## Supporting Information Beyond the Förster formulation for resonance energy transfer: the role of dark states

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### Absorption and fluorescence spectra of P and parametriza-

### tion of the relevant two-state model

The experimental spectra of the dye dissolved in solvents of different polarity are shown in the top panel of Figure S1. **P** were purchased by Exciton and used without any further purification. Spectra-grade solvents were obtained from Aldrich. Absorption spectra were recorded with a Perkin-Elmer Lambda 650 spectrophotometer, while emission spectra were recorded on a Horiba Jobin Ivon FluoroMax-3 spectrofluorometer on dilute solutions (typical concentrations  $\sim 10^{-6}$  M).

Linear optical spectra of **P** can be satisfactorily reproduced based on the standard essential-state model for polar chromophores<sup>59,76,80,85</sup>, which represents an extension of the two-state electronic model described in Section 2 to account for molecular vibrations and polar solvation. According to the procedure explained in detail in a previous work<sup>59</sup>, absorption and fluorescence spectra of polar chromophores and their evolution

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Figure S1: Top panel: experimental absorption and emission spectra of **P** in different solvents (Tol=toluene, CHCl<sub>3</sub>=chloroform, DMSO=dimethylsulfoxide). Bottom Panel: calculated spectra according to the two-state model<sup>59</sup>. Model parameters are listed in Table S1.

Table S1: Essential-state parameters for **P**. Details about the two-state model accounting for the coupling with molecular vibrations and polar solvation are reported in previous works<sup>59,78</sup>

	$\eta$ (eV)	$\sqrt{2}t$ (eV)	$\omega_{v} (eV)$	$\varepsilon_{v} (eV)$	$\gamma$ (eV)	$\mu_0$ (D)
Р	1.52	1	0.16	0.2	0.06	18

with the solvent polarity can be reproduced adjusting the electronic model parameters,  $\eta$  and  $\sqrt{2}t$ , defined in Section 2, the vibrational frequency,  $\omega_v$ , of an effective coupled vibrational mode, and the corresponding relaxation energy,  $\varepsilon_v$ , plus a parameter,  $\gamma$ , that measures the half-width at half-maximum of the Gaussian band assigned to each vibronic transition. All these parameters are kept constant irrespective of the solvent. The spectral evolution with the solvent polarity is finally accounted for by a single parameter,  $\varepsilon_{or}$ , the solvent relaxation energy, that increases with the solvent polarity. The spectra calculated for **P** are shown in the bottom panel of Figure S1, respectively, and relevant model parameters are listed in Table S1.

## Explicit expression of coulombic interaction terms between a polar energy donor and a quadrupolar energy acceptor

The following equations report  $V_{Q_1}$  and  $V_{Q_2}$  as relevant to the geometrical arrangement reported in Figure 2:

$$V_{Q_1} = \frac{e^2}{4\pi\epsilon_0 n^2} \left( -\frac{1}{\sqrt{(r-\frac{l}{2}\sin\phi)^2 + (L-\frac{l}{2}\cos\phi)^2}} - \frac{1}{\sqrt{(r+\frac{l}{2}\sin\phi)^2 + (\frac{l}{2}\cos\phi)^2}} + \frac{1}{\sqrt{(r-\frac{l}{2}\sin\phi)^2 + (\frac{l}{2}\cos\phi)^2}} \right)$$
$$+ \frac{1}{\sqrt{(r+\frac{l}{2}\sin\phi)^2 + (L+\frac{l}{2}\cos\phi)^2}} + \frac{1}{\sqrt{(r-\frac{l}{2}\sin\phi)^2 + (\frac{l}{2}\cos\phi)^2}} \right)$$
$$V_{Q_2} = \frac{e^2}{4\pi\epsilon_0 n^2} \left( -\frac{1}{\sqrt{(r+\frac{l}{2}\sin\phi)^2 + (\frac{l}{2}\cos\phi)^2}} - \frac{1}{\sqrt{(r-\frac{l}{2}\sin\phi)^2 + (L+\frac{l}{2}\cos\phi)^2}} + \frac{1}{\sqrt{(r-\frac{l}{2}\sin\phi)^2 + (L-\frac{l}{2}\cos\phi)^2}} \right)$$
(1)

# Interaction between the transition charge densities of a polar energy donor and a octupolar energy acceptor

The following equations report  $V_{O_1}$ ,  $V_{O_2}$  and  $V_{O_3}$  as relevant to the geometrical arrangement of Figure 4:

$$\begin{split} V_{O_1} &= \frac{e^2}{4\pi\epsilon_0 n^2} \left( -\frac{1}{\sqrt{(r+l\sin\beta)^2 + (l\cos\beta)^2}} - \frac{1}{\sqrt{r^2 + L^2}} + \frac{1}{r} \right. \\ &+ \frac{1}{\sqrt{(r+l\sin\beta)^2 + (L-l\cos\beta\cos\phi)^2 + (l\cos\beta\sin\phi)^2}} \right) \\ V_{O_2} &= \frac{e^2}{4\pi\epsilon_0 n^2} \left( -\frac{1}{\sqrt{(r+l\sin\beta)^2 + (l\cos\beta)^2}} - \frac{1}{\sqrt{r^2 + L^2}} + \frac{1}{r} \right. \\ &+ \frac{1}{\sqrt{(r+l\sin\beta)^2 + (\frac{L}{2} + l\cos\beta\cos\phi)^2 + (\frac{\sqrt{3}L}{2} - l\cos\beta\sin\phi)^2}} \right) \\ V_{O_3} &= \frac{e^2}{4\pi\epsilon_0 n^2} \left( -\frac{1}{\sqrt{(r+l\sin\beta)^2 + (l\cos\beta)^2}} - \frac{1}{\sqrt{r^2 + L^2}} + \frac{1}{r} \right. \\ &+ \frac{1}{\sqrt{(r+l\sin\beta)^2 + (\frac{L}{2} + l\cos\beta\cos\phi)^2 + (\frac{\sqrt{3}L}{2} + l\cos\beta\sin\phi)^2}} \right) (2) \end{split}$$



Figure S2: The ground state optimized geometries of the molecular chromophores. Details of calculations are reported in Section 5.

#### **Results from ab-initio calculations**

Figure S2 shows the ground state optimized geometries of the three chromophores object of analysis, while Figure S3 reports the frontier molecular orbitals for the three dyes. Details about calculations are described in Section 5.



Figure S3: The isosurface of frontier molecular orbitals HOMO, HOMO-1, LUMO and LUMO+1 for the three dyes.



Figure S4: Transition charge density distributions relevant to different excitations of all molecular dyes.

Figure S4 shows the calculated transition densities for the three chromophores. All results refer to the absorption process (i.e. are calculated for the equilibrium geometry relevant to the ground state), with the only exception of **P**, whose transition density refer to the emission process (i.e. was obtained for the equilibrium geometry relevant to the  $S_1$  state). Specifically, as it can be seen from Figure S4, the transition densities for the first two singlet excited states of **Q** are delocalized over the entire molecule, resulting in an optically allowed transition  $S_0 \rightarrow S_1$  with finite transition dipole moment, and an optically forbidden transition  $S_0 \rightarrow S_2$  with vanishing transition dipole moment. For the octupolar dye **O**, the third singlet excitation is forbidden, whereas the first two singlet excitations are one-photon allowed and degenerate, as expected based on the molecular symmetry, and discussed in Section 2 within the essential-state picture.

Table S2 compares transition energies and dipole moments calculated within TDDFT, using different functionals, and results obtained with CIS and 6-31G(d,p) basis. Figure S5 compares RET energies calculated for the **P/Q** pair within TDDFT adopting different functionals, and Figure S6 shows similar results comparing TDDFT-B3LYP with

		B3LYP/6-31G(d,p)		mPW1PW91/6-31G(d,p)		HSE06/6-31G(d,p)		CIS/6-31G(d,p)	
Dye	Transition	Excitation	Oscillator	Excitation	Oscillator	Excitation	Oscillator	Excitation	Oscillator
		Energy (eV)	Strength	Energy (eV)	Strength	Energy (eV)	Strength	Energy (eV)	Strength
Р	$S_0 \rightarrow S_1 \text{ (abs)}$	3.97	0.37	4.06	0.39	4.03	0.39	5.22	0.72
	$S_1 \rightarrow S_0$ (fluo)	3.79	0.39	3.86	0.41	3.84	0.41	4.88	0.73
Q	$S_0 \rightarrow S_1$	2.79	2.26	2.88	2.35	2.77	2.23	3.87	2.89
	$S_0 \rightarrow S_2$	3.26	0.00	3.41	0.00	3.19	0.00	4.91	0.00

Table S2: Results obtained from TDDFT and CIS calculations in vacuum.

CIS results.



Figure S5: Comparison of RET energies calculated within TDDFT adopting different functionals. Black and orange symbols show RET energies towards the allowed and dark state of  $\mathbf{Q}$ , respectively.



Figure S6: Comparison of RET energies calculated within TDDFT and CIS. Black and orange symbols show RET energies towards the allowed and dark state of  $\mathbf{Q}$ , respectively.