Novel anthracene-based organic dyes as co-sensitizers of porphyrins for developing efficient dye-sensitized solar cells

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Contents

1. Experimental section
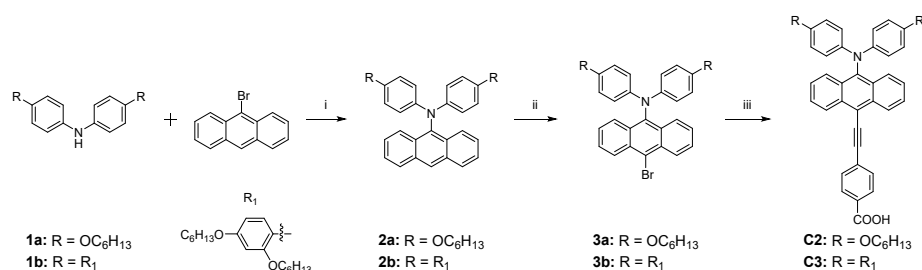
1.1 Materials and Instrumentation

All chemical reagents and solvents of analytical grade were purchased and used without further purification unless otherwise noted. THF was dried over 4 Å molecular sieves and distilled under nitrogen from sodium benzophenone prior to use. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was vacuum-dried for 48 h. The transparent FTO conducting glass (fluorine-doped SnO$_2$, transmission >90% in the visible range, sheet resistance 15 Ω/square) was purchased from Geao Science and Educational Co. Ltd. TiO$_2$ paste (18NR-T and 18NR-AO) was purchased from Dyesol Ltd. The FTO conducting glass was washed with a detergent solution, deionized water, ethanol, and acetone successively under ultrasonication for 20 min before use.

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AM 400 spectrometer at 298 K with tetramethylsilane (TMS) used as the internal standard. High resolution mass spectroscopy (HRMS) measurements were performed using a Waters LCT Premier XE spectrometer. UV-Vis absorption spectra were measured on a Varian Cary 60 spectrophotometer, and fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. The cyclic voltammograms of the dyes were carried out in acetonitrile on a Zahner IM6e electrochemical workstation based on a three electrode system using 0.1 M TBAPF$_6$ (Adamas) as the supporting electrolyte, the sensitizer attached to a nanocrystalline TiO$_2$ film deposited on the conducting FTO glass as the working electrode, a platinum wire as the counter electrode, and a regular saturated calomel electrode (SCE) as the reference electrode. The scan rate was fixed

at 100 mV s^{-1}.

Photovoltaic measurements were performed by employing an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm^{-2} using a Newport Oriel PV reference cell system (model 91150 V). *J–V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a model 2400 source meter (Keithley Instruments, Inc. USA). The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with the frequency range of 0.1 Hz–100 kHz and the alternative signal of 10 mV. The ZSimpWin software was used to fit the experimental EIS data.

1.2 Syntheses of the dyes

1a: R = OC$_6$H$_{13}$
1b: R = R$_1$

2a: R = OC$_6$H$_{13}$
2b: R = R$_1$

3a: R = OC$_6$H$_{13}$
3b: R = R$_1$

C2: R = OC$_6$H$_{13}$
C3: R = R$_1$

Scheme S1. Synthetic routes for **C2** and **C3**. Reaction conditions: (i) Pd$_2$(dba)$_3$, BINAP, *t*-BuONa, xylene; (ii) NBS, CH$_2$Cl$_2$; and (iii) a) methyl 4-ethynylbenzoate, Pd(PPh$_3$)$_2$Cl$_2$, CuI, Et$_3$N, THF; b) LiOH·H$_2$O, THF/H$_2$O.

2a: Under a nitrogen atmosphere, to a solution of **1a** (1.0 g, 2.7 mmol), 9-bromoanthracene (694 mg, 2.7 mmol) in xylene (50 mL) were added $Pd_2(dba)_3$ (163 mg, 0.18 mmol), BINAP (168 mg, 0.27 mmol) and t-BuONa (909 mg, 9.45 mmol). The mixture was stirred overnight at 130 °C. The reaction mixture was suspended in CH_2Cl_2 and washed with water. The aqueous phase was extracted two times with CH_2Cl_2 and the combined organic extracts were dried over Na_2SO_4. The residue was purified by column chromatography on silica gel to give **2a** (1.0 g, yield 68%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 0.87 (t, J = 6.8 Hz, 6H), 1.26-1.31 (m, 8H), 1.36-1.43 (m, 4H), 1.67-1.74 (m, 4H), 3.83 (t, J = 2.8 Hz, 4H), 6.68 (d, J = 8.8 Hz, 4H, phenyl), 6.93 (d, J = 8.8 Hz, 4H, phenyl), 7.34-7.38 (m, 2H, phenyl), 7.40-7.44 (m, 2H, phenyl), 8.03 (d, J = 8.4 Hz, 4H, phenyl), 8.13 (d, J = 8.8 Hz, 4H, phenyl), 8.45 (s, 1H, phenyl). HRMS (ESI, m/z): [M+H]$^+$ calcd for $C_{38}H_{44}NO_2$, 546.3372; found, 546.3363.

2b: It was prepared according to the procedure same as that for **2a**, except that **1b** (2.0 g, 2.7 mmol) was used instead of **1a**. Yield: 1.9 g, 79%. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 0.81 (t, J = 7.2 Hz, 6H), 0.90 (t, J = 7.2 Hz, 6H), 1.21-1.26 (m, 8H), 1.31-1.35 (m, 12H), .142-1.49 (m, 4H), 1.64-1.71 (m, 4H), 1.73-1.80 (m, 4H), 3.90 (t, J = 6.4 Hz, 4H), 3.95 (t, J = 6.4 Hz, 4H), 6.47-6.49 (m, 4H, phenyl), 7.09 (d, J = 8.8 Hz, 4H, phenyl), 7.17 (d, J = 8.8 Hz, 2H, phenyl), 7.32 (d, J = 8.8 Hz, 4H, phenyl), 7.37-7.41 (m, 2H, phenyl), 7.43-7.47 (m, 2H, phenyl), 8.06 (d, J = 8.4 Hz, 2H, phenyl), 8.20 (d, J = 8.4 Hz, 2H, phenyl), 8.51 (s, 1H, phenyl). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.04, 14.09, 22.53, 22.66, 25.73, 25.80, 29.08, 29.34, 31.47, 31.65, 53.46, 68.09, 68.40, 100.46, 105.24, 119.62, 123.23, 124.71, 125.49, 126.60, 126.71, 128.80, 130.08,

130.73, 130.84, 131.10, 132.83, 137.40, 146.06, 156.94, 159.32. HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{62}$H$_{76}$NO$_4$, 898.5774; found, 898.5779.

3a: To a solution of **2a** (786 mg, 1.44 mmol) in CH$_2$Cl$_2$ (10 mL) was added NBS (308 mg, 1.73 mmol). The mixture was stirred for another 1 h at room temperature. Then the reaction mixture was quenched with acetone (1 mL). The solvent was concentrated and the residue was purified by column chromatography on silica gel to give **3a** (270 mg, yield 30%). ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 0.87 (t, J = 6.8 Hz, 6H), 1.27-1.31 (m, 8H), 1.36-1.43 (m, 4H), 1.67-1.74 (m, 4H), 3.83 (t, J = 2.8 Hz, 4H), 6.68 (d, J = 8.8 Hz, 4H, phenyl), 6.92 (d, J = 8.8 Hz, 4H, phenyl), 7.40 (t, J = 6.4 Hz, 2H, phenyl), 7.55 (t, J = 8.0 Hz, 2H, phenyl), 8.16 (d, J = 8.8 Hz, 4H, phenyl), 8.58 (d, J = 8.8 Hz, 4H, phenyl). HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{38}$H$_{43}$BrNO$_2$, 624.2477; found, 624.2477.

3b: It was prepared according to the procedure same as that for **3a**, except that **2b** (1.1 g, 1.22 mmol) was used instead of **2a**. Yield: 600 mg, 23%. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 0.81 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 7.2 Hz, 6H), 1.20-1.48 (m, 24H), 1.64-1.78 (m, 8H), 3.87-3.94 (m, 8H), 6.45-6.50 (m, 4H, phenyl), 7.09 (d, J = 8.8 Hz, 4H, phenyl), 7.16 (d, J = 8.8 Hz, 2H, phenyl), 7.34 (d, J = 8.8 Hz, 4H, phenyl), 7.39-7.43 (m, 2H, phenyl), 7.52-7.56 (m, 2H, phenyl), 8.24 (d, J = 8.8 Hz, 2H, phenyl), 8.60 (d, J = 8.4 Hz, 2H, phenyl). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.10, 14.15, 22.61, 22.72, 25.80, 25.86, 29.15, 29.40, 31.53, 31.71, 53.50, 68.12, 68.43, 100.50, 105.32, 119.70, 122.52, 123.10, 125.21, 127.02, 127.37, 128.44, 130.22, 130.78, 131.48, 131.69, 131.76, 138.07, 145.89, 156.99, 159.46. HRMS (ESI, m/z): [M+H]$^+$ calcd for

$C_{62}H_{75}BrNO_4$, 976.4879; found, 976.48767.

C2: To a solution of **3a** (130 mg, 0.2 mmol), methyl 4-ethynylbenzoate (50 mg, 0.31mmol), in dry THF (5 mL) and Et_3N (1 mL) were added CuI (25 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). The mixture was flushed with nitrogen and stirred at 55 °C for 4.5 h. Then, the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was purified on a silica gel column to give 120 mg crude intermediate. Then the intermediate (120 mg, 0.17 mmol) in THF (5 mL) was mixed with $LiOH·H_2O$ (286 mg, 6.82 mmol) in H_2O (2 mL), and the mixture was heated to reflux for 12 h under nitrogen. Then, the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was purified on a silica gel column to give the desired product (100 mg, yield 72 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.88 (t, J = 6.8 Hz, 6H), 1.25-1.32 (m, 8H), 1.37-1.44 (m, 4H), 1.68-1.75 (m, 4H), 3.84 (t, J = 6.8 Hz, 4H), 3.96 (s, 3H, OMe), 6.70 (d, J = 8.8 Hz, 4H, phenyl), 6.95 (d, J = 8.8 Hz, 4H, phenyl), 7.42 (t, J = 6.4 Hz, 2H, phenyl), 7.58 (t, J = 8.0 Hz, 2H, phenyl), 7.87 (d, J = 8.4 Hz, 4H, phenyl), 8.17 (d, J = 8.0 Hz, 4H, phenyl), 8.21 (d, J = 8.8 Hz, 4H, phenyl), 8.69 (d, J = 8.8 Hz, 4H, phenyl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.05, 22.62, 25.77, 29.36, 31.62, 50.84, 68.33, 89.97, 100.39, 115.29, 121.43, 125.30, 126.77, 126.92, 127.27, 129.10, 130.40, 130.49, 131.63, 134.14, 139.98, 141.96. HRMS (ESI, m/z): [M-H]$^-$ calcd for $C_{47}H_{46}NO_4$, 688.3427; found, 688.34436.

C3: It was prepared according to the procedure same as that for **C2**, except that **3b**

(600 mg, 0.6 mmol) was used instead of **3a**. Yield: 175 mg, 33%. ^{1}H NMR (CDCl$_3$,

400 MHz, ppm): δ 0.82 (t, J = 7.2 Hz, 6H), 0.90 (t, J = 7.2 Hz, 6H), 1.22-1.35 (m, 20H),

1.42-1.47 (m, 4H), 1.65-1.72 (m, 4H), 1.74-1.79 (m, 4H), 3.91 (t, J = 6.4 Hz, 3H), 3.95

(t, J = 6.4 Hz, 3H), 6.47-6.50 (m, 4H, phenyl), 7.10 (d, J = 8.8 Hz, 4H, phenyl), 7.19

(d, J = 8.0 Hz, 2H, phenyl), 7.35 (d, J = 8.8 Hz, 4H, phenyl), 7.46 (t, J = 8.0 Hz, 2H,

phenyl), 7.61 (t, J = 8.0 Hz, 2H, phenyl), 7.82 (d, J = 8.4 Hz, 2H, phenyl), 8.23 (m, 4H,

phenyl), 8.72 (d, J = 8.8 Hz, 2H, phenyl). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.06, 14.09,

22.56, 22.66, 25.74, 25.79, 29.08, 29.34, 29.75, 31.47, 31.64, 68.10, 68.40, 89.98,

100.45, 105.27, 116.64, 119.81, 123.07, 125.35, 127.00, 127.21, 128.87, 129.14,

130.20, 130.40, 130.57, 130.74, 131.48, 131.65, 134.06, 139.38, 146.01, 156.94,

159.39. HRMS (ESI, m/z): [M-H]$^-$ calcd for C$_{71}$H$_{79}$NO$_6$, 1040.5829; found,

1040.58276.

1.3 Fabrication of the solar cells

The procedure for preparation of TiO$_2$ electrodes and fabrication of the sealed cells

for photovoltaic measurements were adapted from that reported by Grätzel and

coworkers.[1] The photoelectrode was made by a screen-printed double layer of TiO$_2$

particles. A 6 μm thick film (for cobalt-based electrolyte) or 10 μm thick film (for

iodine-based electrolyte) of 18-nm-sized TiO$_2$ particles was first printed on the FTO

conducting glass, which was kept in a clean box for 10 minutes, and then dried at 130

°C over 5 min, and further coated with a 3-μm thick second layer of 400-nm light-

scattering anatase particles. Finally, the electrodes coated with the TiO$_2$ pastes were

gradually sintered in a muffle furnace at 275 °C for 5 min, at 325 °C for 5 min, at 375

°C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min, respectively. The size of the TiO$_2$ film was 0.12 cm^2. These films were immersed into a 40 mM aqueous TiCl$_4$ solution at 70 °C for 30 min, washed with water and ethanol, and then heated again at 450 °C for 30 min. The films were then immersed into 0.3 mM solutions of the dyes in a mixture of chloroform and ethanol (3/2, v/v) at 25 °C for 12 h. The counter electrode was prepared according to the procedure reported in our previous work.[2] Finally, the DSSCs were assembled, with a cobalt electrolyte. The cobalt electrolyte is composed of 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 0.5 M 4-tert-butylpyridine (TBP), 0.06 M cobalt(II) tris(2,2'-bipyridine)di[bis(trifluoromethane-sulfonyl)imide] and 0.25 M cobalt(III) tris(2,2'-bipyridine)tris[bis(trifluoromethane-sulfonyl)imide] in CH$_3$CN. For the iodine electrolyte based cells, the TiO$_2$ film consists of 15μm thick film of 13-nm-sized TiO$_2$ particles and 3 μm thick of 400-nm light-scattering anatase particles. The iodine electrolyte is composed of 0.1 M LiI, 0.05 M I$_2$, 0.5 M TBP and 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII) in CH$_3$CN.

For sequential cosensitization, the TiO$_2$ films were first immersed in 0.3 mM solutions of the **C1−C3** in ethanol for 10 h. Then, ethanol was utilized to wash the films, followed by drying in air, and the films were then immersed in a solution of ethanol and toluene (volume ratio of 4:1) containing 0.2mM of **XW66** at 298K for 2 h. At last, the DSSCs were assembled with the cobalt electrolyte.

Dye loading amount measurements

The dye loading amounts were estimated spectroscopically by desorbing the dyes

into 0.1 M solutions of NaOH in THF / H_2O.

1.4 Theoretical calculation details

We employed density functional theory (DFT) calculations to optimize the ground state geometries of the sensitizers, using the hybrid B3LYP functional[3,4] and the 6-31G* basis set[5]. For zinc atoms, the Los Alamos effective core potential basis set (LANL2DZ) was used[6]. All calculations were carried out using the Gaussian09 program package[7].

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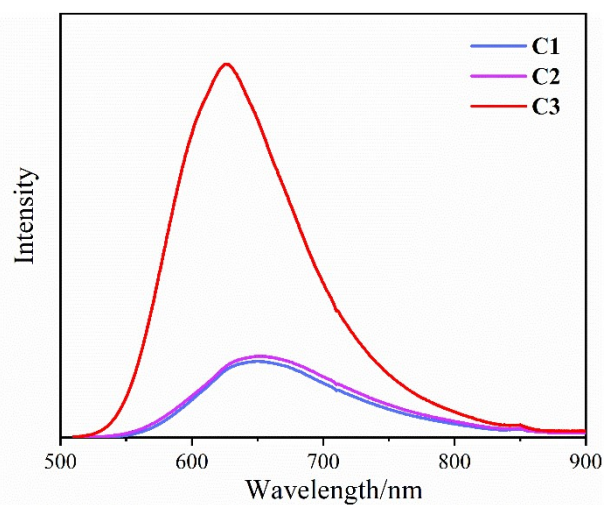
2. Emission spectra

Fig. S1 Emission spectra of **C1**–**C3** in THF. The spectra were used to calculate the wavelengths at the intersection (λ_{inter}) of normalized absorption and emission spectra, and the corresponding E_{0-0} values. Excitation wavelengths: 498 nm (**C1**), 512 nm (**C2**), 498 nm (**C3**).
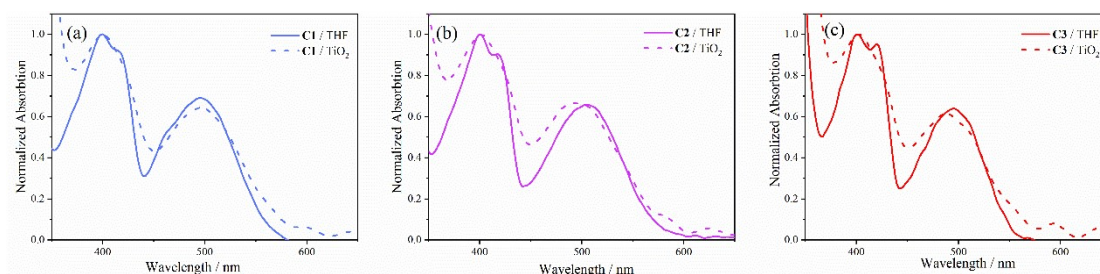
3. Normalized absorption spectra

Fig.S2 Absorption spectra of **C1**−**C3** adsorbed on transparent TiO$_2$ films (3 μm).

4. Cyclic voltammetry curves
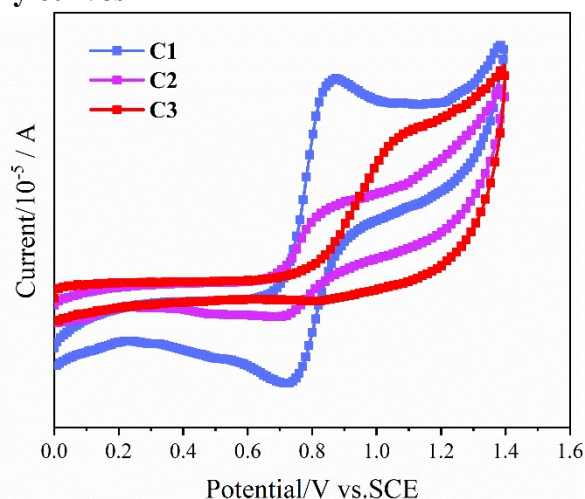
Fig. S3 Cyclic voltammetry curves of **C1**−**C3** adsorbed on the TiO$_2$ films.

Table S1 Electrochemical data of **C1**−**C3**.

Dyes	E_{0-0}, eV[a]	E_{ox}, V[b] (vs NHE)	E_{ox}*, V[c] (vs NHE)
C1	2.18	0.79	-1.39
C2	2.18	0.79	-1.39
C3	2.24	0.94	-1.30

[a] E_{0-0} was estimated from the wavelength at the intersection (λ_{inter}) of normalized absorption and emission spectra using the equation $E_{0-0} = 1240/\lambda_{inter}$.

[b] E_{ox} was obtained from the first oxidation potential measured in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the electrolyte (working electrode: FTO/TiO$_2$/dye; reference electrode: SCE; counter electrode: Pt). Potentials measured vs. ferrocene/ferrocenium (Fc/Fc$^+$) were converted to normal hydrogen electrode (NHE) by addition of +0.63 V.

[c] E_{ox}* was estimated from the equation E_{ox}* = E_{ox} − E_{0-0}.

5. Simulated absorption spectra
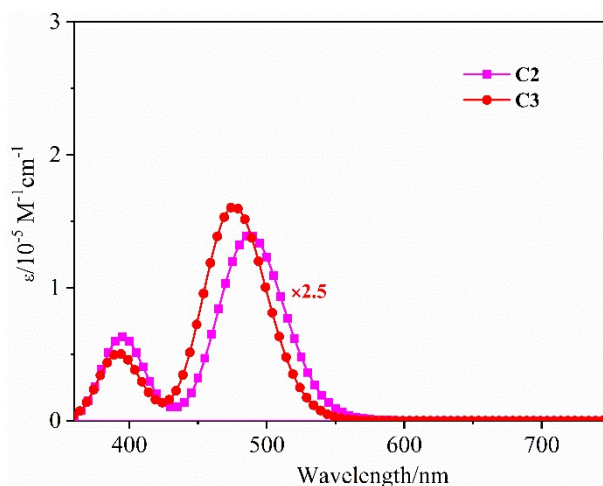
Fig. S4 The calculated absorption spectra of **C2** and **C3**.

6. Computed molecular orbital properties

Table S2 Computed energy levels of frontier molecular orbitals for **C2** and **C3**.

	C2	**C3**
$E_{\text{HOMO-1}}$ (eV)	-5.33	-5.24
E_{HOMO} (eV)	-4.70	-4.67
E_{LUMO} (eV)	-2.27	-2.24
$E_{\text{LUMO+1}}$ (eV)	-1.37	-1.34
HOMO-LUMO gap	2.43	2.43

Table S3 Calculated excitation energies, wavelengths, oscillator strengths and molecular orbital compositions for the lowest excited states of the sensitizer dyes.

Compound	Excited state	Excitation energy	Oscillator strength	MO composition
C2	S1	2.54 eV, 488 nm	0.602	H-0→L+0 (89%)
C3	S1	2.60 eV, 477 nm	0.695	H-0→L+0 (84%)
				H-1→L+0 (6%)

7. Optimized structures
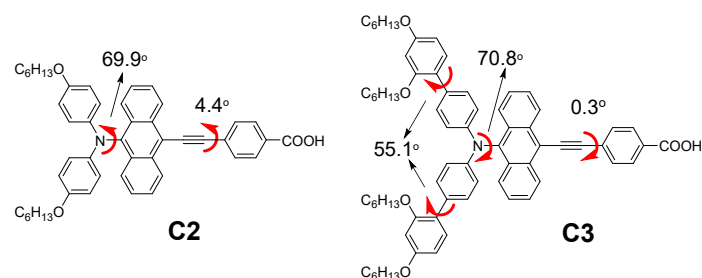
Fig. S5 The optimized dihedral angles for **C2** and **C3**.

8. Dye loading amounts

Table S4 The dye loading amounts for the cells based on individual dyes of **C1–C3** and the corresponding cosensitization systems.

Dyes	Organic dyes (10^{-7} mol·cm^{-2})	Porphyrin dyes (10^{-7} mol·cm^{-2})
C1	2.46	–
C2	2.34	–
C3	2.12	–
C1+XW66	1.52	0.45
C2+XW66	1.44	0.63
C3+XW66	1.30	0.77
XW66	–	2.10

9. The photovoltaic data for the DSSCs

Table S5 Photovoltaic parameters of **C1–C3** sensitized solar cells using an I$^-$/I$_3^-$ electrolyte.

Dyes	V_{oc} / V	J_{sc} / mA cm^{-2}	FF / %	PCE / %	Dye loading amount / $\times 10^{-7}$ mol/cm^{-2}
C1	0.738 ± 0.004	11.94 ± 0.03	70.36 ± 0.35	6.20 ± 0.01	4.74
C2	0.737 ± 0.006	12.08 ± 0.50	73.21 ± 0.94	6.52 ± 0.23	5.15
C3	0.761 ± 0.006	11.23 ± 0.25	71.83 ± 0.34	6.14 ± 0.08	4.10

Table S6 Detailed photovoltaic parameters for the cells based on **C1–C3** coadsorbed with CDCA.

Dyes	CDCA	V_{oc} / V	J_{sc} / mA cm^{-2}	FF / %	PCE / %	Dye loading amount / $\times 10^{-7}$ mol/cm^{-2}
C1	0	0.843 ± 0.005	11.92 ± 0.13	74.20 ± 0.31	7.46 ± 0.07	2.46
	2 mM	0.846 ± 0.004	11.87 ± 0.25	74.05 ± 0.27	7.44 ± 0.29	2.30
	5 mM	0.847 ± 0.008	11.79 ± 0.14	75.31 ± 0.25	7.52 ± 0.23	2.25
	10 mM	0.841 ± 0.004	11.66 ± 0.28	73.98 ± 0.39	7.25 ± 0.32	2.15
C2	0	0.831 ± 0.005	13.03 ± 0.38	70.14 ± 0.27	7.59 ± 0.24	2.34
	2 mM	0.843 ± 0.008	12.95 ± 0.10	71.16 ± 0.16	7.77 ± 0.28	2.27
	5 mM	0.852 ± 0.002	12.89 ± 0.29	71.41 ± 0.31	7.84 ± 0.20	2.10
	10 mM	0.845 ± 0.007	12.66 ± 0.37	71.59 ± 0.33	7.66 ± 0.11	1.98
C3	0	0.857 ± 0.002	13.23 ± 0.12	78.93 ± 1.49	8.95 ± 0.12	2.12
	2 mM	0.859 ± 0.002	12.86 ± 0.22	74.83 ± 0.37	8.27 ± 0.32	2.07
	5 mM	0.863 ± 0.004	12.73 ± 0.12	74.57 ± 0.21	8.19 ± 0.31	2.01
	10 mM	0.854 ± 0.005	12.45 ± 0.39	74.44 ± 0.34	7.91 ± 0.23	1.91

10. Characterization data for the compounds
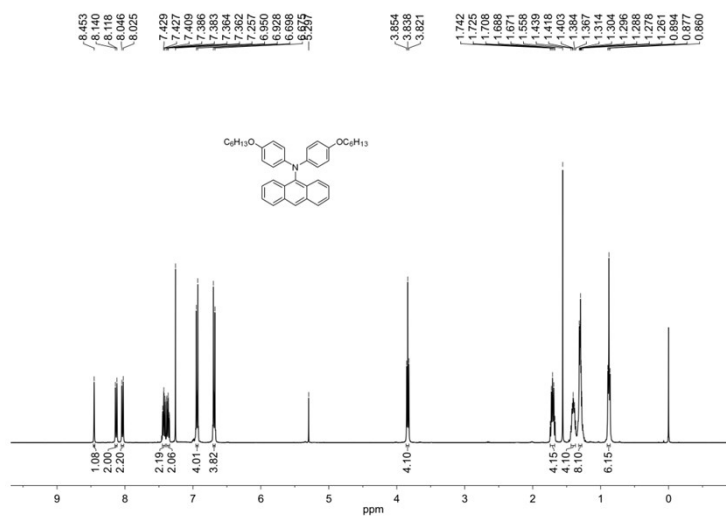
Fig. S6 The ^{1}H NMR spectrum of **2a** in CDCl$_3$
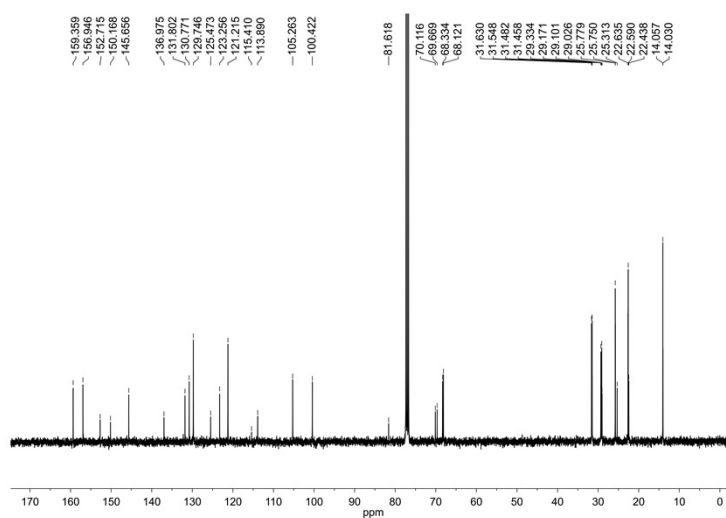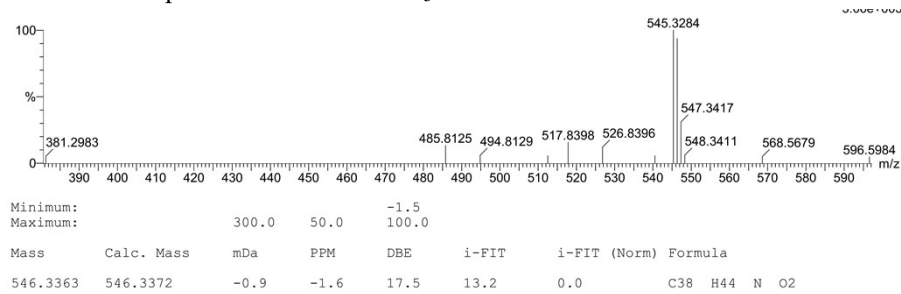

Fig. S7 The ^{13}C NMR spectrum of **2a** in CDCl$_3$

Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
546.3363	546.3372	-0.9	-1.6	17.5	13.2	0.0	C38 H44 N O2

Fig. S8 The HRMS spectrum of **2a**
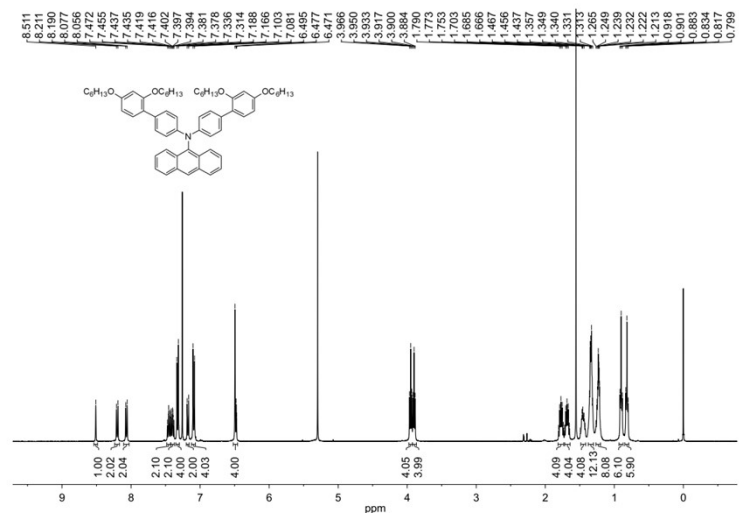
Fig. S9 The ^{1}H NMR spectrum of **2b** in CDCl$_3$
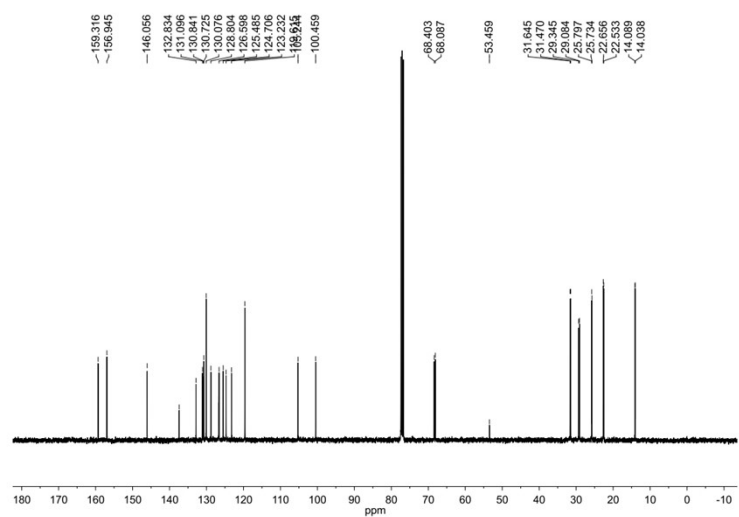
Fig. S10 The ^{13}C NMR spectrum of **2b** in CDCl$_3$

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
898.5779	898.5774	0.5	0.6	25.5	15.6	0.0	C62 H76 N O4
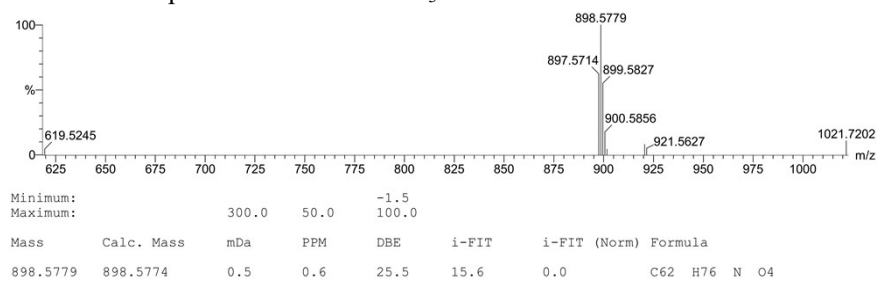
Fig. S11 The HRMS spectrum of **2b**
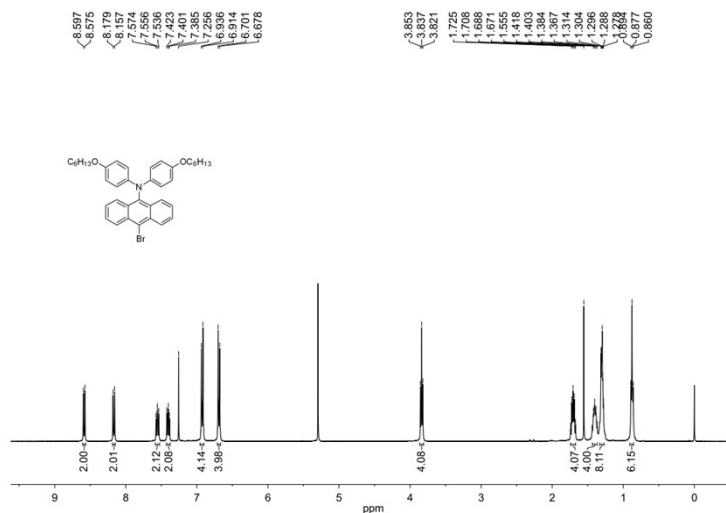
Fig. S12 The ^{1}H NMR spectrum of **3a** in CDCl$_3$
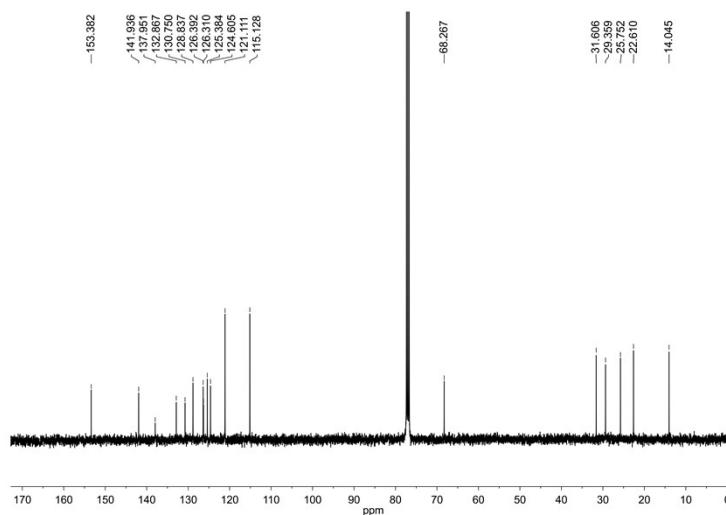
Fig. S13 The ^{13}C NMR spectrum of **3a** in CDCl$_3$

Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
624.2477	624.2477	0.0	0.0	17.5	56.0	0.0	C38 H43 N O2 Br
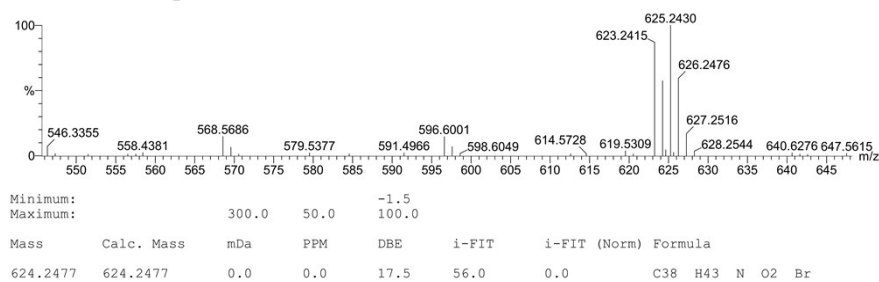
Fig. S14 The HRMS spectrum of **3a**
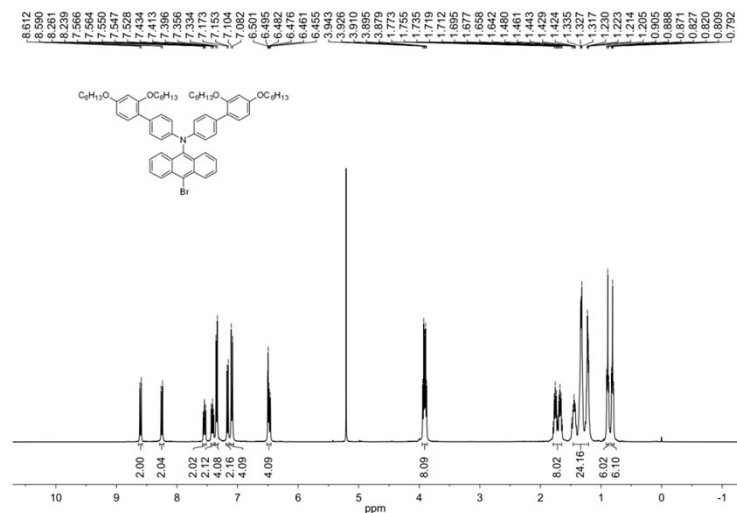
Fig. S15 The ^{1}H NMR spectrum of **3b** in CDCl$_3$
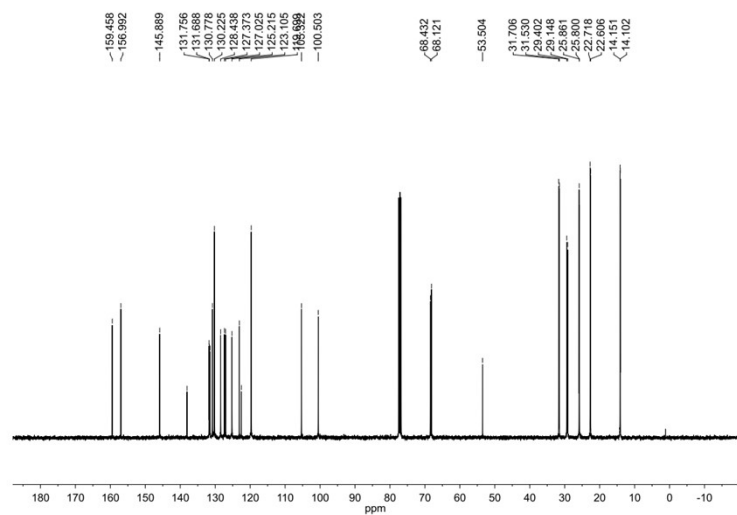
Fig. S16 The ^{13}C NMR spectrum of **3b** in CDCl$_3$
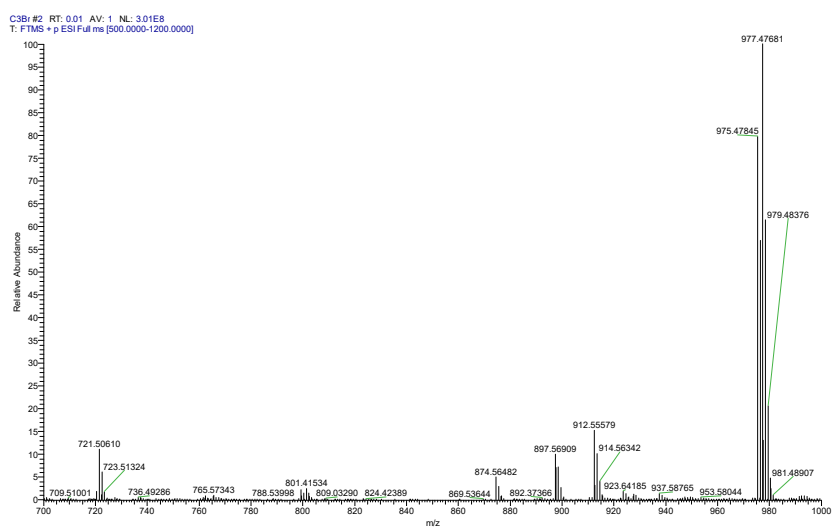
Fig. S17 The HRMS spectrum of **3b**.
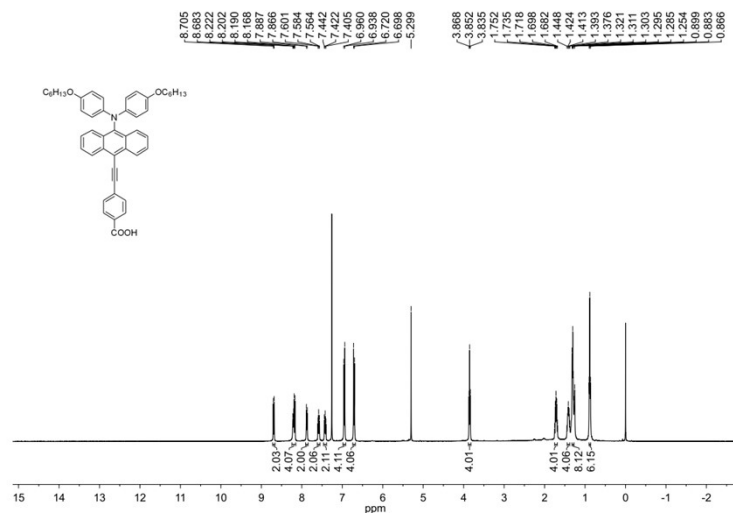
Fig. S18 The ^{1}H NMR spectrum of **C2** in CDCl$_3$.
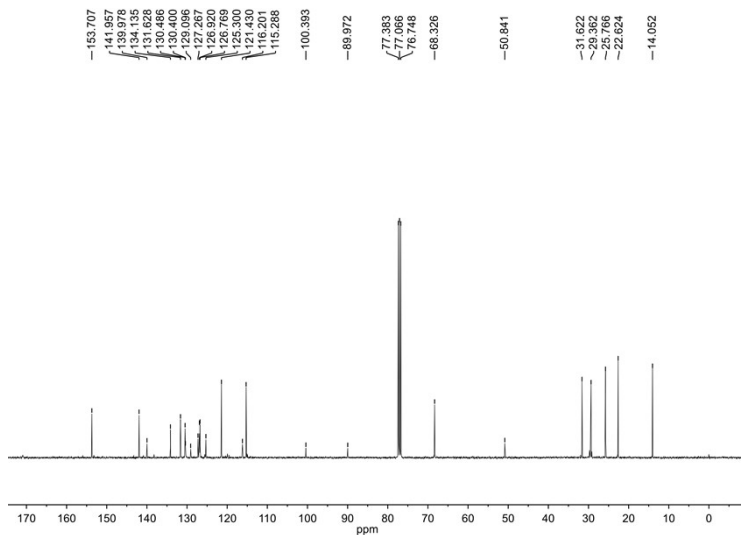
Fig. S19 The ^{13}C NMR spectrum of **C2** in CDCl$_3$.
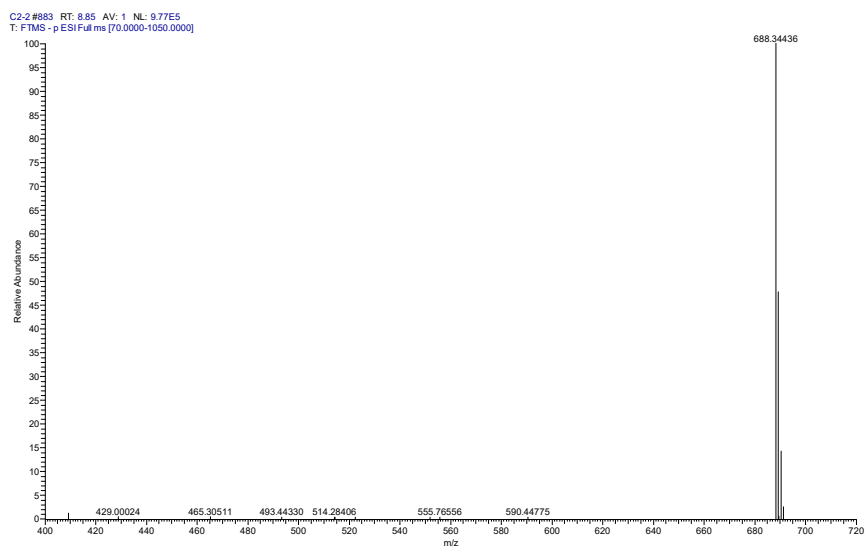
Fig. S20 The HRMS spectrum of **C2**.
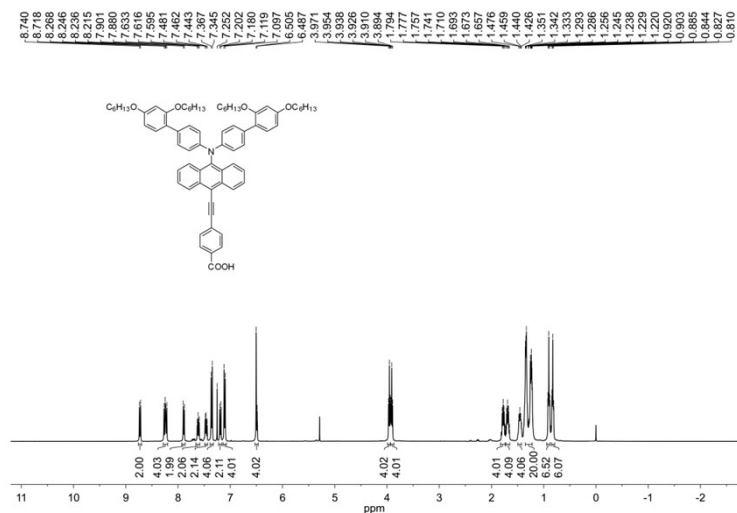
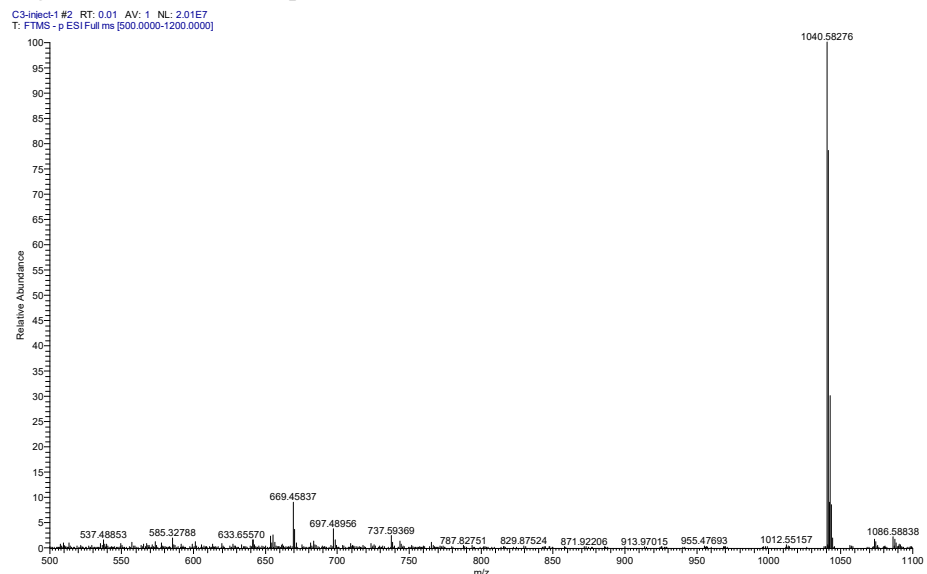Fig. S21 The ^{1}H NMR spectrum of **C3** in CDCl$_3$
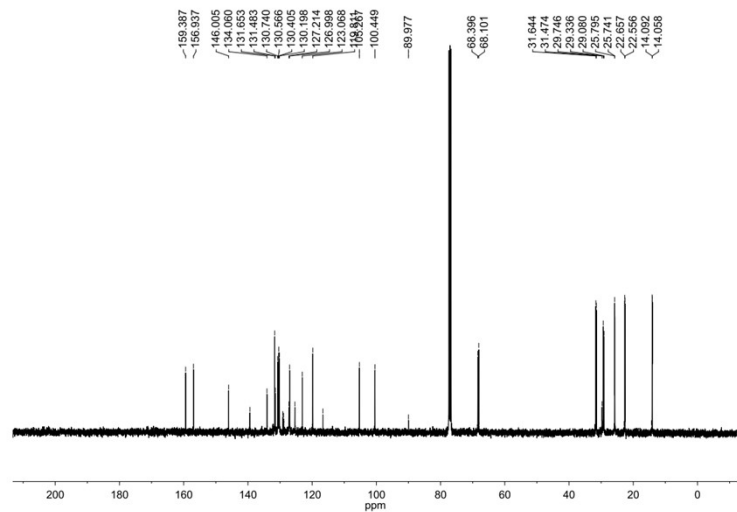
Fig. S22 The ^{13}C NMR spectrum of **C3** in CDCl$_3$

Fig. S23 The HRMS spectrum of **C3**.