Extended Charge-Transfer Excitons in Crystalline Supramolecular Photocatalytic Scaffolds: Supporting Information

Nicholas J. Hestand¹, Roman V. Kazantsev²³, Adam S. Weingarten²³, Liam C. Palmer²³⁷, Samuel I. Stupp²³⁴⁵⁶⁷ * and Frank C. Spano¹ *

¹Department of Chemistry, Temple University, Philadelphia, PA 19122, USA.
²Department of Chemistry, Northwestern University, Evanston, IL 60208, USA.
³Argonne—Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, IL 60208, USA.
⁴Department of Materials Science and Engineering, Evanston, IL 60208, USA.
⁵Department of Biomedical Engineering, Northwestern University, Evanston, IL 60208, USA.
⁶Department of Medicine, Northwestern University, Chicago, IL 60611, USA.
⁷Simpson Querrey Institute for BioNanotechnology, Northwestern University, Chicago, IL 60611, USA.

Corresponding Authors: spano@temple.edu; s-stupp@northwestern.edu
S.I. Multiparticle Basis Set

Here we present the multiparticle basis set\(^{1-4}\) used to represent and solve Eq. (1) of the manuscript. The multiparticle basis set consists of vibrationally dressed Frenkel and charge-transfer (CT) excitation states that can be categorized by the number of vibronic and vibrationally excited molecules in the system. When there are \( n \) excited molecules in the system, the corresponding basis states are part of the \( n \)-particle set. In the simplest approximation, only one-particle states \((n = 1)\) are retained in the basis and higher levels of approximation involve the successive addition of higher \( n \)-particle states \((n = 2, 3, \ldots)\).

The \( n \)-particle states can be further divided based on their electronic character into Frenkel and CT subsets. One-particle Frenkel states consist of a single vibronically excited molecule, \( m = 1, 2, \ldots N \), while all other molecules remain in their ground electronic and vibrational states. In the local basis, one-particle FE states are denoted by

\[
|m, \tilde{\nu}; m+s, \nu_s\rangle_{FE}
\]

where \( \tilde{\nu} (= 0, 1, 2, \ldots) \) denotes the number of vibrational quanta on molecule \( m \). The tilde over \( \nu \) indicates that the vibrations are characterized by the nuclear potential well of the Frenkel Exciton which is shifted from that of the ground state as quantified by the neutral Huang-Rhys parameter, \( \lambda^2 \). Two-particle Frenkel states consider a single vibrationally excited molecule in addition to the vibronically excited molecule present in the one-particle states. These are expressed in the local basis as

\[
|m, \tilde{\nu}; m+s, \nu_s; m+r, \nu_r\rangle_{FE}
\]

where the new terms \( m + s \) and \( \nu_s \) indicate the site of the vibrationally excited molecule and the number of vibrational quanta residing on that molecule. Note that the vibration on molecule \( m + s \) is characterized by the ground state nuclear potential. Furthermore, three-particle states consider a second vibrationally excited molecule and can be expressed in the local basis as

\[
|m, \tilde{\nu}; m+s, \nu_s; m+r, \nu_r\rangle_{FE}
\]

where the new terms \( m + r \) and \( \nu_r \) indicate the site of the second vibrationally excited molecule and the number of vibrational quanta residing on that molecule. The vibrational excitations residing on molecules \( m + s \) and \( m + r \) are characterized by the unshifted potential well of the electronic ground state.

The simplest CT states are two-particle states since the electron and hole reside on different molecules. In the local basis, these states can be denoted by

\[
|m_+ , \nu_+; m_+ + s, \nu_+; m_- + s, \nu_-\rangle_{CT}
\]

where \( m_+ \) denotes the site hosting the hole, and \( m_+ + s, \nu_- \) denotes the site hosting the electron. The ionic molecules can also host vibrational excitations and the terms \( \nu_+ (= 0, 1, 2, \ldots) \) and \( \nu_- (= 0, 1, 2, \ldots) \) denote the number of vibrational quanta on the cation and anion. The vibrations on the ionic molecules are characterized by the shifted potential wells of the ionic states as defined by the ionic Huang Rhys parameters, \( \lambda'^2 \) and \( \lambda'^2 \). Three-particle CT states consider a vibrationally excited molecule in addition to the two ionic molecules. These states are written in the local basis as

\[
|m_+ , \nu_+; m_+ + s, \nu_+; m_- + s, \nu_-\rangle_{CT}
\]

where the new term \( m_+ + s \) denotes the site of the vibrational excitation and \( \nu (= 1, 2, \ldots) \) denotes the number of vibrational quanta in the ground state nuclear potential well of molecule \( m_+ + s \).

The multiparticle basis states contained in Eqs. (S.1)-(S.5) can be transformed to the delocalized basis according to wave vector \( k \). The one-, two-, and three-particle FE states are written in the delocalized basis as

\[
|k, \tilde{\nu}\rangle_{FE} = \frac{1}{\sqrt{N}} \sum_m e^{im\theta} |m, \tilde{\nu}\rangle_{FE}
\]

\[
|k, \tilde{\nu}; s, \nu_s\rangle_{FE} = \frac{1}{\sqrt{N}} \sum_m e^{im\theta} |m, \tilde{\nu}; m+s, \nu_s\rangle_{FE}
\]

\[\text{S1}\]
\[
\left[ k, \tilde{\nu}; s, \nu, \nu \right]_{FE} = \frac{1}{\sqrt{N}} \sum_{m} e^{i \omega m} \left[ m, \tilde{\nu}; m + s, \nu; m + r, \nu \right]_{FE}
\]  
(S.8)

Similarly, the two- and three-particle CT states are written in the delocalized basis as
\[
\left[ k, \tilde{\nu}; s, \nu, \nu \right]_{CT} = \frac{1}{\sqrt{N}} \sum_{m} e^{i \omega m} \left[ m, \tilde{\nu}; m + s, \nu; m + r, \nu \right]_{CT}
\]  
(S.9)
\[
\left[ k, \tilde{\nu}; s, \nu, \nu \right]_{CT} = \frac{1}{\sqrt{N}} \sum_{m} e^{i \omega m} \left[ m, \tilde{\nu}; m + s, \nu; m + r, \nu \right]_{CT}
\]  
(S.10)

The basis set defined by Eqs. (S.6)-(S.10) was used for all numerical calculations within the manuscript.

**S.II. Absorption Calculation**

Once the eigenfunctions, \( |\Psi_i\rangle \), and eigenvalues, \( \omega_i \), of Eq. (1) are found numerically using the delocalized multiparticle basis set (Eqs. (S.6)-(S.10)), the absorption spectrum of the system is calculated according to
\[
A(\omega) = \sum_i f_i \Gamma(\omega - \omega_i)
\]  
(S.11)

where \( f_i \) is the line strength for the transition from the ground state to \( |\Psi_i\rangle \) and \( \Gamma(\omega) \) is a line shape function. The line strength is defined by
\[
f_i = \frac{\omega_i}{|\mu|} \left| \langle G | \hat{\mu} | \Psi_i \rangle \right|^2
\]  
(S.12)

where \( \hat{\mu} \) is the transition dipole moment operator between the ground \( |G\rangle \) and excited Frenkel exciton states
\[
\hat{\mu} = \sum_n \mu_n |G\rangle \langle n| + H.c.
\]  
(S.13)

Eq. (S.13) neglects direct absorption to CT states due to their expected weak oscillator strength.\(^56\) The line strength in Eq. (S.12) is essentially the oscillator strength as it is the product of the square of the transition dipole moment and the transition frequency. Finally, the line shape function is taken to be a normalized Gaussian with standard deviation \( \sigma \)
\[
\Gamma(\omega) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\omega^2}{2\sigma^2}\right)
\]  
(S.14)

**S.III. Exciton Coupling Calculation for 2D Perylene Monoimide Sheets**

The exciton coupling was calculated for (semi-)infinite 2D sheets of perylene monoimide (PMI) aggregates using atomic transition charge densities derived from density functional theory (DFT) calculations.\(^79\) Atomic transition charges were calculated at the DFT/B3LYP level of theory using the cc-pVDZ basis set and were based on a PMI core where the linker group was replaced by a Hydrogen atom. The PMI core was optimized at the DFT/B3LYP level of theory using the cc-pVDZ basis set. Given the transition charges, exciton couplings were calculated between all molecules in a periodic 2D lattice consisting of 10,000 total molecules. The 2D lattice was constructed to contain 100 molecules along both the \( \pi \)-stacking and edge-to-edge stacking dimensions and the packing geometry was set according to the wide angle x-ray scattering (WAXS) measurements of Ref 10. The WAXS measurements provide packing information concerning the edge-to-edge and \( \pi \)-stacking distances, but not the relative displacement along the long molecular axis of neighboring molecules. For simplicity we therefore stacked the PMI molecules in an antiparallel fashion along the \( \pi \)-stacking axis and took the centers of the perylene cores to lie directly above one another. As such, the line connecting \( \pi \)-stacked PMI centers was parallel to the \( \pi \)-stacking axis. We note that in contrast to the CT integrals (see section S.V), the exciton coupling is expected to be relatively insensitive to small displacements along the long molecular axis.\(^11\) In an effort to correct for any
Figure S1. The Coulombic binding energy ($V_{CT}$) as a function of electron/hole separation (s) for several values of the static dielectric constant, $\varepsilon_r$. In all cases, we have set $e^2/4\pi\varepsilon_0d = 1$ eV.

computational error in the calculated exciton couplings, we followed the procedure outlined in Ref. 12: assuming the computational error for PMI is the same as it is for perylene, the calculated exciton couplings were multiplied by the ratio $\mu_{EXP}/\mu_{THEORY}^2 = 2$ where $\mu_{EXP} = 6.09$ Debye and $\mu_{THEORY} = 4.32$ Debye are the experimentally measured and calculated transition dipole moments of perylene, respectively. Finally, we divided the excitonic couplings by an optical dielectric constant of $\varepsilon = 3$ in order to account for optical screening.14,15 After calculating the local exciton couplings in this manner, the $k=0$ Frenkel exciton coupling was evaluated according to $J_{k=0} = \sum_m J_m$. Here $m$ is a vector that labels the displacement between molecules (in units of molecules) in the 2D lattice, ranging from $m = (-49,49)$ to $m = (50,50)$, and $J_m$ is the local excitonic coupling between molecules displaced by the vector $m$. This method resulted in the values of 3850 and 3500 cm$^{-1}$ for L1 and L5, respectively, as reported in the manuscript. The difference in coupling between the two species is due to the closer edge-to-edge packing distance in L1 which serves to increase the magnitude of the coupling.

S.IV. Effect of Static Dielectric Constant on the Coulomb Binding Energy

Figure S1. shows the distance dependent Coulomb binding energy ($V_{CT}(s)$) for an electron and hole for several values of the effective static dielectric constant, $\varepsilon_r$. For this illustration, we have set $e^2/4\pi\varepsilon_0d = 1$ eV. The figure demonstrates how the energy of extended CT states depends on the effective static dielectric constant of the system plus environment. In vacuum the Coulomb force between electron and hole is unscreened ($\varepsilon_r = 1$, blue curve) and the potential well achieves its maximum depth. This results in CT energies that are strongly dependent on the distance between electron and hole. In this case, the electron and hole are strongly bound to one another. In a crystal, the static dielectric constant increases from 1 (green and red curves) resulting in shallower wells. When $\varepsilon_r$ increases, the electron and hole can separate from one another more readily than when the potential is unscreened ($\varepsilon_r = 1$). In the limit of a high dielectric environment (black curve), such as we assume in the manuscript for PMI, the potential well is very shallow. In this case, the energies of the CT states are largely independent of the separation between electron and hole so that the electron and hole behave as free particles.

S.V. Ab-initio Calculation of the Charge-Transfer Integrals

In the manuscript, the CT integrals were set empirically based on the absorption bandwidth. The absorption bandwidth uniquely determines the sum of the CT integrals but gives no indication of their relative magnitudes. Figure S2 (a) and (b) shows the DFT/B3LYP calculated CT integrals for L1 and L5 as a function of long-axis displacement while the $\pi$-stacking distance and short-axis offset were taken from experimental wide angle x-ray scattering experiments. The integrals were extracted from the DFT calculations using the energy splitting method.56-58 As can be appreciated from the figure, the integrals are quite sensitive to displacements along the
Figure S2. The charge-transfer integrals and the sum $|t_e + t_h|$ for (a) L1 and (b) L5 as a function of packing displacement along the long molecular axis. At a displacement of 0 Å, the perylene subunits are eclipsed (e). The spectra calculated for (c) L1 and (d) L5 show only minor differences for the four sets of $t_e$ and $t_h$ corresponding to the geometries for which $|t_e + t_h| = 1250$ cm$^{-1}$, the value extracted from the experimental spectrum. These geometries are indicated by the numbers 1, 2, 3 and 4 in parts (a)-(d).
long molecular axis\textsuperscript{9} which precludes a direct evaluation of these integrals for $L_1$ and $L_5$ in the absence of information about the precise $\pi$-stacking geometry.

Over the range of displacements presented in Fig. S2, the sum of $t_{e}$ and $t_{h}$ equals 1250 cm\textsuperscript{-1}, the value extracted empirically from the experimental spectrum, four times for each compound. The corresponding spectra are shown in Fig. S2 (c) and (d) for $L_1$ and $L_5$, respectively. The spectra were calculated using the same parameters as in Fig 10 of the manuscript with the exception of the charge-transfer integrals, which appear in the insets. That the spectra exhibit only minor changes as the relative magnitudes of the CT integrals vary indicates that the sum of the charge-transfer integrals is an important parameter in determining the spectral profile while the relative magnitudes of $t_{e}$ and $t_{h}$ are of secondary importance. The relative magnitude of $t_{e}$ and $t_{h}$ will be important in determining the relative mobility of electrons and holes within the material, however, the $(k = 0)$ charge separation dynamics and photophysics are governed mainly by the sum.

Figure S2 also implies that $L_1$ and $L_5$ might have very different values of $t_{e}$ and $t_{h}$ even though the sum remains nearly equal for the two systems. If this were true, it would allow for an alternate explanation of different H$_2$ production from the two systems. For example, if the magnitude of $t_{e}$ was significantly larger in one material, it would allow for faster electron transport to the catalytic reduction sites, thereby promoting faster H$_2$ evolution. While this is certainly possible, we think it would be an extraordinary coincidence for $L_1$ and $L_5$ to have significantly different $\pi$-stacking geometries (for instance at positions 1 and 2 in Fig. S2), but somehow still maintain the same sum of $|t_{e} + t_{h}|$ as required by the peak-to-peak splitting in the absorption spectrum. The coincidence is even more extraordinary when considering that Fig. S2 considers only a 1-dimensional phase space of the dimer geometry. The chance of having two geometries where $|t_{e} + t_{h}| = 1250$ cm\textsuperscript{-1} is maintained becomes significantly less when considering the full 3-dimensional dimer geometry phase space. We thus prefer our interpretation presented in the manuscript: the difference in H$_2$ generation is driven mainly by the energy difference between the $k = 0$ Frenkel and charge-transfer excitons, as determined by the Coulomb coupling, which is rationalized based on the experimentally observed molecular packing distances and nanoribbon widths. This energy difference governs the ability of the photogenerated exciton to split into free charges that can proceed to the catalytic reduction sites to participate in H$_2$ generation reactions.

References