Buckybowl polymers: Synthesis of corannulene-containing polymers through post-polymerization modification strategy

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Experimental Details:

1 was synthesized according to the procedure given in *Tetrahedron* **1995,** *51*, 2939-2946. Mercaptocorannulene was prepared according to the procedure given in *Chemical Science*, **2021**, *12*, 4949-4957. Polymer **12** was purchased from Laysan Bio, Inc. All the reactions requiring anhydrous and inert conditions were carried out under an argon atmosphere using oven-dried glassware and standard Schlenk technique. Anhydrous DCM was freshly distilled from CaH_2 under nitrogen, anhydrous THF was freshly distilled from sodium metal and benzophenone under nitrogen. Anhydrous diethyl ether was obtained commercially. All other chemicals were obtained commercially and used as received unless otherwise noted. Column chromatography was carried out on silica gel 40−63 mesh. Reactions were monitored by thin-layer chromatography (TLC) on silica gel-coated aluminium plates (60F254, Merck) and visualized with UV light (λ = 254 and 365 nm). NMR spectra were recorded at 396 or 400 MHz JEOL ECA instruments (and the corresponding frequencies for ^{13}C) in $CDCl_3$, $C_2D_2Cl_4$, DMSO-d_6 or D_2O. Chemical shifts are given in ppm and coupling constants in Hz ($CDCl_3$ ^1H: 7.26 ppm, ^{13}C: 77.23 ppm; $C_2D_2Cl_4$ ^1H: 5.99 ppm, ^{13}C: 73.78 ppm; DMSO-d_6 ^1H: 2.50 ppm; D_2O ^1H: 4.79 ppm). The fullerene complexation studies were done in a Wilmad external reference system NMR tube with ^{13}C-enriched C_{60}. Each complexation experiment was done using 0.8 mg C_{60} in 0.4 mL $C_2D_2Cl_4$ and the respective polymer was added in 4:1 corannulene to C_{60} ratio. The samples were equilibrated for 24 hours before each measurement. The external standard was a saturated solution of C_{60} in $C_2D_2Cl_4$. Gel permeation chromatography (GPC) (against polystyrene standards) was carried out in THF using a Waters system (Waters 1515 pump, Water 2414 refractive 5 index detector) instrument with three shodex HK-404L (2x), HK-450 columns. Gel permeation chromatography (GPC) (against polystyrene standards) was carried out in 1% LiBr in DMF using a Waters system (waters 1515 pump, waters 2414 refractive 5 index detector) instrument with four waters styragel HR 0.5, HR 5E, HR 4, HR5 columns. The UV/Vis measurements were carried out on a Lambda 265 UV/Vis-spectrometer from Perkin-Elmer. Fullerene loading was calculated via the Lambert-Beer law using UV/Vis spectroscopy; $A = \varepsilon cl$ (A = absorbance of the samples, ε = molar absorbance coefficient, l: optical path length.) (molar absorption coefficient of C_{60} ε (340 nm) = 49,000 M^{-1} cm^{-1}).

Synthetic Details:

Polymer **3**: ATRP initiator **1** (242 mg, 1 mmol), glycidyl methacrylate (8.52 g, 60 mmol) and pentamethyldiethylenetriamine (PMDETA, 156 mg, 0.9 mmol) in anisole (14 mL) was degassed by argon bubbling for 20 minutes. CuBr (86 mg, 0.6 mmol) was added and the bubbling was continued for 5 more minutes followed by stirring at room temperature for 1 h under an argon atmosphere. The reaction was quenched by bubbling air through the mixture and the solvent was evaporated *in vacuo*. The residue was dissolved in DCM and passed through a plug of silica and concentrated. The residue was redissolved in a small amount of DCM and precipitated into 400 mL methanol to give 4.1 g of white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 7.39 (t, Ar**H** initiator), 7.25 (t, Ar**H** initiator), 7.05 (d, Ar**H** initiator), 4.30 (br s, COO**CH_2**), 3.79 (br s, COO**CH_2**), 3.23 (br s, CH_2**CH**CH_2O), 2.84 (br s, CH_2CH**CH_2**O), 2.63 (br s, CH_2CH**CH_2**O), 2.34 – 0.65 (br m, backbone). GPC(THF): M_n = 7500, M_w = 9600, PDI = 1.2.

Polymer **4a**: To a solution of polymer **3** (100 mg, 0.70 mmol of epoxide units) and mercaptocorannulene (230 mg, 0.82 mmol) in THF (5 mL) was added $NaBH_4$ (38 mg, 1.0 mmol) in water (1.0 mL) under an argon atmosphere and stirred at room temperature for 2 h. Half of the solvent was evaporated by argon bubbling and the residue was precipitated into 120 mL isopropanol to give 246 mg off-white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.18 – 6.80 (br m, **Corannulene**), 4.14 (br s, COO**CH_2CH**(OH)), 3.21 (br s, CH(OH)**CH_2**S), 2.40 – 0.40 (br m, backbone). GPC(THF): M_n = 10300, M_w = 13600, PDI: 1.3.

Polymer **4b:** To a solution of polymer **3** (150 mg, 1.06 mmol of epoxide units) and mercaptocorannulene (164 mg, 0.58 mmol) in THF (5 mL) was added $NaBH_4$ (28 mg, 0.73 mmol) in water (0.7 mL) under an argon atmosphere and stirred at room temperature for 2.5 h. Half of the solvent was evaporated by argon bubbling and the residue was precipitated into 120 mL isopropanol to give 230 mg off-white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.26 – 6.98 (br m, **Corannulene**), 4.53 – 3.94 (br m, COO**CH_2CH**(OH), COO**CH_2**), 3.71 (br s, COO**CH_2**), 3.46 – 2.95 (br m, CH(OH)**CH_2**S, CH_2**CH**CH_2O), 2.72 (br s, $COOCH_2$CH**CH_2**O), 2.53 (br s, $COOCH_2$CH**CH_2**O), 2.30 – 0.59 (br m, backbone). GPC(THF): M_n = 9800, M_w = 13000, PDI: 1.3.

Polymer **4c**: To a solution of polymer **3** (200 mg, 1.41 mmol of epoxide units) and mercaptocorannulene (110 mg, 0.4 mmol) in THF (6 mL) was added $NaBH_4$ (18 mg, 0.47 mmol) in water (0.5 mL) under an argon atmosphere and stirred at room temperature for 2 h. Half of the solvent was evaporated by argon bubbling and the residue was precipitated into 110 mL MeOH to give 280 mg off-white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.26 – 6.98 (br m, **Corannulene**), 4.53 – 3.94 (br m, COO**CH$_2$CH**(OH), COO**CH$_2$**), 3.71 (br s, COO**CH$_2$**), 3.46 – 2.95 (br m, CH(OH)**CH$_2$**S, CH$_2$**CH**CH$_2$O), 2.72 (br s, COOCH$_2$CH**CH$_2$**O), 2.53 (br s, COOCH$_2$CH**CH$_2$**O), 2.30 – 0.59 (br m, backbone). GPC(THF): M_n = 8800, M_w = 12000, PDI: 1.3.

Polymer **5**: To a solution of polymer **3** (30 mg, 0.07 mmol of OH units), triethylamine (21 µL, 0.15 mmol) and DMAP (0.6 mg, 5 µmol) in DCM (3 mL) was added hexanoyl chloride (21 µL, 0.15 mmol) under an argon atmosphere, ice cooling and stirred at room temperature for 16 h. The mixture was concentrated, redissolved in 10 mL DCM, washed with aq. $NaHCO_3$ and water. The organic layer was dried, filtered and concentrated. The residue was redissolved in 0.6 mL DCM and precipitated into 12 mL hexane to give 4 mg off-white solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.04 – 6.95 (br m, **Corannulene**), 5.33 (OCH$_2$**CH**CH$_2$S), 4.29 (br d, O**CH$_2$**CHCH$_2$S), 3.40 (br s, OCH$_2$CH**CH$_2$**S), 2.02 (br s, CHOCO**CH$_2$**CH$_2$CH$_2$CH$_2$CH$_3$), 1.28 (br s, CHOCOCH$_2$**CH$_2$**CH$_2$CH$_2$CH$_3$), 0.99 (br s, CHOCOCH$_2$CH$_2$**CH$_2$CH$_2$**CH$_3$), 0.61 (br s, CHOCOCH$_2$CH$_2$CH$_2$CH$_2$**CH$_3$**). 2.36 – 0.32 (br m, backbone). GPC(THF): M_n = 12700, M_w = 16000, PDI: 1.2.

Polymer **6**: ATRP initiator **1** (484 mg, 2 mmol), glycidyl methacrylate (8.52 g, 60 mmol), methyl methacrylate (6.0 g, 60 mmol) and pentamethyldiethylenetriamine (PMDETA, 312 mg, 1.8 mmol) in anisole (28 mL) was degassed by argon bubbling for 20 minutes. CuBr (172 mg, 1.2 mmol) was added and the bubbling was continued for 5 more minutes followed by stirring at room temperature for 2 h under an argon atmosphere. The reaction was quenched by bubbling air through the mixture and the solvent was evaporated *in vacuo*. The residue was dissolved in DCM and passed through a plug of silica and concentrated. The residue was redissolved in a small amount of DCM and precipitated into 450 mL methanol to give 6.03 g of white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 7.39 (t, Ar**H** initiator), 7.26 (t, Ar**H** initiator), 7.04 (d, Ar**H** initiator), 4.30 (br s, COO**CH$_2$**), 3.79 (br s, COO**CH$_2$**), 3.59 (br s, O**CH$_3$**), 3.22 (br s, CH$_2$**CH**CH$_2$O), 2.84 (br s, CH$_2$CH**CH$_2$**O), 2.63 (br s, CH$_2$CH**CH$_2$**O), 2.26 – 0.61 (br m, backbone). GPC(THF): M_n = 5600, M$_w$ = 7200, PDI: 1.2. (ratio between MMA:GMA = 1:3)

Polymer **7**: To a solution of polymer **6** (71 mg, 0.37 mmol of epoxide units) and mercaptocorannulene (106 mg, 0.38 mmol) in THF (3 mL) was added $NaBH_4$ (18 mg, 0.47 mmol) in water (0.5 mL) under an argon atmosphere and stirred at room temperature for 2 h. Half of the solvent was evaporated by argon bubbling and the residue was precipitated into 90 mL isopropanol to give 159 mg off-white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.18 – 6.80 (br m, **Corannulene**), 4.14 (br s, br s, COO$\mathbf{CH_2CH}$(OH)), 3.59 (br s, O$\mathbf{CH_3}$), 3.21 (br s, CH(OH)$\mathbf{CH_2}$S), 2.40 – 0.40 (br m, backbone). GPC(THF): M_n = 7800, M_w = 10200, PDI: 1.3.

Polymer **8**: To a solution of polymer **6** (25 mg, 0.04 mmol of OH units), triethylamine (9 µL, 0.09 mmol) and DMAP (0.6 mg, 5 µmol) in DCM (3 mL) was added hexanoyl chloride (13 µL, 0.09 mmol) under an argon atmosphere, ice cooling and stirred at room temperature for 16 h. The mixture was concentrated, redissolved in 10 mL DCM, washed with aq. $NaHCO_3$ and water. The organic layer was dried, filtered and concentrated. The residue was redissolved in 0.6 mL DCM and precipitated into 12 mL hexane to give 14 mg off-white solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.04 – 6.95 (br m, **Corannulene**), 5.33 (br s, $OCH_2\mathbf{CH}CH_2S$), 4.29 (br d, $O\mathbf{CH_2}CHCH_2S$), 3.54 (br s, O$\mathbf{CH_3}$), 3.42 (br s, $OCH_2CH\mathbf{CH_2}S$), 2.09 (br s, $CHOCO\mathbf{CH_2}CH_2CH_2CH_2CH_3$), 1.33 (br d, $CHOCOCH_2\mathbf{CH_2}CH_2CH_2CH_3$), 1.05 (br d, $CHOCOCH_2CH_2\mathbf{CH_2CH_2}CH_3$), 0.69 (br d, $CHOCOCH_2CH_2CH_2CH_2\mathbf{CH_3}$). 2.32 – 0.47 (br m, backbone). GPC(THF): M_n = 10600, M_w = 13700, PDI: 1.2.

Synthesis of thienothiophene methyl sulfide: A solution of thieno(3,2-b)thiophene (280 mg, 2 mmol) in diethyl ether (3 mL) was cooled to 0 °C under an argon atmosphere and *n*-BuLi (2M in cyclohexane, 1.1 mL, 2.2 mmol) was added dropwise and stirred for 30 minutes. Dimethyl disulfide (0.27 mL, 3 mmol) was added dropwise. The mixture was stirred for 30 more minutes in the ice bath then the cooling was removed and stirred for 2 more hours. The reaction was quenched with aq. HCl, diluted with DCM, washed with water, dried over anhydrous Na_2SO_4, filtered ad concentrated. The crude product was purified with column chromatography eluting with cyclohexane to give the product as 289 mg (1.55 mmol) of colourless oil. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 5.1 Hz, 1H), 7.31 (s, 1H), 7.19 (d, J = 5.1 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.36, 124.13, 119.59, 77.55, 77.23, 76.91, 22.76.

Synthesis of mercaptothienothiophene: Thienothiophene methyl sulfide was dissolved in 3 mL of anhydrous DMF and degassed by argon bubbling. Sodium thiomethoxide

(217 mg, 3.1 mmol) was added and the mixture was heated to reflux for 1 h under an argon atmosphere. After cooling to room temperature, the mixture was carefully quenched with degassed aq. HCl, diluted with toluene, washed with water (2x) and brine (1x). The organic layer was dried over anhydrous Na_2SO_4, filtered ad concentrated to give mercaptothienothiophene as 256 mg (1.49 mmol) brown solid. Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 5.2 Hz, 1H), 7.31 (s, 1H), 7.17 (d, J = 5.0 Hz, 1H), 3.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.13, 123.12, 115.99, 74.10, 73.78, 73.46.

polymer **9a**: To a solution of polymer **4b** (30 mg, 0.058 mmol of epoxide units) and mercaptothienothiophene (15 mg, 0.087 mmol) in THF (1.5 mL) under an argon atmosphere was added $NaBH_4$ (5 mg, 0.13 mmol) in water (0.3 mL) and stirred at room temperature for 2 h. The reaction mixture was precipitated into 15 mL isopropanol to give 42 mg off-white solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.14 – 6.64 (br m **Corannulene, Thienothiophene**), 4.47 – 3.63 (br m, COO**CH₂CH**(OH), COO**CH₂**), 3.25 (br s, CH(OH)**CH₂**S), 2.89 (br s, CH(OH)**CH₂**S), 2.33 – 0.61 (br m, backbone). GPC(THF): M_n = 10500, M_w = 14200, PDI = 1.3.

Polymer **9b**: To a solution of polymer **4c** (30 mg, 0.158 mmol of epoxide units) and mercaptothienothiophene (32 mg, 0.186 mmol) in THF (1.5 mL) under an argon atmosphere was added $NaBH_4$ (10.6 mg, 0.28 mmol) in water (0.3 mL) and stirred at room temperature for 2 h. The reaction mixture was precipitated into 15 mL isopropanol to give 42 mg off-white solid. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 8.15 – 6.80 (br m **Corannulene, Thienothiophene**), 4.46 – 3.63 (br m, COO**CH₂CH**(OH), COO**CH₂**), 3.28 (br s, CH(OH)**CH₂**S), 2.92 (br s, CH(OH)**CH₂**S), 2.38 – 0.59 (br m, backbone). GPC(THF): M_n = 10600, M_w = 14300, PDI = 1.3.

Polymer **10**: To a solution of polymer **3** (50 mg, 0.35 mmol of epoxide units) and mercaptobenzene (0.042 mL, 0.045 mmol) in THF (2 mL) was added $NaBH_4$ (20 mg, 0.53 mmol) in water (0.5 mL) under an argon atmosphere and stirred at room temperature for 2 h. Precipitated into isopropanol to give 22 mg off-white powder. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 7.70 – 6.94 (br m, **Benzene**), 4.11 (br s, COOCH₂**CH**(OH)), 3.97 (br s, COO**CH₂**CH(OH)), 3.66 (br s, COOCH₂CH(**OH**)), 3.03 (br s, CH(OH)**CH₂**S), 2.36 – 0.44 (br m, backbone). GPC(THF): M_n = 10400, M_w = 13500, PDI = 1.2.

polymer **11**: To a solution of polymer **4c** (30 mg, 0.158 mmol of epoxide units) and 1-thioglycerol (20 mg, 0.186 mmol) in THF (1.5 mL) under an argon atmosphere was added $NaBH_4$ (10.6 mg, 0.28 mmol) in water (0.3 mL) and stirred at room temperature for 2 h. The reaction mixture was diluted with water and then dialyzed (dialysis tube: cutoff 1 kDa) against DI water for 2 days. The aqueous solution was lyophilized to dryness to give as 45 mg off-white powder. ^1H NMR (400 MHz, DMSO-D_6) δ 8.24 – 7.36 (br m **Corannulene**), 5.44 (br s, $COOCH_2CH(\mathbf{OH})$), 5.15 (br s, $COOCH_2CH(\mathbf{OH})$), 4.78 (br s, $SCH_2CH(\mathbf{OH})$), 4.57 (br s, $CHCH_2\mathbf{OH}$), 4.36 – 3.72 (br m, $COO\mathbf{CH_2CH}(OH)$, $COO\mathbf{CH_2}$), 3.58 (br s, $CH_2SCH_2\mathbf{CH}$), 3.46 – 3.27 (br m, CH(OH) $\mathbf{CH_2}S$, $CH\mathbf{CH_2}OH$), 2.65 (br s, CH(OH) $\mathbf{CH_2}S$), 2.18 – 0.49 (br m, backbone).GPC(DMF): $M_n = 11200$, $M_w = 14500$, PDI = 1.2.

Preparation of polymer-fullerene complex for %loading examination: Polymer **11** (10 mg) and fullerene (C_{60}) (1 eq. per corannulene unit) were dissolved in DMF (0.5 mL) and sonicated for 30 min and added DI water (9.5 mL) under stirring. The solution was then filtered through a 0.8 µm syringe filter (cellulose acetate). The mixture was dialyzed (dialysis tube: cutoff 1 kDa) against deionized water for 2 days to remove the DMF.

Preparation of thick film: To a solution of polymer **4c** (10 mg, 0.05 mmol of epoxide units) and 4-arm-PEG-thiol **12** (10 kDa) (132 mg, 0.01 mmol) in THF (0.2 mL) in a glass vial was added DBU (1.4 mg, 1 wt% of the total mixture) and vortexed immediately. The mixture was kept at room temperature overnight which led to the formation of the thick crosslinked film.

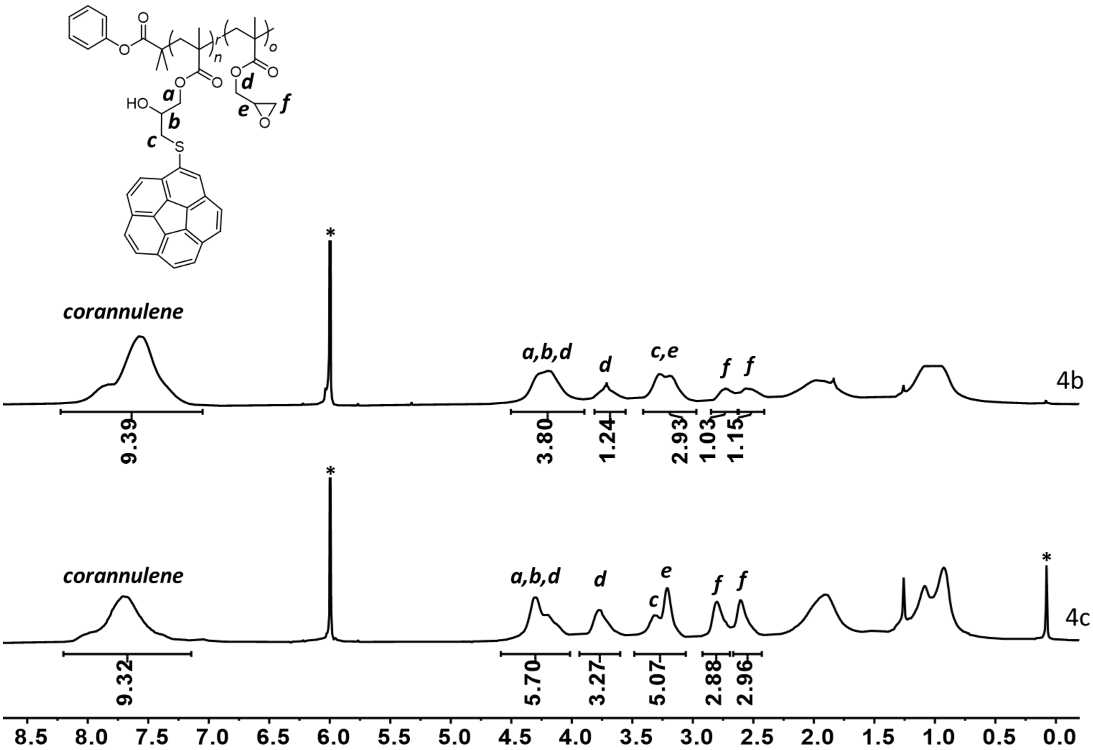

Figure S1. ^{1}H-NMR of polymers **4b** and **4c** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

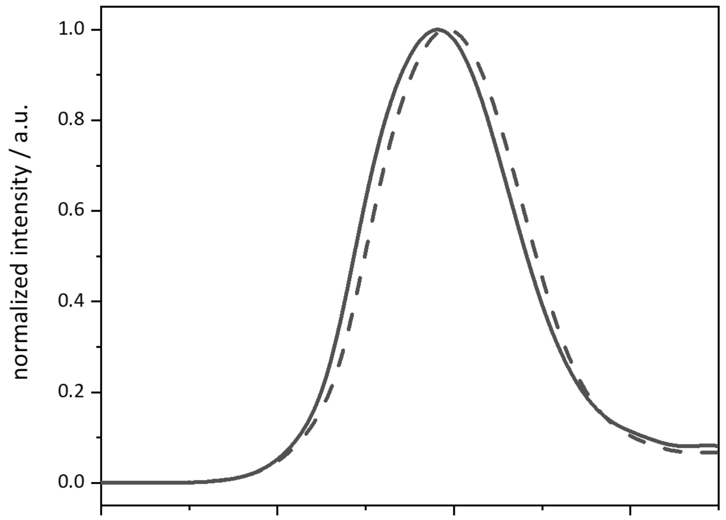

Figure S2. Gel permeation chromatograms for polymers **4b** (dash line) and **4c** (solid line) in THF.

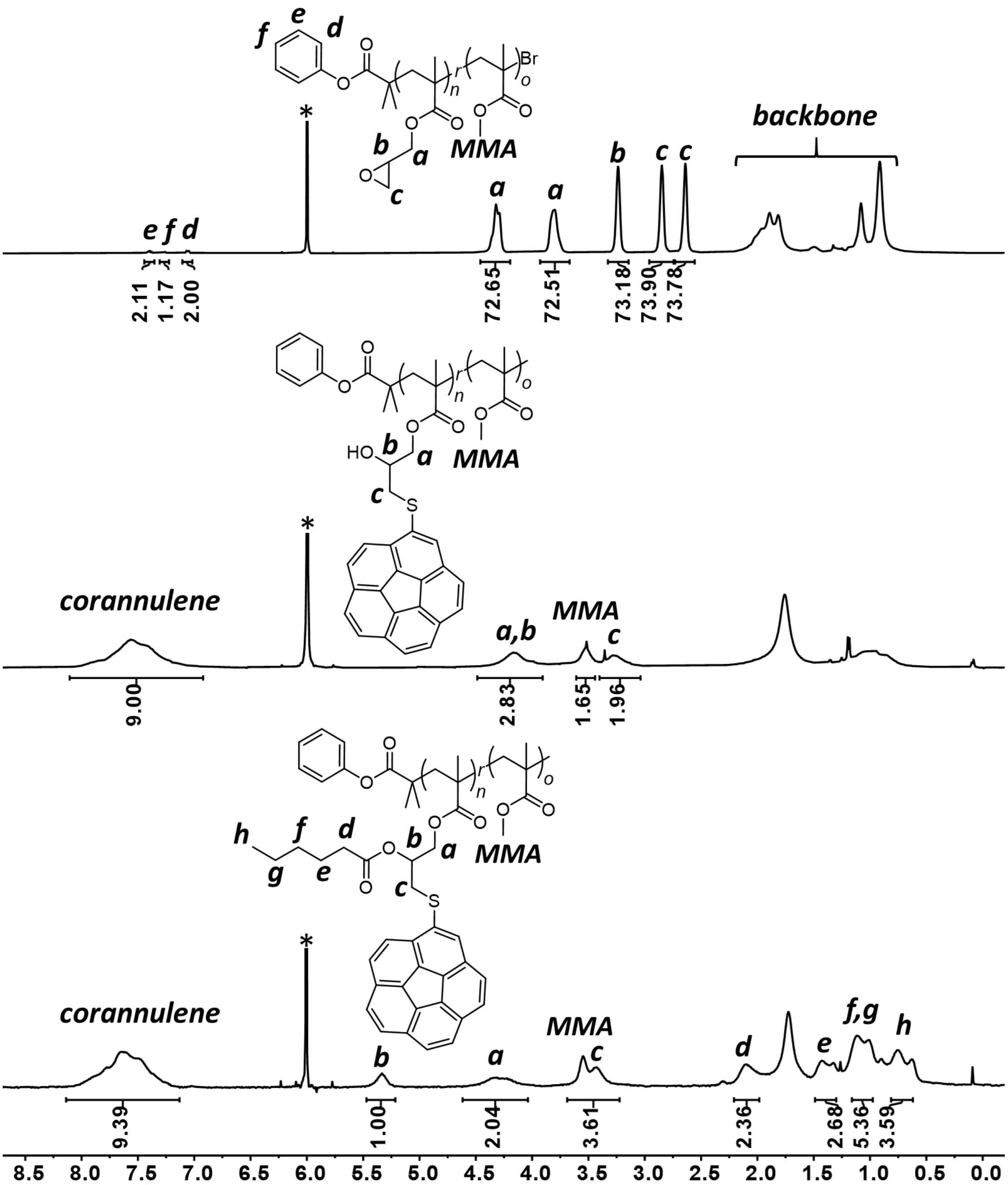

Figure S3. ^{1}H-NMR of polymers **6**, **7**, and **8** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

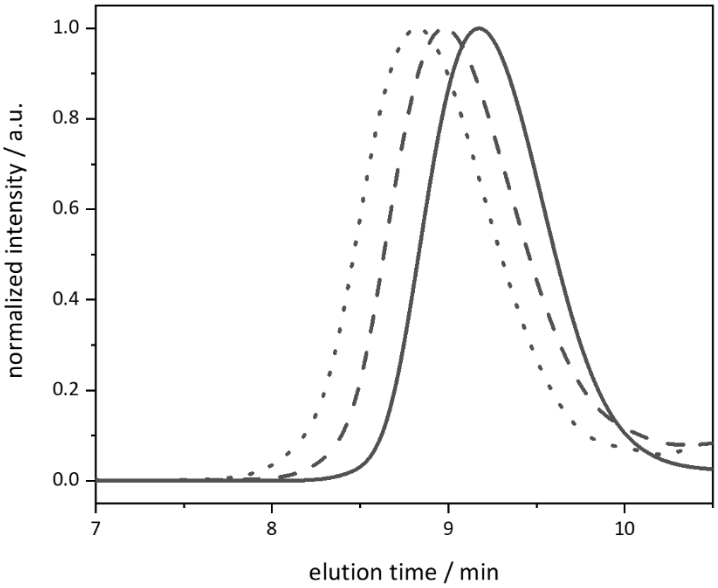

Figure S4. Gel permeation chromatograms for polymers **6** (solid line), **7** (dash line), and **8** (dot line) in THF.

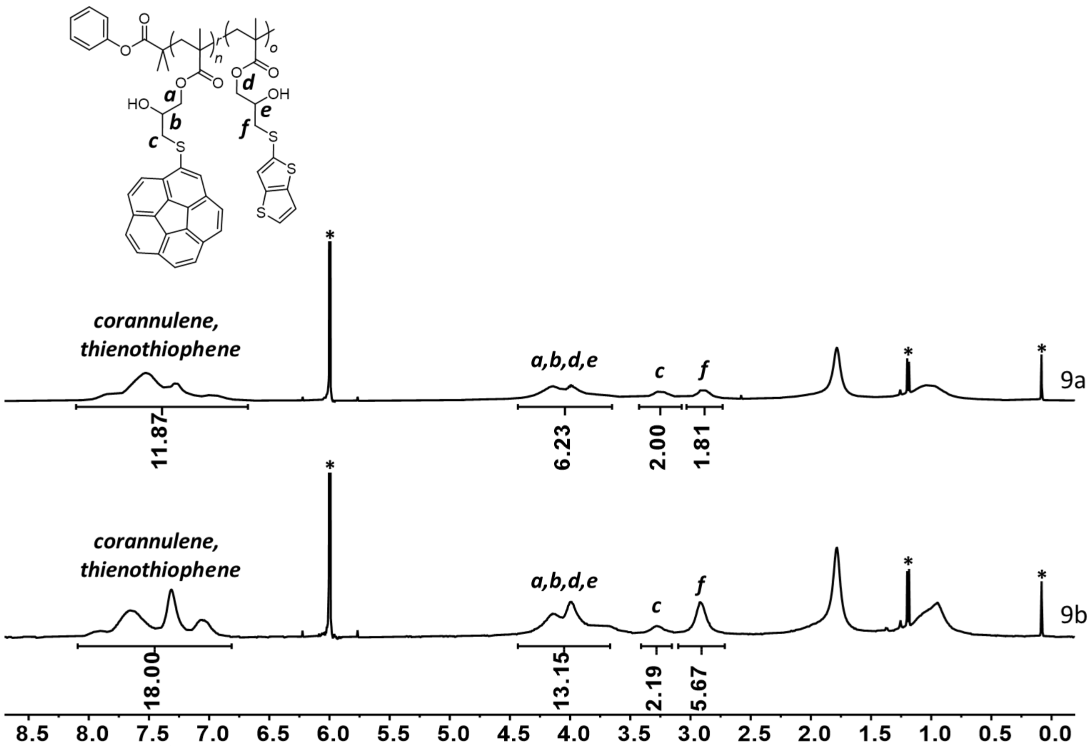

Figure S5. ^{1}H-NMR of polymers **9a** (corannulene:thienothiophene 1:1) and **9b** (corannulene:thienothiophene 1:3) in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

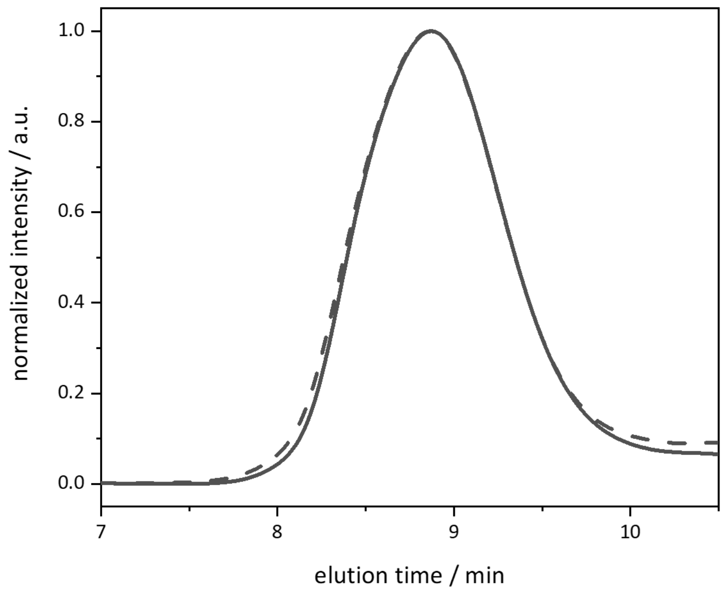

Figure S6. Gel permeation chromatogram of polymers **9a** (solid line) and **9b** (dash line) in THF.

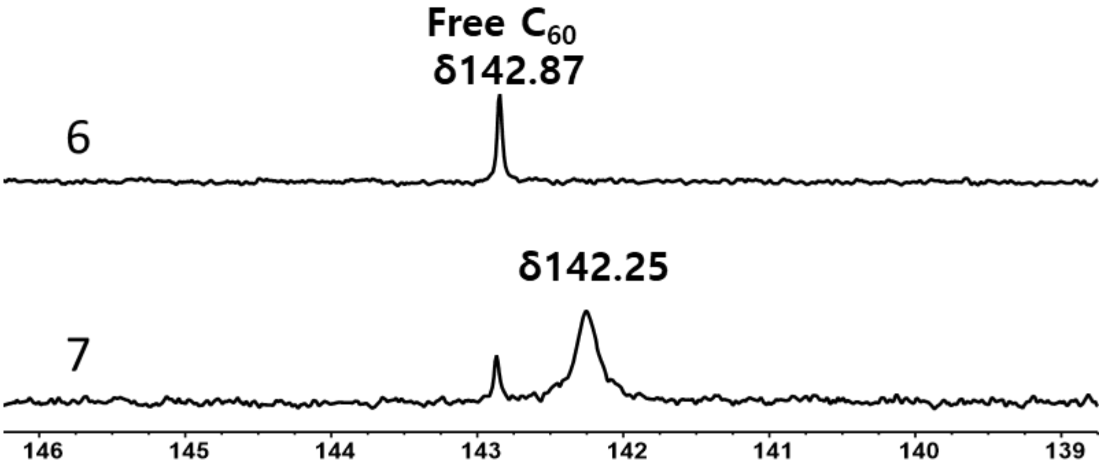

Figure S7. ^{13}C-NMR of fullerene C_{60} in the presence of polymers **6** and **7** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

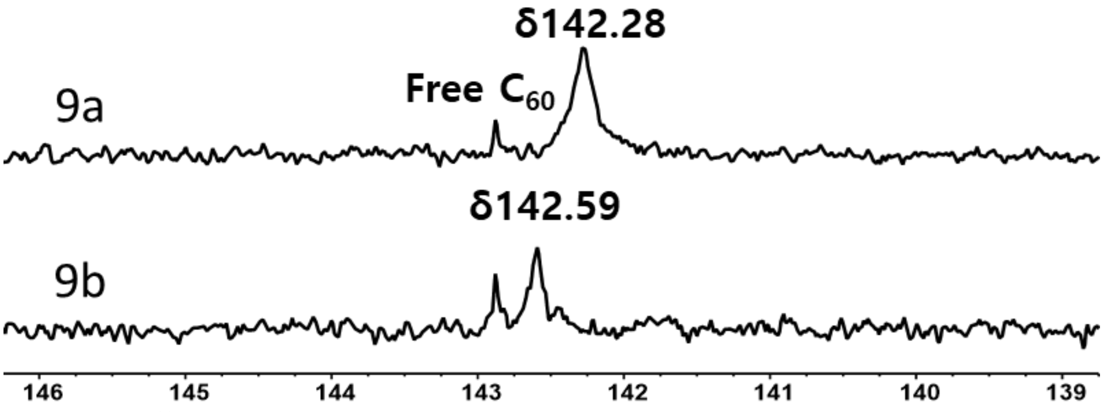

Figure S8. ^{13}C-NMR of fullerene C_{60} in the presence of polymers **9a** and **9b** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

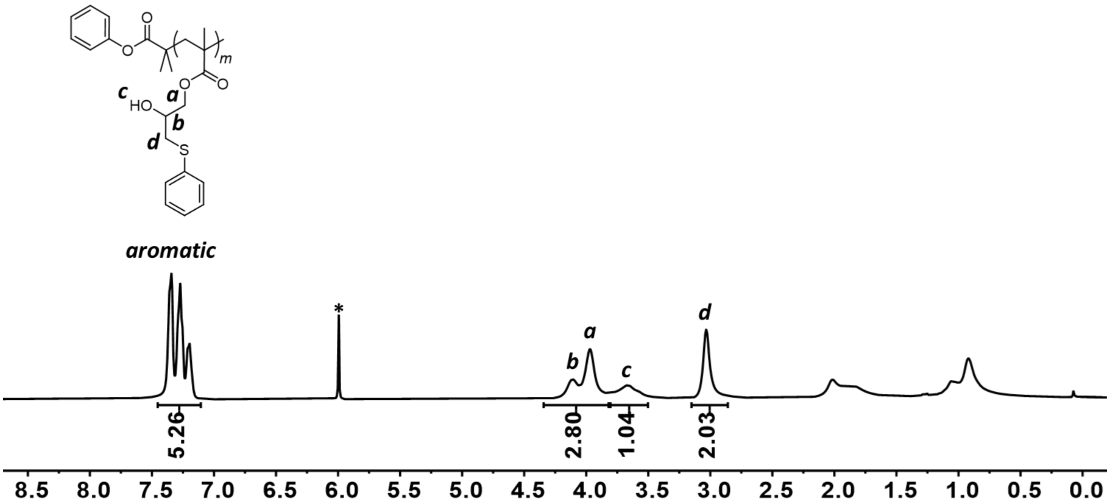

Figure S9. ^{1}H-NMR of polymer **10** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

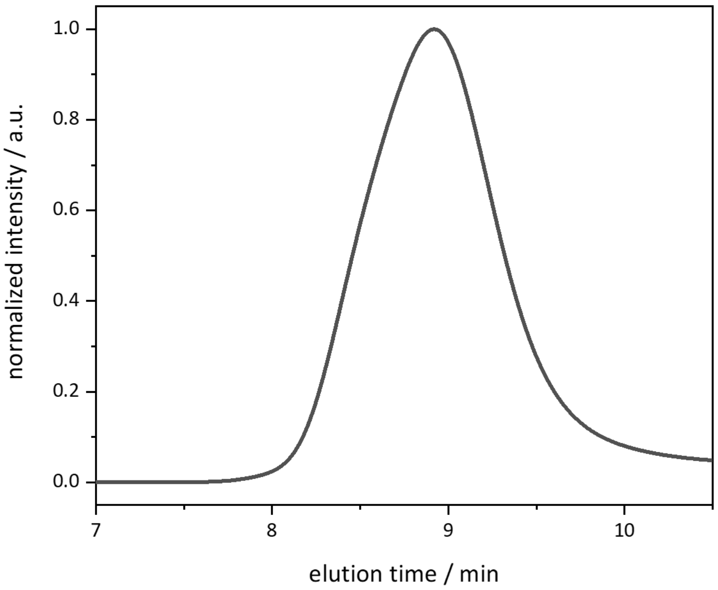

Figure S10. Gel permeation chromatogram of polymer **10** in THF.

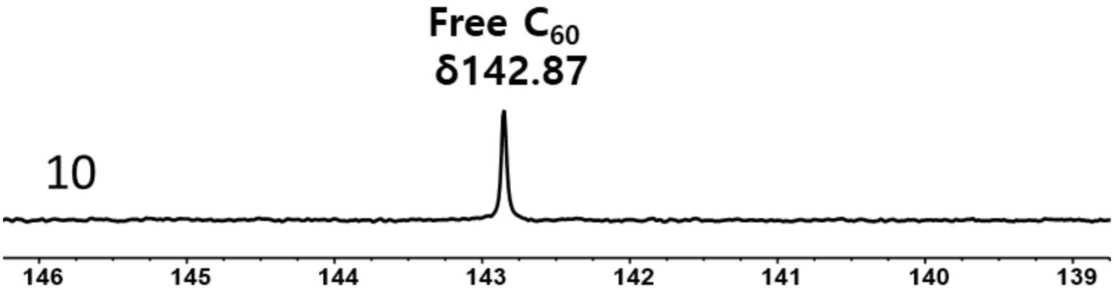

Figure S11. ^{13}C-NMR of fullerene C_{60} in the presence of polymer **10** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

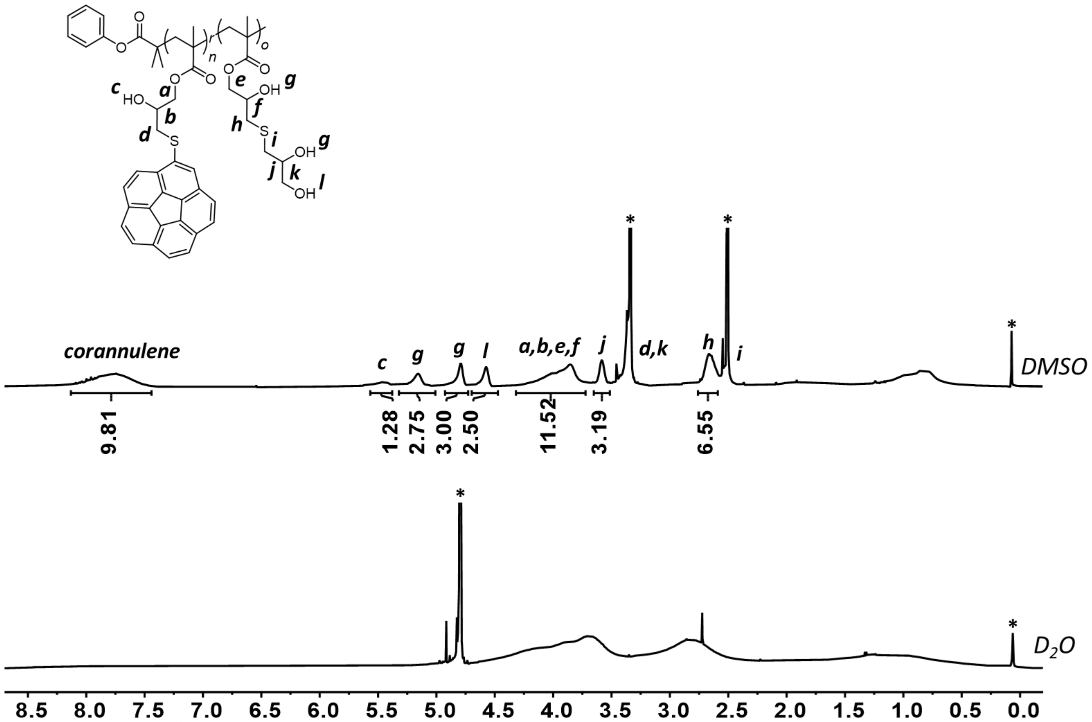

Figure S12. ^{1}H-NMR of polymer **11** in DMSO-d_6 (top) and D_2O (bottom). The chemical shifts are given in δ/ppm scale.

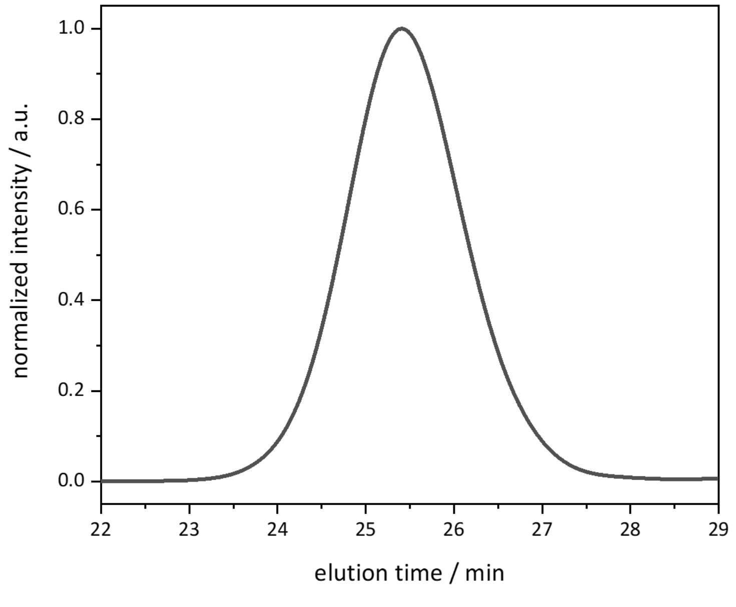

Figure S13. Gel permeation chromatogram of polymer **11** in DMF.

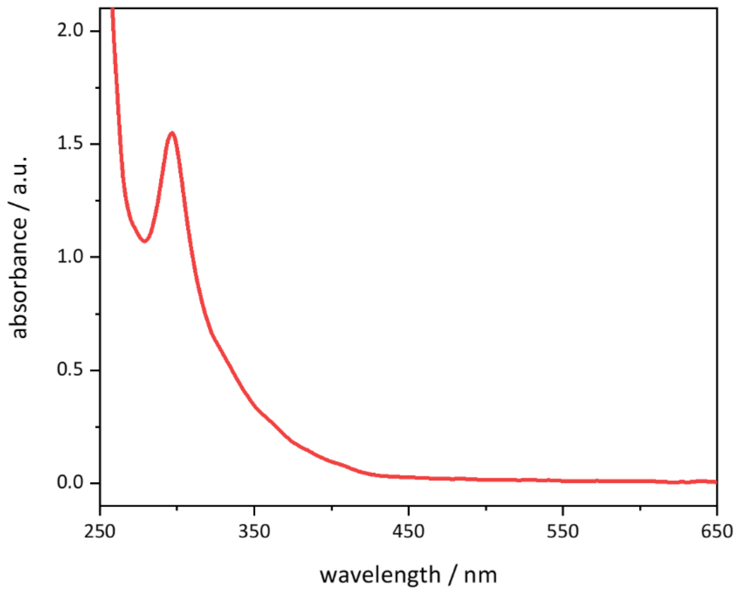

Figure S14. UV-Vis spectrum of polymer **11** and fullerene C_{60} in water.