## **Supporting Information**

## Hot Hole Transfer at Plasmonic Semiconductor/Semiconductor Interface

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**Scheme S1**. Schematic presentation of the plasmon induced transit hole transfer (PITCT) mechanism. The hot hole transfer proceeds through a two-step process of hole trapping followed by transfer of the trapped holes to the acceptor phase.



Figure S1. TEM images of CuS NCs showing the hexagonal shape.



Figure S2. The magnified HR-TEM image of CuS/CdS HNCs.



**Figure S3.** Powder X-ray diffraction (PXRD) patterns of CuS NCs and CdS/CuS HNCs, compared with the reference obtained for *cv*-CuS (JCPDS no 00-006-0464), and *w*-CdS (JCPDS no. 00-041-1049).



**Figure S4.** Time evolution of the TAS of thin films of CuS (EDT) NCs in the visible (A) and (C); and in the NIR (B) and (D) spectral regions at short (0 - 2 ps) and long (2 ps - 1 ns), respectively following excitation at 1500 nm. The arrows indicate the time evolution from 0 to 2 ps and from 2 ps to 1 ns. The roman numerals I and II indicate the spectral position of trap state A and B, respectively. The spectra have been smoothed for clarity of presentation. Note the difference in the  $\Delta OD$  values between the short and long-time windows.



**Figure S5.** Comparison of the transient decays at: A) 440 nm; B) 560 nm; C) 640 nm and D) 900 nm probe wavelengths of thin films of CuS (EDA) NCs at short time window following excitation at 1000 and 1500 nm. The excitation power was 2 mW and the IRF is 80 fs.



**Figure S6.** Comparison of the transient decays at: A) 440 nm; B) 560 nm; C) 640 nm and D) 900 nm probe wavelengths of thin films of CuS (EDA) NCs at long time window following excitation at 1000 and 1500 nm. The excitation power was 2 mW and the IRF is 80 fs.



**Figure S7.** Laser flash photolysis decays at 470 nm for A) CuS (EDA) NCs, B) CuS/CdS (EDA) HNCs and C) CuS/CdS (EDT) HNCs following excitation at 1100 nm. The solid line represents the best bi-exponential fit. Note the difference in the timescales.



**Figure S8**. Time evolution of the TAS of thin films of CuS/CdS (EDT) HNCs in the visible (A) and (C); and in the NIR (B) and (D) spectral regions at short (0 - 2 ps) and long (2 ps – 1 ns), respectively following excitation at 1500 nm. The arrows indicate the time evolution from 0 to 2 ps and from 2 ps to 1 ns. The roman numerals I and II indicate the spectral position of trap state A and B, respectively. The spectra have been smoothed for clarity of presentation. Note the difference in the  $\Delta$ OD values between the short and long-time windows.



**Figure S9.** Comparison of the transient decays at: A) 440 nm; B) 560 nm; C) 640 nm and D) 900 nm probe wavelengths of thin films of CuS/CdS (EDA) HNCs at short time window following excitation at 1000 and 1500 nm. The excitation power was 2 mW and the IRF is 80 fs.



**Figure S10.** Comparison of the transient decays at: A) 440 nm; B) 560 nm; C) 640 nm and D) 900 nm probe wavelengths of thin films of CuS/CdS (EDA) HNCs at long time window following excitation at 1000 and 1500 nm. The excitation power was 2 mW and the IRF is 80 fs.



**Figure S11.** Absorption spectrum of pristine CdS. For more clarity, we have corrected the light dispersion of this sample by subtracting the baseline.



**igure S12.** Comparison of the transient decays at A) and B) 440 nm; C) and D) 560 nm; and E) and F) 900 nm probe wavelengths at short and long time windows of thin films of CuS (EDA) NCs following excitation at 1500 nm using different excitation power. The IRF is 80 fs.



**Figure S13.** Comparison of the transient decays at A) and B) 440 nm; C) and D) 560 nm; and E) and F) 900 nm probe wavelengths at short and long time windows of thin films of CuS/CdS (EDA) HNCs following excitation at 1500 nm using different excitation power. The IRF is 80 fs.