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Regioselective Ultrafast Photoinduced Electron Transfer from Naphthols to Halocarbon Solvents

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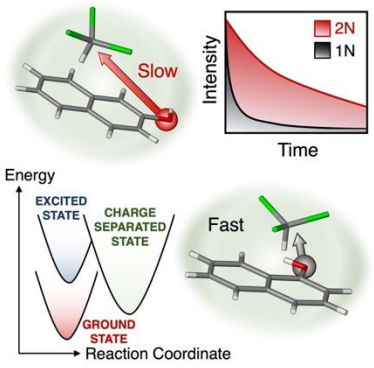
ABSTRACT: Excited state decay of 2-naphthol (2N) in halocarbon solvents has been observed to be significantly slower when compared to 1-naphthol (1N). In this study, we provide new physical insights behind this observation by exploring the regioselective electron transfer (ET) mechanism from photoexcited 1N and 2N to halocarbon solvents at a detailed molecular level. Using state-of-the-art electronic-structure calculations, we explore several configurations of naphthol-chloroform complexes, and find that the proximity of the electron accepting chloroform molecule to the electron-rich –OH group of the naphthol is the dominant factor affecting electron transfer rates. The origin of significantly slower electron transfer rates for 2N is traced back to the notably smaller electronic coupling when the electron accepting chloroform molecule is on top of the aromatic ring distal to the –OH group. Our findings suggest that regioselective photoinduced electron transfer could thus be exploited to control electron transfer in substituted acenes tailored for specific applications.

TOC GRAPHIC



Photoinduced electron transfer plays a key role in light harvesting molecular systems responsible for converting electromagnetic radiation into charge carriers.[1–6] Excited state processes are limited by the excited state lifetimes. The radiative decay pathway competes with the non-radiative pathways and typically involves charge separation and/or chemical changes. Understanding the molecular mechanisms of excited state decay is thus essential for a wide range of applications. One of the most important decay processes is via intermolecular electron transfer (ET), which is the focus of this paper.

Significant efforts have been undertaken to elucidate ET processes by tuning the donor-acceptor interactions through variation of molecular structures,[7] or by control of ET rates through molecular design of donor-acceptor dyad systems.[8–10] Time-resolved spectroscopic studies have revealed the relevant ET time-scales as well as geometric aspects that control the relaxation mechanisms by regulating the arrangement and separation of specific donor and acceptor units.[11] The interplay between fast "on-contact" ET reaction dynamics, and slow diffusional dynamics often makes it difficult to interpret solution-phase ET between freely moving donor and acceptor systems, and further intricacies occur upon the involvement of excited radical ion states.[12] Molecular design of donor-acceptor dyads with fixed donor-acceptor distances has enabled the analysis of electron transfer rates, as a function of free energy changes for a series of electron-acceptor moieties, eliminating the ambiguity that would otherwise be introduced with variable electron donor-acceptor distances.[13–15] However, photoinduced electron transfer from solute to solvent is more difficult to characterize because of the bulk nature of the solvent.[16,17] Many solute-solvent conformations are conducive to faster ET, whereas other configurations would be ineffective. Nevertheless, conformations leading to fast ET often make photoinduced electron transfer the most effective decay pathway. In fact, ET is often dominated by close contact interactions with the

fluctuating first coordination shell of solvent generating a distribution of solute-solvent configurations without significant diffusional character of donor-acceptor partners. This aspect has been understood to play a crucial role in donor-acceptor systems where the aromatic nature of both donor and acceptor makes the $\pi - \pi$ orbital interactions are the dominating factor. Examples for these can be found in important time-resolved ET studies using N,N-dimethylaniline as electron donating solvent and a variety of aromatic electron acceptors.[18–23] The size of such molecular systems makes computations prohibitively expensive with state-of-the-art quantum chemical calculational methodology. Hence, we first study a significantly more compact halocarbon solvent as an electron accepting case, with a moderately sized naphthol as the electron donor. With this, we analyze thermally accessible configurations to identify dominant configurations for efficient ET.

Previous studies have ascribed ET from electronically excited naphthol to the non-polar carbon tetrachloride (CCl_4) solvent as the main mechanism for ultrafast fluorescence decay, as observed by Time-Correlated Single Photon Counting (TCSPC) experiments.[24,25] However, a mechanism that could explain the appreciably slower excited state decay of 2-naphthol (2N) compared to 1-naphthol (1N) remains unknown and is the subject of this paper.

Here, we find new physical evidence for the photoinduced electron transfer mediated decay of the naphthol excited state making the photoinduced electron transfer from 1N much faster than from 2N. We focus on studying ET to the solvent by explicitly modeling the electron accepting solvent in complexation with the solute. We explore a distribution of configurations for the naphthol chromophore in close contact with the electron acceptor solvent in the first coordination sphere, while modeling the rest of the surrounding solvent as a polarizable continuum dielectric.

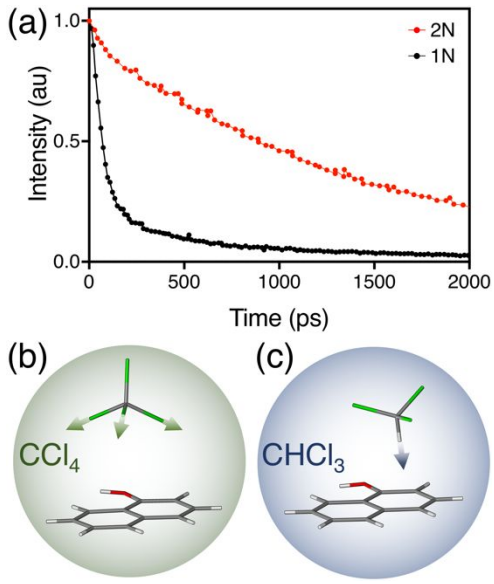


Figure 1. (a) TCSPC measurements of 1N and 2N in $CHCl_3$. **(b)** Optimized ground state geometry of 1N in CCl_4 showing C-Cl bonds forming an umbrella-like configuration on the naphthol. **(c)** $CHCl_3$ with the C-H bond pointing towards the naphthol aromatic ring.

We focus on chloroform since it is a solvent probe with directional character that allows for a systematic exploration of interactions in the electron donor-acceptor complex. Polar solvents like water were ruled out since they would lead to chemical changes resulting from the photoacidic property of naphthols, thus defeating the purpose of studying photoinduced electron transfer. A previous ET-mediated fluorescence quenching study was focused on CCl_4, a solvent without significant directionality.[24] The CCl_4 molecule interacts with the aromatic ring of naphthols, with the three C-Cl bonds forming an umbrella-like arrangement facing the naphthol fluorophore (Figure 1(b)).

Remarkably, the electronic excited state decay times differ by an order of magnitude when comparing 1N and 2N (1.4 ps in 1N *vs*. 13 ps in 2N, as measured by UV/IR pump-probe spectroscopy) in CCl_4. The difference is even more significant in chloroform (70 ps in 1N *vs*. 900

ps-1.9 ns in 2N), with 2N again exhibiting the slower decay (Figure 1(a)). Chloroform ($CHCl_3$) in the first solvation shell has the C-H bond usually pointing towards the naphthol (Figure 1(c)) thus functioning as a directional probe.

The analysis of energetically accessible configurations of naphthol-$CHCl_3$ complexes reveals that proximity of the electron accepting solvent molecule to the proximal aromatic ring ($R^{(1)}$), as the primary factor governing the ET rates. The close contact arrangement provides understanding of configurations that dominate photoinduced electron transfer in naphthols, providing a design principle for modulation of ET with –OH substituted polyacene electron donors.

The configurations of 1N and 2N in contact with $CHCl_3$ were obtained in a continuum dielectric environment, as described by the CPCM[26] model in Q-Chem 5.0.[27] The $CHCl_3$ electron acceptor was found to settle on top of the naphthol (Figure 2(d)) with the C-H bond pointing towards one of the rings ($R^{(1)}$ or $R^{(2)}$), as described by the ground electronic state at the B3LYP[28]-D (empirical dispersion correction from Chai & Head-Gordon[29])/6-31+G(d,p) level of theory.

In non-polar or weakly polar solvents, the ^1L_a state is higher than the ^1L_b state. Thus, following Kasha's rule, only the ^1L_b state emission is observed since fluorescence emission is observed from the lowest lying excited state, S_1.[30–34] The more ionic ^1L_a state[25,35–37] is formed predominantly by a $LUMO \leftarrow HOMO$ transition, whereas the ^1L_b state is primarily a combination of $LUMO \leftarrow HOMO - 1$ and $LUMO + 1 \leftarrow HOMO$.[38] TDDFT was used to generate the excited state configurations at B3LYP-D/6-31+G(d,p) level of theory. However, TDDFT was found to severely underestimate the ^1L_a energy and erroneously label it as the lowest excited state[39] leading to drastic errors in prediction of the emission and absorption spectra for naphthols. To circumvent this problem, all excitation energies were computed at the EOM-CCSD[40–48]/6-31+G(d,p) level of

theory as implemented in Q-Chem 5.0. EOM-CCSD allows us to identify the fluorescent ^1L_b state correctly and obtain all relative energies consistently for the various isomers of naphthols.

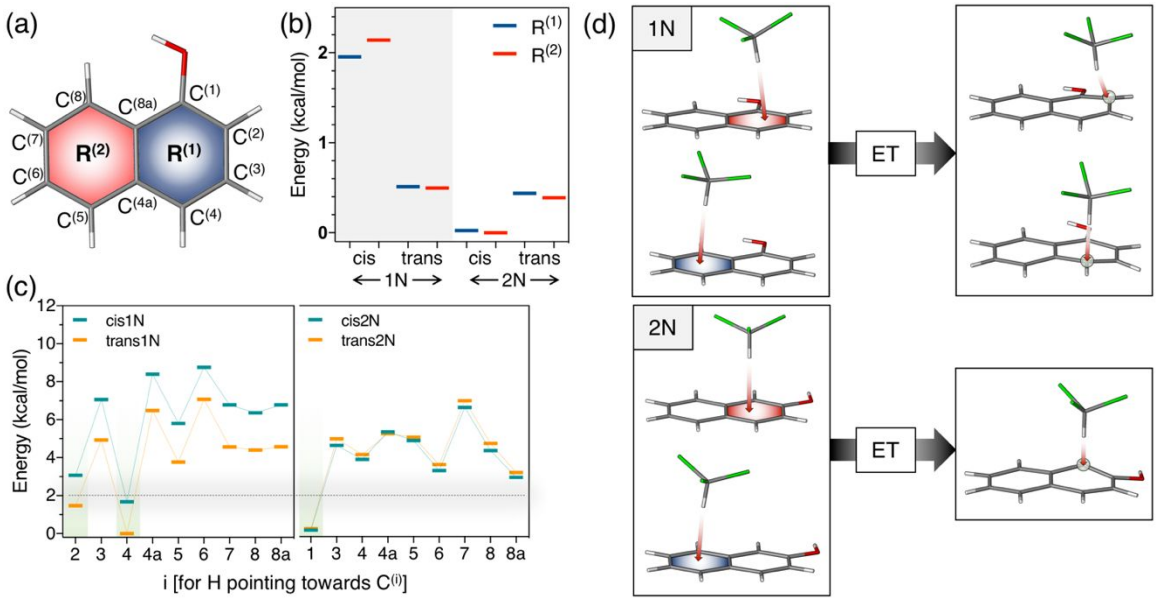


Figure 2. (a) Labelling of the aromatic rings of 1N. Energies of the 1N-$CHCl_3$ complex for various configurations in the (b) ground state and (c) charge-separated state. (d) Representative low energy configurations for cis1N and cis2N before and after electron transfer. Red arrows show the C-H bond pointing (left) towards the center of the ring (in the ground state) or (right) to a carbon atom (in the charge separated state).

Constrained-DFT (CDFT) optimizations provided the charge-separated (CS) state, as generated by photoinduced electron transfer, with the hole (*i.e.*, missing electron) constrained on the naphthol (donor) and the electron on the $CHCl_3$ (acceptor) molecule (Fig. 3). Preliminary CDFT calculations (see SI) show that $CHCl_3^-$ dissociates into $CHCl_2$ and Cl^-, consistent with earlier studies.[49,50] Since the dissociation succeeds the electron transfer, it is not relevant for this study of ultrafast dynamics of photoinduced electron transfer. Therefore, we analyze the CS state with constraints on the C-Cl and C-H bond lengths derived from a separate optimization of $CHCl_3^-$ at the MP2/6-311++G(d,p)

level of theory. This allows us to model the acceptor moiety after ET before pre-dissociation. We find that, in the CS state, $CHCl_3^-$ is placed above the naphthol ring with the C-H bond pointing towards one of the carbons of the naphthol. To gain further insights into stable CS state configurations, we performed optimizations with geometry constraints, and obtained a distribution of configurations with the C-H bond of chloroform pointing towards each of the carbons of naphthol. Due to negligible Boltzmann weights, the higher energy configurations were considered statistically insignificant, and only the energetically favorable configurations were considered for this study (Figure 2(c)). The more favored conformations, correspond to the C-H bond pointing towards $C^{(2)}$ and $C^{(4)}$ of 1N, and $C^{(1)}$ of 2N (Figure 2(d)). Those configurations correspond to resonance structures (see Supporting Information) stabilized by $C^{(2)}$ and $C^{(4)}$ that are the electron-rich centers of 1N and 2N.

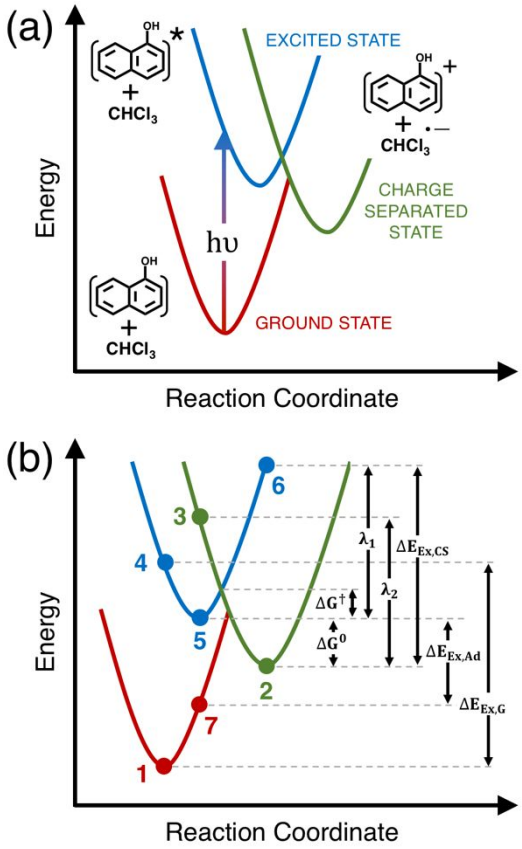


Figure 3. Schematic diagram showing the ground (red), excited (blue) and charge separated (green) energy surfaces, including formal oxidation states (a) and Marcus parameters (b) required to compute photoinduced electron transfer rates.

ET rates were computed, according to Marcus theory, using the computed parameters for the reorganization energy, electronic coupling and free energy change. Therefore, reactants and products are described by harmonic states (Figure 3(a)) at the semiclassical level.[51–53] For weakly coupled donor-acceptor systems, the electron transfer rates (k_{ET}) depend on (i) the free energy of reaction (ΔG^0), (ii) the reorganization energy (λ), and (iii) the electronic coupling (H_{if}), as follows:

$$k_{ET} = \frac{2\pi|H_{if}|^2}{\hbar\sqrt{4\pi\lambda k_B T}} exp\left(-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right), \quad (1)$$

so, the ET times (t_{Comp}) can be readily obtained, as follows:

$$t_{Comp} = \frac{1}{k_{ET}}. \quad (2)$$

The free energy values (ΔG^0) are calculated as the free energy differences between the CS and excited states (Figure 3(b)):

$$\Delta G^0 = E_2 - E_5. \quad (3)$$

The reorganization energy (λ) is computed as a geometric average of the ground and CS state reorganization energies λ_1 and λ_2 (see Figure 3(b)), obtained as follows:

$$\lambda_1 = E_3 - E_2 \quad (4)$$

$$\lambda_2 = E_6 - E_5 \quad (5)$$

Under the displaced harmonic oscillator approximation,[54] $\lambda_1 = \lambda_2$. However, the two reorganization energies are usually slightly different,[55] so the effective reorganization energy (λ) is computed, as follows[55]:

$$\lambda = \frac{\lambda_1 + \lambda_2}{2}. \quad (6)$$

The activation free energy $(\Delta G^\dagger)$ is defined by ΔG^0 and λ, as follows:

$$\Delta G^\dagger = \frac{(\Delta G^0 + \lambda)^2}{4\lambda}. \quad (7)$$

The electronic couplings (H_{if}) are computed with the fragment-charge difference (FCD) method,[56] under the two-state approximation (*i.e.*, assuming that the reactant and product diabatic states are linear combinations of the eigenstates). The naphthol and $CHCl_3$ molecules are defined as the donor and acceptor fragments, respectively. The states are chosen according to the maximum charge differences between the two fragments, as implemented in Q-Chem 5.0 at the DFT ωB97x-D/6-31+G(d,p) level of theory.

Table 1 lists the calculated Marcus parameters and ET rates. The ET from 1N is significantly faster (t_{Comp}=16–269 ps) than from 2N (ns), consistent with TCSPC experiments. In fact, the multiexponential fitting of the decay curves shows that the major decay time for 1N is <100 ps, while that for 2N is 1.9 ns.

Table 1. ET times and Marcus parameters

Ground State	CS State	Isomer	ΔG^0	λ	H_{if}	$\Delta G^\dagger$	t_{Comp}	t_{TCSPC}
H pointing to			eV					ps
$R^{(1)}$	$C^{(2)}$	cis1N	-0.41	1.35	0.01	0.16	269	70 (0.92) 1.5x10^3 (0.08)
		trans1N	-0.45	1.37	0.02	0.15	85	
	$C^{(4)}$	cis1N	-0.48	1.25	0.01	0.12	51	
		trans1N	-0.51	1.27	0.02	0.11	16	
$R^{(2)}$	$C^{(2)}$	cis1N	-0.42	1.34	0.02	0.16	63	
		trans1N	-0.45	1.34	0.02	0.15	53	
	$C^{(4)}$	cis1N	-0.48	1.37	0.02	0.15	39	
		trans1N	-0.51	1.36	0.02	0.13	29	
$R^{(1)}$	$C^{(1)}$	cis2N	-0.31	1.42	0.02	0.16	64	<40 (0.2) 900 (0.4) 1.9x10^3 (0.4)
		trans2N	-0.29	1.40	0.02	0.16	94	
$R^{(2)}$		cis2N	-0.47	1.42	0.002	0.16	15x10^3	
		trans2N	-0.46	1.39	0.001	0.16	55x10^3	

Isomerization times <10 ps were obtained, according to transition state theory (see Table 2 and Figure 4 (a,b)) at the EOM-CCSD/6-31+G(d,p) level, using Q-Chem 5.0, with excited state barriers obtained by scanning the $C^{(8a)}$-$C^{(1)}$-O-H and $C^{(1)}$-$C^{(2)}$-O-H dihedral angles.

Ultrafast isomerization leads to faster ET routes, with isomerization preceding ET. However, we observe a significantly slow component of ET and fluorescence quenching in 2N due to the noticeably slow ET in both cis- and trans-2N (with $CHCl_3$ pointing towards $R^{(2)}$ and nearly identical Boltzmann populations of both isomers in the excited state).

$$k_{cis\rightarrow tans} = \frac{k_B T}{\hbar} exp\left(-\frac{\Delta E_1{}^*}{k_B T} \right) \quad (8)$$

$$k_{trans\rightarrow cis} = \frac{k_B T}{\hbar} exp\left(-\frac{\Delta E_2{}^*}{k_B T} \right) \quad (9)$$

$$\frac{N_{cis}}{N_{trans}} = \frac{k_B T}{\hbar} exp\left(-\frac{\Delta E_3{}^*}{k_B T} \right) \quad (10)$$

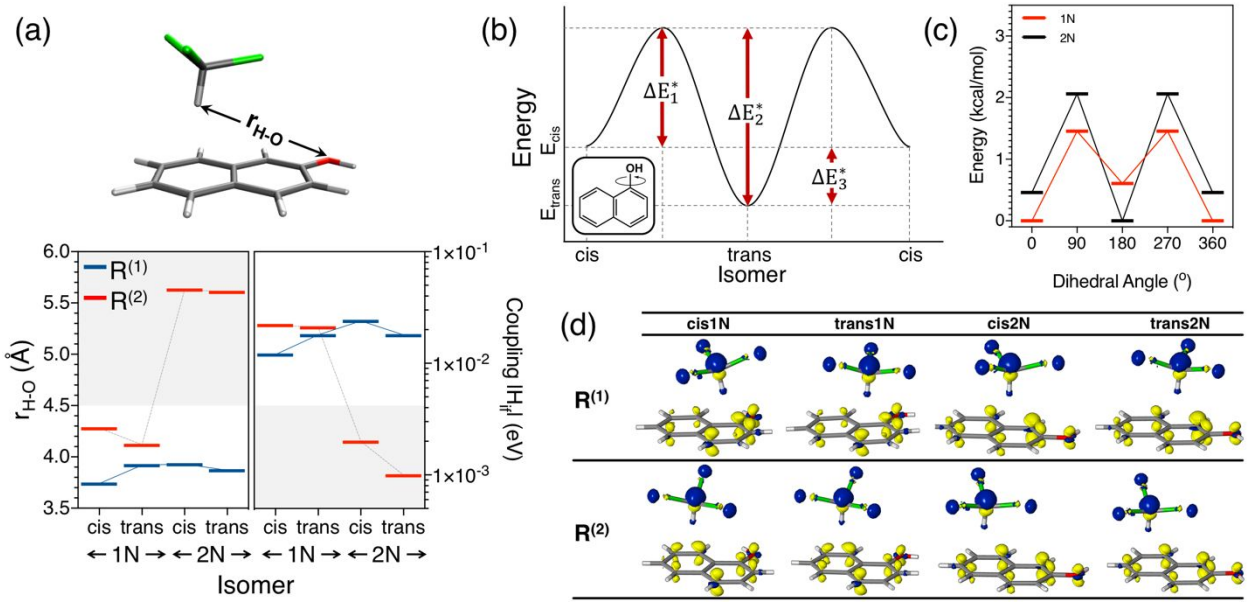


Figure 4. (a) Distances between H of $CHCl_3$ and O of naphthol for different configuration with the solvent on top of $R^{(1)}$ and $R^{(2)}$ and corresponding electronic couplings. **(b)** Schematic diagram of a dihedral scan and relevant energies. **(c)** Dihedral scans of $C^{(8a)}$-$C^{(1)}$-O-H (for 1N) and $C^{(1)}$-$C^{(2)}$-O-H (for 2N) in the excited state. **(d)** Change of electron density before and after electron transfer (density goes from yellow to blue during ET).

Table 2. Excited state isomerization times and Boltzmann populations.

Molecule	Isomer	Isomerization Time ps	Population %
1N	cis	3	76
	trans	1	24
2N	cis	4	52
	trans	8	48

As noted from Table 1, configurations with low ΔG^0 also have low λ, resulting in similar $\Delta G^\dagger$ for all the cases. Electronic couplings are thus important factors that modulate ET rates.

The plot of electron densities differences, before and after ET (Figure 4(d)), shows that the electron density is transferred from the oxygen of the naphthol to the $CHCl_3$ molecule. Being on top of $R^{(1)}$ allows the solvent molecule to accept the electron much faster. However, when the electron accepting solvent molecule is on top of $R^{(2)}$, especially for 2N, ET is slower since the separation between the electron rich oxygen and the $CHCl_3$ is larger and thus the electronic coupling is significantly smaller (Figure 4(c)).

In summary, quantum chemical calculations on several statistically relevant configurations allowed us to elucidate the origin of significantly different fluorescence lifetimes of photoexcited naphthols in halogenated solvents. The observed differences in ET dynamics stem from the differences in electronic couplings, when comparing 1N and 2N. Differences in reorganization energies are nearly compensated by concomitant differences in ET free energy changes. The differences in couplings are controlled by different electron donor-acceptor distances, as determined by the closer contact of the –OH group with $CHCl_3$ in 1N when compare to 2N, thereby rationalizing the significantly different fluorescence quenching lifetimes observed in experiments.

Our findings suggest that increasing the number of fused aromatic rings in the chromophore can allow us to gain control over fluorescence quenching times through modulation of the separation between the electron accepting solvent molecules in the first coordination sphere and the electron rich center of the –OH substituted acenes. The regioselective ET discussed in this study can be utilized for several practical applications, an evident one being the design of photo-switching molecular probes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXXXXXX.

Computational method, information about calculations performed, necessity of using EOM-CCSD for excited states, comparison of free and reorganization energies with and without explicit solvent, coordinates of optimized structures

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The authors declare no competing financial interest.

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