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### Ferric perchlorate-mediated one-step reaction of [60]fullerene<sup>DOI-101</sup>/078<sup>9/C5NJ02503F</sup> primary amides for the synthesis of fullerooxazoles<sup>†</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available: NMR spectra of products **2a-o** as well as UV-vis spectra of **2g**, **2h**, and **2o**. See DOI: XXXX

The facile one-step reaction of [60]fullerene with primary amides promoted by cheap and easily available ferric perchlorate afforded a series of interesting fullerooxazole derivatives. The reaction was tolerant of a large variety of primary amides containing aryl, alkyl, and cinnamyl groups. A possible reaction mechanism for the product formation was proposed.

### Introduction

Over the past two decades, chemical modification of fullerenes to produce various fullerene derivatives with different structural motifs have attracted extensive attention in chemical community because functionalized fullerenes have exhibited remarkable potential in areas such as biological and medicinal chemistry, materials, and nanotechnology.<sup>1</sup> Accordingly, the development of functionalization methods for fullerenes is of great significance. Generally speaking, the majority of chemical

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Wiew Article Online modification of fullerenes includes cycloadditions, nucleophilic additions, Tadical

additions, etc.<sup>1,2</sup> Radical additions are one of the first investigated reaction types of fullerenes and continue to be of interest and important methodologies to functionalize fullerenes.<sup>3</sup> Nevertheless, the radical additions of parent fullerenes induced by traditional peroxide or light tend to result in the generation of multi-addition fullerene products, which would be extremely difficult to separate and characterize. In efforts to avoid the formation of multi-addition products, various types of transition metal salts<sup>3,4</sup> such as Mn(OAc)<sub>3</sub>,<sup>5</sup> Fe(ClO<sub>4</sub>)<sub>3</sub>,<sup>6</sup> FeCl<sub>3</sub>,<sup>7</sup> TBADT[(n-Bu<sub>4</sub>N)<sub>4</sub>W<sub>10</sub>O<sub>32</sub>],<sup>8</sup>  $Cu(OAc)_{2}$ , <sup>5d,9</sup> Pb(OAc)<sub>4</sub>, <sup>5g,10</sup> CoCl<sub>2</sub>dppe, <sup>11</sup> and Ag<sub>2</sub>CO<sub>3</sub><sup>12</sup> were employed as new promoters of fullerene radical reactions. The radical reactions of fullerenes promoted by transition metal salts were found to proceed well under mild conditions and could generate a large number of novel mono-addition fullerene adducts that are relatively easy to isolate and purify. For example, a large variety of rare fullerene derivatives including oxazolines, 1,3-dioxolanes, disubstituted C<sub>60</sub>-fused lactones, boronic esters, 1,2-fullerenols, hemiketals, oxazolidinofullerenes/thiazolidinofullerenes, and dioxanes/dioxepanes could be successfully obtained through the Fe(ClO<sub>4</sub>)<sub>3</sub>-mediated radical reaction of C<sub>60</sub> with nitriles,<sup>6a</sup> aldehydes/ketones,<sup>6b</sup> malonate esters,<sup>6c</sup> arylboronic acids,<sup>6d</sup> acid chlorides,<sup>6e</sup> β-keto esters,<sup>6f</sup> isocyanates/isothiocyanates,<sup>6g</sup> and diols,<sup>6h</sup> respectively. Therefore, the further exploration and development of novel radical reactions of fullerenes promoted by transition metal salts is still demanded.

Fullerooxazoles are a class of oxazoline-containing fullerene derivatives, which may have promising applications in life science because a great number of

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View Article Online oxazoline-containing natural products and biologically active compounds are present in marine organisms.<sup>13</sup> On the other hand, fullerooxazoles may have great benefits for the preparation of a large variety of organic photovoltaic devices because the presence of two electronegative atoms directly connected to the C<sub>60</sub> skeleton enables fullerooxazoles to have better electron acceptor character than  $C_{60}$ .<sup>7c</sup> Initially, fullerooxazoles were prepared via either thermal reactions<sup>14*a*,*b*</sup> of  $C_{60}$  with azidoformates and hydroxamic acid derivatives or photochemical reactions<sup>14c</sup> of C<sub>60</sub> with arylazides, followed by rearrangement of the formed fulleroaziridines to fullerooxazoles. However, these methods undergo a two-step process and require the use of highly toxic and explosive azides. Gao<sup>15a</sup> and Wang<sup>6a</sup> subsequently developed a straightforward approach to the preparation of fullerooxazoles via cycloadditions of  $C_{60}$ with nitriles under electrochemical or  $Fe(ClO_4)_3$ -mediated conditions. Nevertheless, the two methods require a large amount of nitriles (100 equiv. or solvent amounts), and the electrochemical method is only limited to benzonitrile, which dramatically decreases its practicability. Recently, fullerooxazoles were also synthesized via different reactions of C<sub>60</sub> promoted by t-BuOI, <sup>15b</sup> PhI(OAc)<sub>2</sub>/I<sub>2</sub>, <sup>15c</sup> CuI/Phen,<sup>15d</sup> and FeCl<sub>2</sub>,<sup>15e</sup> respectively. However, these methods require expensive and unaccessible reagents as promoters, ligands or reactants. For example, the reaction promoted by FeCl<sub>2</sub> requires the unavailable N-substituted amides as reaction and the PhI(OAc)<sub>2</sub>/I<sub>2</sub>-mediated synthesis must be manipulated under substrates.<sup>15e</sup> photo-irradiation conditions.<sup>15c</sup> Hence, it is still demanding to develop new protocol to obtain fullerooxazoles in a more practical and convenient way with a broad substrate

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scope. In continuation of our interest in fullerene chemistry,  ${}^{6g,h,16}$  herein we describe a one-step reaction of C<sub>60</sub> with primary amides promoted by cheap and easily available Fe(ClO<sub>4</sub>)<sub>3</sub> to afford a variety of interesting fullerooxazoles with a high tolerance of functional groups (Scheme 1).



Scheme 1  $Fe(ClO_4)_3$ -mediated reaction of  $C_{60}$  with primary amides affording fullerooxazoles.

### **Results and discussion**

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Initially, we investigated the reaction of  $C_{60}$  with benzoyl isothiocyanate in the presence of Fe(ClO<sub>4</sub>)<sub>3</sub> by the direct dissolution method, that is, Fe(ClO<sub>4</sub>)<sub>3</sub> was first dissolved in benzoyl isothiocyanate, and then the *o*-dichlorobenzene (ODCB) solution of  $C_{60}$  was added. We found that fullerooxazole **2a** was unexpectedly obtained as the major product in 17% isolated yield at 100 °C for 14 h (Scheme 2). We conjectured that the formation of fullerooxazole **2a** might proceed via the Fe(ClO<sub>4</sub>)<sub>3</sub>-mediated reaction of  $C_{60}$  with benzamide **1a** generated *in situ* by the addition of H<sub>2</sub>O in our system to benzoyl isothiocyanate accompanied with the elimination of CO<sub>2</sub> and H<sub>2</sub>S.<sup>17</sup> Controlled experiments indicated that the reaction of  $C_{60}$  with benzamide **1a** promoted by Fe(ClO<sub>4</sub>)<sub>3</sub> at 100 °C for 13 h produced the desired fullerooxazole **2a** in 19% yield as a major product (Scheme 2). It should be noted that the easy generation of benzamide **1a** from benzoyl isothiocyanate was attributed to the high reactivity of benzoyl isothiocyanate due to the existence of the strong electron-withdrawing

carbonyl group in its molecular structure.



Scheme 2  $Fe(ClO_4)_3$ -mediated reaction of  $C_{60}$  with benzoyl isothiocyanate and benzamide **1a** affording fullerooxazole **2a**.

These experimental results shown in Scheme 2 provided a good idea for us to realize the efficient synthesis of fullerooxazoles via a simple one-step reaction promoted by  $Fe(ClO_4)_3$ . Although benzoyl isothiocyanate and benzamide **1a** can be employed to synthesize fullerooxazole **2a**, benzoyl isothiocyanate as starting materials is relatively expensive and more difficult to attain than the corresponding benzamide. Therefore, amides were selected as the reaction substrates to extend the synthesis of fullerooxazoles.

At the onset, the reaction of  $C_{60}$  with benzamide (**1a**) in the presence of  $Fe(ClO_4)_3$  was chosen to screen the reaction conditions. In our previous study, we have found that the reactions of  $C_{60}$  promoted by metal oxidants such as  $Mn(OAc)_3^{5d}$  under air conditions could result in the generation of  $C_{60}O$ . To avoid the formation of  $C_{60}O$ , herein we have manipulated the  $Fe(ClO_4)_3$ -mediated reaction of  $C_{60}$  with amides under nitrogen atmosphere. As can be seen from Table 1, the reaction of  $C_{60}$ ,

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Fe(ClO<sub>4</sub>)<sub>3</sub>, and **1a** in a molar ratio of 1:1:5 gave fullerooxazole **2a** in 29% <sup>1</sup>Solated<sup>2/C5NJ02503F</sup> yield at 150 °C for 1 h (entry 1, Table 1). Increasing the reaction temperature to 170 <sup>o</sup>C did not improve the yield of product **2a** (entry 2, Table 1). Decreasing the reaction temperature to 130 °C or 100 °C obviously reduced the isolated yield of product 2a (entries 3 and 4, Table 1). The variation of the amount of benzamide (from 3 to 8 equiv.) and  $Fe(ClO_4)_3$  (from 1 to 2 equiv.) had also no benefit to the isolated yield of product 2a (entries 5-8, Table 1). Thus, the reagent molar ratio of  $C_{60}/Fe(ClO_4)_3/1a$  as 1:1:5, the reaction temperature as 150 °C together with the protection of nitrogen were chosen as the optimized reaction conditions. In addition, other metal oxidants such as FeCl<sub>3</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>, CuCl<sub>2</sub>·2H<sub>2</sub>O, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O, and  $Mg(ClO_4)_2$  were also examined under the optimized conditions (entries 9-15, Table 1). Unfortunately, these metal oxidants instead of  $Fe(ClO_4)_3$  only led to the formation of a trace amount or no yield of product 2a, and thus  $Fe(ClO_4)_3$  has been proved to be the best oxidant.

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**Table 1** Optimization of reaction conditions for the  $Fe(ClO_4)_3$ -mediated reaction of  $C_{60}$  with benzamide  $\mathbf{1a}^{a}$ 

$+ \underbrace{1a}^{O} H_{2} \xrightarrow{\text{additive}} V_{O} \xrightarrow{N} O$						
			2	2a		
Entry	Additive	Molar ratio <sup>b</sup>	Temp. (°C)	Time (h)	Yield of $2a^c$	
1	$Fe(ClO_4)_3 \cdot xH_2O$	1:1:5	150	1	29% (94%)	
2	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:5	170	0.5	29% (58%)	
3	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:5	130	3	22% (88%)	
4	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:5	100	5	19% (86%)	
5	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:8	150	1.5	29% (74%)	

6	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:3	150	1	19% (86%)
7	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:1:2	150	1	14% (56%)
8	Fe(ClO <sub>4</sub> ) <sub>3</sub> ·xH <sub>2</sub> O	1:2:5	150	0.5	24% (41%)
9	FeCl <sub>3</sub>	1:1:5	150	4	trace
10	FeCl <sub>3</sub> ·6H <sub>2</sub> O	1:1:5	150	4	0
11	CuCl <sub>2</sub>	1:1:5	150	3	0
12	$CuCl_2 \cdot 2H_2O$	1:1:5	150	4	0
13	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	1:1:5	150	3	0
14	Mn(OAc) <sub>3</sub> ·2H <sub>2</sub> O	1:1:5	150	3	0
15	$Mg(ClO_4)_2$	1:1:5	150	3	0

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<sup>*a*</sup>All reactions were performed under nitrogen conditions. <sup>*b*</sup>Molar ratio refers to  $C_{60}$ /additive/1a. <sup>*c*</sup> Isolated yield; those in parentheses were based on consumed  $C_{60}$ .

To expand the scope of the Fe(ClO<sub>4</sub>)<sub>3</sub>-mediated reaction of  $C_{60}$  with primary amides, the substrates were extended from benzamide (**1a**) to other representative amides. 4-methoxybenzamide (**1b**), 3,4-dimethoxybenzamide (**1c**), 4-methylbenzamide (**1d**), 2,4-dimethylbenzamide (**1e**), 4-chlorobenzamide (**1f**), 2-chlorobenzamide (**1g**), 2,6-dichlorobenzamide (**1h**), 4-nitrobenzamide (**1i**), 3-nitrobenzamide (**1j**), 1-naphthylamide (**1k**), 2-furamide (**1l**), 2-phenylacetamide (**1m**), hexanamide (**1n**), and cinnamamide (**1o**), were chosen to react with C<sub>60</sub> in the presence of Fe(ClO<sub>4</sub>)<sub>3</sub>, and were found to afford the desired fullerooxazoles **2b-o**. The reaction times and yields for the Fe(ClO<sub>4</sub>)<sub>3</sub>-mediated reaction of C<sub>60</sub> with primary amides **1a-o** under the optimized conditions are summarized in Table 2.

**Table 2** Reaction times and yields for the reaction of  $C_{60}$  with primary amides **1a-o** in the presence of  $Fe(ClO_4)_3^a$ 



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Amide 1	Time (h)	Yield of $2^b$
	1	29% (94%)
CH <sub>3</sub> O-CONH <sub>2</sub> 1b	2	23% (92%)
$CH_3O \longrightarrow CONH_2$ $CH_3O$	2	16% (84%)
$CH_3 - CONH_2$ 1d	0.5	27% (93%)
CH <sub>3</sub> -CONH <sub>2</sub> 1e CH <sub>3</sub>	1	25% (89%)
	1	23% (82%)
	1	17% (85%)
	2	18% (82%)
	1.5	20% (91%)
NO <sub>2</sub> CONH <sub>2</sub> 1j	2	17% (89%)
	1.5	16% (84%)
	2	17% (89%)
CH <sub>2</sub> CONH <sub>2</sub> 1m	1.5	21% (84%)
CONH <sub>2</sub> 1n	1	19% (76%)
NH <sub>2</sub>	1.5	10% (83%)

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<sup>a</sup> All reactions were performed at 150 °C under atmosphere, molar nitrogen ratio of  $C_{60}/Fe(ClO_4)_3$ :xH<sub>2</sub>O/1 = 1:1:5. <sup>b</sup> Isolated yield; those in parentheses were based on consumed C<sub>60</sub>.

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As can be seen from Table 2, aromatic amides bearing electron-withdrawing groups<sup>(C5NJ025037)</sup> or electron-donating groups (1a-1), aliphatic amides (1m and 1n), and cinnamamide (1o) could be successfully employed to prepare fullerooxazoles. Aromatic amides (1a-1) and aliphatic amides (1m and 1n) usually gave fullerooxazoles 2a-n in moderate to good yields (16-29% isolated yields), comparable to the previously reported data for most monoadducts. As for cinnamamide (1o), only 10% yield of fullerooxazole 2o was produced probably due to the lower reactivity of 1o owing to the existence of an additional conjugate double bond in its molecular structure. Additionally, functional groups such as Cl and NO<sub>2</sub> could be tolerated under our reaction conditions and could be further transformed to other moieties.

Products **2a-f** and **2i-n** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature.<sup>6a,14c,15a-e</sup> New compounds **2g**, **2h**, and **2o** were unambiguously characterized by their HR MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and UV-vis spectra. All of high-resolution mass spectra of these fullerooxazole products gave the correct  $[M+H]^+$  peaks. Their <sup>1</sup>H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. In their <sup>13</sup>C NMR spectra, the typical peak for the *C*=N carbon appeared at 163.60-164.57 ppm, and no more than 30 peaks in the range of 135-148 ppm for the 58 sp<sup>2</sup>-carbons of the C<sub>60</sub> moiety together with two peaks at 96.17-96.42 ppm and 91.08-91.43 ppm for the two sp<sup>3</sup>-carbons of the C<sub>60</sub> moiety were observed, consistent with the C<sub>s</sub> symmetry of their molecular structures. In their IR spectra, the absorption at 1638-1672 cm<sup>-1</sup> also demonstrated the presence of the C=N moiety. Their UV-vis

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view Article Online spectra exhibited a diagnostic absorption at 415-416 nm for the 1,2-adduct of  $C_{60}^{\text{OI: 10.1039/C5NJ02503F}}$ 

On the basis of the previously suggested mechanisms for the reactions of  $C_{60}$  with nitriles,<sup>6a</sup> aldehydes/ketones,<sup>6b</sup> malonate esters,<sup>6c</sup> arylboronic acids,<sup>6d</sup> acid chlorides,<sup>6e</sup>  $\beta$ -keto esters, <sup>6f</sup> isocyanates/isothiocyanates, <sup>6g</sup> and diols<sup>6h</sup> in the presence of Fe(ClO<sub>4</sub>)<sub>3</sub>. We propose a possible formation mechanism for fullerooxazoles 2 from the reaction of  $C_{60}$  with primary amides 1 promoted by  $Fe(ClO_4)_3$  (Scheme 3). A chosen amide reacts with  $Fe(ClO_4)_3$  to generate Fe(III)-complex 3 accompanied with the elimination of HClO<sub>4</sub>. Homolytical addition of **3** to  $C_{60}$  produces fullerenyl radical **4** with an elimination of Fe(ClO<sub>4</sub>)<sub>2</sub>, followed by coordination with another molecule of  $Fe(ClO_4)_3$  to give Fe(III)-complex 5, in which the radical can either attack the oxygen atom of the carbonyl group with the loss of a Fe(II) species to afford fullerooxazoles 2 (path a) or attack the nitrogen atom to form N-acyl aziridinofullerene 6 (path b), followed by rearrangement to give fullerooxazoles 2. It should be noted that the rearrangement of N-acyl aziridinofullerenes under high temperature conditions (about 150 °C) to produce fullerooxazoles has been experimentally confirmed by different groups in previous literature,<sup>14a-c</sup> and thus the reaction pathway (path b) for the formation of fullerooxazoles is also reasonable although the crucial aziridinofullerene intermediate 6 could not be isolated even by decreasing the reaction temperature and shortening the reaction time.

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Scheme 3 Proposed reaction mechanism for the formation of fullerooxazoles 2.

### Conclusion

In summary, the simple one-step synthesis of fullerooxazoles has been readily achieved via the reaction of  $C_{60}$  with primary amides promoted by  $Fe(ClO_4)_3$ . The current approach to the preparation of fullerooxazoles from cheap and easily accessible  $Fe(ClO_4)_3$  and primary amides is obviously more straightforward and practical than the previous protocols.<sup>6a,14,15</sup> A plausible reaction mechanism for the formation of fullerooxazoles is also suggested.

### **Experimental**

### Materials and instruments

All reagents and solvents were used directly as obtained commercially unless otherwise noted. All of primary amides besides benzamide were synthesized by the reaction of aldehydes with hydroxylamine hydrochloride in the presence of Na<sub>2</sub>CO<sub>3</sub>

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and catalytic quantities of CuBr<sub>2</sub>. All of fullerene products were purified  $B_{y}^{O(25NJO2503F)}$ chromatography over silica gel (200-300 mesh). The UV-vis spectra were measured in CHCl<sub>3</sub> using a Shimadzu UV-2401 spectrometer. IR spectra were taken on a SPECTRUM ONE NTS spectrometer with KBr pellets. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a WIPM 400 spectrometer. Chemical shifts in <sup>1</sup>H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, and chemical shifts in <sup>13</sup>C NMR spectra were referenced to residual CHCl<sub>3</sub> at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

### General procedure for the $Fe(ClO_4)_3$ -mediated reaction of $C_{60}$ with primary amides 1a-o

To a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer was charged with C<sub>60</sub> (36.0 mg, 0.05 mmol),  $Fe(ClO_4)_3 \cdot xH_2O$  (23.0 mg, 0.05 mmol), and primary amide 1a (1b-o, 0.25 mmol). After they were completely dissolved in ODCB (6 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 150 °C under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The reaction mixture was filtered through a silica gel plug in order 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 afford first unreacted C<sub>60</sub> and then fullerooxazole 2a

(2b-o) as an amorphous black solid.

2-Phenyl-oxazolo[4,5:1,2][60]fullerene (2a). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **1a** (30.0 mg, 0.25 mmol) and  $Fe(ClO_4)_3$  xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C<sub>60</sub> (24.9 mg, 69%) and then  $2a^{6a,14c,15a-e}$  (12.2 mg, 29%) as an amorphous black solid. MP > 300 °C: <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/DMSO- $d_6$ )  $\delta$  8.39 (d, J = 7.0 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.61 (t, J = 7.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CS<sub>2</sub>/DMSO- $d_6$  with Cr(acac)<sub>3</sub> as relaxation reagent) (all 2C unless indicated)  $\delta$  164.05 (1C, C=N), 147.12 (1C), 147.06, 146.71 (1C), 145.32 (4C), 145.18, 145.03, 144.97, 144.69, 144.55, 144.41, 144.16, 144.05, 143.79, 143.53, 143.22, 142.61, 141.75, 141.72, 141.64, 141.32 (4C), 141.23, 141.09, 140.95 (4C), 139.39, 138.58, 136.79, 135.10, 131.66 (1C, aryl C), 128.33 (aryl C), 127.98 (aryl C), 125.92 (1C, aryl C), 96.26 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 91.25 (1C, sp<sup>3</sup>-C of C<sub>60</sub>); FT-IR v/cm<sup>-1</sup> (KBr) 1641, 1578, 1492, 1448, 1430, 1325, 1235, 1179, 1141, 1090, 1068, 983, 932, 841, 773, 690, 576, 562, 525.

2-(4-Methoxyphenyl)-oxazolo[4,5:1,2][60]fullerene (2b). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **1b** (38.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>: $xH_2O$  (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C<sub>60</sub> (27.1 mg, 75%) and then  $2b^{6a,14c,15b-d}$  (9.9 mg, 23%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 3.96 (s, 3H).

2-(3,4-Dimethoxyphenyl)-oxazolo[4,5:1,2][60]fullerene (2c). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with 1c (45.0 mg, 0.25

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mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>:xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted  $C_{60}^{039/C5NJ02503F}$ (29.1 mg, 81%) and then  $2c^{6a}$  (7.0 mg, 16%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.04 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.06 (d,

*J* = 8.4 Hz, 1H), 4.06 (s, 3H), 4.02 (s, 3H).

**2-(4-Methylphenyl)-oxazolo[4,5:1,2][60]fullerene** (**2d**). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1d** (34.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·*x*H<sub>2</sub>O (23.0 mg, 0.05 mmol) for 0.5 h afforded first unreacted C<sub>60</sub> (25.4 mg, 71%) and then **2d**<sup>6a</sup> (11.4 mg, 27%) as an amorphous black solid: mp > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.33 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 2.55 (s, 3H).

**2-(2,4-Dimethylphenyl)-oxazolo[4,5:1,2][60]fullerene** (**2e**). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1e** (37.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·*x*H<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C<sub>60</sub> (25.9 mg, 72%) and then **2e**<sup>15c</sup> (10.9 mg, 25%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/DMSO-*d*<sub>6</sub>)  $\delta$  8.21 (d, *J* = 7.4 Hz, 1H), 7.22 (s, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 2.94 (s, 3H), 2.47 (s, 3H).

**2-(4-Chlorophenyl)-oxazolo[4,5:1,2][60]fullerene** (**2f**). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1f** (39.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>:xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C<sub>60</sub> (25.9 mg, 72%) and then **2f**<sup>15b-d</sup> (10.1 mg, 23%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.39 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H).

2-(2-Chlorophenyl)-oxazolo[4,5:1,2][60]fullerene (2g). According to the general

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procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **1g** (39.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C<sub>60</sub> (28.7 mg, 80%) and then 2g (7.3 mg, 17%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  8.36 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.4 Hz, 1H), 7.51-7.61 (m, 2H); <sup>13</sup>C NMR (100 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> with Cr(acac)<sub>3</sub> as relaxation reagent) (all 2C unless indicated)  $\delta$  163.60 (1C, C=N), 147.39 (1C), 146.98 (1C), 146.76, 145.60 (4C), 145.46, 145.29, 145.24, 145.02, 144.84, 144.66, 144.42, 144.32, 144.04, 143.75, 143.45, 142.45, 141.99, 141.95, 141.88, 141.57, 141.47 (4C), 141.32, 141.20, 141.17, 139.63, 138.86, 137.01, 135.49, 133.99 (1C, aryl C), 132.04 (1C, aryl C), 131.56 (1C, aryl C), 130.68 (1C, aryl C), 126.23 (1C, aryl C), 125.52 (1C, aryl C), 96.42 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 91.43 (1C, sp<sup>3</sup>-C of C<sub>60</sub>); FT-IR  $\nu$ /cm<sup>-1</sup> (KBr) 1638, 1591, 1473, 1432, 1326, 1259, 1179, 1141, 1103, 1061, 1041, 981, 951, 931, 776, 763, 728, 562, 526; UV-vis (CHCl<sub>3</sub>)  $\lambda_{max}/nm$  257, 317, 415, 686; MALDI-TOF MS m/z calcd for C<sub>67</sub>H<sub>5</sub>ClNO [M+H]<sup>+</sup> 874.0060, found 874.0059.

2-(2,6-Dichlorophenyl)-oxazolo[4,5:1,2][60]fullerene (2h). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **1h** (48.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C<sub>60</sub> (27.9 mg, 78%) and then **2h** (8.1 mg, 18%) as an amorphous black solid. MP > 300 <sup>o</sup>C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  7.58 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CS<sub>2</sub>/DMSO- $d_6$  with Cr(acac)<sub>3</sub> as relaxation reagent) (all 2C unless indicated)  $\delta$  160.64 (1C, C=N), 147.05 (1C), 146.65 (1C), 146.14, 145.30, 145.26, 145.15, 144.97, 144.91, 144.71, 144.48, 144.37, 144.09, 143.99, 143.69,

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907.9671. 2-(3-Nitrophenyl)-oxazolo[4,5:1,2][60]fullerene (2j). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with 1j (42.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>:xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted  $C_{60}$  (29.2

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mg, 81%) and then  $2j^{15c}$  (7.4 mg, 17%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz,  $CS_2/CDCl_3$ )  $\delta$  9.28 (s, 1H), 8.81 (d, J = 7.6 Hz, 1H), 8.54 (d, J = 8.2Hz, 1H), 7.86 (t, J = 7.9 Hz, 1H). 2-(1-Naphthylphenyl)-oxazolo[4,5:1,2][60]fullerene (2k). According to the

general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with 1k (43.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted  $C_{60}$  (29.1 mg, 81%) and then  $2k^{15c}$  (7.1 mg, 16%) as an amorphous black solid. MP >

143.41, 143.13, 141.89, 141.67, 141.62, 141.56, 141.24, 141.17, 141.14, DP41000, PPC5NJ02503F 140.87 (4C), 139.35, 138.60, 136.63, 135.15, 134.18 (aryl C), 132.14 (1C, aryl C), 127.61 (aryl C), 126.37 (1C, aryl C), 96.17 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 91.08 (1C, sp<sup>3</sup>-C of C<sub>60</sub>); FT-IR v/cm<sup>-1</sup> (KBr) 1672, 1561, 1431, 1384, 1295, 1275, 1236, 1194, 1128, 1084, 1042, 977, 957, 927, 841, 794, 771, 562, 526; UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub>/nm 256, 317, 416, 688; MALDI-TOF MS m/z calcd for C<sub>67</sub>H<sub>4</sub>Cl<sub>2</sub>NO [M+H]<sup>+</sup> 907.9670, found

2-(4-Nitrophenyl)-oxazolo[4,5:1,2][60]fullerene (2i). According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with 1i (42.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>:xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C<sub>60</sub> (28.1 mg, 78%) and then  $2i^{6a,15b-d}$  (8.9 mg, 20%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz,  $CS_2/CDCl_3$ )  $\delta$  8.67 (d, J = 8.8 Hz, 2H), 8.49 (d, J = 8.8 Hz, 2H).

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300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  9.78 (d, J = 8.6 Hz, 1H), 8.70 (d,  $\mathcal{G}^{\pm}$   $\mathcal{G$ 

**2-(2-Furylphenyl)-oxazolo[4,5:1,2][60]fullerene** (**2l**). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1l** (28.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C<sub>60</sub> (29.1 mg, 81%) and then **2l**<sup>15d</sup> (7.1 mg, 17%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  7.81 (d, *J* = 1.8 Hz, 1H), 7.50 (d, *J* = 3.4 Hz, 1H), 6.75 (dd, *J* = 3.4, 1.8 Hz, 1H).

**2-Benzyl-oxazolo**[4,5:1,2][60]**fullerene** (2m). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1m** (34.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·*x*H<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C<sub>60</sub> (27.1 mg, 75%) and then **2m**<sup>6a,15c,d</sup> (8.9 mg, 21%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  7.67 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.87 (s, 2H).

**2-**(*n*-**Pentyl**)-**oxazolo**[**4**,**5**:**1**,**2**][**60**]**fullerene** (**2n**). According to the general procedure, the reaction of C<sub>60</sub> (36.0 mg, 0.05 mmol) with **1n** (29.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>:*x*H<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C<sub>60</sub> (26.9 mg, 75%) and then **2n**<sup>15*c*,*d*</sup> (7.8 mg, 19%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  2.93 (t, *J* = 7.6 Hz, 2H), 2.06-2.17 (m, 2H), 1.64-1.72 (m, 2H), 1.51-1.60 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

2-(1-Styryl)-oxazolo[4,5:1,2][60]fullerene (20). According to the general

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procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **10** (37.0 mg, 0.25 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C<sub>60</sub> (31.6 mg, 88%) and then **20** (4.2 mg, 10%) as an amorphous black solid. MP > 300 °C; <sup>1</sup>H NMR (400 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 16.3 Hz, 1H), 7.68 (d, J = 7.1 Hz, 2H), 7.40-7.48 (m, 3H), 7.13 (d, J = 16.3 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> with Cr(acac)<sub>3</sub> as relaxation reagent) (all 2C unless indicated)  $\delta$  164.57 (1C, C=N), 147.50 (1C), 147.26, 147.08 (1C), 145.68, 145.65, 145.54, 145.38, 145.33, 145.06, 144.81, 144.74, 144.51, 144.41, 144.07, 143.86, 143.56, 142.89, 142.34 (1C), 142.08, 142.04, 141.98, 141.64, 141.61, 141.55, 141.40, 141.29, 141.26, 139.73, 138.92, 137.12, 135.52, 134.23 (1C, aryl C), 129.70 (1C, aryl C), 128.53 (aryl C), 127.44 (aryl C), 113.39 (1C), 96.35 (1C, sp<sup>3</sup>-C of C<sub>60</sub>), 91.29 (1C, sp<sup>3</sup>-C of C<sub>60</sub>); FT-IR  $\nu/cm^{-1}$  (KBr) 1648, 1626, 1604, 1495, 1447, 1423, 1313, 1276, 1178, 1137, 1062, 1024, 982, 970, 941, 852, 769, 752, 691, 575, 562, 525; UV-vis (CHCl<sub>3</sub>) λ<sub>max</sub>/nm 257, 316, 415, 686; MALDI-TOF MS m/z calcd for C<sub>69</sub>H<sub>8</sub>NO [M+H]<sup>+</sup> 866.0606, found 866.0607.

### $Fe(ClO_4)_3$ -mediated reaction of $C_{60}$ with benzoyl isothiocyanate in scheme 2.

A mixture of benzoyl isothiocyanate (336 uL, 2.5 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (115.0 mg, 0.25 mmol) 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 isothiocyanate. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C<sub>60</sub> (36.0 mg, 0.05 mmol). The resulting solution was heated with vigorous stirring in the oil bath at the same temperature for 14 h under nitrogen

atmosphere. 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 afford unreacted C<sub>60</sub> (21.0 mg, 58%) and fullerooxazole  $2a^{6a,14c,15a-e}$  (7.1 mg, 17%) as an amorphous black solid.

### Fe(ClO<sub>4</sub>)<sub>3</sub>-mediated reaction of C<sub>60</sub> with benzamide 1a in scheme 2.

According to the general procedure, the reaction of  $C_{60}$  (36.0 mg, 0.05 mmol) with **1a** (303 mg, 2.5 mmol) and Fe(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O (115.0 mg, 0.25 mmol) at 100 °C for 13 h afforded first unreacted C<sub>60</sub> (25.1 mg, 70%) and then fullerooxazole  $2a^{6a,14c,15a-e}$  (7.9 mg, 19%) as an amorphous black solid.

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## Ferric perchlorate-mediated one-step reaction of [60]fullerene with primary amides for the synthesis of fullerooxazoles

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Reaction of [60]fullerene with amides promoted by cheap and easily available ferric perchlorate affords a series of interesting fullerooxazole derivatives.

Fe(ClO<sub>4</sub>)<sub>3</sub> NH<sub>2</sub> cheap and easily available reagents 15 examples R = aryl, alkyl, and cinnamyl