Supporting Information

A Clear Solution: Semiconductor Nanocrystals as Photoinitiators in Solvent Free Polymerization

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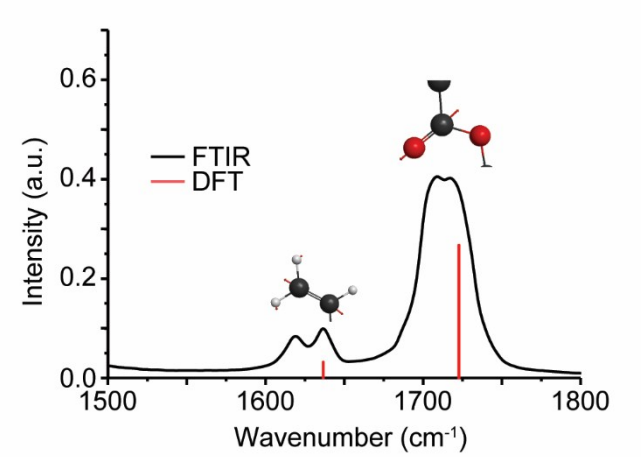
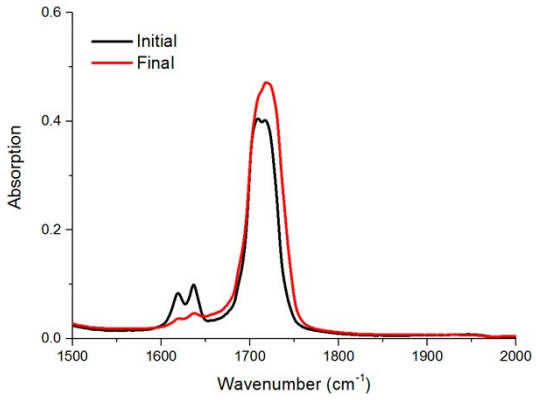
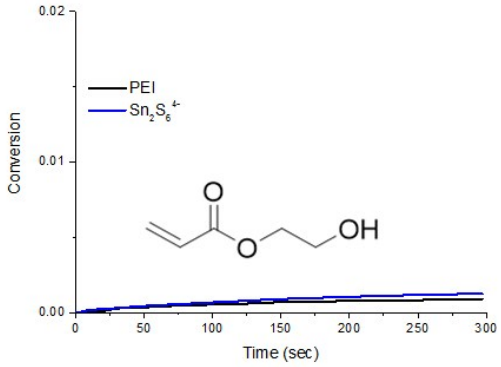


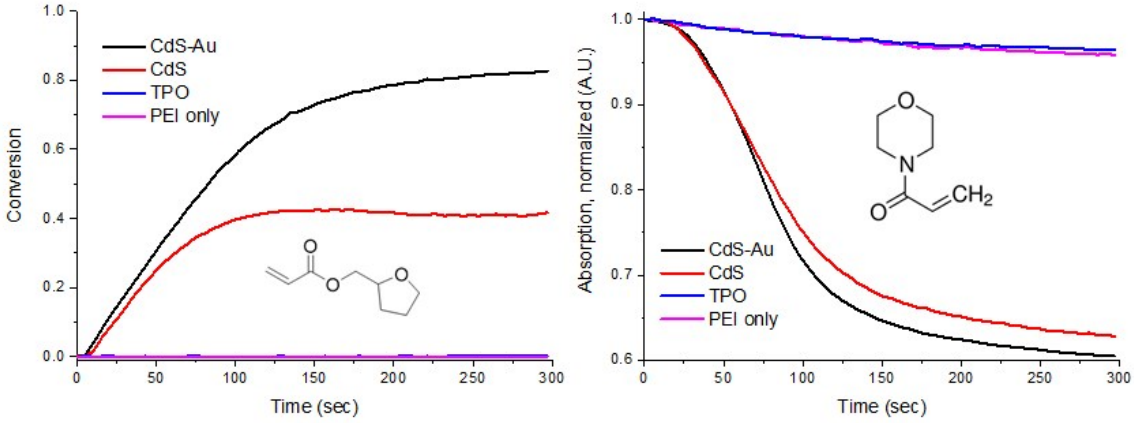
Supplementary Figure S1. HEA spectrum as measured by FTIR (black) and calculated by DFT (red). Insets: relevant vibrations as obtained. Doublets in the FTIR measurements come from s-cis/s-trans isomerism of the monomers in solution[1], while the DFT was optimized and analyzed only for s-cis conformation.



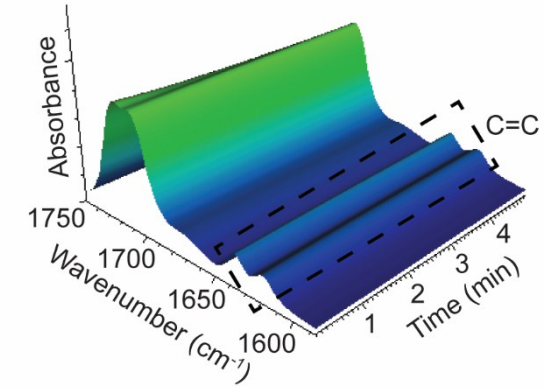
Supplementary Figure S2. Initial (black) and final (red) spectra of HEA, before and after the polymerization.



Supplementary Figure S3. Control experiments of HEA polymerization. Both sole PEI (black) and $Sn_2S_6^{4-}$ (blue) produced no polymerization of HEA in the absence of SCNCs.



Supplementary Figure S4. Conversion of THFA (a) as function of time by HNPs (black) and nanorods (red). Both PEI in the absence of SCNCs (blue) and 5μM TPO in HEA (pink) produced no significant polymerization. Inset: structure of THFA. (b) The decrease in the acrylate absorption peak of ACMO after normalization to the initial absorption value of nanorods (red) and HNPs (black). The conversion could not be deduced from the FTIR spectrum of ACMO. Inset: structure of ACMO. Both PEI in the absence of SCNCs (blue) and 5μM TPO in HEA (pink) produced no significant polymerization. This experiment shows the generality of the quantum PI approach for solvent-free polymerization.

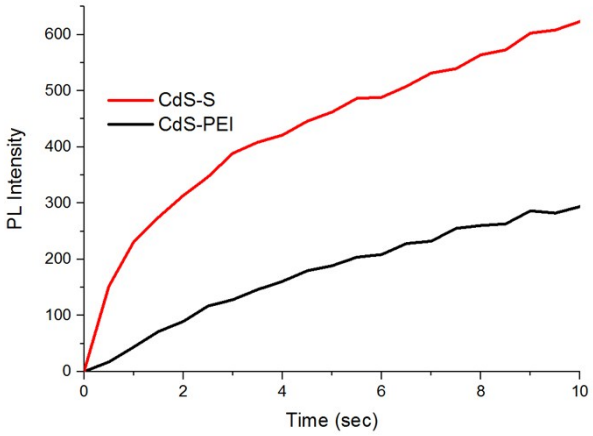


Supplementary Figure S5. 3D FTIR spectrum of the polymerization process of HEA using CdS-S^{2-} without water. The C=C doublet at 1619 cm^{-1} and 1640 cm^{-1}, as confirmed by DFT calculations, is constant over time. The carbonyl stretching is seen at 1708 cm^{-1}.

Terephthalic acid (TPA) assay

TPA assay was used to measure hydroxyl radical production. This assay is based on a chemical reaction between hydroxyl radicals and TPA, producing 2-hydroxyterephthalic acid,

which has a characteristic emission peak at 425 nm.[2] In a typical procedure, 575 μL of 1 mg/mL TPA in water is placed in a quartz cuvette, together with 25 μL of nanoparticles solution with optical density of 1 at 405 nm. The solution, under constant stirring, is irradiated with a 405 nm laser (20mW/cm^2), to excite the nanoparticles, and the oxidation products are simultaneously excited at 310 nm resulting in fluorescence which is measured at 425 nm.



Supplementary Figure S6. PL intensity as measured from hydroxyl radical mediated oxidation of TPA (ex. 310nm/em. 425 nm) of S^{2-} (red) and PEI (black)-capped nanorods.

References:

[1] R. A. Nyquist, S. Fiedler, R. Streck, *Vib. Spectrosc.* **1994**, *6*, 285.

[2] J. C. Barreto, G. S. Smith, N. H. P. Strobel, P. A. McQuillin, T. A. Miller, *Life Sci.* **1994**, *56*, PL89.