# Supporting Information

# Energy redistribution dynamics in triarylamine-triarylborane containing hexaarylbenzenes

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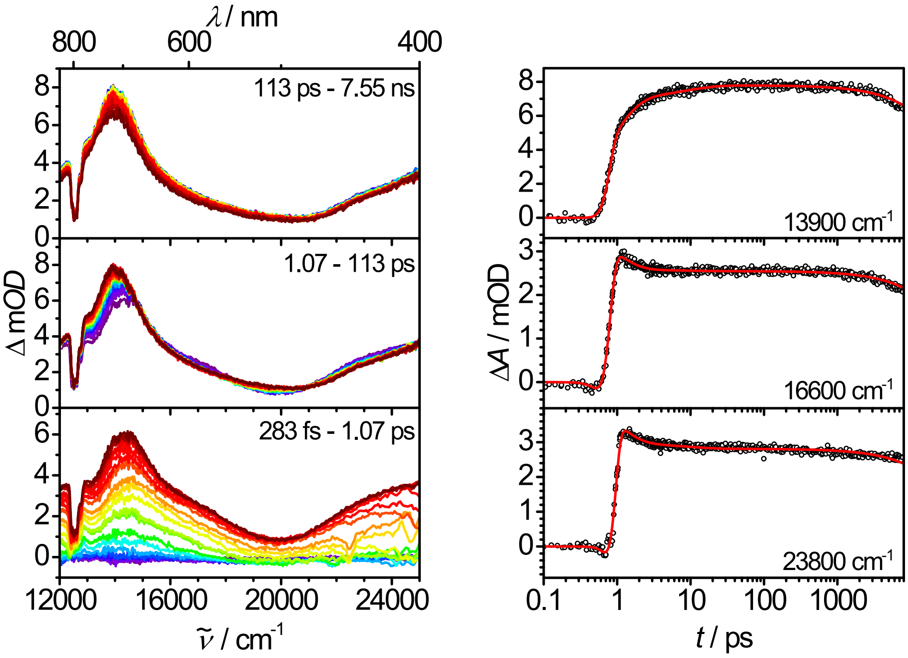

**Fig. S1** Transient spectra and time scans of **1** in DCM at 24700 cm$^{-1}$ excitation. Early spectra are given in blue, late spectra in red.

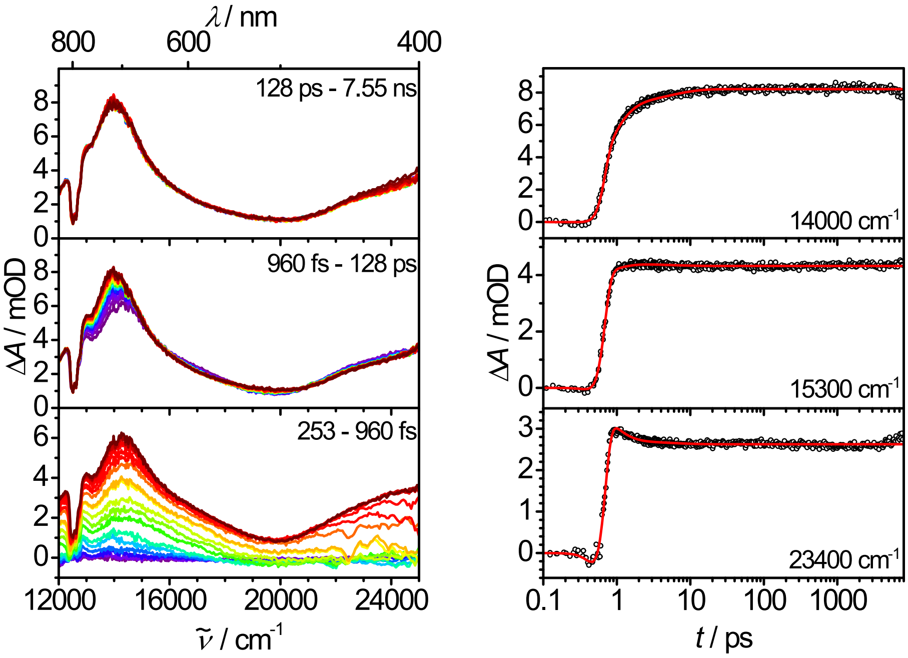

**Fig. S2** Transient spectra and time scans of **2** in DCM at 24700 cm$^{-1}$ excitation. Early spectra are given in blue, late spectra in red.

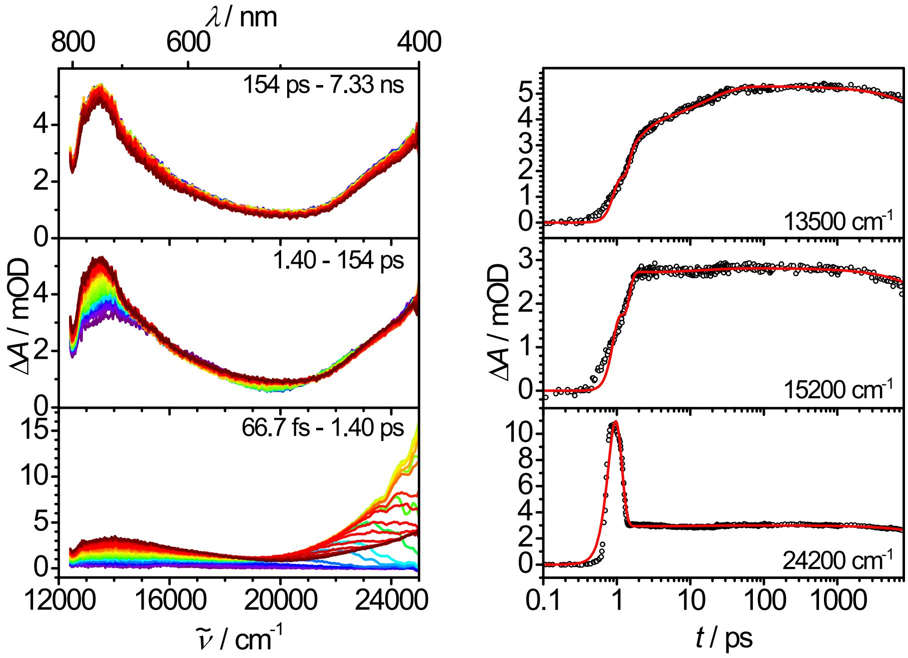

**Fig. S3** Transient spectra and time scans of **3** in PhCN at 26700 cm$^{-1}$ excitation. Early spectra are given in blue, late spectra in red.

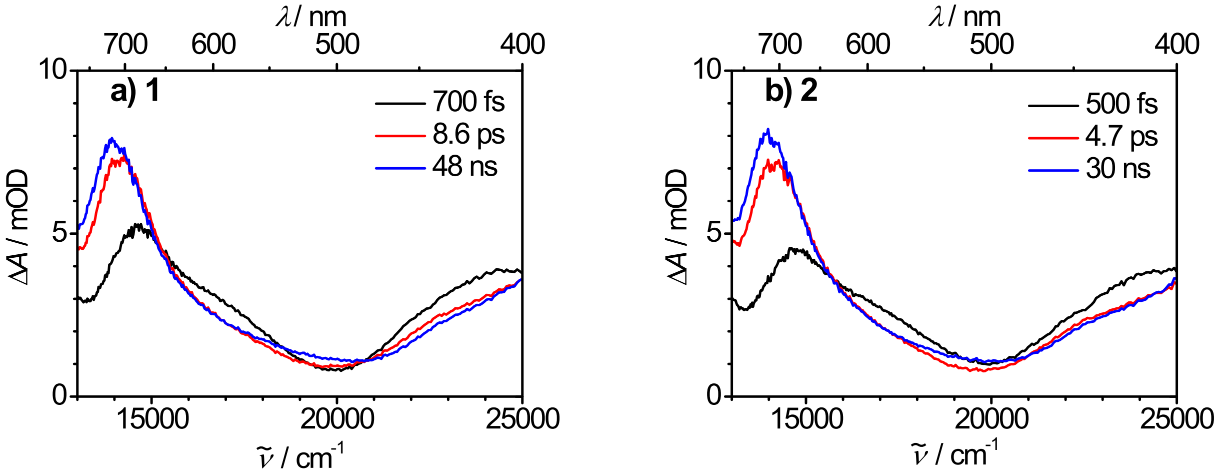

**Fig S4** Evolution associated fs-transient absorption spectra of a) **1** and b) **2** in DCM. The decay times of the respective EADS are given in the legend. The samples were pumped at 24700 cm$^{-1}$.

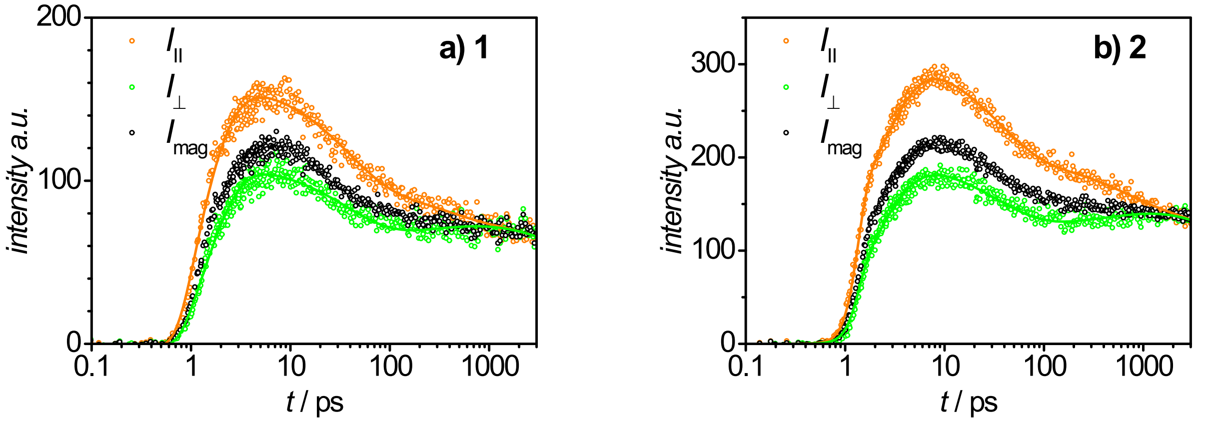

**Fig. S5** The fluorescence upconversion traces (circles) $I_{\parallel}$, $I_{\perp}$ and the calculated $I_{\text{mag}}$ of a) **1** and b) **2** excited at 24700 cm$^{-1}$ (405 nm) in DCM. The global fits are shown in all cases as solid lines.

## Estimation of Förster energy transfer rate in 1 and 2

Population transfer between neighbouring CT states in **1** and **2** could proceed by Förster resonance energy transfer (FRET) theory (eq. S1) which is based on dipolar coupling of transition moments in the weak coupling regime.[1, 2]

$$k_{\text{FRET}} = \frac{9 \cdot 1000 \ln(10) \Phi_{\text{D}} \kappa^2 J}{128 \pi^5 N_{\text{A}} n^4 \tau_{\text{D}} r^6} \qquad \text{(S1)}$$

Accordingly, the energy transfer rate $k_{\text{FRET}}$ depends on the quantum yield $\Phi_{\text{D}}$ and lifetime $\tau_{\text{D}}$ of the donor state in absence of the acceptor state, the factor $\kappa$ describing the mutual orientation of the transition moments of the donor and acceptor states, the centre to centre distance $r$ of the two states, the refractive index $n$ of the solvent and the overlap integral $J$. The latter is defined as the integral over the product of the area normalised fluorescence intensity of the donor $\bar{I}_{\text{fl,D}}(\tilde{\nu})$ and the extinction coefficient of a single acceptor state $\varepsilon(\tilde{\nu})$ (eq S2).

$$J = \int_{-\infty}^{\infty} \bar{I}_{\mathrm{fl,D}}(\tilde{\nu})\,\varepsilon(\tilde{\nu})\,\frac{\partial\tilde{\nu}}{\tilde{\nu}^{4}} \qquad \text{(S2)}$$

With $n$(PhCN) = 1.528, $\Phi_{\mathrm{D}}$ = 0.35 and $\tau_{\mathrm{D}}$ = 63 ns (of **3** in PhCN), $\kappa$ = 1.75 for an angle of 120° between the transition moment directions of two neighbouring CT states, $r_{\mathrm{DA}}$ = 6.279 Å for the distance between the middle points of the C-B separation (from DFT optimised structures) and $J$ = $1.1{\cdot}10^{-18}$ and $3.2{\cdot}10^{-18}$ $\mathrm{dm^3\,mol^{-1}\,cm^3}$ (calculated for the steady state absorption and emission spectra in PhCN and cyclohexane, all data from[3], energy transfer time constants of 42 ns and 79 ns were obtained for **1** and **2**, respectively (see Table S1).

**Table S1:** Overlap integrals $J$ of **1** and **2**, calculated for PhCN and cyclohexane, and the respective energy transfer time constants $1/k_{\mathrm{FRET}} = \tau_{\mathrm{FRET}}$ obtained by eq S1.

|  | $J$ (PhCN) /$\mathrm{dm^3\,mol^{-1}\,cm^3}$ | $J$ (cyclohexane) /$\mathrm{dm^3\,mol^{-1}\,cm^3}$ | $\tau_{\mathrm{FRET}}$ (PhCN) | $\tau_{\mathrm{FRET}}$ (cyclohexane) |
|---|---|---|---|---|
| **1** | $3.2{\cdot}10^{-18}$ | $1.2{\cdot}10^{-15}$ | 42 ns | 89 ps |
| **2** | $1.1{\cdot}10^{-18}$ | $1.5{\cdot}10^{-15}$ | 79 ns | 75 ps |

## Calculation of limiting anisotropy for 1 and 2

To relate the measured anisotropy decay time $\tau_{\mathrm{a1}}$ to a single dynamic hopping process in **1**, we have to solve a set of Pauli master equations. The six donor-acceptor pairs have a time dependent probability to be in an excited CT state $P_{\mathrm{i}}(t)$ (i = 1 – 6) where one pair (i = 1) is initially excited, the energy can be transferred between neighbouring pairs with an uniform rate constant $k_{\mathrm{EN}}$. Each CT state can relax to the ground state with the fluorescence time constant $\tau_{\mathrm{fl}}$ (see Fig. S6).

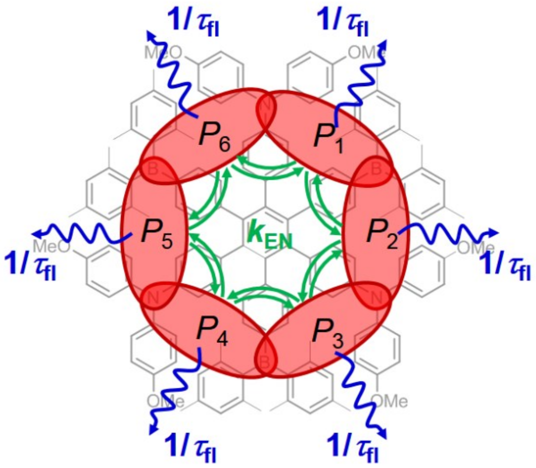

**Fig. S6** Energy transfer pathways in HAB **1**.

The following Pauli master differential equations can be set up for each CT state (equation S3).

$$\frac{\partial P_1(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_1 + k_{\mathrm{EN}}P_2 + k_{\mathrm{EN}}P_6$$

$$\frac{\partial P_2(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_2 + k_{\mathrm{EN}}P_3 + k_{\mathrm{EN}}P_1$$

$$\frac{\partial P_3(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_3 + k_{\mathrm{EN}}P_4 + k_{\mathrm{EN}}P_2$$

$$\frac{\partial P_4(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_4 + k_{\mathrm{EN}}P_5 + k_{\mathrm{EN}}P_3$$

$$\frac{\partial P_5(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_5 + k_{\mathrm{EN}}P_6 + k_{\mathrm{EN}}P_4$$

$$\frac{\partial P_6(t)}{\partial(t)} = -\left(\frac{1}{\tau_{\mathrm{fl}}} + 2k_{\mathrm{EN}}\right)P_6 + k_{\mathrm{EN}}P_1 + k_{\mathrm{EN}}P_5 \qquad \text{(S3)}$$

This system of differential equations can be solved to yield the time dependent probabilities $P_i(t)$ (equation S4)

$$P_1(t) = \frac{P_1(0)}{6} e^{\frac{-t}{\tau_{\mathrm{fl}}}}\left(1 + 2e^{-tk_{\mathrm{EN}}} + 2e^{-3tk_{\mathrm{EN}}} + e^{-4tk_{\mathrm{EN}}}\right)$$

$$P_{2,6}(t) = \frac{P_1(0)}{6} e^{\frac{-t}{\tau_{\mathrm{fl}}}}\left(1 + e^{-tk_{\mathrm{EN}}} - e^{-3tk_{\mathrm{EN}}} - e^{-4tk_{\mathrm{EN}}}\right)$$

$$P_{3,5}(t) = \frac{P_1(0)}{6} e^{\frac{-t}{\tau_{\mathrm{fl}}}}\left(1 - e^{-tk_{\mathrm{EN}}} - e^{-3tk_{\mathrm{EN}}} + e^{-4tk_{\mathrm{EN}}}\right)$$

$$P_4(t) = \frac{P_1(0)}{6} e^{\frac{-t}{\tau_{\mathrm{fl}}}}\left(1 - 2e^{-tk_{\mathrm{EN}}} + 2e^{-3tk_{\mathrm{EN}}} - e^{-4tk_{\mathrm{EN}}}\right) \qquad \text{(S4)}$$

The measured anisotropy $r(t)$ can then be obtained by summation of the anisotropy values of each CT energy transfer step $r_i(t)$ (i = 1 - 6) (with $r_{1,4} = 0.4$ for parallel orientation and $r_{2,3,5,6} = -0.05$ for 120° orientation) weighted by the relative probability of each CT state being excited $w_i$ (equation S5).

$$r(t) = \sum_{i=1}^{6} r_i w_i(t) \text{ with } w_i(t) = \frac{P_i(t)}{\sum_{k=1}^{6} P_k(t)} \qquad \text{(S5)}$$

If rotational diffusion is neglected the predicted anisotropy should then decay with equation S6.

$$r(t) = 0.1 + 0.3e^{-3tk_{\mathrm{EN}}} \qquad \text{(S6)}$$

In the case of the symmetric HAB **1** the observed anisotropy decay time constant $\tau_{a1}$ ascribed to energy transfer is a third of the actual energy transfer time constant $\tau_{EN} = 1/k_{EN}$ between neighbouring donor-acceptor pairs (equation S7).

$$\tau_{a1} = \frac{\tau_{EN}}{3} = \frac{1}{3k_{EN}} \qquad \text{(S7)}$$

In this consideration, it was assumed that energy transfer between donor-acceptor pairs being further apart is negligible in contrast to that between neighbouring chromophores. That is because the energy transfer rate constant decreases rapidly with the distance between the involved chromophores (see equation S1). Furthermore, the derived anisotropy decay can only be observed if the energy transfer ($\tau_{EN}$ ca. 3 ps in **1** and **2**) is faster than the fluorescence lifetime ($\tau_{fl}$ ca. 60 ns) and the rotational diffusion ($\tau_{a2}$ ca 350 – 600 ps), which is the case for all chromophores **1 – 3**. From equation S6, the anisotropy value of 2D delocalisation is expected to be 0.1 for **1**.

In case of the time dependent anisotropy of **2** (see Fig. S7), four cases have to be treated corresponding to the initial population of the four CT states. In the following it is assumed that the population transfer is only observed between adjacent CT states.

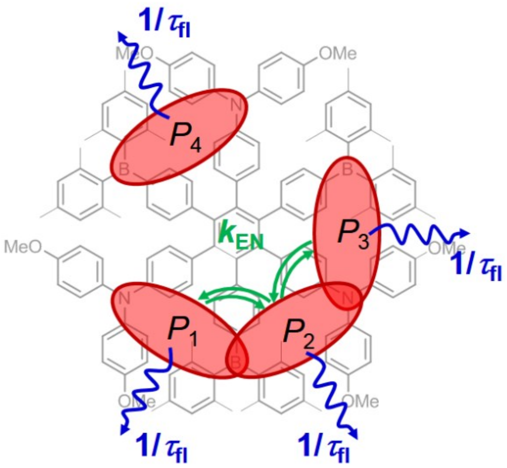

**Fig. S7** Energy transfer pathways in HAB **2.**

**(i) Population of CT state 1:**

The following Pauli master differential equations can be set up for each CT state (equation S8).

$$\frac{\partial P_1(t)}{\partial(t)} = -\left(\frac{1}{\tau_{fl}} + k_{EN}\right)P_1 + k_{EN}P_2$$

$$\frac{\partial P_2(t)}{\partial(t)} = -\left(\frac{1}{\tau_{fl}} + 2k_{EN}\right)P_2 + k_{EN}P_2 + k_{EN}P_3 + k_{EN}P_1$$

$$\frac{\partial P_3(t)}{\partial(t)} = -\left(\frac{1}{\tau_{fl}} + k_{EN}\right)P_3 + k_{EN}P_2$$

(S8)

CT state 4 is not considered as it is not populated in this case. This system of equations is again solved to derive terms for each probability $P_\mathrm{i}(t)$ (equation S9)

$$P_1(t) = \frac{P_1(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 + \mathrm{e}^{-3tk_\mathrm{EN}} + 3\mathrm{e}^{-tk_\mathrm{EN}}\right)$$

$$P_2(t) = \frac{P_1(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 - 2\mathrm{e}^{-3tk_\mathrm{EN}}\right)$$

$$P_3(t) = \frac{P_1(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 + \mathrm{e}^{-3tk_\mathrm{EN}} - 3\mathrm{e}^{-tk_\mathrm{EN}}\right)$$

(S9)

With eq S5 it follows

$$r(t) = 0.1 + 0.225\mathrm{e}^{-tk_\mathrm{EN}} + 0.075\mathrm{e}^{-3tk_\mathrm{EN}}$$

(S10)

**(ii) Population of CT state 2:**

$$\frac{\partial P_1(t)}{\partial(t)} = -\left(\frac{1}{\tau_\mathrm{fl}} + k_\mathrm{EN}\right)P_1 + k_\mathrm{EN}P_2$$

$$\frac{\partial P_2(t)}{\partial(t)} = -\left(\frac{1}{\tau_\mathrm{fl}} + 2k_\mathrm{EN}\right)P_2 + k_\mathrm{EN}P_3 + k_\mathrm{EN}P_1$$

$$\frac{\partial P_3(t)}{\partial(t)} = -\left(\frac{1}{\tau_\mathrm{fl}} + k_\mathrm{EN}\right)P_3 + k_\mathrm{EN}P_2$$

(S11)

CT state 4 is again not considered as it is not populated in this case. The solutions are:

$$P_1(t) = \frac{P_2(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 - 2\mathrm{e}^{-3tk_\mathrm{EN}}\right)$$

$$P_2(t) = \frac{P_2(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 + 4\mathrm{e}^{-3tk_\mathrm{EN}}\right)$$

$$P_3(t) = \frac{P_2(0)}{6}\mathrm{e}^{\frac{-t}{\tau_\mathrm{fl}}}\left(2 - 2\mathrm{e}^{-3tk_\mathrm{EN}}\right)$$

(S12)

With eq S5 it follows

$$r(t) = 0.1 + 0.3\mathrm{e}^{-3tk_{\mathrm{EN}}} \tag{S13}$$

**(iii) Population of CT state 3:**

The same result as in (i) is optained.

**(iv) Population of CT state 4:**

As there is no adjacent CT state, no energy transfer is possible and hence equation S14 is obtained.

$$r(t) = 0.4 \tag{S14}$$

The overall anisotropy (equation S15) is calculated by averaging the cases (i)-(iv).

$$r(t) = \frac{2\left(0.1 + 0.225\mathrm{e}^{-k_{\mathrm{EN}}t} + 0.075\mathrm{e}^{-3k_{\mathrm{EN}}t}\right) + 0.1 + 0.3\mathrm{e}^{-3k_{\mathrm{EN}}t} + 0.4}{4} = 0.175 + 0.11\mathrm{e}^{-k_{\mathrm{EN}}t} + 0.115\mathrm{e}^{-3k_{\mathrm{EN}}t} \tag{S15}$$

Thus, two time constants are expected for the anisotropy decay of **2** caused by energy transfer. However, as these time constants are on the same order of magnitude the observed single time constant may be the average of the calculated biexponential decay. Delocalisation of the CT states in **2** leads to a limiting, calculated anisotropy of 0.175.

## References

1 T. Förster, *Ann. Phys.*, 1948, **437**, 55-75.

2 S. E. Braslavsky, E. Fron, H. B. Rodriguez, E. S. Roman, G. D. Scholes, G. Schweitzer, B. Valeur and J. Wirz, *Photochem. Photobiol. Sci.*, 2008, **7**, 1444-1448.

3 M. Steeger and C. Lambert, *Chem. Eur. J.*, 2012, **18**, 11937-11948.