Efficient Microwave-mediated synthesis of fullerene acceptors for Organic Photovoltaics

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SUPPLEMENTARY MATERIAL

Experimental part

General

General: Chemicals and solvents were purchased from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates (Merck 60 F254) were used and compounds were visualized by irradiation with UV light and/or by treatment with a KMnO₄ solution. Flash chromatography was carried out using Macherey–Nagel silica gel (0.04–0.063 mm). MW-assisted syntheses were carried out with a CEM DISCOVER monomode system in closed vessel in manual mode (no remote PC control) with infrared sensor for temperature control and with no pressure control. Petroleum ether refers to the fraction with the boiling range 40–60 °C. ¹H and ¹³C NMR spectra were recorded with a Bruker 250, Bruker 300 MHz or Bruker Avance II 400 MHz spectrometers. HRMS spectra were recorded on MeOH/CH₂CL₂ or in CH₂CL₂ with a Waters Q-TOF Premier, with atmospheric pressure chemical ionization (APCI) as ion source.

• [70] and [60]PCBM derivatives

Synthesis of methyl 4-Benzoylbutyrate. This compound was prepared on 5g scale starting from 4-benzoylbutyric acid and MeOH using HCl gas following a procedure previously reported in literature.¹ Methyl 4-Benzoylbutyrate was obtained as a colorless oil (yield: 88%).

Synthesis of methyl 4-Benzoylbutyrate p-Tosylhydrazone (1). Methyl 4-Benzoylbutyrate (4.5 g, 21.8 mmol) and p-toluenesulfonyl hydrazide (5.0 g, 1.2 eq) were placed in a round bottom flask and methanol was added (15 mL). The mixture was stirred and refluxed for 6 h and then stirred overnight at room temperature and lastly cooled to -15 °C. The product was collected by filtration, washed with cold methanol and dried under vacuum to obtain 4-Benzoylbutyrate p-Tosylhydrazone as white crystals (yield: 92 %).

General procedure for preparation of 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane. Sodium methoxide (3.73 mg, 0.069 mmol) was added in a glass vial (ca. 10 mL tube) sealed with a teflon septum containing a solution of 4-Benzoylbutyrate p-Tosylhydrazone (17.20 mg, 0.046 mmol) in dry pyridine (2 mL). The mixture was stirred at room temperature for 15 minutes.
Synthesis of PCBM derivatives (2a-c, 3a-c). A solution of $C_{60}$ or $C_{70}$ (50.00 mg) in 3 mL of ODCB (previously sonicated for about 15 minutes) was added to a previously prepared mixture containing the appropriate quantity of 1-Phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane in dry pyridine. The resulting mixture was kept under MW irradiation at 180 °C (48 W) for appropriate time. After cooling down, pyridine was removed under vacuum and the remaining reaction mixture was directly chromatographed on silica gel without removal of the remaining solvent (Silica gel column conditions for $C_{60}$-derivatives: Hexane/Toluene 3:1 up to 9:1 Toluene/Hexane for monoadduct recovery and then dichloromethane for bisadducts. Column conditions for $C_{70}$-derivatives: Hexane/Toluene 3:1 up to 2:1 Toluene/Hexane for monoadduct recovery and then dichloromethane for bisadducts recovery). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol.

(2a) $^1$H NMR (400 MHz, CDCl$_3$/CS$_2$) $\delta$: 7.92 (d, $J$ = 7.2 Hz, 2H; o-H arom), 7.55 (t, $J$ = 7.3 Hz, 2H; m-H arom), 7.51-7.41 (m, 1H; p-H arom), 3.68 (s, 3H; OCH$_3$), 2.92 (t, $J$ = 7.3Hz, 2H; PhCCH$_2$), 2.53 (t, $J$ = 7.3 Hz, 2H; CH$_2$CO$_2$Me), 2.20 (q, $J$ = 7.3 Hz, 2H; CH$_2$CH$_2$CO$_2$Me). $^{13}$C NMR (100 MHz, CDCl$_3$/CS$_2$) $\delta$: 172.65 (C=O), 148.46, 147.51, 145.62, 145.01, 144.86, 144.59, 144.47, 144.28, 143.89, 143.57, 142.82, 142.76, 142.02, 141.94, 140.84, 140.60, 137.87, 137.47, 136.48, 131.85, 128.31, 128.10, 79.60 ($C_{60}$ sp$^3$), 51.64 (OCH$_3$), 51.26 (PhCCH$_2$), 33.69, 33.56 (PhCCH$_2$ and CH$_2$CO$_2$Me), 22.33 (CH$_2$CH$_2$CO$_2$Me). HRMS calculated: 933.0891; found: 933.2404 [M-Na$^+$].

(2b) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.24-7.31 (m, 10H; H arom), 3.81-3.52 (m, 6H; OCH$_3$), 3.23-1.85 (m, 12H; PhCCH$_2$, CH$_2$CO$_2$Me and CH$_2$CH$_2$CO$_2$Me). HRMS calculated: 1123.1885; found: 1123.3757 [M-Na$^+$].

(2c) $^1$H NMR (250 MHz, CDCl$_3$) $\delta$: 8.23-7.29 (m, 15H; H arom), 3.89-3.35 (m, 9H; OCH$_3$), 3.23-1.85 (m, 18H; PhCCH$_2$, CH$_2$CO$_2$Me and CH$_2$CH$_2$CO$_2$Me). HRMS calculated: 1314.2878; found: 1314.6711 [M-Na$^+$].

(3a) $^1$H NMR (250 MHz, CDCl$_3$/CS$_2$) $\delta$: 7.93-7.19 (m, 5H; H arom), 3.75, 3.69, 3.52 (s, 3H; OCH$_3$ isomers mixture), 2.53-2.37 (m, 4H; PhCCH$_2$ and CH$_2$CO$_2$Me), 2-19-1.75 (m, 2H; CH$_2$CH$_2$CO$_2$Me). HRMS calculated: 1053.0891; found: 1053.0590 [M-Na$^+$].

(3b) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.96-7.00 (m,10H; H arom), 4.10-3.22 (m, 6H; OCH$_3$), 2.71-1.93 (m, 12H; PhCCH$_2$, CH$_2$CO$_2$Me and CH$_2$CH$_2$CO$_2$Me). HRMS calculated: 1245.1963; found: 1245.1877 [M-Na$^+$]. (3c) HRMS calculated: 1433.2878; found: 1433.6976 [M-Na$^+$].
Figure S1. $^1$H NMR Spectrum of 2a

Figure S2. $^{13}$C NMR Spectrum of 2a
Figure S3. $^1$H NMR Spectrum of 2b

Figure S4. $^1$H NMR Spectrum of 2c
Figure S5. $^1$H NMR Spectrum of 3a

Figure S6. $^1$H NMR Spectrum of 3b.
Figure S7. From the top: simulated, experimental and full HRMS spectrum of 2a.
Figure S8. From the top: simulated, experimental and full HRMS spectrum of 2b.
Figure S9. From the top: simulated, experimental and full HRMS spectrum of 2c.
Figure S10. From the top: simulated, experimental and full HRMS spectrum of 3a.
**Figure S11.** From the top: simulated, experimental and full HRMS spectrum of 3b.
Figure S12. From the top: simulated, experimental and full HRMS spectrum of 3c.
• [70] and [60]DPM6 derivatives

Synthesis of 4,4’-dihexyloxybenzophenone-p-Tosylhydrazone (4). The synthesis of this compound was carried out following procedures previously reported in literature. This compound was prepared starting from commercially available 4,4’-dihydroxybenzophenone in two synthetic steps and on 5g scale.

General procedure for preparation of 4,4’-(diazomethylene)bis(hexyloxybenzene). Sodium methoxide (3.73 mg, 0.069 mmol) was added in a glass vial (ca. 10 ml tube) sealed with a teflon septum containing a solution of 4,4’-Dihexyloxybenzophenone-p-Tosylhydrazone (25.30 mg, 0.046 mmol) in dry pyridine (2 mL). The mixture was stirred at room temperature for 15 minutes.

Synthesis of DPM6 derivatives (5a-b, 6a-b). A solution of C60 or C70 (50.00 mg) in 3 mL of ODCB (previously sonicated for about 15 minutes) was added to a previously prepared mixture containing the appropriate quantity of 4,4’-(diazomethylene)bis(hexyloxybenzene) in dry pyridine. The resulting mixture was kept under MW irradiation at 180 °C (48 W) for appropriate time. After cooling down, pyridine was removed under vacuum and the remaining reaction mixture was directly chromatographed on silica gel without removal of the remaining solvent (Silica gel column conditions for C60-derivatives: CS2 to recover unaacted C60 and then Hexane/Toluene 4:1 and 3:1 for monoadduct recovery and finally Hexane/toluene 1:1 for bisadducts recovery. Column conditions for C70-derivatives: CS2 to recover unaacted C70 and then Hexane/Toluene 6:1 and 4:1 for monoadduct recovery and finally Hexane/Toluene 2:1 for bisadducts recovery). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (5a) 1H NMR (250 MHz, CDCl3) δ: 7.97 (d, J = 8.6 Hz, 4H), 6.98 (d, J = 8.6 Hz, 4H), 3.98 (t, J = 6.5 Hz, 4H; OCH3), 1.97-1.68 (m, 4H; OCH2CH3), 1.54-1.19 (m, 12H; -CH2-), 0.91 (t, J = 6.6 Hz, 6H; CH3CH3). 13C NMR (62.5 MHz, CDCl3/CS2) δ: 158.68 (C=O), 148.48, 145.34, 145.10, 145.02, 144.63, 144.52, 144.18, 143.78, 142.92, 142.85, 142.23, 142.05, 140.76, 138.17, 131.75, 131.20, 114.60, 79.57 (C60 sp3), 68.00 (OCH3), 57.30 (CDPM), 31.67, 29.35, 25.85, 22.73, 14.09. HRMS calculated: 1087.2637; found: 1087.2247 [M-H]+. (5b) 1H NMR (250 MHz, CDCl3) δ: 8.20-7.50 (m, 8H), 7.12-6.60 (m, 8H), 4.08-3.78 (m, 8H; OCH3), 2.04-1.1 (m, 32H; -CH2-), 1.1-0.64 (m, 12H; CH3CH3). HRMS calculated: 1453.5195; found: 1453.4471 [M-Na]+. (6a) 1H NMR (250 MHz, CDCl3) δ: 7.95, 7.83, 7.46 (d, J = 7.9 Hz, 4H), 6.95, 6.65 (d, J = 7.9 Hz, 4H), 3.99, 3.80 (m, 4H; isomers mixture), 2.09-1.12 (m, 16H; OCH2CH3 and -CH2-), 1.12-0.68 (m, 6H; CH2CH3). 13C NMR (100 MHz, CDCl3/CS2) δ: 158.42, 155.69, 155.41, 151.83, 150.95, 150.61, 150.30, 149.18, 148.99, 148.90, 148.26, 148.05, 147.77, 147.29, 147.19, 146.85, 146.73, 145.82, 145.49, 145.25, 144.26, 143.71, 143.53, 143.11, 142.38, 141.42, 141.35, 139.81, 138.57, 137.16, 136.58, 133.74, 132.56, 131.52, 131.14, 130.99, 130.60, 130.38, 114.53, 114.19, 106.59, 71.72, 69.62, 67.83, 67.65, 65.46, 43.03, 40.73, 31.65, 29.31, 25.83, 22.76, 14.11. HRMS calculated: 1208.2637; found: 1208.2496 [M-H]+. (6b) 1H NMR (250 MHz, CDCl3) δ: 8.21-7.33 (m, 8H), 7.21-6.49 (m, 8H), 4.26-3.60 (m, 8H; OCH3), 2.03-1.08 (m, 32H; -CH2-), 1.08-0.73 (m, 12H; CH2CH3). HRMS calculated: 1570.5195; found: 1570.5037 [M-H]+.
Figure S13. $^1$H NMR Spectrum of 5a

Figure S14. $^{13}$C NMR Spectrum of 5a
Figure S15. $^1$H NMR Spectrum of 5b

Figure S16. $^1$H NMR Spectrum of 6a
Figure S17. $^{13}$C NMR Spectrum of 6a

Figure S18. $^1$H NMR Spectrum of 6b
Figure S19. From the top: simulated, experimental and full HRMS spectrum of 5a.
**Figure S20.** From the top: simulated, experimental and full HRMS spectrum of 5b.
Figure S21. From the top: simulated, experimental and full HRMS spectrum of 6a.
Figure S22. From the top: simulated, experimental and full HRMS spectrum of 6b.
• [70] and [60]BHN derivatives

Synthesis of sultine (7). The synthesis of this compound was carried out following a procedure previously reported in literature.\(^5\) To a solution in DMF (75 mL) of 1,2-bis(bromomethyl)benzene (1.15 g, 4.230 mmol), Sodium hydroxymethanesulfinate (rongalite, 2.60 g, 16.902 mmol) and tetrabutylammonium bromide (413.00 mg, 1.268 mmol) were added. The mixture was stirred at 0°C under argon atmosphere for 4 h. Then water was added and the mixture was extracted three times with dichloromethane. The organic layer was dried over Na\(_2\)SO\(_4\), and the solvent was evaporated at 25°C to give colorless oil (627.35 mg, 88.2%). The crude product was used in the next reaction step without further purification.

Synthesis of BHN derivatives (8a-c, 9a-b). To a solution of C\(_{60}\) or C\(_{70}\) (50.00 mg) in 4 mL of ODCB (previously sonicated for about 20 minutes), the appropriate amount of sultine was added. The resulting mixture was kept under MW irradiation at appropriate temperature (7-10 W) for appropriate time. After cooling down, the reaction mixture was precipitated with methanol. The recovered residue was solubilized in a minimal amount of chloroform and precipitated again with methanol. Methanol was removed and the residue was solubilized in dichloromethane, adsorbed on silica and chromatographed (Silica gel column conditions for C\(_{60}\)-derivatives: Hexane/Toluene from 15:1 to 5:1 for mono- and bisadducts and finally 2:1 for trisadducts. Column conditions for C\(_{70}\)-derivatives: Hexane/Toluene from 15:1 to 5:1 for mono- and bisadducts and finally 2:1). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (8a) \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\): 7.68 (m, 2H), 7.57 (m, 2H), 4.81 (m, 2H), 4.72 (m, 2H). (8b) \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\): 8.00-7.30 (m, 8H), 5.18-3.36 (m, 8H). HRMS calculated: 929.1330; found: 929.0865 [M-H]. (9b) \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\): 7.95-6.96 (m, 8H), 4.74-3.10 (m, 8H). HRMS calculated: 1049.1331; found: 1049.0826 [M-H].

Figure S23. \(^1\)H NMR Spectrum of 8a
Figure S24. $^1$H NMR Spectrum of 8b

Figure S25. $^1$H NMR Spectrum of 9b
Figure S26. From the top: simulated, experimental and full HRMS spectrum of 8b.
Figure S27. From the top: simulated, experimental and full HRMS spectrum of 9b.
• [70] and [60]ICBA derivatives

Synthesis of ICBA derivatives (11a-c, 12a-b). To a solution of C\textsubscript{60} or C\textsubscript{70} (50.00 mg) in 4 mL of ODCB (previously sonicated for about 20 minutes), the appropriate amount of indene (10) was added. The resulting mixture was kept under MW irradiation at 180 °C (25 W) for appropriate time. After cooling down, the reaction mixture was precipitated with methanol. The recovered residue was solubilized in a minimal amount of chloroform and precipitated again with methanol. Methanol was removed and the residue was solubilized in dichloromethane, adsorbed on silica and chromatographed (Silica gel column conditions for C\textsubscript{60}-derivatives: Hexane/Chloroform 25:1 and then 20:1 for monoadduct, 10:1 for bisadducts mixture and finally 1:1 for trisadducts. Column conditions for C\textsubscript{70}-derivatives: Hexane/Chloroform 30:1 and then 25:1 for monoadducts, 15:1 and then 9:1 for bisadducts and finally 5:1 for trisadducts). Both mono and bis-adducts were solubilized and transferred to a centrifuge tube using a minimal amount of chloroform and subsequently precipitated with methanol. (11b) \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}) δ: 8.01-7.12 (m, 8H), 5.41-2.34 (m, 8H). HRMS calculated: 953.1252; found: 953.0886 [M-H]\textsuperscript{+}. (11c) HRMS calculated: 1068.1877; found: 1068.1566 [M-H]\textsuperscript{+}. (12a) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 8.32-7.28 (m, 3H), 7.24-6.88 (m, 1H). 4.94-2.10 (m, 4H; isomers mixture). (12b) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.87-6.72 (m, 8H), 5.19-1.97 (m, 8H). HRMS calculated: 1072.1252; found: 1072.0819 [M-H]\textsuperscript{+}.

![Figure S28. \textsuperscript{1}H NMR Spectrum of 11b](image-url)
Figure S29. $^1$H NMR Spectrum of 12a

Figure S30. $^1$H NMR Spectrum of 12b
Figure S31. From the top: simulated, experimental and full HRMS spectrum of 11b.
Figure S32. From the top: simulated, experimental and full HRMS spectrum of 11c.
Figure S33. From the top: simulated, experimental and full HRMS spectrum of 12b.
References: