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Aggregation Induced Emission and Reversible Mechanofluorochromism Active Carbazole-Anthracene Conjugated Cyanostilbenes with Different Terminal Substitutions

Afrin A[a] and Chinna Ayya Swamy P[a*]

[a]Main group Organometallics Optoelectronic Materials and Catalysis lab, Department of Chemistry, National Institute of Technology, Calicut, India-673601.

Corresponding author: swamy@nitc.ac.in

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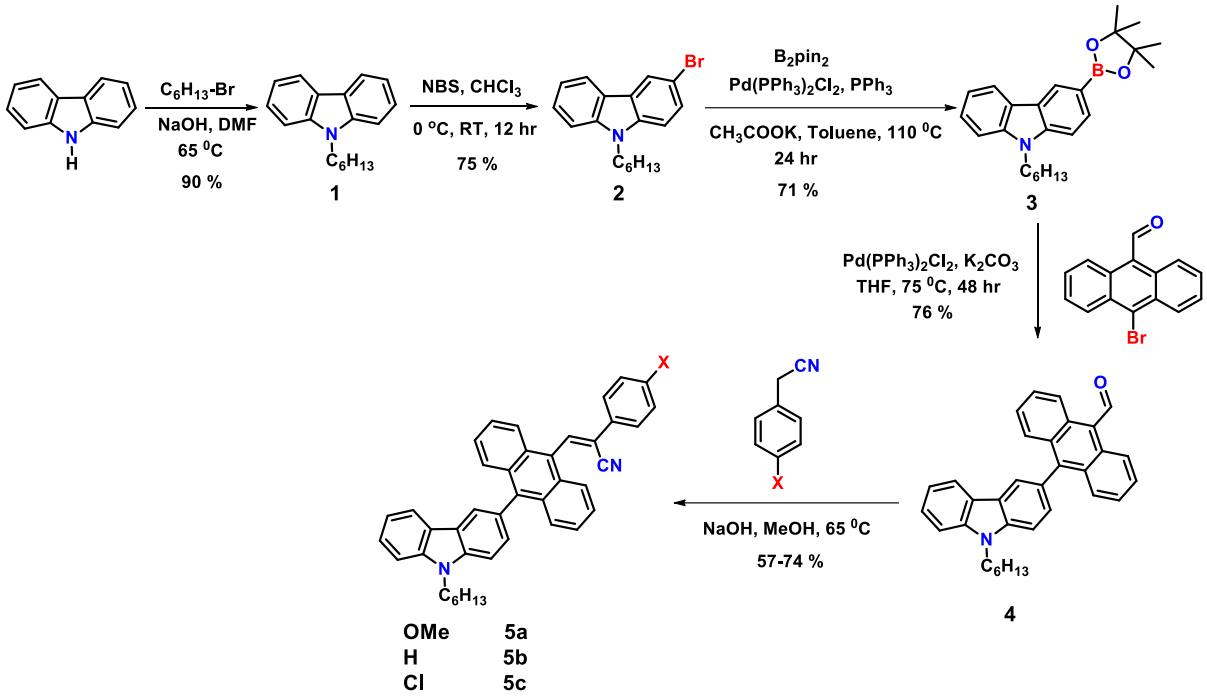
1. Experimental Section

1.1 Materials and measurements

The chemicals and solvents including 9H-carbazole, 1-bromohexane, N-bromosuccinimide (NBS), bis(pinacolato)diboron, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(II), tetrakis (triphenylphosphine) palladium(0), benzyl cyanide, 4-chlorophenylacetonitrile, 4-methoxyphenylacetonitrile, potassium acetate (KOAc), NaOH, K_2CO_3, dimethylformamide, chloroform, tetrahydrofuran (THF) and methanol(MeOH) were purchased from a commercial supplier and used as received. Toluene was dried over sodium and freshly distilled and use. The ^{1}H and ^{13}C NMR spectra of the synthesized compounds were recorded on a JEOL JNM-ECZ-500R/M1 (500 MHz) NMR instrument using $CDCl_3$ as the solvent, and tetramethylsilane (TMS) as an internal standard. The high resolution mass spectrometry (HRMS) was carried out with a data were obtained from a Thermo Scientific Exactive mass spectrometer with Orbitrap analyser and the ions are given in m/z. The UV–vis absorption spectra was measured using a LAMBDA 365 UV/Vis Spectrophotometer with keeping slit width 1. Fluorescent measurements were carried out on perkinelmer LS-55 fluorescence spectrometer. The solid-state measurements were measured on Horiba fluorescence spectrophotometer. The XRD pattern in the 2θ range from 0° to 90° was recorded using a PANalytical X'Pert3 powder X-ray diffractometer, with a CuKα source of 1.5406 A° at a scan rate of 1° min−1. SEM images were obtained using Hitachi SU6600 variable pressure. Atomic force microscopic (AFM) images of samples drop casted on glass slide were obtained by XE-100 (Park Systems). Dynamic light scattering (DLS) measurements of aggregates were performed on the STABINO ZETA. Density functional theory (DFT) calculations were made on B3LYP/6-31G(d) level using the Gaussian 09W program package. TGA measurements were conducted on TGA Q50 V20.13 Build 39 instrument. The DSC curves were obtained using DSC Q20 V24.11 Build 124 model instrument. Quantum yields (ff) of fluorescence were obtained using quinine sulfate (0.545 in 1 N H_2SO_4) as a reference standard.

1.2 Synthesis of target compounds



Synthesis of 9-hexyl-9H-carbazole (**1**)

To a solution of carbazole (20 g, 119.6 mmol) dissolved in DMF (80 mL), NaOH (19.1 g, 478.4 mmol) and 1-bromohexane (25 mL, 179.4 mmol) was added. The reaction mixture was stirred at 70°C for 4 h. The reaction was monitored via thin layer chromatography (TLC) and confirmed the formation of product. After cooling the reaction to room temperature, it was quenched with water and the crude product was extracted with ethyl acetate and brine solution for 5-6 times. The organic fraction was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel column chromatography with hexane/ethylacetate as the eluents. The pure product was obtained as a white solid (27.2 g, 90 %). The NMR data was matches with the literature reported values. ^{1}H NMR (500 MHz; $CDCl_3$): δ ppm 8.13 – 8.09 (m, 2H), 7.49 – 7.45 (m, 2H), 7.43 – 7.40 (m, 2H), 7.25 – 7.21 (m, 2H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.88 (dt, *J* = 19.0, 7.5 Hz, 2H), 1.45 – 1.38 (m, 2H), 1.35 – 1.26 (m, 4H), 0.90 – 0.84 (m, 3H).

Synthesis of 3-bromo-9-hexyl-9H-carbazole (**2**)

To a suspension of n-hexyl carbazole (5 g, 19.9 mmol) in $CHCl_3$ (100 ml) N-bromosuccinimide (3.5 g, 19.9 mmol) was added portion wise at 0 °C within 30 minutes. The reaction mixture was slowly warmed to room temperature and stirred for further 12 h. The reaction was quenched with water and the product was extracted with $CHCl_3$. The organic layer was

collected and dried over Na_2SO_4. The crude product was then purified by flash column chromatography with hexane-ethyl acetate as the eluents. The Solvents were evaporated to yield a sticky white solid (4.97 g, 75 %). The NMR data was matches with the literature reported values. ^{1}H NMR (500 MHz; $CDCl_3$): δ ppm 8.20 (d, *J* = 1.9 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.24 (s, 1H), 4.27 (t, *J* = 7.3 Hz, 2H), 1.84 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.29 (dd, *J* = 6.4, 3.2 Hz, 6H), 0.86 (t, *J* = 7.1 Hz, 3H).

Synthesis of 9-hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3**)

To 100 ml oven dried Schlenk flask cooled under vaccum, 3-bromo-9-hexyl-9H-carbazole (2 g, 6.1 mmol), bis(pinacol-ato)diboron (1.9 g, 7.6 mmol), potassium acetate (1.8 g, 18.2 mmol), triphenylphosphine (63.3 mg,0.25 mmol) were added and dissolved using dry toluene (50 ml) under nitrogen atmosphere. And the reaction mixture is degassed using N_2 gas for 30 minutes. After that dichlorobis(triphenylphosphine)palladium(II) (64 mg, 0.12 mmol) catalyst were added and purged using N_2 gas and the reaction was refluxed at 110 ^{o}C for 24 h. The solvent was evaporated under reduced pressure, crude product was extracted with ethylacetate, and the organic volume were dried over sodium sulfate. 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/ethylacetate as eluents. The solvents were evaporated to obtain as colorless oil (1.63 g, 71 %). The NMR data was matches with the literature reported values. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.66 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 10.2 Hz, 1H), 7.50 (t, *J* = 7.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 4.32 (t, *J* = 7.3 Hz, 2H), 1.95 – 1.85 (m, 2H), 1.44 (s, 12H), 1.35 – 1.27 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H).

Synthesis of 10-(9-hexyl-9H-carbazol-3-yl)anthracene-9-carbaldehyde (**4**)

To a 100 ml Schlenk flask (9-Hexylcarbazol-3-yl) boronic acid pinacol ester (0.7 g, 2.1 mmol), 10-bromoanthracene-9-carbaldehyde (0.55 g, 1.9 mmol) and potassium carbonate (2 M, 10 mL) were dissolved in tetrahydrofuran (50 mL). The reaction mixture was degassed using N_2 gas for 30 minutes then tetrakis (triphenylphosphine) palladium (0) $Pd(PPh_3)_4$ (44.5 mg, 0.03 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 ethylacetate/water and brine solution. The organic layer collected were dried over sodium sulfate. The crude product obtained as yellow powder upon concentrating under reduced

pressured was purified using column chromatography with hexane/EtOAc as eluents. The pure product is obtained as fine yellow powder (640 mg, 76 %). ^{1}HNMR (500 MHz, $CDCl_3$): δ ppm 11.63 (s, 1H), 9.07 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 1.3 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.69 – 7.65 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.48 (d, *J* = 6.6 Hz, 1H), 7.40 (d, *J* = 6.5 Hz, 1H), 7.38 (d, *J* = 5.5 Hz, 1H), 7.25 (d, *J* = 6.1 Hz, 1H), 4.43 (t, *J* = 7.3 Hz, 2H), 2.04 – 1.99 (m, 2H), 1.55 – 1.50 (m, 2H), 1.39 (dd, *J* = 12.7, 5.8 Hz, 4H), 0.93 (d, *J* = 7.1 Hz, 3H). ^{13}CNMR (126 MHz, $CDCl_3$) δ ppm 193.84, 147.40, 141.44, 140.52, 132.35, 131.14, 129.07, 128.72, 128.67, 126.61, 125.80, 125.18, 123.88, 123.31, 123.06, 122.96, 120.99, 119.63, 109.44, 109.04, 107.44, 43.85, 32.10, 29.55, 27.55, 23.07, 14.52. HRMS-ESI Calcd. for $C_{33}H_{29}NO$ Exact Mass: 456.2327; Found 456.2326 $(M+H)^+$.

(Z)-3-(10-(9-hexyl-9H-carbazol-3-yl)anthracen-9-yl)-2-(4-methoxyphenyl)acrylonitrile (**5a**)

To a suspension of 10-(9-hexyl-9H-carbazol-3-yl)anthracene-9-carbaldehyde (300 mg, 0.65 mmol) in 50 ml methanol, sodium hydroxide (55 mg,1.3 mmol) and 4-methoxy phenyl acetonitrile (144 µL, 0.98 mmol) were added. The reaction mixture was stirred at 65 ºC for 6 h. The reaction was monitored via thin layer chromatography (TLC) and the formation of product was confirmed. After cooling the reaction to room temperature, the mixture was filtered and washed with methanol. The pure product was obtained as yellow powder (220 mg, 57 %). ^{1}HNMR (500 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 8.21 – 8.06 (m, 4H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 15.8, 8.1 Hz, 5H), 7.38 – 7.34 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 3.93 (s, 3H), 2.05 – 1.98 (m, 2H), 1.52 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.40 (ddd, *J* = 22.0, 12.0, 5.5 Hz, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}CNMR (126 MHz, $CDCl_3$) δ ppm 161.40, 141.41, 140.83, 140.41, 138.71, 131.19, 129.78, 129.27, 129.17, 128.76, 128.32, 128.03, 126.64, 126.44, 126.41, 125.66, 125.61, 123.55, 123.35, 123.14, 121.21, 121.02, 119.50, 117.35, 115.12, 109.35, 108.99, 56.04, 43.86, 32.13, 29.58, 27.59, 23.10, 14.54. HRMS-ESI Calcd. for $C_{42}H_{37}N_2O$ Exact Mass: 585.2905; Found 585.2911 $(M+H)^+$. FTIR (pallet made with KBr) (cm^{-1}) 3056, 2955, 2925, 2848, 2224, 1605, 1512, 1461, 1377, 1339, 1238, 1183, 1018, 832, 807, 778, 739, 659. M. P. 260-264 ºC (decomposes).

Synthesis of (Z)-3-(10-(9-hexyl-9H-carbazol-3-yl)anthracen-9-yl)-2-phenylacrylonitrile (**5b**)

The synthesis of **5b** was similar procedure of **5a** and data as follows: 10-(9-hexyl-9H-carbazol-3-yl)anthracene-9-carbaldehyde (300 mg, 0.65 mmol), benzyl cyanide (200 µL, 0.98 mmol),

sodium hydroxide (55 mg,1.3 mmol) and 50 mL methanol. The pure product was obtained as yellow powder (270 mg, 74 %). ^{1}HNMR (500 MHz, $CDCl_3$) δ ppm 8.56 (s, 1H), 8.21 – 8.12 (m, 3H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.56 – 7.50 (m, 6H), 7.40 – 7.34 (m, 2H), 7.24 (d, *J* = 5.8 Hz, 1H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.06 – 1.96 (m, 2H), 1.52 (d, *J* = 7.8 Hz, 2H), 1.44 – 1.34 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).^{13}CNMR (126 MHz, $CDCl_3$) δ NMR (126 MHz,) δ ppm 141.41, 141.19, 141.08, 140.41, 133.83, 131.17, 130.29, 129.78, 129.68, 129.23, 129.10, 128.80, 128.00, 126.76, 126.64, 126.43, 125.69, 125.49, 123.53, 123.36, 123.12, 121.76, 121.01, 119.51, 117.17, 109.36, 109.01, 43.85, 32.12, 29.57, 27.57, 23.09, 14.54. HRMS-ESI Calcd. for $C_{41}H_{35}N_2$ Exact Mass: 555.2800; Found 585.2796 $(M+H)^+$. FTIR (pallet made with KBr) (cm^{-1}) 3046, 2963, 2925, 2857, 2226, 1597, 1465, 1386, 1326, 1271, 1233, 1136, 803, 748, 685, 656, 605. M. P. 252-256 ºC (decomposes).

Synthesis of (Z)-2-(4-chlorophenyl)-3-(10-(9-hexyl-9H-carbazol-3-yl)anthracen-9-yl)acrylonitrile (**5c**)

The synthesis of **5c** was similar procedure of **5a** and data as follows: 10-(9-hexyl-9H-carbazol-3-yl)anthracene-9-carbaldehyde (300 mg, 0.65 mmol), 4-chlorophenylacetonitrile (150 µL, 0.98 mmol), sodium hydroxide (55 mg,1.3 mmol) and 50 mL methanol. The pure product was obtained as yellow powder (250 mg, 64 %). Follows the same procedure of 1 in the place of 4-methoxyphenylacetonitrile, is used.^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.53 (s, 1H), 8.24 – 8.01 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 4H), 7.52 (d, *J* = 1.0 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.44 (t, *J* = 7.3 Hz, 2H), 2.09 – 1.97 (m, 2H), 1.56 – 1.49 (m, 2H), 1.47 – 1.33 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}CNMR (126 MHz, $CDCl_3$) δ ppm 141.65, 141.42, 141.36, 140.44, 136.39, 132.34, 131.16, 130.02, 130.00, 129.65, 129.20, 129.01, 128.88, 127.90, 127.59, 126.89, 126.46, 125.73, 125.34, 123.51, 123.36, 123.11, 121.01, 120.64, 119.53, 116.88, 109.38, 109.02, 77.76, 77.50, 77.25, 43.87, 32.13, 29.58, 27.58, 23.10, 14.54. HRMS-ESI Calcd. for $C_{41}H_{34}ClN_2$ Exact Mass: 589.2410; Found 589.2428 $(M+H)^+$. FTIR (pallet made with KBr) (cm^{-1}) 3056, 2955, 2921, 2845, 2229, 1596, 1491, 1381, 1330, 1271, 1229, 1149, 1094, 1014, 807, 739, 651, 621. M. P. 245-248 ºC (decomposes).

1.2 Characterisation data

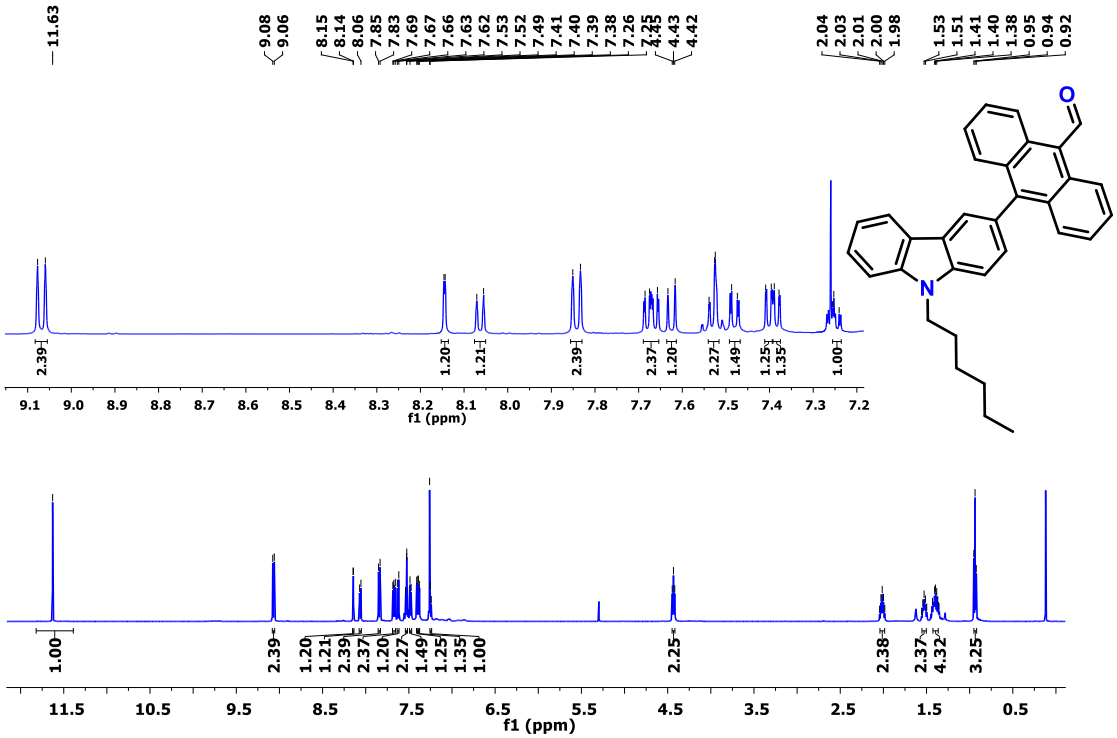


Figure S1: ^{1}H NMR spectrum of **4** ($CDCl_3$, 500 MHz, RT)

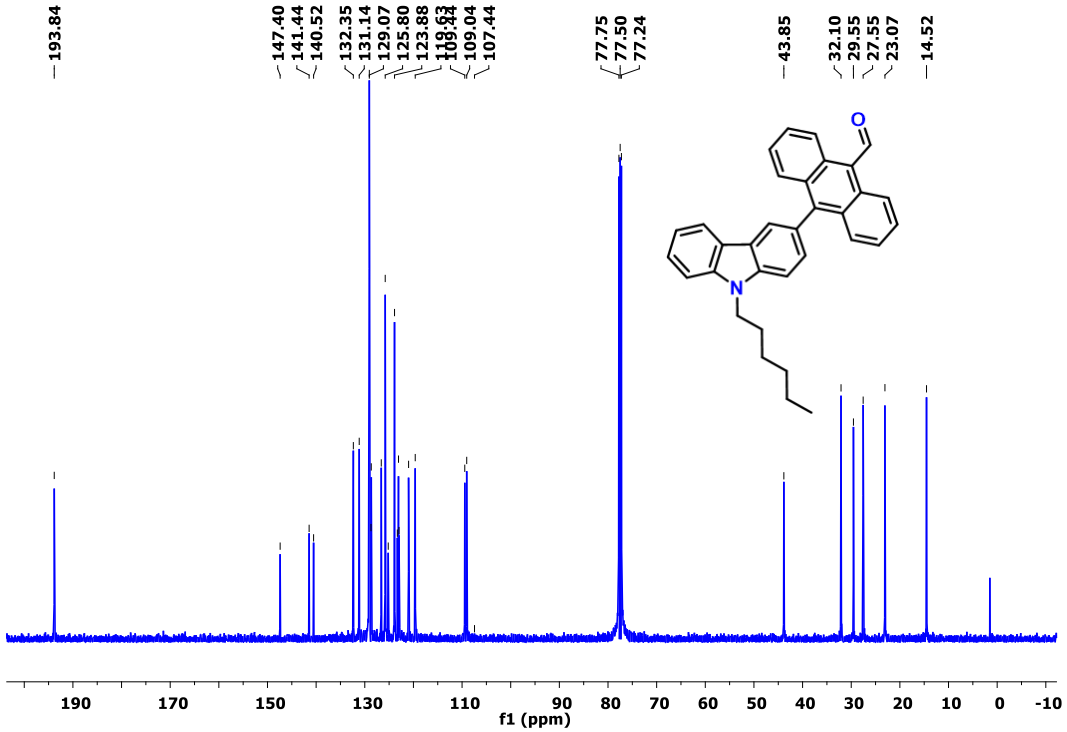


Figure S2: ^{13}C NMR spectrum of **4** ($CDCl_3$, 125 MHz, RT)

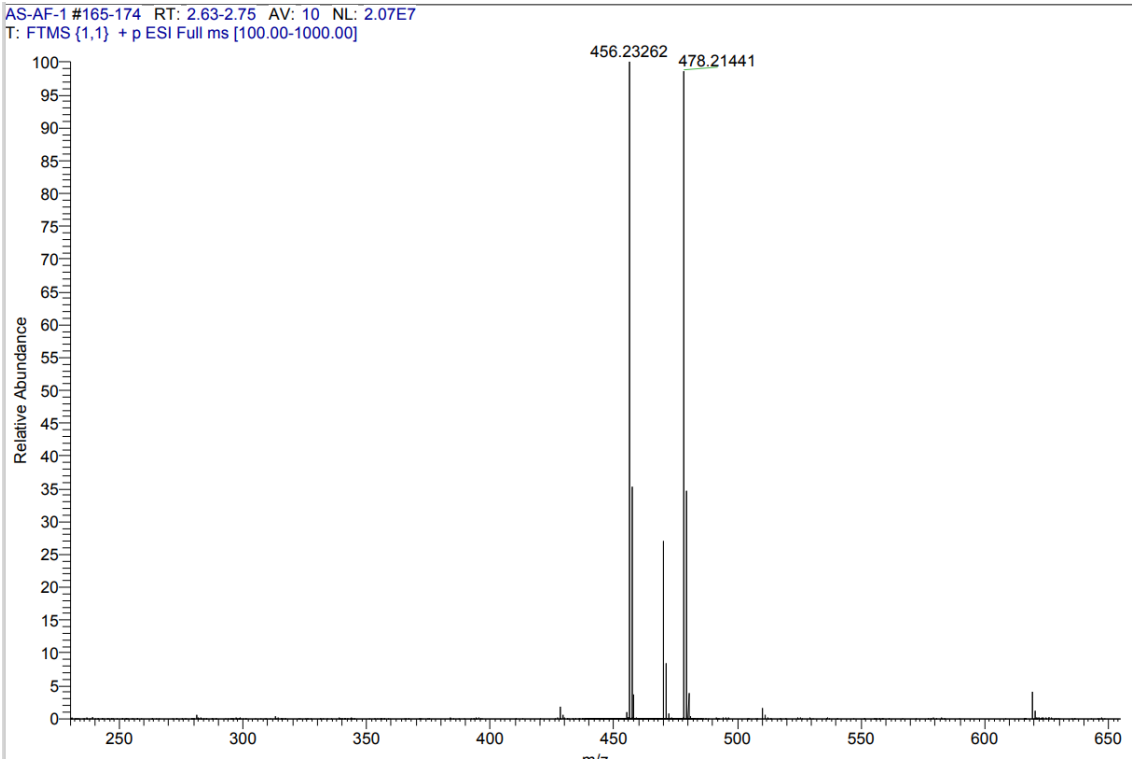


Figure S3: HRMS-ESI spectrum of **4**

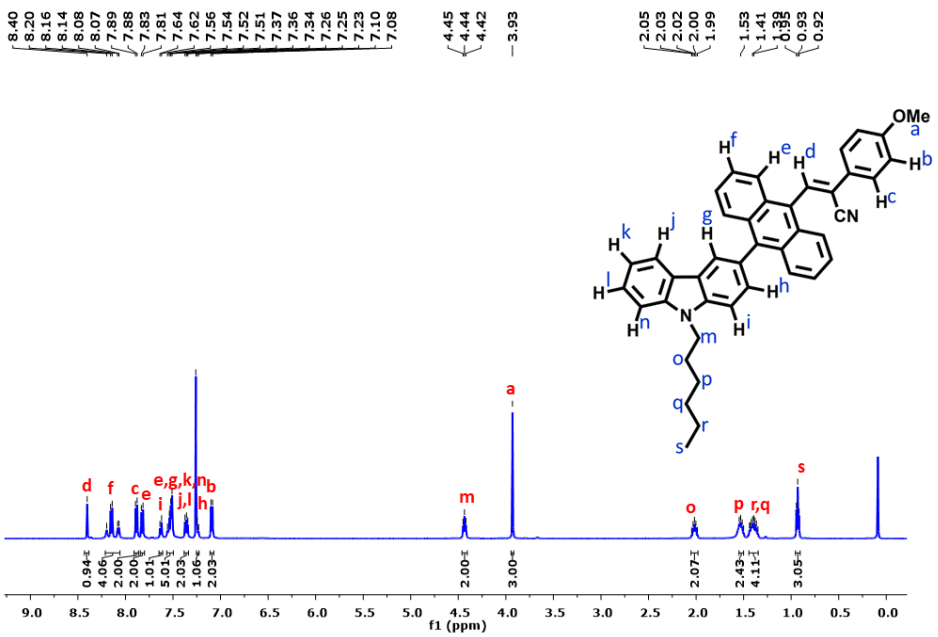


Figure S4: ^{1}H NMR spectrum of **5a** ($CDCl_3$, 500 MHz, RT)

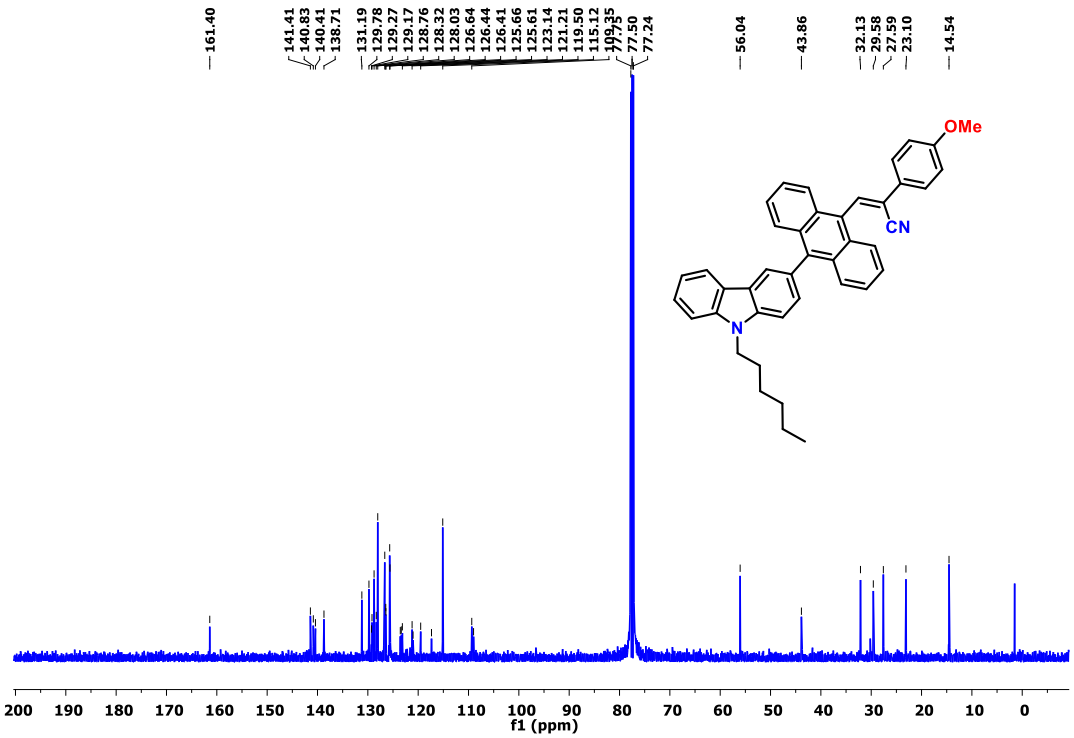


Figure S5: ^{13}C NMR spectrum of **5a** ($CDCl_3$, 125 MHz, RT)

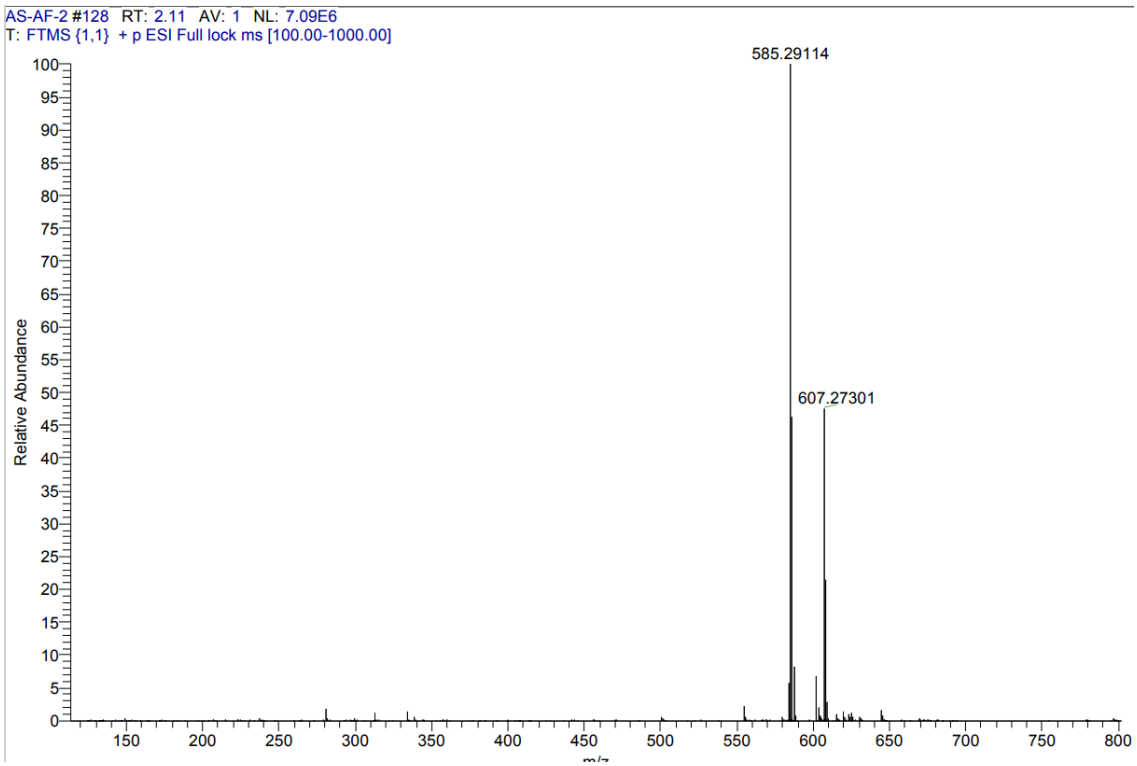


Figure S6: HRMS-ESI spectrum of **5a**

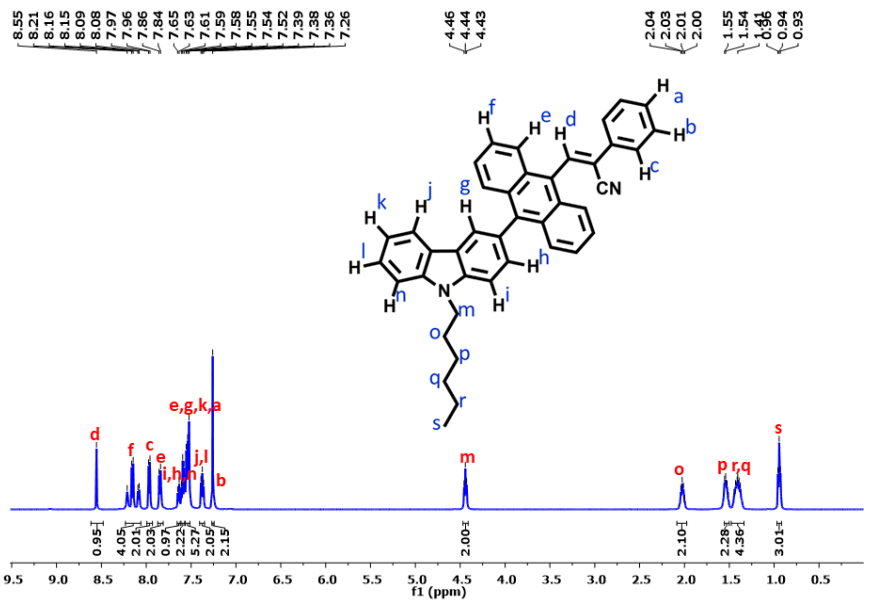


Figure S7: ^{1}H NMR spectrum of **5b** ($CDCl_3$, 500 MHz, RT)

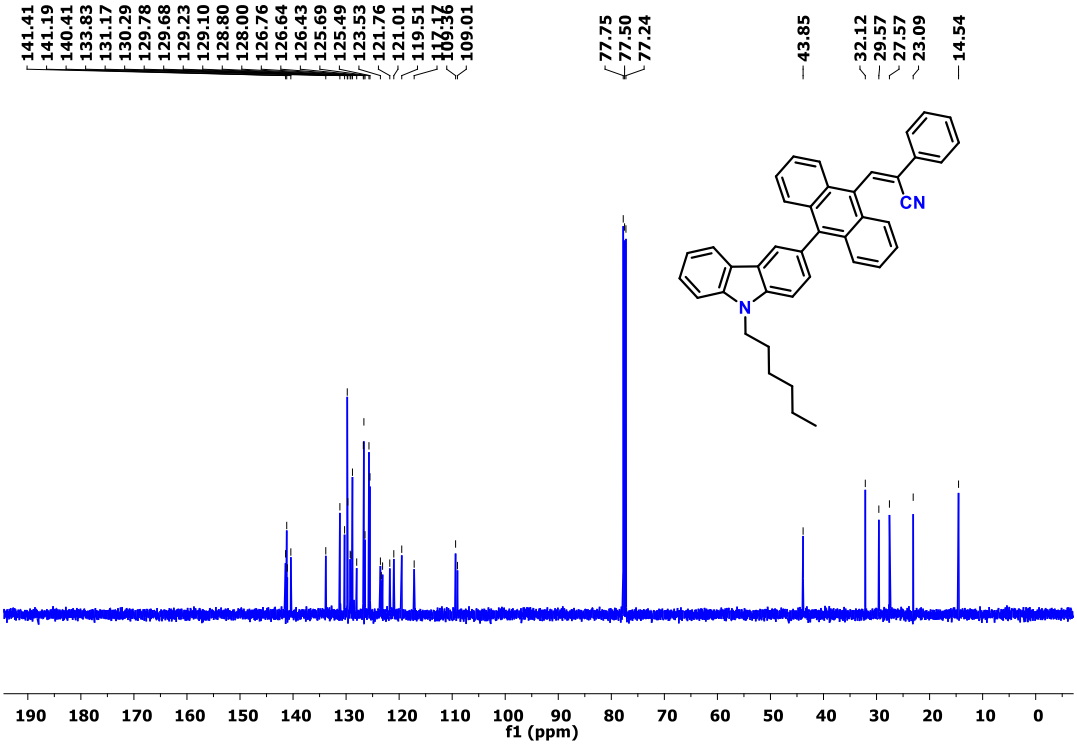


Figure S8: ^{13}C NMR spectrum of **5b** ($CDCl_3$, 125 MHz, RT)

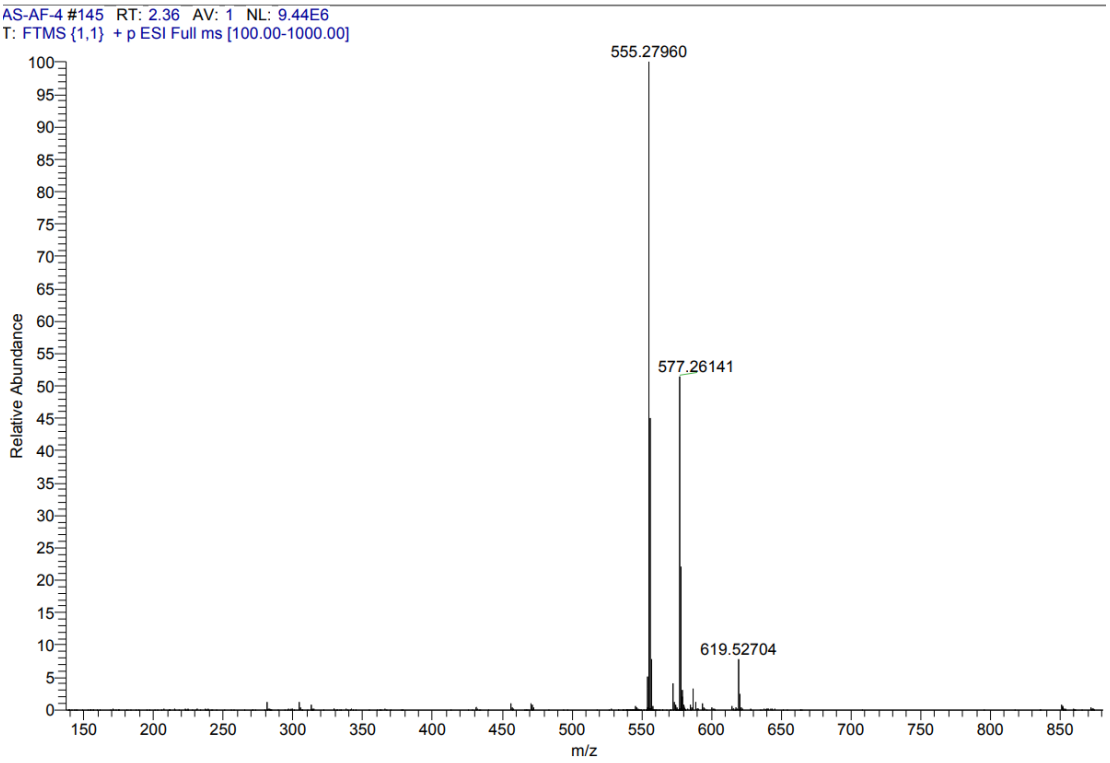


Figure S9: HRMS-ESI spectrum of **5b**

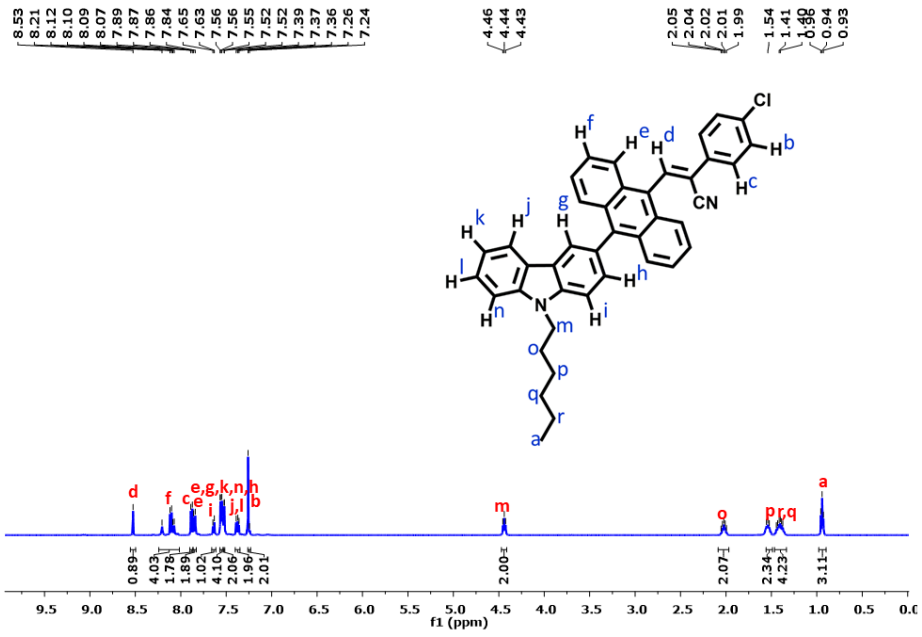


Figure S10: ^{1}H NMR spectrum of **5c** ($CDCl_3$, 500 MHz, RT)

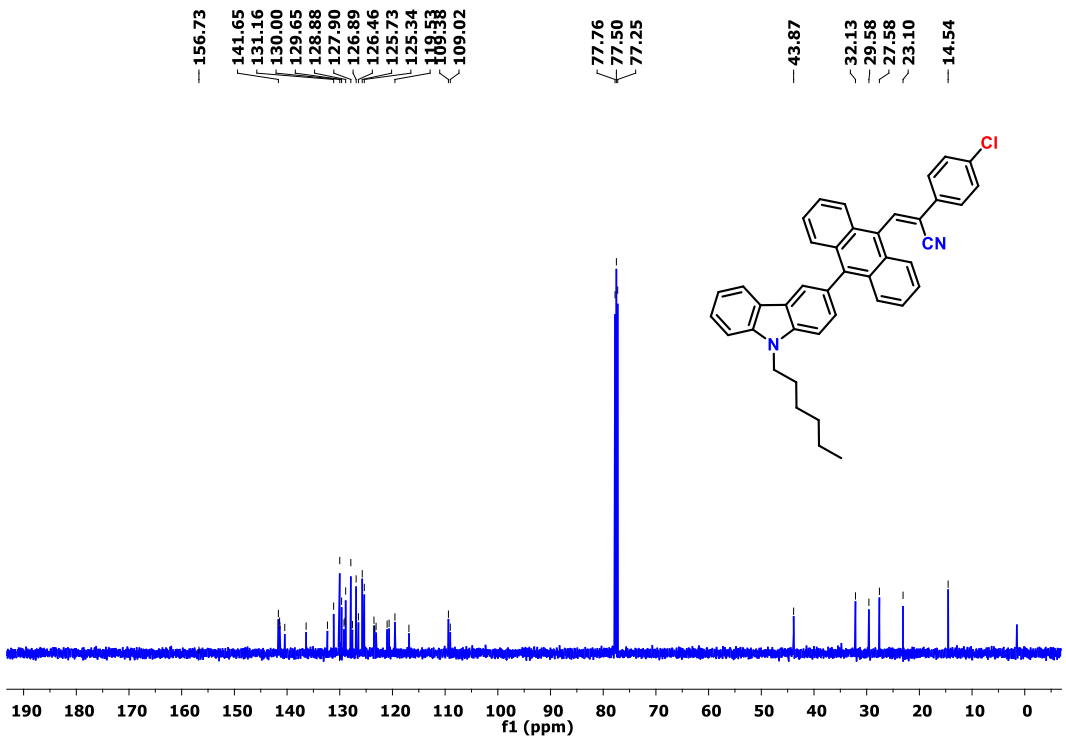


Figure S11: ^{13}C NMR spectrum of **5c** ($CDCl_3$, 125 MHz, RT)

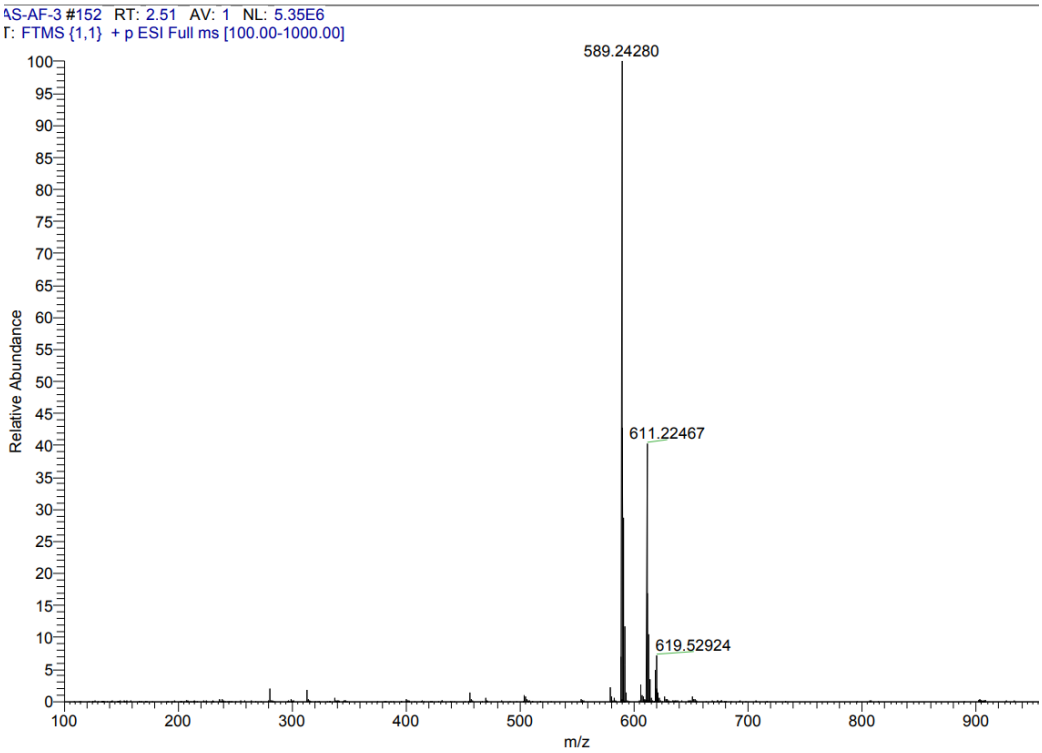


Figure S12: HRMS-ESI spectrum of **5c**

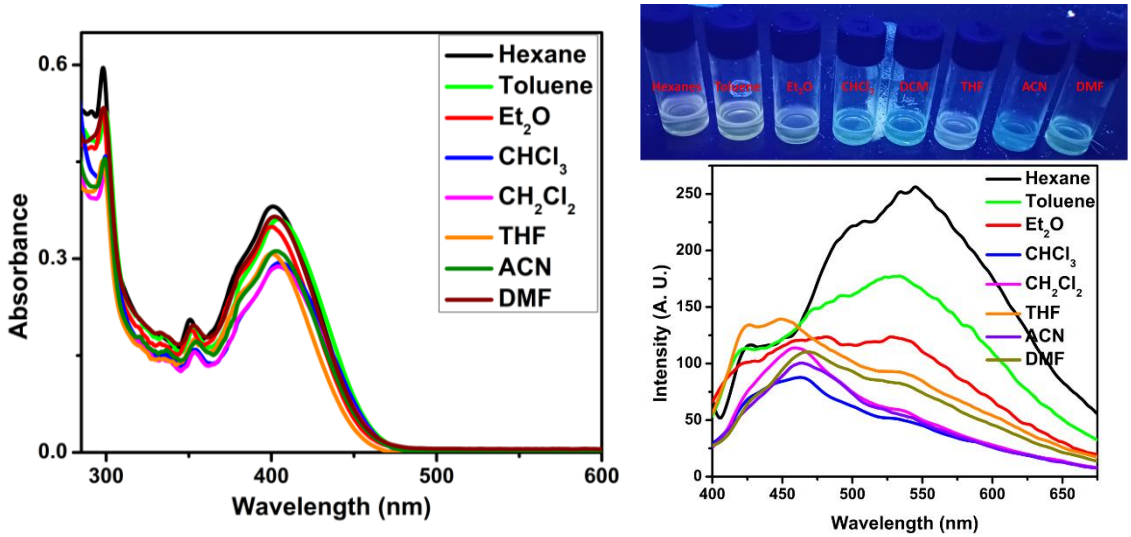


Figure S13. Absorption (left) and emission spectra (right) of **5a** in various polarity of solvents (Con 3 $\times 10^{-5}$ M, λ_{ex} = 385 nm).

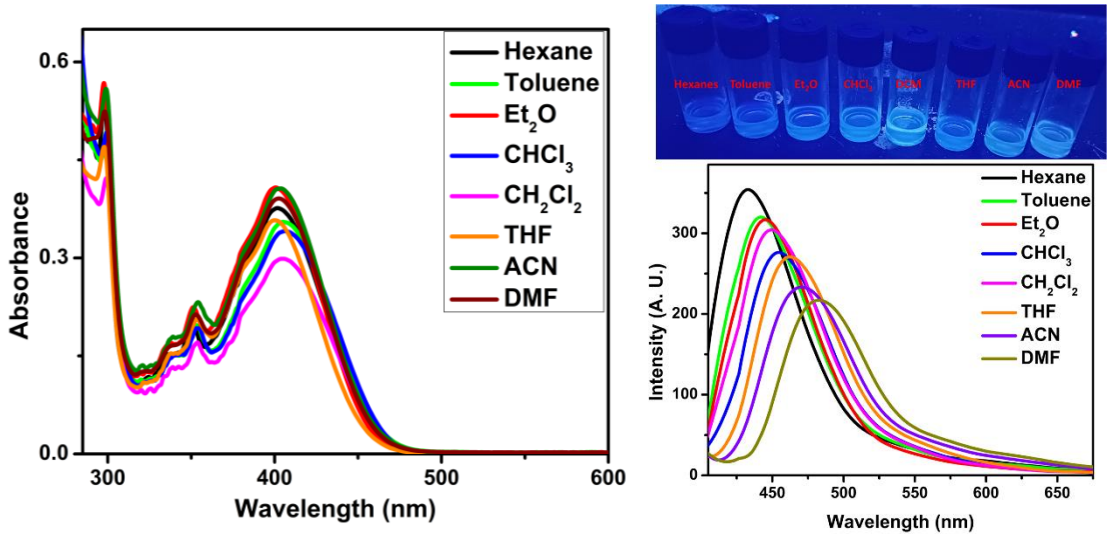


Figure S14. Absorption (left) and emission spectra (right) of **5b** in various polarity of solvents (Con 3 $\times 10^{-5}$ M, λ_{ex} = 385 nm).

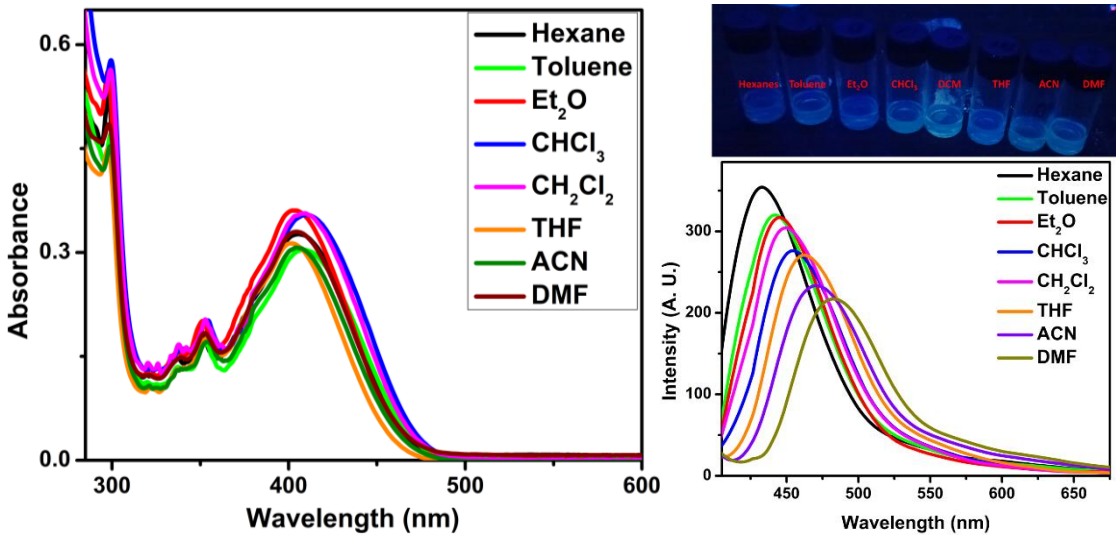


Figure S15. Absorption (left) and emission spectra (right) of **5c** in various polarity of solvents (Con 3 ×10^{-5} M, λ_{ex} = 385 nm).

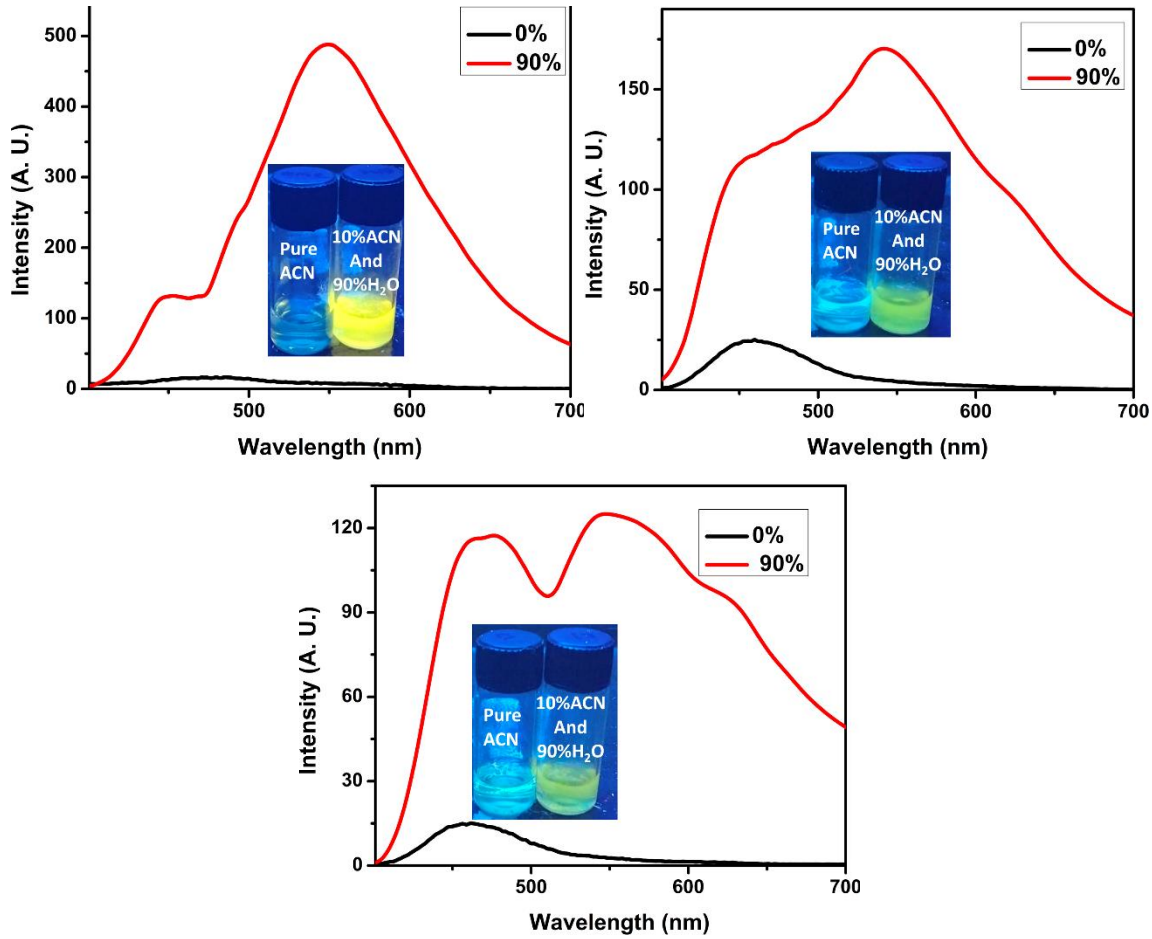


Figure S16: Aggregation studies (ACN:H_2O) of molecule **5a** (top left), **5b** (top right) and **5c** (bottom) (Con 3 ×10^{-5} M, λ_{ex} = 385 nm).

Table S1: Optical data of compound **5a** with different polarity of solvents

Solvent	λ_{abs}	λ_{em}	Stokes shift (cm^{-1})	Quantum yields (%)[a]
Hexane	401	545	6589.03	32
Toluene	404	528	5813.08	27
Et_2O	400	528	6060.60	15
$CHCl_3$	405	463	3093.08	3.2
CH_2Cl_2	405	458	2857.29	2.1
THF	400	448	2678.57	0.32
ACN	403	441	2138.15	0.21
DMF	402	447	2504.25	0.24

Table S2: Optical data of compound **5b** with different polarity of solvents

Solvent	λ_{abs}	λ_{em}	Stokes shift (cm^{-1})	Quantum yields (%)[a]
Hexane	402	433	1780.93	15
Toluene	406	440	1903.26	12
Et_2O	400	449	2728.28	09
$CHCl_3$	406	447	2259.17	07
CH_2Cl_2	405	448	2369.92	4.2
THF	400	457	3118.16	3.6
ACN	403	458	2979.83	3.1
DMF	402	469	3553.66	2.7

Table S3: Optical data of compound **5c** with different polarity of solvents

Solvent	λ_{abs}	λ_{em}	Stokes shift (cm^{-1})	Quantum yields (%)[a]
Hexane	405	433	1596.66	18
Toluene	408	439	1730.76	15
Et_2O	402	443	2302.25	11
$CHCl_3$	408	448	2188.37	08
CH_2Cl_2	408	453	2434.74	3.5
THF	401	462	3292.63	3.1
ACN	405	471	3459.93	2.7
DMF	405	480	3858.02	2.3

[a]Quantum yields are calculated using quinine sulfate (0.1 M in H_2SO_4, Φ_F = 57.7%) solution as reference and using the following formula $\phi = \phi_F \times I/I_R \times A_R/A \times \eta^2/\eta_R^2$ where ϕ = quantum yield, I = integral area of emission peak, A = absorbance at λ_{ex}, η = refractive index of solvent.

Table S4: Summarizing the optical properties of compound **5a-c** in Dichloromethane.

Compounds	**λ_{abs} (nm)/ε**	**Emission (nm)**	**quantum yield[a] (%) in solution state**	**quantum yield (%) in solid state**
5a	404 (2.8×10^5), 350 (1.5×10^5), 298 (4.2×10^5)	473	2.1	28
5b	406 (2.9×10^5), 353 (1.7×10^5), 297 (4.2×10^5)	458	4.2	22
5c	410 (3.5×10^5), 352 (2.0×10^5), 300 (5.6×10^5)	450	3.5	18

Quantum yields are calculated using quinine sulfate (0.1 M in H_2SO_4, Φ_F = 57.7%) solution as reference and using the following formula $\phi = \phi_F \times I/I_R \times A_R/A \times \eta^2/\eta_R^2$ where ϕ = quantum yield, I = integral area of emission peak, A = absorbance at λ_{ex}, η = refractive index of solvent. Solution state quantum yields calculated in dichloromethane.

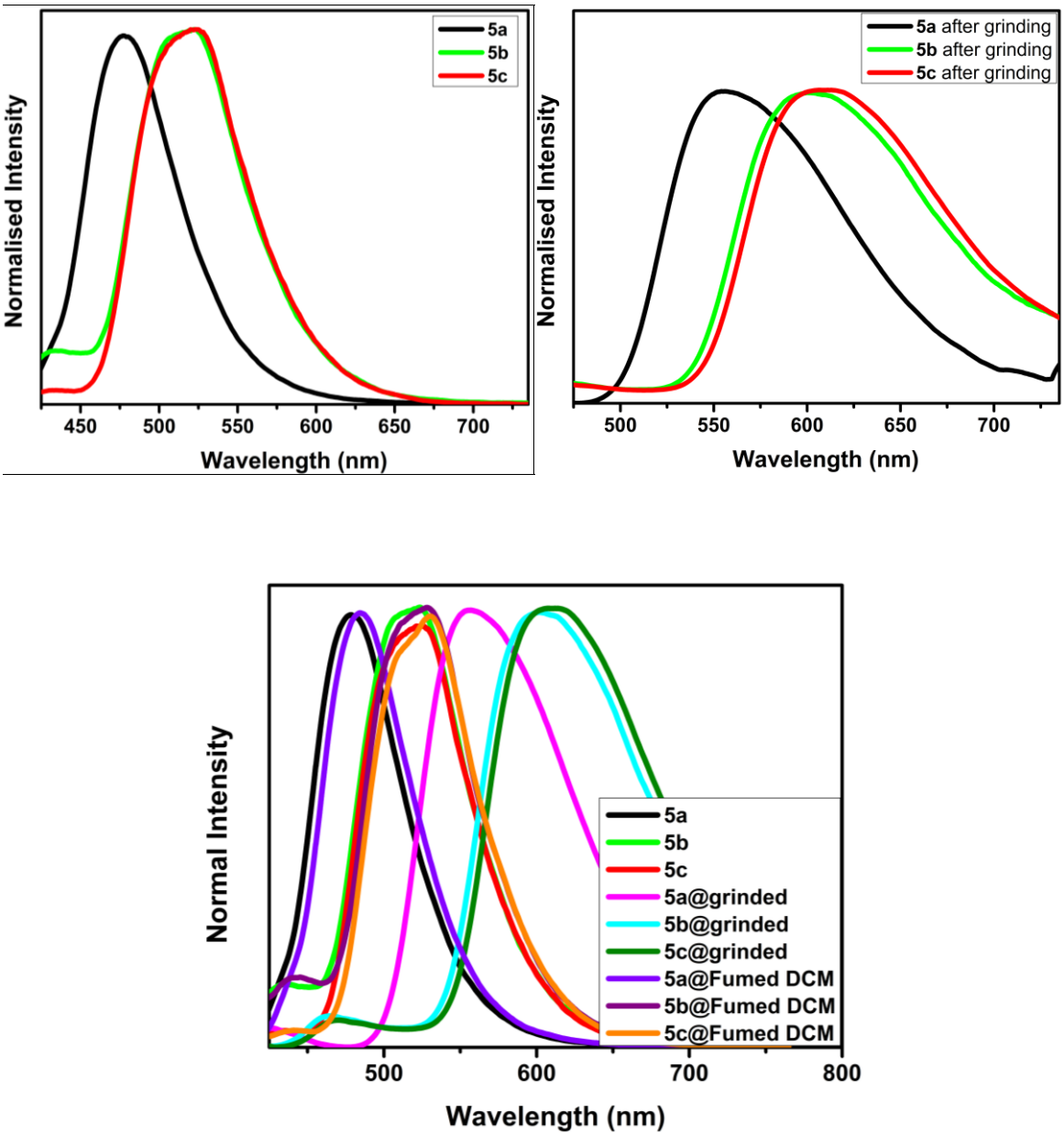


Figure S17: Solid state emission spectra of **5a-c** with grinding and fuming with DCM solvent

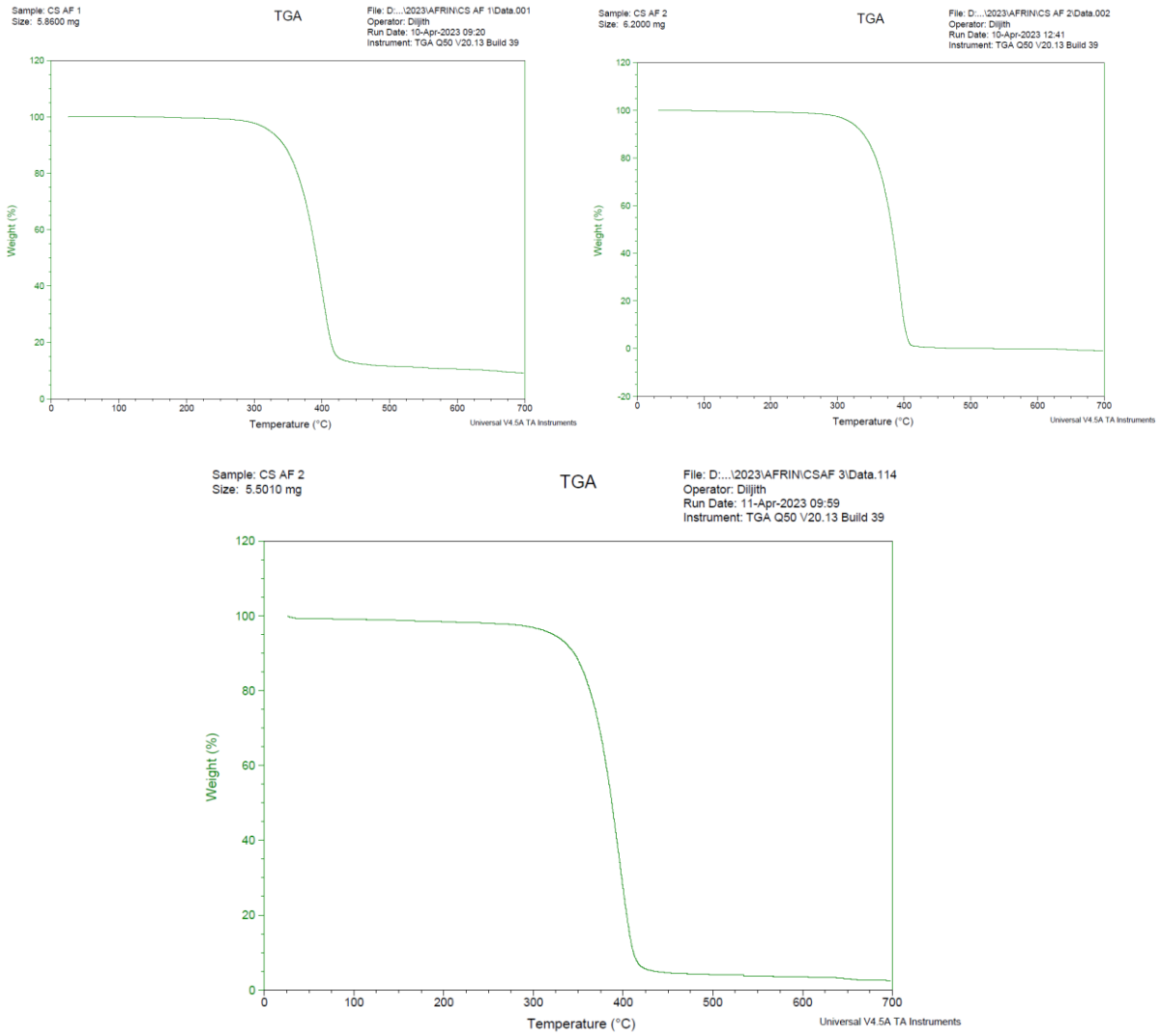


Figure S18: TGA data of **5a** (top left), **5b** (top right) and **5c** (bottom).

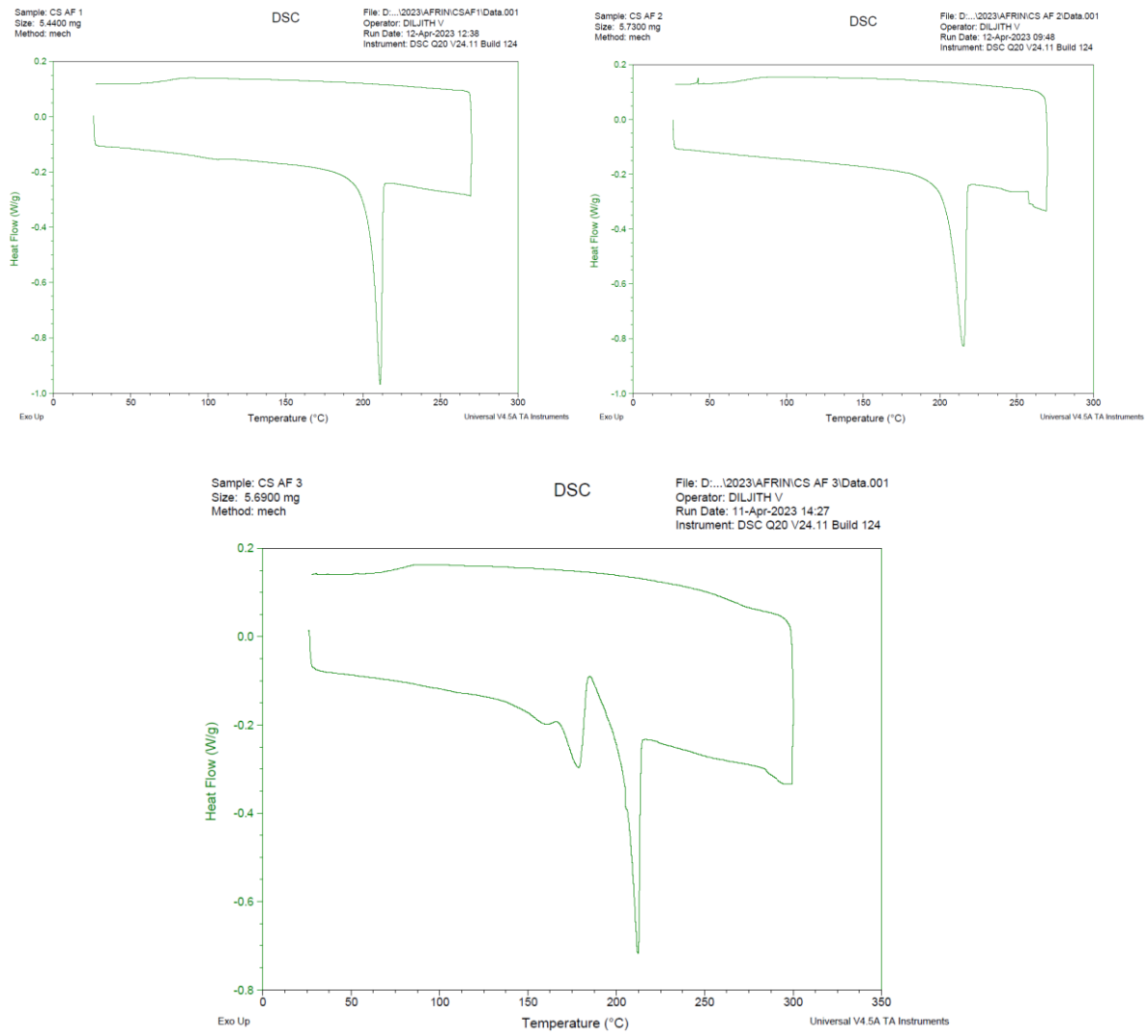


Figure S19: DSC data of **5a** (top left), **5b** (top right) and **5c** (bottom).

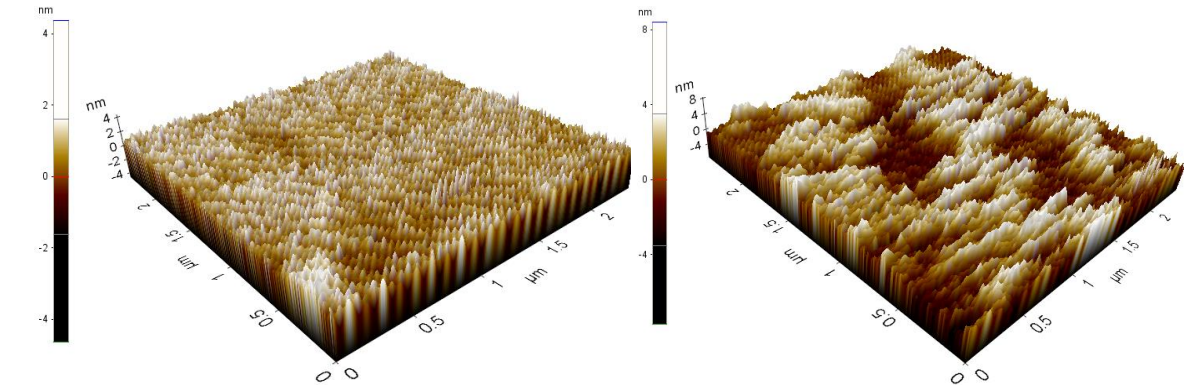


Figure S20: AFM images of **5a** ACN (left) and aggregates (right)

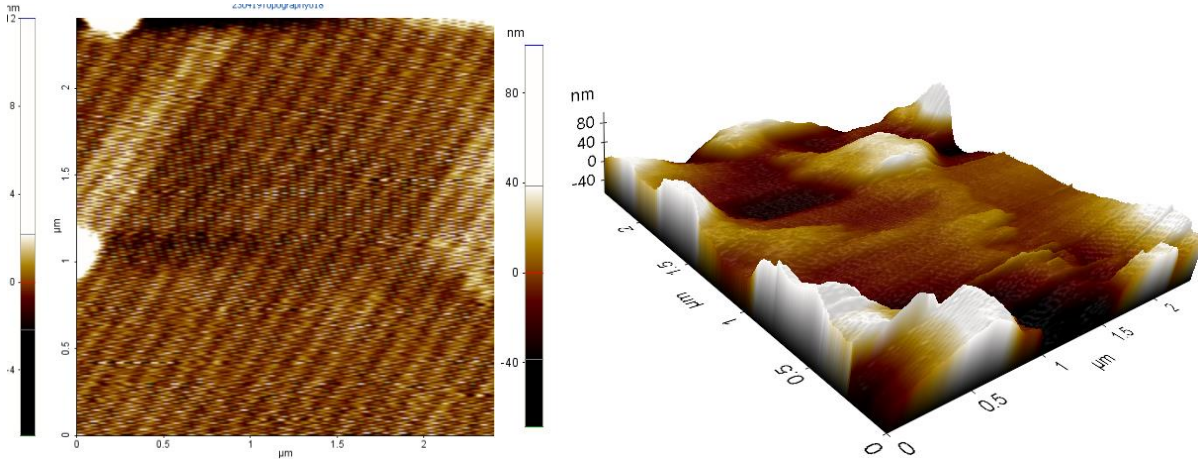


Figure S21: AFM images of **5b** ACN (left) and aggregates (right)

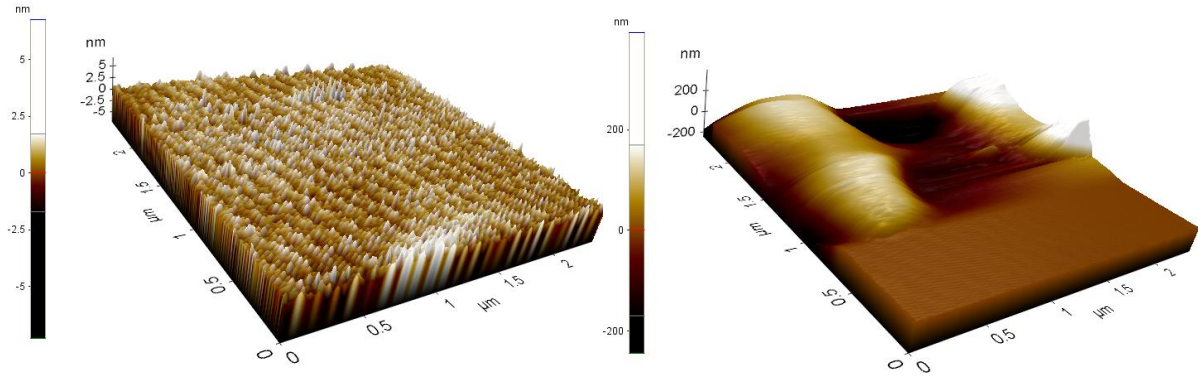


Figure S22: AFM images of **5c** ACN (left) and aggregates (right)

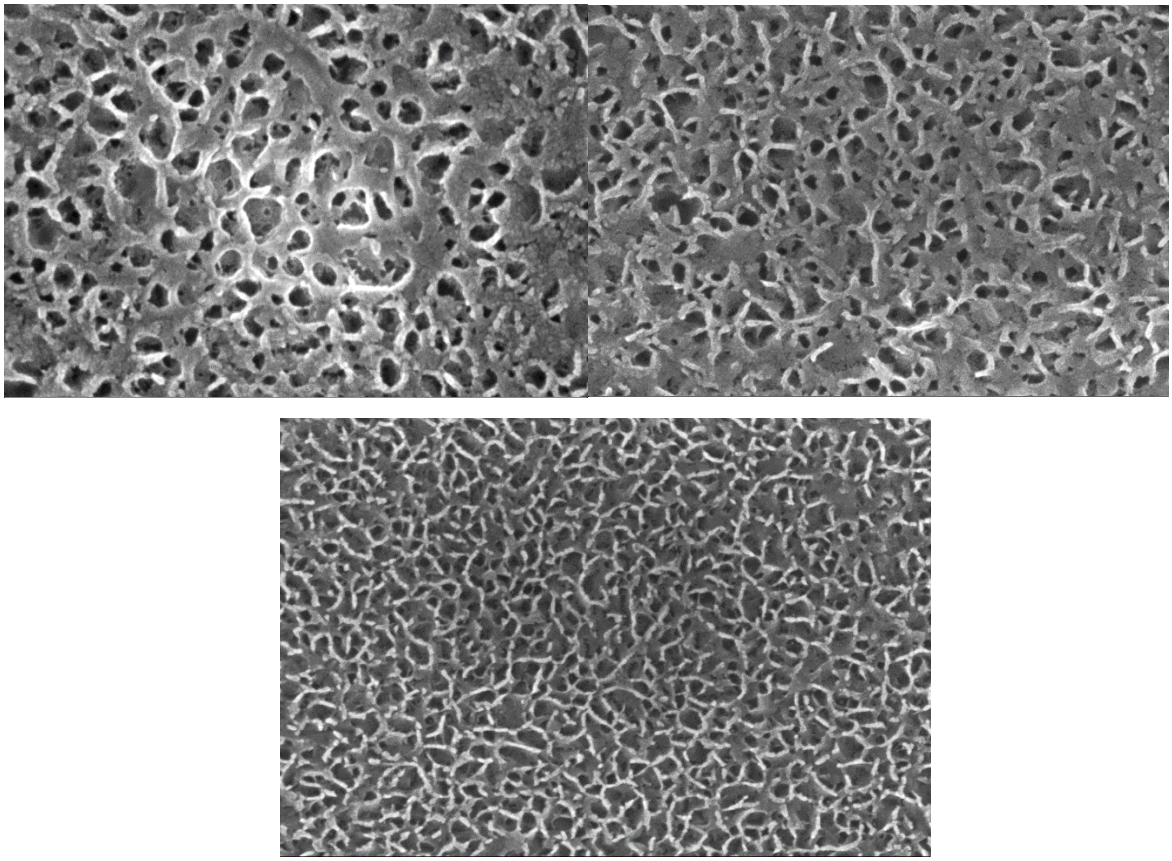


Figure S23: FE-SEM images of **5a** (top left), **5b** (top right) and **5c** (bottom).

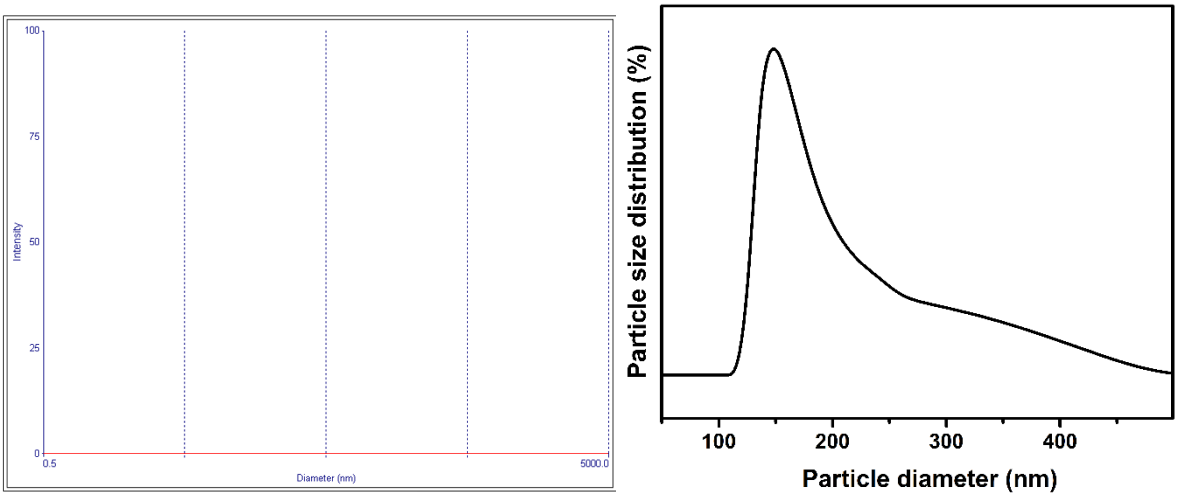


Figure S24: DLS plots of **5a** ACN (left) and aggregates (right)

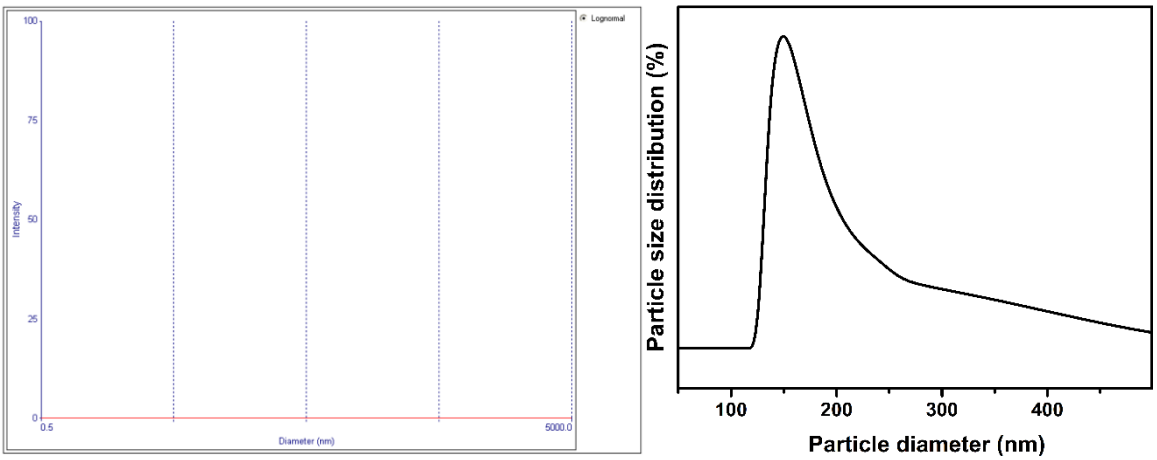


Figure S25: DLS plots of **5b** ACN (left) and aggregates (right)

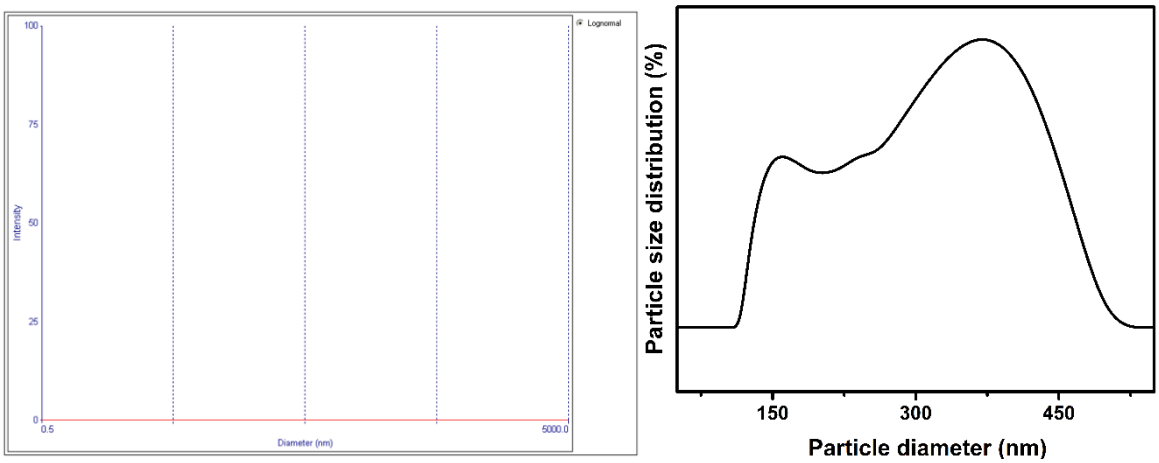


Figure S24: DLS plots of **5c** ACN (left) and aggregates (right)

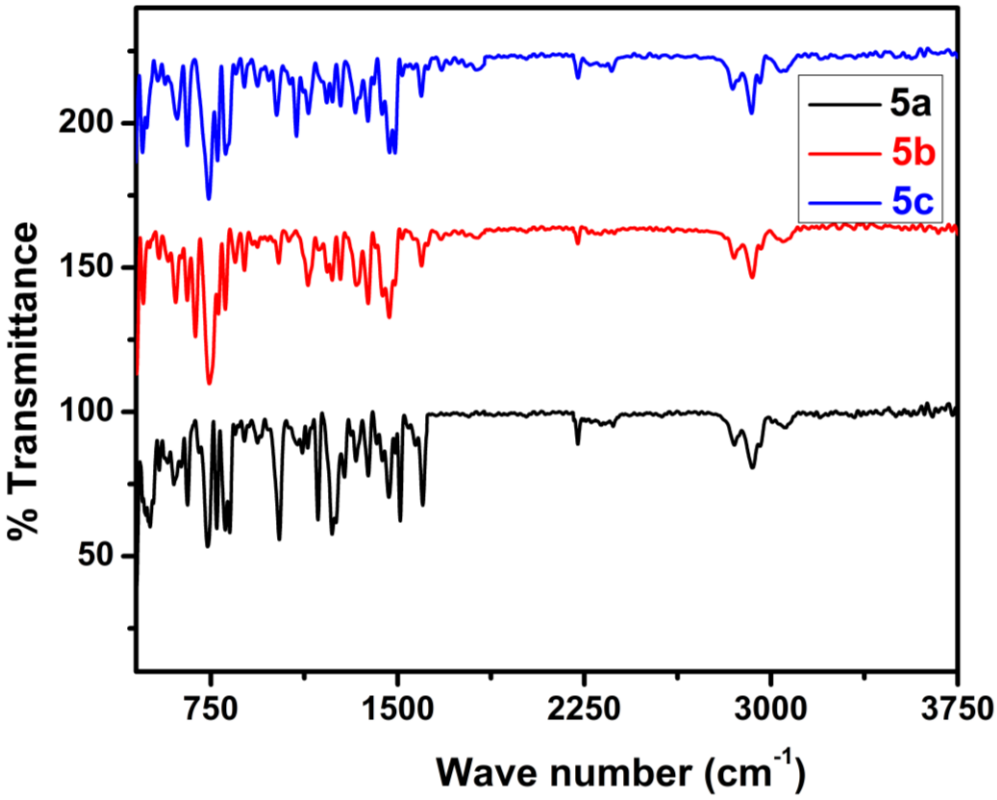


Figure S25: FTIR of **5a**, **5b** and **5c**.

Table S5: DFT data of molecule **5a**

6	2.166112915	0.053120662	0.331185415
6	2.720090887	-0.630629735	1.435770152
6	4.095825218	-0.745522435	1.619281980
6	4.936218545	-0.154385605	0.671174492
6	4.405657836	0.536031904	-0.451165116
6	3.019874048	0.635188703	-0.611155251
1	2.048922496	-1.083775221	2.159974438
1	4.490565157	-1.284424490	2.475485112
1	2.600814970	1.161173817	-1.465077549
6	6.703053446	0.582516019	-0.525911791
6	7.984595222	0.870950609	-1.005830100
6	8.086380085	1.600640880	-2.188524482
6	6.943810944	2.032753306	-2.883996856
6	5.669835979	1.739910162	-2.405064722
6	5.538496726	1.008742215	-1.219093336
1	8.876367845	0.538265964	-0.482990568

1	9.071850789	1.836900191	-2.580945608
1	7.058409251	2.598457882	-3.804164129
1	4.787799456	2.073579944	-2.945612694
7	6.324520207	-0.107368028	0.622245858
6	7.229090981	-0.747604753	1.562528027
1	8.131129324	-0.129064941	1.638933374
1	6.757378148	-0.727871558	2.551774632
6	7.603320210	-2.187951838	1.180416343
1	6.685376016	-2.783392382	1.099046461
1	8.059620279	-2.182675660	0.182661790
6	8.557885904	-2.825280095	2.194312654
1	8.110382454	-2.864550550	3.195096922
1	8.812328931	-3.850144282	1.904649955
1	9.494698866	-2.259761027	2.272023265
6	0.678436746	0.146268277	0.176433603
6	-0.031520601	1.194036143	0.804787953
6	-0.014297212	-0.810177618	-0.597608255
6	-1.467867239	1.267092099	0.682191020
6	0.638532564	2.195951844	1.578240363
6	-1.451978931	-0.728074736	-0.746607153
6	0.681090395	-1.872737302	-1.262180535
6	-2.150786312	2.318898934	1.371538358
6	-2.167606730	0.298496203	-0.080947847
6	-0.053742696	3.201587366	2.199439890
1	1.718011119	2.143880655	1.664357128
6	-2.090667501	-1.675825775	-1.609202778
6	0.021605799	-2.774600424	-2.052269611
1	1.754871256	-1.944523488	-1.132425295
6	-1.469687916	3.260527059	2.098319208
1	-3.234327663	2.357507769	1.330717514
1	0.477600123	3.951590535	2.778985642
1	-3.158821160	-1.597812428	-1.771837970

6	-1.383098219	-2.664163847	-2.239194754
1	0.571423379	-3.570394592	-2.547347768
1	-2.014613797	4.050439850	2.608330610
1	-1.897916556	-3.367750271	-2.887716528
6	-3.630971935	0.443099863	-0.208724100
1	-3.980374242	1.402584896	-0.587598274
6	-4.593712487	-0.447566163	0.144739405
6	-6.046346703	-0.219516641	-0.059822398
6	-6.996336072	-0.846149590	0.758709913
6	-6.518690474	0.638030650	-1.073089730
6	-8.362783756	-0.613558033	0.604011564
1	-6.665574997	-1.525829119	1.538503226
6	-7.873249979	0.879652066	-1.236544369
1	-5.816756327	1.102313612	-1.759421562
6	-8.810292974	0.259044563	-0.394684818
1	-9.061470607	-1.114920911	1.263682086
1	-8.235850326	1.533874042	-2.023098059
8	-10.115812459	0.560074009	-0.638211501
6	-11.109866312	-0.049467900	0.172582777
1	-10.989382601	0.222619165	1.229223318
1	-12.065958365	0.330309755	-0.191556344
1	-11.092687367	-1.142875524	0.076589547
6	-4.231665293	-1.668919150	0.814236265
7	-3.998203986	-2.657884979	1.381434301

Table S6: DFT data of **5b**

6	-6.722392599	1.177987578	2.893295331
6	-7.820442429	0.757499288	2.123030849
6	-7.647165244	0.154114731	0.879036310
6	-6.339109306	-0.025449207	0.418012002
6	-5.219049582	0.398248622	1.182354465
6	-5.421993645	1.001430928	2.428735181
1	-6.892523138	1.645822632	3.858702983

1	-8.827755982	0.907183269	2.502278774
1	-8.505752843	-0.159947367	0.292987239
1	-4.574476364	1.328408042	3.025654187
6	-4.503240920	-0.543529356	-0.789857010
6	-3.607253539	-0.982649909	-1.769253548
6	-2.245558841	-0.813161897	-1.532607038
6	-1.759441025	-0.214071404	-0.349397851
6	-2.668646285	0.225265301	0.618337435
6	-4.041898882	0.066423576	0.407283845
1	-3.949402567	-1.439659711	-2.692997562
1	-1.531647608	-1.147525548	-2.280062817
1	-2.301699345	0.687208039	1.531234014
6	-6.737046046	-1.106316552	-1.837350738
1	-7.634862508	-1.537530540	-1.381869607
1	-6.208761519	-1.934251432	-2.322144452
6	-7.117498347	-0.036068844	-2.866375846
1	-6.224725368	0.383774263	-3.341145858
1	-7.751695901	-0.468924717	-3.648428165
1	-7.667038072	0.783621318	-2.392240932
7	-5.891213682	-0.606288529	-0.765060431
6	-0.284225860	-0.054561707	-0.143687599
6	0.334789820	1.191570404	-0.393726223
6	0.489700923	-1.150256150	0.299290577
6	1.761236740	1.334928834	-0.224369173
6	-0.415344661	2.327028943	-0.840007371
6	1.918747079	-1.010685624	0.483335676
6	-0.117220065	-2.412475426	0.603848763
6	2.352322907	2.602838925	-0.525578575
6	2.543542286	0.229018606	0.195129335
6	0.189403187	3.529654934	-1.093877812
1	-1.484754053	2.216553572	-0.978298077
6	2.639081512	-2.131857875	1.006469394

6	0.618911296	-3.465323740	1.075227553
1	-1.186919714	-2.516401673	0.463839353
6	1.594064266	3.668964893	-0.934358272
1	3.428681004	2.714267360	-0.447052856
1	-0.402198739	4.376590294	-1.430519809
1	3.700839700	-2.030513970	1.194652465
6	2.016102659	-3.317940457	1.288580384
1	0.134667181	-4.411227501	1.301875798
1	2.070194861	4.621199509	-1.152282714
1	2.592088482	-4.149573545	1.685062813
6	3.990765564	0.439590924	0.386215569
1	4.265814059	1.259557605	1.048047607
6	5.020964313	-0.219449094	-0.204195353
6	4.762775712	-1.198261893	-1.225779724
7	4.609298799	-1.979223550	-2.074811398
6	6.451199102	0.057867625	0.096952047
6	7.442134884	-0.169191844	-0.872963144
6	6.842964630	0.556451547	1.351453367
6	8.778734060	0.120523754	-0.605305947
1	7.160304659	-0.570036871	-1.842121504
6	8.179380552	0.847926117	1.615092912
1	6.102558715	0.690708848	2.134618767
6	9.153283283	0.634474557	0.637120195
1	9.528593515	-0.057099097	-1.371294349
1	8.462206212	1.227567840	2.593229960
1	10.196204591	0.855459252	0.846717820

Table S7: DFT data of **5c**

6	-7.243657802	1.528494812	2.878036812
6	-8.370304846	1.073160147	2.171469120
6	-8.242536746	0.362143960	0.979982681
6	-6.950898162	0.110153873	0.506627483

6	-5.802401600	0.567741142	1.206380975
6	-5.959761081	1.279192340	2.401169290
1	-7.378561910	2.080829270	3.803521327
1	-9.363955678	1.281032120	2.559189125
1	-9.122517711	0.022235997	0.442040854
1	-5.090241812	1.633557441	2.948777571
6	-5.158964167	-0.553768973	-0.695578892
6	-4.298213312	-1.095483511	-1.655014599
6	-2.927333197	-0.941212880	-1.465516105
6	-2.397903213	-0.257657865	-0.348609352
6	-3.272044565	0.283587390	0.599778765
6	-4.653355986	0.142268921	0.435007918
1	-4.674034020	-1.619127815	-2.528910921
1	-2.240856683	-1.354259774	-2.199249407
1	-2.871900669	0.810451081	1.462175673
6	-7.431933352	-1.143342364	-1.640289941
1	-8.320785762	-1.526802958	-1.127737938
1	-6.929232322	-2.011924757	-2.078673577
6	-7.830320739	-0.145067485	-2.732906126
1	-6.947556090	0.223908218	-3.265169452
1	-8.496024660	-0.623300837	-3.460382055
1	-8.352147663	0.716143096	-2.303179083
7	-6.546767349	-0.579064439	-0.633372223
6	-0.915338832	-0.116737679	-0.189005401
6	-0.277680326	1.093993781	-0.544717936
6	-0.154049000	-1.192076155	0.321005175
6	1.153975086	1.221392114	-0.411278507
6	-1.015210370	2.205952014	-1.064824521
6	1.280548976	-1.068350598	0.469232811
6	-0.779884247	-2.414347925	0.731588356
6	1.762043677	2.450913052	-0.818592748
6	1.923075817	0.133839036	0.076937886

6	-0.393718182	3.373782347	-1.420367475
1	-2.088547627	2.105306020	-1.177404737
6	1.987731736	-2.160110775	1.066624046
6	-0.055997148	-3.443232807	1.270079988
1	-1.853846151	-2.505899680	0.618158335
6	1.015650286	3.497467310	-1.294727090
1	2.841458885	2.548143513	-0.768657429
1	-0.975656752	4.203523012	-1.811973858
1	3.053982934	-2.066706138	1.231753018
6	1.347044156	-3.308089150	1.449352444
1	-0.554173783	-4.358782088	1.576770631
1	1.505101082	4.420778997	-1.592742291
1	1.913831112	-4.117874008	1.900474514
6	3.375848667	0.329725138	0.224994006
1	3.677425294	1.202510980	0.802266820
6	4.384279589	-0.402202093	-0.316830095
6	4.094878504	-1.461942338	-1.244314607
7	3.919310008	-2.311029888	-2.020532793
6	5.822827366	-0.127997657	-0.061838535
6	6.798363243	-0.481049621	-1.009315992
6	6.245489013	0.493188617	1.125898518
6	8.145365779	-0.199546567	-0.796494507
1	6.500175885	-0.977979279	-1.927435391
6	7.588398946	0.783391216	1.349280719
1	5.523474971	0.731231104	1.900996749
6	8.531563146	0.437687123	0.381561541
1	8.888502884	-0.471545709	-1.538265821
1	7.903926649	1.257873149	2.272299374
17	10.228876365	0.793658355	0.660586851