

[SUPPLEMENTARY MATERIAL]

Modeling Ligand Crosslinking for Interlocking Quantum Dots in Thin-films

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Materials

Anhydrous dichloromethane (DCM), octane-1,8-diol (HO(CH₂)₈OH), and anhydrous triethyl amine (NEt₃) were purchased from Sigma Aldrich. Thionyl chloride (SOCl₂) and the rest of other solvents were purchased from Daejung (Korea). Deuterated chloroform (CDCl₃) for ¹H-NMR and ¹⁹F-NMR measurement was purchased from Cambridge Isotope Laboratories.

These chemicals were used without further purification.

Characterization

To identify the molecular structure of the synthesized products, ^1H -NMR and ^{19}F -NMR spectra were measured by a Bruker Avance III 400 MHz NMR spectrometer and an Agilent 400 MHz FT-NMR spectrometer with CDCl_3 as a solvent. Mass spectrum was obtained by electrospray ionization-mass spectrometry (ESI) technique using an AccuTOF 4G+ DART (JEOL) at UNIST (Ulsan National Institute of Science and Technology) Central Research Facilities, Republic of Korea. UV-Vis absorption spectra of the QD films were measured using a Jasco V-770 UV-Vis-NIR spectrophotometer. Time-resolved photoluminescence (TRPL) characteristics of QD films were measured using a time-correlated single photon counting (TCSPC) system from Becker & Hickl (resolution of 120 ps). The films were excited at 405 nm at a repetition rate of 2 MHz.

Experiments

Synthesis of CdSe/CdZnS QDs

CdSe/CdZnS QDs were synthesized by following literature methods.¹

Synthesis of ethane-1,2-diyl bis(4-azido-2,3,5,6-tetrafluorobenzoate),

2C-LIXER

2C-LIXER was synthesized by following literature methods.²

Synthesis of octane-1,8-diyl bis(4-azido-2,3,5,6-tetrafluorobenzoate), 8C-LIXER

First, 4-azido-2,3,5,6-tetrafluorobenzoic acid was synthesized by following method in the literature.³ A mixture of 4-azido-2,3,5,6-tetrafluorobenzoic acid (0.30 g, 1.28 mmol) and SOCl_2 (0.15 mL, 2.13 mmol) in anhydrous DCM (6 mL) was refluxed in an oil-bath at 70 °C. After 14 hours, the reaction mixture was cooled down to room temperature and then was dried using a rotary evaporator and under vacuum. The resulting acyl chloride compound was diluted using anhydrous DCM (6 mL) and then was transferred dropwise to a mixture of $\text{HO}(\text{CH}_2)_8\text{OH}$ (0.08 g, 0.53 mmol) and anhydrous Et_3N (0.23 mL, 1.60 mmol) in anhydrous DCM (4 mL). After 21 hours under stirring at RT, the reaction mixture was diluted with water (10 mL), and the aqueous phase was extracted with DCM (12 mL) three times. The organic phases were washed with brine (40 mL) and the resulting organic phase was dried using anhydrous MgSO_4 and filtered. The filtrate was dried using a rotary evaporator. The crude product was purified by silica gel column chromatography (ethyl acetate:n-hexane = 10:1 vol.). This afforded pure 8C-LIXER as a white solid (0.28 g, 91 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 4.38 - 4.35$ (t, 4H), $1.77 - 1.72$ (m, 4H), $1.45 - 1.35$ (m, 8H). $^{19}\text{F-NMR}$ (376 MHz, CDCl_3) δ : $-138.85 - -138.94$ (m), $-150.92 - -151.02$ (m). ESI-MS m/z Calcd: 580.1105 Found: 581.1170 (M + H).

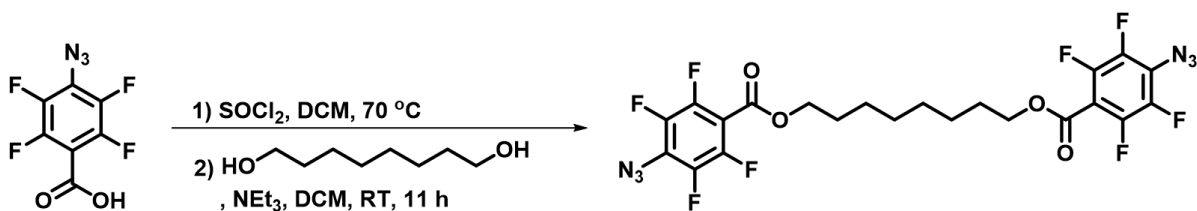


Figure S1: Reaction scheme for synthesis of 8C-LIXER.

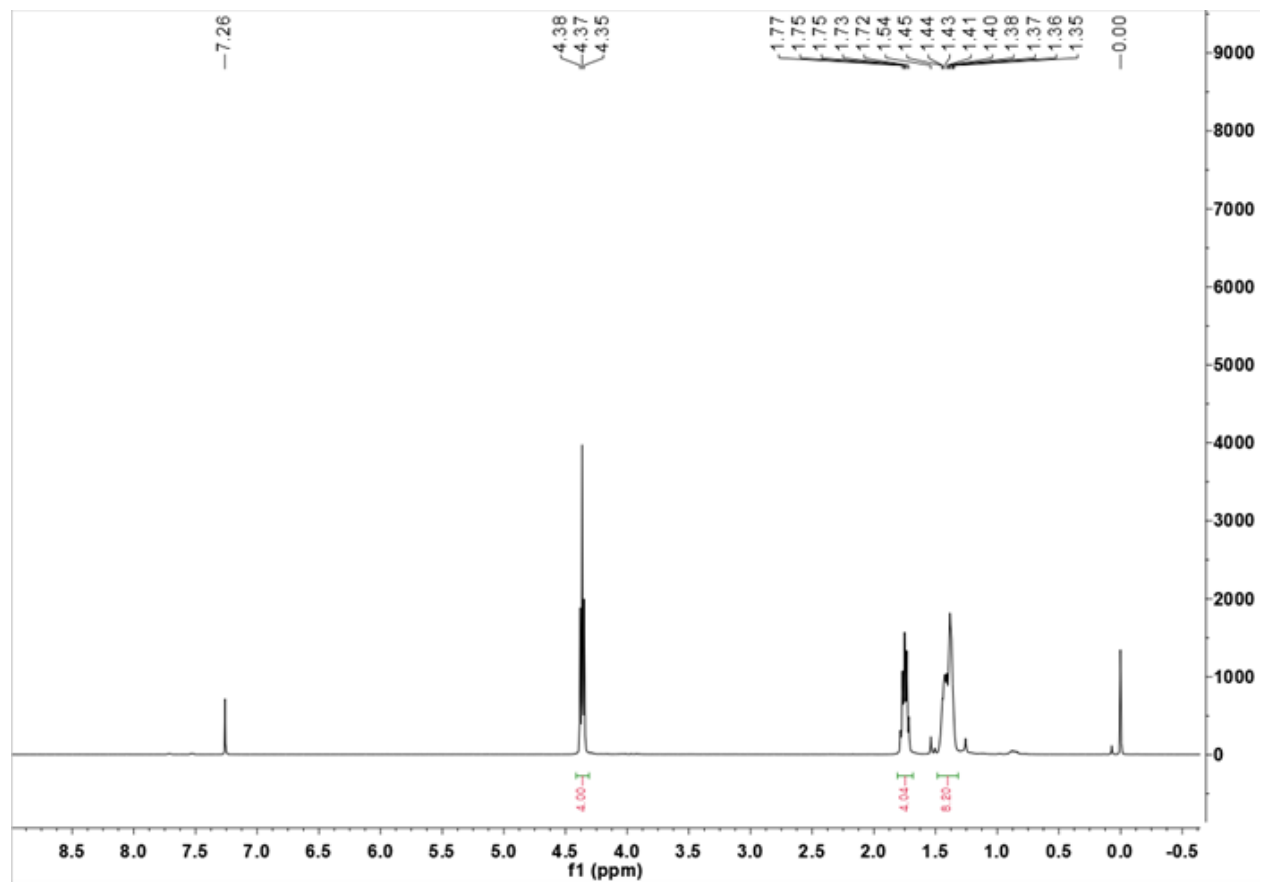


Figure S2: $^1\text{H-NMR}$ spectrum of 8C-LIXER.

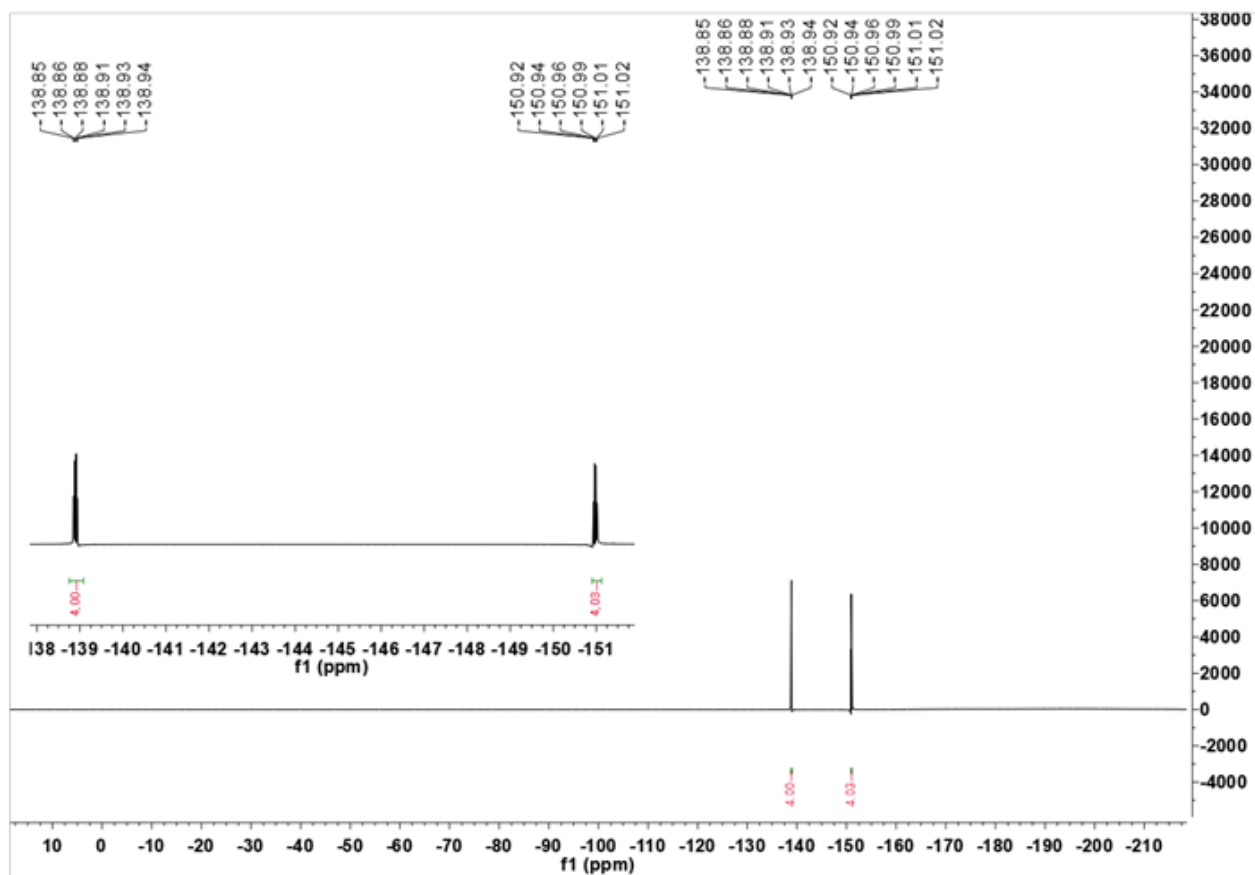


Figure S3: ^{19}F -NMR spectrum of 8C-LIXER.

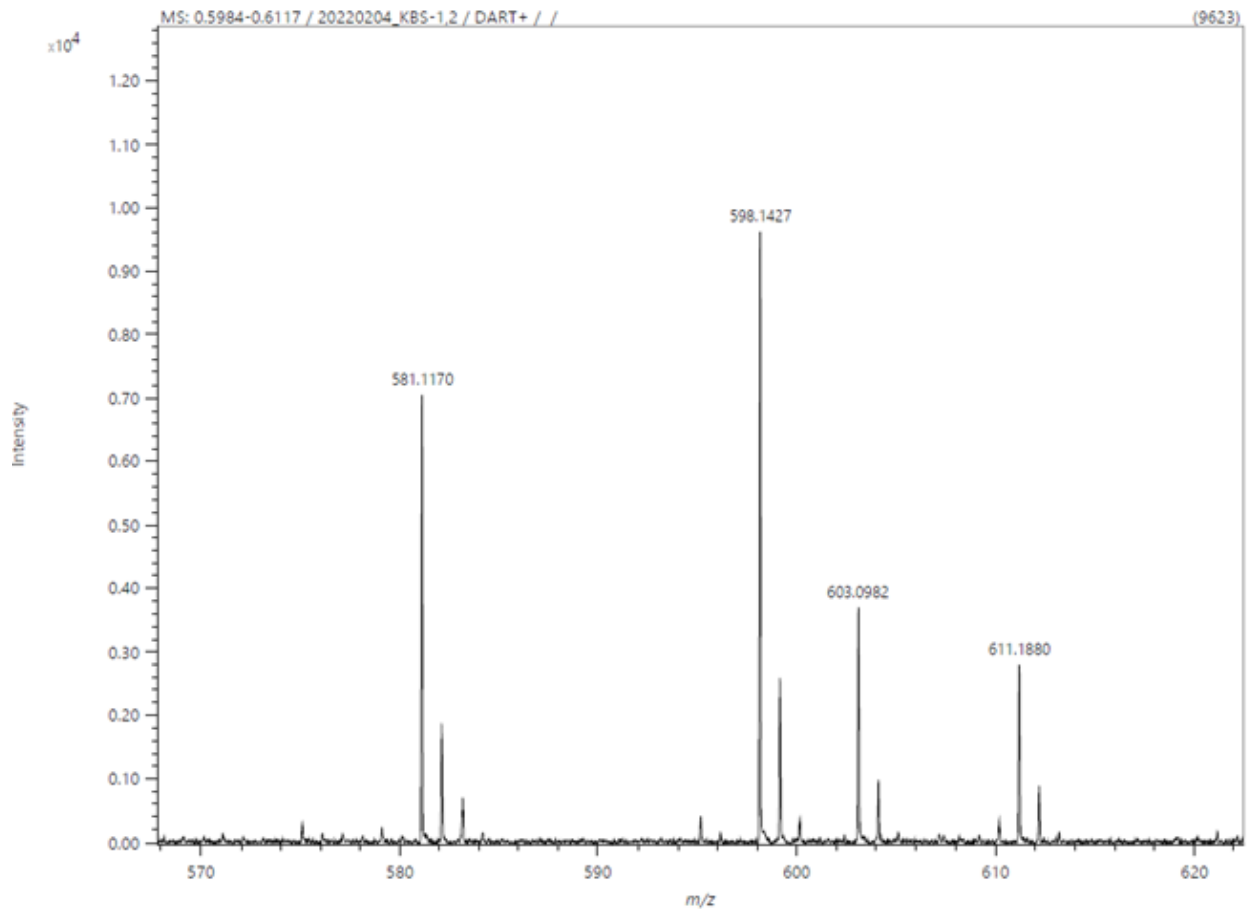


Figure S4: ESI-MS spectrum of 8C-LIXER.

Preparation of crosslinked QD films

Glass substrates were sequentially cleaned with acetone, isopropyl alcohol in an ultrasonic bath for 10 min each. Different weight fractions of LIXER were added to a pristine QD solution of CdSe/CdZnS (20 mg ml^{-1} in toluene). The mixture solution was spin-coated onto the glass substrate at 4000 rpm for 30 sec under nitrogen atmosphere. The QD films were irradiated with a handheld UV-light source (254 nm , 0.5 mW cm^{-2} , exposure dose 2 mJ cm^{-2}) for 5 sec to derive the crosslinking reaction between QDs and LIXER. Subsequently, the resulting films were rinsed with toluene.

References

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- (3) Kim, M. J.; Lee, M.; Min, H.; Kim, S.; Yang, J.; Kweon, H.; Lee, W.; Kim, D. H.; Choi, J.-H.; Ryu, D. Y. *Nature Communications* **2020**, *11*, 1–11.