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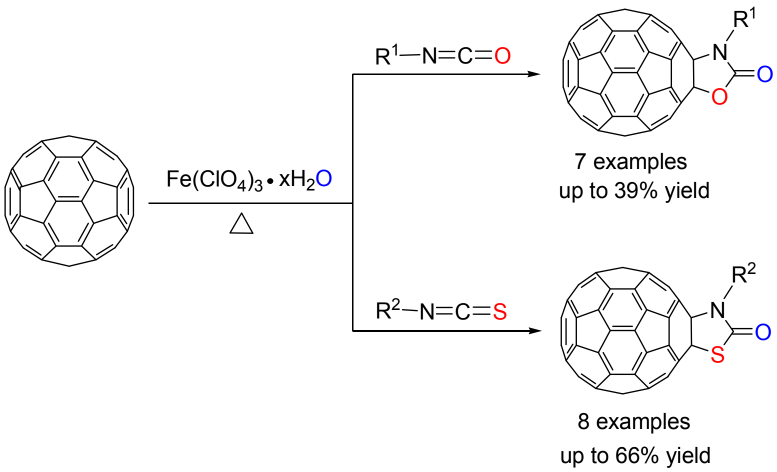

Synthesis of oxazolidinofullerenes/thiazolidinofullerenes: Novel reaction [60]fullerene with isocyanates/isothiocyanates promoted by ferric perchlorate†

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†Electronic supplementary information (ESI) available: NMR spectra of products **2a-g**, **3**, and **5a-h**, UV-vis spectra of **2b** and **5f** as well as HRMS of **2a** and **5a**. See DOI: XXXX

The facile one-step reaction of [60]fullerene with isocyanates/isothiocyanates in the presence of ferric perchlorate generates a series of oxazolidinofullerenes/thiazolidinofullerenes, which will be difficult to prepare by common methods. The direct dissolution approach plays an important role in the efficient synthesis of oxazolidinofullerenes/thiazolidinofullerenes. A possible reaction mechanism for the product formation is proposed.

Introduction

Since the availability of fullerenes in a macroscopic amount, many chemical reactions for the functionalization of fullerenes have been explored and numerous fascinating fullerene derivatives with widely structural diversities have been prepared.[1] Radical reactions[2] are one of the first investigated fullerene reactions and are still important methodologies to functionalize fullerenes.[3] Recently, radical reactions of fullerenes promoted by transition metal salts[2,4] such as $Mn(OAc)_3$,[5] $Fe(ClO_4)_3$,[6] $FeCl_3$,[7] TBADT[$(n\text{–}Bu_4N)_4W_{10}O_{32}$],[8] $Cu(OAc)_2$,[5d,9] $Pb(OAc)_4$,[5g,10] $CoCl_2$dppe,[11] and Ag_2CO_3[12] have attracted extensive attention and have exhibited remarkable advantages over the traditional peroxide- or light-initiated processes. Through which, a large number of novel mono-addition fullerene derivatives have been synthesized. For instance, the reactions of C_{60} with nitriles,[6a] aldehydes/ketones,[6b] malonate esters,[6c] arylboronic acids,[6d] acid chlorides,[6e] and β-keto esters[6f] in the presence of $Fe(ClO_4)_3$ afforded the C_{60}-fused oxazoles, C_{60}-fused 1,3-dioxolanes, C_{60}-fused disubstituted lactones, fullerenyl boronic esters, 1,2-fullerenols, and C_{60}-fused hemiketal and dihydrofuran, respectively.

Although a large variety of fullerene derivatives have been prepared over the past two decades, oxazolidinofullerenes/thiazolidinofullerenes are still relatively scarce until now. Banks[13a] and Luh[13b] almost at the same time reported the synthesis of the first oxazolidinofullerene by chemical transformation of an aziridinofullerene product from cycloaddition of [60]fullerene (C_{60}) with N_3CO_2Et. Minakata and co-workers described the preparation of another four oxazolidinofullerenes by a ring-expansion reaction of aziridinofullerenes with CO_2 catalyzed by PCy_3.[13c] Wang's group recently realized the synthesis of seven oxazolidinofullerenes by the $FeCl_3$-catalyzed reaction of C_{60} with *tert*-butyl *N*-substituted carbamates.[7f] Among the reported oxazolidinofullerene derivatives, only those from Wang's group were prepared directly from C_{60}. However, the one-step methodology of Wang's group mainly afforded alkyl-substituted oxazolidinofullerenes. As for thiazolidinofullerenes, only Gan's group described the synthesis of a few thiazolidinofullerenes through the reaction of aryl isothiocyanates with fullerene epoxides containing four *tert*-butylperoxo groups in the presence of a Lewis acid.[14] It should be noted that the reported methodology for the preparation of thiazolidinofullerenes by Gan et al. required a multi-step procedure starting from C_{60} and gave only thiazolidinofullerenes with multiple addends.[14] On the other hand, oxazolidinofullerenes/thiazolidinofullerenes may have promising applications in life science because oxazolidinones/thiazolidinones have exhibited a wide range of biological activities.[15] Oxazolidinofullerenes/thiazolidinofullerenes are also valuable precursors for further functionalizations.[13a,14] Therefore, it is still demanding to develop new protocol directly from C_{60} to obtain oxazolidinofullerenes/thiazolidinofullerenes, especially the rare aryl-substituted oxazolidinofullerenes as well as the unreported mono-addition thiazolidinofullerenes, in a straightforward and efficient way with a broad substrate scope.

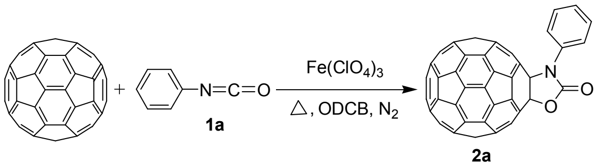
In efforts to extend the $Fe(ClO_4)_3$-mediated radical reactions of C_{60}, herein we describe the one-step reaction of C_{60} with isocyanates/isothiocyanates promoted by $Fe(ClO_4)_3$ to afford a series of scarce aryl-substituted oxazolidinofullerenes and mono-addition thiazolidinofullerenes.

Results and discussion

In our previous study, we found that the direct dissolution[6a-c,6e,6f] of $Fe(ClO_4)_3$ played a crucial role for the efficient synthesis of fullerene derivatives. Similarly, we explored the $Fe(ClO_4)_3$-promoted reaction of C_{60} with various isocyanates by adopting the direct dissolution method, i.e., $Fe(ClO_4)_3$ was first dissolved in a chosen isocyanate, and then the dichlorobenzene (ODCB) solution of C_{60} was added. Much to our satisfaction, we found that the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isocyanates **1a**-**g**, that is, phenyl isocyanate (**1a**), 4-tolyl isocyanate (**1b**), 3-tolyl isocyanate (**1c**), 4-methoxyphenyl isocyanate (**1d**), 3,5-dimethylphenyl isocyanate (**1e**), 4-chlorophenyl isocyanate (**1f**), and 3,4-dichlorophenyl isocyanate (**1g**), afforded oxazolidinofullerenes **2a**-**g**.

Initially, the reaction of C_{60} with phenyl isocyanate (**1a**) in the presence of $Fe(ClO_4)_3$ was chosen to screen the reaction conditions. The details are listed in Table 1. As can be seen from Table 1, the reaction of C_{60}, $Fe(ClO_4)_3$, and **1a** in a molar ratio of 1:2:20 gave oxazolidinofullerene **2a** in 26% of isolated yield at 100 ^{o}C (entry 1, Table 1). Decreasing the reaction temperature to 80 ^{o}C drastically reduced the isolated yield of oxazolidinofullerene **2a** even by extending the reaction time to 22 h (entry 2, Table 1). Increasing the reaction temperature to 120 ^{o}C did not improve the yield of product **2a** (entry 3, Table 1). No benefit to the yield of oxazolidinofullerene **2a** could be achieved by variation of the amount of phenyl isocyanate (entries 4-5, Table 1). Slight lower yield was obtained by increasing or decreasing the amount of $Fe(ClO_4)_3$ (entries 6 and 7 vs entry 1, Table 1). The dissolution of $Fe(ClO_4)_3$ in acetonitrile rather than in **1a** lowered the product yield and gave some unknown highly polar byproducts (entry 8, Table 1). Therefore, the reagent molar ratio of C_{60}/$Fe(ClO_4)_3$/**1a** as 1:2:20 and the reaction temperature as 100 °C together with the direct dissolution method were chosen as the optimized reaction conditions. These optimized reaction conditions could be extended to other isocyanates.

Table 1 Optimization of reaction conditions for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isocyanate **1a**[a]

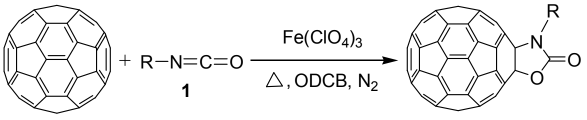


entry	molar ratio[b]	temp. (°C)	time (h)	yield of **2a**[c]
1	**1:2:20**	**100**	**10**	**26% (84%)**
2	1:2:20	80	22	2% (67%)
3	1:2:20	120	10	19% (68%)
4	1:2:10	100	12	7% (64%)
5	1:2:30	100	11	21% (54%)
6	1:1:20	100	12	23% (92%)
7	1:3:20	100	11	19% (40%)
8[d]	1:2:20	100	13	14% (32%)

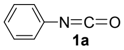
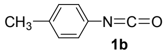
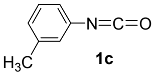
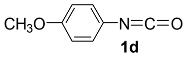
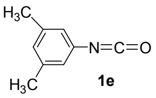
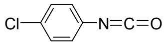
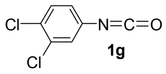
[a] All reactions were performed under protection of nitrogen by the dissolution of $Fe(ClO_4)_3 \cdot xH_2O$ in **1a** (direct dissolution method) unless otherwise indicated. [b] Molar ratio refers to C_{60}/$Fe(ClO_4)_3 \cdot xH_2O$/**1a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] After the mixture of C_{60} with **1a** was dissolved in *o*-dichlorobenzene (6 mL), 2 mL of acetonitrile solution of $Fe(ClO_4)_3 \cdot xH_2O$ was added at the reaction temperature.

The reaction times and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isocyanates **1a-g** under the optimized conditions are summarized in Table 2.

Table 2 Reaction times and yields for the reaction of C_{60} with isocyanates **1a-g** in the presence of $Fe(ClO_4)_3$[a]



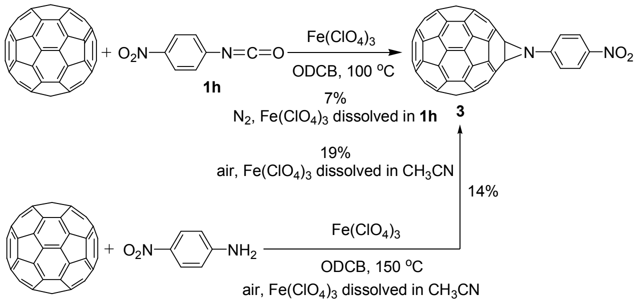
2

isocyanate **1**	time (h)	yield of **2**[b]
 1a	10	26% (84%)
 1b	14	39% (78%)
 1c	24	30% (91%)
 1d	24[c]	20% (65%)
 1e	24	23% (82%)
 1f	10	18% (82%)
 1g	5	9% (41%)

[a] Unless otherwise indicated, all reactions were performed at 100 °C under nitrogen atmosphere, molar ratio of $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{1}$ = 1:2:20. [b] Isolated yield; those in parentheses were based on consumed C_{60}. [c] Molar ratio of $C_{60}/Fe(ClO_4)_3{\cdot}xH_2O/\mathbf{1d}$ = 1:3:20.

As can be seen from Table 2, all of the examined isocyanates **1a-g** bearing either electron-donating groups or electron-withdrawing groups could be successfully utilized to prepare oxazolidinofullerenes **2a-g** in 9-39% yields (41-91% based on consumed C_{60}), comparable to the previously reported data for most monoadducts. In the case of 4-methoxyphenyl isocyanate (**1d**), increasing the amount of $Fe(ClO_4)_3$ to 3 equiv together with prolonging the reaction time to 24 h could provide an acceptable yield (20%) of oxazolidinofullerene **2d**. As for 3,4-dichlorophenyl isocyanate (**1g**), some unknown byproducts besides the desired oxazolidinofullerene **2g** were produced for a long reaction time probably attributed to the higher reactivity of **1g** owing to the existence of two electron-withdrawing chloro groups, and thus shorter reaction time such as 5 h was chosen although the oxazolidinofullerene **2g** was obtained only in 9% yield.

We also investigated the reaction of C_{60} with 4-nitrophenyl isocyanate **(1h)** bearing the stronger electron-withdrawing NO_2 group in the presence of $Fe(ClO_4)_3$ by the dissolution of $Fe(ClO_4)_3$ in **1h** (direct dissolution method), and found that aziridinofullerene **3** was unexpectedly obtained as the major product in 7% of isolated yield under standard experimental conditions for 25 h (Scheme 1). The yield of aziridinofullerene **3** could be increased to 19% (Scheme 1) when the reaction was conducted by the dissolution of $Fe(ClO_4)_3$ in acetonitrile under air conditions for 40 h. To our disappointment, no anticipated oxazolidinofullerene was isolated from the above reaction. Very recently, Yang and co-workers have reported the anhydrous $CuCl_2$-mediated reaction of C_{60} with 4-nitroaniline under air conditions to afford aziridinofullerene **3**.[16] We thus conjectured that the formation of aziridinofullerene **3** should proceed via the $Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitroaniline generated *in situ* by the addition of H_2O in our system to 4-nitrophenyl isocyanate **(1h)** accompanied with the elimination of CO_2. Controlled experiments indicated that the reaction of C_{60}, $Fe(ClO_4)_3$, and 4-nitroaniline by the dissolution of $Fe(ClO_4)_3$ in acetonitrile under air conditions at 150 °C for 22 h produced aziridinofullerene **3** in 14% yield (Scheme 1). It should be noted that controlled experiments were also conducted at 100 °C. Nevertheless, only a trace amount of aziridinofullerene **3** was observed even by prolonging the reaction time to 40 h. The difficulty in preparing aziridinofullerene **3** by the $Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitroaniline was probably attributed to the existence of higher amount of H_2O in the reaction system. In addition, other isocyanates such as *tert*-butyl isocyanate, cyclohexyl isocyanate, methylene diphenyl diisocyanate (MDI), and hexamethylene diisocyanate (HDI) have also be treated with C_{60} and $Fe(ClO_4)_3$ under similar reaction conditions. Unfortunately, the desired oxazolidinofullerenes could not be successfully isolated.



Scheme 1 $Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitrophenyl isocyanate **1h** and 4-nitroaniline affording aziridinofullerene **3**.

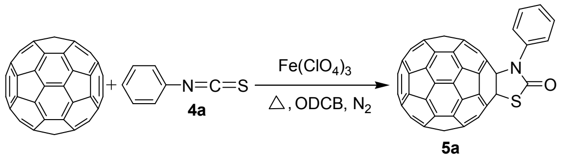
The structures of oxazolidinofullerenes **2a-g** were fully characterized by HR MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-vis spectra. All of high-resolution mass spectra of these oxazolidinofullerene products gave the correct molecular ion peaks. Their ^{1}H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. In their ^{13}C NMR spectra, the peak for the C=O carbon appeared at 152.12-154.51 ppm, and the two sp^3-carbons of the C_{60} skeleton were located at

91.47-93.20 ppm and 78.72-80.17 ppm, close to those of the reported oxazolidinofullerenes in the previous literature.[7*f*,13] No more than 28 peaks including some overlapped ones for the 58 sp^2-carbons of the C_{60} moiety were observed in the range of 136-149 ppm, consistent with the C_s symmetry of their molecular structures. The IR spectra of **2a-g** showed absorptions at 1768-1772 cm^{-1} due to the C=O group. Their UV-vis spectra exhibited a peak at 417-420 nm, which is a diagnostic absorption for the 1,2-adduct of C_{60}, to which the oxygen atom is directly attached.[5*f-h*,6c] Aziridinofullerene **3** is a known compound and its structure was confirmed by comparison of its spectral data with those reported previously.[16]

To expand the scope of the reaction, the substrates were extended from isocyanates to isothiocyanates. Phenyl isothiocyanate (**4a**), 4-fluorophenyl isothiocyanate (**4b**), 4-chlorophenyl isothiocyanate (**4c**), 4-bromophenyl isothiocyanate (**4d**), 4-(trifluoromethyl)phenyl isothiocyanate (**4e**), 4-nitrophenyl isothiocyanate (**4f**), 3-tolyl isothiocyanate (**4g**), and 4-methoxyphenyl isothiocyanate (**4h**) were chosen to react with C_{60} in the presence of $Fe(ClO_4)_3$ by the direct dissolution method, and were found to generate thiazolidinofullerenes **5a-h**.

The reaction conditions were also screened by choosing the reaction of C_{60} with phenyl isothiocyanate (**4a**) promoted by $Fe(ClO_4)_3$. The details are listed in Table 3. As can be seen from Table 3, the reaction of C_{60} with 50 equiv of phenyl isothiocyanate in the presence of 5 equiv of $Fe(ClO_4)_3$ afforded thiazolidinofullerene **5a** in 18% of isolated yield at 100 °C for 18 h (entry 1, Table 3). Decreasing the reaction temperature to 80 ^oC or increasing the reaction temperature to 120 ^oC had no benefit to the isolated yield of product **5a** (entries 2 and 3, Table 3). The variation of the amount of phenyl isothiocyanate and $Fe(ClO_4)_3$ did not improve the isolated yield of thiazolidinofullerene **5a** (entries 4-7, Table 3). The dissolution of $Fe(ClO_4)_3$ in acetonitrile rather than in **4a** obviously reduced the isolated yield of thiazolidinofullerene **5a** even by extending the reaction time to 24 h (entry 8, Table 3). Accordingly, the best molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot xH_2O$:**4a** was 1:5:50, and the reaction temperature was 100 °C. These optimized reaction conditions could also be extended to other isothiocyanates.

Table 3 Optimization of reaction conditions for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isothiocyanate **4a**[a]

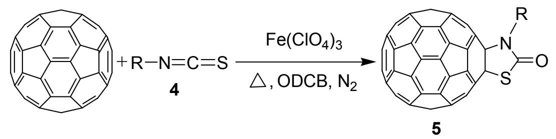


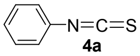
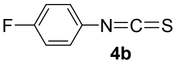
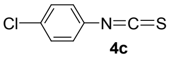
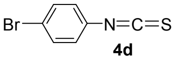
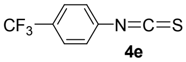
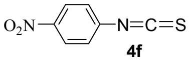
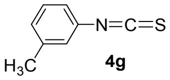
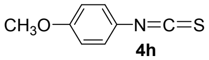
entry	molar ratio[b]	temp. (°C)	time (h)	yield of **5a**[c]
1	**1:5:50**	**100**	**18**	**18% (33%)**
2	1:5:50	80	24	7% (88%)
3	1:5:50	120	2	16% (34%)
4	1:5:30	100	6	12% (27%)
5	1:5:100	100	7	18% (28%)
6	1:3:50	100	24	9% (47%)
7	1:7:50	100	5	18% (23%)
8[d]	1:5:50	100	24	5% (11%)

[a] All reactions were performed under nitrogen conditions by the dissolution of $Fe(ClO_4)_3 \cdot xH_2O$ in **4a** (direct dissolution method) unless otherwise indicated. [b] Molar ratio refers to C_{60}/$Fe(ClO_4)_3 \cdot xH_2O$/**4a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] After the mixture of C_{60} with **4a** was dissolved in *o*-dichlorobenzene (6 mL), 2 mL of acetonitrile solution of $Fe(ClO_4)_3 \cdot xH_2O$ was added at the reaction temperature.

The reaction times and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isothiocyanates **4a-h** under the optimized conditions are summarized in Table 4.

Table 4 Reaction times and yields for the reaction of C_{60} with isothiocyanates **4a-h** in the presence of $Fe(ClO_4)_3$[a]



isocyanate **1**	time (h)	yield of **2**[b]
 **4a**	18	18% (33%)
 **4b**	4	25% (81%)
 **4c**	1	66% (96%)
 **4d**	0.5	59% (82%)
 **4e**	2	26% (62%)
 **4f**	0.5[c]	15% (19%)
 **4g**	4	18% (58%)
 **4h**	14	11% (19%)

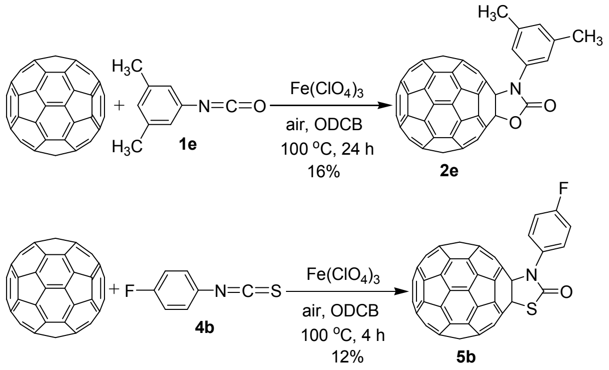
[a] Unless otherwise indicated, all reactions were performed at 100 °C under nitrogen atmosphere, molar ratio of $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/\mathbf{4}$ = 1:5:50. [b] Isolated yield; those in parentheses were based on consumed C_{60}. [c] Molar ratio of $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/\mathbf{4f}$ = 1:2:20 and the reaction temperature = 150 °C.

As can be seen from Table 4, aromatic isothiocyanates bearing either electron-withdrawing or electron-donating groups (**4a-h**) could be successfully employed to prepare thiazolidinofullerenes in 11-66% yields (19-96% based on consumed C_{60}). For the synthesis of thiazolidinofullerene **5f**, higher reaction temperature was required for the melting of **5f** and subsequent dissolution of $Fe(ClO_4)_3$, and thus resulted in the generation of some unknown byproducts even by decreasing the molar ratio of C_{60}:$Fe(ClO_4)_3\cdot xH_2O$:**4f** to 1:2:20. As for 4-methoxyphenyl isothiocyanate (**4h**), an unknown byproduct was produced accompanied with the formation of thiazolidinofullerene **5h**, and accordingly gave the lower product yield. It should be noted the reaction of aliphatic isothiocyanates such as benzyl isothiocyanate and butyl isothiocyanate under the same conditions was also investigated, and found that only less than 5% yield of thiazolidinofullerenes were obtained.

The identities of thiazolidinofullerenes **5a-h** were unambiguously established by HR MS, ^1H NMR, ^{13}C NMR, FT-IR, and UV-vis spectra. Comparing the spectra of **5a-h** with those of **2a-g**, we found that the peak at 152.12-154.51 ppm for the C=O carbon in the ^{13}C NMR spectra of **2a-g** were shifted downfield to 165.72-168.87 ppm in those of **5a-h**, and the peaks at 91.47-93.20 ppm and 78.72-80.17 ppm for the two *sp*^{3}-carbons of the C_{60} skeleton were shifted upfield to 82.62-84.17 ppm and 65.38-67.07 ppm in those of **5a-h**; the absorptions at 1768-1772 cm^{-1} for the carbonyl group in the IR spectra of **2a-g** moved to 1678-1689 cm-1 in those of **5a-h**. The change of the above data agrees well with reported data in the literature.[7*f*,13,14]

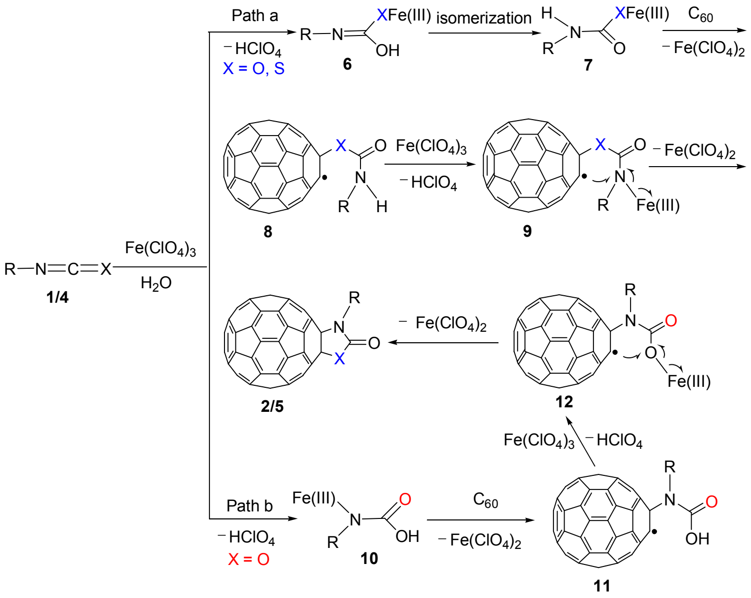
In our previous study, we have found that $C_{60}O$ could be formed via the reaction of

C_{60} with metal oxidants such as $Mn(OAc)_3$[5d] under air conditions. To avoid the formation of $C_{60}O$, the reaction of C_{60} with various organic compounds promoted by metal oxidants such as $Fe(ClO_4)_3$[6] has been manipulated under nitrogen atmosphere in our subsequent study. Therefore, the reaction pathway for the formation of oxazolidinofullerenes/thiazolidinofullerenes **2/5** by the $Fe(ClO_4)_3$-mediated reaction of $C_{60}O$ with isocyanates/isothiocyanates may be excluded under nitrogen atmosphere although the study on the reaction of epoxides with isocyanates/isothiocyanates promoted by different species to result in the generation of oxazolidinones/thiazolidinoes has been reported by different groups.[14,17] To further confirm the plausibility of the above-mentioned conclusion, controlled experiments were also conducted via the reaction of C_{60} with 3,5-dimethylphenyl isocyanate (**1e**) and 4-fluorophenyl isothiocyanate (**4b**) promoted by $Fe(ClO_4)_3$ under air conditions (Scheme 2). Experimental results showed that oxazolidinofullerene **2e** was isolated only in 16% yield when the reaction of C_{60} with 3,5-dimethylphenyl isocyanate (**1e**) was carried out at 100 ^{o}C for 24 h, which are obviously lower than that obtained under nitrogen conditions at 100 ^{o}C for 24 h (23%, Table 2). As for 4-fluorophenyl isothiocyanate (**4b**), the reaction under air conditions produced 12% yield of thiazolidinofullerene **5b** at 100 ^{o}C for 4 h, which are also obviously lower than that obtained under nitrogen conditions at 100 ^{o}C for 4 h (25%, Table 4).



Scheme 2 $Fe(ClO_4)_3$-mediated reaction of C_{60} with 3,5-dimethylphenyl isocyanate **1e** and 4-fluorophenyl isothiocyanate **4b** under air conditions.

On the basis of the previously suggested mechanisms for the reactions of C_{60} with nitriles,[6a] aldehydes/ketones,[6b] arylboronic acids,[6d] and acid chlorides[6e] in the presence of $Fe(ClO_4)_3$ together with the reported results from the reactions[18] of isocyanates with active hydrogen compounds such as H_2O to selectively afford carbonyl derivatives, we propose a possible formation mechanism for oxazolidinofullerenes/thiazolidinofullerenes **2/5** from the reaction of C_{60} with isocyanates/isothiocyanates **1/4** promoted by $Fe(ClO_4)_3$ (Scheme 3, path a). A chosen isocyanate or isothiocyanate reacts with the hydrated water in $Fe(ClO_4)_3{\cdot}xH_2O$ or traces of water in the system to produce Fe(III)-complex **6** accompanied with the elimination of $HClO_4$, and then isomerization to form the more stable Fe(III)-complex **7**. The observed reddening of the mixtures of isocyanates/isothiocyanates and $Fe(ClO_4)_3{\cdot}xH_2O$ hints the formation of complexes between $Fe(ClO_4)_3{\cdot}xH_2O$ and isocyanates/isothiocyanates.[19] Homolytical addition of **7** to C_{60} produces fullerenyl radical **8** with an elimination of $Fe(ClO_4)_2$, followed by coordination with another molecule of $Fe(ClO_4)_3 \cdot xH_2O$ to generate Fe(III)-complex **9**, which undergoes intramolecular cyclization with the loss of a Fe(II) species to afford oxazolidinofullerenes/thiazolidinofullerenes **2**/**5**. It should be noted that the formation of Fe(III)-complex **10** by the reaction of H_2O with carbon–nitrogen double bond of isocyanate in the presence of $Fe(ClO_4)_3$ is also possible (Scheme 3, path b), and then addition of **10** to C_{60} produces fullerenyl radical **11**, which undergoes coordination with another molecule of $Fe(ClO_4)_3 \cdot xH_2O$ to afford Fe(III)-complex **12**, followed by intramolecular cyclization to give oxazolidinofullerenes **2**. As for isothiocyanates, the reaction pathway by addition of H_2O to carbon–nitrogen double bond of isothiocyanate could not afford the corresponding thiazolidinofullerenes **5**, and was thus excluded. The exact reason for the exclusive addition of H_2O to carbon–sulphur double bond of isothiocyanate to afford thiazolidinofullerenes **5** is not quite clear now. Additionally, an oxidative reaction pathway for the formation of oxazolidinofullerenes/thiazolidinofullerenes should also be mentioned, that is, fullerenyl radicals **8** and **11** with the aid of $Fe(ClO_4)_3 \cdot xH_2O$ could be oxidized to the corresponding fullerenyl cations, followed by cyclization with the loss of H^+ to give the **2**/**5**.



Scheme 3 Proposed possible formation mechanism for oxazolidinofullerenes/thiazolidinofullerenes **2**/**5**.

Conclusion

We have synthesized a series of oxazolidinofullerenes/thiazolidinofullerenes via the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isocyanates/isothiocyanates. The current one-step approach to the preparation of oxazolidinofullerenes/thiazolidinofullerenes was obviously more straightforward and practical than the previously reported protocols.[13,14] The direct dissolution of isocyanates/isothiocyanates and $Fe(ClO_4)_3$ proved to be crucial for the efficient synthesis of oxazolidinofullerenes/thiazolidinofullerenes. A plausible reaction mechanism for the formation of oxazolidinofullerenes/thiazolidinofullerenes is suggested.

Experimental section

General procedure for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isocyanates 1a-g

A mixture of isocyanate **1a** (**1b-g**, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (0.10 mmol, 0.15 mmol in the case of **1d**) was added to a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at 100 °C for 10 min to allow ferric perchlorate to dissolve in the liquid isocyanate. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The resulting solution was heated with vigorous stirring in the oil bath at the same temperature under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The resulting solution was directly separated on a silica gel column with carbon disulfide/toluene as the eluent. Oxazolidinofullerene **2a** (**2b-g**) was obtained along with unreacted C_{60}.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isocyanate 1a by the dissolution of $Fe(ClO_4)_3$ in 1a under different conditions

$Fe(ClO_4)_3 \cdot xH_2O$ (0.05-0.15 mmol) and **1a** (0.5-1.5 mmol) was added to a 50-mL three-neck flask, which was equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at desired temperature (80-120 °C) for 10 min to allow $Fe(ClO_4)_3 \cdot xH_2O$ to dissolve in liquid **1a**. Then to the flask was added *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The reaction mixture was vigorously stirred in the oil bath preset at the same temperature under nitrogen atmosphere. The reaction was monitored by TLC and stopped at the designated time (10-22 h). The resulting solution was directly separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and oxazolidinofullerene **2a**.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isocyanate 1a by the dissolution of $Fe(ClO_4)_3$ in acetonitrile

A mixture of C_{60} (36.0 mg, 0.05 mmol) and **1a** (108 μL, 1.0 mmol) was dissolved in *o*-dichlorobenzene (6 mL), and then the resulting solution was deoxygenated by a nitrogen stream for 10 min. After $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol, dissolved in 2 mL of acetonitrile) was added, the reaction mixture was vigorously stirred at 100 ^oC under nitrogen atmosphere for 13 h. The resulting solution was directly separated on a silica gel column with carbon disulfide/toluene as the eluent to give first unreacted C_{60} (20.0 mg, 56%) and then oxazolidinofullerene **2a** (6.0 mg, 14%).

Synthesis of oxazolidinofullerene 2a

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (108 μL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 10 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **2a** (11.2 mg, 26%) as amorphous black solid. mp > 300 ^oC; ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.80 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 152.19 (1C, *C*=O), 147.32 (1C), 147.11 (1C), 145.48 (4C), 145.43, 145.21 (6C), 144.30, 144.14, 144.11 (4C), 143.96, 143.63, 143.53, 143.47, 143.41, 141.79, 141.72 (4C), 141.36, 141.27, 141.03, 140.98, 140.79, 140.51, 138.92, 138.59, 136.57, 136.24, 134.61 (1C, aryl *C*), 128.89 (aryl *C*), 128.66 (aryl *C*), 128.14 (1C, aryl *C*), 91.51 (1C, sp^3-*C* of C_{60}), 78.72 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1771, 1506, 1451, 1430, 1361, 1343, 1227, 1172, 1153, 1087, 1071, 1060, 1016, 954, 857, 832, 738, 689, 546, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 318, 417; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_5NO_2$ [M^+] 855.0320, found 855.0308.

Synthesis of oxazolidinofullerene 2b

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (135 µL, 1.0 mmol) and $Fe(ClO_4)_3·xH_2O$ (46.0 mg, 0.10 mmol) for 14 h afforded first unreacted C_{60} (18.1 mg, 50%) and then **2b** (17.1 mg, 39%) as amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 152.31 (1C, *C*=O), 147.41 (1C), 147.19 (1C), 145.56 (4C), 145.51, 145.30 (4C), 145.27, 144.39, 144.30, 144.23, 144.19, 144.12, 143.71, 143.70, 143.58, 143.51, 141.88, 141.82, 141.80, 141.45, 141.35, 141.11, 141.09, 140.88, 140.61, 139.00, 138.67, 138.18 (1C, aryl *C*), 136.65, 136.27, 132.07 (1C, aryl *C*), 129.42 (aryl *C*), 128.87 (aryl *C*), 91.47 (1C, sp^3-*C* of C_{60}), 78.90 (1C, sp^3-*C* of C_{60}), 20.64 (1C); FT-IR ν/cm^{-1} (KBr) 2916, 2849, 1772, 1512, 1435, 1364, 1352, 1231, 1172, 1155, 1086, 1061, 1014, 954, 864, 809, 793, 742, 546, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 319, 420; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_7NO_2$ [M^+] 869.0477, found 869.0472.

Synthesis of oxazolidinofullerene 2c

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (135 μL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (24.1 mg, 67%) and then **2c** (10.2 mg, 30%) as amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, CS_2/DMSO-*d*$_6$) *δ* 7.55 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-*d*$_6$) (all 2C unless indicated) *δ* 152.24 (1C, *C*=O), 147.32 (1C), 147.10 (1C), 145.47 (4C), 145.42, 145.21 (4C), 145.19, 144.30, 144.17, 144.14, 144.10, 143.98, 143.62, 143.57, 143.46, 143.41, 141.78, 141.72 (4C), 141.35, 141.26, 141.03, 140.98, 140.78, 140.50, 138.91, 138.67 (1C, aryl *C*), 138.58, 136.56, 136.18, 134.52 (1C, aryl *C*), 129.48 (1C, aryl *C*), 128.97 (1C, aryl *C*), 128.46 (1C, aryl *C*), 125.83 (1C, aryl *C*), 91.47 (1C, sp^3-*C* of C_{60}), 78.73 (1C, sp^3-*C* of C_{60}), 20.60 (1C); FT-IR *ν*/cm^{-1} (KBr) 2916, 2848, 1771, 1605, 1488, 1425, 1363, 1350, 1281, 1246, 1188, 1167, 1151, 1086, 1064, 1011, 955, 887, 807, 777, 742, 693, 574, 562, 553, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 319, 418; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_7NO_2$ [M^+] 869.0477, found 869.0476.

Synthesis of oxazolidinofullerene 2d

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (149 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (69.0 mg, 0.15 mmol) for 24 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **2d** (8.9 mg, 20%) as amorphous black solid. mp > 300 °C; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 7.66 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 160.08 (1C, aryl *C*), 154.38 (1C, *C*=O), 148.37 (1C), 148.16 (1C), 146.55, 146.51, 146.48, 145.26 (4C), 146.24, 145.26, 145.19, 145.15, 144.98, 144.82, 144.64, 144.52, 144.48, 144.40, 142.83, 142.75 (4C), 142.39, 142.29, 142.03, 142.01, 141.82, 141.51, 139.97, 139.70, 137.41, 137.04, 130.96 (aryl *C*), 127.72 (1C, aryl *C*), 114.99 (aryl *C*), 92.65 (1C, sp^3-*C* of C_{60}), 80.17 (1C, sp^3-*C* of C_{60}), 55.19 (1C); FT-IR ν/cm^{-1} (KBr) 2973, 2927, 1769, 1607, 1510, 1459,1435, 1369, 1301, 1252, 1169, 1155, 1087, 1049, 1030, 1012, 954, 864, 828, 742, 628, 547, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 417; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_7NO_3$ [M$^+$] 885.0426, found 885.0429.

Synthesis of oxazolidinofullerene 2e

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (141 µL, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 24 h afforded first unreacted C_{60} (25.9 mg, 72%) and then **2e** (10.1 mg, 23%) as amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.35(s, 2H), 7.08 (s, 1H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 154.51 (1C, *C*=O), 148.37 (1C), 148.17 (1C), 146.54, 146.51, 146.47, 146.26 (4C), 146.24, 145.27, 145.19, 145.14, 144.95, 144.76, 144.63, 144.52, 144.46, 144.39, 142.82, 142.75 (4C), 142.38, 142.29, 142.04, 142.00, 141.80, 141.48, 139.98, 139.66, 139.57 (aryl *C*), 137.42, 136.98, 135.01 (1C, aryl *C*), 131.23 (1C, aryl *C*), 127.26 (aryl *C*), 92.86 (1C, sp^3-*C* of C_{60}), 79.99 (1C, sp^3-*C* of C_{60}), 21.42; FT-IR *v*/cm^{-1} (KBr) 2917, 2850, 1771, 1611, 1465, 1435, 1366, 1277, 1230, 1195, 1151, 1088, 1014, 956, 851, 797, 764, 690, 575, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 418; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{69}H_9NO_2$ [M^+] 883.0633, found 883.0641.

Synthesis of oxazolidinofullerene 2f

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (154 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 10 h afforded first unreacted C_{60} (28.1 mg, 78%) and then **2f** (8.1 mg, 18%) as amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 152.13 (1C, *C*=O), 147.33 (1C), 147.11 (1C), 145.48 (4C), 145.43, 145.23 (6C), 144.26, 144.13 (4C), 143.77, 143.73, 143.62, 143.39 (6C), 141.80, 141.73 (4C), 141.35, 141.25, 141.02, 140.91, 140.81, 140.45, 138.92, 138.65, 136.62, 136.43, 134.45 (1C, aryl *C*), 133.16 (1C, aryl *C*), 130.29 (aryl *C*), 128.88 (aryl *C*), 91.62 (1C, sp^3-*C* of C_{60}), 78.57 (1C, sp^3-*C* of C_{60}); FT-IR *v*/cm^{-1} (KBr) 1768, 1490, 1424, 1363, 1349, 1229, 1175, 1154, 1087, 1061, 1010, 953, 863, 820, 810, 736, 725, 541, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 318, 419; HRMS (MALDI-TOF-MS with

4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_4ClNO_2$ [M^+] 888.9931, found 888.9937.

Synthesis of oxazolidinofullerene 2g

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (188 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 5 h afforded first unreacted C_{60} (28.2 mg, 78%) and then **2g** (4.1 mg, 9%) as amorphous black solid. mp > 300 ^oC; ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.07 (s, 1H), 7.78 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 153.86 (1C, *C*=O), 148.41 (1C), 148.21 (1C), 146.58, 146.53 (4C), 146.38, 146.32 (4C), 145.21 (4C), 145.18, 144.65, 144.35, 144.32, 144.27, 144.05 (4C), 142.89, 142.80 (4C), 142.39, 142.31, 142.03, 141.88 (4C), 141.42, 140.06, 139.82, 137.30, 137.29, 134.72 (1C, aryl *C*), 134.16 (1C, aryl *C*), 134.10 (1C, aryl *C*), 131.47 (1C, aryl *C*), 131.30 (1C, aryl *C*), 128.66 (1C, aryl *C*), 93.20 (1C, sp^3-*C* of C_{60}), 79.55 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1769, 1587, 1506, 1470, 1435, 1345, 1226, 1177, 1155, 1086, 1011, 954, 866, 765, 562, 541, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 319, 417; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_3Cl_2NO_2$ [M^+] 922.9541, found 922.9539.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitrophenyl isocyanate 1h by the dissolution of $Fe(ClO_4)_3$ in 1h under nitrogen conditions

According to the general procedure for the preparation of oxazolidinofullerenes **2a-g**, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (164 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) for 25 h afforded first unreacted C_{60} (28.2 mg, 78%) and then aziridinofullerene **3**[16] (3.1 mg, 7%).

$Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitrophenyl isocyanate 1h by the dissolution of $Fe(ClO_4)_3$ in acetonitrile under air conditions

A mixture of C_{60} (36.0 mg, 0.05 mmol) and **1h** (164 mg, 1.0 mmol) was dissolved in *o*-dichlorobenzene (6 mL). After $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol, dissolved in 2 mL of acetonitrile) was added, the reaction mixture was vigorously stirred at 100 °C under air conditions for 40 h. The reaction mixture was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} (28.0 mg, 78%) and then aziridinofullerene **3**[16] (8.1 mg, 19%).

$Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitroaniline by the dissolution of $Fe(ClO_4)_3$ in acetonitrile under air conditions

According to the same procedure as for the preparation of aziridinofullerene **3** by 4-nitrophenyl isocyanate **1h** under air conditions, the reaction of C_{60} (36.0 mg, 0.05 mmol) with 4-nitroaniline (138 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) at 150 °C for 22 h afforded first unreacted C_{60} (30.2 mg, 84%) and then aziridinofullerene **3**[16] (6.0 mg, 14%).

$Fe(ClO_4)_3$-mediated reaction of C_{60} with 3,5-dimethylphenyl isocyanate 1e by the dissolution of $Fe(ClO_4)_3$ in 1e under air conditions

A mixture of 3,5-dimethylphenyl isocyanate **1e** (141 μL, 1.0 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (46.0 mg, 0.10 mmol) was added to a 50-mL round-bottom flask, which was heated in an oil bath preset at 100 °C for 10 min to allow ferric perchlorate to dissolve in the liquid isocyanate. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The reaction mixture was vigorously stirred in the oil bath at the same temperature under air conditions for 24 h. The resulting solution was directly separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} (27.9 mg, 78%) and then oxazolidinofullerene **2e** (7.1 mg, 16%).

General procedure for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with isothiocyanates 4a-h.

A mixture of isothiocyanate **4a** (**4b-h**, 2.5 mmol, 1.0 mmol in the case of **4f**) and $Fe(ClO_4)_3{\cdot}xH_2O$ (0.25 mmol, 0.10 mmol in the case of **4f**) was added to a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at 100 °C (150 °C in the case of **4f**) for 10 min to allow ferric perchlorate to dissolve in the liquid isothiocyanate. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The resulting solution was heated with vigorous stirring in the oil bath at the same temperature under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The reaction mixture was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent. Thiazolidinofullerene **5a** (**5b-h**) was obtained along with unreacted C_{60}.

Fe(ClO$_4$)$_3$-mediated reaction of C$_{60}$ with phenyl isothiocyanate 4a by the dissolution of Fe(ClO$_4$)$_3$ in 4a under different conditions.

$Fe(ClO_4)_3 \cdot xH_2O$ (0.15-0.35 mmol) and **1a** (1.5-5.0 mmol) was added to a 50-mL three-neck flask, which was equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at desired temperature (80-120 ^{o}C) for 10 min to allow $Fe(ClO_4)_3 \cdot xH_2O$ to dissolve in liquid **4a**. Then to the flask was added *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The reaction mixture was vigorously stirred in the oil bath preset at the same temperature under nitrogen atmosphere. The reaction was monitored by TLC and stopped at the designated time (2-24 h). The resulting solution was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and thiazolidinofullerene **5a**.

Fe(ClO$_4$)$_3$-mediated reaction of C$_{60}$ with phenyl isothiocyanate 4a by the

dissolution of $Fe(ClO_4)_3$ in acetonitrile.

A mixture of C_{60} (36.0 mg, 0.05 mmol) and **4a** (296 μL, 2.5 mmol) was dissolved in *o*-dichlorobenzene (6 mL), and then the resulting solution was deoxygenated by a nitrogen stream for 10 min. After $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol, dissolved in 2 mL of acetonitrile) was added, the reaction mixture was vigorously stirred at 100 ^{o}C under nitrogen atmosphere for 24 h. The resulting solution was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give first unreacted C_{60} (19.2 mg, 53%) and then thiazolidinofullerene **5a** (2.3 mg, 5%).

Synthesis of thiazolidinofullerene 5a.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4a** (296 μL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 18 h afforded first unreacted C_{60} (16.1 mg, 45%) and then **5a** (8.0 mg, 18%) as amorphous black solid. mp > 300 ^{o}C; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 167.75 (1C, *C*=O), 150.81, 148.18 (1C), 147.87 (1C), 146.54, 146.32, 146.27, 146.19, 146.09, 145.70, 145.56, 145.26, 145.17, 144.69, 144.58, 144.38, 144.28, 143.10, 143.02, 142.76, 142.68, 142.27, 142.16, 142.02, 141.95, 141.60, 141.56, 140.37, 139.17, 137.04 (1C, aryl *C*), 136.03, 134.34, 131.21 (aryl *C*), 129.64 (aryl *C*), 129.54 (1C, aryl *C*), 84.05 (1C, sp^{3}-*C* of C_{60}), 66.34 (1C, sp^{3}-*C* of

C_{60}); FT-IR *v*/cm^{-1} (KBr) 2918, 2849, 1678, 1487, 1462, 1431, 1313, 1201, 1180, 1154, 1103, 1069, 1051, 882, 842, 814, 743, 690, 548, 524; UV-vis ($CHCl_3$) λ_{max}/nm 258, 319, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_5NOS$ $[M+Na]^+$ 893.9990, found 893.9990.

Synthesis of thiazolidinofullerene 5b.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4b** (308 μL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 4 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **5b** (11.1 mg, 25%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 7.63 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 167.99 (1C, *C*=O), 162.88 (d, $J_{C\text{-}F}$ = 251.5 Hz, 1C, aryl C), 150.68, 148.22 (1C), 147.92 (1C), 146.58, 146.37, 146.31, 146.23, 146.16, 145.67, 145.60, 145.31, 145.21, 144.72, 144.31, 144.29, 144.21, 143.07, 143.05, 142.81, 142.72, 142.27, 142.19, 142.03, 141.97, 141.66, 141.54, 140.42, 139.29, 136.14, 134.30, 133.10 (d, $J_{C\text{-}F}$ = 8.9 Hz, aryl C), 132.89 (d, $J_{C\text{-}F}$ = 3.4 Hz, 1C, aryl C), 116.80 (d, $J_{C\text{-}F}$ = 22.8 Hz, aryl C), 83.98 (1C, sp^3-*C* of C_{60}), 66.29 (1C, sp^3-*C* of C_{60}); FT-IR *v*/cm^{-1} (KBr) 2918, 2849, 1686, 1596, 1504, 1463, 1434, 1315, 1226, 1199, 1150, 1104, 1090, 1050, 885, 860, 816, 551, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 319, 421; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_4FNOS$ $[M+Na]^+$ 911.9895, found 911.9884.

Synthesis of thiazolidinofullerene 5c.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4c** (424 mg, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 1 h afforded first unreacted C_{60} (11.2 mg, 31%) and then **5c** (29.7 mg, 66%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 7.60 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 168.00 (1C, *C*=O), 150.61, 148.23 (1C), 147.93 (1C), 146.59, 146.38, 146.32, 146.24, 146.18, 145.67, 145.61, 145.33, 145.22, 144.72, 144.30, 144.21, 144.18, 143.08, 143.04, 142.82, 142.73, 142.26, 142.19, 142.04, 141.97, 141.69, 141.53, 140.42, 139.34, 136.16, 136.12 (1C, aryl *C*), 135.50 (1C, aryl *C*), 134.30, 132.50 (aryl *C*), 130.06 (aryl *C*), 83.93 (1C, sp^3-*C* of C_{60}), 66.43 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2917, 2849, 1687, 1487, 1463, 1434, 1314, 1199, 1156, 1104, 1087, 1048, 1015, 884, 856, 807, 549, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 320, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_4ClNOS$ $[M+Na]^+$ 927.9600, found 927.9603.

Synthesis of thiazolidinofullerene 5d.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4d** (535 mg, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 0.5 h afforded first unreacted C_{60} (10.2 mg, 28%) and then **5d** (28.1 mg, 59%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.59 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.72 (1C, *C*=O), 149.75, 147.19 (1C), 146.92 (1C), 145.56, 145.35, 145.32, 145.21, 145.17, 144.74, 144.58, 144.31, 144.20, 143.73, 143.43, 143.35, 143.33, 142.14, 142.07, 141.80, 141.72, 141.30, 141.20, 141.08, 140.97, 140.72, 140.57, 139.36, 138.32, 135.38, 135.27 (1C, aryl *C*), 133.54, 132.31 (aryl *C*), 132.04 (aryl *C*), 123.45 (1C, aryl *C*), 82.62 (1C, sp^3-*C* of C_{60}), 65.38 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2918, 2849, 1683, 1484, 1463, 1432, 1314, 1198, 1155, 1102, 1065, 1012, 885, 854, 804, 549, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 320, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_4BrNOS$ $[M+Na]^+$ 971.9095, found 971.9087.

Synthesis of thiazolidinofullerene 5e.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4e** (508 mg, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 2 h afforded first unreacted C_{60} (20.9 mg, 58%) and then **5e** (12.1 mg, 26%) as an amorphous black solid. mp > 300 ^{o}C; ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 168.53 (1C, *C*=O), 150.54, 148.35 (1C), 148.05 (1C), 146.71, 146.51, 146.44, 146.36, 146.32, 145.75, 145.72, 145.46, 145.33, 144.83, 144.37, 144.04 (4C), 143.20, 143.08, 142.94, 142.85, 142.33, 142.29, 142.13, 142.08, 141.79, 141.60, 140.56, 140.33 (1C, aryl *C*), 139.48, 136.37, 134.39, 131.89 (q, $J_{C\text{-}F}$ = 32.8 Hz, 1C, aryl *C*), 131.87 (aryl *C*), 127.02 (q, $J_{C\text{-}F}$ = 3.6 Hz, aryl *C*), 123.45 (q, $J_{C\text{-}F}$ = 271.4 Hz, 1C), 83.98 (1C, sp^3-*C* of C_{60}), 66.80 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2919, 2850, 1689, 1462, 1435, 1322, 1261, 1165, 1125, 1103, 1064, 1041, 1020, 817, 806, 542, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 320, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_4F_3NOS$ $[M+Na]^+$ 961.9863, found 961.9870.

Synthesis of thiazolidinofullerene 5f.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4f** (180 mg, 1.0 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (46.0 mg, 0.10 mmol) at 150 °C for 0.5 h afforded first unreacted C_{60} (8.0 mg, 22%) and then **5f** (6.9 mg, 15%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 8.37 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 168.87 (1C, *C*=O), 150.40, 148.46 (1C), 148.38 (1C, aryl *C*), 148.14 (1C), 146.81, 146.60, 146.52, 146.46, 146.43, 145.81, 145.78, 145.56, 145.42, 144.90, 144.41, 143.85, 143.76, 143.29, 143.08, 143.04, 142.94, 142.82 (1C, aryl *C*), 142.36 (4C), 142.18, 142.16, 141.85, 141.62, 140.66, 139.56, 136.55, 134.41, 132.59 (aryl *C*), 125.19 (aryl *C*), 84.02 (1C, sp^3-*C* of C_{60}), 67.07 (1C, sp^3-*C* of C_{60}); FT-IR *v*/cm^{-1} (KBr) 2922, 2850, 1678, 1606, 1591, 1521, 1490, 1427, 1342, 1313, 1261, 1199, 1155, 1124, 1101, 852, 829, 811, 742, 574, 549, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 320, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{67}H_4N_2O_3S$ $[M+Na]^+$ 938.9840, found 938.9851.

Synthesis of thiazolidinofullerene 5g.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4g**

(338 uL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 4 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **5g** (8.1 mg, 18%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, CS_2/DMSO-*d*$_6$) *δ* 7.39 (s, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 6.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) *δ* 166.78 (1C, *C*=O), 150.08, 147.39 (1C), 147.08 (1C), 145.75, 145.53, 145.49, 145.40, 145.29, 144.93, 144.77, 144.47, 144.40, 143.91, 143.86, 143.72, 143.50, 142.33, 142.24, 141.97, 141.90, 141.49, 141.38, 141.25, 141.17, 140.84, 140.79, 139.59, 139.00 (1C, aryl *C*), 138.38, 136.21 (1C, aryl *C*), 135.19, 133.56, 130.89 (1C, aryl *C*), 129.70 (1C, aryl *C*), 128.84 (1C, aryl *C*), 127.42 (1C, aryl *C*), 83.22 (1C, sp^3-*C* of C_{60}), 65.51 (1C, sp^3-*C* of C_{60}), 20.88 (1C); FT-IR *ν*/cm^{-1} (KBr) 2918, 2849, 1682, 1601, 1488, 1449, 1428, 1314, 1261, 1230, 1174, 1154, 1101, 1069, 775, 761, 691, 574, 548, 524; UV-vis ($CHCl_3$) λ_{max}/nm 257, 320, 422; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_7NOS$ $[M+Na]^+$ 908.0146, found 908.0143.

Synthesis of thiazolidinofullerene 5h.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4h** (345 uL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) for 14 h afforded first unreacted C_{60} (15.2 mg, 42%) and then **5h** (5.1 mg, 11%) as an amorphous black solid. mp > 300 °C; ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) *δ* 7.52 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) *δ* 168.36 (1C, *C*=O), 159.92 (1C, aryl *C*), 150.59, 147.97 (1C), 147.69 (1C), 146.33, 146.12, 146.07, 145.98, 145.89, 145.49, 145.34, 145.06, 144.98, 144.47, 144.39, 144.28, 144.08, 142.90, 142.81, 142.54, 142.47, 142.05, 141.94, 141.81, 141.73, 141.42, 141.34, 140.13, 139.02, 135.77, 134.15, 132.00 (aryl *C*), 129.19 (1C, aryl *C*), 114.80 (aryl *C*), 84.17 (1C, sp^3-*C* of C_{60}), 65.83 (1C, sp^3-*C* of C_{60}), 55.10; FT-IR ν/cm^{-1} (KBr) 2922, 2850, 1686, 1606, 1507, 1462, 1436, 1326, 1297, 1250, 1182, 1156, 1105, 1034, 814, 765, 618, 562, 550, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 321, 427; HRMS (MALDI-TOF-MS with 4-hydroxy-α-cyanocinnamic acid as the matrix) *m*/*z* calcd for $C_{68}H_7NO_2S$ $[M+Na]^+$ 924.0095, found 924.0097.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-fluorophenyl isothiocyanate 4b by the dissolution of $Fe(ClO_4)_3$ in 4b under air conditions.

According to the general procedure for the preparation of thiazolidinofullerenes **5a-h**, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **4b** (308 μL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) under air conditions at 100 °C for 4 h afforded first unreacted C_{60} (29.1 mg, 81%) and then thiazolidinofullerene **5b** (5.2 mg, 12%) as an amorphous black solid.

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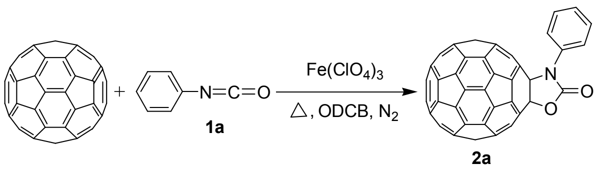
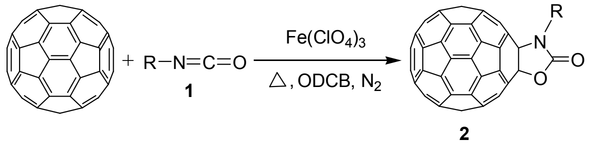
Table 1 Optimization of reaction conditions for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isocyanate **1a**[a]

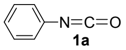
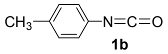
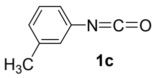
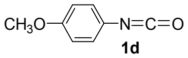
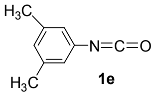
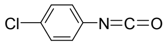
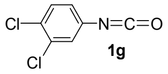


entry	molar ratio[b]	temp. (°C)	time (h)	yield of **2a**[c]
1	**1:2:20**	**100**	**10**	**26% (84%)**
2	1:2:20	80	22	2% (67%)
3	1:2:20	120	10	19% (68%)
4	1:2:10	100	12	7% (64%)
5	1:2:30	100	11	21% (54%)
6	1:1:20	100	12	23% (92%)
7	1:3:20	100	11	19% (40%)
8[d]	1:2:20	100	13	14% (32%)

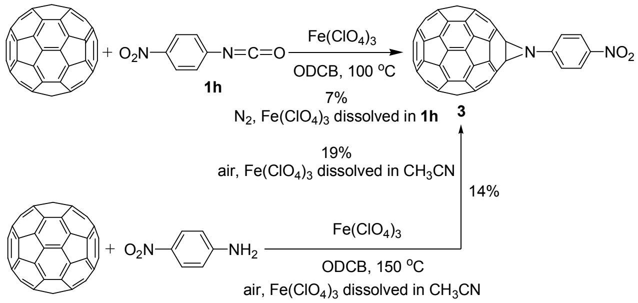
[a] All reactions were performed under protection of nitrogen by the dissolution of $Fe(ClO_4)_3 \cdot xH_2O$ in **1a** (direct dissolution method) unless otherwise indicated. [b] Molar ratio refers to $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/$**1a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] After the mixture of C_{60} with **1a** was dissolved in *o*-dichlorobenzene (6 mL), 2 mL of acetonitrile solution of $Fe(ClO_4)_3 \cdot xH_2O$ was added at the reaction temperature.

Table 2 Reaction times and yields for the reaction of C_{60} with isocyanates **1a-g** in the presence of $Fe(ClO_4)_3$[a]



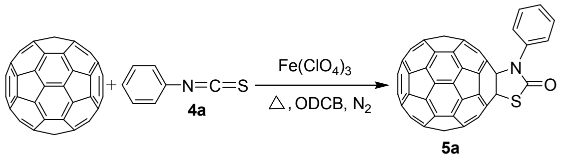
isocyanate **1**	time (h)	yield of **2**[b]
 **1a**	10	26% (84%)
 **1b**	14	39% (78%)
 **1c**	24	30% (91%)
 **1d**	24[c]	20% (65%)
 **1e**	24	23% (82%)
 **1f**	10	18% (82%)
 **1g**	5	9% (41%)

[a] Unless otherwise indicated, all reactions were performed at 100 °C under nitrogen atmosphere, molar ratio of $C_{60}/Fe(ClO_4)_3\cdot xH_2O/\mathbf{1}$ = 1:2:20. [b] Isolated yield; those in parentheses were based on consumed C_{60}. [c] Molar ratio of $C_{60}/Fe(ClO_4)_3\cdot xH_2O/\mathbf{1d}$ = 1:3:20.



Scheme 1 $Fe(ClO_4)_3$-mediated reaction of C_{60} with 4-nitrophenyl isocyanate **1h** and 4-nitroaniline affording aziridinofullerene **3**.

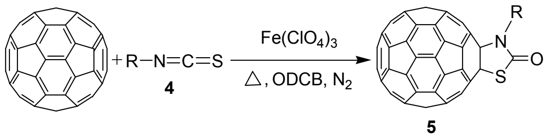
Table 3 Optimization of reaction conditions for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with phenyl isothiocyanate **4a**[a]

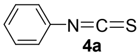
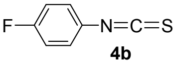
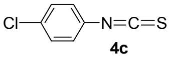
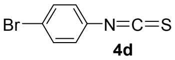
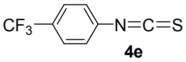
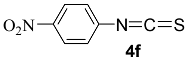
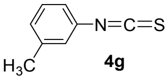
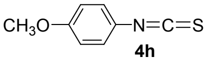


entry	molar ratio[b]	temp. (°C)	time (h)	yield of **5a**[c]
1	**1:5:50**	**100**	**18**	**18% (33%)**
2	1:5:50	80	24	7% (88%)
3	1:5:50	120	2	16% (34%)
4	1:5:30	100	6	12% (27%)
5	1:5:100	100	7	18% (28%)
6	1:3:50	100	24	9% (47%)
7	1:7:50	100	5	18% (23%)
8[d]	1:5:50	100	24	5% (11%)

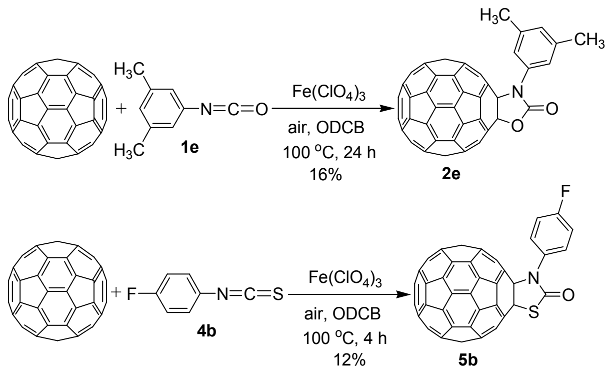
[a] All reactions were performed under nitrogen conditions by the dissolution of $Fe(ClO_4)_3 \cdot xH_2O$ in **4a** (direct dissolution method) unless otherwise indicated. [b] Molar ratio refers to $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/$**4a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] After the mixture of C_{60} with **4a** was dissolved in *o*-dichlorobenzene (6 mL), 2 mL of acetonitrile solution of $Fe(ClO_4)_3 \cdot xH_2O$ was added at the reaction temperature.

Table 4 Reaction times and yields for the reaction of C_{60} with isothiocyanates **4a-h** in the presence of $Fe(ClO_4)_3$[a]

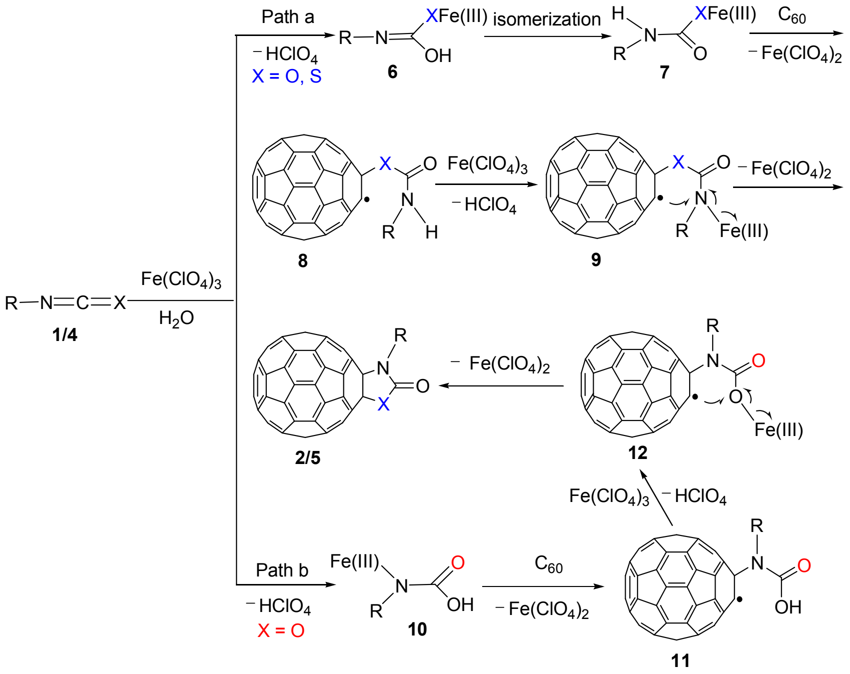


isocyanate **1**	time (h)	yield of **2**[b]
 **4a**	18	18% (33%)
 **4b**	4	25% (81%)
 **4c**	1	66% (96%)
 **4d**	0.5	59% (82%)
 **4e**	2	26% (62%)
 **4f**	0.5[c]	15% (19%)
 **4g**	4	18% (58%)
 **4h**	14	11% (19%)

[a] Unless otherwise indicated, all reactions were performed at 100 °C under nitrogen atmosphere, molar ratio of $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/\mathbf{4}$ = 1:5:50. [b] Isolated yield; those in parentheses were based on consumed C_{60}. [c] Molar ratio of $C_{60}/Fe(ClO_4)_3 \cdot xH_2O/\mathbf{4f}$ = 1:2:20 and the reaction temperature = 150 °C.



Scheme 2 $Fe(ClO_4)_3$-mediated reaction of C_{60} with 3,5-dimethylphenyl isocyanate **1e** and 4-fluorophenyl isothiocyanate **4b** under air conditions.



Scheme 3 Proposed possible formation mechanism for oxazolidinofullerenes/thiazolidinofullerenes **2**/**5**.