

Synthesis and characterization of *meso*-ferrocenylethynyl 5,15-diphenylporphyrins

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Abstract

A series of four *meso*-ferrocenylethynyl (5,15-diphenylporphyrinato)nickel(II) derivatives have been synthesized by Sonogashira coupling reactions. Three of these compounds contain the electron-withdrawing groups including $-\text{CHO}$, $-\text{CH}=\text{C}(\text{CN})_2$, and $-\text{C}\equiv\text{CC}_6\text{H}_4\text{NO}_2$ at the remaining *meso* position, with a view to preparing push–pull chromophores, in which ferrocene serves as the electron donor. All the new compounds have been characterized spectroscopically and the molecular structure of one of these porphyrins (compound **11**) has also been determined. The studies show that although the ferrocenylethynyl group can extend the π system of the central porphyrin core, the cyclopentadienyl rings of ferrocene are almost orthogonal to the porphyrin ring. This hinders ferrocene serving as a good electron donor in these systems.

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Keywords: Porphyrin; Ferrocene; Push–pull; Non-linear optics

1. Introduction

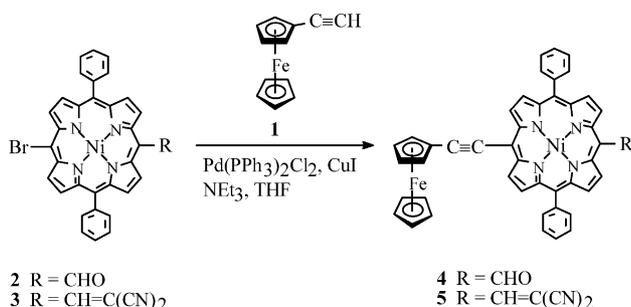
There has been a considerable interest in “push–pull” type chromophores with high dipole moment and molecular non-linearity [1]. These compounds are potential electro-optic materials for applications in high-speed photonic devices for communication, information storage, and optical switching [2]. Different kinds of electron donors, electron acceptors, and conjugated bridges have been employed to construct a wide range of second-order non-linear optical (NLO) chromophores. Detailed theoretical studies have also been performed to elucidate the structural control of the molecular first hyperpolarizability [3]. Among the various conjugated linkers, porphyrins are of particular interest. The macrocycles, which contain a large polarizable π -conjugated system, constitute a two-dimensional platform for electronic communication. The optical properties can also be tuned by changing the metal center, its oxidation state and axial ligands, and the peripheral substituents. Apart

from the architectural flexibility, this class of functional dyes is also thermally stable in general and can be fabricated readily. To date, a substantial number of porphyrin-based NLO chromophores have been reported, focusing on their third-order NLO response [4]. Push–pull porphyrins showing second-order NLO effects are relatively rare [5]. We have recently reported the synthesis and NLO properties of a series of push–pull 5,15-diphenylporphyrins containing electron-releasing ($-\text{C}\equiv\text{CC}_6\text{H}_4\text{NMe}_2$) and $-\text{withdrawing}$ groups [$-\text{CHO}$, $-\text{CH}=\text{C}(\text{CN})_2$, $-\text{CH}=\text{C}(\text{CO}_2\text{Et})_2$, $-\text{CH}=\text{CHCHO}$] in opposite *meso* positions [6]. Such a molecular design facilitates the electronic communication between the donor and the acceptor through the porphyrin framework. Since ferrocene is a well-known electron donor for push–pull NLO chromophores [7], we like to extend the study to *meso*-ferrocenylethynyl 5,15-diphenylporphyrins with an electron withdrawing group at the remaining *meso* position. The preparation and spectroscopic properties of such a series of compounds, as well as the molecular structure of one of the ferrocenyl porphyrins, namely [5-ferrocenylethynyl-15-(4'-nitrophenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (**11**) are reported herein.

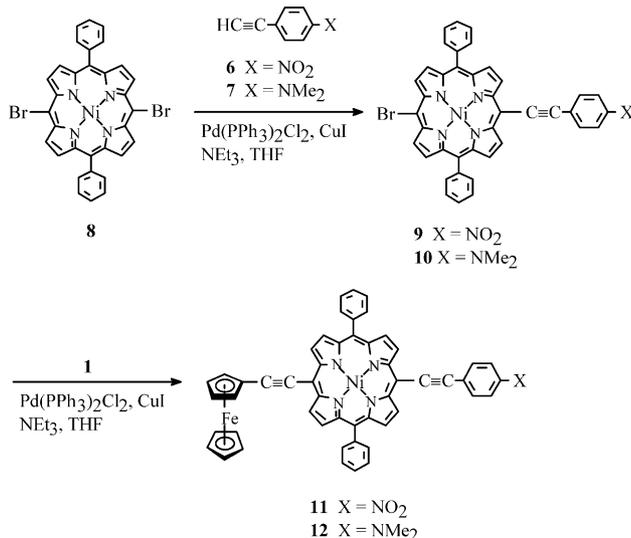
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2. Results and discussion

The synthesis of these ferrocenyl porphyrins involved typical Sonogashira coupling reactions, using ferrocenylethyne (**1**) as a starting material. The porphyrin precursors **2** and **3**, which could be prepared readily by bromination of the corresponding *meso*-formyl or 2,2-dicyanoethenyl derivatives [6], were treated with **1** in the presence of Pd(PPh₃)₂Cl₂, CuI, and triethylamine in tetrahydrofuran (THF) to give porphyrins **4** and **5**, respectively, in good yield (Scheme 1). The bis(alkynyl) analogue **11** was prepared by two sequential palladium-catalyzed coupling reactions from dibromoporphyrin **8** (Scheme 2). As expected, the first coupling reaction using one equiv. of 4-nitrophenylethyne (**6**) gave both the mono- and di-substituted products with a substantial amount of unreacted **8**, leading to a rather low yield of the desired product **9** (32%). This compound also reacted with ferrocenylethyne (**1**) under usual conditions, but the yield of the product **11** (36%) was substantially lower than that for **4** (78%) and **5** (68%). The *N,N*-dimethylamino analogue **12** was prepared in a similar



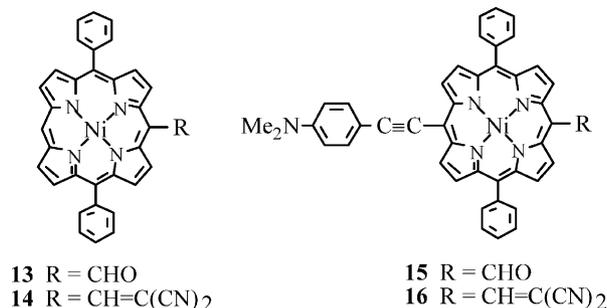
Scheme 1.



Scheme 2.

manner using 4-*N,N*-dimethylaminophenylethyne (**7**) as the coupling reagent (Scheme 2). Compound **12**, which contains the presumably electron donating ferrocenyl and *N,N*-dimethylamino groups, is not a push–pull porphyrin. In attempts to convert this compound to a push–pull counterpart, we tried to oxidize this compound (at the ferrocene center) with iodine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, protonate it (at the amino group) with HCl and HClO₄, and methylate it (at the amino group) with methyl iodide. Unfortunately, all these attempts did not give the desired push–pull porphyrins.

All the ferrocenyl porphyrins are stable and have a good solubility in common organic solvents. Purification of these compounds could be performed readily by column chromatography and recrystallization. All the new compounds were characterized with various spectroscopic methods. Table 1 lists the electronic absorption data of the ferrocenyl porphyrins in CH₂Cl₂. All of them show typical absorptions of metalloporphyrins, giving a strong Soret band at 434–459 nm and one to two Q band(s) at ≈560–570 and 621–649 nm. These bands are significantly red-shifted compared with those of (5,15-diphenylporphyrinato)nickel(II) (400, 515, and 547 nm in CHCl₃) [8]. The data for **4** and **5** are also red-shifted compared with those of the non-ferrocenylethyne analogues **13** (416, 544, and 588 nm in CH₂Cl₂) and **14** (385, 444, and 607 nm in CH₂Cl₂), respectively [6]. However, the lowest-energy Q band of **4** (621 nm) and **5** (649 nm) appears at shorter wavelength compared with that of the (4-*N,N*-dimethylaminophenyl)ethynyl counterparts **15** (630 nm) and **16** (667 nm), respectively [6]. All these observations indicate that the ferrocenylethyne group can extend the π conjugation of the central porphyrin core, but the extent seems to be smaller than the (4-*N,N*-dimethylaminophenyl)ethynyl moiety. Another remarkable feature of the absorption spectra of these ferrocenyl porphyrins is the broadening of signals, in particular for compound **5**, which may suggest a partial mixing of the π–π* transition with an intramolecular charge-transfer character [5c,5e,9].



The molecular structure of porphyrin **11** was also confirmed by X-ray diffraction analysis. The compound crystallizes in the triclinic system with a *P*₁ space group with solvated CHCl₃ and water. Fig. 1 shows a perspec-

Table 1
Electronic absorption data [λ_{\max} nm (log ϵ)] of the ferrocenyl porphyrins in CH_2Cl_2

Compound	Soret band	Q band(s)
4	434 (5.46)	\approx 570 (sh), 621 (4.64)
5	457 (5.49)	-----, 649 (4.78)
11	443 (5.49)	556 (4.33), 621 (4.71)
12	459 (5.36)	557 (4.36), 631 (4.87)

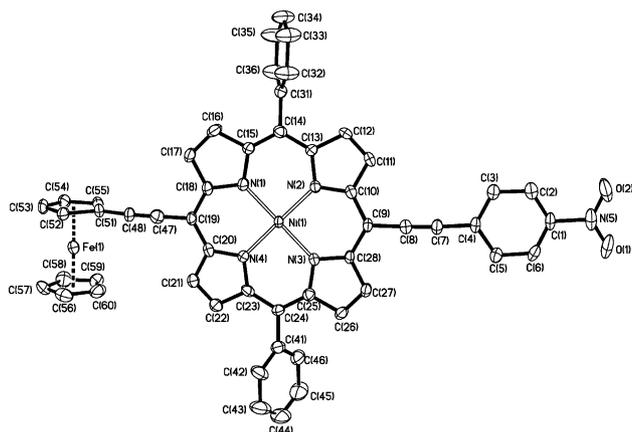


Fig. 1. Molecular structure of **11** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms. Selected bond lengths (Å) and angles (°) are as follows: C(4)–C(7) = 1.426(12), C(7)–C(8) = 1.171(11), C(8)–C(9) = 1.434(11), C(19)–C(47) = 1.426(12), C(47)–C(48) = 1.200(11), C(48)–C(51) = 1.413(12), C(4)–C(7)–C(8) = 176.9(10), C(7)–C(8)–C(9) = 177.6(10), C(19)–C(47)–C(48) = 176.2(11), C(47)–C(48)–C(51) = 174.4(11).

tive view of the structure of **11**, highlighting some important bond lengths and bond angles. The porphyrin core of **11** is relatively planar. The mean deviation from the porphyrin C_{20}N_4 plane is 0.112 Å, which is slightly larger than that of [5,15-bis(4'-fluorophenylethynyl)-10,20-diphenylporphyrinato]zinc(II) and 5,15-bis(4'-methoxyphenylethynyl)-10,20-diphenylporphyrin (<0.05 Å) [10], but substantially smaller than that of the formylated push–pull porphyrins reported by us earlier [6]. The dihedral angle between the porphyrin ring and the aryl C(1)–C(6) plane is 5.6°, showing that the two π systems adopt a nearly coplanar arrangement. The two meso-phenyl groups, however, are tilted with respect to the porphyrin ring by 59.2° and 70.3°. The ferrocene C(51)–C(55) ring is almost orthogonal to porphyrin C_{20}N_4 plane with a dihedral angle of 85.7°. The C \equiv C bond lengths of C(7)–C(8) and C(47)–C(48) are 1.171(11) and 1.200(11) Å, respectively, which are comparable with those in other meso-alkynyl porphyrins [6,10]. A close examination of the neighboring C–C bond distances shows that there is no significant cumulenic character in the molecule. The results suggest that ferrocene is not a good electron donor in these molecules, probably because of the non-coplanarity between the cyclopentadienyl rings of ferrocene and the porphyrin core.

In summary, we have employed the Sonogashira coupling reactions to prepare a series of meso-ferrocenylethynyl 5,15-diphenylporphyrins. On the basis of the absorption spectroscopic and X-ray diffraction studies, it can be concluded that although the ferrocenylethynyl group can extend the π conjugation of the porphyrin core, ferrocene itself may not function as a good electron donor in these systems, as a result of the virtually orthogonal arrangement of the ferrocene and porphyrin π systems.

3. Experimental

3.1. General

Reactions were performed under an atmosphere of nitrogen. THF and triethylamine were distilled from sodium benzophenone ketyl and calcium hydride, respectively. Hexanes used for chromatography was distilled from anhydrous calcium chloride. Chromatographic purifications were performed on silica gel columns (Macherey–Nagel, 70–230 mesh) with the indicated eluents. All other solvents and reagents were of reagent grade and used as received. Alkynes **1** [11], **6** [12], and **7** [13] and porphyrins **2** [6], **3** [6], and **8** [6,8] were prepared according to literature procedures.

^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in CDCl_3 solutions. Chemical shifts were relative to internal SiMe_4 (δ 0). L-SIMS mass spectra were measured on a Bruker APEX 47e FT-ICR mass spectrometer using a 3-nitrobenzyl alcohol matrix. UV–vis absorption spectra were taken on a CARY 5E spectrophotometer. IR spectra were obtained on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets.

3.2. Preparation of meso-alkynyl 5,15-diphenylporphyrins

3.2.1. (5-Ferrocenylethynyl-15-formyl-10,20-diphenylporphyrinato)nickel(II) (**4**)

To a mixture of porphyrin **2** (88 mg, 0.14 mmol), ferrocenylethyne (**1**) (59 mg, 0.28 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (25 mg, 36 μmol), and CuI (3 mg, 16 μmol) in THF (10 ml) was added triethylamine (4 ml). The mixture was stirred at room temperature for 1 h, then the volatiles were removed in vacuo. The residue was purified by chromatography using toluene as eluent. The green band was collected and rotary-evaporated to give **4** as a green solid (83 mg, 78%). ^1H NMR: δ 11.94 (s, 1 H, CHO), 9.68 (d, J = 5.0 Hz, 2H, β -H), 9.38 (d, J = 5.0 Hz, 2H, β -H), 8.72 (d, J = 5.0 Hz, 2H, β -H), 8.60 (d, J = 5.0 Hz, 2H, β -H), 7.90–7.93 (m, 4H, Ph), 7.64–7.72 (m, 6H, Ph), 4.86 (t, J = 1.8 Hz, 2H, Fc-H), 4.45 (t, J = 1.8 Hz, 2H, Fc-H), 4.39 (s, 5H, Fc-H). HRMS (LSI): m/z calcd for $\text{C}_{45}\text{H}_{28}^{56}\text{FeN}_4^{58}\text{NiO}$ (M^+)

754.0966, found 754.1008. IR (KBr): 2194 w (ν C \equiv C), 1672 s (ν C=O) cm^{-1} .

3.2.2. [5-(2',2'-Dicyanoethenyl)-15-ferrocenylethynyl-10,20-diphenylporphyrinato]nickel(II) (**5**)

To a mixture of porphyrin **3** (58 mg, 0.09 mmol), ferrocenylethyne (**1**) (36 mg, 0.17 mmol), Pd(PPh₃)₂Cl₂ (15 mg, 21 μ mol), and CuI (2 mg, 11 μ mol) in THF (10 ml) was added triethylamine (4 ml). The mixture was stirred at room temperature for 4 h, then the volatiles were removed in vacuo. The residue was purified by chromatography using toluene as eluent. The green band was collected and rotary-evaporated to give **5** as a green solid (47 mg, 68%). ¹H NMR: δ 9.87 (s, 1H, CH=C), 9.33 (d, J = 4.8 Hz, 2H, β -H), 9.02 (d, J = 5.1 Hz, 2H, β -H), 8.69 (d, J = 5.1 Hz, 2H, β -H), 8.56 (d, J = 4.8 Hz, 2H, β -H), 7.87–7.90 (m, 4H, Ph), 7.64–7.70 (m, 6H, Ph), 4.85 (t, J = 1.8 Hz, 2H, Fc-H), 4.47 (t, J = 1.8 Hz, 2H, Fc-H), 4.39 (s, 5H, Fc-H). HRMS (LSI): m/z calcd for C₄₈H₂₈⁵⁶FeN₆⁵⁸Ni (M⁺) 802.1078, found 802.1063. IR (KBr): 2219 w, 2193 m (ν C \equiv C and C \equiv N) cm^{-1} .

3.2.3. [5-Bromo-15-(4'-nitrophenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (**9**)

Dibromoporphyrin **8** (400 mg, 0.59 mmol), 4-nitrophenylethyne (**6**) (130 mg, 0.88 mmol), Pd(PPh₃)₂Cl₂ (33 mg, 47 μ mol), and CuI (13 mg, 68 μ mol) were dissolved in THF (40 ml). Triethylamine (15 ml) was then added dropwise into the mixture, which was then stirred at 60 °C for 12 h. After removing the volatiles in vacuo, the residue was chromatographed using toluene/hexanes (1:1) as eluent. The first red band, which contained a trace amount of unreacted porphyrin **8** was discarded. The second reddish-green band was collected and evaporated to give **9** as a green solid (141 mg, 32%). ¹H NMR: δ 9.52 (br. s, 2H, β -H), 8.80–8.85 (m, 4H, β -H), 8.37 (d, J = 7.8 Hz, 2H, C₆H₄), 7.97–8.02 (m, 6H, Ph and β -H or C₆H₄), 7.61–7.79 (m, 8H, Ph and β -H or C₆H₄). UV-vis (CH₂Cl₂) [λ_{max} nm (log ϵ): 435 (5.10), 543 (4.08), 581 (4.13)]. IR (KBr): 2191 w (ν C \equiv C), 1511 m (ν_{asy} NO₂), 1333 s (ν_{sym} NO₂), 849 m (ν C–N) cm^{-1} .

3.2.4. [5-Bromo-15-(4'-N,N-dimethylaminophenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (**10**)

Dibromoporphyrin **8** (200 mg, 0.30 mmol), 4-N,N-dimethylaminophenylethyne (**7**) (78 mg, 0.54 mmol), Pd(PPh₃)₂Cl₂ (17 mg, 24 μ mol), and CuI (8 mg, 42 μ mol) were dissolved in THF (25 ml). Triethylamine (10 ml) was then added dropwise into the mixture, which was then stirred at 50 °C for 12 h. After removing the volatiles in vacuo, the residue was chromatographed using toluene/hexanes (1:1) as eluent. The first red band, which contained a trace amount of unreacted porphyrin

8 was discarded. The second reddish-green band was collected and evaporated to give **10** as a green solid (115 mg, 53%). ¹H NMR: δ 9.52 (d, J = 4.8 Hz, 2H, β -H), 9.41 (d, J = 5.1 Hz, 2H, β -H), 8.67–8.71 (m, 4H, β -H), 7.95–7.98 (m, 4H, Ph), 7.77 (d, J = 8.4 Hz, 2H, C₆H₄), 7.68–7.73 (m, 6H, Ph), 6.82 (d, J = 8.4 Hz, 2H, C₆H₄), 3.08 (s, 6H, NMe₂).

3.2.5. [5-Ferrocenylethynyl-15-(4'-nitrophenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (**11**)

To a mixture of porphyrin **9** (83 mg, 0.11 mmol), ferrocenylethyne (**1**) (36 mg, 0.17 mmol), Pd(PPh₃)₂Cl₂ (6 mg, 9 μ mol), and CuI (3 mg, 16 μ mol) in THF (25 ml) was added triethylamine (10 ml). The mixture was stirred at 60 °C for 12 h, then the volatiles were removed in vacuo. The residue was purified by chromatography using hexanes/CHCl₃ (1:4) as eluent. The green band was collected and rotary-evaporated to give **11** as a green solid (35 mg, 36%). ¹H NMR: δ 9.48 (d, J = 4.8 Hz, 2H, β -H), 9.44 (d, J = 4.2 Hz, 2H, β -H), 8.72–8.75 (m, 4H, β -H), 8.38 (d, J = 7.8 Hz, 2H, C₆H₄), 7.98–8.03 (m, 6H, Ph and C₆H₄), 7.71–7.73 (m, 6H, Ph), 4.87 (s, 2H, Fc-H), 4.45 (s, 2H, Fc-H), 4.39 (s, 5H, Fc-H). HRMS (LSI): m/z calcd for C₅₂H₃₁⁵⁶FeN₅⁵⁸NiO₂ (M⁺) 871.1180, found 871.1115. IR (KBr): 2194 m (ν C \equiv C), 1508 m (ν_{asy} NO₂), 1331 s (ν_{sym} NO₂) cm^{-1} .

3.2.6. [5-Ferrocenylethynyl-15-(4'-N,N-dimethylaminophenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (**12**)

To a mixture of porphyrin **10** (100 mg, 0.14 mmol), ferrocenylethyne (**1**) (57 mg, 0.27 mmol), Pd(PPh₃)₂Cl₂ (24 mg, 34 μ mol), and CuI (3 mg, 16 μ mol) in THF (10 ml) was added triethylamine (4 ml). The mixture was stirred at 60 °C for 12 h, then the volatiles were removed in vacuo. The residue was purified by chromatography using hexanes/CHCl₃ (1:4) as eluent. The green band was collected and rotary-evaporated to give **12** as a green solid (53 mg, 45%). ¹H NMR: δ 9.50 (d, J = 4.8 Hz, 2H, β -H), 9.45 (d, J = 4.8 Hz, 2H, β -H), 8.70 (d, J = 5.1 Hz, 2H, β -H), 8.68 (d, J = 5.1 Hz, 2H, β -H), 7.97–8.00 (m, 4H, Ph), 7.67–7.76 (m, 8H, Ph and C₆H₄), 6.76 (d, J = 8.4 Hz, 2H, C₆H₄), 4.86 (s, 2H, Fc-H), 4.41 (s, 7H, Fc-H). HRMS (LSI): m/z calcd for C₅₄H₃₇⁵⁶FeN₅⁵⁸Ni (M⁺) 869.1752, found 869.1765. IR (KBr): 2178 m (ν C \equiv C) cm^{-1} .

3.3. X-ray crystallographic analysis of **11**·CHCl₃·1.5H₂O

Crystal data and details of data collection and structure refinement are given in Table 2. Data were collected on a Bruker SMART CCD diffractometer with an Mo K α sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode with an increment of 0.3 °. Preliminary unit

Table 2
Crystallographic data for **11** · CHCl₃ · 1.5H₂O

	11 · CHCl ₃ · 1.5H ₂ O
Formula	C ₅₃ H ₃₅ Cl ₃ FeN ₅ NiO _{3.5}
Formula weight	1018.77
Crystal size (mm ³)	0.53 × 0.29 × 0.20
Crystal system	Triclinic
Space group	P ₁
<i>a</i> (Å)	11.2859 (10)
<i>b</i> (Å)	14.6870 (13)
<i>c</i> (Å)	15.2904 (13)
α (°)	108.344 (2)
β (°)	90.698 (2)
γ (°)	106.768 (2)
<i>V</i> (Å ³)	2288.6 (3)
<i>Z</i>	2
<i>F</i> (000)	1042
<i>D</i> _{calcd} (mg m ⁻³)	1.478
μ (mm ⁻¹)	0.956
θ range (°)	1.41–24.00
Total number of reflections	11791
Number of independent reflections	7132 (<i>R</i> _{int} = 0.0497)
Number of parameters	597
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0788
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.2148
Goodness of fit	0.963

cell parameters were obtained from 45 frames. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling [14]; SADABS for absorption correction [15]; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting [16]. Crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-224460. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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