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Thieno[3,2-b]thiophene fused BODIPYs: synthesis, near-infrared luminescence and photosensitive properties

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The fusion of π -sufficient heteroaryl moieties has proven to be an effective strategy for achieving red shift of the main spectral bands of BODIPY. In this paper, thieno[3,2-*b*]thiophene-fused BODIPY derivatives **1** and **2** have been designed and characterized with various spectroscopic methods, and their photosensitive properties have also been explored. Both dyes absorb in the near-infrared region with extremely high molar extinction coefficients, due to extention of π -conjugation by fusion of thieno[3,2-*b*]thiophene moiety. Their fluorescent quantum yields and singlet oxygen generation properties are significantly affected by iodine substitutions, dye **2** displays moderate singlet oxygen generation value of 0.32, providing it as a potential NIR photosensitizer for photodynamic therapy of cancer in future research.

Introduction

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Among many important types of chromophores, BODIPY (4,4difluoro-4-bora-3a,4a-diaza-s-indacene) derivatives have attracted tremendous attention as fluorescence dye due to their unique and famous spectroscopic properties¹ such as: (i) excellent photochemical stabilities, (ii) narrow absorption and emission bands, (iii) large molar absorption coefficients and high fluorescence quantum yields, and (iv) their chemical versatility. BODIPY dyes have significant utility in a variety of applications, such as labeling reagents,² organic photovoltaics (OPVs),³ organic light-emitting diodes (OLEDs),⁴ photodynamic therapy,⁵ etc. However, since their absorption/emission wavelengths typically range between 470 and 530 nm,¹ it restricts some applications such as biological imaging and photosensitizing which generally require dyes that absorb and emit at longer wavelengths in the far-red or NIR region. To solve this research problem, various structural modifications on the skeleton have been reported for BODIPYs^{1,6}: 1) Replacement of the meso carbon atom with a nitrogen atom to form aza-BODIPY dyes; 2) Rigidification of rotatable moieties; 3) Extension of π conjugation by introduction of aryl, vinyl, styryl and arylethynyl substituents; 4) The extension of the π conjugation by the fusion of aryl building blocks to the pyrrole unit. The fusion of π -sufficient heteroaryl moieties on the BODIPY skeleton can be regarded as one of the most effective strategies for the rational design of red/NIR region BODIPYs.⁷ For example, the fusion of furan and thiophene moieties result in significant red-shift of 80 and 63 nm compared to the model BODIPY **1a**, respectively, while the emission band maxima lie at 583 and 571 nm. These dyes have very large molar absorption coefficients rivaling those of cyanine dyes. Although *meso*-position substituent often have only a minor influence on the absorption and emission maxima of BODIPY dyes, it is noteworthy that the introduction of a strong electron-withdrawing CF_3 group results in a red-shift of *ca*. 50 nm without obvious decreasing of molar absorption coefficients.



With this in mind, thieno[3,2-*b*]thiophene, which have strong electron-donating ability and efficient extension of the π system, is employed to fuse the BODIPY core.⁸ Herein we report the synthesis, photophysical properties, and the singlet oxygen generation properties of thieno[3,2-*b*]thiophene-fused

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⁺ Electronic supplementary information (ESI) available: ¹H NMR, ¹⁹F NMR, ¹¹B NMR HR-MS and luminescence spectra of compounds **1** and **2**. CCDC 1875790 for **1**. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x.

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BODIPY derivatives with strong absorption in the NIR region. The electron-withdrawing CF_3 group was introduced at *meso* position for increment of deep red shift.^{7g,h} BODIPY **2** bearing two iodines were prepared to evaluate the heavy-atom effect on the improvement of singlet oxygen generation capability through the enhanced intersystem crossing (ISC) efficiency.

Results and discussion



Scheme 2. Synthetic route of thieno[3,2-*b*]thiophene-fused BODIPY dyes 1 and 2. (i) NaOEt, Ethyl azidoacetate, EtOH, room temperature, 6 h; (ii) toluene, reflux, overnight; (iii) NaOH, ethanol, 1 h; (iv) trifluoroacetic acid, trifluoroacetic anhydride, reflux, 1 h, BF₃-OEt₂, trimethylamine; DCM, room temperature, 1 h; (v) NIS, DCM.

Synthesis and characterization

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The synthetic protocols of thieno[3,2-b]thiophene-fused BODIPY was depicted in Scheme 2. Thieno[3,2-b]thiophene-2carbaldehyde 6 was synthesized in 86% yield according to a procedure.9 published 7H-thieno[2',3':4,5]thieno[3,2b]pyrrole-6-carboxylic acid 5, was obtained following the established Hemetsberger-Knittel¹⁰ synthesis between 6 and ethylazidoacetate, and then upon cyclization gave ethyl 7Hthieno[2',3':4,5]thieno[3,2-b]pyrrole-6-carboxylate 4. 4 was subjected to hydrolysis reaction to give corresponding 3. The BODIPY 1 was then synthesized through boron difluoride chelation of the meso CF₃ substituted dipyrromethene unit, which was obtained through a TFA-mediated condensation of 3 with TFA anhydride, under basic conditions in CH₂Cl₂ at room temperature. 2 was obtained in 60% yield via an iodination reaction of 1 with N-lodosuccinimide (NIS).



Fig.1 (a) Top views of the molecular structure of 1, with the thermal ellipsoids set at 50% probability. (b) Packing diagram of 1. H atoms are omitted for clarity. (c) Side views of the molecular structure. (d) Crystal-packing pattern of BODIPY 1 between the adjacent interlayered crystals. Slip angle of 35.0° for coplanar inclined arrangements of its transition dipole.

X-Ray crystal structure analysis

Single crystals of **1** were obtained for X-ray structure analysis by the slow diffusion of hexane into CHQCl¹oSOLTGORBOX2745 diffraction analysis of **1** confirmed incorporation of thieno[3,2*b*]thiophene groups into the [*b*]-fused positions of pyrrole rings of BODIPY skeleton(Fig. 1). The dihedral angle between the thieno[2',3':4,5]thieno[3,2-*b*]pyrrole moieties is 17.89° (Fig. 1). In the packing structure, the average intermolecular distance between neighbouring thieno[3,2-*b*]thiophene planes is approximately 3.56 Å, molecular packing adopt coplanar inclined arrangements of their transition dipoles moments with slip angles of 35.0° (Fig. 1d), which are characteristic of Jtype solid state packing as previously reported.^{7h}

Spectroscopic properties



Fig. 2 The absorption and emission spectra of 1 and 2 in DCM solution. $\lambda ex=640nm$ for 1, $\lambda ex=650$ nm for 2.

Table 1. Spectroscopic and photophysical properties of 1-2 in various solvents at 298K

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	Solvent	λ _{abs} [nm]	ϵ_{max}	λ _{em} [nm]	$\triangle v_{abs-em}$ [cm ⁻¹]	$arPhi_{ extsf{F}}$	τ [ns]	K _r [10 ⁸ s ⁻¹]	K _{nr} [10 ⁸ s ⁻¹]
	Hexane	690	224600	693	63	0.21	4.49	0.47	1.76
	Toluene	699	216300	704	101	0.19	4.55	0.42	1.78
1	DCM	695	204500	701	123	0.21	4.33	0.48	1.82
	THF	694	194700	699	103	0.13	3.08	0.42	2.82
	MeOH	689	175800	698	187	0.09	2.08	0.43	4.38
	MeCN	688	174100	698	208	0.09	1.85	0.49	4.92
	Hexane	714	233300	716	39	0.03	3.89	0.08	2.49
	Toluene	726	250400	732	113	0.07	2.40	0.29	3.88
2	DCM	720	234900	728	153	0.07	1.90	0.37	4.89
	THF	721	222400	724	57	0.04	1.05	0.38	9.14
	MeOH	714	175800	721	136	0.03	0.54	0.56	17.96
	MeCN	713	213700	721	156	0.07	0.58	1.21	16.03

The spectroscopic properties of thieno[3,2-*b*]thiophene fused BODIPYs investigated in solvents of different polarity are outlined in Figure 2, ESI. S1, S2 and Table 1. In dichloromethane (DCM), **1** and **2** have intensive absorption with large absorption coefficients, the characteristic cyanine-type band of BODIPY dyes is observed at 695 and 720 nm, which can be readily assigned to the S_0 - S_1 transition.¹¹ Few broader, much weaker band around 300-500 nm can be attributed to the second or third transition (Fig.S2 in ESI). The

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absorption maxima of thieno[3,2-b]thiophene fused BODIPYs 1 are red-shifted by 142 and 82 nm, respectively, relative to those observed for the BDP-1b and furan-fused BDP-2b, which suggests that the fusion of thieno[3,2-b]thiophene is a promising way to achieve NIR dyes. Compared to thiophenefused BDP-3b, one more thiophene-fused leads to red-shift of 72 nm and almost three-fold increasing of molar extinction coefficient (ϵ_{max} : 72200 M⁻¹ cm⁻¹ for **BDP-3b**; 194700 M⁻¹ cm⁻¹ for 1 in THF), which is suitable for imaging cell and photosensitizer. The introduction of iodine results in a redshift of 25 nm and 27 nm in the absorption and emission band with lower quantum yield, due to the heavy atom effect and the increased internal conversion. The fluorescent spectra are typical mirror-image relationship of the lowest-energy absorption spectra. The absorptive maxima slightly depend on the polarity of the solvent, with a blue shift of ca. 11 nm when the solvent polarity changes on moving from the relatively non-polar toluene to more highly polar acetonitrile. A similar trend is observed in the emissive maxima. These features suggest that emission occurs from the weakly polar, relaxed Franck-Condon excited state. The very small Stokes shift is observed and generally increases on going from a hexane to an acetonitrile, due to little different of permanent dipole moments between the ground state and the excited state. The fluorescence decay profiles of dyes could be described by a single-exponential fit with fluorescence lifetime in the range of nanosecond in all of the solvents investigated, similar to the lifetime data of reported BODIPY systems.^{7h} The fluorescence quantum yields of 1 had a positive solvatokinetic behavior from 0.21 in hexane to 0.09 in MeCN, this trends is reflected by the rates of nonradiative decay. The fluorescence quantum yields of 2 are considerably lower than those of 1 in different solvent, due to the heavy-atom effect of iodine atoms enhancing the rate of intersystem crossing of the dyes.

Singlet Oxygen generation

In order to estimate the ability of generation of singlet oxygen BODIPY **1** and **2**, 1,3-diphenylisobenzofuran (DPBF), a wellknown singlet oxygen indicator was chosen as a standard.¹² The mixture of BODIPY sensitizer **1** or **2** and DPBF was irradiated with a 690 nm laser beam (100 mW cm⁻², Fig S3). The slope of the graph obtained by plotting the changes in optical density against time is used to calculate the quantum yield of singlet oxygen. Compared to the value that of **1** (0.10), di-iodio substituted **2** gave a better production of singlet oxygen with the value of 0.32. These results were validated by monitoring the phosphorescence spectrum of ${}^{1}O_{2}$ at *ca*.1270 nm (Fig. S3 and S4 in ESI).¹³

DFT Calculation



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Fig.3 Selected transition energies and wave functions of BDP-1b, BDP-3b, 1 and 2 calculated using the DFT method with CAM-B3LYP functional and 6-31G(d, p) basis set (LanL2DZ basis for I atom)

Table 2 Selected transition energies and wave functions of BDP-1b, BDP-3b, 1 and 2 calculated using the TDDFT method with CAM-B3LYP functional and 6-31G(d, p) basis set (LanL2DZ basis for Latom)

	State ^a	Energy [eV]	λ [nm]	f^{b}	Orbitals (coefficient) ^c		
BDP- 1b	S1	2.81	441	0.52	HOMO→LUMO (98%)		
BDP- 3b	S1	2.55	487	0.85	HOMO→LUMO (100%)		
1	S1	2.35	528	0.81	HOMO→LUMO (96%)		
2	S1	2.28	545	0.91	HOMO→LUMO (96%)		
a Excited state. b Oscillator strength. c MOs involved in the transitions.							

In order to gain a deeper understanding of the effect of ring fusion on electronic properties, Nuclear Independent Chemical Shift (NICS (0))^{14,15} values were calculated using the DFT-GIAO method with the 6-31g(d, p) for the optimized structures of classic BODIPY and 1 (Fig. S5 in ESI). The NICS(0) values of pyrrole rings are -6.50 and -6.10 for meso-CF₃-BODIPY and 1, respectively, suggesting the fusion of dithieno[3,2-b]thiophene unit have less influence on the aromatic characteristics of pyrrole rings. The NICS value of thiophene of thieno[3,2b]thiophene rings (0) is -5.63 and -10.20, suggesting the aromatic characteristics of the electronic delocalization in both the thiophene rings significantly differs.¹⁶ The ground-state geometry optimizations were directly taken from the single crystal data and performed by DFT with CAM-B3LYP functional and 6-31G(d, p) basis set (LanL2DZ basis for I atom) (Fig. 3 and Table 2, Table S1-S4 in ESI).¹⁵ UV/Vis spectra were simulated by utilizing the first 20 excited states by TD-DFT with the same approach. For 1-2, the calculated absorption spectra in the gas phase are blue-shifted compared with experimental values, similar to reported BODIPY systems, and their sequence agrees rather well with the measured absorption spectra in solution.¹⁷ It is clear that the narrowing of the HOMO-LUMO gap is due primarily to a destabilization of the HOMO caused by fusion of thieno[3,2-b]thiophene moiety, resulting in a red-shift of absorption and emission bands.

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The lowest energy is mostly consisting of the HOMO-LUMO transition, HOMO and LUMO are all well distributed over the entire conjugated π -system. The TDDFT calculations predict that the lowest energy band of **1** and **2** are red-shift of **87** and **104** nm compared with **BDP-1b**, which is in good agreement with the experimental data.

Conclusions

In conclusion, thieno[3,2-*b*]thiophene-fused BODIPY featuring an intensive absorption in the NIR region have been synthesized and fully characterized. Thieno[3,2-*b*]thiophene fused on the BODIPY core greatly redshifted the absorption and fluorescence band. Diiodio-substituted BODIPY **2** was found to exhibit efficient singlet oxygen generation with a quantum yield of 0.32 upon irradiation with 690 nm laser. Efforts to improve the water solubility and targeting of this type BODIPY dyes for cancer cells are currently underway.

Experimental

Synthesis

Synthesis of thieno[3,2-b]thiophene-2-carbaldehyde (6)

N, N-dimethylformide (16 mL, 210 mmol) was added phosphorus chloride oxide (2.2 mL, 23.6 mmol) under argon at 0 °C. And then it was added to a solution of thieno[3, 2-*b*]thiophene (2.24 g, 16 mmol) in 1,2-dichloroethane (100 mL) and heated for 4 h at 70 °C. Subsequently, it was neutralized with Na₂CO₃, the crude product was extracted with dichloromethane, washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography to yield yellowish powders **6** (1.86 g, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.95(s, 1H) 7.70 (d, *J* = 4 Hz, 1H), 7.33 (d, *J* = 4 Hz, 1H).

Synthesis of ethyl (Z)-2-azido-3-(thieno[3,2-*b*]thiophen-2-yl)acrylate (5)

Thieno[3,2-*b*]thiophene-2-carbaldehyde **6** (1.1 g, 6.63 mmol) and ethyl 2-azidoacetate (1.72 g, 13.3 mmol) were dissolved in 60 mL of ethanol, and the mixture was dropwise added to a solution of sodium ethoxide in ethanol at 0°C and stirred for 2h, then room temperature for 9 h. After the reaction was completed, added 150 mL of saturated NH₄Cl, extracted with dichloromethane, dried over anhydrous sodium sulphate. After removing solvent under reduced pressure, the residue was purified by column chromatography to yield colorless solid **5** (370 mg, 20%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, 2 H), 7.27(s, 1 H), 7.17 (s, 1 H), 4.40 (dd, *J* = 8 Hz, 2 H), 1.42 (m, 3 H).

Synthesis of ethyl 7H-thieno[2',3':4,5]thieno[3,2-*b*]pyrrole-6-carboxylate (4)

Compound **5** (480 mg, 1.72 mmol) was dissolved in 10 mL of *p*-xylene, heated to reflux for 1 h. The solvent was removed under reduced pressure, the residue was purified by column chromatography using silica gel and dichloromethane/petroleum ether (1/1; v/v) as the eluent to obtain a white solid **4** (320 mg, 74%)

yield). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8 Hz, 1H)_{ev}7₄28(s₀1H)_e 7.20(s, 1H), 4.50 (dd, *J* = 8 Hz, 2 H), 1.45 (t, 3H)^[: 10.1039/C9OB00030E]

Synthesis of 7H-thieno[2', 3':4, 5]thieno[3,2-*b*]pyrrole-6-carboxylic acid (3)

Compound **4** (1.38 g, 5.5 mmol) was dissolved in EtOH (50 mL), NaOH (3.1 g, 77.5 mmol) in water (25 mL) was added, and the mixture was refluxed for 1 h. The reaction was then cooled to room temperature and chilled in an ice bath to acidify the mixture with concentrated HCl. The precipitate was filtered, washed with water, and dried under vacuum to afford **3** as grey solid (1.2 g, 98% yield). ¹H NMR (400 MHz, DMSO-d₆) δ 12.61 (s, 1H), 12.05 (s, 1H), 7.17 (d, *J* = 4 Hz, 1H), 6.99 (s, 1H).

Synthesis of 1

Compound 3 (0.8 g, 3.6 mmol) was dissolved in trifluoroacetic acid (TFA) (50 mL) and heated to 40 °C for 10 min. Subsequently, trifluoroacetic anhydride (17 mL) was added and the temperature was then raised to 80°C with continued stirring for 4 h. The resulting deep blue reaction solution was then allowed to cool to room temperature and poured into an aqueous NaHCO₃ solution containing crushed ice. The resultant precipitate was then filtered and dried in vacuo. The dry solid was then dissolved in CH₂Cl₂ (250 mL) and stirred for 5 min at room temperature under a nitrogen atmosphere. Next, boron trifluoride dietherate (7 mL) and triethylamine (5 mL) were added and the reaction mixture was stirred at room temperature for 1 h. Following evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (CH₂Cl₂) to afford **1** as blue solid (300 mg, 17% yield). ¹H NMR (400 MHz, THF-d₈) δ 8.06 (d, J = 4 Hz, 2H), 7.49 (s, 2H), 7.38 (d, J = 4 Hz, 2H). ¹¹B NMR (128 MHz, CDCl₃) δ 0.56 (t, J = 24.3 Hz, BF2) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -51.46 (t, CF3), -160.61 (q, BF2). UV/vis (CH₂Cl₂). λ max (ϵ) = 695 nm (204500 dm³ mol⁻¹ cm⁻¹); HRMS-ESI: m/z: calcd $[C_{18}H_6BF_5N_2S_4]^{\dagger}$ m/z =483.9427, found m/z= 483.9422.

Synthesis of 2

NIS (225 mg, 1 mmol) was added to the dichloromethane solution of **1** (60 mg, 0.124 mmol) and the mixture was then stirred at room temperature overnight, the residue was chromatographed on silica gel to give **2** as green solid (45 mg, 50% yield). ¹H NMR (400 MHz, DMSO-d₆) δ 7.88 (s, 2H), 7.67(s, 2H). ¹¹B NMR (128 MHz, CDCl₃) δ 0.44 (t, J = 23.8 Hz, *B*F2) ppm. ¹⁹F NMR (376 MHz, CDCl₃) δ -51.46 (t, *CF3*), -160.62 (q, *BF2*). UV/vis (CH₂Cl₂), λ max (ϵ) = 720 nm (234900 dm³ mol⁻¹ cm⁻¹); HRMS-ESI: m/z: calcd [C₁₈H₄BF₅I₂N₂S₄]⁺ m/z =735.7358, found m/z= 735.7387.

Spectroscopic Measurements

UV-Vis spectra were recorded on a Shimadzu UV-3000 spectrophotometer. Fluorescence spectra were measured on a Hitachi F-2700 FL spectrophotometer with a 150 W xenon arc lamp as light source. Samples for absorption and emission measurements were contained in 1 cm \times 1 cm quartz cuvettes. For all measurement, the temperature was kept constant at (298 ± 2) K. Dilute solution with an absorbance of less than 0.05 at the excited wavelength was used for the measurement of fluorescent quantum yields, The luminescence quantum yields in solution were measured by using fluorescein with excited wavelength ZnPc (Φ =0.28, in DMF)

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as a reference. $^{18}\,$ The quantum yield Φ as a function solvent polarity is calculated using the following equation. $^{19}\,$

$$\boldsymbol{\Phi}_{sample} = \boldsymbol{\Phi}_{std} \left[\frac{lsample}{lstd} \right] \left[\frac{A \, std}{A \, sample} \right] \left[\frac{n \, sample}{n \, std} \right]^2 \tag{1}$$

Where subscript sample and std denote the sample and standard, respectively, Φ is quantum yield, I is the integrated emission intensity, A stands for the absorbance, n is refractive index.

The fluorescence lifetimes of the samples were determined with a Horiba JobinYvon Fluorolog- 3 spectrofluorimeter. Absorption and emission measurements were carried out in 1×1 cm quartz cuvettes. The goodness of the fit of the single decays as judged by reduced chi-squared (χ^2_R) and autocorrelation function C(j) of the residuals was below χ^2_R <1.2.

When the fluorescence decays were monoexponential, the rate constants of radiative (k_r) and nonradiative (k_{nr}) deactivation were calculated from the measured fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ) according to eqs 2 and 3:

$k_r = \mathcal{D}_F / \tau$	(2)
$k_{nr} = (1 - \mathcal{O}_F) / \tau$	(3)

Computational details

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The ground state structures of compounds **1** and **2** are optimized using the density functional theory (DFT) method with CAM-B3LYP functional and 6-31G(d, p) basis set (LanL2DZ basis for I atom). LanL2DZ basis set was assigned to the elements of I atom, which guarantees a reasonable balance of the computational cost and the reliability of the results. The absorption properties were predicted by time-dependent (TD-DFT) method with the same basis set. All of the calculations were performed with the Gaussian09 program package.¹⁵

X-ray structure determination

The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the ω -20 scan mode. The structure was solved by direct methods and refined on F² by full-matrix least-squares methods using SHELX-2000.²⁰ All calculations and molecular graphics were carried out on a computer using the SHELX-1997 program package and ORTEP2 v2.

Compound 1: $C_{18}H_6B_1F_5N_2S_4$; A brown block-like crystal of the approximate dimensions was measured. Monoclinic, space group P -1, a = 8.209(2) Å, b = 9.719(3) Å, c = 12.587(5) Å, α = 111.424(6), β = 104.496(7), γ = 96.556(4), V = 881.2(5) Å3, Z = 2, F(000) = 484, ρ = 1.825 Mg m⁻³, R1 = 0.0443, wR2 = 0.1154, GOF = 1.095. CCDC No. 1875790 for **1** containing the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223–336–033; E-mail: deposit@ccdc.cam.ac.uk).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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