

Supporting Information for

Semiconductor Nanocrystals in Fluorous Liquids for the Construction of Light-Emitting Diodes

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Experimental

Raw materials and solvents

Heptadecafluoro-1-iodooctane, tridecafluoro-1-iodohexane, 5-hexen-1-ol (98%, TCI), 3-buten-1-ol (98%, TCI), azobisisobutyronitrile (AIBN), sodium bis(2-methoxyethoxy) aluminium dihydride (70% w/w solution in toluene, TCI), imidazole (99%, Alfa Aesar co.), iodine (99.8%, Yakuri), triphenylphosphine (98%, Deajung), thiourea (ACS reagent, >99%, Sigma-Aldrich), aliquat[®] 336 (Aldrich), diethyl ether (anhydrous), tetrahydrofuran (THF), distilled water, hexane, and toluene were used as received.

Equipment

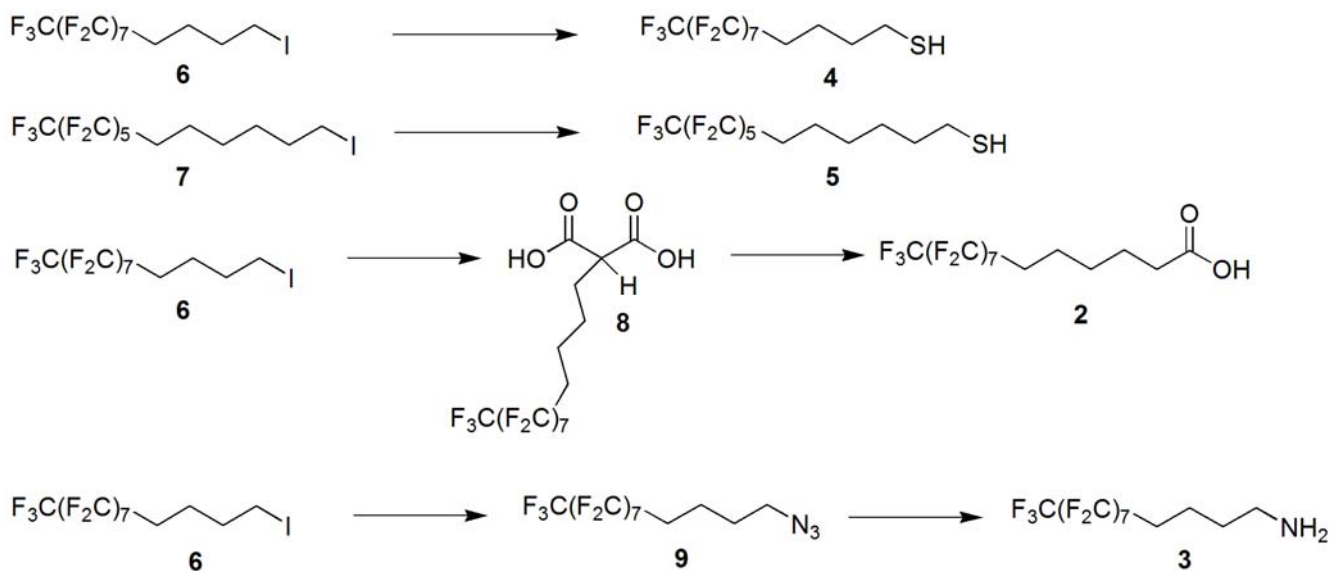
The ¹H NMR spectra were recorded on a Varian Inova-400 (400 MHz) spectrometer at ambient temperature using the chemical shift of the residual protic solvent (CHCl₃ at δ 7.24 ppm and DMSO at δ 2.50 ppm) as an internal reference. All chemical shifts are quoted in parts per million (ppm)

relative to the internal reference and the coupling constants, J , are reported in Hz. The multiplicity of the signal is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dm (doublet of multiplets), tt (triplet of triplets), and br s (broad singlet). The ^{13}C NMR spectra were recorded on a Varian Inova-400 (101 MHz) spectrometer using the central resonance of the triplet of CDCl_3 at δ 77.0 ppm or the septet of DMSO-d_6 at δ 40.0 ppm as a reference. GC-Mass spectrometry was performed on a Varian 1200L Single Quadrupole GC/MS System with 3800GC. A zeta potential analyzer (ELS-Z, Otsuka Electronics) was used to confirm the particle size distribution in a fluorinated solvent. The absorption spectra of the TCTA films with the solvent treatment were obtained using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Technologies) with an integrating sphere system. The ultraviolet photoelectron spectroscopy (UPS) measurements were performed using Kratos AXIS-NOVA, employing He I light source and a hemispherical analyzer. The valence band maximum (VBM) of the nanocrystals was calculated using the following equation:

$$\text{VBM} = 21.2 \text{ eV} - |E_{\text{cutoff}} - E_{\text{onset}}|$$

[He I light photon energy = 21.2 eV; high binding energy cutoff (E_{cutoff}); onset point at valence band region (E_{onset})].

Synthesis of semi-perfluoroalkyl ligands



Scheme S1 Synthesis of semi-perfluoroalkyl ligands.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptafluorododecane-1-thiol **4**

A round bottomed flask was filled with semi-perfluoroalkyl iodide **6**¹ (5.0 g, 8.3 mmol), thiourea (0.95 g, 12.5 mmol), Aliquat 336 (0.21 g, 0.53 mmol) and water (25 cm³). The mixture was heated

under reflux and stirred for 20 h. After the reaction, an aqueous KOH (50 cm³, 0.1 M) solution was added. After 0.5 h, the mixture was cooled to ambient temperature and concentrated HCl was added until the mixture became acidic. The mixture was extracted with CH₂Cl₂ (100 cm³) and then dried over anhydrous MgSO₄. The solution was concentrated under reduced pressure. The light brown oil was purified by flash column chromatography (silica gel, hexanes) to give thiol **4** as opaque crystals (2.6 g, 62%); δ_{H} (400 MHz, CDCl₃) 2.55 (2H, td, $J = 7.0$ Hz, CH₂SH), 2.06 (2H, m, CF₂CH₂), 1.70 (4H, m, CF₂CH₂CH₂CH₂), 1.35 (1H, t, $J = 7.5$ Hz, CH₂SH). ¹³C NMR (101 MHz, CDCl₃, δ) 33.5, 30.42 (t, $J = 22$ Hz), 24.3, 19.3; m/z (GC-MS, EI) 508.0 [M⁺. C₁₂H₉F₁₇S requires M, 508.24].

1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-12-iododecane **7**

I₂ (7.93 g, 31.2 mmol) was added to a magnetically stirred solution of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecan-1-ol² (8.75 g, 20.8 mmol), triphenylphosphine (8.19 g, 31.2 mmol) and imidazole (2.13 g, 31.2 mmol) in THF (200 cm³) in a dry ice/acetone bath under a N₂ atmosphere. The reaction mixture was allowed to warm to ambient temperature. After stirring at that temperature for 2 h, the reaction was quenched by the addition of water (200 cm³) and Et₂O (200 cm³). The organic layer was then separated, washed with brine (200 cm³) and concentrated under reduced pressure. When a large amount of triphenylphosphine oxide precipitated, Et₂O (100 cm³) was added to the flask. The precipitated solid was filtered off through a short plug of silica gel and flushed with copious amounts of Et₂O. The filtrate was concentrated under reduced pressure and the resulting viscous liquid was crystallized from EtOH (90 cm³) to give the iodide **7** as colorless crystals (7.78 g, 71%); δ_{H} (400 MHz, CDCl₃) 3.33 (2H, t, $J = 7$ Hz, CH₂I), 2.20 (2H, td, $J = 9$ Hz, CF₂CH₂), 1.98 (2H, td, $J = 6.5$ Hz, CF₂CH₂CH₂), 1.76 (2H, td, $J = 7.5$ Hz CH₂CH₂I), 1.62 - 1.52 (4H, m, CF₂CH₂CH₂CH₂CH₂).

7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecane-1-thiol **5**

A round bottomed flask was filled with iodide **7** (5.0 g, 9.4 mmol), thiourea (1.08 g, 14.1 mmol), Aliquat 336 (0.25 g, 0.61 mmol), and water (25 cm³). The mixture was heated to 100 °C and stirred for 20 h. After 20 h, an aqueous KOH (50 cm³, 0.1 M) solution was added. After 0.5 h, the mixture was cooled to ambient temperature and concentrated HCl was added until the mixture became acidic. The mixture was extracted with CH₂Cl₂ (150 cm³) and dried over anhydrous MgSO₄. The solution was concentrated under reduced pressure. The light brown oil was purified by flash column chromatography (silica gel, hexanes) to give thiol **5** as opaque crystals (2.2 g, 42%); δ_{H} (400 MHz, CDCl₃) 2.5 (2H, td, $J = 7.5$ Hz, CH₂SH), 2.15 – 1.87 (2H, m, CF₂CH₂), 1.6 (4H, qd, $J = 8.0, 4.0$ Hz, CF₂CH₂CH₂CH₂), 1.48 – 1.16 (5H, m, CF₂CH₂CH₂CH₂CH₂CH₂CH₂SH). The δ_{H} data was in agreement with the literature values.³

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptafluorotetradecanoic acid 2

2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptafluorododecyl)malonic acid **8**⁴ (0.50 g, 0.86 mmol) was dissolved completely in DMF and the solution was heated under reflux at 190 °C. After 1 h, the mixture was distilled to remove the DMF. CHCl₃ was then added to the flask and the unreacted starting material was filtered off. Subsequently, the filtrate was cooled to give the semi-perfluoroalkyl carboxylic acid **2** as brown crystals; δ_{H} (400 MHz, CDCl₃) 2.37 (2H, t, $J = 7.0$ Hz, CH₂COOH), 2.05 (2H, m, CF₂CH₂), 1.68 (2H, m, CH₂CH₂COOH), 1.61 (2H, m, CF₂CH₂CH₂), 1.43 (2H, m, CF₂CH₂CH₂CH₂). The δ_{H} data was in agreement with the literature values.⁴

5,5,6,6,7,7,8,8,9,9,10,10,10,11,11,12,12,12-Heptafluorododecan-1-amine 3

A 100 cm³ round bottomed flask was filled with the semi-perfluoroalkyl iodide **6** (3.5 g, 5.77 mmol) and sodium azide (0.41 g, 6.34 mmol). DMF (anhydrous, 15 cm³) was then added and the solution was stirred at 55 °C for 2 h. After the reaction was complete, the solution was poured into ice/water (100 cm³) and the solid was removed by filtration and washed with ice/water. The solid was dissolved in diethyl ether (100 cm³) and then dried over anhydrous MgSO₄. The solution was then concentrated under reduced pressure. The viscous liquid was chromatographed (silica gel, EA:hexanes = 1:5) to give azide **9** as a colourless viscous liquid. A Schlenk tube was then charged with Pd/C (10%, 0.2 g) and a solution of azide **9** (2.2 g) in an ethanol/TFT 1:1 mixture (20 cm³), purged with H₂ (5 min), and fitted with a 3-layered balloon filled with H₂. The mixture was stirred at 35 °C for 3 h and filtered through a plastic syringe filter (0.45 μm , PFFE). The solvent was removed under reduced pressure and vacuum-dried to give the semi-perfluoroalkyl amine **3** as a white waxy solid (2.2 g, 77%) (400 MHz, CDCl₃) 2.63 (2H, t, $J = 6.5$ Hz, NCH₂), 2.04 (2H, m, CF₂CH₂), 1.63 (2H, m, CF₂CH₂CH₂CH₂), 1.55 (2H, m, CF₂CH₂CH₂CH₂CH₂). The δ_{H} data is in agreement with the literature values.⁵

Preparation of R_F1-NC

In the first place, semi-perfluoroalkyl thiol **4** (1.02 g, 2.01 mmol) and ⁱPr₂EtN (0.52 g, 4.02 mmol) were dissolved in CHCl₃ (40 cm³) and stirred at room temperature for 0.5 h.⁶ To remove the residual oleic acid ligand, a solution of CdSe/CdS/CdZnS core-shell type nanocrystals (**NC**) in toluene (1.5 cm³, 0.103 g cm⁻³) was diluted with 20 parts (by volume) of MeOH. The resulting precipitate was recovered by centrifuge and mixed with the aforementioned thiol **4** and ⁱPr₂EtN solution in CHCl₃. The reaction mixture was sonicated for 15 min at room temperature. The ligand-exchanged nanocrystals were precipitated by pouring excess hexanes, recovered by centrifuge and re-dispersed in CHCl₃. This dispersion-precipitation sequence was repeated two more times to obtain purified **R_F1-NC** (0.04 g). **R_F1-NC** (0.02 g) was then dissolved in HFE-7500 (1 cm³) and filtered through a

syringe filter (0.45 μm , nylon) to prepare a $\text{R}_{\text{F}1}\text{-NC}$ solution for solution casting.

Preparation and measurements of LEDs containing semiconductor nanocrystal light-emitting layers

The MoO_3 and TCTA as a HTL were thermally evaporated sequentially on the patterned ITO substrates. A $\text{R}_{\text{F}1}\text{-NC}$ (or $\text{R}_{\text{F}2}\text{-NC}$) solution in HFE-7500 (0.02 g per 1 cm^3 of HFE-7500) or a NC solution in hexanes (0.02 g per 1 cm^3 of hexanes) was spin-cast on the top of the TCTA / MoO_3 / ITO substrates at 2500 rpm for 40 s (for $\text{R}_{\text{F}1}\text{-NC}$ and $\text{R}_{\text{F}2}\text{-NC}$ solution) and 4000 rpm for 30 s (NC solution). The nanocrystal films were *ca.* 20 nm thick. TPBI as an ETL, LiF and an Al electrode were thermally evaporated sequentially on the former substrates under a pressure of 1×10^{-6} Torr. The current–voltage–luminance characteristics of the devices were measured using a source measurement unit (Keithley 236), a calibrated Si photodiode (Hamamatsu S5227-1010BQ), a photomultiplier tube detector and multimeter (Keithley 2000). The electroluminescence spectra of the devices were obtained using a spectroradiometer (Konica-Minolta CS-1000A).

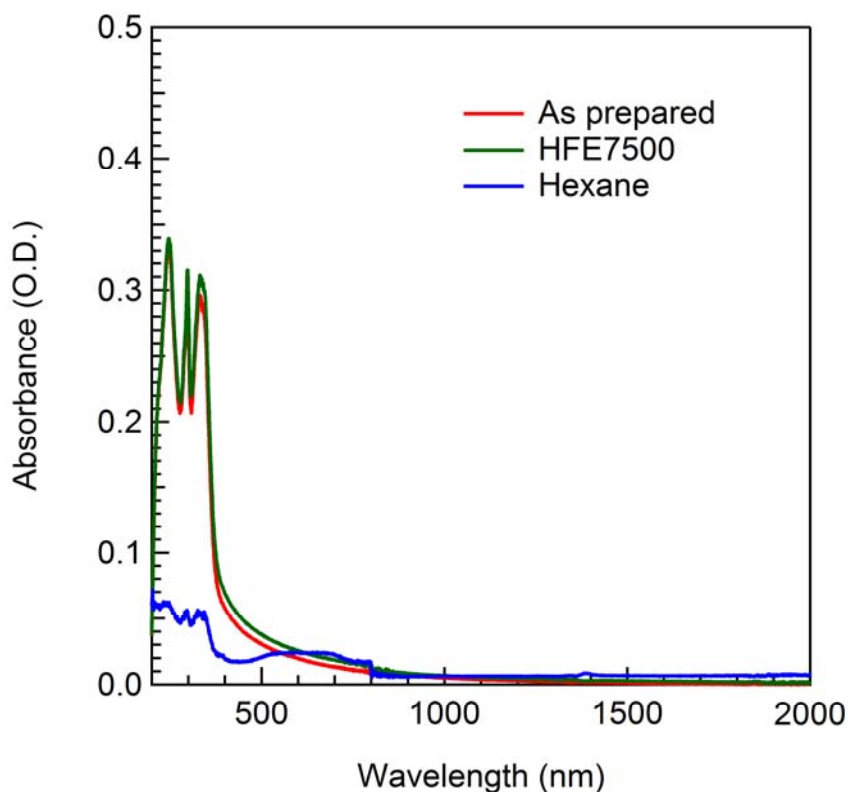


Fig. S1 UV-Vis absorption spectra of the TCTA films with the solvent treatment.

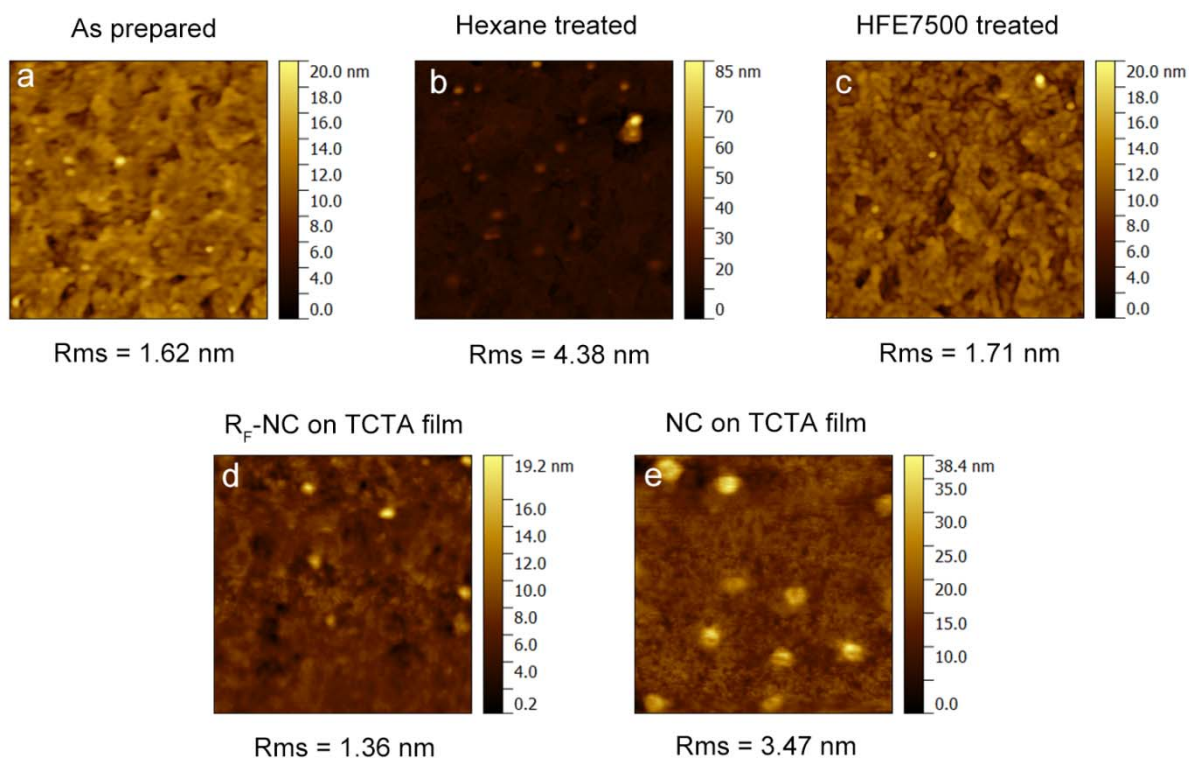


Fig. S2 AFM topography images (image size: 5 μm x 5 μm) of the TCTA films, (a) pristine sample, (b) after dipping in hexanes, (c) after dipping in HFE-7500. AFM topography images of the nanocrystal films, (d) **R_F1-NC** film on top of the TCTA layer, (e) **NC** film on top of TCTA layer.

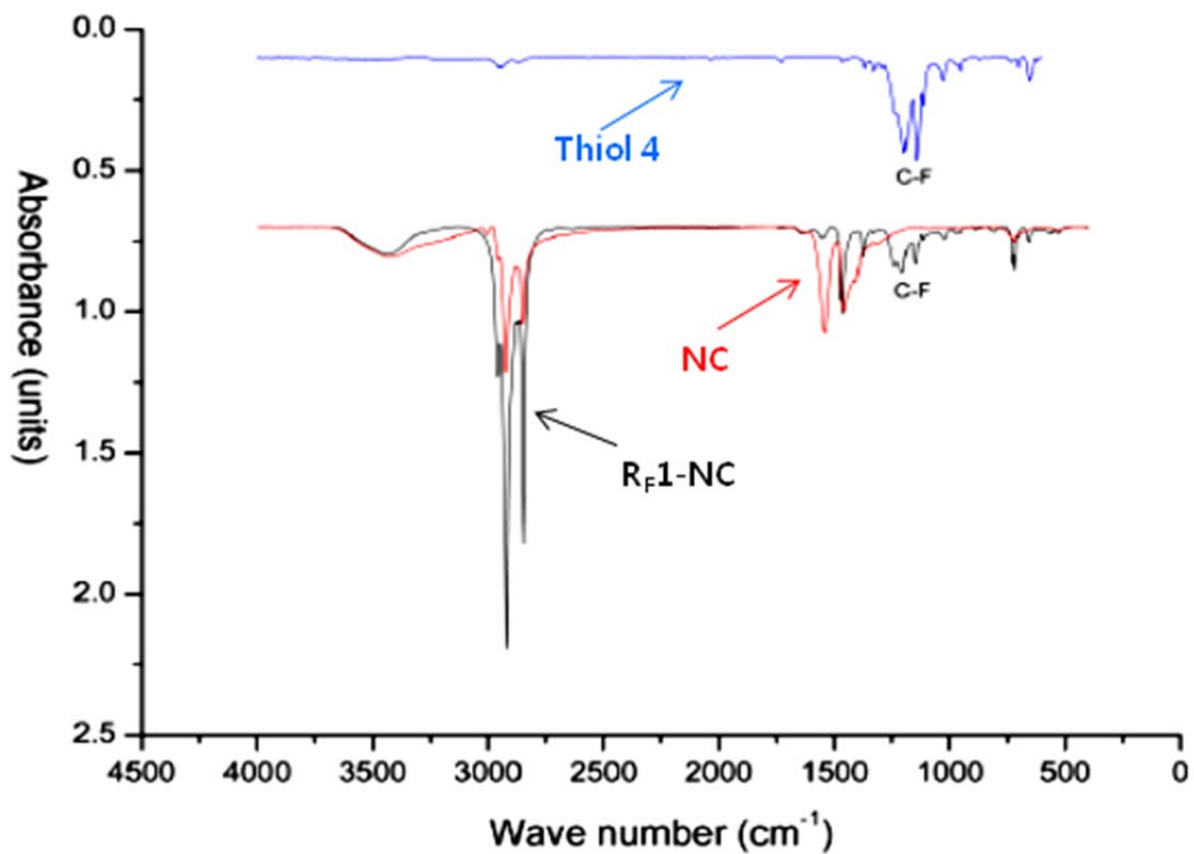


Fig. S3 FT-IR experiments of thiol **4**, NC and **R_F1-NC** in their KBr pellet form.

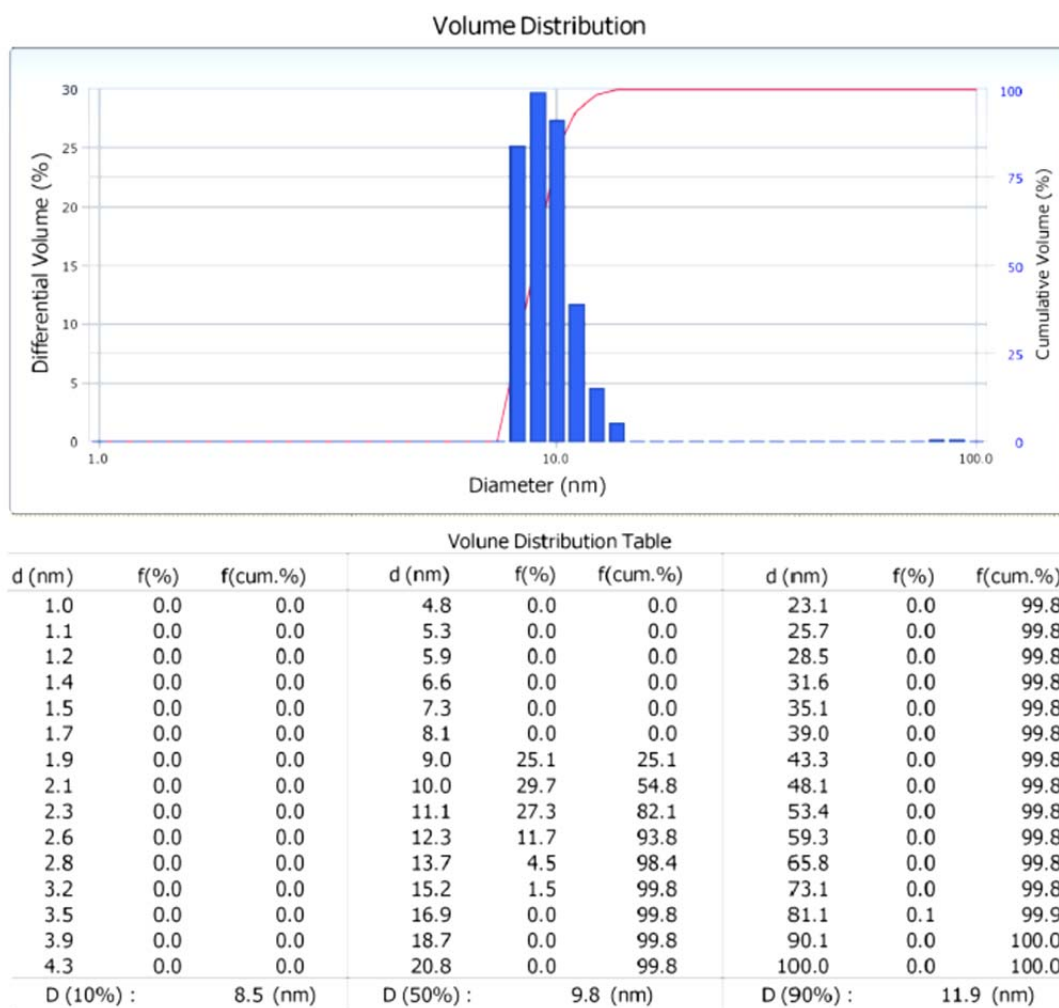


Fig. S4 Particle size distribution of **R_F1-NC** after the ligand exchange reaction (the particle sizes of **NC** before ligand exchange were 8 – 9 nm measured in hexanes). **R_F1-NC** was dissolved and diluted in HFE-7500 to the point suitable for the measurement.

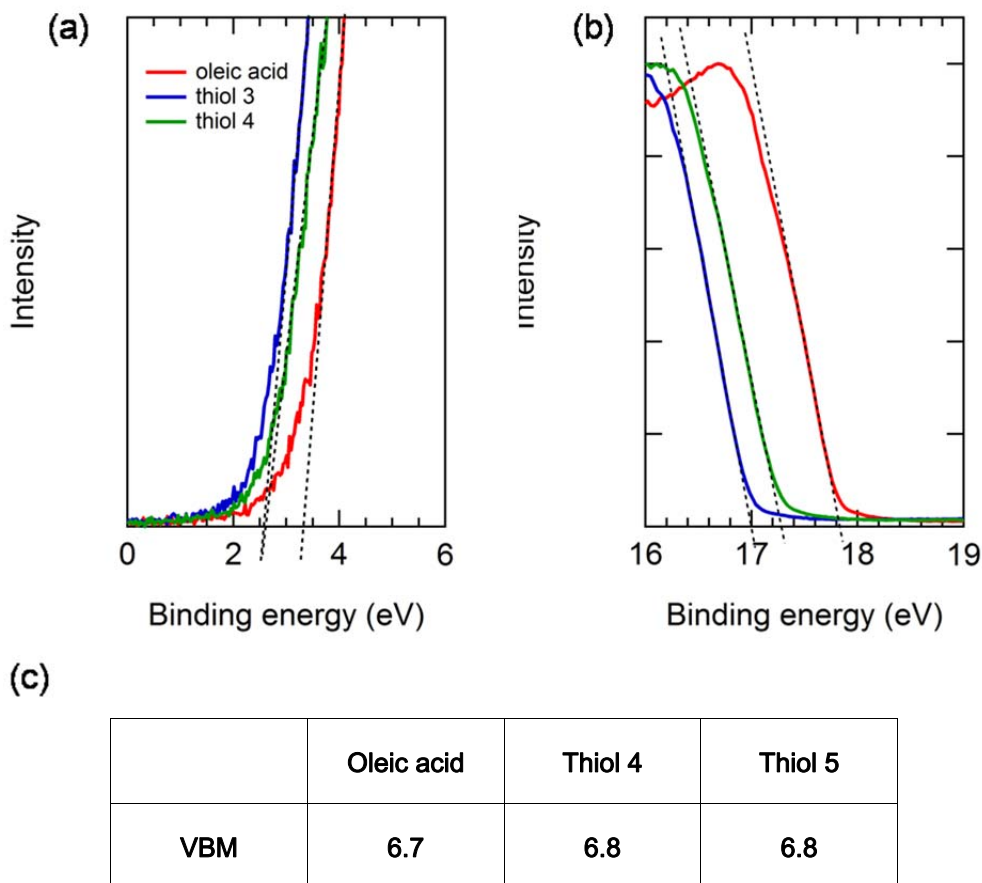


Fig. S5 UPS measurement data of NC, R_F1 -NC and R_F2 -NC, (a) valence band region, (b) high binding energy cut-off region, (c) valence band maximum (VBM) of the semiconductor nanocrystals

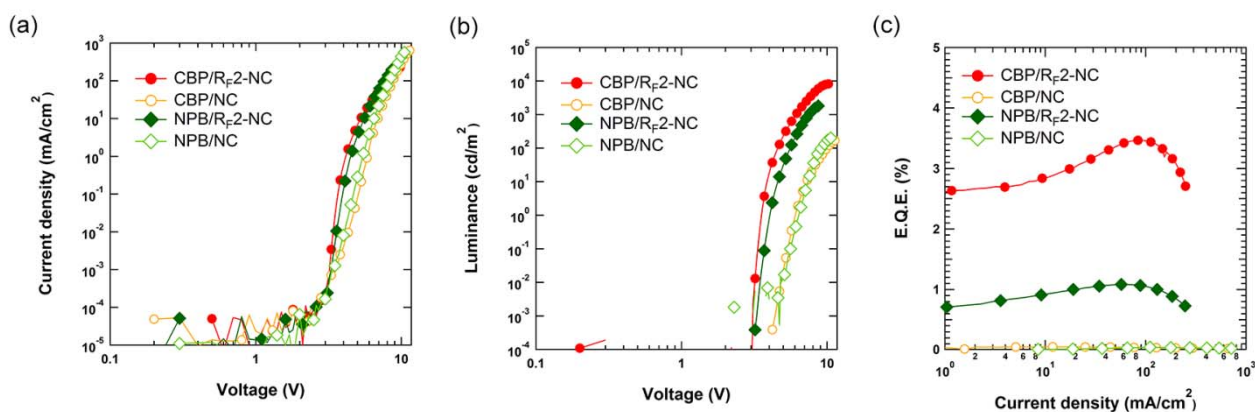


Fig. S6 Electrical characteristics of the LEDs fabricated with other hole-transporting layers in terms of (a) current density-voltage, (b) luminance-voltage characteristics, (c) external quantum efficiency-current density [CBP: 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl, NPB: *N,N*-di-(1-naphthyl)-*N,N*-diphenyl-(1,1'-biphenyl)-4,4'-diamine].

Table S1. LED performances containing NC (Device B), **R_F1-NC** (Device A) and **R_F2-NC** (Device C).

Device	V _{on} (V)	Max. EQE (%)	EQE at 100 cd m ⁻² (%)	Max. LE (cdA ⁻¹)
A	3.6	3.19	0.78	2.27
B	4.5	0.18	0.18	0.13
C	2.7	4.24	3.45	4.40

References

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