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Raman spectra study of photochromic diarylethene in a single crystalline phase

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Abstract

The cyclization and cycloreversion of the photochromic single crystal 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene were investigated by Raman spectroscopy using an excitation wavelength of 785 nm. Polarized Raman spectra of the ring-open form using an excitation wavelength of 514 nm indicated that the ring-open isomers are regularly oriented in the crystal. The depolarization ratio of the Raman band at 740 cm^{-1} was 0.40 in scattered polarization of the Raman spectra when excited with a wavelength of 633 nm. Raman spectra of the ring-open and ring-closed isomers were calculated with the Gaussian 98 program at the B3LYP/6-31G* level, and the results were in good agreement with the recorded Raman spectra. The vibrations were assigned on the basis of the calculations and polarized Raman spectra.

Keywords: Raman spectra; Single crystal; Photochromic; Diarylethene

1. Introduction

Organic photochromic molecules have gained much attention for their potential applications to optical memory and photoswitches [1–3]. So far considerable interest has been focused on photochromic diarylethenes due to the high conversion efficiency of the reversible photochromic reactions, excellent thermal stability of both isomers, and good fatigue resistance [4–12]. Diarylethenes have shown great promise as new materials for optoelectronic devices and molecular switches [13,14].

Raman scattering is an effective technique for elucidating molecular structure. Steady-state Raman spectra provide significant information about the vibrational states and arrangement of a material [15]. By controlling the polarization directions of the incident and scattered light, the Raman polarization selection rules allow identification of the information about the symmetry of vibrations for a particular excitation [16]. The application of polarized Raman spectra would be very useful to investigate the orientation of the photochromic diarylethenes in single crystals.

The photochromic performance of diarylethene has been widely investigated. However, there have been few investigations of the Raman spectra of diarylethene. To the best of our knowledge, the only two published reports by Sekiya and co-worker demonstrated that the Raman spectroscopy is useful to distinguish the open-ring and closed-ring forms of diarylethenes in solution [17,18]. Here we wish to report the Raman spectra of photochromic 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene in single crystals.

The photochromic reaction of a typical diarylethene **1** is shown in Scheme 1. Both the antiparallel and parallel conformers exist in solution [19], but it is possible to prepare only the antiparallel conformer in a single crystal. Therefore, the application of Raman spectroscopy to diarylethenes in single crystals maybe very useful to investigate cyclization and cycloreversion processes. We succeeded in distinguishing the Raman bands of the open-ring and closed-ring isomers. Polarization of the Raman spectra is consistent with the assignment of the vibration.

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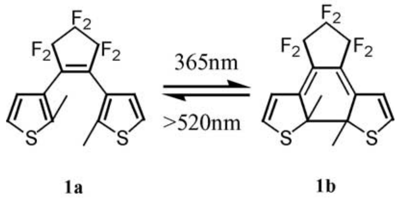

Scheme 1.

2. Experimental

2.1. Synthesis

Diarylethene **1a** was synthesized from 2-methylthiophene according to the procedures in literature [20,21]. Colorless single crystals of **1a** were obtained from *n*-hexane by slow evaporation. The structure was determined by X-ray crystallography, and the crystals belong to triclinic space group $P\bar{1}$.

2.2. Raman spectra

Raman spectra were obtained with a microscopic confocal Raman spectrometer (model RM 2000, Renishaw PLC, England), which used a charge-coupled device (CCD) detector with a resolution of $1\,\text{cm}^{-1}$. The power was always maintained very low to avoid the destruction of the crystal.

Raman spectra of the ring-open and ring-closed form of the crystal were measured with an excitation wavelength of 785 nm, which could avoid the cycloreversion reaction of the ring-closed form.

Polarized Raman spectra of the crystal in the ring-open form were investigated using an excitation wavelength of 514 nm. Raman spectra were recorded when the excitation beam was rotated every 20° with a polarizer.

Raman spectra with scattered polarization were excited with a wavelength of 633 nm. In order to measure a standard depolarisation ratio, two measurements were required. The two states analyzed were those with scattered polarization parallel to that of the polarized excitation beam and perpendicular to that of the excitation beam.

2.3. Computational methods

Raman spectra of the ring-open and ring-closed isomers were calculated with the Gaussian 98 program [22]. The results were obtained using Density Functional Theory (DFT) calculated at the B3LYP/6-31G* level, and C_2 symmetry was imposed. The theoretical values of frequencies were scaled down by a factor of 0.9613.

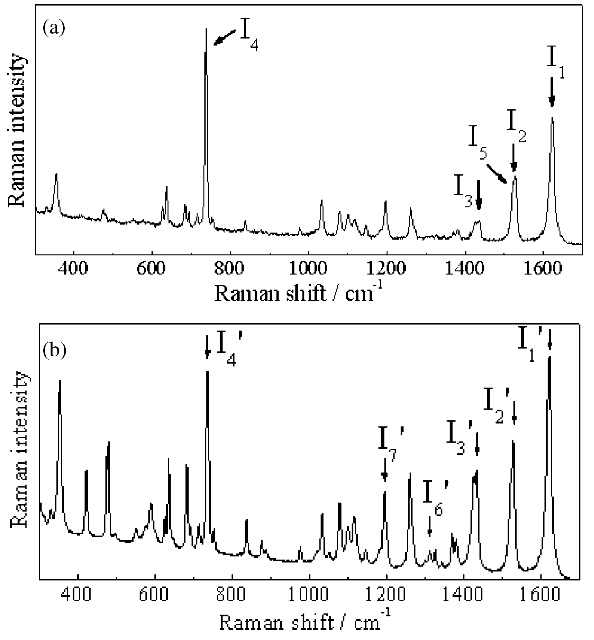

Fig. 1. Raman spectra of single crystal of 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene before (a) and after (b) 365 nm irradiation using an excitation wavelength of 785 nm.

3. Results and discussion

3.1. Observed and calculated Raman spectra

Single crystals of **1a** belong to the triclinic system. The distance between the reacting carbon atoms was 3.58 Å, which is short enough for a photochromic reaction. Upon photoirradiation of 365 nm, the colorless crystals turned red, and in turn, the red crystals became colorless under irradiation of visible light ($\lambda > 500$ nm).

Fig. 1 shows the Raman spectra of **1a** in single crystals before and after UV irradiation using an excitation wavelength of 785 nm. As Fig. 1a and 1b indicate, the Raman spectra of the ring-open and ring-closed isomers are very different. The difference enables us to distinguish the Raman bands of the two isomers. In the open form, there are four prominent Raman bands at 737, 1523, 1529 and $1622\,\text{cm}^{-1}$.

The Raman bands changed greatly upon irradiation with UV light. Table 1 indicates the ratios of Raman intensity relative to $1622\,\text{cm}^{-1}$ of single crystals of diarylethene **1a** before and after UV irradiation. The ratio of the intensities between 737 and $1622\,\text{cm}^{-1}$ decreased from 1.61 for the ring-

Table 1
Ratios of Raman intensity of the prominent bands relative to $1622\,\text{cm}^{-1}$ of single crystals of diarylethene **1a** before and after UV irradiation

Ratio	Ring-open[a]	Ratio	Ring-closed[b]
I_2/I_1	0.52	$I_{2'}/I_{1'}$	0.61
I_3/I_1	0.16	$I_{3'}/I_{1'}$	0.47
I_4/I_1	1.61	$I_{4'}/I_{1'}$	0.86

[a] I_1: $1622\,\text{cm}^{-1}$, I_2: $1529\,\text{cm}^{-1}$, I_3: $1436\,\text{cm}^{-1}$, I_4: $737\,\text{cm}^{-1}$.

[b] $I_{1'}$: $1622\,\text{cm}^{-1}$, $I_{2'}$: $1529\,\text{cm}^{-1}$, $I_{3'}$: $1436\,\text{cm}^{-1}$, $I_{4'}$: $737\,\text{cm}^{-1}$.

Table 2
Observed and calculated Raman bands of the ring-open isomer

Raman band (cm^{-1})			Assignment[a]
Number	Observed	Calculated	
I_1	1622	1613	C=C str of perfluorocyclopene
I_2	1529	1533	C=C asym str of thiophene
I_5	1523	1530	C=C sym str of thiophene
I_3	1436	1437	Str of whole thiophene
I_4	737	738	Twisting of thiophene

open form to 0.86 for the ring-closed form. However, the ratio of the intensities between 1436 and 1622 cm^{-1} increased from 0.16 for the ring-open form to 0.47 for the ring-closed form. In the ring-closed isomer, the 1436 cm^{-1} band was assigned to the C=C stretching of the newly generated conjugated system. Several new bands, such as 418, 590, 883 and 1313 cm^{-1} appeared in the Raman spectra of the ring-closed isomer. These bands can also be used to detect the formation of the ring-closed isomer. Upon irradiation with visible light the intensities of the bands of the ring-closed isomer significantly decreased, while those of the ring-open isomer increased. Thus, cyclization/cyclo-reversion of 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene in single crystals were observed by Raman spectroscopy.

Raman spectra of the ring-open and ring-closed isomers were simulated by density functional theory (DFT) calculations, which were performed with the B3LYP function at the 6-31G* level, and C_2 symmetry was imposed. All the calculations were carried out with the Gaussian 98 program [21]. The theoretical values of frequencies were scaled down by a factor of 0.9613.

As shown in Table 2, the calculated vibrational frequencies of the ring-open isomer are in good agreement with the recorded Raman spectra. The Raman band at 1613 cm^{-1} was assigned to the C=C stretching of the perfluoro-cyclopentene moiety. The character of the 1533 cm^{-1} mode was C=C asymmetric stretching of the thiophene ring, whereas that of the 1530 cm^{-1} mode was C=C symmetric stretching of the thiophene ring. The 1437 cm^{-1} mode involved stretching of the whole thiophene moiety. And the band at 738 cm^{-1} was assigned to twisting of the thiophene moiety. The polarization measurement was consistent with the assignment.

Table 3 shows the calculated spectrum of the ring-closed isomer. Some of the prominent recorded bands were in good agreement with the calculated vibrational frequencies. The 1617 cm^{-1} band was assigned to the C=C asymmetric stretching, whereas the character of the 1565 cm^{-1} mode was C=C symmetric stretching. And the 1209 cm^{-1} band was assigned to the C–C stretching of the reacting carbon atoms.

3.2. *Polarized Raman spectra in a single crystalline phase*

The triclinic-shaped single crystal of **1a** consists of six surfaces of parallelograms. Fig. 2 shows polar plots of the Raman band at 1637 cm^{-1} of single crystal of **1a**. Raman spectra were recorded when the excitation beam was rotated every 20° with a polarizer. It was interesting to see that the intensity of the Raman band changed periodically. Intensity of the Raman shift at 1637 cm^{-1} dramatically changed when the excitation beam was rotated 90°. At a certain angle, 0°, the crystal showed a high intensity of 6797. When the excitation beam was rotated as much as 90°, the crystal showed a relatively lower intensity of 3212. The depolarization ratio of the band at 1637 cm^{-1} ($\rho_{90°/0°}$) was 0.47. The Raman intensity changed periodically as the excitation beam rotated, which indicated that the ring-open isomers are regularly oriented in the crystal.

Table 3
Observed and calculated Raman bands of the ring-closed isomer

Raman band (cm^{-1})			Assignment[a]
Number	Observed	Calculated	
$I_{1'}$	1622	1617	C=C asym str
$I_{2'}$	1529	1565	C=C sym str
		1511	
$I_{3'}$	1436		C=C str
$I_{6'}$	1313	1312	C–C str
$I_{7'}$	1195	1209	C–C str[b]

[a] Str indicates stretching; sym indicates symmetry; asym indicates asymmetry.

[b] C–C stretching of the reacting carbon atoms in the photochromic reaction.

Raman spectra with scattered polarization of **1a** using an excitation wavelength of 633 nm are shown in Fig. 3. Fig. 3a shows Raman spectra of **1a** with scattered polarization parallel to that of the polarized excitation beam. Fig. 3b shows Raman spectra of **1a** with scattered polarization perpendicular to that of the excitation beam. For bands at 1637 cm^{-1} (I_1), 1438 cm^{-1} (I_3) and 740 cm^{-1} (I_4), the Raman intensities shown in Fig. 3b decreased relative to the intensities of the bands in Fig. 3a. The depolarization ratio ($I_\perp/I_{||}$) of the band at 740 cm^{-1} (I_4) was 0.40. However, as shown in Fig. 3b, at 1543 cm^{-1} (I_2), the Raman intensity increased, which was regarded as anti-polarization. The iterative changes of the intensity indicate again the

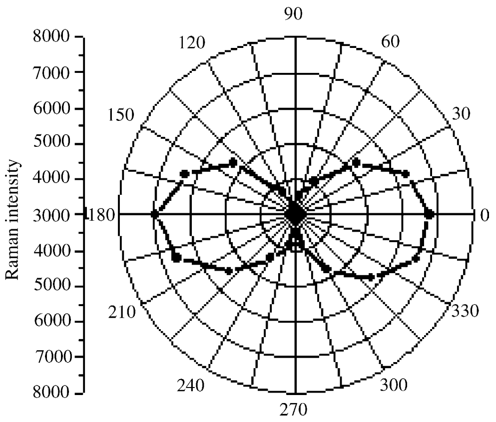

Fig. 2. Polar plots of the Raman band at 1637 cm^{-1} of single crystal of **1a**.

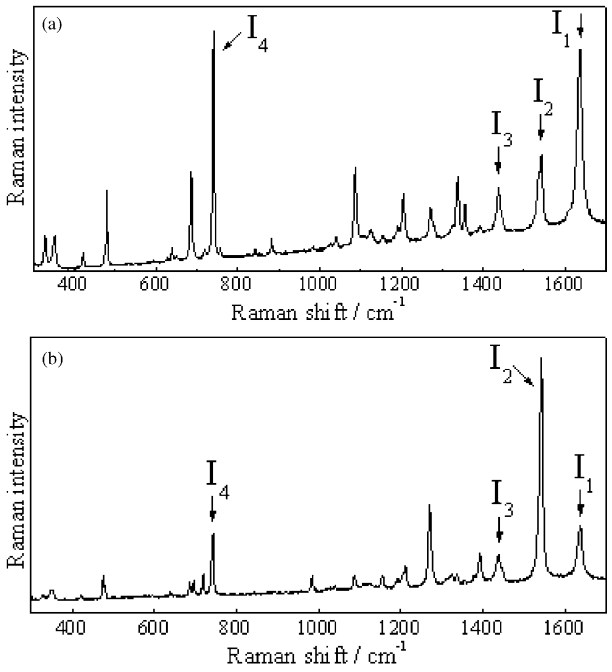

Fig. 3. Raman spectra of **1a** with scattered polarization parallel (a) and perpendicular (b) to that of the polarized excitation beam using excitation wavelength of 633 nm.

regular orientation of the ring-open isomers in single crystals.

4. Conclusions

The difference between the Raman spectra of the two isomers of the photochromic single crystal of 1,2-bis(2-methyl-3-thienyl)perfluorocyclopentene was very apparent. Polarized Raman spectra of the ring-open form indicated that the ring-open isomers are regularly oriented in the crystal. The depolarization ratio of the band at 740 cm^{-1} was 0.40 in scattered polarization of the Raman spectra. Density functional theory calculations at the B3LYP/6-31G* level were in good agreement with the recorded Raman spectra. Based on the calculations and polarized Raman spectra, the vibrations were assigned.

Acknowledgements

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