Carbazole linked phenylquinoline-based fullerene derivatives as an acceptor for bulk heterojunction polymer solar cells: Effect of interfacial contacts on the device performance

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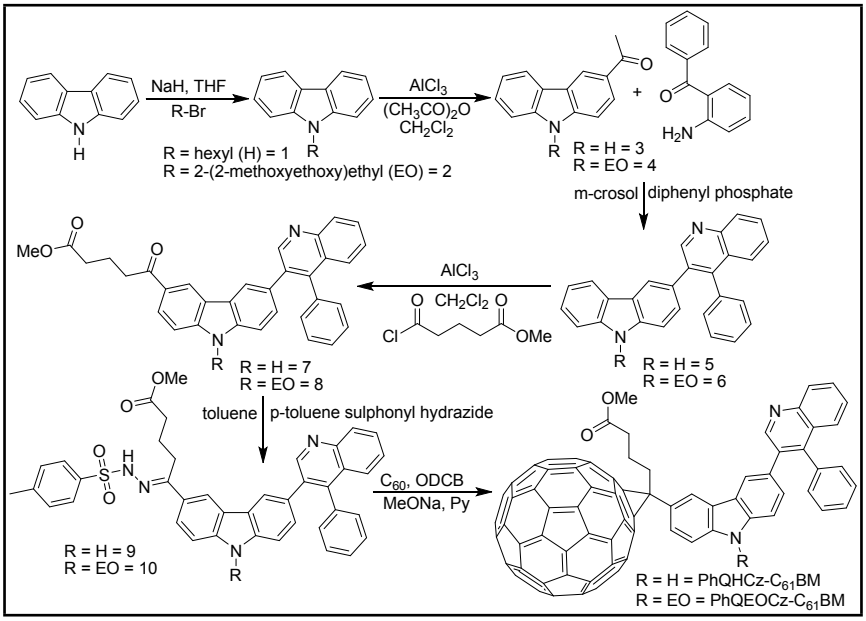

Scheme S1. Synthesis of **PhQHCz-C_{61}BM** and **PhQEOCz-C_{61}BM**.

Synthesis of fullerene derivatives

9-Hexyl-9H-carbazole (**1**), 9-(2-(2-methoxyethoxy)ethyl)-9H-carbazole (**2**), 1-(9-hexyl-9H-carbazol-3-yl)ethanone (**3**), and 1-(9-(2-(2-methoxyethoxy)ethyl)-9H-carbazol-3-yl)ethanone (**4**) were synthesized using a slight modification to the literature procedures.[1,2] Compound **1** (88%, white solid, mp 68-70 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13-8.10 (d, 2H), 7.51-7.41 (m, 4H), 7.24-7.22 (d, 2H), 4.33-4.30 (t, 2H), 1.93-1.83 (m, 2H), 1.56-1.30 (m, 6H), 0.90-0.86 (t, 3H); Compound **2** (70%, colorless liquid). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13-8.10 (d, 2H), 7.50-7.48 (m, 4H), 7.21-7.24 (d, 2H), 4.55-4.50 (t, 2H), 3.90-3.86 (t, 2H), 3.55-3.52 (t, 2H), 3.46-3.43 (t, 2H), 3.34 (s, 3H); Compound **3** (67%, gummy liquid). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.74 (s, 1H), 8.17-8.11 (m, 2H), 7.55-7.49 (m, 1H), 7.45-7.39 (t, 2H), 7.33-7.28 (m, 1H), 4.34-4.29 (t, 2H), 2.73 (s, 3H), 1.90-1.83 (m, 2H), 1.36-1.30 (m, 6H), 0.89-0.84 (t, 3H); Compound **4** (58%, gummy liquid). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.73 (s, 1H), 8.16-8.10 (m, 2H), 7.56-7.42 (m, 3H), 7.33-7.26 (m, 1H), 4.56-4.50 (t, 2H), 3.91-3.85 (t, 2H), 3.52-3.46 (t, 2H), 3.43-3.39 (t, 2H), 3.40 (s, 3H), 2.72 (s, 3H).

Synthesis of 9-hexyl-3-(4-phenylquinolin-2-yl)-9H-carbazole (5)

A mixture of compound **4** (2.93 g, 10 mmol), 2-aminobenzophenone (2.16 g, 11 mmol) and diphenyl phosphate (3.01 g, 12 mmol) in 10 mL of m-cresol was purged with nitrogen, stirred for 30 min at room temperature and refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane:methylene chloride (MC):ethyl acetate (EA), 6:3:1 v/v) to give **5** (90%, yellow solid, mp 113-115 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.94 (s, 1H), 8.39-8.36 (d, 1H), 8.30-8.21 (m, 2H), 8.00 (s, 1H), 7.93-7.90 (d, 1H), 7.78-7.72 (t, 1H), 7.64-7.43 (m, 9H), 7.30-7.28 (d, 1H), 4.38-4.33 (t, 2H), 1.92-1.87 (m, 2H), 1.36-1.29 (m, 6H), 0.88-0.84 (t, 3H).

9-(2-(2-Methoxyethoxy)ethyl)-3-(4-phenylquinolin-2-yl)-9H-carbazole (6)

The compound **6** was synthesized by adopting the similar procedure for compound **5** using the carbazole derivative **4** (15%, brown solid, mp 102-105 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.94 (s, 1H), 8.39-8.36 (d, 1H), 8.30-8.26 (m, 1H), 8.22-8.20 (d, 1H) 8.00 (s, 1H), 7.92-7.90 (d, 1H), 7.78-7.73 (t, 1H), 7.64-7.43 (m, 9H), 7.30-7.25 (d, 1H), 4.59-4.55 (t, 2H), 3.93-3.89 (t, 2H), 3.54-3.51 (t, 2H), 3.45-3.41 (t, 2H) 3.31 (s, 3H).

Synthesis of methyl 5-(9-hexyl-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-oxopentanoate (7)

The compound **5** (3 g, 6.6 mmol) was dissolved in 30 mL of MC and stirred at 0 ºC under N_2 atmosphere for 10 min. $AlCl_3$ (2.64 g, 19.8 mmol) was added to the mixture and methyl 5-chloro-5-oxopentanoate (2.2 g, 13.2 mmol) was slowly added at 0 ºC. The yellow color slowly changed to dark green, and the resulting dark green solution was allowed to warm and was stirred at room temperature overnight. The reaction mixture was poured onto crushed ice and the organic phase was separated. The aqueous layer was extracted with MC (2 x 100 mL). The combined organic layers were washed with 2% aq. NaOH solution (100 mL), brine (100 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane:MC:EA, 6:3:1 v/v) to give **7 (**Yield: 68%, yellow solid, mp 130-132 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.0 (s, 1H), 8.87 (s, 1H), 8.46-8.43 (d, 1H), 8.30-8.27 (d, 1H), 8.19-8.16 (d, 1H), 8.0 (s, 1H), 7.94-7.91 (d, 1H), 7.75-

7.73 (t, 1H), 7.64-7.43 (m, 8H), 4.40-4.36 (t, 2H), 3.70 (s, 3H), 3.25-3.20 (t, 2H), 2.54-2.58 (t, 2H), 2.19-2.14 (m, 2H), 1.93-1.89 (m, 2H), 1.40-1.27 (m, 6H), 0.88-0.83 (t, 3H).

Methyl 5-(9-(2-(2-methoxyethoxy)ethyl)-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-oxopentanoate (8)

The compound **8** was synthesized using the similar procedure for compound **7 (**Yield: 59%, yellow solid, mp 119-121 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.0 (s, 1H), 8.86 (s, 1H), 8.44-8.42 (d, 1H), 8.30-8.20 (d, 1H), 8.18-8.15 (d, 1H), 8.0 (s, 1H), 7.95-7.92 (d, 1H), 7.78-7.73 (t, 1H), 7.60-7.46 (m, 8H), 4.59-4.57 (t, 2H), 3.94-3.90 (t, 2H), 3.70 (s, CO-OCH_3, 3H), 3.52-3.50 (t, 2H), 3.42-3.40 (t, 2H), 3.30 (s, OCH_3, 3H), 3.25-3.20 (t, 2H), 2.54-2.45 (t, 2H), 2.21-2.14 (t, 2H).

Synthesis of methyl5-(9-hexyl-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-(2-tosylhydrazono)pentanoate (9)

A three-neck round-bottom flask was charged with methyl 5-(9-hexyl-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-oxopentanoate (**7**) (3.6 g, 6.17 mmol) and p-toluenesulfonyl hydrazide (2.3 g, 12.36 mmol) was dissolved in 75 mL of dry toluene. The resulting solution was refluxed for 24 h using a Dean-Stark setup. The toluene was removed under reduced pressure and the crude mixture was extracted with MC (2 x 300 mL). The combined organic layers were washed with 2% aq. NaOH solution (100 mL) and brine (100 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexane:MC:EA, 4:4:2 v/v) to give **9** (Yield: 72%, yellow solid, mp 153-155 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.22 (s, 1H), 8.98 (s, NH), 8.40-8.41 (d, 1H), 8.34-8.38 (d, 1H), 7.90-8.01 (m, 5H), 7.71-7.95 (t, 1H), 7.41-7.68 (m, 8H), 7.30-7.40 (m, 3H), 4.30-4.40 (t, 2H), 3.80 (s, 3H), 2.71-2.86 (t, 2H), 2.23-2.48 (m, 5H), 1.71-1.98 (m, 4H), 1.20-1.41 (m, 6H), 0.81-0.90 (t, 3H).

Synthesis of methyl 5-(9-(2-(2-methoxyethoxy)ethyl)-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-(2-tosylhydrazono)pentanoate (10)

The compound **10** synthesized according to the procedure used for compound **9 (**Yield: 61%, yellow solid, mp 148-150 ºC). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.22 (s, 1H), 8.94 (s, NH), 8.39-8.41 (d, 1H), 8.25-8.30 (d, 1H), 7.90-8.01 (m, 5H), 7.71-7.80 (t, 1H), 7.42-7.66 (m, 8H),

7.30-7.36 (d, 3H), 4.48-4.61 (t, 2H), 3.82-3.91 (t, 2H), 3.81 (s, 3H), 3.48-3.51 (t, 2H), 3.38-3.43 (t, 2H), 3.40 (s, OCH3, 3H), 2.70-2.83 (t, 2H), 2.30-2.48 (m, 5H), 1.70-1.90 (m, 2H).

Synthesis of 9-hexyl-3-(4-phenylquinoline-2-yl)-9H-carbazole-6-C61-butyric acid methyl ester (PhQHCz-C_{61}BM)

A mixture of methyl 5-(9-hexyl-6-(4-phenylquinolin-2-yl)-9H-carbazol-3-yl)-5-(2-tosylhydrazono)pentanoate (**9**) (0.44 g, 0.58 mmol), sodium methoxide (0.03 g, 0.58 mmol) and dry pyridine (10 mL) was stirred at room temperature for 30 min under N2 atmosphere. A degassed solution of C_{60} (0.33 g, 0.46 mmol) in *o*-dichlorobenzene (*o*-DCB) (20 mL) was added to the reaction mixture and the homogeneous reaction mixture was stirred at 80 ºC under N2 atmosphere overnight. Then, the solution was heated to reflux for 24 h, the resulting mixture was concentrated in vacuo and the crude solution was cooled to room temperature and poured into MeOH. The solid was collected by filtration and purified by silica gel column chromatography using toluene:hexane (8:2 v/v) as an eluent, give the **PhQHCz-C_{61}BM (**Yield 52%, brown solid). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.70 (s, 1H), 8.42-8.40 (d, 1H), 8.28-8.22 (d, 1H), 8.04-8.02 (d, 1H), 8.0 (s, 1H), 7.88-7.87 (d, 1H), 7.72-7.70 (t, 1H), 7.62-7.61(d, 2H), 7.55-7.53 (t, 4H), 7.50-7.48 (t, 1H), 7.44-7.42 (t, 1H), 4.40-4.38 (t, 2H), 3.63 (s, 3H), 2.99-2.97 (t, 2H), 2.52-2.50 (t, 2H), 2.28-2.23 (m, 2H), 2.01-1.96 (m, 2H), 1.50-1.46 (m, 2H), 1.37-1.30 (m, 4H), 0.90-0.81 (t, 3H); ^{13}C NMR (600 MHz, $CDCl_3$) δ: 173.75, 157.67, 149.28, 149.17, 148.43, 145.00, 144.01, 142.51, 140.84, 138.90, 138.28, 130.17, 129.84, 128.83, 127.60, 125.90, 124.61, 123.34, 120.41, 119.62, 109.47, 109.17, 80.91, 52.63, 51.87, 43.82, 34.53, 34.25, 31.81, 29.33, 27.29, 22.86, 22.82, 14.27. FTIR (KBr, cm^{-1}): 2952, 2925 (double, CH_3 stretch), 2854 (double, CH_2 stretch), 1735 (single, ester C=O), 1587, 1544 (single, aromatic C=C stretch), 1486 (single, CH_2 bend), 526 (single, from C_{60}). HRMS: Calculated for $C_{99}H_{38}N_2O_2$, 1288.63; found, 1288.31. Anal. Calcd for $C_{99}H_{38}N_2O_2$: C 92.80, H 2.95, N 2.16, found, C 93.11, H 2.85, N 2.23.

9-(2-(2-Methoxyethoxy)ethyl)-3-(4-phenylquinoline-2-yl)-9H-carbazole-6-C61-butyric acid methyl ester (PhQEOCz-C_{61}BM)

The **PhQEOCz-C_{61}BM** was synthesized using the similar procedure for **PhQHCz-C_{61}BM** as brown colored solid. Yield: 49% (0.32 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.69 (s, 1H), 8.41-8.39 (d, 1H), 8.26-8.28 (d, 1H), 8.01-8.00 (d, 1H), 7.99 (s, 1H), 7.87-7.86 (d, 1H), 7.73-7.70 (t, 1H), 7.62-7.61(d, 2H), 7.55-7.53 (t, 4H), 7.46-7.44 (t, 1H), 7.43-7.40 (t, 1H), 4.63-

4.61 (t, 2H), 4.00-3.98 (t, 2H), 3.63 (s, 3H), 3.59-3.57 (t, 2H), 3.46-3.45 (t, 2H), 3.31 (s, 3H), 3.00-2.98 (t, 2H), 2.52-2.50 (t, 2H), 2.27-2.23 (m, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ: 173.72, 157.37, 149.32, 149.19, 148.33, 148.23, 145.30, 145.00, 144.61, 144.32, 143.28, 142.50, 141.18, 140.84, 138.90, 138.28, 130.22, 129.82, 128.83, 128.57, 127.20, 125.81, 124.62, 123.41, 120.40, 119.61, 109.74, 109.38, 80.86, 72.24, 71.18, 69.61, 59.37, 52.58, 51.86, 43.83, 34.50, 34.23, 22.85. FTIR (KBr, cm^{-1}): 2944, 2923 (double, CH_3 stretch), 2871 (double, CH_2 stretch), 1735 (single, ester C=O), 1588, 1544 (single, aromatic C=C stretch), 1487 (single, CH_2 bend), 1135, 1102 (single, CH_2-O-CH_2 stretch), 526 (single, from C_{60}). HRMS: Calculated for $C_{98}H_{36}N_2O_4$, 1304.68; found, 1304.0 Anal. Calcd for $C_{98}H_{36}N_2O_4$: C 90.18, H 2.76, N 2.15, found, C 90.07, H 2.82, N 2.18.

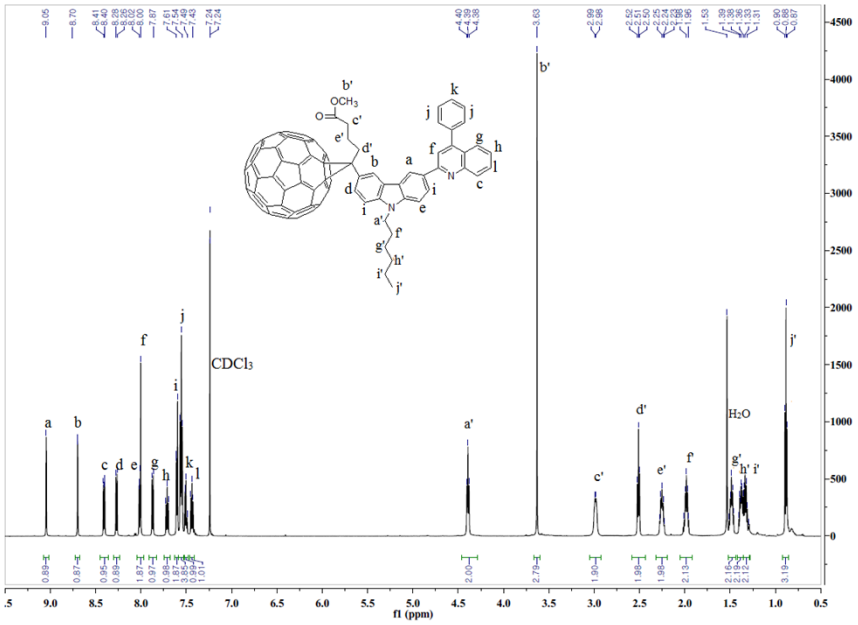

Figure S1. ^{1}H NMR Spectrum of **PhQHCz-C_{61}BM**.

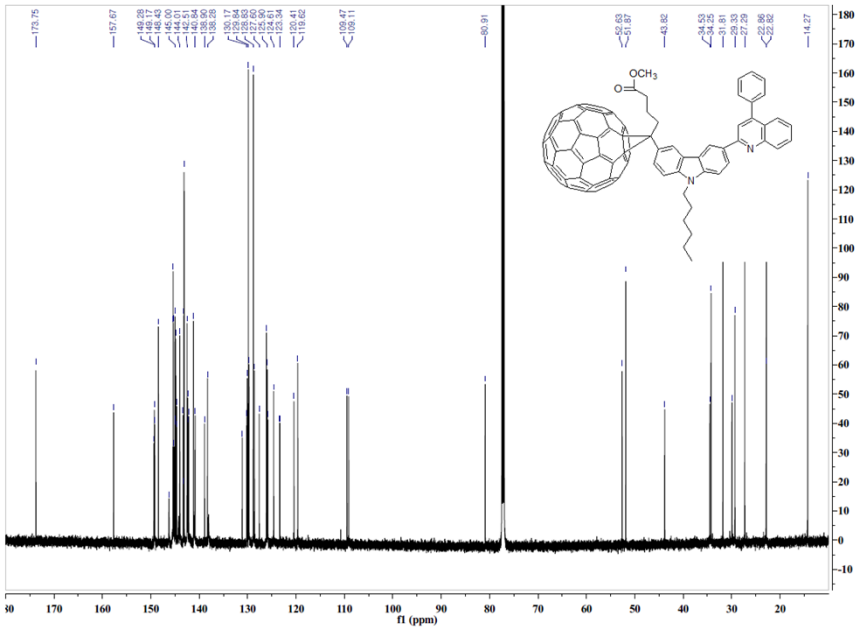

Figure S2. ^{13}C NMR Spectrum of **PhQHCz-C$_{61}$BM**.

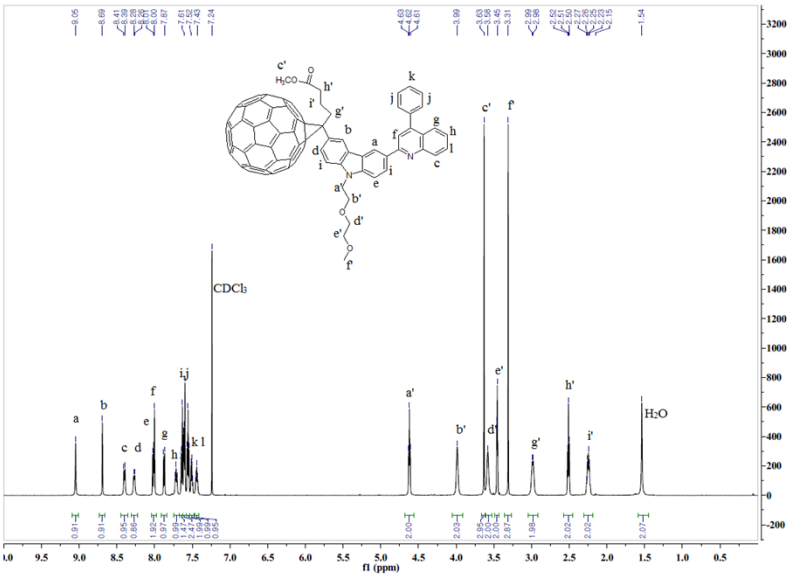

Figure S3. ^{1}H NMR Spectrum of **PhQEOCz-C_{61}BM**.

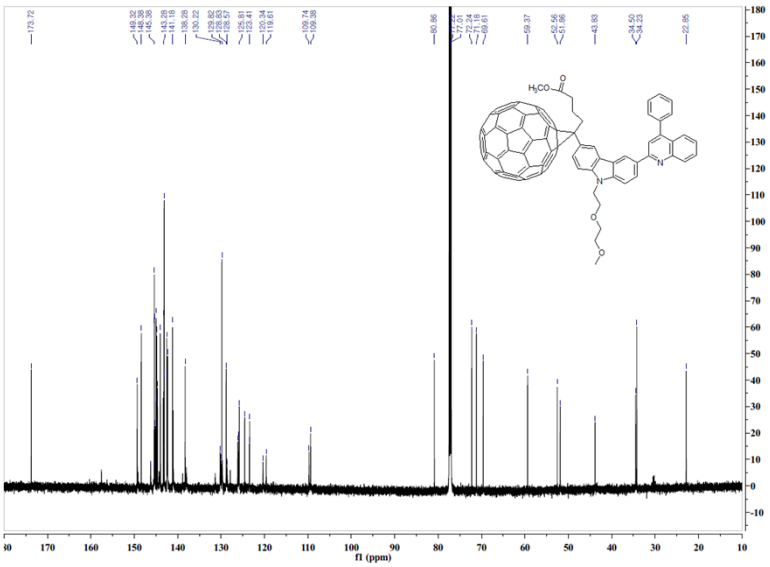

Figure S4. ^{13}C NMR Spectrum of **PhQEOCz-C_{61}BM**.

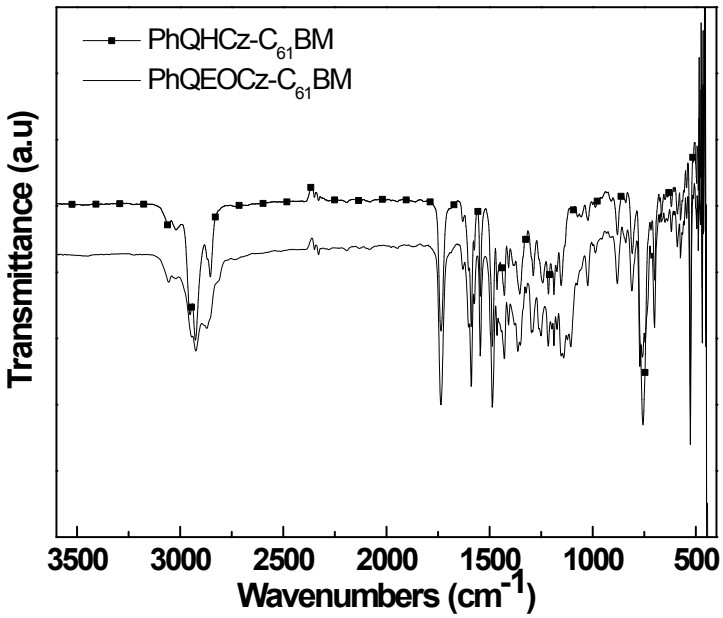

Figure S5. FT IR Spectra of **PhQHCz-C_{61}BM** and **PhQEOCz-C_{61}BM**.

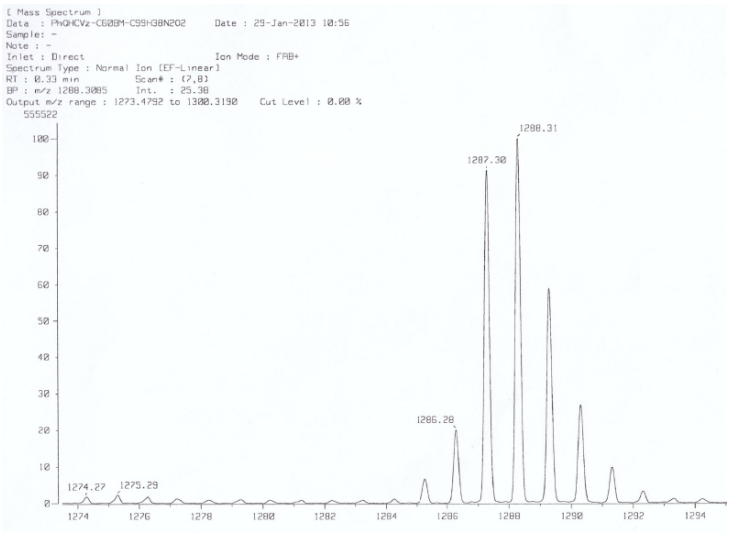

Figure S6. Mass spectrum of PhQHCz-C_{61}BM.

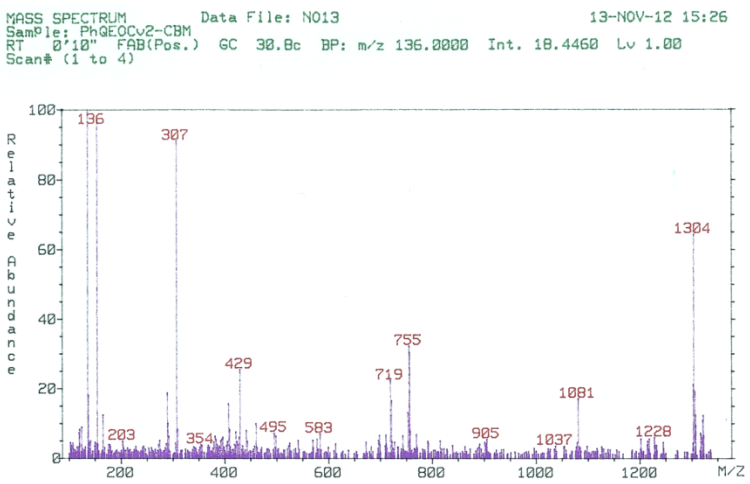

Figure S7. Mass spectrum of PhQEOCz-C_{61}BM.

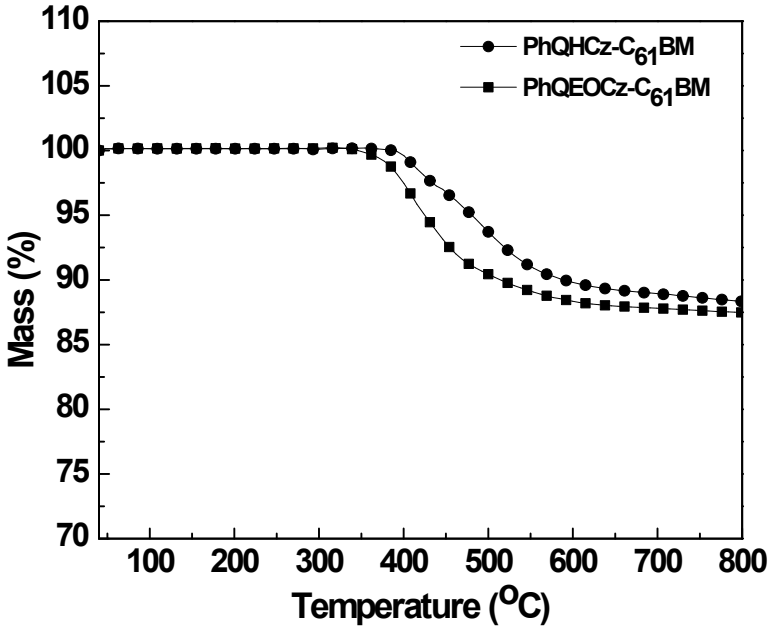

Figure S8. TGA curves of **PhQHCz-C_{61}BM** and **PhQEOCz-C_{61}BM**.

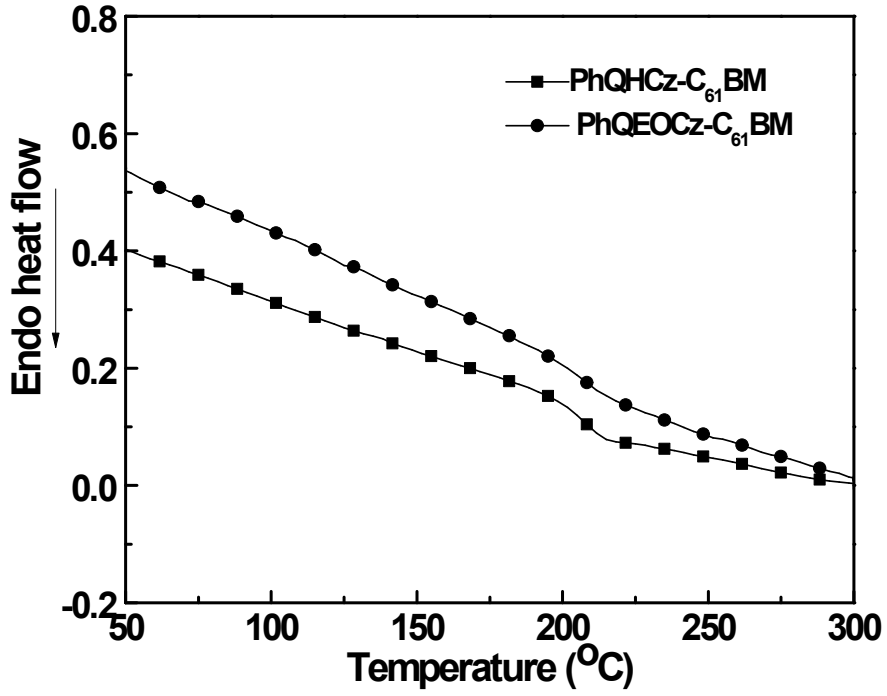

Figure S9. DSC curves of PhQHCz-C_{61}BM and PhQEOCz-C_{61}BM.

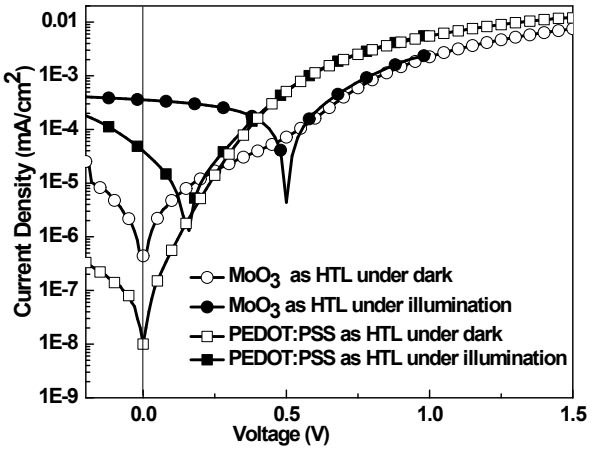

Figure S10. **J**-V curves of **PhQHCz-C_{61}BM** in a logarithmic current scale (dark and illumination).

References

1. S.-J. Lee, J.-S. Park, M. Song, I. A. Shin, Y.-I. Kim, J.W. Lee, J.-W. Kang, Y.-S. Gal, S. Kang, J. Y. Lee, S.-H. Jung, H.-S. Kim, M.-Y. Chae and S.-H. Jin, *Adv. Fun. Mater.*, 2009, **19**, 2205-2212.

2. S. J. Lee, J. S. Park, K.-J. Yoon, Y.-I. Kim, S.-H. Jin, S. K. Kang, Y.-S. Gal, S. Kang, J. Y. Lee, J.-W. Kang, S.-H. Lee, H.-D. Park and J.-J. Kim, *Adv. Fun. Mater.*, 2008, **18**, 3922-3930.