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Exciplex Ensemble Modulated by Excitation Mode in Intramolecular Charge-Transfer Dyad: Effects of Temperature, Solvent Polarity, and Wavelength on Photochemistry and Photophysics of Tethered Naphthalene–Dicyanoethene System

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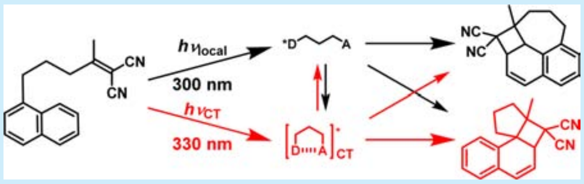
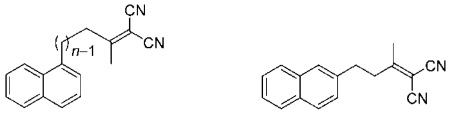
Ⓢ *Supporting Information*

ABSTRACT: Solvent, temperature, and excitation wavelength significantly affected the photochemical outcomes of a naphthalene–dicyanoethene system tethered by different number (*n*) of methylene groups (**1**–**3**). The effect of irradiation wavelength was almost negligible for **2a** but pronounced for **3a**. The temperature dependence and theoretical calculations indicated the diversity of exciplex conformations, an ensemble of which can be effectively altered by changing excitation wavelength to eventually switch the regioselectivity of photoreactions.



Photolysis of a tethered arene–alkene system, leading to efficient [4 + 2], [3 + 2], and/or [2 + 2] cyclization, has attracted much mechanistic and synthetic interest as a tool for constructing complex polycyclic carbon frameworks.[1] Photoreaction of an intramolecular donor (D)–acceptor (A) system has also been investigated extensively[2] to reveal that the formation of folded or compact exciplex (CEX) plays a vital role in determining the fate of an excited D–A pair. In theory, an exciplex is described by a linear combination of the wave functions of locally excited (LE) and radical ion pair (IP) states, the relative contribution of which varies with the redox properties of D and A. In the D–A dyad case, the photophysical and photochemical behaviors are critically controlled not only by the redox properties but also by the tether length connecting the D/A components.[3]

We have recently investigated the effects of excitation wavelength on the stereochemical outcomes of asymmetric photoreactions of several intramolecular[4] and intermolecular[5,6] D–A or charge transfer (CT) systems. The excited species formed upon local and CT-band excitation, i.e., conventional exciplex and excited CT complex, are classified as exciplex in a broader sense but differ in structure, with the latter preserving some original (ground-state) conformation. If the equilibrium between them is comparable to or slower in rate than the subsequent chemical process of each state, the subtle structural difference can be visualized as a stereochemical outcome when employing a chiral D–A system. Indeed, the diastereoselectivity of photoproduct was critically controlled by the excitation wavelength in several D–A systems.[7] In the present study, we achieved the wavelength control of regioselectivity in the intramolecular [2 + 2] photocycloaddition reaction of D–A dyads. Thus, a series of naphthalene–dicyanoethene dyads (**1**–**3**) (Figure 1) was employed to elucidate the effects of tether length and substitution position on the photophysics and photochemistry of the exciplex ensemble formed upon excitation at different wavelengths.



1a (*n* = 1), **2a** (*n* = 2), **3a** (*n* = 3) **2b**

Figure 1. Intramolecular D–A dyads of different tether-length or substitution position.

Intramolecular CT interaction in the ground state was examined by UV–vis spectroscopy. Thus, the spectra of **1**–**3** in acetonitrile at 20 °C were compared with the arithmetic sum of those of the corresponding donor (1- or 2-methylnaphthalene) and acceptor (1,1-dicyano-2-methylpropene) moieties. New absorption bands, assignable to the (intramolecular) CT band, emerged at longer wavelengths (300–350 nm) in these tethered systems (Figure S23, Supporting Information). Selective excitation of the CT band was executed by irradiating at 330 nm through the band-path filter (vide infra). Lacking a distinct CT band in the spectrum, the energy of CT transition (E_{CT}) was tentatively evaluated from the wavelength that gives the molar extinction coefficient (ε) of 100 M^{-1} cm^{-1}. The E_{CT} value turned out to be inversely proportional to the oxidation potential (Figure S23, Supporting Information). This is due to the gradual increase

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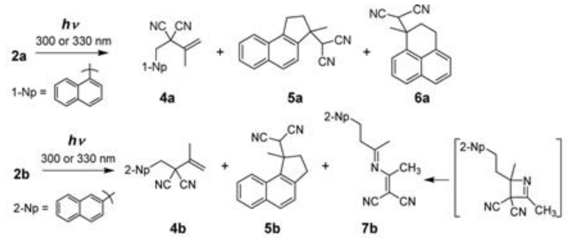
of the tether length in **1**−**3**, or the mean separation r_{AD} of the D and A moieties, leading to a decrease of the electronic coupling between D and A.[8]

In a flexible D−A system like **1**−**3**, all possible conformers are thought to be populated in both ground and excited states at temperatures under experiments. Hence, all possible conformations and their relative energies were investigated by dispersion-corrected DFT method at the DFT-D3-TPSS/def2-QZVP level (Table S1, Supporting Information).[9] For **1a**, only four conformers, arising from the bond rotation of the tether, are possible. The conformational freedoms progressively increase upon elongation of the tether to give 6 conformers for **2a** or **2b** and 18 conformers for **3a**. When both of the two central bonds of the tether in **3a** are in gauche (8 such conformers in total), the molecular orbitals of D and A were found to overlap substantially, while the D−A distance was much larger (>4 Å) for those conformers that possess at least one trans tether bond (10 conformers in total). The former group of conformers may be categorized as folded or compact CT form, while the latter as extended form.[10] It is to note that the energetically most preferred conformer (*pro*-*S*-G$^-$G$^+$) is an immediate precursor (in structure) to ipso product **8a**, the major photoproduct (vide infra). In contrast to the gauche conformations strongly favored in the dispersion-corrected DFT calculations, X-ray crystal structural analyses revealed that trans and trans−gauche conformers (i.e., extended forms) were preferred in the solid state in **2b** and **3a**, respectively (Figure S24, Supporting Information). This is probably because the extended forms are more favorable for crystal packing (due to the intermolecular C−T and/or dispersion interactions) and does not immediately mean that the trans or trans−gauche conformers are the most stable in solution. It is rather reasonable to consider that various conformers coexist in **1**−**3** as an ensemble in both ground and excited states, as indicated by the DFT-D calculations.

Photolysis of **1a** in acetonitrile at 20 °C (at >280 nm) resulted in a recovery of the starting material even upon prolonged irradiations, which is in sharp contrast to the previous observation that the corresponding phenyl derivatives undergo facile di-π-methane rearrangement (upon photoirradiation at 254 nm).[11] This is probably due to a lower oxidation potential of naphthyl derivative, which facilitates the deactivation process through electron transfer (ET) in **1a**. Indeed, the free energy change calculated for ET is significantly negative in the solvent used ($\Delta G_{ET} = -0.13$ eV). ET pathway seems, however, not relevant for the photochemical process in the current systems (Figure S31, Supporting Information).

Photolysis of **2a** led to the competitive rearrangement and cyclization reactions (affording **4a** and **5a**) as was the case with the phenyl analogue (1,1-dicyano-2-methyl-4-phenyl-1-butene), but only in low relative yields (<5% in total).[12] The major process was the intramolecular substitution at the peri position to give cyclization product, 2,3-dihydrophenalene (**6a**), in ≥95% relative yield, irrespective of the excitation wavelength (Table 1). The effect of excitation mode (CT or local) was quite small. Photolysis in solvents of lower polarities and under lower temperature increased the relative yields of **4a** and **5a** (Table S2, Supporting Information), but the excitation wavelength did not greatly affect the product distribution.

Table 1. Effects of Excitation Wavelength on the Photoreactions of 2a and 2b[a]



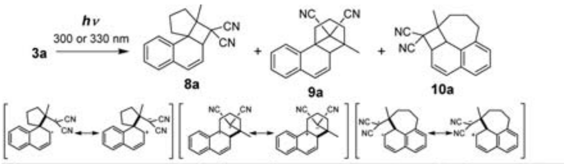
substrate	λ$_{ex}$/nm	*t*/min	conv %	distribution/%	
2a	300	0.8	16	**4a**:**5a**:**6a** =	<0.1:3:97
	330	3	6		<0.1:5:95
2b	300	720	17	**4b**:**5b**:**7b** =	3:77:20
	330	1020	10		14:82:4

[a] Irradiations performed with 0.1 mM acetonitrile solution at 20 °C. λ_{ex}: excitation wavelength. *t*: irradiation time.

Photoreaction of β-substituted **2b** proceeded considerably slow (by a factor of ca. 100), but similarly afforded the corresponding rearrangement and cyclization products (**4b** and **5b**). The cyclization occurred exclusively at the 1-position and was the major reaction pathway (~80%). To our surprise, unexpected azahexadiene (**7b**) was also formed in a substantial yield (up to 20%), when the photoirradiation was carried out in pure and mixed acetonitrile solutions. Variable temperature NMR experiment in deuterated acetonitrile revealed that **7b** (formally acetonitrile-inserted product) is formed most likely through the initial [2 + 2] cycloaddition of the dicyanoethene moiety of excited **2b** to acetonitrile's C≡N bond to afford 1-azetine derivative, which thermally rearranges to the final product (Figure S30, Supporting Information). While the latter process is known for related azacyclobutenes,[13] the cycloaddition of an excited dicyanoethene (or exciplex) to nonactivated C≡N bond is unprecedented,[14] to the best of our knowledge. In the photolysis of **2b**, the product distribution was obviously wavelength-dependent (Table 1). It is to note that the cyclization was much preferred for both **2a** and **2b**, which is in contrast to the photoreaction of phenyl analogues.[15] This is in line with the highly polar nature of the exciplex involved (vide infra), as the cyclization product is formed through a zwitter ionic or polar biradical intermediate, contrary to the nonpolar nature of sigmatropic rearrangement.[16] The relative product distribution was not essentially altered even when the reaction was carried out in the presence of trifluoroacetic acid, suggesting that the cyclization step is rate-determining.

Tethered by a trimethylene chain, **3a** smoothly photocyclized to three isomeric [2 + 2] cycloadducts (**8a**−**10a**) in excellent combined yields (Table 2). These benzotricyclic compounds possess two medium-sized (5- to 7-membered) rings together with a cyclobutane moiety but differs in the position of cycloaddition, i.e., ipso, ortho, or peri. The structures of these products were fully assigned by the 2D NMR techniques (Supporting Information). Solvent polarity significantly affected the product distribution, indicating involvement of a zwitter ionic or polar biradical intermediate. Similarly, altering excitation wavelength from 330 to 300 nm dramatically switched the major product from ipso-product **8a** to peri-product **10a**, for which the different ensembles of exciplex conformers excited are responsible (vide infra). It is to note that a low substrate concentration (0.1 mM) and relatively low conversions (≤20%) were employed in these experiments in order to avoid possible intermolecular interactions in the ground and excited states[4,17] and possible secondary reactions, as the products also absorb light at wavelengths similar to the substrates (Figure S26, Supporting Information). As anticipated from the crystal structure,

Table 2. Effect of Excitation Wavelength on the Photoreaction of 3a in Various Solvents[a]



solvent	λ_{ex}/nm	t/min	conv %	distribution/% (8a:9a:10a)
methylcyclohexane	300	0.3	11	54:6:40
	330	8	11	87:8:5
dichloromethane	300	0.3	15	26:12:62
	330	8	18	71:8:21
acetonitrile	300	0.3	8	46:13:41
	330	8	11	79:9:12

[a] For irradiation conditions, see footnote a in Table 1.

photolysis of **3a** in the solid state did not essentially afford any of these products.

Photophysical properties of **1**−**3** were investigated in acetonitrile at 20 °C to exhibit the dual fluorescence behavior. Thus, in addition to the structured fluorescence at 300−360 nm (which is mirror-imaged against the UV−vis spectrum and hence assignable to the locally excited naphthalene chromophore, LE), less-structured fluorescence of comparable to much stronger intensity was observed at longer wavelengths (360−680 nm);[18] see Figure 2 (left). The lifetime of the LE fluorescence was comparable (11.4 and 9.7 ns for **2a** and **2b**, respectively) for all of the substrates examined and was also very close to those of reference compounds 1- and 2-methylnaphthalene (11.5 and 11.0 ns, respectively) measured under the identical conditions, confirming the LE origin. The apparent exciplex emission observed at longer wavelengths was significantly short-lived (0.7−4.3 ns) and highly sensitive to solvent polarity. The difference in dipole moment between the ground and excited states ($\Delta\mu$) was evaluated from the Lippert−Mataga plots (Figure S27, Supporting Information) as 8.4, 18, and 20 D for **2a**, **2b**, and **3b**, respectively, revealing the highly polar nature of the exciplex. The excitation spectra monitored at the LE and exciplex fluorescence maxima were superimposable to each other and also to the UV−vis spectrum. This means that the excited CT complex and conventional exciplex[7] are indistinguishable from the comparison of excitation spectra due to the rapid relaxation to a common exciplex species or the very fast equilibrium between them (Figure S28, Supporting Information). At lower temperatures, the exciplex fluorescence was enhanced in intensity and shifted to longer wavelengths (Figures 2, right, and S27, Supporting Information), indicating that the relaxation is not greatly decelerated even at −40 °C and more stable (relaxed) conformers are progressively populated. Further details of the photophysical properties of **1**−**3** in less polar solvents are shown in Table S4, Supporting Information.

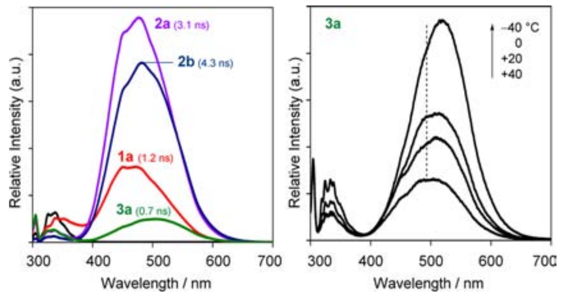


Figure 2. Fluorescence spectra and lifetimes of the exciplex emissions of **1**−**3** in acetonitrile at 20 °C (left) and those of **3a** at varying temperatures (right). λ_{ex} = 280 nm. Black line on the left panel is the fluorescence spectrum of 1-methylnaphthalene, scaled to one-fiftieth.

A temperature-dependence study has frequently been employed to elucidate the nature of intermediate(s) involved in the course of the photoreaction.[19] In the present study, the logarithm of relative rate (yield) of cyclization and rearrangement was plotted against the reciprocal temperature to give a good straight line in the both photolyses performed at different wavelengths. The differential activation parameters were evaluated from the slope and intercept of the least-squares fit (Figure 3 and Table S3, Supporting Information). Interestingly, **2a** and **3a** showed very contrasting behavior; thus, the activation parameters upon local and CT band excitations (at 300 and 330 nm, respectively) were almost the same for **2a** but significantly different and sign-inverted for **3a** (Table 3). The thermal equilibrium (relaxation) in the excited state seems to be much faster in **2a** than in **3a**, due to the smaller conformational freedoms and variations in the former, which allows the photochemical and photophysical processes to undergo in comparable rates. The differences in such ultrafast processes may be explained by a variable conical intersection seam for **2a** and **3a**.[20] Such contrasting photochemical behaviors observed for structurally resembling substrates **2a** and **3a** may indicate that the conformational flexibility is one of the key factors that determine the wavelength-dependent photobehavior of intramolecular CT systems.

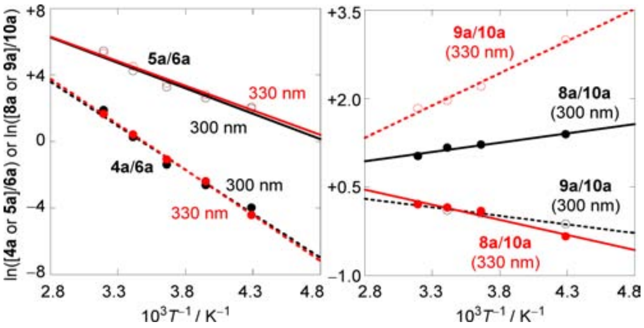


Figure 3. Eyring-type plots for the competitive photorearrangement/cyclization of **2a** (left) and **3a** (right) upon irradiation at 300 nm (local excitation) and 330 nm (CT excitation) in acetonitrile.

Table 3. Differential Activation Parameters for the Preferential Formation of 4a/5a and 8a/9a over peri-Substituted Products (6a/10a) upon Photolysis of 2a or 3a[a]

λ_{ex}/nm	$\Delta\Delta H°$	$T\Delta\Delta S°$	$\Delta\Delta H°$	$T\Delta\Delta S°$
	4a/6a		**5a/6a**	
300	+44	+49	+26	+36
330	+46	+47	+25	+36
	8a/10a		**9a/10a**	
300	+2.6	+0.1	+2.4	+2.7
330	-4.2	+4.6	-9.1	-4.2

[a] λ_{ex}: excitation wavelength. Activation parameters ($\Delta\Delta H°$ and $T\Delta\Delta S°$) in kJ mol^{-1}; T = 293 K.

Figure 4 illustrates the photochemistry and photophysics of the intramolecular CT systems **2** and **3** discussed above. Upon irradiation at 300 nm, the naphthalene chromophore (mostly in the extended form) is locally excited to its singlet state, which immediately stacks to the dicyanoethene moiety to form the compact exciplex (CEX = EX + EX′) as an ensemble of conformers. Irradiation at 330 nm mostly excites the CT band of the compact form to give the excited CT complex, which also relaxes to (different) conformer ensemble of CEX. This mechanism is also in line with the result of a recent investigation, in which locally excited reactant and exciplex are in equilibrium.[21] Judging from the significant temperature effects on the fluorescence of **3a**, it is highly likely that the CEX is variable in structure and reactivity, an ensemble of which can be manipulated and differentiated by many factors, including solvent polarity, temperature, and history of exciplex formation, i.e., local versus CT band excitation. In other words, the exciplex ensemble can keep some memory of the original (ground-state) structure. Such ensemble is indistinguishable in short-tethered dyad **2a**.

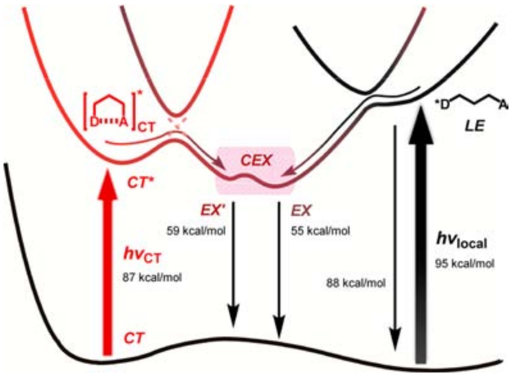


Figure 4. Schematic potential energy surfaces explaining the effects of excitation wavelength in donor−acceptor dyads **2** and **3**. The values are for **3a**.

In summary, the regioselectivity of [2 + 2] photocycloaddition of trimethylene-tethered naphthalene−dicyanoethene dyad **3a** can be switched by simply changing excitation wavelength. Such a wavelength effect was not pronounced in CT dyads **2** with a shorter dimethylene tether. The present exciplex is structurally loose and allows various conformations as an ensemble, which enables us to modify the photophysical and photochemical consequences through manipulation of the conformer population by various environmental factors such as solvent polarity, temperature, and excitation wavelength. We are planning to further explore the effect of wavelength on various photoreactions of CT dyads.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental details, tables of selected results on photoreaction and photophysics, UV−vis and fluorescence spectra, characterization data of all substrates/products, details of DFT calculation and optimized geometries, and copies of ^{1}H, ^{13}C, and 2D NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052−1103. (b) Hoffman, N. *Synthesis* **2004**, *4*, 481−495. (c) Streit, U.; Bochet, C. G. *Beilstein J. Org. Chem.* **2011**, *7*, 525−542.

(2) (a) Mattay, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 663−665. (b) Mukae, H.; Maeda, H.; Mizuno, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 6558−6560.

(3) (a) El-Gezawy, H.; Rettig, W. *Chem. Phys.* **2006**, *327*, 385−394. (b) Slama-Schwok, A.; Blanchard-Desce, M.; Lehn, J. M. *J. Phys. Chem.* **1990**, *94*, 3894−3902.

(4) Nishiuchi, E.; Mori, T.; Inoue, Y. *J. Am. Chem. Soc.* **2012**, *134*, 8082−8085.

(5) (a) Saito, H.; Mori, T.; Wada, T.; Inoue, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1900−1906. (b) Saito, H.; Mori, T.; Wada, T.; Inoue, Y. *Chem. Commun.* **2004**, 1652−1653. (c) Saito, H.; Mori, T.; Wada, T.; Inoue, Y. *Org. Lett.* **2006**, *8*, 1909−1912.

(6) (a) Matsumura, K.; Mori, T.; Inoue, Y. *J. Am. Chem. Soc.* **2009**, *131*, 17076−17077. (b) Matsumura, K.; Mori, T.; Inoue, Y. *J. Org. Chem.* **2010**, *75*, 5461−5469.

(7) Mori, T.; Inoue, Y. *Chem. Soc. Rev.* **2013**, *42*, 8122−8133.

(8) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116−4126.

(9) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104/1−18. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456−1465. (c) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401/1−4.

(10) Lauteslager, X. Y.; van Stokkum, I. H. M.; van Ramesdonk, H. J.; Brouwer, A. M.; Verhoeven, J. W. *J. Phys. Chem. A* **1999**, *103*, 653−659.

(11) Ferreira, A. B. B.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2* **1978**, *21*, 995−1001.

(12) Cookson, R. C.; Sadlar, D. E.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 774−782.

(13) (a) Cantrell, T. S. *J. Am. Chem. Soc.* **1972**, *94*, 5929−5931. (b) Yang, N. C.; Kim, B.; Chiang, W.; Hamada, T. *J. Chem. Soc., Chem. Commun.* **1976**, 729−730. (c) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 4238−4245.

(14) Further studies employing different nitriles, dyad types, excitation wavelength, solvents, and temperature are now underway, but beyond the scope of this communication.

(15) Ito, T.; Nishiuchi, E.; Fukuhara, G.; Inoue, Y.; Mori, T. *Photochem. Photobiol. Sci.* **2011**, *10*, 1405−1414.

(16) Cookson, R. C.; Kemp, J. E. *Chem. Commun.* **1971**, 385−386.

(17) Imoto, M.; Ikeda, H.; Fujii, T.; Taniguchi, H.; Tamaki, A.; Takeda, M.; Mizuno, K. *Org. Lett.* **2010**, *12*, 1940−1943.

(18) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1980**, *102*, 7782−7784.

(19) (a) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107−115. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 875−894.

(20) (a) Gomez, I.; Reguero, M.; Boggio-Pasqua, M.; Robb, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 7119−7129. (b) Zgierskia, M. Z.; Fujiwarab, T.; Lim, E. C. *Chem. Phys. Lett.* **2008**, *463*, 289−299.

(21) (a) Koch, M.; Letrun, R.; Vauthey, E. *J. Am. Chem. Soc.* **2014**, *136*, 4066−4074. (b) Letrun, R.; Vauthey, E. *J. Phys. Chem. Lett.* **2014**, *5*, 1685−1690.