Deciphering Donor-Acceptor Order: Impact of Acceptor Positioning on the Optical Properties of Anthraquinone-Carbazole-Cyanostilbenes

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1. Materials and Measurements

The starting material for the synthetic scheme carbazole, and the chemicals including bromohexane, bis(pinacolato)diboron, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0), benzylcyanide, 2-(4-bromophenyl)acetonitrile, 2-bromoanthracene-9,10-dione, N-Bromosuccinimade, KOAc, NaOH, K_2CO_3, phosphorus oxychloride, dichloroethane, chloroform, tetrahydrofuran and methanol were purchased and used as received. DMF and Toluene was dried by storing it over 4 Å molecular sieves that had been activated by heating in a preheated 150 ºC oven. Dichloroethane were dried over CaH_2, distilled and subsequently stored over 4 Å molecular sieves. Reactions sensitive to oxygen or moisture were conducted under a nitrogen atmosphere. Reflux reactions were carried out using a heating reaction block equipped with a temperature-controlled probe. All chromatographic purifications were done using silica gel (100−200 mesh). The ^{1}H and ^{13}C NMR spectra of the synthesized compounds were recorded on a JEOL JNM-ECZ-500R/M1 (500 MHz) NMR spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal reference. High-resolution mass spectrometry (HRMS) data were acquired on a Waters Synapt XS spectrometer in positive ion mode, with a fragmentor voltage of 3.01 kV, cone voltage of 35 V, source offset of 4.0 V, source temperature of 120 ºC, and cone gas flow rate of 50 L/h, and the ion values are reported as *m/z*. UV-visible absorption spectra were measured using a SHIMADZU-2600 spectrophotometer, maintaining a slit width of 2 nm. Fluorescence measurements were conducted on a PerkinElmer 6500 fluorescence spectrometer. X-ray diffraction (XRD) patterns in the 2θ range of 5º to 50º were recorded on a PANalytical X'Pert3 powder X-ray diffractometer, employing a CuKα radiation source (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were obtained using a ZEISS Gemini Sigma 300 instrument, while dynamic light scattering (DLS) measurements of aggregates were performed on the STABINO ZETA analyzer. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G(d,p) level using the Gaussian 09W software package. Thermogravimetric analysis (TGA) was performed on a PerkinElmer STA 8000 thermal analyzer, and differential scanning calorimetry (DSC) curves were recorded using a DSC Q20 V24.11 Build 124 model. Absolute quantum yields were determined using an integrating sphere.

2. Experimental Section

The synthesis of compounds **1–4** was carried out following the established protocols from our previous work.[1]

Synthesis of 6-(9,10-dioxo-9,10-dihydroanthracen-2-yl)-9-hexyl-9H-carbazole-3-carbaldehyde (**5**)

To a 100 ml Schlenk flask 9-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole-3-carbaldehyde (1.5 g, 3.7 mmol), 2-bromoanthracene-9,10-dione (1.16 g, 4.07 mmol), and potassium carbonate (2 M, 5 mL) were dissolved in tetrahydrofuran (50 mL). The reaction mixture was degassed using N_2 gas for 30 minutes then tetrakis (triphenylphosphine) palladium (0) $Pd(PPh_3)_4$ (50 mg, 0.037 mmol) catalyst was added to the reaction mixture. The reaction mixture was refluxed for 24 h under N_2 atmosphere. After removing the volatiles, the crude product was extracted using DCM/water and brine solution. The organic layer collected were dried over sodium sulfate. The crude product obtained upon concentrating under reduced pressured was purified using column chromatography with hexane/EtOAc as eluents. The pure product was obtained by further washing with hot methanol, yielding a yellowish orange solid powder (1.62 g, 90 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.57 (s, 1H), 8.47 (s, 1H), 8.34 (s, 1H), 8.23 (dd, *J* = 12.7, 6.2 Hz, 3H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.39 (dd, *J* = 14.3, 7.3 Hz, 2H), 1.33 – 1.26 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 192.1, 183.6, 183.1, 147.3, 144.8, 141.7, 134.5, 134.3, 134.1, 133.9, 133.8, 132.3, 131.8, 131.4, 129.3, 128.4, 127.6, 127.4, 126.4, 125.5, 124.9, 124.0, 123.3, 119.9, 110.4, 109.7, 43.9, 31.9, 29.4, 27.3, 25.3, 22.9, 14.4. HRMS-ESI Calcd. for $[M+H]^+$ $C_{33}H_{28}NO_3$ Exact Mass: 486.2069; Found 486.2065.

Synthesis of (Z)-3-(6-(9,10-dioxo-9,10-dihydroanthracen-2-yl)-9-hexyl-9H-carbazol-3-yl)-2-phenylacrylonitrile (**AQCZCS**)

To a suspension of 6-(9,10-dioxo-9,10-dihydroanthracen-2-yl)-9-hexyl-9H-carbazole-3-carbaldehyde (300 mg, 0.62 mmol) in 50/20 ml methanol/THF, sodium hydroxide (99.36 mg,2.484 mmol) and the benzyl cyanide (110 µl, 0.931 mmol) were added. The reaction mixture was stirred at 65 °C up to the complete consumption of reactant. The reaction was monitored via thin layer chromatography (TLC) and the formation of product was confirmed. The reaction mixture was filtered hot and washed with methanol. The pure products were

obtained as orange solid. (0.24 g, 66.6 %).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.44 (d, *J* = 1.8 Hz, 1H), 8.27 (d, *J* = 1.4 Hz, 1H), 8.22 (ddd, *J* = 12.9, 7.3, 5.0 Hz, 3H), 8.09 (d, *J* = 10.1 Hz, 1H), 7.96 (d, *J* = 6.2 Hz, 1H), 7.77 – 7.75 (m, 1H), 7.74 – 7.73 (m, 1H), 7.73 – 7.69 (m, 3H), 7.64 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 15.3, 7.9 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 1H), 4.20 (t, *J* = 7.3 Hz,2H), 1.85 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.38 (dd, *J* = 15.1, 6.7 Hz, 2H), 1.34 – 1.27 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 183.6, 183.0, 147.4, 143.6, 142.3, 141.5, 135.6, 134.4, 134.2, 134.1, 134.0, 133.9, 132.3, 131.6, 130.8, 129.5, 129.0, 128.3, 127.5, 127.5, 127.4, 126.2, 125.7, 125.4, 123.8, 123.5, 123.5, 119.8, 119.5, 110.1, 109.8, 108.1, 43.8, 32.0, 29.4, 27.4, 23.0, 14.5. HRMS-ESI Calcd. for $[M]^+$ $C_{41}H_{32}N_2O_2$ Exact Mass: 584.2464; Found 584.2463.

Synthesis of (Z)-2-(4-bromophenyl)-3-(9-hexyl-9H-carbazol-3-yl)acrylonitrile (**6**)

To a solution of 9-hexyl-9H-carbazole-3-carbaldehyde (1 g, 3.6 mmol) dissolved in MeOH (60 ml) and NaOH (0.5 mg, 14.3 mmol) and 4-Bromo-Phenylacetonitrile (1.1 g, 5.4 mmol) were added and stirred at 65 ^{o}C for 6 h, with the reaction progress monitored using TLC. Upon confirming the complete consumption of reactant, the mixture was filtered, washed with methanol, and dried under vacuum, yielding the pure product as a yellow powder (1.5 g, 88.0 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.13 (dd, *J* = 16.4, 8.2 Hz, 2H), 7.67 (s, 1H), 7.56 (s, 4H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.43 – 1.35 (m, 2H), 1.34 – 1.27 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.3, 142.2, 141.5, 134.7, 132.5, 127.6, 127.6, 127.0, 124.9, 123.7, 123.2, 123.2, 122.9, 121.2, 120.3, 119.3, 109.7, 109.6, 106.5, 43.8, 32.0, 29.4, 27.4, 23.0, 14.5. HRMS-ESI Calcd. for $[M]^+$ $C_{27}H_{25}N_2Br$ Exact Mass: 456.1201; Found 456.1190.

Synthesis of (Z)-3-(9-hexyl-9H-carbazol-3-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (**7**)

To a 100 ml oven dried Schlenk flask cooled under vacuum, (Z)-2-(4-bromophenyl)-3-(9-hexyl-9H-carbazol-3-yl)acrylonitrile (1.5 g, 3.3 mmol), bis(pinacol-ato)diboron (1.1 g, 4.1 mmol), potassium acetate (0.9 g, 9.8 mmol), triphenylphosphine (35 mg, 0.13 mmol) were added and dissolved using dry toluene (55 ml) under nitrogen atmosphere. And the reaction mixture is degassed using N_2 gas for 30 minutes. After that dichlorobis(triphenylphosphine)palladium(II) (23 mg, 0.03 mmol) catalyst were added and purged using N_2 gas and heated at 110 ^{o}C for 24 h. The solvent was evaporated under reduced

pressure, crude product was extracted with EtOAc, and the organic volume were dried over Na_2SO_4. The crude product was obtained as a brown-black liquid upon removal of solvents under vacuo. The product was purified by column chromatography using hexane/ EtOAc (90:10) as eluents. The solvents were evaporated to obtain a yellow color solid (1.4 g, 84.8 %). NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.14 (t, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 3H), 7.51 (dd, *J* = 10.4, 5.9 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 4.25 (t, *J* = 7.3 Hz, 2H), 1.86 (m, 2H), 1.40 (s, 12H), 1.37 – 1.28 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.4, 142.1, 141.4, 138.2, 135.8, 127.6, 126.8, 125.2, 125.0, 123.6, 123.2, 121.1, 120.2, 119.4, 109.6, 109.4, 107.4, 84.4, 43.7, 31.9, 29.3, 27.3, 25.3, 22.9, 14.4.

Synthesis of ((Z)-2-(4-(9,10-dioxo-8a,9,10,10a-tetrahydroanthracen-2-yl)phenyl)-3-(9-hexyl-9H-carbazol-3-yl)acrylonitrile (**CZCSAQ**)

To a 100 ml Schlenk flask (Z)-3-(9-hexyl-9H-carbazol-3-yl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (**6**) (0.45 g, 0.89 mmol), 2-bromoanthracene-9,10-dione (281 mg, 0.98 mmol), and potassium carbonate (2 M, 5 mL) were dissolved in tetrahydrofuran (60 mL). The reaction mixture was degassed using N_2 gas for 30 minutes then tetrakis (triphenylphosphine) palladium (0) $Pd(PPh_3)_4$ (20 mg, 0.01 mmol) catalyst was added to the reaction mixture. The reaction mixture was refluxed for 24 h under N_2 atmosphere. After removing the volatiles, the crude product was extracted using DCM/H_2O and brine solution. The organic layer collected were dried over anhydrous Na_2SO_4. The pure product obtained by washing using hot-methanol (250 mg, 48.0 %). ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.54 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.33 – 8.29 (m, 2H), 8.17 – 8.12 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, J = 16.0, 8.5 Hz, 6H), 7.76 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.44 – 1.36 (m, 2H), 1.35 – 1.25 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 183.6, 183.2, 146.1, 144.3, 142.2, 141.5, 139.1, 136.3, 134.7, 134.6, 134.4, 134.1, 134.0, 132.8, 132.5, 128.6, 128.3, 127.8, 127.7, 127.0, 126.8, 125.8, 125.1, 123.7, 123.3, 123.2, 121.2, 120.4, 119.4, 109.7, 109.6, 106.8, 43.8, 32.0, 29.4, 27.4, 23.0, 14.5. HRMS-ESI Calcd. for $[M]^+$ $C_{41}H_{32}N_2O_2$ Exact Mass: 584.2464; Found 584.2466.

3. Characterization Data

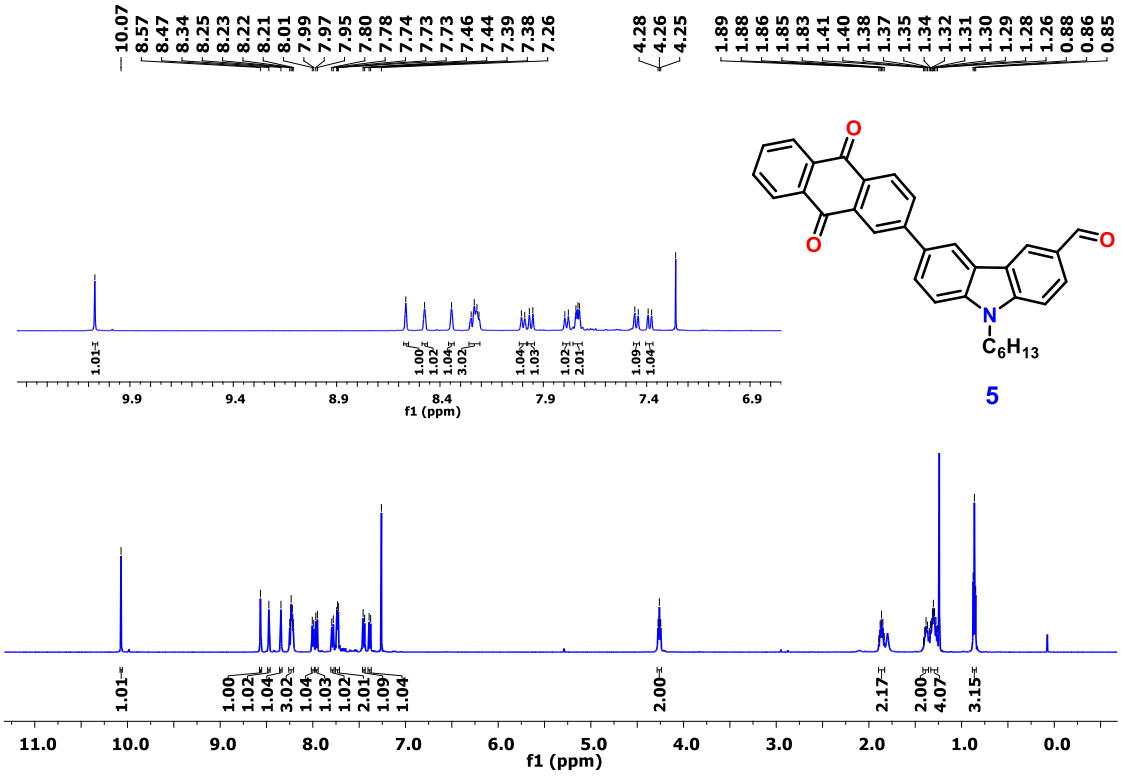

Figure S1. ^{1}H NMR spectrum (500 MHz) of **5** in $CDCl_3$

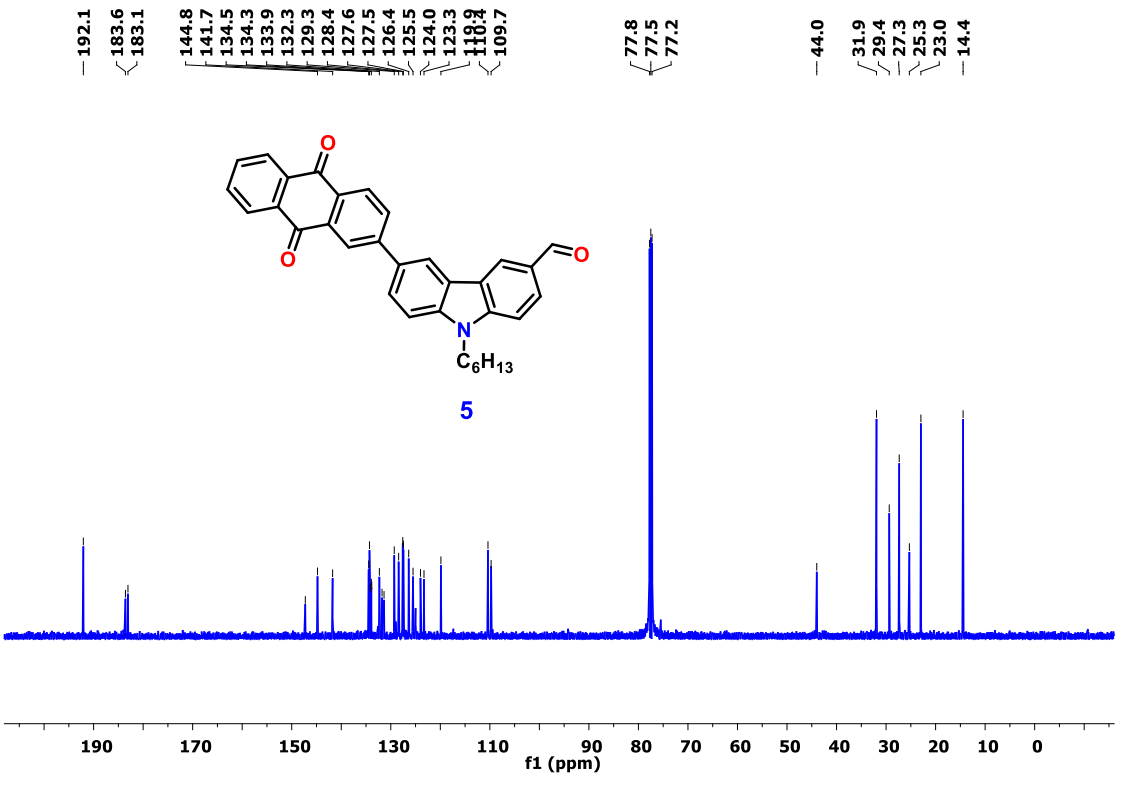

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **5** in $CDCl_3$.

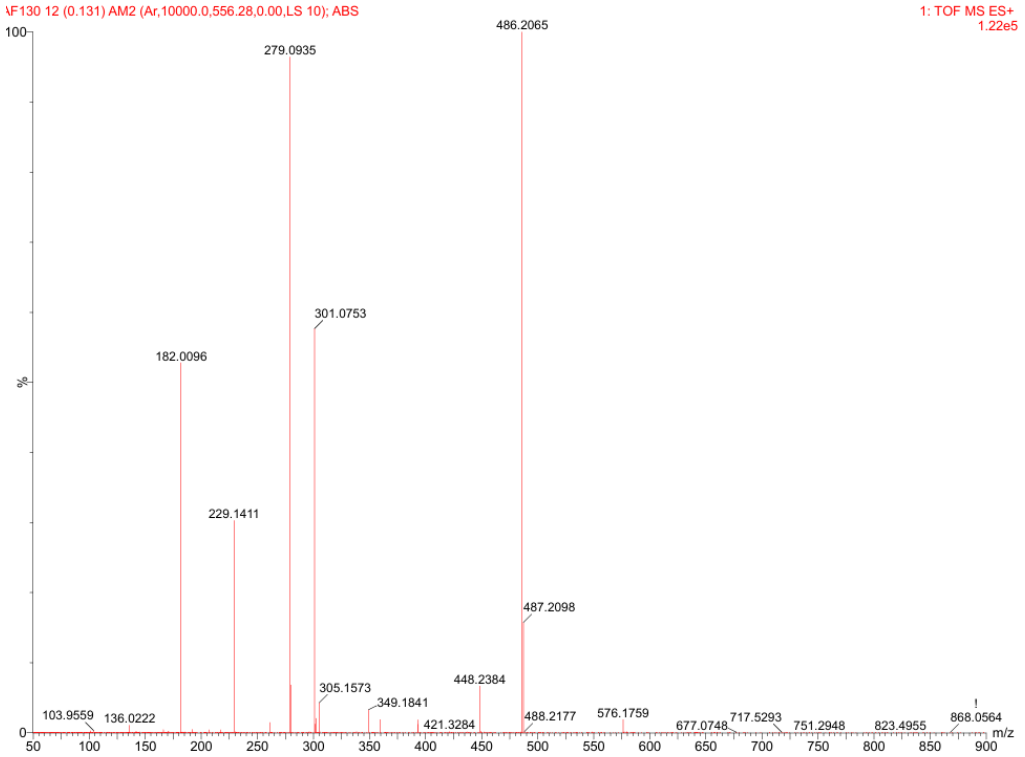

Figure S3. HRMS spectrum of **5**.

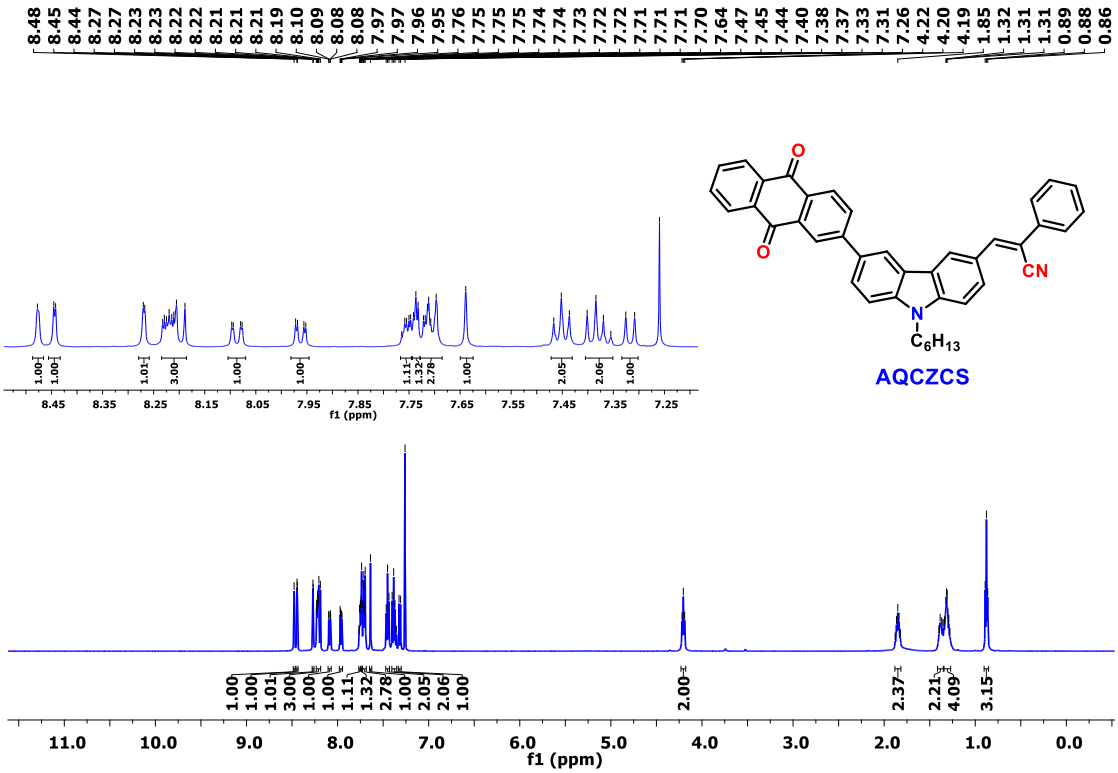

Figure S4. ^{1}H NMR spectrum (500 MHz) of **AQCZCS** in $CDCl_3$

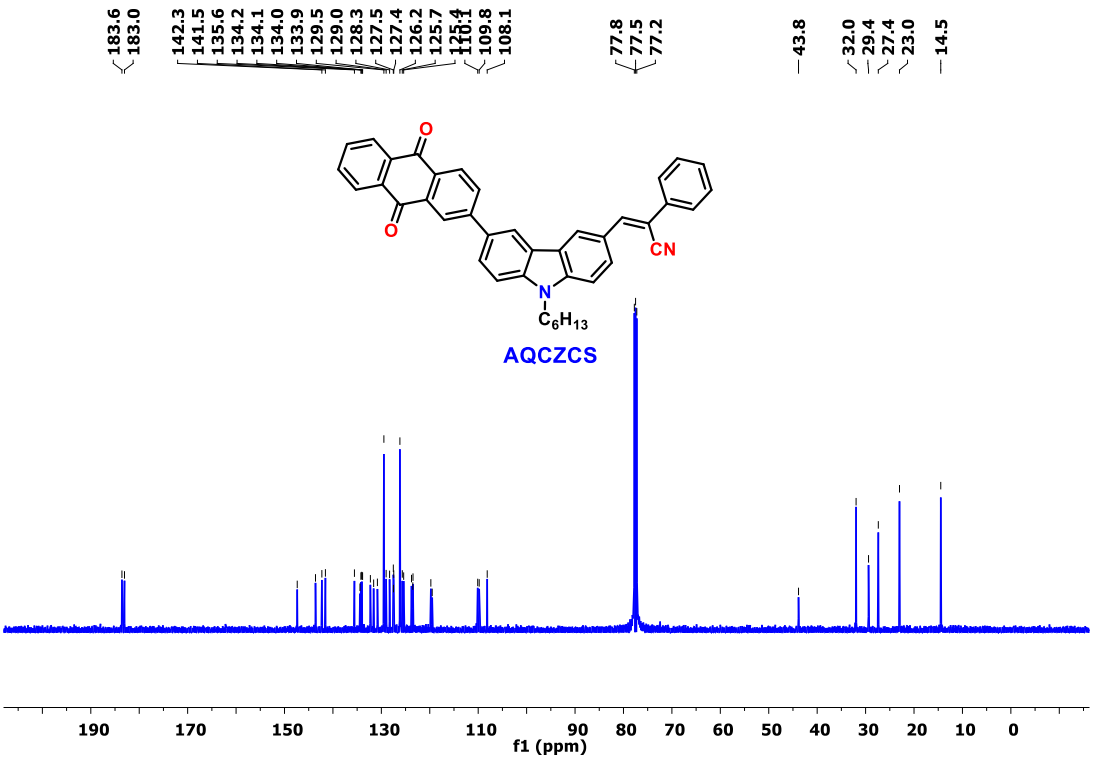

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **AQCZCS** in $CDCl_3$.

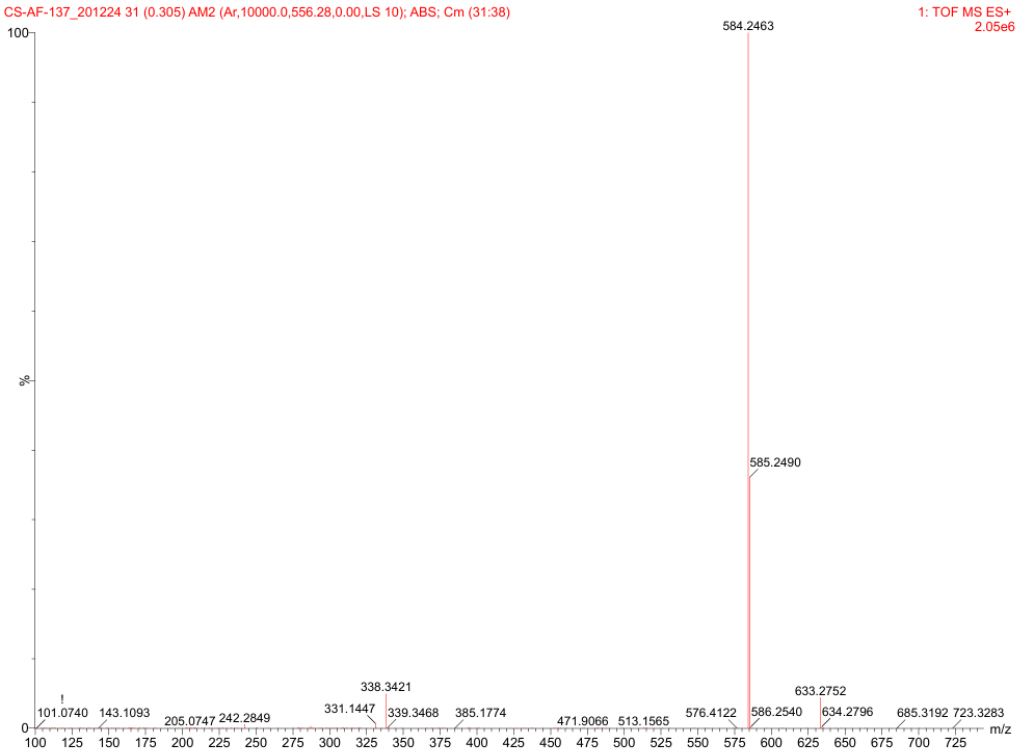

Figure S6. HRMS spectrum of **AQCZCS**.

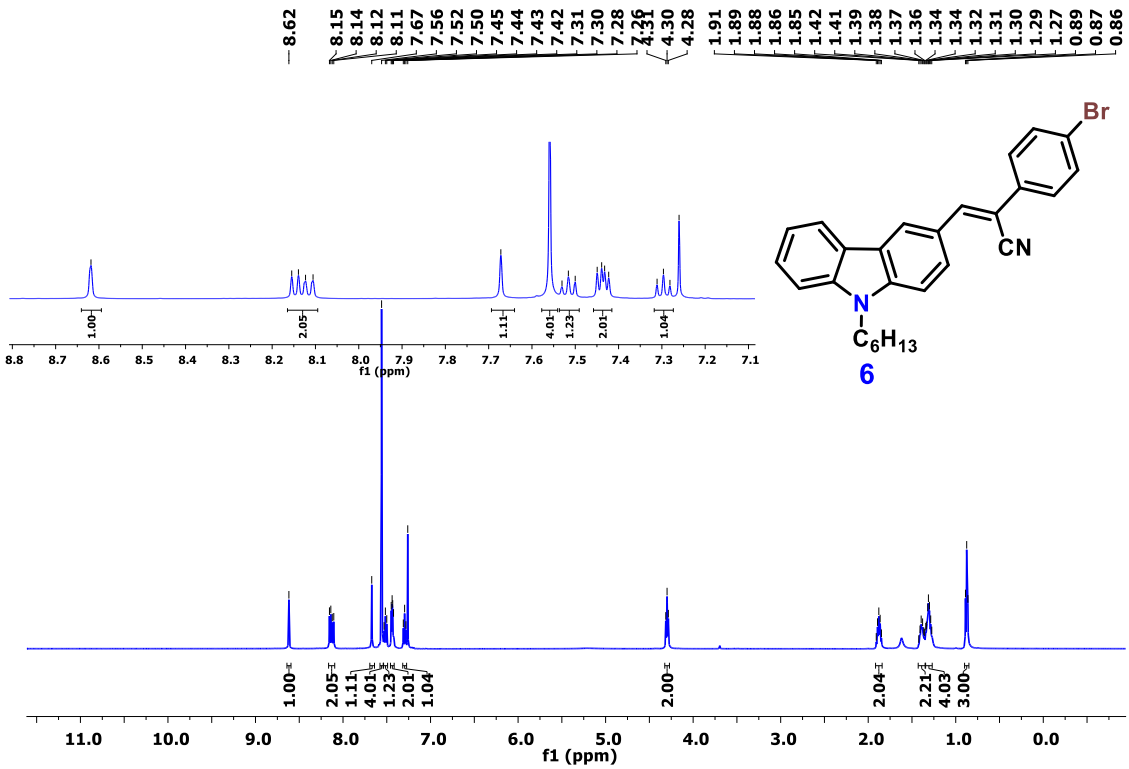

Figure S7. ^{1}H NMR spectrum (500 MHz) of **6** in $CDCl_3$.

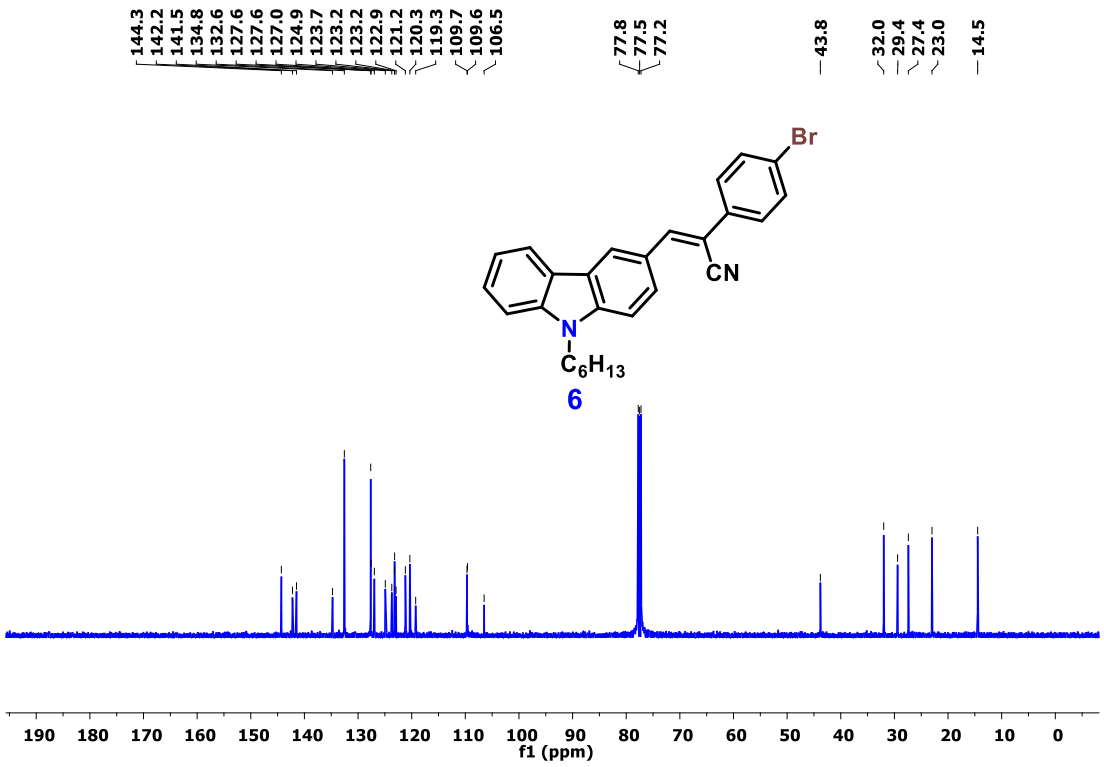

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **6** in $CDCl_3$.

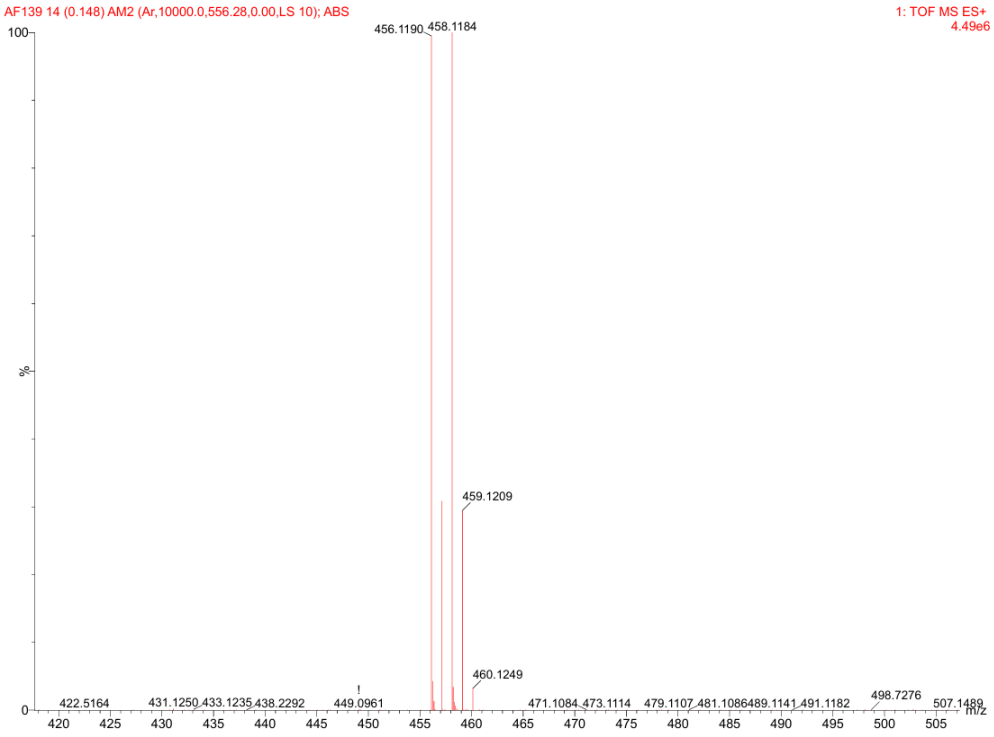

Figure S9. HRMS spectrum of compound **6**.

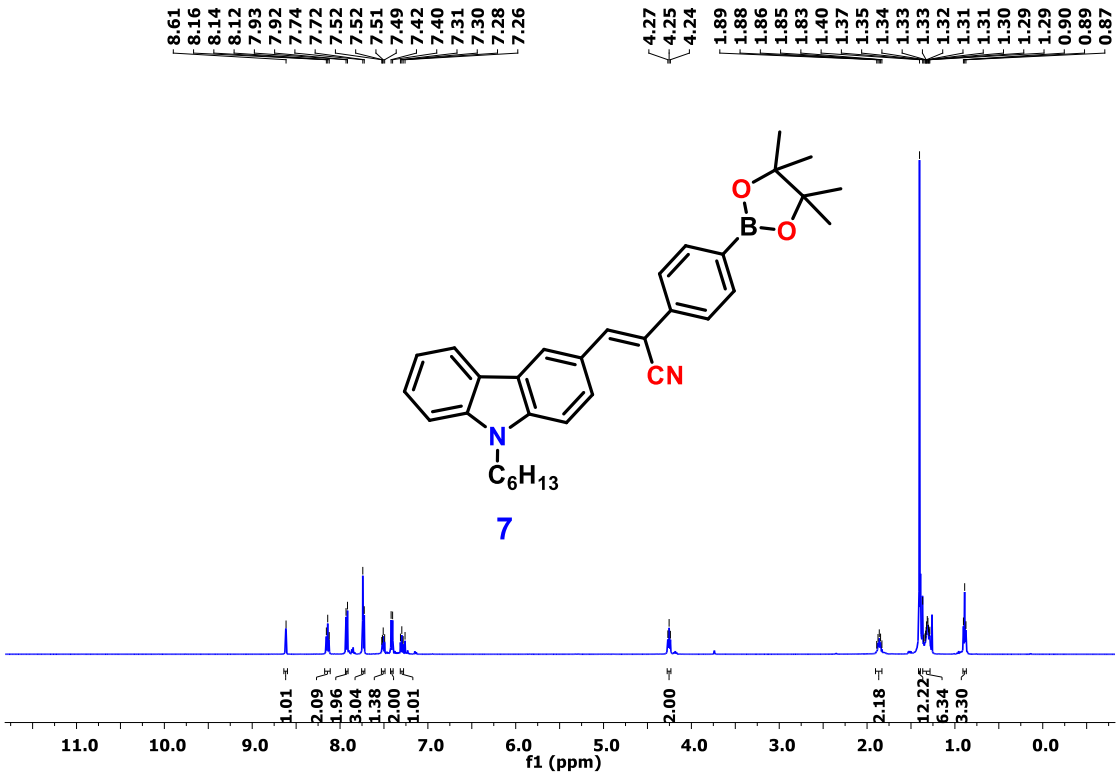

Figure S10. ^{1}H NMR spectrum (500 MHz) of **7** in $CDCl_3$.

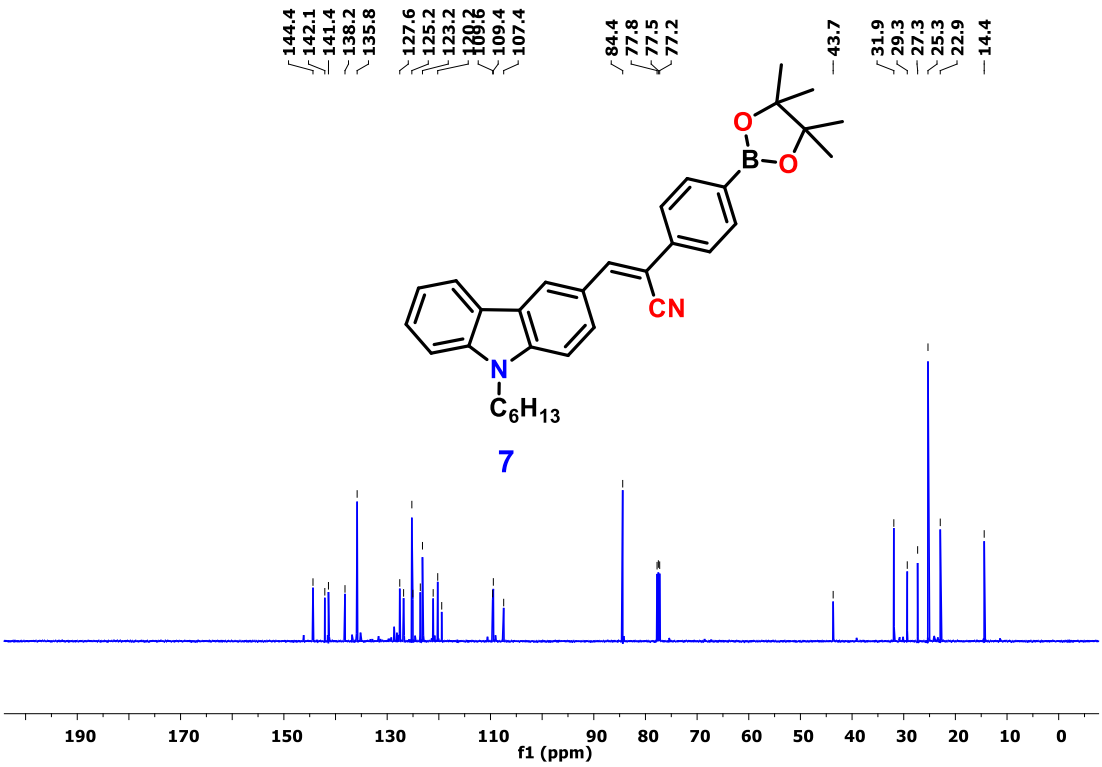

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **7** in $CDCl_3$.

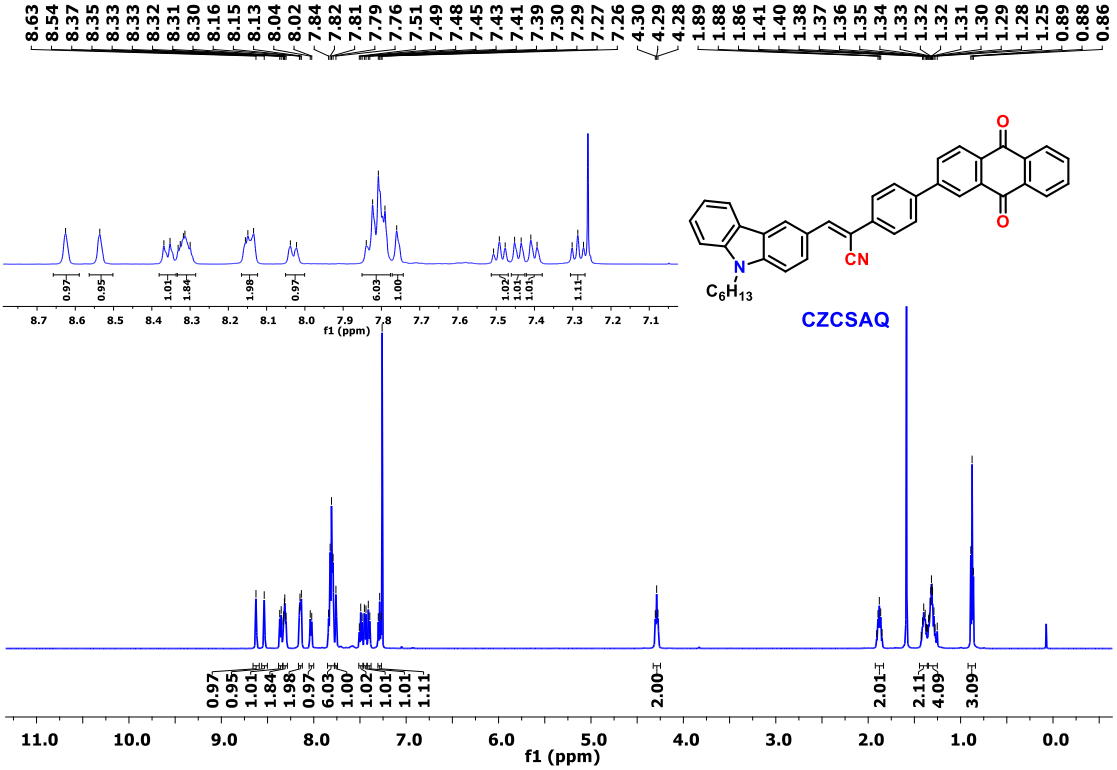

Figure S12. ^{1}H NMR spectrum (500 MHz) of **CZCSAQ** in $CDCl_3$.

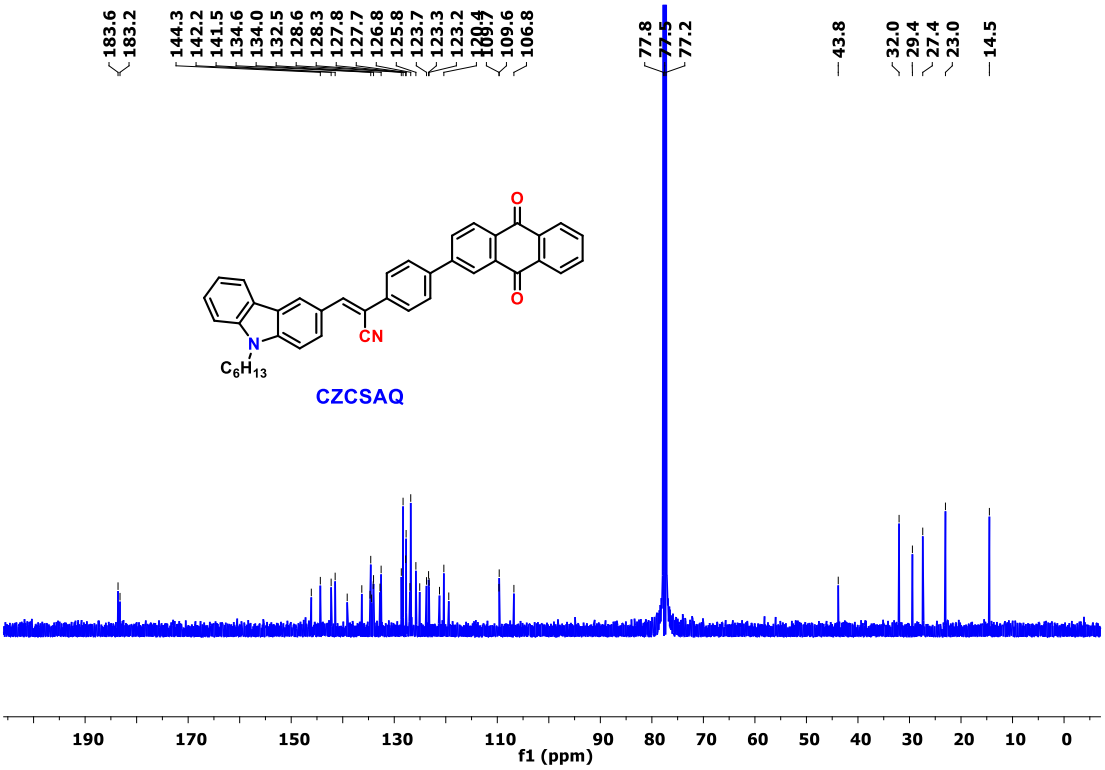

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **CZCSAQ** in $CDCl_3$.

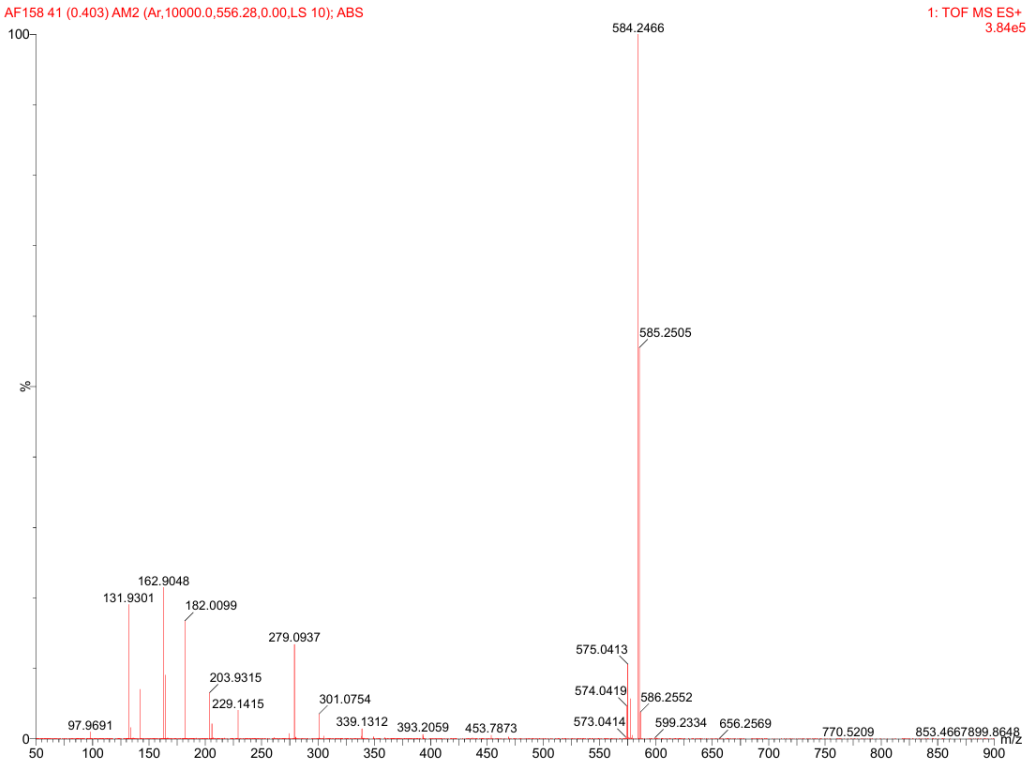

Figure S14. HRMS spectrum of compound **CZCSAQ**.

4. Optical Properties

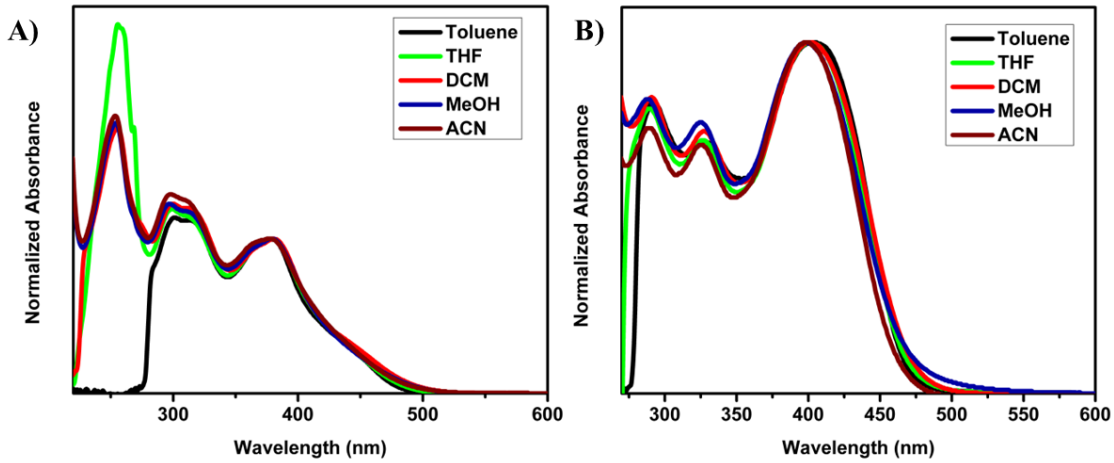

Figure S15. Normalised Absorption spectra of (**A**) **AQCZCS** and (**B**) **CZCSAQ** in different polarity of solvents.

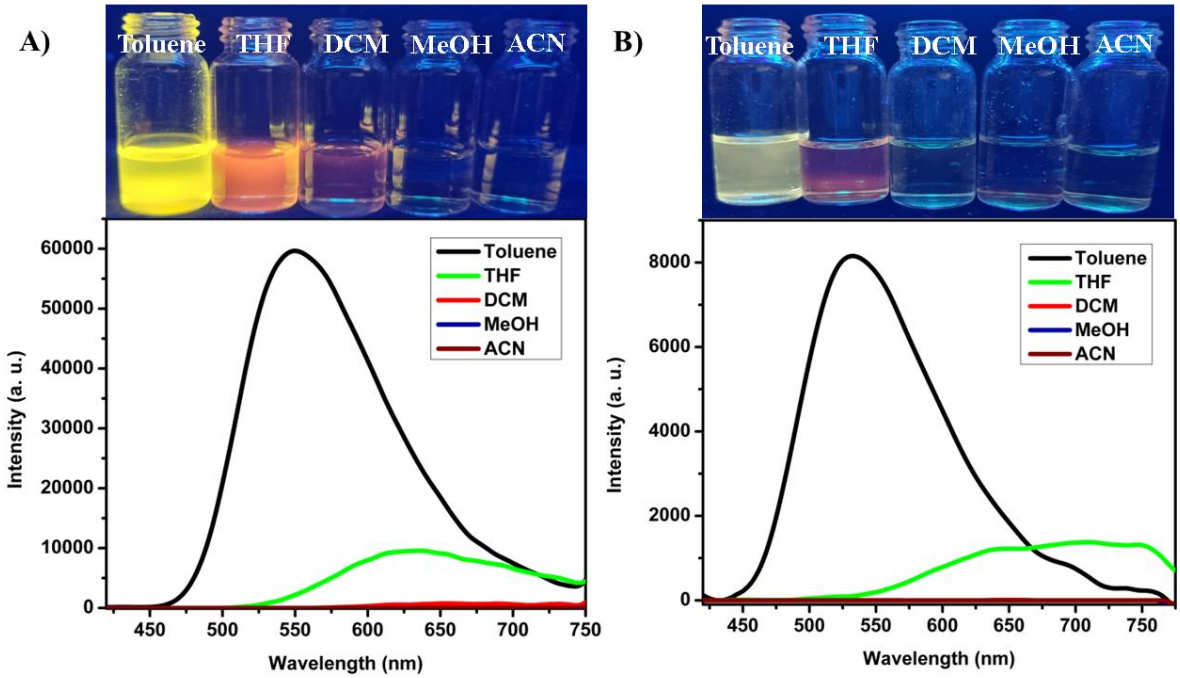

Figure S16. Normalised Emission spectra of (**A**) **AQCZCS** and (**B**) **CZCSAQ** in different polarity of solvents. (Con. 10 μM, λ_{ex} = 380 nm for **AQCZCS** and λ_{ex} = 400 nm for **CZCSAQ**). Digital photos taken under a UV 365 nm lamp are displayed on the top of the spectra. (Instrumental parameters: excitation slit width and emission slit width = 2.5 and 20 nm, respectively).

Table S1. Quantum yields of compounds **AQCZCS** and **CZCSAQ** in different polarity of solvents (λ_{ex} = 380 nm for **AQCZCS** and λ_{ex} = 400 nm for **CZCSAQ**).

Compounds	Solvents	Φ[a]
AQCZCS	Toluene	56.1 %
	THF	6.5 %
	DCM	0.2 %
	MeOH	nd
	ACN	nd
CZCSAQ	Toluene	5 %
	THF	1.8 %
	DCM	nd
	MeOH	nd
	ACN	nd

[a]Absolute Quantum yields calculated in solution states using calibrated integrating sphere. nd = not detectable (Emission is too weak to be accurately determined).

5. SEM images

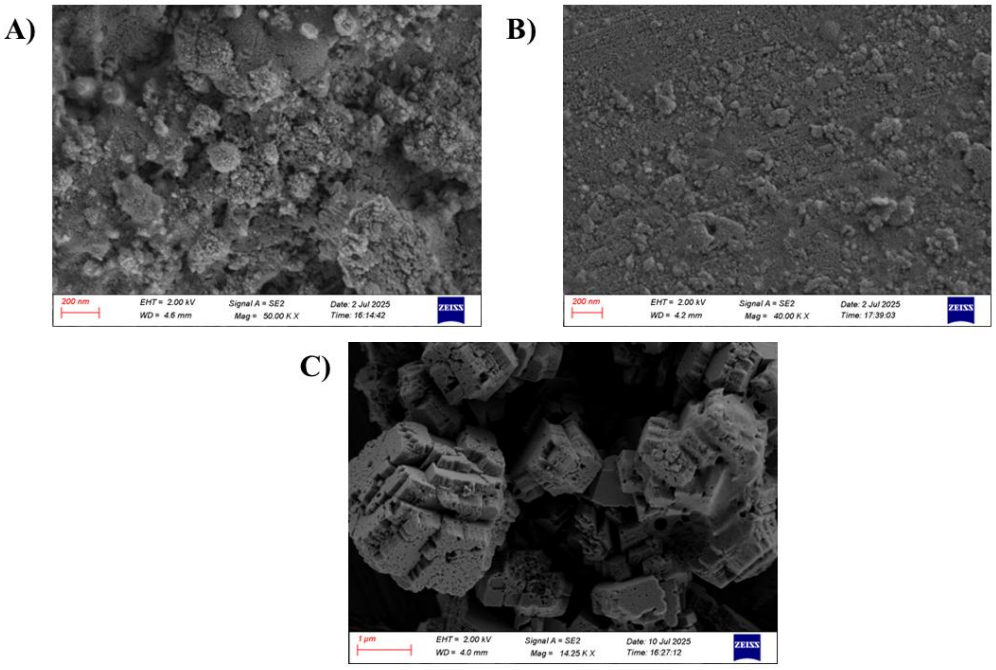

Figure S17. SEM images of (**A**) **AQCZCS** (drop-casted from a 10^{-5} M DMSO/H_2O solution with f_w = 40 % (**B**) **AQCZCS** (drop-casted from a 10^{-5} M DMSO/H_2O solution with f_w = 90 % and (**C**) **CZCSAQ** (drop-casted from a 10^{-5} M DMSO/H_2O solution with f_w = 90 %.

6. Dynamic light Scattering studies

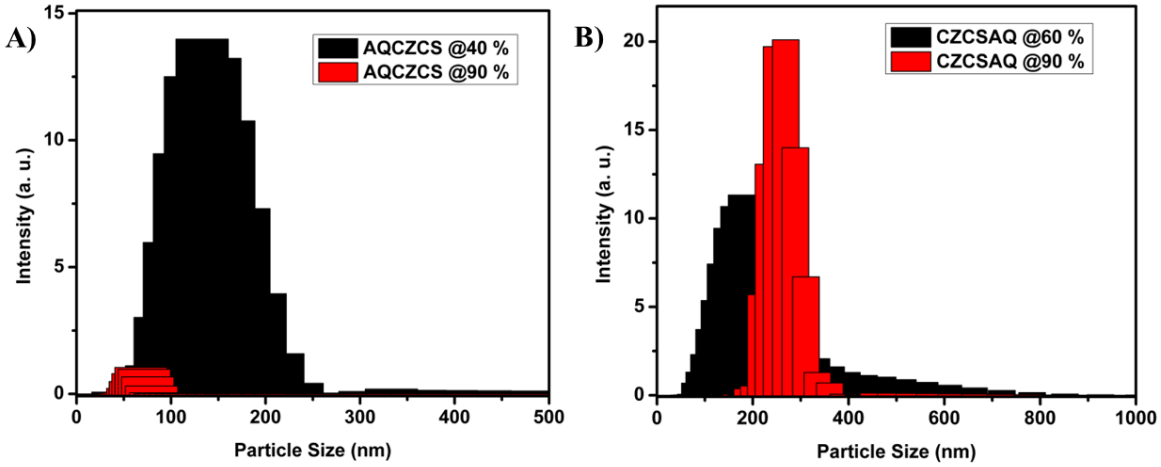

Figure S18. Size distributions of the aggregates of (**A**) **AQCZCS** and (**B**) **CZCSAQ** (drop-casted from a 10^{-5} M DMSO solution with varying water fractions.

7. PXRD data

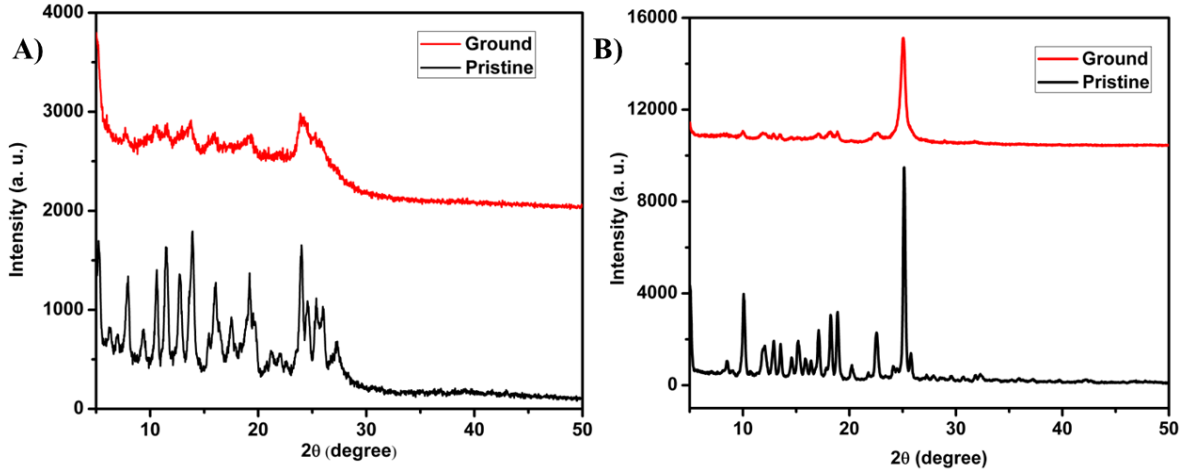

Figure S19. PXRD pattern of compound (**A**) **AQCZCS** and (**B**) **CZCSAQ**.

8. DFT and TD-DFT Calculations

DFT calculation data of Compounds **AQCZCS** and **CZCSAQ**.

Calculation method: B3LYP/6-31G(d, p) using Gaussian 09 with solvent effects modeled via PCM approach.

Table S2. Compound AQCZCS

6	-7.526475000	-0.362189000	0.184147000
6	-8.917050000	-0.210406000	0.223204000
1	-9.527536000	-0.881408000	-0.370828000
6	-9.492908000	0.784103000	1.010291000
1	-10.572250000	0.897080000	1.035588000
6	-8.681939000	1.636782000	1.767648000

1	-9.131654000	2.411535000	2.380685000
6	-7.297018000	1.492600000	1.736073000
1	-6.650447000	2.142247000	2.315465000
6	-6.709500000	0.496856000	0.947270000
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6	-1.161977000	-1.967069000	-0.810365000
6	-0.329620000	-0.843182000	-0.697657000
1	-0.760411000	0.148262000	-0.599449000
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6	2.170161000	-0.073719000	-0.665063000
6	2.255716000	1.305912000	-0.509583000
1	1.348364000	1.890624000	-0.430279000
6	3.521110000	1.925527000	-0.460605000
6	4.680880000	1.109726000	-0.583085000
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6	2.913361000	4.404555000	-0.056889000

6	3.402557000	5.808712000	0.035705000
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1	2.676849000	8.759612000	1.589841000
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1	4.708914000	9.475392000	0.341833000
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6	1.507957000	4.229883000	0.149370000
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7	0.359593000	4.137107000	0.329281000
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1	6.300471000	-7.811691000	3.272749000
6	-6.936125000	-1.434397000	-0.667769000

8	-7.650683000	-2.187321000	-1.328108000

Table S3. Compound CZCSAQ

6	-7.101685000	4.759341000	0.393556000
6	-8.363073000	4.170810000	0.193883000
6	-8.492916000	2.827970000	-0.156513000
6	-7.320708000	2.080660000	-0.306914000
6	-6.039725000	2.658826000	-0.103615000
6	-5.936953000	4.009970000	0.246763000
7	-7.167101000	0.739750000	-0.661064000
6	-5.820881000	0.438245000	-0.669386000
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6	-5.178036000	-0.778215000	-0.944104000
6	-3.794254000	-0.819511000	-0.893012000
6	-3.016303000	0.327328000	-0.568654000
6	-3.685976000	1.536856000	-0.284862000
6	-1.567201000	0.354546000	-0.486661000
6	-0.601105000	-0.565272000	-0.790213000
6	0.845000000	-0.304355000	-0.562987000
6	1.824929000	-0.945508000	-1.341520000
6	3.177893000	-0.694465000	-1.144049000
6	3.614155000	0.207176000	-0.158445000
6	2.634301000	0.838992000	0.627875000
6	1.281793000	0.582548000	0.437852000
6	-11.841145000	-4.472613000	2.347449000
6	-11.409693000	-3.705916000	1.093636000
6	-10.279948000	-2.702998000	1.357997000
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6	-8.703361000	-0.942073000	0.377216000
6	-8.252100000	-0.208157000	-0.893361000
6	-0.909844000	-1.833887000	-1.375849000
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1	3.902483000	-1.186191000	-1.785153000
1	2.933988000	1.505969000	1.430088000
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1	-9.416547000	-3.233769000	1.783457000
1	-10.603726000	-1.985293000	2.124897000
1	-10.696696000	-1.407712000	-0.322716000
1	-9.510242000	-2.658636000	-0.661024000
1	-7.841454000	-1.465764000	0.809214000
1	-9.026032000	-0.203799000	1.121679000
1	-9.087362000	0.341909000	-1.337368000
1	-7.916015000	-0.924577000	-1.649532000
6	5.055809000	0.472362000	0.057116000
6	6.011784000	-0.538145000	-0.126619000
1	5.712958000	-1.540398000	-0.411967000
6	5.508613000	1.746112000	0.457438000
1	4.794533000	2.553617000	0.581479000
6	6.858958000	1.994252000	0.668631000
1	7.203469000	2.977235000	0.970150000
6	7.806199000	0.980484000	0.484490000
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6	8.340256000	-1.412915000	-0.122837000
8	7.962634000	-2.528532000	-0.472845000
6	9.245515000	1.271094000	0.717956000
8	9.623009000	2.388227000	1.066873000
6	10.215032000	0.156831000	0.515190000
6	9.782766000	-1.123894000	0.113873000

6	10.720661000	-2.147002000	-0.066377000
1	10.367324000	-3.124630000	-0.374868000
6	12.074967000	-1.903461000	0.149179000
1	12.797549000	-2.701037000	0.007811000
1	13.559622000	-0.443561000	0.715543000
6	12.503971000	-0.632428000	0.547565000
6	11.577798000	0.391927000	0.729328000
1	11.889362000	1.383631000	1.037830000
1	-7.037777000	5.808079000	0.666169000

Table S4. TD-DFT simulated absorption values corresponding to major transitions

Compounds	λ_{B3LYP}[a] (nm)	λ_{M06}[a] (nm)
AQCZCS	402.47 (0.6732)	389.54(0.7638)
CZCSAQ	409.06 (1.3484)	394.79 (1.3424)

[a] Values obtained from various density functionals (B3LYP and M06)/6-31G (d,p)/PCM (Tetrahydrofuran) levels of theory, and oscillator strength values are given in parenthesis.

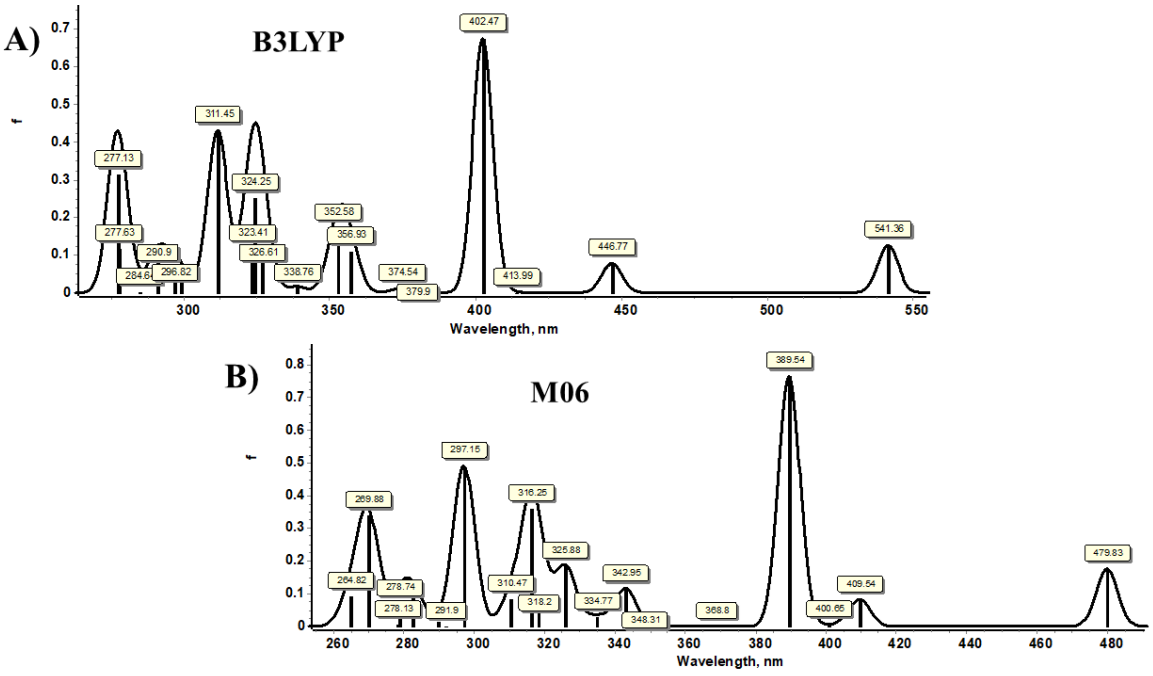

Figure S20. Simulated absorption spectra of compound **AQCZCS** (**A**) **B3LYP** (**B**) **M06** functional with 6-31G (d, p)/PCM (Tetrahydrofuran) level of theory.

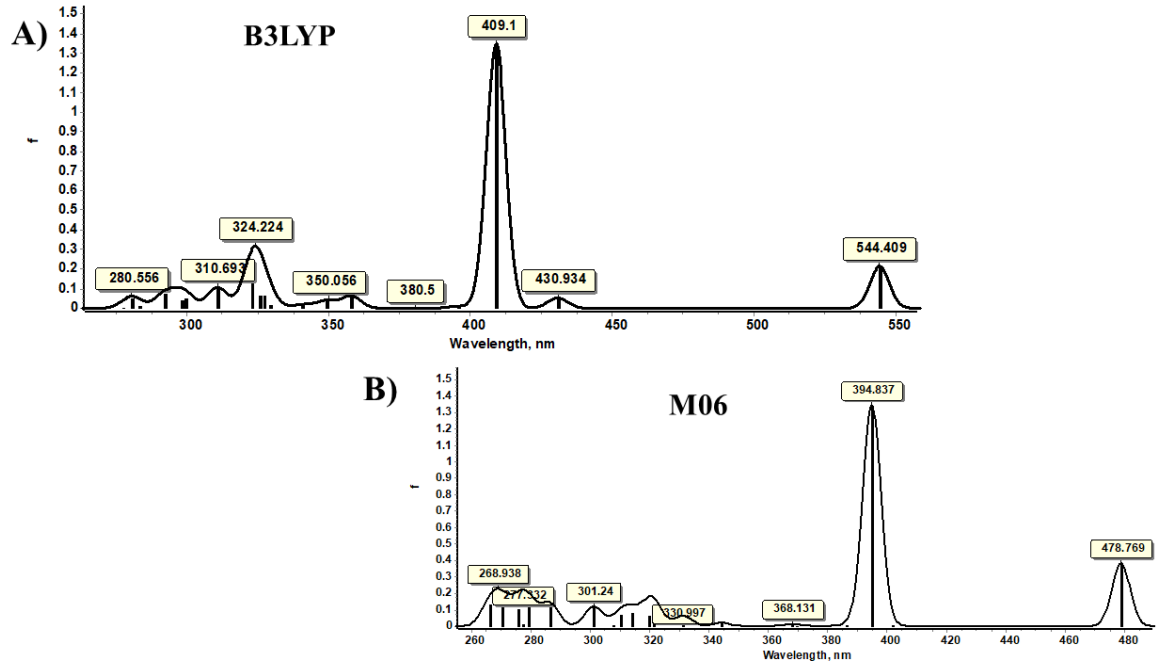

Figure S21. Simulated absorption spectra of compound **CZCSAQ** (**A**) **B3LYP** (**B**) **M06** functional with 6-31G (d, p)/PCM (Tetrahydrofuran) level of theory.

Table S5. Computed singlet vertical transitions involved in Compound **AQCZCS** from TD-DFT calculation using 6-31G (d, p) basis set M06 functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f*** **[a]**	**Major transitions (%)**
S_1	2.5839 eV	479.83 nm	0.1759	HOMO-1→ LUMO (1.73 %) HOMO→ LUMO (46.9 %)
S_2	3.0274 eV	409.54 nm	0.0821	HOMO-1→ LUMO (45.1 %) HOMO→ LUMO (2.25 %)
S_3	3.0946 eV	400.65 nm	0.0053	HOMO-9→ LUMO+2 (1.8 %) HOMO-7→ LUMO (45.98 %)
S_4	3.1828 eV	389.54 nm	0.7638	HOMO-1→ LUMO (1.02 %) HOMO→LUMO+1 (47.35 %)
S_5	3.3619 eV	368.80 nm	0.0004	HOMO-9→ LUMO (44.36 %) HOMO-7→ LUMO+2 (3.65 %)

Table S6. Computed singlet vertical transitions involved in Compound **CZCSAQ** from TD-DFT calculation using 6-31G (d, p) basis set M06 functional in Gaussian09.

Excited States	**E (eV)**	**λ_{max} (nm)**	***f*** **[a]**	**Major transitions (%)**
S_1	2.5901 eV	478.69 nm	0.3819	HOMO-2→LUMO (1.54 %) HOMO→LUMO (46.7 %)
S_2	3.0864 eV	401.71 nm	0.0034	HOMO-9→ LUMO+2 (1.6 %) HOMO-5→LUMO (42.7 %) HOMO-4→LUMO (2.4 %)

S_3	3.1405 eV	394.79 nm	1.3424	HOMO→LUMO (1.3 %) HOMO→LUMO+1 (45.6 %)
S_4	3.2093 eV	386.33 nm	0.0095	HOMO-3→ LUMO (1.2 %) HOMO-2→LUMO (5.1 %) HOMO-1→LUMO (38.9 %) HOMO→LUMO+1 (1.5 %)
S_5	3.3556 eV	369.49 nm	0.0020	HOMO-9→ LUMO (38.3 %) HOMO-5→LUMO+2 (2.7 %) HOMO-2→LUMO (4.01 %) HOMO-1→LUMO (1.26 %)

9.Thermal properties

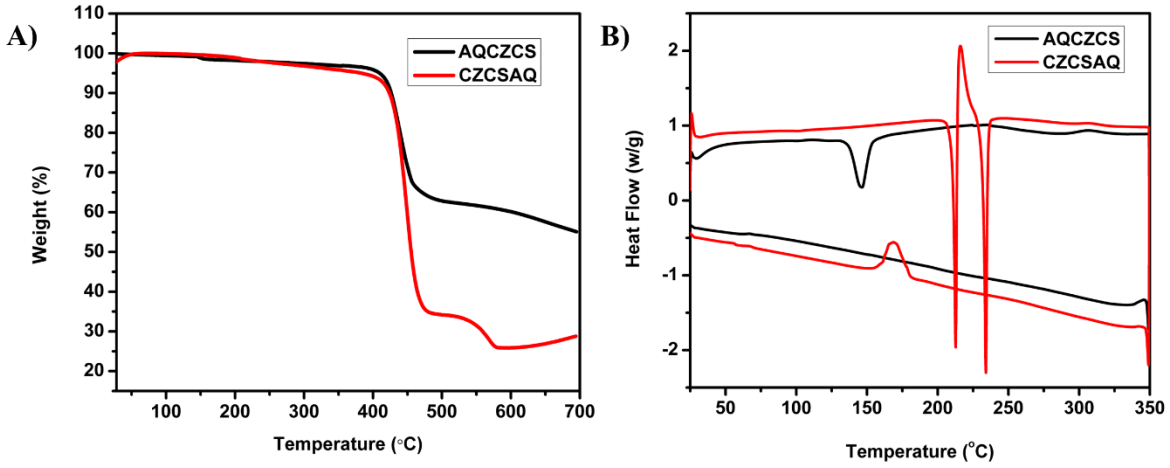

Figure S22. (**A**) TGA and (**B**) DSC curves of the compounds **AQCZCS** and **CZCSAQ**.

10. References

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K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 09, Revision B.01,Gaussian, Inc., Wallingford, CT, 2016.