



Article Reactivity of Open-Shell Metallofullerene Anions: Synthesis, Crystal Structures, and Electrochemical Properties of Benzylated Gd@C_{2v}-C₈₂

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Abstract: The reactivity of the open-shell $Gd@C_{2v}-C_{82}$ with different charge states towards benzyl bromide was investigated. $[Gd@C_{2v}-C_{82}]^{3-}$ exhibited enhanced activity relative to $Gd@C_{2v}-C_{82}$ and $[Gd@C_{2v}-C_{82}]^{-}$. The structural characterizations, including MALDI-TOF MS, UV-vis-NIR, and single crystal X-ray diffraction, indicate the formation of isomeric benzyl monoadducts of $Gd@C_{2v}-C_{82}$. All three monoadducts contain 1:1 mirror-symmetric enantiomers. Additionally, the addition of the benzyl group and its specific position result in distinct electrochemical behavior of the products compared to the parent $Gd@C_{2v}-C_{82}$. Theoretical studies demonstrate that only $[Gd@C_{2v}-C_{82}]^{3-}$ has a HOMO energy level that matches well with the LUMO energy level of the PhCH₂ radical, providing a rationalization for the observed significantly different reactivity.

Keywords: endohedral metallofullerene; open shell; electrosynthesis; fullerene anion; Gd@C_{2v}-C₈₂

1. Introduction

Endohedral metallofullerenes (EMFs) have garnered substantial attention from scientists due to their exceptional chemical and physical properties [1–9]. Since the discovery of the first solvent-extractable EMF, La@C₈₂ [10], there has been a boom in interest in EMFs. According to the electronic structure, EMFs are categorized into two main groups: closedshell EMFs and open-shell EMFs. Closed-shell EMFs possess completely filled electron shells, meaning that all the molecular orbitals are paired with electrons. Consequently, they exhibit a stable and relatively non-reactive structure. In contrast, open-shell EMFs have partially filled electron shells, resulting in the presence of unpaired electrons in their molecular orbitals. This characteristic makes them more reactive and prone to chemical reactions [11–13]. Nevertheless, compared with closed-shell EMFs, the reaction of open-shell EMFs is relatively less studied.

The physical and chemical properties of open-shell EMFs can be altered by functionalization [11,14–17]. By introducing trifluoromethyl, phenyl, or dichlorophenyl groups into the Er@C₈₂ cages, the derived products exhibit distinct photoluminescent properties [18]. Additionally, multi-hydroxylated $Pr@C_{82}$ [19], $Gd@C_{82}$ [20–23], and $Ho_x@C_{82}$ [24] show enhanced solubility, rendering them suitable for use in biomedicine as novel biological radical scavengers, radiographic agents, magnetic resonance imaging agents, and "missile" drugs [20].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Gd@ C_{2v} -C₈₂, with the inner Gd atom capable of transferring three electrons to the C₈₂ cages, represents a typical open-shell molecule. The electronic states of this system can be described as Gd³⁺@C₈₂³⁻ [25–27]. Gd@ C_{2v} -C₈₂ has magnetic properties stemming from the interaction between the spin of the metal atom and the electron spin of the cage [28]. Gd@ C_{2v} -C₈₂ has found widespread use in various biomedical applications, including MRI contrast [20,29,30], antitumor therapeutics [31–33], adjuvant therapeutic agents [34,35], metabolic disease modulation [22,36,37], and so forth. Indeed, the diverse range of applications for Gd@ C_{2v} -C₈₂ in biomedical applications, thereby enhancing its effectiveness and versatility in various medical contexts. In addition, the carbon cage encasing the Gd ion serves as a protective barrier, preventing the release of Gd³⁺ and thereby eliminating potential toxicity concerns. Therefore, expanding the variety of Gd@ C_{2v} -C₈₂ derivatives holds great significance as it allows for a more comprehensive exploration of their potential properties and applications.

In this work, we utilized the electrochemical method to produce $Gd@C_{2v}-C_{82}$ anions, which were then subjected to the benzylization reaction. Interestingly, this reaction has been demonstrated to be ineffective for the neutral form of the molecule. The reduction of $Gd@C_{2v}-C_{82}$ to its trianions resulted in a notable increase in reactivity towards the benzylization reaction. Three benzylated $Gd@C_{2v}-C_{82}$ isomers (**2a**, **2b**, and **2d**) are isolated and characterized. The structures are confirmed through X-ray single crystal diffraction, revealing that they are monoadducts with a benzyl group attached to the [5,6,6] junction of the C_{82} cage. In addition, each isomer exists in a mirror-symmetric form. The electrochemical properties of the benzylated $Gd@C_{2v}-C_{82}$ isomers show distinct characteristics compared to the pristine $Gd@C_{2v}-C_{82}$. Through density functional theory (DFT) calculations, the reactivity of the $Gd@C_{2v}-C_{82}$ trianion towards the benzyl group was unveiled.

2. Results and Discussion

Despite $Gd@C_{2v}-C_{82}$ having an unpaired electron, it does not exhibit reactivity towards benzyl bromide (PhCH₂Br) as shown in Scheme 1. As previously known, Gd@C₈₂ demonstrates its capability as an excellent electron acceptor, with the capacity to accept up to seven electrons [38,39]. Electrochemical reduction can be used to selectively synthesize fullerene anions by controlling the applied potential. To enhance the reactivity, $Gd@C_{2v}-C_{82}$ was subjected to electrochemical reduction, specifically to its monoanion, using controlled potential electrolysis (CPE). The resulting Gd@C_{2v}-C₈₂ monoanion was then subjected to the benzylation reaction. However, it was observed that the monoanion also shows no reactivity toward $PhCH_2Br$ (Scheme 1), indicating that the nucleophilicity of the Gd@ C_{2v} - C_{82} monoanion is not sufficiently strong to attack the carbon cation (C⁺) of PhCH₂Br. Therefore, additional electrons were added to the $Gd@C_{2v}$ -C₈₂ cage through the CPE process. According to the cyclic voltammogram of $Gd@C_{2v}-C_{82}$, the second reduction is a simultaneous two-electron transfer process [27,39]; therefore, it is rational to consider the anions obtained via CPE to be trianions. Once the electrogeneration of $[Gd@C_{2v}-C_{82}]^{3-}$ was completed, PhCH₂Br was added to the solution in one portion and stirred for 3h. High performance liquid chromatography (HPLC) observation confirms the occurrence of the reaction between $[Gd@C_{2v}-C_{82}]^{3-}$ and PhCH₂Br (Scheme 1). It is evident that $[Gd@C_{2v}-C_{82}]^{3-}$ shows enhanced reactivity toward PhCH₂Br.

As observed in Figure 1a, the HPLC results show the synthesis of multiple products through the reaction of $[Gd@C_{2v}-C_{82}]^{3-}$ with PhCH₂Br. To separate and purify the products from the crude mixture, a three-stage HPLC procedure was performed. Initially, the reaction mixtures in toluene were separated using a Buckyprep column to isolate the main fractions 1, 2, and 3 (Figure 1a). Subsequent chromatography employing a Buckyprep column (Figure 1b) and a 5PBB column (Figure 1c) revealed that fraction 2 comprises four compounds: **2a**, **2b**, **2c**, and **2d**. (Figure 1c). Notably, as we only succeeded in getting single crystal structures of **2a**, **2b**, and **2d**, the subsequent discussion in this study was only

focused on these three products. Electrosynthesis has been commonly recognized as an effective strategy for the highly selective synthesis of fullerene derivations. The production of multiple adducts is likely ascribed to the delocalization of charges caused by the low symmetry of the C₈₂ cage and the high reactivity of trianionic Gd@ C_{2v} - C_{82} .



Scheme 1. Benzylation reactions of Gd@ C_{2v} - C_{82} , [Gd@ C_{2v} - C_{82}]⁻, and [Gd@ C_{2v} - C_{82}]³⁻, and the corresponding HPLC profiles of the reaction crude. Conditions: Buckyprep (φ 4.6 × 250 mm), toluene, 1 mL/min. (colors indicate the areas of each fraction).



Figure 1. (a) HPLC profile of the reaction mixture (colors indicate the areas of each fraction). Conditions: Buckyprep (ϕ 4.6 × 250 mm), toluene, 1 mL/min. (b) Recycling HPLC profile of fraction 2. Conditions: Buckyprep (ϕ 20 × 250 mm), toluene, 7 mL/min. (c) HPLC profiles of fractions 2-1 and 2-2. Conditions: 5PBB (ϕ 4.6 × 250 mm), toluene, 1 mL/min.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectrometry gave preliminary speculation on the structure of the three products (Figure 2). The mass spectra of **2a**, **2b**, and **2d** reveal very similar molecular ion peaks, positioned around m/z = 1233. This observation indicates that they are isomers, each featuring a single benzyl group (CH₂C₆H₅) attached to the Gd@C_{2v}-C₈₂ cage, i.e., Gd@C_{2v}-C₈₂(CH₂C₆H₅) (theoretical m/z = 1232.979). The addition pattern is consistent with that of the reported open-shell EMFs derivatives [12,40–44]. This can be attributed to the paramagnetic behavior of Gd@C_{2v}-C₈₂, which leads to specific addition patterns of functional groups in its derivatives.



Figure 2. MALDI-TOF mass spectra of **2a** (**a**), **2b** (**b**), and **2d** (**c**) with TPB as the matrix. (**d**) UV-vis-NIR spectra of **2a**, **2b**, **2d**, and Gd@ C_{2v} - C_{82} in CS₂ solution.

The optical properties that can provide crucial insights into the electronic structures were studied through the analysis of the UV-vis-NIR absorption spectra. As shown in Figure 2, the UV-vis-NIR spectra of **2a**, **2b**, and **2d** show remarkably different behavior compared to that of the parent Gd@C_{2v}-C₈₂, which is attributed to the changes in the electronic structure of the cage caused by the addition of the benzyl groups [45]. The characteristic absorption of Gd@C_{2v}-C₈₂ at $\lambda = 636$ nm undergoes a blue shift upon the addition of the benzyl groups, which can be explained by the reduction of the π -conjugated region in the molecule [44]. The characteristic band of Gd@C₈₂ at 400 nm disappears in all benzyl adducts, which is ascribed to the quenching of unpaired electrons by the odd number of benzyl groups on the Gd@C₈₂ cage. A similar phenomenon was observed in the absorption of Gd@C₈₂ morpholine derivatives [44].

Single crystal X-ray diffraction measurement is widely accepted as the most reliable technique for analyzing the structure of isomers [46–49]. It provides solid evidence for the structure confirmation of **2a**, **2b**, and **2d**. We made efforts to obtain single crystals for all the products, unfortunately, only products **2a**, **2b**, and **2d** were successfully crystallized. Figure 3 displays the single crystal structures of the three isomers, namely, **2a**, **2b**, and **2d**.

Notably, 2a and 2b were co-crystallized with decapyrrylcorannulene (DPC) molecules [50]. The DPC molecules were found to form a V-shaped structure when combined with 2a and **2b**, with the angle between the DPC molecules being 64.9° and 64.8° , respectively. The arrangement of these two molecules is very similar to other reported structures [51–54]. In 2a·2DPC, the distances between the centroid of the C₈₂ cage and the central five-membered rings of DPC molecules are 7.361 Å and 7.394 Å, while they are 7.439 Å and 7.474 Å in **2b**·2DPC. From there, it can be deduced that the distance between the carbon cage and the DPC is approximately 2.8–3.2 Å, indicating the presence of π - π interactions between the carbon cage and DPC molecules. These π - π interactions play a significant role in stabilizing the co-crystallized structure of **2a** and **2b** with DPC molecules. All three crystals feature a monoclinic $P2_1/c$ space group. The carbon cages and embedded Gd atoms (in cyan color) display varying degrees of disorder. An interesting observation is that, irrespective of the location of the benzyl addition, the Gd atoms with major occupancy are consistently found underneath a hexagonal ring along the C_2 axis of the C_{2v} - C_{82} cage (marked in orange in Figure 3). And, the distances between Gd and the adjacent carbon atoms, ranging from 1.9 Å to 2.4 Å, indicate a strong interaction between the endohedral Gd and the outer C_{2v} - C_{82} cage.



Figure 3. Single crystal structures of $2a \cdot 2DPC$ (a), $2b \cdot 2DPC$ (b), and 2d (c) with thermal ellipsoids set at the 20% probability level. The solvent molecules are omitted and only one cage orientation is shown.

As depicted in Figure 3, the benzyl group was added in the form of a single bond at the [5,6,6]-ring junction of the C_{2v} - C_{82} cage. Despite the addition, the C_{2v} symmetry of the cage is preserved, indicating that the attachment of the benzyl group did not disrupt the overall symmetry of the molecule (Figure 4). Interestingly, all three crystal structures of 2a, 2b, and 2d contain mirror-symmetric enantiomers, suggesting that each compound exists in a pair of structures that are mirror images of each other. To gain a better understanding of the addition sites and the arrangement of the benzyl groups in each enantiomer, a Schlegel diagram of the C_{2v} - C_{82} cage was mapped. In this diagram, the addition sites of the benzyl groups in each enantiomer are marked (1–2 for 2a, 3–4 for 2b, and 5–6 for 2d) (Figure 4a), providing valuable insights into the spatial orientation and symmetry of the derivatives. It can be observed that the addition sites in structures that are mutually enantiomeric are mirror-symmetric. The denoted sites 1 and 2 refer to cage 1 and cage 2 of 2a, sites 3 and 4 refer to cage 1 and cage 2 of 2b, and sites 5 and 6 refer to cage 1 and cage 2 of 2d. Figure 4b displays the mirror-symmetric enantiomers for 2a, 2b, and 2d. For every isomer, there is an identical structure that is a mirror image of the original isomer. Owing to the existence of the C_2 axis, the addition sites labeled as 1' to 6' on the cage are equivalent to the corresponding sites of 1 to 6.



Figure 4. (a) Schlegel diagram showing the addition sites of **2a**, **2b**, and **2d**. (b) Structures of enantiomers of **2a**, **2b**, and **2d** with 20% thermal probability. Internal disordered sites of gadolinium atoms were also shown. Benzyl groups are labeled in pink. The co-crystallization and solvent molecules were omitted for clarity.

The crystal packing and molecular organization for each isomer were studied. As shown in Figure 5, the smallest asymmetric unit for the three products consists of four fullerene cages. Furthermore, **2a** and **2b** are arranged in a head-to-tail mode with DPC molecules along the *b*-axis. Additionally, the DPC molecules adopt an S-shape configuration along the *c*-axis. The distances between the two back-to-back DPC molecules are in the range of 3.4–3.8 Å, indicating the existence of π - π interactions. These interactions lead to favorable π -electron overlap and stabilize the crystal packing. The crystal structure of **2d** without DPC co-crystallization reveals the formation of a one-dimensional zigzag supramolecular chain along the *b*-axis. The detailed crystallographic data for these compounds can be found in the experimental section.



Figure 5. The packing structures of (a) **2a**·**2DPC**, (b) **2b**·**2DPC**, and (c) **2d**. The solvent molecules are omitted and only one cage orientation is shown.

The addition of functional groups on the fullerene cages can greatly alter the electrochemical properties of the compounds. Cyclic voltammetry (CV) measurements were conducted for each isomer and compared with the CV curves of the pristine $Gd@C_{2v}-C_{82}$ [27]. As reported in the literature, the pristine $Gd@C_{2v}$ -C₈₂ shows three pairs of reversible redox peaks and two irreversible redox processes in its CV curves, and the second and the fourth reduction are two-electron processes [27]. However, the addition of the benzyl group to form isomers 2a, 2b, and 2d has led to changes in the electrochemical characteristics of the compounds. Moreover, the addition position of the benzyl group was found to have effects on the electrochemical behavior [46,55]. As illustrated in Figure 6, the CV curves of 2a, 2b, and 2d exhibit more redox signals compared with the pristine $Gd@C_{2v}$ -C₈₂, suggesting the presence of distinct electron transfer processes, which is attributed to the addition of the benzyl group and its influence on the electronic structure of $Gd@C_{2v}$ -C₈₂. In the case of 2a, the CV curves display irreversible cathodic electrochemical behavior, with peak potential (E_{pc}) values observed at -0.97, -1.51, -1.66, -1.93, and -2.39 V vs. Fc/Fc⁺ (Table 1). On the other hand, 2a also shows one quasi-reversible oxidation peak with an E_{pa} value of +0.14 V vs. Fc/Fc⁺ and two irreversible oxidations with E_{pa} values of +0.74 and +1.03 V vs. Fc/Fc⁺. For compound 2b, there are three quasi-reversible reductions with E_{pc} values of -1.06, -1.89, and -2.11 V vs. Fc/Fc⁺, while the second reduction is found to be irreversible, with an E_{pc} value of -1.58 V vs. Fc/Fc⁺. The electrochemically anodic behavior of 2b exhibits irreversible characteristics. CV measurements for 2d show

two irreversible reductions with E_{pc} values of -0.86 and -1.52 V vs. Fc/Fc⁺ and two quasi-reversible reductions with E_{pc} values of -1.77 and -2.04 V vs. Fc/Fc⁺. Moreover, compound **2d** exhibits electrochemically irreversible anodic behavior, which is similar to the behavior observed for **2d**. The distinct electrochemical characteristics of **2a**, **2b**, and **2d** may be attributed to the specific addition position of the benzyl group and its influence on the electronic structure of the Gd@ C_{2v} -C₈₂ cage. In addition, compared to the redox behavior of Gd@ C_{2v} -C₈₂, the first reduction potentials of **2a**, **2b**, and **2d** show negative shifts, and the first oxidation potentials show positive shifts, which indicates a decrease in electron-donating/accepting properties after modification with the benzyl group. The enlarged electrochemical gaps in the derivatives **2a**, **2b**, and **2d** demonstrate the enhanced stability of the derivatives relative to the parent Gd@ C_{2v} -C₈₂. The redox potentials for Gd@ C_{2v} -C₈₂ and its benzylated products are summarized in Table 1.



Figure 6. Cyclic voltammograms of **2a**, **2b**, and **2d** recorded in a 0.05 M solution of TBAPF₆ in *o*-DCB at a scan rate of 100 mV s⁻¹. (The redox processes are labeled with a star and each process is indicated in different colors).

Table 1. Redox potentials (V vs. Fc/Fc^+) of Gd@ C_{2v} - C_{82} and **2a**, **2b**, and **2d**.

	$E^{2+/3+}$	E ^{+/2+}	E ^{0/+}	E ^{0/-}	E ^{-/2-}	$E^{2-/3-}$	$E^{3-/4-}$	$E^{4-/5-}$	Egap
Gd@C _{2v} - C ₈₂ a		+1.08 ^b	+0.09 ^c	-0.39 ^c	-1.38 ^{c,d}		-2.22 ^{b,d}		0.48
2a 2b 2d	+1.03 ^b +0.94 ^b	+0.74 ^b +0.73 ^b +0.94 ^b	+0.14 ^c +0.19 ^b +0.26 ^b	$-0.97 \ ^{b}$ $-1.06 \ ^{c}$ $-0.86 \ ^{b}$	$-1.51 \ ^{b}$ $-1.58 \ ^{b}$ $-1.52 \ ^{b}$	$-1.66 \ ^{b}$ $-1.89 \ ^{c}$ $-1.77 \ ^{c}$	$-1.93 \ ^{b}$ $-2.11 \ ^{c}$ $-2.04 \ ^{c}$	-2.39 ^b	1.11 1.25 1.12

^{*a*} From reference [21]; ^{*b*} peak potentials; ^{*c*} quasi-reversible process; and ^{*d*} two-electron process.

Density functional theory calculations at the M06-2X/6-31G*~SDD level were then carried out to disclose the underlying reactivity of $Gd@C_{2v}-C_{82}$ and its anions. Figure 7 illustrates the optimized structures of **2a**, **2b**, and **2d**, which are consistent with the corresponding single crystal structures. For pristine $Gd@C_{2v}-C_{82}$, it is well known that it has an unpaired electron distributed on the outer cage due to the $3e^-$ transfer from the internal metal to the cage. However, our calculations with different spin multiplicities reveal that all three monoadducts have the octet ground state completely stemming from the Gd-4f⁷ electron configuration of their internal Gd³⁺ cation (Table 2). Clearly, the unpaired electron (spin) on the outer cage of Gd@C_{2v}-C₈₂ has been effectively quenched as a result of the formation of a single bond with the benzyl group, which thus leads to the excellent stability of the adducts.



Figure 7. Optimized structures of (a) 2a, (b) 2b, and (c) 2d.

Table 2. Relative energies (kcal/mol) of **2a**, **2b**, and **2d** as well as $[Gd@C_{2v}-C_{82}]^-$ and $[Gd@C_{2v}-C_{82}]^{3-}$ with different spin multiplicities (*M*).

М	6	8	10
2a	21.0	0.0	20.9
2b	17.0	6.8	14.9
2d	22.1	1.8	22.2
[Gd@C _{2v} -C ₈₂] ⁻	58.3	0.0	17.8
$[Gd@C_{2v}-C_{82}]^{3-}$	0.0	18.3	26.7

In addition, the reactivity of different charged forms of $Gd@C_{2v}-C_{82}$ was elaborated through DFT simulations. Figure 8 shows the calculated energy levels of frontier molecular orbitals of $Gd@C_{2v}-C_{82}$ with various charge states (0, -1, -3). Consistent with our experimental findings, only $[Gd@C_{2v}-C_{82}]^{3-}$ demonstrates HOMO (highest occupied molecular orbital) energy levels that are comparable to the LUMO (lowest unoccupied molecular orbital) of PhCH₂ radical, thus enhancing the orbital interactions and charge transfer during the addition reaction. Through the process of electrochemical reduction, the orbital energy levels of $Gd@C_{2v}-C_{82}$ are greatly elevated, resulting in a significant improvement in its reactivity.



Figure 8. Frontier molecular orbital energy levels of PhCH₂ radical and Gd@ C_{2v} - C_{82} in different charge states (occupied: black; unoccupied: cyan).

3. Materials and Methods

Gd@ C_{2v} -C₈₂ was purchased from Xiamen Funano New Material Technology Company LTD, Xiamen, China. PhCH₂Br, anhydrous *o*-DCB, 1,1,4,4-Tetraphenyl-1,3-butadiene (TPB), toluene, CDCl₃, and CS₂ were purchased from Aladdin and used as received. Tetrabutylammonium perchlorate (TBAP) and Tetra-n-butylammonium hexauorophosphate (TBAPF₆) were recrystallized from absolute ethanol and dried under vacuum before use. The purity of the products was verified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Tokyo, Japan) equipped with Buckyprep and 5PBB columns, with toluene used as the eluent. UV-vis-NIR spectra were recorded using a SHIMADZU UV-3600 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). MALDI-TOF MS measurements were conducted using a Bruker autoex speed mass spectrometer. CV studies were conducted in a solution of *o*-DCB containing 0.05 M TBAPF₆ in a one-compartment cell connected to a CHI 760E workstation, Shanghai, China. A 2 mm diameter glassy carbon disk, a Pt wire, and a Ag wire were used as the working, counter, and pseudoreference electrodes, respectively. Ferrocene (Fc) was introduced into the solution at the end of each experiment as an internal standard. All reactions were carried out inside a glove box under Ar protection.

3.1. Synthesis of 2a, 2b, and 2d

A 2 mg (1.75 mmol) sample of Gd@ C_{2v} - C_{82} was electrochemically reduced at -1.36 V versus a silver wire reference electrode in 8 mL of *o*-DCB containing 0.1 M TBAP as the supporting electrolyte under an argon atmosphere. The potentiostat was turned off once the electrogeneration of $[Gd@C_{2v}$ - $C_{82}]^{3-}$ was completed. Subsequently, 100 equivalents of PhCH₂Br (21.5 µL) were added into the solution in one portion under stirring. The reaction was allowed to proceed for 2 h with stirring, and, finally, it was electrochemically oxidized at a potential of 0 V. The solvent was evaporated under a vacuum, and the crude was washed with plenty of methanol to remove the unreacted PhCH₂Br and the supporting electrolyte. The slurry was separated by filtration. The residue was dried at 70 °C under a

vacuum and dissolved in toluene. The soluble fraction was then purified by HPLC using Buckyprep and 5PBB columns.

3.2. Single Crystal X-ray Crystallography

The single crystals of **2a** and **2b** were obtained by co-crystallization with DPC molecules. In a 5.0 mL centrifuge tube, 0.5 mg of **2a** was dissolved in 0.5 mL of carbon disulfide. Then, a toluene solution containing DPC was added to the tube, with a molar ratio of DPC to fullerene in the mixed solution being 2:1. After around three weeks, black sheet-like crystals were formed. A crystal of 0.4 mm × 0.25 mm × 0.03 mm dimension was mounted in the 100 K nitrogen cold stream on an XtaLAB PRO MM007HF diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement, and data reduction. The crystal structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXLTL software package. All the non-hydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically.

Crystal data of **2a**·**2DPC**: C₂₁₆H₉₅Gd_{0.88}N₂₀, $M_w = 3108.89$ amu, monoclinic, $P_{1/C}$, a = 14.6998 (1) Å, b = 32.4984 (3) Å, c = 32.1664 (3) Å, $\alpha = 90^{\circ}$, $\beta = 102.071$ (1)°, $\gamma = 90^{\circ}$, V = 15,026.8 (2) Å³, T = 100 K, Z = 4, R indices (all data) $R_1 = 0.0896$ (23,666), $wR_2 = 0.2647$ (29,671), GOF = 1.054.

Black sheet-like crystals of **2b** were obtained through the same procedures as for **2a**. Crystallographic characterization of a piece of co-crystal ($0.12 \text{ mm} \times 0.1 \text{ mm} \times 0.08 \text{ mm}$) was performed at 100 K by using synchrotron radiation (0.65250 Å) with a MarCCD detector at the beamline BL17B station of Shanghai Synchrotron Radiation Facility.

Crystal data of **2b**·2**DPC**: C₂₁₆H₉₅Gd_{0.87}N₂₀, $M_w = 3106.92$ amu, monoclinic, $P_{21/C}$, a = 14.6857 (4) Å, b = 32.4812 (11) Å, c = 32.1342 (9) Å, $\alpha = 90^\circ$, $\beta = 101.791$ (1)°, $\gamma = 90^\circ$, V = 15,004.9 (8) Å³, T = 100 K, Z = 4, R indices (all data) $R_1 = 0.1054$ (20,309), $wR_2 = 0.3207$ (29,611), GOF = 1.052.

The crystal of **2d** was grown through solvent diffusion in which a near-saturated carbon disulfide solution was injected into the glass tube followed by slow injections of hexane, and the fullerene solution was layered at a height of about 5 cm. At this point, a clear delamination between hexane and carbon disulfide solution appears, creating a diffusion interface that provides favorable conditions for crystal growth. The tube is closed with a cap and left at a low temperature for several weeks until the solvent diffusion is complete and several crystals are attached to the tube walls. The crystal of **2d** (0.1 mm × 0.08 mm × 0.06 mm) was tested using the same instruments and methods as **2b**.

Crystal data of **2d**: $C_{87}H_7Gd_{0.91}$, $M_w = 1233.20$ amu, monoclinic, $P2_{1/C}$, a = 10.891(2) Å, b = 18.946 (4) Å, c = 22.442 (5) Å, $\alpha = 90^\circ$, $\beta = 96.45$ (3)°, $\gamma = 90^\circ$, V = 4601.4 (16) Å³, T = 100 K, Z = 4, R indices (all data) $R_1 = 0.1409$ (6211), $wR_2 = 0.3370$ (8277), GOF = 1.069.

The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre with CCDC numbers 2281483, 2283118, and 2283119 via www.ccdc.cam.ac.uk/data_request/cif (accessed on 1 July 2023).

3.3. Computational Details

The calculations were carried out at the DFT level with the M06-2X [56] function, the 6-31G* all-electron basis set of C and H atoms, the SDD basis set, and the corresponding effective core potentials of Gd [57–59]. All the above DFT calculations were performed using the Gaussian 09 software package [60]. The results were visualized with CYLview [61] and VMD [62] software.

4. Conclusions

In summary, this study presents the first successful synthesis of open-shell $Gd@C_{2v}-C_{82}$ benzyl monoadducts using the electrochemical synthesis method. Three $Gd@C_{2v}-C_{82}$ (PhCH₂) isomers (**2a**, **2b**, and **2d**) were synthesized, isolated, and characterized. The

crystal structures revealed that the benzyl group is attached to the [5,6,6] junction of the cage through a single bond and each isomer contains a mirror-symmetric enantiomer. The addition of the benzyl group and its specific position have notable effects on the electrochemical behavior. DFT calculations reveal that $[Gd@C_{2v}-C_{82}]^{3-}$ has a HOMO energy level that aligns effectively with the LUMO energy levels of the PhCH₂ radical, rationalizing the higher reactivity towards benzyl. The electrochemical method shows great potential in regulating the chemical reactivity of fullerenes, opening up possibilities for creating a wide range of new fullerene products.

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