Supplementary Information

Size-Dependent Photophysical Behaviour of Low Bandgap Semiconducting Polymer Particles

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TEM measurements

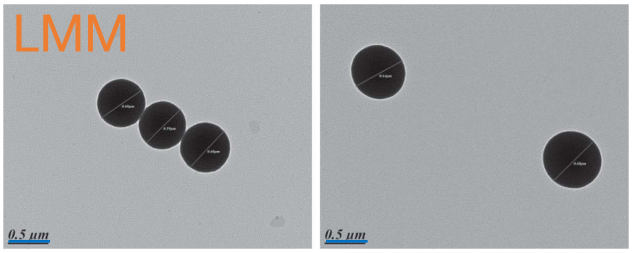

Figure 1S. Transmission electron microscopy (TEM) images for the LMM mesoparticles are reproduced with permission from (Parrenin et al., 2015). Copyright (2015) John Wiley & Sons.

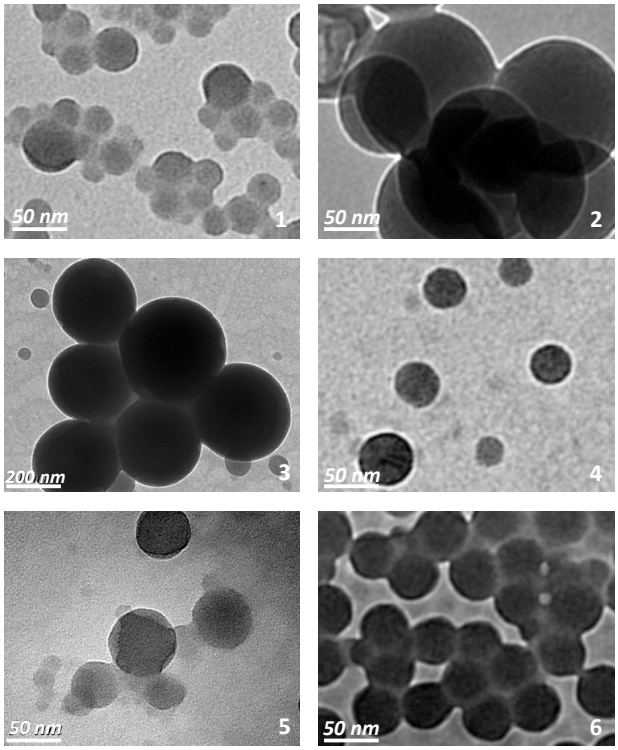

Figure 2S. TEM images for the HMM nanoparticles are reproduced with permission from (Parrenin et al., 2017). Copyright (2017) American Chemical Society.

Emission from the PVP surfactant

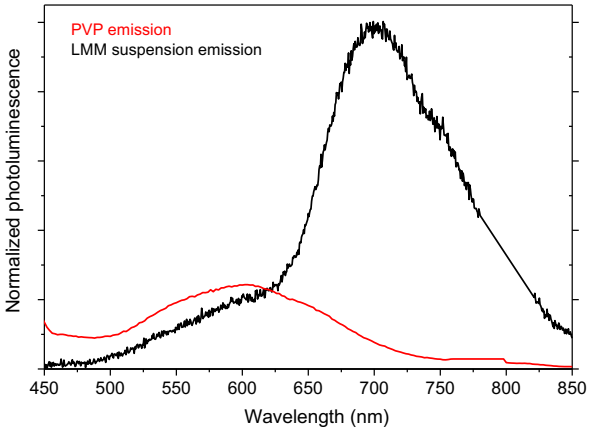

Figure 3S. Comparison between the PL emission of the LMM suspension and the PVP surfactant after excitation at 390 nm.

μRaman measurements on the LMM mesoparticles

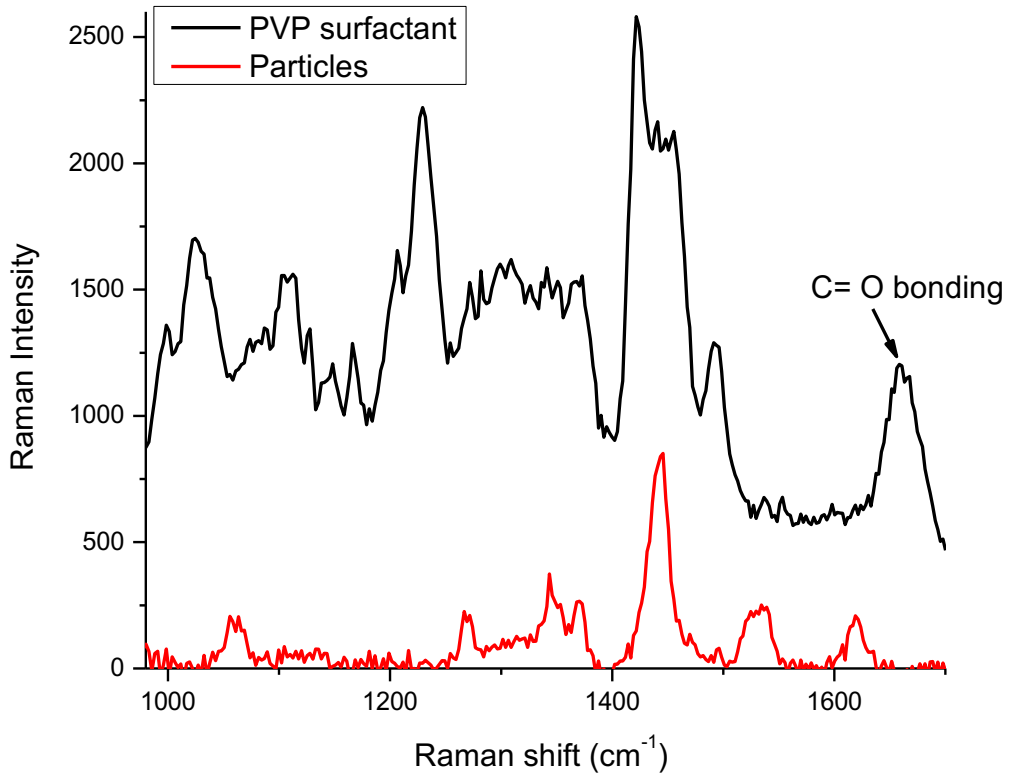

Figure 4S. μRaman spectroscopy measurements were performed on the LMM mesoparticles to check the presence of the PVP surfactant. The spectrum (red line) revealed no PVP presence (black line). The spectrum from the particles resembles that of an earlier one for PCDTBT (Provencher et al., 2014). These experiments were recorded in backscattering mode on a modified HR800 (HORIBA Jobin Yvon) confocal micro-Raman spectrometer. A continuous wave laser operating at 785 nm was used with typical resolution of 2.5 cm^{-1}.

Transient Transmission measurements on the LMM and HMM polymer spin coated films

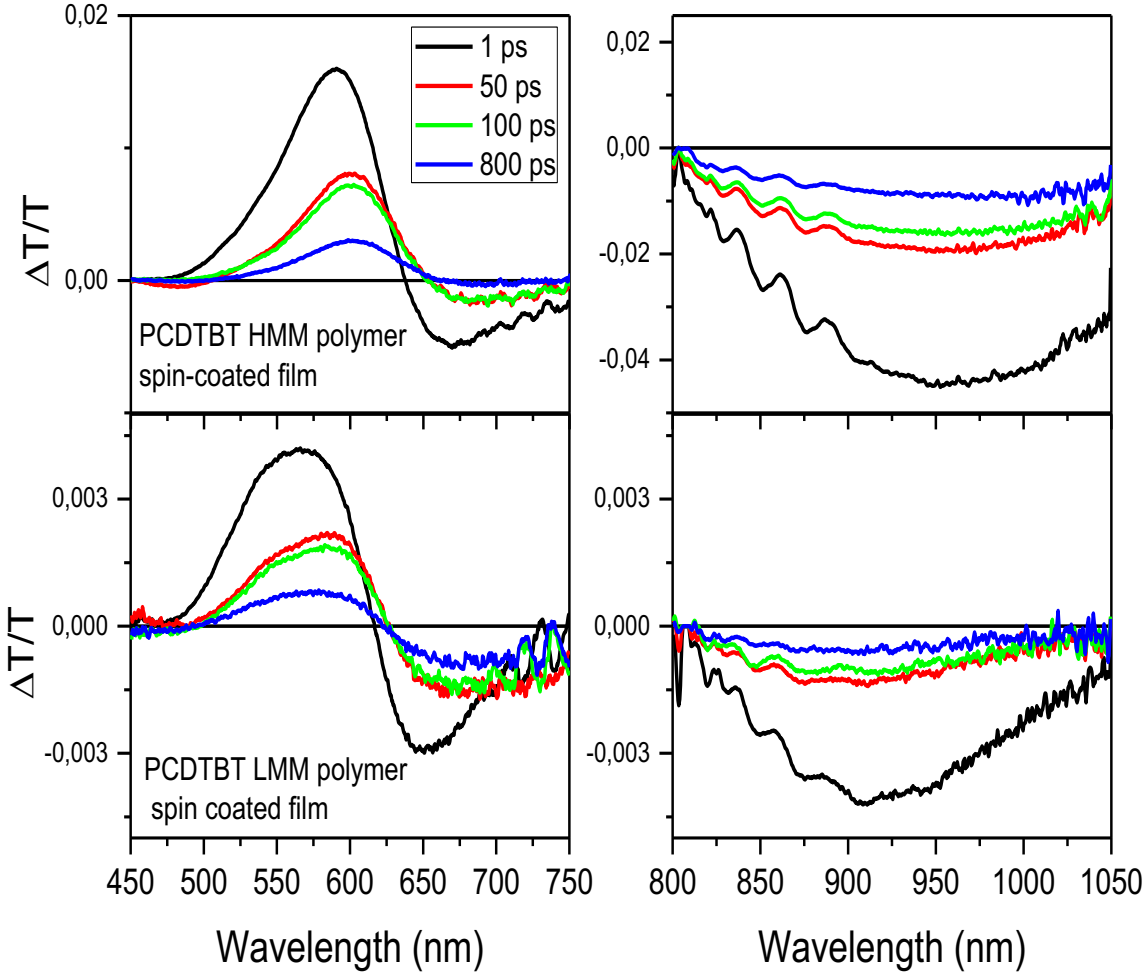

Figure 5S. Pump-probe spectra at different probe delays. In the top/bottom panels the spectra in the visible and near infrared region are shown for the HMM/LMM polymer spin coated films.

References

Parrenin, L., Brochon, C., Hadziioannou, G., and Cloutet, E. (2015). Low bandgap semiconducting copolymer nanoparticles by Suzuki cross-coupling polymerization in alcoholic dispersed media. *Macromol. Rapid Commun.* 36**,** 1816-1821.

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Provencher, F., Bérubé, N., Parker, A.W., Greetham, G.M., Towrie, M., Hellmann, C., Côté, M., Stingelin, N., Silva, C., and Hayes, S.C. (2014). Direct observation of ultrafast long-range charge separation at polymer-fullerene heterojunctions. *Nature Commun.* 5**,** 4288.