

Supporting Information

Cu(OAc)₂-Promoted Reaction [60]Fullerene with Primaryamines and Diamines

Xin-Wei Lu, Meng-Lei Xing,[†] Chun-Bao Miao,[†] Jia-Xing Li,[‡] Xiao-Qiang Sun,^{*,†} and Hai-Tao Yang,^{*,†}

[†] School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

[‡] Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, China

Email: yht898@yahoo.com

General Synthetic Procedure and Identification of the Products	S1-7
UV-vis Spectra of 2e and 3a	S8
¹H NMR, ¹³C NMR Spectra of Products	S9-27
¹ H NMR and ¹³ C NMR spectra of 2a	S9
¹ H NMR and ¹³ C NMR spectra of 3a	S10
¹ H NMR spectra of 2b and 3b	S11
¹ H NMR spectra of 2c and 3c	S12
¹ H NMR and ¹³ C NMR spectra of 2d	S13
¹ H NMR and ¹³ C NMR spectra of 3d	S14
¹ H NMR and ¹³ C NMR spectra of 2e	S15
¹ H NMR and ¹³ C NMR spectra of 2f	S16
¹ H NMR and ¹³ C NMR spectra of 2g	S17
¹ H NMR and ¹³ C NMR spectra of 3g	S18
¹ H NMR and ¹³ C NMR spectra of 2h	S19
¹ H NMR and ¹³ C NMR spectra of 2i	S20
¹ H NMR and ¹³ C NMR spectra of 2j	S21
¹ H NMR and ¹³ C NMR spectra of 2k	S22
¹ H NMR and ¹³ C NMR spectra of 2l	S23
¹ H NMR spectra of 2m and 2n	S24
¹ H NMR and ¹³ C NMR spectra of 5a	S25
¹ H NMR spectra of 5b and 5c	S26
¹ H NMR and ¹³ C NMR spectra of 5d	S27

General Procedure for the Cu(OAc)₂-Promoted Reaction of C₆₀ with Alkyl Amines 1a-f

C₆₀ (72.0 mg, 0.1 mmol) and 20 mL of dry chlorobenzene was added to a big tube (Φ 2.5 cm × 18 cm). After ultrasonic dissolution, DMAP (24.4 mg, 0.2 mmol), Cu(OAc)₂ (36.2 mg, 0.2 mmol), and alkyl amines (**1a-f**, 0.2 mmol) was added sequentially. The mixture was vigorously stirred at 80 °C for 3-6 h. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using CS₂/toluene as the eluent to give unreacted C₆₀ and the products **2a-f** and **3a-d**.

2a (brown solid, 7.8 mg, 9%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.61 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 4.71 (s, 2H), 3.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 159.42, 145.10, 145.06, 144.59, 144.49, 144.43, 143.74, 143.03, 142.85, 142.26, 142.11, 140.74, 130.32, 129.02, 114.28, 85.27 (sp³-C of C₆₀), 55.03, 53.99.

3a (brown solid, 15.9 mg, 16%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.46 (d, *J* = 8.5 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 4.54 (d, *J* = 13.4 Hz, 2H), 4.19 (d, *J* = 13.4 Hz, 2H), 3.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃-CS₂) δ 159.06, 153.38, 149.64, 148.02, 147.02, 146.10, 146.04, 145.73, 145.66, 145.64, 145.21, 145.09, 144.66, 144.07, 144.00, 143.80, 143.50, 143.42, 143.30, 142.87, 142.46, 142.00, 141.67, 141.51, 141.47, 141.24, 140.64, 140.07, 139.70, 129.94, 129.11, 114.15, 77.26 (sp³-C of C₆₀), 72.82 (sp³-C of C₆₀), 55.06, 52.82; UV-vis (CHCl₃) λ_{max}/nm 258, 327, 426, 471, 686; HRMS (MALDI-TOFMS) *m/z*: [M+Na]⁺ Calcd for C₇₆H₁₈N₂O₂Na 1013.1266, found 1013.1260.

2b (brown solid, 11.8 mg, 14%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 5.07 (s, 2H).

3b (brown solid, 15.2 mg, 16%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.56-7.62 (m, 4H), 7.28-7.34 (m, 6H), 4.58 (d, *J* = 13.8 Hz, 2H), 4.31 (d, *J* = 13.8 Hz, 2H).

2c (brown solid, 16.9 mg, 21%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 3.66 (t, *J* = 7.1 Hz, 2H), 2.13 (quint, *J* = 7.3 Hz, 2H), 1.79 (sextet, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).

3c (brown solid, 11.3 mg, 13%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 3.41 (ddd, *J* = 11.8, 8.0, 6.3 Hz, 2H), 3.20 (ddd, *J* = 11.8, 7.9, 6.3 Hz, 2H), 1.93-2.07 (m, 4H), 1.64-1.75 (m, 4H), 1.08 (t, *J* = 7.4 Hz, 6H).

2d (brown solid, 12.4 mg, 14%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.24 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.57 (t, *J* = 6.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃-CS₂) δ 145.22, 145.18, 144.68, 144.61, 144.58, 143.83, 143.13, 143.11, 142.90, 142.25, 142.16, 140.71, 135.35, 135.09, 133.71, 132.81, 129.62, 127.64, 84.43 (sp³-C of C₆₀), 49.77, 33.69; UV-vis (CHCl₃) λ_{max}/nm 258, 325, 424, 500, 682; HRMS (MALDI-TOFMS) *m/z*: [M+H]⁺ Calcd for C₆₈H₈Cl₂N 908.0034, found 908.0022.

3d (brown solid, 23.4 mg, 21%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 2.1 Hz, 2H), 7.20 (dd, *J* = 8.2, 2.1 Hz, 2H), 3.40-3.63 (m, 8H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 153.19, 148.93, 147.53, 147.02, 146.05, 145.69, 145.50, 145.10, 144.96, 144.61, 143.98, 143.90, 143.71, 143.40, 143.35, 143.19, 142.73, 142.32, 142.27, 141.91, 141.52, 141.33, 141.25, 141.22, 140.60, 140.29, 139.62, 138.91, 135.26, 134.96, 133.61, 132.46, 129.45, 127.43, 75.63 (sp³-C of C₆₀), 71.95 (sp³-C of C₆₀), 48.45, 33.45; UV-vis (CHCl₃) λ_{max}/nm 258, 327, 426, 470, 686; HRMS (MALDI-TOFMS) *m/z*: [M+H]⁺ Calcd for C₆₉H₁₁N 1094.9989, found 1094.9983.

2e (brown solid, 14.2 mg, 17%, mp > 300 °C): ¹H NMR (400 MHz, CDCl₃-CS₂) δ 4.17 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.42 (quint, *J* = 6.9 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃-CS₂) δ 172.52, 145.13, 145.09, 144.62, 144.51, 144.48, 143.76, 143.06, 142.85, 142.24, 142.12, 140.78, 85.03 (sp³-C of C₆₀), 60.54, 50.12, 31.94, 24.92, 14.48; UV-vis (CHCl₃) λ_{max}/nm 258, 325, 424, 500, 682; HRMS (MALDI-TOFMS) *m/z*: [M]⁺ Calcd for C₆₆H₁₁NO₂ 849.0790, found 849.0773.

2f (brown solid, 11.1 mg, 14%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 3.84 (t, *J* = 6.1 Hz, 2H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.45 (s, 3H), 2.40 (quint, *J* = 6.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 145.22, 145.18, 144.69, 144.61, 144.57, 143.86, 143.15, 142.95, 142.38, 142.22, 140.86, 85.36 (sp³-C of C₆₀), 70.44, 58.88, 48.34, 30.07; UV-vis (CHCl₃) λ_{max}/nm 258, 325, 424, 499, 682; HRMS (MALDI-TOFMS) *m/z*: [M]⁺ Calcd for C₆₄H₉NO 807.0684, found 807.0663.

General Procedure for the Cu(OAc)₂-Promoted Reaction of C₆₀ with Aryl Amines **1g-n**

C₆₀ (72.0 mg, 0.1 mmol) and 20 mL of dry chlorobenzene was added to a big tube (Φ 2.5 cm × 18 cm). After ultrasonic dissolution, DMAP (24.4 mg, 0.2 mmol), Cu(OAc)₂ (36.2 mg, 0.2 mmol), and aryl amines (**1g-n**, 0.2 mmol) was added sequentially. Then the mixture was vigorously stirred at 80 °C for 8-12 h. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using CS₂/toluene as the eluent to give unreacted C₆₀ and the products **2g-n**.

2g (brown solid, 10.1 mg, 12%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.96 (heptet, *J* = 6.9 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 145.24, 145.16, 145.01, 144.81, 144.76, 144.74, 144.59, 144.53, 144.11, 143.89, 143.34, 143.12, 142.86, 142.32, 142.21, 140.94, 140.76, 127.14, 121.34, 83.75 (sp³-C of C₆₀), 33.85, 24.20; UV-vis (CHCl₃) λ_{max}/nm 258, 326, 405, 423, 454, 507, 683; HRMS (MALDI-TOFMS) *m/z*: [M]⁺ Calcd for C₆₉H₁₁N 853.0891, found 853.0895.

2h (brown solid, 14.6 mg, 18%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.43 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 2.47 (s, 3H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 145.52, 145.23, 145.14, 144.91, 144.80, 144.73, 144.72, 144.57, 144.09, 143.86, 143.09, 142.85, 142.29, 142.19, 140.94, 140.71, 139.05, 129.03, 125.17, 121.95, 118.64, 83.59 (sp³-C of C₆₀), 21.80; UV-vis (CHCl₃) λ_{max}/nm 258, 325, 405, 424, 455, 510, 683; HRMS (MALDI-TOFMS) *m/z*: [M]⁺ Calcd for C₆₇H₇N 825.0578, found 825.0592.

2i (brown solid, 11.9 mg, 14%, mp > 300 °C): ^1H NMR (500 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 7.40 (d, $J = 2.1$ Hz, 1H), 7.35 (dd, $J = 8.0, 2.3$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 145.28, 145.20, 145.15, 144.83, 144.82, 144.78, 144.63, 144.16, 143.93, 143.47, 143.16, 143.14, 142.91, 142.39, 142.25, 140.97, 140.76, 137.52, 132.42, 130.25, 122.63, 118.98, 83.80 ($\text{sp}^3\text{-C}$ of C_{60}), 20.28, 19.41; UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ 258, 326, 405, 423, 455, 508, 684; HRMS (MALDI-TOFMS) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{68}\text{H}_9\text{N}$ 839.0735, found 839.0753.

2j (brown solid, 8.5 mg, 10%, mp > 300 °C): ^1H NMR (400 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 7.55 (d, $J = 8.9$ Hz, 2H), 6.99 (d, $J = 8.9$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 156.32, 145.27, 145.18, 145.00, 144.84, 144.76, 144.75, 144.60, 144.10, 143.91, 143.12, 143.10, 142.89, 142.33, 142.21, 140.94, 140.74, 138.86, 122.52, 114.49, 83.82 ($\text{sp}^3\text{-C}$ of C_{60}), 55.43; UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ 258, 326, 405, 423, 457, 510, 684; HRMS (MALDI-TOFMS) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{67}\text{H}_7\text{NO}$ 841.0528, found 841.0523.

2k (brown solid, 12.6 mg, 14%, mp > 300 °C): ^1H NMR (500 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 7.70 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 8.8$ Hz, 2H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H); ^{13}C NMR (100 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 145.25, 145.16, 144.85, 144.81, 144.75, 144.69, 144.58, 144.08, 143.87, 143.12, 143.10, 142.85, 142.26, 142.19, 140.98, 140.76, 140.37, 137.24, 128.90, 127.86, 127.26, 126.97, 121.88, 83.55 ($\text{sp}^3\text{-C}$ of C_{60}); UV-vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ 258, 324, 405, 424, 458, 510, 684; HRMS (MALDI-TOFMS) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{72}\text{H}_9\text{N}$ 887.0735, found 887.0717.

2l (brown solid, 14.1 mg, 16%, mp > 300 °C): ^1H NMR (500 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 7.59 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.65 (s, 2H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, $\text{CDCl}_3\text{-CS}_2$) δ 171.04, 145.25, 145.17, 144.84, 144.77, 144.73, 144.69, 144.59, 144.51, 144.08, 143.88, 143.12, 143.11, 142.86, 142.27, 142.20, 140.97, 140.74, 130.05, 129.97, 121.55,

83.53 (sp³-C of C₆₀), 60.92, 40.85, 14.39; UV-vis (CHCl₃) λ_{max}/nm 258, 324, 404, 424, 455, 510, 684;

HRMS (MALDI-TOFMS) m/z: [M]⁺ Calcd for C₇₀H₁₁NO₂ 897.0790, found 897.0785.

2m (brown solid, 6.9 mg, 8%, mp > 300 °C): ¹H NMR (300 MHz, CDCl₃-CS₂) δ 8.38 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H).

2n (brown solid, 6.5 mg, 7%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

Cu(OAc)₂-Promoted Reaction of C₆₀ with 4-Isopropylaniline **1g at 120 °C**

C₆₀ (72.0 mg, 0.1 mmol) and 20 mL of dry chlorobenzene was added to a big tube (Φ 2.5 cm × 18 cm). After ultrasonic dissolution, DMAP (24.4 mg, 0.2 mmol), Cu(OAc)₂ (36.2 mg, 0.2 mmol), and 4-isopropylaniline **1g** (0.2 mmol) was added sequentially. Then the mixture was vigorously stirred at 120 °C for 8 h. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using CS₂/toluene as the eluent to give unreacted C₆₀ and the products **2g** (8.6 mg, 10%) and **3g** (7.1 mg, 7%).

3g: ¹H NMR (500 MHz, CDCl₃-CS₂) δ 7.35 (d, *J* = 8.4 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 4H), 2.91 (heptet, *J* = 6.9 Hz, 2H), 1.28 (d, *J* = 6.9 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃-CS₂) δ 152.06, 149.27, 147.64, 147.06, 146.19, 145.98, 145.70, 145.50, 145.42, 145.22, 144.88, 144.62, 144.03, 144.02, 143.94, 143.87, 143.41, 143.38, 143.23, 142.79, 142.62, 142.36, 142.29, 142.26, 142.02, 141.84, 141.67, 141.65, 141.25, 140.09, 140.05, 139.63, 126.86, 121.30, 75.96 (sp³-C of C₆₀), 70.32 (sp³-C of C₆₀), 33.79, 24.15, 24.14; UV-vis (CHCl₃) λ_{max}/nm 258, 325, 424, 470, 683; HRMS (MALDI-TOFMS) m/z: [M]⁺ Calcd for C₇₈H₂₂N₂ 986.1783, found 986.1770.

General Procedure for the Cu(OAc)₂-Promoted Reaction of C₆₀ with Diamines **4a-e**

C₆₀ (72.0 mg, 0.1 mmol) and 20 mL of dry chlorobenzene was added to a big tube (Φ 2.5 cm × 18 cm). After ultrasonic dissolution, DMAP (24.4 mg, 0.2 mmol), Cu(OAc)₂ (36.2 mg, 0.2 mmol), and

diamines (**4a-e**, 0.2 mmol) was added sequentially. The mixture was vigorously stirred at 80 °C for 2.5-4 h. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using CS₂/toluene as the eluent to give unreacted C₆₀ and the products **5a-d**.

5a (brown solid, 11.1 mg, 14%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃) δ 3.92 (s, 4H), 3.41 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 1151.33, 148.22, 146.60, 146.27, 145.88, 145.76, 145.66, 145.38, 144.86, 142.95, 142.78, 142.45, 141.64, 141.53, 138.88, 137.22, 80.64 (sp³-C of C₆₀), 48.62, 44.26.

5b (brown solid, 34.4 mg, 43%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃) δ 4.48-4.61 (m, 4H), 3.53-3.65 (m, 4H).

5c (brown solid, 44.7 mg, 55%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃) δ 4.64 (ddd, *J* = 15.8, 11.6, 5.0 Hz, 2H), 4.45-4.56 (m, 2H), 3.94 (ddd, *J* = 15.8, 6.1, 2.3 Hz, 2H), 3.79-3.90 (m, 2H), 2.63 (dt, *J* = 15.0, 11.5, 6.0 Hz, 1H), 2.63 (dt, *J* = 15.0, 5.0, 2.5 Hz, 1H).

5d (brown solid, 8.5 mg, 10%, mp > 300 °C): ¹H NMR (500 MHz, CDCl₃-CS₂) δ 4.39 (t, *J* = 13.5 Hz, 2H), 3.65 (d, *J* = 14.7 Hz, 2H), 3.57 (s, 6H), 2.84 (qt, *J* = 13.0, 4.1 Hz, 1H), 1.93 (dt, *J* = 13.8, 2.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃-CS₂) δ 154.91, 154.57, 148.39, 146.70, 146.55, 146.24, 146.18, 145.63, 145.62, 145.60, 145.54, 145.46, 145.43, 145.40, 144.94, 143.01, 142.93, 142.77, 142.73, 142.59, 141.66, 141.64, 141.47, 141.19, 139.31, 138.92, 136.71, 136.10, 83.69 (sp³-C of C₆₀), 55.85, 43.08, 27.37; UV-vis (CHCl₃) λ_{max}/nm 257, 312, 698; HRMS (MALDI-TOFMS) *m/z*: [M+H]⁺ Calcd for C₆₅H₁₃N₂ 821.1079, found 821.1099.







































