

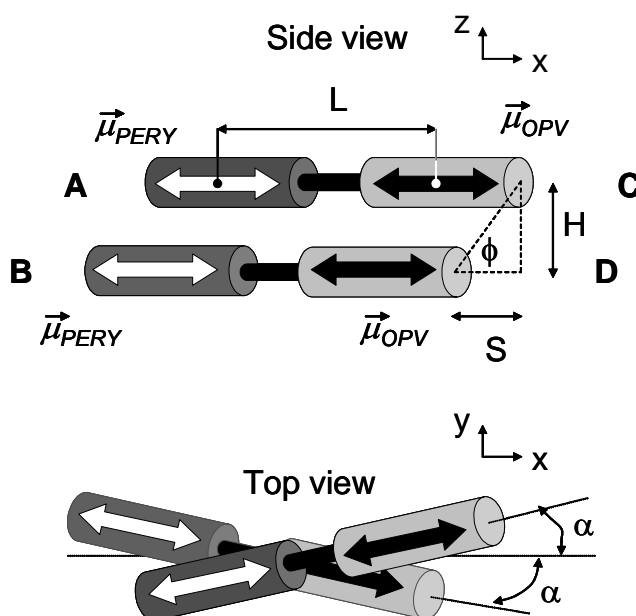
Supporting Information

The Importance of Nanoscopic Ordering on the Kinetics of Photoinduced Charge Transfer in Aggregated π -Conjugated Hydrogen-Bonded Donor-Acceptor Systems

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Calculations on the Excited State Energies of Proposed Aggregated Structures of Dyad Systems

To simulate the absorption and circular dichroism data we use a coupled oscillator model. Here the interchromophoric interactions are approximated by the dipole-dipole interactions between the transition dipole moments of the chromophores. To illustrate the procedure we focus on the calculation of the excited state energies for the aggregates of complex **1**. The spatial arrangement of the transition dipoles for the chromophoric units labeled A, B, C and D can be represented the stacked dyads are as follows:



The transition dipole moments for the OPV and PERY chromophores are known to be oriented along the long axis of the chromophores and here we take the transition dipole moments of the hydrogen bonded PERY-OPV pair to be co-linear. The distance between the centers of the transition dipole moments is taken to be $L = 20 \text{ \AA}$. The height is set $H = 5 \text{ \AA}$. This distance reflects the π - π stacking distance and a lateral translation of the hydrogen-bonded pairs with respect to each other. Note that the bulky phenoxy substituents on the perylene bisimide chromophore prevent tight packing of the PERY moieties.

Chirality is introduced into the model by rotating the OPV-PERY hydrogen bonded dimers in the x - y plane. The angle α between the transition dipole moments μ and the x axis is to ± 5 degrees.

After determination of the transition dipole moments from absorption data and taking positions of the dipoles from the structure model, the interchromophoric couplings (V) can be calculated using:

$$V_{AB} = \frac{1}{4\pi\epsilon_0} \frac{\vec{\mu}_{0,1}^A \cdot \vec{\mu}_{0,1}^B |\vec{R}_A - \vec{R}_B|^2 - 3(\vec{\mu}_{0,1}^A \cdot (\vec{R}_A - \vec{R}_B))(\vec{\mu}_{0,1}^B \cdot (\vec{R}_A - \vec{R}_B))}{|\vec{R}_A - \vec{R}_B|^5} \quad (\text{S1})$$

The couplings from the off diagonal elements in a matrix representation of the Hamiltonian describing the lower excited states of the aggregate. The basis function used in this representation are the states in which the excitations are fully localized on the individual chromophores. The diagonal elements of the Hamilton matrix are the excitation energies of the lowest excited singlet states of the PERY and OPV chromophores.

In first approximation, we may neglect the higher vibronic levels of the OPV and PERY S_1 states. This simplifies the explanation of the calculations as there are now only four basis states. The Hamiltonian described the system of the 4 coupled chromophores now reads

$$H = \begin{bmatrix} E_A & V_{AB} & V_{AC} & V_{AD} \\ V_{AB} & E_B & V_{BC} & V_{BD} \\ V_{AC} & V_{BC} & E_C & V_{CD} \\ V_{AD} & V_{BD} & V_{CD} & E_D \end{bmatrix} \quad (\text{S2})$$

Solving the eigenvalue problem

$$H\psi = E\psi \quad (\text{S3})$$

yields eigenvalues E_i which are the energies of the collective excited states of the complex of chromophores ($I = 1, \dots, N$ in the case of N interacting chromophoric groups). The corresponding eigenvectors ψ_i describe the contribution of each chromophore to the particular excited state

$$\psi_i = \begin{bmatrix} c_{i,A} \\ c_{i,B} \\ c_{i,C} \\ c_{i,D} \end{bmatrix} \quad (\text{S4})$$

where the real coefficient $c_{i,A}$ describes the weight of the S_1 excited state of chromophore A in the collective excited state i of the complex. In the limiting case of $(c_{i,A})^2 = 1$ the excited state i is completely localized on chromophore A, which is only possible if the excited state interactions of chromophore A with the others in the complex are zero.

Transition dipole moment $\mu_{0,i}$ for transition from the ground state to collective state i can be expressed as

$$\bar{\mu}_{0,i} = c_{i,A}\bar{\mu}_{0,1}^A + c_{i,B}\bar{\mu}_{0,1}^B + \dots = \sum_{Q=1}^N c_{i,Q}\bar{\mu}_{0,1}^Q \quad (\text{S5})$$

In the solution the fluctuating solvent environment and the conformational flexibility of the molecules give rise to inhomogeneous broadening resulting in a rather broad bandwidth for the optical absorption. To account for these effects we introduce a band shape function $g(\tilde{\nu})$. For a single transition j with a center frequency $\tilde{\nu}_{0,j}$ and width σ_j

$$g_j(\tilde{\nu}) = \frac{\tilde{\nu}}{\sqrt{2\pi}\sigma_j} \exp\left[-\frac{(\tilde{\nu} - \tilde{\nu}_{0,j})^2}{2\sigma_j^2}\right] \quad (\text{S6})$$

The line shape is defined in such a way that the decadic molar extinction coefficient ε for the inhomogeneously broadened absorption band associated with the excited state j can be described as

$$\varepsilon_j(\tilde{\nu}) = \frac{F_{loc} |\vec{\mu}_j|^2}{C} g(\tilde{\nu}) \quad (\text{S7})$$

Where

$$C = \frac{3 \ln(10) c \varepsilon_0 \hbar}{10 \pi N_A} = 1.022 \times 10^{-61} \text{ Coulomb}^2 \quad (\text{S8})$$

In order to calculate the chiroptical properties associated with the collective excited states we define the magnetic transition dipole moment $\vec{m}_{0,i}$ for transition from the ground state to collective state i : (See e.g. Circular Dichroism Spectroscopy N. Harada, K. Nakanishi Oxford University Press 1984):

$$\vec{m}_{0,i} = i \alpha c_{i,A} (\vec{R}_A \times \vec{\mu}_{0,1}^A) + i \alpha c_{i,B} (\vec{R}_B \times \vec{\mu}_{0,1}^B) + \dots = i \sum_{Q=1}^N \alpha c_{i,Q} (\vec{R}_Q \times \vec{\mu}_{0,1}^Q) \quad (\text{S9})$$

Here the magnetic dipole moment is a purely imaginary quantity. This reflects the fact that in the optical cycle $\vec{m}_{0,i}$ lags 90° behind in phase compared to the electrical transition

dipole moment $\vec{\mu}_{0,i}$. The factor α is related to the optical frequency of the transition in the isolated chromophore: $\alpha = E_{0,1}/\hbar$. Here, $E_{0,1}$ is the energy of the relevant excited state relative to the ground state of the isolated chromophore. With the help of the magnetic transition dipole moments we can calculate the magnitude of the circular dichroism ($\Delta A = A_L - A_R$ with A_L the absorbance of *left* circular polarized light) for the absorptive transition from the ground state to state i

$$\Delta A_{0,i} \propto \text{Im}(\vec{\mu}_{0,i} \cdot \vec{m}_{0,i}) = \left(\sum_{Q=1}^N c_{i,Q} \vec{\mu}_{0,1}^Q \right) \cdot \left(\sum_{P=1}^N \alpha c_{i,P} (\vec{R}_P \times \vec{\mu}_{0,1}^P) \right) \quad (\text{S10})$$

Again we need to introduce the band shape function g . The CD can now be expressed as in terms of the circular differential molar decadic extinction coefficient $\Delta \varepsilon (= \varepsilon_L - \varepsilon_R)$

$$\Delta \varepsilon_j = \frac{F_{loc} \text{Im}(\vec{\mu}_j \cdot \vec{m}_j)}{R} g(\tilde{\nu}) \quad (\text{S11})$$

where $R = C(c/4)$ with C defined above and c the speed of light .

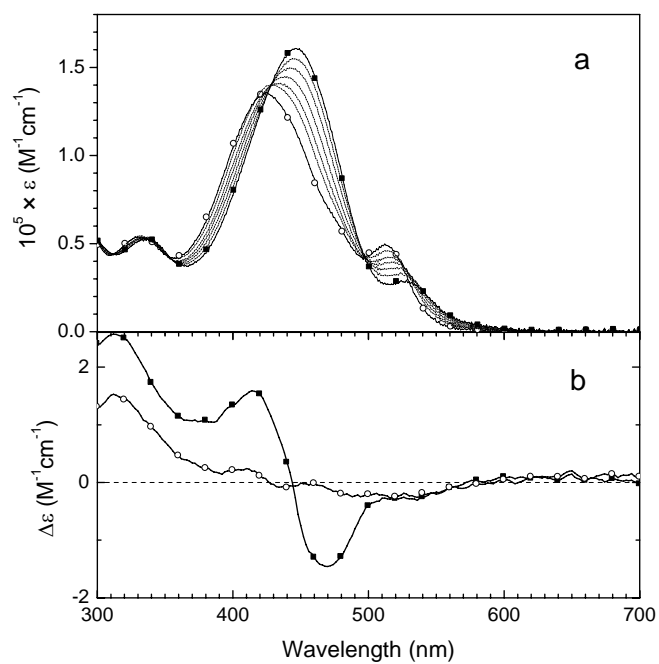


Figure S1. (a) Absorption (1.3×10^{-6} M) and circular dichroism (5×10^{-5} M) spectra of Cl-OPO in MCH at temperatures ranging from 20 °C (solid squares) to 90 °C (open circles).

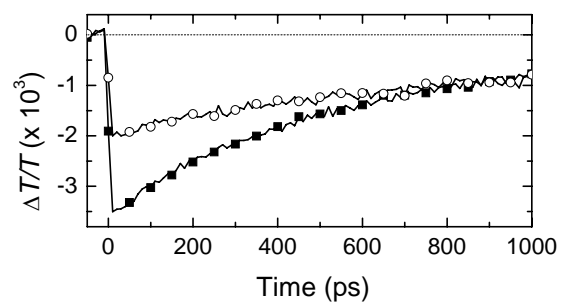


Figure S2. Transient photoinduced absorption traces in MCH for Ph-OPO (5×10^{-5} M). Solid squares: $T = 20^\circ\text{C}$; open circles: $T = 80^\circ\text{C}$. The excitation wavelength is 455 nm and the PIA signal was detected at 1450 nm.