

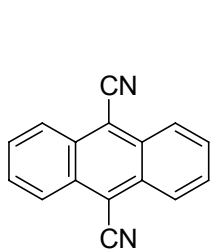
Supporting Information for:

**Free Energy Dependence of the Diffusion-Limited Quenching Rate Constants in
Photoinduced Electron Transfer Processes**

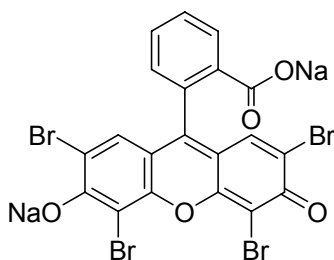
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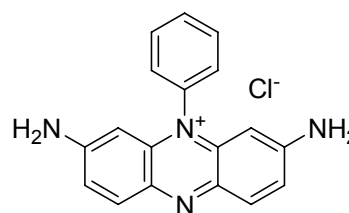
Chart 1: Structure of the fluorophores involved in the study.



9,10-Dicyanoanthracene



Eosin Y



Phenosafranine

Figure 1-SI: Fluorescence decay of DCA in acetonitrile in the presence of TMPD 0.02 M. Lamp profile (curve a, ●) and response function (curve b, ○). The solid line represents the fit of the experimental data to a monoexponential decay model ($\tau=1.69$ ns, $\chi^2 = 1.082$).

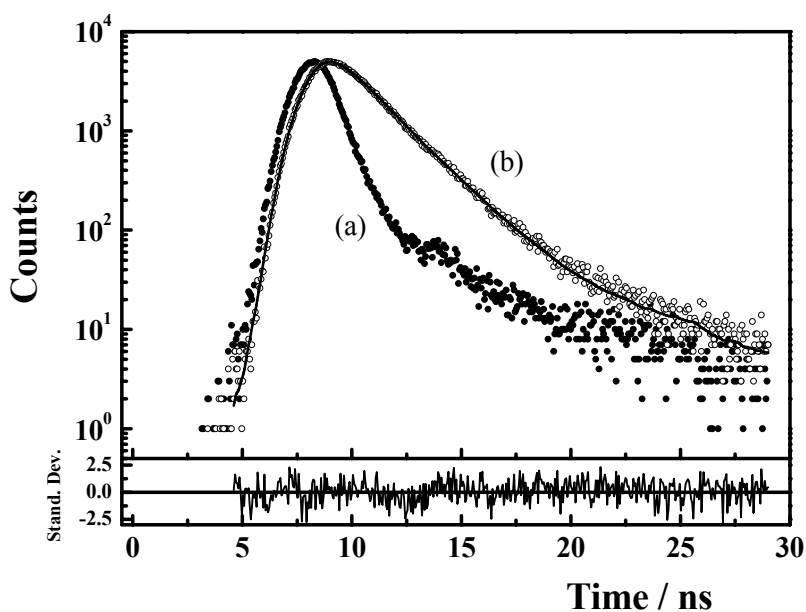


Figure 2-SI: Stern-Volmer (τ_o / τ) plots for the quenching of DCA by anisole (\blacktriangle); 124TMB (\circ) and TMPD (\bullet) in acetonitrile at 298 K.

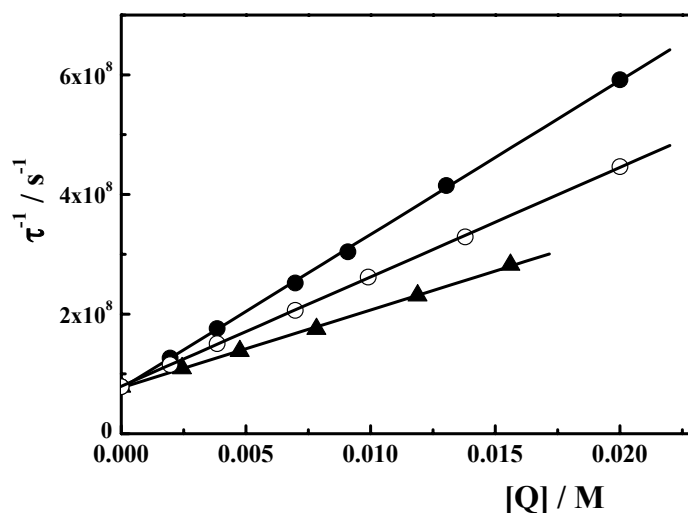


Figure 3 SI: Bimolecular rate constants (k_q) for the quenching of DCA (\square) and PS (\circ) by electron donors, PS (\bullet) and Eosin Y (\blacksquare) by electron acceptors and Rehm and Weller data (\times) as a function of ΔG_{et} . The solid line corresponds to the simulation of the second order diffusion-mediated ET rate constant according to the model developed by Tachiya and Murata. The parameters used for the simulation are: $r_D = r_A = 0.35$ nm, $\lambda_v = 0.35$ eV, $V_o = 100$ cm⁻¹, $\beta = 10$ nm⁻¹ and $D = 3.0 \times 10^{-9}$ m²/s.

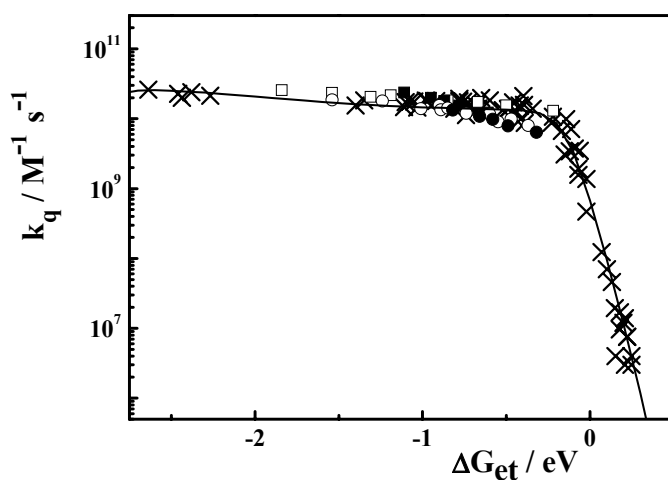


Table 1-SI: Bimolecular rate constants (k_q) for the singlet excited state quenching of Phenoafranine by aromatic electron donors in acetonitrile at 298 K. The data were taken from Ref. 22 (main text).

Quencher	E_{ox} (V vs. SCE)	ΔG_{et} (eV)	$k_q \times 10^{10}$ ($M^{-1} s^{-1}$)	β (nm^{-1})
TMPD	0.16	-1.54	1.87	8.5
TMBZ	0.32	-1.24	1.80	8.8
p-anisidine	0.66	-1.01	1.39	9.2
N,N-dimethylaniline	0.77	-0.90	1.54	9.4
p-toluidine	0.78	-0.89	1.34	9.4
N-methylaniline	0.82	-0.85	1.42	9.4
aniline	0.93	-0.74	1.20	9.6
2-methylindole	1.07	-0.60	1.16	9.8
1,2,4-trimethoxybenzene	1.12	-0.55	0.90	9.8
indole	1.20	-0.47	0.99	9.8
1,4-dimethoxybenzene	1.30	-0.37	0.80	9.8

Table 2-SI: Estimated radii (R) and AM1 theoretically calculated contributions of the internal reorganization energy, λ_v .

Compound	R / nm	λ_{vA} / eV	λ_{vD} / eV
1,9-Dicyanoanthracene	0.37	0.10	-
Phenosafranin	~ 0.41	0.30	0.11
Eosin Y	~ 0.47	-	0.11
Aromatic amines	0.31	-	~0.31
Metoxybenzenes	0.31	-	~0.24
Quinones	0.27	~0.23	

Calculation of the exponential factor (β)

Table 3-SI: Estimated β for the solvent mediated photoinduced ET reaction between DCA and electron donors in acetonitrile.

Quencher	ΔG_{AS}^a (eV)	ΔG_{DS}^b (eV)	ΔG_{eff}^c (eV)	β^d (nm^{-1})	β^e (nm^{-1})
TMPD	3.3	2.7	2.7	15.9	9.4
TMBZ	3.3	2.8	2.8	16.4	9.7
p-anisidine	3.3	3.2	3.2	17.4	10.2
p-toluidine	3.3	3.3	3.3	17.7	10.3
1,2,4-trimethoxybenzene	3.3	3.6	3.3	17.7	10.3
1,4-dimethoxybenzene	3.3	3.8	3.3	17.7	10.3
1,2-dimethoxybenzene	3.3	4.0	3.3	17.7	10.3

Anisole	3.3	4.3	3.3	17.7	10.3
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a) $\Delta G_{AS} = E_{oxS} - E_{redA} - E_{ooA}$, where A is the fluorophore, b) $\Delta G_{DS} = E_{oxD} - E_{redS}$, where D is the quencher, c) $\Delta G_{eff} = \min(\Delta G_{AS}, \Delta G_{DS})$, d) Calculated according to Gamow expression, eq. 10, e) Calculated according to Kibori expression, eq. 11, with $\lambda_{se} = 1$ eV, $\nu_s = 850$ cm⁻¹ and $d_{ss} = 0.5$ nm. The oxidation and reduction potentials of the solvent (acetonitrile) were taken from Ref 27 (main text), $E_{oxS} = +5.21$ V vs SCE and $E_{redS} = -2.51$ vs SCE.

Table 4-SI: Estimated β for the solvent mediated photoinduced ET reaction between phenosafranine and electron donors in acetonitrile.

Quencher	ΔG_{AS} ^a (eV)	ΔG_{DS} ^b (eV)	ΔG_{eff} ^c (eV)	β^d (nm ⁻¹)	β^e (nm ⁻¹)
TMPD	3.5	2.7	2.7	15.9	9.4
TMBZ	3.5	2.8	2.8	16.4	9.7
p-anisidine	3.5	3.2	3.2	17.4	10.2
N,N-dimethylaniline	3.5	3.3	3.3	17.7	10.3
p-toluidine	3.5	3.3	3.3	17.7	10.3
N-methylaniline	3.5	3.3	3.3	17.8	10.4
aniline	3.5	3.4	3.4	18.1	10.5
2-methylindole	3.5	3.6	3.5	18.4	10.6
1,2,4-trimethoxybenzene	3.5	3.6	3.5	18.4	10.6

indole	3.5	3.7	3.5	18.4	10.6
1,4-dimethoxybenzene	3.5	3.8	3.5	18.4	10.6

a) $\Delta G_{AS} = E_{oxS} - E_{redA} - E_{ooA}$, where A is the fluorophore, b) $\Delta G_{DS} = E_{oxD} - E_{redS}$, where D is the quencher, c) $\Delta G_{eff} = \min(\Delta G_{AS}, \Delta G_{DS})$, d) Calculated according to Gamow expression, eq. 10, e) Calculated according to Kibori expression, eq. 11, with $\lambda_{se} = 1$ eV, $\nu_s = 850$ cm⁻¹ and $d_{ss} = 0.5$ nm. The oxidation and reduction potentials of the solvent (acetonitrile) were taken from Ref 27 (main text), $E_{oxS} = +5.21$ V vs SCE and $E_{redS} = -2.51$ vs SCE.

Table 5-SI: Estimated β for the solvent mediated photoinduced ET reaction between Eosin Y and electron acceptors in acetonitrile.

Quencher	ΔG_{AS} ^a (eV)	ΔG_{DS} ^b (eV)	ΔG_{eff} ^c (eV)	β ^d (nm ⁻¹)	β ^e (nm ⁻¹)
chloro-p-benzoquinone	5.55	1.0	1.0	9.8	6.0
p-benzoquinone	5.71	1.0	1.0	9.8	6.0
methyl-p-benzoquinone	5.79	1.0	1.0	9.8	6.0
2,6-dimethylbenzoquinone	5.88	1.0	1.0	9.8	6.0
duroquinone	6.05	1.0	1.0	9.8	6.0

a) $\Delta G_{AS} = E_{oxS} - E_{redA}$, where A is the quencher, b) $\Delta G_{DS} = E_{oxD} - E_{redS} - E_{ooD}$, where D is the fluorophore, c) $\Delta G_{eff} = \min(\Delta G_{AS}, \Delta G_{DS})$, d) Calculated according to Gamow expression, eq. 10, e) Calculated according to Kibori expression, eq. 11, with $\lambda_{se} = 1$ eV, $\nu_s =$

850 cm^{-1} and $d_{ss} = 0.5 \text{ nm}$. The oxidation and reduction potentials of the solvent (acetonitrile) were taken from Ref 27 (main text), $E_{oxS} = +5.21 \text{ V vs SCE}$ and $E_{redS} = -2.51 \text{ vs SCE}$.

Table 6-SI: Estimated β for the solvent mediated photoinduced ET reaction between phenoafranine and electron acceptors in acetonitrile.

Quencher	ΔG_{AS}^a (eV)	ΔG_{DS}^b (eV)	ΔG_{eff}^c (eV)	β^d (nm^{-1})	β^e (nm^{-1})
chloro-p-benzoquinone	5.55	1.5	1.5	11.9	7.2
p-benzoquinone	5.71	1.5	1.5	11.9	7.2
methyl-p-benzoquinone	5.79	1.5	1.5	11.9	7.2
2,6-dimethylbenzoquinone	5.88	1.5	1.5	11.9	7.2
duroquinone	6.05	1.5	1.5	11.9	7.2

a) $\Delta G_{AS} = E_{oxS} - E_{redA}$, where A is the quencher, b) $\Delta G_{DS} = E_{oxD} - E_{redS} - E_{ooD}$, where D is the fluorophore, c) $\Delta G_{eff} = \min(\Delta G_{AS}, \Delta G_{DS})$, d) Calculated according to Gamow expression, eq. 10, e) Calculated according to Kibori expression, eq. 11, with $\lambda_{se} = 1 \text{ eV}$, $\nu_s = 850 \text{ cm}^{-1}$ and $d_{ss} = 0.5 \text{ nm}$. The oxidation and reduction potentials of the solvent (acetonitrile) were taken from Ref 27 (main text), $E_{oxS} = +5.21 \text{ V vs SCE}$ and $E_{redS} = -2.51 \text{ vs SCE}$.

Figure 4-SI: Experimental k_q for the quenching of PS emission by electron donors (○). The solid line corresponds to the simulation of the second order diffusion-mediated electron transfer rate constant according to the model developed by Tachiya and Murata. The parameters used for the simulation are: $r_A = 0.41 \text{ nm}$, $r_D = 0.31 \text{ nm}$, $\lambda_\nu = 0.61 \text{ eV}$, $V_o = 100 \text{ cm}^{-1}$, $\beta = 10 \text{ nm}^{-1}$ and $D = 3.2 \times 10^{-9} \text{ m}^2 / \text{s}$.

