# Supplementary information:

## A) Derivation of Equation 2 for the hopping rates

Within the weak-coupling limit, the energy transfer rate can be expressed according to the Fermi Golden rule (Eq. 1 in the paper):

$$k_{DA} = \frac{2\pi}{\hbar} \left|V_{DA}\right|^2 \left(\mathrm{FCWD}\right) \qquad \text{(A1)}$$

Let us expand the wavefunction associated with the initial state as the antisymmetrized product of donor excited state and acceptor ground state wavefunctions:

$$\left|i\right\rangle = \left|\Psi_{D*}^{m}\Psi_{A}^{n}\right\rangle = \left|\psi_{D*}\chi_{D*}^{m}\psi_{A}\chi_{A}^{n}\right\rangle \qquad \text{(A2)}$$

where $\chi_{D*}^{m}$ represents the $m^{th}$ vibrational state (assuming that only one vibrational mode couples to the electronic transition) of the donor electronic excited state $\psi_{D*}$ and $\chi_{A}^{n}$ is the $n^{th}$ vibrational state of the acceptor in the ground electronic state $\psi_{A}$ . The final state reached by the system after excitation energy transfer from the donor to the acceptor reads similarly:

$$\left| f \right\rangle = \left|\Psi_{D}^{s}\Psi_{A*}^{t}\right\rangle = \left|\psi_{D}\chi_{D}^{s}\psi_{A*}\chi_{A*}^{t}\right\rangle \qquad \text{(A3)}$$

Injecting Eqs. (A2) and (A3) into Eq. (A1) leads to:

$$k_{DA} = \frac{2\pi}{\hbar}\sum_{\{m,n\}}\sum_{\{s,t\}} f\left(E_{D*}^{m}\right) f\left(E_{A}^{n}\right)\left|\left\langle\Psi_{D*}^{m}\Psi_{A}^{n}\left|V_{DA}\right|\Psi_{D}^{s}\Psi_{A*}^{t}\right\rangle\right|^2 \delta\left(E_{D*}^{m}+E_{A}^{n}-E_{D}^{s}-E_{A*}^{t}\right) \qquad \text{(A4)}$$

where $V_{DA}$ is the donor-acceptor interaction, which can be viewed as a measure of the electronic interaction between excitations localized over the donor and acceptor moieties. The double sum runs over vibrational quantum states (labeled $m$ and $n$ ) associated to the initial electronic state with weights $f\left(E_{D*}^{m}\right)$ and $f\left(E_{A}^{n}\right)$ (these functions describe the population of the vibrational states associated to the donor excited state and acceptor ground state); the sum over all possible vibrational states associated to the final electronic state times the delta function allows a selection of the final nuclear states obeying the energy conservation law.

In the Condon approximation, which assumes that the electronic part of the coupling factor does not depend on the nuclear arrangement, the matrix element of the Coulomb operator reduces to an electronic coupling weighted by Franck-Condon overlaps between initial and final vibrational states:

$$\left\langle \Psi^{m}_{D*}\Psi^{n}_{A} \middle| V^{el-el}_{DA} \middle| \Psi^{s}_{D}\Psi^{t}_{A*} \right\rangle = \left\langle \psi_{D*}\psi_{A} \middle| V^{el-el}_{DA} \middle| \psi_{D}\psi_{A*} \right\rangle \left\langle \chi^{m}_{D*} \middle| \chi^{s}_{D} \right\rangle \left\langle \chi^{n}_{A} \middle| \chi^{t}_{A*} \right\rangle \tag{A5}$$

and the energy hopping rate becomes:

$$k_{DA} = \frac{2\pi}{\hbar} \sum_{\{m,n\}} \sum_{\{s,t\}} f\left(E^{m}_{D*}\right) f\left(E^{n}_{A}\right) \left| \left\langle \psi_{D*}\psi_{A} \middle| V^{el-el}_{DA} \middle| \psi_{D}\psi_{A*} \right\rangle \right|^{2} \left\langle \chi^{m}_{D*} \middle| \chi^{s}_{D} \right\rangle^{2} \left\langle \chi^{n}_{A} \middle| \chi^{t}_{A*} \right\rangle^{2} \delta\left(E^{m}_{D*} - E^{s}_{D} + E^{n}_{A} - E^{t}_{A*}\right) \tag{A6}$$

Since the process of resonant excitation energy transfer can be viewed as the simultaneous light emission at the donor and absorption at the acceptor, the transfer rate is generally expressed in terms of donor emission and acceptor absorption spectra. This can be achieved, providing the sets of vibrational coordinates associated to the interacting chromophores are independent, by recasting the delta function ensuring the energy conservation for energy transfer process in two parts :

$$\delta\left(E^{m}_{D*} - E^{s}_{D} + E^{n}_{A} - E^{t}_{A*}\right) = \int_{-\infty}^{+\infty} dE \; \delta\left(E^{m}_{D*} - E^{s}_{D} - E\right) \; \delta\left(E^{n}_{A} - E^{t}_{A*} + E\right) \tag{A7}$$

Combining Eqs. (A6) and (A7), leads to:

$$\begin{aligned} k_{DA} \; = \; & \frac{2\pi}{\hbar} \sum_{\{m,n\}} \sum_{\{s,t\}} f\left(E^{m}_{D*}\right) f\left(E^{n}_{A}\right) \left| \left\langle \psi_{D*}\psi_{A} \middle| V^{el-el}_{DA} \middle| \psi_{D}\psi_{A*} \right\rangle \right|^{2} \left\langle \chi^{m}_{D*} \middle| \chi^{s}_{D} \right\rangle^{2} \left\langle \chi^{n}_{A} \middle| \chi^{t}_{A*} \right\rangle^{2} \times \\ & \int_{-\infty}^{+\infty} dE \; \delta\left(E^{m}_{D*} - E^{s}_{D} - E\right) \delta\left(E^{n}_{A} - E^{t}_{A*} + E\right) \end{aligned} \tag{A8}$$

If we now introduce the donor emission and acceptor absorption lineshapes $D\left(E\right))$ and $A\left(E\right)$, respectively:

$$\begin{aligned} D\left(E\right) \; &= \; \sum_{\{m,s\}} f\left(E^{m}_{D*}\right) \; \left\langle \chi^{m}_{D*} \middle| \chi^{s}_{D} \right\rangle^{2} \; \delta\left(E^{m}_{D*} - E^{s}_{D} - E\right) \\ A\left(E\right) \; &= \; \sum_{\{n,t\}} f\left(E^{n}_{A}\right) \; \left\langle \chi^{n}_{A} \middle| \chi^{t}_{A*} \right\rangle^{2} \; \delta\left(E^{n}_{A} - E^{t}_{A*} - E\right) \end{aligned} \tag{A9}$$

The energy transfer rate finally writes:

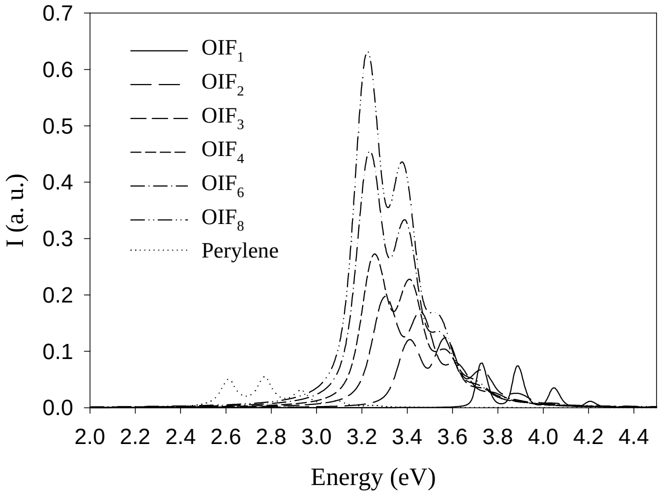
$$k_{DA} \; = \; 1.18 \; \left|V_{DA}\right|^{2} \int_{0}^{\infty} dE \; F_{D}\left(E\right) A_{A}\left(E\right) \; = 1.18 \; \left|V_{DA}\right|^{2} J_{DA} \tag{A10}$$

where $F_{D}\left(E\right)$ and $A_{A}\left(E\right)$ denote the donor fluorescence and acceptor absorption spectrum, respectively, normalised on a cm$^{-1}$ scale;  the electronic matrix element is expressed in cm$^{-1}$ and the transfer rate in ps$^{-1}$.

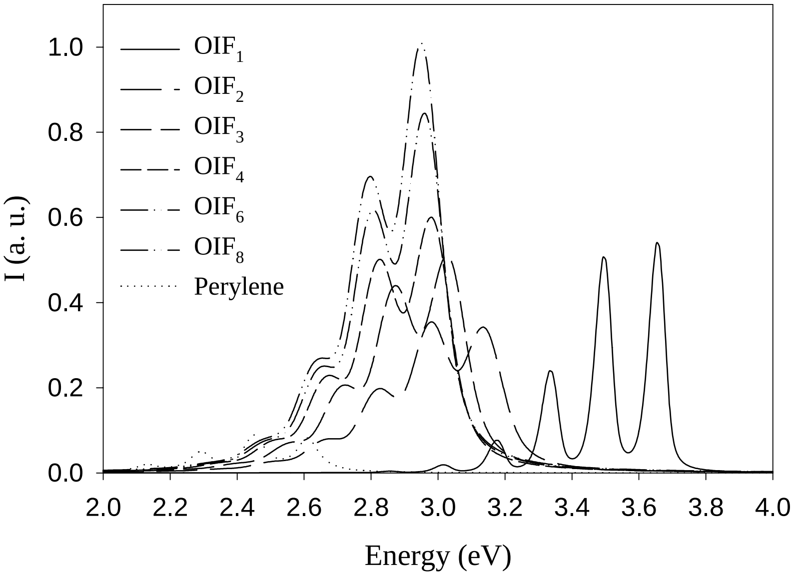
## B) Optical absorption and emission spectra

Optical absorption and emission spectra computed for indenofluorene segments and perylene derivative on the basis of excitation energies, relaxation energies and transition dipole moments obtained at the INDO/SCI level within the Franck-Condon approximation. Coupling of electronic excitation to high–frequency modes (accounting for C-C stretching vibrations) and low-frequency modes (ring-torsional motions) has been considered.

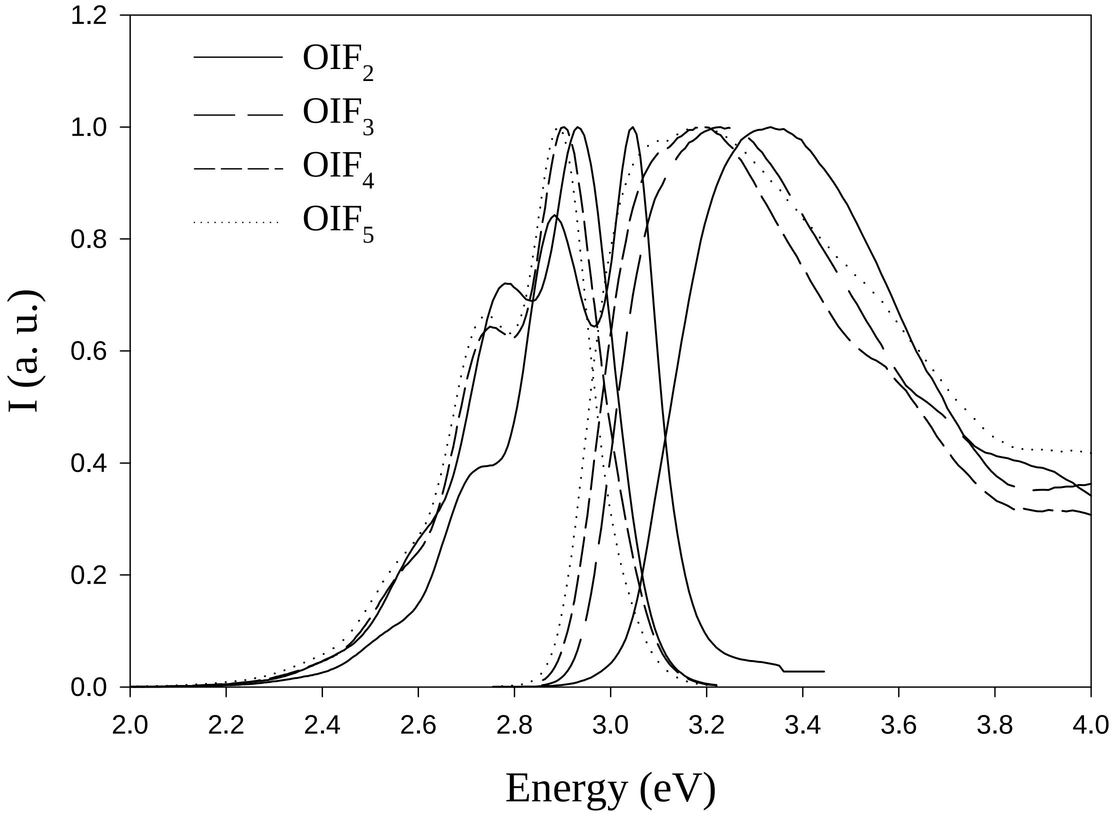
*Absorption spectra:*



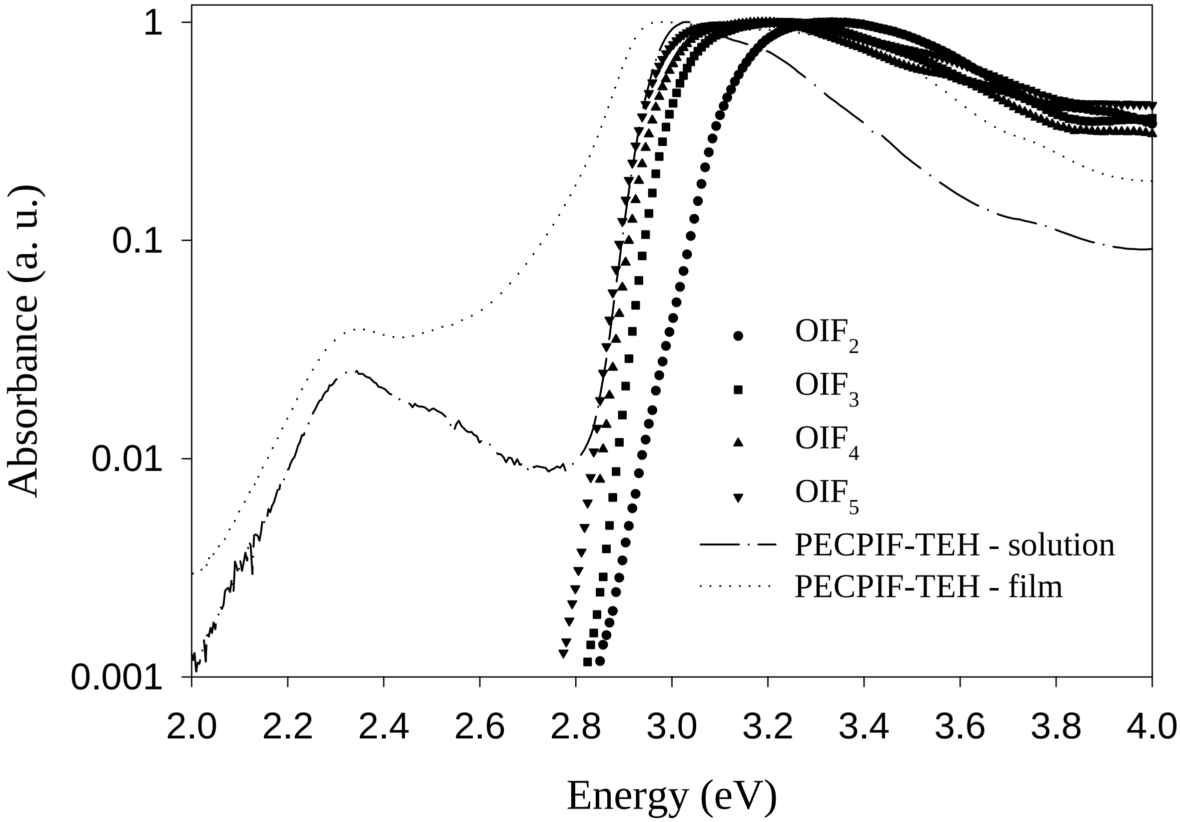
*Emission spectra:*



Measured absorption and emission spectra for oligo(indenofluorene)s in p-xylene solution at room temperature:

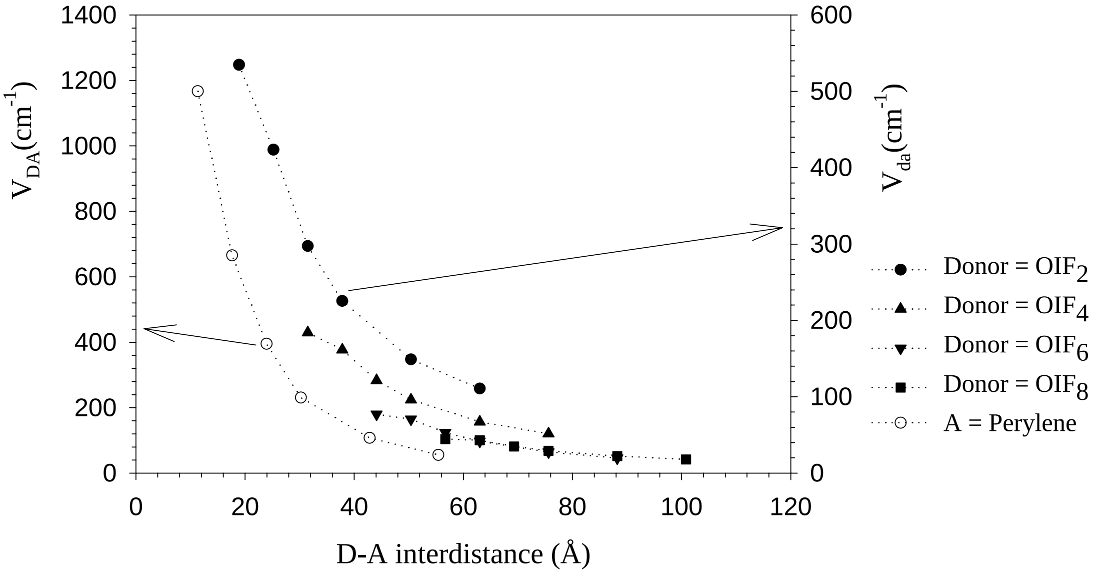


Experimental absorption spectra of PEC-PIFTEH in 1.7 g/L solution in *p*-xylene and in a thin film; absorption spectra of oligo(indenofluorene)s experimentally obtained in *p*-xylene solution are plotted for comparison.

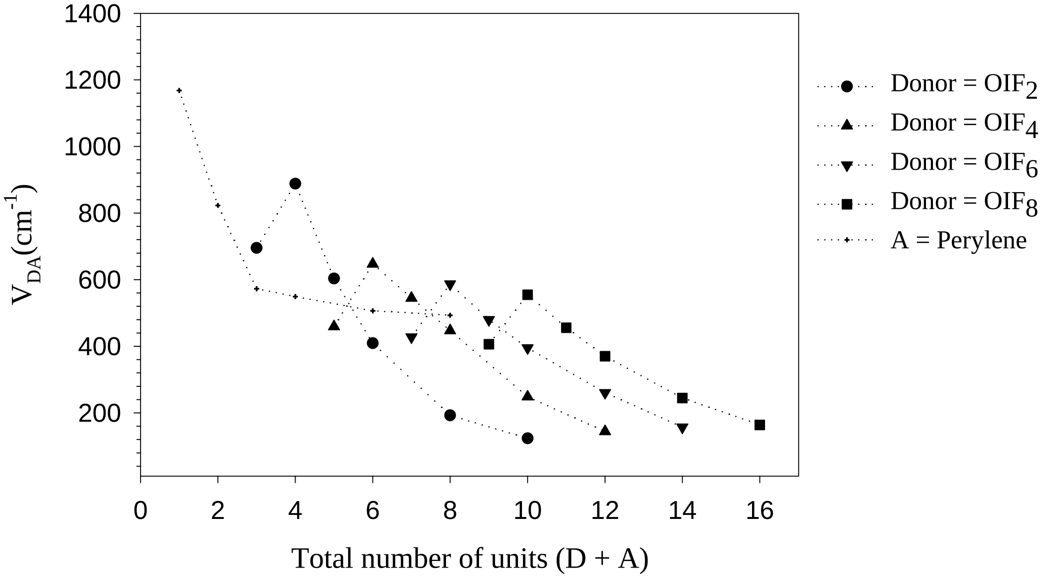


## C. Electronic couplings

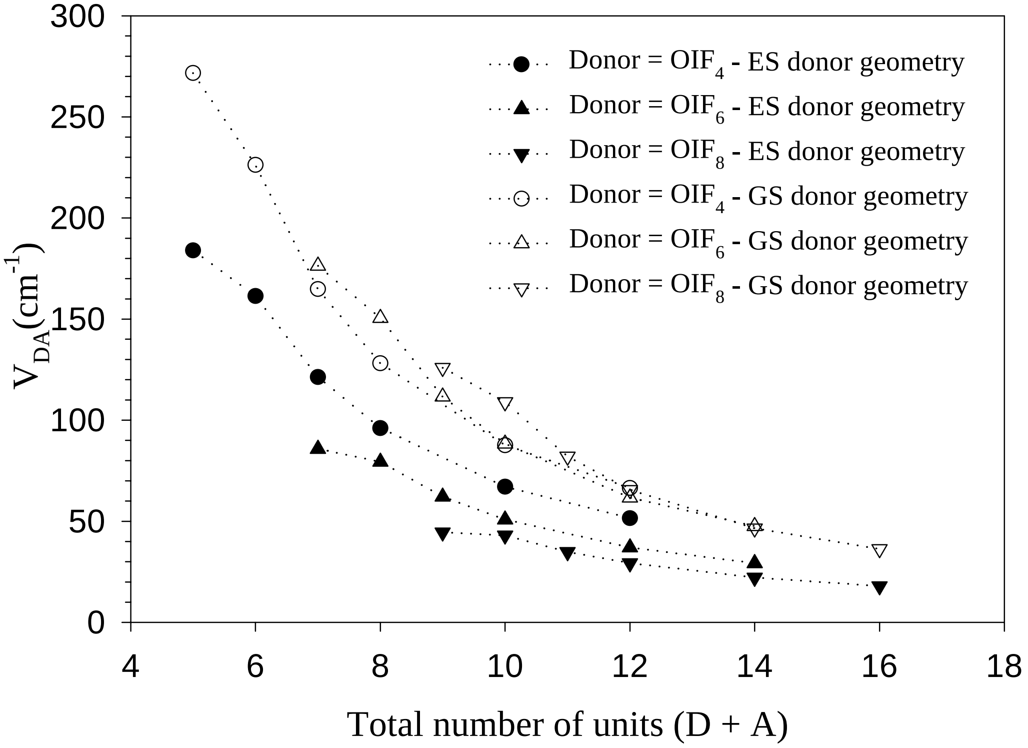
Electronic matrix elements, $V_{DA}$, for exciton hopping along the polyindenofluorene backbone as obtained within the Distributed Monopole Model for covalently linked $\mathrm{OIF_n/OIF_m}$ couples with varying donor and acceptor sizes (filled symbols, right-hand y axis). Geometric relaxation has been accounted for. Electronic coupling factors computed for intrachain transfer from indenofluorene oligomers of increasing size towards an attached perylene group are displayed as open symbols (left-hand y axis).



Electronic matrix elements, $V_{DA}$, as obtained within the Distributed Monopole Model for interchain energy transfer in $OIF_n/OIF_m$ and $OIF_n$/PER cofacial dimers. Geometric relaxation has been accounted for.

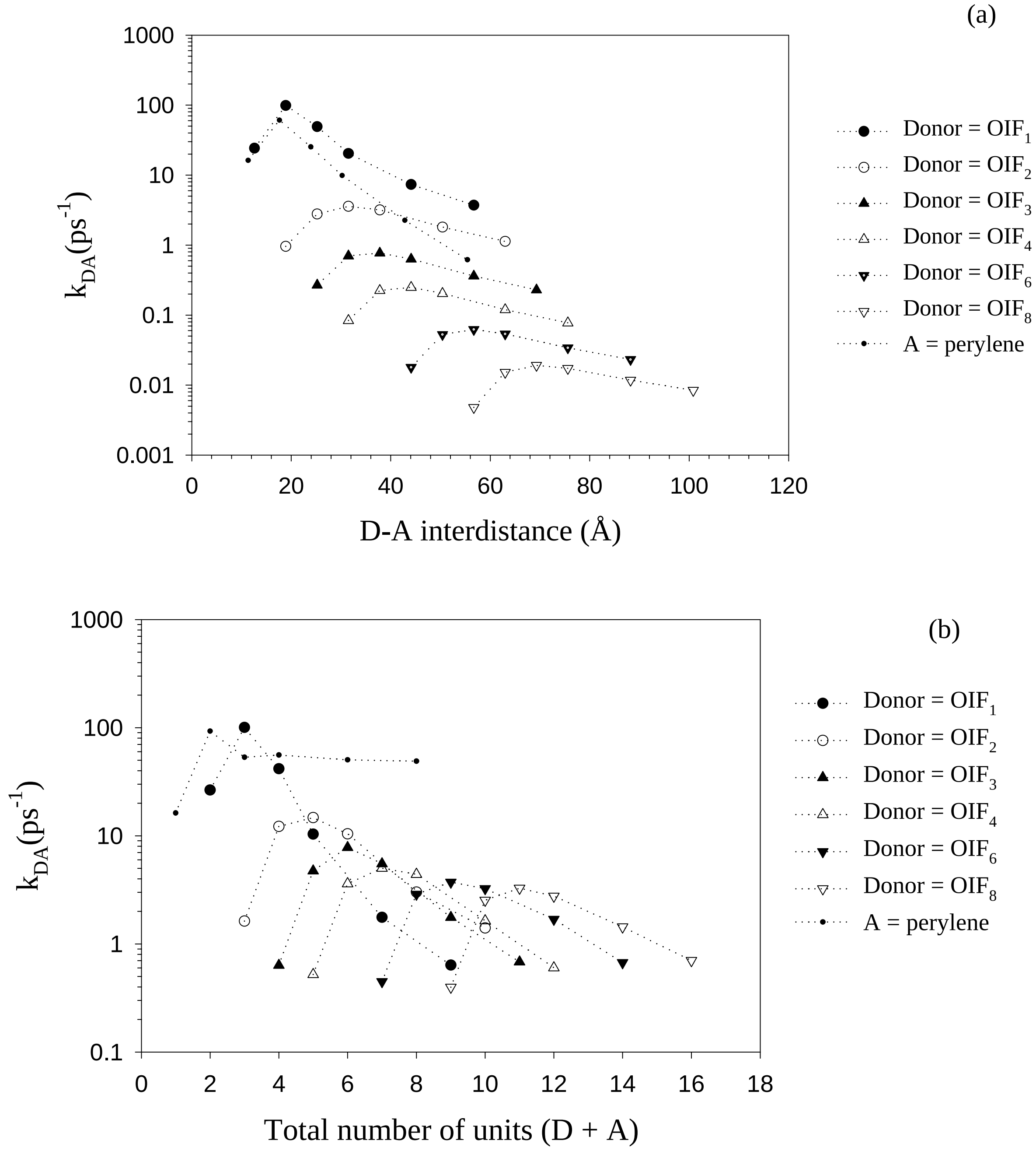


Intramolecular electronic matrix elements, as computed within the distributed monopole model for several $OIF_n/OIF_m$ couples, on the basis of excited-state (filled symbols) and ground-state (open symbols) donor geometries.

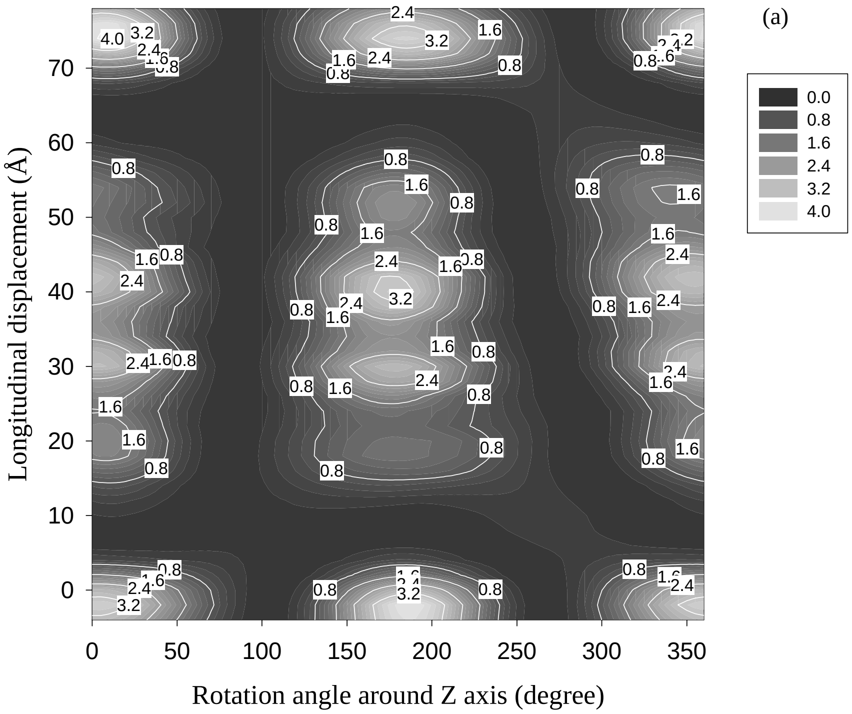


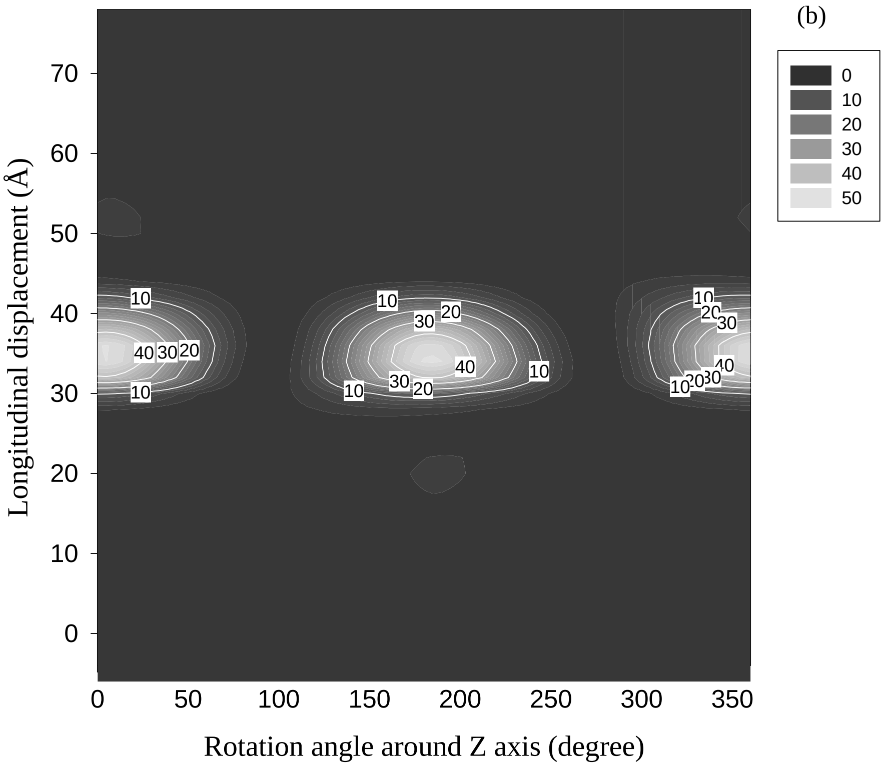
## D) Hopping rates

Intramolecular (a) and intermolecular (b) energy transfer rates computed for different $OIF_n$/$OIF_m$ and $OIF_n$/PEC donor-acceptor pairs differing by the size of the indenofluorene segments.



Interchain transfer rates, $k_{DA}$ (in ps$^{-1}$), as a function of longitudinal (along $X$) and rotational (around $Z$) motions in a OIF$_6$–PEC donor-acceptor pair, as calculated on the basis of the transition densities for the donor ground-state geometry (a); and on the basis of the relaxed excited-state geometry (b). A longitudinal displacement of 35 Å corresponds to a perfect superposition of the donor and acceptor centers.




(b)
Longitudinal displacement (Å)
Rotation angle around Z axis (degree)
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300
350
0
10
20
30
40
50
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10
20
30

## E) Time- resolved PL spectra

Time dependent photoluminescence spectrum computed for a polymer chain of 70 indenofluorene units end-capped at both ends with a perylene derivative.