

Supporting information for

A- π -A, D- π -D and D- π -A Blue Emitting fluorophores based on dispiro[fluorene-9,6'-indeno[1,2-*b*]fluorene-12',9''-fluorene]

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MATERIAL AND METHODS

Synthesis and ^1H NMR studies:

Commercially available reagents and solvents were purchased from Alfa Aesar, Acros Organics or Sigma-Aldrich and used without further purification other than those detailed below. Dichloromethane and acetonitrile were distilled from P_2O_5 drying agent Sicapent© (Merck); THF was distilled from sodium/benzophenone prior to use. Toluene was distilled from sodium prior to use. Light petroleum refers to the fraction with bp 40-70°C. Reactions were stirred magnetically, unless otherwise indicated. Analytical thin layer chromatography was carried out using aluminium backed plates coated with Merck Kieselgel 60 GF254 and visualized under UV light (at 254 and 365 nm). Chromatography was carried out using silica 60A CC 40-63 μm (SDS). ^1H , ^{13}C and ^{19}F NMR spectra were recorded using Bruker 300 MHz (^1H frequency, corresponding ^{13}C frequency is 75 MHz and corresponding ^{19}F frequency is 282MHz) or 500 MHz instruments (^1H frequency, corresponding ^{13}C frequency is 125 MHz); chemical shifts were recorded in ppm and J values in Hz. In the ^{13}C NMR spectra, signals corresponding to CH, CH_2 or Me groups, assigned from DEPT, are noted; all others are C. The residual signals for the NMR solvents are: CDCl_3 ; 7.26 ppm for the proton and 77.00 ppm for the carbon, CD_2Cl_2 ; 5.32 ppm for the proton and 53.80 ppm for the carbon; $[\text{D}_6]\text{DMSO}$; 2.50 ppm for the proton and 39.52 ppm for the carbon. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet, m for multiplet and br for broad. High resolution mass spectra were recorded at the Centre Régional de Mesures Physiques de l'Ouest (Rennes). Names of chemicals have been generated with the naming service of ACD-I lab, which determines the chemical name according to systematic application of the nomenclature rules agreed upon by the International Union of Pure and Applied Chemistry and International Union of Biochemistry and Molecular Biology. The synthesis and the full characterization of the **DSF-IF(t-Bu) $_4$ 1** may be found in our previous works.^[1]

Spectroscopic studies:

UV-visible spectra were recorded in solution using a UV-Visible-NIR spectrophotometer CARY 5000-Varian or SHIMADZU UV-1605 spectrophotometer. The optical band gap was calculated from the absorption edge of the UV-vis absorption spectrum using the formula ΔE^{opt} (eV) = hc/λ , λ being the absorption edge (in meter). With $h = 6.6 \times 10^{-34}$ J.s ($1\text{eV} = 1.6 \times 10^{-19}$ J) and $c = 3.0 \times 10^8$ m.s $^{-1}$, (ΔE^{opt} (eV) = $1237.5 / \lambda$ (in nm)). Photoluminescence spectra were recorded with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a Xenon lamp either in solution (THF) or in thin film. Quantum yields in solution (θ_{sol}) were calculated relative to quinine sulfate ($\theta_{\text{sol}} = 0.546$ in H_2SO_4 1N) using standard procedures.^[2] θ_{sol} was determined according to the following equation (1),

$$\phi_{\text{sol}} = \phi_{\text{ref}} \times 100 \times \frac{(T_s \times A_r)}{(T_r \times A_s)} \left(\frac{n_s}{n_r} \right)^2 \quad (1)$$

where subscripts s and r refer respectively to the sample and reference. The integrated area of the emission peak in arbitrary units is given as T, n is the refracting index of the solvent ($n_s = 1.407$ for THF) and A is the absorbance. IR spectra were recorded on a VARIAN 640-IR using a PIKE Technologies MIRacle(TM) ATR (single Attenuated Total Reflectance) with a diamond crystal.

Electrochemical studies:

All electrochemical experiments were performed under an argon atmosphere, using a Pt disk electrode (diameter 1 mm), the counter electrode was a vitreous carbon rod and the reference electrode was a silver wire in a 0.1 M AgNO₃ solution in CH₃CN. Ferrocene was added to the electrolyte solution at the end of a series of experiments. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal standard. The three electrode cell was connected to a PAR Model 273 potentiostat/galvanostat (PAR, EG&G, USA) monitored with the ECHEM Software. Dichloromethane with less than 100 ppm of water (ref. SDS 02910E21) was used without purification. Activated Al₂O₃ was added in the electrolytic solutions to remove excess moisture. All potentials are referred to the SCE electrode that was calibrated at -0.405 V vs. Fc/Fc⁺ system. The oxidation/reduction onset potential ($E_{onset}^{ox}/E_{onset}^{red}$) were determined on the CVs by the intersection of the tangent of the first oxidation/reduction wave with the potential axis. The estimated errors in the determination of the onset potential values are ± 20 mV for E_{onset}^{ox} and ± 50 mV for E_{onset}^{red} . The electron affinity (LUMO energy level) and the ionization potential (HOMO energy level) of the molecules were determined from their E_{onset}^{red} and E_{onset}^{ox} using the following formula based on an SCE energy level of 4.4 eV relative to the vacuum:^[3] HOMO (eV) = $-[E_{onset}^{ox} \text{ (vs SCE)} + 4.4]$ and LUMO (eV) = $-[E_{onset}^{red} \text{ (vs SCE)} + 4.4]$. The electrochemical gap was calculated from : $\Delta E^{el} = |\text{HOMO-LUMO}|$ (in eV).

Computational Details:

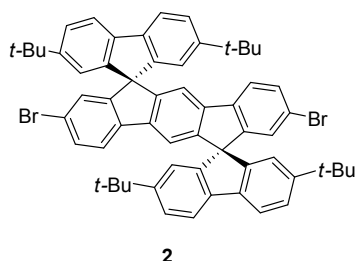
Full geometry optimization with Density functional theory (DFT)^[4, 5] and Time-Dependent Density Functional Theory (TD-DFT) calculations were performed with the hybrid Becke-3 parameter exchange^[6-8] functional and the Lee-Yang-Parr non-local correlation functional^[9] (B3LYP) implemented in the Gaussian 09 (Revision A.02) program suite^[10] using the 6-31G* basis set^[11] and the default convergence criterion implemented in the program. The figures were generated with MOLEKEL 4.3.^[12]

OLED fabrication and testing:

OLEDs were fabricated using the following procedure. Indium-tin oxide (ITO) substrates on glass from Merck underwent a solvent ultrasonic cleansing using acetone, ethanol and isopropanol followed by a 15 min UV-ozone treatment. A layer of poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT/PSS from Aldrich) was then deposited onto ITO by spin-coating at 6000 rpm, from a 3 wt% water dispersion to form a 40 nm-thick layer. PEDOT/PSS was subsequently annealed at 120°C under vacuum for 40 minutes. This layer improves hole injection from the ITO to the HOMO level of the organic material and increases the performances and the lifetime of the device.⁵ The evaporation of the different organic layers was performed under vacuum (ca. 10⁻⁶ mbar) in a Boc Edwards Auto 306. The layer thickness was monitored *in situ* by a piezoelectric quartz balance during the evaporation. Lithium Fluorine-Aluminium cathodes were finally evaporated through a shadow mask by evaporation under vacuum of 0.8 nm of LiF followed by 75 nm of Aluminium or calcium cathodes were evaporated through a shadow mask by evaporation under vacuum of 200 nm of calcium. The OLEDs were then stored and characterized under inert atmosphere in a nitrogen glove box ([O₂] and [H₂O] < 1 ppm). Contacts on ITO and LiF/Al or Ca were taken using a prober (Karl Suss PM5). Current-voltage-luminance (I-V-L) curves were recorded using a Keithley 4200 SCS. Light emission was collected using a calibrated photodiode. Electroluminescence spectra were measured with a CCD spectrometer (Ocean Optics HR 2000).

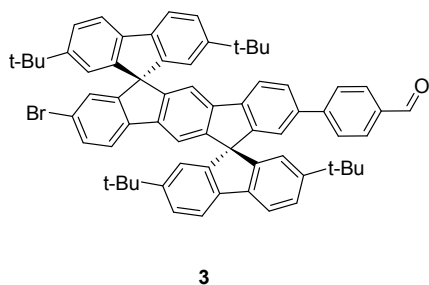
Synthesis

DSF(*t*-Bu)₄-IF(Br)₂ **2**



1^[1] (1.00 g, 1.28 mmol) was dissolved in dichloromethane (650 mL) and stirred at room temperature. Iodine (0.03 g, 0.13 mmol) and sodium carbonate (0.34 g, 3.20 mmol) dissolved in water (50 mL) were added to the mixture and stirred for 10 minutes at room temperature. Bromine (0.17 mL, 3.20 mmol) was added and the solution was allowed to stir overnight at room temperature under exclusion of light. The mixture was then poured into a saturated aqueous solution of sodium bisulfite and extracted with dichloromethane. The combined extracts were dried (MgSO₄), evaporated *in vacuo* and purified by precipitation in a mixture of dichloromethane/hexane to give the title compound **2** (1.08 g, 90%) as a colorless solid. Mp (hexane) >300°C; ¹H NMR (CD₂Cl₂, 300 MHz, ppm) δ 7.80 (4H, d, *J* = 8.1, ArH), 7.50-7.44 (6H, m, ArH), 7.36 (2H, dd, *J* = 8.1 *J* = 2.1, ArH), 7.16 (2H, s, ArH), 6.78 (2H, sd, *J* = 2.1, ArH), 6.72 (4H, sd, *J* = 1.8, ArH), 1.17 (36H, s, Me); ¹³C NMR (CD₂Cl₂, 75 MHz, ppm) δ 151.5 (C), 150.8 (C), 150.0 (C), 149.9 (C), 148.5 (C), 141.5 (C), 139.6 (C), 130.9 (CH), 127.1 (CH), 125.7 (CH), 123.6 (C), 121.9 (CH), 120.8 (CH), 119.8 (CH), 116.0 (CH), 66.3 (C_{spiro}), 35.1 (CMe), 31.5 (Me); HRMS (ESI⁺): (Found: [M+Na]⁺, 957.2631; C₆₀H₅₆⁷⁹Br₂Na required 957.2641); IR (ATR, cm⁻¹) ν = 3067, 3029, 2960, 2902, 2867, 1596, 1572, 1551, 1475, 1455, 1419, 1403, 1361, 1329, 1250, 1164, 1057.

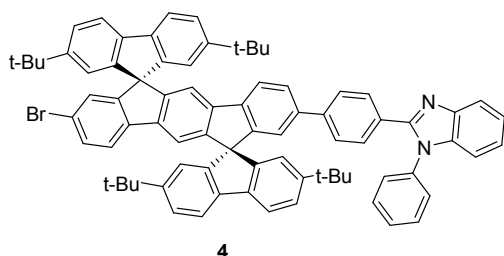
DSF(*t*-Bu)₄-IF(Br)(benzaldehyde) **3**



2 (400 mg, 0.43 mmol), 4-formylbenzene boronic acid (90 mg, 0.60 mmol), Pd₂dba₃ (39 mg, 0.4 mmol) and tritert-butyl phosphine (30 μL, 0.12 mmol) were dissolved in dry toluene (400 mL) under an argon atmosphere. The mixture was stirred at 100°C for 6 hours and, after cooling, poured into a saturated ammonium chloride solution. Ethyl acetate was added, the different layers separated and the residual aqueous solution was extracted with dichloromethane. The combined extracts were dried (MgSO₄), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2. The title compound **3** (124 mg, 30%) was afforded as a yellow solid. Mp

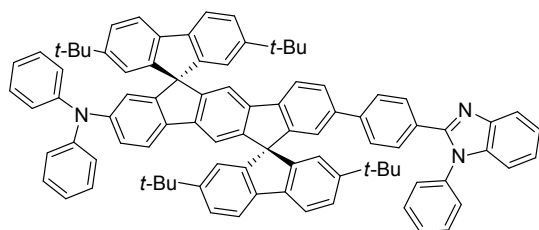
(hexane) >300°C; $^1\text{H NMR}$ (CD_2Cl_2 , 300 MHz, ppm) δ 9.93 (1H, s, H_{ald}), 7.83 (4H, dd, $J = 8.1$ $J = 2.1$, ArH), 7.78 (2H, d, $J = 8.4$, ArH), 7.70 (1H, d, $J = 7.8$, ArH), 7.61-7.54 (3H, m, ArH), 7.50-7.44 (5H, m, ArH), 7.36 (1H, dd, $J = 8.1$ $J = 1.8$, ArH), 7.24 (1H, sd, $J = 0.9$, ArH), 7.20 (1H, sd, $J = 0.6$, ArH), 6.97 (1H, sd, $J = 1.2$, ArH), 6.81-6.74 (5H, m, ArH), 1.18 (18H, s, Me), 1.16 (18H, s, Me); $^{13}\text{C NMR}$ (CD_2Cl_2 , 75 MHz, ppm) δ 191.9 (CO), 152.4 (C), 151.5 (C), 151.5 (C), 151.2 (C), 150.7 (C), 149.8 (C), 149.0 (C), 148.6 (C), 147.0 (C), 142.4 (C), 141.8 (C), 141.5 (C), 141.0 (C), 139.7 (C), 139.6 (C), 139.3 (C), 135.4 (C), 130.9 (CH), 130.2 (CH), 127.7 (CH), 127.3 (CH), 127.1 (CH), 125.7 (CH), 125.6 (CH), 122.8 (CH), 121.9 (CH), 121.4 (C), 121.0 (CH), 120.93 (CH), 120.87 (CH), 119.8 (CH), 119.7 (CH), 116.1 (CH), 116.0 (CH), 66.6 (C_{spiro}), 66.4 (C_{spiro}), 35.13 (C_{Me}), 35.12 (C_{Me}), 31.5 (Me); HRMS (ESI $^+$): (Found: $[\text{M}+\text{Na}]^+$, 983.3794; $\text{C}_{67}\text{H}_{61}\text{O}^{79}\text{BrNa}$ required 983.3798); IR (ATR, cm^{-1}) $\nu = 3060, 3034, 2956, 2902, 2867, 2817, 1703$ (C=O), 1602, 1475, 1456, 1404, 1361, 1251, 1208, 1168.

DSF(*t*-Bu) $_4$ -IF(Br)(phenylbenzimidazole) 4



3 (300 mg, 0.31 mmol) and N-phenyl-ortho-phenylene diamine (63 mg, 0.34 mmol) were dissolved in 2-methoxyethanol (150 mL) and stirred at reflux for 24 hours. After cooling, the mixture was poured into water and extracted with dichloromethane. The combined extracts were dried (MgSO_4), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2. The title compound **4** (227 mg, 65%) was afforded as a pink to violet solid. Mp (hexane) >300°C; $^1\text{H NMR}$ (CD_2Cl_2 , 300 MHz, ppm) δ 7.82 (4H, d, $J = 7.8$, ArH), 7.78 (2H, d, $J = 8.1$, ArH), 7.66 (1H, d, $J = 8.1$, ArH), 7.55-7.42 (11H, m, ArH), 7.38-7.18 (10H, m, ArH), 6.89 (1H, sd, $J = 1.2$, ArH), 6.81-6.74 (5H, m, ArH), 1.18 (18H, s, Me), 1.16 (18H, s, Me); $^{13}\text{C NMR}$ (CD_2Cl_2 , 75 MHz, ppm) δ 152.4 (C), 152.3 (C), 151.5 (C), 151.4 (C), 151.1 (C), 150.6 (C), 149.8 (C), 149.2 (C), 148.6 (C), 143.6 (C), 142.1 (C), 141.9 (C), 141.7 (C), 141.3 (C), 141.1 (C), 139.74 (C), 139.70 (C), 139.6 (C), 137.9 (C), 137.5 (C), 130.9 (CH), 130.2 (CH), 130.0 (CH), 129.2 (C), 128.9 (CH), 127.8 (CH), 127.1 (CH), 126.9 (CH), 125.7 (CH), 125.5 (CH), 123.5 (CH), 123.1 (CH), 122.4 (CH), 121.9 (CH), 121.3 (C), 120.93 (CH), 120.88 (CH), 119.9 (CH), 119.8 (CH), 119.7 (CH), 116.2 (CH), 115.9 (CH), 110.7 (CH), 66.6 (C_{spiro}), 66.4 (C_{spiro}), 35.14 (C_{Me}), 35.12 (C_{Me}), 31.54 (Me); HRMS (ESI $^+$): (Found: $[\text{M}+\text{H}]^+$, 1125.4725; $\text{C}_{79}\text{H}_{70}\text{N}_2^{79}\text{Br}$ required 1125.4717); IR (ATR, cm^{-1}) $\nu = 3063, 3034, 2956, 2903, 2868, 1596, 1499, 1476, 1451, 1427, 1403, 1362, 1324, 1252$.

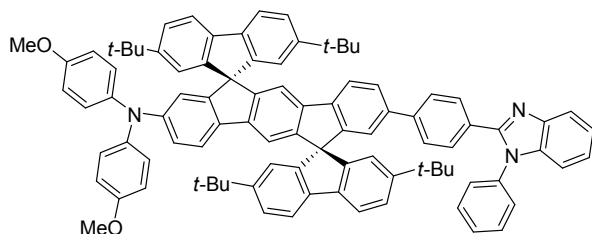
DA1-DSF-IF



DA1-DSF-IF

4 (200 mg, 0.18 mmol), diphenylamine (61 mg, 0.36 mmol), Pd(OAc)₂ (4 mg, 0.02 mmol), tritert-butylphosphine (15 μ L, 0.06 mmol) and potassium *tert*-butoxide (24 mg, 0.22 mmol) were dissolved in dry toluene (200 mL) under an argon atmosphere. The mixture was allowed to stir overnight at 100°C and, after cooling, poured into a saturated solution of ammonium chloride. Ethyl acetate was added, the different layers separated and the residual aqueous solution was extracted with dichloromethane. The combined extracts were dried (MgSO₄), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2 to 7:3. The title compound **DA1-DSF-IF** (10 mg, 5%) was afforded as a green solid. Mp >300°C; ¹H NMR (CD₂Cl₂, 300 MHz, ppm) δ 7.85-7.70 (5H, m, ArH), 7.63 (1H, d, *J* = 8.1, ArH), 7.56-7.13 (20H, m, ArH), 7.11-6.99 (4H, m, ArH), 6.90-6.78 (8H, m, ArH), 6.76 (2H, m, ArH), 6.43 (1H, sd, *J* = 1.2, ArH), 1.21 (18H, s, Me), 1.15 (18H, s, Me); ¹³C NMR (CD₂Cl₂, 75 MHz, ppm) δ 155.1 (C), 153.1 (C), 151.4 (C), 151.3 (C), 151.0 (C), 149.8 (C), 149.3 (C), 149.2 (C), 148.5 (C), 147.3 (C), 145.7 (C), 143.5 (C), 143.3 (C), 140.3 (C), 140.2 (C), 140.0 (C), 139.7 (C), 139.6 (C), 139.2 (C), 137.4 (C), 137.1 (C), 137.0 (C), 136.2 (C), 130.2 (CH), 129.9 (CH), 129.3 (CH), 128.9 (CH), 127.8 (CH), 126.8 (CH), 126.3 (CH), 125.4 (CH), 125.2 (CH), 124.5 (CH), 123.94 (CH), 123.87 (CH), 123.6 (CH), 122.8 (CH), 122.3 (CH), 121.3 (CH), 121.0 (CH), 120.9 (CH), 119.9 (CH), 119.6 (CH), 116.9 (CH), 115.5 (CH), 112.2 (CH), 111.8 (CH), 107.8 (CH), 66.4 (C_{spiro}), 35.13 (CMe), 35.11 (CMe), 31.6 (Me), 31.5 (Me);); HRMS (ESI⁺): (Found: M⁺, 1213.6267; C₇₉H₇₉N₃ required 1213.62685)

DA2-DSF-IF^[13]

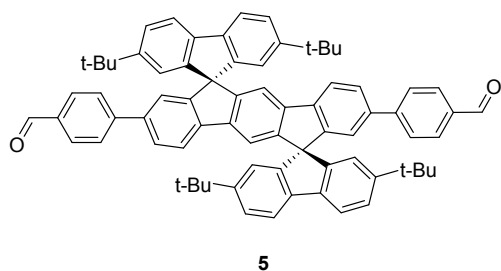


DA2-DSF-IF

4 (200 mg, 0.18 mmol), di(4-methoxyphenyl)amine (82 mg, 0.36 mmol), Pd(OAc)₂ (4 mg, 0.02 mmol), tritert-butylphosphine (15 μ L, 0.06 mmol) and potassium *tert*-butoxide (24 mg, 0.22 mmol) were dissolved in dry toluene (200 mL) under an argon atmosphere. The mixture was allowed to stir overnight at 100°C and, after cooling, poured into a saturated solution of ammonium chloride. Ethyl

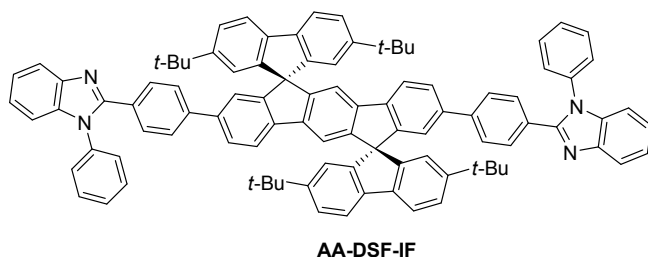
acetate was added, the different layers separated and the residual aqueous solution was extracted with dichloromethane. The combined extracts were dried (MgSO_4), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2 to 7:3, and recrystallization in cyclohexane. The title compound **DA2-DSF-IF** (114 mg, 50%) was afforded as a green solid. Mp (cyclohexane) $>300^\circ\text{C}$; ^1H NMR (CD_2Cl_2 , 300 MHz, ppm) δ 7.81-7.72 (5H, m, ArH), 7.61 (1H, d, $J = 8.1$, ArH), 7.52-7.18 (18H, m, ArH), 7.14 (1H, s, ArH), 7.04 (1H, s, ArH), 6.87-6.72 (10H, m, ArH), 6.62 (4H, m, ArH), 6.30 (1H, sd, $J = 1.2$, ArH), 3.68 (6H, s, Me), 1.21 (18H, s, Me), 1.15 (18H, s, Me); ^{13}C NMR (CD_2Cl_2 , 75 MHz, ppm) δ 155.8 (C), 152.3 (C), 151.5 (C), 151.3 (C), 151.2 (C), 151.0 (C), 150.9 (C), 150.3 (C), 149.7 (C), 149.5 (C), 149.4 (C), 148.7 (C), 147.4 (C), 143.5 (C), 143.3 (C), 142.1 (C), 142.0 (C), 141.4 (C), 140.4 (C), 139.6 (C), 139.5 (C), 139.1 (C), 137.8 (C), 137.4 (C), 130.2 (CH), 129.9 (CH), 129.0 (CH), 128.9 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 125.9 (CH), 125.4 (CH), 125.1 (CH), 123.5 (CH), 123.1 (CH), 122.3 (CH), 120.9 (CH), 120.8 (CH), 120.5 (CH), 119.8 (CH), 119.62 (CH), 119.59 (CH), 117.4 (CH), 115.7 (CH), 114.9 (CH), 114.7 (CH), 110.7 (CH), 66.5 (C_{spiro}), 66.4 (C_{spiro}), 55.6 (MeO), 35.12 ($\underline{\text{C}}\text{Me}$), 35.09 ($\underline{\text{C}}\text{Me}$), 31.59 (Me), 31.52 (Me); HRMS (ESI⁺) : (Found : M^+ , 1273.6479; $\text{C}_{93}\text{H}_{83}\text{N}_3\text{O}_2$ required 1273.6480); The spectroscopic properties are in accordance with those previously reported [13]

DSF(*t*-Bu)₄-IF(benzaldehyde)₂ 5



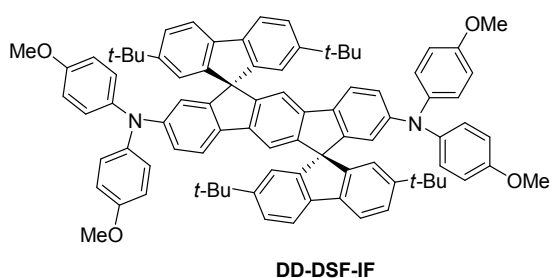
2 (400 mg, 0.43 mmol), 4-formylbenzene boronic acid (180 mg, 1.20 mmol), Pd_2dba_3 (78 mg, 0.8 mmol) and tritert-butyl phosphine (60 μL , 0.24 mmol) were dissolved in dry toluene (400 mL) under an argon atmosphere. The mixture was stirred at 100°C for 15 hours and, after cooling, poured into a saturated ammonium chloride solution. Ethyl acetate was added, the different layers separated and the residual aqueous solution was extracted with dichloromethane. The combined extracts were dried (MgSO_4), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2. The title compound **5** (361 mg, 85%) was afforded as a yellow solid. Mp (hexane) $>300^\circ\text{C}$; ^1H NMR (300 MHz, CD_2Cl_2) δ 9.93 (2H, s, ArH), 7.84 (4H, dd, $J = 8.1$ Hz, $J = 0.3$ Hz, ArH), 7.81 – 7.75 (4H, m, ArH), 7.72 (2H, d, $J = 8.1$ Hz, ArH), 7.63 – 7.53 (6H, m, ArH), 7.48 (4H, dd, $J = 8.1$, $J = 1.8$ Hz, ArH), 7.25 (2H, s, ArH), 6.97 (2H, d, $J = 1.2$ Hz, ArH), 6.79 (4H, d, $J = 1.8$ Hz, ArH), 1.16 (36H, s, Me); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 192.1 (CO), 151.6 (C), 151.4 (C), 150.7 (C), 149.2 (C), 147.2 (C), 142.6 (C), 141.9 (C), 139.8 (C), 139.4 (C), 135.5 (C), 130.3 (CH), 127.8 (CH), 127.4 (CH), 125.7 (CH), 122.9 (CH), 121.0 (CH), 119.8 (CH), 116.2 (CH), 66.7 (C_{spiro}), 35.2 ($\underline{\text{C}}\text{Me}$), 31.6 (Me); HRMS (ESI⁺) : (Found : $[\text{M}+\text{Na}]^+$, 1009.4960; $\text{C}_{74}\text{H}_{66}\text{O}_2\text{Na}$ required 1009.4955); IR (ATR, cm^{-1}) $\nu = 3059, 3031, 2961, 2902, 2867, 2822, 2728, 1705$ (C=O), 1602, 1565, 1477, 1459, 1407, 1361, 1306, 1251, 1210, 1169.

AA-DSF-IF



5 (300 mg, 0.31 mmol) and N-phenyl-ortho-phenylene diamine (126 mg, 0.68 mmol) were dissolved in 2-methoxyethanol (200 mL) and stirred at reflux for 24 hours. After cooling, the mixture was poured into water and extracted with dichloromethane. The combined extracts were dried (MgSO_4), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2. The title compound **AA-DSF-IF** (285 mg, 70%) was afforded as a slightly pink solid. Mp (hexane) > 300°C; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.82 (4H, d, J = 8.1 Hz, ArH), 7.77 (2H, d, J = 7.4 Hz, ArH), 7.66 (2H, d, J = 7.9 Hz, ArH), 7.53 (2H, dd, J = 8.0 Hz, J = 1.7 Hz, ArH), 7.51 – 7.42 (14H, m, ArH), 7.37 – 7.31 (4H, m, ArH), 7.30 – 7.25 (6H, m, ArH), 7.24 – 7.17 (6H, m, ArH), 6.88 (2H, d, J = 1.3 Hz, ArH), 6.77 (4H, d, J = 1.4 Hz, 1H), 1.16 (36H, s, Me); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.3 (C), 151.8 (C), 151.4 (C), 151.1 (C), 150.5 (C), 149.3 (C), 143.5 (C), 141.9 (C), 141.8 (C), 139.8 (C), 139.7 (C), 139.6 (C), 137.9 (C), 137.5 (C), 130.2 (CH), 129.9 (CH), 129.2 (CH), 128.9 (CH), 127.8 (CH), 126.9 (CH), 125.5 (CH), 123.5 (CH), 123.1 (CH), 122.4 (CH), 120.9 (CH), 119.9 (CH), 119.7 (CH), 115.9 (CH), 110.7 (CH), 66.6 (C_{spiro}), 35.1 (C_{Me}), 31.5 (Me); HRMS (ESI⁺): (Found: [M+H]⁺, 1315.6608; $\text{C}_{98}\text{H}_{83}\text{N}_4$ required 1315.6612); IR (ATR, cm^{-1}) ν = 3066, 3034, 2961, 2902, 2867, 1597, 1499, 1477, 1450, 1406, 1376, 1362, 1324, 1253, 1190, 1115.

DD-DSF-IF



2 (200 mg, 0.18 mmol), di(4-methoxyphenyl)amine (123 mg, 0.54 mmol), $\text{Pd}(\text{OAc})_2$ (4 mg, 0.02 mmol), tritert-butylphosphine (15 μL , 0.06 mmol) and potassium *tert*-butoxide (24 mg, 0.22 mmol) were dissolved in dry toluene (200 mL) under an argon atmosphere. The mixture was allowed to stir overnight at 100°C and, after cooling, poured into a saturated solution of ammonium chloride. Ethyl acetate was added, the different layers separated and the residual aqueous solution was extracted with dichloromethane. The combined extracts were dried (MgSO_4), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate 8:2 to 7:3, and recrystallization in cyclohexane. The title compound **DD-DSF-IF** (114 mg, 50%) was afforded as a slightly pink solid. Mp (hexane) > 300°C; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.71 (4H, d, J = 8.0 Hz, ArH), 7.41 (4H, dd, J = 8.0 Hz, J = 1.8 Hz, 1H), 7.35 (2H, d, J = 8.3 Hz, ArH), 6.98 (2H, s, ArH), 6.84 – 6.69 (14H, m,

ArH), 6.65 – 6.58 (8H, m, ArH), 6.28 (2H, sd, $J = 2.0$ Hz, ArH), 3.68 (12H, s, Me), 1.21 (36H, s, Me); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 155.7 (C), 151.3 (C), 151.2 (C), 149.7 (C), 149.6 (C), 148.4 (C), 141.5 (C), 141.0 (C), 139.5 (C), 135.8 (C), 125.8 (CH), 125.1 (CH), 121.8 (CH), 120.9 (CH), 120.5 (CH), 119.6 (CH), 117.6 (CH), 114.7 (CH), 114.6 (CH), 66.3 (C_{spiro}), 55.6 (MeO), 35.1 (CMe), 31.6 (Me); HRMS (ESI⁺) : (Found : M^+ , 1232.6424; $\text{C}_{88}\text{H}_{84}\text{N}_2\text{O}_4$ required 1232.6426); IR (ATR, cm^{-1}) $\nu = 3071, 3037, 3002, 2953, 2903, 2866, 2832, 1605, 1501, 1459, 1439, 1360, 1319, 1270, 1178, 1104, 1034$.

Emission spectroscopy

	Cyclohexane	THF	MeCN
1	56% (300nm)	55% (300nm)	52% (300nm)
AA-DSF-IF	76% (370nm)	74% (372nm)	82% (374nm)
DD-DSF-IF	87% (382nm)	56% (380nm)	26% (380nm)
DA1-DSF-IF	70% (381nm)	50% (379nm)	38% (386nm)
DA2-DSF-IF	97% (397nm)	55% (379nm)	22% (377nm)

Table S1. Quantum yields (with λ_{exc}) in cyclohexane, THF and MeCN (Reference Quinine Sulphate)

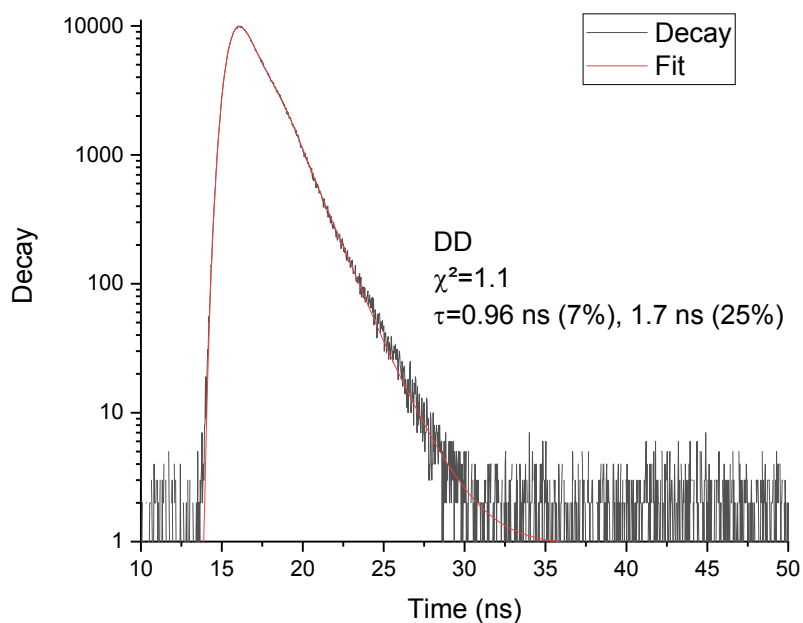


Figure S1. Lifetime measurement of **DD-DSF-IF** ($\lambda_{exc}=310$ nm, $\lambda_{em}=424$ nm)

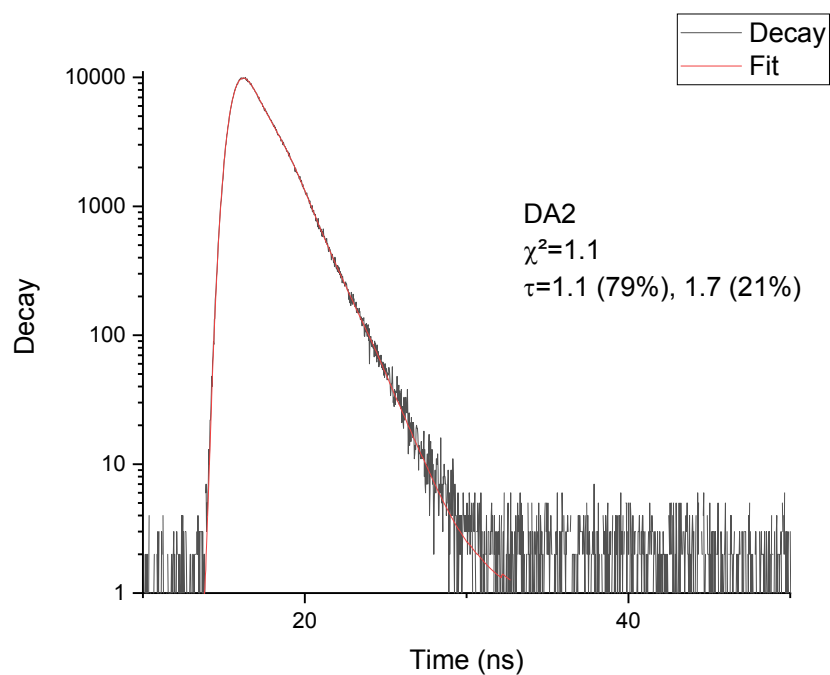


Figure S2 Lifetime measurement of **DA2-DSF-IF** ($\lambda_{exc}=310$ nm, $\lambda_{em}=435$ nm)

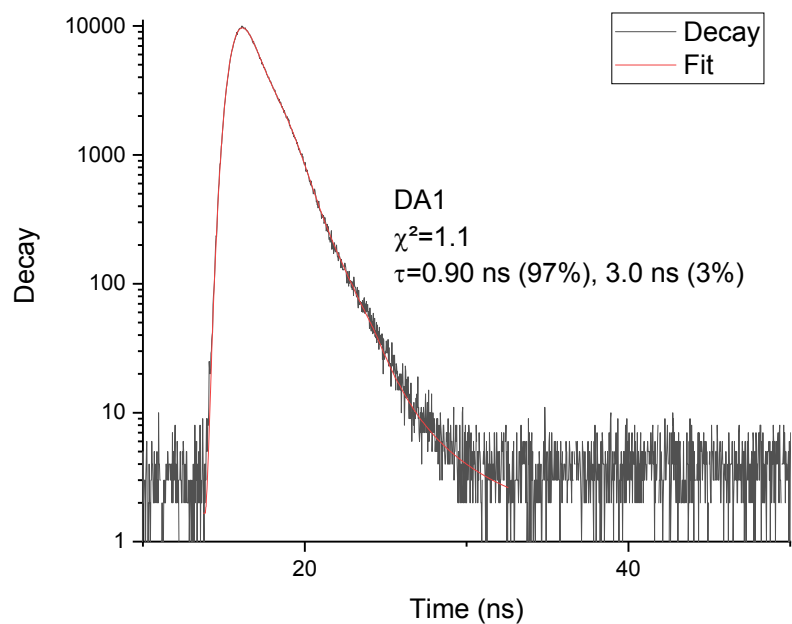


Figure S3 . Lifetime measurement of **DA1-DSF-IF** ($\lambda_{exc}=310$ nm, $\lambda_{em}=420$ nm)

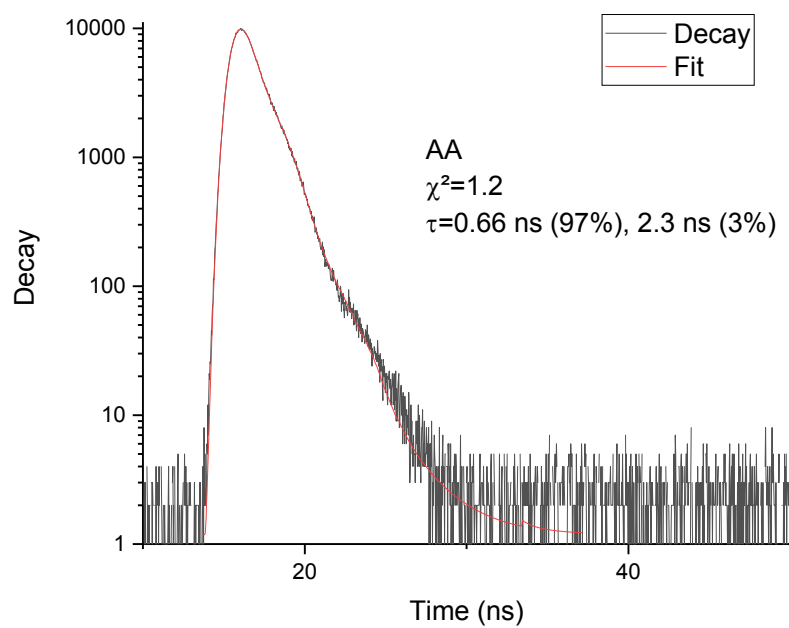


Figure S4 . Lifetime measurement of **AA-DSF-IF** ($\lambda_{exc}=310$ nm, $\lambda_{em}=407$ nm)

Electrochemistry

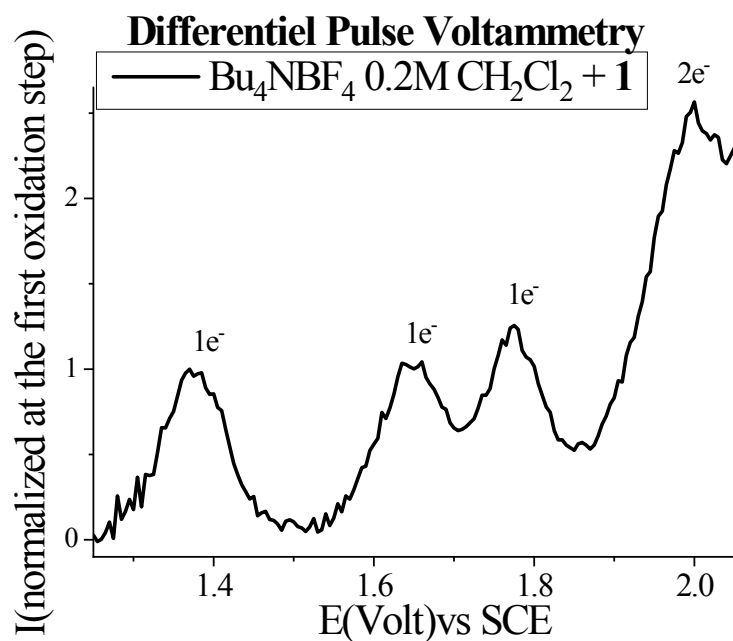


Figure S5. Differential Pulse Voltammetry recorded in Bu_4NPF_6 0.2M in CH_2Cl_2 in presence of **1**. Working platinum disk electrode. Pulse Height: 50 mV, Scan-rate: 10 mV/s.

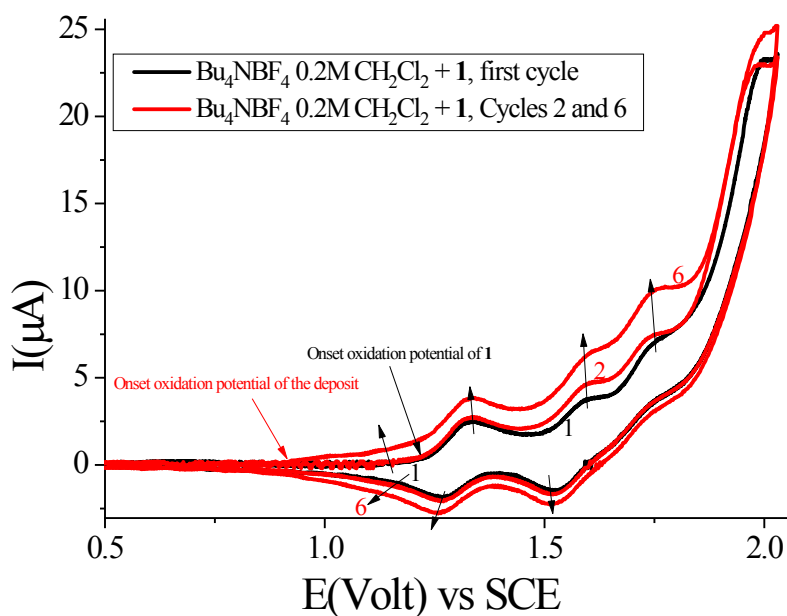


Figure S6. Cyclic voltammeteries recorded in Bu_4NPF_6 0.2M in CH_2Cl_2 in presence of **1** ($1.36 \cdot 10^{-3}\text{M}$) between 0.5 and 2.03 V, First cycle in black, cycles 2 and 6 in red. Working platinum disk electrode, diameter 1mm. Sweep-rate 100 mV/s.

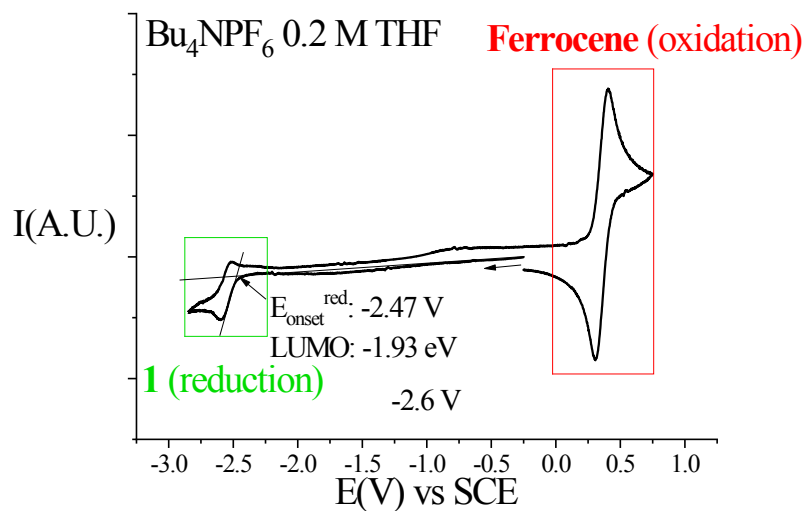


Figure S7. Cathodic behaviour of **1** recorded in presence of ferrocene. The cyclic voltammetry is recorded in THF + Bu_4NPF_6 0.2M from -0.25 to -2.85 V (reduction of **1**) then to 0.75 V (oxidation of ferrocene) and back to -0.25 V. Working platinum disk electrode. Sweep-rate 100 mV/s.

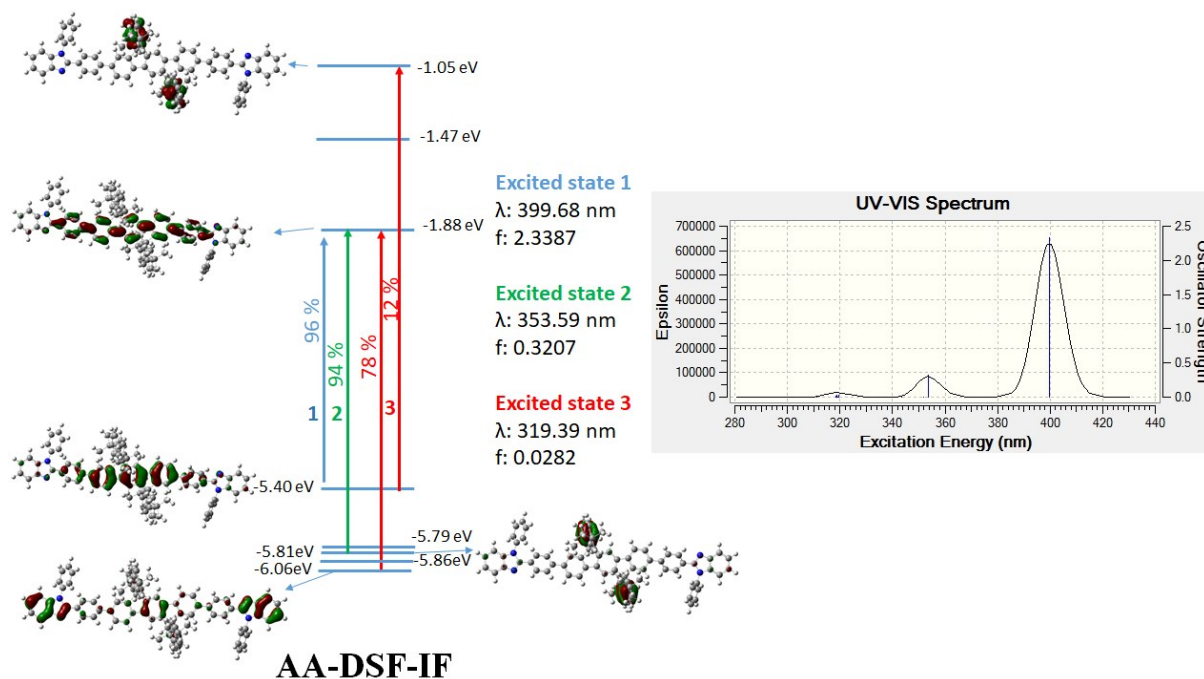


Figure S8. Calculated frontier molecular orbitals by DFT and calculated electronic transitions by TD-DFT of **AA-DSF-IF**, obtained after geometry optimization with DFT RB3LYP/6-31G(d), shown with a cut-off 0.03 [e bohr⁻³]^{1/2} (Left) and calculated UV spectrum (Right).

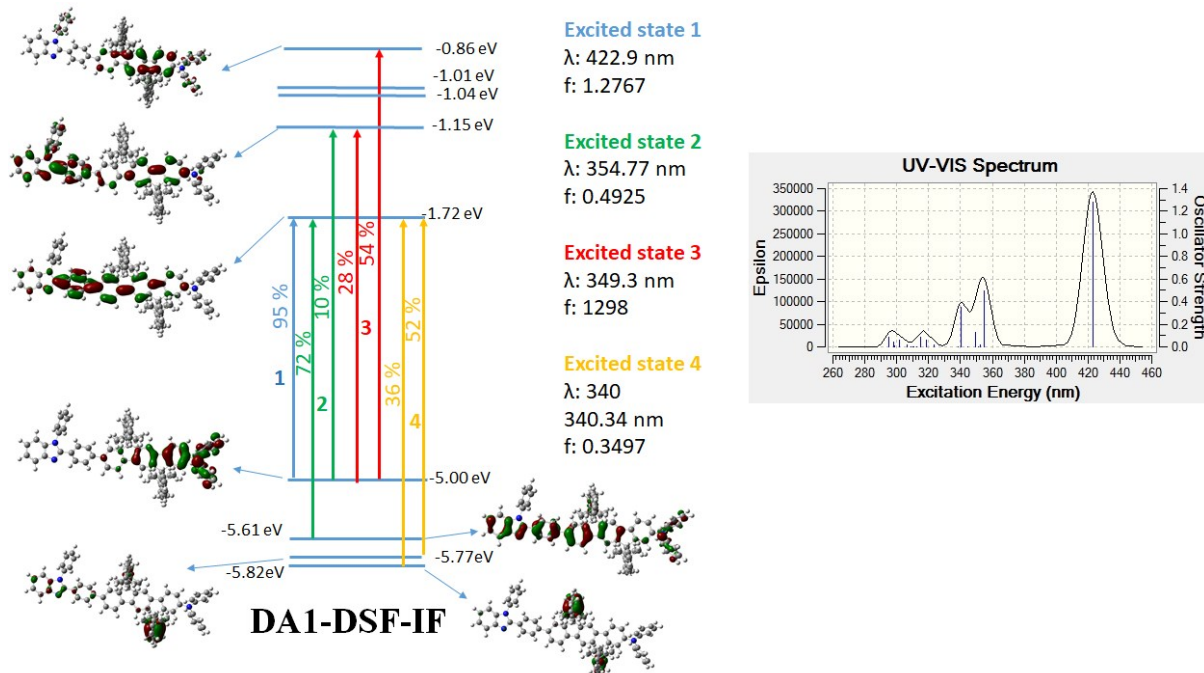


Figure S9. Calculated frontier molecular orbitals by DFT and calculated electronic transitions by TD-DFT of **DA1-DSF-IF**, obtained after geometry optimization with DFT RB3LYP/6-31G(d), shown with a cut-off 0.03 [e bohr⁻³]^{1/2} (Left) and calculated UV spectrum (Right).

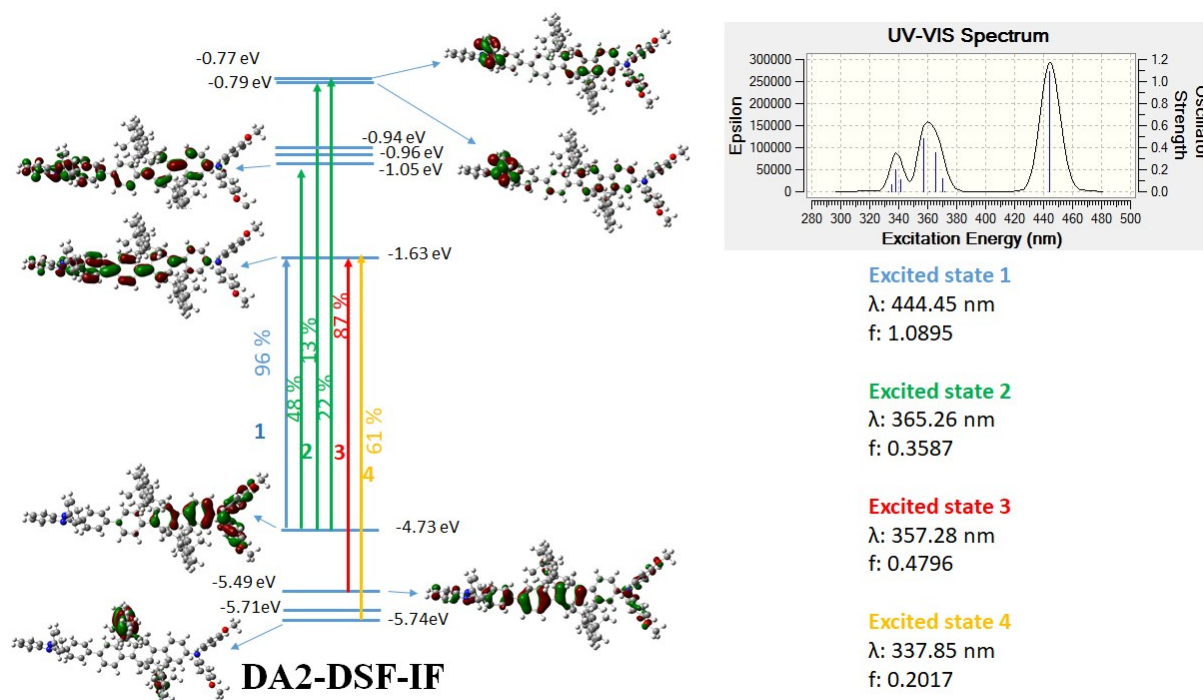


Figure S10. Calculated frontier molecular orbitals by DFT and calculated electronic transitions by TD-DFT of **DA2-DSF-IF**, obtained after geometry optimization with DFT RB3LYP/6-31G(d), shown with a cut-off 0.03 [e bohr⁻³]^{1/2} (Left) and calculated UV spectrum (Right).

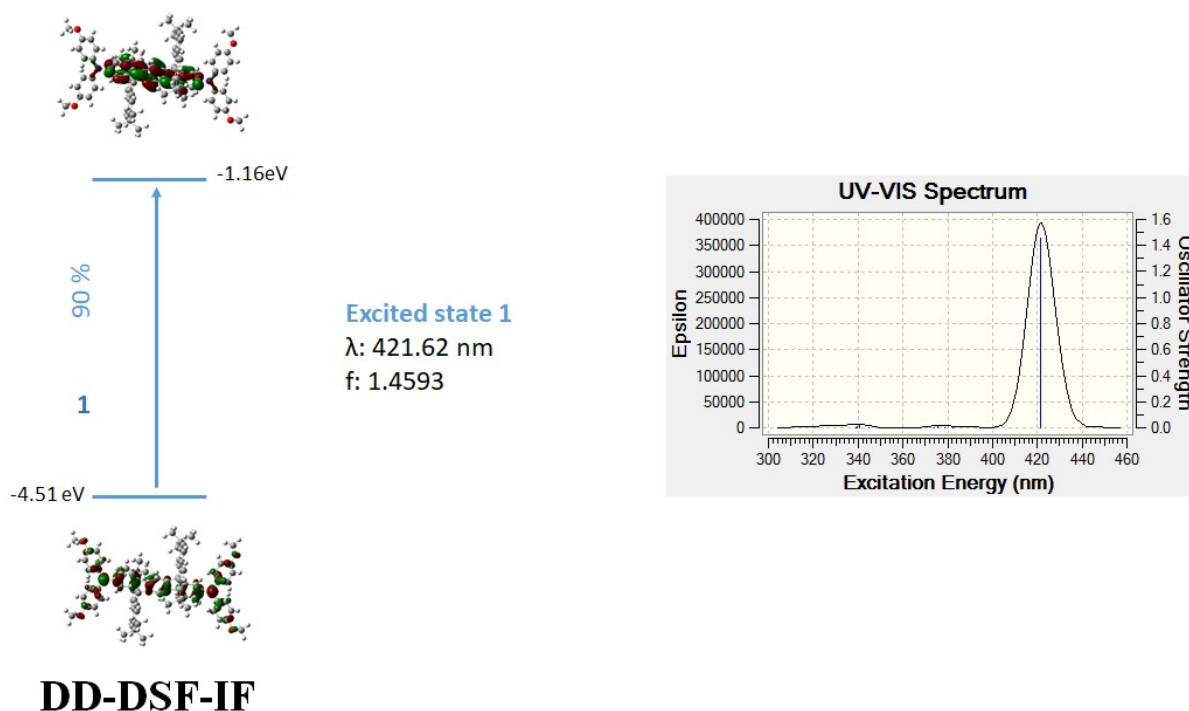


Figure S11. Calculated frontier molecular orbitals by DFT and calculated electronic transitions by TD-DFT of **DD-DSF-IF**, obtained after geometry optimization with DFT RB3LYP/6-31G(d), shown with a cut-off 0.03 [e bohr⁻³]^{1/2} (Left) and calculated UV spectrum (Right).

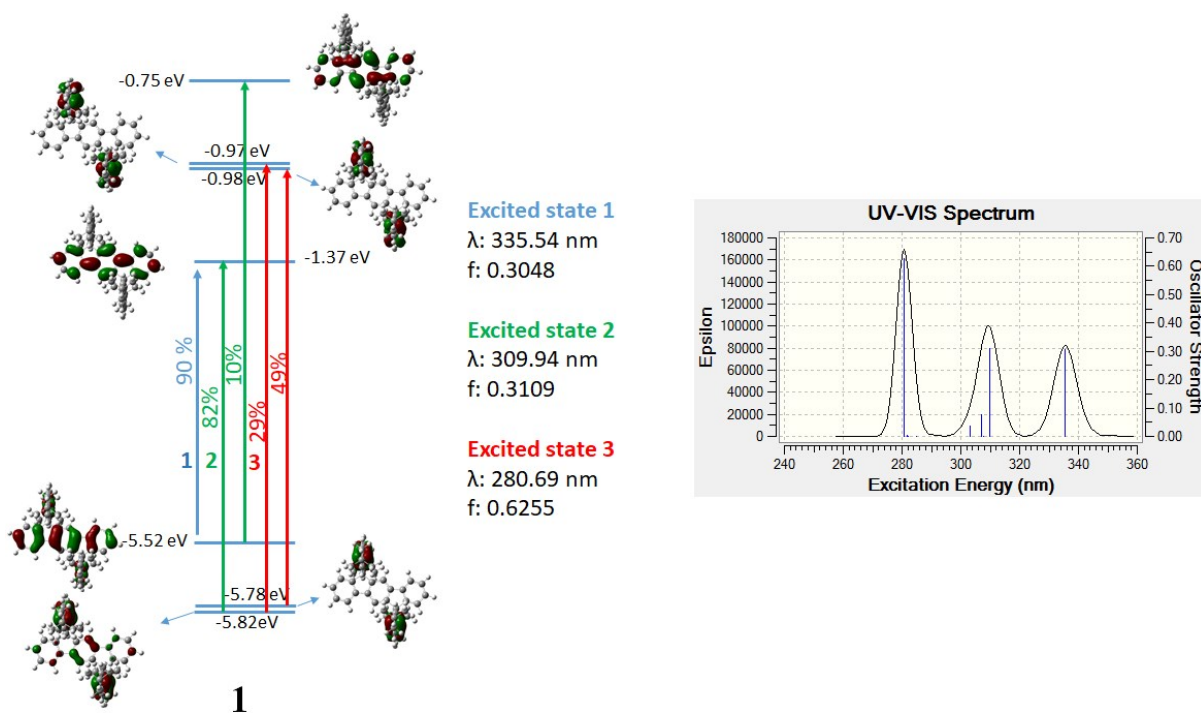
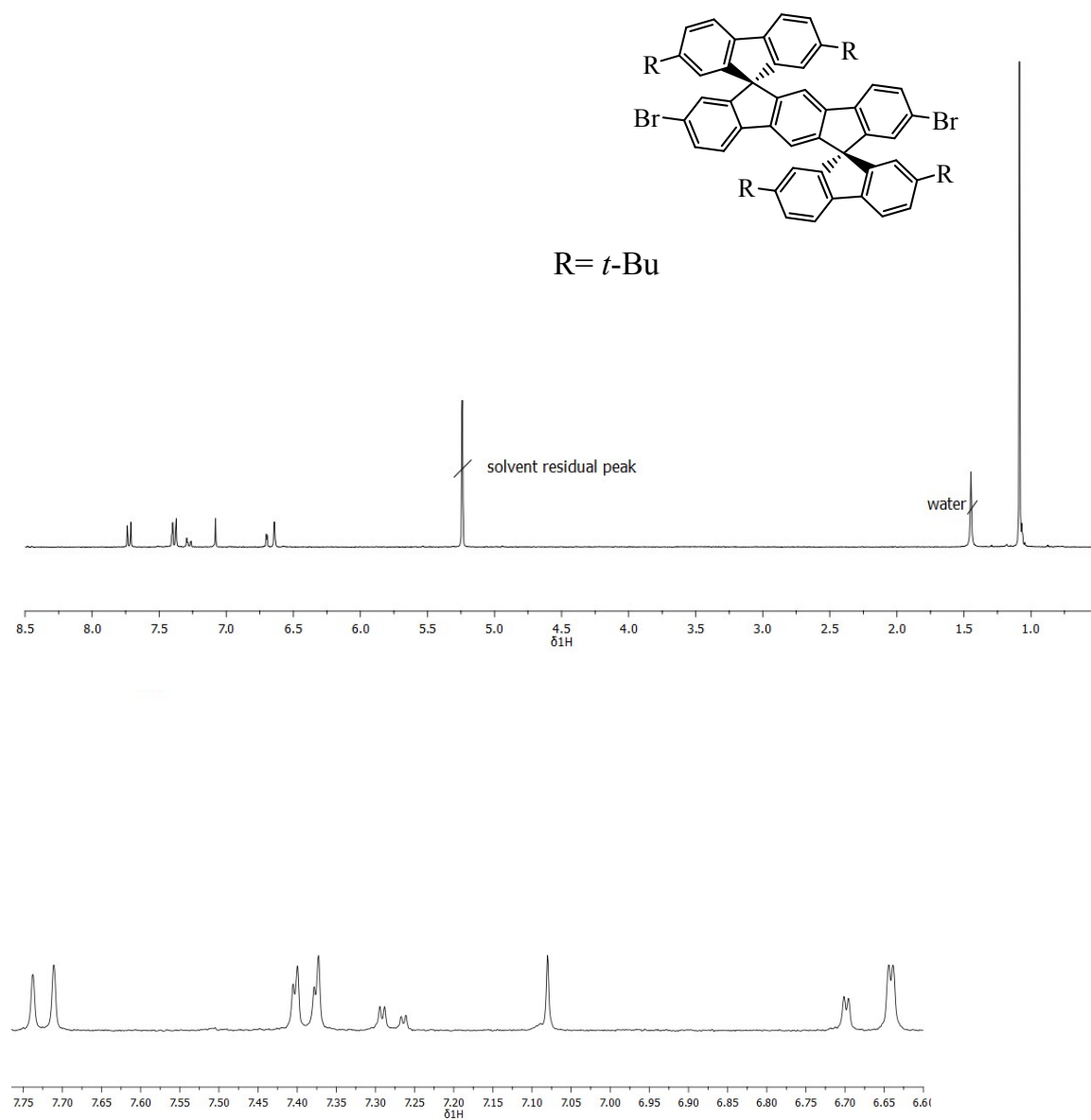


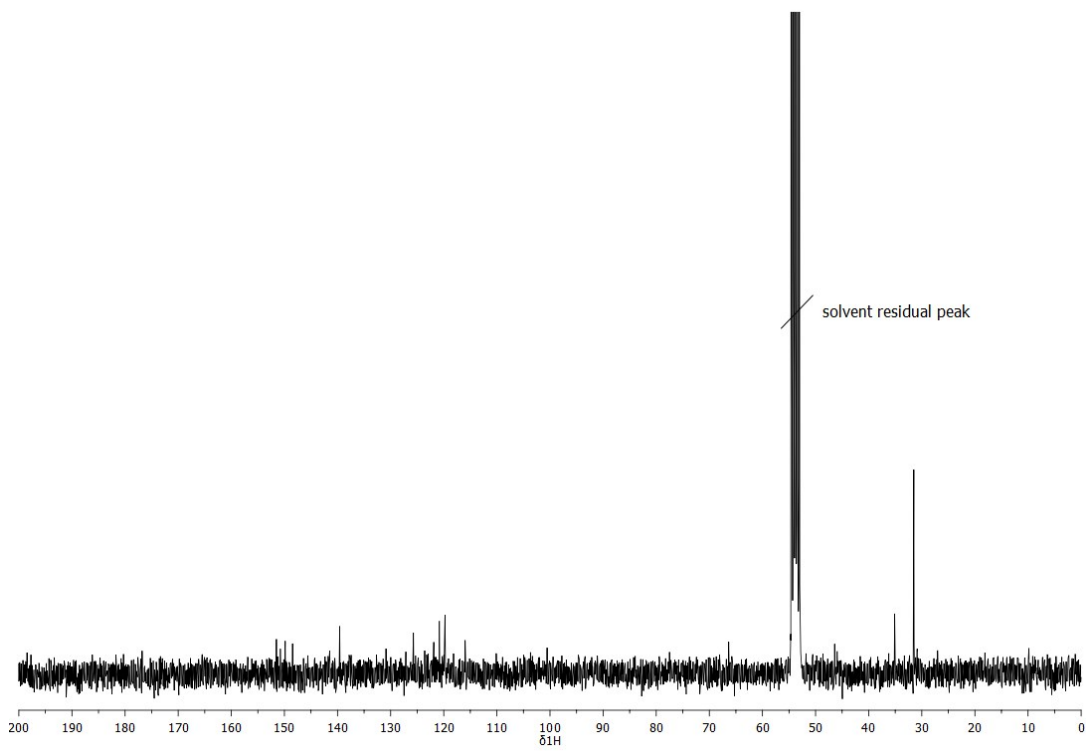
Figure S12. Calculated frontier molecular orbitals by DFT and calculated electronic transitions by TD-DFT of **1**, obtained after geometry optimization with DFT RB3LYP/6-31G(d), shown with a cut-off 0.03 [$e \text{ bohr}^{-3/2}$] (Left) and calculated UV spectrum (Right).

Copy of NMR spectra

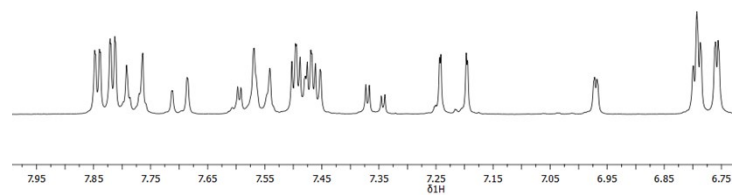
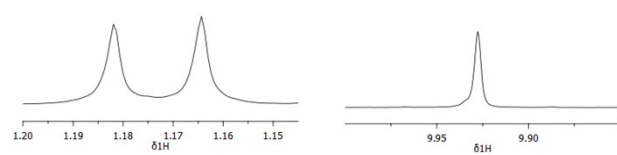
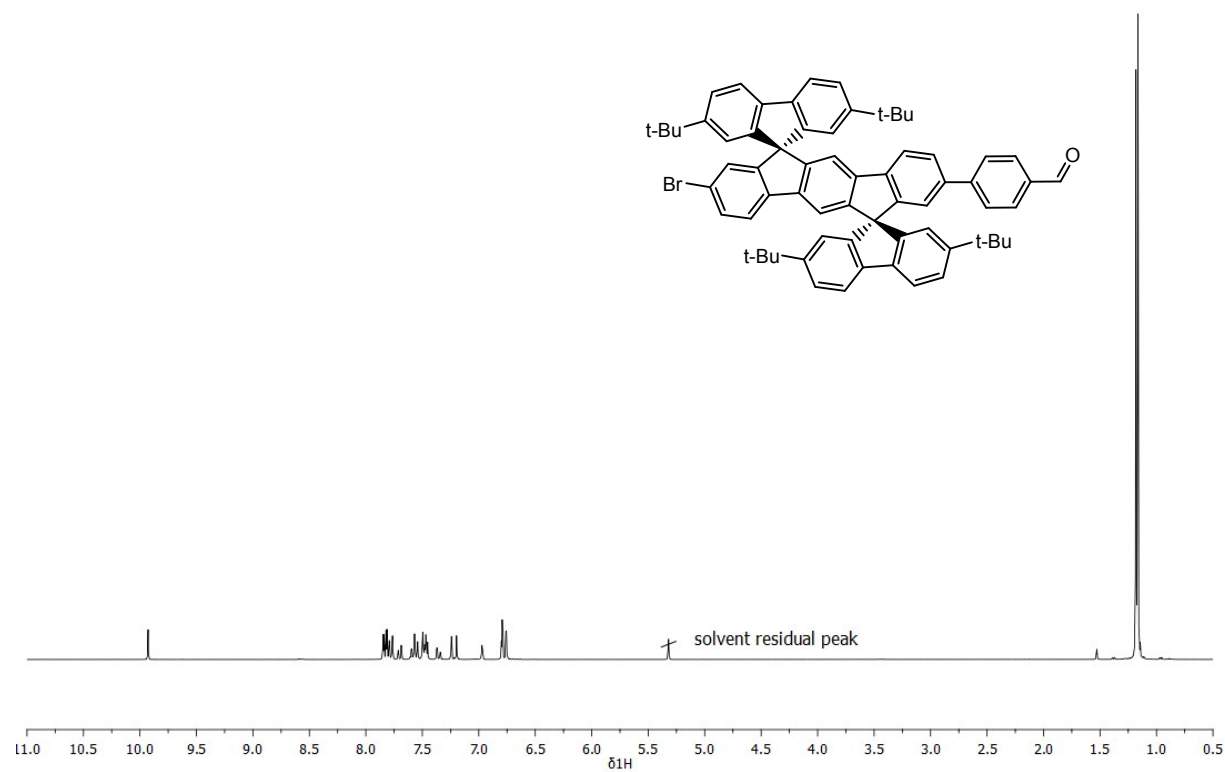
Compound **2** (CD₂Cl₂)¹

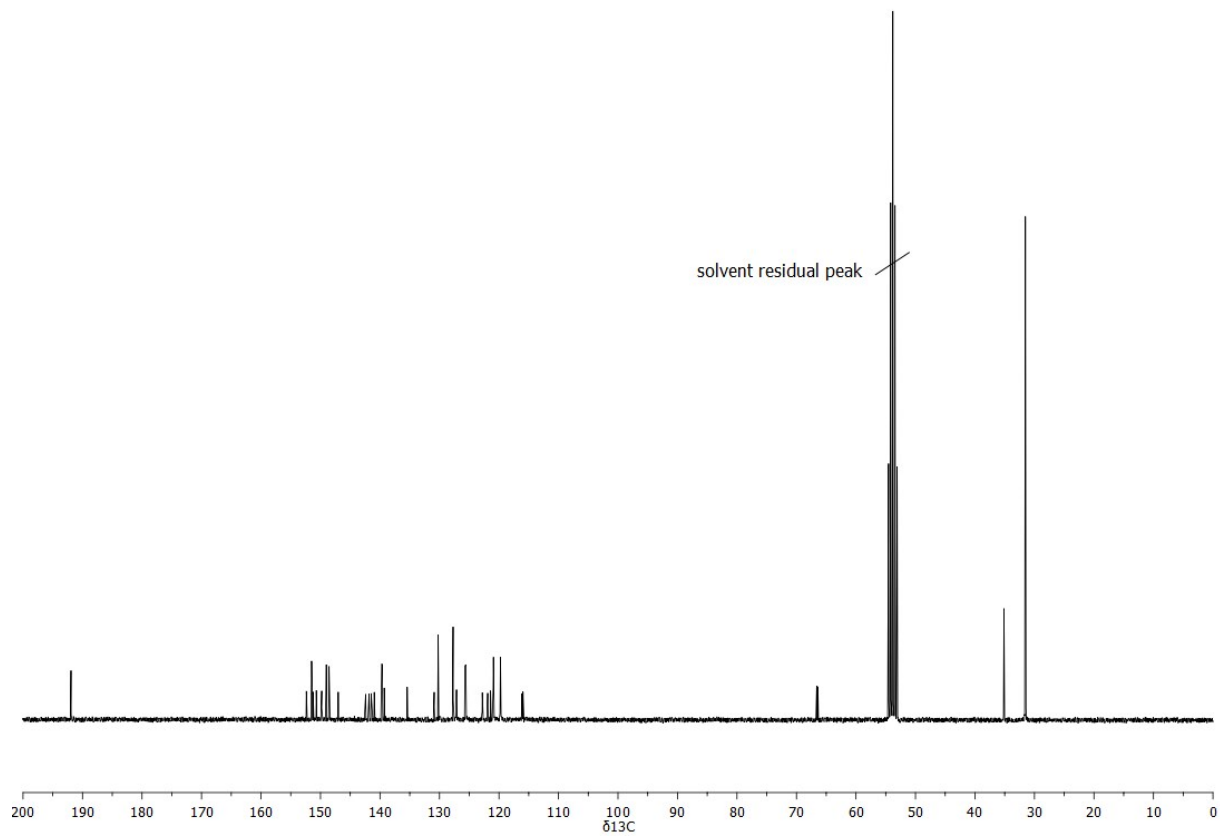


¹ It should be noted that the ¹³C NMR of **2** is poor due its extremely low solubility in all the solvents tested.

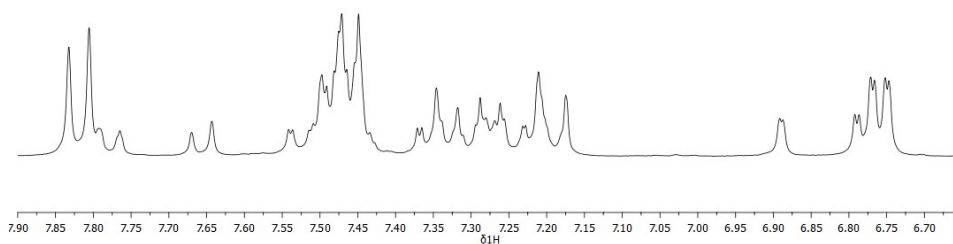
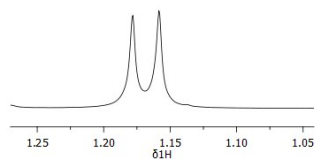
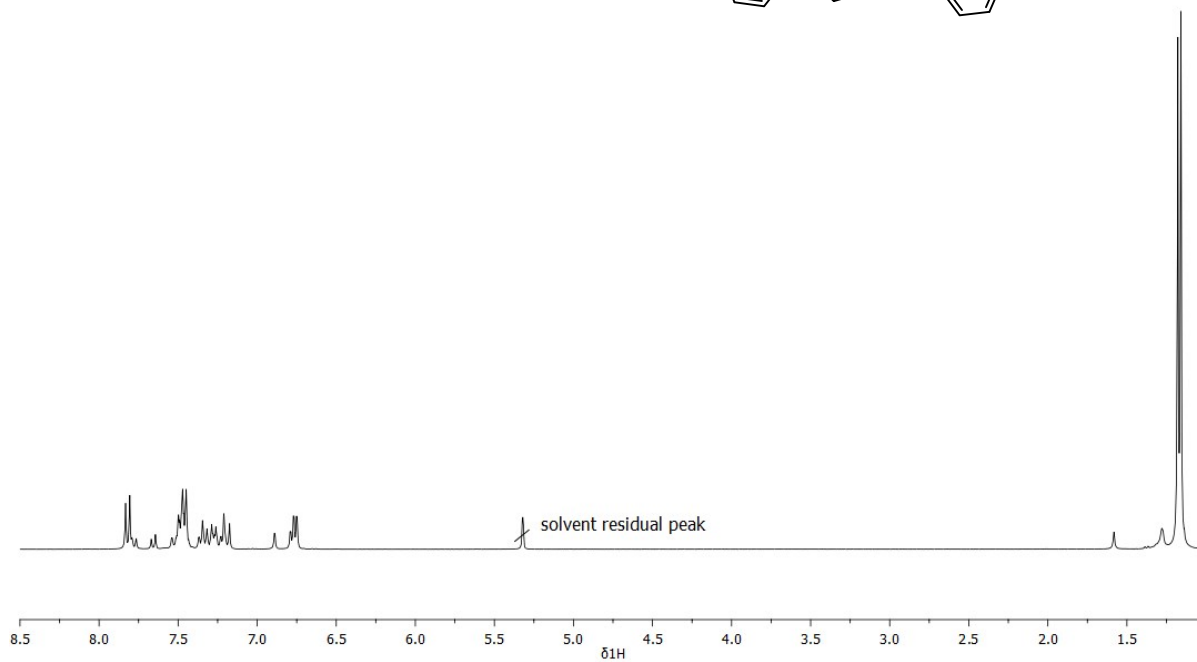
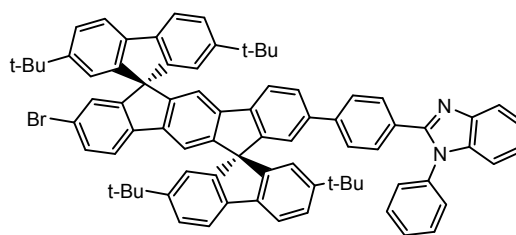


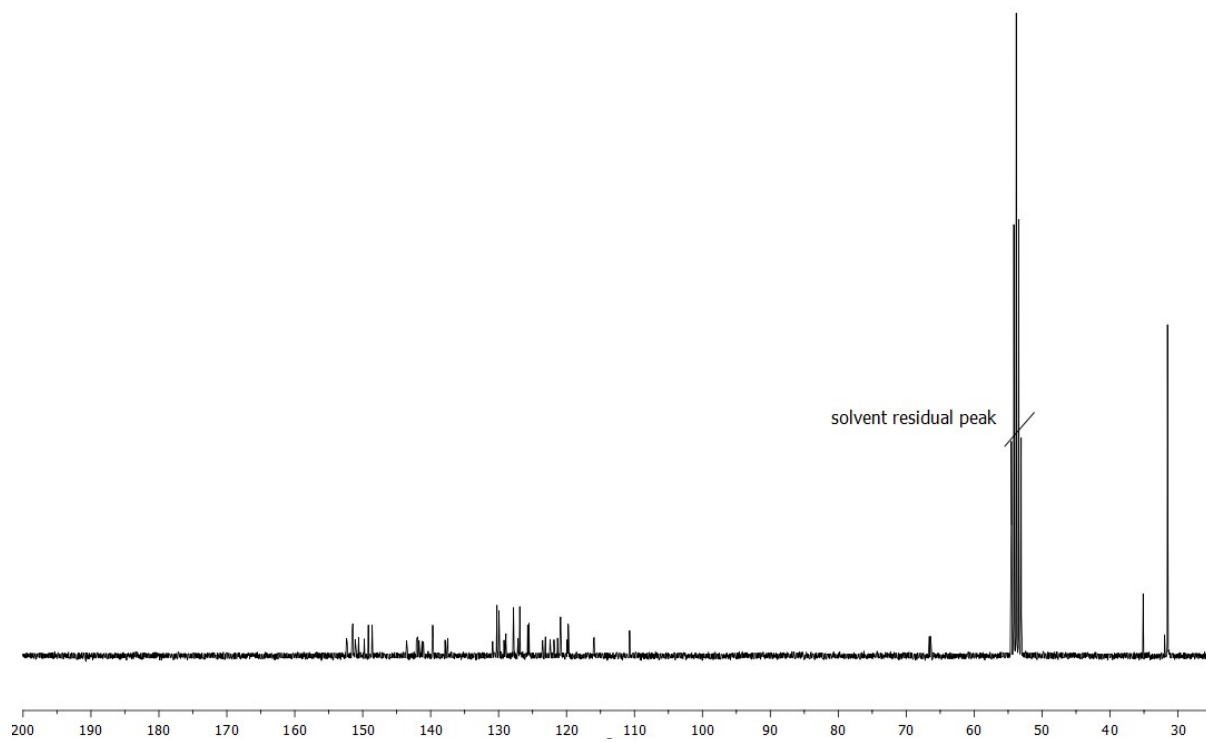
Compound 3 (CD₂Cl₂)



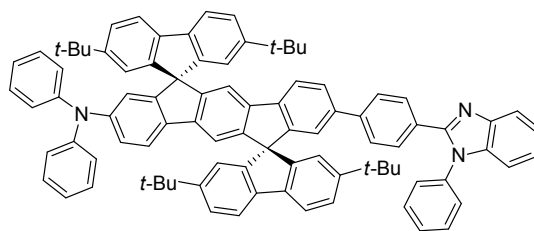


Compound 4 (CD₂Cl₂)

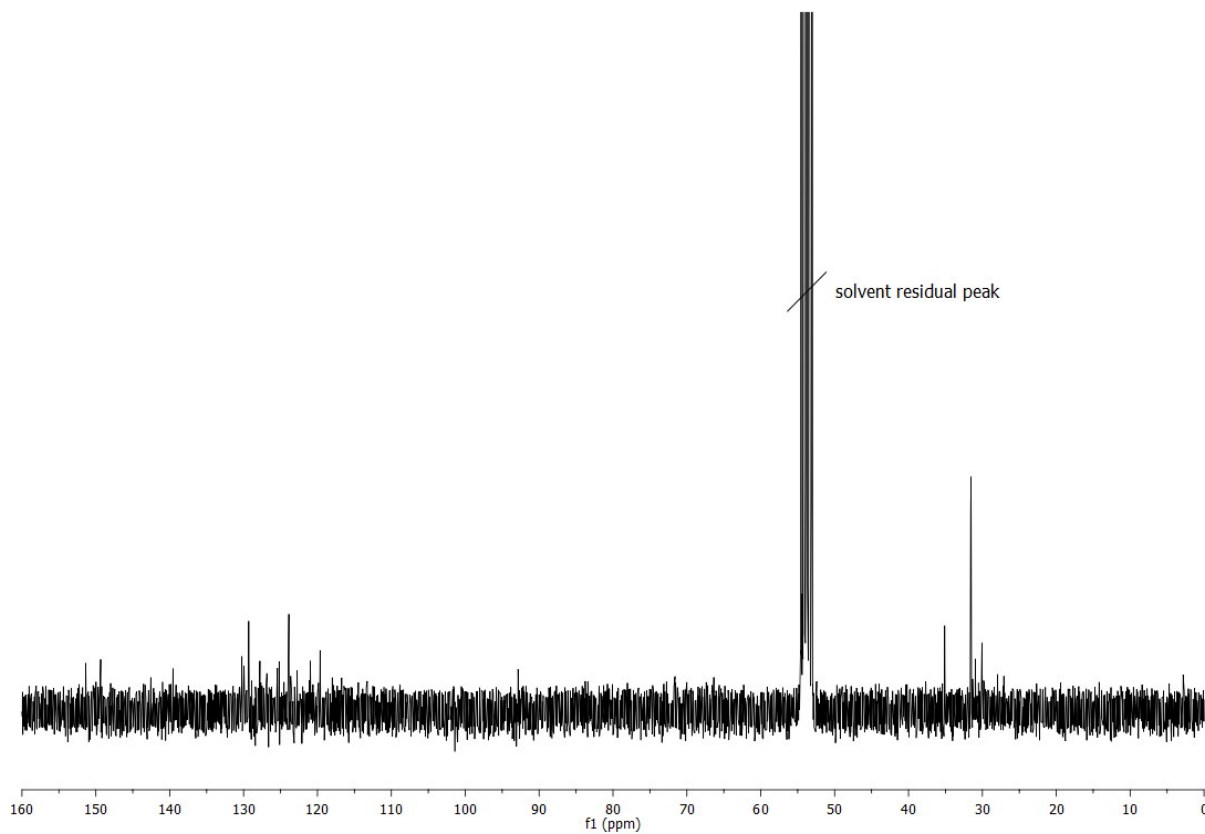
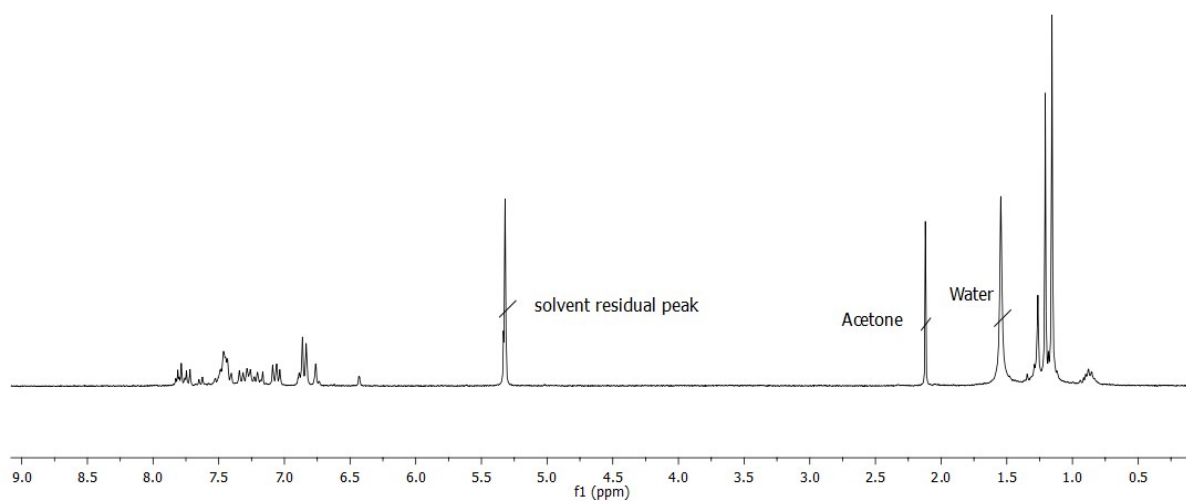




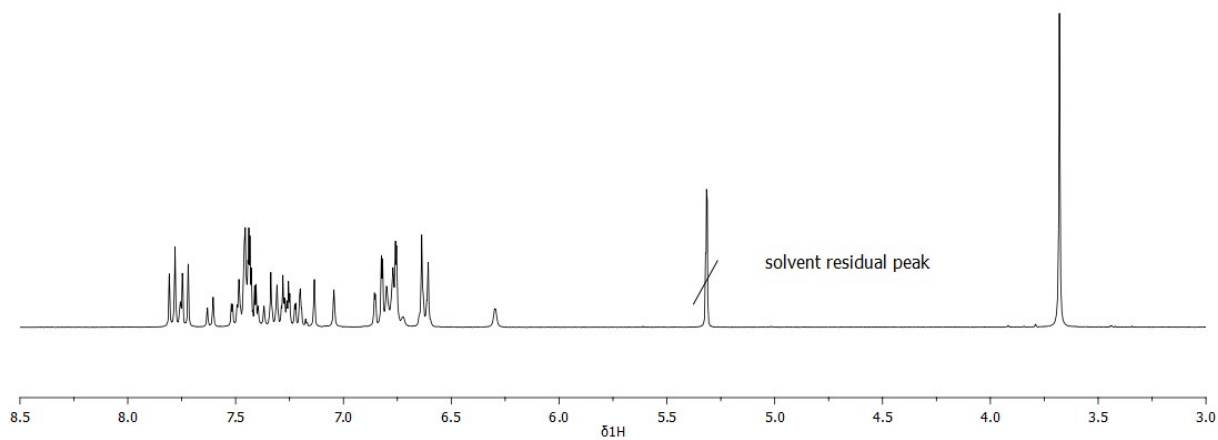
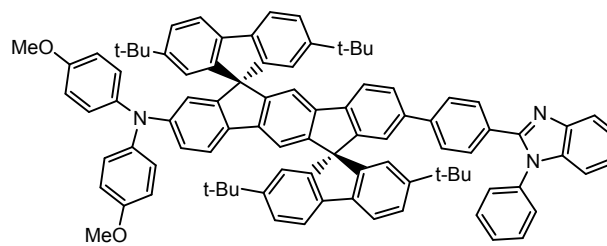
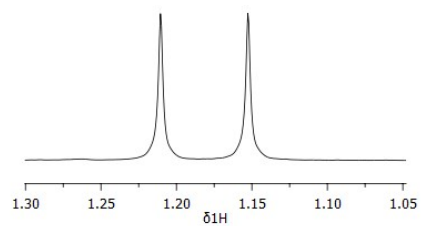
DA1-DSF-IF (CD₂Cl₂)

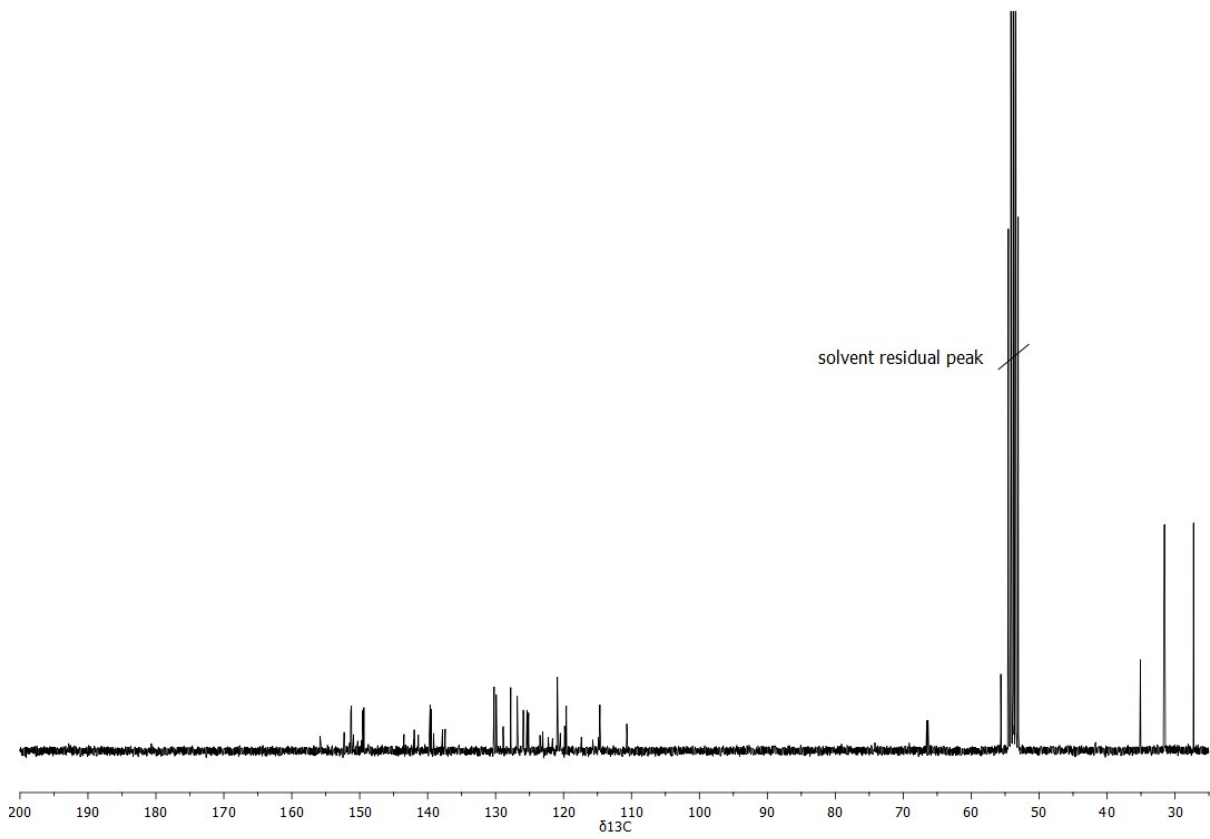
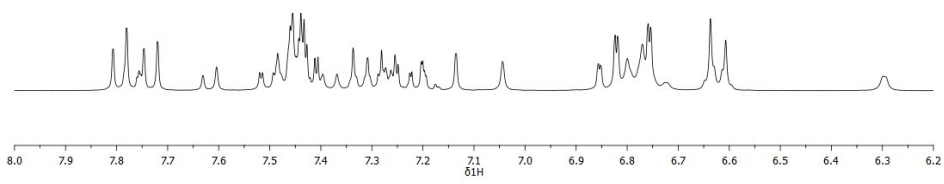
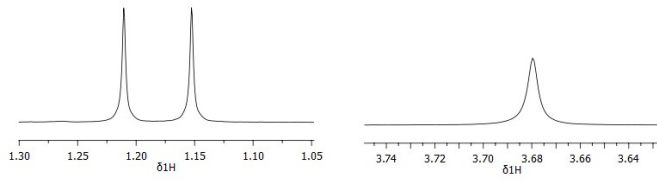


DA1-DSF-IF

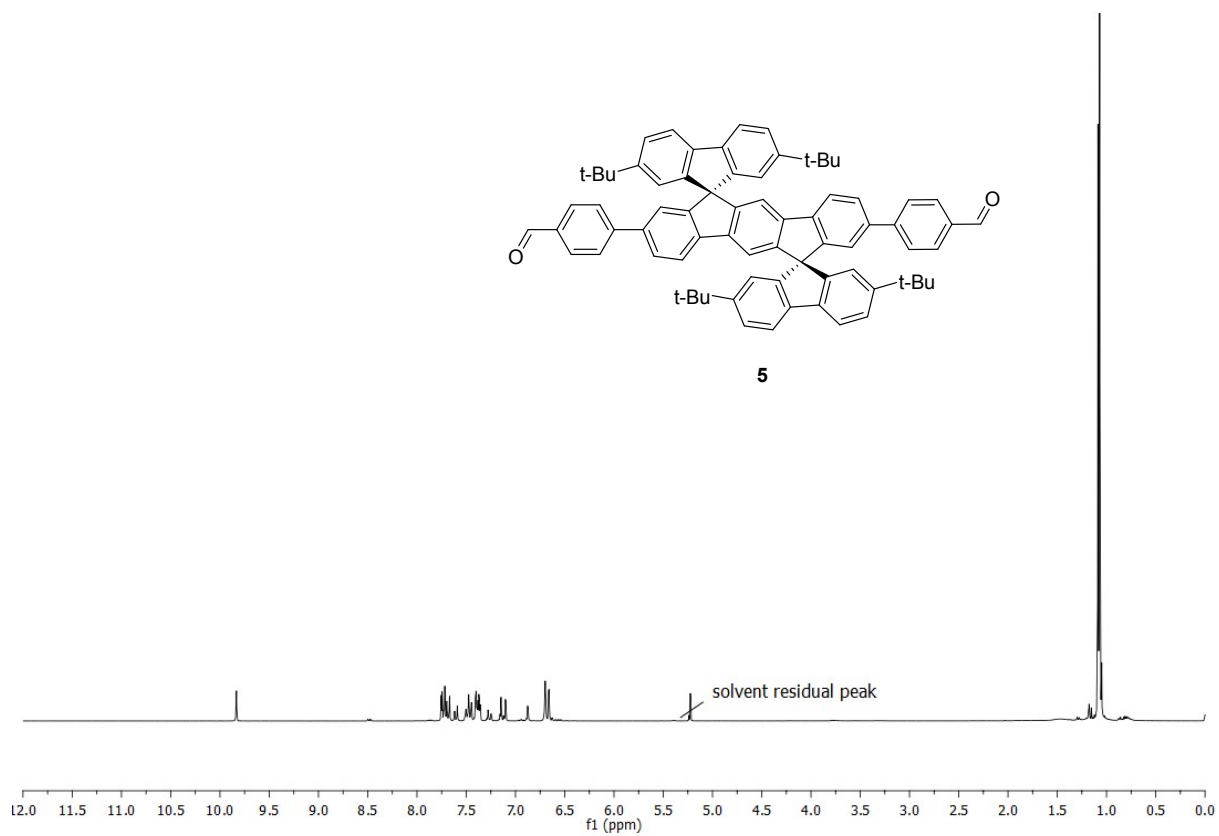
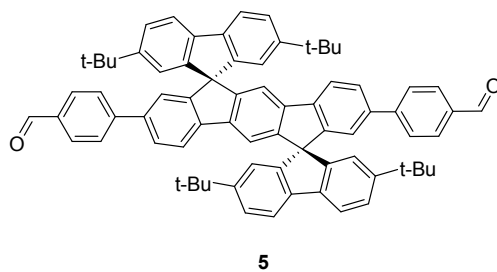


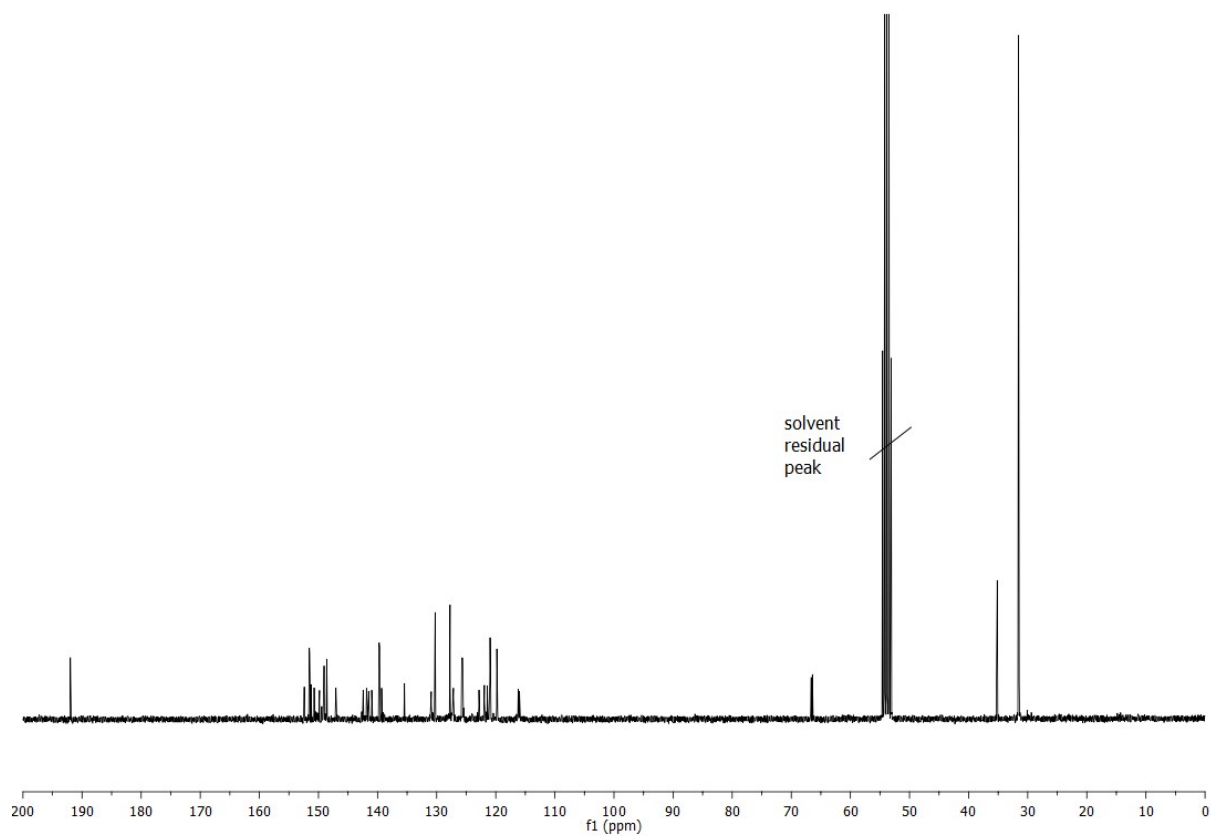
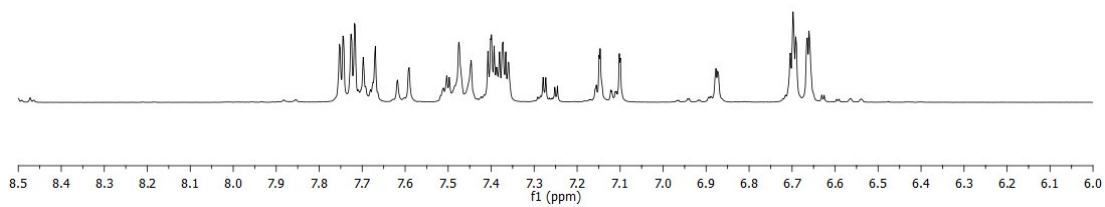
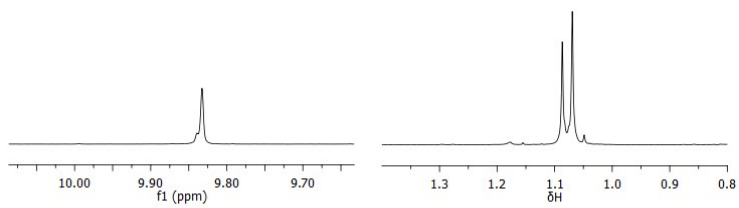
DA2-DSF-IF (CD₂Cl₂)



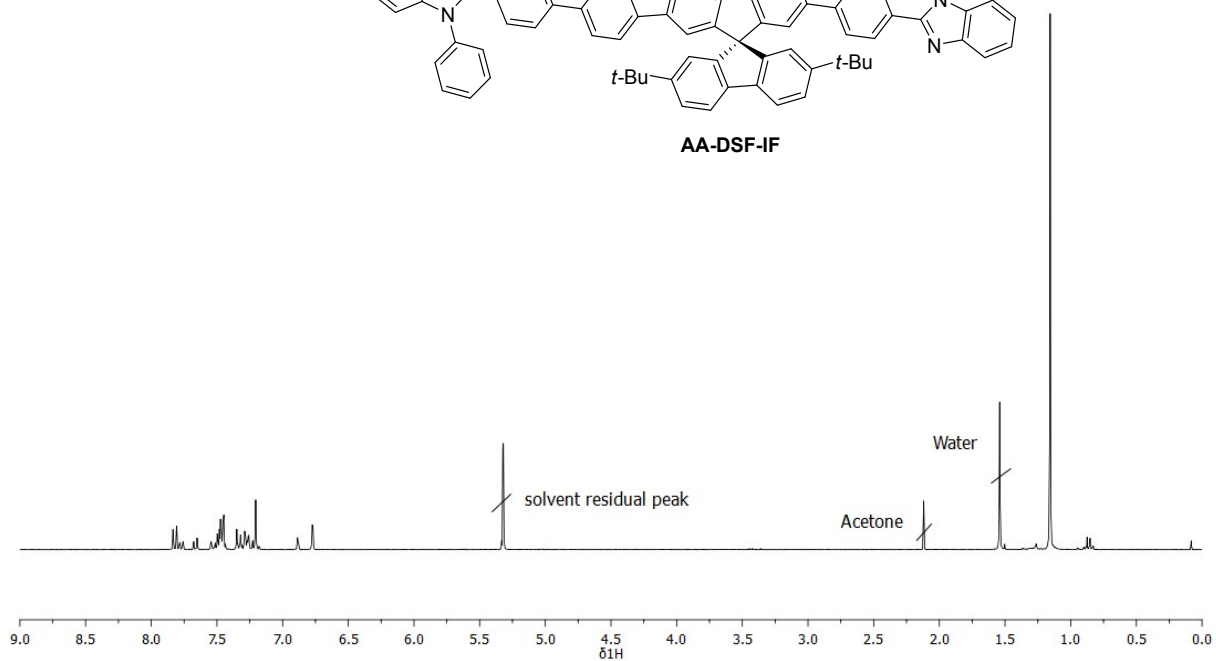
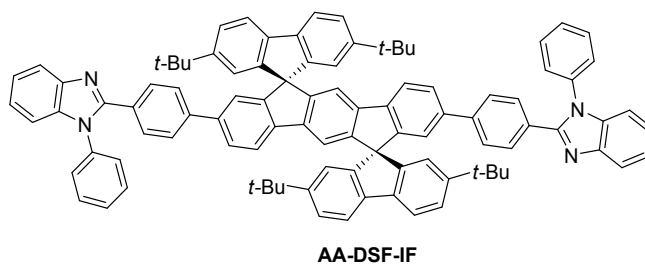


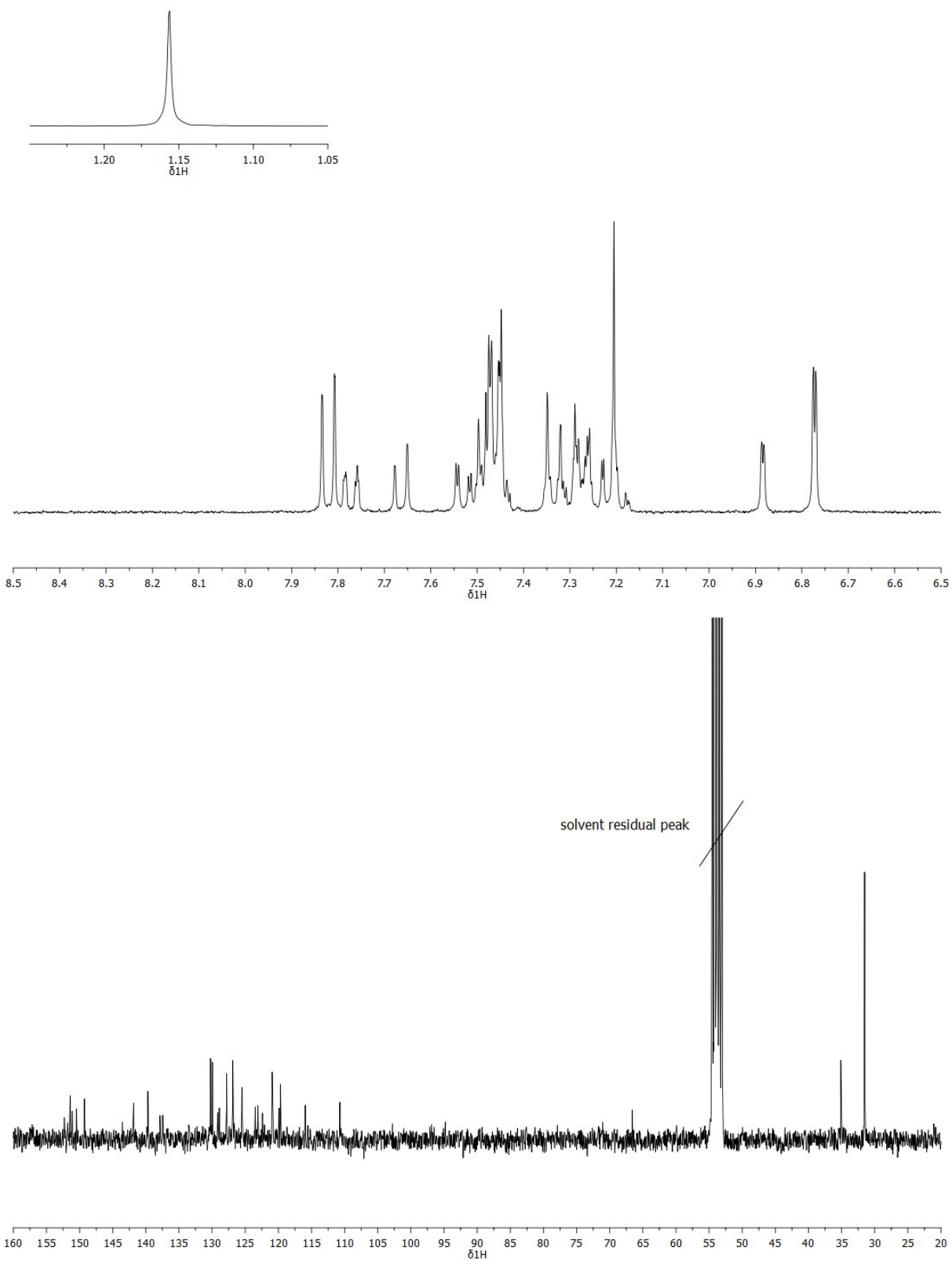
Compound 5 (CD₂Cl₂)



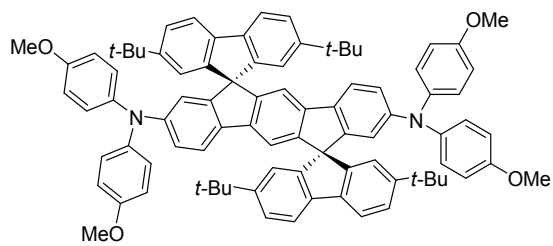


AA-DSF-IF (CD_2Cl_2)

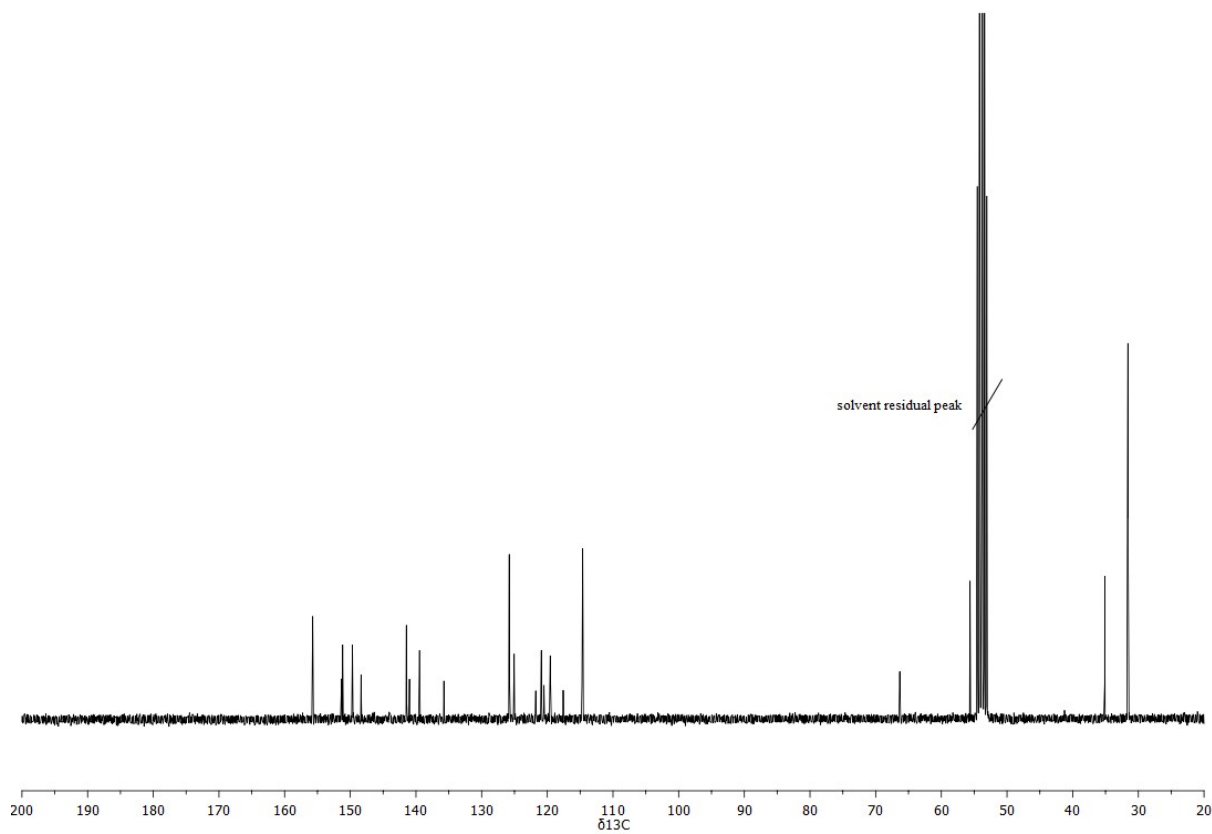
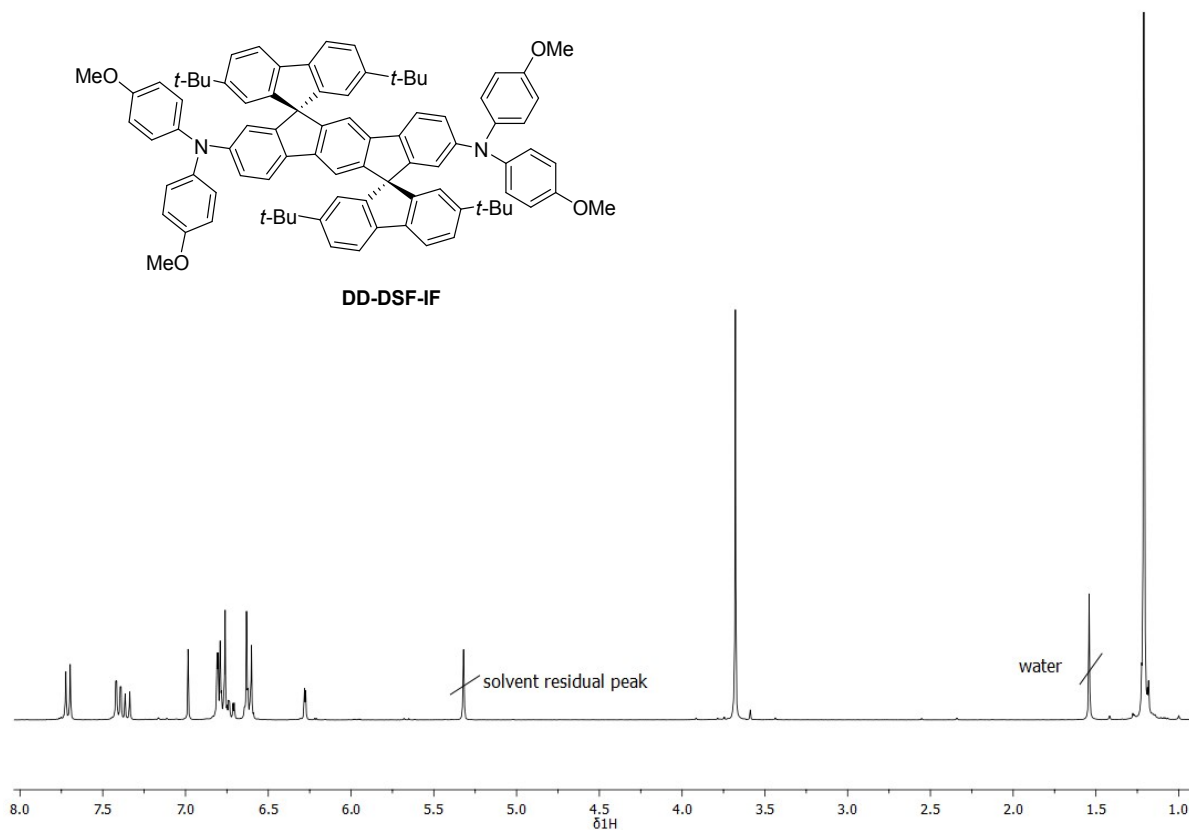




DD-DSF-IF (CD₂Cl₂)



DD-DSF-IF



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