

Effects of solvents on reaction products: synthesis of endohedral metallofullerene oxazoline and epoxide

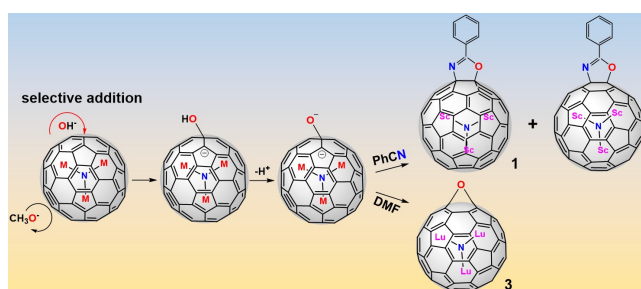
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Abstract: Herein, we performed the reactions of $M_3N@C_{80}$ ($M = Sc, Lu$) with the methanol (CH_3OH) solution of TBAOH (note that both CH_3O^- and OH^- are nucleophiles) in benzonitrile

(PhCN) and dimethylformamide (DMF), respectively. It is found that OH^- ions rather than CH_3O^- ions selectively attacked the fullerene cage to form the $\text{M}_3\text{N}@\text{C}_{80}-\text{O}^-$ intermediate. Although the fullerene cage is initially attacked by OH^- in both PhCN and DMF solvents, the products are quite different. In PhCN, two isomeric $\text{Sc}_3\text{N}@I_{\text{h}}-\text{C}_{80}$ fullerooxazoline heterocyclic products (**1** and **2**) were synthesized. Whereas, in DMF, an epoxide of $\text{Lu}_3\text{N}@I_{\text{h}}-\text{C}_{80}$ (**3**) was obtained. The preference for fullerooxazoline formation over that of fullerene epoxy in PhCN is well explained by density functional theory (DFT) calculations. Plausible reaction mechanisms for the formation of metallofullerene oxazoline and epoxide were proposed based on the experimental and theoretical results.

Introduction

In most chemical reactions, except for neat and solid-solid phase reactions,^{1,2} solvents are needed to dissolve the reacting substances and accelerate the reaction process. The primary requirement for the solvent is to have good solubility for the reactants and to be inert to the chemical process being studied. The reactions of endohedral metallofullerenes (EMFs) are mainly performed in benzene solvents as fullerenes are readily soluble in them and more importantly, the solvents are not reactive towards fullerenes.³ However, on the other hand, the involvement of a solvent as a reagent in the reactions leads to unpredictable results and is well worth investigating. Nevertheless, there are only a few examples of solvents being reactive to EMFs, and the reactions are limited to radical reactions.⁴⁻⁶ For instance, during the high-temperature extraction of fullerene soot, trichlorobenzene and iodobenzene solvents reacted with some metallofullerenes via radicals, resulting in the discovery of some difficult to separate

La@C_{2n} (n = 36–40) cages.^{4,5} Besides, solvents can adjust the polarity of the reaction system, regulating the interaction between the solvents and the reactant molecules and facilitating the progress of a specific process or reaction.⁷⁻⁹ For example, M₃N@I_h-C₈₀ (M = Sc, Lu) does not undergo the Bingel reaction in dichlorobenzene (o-DCB) solvent,^{8,9} but it occurs in the presence of a more polar solvent DMF.¹⁰ By all accounts, the choice of solvent is essential for the reactions of EMFs.

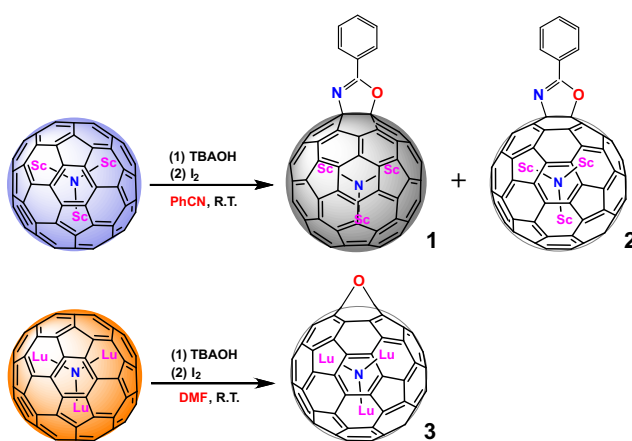
It is well known that the acquisition of EMF derivatives via various chemical reactions^{3,11,12} offer promising solutions to target applications in nanoscience, biochemistry, and energy storage.^{3,13-16} Heterocyclic compounds are an important class of chemicals as many of them such as oxazoline, isoxazoline, and their derivatives show biological functions,^{17,18} and epoxides show the capability of fixing CO₂ into high-value cyclic/polycarbonates.¹⁹⁻²² Modification of EMF skeletons with heterocycles is expected to enrich the reservoir of EMF derivatives and expand their applications. However, heterocyclic derivatives of EMFs are rarely reported due to the limitations of (i) the heteroatomic nucleophiles and (ii) the synthesis methods, mainly relying on the high-temperature 1,3-dipolar addition reaction.²³⁻³⁰ Therefore, developing new methods for synthesizing EMF heterocyclic compounds under mild conditions is desired.

Herein, we report three heterocyclic EMF derivatives through room-temperature reactions of M₃N@I_h-C₈₀ (M = Sc, Lu) with TBAOH stored in CH₃OH (denoted as TBAOH/CH₃OH) in PhCN and DMF, respectively. Unexpected results were obtained due to the modulation of the solvents. In PhCN, isomeric [5,6]- and [6,6]-N,O-heterocyclic Sc₃N@I_h-C₈₀ derivatives were obtained, while in DMF, Lu₃N@I_h-C₈₀ epoxide, instead of the N,O-heterocyclic adduct, was

obtained. The present work outlines the effects of solvents on EMF functionalization. More importantly, the method presented here can serve as an important platform, since the $M_3N@C_{80}^{-}-O^{-}$ intermediate is able to attack a variety of electrophiles, for the production of various heterocyclic adducts, thus expanding the available synthetic methods.

Results and Discussion

In a typical reaction, $M_3N@I_h-C_{80}$ ($M = Sc$ or Lu) was put into a flask equipped with 10 ml solvent (PhCN and DMF). Then, 10 equivalent of 1.0 M TBAOH stored in CH_3OH were injected into the fullerene solution. After stirring for 2 h, the reaction was quenched by the addition of 50 equivalent iodine (I_2). The crude product was washed with methanol to remove excess TBAOH and I_2 . Due to the high reactivity of PhCN, two isomeric oxazoline heterocyclic $Sc_3N@I_h-C_{80}$ fullerenes (**1** and **2**) were synthesized, while one $Lu_3N@I_h-C_{80}$ epoxide (**3**) was obtained in DMF (Scheme 1).



Scheme 1. Results for the reactions of $Sc_3N@I_h-C_{80}$ and $Lu_3N@I_h-C_{80}$ with TBAOH in different solvents at room temperature.

1.1. Synthesis of oxazoline adducts by room-temperature reaction of $Sc_3N@I_h-C_{80}$ with

TBAOH in PhCN.

Although $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ is not very soluble in PhCN ($\text{C}_6\text{H}_5\text{CN}$), injection of TBAOH/ CH_3OH resulted in an immediate change of the solution from brown suspension to transparent dark green and then brown upon I_2 addition (Figure S1). The in-situ UV-Vis-NIR spectra of the reaction mixture (Figure S2) showed that the absorption of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ is red-shifted from 373 nm to 391 nm, and a new peak appears at about 568 nm, indicating the formation of an anionic intermediate. As shown in the High-Performance Liquid Chromatography (HPLC) profile of the reaction crude (Figure 1), two derivatives **1** and **2** along with the unreacted $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ were observed. The products are separated and purified by HPLC (Figure S3). In addition, the reaction was carried out on a larger scale, and products **1** and **2** were also obtained (Figure S4), which demonstrated the practical utility of the method as a synthetic tool.

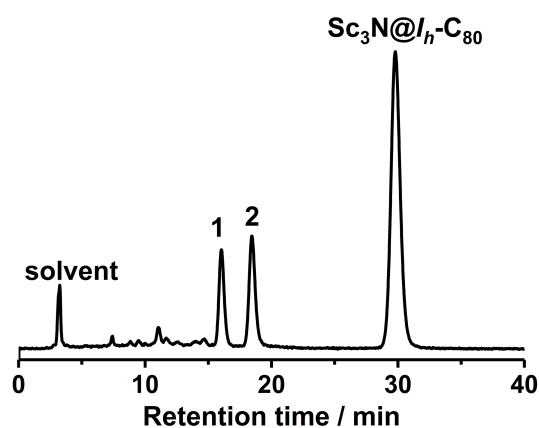


Figure 1. HPLC profile of the reaction mixture of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ with TBAOH (1.0 M in CH_3OH) in PhCN. HPLC (Buckyprep column, ϕ 4.6 $\times$ 250 mm, toluene, flow rate = 1.0 ml/min, λ = 330 nm) tR = 16.0 min (**1**), 18.4 min (**2**).

The MALDI-TOF mass spectrum of **1** shows a molecular ion peak at 1228.035, corresponding to a molecular formula of $\text{Sc}_3\text{N}@C_{80}(\text{C}_6\text{H}_5\text{CNO})$ (theoretical m/z = 1227.918)

(Figure 2a), indicating the possible addition of C₆H₅CN, which was subsequently confirmed by NMR measurements. The ¹H NMR spectrum of **1** (Figure 2b and Figure S5) showed a doublet at 7.97 (d, 2H) ppm and two triplets at 7.36 (t, 1H) and 7.29 (t, 2H) ppm, corresponding to the five phenyl protons of C₆H₅CN group, which suggested that C₆H₅CNO was added in a symmetric [5,6]-addition pattern. The ¹H NMR pattern of **1** is consistent with those of reported symmetric benzene addition derivatives of M₃N@I_h-C₈₀.^{31,32} The proposed addition pattern of **1** was further proven by UV-vis-NIR spectroscopy, which has been widely recognized as a useful tool for addition pattern assignment and does not depend on the nature of the addend but on the regiochemistry of the addend. As shown in Figure 2c, **1** displayed a broad absorption peak at 968 nm, nearly identical to the characteristic absorptions of the reported [5,6]-closed Sc₃N@I_h-C₈₀ monoadducts, such as the [5,6]-*N*-tritylpyrrolidino Sc₃N@I_h-C₈₀ from the Prato reaction,³³ the [5,6]-benzyne Sc₃N@I_h-C₈₀ from the [2+2] reaction,^{34,35} and the [5,6]-carbosilylated Sc₃N@I_h-C₈₀ from the photoreaction.³⁶

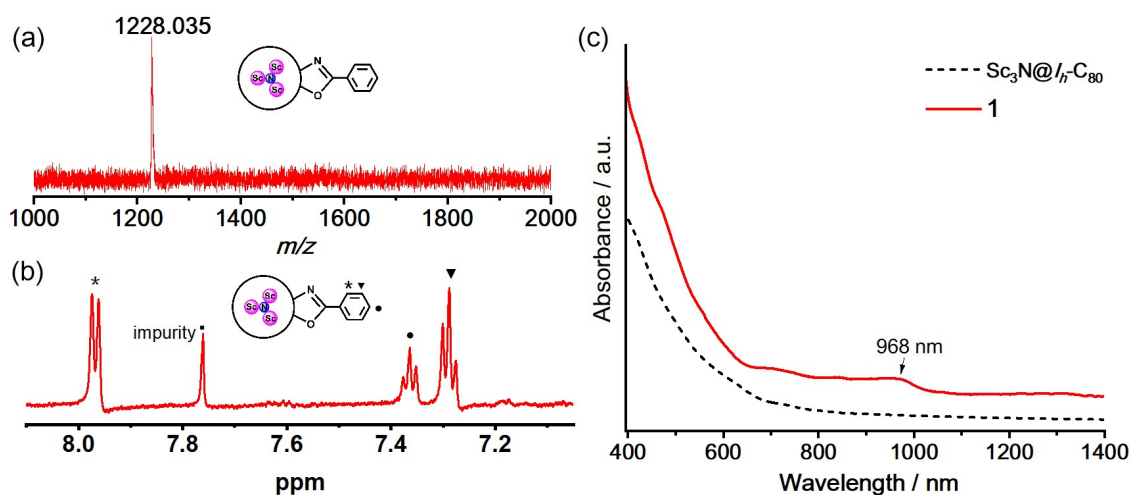


Figure 2. (a) MALDI-TOF MS of **1**, (b) ¹H NMR of **1** in CS₂ with DMSO-*d*₆ as the lock solvent (▪ represents unknown impurity) and (c) UV-vis-NIR spectra of Sc₃N@I_h-C₈₀ and **1** in

CS₂.

The structure of derivative **1** was unambiguously confirmed by X-ray single-crystal diffraction. Crystallography measurement is known as one of the most reliable methods to identify the structure of a compound. Black cube-like co-crystals of **1**•2DPC•toluene were obtained by slow evaporation of toluene solutions of **1** and DPC³⁷ at room temperature (Figure 3a). The two DPC molecules are located at the bottom and side of **1**, respectively, and assembled into a V-shape with an angle of 64.7°. The centroid-centroid distance of the C₈₀ cage with the pentagon of the bottom DPC is 7.466, slightly greater than 7.422 Å with the lateral DPC. As the structure of **1** shows (Figure 3b), an N,O-heterocycle was fused at a [5,6]-ring junction of the C₈₀ cage, which is highly consistent with the structure that was proposed based on the MS, NMR, and UV–vis–NIR results, indicating the reliability of structure inference from the spectral data. The lengths of the O1–C3 and N2=C3 bonds are 1.383 Å and 1.311 Å, respectively. The bond length of C1–C2 at [5,6]-addition site is 1.579 Å, longer than the average C–C single bond distance of the pristine Sc₃N@I_h-C₈₀ (1.437 Å), but shorter than that of other reported [5,6]-five-membered heterocycle derivatives such as the pyrrolidine-fused Sc₃N@I_h-C₈₀ (1.619 Å),³³ pyrazole-fused Sc₃N@I_h-C₈₀ (1.61 Å),²⁶ and isoxazoline-fused Sc₃N@I_h-C₈₀ (1.59 Å),²⁷ further confirming the [5,6]-closed structure of **1**. The orientation of the major Sc₃N cluster in **1** is almost parallel to the heterocycle, and none of the Sc atoms point to the C1-C2 bond.

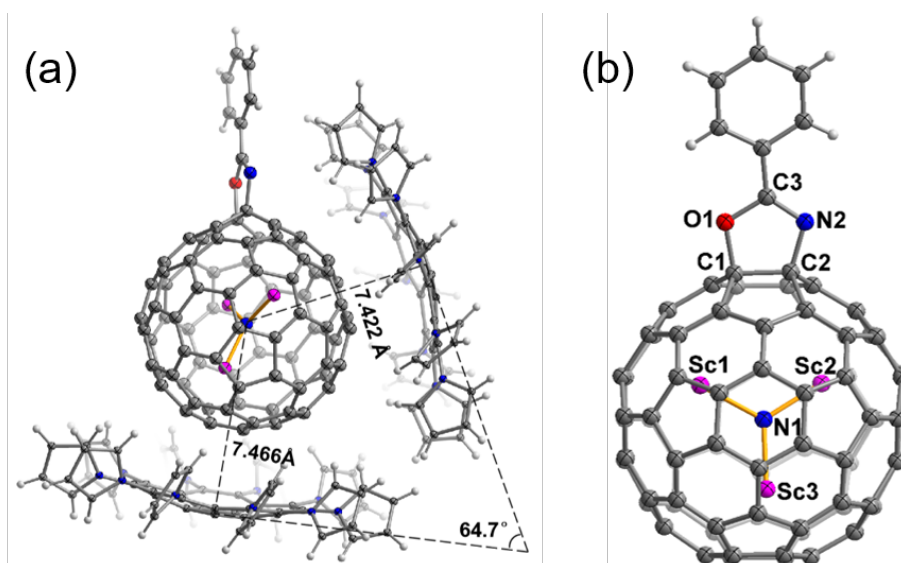


Figure 3. (a) X-ray single crystal structure of the co-crystal **[1]·2DPC** and (b) **1** with thermal ellipsoids at the 10% probability level. Only the major cage and Sc₃N site are shown.

Although the crystallization of compound **2** was unsuccessful, combining the structural information of **1** with the MS, NMR, and UV-vis-NIR data of **2**, we can confirm that product **2** is a regioisomer of **1**, i.e., a [6,6]-heterocyclic oxazoline derivative of Sc₃N@I_h-C₈₀. As displayed in Figure 4a, the MALDI-TOF mass spectrum of **2** showed a molecular ion peak with $m/z = 1227.920$, which is similar to the m/z value of **1** (1228.035), indicative of the isomeric structure of **1** and **2**. ¹H NMR spectrum of **2** (Figure 4b and Figure S6) exhibited a similar pattern to that of **1** since the Ph group can rotate freely. It shows a doublet at 7.76 (d, 2H) ppm and two triplets at 7.29 (t, 1H) and 7.20 (t, 2H) ppm. The UV-vis-NIR spectrum (Figure 4c), in which an absorption peak at 860 nm was observed, is similar to the characteristic absorptions of the reported [6,6]-closed Sc₃N@I_h-C₈₀ monoadducts such as [6,6]-*N*-tritylpyrrolidino,³³ [6,6]-benzyne Sc₃N@I_h-C₈₀,^{34,35} and [6,6]-carbosilylated Sc₃N@I_h-C₈₀.³⁶ Notably, heterocyclic adducts of EMFs are synthesized mainly via 1,3-dipolar reactions under high temperature or irradiation conditions. However, the heterocyclic Sc₃N@I_h-C₈₀ oxazoline

adducts (**1** and **2**) were synthesized under mild conditions. Moreover, the participation of the PhCN solvent as a reagent is critical for the formation of **1** and **2**. It is worth mentioning here that the reaction between $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and TBAOH (stored in CH_3OH) conducted in *o*-DCB unexpectedly yielded two bismethoxyl derivatives of $\text{Sc}_3\text{N}@C_{80}$ ($\text{Sc}_3\text{N}@C_{80}(\text{OCH}_3)_2$) due to the selective nucleophilic addition of CH_3O^- .³⁸ These results indicated the effects of solvents on the selective addition of nucleophiles and thus the final reaction products.

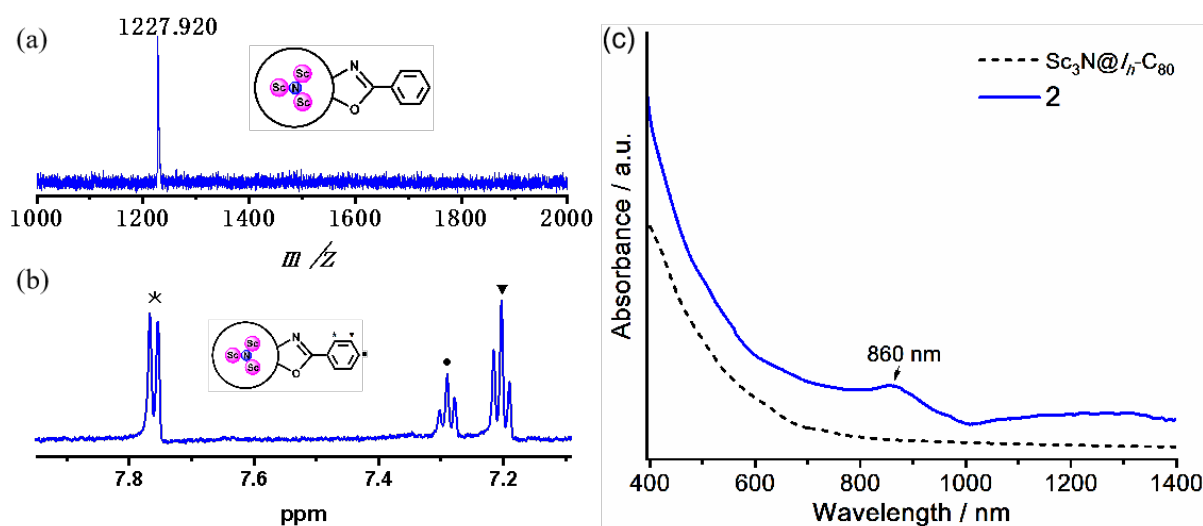


Figure 4. (a) MALDI-TOF MS of **2**, (b) ^1H NMR of **2** in CS_2 with $\text{DMSO-}d_6$ as the lock solvent, and (c) UV-vis-NIR spectra of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and **2** in CS_2 .

The structures and relative energies of regioisomers of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}(\text{C}_7\text{H}_5\text{NO})$ were further studied by density functional theory (DFT) calculations. For each adduct, different orientations of the cluster with respect to the substituted bond were considered (Figure S7). We found that the most favored cluster orientation (the first one at the top of Figure S7) is consistent with that in the crystal of **1** (Figure 3). The addition on a [6,6] bond, due to its asymmetric character, leads to two possible isomers, **2** and **2'**, where the positions of O and N of the oxazoline ring are exchanged. Isomer **2** (the first one at the bottom of Figure S7), with the O

bonded to the [666] C atom and the N bonded to the [665] C atom, is predicted to have somewhat lower energy (2.3 kcal mol⁻¹ with respect to isomer **2'**). It is worth mentioning that isomer **1** is found to be 9.6 kcal mol⁻¹ lower in energy than isomer **2**. Although the substituted C–C bond is elongated with respect to the pristine Sc₃N@I_h-C₈₀, the bond remains formed with C–C distances ranging from 1.61 to 1.69 Å, slightly larger than that found by the X-ray study for **1** (1.579 Å). Structures forced to have the bond broken, i.e., to be open fullerenoids, were found to be more than 15 kcal mol⁻¹ higher in energy. The optimal structures obtained from theoretical calculations are consistent with the experimental results.

The energy gap of a fullerene derivative calculated from the electrochemical cyclic voltammetry curve can reveal its potential applications in solar cells or optoelectronic devices. The electronic modulation normally occurred by the introduction of a functional group on the cage. Both **1** and **2** exhibit three electrochemically irreversible reductions and two quasi-reversible oxidation (Figure S8 and Table S1). The first reduction potentials ($E^{0/-}$) of **1** and **2** were anodically shifted by 170 mV and 290 mV, respectively, relative to the first reduction potential of the pristine Sc₃N@I_h-C₈₀. The addition of PhCNO enhanced the electron-accepting character. Moreover, the first oxidation potentials ($E^{0/+}$) of **1** and **2** were cathodically shifted relative to the counterpart of the pristine Sc₃N@I_h-C₈₀. Thus, their electrochemical gaps are reduced by ca. 300 mV and ca. 500 mV, respectively, relative to that of Sc₃N@I_h-C₈₀, which announced their future development in photovoltaics and optoelectronics.

1.2 Synthesis of epoxy adduct by room-temperature reaction of Lu₃N@I_h-C₈₀ with TBAOH in DMF.

The distinct results from the reaction of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ with TBAOH/ CH_3OH in *o*-DCB³⁸ and in PhCN demonstrate the important effects of solvents on the reactions. The results appear to be related to the polarity of the solvent. Therefore, DMF, as a strong polar anti-solvent for fullerenes, was employed to perform the same reaction. When TBAOH/ CH_3OH was added to the DMF suspension of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$, the solution immediately turned into a clear green color, indicating the formation of a soluble anionic intermediate. However, $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ was recovered from HPLC without obtaining significant product, the reason for which is yet unclear. $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ has long been considered the least reactive species in the EMF family and exhibits lower reactivity than other EMFs.^{8,9,32,39} Based on this, $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ was employed to perform the reaction under identical conditions as for $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$. The suspension of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ in DMF turned into a transparent orange solution after the injection of TBAOH/ CH_3OH , implying the formation of an anionic intermediate. Consistent results were obtained from the UV-vis-NIR spectra of the reaction mixture probed at different times (Figure S9), in which two new peaks at about 294 and 315 nm indicated the formation of an anionic intermediate. After the addition of I_2 , the reaction crude was examined by HPLC, where a new peak (compound **3**) with a longer retention time relative to the pristine $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ was observed (Figure 5a). Notably, most fullerene derivatives have shorter retention times than the corresponding pristine fullerenes (through a Buckyprep column with toluene as the mobile phase). C_{60} and C_{70} epoxides are the only exceptions that appear after the parent fullerenes in the HPLC profile.⁴⁰⁻⁴⁴ We thus speculate that the new product is an epoxide of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$, which was subsequently confirmed by mass spectrometry analysis.

Although the crystallization of **3** was unsuccessful, its spectral data was sufficient to

determine the structure. The high-resolution field desorption mass spectrum (HR–FD MS) of compound **3** shows a molecular ion peak at 1514.8170, consistent with the theoretical value of epoxy Lu₃N@C₈₀ (Lu₃N@C₈₀O m/z = 1514.8203). The fragment peak at 1498.8256 corresponds to Lu₃N@C₈₀ due to the loss of an oxygen atom from Lu₃N@C₈₀O (Figure 5b). The experimental isotopic distribution of Lu₃N@C₈₀O is identical to the theoretical distribution (inset in Figure 5b), further corroborating that the composition of **3** is Lu₃N@C₈₀O. Due to the absence of protons in the molecule, the ¹H NMR study of **3** is not applicable. The addition pattern of **3** was confirmed by absorption spectroscopy. As shown in Figure 5c, compound **3** displays three absorption peaks at 399, 676, and 719 nm, which are very similar to those of pristine Lu₃N@I_h-C₈₀ and other reported [6,6]-Lu₃N@I_h-C₈₀ fullerenes, like Lu₃N@I_h-C₈₀ methanofullerenes (Lu₃N@I_h-C₈₀(>CHPh),³² Lu₃N@I_h-C₈₀-PCBM/PCBH/PCBB/PCBO¹⁶) and Si-bridged fullerene Lu₃N@I_h-C₈₀(>SiDep₂)³⁹. In addition, the spectroscopic results of **3** are highly consistent with a recently reported [6,6]-open Lu₃N@I_h-C₈₀ monoepoxide obtained from a photochemical reaction,⁴⁵ which provides extra evidence for the structure assignment of **3** to be a [6,6]-open Lu₃N@I_h-C₈₀ epoxide. A thermodynamic study of the Lu₃N@I_h-C₈₀ epoxide was performed. Open and closed cages have been computed for the [6,6] isomer at the DFT level. Nevertheless, the closed structure ended up as an open-cage fullerene during the structure optimization (Figure S10), indicating the open-cage Lu₃N@I_h-C₈₀ epoxide is thermodynamically more favorable, consistent with the experimental results.

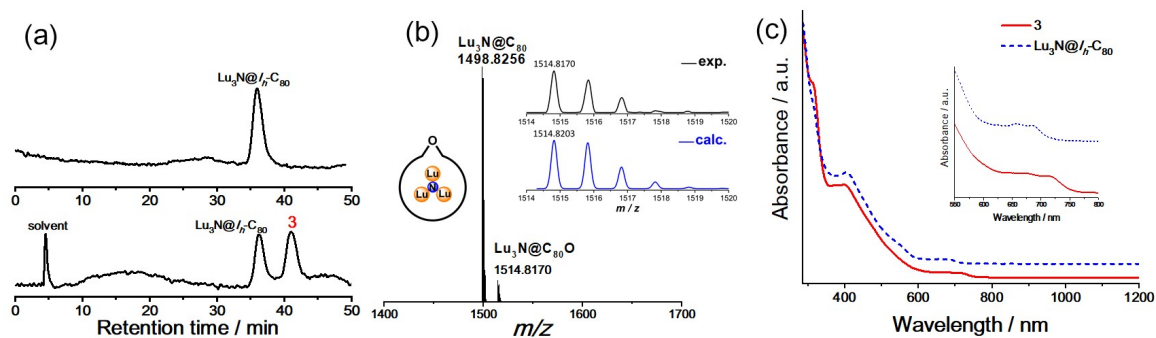


Figure 5. (a) HPLC profiles of pristine $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ and the reaction mixture of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ with TBAOH in DMF. Conditions: HPLC (Buckyprep column, ϕ 10 $\times$ 250 mm, toluene, flow rate = 4.0 ml/min, λ = 330 nm) tR = 41.0 min (**3**). (b) High-resolution field desorption mass spectrum of **3**. (c) UV–Vis–NIR spectra of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ and **3** in CS_2 .

The cyclic voltammogram and the electrochemical redox potentials of **3** were shown in Figure S11 and Table S2. Three irreversible reduction peaks and two quasi-reversible oxidation peaks were observed, which is in good agreement with those of methanofullerenes with [6,6]-open addition pattern. The reduction potentials of **3** were shifted anodically than that of pristine $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$, indicating that the addition of oxygen improves the electron-accepting property. The oxidation potentials of **3** were slightly anodically shifted as well, leading to an electrochemical gap of **3** that is approximately 140 mV smaller than that of $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$.

Epoxy metallofullerenes have been rarely reported. Although the synthesis of $\text{C}_{60}/\text{C}_{70}$ epoxides dates back to the 1990s,^{46–48} the reaction conditions are violent, requiring catalysts^{49,50} and/or strong oxidants (such as ozone, m-chloroperoxybenzoic acid, methyltrioxorhenium-hydrogen peroxide, and dioxirane)^{40,42,51–54} under thermal, photolysis or ultrasonication conditions.^{43,55–57} Moreover, the reactions proceeded in an uncontrolled manner and are detrimental to the control of the number of addends. Nevertheless, our epoxidation reaction was performed under mild conditions, where TBAOH served as both a nucleophile and a

deprotonating agent, resulting in a dianionic intermediate ($\text{Lu}_3\text{N}@\text{I}_h\text{-C}_{80}^{2-}\text{-O}^-$), followed by **oxidation** to form an epoxide. More interestingly, the epoxidation reaction **has** occurred in a controlled manner even a large excess of TBAOH was added. The anion intermediates ensured high regioselectivity of the reaction.

Mechanism Studies

According to the experimental results from the reactions of $\text{M}_3\text{N}@\text{I}_h\text{-C}_{80}$ with TBAOH/ CH_3OH in three different solvents (*o*-DCB,³⁸ PhCN, and DMF) shown in Figure 6, there are two reaction paths at the initial stage, i.e., direct nucleophilic addition of CH_3O^- or OH^- to the cage, depending on the solvent used in the reaction. TBAOH is an ammonium-based ionic liquid (**IL**) and a strong organic base. It is very soluble in aqueous solution and CH_3OH .^{58,59} For the reaction in *o*-DCB, due to the better miscibility of CH_3OH with *o*-DCB than TBAOH, CH_3OH can efficiently approach the fullerene cage and accumulate around the fullerene molecules, promoting the nucleophilic addition of CH_3O^- to the fullerene cage. In contrast, in polar solvents PhCN and DMF, OH^- can be better solvated and tends to be directly added to the fullerene cages to form an anionic intermediate ($\text{M}_3\text{N}@\text{C}_{80}\text{-OH}$),⁻ which is well soluble in polar PhCN and DMF.^{60,61}

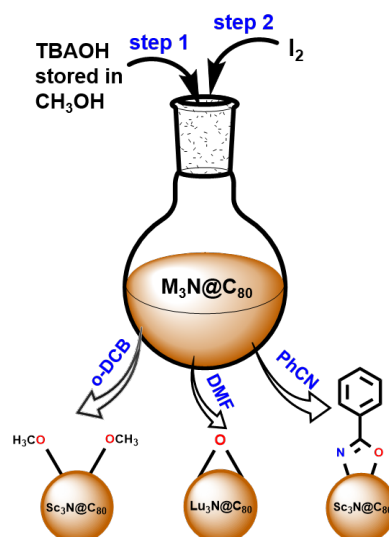


Figure 6. Results for the reactions of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ and $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ with TBAOH/ CH_3OH in different solvents.

In addition, although the fullerene cage was initially attacked by OH^- in both PhCN and DMF, the products from the two reactions are different. Two oxazoline adducts **1** and **2** were obtained in PhCN, and one epoxide was obtained in DMF. DFT calculations confirmed that the fullerooxazoline formation takes precedence over the fullerene epoxide in the presence of PhCN. We explored the reaction mechanism for the formation of these heterocycle adducts, where the metallofullerene reacts with the solvent PhCN at a certain point. Figure 7 shows the energy profiles with the structures of intermediates and transition states (TS) for the different steps of the reactions. $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ initially reacts with TBAOH, leading to an intermediate $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}\text{-OH}]^-$ (**I1-OH**), in which one OH group is attached to a [666] C atom of the fullerene. This is an exothermic process with a reaction energy of $-13.6 \text{ kcal mol}^{-1}$. In the next step, the OH of **I1-OH** was deprotonated by the OH^- of another TBAOH, resulting in a dianionic species $[\text{Sc}_3\text{N}@I_h\text{-C}_{80}\text{-O}]^{2-}$ (**I2-O**) and H_2O . The reaction energy is $-3.5 \text{ kcal mol}^{-1}$. This intermediate **I2-O**, in which the O atom is singly bonded to the carbon cage, plays an

important role in the mechanism since it is a *crossing point* in the road. **I2-O** could generate the epoxide through a TS at 6.8 kcal mol⁻¹ that would make the second C–O bond with the cage (**TS-epox**), but the nucleophilic attack of this O atom to the C atom of the Ph–CN solvent leads to intermediate **I3-oxaz-O** at a much lower energetic cost (3.5 vs 23.9 kcal mol⁻¹, see Figure 7). It should be noted here that we have not been able to locate the TS corresponding to this nucleophilic attack (**TS1-oxaz**), but we estimate that its energy is almost the same as that of intermediate **I3-oxaz-O** (-13.6 kcal mol⁻¹). The large energy difference between the barriers of these two competitive processes, 20.4 kcal mol⁻¹, made us think that the free energy barrier would be favorable to the oxazoline path even though the entropic penalty due to the bimolecular associative process. Even in the limiting case in which the reactants are considered as they were in the gas phase with plenty of translational entropy, the free energy barrier is still favorable for the oxazoline path by 6 kcal mol⁻¹. Intermediate **I3-oxaz-O** makes a new N–C bond with the cage to form the five-membered heterocyclic ring adduct, overcoming a small energy (and free energy) barrier of 4.4 kcal mol⁻¹ (**TS2-oxaz-O**). The reaction energy for the formation of this bis-reduced [6,6] oxazoline adduct, **Oxaz**²⁻, is -20.2 kcal mol⁻¹. Then, an intermediate **I4-oxaz-N** with the O–C_{cage} bond broken at 7.7 kcal mol⁻¹ below **Oxaz**²⁻ would be obtained surpassing a low-energy barrier (**TS3-oxaz-N**, 1.5 kcal mol⁻¹). We could not find the TS that directly connects **I3-oxaz-O** and **I4-oxaz-N**, but our estimation for the barrier would not be lower than 10 kcal mol⁻¹, so the path through intermediate **Oxaz**²⁻ seems to be more feasible. Finally, the oxidation of **I4-oxaz-N** by iodine to obtain fullerooxazoline (**2**) is very exothermic (-58.3 kcal mol⁻¹). The total reaction energy for reactants is -99.8 kcal mol⁻¹, which is somewhat more exothermic than that corresponding to the formation of the epoxide (-74.9

kcal mol⁻¹). The energy profile for the formation of the [5,6] oxazoline adduct, i.e., product 1, would be, within some slight changes in the values of the energies, parallel to that shown for product 2.

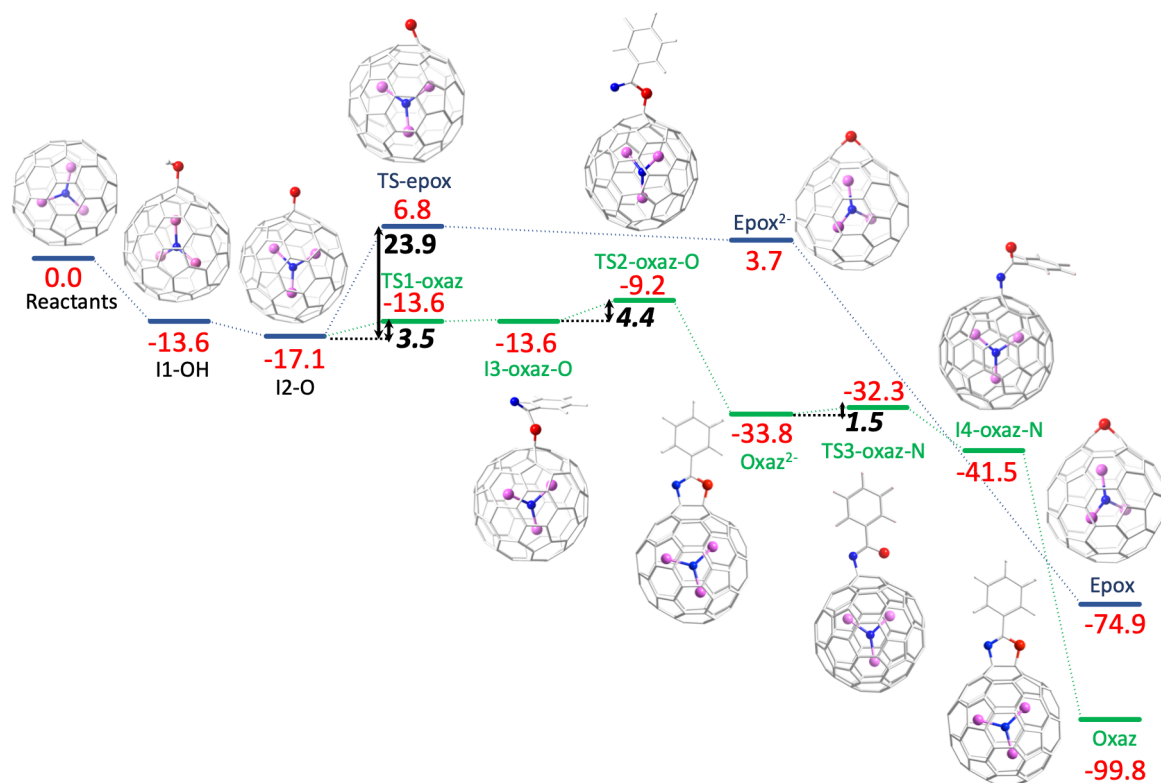
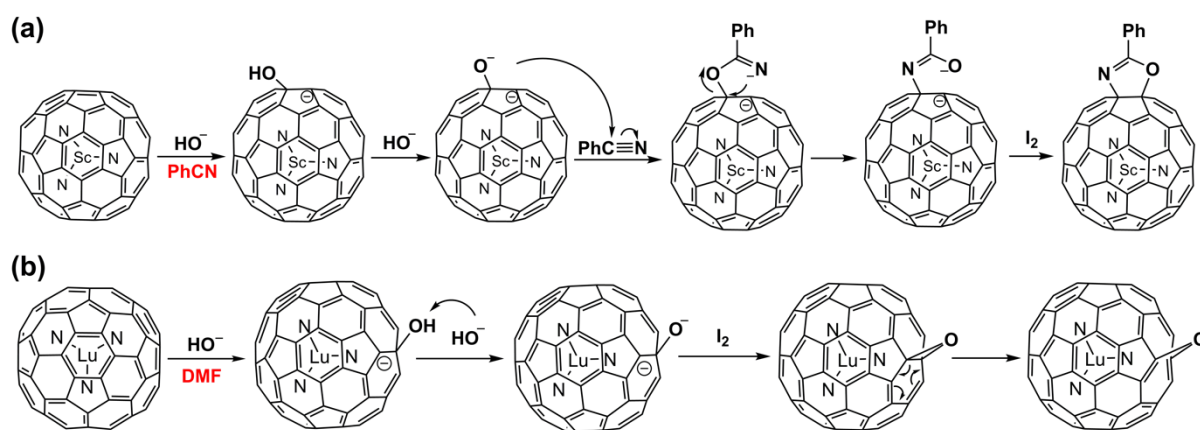


Figure 7. Energy profiles computed for the formation of oxazoline (green lines) and epoxide (blue lines) derivatives of Sc₃N@C₈₀ (energies in kcal mol⁻¹) using PhCN as the solvent.

Based on the structures of 1, 2, and 3, along with previous studies,⁶² the plausible formation mechanisms of the EMF oxazoline and epoxy derivatives were proposed here (Scheme 2). In PhCN (Scheme 2a), as commented above and shown in Figure 7, the C₈₀ cage was attacked by OH⁻ from TBAOH to form a monoanionic fullerene hydroxide (Sc₃N@C₈₀⁻-OH, **I1-OH** in Figure 7), which was then deprotonated by another TBAOH, generating a dianionic Sc₃N@C₈₀⁻-O⁻ intermediate **I2-O**. The intermediate attacked the carbon atom of PhCN to form a dianionic oxazole species (Sc₃N@C₈₀⁻-OCPhN⁻, **I3-oxaz-O**),

which underwent bond rearrangement and was then oxidized by I_2 to generate the $Sc_3N@C_{80}$ oxazoline products (**1** and **2**). In DMF (Scheme 2b), OH^- attacked the C_{80} cage to form a monoanionic fullerene hydroxide $[Lu_3N@C_{80}-OH]^-$ (see energy profile for this mechanism in Figure S12). The hydroxide was then deprotonated by another TBAOH to give a dianionic oxyfullerene intermediate ($Lu_3N@C_{80}^{2-}-O^-$). Due to the absence of PhCN, the O^- attacked the cage carbon, forming the open-cage fullerene epoxide (**3**) via a bond rearrangement process involving the cleavage of the cyclopropane ring.



Scheme 2. Proposed reaction mechanisms of the reactions of $M_3N@C_{80}$ ($M = Sc, Lu$) with TBAOH/ CH_3OH in PhCN (a) and DMF (b).

Conclusion

In summary, the regulation of the reaction pathways and products by the solvents was demonstrated. In PhCN, the $Sc_3N@C_{80}^{2-}-O^-$ intermediate selectively attacked the nitrile carbon of PhCN rather than the fullerene cage carbon, resulting in two isomeric fullerooxazoline heterocyclic products **1** and **2**, which is ascribed to the relatively low energy cost for nucleophilic attack of O^- to the PhCN. While in DMF, the $Lu_3N@C_{80}^{2-}-O^-$ intermediate attacked the fullerene cage carbon to form the epoxide of $Lu_3N@C_{80}$. DFT studies allowed us

to rationalize why an oxazoline adduct instead of epoxide is formed when the solvent is PhCN. Significantly, the dianionic intermediate $C_{\text{fullerene}}^{2-}O^-$ can be used as a potentially versatile nucleophile to electron-deficient unsaturated bonds for the synthesis of diverse heterocyclic EMF derivatives. Given the simplicity and relative mildness of the reaction conditions, the method presented here can serve as an important platform for the production of various heterocyclic adducts that have previously been difficult for fullerenes.

Experimental Section

Materials and methods

Pure $Sc_3N@I_h-C_{80}$ and $Lu_3N@I_h-C_{80}$ were obtained according to the procedures described previously.^{32,34} Tetrabutylammonium hydroxide (TBAOH) (1.0 M in MeOH), I_2 , toluene, DMSO- d_6 and CS_2 were used as received. PhCN was distilled over P_2O_5 under a vacuum at 313 K before use. DMF was distilled over CaH_2 under a vacuum at 305 K before use. Tetra-*n*-butylammonium-hexafluorophosphate (TBAPF₆) was recrystallized from absolute ethanol and dried in a vacuum before use. The purity of the compounds was verified by HPLC using a Buckyprep column and toluene as the eluent. The UV–vis–NIR spectra were recorded using a SHIMADZU UV–3600 spectrophotometer. MALDI–TOF MS was conducted on a Bruker Autoflex speed mass spectrometer. HR–FD MS was carried out on a high-resolution field desorption mass spectrometer. The NMR spectra were recorded using a Bruker Ascend™ 600 MHz NMR spectrometer. All reactions were carried out in a glove box with Ar protection.

Synthesis of compounds 1 and 2

$Sc_3N@I_h-C_{80}$ (5.0 mg, 4.5 μmol) was added to 15 ml of freshly distilled PhCN. Then, 32

μl of TBAOH (1.0 M in CH_3OH , 10 equiv.) was added to the solution under stirring. In a fairly short time, the fullerene solid dissolved, and the color of the solution changed from brown to dark green. After stirring for 2 h, the reaction was quenched by the addition of 50 equiv. I_2 (57.1 mg, 225 μmol). Then, the solvent was evaporated under a vacuum to obtain the crude material which was washed with methanol to remove excess TBAOH and I_2 . The cleaned solid product was finally dissolved in toluene and separated by HPLC with a Buckyprep column.

Compound 1 (amorphous solid, black; 1.5 mg, yield: 30%): ^1H NMR (600 MHz, $\text{CS}_2/\text{DMSO-}d_6$, 25 $^\circ\text{C}$, TMS): δ 7.97 ppm (d, 2H), 7.36 ppm (t, 1H), 7.29 ppm (t, 2H); Vis-NIR (CS_2) $\lambda_{\text{max}}/\text{nm}$ 968; MALDI-TOF MS (negative ionization mode): m/z $[\text{M}]^-$ calcd for $\text{C}_{87}\text{H}_5\text{N}_2\text{OSc}_3$ 1227.918; found 1228.035.

Compound 2 (amorphous solid, black; 1.6 mg, yield: 32%): ^1H NMR (600 MHz, $\text{CS}_2/\text{DMSO-}d_6$, 25 $^\circ\text{C}$, TMS): δ 7.76 ppm (d, 2H), 7.29 ppm (t, 1H), 7.20 ppm (t, 2H); UV-vis-NIR (CS_2) $\lambda_{\text{max}}/\text{nm}$ 860; MALDI-TOF MS (negative ionization mode): $[\text{M}]^-$ calcd for $\text{C}_{87}\text{H}_5\text{N}_2\text{OSc}_3$ 1227.918; found 1227.920.

Scale-up synthesis of 1 and 2

$\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ (25 mg, 22.5 μmol) was added to 75 ml of freshly distilled PhCN followed by addition of 160 μl of TBAOH (1.0 M in CH_3OH , 10 equiv.). After stirring for 30 min, fullerene solid dissolved and the solution color changed from brown to dark green. The mixture was continuously stirred for 6 h, then 250 equiv. I_2 was added. The obtained crude product was washed with methanol to remove excess TBAOH and I_2 . As the HPLC shown (Figure S4), the reaction afforded 1 (6.5 mg, 26%) and 2 (7.5 mg, 30%), which are black amorphous solids.

Synthesis of compound 3

Lu₃N@I_h-C₈₀ (4.0 mg, 2.7 μmol) was added to 20 ml of freshly distilled DMF, and the solid could not be dissolved due to its low solubility. Then, 19 μl of TBAOH (1.0 M in MeOH, 10 equiv.) was added to the suspension of Lu₃N@I_h-C₈₀ in DMF under stirring. The suspension rapidly changed to a clear orange solution. After stirring for 2 h, the reaction was quenched by adding 50 equiv. I₂ (34.3 mg, 135 μmol). After removing the solvent under a vacuum and washing with methanol to remove excess TBAOH and I₂, the obtained solid product was dissolved in toluene for separation by HPLC with a Buckyprep column.

Compound **3** (amorphous solid, black; 0.8 mg, yield: 20%): UV-vis-NIR (CS₂) λ_{max}/nm 399, 676, and 719; HRMS (HR-FD): *m/z* [M]⁻ Calcd for C₈₀NOLu₃ 1514.8203; Found 1514.8170.

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 to 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 with dimensions of 0.1 mm × 0.08 mm × 0.06 mm was mounted in a 100 K nitrogen cold stream on an XtaLAB PRO MM007HF diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement, and data reduction. Crystal structures were solved by the direct methods and refined by the full-matrix method based on *F*² using the SHELXLTL software package.⁶³ All the nonhydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically.

Crystal data: C₂₁₄H₈₈N₂₂OSc₃, *M*_w = 3117.94 amu, monoclinic, *P*2₁/*c*, *a* = 14.7749(1) Å, *b* = 32.1377(3) Å, *c* = 32.2789(2) Å, α = γ = 90°, β = 102.007(1)°, *V* = 14991.7(2) Å³, *T* = 100 K,

$Z = 4$, $R_1 = 0.1281$, $wR_2 = 0.3416$, GOF (on F^2) = 1.063, CCDC 2099830.

Computational details

All computations were performed using density functional theory (DFT) methodology with the ADF 2016 program.^{64,65} The exchange-correlation functionals of Becke and Perdew (BP86) and the Slater triple- ζ +polarization (TZP) basis sets were selected for geometry optimizations, vibrational normal modes, and transition state calculations.^{66,67} Scalar relativistic corrections by means of the zeroth-order regular approximation (ZORA) were included, as well as Grimme dispersion corrections.⁶⁸ Solvent effects were described by the conductor-like screening model (COSMO) approximation for dichlorobenzene ($\epsilon=9.8$), dimethylformamide ($\epsilon=37$) and benzonitrile ($\epsilon=25.4$).⁶⁹⁻⁷²

ASSOCIATED CONTENT

Data Availability Statement

CCDC 2099830 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif. All other data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Digital photos of the reaction of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ with TBAOH (1.0 M in CH_3OH) in PhCN. HPLC profiles for reaction crude and purified products of **1** and **2**. ^1H NMR spectra of **1** and **2**. X-ray crystal structure data (CIF). DFT optimized structures of regioisomers of oxazoline derivatives of $\text{Sc}_3\text{N@C}_{80}$, $\text{Lu}_3\text{N@C}_{80}$ epoxide, and the optimized xyz coordinates.

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Notes

The authors declare no competing financial interest.

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