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THEORETICAL STUDIES ON EXCITED STATE PROTON TRANSFER TAUTOMERISM REACTION AND SPECTROSCOPIC PROPERTIES OF 8-HYDROXYQUINOLINE MONOMERS AND DIMERS© 2009 Z.-Y. Zhou^{1,3*}, G.-G. Shan³, Y.-L. Zhu², X.-J. Yu¹, Y.-H. Dong¹, J.-Y. Zhao³¹College of Chemical Engineering, Shandong University of Technology, Zibo, Shandong, 255049, P. R. China²Department of Chemistry, College of Science, Yanbian University, Yanji, Jilin, 133002, P. R. China³Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials (Huaiyin Teachers College), Huai'an, Jiangsu, 223300, P. R. China

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By means of *ab initio* HF methods, the ground state structures of 8-hydroxyquinoline (8-HQ) monomers and dimers were optimized using the 6-311+g* and 6-31G basis sets, respectively. The lowest singlet excited states of 8-HQ monomers and dimers have been studied by the single-excitation configuration interaction (CIS) approach at the same level. In the studies of the potential energy surface, it was found that all the stable configurations corresponded to enol form. The UV-vis and fluorescence spectra of 8-HQ monomers and dimers under a solvent effect condition were also calculated using the TD-B3LYP/6-31+G* method based on the HF- and CIS-optimized geometries. The computed absorption and fluorescence spectral characteristics for monomers and dimers were in good agreement with previously reported experimental values. The results also show that 8-HQ has very poor fluorescence in solvents.

Key words: 8-hydroxyquinoline, proton transfer, excited state, spectroscopy.

Proton transfer attracts considerable attention because it plays a key role in a wide variety of biological and chemical phenomena [1—4]. Numerous studies have been devoted to monofunctional compounds able to exhibit excited state intermolecular proton transfers and the impact of solvation on these processes has been pointed out. It is well known that the transfers result in significant charge rearrangement [5]. Moreover, during the last few decades, the excited state intermolecular and intramolecular proton transfer reactions have been studied extensively to explore the photophysical phenomena, photodynamics and the application of organic molecules exhibiting proton transfer reactions in various fields [3, 6].

Chelate metal complex of 8-hydroxyquinoline (8-HQ) is one of the most important electroluminescence materials that have been studied from both experimental and theoretical viewpoint [7—9]. Besides its chelating properties, 8-HQ is widely used in analytical chemistry as a fluorogenic ligand . It shows a very weak fluorescence intensity and a low quantum yield in aqueous and organic solutions, possibly because the photoisomerization process generates a nonfluorescent tautomeric form [10—12]. We have reported theoretical studies on ground state proton transfer tautomerism reaction of 8-hydroxyquinoline monomers and dimers [13], and the excited state proton transfer tautomerism reaction and spectroscopic properties of 6-methyl-4-hydroxy-pyrimidine monomers and dimers [14]. In this work, we investigate the intramolecular and intermolecular proton transfer processes of 8-HQ in the excited state.

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COMPUTATIONAL METHOD

All calculations reported in the paper were carried out using the Gaussian-03 suite package [15]. Based on the ground-state geometries which were optimized using the density functional theory method with the Becke3LYP functional [14], the geometric structures of the 8-HQ monomers and dimers were optimized in the first singlet state using configuration interaction with all singly excited determinants (CIS) with the 6-311+g* and 6-31G basis sets, respectively. The frontier molecular orbital characteristics have been analyzed in order to study the electronic transition mechanism in the dimer. The vibrational frequencies were calculated at the same level. To confirm the connection of transition states with designated intermediates, intrinsic reaction coordinate calculations also were performed. The tendencies from transition states to either reactant or product were verified and the results proved that the optimized transition states obtained were reliable. The UV-vis absorption and fluorescence spectra of 8-HQ monomers and dimers under a solvent effect condition were also investigated with hybrid time-dependent density functional theory with 6-31+G* basis set. During the calculations, the default value (10^{-8}) defined by the program was adopted as the convergence precision.

RESULTS AND DISCUSSION

Electronic structure of 8-HQ monomers and dimers in the excited state. The geometric structures of isomers and transition states of 8-HQ monomer in the ground and excited states and their geometric parameters are shown in Fig. 1. The enol form of 8-HQ monomer (MD1) was excited from

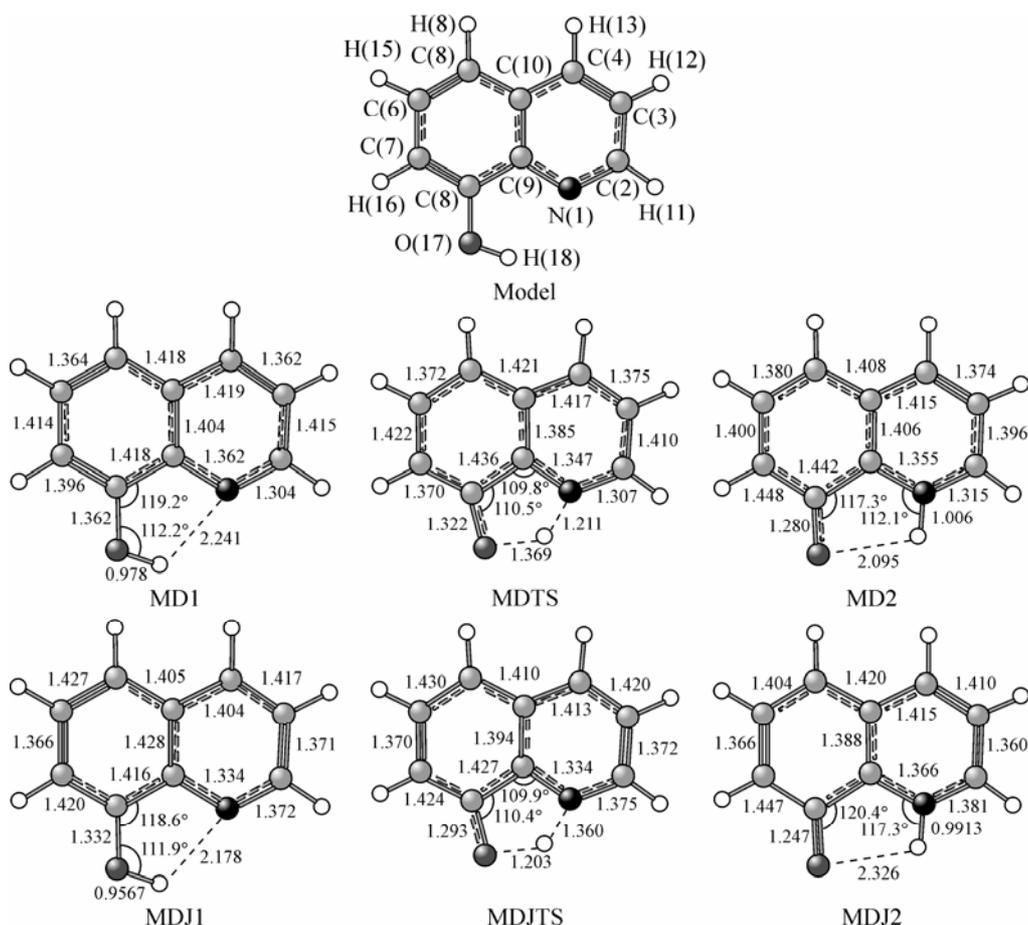


Fig. 1. Geometric structures of isomers and transition states of 8-HQ monomers in the ground state (MD*) and excited state (MDJ*).

Bond lengths and angles in angstroms and degrees, respectively

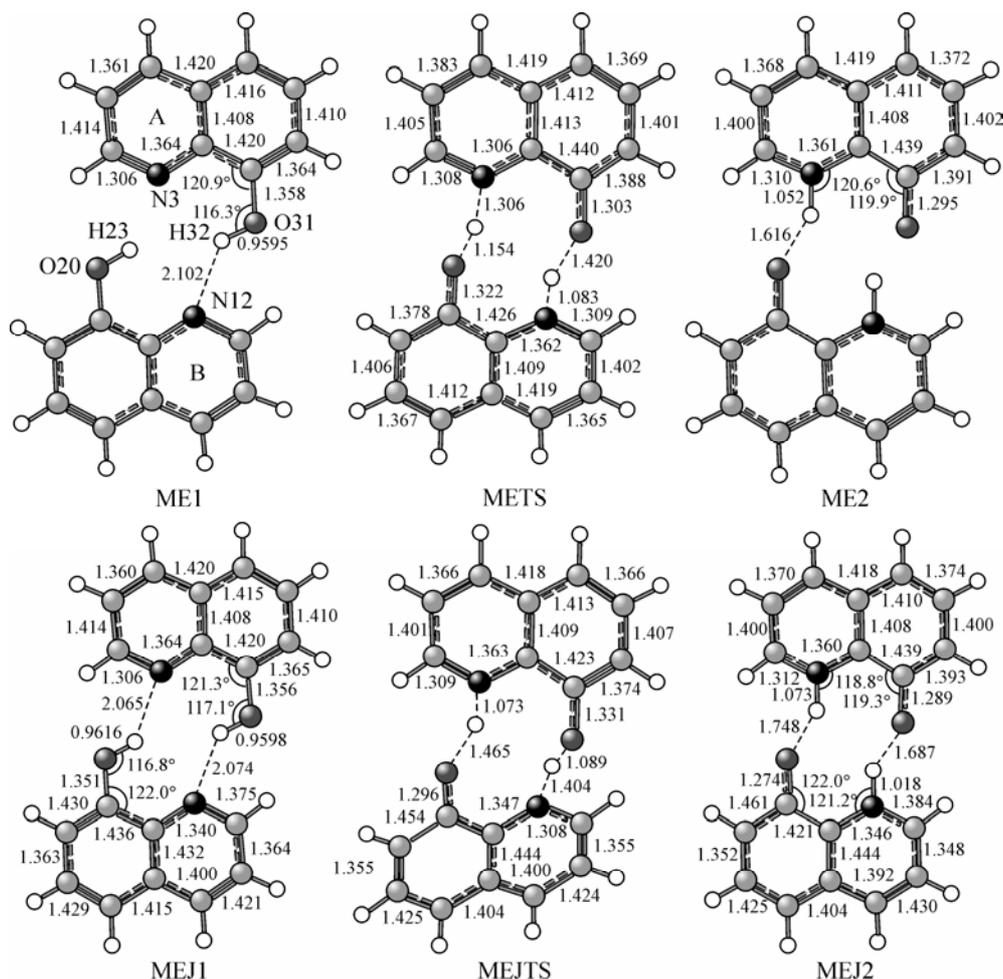


Fig. 2. Geometric structures of isomers and transition states of 8-HQ dimers in the ground state (ME*) and excited state (MEJ*).

Bond lengths and angles in angstroms and degrees, respectively

the ground state to the corresponding lowest singlet excited state (MDJ1). The bond lengths C9—N1 and C8—O17 were shrunk, whereas the bond length C7—C8 and C2—N1 were elongated. The angle C9—C8—O17 decreased leading to the length of the intramolecular hydrogen bond H18—N1 to shrink from 2.241 Å to 2.178 Å, and the distance N1—O17 to reduce by 0.051 Å. This indicates that the energy of hydrogen bonds in the excited state is higher than in the ground state. It also indicates that the intramolecular proton transfer in the excited state is easier than in the ground state. Whereas, comparison of the ground and excited state geometric configuration parameters of keto form (MD2 vs MDJ2) reveals that C8—O17 and N1—H18 distances clearly decreased, the bond angles C9—C8—O17 and C9—N1—H18 increased, resulting in the intramolecular hydrogen bond H18—O17 being elongated from 2.095 Å to 2.326 Å. The discrepancy is more remarkable for the transition state, where the position of proton H18 is close to the nitrogen atom of pyridine ring in the ground transition state, whereas it is close to the oxygen atom of phenol ring in the excited state.

Fig. 2 displays the geometric structures of isomers and transition states of 8-HQ dimers in both the ground and excited states with geometric parameters labeled. The two 8-HQ molecules in the dimer were denoted as A and B. A has the same geometric parameters as B in the ground state, but in the excited state they differ. One reason that causes the difference might be the electron transition from an occupied to a virtual MO. The electronic transition causes some electron density redistribution. For example, analysis of the difference of geometric configuration parameters between the

Zero-point vibration energy E_{zp} (a.u.), total energy E (a.u.), vibrational frequency ν (cm^{-1}) of isomers and transition states of 8-HQ monomers (MD*) and dimers (ME*)

Species	E_{zp}	E	ν	Species	E_{zp}	E	ν
MD1	0.150536	-474.125538	—	ME1	0.303334	-948.064082	—
MD2	0.150508	-474.090239	—	ME2	0.305166	-948.043226	—
MDTS	0.142151	-474.074330	-1752.9	METS	0.297564	-948.032060	-1167.8
MDJ1	0.145550	-474.108328	—	MEJ1	0.280784	-948.046363	—
MDJ2	0.148629	-474.075627	—	MEJ2	0.281960	-948.023192	—
MDJTS	0.142150	-474.064428	-2031.6	MEJTS	0.273746	-948.014651	-521.5

ground and excited states of 8-HQ dimer (ME1 vs MEJ1) shows that A exhibits almost no change, while B changes implying that an electron from B may be excited. In addition, the bond length parameters of the transition state of 8-HQ dimer in the excited state (MEJTS) reveal that the two protons are close to A.

The energy parameters of 8-HQ monomer and dimer in the excited state. The zero-point energy, total energy and vibrational frequency are listed in Table. The results indicate that the enol form (MD1) is moderately more stable than the keto form (MD2) in the ground state. When excited to their corresponding first excited states, they show the same relation as in the ground state. From the energy of the dimers, we also found the dimer of enol form is much more stable than that of keto form in both the ground and excited states.

The isomerization reaction process of 8-HQ monomers and dimers in the excited state. Potential energy surfaces of the ground and excited states of monomers are shown in Fig. 3. It can be seen that the reaction MD1→MDTS→MD2 is an endothermic process, with the direct activation energy and reverse activation energy being 134.1 kJ/mol and 41.8 kJ/mol, respectively. This result indicates that the reverse reaction can occur at room temperature, but direct reaction has a large reaction barrier and is difficult to occur. The excited state reaction MDJ1→MDJTS→MDJ2 is also endothermic (85.9 kJ/mol). The direct activation energy and reverse activation energy are 115.3 kJ/mol and 29.3 kJ/mol, respectively. The reverse reaction can easily proceed at room temperature, while, although the direct activation energy in the excited state is lower than in the ground state, the direct reaction is still difficult to occur. Consequently the reaction pathways of the ground and excited states can explain the fact the UV-vis absorption and fluorescence spectra of monomer and dimers all corresponded to enol form.

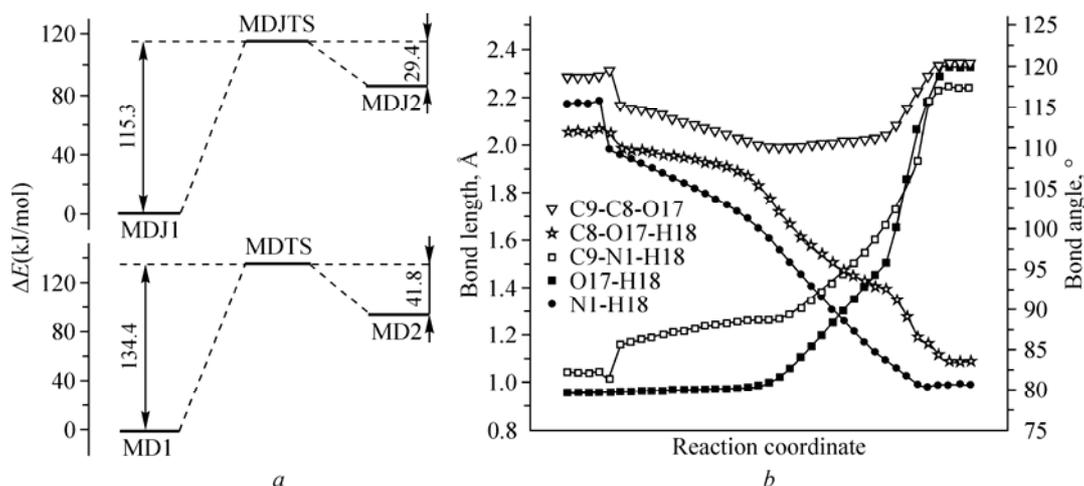


Fig. 3. (a) Schematic diagram of potential energy surfaces describing the ground state and excited state of monomers (kJ/mol, the energy of MD1 and MDJ1 taken as zero). (b) Variations of geometric parameters in the excited state proton transfer tautomerism of 8-HQ monomers analyzed by IRC

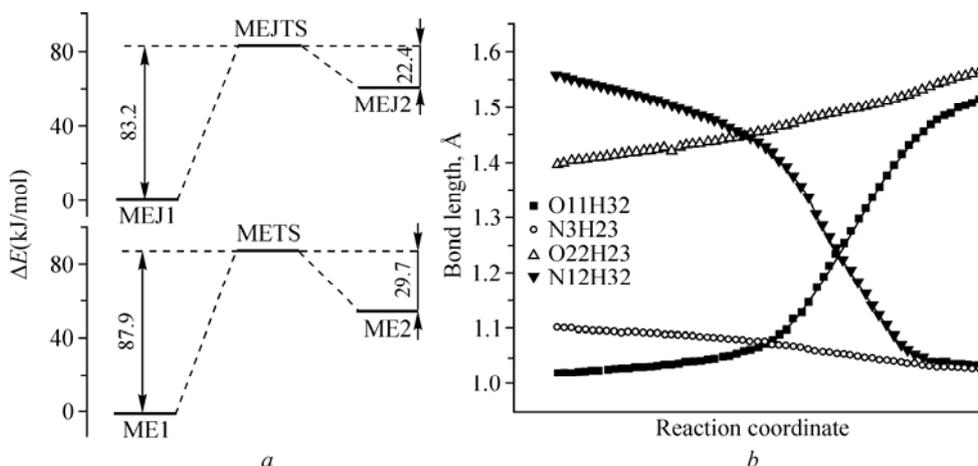


Fig. 4. (a) Schematic diagram of potential energy surfaces describing the ground and excited states of dimers (kJ/mol, the energy of ME1 and MEJ1 taken as zero). (b) Variations of geometric parameters in the excited state proton transfer tautomerism of 8-HQ dimers analyzed by IRC

Fig. 3, *b* shows variations of the geometric parameters for MDJ1→MDJTS→MDJ2 during isomerization process as a function of intrinsic reaction coordinate. As the reaction starts, the bond length O17—H18 is elongated while N1—H18 gradually shrinks. At the same time, the bond angle C8—O17—H18 becomes smaller but C9—N1—H18 grows; the bond angle C9—C8—O17 at first gradually decreases. It shows that the proton is close to the nitrogen atom of pyridine ring. But when the pentanuclear transition state formed, the angle of C9—C8—O17 slowly becomes greater. When H18 reaches N1, the product MDJ2 is formed.

One can see from Fig. 4, *a* that isomerization reactions in both the ground and excited states of 8-HQ dimers are endothermic processes, with the endothermic energy of 58.2 kJ/mol and 60.8 kJ/mol, respectively. From the studies of the potential energy surface, although the direct activation energy and reverse activation energy of 8-HQ dimers in the ground state are smaller than for monomers, they are 87.9 kJ/mol and 29.7 kJ/mol, respectively. It shows that the reverse reaction can readily occur at room temperature, whereas direct reaction can only occur with low probability. According to the Arrhenius equation, the population ratio in the gas phase for the keto form *vs* enol form in the ground state at 298 K is $1:1.6 \times 10^{10}$. In the same way, we can calculate the population ratio in the gas phase for the keto form *vs* enol form in the excited state, to yield $1:4.4 \times 10^{10}$. Thus, this analysis demonstrates that the enol form is the only stable structure that exists both in the excited and ground states. Hence, the fluorescence emission of dimer is from enol form.

Fig. 4, *b* shows the changes in geometric parameters during MEJ1→MEJTS→MEJ2 isomerization process as a function of the intrinsic reaction coordinate. As the reaction starts, the bond lengths N12—H32 and N3—H23 become elongated, while the lengths O11—H32 and O22—H23 gradually shorten. The result of IRC calculation shows that the two protons transfer is a concerted reaction. The two protons are in asymmetric position and the two 8-HQ molecular geometric parameters are different due to the electronic transition in the excited state. The transfer rates of the two protons are different; this causes the transition state during the transition process from MEJ1 to MEJ2 to be not a planar structure. As the two protons reach appropriate positions, the structure converges to the stable planar configuration.

The UV-visible absorption and fluorescence spectra of 8-HQ monomers and dimers. Our results show that the electron density and the orbital energy of HOMO and LUMO for enol form is similar for the ground and excited states of the monomer. This similarity could imply that the monomer would react in a similar way in both ground and excited states. Nevertheless, as shown in Fig. 5, both A and B molecules in the ground state are symmetrical, but in the excited state, the electron density mainly concentrate on A molecule. It indicates that the excited state proton transfer in 8-HQ dimer mainly occurs in B molecule, in agreement with our previous discussion.

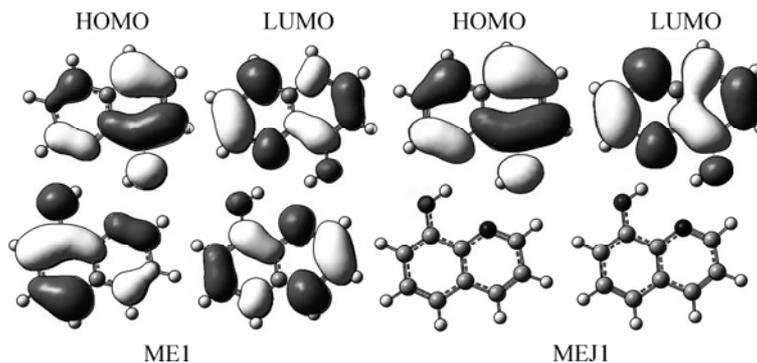


Fig. 5. Frontier molecular orbitals for the enol form of 8-HQ dimer

In the ground state of the monomer, the energy order is the following: enol form > keto form; the reaction barrier is 134.4 kJ/mol. The reaction could hardly proceed at room temperature; enol form should be the most abundant and stable species. Therefore, the absorption and fluorescence spectra of monomer correspond to the enol form.

The UV-vis absorption spectra of 8-HQ monomer under a solvent effect condition also were investigated with hybrid time-dependent density functional theory and 6-31+G* basis. For the monomer, the calculated dominant peak in the CH₂Cl₂ solution located at 308.2 nm (*cf.* experimental 309 nm [10]) indicating that the B3LYP excitation energies were in good agreement with the experimental ones. The result show that the excitation corresponds almost exclusively to the promotion of an electron from HOMO to LUMO (65.5 %).

Apparently, the TD-B3LYP/6-31+g* method provides a better prediction of the absorption wavelengths for 8-HQ monomers. Hence, we conducted similar calculations of absorption wavelengths for the 8-HQ dimer in cyclohexane solvent. The computed result (331 nm) also was in accordance with the experimental value (330 nm [11]).

The fluorescence spectra of the enol form of 8-HQ monomers in the excited state under a solvent effect condition were also investigated with hybrid TD-DFT using the same level, as well as the fluorescence emission spectra in the presence of CH₂Cl₂ solvent. The experimental value (391 nm, fluorescence emission of 8-HQ in CH₂Cl₂ [10]) is close to the calculated emission wavelength of the enol form (384 nm). Bardez and co-workers [10] also suggested that the fluorescence spectra corresponded to the enol form.

The fluorescence spectra of 8-HQ dimer also was calculated using the same method with 6-31+G* basis set in cyclohexane solvent. The calculated emission wavelength (392.0 nm) is obviously in good agreement with the experimental value (384 nm). From our computed data, both 8-HQ monomer and dimer in the excited state have small oscillator strengths (*f*) of fluorescence emission, 0.066 and 0.0951, respectively. This lack of the fluorescence in the organic solvent justifies previously reported quantum yield to be lower than 2×10^{-4} [12].

CONCLUSIONS

The *ab initio* CIS method was adopted to obtain the first singlet excited state structures of 8-hydroxyquinoline monomers and dimers. The solvent effect was modeled using the self-consistent reaction field (SCRF) method with the Tomasi's polarized continuum model (PCM). In this study we found that the absorption and fluorescence spectra of monomers and dimers all corresponded to the enol form. We calculated the spectral data by hybrid time-dependent density functional theory (TD-DFT) method in the presence of solvent, the data being in good agreement with experimental results.

The electronic transition between S₀ and S₁ for dimer was found to be mainly localized on B molecule of 8-hydroxyquinoline as evidenced from structural changes between the excited and ground states and changes in the frontier molecular orbitals. The reverse activation energy for dimerization is very low in the excited state. According to the Arrhenius equation, the population ratio in the gas phase for the keto form vs enol form in the ground and excited states at 298 K are $1:1.6 \times 10^{10}$ and

$1:4.4 \times 10^{10}$, respectively. It shows that the enol form is the stable structure existing both in the ground and excited states. The fluorescence emission and absorption were all produced by enol form. The oscillator strengths (f) from TDDFT calculation for dimer and monomer were very small. Therefore, the poor fluorescence intensity of 8-HQ in the solvents can be understood from these theoretical results.

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REFERENCES

1. Douhal A., Lahmani F., Zewail A.H. // *Chem. Phys.* – 1996. – **207**. – P. 477.
2. Mohammed O.F., Pines D., Pines E. et al. // *Science*. – 2005. – **310**. – P. 83.
3. Tolbert L.M., Solntsev K.M. // *Acc. Chem. Res.* – 2002. – **35**. – P. 19.
4. Kwon O.H., Lee Y.S., Yoo B.K., Jang D.J. // *Angew. Chem. Int. Ed.* – 2006. – **45**. – P. 415.
5. Marcus R.A., Sutin N. // *Biochim. Biophys. Acta.* – 1985. – **811**. – P. 265.
6. Wang S.L., Gao G.Y., Ho T.I., Yang L.Y. // *Chem. Phys. Lett.* – 2005. – **415**. – P. 217.
7. Brinkmann M., Fite B., Pratontep S., Chaumont C. // *Chem. Mater.* – 2004. – **16**. – P. 4627.
8. Ben Khalifa M., Vaufrey D., Tardy J. // *Organic Electronics*. – 2004. – **5**. – P. 187.
9. Mirzaee M., Amini M.M. // *Applied Organomet. Chem.* – 2005. – **19**. – P. 339.
10. Bardez E., Devol I., Larrey B., Valeur B. // *J. Phys. Chem. B.* – 1997. – **101**. – P. 7786.
11. Goldman M., Wehry E.L. // *Anal. Chem.* – 1970. – **42**. – P. 1178.
12. Cheatum C.M., Heckscher M.M., Crim F.F. // *Chem. Phys. Lett.* – 2001. – **349**. – P. 37.
13. Zhao J.Y., Zhou Z.Y., Su Z.M. et al. // *Chin. J. Chem.* – 2006. – **24**. – P. 727.
14. Zhou Z.Y., Zhao J.Y., Liu M. et al. // *Chem. J. Chinese. U.* – 2007. – **28**. – P. 2385.
15. Frisch M.J., Trucks G.W., Schlegel H.B. et al. Gaussian-03, Gaussian, Inc., Pittsburgh PA, 2003.