Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information of

Direct Estimation of the Transfer Integral for Photoinduced Electron Transfer from TD DFT calculations

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Derivation of Eq. (2) $V_{LE,CT}^2 = \left(E_{LE} - E_{CT}\right)^2 \frac{f_{CT} f_{LE} E_{CT} E_{LE}}{\left(f_{LE} E_{CT} + f_{CT} E_{LE}\right)^2}$.

Electronic interaction $V_{LE,CT}$ of two diabatic states φ_{LE} and φ_{CT} with energies ε_{LE} and ε_{CT} leads to adiabatic states ψ_i and ψ_j

$$\begin{aligned} \psi_i &= \varphi_{LE} \cos\omega - \varphi_{CT} \sin\omega \\ \psi_j &= \varphi_{LE} \sin\omega + \varphi_{CT} \cos\omega \end{aligned} \qquad (1)$$

The *diabatic* transition dipole moment μ_{CT} for the state φ_{CT} is usually assumed to be zero. See Ref. 9 cited in the paper. The state φ_{LE} has a large transition dipole moment μ_{LE}, which is responsible for the strong light absorption. By definition, both the adiabatic and the diabatic states are orthonormalized. Usually, the rotation angle ω is small and ψ_i and ψ_j resemble the states φ_{LE} and φ_{CT}. i.e. the state ψ_i and ψ_j correspond to "observed" or computed LE and CT excited states. Hereafter, ψ_i and ψ_j are labelled as ψ_{LE} and ψ_{CT}, respectively.

The *adiabatic* transition dipole moments M_{LE} (M_i) and M_{CT} (M_j) are determined by the contribution of φ_{LE} in the adiabatic states

$$\begin{aligned} M_{LE} &= \mu_{LE} \cos\omega - \mu_{CT} \sin\omega = \mu_{LE} \cos\omega \\ M_{CT} &= \mu_{LE} \sin\omega + \mu_{CT} \cos\omega = \mu_{LE} \sin\omega \end{aligned} \qquad (2)$$

As μ_{CT} is vanishingly small and not accounted for. Note that the borrowing intensity is determined by the square of M_{CT}, where $M_{CT} = \mu_{LE} \sin\omega = M_{LE} \tan\omega$

The matrix element $V_{LE,CT}$ can be written as:

$$V_{LE,CT} = \frac{E_{LE} - E_{CT}}{2} \sin 2\omega, \qquad (3)$$

where E_{LE} and E_{CT} are adiabatic energies, $E_{CT} = \langle \psi_{CT} | H | \psi_{CT} \rangle$ and $E_{LE} = \langle \psi_{LE} | H | \psi_{LE} \rangle$ Note that if ω=45° the diabatic states are in resonance and the matrix element is equal to half the adiabatic energy gap.

From Eq. (2) one directly obtains

$$\frac{|M_{LE}||M_{CT}|}{M_{LE}^2 + M_{CT}^2} = \frac{1}{2} \sin 2\omega, \qquad (4)$$

The oscillator strength f is expressed through the transition energy E and the adiabatic transition dipole moment M

$$f = \frac{2}{3} EM^2$$

Then, using Eq. (3) and (4) we obtain

$$V_{LE,CT} = \left(E_{LE} - E_{CT}\right) \frac{\sqrt{E_{LE} E_{CT} f_{LE} f_{CT}}}{E_{CT} f_{LE} + E_{LE} f_{CT}} \qquad (5)$$

Taking the square of the left and the right sides of Eq. (A5) we finally get

$$V_{LE,CT}^2 = \left(E_{LE} - E_{CT}\right)^2 \frac{f_{CT} f_{LE} E_{CT} E_{LE}}{\left(f_{LE} E_{CT} + f_{CT} E_{LE}\right)^2} \qquad (6)$$

.If the φ_{LE} and φ_{CT} states are in resonance, $\varepsilon_{LE} = \varepsilon_{CT}$, the adiabatic states ψ_{LE} and ψ_{CT} are represented by linear combinations ($\varphi_{LE}+\varphi_{CT}$) and ($\varphi_{LE}-\varphi_{CT}$). In this case, $M_{LE}=M_{CT}$, and $f_{CT}/E_{CT} = f_{LE}/E_{LE}$. On this condition, Eq. (5) reduces to the half-splitting formula

$$\left|V_{LE,CT}\right| = \frac{1}{2}\left|E_{LE} - E_{CT}\right| \qquad (A7)$$

Note that Eq. (1) gives $\left|V_{LE,CT}\right| = \left|E_{LE} - E_{CT}\right|$ overestimating the coupling by a factor of 2.

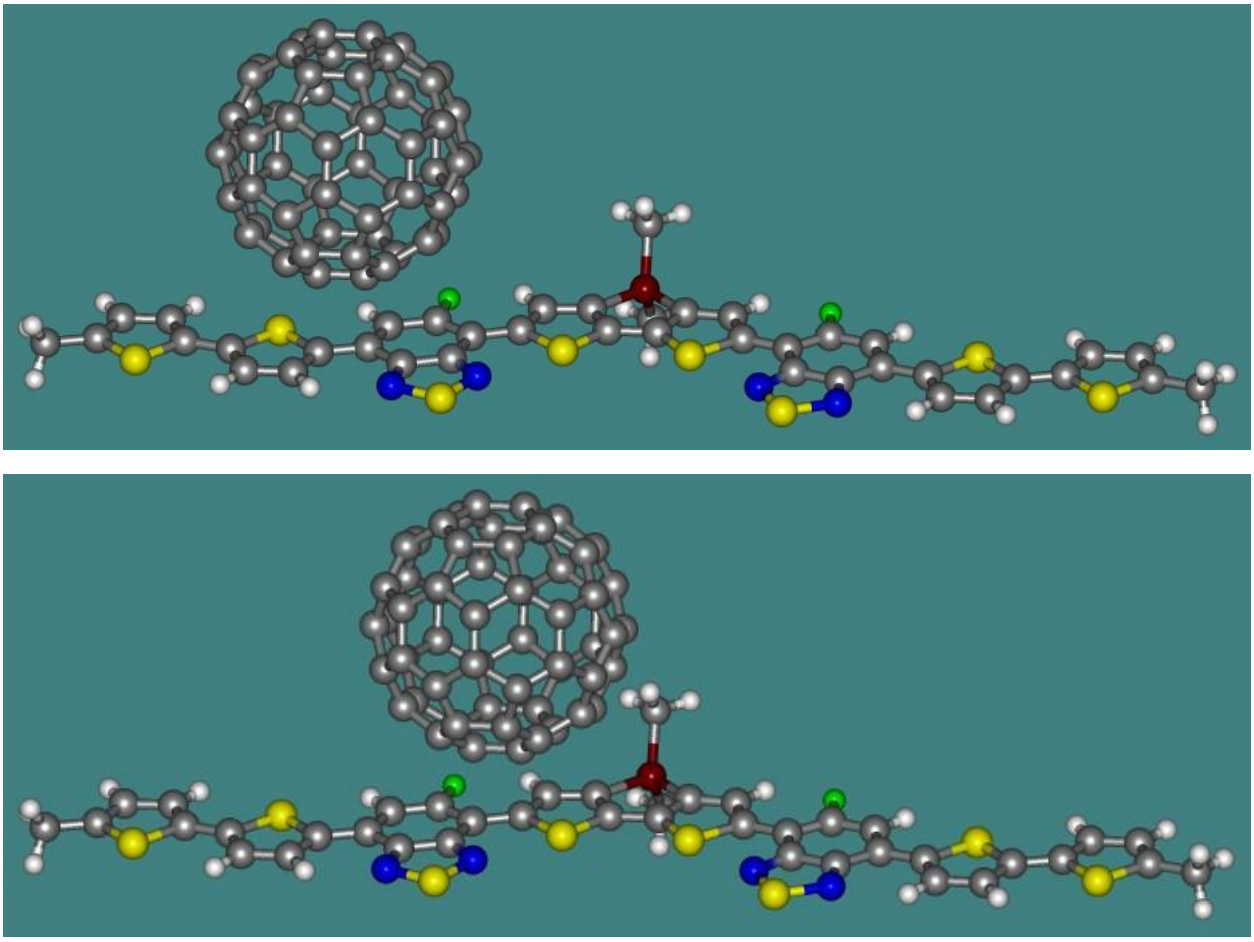

Figure S1. Two conformations I and II of the donor-acceptor complex are shown in the upper and lower panels.

Cartesian coordinates of conformation I

6	3.217000000	1.009000000	0.000000000
6	0.722000000	1.204000000	0.000000000
6	-0.722000000	1.204000000	0.000000000
6	2.752000000	2.326000000	0.000000000
6	1.349000000	2.452000000	0.000000000
16	1.844000000	-0.115000000	0.000000000
1	3.427000000	3.169000000	0.000000000
14	0.000000000	3.778000000	0.000000000
6	0.000000000	4.851000000	-1.554000000
1	0.885000000	5.497000000	-1.586000000
1	-0.885000000	5.497000000	-1.586000000
1	0.000000000	4.234000000	-2.458000000
6	0.000000000	4.851000000	1.554000000
1	0.885000000	5.497000000	1.586000000
1	0.000000000	4.234000000	2.458000000
1	-0.885000000	5.497000000	1.586000000
16	-1.844000000	-0.115000000	0.000000000
6	-3.217000000	1.009000000	0.000000000
6	-2.752000000	2.326000000	0.000000000
6	-1.349000000	2.452000000	0.000000000
1	-3.427000000	3.169000000	0.000000000
6	-4.592000000	0.543000000	0.000000000
6	-5.704000000	1.378000000	0.000000000
6	-7.049000000	0.967000000	0.000000000
9	-5.534000000	2.721000000	0.000000000
6	-4.964000000	-0.853000000	0.000000000
6	-6.352000000	-1.307000000	0.000000000
6	-7.445000000	-0.363000000	0.000000000
7	-4.088000000	-1.858000000	0.000000000
7	-6.467000000	-2.636000000	0.000000000
16	-4.947000000	-3.258000000	0.000000000
1	-7.782000000	1.767000000	0.000000000
6	7.049000000	0.967000000	0.000000000
6	5.704000000	1.378000000	0.000000000
6	4.592000000	0.543000000	0.000000000
6	4.964000000	-0.853000000	0.000000000
6	6.352000000	-1.307000000	0.000000000
1	7.782000000	1.767000000	0.000000000
9	5.534000000	2.721000000	0.000000000
6	7.445000000	-0.363000000	0.000000000
7	4.088000000	-1.858000000	0.000000000
7	6.467000000	-2.636000000	0.000000000
16	4.947000000	-3.258000000	0.000000000

6	8.838000000	-0.765000000	0.000000000
6	9.391000000	-2.033000000	0.000000000
16	10.123000000	0.444000000	0.000000000
6	10.804000000	-2.042000000	0.000000000
1	8.781000000	-2.926000000	0.000000000
6	11.375000000	-0.784000000	0.000000000
1	11.392000000	-2.954000000	0.000000000
6	12.772000000	-0.419000000	0.000000000
16	14.028000000	-1.653000000	0.000000000
6	15.302000000	-0.454000000	0.000000000
6	14.769000000	0.809000000	0.000000000
6	13.347000000	0.834000000	0.000000000
1	12.765000000	1.749000000	0.000000000
1	15.384000000	1.703000000	0.000000000
6	16.745000000	-0.858000000	0.000000000
1	17.378000000	0.035000000	0.000000000
1	17.005000000	-1.454000000	-0.884000000
1	17.005000000	-1.454000000	0.884000000
6	-8.838000000	-0.765000000	0.000000000
16	-10.123000000	0.444000000	0.000000000
6	-11.375000000	-0.784000000	0.000000000
6	-10.804000000	-2.042000000	0.000000000
6	-9.391000000	-2.033000000	0.000000000
1	-8.781000000	-2.926000000	0.000000000
1	-11.392000000	-2.954000000	0.000000000
6	-12.772000000	-0.419000000	0.000000000
6	-13.347000000	0.834000000	0.000000000
6	-14.769000000	0.809000000	0.000000000
6	-15.302000000	-0.454000000	0.000000000
16	-14.028000000	-1.653000000	0.000000000
1	-12.765000000	1.749000000	0.000000000
1	-15.384000000	1.703000000	0.000000000
6	-16.745000000	-0.858000000	0.000000000
1	-17.005000000	-1.454000000	-0.884000000
1	-17.378000000	0.035000000	0.000000000
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6	-7.183000000	-1.915000000	9.660000000
6	-6.490000000	-0.715000000	9.660000000
6	-5.317000000	-0.555000000	8.823000000
6	-4.889000000	-1.602000000	8.022000000
6	-5.614000000	-2.858000000	8.022000000
6	-6.735000000	-3.011000000	8.823000000
6	-6.494000000	-0.679000000	3.194000000

6	-5.318000000	-0.837000000	4.022000000
6	-5.316000000	-2.193000000	4.537000000
6	-5.614000000	-3.376000000	6.668000000
6	-4.888000000	-2.440000000	5.831000000
6	-4.441000000	-1.344000000	6.668000000
6	-4.440000000	-0.048000000	6.174000000
6	-4.888000000	0.211000000	4.820000000
6	-4.888000000	1.047000000	7.012000000
6	-5.317000000	0.799000000	8.307000000
6	-9.325000000	-0.714000000	9.660000000
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6	-7.214000000	0.541000000	9.660000000
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6	-7.182000000	2.372000000	8.024000000
6	-8.632000000	2.372000000	8.024000000
6	-9.325000000	1.477000000	8.824000000
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6	-6.737000000	1.618000000	4.025000000
6	-7.908000000	2.298000000	4.538000000
6	-9.080000000	2.632000000	6.670000000
6	-7.907000000	2.791000000	5.833000000
6	-6.734000000	2.631000000	6.670000000
6	-5.613000000	1.983000000	6.175000000
6	-5.614000000	1.467000000	4.822000000
6	-9.080000000	-3.010000000	8.823000000
6	-10.201000000	-2.857000000	8.023000000
6	-10.202000000	-3.375000000	6.669000000
6	-9.081000000	-4.022000000	6.174000000
6	-7.908000000	-4.183000000	7.011000000
6	-7.907000000	-3.688000000	8.306000000
6	-7.215000000	-1.933000000	3.188000000
6	-6.489000000	-2.871000000	4.019000000
6	-6.735000000	-4.024000000	6.174000000
6	-7.183000000	-3.764000000	4.820000000
6	-8.633000000	-3.764000000	4.820000000
6	-9.326000000	-2.869000000	4.020000000
6	-8.601000000	-1.934000000	3.184000000
6	-10.499000000	-2.191000000	4.537000000
6	-10.927000000	-2.439000000	5.832000000
6	-10.498000000	-0.554000000	8.824000000
6	-10.926000000	-1.602000000	8.023000000
6	-11.374000000	-1.343000000	6.669000000
6	-11.374000000	-0.048000000	6.175000000
6	-10.926000000	1.048000000	7.012000000

6	-10.498000000	0.800000000	8.307000000
6	-8.633000000	0.523000000	3.186000000
6	-9.081000000	1.620000000	4.020000000
6	-10.202000000	1.984000000	6.175000000
6	-10.202000000	1.467000000	4.821000000
6	-10.927000000	0.211000000	4.820000000
6	-10.499000000	-0.837000000	4.020000000
6	-9.326000000	-0.678000000	3.183000000

Cartesian coordinates of conformation II

6	3.217300000	1.009200000	0.000000000
6	0.722300000	1.204100000	0.000000000
6	-0.722300000	1.204100000	0.000000000
6	2.751700000	2.325600000	0.000000000
6	1.348900000	2.452300000	0.000000000
16	1.844300000	-0.114900000	0.000000000
1	3.426600000	3.169000000	0.000000000
14	0.000000000	3.777900000	0.000000000
6	0.000000000	4.850800000	-1.553700000
1	0.885200000	5.497400000	-1.585600000
1	-0.885200000	5.497400000	-1.585600000
1	0.000000000	4.233700000	-2.458300000
6	0.000000000	4.850800000	1.553700000
1	0.885200000	5.497400000	1.585600000
1	0.000000000	4.233700000	2.458300000
1	-0.885200000	5.497400000	1.585600000
16	-1.844300000	-0.114900000	0.000000000
6	-3.217300000	1.009200000	0.000000000
6	-2.751700000	2.325600000	0.000000000
6	-1.348900000	2.452300000	0.000000000
1	-3.426600000	3.169000000	0.000000000
6	-4.592200000	0.542900000	0.000000000
6	-5.703900000	1.378200000	0.000000000
6	-7.049300000	0.966700000	0.000000000
9	-5.534500000	2.720700000	0.000000000
6	-4.964000000	-0.853100000	0.000000000
6	-6.352100000	-1.306800000	0.000000000
6	-7.444800000	-0.362800000	0.000000000
7	-4.088400000	-1.857800000	0.000000000
7	-6.467200000	-2.636200000	0.000000000
16	-4.947000000	-3.258200000	0.000000000
1	-7.782200000	1.766800000	0.000000000
6	7.049300000	0.966700000	0.000000000
6	5.703900000	1.378200000	0.000000000
6	4.592200000	0.542900000	0.000000000
6	4.964000000	-0.853100000	0.000000000
6	6.352100000	-1.306800000	0.000000000
1	7.782200000	1.766800000	0.000000000
9	5.534500000	2.720700000	0.000000000
6	7.444800000	-0.362800000	0.000000000

7	4.088400000	-1.857800000	0.000000000
7	6.467200000	-2.636200000	0.000000000
16	4.947000000	-3.258200000	0.000000000
6	8.838100000	-0.765100000	0.000000000
6	9.391000000	-2.033300000	0.000000000
16	10.123100000	0.444500000	0.000000000
6	10.803900000	-2.042300000	0.000000000
1	8.781000000	-2.925900000	0.000000000
6	11.375000000	-0.784200000	0.000000000
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6	12.772200000	-0.419300000	0.000000000
16	14.028500000	-1.652700000	0.000000000
6	15.302200000	-0.453800000	0.000000000
6	14.768600000	0.808800000	0.000000000
6	13.346900000	0.833600000	0.000000000
1	12.764900000	1.749400000	0.000000000
1	15.383700000	1.703100000	0.000000000
6	16.745500000	-0.857800000	0.000000000
1	17.378100000	0.035300000	0.000000000
1	17.005100000	-1.453500000	-0.883900000
1	17.005100000	-1.453500000	0.883900000
6	-8.838100000	-0.765100000	0.000000000
16	-10.123100000	0.444500000	0.000000000
6	-11.375000000	-0.784200000	0.000000000
6	-10.803900000	-2.042300000	0.000000000
6	-9.391000000	-2.033300000	0.000000000
1	-8.781000000	-2.925900000	0.000000000
1	-11.391500000	-2.954300000	0.000000000
6	-12.772200000	-0.419300000	0.000000000
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6	-14.768600000	0.808800000	0.000000000
6	-15.302200000	-0.453800000	0.000000000
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6	-16.745500000	-0.857800000	0.000000000
1	-17.005100000	-1.453500000	-0.883900000
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6	-2.644800000	-1.043200000	9.666100000
6	-1.951700000	0.157100000	9.666100000
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6	-0.351300000	-0.730600000	8.028300000

6	-1.075900000	-1.986400000	8.028500000
6	-2.197100000	-2.138800000	8.829200000
6	-1.956100000	0.193300000	3.200500000
6	-0.780000000	0.034500000	4.028300000
6	-0.778400000	-1.320700000	4.543100000
6	-1.075800000	-2.504300000	6.674500000
6	-0.350100000	-1.568400000	5.837500000
6	0.097300000	-0.472100000	6.674500000
6	0.097700000	0.823300000	6.180500000
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6	-4.062400000	1.412800000	9.666400000
6	-2.676500000	1.412500000	9.666300000
6	-1.951500000	2.348600000	8.829700000
6	-2.644400000	3.243800000	8.029600000
6	-4.094300000	3.244000000	8.030000000
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6	-2.648400000	1.392000000	3.200500000
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6	-1.075800000	2.338300000	4.827600000
6	-4.542300000	-2.138600000	8.829100000
6	-5.663500000	-1.985400000	8.029100000
6	-5.663900000	-2.502800000	6.674800000
6	-4.542700000	-3.150600000	6.179900000
6	-3.369800000	-3.310800000	7.017100000
6	-3.369600000	-2.816000000	8.311900000
6	-2.677400000	-1.061700000	3.194000000
6	-1.951500000	-1.999000000	4.025500000
6	-2.197000000	-3.152300000	6.180100000
6	-2.645300000	-2.892600000	4.825700000
6	-4.095000000	-2.892500000	4.825600000
6	-4.788500000	-1.997200000	4.026000000
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6	-5.961100000	-1.319600000	4.543300000
6	-6.389000000	-1.566800000	5.838300000
6	-5.959900000	0.317400000	8.829600000
6	-6.388300000	-0.729900000	8.029300000

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6	-4.788300000	0.193700000	3.188600000