Supporting information

Unravelling the Conformations of di-(perylene bisimide acrylate) by combining Time-Resolved Fluorescence-Anisotropy experiments and Molecular Modelling

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I. Time rescaling in MD simulations

Since the focus of our work is comparing the photophysical properties of monomeric PerAcr with those of dimeric $(PerAcr)_2$ we choose the long-time anisotropy decay of the former as a reference time scale. From simulations on a single monomer we obtain the anisotropy decay depicted in figure SI_1. It features a clear mono-exponential tail with a time constant θ_{sim}=1140ps. Comparing with the experimental value θ_{exp}=460ps yields a scaling factor of 2.5. All times obtained from MD simulations were divided by this constant factor without any further adjustments.
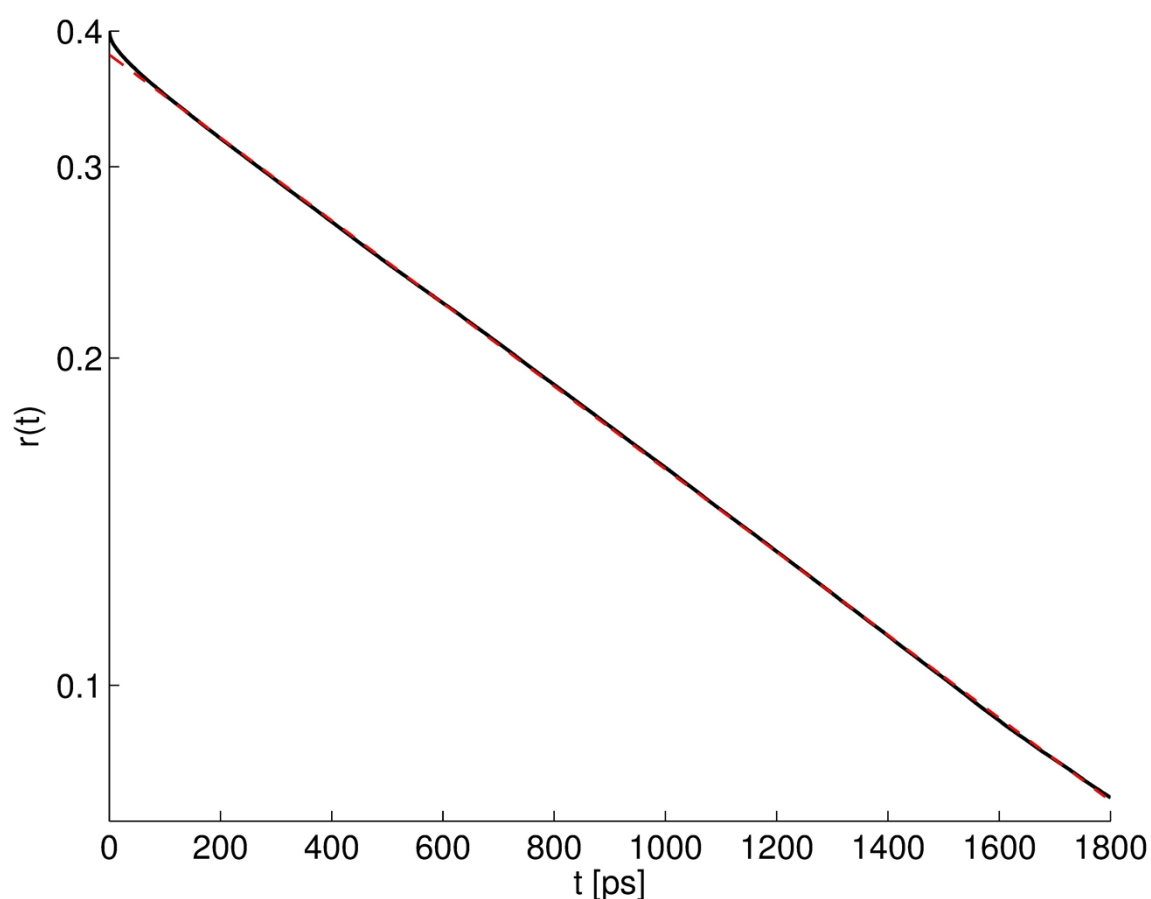
Fig.SI_1: *Anisotropy decay of a single PerAcr monomer (solid line) with a fit to the mono-exponential tail (red dashed line).*

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II. <u>Förster-distance for PBI-PBI homo-ET in (PerAcr)$_2$</u>

Förster resonance energy transfer (FRET) refers to the transfer of electronic excitation energy between a donor (D) and an acceptor (A) molecule, that are only weakly coupled. This allows to take advantage of time-dependent perturbation theory and to derive under several further approximations (restriction of the electrostatic interaction to the leading dipole-dipole term) an expression from Fermi's golden rule for the energy transfer rate from D to A. This yields that the rate depends on the D-A distance as R^{-6}, the reciprocal lifetime of the excited state of the unperturbed donor, and further scaling factors that can be lumped together in a constant termed the Förster radius R_0, which is given as:[1]

$$R_0{}^6 = \frac{9(\ln 10)\kappa^2 Q_D}{128\pi^5 N n^4} \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \qquad (1)$$

Here N denotes Avogadro's constant, n refers to the refractive index of the solvent; F_D is the (normalised) fluorescence spectrum of the donor, Q_D is the fluorescence quantum yield of the unperturbed donor, ε_A denotes the extinction coefficient of the acceptor, and κ^2 is the orientational factor of the two interacting transition-dipole moments. Under the assumption of dynamic random averaging of the donor/acceptor orientation this yields 2/3. The Förster radius corresponds to that distance between the donor and the acceptor where the probability is 50% for energy transfer from D to A during the lifetime of the donor excited state. Using the fluorescence and absorption spectra reported for PerAcr earlier,[2] we find a value of R_0 = 5 nm for the Förster radius between the two PBIs in (PerAcr)$_2$.

III.   Derivation of Eq. 9 of the main text

Let $p_a(t')$ denote the probability that the excitation is located on monomer *a* at time *t'*. With the reaction rate *k*, its rate of change is given by

$$\dot{p}_a(t') = -p_a(t')k + (1 - p_a(t'))k$$
$$= -2p_a(t')k + k$$

(2)

which can be solved by the ansatz

$$p_a(t') = \frac{1}{2} + C_0 e^{-2kt'}$$

(3)

where C_0 is a constant. Assuming that $p_a(t' = 0) = 1$ fixes $C_0 = \frac{1}{2}$.

Thus, the probability that the excitation is located on monomer *a* at time Δt, given that it was on *a* at *t'*=0, is

$$p_a(\Delta t) = \frac{1}{2} + \frac{1}{2} e^{-2k\Delta t}.$$

(4)

This is the resting probability used in the main text.

IV. <u>Calculation of the hopping constant k_0 and the orientation factor κ in Eq. 10 of the main text</u>

The reaction rate $k(t)$ is given by [3]

$$k(t) = \frac{3}{2} \frac{\kappa(t)^2}{\tau} \left(\frac{R_0}{R} \right)^6.$$ (5)

The fluorescence life time τ for the ISO state has been determined to be 3.7ns [2] and the Förster radius R_0 =5nm which leads to k_0=6.33 nm^6/ps.

The orientation factor $\kappa(t)$ is calculated from [3]

$$\kappa(t) = \left(\cos\alpha(t) - 3\cos\theta_D(t)\cos\theta_A(t) \right)^2$$ (6)

where α is the angle between the two dipole vectors as in Fig. 3 of the main text and θ_D (θ_A) is the angle between the acceptor (donor) dipole with the vector connecting the centres-of-mass of the two monomers.

References

1   S. E. Braslavsky et al., *Photochem. Photobiol. Sci.* 7, 1444-1448 (2008).

2   F. Spreitler, M. Sommer, M. Thelakkat, J. Köhler, *Phys. Chem. Chem. Phys.* 14, 7971-7980 (2012).

3   J. R. Lakowicz, Principles of Fluorescence Spectroscopy (Springer, ed. 3, 2006).