Unexpected formation of 1,2- and 1,4-bismethoxyl Sc$_3$N@I$_h$-C$_{80}$ derivatives via regioselective anion addition: an unambiguous structural identification and mechanism study†

Yajing Hu,$^a$ Yang-Rong Yao,$^b$ Xuechen Liu,$^a$ Ao Yu,$^a$ Xiaoming Xie,$^b$ Laura Abella,$^d$$^e$ Antonio Rodríguez-Fortea,$^d$$^e$ Josep M. Poblet,$^d$$^e$ Takeshi Akasaka,$^a$ Ping Peng,$^a$ Qianyan Zhang,$^{ab}$ Su-Yuan Xie,$^b$ Fang-Fang Li$^{ab}$$^a$ and Xing Lu$^{ab}$$^a$

An attempt to achieve heterocyclic cycloadducts of Sc$_3$N@I$_h$-C$_{80}$ via reaction with Ph$_2$C=O, PhC=CH$_2$ or PhCN=N in the presence of tetrabutylammonium hydroxide (TBAAOH) stored in CH$_3$OH led to the formation of the unexpected bismethoxyl adducts of Sc$_3$N@I$_h$-C$_{80}$ (1 and 2). Further studies reveal that TBAAOH in CH$_3$OH can boost the CH$_3$O$^-$ addition efficiently, regardless of the presence of other reagents. Single-crystal X-ray diffraction results firmly assign the molecular structures of 1 and 2 as respective 1,4- and 1,2-bismethoxyl adducts, and reveal unusual relationships between the internal Sc$_3$N cluster and the addition modes, in addition to the unusual packing mode in view of the orientation of the methoxyl groups. Electrochemical results demonstrate smaller electrochemical gaps for 1 and 2, relative to that of Sc$_3$N@I$_h$-C$_{80}$, confirming their better electroactive properties. Finally, a plausible reaction mechanism involving anion addition and a radical reaction was proposed, presenting new insights into the highly selective reactions between the methoxyl anion and metallofullerenes. 1 and 2 represent the first examples of methoxyl derivatives of metallofullerenes. This work not only presents a novel and facile strategy for the controllable synthesis of alkoxyalted metallofullerene derivatives, but also provides new non-cycloadducts for the potential applications of EMFs.

Introduction

Endohedral metallofullerenes (EMFs) are a collection of hybrid molecules with metallic species trapped inside fullerene cages which show novel structures, fascinating properties and promising applications in energy storage/convertion, materials science and biomedicine.$^{1-4}$ Exohedral functionalization of EMFs has shown its effectiveness to broaden their application by generation of a variety of useful derivatives. During the last few decades, many synthetic methods have been applied to modify EMFs, among which cycloadditions, such as the Bingel–Hirsch reaction,$^{5,6}$ [2+2] benzene addition,$^7$ the 1,3-dipolar diene reaction,$^8-12$ the Diels–Alder reaction,$^13$ carbene addition$^{14}$ and so on,$^{15-18}$ have been widely utilized. The results show that the chemical properties of EMFs are much different from those of empty fullerenes, resulting in the fact that some chemical reactions which are effective for C$_{60}$ do not work on EMFs.

In contrast, non-cycloadditions of EMFs are relatively rare, and the addition is generally uncontrollable and has low selectivity. Radical reactions, such as trifluoromethylation and benzylation, represent the most effective strategies that afforded singly-bonded EMF-derivatives with identified structures. However, the high reactivity of radical species normally produced a mixture of numerous isomers, bringing challenges in selectivity and the subsequent isolation of pure adducts. For instance, trifluoromethylation of Sc$_3$N@I$_h$-C$_{80}$, Y$_2$C$_2$@C$_{60}$($^6$)-C$_{82}$ and M@C$_{60}$ (M = Gd, La) afforded plenty of isomers for the respective EMFs, i.e. Sc$_3$N@I$_h$-C$_{80}$([CF$_3$]$^3$)-Cr$^x$$^{17-19}$ Y$_2$C$_2$@C$_{60}$([CF$_3$])$_{16}$ $^{20}$ and M@C$_{60}$([CF$_3$])$_{3}$-I $^{21}$ (M = Gd, La), respectively, in spite that benzyl radical additions to Sc$_3$N@I$_h$-C$_{80}$ $^{22}$ and La$_2$@I$_h$-C$_{80}$ $^{23}$ showed much better selectivity. Unexpectedly, the Bingel–Hirsch reactions of the paramagnetic M@C$_{82}$
(M = La, Y and so on) also afforded singly-bonded adducts, and Lewis acid–base pairs of Sc₃N@I₈-C₈₀/O₂ and N-heterocyclic carbene commonly bear the singly-bonded nature. Additionally, the η¹-complex of Y@C₂₁(9)-C₆₂Re(CO)₅ stands as an example with a metal–carbon single bond. However, each of the above strategies requires a specific category of EMFs. For example, the Bingel–Hirsch reactions of diamagnetic EMFs always produce cycloadducts and Lewis acid–base pairs of mono-EMFs have never been obtained. Accordingly, it is currently urgent and meaningful to search for new synthetic methods to achieve non-cycloadducts of EMFs in a controllable manner so as to obtain useful compounds with novel structures and fascinating properties.

Herein, we report the unexpected addition of the methoxyl anion to Sc₃N@I₈-C₈₀ via reaction with the methanol solution of tetrabutylammonium hydroxide (TBAOH) which produced the methoxy anion ([CH₃O]⁻) in situ. Only two derivatives are obtained (1 and 2), whose structures have been established by single-crystal X-ray diffraction as 1,4- and 1,2-bismethoxyl adducts, respectively. Further studies reveal an anion-radical relay mechanism for the reaction process. To the best of our knowledge, this is the first report on alkoxylated metallofullerenes and the current method differs from those available for the alkylation of fullerenes, which provide new insights into the controlled synthesis and formation mechanism of alkoxyl metallofullerene derivatives.

Results and discussion

In fact, our first attempt was to achieve heterocyclic cycloadducts of Sc₃N@I₈-C₈₀ through the reaction with Ph₂C=O, PhC=CP or PhC=N in the presence of TBAOH, following the procedures for C₆₀ previously reported by Gao and coworkers. 3 mg Sc₃N@I₈-C₈₀ was dissolved in 10 ml anhydrous o-DCB, and then 10 equivalent of TBAOH (stored in CH₃OH) was added into the solution, the color of which rapidly changed from light brown to dark green (Fig. S1, ESI†). The in situ UV-Vis-NIR spectra of the reaction mixture in Fig. S1† showed that the absorption of Sc₃N@I₈-C₈₀ is red-shifted from 371 to 391 nm, and a new peak appears at about 568 nm, indicating the formation of an anionic intermediate. 100 equivalent of Ph₂C= O, PhC=CP or PhC=N was then added into the green solution which was quenched by adding 50 equivalent of I₂ after stirring for 2 h. The obtained solid products from all three reactions were dissolved in toluene and analyzed by HPLC (Fig. 1a-c). To our surprise, the reactions do not afford any cycloadducts which have been found for C₆₀ (according to mass spectrum data). As a matter of fact, we eventually realized that Ph₂C=O, PhC=CP or PhC=N did not participate in the reaction as we expected. Therefore, the reaction of Sc₃N@I₈-C₈₀ and the CH₃OH solution of TBAOH without the addition of Ph₂C=O, PhC=CP or PhC=N was conducted according to the same procedure as described above (Scheme 1, Fig. 1d). As shown in Fig. 1, the HPLC profiles of the reaction mixtures, either with or without Ph₂C=O/PhC=CP/PhC=N, showed that the adduct peaks emerged at around 32 min after stirring for 2 hours. Further separation gave the pure isomers of 1 and 2 (Fig. S2, ESI†), which have singly-bonded structures (vide infra).

1 and 2 are fully characterized by MALDI-TOF MS, NMR, Vis-NIR spectroscopy and single-crystal X-ray diffraction. Fig. 2 displays the mass spectra of 1 and 2 where the peaks at around m/z 1170.6 correspond to the dimethoxylated adducts Sc₃N@I₈-C₈₀(OCH₃)₂. The peaks at around 1139.6 and 1108.6 are ascribed to the fragments of Sc₃N@I₈-C₈₀(OCH₃) and Sc₃N@I₈-C₈₀ due to the loss of one or two OCH₃ groups, respectively, confirming the successful attachment of two methoxyl groups on to Sc₃N@I₈-C₈₀.

1H NMR spectra (Fig. 3a) provide additional structural features of 1 and 2. Only one single signal for the two OCH₃ groups in either 1 or 2 is observed, in detail, 3.76 ppm in 1 and 3.84 ppm in 2, indicative of the highly symmetric placement of the two equivalent OCH₃ groups. Since there are more than 40 possible isomers for Sc₃N@I₈-C₈₀ bisadducts, the formation of merely two derivatives reveals high regioselectivity. The 13C NMR spectrum of product 1 is shown in Fig. 3b. 38 (including one doublet signal) resonances for the 78 sp² I₈-C₈₀ cage carbons are detected from 120.26 to 170.56 ppm, confirming...
a symmetrical addition pattern of 1. Resonance for the two sp³
Ih-C₈₀ cage-carbons bonded to the OCH₃ groups appears at
53.76 ppm, while the peak for the two sp³ OCH₃ carbons
appears at 29.15 ppm. Although, the ¹³C NMR data collection of
2 was not successful due to its relatively low yield, the ¹H NMR
spectra of the two products could alternatively elucidate the
symmetry of the products, and its X-ray structure provided the
absolute structure.

Vis-NIR spectroscopy is a diagnostic tool to estimate the
addition position on fullerenes, especially for the highly
symmetric C₆₀ and Sc₃N@C₈₀ cages. Fig. 4 shows the absorption
spectra of 1 and 2. The characteristic peak at 968 nm of 1 is very
similar to those of the previously reported 1,4-Sc₃N@C₈₀(CH₂-
Ph)₂ (898 nm)²² and 1,4-Sc₃N@C₈₀(CF₃)₂ (920 nm),¹⁷ suggesting
a 1,4-addition pattern. However the absorption curve of 2 is
analogous to those of the [5,6]-adducts of Sc₃N@C₈₀,⁷,⁸,²⁹ indicative of a 1,2-[5,6]-fashion.

Finally, the molecular structures of 1 and 2 are unambigu-
ously established by single crystal X-ray diffraction. The co-
ocrystals of [1]·2DPC and [2]·4DPC·2toluene were obtained by
slow evaporation of the toluene/CS₂ solution of the corre-
sponding derivatives and decapoyrrlycorannulene (DPC).²⁰ Both
crystals fall into the Pı space group with variations in the
asymmetric unit. 1 shows disorder of both the C₈₀ cage and the
Sc₃N cluster. Two orientations of the C₈₀ cage with equal
occupancy and four orientations of the Sc₃N cluster with occup-
cancies of 0.40, 0.35, 0.15 and 0.10 are observed. Interestingly,
the C₈₀ cage of 2 is highly ordered and only two positions of the
Sc₃N cluster with occupancies of 0.82 and 0.18, respectively, are
presented.

Fig. 5 shows the molecular structures of 1 and 2 with only the
major components together with the cocrystallized DPC mole-
cules. The pairs of DPC and 1 or 2 are assembled into a similar
V-shaped configuration with an angle of 61.28° for [1]·2DPC
(Fig. 5a) and 61.86° for [2]·2DPC (Fig. 5b). The distance between
the centroid of the C₈₀ cage and the central five-membered ring
of DPC is 7.313 and 7.308 Å for 1 and 7.382 and 7.313 Å for 2.
The cage-plane distance in 1 and 2 is ca. 3.3–3.6 Å, indicating π-
π interactions between the fullerene cages and DPC.

It is rather evident that two OCH₃ groups are located at the
para-position of a six-membered ring, i.e., 1,4-bisaddition on
[566]-carbons in 1, while in 2 are on a [5,6]-ring junction,
namely, 1,2-bisaddition. It is noteworthy that the addition

---

Fig. 2 MALDI-TOF mass spectra of 1 and 2.

Fig. 3 (a) ¹H NMR spectra of 1 and 2 and (b) ¹³C NMR spectrum of 1 recorded in CS₂ with DMSO-δ₆ as the external lock solvent.

Fig. 4 Vis-NIR spectra of Sc₃N@I₃h-C₈₀: 1 and 2 in CS₂.

© 2021 The Author(s). Published by the Royal Society of Chemistry

Chem. Sci., 2021, 12, 8123–8130 | 8125
patterns show somehow influence on the orientation of the inner cluster. The planar Sc₃N cluster in 1 is orthogonal with the plane crossing the sites of addition, namely, C1–O1–O2–C2, but the metal cluster in 2 is nearly parallel to the plane of C1–O1–O2–C2. Thus, it is proposed that exohedral modification, even merely the addition pattern of bisaddition, is practical to control the cluster orientation.

Notably, the conformations of the two OCH₃ groups in 1 and 2 also differ significantly. The two OCH₃ groups in 1 are unexpectedly arranged towards the same direction, which is unusual and different from the situations observed in the previously reported 1,4-Sc₃N@C₆₀(CH₂Ph)₂ and 1,4-Sc₃N@C₆₀(CF₃)₂ where the two addition groups are aligned in the opposite position to release steric hindrance.17,22 We speculate that only the intermolecular steric effect between DPC and 1, instead of any electronic influence, is responsible for the abnormal alignment of the two OCH₃ groups since there are no C–H···π interactions between OCH₃ and DPC.

The packing mode of [1]-2DPC (Fig. 6a) reveals that one of the OCH₃ groups (labeled as A) points to three DPC molecules with long intermolecular distances (red circle). Accordingly, the other OCH₃ group (labeled as B) is not allowed to point to the opposite position relative to group A, because it will cause large steric hindrance with the other two adjacent DPC molecules. Besides, the addition pattern of the two OCH₃ groups in 2 is also abnormal since they show a back-and-forth arrangement to decrease both the intramolecular and intermolecular repulsive forces. One OCH₃ group is trapped into the cavity of two DPC molecules (red circle in Fig. 6b) so that the other OCH₃ group can only choose the back orientation, facing three DPC molecules without obvious C–H···π interactions. It is thus concluded that the abnormal configurations of the two OCH₃ groups in both 1 and 2 are possibly caused by the intermolecular steric effects of the cocrystallized DPC molecules, which is proved by our theoretical calculations. The optimized structures of 1 and 2 without DPC show that the two OCH₃ are arranged oppositely (Fig. S4, ESI†). In addition, both 1 and 2 are aligned with DPC molecules to form a one-dimensional zigzag supramolecular chain along the c and b axis, respectively. The fullerenes are arranged in a head-to-tail mode in the packing structures of 1 (along the b axis) and 2 (along the c axis), respectively (Fig. 6).

The electrochemical properties of 1 and 2 are studied by cyclic voltammetry (CV) and the results are listed in Fig. 7 and Table 1. The 1,4-adduct 1 displays two irreversible oxidations at +0.40 and +0.59 V and three reversible reductions at /C₀ 1.17, /C₀ 1.33 and /C₀ 1.74 V, respectively, a behavior slightly different from that of the 1,4-Sc₃N@I₈-C₆₀(CF₃)₂ which displays only one reversible anodic process.17 Similarly, the 1,2-bisadduct 2 also

---

**Fig. 5** Single crystal X-ray structures of co-crystals [1]-2DPC (a) and [2]-2DPC (b) with thermal ellipsoids at the 10% probability level. Only the major cage and the major Sc₃N site are shown. The solvent molecules are omitted for clarity.

**Fig. 6** Packing structures of [1]-2DPC (a) and [2]-2DPC (b). Only one cage orientation and the major Sc₃N cluster are shown and the solvent molecules are omitted for clarity.

**Fig. 7** Cyclic voltammograms of Sc₃N@I₈-C₆₀. 1 and 2 recorded in a 0.05 M solution of TBAPF₆ in o-DCB at a scan rate of 100 mV s⁻¹.
exhibits two irreversible oxidations at +0.43 and +0.98 V and three reversible reductions at −1.03, −1.40 and −1.72 V, respectively, which is similar to those of the previous reported Sc$_3$N@I$_3$C$_{80}$ [5,6]-monoadducts.\textsuperscript{7,31,32} Compared with the corresponding redox potentials of pristine Sc$_3$N@I$_3$C$_{80}$ (Table 1), the first reduction potentials of 1 and 2 are less negative and their first oxidation potentials are less positive, resulting in smaller electrochemical gaps of the derivatives (1.57 V for 1 and 1.46 V for 2) than that of Sc$_3$N@I$_3$C$_{80}$ (1.88 V) and accordingly higher reactivities, which are beneficial to their future application in photovoltaics and electronics.

Currently, conversion of halofullerenes to alkoxy fullerenes by substituting Cl/Br groups is the most common approach to obtain alkoxy fullerenes,\textsuperscript{13-39} which is a complex and multi-step process, requiring the synthesis of halofullerenes first. However, neither halo-EMFs nor alkoxyl-EMFs have been reported due to the unrecognized chemical properties of EMFs. Accordingly, our finding presents a novel solution to the controllable synthesis of alkoxyated fullerene derivatives. We then try to understand the reaction mechanism of this unexpected bis-methoxylation process.

In fact, our initial purpose was to synthesize heterocyclic cycloadducts of Sc$_3$N@I$_3$C$_{80}$ following the method reported by Gao and co-workers where C$_{60}$, tetrabutylammonium hydroxide (TBAOH) and benzonitrile (PhCN) were involved.\textsuperscript{28} In the case of C$_{60}$, OH$^-$ from TBAOH acts as an oxygen nucleophile to form a dianionic intermediate C$_{60}$O$^-$ which then attacks the C≡N triple bond of PhCN to produce an ON$_2$-heterocyclic adduct. However, the same process does not occur on Sc$_3$N@I$_3$C$_{80}$ even when the more reactive Ph$_3$C≡O, PhC≡CPh or PhCN were used, and no any cycloadducts have been detected in the reaction mixture, indicating that the reaction mode was changed by the Sc$_3$N cluster.

Based on the experimental facts, we propose an anion-radical relay mechanism for the formation of 1 and 2 (Scheme 2). First, TBAOH, as a strong organic base, deprotonates CH$_3$OH to generate CH$_3$O$^-$ in the less polar solvent o-DCB. Due to the better miscibility of CH$_3$OH with o-DCB than TBAOH, CH$_3$O$^-$ prevails in the addition to Sc$_3$N@C$_{80}$ over OH$^-$ (from TBAOH) in the o-DCB solution. Then, the monoanion [Sc$_3$N@C$_{60}$O(OCH$_3$)$_2$]$^-$ is oxidized to the [Sc$_3$N@C$_{60}$O(OCH$_3$)$_2$]$^+$ radical by I$_2$ which accepts another CH$_3$O$^-$ to form the dimethoxyfullerene anion [Sc$_3$N@C$_{60}$O(OCH$_3$)$_3$]$^-$. Final oxidation by I$_2$ gives the final products of Sc$_3$N@C$_{60}$O(OCH$_3$)$_3$ with either 1,2- or 1,4-addition patterns. This anion radical relay process ensures the high selectivity and controllability of the reaction. The possibility of forming dianionic methoxyfullerene intermediates before I$_2$-oxidation could be reasonably excluded by considering the high charge density on the cage and thus the low stability in solution.

Most electrochemical reactions involving fullerenes or EMFs anions follow the “electron transfer-SN2 reaction” mechanism.\textsuperscript{15,16,40} But there is an exception that the electrochemical reaction of a C$_{60}$ derivative reported by Wang’s group follows a “stepwise one-electron reduction and protonation” mechanism, in which the monoanionic intermediate was protonated to generate a free radical on the adjacent carbon.\textsuperscript{41} The anion radical relay mechanism of methoxylation of Sc$_3$N@C$_{80}$ follows the electron transfer process proposed in most electrochemical reactions, but is followed by a process in which the anion is directly oxidized to a free radical.

It is known that the hydroxylation reactions of C$_{60}$ and EMFs were conducted by adding strong base NaOH containing TBAOH as a catalyst to the fullerene solution. The OH$^-$ as a nucleophile was added on the fullerene cage and a negative charge was transferred to the carbon cage. Then, the negative charge was neutralized by H$^+$ addition.\textsuperscript{42-43} Moreover, the reactions proceeded in an uncontrolled manner and generated multi-hydroxy derivatives,\textsuperscript{44,45} which makes it difficult to perform unambiguous structural identification. However, in our methoxylation reaction of Sc$_3$N@C$_{80}$, TBAOH (1.0 M in CH$_3$OH) acted as a deprotonating agent of CH$_3$OH rather than a nucleophile to participate in the reaction. Therefore, no hydroxyl derivatives were formed, and instead methoxyl derivatives were formed. More importantly, the methoxylation reaction was carried out in a controlled manner. The unique stepwise addition pattern ensured high regioselectivity of the reaction, thereby promoting the separation, purification and structure determination of the products.

### Conclusions

In summary, we discovered for the first time that the methoxyl anion (CH$_3$O$^-$) could react with Sc$_3$N@I$_3$C$_{80}$ in a highly regioselective manner to produce merely two isomers (1,4-adduct for 1 and 1,2-adduct for 2) out of more than 40 possibilities, representing the first examples of bismethoxyl derivatives of metallofullerenes. Their molecular structures and electrochemical properties are systematically investigated by a collection of experimental techniques. Based on the experimental evidence, an anion-radical relay mechanism for the formation of 1 and 2 has been proposed which is highly dependent on the type of solvents used, revealing an unprecedented reaction process for metallofullerenes. Significantly, we provide a facile synthetic

### Table 1  Redox potentials of Sc$_3$N@I$_3$C$_{80}$ and compounds 1 and 2 versus Fc/Fc$^+$

|                 | $E^{1/2}$ [V] | $E^{0}$ [V] | $E^{0/1}$ [V] | $E^{1/2}$ [V] | $E^{0/1}$ [V] | $E_{gap}$ [V] |
|-----------------|---------------|-------------|---------------|---------------|---------------|--------------|
| Sc$_3$N@I$_3$C$_{80}$ | +0.62$^a$     | −1.26$^b$  | −1.62$^b$    | −1.91$^b$    | 1.88          |
| 1               | +0.59$^a$     | +0.40$^b$   | −1.17$^b$    | −1.33$^b$    | −1.74$^b$    | 1.57         |
| 2               | +0.98$^a$     | +0.43$^b$   | −1.03$^b$    | −1.40$^b$    | −1.72$^b$    | 1.46         |

$^a$ Peak potentials. $^b$ Reversible process.
strategy for alkoxylation of metallofullerenes in a highly regioselective manner under mild conditions.

**Experimental**

**Materials and methods**

Sc$_2$N@I$_2$-C$_{60}$ was synthesized by the direct current arc discharge method and isolated by high performance liquid chromatography (HPLC). Tetraethylammonium hydrosyl (TBAOH) (1.0 M in CH$_3$OH), anhydrous o-DCB, Ph$_3$C=O, PhC≡CPh, anhydrous PhC≡N, I$_2$, toluene, DMSO-$d_6$ and CS$_2$ were purchased from Sigma-Aldrich and were used as received. Tetra-n-butyllammonium-hexafluorophosphate (TBAPF$_6$) was recrystallized from absolute ethanol and dried in a vacuum before use. The purity of the products 1 and 2 was verified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Japan) equipped with Buckyprep and SPBB columns with toluene as the eluent. Vis-NIR spectra were recorded using a Bruker Ascend™ 400 MHz NMR spectrometer. The $^{13}$C NMR spectrum was recorded using a Bruker Ascend™ 600 MHz NMR spectrometer. The $^{13}$C NMR spectrum was recorded using a Bruker Ascend™ 400 MHz NMR spectrometer. CV studies were conducted in a one-compartment cell connected to a CHI 760E workstation in a solution of o-DCB containing 0.05 M TBAPF$_6$. A 2 mm diameter glassy carbon disk was used as the working electrode, and a Pt wire and a Ag wire as the counter and pseudo-reference electrodes, respectively. Ferrocene (Fc) was added to the solution at the end of each experiment as an internal standard. All reactions were carried out in a glove box with Ar protection.

**Synthetic procedures of 1 and 2**

3 mg Sc$_2$N@I$_2$-C$_{60}$ was dissolved in 10 ml anhydrous o-DCB, and then 10 equivalent of TBAOH (stored in CH$_3$OH) was added into the solution, which was quenched by the addition of 50 equivalent of I$_2$ after stirring for 2 h. The obtained solid products from the reaction were dissolved in toluene and analyzed by HPLC (Fig. 1d). Products 1 and 2 were isolated and purified by two-step HPLC.

**Compound 1** (yield: 29.7%): MALDI-TOF MS (negative ionization mode): $m/z$ 1170.634; Vis-NIR 968 nm; $^1$H NMR (600 MHz, CS$_2$/DMSO, 25 °C, TMS): $\delta$ = 3.76 ppm (s, 6H, $-$OCH$_3$). $^{13}$C NMR (400 MHz, CS$_2$/DMSO, 25 °C, TMS): $\delta$ = 170.56 (2C), 163.87 (2C), 156.13 (2C), 151.09 (2C), 150.25 (2C), 149.37 (2C), 148.79 (2C), 146.27 (2C), 146.05 (2C), 145.66 (2C), 145.45 (2C), 145.24 (2C), 144.90 (2C), 143.89 (2C), 143.63 (2C), 143.44 (2C), 140.82 (2C), 140.42 (2C), 140.27 (2C), 139.40 (2C), 139.33 (2C), 138.98 (2C), 138.93 (2C), 138.47 (2C), 137.13 (2C), 138.65 (2C), 134.67 (2C), 134.99 (2C), 134.47 (2C), 134.33 (2C), 134.25 (2C), 132.72 (2C), 132.45 (4C), 131.45 (2C), 130.32 (2C), 129.12 (2C), 126.60 (2C), 120.26 (2C), 53.76 (2C, sp$^3$, C$_{cage}$$-$OCH$_3$), 29.15 ppm (2C, sp$^3$, OCH$_3$).

**Compound 2** (yield: 10.9%): MALDI-TOF MS (negative ionization mode): $m/z$ 1170.622; Vis-NIR 992 nm; $^1$H NMR (600 MHz, CS$_2$/DMSO, 25 °C, TMS): $\delta$ = 3.84 ppm (s, 6H, $-$OCH$_3$).

**Single crystal X-ray crystallography**

0.5 mg of 1 was dissolved in 0.5 ml carbon disulfide in a 5.0 ml centrifuge tube. Then, a toluene solution of DPC was added into the tube. The mixed solution, in which DPC and fullerene have a molar ratio of 2 : 1, was kept undisturbed at room temperature for slow evaporation. After two weeks, black sheet-like crystals were formed. A crystal of 0.12 mm $\times$ 0.08 mm $\times$ 0.01 mm dimension was mounted in the 100 K nitrogen cold stream on an XtaLAB PRO MM007HF diffractometer with Cu-K$_x$ radiation ($\lambda$ = 1.5406 Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement, and data reduction. The crystal structure of 1 was 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 [1]**

- $^{2}$DPC: $^{2}$DPC-H$_2$N$_2$O$_2$Sc$_3$, $M_w$ = 3065.93 amu, triclinic, $P\overline{1}$, $a = 14.4947(8)$ Å, $b = 31.8931(18)$ Å, $c = 32.660(2)$ Å, $\alpha = 91.077(1)^{\circ}$, $\beta = 95.165(2)^{\circ}$, $\gamma = 101.899(1)^{\circ}$, $V = 14.703(0.15)$ Å$^3$, $T = 100$ K, $Z = 2$, $R$ indices (all data) $R_1$ = 0.1158, $wR_2$ = 0.3470, GOF (on $F^2$) = 1.045.

**Computational details**

All computations were performed using the density functional theory (DFT) methodology with the ADF 2016 program. The exchange-correlation functionals of Becke and Perdew (BP86) and the Slater triple-$\xi$ + polarization (TZP) basis sets were selected for geometry optimizations.

**Author contributions**

Y. Hu: data collection, writing-originial draft; Y.-R. Yao: crystal structure analysis; X. Liu and A. Yu: synthesis of raw materials; X. Xie, Q. Zhang and S.-Y. Xie: synthesis of DPC; L. Abella, A. Rodriguez-Fortea, and J. M. Poblet: theoretical calculations; T. Akasaka: writing-commenting and editing; P. Peng: project management; F.-F. Li: conceptualization, supervision, writing-commenting and editing; X. Lu: conceptualization, writing-commenting and editing.
Conflicts of interest
The authors declare no conflict of interest.

Acknowledgements
Financial support from the National Natural Science Foundation of China (Grant No. 22071070, 21925104, 21971077, 51772111 and 21672076) and the Spanish Ministry of Science (grant CTQ2017-87269-P) is gratefully acknowledged.

Notes and references
1 S. Yang, T. Wei and F. Jin, Chem. Soc. Rev., 2017, 46, 5005–5058.
2 K. Wang, X. Liu, R. Huang, C. Wu, D. Yang, X. Hu, X. Jiang, J. C. Duchamp, H. Dorn and S. Priya, ACS Energy Lett., 2019, 4, 1852–1861.
3 K. Zhang, C. Wang, M. Zhang, Z. Bai, F.-F. Xie, Y.-Z. Tan, Y. Guo, K.-J. Hu, L. Cao, S. Zhang, X. Tu, D. Pan, L. Kang, J. Chen, P. Wu, X. Wang, J. Wang, J. Liu, Y. Song, G. Wang, F. Song, W. Ji, S.-Y. Xie, S.-F. Shi, M. A. Reed and B. Wang, Nat. Nanotechnol., 2020, 15, 1019–1024.
4 T. Wang and C. Wang, Small, 2019, 15, 1901522.
5 Y. Hu, A. Solé-Daura, Y.-R. Yao, X. Liu, S. Liu, A. Yu, P. Peng, J. M. Poblet, A. Rodríguez-Forteza, L. Echegoyen and F.-F. Li, Chem.–Eur. J., 2020, 26, 1748–1753.
6 W. Shen, L. Yang, B. Li, P. Jin, B. Yu, H. Cong, T. Akasaka and X. Lu, Chem. Commun., 2020, 56, 14357–14360.
7 F.-F. Li, J. R. Pinzón, B. Q. Mercado, M. M. Olmstead, A. L. Balch and L. Echegoyen, J. Am. Chem. Soc., 2011, 133, 1563–1571.
8 G.-W. Wang, T.-X. Liu, M. Jiao, N. Wang, S.-E. Zhu, C. Chen, S. Yang, F. L. Bowles, C. M. Beavers, M. M. Olmstead, B. Q. Mercado and A. L. Balch, Angew. Chem., Int. Ed., 2011, 50, 4658–4662.
9 O. Semivrazhskaya, S. Aroua, M. Yulikov, A. Romero-Rivera, S. Stevenson, M. García-Borrás, S. Osuna and Y. Yamakoshi, J. Am. Chem. Soc., 2020, 142, 12954–12965.
10 Y. Chai, X. Liu, B. Wu, L. Liu, Z. Wang, Y. Weng and C. Wang, J. Am. Chem. Soc., 2020, 142, 4411–4418.
11 O. Semivrazhskaya, A. Romero-Rivera, S. Aroua, S. I. Troyanov, M. García-Borrás, S. Stevenson, S. Osuna and Y. Yamakoshi, J. Am. Chem. Soc., 2019, 141, 10988–10993.
12 S. Yang, M. Chen, R. Guan, B. Li, L. Yang, C. Niu, P. Jin and G.-W. Wang, Angew. Chem., Int. Ed., 2021, 60, 7880–7886.
13 Y. García-Rodeja, M. Solà and I. Fernández, J. Org. Chem., 2018, 83, 3285–3292.
14 M. Yamada, Y. Tanabe, J.-S. Dang, S. Sato, N. Mizorogi, M. Hachiya, M. Suzuki, T. Abe, H. Kurihara, Y. Maeda, X. Zhao, Y. Lian, S. Nagase and T. Akasaka, J. Am. Chem. Soc., 2016, 138, 16523–16532.
15 F.-F. Li, A. Rodríguez-Forteza, J. M. Poblet and L. Echegoyen, J. Am. Chem. Soc., 2011, 133, 2760–2765.
16 F.-F. Li, A. Rodríguez-Forteza, P. Peng, G. A. Campos Chavez, J. M. Poblet and L. Echegoyen, J. Am. Chem. Soc., 2012, 134, 7480–7487.
17 N. B. Shustova, A. A. Popov, M. A. Mackey, C. E. Coumbe, J. P. Phillips, S. Stevenson, S. H. Strauss and O. V. Boltalina, J. Am. Chem. Soc., 2007, 129, 11676–11677.
18 N. B. Shustova, D. V. Peryshkov, I. V. Kuvychko, Y.-S. Chen, M. A. Mackey, C. E. Coumbe, D. T. Heaps, B. S. Confait, T. Heine, J. P. Phillips, S. Stevenson, L. Dunsch, A. A. Popov, S. H. Strauss and O. V. Boltalina, J. Am. Chem. Soc., 2011, 133, 2672–2690.
19 S. Yang, C. Chen, M. Jiao, N. B. Tamm, M. A. Lanskikh, E. Kemnitz and S. I. Troyanov, Inorg. Chem., 2011, 50, 3766–3771.
20 F. Jin, N. B. Tamm, S. I. Troyanov and S. Yang, J. Am. Chem. Soc., 2018, 140, 3496–3499.
21 A. Nakagawa, M. Nishino, H. Niwa, K. Ishino, Z. Wang, H. Omachi, K. Furukawa, T. Yamaguchi, T. Kato, S. Bandow, J. R. Rio, C. Ewels, S. Aoyagi and H. Shinohara, Nat. Commun., 2018, 9, 3073.
22 C. Shu, C. Slobodnick, L. Xu, H. Champion, T. Fuhrer, T. Cai, J. E. Reid, W. Fu, K. Harich, H. C. Dorn and H. W. Gibson, J. Am. Chem. Soc., 2008, 130, 17755–17760.
23 L. Bao, M. Chen, C. Pan, T. Yamaguchi, T. Kato, M. Olmstead, A. Balch, T. Akasaka and L. Xing, Angew. Chem., Int. Ed., 2016, 55, 4242–4246.
24 L. Feng, T. Nakahodo, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, T. Kato, E. Horn, K. Yozu, N. Mizorogi and S. Nagase, J. Am. Chem. Soc., 2005, 127, 17136–17137.
25 M. Chen, L. Bao, M. Ai, W. Shen and X. Lu, Chem. Sci., 2016, 7, 2331–2334.
26 W. Shen, L. Yang, Y. Wu, L. Bao, Y. Li, P. Jin, H. Fang, Y. Xie and X. Lu, J. Org. Chem., 2019, 84, 606–612.
27 Y.-P. Xie, C. Pan, L. Bao, Z. Slanina, T. Akasaka and X. Lu, Organometallics, 2019, 38, 2259–2263.
28 W.-W. Chang, Z.-J. Li, W.-W. Yang and X. Gao, Org. Lett., 2012, 14, 2386–2389.
29 T. Cai, C. Slobodnick, L. Xu, K. Harich, T. E. Glass, C. Chancellor, J. C. Fettinger, M. M. Olmstead, A. L. Balch, H. W. Gibson and H. C. Dorn, J. Am. Chem. Soc., 2006, 128, 6486–6492.
30 Y.-Y. Xu, H.-R. Tian, S.-H. Li, Z.-C. Chen, Y.-R. Yao, S.-S. Wang, X. Zhang, Z.-Z. Zhu, S.-L. Deng, Q. Zhang, S. Yang, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, Nat. Commun., 2019, 10, 485.
31 Y. Maeda, M. Kimura, C. Ueda, M. Yamada, T. Kikuchi, M. Suzuki, W.-W. Wang, N. Mizorogi, N. Karousis, N. Tagmarchis, T. Hasegawa, M. M. Olmstead, A. L. Balch, S. Nagase and T. Akasaka, Chem. Commun., 2014, 50, 12552–12555.
32 J. R. Pinzón, D. C. Gasca, S. G. Sankaranarayanan, G. Bottari, T. Torres, D. M. Guldi and L. Echegoyen, J. Am. Chem. Soc., 2009, 131, 7727–7734.
33 A. G. Avent, P. R. Birkett, A. D. Darwish, S. Houlton, R. Taylor, K. S. T. Thomson and X.-W. Wei, J. Chem. Soc., Perkin Trans. 2, 2001, 782–786.
34 L.-L. Deng, S.-L. Xie, C. Yuan, R.-F. Liu, J. Feng, L.-C. Sun, X. Lu, S.-Y. Xie, R.-B. Huang and L.-S. Zheng, *Sol. Energy Mater. Sol. Cells*, 2013, **111**, 193–199.

35 G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9385–9387.

36 E. A. Khakina, O. A. Kraevaya, M. L. Popova, A. S. Peregudov, S. I. Troyanov, A. V. Chernyak, V. M. Martynenko, A. V. Kulikov, D. Schols and P. A. Troshin, *Org. Biomol. Chem.*, 2017, **15**, 773–777.

37 H. Ueno, K. Uchiyama, Y. Ma, K. Watanabe, K. Yoya, Y. Matsuo and H. Moriyama, *J. Org. Chem.*, 2018, **83**, 10655–10659.

38 N. Lou, Y. Li and L. Gan, *Angew. Chem., Int. Ed.*, 2017, **56**, 2403–2407.

39 Z. Jia, Q. Zhang, Y. Li, L. Gan, B. Zheng, G. Yuan, S. Zhang and D. Zhu, *Tetrahedron*, 2007, **63**, 9120–9123.

40 K. M. Kadish, X. Gao, O. Gorelik, E. Van Caemelbecke, T. Suenobu and S. Fukuzumi, *J. Phys. Chem. A*, 2000, **104**, 2902–2907.

41 X.-X. Yan, B. Li, H.-S. Lin, F. Jin, C. Niu, K.-Q. Liu, G.-W. Wang and S. Yang, *Research*, 2020, **2020**, 2059190.

42 M. Mikawa, H. Kato, M. Okumura, M. Narazaki, Y. Kanazawa, N. Miwa and H. Shinozaka, *Bioconjugate Chem.*, 2001, **12**, 510–514.

43 J. Zhang, Y. Ye, Y. Chen, C. Pregot, T. Li, S. Balasubramaniam, D. B. Hobart, Y. Zhang, S. Wi, R. M. Davis, L. A. Madsen, J. R. Morris, S. M. LaConte, G. T. Yee and H. C. Dorn, *J. Am. Chem. Soc.*, 2014, **136**, 2630–2636.

44 G. M. Sheldrick, *Program for crystal structure solution*, University of Göttingen, Germany, 1997.

45 N. Alegret, A. Rodriguez-Fortea and J. M. Poblet, *Chem.–Eur. J.*, 2013, **19**, 5061–5069.

46 A. Rodriguez-Fortea, J. M. Campanera, C. M. Cardona, L. Echegoyen and J. M. Poblet, *Angew. Chem., Int. Ed.*, 2006, **45**, 8176–8180.