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DMAP-Mediated Synthesis of Fulleropyrrolines: Reaction of [60]Fullerene with Aromatic Aldehydes and Arylmethanamines in the Absence or Presence of Manganese(III) Acetate

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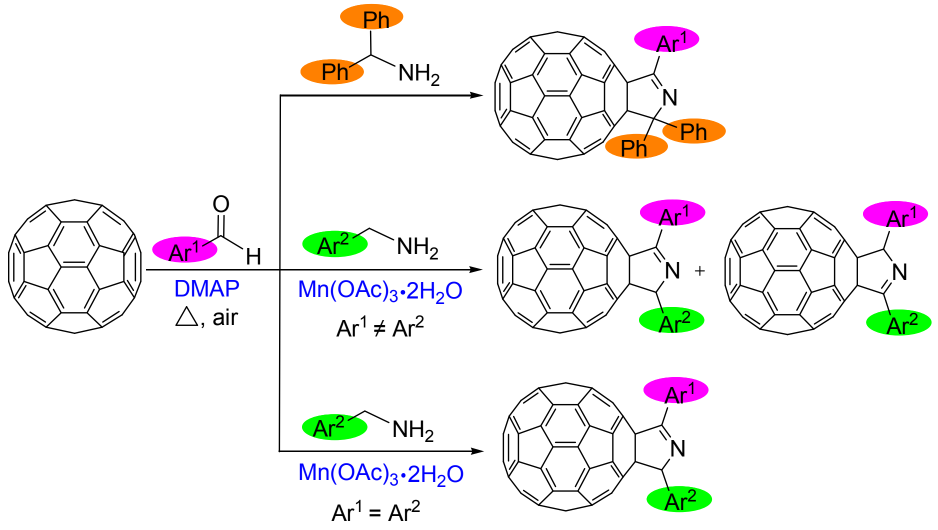


ABSTRACT: A series of scarce fulleropyrrolines were synthesized via DMAP-mediated one-step reaction of [60]fullerene with commercially inexpensive aromatic aldehydes and arylmethanamines in the absence or presence of manganese(III) acetate. In the case of aminodiphenylmethane, novel 2,5,5-trisubstituted fulleropyrrolines could be easily obtained without the addition of manganese(III) acetate. As for arylmethanamines without α-substitutions, the addition of manganese(III) acetate was required to suppress the formation of fulleropyrrolidines, in order to generate the desired 2,5-disubstituted fulleropyrrolines. Two tautomers were produced as expected when different aryl groups ($Ar^1 \neq Ar^2$) from aromatic aldehydes and arylmethanamines were employed in the synthesis. A plausible reaction mechanism for the formation of fulleropyrrolines is proposed.

INTRODUCTION

Fullerenes are a class of three-dimensional all-carbon hollow molecules incorporating conjugated π systems, and have attracted wide attention over the past decades due to their outstanding properties. Among the known fullerenes, [60]fullerene (C_{60}) is one of the most extensively studied fullerenes as a result of its perfect symmetry and easy availability.[1] Nevertheless, the limited solubility of C_{60} in water and/or polar organic solvents has hampered its applications.[2] This limitation required the functionalization of C_{60} with various organic functional groups.[2,3] Chemical modification of C_{60} induced by transition metal salts instead of traditional peroxide or light have proven to be a powerful tool to functionalize fullerenes,[4] and a large variety of novel fullerene derivatives with structural and functional diversities have been successfully prepared under the assistance of diverse types of transition metal salts. Among the reported transition metal salts,[4-7] those from the first-row transition metals, such as Mn(III),[5] Fe(III)/Fe(II)[6] and Cu(II)/Cu(I),[7] have been widely used to functionalize fullerenes owing to their low toxicity, easy availability, inexpensive price, and insensitivity to air and water. Although many fullerene reactions catalyzed/promoted by transition metal salts have been developed to functionalize fullerenes, there is still a demand to explore new transition-metal-salt catalyzed/promoted reactions to prepare a plethora of novel fullerene derivatives including the relatively scarce fulleropyrrolines. Fulleropyrrolines[5c,7,8] are generally classified into two categories according to the relative position of nitrogen atom, namely, pyrroline derivatives with/without a nitrogen atom bonding to the fullerene cage directly. Fulleropyrrolines with a directly attached nitrogen atom can be further divided into two groups, that is, 1-fulleropyrrolines[7b] with a C=N bond and 2-fulleropyrrolines[5c,7a,c] with a C=C bond. Wang and co-workers reported the first synthesis of 1-fulleropyrrolines by Cu(I)-catalyzed heteroannulation of C_{60} with ketoxime acetates.[7b] The same group also realized the first preparation of 2-fulleropyrrolines through $Mn(OAc)_3$-mediated reaction of C_{60} with β-enamino carbonyl compounds.[5c] 2-Fulleropyrrolines could also be synthesized via a $CuCl_2$-promoted three-component reaction of C_{60} with amines and dimethyl acetylenedicarboxylate (DMAD)[7a] or by a $Cu(OAc)_2$-mediated one-step reaction of C_{60} with aldehydes and primary amines.[7c] As for fulleropyrrolines without a directly attached nitrogen atom, only a few papers were reported.[8] However, these known protocols still have some synthetic limitations. For example, 2,5,5-trisubstituted fulleropyrrolines have not been reported. Furthermore, the reaction scope for the preparation of 2,5-disubstituted fulleropyrrolines is also very limited because the starting materials, 2,3-diphenyl-2H-azirine,[8a,b] imidoyl chlorides,[8c-e] and sulfonylhydrazones,[8f] are not readily available and are commonly required to prepare in advance by the complex synthesis process. Accordingly, further exploration and development of new protocols for the preparation of fulleropyrrolines, especially for those with tri-substituted groups, is still demanding.

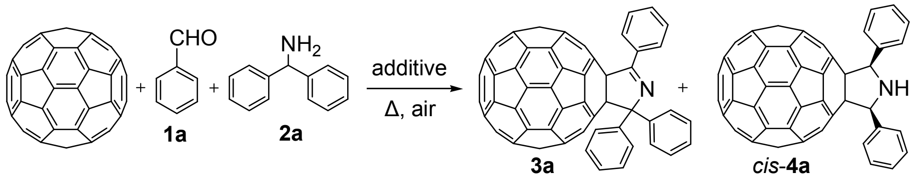
Recently, the functionalization of fullerenes by using commercially inexpensive aldehydes and amines has received increasing attention because large numbers of novel fullerene derivatives have been successfully prepared by adopting this strategy.[6c,7c,9] For example, our group reported the thermal reactions of C_{60} with aromatic aldehydes and arylmethanamines to produce a large variety of 2,5-diaryl fulleropyrrolidines with high stereoselectivity.[9c] However, during the reaction condition optimization, a higher polarity byproduct was observed in the presence of base. This byproduct was identified as a fulleropyrroline without the directly attached nitrogen atom, indicating a competitive reaction between the formation of fulleropyrrolidine and fulleropyrroline. The formation of fulleropyrrolidines can be further suppressed by adding metal oxidants into the reaction system. In continuation of our interest in fullerene chemistry,[6b,c,7c,9c,d,10] here we detailed our investigation results for the reaction of C_{60} with aromatic aldehydes and arylmethanamines in the presence of base promoter, and metal oxidants if required. Considering the easy accessibility of aromatic aldehydes and arylmethanamines, and the simple operation conditions, this synthetic technique would provide a high competitive strategy for the preparation of fulleropyrrolines without a directly attached nitrogen atom.

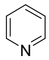
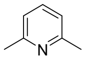
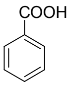
RESULTS AND DISCUSSION

To get started, benzaldehyde **1a** and aminodiphenylmethane **2a** were used for the reaction condition optimization, as summarized in Table 1. Under air conditions, C_{60}, **1a** (5 equiv) and **2a** (5 equiv) were dissolved in *o*-dichlorobenzene (ODCB) and heated at 180 °C for 11.5 h (entry 1, Table 1). The desired fulleropyrroline product, **3a**, was observed and isolated in 12% yield, as well as a fulleropyrrolidine byproduct (*cis*-**4a**, see Supporting Information). This preliminary result encouraged us to further optimize the reaction conditions with a base promoter. By adding 4-dimethylaminopyridine (DMAP, 2 equiv) into the reaction system and heated at 180

°C for 3.5 h, only **3a** was obtained in 51% yield, while *cis*-**4a** was completely suppressed (entry 2, Table 1). By changing the reaction conditions, i.e. temperature, reaction time, reagent molar ratio, etc., no improvement for the synthesis of **3a** was observed (entries 3-11, Table 1). It is worth to mention that only a trace amount of **3a** was obtained by heating at 180 °C under nitrogen atmosphere (entry 10 vs 2, Table 1), indicating the critical role of oxygen to the successful formation of **3a**. Under the best reaction conditions (entry 2, Table 1), other bases, acids, or metal oxidants were also tested to examine their reaction efficiencies (entries 12-23, Table 1). Either lower yields or complete failure to form **3a** was observed, indicating the superior reaction efficiency of DMAP to other bases/acids/metal oxidants. Therefore, entry 2, Table 1 was selected as the optimized reaction conditions to further expand the reaction scope (Table 2). It should be noted that the reaction of C_{60} with **1a** and **2a** was also conducted in the presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP. Unfortunately, no improved yield of **3a** was observed (entry 24, Table 1). In addition, 0.5 g of C_{60} was employed to react with **1a** and **2a** under the assistance of DMAP with the optimized conditions to check if the yield listed in entry 2 is trustable on a larger scale, and was found to produce 46% yield of **3a** (entry 25, Table 1), which is slightly lower than that from 36 mg of C_{60} (entry 25 vs 2, Table 1).

Table 1. **Optimization of Reaction Conditions for the Reaction of C_{60} with Benzaldehyde 1a and Aminodiphenylmethane 2a**[*a*]



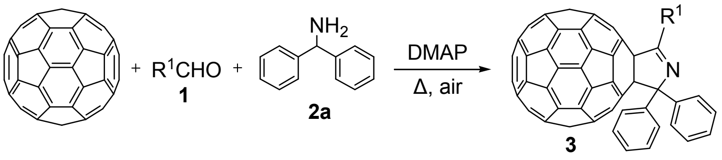
entry	additive	molar ratio^b	temp. (^{o}C)	time (h)	yield (%) of **3a**^{c}	yield (%) of *cis*-**4a**^{c}
1	none	1:5:5:0	180	11.5	12 (75)	< 5
2	**DMAP**	**1:5:5:2**	**180**	**3.5**	**51 (98)**	**0**
3	DMAP	1:5:5:2	160	7	34 (92)	0
4	DMAP	1:5:5:1	180	4	46 (96)	0
5	DMAP	1:5:5:3	180	4	51 (78)	0
6	DMAP	1:5:2:2	180	7	42 (93)	0
7	DMAP	1:5:8:2	180	4	49 (89)	0
8	DMAP	1:2:5:2	180	7	29 (94)	0
9	DMAP	1:8:5:2	180	4	47 (66)	0
10^d	DMAP	1:5:5:2	180	4	trace	0
11^e	DMAP	1:5:5:2	180	3.5	47 (90)	0
12	DABCO	1:5:5:2	180	4.5	35 (92)	0
13	DBU	1:5:5:2	180	4.5	0	0
14	TEA	1:5:5:2	180	7	7 (32)	12 (55)
15		1:5:5:2	180	5	< 5	trace
16		1:5:5:2	180	6.5	trace	< 5
17		1:5:5:2	180	7	trace	33 (73)
18	$Mn(OAc)_3 \cdot 2H_2O$	1:5:5:2	180	4	40 (95)	0
19	$Pb(OAc)_4$	1:5:5:2	180	3	15 (83)	0
20	$Cu(OAc)_2$	1:5:5:2	180	3	7 (28)	0
21	$Fe(ClO_4)_3 \cdot xH_2O$	1:5:5:2	180	2	0	0
22	$Mg(ClO_4)_2$	1:5:5:2	180	3	0	< 5
23	$(NH_4)_2Ce(NO_3)_6$	1:5:5:2	180	0.67	39 (53)	0
24^f	$Mn(OAc)_3 \cdot 2H_2O$/DMAP	1:5:5:2:2	180	3.5	46 (98)	0
25^g	DMAP	1:5:5:2	180	6	46 (90)	0

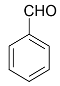
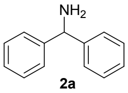
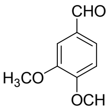
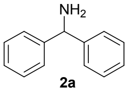
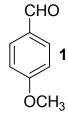
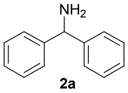
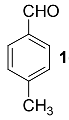
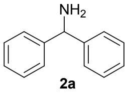
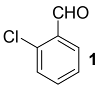
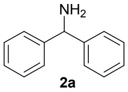
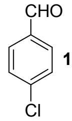
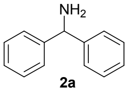
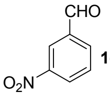
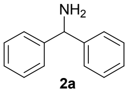
[a]Unless otherwise indicated, all reactions were performed in ODCB under air conditions. [b]Molar ratio refers to C_{60}/**1a**/**2a**/additive. [c]Isolated yield; those in parentheses were based on consumed C_{60}. [d]The reaction was conducted under nitrogen atmosphere. [e]The reaction was carried out under dark conditions, that is, the container flask was wrapped with tin foil. [f]Molar ratio refers to

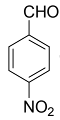
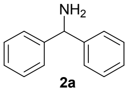
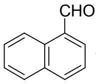
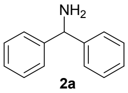
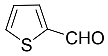
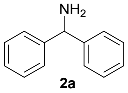
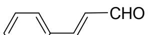
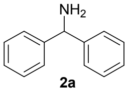
C_{60}/**1a**/**2a**/Mn(OAc)$_3$·2H$_2$O/DMAP. ^{g}0.5 g of C_{60} dissolved in 84 mL of ODCB was used to prepare **3a** on a larger scale.

The reaction scope of C_{60} with aminodiphenylmethane and different aldehydes was collected in Table 2 to produce novel 2,5,5-trisubstituted fulleropyrrolines, which would be difficult to synthesize by known methods.[8] It should be mentioned that a reaction of C_{60} with benzaldehyde (**1a**) and α-methylbenzylamine was also performed under optimized reaction conditions (see Scheme S1 in Supporting Information). However, instead of the formation of desired fulleropyrroline, two products including an unknown product were detected and the structure of unknown product needs further elucidation. As can been seen from Table 2, both electron-donating and electron-withdrawing benzaldehydes (**1b**-**h**), 1-naphthaldehyde (**1i**), 2-thiophenaldehyde (**1j**), and cinnamaldehyde (**1k**) were within the reaction scope, giving moderate to good yields (27-52%). By comparing electron-donating (**1b**-**d**) and electron-withdrawing (**1f**-**h**) benzaldehydes, higher yields were achieved for electron-withdrawing aldehydes. This is reasonable since electron-withdrawing benzaldehydes are easier to be attacked by aminodiphenylmethane, as compared with electron-donating benzaldehydes. A lower yield (30%) from **1e** can be attributed to the neighboring group effect. In the case of **1i** and **1j**, longer reaction times were required to gain reasonable yields. As for cinnamaldehyde **1k**, a 3-hour reaction time is enough to reach a 39% yield, which can be ascribed to its high reactivity and less hindrance, as compared with other aldehydes. Furthermore, phenylacetaldehyde was also employed to react with **2a**. To our disappointment, no desired product was obtained in addition to a 11% yield of fulleropyrroline (see Scheme S2 in Supporting Information).

Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Aldehydes 1 and Aminodiphenylmethane 2a in the Presence of DMAP[a]



aldehyde **1**	amine **2**	product **3**	time (h)	yield[b] (%)
 **1a**	 **2a**	**3a**	3.5	51 (98)
 **1b**	 **2a**	**3b**	6.5	31 (91)
 **1c**	 **2a**	**3c**	4.5	33 (92)
 **1d**	 **2a**	**3d**	5	33 (94)
 **1e**	 **2a**	**3e**	4.5	30 (91)
 **1f**	 **2a**	**3f**	4	52 (87)
 **1g**	 **2a**	**3g**	6	46 (90)

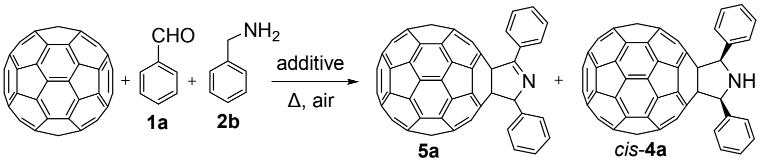
 **1h**	 **2a**	**3h**	3	41 (72)
 **1i**	 **2a**	**3i**	6.5	31 (89)
 **1j**	 **2a**	**3j**	7	27 (87)
 **1k**	 **2a**	**3k**	3	39 (64)

[a] All reactions were performed in ODCB (6 mL) under air conditions at 180 °C unless otherwise indicated, molar ratio refers to C_{60}/**1**/**2a**/DMAP = 1:5:5:2. [b] Isolated yield, those in parentheses were based on consumed C_{60}.

The structures of novel fulleropyrrolines **3a-k** were unambiguously characterized by MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR, FT−IR, and UV−vis spectra. The correct $[M+H]^+$ peak of each fulleropyrroline was observed by their MALDI-TOF MS. Expected chemical shifts and splitting patterns were also displayed in their ^{1}H NMR spectra. In their ^{13}C NMR spectra, the peak for the C=N carbon appeared at 159.34-166.68 ppm, and the two sp^3-carbons from C_{60} moiety were located at 83.69-86.41 and 81.60-83.03 ppm, within the reported chemical shifts of fulleropyrrolines.[8] No more than 29 peaks including possible overlaps for the rest 58 sp^2-carbons were observed in the range of 135.23-153.51 ppm, agreeing well with the C_s symmetry of their molecular structures. Diagnostic absorptions at 1620−1666 cm^{-1} were detected in IR spectra, attributing to the stretching C=N vibrations. Characteristic absorption peaks at 430−431 nm were observed in UV-vis spectra, indicating the 1,2-adducts of C_{60}.

Although the above-mentioned reaction with aminodiphenylmethane **2a** successfully afforded the novel fulleropyrrolines (Table 2), the reaction with α-methylbenzylamine failed to produce the desired fulleropyrroline (see Scheme S1 in Supporting Information). An attempt to prepare fulleropyrroline from C_{60} with benzaldehyde (**1a**) and benzylamine (**2b**) was thus carried out, as listed in Table 3. In the presence of DMAP, 29% fulleropyrroline and 20% fulleropyrrolidine were isolated after heating 10 h at 180 ^{o}C in ODCB under air conditions (entry 1, Table 3). To suppress the formation of fulleropyrrolidine (*cis*-**4a**), the addition of $Mn(OAc)_3{\cdot}2H_2O$ (2 equiv) was tested, and expected suppression effect was observed (entry 2, Table 3), however, with a lower yield of fulleropyrroline (24%). Increasing the equivalents of **1a** and **2b** (from 5 to 8 equiv) exhibited a positive effect by increasing the yield to 37% (entry 3, Table 3), while decreasing the reaction temperature would dramatically lower the yield to 10% (entry 4 vs 3, Table 3). The involvement of oxygen in the reaction was also confirmed by carrying out the reaction under nitrogen atmosphere (entry 5, Table 3). In this case, only 6% fulleropyrroline was isolated as compared to 37% yield in entry 3. By changing the reagent equivalents and reaction time, decreased or slightly increased yields were observed (entries 6-14, Table 3). The highest yield of fulleropyrroline was achieved from entry 11 with a molar ratio of 1:8:8:2:1 for C_{60}:**1a**:**2b**:$Mn(OAc)_3{\cdot}2H_2O$:DMAP, however, 10% undesired fulleropyrrolidine *cis*-**4a** was also isolated. Considering the overall reaction efficiency and the purification process, entry 13, Table 3 was selected as the optimum reaction conditions. Other metal oxidants and bases were also tested, i.e., entries 15-19, Table 3 for different metal oxidants with DMAP and entries 20-22, Table 3 for a combination of $Mn(OAc)_3{\cdot}2H_2O$ with different bases in a molar ratio of C_{60}:**1a**:**2a**:metal oxidant:base as 1:8:8:2:2. While $(NH_4)_2Ce(NO_3)_6$ and pyridine would slightly lower the reaction yields (entries 19 and 22 vs entry 3, Table 3), dramatic yield decrease was observed for $Pb(OAc)_4$ and DABCO (entries 15 and 20 vs entry 3, Table 3). The other metal oxidants or bases presented a trace amount of desired fulleropyrroline (entries 16-18 and 21 vs entry 3, Table 3). Overall, the optimum reaction conditions were set as entry 13, Table 3 for reaction scope study (Table 4). With the optimized conditions, 0.5 g of C_{60} was also used to react with **1a** and **2b**, and was found to generate 41% yield of **5a** (entry 23, Table 3), comparable to the obtained data from 36 mg of C_{60} although 4% yield of *cis*-**4a** was also formed (entry 23 vs 13, Table 3).

Table 3. **Optimization of Reaction Conditions for the Reaction of C_{60} with Benzaldehyde 1a and Benzylamine 2b**[a]

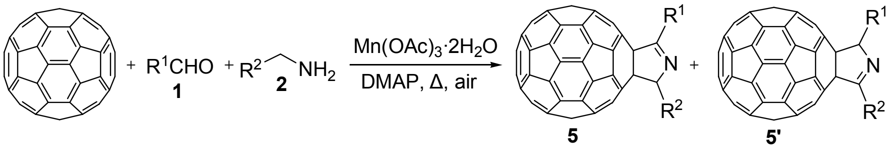


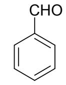
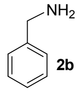
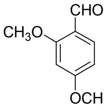
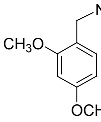
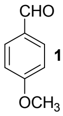
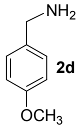
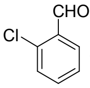
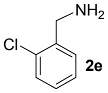
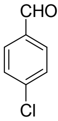
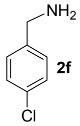
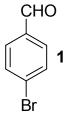
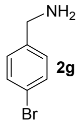
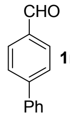
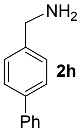
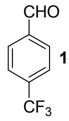
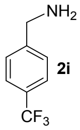
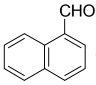
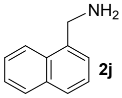
entry	additive	molar ratio[b]	temp. (ºC)	time (h)	yield (%) of **5a**[c]	yield (%) of *cis*-**4a**[c]
1	DMAP	1:5:5:0:2	180	10	29 (48)	20 (33)
2	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:5:5:2:2	180	9	24 (77)	trace
3	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:2:2	180	10	37 (65)	trace
4	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:2:2	160	11	10 (40)	4 (16)
5[d]	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:2:2	180	10	6 (33)	trace
6	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:10:8:2:2	180	8.5	34 (97)	trace
7	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:5:8:2:2	180	9	29 (78)	6 (16)
8	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:10:2:2	180	6.5	37 (69)	trace
9	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:5:2:2	180	8	18 (64)	trace
10	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:2:3	180	8	36 (77)	trace
11	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:2:1	180	7	43 (73)	10 (17)
12	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:3:2	180	8	37 (71)	trace
13	**$Mn(OAc)_3{\cdot}2H_2O$/DMAP**	**1:8:8:1:2**	**180**	**8**	**38 (78)**	**trace**
14	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:0.5:1	180	6	38 (59)	7 (11)
15	$Pb(OAc)_4$/DMAP	1:8:8:2:2	180	5	14 (82)	trace
16	$Cu(OAc)_2$/DMAP	1:8:8:2:2	180	0.5	trace	trace
17	$Fe(ClO_4)_3{\cdot}xH_2O$/DMAP	1:8:8:2:2	180	0.5	trace	52 (84)
18	$Mg(ClO_4)_2$/DMAP	1:8:8:2:2	180	0.67	trace	49 (84)
19	$(NH_4)_2Ce(NO_3)_6$/DMAP	1:8:8:2:2	180	0.83	32 (47)	trace
20	$Mn(OAc)_3{\cdot}2H_2O$/DABCO	1:8:8:2:2	180	2.5	13 (24)	20 (36)
21	$Mn(OAc)_3{\cdot}2H_2O$/TEA	1:8:8:2:2	180	2	trace	34 (85)
22	$Mn(OAc)_3{\cdot}2H_2O$/Py	1:8:8:2:2	180	5	35 (64)	17 (31)
23[e]	$Mn(OAc)_3{\cdot}2H_2O$/DMAP	1:8:8:1:2	180	12	41 (57)	4 (6)

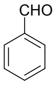
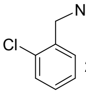
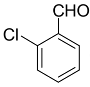
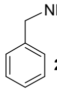
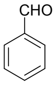
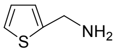
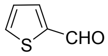
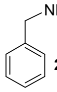
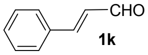
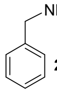
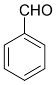
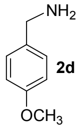
[a] Unless otherwise indicated, all reactions were performed in ODCB (6 mL) under air conditions. [b] Molar ratio refers to C_{60}/**1a**/**2a**/metal oxidant/base. [c] Isolated yield; those in parentheses were based on consumed C_{60}. [d] The reaction was conducted under nitrogen conditions. [e] 0.5 g of C_{60} dissolved in 84 mL of ODCB was used to prepare **5a** on a larger scale.

The reaction scope was initially expanded to the aldehydes and amines with the same aryl groups (Ar^1 = Ar^2). Both electron-donating and electron-withdrawing functional groups on aryl groups were examined, producing the desired fulleropyrrolines **5a-i** in moderate yields. However, in this case, lower yields were isolated with electron-withdrawing groups, while higher yields were obtained for electron-donating groups, which is opposite to the previous observations. This can be explained by the lower nucleophilicity of electron-withdrawing amines towards aldehydes. By using two different aryl groups ($Ar^1 \neq Ar^2$), tautomers **5** and **5'** will be obtained. For example, the reaction of C_{60} with **1a** and **2e** isolated **5j** and **5j'** in 28% and 16% yields, respectively, while **1e** and **2b** produced **5j'** and **5j** in 17% and 27% yields, respectively. As for **1a** and **2k**, a trace amount of **5k** (see Supporting Information) as well as 17% yield of **5k'** was obtained, yet **1j** and **2b** generated 20% yield of **5k'** along with a trace amount of **5k**. However, in the case of **1k** and **2b**, fulleropyrroline **5l** was collected as expected. Tautomer **5l'** was not detected, but replaced by a new tautomer **6** (Scheme 1). This is due to the natural preference of conjugated systems over non-conjugated systems, i.e. the preferred conjugation system of CH_2-CH=C-N=C (**6**) over the nonconjugation system of CH=CH-CH-N=C (**5l'**). In addition, both **5m** and **5m'** from **1a** and **2d** were unable to be separated by column chromatography due to the similar polarity, and the tautomer ratio was determined based on the ^{1}H NMR integration. As for **1h** and **2b**, no obvious fulleropyrrolines were observed in addition to fulleropyrrolidine *cis*-**4b** (Scheme 2), and the exact reason for this phenomenon is not quite clear. It is noteworthy that phenylacetaldehyde with **2b**, **1a** with *n*-butylamine, and phenylacetaldehyde with *n*-butylamine were also studied under the optimized conditions (see Schemes S3-5 in Supporting Information). To our disappointment, no desired fulleropyrrolines were successfully isolated.

Table 4. Reaction Conditions and Yields for the Reaction of C_{60} with Aldehydes 1 and Amines 2 in the Presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP[a]

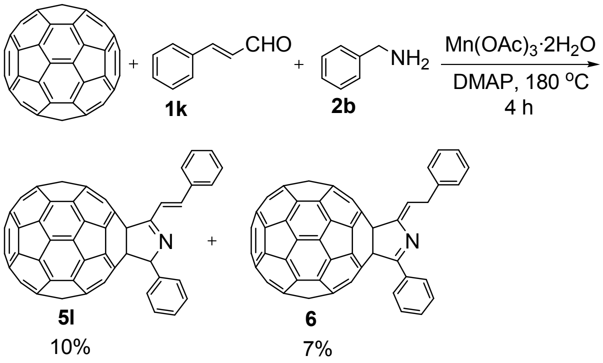


aldehyde **1**	amine **2**	time (h)	product **5**	yield[b] (%)	product **5'**	yield[b] (%)
 **1a**	 **2b**	8	**5a**	38 (78)	/	/
 **1l**	 **2c**	3	**5b**	49 (68)	/	/
 **1c**	 **2d**	2.5	**5c**	36 (92)	/	/
 **1e**	 **2e**	6	**5d**	26 (46)	/	/
 **1f**	 **2f**	6	**5e**	23 (59)	/	/
 **1m**	 **2g**	5	**5f**	30 (60)	/	/
 **1n**	 **2h**	4	**5g**	34 (67)	/	/
 **1o**	 **2i**	5	**5h**	23 (39)	/	/
 **1i**	 **2j**	4.5	**5i**	33 (77)	/	/

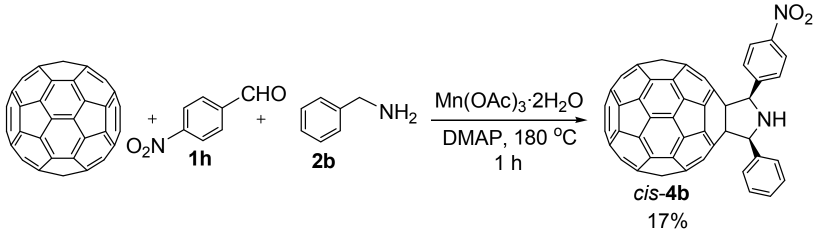
 **1a**	 **2e**	10	**5j**	28 (58)	**5j'**	16 (33)
 **1e**	 **2b**	9	**5j'**	17 (38)	**5j**	27 (60)
 **1a**	 **2k**	3	**5k**	trace	**5k'**	22 (79)
 **1j**	 **2b**	3	**5k'**	20 (65)	**5k**	trace
 **1k**	 **2b**	4	**5l**	10 (18)	**5l'**	0
 **1a**	 **2d**	4	**5m**/**5m'**		42^c (71)	

[a] All reactions were performed in ODCB (6 mL) under air conditions at 180 °C unless otherwise indicated, molar ratio refers to C_{60}/**1**/**2**/$Mn(OAc)_3 \cdot 2H_2O$/DMAP = 1:8:8:1:2. [b] Isolated yield, those in parentheses were based on consumed C_{60}. [c] Total isolated yield including both **5m** and **5m'**, the **5m**/**5m'** ratio was determined as 2.6:1 based on the ^{1}H NMR spectrum.

Scheme 1. Reaction of C_{60} with Cinnamaldehyde 1k and Benzylamine 2b in the Presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP



Scheme 2. Reaction of C_{60} with 4-Nitrobenzaldehyde 1h and Benzylamine 2b in the Presence of $Mn(OAc)_3{\cdot}2H_2O$ and DMAP

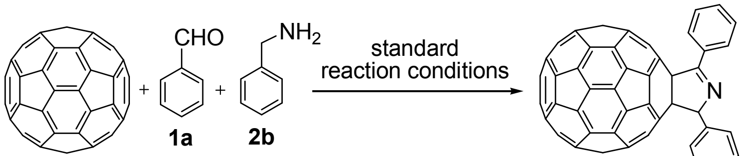


Structural elucidations of novel fulleropyrrolines **5a-m**, **5j',k',m'**, and **6** were performed with the aid of MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR, FT−IR, and UV−vis spectra. All MALDI-TOF MS of these fulleropyrrolines gave the correct $[M+H]^+$ or $[M]^+$ peaks. Their ^{1}H NMR spectra displayed the expected chemical shifts and splitting patterns for all protons. In addition, the ^{1}H NMR spectra of **5j**/**5j'**, **5k**/**5k'**, and **5m**/**5m'** showed a similar pattern, and the signals for the two ortho-position protons from the phenyl ring of **5j**,**k**,**m** were shifted downfield relative to those in tautomers **5j'**,**k'**,**m'** probably due to the strong electron-withdrawing property of the C=N group, which is consistent with the previous observations.[8c,e] In their ^{13}C NMR spectra, besides the peaks for the addends including the signals at 161.65-170.05 ppm for the C=N carbon, there were at least 40 peaks containing some overlapped ones in the range of 131.92-159.53 ppm for the 58 sp^2-carbons of the C_{60} moiety and two peaks at 80.70-85.00 and 75.27-77.54 ppm for the two sp^3-carbons of the C_{60} skeleton for fulleropyrrolines **5a-m** and **5j'**,**k'**,**m'**, consistent with the C_1 symmetry of their molecular structures, whereas there existed only 26 lines including four overlapping ones in the range of 133.05-155.65 ppm for the 58 sp^2-carbons of the C_{60} skeleton and two peaks at 82.79 and 73.66 ppm for the two sp^3-carbons of the C_{60} cage for fulleropyrroline **6**, agreeing well with its C_s symmetry. In their IR spectra, the absorption at 1610−1669 cm^{-1} also demonstrated the presence of C=N group. Their UV-vis spectra exhibited diagnostic absorption at 429−430 nm for the 1,2-adducts of C_{60}. As for *cis*-**4a**,**b**, their structures were well established by comparing their spectral data with those reported in the literature.[6c,9c,d]

The formation of fulleropyrrolines can be either via a 1,3-dipolar cycloaddition reaction of nitrile ylides[8a-e] or through a single electron transfer process.[8a,f] The requirement of oxygen atmosphere for this reaction conditions excluded the 1,3-dipolar cycloaddition mechanism, making it high possible to be a single electron transfer process. To further confirm the single electron transfer mechanism, radical trapping experiments were conducted by the addition of typical radical scavenger 2,6-di-tert-butyl-4-methylphenol (BHT) to the reaction system of C_{60} with benzaldehyde (**1a**) and benzylamine (**2b**) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP (Scheme 3). Experimental results indicated that 2 equiv of BHT dramatically decreased the yield of product **5a**, while 5 equiv of BHT completely suppressed the formation of fulleropyrroline **5a**, indicating that a radical pathway was involved into the present reaction. In addition, the detection of fulleropyrrolidines from aromatic aldehydes and arylmethanamines **2b**-**k** during the reaction process and their subsequent suppression/conversion to the corresponding fulleropyrrolines is an indication of another possible reaction pathway. To confirm this speculation, fulleropyrrolidine, *cis*-**4a**, as a starting material, was heated in ODCB at 180 °C for

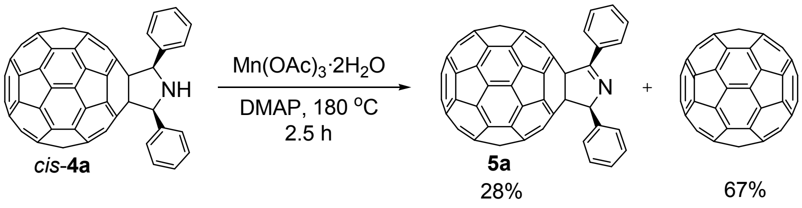
2.5 h under air conditions in the presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP (Scheme 4). As expected, fulleropyrroline, **5a**, was successfully obtained in 28% yield, together with 67% recovered C_{60}, which can be considered as the retro-1,3-dipolar cycloaddition reaction product. However, in comparison with arylmethanamines **2b-k**, aminodiphenylmethane **2a** could not produce the corresponding fulleropyrrolidines during the reaction process (Tables 1 and 2), and thus the possible reaction pathway by the transformation of fulleropyrrolidines to fulleropyrrolines **3a-k** was excluded.

Scheme 3. Radical Trapping Experiments



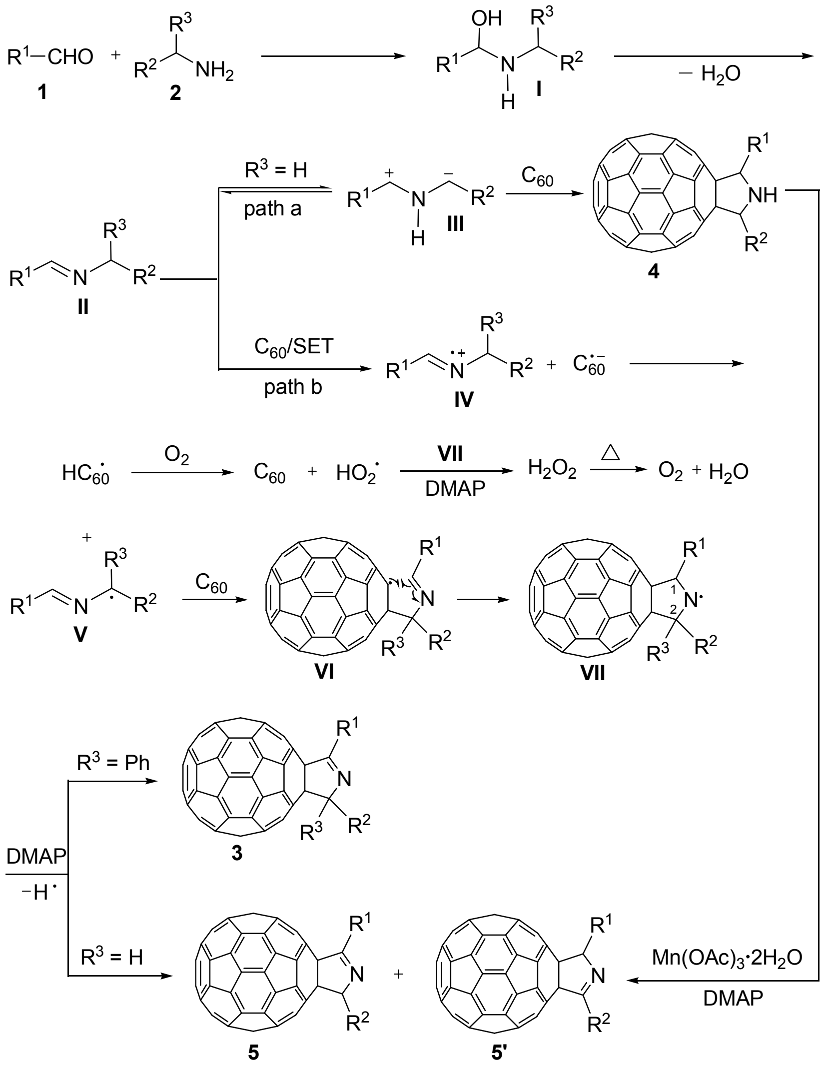
additive	equivalent	5a
BHT	0	38%
	2	15%
	5	0%

Scheme 4. Transformation of *cis*-4a to Fulleropyrroline 5a in the Presence of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP



Based on the previously reported mechanisms[8,11-13] together with the above experimental results, we proposed two plausible pathways for the formation of fulleropyrrolines, as depicted in Scheme 5. Aldehyde **1** first reacts with amine **2** to form α-hydroxyamine intermediate **I**, which can undergo dehydration to produce Schiff-base imine **II**, followed by either tautomerization to a 1,3-dipole (**III**, path a for $R^3 = H$, Table 4) or single electron transfer to C_{60} to form a cationic radical **IV** and an anionic radical $C_{60}^{\cdot-}$ [11-13] (path b for both Tables 2 and 4). 1,3-Dipole **III** will react with C_{60} to produce observed fulleropyrrolidine, **4**, which will further undergo dehydrogenation to give the desired fulleropyrrolines, **5** and **5'**, with the aid of $Mn(OAc)_3 \cdot 2H_2O$ and DMAP under air conditions. The oxidative dehydrogenation reactions of amines in the presence of metal oxidants have been extensively reported in previous literature.[6c,14] As for path b, a proton transfer process would happen between the cationic radical intermediate **IV** and $C_{60}^{\cdot-}$, producing radical intermediate **V** and $HC_{60}^{\cdot}$. A radical reaction between **V** and C_{60} will generate fulleropyrroline radical intermediate **VI**, followed by cyclization to give fullerenyl radical **VII**, while $HC_{60}^{\cdot}$ reacts with oxygen to produce hydrogen hyperoxide radical $HO_2^{\cdot}$. With the aid of DMAP, hydrogen hyperoxide radical $HO_2^{\cdot}$ would further abstract one hydrogen radical from **VII** to form hydrogen peroxide, together with the desired fulleropyrroline **3** ($R^3 = Ph$) or **5** and **5'** ($R^3 = H$). By heating, hydrogen peroxide can be easily decomposed to water and oxygen. As for *cis*-**4a**, its formation mechanism has been outlined in Scheme S6 in Supporting Information.

Scheme 5. Proposed Formation Mechanism for Fulleropyrrolines 3 and 5/5'



CONCLUSION

In summary, the simple one-step synthesis of fulleropyrrolines without the directly attached nitrogen atom has been successfully achieved by the facile DMAP-mediated reaction of C_{60} with aromatic aldehydes and arylmethanamines with/without the aid of $Mn(OAc)_3 \cdot 2H_2O$. The current synthetic protocol for the fulleropyrrolidines, from inexpensive and commercially available aromatic aldehydes and arylmethanamines, is more practical and versatile than the previous ones.[8] In addition, the successful synthesis of novel 2,5,5-triaryl fulleropyrrolines would provide a great opportunity for researchers to design and synthesize a series of new type of organic photovoltaic materials based on the 2,5,5-trisubstituted fulleropyrroline derivatives.

EXPERIMENTAL SECTION

General Methods. Reagents and solvents employed were commercially available and used directly as received without further purification. Purified fullerene products were obtained by flash chromatography over silica gel. The UV-vis spectra were measured in $CHCl_3$. IR spectra were taken with KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a 500 or 600 MHz NMR spectrometer. Chemical shifts in ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, while chemical shifts in ^{13}C NMR spectra were referenced to residual 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 Synthesis of Fulleropyrrolines 3. C_{60} (36.0 mg, 0.05 mmol), aldehydes **1** (0.25 mmol), aminodiphenylmethane **2a** (43 μL, 0.25 mmol), and DMAP (12.2 mg, 0.10 mmol) were added to a 50 mL three-neck flask. After the mixed compounds were completely dissolved in 6 mL of *o*-dichlorobenzene by sonication, the resulting solution was put into an oil bath preset at 180 °C and stirred under air conditions. Thin-layer chromatography (TLC) was employed to carefully monitor the reaction and to stop the reaction at the designated time. The reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After the solvent evaporation in vacuo was completed, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60}, and then fulleropyrrolines **3**.

Fulleropyrroline 3a: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (26 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 3.5 h afforded first unreacted C_{60} (17.1 mg, 48%) and then **3a** (25.6 mg, 51%) as an amorphous brown solid: mp >300 °C.

3a: ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 8.22-8.20 (m, 2H), 8.13 (d, J = 7.7 Hz, 4H), 7.54-7.53 (m, 3H), 7.47 (t, J = 8.0 Hz, 4H), 7.35 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 166.60 (1C, *C*=N), 153.14, 148.55, 145.84 (1C), 145.75 (1C), 145.65, 145.23, 144.75, 144.73, 144.65, 144.36, 144.27, 144.23, 144.19, 143.93, 143.67, 143.19, 142.97, 141.97, 141.67, 141.58, 141.38, 141.10, 141.06, 140.88, 140.72 (4C), 140.42, 138.84, 138.07, 135.54, 133.60 (1C, aryl *C*), 133.49 (aryl *C*), 129.53 (1C, aryl *C*), 128.83 (4C, aryl *C*), 128.55 (aryl *C*), 127.76 (aryl *C*), 127.31 (4C, aryl *C*), 127.04 (aryl *C*), 94.38 (1C), 84.40 (1C, sp^3-*C* of C_{60}), 82.53 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1653, 1513, 1492, 1445, 1430, 1272, 1265, 1183, 1045, 1027, 907, 753, 696, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{80}H_{16}N$ 990.1277; Found 990.1271.

Fulleropyrroline 3b: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (41.5 mg, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 6.5 h afforded first unreacted C_{60} (23.7 mg, 66%) and then **3b** (16.3 mg, 31%) as an amorphous brown solid: mp >300 °C.

3b: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.05 (dd, J = 8.5, 1.1 Hz, 4H), 7.88 (dd, J = 8.4, 2.1 Hz, 1H), 7.74 (d, J = 2.1 Hz, 1H), 7.41 (t, J = 7.8 Hz, 4H), 7.30 (t, J = 7.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.71 (1C, *C*=N), 153.51, 150.72 (1C, aryl *C*), 149.13, 148.48 (1C, aryl *C*), 146.03, 145.99 (1C), 145.94 (1C), 145.41, 144.92 (4C), 144.82, 144.58, 144.52, 144.40, 144.34, 144.12, 143.81, 143.40, 143.16, 142.16, 141.87, 141.79, 141.58, 141.35, 141.30, 141.02, 140.89, 140.87, 140.65, 138.73, 138.26, 135.69, 133.67 (aryl *C*), 129.08 (4C, aryl *C*), 127.41 (4C, aryl *C*), 127.14 (aryl *C*), 126.09 (1C, aryl *C*), 122.34 (1C, aryl *C*), 113.06 (1C, aryl *C*), 110.65 (1C, aryl *C*), 94.13 (1C), 84.34 (1C, sp^{3}-*C* of C_{60}), 83.03 (1C, sp^{3}-*C* of C_{60}), 54.89 (1C), 54.81 (1C); FT-IR ν/cm^{-1} (KBr) 1648, 1600, 1515, 1446, 1421, 1294, 1269, 1218, 1189, 1168, 1140, 1023, 887, 855, 705, 527; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{82}H_{20}NO_2$ 1050.1489; Found 1050.1484.

Fulleropyrroline 3c: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (30 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 4.5 h afforded first unreacted C_{60} (23.0 mg, 64%) and then **3c** (17.0 mg, 33%) as an amorphous brown solid: mp >300 °C.

3c: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.21 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 7.8 Hz, 4H), 7.42 (t, J = 7.7 Hz, 4H), 7.31 (t, J = 7.3 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.77 (1C, *C*=N), 160.38 (1C, aryl *C*), 153.39, 149.00, 145.91 (1C), 145.88, 145.85 (1C), 145.32, 144.85, 144.82, 144.74, 144.49, 144.42, 144.32, 144.26, 144.03, 143.74, 143.32, 143.08, 142.08, 141.78, 141.70, 141.49, 141.30, 141.20, 140.96, 140.81 (4C), 140.57, 138.84, 138.17, 135.63, 133.59 (aryl *C*), 130.46 (aryl *C*), 128.98 (4C, aryl *C*), 127.32 (4C, aryl *C*), 127.04 (aryl *C*), 125.97 (1C, aryl *C*), 113.27 (aryl *C*), 94.11 (1C), 84.36 (1C, sp^3-*C* of C_{60}), 82.83 (1C, sp^3-*C* of C_{60}), 54.33 (1C); FT-IR ν/cm^{-1} (KBr) 1646, 1605, 1510, 1446, 1253, 1174, 1029, 705, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{81}H_{18}NO$ 1020.1383; Found 1020.1377.

Fulleropyrroline 3d: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (30 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 5 h afforded first unreacted C_{60} (23.5 mg, 65%) and then **3d** (16.4 mg, 33%) as an amorphous brown solid: mp >300 °C.

3d: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.08-8.05 (m, 6H), 7.41 (t, J = 7.8 Hz, 4H), 7.30 (t, J = 7.3 Hz, 4H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 166.68 (1C, *C*=N), 153.43, 148.95, 146.05 (1C), 145.96 (3C), 145.44, 144.96, 144.93, 144.86, 144.59, 144.52, 144.43, 144.38, 144.15, 143.87, 143.41, 143.20, 142.18, 141.88, 141.80, 141.60, 141.37, 141.29, 141.09, 140.93 (4C), 140.66, 139.66 (1C, aryl *C*), 139.00, 138.27, 135.71, 133.71 (aryl *C*), 131.03 (1C, aryl *C*), 129.04 (4C, aryl *C*), 128.82 (aryl *C*), 128.61 (aryl *C*), 127.46 (4C, aryl *C*), 127.18 (aryl *C*), 94.49 (1C), 84.62 (1C, sp^3-*C* of C_{60}), 82.78 (1C, sp^3-*C* of C_{60}), 21.00 (1C); FT-IR *ν*/cm^{-1} (KBr) 1664, 1490, 1445, 1429, 1183, 1044, 1021, 906, 699, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{81}H_{18}N$ 1004.1433; Found 1004.1429.

Fulleropyrroline 3e: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (28 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 4.5 h afforded first unreacted C_{60} (24.1 mg, 67%) and then **3e** (15.2 mg, 30%) as an amorphous brown solid: mp >300 °C.

3e: ^{1}H NMR (500 MHz, CS_2/DMSO-*d*$_6$) *δ* 8.12 (d, *J* = 7.8 Hz, 4H), 7.84 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.50-7.42 (m, 6H), 7.32 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-*d*$_6$) (all 2C unless indicated) *δ* 166.14 (1C, *C*=N), 153.06, 148.18, 146.05 (1C), 145.88 (1C), 145.31, 145.18, 144.85 (4C), 144.79, 144.41, 144.38, 144.31 (4C), 144.06, 143.90, 143.28, 143.13, 142.11, 141.75, 141.63, 141.48, 141.10 (4C), 141.06, 140.86, 140.79, 140.48, 138.29, 138.10, 135.62, 133.76 (aryl *C*), 132.60 (1C, aryl *C*), 132.40 (1C, aryl *C*), 130.19 (1C, aryl *C*), 129.79 (1C, aryl *C*), 129.60 (1C, aryl *C*), 129.09 (4C, aryl *C*), 127.37 (4C, aryl *C*), 127.14 (aryl *C*), 125.66 (1C, aryl *C*), 95.79 (1C), 85.74 (1C, sp^3-*C* of C_{60}), 81.60 (1C, sp^3-*C* of C_{60}); FT-IR *ν*/cm^{-1} (KBr) 1666, 1492, 1446, 1431, 1287, 1247, 1184, 1075, 1030, 912, 749, 700, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 315, 430; HRMS (MALDI-TOF) m/z: [M +

H]$^+$ Calcd for $C_{80}H_{15}ClN$ 1024.0887; Found 1024.0881.

Fulleropyrroline 3f: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (35.4 mg, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 4 h afforded first unreacted C_{60} (14.3 mg, 40%) and then **3f** (26.5 mg, 52%) as an amorphous brown solid: mp >300 °C.

3f: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.20 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 7.9 Hz, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.7 Hz, 4H), 7.32 (t, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.82 (1C, *C*=N), 153.15, 148.41, 146.03 (1C), 145.95 (1C), 145.62, 145.42, 144.94, 144.90, 144.84, 144.49, 144.41(4C), 144.38, 144.11, 143.85, 143.37, 143.12, 142.15, 141,86, 141.77, 141.55, 141.21, 141.09, 141.02, 140.92, 140.88, 140.55, 139.07, 138.26, 136.12 (1C, aryl *C*), 135.87, 133.63 (aryl *C*), 132.16 (1C, aryl *C*), 130.23 (aryl *C*), 128.95 (4C, aryl *C*), 128.17 (aryl *C*), 127.49 (4C, aryl *C*), 127.25 (aryl *C*), 94.49 (1C), 84.32 (1C, sp^3-*C* of C_{60}), 82.73 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1665, 1594, 1489, 1446, 1430, 1265, 1183, 1092, 1044, 1013, 907, 747, 698, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 316, 430; HRMS (MALDI-TOF) m/z: [M + H]$^+$ Calcd for $C_{80}H_{15}ClN$ 1024.0887; Found 1024.0881.

Fulleropyrroline 3g: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (37.8 mg, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 6 h afforded first unreacted C_{60} (17.6 mg, 49%) and then **3g** (23.8 mg, 46%) as an amorphous brown solid: mp >300 °C.

3g: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 9.04 (s, 1H), 8.63 (d, J = 7.6 Hz, 1H), 8.39 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 7.9 Hz, 4H), 7.81 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 4H), 7.34 (t, J = 7.3 Hz, 2H); ^{13}C NMR (150 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.08 (1C, *C*=N), 152.83, 147.80, 147.18 (1C, aryl *C*), 146.02 (1C), 145.93 (1C), 145.40, 145.20, 144.91, 144.88, 144.82, 144.45, 144.41 (4C), 144.26, 144.07, 143.85, 143.34, 143.07, 142.12, 141.83, 141.72, 141.51, 141.16, 140.95, 140.90, 140.84, 140.75, 140.44, 139.14, 138.24, 136.12, 135.03 (1C, aryl *C*), 134.40 (1C, aryl *C*), 133.63 (aryl *C*), 129.48 (1C, aryl *C*), 128.90 (4C, aryl *C*), 127.57 (4C, aryl *C*), 127.37 (aryl *C*), 124.48 (1C, aryl *C*), 123.35 (1C, aryl *C*), 94.58 (1C), 84.00 (1C, sp^3-*C* of C_{60}), 82.68 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1643, 1529, 1515, 1494, 1446, 1430, 1347, 1261, 1189, 1100, 1058, 884, 750, 698, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 316, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{80}H_{15}N_2O_2$ 1035.1128; Found 1035.1124.

Fulleropyrroline 3h: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (37.8 mg, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 3 h afforded first unreacted C_{60} (15.4 mg, 43%) and then **3h** (21.2 mg, 41%) as an amorphous brown solid: mp >300 °C.

3h: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.57 (d, J = 8.8 Hz, 2H), 8.49 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 7.5 Hz, 4H), 7.58 (t, J = 7.8 Hz, 4H), 7.47 (t, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 165.48 (1C, *C*=N), 152.72, 147.87 (1C, aryl *C*), 147.69, 145.93 (1C), 145.85 (1C), 145.32, 145.18, 144.83, 144.79, 144.74, 144.32 (6C), 144.15, 143.98, 143.77, 143.24, 142.96, 142.04, 141.75, 141.65, 141.42, 141.04, 140.87, 140.80, 140.76, 140.71, 140.35, 139.32 (1C, aryl *C*), 139.05, 138.17, 135.95, 133.49 (aryl *C*), 129.88 (aryl *C*), 128.80 (4C, aryl *C*), 127.51 (4C, aryl *C*), 127.29 (aryl *C*), 122.92 (aryl *C*), 94.68 (1C), 84.07 (1C, sp^3-*C* of C_{60}), 82.50 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1656, 1598, 1523, 1490, 1446, 1345, 1315, 1274, 1190, 1044, 858, 748, 700, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 316, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{80}H_{15}N_2O_2$ 1035.1128; Found 1035.1124.

Fulleropyrroline 3i: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (34 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 6.5 h afforded first unreacted C_{60} (23.5 mg, 65%) and then **3i** (16.1 mg, 31%) as an amorphous brown solid: mp >300 °C.

3i: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.50 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 7.6 Hz, 4H), 8.01 (d, J = 7.1 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.9 Hz, 4H), 7.35 (t, J = 7.4 Hz, 2H); ^{13}C NMR (150MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 166.49 (1C, *C*=N), 153.09, 148.53, 146.01 (1C), 145.82 (1C), 145.44, 145.26, 144.87, 144.83, 144.79, 144.43, 144.41, 144.31, 144.24, 144.04, 143.91, 143.25, 143.08, 142.06, 141.77, 141.69, 141.61, 141.49, 141.13, 141.03, 140.81 (4C), 140.45, 139.25, 138.10, 135.23, 133.75 (aryl *C*), 132.93 (1C, aryl *C*), 130.90 (1C, aryl *C*), 130.68 (1C, aryl *C*), 129.31 (1C, aryl *C*), 128.81 (4C, aryl *C*), 127.97 (1C, aryl *C*), 127.56 (4C, aryl *C*), 127.14 (aryl *C*), 126.41 (1C, aryl *C*), 125.94 (1C, aryl *C*), 125.85 (1C, aryl *C*), 125.03 (1C, aryl *C*), 123.77 (1C, aryl *C*), 95.90 (1C), 86.41 (1C, sp^3-*C* of C_{60}), 81.73 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1655, 1427, 1183, 1108, 1023, 782, 699, 526; UV-vis ($CHCl_3$) λ_{max}/nm 260, 315, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{84}H_{18}N$ 1040.1433; Found 1040.1429.

Fulleropyrroline 3j: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (23 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 7 h afforded first unreacted C_{60} (25.0 mg, 69%) and then **3j** (13.5 mg, 27%) as an amorphous brown solid: mp >300 °C.

3j: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.34 (d, J = 3.4 Hz, 1H), 8.02 (d, J = 7.8 Hz, 4H), 7.66 (d, J = 4.8 Hz, 1H), 7.40 (t, J = 7.7 Hz, 4H), 7.30 (t, J = 7.3 Hz, 2H), 7.17 (t, J = 4.3 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 159.34 (1C, *C*=N), 153.17, 148.82, 145.96 (4C), 145.41, 144.90 (4C), 144.80, 144.53, 144.44 (4C), 144.38, 144.09, 143.75, 143.40, 143.12, 142.13, 141.87, 141.79, 141.56, 141.31, 140.94 (4C), 140.84 (5C), 140.65, 138.76, 138.29, 137.10 (1C, aryl *C*), 136.04, 133.61 (aryl *C*), 130.61 (1C, aryl *C*), 129.05 (4C, aryl *C*), 127.39 (5C, aryl *C*), 127.17 (aryl *C*), 93.37 (1C), 84.42 (1C, sp^3-*C* of C_{60}), 82.87 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1620, 1422, 1254, 1182, 1060, 1033, 940, 897, 745, 705, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 313, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{78}H_{14}NS$ 996.0841; Found 996.0838.

Fulleropyrroline 3k: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1k** (32 μL, 0.25 mmol) and **2a** (43 μL, 0.25 mmol) in the presence of DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 3 h afforded first unreacted C_{60} (14.1 mg, 39%) and then **3k** (19.6 mg, 39%) as an amorphous brown solid: mp >300 °C.

3k: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.33 (d, J = 15.6 Hz, 1H), 8.03 (d, J = 7.5 Hz, 4H), 7.76 (d, J = 15.6 Hz, 1H), 7.65 (d, J = 6.7 Hz, 2H), 7.40 (t, J = 7.8 Hz, 4H), 7.37-7.32 (m, 3H), 7.29 (t, J = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 162.69 (1C, *C*=N), 153.21, 149.16, 145.99 (1C), 145.86 (1C), 145.40, 145.30, 144.82, 144.77 (4C), 144.49, 144.38, 144.33, 144.31, 144.04, 143.78, 143.29, 143.10, 142.09, 141.72, 141.64, 141.60, 141.44, 141.07 (4C), 140.96, 140.71, 140.67 (3C), 139.53, 138.09, 135.72, 134.60 (1C, aryl *C*), 133.65 (aryl *C*), 129.03 (1C, aryl *C*), 128.94 (4C, aryl *C*), 128.14 (aryl *C*), 127.27 (4C, aryl *C*), 127.25 (aryl *C*), 126.95 (aryl *C*), 117.57 (1C), 94.75 (1C), 83.69 (1C, sp^{3}-*C* of C_{60}), 82.03 (1C, sp^{3}-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1644, 1610, 1491, 1446, 1430, 1332, 1183, 1038, 966, 892, 746, 694, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259, 316, 431; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{82}H_{18}N$ 1016.1433; Found 1016.1427.

General Procedure for the Synthesis of Fulleropyrrolines 5/5'. C_{60} (36.0 mg, 0.05 mmol), aldehydes **1** (0.40 mmol), amines **2** (0.40 mmol), $Mn(OAc)_3\cdot 2H_2O$ (13.4 mg, 0.05 mmol), and DMAP (12.2 mg, 0.10 mmol) was added to a 50 mL three-neck flask. After they were completely dissolved in 6 mL of *o*-dichlorobenzene by sonication, the mixture was heated in an oil bath preset at 180 ^{o}C and stirred under air conditions. 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 to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/dichloromethane as the eluent to afford first unreacted C_{60}, and then fulleropyrrolines **5/5'**.

Fulleropyrroline 5a: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 8 h afforded first unreacted C_{60} (18.2 mg, 51%) and then **5a** (17.5 mg, 38%) as an amorphous brown solid: mp >300 °C.

5a: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.17 (d, J = 7.7 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.51-7.47 (m, 3H), 7.41 (t, J = 7.8 Hz, 2H), 7.31 (t, J = 8.1 Hz, 1H), 7.15 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 169.15 (*C*=N), 154.49, 151.94, 148.05, 146.95, 146.39, 146.04 (2C), 145.73, 145.47, 145.41, 145.07 (3C), 144.99 (2C), 144.87, 144.83 (2C), 144.74, 144.61, 144.46 (3C), 144.30, 144.21, 144.19, 144.11, 144.01, 143.55, 143.47, 143.16 (2C), 142.28 (2C), 141.86, 141.81 (2C), 141.74, 141.67, 141.40 (2C), 141.30 (3C), 141.14 (2C), 141.00, 140.93, 140.86, 140.76, 139.63, 139.33, 139.22, 138.92 (2C), 135.45, 135.41, 134.00, 133.73, 133.05, 129.80 (aryl *C*), 128.60 (2C, aryl *C*), 128.18 (2C, aryl *C*), 127.90 (2C, aryl *C*), 127.56 (aryl *C*), 127.51 (2C, aryl *C*), 87.35, 83.86 (sp^{3}-*C* of C_{60}), 77.05 (sp^{3}-*C* of C_{60}); FT-IR v/cm^{-1} (KBr) 1636, 1428, 1155, 1099, 1045, 983, 753, 695, 527; UV-vis ($CHCl_3$)

λ_{max}/nm 258, 311, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{12}N$ 914.0964; Found 914.0957.

Fulleropyrroline 5b: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1l** (66.5 mg, 0.40 mmol) and **2c** (60 μL, 0.40 mmol) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 3 h afforded first unreacted C_{60} (10.1 mg, 28%) and then **5b** (25.3 mg, 49%) as an amorphous brown solid: mp >300 °C.

5b: ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.52 (d, J = 8.9 Hz, 1H), 7.41-7.40 (m, 2H), 6.55-6.52 (m, 3H), 6.39 (s, 1H), 3.80 (s, 6H), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 167.36 (*C*=N), 160.82 (aryl *C*), 159.53, 157.21 (aryl *C*), 155.81, 154.88 (aryl *C*), 152.26, 149.34 (aryl *C*), 147.95, 145.97, 145.70 (2C), 145.60, 145.04 (2C), 144.96, 144.76, 144.68, 144.63, 144.60, 144.52 (2C), 144.51 (2C), 144.37, 144.01, 143.90 (3C), 143.81 (2C), 143.73, 143.59, 143.15 (2C), 142.93 (2C), 141.87 (2C), 141.56, 141.46, 141.34 (3C), 141.19, 141.13, 141.07, 140.85 (2C), 140.74, 140.69, 140.55, 140.51, 140.32 (2C), 139.06, 138.68, 138.08, 138.00, 134.15 (2C), 133.54, 132.91, 129.68 (aryl *C*), 127.84 (aryl *C*), 121.47 (aryl *C*), 115.51 (aryl *C*), 104.10 (aryl *C*), 103.99 (aryl *C*), 98.21 (aryl *C*), 97.27 (aryl *C*), 85.13, 80.70 (sp^3-*C* of C_{60}), 75.60 (sp^3-*C* of C_{60}), 54.53, 54.37, 54.17, 53.96; FT-IR ν/cm^{-1} (KBr) 1610, 1506, 1462, 1435, 1279, 1208, 1182, 1159, 1032, 983, 834, 527; UV-vis ($CHCl_3$) λ_{max}/nm 259, 310, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{78}H_{20}NO_4$ 1034.1386; Found 1034.1381.

Fulleropyrroline 5c: According to the general procedure, the reaction of C_{60} (36.0

mg, 0.05 mmol) with **1c** (49 μL, 0.40 mmol) and **2d** (52 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 2.5 h afforded first unreacted C_{60} (22.1 mg, 61%) and then **5c** (17.7 mg, 36%) as an amorphous brown solid: mp >300 °C.

5c: ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.20 (d, J = 8.9 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.05 (s, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 167.62 (*C*=N), 160.57 (aryl *C*), 158.51, 154.83, 152.44 (aryl *C*), 148.55, 147.37, 146.53, 146.04, 145.99, 145.88, 145.45, 145.40, 145.04 (3C), 144.95 (3C), 144.84 (2C), 144.77, 144.57, 144.43 (3C), 144.38 (2C), 144.10 (2C), 143.98, 143.57, 143.52, 143.15 (2C), 142.28 (2C), 141.85, 141.81 (2C), 141.74, 141.70, 141.42, 141.39, 141.32 (3C), 141.14 (2C), 141.00 (2C), 140.83, 140.71, 139.64, 139.11, 139.02, 138.73, 135.44 (2C), 133.89, 132.92, 131.55 (aryl *C*), 130.45 (2C, aryl *C*), 128.62 (2C, aryl *C*), 126.06 (aryl *C*), 113.51 (2C, aryl *C*), 113.36 (2C, aryl *C*), 86.67, 83.52 (sp^3-*C* of C_{60}), 77.54 (sp^3-*C* of C_{60}), 54.44, 54.16; FT-IR ν/cm^{-1} (KBr) 1630, 1606, 1510, 1460, 1437, 1250, 1175, 1034, 983, 827, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 310, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{76}H_{16}NO_2$ 974.1176; Found 974.1170.

Fulleropyrroline 5d: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (45 μL, 0.40 mmol) and **2e** (48 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 6 h afforded first unreacted C_{60} (15.8 mg, 44%) and then **5d** (12.9 mg, 26%) as an amorphous brown solid: mp >300 °C.

5d: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.88 (d, J = 8.5 Hz, 1H), 7.74-7.72 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.48-7.41 (m, 4H), 7.31 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 168.59 (C=N), 153.68, 150.98, 147.41, 146.42, 146.09, 145.99, 145.83, 145.63, 145.46, 145.37, 145.12, 145.07, 145.00, 144.94 (4C), 144.76, 144.59, 144.53, 144.40 (4C), 144.34, 144.19 (2C), 144.13, 143.52, 143.37, 143.15, 143.12, 142.21 (2C), 141.81, 141.75, 141.68, 141.64, 141.59, 141.45, 141.41, 141.29, 141.12, 141.08 (2C), 140.97, 140.84, 140.78, 140.72 (2C), 139.52, 139.25, 138.88, 138.49, 137.62 (aryl C), 135.35 (2C), 133.94 (aryl C), 133.38, 132.87, 132.53, 132.10, 130.33 (aryl C), 129.62 (2C, aryl C), 129.52 (aryl C), 128.98 (2C, aryl C), 126.82 (aryl C), 125.86 (aryl C), 85.52, 84.07 (sp^3-C of C_{60}), 75.27 (sp^3-C of C_{60}); FT-IR ν/cm^{-1} (KBr) 1659, 1474, 1433, 1291, 1188, 1076, 1032, 984, 939, 751, 734, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 312, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{10}Cl_2N$ 982.0184; Found 982.0175.

Fulleropyrroline 5e: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (56.2 mg, 0.40 mmol) and **2f** (49 μL, 0.40 mmol) in the presence of $Mn(OAc)_3\cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 6 h afforded first unreacted C_{60} (22.0 mg, 61%) and then **5e** (11.4 mg, 23%) as an amorphous brown solid: mp >300 °C.

5e: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.21 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.16 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 168.55 (C=N), 154.02, 151.29, 147.49, 146.37, 146.05, 146.01, 145.99, 145.41, 145.38 (2C), 145.02 (3C), 144.95 (2C), 144.83, 144.67, 144.60 (2C), 144.45 (2C), 144.42, 144.39, 144.25, 144.13, 144.06 (2C), 143.95, 143.48, 143.39, 143.07, 143.04, 142.23 (2C), 141.81 (2C), 141.75, 141.70, 141.50, 141.34, 141.30, 141.21 (2C), 141.14, 141.09, 140.99, 140.95, 140.78 (2C), 140.71, 139.57, 139.21, 139.01, 138.91, 137.76, 136.26, 135.55, 135.41, 133.94, 133.59, 133.00, 131.92, 130.09 (2C, aryl *C*), 128.90 (2C, aryl *C*), 128.27 (2C, aryl *C*), 128.15 (2C, aryl *C*), 86.29, 83.50 (sp^3-*C* of C_{60}), 76.76 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1630, 1593, 1489, 1428, 1275, 1180, 1092, 1042, 1014, 985, 823, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 313, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{10}Cl_2N$ 982.0184; Found 982.0175.

Fulleropyrroline 5f: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1m** (74 mg, 0.40 mmol) and **2g** (51 μL, 0.40 mmol) in the presence of $Mn(OAc)_3\cdot2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 5 h afforded first unreacted C_{60} (18.0 mg, 50%) and then **5f** (15.9 mg, 30%) as an amorphous brown solid: mp >300 °C.

5f: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.13 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.15 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 168.65 (*C*=N), 153.93, 151.18, 147.38, 146.26, 145.97, 145.92 (2C), 145.33, 145.29 (2C), 144.94 (4C), 144.87 (2C), 144.75, 144.61, 144.52 (2C), 144.37 (2C), 144.33, 144.16, 144.04, 143.98 (2C), 143.89, 143.40, 143.31, 142.99, 142.96, 142.14 (2C), 141.72 (2C), 141.66, 141.61, 141.42, 141.25, 141.22, 141.13 (2C), 141.07, 141.02, 140.90, 140.88, 140.70 (2C), 140.63, 139.47, 139.13, 138.94, 138.84, 138.16, 135.48, 135.33, 133.88, 132.93, 132.27, 131.16 (2C, aryl *C*), 131.08 (2C, aryl *C*), 130.22 (2C, aryl *C*), 129.19 (2C, aryl *C*), 124.86 (aryl *C*), 122.03 (aryl *C*), 86.25, 83.42 (sp^3-*C* of C_{60}), 76.57 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1629, 1587, 1486, 1430, 1276, 1182, 1072, 1042, 1010, 986, 821, 527; UV-vis ($CHCl_3$) λ_{max}/nm 258, 313, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{10}Br_2N$ 1069.9174; Found 1069.9166.

Fulleropyrroline 5g: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1n** (72.9 mg, 0.40 mmol) and **2h** (73.3 mg, 0.40 mmol) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 4 h afforded first unreacted C_{60} (17.7 mg, 49%) and then **5g** (18.0 mg, 34%) as an amorphous brown solid: mp >300 °C.

5g: ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.31 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.9 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 168.55 (*C*=N), 154.31, 151.68, 147.87, 146.75, 146.21, 145.81, 145.79, 145.55, 145.24, 145.18, 144.83 (3C), 144.76 (2C), 144.62 (3C), 144.52, 144.40, 144.25, 144.23, 144.20, 144.07, 143.99, 143.95, 143.87 (2C), 143.33, 143.23, 142.93, 142.91, 142.20, 142.06, 142.03, 141.62, 141.60, 141.57, 141.51, 141.43, 141.18, 141.15, 141.08 (3C), 140.93 (2C), 140.78, 140.72, 140.63, 140.54, 139.79, 139.41, 139.13, 138.99, 138.84, 138.78, 138.69, 138.20, 135.30, 135.27, 133.88 (aryl *C*), 132.82 (aryl *C*), 132.32 (aryl *C*), 129.11 (2C, aryl *C*), 128.14

(2C, aryl *C*), 128.02 (2C, aryl *C*), 127.94 (2C, aryl *C*), 127.15 (aryl *C*), 126.64 (aryl *C*), 126.54 (2C, aryl *C*), 126.32 (2C, aryl *C*), 126.27 (2C, aryl *C*), 126.14 (2C, aryl *C*), 86.78, 83.60 (sp^3-*C* of C_{60}), 76.92 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1630, 1605, 1486, 1428, 1276, 1188, 1046, 830, 762, 695, 526; UV-vis ($CHCl_3$) λ_{max}/nm 260, 309, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{86}H_{20}N$ 1066.1590; Found 1066.1587.

Fulleropyrroline 5h: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1o** (55 μL, 0.40 mmol) and **2i** (57 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^oC for 5 h afforded first unreacted C_{60} (14.7 mg, 41%) and then **5h** (12.0 mg, 23%) as an amorphous brown solid: mp >300 °C.

5h: ^1H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.37 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.32 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 169.17 (*C*=N), 153.71, 150.73, 147.02, 145.98 (3C), 145.86, 145.40, 145.35, 145.16, 145.01 (3C), 144.92 (2C), 144.83, 144.64, 144.59, 144.52, 144.44, 144.38 (2C), 144.27, 144.23, 144.14, 144.05 (2C), 143.86, 143.44, 143.30, 143.00 (3C), 142.21, 142.18, 141.78 (2C), 141.72, 141.67, 141.43, 141.29, 141.26, 141.17, 141.15, 141.05 (2C), 140.93 (2C), 140.76, 140.71, 140.67, 139.50, 139.25, 139.01, 138.98, 136.89, 135.63, 135.42, 134.02, 133.07, 131.20 (q, $J_{C\text{-}F}$ = 32 Hz, aryl *C*), 129.44 (q, $J_{C\text{-}F}$ = 32 Hz, aryl *C*), 129.13 (2C, aryl *C*), 128.11 (2C, aryl *C*), 124.99 (2C, aryl *C*), 124.81 (2C, aryl *C*), 122.91 (q, $J_{C\text{-}F}$ = 271 Hz), 122.68 (q, $J_{C\text{-}F}$ = 271 Hz), 86.39, 83.66 (sp^3-*C* of C_{60}), 76.38 (sp^3-*C* of C_{60}); FT-IR *ν*/cm^{-1} (KBr) 1619, 1419, 1405, 1325, 1167, 1128, 1069, 1017, 986, 847, 830, 527; UV-vis ($CHCl_3$) λ_{max}/nm 257, 313, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{76}H_{10}F_6N$ 1050.0711; Found 1050.0706.

Fulleropyrroline 5i: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (54 μL, 0.40 mmol) and **2j** (59 μL, 0.40 mmol) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 4.5 h afforded first unreacted C_{60} (20.6 mg, 57%) and then **5i** (16.6 mg, 33%) as an amorphous brown solid: mp >300 °C.

5i: ^{1}H NMR (600 MHz, CS_2/DMSO-*d*$_6$) *δ* 8.61 (d, *J* = 8.8 Hz, 1H), 8.58 (d, *J* = 8.6 Hz, 1H), 8.27 (s, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.66-7.62 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-*d*$_6$) (all 1C unless indicated) *δ* 168.99 (*C*=N), 153.45, 151.30, 147.72, 147.13, 145.84, 145.73, 145.70, 145.35, 145.21, 145.18, 144.92, 144.91, 144.75 (4C), 144.64, 144.53, 144.37, 144.29, 144.20 (2C), 144.18 (2C), 144.11, 144.02, 143.93, 143.80, 143.22, 143.11, 142.96 (2C), 142.00, 141.98, 141.56, 141.47 (4C), 141.13 (2C), 141.09, 140.93 (2C), 140.70, 140.65, 140.62 (3C), 140.51, 139.36, 138.94, 138.50, 138.39, 135.97 (aryl *C*), 134.85, 134.75, 133.61, 133.55, 133.03 (aryl *C*), 132.83 (aryl *C*), 130.84 (aryl *C*), 130.47 (aryl *C*), 130.40 (aryl *C*), 129.24 (aryl *C*), 128.27 (aryl *C*), 128.08 (aryl *C*), 127.87 (aryl *C*), 126.35 (aryl *C*), 126.04 (aryl *C*), 125.83 (aryl *C*), 125.76 (aryl *C*), 125.33 (aryl *C*), 125.18 (aryl *C*), 125.06 (2C, aryl *C*), 123.79 (aryl *C*), 123.67 (aryl *C*), 86.15, 83.34 (sp^3-*C* of C_{60}), 75.90 (sp^3-*C* of C_{60});

FT-IR ν/cm^{-1} (KBr) 1653, 1508, 1463, 1426, 1278, 1246, 1182, 1110, 793, 771, 527; UV-vis ($CHCl_3$) λ_{max}/nm 259, 311, 430; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{82}H_{16}N$ 1014.1277; Found 1014.1279.

Fulleropyrroline 5j and 5j': Method A: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2e** (48 μL, 0.40 mmol) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 10 h afforded first unreacted C_{60} (18.7 mg, 52%), then **5j** (13.2 mg, 28%) and **5j'** (7.6 mg, 16%) as amorphous brown solid: mp >300 °C. Method B: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (45 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 9 h afforded first unreacted C_{60} (19.8 mg, 55%), then **5j** (13.0 mg, 27%) and **5j'** (8.0 mg, 17%) as amorphous brown solid: mp >300 °C.

5j: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.16 (d, J = 7.1 Hz, 2H), 7.65-7.64 (m, 2H), 7.49-7.48 (m, 3H), 7.42-7.41 (m, 2H), 7.30 (t, J = 7.8 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 170.05 (*C*=N), 153.73, 151.39, 147.76, 147.00, 146.15, 145.93 (3C), 145.66, 145.42, 145.36, 145.04, 144.97 (2C), 144.89, 144.85 (3C), 144.76, 144.52, 144.47, 144.39, 144.33 (2C), 144.22, 144.15, 144.08, 143.93, 143.47, 143.37, 143.04 (2C), 142.14 (2C), 141.78, 141.72, 141.67 (2C), 141.45, 141.38 (2C), 141.18, 141.14, 141.08 (2C), 140.95, 140.76 (3C), 140.64, 139.16, 138.92, 138.82, 138.63, 137.77 (aryl *C*), 135.29 (2C), 133.59 (aryl *C*), 133.49, 133.19, 132.92 (aryl *C*), 129.80 (aryl *C*), 128.98 (aryl *C*), 128.86 (2C, aryl *C*), 128.53 (2C, aryl *C*), 127.84 (2C, aryl *C*), 126.71 (aryl *C*), 83.85, 82.70 (sp^3-*C* of C_{60}), 76.41 (sp^3-*C* of C_{60}); FT-IR *v*/cm^{-1} (KBr) 1630, 1572, 1440, 1427, 1276, 1183, 1044, 984, 752, 693, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 312, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{11}ClN$ 948.0574; Found 948.0570.

5j': ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.76 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.47-7.40 (m, 4H), 7.31 (t, J = 7.7 Hz, 1H), 7.22 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 167.13 (*C*=N), 153.90, 151.00, 147.02, 145.87, 145.67, 145.60, 145.54, 145.01, 144.91, 144.65, 144.64, 144.58 (2C), 144.55, 144.51 (2C), 144.47, 144.32, 144.23 (2C), 144.01, 143.98, 143.94, 143.85 (2C), 143.81, 143.70 (2C), 143.08, 142.97, 142.79, 142.72, 141.85 (2C), 141.38, 141.34, 141.30, 141.25 (2C), 140.96 (2C), 140.91, 140.73 (2C), 140.66, 140.62, 140.48, 140.44, 140.39, 140.31, 139.07, 139.03, 138.80, 138.68, 138.34 (aryl *C*), 135.05, 134.91, 133.83, 132.72, 132.28 (aryl *C*), 131.84 (aryl *C*), 130.05 (aryl *C*), 129.30 (aryl *C*), 129.08 (aryl *C*), 127.86 (2C, aryl *C*), 127.27 (aryl *C*), 127.23 (2C, aryl *C*), 125.59 (aryl *C*), 88.14, 85.00 (sp^3-*C* of C_{60}), 75.43 (sp^3-*C* of C_{60}); FT-IR *v*/cm^{-1} (KBr) 1657, 1453, 1431, 1182, 1075, 1035, 983, 751, 698, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 312, 429; HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{74}H_{11}ClN$ 948.0574; Found 948.0570.

Fulleropyrroline 5k': Method A: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2k** (41 μL, 0.40 mmol) in the presence of $Mn(OAc)_3{\cdot}2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10

mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 3 h afforded first unreacted C_{60} (25.5 mg, 71%) and then **5k** (trace) and **5k'** (10.2 mg, 22%) as amorphous brown solid: mp >300 °C. Method B: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (37 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 3 h afforded first unreacted C_{60} (24.7 mg, 69%) and then **5k** (trace) and **5k'** (9.4 mg, 20%) as amorphous brown solid: mp >300 °C.

5k: ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.16-8.14 (m, 2H), 7.53-7.46 (m, 3H), 7.42-7.41 (m, 1H), 7.35-7.33 (m, 2H), 7.05-7.04 (m, 1H).

5k': ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.31 (d, J = 3.4 Hz, 1H), 7.65 (d, J = 5.2 Hz, 1H), 7.63 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.14 (t, J = 4.5 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 161.65 (*C*=N), 154.31, 151.73, 147.85, 146.91, 146.33, 146.00, 145.91, 145.82, 145.37 (2C), 144.96 (4C), 144.88, 144.75 (3C), 144.62, 144.47, 144.34 (2C), 144.20, 144.11, 144.04, 144.00, 143.85, 143.50, 143.42, 143.06 (2C), 143.03, 142.19, 142.17, 141.75 (4C), 141.69, 141.50, 141.30, 141.28 (2C), 141.06 (2C), 141.01, 140.91 (2C), 140.71, 140.61, 139.62, 138.99, 138.96, 138.90, 138.58, 137.01, 135.61 (2C), 133.88, 132.89, 130.65 (aryl *C*), 130.42 (aryl *C*), 128.09 (2C, aryl *C*), 127.50 (3C, aryl *C*), 127.29 (aryl *C*), 86.33, 82.08 (sp^{3}-*C* of C_{60}), 77.50 (sp^{3}-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1613, 1426, 1267, 1188, 1059, 837, 709, 701, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 310, 429; HRMS (MALDI-TOF) m/z: $[M + H]^{+}$ Calcd for $C_{72}H_{10}NS$ 920.0528; Found 920.0533.

Fulleropyrroline 5l and 6: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1k** (50 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3 \cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 ^{o}C for 4 h afforded first unreacted C_{60} (16.0 mg, 44%), then **6** (3.1 mg, 7%) and **5l** (4.8 mg, 10%) as amorphous brown solid: mp >300 °C.

5l: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.26 (d, J = 16.1 Hz, 1H), 7.63 (d, J = 6.8 Hz, 4H), 7.61 (d, J = 16.1 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.36-7.28 (m, 4H), 7.11 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 165.16 (*C*=N), 154.29, 151.68, 148.28, 147.23, 145.93, 145.87, 145.84, 145.27, 145.22, 145.17, 144.81 (3C), 144.78 (3C), 144.67, 144.54, 144.45 (2C), 144.31, 144.20 (3C), 144.09, 144.00, 143.90, 143.81, 143.32, 143.24, 142.98 (2C), 142.08 (2C), 141.58, 141.54 (3C), 141.49, 141.14 (3C), 141.00 (3C), 140.81 (2C), 140.77, 140.68 (2C), 140.37, 139.63, 139.58, 139.26 (2C), 138.59, 135.27, 135.18, 134.52, 133.85, 132.93, 129.04 (aryl *C*), 128.14 (2C, aryl *C*), 127.97 (2C, aryl *C*), 127.40 (aryl *C*), 127.32 (2C, aryl *C*), 127.20 (2C, aryl *C*), 117.43, 87.35, 83.09 (sp^3-*C* of C_{60}), 76.11 (sp^3-*C* of C_{60}); FT-IR v/cm^{-1} (KBr) 1638, 1607, 1450, 1427, 1335, 1267, 1182, 1169, 1157, 1043, 967, 745, 697, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 314, 430; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{76}H_{13}N$ 939.1043; Found 939.1052.

6: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.43 (d, J = 7.7 Hz, 2H), 7.53-7.48 (m, 3H), 7.32 (d, J = 7.6 Hz, 2H), 7.25 (t, J = 7.9 Hz, 2H), 7.14 (t, J = 8.3 Hz, 1H), 6.63 (t, *J* = 7.7 Hz, 1H), 4.25 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 168.73 (1C, *C*=N), 155.65 (1C), 152.82, 146.07, 146.02 (1C), 145.35 (4C), 145.05, 144.97 (4C), 144.90, 144.87, 144.44 (4C), 144.15, 143.99, 143.52, 143.08, 142.25, 142.15 (1C), 141.89, 141.82, 141.58. 141.39 (4C), 141.25, 141.02, 140.70, 139.91, 139.13 (3C), 135.82, 133.32 (1C), 133.05, 130.51 (1C, aryl *C*), 129.10 (aryl *C*), 128.00 (aryl *C*), 127.95 (4C, aryl *C*), 125.61 (1C, aryl *C*), 125.36 (1C, aryl *C*), 82.79 (1C, sp^3-*C* of C_{60}), 73.66 (1C, sp^3-*C* of C_{60}), 34.50 (1C); FT-IR *v*/cm^{-1} (KBr) 1669, 1628, 1599, 1540, 1492, 1450, 1441, 1426, 1272, 1263, 1182, 1157, 1109, 1060, 861, 695, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 308, 429; HRMS (MALDI-TOF) m/z: $[M]^+$ Calcd for $C_{76}H_{13}N$ 939.1043; Found 939.1052.

Fulleropyrroline 5m and 5m': According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2d** (52 μL, 0.40 mmol) in the presence of $Mn(OAc)_3\cdot 2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 4 h afforded first unreacted C_{60} (14.9 mg, 41%) and then **5m/5m'** (19.7 mg, 42%) as amorphous brown solid: mp >300 °C. The ratio of **5m/5m'** was determined as 2.6:1 based on the ^{1}H NMR spectrum.

5m: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{75}H_{14}NO$ 944.1070; Found 944.1063.

5m': ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.16 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.50-7.46 (m, 3H), 7.09 (s, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H); HRMS (MALDI-TOF) m/z: $[M + H]^+$ Calcd for $C_{75}H_{14}NO$ 944.1070; Found 944.1063.

Fulleropyrrolidine *cis*-4b: According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (60.4 mg, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 1 h afforded first unreacted C_{60} (21.1 mg, 59%) and then ***cis*-4b**[9d] (8.0 mg, 17%)

Reaction of C_{60} with 1a and 2b in the Presence of 2 equiv of BHT under the Assistance of $Mn(OAc)_3·2H_2O$ and DMAP. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) with the addition of BHT (22.0 mg, 0.10 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 3 h afforded first unreacted C_{60} (25.0 mg, 69%) and then **5a** (7.0 mg, 15%) as an amorphous brown solid.

Reaction of C_{60} with 1a and 2b in the Presence of 5 equiv of BHT under the Assistance of $Mn(OAc)_3·2H_2O$ and DMAP. According to the general procedure, the reaction of the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (41 μL, 0.40 mmol) and **2b** (44 μL, 0.40 mmol) in the presence of $Mn(OAc)_3·2H_2O$ (13.4 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) with the addition of BHT (55.1 mg, 0.25 mmol) in *o*-dichlorobenzene (6 mL) at 180 °C for 3 h, and no desired **5a** was observed.

Transformation of *cis*-4a to 5a in the Presence of $Mn(OAc)_3·2H_2O$ and DMAP.

A mixture of fulleropyrrolidine *cis*-**4a**[6c,9c,d] (18.3 mg, 0.02 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.02 mmol) and DMAP (4.9 mg, 0.04 mmol) was added to a 50 mL three-neck flask. After they were completely dissolved in *o*-dichlorobenzene (6 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 180 °C under air conditions for 2.5 h. 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/dichloromethane as the eluent to give first unreacted C_{60} (9.6 mg, 67%) and then **5a** (5.2 mg, 28%) as an amorphous brown solid.

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Supporting Information

Schemes S1-5 for the reaction of C_{60} with aldehydes and amines, proposed formation mechanism of compound *cis*-**4a**, HRMS of **3a**, **5e**, and **6**, UV-vis spectra of **3c**, **3e**, **3h**, **3k**, **5j**, **5l**, and **6**, ^1H and ^{13}C NMR spectra of products **3a-k**, *cis*-**4a**,**b**, **5a-l, 5j'**,**k'**, **5m/5m'**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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