Electronic Supplementary Information for

Crosslinked Dendronized Polyols as a General Approach to Brighter and More Stable fluorophores

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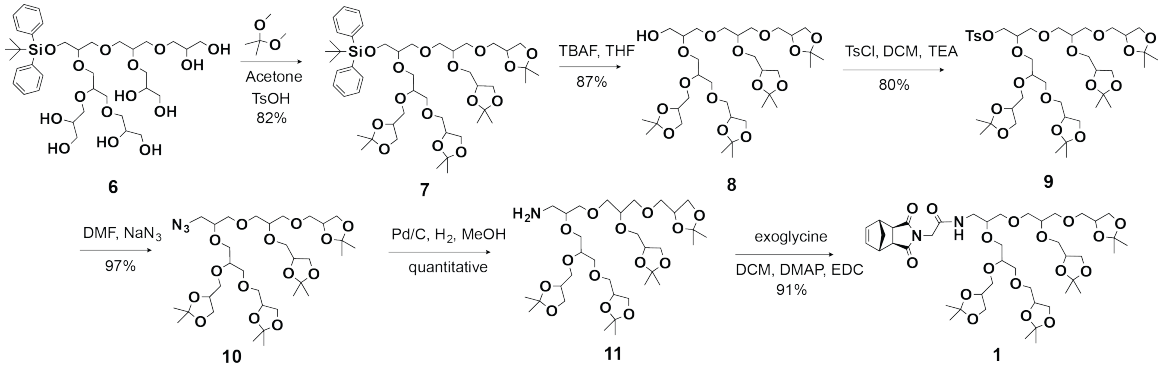
General Methods

Materials. All reagents were purchased from Acros Organics, Fisher Scientific, AK Scientific, TCI America, or Sigma-Aldrich, and used without further purification unless otherwise noted. Dichloromethane (DCM), pyridine, tetrahydrofuran (THF), toluene, dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were stored over activated 4 Å molecular sieves. All other solvents, such as ethanol (EtOH), methanol (MeOH), ethyl acetate (EtOAc) and hexanes (Hx) were of reagent grade and used without further purification. Pyridine-modified Grubbs 2nd generation catalyst for ROMP polymerization,[1] *N*-glycine *cis*-5-norbornene-*exo*-2,3-dicarboximide,[2] fluorescein monomer,[2] and tris(allyloxymethyl)-aminomethane (triallyl-*O*-tris)[3] were synthesized according to reported procedures. All reactions were carried out under dry N_2 atmosphere. Reported reaction temperatures refer to the temperature of the heating medium. The progress of reactions was monitored by silica gel thin layer chromatography (SiO_2 TLC) using 0.2 mm silica 60 coated, plastic plates with F254 indicator. Flash and gravity chromatography was performed using 230-400 mesh (40-63 μm) silica gel. Ratios of solvents for NMR solvents and flash chromatography are reported as volume percentages. Chemical shifts (δ) and coupling constants (J) are reported in parts per million (ppm) and hertz (Hz), respectively. ^{1}H NMR chemical shifts were referenced to the residual solvent peak at 7.26 ppm in chloroform-*d* ($CDCl_3$), 5.32 ppm in dichloromethane-d_2 (CD_2Cl_2) and 3.35 ppm in methanol-d_4 (CD_3OD). For ^{13}C spectra, chemical shifts were referenced to the solvent peak at 77.0 ppm in $CDCl_3$, 53.5 ppm in CD_2Cl_2 and 49.3 ppm in CD_3OD.

Instrumentation. NMR spectra were recorded using a Varian U400, UI400, U500, VXR500 or UI500NB spectrometer in the NMR Laboratory, School of Chemical Science, University of Illinois. The data was processed in iNMR reader (3.5.0) or MestReC 4.8.1.1. Some spectra were treated with the smoothing function of the software to obtain a better baseline. NMR images were screenshots taken from the NMR processing software. Mass spectral analyses were provided by the Mass Spectrometry Laboratory, School of Chemical Science, University of Illinois, using ESI

on a Waters Micromass Q-Tof spectrometer, or MALDI-TOF on an Applied Biosystems Voyager-DE STR spectrometer. Elemental analyses were performed at the Microanalysis Lab, School of Chemical Sciences at University of Illinois. Analytical gel permeation chromatography (GPC) experiments were performed on a hybrid system equipped with a Waters 1515 isocratic pump, a Waters 2414 refractive index detector, a Waters 2998 photodiode array detector, and a miniDAWN TREOS 3-angle laser light scattering detector (MALLS, Wyatt Technology, CA). The detection wavelength of the TREOS detector was set at 658 nm. The MALLS detector was calibrated using pure toluene and used for the determination of the absolute molecular weights. Separations were performed at 50 °C using DMF containing 0.1 M LiBr as the mobile phase (flow rate = 1.0 mL/min). The absolute molecular weights of all linear polymers were determined based on the *dn/dc* value of each sample. The *dn/dc* value of the polymer, which is the slope of polymer solution's refractive index plotted against concentration, was calculated offline using the ASTRA software (version 6.1, Wyatt Technology CA) assuming 100% mass recovery. GPC data points were exported as ASCII files, re-imported into OriginPro 8, plotted, saved as vector image files (*.ai) and colored and annotated in Adobe Illustrator CS6. DLS analysis was performed on a Brookhaven ZetaPALS instrument. UV-Vis absorbance spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. Fluorescence spectra were recorded on a Horiba Jobin Yvon Fluoromax-3 spectrophotometer and quantum yields were determined using fluorescein ($\Phi = 0.95$ in 0.1 M aqueous NaOH solution) as the reference.[4]

Synthesis of Monomers



Scheme S1. Synthetic scheme for 3rd generation polyglycerol dendron monomer.

Compound 6. This compound was prepared according to a previously reported procedures.[5]

Compound 7. To a solution of **6** (1.24 g, 1.6 mmol) and 2,2'-dimethoxypropane (8 mL, 65 mmol) in 10 mL of DMF was added 4-toluenesulfonic acid (1.04 g, 6.0 mmol). The mixture was stirred overnight at 60 ^{o}C. The reaction was quenched by adding TEA (0.5 mL, 3.6 mmol) and the solvents removed using a rotary evaporator. The mixture was re-dissolved in DCM and washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by gradient column chromatography (EtOAc:hexanes = 1:4 to 1:1) to give 1.2 g (82%) of the product as a brown oil. ^{1}H NMR δ 7.65 (br, 4H), 7.41 (br, 2H), 7.38 (br, 4H), 4.21 (br, 4H), 4.01 (br, 4H), 3.75-3.40 (br, 28 H), 1.39 (m, 12H), 1.10 (m, 12H), 1.04 (s, 9H).

Compound 8. To a solution of **7** (2 g, 2.1 mmol) in 15 mL of THF was added TBAF (1 M in THF, 4 mL, 4 mmol). The mixture was stirred at room temperature overnight and concentrated using a rotary evaporator. The mixture was re-dissolved in DCM and washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by gradient column chromatography (EtOAc:hexanes = 1:4 to 1:0) to give 1.3 g (87%) of the product as a yellow oil. ^{1}H NMR δ 4.27 (br, 4H), 4.05 (br,

4H), 4.00 (m, 2H), 3.72 (m, 4H), 3.63-3.48 (br, 20 H), 2.65 (br, 2H), 1.42 (br, 12H), 1.36 (br, 12H). ESI-LRMS (*m*/*z*): calcd for $[M+H]^+$ 697.4; found, 697.6.

Compound 9. To a solution of **8** (1.31 g, 1.9 mmol) and 4-toluenesulfonyl chloride (1.43 g, 7.5 mmol) in 10 mL of DCM was added triethylamine (3.2 mL, 23 mmol). Upon completion of the reaction, the mixture was washed with saturated aqueous NH_4Cl solution and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by gradient column chromatography (EtOAc:hexanes = 1:4 to 2:1) to give 1.28 g (80%) of the product as a yellow oil. ^{1}H NMR δ 7.79 (d, *J*=8.5 Hz, 2H), 7.35 (d, *J*=8.5 Hz, 2H), 4.25 (m, 4H), 4.04 (m, 4H), 3.75-3.40 (br, 27 H), 2.46 (s, 3H), 1.41 (br, 12H), 1.34 (br, 12H). ESI-LRMS (*m*/*z*): calcd for $[M+H]^+$, 851.4; found, 851.5.

Compound 10. To a solution of **9** (3.4 g, 4.0 mmol) in 10 mL of DMF was added sodium azide (4 g, 62 mmol). The mixture was stirred and heated overnight at 90 ^{o}C and the solvents was removed using a rotary evaporator. The crude product was purified by gradient column chromatography (EtOAc:hexanes = 1:4 to 1:2) to give 2.8 g (97%) of the product as a light yellow oil. ^{1}H NMR δ 4.25 (br, 4H), 4.04 (m, 4H), 3.78-3.43 (br, 25 H), 3.38 (br, 1H), 3.30 (br, 1H), 1.41 (br, 12H), 1.35 (br, 12H). ESI-LRMS (*m*/*z*): calcd for $[M]^+$ 721.4; found, 744.3 $[M+Na]^+$.

Compound 11. To a solution of **10** (0.5 g, 0.69 mmol) in 10 mL of MeOH was bubbled through N_2 for 30 min and added 10% palladium on carbon (30 mg, 0.028 mmol). The mixture was charged with H_2 up to 200 psi and stirred overnight at room temperature. The reaction bomb was vented and the mixture was filtered through a Celite plug. The filtrate was concentrated using a rotary evaporator and the residual crude product was used without further purification. ^{1}H NMR δ 4.25 (br, 4H), 4.04 (m, 4H), 3.78-3.38 (br, 25 H), 2.85 (br, 1H), 2.73 (br, 1H), 1.50 (br, 2H), 1.40 (br, 12H), 1.35 (br, 12H). ESI-LRMS (*m*/*z*): calcd for $[M+H]^+$ 696.4; found, 696.4.

Compound 1. To a solution of **11** (695.8 mg, 1 mmol) and *N*-glycine *cis*-5-norbornene-*endo*-2,3-dicarboximide (230 mg, 1.04 mmol) in 10 mL of DCM was added DMAP (12 mg, 0.1 mmol) and

EDC (0.4 mg, 2 mmol). The mixture was stirred overnight at room temperature and washed with brine. The organic layer was dried over Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by gradient column chromatography (EtOAc:hexanes = 1:4 to 2:1) to give 819 mg (91%) of the product as an orange oil. ^{1}H NMR δ 6.29 (s, 2H), 4.24 (br, 4H), 4.13 (br, 2H), 4.04 (m, 4H), 3.78-3.42 (br, 28 H), 3.30 (s, 2H), 2.71 (s, 2H), 1.88 (d, *J* = 10 Hz, 1H), 1.51 (d, *J* = 10 Hz, 1H), 1.41 (br, 12H), 1.35 (br, 12H). ESI-LRMS (*m*/*z*): calcd for $[M+H]^+$ 899.5; found, 899.4, 921.4 $[M+Na]^+$; Anal. Calcd for $C_{44}H_{70}N_2O_{17}$: C, 58.78; H, 7.85; N, 3.12. Found: C, 57.59; H, 7.71; N, 2.95. LC-MS: see below.

LC-MS Analysis

High-performance liquid chromatography (HPLC) coupled to a diode array UV-vis detector and mass spectrometer was utilized to confirm the purity of the 3rd generation polyglycerol dendron monomer.

Compound 1 (dissolved in DMSO/MeOH)

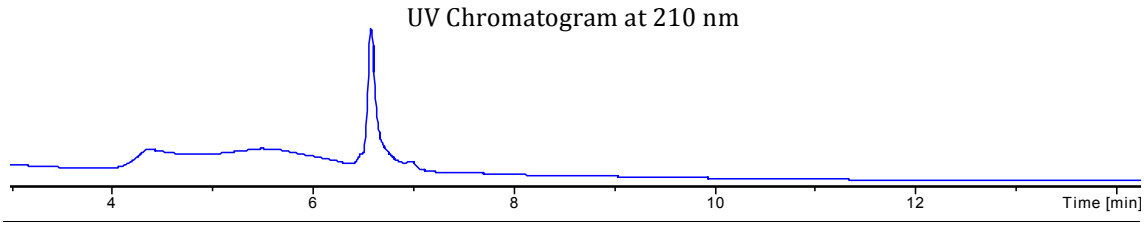


Fig. S1. HPLC spectrum for 3rd generation polyglycerol dendron monomer.

Mass Spectrum for the above Peak at 6.6 min (positive electrospray ionization)

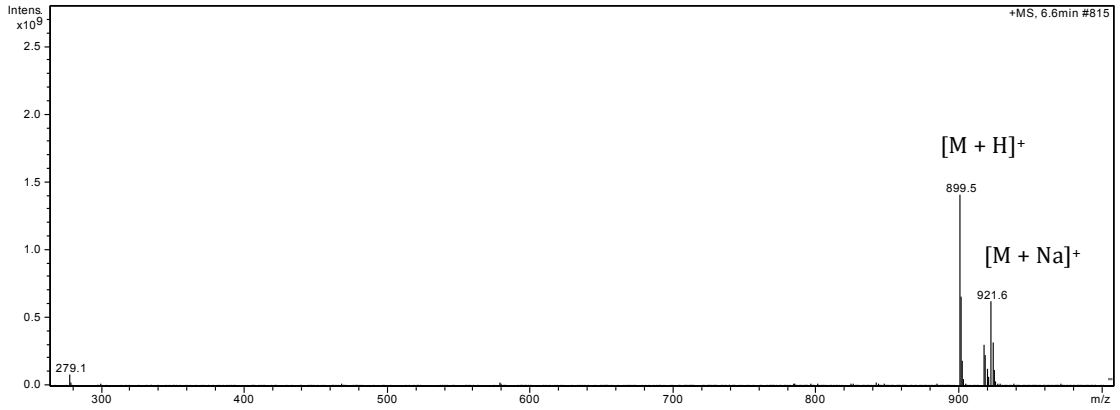
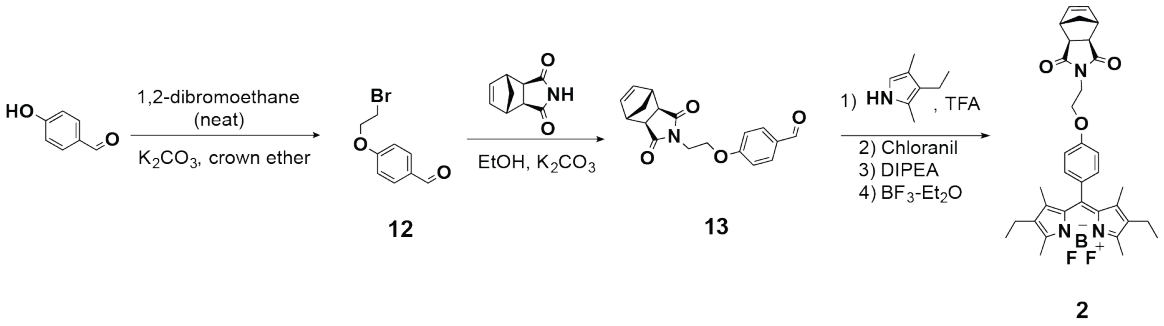


Fig. S2. Mass spectrum for 3rd generation polyglycerol dendron monomer.



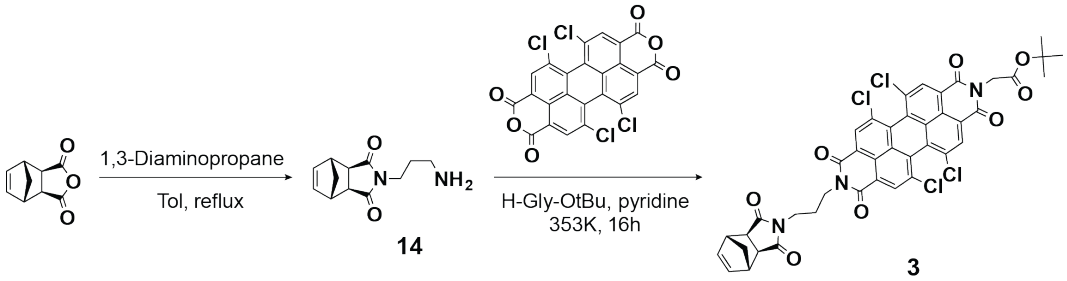
Scheme S2. Synthetic scheme for BODIPY monomer.

Compound 12. This compound was prepared similar to a reported procedure.[6]

Compound 13. A mixture of *cis*-5-norbornene-*exo*-2,3-dicarboximide (1.5 g, 9.2 mmol), **12** (2.1 g, 9.2 mmol) and K_2CO_3 (3.0 g, 21.7 mmol) in 25 mL of ethanol was refluxed for 15 h. The solvent was removed by rotary evaporation and the resulting residue was purified by column chromatography (EtOAc:hexanes = 4:5) to give 2.1 g (73%) of the product as a yellow oil. ^{1}H NMR (400 MHz): δ 9.85 (s, 1H), 7.80 (d, J = 8.7, 2H), 6.93 (d, J = 8.7, 2H), 6.25 (t, J = 1.6, 2H), 4.22 (t, J = 5.6, 2H), 3.93 (t, J = 5.6, 2H), 3.25 (broad s, 2H), 2.68 (broad s, 2H), 1.44 (dt, J = 9.5, 1.5, 1H), 1.23 (d, J = 9.5, 1H). ^{13}C NMR (400 MHz): δ 191.0, 178.1, 163.3, 138.0, 132.2, 130.6, 115.0, 64.3, 48.1, 45.5, 42.8, 37.8. HR-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{17}NO_4$, 311.1230; found, 312.1244, $[M+H]^+$.

Compound 2. The preparation of BODIPY monomer was analogous to a previously published protocol.[7] Briefly, **13** (1.26 g, 4.0 mmol) was mixed with cryptopyrrole (1.0 g, 8.1 mmol) in 20 mL of DCM. A few drops of trifluoroacetic acid were added. The dark reaction mixture was stirred at room temperature until total disappearance of the aldehyde. Chloranil (0.98 g, 4.0 mmol) was added and the mixture stirred for 5 min. DIPEA (3.62 g, 28 mmol) and trifluoroborate etherate (6.24 g, 44 mmol) were added successively. The mixture was stirred at room temperature overnight. The filtrate was concentrated using a rotary evaporator and the residue was purified by chromatography (DCM:hexanes = 5:1). The resultant orange-red solid was then suspended in 25

mL of 1:1 ether:hexanes, sonicated, and filtered to give the pure product (1.4 g, 60%). ^{1}H NMR δ 7.15 (d, *J* = 8.6, 2H), 6.95 (d, *J* = 8.6, 2H), 6.32 (t, *J* = 1.7, 2H), 4.22 (t, *J* = 5.8, 2H), 3.97 (t, *J* = 5.8, 2H), 3.32 (t, *J* = 1.5, 2H), 2.75 (d, *J* = 1.0, 2H), 2.53 (s, 6H), 2.30 (q, *J* = 7.5, 4H), 1.48 (dt, *J* = 9.8, 1.5, 1H), 1.34 (d, *J* = 9.8, 1H), 1.31 (s, 6H), 0.99 (t, *J* = 7.5, 6H). ^{13}C NMR δ 178.09, 158.60, 153.71, 140.11, 137.97, 132.81, 131.25, 129.65, 128.61, 115.15, 63.90, 48.03, 45.48, 42.72, 37.85, 17.21, 14.78, 12.63, 11.96. ^{11}B NMR (128 MHz, $CDCl_3$): 0.85 (t, *J* = 33.4). ^{19}F NMR (376 MHz, $CDCl_3$): -146.3 (q, *J* = 33.5). HR-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{34}H_{39}BF_2N_3O_3$, 586.3053; found, 586.3047, $[M+H]^+$; Anal. Calcd for $C_{34}H_{38}BF_2N_3O_3$: C, 69.75; H, 6.54; N, 7.18. Found: C, 68.19; H, 6.35; N, 7.02.

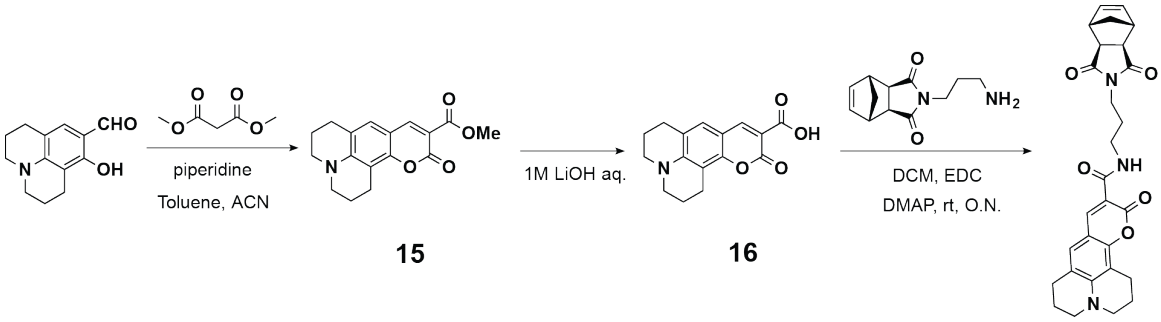


Scheme S3. Synthetic scheme for PDI monomer.

Compound 14. This compound was prepared analogous to a reported procedure.[2]

Compound 3. Tetrachloroperylene tetracarboxylic acid dianhydride (532 mg, 1.00 mmol), *N*-(3-aminopropyl) *cis*-5-norbornene-*exo*-2,3-dicarboximide (231 mg, 1.05 mmol) and *tert*-butyl aminoacetate hydrochloride (176 mg, 1.05 mmol) were mixed in 15 mL of dry pyridine. The mixture was heated to 80 ^{o}C to generate a homogeneous solution, and was kept stirring for 20 h. Solvent was removed using a rotary evaporator, and the residue was purified by gradient column chromatography (EtOAc:hexanes = 1:5 to 1:3) to give 210 mg (25%) of the product as a bright orange powder. ^{1}H NMR δ 8.71 (s, 2H), 8.68 (s, 2H), 6.32 (t, *J* = 1.5, 2H), 4.89 (s, 2H), 4.25 (t, *J* = 7.4, 2H), 3.66 (t, *J* = 6.9, 2H), 3.32 (t, *J* = 1.9, 2H), 2.74 (d, *J* = 1.0, 2H), 2.07 (tt, *J* = 7.4, 6.9, 2H), 1.59 (d, *J* = 9.4, 1H), 1.53 (s, 9H), 1.34 (d, *J* = 9.4, 1H). ^{13}C NMR δ 178.22, 178.07, 166.65,

162.30, 162.09, 138.01, 137.96, 135.63, 135.53, 133.35, 133.15, 131.58, 131.55, 129.02, 128.81, 123.55, 123.40, 123.19, 122.91, 82.94, 48.05, 48.04, 47.99, 45.36, 45.30, 42.98, 42.95, 42.45, 38.69, 36.59, 36.35, 28.20, 26.85, 26.48. MALDI-TOF (*m/z*): calcd for $[M+H]^+$ 846.1; found 846.1, 791.1 [M minus *tert*-butyl]$^+$; Anal. Calcd for $C_{42}H_{29}Cl_4N_3O_8$: C, 59.66; H, 3.46; N, 4.97; Cl, 16.77. Found: C, 58.53; H, 3.08; N, 4.88; Cl, 16.40.



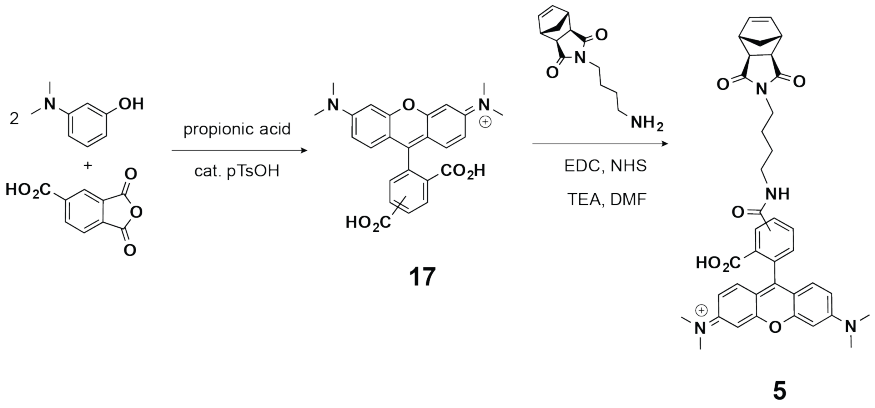
Scheme S4. Synthetic scheme for coumarin monomer.

Compound 15. This compound was prepared using a reported procedure.[8]

Compound 16. To a suspension of **15** (2 g, 6.7 mmol) in 30 mL of MeOH was added 10 mL of 4 M LiOH aqueous solution. The mixture was stirred at room temperature for 2 h and became a clear solution. The solution was acidified with 4 M aqueous HCl and extracted with DCM multiple times. The organic layers were combined, dried over Na_2SO_4 and the solvent removed by rotary evaporator to afford 580 mg (30%) of the product as a brown solid. The crude product was used in the next step without further purification. The ^{1}H NMR was consistent with that in the literature.[8]

Compound 4. To a solution of **16** (200 mg, 0.70 mmol) and **14** (183.9 mg, 0.83 mmol) in 4 mL of DCM was added DMAP (40 mg, 0.16 mmol) and EDC (400 mg, 2.1 mmol). The mixture was stirred overnight at room temperature, washed with brine, dried over Na_2SO_4 and the solvent was removed using a rotary evaporator. The crude product was purified by gradient column

chromatography (EtOAc:hexanes = 1:4 to 1:1) to give 315 mg (92%) of the product as a dark yellow solid. ^{1}H NMR δ 9.03 (br, 1H), 8.56 (s, 1H), 6.98 (s, 1H), 6.27 (s, 2H), 3.58 (m, 2 H), 3.41 (m, 2H), 3.31 (m, 4H), 3.27 (s, 2H), 2.87 (m, 2H), 2.76 (m, 2H), 2.69 (s, 2H), 1.96 (br, 4H), 1.87 (m, 2H), 1.51 (d, J = 10 Hz, 1H). ^{13}C NMR δ 178.14, 163.76, 162.99, 152.70, 148.04, 137.89, 127.04, 119.63, 109.00, 108.26, 105.70, 53.55, 50.29, 49.87, 47.90, 45.24, 42.89, 37.04, 36.42, 28.19, 27.52, 21.21, 20.27, 20.15. ESI-HRMS (m/z): calcd for $[M+H]^+$ 488.2185; found, 488.2178; Anal. Calcd for $C_{28}H_{29}N_3O_5$: C, 68.98; H, 6.00; N, 8.62. Found: C, 63.84; H, 5.25; N, 7.71.



Scheme S5. Synthetic scheme for rhodamine monomer.

Compound 17. To a suspension of *N,N*-dimethyl 3-aminophenol (9.999 g, 73.0 mmol) and 1,2,4-benzenetricarboxylic anhydride (7.008g, 36.5 mmol) in 500 mL of propionic acid was added p-toluenesulfonic acid monohydrate (322 mg, 1.6 mmol). The mixture was refluxed for 2 d. The solvent was removed via rotary evaporator and the residual propionic acid was removed by azeotropic distillation with water using a rotary evaporator. The crude product was purified by gradient column chromatography (MeOH:DCM = 1:4 to 3:2) to give 1.88 g (12%) of the product as a dark purple solid (a mixture as 5/6 isomer in an approx. 4:5 ratio, 1.88 g, 4.35 mmol). ^{1}H NMR (500 MHz; CD_3OD): δ 8.79 (d, J = 1.5, 1H), 8.27 (d, J = 1.2, 1H), 8.25 (d, J = 1.6, 1H), 8.17 (d, J = 8.2, 1H), 7.86 (d, J = 1.6, 1H), 7.38 (d, J = 7.9, 1H), 7.25 (d, J = 9.5, 2H), 7.23 (d, J =

9.5, 2H), 7.032 (dd, *J* = 9.5, 1.0 2H), 7.027 (dd, *J* = 9.4, 0.8, 2H), 6.93 (d, *J* = 2.6, 2H), 6.92 (d, *J* = 2.6, 2H), 3.28 (s, 24H). ESI-LRMS (*m*/*z*): calcd for $[M+H]^+$ 431.1; found 431.0.

Compound 5. To a solution of **17** (578 mg, 1.38 mmol) and NHS (168 mg, 1.46 mmol, 1.05 eq.) in 15 mL of dry DMF was added EDC·HCl (315 mg, 1.85 mmol, 1.3 eq.). The mixture was allowed to stir at room temperature for 20 min. *N*-(4-Aminobutyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (350 mg, 1.49 mmol, 1.08 eq.) was added to the mixture and the reaction was stirred overnight at room temperature. DMF was removed via rotary evaporator and the residue was re-dissolved in EtOAc and washed with water, 0.1 M HCl, and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed using a rotary evaporator. The crude product was purified via gradient column chromatography (MeOH:DCM = 1:9 to 1:3) to give a dark purple solid (a mixture of 5/6 isomers, 700 mg, 79%). Note: isomers could be separated with careful chromatography although it was not necessary. Isomer **5**: ^{1}H NMR (CD_3OD): δ 8.66 (d, *J* = 1.5, 1H), 8.16 (dd, *J* = 7.9, 1.5 1H), 7.45 (d, *J* = 7.9, 1H), 7.18 (d, *J* = 9.5, 2H), 7.04 (dd, *J* = 9.5, 2.4, 2H), 6.96 (d, *J* = 2.4, 2H), 6.33 (t, *J* = 1.7, 2H), 3.55 (m, 2H), 3.48 (m, 2H), 3.30 (s, 12H), 3.19 (t, *J* = 1.7, 2H), 2.73 (d, *J* = 1.1, 2H), 1.68 (m, 4H), 1.50 (dt, *J* = 9.8, 1.4, 1H), 1.26 (d, *J* = 9.8, 1H). Isomer **6**: ^{1}H NMR (CD3OD): 8.27 (d, *J* = 8.2, 1H), 8.12 (dd, *J* = 8.2, 1.8, 1H), 7.74 (d, *J* = 1.8, 1H), 7.20 (d, *J* = 9.5, 2H), 7.04 (dd, *J* = 9.5, 2.5, 2H), 6.96 (d, *J* = 2.5, 2H), 6.30 (t, *J* = 1.7, 2H), 3.48 (m, 2H), 3.40 (m, 2H), 3.30 (s, 12H), 3.12 (t, *J* = 1.6, 2H), 2.68 (d, *J* = 1.0, 2H), 1.60 (m, 4H), 1.42 (dt, *J* = 9.8, 1.4, 1H), 1.18 (d, *J* = 9.8, 1H). ESI-HRMS (*m*/*z*): calcd for $[M+H]^+$ 647.2864; found: 647.2893; Anal. Calcd for $C_{38}H_{39}ClN_4O_6$: C, 66.81; H, 5.75; N, 8.20; Cl, 5.19. Found: C, 61.03; H, 5.16; N, 7.75; Cl, 5.71.

Synthesis of Polymers

Typical synthetic procedure for pX-1 (X= **C**, **B**, **F**, **P** and **R**)

M_X (12 nmol, 2 eq), M_1 (0.15 mmol, 25 eq) and M_2 (0.3 mmol, 50 eq) were dissolved in anhydrous DCM (5 mL). Pyridine-modified Grubbs 2nd generation catalyst (0.03 M in DCM, 0.02 mL, 6 nmol, 1 eq) was added. The solution was stirred at room temperature for 30 min before butyl vinyl ether (1 mL) was added to quench the catalyst. Solvent was removed using a rotary evaporator. The solid residue was dissolved in DCM, precipitated in 14 mL of a 30:1 hexanes:ether and centrifuged for 10 min at 5000 rpm. This process was repeated two times. The precipitate was dried to give a brown transparent film.

To a solution of the above polymer (23 mg) in a mixture of DCM (5 mL) and nitrobenzene (0.1 mL) was added triallyl-*O*-tris (0.1 mL). The solution was stirred at 40 °C overnight and concentrated via rotary evaporator. The viscous residue was dissolved in DCM, precipitated in 14 mL of 27:1 hexanes:ether and centrifuged for 10 min at 5000 rpm. This process was repeated two times. The precipitate was dried to give a brown transparent film.

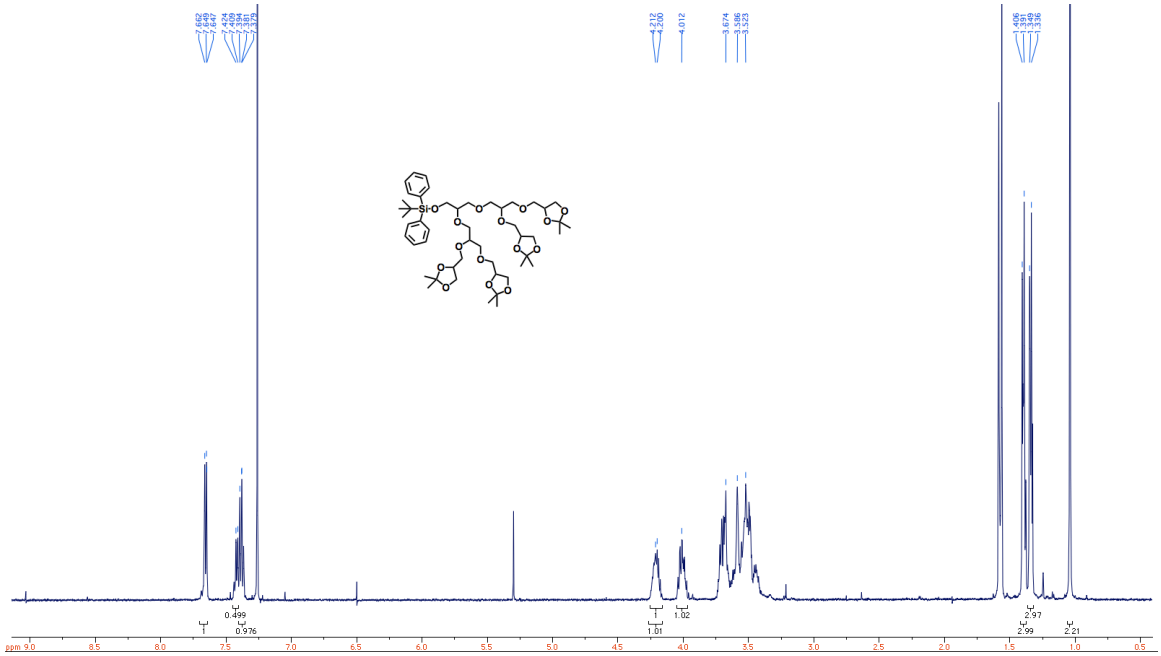
Typical synthetic procedure for pX-2 (X= **C**, **B**, **F**, **P** and **R**)

To a solution of **pX-1** (20 mg) in 500 mL of anhydrous DCM under nitrogen atmosphere was added Grubbs 1st generation catalyst (12 mg) in 1 mL of DCM. The mixture was stirred at 35 ^{o}C for a total of 48 h, during which time additional catalyst was added to the solution portion-wise (6 mg in 1 mL of DCM at the time point of 6 h, and another 3 mg at the time point of 30 h). The reaction was quenched by adding 15 mL of butyl vinyl ether, stirred for 30 min and concentrated using a rotary evaporator. The oily residue was dissolved in DCM, precipitated in 14 ml of 27:1 hexanes:ether and centrifuged for 10 min at 5000 rpm. This process was then repeated for a second time. The crude was further purified by passing through silica gel eluted by DCM. The solvent was removed via rotary evaporator to afford a brown transparent film.

Typical synthetic procedure for pX (X= **C**, **B**, **F**, **P** and **R**)

To a solution of **pX-2** (20 mg) in a mixture of DCM (2 mL), Acetone (2 mL) and Water (1 mL) was added TFA (0.2 mL). The mixture was stirred at 40 ^{o}C for 2 h and concentrated via rotary evaporator. The crude product was purified by dialysis against aqueous solution of K_2CO_3 (4 L, 0.05 wt%) for 6 h, and twice against water (4 L) for 6 h. The solution was lyophilized to afford a solid foam.

NMR Spectra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2.99
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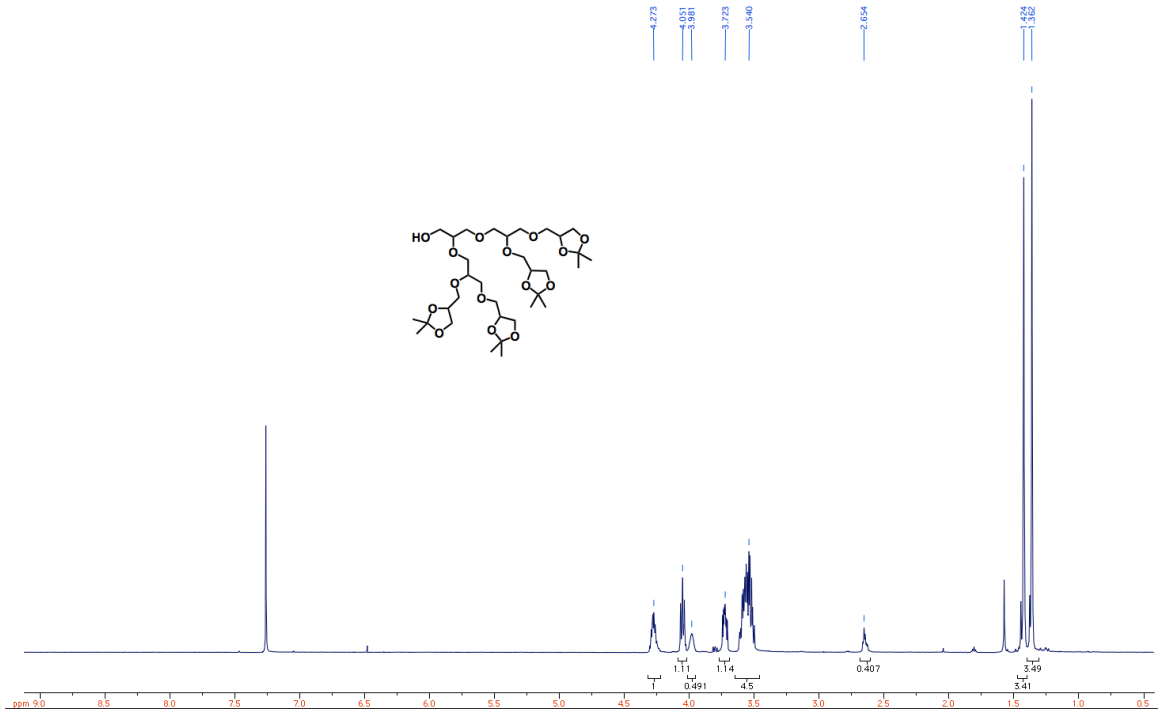
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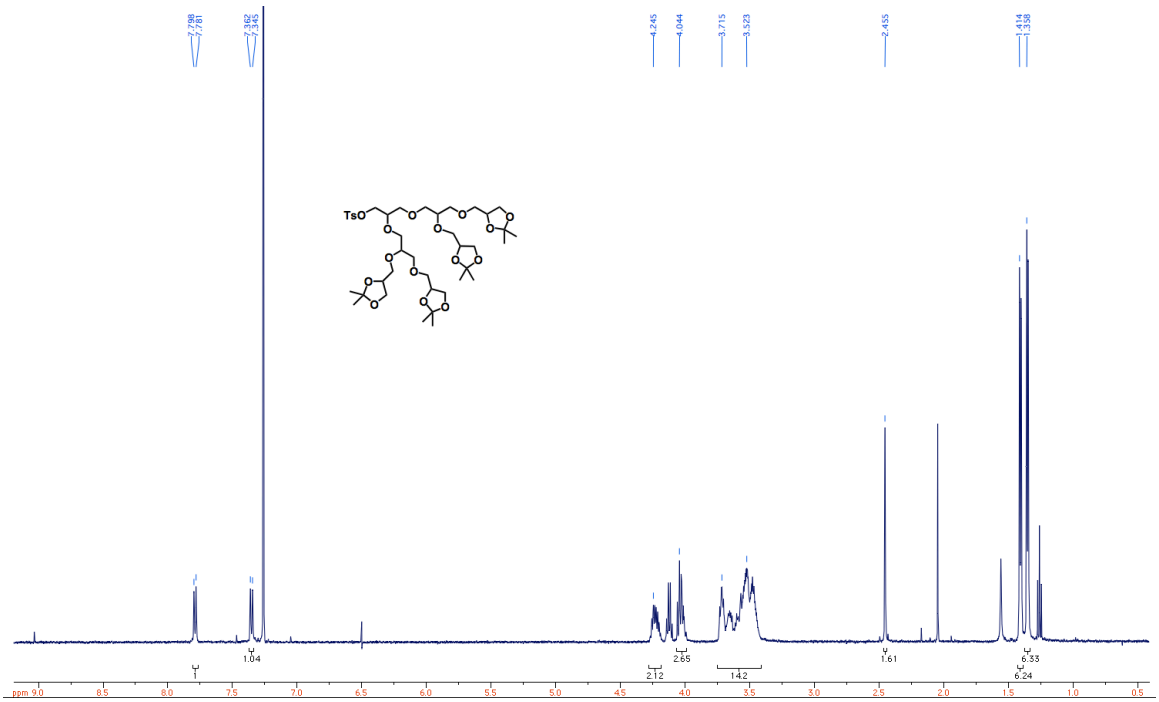
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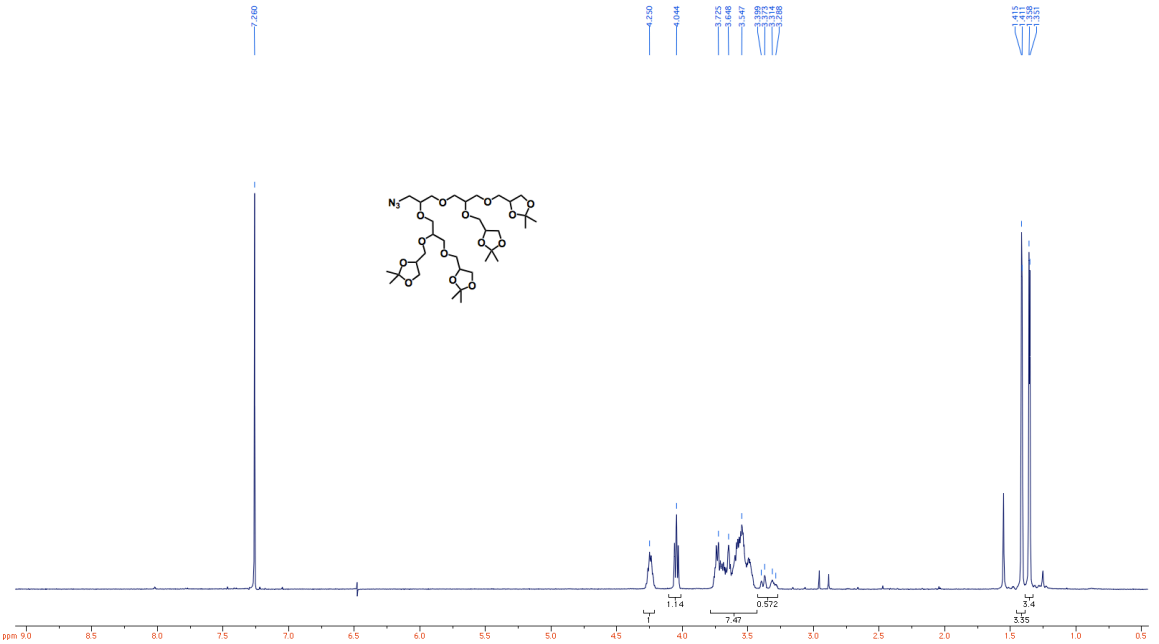
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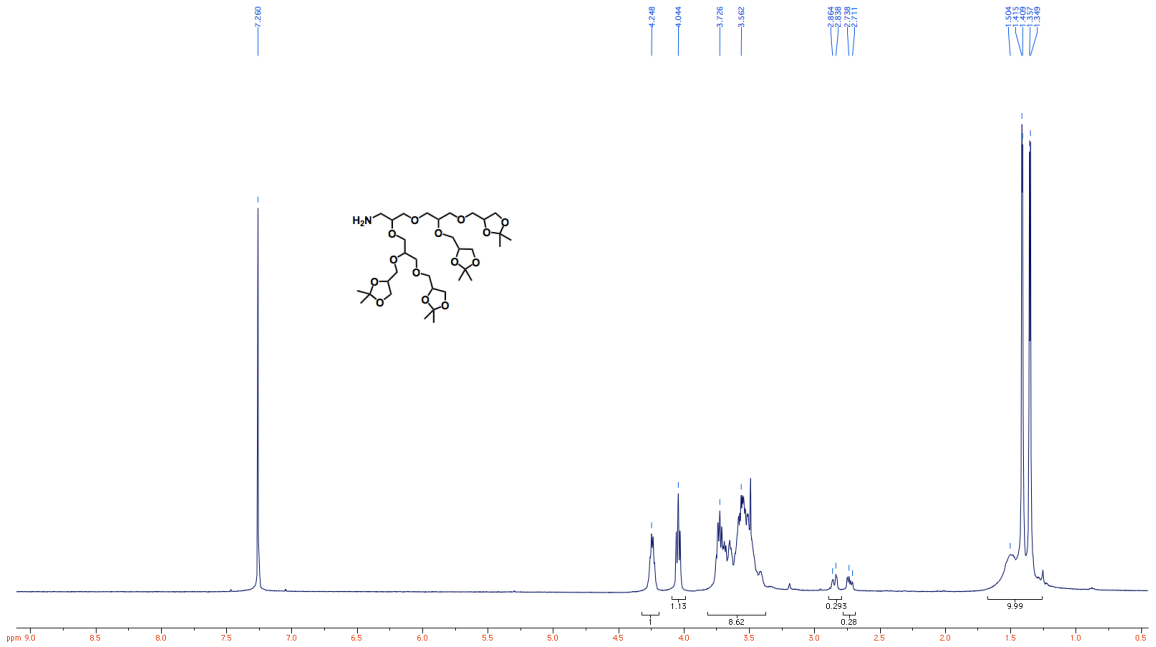
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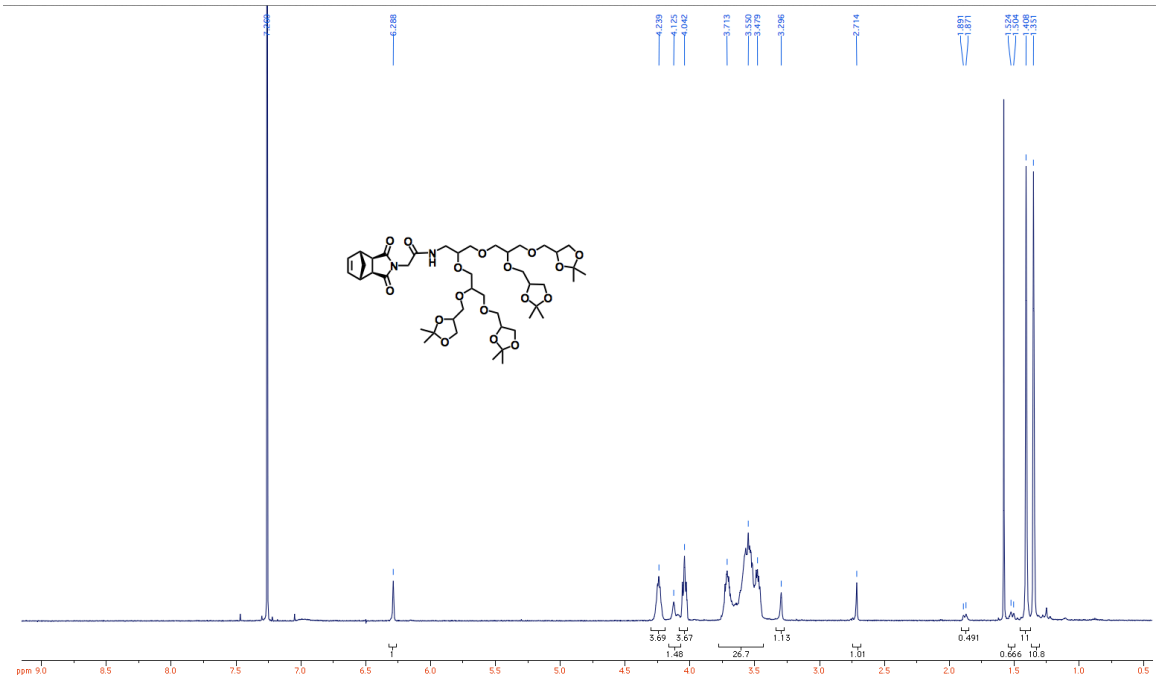
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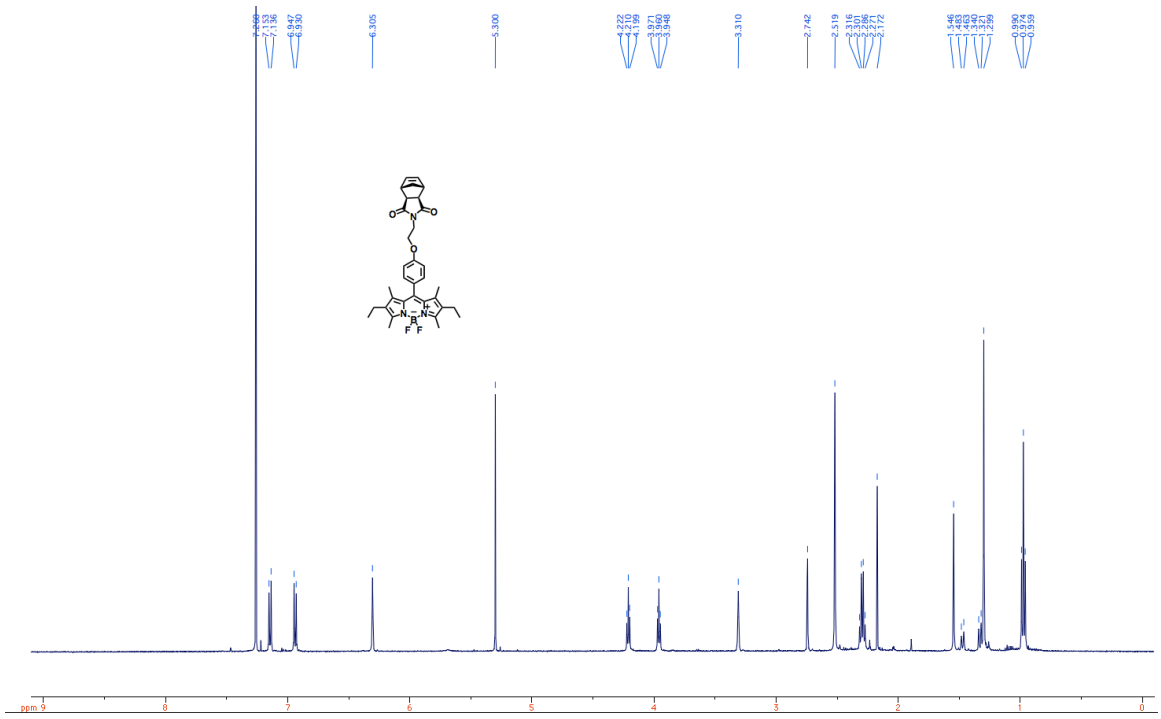
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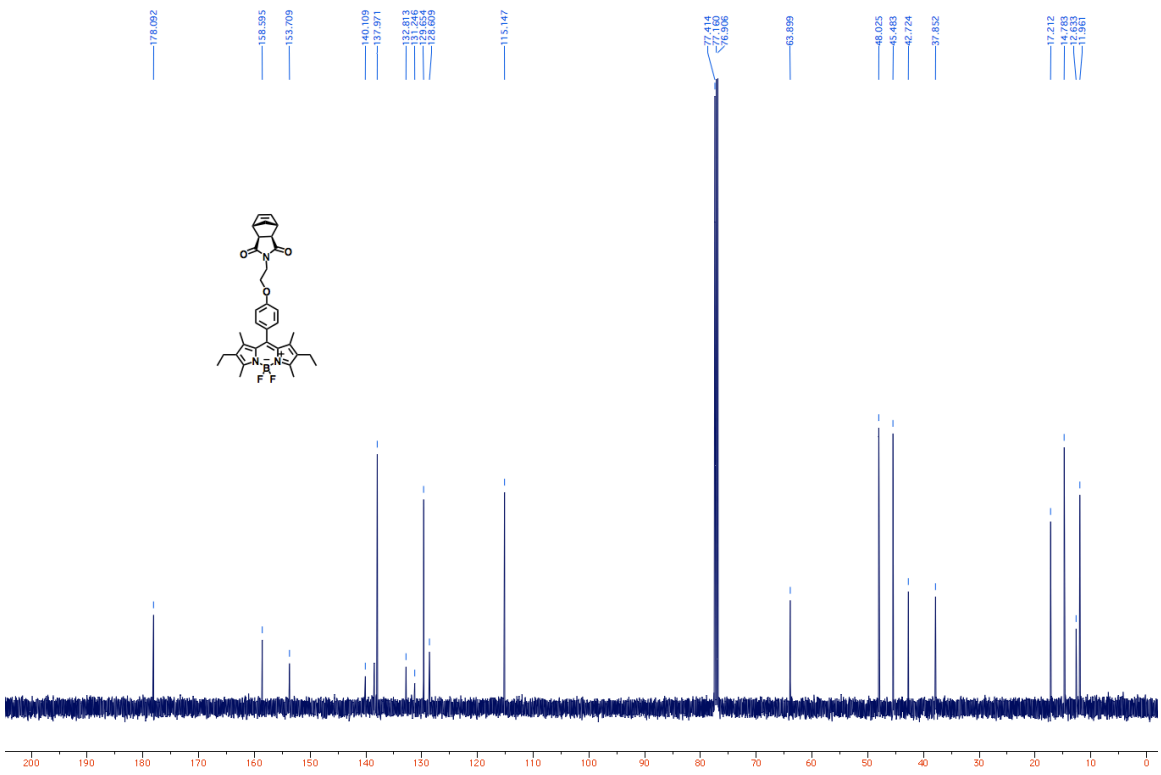
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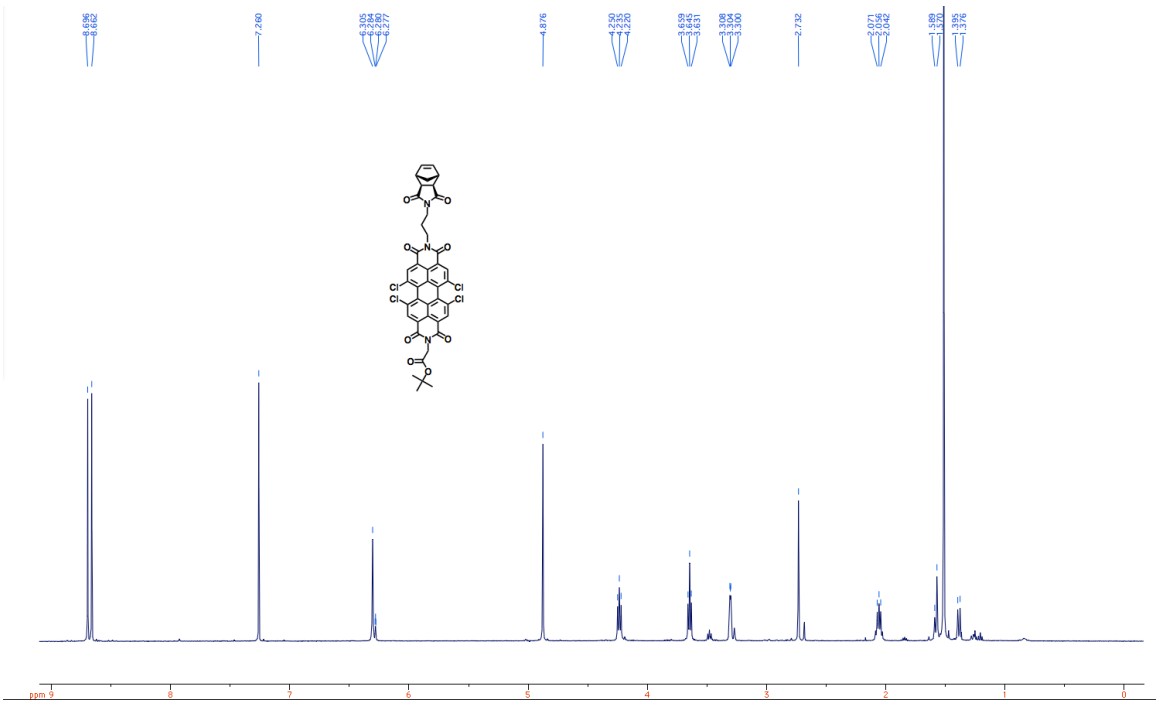
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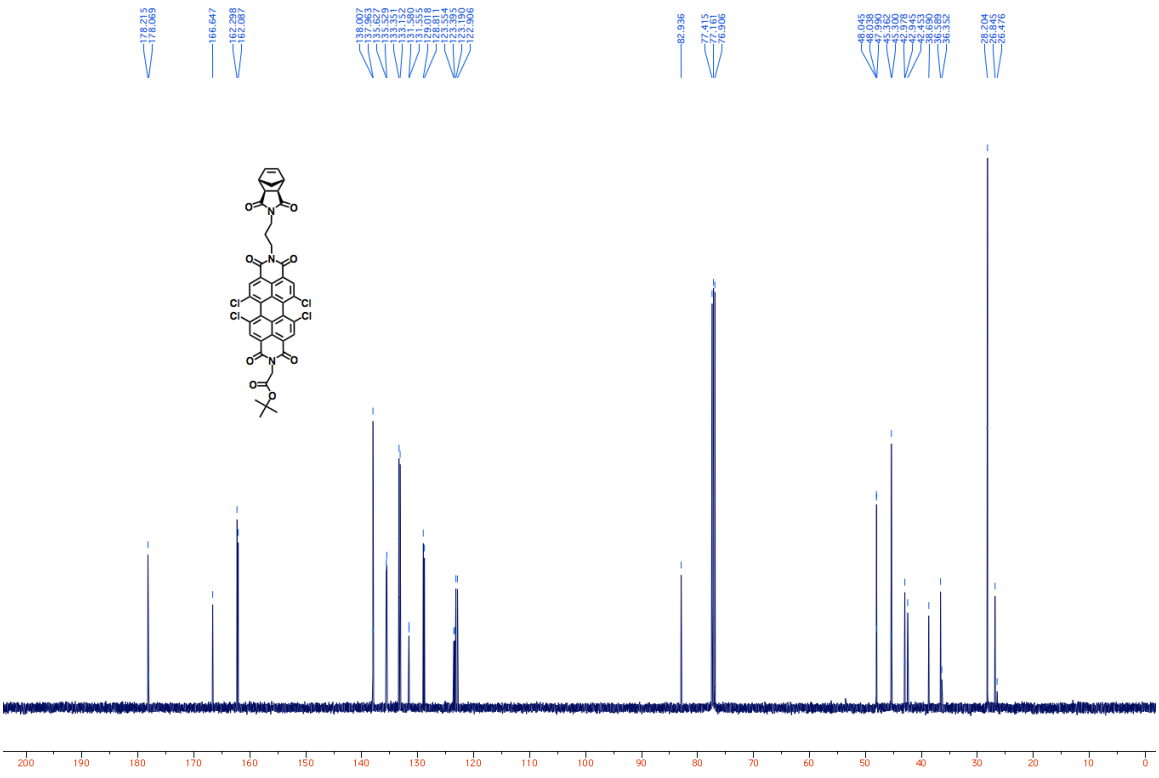
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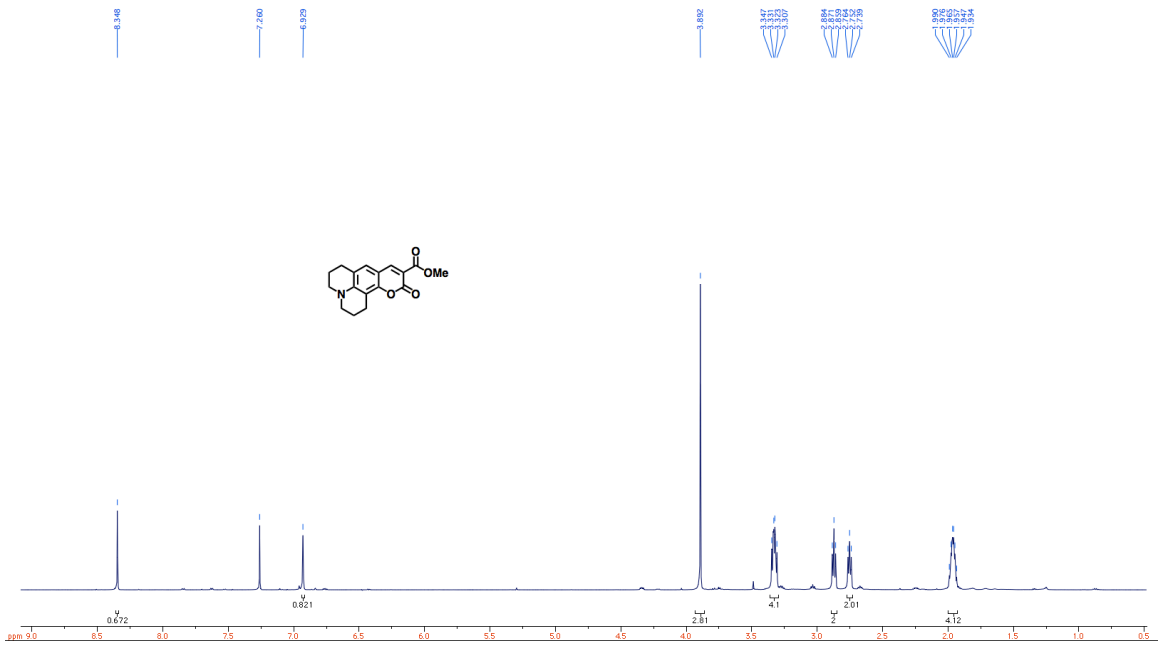
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1.934
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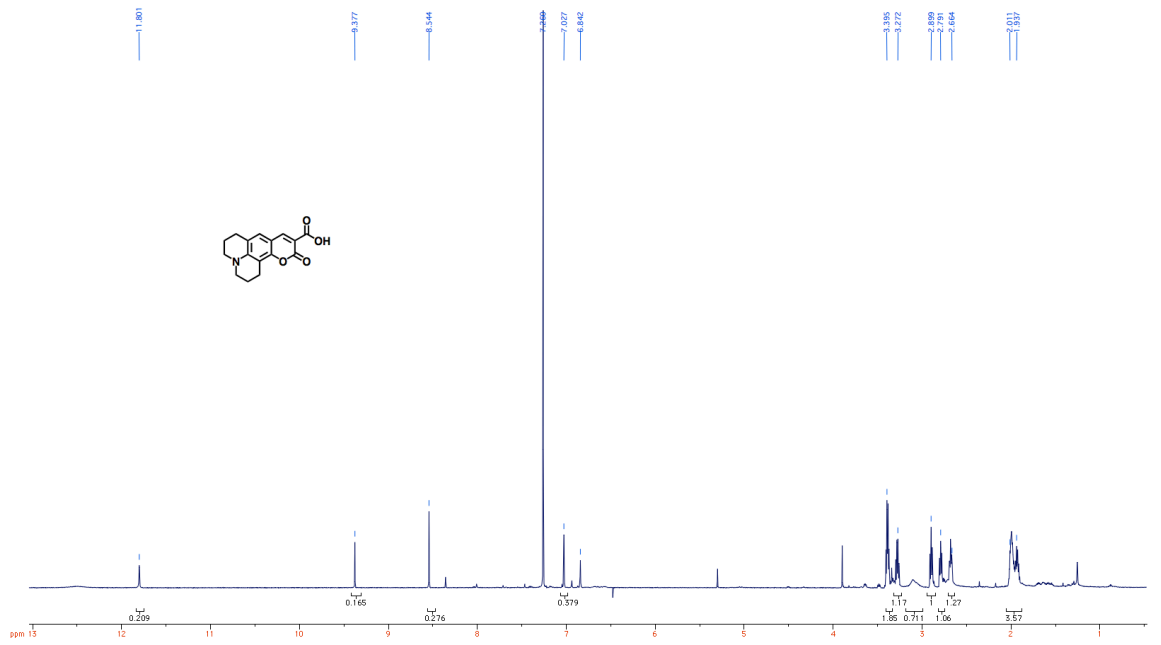
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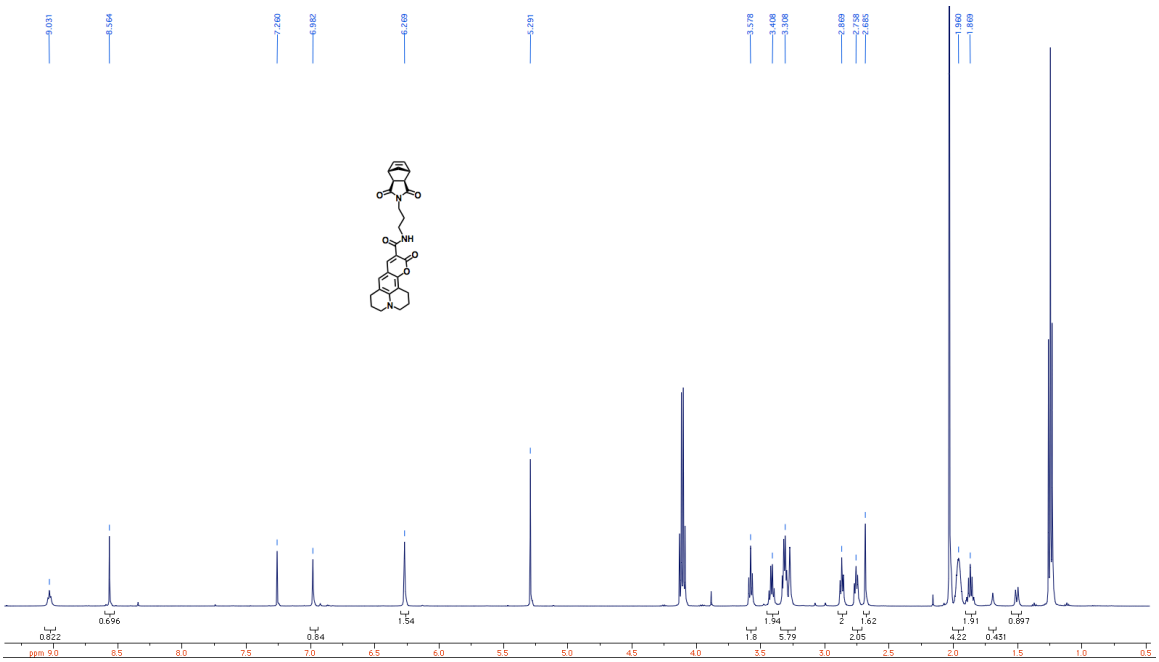
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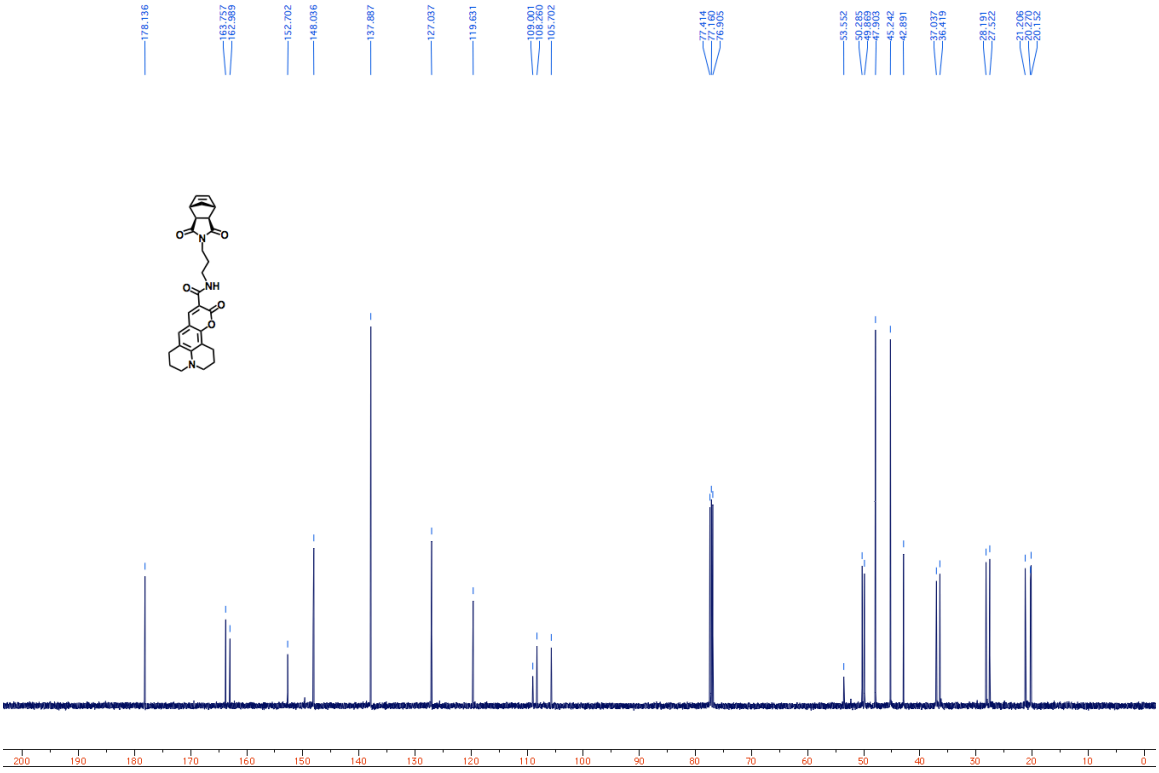
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Polymer Characterizations

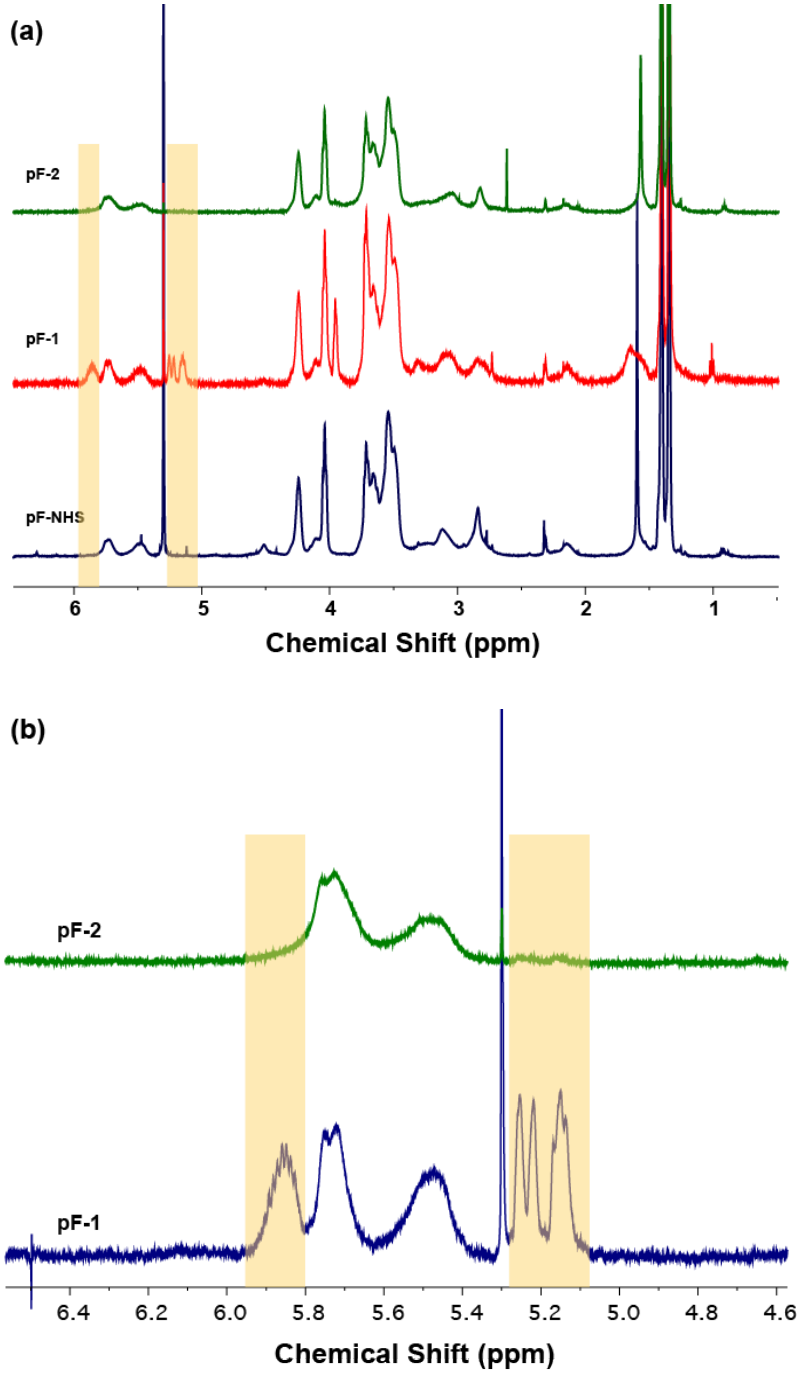

Fig. S3. Overlay of ^{1}H NMR spectra of polymers after polymerization (**pF-NHS**), triallyl-*O*-tris incorporation (**pF-1**) and RCM (**pF-2**). The changes of the proton signals are highlighted: (a) full spectra; (b) truncated spectra.

GPC Traces

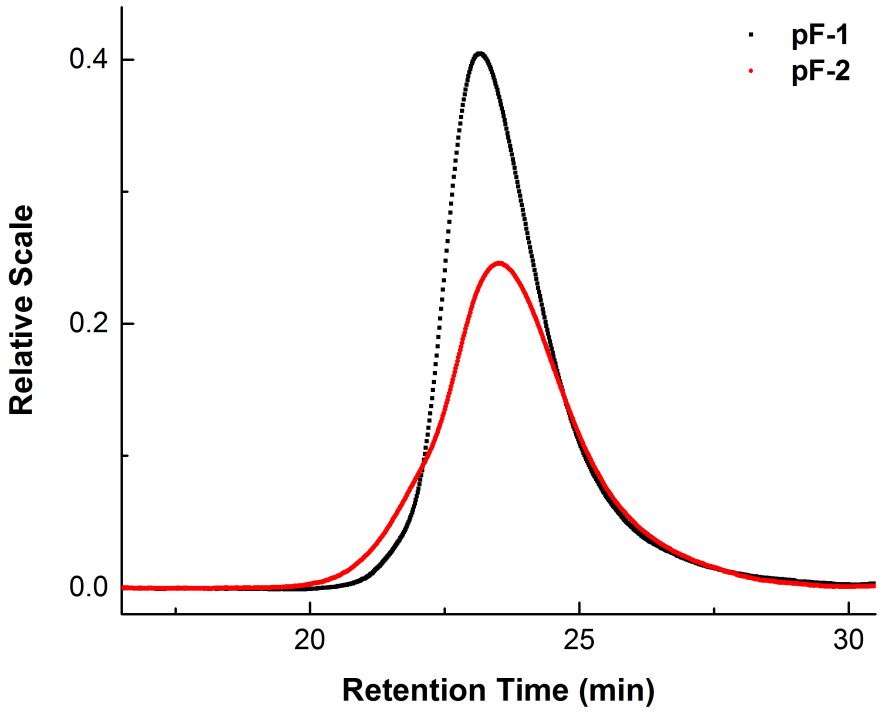

Fig. S4. GPC traces of **pF-1** and **pF-2**.

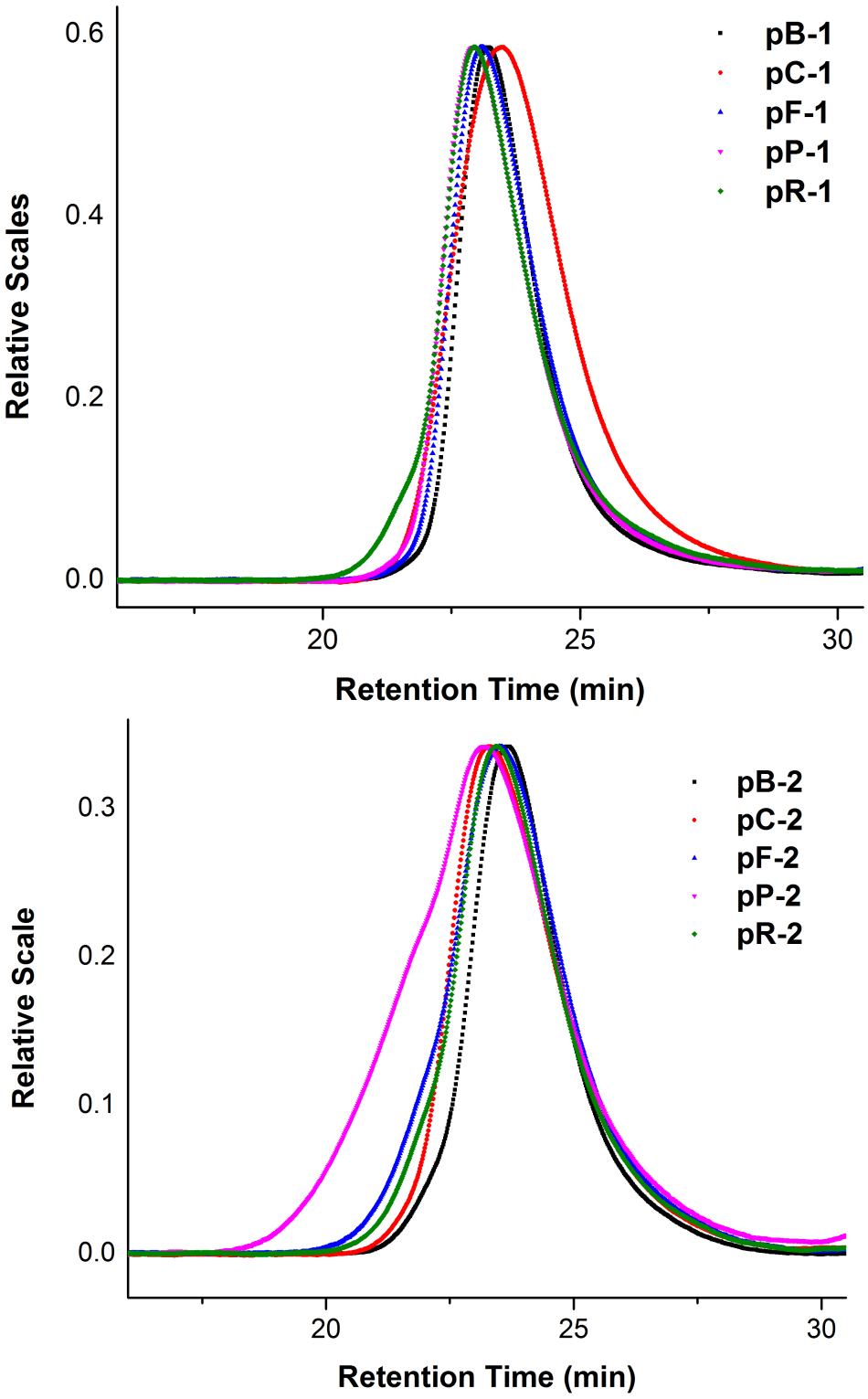

Fig. S5. GPC traces of **pX-1** (top) and **pX-2** (bottom) (X= **C**, **B**, **F**, **P** and **R**).

Dynamic Light Scattering (DLS) Analysis

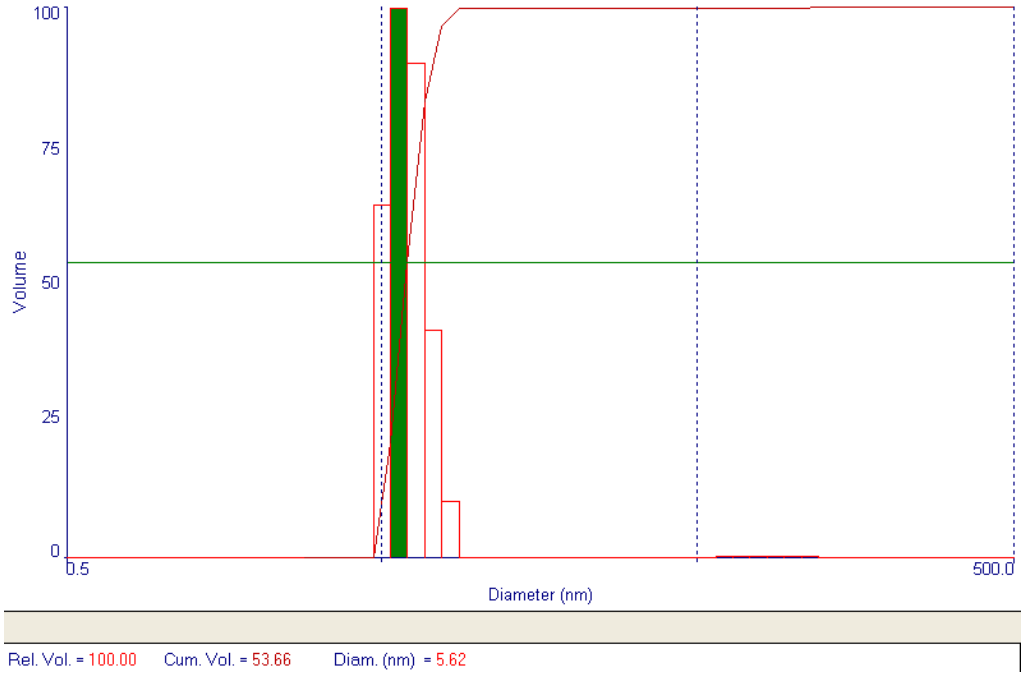

Fig. S6. DLS analysis of **pF**.

pP UV-vis

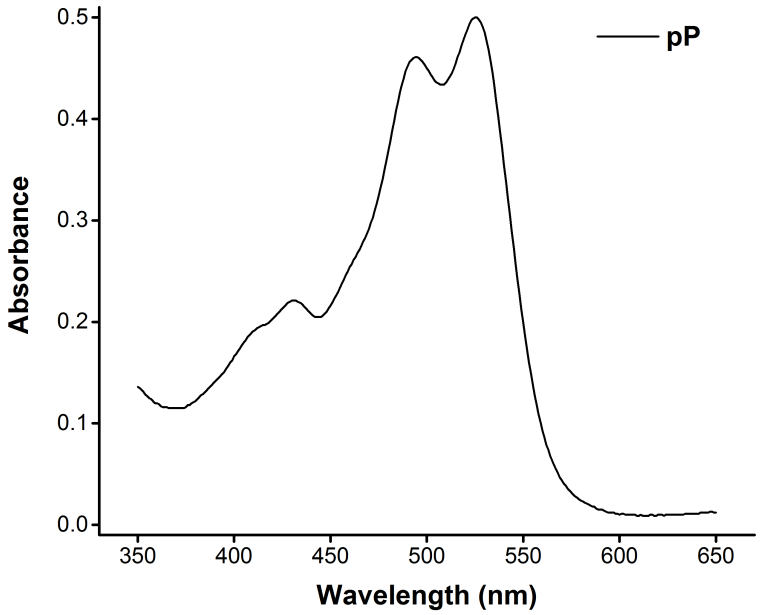

Fig. S7. UV-vis spectrum (350-650 nm) of **pP**.

Although the QY of pP is low, however, it is not likely a result of intermolecular π-π stacking, rather it may arise from the microenvironment within the CDP (*e.g.* the chemical structures around the dye is quenching the fluorophore – this is very common for most dyes. for example, many dyes give significantly lower QY when they are conjugated to a protein). The UV-vis absorbance at ca. λ_{max} 523 nm is higher than that at λ_{max} 492 nm. The reverse is true when the PDIs are aggregated as reported by us (Zimmerman *et al.*, *J. Am. Chem. Soc.*, 2011, 133, 9964) and by Haag group (Haag *et al., Chem. Commun.*, 2010, 46, 1884). Therefore, the CDP architecture should have successfully prevented or significantly relieved the aggregation and self-quenching of the hydrophobic PDI dyes. Internal functionalization of the CDPs or chemical modifications on the PDI structure may help further improve the quantum yield.

Photobleaching Studies

Polymer or free-dye samples (0.2 μM, 500 μL in 1x PBS) in cuvettes were placed in a black box equipped with a high-power LED (470 nm wavelength, 15 V x 700 mA). The distance between samples and light source was 10 cm. The cuvettes were capped to prevent solvent evaporation and concentration change. Every 30 min, the samples were taken out of the box and directly measured in a fluorospectrometer. The caps were removed after each measurement for 1 min to allow air exchange so that oxygen in the solution would not be reduced or exhausted. The samples were re-capped and moved back into the black box. The fluorescence intensity of each measurement was recorded and plotted against irradiation time.

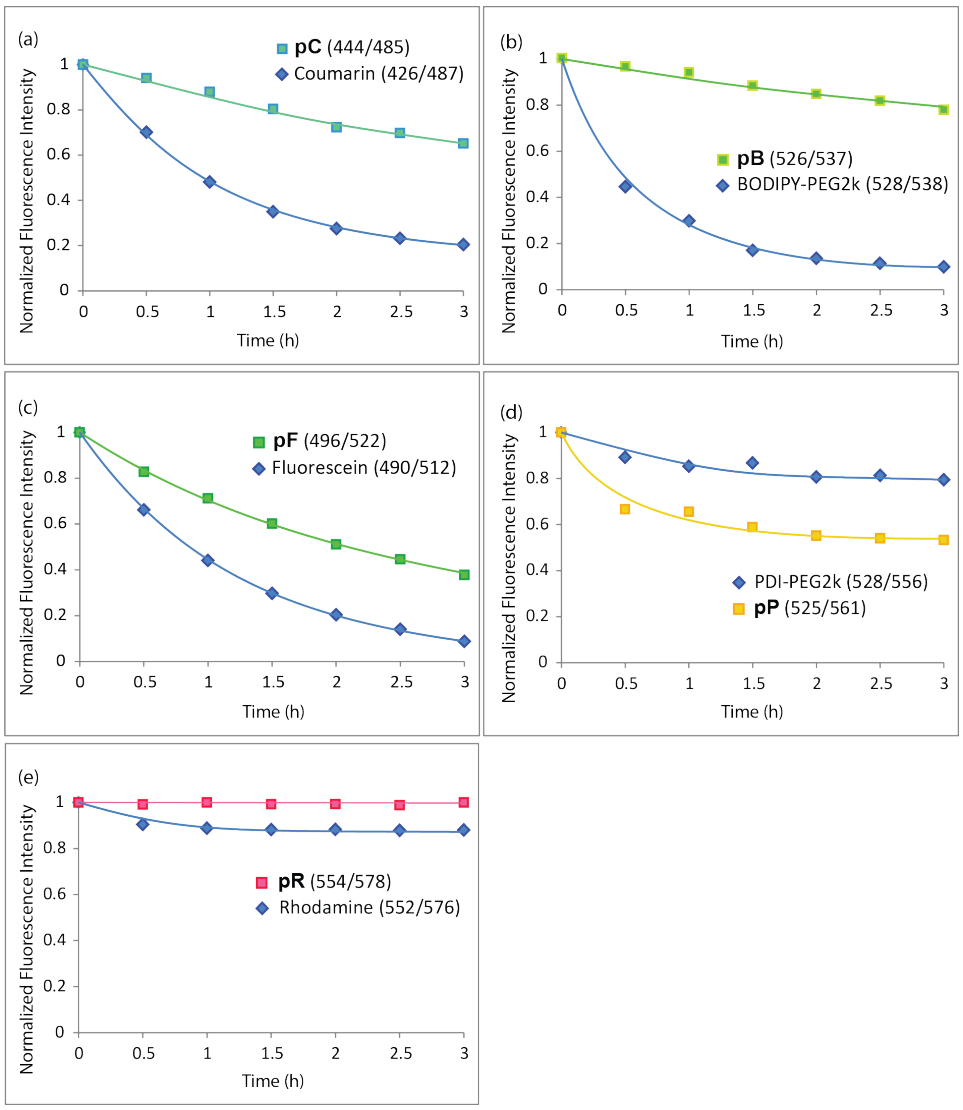

Fig. S8. Normalized fluorescence intensity over time during photobleaching study of **pX** compared with free dyes: (a) **pC** and coumarin; (b) **pB** and BODIPY-PEG2k; (c) **pF** and fluorescein; (d) **pP** and PDI-PEG2k; (e) **pR** and rhodamine. The corresponding excitation and maximum emission wavelengths are indicated.

Cell Cytotoxicity

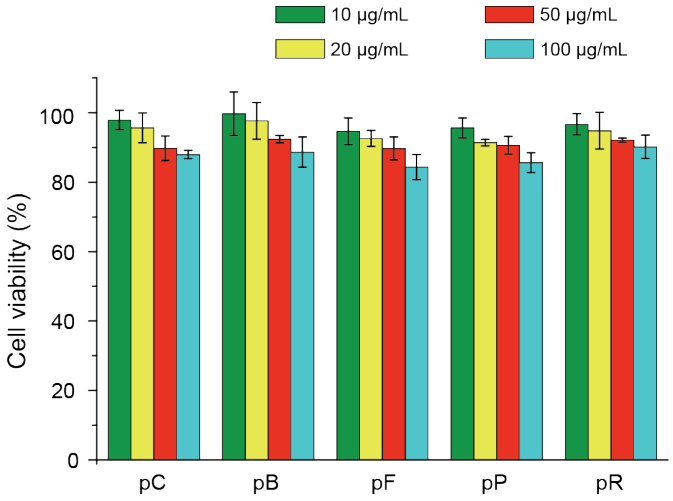

Fig. S9. MTT toxicity study of **pX**. The Y-axis shows % cell viability.

Protocol: HeLa cells were seeded on 96-well plates at 1×10^4 cells/well and cultured in serum-containing media for 24 h. The medium was replaced with fresh DMEM containing serum (100 µL/well), into which polymers were added at the final concentrations of 100, 50, 20, and 10 µg/mL, respectively. After incubation at 37°C for 4 h, the medium was changed to fresh serum-containing DMEM and cells were further cultured for 24 h before viability assessment by the MTT assay. Results were represented as percentage viability of control cells that did not receive polymers treatment.

Cell Uptake and Confocal Images

Protocol (live-cell imaging): HeLa cells cultured on coverslips in 6-well plate were incubated with polymers in DMEM (2 mL) at 15 μg polymer/well. Following incubation for 4h, cells were washed three times with PBS, and stained with Hoechst 33258 (2 μg/mL) before observation by confocal laser scanning microscopy (CLSM, LSM700, Zeiss, Germany).

Protocol (fixed-cell imaging): HeLa cells cultured on coverslips in 6-well plate were incubated with polymers in DMEM (2 mL) at 15 μg polymer/well. Following incubation for 4 h, cells were washed three times with PBS, fixed with 4% paraformaldehyde and stained with Hoechst 33258 (2 μg/mL) before observation by confocal laser scanning microscopy (CLSM, LSM700, Zeiss, Germany).

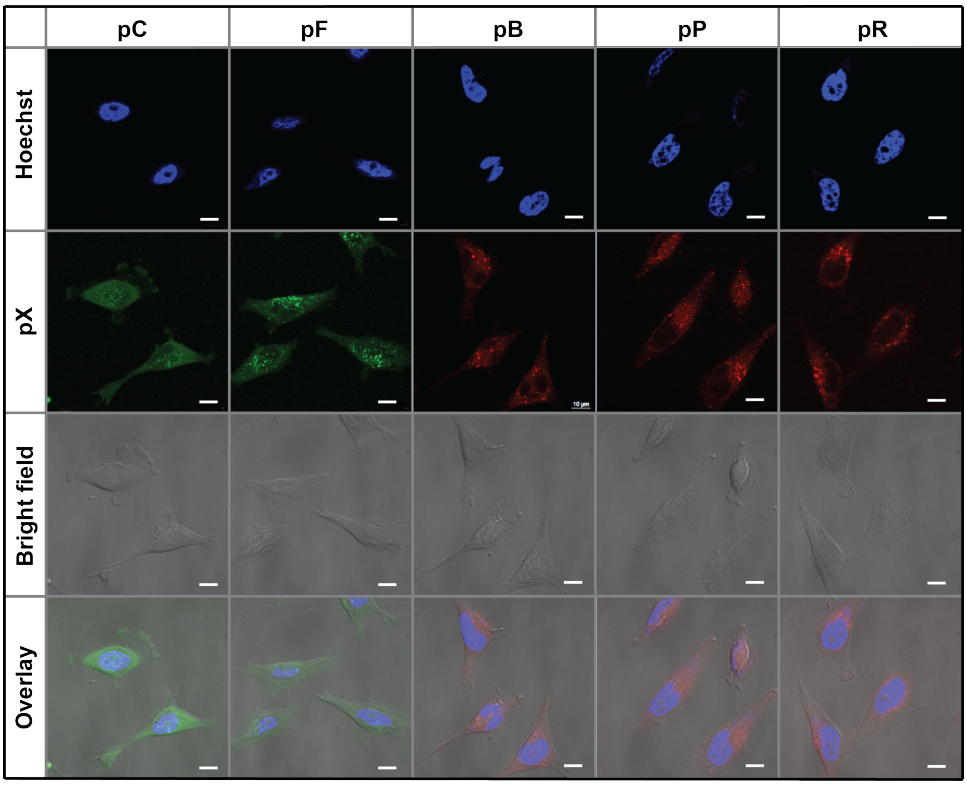

Fig. S10. Confocal microscopy images of live HeLa cells treated with **pX**. First row: blue channel images showing nucleus staining with Hoechst; second row: fluorescence from **pX**; third row: bright-field images; fourth row: overlay of nucleus and fluorescence from **pX**. (X = **C**, **F**, **B**, **P** and **R**); scale bar: 10 μm.

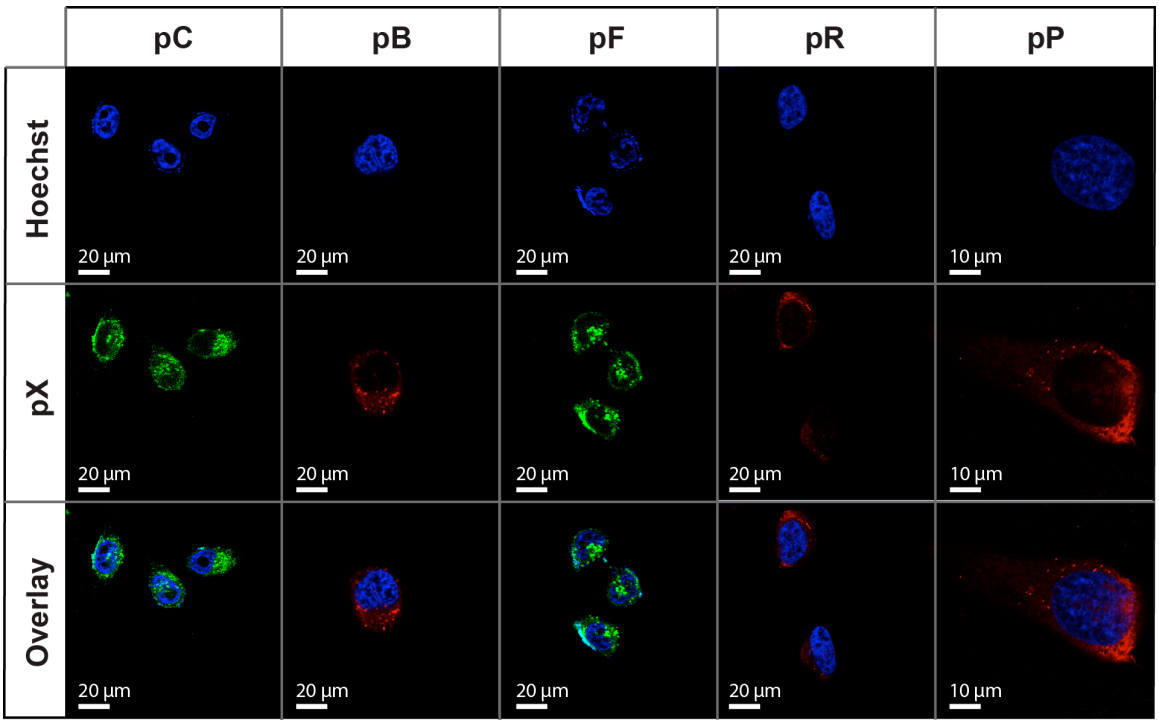

Fig. S11. Confocal microscopy images of fixed HeLa cells treated with **pX**. First row: blue channel images showing nucleus staining with Hoechst; second row: fluorescence from **pX**; third row: overlay of nucleus and fluorescence from **pX**. (X = **C**, **F**, **B**, **P** and **R**); scale bar: 10 µm.

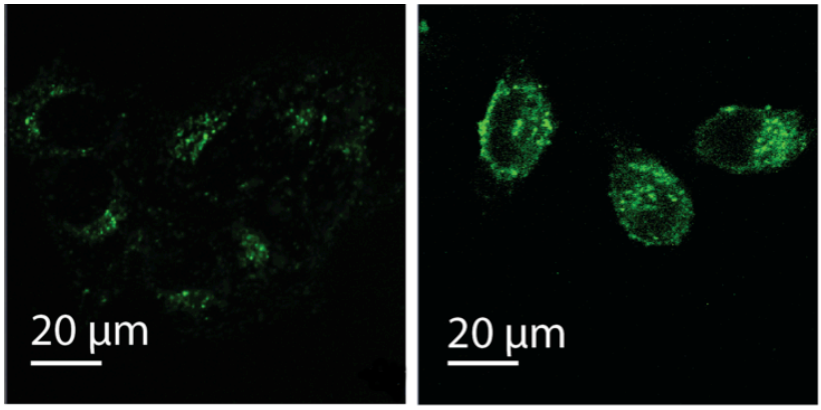

Fig. S12. Confocal microscopy images of HeLa cells treated with polymers. Left: non-dendronized organic nanoparticles[2] (5 µM, 6 h incubation, fixed cells); right: CDPs (95 nM, 4 h incubation, fixed cells).

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1. J. A. Love, J. P. Morgan, T. M. Trnka and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2002, **41**, 4035-4037.

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