

SUPPORTING INFORMATION ACCOMPANYING:

**Direct Synthesis of CdSe Nanocrystals within a Conducting Metallopolymer:
Toward Improving Charge Transfer in Hybrid Nanomaterials**

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General Methods

Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry nitrogen or argon. All solvents were dried using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. NMR spectra were recorded on a Mercury 400 MHz spectrometer (^1H , 400 MHz) and/or a Varian 300 Unity Plus spectrometer (^1H , 300 MHz). ^1H NMR signals are reported relative to residual solvent peaks. All NMR peaks are reported in ppm and coupling constants are reported in Hz. Elemental analyses were performed by QTI, Whitehouse, NJ (www.qtionline.com). Low-res and high-res mass spectrometry were carried out by Thermo Finnigan TSQ 700 and Waters Autospec Ultima, respectively. Infrared spectra were recorded using a Nicolet IR 200 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5700 XPS system equipped with a dual Mg X-ray source and monochromatic Al X-ray source complete with depth profile and angle-resolved capabilities. 3',4'-dinitro-2,2':5',2''-terthiophene was prepared as reported in the literature.¹ The starting material, 2-hydroxy-4-methylbenzaldehyde (from Aldrich), and other commercially available reagents were used without further purification.

Syntheses of ligand (L) and monomer (M1)

3',4'-diamino-2,2':5',2''-terthiophene

3',4'-dinitro-2,2':5',2''-terthiophene (1.0 g), iron powder (250 mesh, 2.2 g), and acetic acid (45 mL) were mixed and heated at 60 °C for 30 minutes. The reaction mixture was cooled and poured into deionized H_2O (100 mL) and extracted with diethyl ether (3x 50 mL). The organic layer was washed with a sodium bicarbonate solution and then rinsed 3 times with brine and water. After drying over anhydrous Na_2SO_4 , the solvent was removed by rotary evaporation to

afford the desired product as a brown-yellow solid (0.7 g, 84%). ^1H NMR (CDCl_3): δ 7.25 (dd, 2H, $J = 1.6, 4.5$), 7.07–7.01 (m, 4H), 3.80 (s, 4H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) 135.9, 133.5, 127.8, 124.0, 123.9, 110.0.

***N,N'*-Bis(4-methylsalicylidene)-3',4'-diamino-2,2':5',2''-terthiophene (L)**

To a solution of 3',4'-diaminoterthiophene (1.07 g, 5 mmol) in ethanol (20 mL) was added 2-hydroxy-4-methylbenzaldehyde (1.36 g, 10 mmol). The reaction mixture was brought to reflux for 20 hours. The mixture was cooled to room temperature, concentrated, and stored in the refrigerator (5 °C) overnight. The precipitate was collected by vacuum filtration to give the desired product (1.8 g, 71%). ^1H NMR ($\text{DMSO}-d_6$): δ 11.45 (s, 2H), 8.77 (s, 2H), 7.57 (dd, 2H, $J = 1.1, 5.2$), 7.41 (d, 2H, $J = 2.2$), 7.32 (dd, 2H, $J = 1.1, 3.6$), 7.20 (dd, 2H, $J = 2.2, 8.4$), 7.09 (dd, 2H, $J = 3.6, 5.2$), 6.82 (d, 2H, $J = 8.4$), 2.20 (s, 6H). ^{13}C $\{^1\text{H}\}$ NMR: compound was not sufficiently soluble in any common organic solvent to obtain a spectrum. HRMS (CI+) m/z calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_3$ 514.0843, found 514.0839.

***N,N'*-Bis(4-methylsalicylidene)-3',4'-diamino-2,2':5',2''-terthiophene cadmium(II) (M1)**

To a solution of ligand L (0.206 g, 0.4 mmol) in methylene chloride (20.0 mL) was added a solution of NaOMe (0.046 g, 0.85 mmol) in 5 mL of methanol. The mixture was stirred for three hours before adding a solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.106 g, 0.4 mmol) in 6 mL of methanol. The reaction mixture was stirred at room temperature for 20 hours then the methylene chloride was removed *in vacuo*, resulting in a suspension in methanol. The dark yellow solid was collected by filtration and dried to give the desired product (0.17 g, 68%). ^1H NMR ($\text{DMSO}-d_6$): δ 8.32 (s, 2H), 7.63 (d, 2H, $J = 5.2$), 7.29 (d, 2H, $J = 3.6$), 7.13 (dd, 2H, $J = 3.6, 5.2$), 6.95 (d, 2H, $J = 8.4$), 6.54 (s, 2H), 6.48 (d, 2H, $J = 8.4$), 2.07 (s, 6H). ^{13}C $\{^1\text{H}\}$ NMR: compound was not sufficiently

soluble in any common organic solvent to obtain a spectrum. HRMS (CI+) m/z calculated for $C_{28}H_{20}CdN_2O_2S_3$ 625.9809, found 625.9807.

Electrochemistry

Electrochemical syntheses and studies were performed in a dry-box under a nitrogen atmosphere using a GPES system from Eco. Chemie B. V. All the electrochemical experiments were carried out in a three-electrode cell with a Ag/AgNO₃ reference electrode (silver wire dipped in a 0.01 M silver nitrate solution with 0.1 M [(*n*-Bu)₄N][PF₆] in CH₃CN), a Pt button working electrode, and a Pt wire coil counter electrode. Potentials were referenced relative to the 0.01 M Ag/AgNO₃ reference electrode. Ferrocene was used as an external reference to calibrate the reference electrode before and after experiments were performed, and that value was used to correct the measured potentials. The supporting electrolyte was 0.1 M [(*n*-Bu)₄N][PF₆] (TBAPF₆) that was purified by recrystallization three times from hot ethanol before being dried for 3 days at 100-150 °C under dynamic vacuum. Electrosyntheses of the films were performed from 5×10^{-4} M monomer solutions by continuous cycling between -0.5 V and 1.5 V at 100 mVs⁻¹. The films obtained were then repeatedly washed with fresh CH₂Cl₂ before continuing on to the next set of experiments.

UV-vis-NIR spectroelectrochemistry

The spectroelectrochemical measurements were performed using the previously described cell arrangement on a polymer film deposited on ITO coated glass substrate as working electrode, a platinum mesh as the counter electrode, and Ag/AgNO₃ as reference electrode. Experiments were carried out in an optical cuvette inside the glovebox. Absorption spectra were recorded on a Varian Cary 6000 UV-vis-NIR spectrophotometer within the NIR/visible spectra ($1600 \geq \lambda \geq 400$ nm) under several applied potentials.

Electron paramagnetic resonance spectroscopy (EPR)

EPR experiments were recorded on a Bruker EMX-Plus X-band spectrometer at 100 K. *Ex-situ* EPR of metallopolymer films were recorded by first depositing the polymer film on platinum mesh in the glovebox. In a pure electrolyte solution, a potential of 1.0 V was applied to the films for one minute. The polymer films were then put into EPR tubes and capped carefully. The samples were then taken out of the glove box and kept in liquid nitrogen until performing the EPR measurement. Deconvolution of EPR spectra of two polymer types was done using the Bruker WinEPR Processing software.

Light-induced EPR was recorded for metallopolymers containing CdSe NCs. The film was put into an EPR tube and annealed at 90 °C for 30 seconds. The annealed tube was then introduced to the cavity and cooled to 90 K before the dark spectrum was recorded. Subsequently, the sample was excited with 543.5 nm laser light and the excited spectrum was recorded.

Se²⁻ solution preparation

The Se²⁻ solution was synthesized according to a literature procedure.² Briefly, 0.1 g of SeO₂ is dissolved in 30 mL ethanol (30 mM), and purged with N₂, while stirring, for 15 minutes. Then NaBH₄ (0.068 g, 60 mmol) was added quickly to the reaction flask containing SeO₂ and stirred under N₂ flow until the solution became clear. The flask was transferred to the glove box and the solution was diluted with dry acetonitrile to obtain the desired concentration.

CdSe nanocrystal growth

The electropolymerized thin films were treated with a 2x10⁻⁴ M Se²⁻ solution in acetonitrile for one minute then rinsed thoroughly with dry acetonitrile. The film was then treated with a solution of Cd(NO₃)₂ in acetonitrile (2x10⁻⁴ M) for one minute followed by another rinse with

acetonitrile. The films were treated one more time with Se^{2-} solution, followed by rinsing. This process constitutes one cycle of the growth process, which was repeated up to six times.

Transmission Electron Microscopy (TEM)

TEM experiments were carried out on a JEOL 2010F microscope. Films were grown electrochemically onto 400 mesh carbon coated gold grids purchased from Electron Microscopy Sciences. Films were made by electropolymerization of **M1**, by cycling between -0.5 and 1.5 V four times. TEM grids containing the polymer film were kept in an air free environment and CdSe NCs were grown directly within the resulting polymer film. Analysis of the nanocrystals was done using Gatan Digital Micrograph software.

Energy-dispersive X-ray spectroscopy (EDS) elemental mapping

Scanning transmission electron microscopy (STEM)-EDS experiments were carried out on a Hitachi S-5500 SEM/STEM microscope. Films used in this measurement were prepared in the same manner as in the TEM experiment. The elemental map was recorded in a 10-second exposure time to avoid overshadowed signals. The fact that Cd and Se signals are not localized on the same nanocrystal in Fig. 4 could be due to two reasons: (i) The short time of measurement did not give enough statistics of Cd and Se signals for a single nanocrystal although it is sufficient to show the distribution of these two elements throughout the entire film; (ii) As the polymer film is contains Cd(II) centers before the NC growth, some EDS signals for Cd can also be derived from Cd(II) sites of the metallopolymer which do not act as nucleation points in the NC growth.

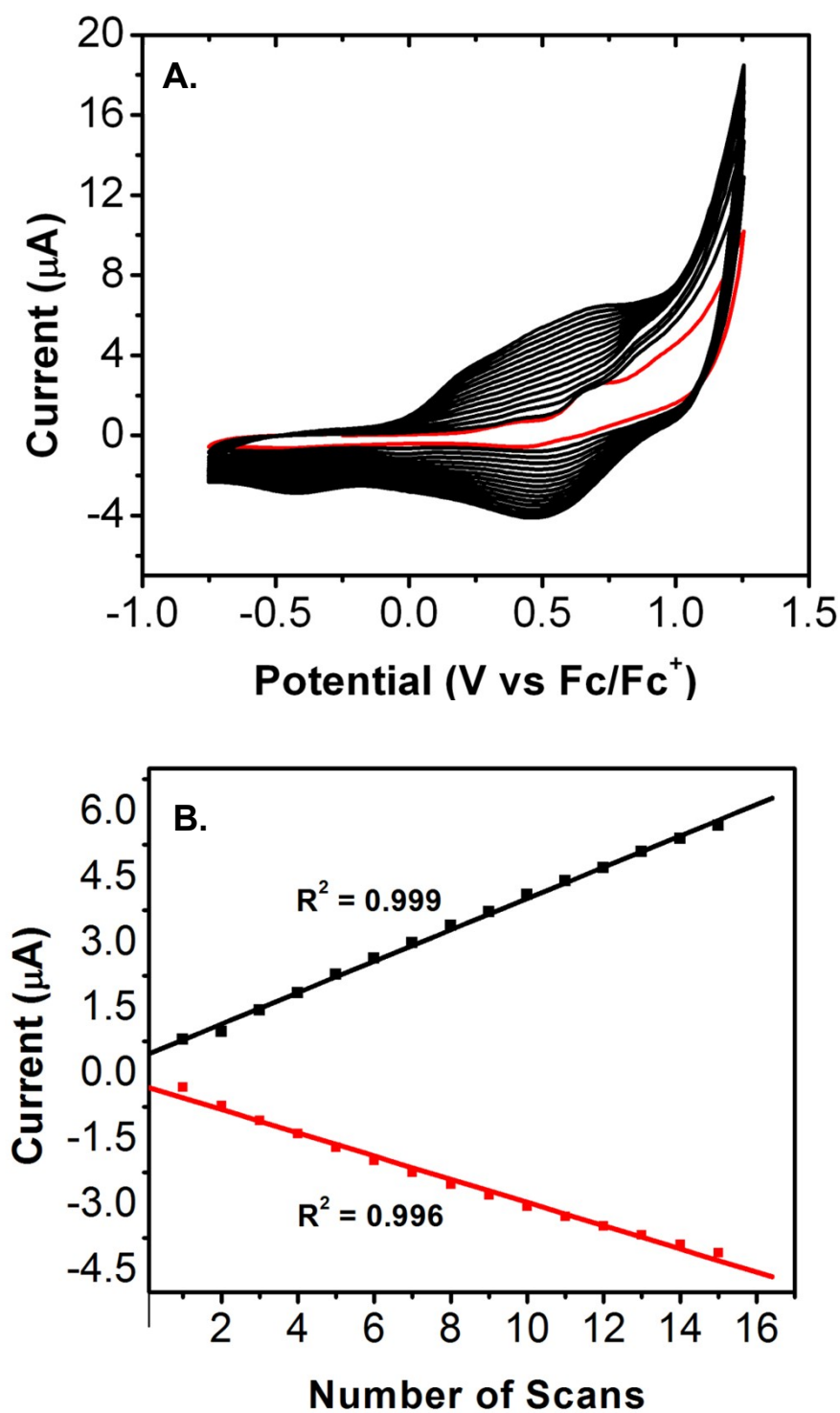


Figure S1. (A) Electropolymerization of M1 from a 2×10^{-4} M CH_2Cl_2 solution, 0.1 M TBAPF₆, Pt button electrode. (B) The peak current versus the number of scans.

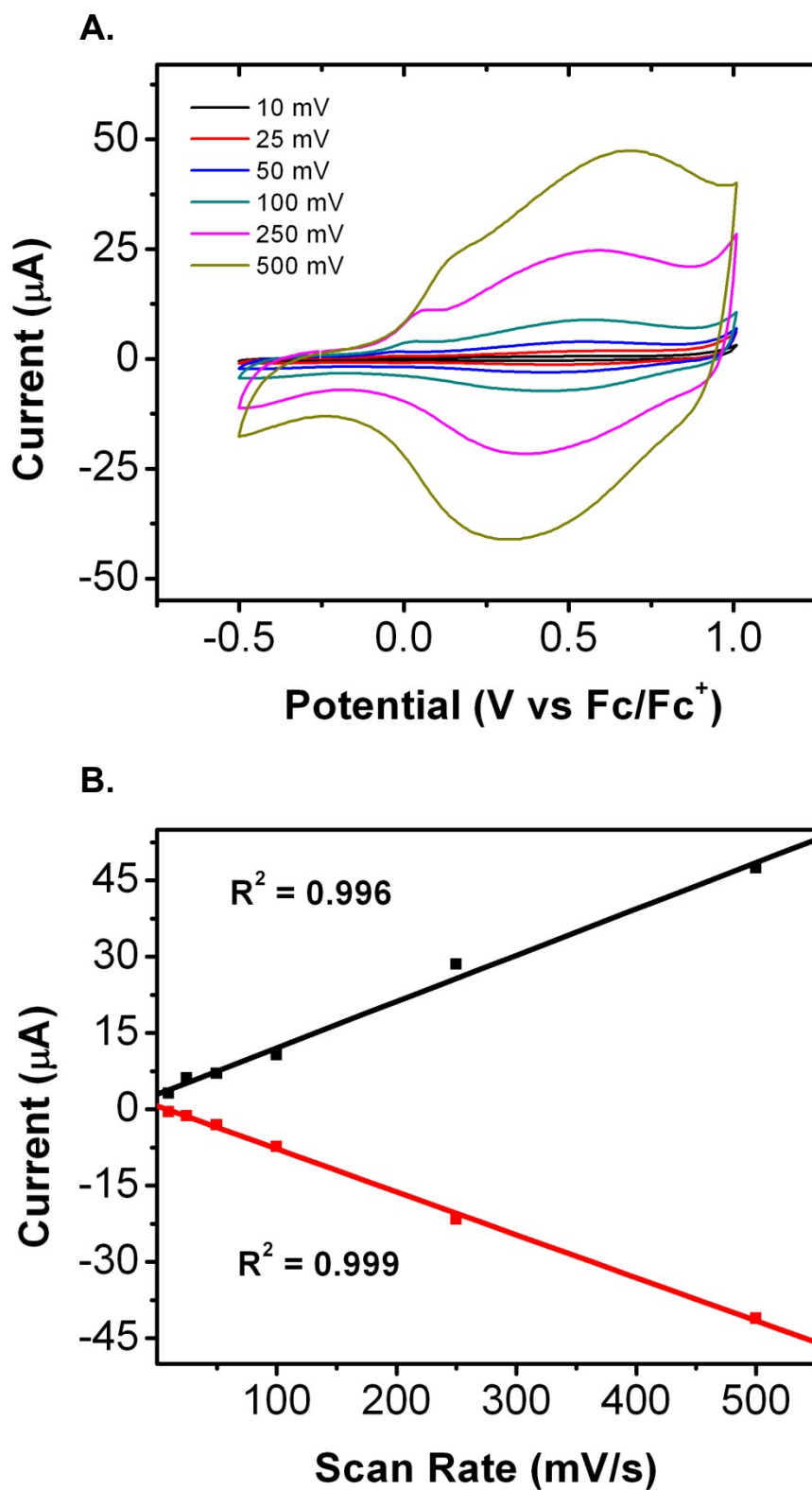
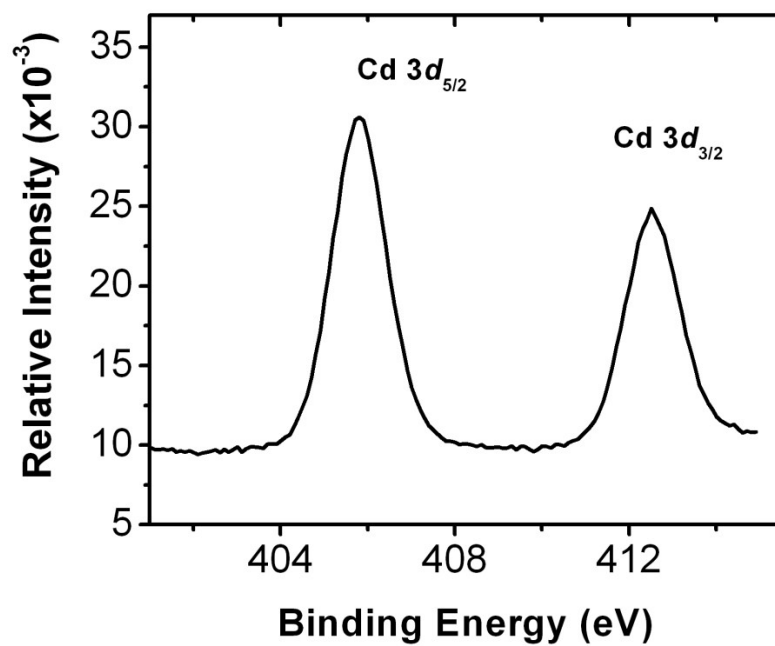


Figure S2. (A) Scan rate dependence of an electrode-confined film of **poly-1** using a 0.1 M TBAPF₆/CH₂Cl₂ electrolyte solution. (B) The peak current versus the scan rates.

A.



B.

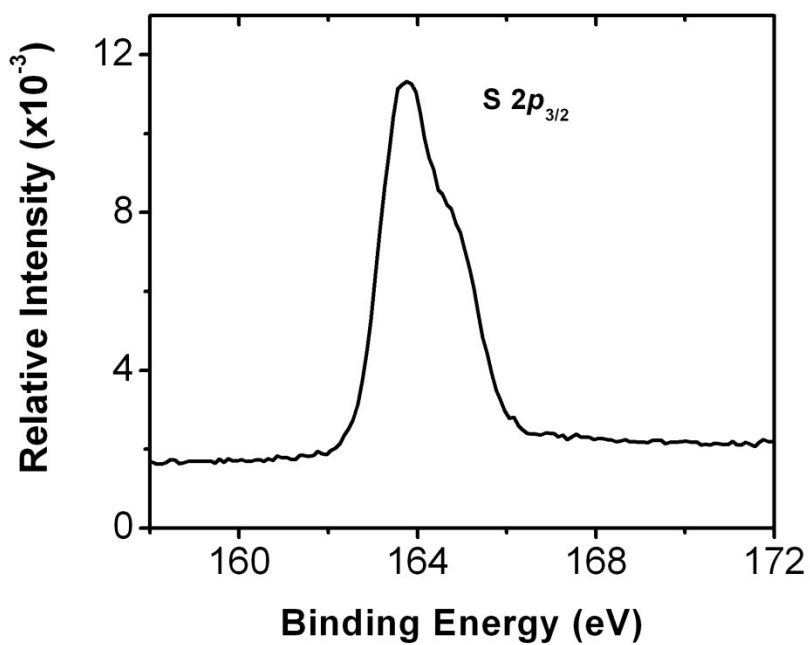


Figure S3. XPS data of **poly-1** (A) Cd 3d (B) S 2p.

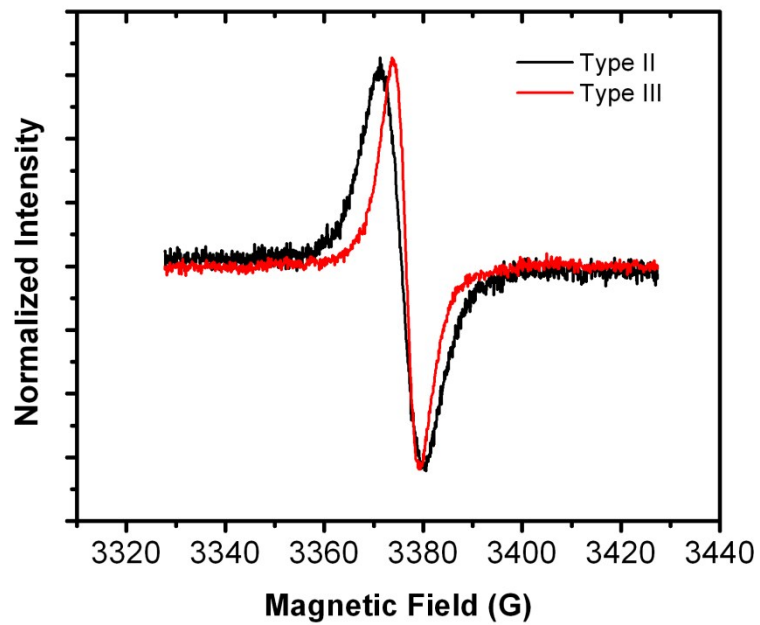


Figure S4. *Ex-situ* EPR spectra of the Wolf Type II (black line) and Type III (red line) conducting metallopolymers recorded at 100 K, microwave power: 2 mW, modulation amplitude: 2 G.

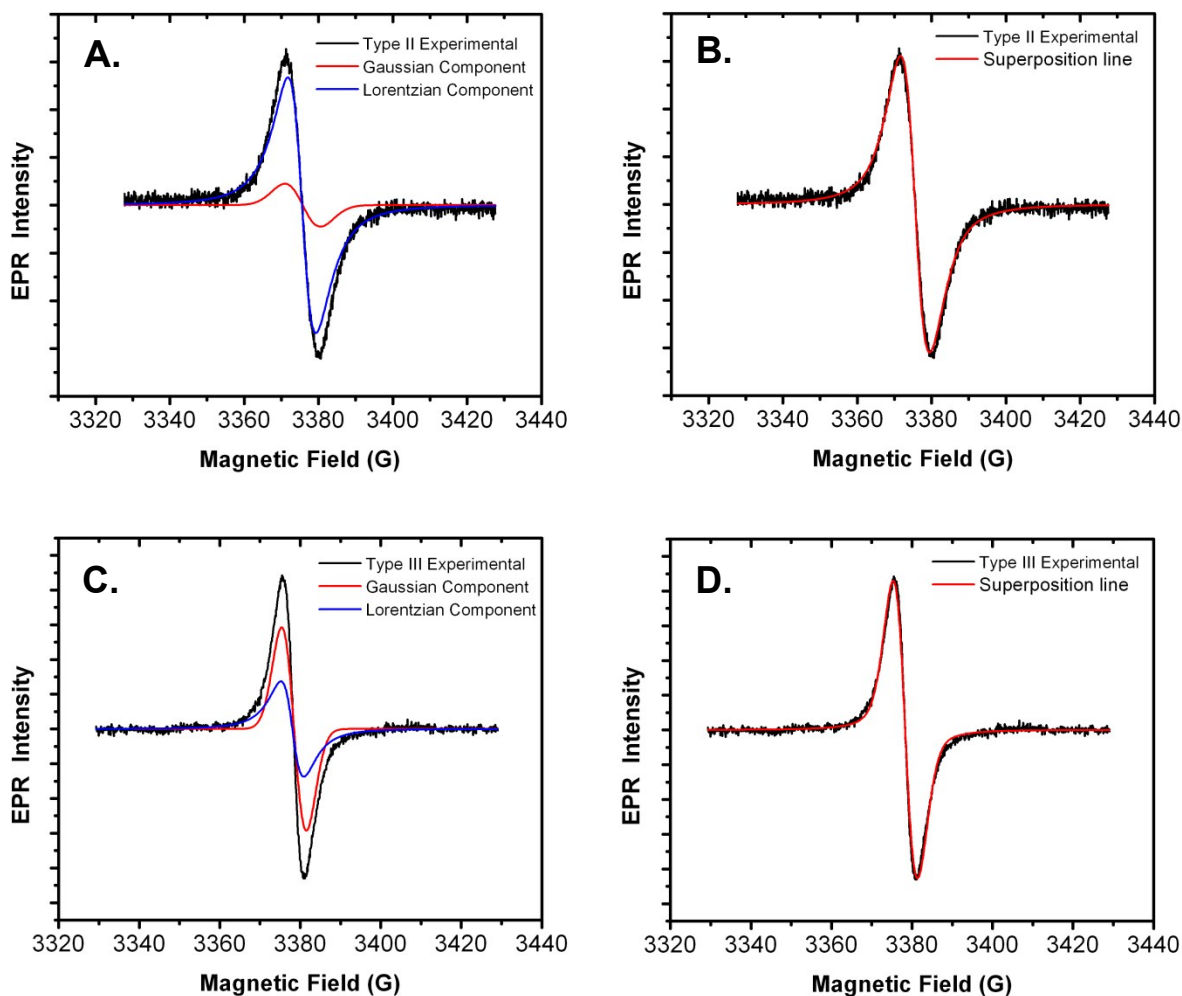


Figure S5. Deconvolution of EPR spectra of the Wolf Type II and Type III conducting metallopolymer into Lorentzian and Gaussian components. (A) Type II polymer, Gaussian linewidth: 13.00 G, Lorentzian linewidth: 9.57 G. (B) Gaussian/Lorentzian superposition of Type II conducting metallopolymer. (C) Type III polymer, Gaussian linewidth: 9.84 G, Lorentzian linewidth: 6.13 G. (D) Gaussian/Lorentzian superposition of Type III conducting metallopolymer.

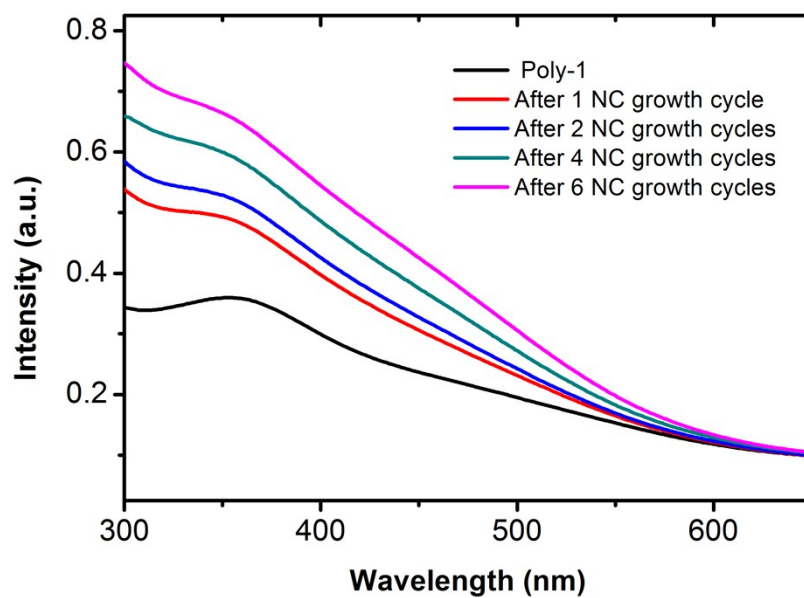


Figure S6. UV-vis spectra of **poly-1** films measured before and after treatment with 1-6 CdSe NC growth cycles.

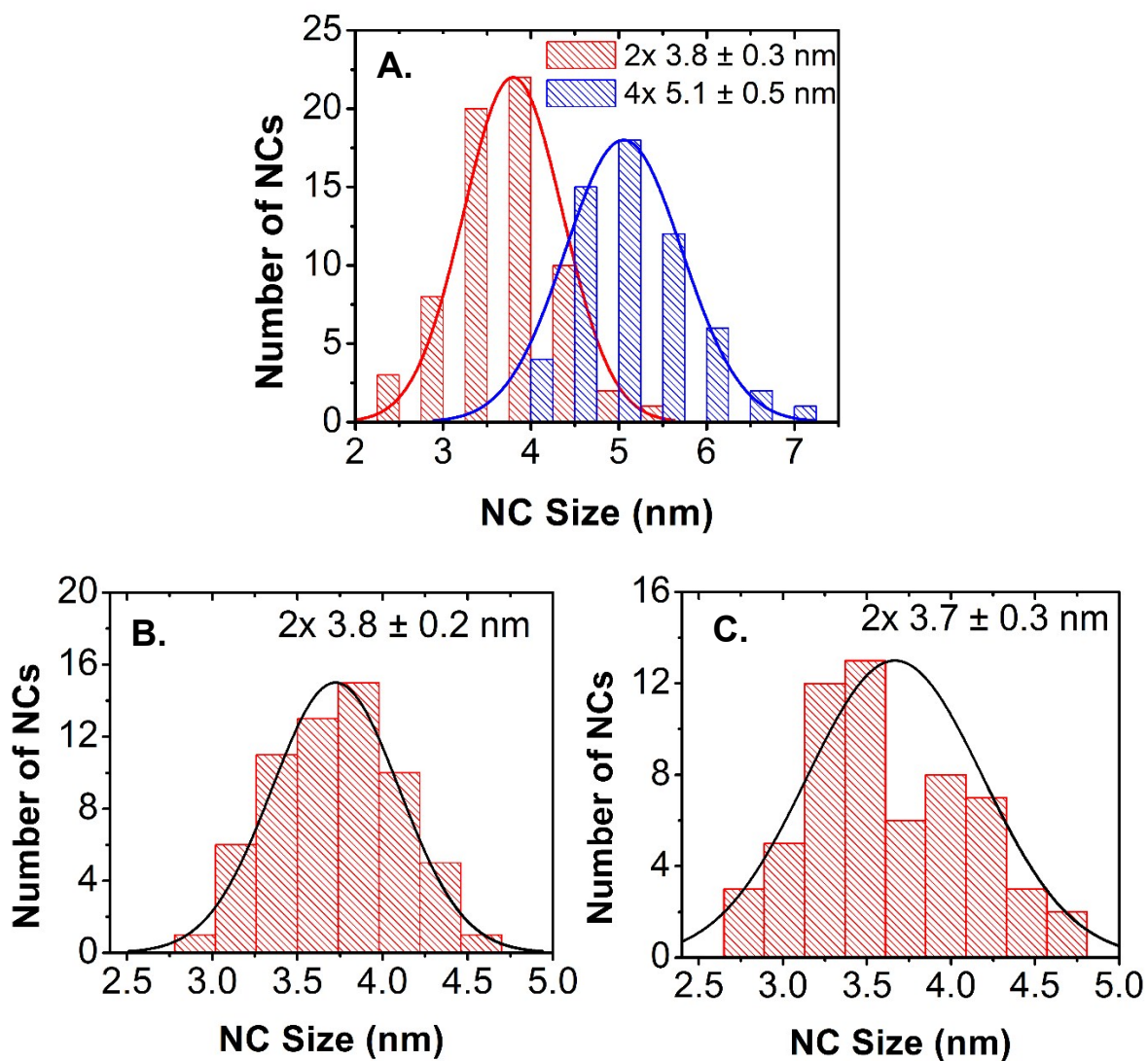


Figure S7. CdSe NCs size distribution in **poly-1** films (A) with the same thickness and different NC growth cycles, 2x vs. 4x (B) film thickness: 1 CV scan, 2x NC growth cycles (C) film thickness: 4 CV scan, 2x NC growth cycles.

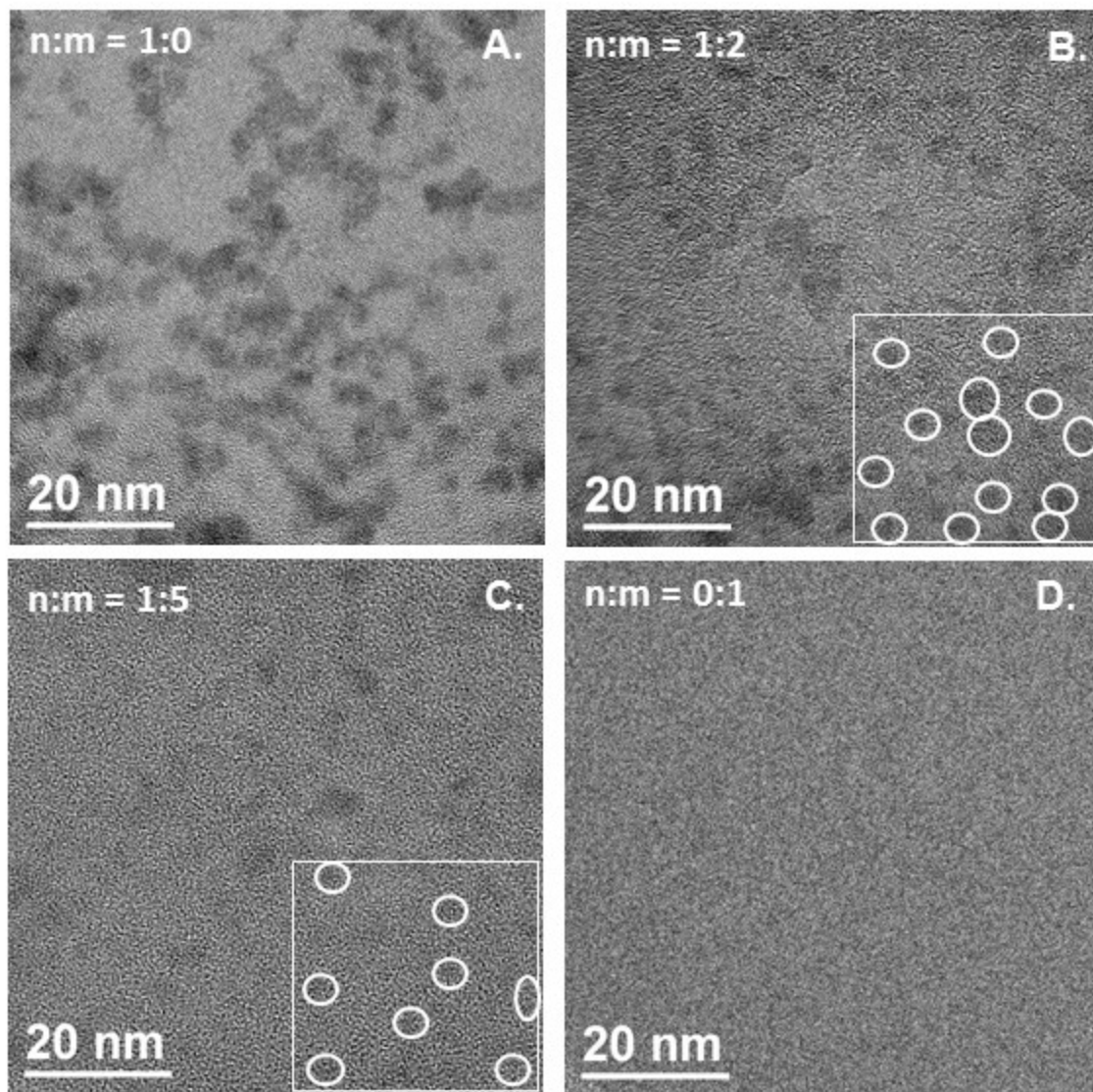


Figure S8. TEM images of $[\mathbf{M1}]_n[\text{bithiophene}]_m$ copolymer films at different ratios treated with 2x NC growth cycles (A) pure **poly-1**, $n:m = 1:0$ (B) copolymer, $n:m = 1:2$ (C) copolymer, $n:m = 1:5$ (D) pure polybithiophene, $n:m = 0:1$.

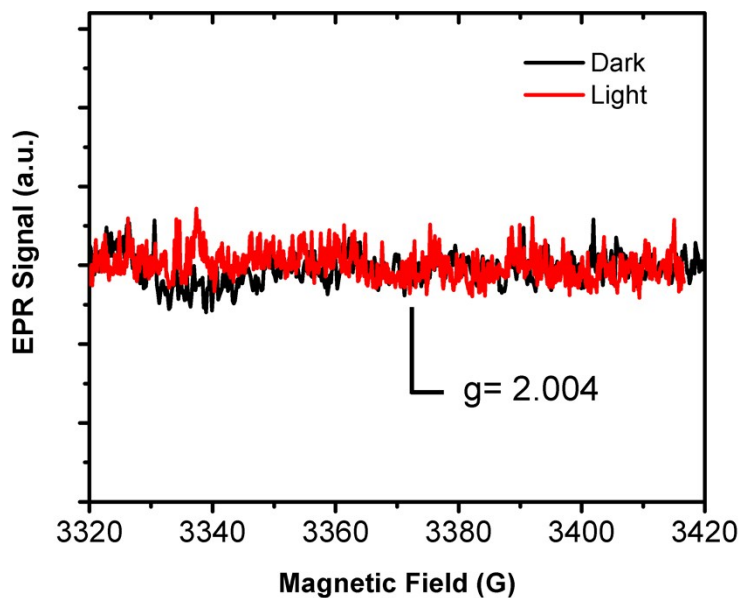


Figure S9. EPR spectra of the Wolf Type II metallopolymer recorded at $P_{\text{microwave}} = 6$ mW in the dark (black line) and under 543 nm laser excitation (red line).

References

- 1) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570-578.
- 2) Lee, L.; Wang, M.; Chen, P.; Gamelin, D. R.; Zakeeruddin, S. M.; Gratzel, M.; Nazeeruddin, M. K. *Nano Lett.* **2009**, *9*, 4221-4227.