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$CuCl_2$-Mediated Reaction of [60]Fullerene with Amines in the Presence or Absence of Dimethyl Acetylenedicarboxylate: Preparation of Fulleropyrroline or Aziridinofullerene Derivatives

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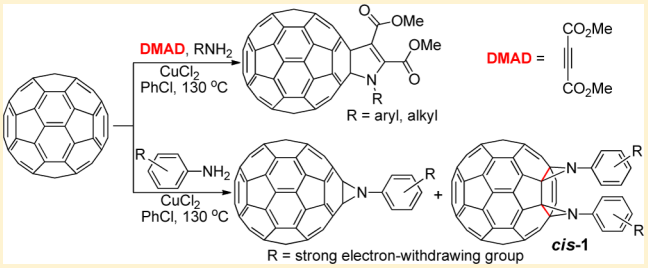
Supporting Information

ABSTRACT: The $CuCl_2$-mediated three-component reaction of C_{60} with amines and dimethyl acetylenedicarboxylate afforded the fulleropyrrolines in moderate yields. Furthermore, the $CuCl_2$-mediated oxidative [2 + 1] reaction of C_{60} with aromatic amines bearing a strong electron-withdrawing group provided the aziridinofullerenes and the selective *cis*-1-bisaziridinofullerenes.



INTRODUCTION

Extensive studies on the chemical functionalization of fullerenes have been made for further investigation on their properties and applications up to now, involving various radical additions, nuclophilic additions, [2 + *n*] (*n* = 1−4) cycloadditions, and multiadditions.[1] The 1,3-dipolar cycloaddition reaction is widely used for the preparation of five-membered heterocyclic ring-fused [60]fullerene derivatives. C_{60}-fused pyrrolidine/pyrroline derivatives can be easily prepared from the reaction of [60]fullerene with azomethine ylides or nitrile ylides. However, the nitrogen atom does not link with the fullerene skeleton directly. So far, there were only a few reports on the synthesis of C_{60}-fused pyrroline derivatives with a nitrogen atom bonding to the fullerene cage.[2] In recent years, C−C and C−N bond forming reactions mediated by zwitterionic species, generated by addition of various nucleophiles to electron-deficient alkynes, allenes, or diethyl azodicarboxylate, have been investigated intensively.[3] This method has also been applied in fullerene chemistry by performing the reaction of C_{60} with dimethyl acetylenedicarboxylate (DMAD) in the presence of different additives such as phosphine,[4] isocyanide,[5] quinoline,[6] or DMAP[7] to prepare three- or five-membered ring fused fullerene derivatives. In continuation of our interest in fullerene chemistry,[8] we reported here the $CuCl_2$-mediated reaction of C_{60} with amines in the presence or absence of DMAD to afford fulleropyrrolines or aziridinofullerenes.

It has been well reported that copper-mediated inter- or intramolecular reaction of *β*-enamino carbonyl compounds can afford a variety of azaheterocycles. Intramolecular reactions form indoles, oxazoles, or 3-azabicyclo[3.1.0]hex-2-enes,[9] and intermolecular reactions with alkynes or nitirles produce pyrroles or pyrazoles.[10] Nevertheless, the intermolecular reaction of *β*-enamino carbonyl compounds with alkenes to generate a pyrrole skeleton has seldom been investigated, and the substrates are mostly limited to nitroalkenes.[2a,11] Furthermore, in these methods, it is a prerequisite to prepare *β*-enamino carbonyl derivatives from *β*-dicarbonyl compounds and amines beforehand. We hypothesize that, if the *β*-enamino carbonyl compounds can be generated in situ from the readily available amines and DMAD, a tandem synthesis of fulleropyrrolines will be realized.

RESULTS AND DISCUSSION

At the onset, the reaction of C_{60} with 4-methylaniline **1a** and DMAD was carried out in the presence of different additives to screen the optimized reaction conditions (Table 1). When the mixture of C_{60} (0.05 mmol), 4-methylaniline **1a** (0.1 mmol), DMAD (0.1 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (0.1 mmol) was stirred in 10 mL of chlorobenzene at 130 °C for 10 h, to our delight, the desired product **2a** was obtained in 14% yield (Table 1, entry 1). CuO, $CuBr_2$, and $CuCl_2$ were also effective in this reaction, and $CuCl_2$ gave the best yield of **2a** (24%, Table 1, entries 3−5). $CuSO_4$, CuCl, and CuI only provided trace amount of **2a** (Table 1, entries 2, 10, and 11). A catalytic amount of $CuCl_2$ led to a noticeable decrease in the yield, and O_2 had no dramatic influence on the reaction (Table 1, entries 6 and 7). Increasing the amount of $CuCl_2$ to 4 equiv resulted in a significant increase of the yield to 34% (Table 1, entry 8). Although $Mn(OAc)_3{\cdot}2H_2O$ was also effective in this reaction (Table 1, entry 12), $CuCl_2$ was much cheaper and easily available. Other oxidants such as $FeCl_3$ and $PhI(OAc)_2$ could not initiate the reaction. An envision with aerobic oxidation catalyzed by $Pd(OAc)_2$ also failed (Table 1, entries 13−15). Reducing the temperature to 70 °C gave only trace amount of **2a** (Table 1, entry 9).

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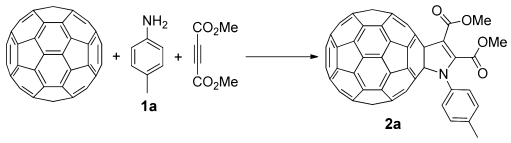
Table 1. Screening of the Reaction Conditions[a]



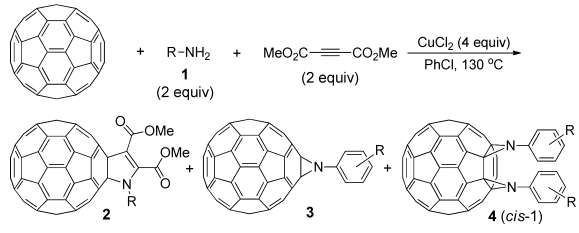
entry	additive	molar ratio[b]	temp (°C)	time (h)	yield (%)[c]
1	$Cu(OAc)_2\ H_2O$	1:2:2:2	130	10	14 (90)
2	$CuSO_4$	1:2:2:2	130	24	trace
3	CuO	1:2:2:2	130	12	13 (92)
4	$CuBr_2$	1:2:2:2	130	12	18 (82)
5	$CuCl_2$	1:2:2:2	130	12	24 (88)
6[d]	$CuCl_2$	1:2:2:2	130	12	22 (93)
7	$CuCl_2$	1:2:2:0.2	130	12	6 (90)
8	**$CuCl_2$**	**1:2:2:4**	130	**12**	**34 (86)**
9	$CuCl_2$	1:2:2:4	70	24	trace
10	CuCl	1:2:2:4	130	24	trace
11	CuI	1:2:2:4	130	24	trace
12	$Mn(OAc)_3\ 2H_2O$	1:2:2:2	130	3	27 (83)
13	$Pd(OAc)_2$	1:2:2:0.2	130	24	0
14	$PhI(OAc)_2$	1:2:2:2	130	24	0
15	$FeCl_3$	1:2:2:2	130	24	0

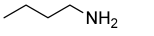
[a]Conditions: C_{60} (0.05 mmol), other starting materials, and 10 mL of chlorobenzene. [b]C_{60}/**1a**/DMAD/additive. [c]Isolated yield. Values in parentheses are based on consumed C_{60}. [d]N_2 atmosphere.

Under the optimal conditions (Table 1, entry 8), we examined the generality of this kind of three-component reaction (Table 2). Both aromatic amines and aliphatic amines could be successfully utilized to prepare fulleropyrrolines **2** in moderate yields. In terms of the aromatic amines, the substituent groups on the phenyl ring had great influence on the reaction. All electron-donating and weak electron-withdrawing groups gave moderate yield of **2** (Table 2, entries 1−5). However, when a strong electron-withdrawing group (NO_2) was linked with a phenyl ring, only 6% of the pyrroline product **2i** was isolated. Meanwhile, aziridinefullerene **3i** and the selective *cis*-1-bisaziridinefullerene **4i** were generated in 14% and 11% yield, respectively (Table 2, entry 9). In order to investigate the trend of influence of the electronic effect of the substituent group, more aromatic amines (**1f−h**) were introduced to this reaction (Table 2, entries 6−8). As for **1f** and **1g**, pyrroline products **2f** (21%) and **2g** (14%) were generated as the main products accompanying with minor products **3f** (12%), **4f** (10%), and **3g** (5%). However, when ethyl 4-aminobenzoate **1h** was employed in the reaction, aziridinofullerene **3h** (17%) was produced as the main product along with minor products **2h** (7%) and **4h** (5%) (Table 2, entry 8). Large steric hindrance amine (**1j**) afforded only 8% yield of **2j** (Table 2, entry 10). Alkyl amines **1k** and **1l** were also applicable in this reaction and gave the products in moderate yields (Table 2, entries 11 and 12).

We are inquisitive about the formation of mono/bisaziridinofullerenes **3** and **4** in the three-component reaction because it seemed that the DMAD did not participate in the reaction (Table 2, entries 6−9). Therefore, we performed the reaction of C_{60} with 4-nitroaniline **1i** and $CuCl_2$ in the absence of DMAD (Table 3). To our surprise, monoaziridinofullerene **3i** was also generated in 19% yield along with 16% yield of bisaziridinofullerene **4i** (Table 3, entry 1). However, no similar reaction occurred for 4-methylaniline **1a** or 4-chloroaniline **1d**,

Table 2. $CuCl_2$-Mediated Three-Component Reaction of C_{60} with DMAD and Amines[a]



entry	substrate	time (h)	product and yield (%)[b] 2	3	4
1	**1a** Me−C6H4−NH_2	8	34 (86)	0	0
2	**1b** C6H5−NH_2	8	27 (88)	0	0
3	**1c** MeO−C6H4−NH_2	8	30 (79)	0	0
4	**1d** Cl−C6H4−NH_2	8	33 (87)	0	0
5	**1e** F−C6H4−NH_2	8	25 (92)	0	0
6[c]	**1f** F_3C−C6H4−NH_2	12	21 (40)	12 (23)	10 (19)
7[c]	**1g** MeC(=O)−C6H4−NH_2	12	14 (55)	5 (20)	0
8[c]	**1h** EtOC(=O)−C6H4−NH_2	12	7 (17)	17 (41)	5 (12)
9[c]	**1i** O_2N−C6H4−NH_2	12	6 (14)	14 (33)	11 (26)
10	**1j** 2,6-Me2−C6H3−NH_2	8	8 (90)	0	0
11	**1k** C6H5−CH_2NH_2	8	27 (84)	0	0
12	**1l** 	8	21 (81)	0	0

[a]C_{60} (36 mg)/**1**/DMAD/$CuCl_2$ = 1:2:2:4, 10 mL of chlorobenzene, 130 °C. [b]Isolated yield. The values in parentheses are based on consumed C_{60}. [c]72 mg of C_{60} and 20 mL of chlorobenzene were used.

and the formation of azo compounds was observed.[12] These results indicated that only those aromatic amines bearing strong electron-withdrawing groups were suitable in this kind of conversion. CuO and $CuSO_4$ failed to give any of the products, and $Cu(OAc)_2{\cdot}H_2O$ only produced 5% of **3i** (Table 3, entries 2−4). A catalytic amount of $CuCl_2$ led to dramatic decrease in the yield, and low temperature resulted in no reaction (Table 3, entries 5 and 6).

It is worth noting that the generation of mono- and bisaziridinefullerenes (**3f−i**, **4f**, **4h**, and **4i**) in the three-component reaction was due to the incomplete Michael addition reaction of the amines with DMAD (Scheme 1). When 4-methylaniline **1a** was treated with an equal amount of

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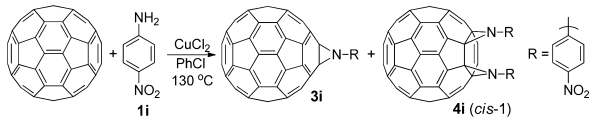
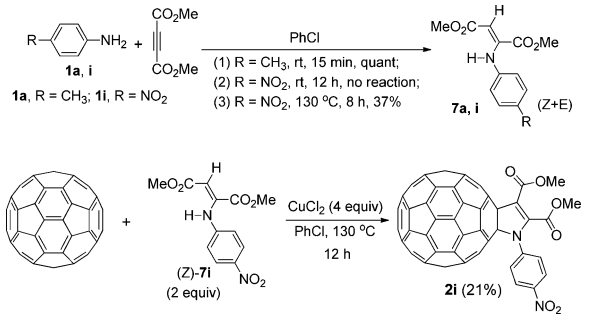
Table 3. Reaction of C_{60} with 4-Nitroaniline[a]



entry	[Cu]	molar ratio[b]	temp (°C)	time (h)	3[c]	4[c]
1	**$CuCl_2$**	**1:2:4**	**130**	**6**	**19 (47)**	**16 (40)**
2	$Cu(OAc)_2$ H_2O	1:2:4	130	6	5 (91)	0
3	$CuSO_4$	1:2:4	130	6	0	0
4	CuO	1:2:4	130	6	0	0
5	$CuCl_2$	1:2:0.2	130	6	<5	0
6	$CuCl_2$	1:2:4	80	6	0	0

[a]Conditions: C_{60} (72 mg), 20 mL of chlorobenzene. [b]C_{60}/**1i** /$CuCl_2$. [c]Isolated yield. The values in parentheses are based on consumed C_{60}.

Scheme 1

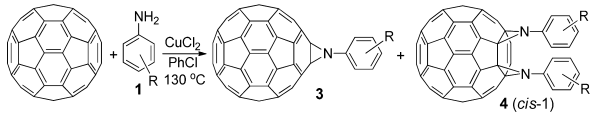


DMAD in PhCl under the same concentration as that of the three-component reaction, quantitative conversion to **7a** was observed at room temperature within a short time (15 min). In the case of the 4-nitroaniline **1i**, no addition reaction was observed even stirring at room temperature for 12 h. Increasing the temperature to 130 °C, only 37% of the addition product **7i** was formed after 8 h, as determined by ^{1}H NMR. When the pure **7i**[13] was treated with C_{60} in the presence of 4 equiv of $CuCl_2$ in PhCl at 130 °C for 12 h, the single fulleropyrroline **2i** was generated in 21% yield without the formation of **3i** or **4i** (Scheme 1). This result demonstrated that the aziridinefullerenes could not be generated from the reaction of enamines with C_{60} through release of DMAD. In the one-pot three-component reaction, the electron-withdrawing group on the phenyl ring led to the decrease of nucleophilicity of the nitrogen atom, which resulted in the slow Michael addition reaction of amines with DMAD. Thus, the competitive reaction of C_{60} with amines and enamines occurred, which led to the complex of products (Table 2, entries 6–9).

The aziridinofullerenes have been hitherto mainly synthesized from the reaction of C_{60} with organic azides, followed by photolysis or thermolysis of the triazole-fused fullerenes.[14] However, azafulleroid was always generated as a byproduct, and the substituent on the nitrogen atom had great influence on the distribution of azafulleroid and aziridinofullerene. Furthermore, azides had major associated problems with respect to their explosibility and toxicity. Although some new synthetic methods to aziridinefullerenes starting from chloramines,[15] sulfilimines,[16] iminophenyliodinanes,[17] and *N*,*N*-dihalosulfonamides[18] were recently reported, the products were mostly restricted to those aziridinefullerenes binding a strong electron-withdrawing group on the nitrogen atom such as carbonyl, sulfonyl, and phosphonyl groups. On the other hand, controlled diversity of the addition degree and the addition pattern allowed tuning of the electronic and chemical properties of fullerenes slightly, which was significant for the preparation of functional advanced materials. The regioselective bisadducts of fullerenes was difficult to be prepared because eight possible isomers existed. In order to control the regioselectivity of bisadditions to fullerene, an elegant protocol was introduced through tether-directed remote functionalization.[19] As for the *cis*-1-bisaziridinofullerene, up to now, only the Akasaka and Nagase group reported the selective synthesis of *cis*-1-bisaziridinofullerenes from sulfilimine.[16b] In addition, only the alkyl substituent of sulfilimine could afford the target compounds. Aryl substituent of sulfilimine gave the major azafulleroid product. In an earlier period, the Hirsch group reported the synthesis and isolation of eight isomers of $C_{60}(NCO_2R)_2$.[20] Nevertheless, the *cis*-1 isomer contained two open transannular [6,6] bonds. Herein, we developed a new method to prepare aziridinofullerenes and selective *cis*-1-bisaziridinofullerenes from the easily available aromatic amines mediated by $CuCl_2$.

Under the optimal conditions (Table 3, entry 1), different aromatic amines bearing a strong electron-withdrawing group took place in a similar reaction with C_{60} to generate the desired mono- and bisaziridinefullerenes products **3** and **4** (Table 4). 4-Aminoacetophenone had a poor reactivity and only gave the monoadduct **3g** in 7% yield.

Table 4. $CuCl_2$-Mediated Reaction of C_{60} with Electron-Deficient Aromatic Amines[a]



entry	substrate	R	time (h)	3[b]	4[b]
1	**1f**	4-CF_3	12	16 (51)	12 (39)
2	**1g**	4-$COCH_3$	12	7 (79)	trace
3	**1h**	4-CO_2Et	12	19 (67)	6 (21)
4	**1i**	4-NO_2	6	19 (47)	16 (40)
5	**1m**	3-NO_2	7	18 (41)	19 (44)
6	**1n**	4-CN	12	14 (58)	5 (21)

[a]All the reactions were carried out with 0.1 mmol of C_{60} in 20 mL of chlorobenzene at 130 °C with a molar ratio of C_{60}/**1**/$CuCl_2$ = 1:2:4. [b]Isolated yield. The values in parentheses are based on consumed C_{60}.

Structures of the bisadducts **4** were inferred from the NMR and UV–vis spectra. Taking **4i** as an example, the ^{13}C NMR spectrum of **4i** showed 29 signals (24 × 2C, 1 × 4C, 4 × 1C) in the range of 138–151 ppm for the sp^2 carbon of the fullerene cage and two signals at 70.44 and 76.51 ppm (each 2C) for the sp^3 carbon of the fullerene cage. These data demonstrate that the bisaziridinofullerene **4i** has a C_s symmetry with a symmetrical plane between the two aziridine addends. Among the possible eight isomers of bisadducts, only the *cis*-1, *cis*-2, and *trans*-4 isomers have this kind of C_s symmetry and ^{13}C NMR spectra patterns. Further determination of the structure was depended on the UV–vis spectroscopy analysis. UV–vis spectral patterns in the region 400–700 nm are extremely useful for fullerene structural assignments. It is well known that different types of fullerene bisadducts have entirely different UV–vis spectral patterns, whereas the same type of fullerene bisadducts display similar UV–vis absorption patterns.[16b,21]

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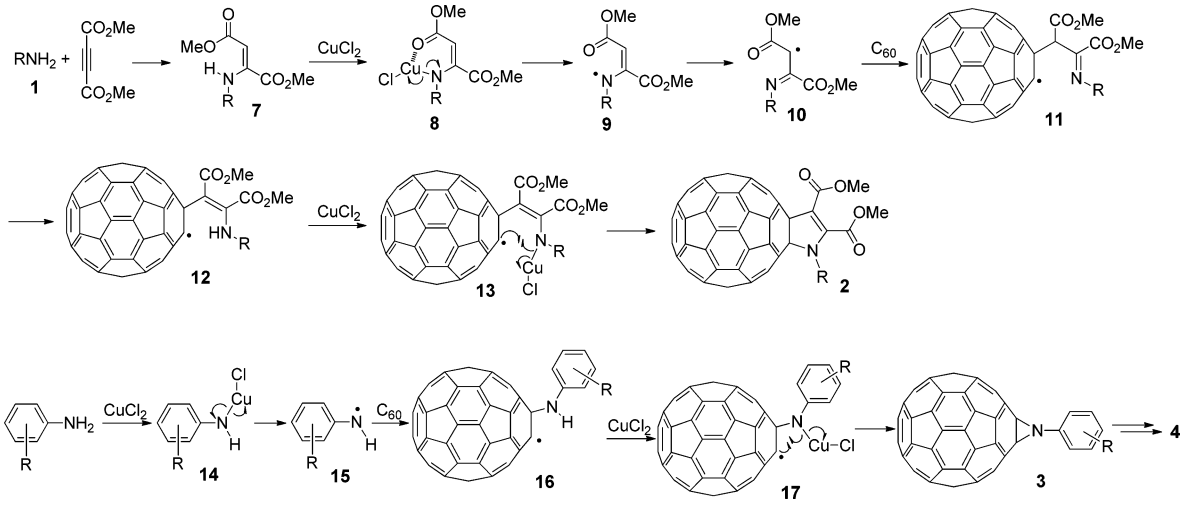
Scheme 2. Proposed Mechanism



The UV−vis spectrum of **4i** showed similarity with that of those reported *cis*-1-bisadducts in the literature and obvious difference with that of *cis*-2 or *trans*-4 isomers,[16b,21a,b] which strongly suggests that **4i** is a *cis*-1 isomer (see the Supporting Information). Hirsch also concluded that two-fold addition to [6,6]-bonds of C_{60} preferably attacked the *cis*-1 site for sterically less demanding addends.[22] The energetically favorable frontier orbital of the [6,6]-closed monoadduct displayed a high coefficient at *cis*-1 and the *e*-position, and the length of the *cis*-1 bond in the monoadduct was shorter than that of the *e*-bond due to the disruption of conjugation within the six-membered rings involving the *cis*-1 bonds. As a result, the *cis*-1 bond was more reactive than those of intact Kekulé rings within the fullerene cage.[23]

A proposed mechanism for the formation of fulleropyrroline **2** or aziridinofullerene **3** or **4** is described in Scheme 2. Michael addition reaction of amine with DMAD generates enamine **7**, which is chelated with $CuCl_2$ to yield **8**. Homolytical addition of **8** to C_{60} gives fullerene radical **12** accompanying with the loss of CuCl, followed by coordination with $CuCl_2$ to generate **13**; further intramolecular cyclization along with release of CuCl yields product **2**. In the case of the reaction between C_{60} and aromatic amines bearing a strong electron-withdrawing group, $CuCl_2$ reacted with amine to produce complex **14**. Homolytical cleavage of the C−Cu bond generates nitrogen radical **15**, which is captured by C_{60} to form fullerene radical **16**. Subsequent coordination of **16** with $CuCl_2$ generates complex **17**; following intramolecular cyclization with the concomitant discharge of CuCl affords aziridinofullerene product **3**. A similar reaction pathway starting from **3** provides the *cis*-1-bisaziridinofullerene **4**.

CONCLUSION

In summary, we have successfully developed a convenient three-component reaction for the synthesis of fulleropyrrolines from easily available amines and DMAD mediated by $CuCl_2$. In addition, we exploited a $CuCl_2$-mediated reaction of C_{60} with electron-deficient aromatic amines for the easy preparation of aziridinofullerenes and *cis*-1-bisaziridinofullerenes. It is the first time realizing the oxidative [2 + 1] reaction of aromatic amines with alkenes.

EXPERIMENTAL SECTION

General Procedure for the Three-Component Reaction of C_{60} with DMAD and Amines (1a−e and 1j−l) Mediated by $CuCl_2$. A mixture of C_{60} (36.0 mg, 0.05 mmol), DMAD (14.2 mg, 0.1 mmol), amines (**1a−e** and **1j−l**, 0.1 mmol), and $CuCl_2$ (27.0 mg, 0.2 mmol) was stirred vigorously in 10 mL of PhCl at 130 °C in a 25 mL round-bottomed flask equipped with a reflux condenser. The reaction was monitored by TLC and stopped at the designated time. The mixture was passed through a short silica gel column to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and fulleropyrrolines **2**. (**2a**: 16.4 mg, 34%; **2b**: 12.9 mg, 27%; **2c**: 14.7 mg, 30%; **2d**: 16.1 mg, 33%; **2e**: 12.1 mg, 25%; **2j**: 4.2 mg, 8%; **2k**: 13.2 mg, 27%; **2l**: 10.0 mg, 21%.)

General Procedure for the Three-Component Reaction of C_{60} with DMAD and Amines (1f−i) Mediated by $CuCl_2$. A mixture of C_{60} (72.0 mg, 0.1 mmol), DMAD (28.4 mg, 0.2 mmol), amines (**1f−i**, 0.2 mmol), and $CuCl_2$ (54.0 mg, 0.4 mmol) was stirred vigorously in 20 mL of PhCl at 130 °C in a 50 mL tube equipped with a reflux condenser. The reaction was monitored by TLC and stopped at the designated time. The mixture was passed through a short silica gel column 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/ethyl acetate as the eluent to give unreacted C_{60}, fulleropyrrolines **2**, aziridinofullerenes **3**, and the *cis*-1-bisaziridinofullerene **4**. (**2f**: 21.7 mg, 21%; **3f**: 10.7 mg, 12%; **4f**: 10.2 mg, 10%; **2g**: 14.1 mg, 14%; **3g**: 4.6 mg, 5%; **2h**: 7.5 mg, 7%; **3h**: 15.4 mg, 17%; **4h**: 5.1 mg, 5%; **2i**: 5.8 mg, 6%; **3i**: 12.2 mg, 14%; **4i**: 10.7 mg, 11%.)

General Procedure for the Reaction of C_{60} with Electron-Deficient Aromatic Amines (1f−i, 1m, and 1n) Mediated by $CuCl_2$. A mixture of C_{60} (72.0 mg, 0.1 mmol), amines (**1f−i**, **1m**, and **1n** 0.2 mmol), and $CuCl_2$ (54.0 mg, 0.4 mmol) was stirred vigorously in 20 mL of PhCl at 130 °C in a 50 mL tube equipped with a reflux condenser. The reaction was monitored by TLC and stopped at the designated time. The mixture was passed through a short silica gel column 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/ethyl acetate as the eluent to give unreacted C_{60}, aziridinofullerenes **3**, and the *cis*-1-bisaziridinofullerene **4**. (**3f**: 14.5 mg, 16%; **4f**: 12.7 mg, 12%; **3g**: 6.1 mg, 7%; **3h**: 16.6 mg, 19%; **4h**: 6.4 mg, 6%; **3i**: 16.1 mg, 19%; **4i**: 16.3 mg, 16%; **3m**: 15.2 mg, 18%; **4m**: 18.4 mg, 19%; **3n**: 11.5 mg, 14%; **4n**: 4.9 mg, 5%.)

Reaction of C_{60} with Enamine 7i[24] Mediated by $CuCl_2$. A mixture of C_{60} (36.0 mg, 0.05 mmol), **7i** (28.0 mg, 0.1 mmol), and $CuCl_2$ (27.0 mg, 0.2 mmol) was stirred vigorously in 10 mL of PhCl at 130 °C in a 25 mL round-bottomed flask equipped with a reflux

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condenser. The reaction was monitored by TLC and stopped at the designated time. The mixture was passed through a short silica gel column to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and fulleropyrrolines **2i** (10.6 mg, 21%).

2a: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.19, 162.29, 151.91, 147.92, 147.89, 147.33, 147.21, 146.46, 146.16, 146.03, 145.98, 145.95, 145.90, 145.42, 145.19, 145.08, 145.00, 144.67, 144.04, 143.41, 142.97, 142.83, 142.67, 142.63, 142.49, 142.10, 142.01, 141.85, 141.82, 139.69, 139.65, 139.61, 136.92, 135.17, 133.89, 130.63, 130.38, 99.58, 91.14, 73.10, 53.10, 51.41, 21.47; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 427, 456, 688; FT-IR (KBr) ν/cm^{-1} 2941, 1750, 1691, 1596, 1508, 1431, 1417, 1331, 1248, 1220, 1090, 980, 577, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{73}H_{13}NO_4$ 967.0845, found 967.0833.

2b: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.69 (d, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.14, 162.22, 151.71, 147.93, 147.92, 147.38, 147.26, 146.51, 146.22, 146.08, 146.03, 145.98, 145.95, 145.47, 145.25, 145.13, 144.93, 144.71, 144.08, 143.40, 143.01, 142.88, 142.72, 142.67, 142.52, 142.14, 142.05, 141.89, 141.85, 139.75, 139.65, 136.99, 136.76, 135.20, 130.91, 129.73, 129.50, 100.21, 91.12, 73.25, 53.08, 51.42; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 426, 455, 688; FT-IR (KBr) ν/cm^{-1} 2945, 1747, 1690, 1588, 1493, 1434, 1410, 1340, 1260, 1209, 1094, 904, 799, 729, 695, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{72}H_{11}NO_4$ 953.0688, found 953.0682.

2c: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.59 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.24, 162.35, 160.19, 152.17, 148.04, 147.95, 147.40, 147.28, 146.51, 146.22, 146.09, 146.04, 146.00, 145.96, 145.47, 145.25, 145.13, 145.04, 144.72, 144.10, 143.49, 143.02, 142.87, 142.72, 142.68, 142.55, 142.15, 142.07, 141.90, 141.88, 139.74, 139.70, 136.97, 135.21, 132.28, 128.97, 114.85, 99.30, 91.35, 73.09, 55.40, 53.12, 51.40; UV−vis ($CHCl_3$) λ_{max}/nm 257, 315, 427, 457, 689; FT-IR (KBr) ν/cm^{-1} 2943, 1745, 1684, 1606, 1508, 1433, 1345, 1249, 1214, 1094, 729, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{73}H_{13}NO_5$ 983.0794, found 983.0788.

2d: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 163.66, 161.80, 151.09, 147.86, 147.64, 147.30, 147.14, 146.44, 146.15, 146.02, 145.97, 145.93, 145.83, 145.40, 145.19, 145.05, 144.63, 143.98, 143.00, 142.96, 142.83, 142.67, 142.60, 142.42, 142.05, 142.01, 141.80, 141.73, 139.67, 137.00, 135.82, 135.29, 135.04, 132.08, 129.94, 100.97, 90.90, 73.12, 53.02, 51.32; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 427, 455, 688; FT-IR (KBr) ν/cm^{-1} 2944, 1748, 1693, 1606, 1489, 1433, 1336, 1259, 1088, 729, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{72}H_{10}ClNO_4$ 987.0298, found 987.0291.

2e: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.69 (dd, J = 8.9, 4.8 Hz, 2H), 7.17 (t, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 163.81, 161.93, 162.80 (d, $J_{1,C-F}$ = 252 Hz), 151.42, 147.88, 147.74, 147.32, 147.17, 146.46, 146.17, 146.04, 145.99, 145.93, 145.86, 145.42, 145.21, 145.07, 144.67, 144.65, 144.00, 143.06, 142.98, 142.85, 142.68, 142.62, 142.45, 142.06, 142.02, 141.83, 141.77, 139.70, 139.67, 137.01, 135.07, 132.92 (d, $J_{3,C-F}$ = 8.8 Hz), 132.55 (d, $J_{4,C-F}$ = 3.4 Hz), 116.70 (d, $J_{2,C-F}$ = 22.7 Hz), 100.41, 91.01, 73.07, 53.03, 51.34; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 427, 457, 688; FT-IR (KBr) ν/cm^{-1} 2947, 1749, 1689, 1606, 1506, 1435, 1341, 1265, 1209, 1092, 729, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{72}H_{10}FNO_4$ 971.0594, found 971.0599.

2f: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 163.67, 161.86, 150.69, 147.89, 147.47, 147.32, 147.09, 146.48, 146.18, 146.05, 146.01, 145.97, 145.83, 145.43, 145.23, 145.08, 144.64, 144.48, 143.98, 142.99, 142.87, 142.71, 142.62, 142.38, 142.07, 142.03, 141.82, 141.70, 140.35, 139.73, 139.70, 137.11, 135.08, 131.30 (q, $J_{2,C-F}$ = 33.2 Hz), 130.95, 126.81 (q, $J_{3,C-F}$ = 3.5 Hz), 123.39 (q, $J_{1,C-F}$ = 272 Hz), 102.10, 90.79, 73.29, 53.18, 51.49; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 427, 457, 685; FT-IR (KBr) ν/cm^{-1} 2946, 1749, 1694, 1605, 1515, 1435, 1417, 1321, 1260, 1214, 1169, 1127, 1066, 730, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{73}H_{10}F_3NO_4$ 1021.0562, found 1021.0554.

2g: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 195.85, 163.77, 161.98, 150.78, 147.92, 147.58, 147.35, 147.14, 146.50, 146.21, 146.08, 146.03, 145.97, 145.89, 145.46, 145.25, 145.11, 144.68, 144.64, 144.01, 143.07, 143.01, 142.90, 142.73, 142.65, 142.42, 142.11, 142.04, 141.86, 141.75, 141.32, 139.75, 139.65, 137.33, 137.09, 135.13, 130.57, 129.67, 102.09, 90.87, 73.36, 53.17, 51.49, 26.46; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 426, 455, 687; FT-IR (KBr) ν/cm^{-1} 2922, 2850, 1746, 1710, 1683, 1597, 1513, 1432, 1262, 1094, 802, 599, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{74}H_{13}NO_5$ 995.0794, found 995.0781.

2h: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.97, 163.70, 161.86, 150.84, 147.88, 147.60, 147.32, 147.14, 146.46, 146.18, 146.04, 145.99, 145.94, 145.87, 145.42, 145.21, 145.08, 144.64, 144.00, 143.08, 142.97, 142.86, 142.69, 142.62, 142.41, 142.09, 142.02, 141.83, 141.73, 141.05, 139.71, 139.62, 137.04, 135.10, 131.24, 130.95, 130.34, 101.83, 90.85, 73.32, 61.34, 53.07, 51.41, 14.46; UV−vis ($CHCl_3$) λ_{max}/nm 256, 316, 427, 457, 685; FT-IR (KBr) ν/cm^{-1} 2945, 1749, 1716, 1690, 1598, 1506, 1435, 1271, 1094, 911, 730, 703, 526; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{75}H_{15}NO_6$ 1025.0899, found 1025.0906.

2i: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 163.39, 161.68, 149.99, 147.91, 147.54, 147.33, 147.27, 147.03, 146.50, 146.21, 146.08, 146.03, 146.00, 145.78, 145.46, 145.26, 145.10, 144.65, 144.29, 143.96, 143.18, 143.02, 142.92, 142.75, 142.70, 142.63, 142.34, 142.07, 142.04, 141.83, 141.66, 139.76, 139.70, 137.20, 135.05, 130.97, 124.93, 103.69, 90.74, 73.44, 53.23, 51.54; UV−vis ($CHCl_3$) λ_{max}/nm 256, 316, 426, 457, 686; FT-IR (KBr) ν/cm^{-1} 2920, 1742, 1697,1589, 1523, 1494, 1434, 1343, 1258, 1093, 729, 527; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{72}H_{10}N_2O_6$ 998.0539, found 998.0528.

2j: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 6.94 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 2.62 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.19, 162.20, 153.15, 148.70, 147.85, 147.31, 147.25, 146.39, 146.15, 146.00, 145.90, 145.86, 145.43, 145.12, 145.05, 144.66, 144.59, 144.02, 143.27, 143.01, 142.79, 142.60, 142.57, 142.47, 142.07, 142.00, 141.81, 141.42, 139.66, 139.64, 139.59, 139.56, 136.76, 134.96, 131.50, 130.40, 98.59, 92.24, 73.23, 52.90, 51.25, 21.26, 20.08; UV−vis ($CHCl_3$) λ_{max}/nm 256, 314, 427, 457, 689; FT-IR (KBr) ν/cm^{-1} 2945, 2920, 1751, 1692, 1596, 1434, 1340, 1249, 1208, 1135, 1091, 915, 729, 527; HRMS (MALDI-FTMS) m/z: M$^+$ calcd for $C_{75}H_{17}NO_4$ 995.1158, found 995.1164.

2k: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 5.29 (s, 2H), 3.93 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.54, 163.45, 152.49, 148.87, 148.04, 147.49, 147.36, 146.62, 146.30, 146.20, 146.13, 146.11, 146.05, 145.53, 145.37, 145.23, 144.84, 144.72, 144.16, 143.13, 142.95, 142.83, 142.73, 142.53, 142.27, 142.18, 142.02, 141.91, 139.82, 139.59, 137.15, 136.20, 135.21, 128.93, 128.43, 128.37, 98.52, 89.86, 73.53, 53.54, 51.58, 50.06; UV−vis ($CHCl_3$) λ_{max}/nm 257, 315, 427, 456, 685; FT-IR (KBr) ν/cm^{-1} 2944, 1744, 1687, 1595, 1423, 1330, 1235, 1135, 1080, 904, 729, 696, 526; HRMS (MALDI-TOFMS) m/z: [M + Na]$^+$ calcd for $C_{73}H_{13}NNaO_4$ 990.0742, found 990.0751.

2l: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 4.19 (s, 3H), 4.04 (t, J = 8.1 Hz, 2H), 3.81 (s, 3H), 2.00 (quint, J = 7.8 Hz, 2H), 1.45 (sext, J = 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.57, 163.55, 152.61, 148.77, 148.10, 147.53, 147.36, 146.67, 146.29, 146.23, 146.17, 146.13, 145.52, 145.40, 145.26, 144.92, 144.64, 144.19, 143.19, 143.16, 142.99, 142.89,

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142.78, 142.61, 142.30, 142.28, 142.06, 139.93, 139.86, 137.35, 135.17, 97.41, 89.79, 73.55, 53.63, 51.47, 45.89, 33.14, 20.40, 13.88; UV−vis ($CHCl_3$) λ_{max}/nm 256, 315, 427, 456, 689; FT-IR (KBr) ν/cm^{-1} 2945, 1749, 1683, 1592, 1422, 1339, 1247, 1134, 1081, 904, 728, 526; HRMS (MALDI-TOFMS) m/z: $[M + Na]^+$ calcd for $C_{70}H_{15}NNaO_4$ 956.0899, found 956.0891.

3f: Brown solid, mp > 300 °C; ^{1}H NMR (300 MHz, CS_2−$CDCl_3$) δ 7.71−7.78 (m, 4H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 148.48, 145.32, 145.23, 144.95, 144.86, 144.62, 144.52, 144.01, 143.99, 143.88, 143.19, 143.16, 142.90, 142.20, 142.18, 141.10, 140.77, 126.49 (q, $J_{3,C-F}$ = 3.7 Hz), 126.38 (q, $J_{2,C-F}$ = 32.7 Hz), 125.79 (q, $J_{1,C-F}$ = 271.2 Hz), 121.45, 83.08; UV−vis ($CHCl_3$) λ_{max}/nm 258, 327, 424, 500; FT-IR (KBr) ν/cm^{-1} 2920, 1612, 1510, 1428, 1319, 1161, 1122, 1107, 1065, 1012, 902, 835, 729, 576, 526; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{67}H_4F_3N$ 879.0296, found 879.0288.

3g: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.11 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 195.80, 149.66, 145.32, 145.23, 144.95, 144.86, 144.63, 144.56, 144.08, 144.02, 143.89, 143.19, 143.16, 142.91, 142.21, 142.18, 141.10, 140.71, 133.36, 129.83, 121.29, 83.18, 26.37; UV−vis ($CHCl_3$) λ_{max}/nm 256, 320, 424, 496; FT-IR (KBr) ν/cm^{-1} 2920, 1676, 1598, 1504, 1426, 1263, 1166, 902, 834, 730, 526; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{68}H_7NO$ 853.0528, found 853.0542.

3h: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 165.63, 149.47, 145.33, 145.24, 144.95, 144.86, 144.64, 144.60, 144.21, 144.06, 143.91, 143.20, 143.18, 142.92, 142.23, 142.22, 141.10, 140.73, 130.97, 126.53, 121.13, 83.28, 60.93, 14.58; UV−vis ($CHCl_3$) λ_{max}/nm 258, 319, 424, 500; FT-IR (KBr) ν/cm^{-1} 2921 17065, 1602, 1504, 1386, 1363, 1272, 1164, 1106, 1015, 912, 766, 724, 704, 526; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{69}H_9NO_2$ 883.0633, found 883.0626.

3i: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.40 (d, J = 8.9 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 151.09, 145.43, 145.34, 145.11, 144.99, 144.71, 144.47, 144.27, 144.01, 143.94, 143.51, 143.30, 143.26, 143.00, 142.26, 142.16, 141.26, 140.80, 125.26, 121.53, 83.01; UV−vis ($CHCl_3$) λ_{max}/nm 258, 325, 424, 500; FT-IR (KBr) ν/cm^{-1} 2920, 1588, 1508, 1489, 1337, 1108, 902, 843, 728, 526; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{66}H_4N_2O_2$ 856.0273, found 856.0263.

3m: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.51 (t, J = 2.0 Hz, 1H), 8.10 (dd, J = 8.2, 1.5 Hz 1H), 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 148.89, 146.77, 145.43, 145.34, 145.12, 144.98, 144.71, 144.58, 144.02, 143.96, 143.28, 143.25, 143.16, 142.98, 142.27, 142.19, 141.24, 140.85, 130.02, 127.07, 119.13, 116.32, 83.06; UV−vis ($CHCl_3$) λ_{max}/nm 258, 323, 424, 499; FT-IR (KBr) ν/cm^{-1} 2920, 1523, 1476, 1427, 1392, 1345, 1183, 1076, 822, 797, 735, 526; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{66}H_4N_2O_2$ 856.0273, found 856.0280.

3n: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.79 (d, J = 8.9 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 149.32, 145.39, 145.30, 145.05, 144.94, 144.68, 144.46, 143.99, 143.91, 143.63, 143.26, 143.21, 142.97, 142.23, 142.15, 141.20, 140.77, 133.35, 121.93, 118.36, 108.01, 82.95; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 424, 500; FT-IR (KBr) ν/cm^{-1} 2919, 2224, 1601, 1503, 1427, 1395, 1264, 1182, 1164, 835, 572, 554, 525; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{67}H_4N_2$ 836.0374, found 836.0368.

4f: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 4H), 7.59 (d, J = 8.5 Hz, 4H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 151.04, 148.96, 147.98, 147.38, 147.25, 146.44, 146.15, 145.91, 145.74, 145.51, 145.43, 144.85, 144.81, 144.33, 144.12, 144.08, 143.57, 143.49, 143.42, 142.83, 142.68, 142.36, 142.23, 141.97, 141.91, 141.73, 141.65, 141.33, 140.53, 138.64, 138.46, 126.39 (q, $J_{3,C-F}$ = 3.9 Hz), 126.21 (q, $J_{2,C-F}$ = 32.9 Hz), 123.96 (q, $J_{1,C-F}$ = 271 Hz), 121.43, 75.61, 69.79; UV−vis ($CHCl_3$) λ_{max}/nm 258, 324, 425, 470; FT-IR (KBr) ν/cm^{-1} 2921, 1613, 1514, 1429, 1321, 1162, 1121, 1107, 1065, 1012, 904, 837, 730, 527; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{74}H_8F_6N_2$ 1038.0592, found 1038.0588.

4h: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.10 (d, J = 8.7 Hz, 4H), 7.54 (d, J = 8.8 Hz, 4H), 4.36 (q, J = 7.1 Hz, 4H), 1.40 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 165.69, 151.15, 149.03, 149.01, 147.43, 147.23, 146.41, 146.13, 145.89, 145.70, 145.51, 145.42, 144.83, 144.82, 144.29, 144.11, 144.08, 143.57, 143.46, 143.45, 142.81, 142.64, 142.38, 142.26, 141.93, 141.82, 141.75, 141.56, 141.38, 140.49, 138.98, 138.77, 130.85, 126.30, 121.15, 75.78, 69.99, 60.94, 14.54; UV−vis ($CHCl_3$) λ_{max}/nm 258, 324, 425, 469; FT-IR (KBr) ν/cm^{-1} 2920, 1708, 1602, 1505, 1387, 1364, 1271, 1164, 1162, 1016, 906, 848, 767, 728, 704, 527; HRMS (MALDI-TOFMS) m/z: $[M + Na]^+$ calcd for $C_{78}H_{18}N_2NaO_4$ 1069.1164, found 1069.1152.

4i: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.31 (d, J = 9.0 Hz, 4H), 7.62 (d, J = 9.0 Hz, 4H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 150.42, 150.16, 148.64, 147.26, 147.03, 146.44, 146.13, 145.95, 145.76, 145.53, 145.45, 144.93, 144.70, 144.44, 144.18, 144.07, 143.66, 143.62, 143.40, 142.93, 142.82, 142.31, 142.16, 142.09, 141.82, 141.79, 141.39, 141.28, 140.74, 138.00, 137.98, 125.14, 121.23 76.51, 70.44; UV−vis ($CHCl_3$) λ_{max}/nm 256, 325, 425, 470; FT-IR (KBr) ν/cm^{-1} 2922, 1589, 1509, 1492, 1336, 1109, 904, 848, 728, 525; HRMS (MALDI-FTMS) m/z: M^+ calcd for $C_{72}H_8N_4O_4$ 992.0546, found 992.0535.

4m: Brown solid, mp > 300 °C; ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.33 (t, J = 2.1 Hz, 2H), 8.03−8.06 (m, 2H), 7.87−7.90 (m, 2H), 7.63 (t, J = 8.1 Hz, 2H); ^{13}C NMR (500 MHz, CS_2−$CDCl_3$) δ 150.74, 149.07, 148.77, 147.46, 147.37, 146.59, 146.28, 146.16, 146.05, 145.94, 145.64, 145.55, 144.99, 144.83, 144.53, 144.21, 143.69, 143.63, 143.49, 142.94, 142.92, 142.36, 142.25, 142.15, 141.93, 141.82, 141.66, 141.43, 140.79, 138.19, 138.07, 130.04, 127.23, 119.13, 116.25, 75.78, 69.78; UV−vis ($CHCl_3$) λ_{max}/nm 258, 324, 425, 470; FT-IR (KBr) ν/cm^{-1} 2923, 1527, 1477, 1394, 1346, 1261, 1076, 823, 799, 735, 525; HRMS (MALDI-FTMS) m/z: M^+ calcd for $C_{72}H_8N_4O_4$ 992.0546, found 992.0551.

4n: (It cannot be characterized by NMR due to its very poor solubility in commonly used solvents such as CS_2, 1,2-dichlorobenzene, $CHCl_3$, and $ClCH_2CH_2Cl$.) Brown solid, mp > 300 °C; FT-IR (KBr) ν/cm^{-1} 2922, 2222, 1600, 1503, 1463, 1378, 1262, 1181, 1163, 804, 572, 550, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 325, 424, 469; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{74}H_8N_4$ 952.0749, found 952.0736.

■ ASSOCIATED CONTENT

Supporting Information

Comparison of UV−vis spectra of **3h** and **4h** with those of reported bisadducts in the literature. ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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