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Supporting Information for "Structural and Dynamical Heterogeneity of Dyes on TiO_2: Implications for Charge Transfer across Organic-Inorganic Interfaces"

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Atomic centered basis set for projection. As demonstrated by Dunnington and Schmidt,[1] large basis sets are not necessary for a qualitatively good projection from plane waves to an atomic centered basis set. Thus, the 3-21G basis set was used for all atoms except Re, for which there is no such basis set. The fractional localization of the dye LUMO on the dye should not depend much on the Re basis set since there is just one such atom in the system, and it is buried inside the dye molecule. However, to maintain a balanced approach, the Tc 3-21G basis set was used for Re.

Correlation of ReEtC LB with bipyridine-surface distance.

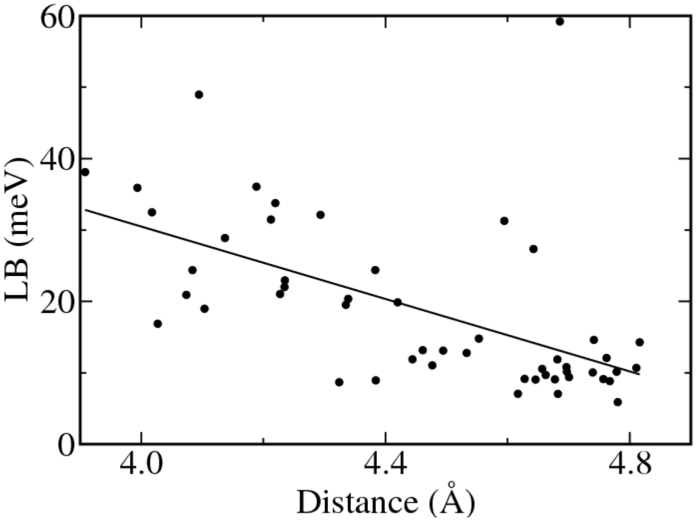

Figure S1. LB (solid points) plotted as a function of the average distance of the bipyridine heavy atoms from the surface. A linear regression (solid line) is shown as a guide to the eye.

Autocorrelation functions.

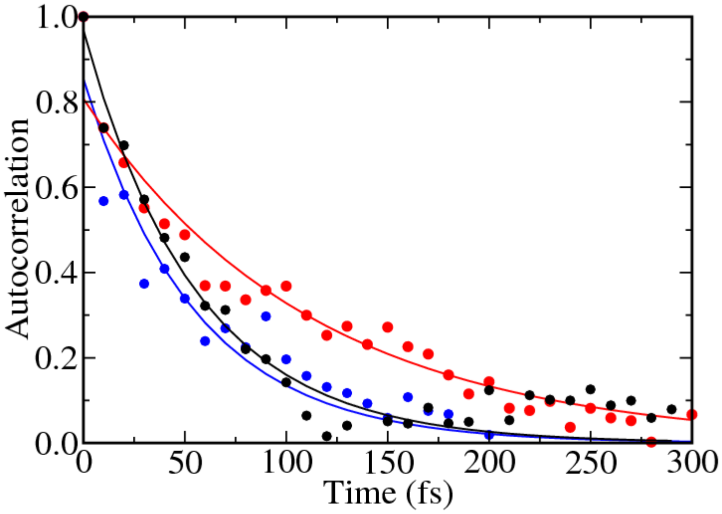

Figure S2. Autocorrelation of E_{LUMO} - E_{CBM} fluctuations (solid points) fit to an exponential decay (solid line) for bulk acetonitrile (black, time constant = 56 fs, reproduced from the manuscript Figure 6a), monolayer acetonitrile (red, 110 fs), and bulk DMF (blue, 54 fs).

References

1. B. D. Dunnington and J. R. Schmidt, *J. Chem. Theory Comput.*, 2012, **8**, 1902–1911.