Supplementary Information for

Enhanced Charge Separation in Ternary P3HT/PCBM/CuInS$_2$ Nanocrystals Hybrid Solar Cells

Aurélie Lefrançois,¹ Beata Luszczynska,¹,² Brigitte Pepin-Donat,¹ Christian Lombard,¹ Benjamin Bouthinon,² Jean-Marie Verilhac,² Marina Gromova,³ Jérôme Faure-Vincent,¹ Stéphanie Pouget,² Frédéric Chandezon,¹ Saïd Sadki,¹ Peter Reiss¹*  

CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble cedex 9, France. ¹INAC-UMR5819 SPrAM (CEA-CNRS-UJF), LEMOH; ²Liten/DTNM; ³INAC/SCIB/RICC; ⁴INAC/SP2M/SGX * email: peter.reiss@cea.fr

Figure S1: Powder X-ray difractogram of 7.4 nm CuInS$_2$ nanocrystals (Cu Kα radiation, $\lambda = 1.5418$ Å). For comparison the diffraction pattern of bulk CuInS$_2$ in the cubic phase is given (red bars).
**Figure S2:** TEM image of EHT-capped CuInS$_2$ nanocrystals. The mean size is 7.4 +/- 1.0 nm.

**Figure S3:** $^1$H-NMR spectra (500 MHz, toluene-d$_8$) of CuInS$_2$ NCs with initial dodecanethiol (DDT) surface ligands (a) and after ligand exchange with 1,2-ethylhexanethiol (EHT) (b). For comparison the spectra of the free ligands are also shown. Solvent and impurity peaks are assigned with an asterisk (*) and an octothorpe (#), respectively.
**Figure S4:** DPV measurements of CuInS$_2$ NCs after ligand exchange with EHT and of pure EHT (a: oxidation; b: reduction), carried out in ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) vs. Ag wire pseudoreference electrode.

**Figure S5:** UV-vis absorption spectra of a) thin films of P3HT:PCBM and P3HT:PCBM:NCs-EHT (film thicknesses: 200-250 nm) and of CuInS$_2$ NCs in chloroform solution; b) P3HT:PCBM:NCs solar cells using the indicated mass ratios, compared to the P3HT:PCBM film on a glass substrate.
Figure S6: Relaxation spectra for the three blends taken 2 or 6 min after switching off the light source, compared to the spectra under 473 nm irradiation (T = 20 K).
Figure S7: Energy levels of poly(triarylamine) (PTAA) and of the used CuInS$_2$ nanocrystals. For comparison the levels of P3HT and PCBM are also indicated.

Figure S8: $J(V)$ curves obtained under simulated solar light (AM1.5 one sun conditions) of solar cells containing blends of PTAA, PCBM and DDT-capped CuInS$_2$ NCs using the indicated mass ratios. The film thickness was in all cases 200 ± 20 nm.

Table S1: Solar cell characteristics obtained with PTAA:PCBM and with PTAA:PCBM:CuInS$_2$ NCs blends, measured under AM1.5 one sun conditions (device active area 3.14 mm$^2$). Best values and average values out of four cells (in brackets).

| Blend                | FF   | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | Efficiency (%) |
|----------------------|------|--------------|---------------------|----------------|
| PTAA:PCBM 1:1        | 0.36 | 0.23         | -0.046              | 0.0037         |
|                      | (0.36) | (0.23)       | (-0.045)            | (0.0036)       |
| PTAA:PCBM:NCs 1:1:1  | 0.27 | 0.46         | -0.11               | 0.013          |
|                      | (0.27) | (0.45)       | (0.09)              | (0.011)        |
| PTAA:PCBM:NCs 1:1:0.5| 0.29 | 0.53         | -0.31               | 0.048          |
|                      | (0.26) | (0.53)       | (-0.29)             | (0.040)        |
| PTAA:PCBM:NCs 1:1:0.25| 0.41 | 0.30         | -0.38               | 0.047          |
|                      | (0.40) | (0.30)       | (-0.35)             | (0.042)        |
Figure S9: UV-vis absorption spectra of the solar cells used in Fig. S8 / Table S1.