Supplementary Materials: Effect of the Donor Size on the Rate of the Photo-Induced Electron Transfer

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1. Electronic coupling

To the first approximation, the electronic coupling can be expressed as

$$H_{el} =< \psi_P|\hat{H}|\psi_R >\approx a A_P A_R S_{ol} \tag{S1}$$

where ψ_P and ψ_R are the wave functions of the product and reactant states, A_P and A_R are the amplitudes of corresponding wave functions, S_{ol} is the overlap volume of the wave functions, and a is a constant having units of energy (note that $A_f A_i S_{ol}$ is a dimensionless term) .

We assume that the donor and acceptor are spheres with radii R_D and R_A, respectively. Ignoring all specific features of the wave functions, the normalization condition is

$$\int \psi^2 ds \approx A^2 \frac{4\pi}{3} R^3 = 1 \tag{S2}$$

or $A = \sqrt{\frac{3}{4\pi R^3}} \propto R^{-3/2}$, where R is the radius of the donor or acceptor.

2. Overlap area

Considering an exponentially decaying $H_{el}^2 \propto \exp(-\beta x)$ and assuming that it results from exponential decay of wave function ψ_P and ψ_R, we can evaluate dependence of the H_{el}^2 on radii of the D and A from a simplified geometrical presentation shown in Figure S1.

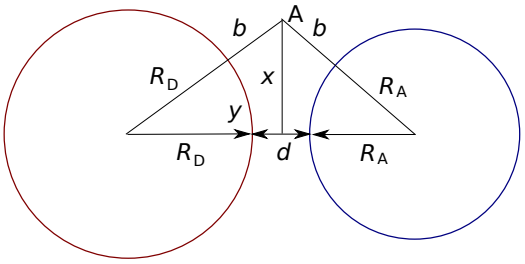

Figure S1. Schematic presentation of geometry used to estimate the overlap area. Point A is located at crossing of two circles with radii $R_D + b$ and $R_A + b$ with $b = (d + \beta^{-1})/2$.

The center-to-center distance is $D_{cc} = R_D + d + R_A$. The point A is places so that the distance from the D center is $R_D + b$ and from A center is $R_D + b$, where $b = (d + \beta^{-1})/2$ or half separation distance d plus the wave function decrement length β^{-1}. We need to evaluate its distance x from the line connecting centers. Let the distance from the center of D to the normal from point A to the line connecting centers of the D and A be y. Then

$$x^2 = (R_D + b)^2 - y^2 = (R_A + b)^2 - (D_{cc} - y)^2 \tag{S3}$$

then

$$2y = \frac{(R_D + b)^2 - (R_A + b)^2}{D_{cc}} + D_{cc} = \frac{R_D^2 - R_A^2 + 2b(R_D - R_A)}{D_{cc}} + D_{cc} \tag{S4}$$

or

$$y = \frac{(R_D - R_A)(R_D + R_A + 2b)}{2D_{cc}} + \frac{1}{2} D_{cc} \tag{S5}$$

Since

$$x = \sqrt{(R_D + b)^2 - y^2} \tag{S6}$$

we get

$$x = \sqrt{(R_D + b)^2 - \frac{1}{4}\left[\frac{(R_D - R_A)(R_D + R_A + 2b)}{D_{cc}} + D_{cc}\right]^2} \tag{S7}$$

The modeled x values calculated for $d = 0.1$, 0.4 and 0.8 nm are presented in Figure S2. The value of x, or the radius of overlapping does not change much on the R_D changing from 0.4 to 4 nm, which is roughly the difference between porphyrin and quantum dot donors. For $d = 0.1$ nm, x increases by roughly 35%. However, the overlapping volume is roughly $V_{ol} \approx \pi x^2 \beta^{-1}$, and since $k_{ET} \propto H_{ei}^2$, the expected dependence of the ET rate constant is $k_{ET} \propto x^4$, which results in 3.3 times difference between donors with 0.4 and 4 nm radii.

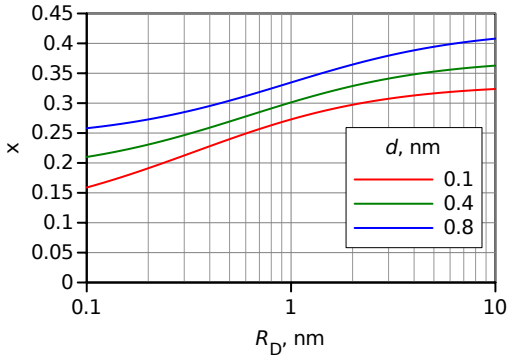

Figure S2. Radius of the overlap area calculated according to eq.(7).

Figure S3 (similar to Figure 4 in the main text) presents the dependence of the overlap volume square on the donor radius, or (relative) x^4 on R_D. It ignores completely any specific features of the wave function and can be considered as a general trend only. The trend shows that if only wave function amplitude is accounted for, the rate of ET is underestimated for large donors, such as QDs, relative to small ones, such as molecular, donors by factor 2–4.

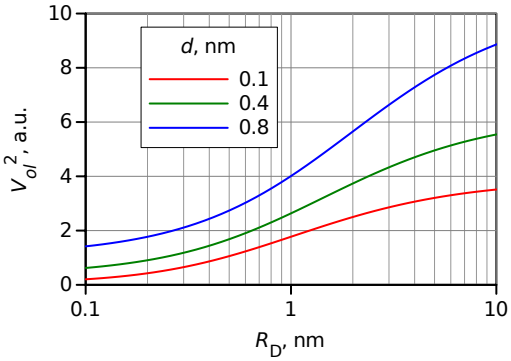

Figure S3. The dependence of V_{ol}^2 on donor radius.