Electronic Supplementary Information (ESI) for: An Effective Potential for Frenkel Excitons

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1 Diagonal Hamiltonian Matrix Elements

In the EOP-TI/CIS model, the E_1 and E_2 matrix elements are approximated by neglecting the influence of environment, quantified by $\Delta E^{X}_{e\to g}(Y)$, because we found it to be a relatively small contribution, even at very close inter-chromophore distances. The E_3 and E_4 matrix elements require evaluation of the Coulombic interaction between HOMO and LUMO orbitals of isolated monomers. In the EOP-TI/CIS model, this contribution is represented by the cumulative atomic multipole moments (CAMM) expansion of the HOMO and LUMO electron densities, including all the terms having up to R^{-5} distance dependence. In Table S1 all these diagonal matrix elements are shown for ethylene and 7AC dimers at selected geometries.

Table S1 Comparison of the diagonal Hamiltonian matrix elements for the studied TI/CIS models. The results (given in eV) were obtained for the ethylene and 7AC dimers at three selected geometries at the CIS/6-31G(d) level. Due to symmetry of the studied model systems, $E_1 = E_2$ and $E_3 = E_4$. References to equations in the main text, that were used to compute the matrix elements, are also given.

		(Ethylene)$_2$			(7AC)$_2$		
		$R_{\mathrm{AB}} = 3.0$	4.169	6.0	2.6	3.6	4.6
E_1	Eq. (4a)	8.660	8.575	8.582	5.205	5.082	5.083
$E^{A}_{e\to g}$	Eq. (14a)	8.584	8.584	8.584	5.074	5.074	5.074
$\Delta E^{A}_{e\to g}(B)$	Eq. (5)	0.076	-0.009	-0.002	0.131	0.008	0.009
E_3	Eq. (7a)	10.024	11.426	12.520	6.093	6.822	7.337
E_3^{EOP}	Eq. (23a)	10.010	11.427	12.520	6.083	6.822	7.337

Table S2 Comparison of the diagonal Hamiltonian matrix elements for the studied TI/CIS models. The results (given in eV) were obtained for the two chlorophylls of the special pair of the PS-I system at the CIS/6-31G(d) level. References to equations in the main text, that were used to compute the matrix elements, are also given.

		(PS-I)$_2$
E_1	Eq. (4a)	2.459
$E^{A}_{e\to g}$	Eq. (14a)	2.433
$\Delta E^{A}_{e\to g}(B)$	Eq. (5)	0.026
E_2	Eq. (4b)	2.575
$E^{B}_{e\to g}$	Eq. (14b)	2.537
$\Delta E^{B}_{e\to g}(A)$	Eq. (5)	0.038
E_3	Eq. (7a)	3.878
E_3^{EOP}	Eq. (23a)	3.878
E_4	Eq. (7b)	3.839
E_4^{EOP}	Eq. (23b)	3.839

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2 Timings for Computations of TI/CIS EET Couplings

Table S3 Comparison of the CPU times of V^{TI} coupling computation for the studied TI/CIS models. The results (given in s) were obtained for the ethylene and 7AC dimers at their equilibrium geometries at the CIS/6-31G(d) level. The reported timings, calculated as an average of 10 runs (except PS-I), do not include the time to solve SCF or CIS problems for the monomers but in the case of $V^{\mathrm{TI}}(\mathscr{F})$ the time to solve the SCF problem for the whole complex is obviously included. All calculations were performed on a single core of 1.2 GHz AMD EPYC™ 7301 16-Core processor with the same SCF and CIS convergence settings and thresholds. Only in the case of PS-I calculations we used the more efficient 3.1 GHz Intel Xeon™ E5-2687W CPU.

	$(\mathrm{Ethylene})_2$	$(\mathrm{7AC})_2$	PS-I
$V^{\mathrm{TI}}(\mathscr{F})$	9.20	$3.70 \cdot 10^{3}$	-
$V^{\mathrm{TI}}(\mathscr{F}_0^{\mathrm{DFI}})$	3.22	$1.55 \cdot 10^{3}$	-
$V^{\mathrm{TI}}(\mathscr{F}_0)$	3.18	$1.53 \cdot 10^{3}$	$4.92 \cdot 10^{5}$
$V^{\mathrm{TI}}(\mathscr{F}_0^{\mathrm{EOP}})$	$5.82 \cdot 10^{-3}$	$7.89 \cdot 10^{-2}$	5.69
$V_{\mathrm{Coul}}^{\mathrm{TrCAMM}}$	$2.80 \cdot 10^{-5}$	$6.74 \cdot 10^{-5}$	$3.10 \cdot 10^{-2}$

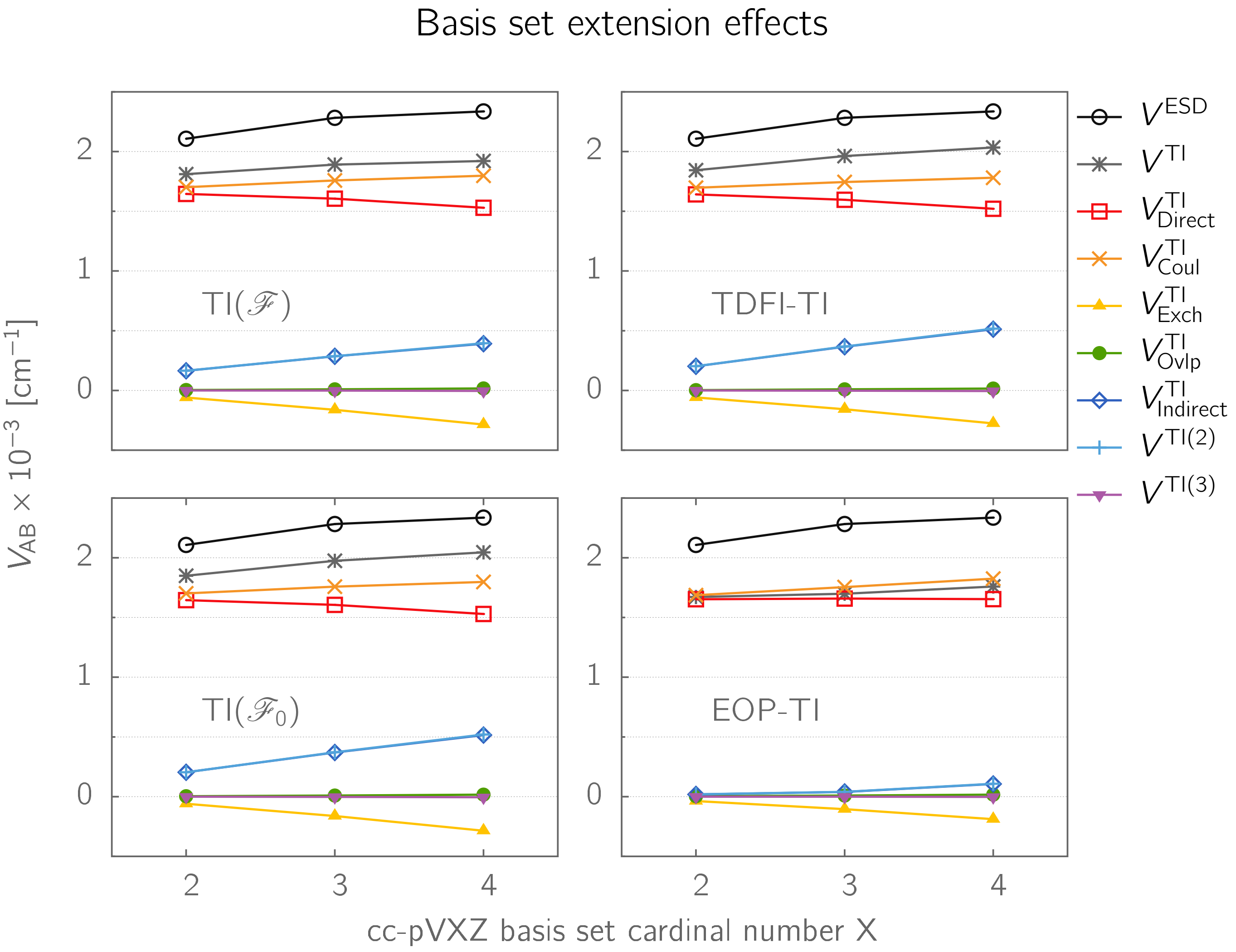
3 Basis Set Extension Effects

All the results in the main article were obtained assuming 6-31G(d) basis set and in the case of EOP-TI/CIS calculations aug-cc-pVDZ-JKFIT auxiliary EOP basis set. In Figure S1 the values of TI/CIS EET couplings and their selected components, calculated assuming cc-pVXZ basis sets for X=D,T,Q, are plotted with respect to growing basis set cardinal number.

All the EOP-TI/CIS results were obtained assuming the corresponding aug-cc-pVXZ-JKFIT auxiliary EOP basis set. However, the differences between results obtained using aug-cc-pVDZ-JKFIT auxiliary basis and the one corresponding to a given orbital basis were negligible. In particular we noticed that using larger JKFIT basis than the one dedicated to a given orbital basis resulted in differences below 1 cm^{-1}. In case of calculations assuming smaller JKFIT basis (for instance aug-cc-pVDZ-JKFIT instead of aug-cc-pVTZ-JKFIT) led to differences not exceeding a few reciprocal centimeters. Thus we would recommend using aug-cc-pVDZ-JKFIT set as EOP auxiliary basis if available.

The choice of orbital basis is more important, however, also does not seem to be critical considering the overall accuracy of the TI/CIS approach. Analysis of the trends obtained for various components shows that the $V_{\mathrm{Direct}}^{\mathrm{TI}}$ is almost independent of basis set choice due to opposite trends for the Coulomb and exchange contributions. The indirect components are much more sensitive to the basis set choice. For instance the cc-pVDZ value of $V_{\mathrm{Indirect}}^{\mathrm{TI}}$ is roughly 55% of that obtained in the cc-pVTZ and 40% of that for cc-pVQZ, however, it seems to saturate rather quickly with the basis set extension. Note also that for the studied model systems the indirect contribution at equilibrium geometries constitutes only roughly 20-30% of the total TI/CIS coupling. Finally, it is interesting to note that the TI/CIS values converge quickly to the exact ESD coupling with basis set extension.

Fig. S1 TI/CIS EET couplings and their components calculated at various level of approximation (indicated by labels in the center of a given panel) for symmetric stacked ethylene dimer at its equlibrium geometry as a function of cc-pVXZ orbital basis set cardinal number. In the case of EOP-TI calculation the corresponding aug-cc-pVXZ-JKFIT basis set was used.



4 Partitioning of EET couplings in the special pair of PS-I

Table S4 Partitioning of EET couplings computed between the lowest-lying bright $^1\pi\pi^*$ states of two chlorophylls of the special pair of PS-I at various levels of approximation to TI/CIS method. Indentation indicates constituents of a given term or it's approximation. All the results, given in cm^{-1}, were computed assuming 6-31G(d) basis set. The superscript 'M' indicates values estimated using the Mulliken approximation: Eq. (53) for the EOP-TI model, and Eq. (51) for remaining models (see main text). The $V^{\mathrm{TI}(3)}$ values in the EOP-TI results were computed assuming either the distributed multipolar expansion truncated on $|R|^{-5}$ terms or on atomic monopoles (values in parentheses) in V_{CT} calculations.

TI/CIS model	TI($\mathscr{F}_0$)	EOP
V^{TI}	170.9	177.7 (177.7)
V_{Direct}	155.1	160.1
V_{Coul}	156.7	-
$V_{\mathrm{Coul}}^{\mathrm{TrCAMM}}$	160.7	160.7
V_{Exch}	-1.6	-
$V_{\mathrm{Exch}}^{\mathrm{M}}$	-0.8	-0.6
V_{Ovlp}	0	0
V_{Indirect}	15.8	17.6 (17.6)
$V^{\mathrm{TI}(2)}$	15.8	17.6
$V^{\mathrm{TI}(3)}$	0	-
$V^{\mathrm{TI}(3),\mathrm{M}}$	0	0 (0)

5 Cartesian coordinates of the studied model systems

Cartesian coordinates (in Å) of minimum energy structure of stacked ethylene dimer optimized using the MP2/6-31G(d) method assuming D_{2h} symmetry. The potential energy scans were obtained by translation of thus obtained rigid ethylene molecules along intermolecular axis.

C	-2.08448	0.66814	0.00000
C	-2.08448	-0.66814	0.00000
H	-2.08296	1.23821	0.92328
H	-2.08296	-1.23821	0.92328
H	-2.08599	-1.23821	-0.92328
H	-2.08599	1.23821	-0.92328
C	2.08448	0.66814	0.00000
C	2.08448	-0.66814	0.00000
H	2.08296	1.23821	0.92328
H	2.08296	-1.23821	0.92328
H	2.08599	-1.23821	-0.92328
H	2.08599	1.23821	-0.92328

Cartesian coordinates (in Å) of stacked 7-aminocoumarin (7AC) dimer. The structure was obtained by superposition of two flat 7AC molecules at their equilibrium geometries located at MP2/6-31g(d) level and shifted with respect to intermolecular axis. Such a rigid potential energy scan shows minimum at $R_{\mathrm{AB}} = 3.6$ Å. The corresponding structure is reported below.

C	1.15427	1.09400	0.00000
C	-0.04215	0.38435	0.00000
C	-0.08115	-1.01874	0.00000
C	1.14783	-1.70347	0.00000
C	2.34913	-1.01715	0.00000
C	2.36815	0.39668	0.00000
O	-1.19462	1.13458	0.00000
C	-2.46341	0.54836	0.00000
C	-2.50237	-0.90913	0.00000
C	-1.36926	-1.65288	0.00000
O	-3.43016	1.28747	0.00000
H	-3.49236	-1.35196	0.00000
H	-1.42347	-2.74082	0.00000
H	1.14741	-2.79222	0.00000
H	3.28959	-1.56439	0.00000
N	3.56465	1.07202	0.00000
H	1.12173	2.18078	0.00000
H	3.59479	2.07912	0.00000
H	4.44182	0.57685	0.00000
C	1.15427	1.09400	3.60000
C	-0.04215	0.38435	3.60000
C	-0.08115	-1.01874	3.60000
C	1.14783	-1.70347	3.60000
C	2.34913	-1.01715	3.60000
C	2.36815	0.39668	3.60000
O	-1.19462	1.13458	3.60000
C	-2.46341	0.54836	3.60000
C	-2.50237	-0.90913	3.60000
C	-1.36926	-1.65288	3.60000
O	-3.43016	1.28747	3.60000
H	-3.49236	-1.35196	3.60000
H	-1.42347	-2.74082	3.60000
H	1.14741	-2.79222	3.60000
H	3.28959	-1.56439	3.60000
N	3.56465	1.07202	3.60000
H	1.12173	2.18078	3.60000
H	3.59479	2.07912	3.60000
H	4.44182	0.57685	3.60000

Cartesian coordinates (in Å) of the special pair of PS-I chlorophylls (residues B1021 and A1011). The updated 1JB0.pdb structure was assumed, reported by Madjet et al.,[1] augmented with hydrogen atoms using reduce 3.23, whose coordinates were then optimized using PM6 Hamiltonian as implemented in Gaussian 09.

C	97.949	119.795	91.053
C	98.120	119.958	89.609
N	98.992	120.987	89.372
C	99.384	121.498	90.588
C	98.720	120.742	91.656
C	97.489	119.162	88.611
C	97.640	119.301	87.236
N	98.437	120.255	86.607
C	98.294	120.123	85.261
C	97.474	118.930	84.993
C	97.068	118.431	86.224
Mg	99.336	121.925	87.514
N	100.789	122.957	88.441
C	101.668	123.751	87.770
C	102.352	124.615	88.705
C	101.910	124.252	89.975
C	100.958	123.235	89.758
C	103.335	125.266	87.931
C	103.434	124.256	86.780
C	102.062	123.986	86.373
C	101.326	123.339	85.393
C	101.427	123.620	83.900
C	100.341	122.718	83.321
C	99.839	121.917	84.458
N	100.337	122.381	85.623
C	102.786	123.133	83.290
C	102.976	123.313	81.828
C	104.172	122.578	81.314
O	105.290	122.411	82.063
C	106.387	121.561	81.575
C	98.883	120.885	84.320
C	99.210	123.642	82.915
O	104.114	126.202	88.127
C	104.641	124.342	85.882
O	104.839	125.208	84.939
C	106.077	125.063	84.158
C	100.274	122.535	90.768
C	102.386	124.806	91.325
C	96.372	117.156	86.252
C	95.111	116.996	86.302
C	97.250	118.326	83.592
C	98.837	121.034	93.122
C	97.687	121.972	93.514
C	97.085	118.772	91.744
O	105.473	123.533	86.125
O	104.143	122.117	80.184
H	101.546	125.206	91.901
H	96.037	118.873	91.435
H	96.817	119.074	82.919
H	98.862	124.275	83.744
H	106.934	124.988	84.837
H	97.730	122.913	92.953
H	102.883	124.023	91.907
H	97.416	117.754	91.498
H	98.209	117.993	83.179
H	99.508	124.314	82.099
H	105.987	124.166	83.532
H	96.712	121.514	93.305
H	94.612	116.030	86.290
H	102.093	122.959	81.239
H	98.790	120.095	93.710
H	103.604	123.665	83.829
H	105.995	120.753	80.949
H	103.107	125.620	91.164
H	97.124	118.883	92.834
H	96.570	117.469	83.638
H	98.330	123.089	82.555
H	106.083	125.990	83.579
H	97.720	122.217	94.581
H	94.385	117.806	86.358
H	103.073	124.393	81.559
H	99.815	121.493	93.363
H	102.923	122.065	83.577
H	107.066	122.205	81.011
H	100.489	122.839	91.805
H	96.838	118.360	88.971
H	98.635	120.652	83.273
H	97.078	116.305	86.207
H	100.682	122.095	82.461
H	101.294	124.703	83.696
H	106.823	121.199	82.512
H	103.774	123.264	87.318
C	96.141	114.161	83.765
C	102.652	120.201	86.174
C	100.187	116.928	93.386
C	95.253	112.657	88.534
N	98.592	115.041	86.004
C	96.009	113.938	82.325
C	103.904	120.295	86.349
C	101.133	115.821	93.859
C	95.447	112.993	87.013
N	100.532	117.155	86.819
O	94.314	111.961	88.929
C	94.857	114.638	81.751
C	95.270	111.763	86.140
N	98.065	114.733	88.893
C	93.426	110.957	84.808
C	96.826	113.631	86.934
C	100.095	116.363	84.591
C	101.512	118.386	88.725
C	98.586	115.346	91.180
C	99.707	113.454	83.425
C	101.712	118.840	83.659
C	102.044	119.012	91.800
C	96.167	113.420	91.878
C	92.589	115.436	81.798
C	97.575	114.114	85.868
C	100.691	117.179	85.457
C	100.883	117.702	89.788
C	97.841	114.625	90.224
O	94.972	115.154	80.655
O	95.856	110.740	86.350
C	97.481	113.682	84.429
C	101.489	118.343	85.090
C	101.116	117.953	91.221
C	96.745	113.780	90.503
O	93.689	114.700	82.395
O	94.436	111.919	85.122
C	98.597	114.475	83.763
C	101.907	118.934	86.265
C	100.307	117.089	91.914
C	96.285	113.346	89.243
C	99.117	115.368	84.819
C	101.342	118.140	87.362
C	99.565	116.309	90.916
C	97.121	113.958	88.280
N	99.975	116.700	89.648
Mg	99.587	115.599	87.869
H	96.923	112.930	92.499
H	103.056	118.902	91.395
H	102.101	118.034	83.026
H	100.027	112.889	84.309
H	93.848	109.945	84.780
H	100.901	114.862	93.380
H	95.803	114.316	92.391
H	101.678	120.015	91.549
H	100.761	119.187	83.235
H	99.362	112.733	82.675
H	92.634	111.035	85.563
H	102.176	116.059	93.615
H	104.474	121.217	86.253
H	96.924	114.266	81.759
H	100.428	117.881	93.903
H	95.292	113.668	84.305
H	92.533	115.239	80.721
H	95.322	112.726	91.758
H	102.104	118.930	92.891
H	102.428	119.668	83.631
H	100.598	113.947	83.016
H	93.077	111.278	83.819
H	101.068	115.678	94.943
H	104.559	119.465	86.611
H	95.933	112.844	82.087
H	99.142	116.692	93.675
H	96.017	115.241	84.017
H	91.724	115.041	82.341
H	98.356	115.147	92.235
H	102.183	119.204	89.001
H	100.347	116.490	83.525
H	94.682	113.767	86.741
H	101.998	121.051	85.920
H	98.284	115.017	82.840
H	97.571	112.578	84.331
H	92.748	116.502	81.989

The cartesian coordinates of all the studied systems are also provided as the electronic supplementary material in the XYZ format.

Notes and references

1 M. E.-A. Madjet, F. Müh and T. Renger, *J. Phys. Chem. B*, 2009, **113**, 12603–12614.