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Volume-conserved Twist Excited-state of π-Conjugated Molecules

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The excited state characters of HY103 have been studied by means of time-resolved photon emission (time-correlated single photon counting) and time dependent density functional theory calculations. The experimental and theoretical results demonstrate that HY103 dyes undergo an efficient one-bond-flip motion after photoexicitation at room temperature, which leads to a very short lifetime of the normal fluorescence state, and a weak fluorescence emission around 670 nm. However, when HY103 are excited in amorphous glasses at 77 K, the normal fluorescence emission is prolonged to nanoseconds time scale about 2 ns, and the fluorescence emission is enhanced. Furthermore, a new emission state is produced, which is characterized as a volume-conserved twisted (VCT) state. This is the first observation of a VCT state. The experiment indicates that the VCT motion of excited state of π-conjugated molecules in restricted environment can form a stable emission state, and the excited state character of π-conjugated molecules in restricted environment is complex.

Key words: Volume-conserved twisted state, Time-resolved photon emission, Photoisomerization

I. INTRODUCTION

π-conjugated molecules have been attracting intensive attention because of their various photochemical and photophysical properties [1, 2]. π-conjugated molecules are widely used in man-made system [3, 4], such as sensitizers in dye sensitized solar cells (DSSCs) [5, 6], and biological system, such as photosynthesis system [7], and vision process [8]. After photoexcitation, π-conjugated molecules take various photochemical and photophysical processes, which are caused by electrons or nucleuses motion, *e.g.* charger transfer, photoisomerization. The nucleuses motion as one of the most important processes in the excited state of which π-conjugated molecules has been extensively studied, *e.g.* the photoinduced isomerization process of π-conjugated molecules in flexible media at room temperature, which has been extensively investigated using time-resolved spectroscopy or by performing quantum chemical calculations of the excited state [9−12]. After photoexcitation, the molecules tend to take a torsion relaxation around the π-conjugated linkage (C=C) to form a strong coupling between the excited state and ground state potential energy surfaces in flexible media [13−15], and the isomerized product is produced. All

these reports have a perfect matching both in experiment and theory. While referring to the nucleuses motion in restricted media, *e.g.* the vision process beginning with photoexcitation of the retinal chromophore in rhodopsion protein [7, 8], the photoisomerization of 1,4-dimethyl-1,4-diphenylbutadines in amorphous glass at 77 K [16], rational conclusion has not been reached, even though a lot of studies in this field have been done [17−19]. Recently, Liu *et al.* have proposed a new photoisomerization mechanism to explain the photoisomerization process of π-conjugated molecules in restricted environment, such as amorphous glass and protein [20]. This mechanism is called as Hula-twist, according to Hula-twist, the volume of π-conjugated molecules is conserved during the photoisomerization process.

In this work, we just can point out that an unstable conical intersection can be formed to lead a photoisomerization process in restricted media, but have no idea whether π-conjugated molecules possess other photochemical and photophysical properties in restricted media. The excited state character of a π-conjugated dye HY103 which was designed as sensitizers for DSSCs devices by Sun *et al.* [21] and is shown in Fig.1, in acetonitrile was studied. The experimental and theoretical results show that after photoexcitation, HY103 takes an ultrafast photoisomerization process in flexible media, but in amorphous glass at 77 K, this ultrafast photoisomerization process (one-bond-flip) is inhibited, and a new emission state has been observed.

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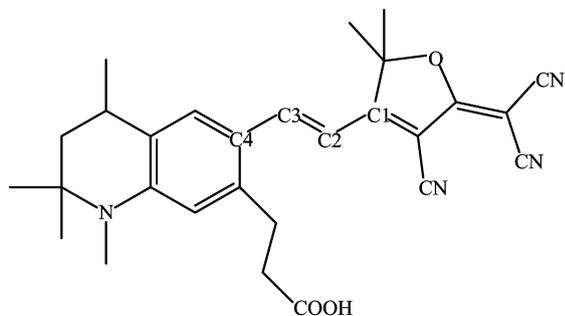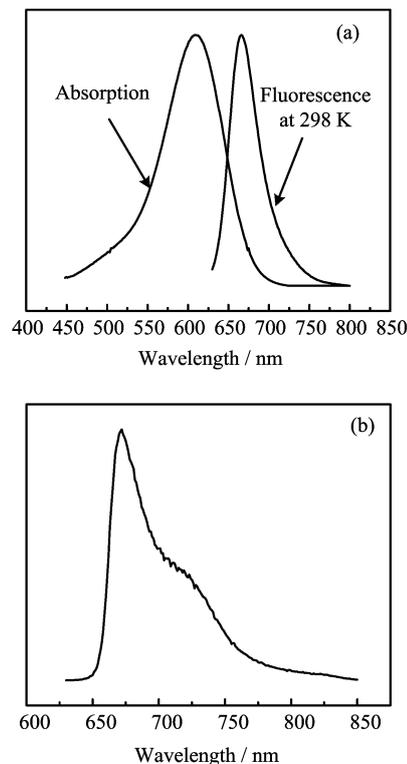
FIG. 1 The molecular structure of HY103 [21].

FIG. 2 (a) The steady state absorption spectra and fluorescence spectra of HY103 in acetonitrile (0.1 mmol/L) at room temperature, (b) the fluorescence spectra of HY103 at 77 K. All the fluorescence spectra are excited at 460 nm.

II. EXPERIMENTS

The steady-state absorption spectra were recorded using a UV-visible absorption spectrophotometer (HP8453, Hewlett-Packard Corp). The fluorescence spectra were measured with a FluoroMax-4P Spectrofluorometer (HORIBA JOBIN YVON Corp). The time-resolved photon emission dynamics are obtained with a nanosecond laser time-correlated single photon counting (TCSPC) setup (HORIBA JOBIN YVON Corp). The instrument response function of the laser system has an FWHM of 1 ns and the time resolution is estimated at 200 ps. The time ranges are 55 ps/channel, in 4096 effective channels. The time-resolved photon emission dynamics are fitted to the exponentials function using a least-squares algorithm with the commercial IBH software. The solutions were degassed with N_2 for at least 30 min prior to data collection and sealed during the measurements.

III. COMPUTATIONAL METHODS

All the structure and potential energy curve calculations in this work have been performed with the Gaussian 09 package [22]. The initial geometry optimization was done by density functional theory (DFT) with the hybrid function B3LYP and 6-31G(d) basis set. The study of the excited state properties has been carried out by time dependent density functional theory (TDDFT) [23−25] using B3LYP/6-31G(d). TDDFT method has been used to study the excited state properties by many groups [26−30]. Poprawa-Smoluch *et al.* showed that the TDDFT method could properly describe the excited-state potential energy surface [31], and Fantancci *et al.* proposed that the geometry with very low TDDFT excited energy corresponded to the conical intersection using the CASPT2 method [32]. In this study, we did not perform a CASPT2 calculation for its time exhausting applying in big system as HY103.

IV. RESULTS AND DISCUSSION

A. Absorption and fluorescence spectra

The structure of HY103 is shown in Fig.1. It is composed by a double bond C2=C3 as the π-conjugated linkage between a tetrahydronquinoline unit and a multi-cyano group [21].

Figure 2(a) presents the steady state absorption spectra and fluorescence spectra of HY103 at room temperature. The maximum of absorption spectra is about 609 nm and the maximal fluorescence emission is about 665 nm. During the fluorescence emission measurement, we found that the fluorescence emission intensity is very weak. In order to obtain a strong fluorescence emission we measured the fluorescence spectra of HY103 at 77 K, shown in Fig.2(b). Figure 2(b) displays the fluorescence emission peak of HY103 at 77 K about 670 nm, which is tiny red shift in comparison to that at room temperature. Besides this normal fluorescence emission around 670 nm, there is a shoulder at the wavelength region from 690 nm to 730 nm in Fig.2(b). This indicates that there is another emission spectrum in this region and overlap with the fluorescence emission (maximum at 670 nm). It is well known that the phosphorescence emission from a triplet excited state will be present at 77 K, but absent at room tempera-
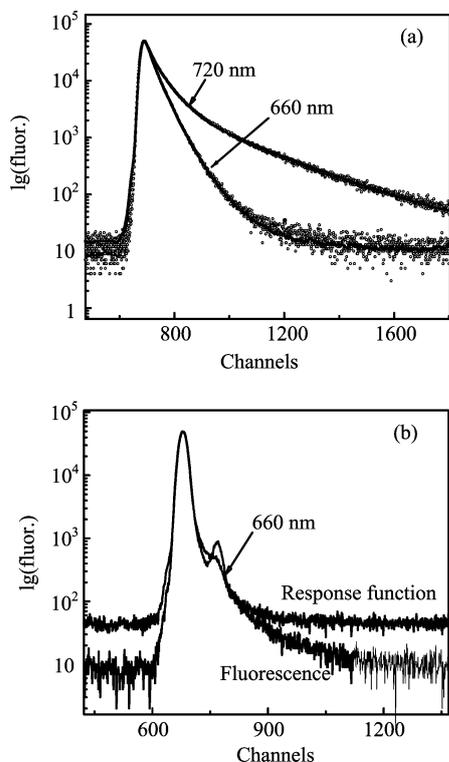
FIG. 3 (a) The time-resolved photon emission dynamics of HY103 in acetonitrile at 77 K. The solid lines are fits and the circles are experimental data. (b) The time-resolved photon emission dynamics of HY103 in acetonitrile at room temperature (fluor. standing for fluorescence intensity).

ture. So it is not surprising if this new emission spectra are from the triplet emission.

B. Lifetime measurement at low temperature

The lifetime of triplet state emission is considered to be on the microsecond time scale in absence of quenching medium. If this new emission spectrum is from the triplet emission, its lifetime must be on the microsecond time scale in our measurement condition (degassed by N_2 for 1.5 h). In order to figure out the origin of this new emission spectrum, we measured the photon emission dynamics of HY103 at 77 K in nitrogen environment. Figure 3(a) presents the time-resolved photon emission curve at 720 nm. This wavelength lies in the new state emission wavelength region (690−730 nm). Therefore, it can represent the character of this new emission state. This emission curve can be reconstructed by a tri-exponential function convolution with the instrument response function. From the fitting components, we found that most of the contributions to this emission curve are from two components, one is about 2.7 ns and the other one is about 12.8 ns, both are far away from the microsecond time scale. These reveal that the new emission spectra cannot be caused by the triplet state

emission. For the time-resolved photon emission curves at 660 nm, we found that this emission curve is mainly contributed by two components and these two components are all about 2 ns. This indicates that the lifetime of normal fluorescence state is about 2 ns. From these time components obtained at 720 and 660 nm, we can infer that the time component of 2.7 ns in photon emission curve at 720 nm must be from normal fluorescence state, because of the spectra overlap of the normal fluorescence emission and new state emission. Therefore, the other time component about 12.8 ns corresponds to the lifetime time of the new emission state.

C. Lifetime measurement at room temperature

From above discussion, we know that the new state emission at the wavelength region from 690 nm to 730 nm at 77 K cannot be caused by triplet state. The difference in spectral behavior at 77 K and room temperature must be caused by the difference in the excited state processes at 77 K and room temperature. Therefore, we measured the photon emission dynamics of HY103 at room temperature in nitrogen environment, shown in Fig.3(b). We found that the time-resolved photon emission curve at 660 nm is nearly the same as our instrument response function. This reveals that the lifetime of fluorescence state at room temperature is beyond our experiment time resolution (about 200 ps). From our further measurement by using femtosecond time-resolved transient absorption spectroscopy, we know that the lifetime of fluorescence state is about 13 ps and the recovery ground state bleach is about 14 ps (the details will be published elsewhere). The recovery of the ground state bleach is remarkably short. This reveals an ultrafast and efficient radiationless process is present after photoexcitation, which quenches the fluorescence emission process. We infer that this ultrafast radiationless process is caused by the torsion relaxation around the C2=C3 double bond. This kind of radiationless process is common in π-conjugated molecules [33]. Such a torsion relaxation is also confirmed by our TDDFT calculations.

D. Theoretical analysis of HY103

In order to provide information about the potential energy curves of the ground and excited states in flexible media, quantum chemical calculations were carried out by TDDFT. The potential energy of HY103 is shown in Fig.4. There is a shallow well where the C1−C2=C3−C4 dihedral angle is about 0°. Therefore, an excited state is restricted to this shallow well. This is consistent with the experimental results, which shows that a normal fluorescence state has been measured. Furthermore, when the C1−C2=C3−C4 dihedral angle twists to 90°, the two curves become very close, which
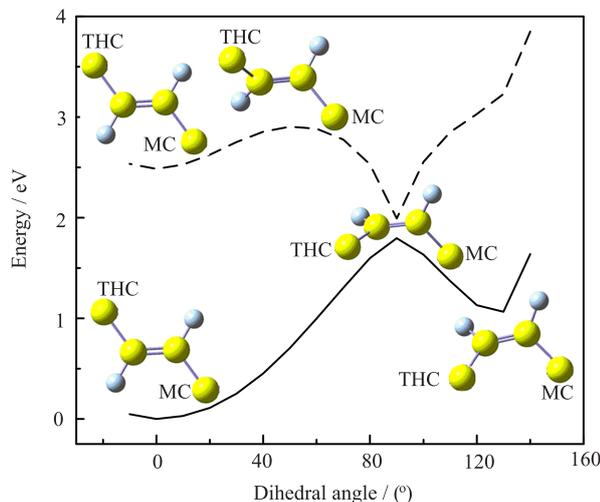

FIG. 4 The energies of S_0 (solid line) of HY103 along the rotation pathway (C1−C2=C3−C4 dihedral angles) and the energies of S_1 (dashed line) calculated as TDDFT excitation energy at the corresponding ground-state geometries in flexible solution. For clarity, we used THQ and MC standing for tetrahydronquinoline unit and a multi-cyano group in this figure. But there are no any simplifications of HY103 structure during the calculation.

suggests that a conical intersection between the S_0 and S_1 potential energy curve is formed at this point. Therefore the excited molecules (HY103) would decay to the ground state rapidly and efficiently at this region, so the fluorescence emission process is strong quenched.

V. DISCUSSION

According to the experimental and computational results, we know that at room temperature the HY103 molecules can take an ultrafast torsion relaxation around C2=C3 double bonds, which leads to an ultrafast and efficient radiationless process. This ultrafast torsion relaxation competed with the fluorescence state emission. However, when HY103 molecules are excited in amorphous glasses at 77 K, the lifetime of fluorescence state can be prolonged to ∼2 ns. The torsion relaxation around the C2=C3 double bonds is also called as one-bond-flip mechanism [20]. One-bond-flip means that during the torsion relaxation process one-half of the molecules have to turn over in space. Therefore, in amorphous glasses environment at 77 K, the space around HY103 is restricted, the torsion relaxation around the C2=C3 double bonds is inhibited and the lifetime of fluorescence is about 2 ns.

While our experiment results also present that an undeniable new state emission appears when the solution is cold to 77 K. It reveals that a new emission state is produced, while such a state is absent in flexible medium at room temperature. As far as we know

that a new state formation can be caused by two kinds of motion. One is electron motion or electron spin reverse, *e.g.* intermolecular charge transfer (ICT) state or triplet state; the other is the relative motion of nucleuses, *e.g.* the one-bond-flip motion. From above discussion we know that this new emission state at 77 K cannot be a triplet state. For the electron motion, it is along the skeleton of the molecules, so its motion is independent on the temperature varying. If a state is caused by the electron motion, it will be present in flexible medium at room temperature; also will be present in amorphous glasses at 77 K. Furthermore, our further femtosecond transient absorption experiments demonstrate that ICT state cannot be formed in solution at room temperature. This means that the new emission state observed at 77 K in our experiment cannot be caused by the election motion. In another condition of the nucleuses motion, usually it refers to the one-bond-flip that causes large volume changes of the molecules. Therefore such a motion is dependent on the temperature varying in solution. If a state is caused by such a nucleus motion, it will be inhibited in amorphous glasses at low temperatures such as 77 K. This is the explanation that the lifetime of fluorescence state is prolonged from 13 ps to 2 ns as temperature varying from room temperature to 77 K. Obviously, the new emission state observed at 77 K cannot be caused by such a kind of motion (one-bond-flip).

From above discussion, we know that this new emission state cannot be explained as an ICT, triplet state or other general excited state. This new emission state must be caused by a motion that makes the volume of the molecules a little change, which just as the Hula-twist proposed by Liu *et al.* The difference is that this kind of motion in our experiment can lead the molecules from one equilibrium state to another equilibrium state; therefore, a new state will be produced in amorphous glasses at 77 K. Therefore, we called this kind of motion as volume-conserved twist (VCT) motion, which is different from the nucleuses relaxation from Franck-Condon state to the equilibrium state, and the new emission state produced by this kind of motion is called VCT state. Figure 5 shows the potential energy curve of the Franck-Condon relaxation and the VCT motion.

According to above discussion, we know that when HY103 is excited in flexible solution at room temperature, an ultrafast on-bond-flip motion will take the fluorescence state to conical intersection as shown in Fig.4. So in flexible solution there is only one fluorescence emission band. But when HY103 is excited in amorphous glasses at 77 K, the ultrafast on-bond-flip motion is inhibited. A VCT motion will take place from the fluorescence state to produce a VCT state as shown in Fig.5. Therefore, two fluorescence emission bands can be observed in amorphous glasses at 77 K.
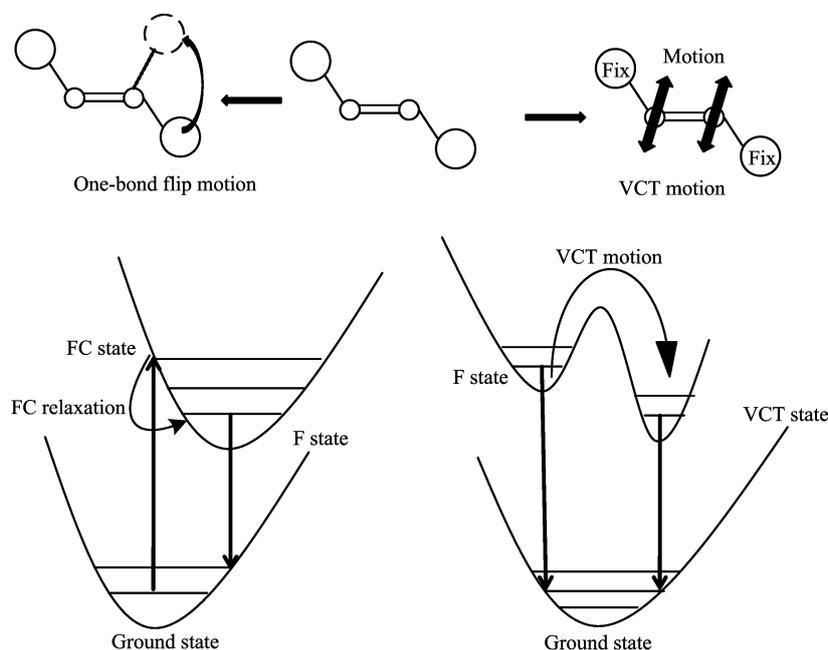
FIG. 5 The schematic potential energy curve. The right displays the VCT motion and the left displays the FC motion. FC state: Franck-Condon state, F state: Fluorescence state.

VI. CONCLUSION

The excited state characters of HY103 have been studied by means of time-resolved photon emission and TDDFT calculations. The results obtained reveal that (i) HY103 dyes undergo an efficient one-bond-flip after photoexcitation at room temperature, which leads to very short lifetime of the fluorescence state, and a weak fluorescence emission. (ii) The lifetime of HY103 is prolonged to ∼2 ns in amorphous glasses at 77 K. Furthermore, a new emission state (VCT state) is formed via a kind of VCT motion. As far as we know, this is the first observation of a VCT state. We see that the VCT nucleuses motion of excited state π-conjugated molecules in restricted environment is no longer just an isomerization motion to form an unstable conical intersection as observed before [17−20], it also can form a stable emission state. The excited state character of π-conjugated molecules in restricted environment is more complex than our usual thought. More and more studies have to be done to figure out the VCT mechanisms: in experiment *e.g.*, the time-resolved UV-Vis spectra were far from enough, the time-resolved IR spectra is really needed to discover the VCT nucleuses motion; in theory, as far as we know, there was no such a theory method which can give a rational simulation of the VCT mechanisms [17]. This must be caused by the complicacy of the VCT motion and the approximation of the current theory method. Therefore, more advanced and accurate theory method is needed to be developed to get a rational explanation of the VCT mechanism.

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