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ABSTRACT

A new crystal of N-2-flurobenzoyl-N'-4-tolylthiourea (FBTT) was obtained from slow evaporation of solvent benzene and the crystal structure of FBTT was determined by X-ray diffraction method. The packing mode of FBTT molecules was affected by crystallization conditions. The new crystal of FBTT crystallizes in the monoclinic with the space group C2/c, and it was stabilized by two pairs of intermolecular interactions. The first pair of intermolecular hydrogen bonds are N(1[#])-H(1[#])...S(1) and N(1)-H(1)...S(1^{#1}), the second pair of intermolecular hydrogen bonds, are C(11[#])-H(11[#])...O(1) and C(11)-H(11)...O(1^{#1}). There also have other unpaired intermolecular hydrogen bonds C(15)-H(15C)...O(1^{#1}) and C(15^{#2})-H(15^{#2})...O(1). Double fluorescence bands are observed in both non-polar and polar solvents. The fluorescence emission at 350–360 nm originates from the transitions of $\pi^* \to \pi$ state and is assigned to S₂ fluorescence for the nature of LE state. The long wavelength fluorescence emission with large Stokes shift is the characteristic of ESIPT state. All experimental results are supported by MP2 and CASSCF calculations.

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1. Introduction

Benzoylthiourea derivatives have been intensively studied due to their applications as 'host' molecules for recognition of 'guest' anions in the field of supramolecular chemistry [1–8]. Over the past few years, fluorescent and luminescent chemosensors for the detection of anions have been successfully developed. Especially, a variety of fluorescence anion chemosensors, such as N-substituted N'-carbonyl thiourea type compounds, have been designed and prepared in recent years [9–15].

Benzoylthiourea derivatives usually show interesting luminescent properties, with a very strong impact of the molecular structure, especially the tilt angle, on their properties. Recently, we had investigated the structure and luminescence properties of N-2-fluorobenzoyl-N'-4-methoxylphenylthiourea (FBMPT) [16], and detected dual fluorescence emissions in several solvents. It reveals that, the high energy fluorescence derived from deactivation of local excited state and the long wavelength fluorescence of the large Stokes shift resulted from excited state intramolecular proton transfer (ESIPT) or twisted intra-molecular charge transfer (TICT). However, the interpretation on the fluorescence emission is ambiguous. It has not been clear which intramolecular charge transfer (ICT) the large Stokes shift fluorescence belongs to, TICT or ESIPT.

Density function theory (DFT) method, Beck's three-parameter hybrid method (B3LYP) [17–19] had been employed to optimize

the ground structure of FBMPT at the level of 6-31G(d). The first excited state of FBMPT had been optimized by configuration interaction singles (CIS) method with a minimal basis set, STO-3G. With the development of the calculation resource, it is possible to perform a higher precise quantum chemical calculation. A large size molecular structure can be optimized by ab initio MP2 method with a middle scale, Pople basis set, 6-31G(d). Complete active space self-consistent field (CASSCF) method instead of CIS method can be used to optimize an excited state of a large scale molecule.

We had already obtained one crystal structure of FBTT [20], and it crystallized in triclinic with $P\bar{1}$ space group, a = 8.413(5) Å, b = 9.532(5) Å, c = 9.927(6) Å, $\alpha = 66.24(2)^\circ$, $\beta = 85.40(2)^\circ$, $\gamma = 72.27(2)^\circ$ V = 693.2(7) Å³, and Z = 2. Recently, we re-synthesized the sample of FBTT, and obtained unexpectedly a new crystal structure. Determining the fluorescence spectra of FBTT in non-polar and polar solvents, we observed the fluorescence properties of FBTT are different from that of FBMPT. Herein, combining with quantum chemical calculation, it is expected to obtain a clear mechanism of fluorescence emissions to provide guidance theoretically and experimentally for searching new fluorescence materials and further applications in the future.

2. Experimental methods

2.1. Experiments

New single crystal of FBTT was obtained by slow evaporation of benzene solvent at 5 $^\circ$ C. The data are corrected for Lorentz and



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Table 1

Crystallographic data of N-2-flurobenzoyl-N'-4-tolylthiourea.

Crystal system	Triclinic ^a	Monoclinic
Empirical formula	C ₁₅ H ₁₃ N ₂ OFS	C ₁₅ H ₁₃ N ₂ OFS
Formula weight	288.34	288.34
Lattice parameters	a = 8.413(5) Å	a = 20.813(4) Å
-	b = 9.532(5) Å	b = 5.7211(8) Å
	c = 9.927(6) Å	c = 24.165(4) Å
	$\alpha = 66.24(2)^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 85.40(2)^{\circ}$	$\beta = 99.396(4)^{\circ}$
	$\gamma = 72.27(2)^{\circ}$	$\gamma = 90^{\circ}$
	$V = 693.2(7) Å^3$	$V = 2838.8(8) \text{ Å}^3$
Space group	P1 (#2)	C2/c
Z value	2	8
D _{calc}	1.381 g/cm ³	1.349 g/cm ³
F ₀₀₀	300.00	1200
$2\theta_{\rm max}$	54.9	55.0
No. of reflections measured	Total: 5522/3021	Total: 7680/3232
	$(R_{int} = 0.025)$	$(R_{\rm int} = 0.0297)$
Corrections Lorentz-	(trans. factors:	0.648-0.954
polarization absorption	0.7469-1.0000)	
Structure solution and	Direct methods	Shelxl
refinement	(SIR97)	
Refinement	Full-matrix least-	Full-matrix least-
	squares on F ²	squares on F^2
Residuals	R1 (I > 3.00,	R1 (I > 2,
	$\sigma(I)) = 0.051$	$\sigma(I)) = 0.0548$
		R1 (all data) = 0.0777
	wR2 (I > 3.00,	wR2 (I > 2,
	$\sigma(I)) = 0.118$	$\sigma(I)) = 0.1409$
		wR2 (all
		date) = 0.1573
Goodness of fit indicator	0.92	1.09

^a Data from Ref. [20].

polarization effects. The structure is solved by direct methods [21] and expanded using Fourier techniques [22]. The non-hydrogen atoms are refined anisotropically. Hydrogen atoms are refined using the riding model. The absorption spectra are recorded on a UV–VIS spectrophotometer, CARY50. Fluorescence measurements were carried out on an FLS920 analytical instrument. The absorption and fluorescence spectra of FBTT have been determined in five different solvents at 1×10^{-5} mol L⁻¹. The fluorescence quantum yield is detected by using quinine sulfate in 0.05 mol L⁻¹ sulfuric acid as the standard.

2.2. Method of calculations

The ground-state minimum structures and the complexes with the first solvent shell are obtained by MP2 [23] method. A Pople basis set, 6-31G(d), is used in all calculations of MOLPRO electronic code package [24]. The calculated harmonic vibration frequencies confirm the stability of the structures. The excited-state structures are optimized by complete active space self-consistent field (CASS-CF) [25,26] method. The active space consists of 12 electrons in ten orbitals (6 + 4). After obtaining geometries, single-point calculations have been carried out by CASPT2 [27,28] method. During the CASPT2 calculations, 65 orbitals have been kept frozen to make the calculation numerically feasible. The results are, however, not particularly sensitive to the exact number of orbitals kept frozen. The calculations are essentially stable with respect to change of the active size and the number of states.

3. Results and discussion

3.1. Crystal structure

The new crystal belongs to monoclinic, space group: C2/c, a = 20.813(4) Å, b = 5.7211(8) Å, c = 24.165(4) Å; $\alpha = 90^{\circ}$, $\beta = 99.396(4)^{\circ}$, $\gamma = 90^{\circ}$; V = 2838.8(8) Å³, Z = 8. The crystal data and the refinement details are given in Table 1. The monoclinic crystal structure of FBTT is shown in Fig. 1. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters are listed in Table 2. The structural parameters of monoclinic crystal are listed in Table 3. The structural parameters of triclinic crystal are also listed for comparison. Intra-molecular and intermolecular hydrogen bonding interactions of both crystals are compiled in Table 4.

As shown in Table 3, different intra-molecular hydrogen bond interactions lead to different molecular configurations for both crystals. In the molecular structure of triclinic crystal, all of atoms are almost co-planar. The intra-molecular hydrogen bonds include: $N(1)-H(1)\cdots F(1)$, the distance of $N(1)\cdots F(1)$, 2.384 Å, the distance of $H(1) \cdots F(1)$, 1.926 Å and the angle of $N(1)-H(1) \cdots F(1)$, 135.1°; $N(2)-H(2)\cdots O(1)$: the distance of $N(2)\cdots O(1)$, 2.640 Å, the distance of $H(2) \cdots O(1)$ is, 1.832 Å, the angle of $N(2)-H(2) \cdots O(1)$, 141.2°. A coplanar form is obtained directed by the hydrogen bonding. The monoclinic FBTT crystal is composed of three parts, with benzoyl ring as left part, toluidine plane as right part, and the middle carbonylthiourea part cyclized by an intra-molecular hydrogen bond, $N(2)-H(2)\cdots O(1)$. The dihedral angle, between the benzoyl plane and the carbonylthiourea plane is 39.9°, and the dihedral angle between carbonylthiourea plane and toluidine plane is 58.6°. The intramolecular hydrogen bond, $N(1)-H(1)\cdots F(1)$ is weaker than that in triclinic crystal. The distance of $N(1) \cdots F(1)$ is 2.781 Å, the distance of $H(1) \cdots F(1)$ is 2.300 Å, and the angle of N(1)- $H(1) \cdots F(1)$ is 114.1°. And the intramolecular hydrogen bond,



(a) The structure of FBTT by X-ray, displace ellipsoids were plotted at the 40% probability



(b) The crystal of packing by an axis a

Table 2						
Atomic coordinates	(×10 ⁴)	and	equivalent	isotropic	displacement	parameters
$(A^2 \times 10^3)$.						

Atom	x	у	Z	$U_{\rm eq}$
S(1)	5807(1)	0.9012(1)	0.4561(1)	38(1)
F(1)	4362(1)	15,058(3)	4411(1)	58(1)
O(1)	3915(1)	9829(4)	3340(1)	58(1)
N(1)	4628(1)	10,467(3)	4145(1)	33(1)
N(2)	5113(1)	8129(3)	3553(1)	34(1)
C(1)	3286(1)	15,718(5)	4525(1)	47(1)
C(2)	2646(1)	15,014(5)	4430(1)	51(1)
C(3)	2453(1)	13,008(5)	4129(1)	50(1)
C(4)	2918(1)	11,693(5)	3922(1)	43(1)
C(5)	3571(1)	12,327(4)	4017(1)	34(1)
C(6)	3731(1)	14,349(4)	4318(1)	39(1)
C(7)	4047(1)	10,783(4)	3794(1)	36(1)
C(8)	5162(1)	9138(4)	4051(1)	29(1)
C(9)	5599(1)	6672(4)	3372(1)	32(1)
C(10)	5853(1)	7315(4)	2900(1)	36(1)
C(11)	6314(1)	5887(4)	2711(1)	38(1)
C(12)	6524(1)	3839(4)	2988(1)	35(1)
C(13)	6258(1)	3231(4)	3461(1)	37(1)
C(14)	5795(1)	4625(4)	3652(1)	37(1)
C(15)	7031(1)	2316(4)	2790(1)	45(1)

 U_{eq} is defined as one third of the trace of the orthogonalized U_{ii} tensor.

 $N(2)-H(2)\cdots O(1)$ is slightly weaker than that in triclinic crystal. The distance of $N(2)\cdots O(1)$ is 2.648 Å, the distance of $H(2)\cdots O(1)$ is 1.950 Å and the angle of $N(2)-H(2)\cdots O(1)$ is 136.2°.

Different intermolecular interaction results in different packing form of the crystals. Some important intermolecular interactions are shown in Fig. 2. Two pairs of the intermolecular hydrogen bonds are found in the monoclinic crystal. One is N(1[#])– H(1[#])···S(1) and N(1)–H(1)···S(1^{#1}), d(H···S), 2.700 Å, d(N···S), 3.409 Å, \angle N–H···S, 139.6°, which similar to that of N-(2-furoyl)-N'-(2-tolyl)thiourea [29]. The other is C(11[#])–H(11[#])···O(1) and C(11)–H(11)···O(1[#]), d(H···O), 2.710 Å, d(C···O), 3.371 Å, \angle C– H···O, 128°. The other intermolecular hydrogen bonds interactions are C(15)–H(15C)···O(1^{#1}) and C(15^{#2})–H(15^{#2})···O(1), d(H···O), 2.490 Å, d(C···O), 3.405 Å, \angle C–H···O, 155.3°. For triclinic crystal, there is only a pair of intermolecular hydrogen bonding interactions C(15)–H(15)···O(1[#]) and C(15[#])–H(15[#])···O(1), d(H···O), 2.640 Å, d(C···O), 3.49 Å, \angle C–H···O, 148.9°. An intense short distance interaction is F(1)–F(1[#]), d(F···F), 2.720 Å.

The optimized molecular structures of FBTT for ground state by MP2/6-31G(d) method and the first excited state by CASSCF method are exhibited in Fig. 3. The structure parameters by MP2 method are listed in Table 3. If we consider the different states between optimized molecular structure and two crystal structures (monoclinic and triclinic), some differences are certainly existed. On the whole, the optimized structure is between two crystal structures.

3.2. NMR spectra

The NMR spectrum was recorded in solvents of CDCl₃ and CD₃OD at room temperature at 400.00 MHz on an INOVA 400 instrument. In CDCl₃, the two most de-shielded signals were broad. They were assigned to NH protons, as reported by Otazo et al. [30] and Macy'as et al. [31] for aromatic 3-substituted aroylthioureas. In most compounds with aromatic substituents at N(2), the hydrogen bonded proton N(2)H has a higher δ^{1} H value between 12 and 13 ppm. ¹H NMR studies in CDCl₃ show that the chemical shift is found about δ = 12.41 ppm for the hydrogen bonded proton N(2)H. Usually, for a very acidic proton on N(1) reported by Macy'as et al. [32], it should show their δ^{1} H values between 11 and 12 ppm. But, the chemical shift of acidic proton on N(1) is about 9.67 ppm. The presence of strong electron-withdrawing groups (-F) in the phenyl group seems to inhibit the formation of the intra-molecular hydrogen bond N–H \cdots F. The proton on C(4), δ = 8.05 ppm, appears in downfield due to weak intra-molecular hydrogen bond C(4)–H···O(1). The other protons at benzene ring resonance come out in downfield at about δ = 7–8 ppm. The peak of the protons of $-CH_3$ shows at $\delta = 2.34$ ppm. In CD₃OD, the signs of both protons of NH in downfield disappear. Because the formation of the intermolecular hydrogen bond between the oxygen atom of carbonyl and -OD of CD₃OD decreases the weak intramolecular hydrogen bond interaction of C(4)–H···O(1). The sign of the proton on C(4), δ = 8.05 ppm in CCl₃D return to 7.65 ppm in CD₃OD. The chemical shift of CD₃OH result from exchange of the proton between the active hydrogen of NH and CD₃OD appears at δ = 3.30 ppm. The peak at 4.85 is considered the chemical shift of the proton of residual water. The protons at benzene ring resonance come out in downfield at about δ = 7–8 ppm, which similar to that in CDCl₃. The proton peaks of -CH₃ always show at δ = 2.34 ppm.

3.3. UV-visible and fluorescence of steady state

The UV-visible spectral curves of FBTT in several solvents are shown in Fig. 4. The data are collected from 250 nm to 400 nm. Generally, a B band of $\pi \to \pi^*$ transition exhibits a red shift of

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Id	DIC	

The selected structure p	parameters of MP2	methods and X-ray.
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Bond lengths (Å)	Triclinic ^a	Monoclinic	MP2	Bond angles (°)	Triclinic ^a	Monoclinic	MP2
S(1)-C(8)	1.660	1.667	1.657	C(7)-N(1)-C(8)	129.4(2)	128.13	129.9
F(1)-C(6)	1.357	1.357	1.371	C(8)-N(2)-C(9)	132.2(2)	125.16	137.7
O(1)-C(7)	1.220	1.216	1.243	N(2)-C(8)-N(1)	114.2	116.04	113.5
N(1)-C(7)	1.370	1.370	1.372	N(2)-C(8)-S(1)	129.3	125.93	129.5
N(1)- C(8)	1.405	1.396	1.416	N(1)-C(8)-S(1)	116.5	118.01	117.1
N(2)-C(8)	1.332	1.324	1.349	O(1)-C(7)-N(1)	129.9	123.1	123.6
N(2)-C(9)	1.403	1.383	1.412	O(1)-C(7)-C(5)	122.5	121.6	119.7
Torsion angles				N(1)-C(7)-C(5)	117.1	115.20	116.6
C(6)-C(5)-C(7)-O(1)	167.9	142.3	167.6	F(1)-C(6)-C(1)	117.2	117.6	116.7
C(4)-C(5)-C(7)-O(1)	12.0	38.2	10.7	F(1)-C(6)-C(5)	119.4	118.9	120.5
C(6)-C(5)-C(7)-N(1)	12.4	39.9	14.6	C(14)-C(9)-N(2)	126.0	120.8	123.3
C(8)-N(2)-C(9)-C(14)	7.6	58.6	39.4	C(10)-C(9)-N(2)	115.3	118.7	116.7
C(8)-N(2)-C(9)-C(10)	172.2	119.2	145.3				

^a Data from Ref. [20].

Table	4
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Some hydrogen bond interactions (distance: Å, angle: °) in crystal.

$N(1)-H(1)\cdots F(1)$	Distances	Triclinic ^a	Monoclinic	MP2
	$\begin{array}{l} N(1) \cdots F(1) \\ H(1) \cdots F(1) \\ \angle N(1) - H(1) \cdots F(1) \end{array}$	2.384 Å 1.926 Å 135.1°	2.781 Å 2.30 Å 114.6°	2.710 Å 1.906 Å 133.8°
N(2)−H(2)···O(1)	Distances $N(2) \cdots O(1)$ $H(2) \cdots O(1)$ $\angle N(2)-H(2) \cdots O(1)$	2.640 Å 1.832 Å 141.2°	2.648 Å 1.950 Å 136.2°	2.679 Å 1.806 Å 140.6°
N(1)-H(1)···S(1 [#]) Symm. op. $(1 - x, 2 - y, 1 - z)$	Distances N(1)S(1 [#]) H(1)S(1 [#]) \angle N(1)-H(1)S(1 [#])		3.409 Å 2.700 Å 139.6°	
$N(1^*)-H(1^*)\cdots S(1)$ Symm. op. $(1 - x, 2 - y, 1 - z)$	Distances $N(1^{#}) \cdots S(1)$ $H(1^{#}) \cdots S(1)$ $\angle N(1^{#}) - H(1^{#}) \cdots S(1)$		3.409 Å 2.700 Å 139.6°	
$C(15^{\#})$ -H $(15^{\#})$ ···O (1) Symm. op. $(1 - x, y + 1, 1/2 - z)$	Distances $C(15^{#}) \cdots O(1)$ $H(15^{#}) \cdots O(1)$ ∠ $C(15^{#}) - H(15^{#}) \cdots O(1)$		3.405 Å 2.490 Å 155.3°	
C(15)-H(15)···O(1 [#]) Symm. op. $(1 - x, y - 1, 1/2 - z)$	Distances $C(15) \cdots O(1^{#})$ $H(15) \cdots O(1^{#})$ ∠ $C(15)$ - $H(15) \cdots O(1^{#})$		3.405 Å 2.490 Å 155.3°	
$C(11^{#})-H(11^{#})\cdots O(1)$ Symm. op. $(1 - x, y, 1/2 - z)$	Distances C (11 [#])···O(1) H(11 [#])···O(1) \angle C(11 [#])-H(11 [#])···O(1)		3.371 Å 2.710 Å 128.0°	
C(11)-H(11)···O(1 [#]) Symm. op. $(1 - x, y, 1/2 - z)$	Distances $C(11) \cdots O(1^{#})$ $H(11) \cdots O(1^{#})$ $\angle C(11) - H(11) \cdots O(1^{#})$		3.371 Å 2.710 Å 128.0°	
C(3)-H(2)···O(1 [#]) Symmetry $(-1 - x, 1 - y, -z)$	Distances $C(3) \cdots O(1^{#})$ $H(2) \cdots O(1^{#})$ $\angle C(3) - H(2) \cdots O(1^{#})$	3.490 Å 2.640 Å 148.9°		
$C(3^{*})-H(2^{*})\cdots O(1)$ Symmetry $(-1 - x, 1 - y, -z)$	Distances $C(3^{*}) \cdots O(1)$ $H(2^{*}) \cdots O(1)$ $\angle C(3^{*}) - H(2^{*}) \cdots O(1)$	3.490 Å 2.640 Å 148.9°		
Short distance interactions $F(1) \cdots F(1^{\#})$, symm. op. $(x, y - 1, z)$	Distances $F(1) \cdots F(1^{\#})$	2.720 Å		

^a Data from Ref. [20].



Fig. 2. Important intermolecular hydrogen bonding interactions in crystals.

absorption band and an R band of $n \rightarrow \pi^*$ transition exhibits a blue shift of absorption band as the polarity of the solvent increases. The first maximum absorption peak at 325 nm in cyclo-hexane shifts

blue to 310 nm in dichloromethane, to 312 nm in THF, and to 305 nm in both acetonitrile and methanol with the increase of the polarity of the solvent, which indicates the property of



The ground state of by MP2

The first excited state by CASSCF

Fig. 3. The optimized molecular structures of both tautomers of FBTT.



Fig. 4. Absorption spectra of FBTT in five organic solvents.

 $n \rightarrow \pi^*$ transition. Obvious solvent effect of the second absorption band is not observed. The maximum wavelengths almost appear about at 268 nm in all solvent.

Fluorescence quantum yield (QY) is determined by Parker's method [33]. Dilute solutions of FBTT is prepared in an appropriate solvent and the absorbance is maintained below 0.05. Quinine sulfate in 0.05 mol L⁻¹ H₂SO₄ is used as the fluorescence standard ($\Phi = 0.545$) [34]. The fluorescence emission curves of FBTT are shown in Fig. 5. The maximum wavelengths of the double fluorescence emissions are compiled in Table 5.

Similar to other benzoylthioureas, FBTT also exhibits faint fluorescence emissions. In non-polar solvent cyclo-hexane, the fluorescence emission curve of FBTT is different from that of FBMPT [16]. In cyclo-hexane, weak double fluorescence emission is observed, and the maximum emissions are at 363 nm and 411 nm. However, only single fluorescence band at 342 nm is observed for FBMPT. If

compared the structures of FBTT and FBMPT, the co-planarity of FBTT is worse than that of FBMPT. Thus, different fluorescence properties are resulted from different molecular configurations. Increasing the polarity of solvent, such as THF (ε = 7.58), excited at 300 nm, the maximum emission wavelength λ_{f2} of the large Stokes shift fluorescence locates at 482 nm, while the maximum emission wavelength λ_{f1} of the high energy fluorescence is observed at 356 nm. The fluorescence emission curve in THF is similar to that of FBMPT. Both fluorescence bands are broadened in THF. In the solvent dichloromethane ($\varepsilon = 8.93$), λ_{f1} shifts red to 373 nm. Compared with the fluorescence emission at 348 nm of FBMPT, a red-shift of 25 nm for λ_{f1} is observed. Additionally, the large Stokes shift fluorescence band is almost covered by the high energy emission band so as to cannot be detached. The faint fluorescence emissions are also determined by a more careful detection in solvent acetonitrile and methanol, which is different from our previous experimental results [20]. The red shifts of the high energy emission bands go on with the increase of the polarity of solvent further. The emissions appear at 402 nm in acetonitrile and 405 nm in methanol. Simultaneously, the fluorescence quantum yields decrease greatly. Large Stokes shift fluorescence band cannot be detected.

As the polarity of the solvent increases, the change of the fluorescence quantum yield of FBTT is different from that of FBMPT. In less polar solvent, the intensity of the fluorescence emissions for FBTT increases with the increase of the solvent polarity, whereas that for FBMPT is almost constant. Double fluorescence bands in cyclo-hexane have low quantum yields, 0.001 for the high energy emission and 0.003 for the large Stokes shift emission. In the polar solvent THF, the fluorescence intensity of the high energy fluorescence increases. The intensity increase for the high energy emission is larger than that for large Stokes shift emission. The fluorescence quantum yield for high energy fluorescence is 0.04, and for long-wavelength fluorescence is 0.02. In dichloromethane, the intensity of double fluorescence emission decreases slightly.



Fig. 5. Fluorescence spectra of FBTT in several solvents.

Table 5

The maximum fluorescence emission wavelengths (nm), λ_{f1} and λ_{f2} , the emission energies, E_{f1} and E_{f2} , fluorescence quantum yields, QY, the energy gaps by CASPT2 calculations.

Solvents	λ_{e}	λ_{f1}	$E_{\rm f1}~({\rm eV})$	QY	λ_{f2}	$E_{\rm f2}~(\rm eV)$	QY
Cyclo-hexane	302	363	3.40	0.001	411	3.00	0.003
Dichloromethane	310	373	3.21	0.03			
THF	300	356	3.48	0.04	482		0.02
Acetonitrile	340	402	3.08	< 0.001	425	2.91	< 0.001
Methanol	344	405	3.06	0.001	425	2.91	0.001
S_0/S_1 gap						1.87	
S_0/S_2 gap			3.03				
S_1/S_1^a gap						3.29	

^a The imidol tautomer of FBTT.

Similar to that in THF, the high energy emission is stronger than the large Stokes shift emission.

The optimized complexes of FBTT with solvents, methanol and acetonitrile molecules by MP2 method are displayed in Fig. 6. We can only consider the short-range interactions of the first solvent-shell as the intermolecular hydrogen bonds between FBTT and solvent molecules. Because the formations of intermolecular hydrogen bonding interactions between FBTT and solvent molecules hinder the rotating of the molecule, the fluorescence has the good band structures in acetonitrile and methanol. As shown in Fig. 6, it is clear that the solvato complexes are stabilized by the different types of H-bonds. It has been demonstrated that the hydrogen bond strengthening behavior in electronic excited states can be responsible for the red shift of the absorption spectrum,

while the hydrogen bond weaken behavior in electronic excited state results in the blue shift of the absorption spectrum. Thus, the intermolecular hydrogen bonds in the first excited state (S_1) must be weaker than that in the ground state (S_0) . Limited in the computer resources and molecules size, we cannot obtain the information on intermolecular hydrogen bonds of the excited state.

The short-wavelength fluorescence is assigned to the local excited (LE) state due to the modest Stokes shift. The Stokes shift of it is about 50 nm. It is related to the origin of the $S_2 \rightarrow S_0$ fluorescence. In many of thiocarbonyls, because of the large energy gap between the S_2 and S_1 states, strong S_2 -fluorescence (much stronger than S_1 fluorescence) is a common and regular feature of this class of compounds [35,36]. In which the $S_2 \rightarrow S_0$ electronic transition band is much stronger than the $S_1 \rightarrow S_0$ transition band. From Table 5, the energy gap between S_0 and S_2 is 3.03 eV. Comparing with the high-wave fluorescence band, 3.40 eV in cyclohexane, the error is 0.37 eV.

Generally, the low fluorescence quantum yields of the molecules in which the lowest excited state is $\pi^* \rightarrow n$ in nature and a $\pi^* \rightarrow \pi$ type transition is always characterized by relatively high fluorescence quantum yields. Frontier Molecular Orbitals (FMOs) of FBTT molecule by calculation are shown in Fig. 7. Lowest unoccupied molecular orbitals (LUMO) are obtained by CASSCF method. And the highest occupied molecular orbital (HOMO) and the next highest occupied molecular orbital (HOMO-1) are acquired by MP2 method. As shown in Fig. 7, LUMO is a π conjugated orbital, which localize at the acylthiourea moiety. HOMO locates partly on aniline, thiocarbonyl and methyl. HOMO involves the lone pairs of sulfur. The lone pairs of electrons of sulfur, twisted out of the



Fig. 6. The complexes of FBTT and methanol and acetonitrile molecules in the first solvation shell.



Fig. 7. Molecular orbitals obtained by MP2/6-31G(d) and CASSCF/6-31G(d).

plane of the aromatic ring, cannot conjugate with the aromatic ring. So, the first transition of HOMO \rightarrow LUMO possesses the property of $\pi^* \rightarrow n$. The next highest occupied molecular orbital (HOMO-1) is a π conjugated orbital including the part of anilinethiourea. So, the second transition of HOMO-1 \rightarrow LUMO should be a $\pi^* \to \pi$ transition. The $\pi^* \to \pi$ states de-active by the appropriate intense fluorescence at 354 nm in THF and 373 nm in dichloromethane. Additionally, a red shift in the polar solvent from 356 nm in THF to 373 nm in dichloromethane and 402 nm in acetonitrile and 405 nm in methanol shows the property of $\pi^* \rightarrow \pi$ transition. Corresponding to other $\pi^* \rightarrow \pi$ transitions, the fluorescence quantum yield is relative low, which could result from the intra-molecular hydrogen bonds. From Fig. 2, we know that two types of intra-molecular hydrogen bonds exist in the FBTT molecule. The formation of intra-molecular hydrogen bonds can decrease dipolar moment and transition dipolar moment of FBTT molecule.

The long wavelength fluorescence can be attributed to the charge transfer transition due to the large Stokes shift and the widener of the emission band. The Stokes shift of long wavelength fluorescence is 182 nm in THF. The fluorescence band from 425 nm to 600 nm is very broad. Is the fluorescence the TICT, ESIPT or the other ICT? As shown in Fig. 3, the large structural difference between the first excited state and the ground-state, the transition of S_1/S_0 can be assigned to twisted intramolecular charge transfer (TICT) transition. In other words, the first excited state belongs to TICT state. From Table 5, the energy gap of S_1/S_0 is 1.82 eV. However, we cannot observe any fluorescence band corresponding to the energy gap of S_1/S_0 . So, the $\pi^* \rightarrow$ n transition as a twisted intramolecular charge transfer (TICT) state does not emit fluorescence. In the other words, the large Stokes shift fluorescence band cannot result from $\pi^* \rightarrow$ n transition of TICT state.

ESIPT is a phototautomerization in the excited state via an intramolecular hydrogen bond involving the transfer proton to the electronegative atom. It indicates that a significant intramolecular relaxation takes place upon photo-excitation. The relaxation should increase Stokes shift. We consider the fluorescence band as ESIPT fluorescence. The imidol tautomer of FBTT relative

to the intra-molecular proton transfer has been observed in IR spectrum [16]. The optimized molecular structures of the imidol tautomer for ground state by MP2/6-31G(d) method and the first excited state by CASSCF method are exhibited in Fig. 3. Frontier Molecular Orbitals (FMOs) of the imidol tautomer are shown in Fig. 7. As shown in Table 5, the energy gap between the first single states of both tautomers is 3.29 eV. Compared with the emission energy of the long wavelength fluorescence in cyclo-hexane, 3.0 eV, the error is 0.29 eV.

In a word, all fluorescence bands in different non-polar and polar solvents experimental are supported by MP2 and CASSCF calculation results. The error between the calculation and experiments must exist. The error can result from the selected different system. The calculations only consider a single molecule system, while it is a solution system in experiment with a large number of solvent molecules and some solute molecules. The intermolecular interactions are ignored.

4. Conclusion

Different crystallization conditions lead to the formation of new monoclinic crystals. The monoclinic crystal of FBTT can be stabilized by the intermolecular interactions. Two pairs of intermolecular hydrogen bonds are found in the monoclinic crystal. One is $N(1^{\#})-H(1^{\#})\cdots S(1)$ and $N(1)-H(1)\cdots S(1^{\#1})$. Another is $C(11^{\#})-H(11^{\#})\cdots O(1)$ and $C(11)-H(11)\cdots O(1^{\#1})$. The other unpaired intermolecular hydrogen bonding interactions are $C(15)-H(15C)\cdots O(1^{\#1})$ and $C(15^{\#2})-H(15^{\#2})\cdots O(1)$. Large Stokes shift fluorescence band at 480 nm presents ESIPT fluorescence character. The short wave-length fluorescence band at 350–360 nm is assigned to the S₂ fluorescence of LE state. The proposed mechanism of the fluorescence emissions is supported by theoretical studies at CASSCF level.

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