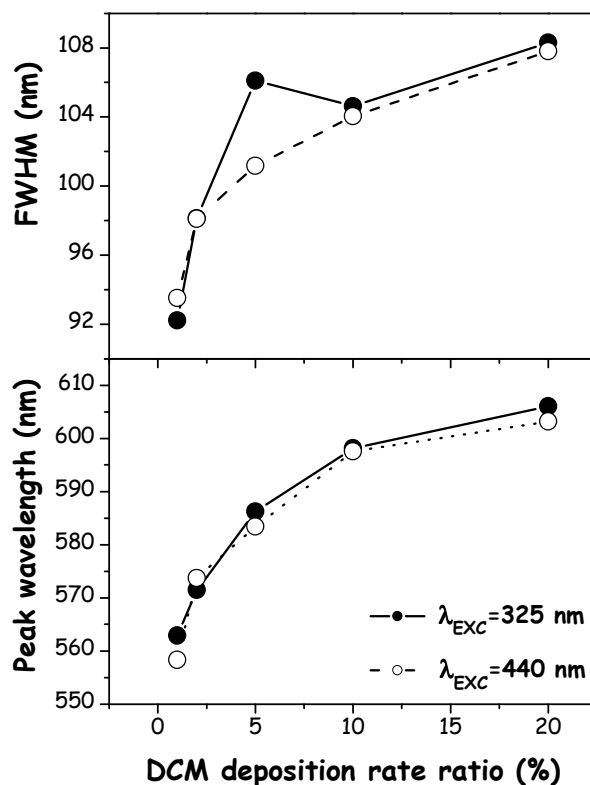


## Supporting Information

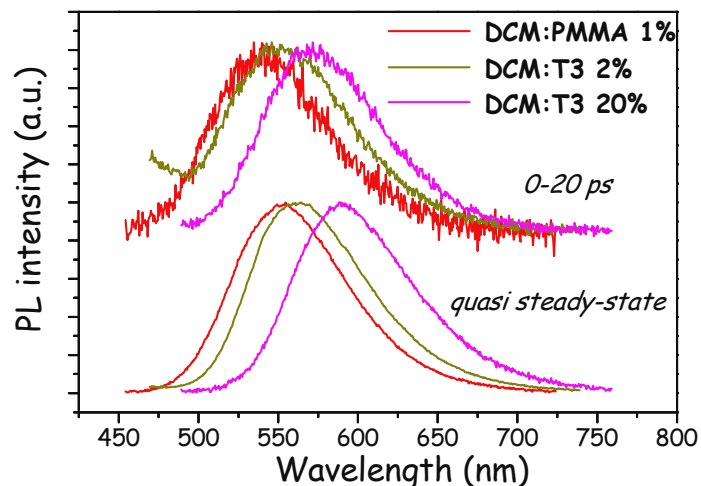


**Figure S1.** Full width at half maximum (FWHM) values and peak wavelengths of DCM photoluminescence maxima with increasing DCM concentration. Donor and the acceptor molecules are selectively excited at 325 nm and 440 nm.

PL measurements performed exciting only the guest molecules in the blends show that the DCM peak wavelengths and FWHM values are almost the same regardless the fact that the time scale of the energy transfer process is much more rapid than the interaction dynamics among guest molecules. We can deduce that even at high guest concentration the guest aggregate distribution is uniform and homogeneous in size around T3 emitting centres, and consequently the energy-transfer process is isotropic.

The energetic mismatch between the T3 and DCM HOMO levels (around 0.2 eV), might promote, upon selective excitation of the guest in the blend, a photo-induced hole-transfer from the DCM HOMO level to the T3 HOMO level. The absence of additional PL peaks in the low-energy spectral

region together with the enhanced blend PLQY (see Table 2) obtained by exciting directly the guest molecules show that there is no significant excited state interaction between the two molecules.



**Figure S2.** Emission of the DCM component in 2% and 20% blends in the first 20 ps (upper) and in almost steady-state times (lower). Emission from DCM molecules dispersed in PMMA matrix is reported for comparison.

For the 20% sample we observe a red-shift of the maximum peak wavelength of about 13 nm without a significative increase of FWHM, which can be ascribed to intramolecular energy relaxation. These spectroscopic features can indicate the enhancement with time of the local static disorder around T3 molecules with the formation of weakly emissive DCM aggregates. Regarding the 2% sample the wavelength redshift and FWHM variation roughly do not increase in early times with respect to the solution-like sample.