Capturing the Long-Sought Dy@C_{2v}(5)-C_{80} via Benzyl Radical Stabilization

Xinyi Han 1,2, Jinpeng Xin 2, Yangrong Yao 2, Zhihui Liang 1, Yongfu Qiu 1, Muqing Chen 1,2,* and Shangfeng Yang 2,*

1 School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China
2 Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion, Anhui Laboratory of Advanced Photon Science and Technology, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China
* Correspondence: mqchen@ustc.edu.cn (M.C.); sfyang@ustc.edu.cn (S.Y.)

Abstract: Endohedral metallofullerenes (EMFs) are one type of intriguing metal/carbon hybrid molecule with the molecule configuration of sphere cavity-encapsulating metal ions/metal clusters due to their unique physicochemical properties and corresponding application in the fields of biological materials, single molecule magnet materials and energy conversion materials. Although the EMF family is growing, and versatile EMFs have been successfully synthesized and confirmed using crystal structures, some expected EMF members have not been observed using the conventional fullerene separation and purify strategy. These missing EMFs raise an interesting scientific issue as to whether this is due to the difficulty in separating them from the in situ formed carbon soot. Herein, we successfully captured a long-sought dysprosium-based EMF bearing a C_{2v}(5)-C_{80} cage (Dy@C_{2v}(5)-C_{80}) in the form of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph)(Ph = –C_{6}H_{5}) from carbon soot containing versatile EMFs using simple benzyl radical functionalization and unambiguously confirmed the molecule structure using single crystal X-ray diffraction characterization. Meanwhile, the crystal structure of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) showed that a single benzyl group was grafted onto the (5,6,6)-carbon, suggesting the open-shell electronic configuration of Dy@C_{2v}(5)-C_{80}. The theoretical calculations unveiled that the benzyl radical addition enables the modulation of the electronic configuration of Dy@C_{2v}(5)-C_{80} and the corresponding stabilization of Dy@C_{2v}(5)-C_{80} in conventional organic solvents. This facile stabilization strategy via benzyl radical addition exhibits the considerable capability to capture these missing EMFs, with the benefit of enriching the endohedral fullerene family.

Keywords: endohedral metallofullerenes; missing fullerene; Dy@C_{2v}(5)-C_{80}; crystal structure; benzyl radical

1. Introduction

Endohedral metallofullerenes (EMFs) featuring versatile metallic ions/metallic clusters encapsulated in a spherical cavity have been attracting considerable interest due to the fact that they not only act as a metal/carbon hybrid molecule model to explore the structure-properties relationship but also provide a series of novel nanomaterials which can be applied in the fields of catalysts, biomaterials and energy conversion devices [1-3]. For instance, the non-IPR Sc@C_{8}N@D_{3}(6140)-C_{68} was reported to possess superior hydrogen evolution reaction (HER) performance with an onset potential of −38 mV vs. RHE due to fused pentagon rings, representing a new and promising HER catalytic motif [4]. Furthermore, the most conventional EMF, such as Sc@C_{8}, was used as ionic dopant by accepting transfer electrons from spiro-OMeTAD, leading to drastically improved conductivity and a lower Fermi level of the hole transfer layer (HTL) to minimize the Schottky barrier. As a result, the perovskite solar cells based on Sc@C_{8}/spiro-OMeTAD HTL exhibit an energy conversion efficiency of 20.77% (with the champion cell exhibiting 21.09%) and improved device stability [5]. With regards to fullerene derivatives, they have been applied as electron transport layers within perovskite solar cells or organic solar cells [6,7], enabling
improved device performance and suggesting the enormous prospect of EMF-derivatives in the field of energy conversion devices. Another EMF, such as Gd$_3$N@C$_{80}$ modified by oligoethylene glycol groups, exhibits enhanced magnetic resonance imaging contrast properties [2]. Since the first EMF, such as La@C$_{82}$ reported in 1991 [8], the EMF family has been growing and was expanded to carbide clusterfullerenes [9,10], trimetallic nitrogen clusterfullerenes [11], sulfur/oxygen metallic clusterfullerenes [12,13] and so on. However, according to theoretical predication regarding possible EMFs, only a few of them are being observed or confirmed using NMR or single crystal characterization. For example, EMFs with a C$_{80}$ cage obeying the isolated pentagon rule (IPR) were proposed to have seven types of isomeric structure including $D_{5d}$, $D_2$, $C_{2v}(3)$, $D_3$, $C_{2v}(5)$, $D_{5h}$ and $I_8$ based on theoretical predictions, while the observed or confirmed species were only $C_{2v}(3)$, $C_{2v}(5)$, $D_{5h}$ and $I_8$ using experimental approaches. The stable formation of EMFs was attributed to the synergistic influence of the transferred charge number from the endohedral metallic ions/clusters to the outer fullerene cages as well as the matched energy levels between the inner metals/clusters and outer fullerene cages [14]. For example, $I_8$-C$_{80}$ can be stabilized by accepting six electrons from the encapsulating metal ions/clusters including M$_2$N clusters ($M = $ Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu) and M$_2$TiC clusters ($M = $ Sc, Y, Tb, Dy, Lu) [15]. When anomalous five-electron transfer occurs on $M_2@I_8$-C$_{80}$ ($M = $ Y, Gd, Tb, Ho, Er, Tm and TbGd) [16,17], a benzyl radical was verified to be the efficient approach to stabilize the missing $M_2@I_8$-C$_{80}$ using bromide benzyl in mild experimental conditions [18].

With regards to EMFs with a $C_{2v}(5)$-C$_{80}$ cage, the two-electron transfer from the endohedral divalent metal ions to the $C_{2v}(5)$-C$_{80}$ cage enable the stabilization of M$^{2+}@[C_{2v}(5)-C_{80}]^{-2}$ ($M = $ Sm, Yb) [19,20]. However, with the trivalent rare earth metal ions encapsulated within the $C_{2v}(3)$-C$_{80}$ cage along with the three-electron transfer, the corresponding M$^{3+}@[C_{2v}(3)-C_{80}]^{-3}$ is difficult to stabilize and obtain only if chemical modification is adopted to stabilize them [21,22]. The first and only case of missing M$^{3+}@[C_{2v}(3)-C_{80}]^{-3}$ is La$^{3+}@[C_{2v}(3)-C_{80}]^{-3}$- reported by Nagase et al., showing that the dichlorobenzene radical formed in situ from the 1, 2, 4-trichlorobenzene solution under thermal conditions enables the stabilization of La$^{3+}@[C_{2v}(3)-C_{80}]^{-3}$- in the form of La@C$_{80}$(C$_6$H$_5$Cl$_2$). The theoretical calculations revealed that La@C$_{2v}(3)$-C$_{80}$ is an open-shell electron configuration and has high reactivity resulting from its small ionization potential (Ip) and electron affinity (Ea), which is efficiently stabilized by the addition of the dichlorobenzene radical [23]. In addition, EMFs with a $C_{2v}(5)$-C$_{80}$ carbon cage can be stabilized by accepting four electrons from the endohedral carbide clusters (Sc$_2$C$_2$, Er$_2$C$_2$) or oxygen clusters (Sc$_2$O, Lu$_2$O) [24–27]. Considering the missing La$^{3+}@[C_{2v}(3)-C_{80}]^{-3}$-, it was stabilized with three-electron transfer and entrapped in the form of La@C$_{2v}(3)$-C$_{80}$(C$_6$H$_5$Cl$_2$) using facile radical addition. Therefore, whether the long-sought monometallic M$^{3+}@[C_{2v}(5)-C_{80}]^{-3}$- ($M = $ Sc, Y, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Lu) can be stabilized and entrapped using facial chemical functionalization is an interesting issue. To address the issue mentioned above, we performed a study searching for the missing M$^{3+}@[C_{2v}(5)-C_{80}]^{-3}$- ($M = $ rare earth metals) EMFs using the facile benzyl radical stabilization strategy.

Herein, we adopted the freshly prepared dysprosium (Dy)-based raw soot as the research target and successfully captured the missing Dy@C$_{80}$ in the existing form of Dy@C$_{60}$(C$_7$H$_7$). More importantly, the molecular structure of Dy@C$_{80}$ was unambiguously confirmed using single crystal X-ray diffraction characterization, showing that the C$_{80}$ cage is a $C_{2v}(5)$ symmetry and the addition site is on a pentagon–hexagon–hexagon junction ([5,6,6]-junction) carbon atom. Dy@C$_{2v}(5)$-C$_{80}$ is the first reported case of a monometallic EMF isomer composed of trivalent M$^{3+}$ ($M = $ rare earth metals) and a $C_{2v}(5)$-C$_{80}$ carbon cage. The theoretical calculations indicated that the benzyl radical addition clearly alters the energy level and enlarges the bandgap, leading to the stabilization of Dy@C$_{2v}(5)$-C$_{80}$.
2. Experiment

2.1. Characterization Techniques

Soot containing Dy-EMFs was produced using a modified Krätschmer–Huffman DC-arc discharge method, and after the radical addition, the extracted EMF derivatives were isolated and purified using high performance liquid chromatography (HPLC, LC-9104, Japan Analytical Industry, Akishima, Japan). Regarding the Dy@C$_{80}$(CH$_2$Ph), the corresponding purification was performed using a multistep HPLC separation procedure with toluene as the eluent. The pure Dy@C$_{80}$(CH$_2$Ph) was further verified using analytical HPLC and matrix-assisted laser desorption ionization time-of-flight mass spectrum (MALDI-TOF MS) with 1,1,4,4-tetraphenyl-1,3-butadiene as a matrix (Biflex III, Bruker Daltonics Inc., Germany). Absorption spectrum of Dy@C$_{80}$(CH$_2$Ph) in toluene was recorded on a UV−vis−NIR 3600 spectrometer (Shimadzu, Kyoto, Japan) using a quartz cell of 1 mm thickness. Electrochemical studies of Dy@C$_{80}$(CH$_2$Ph) were performed in o-DCB (anhydrous, 99%, Aldrich, St. Louis, MI, USA). The supporting electrolyte was TBAPF$_6$ (electrochemical grade, Fluka) which was dried under reduced pressure at 340 K for 24 h and stored in glovebox. Cyclic voltammogram experiments were performed using a CHI660D electrochemical workstation (CHI Instrument, Austin, TX, USA) at room temperature. A standard three-electrode arrangement including a platinum disc as working electrode, a platinum wire as counter electrode and a silver wire as a reference electrode was used. In a control experiment, ferrocene (Fc) was added as the external standard, and all potentials were referred to as Fc/Fc$^+$ couple.

2.2. The Capturing and Separation of Dy@C$_{80}$(CH$_2$Ph)

The composite rods of graphite and Dy$_2$O$_3$ (molar ratio of Dy:C = 1:15) were evaporated using DC-arc discharge method under a 180 mbar He atmosphere and 110A DC, delivering the raw soot containing a series of Dy-EMFs. Before entrapping the missing Dy@C$_{80}$ derivative, the collected freshly prepared carbon soot was treated with N,N-Dimethylformamide (DMF) due to its reduction properties, enabling the missing EMFs to dissolve in solution through transferring electrons as per the same strategy applied in M$_2$@I$_h$-C$_{80}$ (M = Y, Gd, Tb, Dy, Ho, Er, Dy, Tb, Gd), as previously reported [16,17]. In detail, the raw soot obtained from arc discharge procedure was dispersed in DMF and purged using nitrogen for 20 min, and then the mixture solution was heated to 150 $^\circ$C for 20 h under nitrogen atmosphere. Then, the solution temperature was decreased to 110 $^\circ$C, and benzyl bromide was injected into the mixture solution via syringe to avoid the entrance of air. The radical addition reaction occurred, and the corresponding reaction process lasted 20 h under 110 $^\circ$C. When the reaction finished, the reaction solution was cooled to room temperature, and the insoluble solid mixture was filtrated using reduced pressure. The obtained DMF solution containing pristine and functionalized EMFs was dried to remove DMF solvent using a rotary evaporator, and the residual black solid was washed with methanol. Finally, the solid was dissolved in toluene for further isolation using multistep HPLC procedure.

2.3. Crystal Growth and Measurements

The black crystals of Dy@C$_{80}$(CH$_2$Ph) suitable for single crystal X-ray diffraction measurements were obtained using the slow volatilization of toluene/CS$_2$ solution containing Dy@C$_{80}$(CH$_2$Ph) and decapryrylcorannulene (DPC) as host for about two weeks [28]. The black crystals were subjected to the Shanghai Synchrotron Radiation Facility (beamline station BL17B at 100 K) for crystal data collection. The crystal structure was refined using all data (based on F$^2$) utilizing SHELXL 2015 within OLEX2. The corresponding crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC numbers: 2195196).
Scheme 1. The activation and stabilization of missing Dy@C_{2v}(5)-C_{80}.
Figure 1. Isolation and purification of Dy@C$_{80}$(CH$_2$Ph) via four-step HPLC process. (a) Collected fraction A contained Dy@C$_{80}$(CH$_2$Ph) and labelled as the red region. Conditions: Buckyprep column (ø 20 × 250 mm), a flow rate of 4 mL/min, injection volume of 4 mL, toluene as eluent at 40 °C. (b) Recycling HPLC profile of fraction A for fraction A-2. Conditions: Buckyprep column (ø 20 × 250 mm), a flow rate of 8 mL/min, injection volume of 8 mL, toluene as eluent at 40 °C. (c) Recycling HPLC profile of fraction A-2 for A-2-2. Conditions: Buckyprep column (10 × 250 mm), a flow rate of 4 mL/min, injection volume of 4 mL, toluene as eluent at 40 °C. (d) HPLC profile of fraction A-2-2 for consequence A-2-2-2. Conditions: Buckyprep-M column (10 × 250 mm), a flow rate of 4 mL/min, injection volume of 4 mL, toluene as eluent at 40 °C.

Figure 2. MALDI-TOF MS of the fraction A-2-2-2 with 1,1,4,4-tetraphenyl-1,3-butadiene as matrix.
The relative orientation of the Dy@C₈₀(CH₂Ph) and two DPC molecules is shown in Figure 3a, in which the two DPC molecules present a V-shape geometry with the dihedral angle of 65.5°. In contrast to the pristine Sc³⁺@I₆-C₈₀·2DPC complex with a dihedral angle of 1.49°, the enlarged dihedral angle of Dy@C₈₀(CH₂Ph) was perhaps attributable to the steric hindrance of the grafted benzyl group. Furthermore, the crystal structure of Dy@C₈₀(CH₂Ph) shows that one benzyl group was grafted onto the fullerene cage with the addition site of the [5,6,6]-carbon (Figure 3b,d). The detailed analysis of the carbon cage indicates that the symmetry of C₈₀ is C₂ᵥ(5), which is the first case of an EMF composed of a trivalent rare earth metal ion and C₂ᵥ(5)-C₈₀ carbon cage.

![Figure 3](image-url)

Figure 3. Drawing of (a) Dy@C₂ᵥ(5)-C₈₀(CH₂Ph)·2DPC and (b) Dy@C₂ᵥ(5)-C₈₀(CH₂Ph). (c) Fragment view showing the interaction of the major Dy1 with the closest carbon atoms of the cage and (d) the addition site of benzyl. Only major Dy site is shown. Solvent molecules and H atoms are omitted for clarity. Gray: C; blue: N; fuchsia: Dy.

Regarding the endohedral Dy³⁺ ion, there are four position disorders in the C₂ᵥ(5)-C₈₀ cage with the occupancy ratio of Dy1 0.79, Dy2 0.10, Dy3 0.06 and Dy4 0.05, respectively (as seen in Figure S4 and Table S1). The major occupancy Dy1 is located underneath the [6,6]-bond (the bond shared by two hexagonal rings) with the shortest distances of 2.250(13) Å (Dy1-C30) and 2.236(13) Å (Dy1-C29) between Dy1 and the adjacent carbon atoms (Figure 3c), respectively, and indicates the strong interaction between the endohedral metal ion and the outer C₂ᵥ(5)-C₈₀. Conventionally, the encapsulated metal ion is located at the symmetric plane or the symmetric center of the EMF cages [29], and the main occupancy of endohedral Dy1 clearly deviated from the normal position of pristine Dy@C₂ᵥ(5)-C₈₀ after the benzyl functionalization, indicating the remarkable electron configuration change in Dy@C₂ᵥ(5)-C₈₀(CH₂Ph) (Figure S5).

To reveal the absorption and electrochemical properties of Dy@C₂ᵥ(5)-C₈₀(CH₂Ph), the corresponding UV-vis-NIR absorption and cyclic voltammetry measurements were performed, as shown in Figure 4a. The absorption spectrum of Dy@C₂ᵥ(5)-C₈₀(CH₂Ph) in toluene exhibits six obvious absorption peaks at 489, 536, 643, 769, 908 and 1064 nm. The absorption onset at 1123 nm suggests that the calculated optical bandgap (ΔE-gap, optical) of Dy@C₂ᵥ(5)-C₈₀(CH₂Ph) is 1.10 eV. Compared with the absorption profile of C₂ᵥ(5)-C₈₀
embedding Sc$_2$C$_2$, Sc$_2$O, Er$_2$C$_2$ and Lu$_2$O clusters with four-electron transfer to the outer carbon cage, Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) exhibits a remarkable absorption difference which is attributed to the three-electron transfer and benzyl radical addition. The electrochemical characterization of Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) was obtained using cyclic voltammograms with tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the electrolyte in o-dichlorobenzene (o-DCB). The redox potentials of Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) show three reversible reduction peaks and two irreversible oxide peaks. The corresponding differential pulse voltammetry (DPV) in Figure 4b shows that the first reduction potential and first oxide potential are $-0.88$ V and $0.17$ V, respectively, delivering a narrow bandgap of $1.05$ eV. To understand the redox change before and after the benzyl radical addition of Dy@C$_{2v}$(5)-C$_{80}$, the analogous monometallic EMFs, such as La@C$_{2v}$-C$_{82}$ and La@C$_{2v}$-C$_{82}$-benzyl adduct, were applied to analogize the variation tendency of electrochemical properties. After the benzyl radical modification, the first oxide and reduction potentials of La@C$_{2v}$-C$_{82}$ at $0.07$ V and $-0.42$ V positively shift about $0.10$–$0.63$ V to $0.15$–$0.25$ V for the first oxide potential and $-1.05$–$-0.68$ V for the first reduction potential. According to this change tendency, the first oxide potential of Dy@C$_{2v}$(5)-C$_{80}$ is perhaps close to zero potential, even approaching the negative value, which is possibly responsible for the instability of the Dy@C$_{2v}$(5)-C$_{80}$.

Theoretical calculations of Dy@C$_{2v}$(5)-C$_{80}$ and Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) were performed, as shown in Figure 5. The highest occupied molecular orbital (HOMO) energy level and lowest unoccupied molecular orbital (LUMO) energy level calculated are: $-5.27$ eV and $-4.16$ eV, respectively, for Dy@C$_{2v}$(5)-C$_{80}$; and $-5.10$ eV and $-3.29$ eV, respectively, for Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph). The corresponding bandgap for Dy@C$_{2v}$(5)-C$_{80}$ and Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) are $1.11$ eV and $1.86$ eV, respectively. The change tendency of LUMO, HOMO energy levels and bandgap for Dy@C$_{2v}$(5)-C$_{80}$ and Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) indicate that the benzyl radical addition enlarges the bandgap from $1.11$ eV to $1.86$ eV and elevates the LUMO energy level to about $0.87$ eV which is beneficial for the stabilization of the missing Dy@C$_{2v}$-C$_{80}$.

**Figure 4.** (a) UV-Vis-NIR absorption spectrum of Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph). (b) Cyclic voltammograms of Dy@C$_{2v}$(5)-C$_{80}$(CH$_2$Ph) in o-DCB solution with ferrocene (Fc) as the standard under different scan regions. Scan rate: $100$ mV/s, TBAPF$_6$ as supporting electrolyte. The half-wave potentials ($E_{1/2}$) of each redox step are marked with a solid dot to aid comparison.
Figure 5. The electronic configuration (HOMO and LUMO energy levels) of (a) Dy@C_{2v}(5)-C_{80} and (b) Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) using density functional theory.

4. Conclusions

The long-sought Dy@C_{2v}−C_{80} was successfully trapped in the form of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) using a facile reduction and radical addition strategy. After a four-step HPLC isolation procedure, the pure Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) was obtained and unambiguously confirmed using single crystal X-ray diffraction measurements. The crystal structure of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) shows that one benzyl group was grafted onto the [5,6,6]-carbon atom, suggesting that the Dy@C_{2v}(5)-C_{80} is an open-shell electron configuration and a three-electron transfer configuration of Dy^{3+}@C_{2v}(5)-C_{80}. More importantly, the carbon cage symmetry was unveiled to be a rare C_{2v}(5)-C_{80} which is the first case of an EMF composed of a monometal rare earth ion encapsulated within a C_{80} cage. Meanwhile, the encapsulated Dy^{3+} ion of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) is located underneath the [6,6]-bond and is deviated from the symmetry plan of C_{2v}(5)-C_{80}, indicating the remarkable electronic configuration change after the benzyl radical addition. A cyclic voltammogram of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph) shows that the narrow bandgap of 1.10 eV is responsible for the instability of Dy@C_{2v}(5)-C_{80}. The theoretical calculations showed that benzyl radical addition to Dy@C_{2v}(5)-C_{80} enlarges the bandgap from 1.11 eV to 1.86 eV and the clearly elevated LUMO energy level to about 0.87 eV, which synergistically stabilizes the missing Dy@C_{2v}(5)-C_{80}. Therefore, the benzyl radical strategy was verified as an efficient chemical method to trap some long-sought EMFs proposed by theoretical predictions, and there may be benefits to exploring the novel EMFs hidden within raw soot.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12193291/s1, Figure S1. MALDI-TOF mass spectrum of raw soot containing Dy@C_{80}; Figure S2. MALDI-TOF mass spectrum of fraction A with the matrix of 1,1,4,4-tetraphenyl-1,3-butadiene; Figure S3. HPLC chromatograms of purified Dy@C_{80}(CH_{2}Ph). Condition: Buckyprep column (ø 4.6 mm × 250 mm), UV-detector (320 nm), toluene as eluent with the flow rate of 1.0 mL/min; Figure S4. The disordered positions of dysprosium sites in Dy@C_{2v}(5)-C_{80}(CH_{2}Ph). Gray: C; Fuchsia: Dy; Figure S5. Relative orientation between endohedral Dy ion and C_{2v}(5)-C_{80} carbon cage of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph). Gray: C; Fuchsia: Dy; Table S1. Crystal data of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph); Table S2. The occupancy of disordered metal ions encapsulated within Dy@C_{2v}(5)-C_{80}(CH_{2}Ph); Table S3. Redox Potentials (V vs. Fc+/Fc) and Electrochemical Gaps (ΔE_{gap}, EC) of Dy@C_{2v}(5)-C_{80}(CH_{2}Ph).

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. Meanwhile, the detailed crystal data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 5 August 2022).

Conflicts of Interest: The authors declare no conflict of interest.

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