Supporting information for

Double-caged fullerene acceptors: effect of alkyl chain length on photovoltaic performance

Victor A. Brotsman, Alexey V. Rybalchenko, Dmitry N. Zubov, Dmitry Yu. Paraschuk, Alexey A. Goryunkov

Table of Contents

General procedure for the preparation of the glycine alkyl ester and double-caged fullerene derivatives dFR

Fig. S1 MALDI mass spectra of dFHex, dFOct, and dFNon

Fig. S2 1H NMR spectrum of dFHex

Fig. S3 13C NMR spectrum of dFHex

Fig. S4 1H NMR spectrum of dFOct

Fig. S5 13C NMR spectrum of dFOct

Fig. S6 1H NMR spectrum of dFNon

Fig. S7 13C NMR spectrum of dFNon

Fig. S8 UV-Vis spectra of dFHex, dFOct, and dFNon

Fig. S9 Registered and deconvoluted CV curves of dFHex, dFOct, and dFNon

Fig. S10 Contact angle measurements for P3HT, P3HT/dFBn, P3HT/dFNon, P3HT/dFODec as oDCB solutions.

Fig. S11 The series and shunt resistances for the best P3HT/dFR and P3HT/PCBM devices as well as their dependences from selected photovoltaic parameters

Fig. S12 $R_{sh}/R_s$ ratio as a function of dFR solubility.

Fig. S13 AFM height and magnitude images of P3HT/dFR active layers

Fig. S14 Correlation plot between maximum domain sizes ($h_{max}$) and roughness ($R_a$ and $R_q$ values) of P3HT/acceptor bulk heterojunctions according to AFM data

Fig. S15 Correlation plot between PV parameters and the maximum domain size ($h_{max}$).

Fig. S16 Dependences of the maximum domain size ($h_{max}$) vs (a) chain length in alkyl moiety and (b) dFR solubility.
General procedure for the preparation of the glycine alkyl ester p-toluenesulfonates

The glycine alkyl ester p-toluenesulfonates were prepared according to work [46]. Into a 250-mL round-bottom flask were placed glycine (3 g, 0.04 mol), p-toluenesulfonic acid monohydrate (7.6 g, 0.04 mol), alkyl alcohol (0.16 mol), and benzene (150 mL). The mixture was then heated under reflux, with the liberated water being removed azeotropically and trapped with the aid of a Stark and Dean distilling receiver. A clear solution was obtained soon after reflux began. When water (about 5–10 mL) was no longer distilled off (about 4–5 h), the reaction mixture was permitted to cool to room temperature and 50 mL of benzene plus 200 ml of dry diethyl ether added thereto. After standing for about 2 h at 4°C, the crystalline alkyl glycinate p-toluenesulfonate was filtered, washed with anhydrous diethyl ether, and recrystallized from methanol/ether.

**Glycine n-hexyl ester p-toluenesulfonate.** Yield 94%. ¹H NMR (600 MHz, CDCl₃, ppm): δ 8.01 (3H, br, t, ³JHH 5.1 Hz, NH₃⁺), 7.71 (2H, dm, ²JHH 8.1 Hz, para-CH₃, Ts), 7.10 (2H, dm, ²JHH 8.1 Hz, meta-CH₃, Ts), 3.97 (2H, t, ³JHH 6.9 Hz, CH₂, n-hexyl), 3.66 (2H, q, ²JHH 5.9 Hz, CH₂), 2.33 (3H, br, s, CH₃, Ts), 1.48 (2H, m, CH₂, n-hexyl), 1.26 (2H, m, CH₂, n-hexyl), 1.22 (4H, m, CH₂, n-hexyl), 0.87 (3H, t, ³JHH 7.1 Hz, CH₃, n-hexyl). ¹³C NMR (150 MHz, CDCl₃, ppm): δC 167.44 (C=O), 141.17 (Ts, ipso-CH₃), 140.36 (Ts, para-CH₃), 128.87 (Ts, ortho-CH₃), 125.96 (Ts, meta-CH₃), 66.28 (CH₂, n-hexyl), 40.37 (CH₂), 31.35 (CH₂, n-hexyl), 28.14 (CH₂, n-hexyl), 25.31 (CH₂, n-hexyl), 22.46 (CH₂, n-hexyl), 21.28 (CH₃, Ts), 13.97 (CH₃, n-hexyl).

**Glycine n-octyl ester p-toluenesulfonate.** Yield 92%. ¹H NMR (600 MHz, CDCl₃, ppm): δ 8.04 (3H, br, t, ³JHH 5.1 Hz, NH₃⁺), 7.71 (2H, dm, ²JHH 8.1 Hz, para-CH₃, Ts), 7.11 (2H, dm, ²JHH 8.1 Hz, meta-CH₃, Ts), 3.99 (2H, t, ³JHH 7.0 Hz, CH₂, n-octyl), 3.67 (2H, q, ²JHH 5.7 Hz, CH₂), 2.34 (3H, br, s, CH₃, Ts), 1.50 (2H, p, ²JHH 6.7 Hz, CH₂, n-octyl), 1.28 (2H, m, CH₂, n-octyl), 1.24 (8H, m, CH₂, n-octyl), 0.89 (3H, t, ³JHH 7.1 Hz, CH₃, n-octyl). ¹³C NMR (150 MHz, CDCl₃, ppm): δC 167.43 (C=O), 141.08 (Ts, ipso-CH₂), 140.45 (Ts, para-CH₂), 128.90 (Ts, ortho-CH₂), 125.99 (Ts, meta-CH₂), 66.34 (CH₂, n-octyl), 40.37 (CH₂), 31.78 (CH₂, n-octyl), 29.19 (CH₂, n-octyl), 29.16 (CH₂, n-octyl), 28.22 (CH₂, n-octyl), 25.67 (CH₂, n-octyl), 22.62 (CH₂, n-octyl), 21.31 (CH₃, Ts), 14.08 (CH₃, n-octyl).

**Glycine n-nonyl ester p-toluenesulfonate.** Yield 89%. ¹H NMR (600 MHz, CDCl₃, ppm): δ 7.99 (3H, br, t, ³JHH 5.3 Hz, NH₃⁺), 7.71 (2H, dm, ²JHH 8.2 Hz, ortho-CH₃, Ts), 7.09 (2H, dm, ²JHH 8.2 Hz, meta-CH₃, Ts), 3.97 (2H, t, ³JHH 7.0 Hz, CH₂, n-nonyl), 3.65 (2H, q, ²JHH 5.7 Hz, CH₂), 2.33 (3H, br, s,CH₃, Ts), 1.48 (2H, p, ²JHH 7.0 Hz, CH₂, n-nonyl), 1.29 (2H, m, CH₂, n-nonyl), 1.25 (4H, m, CH₂, n-nonyl), 1.22 (6H, m, CH₂, n-nonyl), 0.89 (3H, t, ³JHH 7.1 Hz, CH₃, n-nonyl). ¹³C NMR (150 MHz, CDCl₃, ppm): δC 167.44 (C=O), 141.20 (Ts, ipso-CH₃), 140.26 (Ts, para-CH₃), 128.82 (Ts, ortho-CH₃), 125.96 (Ts, meta-CH₃), 65.24 (CH₂, n-nonyl), 40.33 (CH₂), 31.81 (CH₂, n-nonyl), 29.43 (CH₂, n-nonyl), 29.22 (CH₂, n-nonyl), 28.18 (CH₂, n-nonyl), 25.64 (CH₂, n-nonyl), 22.61 (CH₂, n-nonyl), 21.24 (CH₃, Ts), 14.05 (CH₃, n-nonyl).
Synthesis of double-caged fullerene derivatives dFR

The double-caged fullerene derivatives dFR were prepared via lithium-salt assisted [2+3]-cycloaddition.[26] Typically, triethylamine (46 µL, 0.34 mmol) was added to a suspension of glycine ester p-toluenesulfonate (0.34 mmol) in CH₂Cl₂ (2 mL). Obtained solution was added to fullerene C₆₀ (200 mg, 0.28 mmol) dissolved in the toluene (150 mL). Then paraformaldehyde (84 mg, 2.80 mmol), lithium perchlorate (36 mg, 0.34 mmol) and triethylamine (46 µL, 0.34 mmol) were added, and the mixture was refluxed for 3–5 h. The double-caged fullerene derivatives dFR were isolated by means of column chromatography (sequentially employing toluene/hexane 3:1 v/v mixture and then toluene). Finally, products were purified using preparative scale HPLC and characterized by means of MS and NMR spectroscopy.

n-Hexyl (RS)-1''-azabicyclo[3'',3'',0]octan[3'',4'':1,9;6'',7'':1',9']cyclobuta[2,12:2',12']di(C₆₀-I₅)fullerene-5''-carboxate (dFHHex). Yield 45%. tᵣ 5.9 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 2 mL·min⁻¹). λₘₐₓ (toluene, nm): 328, 432. m/z (MALDI-TOF-MS, negative ion mode): 1623.1 (C₁₃₀H₁₇NO₂⁻, M⁻, 100%), 720.0 (C₆₀⁻, 73%). HRMS (ESI) calculated for [M+H]⁺, C₁₃₀H₁₈NO₂, 1624.1332, found 1624.1354. ¹H NMR (600 MHz, 1,2-C₆D₄Cl₂, ppm): δH 5.68 (2H, d, ²J₁₁ 11.5 Hz, CH₂N), 5.65 (2H, d, ²J₁₁ 11.5 Hz, CH₂N), 4.12 (2H, t, ³J₁₁ 6.5 Hz, CH₂O), 1.32 (4H, m, CH₂, n-hexyl), 0.97 (4H, m, CH₂, n-hexyl), 0.70 (3H, t, ³J₁₁ 7.2 Hz, CH₃, n-hexyl). ¹³C NMR (150 MHz, 1,2-C₆D₄Cl₂, ppm): δC 169.96 (C=O), 154.55, 153.04, 149.38, 149.13, 148.92, 148.46, 148.27, 148.16, 148.01, 147.20, 146.99, 146.93, 146.92, 146.43, 146.38, 146.29, 146.15, 145.71, 145.64, 145.57, 145.07, 144.88, 144.87, 144.84, 144.79, 144.60, 144.53, 144.48, 144.45, 144.29, 144.10, 144.01, 143.89, 143.85, 143.52, 143.46, 142.95, 142.82, 142.59, 142.56, 142.48, 142.35, 142.29, 141.43, 141.30, 141.16, 138.67, 137.77, 137.35, 137.21, 132.76 (sp²-C, cage C₆₀), 109.63 (CCOO), 84.71 (sp³-C, cage C₆₀), 77.18 (sp³-C of cyclobutan moiety, cage C₆₀), 71.87 (CH₂N), 70.72 (sp³-C of cyclobutan moiety, cage C₆₀), 69.44 (sp³-C, cage C₆₀), 66.11 (CH₂O), 31.55 (CH₂, n-hexyl), 28.82 (CH₂, n-hexyl), 26.27 (CH₂, n-hexyl), 22.84 (CH₂, n-hexyl), 14.10 (CH₃, n-hexyl).

n-Octyl (RS)-1''-azabicyclo[3'',3'',0]octan[3'',4'':1,9;6'',7'':1',9']cyclobuta[2,12:2',12']di(C₆₀-I₅)fullerene-5''-carboxate (dFOct). Yield 42%. tᵣ 5.6 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 2 mL·min⁻¹). λₘₐₓ (toluene, nm): 328, 432. m/z (MALDI-TOF-MS, negative ion mode): 1651.2 (C₁₃₂H₂₁NO₂⁻, M⁻, 100%), 931.2 (C₇₂H₁₂NO₂⁻, [M-C₆₀⁻], 13%), 720.0 (C₆₀⁻, 95%), 1901.3 (C₆₀⁺DCTB⁻, 19%). HRMS (ESI) calculated for [M+H]⁺, C₁₃₂H₂₂NO₂, 1652.1645, found 1652.1646. ¹H NMR (600 MHz, 1,2-C₆D₄Cl₂, ppm): δH 5.68 (2H, d, ²J₁₁ 11.5 Hz, CH₂N), 5.65 (2H, d, ²J₁₁ 11.5 Hz, CH₂N), 4.12 (2H, t, ³J₁₁ 6.5 Hz, CH₂O), 1.34 (2H, m, CH₂, n-octyl), 1.22 (2H, m, CH₂, n-octyl), 1.14 (4H, m, CH₂, n-octyl), 1.00 (6H, m, CH₃, n-octyl), 0.79 (3H, t, ³J₁₁ 7.3 Hz, CH₃, n-octyl). ¹³C NMR (150 MHz, 1,2-C₆D₄Cl₂, ppm): δC 169.96 (C=O), 154.55, 153.04, 149.38, 149.13, 148.92, 148.46, 148.27, 148.17, 148.01, 147.20, 146.99, 146.93, 146.44, 146.38, 146.29, 146.15, 145.72, 145.65, 145.58, 145.07, 144.90, 144.88, 144.84, 144.79, 144.60, 144.53, 144.45, 144.46, 144.57, 144.40, 144.14, 143.89, 143.85, 143.52, 143.46, 142.95, 142.82, 142.59, 142.56, 142.48, 142.35, 142.29, 141.43, 141.30, 141.16, 138.67, 137.77, 137.35, 137.21, 132.76 (sp²-C, cage C₆₀), 109.63 (CCOO), 84.71 (sp³-C, cage C₆₀), 71.87 (CH₂N), 70.72 (sp³-C of cyclobutan moiety, cage C₆₀), 69.44 (sp³-C, cage C₆₀), 66.11 (CH₂O), 31.55 (CH₂, n-hexyl), 28.82 (CH₂, n-hexyl), 26.27 (CH₂, n-hexyl), 22.84 (CH₂, n-hexyl), 14.10 (CH₃, n-hexyl).
143.47, 142.95, 142.82, 142.57, 141.30, 141.16, 138.67, 137.77, 137.35, 137.22, 132.76 ($sp^2$-C, cage C$_{60}$), 109.63 (C=CO$_2$), 84.72 ($sp^3$-C, cage C$_{60}$), 77.19 ($sp^3$-C of cyclobutan moiety, cage C$_{60}$), 71.88 (CH$_2$N), 70.69 ($sp^3$-C of cyclobutan moiety, cage C$_{60}$), 69.44 ($sp^3$-C, cage C$_{60}$), 66.13 (CH$_2$O), 31.96 (CH$_2$, n-octyl), 29.52 (CH$_2$, n-octyl), 29.44 (CH$_2$, n-octyl), 28.89 (CH$_2$, n-octyl), 26.57 (CH$_2$, n-octyl), 23.01 (CH$_2$, n-octyl), 14.35 (CH$_3$, n-octyl).

$n$-Nonyl (RS)-1"-azabicyclo[3".3".0]octan[3".4".9]cyclobuta[2,12.2.12]di(C$_{60}$-I)$_h$fullerene-5"-carboxate (dFNon). Yield 48%. $t_R$ 5.3 min (Cosmosil Buckyprep 4.6 mm I.D. × 25 cm, toluene, 2 mL min$^{-1}$). $\lambda_{max}$ (toluene, nm): 328, 432. $m/z$ (MALDI-TOF-MS, negative ion mode): 1665.2 (C$_{133}$H$_{23}$NO$_2^-$, M$^-$, 100%), 720.0 (C$_{60}$, 46%), 1915.4 ([M+DCTB]$^-$, 13%). HRMS (ESI) calculated for [M+H]$^+$, C$_{133}$H$_{24}$NO$_2$, 1666.1801, found 1666.1804.

$^1$H NMR (600 MHz, 1,2-C$_6$D$_4$Cl$_2$, ppm): $\delta$H 5.69 (2H, d, $^2J_{HH}$ 11.5 Hz, CH$_2$N), 5.66 (2H, d, $^2J_{HH}$ 11.5 Hz, CH$_2$N), 4.12 (2H, t, $^3J_{HH}$ 6.5 Hz, CH$_2$O), 1.35 (2H, m, CH$_2$, n-nonyl), 1.17 (2H, m, CH$_2$, n-nonyl), 1.08 (4H, m, CH$_2$, n-nonyl), 1.00 (6H, m, CH$_2$, n-nonyl), 0.82 (3H, t, $^3J_{HH}$ 7.3 Hz, CH$_3$, n-nonyl). $^{13}$C NMR (150 MHz, 1,2-C$_6$D$_4$Cl$_2$, ppm): $\delta$C 169.96 (C=O), 154.55, 153.04, 149.38, 149.13, 148.92, 148.46, 148.27, 148.18, 148.01, 147.21, 147.04, 146.99, 146.93, 146.44, 146.38, 146.30, 146.15, 145.72, 145.65, 145.58, 145.08, 145.07, 144.91, 144.88, 144.85, 144.79, 144.60, 144.53, 144.45, 144.29, 144.27, 144.19, 144.10, 144.03, 143.89, 143.85, 143.53, 143.47, 142.97, 142.82, 142.59, 142.57, 142.48, 142.35, 142.29, 141.44, 141.30, 141.16, 138.67, 137.77, 137.35, 137.22, 132.76 ($sp^2$-C, cage C$_{60}$), 109.64 (C=CO$_2$), 84.73 ($sp^3$-C, cage C$_{60}$), 77.19 ($sp^3$-C of cyclobutan moiety, cage C$_{60}$), 71.88 (CH$_2$N), 70.87 ($sp^3$-C of cyclobutan moiety, cage C$_{60}$), 69.44 ($sp^3$-C, cage C$_{60}$), 66.13 (CH$_2$O), 32.19 (CH$_2$, n-nonyl), 29.82 (CH$_2$, n-nonyl), 29.51 (CH$_2$, n-nonyl), 29.49 (CH$_2$, n-nonyl), 28.89 (CH$_2$, n-nonyl), 26.60 (CH$_2$, n-nonyl), 23.01 (CH$_2$, n-nonyl), 14.35 (CH$_3$, n-nonyl).
Figure S1. MALDI mass spectra of dFHex (a), dFOct (b), and dFNon (c).
Figure S2. $^1$H NMR spectrum of dFHex
Figure S3. $^{13}$C NMR spectrum of dFHex
Figure S4. $^1$H NMR spectrum of dFOct
Figure S5. $^{13}$C NMR spectrum of dFOct
Figure S6. $^1$H NMR spectrum of dFNon
Figure S7. $^{13}$C NMR spectrum of dFNon
Figure S8. UV-Vis spectra of dFHex (a), dFOct (b) and dFNon (c) in toluene solution.
Figure S9. Registered and deconvoluted CV curves of dFHex (a–b), dFOct (c–d), dFNon (e–f) (0.9–1.2 mM, 0.20 M Bu$_4$NBF$_4$, oDCB, 100 mV s$^{-1}$, RT).
Figure S10. Contact angle measurements for P3HT (a), P3HT/dFBn (b), P3HT/dFNon (c), P3HT/dFODec (d) as oDCB solutions.
Figure S11. The series ($R_S$) and shunt ($R_{SH}$) resistances for the best P3HT/dFR and P3HT/PCBM devices as well as their dependences from selected photovoltaic parameters: (a) $R_S$ versus $R_{SH}$ values; (b) correlation between experimental FF values and FF values estimated using $R_S$ and $R_{SH}$ values; (c and d) correlation plots between $J_{SC}$ and FF values vs $R_S$ resistances; (e and f) correlation plots between FF and $V_{OC}$ values vs $R_{SH}$ resistances.
Figure S12. The series ($K_S$) to shunt ($K_{SH}$) resistances ratio ($K_{sh}/K_s$) as a function of dFR solubility in oDCB.
Figure S13. AFM height (top) and magnitude (bottom) images (5×5 μm²) of P3HT/dFR active layers (2.5:1, w/w, pre-annealed at 110 °C for 5 min, R=n-hexyl, benzyl, n-octyl, n-nonyl, n-decyl, and n-octadecyl, a–f).

Figure S14. Correlation plot between maximum domain sizes ($h_{\text{max}}$) and roughness ($R_a$ and $R_q$ values) of P3HT/acceptor bulk heterojunctions according to AFM data.
Figure S15. Correlation plot between PV parameters and the maximum domain size ($h_{\text{max}}$).
Figure S16. The maximum domain size ($h_{\text{max}}$) as a function of (a) chain length in alkyl moiety and (b) dFR solubility.