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Theoretical study on novel quantum yields of dithienylethenes cyclization reactions in crystals

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Abstract

Novel quantum yields (QYs) of photochromic cyclization reactions are studied for 1,2-bis (2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (**1**) and 1,2-bis (2-methyl-1-benzothiophen-3-yl) perfluorocyclopentene (**2**). The difference of the QYs in crystals and hexane solution for the molecules **1** and **2** is explained by their initial geometries, the relaxation from the Franck–Condon states, the shapes of the potential energy surfaces of the ground state, and the geometry change by the large amplitude motions.
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1. Introduction

Dithienylethenes with heterocyclic aryl groups show photochromism, which is defined as a reversible transformation between two isomers with different absorption spectra by photon irradiation [1]. These photochromic compounds have recently attracted much attention owing to their potential application to optoelectronic devices, such as optical memories and optical switches [2,3]. For such applications, photochromic compounds are expected to have large quantum yields (QYs) as well as large absorption cross-sections. It has already been studied that the QYs of dithienylethenes depend on substituents introduced to the aryl groups [2,4–8,10,11]. However, the dependency of the QYs to the molecular environment remains to be investigated.

There are typical experimental data of two dithienylethene molecules, 1,2-bis (2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (**1**) and 1,2-bis (2-methyl-1-benzothiophen-3-yl) perfluorocyclopentene (**2**). They show normal photochromic cyclization

Table 1
Quantum yields for the cyclization reactions of the molecules **1** and **2** under irradiation with 70 nm light in crystals and with 313nm in hexane solution

	In crystals	In hexane solution	Refs.
1	1.0	0.59	[13,15]
2	0.0	0.35	[5,14]

in hexane solution, having the QYs of 0.59 and 0.35, respectively (Table 1) [5,15]. Surprisingly, the QY of the molecule **1** in crystals records 1.0 without any loss, by contrast, that of the molecule **2** turns out to be 0.0 [13,14]. These experimental facts provide unique opportunity to carry out a theoretical study in order to understand the mechanisms.

This paper presents a study with ab initio and DFT methods in an attempt to shed light on the novel QYs in solid phase, as a natural extension of our previous studies [9–12]. We have calculated the optimized structures and the potential energy surfaces of the open-ring isomers in the ground state, and performed the frequency analysis. The relaxation in their excited states from the Franck–Condon (FC) regions has also been traced. Then the origin of the different QYs in crystals and in hexane solution has been clarified.

2. Computational methods

We used the 6-31G basis sets for all the calculations and the B3LYP functionals for the DFT calculations. We obtained the optimized structures of the several important open-ring conformers of the molecules **1** and **2** with the HF and DFT methods. Potential energy surfaces were calculated as a function of the torsion angle ϕ_1 between the thiophene and perfluorocyclopentene rings (see Fig. 1) with the DFT method. Frequency analyses were also performed to verify the optimized conformers as minima with the DFT method. We examined the structure relaxation from the FC states with the CIS method, to see whether the photochromic cyclization reactions can proceed. All the calculations were performed with the GAUSSIAN 98 program package [16].
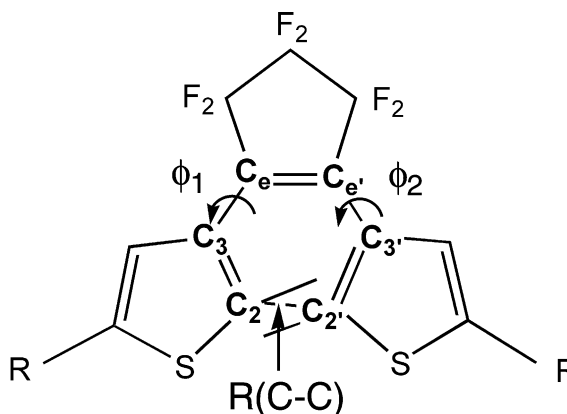

Fig. 1. Atom numberings about the central cyclohexane rings of the molecules **1** and **2**. In this work, $R(C-C)$ is defined as the distance between two reactive carbon atoms, 2 and $2'$. Torsion angles between the thiophene and perfluorocyclopentene rings, ϕ_1 and ϕ_2 are chosen as $\angle 2\text{-}3\text{-}e\text{-}e'$ and $\angle 2'\text{-}3'\text{-}e'\text{-}e$, respectively.

3. Results and discussion

Dithienylethenes have two conformers; one has two aryl groups in the mirror (C_s) symmetry (the parallel (p) conformer) and the other has the groups in the C_2 symmetry (the anti-parallel (ap) conformer) (see Schemes I and II). It has been known that the ap conformer is reactive for the photochemical cyclization reaction and the p conformer is non-reactive, as seen from the Woodward–Hoffmann rules [2,9].

Experimental QYs of the cyclization reactions in crystals and in hexane solution are shown in Table 1, for the current molecules. In crystals, the cyclization reaction occurs only for the molecule **1**, while in hexane solution the reactions are observed for both of the molecules **1** and **2**. The origin of the difference is the main subject of the current study. The cyclization reaction occurs via the HOMO–LUMO ($\pi \to \pi^*$) single-excitation state corresponding to the excitation from the 1A to 1B state under the C_2 symmetry [10, 11]. We will analyse these features focusing on the initial geometries in the ground state and on the relaxation from the FC states.[1]

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[1] Although it is important to analyse the relaxation mechanism from the FC state (the allowed 1B state) to the 1A ground state in detail as well as the internal conversion mechanism from the 1B to 2A state (see our previous work in Ref. [11]), the complete analysis including dynamics will be a future subject.
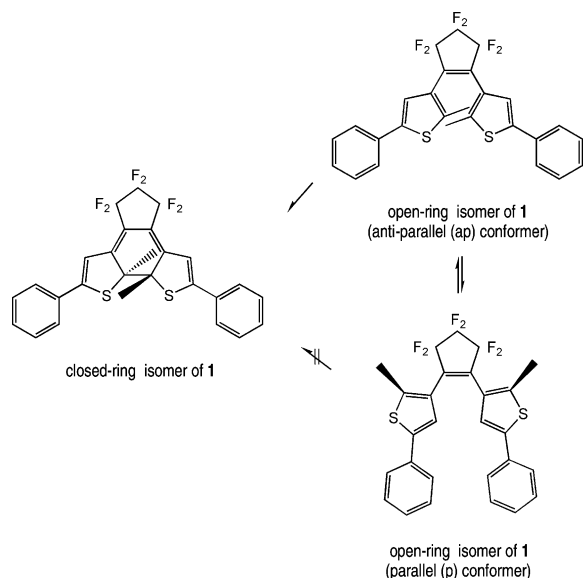
Scheme 1.

3.1. Conformers in the ground state

Table 2 shows the optimized structures for the open-ring isomers of the molecules **1** and **2**. The important internal coordinates are shown in Fig. 1. The molecule **1** has two stable ap(1) and ap(2)
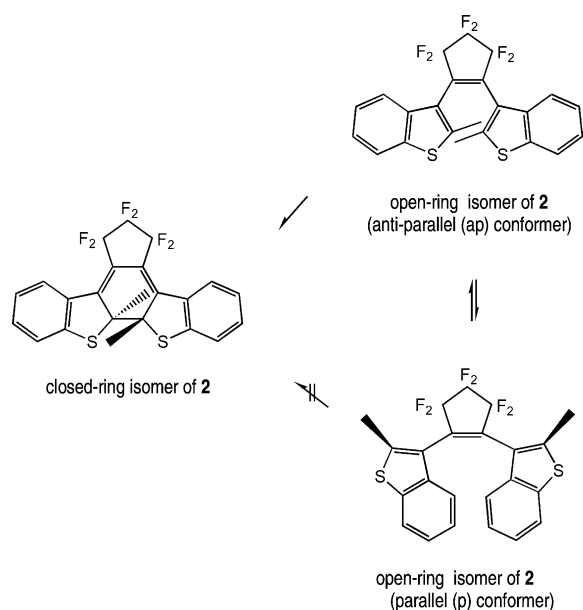
Scheme 2.

conformers (ϕ_1 having the same sign as ϕ_2), and one stable parallel (p) conformer (ϕ_1 having the opposite sign to ϕ_2). These two ap conformers have approximately the C_2 symmetry, while the p conformer is much distorted from the C_s symmetry, because the phenyl groups to the 5 and 5′ positions of the thiophene rings can easily rotate. The energy difference in these three conformers is small (~ 1.1 kcal/mol with the DFT method as shown in Table 2).

On the other hand, the molecule **2** has one stable ap and one stable p conformers. The ap and p conformers have approximately the C_2 and C_s symmetries, respectively. The energy difference in these conformers is fairly small (~ 0.4 kcal/mol with the DFT method as shown in Table 2).

3.2. Cyclization reactions in crystals

In crystals, the most stable structure exclusively appears in general. The structure of the molecule **1** in crystals is similar to that of the ap(1) conformer in the ground state, which is the more stable and closer to the closed-ring isomer of the two optimized ap conformers (Table 2). As shown in Fig. 2, the relaxation from the FC state of the most stable ap(1) conformer led to the closed-ring structure of the $1B_C$ geometry[2] without any barrier. It is still not known in detail how this excited state relaxes to the ground state. At least, the final geometry already having the closed-ring form implies that the destination is the closed-ring form via any kind of the following process such as emission or non-radiative transitions. Since there is only this reactive ap(1) conformer in crystals with no population of the non-reactive conformers, the experimental QY is expected to be very high, which is in fact 1.0 [13].

The structure of the molecule **2** in crystals resembles the optimized ap conformer of the ground state (Table 2). As shown in Fig. 2, the relaxed structure from the FC state of the most stable ap

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[2] The relaxation from the FC state of the ap(1) conformer of the molecule **1** approached to the $1B_C$ geometry ($R(C-C) = 1.571$ Å, $\phi_1 = 12.5$ degrees, and $\phi_2 = 13.5$ degrees), that of the ap(2) conformer reached the open-ring ap structure ($R(C-C) = 5.385$ Å, $\phi_1 = 113.9$ degrees, and $\phi_2 = 142.4$ degrees), and that of the p conformer led to the open-ring p structure ($R(C-C) = 4.237$ Å, $\phi_1 = 61.5$ degrees, and $\phi_2 = -119.6$ degrees).

Table 2

Optimized structures obtained without symmetry constraint for the open-ring anti-parallel (ap) and parallel (p) conformers of the molecules **1** and **2** with the HF and DFT methods

		1			**2**	
		ap(1)	ap(2)	p	ap	p
HF	R(C–C) (Å)	3.797	5.112	4.211	4.477	4.146
	ϕ_1 (degrees)	54.9	112.0	61.0	82.8	76.3
	ϕ_2 (degrees)	57.4	112.5	−121.3	84.2	−105.3
	Relative energy (kcal/mol)	0.00	1.44	0.50	0.00	0.89
DFT	R(C–C) (Å)	3.644	5.559	4.272	4.078	4.129
	ϕ_1 (degrees)	44.9	122.7	46.9	66.1	60.8
	ϕ_2 (degrees)	47.0	153.6	−133.7	66.9	−118.9
	Relative energy (kcal/mol)	0.00	1.07	1.01	0.00	0.36
	Relative Gibbs free energy (kcal/mol)	0.00	1.31	1.05	0.00	1.00
	Dipole moment (debye)	4.97	5.29	5.12	4.03	4.14
Experiment [13,14]	R(C–C) (Å)	3.507/3.578			4.353	
	ϕ_1 (degrees)	45.8/46.5			71.7	
	ϕ_2 (degrees)	46.6/44.6			74.8	

Energy for the ap(1) conformer of the molecule **1** is −2423.9271 Hartree with the HF method and −2434.6790 Hartree with the DFT method. Energy for the ap conformer of the molecule **2** is −2270.1998 Hartree with the HF method and −2279.8937 Hartree with the DFT method. Gibbs free energy for the ap(1) conformer of the molecule **1** is −2434.3612 Hartree and that of the ap conformer of the molecule **2** is −2279.6366 Hartree.

conformer remained in the open-ring ap geometry[3]. The reactive carbon atoms of this ap conformer are separated from each other with a long distance (R(C–C) = 4.353 Å, much larger than 3.6 Å for the molecule **1** in Table 2). It is experimentally known [14] that the cyclization reaction is difficult when the distance R(C–C) is longer than 4.0 Å. Contrasting with the flexible situation in hexane solution, the starting geometry for the cyclization reaction in crystals is fixed at the most stable ap structure and the geometry change induced by the thermal energy vibrations cannot be expected. This ap conformer is non-reactive and the experimental QY is expected to be very small, which is in fact 0.0 [14].

Thus, the novel QYs in crystals are attributed to the significant difference in R(C–C), namely the initial geometries for the cyclization reactions. Although a collective effect on the reaction in crystals is expected as is often argued, the current

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[3] The relaxation from the FC state of the ap conformer of the molecule 2 approached to the open-ring ap conformer (R(C–C) = 3.647 Å, ϕ_1 = 51.3 degrees, and ϕ_2 = 58.7 degrees), and that of the p conformer reached the open-ring p structure (R(C–C) = 4.160 Å, ϕ_1 = 50.3 degrees, and ϕ_2 = −128.6 degrees).

analysis on the molecules **1** and **2** shows that it does not seem to be important. A study based on the band calculation to confirm this argument and to compare with other crystals is now in progress [17].

3.3. Cyclization reactions in hexane solution

In hexane solution, there can be a population distribution of various stable structures, which is obviously less likely in crystals. The ground state potential energy surface for the ap conformers of the molecule **1** shows two kinds of minima, ap(1) and ap(2), as shown in Fig. 3. The dipole moments do not depend significantly on the molecular structures as shown in Table 2. Since the energy difference in the optimized ap(1), ap(2), and p conformers is small (∼1.1 kcal/mol as shown in Table 2), there is a population distribution among these conformers in hexane solution at the room temperature according to the canonical Boltzmann statistics.

The relaxation from the FC state of the ap(1) conformer led to the closed-ring structure, shown as $1B_C$ in Fig. 2, while the ap(2) and p
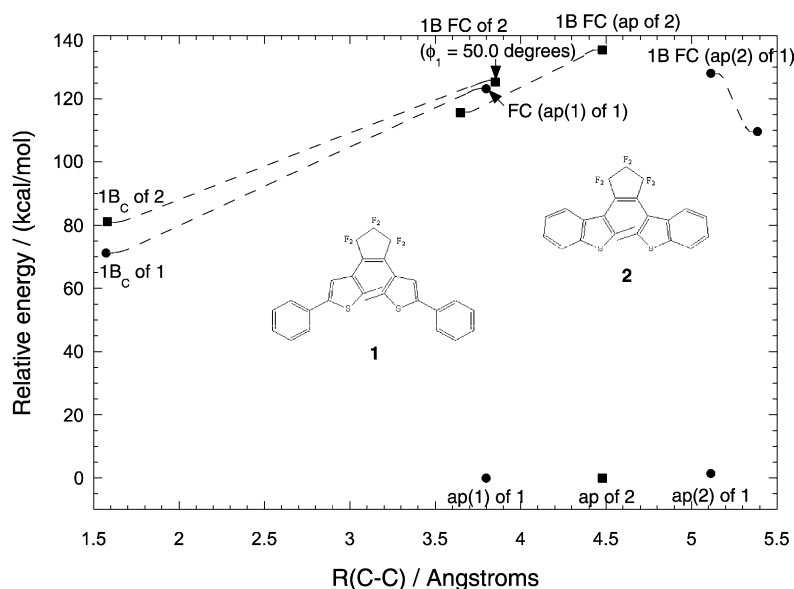
Fig. 2. Overview of the cyclization reactions of the molecules **1** and **2** as a function of the $R(C-C)$ distance. Each arrow shows the relaxation path from the FC state of each of the ground state geometries. Each structure was optimized with the HF or CIS method. It was verified that the same relaxed structures are obtained from the FC states of the optimized geometries with the DFT method. Each state is denoted on the basis of the C_2 symmetry since each conformer has approximately the C_2 symmetry (see also footnotes 2 and 3).

conformers remained in the open-ring ap and p structures, respectively[2]. These results indicate that the ap(1) conformer is reactive for the cyclization reaction, while the ap(2) and p conformers are non-reactive, although the detailed processes of the relaxation to the ground state are still to be clarified.

The QY will be strongly influenced by the ground state distribution. In fact, Irie et al. [4] observed that the ap and p conformers exist in the ratio of 1:1 for 1,2-bis (2,4-dimethyl-5-phenylthiophen-3-yl) perfluorocyclopentene, which is a similar molecule to the molecule **1**, having methyl groups to the 4 and 4′ positions of the thiophene rings instead of hydrogens in the molecule **1**. They discussed that the closed-ring isomer is not produced from the photoexcited p conformer, and the QYs of the cyclization reaction is very close to 0.5, the maximum value generated from the ap conformer.

Reflecting the relative energies shown in Table 2, the population of the ap(1) conformer is superior to that of the ap(2) and p conformers. In fact, the ratio of the reactive to non-reactive conformers, the ap(1)/(ap(2) + p) ratio can be estimated as 3.57 from
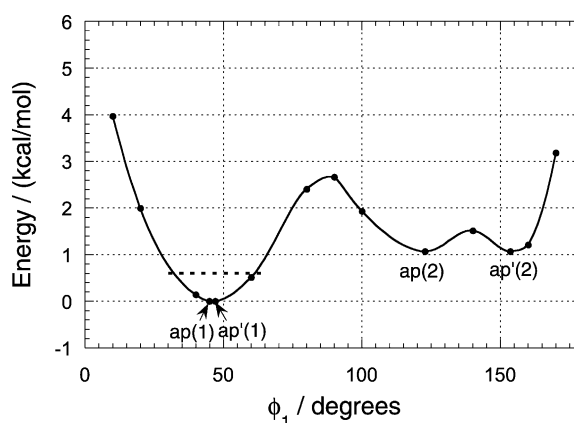

Fig. 3. Calculated potential energy surface for the open-ring anti-parallel (ap) conformer of the ground state of the molecule **1** as a function of the torsion angle ϕ_1 with the DFT method. It has two kinds of minima for the ap(1) and ap(2) structures. The ap′(1) and ap′(2) conformers have the structures where ϕ_1 replaces ϕ_2 in the ap(1) and ap(2) conformers, respectively. A broken line shows the thermal energy corresponding to the room temperature (about 0.59 kcal/mol) from the potential bottom (see footnote 5).

the Boltzmann distribution, as follows [5]:

$$\frac{ap(1)}{ap(2) + p} = \frac{1}{\exp\left(-\dfrac{\Delta G_{ap(2)}}{RT}\right) + \exp\left(-\dfrac{\Delta G_p}{RT}\right)} \quad (1)$$

where ΔG is the Gibbs free energy difference of a given conformer relative to the ap(1) conformer, and T is the room temperature. The QY estimated from this ratio is 0.78 and in comparable with the experimental value of 0.59.

There are two reasons why the estimated QY is slightly larger than the experimental one. The first is the reactivity of the ap(1) conformer. All the excited ap(1) molecules are not necessarily led to the cyclization reaction, on account of non-radiative or radiative decay due to efficient collisions in solution. The second is that this overestimate might partially come from the error in the Gibbs free energy evaluated under the rigid rotor and harmonic approximations together with the accuracy of the B3LYP energy and basis set error. Solvent effects are considered to be small particularly in non-polar hexane solution. Anyway, the experimental QY of 0.59 can be interpreted reflecting the population ratio of the ground state conformers in hexane solution.

The QY of 0.35 of the molecule **2** (Table 1) is discussed hereafter. The potential energy surface for the ap conformers of the ground state shows only one minimum, as shown in Fig. 4. The dipole moments do not depend significantly on the molecular geometries as shown in Table 2. The population of the molecule **2** in hexane solution is distributed to the ap and p conformers at the room temperature, because the energy difference in the two conformers is fairly small (~ 0.4 kcal/mol) as shown in Table 2. The relaxation from the FC states of the optimized ap and p conformers both led to the open-ring ap and p structures, respectively[3]. It is consistent with the experimental criterion [14] that no reaction can occur if $R(C-C)$ is larger than 4.0 Å (see Table 2). The system is likely to go back to the initial open-ring structure of the ground state and no reaction might be observed, neither in crystals nor in hexane solution.

The question is to understand the experimentally observed QY of 0.35 in hexane solution. The frequency analysis has shown that the molecule **2** can change the structure significantly from the minimum of the ap conformer by the thermal energy vibrations, owing to the shallow potential surface. There are some vibrational states[4] in the room temperature fluctuation of about 207 cm^{-1} at the optimized ap conformer of the molecule **2**, whose vibrational modes include the torsion mode between the fluorocyclopentene and cyclohexane rings[5]. As seen in Fig. 4, the torsion angle ϕ_1 of the molecule **2** could roughly move from 45 to 100 degree at the room temperature by the aid of the thermal energy vibrations.[6]

We have examined that the relaxation from the FC state at the calculated structure at $\phi_1 = 50.0$degree, which is about the turning point of these thermal energy vibrations. Indeed, the calculated structure relaxation led to the closed-ring structure of the $1B_C$ geometry,[7] indicating that the cyclization reaction eventually occurs. These results show that the thermal energy vibrations cover the molecular configurations in both the reactive and non-reactive regions of ϕ_1 for the cyclization reaction.

The experimental ap/p ratio by NMR was observed as 1.86 by Uchida et al. [5]. The ap/p ratio can be estimated as 5.39 from the Boltzmann distribution, as follows [5]:

$$\frac{ap}{p} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (2)$$

where ΔG is the Gibbs free energy difference between the ap and p conformers. Assuming that all of the ap conformers are reactive, the QYs are estimated from this calculated ratio and

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[4] The corresponding frequencies including the torsion mode are 18.1, 37.8, and 40.2 cm^{-1}.

[5] Strictly speaking, the thermal correction should be taken into account from the zero-point energy, not from the potential bottom shown in Figs. 3 and 4.

[6] In the molecule **1**, on the other hand, the structure could hardly change from the ap(1) to non-reactive conformer by the aid of the thermal energy vibrations, because of the relatively steep potential surface around it.

[7] The $R(C-C)$ value of the calculated structure at $\phi_1 = 50.0$ degrees of the molecule 2 is 3.851 Å and the molecule **2** with this geometry is expected to be reactive [14]. The relaxed structure from the FC state led to the $1B_C$ geometry ($R(C-C) = 1.579$ Å, $\phi_1 = 6.5$ degrees, and $\phi_2 = 18.3$ degrees).
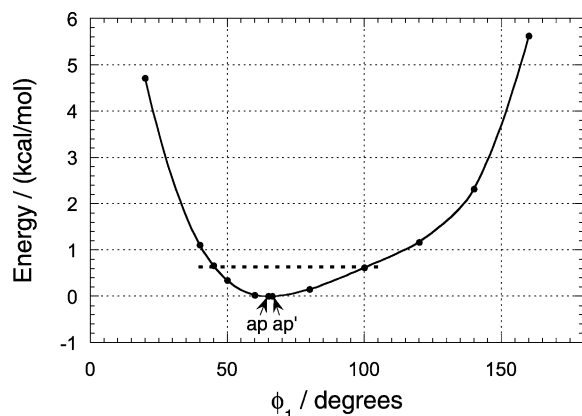
Fig. 4. Calculated potential energy surface for the open-ring anti-parallel (ap) conformer of the ground state of the molecule **2** as a function of the torsion angle ϕ_1 with the DFT method. It has only one minimum for the ap structure and is shallower than that of the molecule **1**. The ap$'$ conformer has the structure where ϕ_1 replaces ϕ_2 in the ap conformer. A broken line shows the thermal energy corresponding to the room temperature (about 0.59 kcal/mol) from the potential bottom (see footnote 5).

the experimental ratio by NMR as 0.84 and 0.65 [5], respectively. These QYs are larger than the observed QY of 0.35. The difference may be explained by the reason that only portions with small ϕ_1 of the ap conformers are reactive by the aid of the thermal energy vibrations.

4. Conclusion

The QYs for the cyclization reactions of 1,2-bis (2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (**1**) and 1,2-bis (2-methyl-1-benzothiophen-3-yl) per-fluorocyclopentene (**2**) have been explained by their initial geometries and the properties of the potential energy surfaces.

In crystals, there is only the reactive ap(1) conformer of the molecule **1** and the experimental QY is 1.0, while the ap conformer of the molecule **2** is non-reactive and the experimental QY is 0.0. The relaxation from the FC states explained these experimental values.

In hexane solution, the experimental QY of 0.59 for the molecule **1** is interpreted reflecting the population of the other non-reactive conformers. On

the other hand, although both the optimized ap and p conformers are non-reactive, the QY of 0.35 for the molecule **2** is explained by the geometry change induced by the thermal energy vibrations, owing to the shallow potential energy surface around the optimized ap conformer. The detailed analysis including conical intersections and band calculations in crystals is in progress.

Acknowledgements

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