Supramolecular Functionalization of Electron Beam-Generated Nanostructures
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Supporting Information:

S1: (a) AFM image of a pattern after assembly of Thy-QD, (b) AFM image of S1a after incubation in thymine acetate solution, showing complete erasure of QDs, and (c) AFM image image of S1a after incubation in N-methylated thymine acetate solution showing no change in topology.

PS-Triaz preparation:

Poly(styrene-p-(chloromethyl)styrene, co-PS-CH2Cl, (1)
AIBN (4.00 g, 24.4 mmol) was added to a solution of styrene (24.54 g, 235 mmol) and p-(chloromethyl)styrene (35.73 g, 234 mmol) in chlorobenzene (200 mL). The reaction mixture was heated at 78 ºC for 20 h, followed by cooling to room temperature. The reaction mixture was then added to methanol (800 mL); vigorous mixing resulted in precipitation of a white solid (40.95 g, 68%), which was collected by filtration and washed with methanol. The product was dried in vacuo. GPC: Mn: 4548, Mw: 7771, PDI: 1.7.

Poly(styrene-p-(cyanomethyl)styrene, co-PS-CH2CN (2)
A solution of polymer 1 (1.70 g, 0.325 mmol), sodium cyanide (0.605 g, 12.34 mmol), and DMF (10 mL) was heated at 70 ºC for 48 h under argon. The resulting heterogeneous mixture was filtered and the filtrate concentrated under reduced pressure. The concentrated solution was precipitated into water. The cream-colored solid product (1.39 g, 83%) was collected by filtration, washed with water and CH2Cl2, and dried in vacuo.

Poly(styrene-p-(methylidiaminotriazine)styrene, co-PS-CH2C3N5H4
A solution of polymer (2) (0.76 g, 0.14 mmol), dicyandiamide dicyandiamide (0.525 g, 6.2 mmol), and KOH (0.078 g, 1.4 mmol) in 1-propanol (6 mL) was refluxed for 20 h. A precipitate formed as the reaction proceeded. After evaporating 1-propanol under reduced pressure, the resulting crude product was stirred in boiling water for 30 min. The solution was cooled to room temperature and then filtered to collect a cream-colored solid (0.768 g, 87%).
NMR of Poly(styrene-p-(cyanomethyl)styrene, co-PS-CH2CN (2)
NMR of Poly(styrene-p-(methylidiaminotriazine)styrene, co-PS-CH2C3N5H4

Synthesis of CdSe-ZnS QDs

CdSe-ZnS core-shell QDs were prepared according to the reported procedure. CdO (0.0514 g, 0.4 mmol), tetradecyl phosphonic acid (TDPA) (0.2232 g, 0.8 mmol) and trioctylphosphine oxide (TOPO) (3.7768 g, 9.77 mmol) were loaded into a 50 ml three-neck flask and heated to 350 °C under Ar flow. After 3 hrs the solution becomes optically clear and the Se solution (Se (0.042 g, 0.53 mmol) in 2.4 ml tributyl phosphine (TOP)) was swiftly injected into the hot solution at 290 °C. The CdSe QDs were purified and precipitated with CHCl3 and MeOH, and finally dissolved in CHCl3. Then, the CdSe core solution is mixed with TOPO (4g, 10.3 mmol) and hexadecylamine (HDA) (1.5 g, 6.2 mmol) and heated to 150 °C for 1 hr. Diethylzinc (ZnEt2) (1.6 ml, 1.6 mmol) in 2.4 ml TOP and and hexamethyl-disilathiane (TMS2S) (0.278 ml, 1.3 mmol) in 5.25 ml TOP were used as shell solution. After injecting the shell solution the QD mixture was reacted for 1 hr at 100 °C. The resulting CdSe-ZnS QDs were purified and precipitated with CHCl3 and MeOH, and finally stored in toluene.

Synthesis of Thy and N-Methylthymine-Functionalized CdSe-ZnS QDs

TOPO/TOP coated CdSe-ZnS QDs (ca. 10 mg) were mixed with HS-C12 ligands (0.422 mg) and Thy–thiol ligand (30 mg) in a dichloromethane solution (ca. 10 mL) was added and stirred for 24 hrs under Ar. QDs were precipitated in hexanes and redissolved in CHCl3. N-methylthymine-functionalized QDs were made using the same procedure.