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Correction to "Charge Recombination Suppressed by Destructive Quantum Interference in Heterojunction Materials"

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The analysis of recombination of triplet charge transfer states (^{3}CT) presented in the manuscript is incomplete, as it implicitly assumes conditions that do not generally hold. Here, we clarify under what conditions the results given in the manuscript are valid and indicate what steps are to be taken to extend the theory to the most general situation. First, however, we stress that, when applied to recombination of singlet charge transfer states (^{1}CT), the analysis and results presented in the manuscript are complete and correct. We would also like to take the opportunity to highlight their importance to geminate recombination and their potential role in supporting the initial charge separation event in organic photovoltaics, because the involved charge transfer states are entirely composed of ^{1}CT.

The complete formulation of the recombination of ^{3}CT state α (eq 4) is given by

$$\Gamma_\alpha = \frac{2\pi}{\hbar}\sum_\beta \left| \sum_{\vec{m}\in \mathrm{D},\vec{n}\in \mathrm{A}} \langle \beta | d_{\vec{m}}^\dagger b_{\vec{m}} c_{\vec{n}} t_1 \delta(\vec{m}, \vec{n} - \hat{x}) | \alpha \rangle \right|^2 \rho(\omega_\alpha - \omega_\beta) \tag{C1}$$

where the first summation extends over all product triplet states β in the recombined (R) manifold, and we use $\rho(\omega)$ to represent the associated spectral density. The operator $d_{\vec{m}}^\dagger$ creates the local triplet excitation $|r_{\vec{m}}\rangle$ at donor site $\vec{m}$. Expressed in the local basis, R states can generally be formulated as $|\beta\rangle = \sum_{\vec{m}} c_{\vec{m}}^\beta |r_{\vec{m}}\rangle$. Consequently

$$\Gamma_\alpha \propto \sum_\beta \left| \sum_{y,z} c_{(N,y,z)}^\beta c_{(N,y,z),(N+1,y,z)}^\alpha \right|^2 \rho(\omega_\alpha - \omega_\beta) \tag{C2}$$

The results presented in Figure 3 are retained when $\rho(\omega_\alpha - \omega_{\beta'}) = \rho_\mathrm{R}$, whereas $\rho(\omega_\alpha - \omega_\beta) = 0$ for all $\beta \neq \beta'$, and the state β' satisfies $c_{(N,y,z)}^{\beta'} = c_0^{\beta'}$ for all x,y. In words, they are retained when the spectral density exclusively supports recombination toward a triplet state that is homogeneously delocalized and in-phase over the heterojunction interface. Furthermore, the results presented in Figure 4 are retained when such selectivity of the triplet states applies to all ^{3}CT states within thermal reach, which requires the splitting between triplet states to exceed $k_\mathrm{B}T$.

As outlined above, the applicability of the results for ^{3}CT presented in the manuscript puts restrictions on the nature of the R states and the spectral density. However, the restrictions expectedly are less severe than the "idealized" cases shown in Figures 3 and 4 might suggest. For example, a delocalization of the R states over two sites suffices to show the type of interference effects reported in the manuscript (as suggested by the Supporting Information). Also, instead of the rigid selectivity assumed for the figures, the spectral density can realistically weigh additional R states close in energy, as long as these states have similar phase behavior. For instance, when the thermalized ^{3}CT states are sign-alternating, recombination toward a variety of triplet states will be coherently suppressed provided that these states change phase slowly along the heterojunction interface. This additionally allows for the triplet splittings to be smaller than the thermal quantum. To further explore this, we plan to extend our microscopic analysis to explicitly include the full band of recombined states and a physically motivated spectral density in a future study. Nevertheless, our results suggest that detailed knowledge about the nature of product triplet states (e.g., through ab initio calculations) is required to fully understand ^{3}CT recombination in realistic materials.

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