

Electronic supplementary information for

A structurally simple perylene dye with ethynylbenzothiadiazole-benzoic acid as the electron-acceptor achieves an over 10% power conversion efficiency

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1. Experimental section

1.1. Materials

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, DMFC, FC, and 4-*tert*-butylpyridine (TBP) were purchased from Sigma-Aldrich. 4,4,4',4',5,5,5',5'-Octamethyl-2,2'-bi(1,3,2-dioxaborolane), NBS, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl₂), palladium(II) acetate (Pd(OAc)₂), tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃), Sphos, tris(*tert*-butyl)phosphine (P(*t*-Bu)₃), potassium hydroxide (KOH), potassium acetate (KOAc), potassium phosphate (K₃PO₄), and cesium carbonate (Cs₂CO₃) were purchased from Sigma-Aldrich and used without further purification. Phosphorus oxychloride (POCl₃), *N,N*-dimethylformide (DMF), dimethyl sulfoxide (DMSO), dioxane, THF, 1,2-dichloroethane (DCE), acetonitrile (ACN), toluene, and ethanol were dried and distilled before use. 2-Hexyldecyl 4-methylbenzenesulfonate,^{S1} 3-bromo-1-(2-hexyldecyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole,^{S2} and butyl 4-(7-ethynylbenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate^{S3} were synthesized according to the respective literature procedures. The synthetic routes of **C271** and **C272** are illustrated in Scheme 1 and preparation details are described as follows.

1-((2-Hexyldecyl)oxy)-4-iodobenzene (2): **1** (2.00 g, 9.09 mmol), 2-hexyldecyl 4-methylbenzenesulfonate (3.60 g, 9.09 mmol), and KOH (2.55 g, 45.45 mmol) were dissolved in DMF (50 mL) in a three-neck round-bottom flask. The resulting mixture was stirred for 5 h at 100 °C and then cooled to room temperature. Dichloromethane (30 mL) was added and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, 1/50, *v/v*) on silica gel to afford a colorless oil as the desired product **2** (4.04 g, 97% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.55 (d, *J* = 8.9 Hz, 2H), 6.69 (d, *J* = 8.9 Hz, 2H), 3.80 (d, *J* = 5.7 Hz, 2H), 1.80–1.77 (m, 1H), 1.44–1.41 (m, 4H), 1.35–1.30 (m, 20H), 0.91 (t, *J* = 6.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.47, 138.30, 117.17, 82.49, 71.22, 38.09, 32.12, 32.06, 31.56, 31.54, 30.22, 29.80, 29.55, 27.04, 27.02, 22.90, 14.33. MS (ESI) *m/z* calcd. for (C₂₂H₃₇IO): 444.19. Found: 445.19 ([M+H]⁺). Anal. calcd. for C₂₂H₃₇IO: C, 59.45; H, 8.39. Found: C, 59.46; H, 8.37.

2-(4-((2-Hexyldecyl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3): **2** (3.00 g, 6.75 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.23 g, 8.78 mmol), Pd(dppf)Cl₂ (247 mg, 0.34 mmol), KOAc (1.91 g, 19.50 mmol), and DMSO (10 mL) were added to a three-neck round-bottom flask under argon. The reaction mixture was stirred at 45 °C for 5 h and then cooled to room temperature. The resultant mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60–90 °C, *v/v*, 1/2) on silica gel to afford a colorless oil as the desired product **3** (2.82 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ: 7.76 (d, *J* = 5.6 Hz, 2H), 6.90 (d, *J* = 5.6 Hz, 2H), 3.87 (d, *J* = 5.7 Hz, 2H), 1.81–1.78 (m, 1H), 1.50–1.39 (m, 4H), 1.34 (br, 14H), 1.28 (br, 18H), 0.90 (t, *J* = 6.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 162.32, 136.69, 114.18, 83.67, 71.03, 38.20, 32.06, 31.67, 30.22, 29.89, 29.78, 29.52, 27.06, 25.07, 22.87, 14.27. MS (ESI) *m/z* calcd. for (C₂₈H₄₉BO₃): 444.38. Found: 444.33 ([M]⁺). Anal. calcd. for C₂₈H₄₉BO₃: C, 75.66; H, 11.11. Found: C, 75.64; H, 11.10.

*1-(2-Hexyldecyl)-3-(4-((2-hexyldecyl)oxy)phenyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole (4):* **3** (2.00 g, 4.50 mmol), 3-bromo-1-(2-hexyldecyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole (2.69 g, 4.50 mmol), Pd(OAc)₂ (20 mg, 0.09 mmol), Sphos (37 mg, 0.09 mmol), K₃PO₄ (4.78 g, 22.50 mmol) and dioxane/H₂O (30 mL, *v/v*, 5/1) were added to a three-neck round-bottom flask under argon. The reaction mixture was refluxed for 3 h and then cooled to room temperature. The resultant mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60–90 °C, *v/v*, 1/2) on silica gel to yield a yellow oil as the desired product **4** (3.01 g, 83% yield). ¹H NMR (400 MHz, CDCl₃) δ: 8.69–8.66 (m, 2H), 8.15–8.12 (m, 2H), 7.91 (d,

$J = 8.7$ Hz, 1H), 7.84–8.74 (m, 3H), 7.72 (s, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 4.57 (d, $J = 7.2$ Hz, 2H), 3.96 (d, $J = 5.5$ Hz, 2H), 2.31–2.30 (m, 1H), 1.88–1.84 (m, 1H), 1.60–1.51 (m, 4H), 1.47–1.27 (m, 30H), 1.19–1.17 (m, 14H), 0.92–0.88 (m, 6H), 0.85–0.79 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 158.98, 137.48, 134.43, 132.41, 132.32, 131.48, 130.74, 130.69, 128.93, 128.24, 125.17, 125.05, 124.92, 124.65, 124.53, 123.51, 120.97, 120.74, 117.59, 116.73, 114.66, 114.21, 113.59, 71.25, 50.17, 40.07, 38.32, 32.17, 32.06, 31.99, 31.95, 31.71, 30.32, 30.13, 29.99, 29.84, 29.71, 29.61, 29.47, 27.15, 26.66, 22.95, 22.83, 14.37, 14.31, 14.26. MS (ESI) m/z calcd. for ($\text{C}_{58}\text{H}_{79}\text{NO}$): 805.62. Found: 806.61 ($[\text{M}+\text{H}]^+$). Anal. calcd. for $\text{C}_{58}\text{H}_{79}\text{NO}$: C, 86.40; H, 9.88; N, 1.74. Found: C, 86.41; H, 9.86; N, 1.73.

1-(2-Hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1H-phenanthro[1,10,9,8-cdefg]carbazole-3-carbaldehyde (5): In a three-neck round bottom flask was dissolved **4** (340 mg, 0.42 mmol) in DCE (10 mL) and cooled to 0 °C using an ice salt bath. DMF (0.17 mL, 2.11 mmol) and POCl_3 (0.051 mL, 0.55 mmol) were added to the cooled solution. The reaction solution was stirred at room temperature for 12 h. Saturated sodium acetate aqueous solution (10 mL) was added and the mixture was stirred for another 2 h. Then the mixture was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate /petroleum ether 60–90 °C, v/v , 1/2) on silica gel to yield a red oil as the desired product **5** (287 mg, 85% yield). ^1H NMR (400 MHz, CDCl_3) δ : 10.25 (s, 1H), 9.10 (d, $J = 8.3$ Hz, 1H), 8.59 (d, $J = 7.6$ Hz, 1H), 8.52 (d, $J = 7.6$ Hz, 1H), 8.17 (d, $J = 8.2$ Hz, 1H), 7.84–7.78 (m, 2H), 7.73 (s, 1H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.51 (s, 1H), 7.17 (d, $J = 8.6$ Hz, 2H), 4.12 (d, $J = 7.4$ Hz, 2H), 4.01 (d, $J = 5.6$ Hz, 2H), 2.07–2.06 (m, 1H), 1.93–1.88 (m, 1H), 1.62–1.55 (m, 2H), 1.53–1.33 (m, 24H), 1.223–1.16 (m, 22H), 0.97–0.92 (m, 6H), 0.85–0.79 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 192.69, 159.36, 140.99, 140.98, 135.51, 133.65, 131.41, 130.51, 130.47, 130.25, 130.07, 128.45, 128.43, 127.94, 127.03, 126.87, 125.31, 125.03, 124.39, 124.07, 123.92, 122.12, 121.57, 121.51, 121.18, 115.68, 115.66, 114.79, 113.79, 71.32, 49.92, 39.95, 38.31, 32.16, 32.14, 32.01, 31.94, 31.88, 31.85, 31.70, 30.31, 30.06, 29.98, 29.87, 29.77, 29.66, 29.60, 29.43, 27.15, 27.13, 26.56, 22.94, 22.93, 22.80, 22.79, 14.36, 14.27, 14.22. MS (ESI) m/z calcd. for ($\text{C}_{59}\text{H}_{79}\text{NO}_2$): 833.61. Found: 834.60 ($[\text{M}+\text{H}]^+$). Anal. calcd. for $\text{C}_{59}\text{H}_{79}\text{NO}_2$: C, 84.94; H, 9.54; N, 1.68. Found: C, 84.96; H, 9.52; N, 1.71.

2-Cyano-3-(1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1H-phenanthro[1,10,9,8-cdefg]carbazol-3-yl)acrylic acid (C271): In a three-neck round bottom flask were dissolved **5** (250 mg, 0.28 mmol) and cyanoacetic acid (240 mg, 2.83 mmol) in acetonitrile/chloroform (20 mL, v/v , 1/2). Then ammonium acetate (20 mg, 0.28 mmol) was added to the reaction mixture, which was stirred at reflux for 48 h. After cooling to room temperature, Water and Chloroform was added. The organic phase was washed with 0.2 M phosphoric acid aqueous solution and water in turn, and then dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, v/v , 15/1) on silica gel to afford a black solid as the final product **C271** (242 mg, 96% yield). ^1H NMR (400 MHz, $\text{THF}-d_8$) δ : 9.08 (s, 1H), 8.73 (d, $J = 4.2$ Hz, 1H), 8.64 (d, $J = 7.4$ Hz, 1H), 8.53 (d, $J = 7.2$ Hz, 1H), 8.15 (d, $J = 8.2$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.76 (t, $J = 7.9$ Hz, 1H), 7.72–7.64 (m, 4H), 7.15 (d, $J = 8.1$ Hz, 2H), 4.27 (br, 2H), 4.01 (d, $J = 5.1$ Hz, 2H), 2.18 (br, 1H), 1.89–1.88 (m, 1H), 1.63–1.57 (m, 2H), 1.52–1.47 (m, 6H), 1.36–1.29 (m, 24H), 1.17–1.13 (m, 16H), 0.93–0.90 (m, 6H), 0.82–0.76 (m, 6H). ^{13}C NMR (100 MHz, $\text{THF}-d_8$) δ : 165.03, 160.36, 151.37, 141.91, 136.64, 134.64, 132.24, 131.73, 130.96, 129.71, 128.91, 126.67, 125.83, 125.36, 124.75, 124.51, 123.08, 122.09, 121.89, 121.30, 118.11, 116.54, 116.29, 115.47, 114.78, 100.82, 71.76, 50.58, 40.93, 39.37, 33.07, 32.95, 32.88, 32.83, 32.63, 31.25, 31.00, 30.92, 30.79, 30.75, 30.52, 30.37, 28.05, 27.43, 23.77, 23.65, 14.67, 14.61. HR-MS (MALDI) m/z calcd. for ($\text{C}_{62}\text{H}_{80}\text{N}_2\text{O}_3$): 900.61689. Found: 900.61782. Anal. calcd. For $\text{C}_{62}\text{H}_{80}\text{N}_2\text{O}_3$: C, 82.62; H, 8.95; N, 3.11. Found: C, 82.64; H, 8.90; N, 3.14.

3-Bromo-1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1H-phenanthro[1,10,9,8-cdefg]carbazole (6): In a three-neck round bottom flask was dissolved **4** (3.00 g, 3.33 mmol) in THF (20 mL) and cooled to 0 °C using an ice salt bath. NBS (592 mg, 3.33 mmol) in

THF (5 mL) was added to the reaction mixture dropwise. Then the resulting solution was stirred at the same temperature for 0.5 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60–90 °C, *v/v*, 1/50) on silica gel to yield a yellow solid as the desired product **6** (2.80 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ: 8.45 (d, *J* = 7.7 Hz, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.69–7.66 (m, 4H), 7.51 (s, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 4.08–4.03 (m, 4H), 2.06 (br, 1H), 1.97–1.94 (m, 1H), 1.65–1.61 (m, 4H), 1.52–1.42 (m, 20H), 1.34–1.23 (m, 24H), 1.04–1.00 (m, 6H), 0.92–0.88 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.00, 137.61, 134.62, 132.10, 131.42, 131.18, 130.15, 129.81, 127.83, 127.47, 124.98, 124.58, 124.48, 124.26, 123.89, 121.04, 120.96, 117.09, 116.66, 116.29, 115.77, 114.64, 113.81, 71.19, 49.73, 39.77, 38.34, 32.20, 32.18, 32.07, 32.00, 31.79, 31.74, 30.35, 29.90, 29.81, 29.72, 29.64, 29.49, 27.18, 26.51, 22.98, 22.85, 14.40, 14.33, 14.28. MS (ESI) *m/z* calcd. for (C₅₈H₇₈BrNO): 883.53. Found: 884.53 ([M+H]⁺). Anal. calcd. for C₅₈H₇₈BrNO: C, 78.70; H, 8.88; N, 1.58. Found: C, 78.71; H, 8.87; N, 1.59.

Butyl 4-(7-((1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1H-phenanthro[1,10,9,8-cdefg]carbazol-3-yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)benzoate (7): To a dried Schlenk tube were added **6** (459 mg, 0.57 mmol), butyl 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)benzoate (148 mg, 0.57 mmol), Pd₂(dba)₃ (15 mg, 0.016 mmol), P(*t*-Bu)₃ (6.5 mg, 0.032 mmol), Cs₂CO₃ (212 mg, 0.65 mmol), and dioxane (16 mL) in a nitrogen-filled glovebox. The reaction mixture was refluxed under argon for 5 h. Water was added and the mixture was extracted three times with chloroform. The organic phase was washed with water and then dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60–90 °C, *v/v*, 1/1) on silica gel to afford a red solid as the desired product **7** (539 mg, 83% yield). ¹H NMR (400 MHz, THF-*d*₈) δ: 8.81–8.74 (m, 1H), 8.69–8.52 (m, 2H), 8.15–8.08 (m, 5H), 7.94–7.87 (m, 3H), 7.71–7.67 (m, 2H), 7.61–7.57 (m, 3H), 7.12–7.06 (m, 2H), 4.52–4.32 (m, 4H), 3.98–3.94 (m, 2H), 2.18–2.17 (m, 1H), 1.86–1.85 (m, 1H), 1.77–1.69 (m, 3H), 1.56–1.34 (m, 32H), 1.12–1.09 (m, 16H), 1.04–0.90 (m, 8H), 0.77–0.74 (m, 6H). ¹³C NMR (100 MHz, THF-*d*₈) δ: 166.46, 160.10, 156.68, 156.60, 154.10, 154.00, 142.31, 142.25, 142.16, 139.88, 139.80, 135.04, 134.76, 132.56, 132.43, 132.21, 131.45, 131.26, 130.60, 130.38, 130.15, 130.07, 129.36, 129.22, 129.05, 126.29, 126.21, 125.61, 125.56, 125.14, 124.84, 122.23, 122.03, 119.16, 118.92, 118.74, 117.09, 116.53, 115.35, 114.99, 114.91, 98.95, 91.05, 71.72, 65.46, 50.65, 50.57, 40.78, 39.35, 33.08, 32.96, 32.91, 32.70, 32.62, 32.02, 31.25, 31.06, 30.79, 30.62, 30.52, 30.42, 28.05, 27.41, 23.78, 23.65, 20.37, 14.68, 14.62, 14.36. MS (ESI) *m/z* calcd. for (C₇₇H₉₃N₃O₃S): 1139.69. Found: 1140.69 ([M+H]⁺). Anal. calcd. for C₇₇H₉₃N₃O₃S: C, 81.08; H, 8.22; N, 3.68. Found: C, 81.09; H, 8.25; N, 3.65.

4-(7-((1-(2-Hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1H-phenanthro[1,10,9,8-cdefg]carbazol-3-yl)ethynyl)benzo[c][1,2,5]thiadiazol-4-yl)benzoic acid (C272): In a three-neck round bottom flask, **7** (137 mg, 0.12 mmol) and KOH (40 mg, 0.72 mmol) were dissolved in THF/H₂O (8 mL, *v/v*, 3/1). The mixture was stirred at reflux under argon for 8 h. Water and Chloroform was added. The organic phase was washed with 0.2 M phosphoric acid aqueous solution and water in turn, and then dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, *v/v*, 15/1) on silica gel to afford a black solid as the final product **C272** (130 mg, 99% yield). ¹H NMR (400 MHz, THF-*d*₈) δ: 8.81 (d, *J* = 6.3 Hz, 1H), 8.66 (d, *J* = 4.0 Hz, 2H), 8.16–8.05 (m, 6H), 7.93–7.89 (m, 3H), 7.72–7.68 (m, 2H), 7.59 (d, *J* = 5.6 Hz, 2H), 7.09 (d, *J* = 5.0 Hz, 2H), 4.49 (br, 2H), 3.99 (br, 2H), 2.26 (br, 2H), 2.09–2.02 (m, 2H), 1.87 (m, 2H), 1.57–1.29 (m, 30H), 1.15–1.13 (m, 14H), 0.91 (br, 6H), 0.77 (br, 6H). ¹³C NMR (100 MHz, THF-*d*₈) δ: 167.67, 160.14, 156.70, 154.15, 142.10, 139.93, 135.05, 134.87, 133.40, 132.59, 132.20, 131.78, 131.57, 131.31, 130.75, 130.09, 129.33, 129.12, 126.29, 125.70, 125.55, 125.15, 124.96, 122.31, 122.14, 119.29, 119.08, 118.67, 117.18, 116.59, 115.37, 114.99, 98.77, 91.02, 71.71, 50.66, 40.82, 39.35, 36.38, 33.07, 32.95, 32.91, 32.72, 32.62, 31.25, 31.06, 30.90, 30.79, 30.62, 30.51, 30.40, 28.18, 28.04, 27.41, 26.59, 23.77, 23.65, 14.67, 14.60.

HR-MS (MALDI) m/z calcd. For (C₇₃H₈₅N₃O₃S): 1083.63116. Found: 1083.63457. Anal. calcd. for C₇₃H₈₅N₃O₃S: C, 80.84; H, 7.90; N, 3.87. Found: C, 80.85; H, 7.90; N, 3.86.

1.2. Theoretical calculations

The Gaussian 09 software package was used for all quantum chemical calculations with a selection of the 6-311G(d, p) basis set. The conductor-like polarized continuum model (C-PCM) was picked for the simulation of solvent effects.^{S4} The ground-state geometries were optimized by virtue of the popular B3LYP exchange-correlation functional.^{S5} The TD-MPW1K hybrid functional,^{S6} which includes 42% of Hartree-Fock exchange was employed for the vertical electron transition calculations and excited-state geometry optimizations.^{S7}

1.3. Device fabrication and measurements

A fluorine doped tin oxide (FTO) conducting glass (NSG, Solar) partly screen-printed with a titania bilayer film was used as the negative electrode of DSCs. The bilayer semiconducting film is composed of a 4.2- μm -thick translucent layer of small particles (25 nm) and a 5.0- μm -thick light-scattering layer of large particles (350–450 nm). Its preparation details can be found from a previous paper.^{S8} Dye-loading was performed by immersing a titania film into a solution of 150 μM dye in the solvent mixture of toluene/ethanol (v/v, 3/7) overnight. Note that for the co-sensitized cells, we used a dyeing solution with 150 μM C272 (or C271) and 150 μM YD2-o-C8 dissolved in the solvent mixture of toluene/ethanol (v/v, 3/7). According to our previous experience, the dye ratios do have an influence on the efficiency of co-sensitized DSCs. In this short communication paper, the ratio of co-sensitized dyes is not optimized, we leave this issue for a future study. A 25- μm -thick Surlyn ring was heated at 130 °C to adhere a dyed titania electrode and a gold coated FTO electrode. The internal space of a partly sealed cell was infiltrated with a cobalt electrolyte. The recipe of a cobalt electrolyte: 0.25 M tris(1,10-phenanthroline)cobalt(II) di[bis(trifluoromethanesulfonyl)imide], 0.05 M tris(1,10-phenanthroline)cobalt(III) tris[bis(trifluoromethanesulfonyl)imide], 0.7 M TBP, and 0.05 M LiTFSI in ACN. The EQE, $J-V$, CE, and TPD measurements have been detailed in our previous papers.^{S9,S10}

1.4. Voltammetric and electronic absorption measurements

Cyclic voltammogram (CV) of a THF dye solution was recorded on a CHI660C electrochemical workstation in combination with a three-electrode electrolytic cell, which consisted of a glassy carbon working electrode, a platinum gauze counter electrode, and a silver wire quasi-reference electrode. The iR drop was compensated and the potential scan rate was 5 mV s⁻¹. Steady electronic absorption measurements were carried out on an Agilent G1103A spectrometer. For spectroscopic measurements of dye molecules grafted onto titania, a dyed mesoporous oxide film deposited on FTO was stuck to a bare FTO, and the internal space was filled with a cobalt electrolyte employing the same procedure for DSC fabrication.

1.5 Notes and references

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2. Additional data

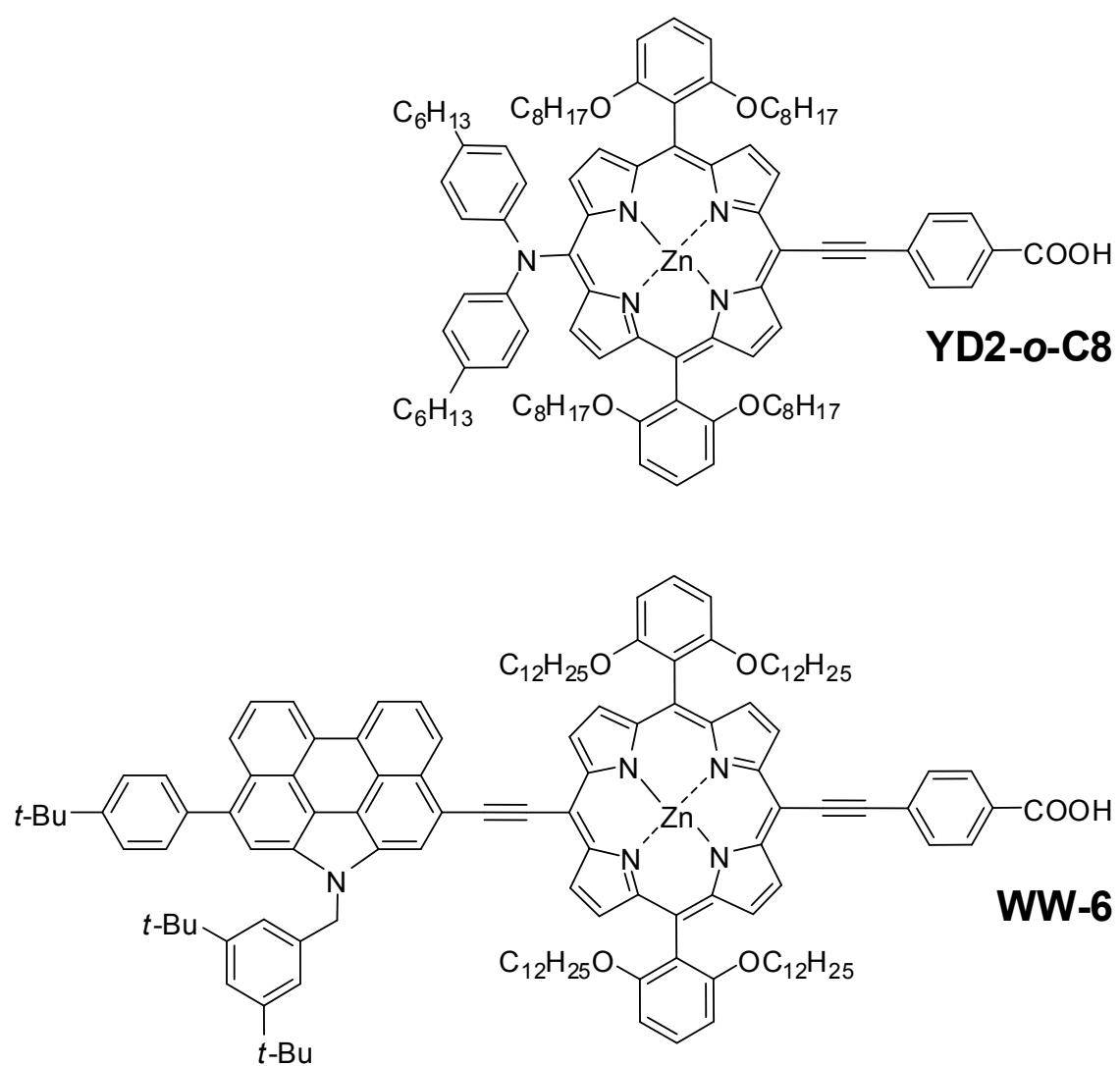


Fig. S1 Chemical structures of zinc porphyrin dyes **YD2-o-C8** and **WW-6**.

Table S1 Energy levels and electronic absorption properties

Dye	E_L^{CV} [eV] ^{a)}	E_L^{B3LYP} [eV] ^{b)}	E_H^{CV} [eV] a)	E_H^{B3LYP} [eV] ^{b)}	$\lambda_{ABS,MAX}^{MEAS}$ [nm] ^{c)}	$\lambda_{ABS,MAX}^{TD-MPW1K}$ [nm] ^{d)}	$\epsilon_{ABS,MAX}^{MEAS}$ [mM ⁻¹ cm ⁻¹] ^{c)}	$f^{TD-MPW1K}$ ^{d)}
C271	-3.26	-2.93	-5.30	-5.43	508	499	34.7	1.2
C272	-3.29	-2.97	-5.15	-5.15	512	523	36.1	1.5

^{a)} Measured molecular orbital energies (E_L^{CV} and E_H^{CV}) vs vacuum are calculated via $E = -4.88 - eE_{onset}$, where E_{onset} is the onset potential (Figure 2a) of reduction and oxidation of a ground-state dye in THF. H and L represent HOMO and LUMO, respectively. ^{b)} Theoretical molecular orbital energies (E_L^{B3LYP} and E_H^{B3LYP}) vs vacuum are calculated at the B3LYP/6-311G(d,p) level for a dye in THF. ^{c)} Measured maximum absorption wavelength ($\lambda_{ABS,MAX}^{MEAS}$) and maximum molar absorption coefficient ($\epsilon_{ABS,MAX}^{MEAS}$) are derived from Figure 2b. ^{d)} Theoretical maximum absorption wavelength ($\lambda_{ABS,MAX}^{TD-MPW1K}$) and oscillator strengths (f) are calculated at the TD-MPW1K/6-311G(d,p) level for a dye in THF.

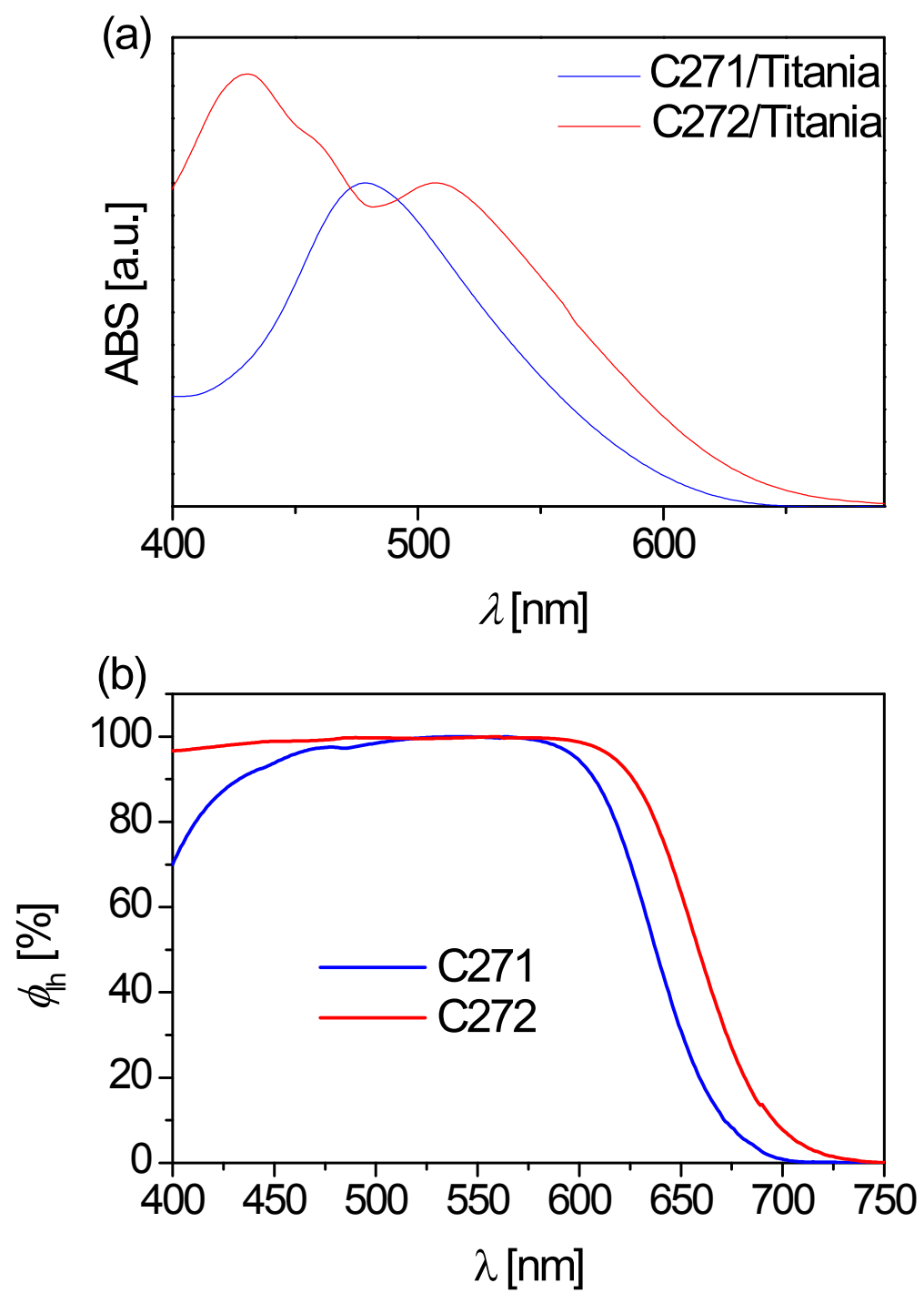


Fig. S2 (a) Normalized electronic absorption spectra of **C271** and **C272** grafted on a mesoporous titania film immersed in a cobalt electrolyte. The absorption of a titania film has been subtracted for clarity of presentation. (b) Light-harvesting yields (ϕ_h) plotted versus wavelength (λ) for the 4.2- μm -thick, dye-grafted mesoporous titania films immersed in a cobalt electrolyte for DSC fabrication.

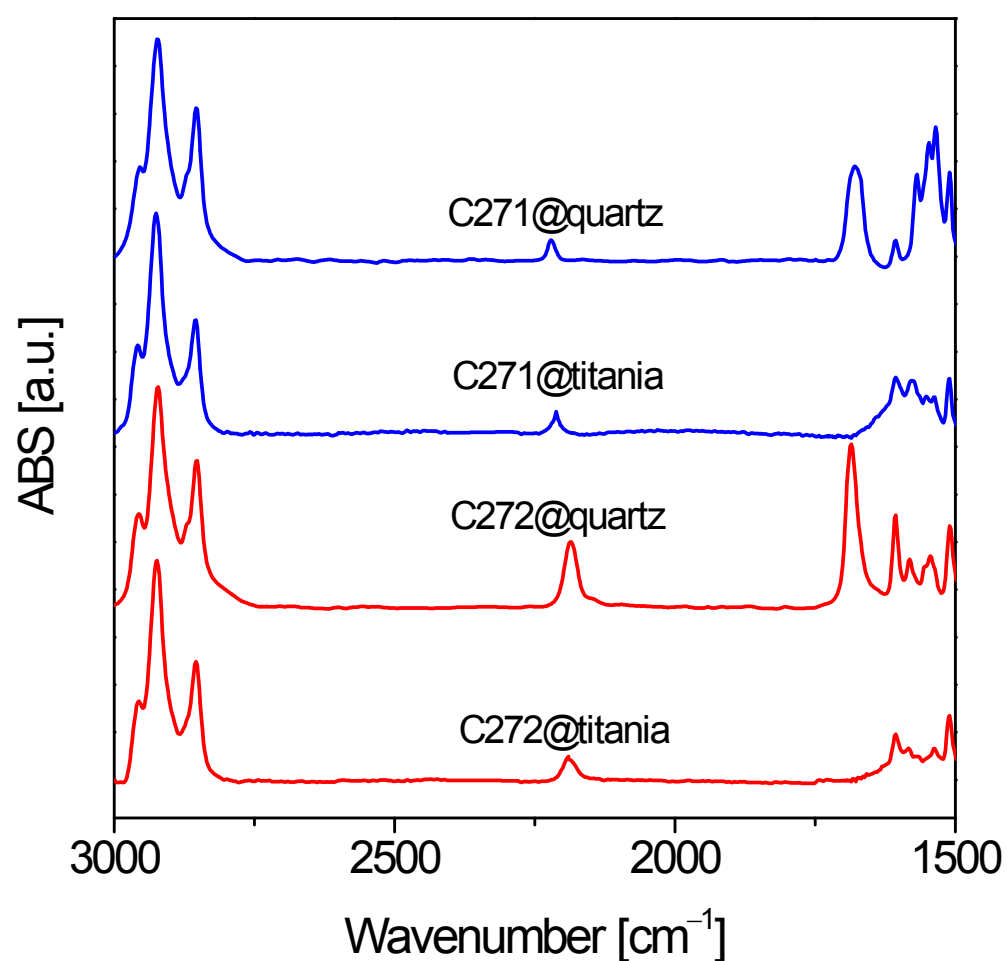


Fig. S3 ATR-FTIR spectra of diverse samples made from **C271** and **C272**. The pristine dyes are characteristic of a vibrational peak of carboxylic acid (COOH) at 1681 ± 4 cm^{-1} . The absence of carboxylic acid absorptions for the dyed titania films has excluded the possibility of physical adsorption of dye molecules on titania. The signals of $\text{-C}\equiv\text{N}$ for the two **C271** samples both occur at 2217 ± 3 cm^{-1} , suggesting that the electron-withdrawing cyano group conjugated to the double bond is maintained during the deprotonation and adsorption processes. Also, the $\text{-C}\equiv\text{C-}$ signals at 2185 ± 2 cm^{-1} for the two **C272** samples do not change during the deprotonation and adsorption processes. The saturated aliphatic chains are easily identified from their C-H stretch modes in the $2800\text{--}3000$ cm^{-1} region. Peaks at 2861 ± 5 and 2929 ± 1 cm^{-1} are due to the symmetric and asymmetric $\text{-CH}_2\text{-}$ stretch vibrations and the corresponding -CH_3 peaks are observed at 2953 ± 2 cm^{-1} .

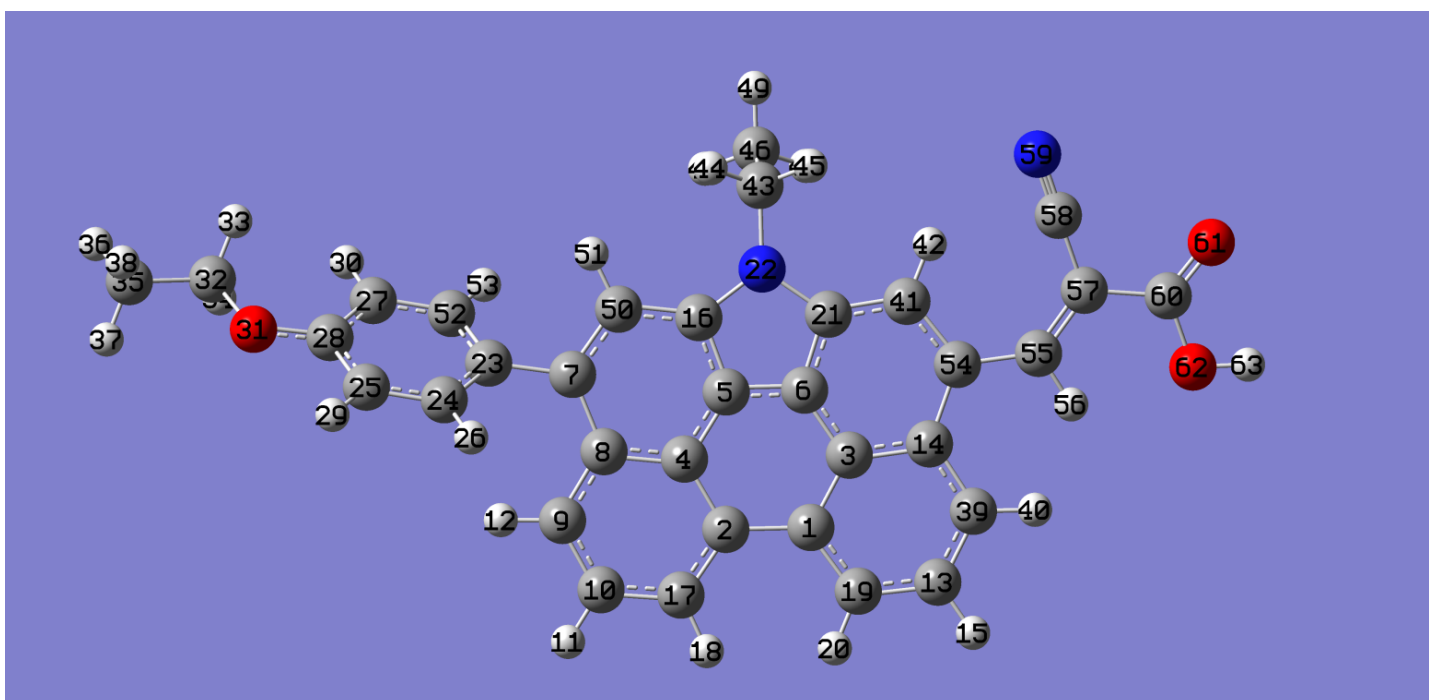


Fig. S4 Geometry of the S₀ state of C₂₇₁ in THF optimized at the B3LYP/6-311G(d,p) level of theory.

Table S2 Geometry parameters and Mulliken atomic charges of the S₀ state of **C271** in THF computed at the B3LYP/6-311G(d,p) level of theory

Center number	Atom	Coordinates [Å]			Mulliken atomic charges
		x	y	z	
1	C	1.516024	2.800978	0.117212	0.049763
2	C	0.022805	2.8254	0.113834	0.053232
3	C	2.198025	1.538968	0.053968	-0.01918
4	C	-0.69543	1.589902	0.0292	-0.00793
5	C	0.042756	0.418898	-0.01927	-0.17183
6	C	1.419208	0.395537	-0.01049	-0.15723
7	C	-2.65222	0.095109	-0.08397	-0.00337
8	C	-2.10792	1.450536	0.010876	-0.01717
9	C	-2.84179	2.652052	0.124366	-0.09847
10	C	-2.17269	3.868001	0.210948	-0.07694
11	H	-2.7552	4.778224	0.29736	0.110251
12	H	-3.92334	2.638837	0.154005	0.114254
13	C	3.738944	3.771606	0.170389	-0.06824
14	C	3.605822	1.349808	0.052506	-0.00228
15	H	4.353487	4.66377	0.212985	0.110936
16	C	-0.43075	-0.88622	-0.08643	0.288006
17	C	-0.76995	3.969958	0.198682	-0.09517
18	H	-0.32109	4.953775	0.269	0.104406
19	C	2.341958	3.921263	0.178092	-0.09877
20	H	1.925736	4.920206	0.22794	0.102999
21	C	1.845327	-0.93119	-0.07632	0.231904
22	N	0.685158	-1.72995	-0.13057	-0.58147
23	C	-4.12484	-0.11115	-0.14088	-0.12971
24	C	-4.92115	0.524994	-1.11059	-0.07856
25	C	-6.28563	0.296115	-1.18302	-0.10713
26	H	-4.46068	1.189455	-1.83228	0.114456
27	C	-6.13485	-1.2198	0.691555	-0.14662
28	C	-6.9087	-0.57677	-0.27949	0.185177
29	H	-6.89254	0.778844	-1.93975	0.111455
30	H	-6.58399	-1.89482	1.406957	0.126621
31	O	-8.25186	-0.72863	-0.42867	-0.36684
32	C	-8.95802	-1.61071	0.459263	-0.0524
33	H	-8.55002	-2.62356	0.369907	0.123191

34	H	-8.8221	-1.27444	1.493031	0.123257
35	C	-10.4211	-1.57754	0.065041	-0.29702
36	H	-10.9963	-2.23726	0.718903	0.118264
37	H	-10.8226	-0.56588	0.155205	0.117368
38	H	-10.5512	-1.91379	-0.96592	0.11739
39	C	4.370928	2.534313	0.106936	-0.10356
40	H	5.452918	2.515643	0.094067	0.103083
41	C	3.22358	-1.1485	-0.07708	0.048691
42	H	3.629763	-2.14843	-0.10827	0.141517
43	C	0.655733	-3.19331	-0.14696	-0.10201
44	H	-0.21323	-3.49943	-0.73295	0.141119
45	H	1.538724	-3.53424	-0.69092	0.142493
46	C	0.61054	-3.8127	1.250933	-0.28018
47	H	1.48992	-3.53015	1.833876	0.119918
48	H	-0.28169	-3.49191	1.793278	0.118005
49	H	0.58929	-4.90231	1.170955	0.122895
50	C	-1.83769	-1.04145	-0.12307	-0.01529
51	H	-2.30495	-2.01464	-0.2075	0.116008
52	C	-4.76135	-0.9843	0.747933	-0.07013
53	H	-4.17795	-1.4816	1.514642	0.109322
54	C	4.10604	-0.03882	-0.01473	-0.07586
55	C	5.529172	-0.224	0.011459	0.045135
56	H	6.10094	0.674867	0.197085	0.143146
57	C	6.336785	-1.32269	-0.15608	-0.20794
58	C	5.885659	-2.6383	-0.45423	0.051859
59	N	5.525081	-3.71043	-0.69957	-0.27775
60	C	7.810392	-1.21561	-0.05727	0.437583
61	O	8.571329	-2.14649	-0.21455	-0.37069
62	O	8.240811	0.032857	0.227785	-0.34529
63	H	9.20828	-0.00272	0.26283	0.28131

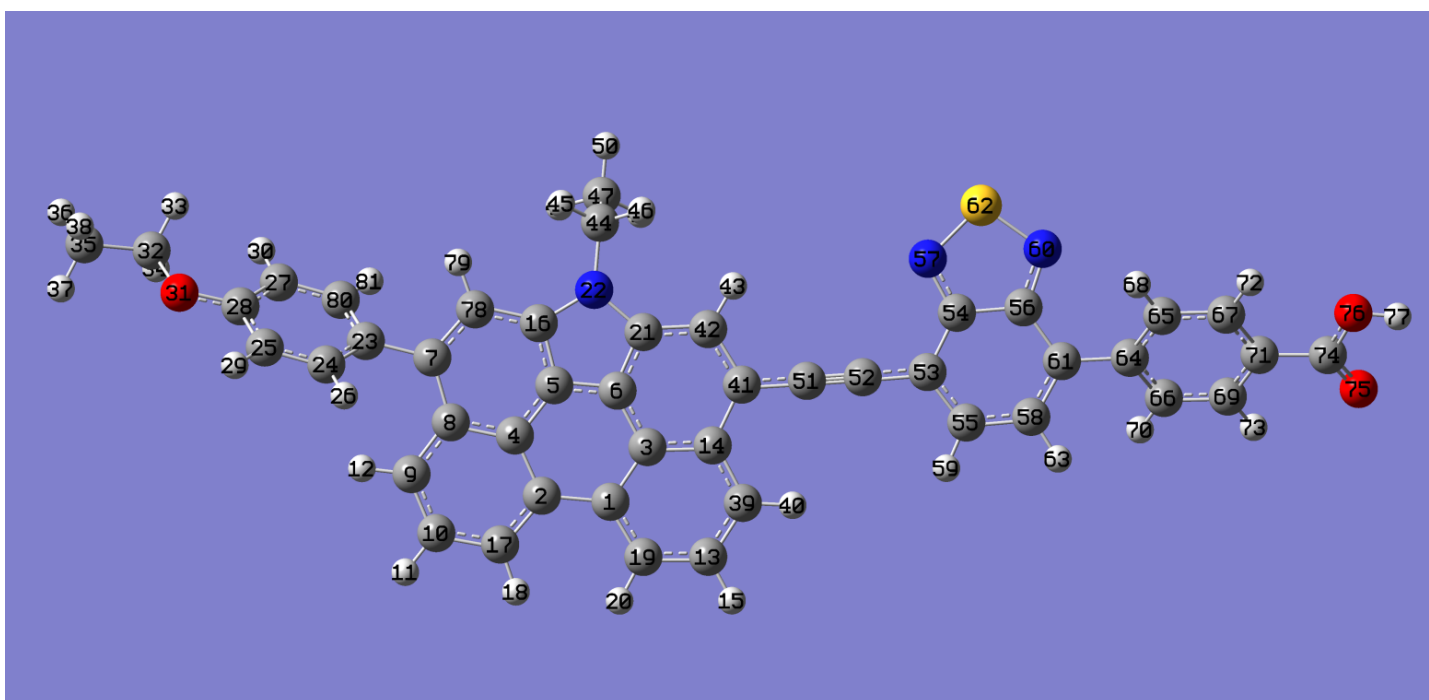


Fig. S5 Geometry of the S_0 state of C272 in THF optimized at the B3LYP/6-311G(d,p) level of theory.

Table S3 Geometry parameters and Mulliken atomic charges of the S₀ state of **C272** in THF computed at the B3LYP/6-311G(d,p) level of theory

Center number	Atom	Coordinates [Å]			Mulliken atomic charges
		x	y	z	
1	C	-2.45523	3.111806	0.019296	0.052424
2	C	-3.94449	2.980841	0.013491	0.043988
3	C	-1.6523	1.923723	-0.00961	-0.04012
4	C	-4.53049	1.672441	-0.0365	-0.00845
5	C	-3.67645	0.582083	-0.05337	-0.18714
6	C	-2.30179	0.701067	-0.04195	-0.12195
7	C	-6.32418	-0.01782	-0.10147	-0.01162
8	C	-5.92246	1.386961	-0.04927	-0.01663
9	C	-6.77649	2.511156	0.027692	-0.10332
10	C	-6.23715	3.790837	0.078396	-0.07962
11	H	-6.91107	4.638274	0.136734	0.107457
12	H	-7.8513	2.387744	0.056044	0.110616
13	C	-0.33258	4.304406	0.05935	-0.08116
14	C	-0.2354	1.888426	-0.00323	-0.00752
15	H	0.184267	5.257256	0.0861	0.108127
16	C	-4.01205	-0.76385	-0.08358	0.277961
17	C	-4.85129	4.037953	0.064749	-0.10082
18	H	-4.50678	5.064713	0.106425	0.10132
19	C	-1.74119	4.308712	0.053813	-0.09862
20	H	-2.25556	5.262346	0.076664	0.10096
21	C	-1.73882	-0.57101	-0.07003	0.269361
22	N	-2.80809	-1.48691	-0.10561	-0.58003
23	C	-7.76891	-0.3769	-0.14373	-0.12997
24	C	-8.62674	0.13186	-1.13564	-0.07901
25	C	-9.96156	-0.2364	-1.19209	-0.10812
26	H	-8.23641	0.809262	-1.88627	0.112108
27	C	-9.65686	-1.64862	0.742513	-0.14729
28	C	-10.4925	-1.12954	-0.25074	0.183
29	H	-10.6144	0.150809	-1.96549	0.110067
30	H	-10.0342	-2.3358	1.487457	0.125335
31	O	-11.8141	-1.42495	-0.38759	-0.36814
32	C	-12.4228	-2.33934	0.538117	-0.05177
33	H	-11.9095	-3.30613	0.488506	0.122237

34	H	-12.3236	-1.94936	1.557186	0.122446
35	C	-13.8813	-2.47733	0.149292	-0.29701
36	H	-14.3834	-3.16816	0.830713	0.117805
37	H	-14.3878	-1.51111	0.201725	0.117089
38	H	-13.9752	-2.8654	-0.86732	0.116982
39	C	0.419764	3.135897	0.032336	-0.0703
40	H	1.502022	3.187631	0.038594	0.108667
41	C	0.399399	0.569926	-0.0336	-0.1063
42	C	-0.33359	-0.63538	-0.06656	0.02956
43	H	0.211574	-1.57072	-0.08543	0.114109
44	C	-2.6836	-2.9436	-0.08029	-0.10027
45	H	-3.52217	-3.35729	-0.64431	0.138834
46	H	-1.77572	-3.20702	-0.62696	0.139178
47	C	-2.64719	-3.52496	1.334533	-0.28106
48	H	-1.79869	-3.13059	1.898099	0.118726
49	H	-3.56377	-3.2879	1.879471	0.117757
50	H	-2.54977	-4.61244	1.285787	0.120405
51	C	1.81223	0.487709	-0.02519	0.008763
52	C	3.023805	0.408476	-0.01596	0.052822
53	C	4.430335	0.297084	-0.00358	-0.23345
54	C	5.069191	-0.98932	-0.08964	0.161558
55	C	5.273442	1.392027	0.091765	-0.02471
56	C	6.51525	-1.10641	-0.0852	0.115318
57	N	4.438374	-2.16066	-0.16975	-0.4895
58	C	6.683362	1.268294	0.101617	-0.06875
59	H	4.840721	2.382642	0.154222	0.117089
60	N	6.931155	-2.37543	-0.15461	-0.49828
61	C	7.348512	0.059727	0.01409	0.002436
62	S	5.595482	-3.31959	-0.22919	0.569888
63	H	7.263468	2.181544	0.157664	0.120085
64	C	8.82521	-0.0124	0.030074	-0.02601
65	C	9.528093	-0.92039	-0.78007	-0.04784
66	C	9.565188	0.858784	0.849624	-0.07653
67	C	10.91612	-0.94845	-0.77981	-0.03571
68	H	8.983102	-1.60127	-1.41858	0.117125
69	C	10.95114	0.828077	0.854729	-0.0414
70	H	9.047818	1.548239	1.505614	0.118566

71	C	11.64125	-0.07478	0.03867	-0.21271
72	H	11.44069	-1.64709	-1.418	0.116812
73	H	11.51449	1.495065	1.495058	0.113165
74	C	13.12588	-0.07141	0.079398	0.43338
75	O	13.79592	0.66353	0.772469	-0.36957
76	O	13.67957	-0.98437	-0.74726	-0.34033
77	H	14.64137	-0.90879	-0.65469	0.276527
78	C	-5.39545	-1.06441	-0.11057	-0.01581
79	H	-5.76044	-2.08302	-0.16186	0.111395
80	C	-8.31447	-1.27082	0.783791	-0.07168
81	H	-7.68379	-1.67345	1.568554	0.107036

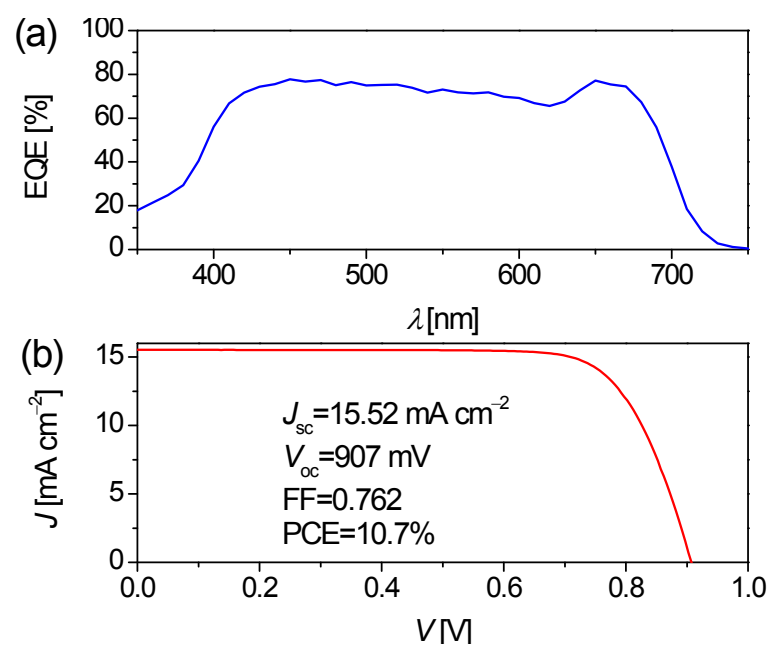


Fig. S6 (a) EQE plotted against λ for a co-sensitized cell with **C271** and **YD2-o-C8**. (b) $J-V$ curve measured under an irradiance of 100 mW cm^{-2} , simulated AM1.5G sunlight. The inset gives the detailed photovoltaic parameters.

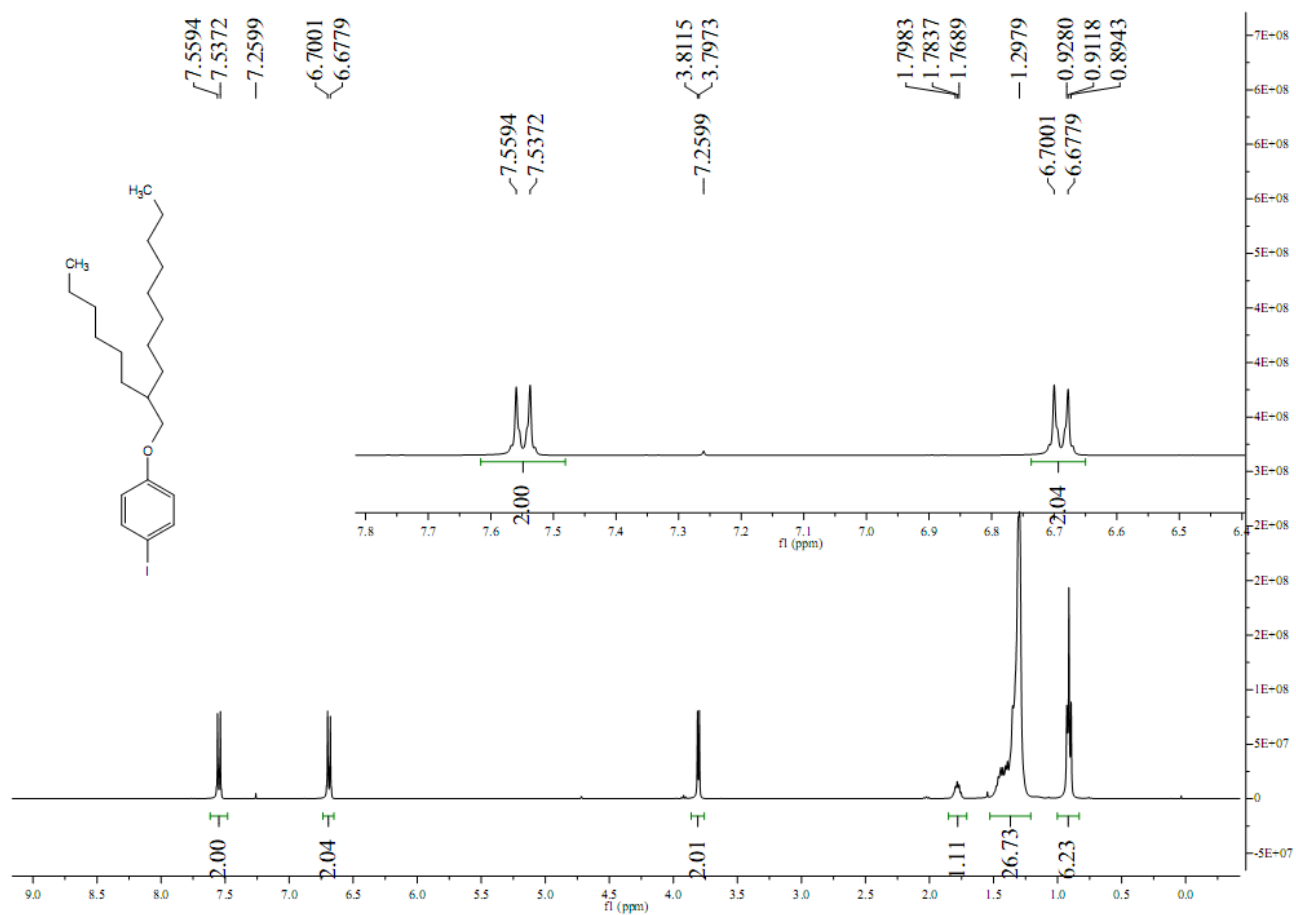


Fig. S7 The ¹H NMR (400 MHz) spectrum of **2** in CDCl₃.

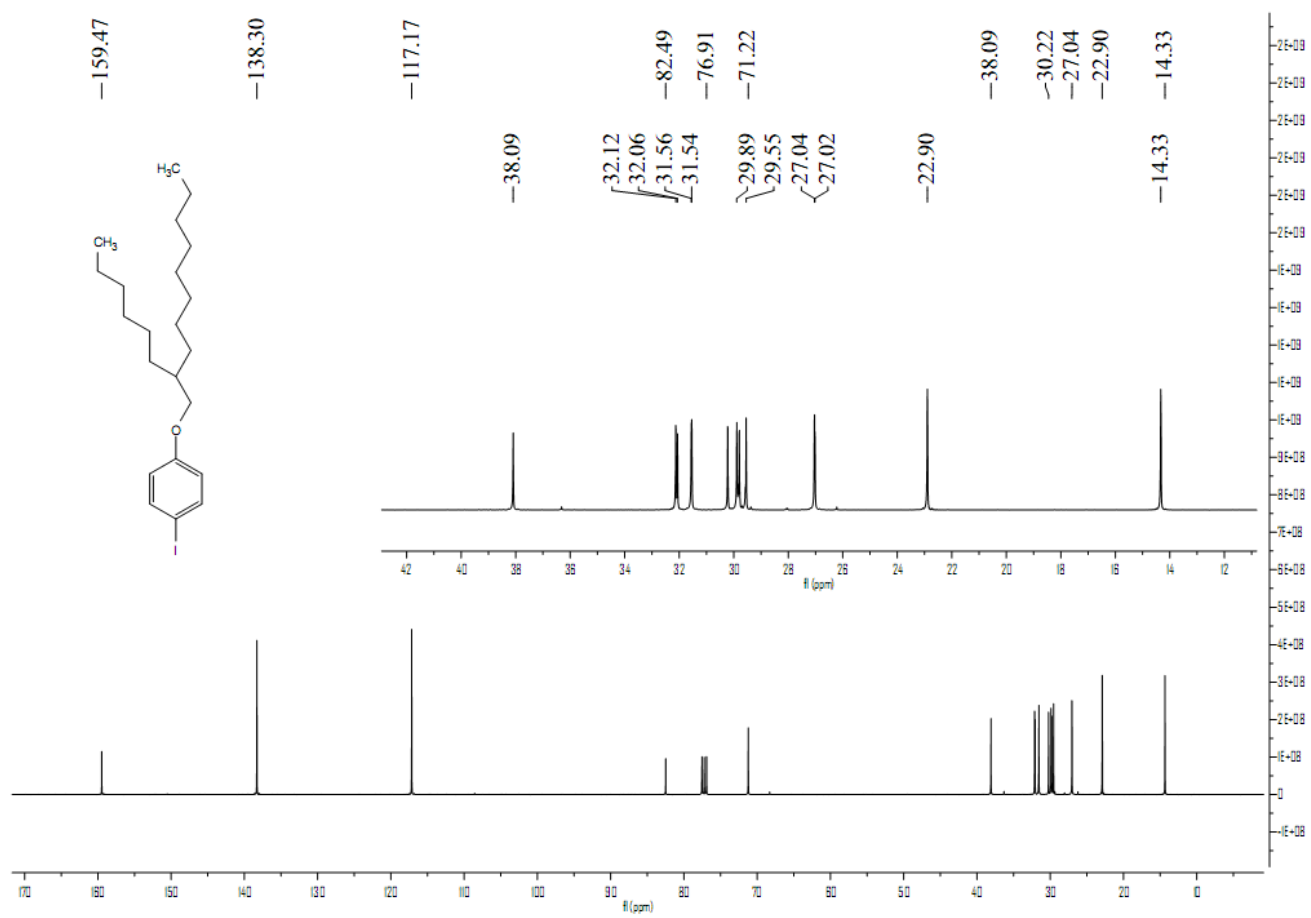


Fig. S8 The ¹³C NMR (100 MHz) spectrum of **2** in CDCl₃.

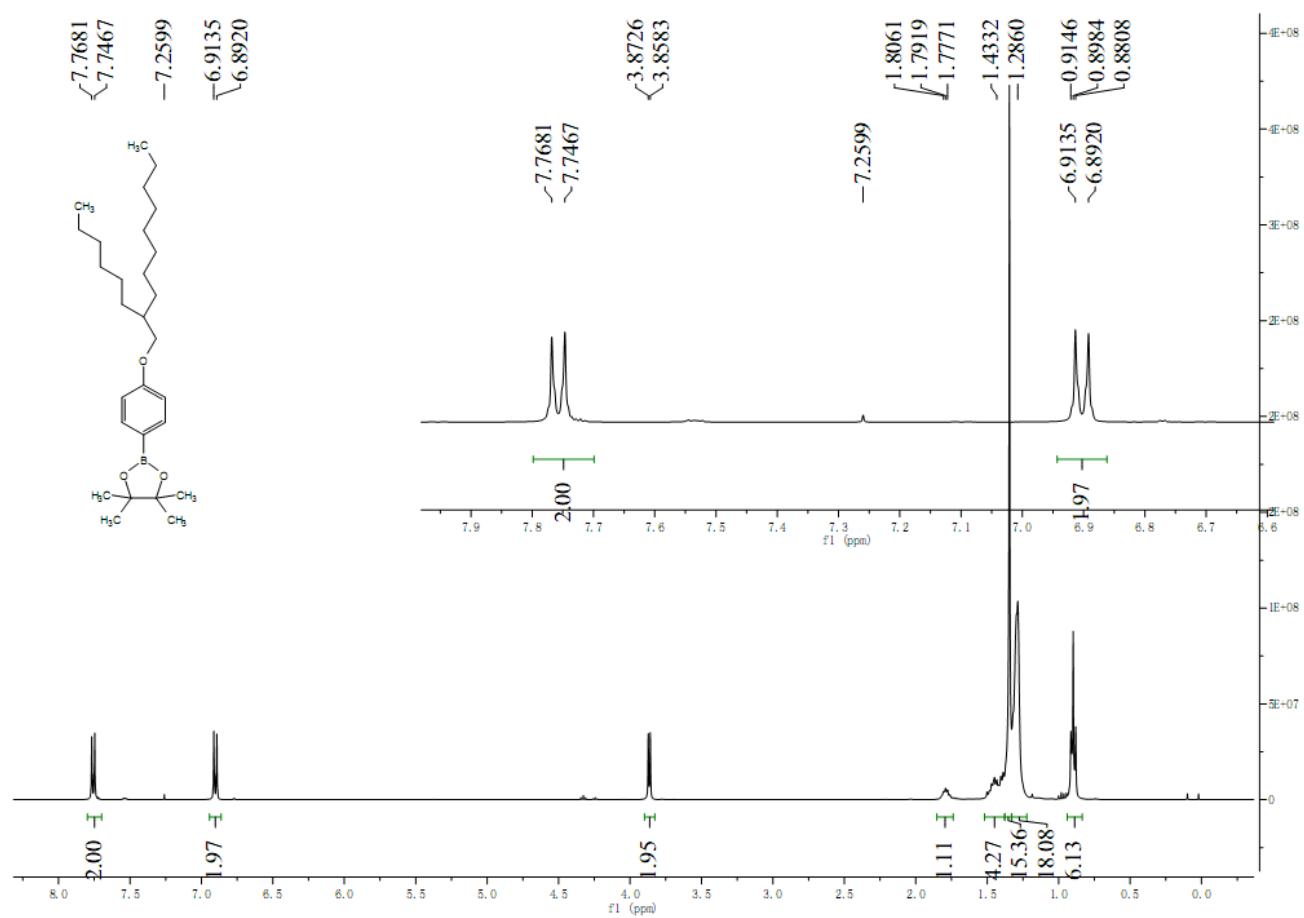


Fig. S9 The ¹H NMR (400 MHz) spectrum of **3** in CDCl₃.

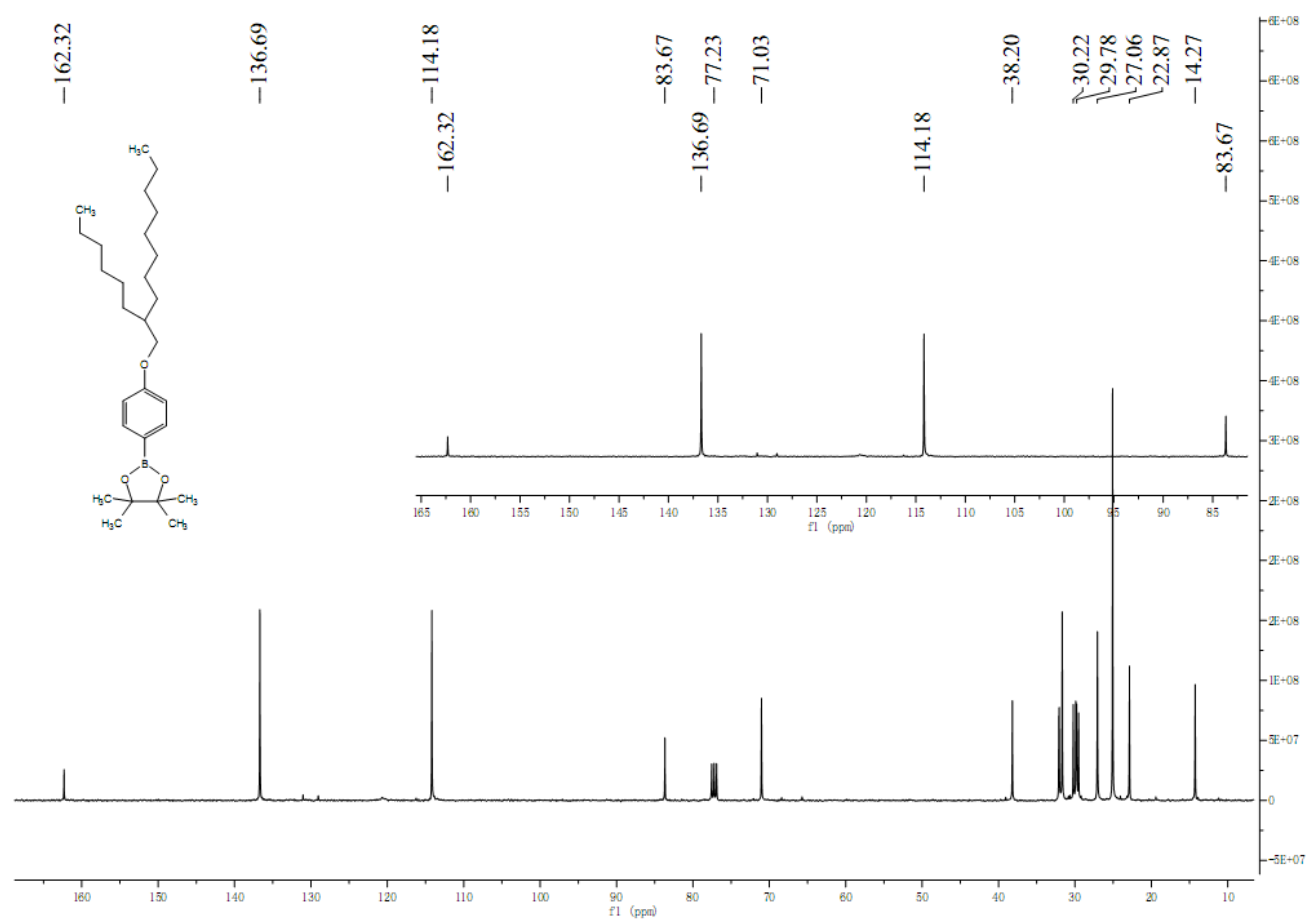


Fig. S10 The ^{13}C NMR (100 MHz) spectrum of **3** in CDCl_3 .

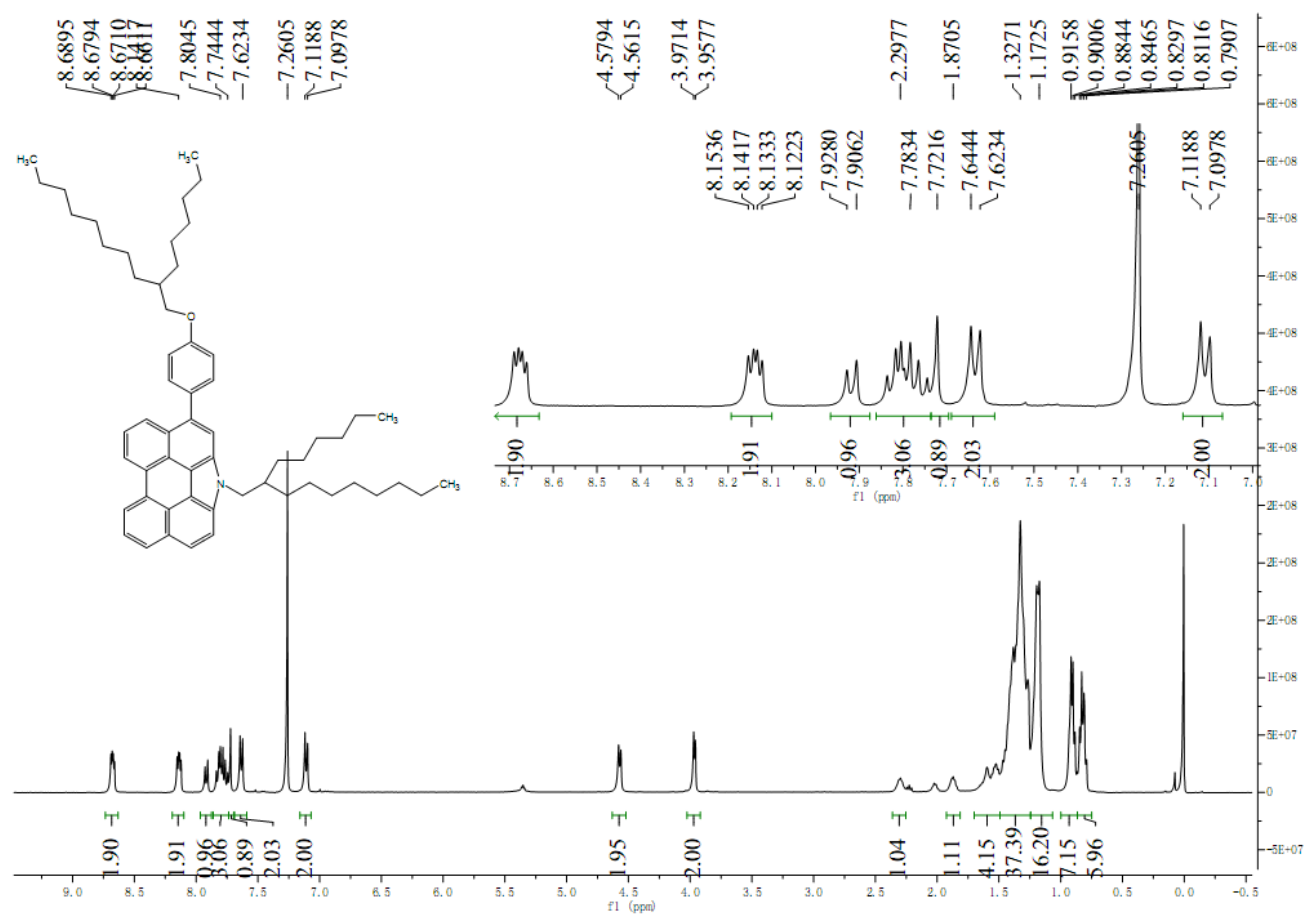


Fig. S11 The ^1H NMR (400 MHz) spectrum of **4** in CDCl_3 .

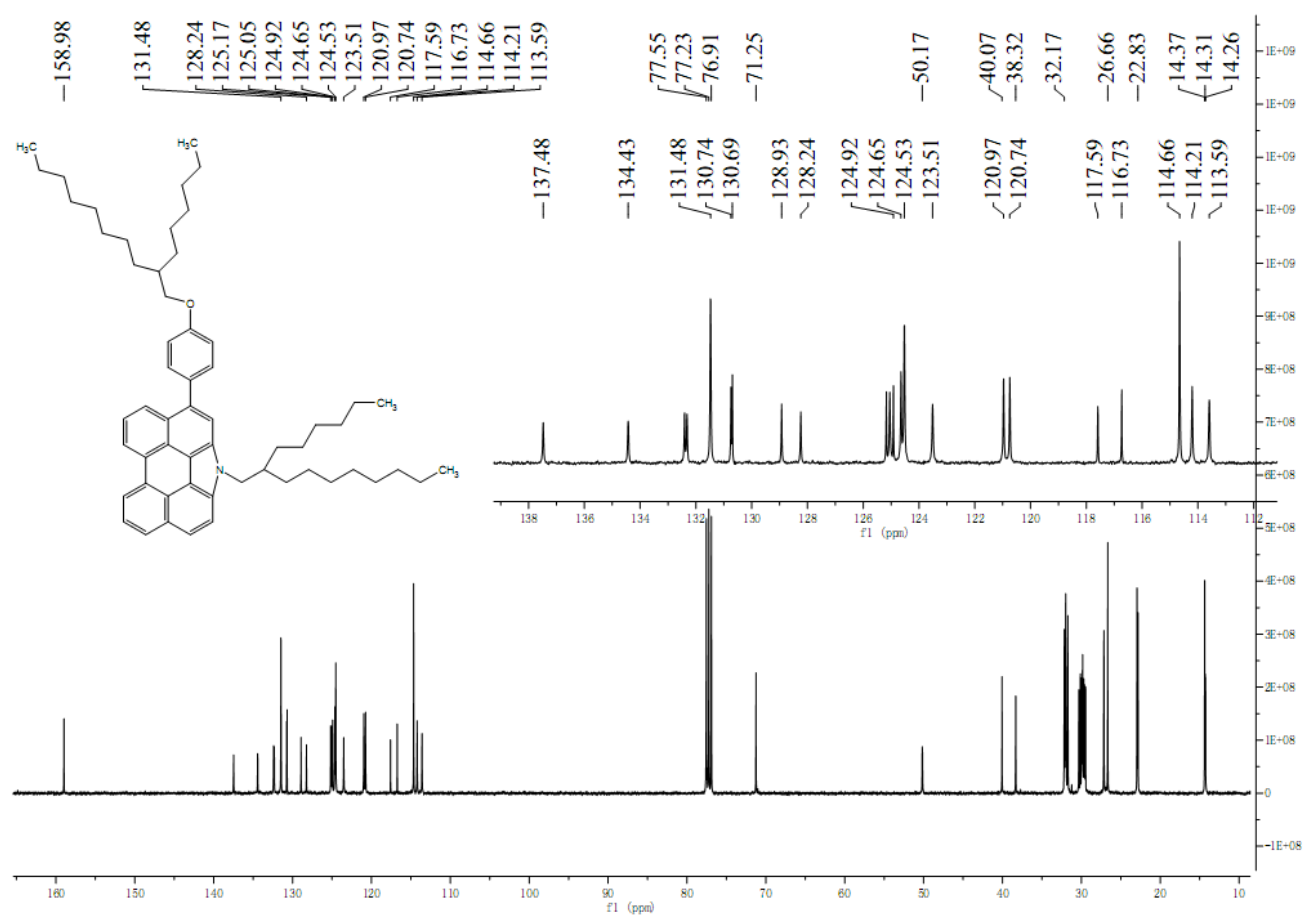


Fig. S12 The ^{13}C NMR (100 MHz) spectrum of **4** in CDCl_3 .

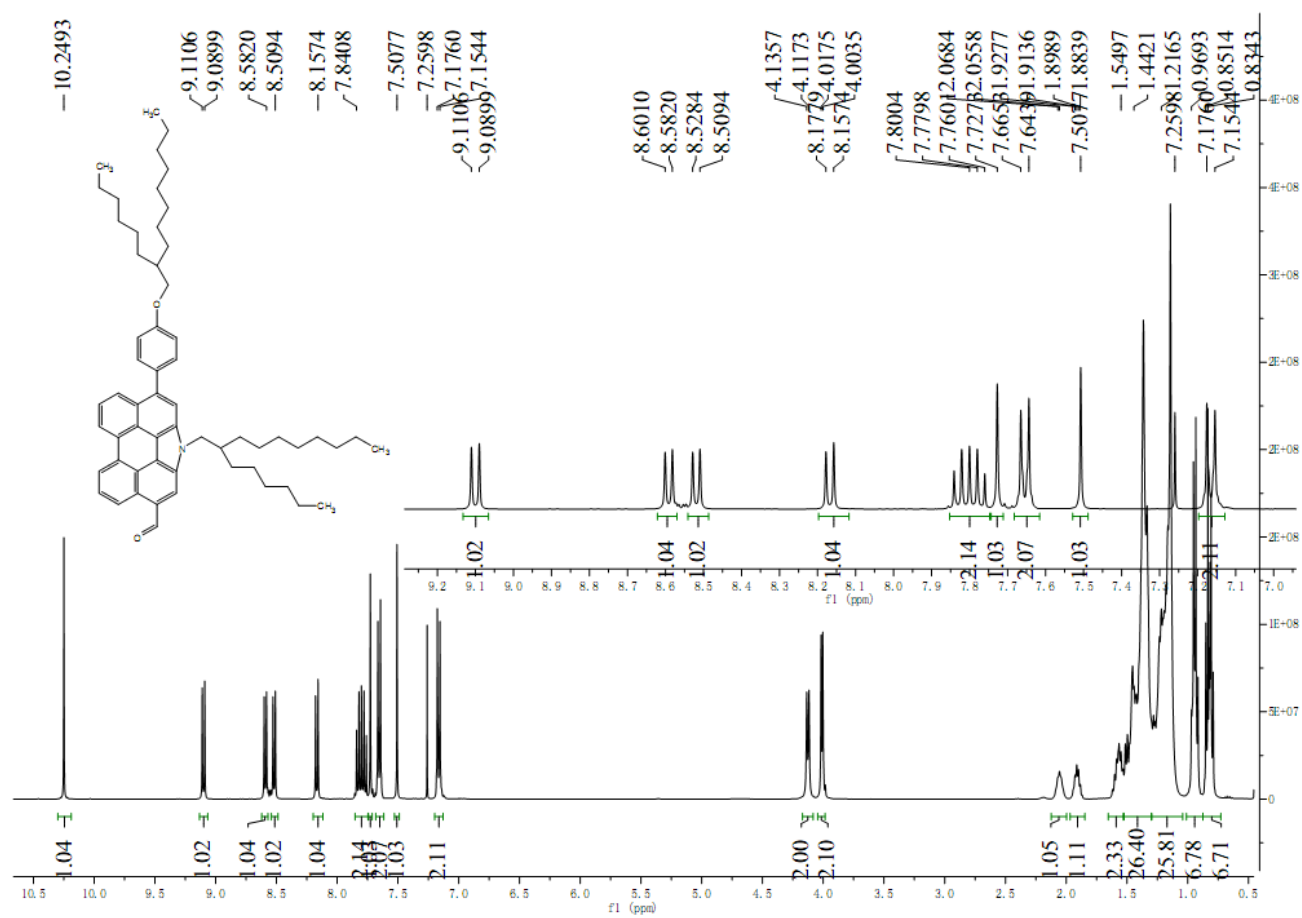


Fig. S13 The ^1H NMR (400 MHz) spectrum of **5** in CDCl_3 .

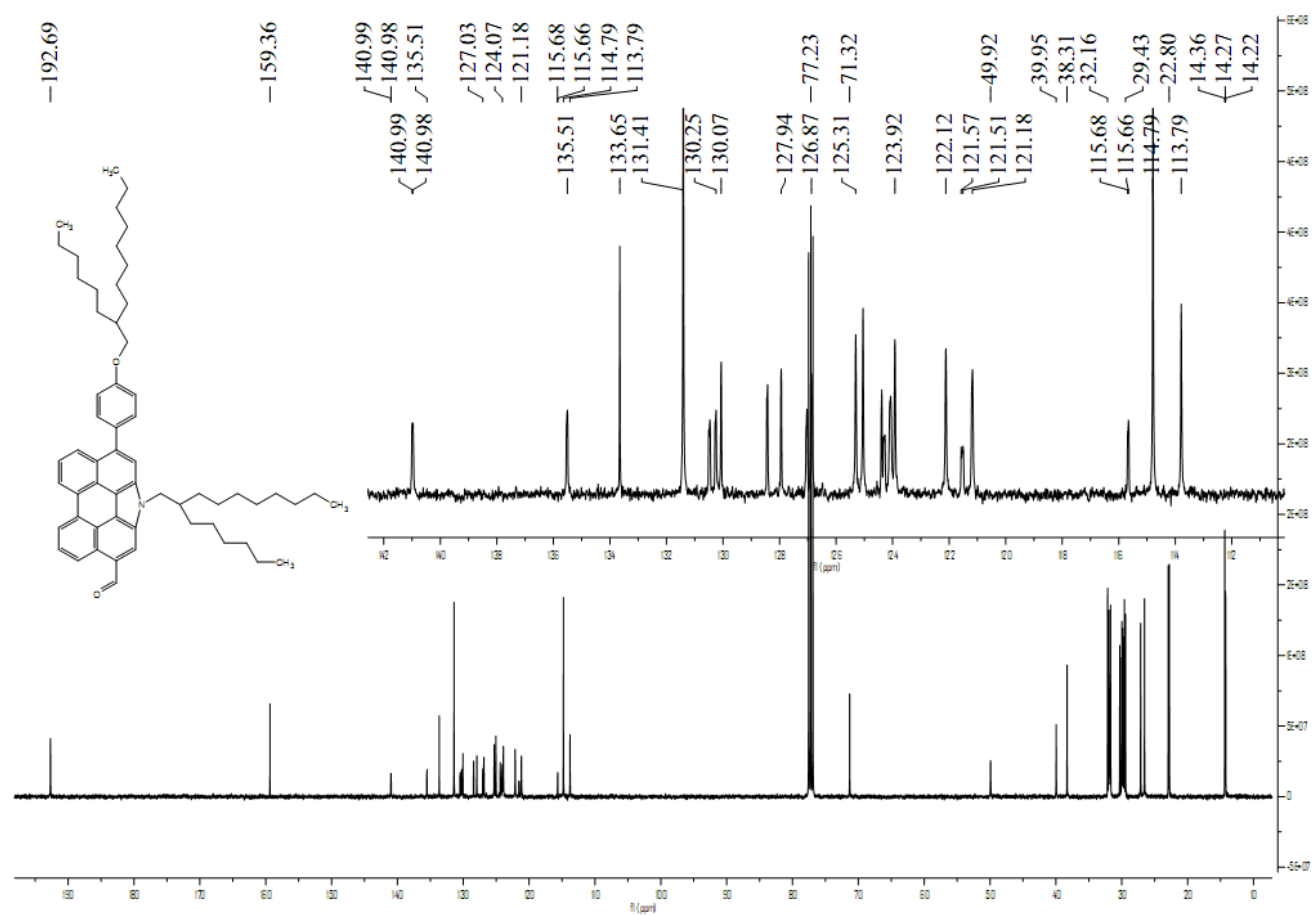


Fig. S14 The ^{13}C NMR (100 MHz) spectrum of **5** in CDCl_3 .

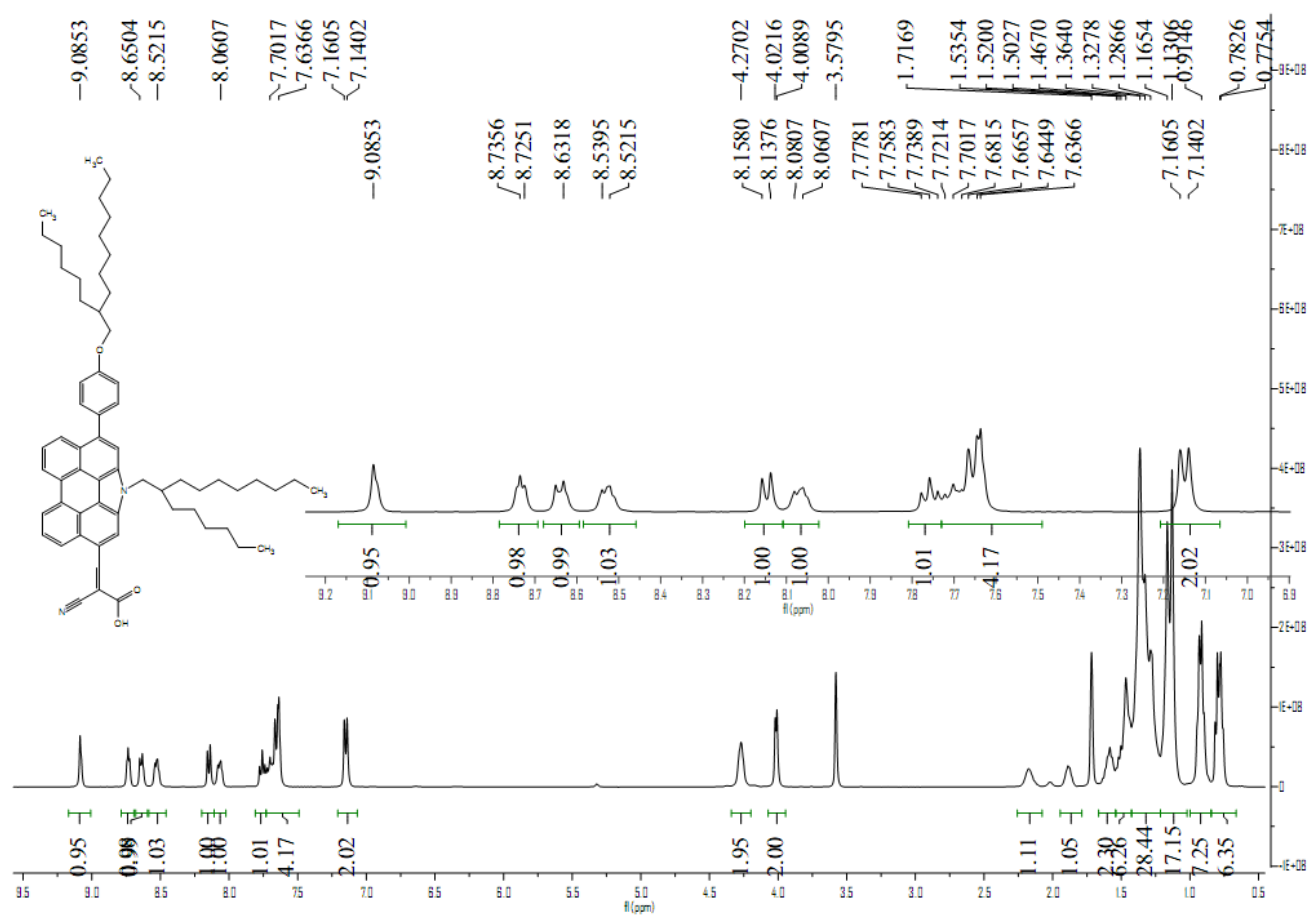


Fig. S15 The ¹H NMR (400 MHz) spectrum of C271 in THF-d₈.

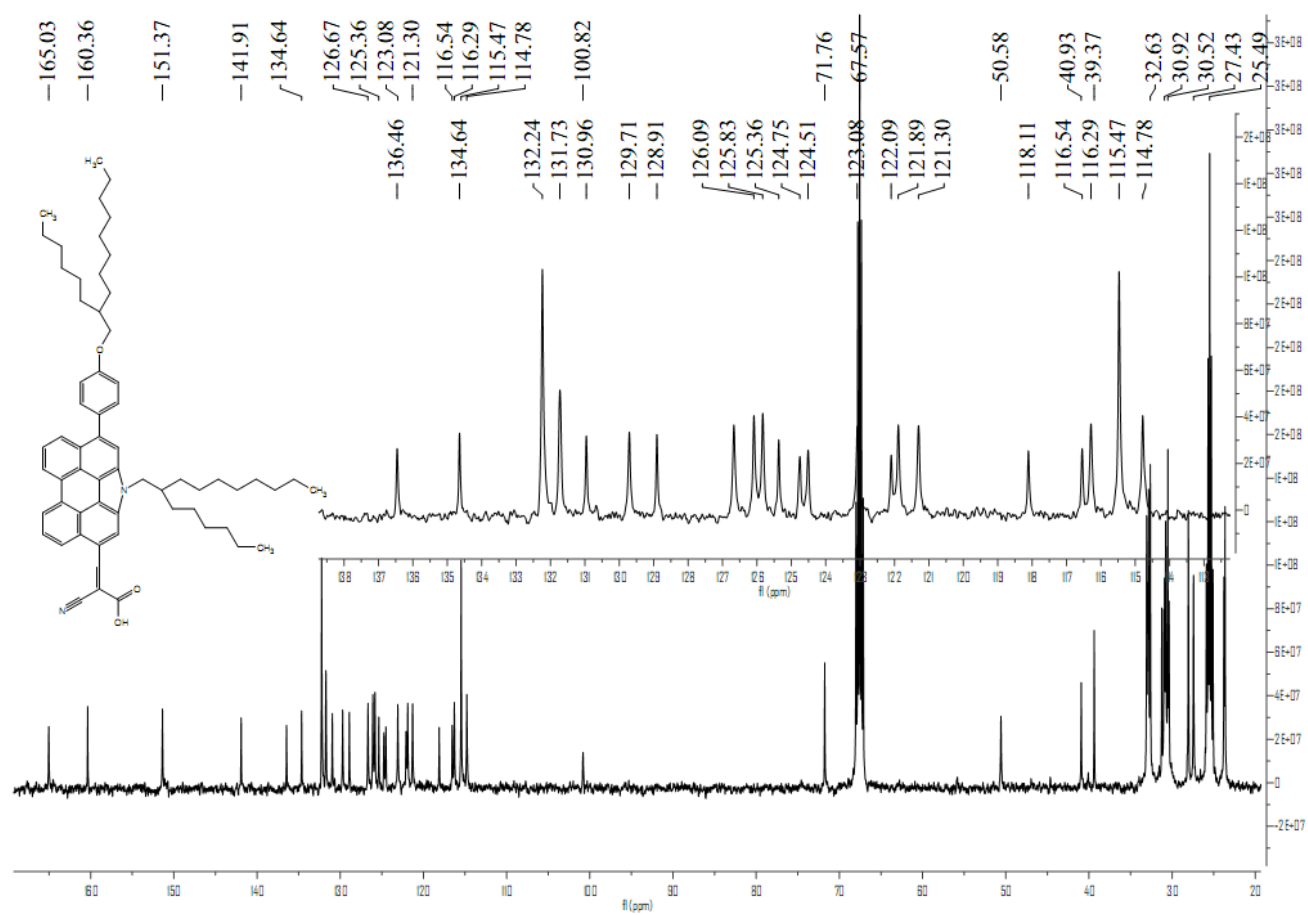


Fig. S16 The ^{13}C NMR (100 MHz) spectrum of **C271** in $\text{THF-}d_8$.

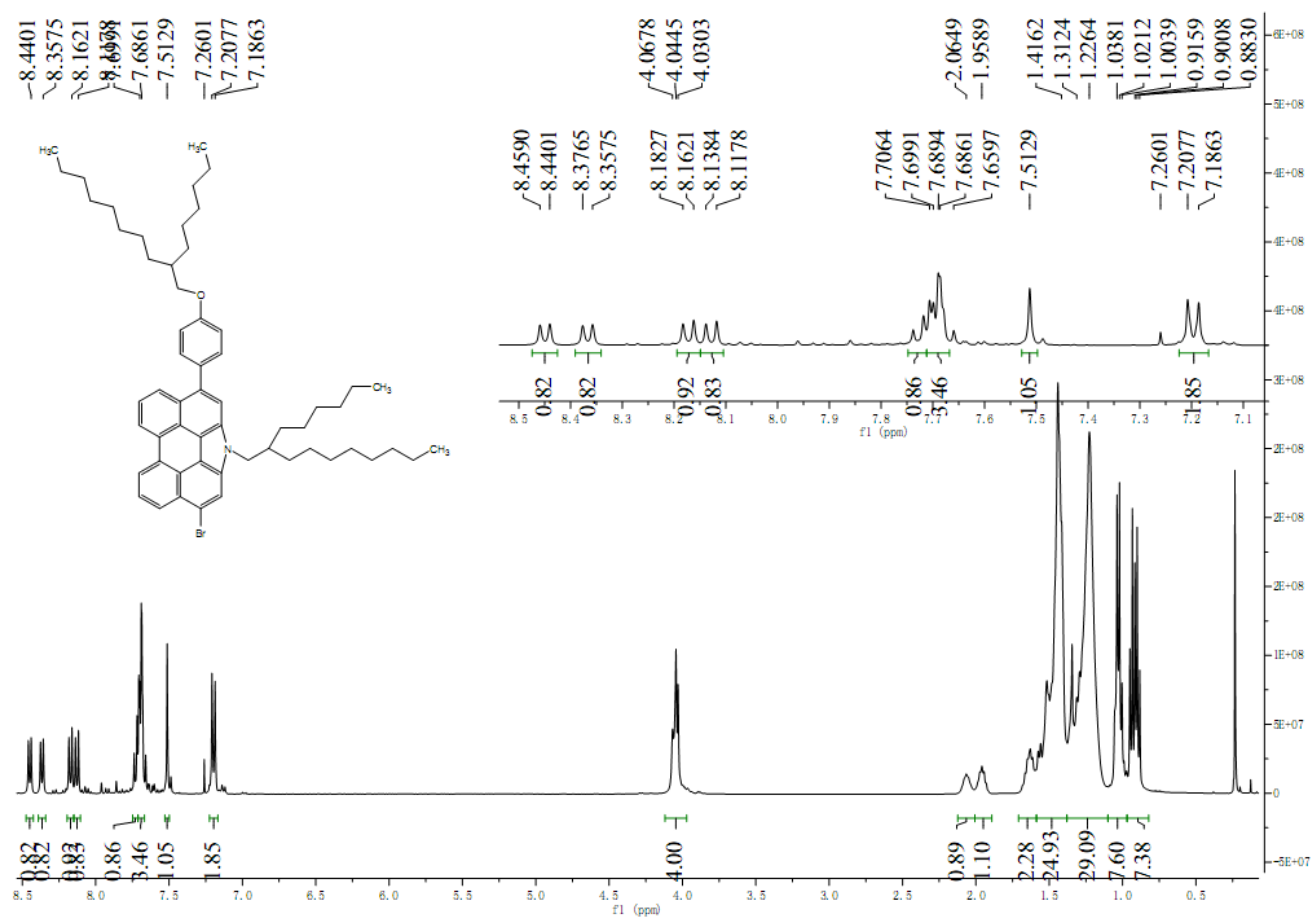


Fig. S17 The ^1H NMR (400 MHz) spectrum of **6** in CDCl_3 .

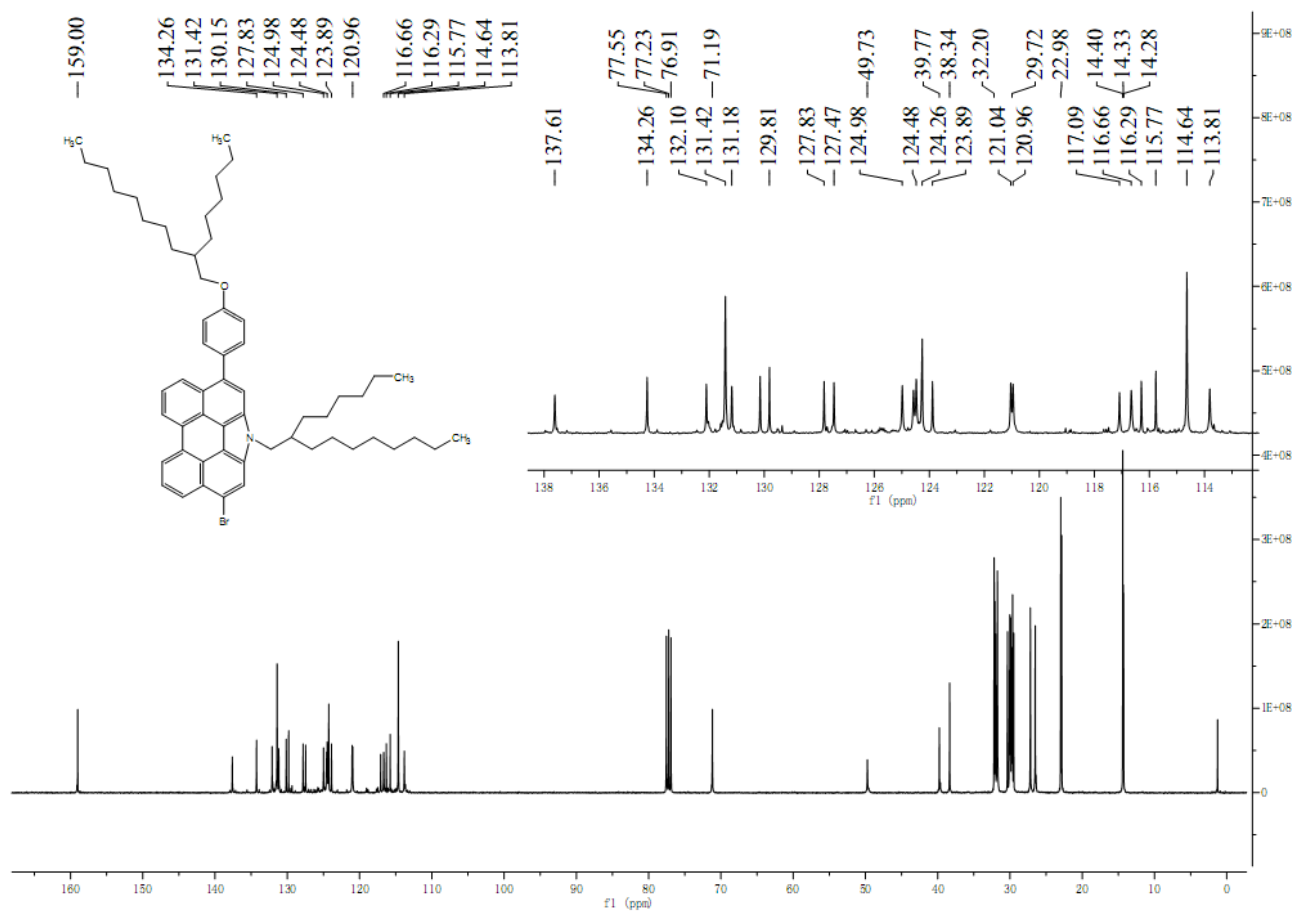


Fig. S18 The ¹³C NMR (100 MHz) spectrum of **6** in CDCl₃.

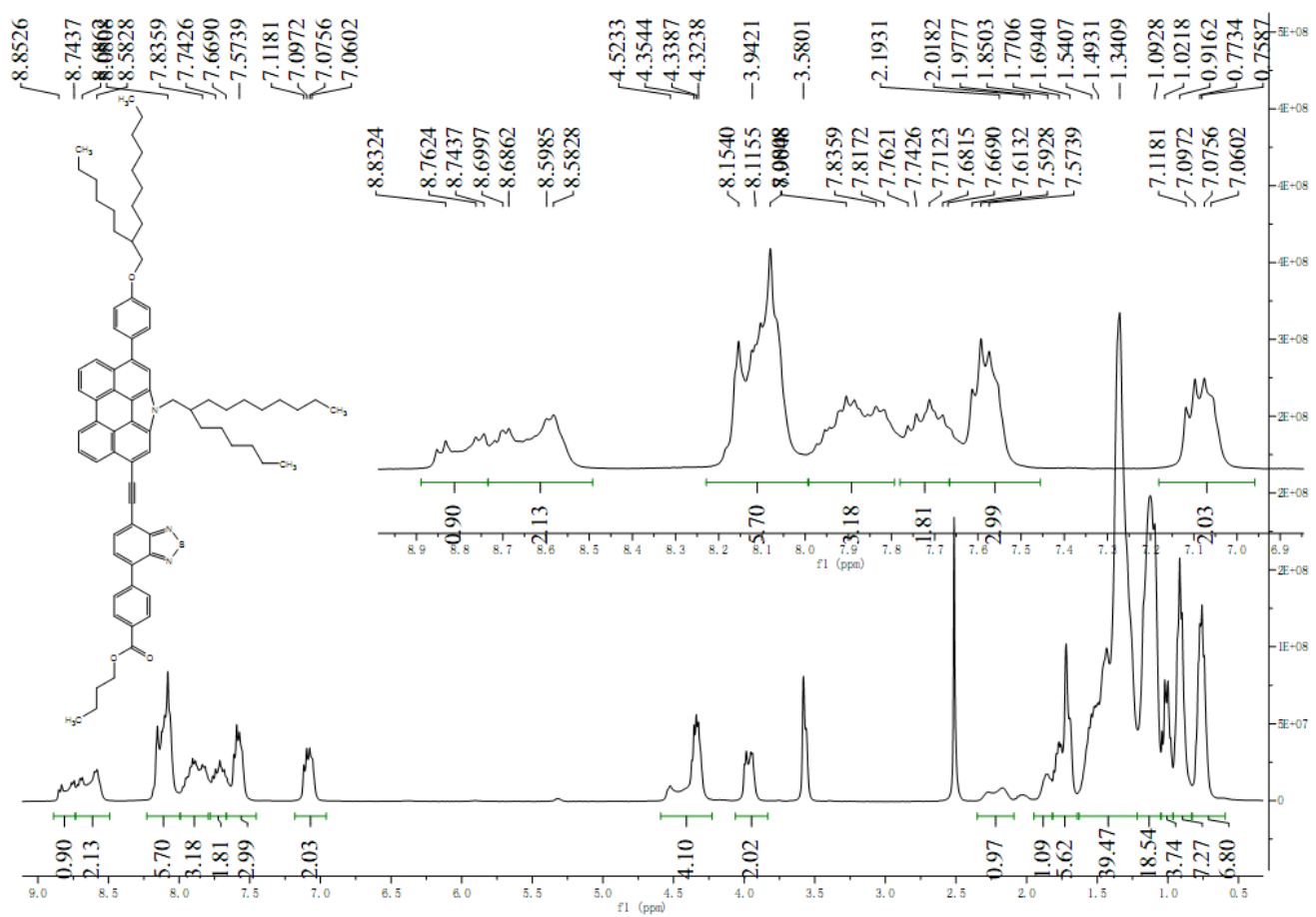


Fig. S19 The ¹H NMR (400 MHz) spectrum of 7 in THF-d₈.

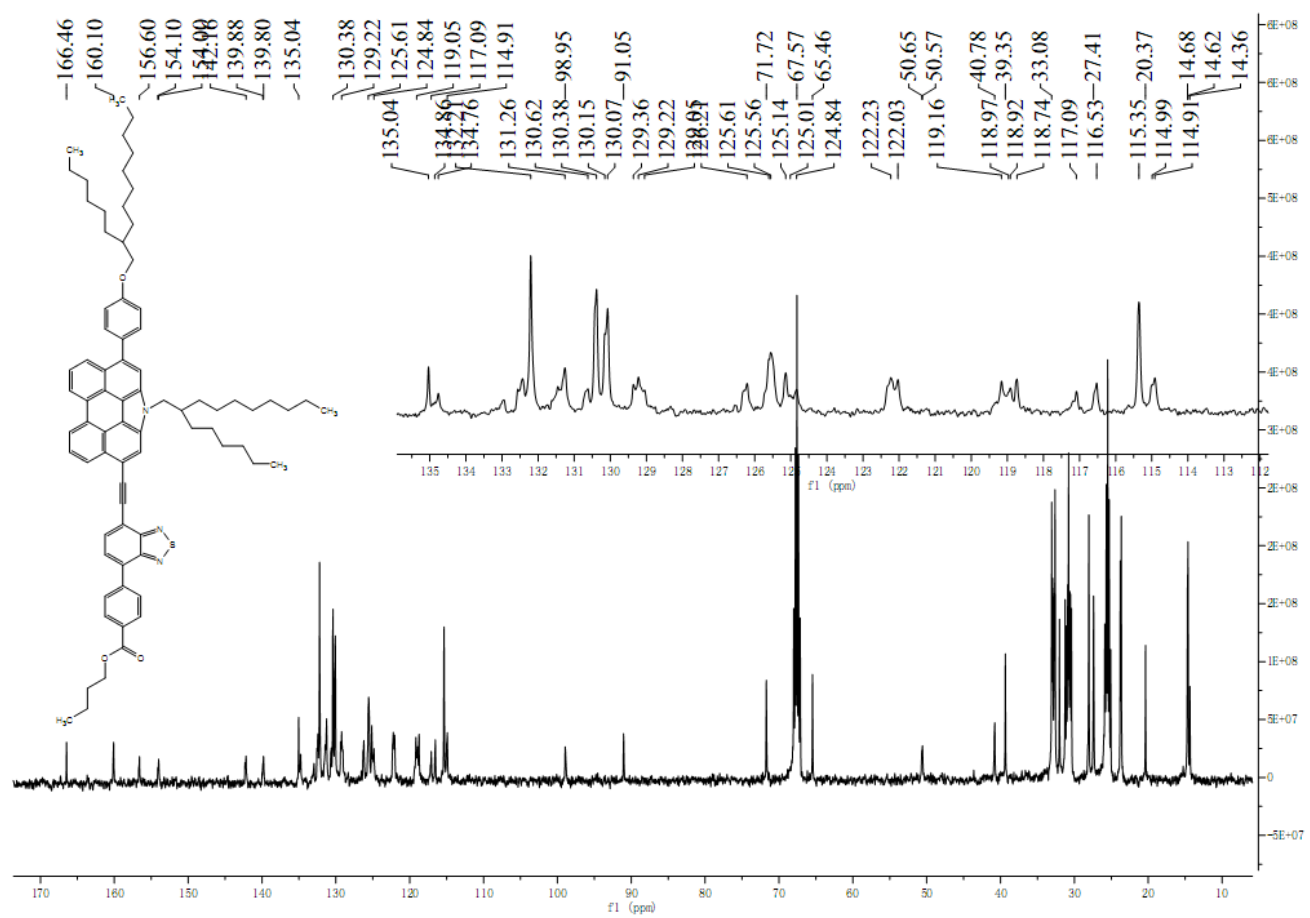


Fig. S20 The ^{13}C NMR (100 MHz) spectrum of **7** in $\text{THF-}d_8$.

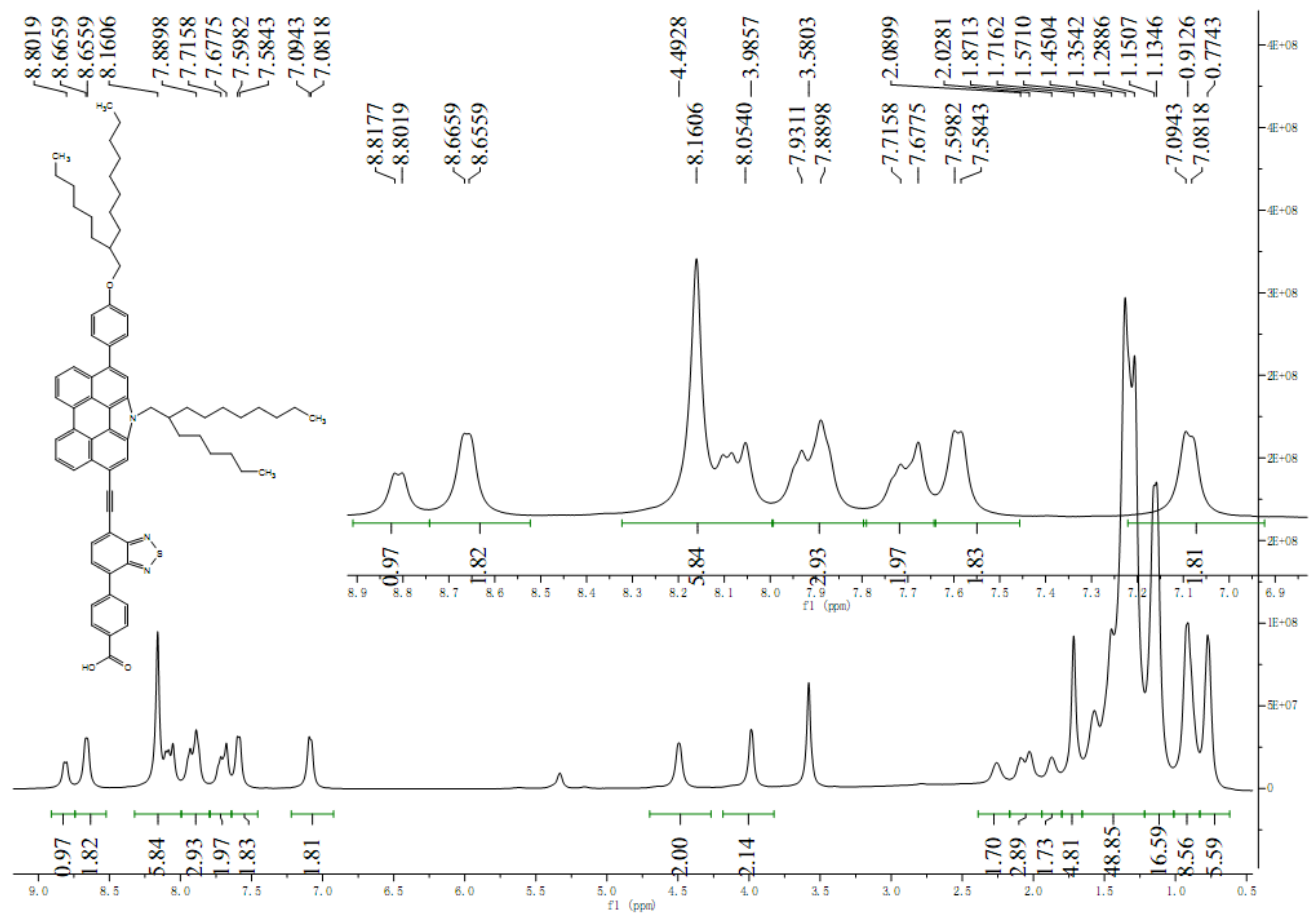


Fig. S21 The ^1H NMR (400 MHz) spectrum of **C272** in $\text{THF-}d_8$.

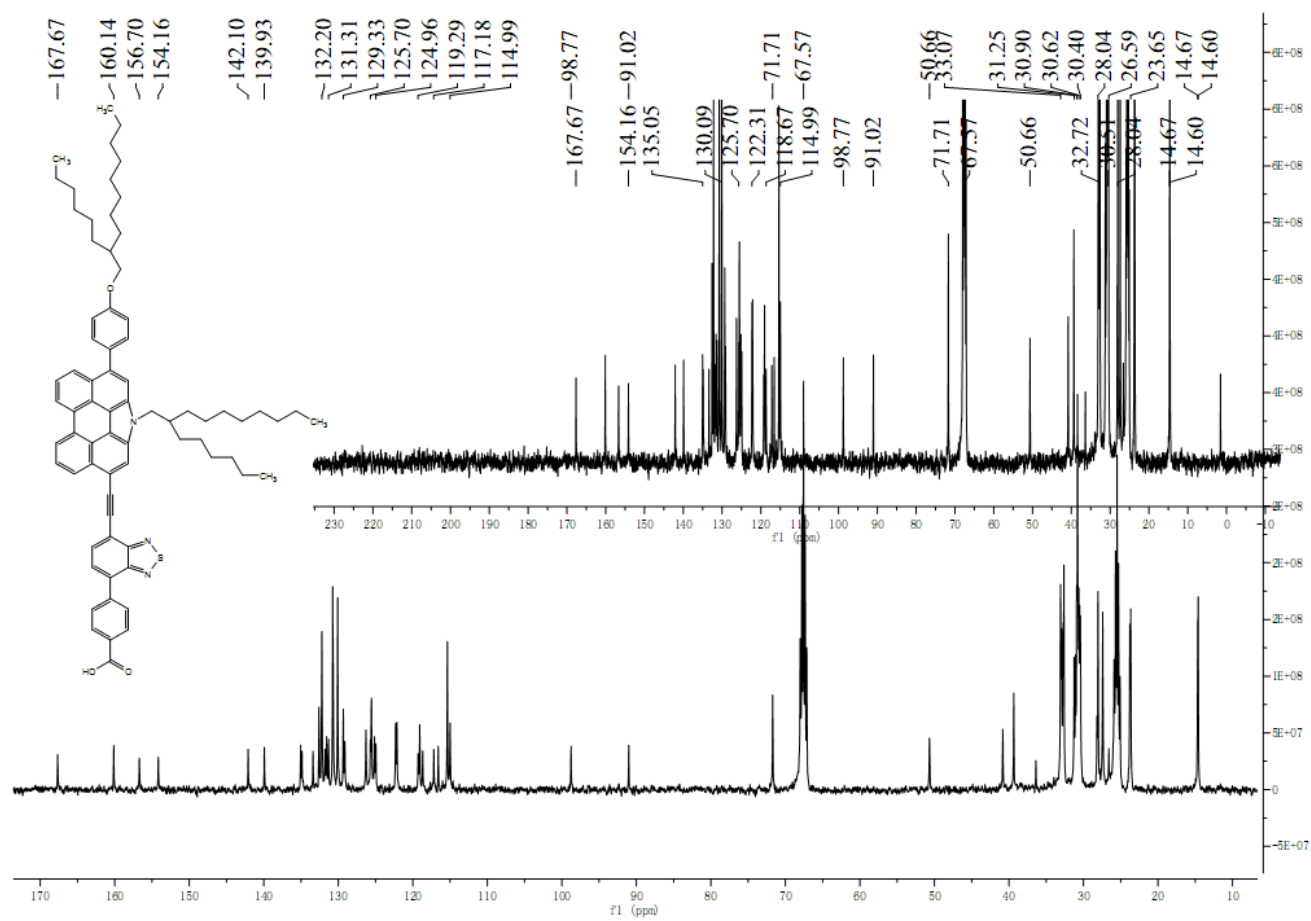


Fig. S22 The ¹³C NMR (100 MHz) spectrum of C272 in THF-*d*₈.