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Reply to "Comment on 'Exothermic Rate Restrictions in Long-Range Photoinduced Charge Separations in Rigid Media'"

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The Comment (DOI 10.1021/jp111064q) by Angulo, Rosspeintner, and Vauthey (ARV) on the electron transfer rates in glycerol:methanol (9:1) matrices at 255 K reported by us,[1] and later corrected,[2] raises interesting issues on the analysis of the fluorescence decays (kinetic model, scaling procedure, parameters) and on its consistency with steady-state fluorescence.

Various kinetic models have been proposed to describe the dynamic quenching of luminescence by electron transfer in rigid matrices.[3−6] These models typically involve the minimum contact distance between electron donor and acceptor (r_0), the rate constant at contact (k_{ET}^0), and a distance decay factor (β). Additionally, they may also include properties of the matrix or a spatial distribution function of the quencher, but when convolution with the instrumental response is required to extract the parameters of the model, the role of these additional parameters cannot be assessed reliably.

The kinetic model employed in refs 1 and 2 is appropriate for a low concentration of quencher in a continuous medium. The concentrations employed in ref 1 range between 0.04 and 0.16 M and can be considered small. The medium is not homogeneous in the space probed by the electron transfer (less than 20 Å), but the nonnegligible fluidity (diffusion coefficient $D_a = 0.002$ Å^2 ns^{-1}) lessens the nonhomogeneity. In view of the experimental conditions chosen to measure electron transfer rates, the kinetic model is appropriate and has the advantage of fitting only two parameters to the decays, because the values of r_0 were calculated with molecular modeling. In fact, β was kept constant for all the systems (eight fluorophore/quencher pair and at least three concentrations per pair) and only k_{ET}^0 was fitted to the kinetic data in refs 1 and 2.

The SPC decays of a given fluorophore at different quencher concentrations were scaled by the fluorescence intensities measured by steady state (I/I_0) and the same was done for the calculated decays. The fact that I/I_0 was employed to multiply both experimental and calculated decays makes the actual value of I/I_0 irrelevant for the minimization of the sum of the squared residuals used as best-fit criterion. The same values of β and k_{ET}^0 are fitted without any scaling and the scaling only improves the visualization. Figure 1 presents the SPC decays for the quenching of pyrene by fumaronitrile without any scaling, in linear and logarithmic scales, together with the calculations with the values of β and k_{ET}^0 for this system reported in ref 2. The calculations were extended to earlier times, where scatter interferes with the decays and was removed from the experimental points, to emphasize that for $t = 0$ these decays tend to unity.

The kinetic parameters fitted to the SPC decays are totally independent of the steady-state data but, as rightfully pointed out by ARV, the time integrals of the decays should be identical to I/I_0 for all quencher concentrations. As explained in detail in ref 2, the authors of this Reply were able to retrieve all the original SPC decays and tested the reproducibility of some of the decays. However, the intensive use of the fluorimeter and the procedures

of its data storage did not facilitate the retrieval all the steady-state data. The recovered absorption spectra are even more fragmentary. The absorption spectra are necessary to correct the fluorescence spectra by absorption intensities differences at the excitation wavelength. The fluorescence spectra presented in the Supporting Information of ref 2 are the recovered spectra, when available, or the fluorescence spectra of ref 1, when the spectra were not recovered. However, in the absence of reliable absorption spectra, the Perrin plots in ref 2 made use of the original fluorescence spectra. They are only indicative of critical radii between 8 and 15 Å. The most important differences between the intensities of the fluorescence spectra in refs 1 and 2 were observed for pyrene in the presence of fumaronitrile. Figure 2 presents the corresponding Perrin plots. In passing, we take the opportunity to clarify the odd presentation of eq 5, where parentheses in the denominator were omitted in ref 1 although the calculations were correctly performed, which should be read as

$$\frac{I}{I_0} = \exp\left(\frac{[Q]}{3/(4\pi R_c{}^3)}\right) = \exp\left(\frac{4}{3}\pi R_c{}^3 [Q]\right)$$

Unfortunately we cannot tell whether the differences in Figure 2 are due to appropriate corrections for absorption differences or to intentional bias of the first author of ref 1. However, the values of β and k_{ET}^0 reported in ref 2 are totally independent of these data.

It should be noted that other authors using the same kinetic model employed a different scaling procedure.[7,8] Consistency between the kinetic decays and the steady-state fluorescence intensities at different quencher concentrations was obtained scaling the integrated luminescence decays by the relative quantum yields of the steady-state luminescence.[9] The representation of the decays in a linear scale (Figure 1) shows that the first few nanoseconds of a hundreds of nanosecond decay make only a small contribution to the integrated decay and can be neglected in such cases, avoiding the difficulties of the convolution with the instrumental response. Decoupling between β and k_{ET}^0 in our work is not critically dependent on scaling because the compensation between β and k_{ET}^0 breaks down for $\beta < 1.2$ Å^{-1} for the slowest systems (e.g., Py + MN) and for $\beta > 1.5$ Å^{-1} for the fastest systems (e.g., Np + FN). Using $\beta = 1.3$ Å^{-1} it was possible to fit very well all the decays with the rate constants reported in ref 2. Further refinement of the value of β in the interval $1.2 < \beta < 1.5$ Å^{-1} could benefit from the scaling by the integrated luminescence decays and may become relevant for long-range electron transfers experienced by long-lived luminescent probes.

In summary, the absorption and steady-state fluorescence spectra of ref 1 were only partially recovered and this limits our ability to evaluate their consistency with the kinetic data. However, the SPC
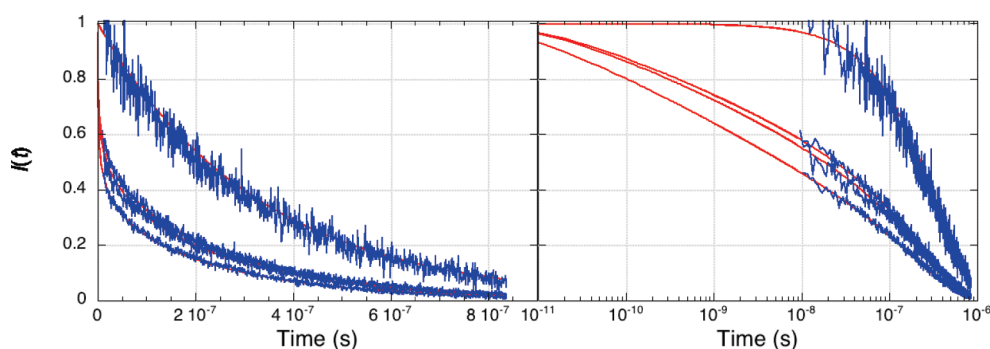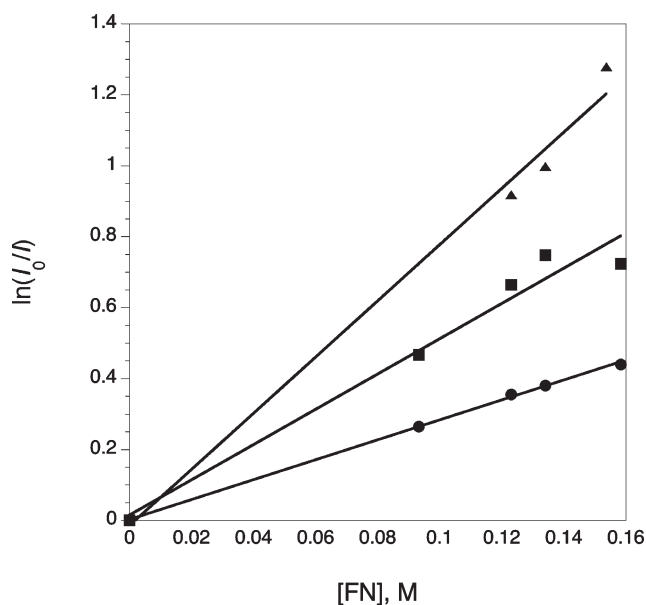
Figure 1. Single photon counting of pyrene ($\tau_0 = 325$ ns) and its quenching by fumaronitrile ([FN] = 0.123, 0.134, and 0.154 M), compared with fits using $\beta = 1.3$ Å^{-1} and $k_{ET}^0 = 1 \times 10^{11}$ s^{-1} (lowest and intermediate concentrations) or 2×10^{11} s^{-1} (highest concentration).

Figure 2. Perrin plots from steady-state and time-resolved data for the quenching of pyrene by fumaronitrile: (●) fluorescence intensities in ref 1, presumably corrected for absorption differences; (■) fluorescence intensities of spectra directly retrieved from the fluorimeter; (▲) calculated with the parameters used to fit the decays in Figure 1.

data were totally recovered and confirmed, and the fitting of β and k_{ET}^0 to these data is completely independent of the less reliable steady-state data. The data analysis of ref 2 was correctly performed, the two fitted parameters are physically meaningful and are independent of scaling procedures. In fact, the value of β is indistinguishable from the value reported for a very similar system,[6] and we can consider that only k_{ET}^0 was fitted to the nonexponential decays reported in ref 2. Perhaps more importantly, the experimental systems were correctly designed to interrogate the existence of exothermic rate restrictions in long-range charge separations and a proper data analysis was described for such systems. In view of the events described in ref 2, rather than pursuing the investigation of rate restrictions with such systems ourselves, we believe that our original paper should be regarded as a guide to look for the Marcus inverted region in matrices.

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(9) We thank a reviewer for pointig out this fact.