Electronic Supplementary Information: The detailed balance limit of photochemical energy conversion

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Parameters of the evolutionary algorithms

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Table SM1: Parameters of the evolutionary algorithms

EA parameters	(μ,λ)-CMA-ES	NSGAII
no. of individuals λ	8	10000
reproducing ind. μ	4	10000
no. of generations	$\Delta\Phi_{RU} < 1 \cdot 10^{-12}$	500
mutation probability	-	0.01
crossover probability	-	0.9
no. of restarts	4	-
increase of pop. size	3	-
time [s]	10^{-3}	1

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Second order electronic coupling V_{i0}

The electronic coupling of charge recombination V_{io} is
20 calculated according to an extended SE model: electron- hole recombination occurs by concerted tunneling through all barriers, which lie between chromophore i and the initial electron donor 0. The electronic coupling matrix element V_{i0} is evaluated up to second order perturbation theory.

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$$V_{i0} = V^{(0)} + V^{(1)} + V^{(2)} \qquad (A1)$$

The extent and energetic position of inbetween lying chromophores is taken into account (see Fig. SM 1).
30 The zeroth-order coupling $V^{(0)}$ between electron carrier i and initial donor 0 is evaluated according to

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$$V_{i0}^{(0)} = \prod_{j=0}^{i-1} V_{ij} \cdot \exp((i-2)\beta_W W)$$

$$\text{with} \quad \beta_W = \beta \cdot \sqrt{\frac{\Delta G_{ij}}{E_B + \Delta G_{ij}}}, \qquad (A2)$$

40 where E_B is the relative *vacuo* level and β_W is an energy

corrected exponential decay parameter of the wave function within the extent of the charge carrier. The additional first order coupling terms $V^{(1)}$ can be identified as super-exchange (SE) coupling

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$$V_{i0}^{(1)} = V_{i0}^{(SE)} = \sum_{j\neq 0, j\neq i} V_{j0}^{(0)} \frac{V_{ij}}{\Delta G_{ij}} . \qquad (A3)$$

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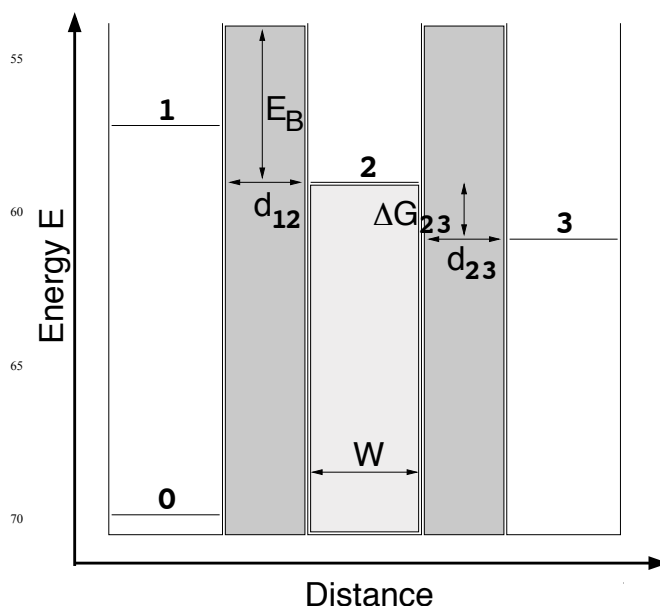Fig. SM 1: extend and energetic position of three chromophores, contributing to the electronic coupling element V_{i0} for charge recombination

80 If charge recombination occurs over large distances ($d_{i0} >$ 5-10 Å) the overlap between the tail of the wave-functions is almost negligible. High lying electronic states can mix and SE-coupling contributes significantly to the overall coupling strength. In the model of a linear chain of n chromophores
85 (n>3) (see Fig. 2) contributions to the electronic coupling V_{i0} arise from more than a single chromophore. These contributions are considered as second order terms $V^{(2)}$ and

are calculated according to

$$V_{i0}^{(2)} = V_{i0}^{(ExSE)} = \sum_{j\neq 0, j\neq i} V_{j0}^{(0)} \left(\sum_{j\neq k, i\neq k} \frac{V_{ik} \cdot V_{kj}}{\Delta G_{ij} \cdot \Delta G_{ik}} - \frac{V_{ij} \cdot V_0}{\Delta G_{ij}^2} \right)$$

$$\text{(A4)}$$

This contribution improves the first order treatment of the coupling matrix element for the loss channels. We designate the second order contribution as extended super-exchange coupling V(ExSE).

Notes and references

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