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KO^{t}Bu-Mediated Coupling of Indoles and [60]Fullerene: Transition-Metal-Free and General Synthesis of 1,2-(3-Indole)(hydro)[60]fullerenes

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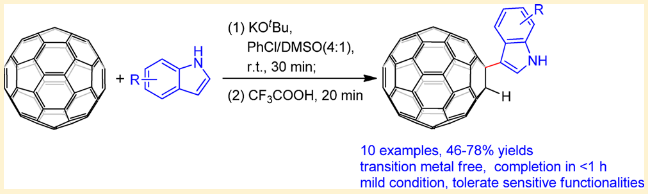
Supporting Information

ABSTRACT: Direct coupling of indoles with C_{60} has been achieved for the first time. Transition-metal-free KO^{t}Bu-mediated reaction of indoles to [60]fullerene has been developed as a practical and efficient method for the synthesis of various 1,2-(3-indole)(hydro)[60]fullerenes that are otherwise difficult to direct synthesize in an efficient and selective manner. This methodology tolerates sensitive functionalities such as chloro, ester, and nitro on indole and builds molecular complexity rapidly, with most reactions reaching completion in <1 h. A plausible reaction mechanism is proposed to explain the high regioselectivity at the 3-position of the indoles and the formation of 1,2-(3-indole)(hydro)[60]fullerenes.



10 examples, 46-78% yields
transition metal free, completion in <1 h
mild condition, tolerate sensitive functionalities

■ INTRODUCTION

Chemically functionalized [60]fullerene(C_{60}) derivatives have been extensively used for applications including optoelectronic materials,[1] nanoscience,[2] and biomedicine.[3] Among the various types of reactions for the functionalization of C_{60}, metal salt-mediated or -catalyzed reactions have emerged as one of the most important methodologies.[4−8] Extensive efforts have focused on using transition-metal salts, such as Mn,[4] Fe,[5] Cu,[6] Pd,[7] Co,[8] which have allowed the development of a broad range of innovative fullerene reactions. For continuing the exploration of metal salt-mediated or -catalyzed reactions of fullerene, developing transition-metal-free alkali-metal salt-mediated effective protocols to synthesize novel fullerene derivatives has attracted our interest. On the other hand, indole derivatives constitute a large number of biologically important pharmaceuticals, fragrances, agrochemicals, conducting polymers, and ligands.[9] As a result, numerous methodologies for the preparation and functionalization of indole derivatives have been developed.[10] However, to the best of our knowledge, direct reaction between indoles and fullerene has rarely been reported. We envisioned that the use of a transition-metal-free approach would allow the coupling of the most electron density C-3 site of indoles and the electron-deficient carbon−carbon double bonds on C_{60}. Herein, this challenge has been addressed, and we present a one-pot transition-metal-free efficient synthesis of 1,2-(3-indole)(hydro)[60]fullerenes by unprecedented KO^{t}Bu-mediated direct coupling of indoles with C_{60}.

■ RESULTS AND DISCUSSION

To begin our study, the readily available indole (**1a**) was chosen as the model substrate. Various metal salts and solvents were screened to optimize the reaction conditions, and the representative results are summarized in Table 1. Bases such as K_2CO_3, Na_2CO_3, Cs_2CO_3, KOAc, NaOAc did not provide any product **2a**, and reactant C_{60} was recovered almost quantitatively from the reaction (Table 1, entries 1−5). Further examination of stronger bases, such as sodium and potassium hydroxide, afforded only 7% and 11% yields of **2a**, respectively (Table 1, entries 6−7). To our delight, employing sodium and potassium tertbutoxides greatly improved the yields of **2a** to 65% and 78%, respectively (Table 1, entries 8 and 9). Sodium and calcium hydrides were also effective for the reaction and provided yields of 61% and 49% (Table 1, entries 10−11). A notable cosolvent effect was observed on this present reaction. It was found that the absence of a polar cosolvent under otherwise identical conditions did not produce any **2a** (Table 1, entry 12). In sharp contrast to this result, addition of the polar cosolvents, such as DMSO and DMF, improved the yields of **2a** drastically to 78% and 67%, respectively (Table 1, entries 9 and 15). Other cosolvents, such as CH_3CN, THF, DME, 1,4-dioxane, and chloroform, did not exert any influences to realize the reaction (Table 1, entries 13−14, 16−18). It should be noted that a similar experiment using KO^{t}Bu as base and a mixture of chlorobenzene(PhCl) (8 mL) and DMSO (2 mL) as solvent in air reduced the product yield significantly to 19%. With the optimized reaction conditions in hand, the substrate scope was investigated by employing different indoles. As shown in Table 2, a variety of indoles reacted efficiently with C_{60} to regioselectively afford the desired products in good yields. The substrates **1b−1d** having a electron-donating methyl group at the 5- or 7- or 2-position of indole afforded the corresponding products **2b−d** in 51−68% yields (Table 2, entries 2−4). Withdrawing groups, such as ester, nitro, and

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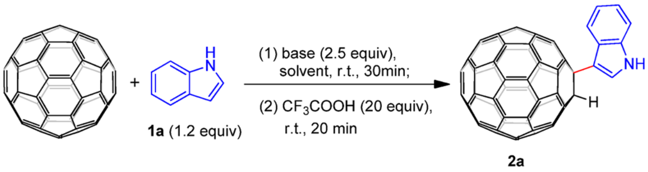
Table 1. Optimization of Reaction Conditions[a]



entry	base	solvent	yield (%)[b]
1	K_2CO_3	PhCl/DMSO (4:1)	NR
2	Na_2CO_3	PhCl/DMSO (4:1)	NR
3	Cs_2CO_3	PhCl/DMSO (4:1)	NR
4	KOAc	PhCl/DMSO (4:1)	NR
5	NaOAc	PhCl/DMSO (4:1)	NR
6	NaOH	PhCl/DMSO (4:1)	7(7)
7	KOH	PhCl/DMSO (4:1)	11(11)
8	NaO^{t}Bu	PhCl/DMSO (4:1)	65(71)
9	**KO^{t}Bu**	**PhCl/DMSO** (4:1)	**78(80)**
10	NaH	PhCl/DMSO (4:1)	61(72)
11	CaH	PhCl/DMSO (4:1)	49(71)
12	KO^{t}Bu	PhCl	NR
13	KO^{t}Bu	PhCl/CH_3CN (4:1)	NR
14	KO^{t}Bu	PhCl/THF (4:1)	NR
15	KO^{t}Bu	PhCl/DMF (4:1)	67(70)
16	KO^{t}Bu	PhCl/DME (4:1)	NR
17	KO^{t}Bu	PhCl/1,4-dioxane (4:1)	NR
18	KO^{t}Bu	PhCl/$CHCl_3$ (4:1)	NR

[a] Reactions were carried out using C_{60} (0.05 mmol, 1 equiv), indole (0.06 mmol, 1.2 equiv), base (0.125 mmol, 2.5 equiv) in Schlenk tubes under Ar atmosphere for 30 min, and then CF_3COOH (1.0 mmol, 20 equiv) was added and stirred for another 20 min. [b] Isolated yield by column chromatography. Values in parentheses were based on consumed C_{60}.

chloro, at various positions in the benzene ring of indole could be tolerated under the reaction conditions and gave the expected products **2e**−**2h** in good yields (Table 2, entries 5−8). A strong electron-donating methoxy group at the 5- or 7-position exhibited lower reactivity to afford the corresponding products **2i**−**2j** in 46−49% yields, even though the reaction temperature was increased to 80 °C (Table 2, entries 9−10). It is important to note that all the reactions are regioselective, giving products substituted at the 3-position of the indoles. Additionally, the indoles and hydrogen atoms on the [60] fullerene core are also regioselective, giving sole 1,2-adducts **2a**−**2j**.

The structures of **2a**−**2j** were unambiguously characterized by MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectroscopy. All of the mass spectra of these products gave the correct molecular ion peaks. The ^{1}H NMR spectra of **2a**−**2j** showed all expected signals. In the ^{13}C NMR spectra of **2a**−**2j**, there were 27−29 peaks including two half-intensity ones in the 134.62−154.87 ppm region for the 58 sp^2-carbons of the C_{60} moiety, consistent with their Cs symmetry. The two sp^3-carbons of the C_{60} skeleton were located at 61.46−62.79 ppm and 61.12−62.24 ppm, close to those of the previously reported hydrofullerene derivatives.[4h,7h,11] Their UV−vis spectra exhibited a peak at 428−430 nm, which is a characteristic absorption for the 1,2-adducts of C_{60}.[4−8]

Our attempts to employ N-substituted indoles, such as *N*-methylindole and *N*-Boc-indole, failed to generate corresponding products. It seems that the presence of the N−H group in indole is crucial for the coupling with the C_{60}. A vis-NIR spectrum study was performed to gain more insight into the reaction mechanism. As shown in Figure 1, when KO^{t}Bu was added to the solution of C_{60} and indole in a mixture of PhCl/DMSO = 4:1 under argon, the color of the solution changed from purple to dark green in 10 min. Dark green is the typical color for the monoanion RC_{60}^-.[12] The vis-NIR spectrum of the corresponding dark green solution shows strong absorption bands at 649 and 984 nm and is very similar to that of the RC_{60}^- of a C_{60} fullerosulfonic acid derivative (648 and 983 nm)[13] and a C_{60} oxazoline derivative (645 and 963 nm).[14] This result, therefore, indicates the addition of indole to C_{60} and the formation of a monoanion C_{60}^--C_8H_7N.

Previous work has shown that C_{60} is an excellent electrophile reacting with a variety of neutral and charged nucleophilic reagents.[15] On the basis of the above observed experimental results, a proposed anion addition mechanism is illustrated in Scheme 1. Initially, the N−H group reacts with KO^{t}Bu forming the indol-1-ide **A**, which subsequently forms indol-3-ide **B** as a resonance structure.[16] Further nucleophilic attack of **B** to C_{60} would lead to intermediate **C**. **C** may be easily quenched by CF_3COOH which converts into the desired adduct **2a**. Since the reaction provided poor yield (19%) of product under air, we supposed that the oxygen may oxidize intermediate **C**, which greatly lowers the yield, and the moisture in air will also lead to a low yield by quenching the base.

According to the optimized proceduce, the sacle-up of one of the KO^{t}Bu-mediated reactions of indoles to [60]fullerene has been examined. As shown in Scheme 2, the reaction of C_{60} (0.5 g, 0.69 mmol) with indole **1a** (0.098 g, 0.84 mmol) in the presence of KO^{t}Bu (0.195 g, 1.78 mmol) under identical conditions afforded corresponding product **2a** in 74% yield, demonstrating that the efficiency of the present method stays high at large scale.

Fulleroindoles **2a**−**2j** (except **2f**) have good solubility in common solvents for fullerenes, such as CS_2, chlorobenzene, *o*-dichlorobenzene, benzene, and toluene. The electrochemical properties of representative products **2a**, **2h**, **2j** along with C_{60} and PCBM have been investigated by cyclic voltammetry (CV), and their half-wave reduction potentials are summarized in Table 3. The electrochemical properties of **2a**, **2h** and **2j** are quite similar and show two quasi-reversible redox processes. It should be noted that the first reduction potentials of these (3-indole)(hydro)[60]fullerenes are more negative than that of C_{60} and are close to that of PCBM. Particularly, the first reduction potential (−1.201 V) of **2j** is even more cathodically shifted relative to PCBM (−1.158 V). It means that these (3-indole)(hydro)[60]fullerenes possess higher LUMO energy levels than that of PCBM and may have potential application as acceptors in organic photovoltaic devices.[11]

■ CONCLUSION

In conclusion, transition-metal-free direct coupling of readily available indoles with C_{60} mediated by inexpensive KO^{t}Bu at room temperature has been developed as a practical method for the one-pot effective synthesis of various 1,2-(3-indole)(hydro)[60]fullerenes that are otherwise difficult to directly synthesize in an efficient and selective manner. Because of the mild conditions, this methodology tolerates sensitive functionalities such as chloro, ester, and nitro on indole. Furthermore, it builds molecular complexity rapidly, with most reactions reaching completion in <1 h. A plausible reaction mechanism is proposed to explain the high regioselectivity at the 3-position of the indoles and the formation of 1,2-(3-indole)(hydro)[60]fullerenes.

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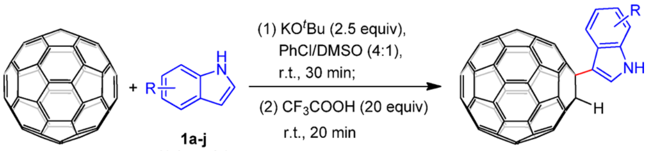
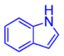
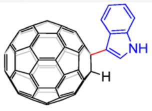
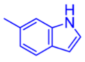
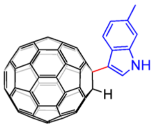
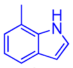
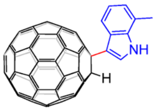
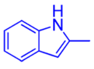
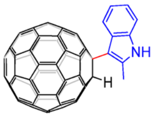
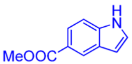
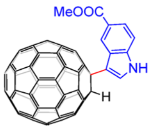
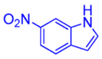
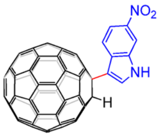
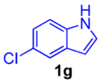
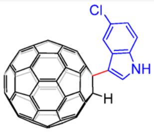
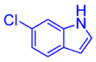
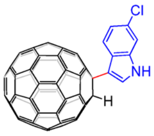
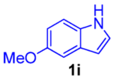
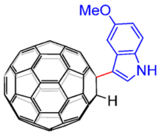
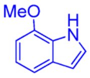
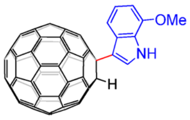
Table 2. Synthesis of (3-Indole)(hydro)[60]fullerenes[a]



1a-j
(1.2 equiv)

2a-j

entry	substrate 1	product 2	Yield(%)[b]
1	 **1a**	 **2a**	78(80)
2	 **1b**	 **2b**	68(75)
3	 **1c**	 **2c**	62(73)
4	 **1d**	 **2d**	51(57)
5	 **1e**	 **2e**	55(64)
6	 **1f**	 **2f**	69(73)
7	 **1g**	 **2g**	72(74)
8	 **1h**	 **2h**	70(72)
9[c]	 **1i**	 **2i**	49(68)
10[c]	 **1j**	 **2j**	46(67)

[a] Reaction conditions: C_{60} (0.05 mmol, 1 equiv), **1** (0.06 mmol, 1.2 equiv) and KO^{t}Bu (0.125 mmol, 2.5 equiv), PhCl (8 mL), DMSO (2 mL) under an argon atmosphere for 30 min at room temperature, and then CF_3COOH (1.0 mmol, 20 equiv) was added and stirred for another 20 min. [b] Isolated yield by column chromatography. Values in parentheses were based on consumed C_{60}. [c] The reactions were carried out at 80 °C.

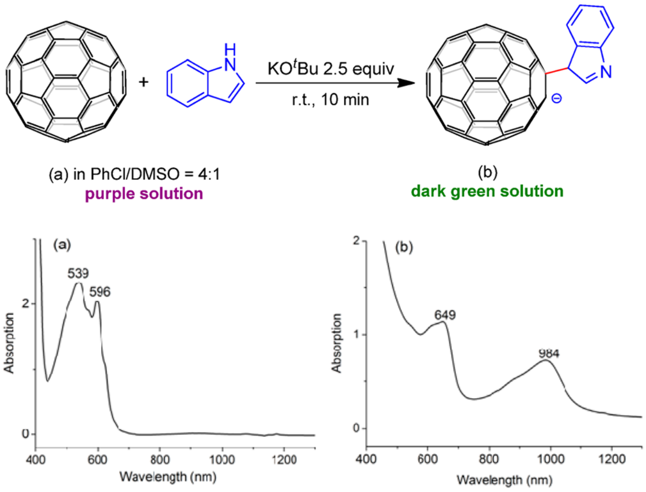
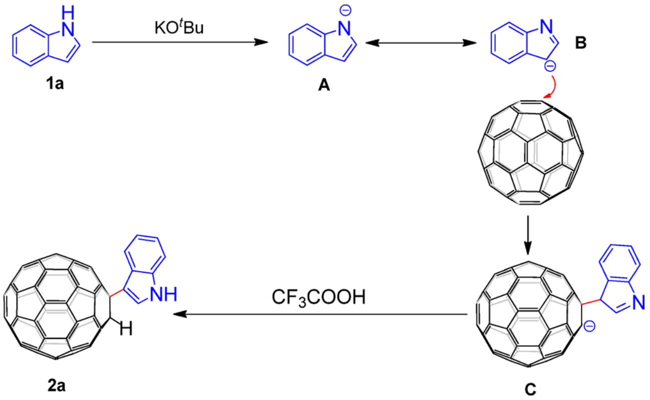


Figure 1. (a) The vis-NIR spectrum of C_{60} (0.05 mmol) and indole (0.06 mmol) in a mixture of PhCl (16 mL) and DMSO (4 mL) as the solvent. (b) The vis-NIR spectrum of the solution after KO^{t}Bu (2.5 equiv) is added and stirred for 10 min under Ar atmosphere.

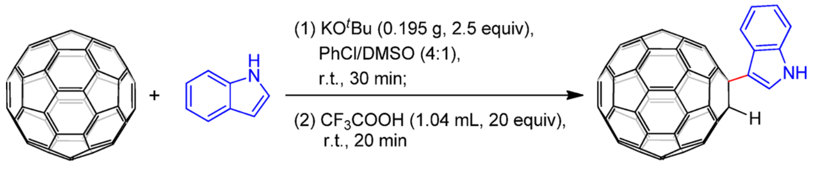
Scheme 1. Proposed Reaction Mechanism



EXPERIMENTAL SECTION

General Methods. All reactions were carried out using standard Schlenk technique under an argon or nitrogen atmosphere. Chlorobenzene (AR grade) and DMSO (AR grade) were dried over CaH_2, distilled under reduced pressure, and stored under an argon atmosphere

Scheme 2. Scale-up Synthesis of 1,2-(3-Indole)(hydro)[60]fullerene 2a



C_{60} (0.5 g, 1 equiv)

1a (0.098 g, 1.2 equiv)

2a (0.431 g, 74%)

Table 3. Half-Wave Reduction Potentials (V) of C_{60}, PCBM, and (3-Indole)(hydro)[60]fullerenes 2a, 2h, 2j[a]

compd	E_1	E_2
C_{60}	−1.078	−1.463
PCBM	−1.158	−1.537
2a	−1.187	−1.561
2h	−1.179	−1.559
2j	−1.201	−1.578

[a] Versus ferrocene/ferrocenium. Experimental conditions: 1 mM of compound and 0.1 M of n-Bu_4NClO_4 in anhydrous o-dichlorobenzene; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 50 mV·s^{-1}.

over activated 4 Å molecular sieves in Teflon screwed Schlenk flasks before using them. ^{1}H NMR spectra were referenced to residual DMSO at 2.50 ppm, and ^{13}C NMR spectra were referenced to residual DMSO at 39.52 ppm.

Cyclic Voltammetry of 2a, 2h, 2j. 1,2-(3-Indole)(hydro)[60]-fullerene(**2a**, **2h**, or **2j**) dissolved in anhydrous o-dichlorobenzene ($c = 2 \times 10^{-4}$ M) containing 0.1 M TBAP was added into an electrochemical cell under an argon atmosphere. CV measurements were then undertaken.

General Procedure for the Synthesis of 1,2-(3-Indole)(hydro)[60]fullerene 2a−2h. C_{60} (0.05 mmol), indole **1** (0.06 mmol), and KO^{t}Bu (0.125 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. Then dry DMSO (2 mL) was added to the mixture, and the color of the solution changed gradually from purple to dark green. After being stirred for 30 min, CF_3COOH (0.075 mL, 1.0 mmol) was added to the mixture, and the color of the solution changed immediately from dark green to reddish brown. The reaction mixture was stirred for 20 min, and the resulting brown solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} subsequent elution with carbon disulfide/dichloromethane (5:1) afforded **2**.

General Procedure for the Synthesis of 1,2-(3-Indole)(hydro)[60]fullerene 2i−2j. C_{60} (0.05 mmol), indole **1** (0.06 mmol), and KO^{t}Bu (0.125 mmol) were dissolved in chlorobenzene (8 mL) at room temperature under Ar atmosphere. The mixture was heated to 80 °C, and then dry DMSO (2 mL) was added to the mixture, and the color of the solution changed gradually from purple to dark green. After being stirred for 30 min, CF_3COOH (0.075 mL, 1.0 mmol) was added to the mixture. The reaction mixture was stirred at 80 °C for 20 min, and the resulting brown solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60}, and subsequent elution with carbon disulfide/dichloromethane (3:1) afforded **2**.

1,2-(3-Indole)(hydro)[60]Fullerene 2a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (7.2 mg, 0.06 mmol) and KO^{t}Bu (14.2 mg, 0.125 mmol) afforded first unreacted C_{60} (1.1 mg, 3%) and then **2a** (32.5 mg, 78%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.19 (s, N−H, 1H), 8.66−8.64 (m, 1H), 7.70−7.69 (m, 1H), 7.52−7.50 (m, 1H), 7.26−7.24 (m, 2H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.24, 152.87, 146.64(1C), 146.47(1C), 146.24, 145.75, 145.59, 145.52, 145.38, 145.33, 145.13, 144.70, 144.66, 144.60, 144.58, 143.98, 143.89, 142.44, 141.77, 141.76, 141.54, 141.35(4C), 141.26, 140.94, 140.90, 139.69, 139.43, 137.13, 135.76, 134.53 (1C, aryl C), 125.04 (1C, aryl C), 122.16 (1C, aryl C), 121.99 (1C, aryl C), 121.74 (1C, aryl C), 119.51 (1C, aryl C), 118.26 (1C, aryl C), 112.11 (1C, aryl C), 62.01 (1C, sp^3-C of C_{60}), 61.36(1C, sp^3-C of C_{60}); FT-IR (KBr) ν 3449, 2920, 1721, 1686, 1655, 1640, 1582, 1562, 1458, 1389, 1265, 1111, 1038, 791, 741, 528 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 262 (4.87), 328 (4.15), 428 (3.27), 702 (2.19) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{68}H_7N$ 837.0578; found 837.0585.

1,2-(3-Indole)(hydro)[60]Fullerene 2b. According to the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1b** (7.9 mg, 0.06 mmol) and KO^{t}Bu (14.1 mg, 0.125 mmol) afforded first unreacted C_{60} (3.4 mg, 9%) and then **2b** (28.8 mg, 68%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.12 (s, N−H, 1H), 8.59 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 2.4 Hz, 1H), 7.40−7.39 (m, 1H), 7.16 (dd, J = 2.4, 8.0 Hz, 1H), 7.07 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.36, 152.94, 146.65(1C), 146.48(1C), 146.27, 145.80, 145.60, 145.53, 145.38, 145.33, 145.15, 144.70, 144.66, 144.60, 144.59, 143.99, 143.91, 142.44, 141.78, 141.77, 141.56, 141.37(4C), 141.28, 140.95, 140.91, 139.70, 139.42, 137.67, 135.79, 134.50(1C, aryl C), 131.10(1C, aryl C), 123.09(1C, aryl C), 121.68(1C, aryl C), 121.58(1C, aryl C), 121.31(1C, aryl C), 117.10(1C, aryl C), 112.18(1C, aryl C), 62.07(1C, sp^3-C of C_{60}), 61.39(1C, sp^3-C of C_{60}), 21.47(1C, $-CH_3$); FT-IR (KBr) ν 3449, 2920, 1655, 1628, 1508, 1458, 1423, 1242, 1180, 1096, 1022, 879, 795, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 262 (5.03), 327 (4.26), 428 (3.15), 698 (2.08) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_9N$ 851.0735; found 851.0749.

1,2-(3-Indole)(hydro)[60]Fullerene 2c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (8.0 mg, 0.06 mmol) and KO^{t}Bu (14.2 mg, 0.125 mmol) afforded first unreacted C_{60} (5.4 mg, 15%) and then **2c** (26.4 mg, 62%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.22 (s, N−H, 1H), 8.58 (d, J = 7.2 Hz, 1H), 7.78 (dd, J = 0.4, 2.8 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.12 (dd, J = 0.4, 7.2 Hz, 1H), 7.08 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.33, 152.93, 146.63(1C), 146.46(1C), 146.25, 145.77, 145.58, 145.52, 145.36, 145.32, 145.13, 144.68, 144.65, 144.59, 144.57, 143.98, 143.89, 142.43, 141.77, 141.75, 141.54, 141.35(4C), 141.26, 140.93, 140.89, 139.68, 139.41, 136.68, 135.78, 134.53(1C, aryl C), 124.80(1C, aryl C), 122.71(1C, aryl C), 122.11(1C, aryl C), 121.95(1C, aryl C), 121.15(1C, aryl C), 119.89(1C, aryl C), 115.97(1C, aryl C), 62.10(1C, sp^3-C of C_{60}), 61.38(1C, sp^3-C of C_{60}), 16.81(1C, $-CH_3$); FT-IR (KBr) ν 3449, 2920, 1686, 1655, 1562, 1543, 1508, 1477, 1458, 1423, 1184, 1141, 1092, 1049, 1022, 1003, 880, 795, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 272 (4.84), 308(4.10), 429 (3.19), 704 (2.25) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_9N$ 851.0735; found 851.0744.

1,2-(3-Indole)(hydro)[60]Fullerene 2d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (7.9 mg, 0.06 mmol) and KO^{t}Bu (14.0 mg, 0.125 mmol) afforded first unreacted C_{60} (4.5 mg, 11%) and then **2d** (21.3 mg, 51%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.06 (s, N−H, 1H), 8.66−8.64 (m, 1H), 7.48−7.46 (m, 1H), 7.25−7.21 (m, 2H), 7.08 (s, 1H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.87, 153.45, 146.63(1C), 146.43(1C), 146.26, 145.62, 145.53, 145.48, 145.36, 145.33, 145.13, 144.67, 144.61, 144.54(4C), 143.95, 143.90, 142.52, 141.80, 141.76, 141.42, 141.31, 141.29, 141.04, 141.02, 140.89, 139.46, 139.40, 135.96, 135.06, 134.37(1C, aryl C), 131.63(1C, aryl C), 126.86(1C, aryl C), 120.87(1C, aryl C), 119.32(1C, aryl C), 118.23(1C, aryl C), 115.28(1C, aryl C), 110.87(1C, aryl C), 62.79(1C, sp^3-C of C_{60}), 62.24(1C, sp^3-C of C_{60}), 14.83(1C, $-CH_3$); FT-IR (KBr) ν 3449, 2924, 1720, 1701, 1686, 1655, 1578, 1562, 1543, 1524, 1508, 1477, 1458, 1423, 1377, 1184, 1103, 1045, 1022, 880, 737, 528 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 269 (5.06), 326 (4.53), 429 (3.15), 704(2.13) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_9N$ 851.0735; found 851.0740.

1,2-(3-Indole)(hydro)[60]Fullerene 2e. According to the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1e** (10.6 mg, 0.06 mmol) and KO^{t}Bu (14.3 mg, 0.125 mmol) afforded first unreacted C_{60} (5.1 mg, 14%) and then **2e** (24.6 mg, 55%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.69 (s, N−H, 1H), 9.452−9.447 (m, 1H), 8.02 (dd, J = 1.6, 8.8 Hz, 1H), 7.92 (d, J = 2.8 Hz, 1H), 7.66 (dd, J = 0.6, 8.8 Hz, 1H), 7.11 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 165.85(1C, acyl C), 153.80, 152.72, 146.68(1C), 146.47(1C), 146.26, 145.58(4C), 145.55, 145.39, 145.35, 145.13, 144.70(4C), 144.61(4C), 144.00, 143.85, 142.43, 141.80, 141.77, 141.58, 141.38, 141.33, 141.26, 140.94, 140.93, 139.74, 139.66, 139.49(1C, aryl C), 135.62, 134.62, 124.56(1C, aryl C), 123.86(1C, aryl C), 123.28(1C, aryl C), 123.07(1C, aryl C), 121.40(1C, aryl C), 121.05(1C, aryl C), 111.77(1C, aryl C), 61.74(1C, sp^3-C of C_{60}), 61.39(1C, sp^3-C of C_{60}), 50.71(1C, -Me); FT-IR (KBr) ν 3449, 2924, 1751, 1720, 1701, 1686, 1655, 1620, 1562, 1543, 1524, 1508, 1478, 1458, 1439, 1423, 1377, 1319, 1265, 1234, 1188, 1110, 983, 880, 764, 528 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 261 (4.96), 328 (4.20), 428 (3.14), 702 (2.07) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{70}H_9NO_2$ 895.0633; found 895.0639.

1,2-(3-Indole)(hydro)[60]Fullerene 2f. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (9.8 mg, 0.06 mmol) and KO^{t}Bu (14.2 mg, 0.125 mmol) afforded first unreacted C_{60} (2.1 mg, 6%) and then **2f** (30.3 mg, 69%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 12.21 (s, N−H, 1H), 8.86 (d, J = 8.8 Hz, 1H), 8.61 (d, J = 1.8 Hz, 1H), 8.24−8.21 (m, 2H), 7.07 (s, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 153.33, 152.44, 146.71(1C), 146.50(1C), 146.16, 145.63, 145.61, 145.43(4C), 145.40, 145.09, 144.78, 144.75, 144.65, 144.63, 144.00, 143.83, 142.84, 142.50, 141.85, 141.82, 141.52, 141.37, 141.27, 141.23, 140.97, 140.94, 139.71, 139.56, 135.92, 135.52(1C, aryl C), 134.67(1C, aryl C), 129.19(1C, aryl C), 128.44(1C, aryl C), 122.60(1C, aryl C), 118.16(1C, aryl C), 114.54(1C, aryl C), 109.07(1C, aryl C), 61.46(1C, sp^3-C of C_{60}), 61.38(1C, sp^3-C of C_{60}); FT-IR (KBr) ν 3449, 2920, 1870, 1774, 1736, 1720, 1686, 1655, 1640, 1578, 1562, 1543, 1524, 1508, 1478, 1458, 1439, 1423, 1408, 1381, 1338, 1092, 1069, 1002, 876, 821, 671, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 266 (4.82), 329 (4.03), 430(3.15), 702 (2.02) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{68}H_6N_2O_2$ 882.0429; found 882.0437.

1,2-(3-Indole)(hydro)[60]Fullerene 2g. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (9.1 mg, 0.06 mmol) and KO^{t}Bu (14.1 mg, 0.125 mmol) afforded first unreacted C_{60} (1.0 mg, 3%) and then **2g** (31.3 mg, 72%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.53 (s, N−H, 1H), 8.63 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.29 (dd, J = 2.0, 8.8 Hz, 1H), 7.04 (s, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 153.80, 152.70, 146.68(1C), 146.49(1C), 146.24, 145.60(4C), 145.57, 145.41, 145.36, 145.14, 144.73, 144.71, 144.62(4C), 144.00, 143.86, 142.45, 141.81, 141.78, 141.58, 141.38, 141.33, 141.27, 140.96, 140.94, 139.70, 139.50, 135.63, 135.62, 134.56(1C, aryl C), 126.00(1C, aryl C), 125.27(1C, aryl C), 123.88(1C, aryl C), 122.21(1C, aryl C), 121.48(1C, aryl C), 117.60(1C, aryl C), 113.37(1C, aryl C), 61.70(1C, sp^3-C of C_{60}), 61.29(1C, sp^3-C of C_{60}); FT-IR (KBr) ν 3437, 2916, 1721, 1701, 1686, 1655, 1620, 1562, 1543, 1512, 1458, 1423, 1389, 1331, 1288, 1258, 1234, 1184, 1096, 1060, 879, 845, 799, 764, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 261 (5.17), 328 (4.40), 428 (3.22), 702 (2.26) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{68}H_6ClN$ 871.0189; found 871.0196.

1,2-(3-Indole)(hydro)[60]Fullerene 2h. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (9.2 mg, 0.06 mmol) and KO^{t}Bu (14.3 mg, 0.125 mmol) afforded first unreacted C_{60} (1.0 mg, 3%) and then **2h** (30.5 mg, 70%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.49 (s, N−H, 1H), 8.68 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.63 (dd, J = 0.6, 2.0 Hz, 1H), 7.30 (dd, J = 2.0, 8.4 Hz, 1H), 7.05 (s, 1H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 153.89, 152.68, 146.68(1C), 146.49(1C), 146.21, 145.63, 145.61, 145.56, 145.41, 145.36, 145.12, 144.72(4C), 144.61(4C), 143.99, 143.88, 142.46, 141.81, 141.79, 141.54, 141.36, 141.30, 141.27, 140.96, 140.92, 139.70, 139.48, 137.74, 135.65, 134.55(1C, aryl C), 127.82(1C, aryl C), 123.63(1C, aryl C), 123.22(1C, aryl C), 121.92(1C, aryl C), 119.98(1C, aryl C), 119.17(1C, aryl C), 112.12(1C, aryl C), 61.77(1C, sp^3-C of C_{60}), 61.36(1C, sp^3-C of C_{60}); FT-IR (KBr) ν 3442, 2915, 1720, 1686, 1655, 1620, 1562, 1543, 1477, 1456, 1379, 1286, 1256, 1234, 1186, 1100, 880, 798, 757, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 262 (4.87), 328 (4.26), 428 (3.15), 704 (2.05) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{68}H_6ClN$ 871.0189; found 871.0194.

1,2-(3-Indole)(hydro)[60]Fullerene 2i. According to the general procedure, the reaction of C_{60} (36.1 mg, 0.05 mmol) with **1i** (8.9 mg, 0.06 mmol) and KO^{t}Bu (14.1 mg, 0.125 mmol) afforded first unreacted C_{60} (10.4 mg, 29%) and then **2i** (21.1 mg, 49%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.13 (s, N−H, 1H), 8.16 (d, J = 2.5 Hz, 1H), 7.75 (d, J = 2.5 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.09 (s, 1H), 6.98 (dd, J = 2.5, 8.8 Hz), 4.00 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.20, 153.60, 152.99, 146.63(1C), 146.47(1C), 146.24, 145.77, 145.59, 145.51, 145.38, 145.32, 145.12, 144.68, 144.64, 144.60, 144.58, 143.97, 143.90, 142.43, 141.79, 141.77, 141.58, 141.35(4C), 141.28, 140.95, 140.89, 139.71, 139.43, 135.61, 134.37(1C, aryl C), 132.24(1C, aryl C), 125.33(1C, aryl C), 122.63(1C, aryl C), 121.34(1C, aryl C), 112.77(1C, aryl C), 112.09(1C, aryl C), 100.13(1C, aryl C), 62.00(1C, sp^3-C of C_{60}), 61.12(1C, sp^3-C of C_{60}), 54.68(1C, $-OCH_3$); FT-IR (KBr) ν 3449, 2925, 1871, 1736, 1686, 1655, 1640, 1627, 1562, 1543, 1524, 1508, 1478, 1458, 1439, 1423, 1381, 1342, 1211, 1176, 1092, 1045, 879, 767, 529 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 262 (5.04), 308 (4.36), 429 (3.18), 702 (2.25) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_9NO$ 867.0684; found 867.0688.

1,2-(3-Indole)(hydro)[60]Fullerene 2j. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (9.0 mg, 0.06 mmol) and KO^{t}Bu (14.4 mg, 0.125 mmol) afforded first unreacted C_{60} (11.5 mg, 32%) and then **2j** (19.9 mg, 46%) as an amorphous black solid: mp > 300 °C; ^{1}H NMR (400 MHz, CS_2/d_6-DMSO) δ 11.26 (s, N−H, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 2.8 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 7.08 (s, 1H), 6.84 (d, J = 7.8 Hz), 4.13 (s, 3H); ^{13}C NMR (100 MHz, CS_2/d_6-DMSO) (all 2C unless indicated) δ 154.23, 152.86, 146.62(1C), 146.45(1C), 146.22, 146.14, 145.72, 145.57, 145.50, 145.35, 145.30, 145.12, 144.67, 144.65, 144.57, 144.56, 143.96, 143.89, 142.41, 141.75, 141.74, 141.53, 141.32(4C), 141.26, 140.93, 140.88, 139.67, 139.40, 135.77, 134.50(1C, aryl C), 127.40(1C, aryl C), 126.65(1C, aryl C), 122.17(1C, aryl C), 122.06(1C, aryl C), 120.16(1C, aryl C), 111.38(1C, aryl C), 102.17(1C, aryl C), 61.96(1C, sp^3-C of C_{60}), 61.38(1C, sp^3-C of C_{60}), 54.32(1C, $-OCH_3$); FT-IR (KBr) ν 3449, 2920, 1870, 1721, 1686, 1655, 1640, 1625, 1562, 1543, 1508, 1477, 1458, 1439, 1423, 1381, 1210, 1172, 1092, 1045, 879, 767, 525 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ε) 264 (5.11), 327 (4.42), 429 (3.36), 703 (2.32) nm; HRMS (MALDI-TOF-MS, DCTB as matrix, negative mode): m/z [M]$^-$ calcd for $C_{69}H_9NO$ 867.0684; found 867.0691.

Scale-up Procedure for Synthesis of 1,2-(3-Indole)(hydro)[60]fullerene 2a. C_{60} (0.5 g, 0.694 mmol), **1a** (98 mg, 0.838 mmol, 1.2 equiv), and KO^{t}Bu (195 mg, 1.741 mmol, 2.5 equiv) were dissolved in chlorobenzene (120 mL) at room temperature under Ar atmosphere in a dry round-bottom 250 mL Schlenk flask. Then dry DMSO (30 mL) was added to the mixture, and the color of the solution changed gradually from purple to dark green. After being stirred for 30 min,

CF_3COOH(1.04 mL, 13.9 mmol, 20 equiv) was added to the mixture, and the color of the solution changed immediately from dark green to reddish brown. The reaction mixture was stirred for 20 min, and the resulting brown solution was washed with water and then evaporated in vacuo. The residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60}(52.7 mg, 11%), and subsequent elution with carbon disulfide/dichloromethane (5:1) afforded **2a**(0.431 g, 74%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01725.

^{1}H NMR and ^{13}C NMR spectra of products **2a−2j**. CVs of compounds **2a**, **2h**, **2j** along with C_{60} and PCBM (PDF)

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Notes

The authors declare no competing financial interest.

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