

## COMMUNICATION

### A theoretical study on ESPT mechanism of DALL-AcOH complex

Jinfeng Zhao, Yang Yang\*

*\*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, China.*

Received 5 June 2016; Accepted (in revised version) 21 June 2016

---

**Abstract:** In the present work, the excited-state intermolecular proton transfer (ESIPT) process of DALL-AcOH complex in AcOH solvent has been investigated theoretically using DFT/TDDFT methods. Based on comparing bond lengths, bond angles and infrared vibrational spectra involved in the two intermolecular hydrogen bonds ( $N_1-H_2\cdots O_3$  and  $O_5-H_6\cdots N_7$ ), we find that the photoexcitation has insignificant on intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ). Oppositely, the intermolecular hydrogen bond  $N_1-H_2\cdots O_3$  was testified to be strengthened in the  $S_1$  state. In addition, intramolecular charge transfer occurring in DALL part, which facilitates ESIPT process. In the end, our constructed PESs provided the reasonable ESIPT mechanism that only excited-state single proton transfer exists in DALL-AcOH complex.

**AMS subject classifications:** 78M50, 74E40, 65D18

**Keywords:** Infrared spectra, ESIPT, TICT, Frontier molecular orbitals.

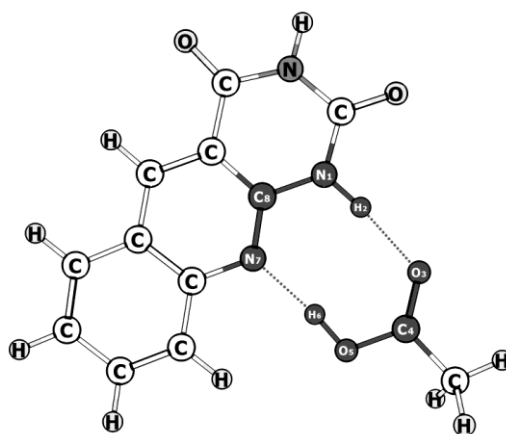
---

Lumichrome, the main product of the photodecomposition and biodegradation of riboflavin, has been extensively studied because its alloxazine scaffold undergoes photoinduced tautomerization, changing its lumichrome-like emission into isoalloxazine-like mission [1-3].  $F_0$  and  $F_{420}$  are unique 5-deazaflavin-containing coenzyme and methanogenic signature molecules, essential for a variety of biochemical transformations associated with methane biosynthesis and light-dependent DNA repair [4]. 5-Deazaflavins (5-deazaalloxazine) are potential riboflavin antagonists with their own redox system, different from that of riboflavin [5]. 5-Deazaflavin and its homologues with the 5-deazaalloxazine (5-DALL) structure were also reported having in vitro antitumor activity [6-9]. Dezaalloxazines (DALL) are analogues of 5-deazaflavins, compounds that are cofactors in yellow chromophores [10]. There is an increasing interest in their photochemical properties since their discovery as chromophores in

---

\* Corresponding author. E-mail: light\_yang@dicp.ac.cn  
<http://www.global-sci.org/cicc>

blue-light-sensing photoreceptors [11]. Particularly, recent years, lumichrome photophysical properties have changed to be hot [12-15], the investigations about DALL also changed to be high-profile. Peculiarly, the properties of excited-state proton transfer (ESPT) about 5-DALL sensor in acetic acid solution was provided by Sikorshi *et al.* [15, 16], the in-depth study about lumichrome has become more and more valuable. In fact, the ESPT mechanism of DALL is ambiguous theoretically. In addition, it is worth mentioning that ESPT processes are important in chemical and biological systems including photosynthesis and DNA based-pair tautomerization [17-20]. As far as we know, its optoelectronic applications attract extensive researchers such as fluorescence sensor, molecular switches, UV filters and so forth [21-23]. Therefore, in this present work, it is necessary to provide an in-detail theoretical investigation about excited-state dynamics of DALL in acetic acid solvent.



**Figure 1:** The optimized structures of DALL-AcOH.

Based on density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, DALL couple with acetic acid molecule (DALL-AcOH) have been optimized to clarify the fundamental aspects concerning the structures occurring in both  $S_0$  and  $S_1$  state (seen in **Figure 1**). All the calculations about electronic structures were dependent on the Gaussian 09 program suite [24]. Becke's three-parameter hybrid exchange function with the Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) [25] as well as the triple- $\zeta$  valence quality with one set of polarisation functions (TZVP) [26] have been selected after testing other basis sets. In addition, in all our calculations, the solvent effect (acetic acid (AcOH)) has been selected based on the Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [27, 28]. **Table 1** lists the primary bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of DALL-AcOH in  $S_0$  and  $S_1$  states based on the DFT/TDDFT methods in AcOH solvent, respectively. One should be noticed that  $N_1\text{-}H_2$  bond is lengthened from 1.029  $\text{\AA}$  in the  $S_0$  state to 1.036  $\text{\AA}$  in the  $S_1$  state, and the  $H_2\cdots O_3$  bond is shortened from 1.836  $\text{\AA}$  to 1.790  $\text{\AA}$ . Furthermore, the  $N_1\text{-}H_2\cdots O_3$  angle is also enlarged from 173.7 $^\circ$  to 177.6 $^\circ$ .

based on the photoexcitation. The decrease of  $H_2\cdots O_3$  bond length and the increase of  $\delta(N_1-H_2\cdots O_3)$  bond angle indicate the formation of a relative stronger hydrogen bond in the  $S_1$  state. However, when it comes to the intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ), almost no obvious variations can be found for both bond length and bond angle, which demonstrates that photoexcitation has insignificant on intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ).

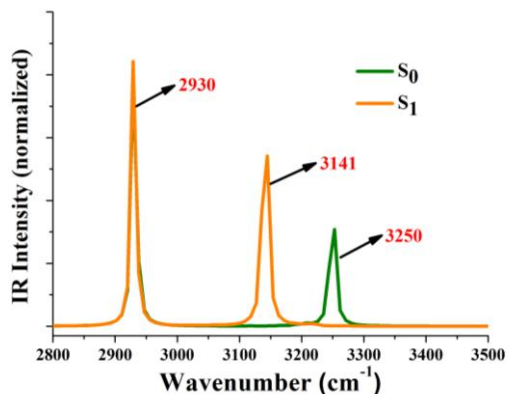
**Table 1** The primary bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) of DALLL-AcOH in  $S_0$  and  $S_1$  states based on the DFT/TDDFT methods in AcOH solvent, respectively.

	$S_0$	$S_1$
$N_1-H_2$	1.029	1.036
$H_2-O_3$	1.836	1.790
$O_3-C_4$	1.223	1.224
$C_4-O_5$	1.328	1.327
$O_5-H_6$	1.009	1.009
$H_6-N_7$	1.751	1.749
$N_7-C_8$	1.318	1.350
$C_8-N_1$	1.377	1.354
$\delta(N_1-H_2-O_3)$	$173.7^\circ$	$177.6^\circ$
$\delta(O_5-H_6-N_7)$	$173.5^\circ$	$173.7^\circ$

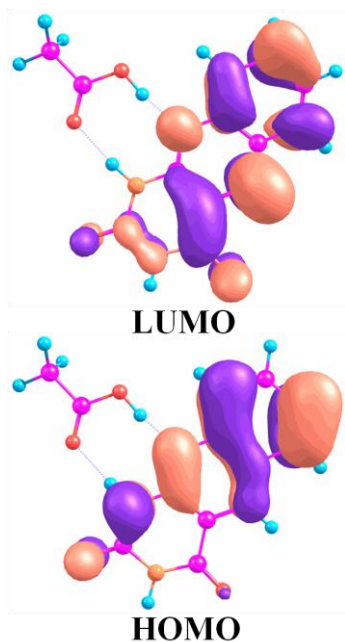
Further, the infrared (IR) spectra of DALL-AcOH were calculated in both  $S_0$  state and  $S_1$  state, particularly, the IR spectra in electronically excited states are difficult and time-consuming (shown in **Figure 2**). It should be noticed that the calculated  $O_5-H_6$  stretching vibrational frequency is coincident ( $2930\text{ cm}^{-1}$ ) in both  $S_0$  and  $S_1$  states, which indicate again that photoexcitation has insignificant on intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ). While for  $N_1-H_2$  stretching band, upon the electronic excitation, it changes to be  $3141\text{ cm}^{-1}$  in the  $S_1$  state from  $3250\text{ cm}^{-1}$  in the  $S_0$  state. The apparent red-shift  $109\text{ cm}^{-1}$  of  $N_1-H_2$  stretching frequency further manifests the intramolecular hydrogen bonds  $N_1-H_2\cdots O_3$  is strengthened in the  $S_1$  state [29-36].

In order to qualitatively discuss the charge distribution and charge transfer, the frontier MOs of DALL-AcOH have been presented in **Figure 3**. Herein, we only show the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), since the  $S_1$  state is mainly associated with these two orbitals. Clearly, the  $S_1$  state is a dominant  $\pi\pi^*$ -type transition from HOMO to LUMO due to the  $\pi$  character for the HOMO as well as the  $\pi^*$  character for LUMO. The one should be noted that the HOMO and LUMO are localized on different parts. Especially, the part involved in the intermolecular hydrogen

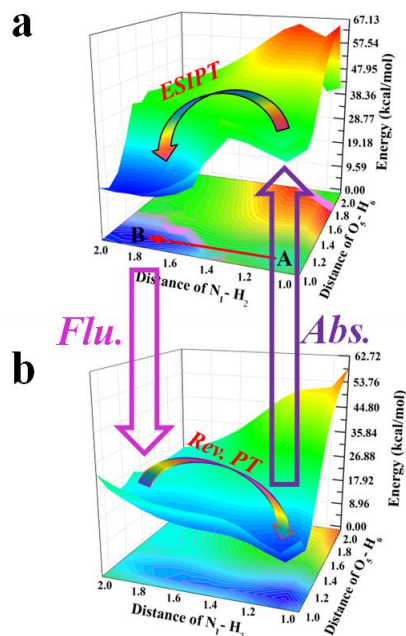
bonds  $N_1-H_2 \cdots O_3$  and  $O_5-H_6 \cdots N_7$ , the electron density of the hydroxide radical moiety changes after the transition from HOMO to LUMO. That is to say, the first excited state involves the intramolecular charge transfer (AcOH part still staying in the  $S_0$  state). As a consequence, the  $H \cdots O$  bond length could be shortened upon excitation to the first excited state. So the ES IPT process could happen due to the intramolecular charge transfer.



**Figure 2:** The calculated IR spectra of DALL-AcOH structure in AcOH solvent at the spectral region of  $N_1-H_2$  and  $O_5-H_6$  stretching bands.



**Figure 3:** View of frontier molecular orbitals, HOMO and LUMO, for DALL-AcOH complex based on TDDFT/B3LYP/TZVP/IEFPCM(AcOH) theoretical level.



**Figure 4:** PESs of the  $S_0$  and  $S_1$  states for DALL-AcOH along with  $N_1-H_2$  and  $O_5-H_6$  bond lengths.

To reveal the detailed dynamic process in both  $S_0$  and  $S_1$  state, the three dimensional potential energy surfaces (PESs) have been scanned based on scanning both  $N_1-H_2$  and  $O_5-H_6$  bond lengths from 0.91 Å to 2.01 Å and from 0.93 Å to 2.03 Å in step, respectively (shown in **Figure 4**). It can be seen clearly that the proton transfer process can not occur on the  $S_0$  PES no matter along with  $N_1-H_2$  or  $O_5-H_6$ . Upon the photoexcitation, DALL-AcOH can be excited to the  $S_1$  state PES (point A). Then, crossing an about 4-5 kcal/mol potential energy barrier to point B, which is the only way to occur ESIPT reaction in the  $S_1$  state. In turn, B point form decays to the ground state through radiating fluorescence, subsequently, undergo the reverse ground state proton transfer process back to DALL-AcOH form with the inappreciable potential barrier.

In summary, in the present work, the excited-state dynamic process of DALL-AcOH complex has been investigated theoretically using DFT/TDDFT methods. Two changes of intermolecular hydrogen bonds ( $N_1-H_2\cdots O_3$  and  $O_5-H_6\cdots N_7$ ) were compared based on bond length and bond angles, which demonstrates that photoexcitation has insignificant on intermolecular hydrogen bond ( $O_5-H_6\cdots N_7$ ). The strengthened hydrogen bond  $N_1-H_2\cdots O_3$  in the  $S_1$  state facilitate ESIPT process, which has been also verified by intramolecular charge transfer. In the end, our constructed PESs provided the reasonable ESIPT mechanism.

## Acknowledgments:

We sincerely thank the financial support from the National Basic Research Program of China (2013CB834604) and National Natural Science Foundation of China (21473195 and 21321091)

## Reference

- [1] W. Holzer, J. Shirdel, P. Zirak, A. Penzkofer, P. Hegemann, R. Deutzmann and E. Hochmuth, Photo-induced degradation of some flavins in aqueous solution, *Chem. Phys.*, 308 (2005), 69-78.
- [2] I. Ahmad, Q. Fasihullah and F. H. M. Vaid, Effect of phosphate bugger on photodegradation reactions of riboflavin in aqueous solution, *J. Photochem. Photobiol. B.*, 78 (2005), 229-234.
- [3] I. Ahmad, Q. Fasihullah and F. H. M. Vaid, A study of simultaneous photolysis and photoaddition reactions of riboflavin in aqueous solution, *J. Photochem. Photobiol. B.*, 75 (2004), 13-20.
- [4] A. F. Glas, M. J. Manu, M. Cryle, T. R. M. Barends, S. Schneider, E. Kaya, I. Schlichting and T. Carell, The archaeal cofactor F-0 is a light-harvesting antenna chromophore in eukaryotes, *PNAS*, 106 (2009), 11540-11545.
- [5] P. Hemmerich, V. Massey and H. Fenner, Flavin and 5-deazaflavin – chemical evaluation of modified flavoproteins with respect to mechanisms of redox biocatalysis, *FEBS Lett.*, 84 (1977), 5-21.
- [6] H. I. Ali, N. Ashida and T. Nagamatsu, Design, synthesis, antitumor activity, and molecular docking

- study of novel 2-substituted 2-deoxoflavin-5-oxides, 2-deoxoalloxazine-5-oxides, and their 5-deaza analogs, *Bioorg. Med. Chem.*, 16 (2008), 992-940.
- [7] Y. Kanaoka, Y. Ikeuchi, T. Kawamoto, K. Bessho, N. Akimoto, Y. Mikata, M. Nishida, S. Yano, T. Sasaki and F. Yoneda, Synthesis and antitumor activities of novel 5-deazaflavin-sialic acid conjugate molecules, *Bioorg. Med. Chem.*, 8 (2000), 2027-2035.
- [8] Y. Kanaoka, Y. Ikeuchi, T. Kawamoto, K. Bessho, N. Akimoto, Y. Mikata, M. Nishida, S. Yano, T. Sasaki and F. Yoneda, Synthesis and evaluation of nitro 5-deazaflavinpyrrolicarboxamides(s) hybrid molecules as novel DNA targeted bioreductive antitumor agents, *Bioorg. Med. Chem.*, 6(1998), 301-314.
- [9] J. M. Wilson, G. Henderson, F. Black, A. Sutherland, R. L. Ludwig, K. H. Vousden and D. J. Robins, Synthesis of 5-deazaflavin derivatives and their activation of p53 in cells, *Bioorg. Med. Chem.*, 15 (2007), 77-86.
- [10] L. V. Bystrykh, N. I. Govorukhina, L. Dijkhuizen and J. A. Duine, Tetrazolium-dye-linked alcohol dehydrogenase of the methylotrophic actinomycete *amycolatopsis methanolica* is a three-component complex, *Eur. J. Biochem.*, 247 (1997), 280-287.
- [11] W. R. Briggs and J. M. Christie, Phototropins 1 and 2: Versatile plant blue-light receptors, *Trends Plant Sci.*, 7 (2002), 204-210.
- [12] D. Prukala, E. Sikorska, J. Koput, I. Khmelinskii, J. Karolczak, M. Gierszewski and M. Sikorshi, Acid-base equilibriums of lumichrome and its 1-methyl, 3-methyl, and 1,3-dimethyl derivatives, *J. Phys. Chem. A.*, 116 (2012), 7474-7490.
- [13] M. Sikorshi, D. Prukala, I. Khmelinshii, D. R. Worrall, S. L. Williams, J. Hernando, J. L. Bourdelande, J. Koput and E. Sikorska, Spectroscopy and photophysics of dimethyl-substituted alloxazines, *J. Photochem. Photobiol. A*, 200 (2008), 148-160.
- [14] D. Prukala, M. Taczkowsha, M. Gierszewshi, T. Pedzinski and M. Sikorshi, Spectroscopy and photophysics of monomethyl-substituted derivatives of 5-deazaalloxazine and 10-ethyl-5-deaza-isoalloxazine, *J. Fluoresc.*, 24 (2014), 505-521.
- [15] D. Prukala, I. Khmelinshii, J. Koput, M. Gierszewshi, T. Pedzinski and M. Sikorshi, Photophysics, excited-state double-proton transfer and hydrogen-bonding properties of 5-deazaalloxazines, *Photochem. Photobiol.*, 90 (2014), 972-988.
- [16] E. Sikorsha, I. Khmelinshii, M. Hoffmann, I. F. Machado, L. F. V. Ferreira, K. Dobek, J. Karolczak, A. Krawczyk, M. Insinska-Rak and M. Sikorshi, Ground- and Excited- state double proton transfer in lumichrome/acetic acid system: Theoretical and experimental approach, *J. Phys. Chem. A*, 109 (2005), 11707-11714.
- [17] P. T. Chou, S. L. Studer and M. L. Martinez, Practical and convenient 355-nm and 337-nm sharp-cut filters for multichannel raman-spectroscopy, *Appl. Spectrosc.*, 45 (1991), 513-515.
- [18] P. T. Chou, S. L. Studer and M. L. Martinez, The design of an effective fluorescence filter for raman-spectroscopy, *Appl. Spectrosc.*, 45 (1991), 918-921.
- [19] J. F. Zhao and P. Li, The investigation of ESIPT for

- 2,8-diphenyl-3,7-dihydroxy-4H,6H-pyrano[3,2-g]-chromene-4,6-dione: Single or double? RSC. Adv., 5 (2015), 73619-73625.
- [20] C. C. Hsieh, C. M. Jiang and P. T. Chou, Recent experimental advances on excited-state intramolecular proton transfer coupled electron transfer reaction, *Acc. Chem. Res.*, 43 (2010), 1364-1374.
- [21] J. F. Zhao, J. S. Chen, J. Y. Liu and M. R. Hoffmann, Competitive excited-state single or double proton transfer mechanism for bis-2,5-(2-benzoxazolyl)-hydroquinone and its derivatives, *Phys. Chem. Chem. Phys.*, 17 (2015), 11990-11999.
- [22] G. Y. Li and T. S. Chu, TD-DFT study on fluoride-sensing mechanism of 2-(2'-Phenylureaphenyl)benzoxazole: The way to inhibit the ESIPT process, *Phys. Chem. Chem. Phys.*, 13 (2011), 20766-70771.
- [23] F. B. Yu, P. Li, B. S. Wang and K. L. Han, Reversible near-infrared fluorescent probe introducing tellurium to mimetic glutathione peroxidase for monitoring the redox cycles between peroxynitrite and glutathione in Vivo, *J. Am. Chem. Soc.*, 135 (2013), 7674-7680.
- [24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.; Scalmani, G. Cheeseman, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- [25] C. T. Lee, W. T. Yang and R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density, *Phys. Rev. B.*, 37 (1988), 785-789.
- [26] D. Feller, The role of databases in support of computational chemistry calculations. *J. Comput. Chem.*, 17 (1996), 1571-1586.
- [27] B. Mennucci, E. Cancès and J. Tomasi, Evaluation of solvent effects in isotropic and anisotropic dielectrics and in ionic solutions with a unified integral equation methods: Theoretical bases, computational implementation, and numerical applications, *J. Phys. Chem. B*, 101 (1997), 10506-10517.
- [28] E. Cancès, B. Mennucci and J. Tomasi, A new intragrual equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics, *J. Chem. Phys.*, 107 (1997), 3032-3041.
- [29] G. J. Zhao and K. L. Han, Novel infrared spectra for intermolecular dihydrogen bonding of the phenol-borane-trimethylamine complex in electronically excited state, *J. Chem. Phys.*, 127 (2007), 024306-024312.
- [30] J. F. Zhao, P. Song and F. C. Ma, A new excited-state intramolecular proton transfer mechanism for C2

- symmetry of 10-hydroxybenzoquinoline, *Commun. Comput. Chem.*, 2 (2014), 117-130.
- [31] G. J. Zhao, J. Y. Liu, L. C. Zhou and K. L. Han, Site-selective photoinduced electron transfer from alcoholic solvents to the chromophore facilitated by hydrogen bonding: A new fluorescence quenching mechanism, *J. Phys. Chem. B.*, 111 (2007), 8940-8945.
- [32] G. J. Zhao, R. K. Chen, M. T. Sun, G. Y. Li, J. Y. Liu, Y. L. Gao, K. L. Han, X. C. Yang and L. C. Sun, Photoinduced intramolecular charge transfer and s-2 fluorescence in thiophene-pi-conjugated donor-acceptor systems: Experimental and TDDFT studies, *Chem. Eur. J.*, 14 (2008), 6935-6947.
- [33] M. Z. Zhang, B. P. Ren, Y. Wang and C. X. Zhao, Excited-state intramolecular proton transfer of HDI and HBF: Excited-state hydrogen-bonding dynamics and electronic structures, *Commun. Comput. Chem.*, 1 (2013), 216-224.
- [34] S. Chai, G. J. Zhao, P. Song, S. Q. Yang, J. Y. Liu and K. L. Han, Reconsideration of the excited-state double proton transfer (ESDPT) in 2-aminopyridine/acid systems: role of the intermolecular hydrogen bonding in excited states, *Phys. Chem. Chem. Phys.*, 11 (2009), 4385-4390.
- [35] Y. Liu and S. C. Lan, Polarity effect of solvents on ground- and excited- state hydrogen bonds, *Commun. Comput. Chem.*, 1 (2013), 235-243.
- [36] G. J. Zhao and K. L. Han, Hydrogen bonding in the electronic excited state, *Acc. Chem. Res.*, 45 (2012), 404-413.