Supporting Information for

Nucleobase-grafted Supramolecular Polymers for Tuning the Surface Properties

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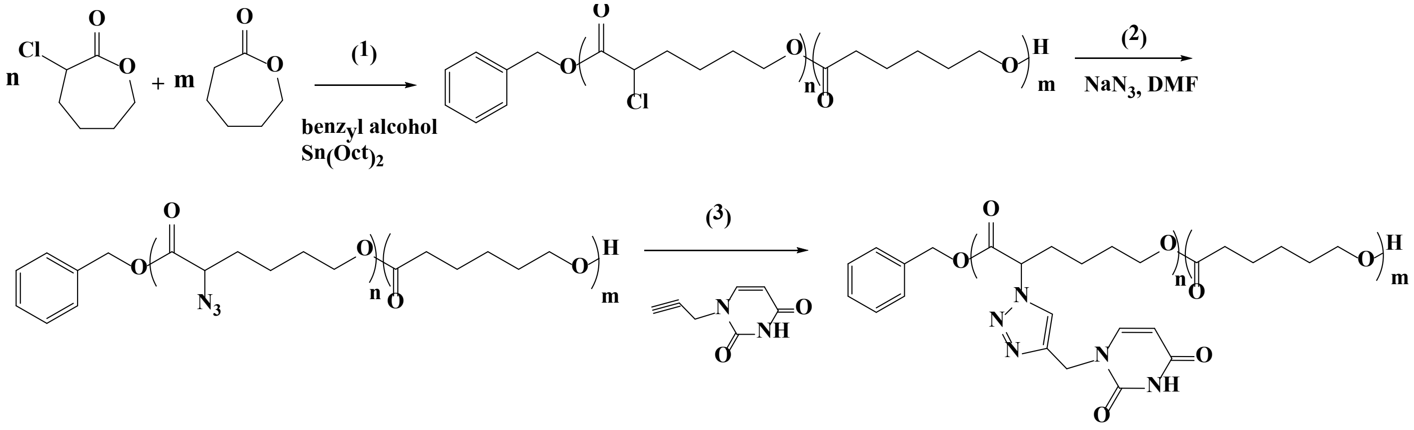
Experimental Section

Materials. *ε*-Caprolactone (*ε*-CL, 99.5 %, ACROS), dichloromethane (DCM, 99 % ACROS), and dimethyl formamide (DMF, 99 %, Fisher Chemical) were dried over calcium hydride (CaH_2, 95 %, ACROS) for 24 h and then distilled under reduced pressure prior to use. Uracil (U, 99 %, ACROS), tetrahydrofuran (THF, HPLC grade, TEDIA), acetonitrile (ACN, anhydrous, Aldrich), ethyl acetate (EtOAc, ACS reagent, Sigma-Aldrich), hexane (HPLC grade, Sigma-Aldrich), sodium azide (SHOWA, 98 %), propargyl bromide (Fluka, 80 % in Toluene), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, ACROS, 98 %), *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich), and 3-Chloroperbenzoic acid (*m*-CPBA, 77 %, Aldrich), benzyl alcohol (99 %, ACROS), 2-Chlorocyclohexane (98 %, ACROS), and sodium hydrosulfite ($Na_2S_2O_4$, 85 %, SHOWA), 2-(4-Hydroxyphenylazo)benzoic acid (HABA, 98 %, Aldrich) were all used as received. Copper(I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and then rinsed with absolute ethanol under a blanket of argon and dried under vacuum at 60 °C overnight. Tin(II) 2-ethylhexanoate (~95%) was purchased from Sigma-Aldrich and azeotropically distilled from toluene three times prior to use. 2,6-Diaminopyridine was purchased from Aldrich and recrystallized from chloroform.

Syntheses and characterizations of nucleobase-functional polycaprolactone. Nucleobase-functional polycaprolactone was synthesized in three steps as shown in Scheme 1. First, the ring-opening copolymerization of *α*Cl*ε*CL and *ε*CL was carried out using tin octoate as transesterification catalyst. This metal catalyst is one of the most common catalysts for the polymerization of lactones and lactides. The pendent chlorides of poly(*α*Cl*ε*CL-*co*-*ε*CL) was then converted into azides by reacting with excess sodium azide in DMF at 60 °C overnight. The IR spectrum shows a new absorption at 2106 cm^{-1} characteristic of the azide in Figure S1. ^{1}H NMR confirms that the resonance peak at 4.25 ppm for the CHCl protons disappears completely and a new peak at 3.8 ppm corresponding CH-N_3 protons appears (Figure S2). Finally, the click reaction was performed first by introduction of the azide-functional prepolymer as a concentrated solution in DMF to a vigorously stirring solution of poly(*α*N_3*ε*CL-*co*-*ε*CL) at 60 °C, followed by the addition of CuBr and PMDETA. Uracil-grafted random copolymer with 1,2,3-triazole linkages were passed through neutral aluminum oxide, followed by precipitation into methanol. Successful incorporation of side-chain uracil moieties was confirmed using ^{1}H NMR and FT-IR spectroscopy. Upon triazole formation with propargyl uracil, the azide stretch at 2106 cm^{-1} was completely disappeared, direct evidence of complete functionalization of all the azide sites of the poly(*α*N_3*ε*CL-*co*-*ε*CL). Fives new resonances characteristic peaks of the poly(*ε*CL-*g*-Uracil) were observed in ^{1}H NMR spectrum at 11.28 ppm (o, −CO−N*H*−CO−), 8.19 (k, −N−C*H*−), 7.71(m, −N−C*H*−), 5.57 (n, −CO−C*H*−), and 4.95 (l, −N−CH_2−). Molecular weights and molecular weight distributions of these nucleobase-functional polycaprolactones are listed in Table S1. In addition, number of repeats units for *α*Cl*ε*CL and *ε*CL segments are also calculated from the ^{1}H NMR integration of the signal at 4.2–4.3 ppm (poly(*α*Cl*ε*CL-*co*-*ε*CL), 1H per repeating unit, –CO–Cl*H*–) and 4.1–4.2 ppm (poly(*α*Cl*ε*CL-*co*-*ε*CL), 2H per repeating unit, –COO–CH_2–). In terms of nomenclature, the descriptor U30-PCL, for example, represents a copolymer containing 30 mol % of uracil. Table S1 summarizes the monomer feed ratios and the compositions, molecular weights, glass transition temperatures, and thermal decomposition temperatures of the synthesized copolymers.

Scheme 1. Synthetic route of the poly(*ε*CL-*g*-Uracil) copolymer. Reagents and conditions: (1) benzyl alcohol, Sn(Oct)$_2$, toluene, 120 °C; (2) NaN$_3$, DMF, 60 °C; (3) alkynyl nucleobase, CuBr, PMDETA, DMF, 60 °C.



Synthesis of N^1-(Prop-2-yne-1-yl)uracil This compound was prepared according to the literature procedure.[1] (yield = 78 %). ^{1}H NMR (500 MHz, DMSO, δ): 11.35 (br s, 1H, –N*H*–), 7.68 (d, *J* = 6.0 Hz, 1H, –N–C*H*–), 5.61 (d, *J* = 6.0 Hz, 1H, –CO–C*H*–), 4.49 (d, *J* = 3.0 Hz, 2H, –CH_2–), 3.37 (t, *J* = 3.0 Hz, 1H, –C≡C*H*).

Synthesis of *α*-Chloro-*ε*-caprolactone[2] 2-chlorocyclohexane (10 g, 75 mmol) and *m*-CPBA (20 g, 81 mmol) were dissolved in 300 mL dichloromethane and stirred for 48 h at 25 °C. The reaction flask was then cooled to 0 °C for precipitation of *m*-chlorobenzoic acid. The solution was filtered and washed in succession with $Na_2S_2O_4$ and saturated $NaHCO_3$ aqueous solution for three times, respectively. After being dried over $MgSO_4$, the organic phase was concentrated under reduced pressure. The residue was distilled under reduced pressure, the *α*-chloro-*ε*-caprolactone (bp = 75–77 °C at 0.1 mmHg) was collected. Yield: 84 %. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.6–4.75 (1H, m, –C*H*ClCO–), 4.20–4.40 (1H, m, –CH_2O–), 1.60–2.10 (6H, m, –CH_2CH_2CH_2–).

Synthesis of Poly(αClεCL-*co*-εCL) Copolymer Random copolymerization was carried out at 120 °C in toluene in a dried glass reactor. 3 g (20 mmol) of *α*-chloro-ε-caprolactone, 7 g (61 mmol) ε-caprolactone, 20 mL toluene, $Sn(Oct)_2$ (0.743 g, 1.83 mmol), and 23 μL benzyl alcohol (1 mmol) were sequentially added to the reactor through a rubber septum with a syringe. After 24 h of polymerization, an excess acetic acid (0.2 mL acetic acid/0.8 ml toluene) was added, and the copolymer was recovered by precipitation in cold methanol. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.2–4.3 (poly(*α*ClεCL-*co*-εCL), 1H per repeating unit, –C=O–Cl*H*–), 4.1–4.2 (poly(*α*ClεCL-*co*-εCL), 2H per repeating unit, –COO–CH_2–), 3.9–4.1 (polycaprolactone, 2H per repeating unit, –COOCH_2–), 2.1–2.4 (polycaprolactone, 2H per repeating unit, –CO=C$H_2$$CH_2$–), 1.8–2.0 (poly(*α*ClεCL-*co*-εCL), 2H per repeating unit, –CClH–CH_2–), 1.2–1.6 (polycaprolactone and poly(αClεCL-*co*-εCL), 10 H per repeating unit, –$COCH_2$CH_2CH_2CH_2– and –$COCH_2$CH_2CH_2–).

Synthesis of the Poly(*α*AzεCL-*co*-εCL) Copolymer Poly(*α*ClεCL-*co*-εCL (2g, 0.067 mmol) was dissolved in 10 mL of DMF, and then NaN_3 (0.044g, 0.67 mmol) was added to the solution. The resulting solution was allowed to stir at 60 °C overnight and precipitated in excess methanol. After filtration, the polymer was dried for 24 h in a vacuum oven at 25 °C (yield = 83.5 %). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.1–4.2 (poly(*α*ClεCL-*co*-εCL), 2H per repeating unit, –COO–CH_2–), 3.9–4.1 (polycaprolactone, 2H per repeating unit, –COOCH_2–), 3.7–3.8 (poly(*α*AzεCL-*co*-εCL), 2H per repeating unit, $–COC\mathit{H}–CH_2–$), 2.1–2.4 (polycaprolactone, 2H per repeating unit, $–CO{=}C\mathit{H}_2CH_2–$), 1.7–1.8 (poly(*α*Az*ε*CL-*co*-*ε*CL), 2H per repeating unit, $–CNH–C\mathit{H}_2–$), 1.2–1.6 (polycaprolactone and poly(αAzεCL-*co*-εCL), 10 H per repeating unit, $–COCH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2–$ and $–COCH_2C\mathit{H}_2C\mathit{H}_2–$).

Synthesis of Poly(εCL-*g*-Uracil) Poly(*α*Az*ε*CL-*co*-*ε*CL) (3 g, 0.25 mmol), N^1-(Prop-2-yne-1-yl)uracil (0.94 g, 6.3 mmol), and 50 µL PDMETA were dissolved in 30 mL of DMF in a dried glass reactor. Then, the reactor was subjected to two freeze-pump-thaw cycles, N_2 was introduced into the reactor when the mixture was frozen, and Cu(I)Br (30 mg) was quickly added under N_2 atmosphere. Finally the reactor was stirred at 60 °C for 24 h. The mixture was diluted with DMF and passed through a short column of neutral aluminum oxide. The solution was distilled under reduced pressure and purified by dialysis in DMF to completely remove the excess N^1-(Prop-2-yne-1-yl)uracil. Drying under vacuum gave pure nucleobase-grafted polycaprolactone. Yield: 71 %. ^{1}H NMR (500 MHz, DMSO, δ): 11.2–11.4 (1H, $–CO–N\mathit{H}–CO–$), 8.0–8.2 (1H, $–N–C\mathit{H}–$), 7.56–7.8 (1H, $–N–C\mathit{H}–$), 5.5–5.7 (1H, $–CO–C\mathit{H}–$). 5.0–5.1 ($–NC\mathit{H}_2–$).

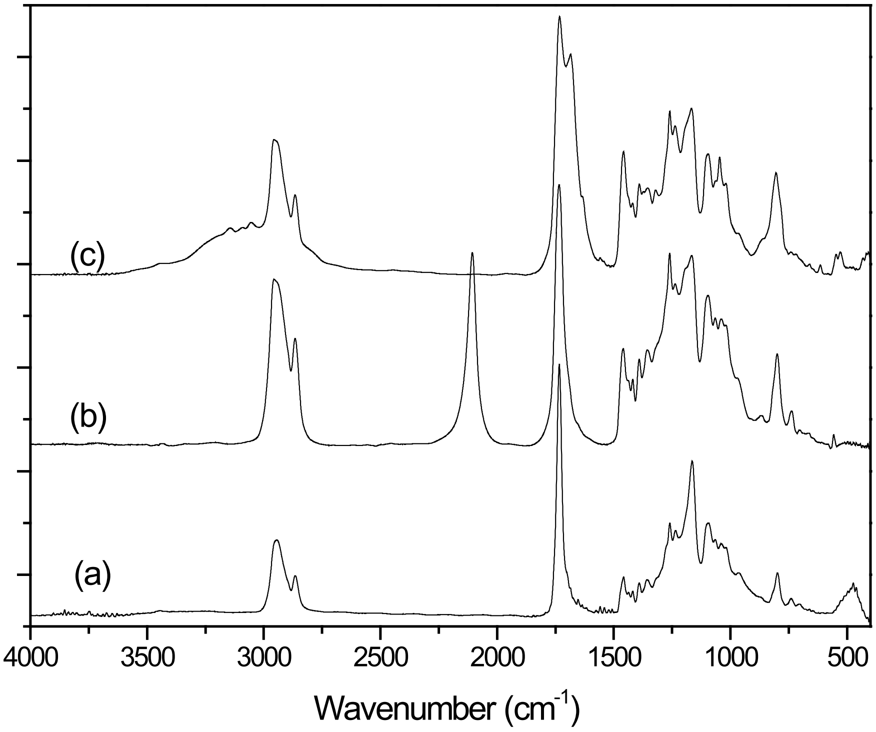


Figure S1. IR spectra of (a) poly(*α*Cl*ε*CL-*co*-εCL) (b) poly(*α*Az*ε*CL-*co*-*ε*CL) (c) poly(*ε*CL-*g*-Uracil).

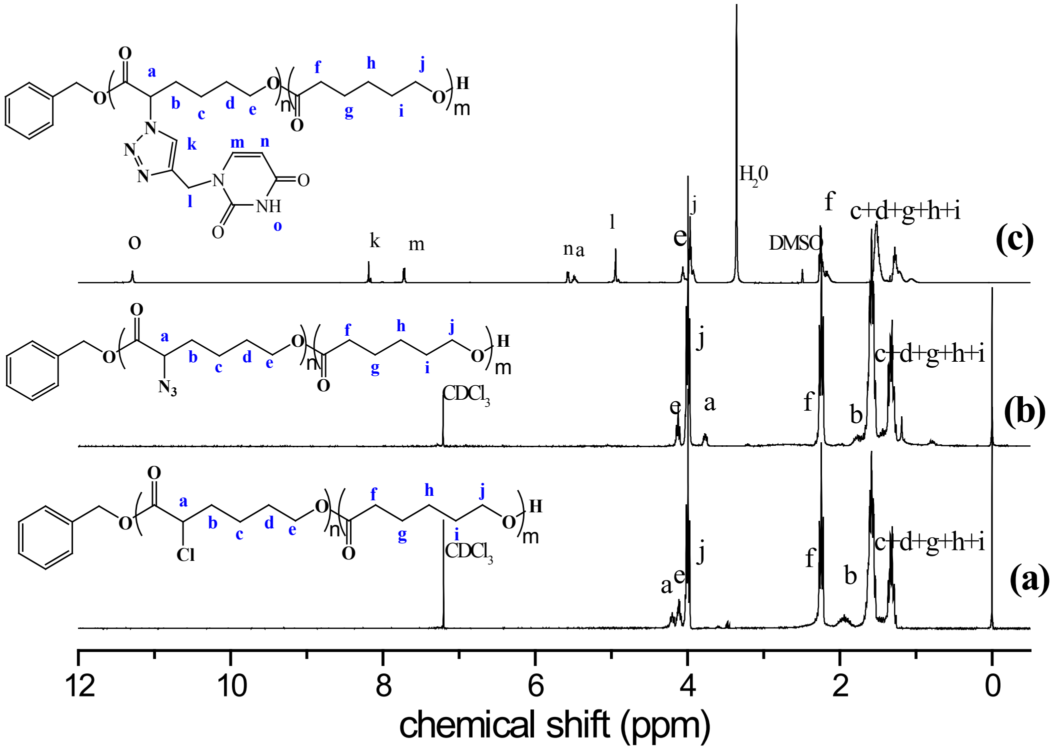


Figure S2. ^{1}H NMR spectra of (a) poly(*α*Cl*ε*CL-*co*-*ε*CL) (b) poly(*α*Az*ε*CL-*co*-*ε*CL) (c) poly(*ε*CL-*g*-Uracil).

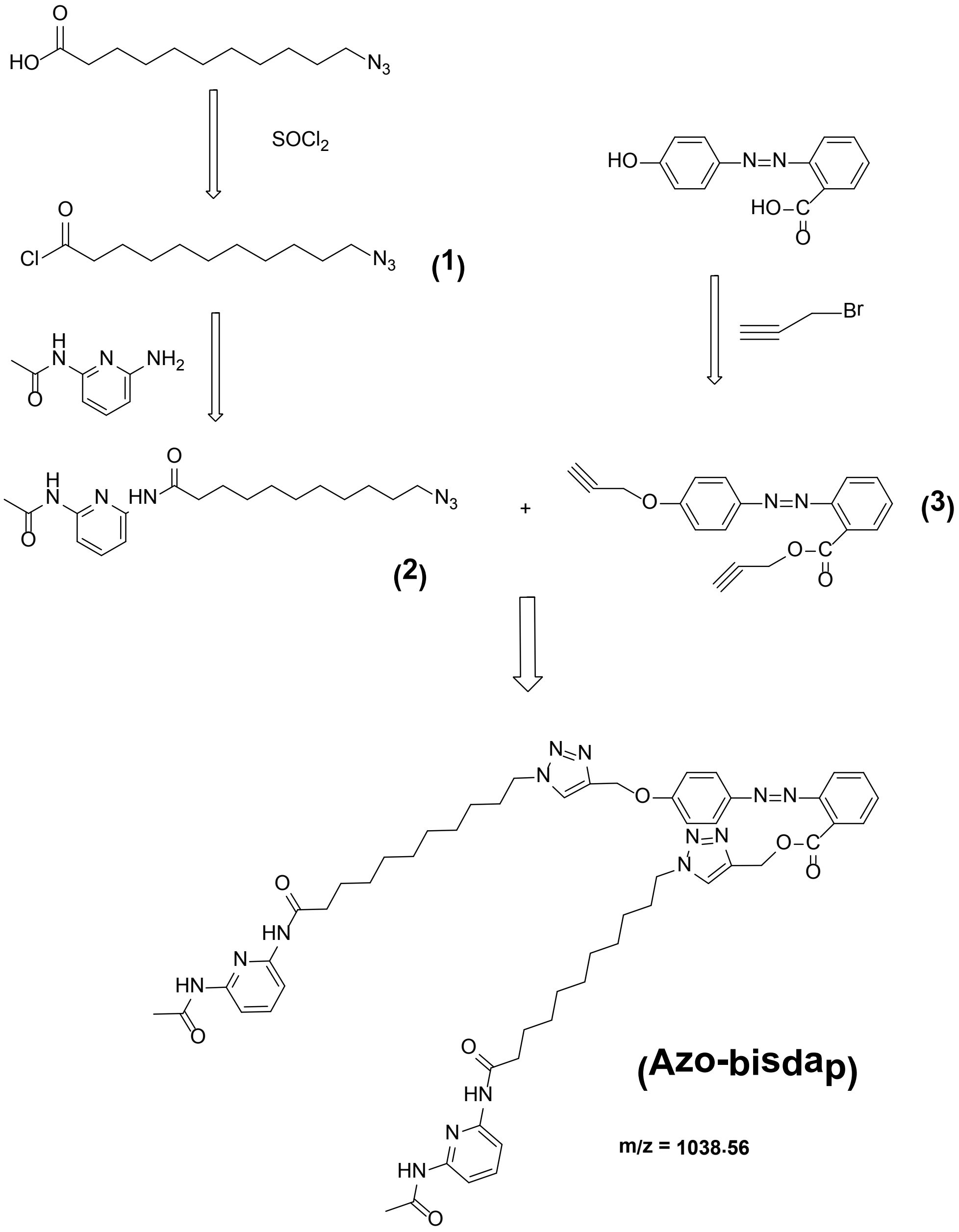
Table S1. Properties of the poly(*ε*CL-*g*-Uracil) copolymers.

Entry	Poly(nucleobase-*co*-*ε*CL)			Thermal properties	
	*α*Cl*ε*CL/*ε*CL[a]	M_n GPC[b]	M_w/M_n[b]	T_d,[c] °C	T_g,[d] °C
U30-PCL	32/68	37598	4.9	277	15.2
Cl30-PCL	29/71	17852	1.5	320	-50.8
Az30-PCL	29/71	18663	1.5	317	-59.4

[a] Obtained from integration of the signal at 4.2–4.3 ppm (poly(*α*Cl*ε*CL-*co*-*ε*CL), 1H per repeating unit, –CO–Cl*H*–) and 4.1–4.2 ppm (poly(*α*Cl*ε*CL-*co*-*ε*CL), 2H per repeating unit, –COO–CH_2–).

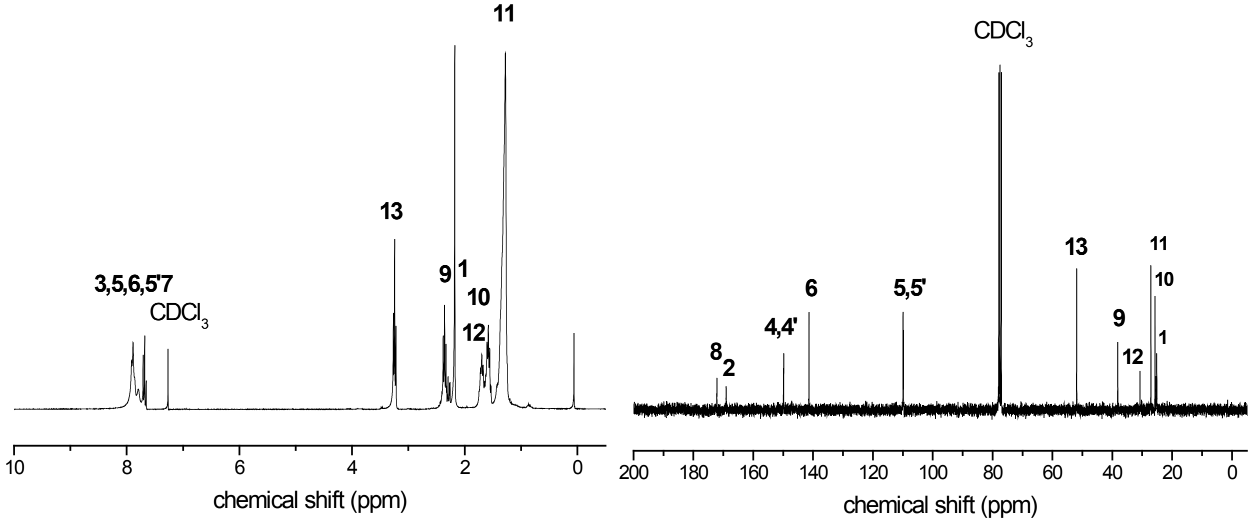
[b] Obtained from GPC trace (eluent: DMF; 0.6 mL/min; PS-standard calibration): M_n, number-average molecular mass with the highest RI intensity; PDI, molecular mass distribution.

[c] Obtained from TGA thermograms recorded at heating rate of 20 °C/min.

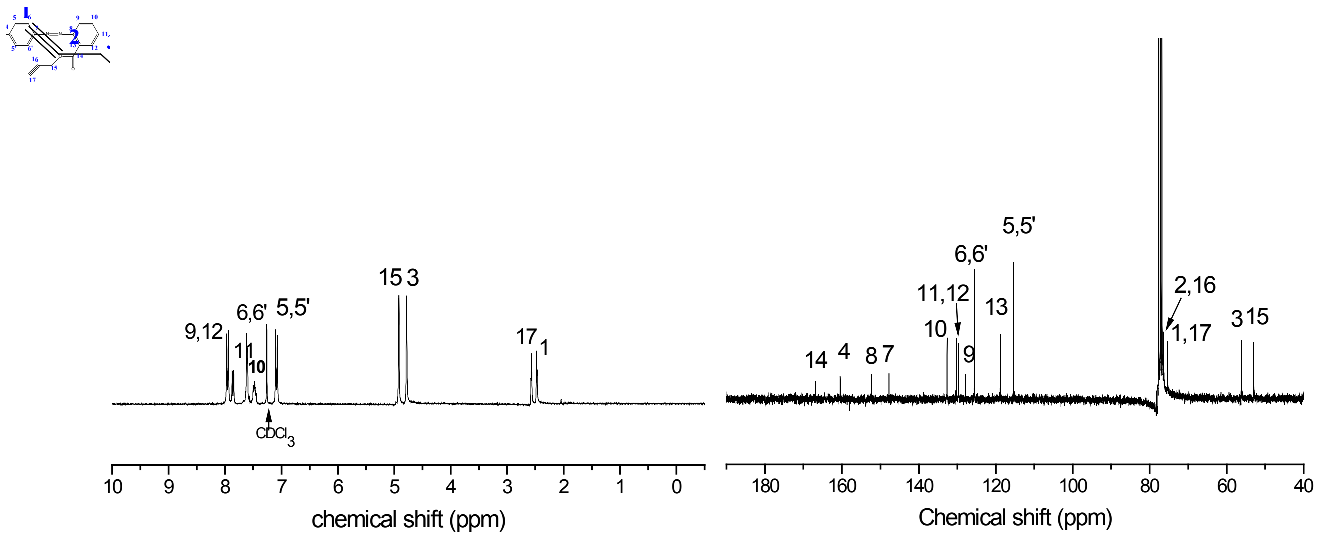


Scheme S2. Synthesis route for Azo-bisdap.

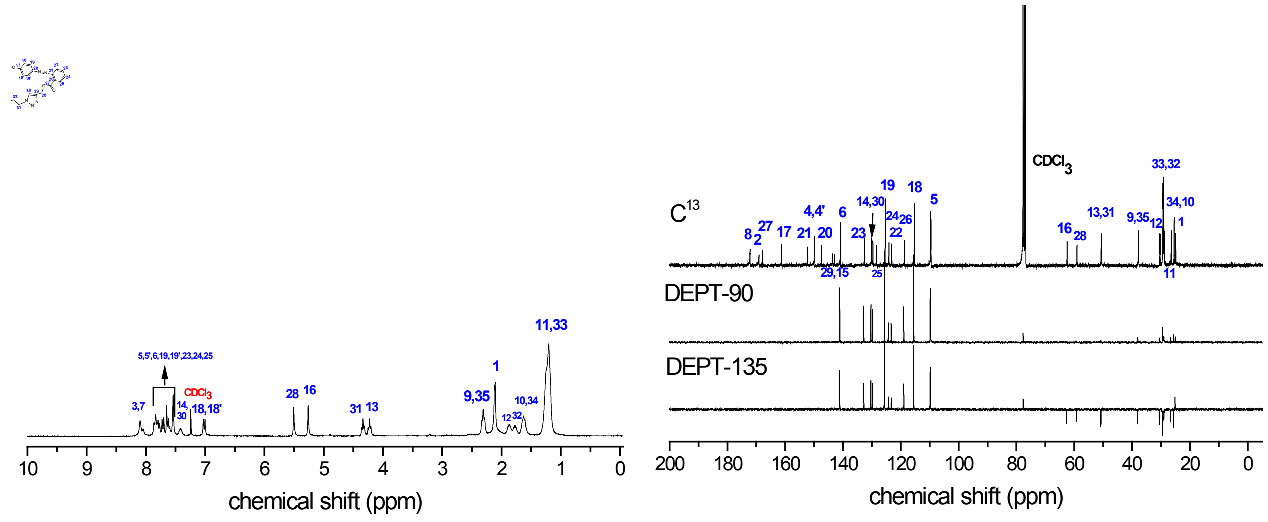
N-(6-acetamidopyridin-2-yl)-11-azidoundecanamide [2]. 11-azidoundecanoic acid was synthesis from commercial 11-bromoundecanoic acid according to the procedures described previously.[3] 11-azidoundecanoic acid (1.00 g, 4.4 mmol, 100 mol %) was first treated with an excess of thionyl chloride (5 mL, 68.0 mmol) and reflux for 6 h, then 11-azidoundecanoyl chloride **[1]** (1.1 g) was obtained by evaporating the thionyl chloride and dried under vacuum. N-(6-aminopyridin-2-yl) acetamide (1 g, 6.6 mmol, 150 mol %) and triethylamine (0.66 g, 6.6 mmol, 150 mol %) were dissolved in dry THF (40 mL) cooled to 0 °C in an ice bath. A solution of 11-azidoundecanoyl chloride in dry THF (10 mL) was added dropwise through syringe over a period of 1 h and the reaction mixture was stirred at 0 °C for 3 h and then maintained at room temperature for an addition 12 h. After evaporating the solvent, the residue was subjected to chromatography (SiO_2; 30 % *n*-hexane/ethyl acetate) and then the product was dried under vacuum, yield: 91 %; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.28 (H11), 1.60 (H10), 1.69 (H12), 2.19 (H1), 2.36 (H9), 3.24 (H13), 7.63-8.1 (H3,H5,H6,H5',H7) ppm. ^{13}C NMR ($CDCl_3$): 24.84 (C1), 25.5 (C10), 26.8 (C11), 30.6 (C12), 38.3 (C9), 51.5 (C13), 110.1 (C5, C5'), 141.7 (C6), 149.6 (C4, C4'), 168.8 (C2), 171.6 (C8) ppm.



Prop-2-ynyl 2-((4-(prop-2-ynyloxy)phenyl)diazenyl)benzoate [3]. A solution of HABA (5 g, 20.6 mmol), propargyl bromide (7.31 g, 61.8 mmol), and K_2CO_3 (8.55 g, 61.8 mmol) in dry acetone (180 mL), was refluxed under a nitrogen atmosphere for 36 h. The reaction was cooled and concentrated in vacuum, and the residue was partition between ethyl acetate (200 mL) and water (100 mL). The organic extract was dried over $MgSO_4$ and concentrated in vacuum. Yield: 81 %. ^{1}H NMR ($CDCl_3$): δ = 2.46 (H1), 2.56 (H17), 4.76 (H3), 4.92 (H15), 7.08 (H5, H5'), 7.47 (H10), 7.59 (H6, H6'), 7.84 (H11), 7.94 (H9, H12) ppm. ^{13}C NMR ($CDCl_3$): δ = 53.14 (C15), 56.28 (C3), 75.49 (C1, C17), 76.37 (C2, C16), 115.17 (C5, C5'), 118.74(C13), 125.59 (C6, C6'), 127.76 (C9), 129.58 (C12), 130.33 (C11), 132.76 (C10), 147.72 (C7), 152.26 (C8), 160.40 (C4), 166.93 (C14).



Synthesis of (1-(11-(6-acetamidopyridin-2-ylamino)-11-oxoundecyl)-1H-1,2,3,-triazol-4-yl)methyl 2-((4-((1-(11-(6-acetamidonpyridin-2-ylamino)-11-oxoundecyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)diazenyl)benzoate (Azo-bisdap). N-(6-acetamidopyridin-2-yl)-11-azidoundecanamide **[2]** (1 g, 2.78 mmol), prop-2-ynyl 2-((4-(prop-2-ynyloxy)phenyl)diazenyl)benzoate **[3]** (1.06 g, 3.34 mmol), and 50 µL PDMETA were dissolved in 30 mL of THF in a dried glass reactor. Then, the reactor was subjected to two freeze-pump-thaw cycles, N_2 was introduced into the reactor when the mixture was frozen, and Cu(I)Br (30 mg) was quickly added under N_2 atmosphere. Finally the reactor was stirred at 50 °C for 24 h. The mixture was diluted with THF and passed through a short column of neutral aluminum oxide. The solution was distilled under reduced pressure and precipitated into ethyl ether to completely remove the excess monomer **3**. The product was obtained by filtration and dried under vacuum. Yield: 92 %. ^{1}H NMR ($CDCl_3$): δ = 1.19 (H11, H33), 1.62 (H10, H34), 1.76 (H32), 1.86 (H12), 2.10 (H1), 2.31 (H9, H35), 4.22 (H13), 4.33 (H31), 5.26 (H16), 5.49 (H28), 7.01 (H18, H18’), 7.41 (H14, H30), 7.52-7.85 (5,5',6,19,19',23,24,25), 8.05-8.1 (H3, H7) ppm. ^{13}C NMR ($CDCl_3$): ($CDCl_3$): δ = 24.84 (C1), 25.5 (C10, C34), 26.8 (C11), 29.18 (C32, C33), 30.6 (C12) 37.88 (C9, C35), 50.69 (C13, C31), 59.07 (C28), 62.67 (C16), 109.62 (C5), 115.30 (C18), 118.76 (C26), 123.11 (C22), 124.12 (C24), 125.54 (C19), 128.47 (C25), 129.67 (C30), 130.24 (C14), 132.59 (C23), 140.93 (C6), 143.06 (C15), 143.63 (C29), 147.41 (C20), 149.75 (C4,C4'), 152.19 (C21), 161.15 (C17), 167.94 (C27), 169.18 (C2), 172.19 (C8) ppm.



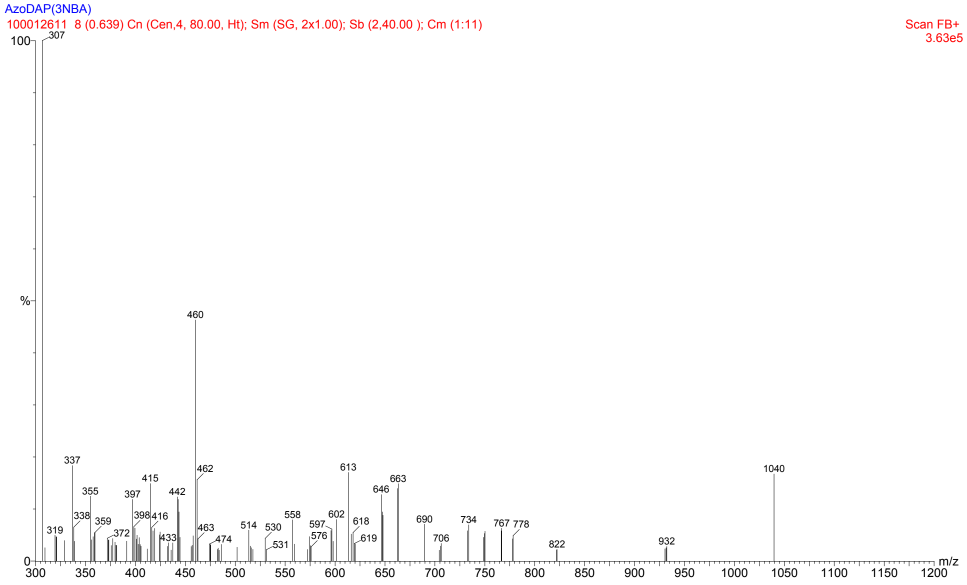


Figure S3. Structural identification of a mixture of Azo-bisdap using mass spectrometry.

Characterizations. Analytical TLC was performed on commercial Merck Plates coated with silica gel GF254 (0.24 mm thick). Silica gel for flash chromatography was from Merck Kieselgel 60 (230-400 mesh, ASTM). ^{1}H NMR spectra were recorded in $CDCl_3$ and d_6-DMSO solution using a Varian Inova 500 MHz spectrometer equipped with a 9.395 T Bruker magnet and operated at 500 MHz. Thermal analysis was carried out using a DSC instrument (TA Instruments Q-20) under an atmosphere of dry N_2.

Samples were weighed (3-5 mg) and sealed in an aluminum pan, which was scanned from -90 to 160 °C at a scan rate of 20 °C/min. AFM micrographs were recorded at 25 °C in air using a Digital Instrument Multimode Nanoscope IV operating in the tapping regime mode using silicon cantilever tips (PPP-NCH-50, 204-497 kHz, 10-130 N/m). Sample irradiation was carried out with a UVP CL-1000 UV cross-linker (UVP, Cambridge, UK) at 365 nm. The films were analyzed with a UV-Vis spectrometer (HP 8453 diode-array spectrophotometer) in the initial state and after each irradiation step with UV or visible light. The spectra background was corrected by subtraction of the spectrum of the quartz substrate. The static water contact angle measurements were carried out using a VCA Optima XE Dynamic Contact Angle Analyzer (AST Products Inc., Billerica, MA) at ambient condition. The image was recorded by a CCD camera immediately after the water drop was deposited onto the film surface. At least five measurements were averaged for each sample. DLS measurements were performed in $CDCl_3$ solution using a Malvern Zetasizer Nano S90 at a wavelength of 532 nm, at angular range of 90 ° and temperature at 25 °C. The measured intensity correlation functions were subjected to CONTIN analysis. Apparent hydrodynamic diameters of aggregations were calculated according to the Stokes-Einstein equation. The cumulant and CONTIN methods are valid for rigid polymers.

Blend Preparation. Blends of the copolymers poly(*ε*CL-*g*-Uracil) and Azo-bisdap were prepared through solution blending. DCM solutions containing 5 wt % of the polymer mixture were stirred for 6-8 h; the solvent was then left to evaporate slowly at room temperature for 24 h. The resulting blend films were dried at 50 °C for 1 day.

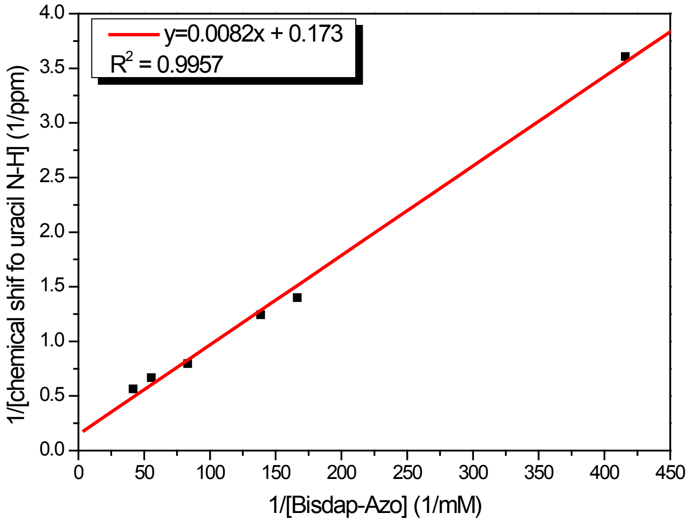


Figure S4. Benesi-Hildebrand plots for the U-PCL/Azo-bisdap association in $CDCl_3$ at 25 ºC.

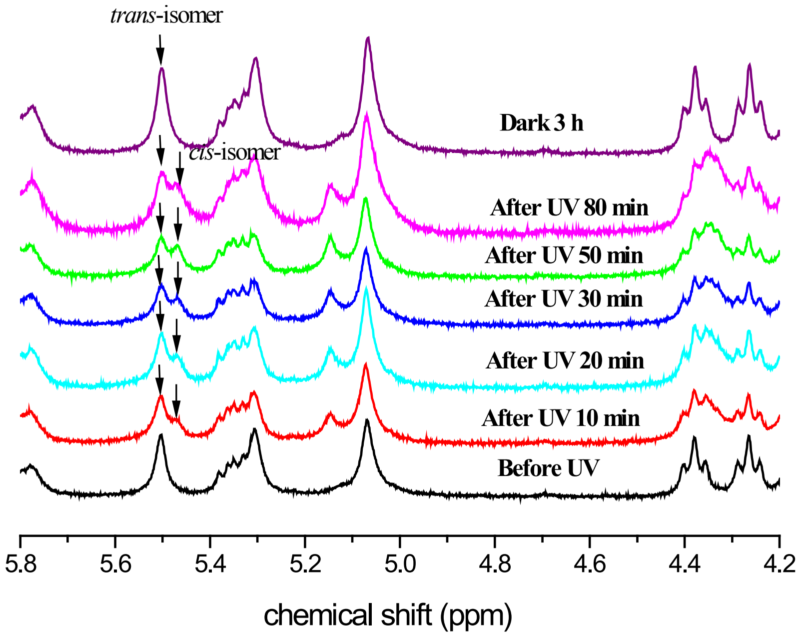


Figure S5. ^1H NMR spectra of the methylene protons of Azo-bisdap after 365 nm irradiation. Conditions: $CDCl_3$, 24 mM, 500 MHz, 22 ºC.

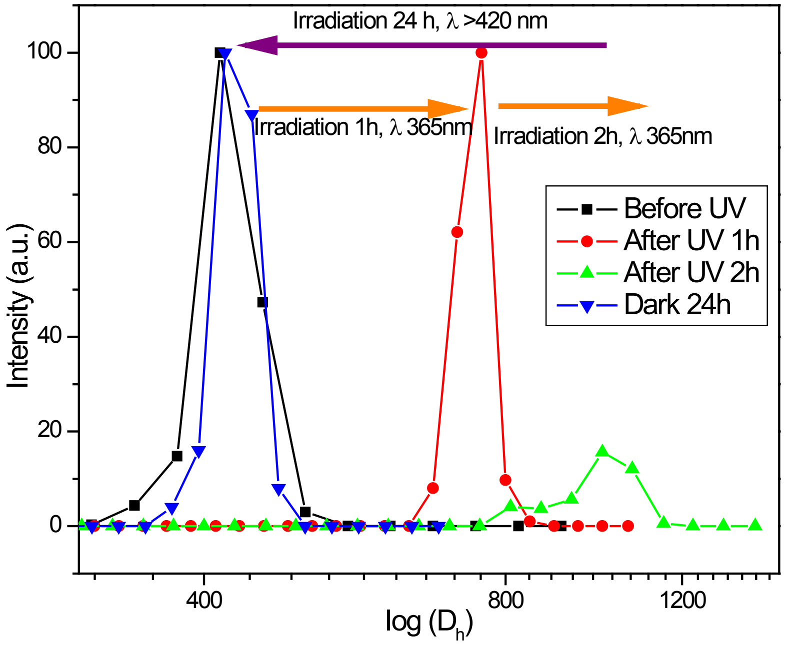


Figure S6. The sizes of aggregated 3/1 U-PCL/Azo-bisdap irradiated with 365 nm UV and visible light measured by DLS (Concentration of each sample: 50 mg/L in CDCl3).

According to Figure S6, we attributed this larger particle of the 3/1 U-PCL/Azo-bisdap blend, having D_h values ranging from around 320 nm to 560 nm, to the large aggregates formed through complementary uracil-diamidopyridine (U-DAP) interactions. After 2 h of UV exposure, the DLS analysis shows substantial changes in size and distribution of the aggregates. The appearance of a broad distribution peak with an average particle size of 1080 nm comes from the diasociation of U-PCL with Azo-bisdap and causes disappearance of U-PCL/Azo-bisdap peak. More interestingly, the D_h is switched back to its "original" state under visible-light irradiation (or in the dark), indicating the *reformation* of U-DAP pairs by induced sepcific self-assembly.

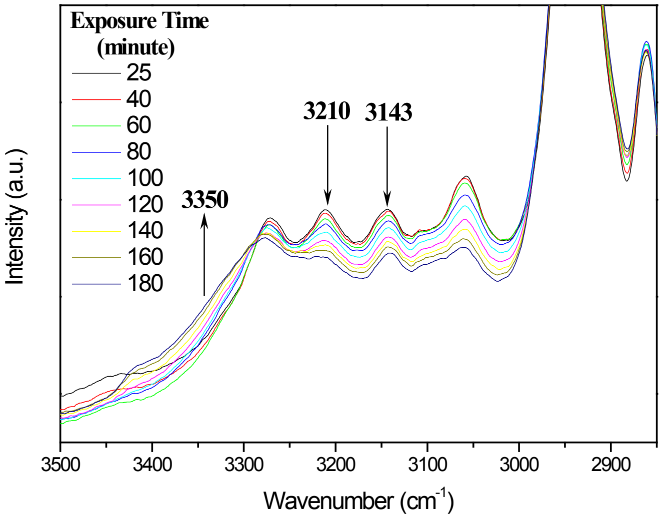


Figure S7. FTIR spectra recorded at room temperature, during the UV exposure period for 3/1 U-PCL/Azo-bisdap in the bulk state.

Reference:

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