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Exciton diffusion enhancement in triphenylamines *via* incorporation of phenylethenyl sidearms

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Relative fluorescence quenching efficiency

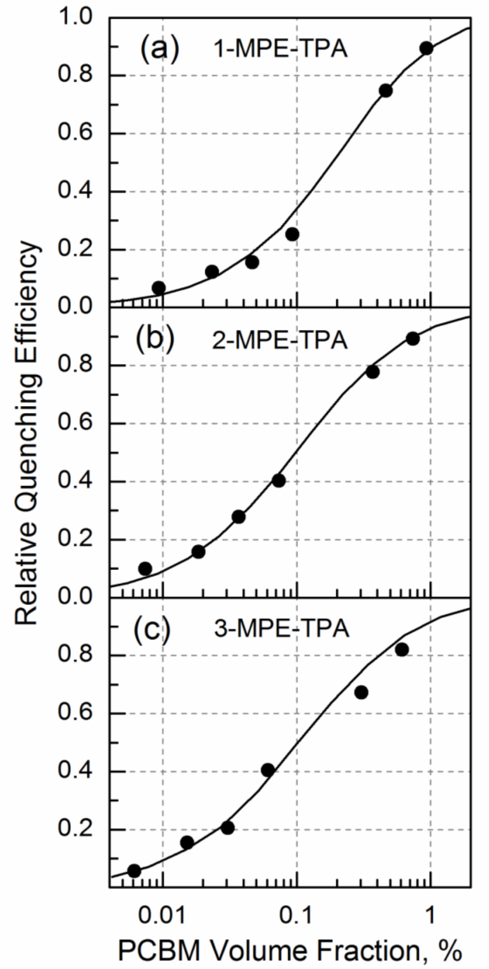

Fig. S1 Relative quenching efficiency *vs*. PCBM volume fraction in TPA:PCBM blends containing mono-substituted TPA (1-MPE-TPA) (a), di-substituted TPA (2-MPE-TPA) (b) and tri-substituted TPA (3-MPE-TPA) (c). Points and lines depict experimental and modelled results, respectively.

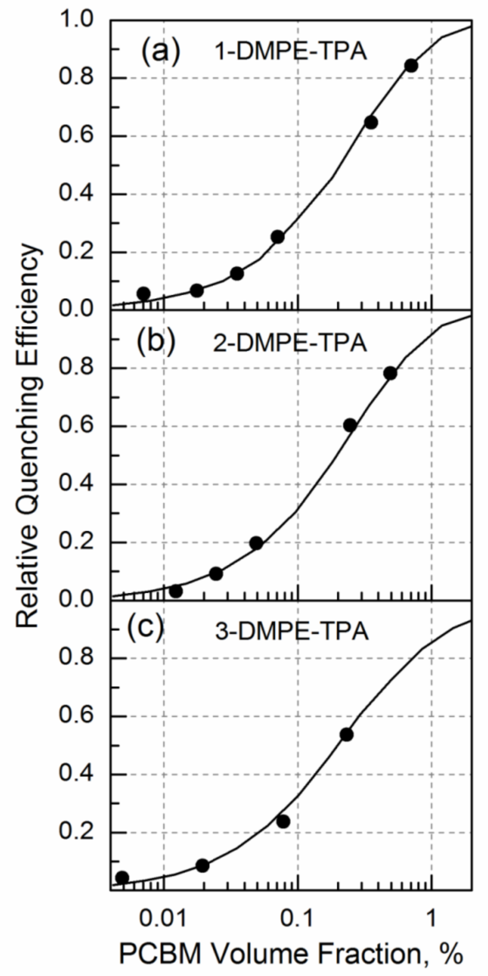

Fig. S2 Relative quenching efficiency *vs*. PCBM volume fraction in TPA:PCBM blends containing mono-substituted TPA (1-DMPE-TPA) (a), di-substituted TPA (2-DMPE-TPA) (b) and tri-substituted TPA (3-DMPE-TPA) (c). Points and lines depict experimental and modelled results, respectively.

Small angle X-ray scattering (SAXS)

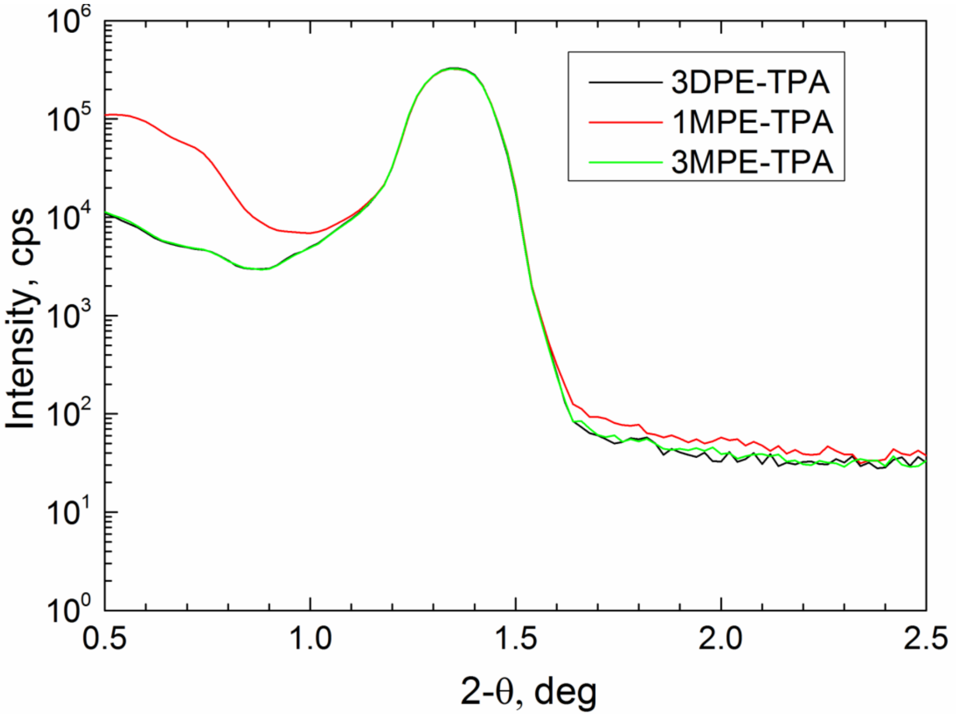

Fig. S3 X-ray scattering intensity as a function of 2-theta angle for 1-MPE-TPA, 3-MPE-TPA, 3-DPE-TPA and PCBM blends at the highest PCBM concentration.

Absorption and fluorescence spectra

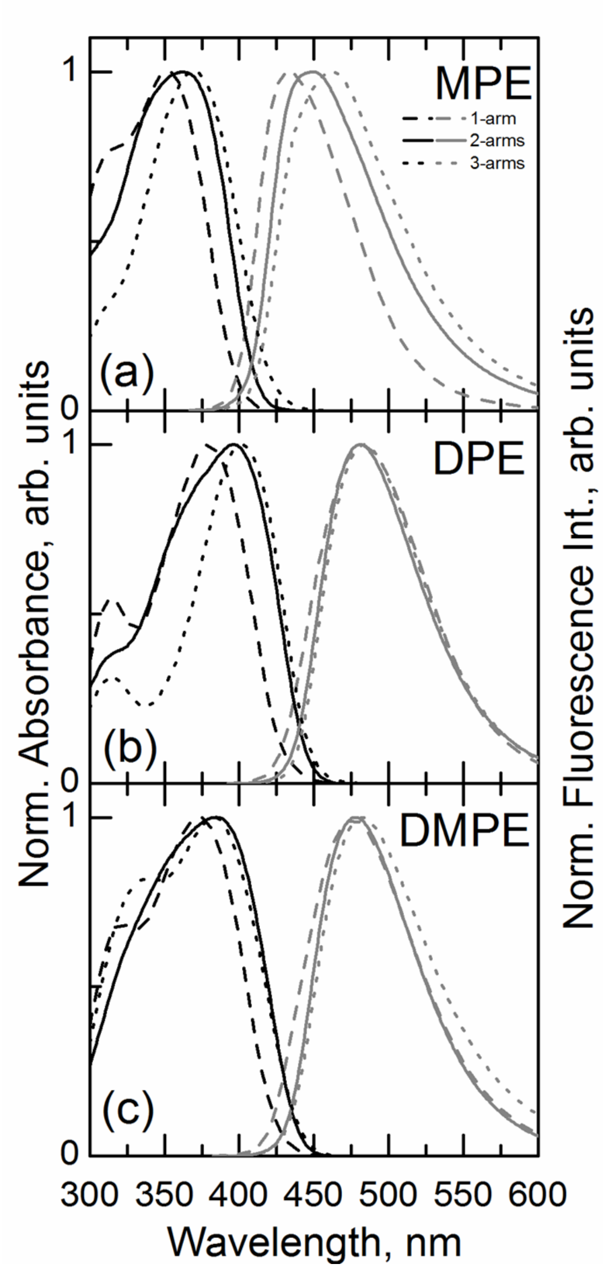

Fig. S4 Normalized absorption and fluorescence spectra of the TPA compounds bearing MPE (a), DPE (b) and DMPE (c) sidearms.

Fig. S4 shows normalized absorption and fluorescence spectra of the TPA compounds with different type of MPE, DPE and DMPE sidearms of the neat incapsulated films. The addition of the larger number of the sidearms redshifts absorption spectra, meanwhile fluorescence spectra are almost unaffected for the compounds with DPE and DMPE sidearms, except for MPE sidearms containing compounds, for which fluorescence are redshifted likely due to the formation of excimers.

Spectral overlap of the TPA compounds

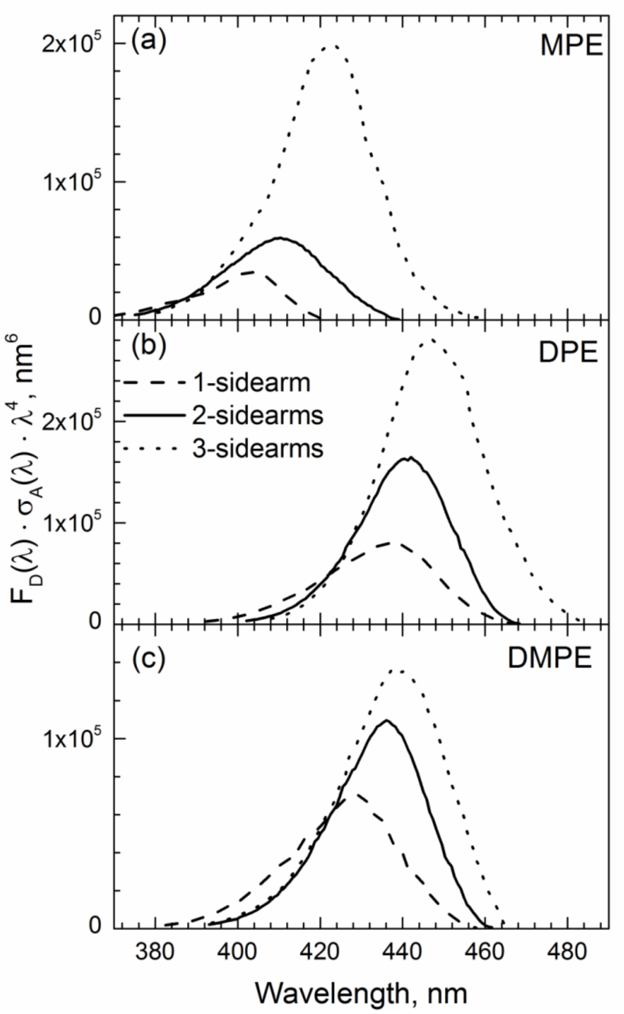

Fig. S5 Spectral overlap of absorption and fluorescence spectra of the TPA compounds.

Absorption and fluorescence spectroscopy in different polarity solvents

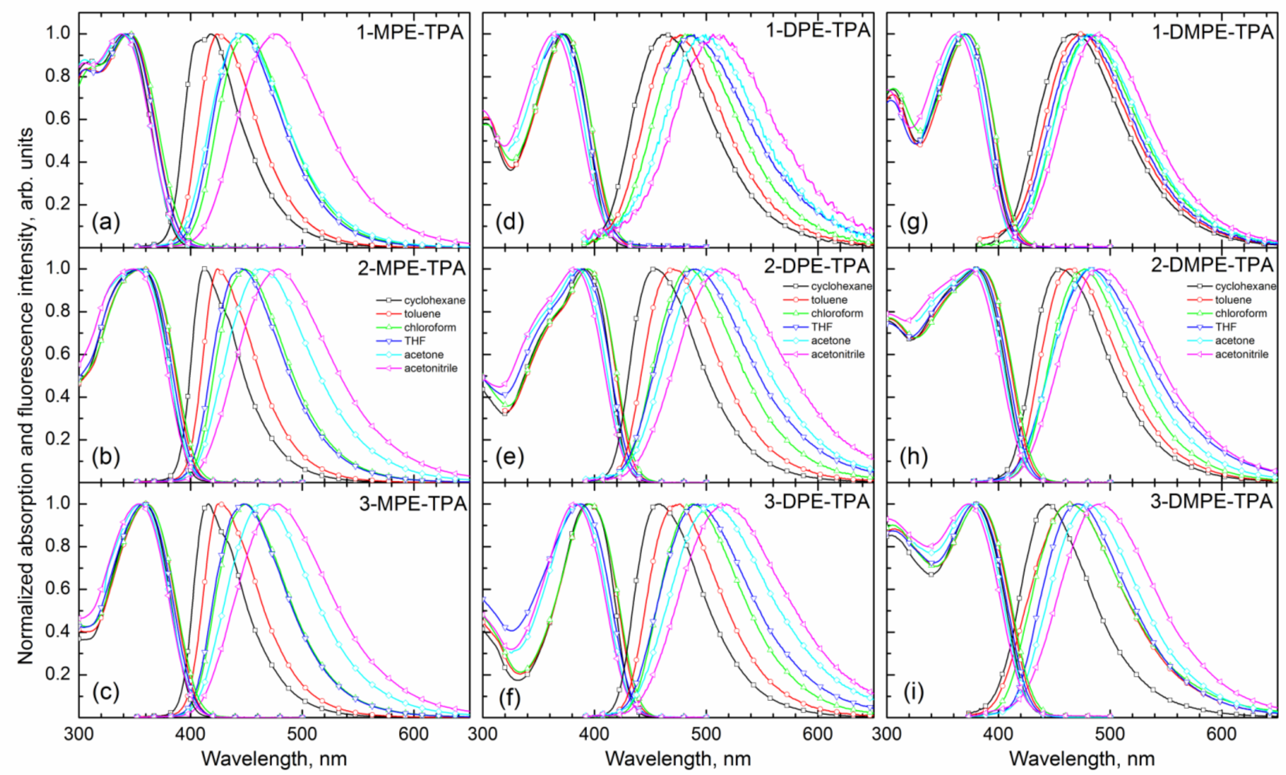

Fig. S6 Absorption and fluorescence spectra of the compounds (a) 1-MPE-TPA, (b) 2-MPE-TPA, (c) 3-MPE-TPA, (d) 1-DPE-TPA, (e) 2-DPE-TPA, (f) 3-DPE-TPA, (g) 1-DMPE-TPA, (h) 2-DMPE-TPA, (i) 3-DMPE-TPA in different polarity solvents.

To prove emitting state localization on one of the sidearms of our TPA compounds, absorption and fluorescence spectroscopy as a function of solvent polarity was performed. The spectra of all the TPA compounds with different type and number of the sidearms are displayed in Fig. S6. The obtained data indicate negligible changes of the absorption spectra and significant red shift of the fluorescence spectra with increasing solvent polarity. To quantify solvent polarity induced changes, the estimated Stokes shift was plotted against orientation polarizability (Δf)

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \tag{S1}$$

which characterizes solvent by its refractive index (n) and dielectric constant (ε). The plots are presented in Fig. S8. According to Lippert-Mataga equation, the Stokes shift ($\bar{\nu}_A - \bar{\nu}_F$) can be expressed as a function of Δf and the change in the dipole moments of excited and ground states, μ_E and μ_G, respectively,

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc}\Delta f \frac{(\mu_E - \mu_G)^2}{a^3}. \tag{S2}$$

Here $\bar{\nu}_A$ and $\bar{\nu}_F$ are absorption and fluorescence maxima in cm^{-1}, h is Planck's constant, c – speed of light, a is the radius of the cavity in which the fluorophore resides. Fig. S8 illustrates that the slopes of the plots, which are proportional to $\Delta\mu^2$ according to eqn S2, are very similar for the TPA compounds bearing the same type but different number of sidearms. This is only possible for the compounds exhibiting similar dipole moments, and thus, for our compounds can be achieved if the excited state is localized on one of the sidearms. To compare, relatively small spectral shifts *vs.* solvent polarity, and thus minimal slope have been obtained for the unsubstituted TPA (Fig. S8). Assumption of the increasing/decreasing *a* with increasing the number of sidearms is improbable, since this would result in the enhanced/reduced conjugation, and thus, in the fluorescence spectrum shift, which was not observed.

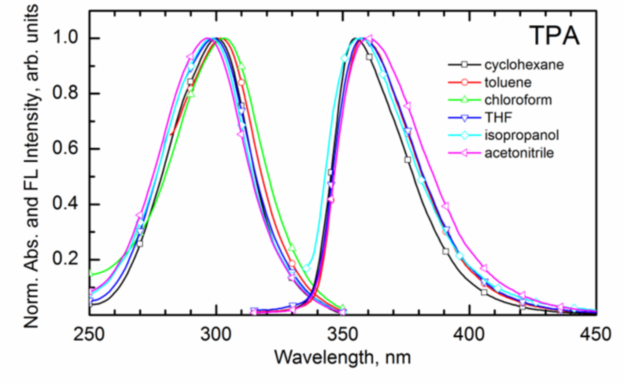

Fig. S7 Absorption and fluorescence spectra of the unsubstituted TPA in different polarity solvents.

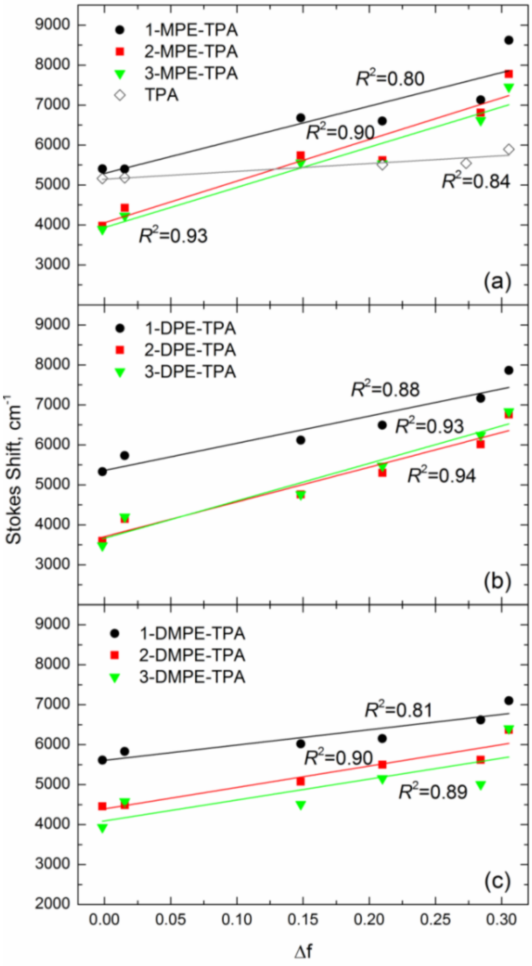

Fig. S8. Stokes shift as a function of orientation polarizability for the TPA compounds as well as for the unsubstituted TPA. R^2 shows the accuracy of the linear fit (R^2=1 indicates perfect fit).

Estimation of the relative contribution of various factors to an overall increase in L_D

The enhancement of exciton diffusivity and diffusion length in the TPA compounds according to eqn (5) can be due to the several factors: (i) reduced intermolecular distance between exciton hopping sites, (ii) increased fluorescence quantum yield or (iii) increased spectral overlap integral (J). The latter can be enhanced due to: (i) increased absorption intensity and (ii) reduced Stokes shift.

To determine the relative contribution of all these factors to an overall increase in L_D, $(J)^{1/2}$, $(\Phi_F)^{1/2}$ and $1/d^2$ were calculated (Fig. S9). Obviously, the major factor causing the increase of L_D (in the case of the TPA compounds with MPE and DPE sidearms) is J, whereas for the compounds with DMPE sidearms J and $1/d^2$ contribute equally. Φ_F either does not change (for the compounds with MPE and DPE sidearms) or even decreases for DMPE sidearms.

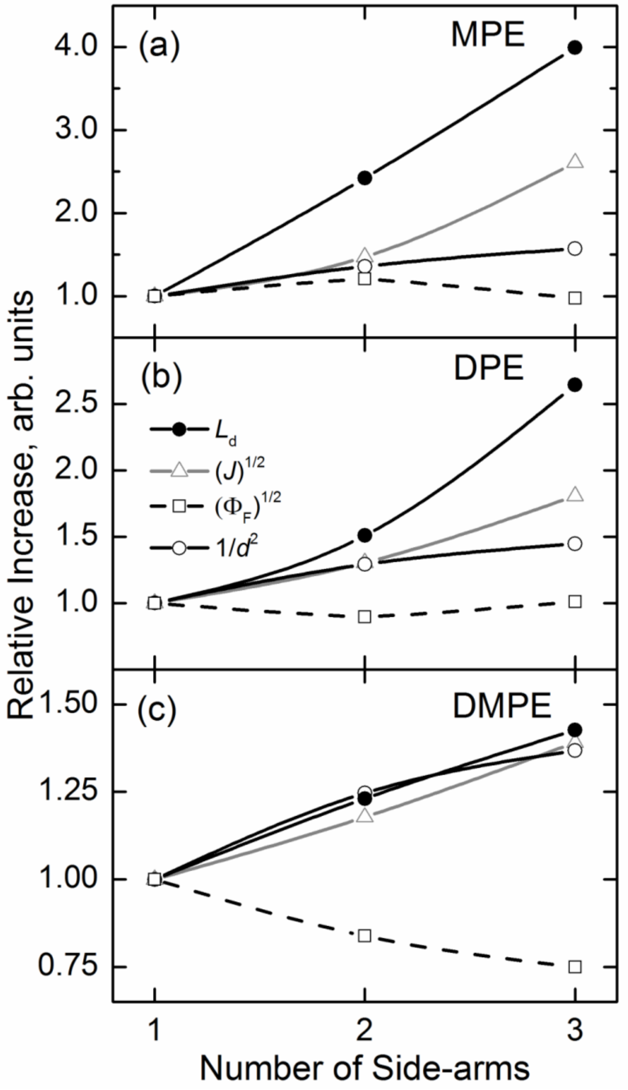

Fig. S9 Relative increase in the exciton diffusion length L_D, as well as in the square root of spectral overlap integral $(J)^{1/2}$, fluorescence quantum yield $(\Phi_F)^{1/2}$ and intermolecular distance term $1/d^2$, as a function of the number of sidearms.

To reveal the dominant mechanism mostly affecting increase of *J,* the relative contributions of increasing absorbance and decreasing Stokes shift were evaluated. Fig. S10 shows the relative increase of *J*, absorption intensity, which was calculated by integrating absorption cross-section spectra, and the overlap integral of normalized fluorescence and absorption spectra, which indicates the influence of Stokes shift. Clearly, decreasing Stokes shift was decisive in causing increased L_D for the compounds with MPE sidearms. For the compounds with DPE sidearms, both Stokes shift and absorption intensity contributed equally, whereas for the compounds with DMPE sidearms the absorption intensity was found to play the major role in the increase of spectral overlap integral.

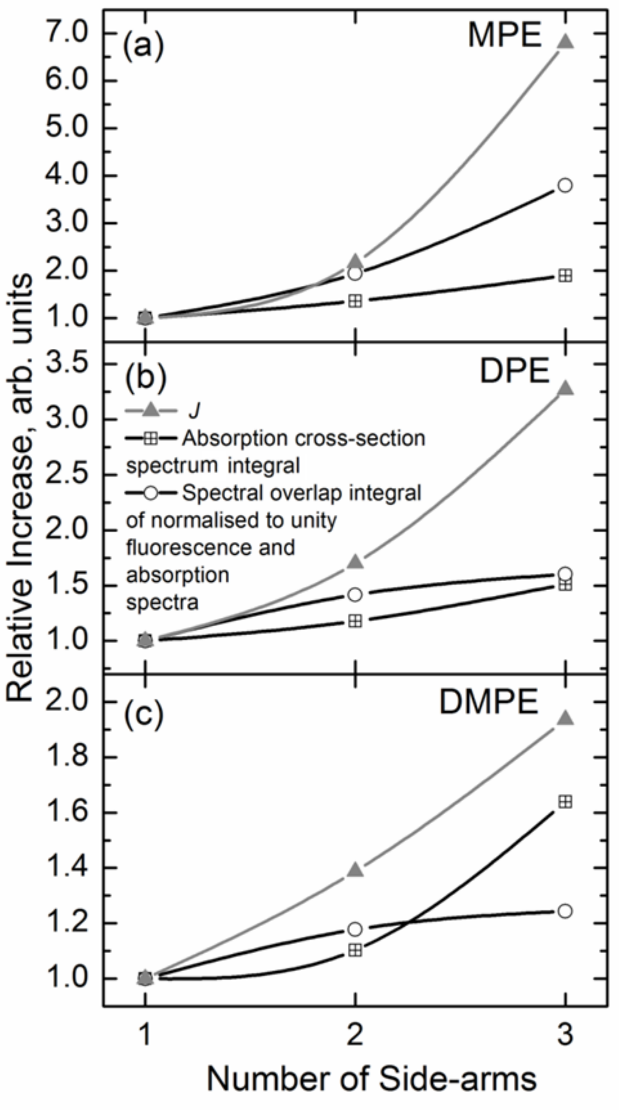

Fig. S10 Relative increase in the spectral overlap integral *J*, absorption cross-section spectrum integral and overlap integral of normalized absorption and fluorescence spectra, which corresponds to Stokes shift.