Supporting Information

Non-volatile Transistor Memory Devices using Charge Storage Cross-Linked Core-Shell Nanoparticles

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Experimental

Materials

Poly(PEGMA) ($M_n \sim 38000$ and 17000 g mol^{-1}) and the block copolymer poly(PEGMA)$_m$-b-poly(DB3VT)$_n$ were prepared through two-step RAFT polymerization according to our previous report.[33] The information of synthesis is simply tabulated both in Table 1 and Table S1 of the *Supporting Information* (*SI*). The molecular weights of poly(DB3VT) segment in the two block copolymers were adjusted to be almost the same ($M_n \sim 4000$ g mol^{-1}), whereas the chain length of the hydrophilic poly(PEGMA) segment and comonomer composition were different. Poly(DB3VT) ($M_n \sim 9000$ g mol^{-1}) was also prepared for comparison with those of block copolymers. Subsequently, the cross-linked core-shell poly(PEGMA)$_m$-b-poly(DB3VT)$_n$ nanoparticles with two different m:n ratios of 90:10 (**P1**) and 77:23 (**P2**) were synthesized through Suzuki coupling reaction as we previously reported.[33] Pentacene was purchased from Luminescence Technology corp. (Hsinchiu, Taiwan). Other chemicals were used as received unless otherwise stated.

Synthesis of poly(DB3VT) by RAFT polymerization

Poly(DB3VT) homopolymer was prepared by following the reaction scheme illustrated in Scheme S3, 2,5-Dibromo-3-vinylthiophene (0.67 g, 2.5 mmol), cumyl dithiobenzoate as the chain transfer agent (CTA, 6.8 mg, 0.025 mmol), AIBN (0.82 mg, 0.005 mmol), and dry 1,4-dioxane (1.3 mL) were placed in a dry glass ampule equipped with a magnetic stir bar, and then the solution was degassed by three freeze-evacuate-thaw cycles. After flame-sealed under vacuum, the ampule was stirred at 60 °C for 24 h in the dark. The reaction was stopped by rapid cooling with liquid nitrogen, and the reaction mixture was then precipitated in a large excess of *n*-hexane and isolated by filtration. The resulting product was finally dried under vacuum at room temperature to yield a pale red powder (160 mg, 24%). ^{1}H NMR (CDCl$_3$, δ, ppm): 6.22-6.72 (m, 1H), 2.03-2.72 (m, 1H), 1.11-1.89 (m, 2H). M_n and M_w/M_n calculated by GPC (THF) were 3700 and 1.03 g mol^{-1}, respectively. The ^{1}H NMR spectrum is shown in Figure S1 (*Supporting Information, SI*), in which the characteristic peak corresponding to DB3VT unit is clearly recognized at 6.3 to 6.7 ppm. The molecular weight calculated by ^{1}H NMR was 9000 g mol^{-1}.

Synthesis of Poly(PEGMA)$_m$-b-Poly(DB3VT)$_n$

A two-step RAFT polymerization, first introduced by our previous work,[32,33] was carried out for preparing the amphiphilic block copolymers composed of PEGMA and DB3VT, poly(PEGMA)-b-poly(DB3VT). The details of synthesis are tabulated in both Table 1 and

Table S1(*Supporting Information, SI*), where the synthetic route was provided in Scheme S1. In the first step, poly(PEGMA) with two different values of molecular weight were prepared from PEGMA using cumyl dithiobenzoate as CTA: $M_{n,NMR}$ = 38 000 (M_w/M_n = 1.26) and 17 000 (M_w/M_n = 1.11) g mol^{-1}. In the second step, poly(PEGMA)$_m$-*b*-poly(DB3VT)$_n$ with two block compositions (m:n = 90:10 and 77:23) were synthesized by RAFT polymerization of DB3VT using two poly(PEGMA) as macro-CTA under suitable conditions, respectively. According to our previous study, the block compositions (m:n) of each segment in the block copolymers can be precisely controlled by adjusting the [M]:[macro-CTA] ratios.[33] While the ratio of [macro-CTA]:[AIBN] was maintained as 5:1, the polymerization was thus carried out at 60 °C for 24 h with different ratios of [M]:[macro-CTA], 140:1 and 30:1, and resulted in the block copolymers, poly(PEGMA)$_m$-*b*-poly(DB3VT)$_n$, with two different m:n ratios, i.e. 90:10 and 77:23, respectively. For the synthesis of block copolymer with77:23 molar ratio, poly(PEGMA) macro-CTA (0.45 g, 0.026 mmol, $M_{n,NMR}$ = 17000), DB3VT (0.211 g, 0.79 mmol), AIBN (0.86 mg, 0.005 mmol), and dry 1,4-dioxane (0.79 mL) were placed in a dry glass ampule equipped with a magnetic stir bar. After the solution was degassed using three freeze-evacuate-thaw cycles, the reaction was carried out at 60 °C for 24 h with stirring. The reaction mixture was poured into hexane, and then the precipitate was collected with decantation and dried *in vacuo* at room temperature to yield light red viscous product (60%, 0.398 g). The compositions of each segment (m:n) was evaluated using by comparison of the area of the peak at 6.2-6.7 ppm attributed to the heterocyclic proton (1H) of DB3VT unit and 3.9-4.2 ppm corresponding to the methylene protons (2H) of poly(PEGMA) unit (Figure S1, *SI*). Herein, DB3VT was successfully polymerized from the dithiobenzoate-terminated macro-CTA to yield amphiphilic block copolymers with narrow polydispersities (M_w/M_n = 1.26 to 1.43).

Preparation of Cross-Linked Nanoparticles

Following by the Suzuki coupling reaction (Scheme S2),[33] the cross-linked nanoparticles with different m:n ratios was respectively carried out using the poly(PEGMA)$_m$-*b*-poly(DB3VT)$_n$ and 2,5-thiophenediboronic acids in a THF/H$_2$O solution in the presence of the catalytic amount of Pd(dppf)Cl$_2$ at 70 °C for 24 h. Considering the solvent is a dominant factor in the preparation of well-defined nanoparticles,[33] the volume ratio of the THF/H$_2$O solution was fixed as 3:7 vol %, in which the poly(PEGMA)-*b*-poly(DB3VT) can form well-defined micelles consisting of a hydrophobic core of poly(DB3VT) covered with a hydrophilic shell of poly(PEGMA) segments. The inter- and intra-molecular coupling reaction to form polythiophene segments within micelles thus led to the formation of cross-

linked core-shell nanoparticles under the Suzuki coupling reaction. A typical procedure (P2 in Table 1) is as follows; The THF solution (15 mL) of poly(PEGMA)$_{77}$-b-poly(DB3VT)$_{23}$ (48 mg, 0.2 mmol based on the repeating unit), 2,5-thiophenedibronic acid (0.172 g, 1.0 mmol), NaHCO$_3$ (0.34 g, 4.0 mmol) was stirred at room temperature under argon atmosphere. After the block copolymer was completely dissolved, Pd(dppf)Cl$_2$ (16.3 mg, 0.02 mmol) and water (35 mL) was added, and the reaction mixture was carried out at 70 °C for 24 h in the dark. Thereafter, dialysis in sequence with water and then with THF was employed to yield brown viscous product (85%, 48 mg). The products are soluble in common organic solvent, such as THF, chloroform, and dichloromethane regardless of the block composition.

Device fabrication

The pentacene-based transistor-type memory devices were fabricated on the wafer with a thermally grown 100-nm-thick SiO$_2$ dielectric on highly doped n-type Si as gate electrode. The solutions of poly(PEGMA), poly(DB3VT), and cross-linked poly(PEGMA)$_m$-b-poly(DB3VT)$_n$ nanoparticles with the concentration of 3 mg mL^{-1} in chloroform was respectively spin-coated at 1000 rpm for 60 s on wafers. Prior to the spin-coating process, the polymer solutions were filtered using Millipore Teflon Filters with a pore size of 0.2 μm into a dust-free cylindrical cuvette and the substrates were rinsed with toluene, acetone, and IPA in sequence. Thereafter, the polymer thin films were dried under vacuum (10^{-6} torr) at room temperature for 6 h to remove residual solvents. Thin films were thus prepared on the SiO$_2$/Si substrates for OFET memory devices as well as for the following characterizations. The thickness of the prepared thin film was estimated to be around 50 nm. A 50-nm-thick pentacene active layer was prepared by thermal deposition with a rate of 0.5 Å s^{-1} under 90 °C and 5 × 10^{-7} torr. The top-contact source and drain electrodes were defined by 80-nm-thick gold through a regular shadow mask and the channel length (L) and width (W) were 50 and 1000 μm, respectively. The current-voltage ($I-V$) characteristics of the devices measured using a Keithley 4200-SCS semiconductor parameter analyzer in a N$_2$-filled glove box. $I_{ds} = \mu(WC/2L)(V_{gs}-V_t)^2$, where I_{ds} is the source–drain current, V_{gs} and V_t gate and threshold voltage, respectively, C the capacitance of the device, W and L the channel width and length.

Characterization

^{1}H NMR (400 MHz) spectrum was recorded JEOL JNM-ECX400. The UV-vis spectra were recorded with a on a JASCO V-630BIO UV-vis spectrophotometer. The thickness of the thin film prepared for UV-vis analysis was estimated to be around 50 nm. Fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. Number-average

molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by GPC using a system consisting of a Tosoh DP-8020 pump and Viscotek. The column set was as follows: a guard column [TSK guard column HXL-H (4.0 cm) and four consecutive columns (Tosoh TSK-GELs (exclusion limited molecular weight): GMHXL (4×10^8), G4000HXL (4×10^5), G3000HXL (6×10^4), and G2500HXL (2×10^4), 30 cm each) eluted with THF at a flow rate of 1.0 mL/min, where polystyrene standards were employed for calibration. DLS measurement was performed by using a Sysmex Zatasizwer Nano with a He−Ne laser ($\lambda_0 =$ 632.8 nm) and a scattering angle of 90°. Prior to the light scattering measurement, the polymer solutions were filtered using Millipore Teflon Filters with a pore size of 0.2 μm into a dust-free cylindrical cuvette.

The thickness of polymer films was measured with a microfigure measuring instrument (Surfcorder ET 3000, Kosaka Laboratory Ltd.). The thin-film samples for morphology analysis were prepared from the same condition with device fabrication, which are respectively spin-coated from the solutions with of 3.0 mg mL^{-1} in chloroform. Atomic force microscopy (AFM) measurement was performed with a NanoScope IIIa AFM (Digital Instrument) at room temperature, where the commercial silicon cantilevers with typical spring constraints of 21−78 N m^{-1} was employed to operate the AFM in tapping mode. Transmission electron microscope (TEM) images were obtained using a JOEL JEM-1230 operated at 100 kV, equipped with a Gatan Dual Vision CCD. The samples for TEM characterization were prepared by spin-coating at 1000 rpm for 60 s onto the carbon-coated copper grids. Note that the surface energies of carbon (62 mJ m^{-2}) and SiO$_2$ (54 mJ m^{-2}) are similar, and thus carbon-coated grids are generally regarded as reliable substrate to simulate the morphology on the SiO$_2$/Si surface. For the capacitance analysis, a metal-insulator-semiconductor (MIS) capacitor was fabricated by depositing gold electrodes on the polymer-coated n-type Si(100) wafers. The capacitance of the bilayer dielectrics was measured on the MIS structure using Keithley 4200-SCS equipped with a digital capacitance meter (model 4210-CVU).

Table S1. Synthesis of block copolymer, poly(PEGMA)$_m$-b-poly(DB3VT)$_n$, by RAFT polymerization of DB3VT using poly(PEGMA) macro-CTA[a]

Run	Macro-CTA M_n	[M]/ [CTA]/ [AIBN]	Yield[b] (%)	M_n Theory[c]	NMR[d]	SEC[e]	M_w/M_n[e]	m : n[d]
1	38000 [f]	700/5/1	59	44000	42000	40000	1.26	90:10[h] (126:14)[i]
2	17000 [g]	150/5/1	60	25000	21000	23000	1.43	77:23[h] (56:16)[i]

[a] Polymerization was carried out in 1,4-dioxane ([M] = 1.0 mol/L) at 60 °C for 24 h. [b] n-Hexane insoluble part. [c] The theoretical molecular weight = [M]$_0$/[CTA]$_0$ × (MW of monomer) × yield + (MW of CTA). [d] Calculated by ^{1}H NMR in CDCl$_3$. [e] Determined by SEC using polystyrene standards in THF. [f] Prepared by RAFT polymerization at [M]/[CTA]/[AIBN] = 2000/5/1 (Yield = 79%, M_w/M_n = 1.26). [g] Prepared by RAFT polymerization at [M]/[CTA]/[AIBN] = 500/5/1 (Yield = 57%, M_w/M_n = 1.11). [f,g] Both polymerizations were conducted in 1,4-dioxane ([M] = 1.0 mol/L) at 60 °C for 12 h. [h] Molar composition ratios. [i] Precise number of repeating units.

Table S2. Preparation of cross-linked poly(PEGMA)$_m$-*b*-poly(DB3VT)$_n$ nanoparticles by Suzuki coupling reaction.[a]

Sample	M_n [b] poly(PEGMA)/ block copolymer	M_w/M_n [b]	m : n [c]	yield [d] (%)	D_h [e] (nm)	D (core) [f] (nm)
P1	38000/42000	1.26	90 : 10	79	230	12
P2	17000/21000	1.43	77 : 23	85	92	25

[a] Catalyst: Pd(dppf)Cl$_2$, [Pd]:[NaHCO$_3$]$_0$:[Br]$_0$ = 0.1 : 20 : 1, [Block of Br] = 0.004 mol/L, THF : H$_2$O = 3 : 7. [b] Molecular weights of poly(PEGMA) segment and block copolymer (see Table S1 for detailed synthetic information). [c] Molecular weights distribution and comonomer composition of the block copolymers determined by SEC in THF and ^{1}H NMR in CDCl$_3$. [d] After dialysis with water and THF, the value is determined by the amount of the product compared with the sum of the amounts of reacted boronic acid compound and block copolymer that has been cross-linked. [e] Determined by DLS measurement in THF solution (conc. = 2.0 mg/mL) at 25 °C. [f] Determined by TEM images.

Table S3. Electrical performance of the studied transistor-type memory devices using cross-linked poly(PEGMA)$_m$-b-poly(DB3VT)$_n$ nanoparticles as dielectric layer. [a]

Dielectric layer	m : n	D (core) (nm) [b]	Mobility $\times 10^{-3}$ (cm^2 V^{-1} s^{-1})	I_{ON}/I_{OFF} [c]	V_{th}^P (V) [d]	V_{th}^E (V) [d]	Memory window (V) [e]
Poly(PEGMA)	-	-	3.9 ± 0.14	3.3×10^5	3	3	-
P1	90 : 10	12	1.4 ± 0.62	3.4×10^5	−25	0	25 (FLASH)
P2	77 : 23	25	2.5 ± 0.21	5.1×10^5	−34	0	34 (FLASH)
Poly(DB3VT)	-	-	6.6 ± 0.20	9.7×10^6	−10	−10	10 (WORM)

[a] The data were averaged from at least 10 devices of two different batches. [b] Determined by TEM images. [c] On/off drain current ratios of reading at $V_g = -5$ V. [d] V_{Th}^P is the threshold voltage after programming progress and V_{Th}^H is that after erasing progress. [e] Memory window is defined as $V_{Th}^P - V_{Th}^E$ for reversible device and as $V_{Th}^P - V_{Th}^{Initial}$ for WORM-type device.
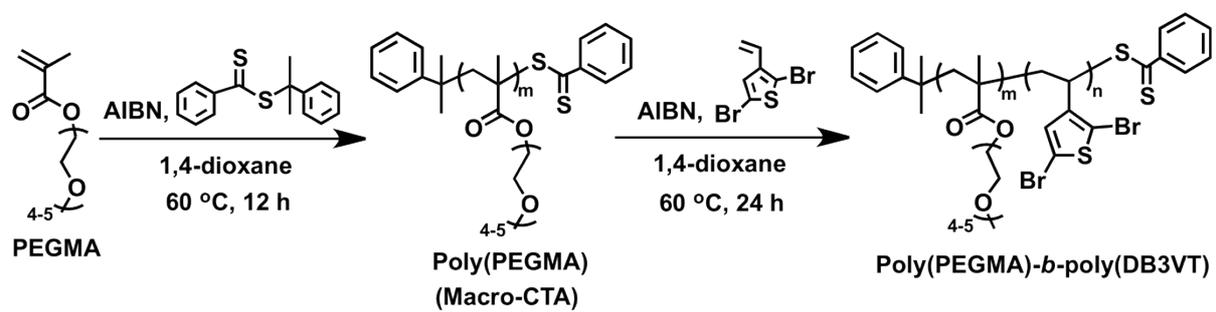
Scheme S1. Synthesis of poly(PEGMA)-*b*-poly(DB3VT).
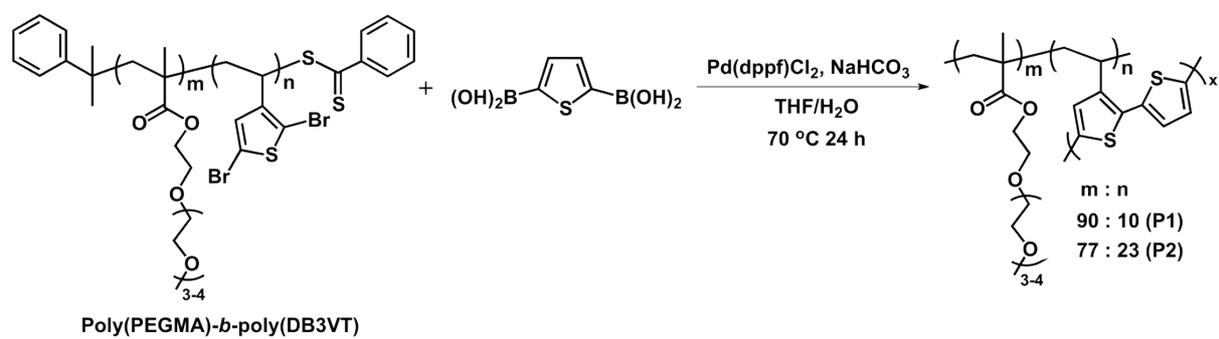
Scheme S2. Preparation of cross-linked core-shell nanoparticles by the Suzuki coupling reaction.
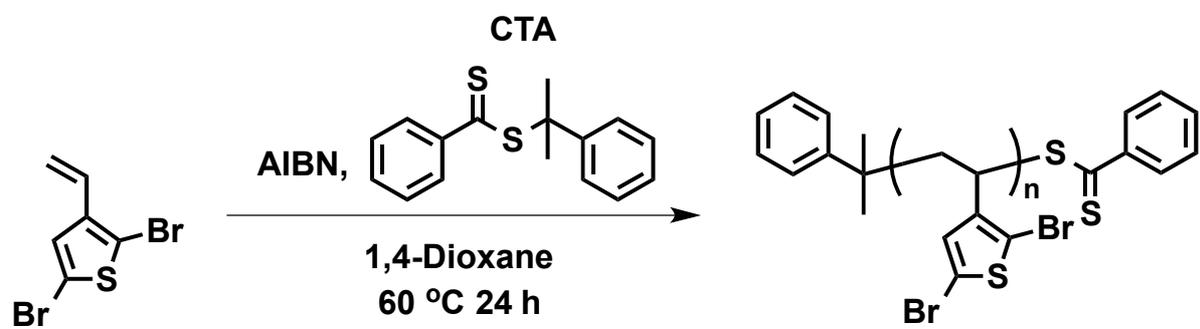
Scheme S3. Preparation of poly(DB3VT) homopolymer by the RAFT polymerization.
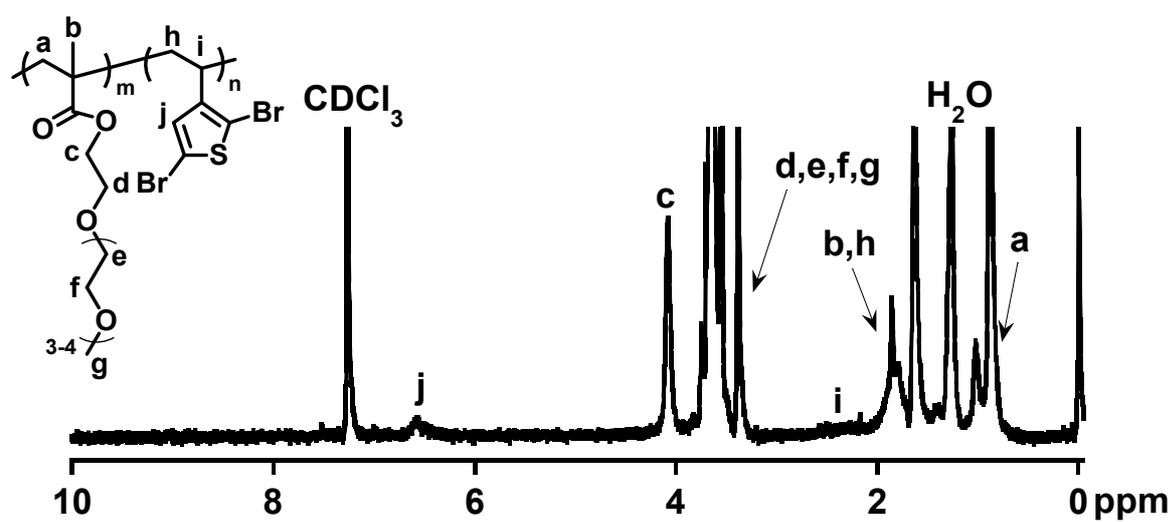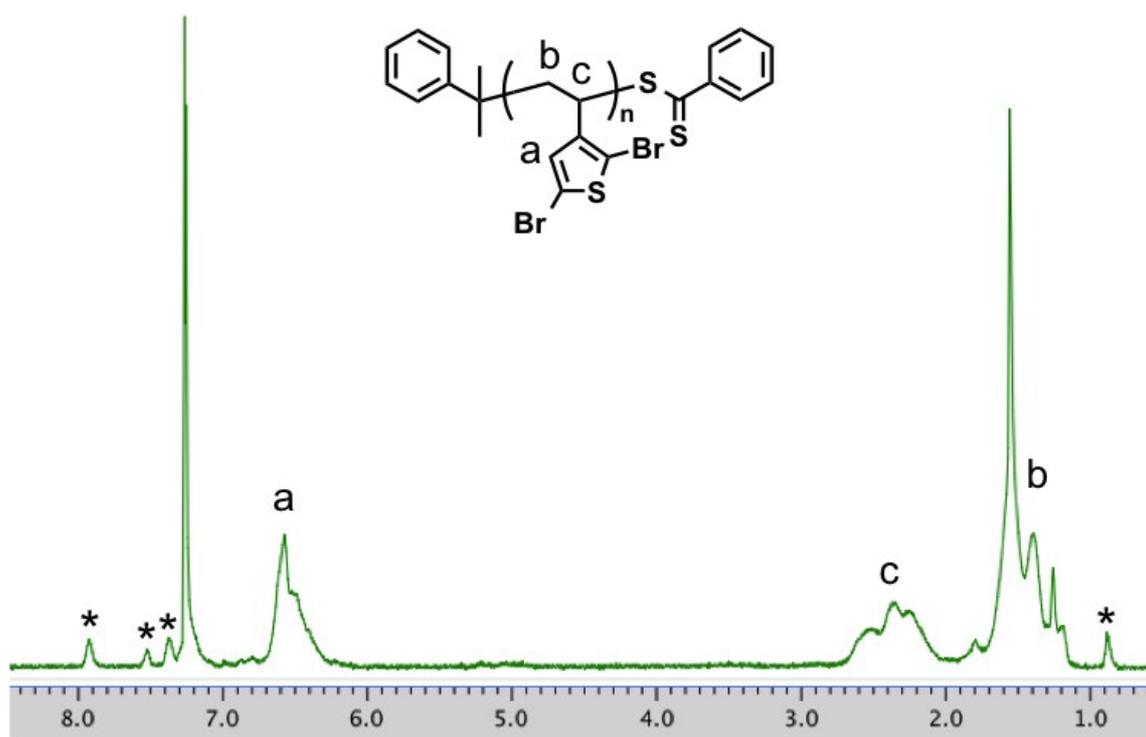
Figure S1. ^{1}H NMR spectra of (a) poly(DB3VT) (top), the peaks corresponding to terminal CTA are marked, and (b) poly(PEGMA)$_{77}$-b-Poly(DB3VT)$_{23}$ (bottom) in CDCl$_3$.
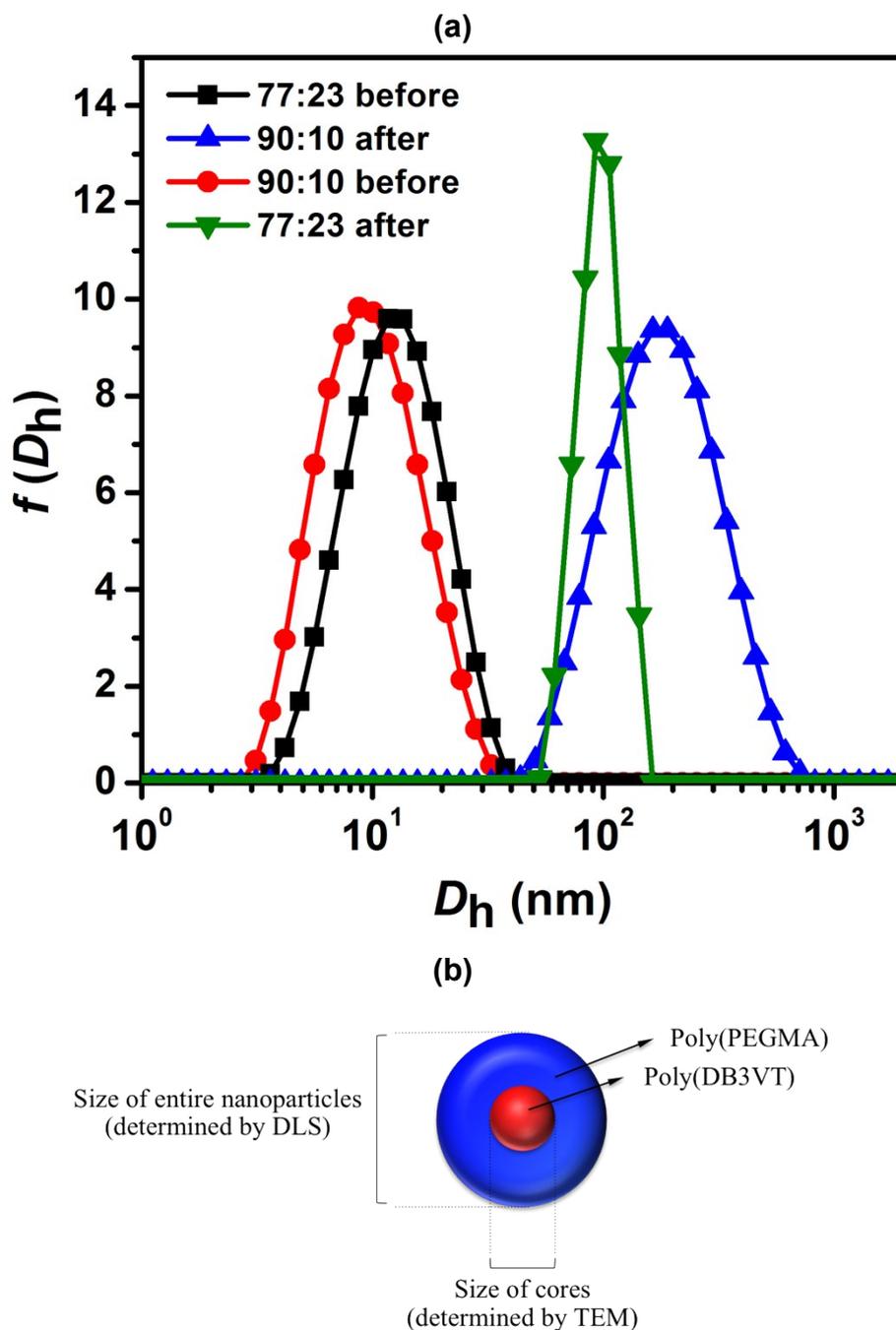
Figure S2. (a) DLS profiles of the block copolymer with different PEGMA:DB3VT ratios before and after cross-linking reaction. The sample solutions were prepared in the concentration of 2.0 mg/mL in THF. (b) The structures of a core-shell cross-linked poly(PEGMA)$_m$-*b*-Poly(DB3VT)$_n$ nanoparticle.
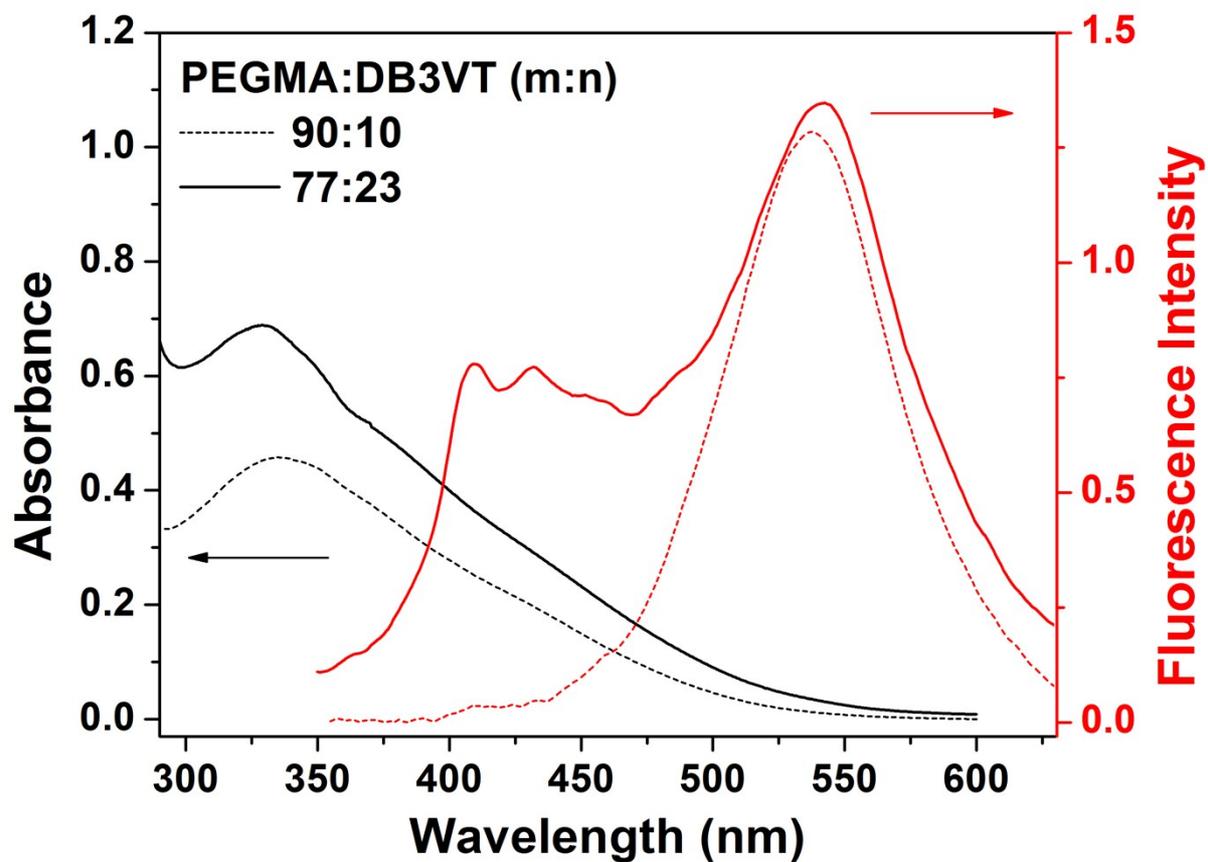
Figure S3. UV-vis absorption (black) and fluorescence (red) spectra of the cross-linked nanoparticles based on different PEGMA:DB3VT ratios: 90:10 (dash line) and 77:23 (solid line). The sample solutions were prepared in the concentration of 2.0 mg/mL in chloroform.
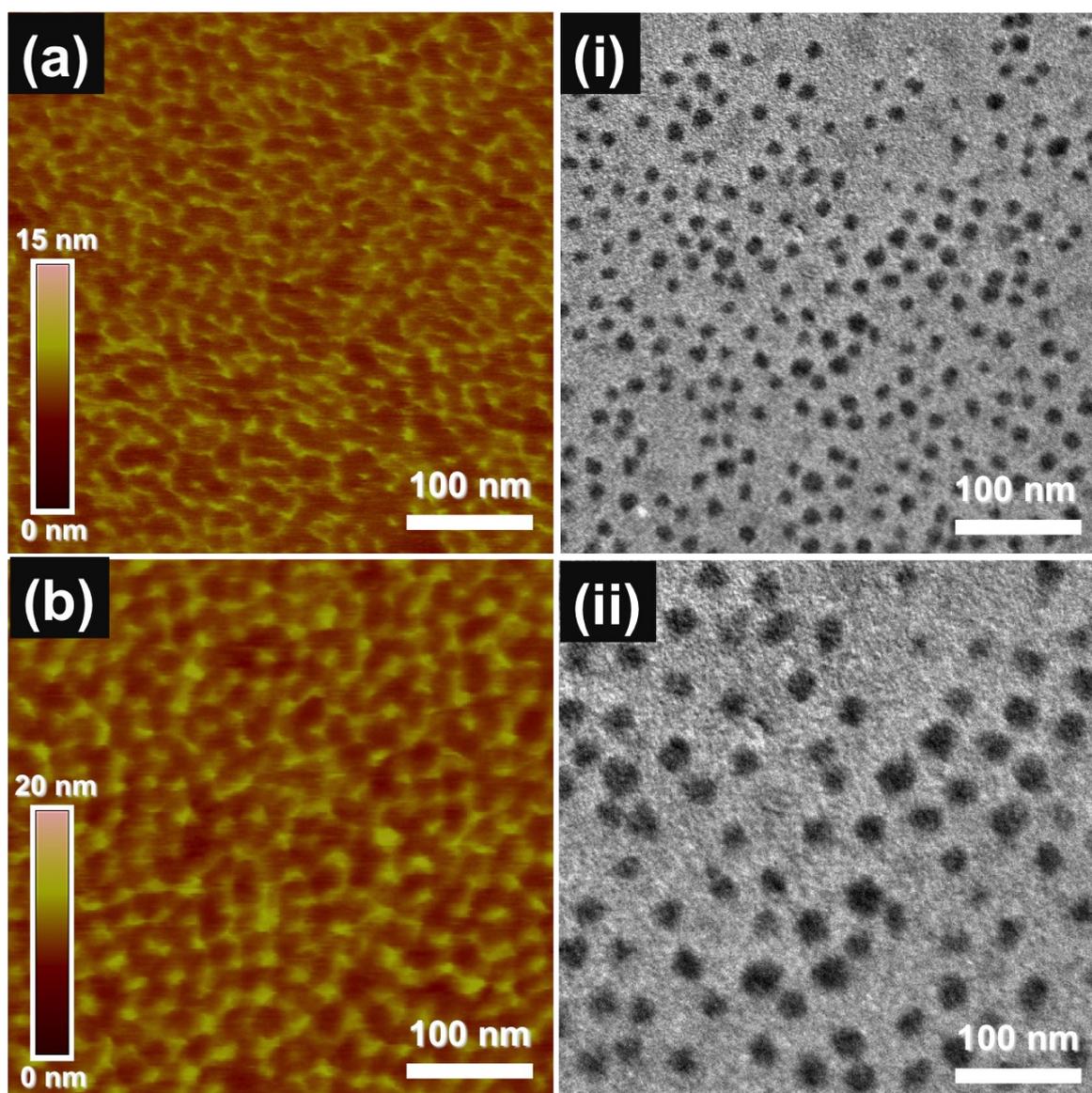
Figure S4. AFM height (a-b) and TEM (i-ii) images of the spin-coat thin film of studied nanoparticles (from 3.0 mg/mL in chloroform) with different PEGMA:DB3VT ratios: (a)(i) 90:10 and (b)(ii) 77:23.
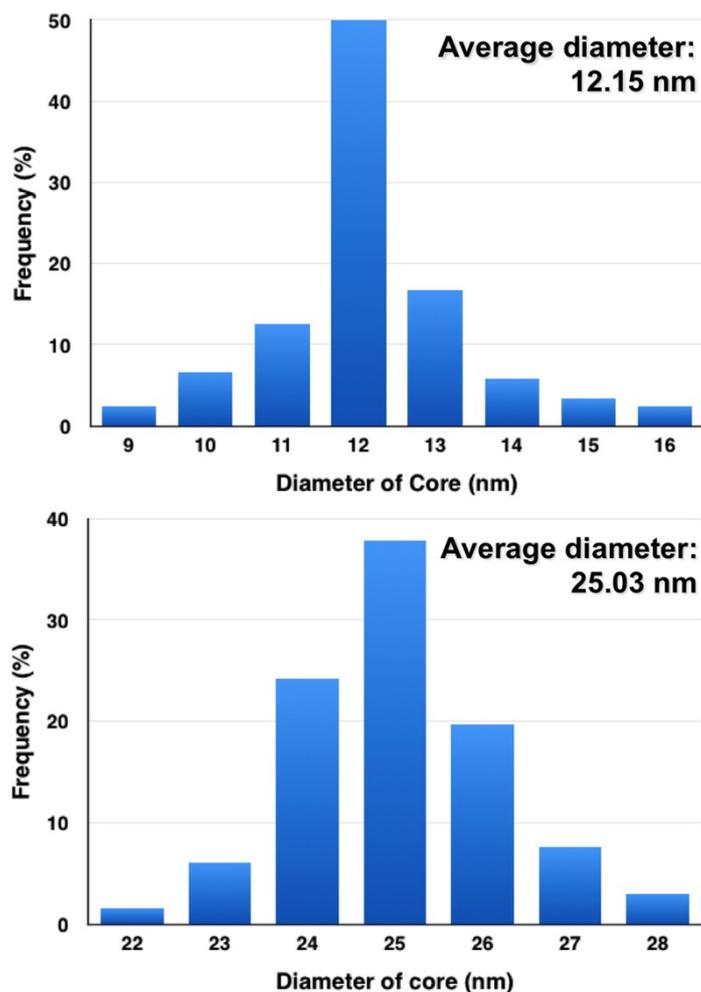
Fig S5. The particle size distribution histograms based on the TEM images of the spin-coat thin films from the cross-linked poly(PEGMA)$_m$-b-poly(DB3VT)$_n$ nanoparticles: P1 (upper) and P2 (lower).
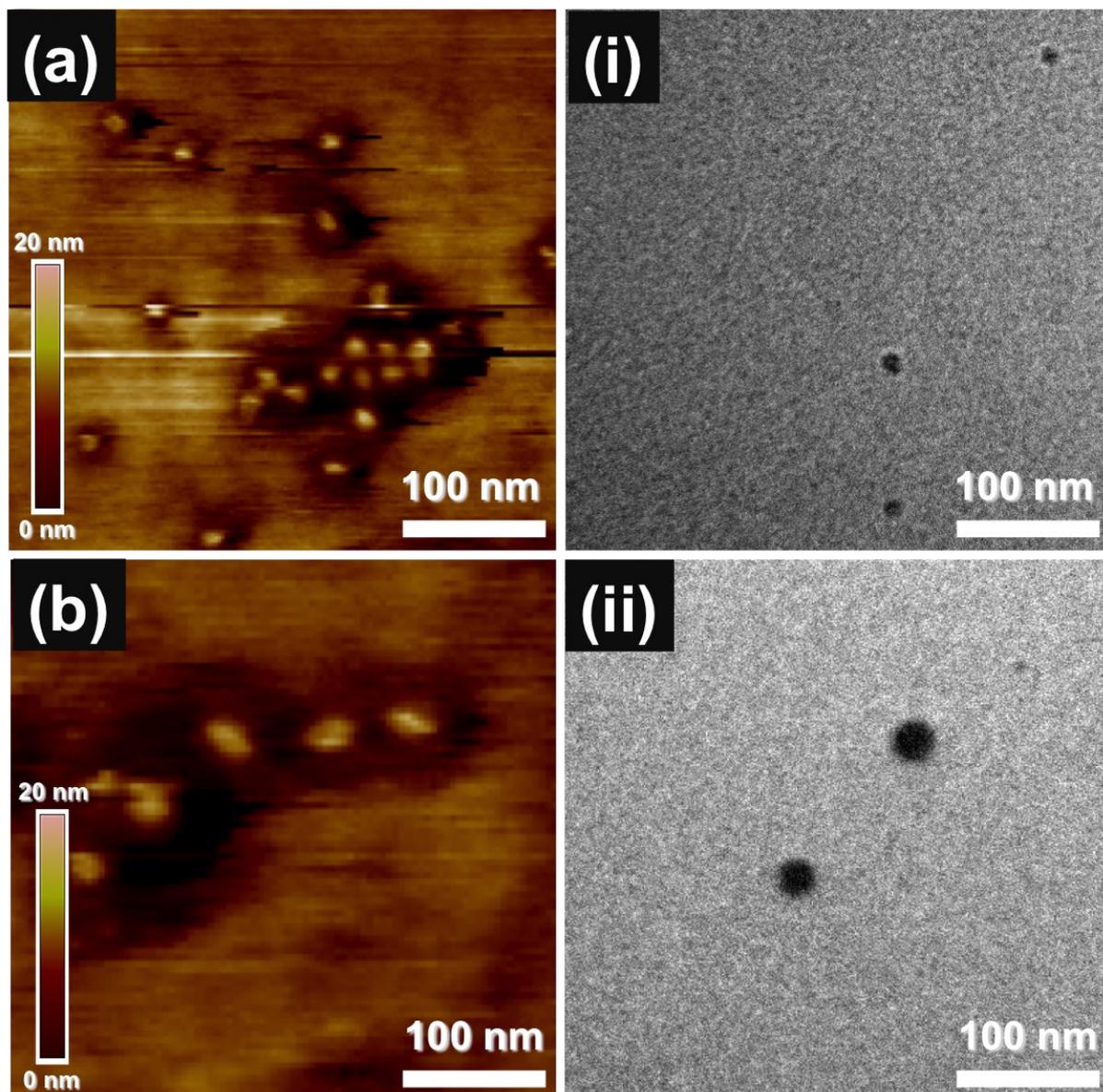
Figure S6. AFM height (a-b) and TEM (i-ii) images of the spin-coat thin film of studied nanoparticles (from 1.0 mg/mL in chloroform) with different PEGMA:DB3VT ratios: (a)(i) 90:10 and (b)(ii) 77:23.
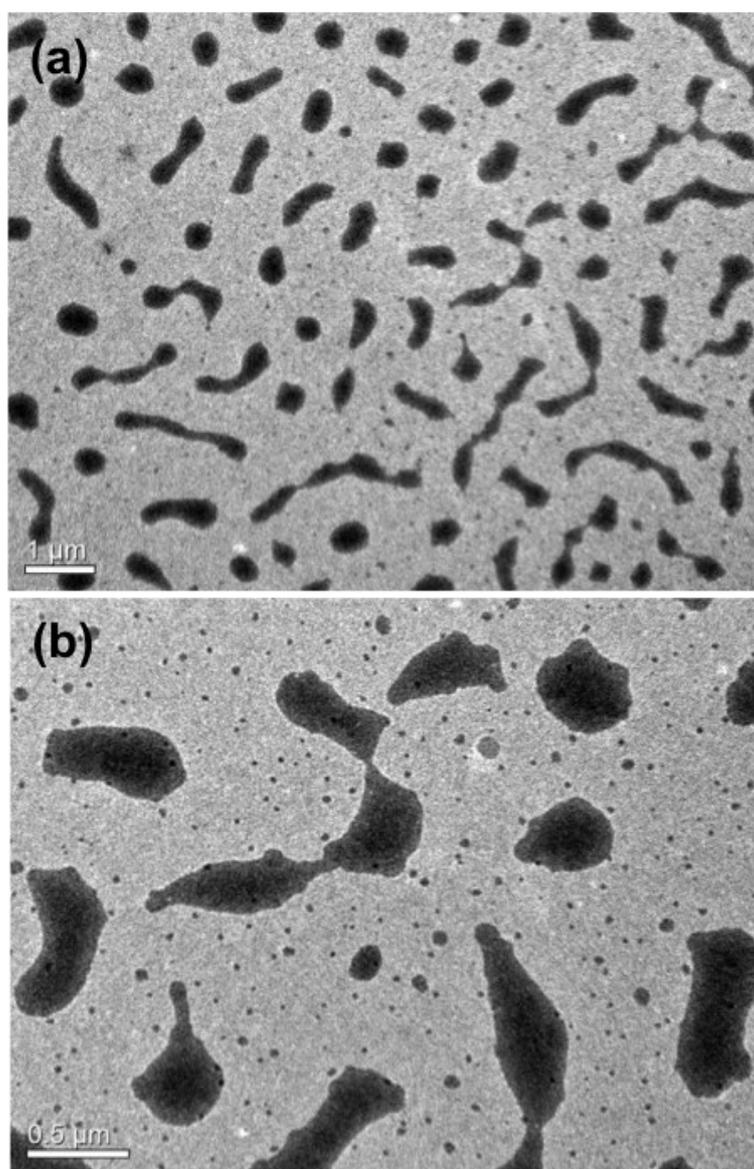
Figure S7. TEM images of the spin-coat thin film of studied poly(DB3VT) homopolymer in two different scales (3.0 mg/mL in chloroform).
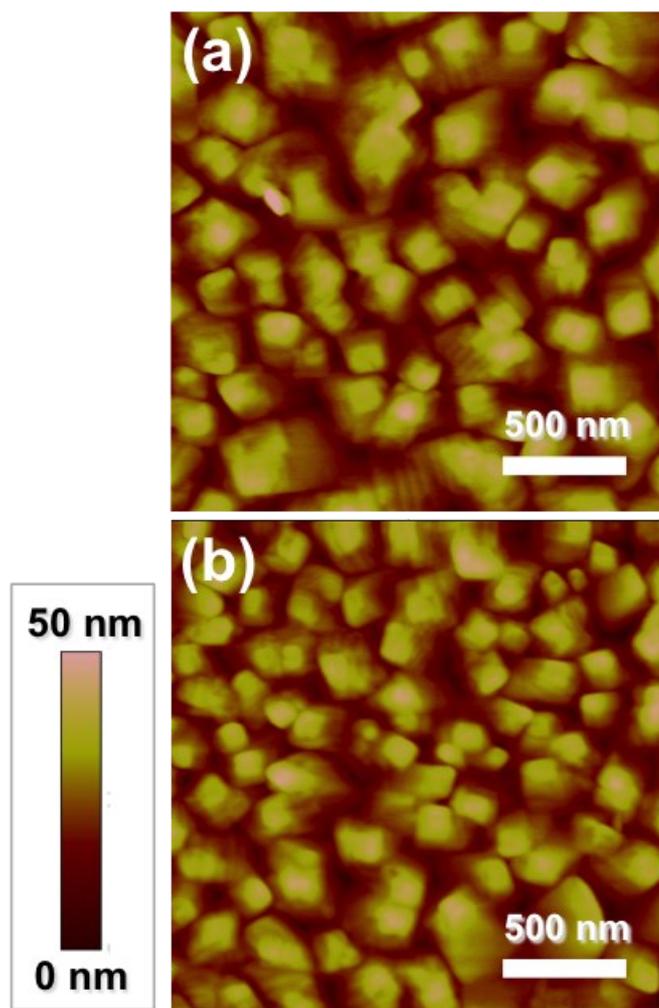
Figure S8. AFM height images of the pentacene layer deposited onto the spin-coat thin films of studied nanoparticles (from 3.0 mg/mL in chloroform) with different PEGMA:DB3VT ratios: (a) 90:10 and (b) 77:23.
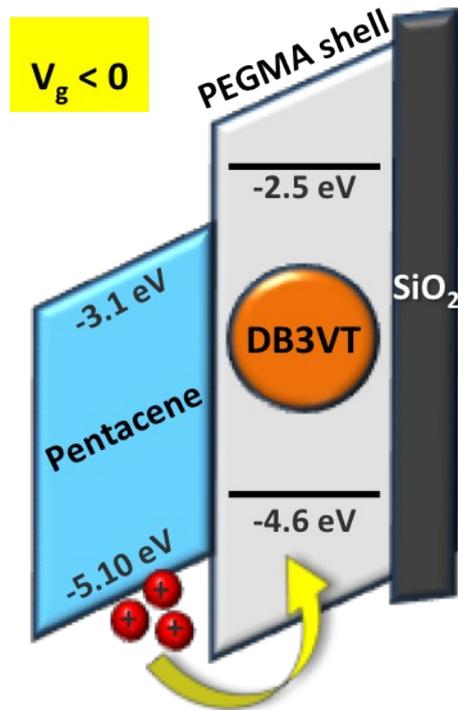
Figure S9. Energy diagram and the proposed charge-trapping mechanism: pentacene and both moieties of the studied cross-linked poly(PEGMA)$_m$-*b*- poly(DB3VT)$_n$ nanoparticles.
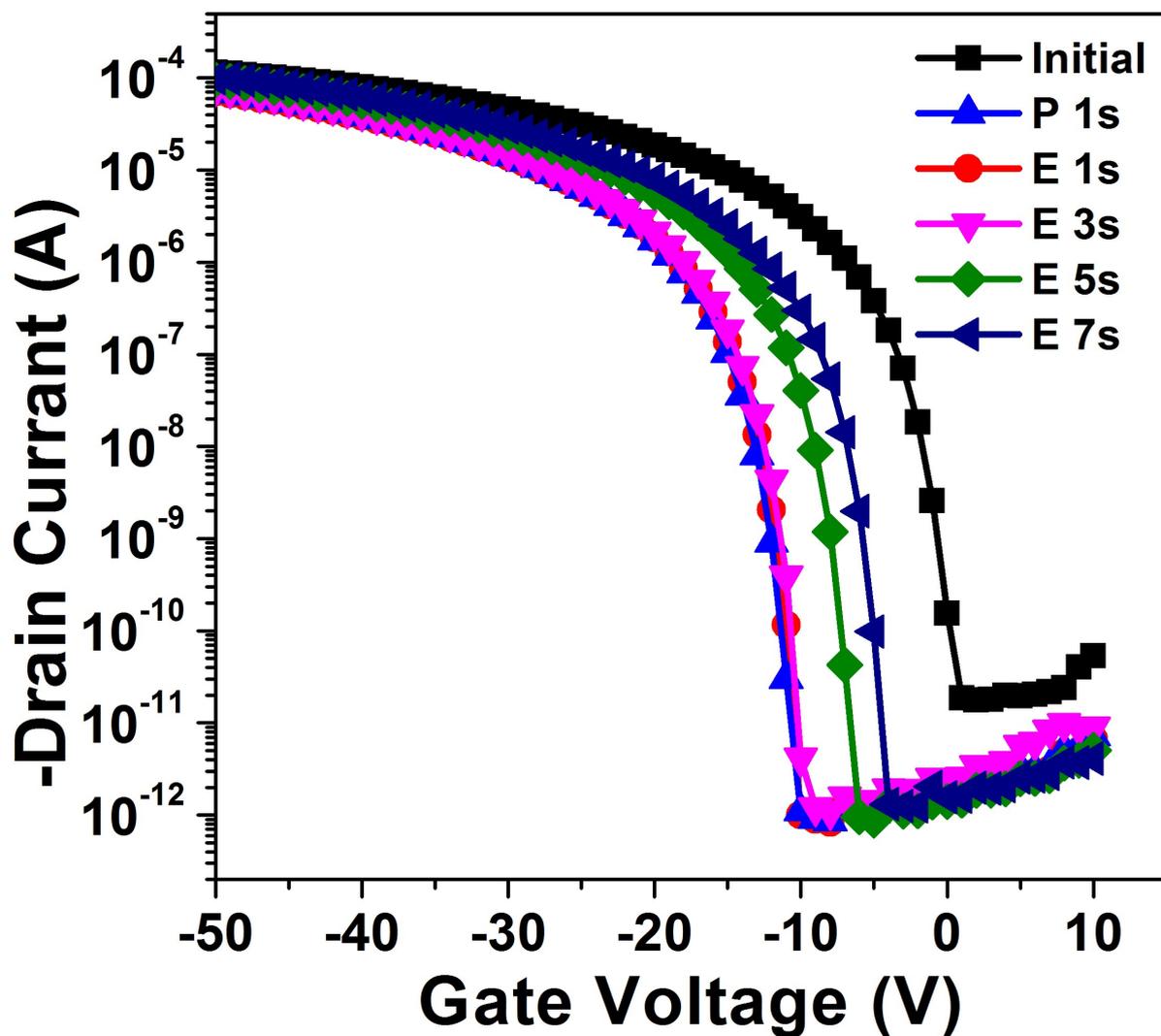
Figure S10. Transfer characteristics of the OFET memory devices using poly(DB3VT) homopolymer as dielectric layer: the device was first programmed using −50 V gate bias (P) for 1 s, and then was respectively erased using 50 V gate bias (E) for 1 s, 3 s, 5 s, and 7 s.
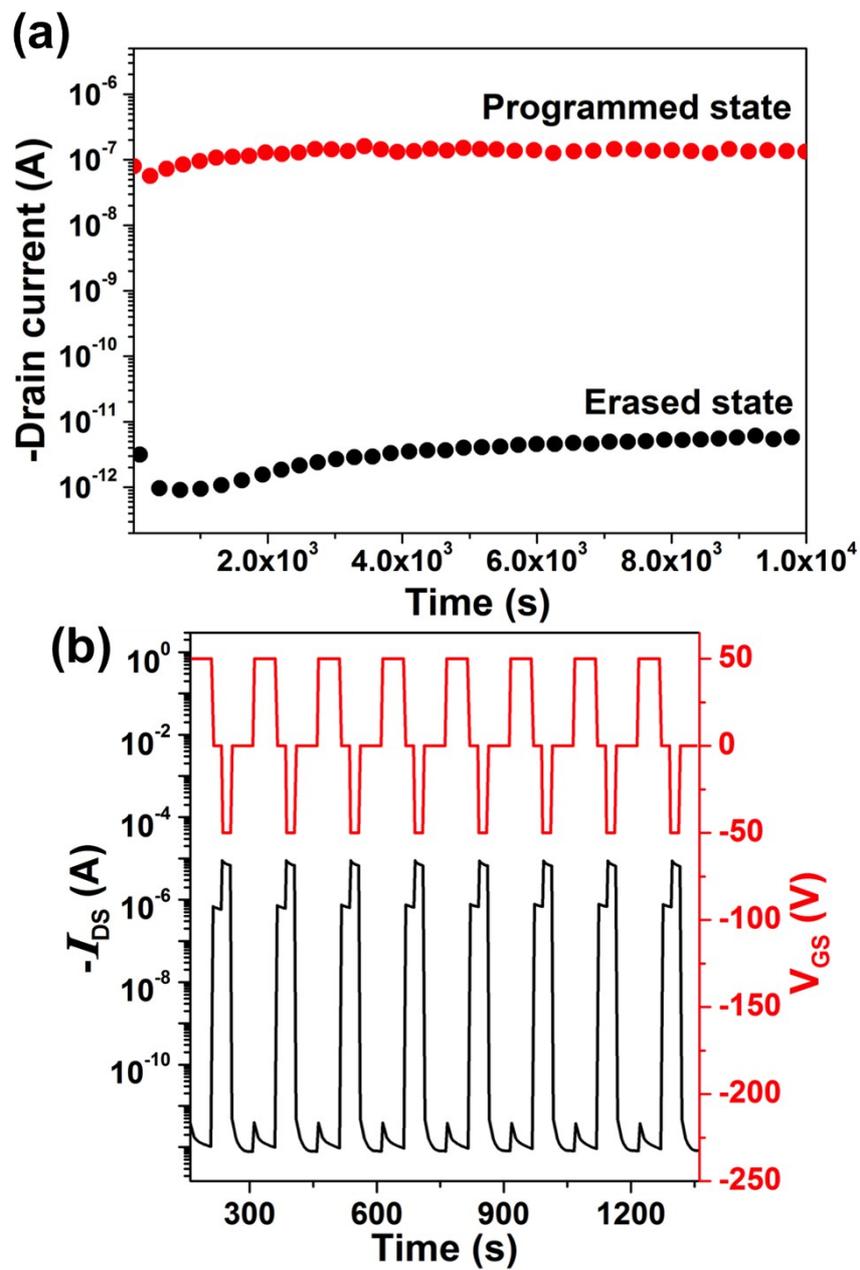
Figure S11. (a) Retention characteristics and (b) reversible current response to the WRER cycles of the cross-linked poly(PEGMA)$_{77}$-b-poly(DB3VT)$_{23}$ nanoparticle devices.
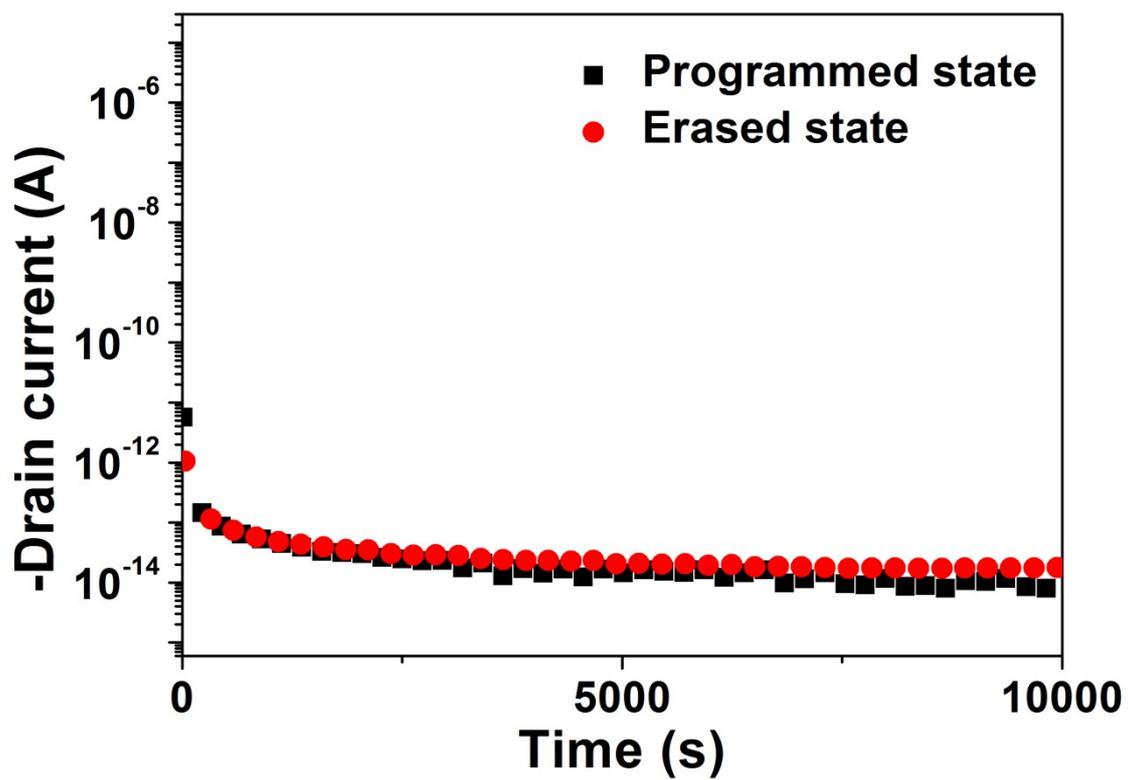
Figure S12. Retention characteristics of the device using poly(DB3VT) homopoylmer as dielectric layer.