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Electronic Supplemental Information (ESI)

Quantifying chloride binding and salt extraction with poly(methyl methacrylate) copolymers bearing aryl-triazoles as anion receptor side chains

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S1. General Methods

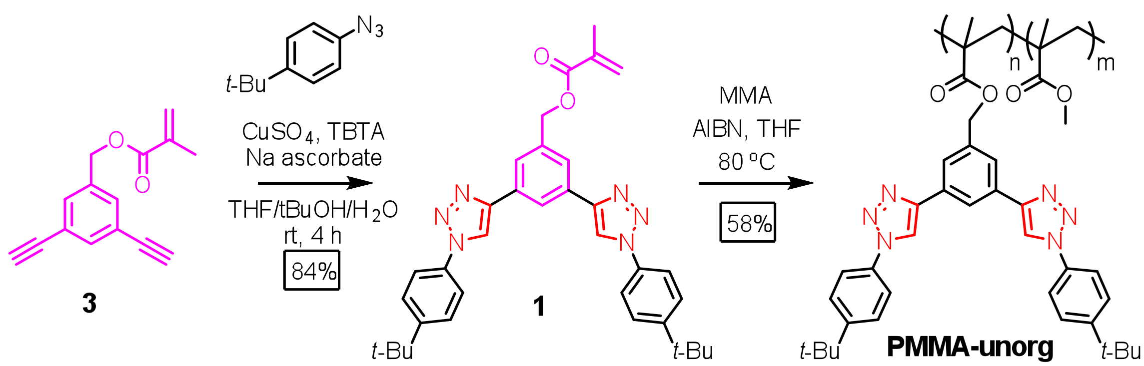
All reagents were obtained from commercial suppliers and used as received unless otherwise noted. 3,5-Diethynylbenzenemethanol,[S1] 1-azido-4-*tert*-butylbenzene,[S2] 4-azidobenzyl alcohol[S3] and tris-[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA)[S4] were prepared according to literature procedures. Methyl methacrylate (contains ≤30 ppm MEHQ as inhibitor, 99%, Aldrich) and styrene (ReagentPlus, contains 4-*tert*-butylcatechol as stabilizer, ≥99%, Aldrich) were eluted over a column of basic Al_2O_3 prior to use. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol. Column chromatography was performed on silica gel (160 – 200 mesh), and thin-layer chromatography (TLC) was performed on precoated silica gel plates (0.25 mm thick, #1615126, Sorbent Technologies, USA) and observed under UV light. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Inova (500, 400 MHz), Varian VXR (400 MHz) and Varian Gemini (300 MHz) spectrometers at room temperature (298 K). Chemical shifts were referenced on tetramethylsilane (TMS) or residual solvent peaks. High-resolution electrospray ionization (ESI), electron impact (EI), or chemical ionization (CI) mass spectrometry was performed on a Thermo Electron Corporation

MAT 95XP-Trap mass spectrometer. Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA Q5000 IR Thermogravimetric Analyzer under a N_2 atmosphere at a ramp rate of 10°C / minute. Gel permeation chromatography (GPC) was performed using an Agilent HPLC equipped with two ResiPore (300 × 7.5 mm) columns in series and stabilized tetrahydrofuran (THF) as the solvent unless otherwise noted. Relative molecular weights were determined based on polymethyl(methacrylate) (PMMA) standards (EasiVial, Agilent). Dynamic light scattering (DLS) measurements were made on Zetasizer Nano-ZS using a quartz cuvette.

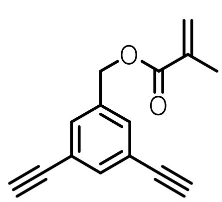
List of Abbreviations

AIBN	2,2′-Azobis(2-methylpropionitrile)
DIPA	Diisopropylamine
Na_2EDTA	Ethylenediaminetetracetic acid, disodium salt
PMMA	Polymethyl(methacrylate)
TBA	Tetra-*n*-butylammonium
TBTA	Tris-[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine
THF	Tetrahydrofuran
TMS	Tetramethylsilane
TMSA	Trimethylsilylacetylene

S2. Synthesis and Compound Characterization

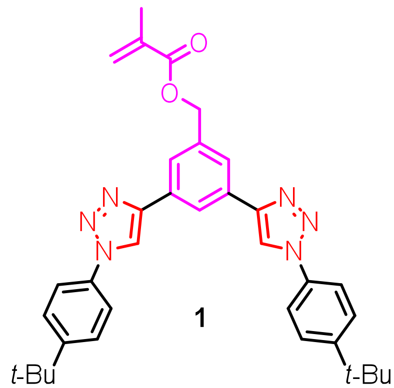


Scheme S1. Two-step preparation of **PMMA-unorg** from symmetric methacrylate **1**

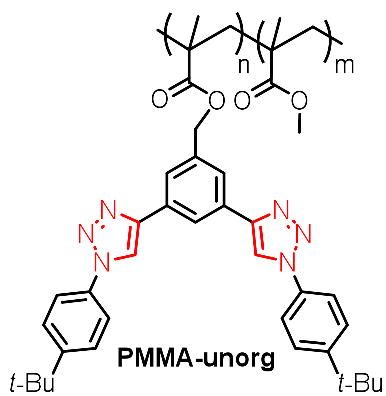


3

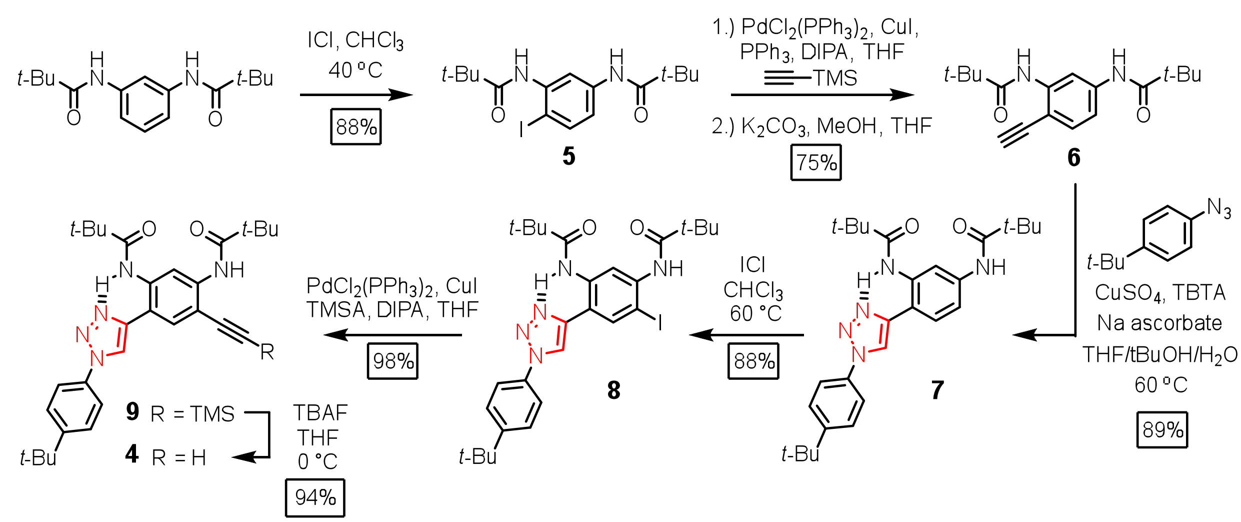
3,5-Diethynylbenzyl methacrylate (3): 3,5-Diethynylbenzenemethanol[S1] (1.23 g, 7.88 mmol) was dissolved in dry CH_2Cl_2 (50 mL), triethylamine (2.25 mL) and cooled to 0 °C. Methacryloyl chloride (860 mg, 8.27 mmol) was then added and the solution was allowed to warm slowly to room temperature over 90 minutes. After the starting material was consumed, the solution was washed with $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. The crude product was chromatographed over SiO_2 (2% ethyl acetate/hexanes) to yield **3** (1.15 g, 64%) in addition to an unidentified byproduct that could be converted back to starting material upon hydrolysis in K_2CO_3/MeOH. Based on recovered starting material (185 mg), the product was obtained in a 77% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (s, 1H), 7.47 (s, 2H), 6.17 (s, 1H), 5.62 (s, 1H), 5.14 (s, 2H), 3.11 (s, 2H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.89, 136.82, 135.87, 135.18, 131.68, 126.21, 122.81, 82.20, 78.30, 65.12, 18.29. HR-ESI-MS: $C_{15}H_{13}O_2$ [M + H^+], Calculated: 225.0914, Found: 225.0910.



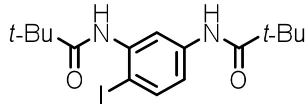
Unorganized pentad (1): **3** (78 mg, 0.35 mmol), 1-azido-4-*tert*-butylbenzene[S2] (135 mg, 0.77 mmol), and TBTA (18 mg) was dissolved in THF (7 mL), *t*-butanol (3 mL), and H_2O (2 mL). The solution was degassed with argon for 15 minutes followed by the addition of $CuSO_4$•$5H_2O$ (9 mg dissolved in 500 μL H_2O) and sodium ascorbate (14 mg dissolved in 500 μL H_2O). The solution was stirred at room temperature for 4 hours. After removing the solvents in vacuo, the crude product was dissolved in CH_2Cl_2 (50 mL), washed with Na_2EDTA, brine, and then dried over $MgSO_4$. The product was then purified over SiO_2 (15% ethyl acetate/hexanes) to yield **1** (167 mg, 84%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.37 (m, 3H), 7.93 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 1.96 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.09, 152.01, 147.39, 137.66, 136.01, 13.44, 131.32, 126.58, 126.10, 125.01, 122.73, 119.93, 118.26, 65.98, 34.70, 31.20, 18.34. HR-ESI-MS: $C_{35}H_{38}N_6O_2Cl$ [M + Cl^-], Calculated: 609.2745, Found: 609.2746.



PMMA-unorganized pentad copolymer (PMMA-unorg): 1 (200 mg, 0.35 mmol) and methyl methacrylate (350 mg) were dissolved in THF (10 mL) and degassed with argon. AIBN (6 mg, 0.03 mmol) was then added and the solution was warmed to 70 °C and stirred for 48 hours. The resulting solution was cooled and precipitated in CH_3OH (150 mL) to yield **PMMA-unorg** as a white solid (320 mg) in a 58% yield. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.67 – 8.23 (br, 3H), 8.00-7.85 (br, 2H), 7.84-7.65 (br, 4H), 7.60-7.45 (br, 4H), 5.14 (br, *2*H), 3.58 (br, 28H), 1.85 (br, 19.6 H), 1.37 (br, 27.4H), 0.99, 0.82 (br, 29.9 H).

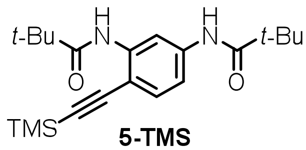


Scheme S2. Preparation of alkyne **4** through a stepwise desymmetrization of the central bisamidophenylene



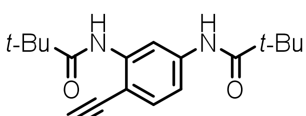
5

***N,N'*-(4-Iodo-1,3-phenylene)bis(2,2-dimethylpropanamide) (5):** *N,N'*-(1,3-Phenylene)bis(2,2-dimethylpropanamide)[5] (1.00 g, 3.61 mmol) was dissolved in $CHCl_3$ (50 mL) and cooled to 0 °C in an ice-water bath. Iodine monochloride (ICl, 700 mg) dissolved in $CHCl_3$ (25 mL) and added dropwise over 30 minutes. After addition was complete, the solution was slowly warmed to 40 °C. Once the staring material was consumed, the solution was neutralized with Na_2CO_3, washed with $Na_2S_2O_3$, and dried over $MgSO_4$. The volatiles were removed in vacuo and the crude material was chromatographed over SiO_2 (10% ethyl acetate/hexanes) to yield **5** (1.28 g, 88%) as a white solid. mp = 201-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, J = 2.4 Hz, 1H), 7.83 (br s), 7.67 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.8, 2.4 Hz, 1H), 7.47 (br s), 1.37 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.04, 176.73, 139.20, 138.72, 138.20, 117.73, 112.57, 82.58, 40.16, 39.67, 27.60, 27.48. HR-ESI-MS: $C_{16}H_{24}N_2O_2I$ [M + H^+], Calculated: 403.0882, Found: 403.0894.



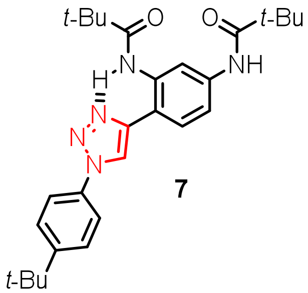
5-TMS

***N,N'*-(4-((Trimethylsilyl)ethynyl)-1,3-phenylene)bis(2,2-di-methyl-propanamide) (5-TMS): 5** (3.0 g, 7.46 mmol) was dissolved in THF/DIPA (5:1, 60 mL) and degassed with argon for 15 minutes. To the solution was then added $PdCl_2(PPh_3)_2$ (160 mg, 0.22 mmol), CuI (42 mg, 0.22 mmol) and TMSA (1.6 mL, 11 mmol). The solution was stirred for 16 hours at rt. The resulting suspension was filtered over Celite, washed with THF, and concentrated in vacuo. The crude material was chromatographed over SiO_2 (5% ethyl acetate/hexanes) to yield **5-TMS** (2.25, 81%) as a light brown, waxy, solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (br s, 1H), 8.31 (d, J = 1.9 Hz, 1H), 7.80 (dd, J = 8.6, 2.0 Hz, 1H), 7.60 (br s, 1H), 7.37 (d, J = 8.6 Hz, 1H), 1.34 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.69, 176.61, 139.79, 139.59, 132.34, 114.61, 109.47, 107.09, 101.18, 100.20, 40.09, 39.64, 27.48, 27.41, –0.08. HR-CI-MS: $C_{21}H_{33}N_2O_2Si$ [$M^{\bullet+}$], Calculated: 372.2225, Found: 372.2228.



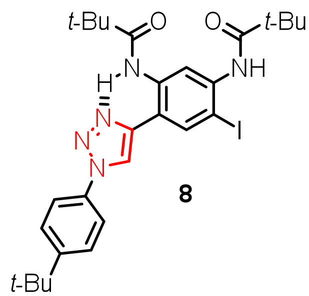
6

***N,N'*-(4-Ethynyl-1,3-phenylene)bis(2,2-dimethylpropanamide) (6): 5-TMS** (2.24 g, 6.01 mmol) was dissolved in THF (70 mL) and saturated K_2CO_3/MeOH (10 mL) and stirred for 10 minutes. After consumption of the starting material, NH_4Cl (150 mL) was added and extracted with dichloromethane. After drying over $MgSO_4$, the crude material was purified over SiO_2 (10-15% acetone/hexanes) to yield **6** (1.68 g, 93%) as an off-white solid. mp = 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (br s, 1H), 8.27 (d, J = 1.6 Hz, 1H), 7.88 (dd, J = 8.6, 2.0 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.40 (br s, 1H), 3.52 (s, 1H), 1.34 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.13, 176.66, 140.13, 139.78, 114.63, 109.43, 105.95, 83.79, 79.24, 40.24, 39.75, 27.51, 27.49. HR-ESI-MS: $C_{18}H_{25}N_2O_2$ [M + H^+], Calculated: 301.1916, Found: 301.1918.



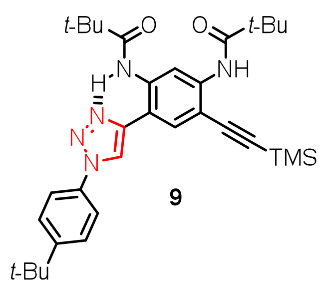
7

Triad-H (7): 6 (100 mg, 0.33 mmol) and 4-azido-*tert*-butylbenzene (58 mg, 0.33 mmol) were dissolved in THF (10 mL), *t*-BuOH (3 mL), and H_2O (3 mL). After degassing the solution for 15 minutes, TBTA (9 mg), $CuSO_4•5H_2O$ (4 mg), and sodium ascorbate (13 mg) were added sequentially. The solution was warmed to 60 °C and stirred for 2 hours. After consumption of the starting materials, the solution was concentrated, diluted with dichloromethane, washed with Na_2EDTA(aq), brine, and dried over $MgSO_4$. After removal of the solvent in vacuo, the crude material was purified over SiO_2 (10-25% ethyl acetate/hexanes) to yield **7** (149 mg, 94%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.59 (br s, 1H), 8.53 (d, J = 2.0 Hz, 1H), 8.26 (s, 1H), 7.99 (dd, J = 8.4, 1.6 Hz, 1H), 7.73 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.9 Hz, 2H), 7.52 (br s, 1H), 1.40 (s, 9H), 1.37 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.56, 176.82, 152.66, 147.87, 138.91, 137.29, 134.18, 127.88, 126.72, 120.36, 118.45, 114.89, 113.11, 111.54, 40.43, 39.68, 34.81, 31.21, 27.70, 27.54. HR-ESI-MS: $C_{28}H_{38}N_5O_2$ [M + H$^+$], Calculated: 476.3026, Found: 476.3044.



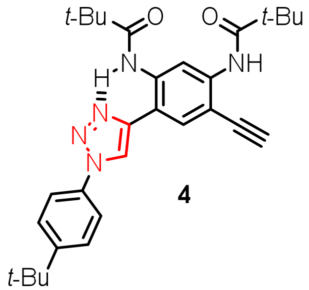
8

Triad-I (8): 7 (430 mg, 0.91 mmol) and ICl (177 mg, 1.1 mmol) was dissolved in $CHCl_3$, warmed to 70 °C and stirred for 16 hours. After cooling, the dark red solution was neutralized with Na_2CO_3 (aq), washed with $Na_2S_2O_3$ (aq) and concentrated in vacuo. The crude material was chromatographed over SiO_2 (10-20% ethyl acetate/hexanes) to yield **7** (480 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.33 (s, 1H), 9.61 (s, 1H), 8.38 (s, 1H), 7.85 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H), 7.53 (d, J = 8.6 Hz, 2H), 1.35 (s, 9H), 1.34 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 177.51, 176.15, 152.56, 146.36, 138.54, 137.99, 136.10, 134.12, 126.66, 120.29, 118.93, 115.54, 114.55, 82.16, 40.42, 40.04, 34.79, 31.23, 27.69, 27.66. HR-ESI-MS: $C_{28}H_{37}N_5O_2I$, [M + H$^+$], Calculated: 602.1992, Found: 602.1985.

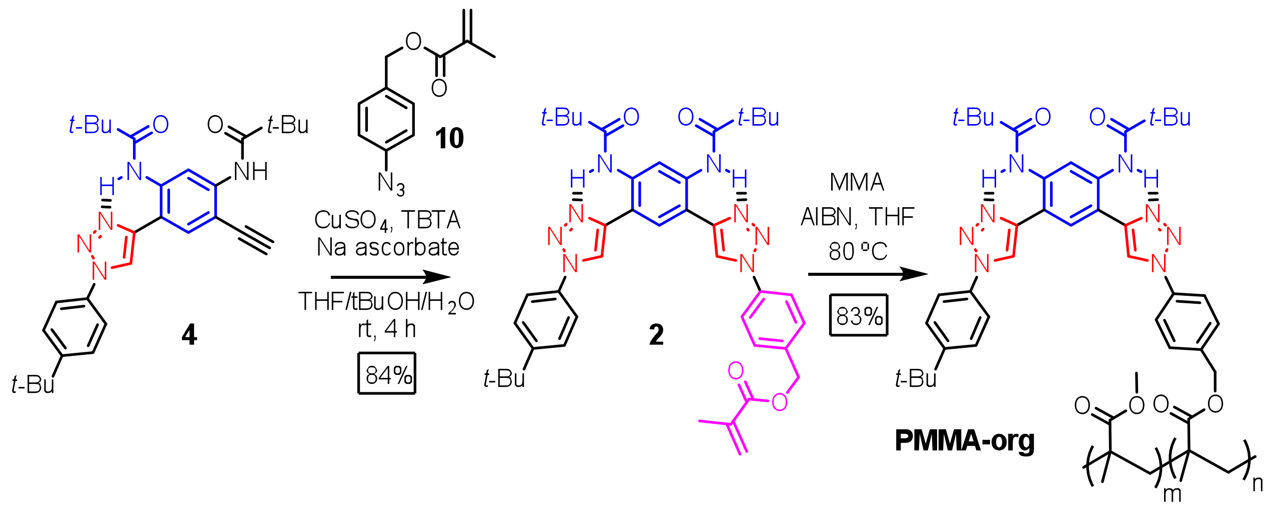


9

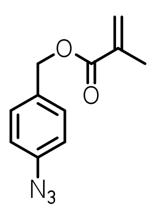
Triad-TMS (9): 8 (480 mg, 0.80 mmol) was dissolved in THF/DIPA(4:1, 25 mL) and degassed for 15 minutes. $PdCl_2(PPh_3)_2$ (30 mg, 0.04 mmol), CuI (8 mg, 0.04 mmol) and (trimethylsilyl)acetylene (250 µL, 1.60 mmol) were then added and the solution was stirred for 16 h. The resulting suspension was filtered over Celite, washed with THF, concentrated in vacuo and purified over SiO_2 (0-3% acetone/dichloromethane) to yield **9** (446 mg, 98%) as a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.46 (s, 1H), 9.91 (s, 1H), 8.34 (br s, 1H), 8.24 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.64 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 1.39 (s, 9H), 1.38 (s, 9H), 1.34 (s, 9H), 0.30 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ = 177.61, 175.97, 152.72, 147.35, 140.34, 138.64, 134.16, 129.94, 126.74, 120.31, 118.28, 112.17, 111.22, 106.23, 101.17, 100.10, 40.50, 40.23, 34.83, 31.22, 27.69, 27.62, -0.01. HR-ESI-MS: $C_{33}H_{46}N_5O_2Si$ [M + H$^+$], Calculated: 572.3421, Found: 572.3428.



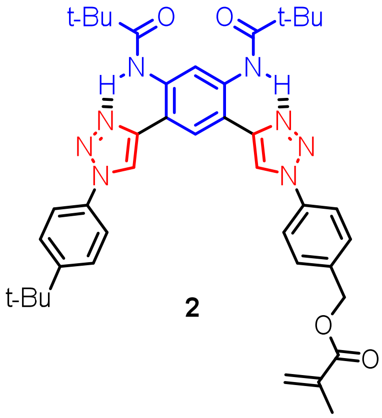
Triad-alkyne (4): 8 (446 mg, 0.780 mmol) was dissolved in THF (20 mL) and saturated K_2CO_3/MeOH (5 mL) was added. After stirring for two minutes, NH_4Cl (75 mL) was added and the resulting suspension was extracted with dichloromethane, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified over SiO_2 (2% acetone in dichloromethane) to yield **4** (366 mg, 94%) as a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.46 (s, 1H), 9.87 (s, 1H), 8.26 (br s, 1H), 8.25 (s, 1H), 7.73 (d, J = 8.6 Hz, 2H), 7.64 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 3.51 (s, 1H), 1.38 (s, 18H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.67, 176.10, 152.72, 147.18, 140.46, 138.82, 134.14, 130.27, 126.74, 120.34, 118.41, 112.41, 111.60, 105.17, 83.51, 79.21, 40.49, 40.21, 34.82, 31.21, 27.66, 27.56. HR-ESI-MS: $C_{30}H_{38}N_5O_2$ [M + H$^+$], Calculated: 500.3026, Found: 500.3037.



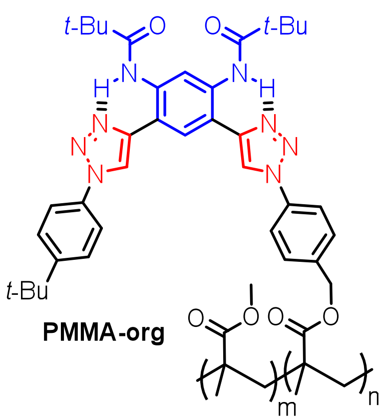
Scheme S3. Two-step preparation of **PMMA-org** from alkyne **4** and azido-methacrylate **10**



4-Azido-benzylmethacrylate (10): 4-Azidobenzyl alcohol (1.13 g, 7.57 mmol) and 4-*N*,*N*'-dimethylaminopyridine (DMAP, 93 mg, 0.75 mmol) were dissolved in CH_2Cl_2/Et_3N (10:1, 20 mL) and cooled to 0 °C. Methacryloyl chloride (940 mg, 8.99 mmol) was then added and the solution was slowly warmed to rt over 4 hours. After the starting material had been consumed, $NaHCO_3$(aq) was added, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the crude material was purified over SiO_2 (1% ethyl acetate/hexanes) to yield **10** (1.23 g, 75%) as a yellow oil. **Note:** This compound should be stored in the dark at –20 °C to hinder self-polymerization. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 6.15 (s, 1H), 5.80 (s, 1H), 5.17 (s, 2H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.14, 139.97, 136.13, 132.84, 129.75, 125.89, 119.11, 65.77, 18.31. HR-CI-MS: $C_{11}H_{12}C_2N_3$ [M + H$^+$], Calculated: 218.0924, Found: 218.0932.



Methacrylate-preorganized pentad (2): 4 (106 mg, 0.21 mmol) and **10** (51 mg, 0.23 mmol) were dissolved in THF (10 mL), *t*-BuOH (3 mL), and H_2O (2 mL) and degassed with argon. TBTA (6 mg, 0.01 mmol), $CuSO_4$•$5H_2O$ (3 mg, 0.01 mmol), and sodium ascorbate (4 mg, 0.02 mmol) were then added sequentially, and the solution was stirred for 16 hours at rt. After consumption of the starting material, NH_4Cl (75 mL) was added and extracted with dichloromethane. After washing with Na_2EDTA (aq), the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude material was purified over SiO_2 (15% acetone/hexanes) to yield **2** (128 mg, 84%) as an off-white solid. ^1H NMR (400 MHz, $CDCl_3$) δ = 11.09 (s, 1H), 11.08 (s, 1H), 9.88 (s, 1H), 8.46 (s, 1H), 8.27 (s, 1H), 7.89 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 7.61 (s, 1H), 7.57 (d, J = 6.2 Hz, 2H), 7.55 (d, J = 7.0 Hz, 2H), 6.21 (s, 1H), 5.65 (s, 1H), 5.28 (s, 2H), 2.01 (s, 3H), 1.38 (s, 9H), 1.32 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 177.60, 177.48, 167.06, 152.60, 147.60, 147.38, 137.44, 137.40, 137.25, 136.45, 136.00, 134.24, 129.27, 126.64, 126.20, 125.71, 120.85, 120.56, 118.83, 118.68, 114.18, 113.10, 112.91, 65.43, 40.30, 40.29, 34.83, 31.24, 27.68, 18.33. HR-ESI-MS: $C_{41}H_{48}N_6O_4Cl$ [M + Cl^-], Calculated: 751.3487, Found: 751.3458.



PMMA-org

PMMA-organized pentad copolymer (PMMA-org): PMMA-org was prepared following a similar procedure as **PMMA-unorg** using **2** as the comonomer (1:10 feed ratio) with methyl methacrylate. 83% yield. ^1H NMR (400 MHz, CD_2Cl_2) δ = 11.15 (br, 2H), 9.96 (br, 1H), 8.44 (br, 2H), 7.87-7.50 (br, 9H), 5.08 (br, 2H), 3.60 (br, 22H), 2.05-1.7 (br, 13.9H), 1.51-1.14 (br, 36.7H), 1.02-0.84 (br, 23.5H).

S3. 2D ROESY NMR – Monomer 2

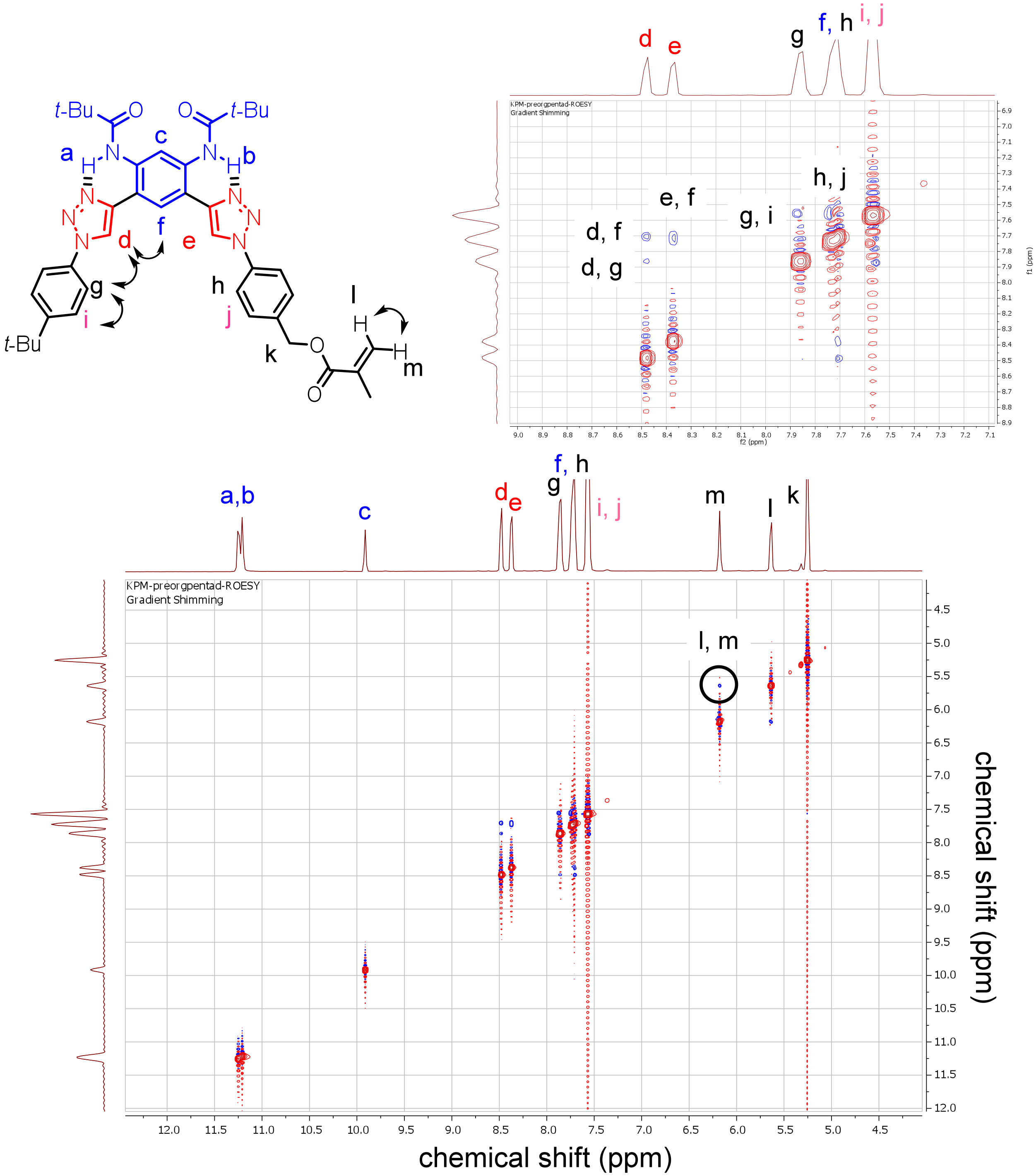


Figure S1. 2D ROESY NMR spectrum for monomer **2** (CD_2Cl_2, 298 K, 500 MHz)

S4. Anion Titrations

Dried polymer samples were dissolved in CD_2Cl_2 (400 μL) in a septum-lined screw capped NMR tube to achieve the effective concentration of the receptor. An initial ^{1}H NMR spectrum was recorded and additional spectra were obtained after aliquots of a TBA^+ halide solution (in CD_2Cl_2) was injected sequentially using a microsyringe. The ^{1}H NMR peak data was fit to a binding model including K_1, K_2, and K_{ion} using HypNMR.[6] For **PMMA-org**, changes in the triazole ($H_{d,e}$), terminal phenylene ($H_{i,j}$) and α-TBA^+ resonances were used in the data fitting while the triazole (H_a), and central phenylene (H_b) resonances were used in determining K_{eff} for **PMMA-unorg**. The effective concentration of the receptor was determined based on the average weight percentage of the receptor relative to methyl methacrylate as determined by ^{1}H NMR integration.

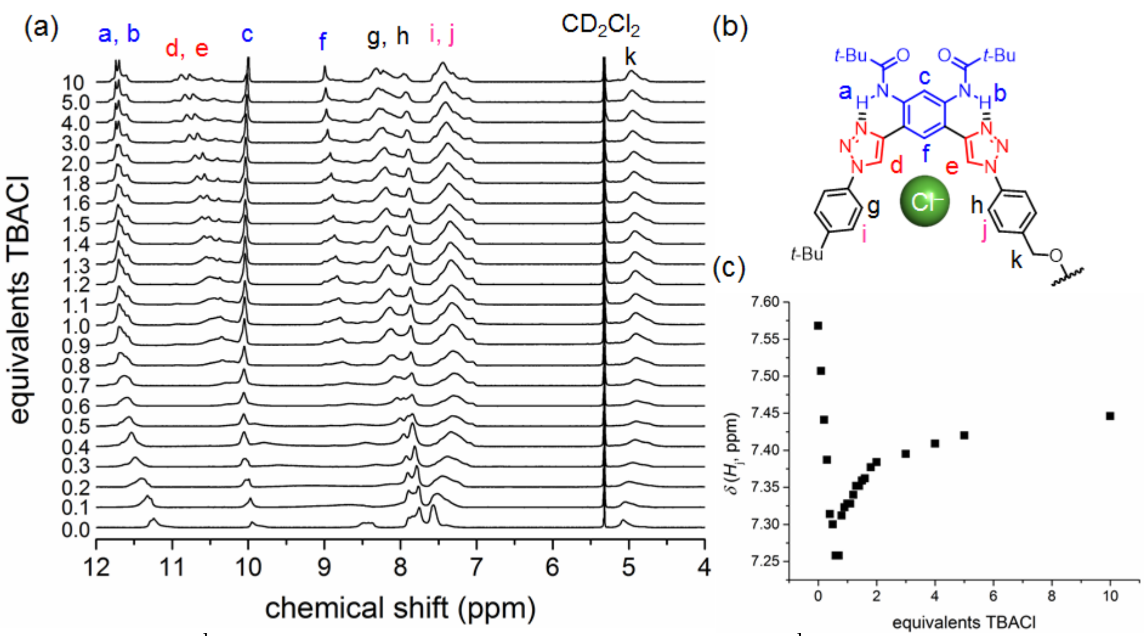


Figure S2. (a) ^{1}H NMR titration of **PMMA-org** (36 mg mL^{-1}, CD_2Cl_2, [receptor]$_{eff}$ = ~24 mM, CD_2Cl_2, 298 K) with TBACl. (b) Resonances assigned for **PMMA-org** based upon the corresponding monomer. (c) Plot of $\delta(H_{i,j})$ vs. equivalents TBACl.

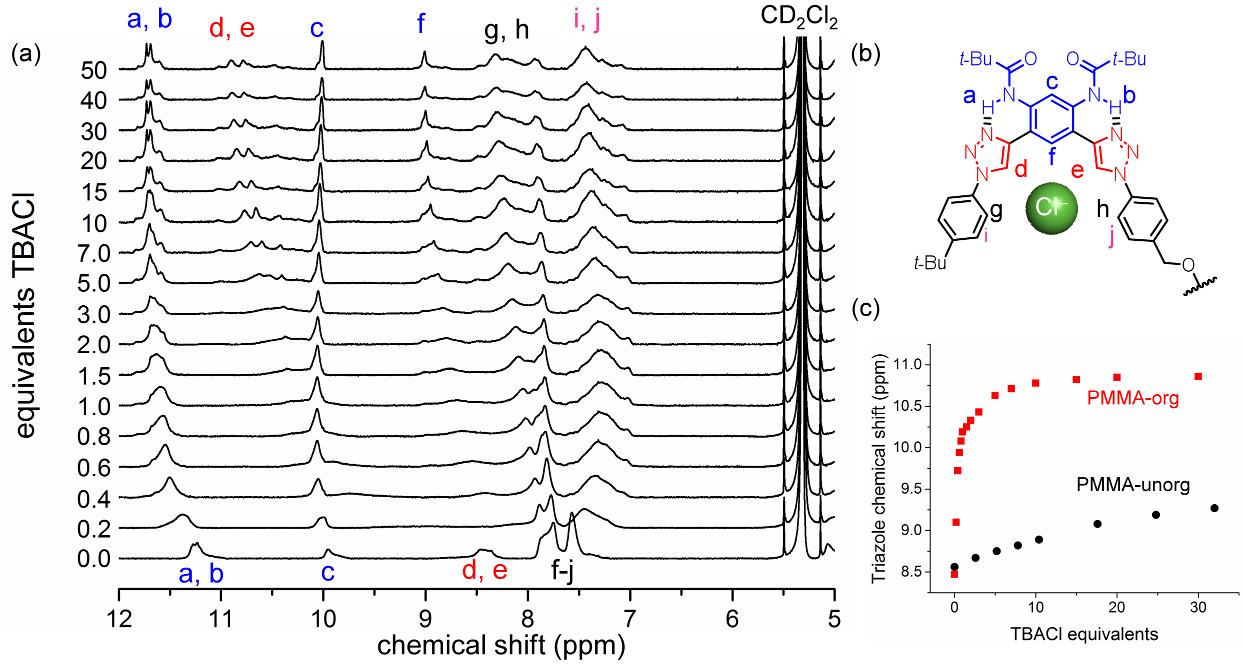


Figure S3. (a) ^{1}H NMR titration of **PMMA-org** (6 mg mL^{-1}, [receptor]$_{eff}$ = ~4 mM, CD_2Cl_2, 298 K) with TBACl. (b) Resonances assigned for **PMMA-org** based upon the corresponding monomer. (c) Plot of triazole chemical shift vs. equivalents TBACl compared to **PMMA-unorg**.

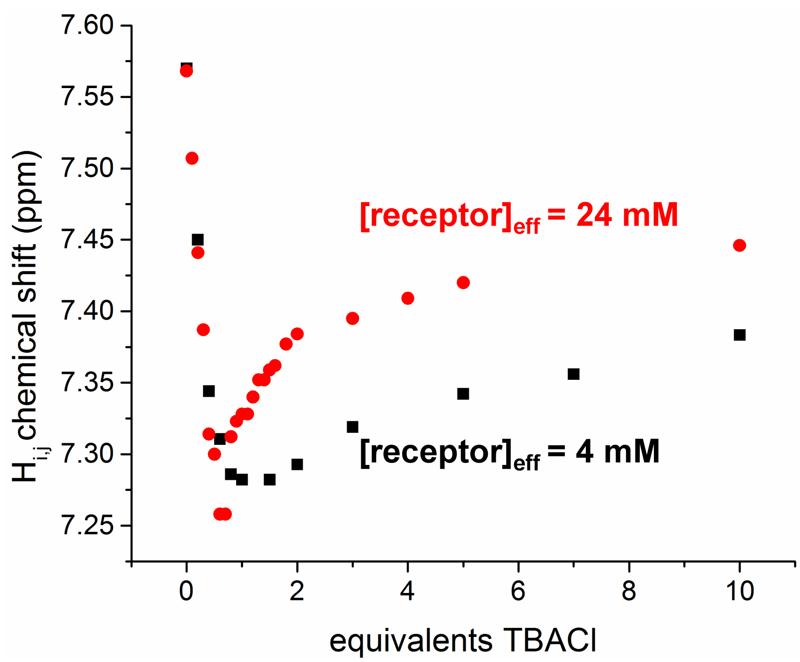


Figure S4. Comparison of the terminal phenylene (H$_{i,j}$) signals for **PMMA-org** at two different polymer concentrations ([receptor]$_{eff}$ = ~4 and ~24 mM; 6 and 36 mg mL^{-1}) during ^{1}H NMR titrations. The earlier inflection point and higher upfield change in chemical shift for the ~24 mM titration is consistent with a higher concentration of 2:1 cross-links formed.

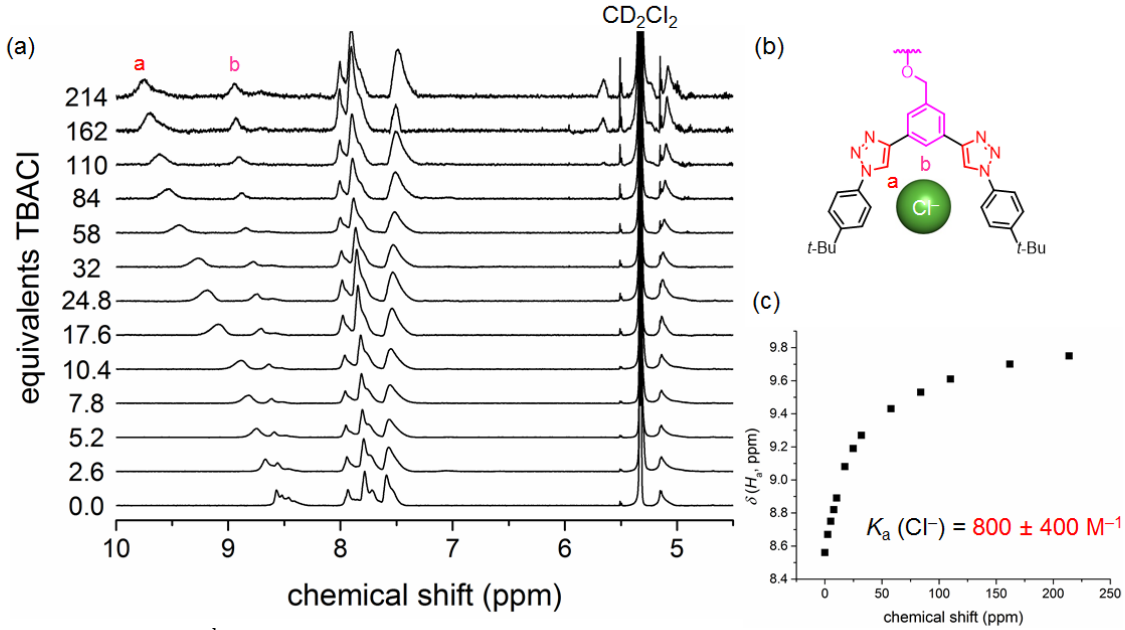


Figure S5. (a) [1]H NMR titration of **PMMA-unorg** (~4 mM receptor, CD_2Cl_2, 298 K) with TBACl. (b) Resonances assigned for **PMMA-unorg** based upon the corresponding monomer. (c) Plot of $\delta(H_a)$ vs. equivalents TBACl and the corresponding binding affinity obtained from fitting to an approximate 1:1 binding model with ion-pairing (TBACl) and ion-pair complexes included.[S7] Relative to known binding models for aryl-triazoles, K_2 was not included as no inflection point was observed in the signal @ 7.5 ppm stemming from the terminal phenylenes.

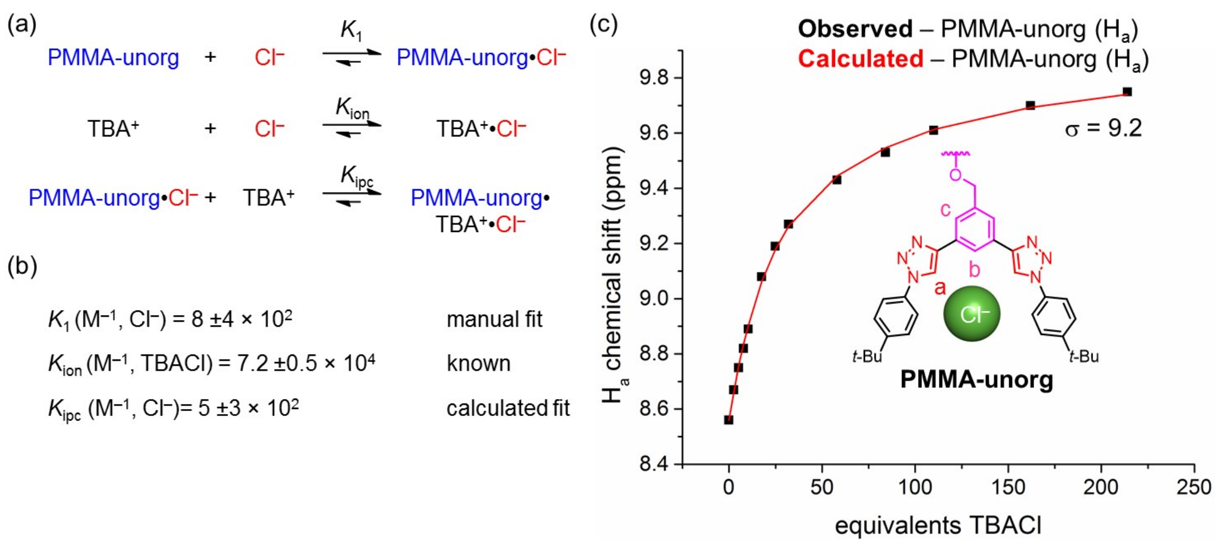


Figure S6. (a) Chloride binding model for unorganized aryl-triazole pentad including K_1 (1:1 binding), K_{ion} (ion pairing between the TBA^+ and chloride), and K_{ipc} (ion pairing between the chloride complex and TBA^+). (b) Fitting obtained from the [1]H NMR data of **PMMA-unorg**. The known value for K_{ion} was fixed while K_1 was changed systematically. The range of K_{ipc} values were obtained from this scan of K_1. (c) Plot of observed and calculated chemical shift positions for the triazole (H_a) resonance in **PMMA-unorg**.

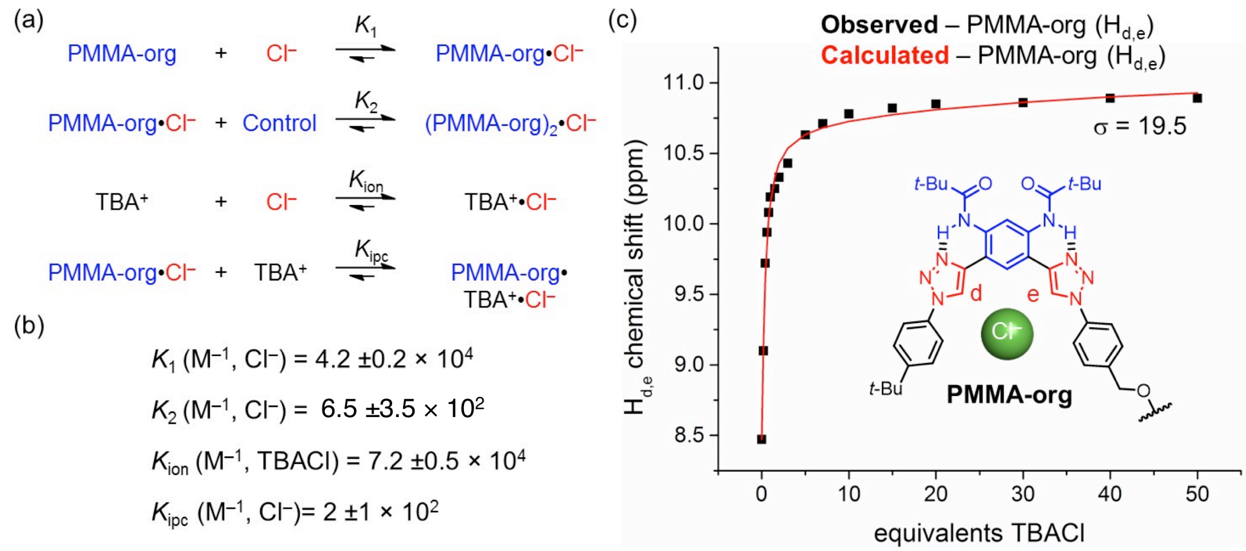


Figure S7. (a) Chloride binding model for **PMMA-org** and (b) values obtained from fitting [1]H NMR data using the triazole ($H_{d,e}$), terminal pheneylene ($H_{i,j}$) and the α-CH_2 resonance from the TBA^+ cation. (c) Plot of observed and calculated triazole ($H_{d,e}$) chemical shifts in **PMMA-org**.

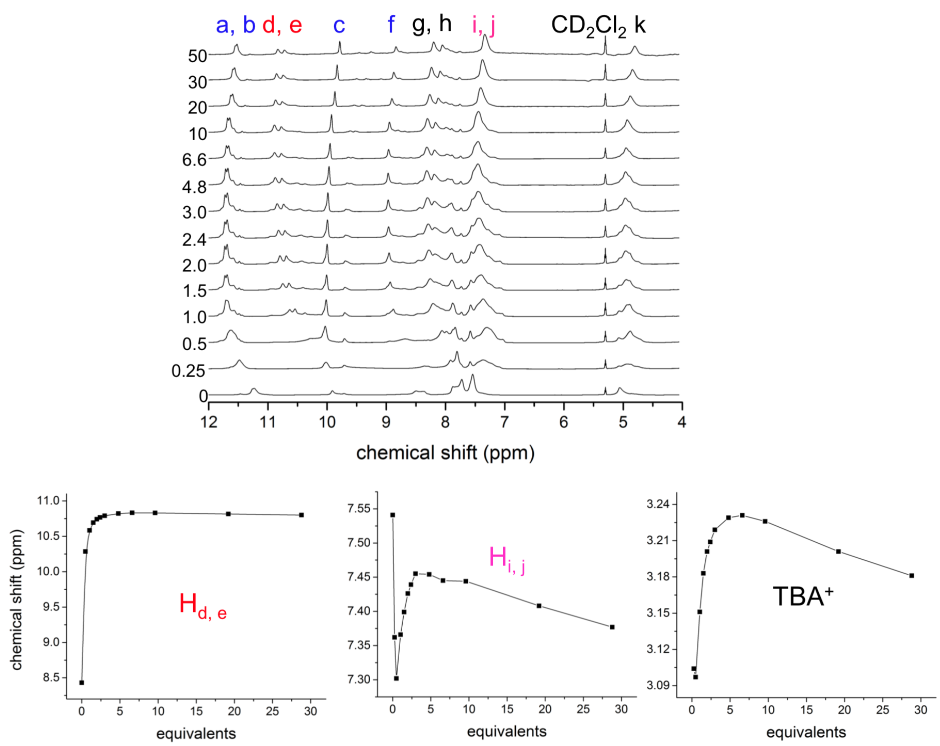


Figure S8. [1]H NMR titration of **PMMA-org** (100 mg mL^{-1}, $[receptor]_{eff}$ = ~70 mM, CD_2Cl_2, 298 K) with TBACl and plots of chemical shift vs. equivalents. The $H_{d,e}$ signals saturate upon addition of 1-2 eq. TBACl while Hi,j shows an inflection point at 0.5 eq. of added TBACl. The α proton of the TBA^+ cation also shows an inflection point at 0.5 eq. that indicates a free TBA^+ that is not associating with the Cl^- anion. Its shift back downfield is associated with pairing to form TBACl.

S5. Monomer Binding Comparison

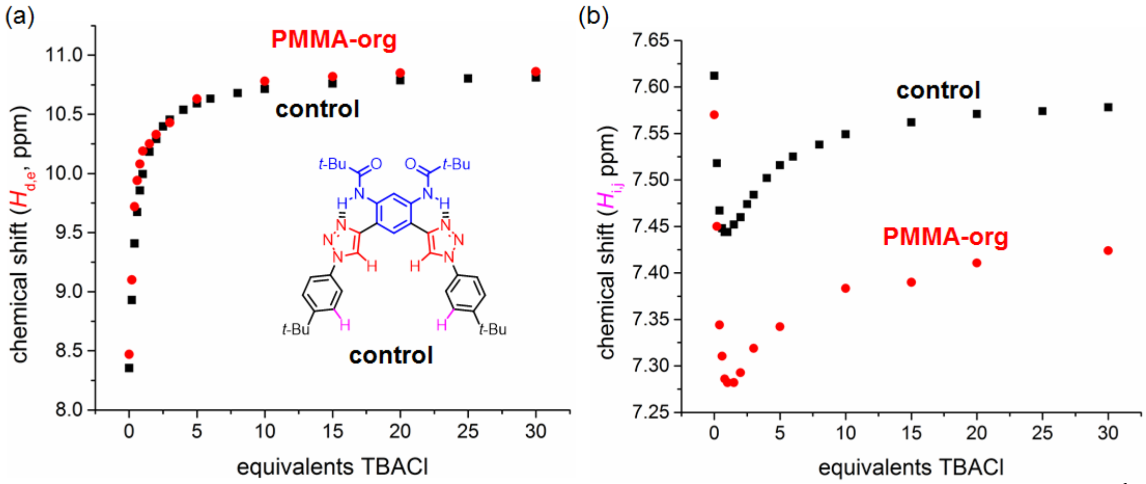


Figure S9. Comparison of titration data for the (a) triazole and (b) terminal phenylene ^{1}H NMR peak shifts observed for **PMMA**-org (~4 mM, CD_2Cl_2) and for a monomeric analogue (**control**, 5 mM, CD_2Cl_2). The similar trends in triazole peak migration shows that the binding affinity of the aryl-triazole receptor is unchanged after incorporation into the polymer ($K_{eff} \sim 5 \times 10^4$ M^{-1}. The trends in chemical shift change observed for $H_{i,j}$ show the same inflection point which correlates to similar stabilities of the 2:1 complexes formed.

S6. Diffusion NMR

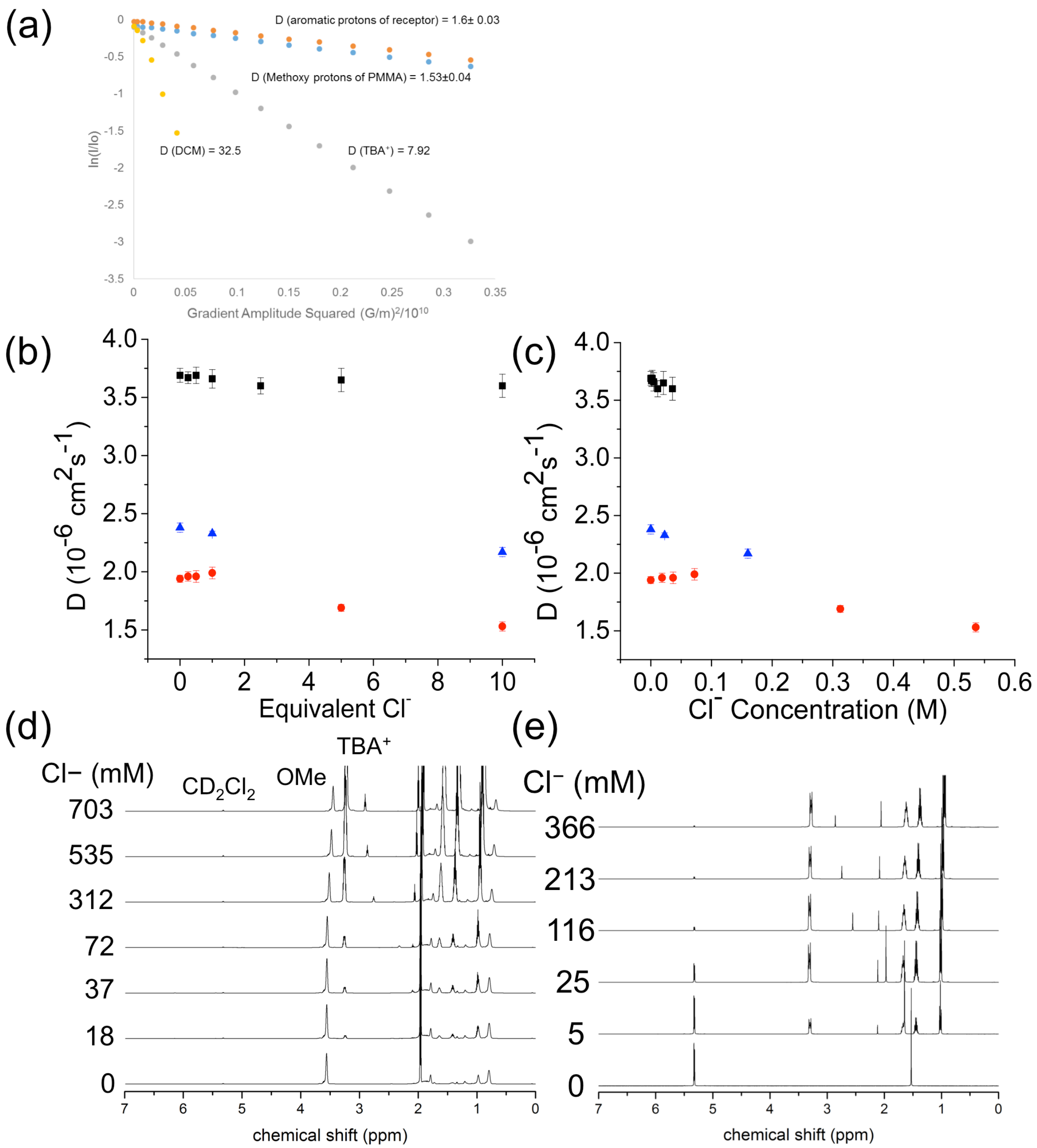


Figure S10. (a) Representative plots of peak intensity, ln (I/I_o), against the gradient squared (G^2) for **PMMA-org** with 10 eq. TBACl ([receptor]$_{eff}$ = ~70 mM, CD_2Cl_2, 298 K). (b) *D* values for the TBACl titration with **PMMA-org** at ~4 mM (squares, 600 MHz), ~24 mM (triangles, 500 MHz) and ~70 mM (circles, 600 MHz) (CD_2Cl_2, 298 K). *D* values are based on the OMe proton from MMA. (c) The same plot as part (b) but redrawn vs. TBACl concentration. ^{1}H NMR spectra upon addition of TBACl that correspond to the diffusion data in Tables S1 and S2 for the (d) PMMA homopolymer (25 mg mL^{-1}) and (e) neat CD_2Cl_2.

Table S1. Summary of diffusion coefficients for selected peaks in the **PMMA-org** (~70 mM) and the PMMA homopolymer (25 mg mL^{-1}) upon addition of TBACl salt (600 MHz)

Cl^- concentration (mM)	D (10^{-6} cm^2 s^{-1})				
	PMMA-org			PMMA	
	OMe[a]	receptor[b]	α-H TBA^+	OMe[a]	α-H TBA^+
0	1.94 ±0.03	1.66 ±0.03	-	4.18 ±0.08	-
18.5	1.96 ±0.04	1.66 ±0.04	6.27 ±0.03	4.13 ±0.08	14.5 ±0.4
36.8	1.96 ±0.05	1.68 ±0.06	6.2 ±0.1	4.07 ±0.07	15.8 ±0.8
72.1	1.99 ±0.05	1.69 ±0.04	7.97 ±0.07	3.98 ±0.07	14.4 ±0.1
312	1.69 ±0.03	1.3 ±0.1	8.92 ±0.03	3.45 ±0.06	12.3 ±0.1
535	1.53 ±0.04	1.2 ±0.01	7.99 ±0.01	2.94 ±0.03	10.3 ±0.1
703	-	-	-	2.55 ±0.02	8.9 ±0.1

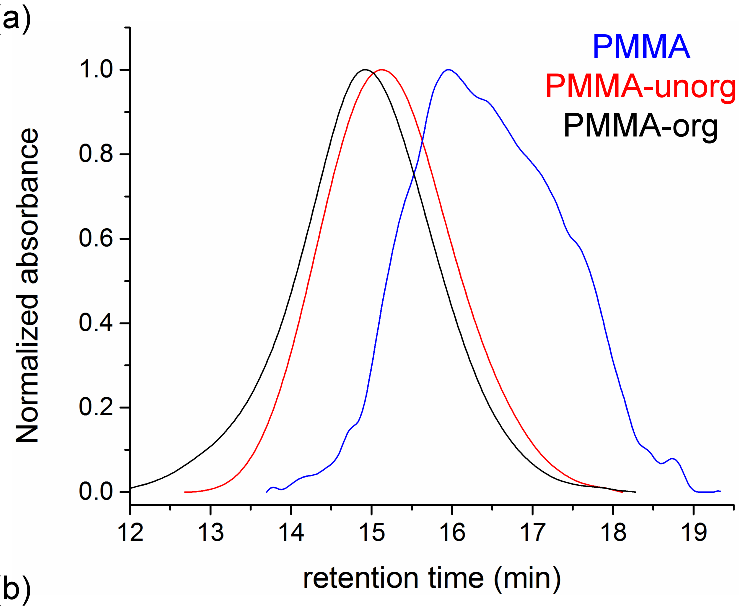
[a] Methoxy protons on PMMA.
[b]Amide protons on the receptor.

Table S2. Summary of diffusion coefficients associated with the addition of TBACl salt to neat CD_2Cl_2 (600 MHz)

Cl^- concentration (mM)	D (10^{-6} cm^2 s^{-1})	
	$CHDCl_2$	TBA-α
0.0	46 ±1	-
5.1	48 ±2	17 ±1
25.1	45 ±2	15.9 ±0.3
116	47 ±2	14.4 ±0.3
213	41 ±2	13.3 ±0.2
366	42 ±2	11.6 ±0.2

S7. Gel Permeation Chromatography (GPC)

(a)



(b)

	M_w	M_n	PDI	$\overline{DP}$
PMMA	6150	3250	1.89	32
PMMA-unorg	16800	10200	1.66	70
PMMA-org	24200	12600	1.92	72

Figure S11. GPC elugrams for (a) methacrylate-based copolymers. Relative molecular weights (b) were determined from calibration curves obtained from PMMA standards. The degree of polymerization (DP) was calculated from the average M_n values and the molar ratios (m, n) of the two monomers.

S8. Thermal Gravimetric Analysis

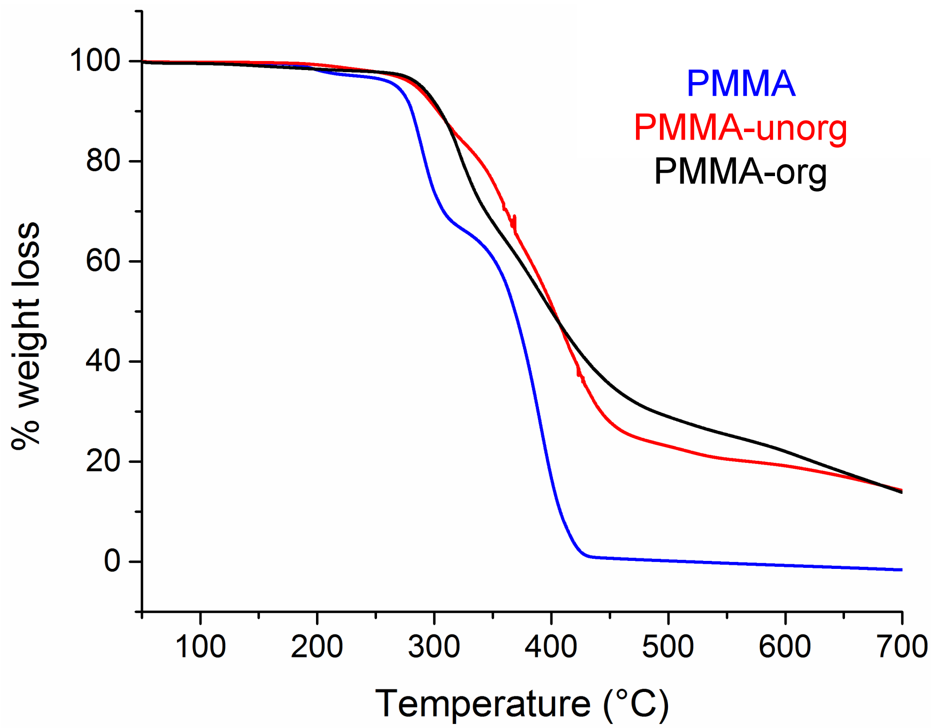


Figure S12. Thermogram of PMMA-based homo- and copolymers taken under an atmosphere of nitrogen at a scan rate of 10 °C / min. The decrease in % weight loss for the copolymers provides indirect evidence for incorporation of the aryl-triazole oligomer into the polymer.

S9. Extraction

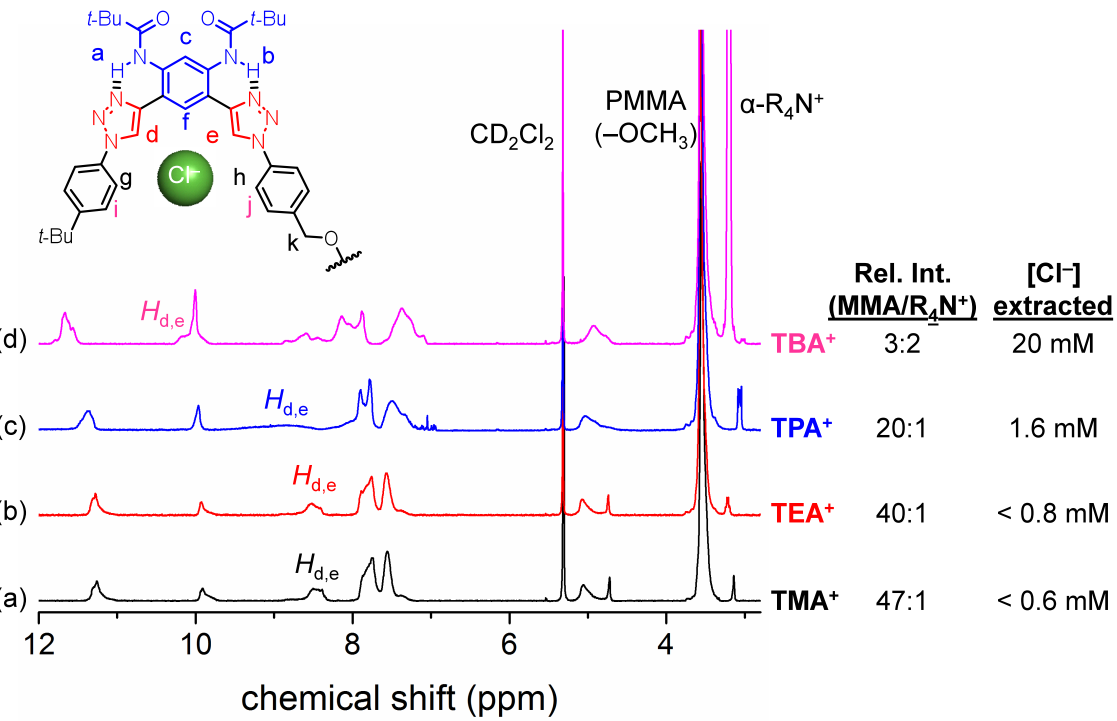


Figure S13. [1]H NMR spectra (CD_2Cl_2, 298 K) collected of **PMMA-org** ($[\text{receptor}]_{eff}$ = 8.8 mM) after extraction with D_2O solutions (100 mM) of (a) TMACl, (b) TEACl, (c) TPACl, and (d) TBACl. The extent of extraction was determined by comparison of the peak intensities of the tetraalkylcation (R_4N^+) and the methoxy signal ($-OCH_3$) of methyl methacrylate.

The ability of **PMMA-org** to extract salt was determined using liquid-liquid extractions experiments and subsequent analysis was conducted using ^{1}H NMR. Samples of a PMMA homopolymer (5 mg, M_n = 3,520) and **PMMA-org** (10 mg, M_n = 12,600) were dissolved in CD_2Cl_2 (750 μL, $[\text{receptor}]_{eff}$ = 10 mM). These concentrations were selected so that the amount of PMMA in solution would be equal. Tetrapropylammonium chloride (TPACl, 16.5 mg) was dissolved in D_2O (750 µL, [TPACl] = 100 mM). The salt and polymer solutions were added to a glass vial, sealed, and stirred for 12 h (25 ºC, 1000 rpm). The mixture was then allowed to phase separate for 30 min before the organic phase was transferred into an NMR tube for analysis. Determination of extraction efficacy was done by comparing integration of the PMMA methyl group (~3.6 ppm) to the α-proton of the tetraalkylammonium cation (~3.2 ppm).

A countercation effect was demonstrated. The extraction of salts using neutral organic receptors is related to the corresponding partition coefficients (Figure 5, main text). Control experiments with the PMMA homopolymer showed this effect to be related to increased partitioning of the larger, hydrophobic cation (Figure S14). Minimal partitioning was observed for TMA, TEA, or TPACl. However, integration of the TBA^+ resonance following extraction with the PMMA homopolymer was found to be identical to that seen in extraction experiments with **PMMA-org**.

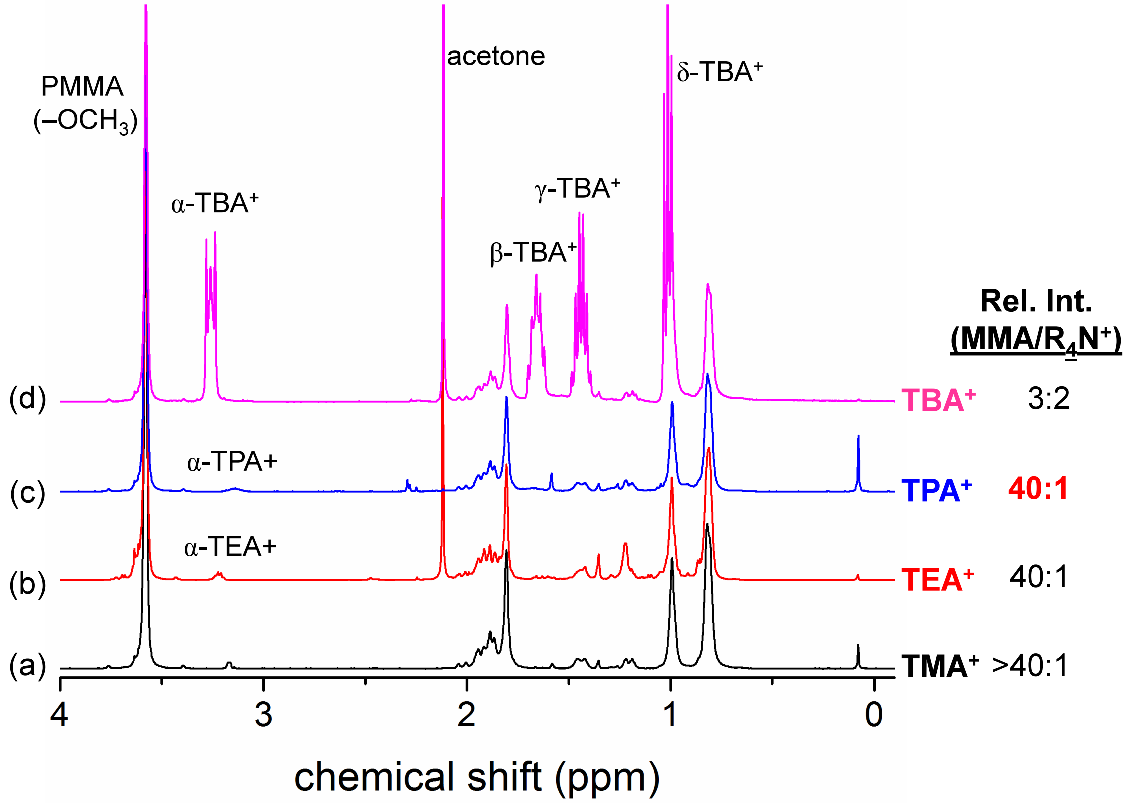


Figure S14. [1]H NMR spectra (CD_2Cl_2, 298 K) collected after extraction experiments involving various chloride salts with the PMMA homopolymer (10 mg / mL, M_n = 3520). The role of the cation in effecting extraction was explored by comparing the relative integration of methyl methacrylate (MMA) to the cation (a) TMACl, (b) TEACl, (c), TPACl, and (d) TBACl.

Table S3. Chloride concentrations and enhancement factors observed in the extraction of chloride salts by **PMMA-org** and the PMMA homopolymer

	Relative Integration (MMA/R_4N^+)		Enhancement Factor
	PMMA-org	**PMMA**	$\frac{[Cl^-]_{PMMA\text{-}org}}{[Cl^-]_{PMMA}}$
TBACl	3:2 (20 mM)	3:2 (20 mM)	1.0
TPACl	20:1 (1.6 mM)	40:1 (0.8 mM)	2.0
TEACl	40:1 (0.8 mM)	40:1 (0.8 mM)	1.0
TMACl	47:1 (0.6 mM)	40:1 (0.8 mM)	1.2

S10. X-Ray Crystallographic Analysis of 2:1 Chloride Complex with Control

Data collection

Single crystals of a 2:1 complex of **control**[S5] and TEACl was grown by slow diffusion of diethyl ether into a solution of 1,2-dichloroethane. A colorless crystal (approximate dimensions 0.425 × 0.121 × 0.074 mm^3) was placed onto the tip of MiTeGen and mounted on an Apex Kappa Duo diffractometer and measured at 100 K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 339 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with 0.50º steps in ω and ϕ scans. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 7334 strong reflections from the actual data collection after integration (SAINT).[S8] The intensity data were corrected for absorption (SADABS).[S9] Please refer to Table S4 for additional crystal and refinement information.

Structure solution and refinement

The space group P–1 was determined based on intensity statistics and systematic absences. The structure was solved using SIR-92[S10] and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system.[S11] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The structure of **control$_2$•Cl$^-$** exhibits structural disorder on one of the tetraethylammonium cations as well as solvent 1,2-dichloroethane. On account of a low reflection-to-parameter ratio as well as severe solvent disorder that could not be modeled successfully, Platon SQUEEZE[12] was implemented to treat the solvents with neutral charge, with tetraethylammonium being refined isotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. The final full matrix least squares refinement converged to R1 = 0.0717 and wR2 = 0.2423 (F^2, all data).

Table S4. **Crystal data and structure refinement for control$_2$•TEACl**

Empirical formula	$C_{176} H_{240} Cl_2 N_{34} O_8$	
Formula weight	3030.99	
Crystal color, shape, size	colorless block, 0.425 × 0.121 × 0.074 mm^3	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P–1	
Unit cell dimensions	a = 20.868(4) Å	α= 79.546(3)°.
	b = 22.184(4) Å	β= 81.047(4)°.
	c = 22.207(5) Å	γ = 77.042(3)°.
Volume	9781(3) $Å^3$	

Z	2
Density (calculated)	1.026 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	3264
Data collection	
Diffractometer	Bruker Apex Kappa Duo, Bruker
Theta range for data collection	1.009 to 25.153°.
Index ranges	$-24 \leq h \leq 24$, $-25 \leq k \leq 26$, $0 \leq l \leq 26$
Reflections collected	34411
Independent reflections	34411 [R(int) = 0.000]
Observed Reflections	13009
Completeness to theta = 25.153°	98.2 %
Solution and Refinement	
Absorption correction	Numerical
Max. and min. transmission	0.99 and 0.99
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with
	$P = (Fo^2 + 2\ Fc^2)/3$, A = 0.136, B = 0.000
Data / restraints / parameters	34411 / 142 / 1912
Goodness-of-fit on F^2	0.8877
Final R indices [I>2sigma(I)]	R1 = 0.0717, wR2 = 0.1864
R indices (all data)	R1 = 0.1685, wR2 = 0.2423
Largest diff. peak and hole	1.48 and –1.43 e.Å^{-3}

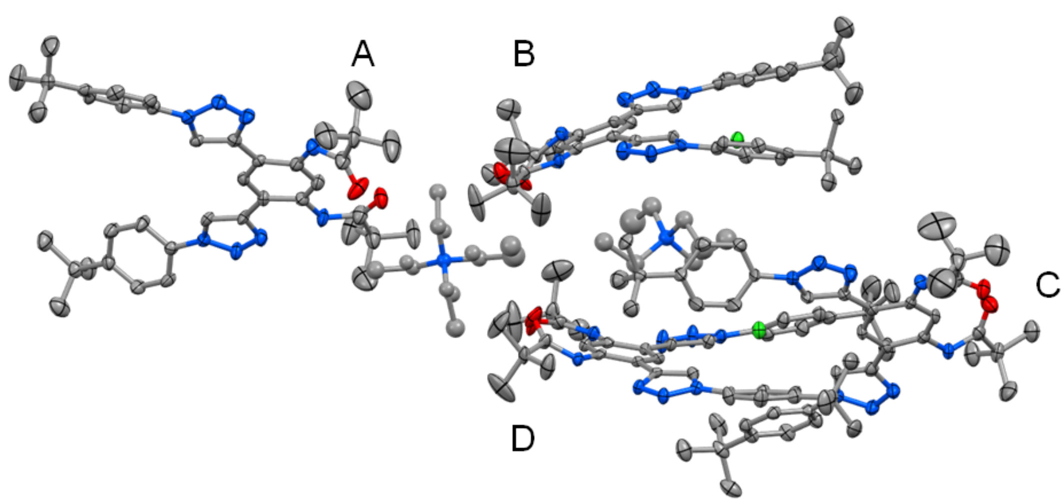


Figure S15. Asymmetric unit of **control$_2$**•TEACl crystal structure containing four pentads and two TEACl salt molecules (50% ellipsoids, hydrogen atoms omitted for clarity).

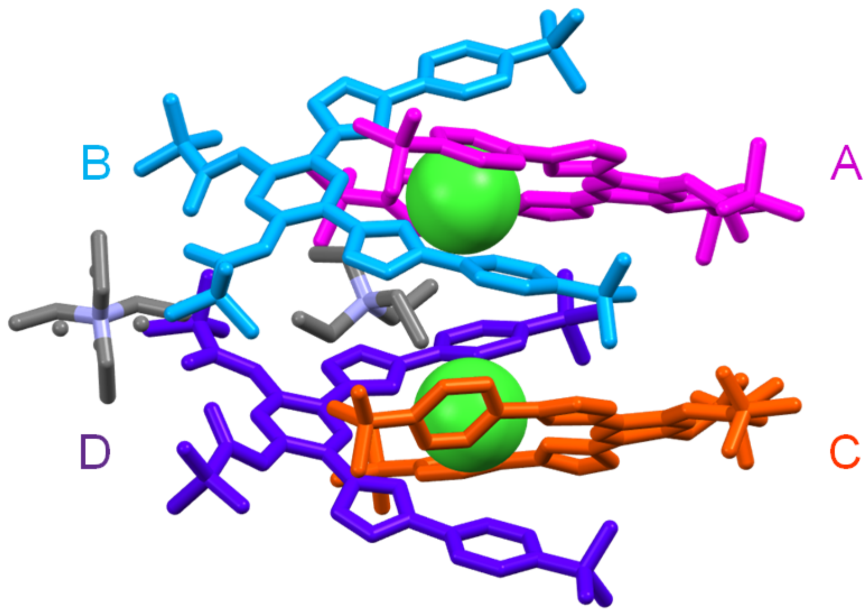


Figure S16. Two pairs of **control$_2$**•TEACl complexes stacked on top of one another (hydrogen atoms omitted for clarity).

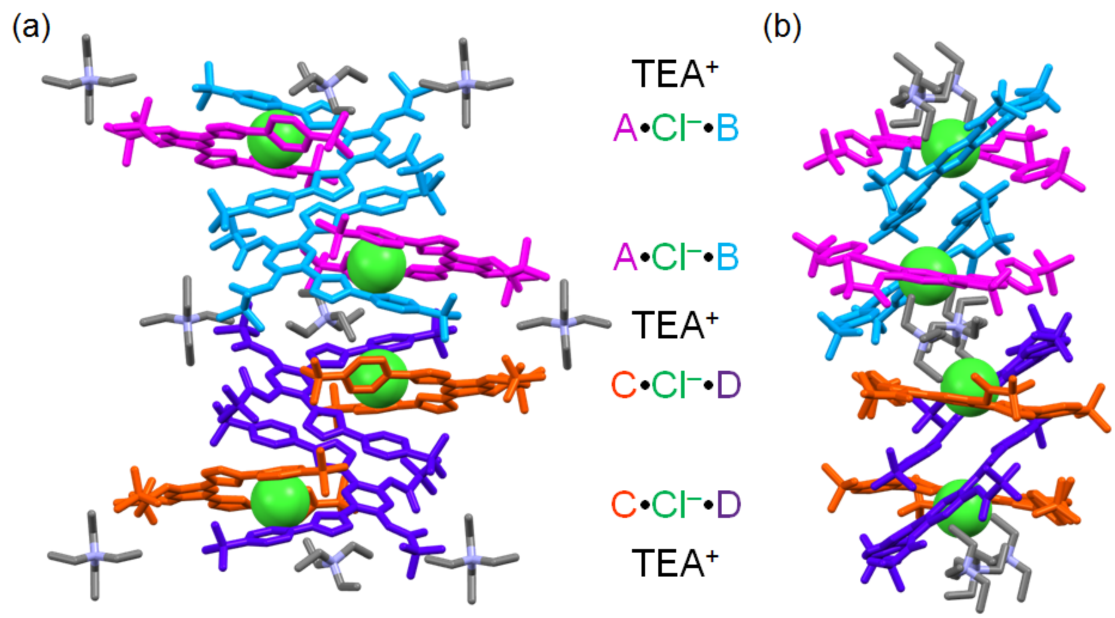


Figure S17. Columnar stacking of **control$_2$**•TEACl complexes in the crystal structure (hydrogen atoms omitted for clarity).

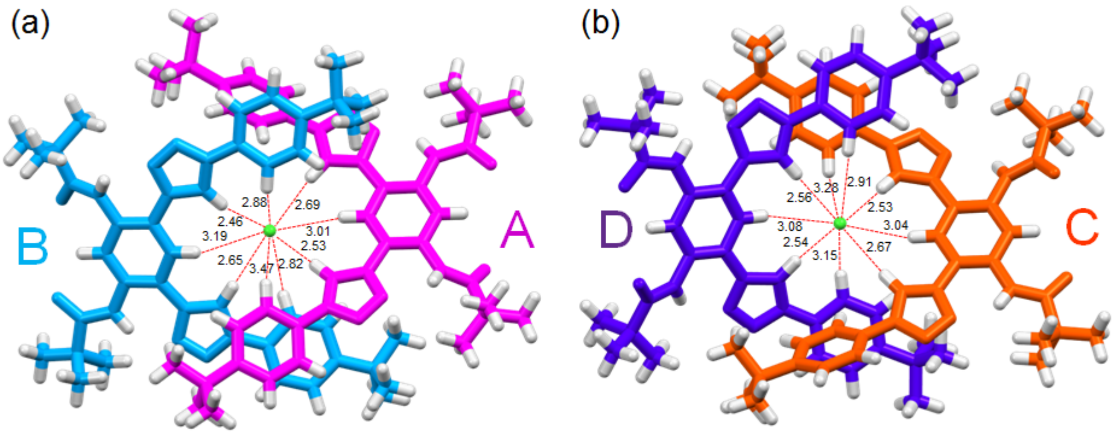
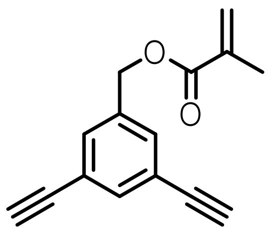


Figure S18. C–H•••Cl⁻ distances within **control**$_2$•Cl⁻ pairs (a) AB and (b) CD.

S11. ^{1}H and ^{13}C NMR Spectra



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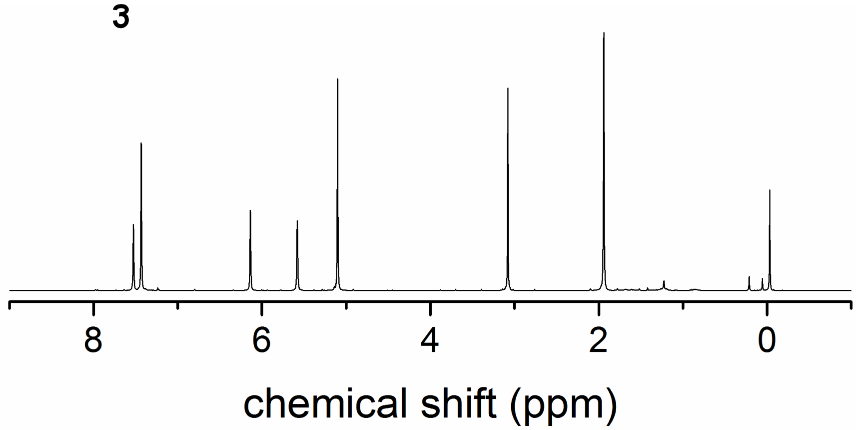

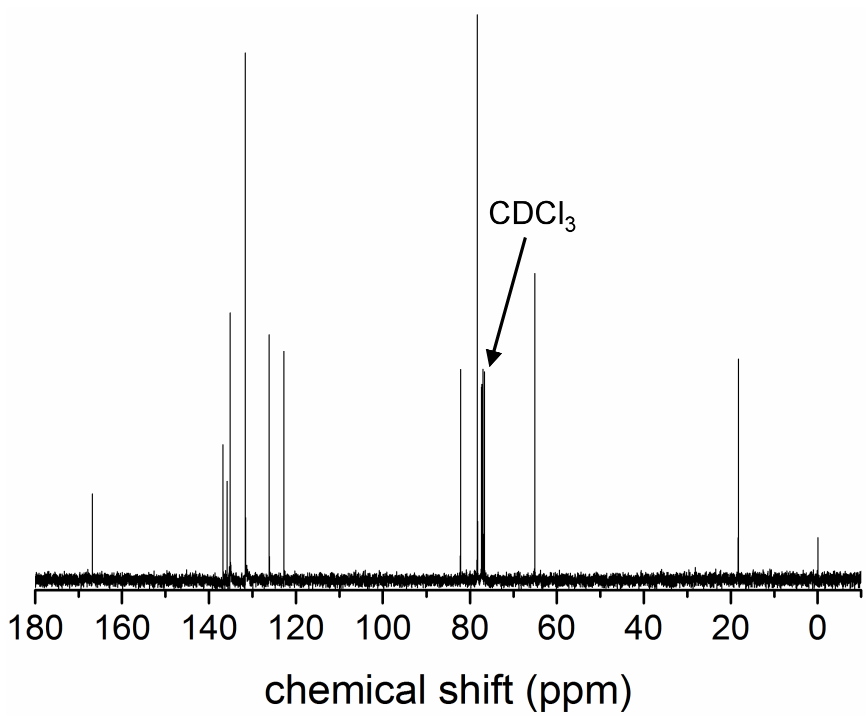

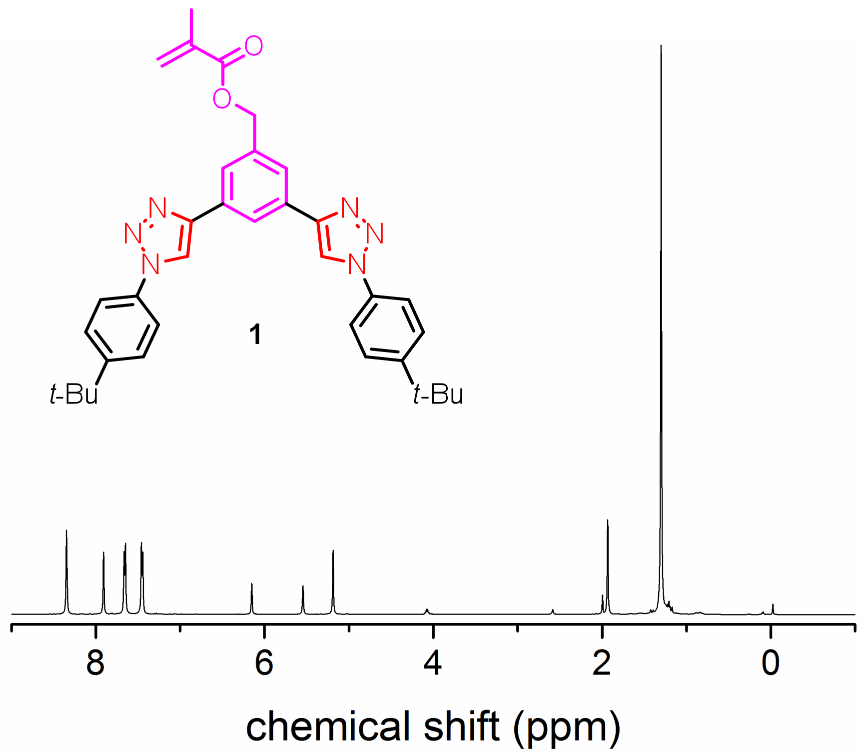
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N
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O
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8
6
4
2
0
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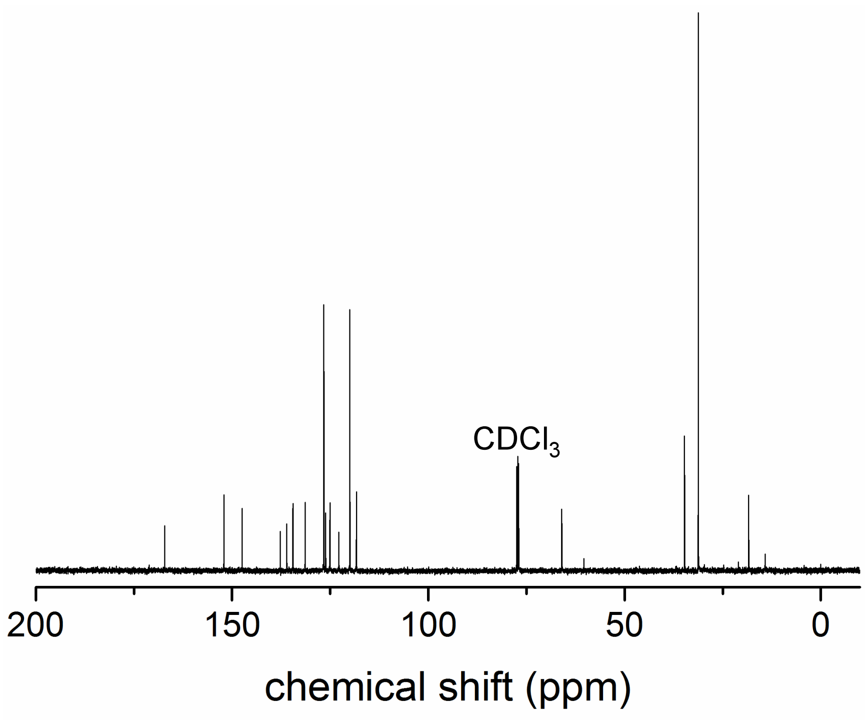
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200
150
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50
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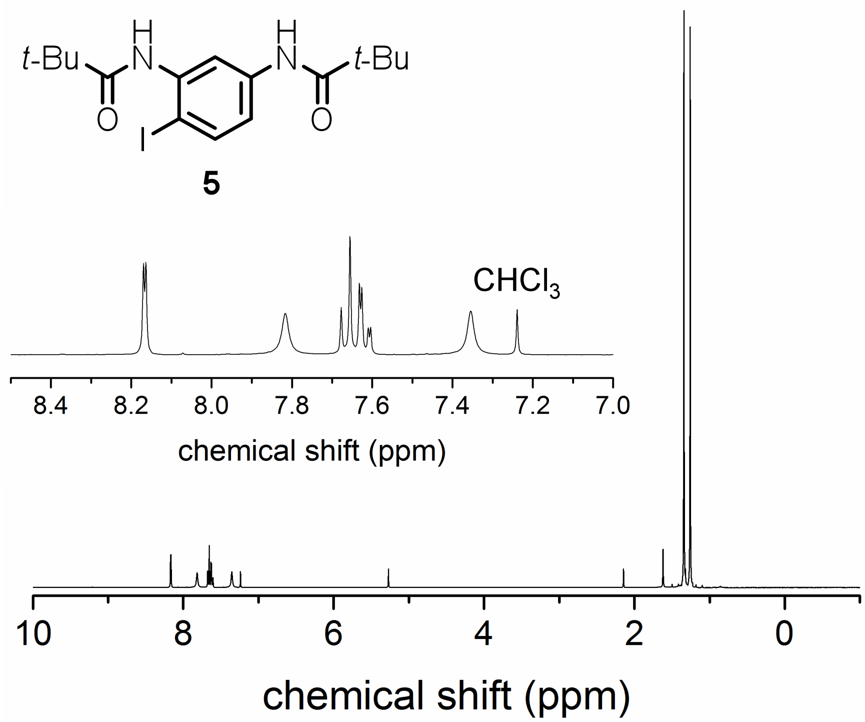
chemical shift (ppm)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H
N
t-Bu
O
O
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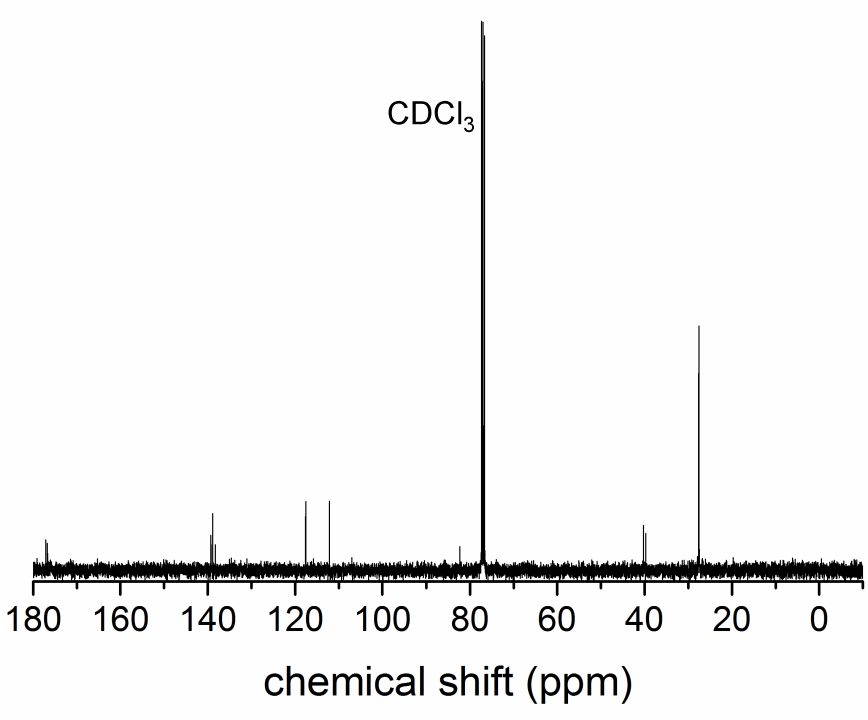
chemical shift (ppm)
10
8
6
4
2
0
chemical shift (ppm)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20
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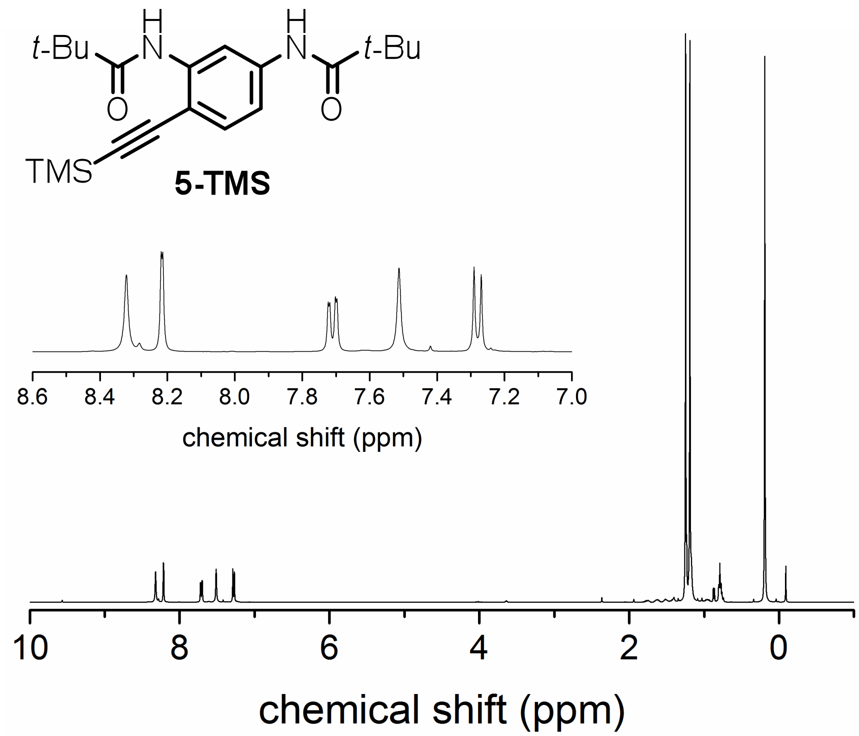
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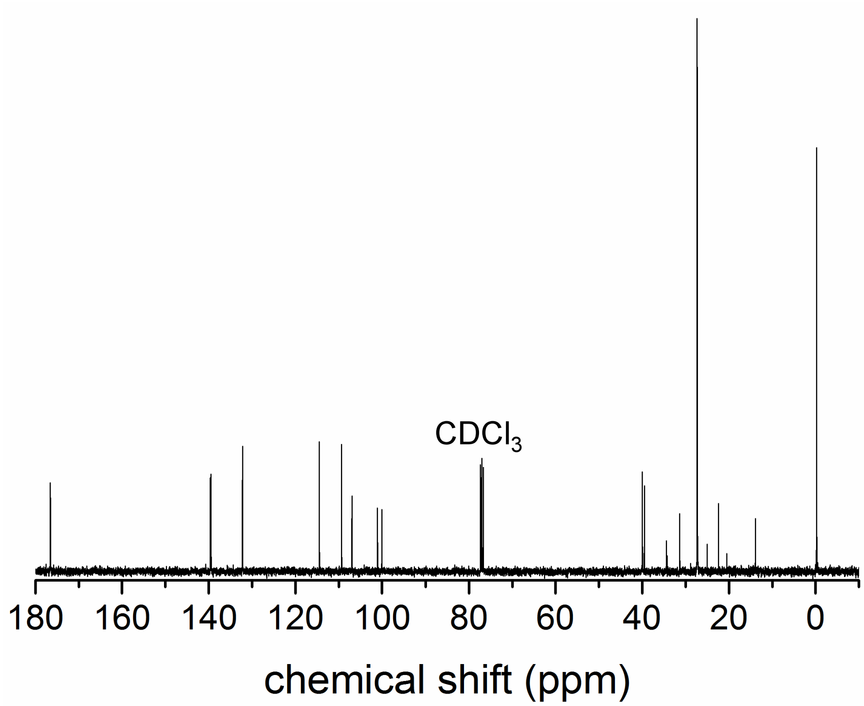
H N
t-Bu
O
O
TMS
5-TMS
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
chemical shift (ppm)
10 8 6 4 2 0
chemical shift (ppm)


CDCl3
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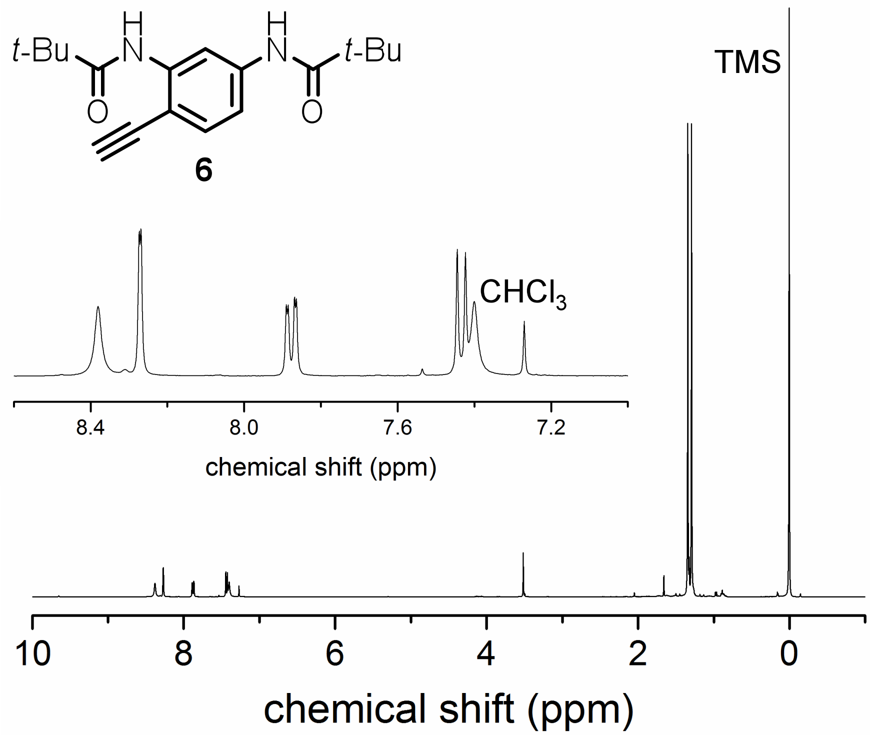
chemical shift (ppm)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N
H
N
t-Bu
O
O
6
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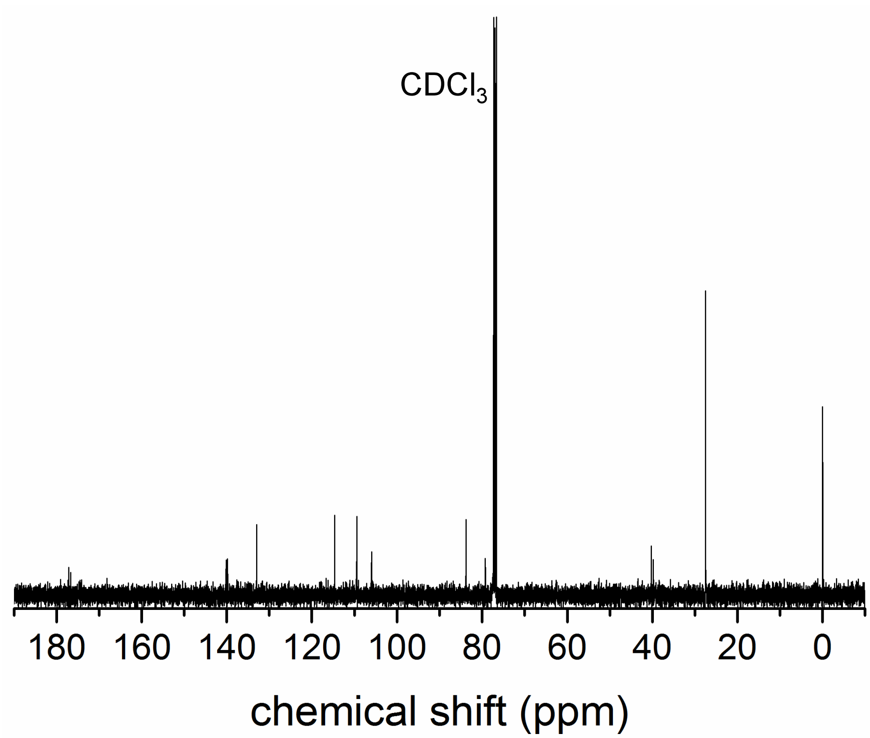
7.2
chemical shift (ppm)
10
8
6
4
2
0
chemical shift (ppm)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20
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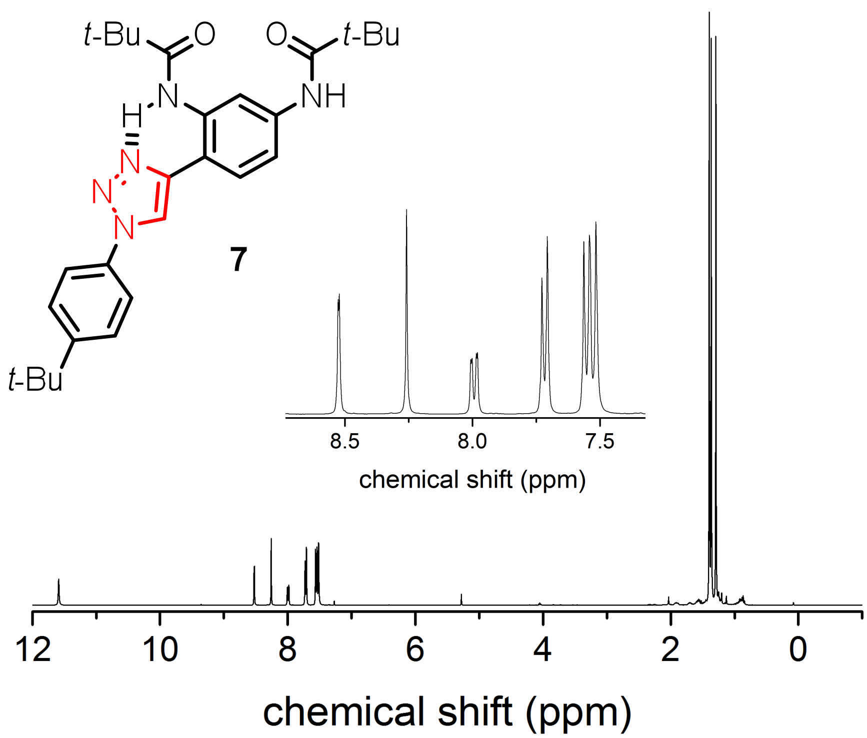
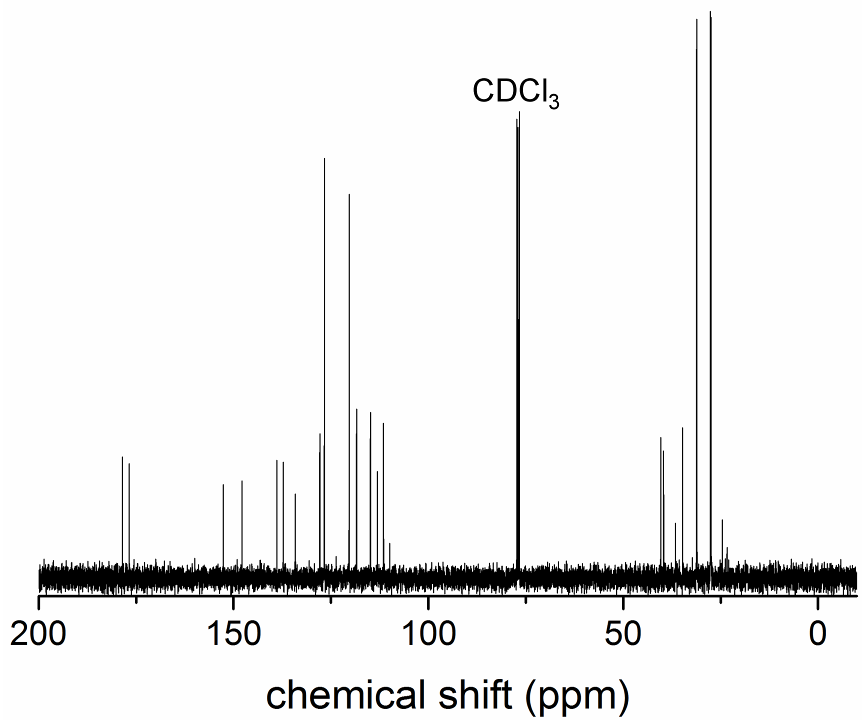
chemical shift (ppm)



t-Bu
O
O
t-Bu
N
NH
H
N
N
N
7
t-Bu
8.5
8.0
7.5
chemical shift (ppm)
12
10
8
6
4
2
0
chemical shift (ppm)



CDCl3
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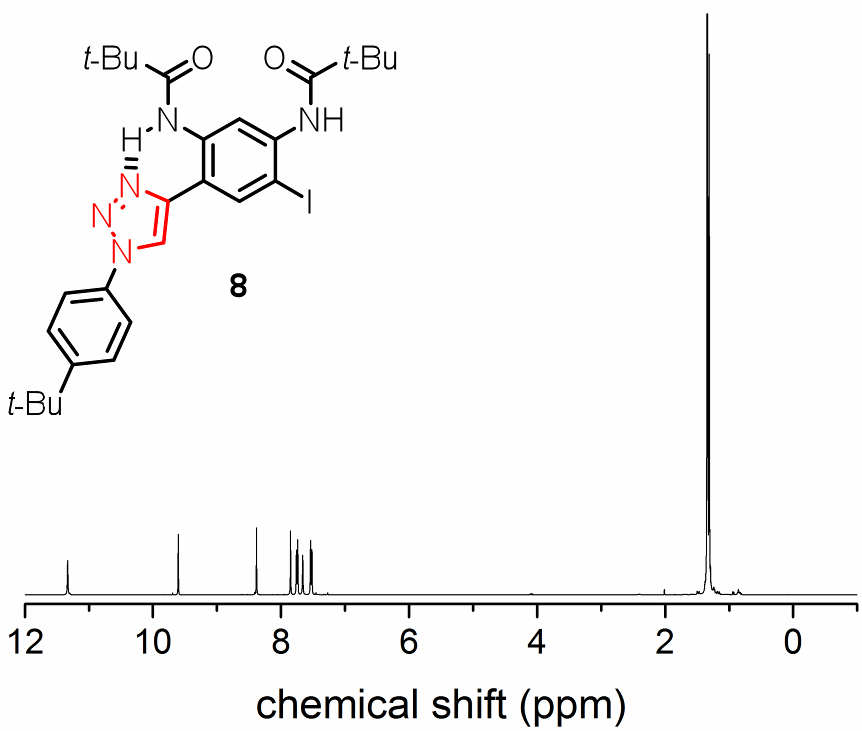
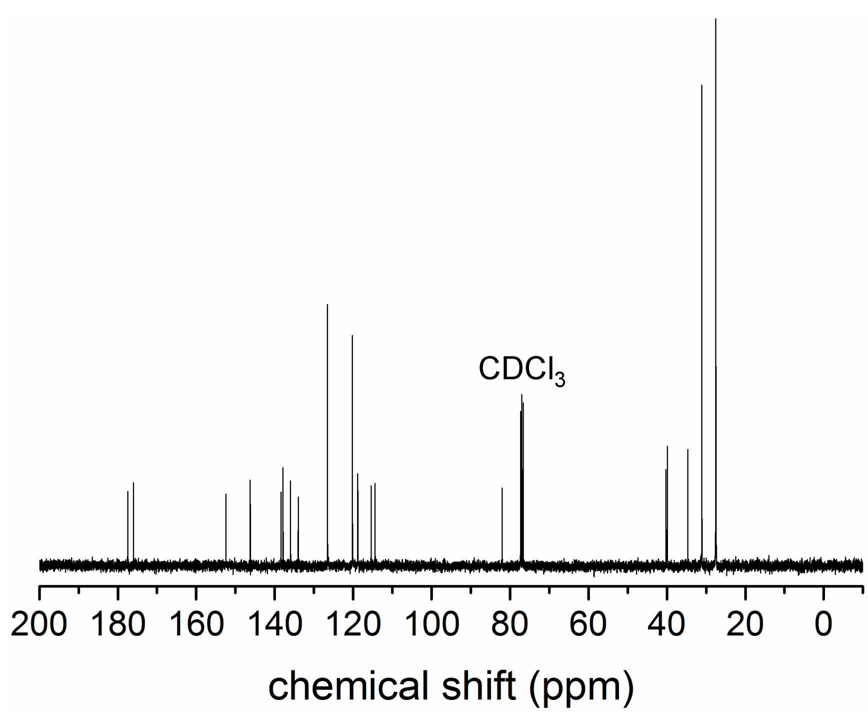
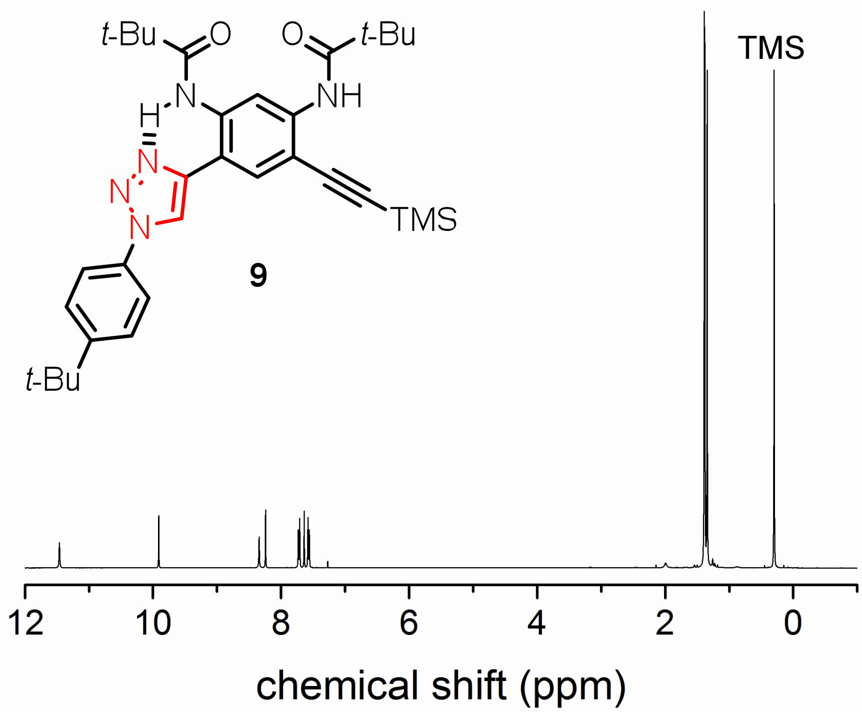
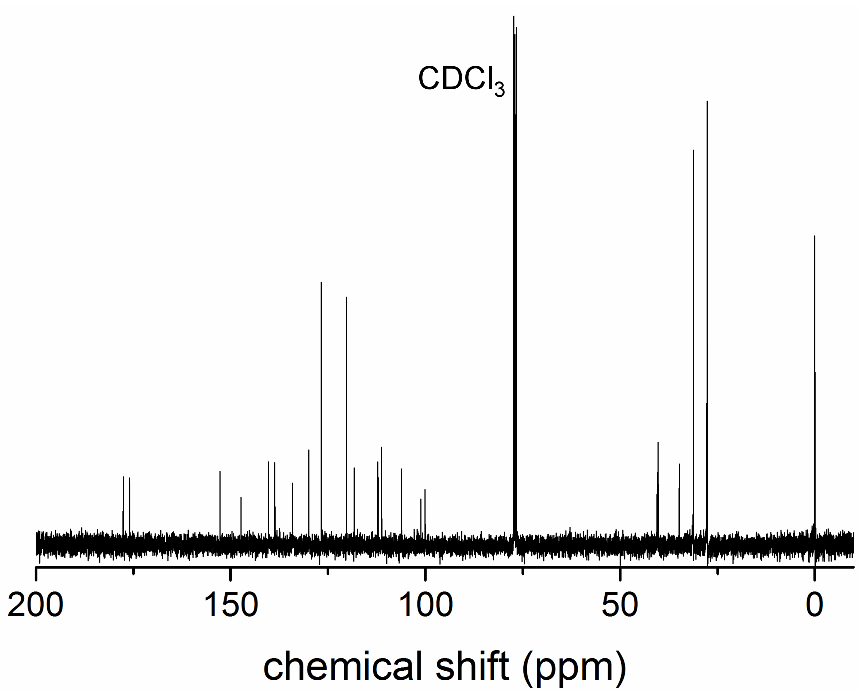
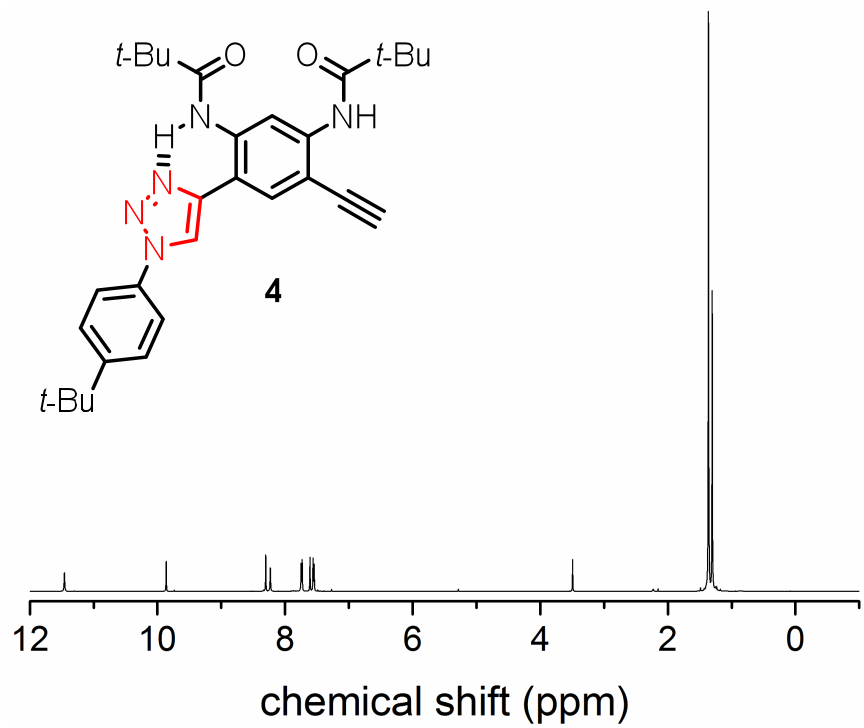
50
0
chemical shift (ppm)

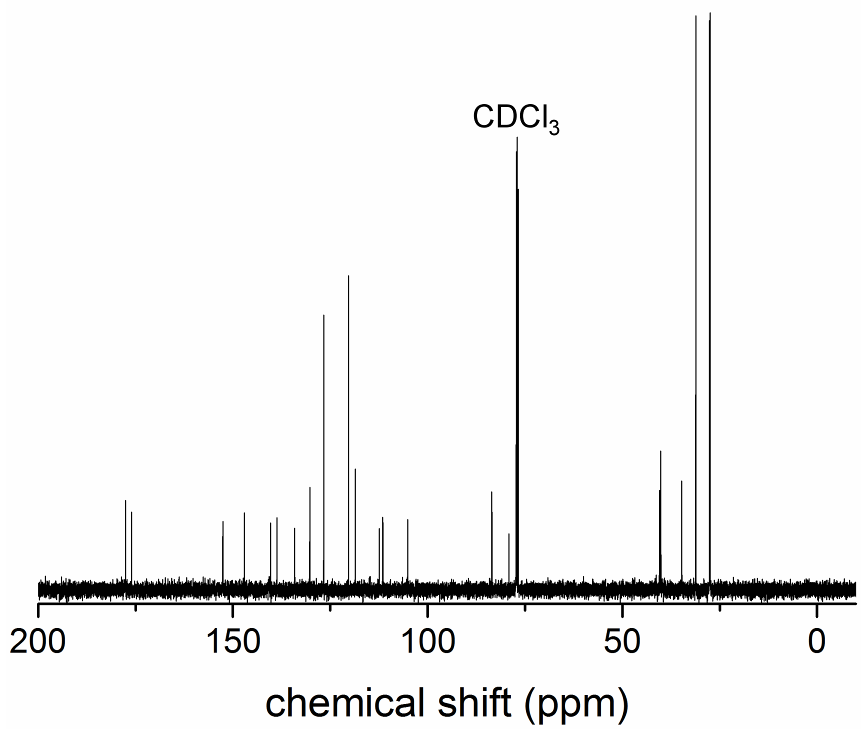

t-Bu
O
O
t-Bu
N
NH
H
N
N
N
I
8
t-Bu
12
10
8
6
4
2
0
chemical shift (ppm)

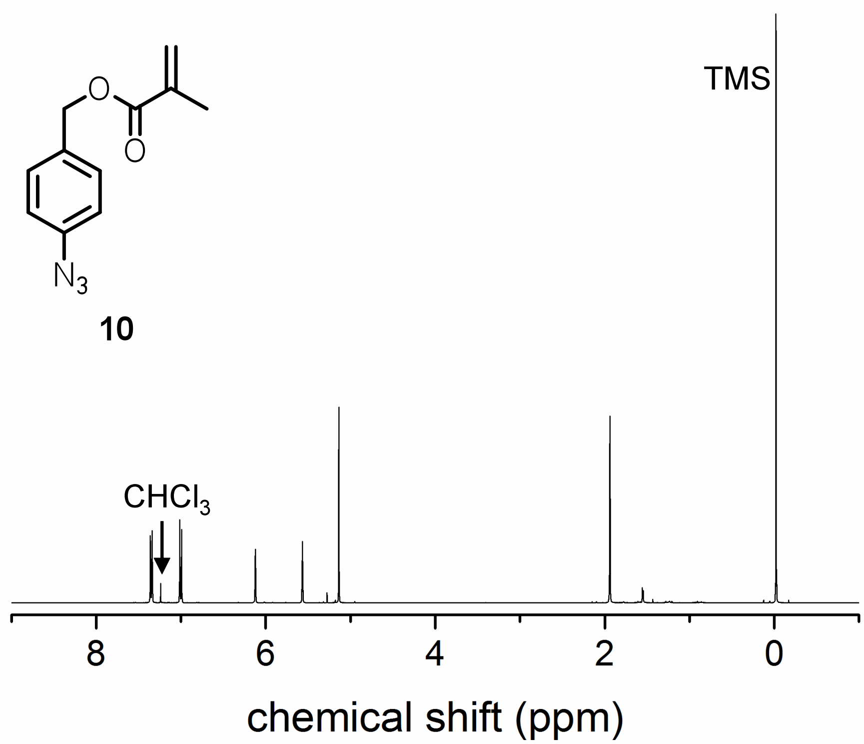

CDCl3
200
180
160
140
120
100
80
60
40
20
0
chemical shift (ppm)


t-Bu
O
O
t-Bu
N
NH
H
N
N
N
TMS
9
t-Bu
TMS
12
10
8
6
4
2
0
chemical shift (ppm)

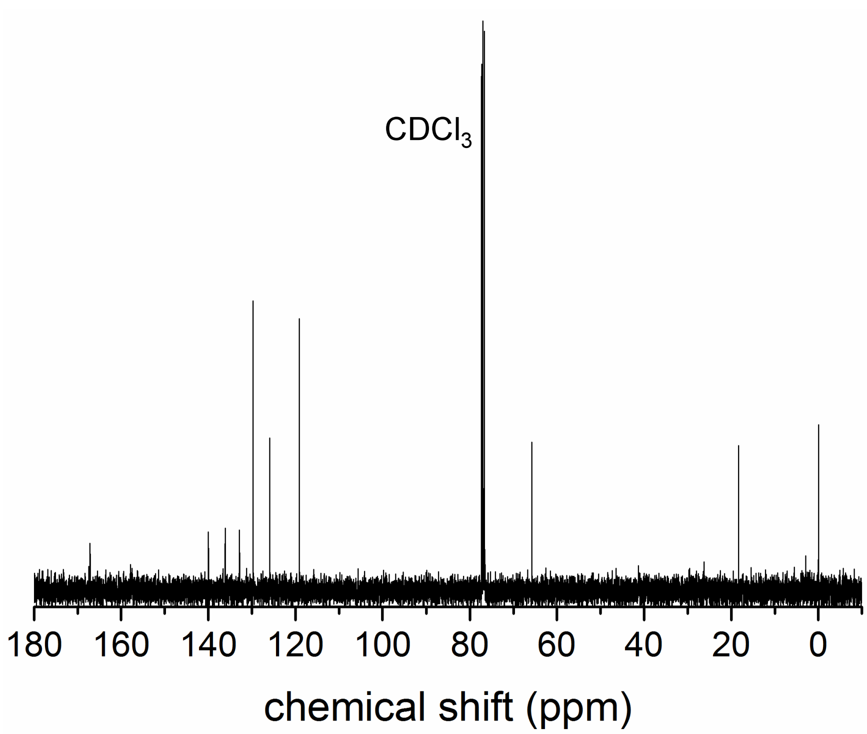

CDCl3
200
150
100
50
0
chemical shift (ppm)


t-Bu
O
O
t-Bu
N
NH
H
N
N
N
4
t-Bu
12
10
8
6
4
2
0
chemical shift (ppm)

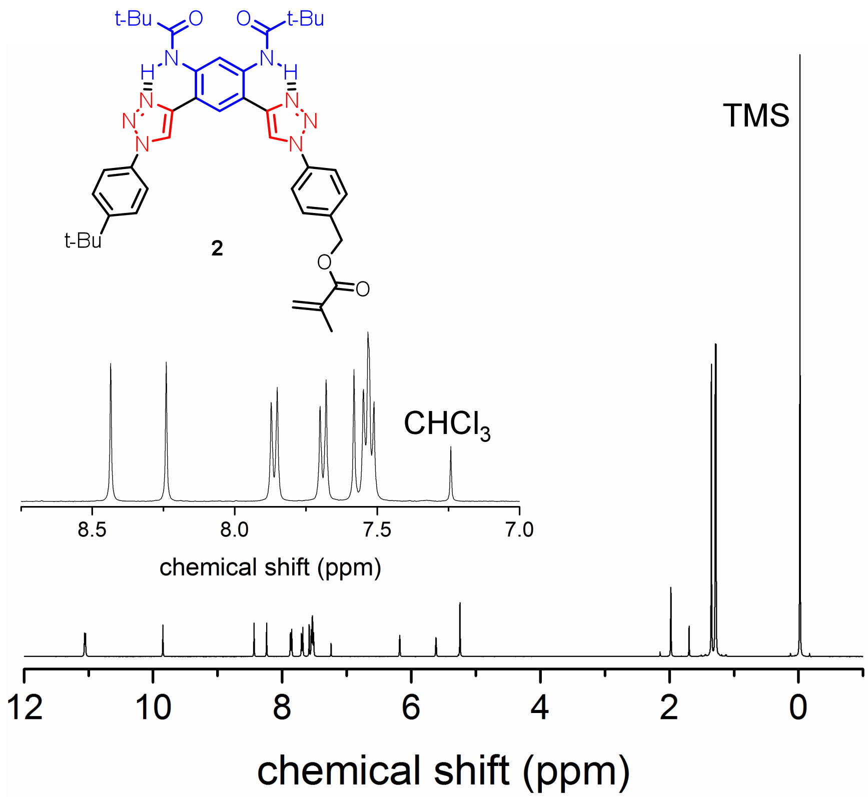

CDCl3
200
150
100
50
0
chemical shift (ppm)

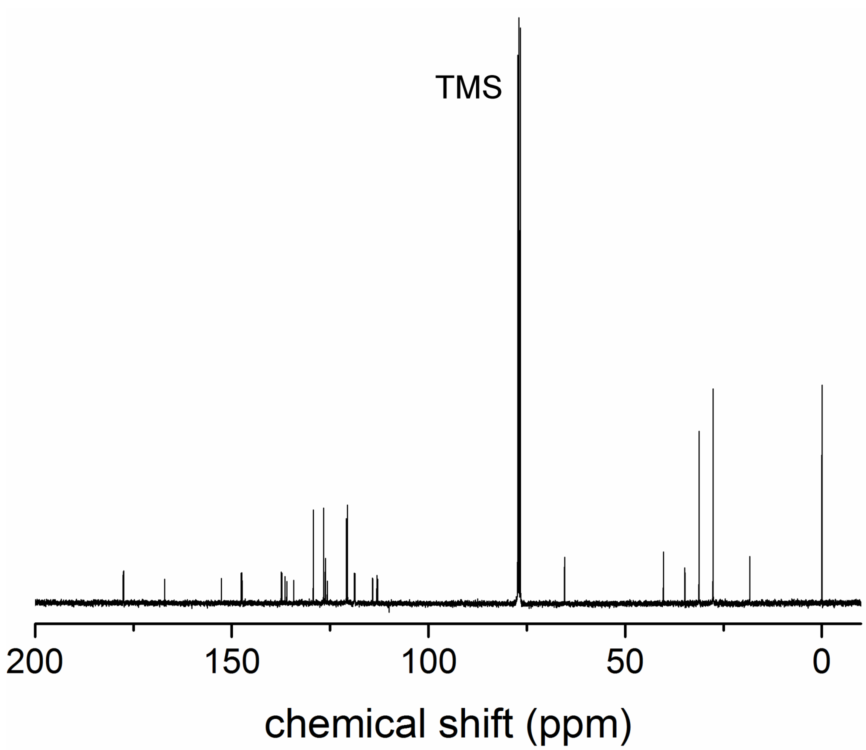


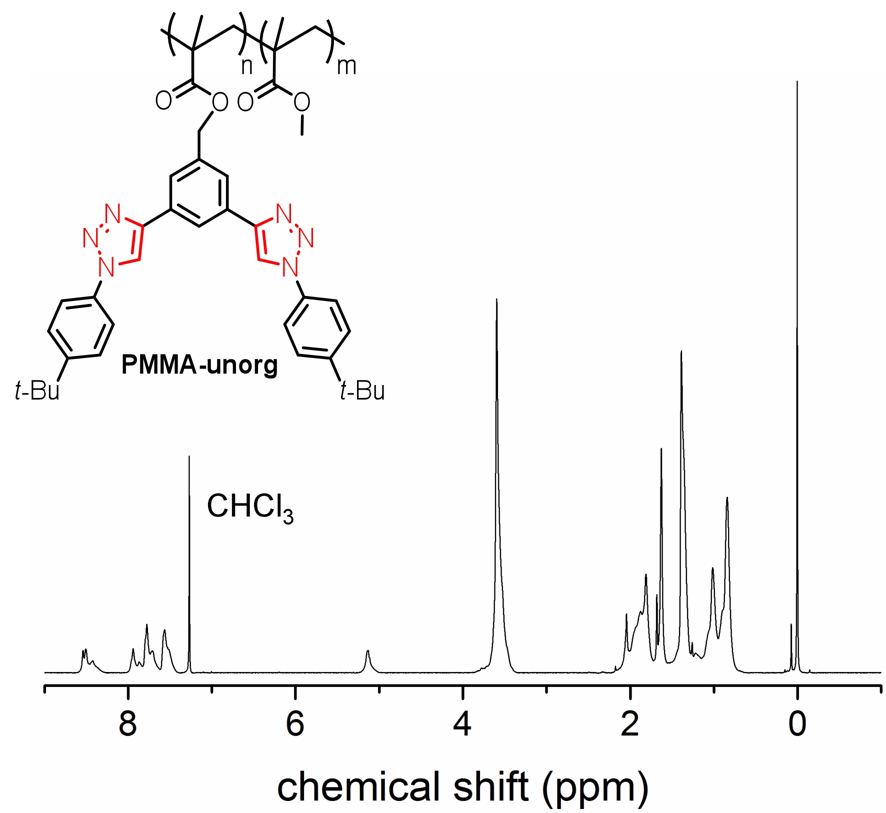
N3
10
TMS
CHCl3
8
6
4
2
0
chemical shift (ppm)

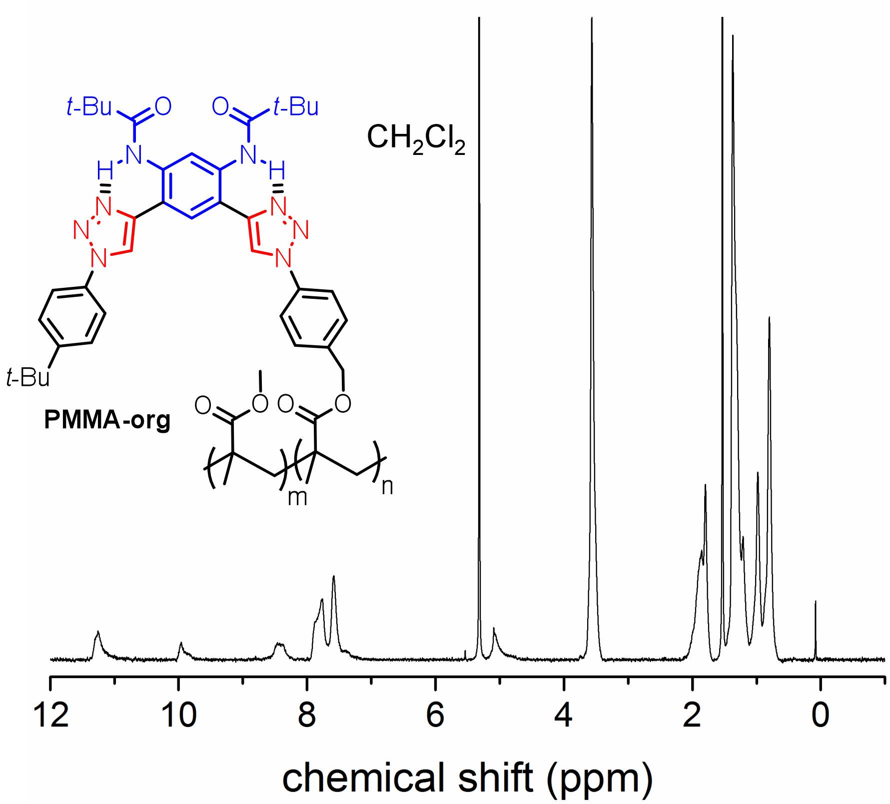


CDCl3
180
160
140
120
100
80
60
40
20
0
chemical shift (ppm)


t-Bu
O
N
H
t-Bu
2
O
TMS
CHCl3
8.5
8.0
7.5
7.0
chemical shift (ppm)
12
10
8
6
4
2
0
chemical shift (ppm)


TMS
200
150
100
50
0
chemical shift (ppm)


PMMA-unorg
t-Bu
t-Bu
CHCl$_3$
chemical shift (ppm)


t-Bu
t-Bu
t-Bu
PMMA-org
CH$_2$Cl$_2$
chemical shift (ppm)

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