

Anionic polymerization by electron transfer process from a CdSe quantum dots - perylenediimide (PDI) system

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Materials and general methods

The authors thank BASF AG, Ludwigshafen, for providing 1,6,7,12-tetrachloroperylene-tetracarboxylic dianhydride.

The UV-Vis spectra were recorded using a Jasco V-500 spectrophotometer equipped with a temperature controlling unit. The fluorescence spectra were registered using a Jasco FP-6500 Able Jasco spectrofluorimeter.

The high resolution transmission electron microscopy (**HRTEM**) studies were performed on an atomic resolution analytical JEOL JEM-ARM 200F electron microscope, operating at 200 kV. Specimens for TEM were prepared in the following way: 5 drops from the CdSe colloid and 3 drops from the PDI-CdSe colloid were put on carbon coated copper grids and let dry in air on filter paper. The number of drops was chosen on trial, depending on the concentration of the colloidal solutions.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 300 spectrometer (¹H: 300 MHz; ¹³C: 75 MHz) and Bruker Avance DRX 500 for HMQC experiment. Chemical shifts are expressed in parts per million (ppm) downfield from residual THF residue. The following abbreviations are used: s, singlet; quint., quintuplet; m, multiplet. IR spectra were performed on a Bruker Vertex 70 spectrophotometer. Matrix-assisted laser-desorption/ionization mass spectrometry was performed on a Bruker Daltonics BIFLEX III spectrometer by using dithranol as the matrix. Elemental analysis was performed on a Thermo Fisher Scientific Flash 2000 CHNS/O analyzer.

The molecular weights of the resulted polymers and oligomers were analyzed using PL-GPC 50 Integrated GPC/SEC System (Agilent Technologies) using a 1 mL/min THF flow rate.

Experimental section

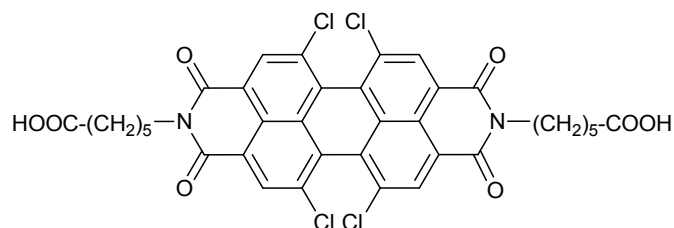
CdSe synthesis was realized using an aqueous-phase approach. The CdSe quantum dots were generated by directly mixing a solution Cd^{2+} (solution A) with another solution containing Se source as sodium hydrogen selenide (NaHSe) (Solution B).

Solution A: 0.07g (0.38 mmole) CdCl_2 were dissolved in 150 mL ultrapure water and 5 mL 2-mercaptoethanol; then the pH was adjusted to 11 using a NaOH solution. Prior to the addition of solution B the mixture was deoxygenated by bubbling nitrogen and heated to 80°C .

Solution B: 0.03 g (0.38 mmole) Se and 0.015 g (0.39 mmole) NaBH_4 were added to 100 mL ultrapure water and kept under continuous stirring until the dark colour disappeared.

After addition of solution B to the solution A the mixture was kept at 80°C for 30 minutes then cooled to 4°C and stored for further use.

Synthesis of PDI **1a** and characterizations:



6-Aminohexanoic acid (2.1g, 16 mmol) was added to a solution of 1,6,7,12- tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride (2.12 g, 4 mmol) in propionic acid (30 mL). The reaction mixture was heated under reflux for 48h. After cooling, the reaction mixture was poured into a mixture of THF (200 mL) and saturated NH_4Cl aqueous solution (50 mL). Following a first extraction, the organic layer was washed with a saturated NH_4Cl aqueous solution (3x50 mL), dried (MgSO_4) and concentrated under vacuum. After addition of methanol, the precipitate was filtered, washed with a HCl 1N aqueous solution (100 mL), then methanol. The solid was washed overnight with diethyl ether using a Soxhlet extractor. After drying under vacuum at 50°C for 2 h, 1.26 g of PDI **1a** was isolated as a red powder (42 % yield).

^1H NMR (THF- d_8 , 300 MHz) δ = 8.64 (s, 4H), 4.19 (t, $^3J = 7.3$ Hz, 4H), 2.26 (t, $^3J = 7.3$ Hz, 4H), 1.77 (m, 4H), 1.67 (m, 4H), 1.47 (quint., $^3J = 7.3$ Hz, 4H); the signal for the COOH proton was broad and centred around 2.6 ppm.

^{13}C NMR (THF-d₈, 300 MHz) δ = 174.2, 162.6, 135.5, 132.6, 132.2, 129.0, 124.8, 124.3, 40.9, 33.9, 28.4, 27.2, 25.7.

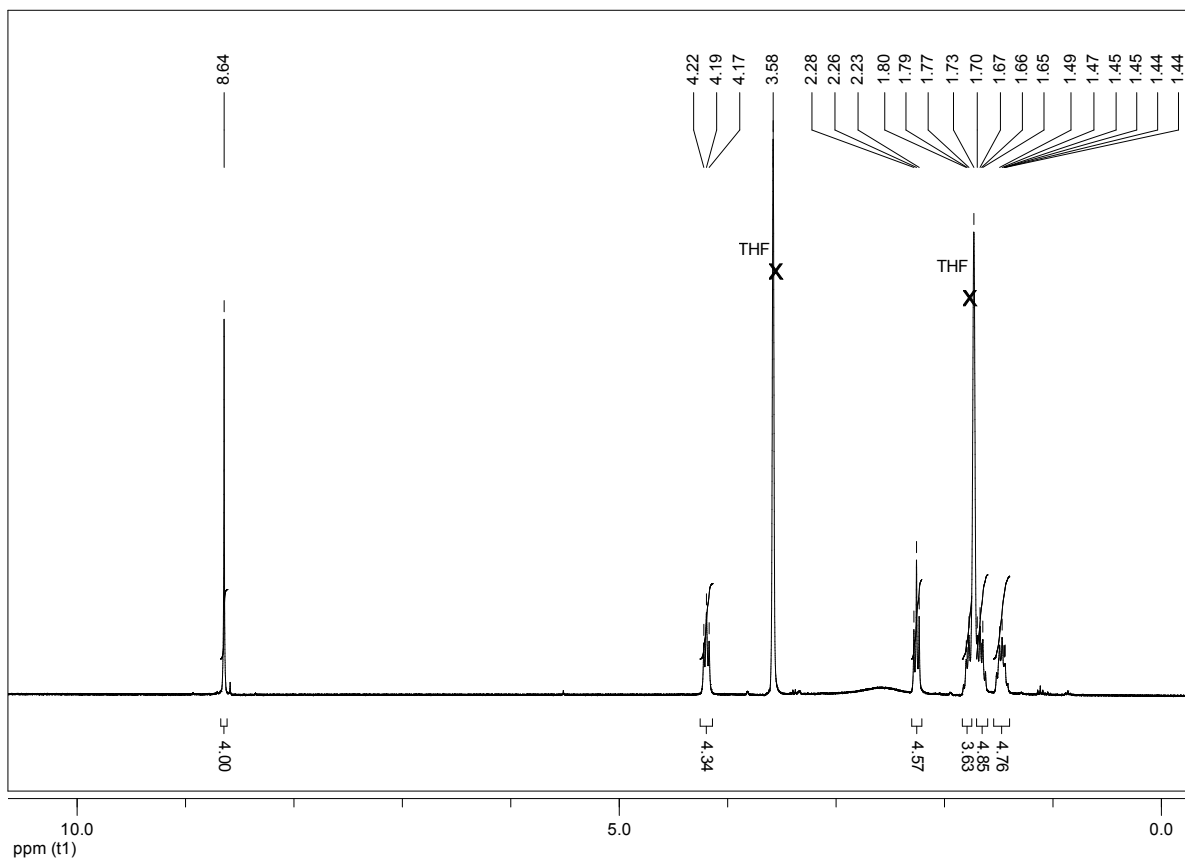
To demonstrate the presence of the peak of one -CH₂-group partially hidden under the peak of THF, a HMQC experiment was performed. One spot corresponding to a ^1H - ^{13}C correlation was unambiguously evidenced for this signal between the five peaks of THF.

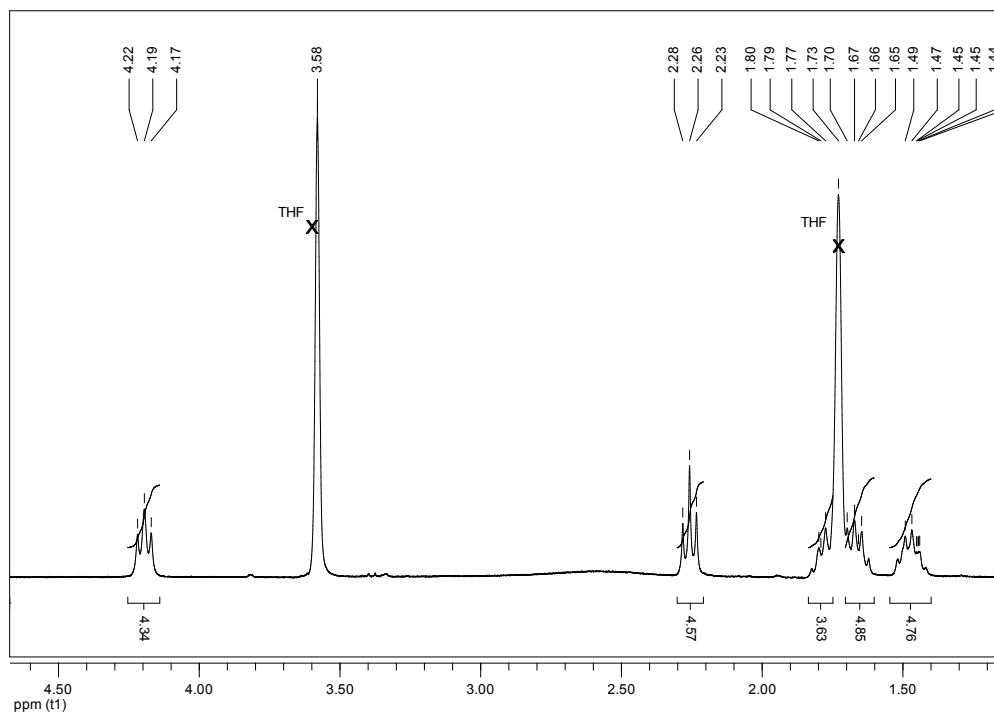
IR (neat, cm⁻¹): $\bar{\nu}$ = 1701 (C=O), 1659 (C=O), 1585 (C=C).

MS (MALDI-TOF) for C₃₆H₂₆Cl₄N₂O₈: 754.0

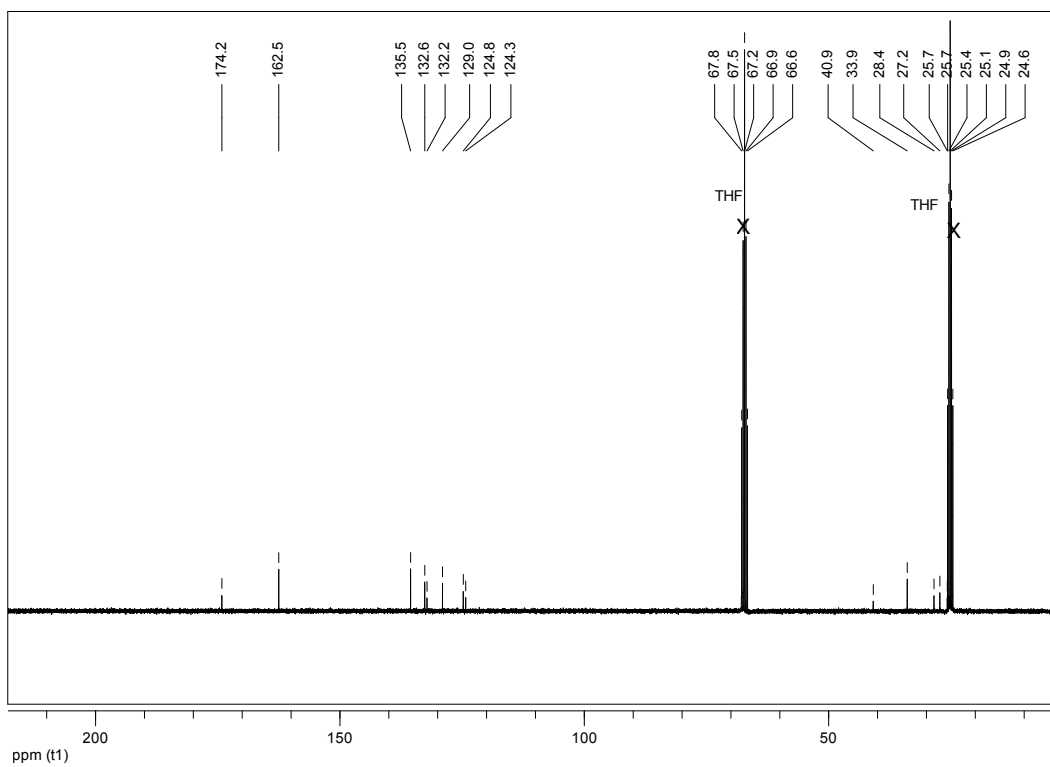
Anal. Calcd. for: C, 57.16; H, 3.46; N, 3.70. Found: C, 56.78; H, 3.49; N, 3.64.

^1H NMR (300 MHz, THF-d₈):

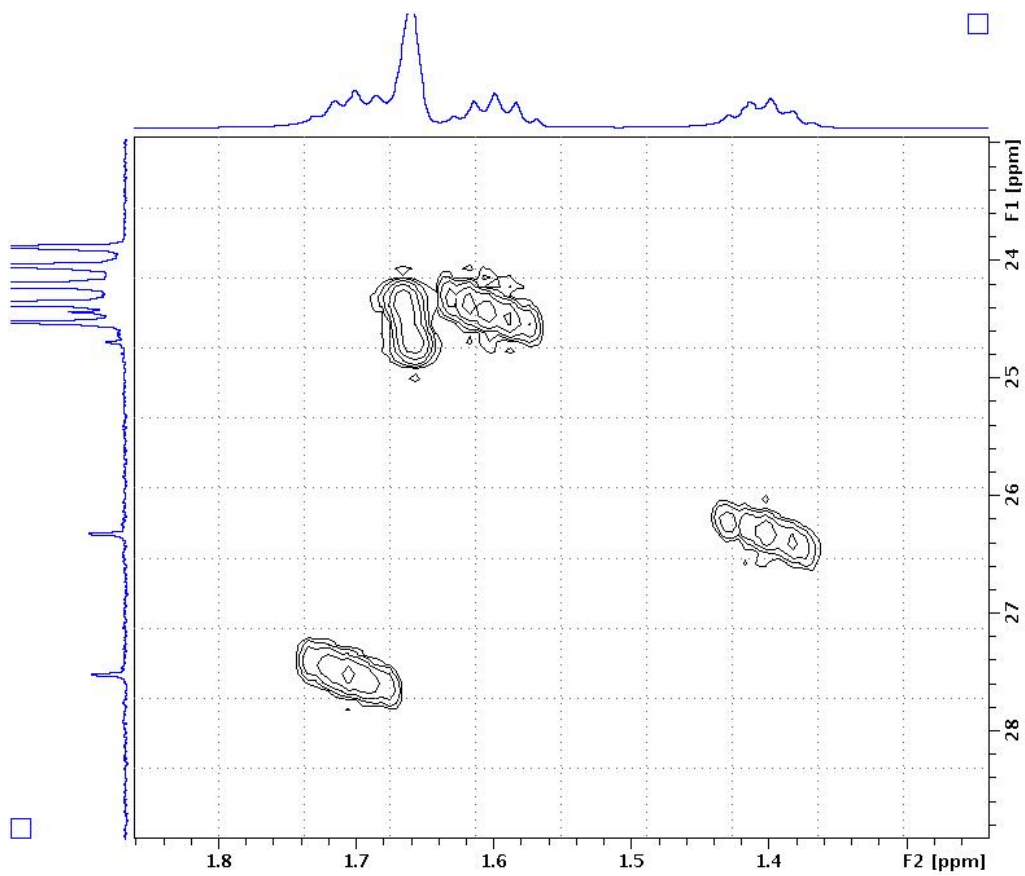
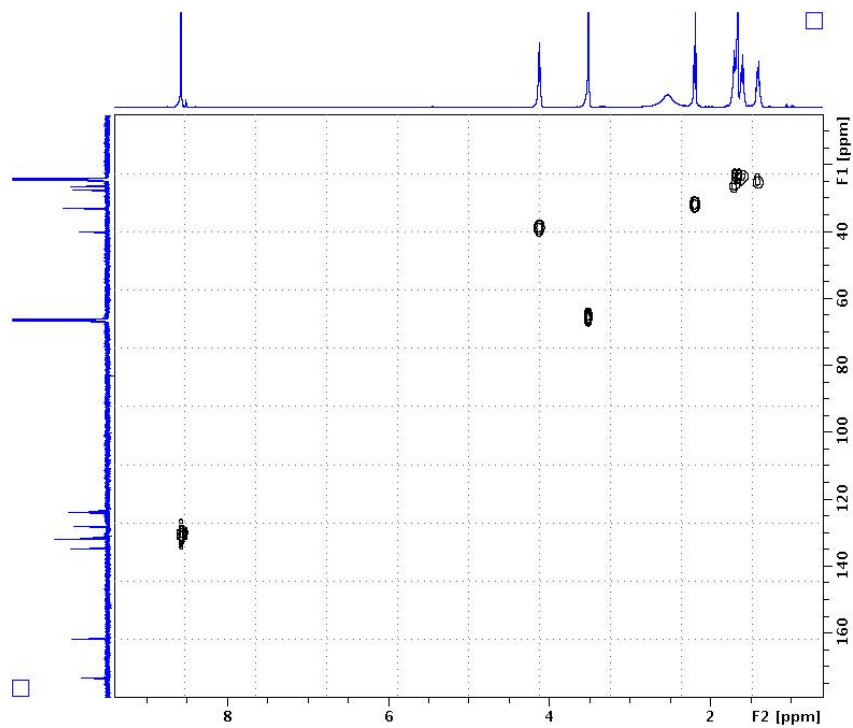




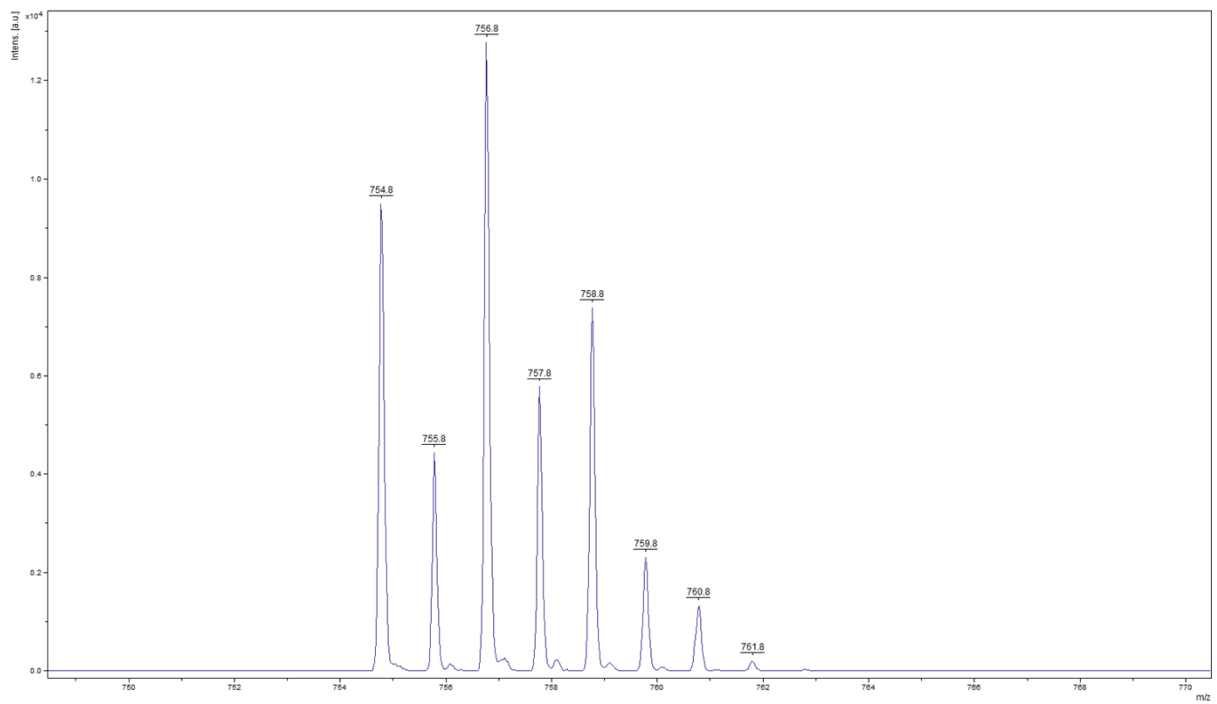
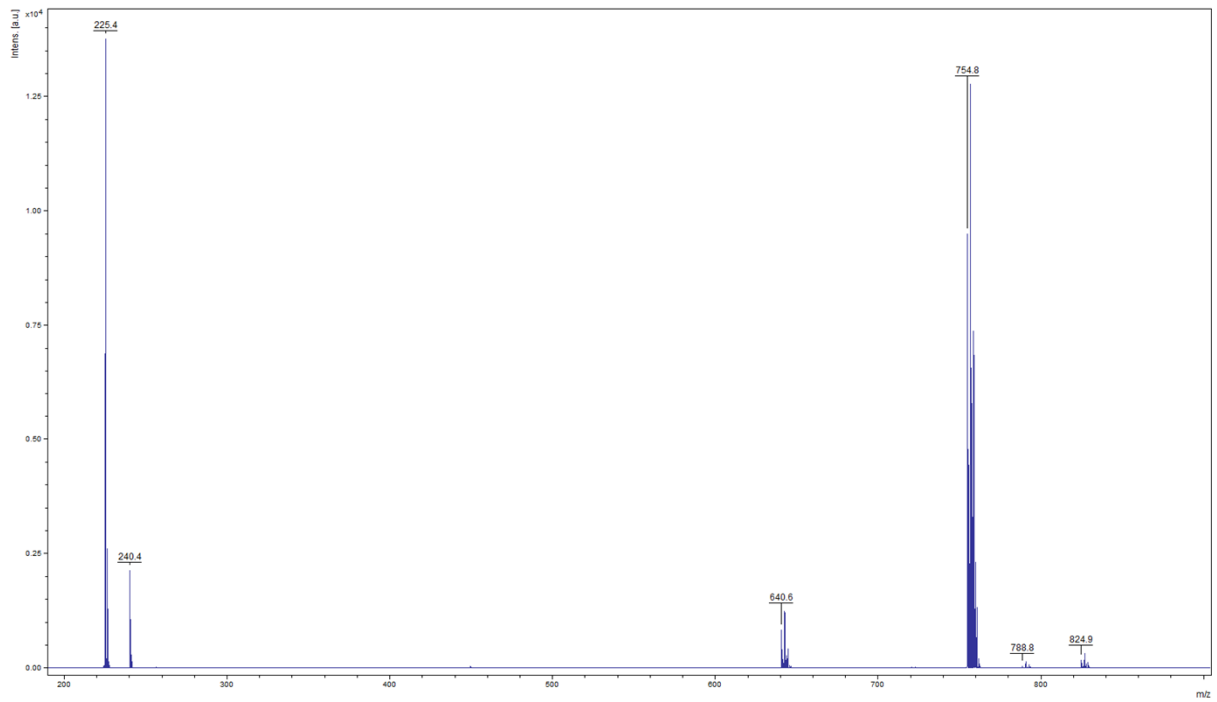
¹³C NMR (75 MHz, THF-d₈):



HMQC (^1H : 500 MHz; ^{13}C = 125 MHz, THF-d8):



Mass spectrum MALDI-TOF (negative mode, matrix = dithranol)



Preparation of PDI 1b

PDI **1b** solution was prepared by dispersing PDI **1a** in water followed by the adjusting of the pH to 12 under continuous stirring using a NaOH 0.5% solution.

Results

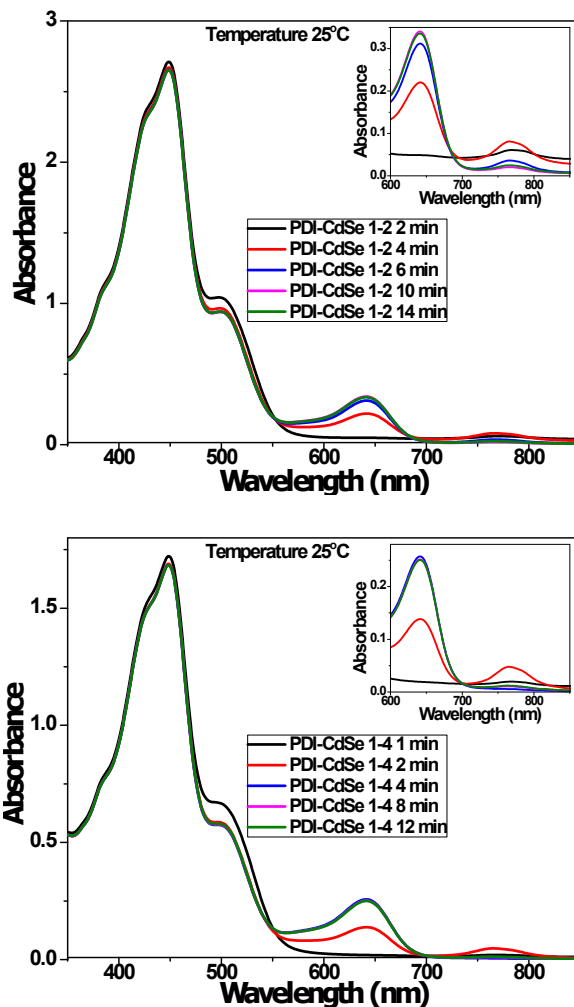


Figure S1: UV-Vis spectra PDI **1b** (conc. $4 \cdot 10^{-4} \text{ M}$ and $2.4 \cdot 10^{-4} \text{ M}$ respectively)-CdSe at different molar ratios at 25°C;

The high resolution transmission electron microscopy (**HRTEM**) studies were performed on an atomic resolution analytical JEOL JEM-ARM 200F electron microscope, operating at 200 kV. Specimens for TEM were prepared in the following way: 5 drops from the CdSe colloid and 3 drops from the PDI-CdSe colloid were put on carbon coated copper grids and let dry in air on

filter paper. The number of drops was chosen on trial, depending on the concentration of the colloidal solutions.

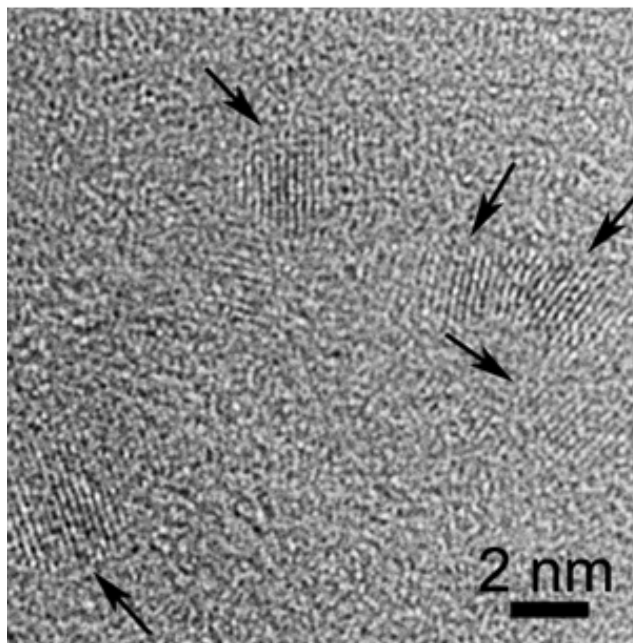


Figure S2: HRTEM image of the CdSe colloidal sample. Black arrows indicate the CdSe nanoparticles revealed by their fringe contrast at the crystalline planes. The interfringe distance of most of the crystallites is 0.2 nm, which corresponds to the (220) planes in the sphalerite (cubic) CdSe structure, or (110) in the wurtzite (hexagonal) CdSe structure. The average size of the CdSe nanoparticles as determined from several HRTEM images is 2 nm.

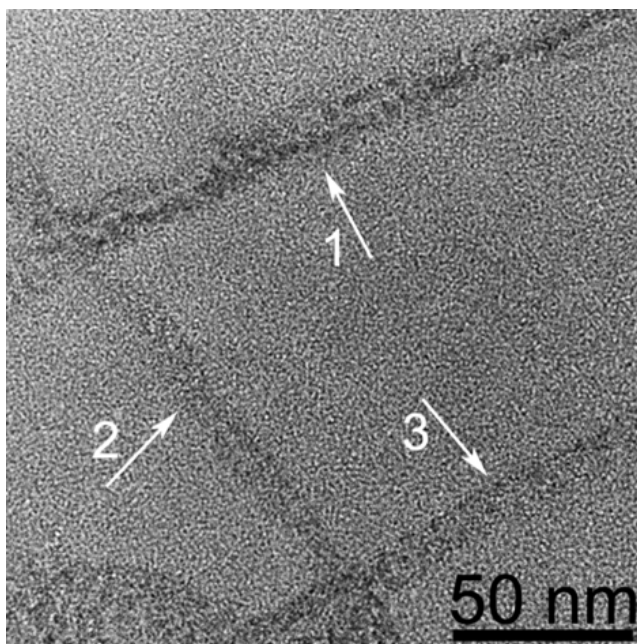


Figure S3 TEM image of an intersection of PDI fibers showing different covering with CdSe nanoparticles: arrow 1 indicates PDI fiber completely covered with CdSe QDs; arrow 2 indicates a fiber without CdSe nanoparticles while the fiber indicated by arrow 3 is partially covered with CdSe nanocrystals. Note that, since the CdSe nanoparticles are crystalline, they give a darker contrast in the TEM image.

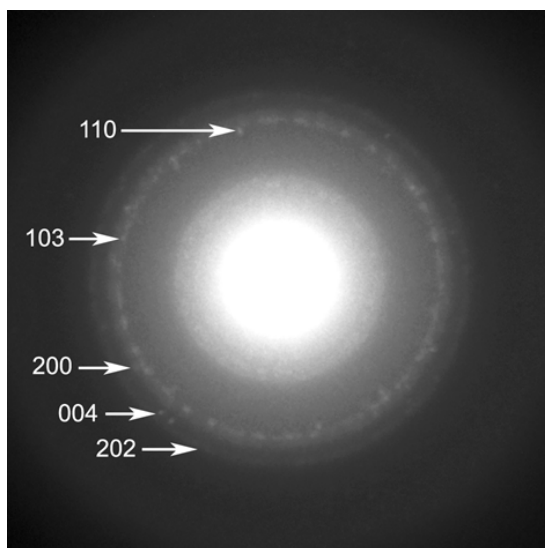


Figure S4 Electron diffraction pattern of the PDI aggregates covered with CdSe nanoparticles. The diffraction pattern is indexed with the wurtzite structure of CdSe, proving that, indeed, the nanocrystallites covering the PDI aggregates are of CdSe.

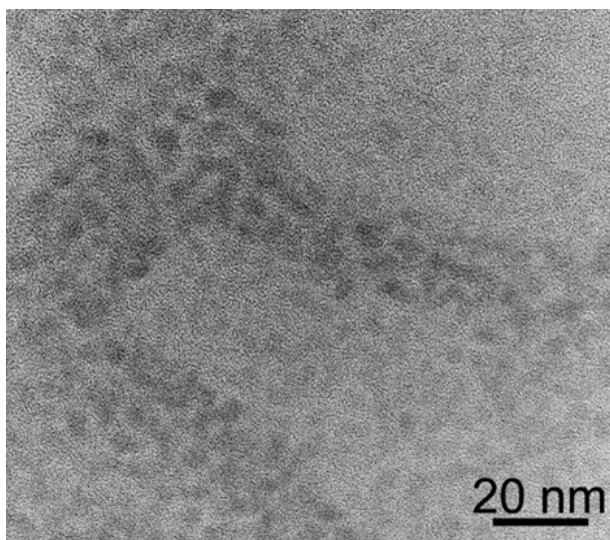


Figure S5. HRTEM image showing the preferential self-assembling of the CdSe QDs in rows of distinct nanoparticles along the PDI fibers.

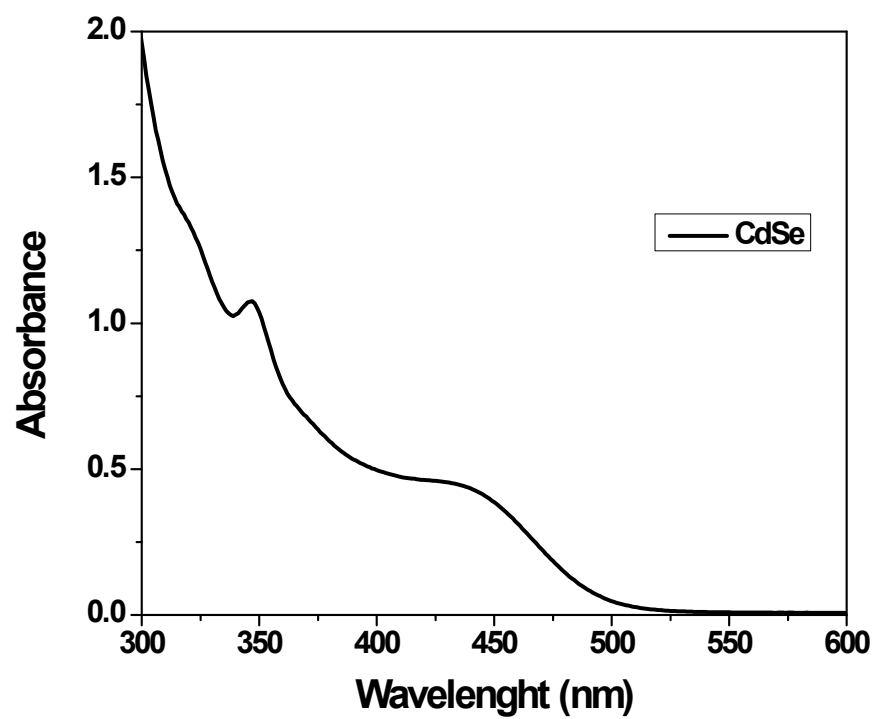


Figure S6. UV-Vis absorption spectra CdSe solution