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Supporting Information

Uniform Multi-Nanoparticles Hierarchical Manipulating by Electro-chemical Coupling Assembly

Jian Zhang,[†,‡] Ji Qi,[†] Shusen Kang,[†] Haizhu Sun,[*,‡] Mao Li[*,†]

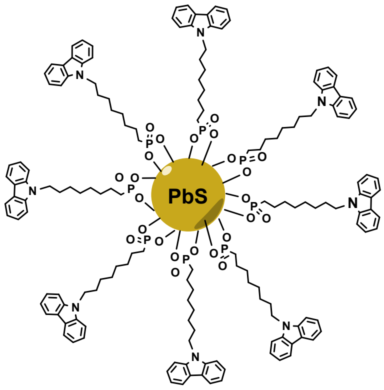
[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

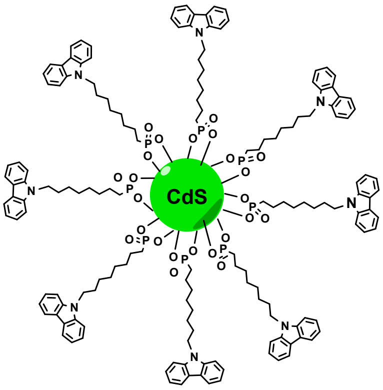
[‡]College of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

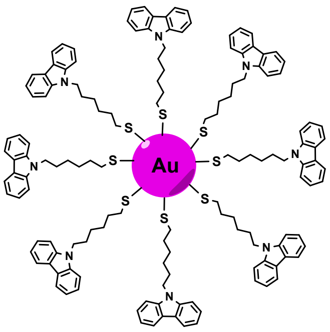
Contents

1. Materials

Materials and reagents used in this study were purchased from Aldrich Chemical Co., Aladdin Chemistry Co., Adamas Reagent Co., and Tokyo Chemical Industry Co., and used without further purification. The solvents were refined and dried by standard methods prior to use. The structures of NPs studied in this article are shown as below and the synthesis procedures are described in section 4.







2. Description on experimental techniques

2.1 General techniques

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were obtained at room temperature using a Bruker Avance 400 NMR spectrometer. Electronic absorption spectra were measured using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. SEM images were obtained using a FEL XL30ESEM-FEG scanning electron microscope operating at an accelerating voltage of 10 kV. TEM images were obtained using a JEOL-JEM2100 operating at 200 kV. AFM study was carried out using a commercial AFM unit (SPA 300HV with a SPI 3800N Probe Station, Seiko

Instruments Inc., Japan). All AFM images were taken in dynamic force mode (DFM, i.e., tapping mode) at optimal force. XPS (X-ray photoelectron spectra) were recorded using a Thermo ESCALAB 250 Electron Spectrometer.

2.2 Electrochemical experiments

For the electrochemical experiments, the supporting electrolyte $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) was dried for 24 h at 80°C under vacuum before use. Cyclic voltammetry (CV) experiments were performed using a standard one-compartment, three-electrode electrochemical cell driven by CHI 660b electrochemical workstation. In all cases, Ag/0.01M $AgNO_3$ ($E_{1/2} = 0.26$ V *vs* Fc/Fc^+) was used as reference. Indium tin oxide (ITO) (8-12 Ω/□, Aldrich) (deposition area: ~ 1.0 cm^2) was used as working electrode; the counter electrode was a gold foil (area: ~ 2.0 cm^2). The scan rate was set as 200 mV/s. The concentration of monomer in CH_2Cl_2 is 1.0 mg/mL. After electrochemical processes, the resulting films were rinsed with CH_2Cl_2 to remove any unreacted precursors.

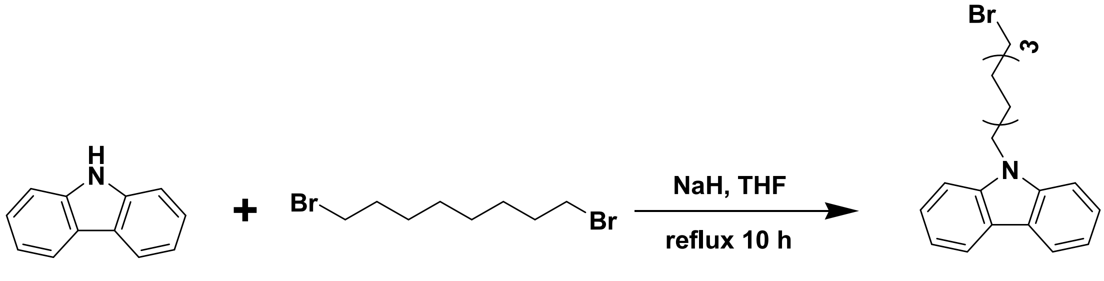
2.3 Device characterization

All measurements were carried out under ambient conditions. EQE was measured using a tungsten lamp (250 W) and a monochromator chopped at 160 Hz with a lock-in amplier (SR830, Stanford Research Systems) to eliminate background noise. The reference was a calibrated Si photodiode (S1337-1010BQ, Hamamatsu, calibrated by the National Institute of Metrology of China) with known EQE spectra. Reverse bias on the device was provided by a Keithley 236 Source Measure Unit. For the dark current measurement, current–voltage characteristics were recorded using a Keithley

236 source measurement unit. The light current characteristics were measured under 430 nm monochromatic light illumination.

3. Syntheses and characterization of organic electroactive ligand

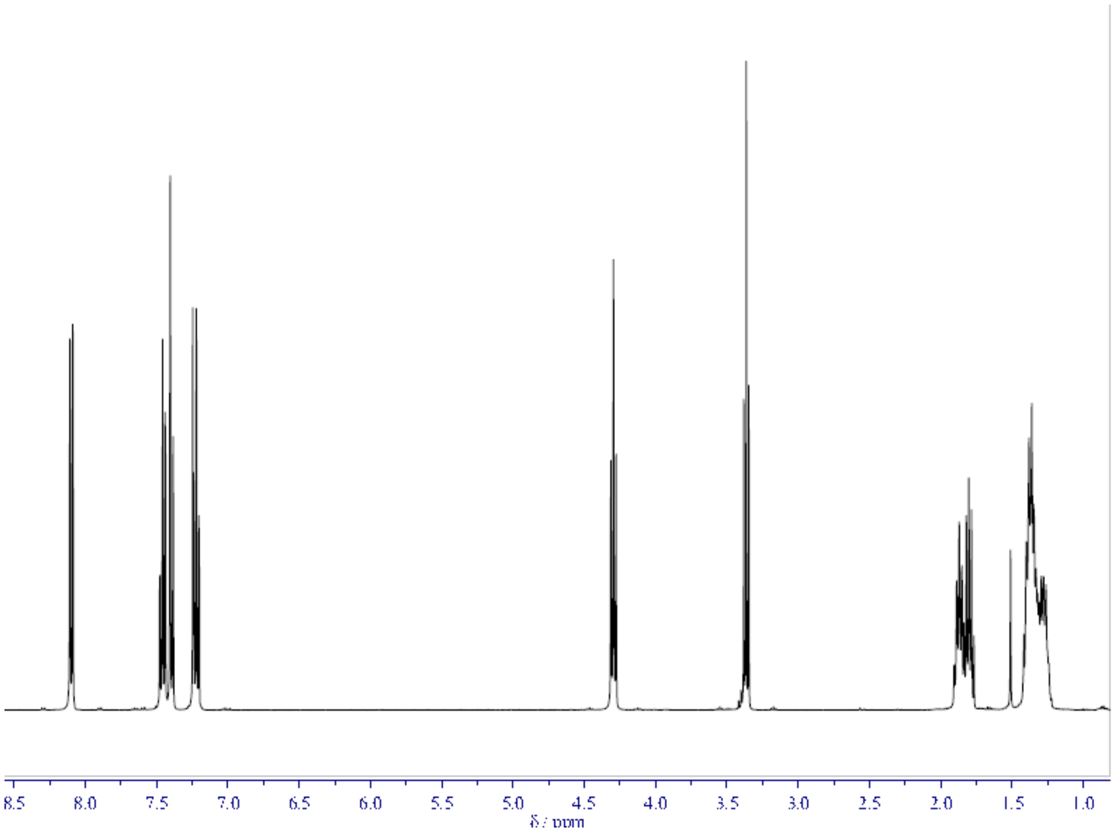
N-(8-bromooctyl)-carbazole **(1)**



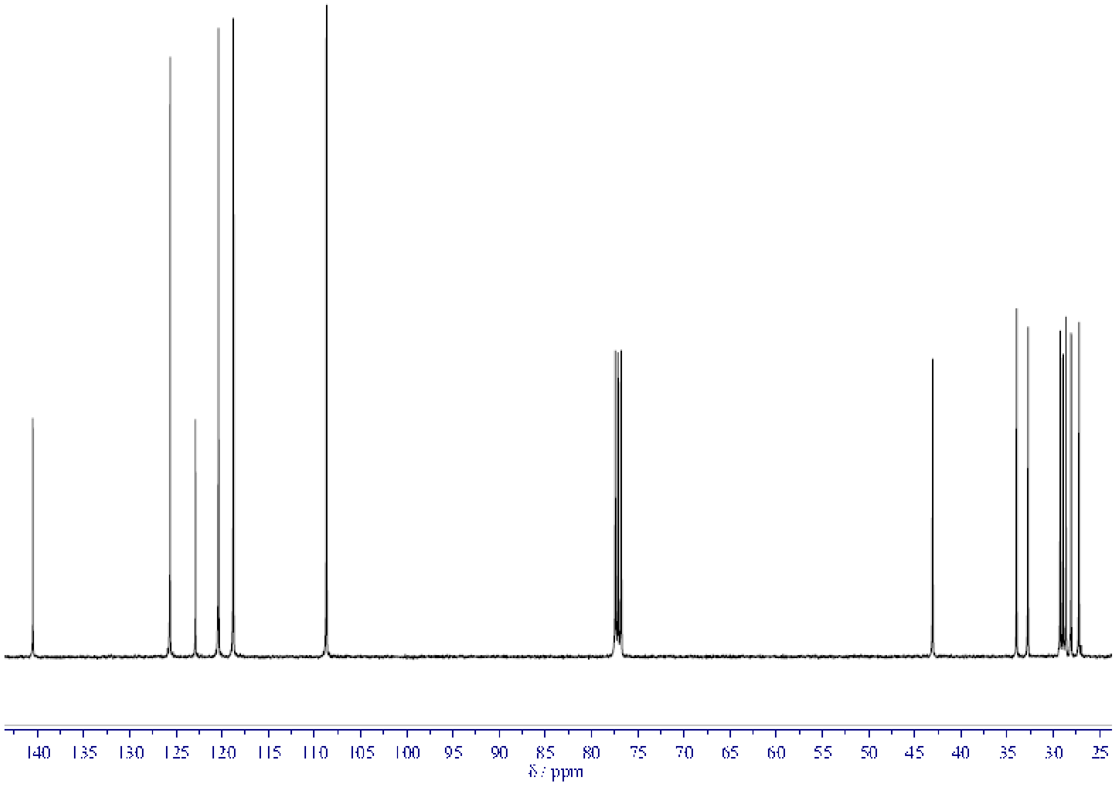
(1)

To a solution of carbazole (2.0 g, 12 mM) in THF (25 mL), was added sodium hydride (0.56 g, 24 mM, 60%) and stirred for 3 h at room temperature. The resulting solution was slowly introduced through a dropping funnel into the THF solution of 1,8-dibromooctane (6.53 g, 24 mM) and refluxed for 10 h under Argon atmosphere. The reaction was quenched by adding water, then the organic phase was separated and washed with water, dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was subjected to silica gel column chromatography (eluent: petroleum ether/CH_2Cl_2= 5/1) to afford compound **(1)** (2.51 g, 7 mM, 58%) as a colorless viscous liquid. ^{1}H-NMR (ppm, $CDCl_3$, 300 MHz): δ = 8.10 (d, 2H, Ar-H), 7.46 (t, 2H, Ar-H), 7.39 (d, 2H, Ar-H), 7.22 (t, 2H, Ar-H), 4.30 (t, 2H, NCH_2), 3.36 (t, 2H, CH_2Br), 1.87 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 1.36 (m, 8H, CH_2). ^{13}C-NMR (ppm, $CDCl_3$, 300 MHz): δ = 140.5, 125.6, 122.9, 120.4, 118.8, 108.7, 43.1, 34.0, 32.7, 29.2, 29.0, 28.6, 28.1, 27.2.

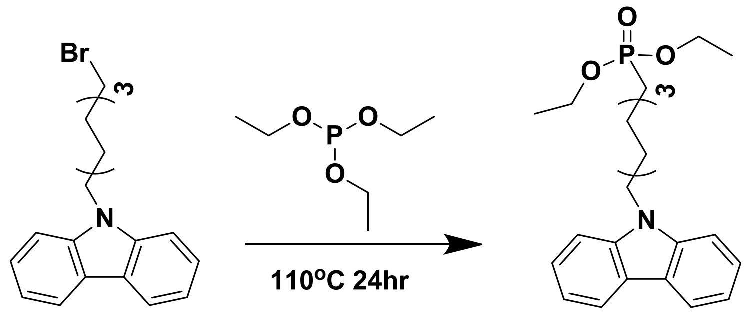
^{1}H-NMR spectrum of *N*-(8-Bromooctyl)-carbazole **(1)**



^{13}C-NMR spectrum of *N*-(8-Bromooctyl)-carbazole **(1)**



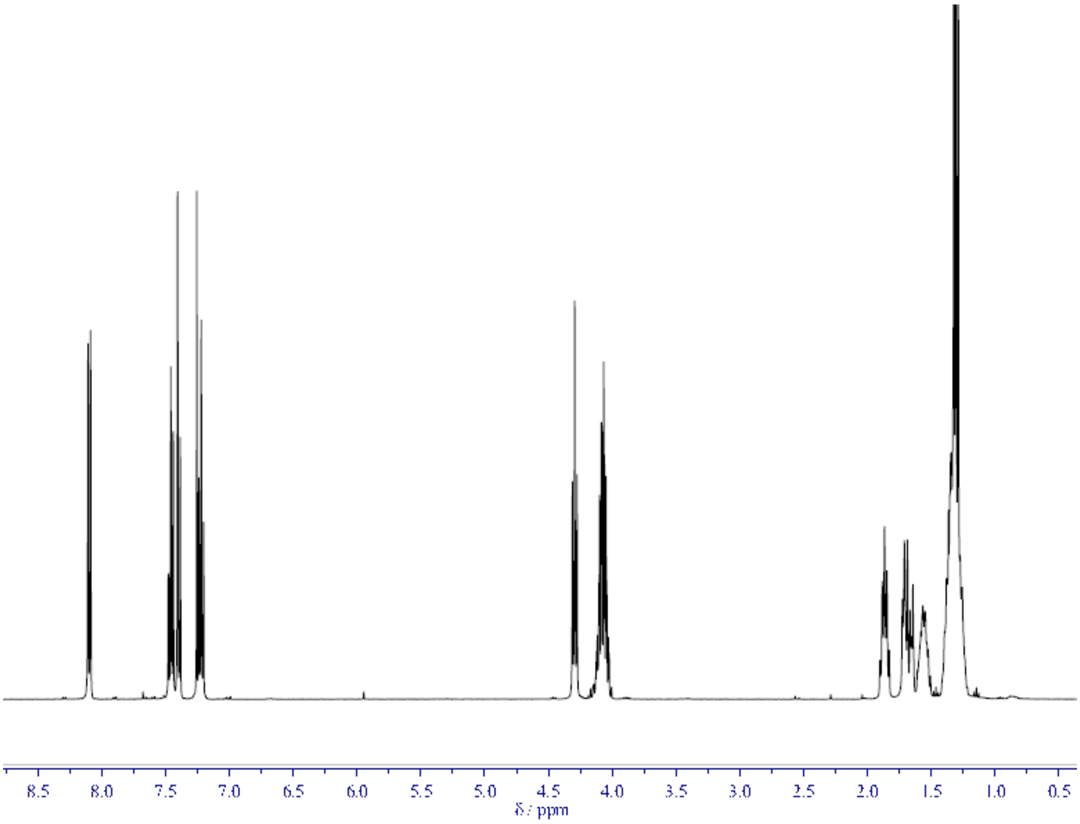
Diethyl 8-(9H-carbazol-9-yl)octylphosphonate **(2)**



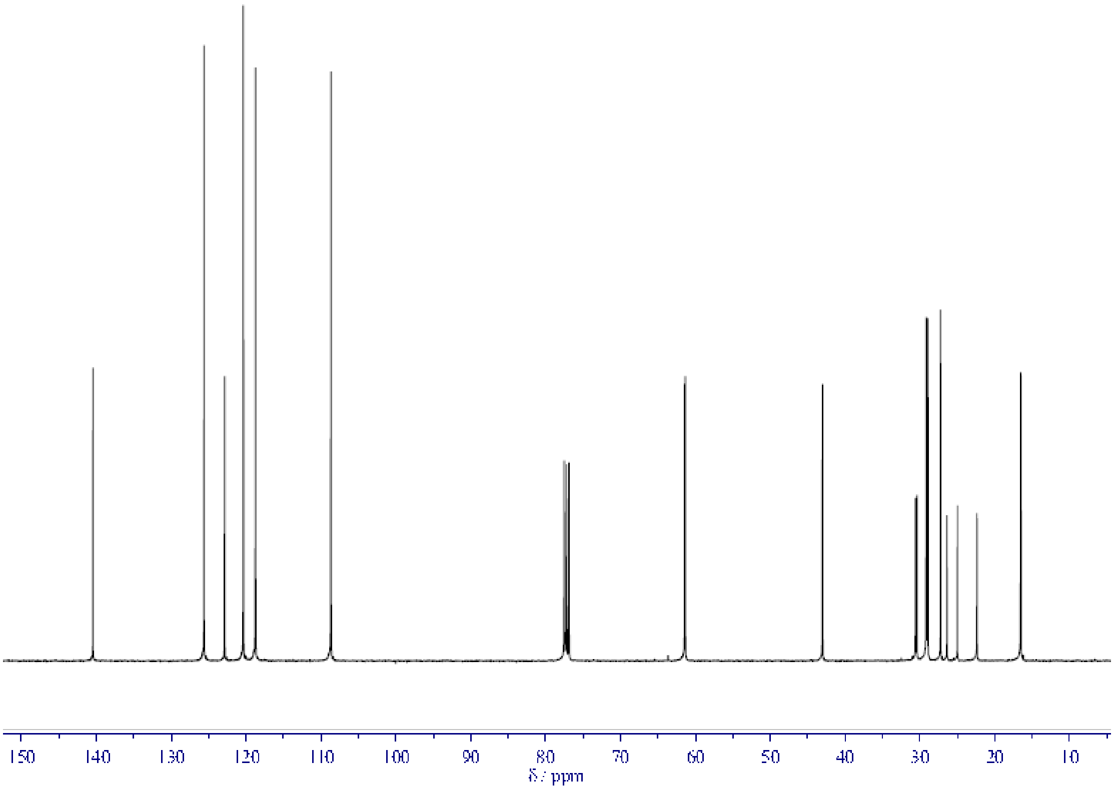
(1) **(2)**

A mixture of compound **(1)** (2.51 g, 7 mM) and triethyl phosphate (1.34 mL, 8 mM) was stirred under Argon atmosphere at 110°C for 24 h to complete the reaction. The crude product was dissolve with CH_2Cl_2 and purified by chromatography (eluent: CH_2Cl_2/ethyl acetate = 10/1) to give a colorless viscous liquid. Yield: 1.93 g, 66%. ^{1}H-NMR (ppm, $CDCl_3$, 300 MHz): δ = 8.10 (d, 2H, Ar-H), 7.46 (t, 2H, Ar-H), 7.39 (d, 2H, Ar-H), 7.22 (t, 2H, Ar-H), 4.29 (t, 2H, NCH_2), 4.07 (m, 4H, OCH_2), 1.86 (p, 2H, CH_2), 1.69 (m, 2H, PCH_2), 1.56 (m, 2H, CH_2), 1.31(m, 14H, CH_2, CH_3) . ^{13}C-NMR (ppm, $CDCl_3$, 300 MHz): δ = 140.4, 125.6, 122.8, 120.3, 118.7, 108.7, 61.4, 43.0, 30.6, 29.1, 27.2, 26.4, 25.0, 22.4, 16.5. ^{31}P-NMR (ppm, $CDCl_3$, 300 MHz): δ = 32.4.

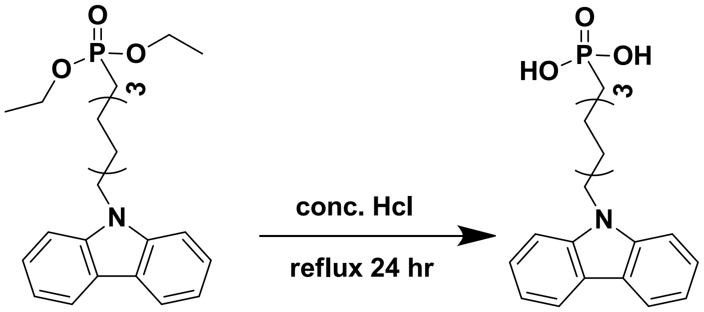
^{1}H-NMR spectrum of Diethyl 8-(9H-carbazol-9-yl)octylphosphonate **(2)**



^{13}C-NMR spectrum of Diethyl 8-(9H-carbazol-9-yl)octylphosphonate **(2)**



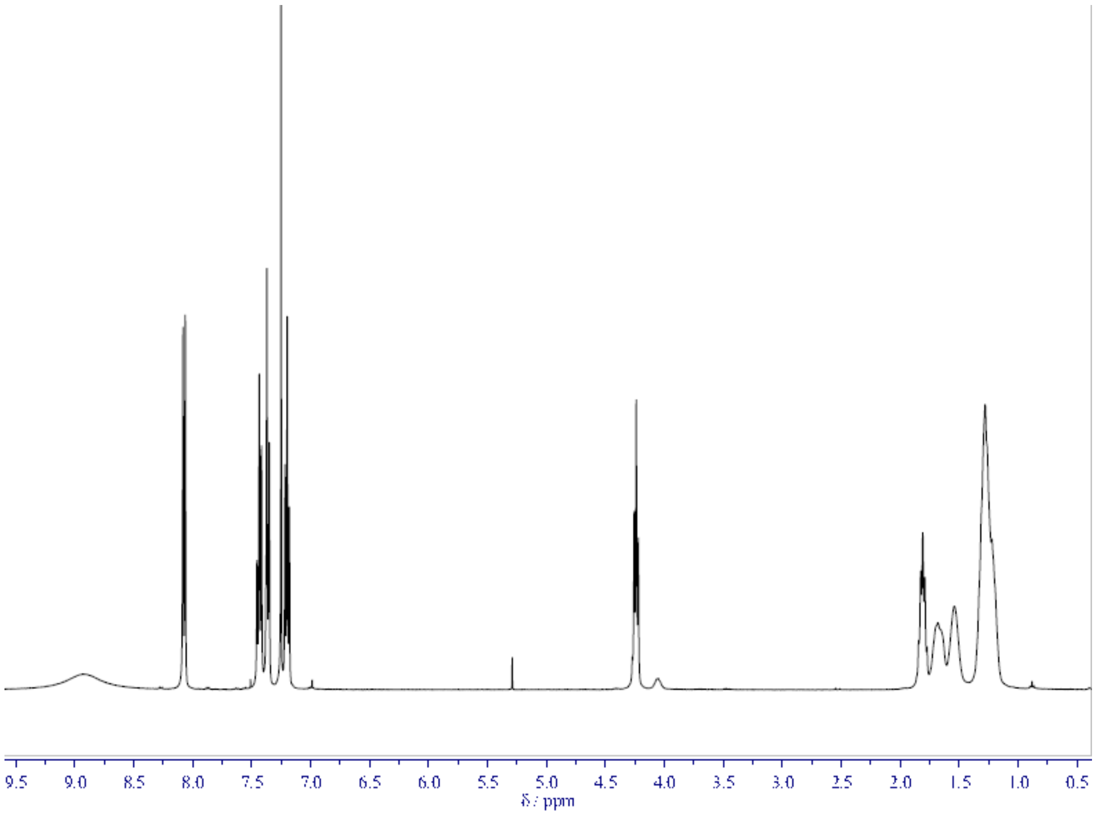
8-(9H-carbazol-9-yl)octylphosphonic acid (COPA) **(3)**



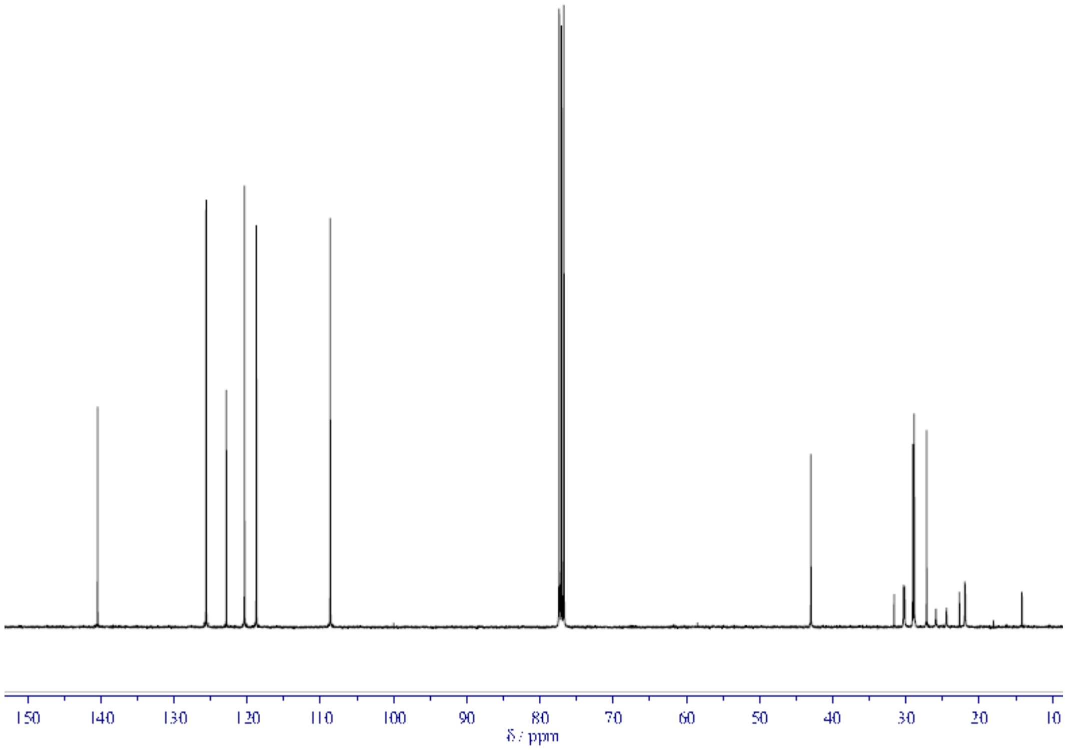
(2) **(3)**

Compound **(2)** (0.915 g, 2.20 mM) was added to concentrated hydrochloric acid (2 mL) and the mixture was refluxed for 24 h. After cooling to room temperature, the crude product was extracted with CH_2Cl_2, then concentrated the solution with reduced pressure distillation and added hexane to precipitate compound **(3)**, filtered and dried in vacuum oven to get pale green powder. Yield: 0.634 g, 80%. ^{1}H-NMR (ppm, $CDCl_3$, 300 MHz): δ = 8.9 (s, 2H, POOH), 8.10 (d, 2H, Ar-H), 7.46 (t, 2H, Ar-H), 7.39 (d, 2H, Ar-H), 7.22 (t, 2H, Ar-H), 4.24 (t, 2H, NCH_2), 1.81 (p, 2H, CH_2), 1.68 (m, 2H, PCH_2), 1.54 (m, 2H, CH_2), 1.28 (m, 8H, CH_2). ^{13}C-NMR (ppm, $CDCl_3$, 300 MHz): δ = 140.4, 125.6, 122.8, 120.3, 118.7, 108.7, 43.0, 31.6, 30.3, 29.0, 28.9, 28.6, 27.2. ^{31}P-NMR (ppm, $CDCl_3$, 300 MHz): δ = 37.3.

^{1}H-NMR spectrum of 8-(9H-carbazol-9-yl)octylphosphonic acid **(3)**



^{13}C-NMR spectrum of 8-(9H-carbazol-9-yl)octylphosphonic acid **(3)**



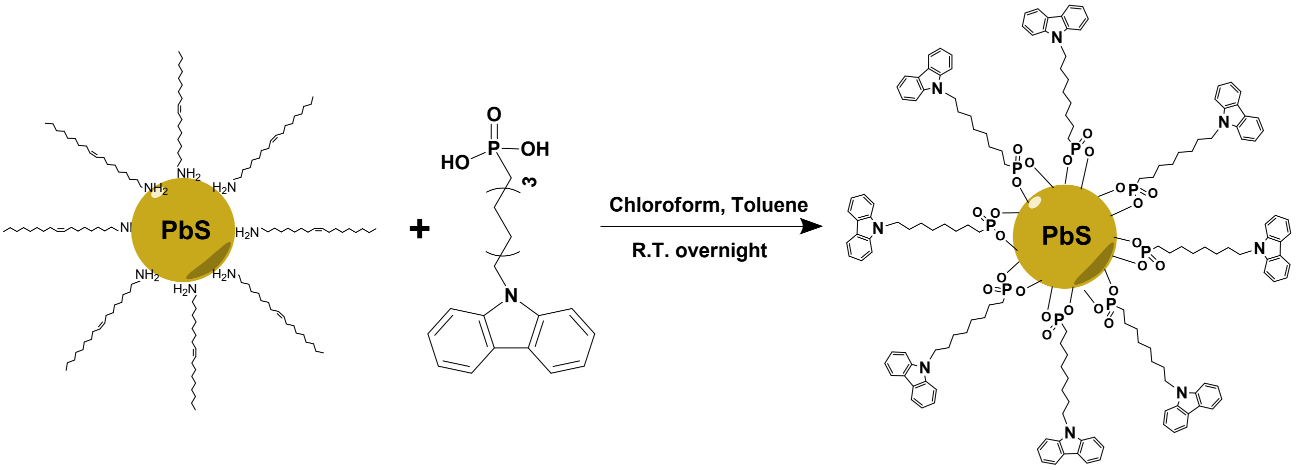
4. Syntheses of PbS, CdS and Au NPs

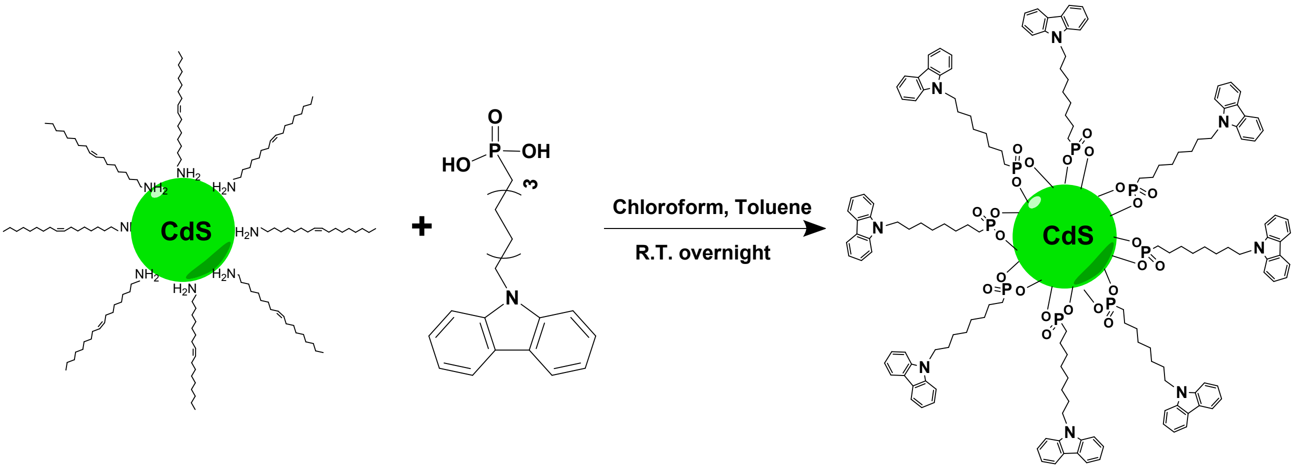
Oleylamine (OLA) capped PbS and CdS NPs

The synthesis of PbS and CdS NPs was according to reported method[S1,S2,S3] with minor modification. Specifically, $PbCl_2$ (167 mg, 0.6 mM) was added to 2.5 mL of oleylamine (OLA) at room temperature and the resulting solution was heated to 90°C under vacuum, forming a homogeneous and clear solution. At the same time, sulfur (32 mg, 1.0 mM) was dissolved in 6.7 mL OLA and the solution was heated at 80 °C. 1.0 mL of the sulfur-OLA solution (0.15 mM sulfur) is then quickly injected into Pb-oleylamine complex solution (S:Pb = 1:4) at 90°C under Argon atmosphere. The resulting mixture was then heated to 120°C and aged at that temperature for 30 min, resulting in a black colloidal solution. Ethanol was added to precipitate PbS NPs, and centrifugation was performed to purify the NPs to give black solid, dissolved in toluene for subsequent ligand exchange process.

In term of CdS NPs, Sulfur (0.15 mM) in 1 mL of oleylamine was injected into the oleylamine solution containing 0.30 mM of $CdCl_2$ (S:Pb = 1:2) at 160 °C. The reacting mixture was aged for 6 h at that temperature. The resulting CdS nanocrystals were retrieved by adding ethanol followed by centrifugation.

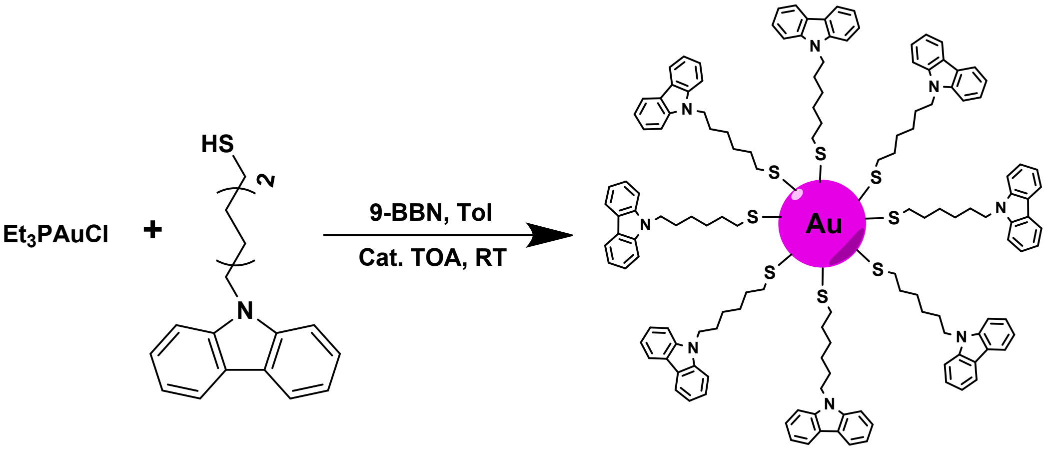
Ligand exchange for electrochemical cross-linkable NPs





A mixture of as synthesized PbS (CdS) NPs in toluene and electroactive ligand **(3)** in chloroform was stirred overnight at room temperature under Argon gas to complete the ligand exchange. The resulting solution was precipitated with ethanol and centrifuged to purify the NPs. The resulting solid was dried with Argon flow, and dissolved in refined CH_2Cl_2 for electrochemical assembly.

Carbazyl thiol capped Au NPs



Au NPs was synthesized based on our previous paper for experimental details.[S4]

5. Supporting information figures

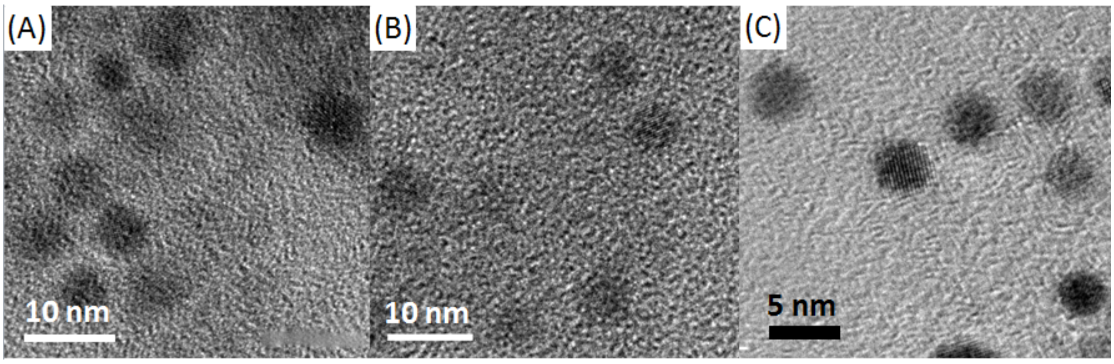


Fig. S1 TEM images of (A) PbS, (B) CdS and Au NPs.

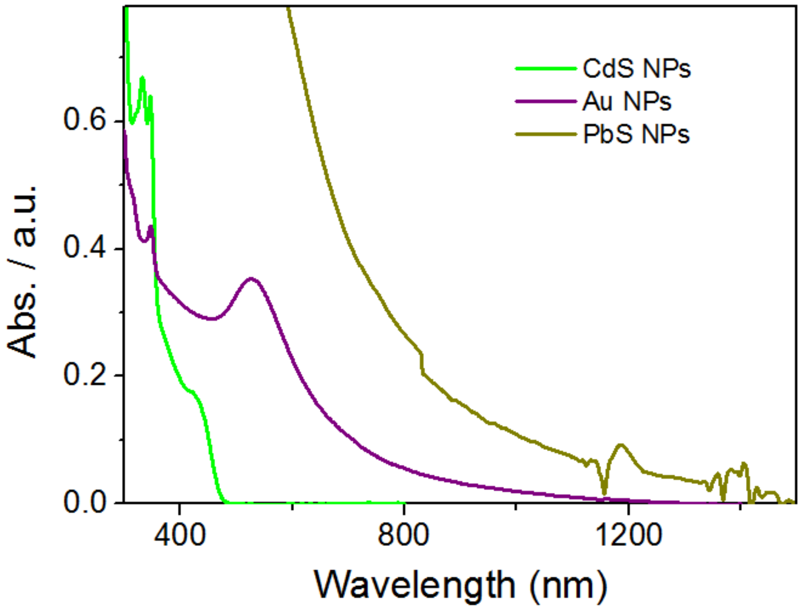


Fig. S2 Absorption spectra of CdS, Au and PbS NPs in CH_2Cl_2 solution.

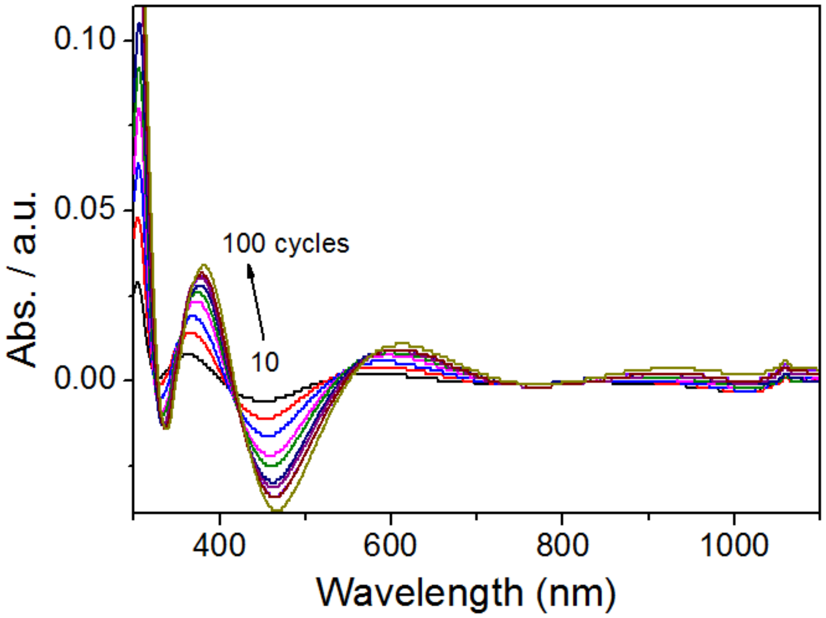


Fig. S3 Absorption spectra of CdS NPs assembly film at relative low positive potential of 0.9 V.

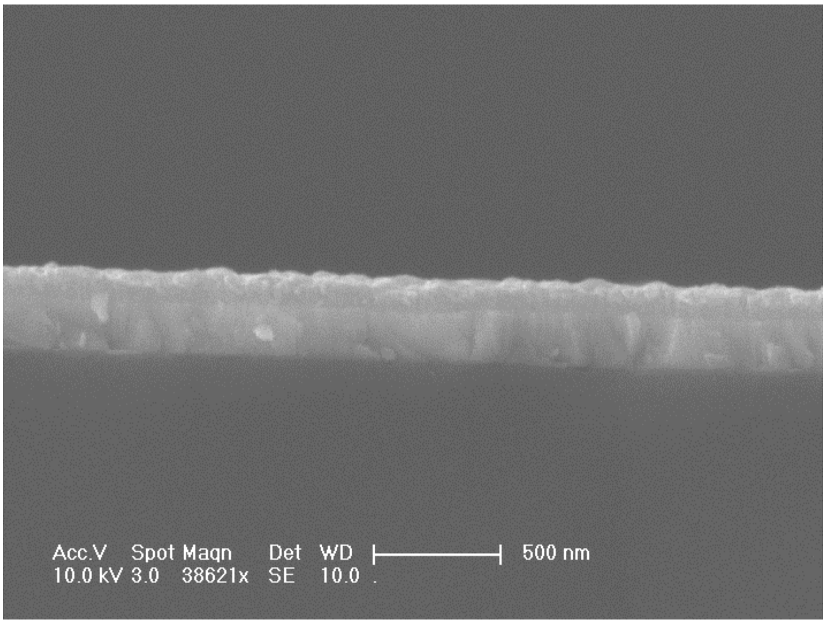


Fig. S4 Cross-section SEM image of CdS NPs electrochemical assembly film.

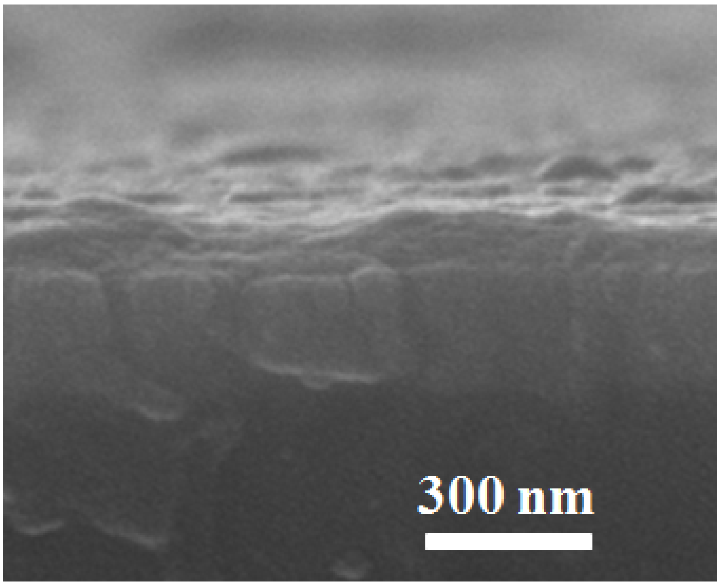


Fig. S5 Cross-section SEM image of Au/PbS NPs hybrid assembly film.

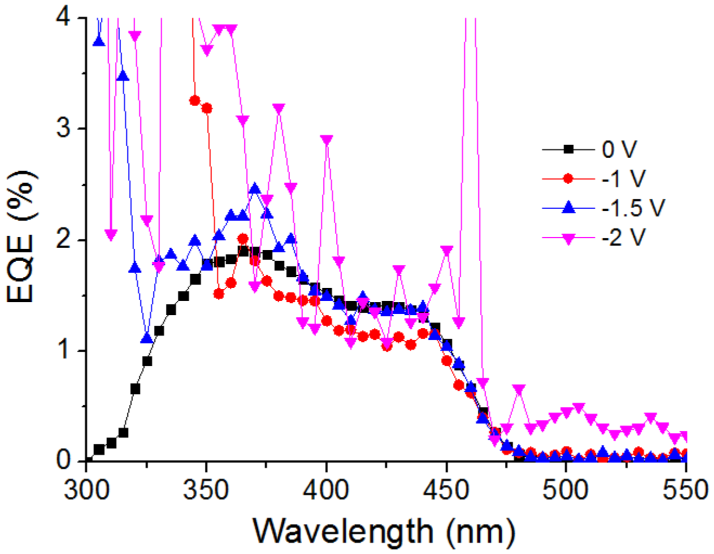


Fig. S6 EQE of CdS NPs single layer device. Applied more than -1 V bias, EQE curve fluctuates much.

6. References

S1 Weidman, M. C.; Beck, M. E.; Hoffman, R. S.; Prins, F.; Tisdale, W. A. *ACS nano* **2014**, *8*, 6363–6371.

S2 Cademartiri, L.; Bertolotti, J.; Sapienza, R.; Wiersma, D. S.; von Freymann, G.; Ozin, G. A. *J. Phys. Chem. B* **2006**, *110*, 671–673.

S3 Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F.; Zhang, J. Z.; Hyeon, T. *J. Am. Chem. Soc.* **2003**, *125*, 11100–11105.

S4 Gao, Y.; Qi, J.; Zhang, J.; Kang, S.; Qiao, W.; Li, M.; Sun, H.; Zhang, J.; Ariga, K. *Chem. Commun.* **2014**, *50*, 10448–10451.