 (m, 2H), 1.49 (m, 4H), 1.33 (m, 26H), 0.86

(t, J = 7.0 Hz, 3H), 0.21 (s, 18H); ¹³C NMR (CDCl₃, 100 MHz): 171.9, 138.2, 131.3, 124.2, 123.1, 103.9, 95.4, 77.9, 77.7, 65.6, 65.5, 37.8, 32.2, 31.8, 29.9 (3C), 29.7, 29.6 (2C), 29.4, 29.3, 29.1 (2C), 28.9, 28.6, 28.5, 25.7, 22.9, 19.4, 14.4, 0.09; HRMS (APPI-TOF) m/z calcd for C₄₁H₆₃NOSi₂[M+H]⁺: 642.4521, found 642.4525; FTIR (ATR): 3295w, 2924m, 2854m, 1663m, 1429m, 1249m, 842m.



Compound 5b. A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **4b** (750 mg, 1.17 mmol), potassium hydroxide (197 mg, 3.50 mmol), THF (2.9 mL) and MeOH (2.9 mL). The reaction mixture was stirred until complete disappearance of the starting product by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 , washed with 10% aqueous HCl (2x), dried with sodium sulfate and the solvent was removed under reduced pressure. The resulting product was charged without further purification in a 25 mL round bottom flask equipped with a magnetic stir bar with 3,5-diiodooctylbenzene (1.33 g, 3.01 mmol), degassed THF (10 mL), degassed DIPEA (1.4 mL, 8.04 mmol), PdCl₂(PPh₃)₂ (28 mg, 0.04 mmol) and CuI (8 mg, 0.04 mmol). The reaction mixture was stirred overnight and diluted with CH₂Cl₂. The organic layer was washed with saturated aqueous NH₄Cl (3x), dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using hexanes to 10% acetone/hexanes as eluents to afford compound **5b** (732 mg, 65% yield) as a dark orange oil. ¹H NMR (CDCl₃, 400 MHz): 7.68 (s, 2H), 7.66 (s, 2H), 7.49 (s, 2H), 7.38 (m, 2H), 7.27 (s, 2H), 2.52 (t, *J* = 7.6 Hz,

4H), 2.37 (t, J = 7.6 Hz, 2H), 2.23 (t, J = 6.7 Hz, 6H), 1.72 (m, 2H), 1.58 (m, 4H), 1.49 (m, 6H), 1.26 (m, 42H), 0.87 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz): 171.9, 145.4, 138.4, 137.9, 137.7, 131.2 (2C), 124.8, 124.2, 122.8, 93.9, 89.2, 89.0, 77.9, 77.7, 65.6, 65.5, 37.9, 35.6, 32.2, 32.1, 31.3, 29.9 (3C), 29.7 (2C), 29.6 (2C), 29.5 (3C), 29.4 (2C), 29.1, 29.0, 28.6, 28.5, 25.7 (2C), 22.9 (2C), 19.4 (2C), 14.4: HRMS (APPI-TOF) *m*/*z* calcd for C₆₃H₈₅I₂NO[M+H]⁺: 1126.4793, found 1126.4817; FTIR (ATR): 3294w, 2923m, 2852m, 1664m, 1599m, 1553m.



Compound 6b. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **5b** (2.10 g, 1.87 mmol), degassed THF (18 mL), degassed Et₃N (1.03 mL, 7.46 mmol), PdCl₂(PPh₃)₂ (65 mg, 0.09 mmol), CuI (18 mg, 0.09 mmol) and triisopropylsilyl acetylene (1.67 mL, 7.46 mmol). The reaction mixture was stirred overnight, diluted with CH₂Cl₂, washed with NH₄Cl and dried with sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel using hexanes to 4 % acetone/hexanes as eluents to afford compound **5b** (1.67 g, 73% yield) as an orange oil. ¹H NMR (CDCl₃, 400 MHz): 7.69 (s, 2H), 7.45 (s, 2H), 7.42 (s, 1H), 7.39 (s, 1H), 7.27 (s, 2H), 7.25 (s, 2H), 2.56 (t, *J* = 7.4 Hz, 4H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.22 (t, *J* = 6.8 Hz, 4H), 1.70 (m, 2H), 1.60 (m, 4H), 1.48 (m, 4H), 1.27 (m, 46H), 1.13 (s, 42H), 0.88 (m, 9H); ¹³C NMR (CDCl₃, 100 MHz): 171.9, 143.5, 138.5, 132.8, 132.3, 131.8, 130.6, 124.4, 123.9, 123.1, 122.7, 106.6, 91.1, 89.9, 88.6, 77.8, 77.7, 65.6 (2C), 37.9, 35.8, 32.2, 32.1, 31.4, 29.9 (3C), 29.8, 29.7, 29.6,

29.5 (3C), 29.4 (2C), 29.3, 29.1 (2C), 29.0, 28.6, 28.5, 25.7, 22.9 (2C), 19.4 (2C), 18.9, 14.4, 11.6; HRMS (APPI-TOF) m/z calcd for $C_{85}H_{127}NOSi_2[M+H]^+$: 1234.9529, found 1234.9556; FTIR (ATR): 3294w, 2923m, 2854m, 1663m, 1586m, 880m.



PAM 1b. A 50 mL round bottom flask equipped with a magnetic stir bar was charged with **6b** (1.00 g, 0.81 mmol), THF (16 mL) and TBAF 1.0M solution in THF (2.40 mL, 2.43 mmol). The reaction mixture was stirred until complete disappearance of the starting product by TLC, diluted with CH_2Cl_2 , washed with water (3x) and dried with sodium sulfate. The solvent was removed under reduced pressure. The resulting product was charged without further purification in a 100 mL round bottom flask equipped with a magnetic stir bar was charged with CuCl (6.09 g, 61.6 mmol), CuCl₂ (1.28 g, 9.54

mmol) and degassed pyridine (123 mL) under N₂ atmosphere. The first solution was added dropwise to the catalyst solution over 4 days and the reaction mixture was stirred for an additional 7 days. The reaction mixture was diluted with CHCl₃ and poured in water. The organic phase was extracted successively with water, 25% aqueous NH₄OH, water, 10% aqueous CH₃COOH, water, 10% aqueous NaOH and brine. The organic layer was dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel using 20% hexanes/CHCl₃ to CHCl₃ as eluents to afford PAM **1b** (390 mg, 49% yield) as a white viscous solid. m.p: >150°C; ¹H NMR (CDCl₃, 400 MHz): 7.67 (s, 4H), 7.58 (s, 4H), 7.48 (s, 2H), 7.33 (s, 4H), 7.29 (s, 4H), 7.16 (s, 2H), 2.59 (t, J = 7.6 Hz, 8H), 2.39 (t, J = 7.3Hz, 4H), 2.25 (q, J = 6.9 Hz, 8H), 1.75 (m, 4H), 1.63 (m, 8H), 1.51 (m, 8H), 1.29 (m, 92H), 0.89 (m, 18H); ¹³C NMR (CDCl₃, 100 MHz): 172.3, 143.3, 137.9, 133.6, 132.2, 132.1, 124.3, 123.5, 123.1 (2C), 122.2, 89.6, 88.9, 81.2, 77.9, 77.7, 74.5, 65.6, 65.5, 37.8 (2C), 35.7, 32.2, 31.2, 29.9 (4C), 29.8, 29.7, 29.6 (2C), 29.4, 29.2, 29.1, 29.0, 28.6 (2C), 28.5, 25.8, 22.9 (2C), 19.5, 17.9, 14.4 (2C), 12.5; MS (MALDI-TOF): calcd for $C_{134}H_{170}N_2O_2[M+H]^+$: 1840.3, found 1842.4; FTIR (ATR): 3300w, 2921m, 2852m, 1668m, 1584m, 1436m.





Figure S1. ¹H NMR of compound **3a** in CDCl₃



Figure S2. ¹³C NMR of compound **3a** in CDCl₃



Figure S3. ¹H NMR of compound **4a** in CDCl₃



Figure S4. ¹³C NMR of compound **4a** in CDCl₃



Figure S5. ¹H NMR of compound **5a** in CDCl₃



Figure S6. ¹³C NMR of compound **5a** in CDCl₃



Figure S7. ¹H NMR of compound **6a** in CDCl₃



Figure S8. ¹³C NMR of compound **6a** in CDCl₃



Figure S9. ¹H NMR of PAM **1a** in CDCl₃



Figure S10. ¹³C NMR of PAM **1a** in CDCl₃



Figure S11. ¹H NMR of compound **3b** in CDCl₃



Figure S12. ¹³C NMR of compound **3b** in CDCl₃



Figure S13.¹H NMR of compound **4b** in CDCl₃



Figure S14. ¹³C NMR of compound **4b** in CDCl₃



Figure S15. ¹H NMR of compound **5b** in CDCl₃



Figure S16. ¹³C NMR of compound **5b** in CDCl₃



Figure S17. ¹H NMR of compound **6b** in CDCl₃



Figure S18. ¹³C NMR of compound **6b** in CDCl₃



Figure S19. ¹H NMR of PAM 1b in CDCl₃



Figure S20. ¹³C NMR of PAM **1b** in CDCl₃

4. MALDI-ToF analysis



Figure S21. MALDI-ToF spectrum of PAM 1a.



Figure S22. MALDI-ToF spectrum of PAM 1b.



Figure S23. MALDI-ToF spectrum of PAM 2a.



Figure S24. MALDI-ToF spectrum of PAM 2b.

5. XRD analysis



Figure S25. X-ray diffraction spectrum of gel of PAM 1a in toluene (10 mg/mL)



Figure S26. X-ray diffraction spectrum of PAM **1b** in toluene (10 mg/mL)



Figure S27. X-ray diffraction spectrum of PAM 2a in cyclohexane (10 mg/mL)



Figure S28. X-ray diffraction spectrum of PAM 2a in ethyl acetate (10 mg/mL)



Figure S29. X-ray diffraction spectrum of PAM 2b in ethyl acetate (10 mg/mL)



Figure S30. X-ray diffraction spectrum of PAM 2b in cyclohexane (10 mg/mL)

6. Raman spectroscopy



Figure S31. Raman spectra of Poly-2a.



Figure S32. Raman spectra of Poly- 2b.

7. References

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