Supporting Online Material:

Energetics and decay dynamics of hot electrons in a CdSe QD solid studied by Two-Photon-Photoemission Spectroscopy

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Materials:

TEM

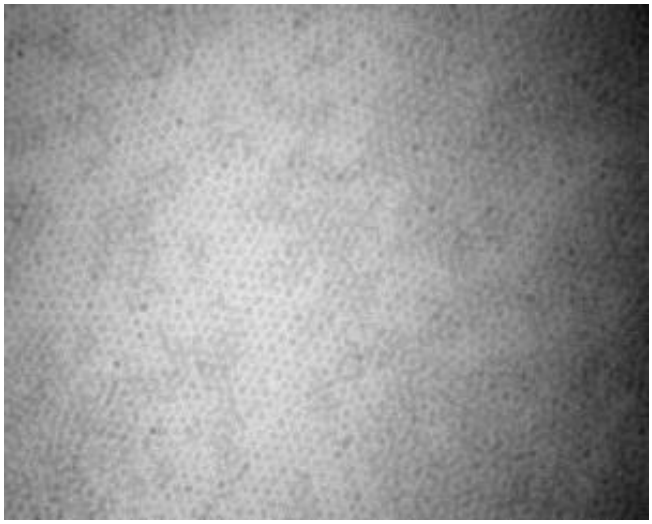

Figure S1. TEM image of 4.2 nm sized CdSe QDs in solution.

2PPE measurements:

Backward process

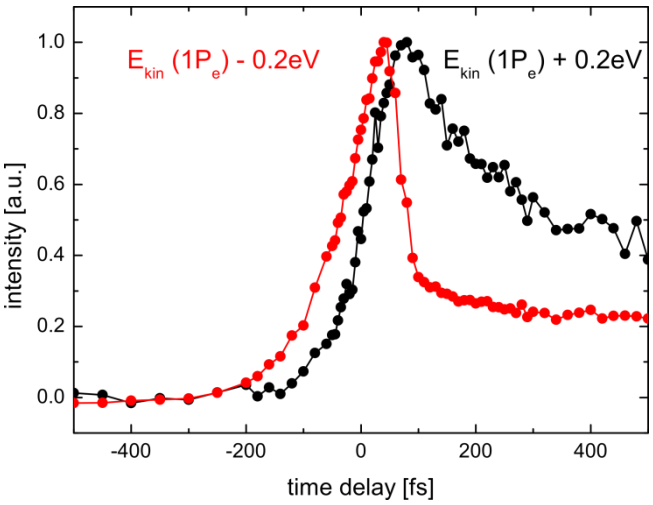

Figure S2. Transients at E_{kin} ($1P_e$) – 0.2eV (red curve) and at E_{kin} ($1P_e$) + 0.2 eV (black curve) for HDT capped QDs around $\Delta t = 0$. The decay for the transient at lower kinetic energy takes course at negative time delays whereas the opposite is true for the transient at higher kinetic energy.

An additional influence of the 2PPE spectra is the already mentioned backward process occurring at lower kinetic energy regions around $\Delta t = 0$ in which the roles of the laser pulses are exchanged. Hence, in this process, the probe pulse pumps and the pump pulse probes. Since the probe pulse is in the UV energy range, higher QD or ligand states can be excited. This process can be seen as the reverse process of 'normal' 2PPE and thus a corresponding decay is seen at negative time delays when the probe pulse comes before the pump pulse. Figure S2 shows the comparison of two transients at different kinetic energies for HDT capped QDs. The transient at lower kinetic energies decays at negative time delays which results from the reverse 2PPE process. The transient at higher kinetic energies shows the opposite behavior indicating a 'normal' 2PPE process.

Comparison of oleic acid and HDT capped QDs at different timescales

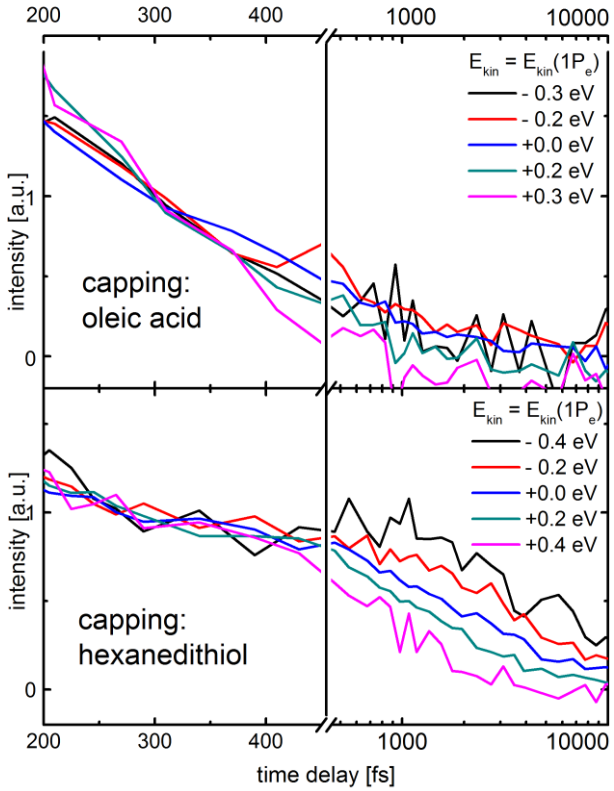

Figure S3. Transients at different kinetic energies for samples with oleic acid and HDT capping. Note that the time scale in the right part of the spectra is logarithmic.

In Figure S3 transient at different kinetic energies are shown. In the case of oleic acid capped samples, almost no prominent dependence on the kinetic energy can be observed at any timescale. The transients of the HDT capped QDs show a very similar behavior at early times up to ~ 400 fs. However, at longer time delays these samples exhibit strongly energy dependent dynamics. This is

probably due to the influence of intermediate states between $1P_e$ and $1S_e$ related to the surface or the capping molecules.