

Supporting Information

Design of Cross-Linked Polyisobutylene Matrix for Efficient Encapsulation of Quantum Dots

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Chemicals: diethyl ether (Et₂O, ≥99%), 1,4-Bis(2-hydroxyisopropyl)benzene, (dicumyl alcohol, 97%), FeCl₃ (97%), TiCl₄ (99.9%), NH₄Cl (99.5%), Na₂SO₄ (99%), CH₃MgI (3M solution in Et₂O), trimethyl 1,3,5-benzenetricarboxylate (98%), lauryl methacrylate (96%) were purchased from Sigma–Aldrich. *i*-PrOH (99.5, Sigma–Aldrich) was boiled and distilled over SnCl₂·H₂O (98%, Sigma–Aldrich). Pyridine, TiCl₄, and lauryl methacrylate were distilled right before using. All other chemicals were used as received. Styrene (stabilised for synthesis) washed with 10% solution of KOH, dried over Na₂SO₄ and distilled.

Synthesis of poly(styrene-*block*-isobutylene-*block*-styrene) (SIBS) was carried out according to the previously published method,¹ by using pyridine instead of 2,6-di-*tert*-butylpyridine. Briefly, 0.2 mL of TiCl₄ were added to a mixture of 2 mL *o*-isobutylene (1.35 g, 24.1 mmol), 12.6 mL of *n*-hexane, 9.6 mL of CH₂Cl₂, 1.1 mL of a solution of pyridine in *n*-hexane (0.1 M), and a solution of 0.7 mL of dicumyl chloride in *n*-hexane (0.1 M) at –80 °C. After 35 min, 3.5 mL of a 2 M styrene

solution in a mixture of *n*-hexane/CH₂Cl₂ (3/2, v/v) cooled to -30 °C was added to the mixture. The reaction was quenched by 2 mL of prechilled methanol and the product was precipitated into a tenfold excess of cooled ethanol. The obtained copolymer was purified by reprecipitation into ethanol and dried overnight under vacuum at 55–60 °C/2 bar.

Synthesis of poly(lauryl methacrylate) (PLMA). 2.91 mL of freshly distilled lauryl methacrylate (9.93 mmol) were polymerized in the presence of 37.7 mg of AIBN (0.23 mmol) at 60 °C for 24 h. The product was precipitated twice from toluene into ethanol and dried under vacuum at 40 °C/0.01 bar to constant weight.

Synthesis of tricumyl alcohol. 7.88 g of trimethyl 1,3,5-benzenetricarboxylate dissolved in 100 mL of THF was slowly added to 62.5 mL of solution CH₃MgI (3M) in Et₂O under vigorous stirring at room temperature. Then, the reaction mixture was refluxed for 1 hour and cooled to 0 °C followed by the addition of solution of 20 g of NH₄Cl in 200 mL of water. The product was extracted with 120 mL of diethyl ether, recrystallized from methylene chloride and dried in vacuum. The purity of prepared tricumyl chloride was confirmed by ¹H NMR spectroscopy.

Synthesis of tricumyl chloride. Tricumyl chloride was prepared via passing gaseous HCl through a solution of 2 g of 1,3,5-tri(2-hydroxyisopropyl)benzene (tricumyl alcohol) in 30 mL of CH₂Cl₂ at 0 °C under stirring. Then the product of the synthesis was twice recrystallized from *n*-hexane and dried in vacuum. The purity of the prepared tricumyl chloride was confirmed by ¹H NMR spectroscopy.

Dicumyl chloride was obtained by a similar method as tricumyl chloride.

Synthesis of FeCl₃·1.4*i*-PrOH. Complexes of FeCl₃ with *i*-PrOH (as 0.22 M solution in CH₂Cl₂) were synthesized following a recipe described in ref.²

Characterization. *Size exclusion chromatography* was performed on an Ultimate 3000 device with PLgel MIXED-C column (7.5×300 mm, particle size 5 μm) and one pre-column (Agilent PLgel 5 μm guard) thermostated at 30 °C, equipped with a differential refractometer. Solutions of the polymers in THF were eluted at flow rate of 1 mL/min. The calculation of molecular weight and polydispersity was based on polystyrene standards (Polymer Labs) with M_w/M_n ≤ 1.05 and using Chromeleon 7.0 program.

¹H NMR (500 MHz) spectra were recorded in CDCl₃ at 25 °C on a Bruker AC-500 spectrometer calibrated relative to the residual solvent resonance. NMR analysis of the QDs' ligand shell was performed using the dispersion of well purified QDs (60 mg/mL) in CDCl₃. QDs were purified through three-time precipitation from chloroform using acetonitrile as a non-solvent. The final precipitate was dried under vacuum and dissolved in CDCl₃.

Transmission electron microscopy (TEM) was performed on a JEOL JEM-1400 Plus microscope operated at 120 kV.

Estimation of the size of PIB unit cells. To estimate the size of the polymer cell we used the following prerequisites:

- 1) Storey and co-workers showed that with a decrease in the mass of the PIB macromer, the crosslink density increases.³
- 2) Bag et al. demonstrated that when self-healing PIB networks were used as coatings for oxygen-sensitive solar cells, the greatest stability was observed when using PIB monomers with the lowest mass (2kDa). It is also associated with a denser packing.⁴
- 3) FTIR analysis of our polymer films with QDs before and after crosslinking revealed the absence of uncrosslinked chains (see Figure SI9).
- 4) Kuhn's segment for PIB is 1.83 nm or 7.3 monomer units.⁵
- 5) To simplify the calculations, the size of the network nodes was taken equal to the size of the PIB link.

Taking into account these considerations, upon formation of networks around QDs, close-packed structures with a close to linear segments are formed, as schematized in Figure 1b, in which the size of PIB-shaft is approx. 1200 Da (5.37 nm) and 1870 Da (8.37 nm) for 4K and 5K PIBs, respectively. Therefore, an “ideal” (i.e. stretched) chain length between network nodes is 2400 Da (10.74 nm) and 3740 Da (16.74) for 4K and 5K, respectively. The molecular mass of the PIB-SH ligand is approx. 1000 Da or 4.48 nm in straight (unfolded) conformation and QD size is 2.6 nm, giving a total QD diameter of 11.56 nm. Since the PIB chain on the surface of QDs is not rigid and can thus can easily fold, the whole size will be smaller and thus will ideally fit into the 4K polymer cell.

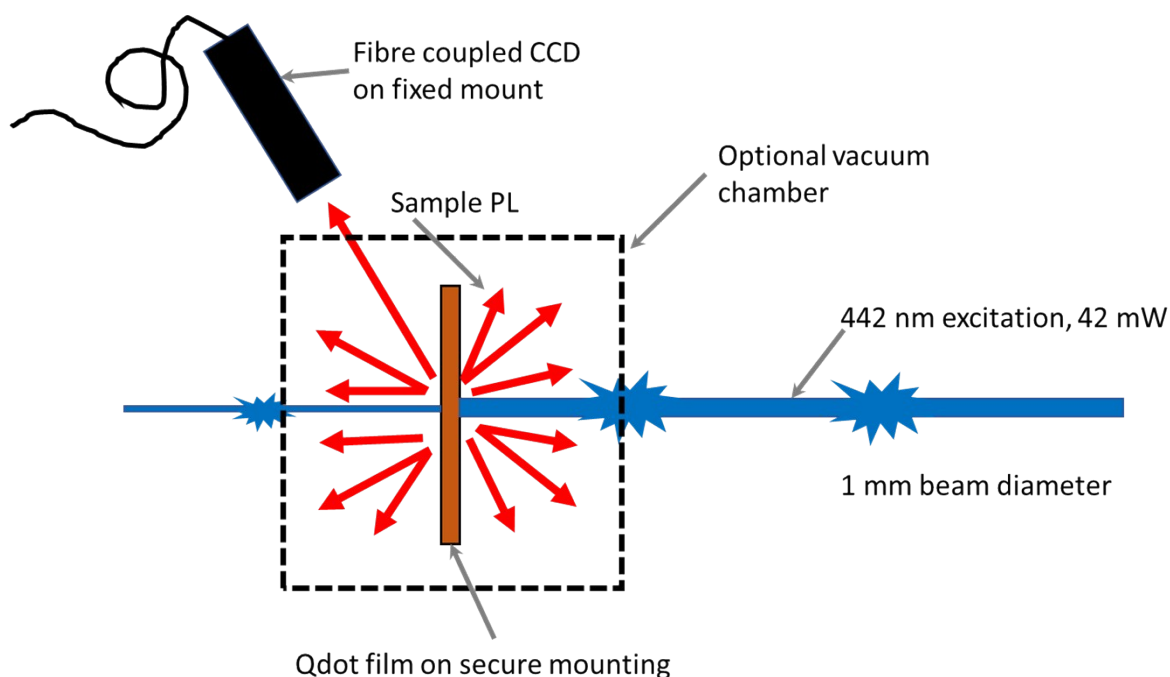


Figure SI1. The experimental setup for the photostability measurements.

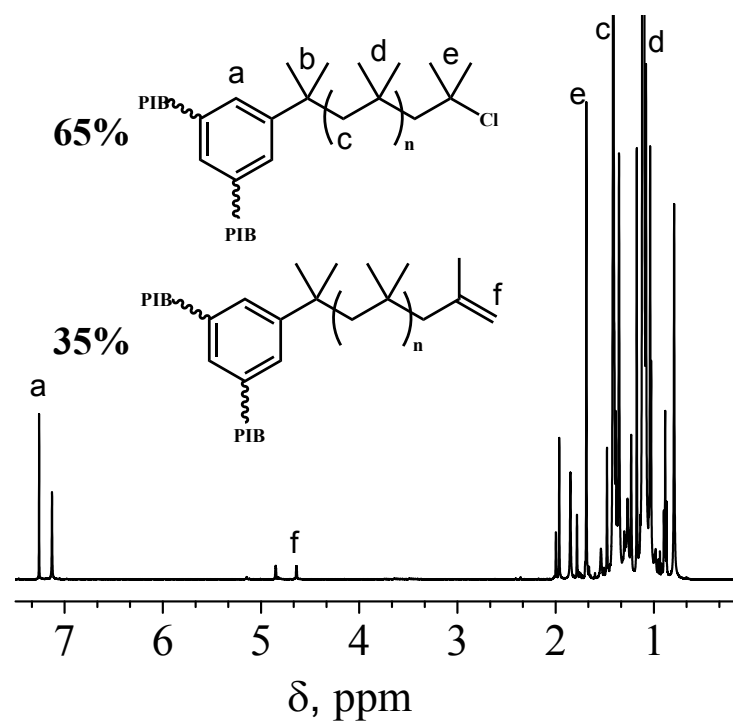


Figure SI2. ^1H NMR spectrum of three-arm star polyisobutylene terminated with exo-olefin (35 mol%) and tertiary chloride (65 mol%) end groups ($M_n = 3500$ g/mol).

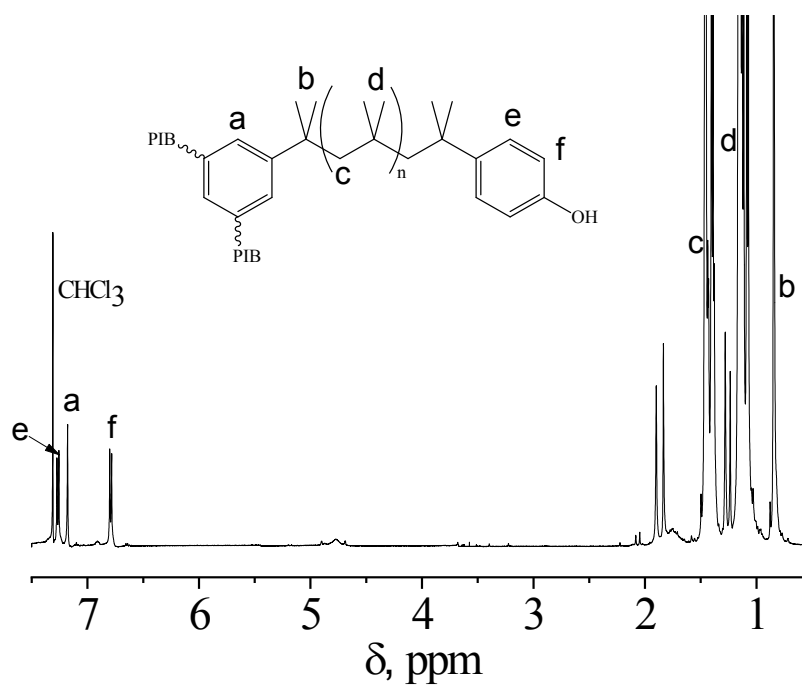


Figure SI3. ^1H NMR spectrum of hydroxyl-terminated three-arm star-shaped polyisobutylene ($M_n = 4000$ g/mol).

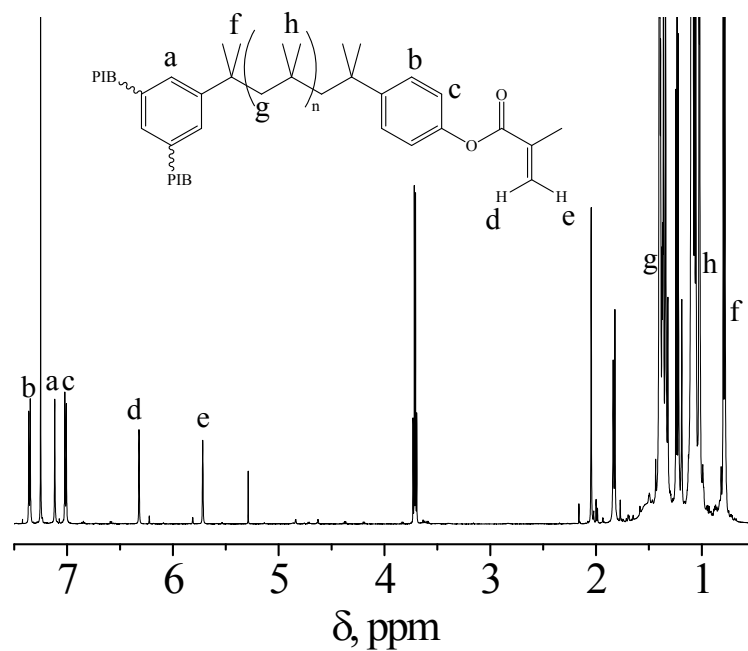


Figure SI4. ^1H NMR spectrum of methacrylate-terminated three-arm star-shaped polyisobutylene (PIB-MA) ($M_n = 4200$ g/mol).

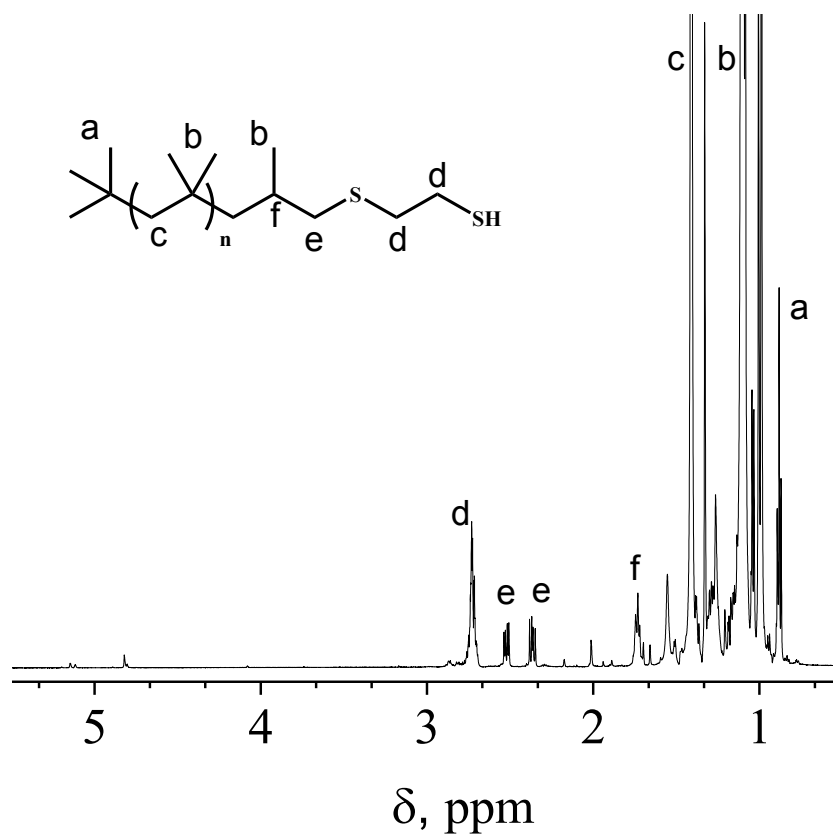


Figure SI5. ^1H NMR spectrum of ((2-mercaptoethyl)thio)polyisobutylene (PIB-SH).

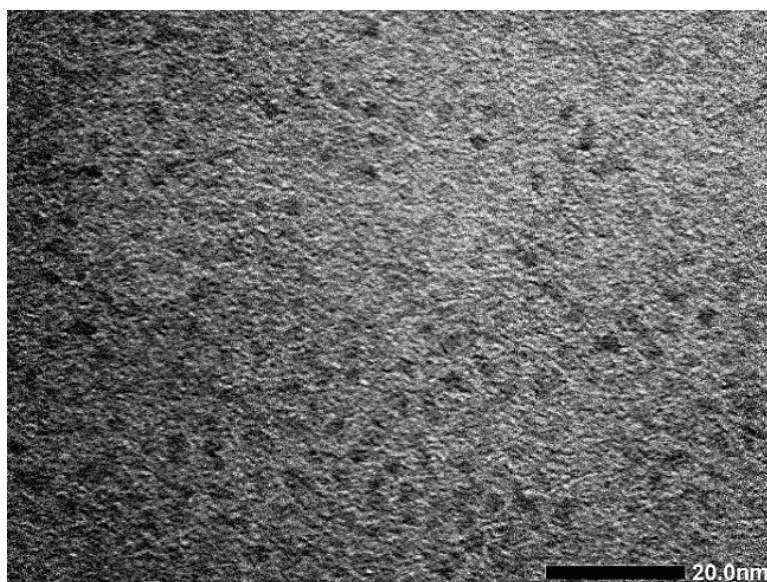


Figure SI6. TEM image of CZIS QDs.

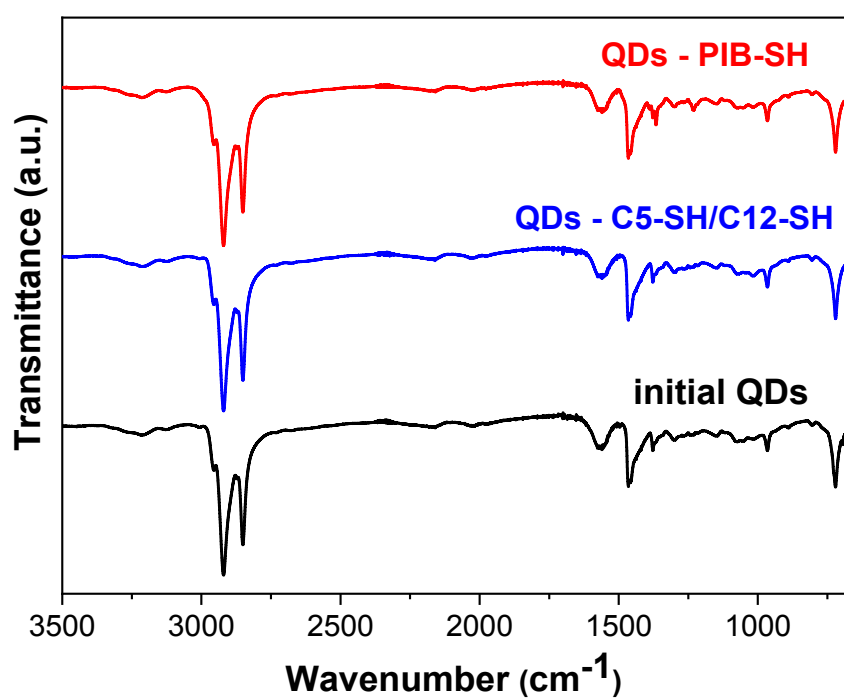


Figure SI7. FTIR spectra of CZIS QDs before and after treatment with thiols.

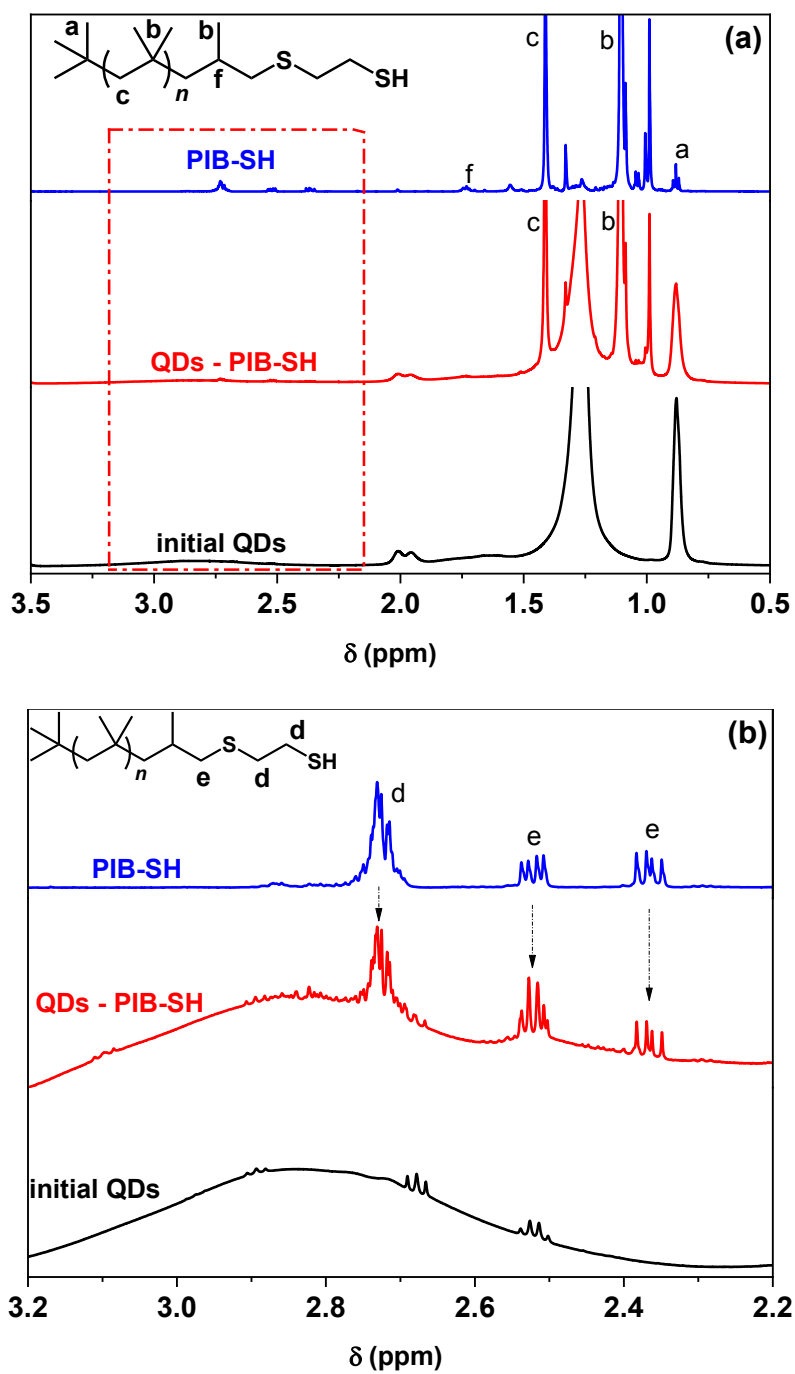


Figure SI8. (a) ^1H NMR spectra of PIB-SH and well-purified dispersions of CZIS QDs in CDCl_3 before and after treatment with PIB-SH. (b) The scaled spectra in the range 2.2-3.2 ppm.

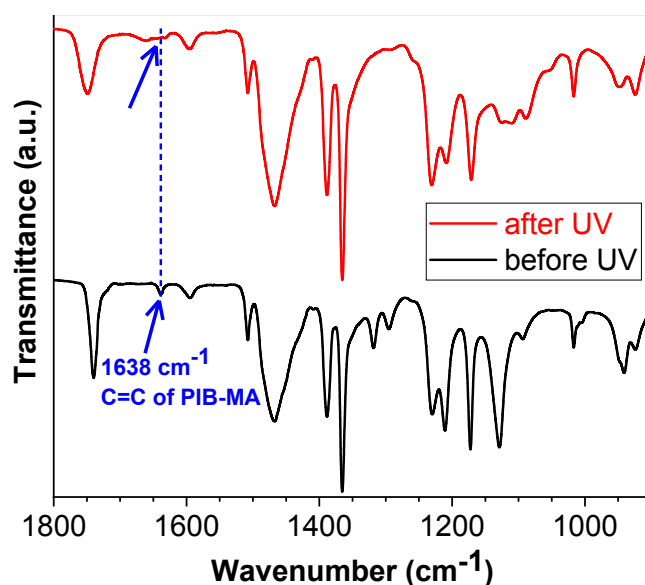


Figure SI9. FTIR spectra of PIB-MA ($M_n = 4200$ g/mol) with PIB-SH-capped CZIS QDs before and after exposure to UV-source (365 nm, 6W) for 1 hour.



Figure SI10. A photo of a free-standing film of CL-PIB4K with embedded CZIS QDs in chloroform under UV-light after one month. (The film peeled off from the substrate and broke into several parts. Despite this, the film was solid, and no extraction of QDs into chloroform was observed.)

References:

- (1) Shiman, D. I.; Sayevich, V.; Meerbach, C.; Nikishau, P. A.; Vasilenko, I. V.; Gaponik, N.; Kostjuk, S. V.; Lesnyak, V. Robust Polymer Matrix Based on Isobutylene (Co)Polymers for Efficient Encapsulation of Colloidal Semiconductor Nanocrystals. *ACS Appl. Nano Mater.* **2019**, *2*, 956–963.
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