

Supporting Information

for

Synthesis and properties of a blue bipolar Indenofluorene emitter based on a D- π -A design

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MATERIAL AND METHODS

Synthesis: Commercially available reagents and solvents were used without further purification other than those detailed below. Dichloromethane was distilled from P₂O₅ 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 40-60°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 360 nm). Chromatography was carried out using silica 60A CC 40-63 µm (SDS). ¹H and ¹³C NMR spectra were recorded using Bruker 300 MHz instruments (¹H frequency, corresponding ¹³C frequency: 75 MHz); chemical shifts were recorded in ppm and J values in Hz. In the ¹³C NMR spectra, signals corresponding to CH, CH₂ or Me groups, assigned from DEPT, are noted; all others are C. The residual signals for the NMR solvents are: CDCl₃; 7.26 ppm for the proton and 77.00 ppm for the carbon, CD₂Cl₂; 5.32 ppm for the proton and 53.80 ppm for the carbon. The following abbreviations have been used for the NMR assignment: s for singlet, d for doublet, t for triplet and m for multiplet. High resolution mass spectra were recorded at the Centre Régional de Mesure Physique de l'Ouest (Rennes). The synthesis and the full characterization of the **DSF-IF(*t*-Bu)₄ 1** may be found in our previous works.¹

Spectroscopic studies: Dichloromethane was distilled from P₂O₅ drying agent Sicapent© (Merck); THF was distilled from sodium/benzophenone prior to use. Toluene was distilled from sodium prior to use. Cyclohexane (reagent grade, Acros) was used without further purification. UV-visible spectra were recorded using a UV-Visible spectrophotometer SHIMADZU UV-1605. 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 (1eV = 1.6×10^{-19} J) and $c = 3.0 \times 10^8$ m.s⁻¹, this equation may be simplified as: 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. Quantum yields in solution (ϕ_{sol}) were calculated relative to quinine sulfate ($\phi_{\text{sol}} = 0.546$ in H₂SO₄ 1N) using standard procedures. ϕ_{sol} was determined according to the following equation (1),

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

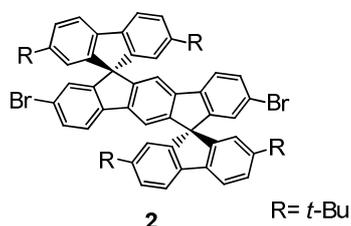
where, subscripts s and r refer respectively to the sample and reference. The integrated area of the emission peak in arbitrary units is given as T, n is the refracting index of the solvent ($n_s = 1.4266$ for cyclohexane, $n_s = 1.4072$ for THF, $n_s = 1.4941$ Toluene) and A is the absorbance ($A < 0.1$). IR spectra were recorded on a Bruker Vertex 70 using a diamond crystal MIRacle ATR (Pike).

AFM studies: Thin films of **DA-DSF-IF** (40 nm) were prepared by vacuum sublimation on a sapphire wafer (monocrystalline Al₂O₃; Ra = 0.063 nm) at the ENSCBP in Bordeaux. The film was heated gradually from room temperature up to 130°C (1h at each stage) in a Schlenk tube under an ambient atmosphere. For each temperature, the film was cooled until RT (around 10 minutes of cooling) and its topography was analyzed by Atomic Force Microscopy imaging (5 × 5 μm and 1 × 1 μm) using acoustic AC mode with a silicon nitride tip (resonance frequency of 295 kHz), in order to evaluate the effect of thermal stress on the thin film morphology. Atomic Force Microscopy imaging was performed using a commercial AFM microscope (Molecular Imaging Picoplus 5500) equipped with a 100 μm scanner. Images were processed with Gwyddion software (<http://gwyddion.net/>).

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 0.1M 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. Activated Al₂O₃ was added in the electrolytic solution to remove excess moisture. For a further comparison of the electrochemical and optical properties, all potentials are referred to the SCE electrode that was calibrated at - 0.405 V vs. Fc/Fc⁺ system. Following the work of Jenekhe,² we estimated the electron affinity (EA) or lowest unoccupied molecular orbital (LUMO) and the ionisation potential (IP) or highest occupied molecular orbital (HOMO) from the redox data. The LUMO level was calculated from: LUMO (eV) = -[E_{onset}^{red} (vs SCE) + 4.4] and the HOMO level from: HOMO (eV) = -[E_{onset}^{ox} (vs SCE) + 4.4], based on an SCE energy level of 4.4 eV relative to the vacuum. The electrochemical gap was calculated from : ΔE^{el} = |HOMO-LUMO| (in eV).

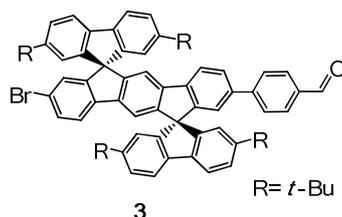
EL fabrication and testing: OLEDs were fabricated using the following procedure. Indium-tin oxide (ITO) substrates on glass from Merck underwent a solvent ultrasonic cleaning using acetone, ethanol and isopropanol followed by a 15 min UV-ozone treatment. A layer of poly(3,4-ethylene dioxythiophene) doped 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. Then a **DA-DSF-IF** layer or a NPB (N,N'-di(1-naphtyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) layer followed by a **DSF-IF(*t*-Bu)₄ 1** layer, were thermally evaporated under vacuum (ca. 10⁻⁶ mbar). The layer thickness was monitored in-situ during the evaporation via a piezoelectric quartz. Lithium Fluorine (0.8 nm)-Aluminium (75 nm) cathodes for **DA-DSF-IF** diodes were finally thermally evaporated through a shadow mask. LiF acts as an electron injection layer and slightly lowers the work function of Al to favour electron injection. Calcium cathodes (200 nm) for **DSF-IF(*t*-Bu)₄ 1** were evaporated through a shadow mask. The OLEDs were then stored and characterized under inert atmosphere in a nitrogen glove box ([O₂] and [H₂O] < 1 ppm). 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



Compound **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) and evaporated *in vacuo*. Precipitation in a mixture of dichloromethane/hexane gave the title compound **2** (1.08 g, 90%) as a colorless solid.

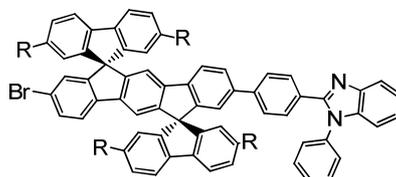
mp (hexane) >300°C; ¹H NMR (CD₂Cl₂, 300 MHz, ppm) δ 7.80 (4H, d, *J* = 8.1, ArH), 7.50-7.44 (6H, m, ArH), 7.36 (2H, dd, *J* = 8.1 *J* = 2.1, ArH), 7.16 (2H, s, ArH), 6.78 (2H, d, *J* = 2.1, ArH), 6.72 (4H, d, *J* = 1.8, ArH), 1.17 (36H, s, Me); ¹³C NMR (CD₂Cl₂, 75 MHz, ppm) δ 151.5 (C), 150.8 (C), 150.0 (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 (C_{Me}), 31.5 (Me); HRMS (ESI⁺, CH₂Cl₂/CH₃OH 95/5): (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.



Compound **2** (400 mg, 0.43 mmol), 4-formylbenzene boronic acid (90 mg, 0.60 mmol), Pd₂dba₃ (39 mg, 0.4 mmol) and *tert*-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; ¹H NMR (CD₂Cl₂, 300 MHz, ppm) δ 9.93 (1H, s, CHO), 7.835 (2H, d, *J* = 8.1, ArH), 7.825 (2H, d, *J* = 8.1, 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, s, ArH), 7.20 (1H, s, ArH), 6.97 (1H, d, *J* = 1.2, ArH), 6.81-6.74 (5H, m, ArH), 1.18 (18H, s, Me), 1.16 (18H, s, Me); ¹³C NMR (CD₂Cl₂, 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

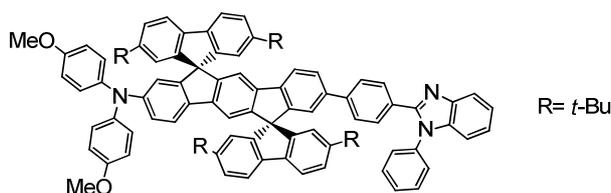
(CH), 130.2 (CH), 127.7 (CH), 127.3 (CH), 127.1 (CH), 125.7 (CH), 125.6 (CH), 122.8 (CH), 121.9 (CH), 121.4 (C), 121.0 (CH), 120.93 (CH), 120.87 (CH), 119.8 (CH), 119.7 (CH), 116.1 (CH), 116.0 (CH), 66.6 (C_{spiro}), 66.4 (C_{spiro}), 35.13 (CMe), 35.12 (CMe), 31.5 (Me); HRMS (ESI⁺, CH₃OH/CH₂Cl₂ 90/10): (Found : [M+Na]⁺, 983.3794; C₆₇H₆₁O⁷⁹BrNa required 983.3798); IR (ATR, cm⁻¹) ν = 3060, 3034, 2956, 2902, 2867, 2817, 1703 (C=O), 1602, 1475, 1456, 1404, 1361, 1251, 1208, 1168.



4 R= *t*-Bu

Compound **3** (300 mg, 0.31 mmol) and *N*-phenyl-*ortho*-phenylenediamine (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 (MgSO₄), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate (8:2). The title compound **4** (268 mg, 70%) was afforded as a pink to violet solid.

mp (hexane) >300°C; ¹H NMR (CD₂Cl₂, 300 MHz, ppm) δ 7.82 (4H, d, *J* = 7.8, ArH), 7.78 (1H, 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, d, *J* = 1.2, ArH), 6.81-6.74 (5H, m, ArH), 1.18 (18H, s, Me), 1.16 (18H, s, Me); ¹³C NMR (CD₂Cl₂, 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 (CMe), 35.12 (CMe), 31.54 (Me); HRMS (ESI⁺, CH₃OH/CH₂Cl₂ 90/10): (Found : [M+H]⁺, 1125.4725; C₇₉H₇₀N₂⁷⁹Br required 1125.4717); IR (ATR, cm⁻¹) ν = 3063, 3034, 2956, 2903, 2868, 1596, 1499, 1476, 1451, 1427, 1403, 1362, 1324, 1252.

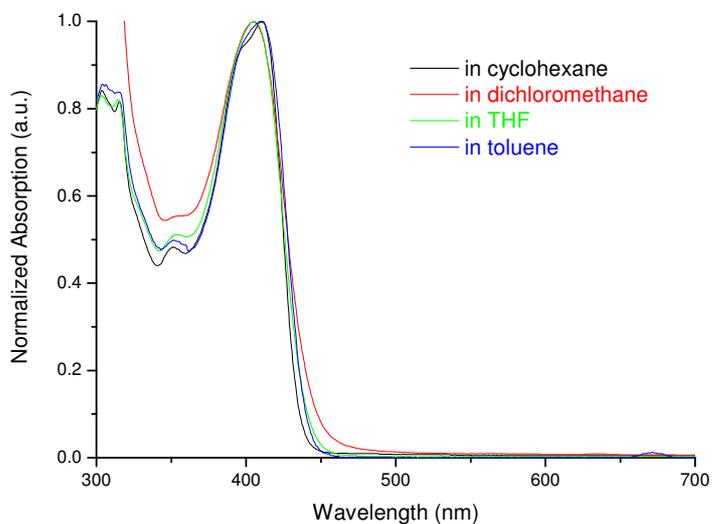


DA-DSF-IF

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 (MgSO₄), evaporated *in vacuo* and purified by column chromatography on silica gel, eluting with light petroleum-ethyl acetate (8:2 to 7:3). After recrystallization in cyclohexane, the title compound **5** (114 mg, 50%) was afforded as a green solid.

mp (cyclohexane) >300°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, d, $J = 1.2$, 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 (CMe), 35.09 (CMe), 31.59 (Me), 31.52 (Me); HRMS (ESI^+ , CH_2Cl_2): (Found: M^+ , 1273.6479; $\text{C}_{93}\text{H}_{83}\text{N}_3\text{O}_2$ required 1273.6480); IR (ATR, cm^{-1}) $\nu = 3068, 3034, 3005, 2954, 2924, 2904, 2867, 2850, 1600, 1501, 1477, 1440, 1406, 1361, 1238, 1104, 1039$.

Spectroscopic studies



UV/visible spectra of **DA-DSF-IF** in different solvents

Regarding the solvatochromic study (see Figure 3 within the manuscript), the quantum yield of **DA-DSF-IF** has been calculated in each solvent (with Quinine Sulphate as reference, $\lambda_{\text{exc}} = 375 \text{ nm}$)

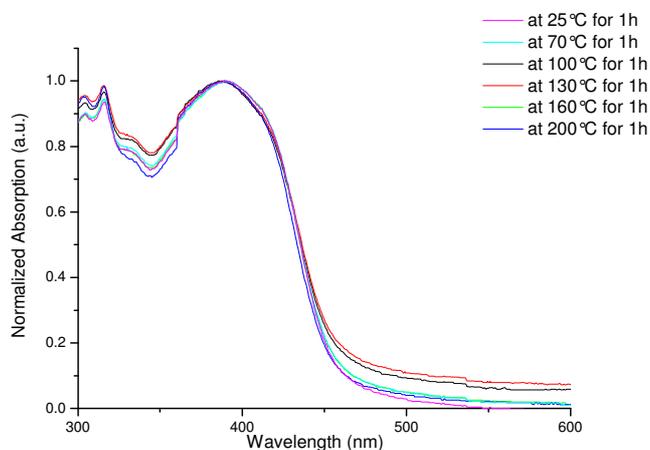
Quantum yield in Cyclohexane: 0.85

Quantum yield in Toluene: 0.91

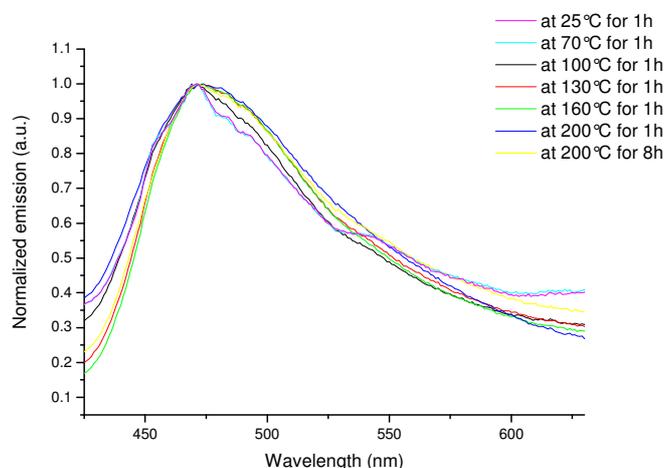
Quantum yield in THF: 0.86

Quantum yield in Dichloromethane: 0.83

A vacuum evaporated thin-film of **DA-DSF-IF** on a sapphire wafer (monocrystalline Al_2O_3 ; $R_a = 0.063 \text{ nm}$) was heated, in a Schlenk tube, under an argon atmosphere. The film was gradually heated from room temperature up to 200°C , one hour at each stage (rt, 70°C , 100°C , 130°C , 160°C , 200°C) and finally 8h at 200°C . For each temperature, the film was cooled to RT (around 10 minutes of cooling) prior to record the absorption and emission spectra.



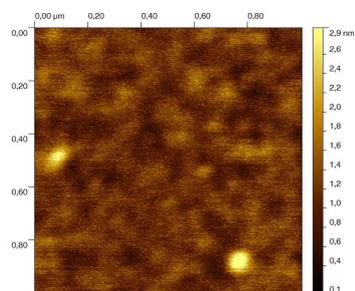
UV/visible spectra of **DA-DSF-IF** in thin film solid, annealed from room temperature to 200°C under argon atmosphere



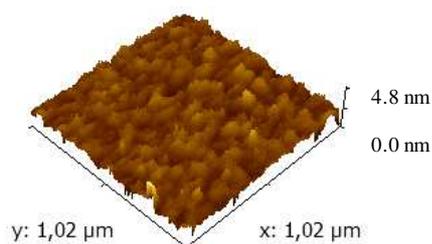
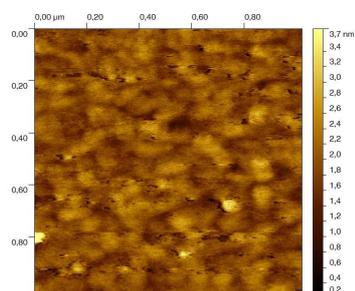
Emission spectra of **DA-DSF-IF** in thin-film, annealed from room temperature to 200°C under argon atmosphere (excitation wavelength 350 nm)

AFM studies

A
(20 °C)
Ra = 0.23 nm

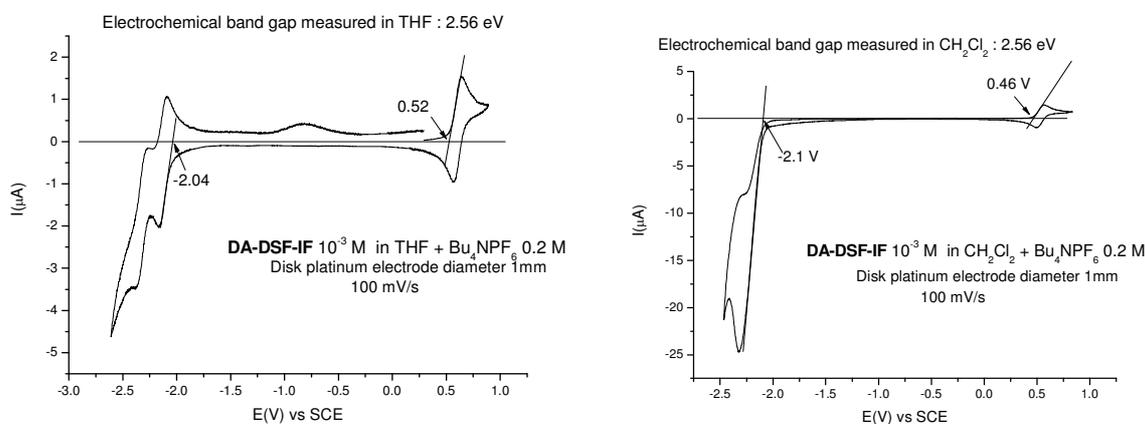


B
(130 °C)
Ra = 0.26 nm

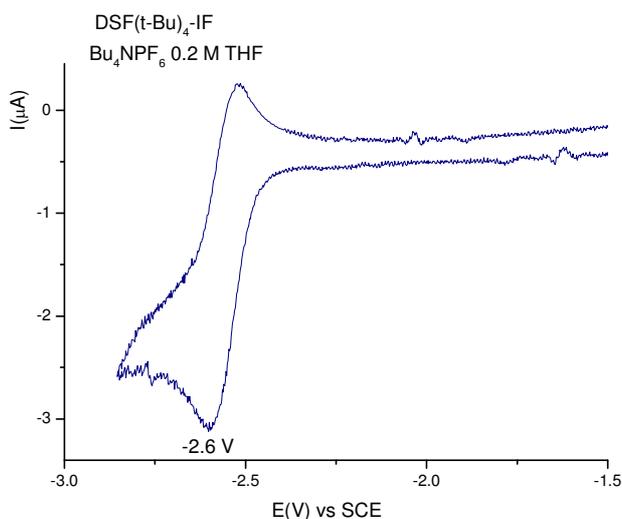


AC-AFM images of a thin-film of **DA-DSF-IF** on a sapphire wafer (left: 2D, right: 3D; $1 \times 1 \mu\text{m}$): (A) non-heated film. (B) film heated in air, at 130 °C, for 1 h.

Electrochemical studies



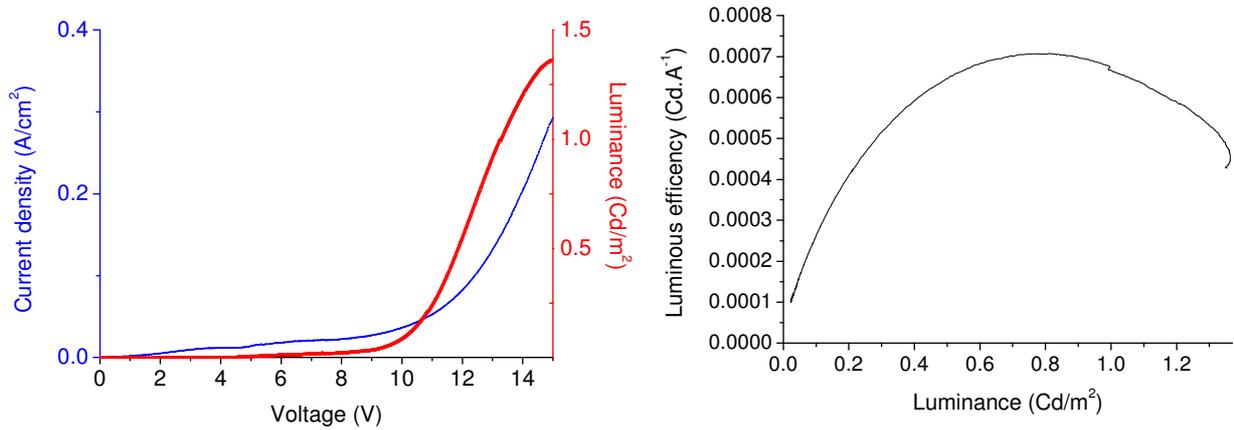
Cyclic Voltammeteries of **DA-DSF-IF** 10⁻³ M in CH₂Cl₂ (right) and in THF (left) both containing *n*-Bu₄NPF₆ 0.2 M. Electrochemical band gaps are determined from the oxidation and reduction onset potentials. Scan-rate: 100 mV/s ; working electrode:platinum disk electrode.



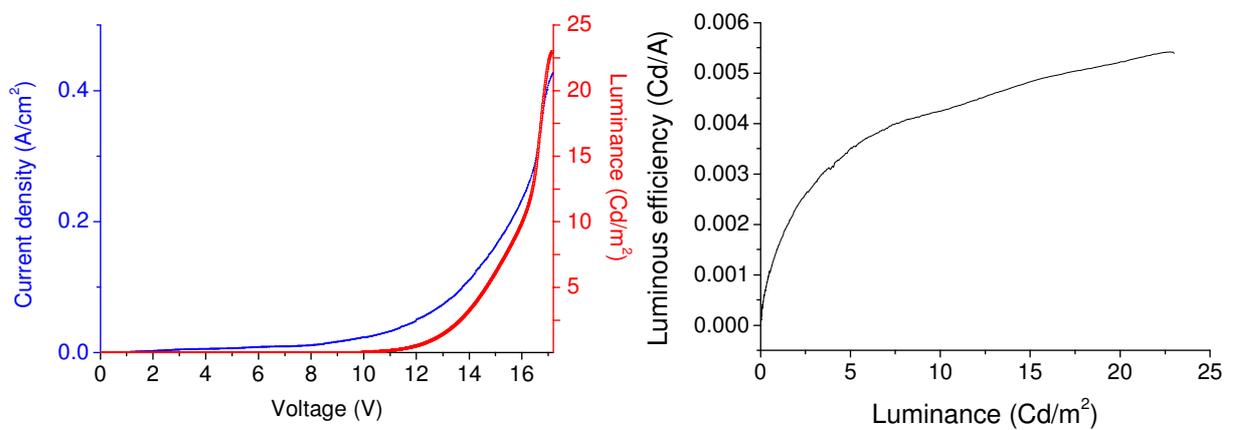
Cyclic Voltammeteries of **DSF-IF(t-Bu)₄** 1 10⁻³ M in THF containing *n*-Bu₄NPF₆ 0.2 M. Sweep-rate 100 mV/s. Working electrode:platinum disk electrode.

EL fabrication and testing

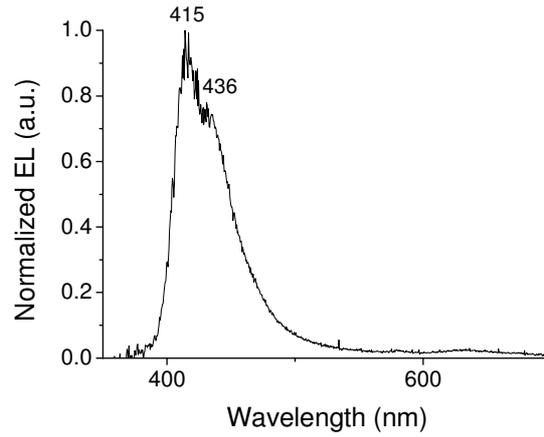
Emitting layer : DSF-IF(*t*-Bu)₄ **1**



ITO/PEDOT/DSF-IF(*t*-Bu)₄ **1** (40 nm)/Ca device.
Left: I-V-L characteristics; Right: Luminous efficiency.

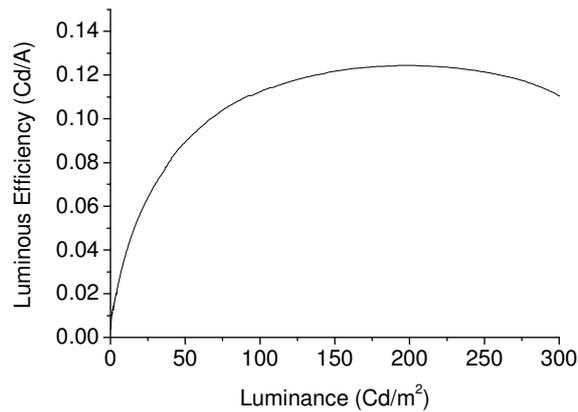


ITO/PEDOT/NPB (35 nm)/DSF-IF(*t*-Bu)₄ **1** (40 nm)/Ca device.
Left: I-V-L characteristics; Right: Luminous efficiency.



Normalized EL spectrum of ITO/PEDOT/NPB (35 nm)/**DSF-IF(*t*-Bu)₄** (40 nm)/Ca device.

Emitting layer : **DA-DSF-IF**



Luminous efficiency of ITO/PEDOT/**DA-DSF-IF** (40 nm)/LiF(0.8 nm)/Al device

Luminous efficiencies have been calculated, from the I-V-L characteristics, as follows:

$$\mathbf{Re = (L * 10^{-4}) / J}$$

With

Re = Luminous efficiency in Cd.A⁻¹

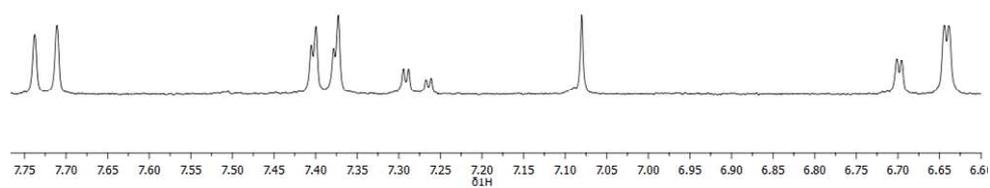
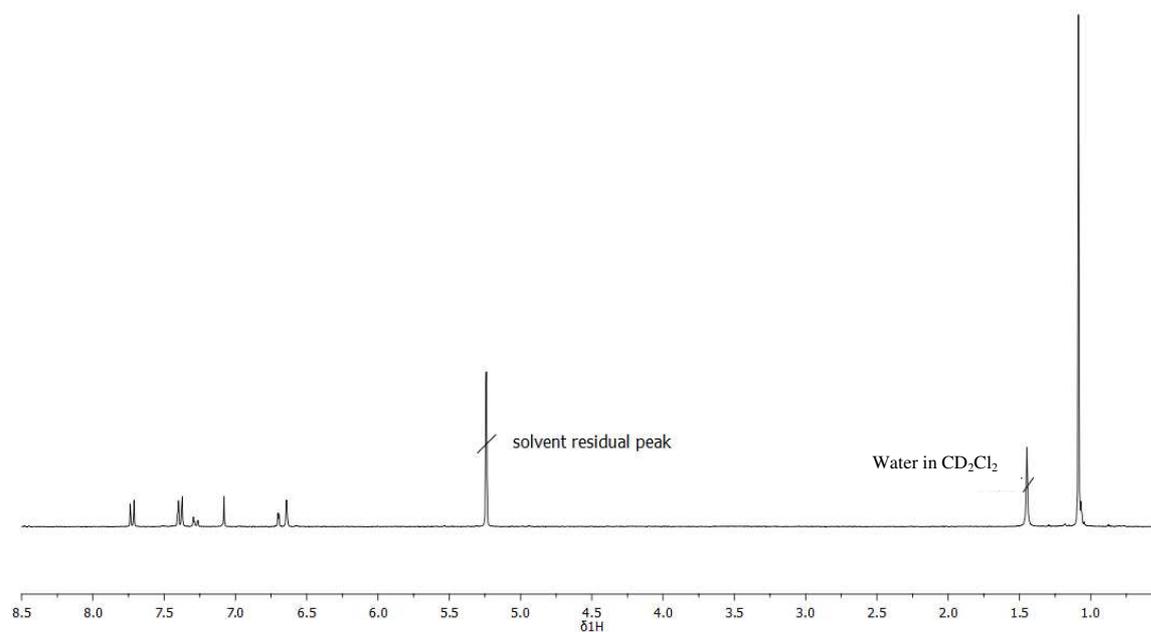
L = Luminance in Cd.m⁻²

The surface of the device is 0.1 cm²

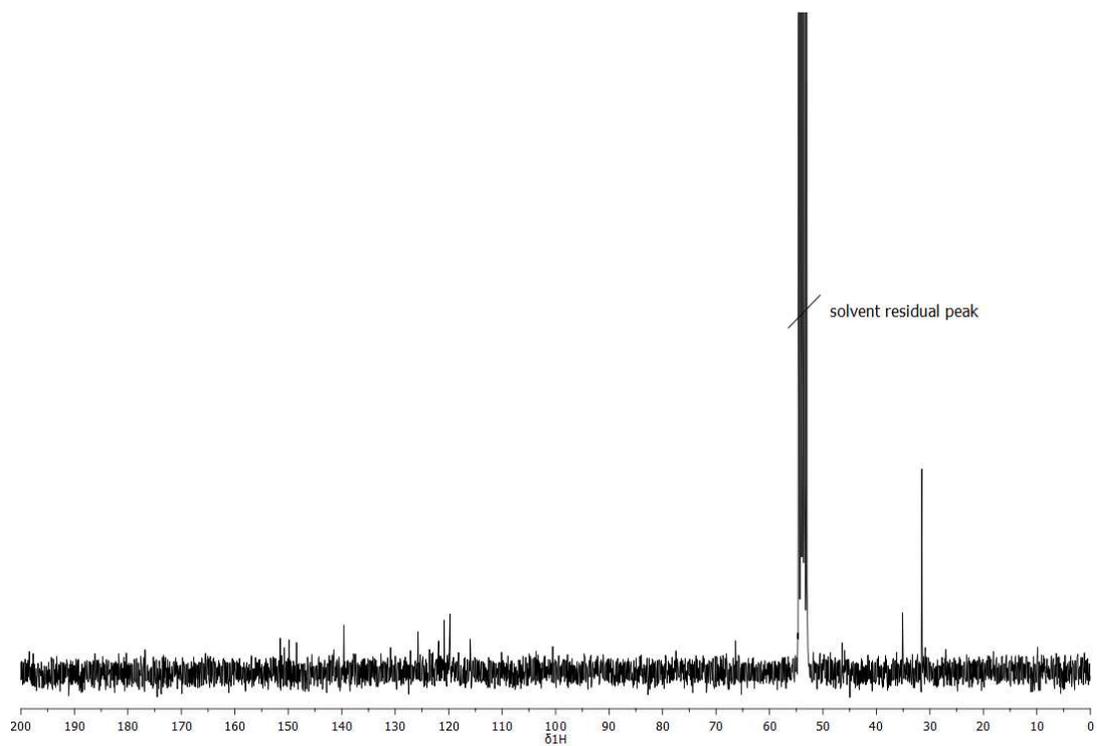
J = current density (A.cm⁻²)

Copy of NMR spectra

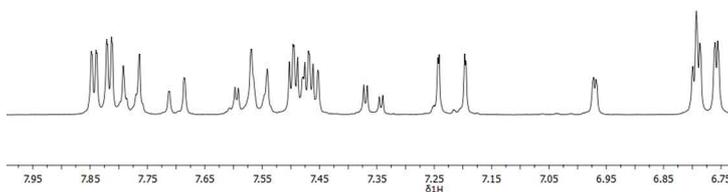
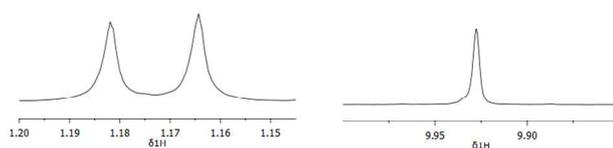
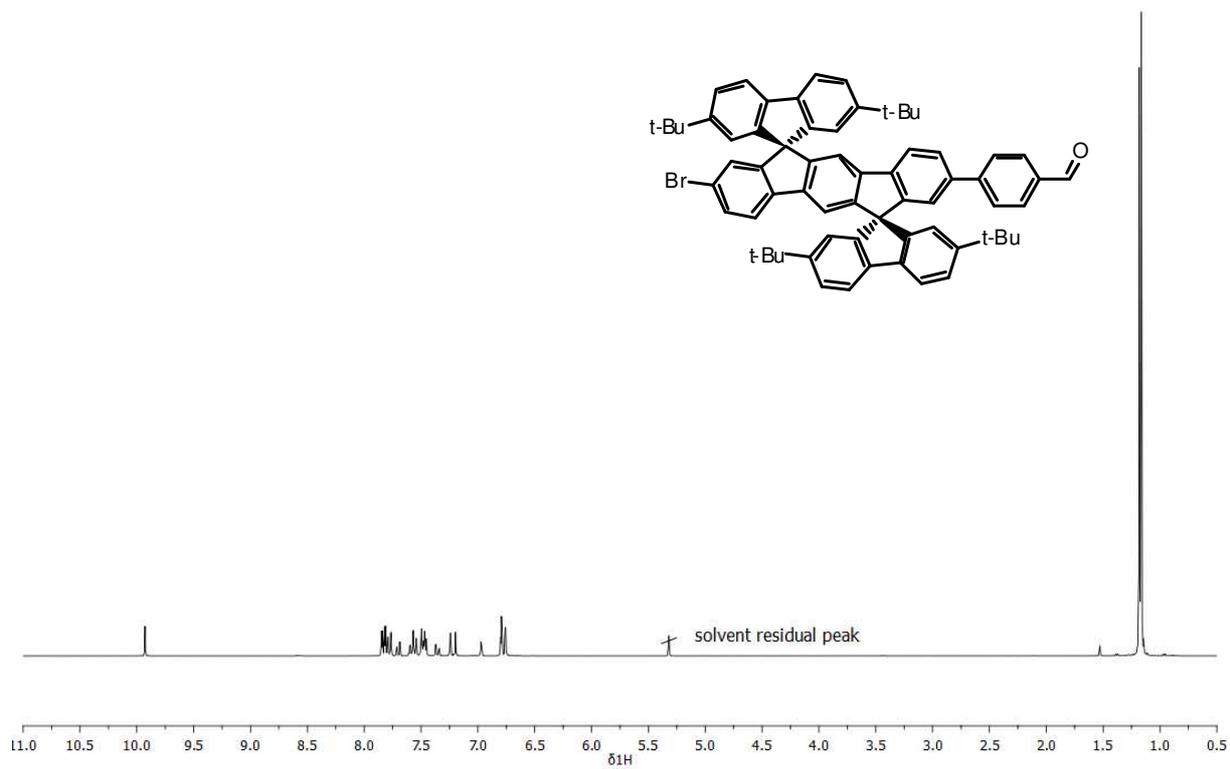
Compound **2** (CD₂Cl₂)*

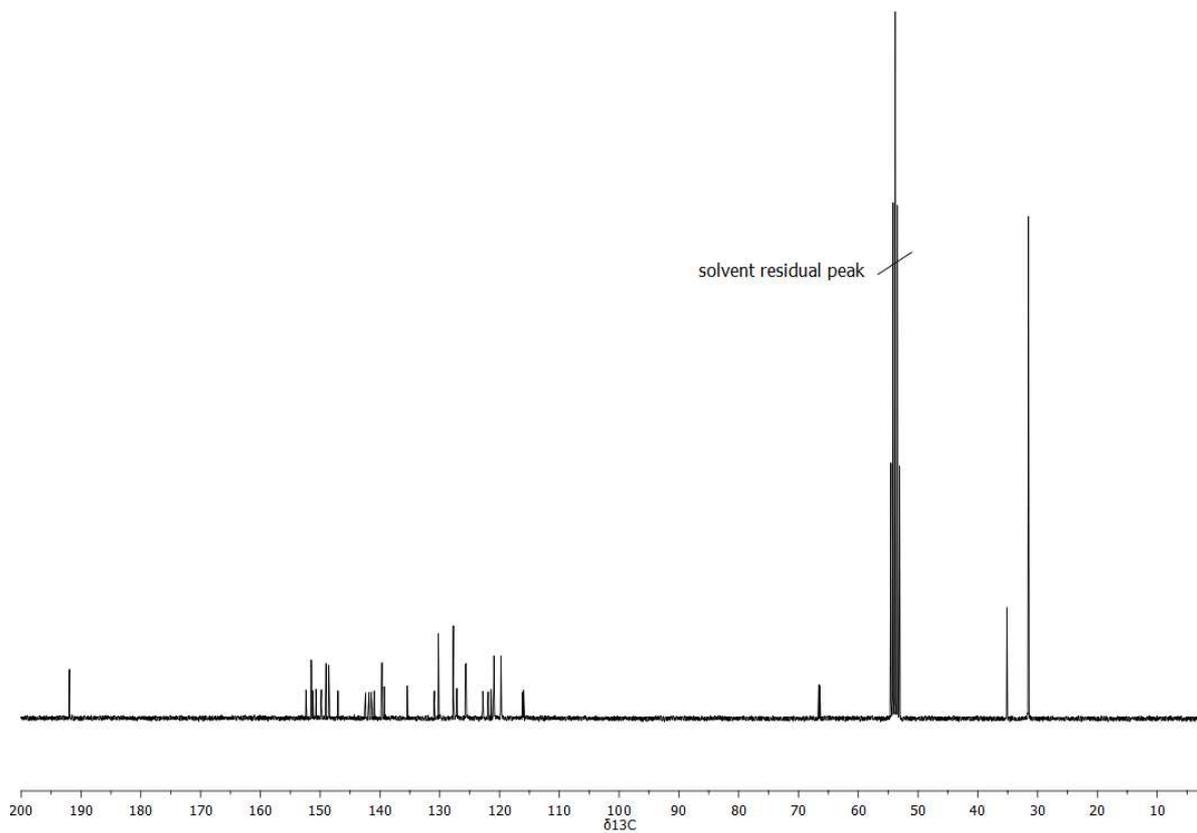


* It should be noted that the ¹³C NMR of **2** is poor due its extremely low solubility in all the solvents tested.

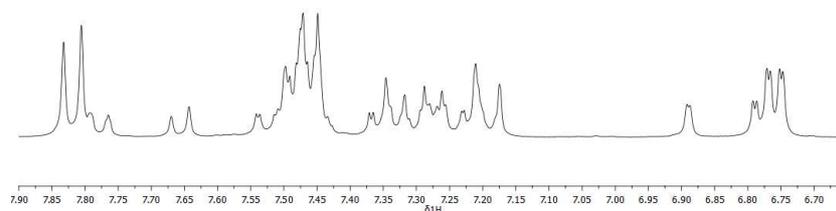
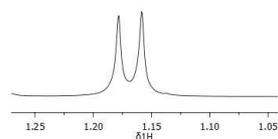
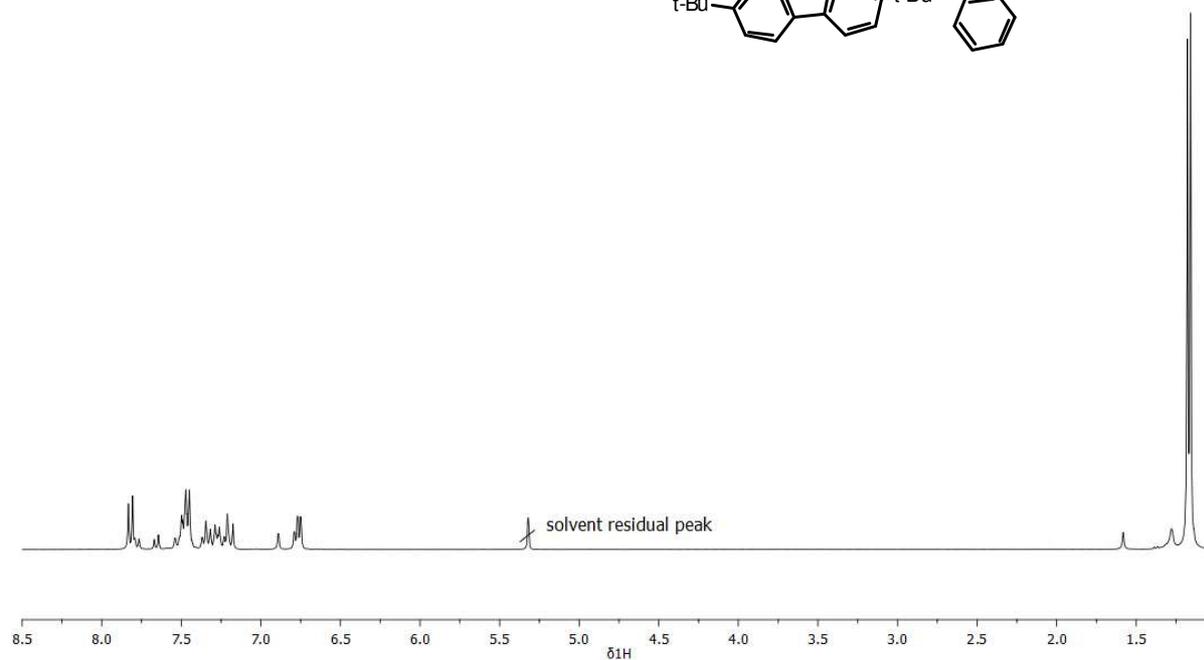
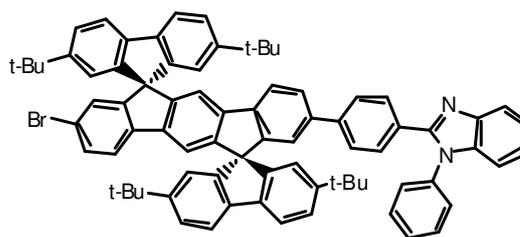


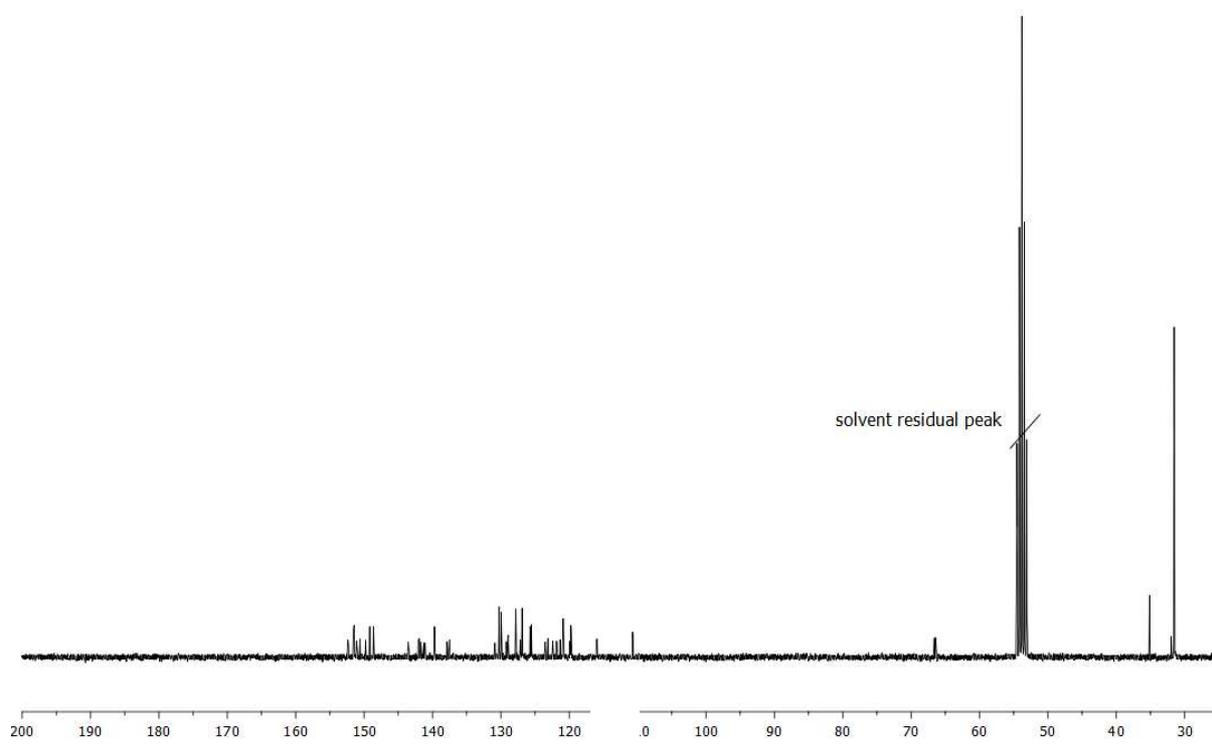
Compound 3 (CD₂Cl₂)

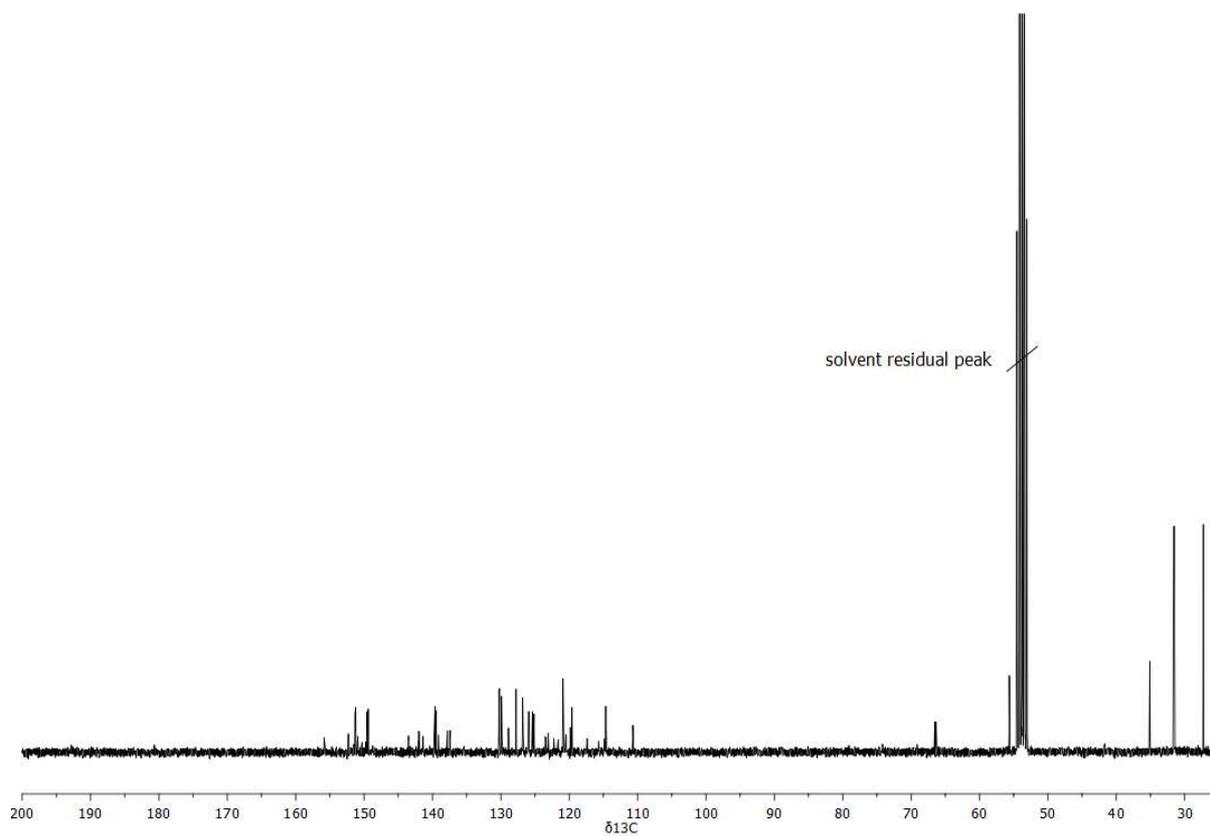




Compound 4 (CD₂Cl₂)







REFERENCES

- (1) Poriel, C.; Rault-Berthelot, J.; Barrière, F.; Slawin, A. M. Z. *Org. Lett.* **2008**, *10*, 373-376.
- (2) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556-4573.