Commun. Comput. Chem.
doi: 10.4208/cicc.2016.v4.n4.3

Vol.4, No.4, pp.130-142
Dec 2016

REGULAR ARTICL

Excited-state proton transfer and charge transfer study in 6-amino-2-(2′-methoxyphenyl)benzoxazole

Can Du[a], Xiao Zhou[a], Peng Song*,[a,b] and Fengcai Ma[a,*]

[a] *Department of Physics, Liaoning University, Shenyang, China.*

[b]*Liaoning Key Laboratory of Semiconductor Light Emitting and Photocatalytic Materials, Liaoning University, Shenyang 110036, P. R. China*

Received 6 Dec 2016; Accepted (in revised version) 30 Dec 2016

Abstract： The proton transfer coupled charge transfer in the excited state of 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO) were investigated, using the time-dependent density functional theory with IEFPCM model by choosing n-heptane and dichloromethane (DCM) as solvent. The primary bond length and angles, the frontier molecular orbitals, absorption and fluorescence spectrum and the potential energy curves in the ground and excited state were calculated. The simulated absorption spectra were found to accord with the experimental data, which suggested that the calculated method is valid. And the fluorescence spectra show a normal Stokes shift, which gradually became larger with increasing the solvent polarity. This indicated that the charge transfer process taking place in the 6A-MBO upon photo-excited. The calculated frontier molecular orbitals confirmed the fact that the intramolecular proton transfer was promoted by charge transfer and redistribution. From the construction of two abrupt veers on the excited-state potential energy curves of 6A-MBO in both n-heptane and dichloromethane (DCM) solvent, it can be concluded that the ESIPT of 6A-MBO cannot happen in the excited state, only charge transfer occurred by photo excitation.

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

Keywords: 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO), Proton transfer, Charge transfer.

---

* Corresponding author *E-mail address*: songpeng@lnu.edu.cn (P. Song)
fcma@lnu.edu.cn (F.C. Ma)

1. Introduction

N.J.Turro has pointed out that the study of photochemical concentrates on chemical behavior and physical process of the electronic excited-state molecules [1]. It is easy for the excited-state molecules in the high energy and unstable state to release energy and then back to the relatively stable ground state in various ways. These behaviors of the excited state molecular were known as the deactivation process, in which the excited-state molecules release energy, and it could occur within a single molecule and also between the molecules [2]. It is worth to mention that hydrogen bonding play an important role in these processes. In the past decades, studies of hydrogen were mainly concentrated in the thermodynamic properties of hydrogen and the nature of the bonding issue [3-6]. With Han et al proposing the excited-state hydrogen bond dynamics [3,4,7-12,23,25,52-54], it attracted more and more attention in both theoretical and experimental ways. The studies mentioned above further explain the luminescence materials fluorescence or phosphorescence emission problems [12-16], intermolecular and intramolecular charge transfer [17-27], excited state proton transfer [28-30], intersystem crossing [14-16] and so on. The explore of these problems would facilitate physical chemists in understanding the essence of the hydrogen bonds by studying the interaction between light and hydrogen bonding, and help organic chemists design more kinds of stable and efficient luminescent material. Excited state proton transfer (ESPT) is an important reaction of photochemical and light physical process, and a hot topic in the field of dynamics. The target molecular could produce isomers after the proton transfer. This feature of the target molecular attracted researchers to design, and applied to light-emitting diodes (leds), laser fuel and ultraviolet filter [31-35], etc. Charge transfer is another important topic in biological, chemical and physical fields. Photo-excited charge transfer reaction is the basis of the solar energy conversion, widely applied in the field of solar cells [36-40]. As a result, the theoretical and experimental researches on proton and charge transfer are continuous.

6-amino-2-(2′-hydroxyphenyl)benzoxazole (6A-HBO) and its derivative which are typical intramolecular proton transfer dye show remarkable changes in the ESIPT process and correlated spectroscopy, due to it has both proton donor (-OH) in the phenol part and the proton acceptor (-N=) in the benzazole ring. It has been studied comprehensively by Cukier group and Gutierrez group from theory and experiment; they studied the problem of couple proton and electron transfer from different perspectives [41-44]. However, 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO) as a kind methoxy derivative of 6A-HBO did not attract a lot of attention. Only Alarcos et al. researched the subtle associations between intramolecular proton transfer and charge transfer; it showed that 6A-MBO cannot undergo an ESIPT process [42]. To understand the behavior of 6A-MBO better, we study the excited-state charge and proton transfer mechanisms of 6A-MBO in theory.

This paper explored proton transfer or charge transfer of 6A-MBO occurred in the excited state in both n-heptane and DCM solvents. Base on density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods with B3LYP gradient corrected function and TZVP basis set; we optimized the configurations of S_0 and S_1 states, and analyzed the frontier molecular orbitals (MOs), absorption and fluorescence spectra, and potential energy curves. The data reveals the details of 6A-MBO in the ground state and excited state.

2. Computational details

For this theoretical study, all the structure optimizations of 6A-MBO were based on Gaussian 09 suit of program [45]. The detailed ground and excited states geometric optimization employing the DFT and TD-DFT methods, respectively. Becke's three-parameter (B3) hybrid exchange functional [46] and Lee-Yang-Parr (LYP) gradient corrected function (B3LYP) [47,48] was selected with the DFT and TD-DFT. Polarization functions (TZVP) basis set was used , which with the triple-ξ valence electrons quality, after testing the basis sets. Based on the polarizable continuum model (PCM), the n-heptane / dichloromethane (DCM) was selected as the solvent during our calculation, using the integral equation formalism variants (IEFPCM). The geometric optimization of 6A-MBO in the S_0 and S_1 states without constrain any atoms, bonds and angles. The vibration frequency was calculated to confirm the local minimum by the absence of an imaginary mode. The potential energy curves (PECs) were structured by fixing the distance of N...H bond in a series values at a step of 0.1 Å, the potential curves of the S_0 and S_1 states have been scanned and analysis. Fine quadrature grids 4 were used. Diagonalization of the Hessian decided the harmonic vibrational frequencies of the S_0 and S_1 states [49]. The excited state Hessian was calculated, using default displacements of 0.02 Bohr and central differences, by numerical differentiation of the analytical gradients [50]. Using the gradients of the dipole moment determined the infrared intensities.

3. Results discussion

3.1 Geometric structure of 6A-MBO

The geometric structure optimization of 6A-MBO was obtained based on the DFT and TDDFT methods with the B3LYP function and TZVP basis set. The n-heptane/dichloromethane (DCM) was selected as the solvents during our calculation, using the IEFPCM model. The stable structure of 6A-MBO was shown in **Figure 1**, and the relevant data was listed in the **Table 1**.

From these data in **Table 1**, we can see that, for 6A-MBO in the n-heptane solvent form, the bond length of C_{27}-H_{30} and N_8...H_{30} bond were 1.0866 Å and 2.4921 Å in the S_0 state, then changed to 1.0890 Å and 2.4382 Å in the S_1 state, respectively. For 6A-MBO in the DCM solvent form, the bond length of C_{27}-H_{30} and N_8...H_{30} changed from 1.0913 Å and 2.7831 Å in the S_0 state to 1.0908 Å and 2.5436 Å in the S_1 state, respectively. Obviously, the length of N_8...H_{30} bond was shortened, while the length of C_{27}-H_{30} bond had no significant changes. Furthermore, we calculated the δ(C_{27}-H...N_8) angle of 6A-MBO, from the S_0 to the S_1 state, the angle changed from 97.2676° to 98.3115° and from 109.6739° to 114.8956° in the n-heptane and DCM solvent, respectively. These changes, including the increase of bond angles and the shortening of the bond length, indicated the intramolecular hydrogen bonds were strengthened in the S_1 state，which also would promote the occurrence rate of the ICT and the ESIPT. In addition, there were more significant changes of the bond length and bond angle in the polar solvent. As a result, the intramolecular hydrogen bond of 6A-MBO was markedly enhanced in the excited state, and the changes of 6A-MBO geometric structure were larger in the polar solvent.

Table 1 The calculated bond lengths (Å) and angles (º) of 6A-MBO in the S_0 and S_1 states based on the DFT and TDDFT methods, respectively.

Solvent	n-heptane		DCM	
Electronic state	S_0	S_1	S_0	S_1
C_{27}-H_{30}	1.0866	1.0890	1.0913	1.0908
N_8...H_{30}	2.4921	2.4382	2.7831	2.5436
δ(C_{27}-H_{30}...N_8)	97.2676	98.3115	109.6739	114.8956

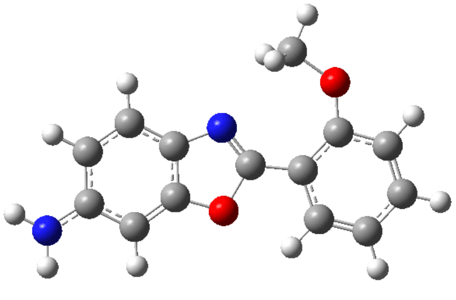
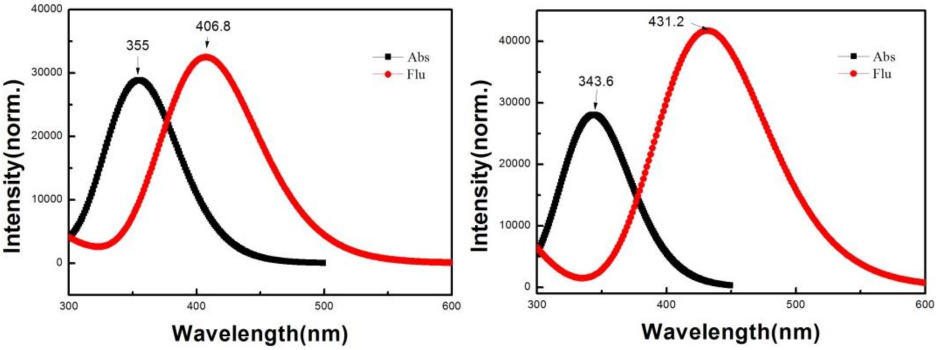


Figure 1: Optimized structures for 6A-MBO based on the B3LYP/TZVP theoretical level.

3.2. Electronic spectrum

Alarcos et al have measured the experiment value of the steady-state spectrum of

6A-MBO[42], while the theoretical study was not included. Based on the TDDFT/B3LYP/TZVP basis sets, we calculated the steady-state absorption and fluorescence spectrum of 6A-MBO, the n-heptane and dichloromethane (DCM) were selected as the solvent, the results shown in the **Figure 2**. We chose 300-6000nm wavelength range to display our spectral details. We can see the absorption peaks were located in the 355nm and 343.6nm, respectively, in the n-heptane and DCM solvent (see in **Figure 2 (a)** and **(b)**). The results of the absorption spectrum were in accord with the experimental data (327nm in n-heptane and 330nm in DCM) [42], which suggest that the calculated method is feasible. The peaks of the fluorescence spectrum occurred at 406.8nm and 431.2nm in the n-heptane and DCM solvent, separately. These calculated fluorescence spectrum data show a normal Stokes shift, which are in agreement with the experiments (385nm in the n-heptane solvent and 413nm in DCM solvent[42]). In addition, the variation ranges of the spectral Stokes shift were also consistent with the experimental values. There is a larger Stokes shift in DCM solvent than that in the n-heptane solvent in both theoretical and experimental calculation. Obviously the Stokes shift grows larger with the solvent polarity increase, which indicated that there was photo-excitation intramolecular charge transfer (ICT) process in the 6A-MBO. Just as some paper suggested that the solvent polarity played a critical role in the process of intramolecular charge transfer (ICT) [51-54]. We will further confirm the intramolecular charge transfer (ICT) in the section 3.3 in detail.

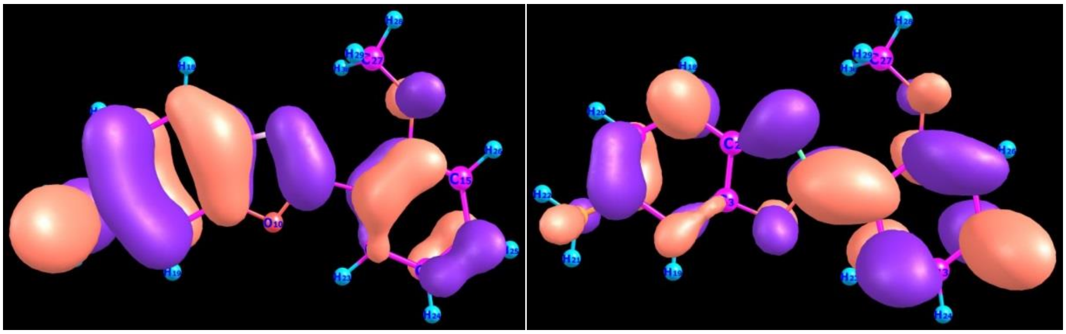


(a) (b)

Figure 2: The absorption and fluorescence spectral of 6A-MBO in the (a) n-heptane and (b) DCM solvent, base on the the TDDFT / B3LYP / TZVP basis sets.

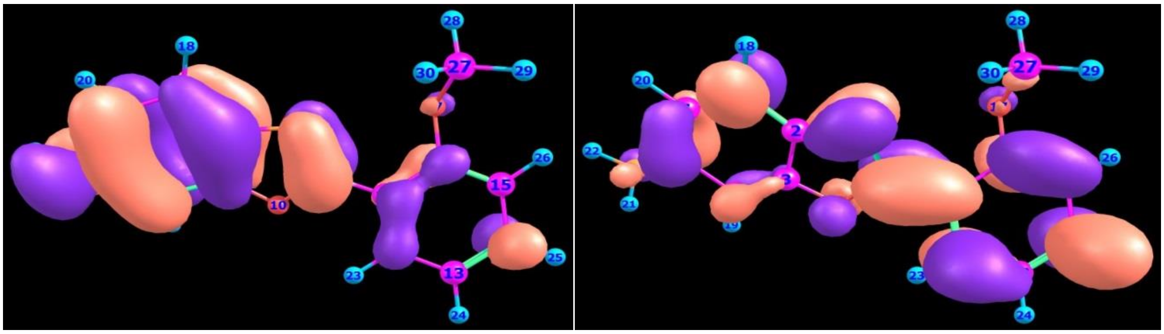
3.3 The frontier molecular orbitals (MOs)

The frontier MOs are able to help uncover the excited state characteristics [55-60]. We displayed the MOs of 6A-MBO in **Figure 3**, to further research the feature of charge distribution before and after photo-excitation, then explored the evidence of the excited state intramolecular proton transfer. Based on TDDFT / B3LYP / TZVP theoretical level, we calculated the electronic excitation energy (nm), oscillator strengths and a series of data of 6A-MBO, listed in **Table 2**. The analysis of CI and oscillator strengths indicated that the first excited state of 6A-MBO was in step with the orbital transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, **Figure 3** demonstrates HOMO and LUMO orbitals only. It is clearly that the HOMO is of π orbital characteristic, while the LUMO is of π* orbital characteristic, so from HOMO to LUMO transition is π-π* type. Electron distribution delocalized on different parts of the 6A-MBO for HOMO and LUMO. In detail, from HOMO to LUMO, the charge density around O atom of phenolic group is decrease, at the same time, the increase of negative charge distributed in N atom was obvious. From the viewpoint of Mulliken's charge distribution, these changes of charge density lead to strengthen the N...H bond, as mentioned before, the length of N...H bond got shorter in the excited state. Obviously, after the photo excitation, the charge transfer occurred.



HOMO LUMO

(a)



HOMO LUMO

(b)

Figure 3: Frontier molecular orbitals (HOMO and LUMO) of 6A-HBO in n-heptane(a) and DCM(b).

3.4. Potential energy curves (PECs)

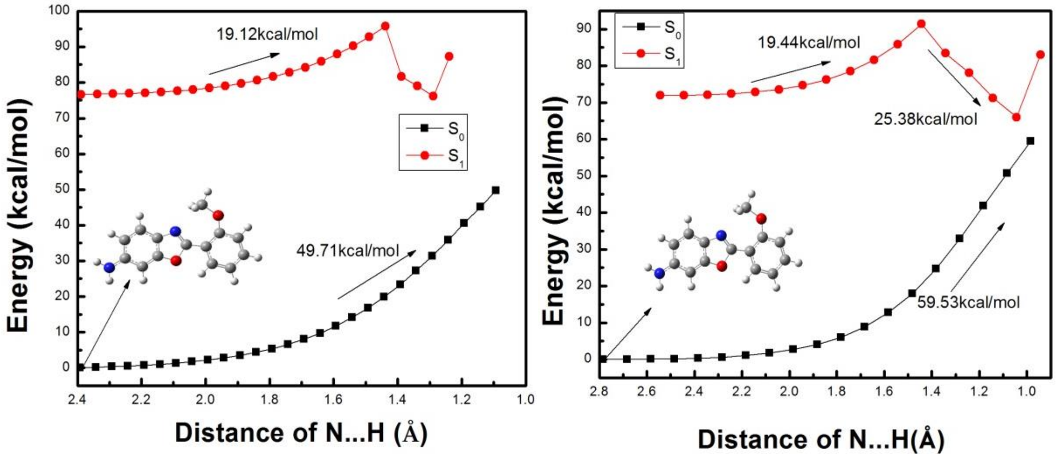
In order to further explore whether excited state intramolecular proton transfer has occurred in 6A-MBO, we studied the potential energy curves in the ground and excited states. The n-heptane and dichloromethane (DCM) were still selected as the solvents, and used DFT /TDDFT / B3LYP / TZVP theoretical level to calculate, this levels have been proved to be reliable by previous study in providing the potential energy curves. We fixed the N...H bond in a series of values to construct the potential energy curves (as shown in **Figure 4**), the length of the N...H bond shorten in a step of 0.1Å. The ground potential energy curves showed that energy monotonically increase with the shortening of N...H bond in both n-heptane and DCM solvent. There is no stable point in the ground state potential curves, which means that proton transfer process couldn't happen in the ground state. The PECs in S_1 state were very strange, for 6A-MBO in n-heptane form, energy increased 19.12kcal/mol with the shortening N...H bond, it's worth to note that while the length of N...H bond shorten to 1.44 Å, the energy reached the maximum and then fell sharply, it decreased to the minimum at 1.29Å, and then suddenly reverse to increased again. The unusual excited state potential curves also occurred in the DCM solvent, the energy grew firstly along with the N...H bond shortening, it had grown 19.44kcal/mol at the distance of N...H bond shorten to 1.44 Å, reaching the maximum, then reversed to drop 25.38kcal/mol sharply, at 1.04 Å reached the minimum reversed again. Although there were two minimum points in the PECs of 6A-MBO in the excited state, in both n-heptane and DCM solvent, and the barrier was lower than that in the ground state, the energy barrier in the excited state were still large, and the two unusual veers occurred in the potential energy curves in the excited state suggested that the molecular state was not stable. Therefore, we suspect that 6A-MBO could not realize excited state intramolecular proton transfer in both n-heptane and DCM solvent. Seems to come to the conclusion that, both in the ground and excited state, the polarity of solvent scarcely affect the potential energy of 6A-MBO, and the 6A-MBO cannot realize excited state intramolecular proton transfer.

4. Conclusion

In summary, in order to explore the proton transfer or charge transfer occurred in the 6-amino-2-(2′-methoxyphenyl)benzoxazole (6A-MBO) upon photo excitation, we chose DFT / TDDFT/ B3LYP / TZVP theoretical level, calculated the molecular geometric structure, the frontier molecular orbitals, electronic spectrum and the potential energy curves. The changes of primary bond length and angles proved that the intramolecular hydrogen bond was strengthened in the excited state. Through the analysis of calculated absorption and fluorescence spectra, which was in good agreement with the experimental data, we found the fluorescence spectra show a normal Stokes shift, and the Stokes shift grow larger with the solvent polarity increase, which indicated that photo-excitation intramolecular charge transfer (ICT) process occurred in the 6A-MBO dye. Then we further explored the possibility of the charge transfer or proton transfer in the excited state specifically. The calculation of frontier molecular orbitals provided intramolecular charge transfer and redistribution by photo excitation with evidence, which promote the intramolecular proton transfer. However, the unusual excited-state potential energy curves data indicated that proton transfer cannot occur in the excited state. Thus, we concluded that the ESIPT of 6A-MBO cannot happen by photo excitation, only charge transfer occurred in the excited state.

Table 2. The calculated electronic excitation energy (nm), oscillator strengths and the corresponding compositions of 6A-MBO in n-heptane and DCM solvent at TDDFT / B3LYP / TZVP theoretical level. H: the highest occupied molecular orbital (HOMO), L: the lowest unoccupied molecular orbital (LUMO).

Solvent	λ(nm)	f	Composition	CI(%)
n-heptane	355.1	0.7112	H→L	98.62%
	297.42	0.0275	H-1→L	82.47%
			H→L+1	7.53%
			H→L+2	5.18%
DCM	343.71	0.6926	H→L	99.15%
	280.03	0.0029	H-2→L	21.23%
			H→L+1	71.65%
			H→L+2	2.75%



(a) (b)

Figure 4: Potential energy curves of the ground and excited states for 6A-MBO in(a) n-heptane and (b) DCM solvent with the N...H bond shorten.

Acknowledge

This work was financially supported by the National Natural Science Foundation of China (Grant No. 11304135 and 21271095), the Doctor Subject Foundation of the Ministry of Education of China (20132101110001), and the Shenyang Natural Science Foundation of China (F15-199-1-04). Liaoning Provincial Department of Education Project (Grant No. L2015200) and the Natural Science Foundation of Liaoning Province (Grant No. 201602345).

References

[1] N. J. Turro, Molecular photochemistry. University Science Books: Sausalito, CA, 1991.

[2] M. G. Pan, J. N. Yao and Z. H. Tong, Molecular photo chemistry and optical functional materials science, Science press, Beijing, 2009.

[3] G.J. Zhao and K. L. Han, Hydrogen bonding in the electronic excited state, Acc. Chem. Res., 45 (2012), 404-413.

[4] K.L. Han and G.J. Zhao, Hydrogen bonding and transfer in the electronic excited state, John Wiley & Sons, Ltd, Chichester, 2011.

[5] J. C. Dore and J. Teixira, Hydrogen-bonded liquids, Kluwer Academic, Boston, 1991.

[6] G. R. Desiraju and T.Steiner, The weak hydrogen bond in structural chemistry and biology, Oxford University Press, New York., 1999.

[7] G. J. Zhao, K. L. Han and P. J. Stang, Theoretical insights into hydrogen bonding and its influence on the structural and spectral properties of Aquo palladium(II) complexes: *cis*-$[(dppp)Pd(H_2O)_2]^{2+}$, *cis*-$[(dppp)Pd(H_2O)(OSO_2CF_3)]^{+}(OSO_2CF_3)^{-}$, and *cis*-$[(dppp)Pd(H_2O)_2]^{2+}(OSO_2CF_3)^{-}_2$, J. Chem. Theory Comput., 5 (2009), 1955–1958.

[8] G. J. Zhao and K. L. Han, Early time hydrogen-bonding dynamics of photo excited coumarin 102 in hydrogen-donating solvents: Theoretical study, J. Phys. Chem. A, 111 (2007), 2469-2474.

[9] 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.

[10] F. B. Yu, P. Li, G. J. Zhao, T. S. Chu and K. L. Han, A near-IR reversible fluorescent probe modulated by selenium for monitoring peroxynitrite and imaging in living cells, J. Am. Chem. Soc., 133 (2011), 11030-11033.

[11] 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., 20 (2013), 7674-7680.

[12] K. L. Han and G. Z. He, Photochemistry of aryl halides: Photodissociation dynamics, J. Photochem. Photobiol. C, 8 (2007), 55-66.

[13] J. Mack and J. R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: a review, J.

Photochem. Photobiol.A, 128 (1999), 1-13.

[14] T. E.Bitterwolf, Organometallic photochemistry at the end of its first century, J. Organomet. Chem., 689 (2004), 3939-3952.

[15] V. Vaida, Sunlight initiated atmospheric photochemical reactions, Int. J. Photoenergy, 7 (2005), 61-70.

[16] M. Garavelli, Computational organic photochemistry: strategy, achievements and perspectives, Theor. Chem. Acc., 116 (2006), 87-105.

[17] M. R. Wasielewski, Photoinduced electron transfer in supramolecular systems for artificial photosynthesis, Chem. Rev., 92 (1992), 435-461.

[18] N. Mataga, H. Chosrowjan and S. Taniguchi, Ultrafast charge transfer in excited electronic states and investigations into fundamental problems of exciplex chemistry: Our early studies and recent developments, J. Photochem. Photobiol. C, 6 (2005), 37-79.

[19] P. F. Barbara, T. J. Meyer and M. A. Ratner, Contemporary issues in electron transfer research, J. Phys. Chem., 100 (1996), 13148-13168.

[20] R. A. Bissell, Fluorescent PET (photoinduced electron transfer) sensors, Cheminform, 168 (2006), 223-264.

[21] H. B.Gray and J. R. Winkler, Electron transfer in proteins, Annu. Rev. Biochem., 65 (1996), 537-561.

[22] M. J. Weaver, Dynamical solvent effects on activated electron-transfer reactions: principles, pitfalls, and progress, Chem. Rev., 92 (1992), 463-480.

[23] G. J. Zhao and K. L. Han, Ultrafast hydrogen bond strengthening of the photoexcited fluorenone in alcohols for facilitating the fluorescence quenching, J. Phys. Chem. A, 111 (2007), 9218-9223.

[24] P. Piotrowiak, Photoinduced electron transfer in molecular systems: recent developments, Chem. Soc. Rev., 28 (1999), 143-150.

[25] G. J. Zhao, J. Y. Liu and L. C. Zhou, 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.

[26] Z. R.Grabowski, K.Rotkiewicz and W. Rettig, Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures, Chem. Rev., 34 (2003), 3899-4032.

[27] R. K. Chen, G. J. Zhao, X. C. Yang, X. Jiang, J. F. Liu, H. N. Tian, Y. Gao, X. Liu, K. L. Han, M. T. Sun and L. C. Sun, Photoinduced intramolecular charge-transfer state in thiophene-π-conjugated donor–acceptor molecules, J. Mol. Struct., 876 (2008), 102-109.

[28] A. C. Legon, The nature of ammonium and methylammonium halides in the vapour phase: hydrogen bonding versus proton transfer, Chem. Soc. Rev., 22 (1993), 153-163.

[29] R. I. Cukierand D. G. Nocera, Proton-coupled electron transfer, Annu. Rev. Phys. Chem., 49 (1998), 337-369.

[30] K. Bhattacharyya, Solvation dynamics and proton transfer in supramolecular assemblies, Acc. Chem. Res., 36 (2003), 95-101.

[31] D. Ma, F. Liang, L. Wang, S. T. Lee and L. S. Hung, Blue organic light-emitting devices with an

oxadiazole-containing emitting layer exhibiting excited state intramolecular proton transfer, Chem. Phys. Lett.,358 (2002), 24-28.

[32] D. G. 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.

[33] J. Catalan, J. C. D. Valle, F. Fabero and N. A. Garcia, The influence of molecular conformation on the stability of ultraviolet stabilizers toward direct and dye-sensitized photo irradiation: The case of 2-(2'-hydroxy-5'-methyphenyl) benzotriazole, Photochem. Photobiol., 61 (1995), 118-123.

[34] P. T. Chou, M. L. Martine and S. L. Studer, The design of an effective 'fluorescence filter' for Raman spectroscopy, Appl. Spectrosc., 45 (1991), 918-921.

[35] M. Irie, Photochromism: memories and switches-introduction, Chem. Rev., 100 (2000), 1683-1684.

[36] Y. Nagaswa, A. P. Yartsev, K. Tominagea，P. B. Bisht, A. E. Johnson and K. Yoshihara, Dynamic aspects of ultrafast intermolecular electron transfer than solvation process: Substituent effects and energy gap dependence, J. Phys. Chem., 99 (1995), 653-662.

[37] H. Pal, Y. Nagaswa, A. K. Tominaga and K. Yoshihara, Deuterium isotope effect on ultrafast intermolecular electron transfer, J. Phys. Chem., 100 (1996), 11964-11974.

[38] H. Shirota, H. Pal, A. K. Tominaga and K. Yoshihara, Substituent effect and deuterium isotope effect of ultrafast intermolecular electron transfer: coumarin in eletron-donating solvent, J. Phys. Chem. A, 102 (1998), 3089-3102.

[39] O. F. Mohammed, N. Banerji, B. Lang, E. T. J. Nibbering and E. Vauthey, Photoiduced bimolecular electron transfer investigated by femtosecond time-resolved infrared spectroscopy, J. Phys. Chem. A, 110 (2006), 13676-13680.

[40] O. F. Mohammed, K. Adamczyk, N. Banerji, J. Dreyer, B. Lang, E. T. Nibbering and E. Vauthey, Direct femtosecond observation of tight and loose ion pairs upon photoinduced bimolecular electron transfer, Angew. Chem. Int. Ed., 47 (2008), 9044-9048.

[41] M. Gutierrez, N. Alarcos, M. Liras, F. Sanchez and A. Douhal, Switching to a reversible proton motion in a charge-transferred dye, J. Phys. Chem. B, 119 (2015), 552-562.

[42] N. Alarcos, M. Gutierrez, M. Liras, F. Sanchez and A. Douhal, An abnormally slow proton transfer reaction in a simple HBO derivative due to ultrafast intramolecular-charge transfer events, Phys. Chem. Chem. Phys., 17 (2015), 16257-16269.

[43] R. I. Cukier and D. G. Nocera, Proton-coupled electron transfer, Chem. Rev., 112 (2012), 337-369.

[44] S. Hammes-Schiffer and A. A. Stuchebrukhov, Theory of coupled electron and proton transfer reactions, Chem. Rev., 42 (2010), 6939-6960.

[45] 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, J. 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 and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.

[46] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys., 98 (1993), 5648-5652.

[47] C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B: Condens. Matter, 37 (1988), 785-789.

[48] B. Miehlich, A. Savin, H. Stoll and H. Preuss, Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr, Chem. Phys. Lett., 157 (1989), 200-206.

[49] O. Treutler and R. Ahlrichs, Efficient molecular numerical integration schemes, J. Chem. Phys., 102 (1995), 346-354.

[50] F. Furche and R. Ahlrichs, Adiabatic time-dependent density functional methods for excited state properties, J. Chem. Phys., 117 (2002), 7433-7447.

[51] J. Seo, S. Kim and S. Y. Park, Strong solvatochromic fluorescence from the intramolecular charge-transfer state created by excited-state intramolecular proton transfer, J. Am. Chem. Soc., 126 (2004), 11154-11155.

[52] C. C. Hsieh, Y. M. Cheng, C. J. Hsu, K. Y. Chen and P. T. Chou, Spectroscopy and femtosecond dynamics of excited-state proton transfer induced charge transfer reaction, J. Phys. Chem. A, 112 (2008), 8323-8332.

[53] C. H. Kim, J. Park, J. Seo, S. Y. Park and T. Joo, Excited state intramolecular proton transfer and charge transfer dynamics of a 2-(2′-Hydroxyphenyl) benzoxazole derivative in solution, J. Phys. Chem. A, 114 (2010), 5618-5629.

[54] M. Gutierrez, N. Alarcos, M. Liras, F. Sánchez and A. Douhal, Switching to a reversible proton motion in a charge-transferred dye, J. Phys. Chem. B, 119 (2015), 552-562.

[55] Y. M. Dai, J. F. Zhao, Y. L. Cui, Q. Y. Wang, P. Song, F. C. Ma and Y. Y. Zhao, Study of fluorescence probe transfer mechanism based on a new type of excited-state intramolecular proton transfer, Spectrochim. Acta, Part A , 144 (2015), 76-80.

[56] G. J. Zhao and K. L. Han, Site-specific solvation of the photo excited proto chlorophyllide a in methanol: formation of the hydrogen-bonded intermediate state induced by hydrogen-bond strengthening, Biophys. J., 94 (2008), 38-46.

[57] G. J. Zhao and K. L. Han, Time-dependent density functional theory study on hydrogen-bonded intramolecular charge-transfer excited state of 4-dimethylamino-benzonitrile in methanol, J. Comput. Chem., 29 (2008), 2010-2017.

[58] G. J. Zhao and K. L. Han, PH-Controlled twisted intramolecular charge transfer (TICT) excited state via changing the charge transfer direction, Phys. Chem. Chem. Phys., 12 (2010), 8914-8918.

[59] J. F. Zhao, P. Song, Y. L. Cui, X. M. Liu, S. W. Sun, S. Y. Hou and F. C. Ma, Effects of hydrogen bond on

2-aminopyridine and its derivatives complexes in methanol solvent, Spectrochim. Acta, Part A, 131 (2014), 282-287.

[60] M. Zhou, J. F. Zhao, Y. L. Cui, Q. Y. Wang, Y. M. Dai, P. Song and L. X. Xia, Theoretical study on the excited-state intramolecular proton-transfer reaction of 10-hydroxybenzo [h] quinoline in methanol and cyclohexane, J. Lumin., 161 (2015), 1-6.