

Electronic Supplementary Information (ESI)

4,5-Diazafluorene co-oligomers as electron-deficient light-emitting materials and selective fluorescence sensors for mercury(II) cations

Sanjay Ghosh, Abdulaziz S. Alghunaim, Mohammed H. Al-mashhadani, Michal P. Krompiec, Megan Hallett, and Igor F. Perepichka*

School of Chemistry, Bangor University, Bangor, LL57 2UW, UK

*E-mail: i.perepichka@bangor.ac.uk; i_perepichka@yahoo.com; Tel: +44-(0)1248-382386

Materials and Instrumentations

All chemicals and solvents were purchased from either Aldrich, Alfa Aesar or Fischer Scientific and were used without further purification unless stated otherwise. Tetrahydrofuran (THF) was refluxed over sodium benzophenone ketyl (sodium metal + benzophenone) under argon and distilled off directly prior using the solvent for cyclic voltammetry and absorption/emission spectral measurements. Manual purification of the products was performed by column chromatography silica gel LC60 (40–60 μM). Some products were purified using Telydyne Isco automatic flash chromatograph, model Combiflash Rf 200 using Biotage disposable PTFE columns, hand-filled with silica gel LC60 (40–60 μM). For monitoring the progress of the reactions and control the products, thin layer chromatography (TLC) on pre-coated silica gel (Merck, 20 \times 20 cm, Silica gel 60 F₂₅₄) was used.

¹H NMR, ¹³C NMR and DEPT-135 C NMR spectra were recorded either on a Bruker Avance 400 MHz or Bruker Avance 500 MHz in CDCl₃ or DMSO-*d*₆. Chemical shifts are reported in ppm, relative to tetramethylsilane (TMS) reference ($\delta = 0.00$ ppm). The following abbreviations were used to assign NMR spectra: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = doublet of triplet. Mass spectra were recorded on GC-MS 5890 (Hewlett Packard Series II) or microTOF LC Bruker Daltonics mass spectrometers. Microwave assisted reactions were performed on a CEM Discover SP microwave reactor. Spin-coated films were prepared using spin coater from Laurel Technologies, Model WS-650Mz-23NPP/LITE.

Absorption and emission spectra, and the photoluminescence quantum yields

Shimadzu UV-3600 UV-Vis-NIR spectrophotometer and Horiba Yvon Fluoromax-4 spectrofluorometer were used for recording absorption and photoluminescence spectra at room temperature. Absorption and emission spectra in solutions were measured using HPLC grade solvents in 10 mm path length quartz cells. Solid state measurements were performed for spin-coated films deposited on 12.5 mm circular quartz windows. The films were prepared by spin coating from oligomer solutions (1–3 mg per 1 mL of DCM) at 3000–4000 rpm. Photoluminescence quantum yields (PLQY, Φ_{PL}) in solutions for all oligomers were measured in HPLC grade dichloromethane (DCM) at room temperature according to the described method.¹ The values of Φ_{PL} were calculated according to the following formula:

$$\Phi_{\text{PL}} = \Phi_{\text{r}} \times (A/A_{\text{r}}) \times (\text{OD}_{\text{r}}/\text{OD}) \times (n^2/n_{\text{r}}^2)$$

where Φ_{PL} is a photoluminescence quantum yield, A is an integral intensity of the emission, OD is an optical density, and n is a refractive index of the used solvent. The subscript *r* refers to the reference fluorophore of known quantum yield [9,10-diphenylanthracene (DPA), diluted solution in cyclohexane, $\Phi_{\text{r}} = 90\%$). The solutions were deoxygenated by bubbling with argon for about 10 minutes before the measurements. Corrected emission and absorption spectrum was used to

calculate the quantum yields. Absolute Φ_{PL} in solutions and in the solid state were measured for spin-coated films on quartz substrates using calibrated integrating sphere Horiba F-3018 on Horiba Jobin Yvon Fluoromax-4 spectrofluorometer at room temperature, and calculated by Horiba Yvon quantum yield calculator software. CIE 1931 color space have been calculated using OSRAM Color Calculator v. 7.23.

Table S1 Determination of photoluminescence quantum yields (PLQY, Φ_{PL}) of oligomers in degassed DCM.

Compound	Integral intensity of the emission $A (\lambda_{\text{ex}} = 350 \text{ nm})$	Optical density OD (a.u.)	PLQY, Φ_{PL} (%)
9,10-DPA ^a	7.53×10^7	0.05	(90)
FNoF ^b	9.75×10^5	0.05	1
FFNFF	1.04×10^8	0.07	84
FNF	1.13×10^8	0.07	93
SNS	1.21×10^8	0.07	101
NSN	8.54×10^7	0.05	89

^a Diluted solution of DPA in degassed cyclohexane ($\Phi_{\text{r}} = 90\%$) was used as fluorophore standards.²

^b $\lambda_{\text{ex}} = 370 \text{ nm}$

Experimental procedure for the metal cations sensing study of FNF.

The metal salts used in these studies LiClO_4 , NaClO_4 , AgClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$, $\text{Cu}(\text{BF}_4)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pb}(\text{ClO}_4)_2$ and $\text{Hg}(\text{ClO}_4)_2$ were dried under high vacuum (10^{-3} mbar) for at least 24 hours prior to using them for preparation of solutions in dry THF [hygroscopic salts were preliminary dried in an oven at 170°C for several hours]. The stoichiometry of the coordination complex with Hg^{2+} was determined using Job's method.^{3,4} The absorption and photoluminescence spectra for titration of **FNF** with HgClO_4 are shown in Figure S10. The corresponding Job's plot using both fluorescence and absorption intensity (Figure S11) reveal 2:1 (**FNF**: Hg^{2+} , mole ratio) stoichiometry for the [**FNF**- Hg^{2+}] adduct. The corresponding structure of the possible complex formation is shown on Figure S12.

Measurements of known concentrations of 2[**FNF**]: Hg^{2+} complex emission intensity can be used to determine the unknown concentration of Hg^{2+} in a given sample by plotting calibration graph of the emission intensity vs concentration. Photoluminescence titration of **FNF** with Hg^{2+} ions showed that an intensity of the long wavelength emission band at 507 nm of **FNF**- Hg^{2+} complex gradually increased with an increase of Hg^{2+} ions up to certain limit that corresponds to the 2:1 ratio (Figure S13b). Linear increase in the fluorescence intensity with an increase of Hg^{2+} concentration added to the **FNF** solution in THF is observed in the range of ca. 0 – 2.5 μM that allowed to estimate the detection limit to be ca. $1.5\text{--}2 \times 10^{-7}$ M.

Cyclic voltammetry

Cyclic voltammetry experiments were conducted in a standard three-electrode configuration, using Metrohm Autolab PGSTAT-302N potentiostat/galvanostat, with iR drop compensation. Platinum disk electrode ($d = 1.5$ or 2 mm) and platinum wire ($d = 0.2 \text{ mm}$) were used as the working and counter electrodes, respectively. The reference electrode was Ag/Ag^+ (silver wire immersed in a mixture of 0.01 M AgNO_3 and $0.1 \text{ M Bu}_4\text{NPF}_6$ in acetonitrile, separated from the solution by a Vycor frit). Potentials are referenced to half-wave potential ($E_{1/2}$) of ferrocene, which was used as an internal standard. The average potentials of Fc/Fc^+ vs Ag/Ag^+ in our conditions were $E_{1/2} = 0.20\text{--}0.22 \text{ V}$ (in DCM) and $0.19\text{--}0.21 \text{ V}$ (in THF). Oxidation scans were performed in DCM containing $0.2 \text{ M Bu}_4\text{NPF}_6$, reduction scans were carried out in a freshly distilled THF containing $0.2 \text{ M Bu}_4\text{NPF}_6$, under argon. The CV were recorded at the scan rate of 100 mV/s .

Computational studies

All the computational studies were performed with Gaussian 09 package of programs⁵ using the density functional theory method (DFT). The hybrid functional B3LYP, which combines Becke's exchange⁶ and Lee, Yang, Paar's correlation functional⁷ with 6-31G or 6-311G basis sets supplemented by (d) or (d,p) polarization functions were used for calculations. The calculations were performed either in a gas phase or in acetonitrile (using polarizable continuum model, PCM). The restricted Hartree-Fock formalism was used. No constraints were used and all structures were free to optimize. The force constants and vibrational frequency for stationary points have been calculated after optimizations to check that they are true minima. To decrease the computation time, all the oligomers geometries were optimized with ethyl substituents at the positions 9,9- of fluorene and 4,5-diazafluorene (instead of longer hexyl or octyl substituents in experimental work). This was shown have no effect on the HOMO/LUMO energy levels of the co-oligomers. The visualization of the orbital coefficients was performed with GaussView 5.0 software.

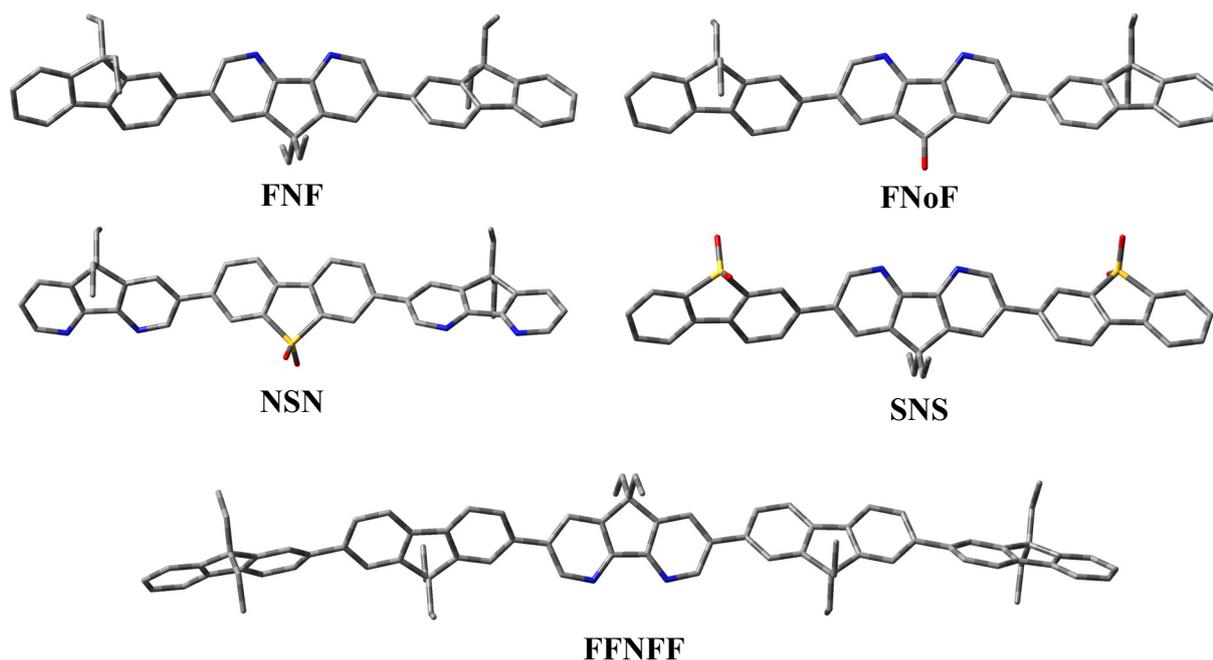


Figure S1. Optimized structures of conjugated oligomers calculated at DFT/B3LYP/6-31G(d) level. For simplicity, H atoms are omitted and tube framework used with colors blue = nitrogen, red = oxygen, and yellow = sulphur atoms using GaussView 05 software.

Table S2. Dipole moments of the optimized geometries of studied co-oligomers calculated by DFT/B3LYP using different basis sets in a gas phase and in ACN.

Compound	6-31G(d)	6-31G(d,p)	6-311G(d,p)	6-311G(d,p)
	gas phasese	ACN	gas phase	ACN
FNoF	0.02	0.16	0.07	0.10
FFNFF	3.50	5.43	3.47	5.38
FNF	3.44	5.06	3.43	5.01
SNS	12.54	17.44	12.76	18.23
NSN	11.51	18.88	11.51	17.08

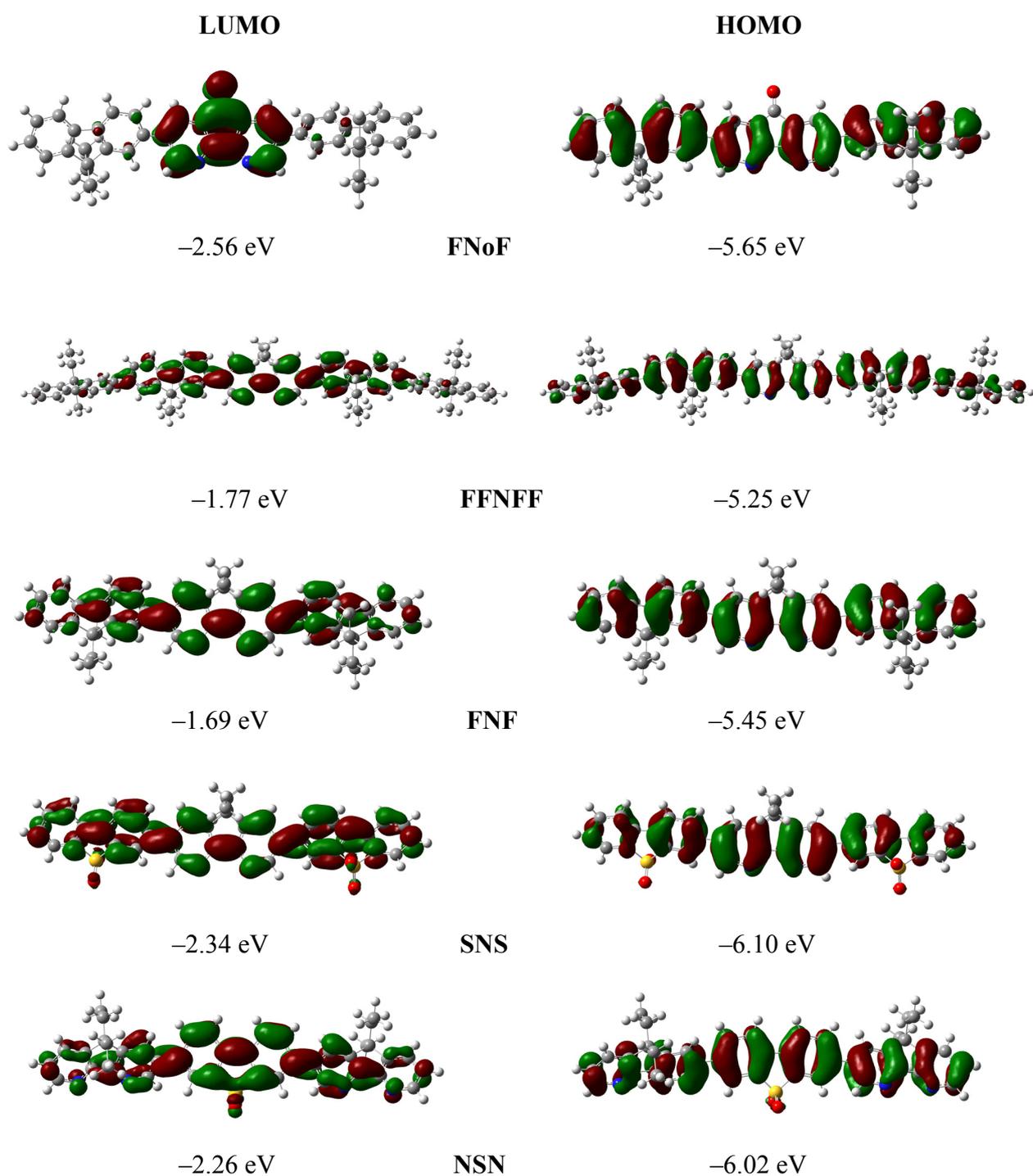


Figure S2. HOMO and LUMO orbital coefficients of 4,5-diazafluorene co-oligomers **FNoF**, **FFNFF**, **FNF**, **SNS**, and **NSN** by DFT/B3LYP/6-31G(d) calculations in a gas phase (surface isovalue = 0.02).

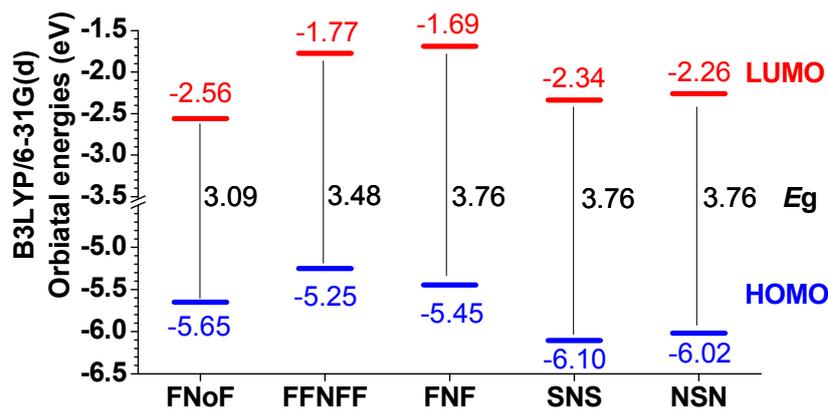


Figure S3 Frontier orbital energy levels of 4,5-diazafluorene co-oligomers by DFT/B3LYP/6-31G(d) calculations in a gas phase.

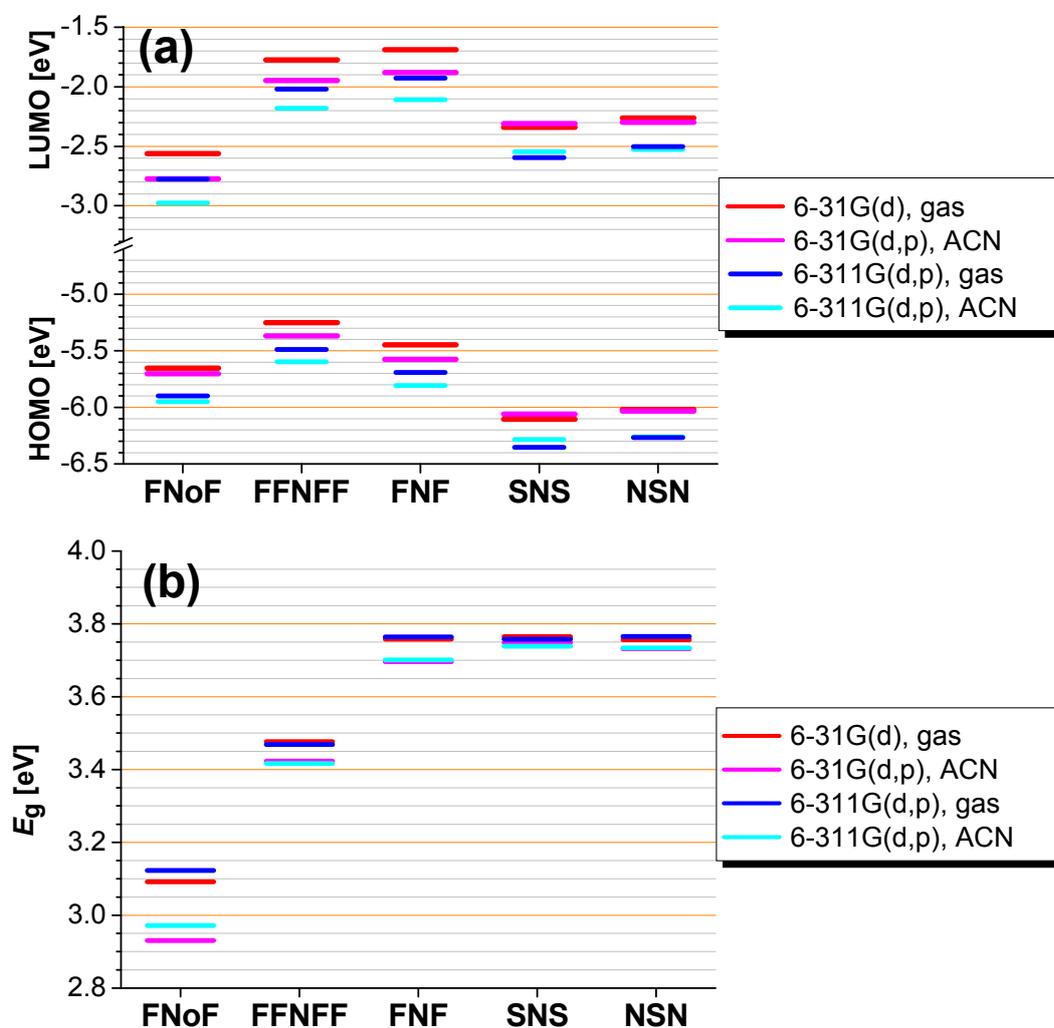


Figure S4 HOMO, LUMO (a) and HOMO–LUMO gaps, E_g (b) of 4,5-diazafluorene co-oligomers calculated by DFT/B3LYP using different basis sets and polarization functions [6-31G(d), 6-31G(d,p) and 6-311G(d,p)] in a gas phase and in acetonitrile, ACN (by PCM model).

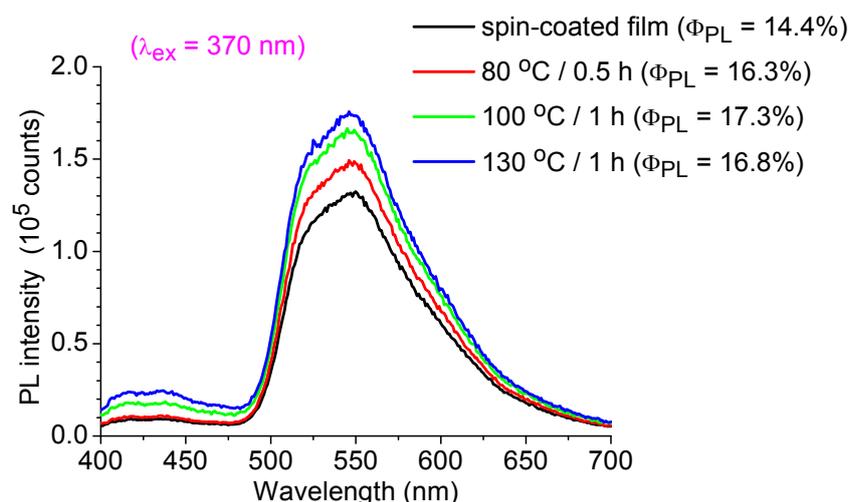


Figure S5 Photoluminescence spectra of **FNF** in the solid state (spin-coated-films from chloroform solution) before and after thermal annealing on an air. The measurements have been performed on an integrating sphere (the shown spectra have not corrected on the sphere background).

Table S3 Absorption and photoluminescence maxima of **FNF**, **FFNFF** and **FNoF** co-oligomers in different solvents.^a

Solvent	FNF		FFNFF		FNoF	
	λ_{abs} (nm)	λ_{PL} (nm)	λ_{abs} (nm)	λ_{PL} (nm)	λ_{abs} (nm)	λ_{PL} (nm)
Hexane	358.5	398, 418, 445sh	324, 372	413.5 , 436	359 , 417sh	500sh, 529 , 560sh
Toluene	363	404.5 , 426, 450sh	326, 377	420.5 , 443	364.5 , 422sh	558
DCM	366	409 , 430sh	328, 378	429 , 446sh	366 , 440sh	575
THF	365	404 , 426, 450sh	–	–	–	–
ACN	364	407 , 424, 450sh	–	–	363 , 427sh	606
EtOH	367	415 , 430sh	327, 379	446	–	–

^a The data are from the spectra shown on Figures 2a,b, 3a-c and 6a,b.

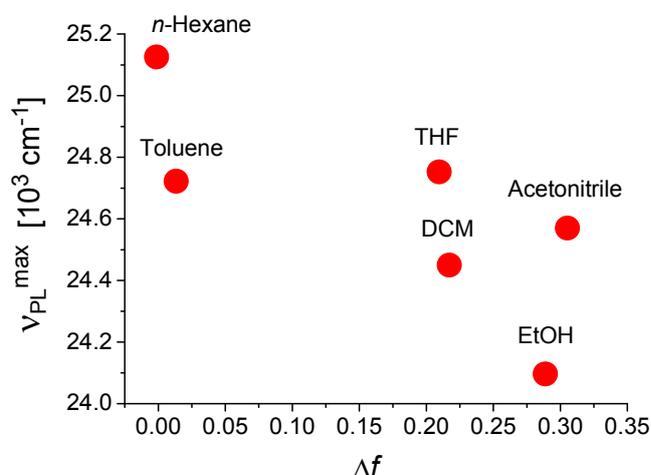
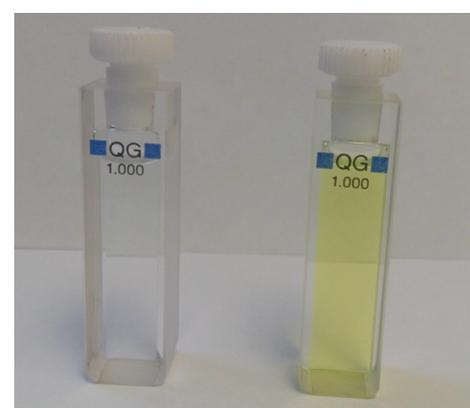
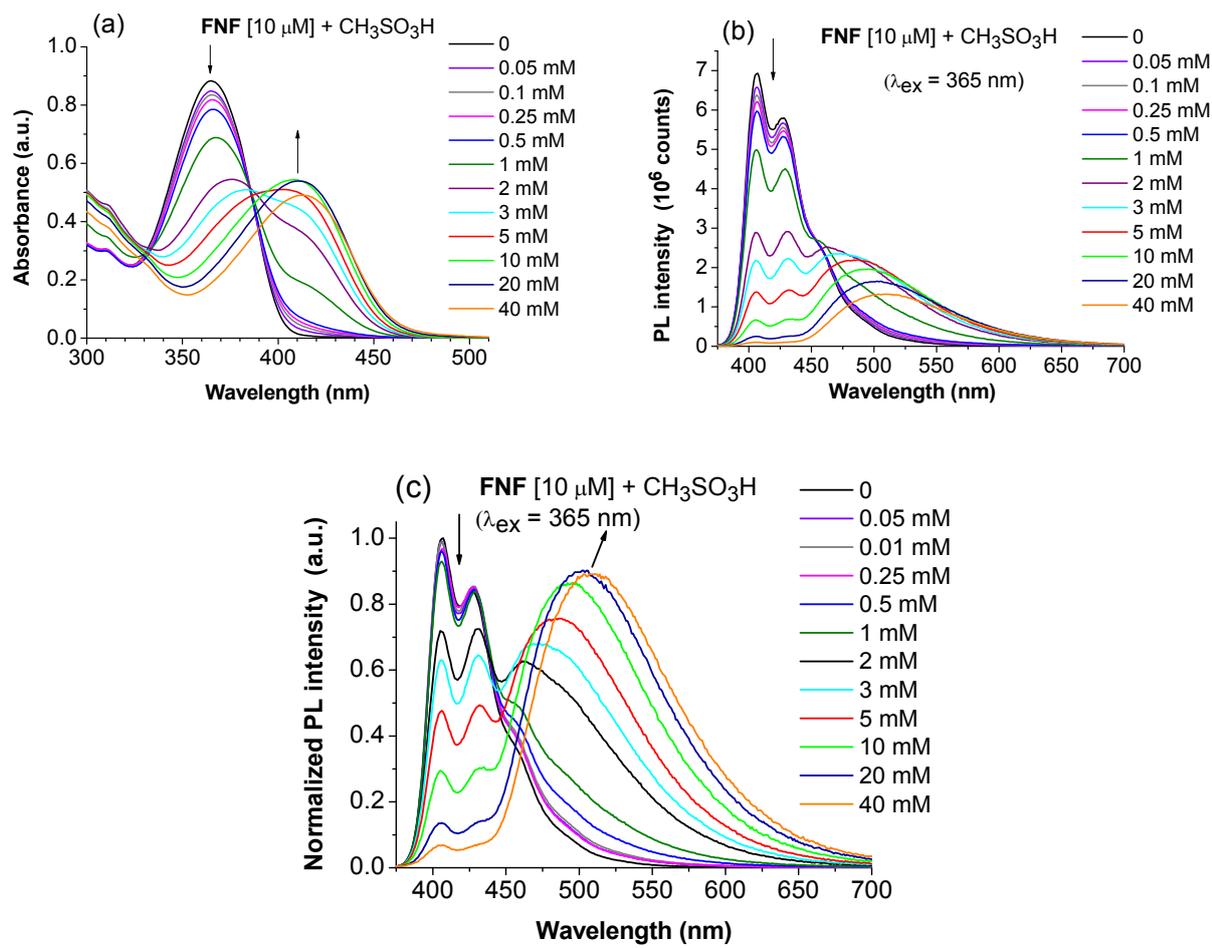


Figure S6. Solvatochromic shifts of the emission maxima ($v_{\text{PL}}^{\text{max}} = 1/\lambda_{\text{PL}}^{\text{max}}$) for **FNF** against the solvent polarity parameter [Lippert-Mataga equation, $\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(n^2 + 1)$, where ϵ is a dielectric permittivity and n is a refractive index of a solvent].



(d) FNF FNF+CH₃SO₃H



(e) FNF FNF+CH₃SO₃H

Figure S7 Changes in UV-Vis absorption (a) and photoluminescence (b) spectra of **FNF** [$\sim 10 \mu\text{M}$] in THF at various concentrations of methanesulfonic acid (0.05 – 40 mM).

(c) As seen in Figure S7b, the intensity of PL (at $\lambda_{\text{PL}} = 510 \text{ nm}$) of the protonated **FNF** is lower than PL intensity of the neutral **FNF** ($\lambda_{\text{PL}} \sim 410 \text{ nm}$). This is, partially, because the absorption of **FNF** at the excitation wavelength ($\lambda_{\text{ex}} = 365 \text{ nm}$) is decreased on protonation (see Figure S7a). Therefore, on the graph (c) we have corrected PL spectra to their absorption intensities at 365 nm: the intensities of PL have been multiplied by $[\text{Abs}^{365}(\text{FNF}+\text{CH}_3\text{SO}_3\text{H})/\text{Abs}^{365}(\text{FNF})]$ and normalized to PL intensity of **FNF**.

(d,e) The bottom photographs show changes of the color of **FNF** solution in THF upon addition of a large excess of CH₃SO₃H: (e) under day light illumination [from colorless to light yellow] and (f) under 366 nm UV-lamp irradiation [from deep blue to green fluorescence].

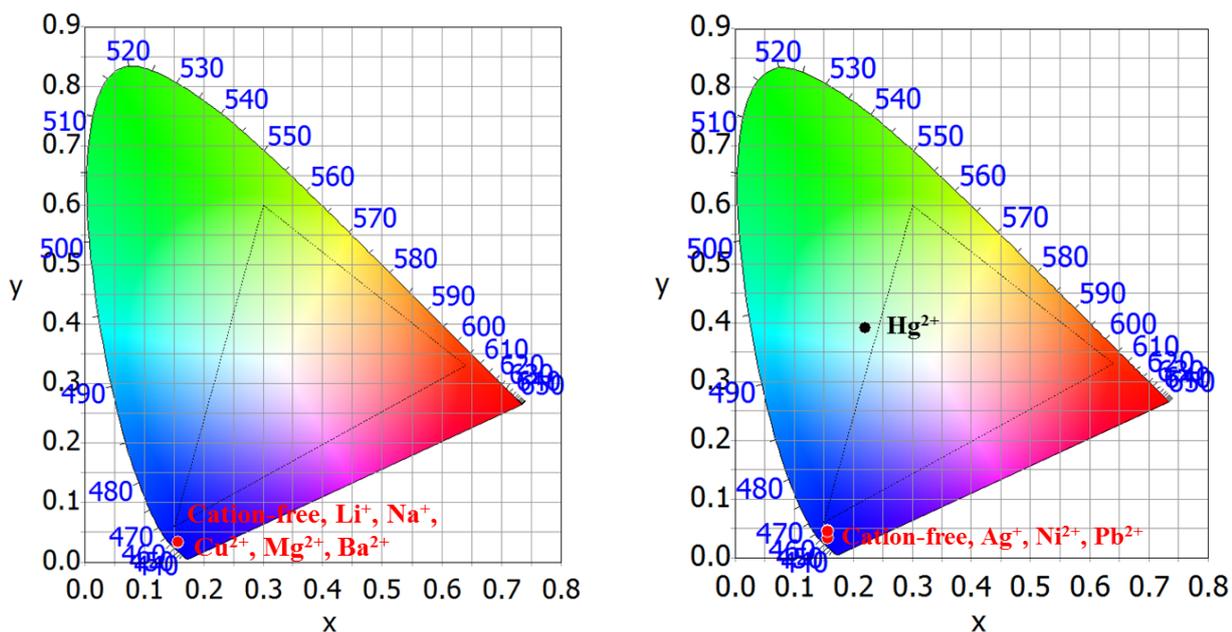


Figure S8. CIE 1931 color space diagrams of the emission spectra of FNF [$\sim 1.4 \mu\text{M}$] solutions in THF in presence of various metal cations [$\sim 14 \mu\text{M}$]. The PL spectra have been taken from Figures 7b (left diagram) and Figure 7d (right diagram). Triangle corresponds to sRGB gamut.

For PL spectra, excitations are at the wavelengths close to the absorption maxima: $\lambda_{\text{ex}} = 365 \text{ nm}$ (cation-free, Li^+ , Na^+ , Cu^{2+} , Mg^{2+} , Ba^{2+}), 367 nm (Ag^+), 371 nm (Ni^{2+}), 379 nm (Pb^{2+}), 395 nm (Hg^{2+}).

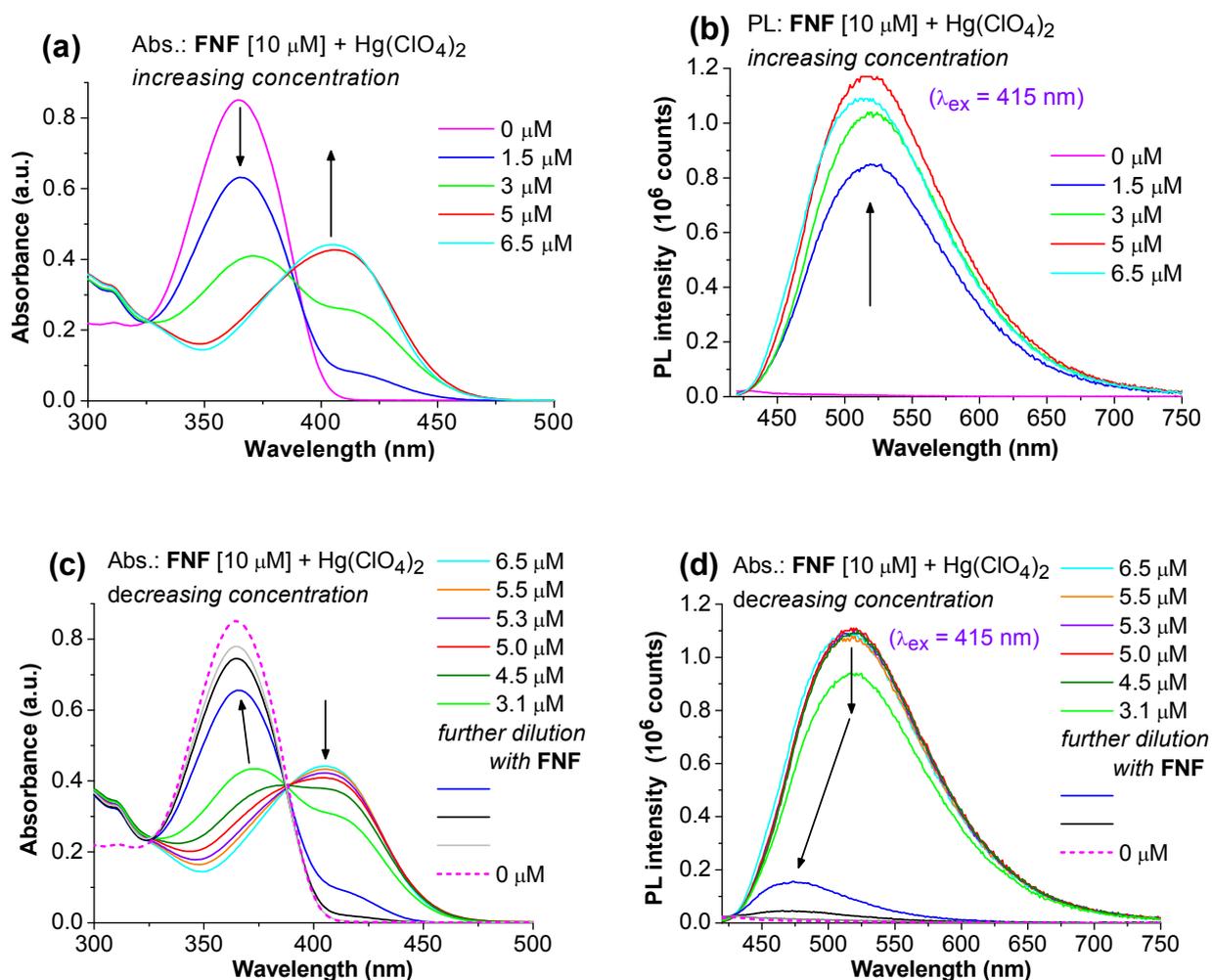


Figure S9. Changes in the absorption (a,c) and photoluminescence (b,d) spectra of **FNF** [$\sim 10 \mu\text{M}$] solutions in THF in presence of $\text{Hg}(\text{ClO}_4)_2$ to demonstrate the reversibility of complexation.

(a,b) Concentration of $\text{Hg}(\text{ClO}_4)_2$ was increased for 0 to $6.5 \mu\text{M}$:

(a) an absorption of **FNF** at 365 nm disappear on the cost of an appearance of red-shifted absorption of the complex **FNF**/ Hg^{2+} at 405 nm;

(b) no emission is observed for an excitation of **FNF** 415 nm; and addition of $\text{Hg}(\text{ClO}_4)_2$ results in an appearance of emission at $\sim 515 \text{ nm}$ (OFF \rightarrow ON).

(c,d) The $\{\text{FNF} [\sim 10 \mu\text{M}] + \text{Hg}(\text{ClO}_4)_2 [6.5 \mu\text{M}]\}$ from experiments (a,b) was diluted with a solution of **FNF** [$\sim 10 \mu\text{M}$]. This kept the concentration of **FNF** constant, but the concentration of $\text{Hg}(\text{ClO}_4)_2$ was decreased from $6.5 \mu\text{M}$ to $< 1 \mu\text{M}$:

(c) long-wavelength absorption of the complex **FNF**/ Hg^{2+} is decreased and an absorption of free **FNF** is growing;

(d) on decrease of the concentration of $\text{Hg}(\text{ClO}_4)_2$, the emission of the complex is decreased and then disappear.

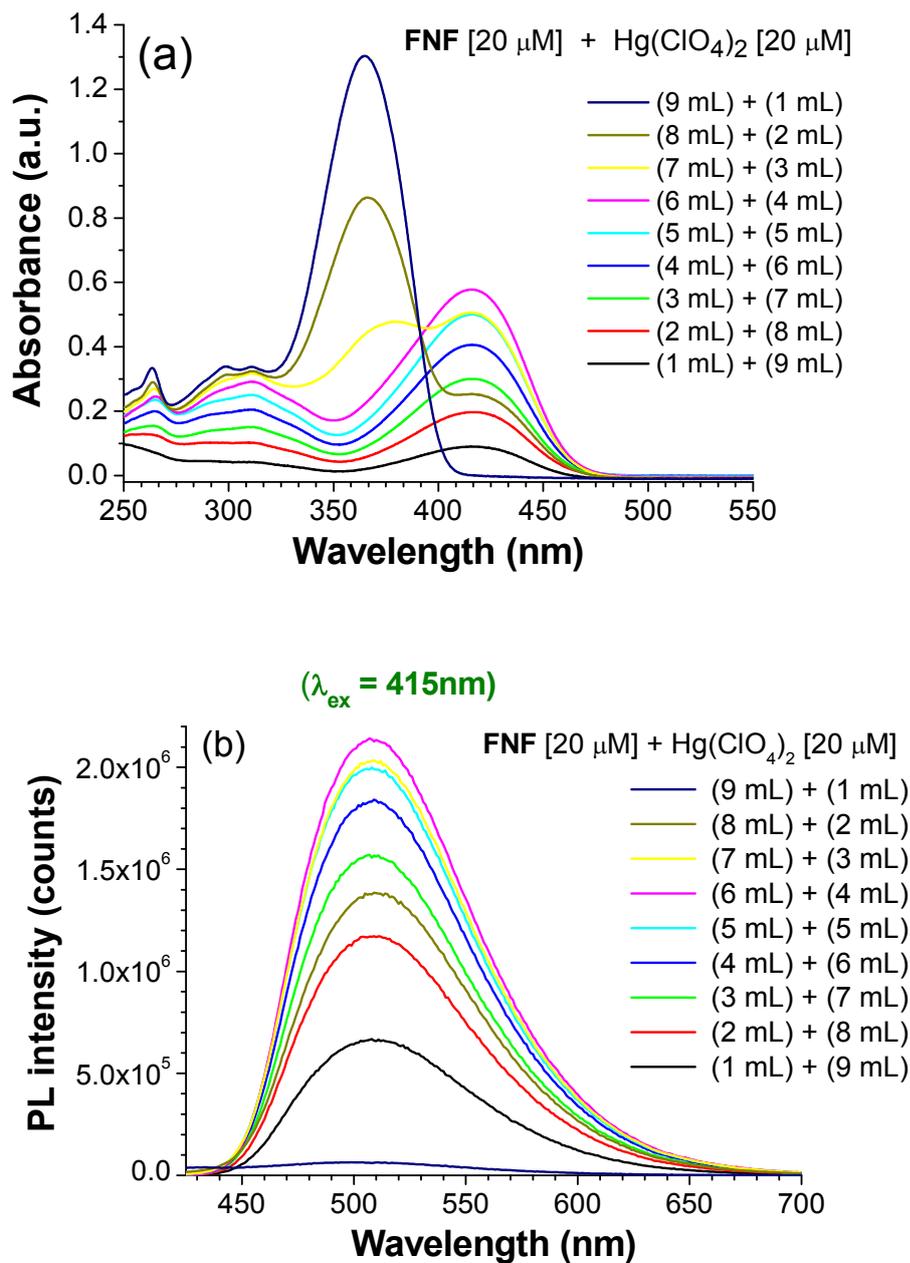


Figure S10. (a) UV-Vis absorption and (b) emission spectra of mixtures of equal concentrations (20 μ M each) of FNF and Hg(ClO₄)₂ in different ratios (in THF) keeping the total volume of the solution

$V_{\text{FNF}} + V_{\text{Hg(ClO}_4)_2} = 10 \text{ mL}$; $\lambda_{\text{ex}} = 415 \text{ nm}$.

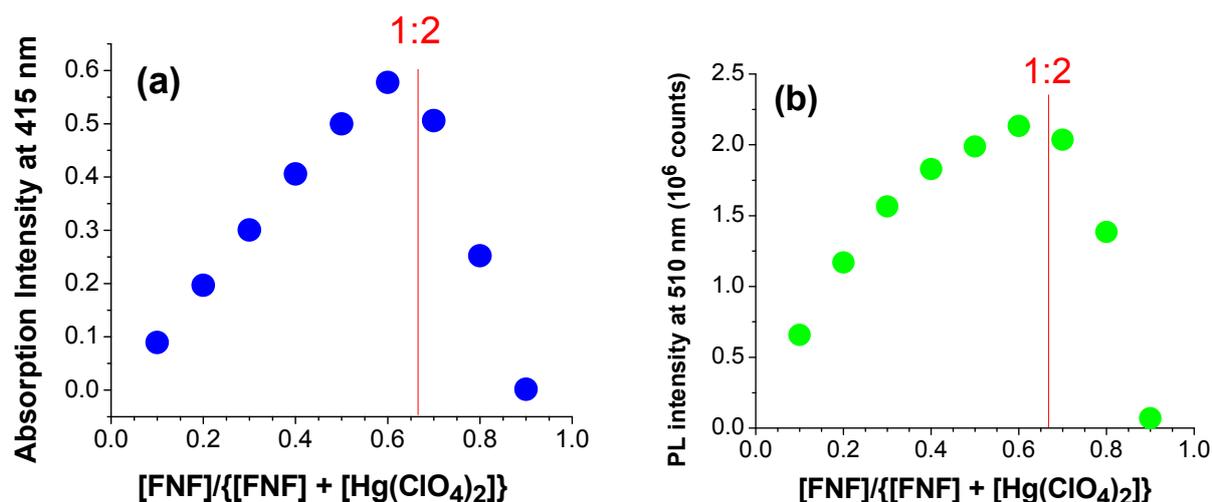


Figure S11. Job's plots for the mixtures of **FNF** (20 μ M) and $Hg(ClO_4)_2$ (20 μ M) at different ratios in THF: (a) absorption intensities at 415 nm; (b) PL intensities at 510 nm ($\lambda_{ex} = 415$ nm). The values have been taken from the data in Figure S5a,b.

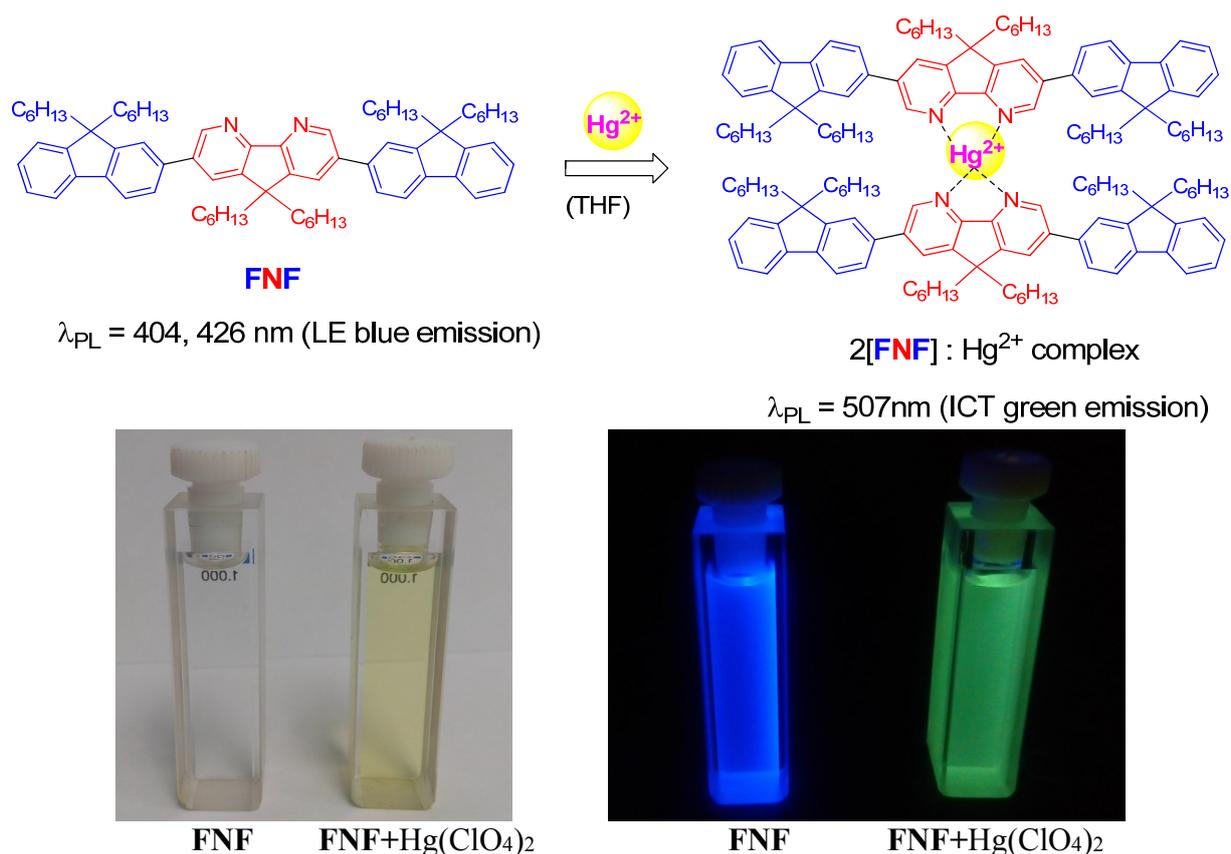


Figure S12. (Top) The reaction scheme of 2[FNF]: Hg^{2+} complex formation. (Bottom) The photographs show changes of the color of **FNF** solution in THF upon addition of $Hg(ClO_4)_2$: (left) under day light illumination [from colorless to light yellow] and (right) under 365 nm UV-lamp irradiation [from deep blue to green fluorescence].

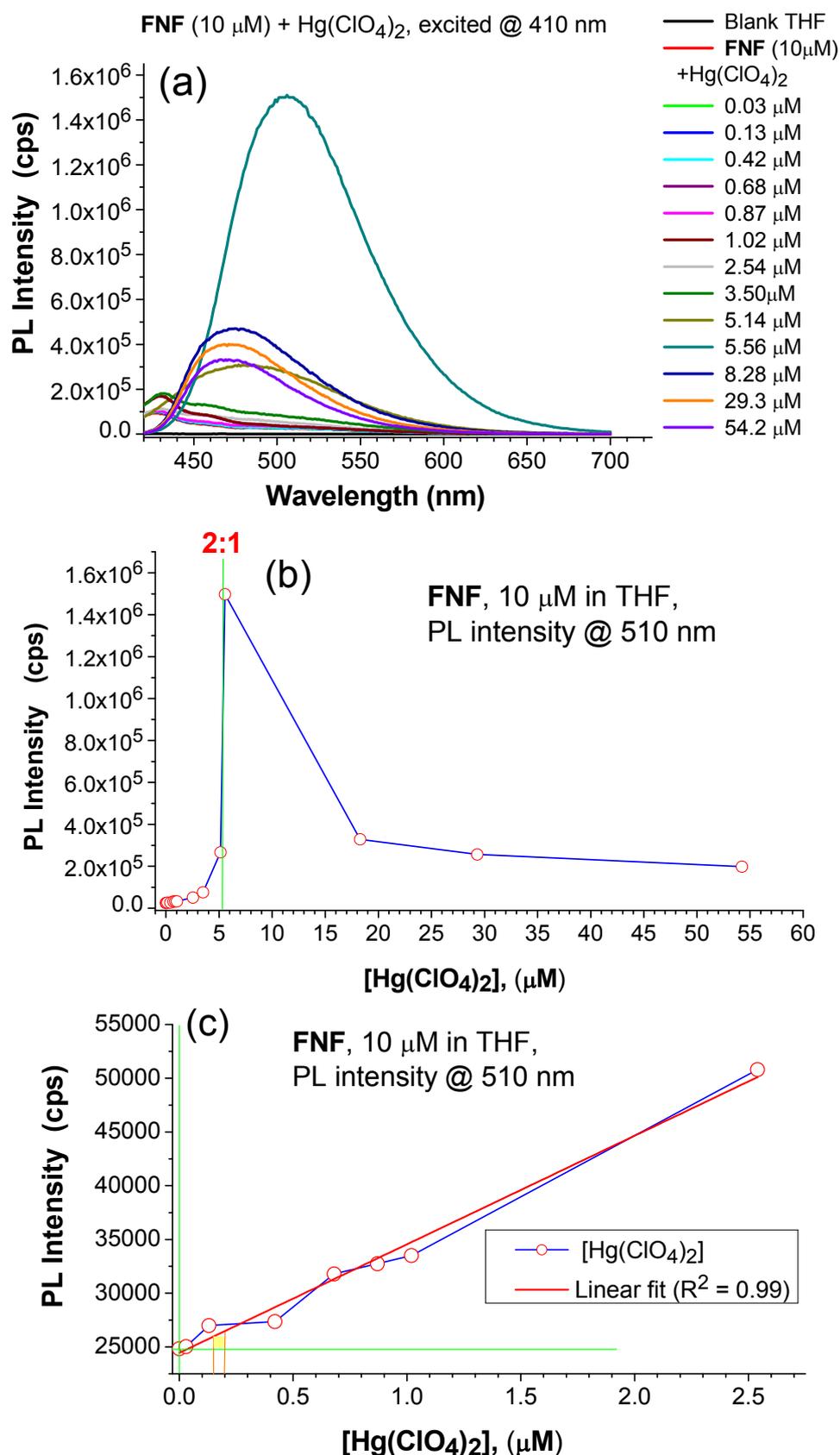


Figure S13 (a) Changes in the photoluminescence spectra of **FNF** (10 μM) on titration with $\text{Hg}(\text{ClO}_4)_2$ (0 - 54.2 μM) in THF (excited at 410 nm). (b) PL intensity measured at 510 nm versus concentration of $\text{Hg}(\text{ClO}_4)_2$ (0-54.25 μM), (PL_{max} is observed at [**FNF**]:[$\text{Hg}(\text{ClO}_4)_2$] \sim 2:1). (c) Linear dependence of the intensity of PL measured at 510 nm versus [$\text{Hg}(\text{ClO}_4)_2$] at low concentrations of 0 - 2.54 μM .

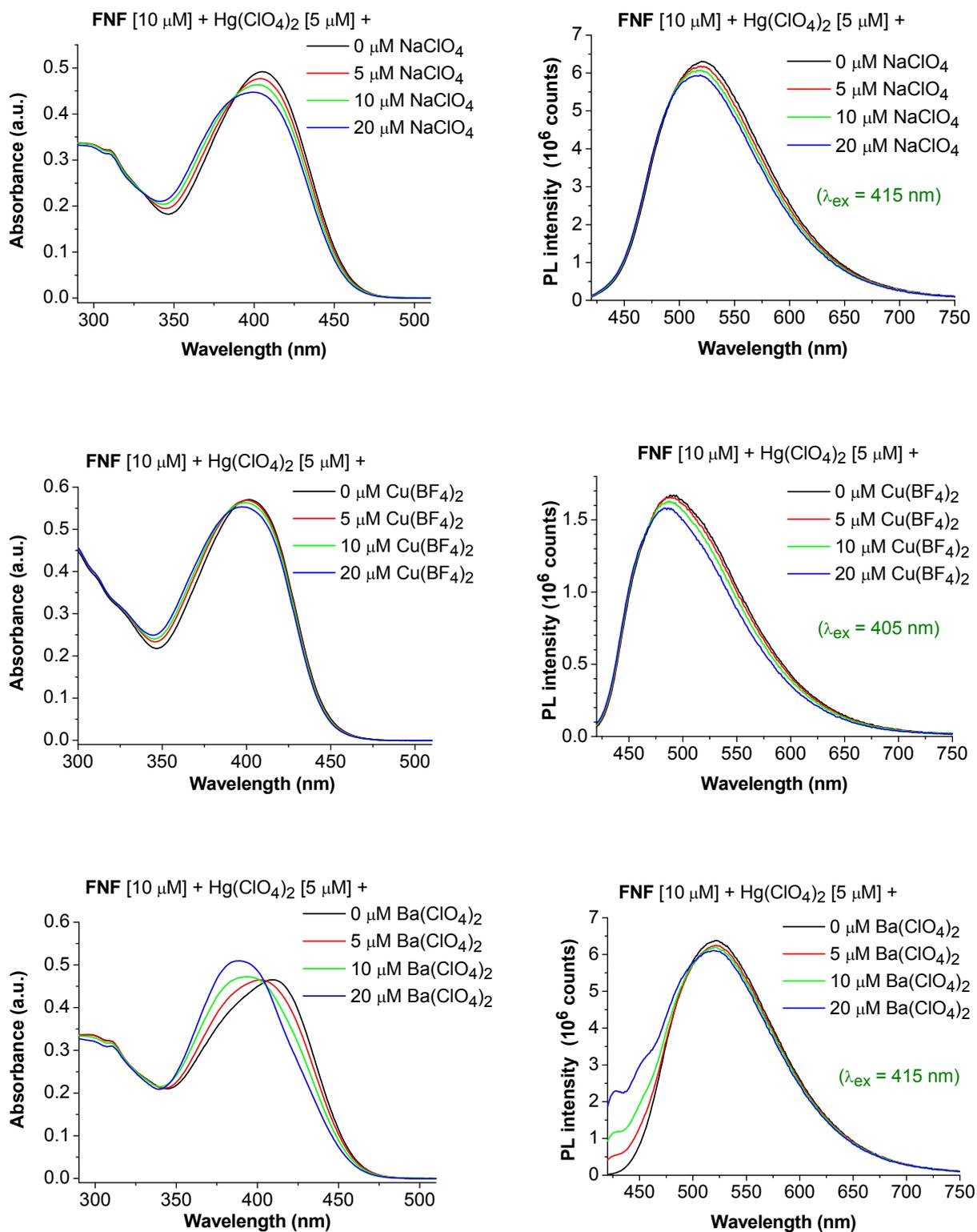


Figure S14 Absorption and photoluminescence spectra of THF solutions of **FNF** [$\sim 10 \mu\text{M}$] and $\text{Hg}(\text{ClO}_4)_2$ [$\sim 5 \mu\text{M}$]} in presence of NaClO_4 , $\text{Cu}(\text{BF}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ salts to show the interference of Hg^{2+} detection by other cations (Na^+ , Cu^{2+} and Ba^{2+}).

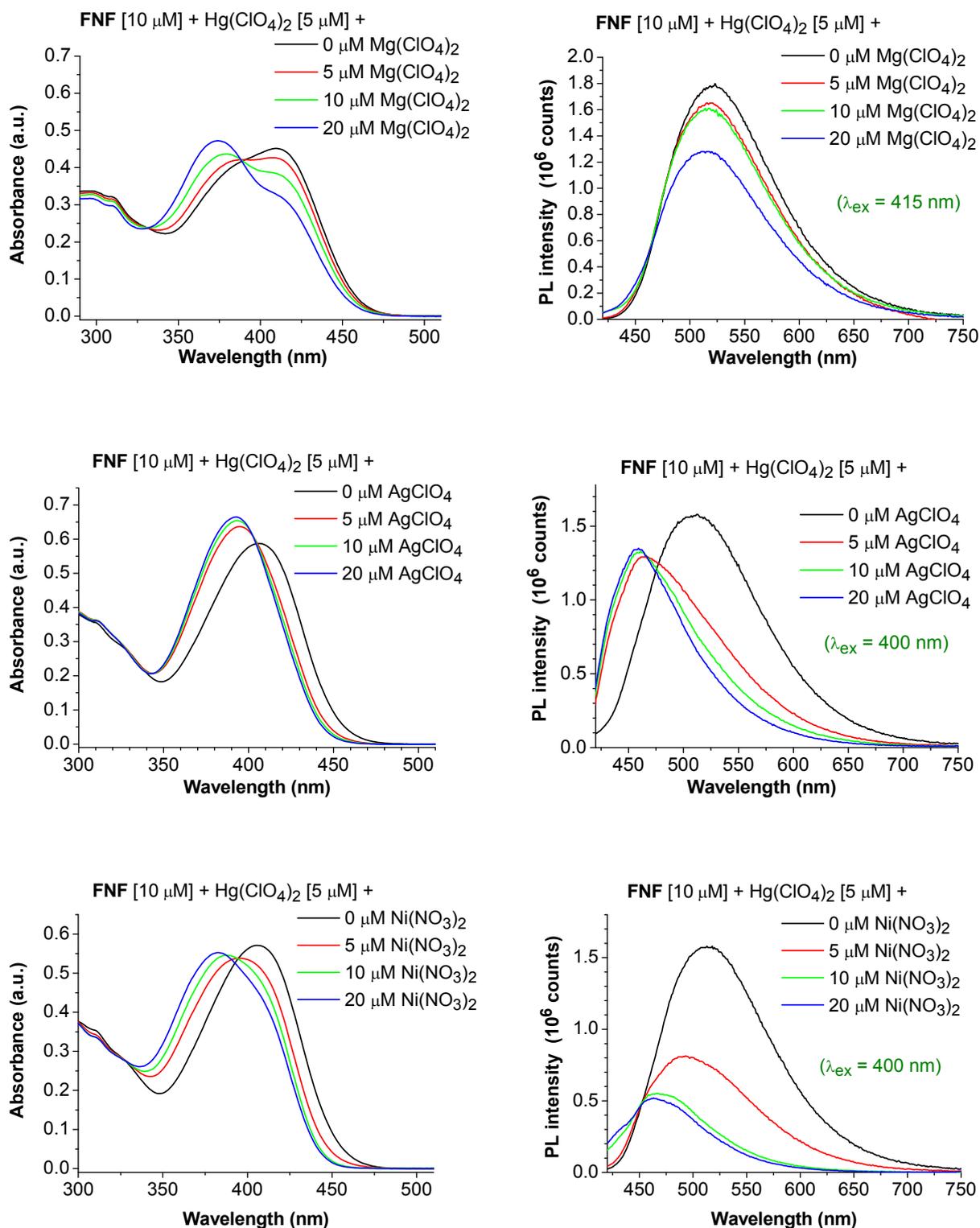
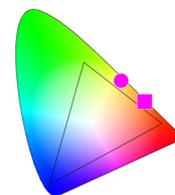
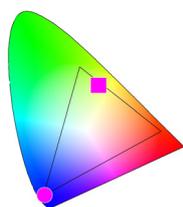
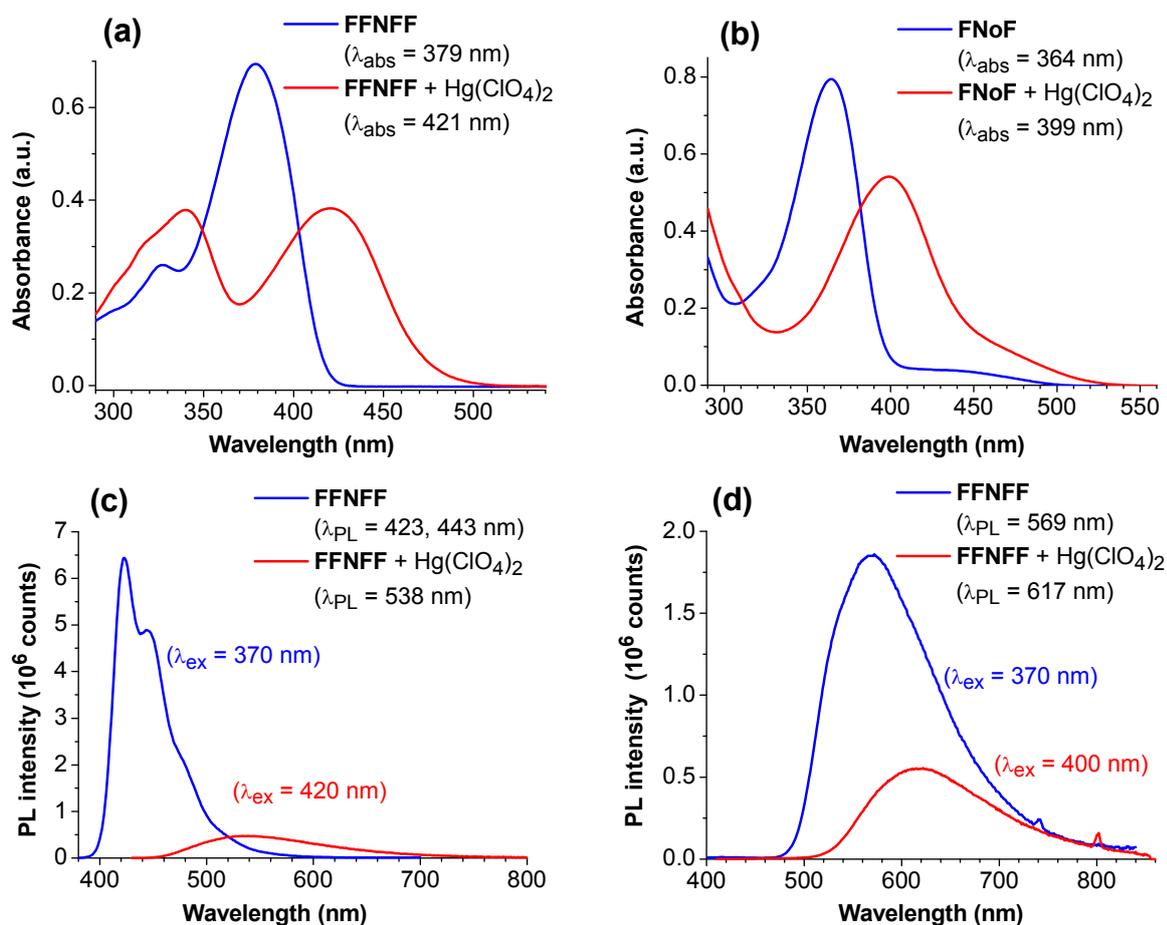


Figure S15 Absorption and photoluminescence spectra of THF solutions of **FNF** [$\sim 10 \mu\text{M}$] and $\text{Hg}(\text{ClO}_4)_2$ [$\sim 5 \mu\text{M}$] in presence of $\text{Mg}(\text{ClO}_4)_2$, AgClO_4 and $\text{Ni}(\text{NO}_3)_2$ salts to show the interference of Hg^{2+} detection by other cations (Mg^{2+} , Ag^+ and Ni^{2+}).



(e) FFNFF FFNFF+Hg(ClO₄)₂ **(f)** FNoF FNoF+Hg(ClO₄)₂

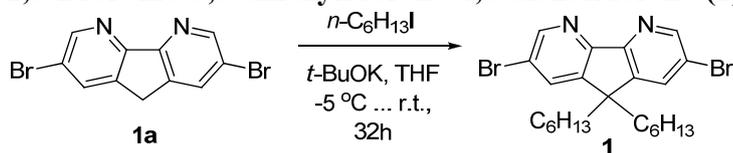
Figure S16 Absorption (a,b) and photoluminescence (c,d) spectra of FFNFF (a,c) FNoF (b,d) in THF in cation-free solutions and in presence of Hg(ClO₄)₂.

The photographs of FFNFF (e) and FNoF (f) solutions in THF under 365 nm UV-lamp irradiation before (left photographs) and after (right photographs) addition of Hg(ClO₄)₂. CIE 1931 color space diagrams on the top of the photographs show the changes of the emission colors (calculated from Figures S16c,d) of FFNFF and FNoF (circles) upon addition of Hg(ClO₄)₂ (squares).

Synthesis

Synthesis of intermediate compounds 1 – 8. 9,9-Dihexylfluorene-2-yl boronic acid **2**,⁸ 2,7-dibromo-4,5-diazafluorene-9-one **3**,⁹ compounds **4**,⁸ **5**,⁸ and **7**⁸ were obtained as described previously. Synthesis of compound **6** and **8** was performed similar to literature procedure¹⁰ with slight modification described below.

2,7-Dibromo-9,9-dihexylfluorene-4,5-diazafluorene (**1**)



Under nitrogen, to a stirred solution of 2,7-dibromo-4,5-diazafluorene (**1a**) (1.00 g, 3.06 mmol) in dry THF (20 mL), *n*-iodohexane (0.95 mL, 6.44 mmol) was added at -5 °C. After that, a solution of potassium *tert*-butoxide (720 mg, 6.44 mmol) in dry THF (15 mL) was added over a period of 50 min keeping the temperature at -5 °C. The reaction mixture was allowed to warm up slowly to room temperature and stirred at room temperature for 32 hours. The solvent was removed on rotary evaporator and the residue was purified by column chromatography on silica gel (column size = 2 × 20 cm) eluting with isooctane:ethyl acetate(EA) = 10:1, v/v to afford the crude product (1.21 g) as a yellow solid. The crude product was further purified by recrystallization from a mixture of isopropanol:water, 5:1 (25 mL) to yield compound **1** (1.04g, 69%) as a light yellow solid.

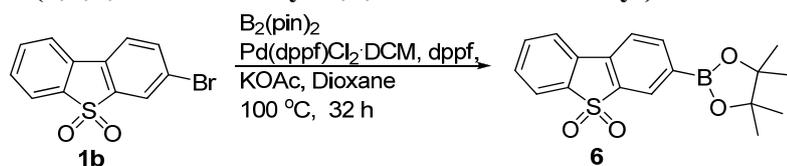
¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.75 (2H, d, *J* = 2.0 Hz), 7.84 (2H, d, *J* = 2.0 Hz), 2.06–1.87 (4H, m, CH₂C₃H₁₁), 1.22–0.97 (12H, m, C₂H₄(CH₂)₃CH₃), 0.79 (6H, t, *J* = 7.1 Hz, C₅H₁₀CH₃), 0.73–0.60 (4H, m, CH₂CH₂C₄H₉).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 155.93, 150.93, 146.59, 133.50, 120.79, 51.56, 39.01, 31.35, 29.45, 24.01, 22.49, 13.93.

DEPT-135 ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 156.04, 150.93 (CH), 146.59, 133.50 (CH), 120.79, 51.70 (C-9), 39.01 (CH₂C₃H₁₁), 31.35 (C₂H₄CH₂C₃H₇), 29.45(C₃H₆CH₂C₂H₅), 24.01 (CH₂CH₂C₄H₉), 22.49 (C₄H₈CH₂CH₃), 13.93 (C₅H₁₀CH₃).

MS (ESI⁺) *m/z*: 491.97 ([M+H]⁺, 50%, ⁷⁹Br/ ⁷⁹Br), 494.00 ([M+H]⁺, 100%, ⁷⁹Br/ ⁸¹Br), 495.92 ([M+H]⁺, 51%, ⁸¹Br, ⁸¹Br). Calcd. for C₂₃H₃₀Br₂N₂: 492.08.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophenes-*S,S*-dioxide (**6**)



Under argon, a two-necked flask (100 mL) was charged with 3-bromodibenzothiophene-*S,S*-dioxide (**1b**) (1.01 g, 3.39 mmol), bis(pinacolato)diboron (1.29 g, 5.08 mmol), anhydrous KOAc (1.25 g, 12.73 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (70 mg, 0.13 mmol) and dry dioxane (50 mL). The mixture was degassed by bubbling with argon for 15 minutes before Pd(dppf)Cl₂·DCM (104 mg, 3 mol%) was added and the mixture was degassed for another 15 minutes. The mixture was heated at 100 °C for 32 hours under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was diluted with water (50 mL). The aqueous solution was then extracted with DCM (2 × 50 mL), washed with water (2 × 20 mL) and dried over anhydrous MgSO₄. The DCM solution (dark color) was then passed through a short silica gel bed eluting with DCM (100 mL) to give a clear solution which was concentrated to afford the product **6** as an off white solid (1.05 g, 91%). According to ¹H NMR, the purity of the sample is >80%, with the main other component being the unreacted excess of bis(pinacolato)diboron. The product was used in the next reaction step without further purification.

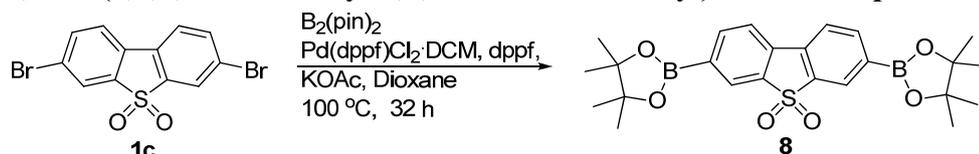
¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.28 (1 H, s), 8.05 (1 H, dd, *J* = 7.7, 0.7 Hz), 7.80 (3 H, m), 7.64 (1 H, td, *J* = 7.7, 1.0 Hz), 7.54 (1H, td, *J* = 7.6, 0.8 Hz), 1.36 (12 H, s).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 140.12, 138.10, 137.13, 133.81, 133.80, 132.03(br.), 131.54, 130.75, 128.34, 122.16, 121.93, 120.75, 84.56, 24.87.

DEPT-135 ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 140.12(CH), 138.10, 137.13, 133.81(CH), 131.54, 130.75(CH), 128.35(CH), 122.17(CH), 121.93(CH), 120.75(CH), 83.50, 24.87(CH₃).

MS (EI⁺) *m/z*: 341.99 ([M]⁺, 100%). Calcd. for C₁₈H₁₉BO₄S: 342.11.

3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-*S,S*-dioxide (8)



Under nitrogen, a two-necked flask (100 mL) was charged with 3,8-dibromodibenzothiophene-*S,S*-dioxide (**1c**)⁸ (1.01 g, 2.70 mmol), bis(pinacolato)diboron (1.49 g, 5.88 mmol), anhydrous KOAc (1.57 g, 15.99 mmol), dppf (89 mg, 0.16 mmol) and dry dioxane (50 mL) and degassed with argon for 15 min. Pd(dppf)Cl₂·DCM (131 mg, 0.16 mmol) was added and the mixture was degassed for another 15 min. The mixture was heated at 100 °C for 32 hours under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was diluted with water (50 mL). The aqueous solution was extracted with DCM (2 × 50 mL), washed with water (2 × 20 mL) and dried with anhydrous MgSO₄. The DCM solution (dark color) was then passed through a short silica gel bed eluting with dichloromethane (100 mL) to give a clear solution which was concentrated to afford the product **8** as an off white solid (1.01 g, 85%).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.28 (1H, s), 8.05 (1H, d, *J* = 8.1 Hz), 7.80 (1H, d, *J* = 7.7 Hz), 1.36 (12H, s).

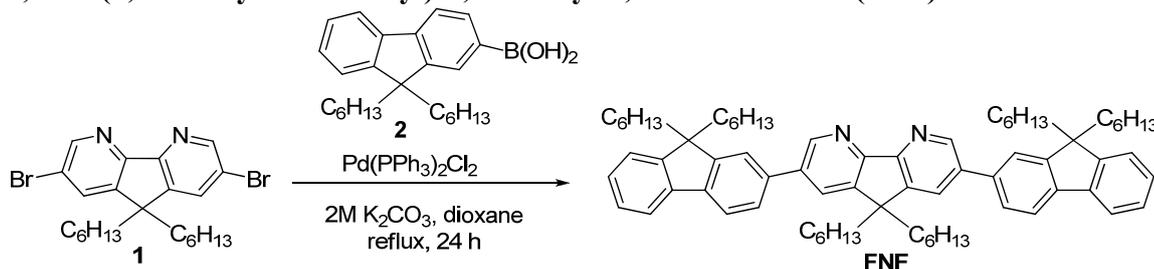
¹³C NMR (101 MHz, CDCl₃): δ (ppm) 140.05 (CH), 137.50, 133.73, 132.37 (br.), 128.33 (CH), 121.09 (CH), 84.56, 24.87 (CH₃).

DEPT-135 ¹³C NMR (101 MHz, CDCl₃): δ (ppm) (101 MHz, CDCl₃) 140.05 (CH), 137.49, 133.73, 128.33 (CH), 121.09 (CH), 84.56, 24.87 (CH₃).

MS (EI⁺) *m/z*: 468.12 ([M]⁺, 100%). Calcd. for C₂₄H₃₀B₂O₆S: 468.19.

Synthesis of the oligomers. General procedure of Pd-catalyzed C–C coupling in the synthesis of conjugated oligomers: under inert atmosphere, flame heated three-neck flask fitted with argon (or nitrogen inlet) was charged with aryl boronic acid (or ester), arylbromide, base and degassed solvents. The mixture was degassed with argon for 15 minutes before adding Pd catalyst and degassed again for another 15–20 minutes. The degassed mixture was stirred under reflux for a required time. After cooling, the solvent was removed under reduced pressure on a rotary evaporator. The residue was dissolved in EA/DCM, washed with water, dried over MgSO₄, and evaporated to afford the crude product, which was then purified by flash/column chromatography on silica gel eluting with appropriate solvents.

3,7-Bis(9,9-dihexylfluoren-2-yl)-9,9-dihexyl-4,5-diazafluorene (FNF)



Under nitrogen, to a mixture of 2,7-dibromo-9,9-dihexyl-4,5-diazafluorene (**1**) (245 mg, 0.49 mmol), 9,9-dihexylfluorene-2-boronic acid (**2**)⁸ (382 mg, 1.01 mmol) and Pd(PPh₃)₂Cl₂ (7 mg, 2 mol%), degassed 2M aqueous K₂CO₃ (4 mL, 8 mmol) and 1,4-dioxane (10 mL) were added via syringe. The mixture was stirred under nitrogen with heating at 110 °C (oil bath) for 24 hours with protection from the sunlight. The mixture was cooled down to room temperature and the resulting slurry was poured into 5% NaCl aqueous solution (50 mL). The precipitate was collected by filtration, washed with water (3 × 20 mL), dried *in vacuo* to afford the crude product (448 mg, 88%) as a brown solid. The crude product was purified by column chromatography on silica gel, eluting first with PE to remove byproducts and then with PE:EA mixture, with gradual increase of EA contents from 2% to 6%, to yield product **FNF** (353 mg, 70.5%) as a light yellow solid.

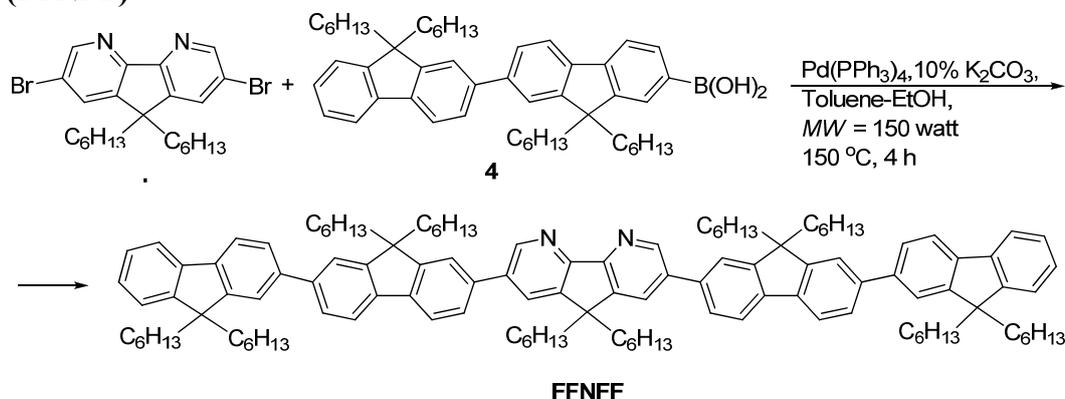
¹H NMR (500 MHz, CDCl₃): δ (ppm) 9.01 (2H, d, *J* = 1.9 Hz), 7.93 (2H, d, *J* = 2.0 Hz), 7.83 (2H, d, *J* = 7.8 Hz), 7.78–7.76 (2H, m), 7.67–7.63 (4H, m), 7.40–7.34 (6H, m), 2.16–2.12 (4H, m), 2.08–2.03 (8H, m), 1.24–1.01 (36H, m), 0.89–0.82 (4H, m) 0.81–0.64 (26H, m).

¹³C NMR (100 MHz, CDCl₃): δ (ppm) 151.92, 151.07, 148.38 (CH), 145.72, 141.47 (× 2), 140.37 (× 2), 136.78, 128.93 (CH), 127.45 (CH), 126.91 (CH), 126.32 (CH), 123.01 (CH), 121.53 (CH), 120.26 (CH), 119.96 (CH), 55.33, 51.63, 40.29, 39.23, 31.44, 31.35, 29.62, 29.52, 24.13, 23.77, 22.52, 22.45, 13.97, 13.93.

DEPT-135 ¹³C NMR (100MHz, CDCl₃): δ (ppm) 151.87, 151.05, 148.72 (CH), 145.42, 141.32, 140.42, 137.05, 136.52, 128.66 (CH), 127.40 (CH), 126.90 (CH), 126.32 (CH), 123.01 (CH), 121.48 (CH), 120.23 (CH), 119.94 (CH), 55.31 (C-9), 40.30, 39.29, 31.46, 31.39, 29.64, 29.56, 24.13, 23.77, 22.54, 22.48, [14.00, 13.96 (CH₃)].

MS (ESI⁺) *m/z*: 1001.76 ([M + H]⁺, 100%). Calcd. for C₇₃H₉₆N₂: 1000.76.

9,9-Dihexyl-2,7-bis(9,9,9',9'-tetrahexyl-9H,9'H-[2,2'-bifluoren]-7-yl)-9H-4,5-diazafluorene (FFNFF)



Under nitrogen, to a 35 mL thick-wall glass microwave reaction tube, 2,7-dibromo-9,9-dihexyl-4,5-diazafluorene (**1**) (10 mg, 0.02 mmol), 9,9,9',9'-tetrahexyl-2,2'-bifluoren-7-ylboronic acid (**4**) (41 mg, 0.057 mmol), Pd(PPh₃)₄ (3 mg, 10 mol%), 10% K₂CO₃ aqueous solution (0.5 mL, 0.4 mmol), ethanol (0.5 mL) and toluene (3 mL) were added. The reaction mixture was degassed for 15 minutes with argon and then irradiated with microwave (150 W) keeping the temperature at 150 °C in a microwave reactor for 4 hours. The reaction mixture was cooled down to room temperature and the solvent was evaporated. The residual slurry was poured into 5% NaCl aqueous solution, the product was extracted with chloroform (2 × 15 mL), the combined organic layers were washed with water until pH = 7, dried over anhydrous MgSO₄ and the solvent was evaporated to afford the crude product (45 mg) as a yellowish solid. The crude product was purified by flash chromatography on silica gel, eluting first with PE, then with gradient increase to PE:EA, 4:1 to yield pure product **FFNFF** (21 mg, 61%) as a light yellow solid.

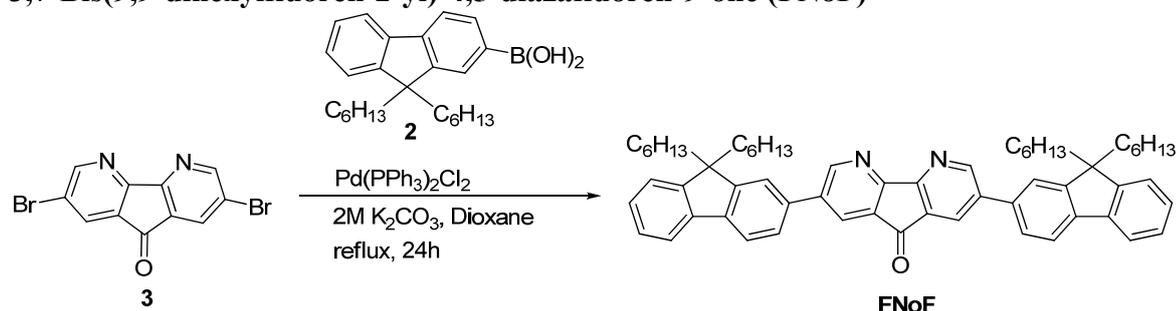
¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.04 (2H, d, *J* = 1.8 Hz), 7.96 (2H, d, *J* = 1.8 Hz), 7.89–7.63 (20H, m), 7.39–7.29 (6H, m), 2.18–1.98 (20H, m), 1.22–1.02 (60H, m), 0.92–0.64 (50H, m).

^{13}C NMR (101 MHz, CDCl_3): δ 157.22, 152.20, 151.84, 151.52, 151.02, 148.73, 145.55, 141.05, 141.01, 140.76, 140.45, 140.37, 139.57, 137.02, 136.55, 128.68, 127.05, 126.81, 126.44, 126.28, 126.07, 122.95, 121.61, 121.59, 121.46, 120.32, 120.20, 119.92, 119.75, 55.48, 55.19, 51.51, 40.38, 40.29, 39.32, 31.48, 31.44, 31.41, 29.70, 29.61, 29.58, 24.16, 23.85, 23.79, 22.57, 22.54, 22.50, 14.02, 13.98.

DEPT-135 ^{13}C NMR (101 MHz, CDCl_3): δ 157.21, 152.20, 151.84, 151.52, 151.02, 148.73 (CH), 145.55, 141.05, 141.01, 140.76, 140.45, 140.37, 139.57, 137.02, 136.55, 128.68 (CH), 127.05 (CH), 126.81 (CH), 126.44 (CH), 126.27 (CH), 126.07 (CH), 122.95 (CH), 121.60 (CH), 121.59 (CH), 121.46 (CH), 120.32 (CH), 120.20 (CH), 119.92 (CH), 119.75 (CH), [55.48, 55.19 (C-9)], 51.51 (CH₂) [40.38, 40.29, 39.32 (CH₂)], [31.48, 31.44, 31.41 (CH₂)], [29.70, 29.61, 29.58 (CH₂)], [24.16, 23.85, 23.79 (CH₂)], [22.57, 22.54, 22.50 (CH₂)], [14.02, 13.98 (CH₃)].

MS (MALDI TOF) m/z : 1666.81 ($[\text{M} + \text{H}]^+$, 100%). Calcd. for $\text{C}_{123}\text{H}_{160}\text{N}_2$: 1665.26.

3,7-Bis(9,9-dihexylfluoren-2-yl)-4,5-diazafluoren-9-one (FNoF)



Under nitrogen, to a three-necked flask containing 2,7-dibromo-4,5-diazafluoren-9-one (**3**) (201 mg, 0.581 mmol), 9,9-dihexylfluoren-2-boronic acid (**2**)⁸ (453 mg, 1.20 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (9 mg, 2 mol%), degassed 2M aqueous K_2CO_3 (4 mL, 8 mmol) and 1,4-dioxane (10 mL) were added via a syringe. The reaction mixture was stirred under reflux (oil bath, 110 °C) for 24 hours under nitrogen, with protection from the sunlight. The reaction mixture was cooled down to room temperature and the resulting slurry was poured into 5% NaCl aqueous solution. The product was extracted with DCM (2 × 25 mL), the combined organic layer was washed with water until pH = 7, dried over anhydrous MgSO_4 , filtered off and the solvent was evaporated to afford the crude product (405 mg, 79%) as a yellow solid. The crude product was purified by flash chromatography on silica gel, eluting first with PE and then with PE:DCM mixture (gradient from 1:1 to 1:4 v/v ratio) to yield pure product FNoF (252 mg, 49%) as a yellow solid.

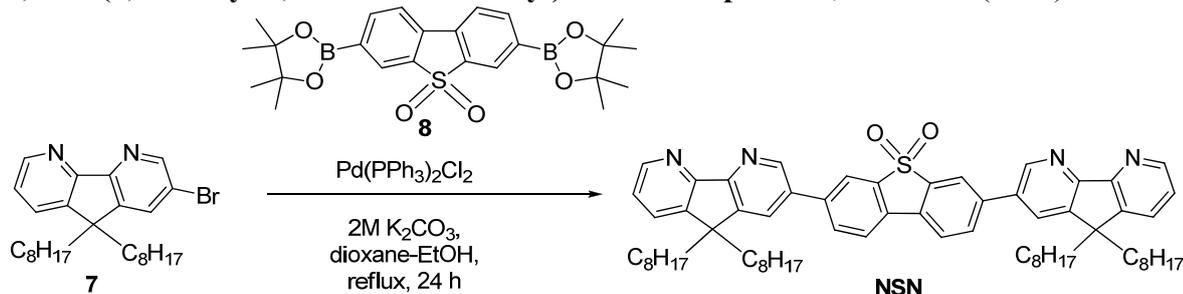
^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.12 (2H, d, $J = 2.1$ Hz), 8.28 (2H, $J = 2.1$ Hz, s), 7.83 (2H, d, $J = 7.9$ Hz), 7.77–7.75 (2H, m), 7.65 (2H, dd, $J = 7.8, 1.5$ Hz), 7.60 (2H, d, $J = 1.2$ Hz), 7.40–7.36 (6H, m), 2.06–2.02 (8H, m, $\text{CH}_2\text{C}_5\text{H}_{11}$), 1.13–1.02 (24H, m, $\text{C}_2\text{H}_4(\text{CH}_2)_3\text{CH}_3$), 0.77 (12H, t, $J = 6.8$ Hz, CH_3), 0.70–0.61 (8H, m, $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$).

^{13}C NMR (100MHz, CDCl_3): δ (ppm) 190.18 (CO), 161.71, 153.77 (CH), 152.08, 151.07, 142.18, 140.15, 138.50, 135.23, 130.02, 129.65 (CH), 127.72 (CH), 126.98 (CH), 125.95 (CH), 123.00 (CH), 121.27 (CH), 120.48 (CH), 120.11 (CH), 55.38 (C-9), 40.39, 31.49, 29.66, 23.79, 22.56, 13.99 (CH₃).

DEPT-135 ^{13}C NMR (100MHz, CDCl_3): δ (ppm) 161.73, 153.79 (CH), 152.09, 151.08, 142.18, 140.16, 138.51, 135.25, 130.03, 129.66 (CH), 127.72 (CH), 126.99 (CH), 125.95 (CH), 123.01 (CH), 121.28 (CH), 120.48 (CH), 120.11 (CH), 55.39 (C-9), 40.40 (CH₂), 31.49 (CH₂), 29.67 (CH₂), 23.79 (CH₂), 22.57 (CH₂), 14.00 (CH₃).

MS (ESI⁺) m/z : 847.55 ($[\text{M} + \text{H}]^+$, 100%). Calcd. for $\text{C}_{61}\text{H}_{70}\text{N}_2\text{O}$: 846.55.

3,7-Bis(9,9-dioctyl-4,5-diazafluoren-2-yl)dibenzothiophene-*S,S*-dioxide (NSN)



Under nitrogen, to a three-necked flask containing 2-bromo-9,9-dioctyl-4,5-diazafluorene (**7**) (402 mg, 0.854 mmol), 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-*S,S*-dioxide (**8**) (200 mg, 0.427 mmol), 2M aqueous K₂CO₃ (4 mL, 8 mmol), 1,4-dioxane (20 mL) and ethanol (2 mL) were added. The mixture was degassed with argon for 15 minutes before adding Pd(PPh₃)₂Cl₂ (10 mg, 0.014 mmol, 3 mol%) and then degassed for another 15 minutes. The mixture was stirred under reflux (oil bath, 115 °C) for 24 hours under nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure on a rotavapor. The residue was dissolved in ethyl acetate (100 mL), washed with water (2 × 50 mL), dried over anhydrous MgSO₄, filtered off and evaporated to afford the crude product (788 mg) as a brown oil. The crude product was purified by flash chromatography on silica gel eluting with PE:EA (gradient from 1:1 to 1:9) to afford pure oligomer **NSN** as a yellow solid (152 mg, 59%).

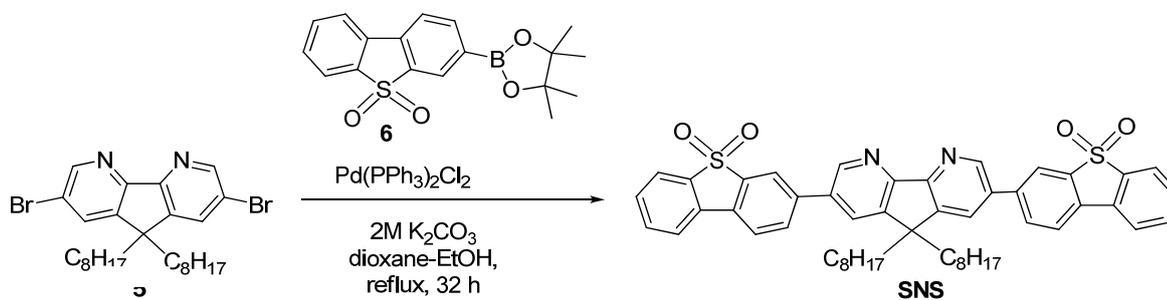
¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.00 (2H, d, *J* = 2.0 Hz), 8.74 (2H, dd, *J* = 4.8, 1.2 Hz), 8.16 (2H, d, *J* = 0.8), 8.05–7.99 (4H, m), 7.95 (2H, d, *J* = 2.0 Hz), 7.76 (2H, dd, *J* = 7.6, 1.2 Hz), 7.33 (2H, dd, *J* = 7.6, 4.8 Hz), 2.10–2.06 (8H, m, CH₂C₇H₁₅), 1.25–0.98 (40H, m, C₂H₄(CH₂)₅CH₃), 0.81 (12H, t, *J* = 7.2 Hz, C₇H₁₄CH₃), 0.72–0.66 (8H, m, CH₂CH₂C₆H₁₃).

¹³C NMR (100MHz, CDCl₃): δ (ppm) 159.01, 157.78, 149.88 (CH), 148.18 (CH), 145.64, 145.55, 141.17, 139.00, 133.65, 132.87 (CH), 130.79, 130.65 (CH), 128.69 (CH), 123.37 (CH), 122.52 (CH), 121.03 (CH), 51.66 (C-9), 39.31 (CH₂), 31.72 (CH₂), 29.90 (CH₂), 29.18 (CH₂), 29.14 (CH₂), 24.16 (CH₂), 22.58 (CH₂), 14.05 (CH₃).

DEPT-135 ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 159.01, 157.82, 149.91 (CH), 148.20 (CH), 145.61, 145.52, 141.19, 138.98, 133.63, 132.86 (CH), 130.76, 130.64 (CH), 128.66 (CH), 123.35 (CH), 122.51 (CH), 121.03 (CH), 51.66 (C-9), 39.35 (CH₂), 31.72 (CH₂), 29.18 (CH₂), 29.14 (CH₂), 24.16 (CH₂), 22.57 (CH₂), 14.05 (CH₃).

MS (ESI⁺) *m/z*: 1020.42 ([M+Na]⁺, 100%). Calcd. for C₆₆H₈₄N₄O₂S: 996.63.

2,7-Bis(dibenzothiophene-*S,S*-dioxide-3-yl)-4,5-diazafluorene (SNS)



A three-necked flask (50 mL) was charged with 2,7-dibromo-9,9-dioctyl-4,5-diazafluorene (**5**) (150 mg, 0.272 mmol), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzothiophene-*S,S*-dioxide (**6**) (373 mg, 1.090 mmol), 2M aqueous K₂CO₃ (4 mL, 8 mmol), dioxane (20 mL) and ethanol (4 mL) and degassed with argon for 15 minutes. Then Pd(PPh₃)₂Cl₂ (6 mg, 0.008 mmol) was added and the mixture was degassed for another 15 minutes. The mixture was stirred under reflux (oil bath, 115 °C) for 32 hours under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with water (15 mL) and then extracted with DCM (2 × 100 mL). The combined DCM layers

were washed with water (2 × 20 mL), dried with anhydrous MgSO₄, filtered off and evaporated on a rotavapor to afford the crude product (580 mg) as a brown oil. The crude product was purified by flash chromatography on silica gel eluting with DCM:MeOH mixture (gradient ratio of 100:1 to 100:2) to afford pure oligomer SNS as an off yellow solid (60 mg, 26%).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.03 (2H, d, *J* = 1.9 Hz), 8.15 (2H, d, *J* = 1.1 Hz), 8.00–7.95 (6H, m), 7.89 (4H, d, *J* = 8.0 Hz), 7.72 (2H, t, *J* = 7.5 Hz), 7.60 (2H, t, *J* = 7.6 Hz), 2.16–2.12 (4H, m, CH₂C₇H₁₅), 1.24–0.98 (20H, m, C₂H₄(CH₂)₅CH₃), 0.79 (6H, t, *J* = 6.0 Hz, C₇H₁₄CH₃), 0.78–0.69 (4H, m, CH₂CH₂C₆H₁₃).

¹³C NMR (100MHz, CDCl₃): δ (ppm) 158.14, 148.50 (CH), 146.13, 140.72, 138.92, 137.92, 134.15, 134.12 (CH), 132.66 (CH), 131.22, 131.18, 130.68 (CH), 128.78 (CH), 122.41(CH), 122.34 (CH), 121.87 (CH), 120.91 (CH), 51.94, 39.39 (CH₂), 31.63 (CH₂), 29.92 (CH₂), 29.19 (CH₂), 29.16 (CH₂), 24.30 (CH₂), 22.57 (CH₂), 14.04 (CH₃).

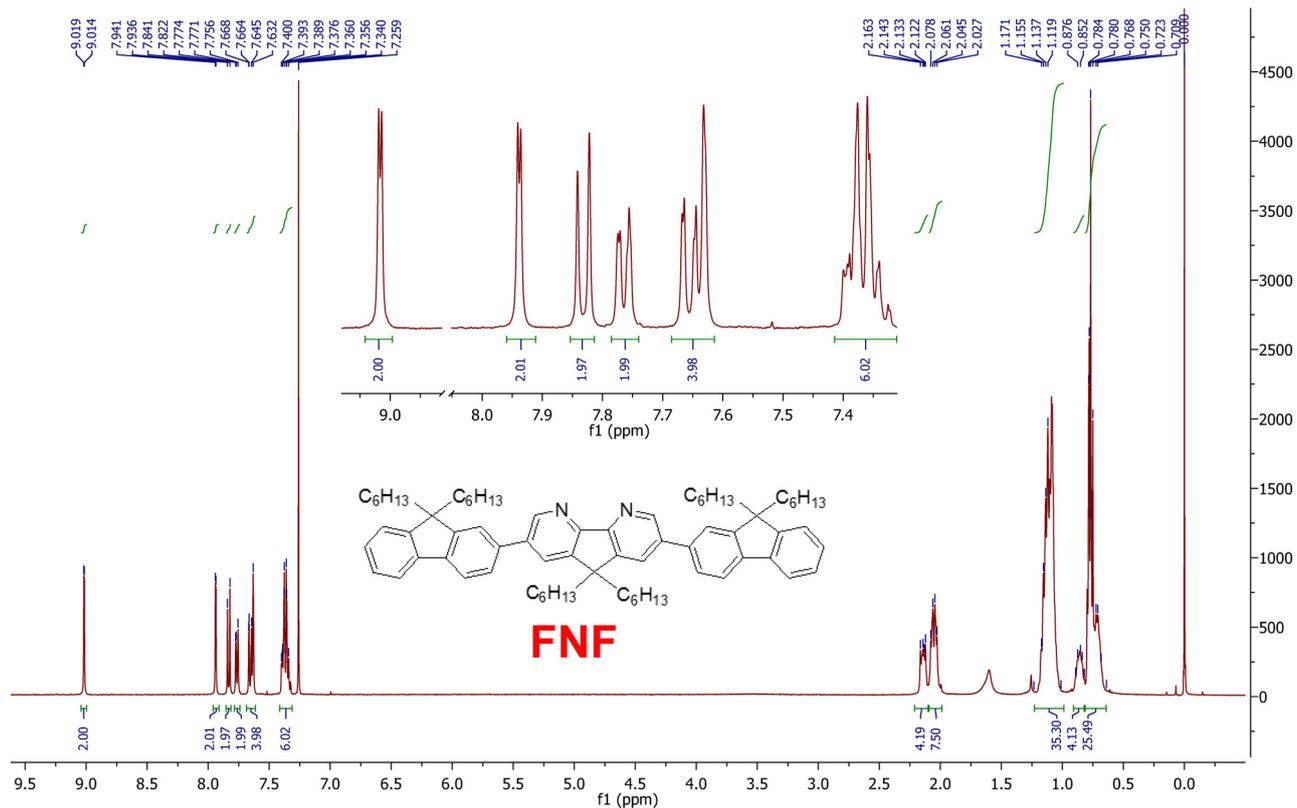
DEPT-135 ¹³C NMR (100MHz, CDCl₃): δ (ppm) 158.14, 148.50 (CH), 146.13, 140.73, 138.92, 137.92, 134.16, 134.12 (CH), 132.70 (CH), 131.19, 130.69 (CH), 128.79 (CH), 122.42 (CH), 122.33 (CH), 121.86 (CH), 120.92 (CH), 51.94, 39.39 (CH₂), 31.70 (CH₂), 29.92 (CH₂), 29.19 (CH₂), 29.17 (CH₂), 24.29 (CH₂), 22.57 (CH₂), 14.04 (CH₃).

MS (ESI⁺) *m/z*: 843.39 ([M+Na]⁺, 100%). Calcd. for C₅₁H₅₂N₂O₄S₂: 820.34.

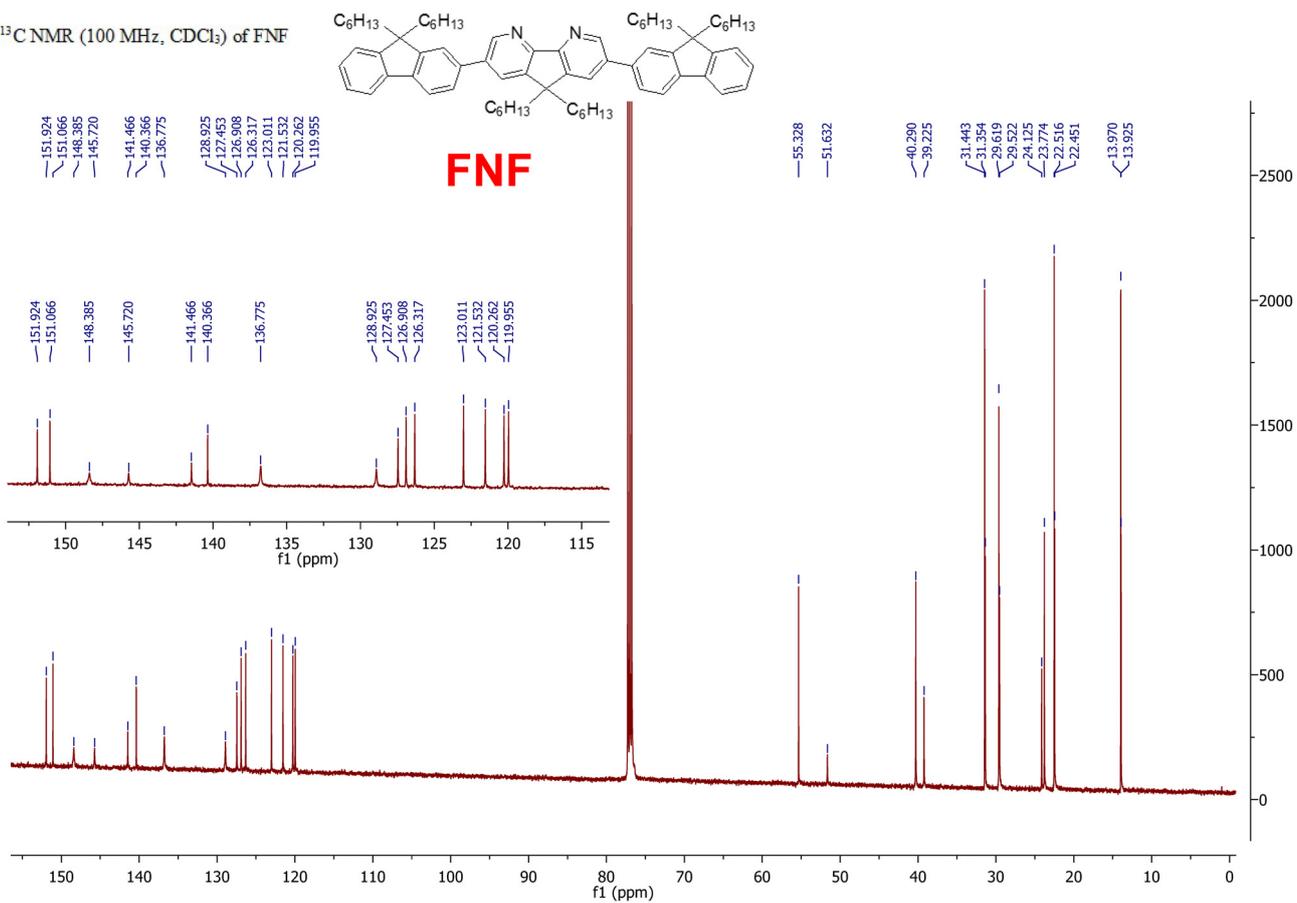
References

- 1 (a) Y. Yang, Q. Pei, and A. J. Heeger, *J. Appl. Phys.*, 1996, **79**, 934; (b) J. Stampfl, S. Tasch, G. Leising, and U. Scherf, *Synth. Met.*, 1995, **71**, 2125–2128.
- 2 S. Hamai and F. Hirayama, *J. Phys. Chem.*, **1983**, *87*, 83–89.
- 3 C. Y. Huang, *Methods in Enzymology*, 1982, **87**, 509–525.
- 4 P. Job, *Annali di Chimica Applicata*, 1928, **9**, 113–203.
- 5 Gaussian 09, Revision A02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 6 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100. (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 7 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- 8 I. I. Perepichka, I. F. Perepichka, M. R. Bryce and L.-O. Pålsson, *Chem. Commun.*, 2005, 3397–3339.
- 9 (a) J. Mlochowski and Z. Szulc, *J. Prakt. Chem.*, 1980, **322**, 971; (b) W.-J. Li, H.-M. Wu, Y.-B. Li, C.-P. Hu, M.-D. Yi, L.-H. Xie, L. Chen, J.-F. Zhao, X.-H. Zhao, N.-E. Shi, Y. Qian, C. Wang, W. Wei, and W. Huang, *Tetrahedron*, 2012, **68**, 8216–8221.
- 10 K. C. Moss, K. N. Bourdakos, V. Bhalla, K. T. Kamatekar, M. R. Bryce, M. A. Fox, H. L. Vaughan, F. B. Dias and A. P. Monkman, *J. Org. Chem.*, 2010, **75**, 6771–6781.

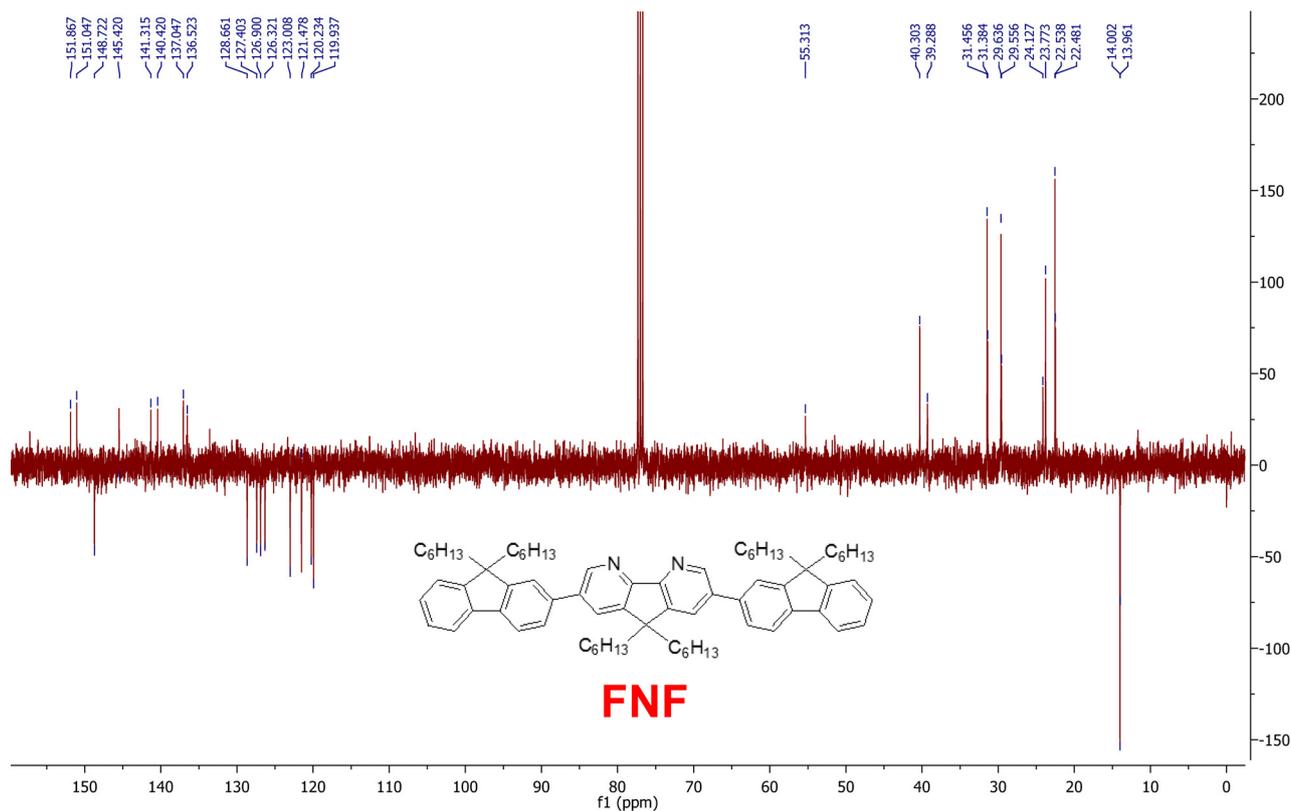
^1H NMR (400 MHz, CDCl_3) of FNF



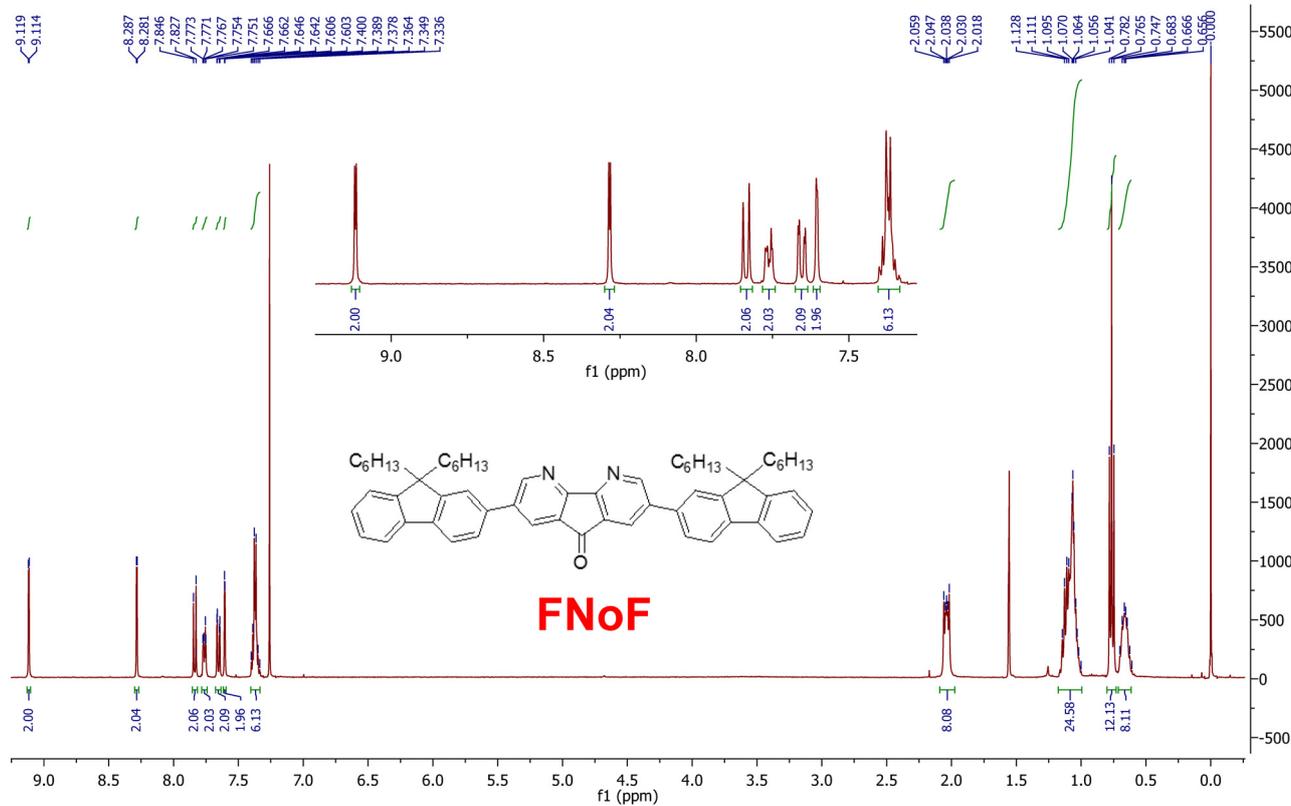
^{13}C NMR (100 MHz, CDCl_3) of FNF



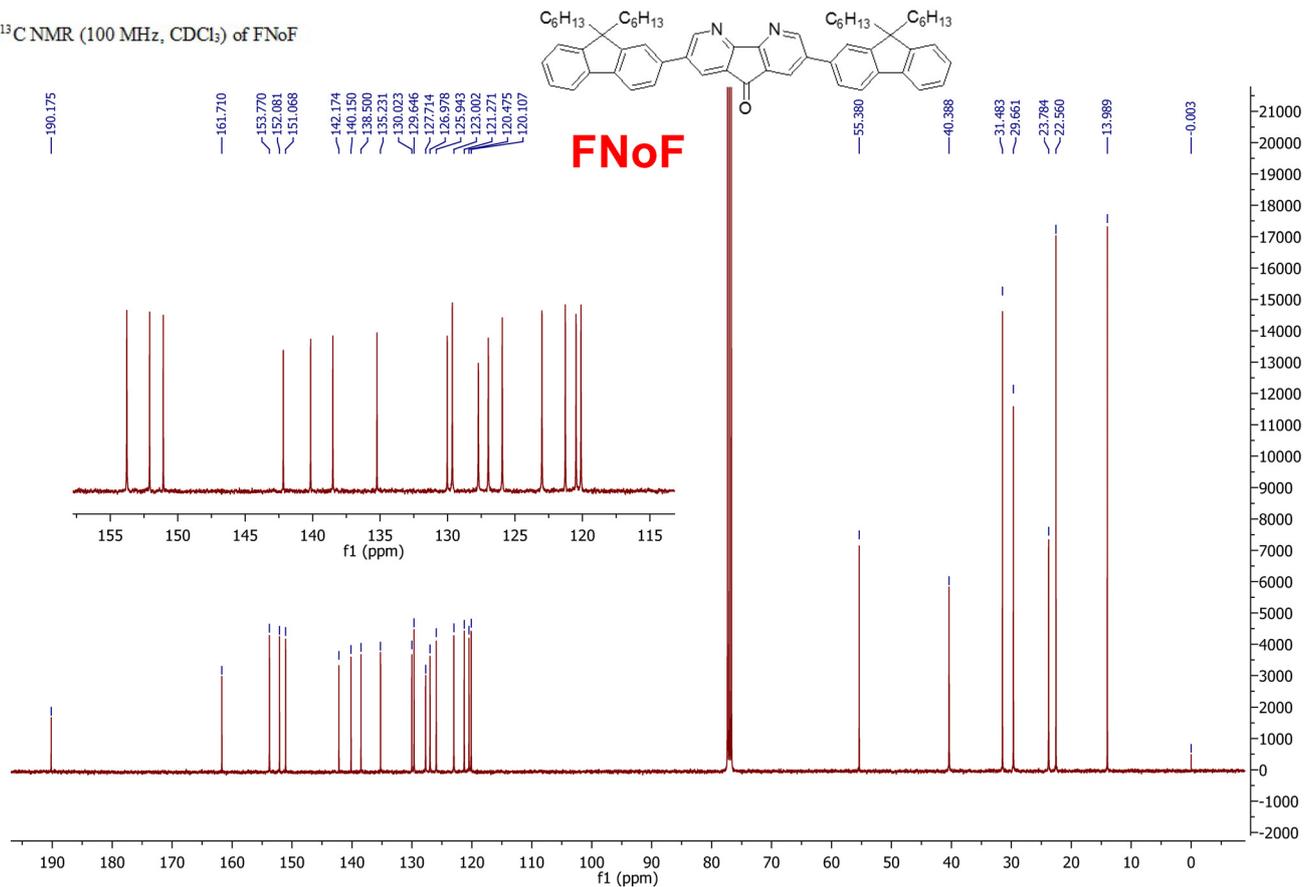
DEPTQ NMR (100MHz, CDCl₃) of FNf



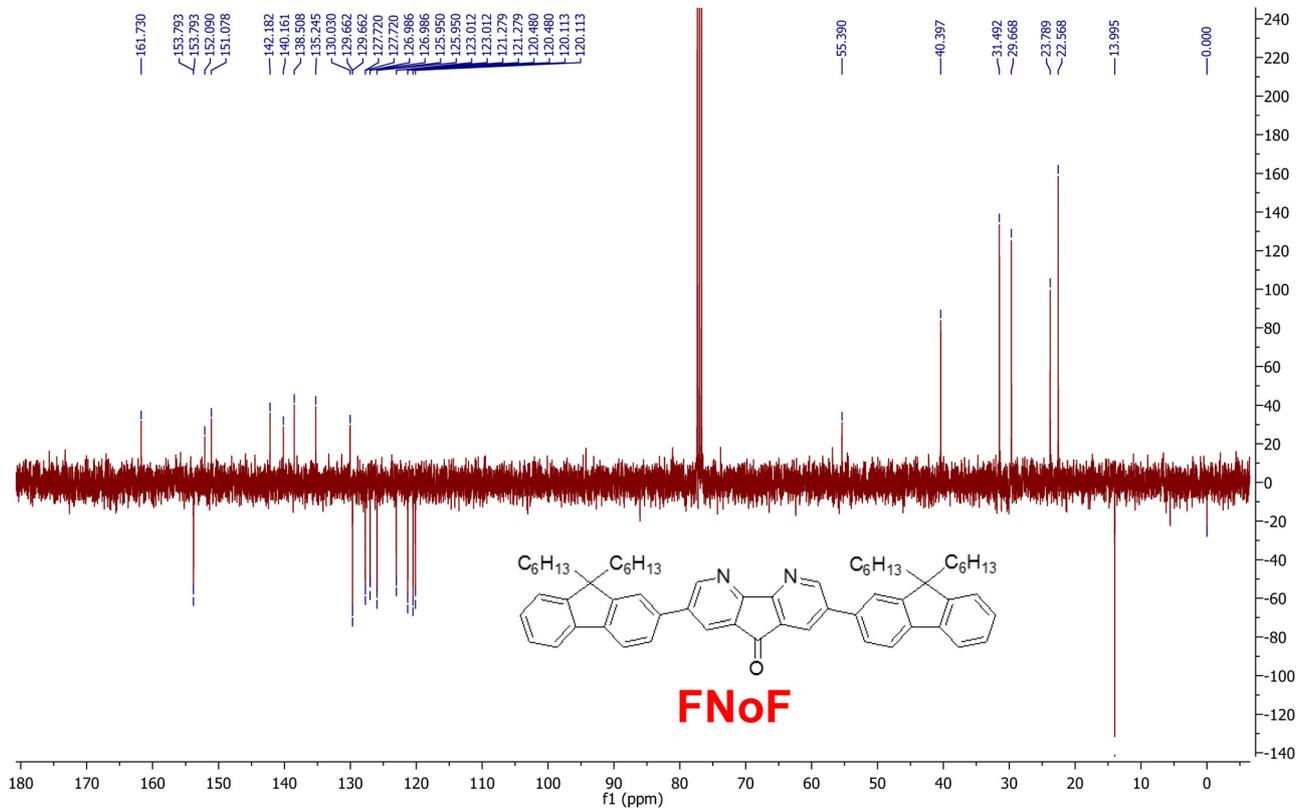
¹H NMR (400 MHz, CDCl₃) of FNof



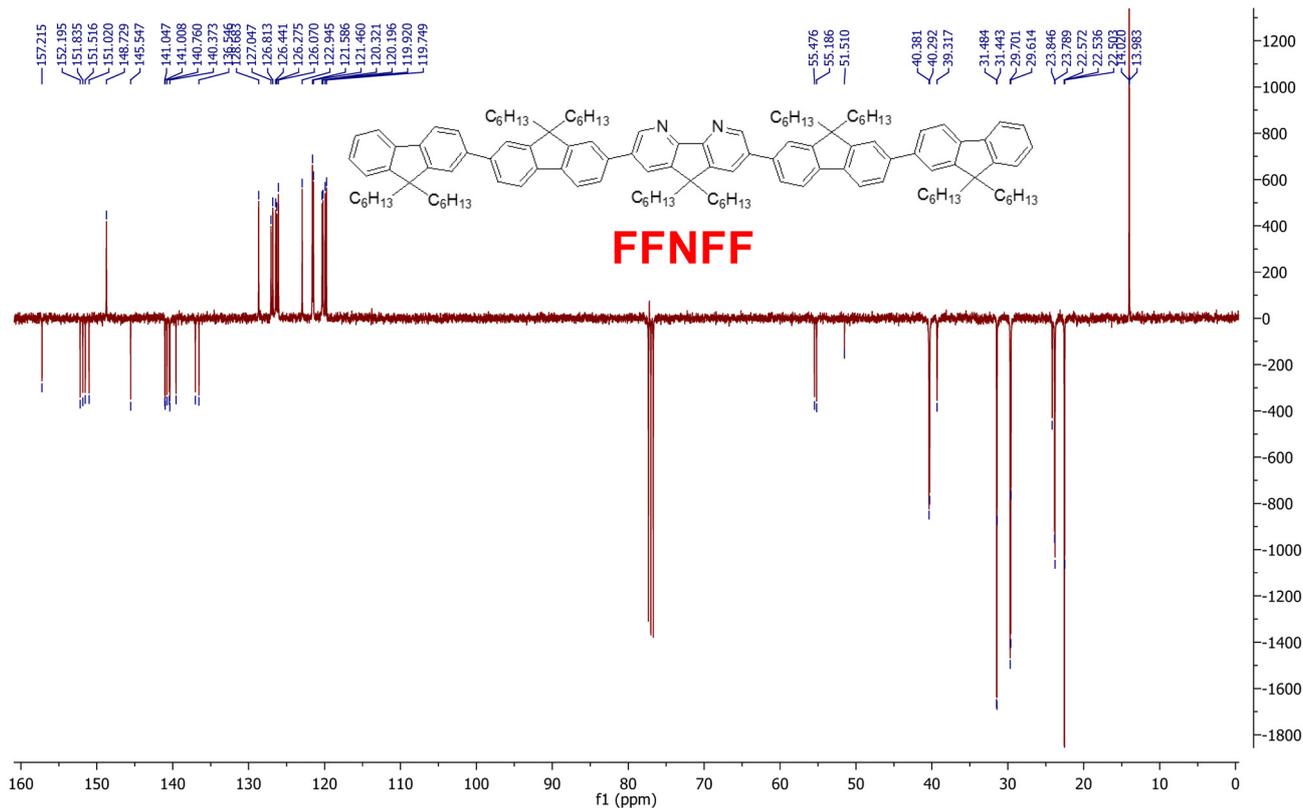
^{13}C NMR (100 MHz, CDCl_3) of FNoF



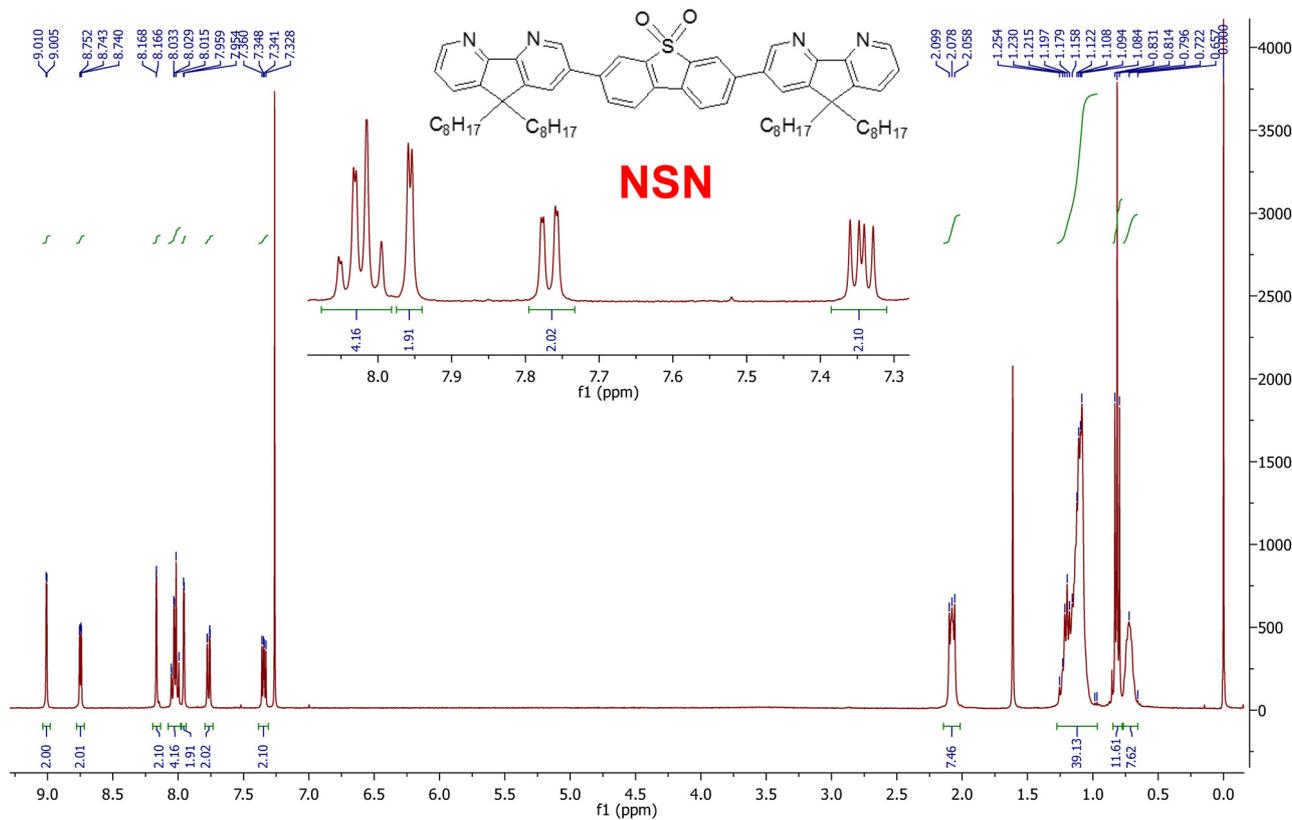
DEPTQ NMR (100MHz, CDCl_3) of FNoF



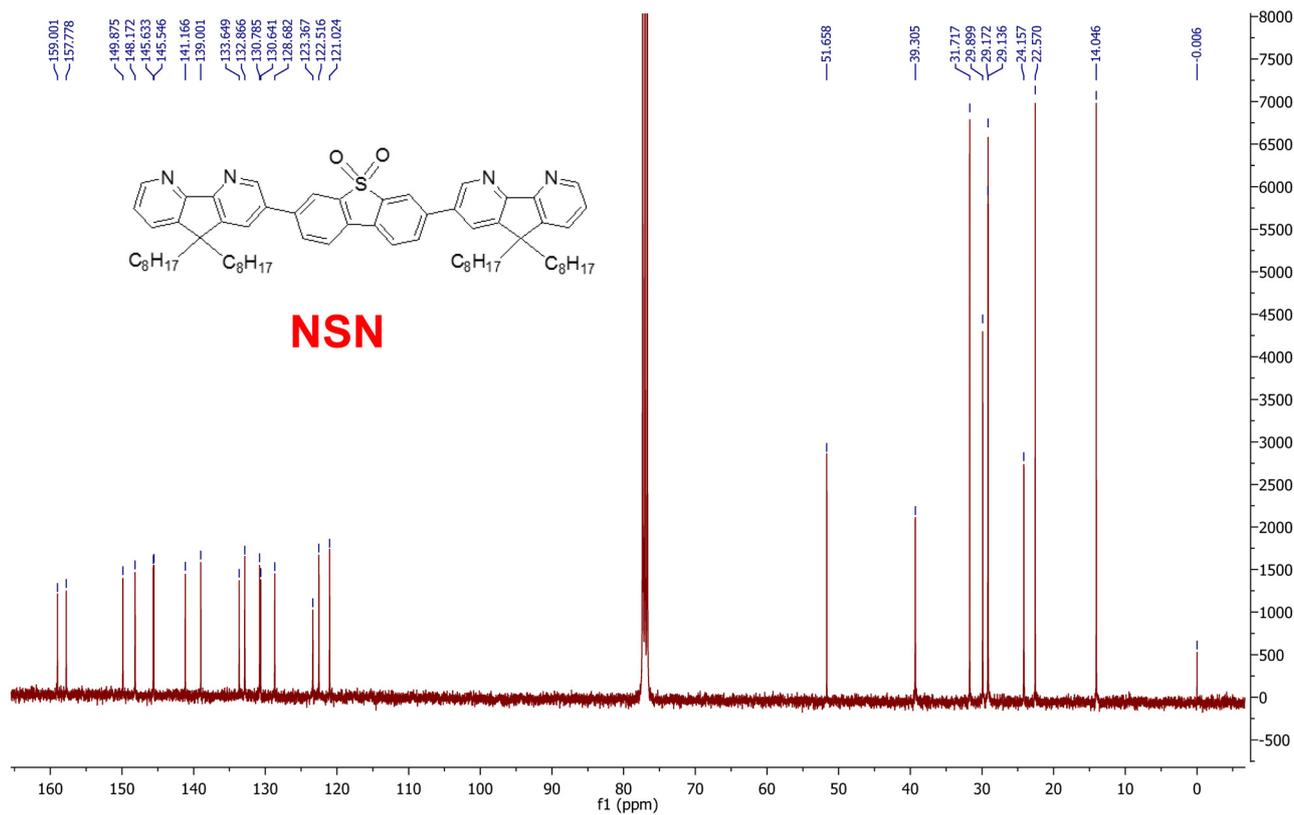
DEPTQ NMR (100MHz, CDCl₃) of FFNFF



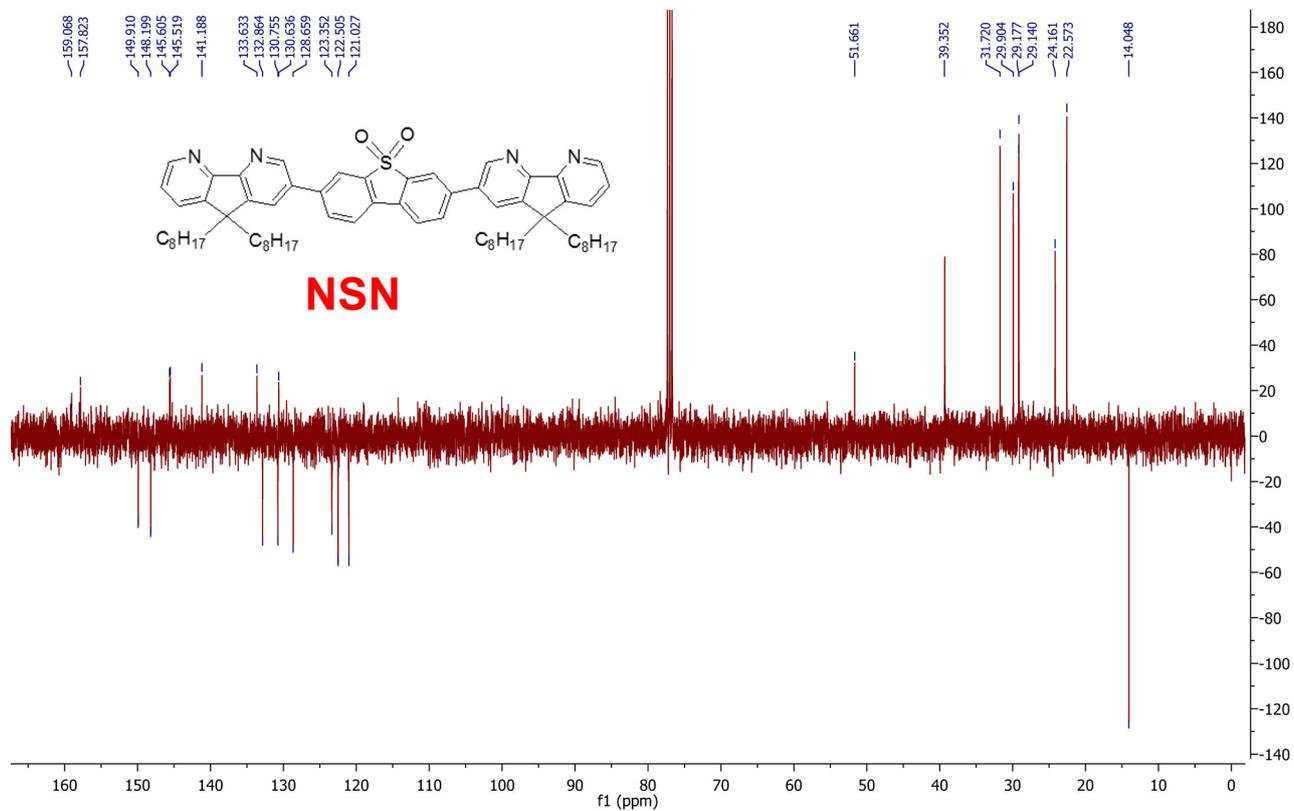
¹H NMR (400 MHz, CDCl₃) of NSN



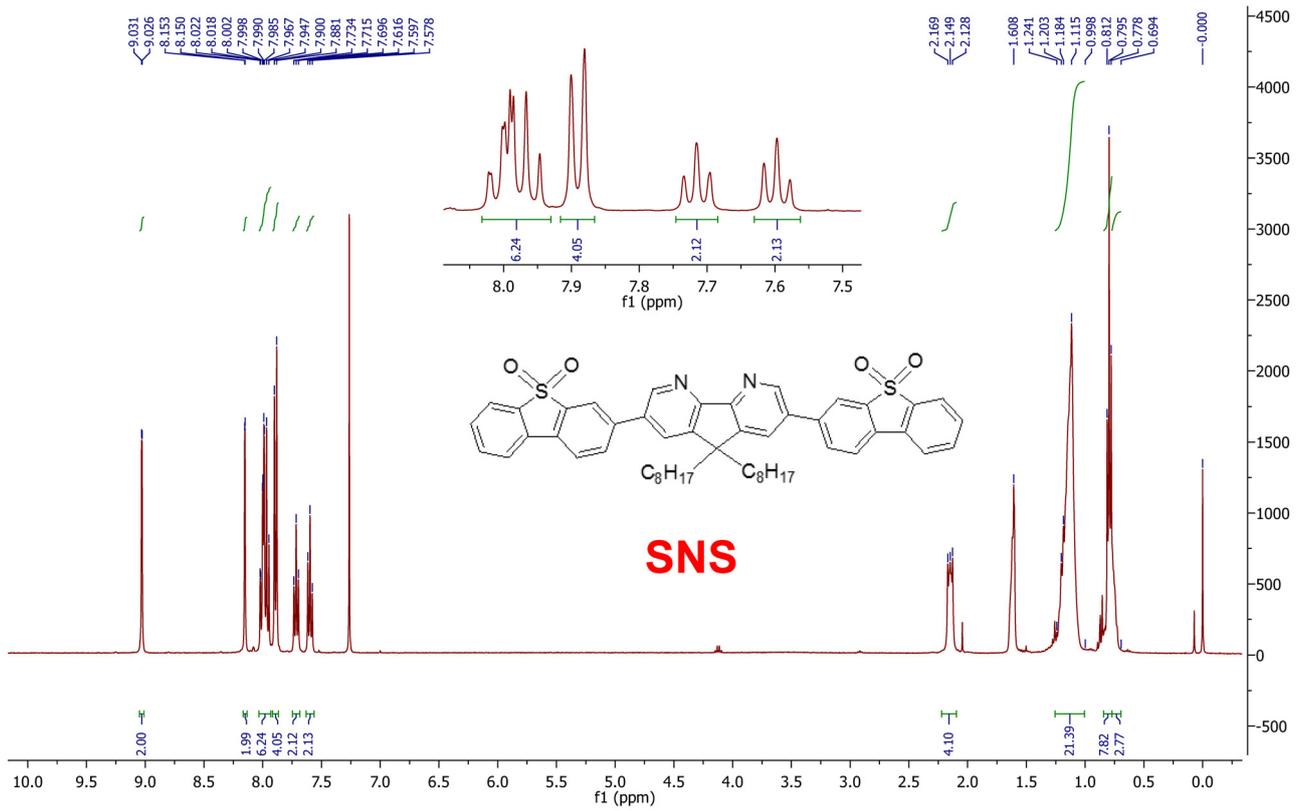
¹³C NMR (101 MHz, CDCl₃) of NSN



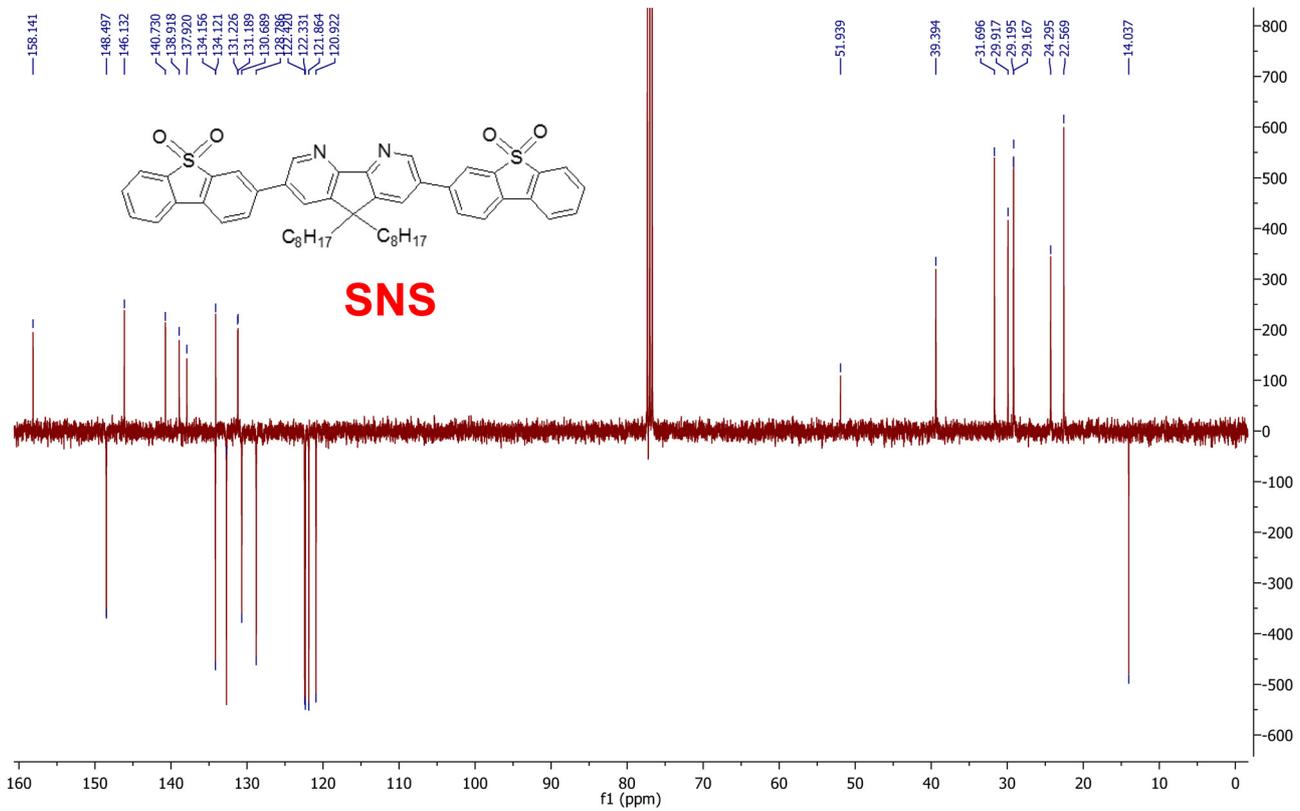
DEPTQ NMR (100MHz, CDCl₃) of NSN



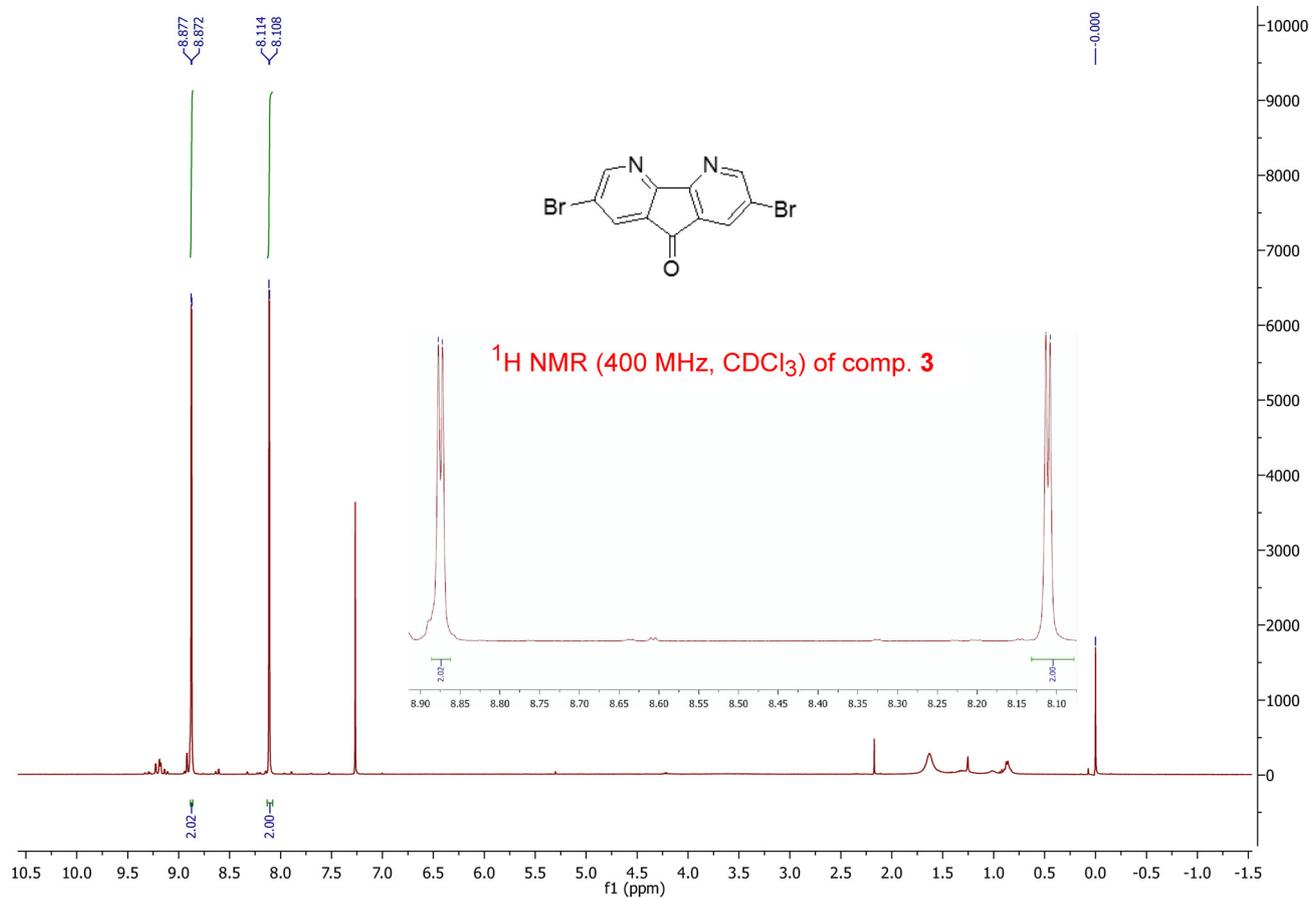
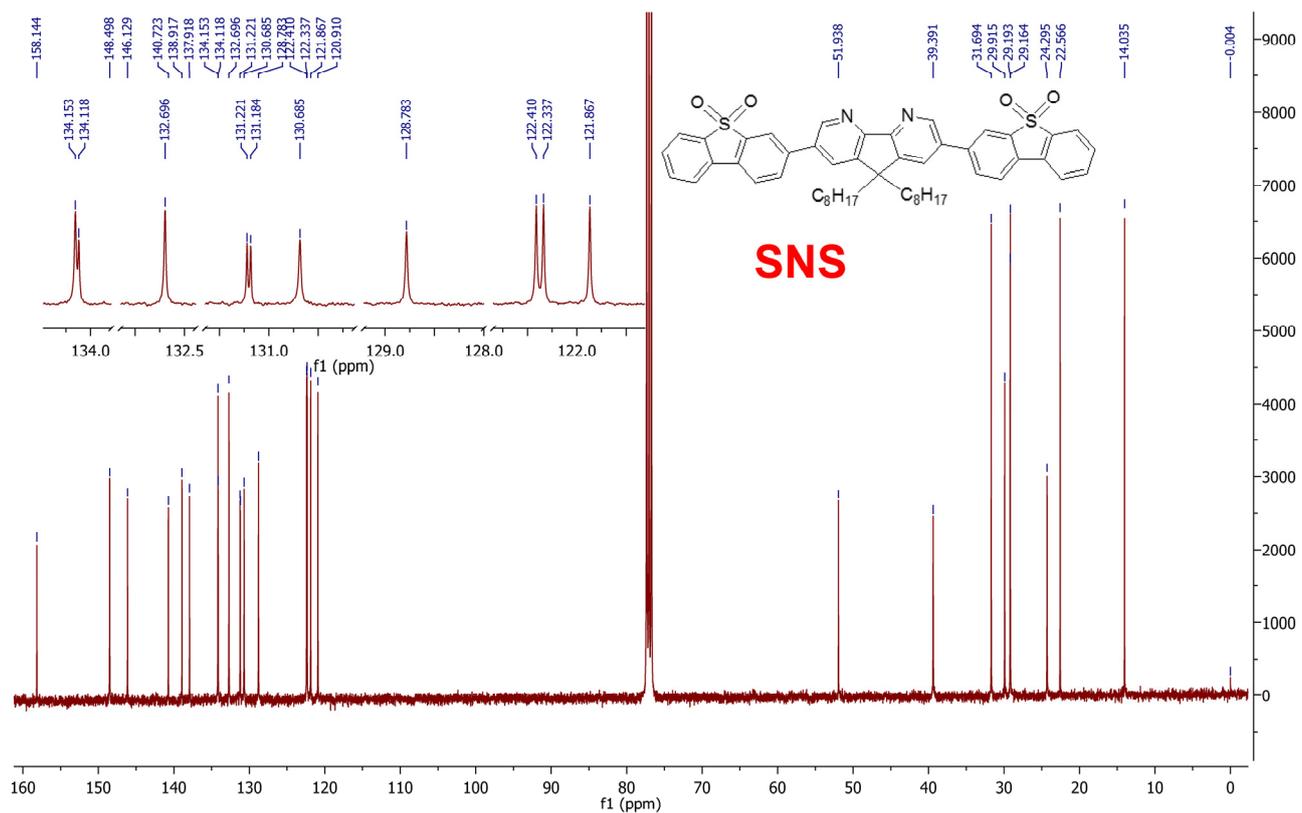
¹H NMR (400 MHz, CDCl₃) of SNS

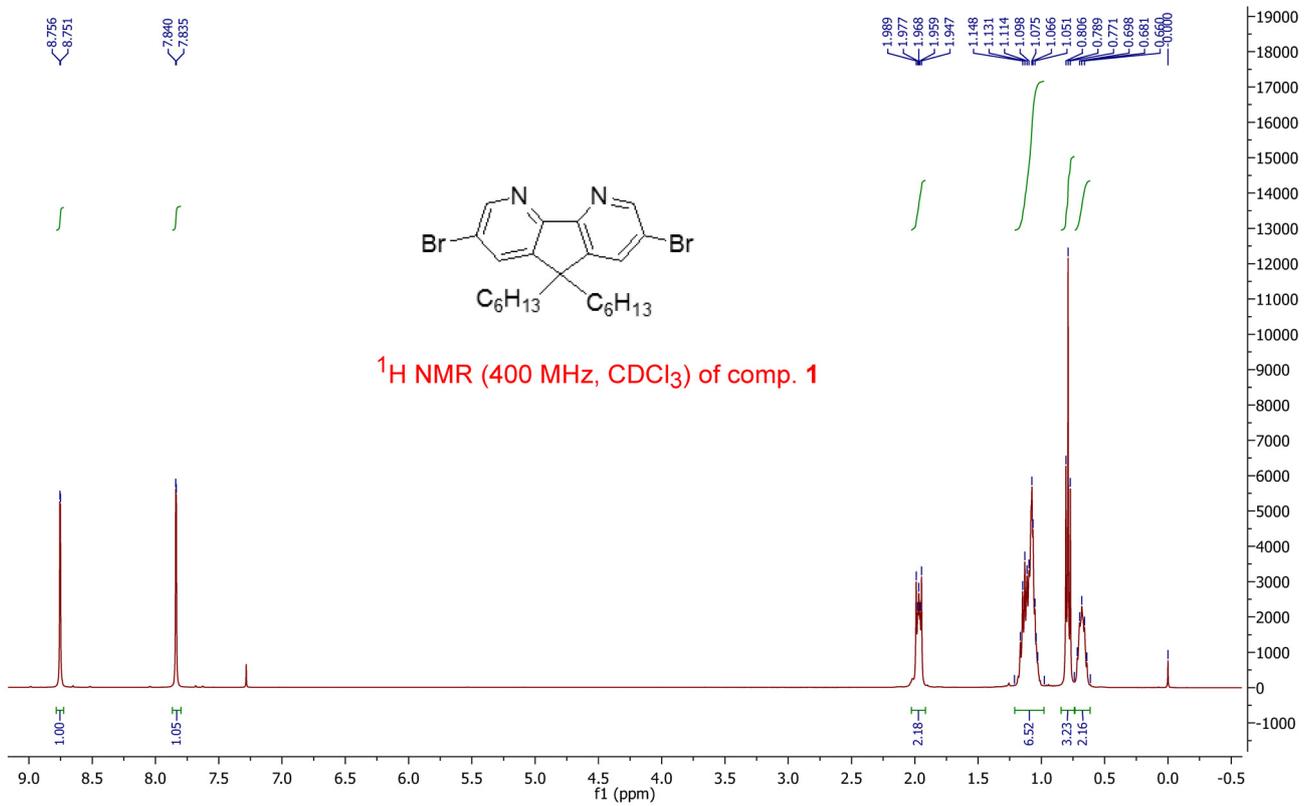
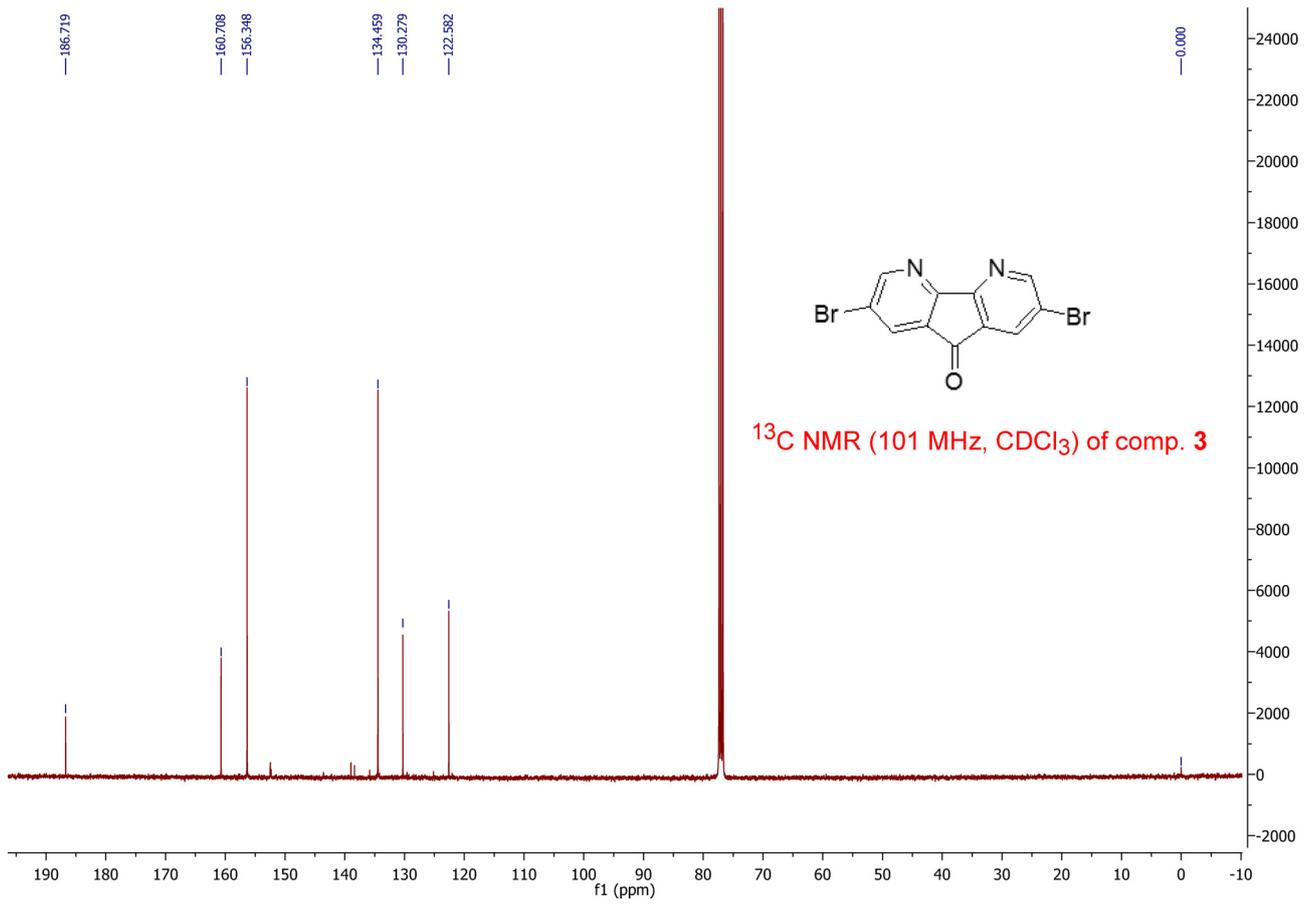


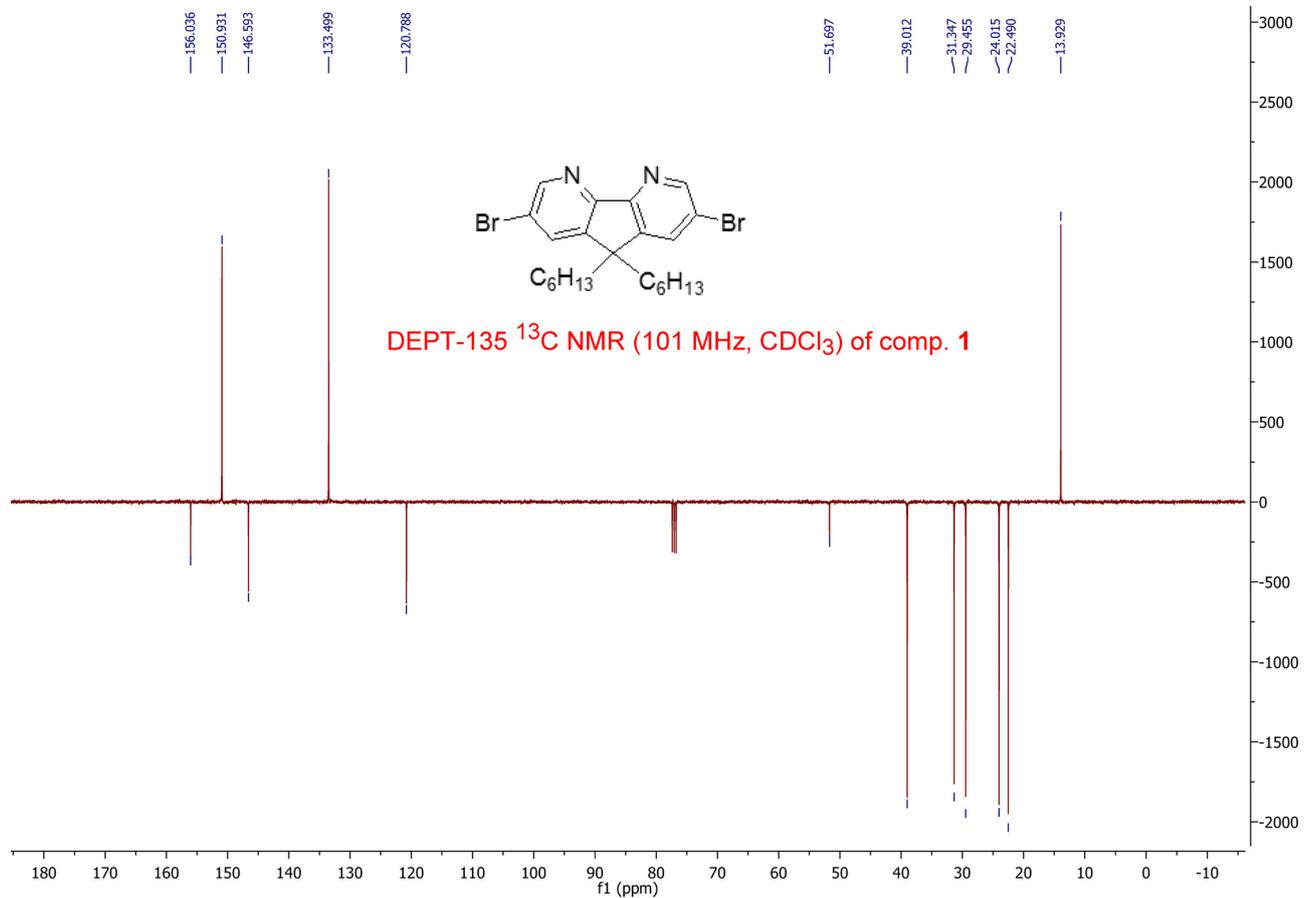
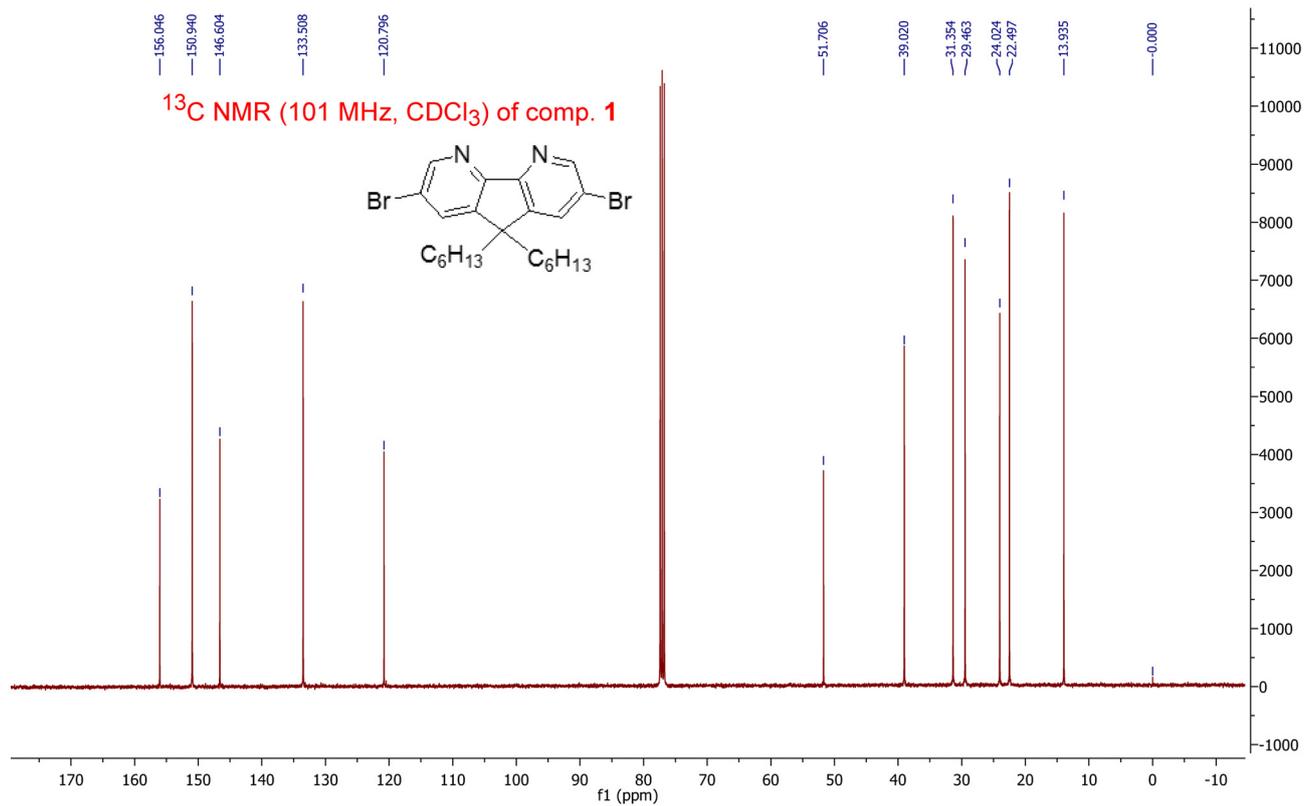
DEPTQ NMR (100MHz, CDCl₃) of SNS

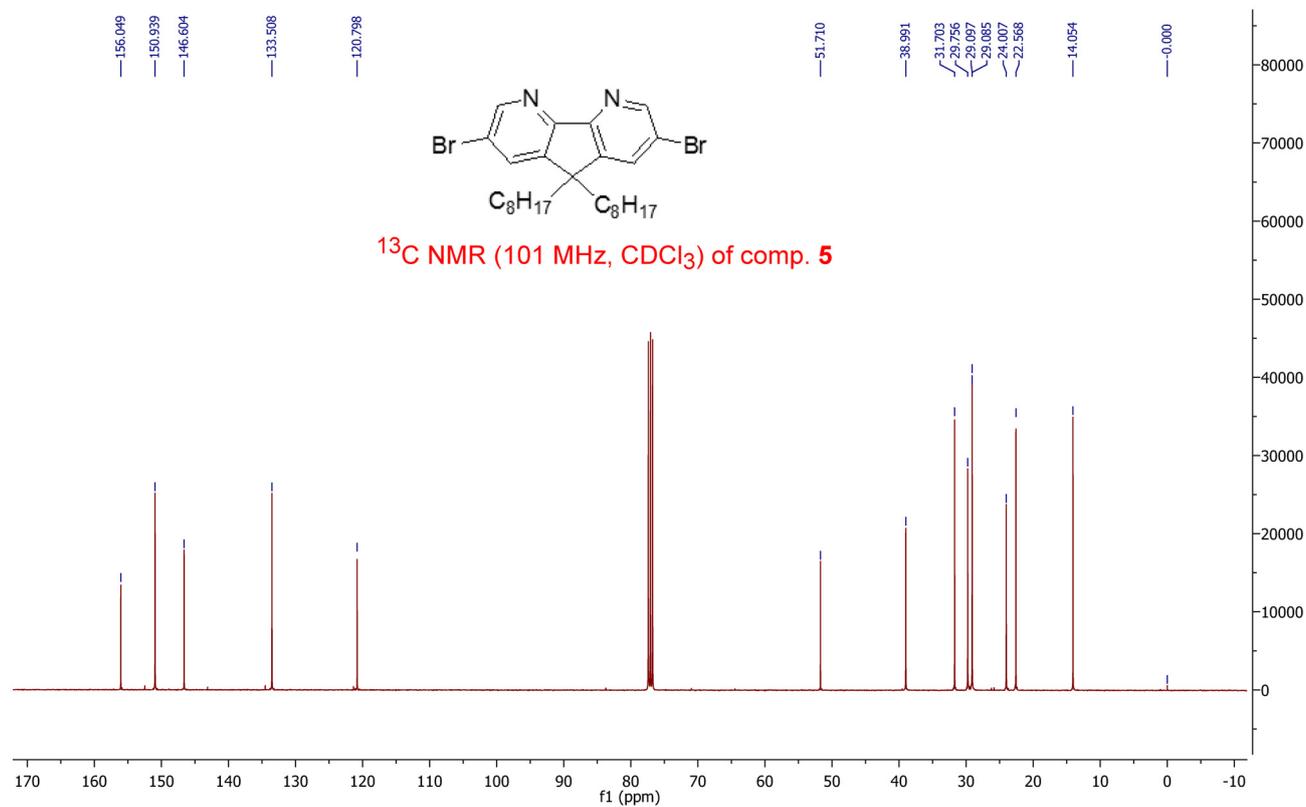
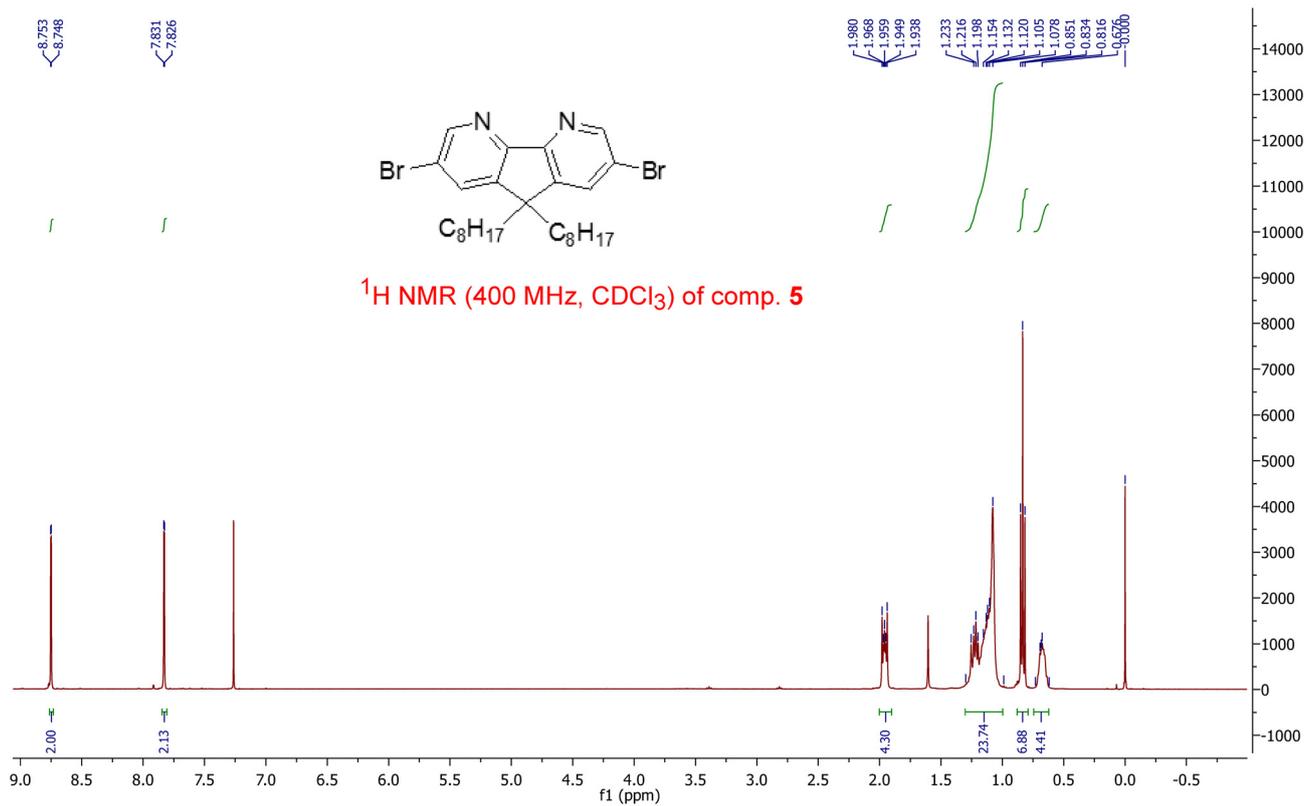


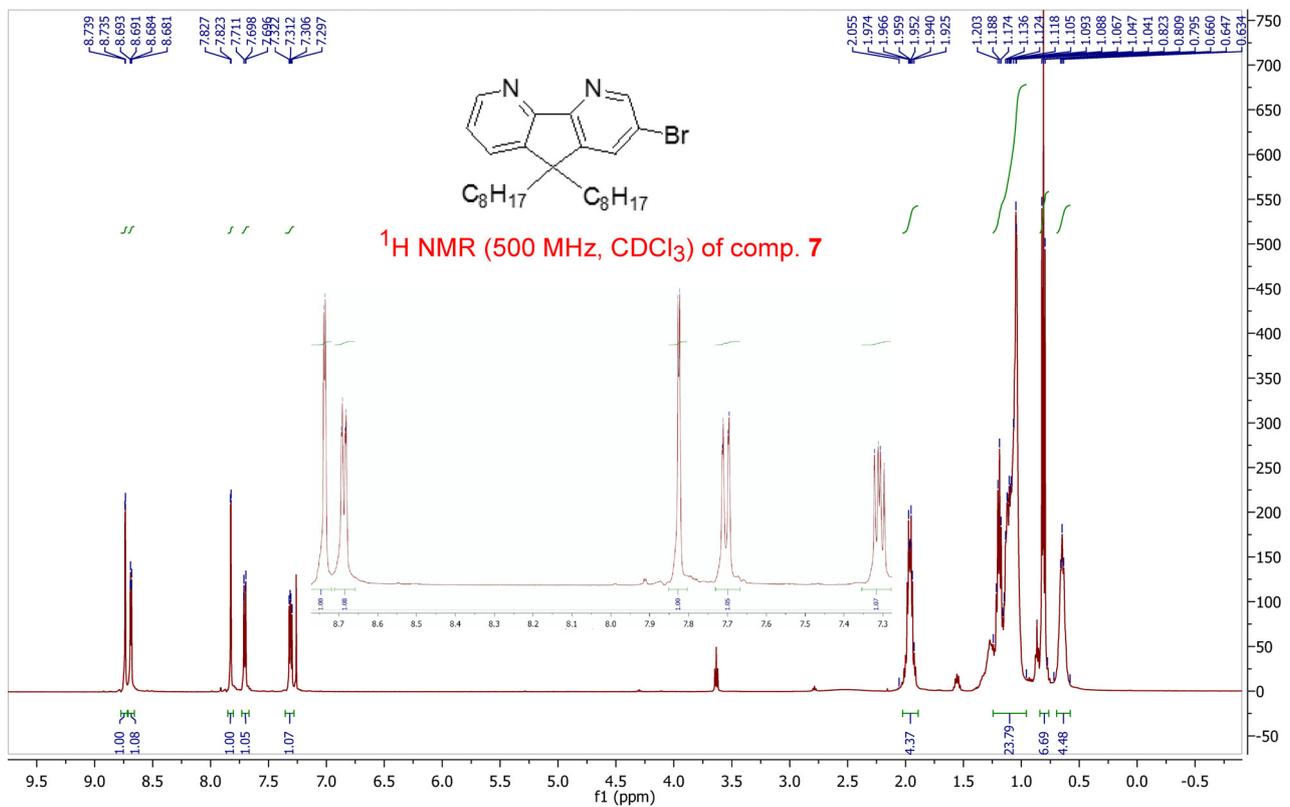
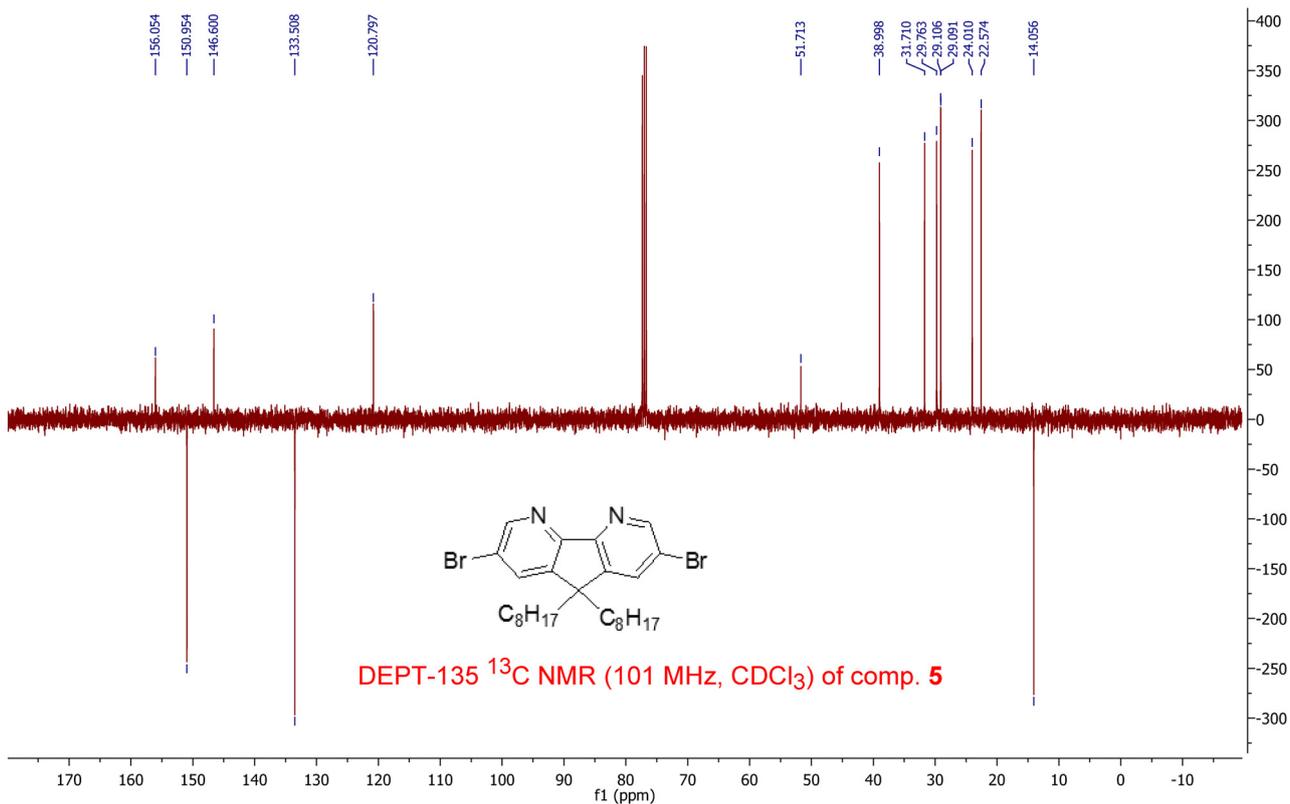
¹³C NMR (101 MHz, CDCl₃) of SNS

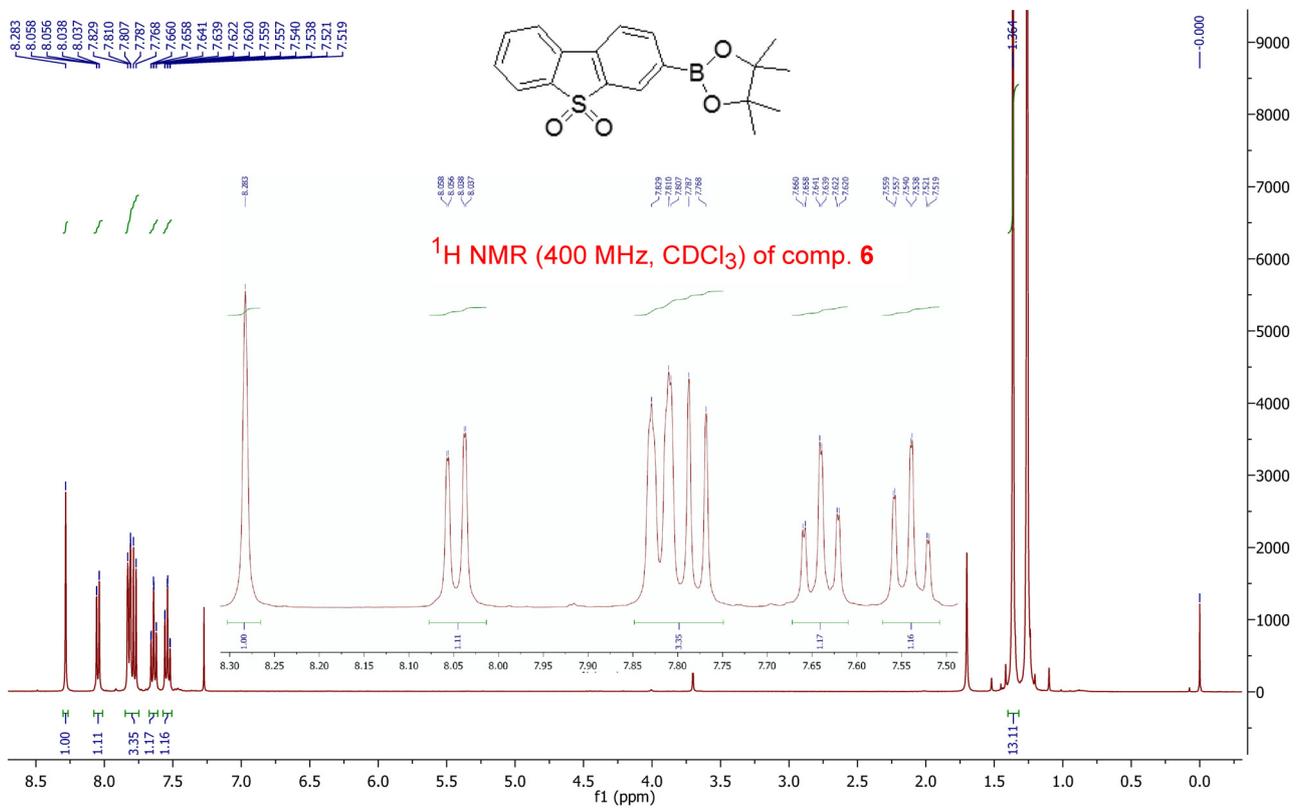
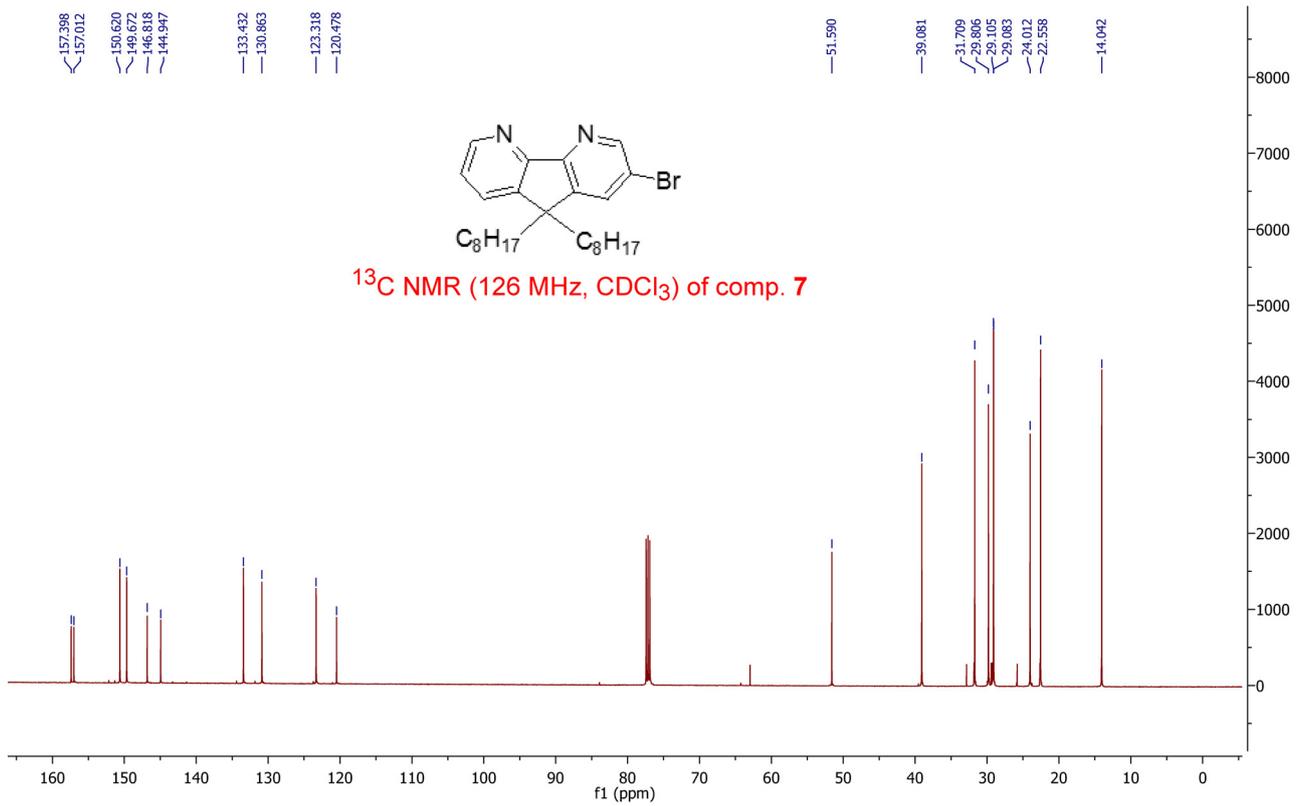


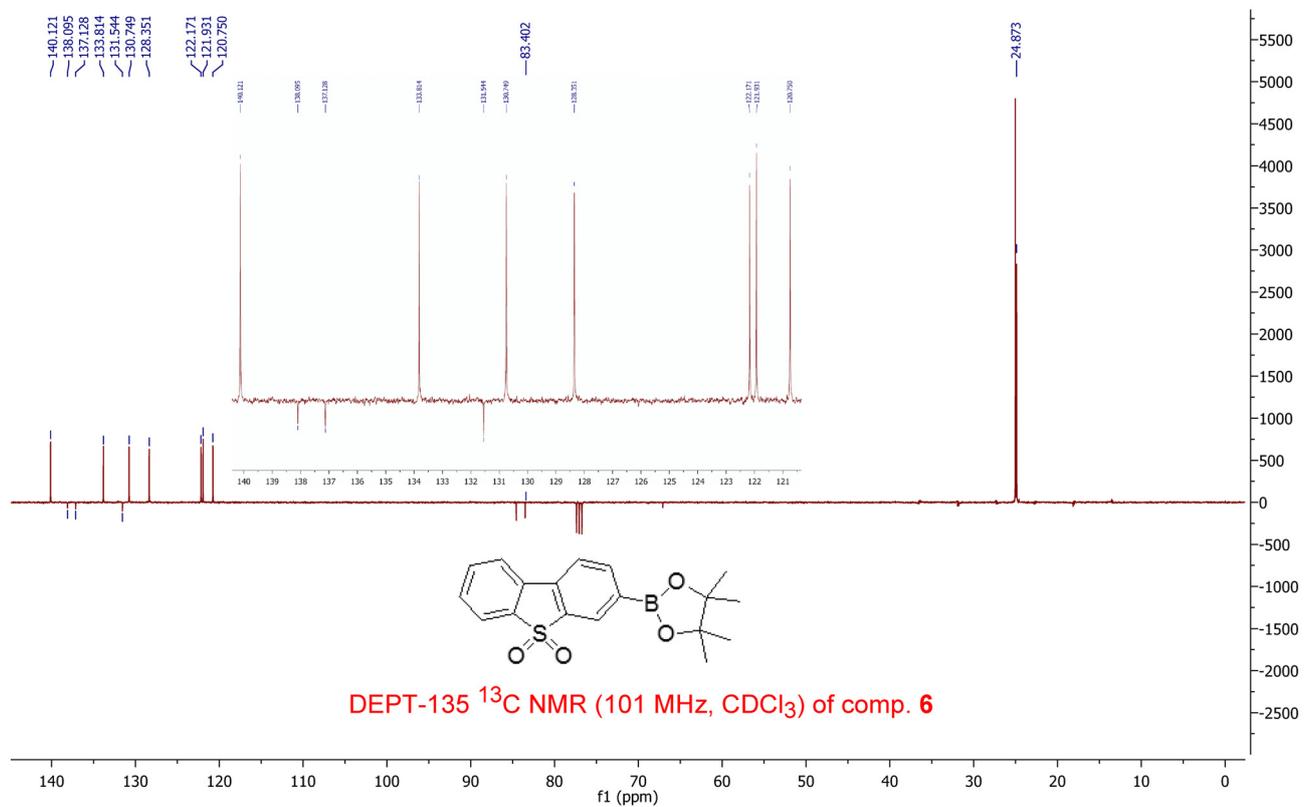
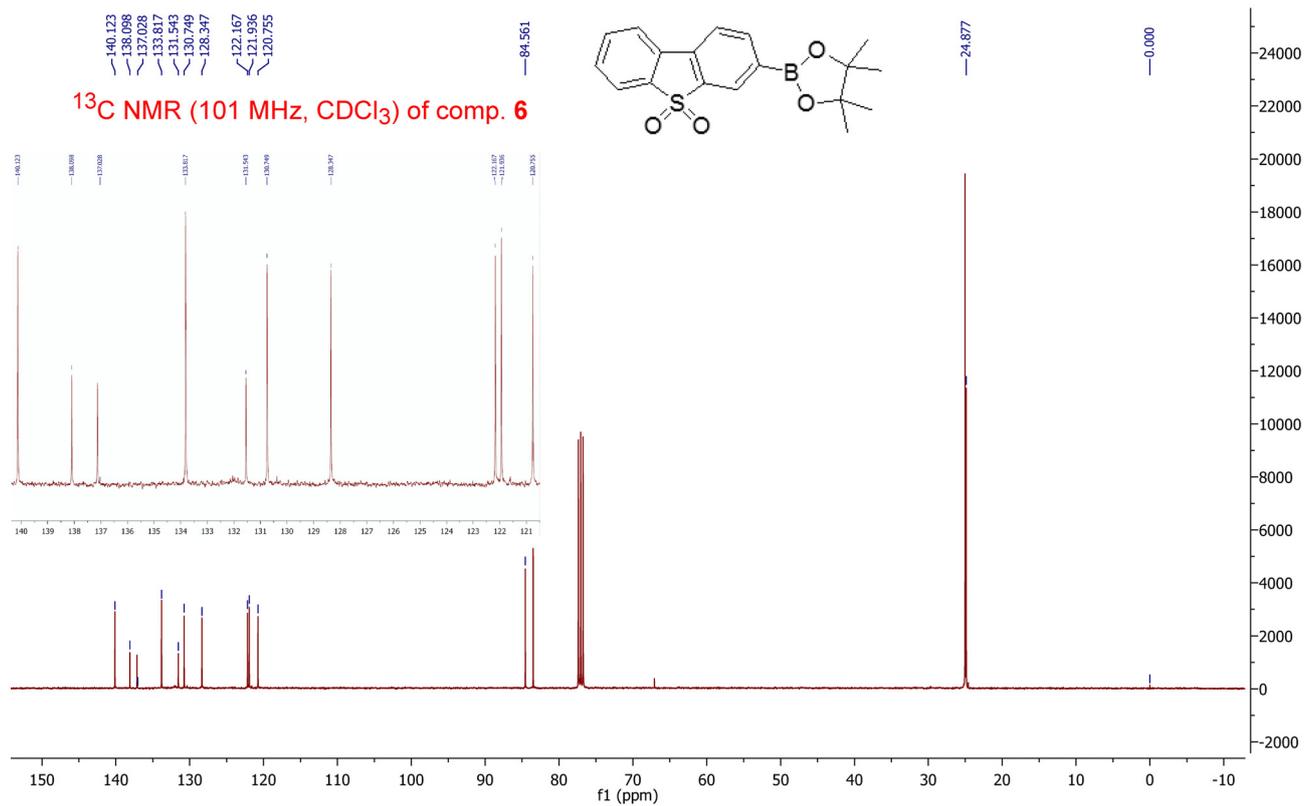


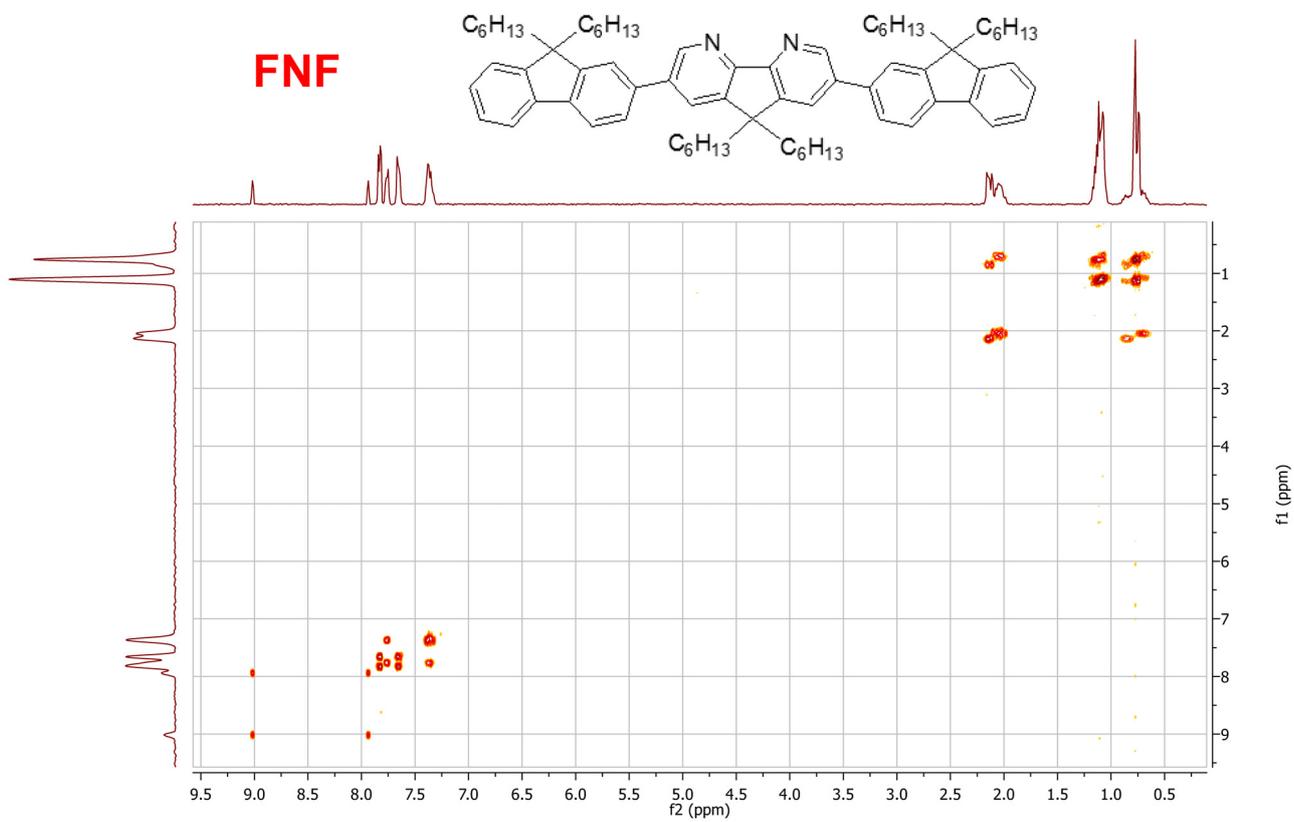
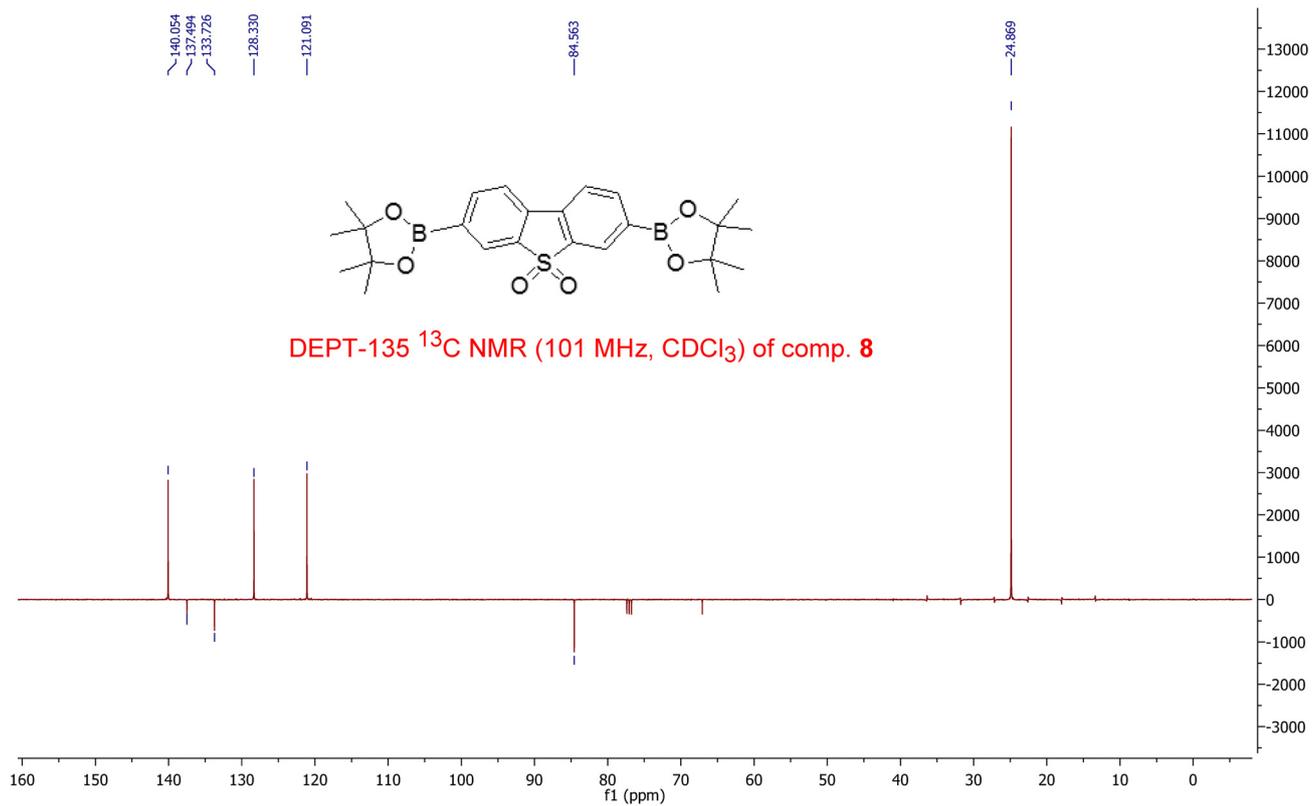








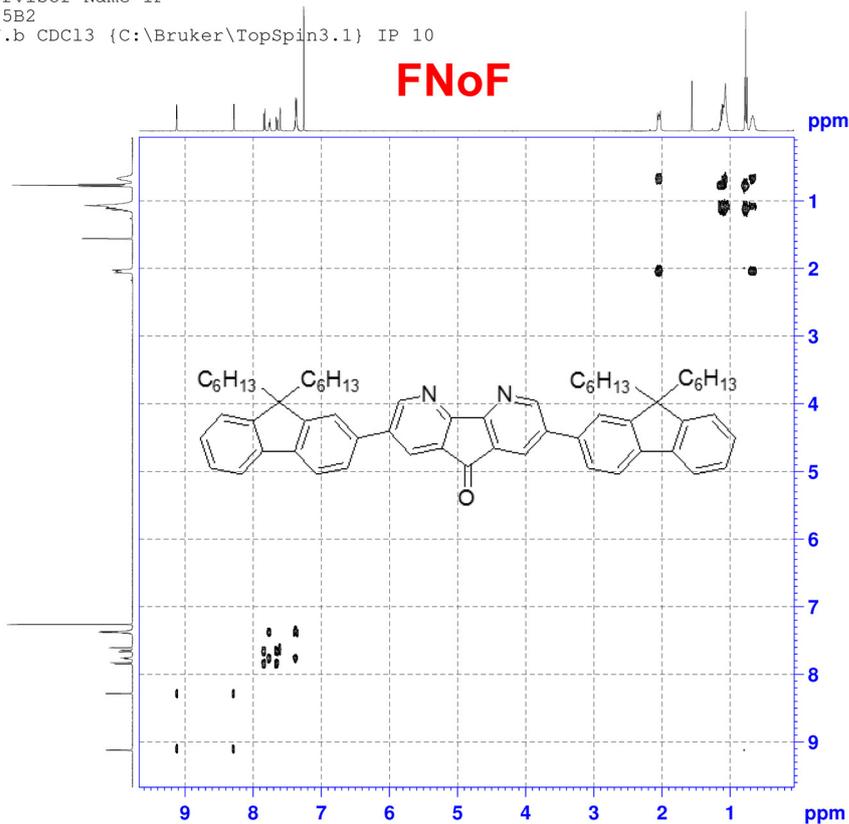




Supervisor Name IP
 SG005B2
 COSY.b CDC13 {C:\Bruker\TopSpin3.1} IP 10



FNoF



Current Data Parameters
 NAME Sep26-2012-IP
 EXPNO 22
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120926
 Time 14.16
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG cosygmrfqf
 TD 2048
 SOLVENT CDC13
 NS 2
 DS 8
 SWH 3846.154 Hz
 FIDRES 1.878005 Hz
 AQ 0.262400 sec
 RG 209.34
 DW 130.000 usec
 DE 8.33 usec
 TE 298.0 K
 D0 0.0000000 sec
 D1 1.92545199 sec
 D13 0.00000400 sec
 D16 0.00020000 sec
 INO 0.00026000 sec

===== CHANNEL f1 =====
 SFO1 400.1319567 MHz
 NUC1 1H
 P1 10.00 usec
 PLW1 28.00000000 W

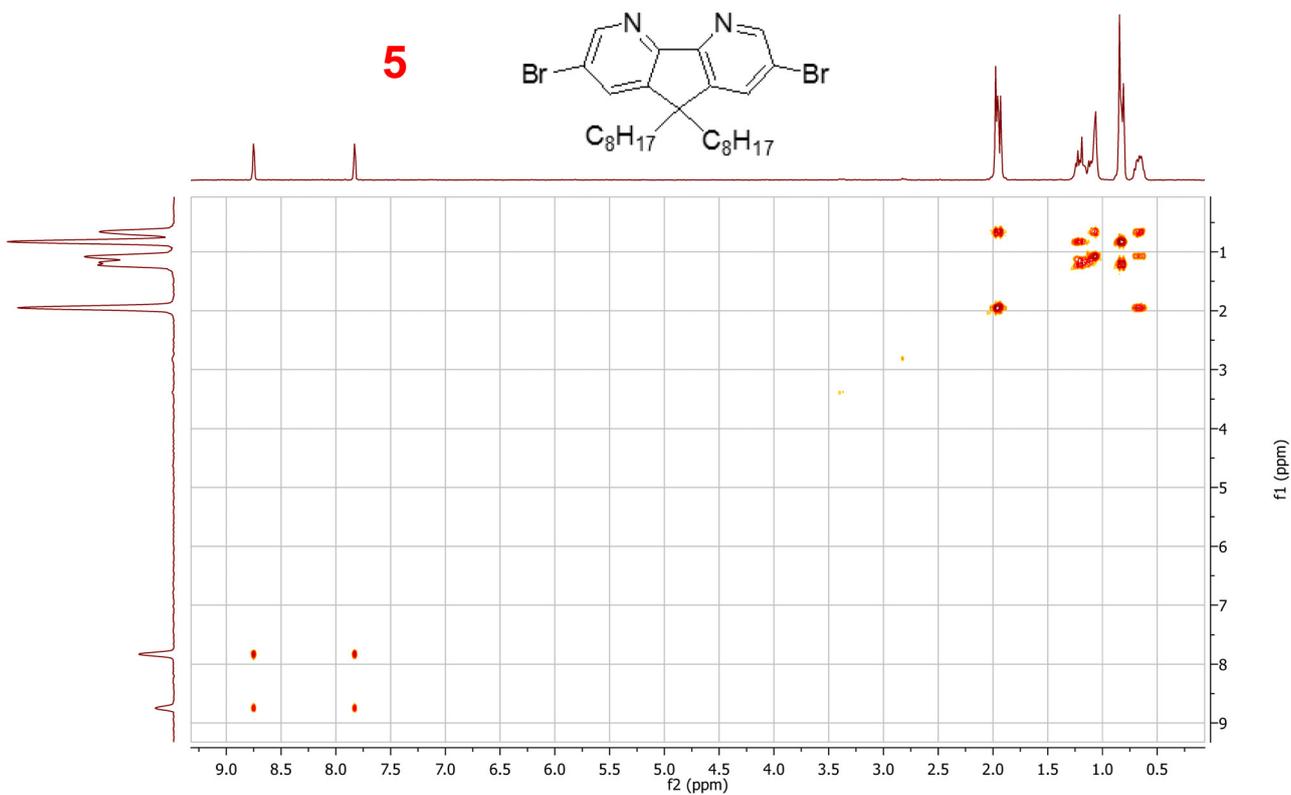
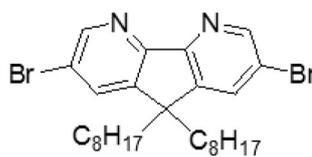
===== GRADIENT CHANNEL =====
 GPNAM1 SMSQ10.100
 GPNAM2 SMSQ10.100
 GPNAM3 SMSQ10.100
 GPZ1 16.00 %
 GPZ2 12.00 %
 GPZ3 40.00 %
 P16 1000.00 usec

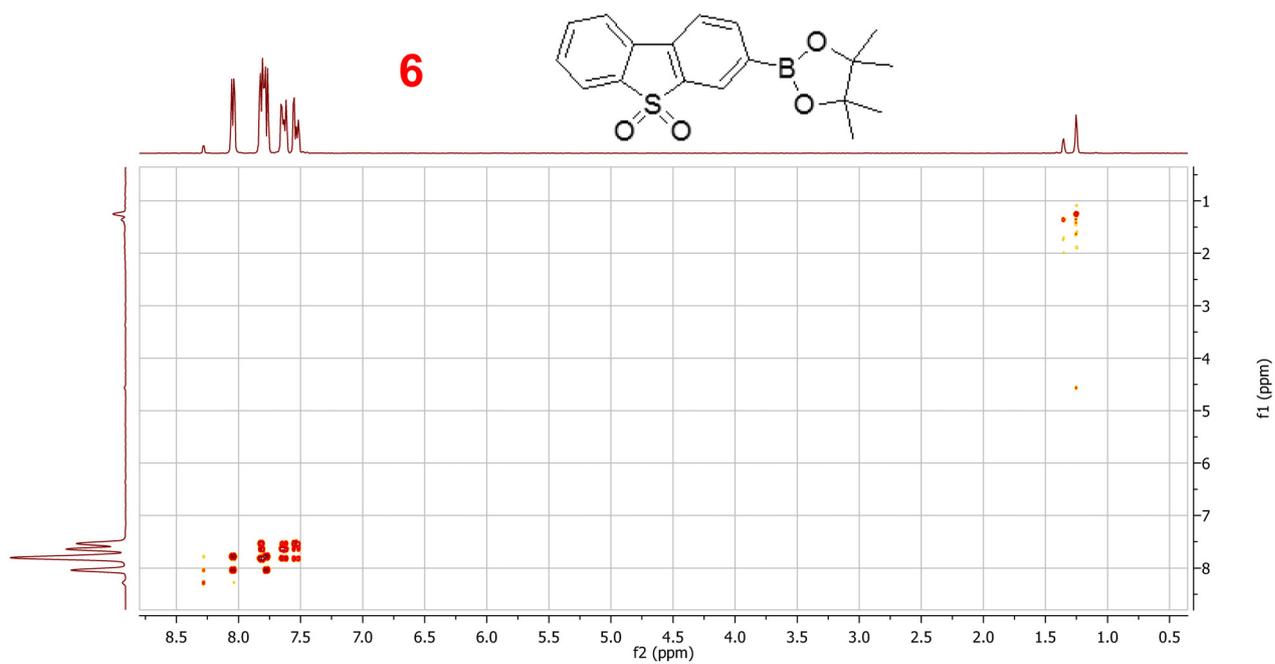
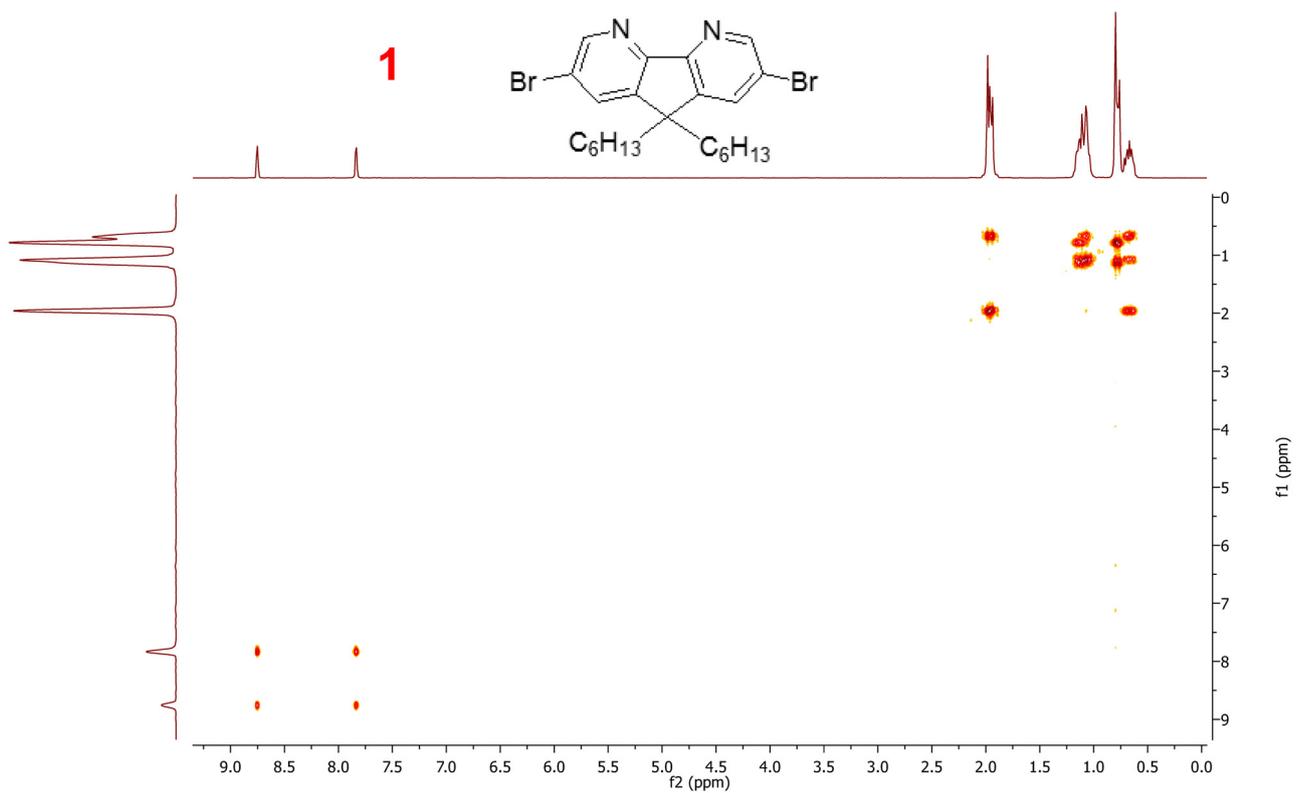
F1 - Acquisition parameters
 TD 128
 SFO1 400.132 MHz
 FIDRES 30.048077 Hz
 SW 9.612 ppm
 FMODE CF

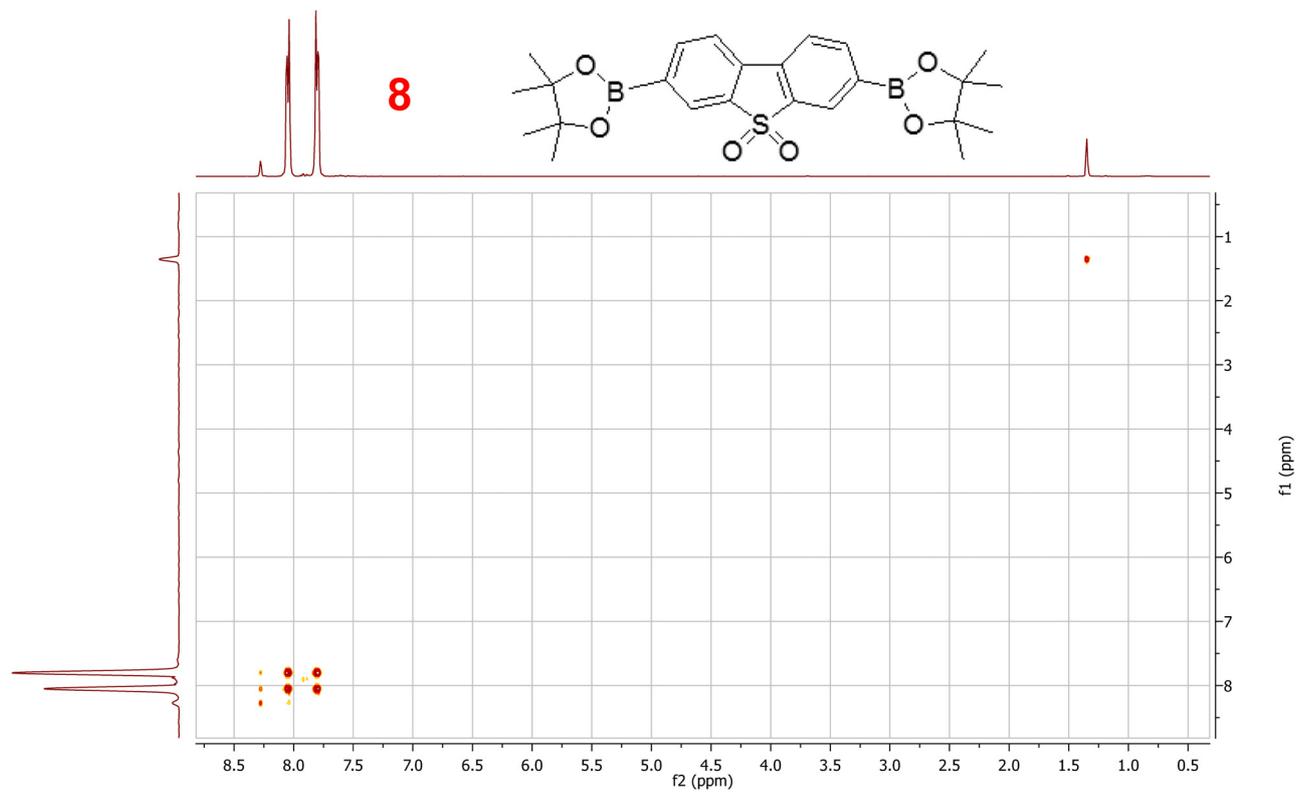
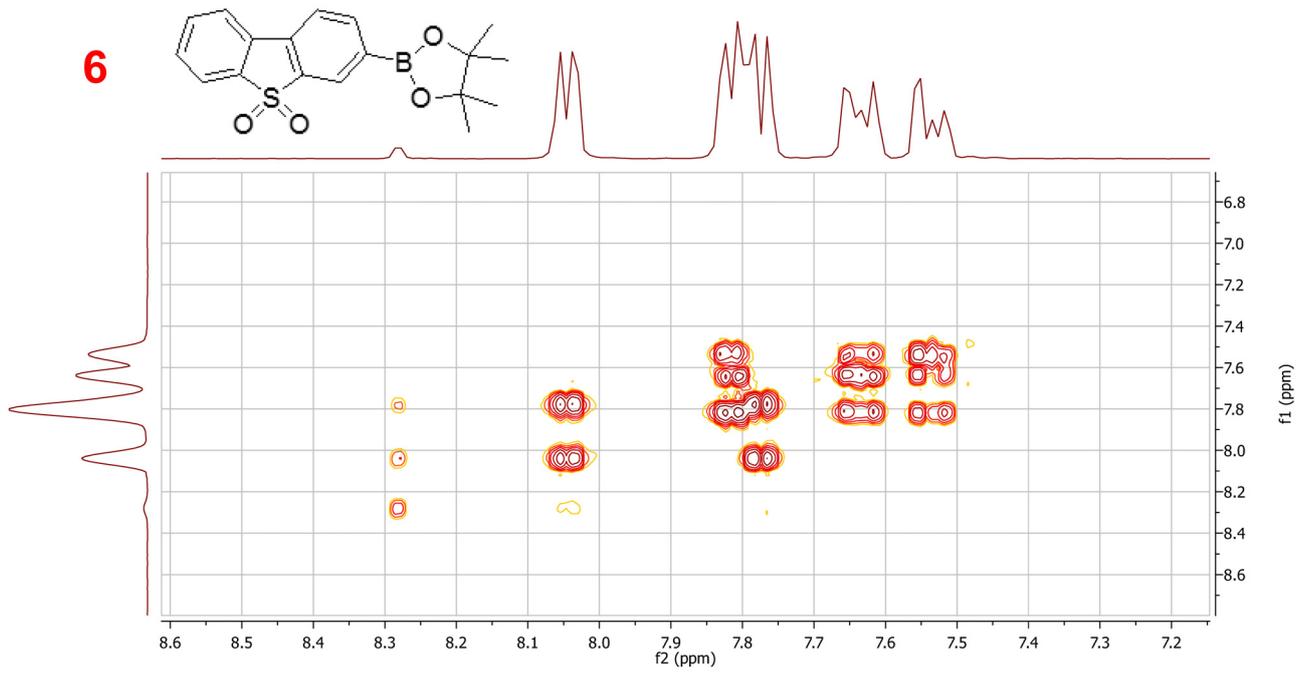
F2 - Processing parameters
 SI 1024
 SF 400.1300098 MHz
 WDW SINE
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.40

F1 - Processing parameters
 SI 1024
 NC2 CF
 SF 400.1300098 MHz
 WDW SINE
 SSB 0
 LB 0 Hz
 GB 0

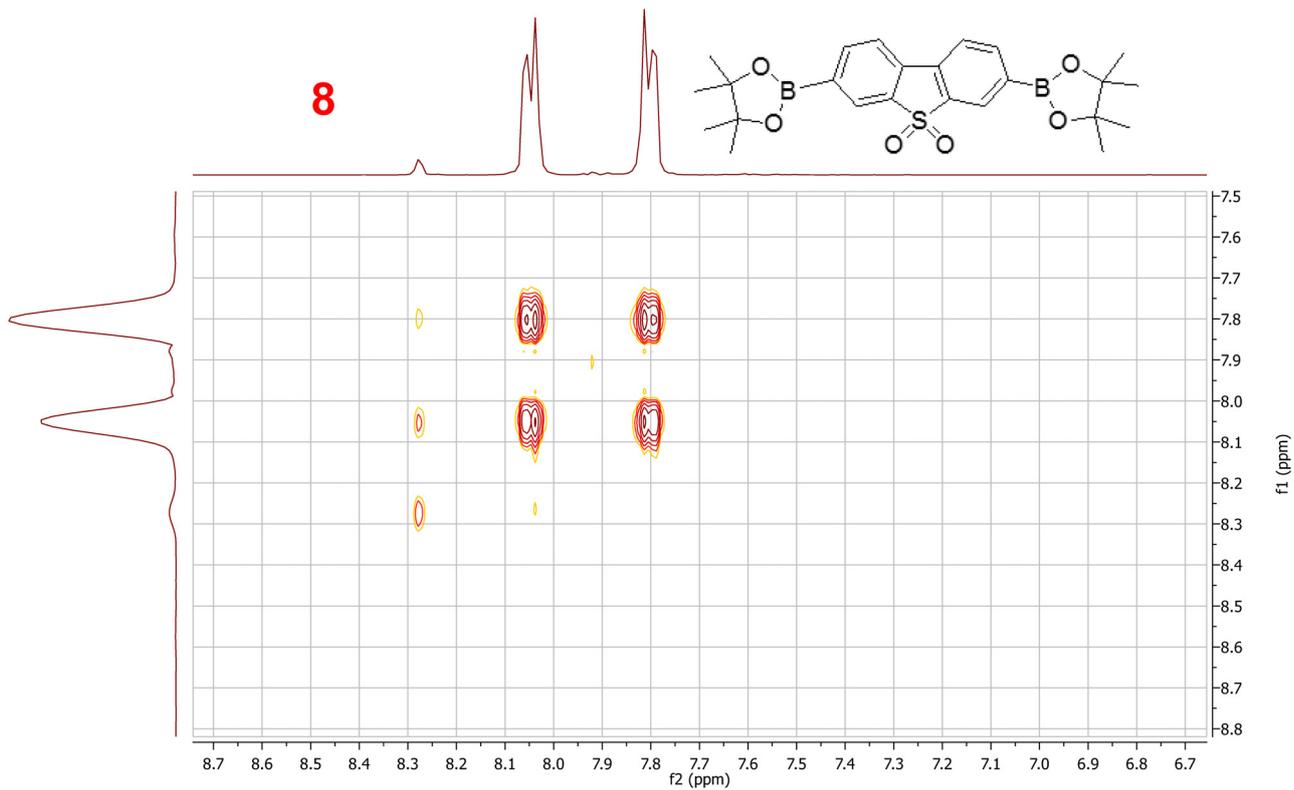
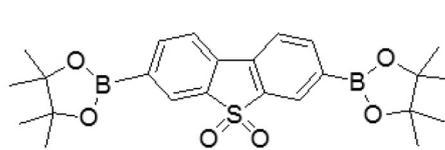
5







8

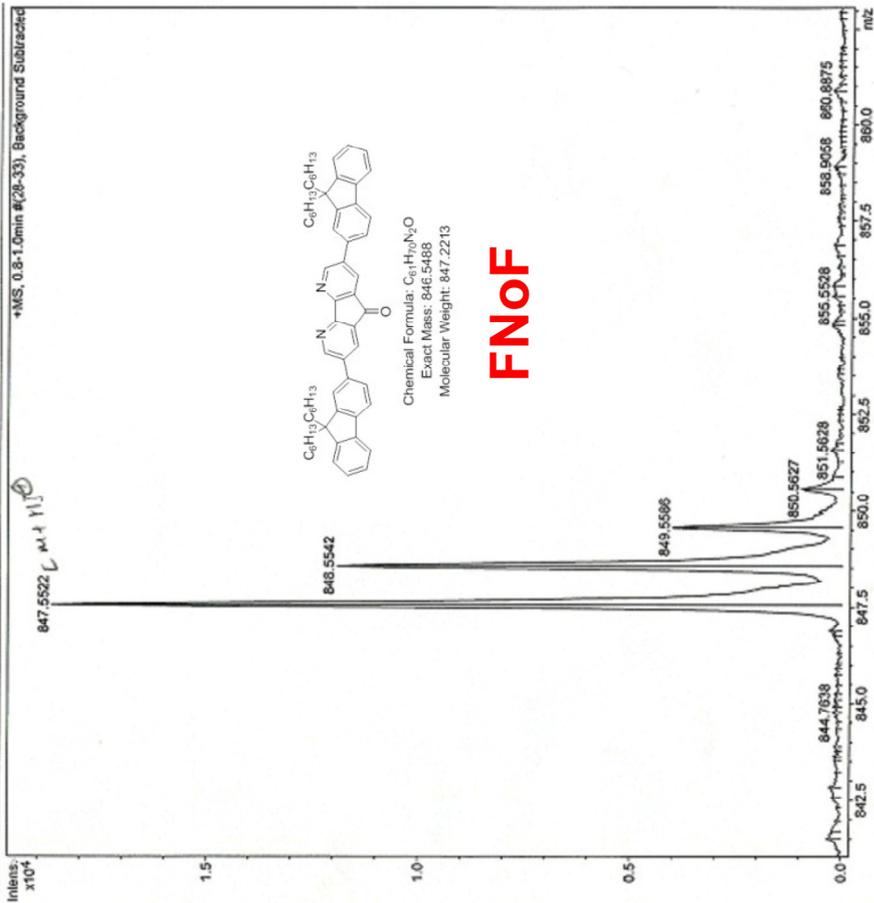


Display Report

Analysis Info
 Analysis Name: D:\data\502197_SG-005-B1.d
 Method: Nov 11 200-1000 Da positive.m
 Sample Name:
 Comment:

Acquisition Date: 11/16/2010 04:52:53 PM
 Operator: bruker
 Instrument: microTOF 0

Acquisition Parameter
 Source Type: ESI
 Scan Range: Standard
 Scan Begin: 50 m/z
 Scan End: 1500 m/z
 Ion Polarity: Positive
 Capillary Exit: 150.0 V
 Hexapole RF: 400.0 V
 Skimmer 1: 80.0 V
 Hexapole 1: 40.7 V
 Set Collector Fill: 80.0 V
 Set Pulsar Pull: 402 V
 Set Pulsar Push: 402 V
 Set Reflector: 1311 V
 Set Flight Tube: 9008 V
 Set Detector TOF: 2850 V

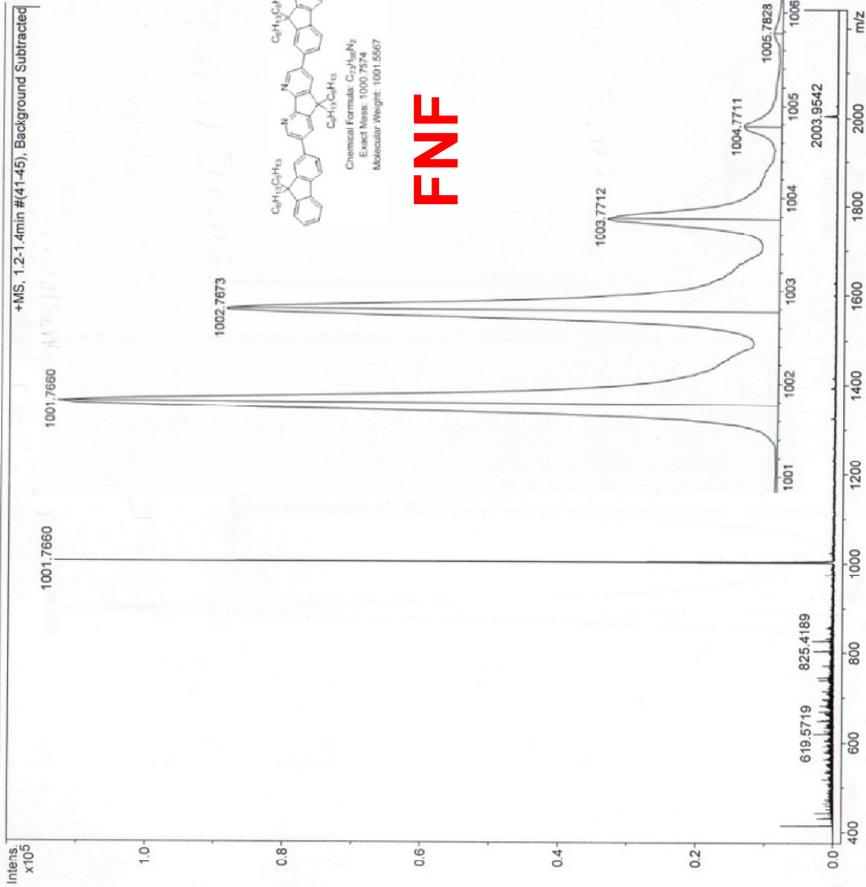


Display Report

Analysis Info
 Analysis Name: D:\data\SANJAY_GHOSH_MS_2nov2010.d
 Method: Oct 9th 2010400 to 1500 Da positive.m
 Sample Name:
 Comment:

Acquisition Date: 11/02/2010 04:05:33 PM
 Operator: bruker
 Instrument: microTOF 0

Acquisition Parameter
 Source Type: ESI
 Scan Range: Standard
 Scan Begin: 50 m/z
 Scan End: 1500 m/z
 Ion Polarity: Positive
 Capillary Exit: 150.0 V
 Hexapole RF: 500.0 V
 Skimmer 1: 80.0 V
 Hexapole 1: 40.7 V
 Set Collector Fill: 80.0 V
 Set Pulsar Pull: 402 V
 Set Pulsar Push: 402 V
 Set Reflector: 1311 V
 Set Flight Tube: 9008 V
 Set Detector TOF: 2650 V



Display Report

Analysis Info

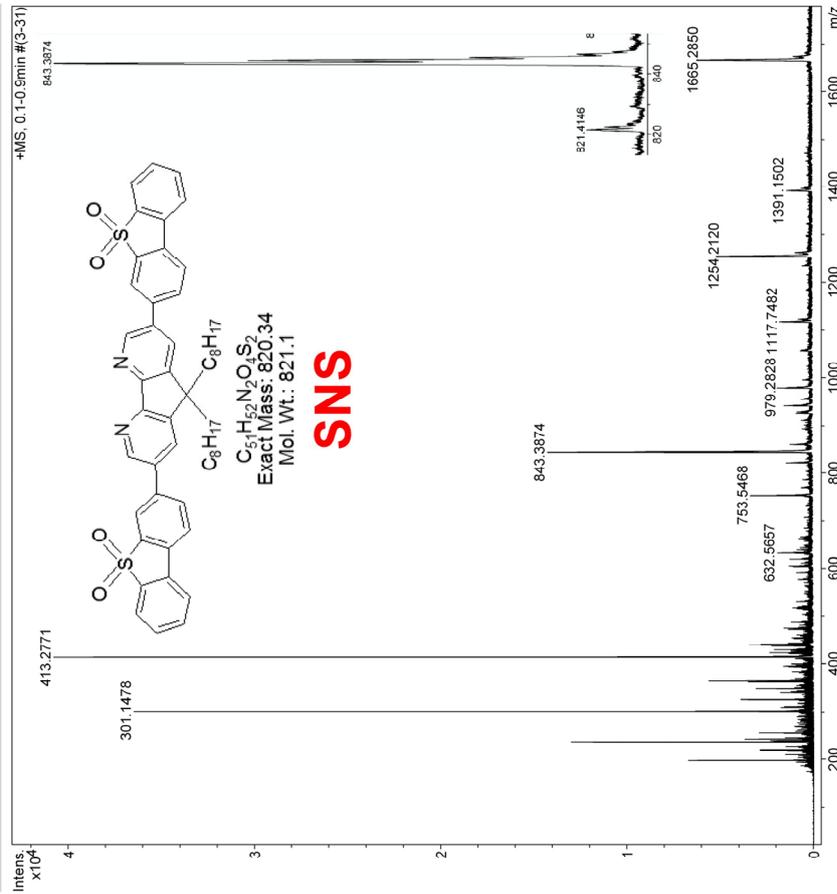
Analysis Name 800610_SG-145.L.d
 Method DJW_300 to 2000da Apr 2012.m
 Sample Name Tetraalanine
 Comment

Acquisition Date 16/04/2013 14:54:11
 Operator bruker
 Instrument microTOF

Acquisition Parameter

Source Type ESI
 Scan Range 50 m/z
 Scan Begin 3000 m/z
 Scan End
 Ion Polarity Positive
 Capillary Exit 150.0 V
 Hexapole RF 100.0 V
 Skimmer 1 100.0 V
 Hexapole 1 38.5 V

Set Corrector Fill 80.0 V
 Set Pulsar Pull 402 V
 Set Pulsar Push 402 V
 Set Reflector 1311 V
 Set Flight Tube 9008 V
 Set Detector TOF 2900 V



Display Report

Analysis Info

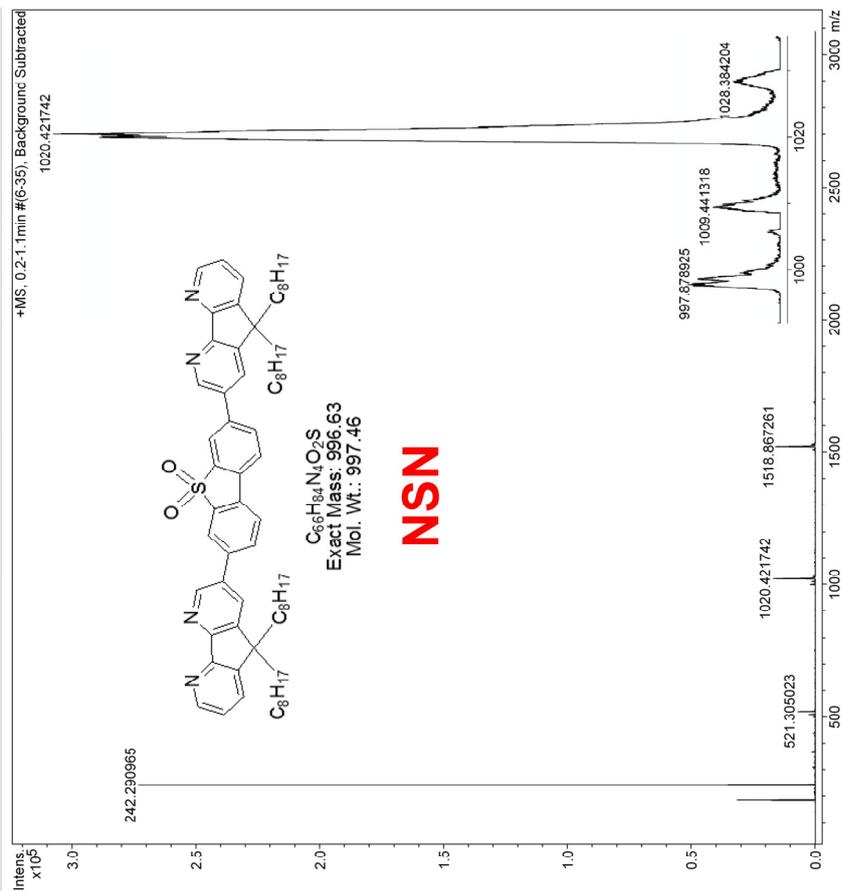
Analysis Name 800611_SG-146.C.d
 Method DJW_300 to 2000da Apr 2012.m
 Sample Name Tetraalanine
 Comment

Acquisition Date 16/04/2013 14:58:02
 Operator bruker
 Instrument microTOF

Acquisition Parameter

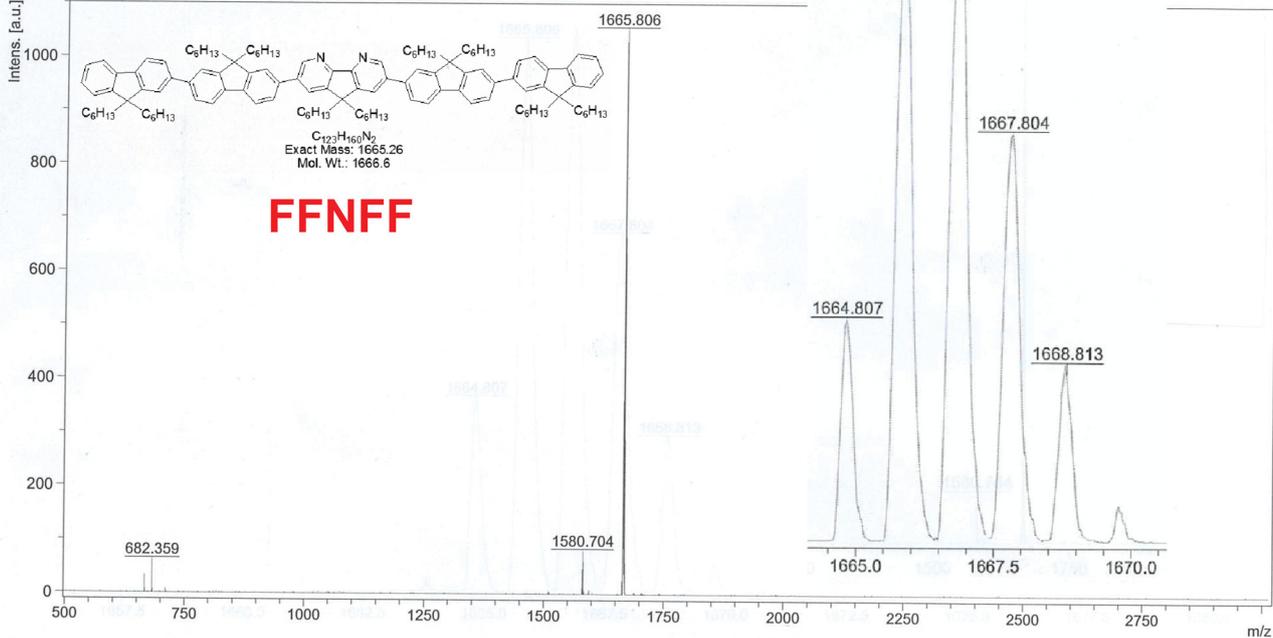
Source Type ESI
 Scan Range 50 m/z
 Scan Begin 3000 m/z
 Scan End
 Ion Polarity Positive
 Capillary Exit 150.0 V
 Hexapole RF 100.0 V
 Skimmer 1 100.0 V
 Hexapole 1 38.5 V

Set Corrector Fill 80.0 V
 Set Pulsar Pull 402 V
 Set Pulsar Push 402 V
 Set Reflector 1311 V
 Set Flight Tube 9008 V
 Set Detector TOF 2900 V



M:IMALDI\SG_185A3 01\0_L9\1

Comment 1
Comment 2



Bruker Daltonics flexAnalysis

printed: 29/10/2013 15:11:53

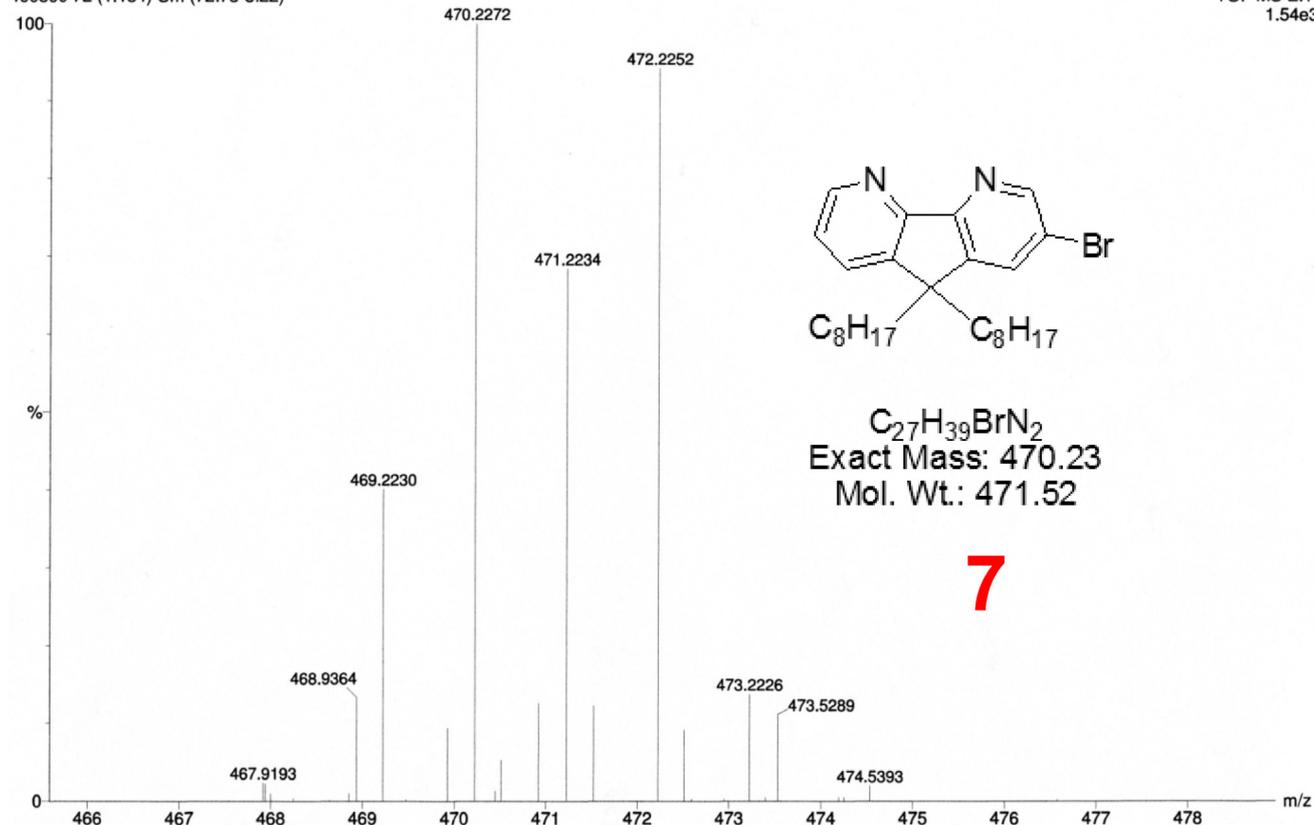
GCTOF

Bangor University - School of Chemistry
S Ghosh SG-040-B

08-Jun-2011

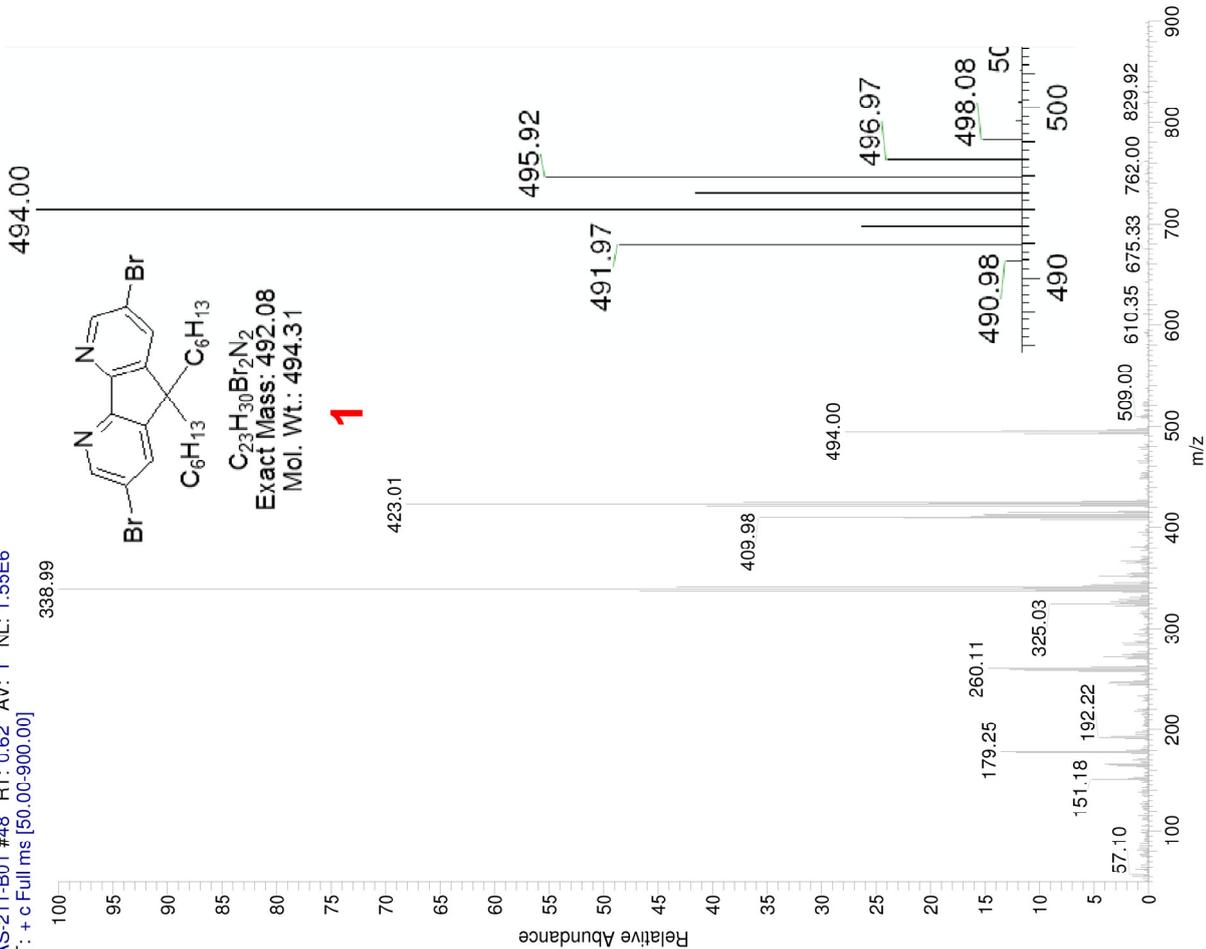
400800 72 (1.184) Cm (72:73-8:22)

TOF MS EI+
1.54e3



AS-211-B01 #48 RT: 0.62 AV: 1 NL: 1.55E6

T: + c Full ms [50.00-900.00]



Display Report

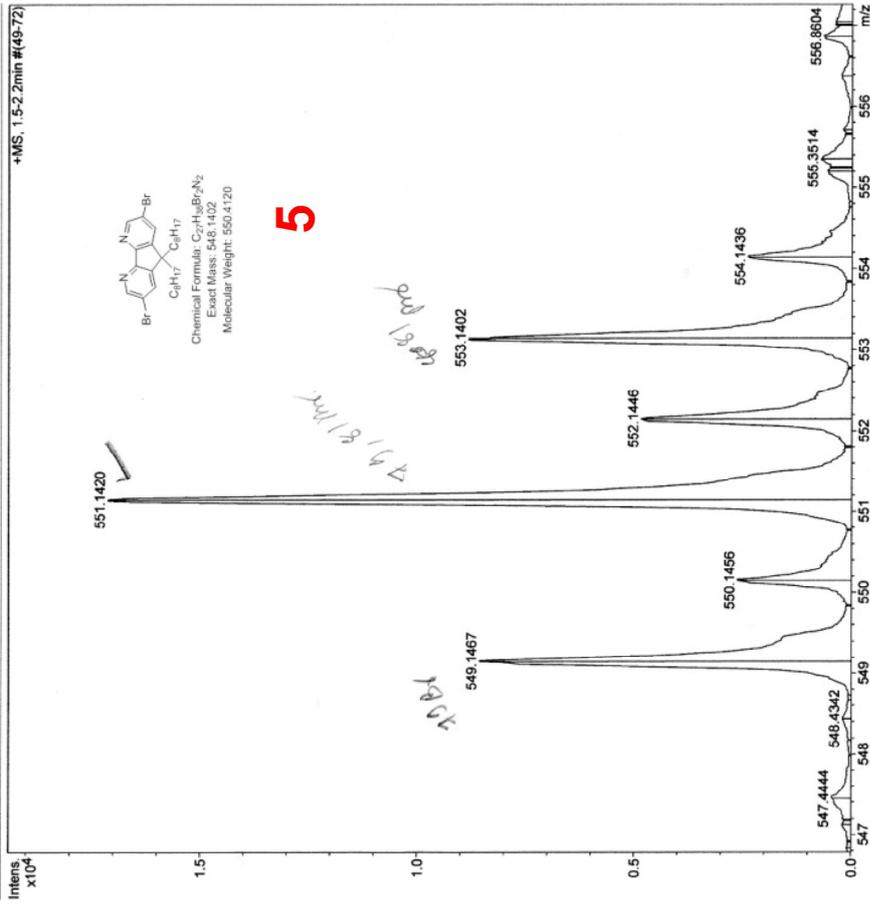
Analysis Info
 Analysis Name D:\data\502225_SG-011-B.d
 Method standard_loop_2164.m
 Sample Name < No Sample >
 Comment

Acquisition Parameter
 Source Type ESI
 Scan Range Standard
 Scan Begin 50 m/z
 Scan End 1500 m/z

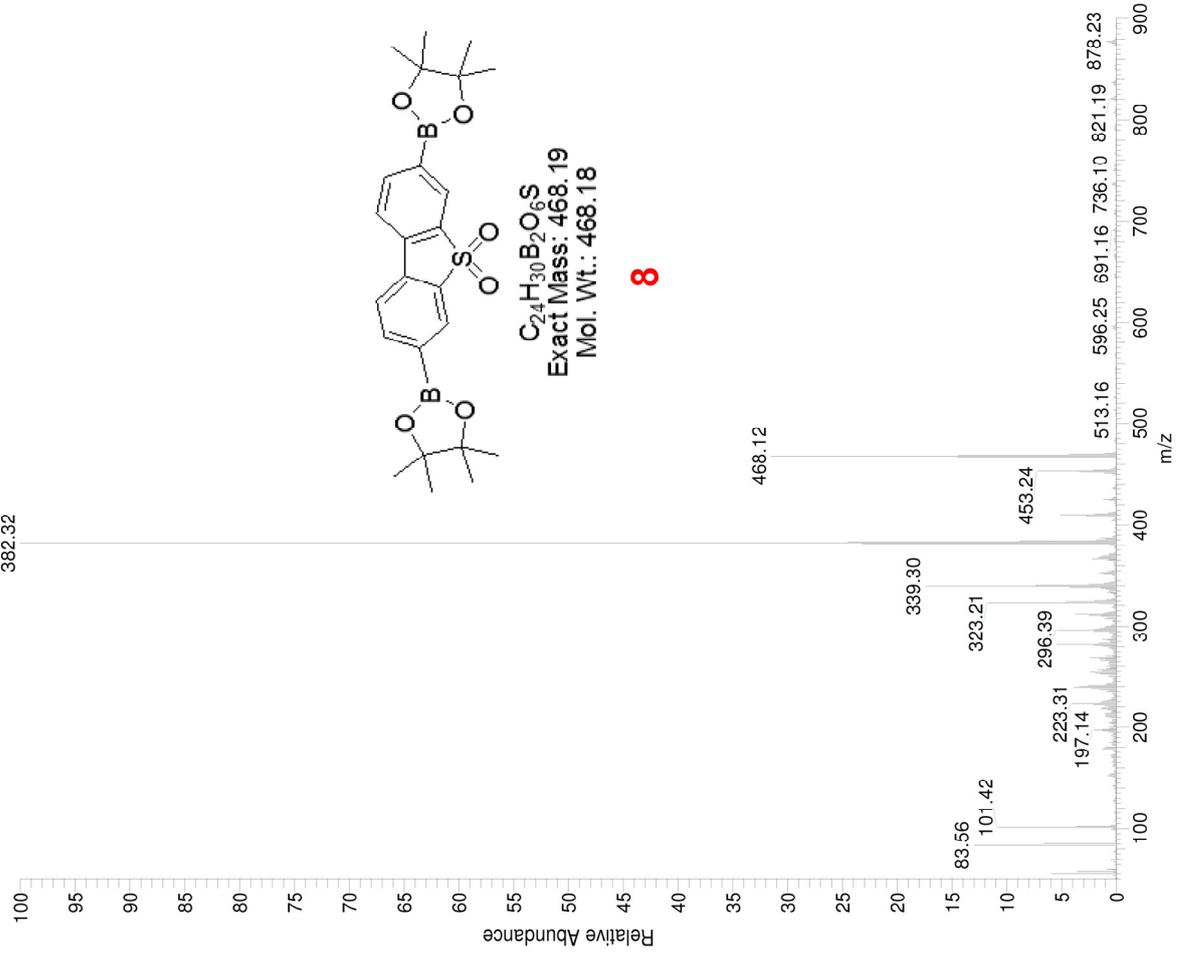
Acquisition Parameters
 Ion Polarity Positive
 Capillary Exit 150.0 V
 Hexapole RF 200.0 V
 Skimmer 1 80.0 V
 Hexapole 1 40.7 V

Acquisition Parameters
 Set Corrector Fill 80.0 V
 Set Pulsar Pull 402 V
 Set Pulsar Push 402 V
 Set Reflector 1311 V
 Set Flight Tube 9008 V
 Set Detector TOF 2650 V

Chemical Structure
C1=CN2C(=C1)N(C2)C3=CC=CC=C3Br
 $C_{17}H_{17}Br$
 Chemical Formula: $C_{17}H_{17}BrN_2$
 Exact Mass: 548.1402
 Molecular Weight: 550.4120



SG144-B01 #45 RT: 0.57 AV: 1 NL: 9.92E7
T: + c Full ms [50.00-900.00]



SG-143B01 #59-63 RT: 0.73-0.79 AV: 5 NL: 1.13E7
T: + c Full ms [50.00-900.00]

