

Surface Modification of CdSeS Nanocrystals for Polymer Hybrid Solar Cells

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S-1. Materials

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Carbazole, 2,7-dibromo-9H-fluorene, [4-(9H-carbazol-9-yl)phenyl]boronic acid, 1,2-dimethoxyethane and (4-cyanophenyl)boronic acid were purchased from Fluka; Acetone, dichloromethane, toluene, DMSO, 1,2-dimethoxyethane, tetrahydrofuran (THF), thiourea, ethanol, CdO, myristic acid, oleic acid, NaBH₄, Selenium powder were purchased from Merck. Potassium carbonate, NaH and [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) were purchased from Riedel de Haen.

S-2. Instrumentation

Electrochemical measurements for L1, MC1 and MC2 ligands were carried out with Bas Epsilon potentiometer. FT-IR spectra were recorded on a Bruker VERTEX 70 FT-IR Spectrometer using an ATR system (4000–400 cm⁻¹). ¹H and ¹³C NMR (Varian-400 MHz) data were recorded at 25°C using CHCl₃-d and d₆-DMSO as solvents and TMS as an internal standard. Bruker New Advanced8 model X-Ray diffractometer was used for structural analysis of CdSeS nanocrystals. NT-MDT NTEGRA Solaris model AFM was used for surface analysis of film layers.

Laurel brand spin coating system was used in coating. All cell fabrication and characterisation works are performed inside Mbraun^(R) brand glove box. For metal coating, a glove box integrated Leybold brand PVD is used. An Atlas brand AM 1,5 solar simulator and Keithley 2100 sourcemeter were used in performance tests of cells. For solar cells characterization and for obtaining the *J-V* curves, the samples were illuminated with Xe light using a Solar Light Co. solar simulator (model 16S-300) equipped with AM 0 and AM 1.5 direct Air Mass filters to simulate solar radiation at the surface of the earth. The light intensity was kept constant at 1000 W/m² measured with a Newport power meter (843-R). Finally, the *J-V* curves were recorded by connecting the cells to a Keithley Source Meter (model 2601A) which was controlled by Keithley computer software (LabTracer). We made three cells for each ligands which were tested under the same conditions in order to avoid any misleading estimation of their efficiency. Cell performance parameters, including short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), maximum power (P_{max}), fill factor (FF) and overall cell conversion efficiency η , were determined from each *J-V* characteristic curve.

S-3. Ligands and synthetic route

The chemical structures of the newly synthesized ligands are presented in Scheme 1. The electron donor in L1 is a carbazole group which in the case of MC1 and MC2 are coupled to an additional electron acceptor groups. The electron acceptor is a cyano group. The synthesis of the ligands is described below and briefly the procedure is presented in Scheme 1:

Synthesis of 4-[6-(4-isocyanophenyl)-9H-carbazol-3-yl]benzonitrile (1). In a round bottomed flask a mixture of (4-cyanophenyl)boronic acid (200 mg; 1,35 mmol), 3,6-dibromo-9H-carbazole (200 mg; 0,61 mmol) was added and dissolved in 1,2-dimethoxyethane (15mL). After that, Pd(dppf)Cl₂ (50 mg; 0,06 mmol) and potassium carbonate aqueous solution (1M, 3mL) were added. The system was isolated under argon atmosphere, heated up to boiling temperature and stirred overnight. The reaction was controlled and ended with TLC, extracted with, dichloromethane (3x20mL) and water (3x20mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated. The crude product was purified by column chromatography (dichloromethane/hexane: 1/1, V/V) on silica gel to afford white solid. ¹H NMR (400 MHz d₆ -DMSO): δ 8.88 (m, 1H), 8.71 (t, 1H), 8.56 (m, 1H), 8.46 (m, 1H), 8.45 (m, 1H), 8.20 (m, 1H), 8.09 (m, 1H), 8.08 (m, 1H), 7.98 (m, 1H), 7.91 (m, 1H), 7.89 (m, 1H), 7.85 (s, 1H), 4.00 (s, 3H). ¹³C NMR (400 MHz CDCl₃):

Synthesis of Sodium 4-[3-(4-cyanophenyl)-6-(4-isocyanophenyl)-9H-carbazol-9-yl]butane-1-sulfonate salt (2). Solid NaH (30mg; 1.3mmol) was added in small portions into a solution of 4-[6-(4-isocyanophenyl)-9H-carbazol-3-yl]benzonitrile (370mg; 1mmol) in dry THF (20 ml). After the generation of hydrogen gas subsided, the reaction mixture was stirred at room temperature for 50 min, and then 1,4-butane sultone (180mg; 1.3mmol) was introduced into the reaction through the septum via a syringe. The resulting mixture was subsequently stirred at room temperature for 20 h, diluted with CH₂Cl₂ (15 ml), and filtered to give a pale pink powder. The crude product was dissolved in a minimum amount of methanol and precipitated out with EtOAc. The precipitate was filtered and washed with EtOAc to give the desired product Sodium 4-[3-(4-cyanophenyl)-6-(4-isocyanophenyl)-9H-carbazol-9-yl]butane-1-sulfonate salt. ¹H NMR (400 MHz d₆ -DMSO): δ 8.88 (m, 1H), 8.71 (t, 1H), 8.56 (m, 1H), 8.46 (m, 1H), 8.45 (m, 1H), 8.20 (m, 1H), 8.09 (m, 1H), 8.08 (m, 1H), 7.98 (m, 1H), 7.91 (m, 1H), 7.89 (m, 1H), 7.85 (s, 1H), 4.00 (s, 3H)..

Synthesis of 4,4'-(9H-fluorene-2,7-diyl)dibenzonitrile (3). In a round bottomed flask a mixture of (4-cyanophenyl)boronic acid (200 mg; 1,35 mmol), 2,7-dibromo-9H-fluorene (198 mg;

0.61 mmol) was added and dissolved in 1,2-dimethoxyethane (16mL). After that, Pd(dppf)Cl₂ (50 mg; 0,06 mmol) and potassium carbonate aqueous solution (1M, 3mL) were added. The system was isolated under argon atmosphere, heated up to boiling temperature and stirred overnight. The reaction was controlled and ended with TLC, extracted with, CH₂Cl₂/H₂O (20mL)/(20mL) three times. The organic phase was separated, dried over sodium sulphate and the solvent was evaporated. The crude product was purified by column chromatography (dichloromethane/hexane: 1/1, V/V) on silica gel to afford white solid and then passed to the next step immediately.

Synthesis of sodium 4,4'-[2-(4-cyanophenyl)-7-(4-isocyanophenyl)-9H-fluorene-9,9-diyl]dibutane-1-sulfonate salt (4). Solid NaH (30mg; 1.3mmol) was added in small portions into a solution of 4,4'-(9H-fluorene-2,7-diyl)dibenzonitrile (368mg; 1mmol) in dry THF (20 ml). After the generation of hydrogen gas subsided, the reaction mixture was stirred at room temperature for 50 min, and then 1,4-butane sultone (180mg; 1.3mmol) was introduced into the reaction through the septum via a syringe. The resulting mixture was subsequently stirred at room temperature for 20 h, diluted with CH₂Cl₂ (15 ml), and filtered to give a pale pink powder. The crude product was dissolved in a minimum amount of methanol and precipitated out with EtOAc. The precipitate was filtered and washed with EtOAc to give the desired product Sodium 4,4'-[2-(4-cyanophenyl)-7-(4-isocyanophenyl)-9H-fluorene-9,9-diyl]dibutane-1-sulfonate. ¹H NMR (400 MHz *d*₆-DMSO).

In synthesis of 9,9'-[9H-fluorene-2,7-diylbis(4,1-phenylene)]bis-9H-carbazole (5). In a round bottomed flask a mixture of [4-(9H-carbazol-9-yl)phenyl]boronic acid (421 mg; 1,45 mmol), 2,7-dibromo-9H-fluorene (190 mg; 0,66 mmol) was added and dissolved in 1,2-dimethoxyethane (20mL). After that, Pd(dppf)Cl₂ (50 mg; 0,06 mmol) and potassium carbonate aqueous solution (1M, 3mL) were added. The system was isolated under argon atmosphere, heated up to boiling temperature and stirred overnight. The reaction was controlled and ended with TLC, extracted with, CH₂Cl₂/H₂O (20mL)/(20mL) three times. The organic phase was separated, dried over sodium sulphate and the solvent was evaporated. The crude product was purified by column chromatography (dichloromethane/hexane: 1/1, V/V) on silica gel to afford white solid.

A synthesis of sodium 4,4'-{2,7-bis[4-(9H-carbazol-9-yl)phenyl]-9H-fluorene-9,9-diyl}dibutane-1-sulfonate (6). Solid NaH (30mg; 1.3mmol) was added in small portions into a solution of 9,9'-[9H-fluorene-2,7-diylbis(4,1-phenylene)]bis-9H-carbazole (200 mg; 1.2

mmol) in dry THF (20 ml). After the generation of hydrogen gas subsided, the reaction mixture was stirred at room temperature for 50 min, and then 1,4-butane sultone (180mg; 1.3mmol) was introduced into the reaction through the septum via a syringe. The resulting mixture was subsequently stirred at room temperature for 20 h, diluted with CH₂Cl₂ (18 ml), and filtered to give a pale reddish powder. The crude product was dissolved in a minimum amount of methanol and precipitated out with EtOAc. The precipitate was filtered and washed with EtOAc to give the desired product sodium 4,4'-{2,7-bis[4-(9*H*-carbazol-9-yl)phenyl]-9*H*-fluorene-9,9-diyl}dibutane-1-sulfonate. ¹H NMR (400 MHz *d*₆-DMSO).

S-4.Synthesis of CdSeS Nanocrystals

First, oleic acid coated CdSeS is synthesized which is used as a reference material. The methods followed are summarized in the following subsections.

S-4.1 Synthesis of cadmium myristate.

This first step is the synthesis of the main structure that is used as cadmium source. Hence, these products are used in all colloidal synthesis phases. As of source of cadmium, cadmium myristate has been used in the following way. One of equivalent mol cadmium oxide has been heated within two equivalent moles of myristic acid. As container, a balloon is used in which contents are treated at 200°C. We enabled the cadmium oxide completely transform into cadmium myristate. The acquired solid product is checked whether it is the cadmium myristate molecule. This is directly used in synthesis without needing any purification steps.

S-4.2 Synthesis of NaHSe.

As of source of selenium, NaHSe has been used in the following way. 10 mg of powder selenium and 12 mg of Sodium borohydride (NaBH₄) are together carefully put into the experiment tube which is completely saturated by nitrogen (N₂) gas. Over them, reaction balloon is saturated with Nitrogen gas and 4ml distilled water is added. The reaction is continued as long as the gas emit is over. Immediately after, the reaction is ended. The final product of sodium hydrogen selenium (NaHSe) which is a transparent solution has been used in intended reactions without direct contact with air.

S-4.3 Synthesis of CdSeS nanocrystals.

CdSeS nanocrystals are synthesized by use of double phase method. First 0.4 g cadmium myristate that is used as cadmium source has been treated. Two grams of oleic acid that is

used as surface active agent is solved in 80 ml of toluene solvent at 80°C. The contents are kept aside for a moment to be used in the following step. The other side 60 mg of thiourea were dissolved in 80 ml distilled water and heated till it reaches 100°C under nitrogen gas for 30 minutes. The previously derived NaHSe is injected into the reaction balloon in amount of 1ml (3 mg). As soon as nitrogen is saturated with ? and temperature is fixed at 100 °C the solution in toluene phase has been added into the water phase in company with stirrer. In half an hour, CdSeS quantum nanocrystals start to form on interfaces. In order to investigate its optical properties, samples are taken at different times. Those samples are analyzed using UV-VIS. Immediately after the samples are reached the targeted size of 5 nm, the reaction is stopped intentionally. The double phased mixture inside the reaction balloon has been separated inside the separation funnel. The organic phase contains product nanocrystals sediment by help of added ethanol. And followed by, the nanocrystals are centrifuged and final sediment is washed with acetone. Finally, the product is left aside for drying.

S-4.4 Enveloping the ligands on nanocrystal surfaces.

The product nanocrystal surfaces are enveloped by synthesized groups which are rich of electrons. For this process, the use of ligand replacement method is planned. On the other side, some trials are made by use of direct synthesis methods, as well.

S-4.5 Processing the ligand replacement method (Ligand Exchange with Organic Molecules).

The general methodology for ligand replacement is given as follows. Described method is common for entire three molecules, which are named as L1, MC1 and MC2, respectively. Molecules are taken in amount of 50 mg and put into the experimental tube. Meanwhile, 4ml chloroform is added. By this way, the solution of molecules are ensured. We note that, an extra 1 ml of hexane is added into the MC1 tube due to the reason that it does not completely dissolved inside the chloroform. The previously synthesized oleic acid coated CdSeS nanocrystals which are dissolved inside the chloroform solution has been added into the prepared ligands in amount of 1 ml. The reaction balloon is stirred for 72 hours. Finally, derived nanocrystals are subsided by use of ethanol. The ethanol is drawn away from the derived sediment by processing it inside the centrifuge machine. Following the dry process finished inside the vacuumed drying oven, FTIR results are taken from the product nanocrystals. FTIR measurements are compared to that of CdSeS of which surface is enveloped by oleic acid (see Figure 7 a-c).

S-4.6 Direct synthesis by use of surface active agents.

CdSeS nanocrystals are synthesized by use of double phase method. As of cadmium source, 0.4 g of cadmium myristate is used. As of surface active agent, either 300 mg of MC1 or 300 mg of MC 2 is dissolved inside 80 ml of toluene solvent. Due to the distress of solubility, 10 ml of chloroform is added into the both nanocrystal synthesis. The prepared mixture is kept aside ready for the next step. In the other side, 60 mg of thiourea which is used as S source dissolved in 80 ml of water. They are heated till reaches 100°C. One ml (3 mg) of the previously derived NaHSe has been injected into the reaction balloon. The contents are saturated with nitrogen and temperature is kept fixed at 100 °C. Thereafter, the solution in form of toluene phase is added into the water phase solution in company with the stirrer operation.

The reaction is stopped intentionally by cutting the heat source, immediately after the samples are thought to be reached the targeted size. Meanwhile, the double phased mixture inside the main reaction balloon has been separated inside the separation funnel. The organic phase contains product nanocrystals sediment by help of added ethanol. And followed by, the nanocrystals are centrifuged and final sediment is washed with acetone. Finally, the product is left aside for dry.

S-5. Electrochemical analysis

The electrochemical properties of L1, MC1 and MC2 ligands were examined by the cyclic voltammetry method in a 0.1 M solution of Bu₄NPF₆ in acetonitrile with a scan rate of 100mVs⁻¹. A glassy-carbon was used as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode.

S-6.Fabrication of Solar cells

In this section, solar cell production is summarized and measurement results are examined.

S-6.1 Cleaning of ITO coated glasses

ITO coated glasses are cut into 1.5 x 1.5 cm dimensions. Taking one side as reference, 3 mm of ITO coat is etched by use of an acid. For this process, a concentrated mix of hydrochloric acid and nitric acid has been used. The mixture had a ratio of 9:1. After the etching process,

the ITO surfaces are carefully directed upward and the glasses are located into an apparatus in a beaker so that the glasses are vertically set. They are washed inside an ultrasonic cleaning machine with distilled water, acetone, ethanol and isopropyl alcohol respectively. The cleaning time was 20 minutes for each. ITO coated surfaces are dried by spraying nitrogen gas and kept inside a plasma machine for surface activation.

S-6.2 Film coating

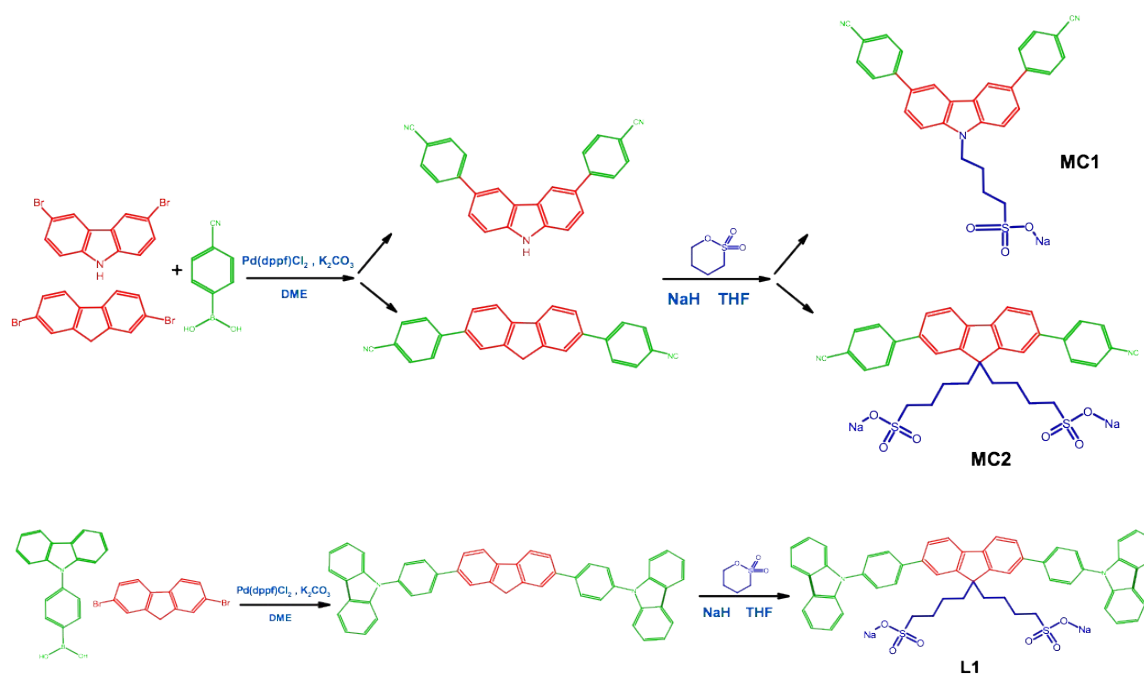
The one side of ITO glasses which are etched by means of acid is coated by PEDOT:PSS. The material is obtained from HCStarck[®] company. As of method, we have used spin coating machine with a radial speed of 2000 rpm. The output waited for 30 minutes at 120°C temperature. Meanwhile, P3HT and nanocrystal mixtures are prepared in ratio of given amounts (see Table 1). They are spin coated at a radial speed of 1500 rpm and dried for 30 minutes at 100°C. The dried samples are masked and put into thermal evaporation system. The previously designed metal masks contain three upper side and single down side electrode gaps. Evaporation is ended as soon as enough Al metal is evaporated. The final product moved to the characterization measurements.

Here, we note that, nanocrystals, as well as organic materials are used in amount of 1 mg per ml in solutions. Hybrid solar cell device structure depends on ITO/PEDOT:PSS/CdSeS:P3HT blend/ Au or Al schematics.

Table 1. Device geometry, ratio and results of fabricated solar cells

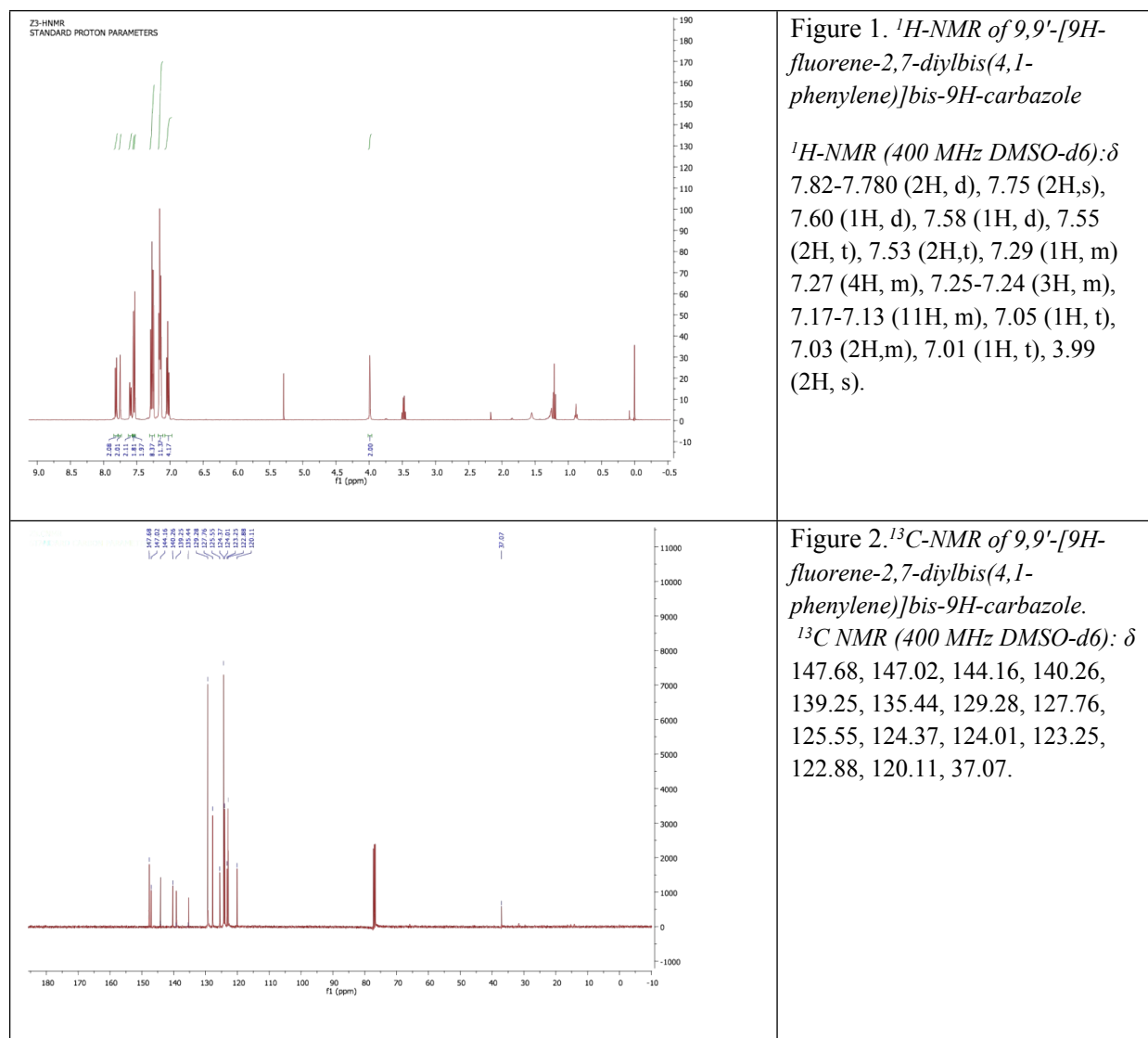
	QD: P3HT	I_{sc} mA/cm ²	V_{oc} mV	PCE %
L1(LE)CdSeS:P3HT	1:1	0,27	220	0,18
	1:3	0,29	280	0,26
MC1(LE)CdSeS:P3HT	1:1	0,43	500	0,71
	1:3	0,47	300	0,42
MC2(LE)CdSeS:P3HT	1:1	0,26	380	0,30
	1:3	0,17	300	0,18
L1(S)CdSeS:P3HT	1:1	0,24	200	0,14
	1:3	0,25	220	0,17
MC1(S)CdSeS:P3HT	1:1	0,35	400	0,43
	1:3	0,3	280	0,26
MC2(S)CdSeS:P3HT	1:1	0,28	220	0,19
	1:3	0,12	180	0,06
PryCdSeS:P3HT (Reference Cell)	1:1	0,50	230	0,38

Schemes



Scheme 1. Synthetic procedures of the MC1, MC2 and L1

Figure S-1. ^1H -NMR and ^{13}C -NMR spectra of synthesized molecules



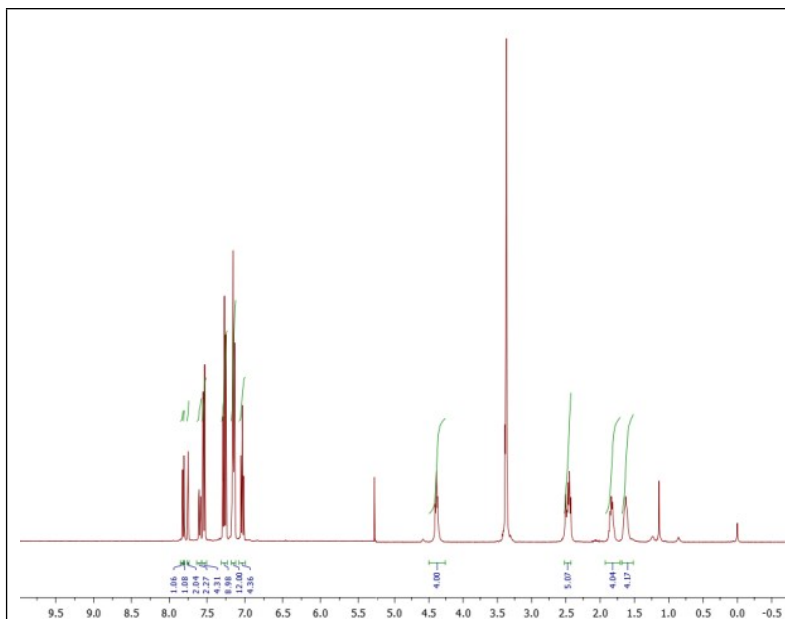


Figure 3. $^1\text{H-NMR}$ of sodium 4,4'-{2,7-bis[4-(9H-carbazol-9-yl)phenyl]-9H-fluorene-9,9-diyl}dibutane-1-sulfonate (L1)

$^1\text{H NMR}$ (400 MHz DMSO- d_6): δ 7.78-7.77 (2H,d), 7.75 (2H,s), 7.61-7.60 (2H, d), 7.53-7.52 (2H, d), 7.28-7.25 (9H, t), 7.20-2.18 (12H,d), 7.00-7.02 (3H, t), 4.42-4.40 (4H, t), 2.50-2.47 (5H, m), 1.82-1.80 (4H, t), 1.69 (4H,s).

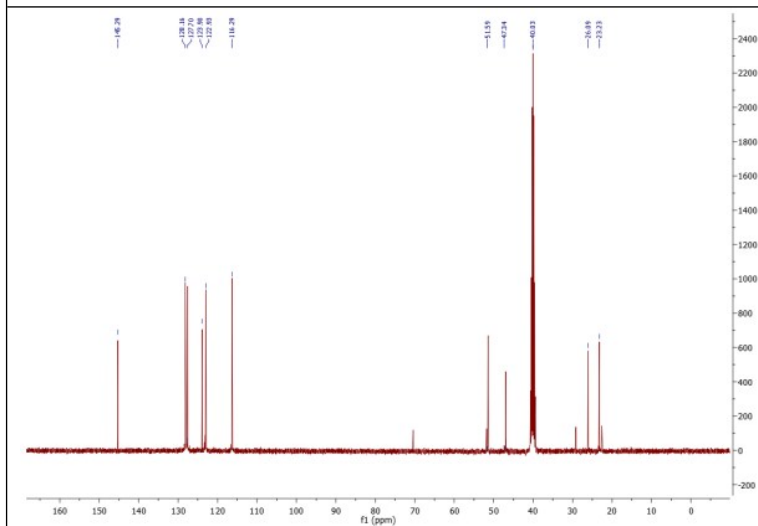


Figure 4. $^{13}\text{C-NMR}$ of sodium 4,4'-{2,7-bis[4-(9H-carbazol-9-yl)phenyl]-9H-fluorene-9,9-diyl}dibutane-1-sulfonate (L1)

$^{13}\text{C NMR}$ (400 MHz DMSO- d_6): δ 145.29, 128.16, 127.70, 123.90, 122.93, 116.29, 51.59, 47.34, 40.03, 26.09, 23.23.

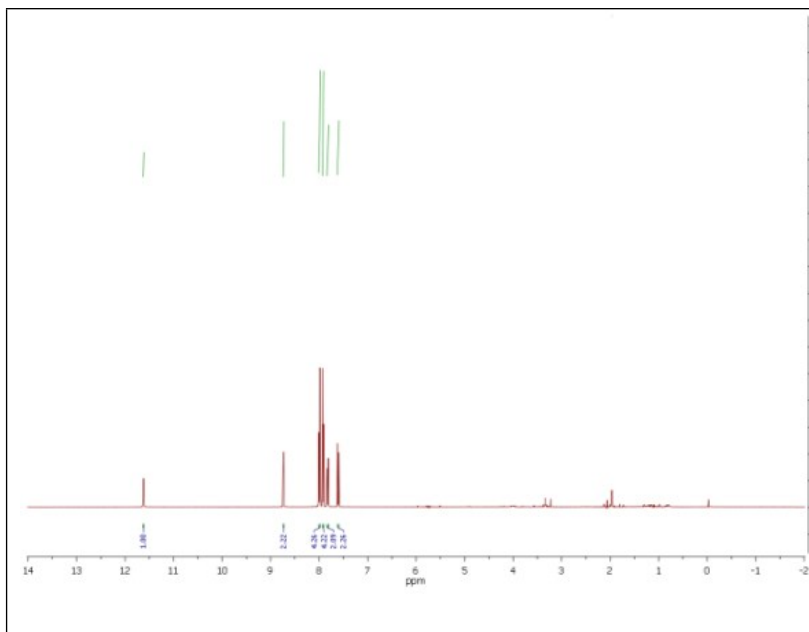


Figure 5. $^1\text{H-NMR}$ of 4-[6-(4-isocyanophenyl)-9H-carbazol-3-yl]benzotrile

$^1\text{H NMR}$ (400 MHz CDCl_3): δ 11.64 (1H, s), 8.72 (2H, s), 8.0-7.99 (4H, d), 7.92-7.91 (4H, d), 7.81-7.80 (2H, d), 7.63-7.62 (2H, d).

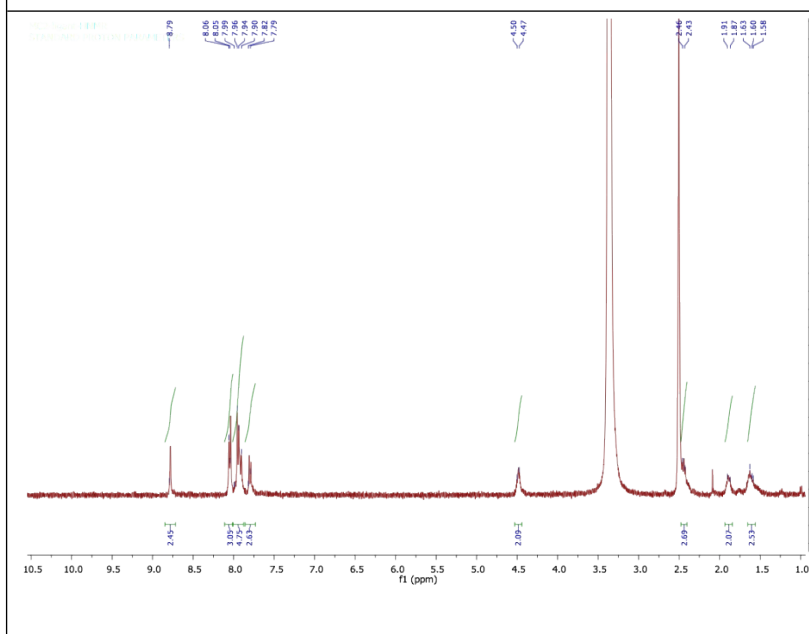


Figure 6. $^1\text{H-NMR}$ of sodium 4-[3-(4-cyanophenyl)-6-(4-isocyanophenyl)-9H-carbazol-9-yl]butane-1-sulfonate salt (MCl)

$^1\text{H NMR}$ (400 MHz DMSO-d_6): δ 8.79 (2H, s), 8.06-7.99 (3H, t), 7.96-7.90 (5H, t), 7.82-7.79 (3H, d), 4.5-4.47 (2H, d), 2.46-2.43 (3H, d), 1.91-1.87 (2H, d), 1.63-1.58 (3H, t).

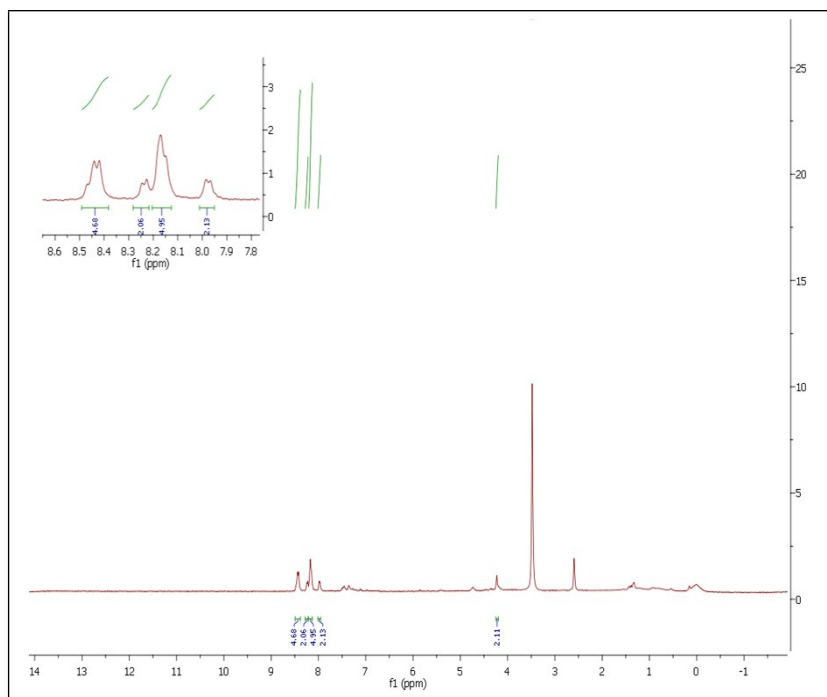


Figure 7. $^1\text{H-NMR}$ of 4,4'-(9H-fluorene-2,7-diyl)dibenzonitrile
 $^1\text{H NMR}$ (400 MHz DMSO- d_6): δ 8.44-8.43 (5H, d), 8.24-8.23 (2H, d), 8.16-8.14 (5H, d), 7.97-7.96 (2H, d), 4.22 (2H, s).

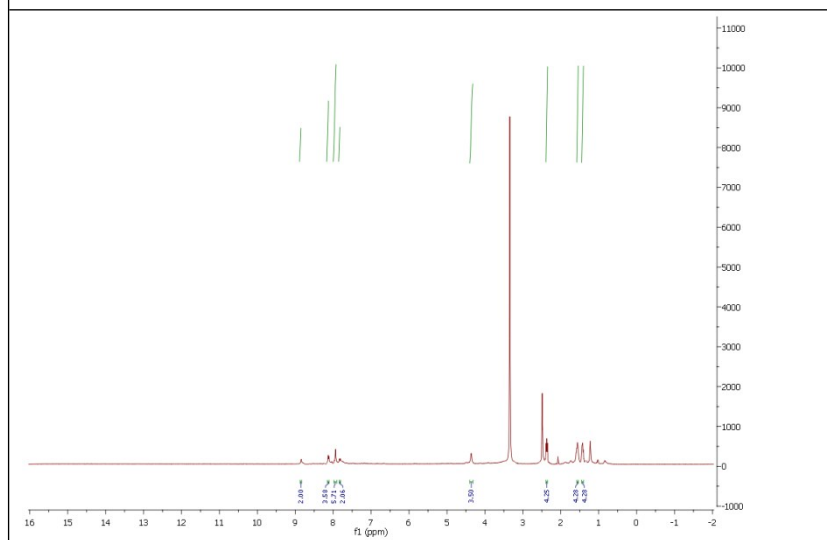


Figure 8. $^1\text{H-NMR}$ of 4,4'-(9H-fluorene-2,7-diyl)dibenzonitrile dibutane-1-sulfonate
 $^1\text{H NMR}$ (400 MHz DMSO- d_6): δ 8.82 (2H, s), 8.13-8.12 (4H, d), 7.93 (6H), 7.78-7.77 (2H, d), 4.33 (4H, s), 2.46-2.44 (4H, t), 1.52 (4H, m), 1.48-1.47 (4H, d)

Verification of products through XRD and FT-IR

The Figure S-2 shows the XRD result that verifies the product nanocrystals are in alloy form. In the figure, the alloy structure is clearly distinguished since peaks lay between the diffraction angles of pure CdSe and pure CdS nanocrystals.

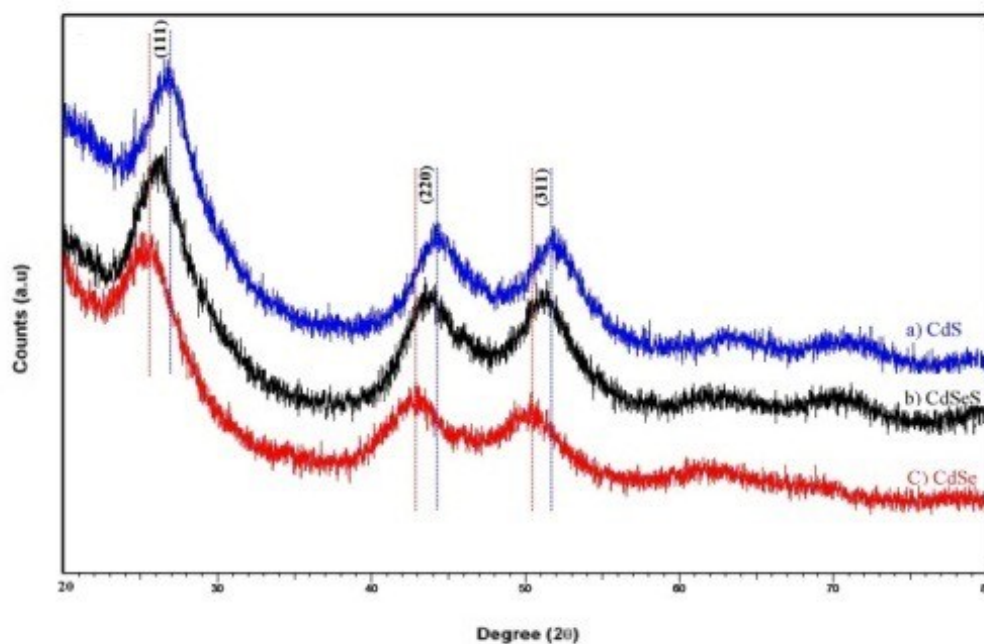


Figure S-2 . XRD spectra of CdSeS nanocrystals (CdS and CdSe as references)

TEM images of Nanocrystals were given in Figure S-3.

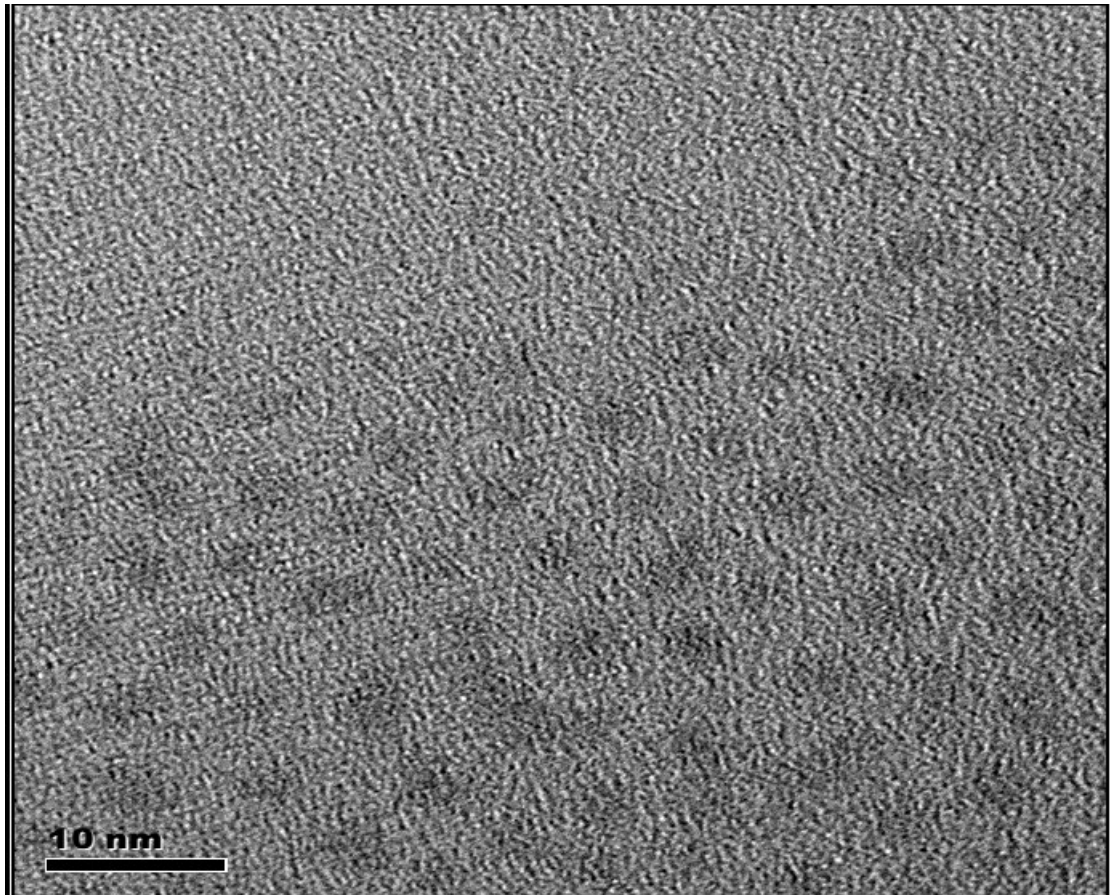


Figure S-3. TEM images of oleic acid capped CdSeS nanocrystals

The dried nanocrystals of MC1:CdSeS and MC2:CdSeS were characterized by FT-IR. The corresponding comparative results are given in Figure S-4.

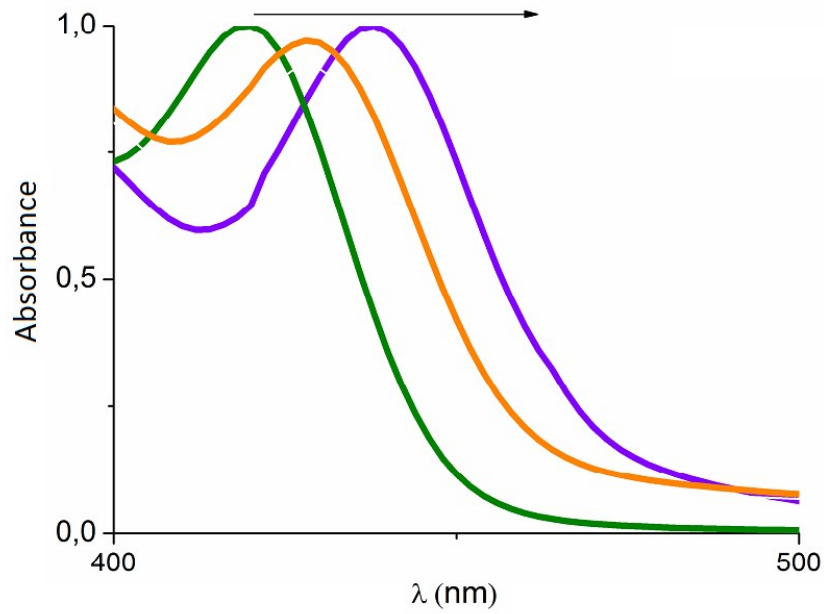


Figure S-4: Absorption spectra of oleic acid capped CdSeS nanocrystals during synthesis. Particle growth can be clearly seen from figure.

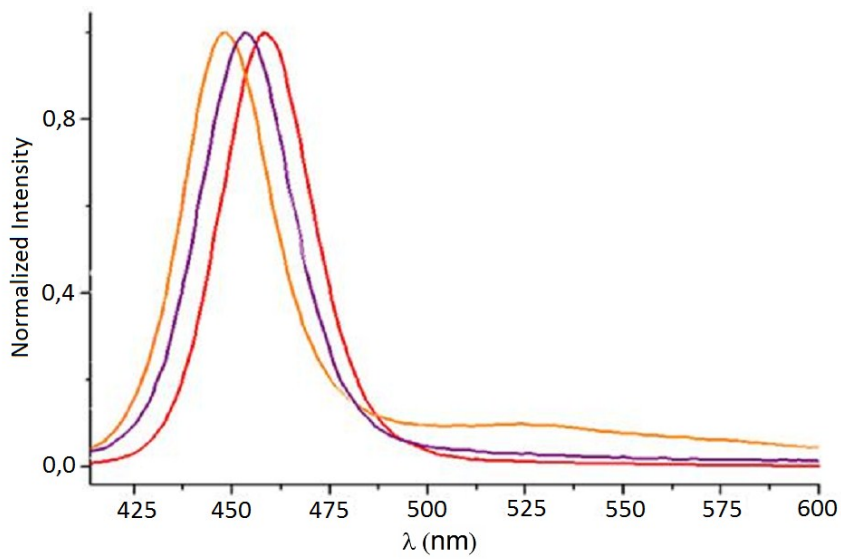


Figure S-5: Normalized fluorescence spectra of oleic acid capped CdSeS nanocrystals during synthesis. Red shift on fluorescence peaks is clear depending on particle growth.

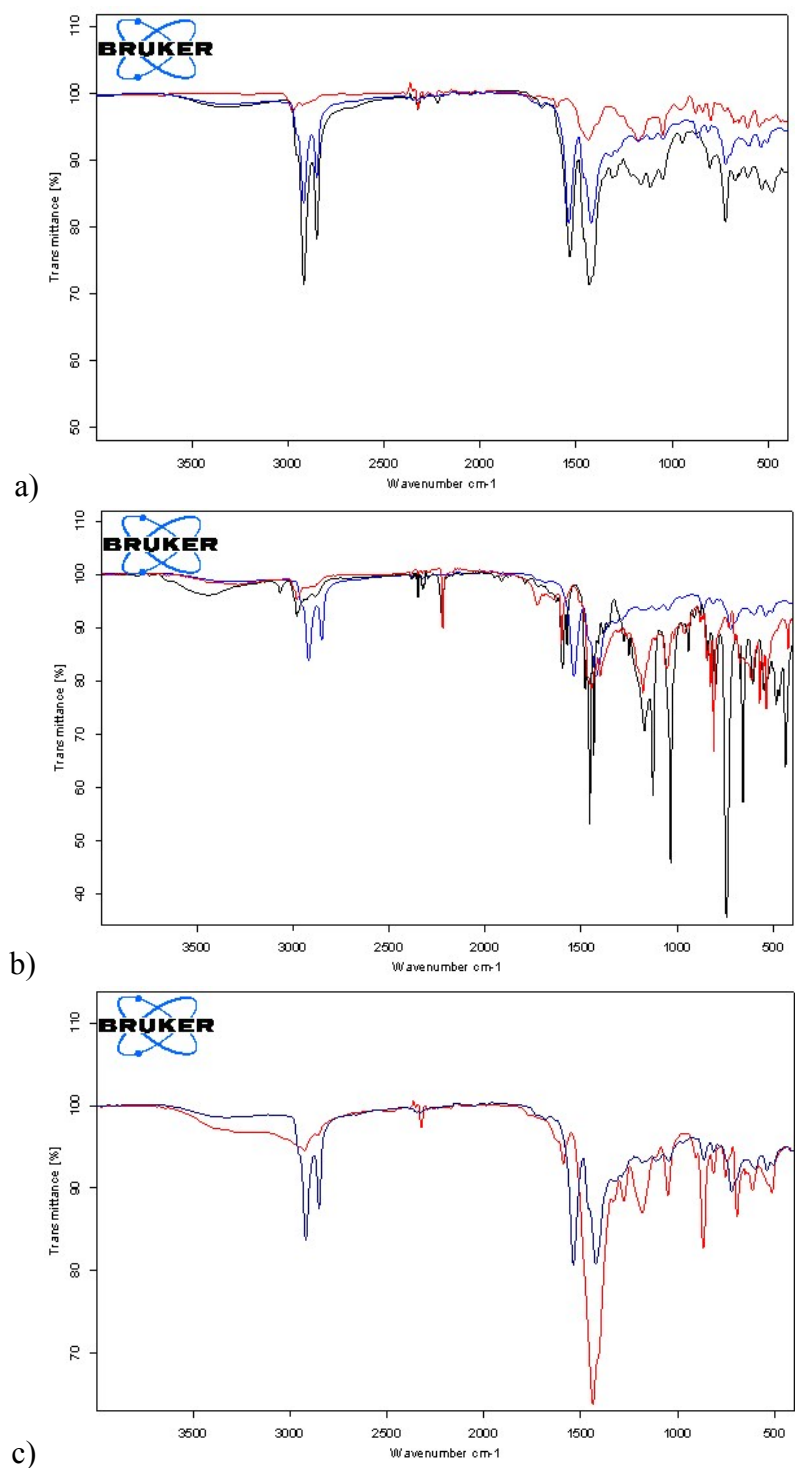


Figure S-6. a) FT-IR spectra for MC1:CdSeS (synthesis, black), MC1:CdSeS (ligand replacement, red), oleic acid coated CdSeS (blue); b) MC2:CdSeS (synthesis, black), MC2:CdSeS (ligand replacement, red), oleic acid coated CdSeS (blue); c) L1:FT-IR spectra for CdSeS (ligand replacement, red), oleic acid coated CdSeS

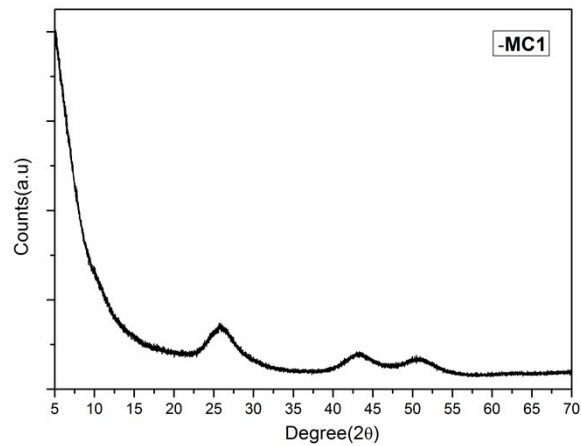
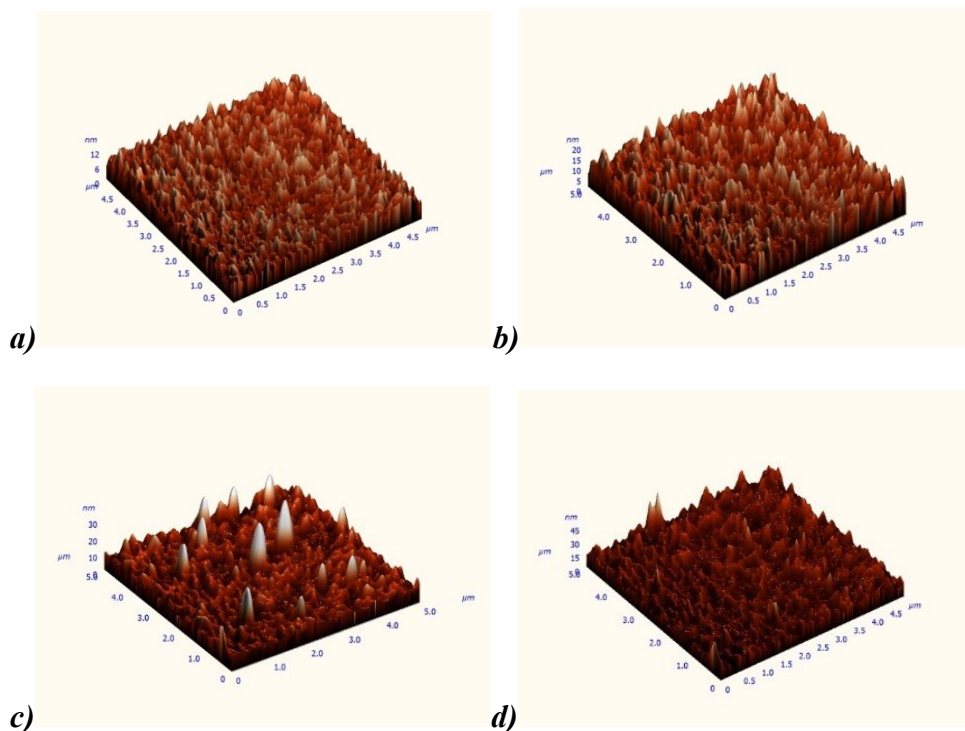


Figure S-7. XRD image for CdSeS nanocrystals which are directly synthesized and used with MC1 as active surface material .

AFM surface analysis

Ligand capped hybrid nanocrystals (generally LX-QD; specifically L1-QD, MC1-QD and MC2-QD) were mixed with P3HT in definite proportions. Using these mixtures, the solar devices were fabricated. Figure S-6 shows the AFM images of coated surfaces prepared in the order of ITO/PEDOT-PSS/LX-QD-P3HT layers. Comparing the images, the surfaces become regular together with the increase in the ratio of P3HT. In account of the same reason, the agglomerations of nanocrystals are lowered, as well.



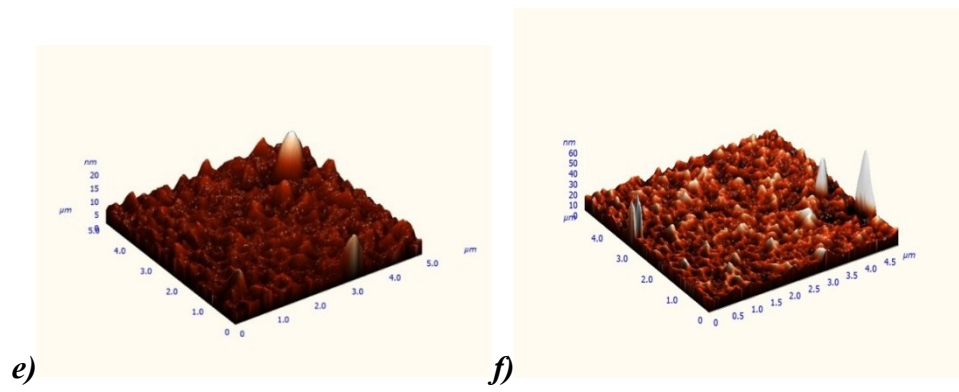


Figure S-8. AFM image of oleic acid coated nanocrystals that are mixed in different proportions of P3HT a) 1:1 (oleic acid-P3HT), b) 1:3 (oleic acid-P3HT) c) 1:1 (L1-P3HT), d) 1:3 (L1-P3HT), e) 1:1 (MC1-P3HT), f) 1:3 (MC1 -P3HT)