Electronic Supplementary Information

Performance Improvement in Near-infrared Quantum-dot Photodetectors by Controlling Molecular Structure of Conjugated Polyelectrolytes

Moon-Ki Jeong,[a,†] *Jinhyeon Kang,*[a,†] *Dasom Park,*[a] *Sanggyu Yim,*[a] *and In Hwan Jung**[a]

[a] Department of Chemistry, Kookmin University, 77 Jeongneung-ro, Seongbuk-gu, Seoul 02707, Republic of Korea. E-mail address: ihjung@kookmin.ac.kr

Synthesis of PbS CQDs

Lead oxide (PbO, 0.943 g, 99.999%, Aldrich) and 3 ml of oleic acid (OA, technical grade, 90%, Aldrich) were dissolved in 40 ml of 1-octadecene (ODE, 90%, Aldrich) in a three-necked flask by heating the mixture to 100 ˚C in a vacuum. Then, 0.36 ml of bis(trimethylsilyl)sulfide (TMS, synthesis grade, Aldrich) and 10 ml of the ODE mixture were injected into the hot solution. After 3 min, the solution was transferred to a water bath, and 10 ml of toluene was injected into the solution. After cooling down, the CQDs were washed by centrifugation with toluene and methanol. Then, the precipitated CQDs were dried in a vacuum to remove any residual solvent. Before fabrication of the CQD photodetector, the CQDs were dispersed in n-octane. The concentration of the CQD solution was 50 mg/ml."

Preparation of ZnO-based n-Type Layer

The indium-tin oxide coated glass (ITO) substrates were sonicated for 20 min with acetone, water, ethanol. The cleaned ITO substrates were treated with UV-O_3 treatment for 20 min. For preparation of the ZnO precursor solution, the zinc acetate dehydrate ($Zn(Ac)_2 \cdot 2H_2O$, Aldrich) and ethanolamine ($NH_2CH_2CH_2OH$, Aldrich) in 2-methoxyethanol (0.45 M) under vigorous stirring for 3 h at 60 °C. The ZnO precursor solution was spin-coated onto the ITO substrates at 2500 rpm for 30 s. Then, the substrates were placed on a plate which was at room temperature. The plate was then heated to 240 °C, and the temperature was reached, the substrates were immediately removed from the hot plate to cool down to room temperature. This spin-coating process was done twice. To coat the buffer layer onto the ZnO n-type layer, the buffer solutions was prepared by dissolving the each materials in N,N-dimethylformamide (DMF) for concentration of 0.01 wt%. The buffer solution was spin-coated onto the ZnO layer at 5000 rpm for 1 min. After spin-coating, the substrates were annealed at 100 ^{o}C for 10 min.

Fabrication of CQD Photodetector

The synthesis of lead sulfide colloidal quantum dots (PbS CQDs) and fabrication of PbS CQD Photodetectos (PbS QPDs) proceed in a similar way to the previous article.[S1] PbS CQDs were spin-coated onto the prepared n-type layer 10 times. The first 8 layers of PbS CQDs were ligand-exchanged by 20 mM TBAI (tetrabutylammonium iodide, Aldrich) solution in methanol (MeOH, DAEJUNG) and rinsed by MeOH 2 times. The last 2 layers were ligand exchanged by 4 mM EDT (1,2-ethanedithiol, Aldrich) solution in acetonitrile (ACN, DAEJUNG) and rinsed by ACN 2 times. During the process, the each PbS CQDs layer was spin-coated with a thickness of about 30 nm onto the prepared substrates at 3000 rpm for 10 s. All spin-coating processes were performed under ambient conditions. The films were stored in a desiccator (<25 % of humidity) overnight. MoO_x (~15 nm) and Ag (~80 nm) were deposited onto the CQDs layer using a thermal evaporator (base pressure of 10^{-6} Torr) as the hole transporting layer (HTL) and the electrode, respectively. The resulted active area was measured to be 0.071 cm^2.

Device Characterization

The current density-voltage (J-V) characteristics were measured using a Keithley 2602B source unit under IR LED light (Thorlabs, M940L3). The intensity of the light was calibrated by using a standard photodiode power sensor (Thorlabs, S120C) with a compact power and energy meter console (Thorlabs, PM200). Optical absorption measurements were performed using a UV-vis-NIR spectrometer (S-3100, Sinco Co., LTD.). An AFM in tapping mode was used to investigate the surface morphology and roughness. The hydrophilicities and work functions of the ZnO films with and without various buffer layers were measured by a contact angle analyzer (Phoenix 300 system) and UPS which performed using an AXIS-NOVA (Kratos) system with HeI α radiation ($h\nu = 21.22$ eV) at a base pressure of 5×10^{-8} Torr, respectively. The cross-sectional SEM images of the devices were obtained using field emission scanning electron microscopy (FE-SEM) (Jeol JSM-7401F, JEOL Ltd.).

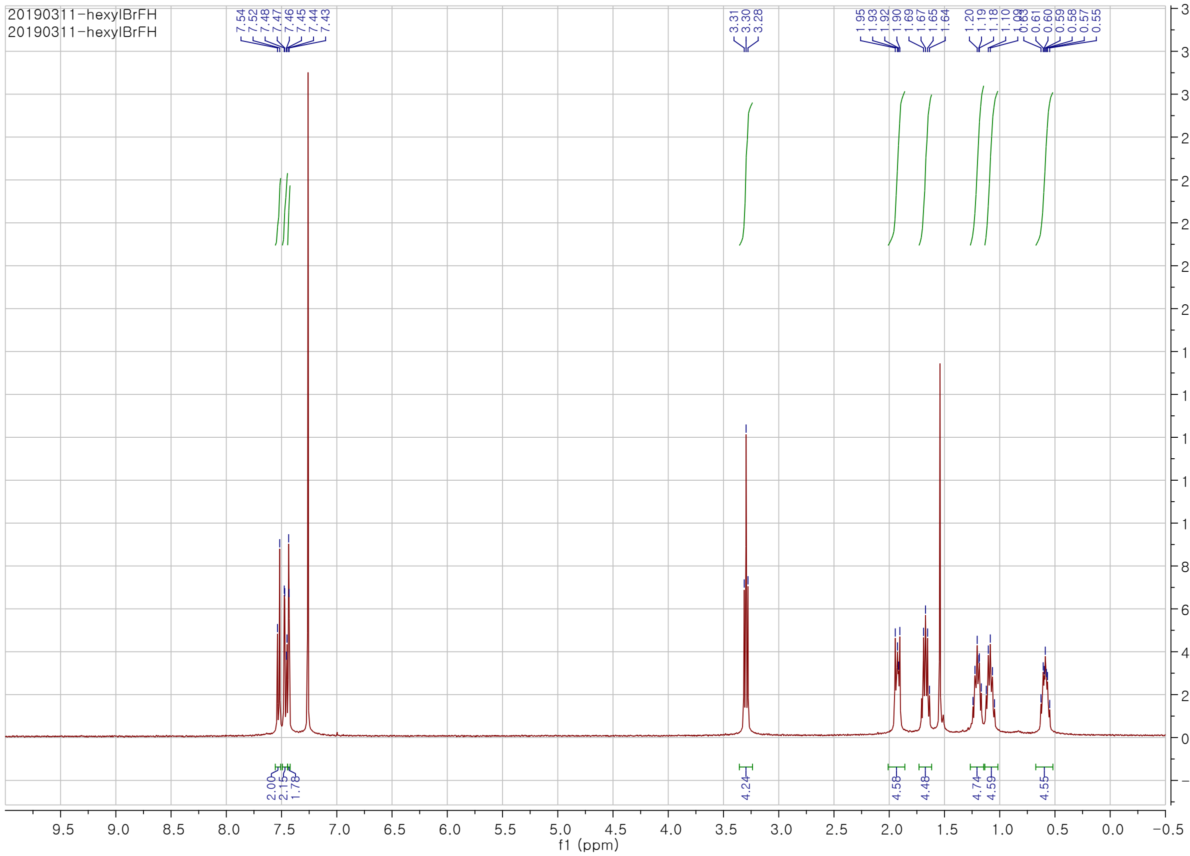

Figure S1. ^{1}H NMR of Compound 1

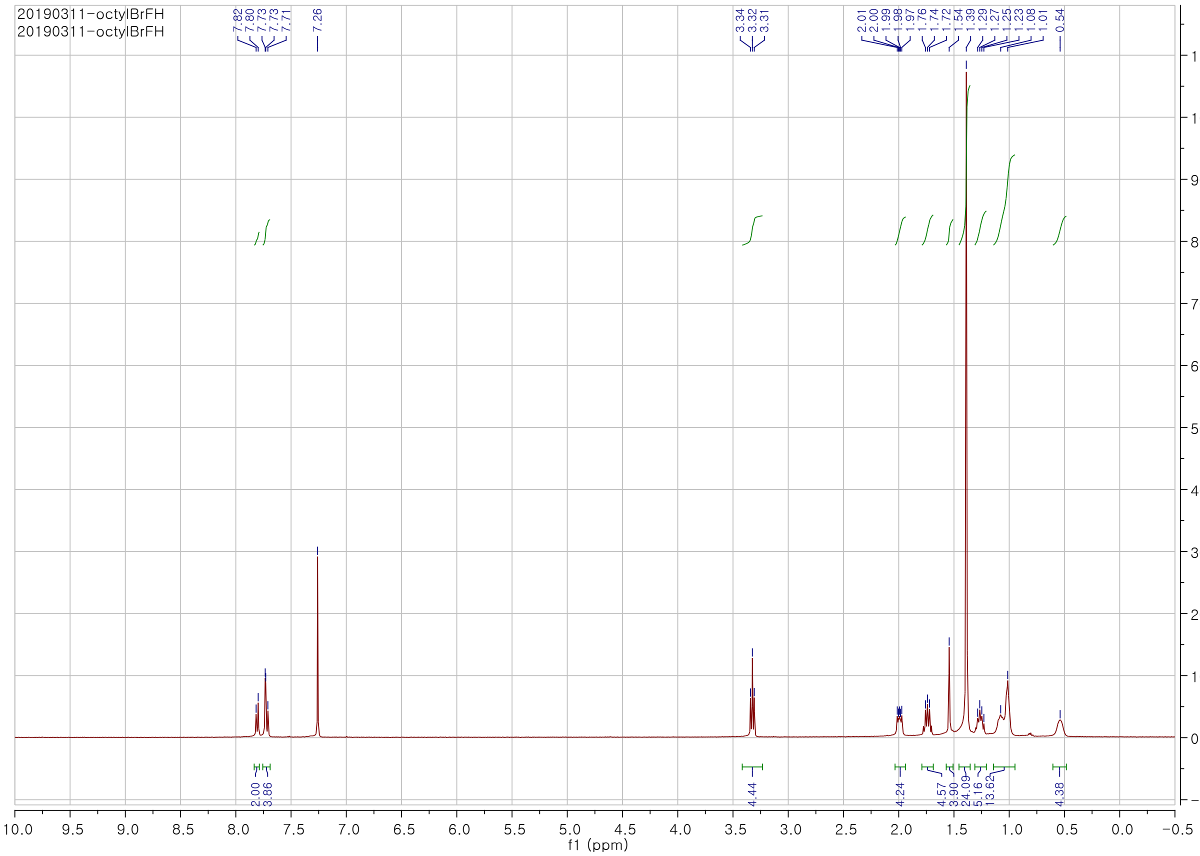

Figure S2. ^{1}H NMR of Compound 2

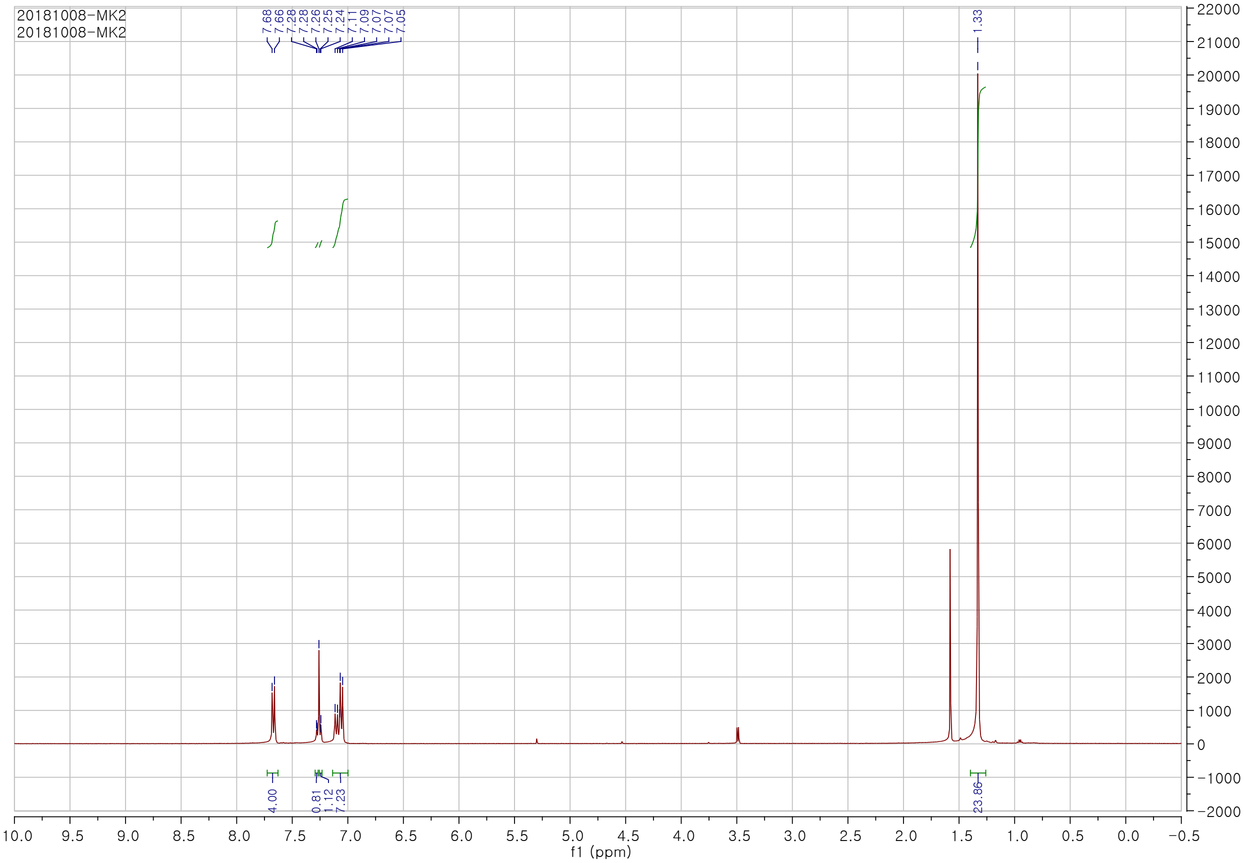

Figure S3. ^{1}H NMR of Compound 4.

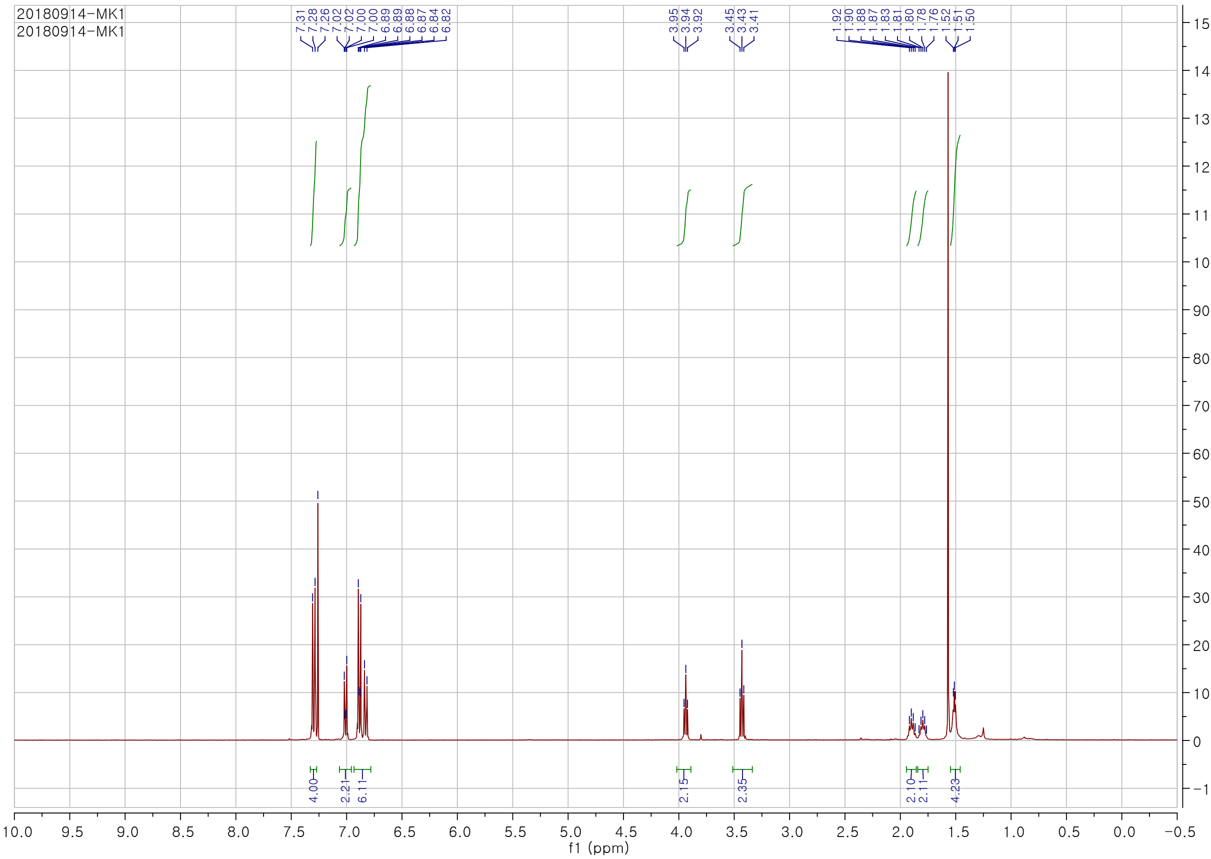

Figure S4. ^{1}H NMR of Compound 7.

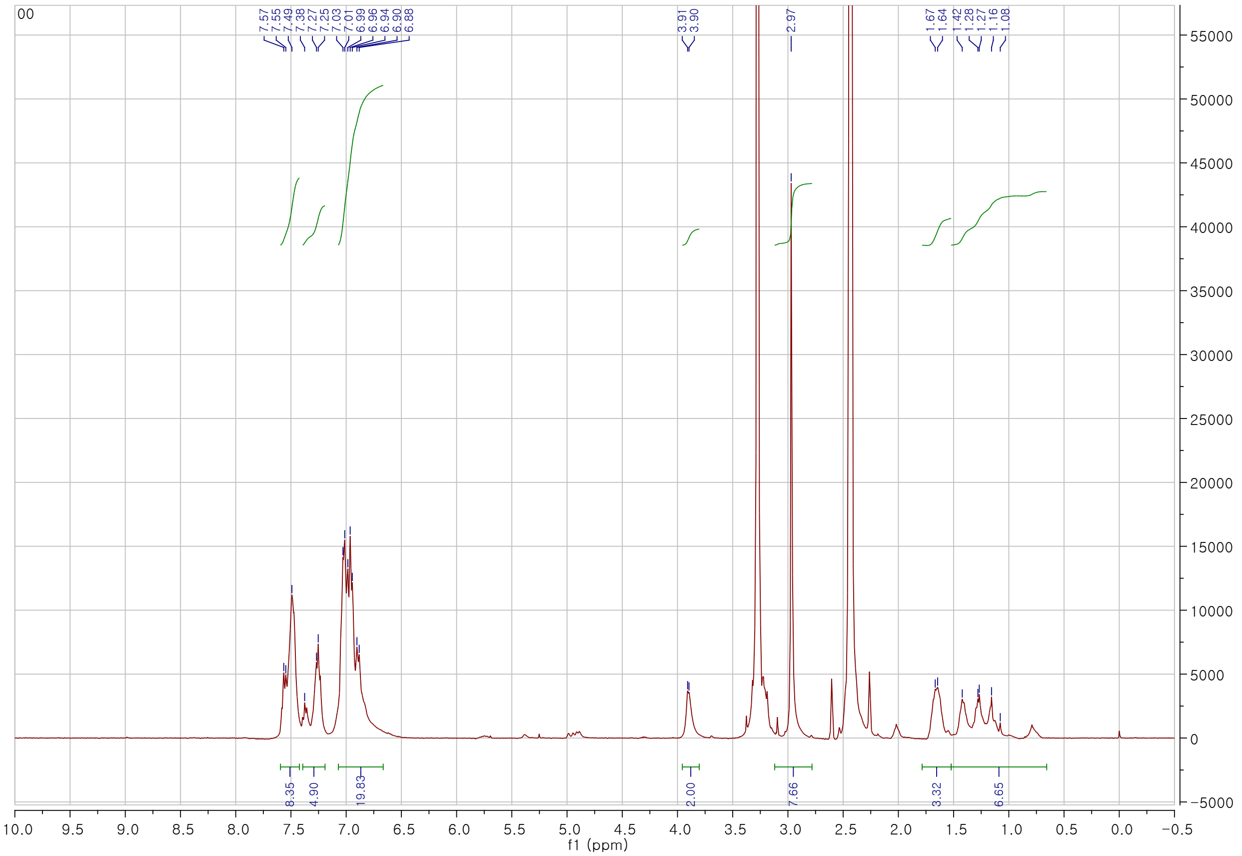

Figure S5. ^{1}H NMR of CCP1.

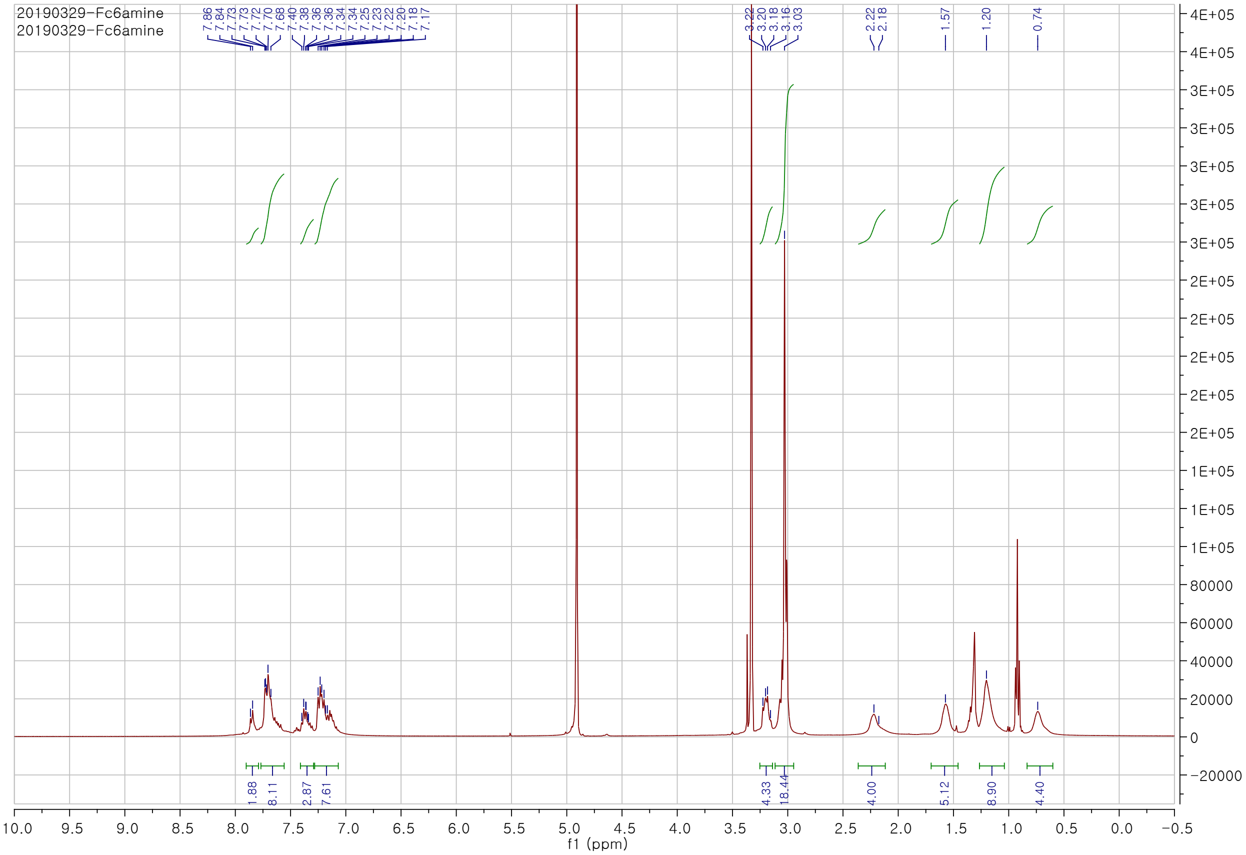

Figure S6. ^{1}H NMR of CCP2.

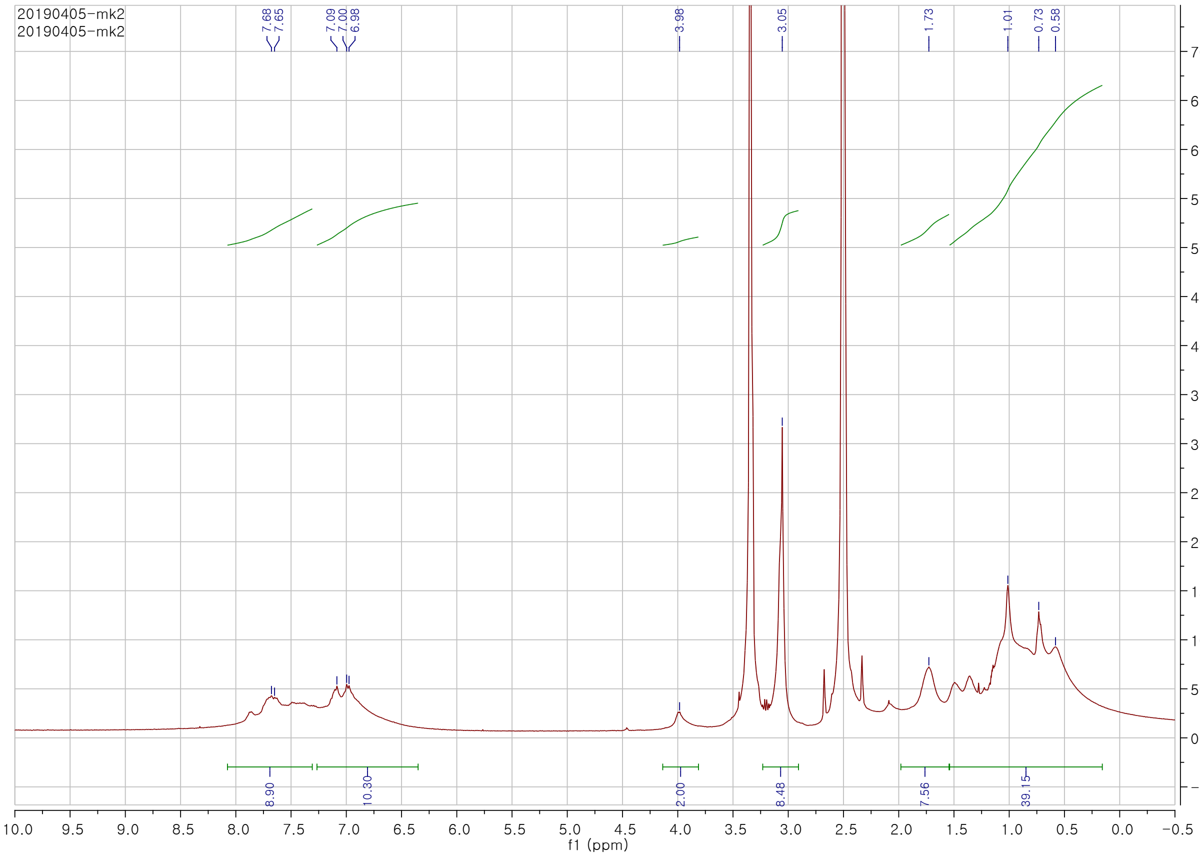

Figure S7. ^{1}H NMR of CCP3.

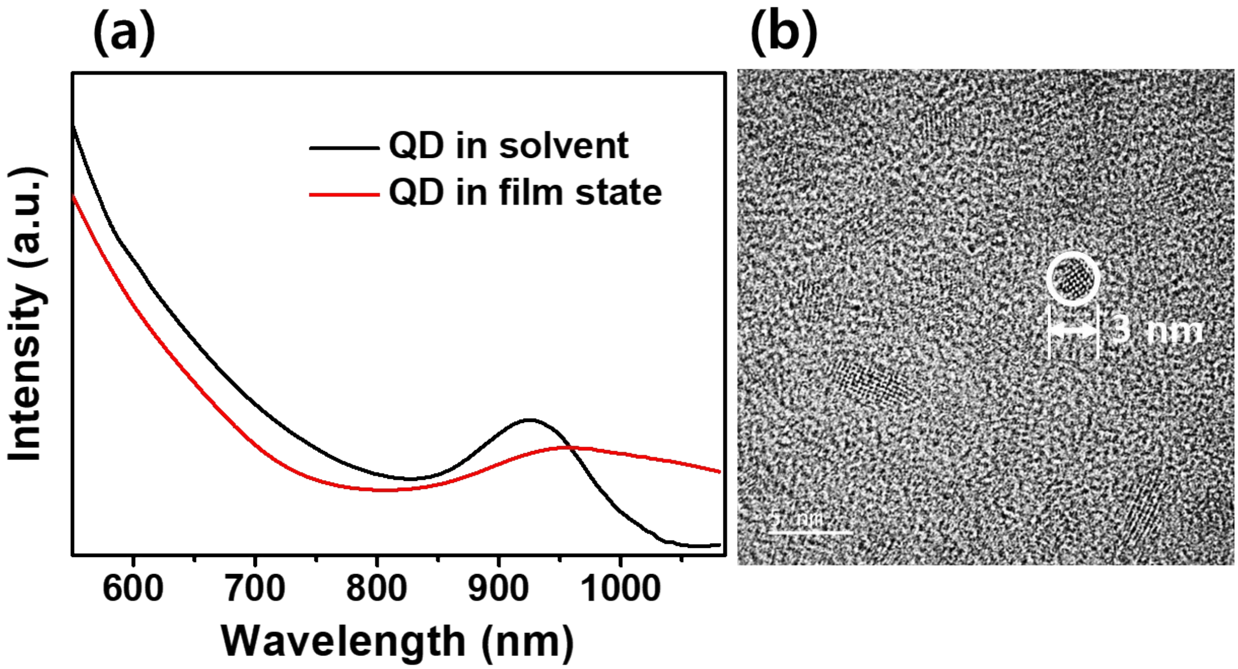

Figure S8. (a) UV/VIS absorption spectrum of synthesized QDs and (b) QD size measured in a TEM image

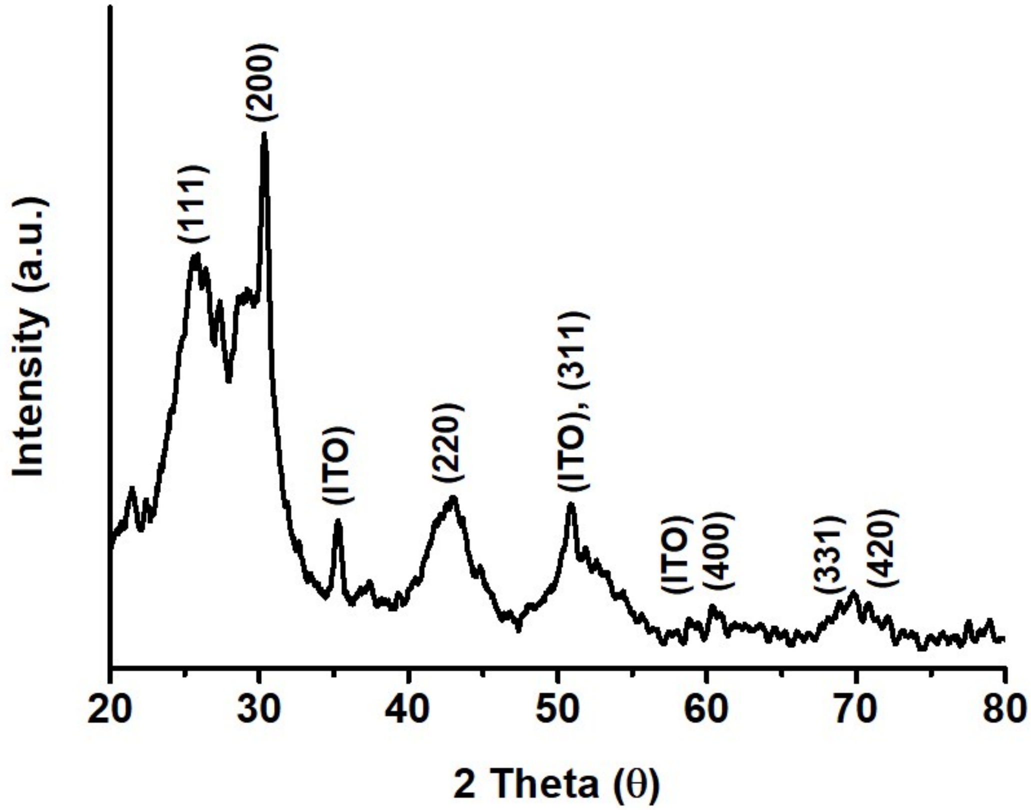

Figure S9. X-ray diffraction patterns of the synthesized PbS QDs

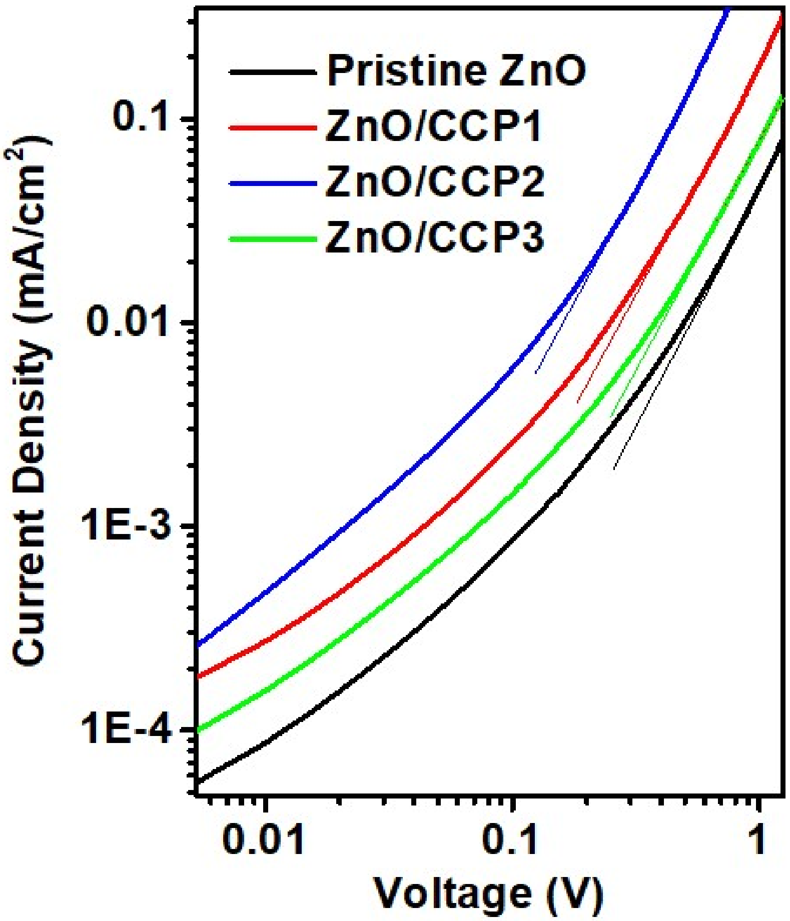

Figure S10. Space-charge-limited-current (SCLC) mobility of the electron-only devices with a structure of ITO/ZnO/CCP1-3/PbS QDs/Al.

Table S1. The photodetecting properties at -0.5 V and -0.1 V as a function of the light intensity

CBL	Bias	P_{NIR} (mW/cm^2)	Jd ($\times 10^{-7}$ A/cm^2)	Jph ($\times 10^{-4}$ A/cm^2)	R (A/W)	D* ($\times 10^{10}$ Jones)
ZnO	-0.5	0.109	16.4	0.0516	0.0473	6.53
		1.04	16.4	0.534	0.0513	7.08
		5.20	16.4	2.60	0.0500	6.90
	-0.1	0.109	1.99	0.0391	0.0359	14.2
		1.04	1.99	0.423	0.0213	16.1
		5.20	1.99	1.95	0.375	14.9
CCP1	-0.5	0.106	1.42	0.174	0.164	77.0
		1.06	1.42	1.55	0.146	68.6
		5.20	1.42	6.90	0.133	62.2
	-0.1	0.106	0.280	0.125	0.118	125
		1.06	0.280	1.16	0.109	116
		5.20	0.280	5.12	0.098	104
CCP2	-0.5	0.106	1.40	0.357	0.337	159
		1.06	1.40	3.17	0.299	141
		5.20	1.40	14.7	0.283	133
	-0.1	0.106	0.530	0.301	0.284	218
		1.06	0.530	2.68	0.253	194
		5.20	0.530	12.1	0.233	179
CCP3	-0.5	0.106	1.69	0.168	0.158	68.1
		1.04	1.69	1.48	0.142	61.1
		5.20	1.69	6.67	0.128	55.1
	-0.1	0.106	0.410	0.133	0.125	109
		1.04	0.410	1.18	0.113	98.9
		5.20	0.410	5.31	0.102	89.1

REFERENCE

S1. J. Kang, D. Park, M.-K. Jeong, J. Kim, S. H. Eom, S.-Y. Jang, S. Yim and I. H. Jung, *Adv. Mater. Interfaces*, 2019, **6**, 1801666.