Supplementary Information

Electron Transfer in Silicon-Bridged Adjacent Chromophores. Source for Blue-Green Emission

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Absorption and Fluorescence Spectra in BUN





Fig. S2 Normalized fluorescence spectra of compound 1 in BUN measured at room temperature (red curve) and at 77 K (black curve)

Determination of Onsager Radius, σ (DFT)

The radius σ used in the Onsager solvent reaction field model was determined basing on the molecular volume inside a fixedelectron-density contour, as implemented in the Gaussian G09 package.¹ The electron density was calculated by the DFT method.

Derivation of Equation 16

Following the description of Marcus for the potential energy surfaces (PES) of reactants and products in terms of the polarization of the low frequency modes of the reacting system (mostly from the solvent), the adiabatic PES can be obtained from the solution of the secular equation:

$$\begin{vmatrix} \lambda_S X^2 - E & V \\ V & \lambda_S (X-1)^2 + \Delta G - E \end{vmatrix} = 0$$
(S1)

In which λ_s is the reorganization energy of the low frequency modes, X the reaction coordinate, ΔG the free energy difference between reactants and products in their most stable configuration in the diabatic description (no-coupling), V the coupling between the initial and final states and E the energy of the states. Equation S1 has two solutions corresponding to un upper state and a lower state. If the coupling is large enough the reaction proceeds adiabatically over the lower PES meaning that the probability for passing to the higher PES is very small. The solution corresponding to the lower PES is:

$$E_{lower}(X) = \frac{\lambda_s (2X^2 - 2X + 1) + \Delta G}{2} - \frac{1}{2} \{ [\lambda_s (2X - 1) - \Delta G]^2 + 4V^2 \}^{1/2}$$
(S2)

If the coupling is large enough the activation energy for the reaction doesn't coincide with the Marcus result, but it is smaller. It is in principle possible to obtain the energy of activation by finding the energy of the transition state, as defined by the maximum between the two equilibrium configurations. As it is located in a maximum, the coordinate for this point can be obtained by finding the poles of the first derivative of eq. S2:

$$\frac{d\mathcal{L}_{lower}(X)}{dX} = 2\lambda_S X - \lambda_S - \left(-\Delta G\lambda_S + 2\lambda_S^2 X - \lambda_S^2\right) / \left\{ \left[\lambda_S(2X-1) - \Delta G\right]^2 + 4V^2 \right\}^{1/2}$$
(S3)

This leads to a quartic equation:

(17)

1 -

$$0 = 2\lambda_{S}X_{max} - \lambda_{S} - \left(-\Delta G\lambda_{S} + 2\lambda_{S}^{2}X_{max} - \lambda_{S}^{2}\right) / \left\{ \left[\lambda_{S}(2X_{max} - 1) - \Delta G\right]^{2} + 4V^{2} \right\}^{1/2}$$
(S4)

Which has analytical solutions but are extremely complex. We prefer to apply an approximation in order to find a easier to handle expression.

For low reaction free energies and for not too large values of the coupling between the states, the position of the transition state must be close to 0.5. Near this value the following ratio is much smaller than 1:

$$\frac{\left[\lambda_{S}(2X_{max}-1)-\Delta G\right]^{2}}{4V^{2}} = \left(\frac{\lambda_{S}(2X_{max}-1)-\Delta G}{2V}\right)^{2} \ll 1$$
(S5)

Taking this into account the equation S4 can be simplified to:

$$0 = 2X_{max} - 1 - \frac{\left(-\Delta G + 2\lambda_S X_{max} - \lambda_S\right)}{2V}$$
(S6)

And its solution is:

$$X_{max} = \frac{1}{2} \left(1 + \frac{\Delta G}{\lambda_s - 2V} \right) \tag{S7}$$

Substituting eq. S7 into eq. S2 gives the energy of the transition state:

$$E_{lower}(X_{max}) = \frac{1}{2} \left[\frac{\lambda_S}{2} \left(\frac{\Delta G^2}{\left(\lambda_S\right)^2} + 1 \right) \right] + \frac{\Delta G}{2} - \frac{1}{2} \sqrt{\Delta G^2 \left(\frac{\lambda_S}{\lambda_S - 2V} - 1 \right)^2 + 4V^2}$$
(S8)

Still we need to obtain this energy respect to that of the reactants in equilibrium. Assuming that their coordinate is equal to zero:

$$E_{lower}(X=0) = \frac{\lambda_{S} + \Delta G}{2} - \frac{1}{2}\sqrt{\left[-\lambda_{S} - \Delta G\right]^{2} + 4V^{2}}$$
(S9)

Thus, the activation energy is given by the difference between eqs. S8 and S9:

$$E_{A} = \frac{1}{2} \left\{ \frac{\lambda_{S}}{2} \left(\frac{\Delta G^{2}}{(\lambda_{S} - 2V)^{2}} - 1 \right) - \frac{1}{2} \sqrt{\Delta G^{2} \left(\frac{\lambda_{S}}{\lambda_{S} - 2V} - 1 \right)^{2} + 4V^{2} + \frac{1}{2} \sqrt{(\lambda_{S} + \Delta G)^{2} + 4V^{2}} \right\}$$
(S10)

To test the applicability of the eq. S10 we have compared it to the numerical exact results of eq. S4 for a free energy of the reaction of -0.11 eV and a reorganization energy of 0.6 eV for increasing values of the coupling.



Fig. S3 Left panel: Lower adiabatic PES obtained from eq. S2 at increasing values of the coupling. Right panel: Blue line: numerical result from eq. S4 for the activation energy. Green line: analytical solution from eq. S10.

Further calculations show that this approximation works quite reasonably only in the normal region and starts failing as we approach the barrier-less point.

A very similar equation was obtained by Brunschwig and Sutin in 1999.² Their result reads:

$$E_A = \frac{\lambda_S}{4} + \frac{\Delta G^2}{4(\lambda_S - V)} + \frac{\Delta G}{2} - V + \frac{V^2}{\lambda_S + \Delta G}$$
(S11)

At the values of free reaction enthalpy used in the Figure S3 the results from eq. S10 and S11 are very similar. However, at larger values of the free reaction enthalpy the equation S11 deviates from the numerical result from eq. S4 much more and at much lower values than eq. S10.



Fig. S4 Same as right panel in Fig. S3, but for a free reaction energy of -0.3 eV, and adding the results from eq. S11 in red.

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DFT calculations

Table 1S Vertical absorption energies (ΔE , in eV), transition oscillator strengths (f), excitation characters ($o \rightarrow v^*$), and electric dipole moments (μ , in D) of the low-lying singlet electronic excited states of **1**, predicted at the TD-DFT/aug-cc-pVDZ level of theory

	PBEO			CAM-B3LYP			ωB97X-D		
State	$\Delta E(f)$	o→v*	μ	ΔE (f)	o→v*	μ	ΔE (f)	o→v*	μ
1	3.80 (0.002)	H→L	30.5	4.21 (0.032)	H→L+1	3.6	4.23 (0.031)	H→L+1	3.5
2	3.95 (0.026)	H→L+1	4.1	4.35 (1.015)	H-1→L	3.0	4.39 (1.008)	H-1→L	2.9
3	4.08 (0.924)	H-1→L	5.9	4.64 (0.113)	H-2→L+1	3.6	4.67 (0.117)	H-2→L+1	3.6
4	4.18 (0.108)	H-2→L	27.5	4.72 (0.002)	H-4→L	2.7	4.74 (0.002)	H-4→L	2.6
5	4.41 (0.069)	H-2→L+1	3.4	5.06 (0.014)	H→L	27.8	5.18 (0.462)	H→L+11	3.2
6	4.49 (0.001)	H-4→L	2.1	5.16 (0.449)	H→L+11	3.4	5.39 (0.003)	H→L	25.1

 $o \rightarrow v^*$ is the excitation character (from occupied o to virtual v* molecular orbital), the orbitals H-2, H, L+1, L+11 are localized on the CBL moiety, the orbitals H-4, H-1, L are localized on the DVB moiety (H=HOMO, L=LUMO)

Table 2S Relative energies (E, in eV)^{*a*}, transition oscillator strengths (f), excitation characters ($0 \rightarrow v^*$), and electric dipole moments (μ , in D) of the low-lying singlet electronic excited states of 1 in acetonitrile solution, predicted at the CAM-B3LYP /aug-cc-pVDZ level of theory including the macroscopic solvent effect.

State	absorption			emission (S1) ^b			emission (S3) ^b		
	E (f)	o→v*	μ	E (f)	o→v*	μ	E (f)	o→v*	μ
0	0.		3.1	0.37		3.0	0.46		2.8
1	4.18 (0.047)	H→L+1	4.7	3.92 (1.178)	H-1→L	3.6	4.01 (1.265)	H-1→L	3.7
2	4.27 (1.153)	H-1→L	3.6	4.55 (0.041)	H→L+1	4.7	4.49 (0.143)	H→L+1	4.3
3	4.62 (0.166)	H-2→L+1	4.2	4.84 (0.003)	H-4→L	3.8	4.57 (0.034)	H→L	27.2
4	4.73 (0.002)	H-4→L	3.5	4.88 (0.013)	H→L	33.0	5.00 (0.015)	H-4→L	3.4
5	5.00 (0.020)	H→L	30.2	4.98 (0.171)	H-2→L+1	4.8			

^a Relatively to the energy of the S₀ state at equilibrium. ^b At the equilibrium configuration of the corresponding excited state. All of the equilibrium structures were determined at the CAM-B3LYP /6-31++G(d,p) level of theory.