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Photochromic properties and crystal structure of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-(4-(azidomethyl)phenyl)-2-methylthiophene), C₂₉H₂₀F₆N₆S₂

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.32 × 0.28 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.25 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω
$\theta_{\max}$, completeness:	27.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11997, 3142, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2514
$N(\text{param})_{\text{refined}}$:	227
Programs:	SHELX [1–3], Bruker [4]

Source of material

The title compound was synthesized following the procedure in previous reported references [5, 6]. Later, a colorless solid was obtained with 41% yield. The title compound crystallized from hexane at room temperature.

Experimental details

The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The occupancies of the disordered fluorine atoms are refined to 0.5:0.5 for F₁:F₁' and F₂:F₂'.

Comment

Photochromic compounds have attracted remarkable interests because these compounds can exhibit different physical and chemical characteristics when they are irradiated by light with different special wavelength [7]. In recent years, various photochromic compounds have been designed with different functional groups [8, 9]. There are many methods that have been reported to connect functional groups with photochromic moieties, such as Suzuki coupling [10], Heck reaction [11] and Click reaction [12, 13]. To date, some photochromic compounds with different coupling methods to

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Abstract

C₂₉H₂₀F₆N₆S₂, monoclinic, C2/c (no. 15), $a = 26.2504(11)$ Å, $b = 8.6981(4)$ Å, $c = 13.3064(6)$ Å, $\beta = 107.659(2)^\circ$, $V = 2895.1(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0436$, $wR_{\text{ref}}(F^2) = 0.1314$, $T = 296(2)$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} ^a / <i>U</i> _{eq}
C1	0.17504(11)	0.2751(4)	0.2568(2)	0.0883(9)
H1A	0.151301	0.276546	0.300271	0.106*
H1B	0.177131	0.378989	0.231830	0.106*
C2	0.22986(9)	0.2251(3)	0.32319(17)	0.0641(6)
C3	0.23566(8)	0.1109(3)	0.39687(17)	0.0602(5)
H3	0.205538	0.062367	0.404775	0.072*
C4	0.28623(7)	0.0670(2)	0.45989(15)	0.0528(5)
H4	0.289418	−0.010049	0.509896	0.063*
C5	0.33176(7)	0.1358(2)	0.44948(14)	0.0465(4)
C6	0.32547(10)	0.2502(3)	0.37376(19)	0.0707(6)
H6	0.355423	0.297728	0.364325	0.085*
C7	0.27478(11)	0.2939(3)	0.3121(2)	0.0795(8)
H7	0.271245	0.371512	0.262384	0.095*
C8	0.38518(7)	0.0901(2)	0.51767(13)	0.0426(4)
C9	0.39960(7)	−0.0361(2)	0.57976(13)	0.0420(4)
H9	0.375299	−0.110430	0.586185	0.050*
C10	0.45552(6)	−0.0445(2)	0.63436(12)	0.0391(4)
C11	0.48320(7)	0.0781(2)	0.61161(13)	0.0406(4)
C12	0.54160(7)	0.1122(2)	0.64743(15)	0.0501(4)
H12A	0.550257	0.170911	0.711506	0.075*
H12B	0.550812	0.170148	0.594030	0.075*
H12C	0.561342	0.017573	0.659838	0.075*
C13	0.48039(7)	−0.1729(2)	0.70350(14)	0.0419(4)
C14	0.46238(8)	−0.3340(2)	0.67032(16)	0.0547(5)
C15 ^a	0.5054(4)	−0.4382(4)	0.7316(5)	0.0581(19)
F1 ^a	0.4504(2)	−0.3603(8)	0.5659(6)	0.0796(17)
F2 ^a	0.4149(5)	−0.3560(14)	0.6921(5)	0.0790(17)
F1 ^{1a}	0.4755(3)	−0.3745(8)	0.5837(5)	0.0904(18)
F2 ^{2a}	0.4111(4)	−0.3660(13)	0.6498(5)	0.086(3)
F3 ^a	0.53783(14)	−0.4792(5)	0.6759(3)	0.0950(10)
F4 ^a	0.4876(2)	−0.5644(3)	0.7626(7)	0.107(3)
N1	0.19738(15)	0.1591(4)	0.0399(3)	0.1237(11)
N2	0.17713(10)	0.1704(3)	0.10356(19)	0.0853(7)
N3	0.15218(9)	0.1727(4)	0.1648(2)	0.0994(8)
S1	0.44059(2)	0.20174(5)	0.52540(4)	0.04774(17)

^aOccupancy: 0.5.

bridge functional groups have been reported, but only some crystal structures have been investigated [14, 15].

The title compound C₂₉H₂₀F₆N₆S₂ owns photochromic properties and contains two azido groups which can be used for the Click reaction [13].

The molecule adopts an antiparallel conformation, and the distance between the photoactive carbon atoms (C11⋯C11A) is 3.517 Å which is less than 4.2 Å, which means that this compound can be irradiated by light to produce a photochromic reaction [16, 17]. Based on the empirical rule, the crystal displayed a notable color change upon UV irradiation. The colorless crystal turned blue upon irradiation with 297 nm light, and the colored crystals reverted to a colorless state upon irradiation with visible light. The photochromism was highly consistent in crystalline phase even after 100

repeat cycles, indicating that it is favorable for applications in a certain optoelectronic device [18]. In the perfluorocyclopentene ring, both thiophene rings are linked by the C13=C13A double bond 1.348(2) Å. The molecule includes three kinds of planar rings and they can form two dihedral angles between every two adjacent planar rings. The dihedral angles between the perfluorocyclopentene ring and the adjacent thiophene ring is 36.7°, and dihedral angle between the thiophene ring and benzyl ring is 14.0°.

The absorption spectrum of the open-form of the title compound exhibited an intense band centered at 296 nm in hexane. Irradiation with UV light (297 nm) resulted in the emergence of a new absorption band centered at 597 nm with a color change from colorless to blue due to the formation of closed-ring isomer. The blue color faded to colorless upon irradiation with visible light (>510 nm), and the absorption spectrum returned to the initial state.

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References

- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
- Sheldrick, G. M.: SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
- Sheldrick, G. M.: SADABS. University of Götting, Germany (2014).
- Bruker. APEX-II, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2008).
- Fu, Y. L.; Fan, C. B.; Liu, G.; Pu, S. Z.: A colorimetric and fluorescent sensor for Cu²⁺ and F[−] based on diarylethene with a 1,8-naphthalimide Schiff base unit. *Sens. Actuators, B* **239** (2017) 295–303.
- Ding, H. C.; Liu, G.; Pu, S. Z.; Zheng, C. H.: Multi-addressable fluorescent switch based on a photochromic diarylethene with triazole-bridged methylquinoline group. *Dyes Pigments* **103** (2014) 82–88.
- Fan, C. B.; Liu, Z. Q.; Gong, L. L.; Zheng, A. M.; Zhang, L.; Yan, C. S.; Wu, H. Q.; Feng, X. F.; Luo, F.: Photoswitching adsorption selectivity in a diarylethene-azobenzene MOF. *Chem. Commun.* **53** (2017) 763–766.
- Feng, E. T.; Fan, C. B.; Wang, N. S.; Liu, G.; Pu, S. Z.: A highly selective diarylethene chemosensor for colorimetric detection of CN[−], and fluorescent relay-detection of Al³⁺/Cr³⁺. *Dyes Pigments* **151** (2018) 22–27.
- Zhuge, Y. X.; Xu, D. M.; Zheng, C. H.; Pu, S. Z.: An ionic liquid-modified diarylethene: synthesis, properties and sensing cyanide ions. *Anal. Chim. Acta* **1079** (2019) 153–163.
- Liu, F. F.; Li, H.; Pu, S. Z.: Structure and photochromism of 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl] 3,3,4,4,5,5-hexafluorocyclopent-1-ene, C₂₇H₁₆ClF₆S₂. *Z. Kristallogr. NCS* **234** (2019) 49–51.

11. Jing, S. H.; Zheng, C. H.; Pu, S. Z.; Fan, C. B.; Liu, G.: A highly selective ratiometric fluorescent chemosensor for Hg^{2+} based on a new diarylethene with a stilbene-linked terpyridine unit. *Dyes Pigments* **107** (2014) 38–44.
12. Pu, S. Z.; Ding, H. C.; Liu, G.; Zheng, C. H.; Xu, H. Y.: Multiaddressing fluorescence switch based on a new photochromic diarylethene with a triazole-linked rhodamine B unit. *J. Phys. Chem. C* **118** (2014) 7010–7017.
13. Li, Y. J.; Zheng, C. H.; Pu, S. Z.: Crystal structure and photochromic properties of a novel photochromic perfluorodiarylethene containing a triazole bridged pyridine group moiety, $C_{24}H_{18}F_6N_4S_2$. *Z. Kristallogr. NCS* **234** (2019) 939–941.
14. Fan, C. B.; Liu, Y.; Zhang, D. B.; Pu, S. Z.: Crystal structure and crystalline state multiphotochromism properties of a fused diarylethene dimer. *Chin. J. Struct. Chem.* **38** (2019) 251–256.
15. Lv, J. F.; Li, H.; Pu, S. Z.: Structure and photochromism of 1,2-bis[2-methyl-5-(3-quinolyl)-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene, $C_{33}H_{20}F_6N_2S_2$. *Z. Kristallogr. NCS* **233** (2018) 999–1002.
16. Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S.: Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem. Rev.* **114** (2014) 12174–12277.
17. Xu, D. M.; Zheng, C. H.; Pu, S. Z.: Crystal structure and photochromic properties of 1-(2-methyl-5-phenyl-3-thienyl)-2-{2-methyl-5-[4-(9-fluorenone hydrazone)-phenyl]-3-thienyl}perfluorocyclopentene, $C_{41}H_{26}F_6N_2S_2$. *Z. Kristallogr. NCS* **234** (2019) 979–981.
18. Cheng, H. B.; Zhang, H. Y.; Liu, Y.: Dual-stimulus luminescent lanthanide molecular switch based on an unsymmetrical diarylperfluorocyclopentene. *J. Am. Chem. Soc.* **135** (2013) 10190–10193.