SUPPORTING INFORMATION

Near-Infrared Quantum Dot Emission Enhanced by Stabilized Self-Assembled J-aggregate Antennas

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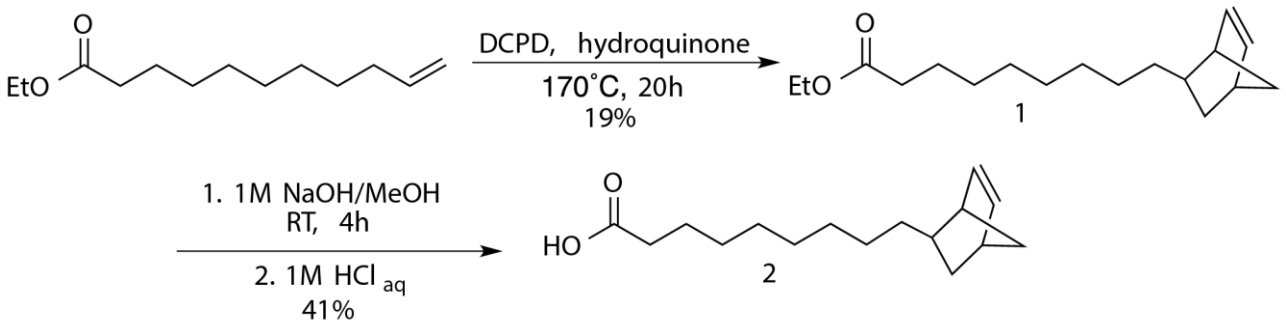
Ligand Synthesis Procedure

Norbornene mono acid ligand synthesis

^{1}H NMR spectra, and ^{13}C NMR spectra with complete proton decoupling were recorded on a Bruker DRX 400 NMR spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, and using the solvent resonance as the internal standard ($CDCl_3$:^{1}H NMR δ 7.26, ^{13}C NMR δ 77.16) (Appendix A).[1]



Scheme S1 Norbornene mono acid ligand synthesis.

ethyl 10-(norborn-2-en-5-yl)decanoate (1)

Caution! This reaction involves the use of a pressure vessel. The use of a blast shield is recommended. Dicyclopentadiene (DCPD, 15.73 g 0.119 mol), ethyl undecylenoate (30.30 g, 0.143 mol) and hydroquinone (39.3 mg, 0.36 mmol) were added to a 65 mL pressure vessel equipped with a Teflon valve. The temperature was increased to 170˚C and the sample was left to react for 20h under constant stirring. After cooling to room temperature, the solution was distilled under vacuum (200 mTorr). A fraction containing compound (1) with vapor temperature of 120-130 ˚C was collected, and set aside for 4 hours to allow for a solid side-product to precipitate, which was then filtered out of the solution using a fritted glass filter funnel. The filtrate was collected and stored at

4˚C overnight to induce a second precipitation event. Another filtration step yields 1 as a clear, colorless oil. (7.69 g, 0.028 mol, 19% yield): mixture of exo and endo (2:8, respectively).

^{1}H NMR (400 MHz, $CDCl_3$) MAJOR ISOMER (endo) δ (ppm) 6.09 (m, 1H), 5.89 (m, 1H), 4.11 (q, J = 7.6 Hz, 2H), 2.73 (m, 2H), 2.27 (t, J = 7.4 Hz, 2H), 1.94 (m, 1H), 1.81 (m, 1H), 1.60 (m, 2H), 1.38 – 1.22 (br, 11H), 1.24 (t, J = 7.1 Hz, 3H), 1.19 (d, J = 8.0 Hz, 1H), 1.03 (m, 2H), 0.47 (m, 1H); ^{13}C{^{1}H} (100MHz, $CDCl_3$) δ (ppm) 174.0, 137.0, 132.6, 60.3, 49.7, 45.5, 42.6, 38.9, 34.9, 34.5, 32.6, 30.0, 29.6, 29.4, 29.3, 28.7, 25.1, 14.4; HRMS (DART/FT-MS): m/z $[M + H]^+$ Calcd for $C_{18}H_{31}O_2$ 279.2319; Found 279.2310.[1]

10-(norborn-2-en-5-yl)decanoic Acid (2)

Compound 1 (6.81g, 0.024mol) was added dropwise to a 1M NaOH solution in methanol (105 mL), and stirred for 4 hours at room temperature. The solution was transferred into a separation funnel and washed with hexanes (150 mL, 3X) to remove any unreacted material. The methanol phase was then acidified to pH 3 using a 1M HCl aqueous solution, and the product was extracted into hexanes (150 mL, 3X). The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to obtain compound (2) as a white solid. (2.82 g, 0.011 mol, 47% yield): mixture of exo and endo (2:8, respectively).

^{1}H NMR (400 MHz, $CDCl_3$) MAJOR ISOMER (endo) δ (ppm) 11.53 (br, 1H), 6.10 (m, 1H), 5.90 (m, 1H), 2.74 (m, 2H), 2.34 (t, J = 7.4 Hz, 2H), 1.96 (m, 1H), 1.82 (m, 1H), 1.63 (m, 2H), 1.39 – 1.23 (br, 11H), 1.20 (d, J = 8.0 Hz, 1H), 1.04 (m, 2H), 0.48 (m, 1H); ^{13}C{^{1}H} (100MHz, $CDCl_3$) δ (ppm) 180.5, 137.0, 132.6, 49.7, 45.5, 42.7, 38.9, 34.9, 34.2, 32.6, 30.0, 29.6, 29.4, 29.2, 28.8, 24.8; HRMS (DART/FT-MS): m/z $[M - H]^-$ Calcd for $C_{16}H_{25}O_2$ 249.1860; Found 249.1856.[1]

We have successfully performed the synthesis of compound (1) and compound (2) at six times the scale described above and have obtained similar reaction yields.

2-(4-(1,2,4,5-tetrazin-3-yl)phenyl)acetic acid (3)

The amine-reactive tetrazine was prepared according to the method described by Yang et al.[2] We found it very difficult to completely wash away the $Ni(OTf)_2$ catalyst—a powerful quencher of QD fluorescence—from the final product, thus, we omitted it from the synthesis.[1]

Tetrazine-PEG$_{500}$ (Tz-PEG)

Compound (3) (0.50 g, 2.33 mmol), DCC (0.58 g, 2.79 mmol), and NHS (0.32 g, 2.79 mmol) were dissolved in DCM (40 mL) and the resulting solution was allowed to react at room temperature for two hours under constant stirring. The mixture was filtered using a 0.45 μm PTFE syringe filter and added to a solution containing O-(2-Aminoethyl)-O'-methylpolyethylene glycol (1.0 g, 1.94 mmol) in DCM (5 mL), which was kept at room temperature under constant stirring for 12 hours. The organic phase was then washed thrice with water (20 mL) and dried over Na_2SO_4. The solvent was evaporated in vacuum and the resulting solid was purified using silica gel chromatography (dichloromethane/methanol gradient 92:8 to 90:10, v/v), to obtain Tz-PEG as a pink solid.[1]

Physico-Chemical Characterization of Water-Soluble QDs

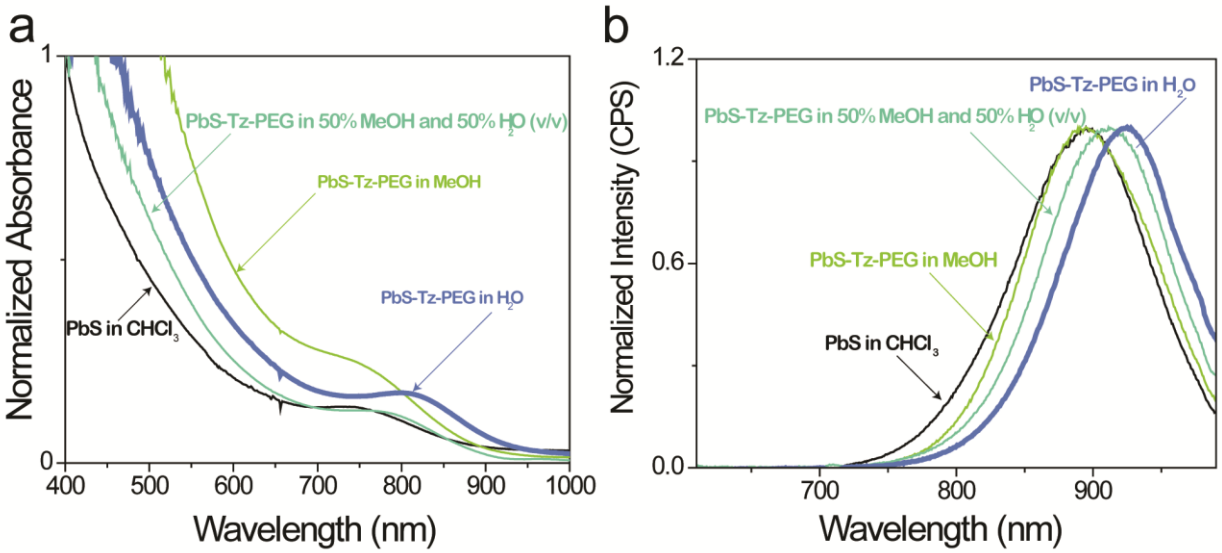


Figure S1. Optical spectra of PbS_{770} QDs from $CHCl_3$ to H_2O through methanol as intermediate solvent: PbS_{770} QDs in chloroform (BLACK line), PbS_{770} QDs after clicking tetrazine-PEG to the QDs surface in methanol (green line), in solution 50%vv of methanol and 50%vv in water (green-blue line) and in water (blue line). (a) UV-vis absorbance spectra; (b) PL spectra

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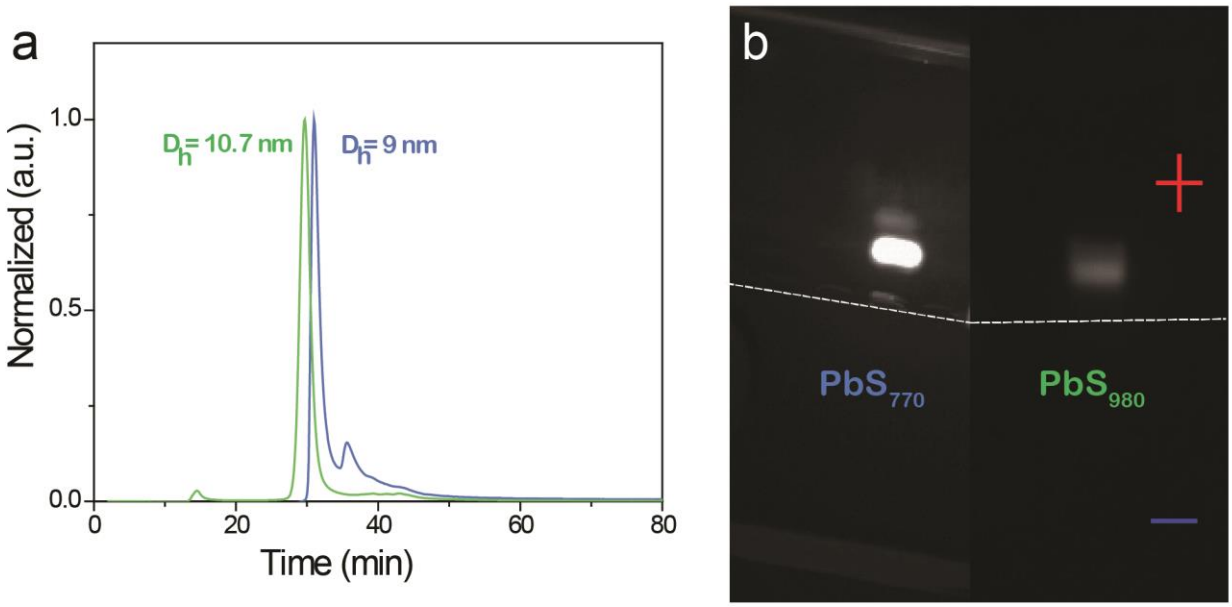


Figure S2. (a) GFC particle size distribution of PbS_{770} (blue line) and PbS_{980} (green line), D_h indicates hydrodynamic diameter; (b) Agarose gel electrophoresis shows PbS QDs migrating to the positive electrode, which indicates an overall negative charge on the particles surface.

Table S1. Summary of optical properties of synthetized QDs by mixing NA and OA. Last sample is not reported in this paper.

Samples	QY (%) in $CHCl_3$	QY (%) in H_2O
PbS_{770}	65	38
PbS_{790}	73	40
PbS_{980}	55	19
PbS_{1242}	12	6

Double Walled LHNS Coupled to QDs in Liquid System

The distance from acceptors and donors (LHNs/QDs) was measured on cryo-TEM images, by assuming that sample distribution in solution is not affected during the cryo-procedure.

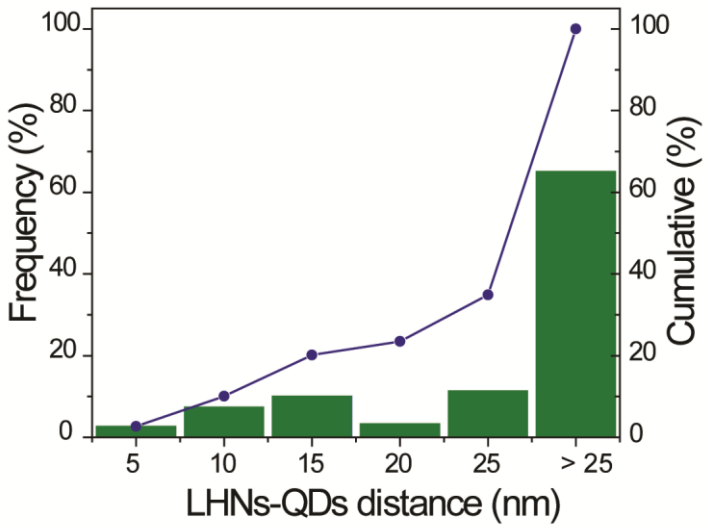


Figure S3. Distance from LHNs and PbS_{770} based on cryo-TEM images

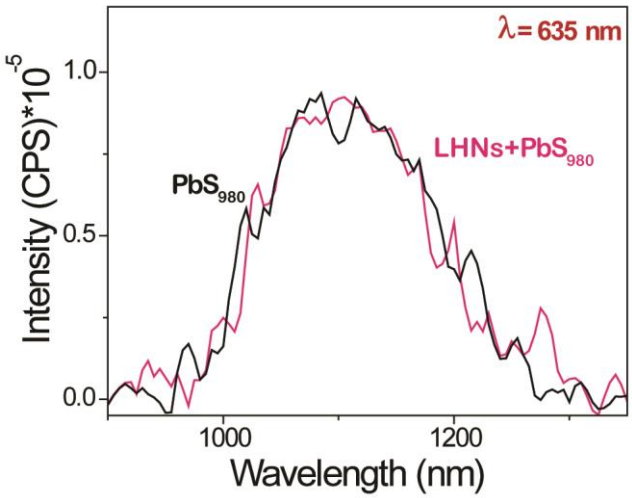


Figure S4. PL spectra of LHNs coupled with PbS_{980} (purple line) and PbS_{980} control sample (back line), excited at 635 nm.

Excitation measurement of LHNs Coupled to QDs

The excitation spectra were collected with a custom-built spectrofluorometer. We used a XBO R 300W/60 C OFR Arc Lamp, Xe/HgXe as excitation source, which was coupled to a monochromator, and chopped at 210 Hz. In order to collect the PL, we used a calibrated InGaAs detector through a Stanford Research Systems lock-in amplifier system. A 850 nm long pass filter was used to spectrally collect only the fluorescence from the QDs.

The excitation spectrum of the QDs in the presence of the LHNs follows a shape that mimics the absorption spectrum of the LHNs (Figure S5), suggesting efficient energy transfer from the organic molecules to the nanocrystals.

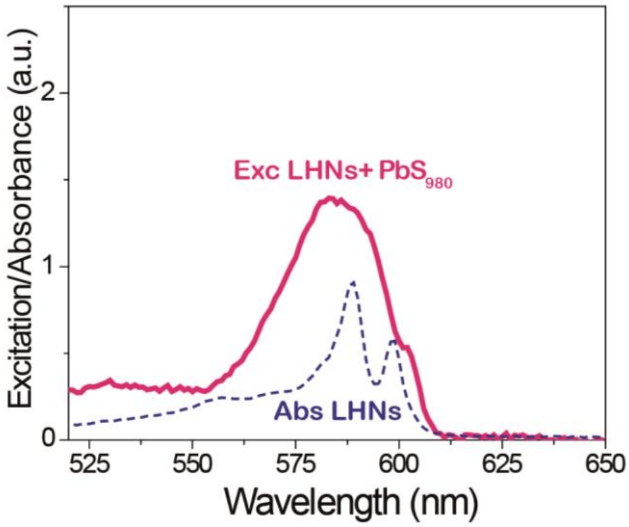


Figure S5. Excitation spectrum of PbS_{980} in the presence of LHNs (purple line) in comparison to the absorption spectrum of the LHNs alone (dotted blue line). The overestimation of the band broadening in the excitation spectrum is ascribable to the low spectral resolution of the experimental setup.

Bundled LHNS Coupled to QDs in Liquid System

Previous studies show that doubled walled nanotubes further aggregate into bundled structures, either over time or via the addition of surfactants.[3,4]

For both sizes of QDs, we found that the QD PL emission was also enhanced in the presence of bundled-like structure that formed either over time or promoted by the addition of QDs in high concentrations (Figure S6). Bundled close-packed structures maintain large exciton delocalization with a high degree of internal order and strong excitation transfer interactions,[5] which permit the energy transfer from J-aggregates to QDs. However, after storing the sample in dark conditions over two months during which the formation of bundles keeps going, we observe PL enhancement dropping by ~35% (inset Figure S6a).

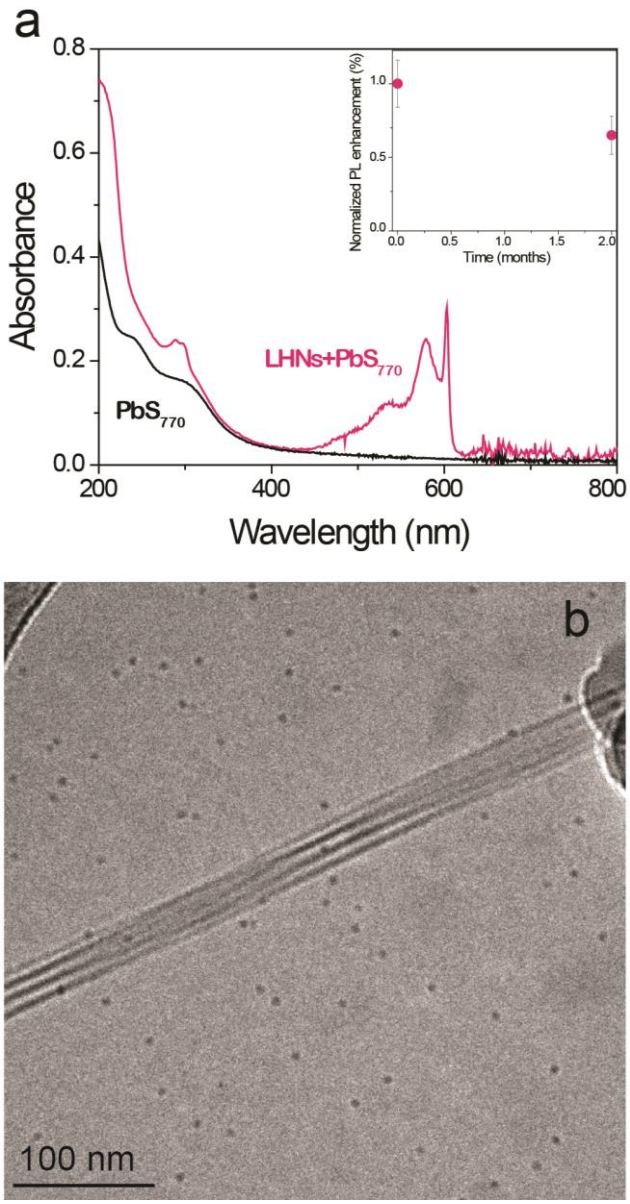


Figure S6. (a) Absorption spectra PbS_{770} coupled to LHNs with a bundled-like structure (purple), PbS_{770} control sample (black line); inset: normalized PL enhancement of QDs over time. The samples were in dark over 2 months. (b) cryo-TEM of bundled LHNs+PbS_{770}

LHNS Coupled to QDs in Solid System

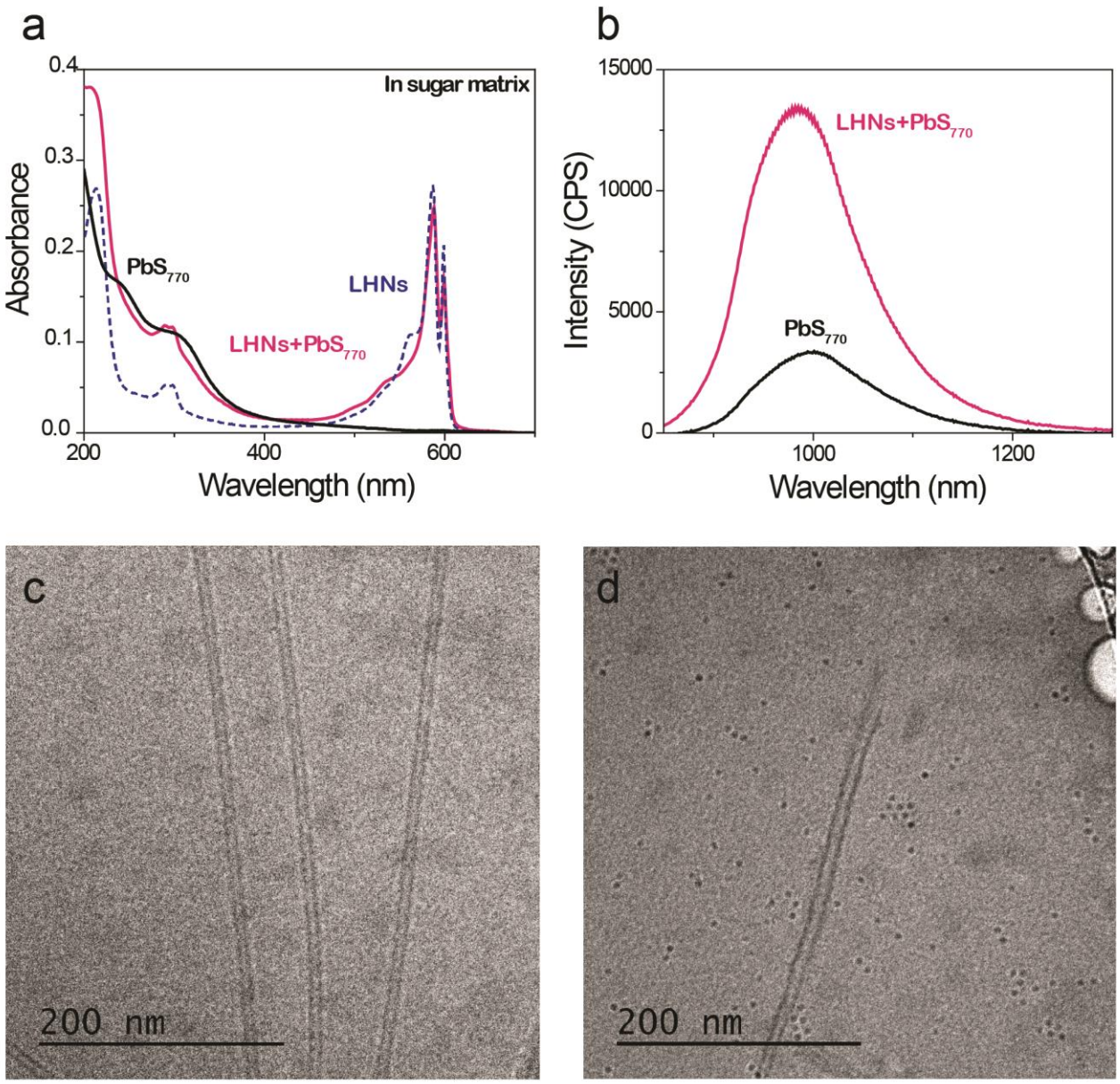
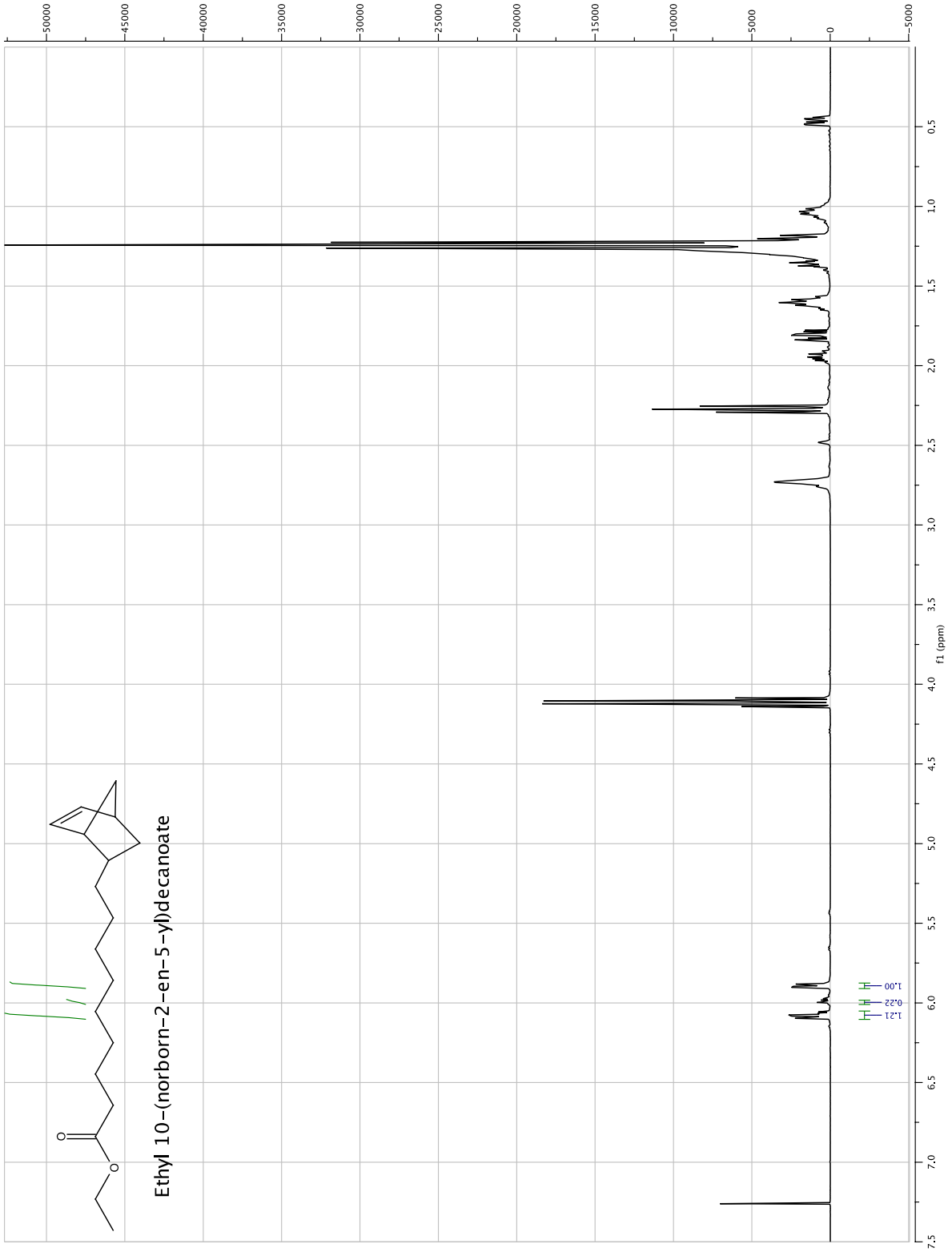
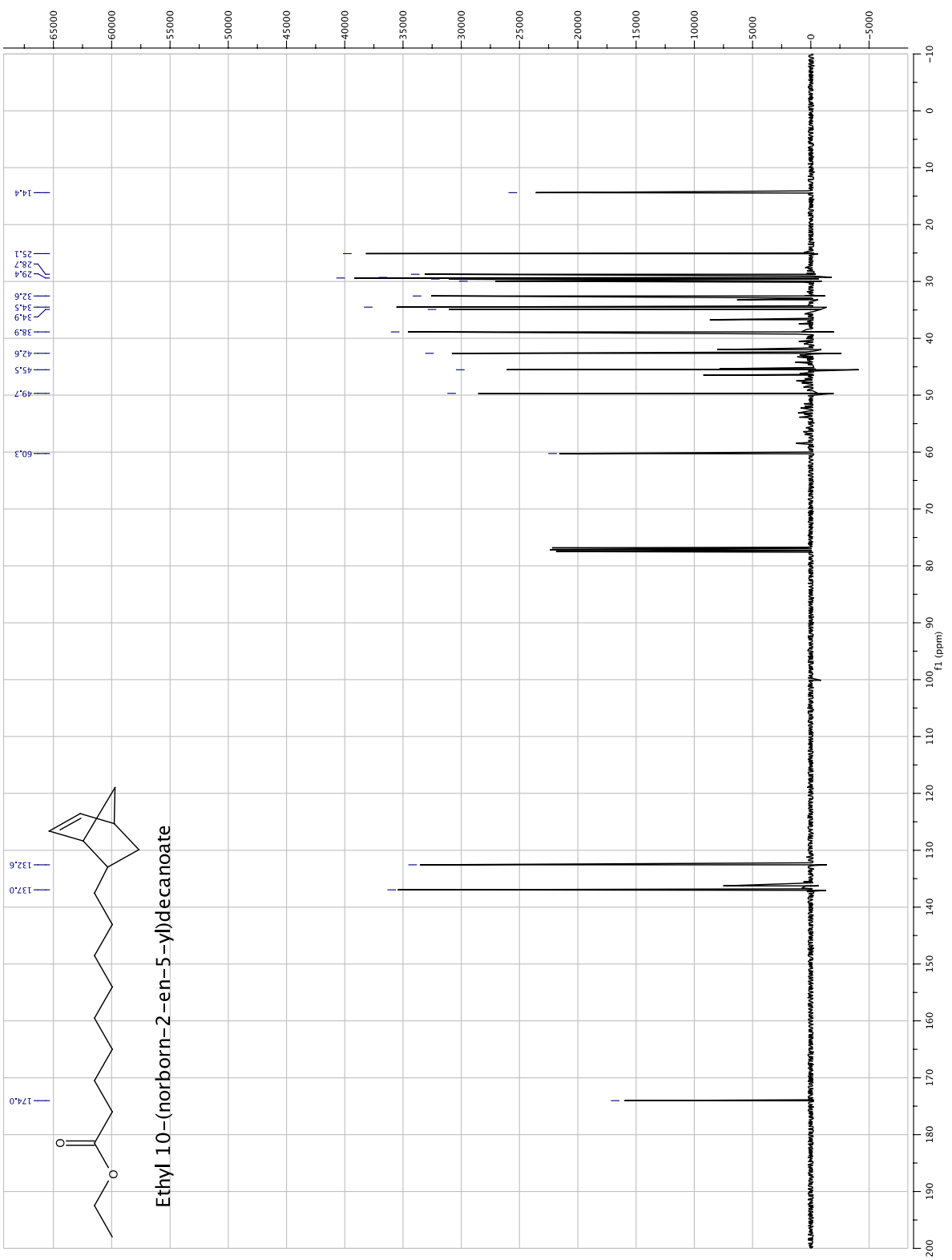


Figure S7. Optical properties of LHNs coupled with PbS_{770} QDs in sugar matrix, LHNs coupled with PbS_{770} QDs (purple line), LHNs control sample (blue line), PbS_{770} QDs control sample (black line): (a) UV-vis absorption spectra of the three samples; (b) PL spectra of LHNs coupled with PbS_{770} and PbS_{770} control sample excited at 532 nm; (c) cryo-TEM image of LHNs in sugar solution; (d) cryo-TEM image of LHNs coupled with QDs in sugar solution.

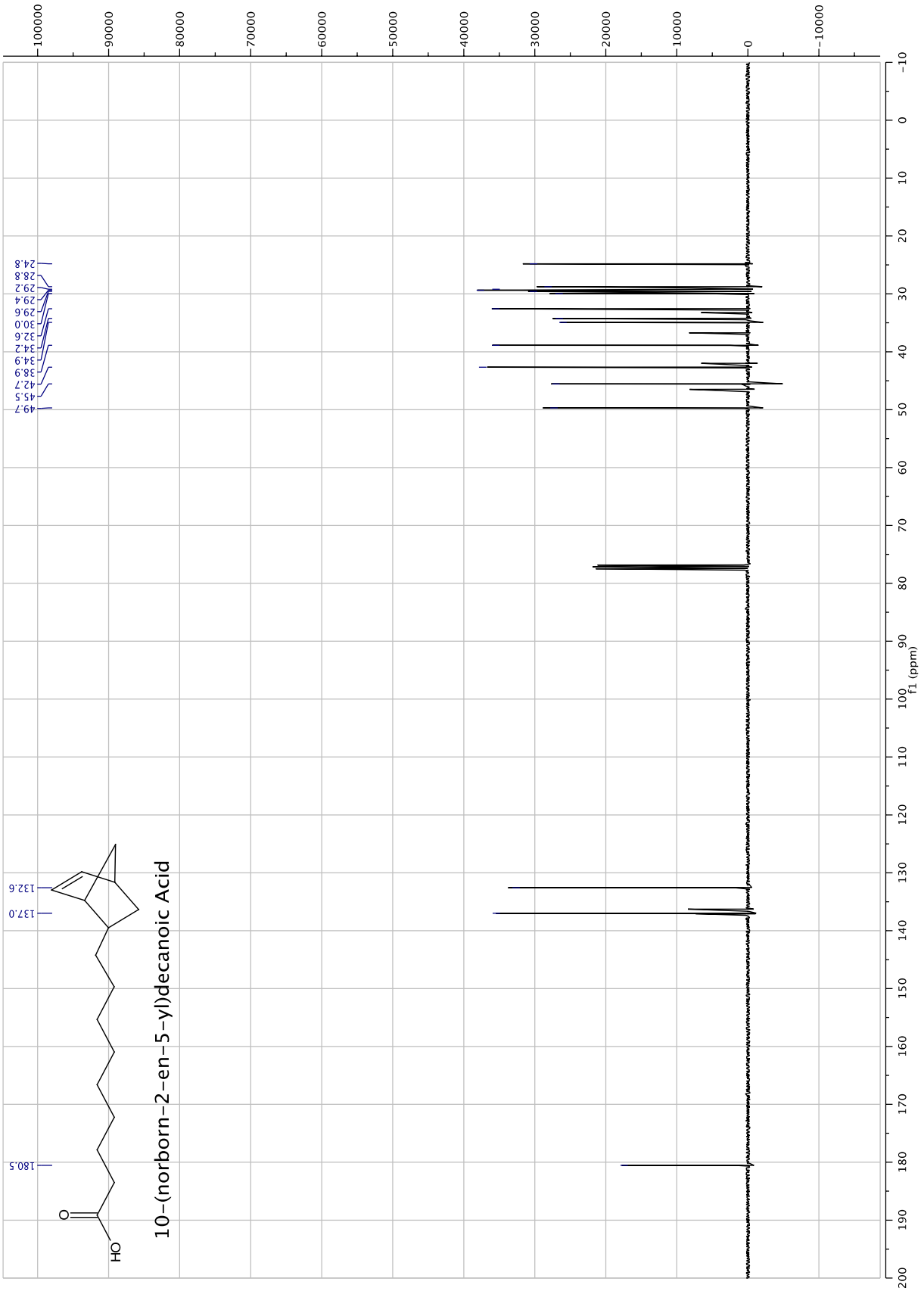
Appendix A.

^{1}H NMR, ^{13}C{^{1}H} NMR Spectra of Chemical Compounds




Ethyl 10-(norborn-2-en-5-yl)decanoate
174.0
137.0
132.6
60.3
49.7
45.5
42.6
38.9
34.9
34.5
32.6
29.4
28.7
25.1
14.4
f1 (ppm)


10-(norborn-2-en-5-yl)decanoic Acid
HO
O
1.00
0.20
0.81
f1 (ppm)


10-(norborn-2-en-5-yl)decanoic Acid
OH
O
180.5
137.0
132.6
49.7
45.5
42.7
38.9
34.9
34.2
32.6
30.0
29.6
29.4
29.2
28.8
24.8
f1 (ppm)

References

(1) Cordero Hernández, J. M. Synthesis of derivatizable semiconductor nanocrystals through rational ligand design, and applications thereof, Massachusetts Institute of Technology, 2016.

(2) Yang, J.; Karver, M. R.; Li, W.; Sahu, S.; Devaraj, N. K. *Angew. Chemie - Int. Ed.* **2012**, *51* (21), 5222–5225.

(3) von Berlepsch, H.; Kirstein, S.; Hania, R.; Pugžlys, A.; Böttcherr, C. *J. Phys. Chem. B* **2007**, *111* (7), 1701–1711.

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(5) Eisele, D. M.; Arias, D. H.; Fu, X.; Bloemsma, E. A.; Steiner, C. P.; Jensen, R. A.; Rebentrost, P.; Eisele, H.; Tokmakoff, A.; Lloyd, S.; Nelson, K. A.; Nicastro, D.; Knoester, J.; Bawendi, M. G. *Proc. Natl. Acad. Sci.* **2014**, *111* (33), E3367–E3375.