Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Patterned Polymer Brushes via Electrodeposited ATRP, ROMP, and RAFT Initiators on Colloidal Template Arrays

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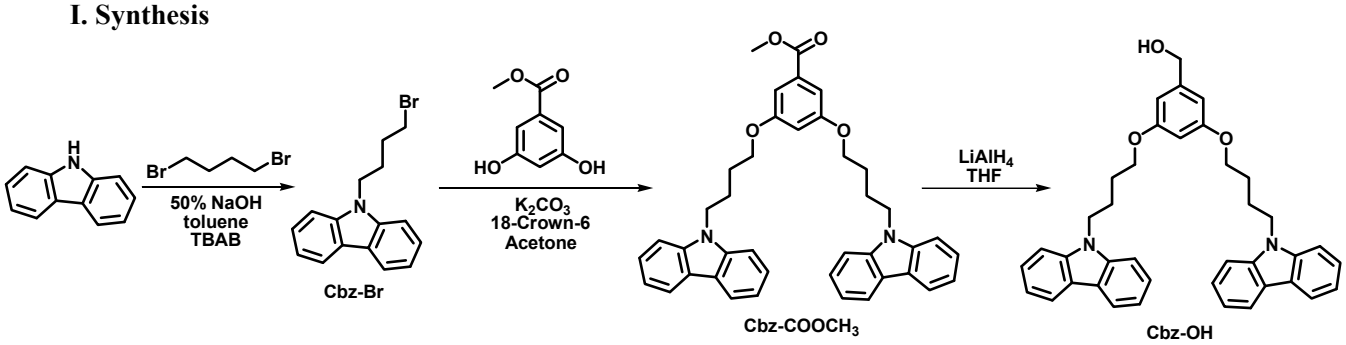
I. Synthesis



Scheme S1. Synthesis of methyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl alcohol [Cbz-OH].

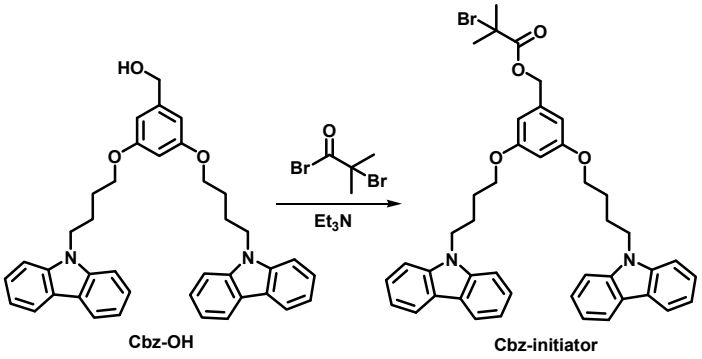
Synthesis of 9-(4-bromobutyl)-9H-carbazole [Cbz-Br]. The synthesis of Cbz-Br was done according to literature.[1] The synthesis of Cbz-Br was done by combining carbazole (20.64 g, 0.1236 mol), 1,4 dibromobutane (132 mL, 1.095 mol), tetrabutylammonium bromide (4 g, 0.0124 mol), toluene (200 mL), and 50% NaOH (200 mL). The resulting mixture was stirred at 45 ^{o}C for 3 hrs and continuously stirred at room temperature overnight. The clear, yellow organic layer was then washed with 100-mL portions H_2O followed by 100 mL brine solution. This was then dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporator and the excess 1,4-dibromobutane via vacuum distillation. After which, the

resulting cream-like solid residue was slowly dissolved in small portions of CH_2Cl_2. The yellow-brown solution was *reprecipitated* using ethanol. *The resulting white solid residue was dried under vacuum overnight to give 33.4 g (89%) of the product.* ^{1}H NMR (δ ppm in $CDCl_3$): 8.12 (d, 2H), 7.22-7.48 (m, 6H), 4.36 (t, 2H), 3.38 (t, 2H), 1.95-2.07 (m, 4H).

Synthesis of methyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzoate [Cbz-COOCH$_3$]. The synthesis of Cbz-$COOH_3$ was done according to literature.[1] The synthesis of compound Cbz-$COOCH_3$ was done by combining Cbz-Br (27.93 g, 0.0923 mol), methyl-3,5-dihydroxybenzoate (6.49 g, 0.0386 mol), and 18-crown-6 (2.416 g) in acetone. To the resulting yellow solution mixture was added K_2CO_3 (29.46 g) and this was left at reflux for 3 days. The solvent was then removed using a rotary evaporator. Water was added to the cream solid residue and the desired compound extracted with dichloromethane. The organic layer was subjected to rotary evaporation until 20-25 mL was left just to dissolve the solid residue. To this was added ethyl acetate to precipitate out the desired white solid compound *in 70 % yield*. ^{1}H NMR (δ ppm in $CDCl_3$): ^{1}H NMR (δ ppm in $CDCl_3$): 8.20 (d, 4H), 7.49-7.12 (m, 16H), 6.54 (s, 1H), 4.40 (t, 4H), 3.95 (t, 4H), 3.88 (s,3H) 2.11-2.04 (m, 4H), 1.87-1.82 (m, 4H).

Synthesis of methyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl alcohol [Cbz-OH]. The synthesis of Cbz-OH was done according to literature.[1] The synthesis of compound Cbz-OH was carried out by first dissolving Cbz-$COOCH_3$ (10.5 g, 0.01719 mol) in dry THF. Into a 3-necked flask flowed with nitrogen was placed 100 mL THF and this was cooled in an ice bath. Approximately 1 g $LiAlH_4$ was put into the flask and the Cbz-$COOCH_3$ solution added dropwise through a dropping funnel. The resulting mixture was then stirred overnight. After which, the reaction was quenched by adding water until all $LiAlH_4$ was consumed. This was then acidified using concentrated HCl and extracted with dichloromethane. The organic layer was further washed with water for several times and then dried with Na_2SO_4. The dicholoromethane was evaporated using a rotary evaporator and the desired white solid compound was further dried under vacuum 90 % yield. ^{1}H NMR (δ ppm in $CDCl_3$): 8.09 5 (d, 4H, J = 7.5), 7.47-7.18 (m,

12H), 6.43 (s, 2H), 6.27 (s, 1H), 4.57 (d, 2H, *J* = 5.7), 4.38 (t, 4H, *J* = 6.9), 3.90 (t, 4H, *J* = 5.9), 2.09-2.01 (m, 4H), 1.84-1.79 (m, 4H).



Scheme S2. Synthesis of 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl 2-bromo-2-methylpropanoate (Cbz-Initiator).

Synthesis of 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl 2-bromo-2-methylpropanoate [Cbz-initiator]. In a round bottom flask both Cbz-OH (*338* mg, 0.58 mmol) and Et_3N (58.4 mg, 0.58 mmol) were added along with 50 ml of dry THF. A solution of 2-bromoisobutyryl bromide (*133* mg, 0.58 mmol) in 10 ml dry THF was added dropwise to the mixture under constant stirring. The reaction was allowed to proceed overnight. The reaction mixture was then filtered to remove the white solid byproduct. The organic phase was extracted 3 times with H_2O and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product mixture was first then purified by column chromatography on silica gel with dichloromethane:hexane (2:1, v/v). The solvent was removed by rotary evaporation to yield Cbz-initiator as a white solid (0.36 g, 86%). ^{1}H NMR (δ ppm in $CDCl_3$): 8.09 (d, 4H, *J* = 7.5), 7.47-7.18 (m, 12H), 6.45 (s, 2H), 6.32 (s, 1H), 5.10 (s, 2H), 4.38 (t, 4H, *J* = 6.9), 3.90 (t, 4H, *J* = 5.9), 2.09-2.01 (m, 4H), 1.94 (s, 6H), 1.84-1.79 (m, 4H). ^{13}C (δ ppm in $CDCl_3$): *171.5,* 161.2, 140.4, 137.5, 125.8, 122.9, 120.5, 118.9, 108.7, 106.0, 101.23, 67.7, 67.4, 55.9, 42.8, 30.9, 27.0, 26.0. *Anal. Calcd for $C_{43}H_{43}BrO_2N_4$: C, 70.58; H, 5.92; Br, 10.92; N, 3.83. Found: C, 70.51; H, 6.03; Br, 10.80; N, 3.80.*

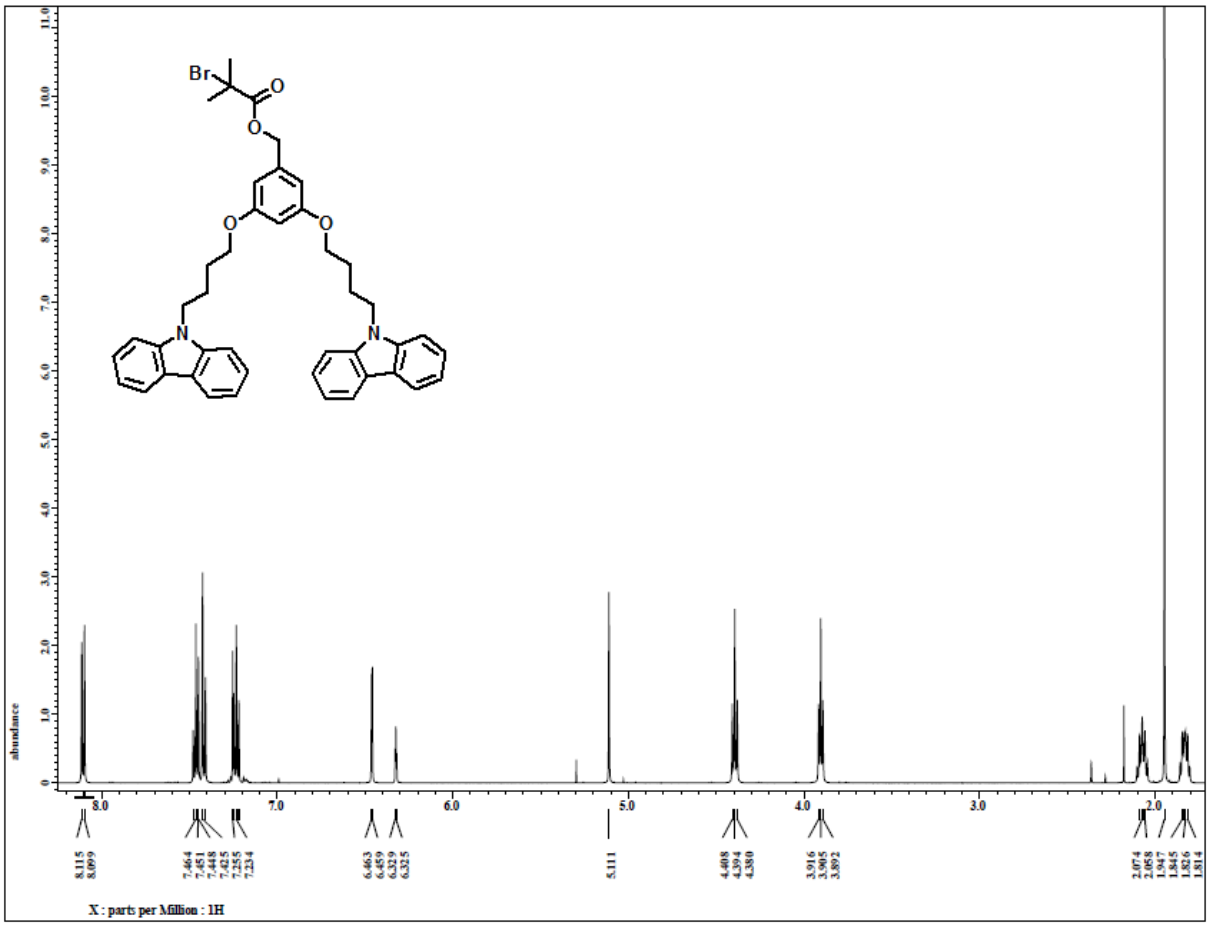


Fig. S1 ^{1}H NMR spectra of Cbz-initiator.

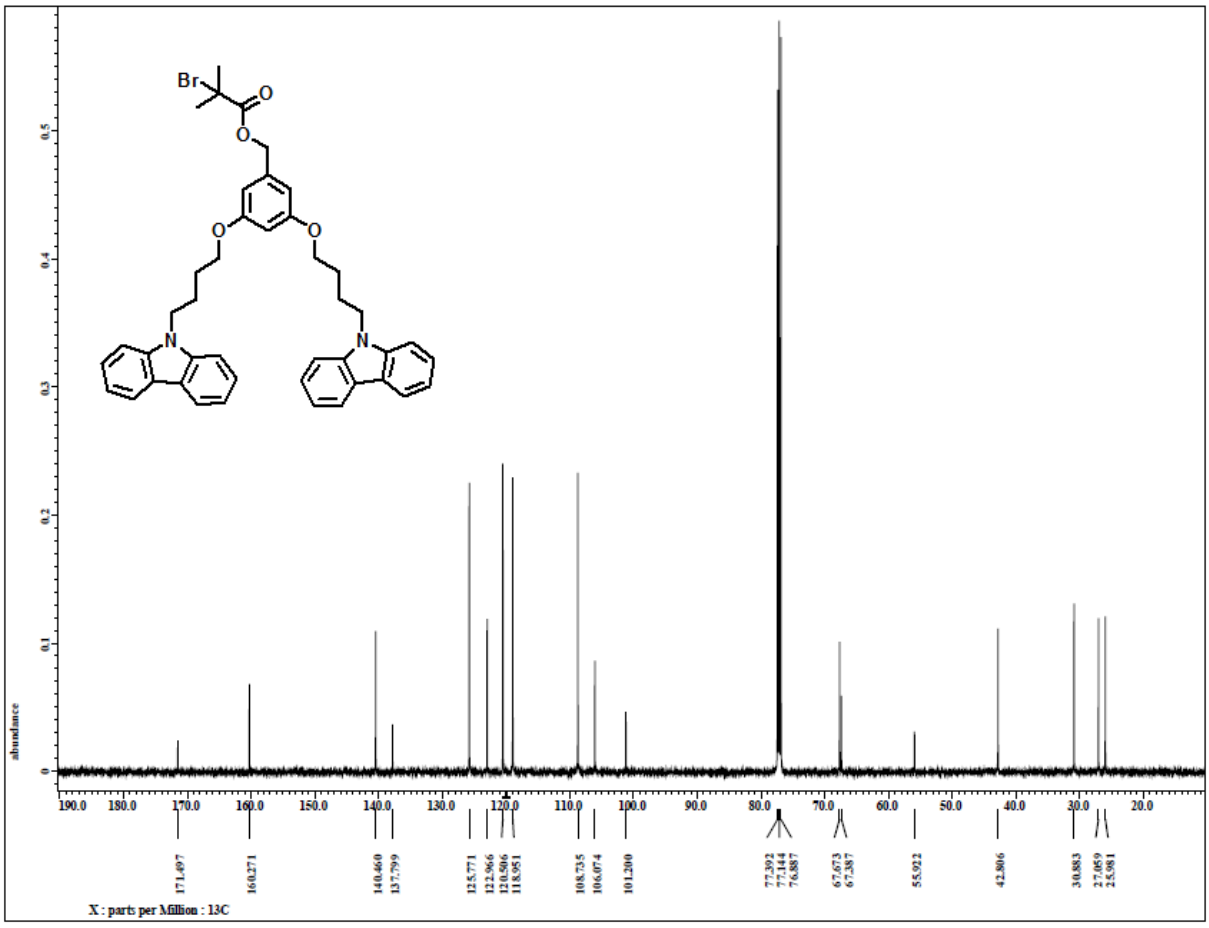
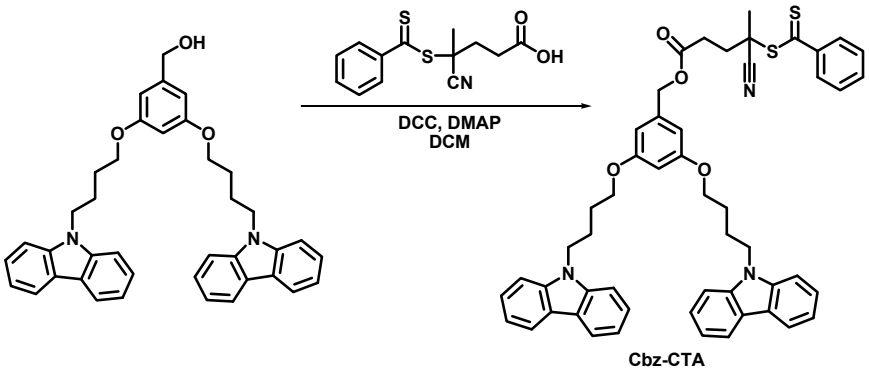


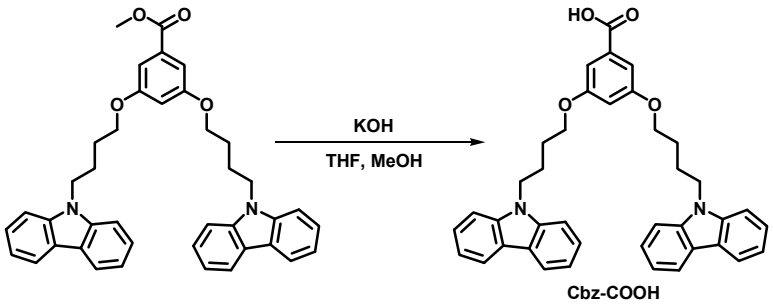
Fig. S2 ^{13}C NMR spectra of Cbz-initiator.



Scheme S3. Synthesis of 3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzyl 4-cyano-4 (phenylcarbonothioylthio)pentanoate (Cbz-CTA).

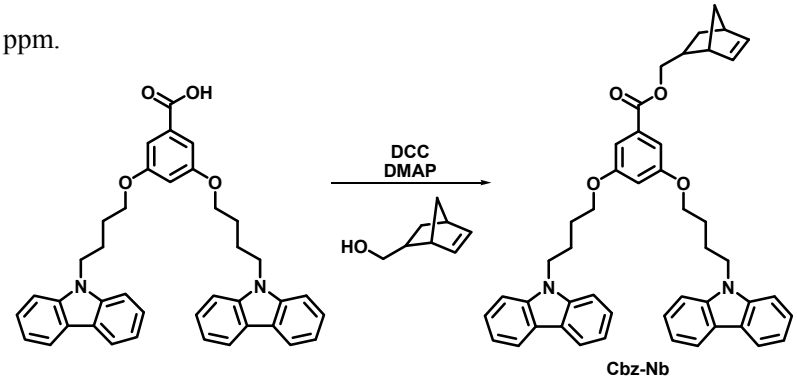
Synthesis of 4-Cyano-4-((thiobenzoyl)sulfanyl)-pentanoic acid. 4-Cyano-4-((thiobenzoyl)sulfanyl)-pentanoic acid was prepared as previously reported.[3]

Synthesis of 3,5-bis(4-(9*H*-carbazol-9-yl)butoxy)benzyl 4-cyano-4 (phenylcarbonothioylthio)pentanoate (Cbz-CTA). The synthesis of Cbz-CTA was done according to literature.[2] A solution of Cbz-OH (0.78 g, *1.34* mmol), 4-Cyano-4-((thiobenzoyl)sulfanyl)-pentanoic acid (0.401 mg, *1.44* mmol), and 4-(dimethylamino) pyridine (DMAP) (*25* mg, *0.20* mmol) was dissolved in anhydrous dichloromethane (15 mL) under N_2. Dicyclohexylcarbodiimide (DCC) (*412* mg, *2.0* mmol) in 5 mL of DCM was added dropwise to the reaction mixture at 0 °C. The reaction was stirred vigorously at 0 °C for 5 min and then warmed to room temperature and stirred overnight. The reaction mixture was filtered to remove the white solid byproduct. The organic phase was washed with dilute $NaHCO_3$ and dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The crude product mixture was first washed with ethyl acetate and then purified by column chromatography on silica gel with dichloromethane:hexane (4:1, v/v). The solvent was removed by rotary evaporation to yield Cbz-CTA as a pink-orange solid (*0.79* g, 70%). ^{1}H NMR (δ ppm in $CDCl_3$): 8.13 (d, 4H); 7.88 (d, 2H); 7.6-7.24 (m, 15H); 6.48 (s, 2H); 6.37 (s, 1H); 5.08 (s, 2H); 4.40 (t, 4H,); 3.92 (t, 4H); 2.76-2.40 (m, 4H); 2.12-2.00 (m, 4H); 1.92-1.76 (m, 7H).



Scheme S4. Synthesis of 3,5-Bis[4-(9H-carbazol-9-yl)butoxy]benzoic Acid (Cbz-COOH).

3,5-Bis[4-(9H-carbazol-9-yl)butoxy]benzoic Acid (Cbz-COOH). The synthesis of Cbz-COOH was done according to literature.[3] A mixture of Cbz-$COOCH_3$ (3.00 g, 4.91 mmol) and KOH (2.76 g, 49.12 mmol) in tetrahydrofuran/methanol (30 mL/60 mL) was refluxed with vigorous stirring for overnight. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was acidified to pH 2-3 with HCl, and then the precipitate was filtered and washed with ether to afford a white solid (2.76 g, 94 % yield). ^{1}H NMR (δ ppm in $CDCl_3$): 8.09 (d, 4H, J = 7.8), 7.84-7.39 (m, 8H), 7.24-7.17 (m, 4H), 7.16 (s, 2H), 6.57 (s, 1H), 4.40 (t, 4H, J = 6.3), 3.94 (t, 4H, J = 6.0), 2.08 (m, 4H), 1.84 (m, 4H) ppm.



Scheme S5. Synthesis of Bicyclo[2.2.1]hept-5-en-2-ylmethyl 3,5-Bis- (4-(9H-carbazol-9-yl) butoxy)benzoate (Cbz-Nb).

Synthesis of Bicyclo[2.2.1]hept-5-en-2-ylmethyl 3,5-Bis- (4-(9H-carbazol-9-yl) butoxy)benzoate (Cbz-Nb). The synthesis of Cbz-Nb was done according to literature.[4] In a 100 mL round-bottom flask

equipped with a stir bar and an addition funnel, a solution of Cbz-COOH (1.93 g, 3.23 mmol), 5-norbornene- 2-methanol (mixture of endo and exo) (0.48 g, 3.88 mmol), and DMAP (40 mg, 0.323 mmol) in 40 mL of dry CH_2Cl_2 was cooled to 0 ^oC under N_2. DCC (0.800 g, 3.88mmol) was dissolved in 10 mL of CH_2Cl_2 and added dropwise to the reaction flask under stirring. After complete addition of DCC, the reaction was stirred for 10 min at 0 ^oC and then allowed to stir at room temperature overnight. Then, the white solids were removed by gravity filtration, and the filtrate was washed with dilute sodium bicarbonate (40 mL) and water (2 X 30 mL) and finally dried over anhydrous Na_2SO_4. The solution was filtered, and the solvent was removed to yield the white crude product mixture, which was further purified by column chromatography on silica gel using 4:1 CH_2Cl_2/hexane as the eluent. The final yield was 1.58 g (69.6%). ^1H NMR (δ ppm in $CDCl_3$): 8.15 (d, 4H, *J=7.8*),7.39-7.57 (m, 8H), 7.20-7.34 (m, 6H), 6.60 (t, 1H, *J=2.1*), 6.25 (q, 0.6 H, *J=3.0*), 6.17 (m, 0.8H), 6.06 (q, 0.6 H, *J=3.0*), 4.46 (dd, 0.5H, *J=6.9*),4.37 (t, 4H, *J=6.9*), 4.27 (t, 0.6H, *J=10.5*), 3.94 (t, 4H, *J=5.7*), 3.03 (s, 0.6H), 2.90 (s, 0.9H), 2.86 (s, 0.4H), 2.08 (m, 4H), 1.86 (m, 5H), 1.42 (m, 3H), 1.00 (m, 0.2H), 0.70 (m, 0.6H).

Synthesis of 11-(2-bromo-2-methyl)-propionyloxy)-undecyl-trichlorosilane (ATRP-silane). The synthesis of 11-(2-bromo-2-methyl)-propionyloxy)-undecyl-trichlorosilane was done according to literature.[5]

II. Additional Supporting Data

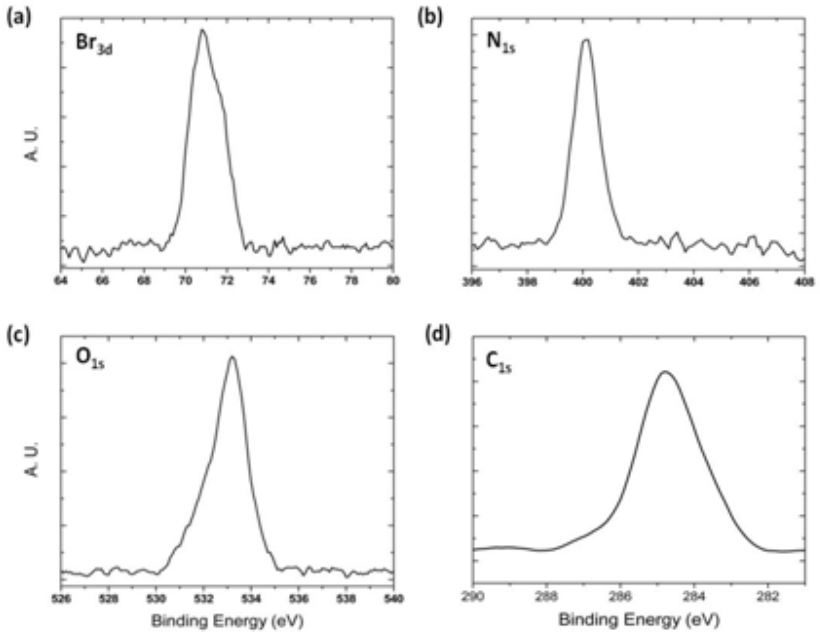


Fig. S3 High resolution XPS scans of the bromine (Br 3d) (a), nitrogen (N 1s) (b), oxygen (O 1s) (c), and carbon (C 1s) (d) signature peaks of the inverse colloidal Cbz-intitator arrays.

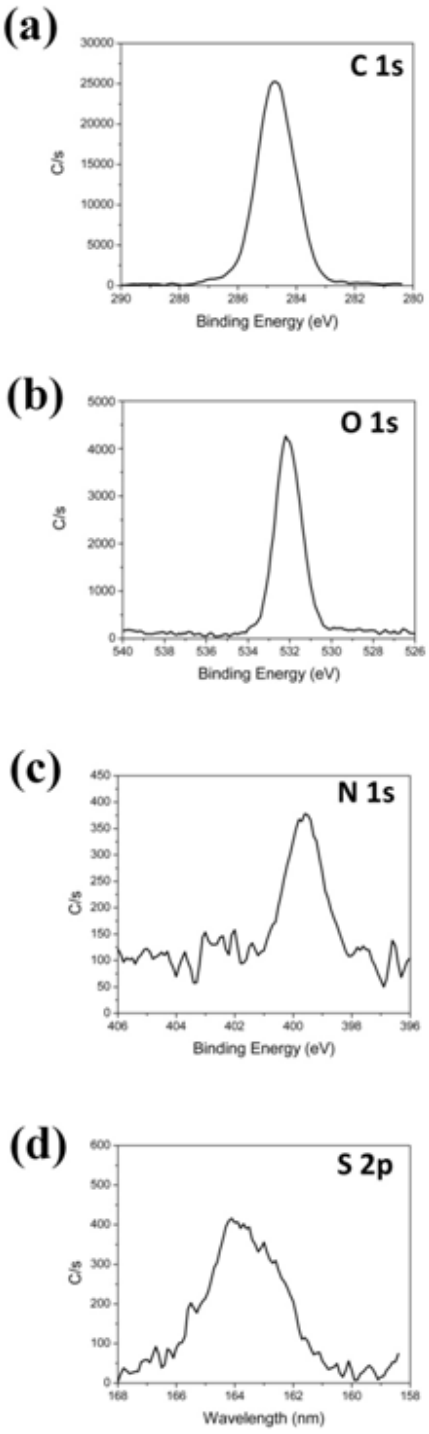


Fig. S4 High resolution XPS scans of the (a) carbon (C 1s), (b) oxygen (O 1s), (c) nitrogen (N1s), and (d) sulfur (S 2p) signature peaks of the inverse colloidal Cbz-CTA arrays.

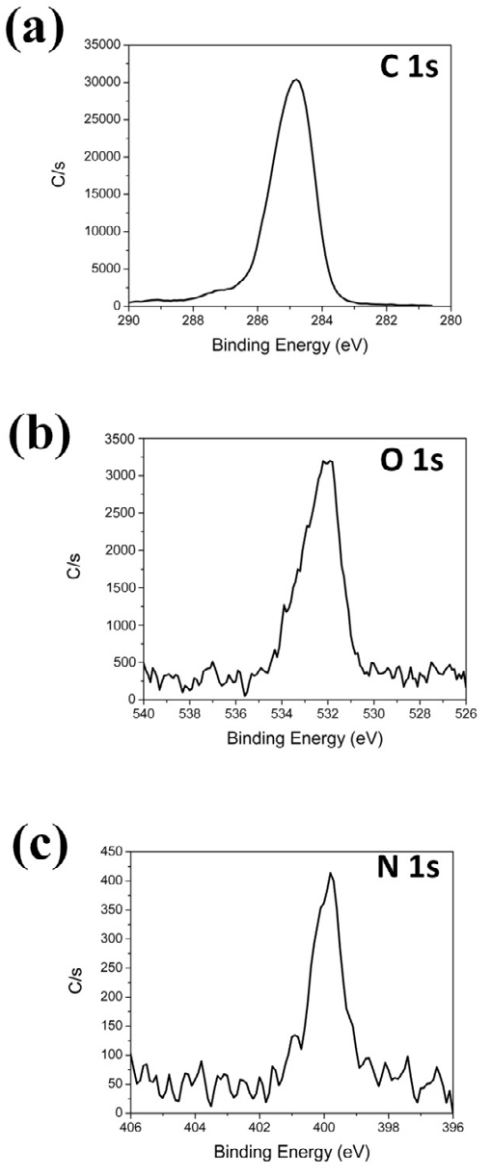


Fig. S5 High resolution XPS scans of the (a) carbon (C 1s), (b) oxygen (O 1s), and (c) nitrogen (N1s), and signature peaks of the inverse colloidal Cbz-Nb arrays.

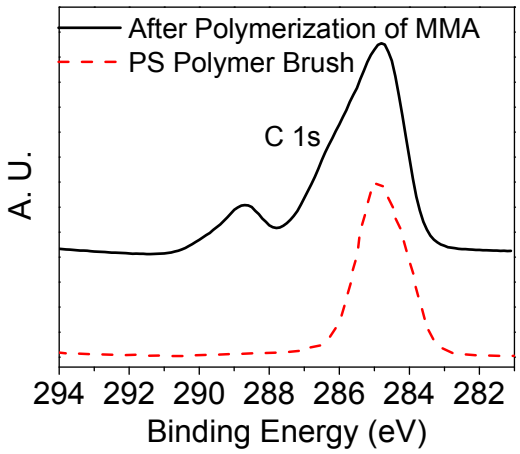


Fig. S6 High resolution XPS scans of the carbon (C 1s) signature peaks of the Cbz-CTA after polymerization of PS and after polymerization of MMA.

III. References

1 P**.** Taranekar, T. Fulghum, D. Patton, R. Ponnapati, G. Clyde, R. Advincula, *J. Am. Chem. Soc*., 2007, **129**, 12537−1254.

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3 C. Kaewtong, G. Jiang, M. J. Felipe, B. Pulpoka, R. Advincula, *ACS Nano*, 2008, **2**, 1533−1542.

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