Supporting Information for

Charge Recombination Suppressed by Destructive Quantum Interference in Heterojunction Materials

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Recombination of a singlet CT state towards the ground state

In the main text, we restricted ourselves to recombination of ^{3}CT towards triplet excitons, which based on spin statistics is expected to be the dominant channel for bimolecular recombination. Here, we present a brief derivation showing that the case of recombination of ^{1}CT towards the ground state is formally equivalent to that of ^{3}CT towards triplets.

For ^{1}CT, the recombination rate is given by

$$\Gamma_{^1\mathrm{CT}} = \frac{2\pi}{\hbar} |\langle \mathrm{G}|H_\mathrm{r}|^1\mathrm{CT}\rangle|^2 \rho_\mathrm{G}, \tag{S1}$$

with $|\mathrm{G}\rangle$ denoting the ground state, and ρ_G the associated density of (vibrationally dressed) states. The recombination Hamiltonian is identical to eq 3, except that the triplet exciton creation operator is omitted,

$$H_\mathrm{r} = \sum_{\vec{m}\in D, \vec{n}\in \mathrm{A}} b_{\vec{m}} c_{\vec{n}}\, t_\mathrm{i} \delta(\vec{m}, \vec{n} - \hat{x}). \tag{S2}$$

Since the CT Hamiltonian, given by eq 2, is spin-independent, its ^{1}CT eigenstates are identical to ^{3}CT eigenstates. Hence, also the ^{1}CT eigenstates can be expressed as $|\alpha\rangle = \sum_{\vec{m}\in \mathrm{D}, \vec{n}\in \mathrm{A}} c^\alpha_{\vec{m},\vec{n}} |\vec{m}, \vec{n}\rangle$. Combining this expression with eqs S1 and S2, we obtain

$$\begin{aligned} \Gamma_\alpha &= \frac{2\pi}{\hbar} |\sum_{\vec{m}\in \mathrm{D}, \vec{n}\in \mathrm{A}} \langle \mathrm{G}| b_{\vec{m}} c_{\vec{n}}\, t_\mathrm{i} \delta(\vec{m}, \vec{n} + \hat{x}) |\alpha\rangle|^2 \rho_\mathrm{G} \\ &\propto |\sum_{y,z} c^\alpha_{(N,y,z),(N+1,y,z)}|^2, \end{aligned} \tag{S3}$$

which is identical to the ^{3}CT result given by eq 4. Hence, the results for ^{3}CT presented in the main text hold equally well for ^{1}CT.

Analytical derivation for an unbound CT state in a 2×1×2 heterojunction

The coherent suppression of charge recombination upon wavefunction delocalization in an idealized heterojunction can be demonstrated analytically when the Coulomb interaction between the electron and hole is neglected. The Hamiltonian in the subspace of CT states can then be expressed as a sum of a hole and electron contribution,

$$H_0 = H_{\mathrm{h}} \oplus H_{\mathrm{e}}. \tag{S4}$$

Consequentially, each CT state can be expressed as a product of states in the hole and electron subspaces, $|\alpha\rangle = |\beta\rangle_{\mathrm{h}} \otimes |\gamma\rangle_{\mathrm{e}}$.

For the sake of simplicity, we restrict ourselves to a $2 \times 1 \times 2$ heterojunction as shown in Figure S1; the smallest setup in which charge delocalization can occur. Since for such a configuration the charge movements are restricted to the z-direction, the hole and electron

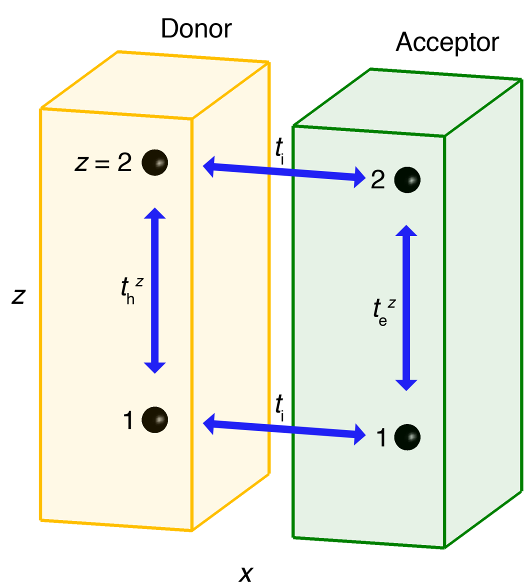

Figure S1: Representation of the hole and electron transfer integrals, analoguous to Figure 2. For an idealized $2 \times 1 \times 2$ heterojunction as depicted here, and neglecting the Coulomb interaction, the coherent suppression of charge recombination can be demonstrated analytically.

Hamiltonians can be formulated as

$$H_{\mathrm{h}} = t_{\mathrm{h}}^{z}(b_1^{\dagger}b_2 + b_2^{\dagger}b_1) \tag{S5}$$

and

$$H_{\mathrm{e}} = t_{\mathrm{e}}^{z}(c_1^{\dagger}c_2 + c_2^{\dagger}c_1). \tag{S6}$$

Here, the subscript of the creation and annihilation operators refers to the z-coordinate, while it is understood that the hole and electron reside inside the donor and acceptor regions, respectively. Furthermore, the recombination rate is given by

$$\Gamma_{\alpha} = \frac{2\pi}{\hbar}|\sum_{z=1,2}\langle \mathrm{R}_z|d_z^{\dagger}b_z c_z t_{\mathrm{i}}|\alpha\rangle|^2\rho_{\mathrm{R}}. \tag{S7}$$

Diagonalization of the hole and electron Hamiltonians is trivial, yielding the well-known symmetric (+) and antisymmetric (−) wavefunctions. Accordingly, the hole eigenfunctions are given by

$$|\pm\rangle_{\mathrm{h}} = \frac{|1\rangle_{\mathrm{h}} \pm |2\rangle_{\mathrm{h}}}{\sqrt{2}}, \tag{S8}$$

with the associated eigenenergies $E_{\mathrm{h}}^{\pm} = \pm t_{\mathrm{h}}^{z}$. The electron eigenfunctions and eigenenergies take up an analogues form. The CT eigenstates are given by different combinations of the product of hole and electron wavefunctions. An example of such a product state is

$$\begin{aligned} |\alpha\rangle &= |+\rangle_{\mathrm{h}} \otimes |-\rangle_{\mathrm{e}} \\ &= \frac{(|1\rangle_{\mathrm{h}} + |2\rangle_{\mathrm{h}}) \otimes (|1\rangle_{\mathrm{e}} - |2\rangle_{\mathrm{e}})}{2}, \end{aligned} \tag{S9}$$

which we denote simply as $(+,-)$, referring to the symmetric and antisymmetric character of the hole and electron wavefunctions, respectively. Substitution of this CT state into eq

S7 yields a recombination rate rigorously equal to zero,

$$\begin{aligned}\Gamma_{(+,-)} &= \frac{\pi t_{\mathrm{i}}^2}{2\hbar} \left| \langle \mathrm{R} | d_1^\dagger b_1 c_1 | 1 \rangle_{\mathrm{h}} \otimes | 1 \rangle_{\mathrm{e}} - \langle \mathrm{R} | d_2^\dagger b_2 c_2 | 2 \rangle_{\mathrm{h}} \otimes | 2 \rangle_{\mathrm{e}} \right|^2 \rho_{\mathrm{R}} \\ &= 0. \end{aligned} \tag{S10}$$

Hence, a complete cancellation of recombination occurs due to the neighboring electron-hole pairs located at $z = 1$ and those located at $z = 2$ being in antiphase. It follows readily that a similar cancellation affects recombination of the CT state $(-,+)$, while $(+,+)$ and $(-,-)$ experience a recombination rate of $\pi\, t_{\mathrm{i}}^2 \rho_{\mathrm{R}}/\hbar$.

The CT energies, on the other hand, are given by a sum of the hole and electron energies,

$$E_\alpha = E_{\mathrm{h}}^{\pm} + E_{\mathrm{e}}^{\pm} = \pm t_{\mathrm{h}}^z \pm t_{\mathrm{e}}^z. \tag{S11}$$

Since typically $t_{\mathrm{h,e}}^z \gg k_{\mathrm{B}}T$ at room temperature, the occurrence of charge recombination in a thermalized heterojunction depends on whether the band-bottom state is of the form $(+,-)$ or $(-,+)$, or of the form $(+,+)$ or $(-,-)$. This in turn depends on the sign of the hole and electron transfer integrals. More specifically, the lowest-value eigenenergy is given by

$$\begin{aligned} &E_{\mathrm{h}}^- + E_{\mathrm{e}}^-, \quad \text{if } t_{\mathrm{h}}^z, t_{\mathrm{e}}^z > 0, \\ &E_{\mathrm{h}}^+ + E_{\mathrm{e}}^+, \quad \text{if } t_{\mathrm{h}}^z, t_{\mathrm{e}}^z < 0, \\ &E_{\mathrm{h}}^- + E_{\mathrm{e}}^+, \quad \text{if } t_{\mathrm{h}}^z > 0,\ t_{\mathrm{e}}^z < 0, \\ &E_{\mathrm{h}}^+ + E_{\mathrm{e}}^-, \quad \text{if } t_{\mathrm{h}}^z < 0,\ t_{\mathrm{e}}^z > 0. \end{aligned} \tag{S12}$$

This demonstrates that a coherent suppression of charge recombination through either $(+,-)$ or $(-,+)$ requires the hole and electron transfer integrals (in the direction perpendicular to the donor-acceptor interface) to be of opposite sign. Generalized in more dimensions, this condition needs to be fulfilled *at least* in one direction.