A new family of fullerene derivatives: Fullerene-curcumin conjugates for biological and photovoltaic applications

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General Methodology

All chemicals were reagent grade, purchased from Sigma Aldrich. Silica gel (40-60 µ, 60 Å) was used to purify the products from the pristine fullerene. MALDI-TOF mass spectrometry was conducted on a Bruker Microflex LRF mass spectrometer, positive mode, samples dissolved in carbon disulfide, matrix THA and TPB. NMR spectra were recorded using a Bruker 400 MHz spectrometer, a Bruker 400 MHz Avance spectrometer III equipped with cryoprobe (2014) and a JEOL 600 MHz spectrometer. The UV-vis-NIR spectra were taken using a Cary 5000 UV-vis-NIR spectrophotometer in chloroform solutions. Cyclic voltammetry (CV) experiments were carried out under an Argon atmosphere at room temperature using a CH Instrument Potentiostat. Scan rate for CV experiments was 100 mV/s. A one compartment cell with a standard three-electrode set up was used, consisting of a 1 mm diameter glassy carbon disk as the working electrode, a platinum wire as the counter electrode and a silver wire as the pseudo-reference electrode, in a solution of anhydrous o-DCB containing 0.05 M n-Bu₄NPF₆. Ferrocene was added to the solution at the end of each experiment as an internal standard.

Synthesis of Curcuminoids (1b-k)

Synthesis of Compound 1b. Acetylacetone (0.40 mL, 4 mmol) and B₂O₃ (210.3 mg, 3 mmol) were mixed in 8 mL of EtOAc and stirred at 50 °C for 30 min. 4-dodecyloxybenzaldehyde (2.9 mL, 10 mmol) was added and stirred for 15 min, subsequently, tributylborate (2.4 mL, 9 mmol) and 0.24 mL of n-butylamine were added and the reaction mixture was stirred at 50 °C for 2 h. Then, the reaction was cooled to room temperature and stirred for 3 h. This suspension was filtered and dried to afford a yellowish red solid, which was suspended in 30 mL of H₂O and stirred at room temperature for 24 h. The yellow solid was filtered, washed with ethanol-water (1:1) and dried under vacuum. The dry solid was recrystallized from n-heptane to afford 2.5 g of 1b as a yellow solid. Yield: 39 %. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 15.8 Hz, 2H), 7.49 (d, J = 8.6 Hz, 4H), 6.90 (d, J = 8.6 Hz, 4H), 6.49 (d, J = 15.8 Hz, 2H), 5.77 (s, 1H), 3.98 (t, J = 6.5 Hz, 4H), 1.89-1.65 (m, 4H), 1.65-1.39 (m, 4H), 1.29-1.16 (m, 32H), 0.88 (t,
$J = 6.7 \text{ Hz, 6H}$. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.5, 161.1, 140.3, 129.9, 127.7, 121.8, 115.1, 101.5, 68.3, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.2, 22.8, 14.3.

**Synthesis of Compound 1c.** Acetylacetone (0.40 mL, 4 mmol) and B$_2$O$_3$ (210.3 mg, 3 mmol) were mixed in 8 mL of EtOAc and stirred at 50 °C for 30 min. 4-hexyloxybenzaldehyde (2.2 mL, 10 mmol) was added and stirred for 15 min, subsequently, tributylborate (2.4 mL, 9 mmol) and 0.24 mL of $n$-butylamine were added and the reaction mixture was stirred at 50 °C for 2 h. Then, the reaction was cooled to room temperature and stirred for 3 h. The reaction turned to a yellowish red color. This suspension was filtered and dried to afford a yellowish red solid, which was suspended in 30 mL of H$_2$O and stirred at room temperature for 24 h. Then the yellow solid was filtered, washed with ethanol-water (1:1) and dried under vacuum. The dry solid was recrystallized from $n$-hexane to afford 0.76 g of 1c as a crystalline yellowish-orange solid. Yield: 40 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 15.8$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 4H), 6.90 (d, $J = 8.5$ Hz, 4H), 6.49 (d, $J = 15.8$ Hz, 2H), 5.77 (s, 1H), 3.99 (t, $J = 6.5$ Hz, 4H), 1.79 (p, $J = 6.7$, 4H), 1.53-1.281 (m, 12H), 0.91 (t, $J = 6.5$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 183.5, 161.1, 140.3, 129.9, 127.7, 121.8, 115.0, 101.5, 68.3, 31.7, 29.3, 25.8, 22.7, 14.2.

**Synthesis of Compound 1d.** Acetylacetone (0.72 mL, 7 mmol) and B$_2$O$_3$ (348.1 mg, 5 mmol) were mixed in 10 mL of EtOAc and stirred at 50 °C for 30 min. Tributylborate (3.77 mL, 14 mmol) was added and stirred for 15 min, subsequently, compound 4-(methylthio)benzaldehyde (1.86 mL, 14 mmol) was added and the reaction mixture was stirred at 50 °C for 3 h. Then, the reaction was cooled to room temperature for about 1 h, and a solution of $n$-butylamine (0.4 mL, 4 mmol) in 2 mL of EtOAc was added dropwise, and the reaction was stirred overnight at room temperature. This suspension was filtered and dried to afford a red solid, which was suspended in 200 mL of H$_2$O, stirred at room temperature for 8 h, filtered, washed with water and dried under vacuum to afford 2.11 g of 1d as an orange precipitate. Yield: 82%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 15.97 (s, 1H), 7.61 (d, $J = 15.8$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.24 (d, $J = 8.4$ Hz, 4H), 6.58 (d, $J = 15.8$ Hz, 2H), 5.81 (s, 1H), 2.51 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 183.4, 141.9, 140.1, 131.7, 128.6, 126.2, 123.3, 101.9, 15.4.
Synthesis of Compound 1e. Acetylacetonate (1g, 9.98 mmol) and B$_2$O$_3$ (0.5 g, 5.14 mmol) were mixed in EtOAc (10 mL) and the reaction mixture was warmed up at 40 °C for 30 min. Then, in a separate flask a solution of ferrocene-carboxaldehyde (4.1 g, 19.15 mmol) and tributylborate (9.2 g, 39.39 mmol) was prepared in EtOAc (10 mL) and added to the previous solution. The mixture was stirred and gently heated at 40 °C for 3 h. After cooling down, n-butylamine (0.5 mL, 50 mM) in EtOAc (10 mL) was added dropwise. The final reaction was stirred at room temperature for two days. After that, a violet-green solid was formed. Then, a solution of 10 % of HCl was added and the mixture heated at 60 °C for 2 h. A color change was observed to light violet and the final mixture was filtered. The solid was washed with H$_2$O, MeOH and Et$_2$O to remove impurities. Yield: 68 %. $^1$H-RMN (300 MHz CDCl$_3$, window from 16 to 0 ppm): δ 16.13 (s, 1H), 7.53 (d, 2H), 6.21 (d, 2H), 5.63 (s, 1H), 4.52 (d, 4H), 4.48 (d, 4H), 4.17 (s, 10H).

Synthesis of Compound 1f: Following a modified procedure from literature.¹ Acetylacetone (0.72 mL, 7 mmol) and B$_2$O$_3$ (348.1 mg, 5 mmol) were dissolved in 10 mL of EtOAc. The reaction mixture was heated at 50 °C for 30 min until a white suspension was formed. Then, a solution containing 2-thiophenecarboxaldehyde (1.3 mL, 14 mmol) and tributyl borate (3.77 mL, 14 mmol) in EtOAc was added to the reaction mixture and stirred for 3 h at 50 °C. After cooling down for 1 h, a solution of $n$-butylamine (0.4 mL, 4 mmol) in EtOAc was added dropwise, and the reaction mixture was stirred at room temperature for 2 d. At this point, a red precipitate was formed corresponding to the boron complex, which was filtered and suspended in water to break the complex. After a day, the pure ligand was filtered and dried under vacuum to afford 1f as an orange solid. Yield: 79%. $^1$H NMR (400 MHz, CDCl$_3$): δ 15.87 (s, 1H), 7.77 (d, $J = 15.5$ Hz, 2H), 7.38 (d, $J = 5.0$ Hz, 2H), 7.27 (d, $J = 3.7$ Hz, 2H), 7.07 (dd, $J = 5.0$, 3.7 Hz, 2H), 6.41 (d, $J = 15.5$ Hz, 2H), 5.75 (s, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 182.6, 139.9, 133.3, 132.1, 130.1, 128.8, 122.8, 101.6.

Synthesis of Compound 1g: Following a modified procedure from literature.¹ Acetylacetone (0.72 mL, 7 mmol) and B$_2$O$_3$ (348.1 mg, 5 mmol) were dissolved in 10 mL of EtOAc. The reaction mixture was heated at 50 °C for 30 min until a white suspension was formed. Then, a solution containing 3-thiophenecarboxaldehyde (1.3 mL, 14 mmol)
and tributyl borate (3.77 mL, 14 mmol) in EtOAc was added to the reaction mixture, and stirred for 3 h at 50 °C. After cooling down for 1 h, a solution of n-butylamine (0.4 mL, 4 mmol) in EtOAc was added dropwise, and stirred at room temperature for 2 d. At this point, an orange precipitate was formed, which was filtered and suspended in water for a day to break the boron complex. The final ligand was filtered and dried under vacuum to afford 1g as a yellow solid. Yield: 69%. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 15.8 Hz, 2H), 7.51 (d, J = 3.7 Hz, 2H), 7.38-7.30 (m, 4H), 6.44 (d, J = 15.7 Hz, 2H), 5.79 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆): δ 183.4, 138.1, 134.3, 129.7, 127.9, 125.7, 123.9, 101.4.

Synthesis of Compound 1h: Acetylacetonate (152.2 mg, 1.5 mmol) and B₂O₃ (75.6 mg, 1.08 mmol) were mixed in 4 mL of EtOAc and the mixture was heated at 40 ℃ for 2 h. Then, tributylborate (1.4 g, 6.3 mmol) was dissolved in 2 mL of EtOAc and added to the former followed by the addition of 1,2,3-benzothiadiazole-4-carbaldehyde (0.5 g, 3.1 mmol). The mixture was stirred at 50 ℃ for two extra hours. After cooling down, n-butylamine (78.7 µL, 0.8 mmol) in 1 mL of EtOAc was added dropwise, leaving the solution at room temperature and under stirring for few days. Afterward, a dark orange precipitate was obtained. Hydrolysis of the boron intermediate by the addition of 80 mL of H₂O to the solid under stirring for several hours provided a yellow precipitated that was filtered and washed with MeOH. Yield: 20 %. ¹H-RMN (300 MHz CDCl₃, window from 20 to 0 ppm): δ 15.79 (s, 1H), 8.07 (d, J = 1 Hz, 1H), 8.05 (d, J = 1 Hz, 1H), 8.03 (d, J = 15.4 Hz, 1H), 7.87 (d, J = 15.8 Hz, 2H), 7.76 (m, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.66 (d, J = 1.1 Hz, 1H), 6.11 (s, 1H).

Synthesis of Compound 1i: Acetylacetone (1.0 g, 10.0 mmol) was added in a bottom flask with an excess of B₂O₃ (0.5 g, 7.1 mmol) in 10 mL of EtOAc. The mixture was heated at 40 ℃ for 30 min until a white paste was formed. Then, in a separated flask, a solution of 1-pyrenecarboxaldehyde (4.6 g, 10.0 mmol) and tributylborate (9.2 g, 40 mmol) in EtOAc (40 mL) was prepared and added to the previous solution. The mixture was stirred at 40 ℃ for three hours. After cooling down, n-butylamine (0.5 mL, 1.3 mmol) in 10 mL of EtOAc was added dropwise. Initially, the solution displayed dark red color which changed to almost black over time; meanwhile a precipitated came out. The solid, after
washing with H$_2$O and MeOH and drying with Et$_2$O was orange. Yield: 40 %. $^1$H-RMN (300 MHz DMSO, window from 20 to 0 ppm): δ 8.90 (d, $J = 15.3$ Hz, 2H), 8.60 (d, $J = 9.2$ Hz, 2H), 8.39 (d, $J = 8.4$ Hz, 2H), 8.23 (m, 8H), 8.15 (d, $J = 9.0$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 8.05 (t, $J = 7.5$ Hz, 2H), 7.99 (d, $J = 15.5$ Hz, 2H), 6.10 (s, 1H).

Synthesis of Compound 1j: Acetylacetonate (259.8 mg, 2.6 mmol) and B$_2$O$_3$ (129.5 mg, 1.9 mmol) were mixed in 4 mL of EtOAc and the mixture was heated at 40 °C for 2 h. Then, tributylborate (2.4 g, 10.4 mmol) was dissolved in 2 mL of EtOAc and added to the former followed by the addition of fluorene-2-carboxaldehyde (1.0 g, 5.2 mmol). The mixture was stirred at 50 °C for two extra hours. After cooling down, n-butylamine (0.2 mL, 1.3 mmol) in 1 mL of EtOAc was added dropwise, leaving the solution at room temperature and under stirring for few days. Afterward, an orange precipitate was obtained. 80 mL of H$_2$O were added to the solid and the mixture was stirred for eight hours. Finally, a yellow solid was separated by filtration and washed with MeOH. Yield: 70 %. $^1$H-RMN (300 MHz CDCl$_3$, window from 20 to 0 ppm): δ 16.15 (s, 1H), 7.80 (m, 6H), 7.76 (d, $J = 15.8$ Hz, 2H), 7.60 (d, $J = 12.1$ Hz, 2H), 7.58 (d, $J = 11.8$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 2H), 6.72 (d, $J = 15.8$ Hz, 2H), 5.90 (s, 1H), 3.97 (s, 4H).

Synthesis of Compound 1k: Acetylacetone (0.72 mL, 7 mmol) and B$_2$O$_3$ (348.1 mg, 5 mmol) were mixed in 10 mL of EtOAc. The reaction mixture was heated at 50 °C for 30 min. until the formation of a white suspension. Then, a solution containing 3-pyridinecarboxaldehyde (1.31 mL, 14 mmol) and tributyl borate (3.77 mL, 14 mmol) in EtOAc was added to the reaction mixture, and stirred for 3 h at 50 °C. After cooling down for 1 h a solution of n-butylamine (0.4 mL, 4 mmol) of EtOAc was added dropwise, and stirred at room temperature for 2 days. At this point a light brown precipitate was formed, which was filtered and suspended in water for a day to break the boron complex. The final ligand was filtered and dried under vacuum to afford 1k as a yellow solid. Yield: 65%. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 8.75 (s, 2H), 8.45 (dd, $J = 4.7$, 1.4 Hz, 2H), 8.04 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 16.1$ Hz, 2H), 7.34 (dd, $J = 7.9$, 4.8 Hz, 2H), 6.98 (d, $J = 16.1$, 2H), 6.08 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 183.1, 150.9, 150.0, 137.3, 134.7, 130.6, 126.2, 124.2, 102.4. ppm.
Synthesis of Curcuminoids 2a-k

**Synthesis of Compound 2a:** To a solution of 50 mg of C\textsubscript{60} (0.069 mmol, 1 eq), curcumin 1\textsubscript{a} (38.4 mg, 0.104 mmol, 1.5 eq) and tetrabromomethane (69.1 mg, 0.208 mmol, 3 eq) in 6 mL of o-DCB, was added DBU (15 μL, 0.104 mmol, 1.5 eq) under N\textsubscript{2} atmosphere and stirred at room temperature for 30 min. The reaction was stopped using 1 drop of acetic acid, followed by extraction with sodium bicarbonate saturate solution and sodium chloride saturate solution. The solvent from the reaction mixture was removed under vacuum and the crude product was purified by silica gel column using initially CS\textsubscript{2} to recover the unreacted C\textsubscript{60}, followed by CS\textsubscript{2}:CHCl\textsubscript{3} 1:1 to recover 2a (54% yield). \textsuperscript{1}H-NMR (600 MHz; CDCl\textsubscript{3} 298 K): δ 8.27 (d, 1H, \textit{J} = 15.92), 7.28 (m, 1H), 7.25 (s, 1H), 7.21 (m, 1H), 6.97 (d, 1H, \textit{J} = 8.24), 6.04 (s, 1H, -OH), 3.98 (s, 3H, O-CH\textsubscript{3}) ppm. \textsuperscript{13}C-NMR (150 MHz; CDCl\textsubscript{3}, 298 K); δ 186.3, 149.8, 149.0, 147.1, 146.1, 145.7, 145.3, 144.0, 144.9, 144.9, 144.6, 143.9, 143.3, 143.1, 143.1, 142.3, 142.2, 141.3, 137.9, 126.7, 125.7, 120.7, 115.2, 110.1, 74.4, 68.2, 56.4 ppm. C\textsubscript{81}H\textsubscript{18}O\textsubscript{6} Calc. 1086.2650, found 1086.1103.

**Synthesis of Compound 2b:** To a solution of 72 mg of C\textsubscript{60} (0.1 mmol, 1 eq), curcuminoid 1\textsubscript{b} (59 mg, 0.1 mmol, 1 eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) at room temperature and the reaction was stirred for 3 min and poured into a silica gel column to stop the reaction and to purify compound 2b. Initially, CS\textsubscript{2} was used to recover the unreacted C\textsubscript{60}, followed by CS\textsubscript{2}:CHCl\textsubscript{3} 1:1 to recover 2a (34% yield). \textsuperscript{1}H-NMR (400 MHz; CDCl\textsubscript{3} 298 K): δ 8.34 (d, 2H), 7.70 (d, 4H), 7.29 (d, 2H), 6.97 (d, 4H), 4.03 (t, 4H), 1.82 (m, 4H), 1.48 (m, 4H), 1.28 (bs, 32H), 0.90 (t, 6H) ppm. \textsuperscript{13}C-NMR (100 MHz; CDCl\textsubscript{3}, 298 K); δ 186.2, 162.4, 148.5, 146.1, 145.6, 145.1, 144.9, 144.7, 144.7, 143.8, 143.1, 142.9, 142.2, 141.1, 137.8, 131.4, 126.4, 120.6, 115.2, 74.3, 68.2, 68.2, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.1, 25.6, 22.7, 14.2 ppm. C\textsubscript{103}H\textsubscript{62}O\textsubscript{4} Calc. 1362.4650, found 1362.4645.

**Synthesis of Compound 2c:** To a solution of 72 mg of C\textsubscript{60} (0.1 mmol, 1 eq), curcuminoid 1\textsubscript{c} (47 mg, 0.1 mmol, 1 eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) at room temperature and the reaction was stirred for 5 min and poured into a silica gel column to stop the reaction and to purify compound 2c. Initially, CS\textsubscript{2} was used to recover the unreacted C\textsubscript{60}, followed by CS\textsubscript{2}:CHCl\textsubscript{3} 1:1 to recover
2c (30% yield). $^1$H-NMR (400 MHz; CDCl$_3$ 298 K): δ 8.34 (d, 2H), 7.70 (d, 4H), 7.29 (d, 2H), 6.96 (d, 4H), 4.03 (t, 4H), 1.82 (m, 4H), 1.48 (m, 4H), 1.37 (m, 8H), 0.93 (t, 6H) ppm.

$^{13}$C-NMR (100 MHz; CDCl$_3$, 298 K); δ 186.2, 162.4, 148.5, 146.1, 145.6, 145.1, 144.9, 144.7, 144.7, 143.8, 143.1, 142.9, 142.2, 141.1, 137.8, 131.4, 126.5, 120.6, 115.2, 74.3, 68.4, 68.2, 31.6, 29.1, 25.7, 22.6, 14.1 ppm. C$_{91}$H$_{38}$O$_4$ Calc. 1194.2765, found 1194.2765.

**Synthesis of Compound 2d:** To a solution of 72 mg of C$_{60}$ (0.1 mmol, 1 eq), 1d (31 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) and stirred at room temperature for 20 min and poured into a silica gel column to stop the reaction and to purify compound 2d. Initially, CS$_2$ was used to recover the unreacted C$_{60}$, followed by CS$_2$:CHCl$_3$ 1:1 to recover 2d (50% yield). $^1$H-NMR (600 MHz; CDCl$_3$, 298 K); δ 8.33 (d, 1H, $J = 16.05$), 7.66 (d, 2H, $J = 8.47$), 7.36 (d, 2H, $J = 16.03$), 7.30 (d, 2H, $J = 9.12$), 2.55 (s, 3H) ppm. $^{13}$C-NMR (150 MHz; CDCl$_3$, 298 K); δ 186.2, 148.2, 145.9, 145.5, 145.2, 144.7, 144.6, 144.5, 143.8, 143.0, 142.2, 142.2, 141.2, 137.8, 130.2, 130.1, 129.7, 125.8, 122.0, 74.1, 67.9, 15.0 ppm. C$_{81}$H$_{18}$O$_2$S$_2$ Calc. 1086.0748, found 1086.0741.

**Synthesis of Compound 2e:** To a solution of 72 mg of C$_{60}$ (0.1 mmol, 1 eq), compound 1e (49 mg, 0.1 mmol, 1 eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) and stirred at room temperature for 5 min and poured into a silica gel column to stop the reaction and to purify compound 2e. Initially, CS$_2$ was used to recover the unreacted C$_{60}$, followed by CS$_2$:CHCl$_3$ 1:1 to recover 2e (52% yield). $^1$H-NMR (600 MHz; CDCl$_3$, 298 K); δ 8.42 (d, 1H, $J = 15.86$), 6.90 (d, 1H, $J = 15.87$), 4.71 (t, 2H, $J = 1.90$), 4.60 (m, 2H), 4.14 (s, 5H) ppm. $^{13}$C-NMR (150 MHz; CDCl$_3$, 298 K); δ 185.6, 152.3, 145.6, 145.3, 145.2, 144.8, 144.6, 143.9, 143.9, 143.1, 143.0, 142.3, 142.3, 141.3, 137.3, 120.6, 77.9, 74.2, 72.9, 70.4, 70.0, 67.9 ppm. C$_{87}$H$_{22}$FeO$_6$ Calc. 1210.0412, found 1210.0650.

**Synthesis of Compound 2f:** To a solution of 72 mg of C$_{60}$ (0.1 mmol, 1 eq), 1f (29 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) and stirred at room temperature for 30 min and poured into a silica gel column to stop the reaction and to purify compound 2f. Initially, CS$_2$ was used to
recover the unreacted $\text{C}_6\text{O}_3$, followed by $\text{CS}_2:\text{CHCl}_3$ 1:1 to recover $2f$ (48% yield). $^1\text{H}$-NMR (600 MHz; CDCl$_3$, 298 K); $\delta$ 8.45 (d, 1H, $J = 15.73$), 7.55 (dd, 2H, $J = 4.17, 9.10$), 7.15 (d, 1H, $J = 15.73$), 7.14 (dd, 1H, $J = 3.76, 5.06$) ppm. $^{13}\text{C}$-NMR (150 MHz; CDCl$_3$, 298 K); $\delta$ 185.8, 145.8, 145.6, 145.2, 144.8, 144.7, 144.5, 143.8, 143.1, 143.0, 143.0, 142.2, 142.2, 141.2, 140.8, 139.5, 137.8, 134.1, 131.4, 128.8, 121.8, 73.9, 67.5 ppm. $\text{C}_{75}\text{H}_{10}\text{O}_2\text{S}_2$ Calc. 1006.1220, found 1005.6770.

**Synthesis of Compound 2g:** To a solution of 72 mg of C$_6$O (0.1 mmol, 1 eq), 1g (29 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of $\alpha$-DCB, was added DBU (2 drops) and stirred at room temperature for 30 min and poured into a silica gel column to stop the reaction and to purify compound 2g. Initially, CS$_2$ was used to recover the unreacted C$_6$O, followed by CS$_2$:CHCl$_3$ 1:1 to recover 2g (51% yield). $^1\text{H}$-NMR (600 MHz; CDCl$_3$, 298 K); $\delta$ 8.36 (d, 1H, $J = 16.21$), 7.83 (s, 1H), 7.51 (m, 1H), 7.44 (m, 1H), 7.20 (d, 1H, $J = 15.96$) ppm. $^{13}\text{C}$-NMR (150 MHz; CDCl$_3$, 298 K); $\delta$ 186.4, 145.8, 145.5, 145.2, 144.9, 144.8, 144.5, 143.8, 143.2, 143.0, 143.0, 142.4, 142.2, 141.6, 141.2, 137.8, 137.5, 131.9, 127.6, 125.5, 122.9, 74.0, 67.7 ppm. $\text{C}_{79}\text{H}_{10}\text{O}_2\text{S}_2$ Calc. 1110.0245, found 1110.0251.

**Synthesis of Compound 2h:** To a solution of 72 mg of C$_6$O (0.1 mmol, 1 eq), 1h (39 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of $\alpha$-DCB, was added DBU (2 drops) and stirred at room temperature for 5 min and poured into a silica gel column to stop the reaction and to purify compound 2h. Initially, CS$_2$ was used to recover the unreacted C$_6$O, followed by toluene to recover 2h (29% yield). $^1\text{H}$-NMR (400 MHz; CDCl$_3$, 298 K); $\delta$ 8.60 (d, 1H), 8.58 (d, 1H), 8.13 (d, 1H), 7.96 (d, 1H), 7.51 (m, 1H), 7.44 (m, 1H), 7.20 (d, 1H, $J = 15.96$) ppm. $^{13}\text{C}$-NMR (100 MHz; CDCl$_3$, 298 K); $\delta$ 186.3, 149.2, 146.0, 145.8, 145.2, 144.9, 144.8, 144.7, 144.5, 144.2, 144.0, 143.8, 143.1, 143.0, 142.2, 141.2, 140.7, 137.9, 132.4, 129.1, 128.0, 127.1, 125.6, 125.3, 122.1, 120.8, 120.5, 74.3, 68.1 ppm. $\text{C}_{79}\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$ Calc. 1110.0245, found 1110.0251.

**Synthesis of Compound 2i:** To a solution of 50 mg of C$_6$O (0.069 mmol, 1 eq), 1i (54.6 mg, 0.104 mmol, 1.5 eq) and tetrabromomethane (69.1 mg, 0.208 mmol, 3 eq) in 6 mL of $\alpha$-DCB, was added DBU (20 μL, 0.139 mmol, 2 eq) under N$_2$ atmosphere and stirred at room temperature for 30 min. The reaction was stopped using 1 drop of acetic acid,
followed by extraction with sodium bicarbonate saturate solution and sodium chloride saturate solution. The solvent from the reaction mixture was removed under vacuum and the crude product was purified by silica gel column using initially CS$_2$ to recover the unreacted fullerene, followed by CS$_2$:CHCl$_3$ 1:1 to recover 2i (55% yield). $^1$H-NMR (600 MHz; CDCl$_3$, 298 K); δ 9.84 (d, 1H, $J = 15.89$), 8.84 (d, 1H, $J = 9.49$), 8.57 (d, 1H, $J = 8.27$), 8.24 (m, 5H), 8.10 (m, 2H), 7.72 (d, 1H, $J = 15.89$) ppm. $^{13}$C-NMR (150 MHz; CDCl$_3$, 298 K); δ 186.6, 146.1, 145.6, 145.5, 145.2, 145.2, 144.9, 144.8, 144.8, 144.6, 143.9, 143.2, 143.0, 142.2, 141.3, 138.0, 134.1, 131.3, 131.3, 130.7, 129.7, 129.6, 127.5, 127.4, 126.7, 126.6, 126.6, 125.4, 125.1, 124.7, 124.6, 124.6, 122.4, 74.3, 67.9 ppm. C$_{99}$H$_{22}$O$_2$ Calc. 1242.1618, found 1242.1625.

**Synthesis of Compound 2j:** To a solution of 72 mg of C$_{60}$ (0.1 mmol, 1 eq), 1j (45 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) and stirred at room temperature for 5 min and poured into a silica gel column to stop the reaction and to purify compound 2j. Initially, CS$_2$ was used to recover the unreacted C$_{60}$, followed by CS$_2$:CHCl$_3$ 2:1 to recover 2j (31% yield). $^1$H-NMR (400 MHz; CDCl$_3$, 298 K); δ 8.49 (d, 1H), 7.97 (s, 1H), 7.86 (m, 2H), 7.78 (d, 1H), 7.61 (d, 1H), 7.49 (d, 1H), 7.42 (m, 2), 3.99 (s, 2H) ppm. $^{13}$C-NMR (100 MHz; CDCl$_3$, 298 K); δ 186.3, 149.2, 146.0, 145.8, 145.6, 145.2, 144.9, 144.8, 144.7, 144.5, 144.2, 144.0, 143.8, 143.1, 143.0, 142.2, 141.2, 140.7, 137.9, 132.4, 129.1, 128.0, 127.1, 125.6, 125.3, 124.1, 120.8, 120.5, 74.3, 68.1, 36.8 ppm. C$_{93}$H$_{22}$O$_2$ Calc. 1170.1620, found 1170.1625.

**Synthesis of C$_{60}$ Compound 2k:** To a solution of 72 mg of C$_{60}$ (0.1 mmol, 1 eq), 1k (28 mg, 0.1 mmol, 1eq) and tetrabromomethane (33 mg, 0.1 mmol, 1 eq) in 10 mL of o-DCB, was added DBU (2 drops) and stirred at room temperature for 30 min and poured into a silica gel column to stop the reaction and to purify compound 2k. Initially, CS$_2$ was used to recover the unreacted C$_{60}$, followed by CHCl$_3$/MeOH 25:1 to recover 2k (23% yield). $^1$H-NMR (600 MHz; CDCl$_3$, 298 K); δ 8.95 (d, 1H), 8.73 (dd, 1H), 8.37 (d, 1H), 8.10 (m, 1H), 7.49 (d, 1H), 7.45 (m, 1H), 7.42 (m, 2) ppm. $^{13}$C-NMR (150 MHz; CDCl$_3$, 298 K); δ 185.9, 166.8, 152.4, 151.0, 145.4, 145.3, 145.1, 144.8, 144.6, 143.8, 143.1, 143.0, 142.2, 141.3, 140.7, 137.8, 135.1, 129.6, 124.7, 124.0, 73.6, 67.2 ppm. C$_{77}$H$_{12}$N$_2$O$_2$ Calc. 996.0899, found 996.0885.
Figure S1. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1b.
Figure S2. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1c.
Figure S3. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1d.
Figure S4. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1e.
Figure S5. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1f.
Figure S6. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1g.
Figure S7. a) $^1$H-NMR of compound 1h.

Figure S8. a) $^1$H-NMR 1i.
Figure S9. a) $^1$H-NMR 1j.

Figure S10. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 1k.
Figure S11. MALDI-TOF spectrum of compound 2a using 1,8,9-trihydroxyanthracene (THA) as matrix.

Figure S12. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 2a.
**Figure S13.** MALDI-TOF spectrum of compound 2b using THA as matrix.

**Figure S14.** a) $^1$H-NMR and b) $^{13}$C-NMR of compound 2b.
Figure S15. MALDI-TOF spectrum of compound 2c using THA as matrix.

Figure S16. a) $^1$H-NMR and b) $^{13}$C-NMR of compound 2c.
Figure S17. MALDI-TOF spectrum of compound 2d using THA as matrix.

Figure S18. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2d.
Figure S19. MALDI-TOF spectrum of compound 2e using THA as matrix.

Figure S20. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2e.
Figure S21. MALDI-TOF spectrum of compound 2f using THA as matrix.

Figure S22. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2f.
Figure S23. MALDI-TOF spectrum of compound 2g using THA as matrix.

Figure S24. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2g.
Figure S25. MALDI-TOF spectrum of compound 2h using THA as matrix.

Figure S26. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2h.
Figure S27. MALDI-TOF spectrum of compound 2i using THA as matrix.

Figure S28. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2i.
Figure S29. MALDI-TOF spectrum of compound 2j using THA as matrix.

Figure S30. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2j.
Figure S31. MALDI-TOF spectrum of compound 2k using THA as matrix.

Figure S32. a) $^1$H-NMR b) $^{13}$C-NMR of compound 2k.
**Figure S33.** UV-Vis absorption spectra of compounds 2a-k in chloroform solutions.
Figure S34. Cyclic voltammetry of compounds 2a-k at a scan rate of 100 mV/s. a) 2a, b) 2b, c) 2c, d) 2d, e) 2e, f) 2f, g) 2g and h) 2h.
Figure S35. SEM image of the perovskite grain size (surface scan).

Figure S36. XRD spectrum of the perovskite film.

Analysis of compound 2a as a cytoprotective reagent

To determine the potential cytoprotective activity of compound 2a in cells undergoing to H₂O₂-induced oxidative stress, the differential nuclear staining (DNS) assay and a high throughput bioimager system (GE Healthcare, Piscataway, NJ) were used. In addition, this strategy was used to measure the potential cytotoxicity of compound 2a alone. Human
dopaminergic neuron SH-SY5Y cells growing in exponential phase were seeded on 96-well plate format at a density of 10,000 cells/well in 100 µL of culture media; DMEM and Ham’s F12 media mixture (1:1) supplemented with 10% heat-inactivated fetal bovine serum (HyClone) and 100 U/mL penicillin and 100 µg/mL streptomycin (Lonza, Walkersville, MD). To test the cell protection activity under an inflicted oxidative stress damage, cells were pretreated for 1 h with a compound 2a concentration gradient (0.3, 3, 10, and 30 µM), followed by addition of 100 µM of H₂O₂ and incubated additionally for 24 h. 1 h prior to experiment completion and image capture, cells were added with Hoechst 33342 and propidium iodide (PI) mixture for staining purposes; both to a final concentration of 1 µg/mL. Hoechst is a permeable dye staining both living and dead cells, providing with the total number of cells, whereas PI solely stains the dead cells since it can only permeate compromised cell membranes, providing with the total number of dead cells (Santiago-Vazquez et al 2016). Both untreated cells and DMSO-treated cells (solvent control) were used as negative controls, whereas H₂O₂-treated cells were used as the positive control for cytotoxicity. Eight replicas were analyzed for each experimental point.

**Anticancer experiments**

To assess the cytotoxic activity of compound 2a the previously validated differential nuclear staining assay²⁻⁴ was used. MDA-MB-231 and CEM cells were plated at a density of 10,000 cells/well in 100 µL of culture media (RPMI1640 and/or DMEM, both supplemented with 10% FBS and 1% penicillin-streptomycin for CEM and MDA-MB-231, respectively) in black flat-bottomed plastic 96-well plates (BD Biosciences, Rockville, MD). 24 h later cells were treated with increasing concentrations of compound 2a; from 1-10 µM final concentration (diluted in 1% DMSO). As a vehicle and positive control for death, cells were treated with 1% DMSO and 1 mM of H₂O₂ respectively. Untreated cells were also included as negative controls. Each treatment was included in tetraplicate. Treated cells were incubated for 48 h, at 37 °C in humidified 5% carbon dioxide (CO₂) atmosphere. 2 h prior to the incubation end, cells were stained with a mixture of Hoechst 33342 and Propidium iodide (PI) (1µg/mL final concentration for each dye) and incubated for 2 h. Image acquisition was performed using the IN Cell Analyzer 2000 bioimager system (GE Healthcare) and image analysis was accomplished by using the IN cell Investigator workstation 3.2 (GE Healthcare). Cells positive for Hoechst 33342,
but negative to PI, were counted as living cells, whereas cells emitting PI signal were considered as dead cells.

**Device Fabrication**

PC$_{61}$BM (99%) was bought from SES Research. Methylammonium iodide (CH$_3$NH$_3$I, 99.5%) was bought from Greatcellsolar. PbI$_2$ (99%) was bought from Sigma-Aldrich. The configuration used for the fabrication of the PSCs was ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_3$/ETM/Ag. The patterned ITO glass substrates were cleaned sequentially with detergent, deionized water and acetone, each step for 30 min, then dried with nitrogen gas and finally treated in a UV-ozone oven for 30 min. After passing through a 0.45 μm PVDF filter, the PEDOT:PSS solution (Baytron P VP AI 4083) was spin-coated onto the treated ITO substrates at 5000 rpm for 30 s and heated at 150 °C for 15 min in air. Then the substrates were transferred to a N$_2$-filled glovebox where CH$_3$NH$_3$PbI$_3$ (1 M solution in DMF) was spin-coated on top of the PEDOT:PSS coated substrates at 800 rpm for 10 s and at 4000 rpm for 25 s. 80 µL of toluene were added 5 s after the second step and then the devices were annealed at 70 °C for 60 min. The fullerene derivatives dissolved in CB (20 mg/mL) were spin-coated onto the CH$_3$NH$_3$PbI$_3$ layer at 5000 rpm for 30 s. Finally, Ag electrodes (100 nm) were deposited by thermal evaporation under a pressure of 1×10$^{-6}$ Torr through a shadow mask. The active area of the fabricated devices was 6 mm$^2$. The Al electrodes were encapsulated with a UV-curable epoxy resin and a glass slide before testing. Stability studies were conducted on unencapsulated devices.

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