

## Supporting Information

### Highly Coplanar very long oligo(alkylfuran)s: A Conjugated System with Specific Head-To-Head Defect

Xu-hui Jin,<sup>\*,[a]</sup> Dennis Sheberla,<sup>[a]</sup> Linda J. W. Shimon<sup>[b]</sup> and Michael Bendikov<sup>†[a]</sup>

In memory of Professor Michael Bendikov

<sup>[a]</sup> Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, 76100, Israel

<sup>[b]</sup> Chemical Research Support Unit, Weizmann Institute of Science, Rehovot 76100, Israel

† Deceased: July 2, 2013.

E-mail: [xuhui.jin@weizmann.ac.il](mailto:xuhui.jin@weizmann.ac.il)

## Table of Contents

Experimental Details.....	3
Synthetic procedures .....	5
3,3'-dibromo-2,2'-bifuran. ....	5
3,3'-dihexyl-2,2'-bifuran. ....	5
5,5'-dibromo-3,3'-dihexyl-2,2'-bifuran. ....	6
4F-2C <sub>6</sub> . ....	6
6F-2C <sub>6</sub> . ....	7
8F-2C <sub>6</sub> . ....	8
2-(tributylstannyl)-3'',4'-dihexyl-2,2':5'',2'':5'',2'''-quaterfuran (Compound 6). ....	8
Compound 7 .....	9
16F-6C <sub>6</sub> . ....	10
Thermal properties .....	10
General X-ray Procedures:.....	11
Details of computations. ....	14
FTIR-ATR spectra.....	19
<sup>1</sup> H and <sup>13</sup> C NMR spectra .....	21

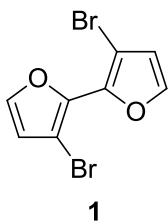
## Experimental Details

**General:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in solution on 300 and 500 MHz spectrometers (Brücker) using tetramethylsilane (TMS) as the external standard. Chemical shifts are expressed in ppm. High resolution mass spectra were measured on a waters Micromass GCT\_Premier Mass Spectrometer using field desorption (FD) ionization. Differential scanning calorimetry (DSC) measurements and thermogravimetric analysis (TGA) were performed on TA Q200 DSC and SDT Q600 instruments, respectively. UV-vis absorption and steady state fluorescence measurements of solution and films were performed on a Cary-5000 spectrometer (Varian) and a Cary Eclipse fluorometer (Varian) respectively. Fluorescence quantum yields in solution were determined using a standard procedure.<sup>1</sup> Coumarine 30 in acetonitrile ( $\lambda_{\text{abs}} = 403 \text{ nm}$ ,  $\lambda_{\text{em}} = 480 \text{ nm}$ ,  $\Phi_{\text{f}} = 0.67$ ) was used as a reference for  $\Phi_{\text{f}}$  measurements.<sup>2</sup> Quantum yield measurements were made using four excitation wavelengths and the quantum yields were averaged across 12 measurements. Solid-state fluorescence quantum yields were measured by an absolute PL quantum yield spectrometer (Hamamatsu, Quantaaurus-QY C11347). The fluorescence lifetime was measured by the time correlated single photon counting technique using FluoroCube (HORIBA Jobin Yvon) station equipped with TBX-04 detection module of less than 180 ps typical timing jitter and less than 100 ps overall time resolution. Cyclic voltammetry (CV) and electrochemical polymerization were performed using a Bio-Logic SAS (model VSP) Potentiostat/Galvanostat in a standard three-electrode setup. Pt wire, Ag/AgCl wire, and Pt disk electrode or an ITO-coated glass slide were used as the counter electrode, pseudo-reference electrode, and working electrode, respectively. 1,2-Dichloroethene (DCE) containing 0.1 M tetra-n-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) was used as the solvent. A ferrocene/ferrocenium redox couple was used as an internal reference for all measurements. Spectroelectrochemical experiments on electrodeposited poly(**16F-6C<sub>6</sub>**) and on films of **16F-6C<sub>6</sub>** monomer on ITO glass were performed with 0.1 M TBABF<sub>4</sub>/DCE respectively, on a PAR 263A potentiostat. Spectra were taken in a UV-vis-NIR quartz optical cell (100-QX, Hellma)

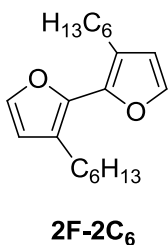
with a JASCO V-570 UV-vis-NIR spectrophotometer. Atom Force Microscopy (AFM) topography images were collected using a P47 AFM (NT-MDT) equipped with a small scanner. Images were recorded in tapping mode in the air at room temperature using silicon micro cantilevers (force constant 42 N/m, resonance frequency 330 kHz, length 160  $\mu\text{m}$ ). Imaging was carried out in different scan directions and at different scales to verify the consistency and robustness of the evaluated structures. HPLC was performed on a 1260 infinity instrument equipped with a diode array detector and a Eclipse plus C18 reversed-phase column (3.5  $\mu\text{m}$ , 4.6 x 100 mm) maintained at room temperature. Acetonitrile/H<sub>2</sub>O (acetonitrile from 0%-90%) was used as eluent.

**Materials:** All solvents and reagents were purchased from commercial sources. All chemicals were from Aldrich except for 3-bromofuran (bought from China). All synthesized compounds used for quantum yield measurement were purified by repetitive column chromatography. Columns were prepared with silica gel (70-200 and 230-400 mesh). Basified silica was obtained by repetitive washing with hexane/NEt<sub>3</sub> (1:4; where NEt<sub>3</sub> is N,N-diethylethanamine). Tetrahydrofuran (THF), diethyl ether, and toluene were distilled from sodium/benzophenone under an atmosphere of dry nitrogen prior to use. Ag/AgCl wire was prepared by dipping silver wire in a solution of FeCl<sub>3</sub> and HCl. Films were washed with ethanol before performing spectroelectrochemistry. 2-(Tributylstannyl)-2,2'-bifuran and 2-(tributylstannyl)terfuran-2,2':5',2''-terfuran was prepared by a reported procedure.<sup>3</sup>

## Synthetic procedures

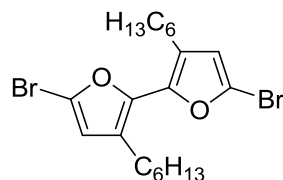


**3,3'-dibromo-2,2'-bifuran.** A solution of Lithium diisopropylamide (LDA) (56 mL, 2.0 M in hexane) was added dropwise to a solution of 3-bromo-furan (15 g, 102 mmol) in 65 mL dry tetrahydrofuran at -78 °C under N<sub>2</sub>. The reaction mixture was then stirred under the same conditions. After 1.5 h, CuCl<sub>2</sub> (15 g, 112 mmol) was added and the resulting solution was allowed to reach room temperature slowly and was stirred overnight. The reaction mixture was then added into 100 mL water with 5 g glycine at 0 °C, filtered, extracted with diethyl ether, dried (MgSO<sub>4</sub>) and evaporated. Flash column chromatography (silica gel, hexane) yielded **1** as a white powder (8.3 g, 55.7% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.47 (d, J = 1.9 Hz, 2H), 6.55 (d, J = 1.9 Hz, 2H).



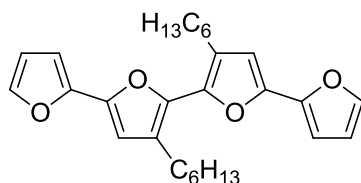
**3,3'-dihexyl-2,2'-bifuran.** A 2.0 M solution of C<sub>6</sub>H<sub>13</sub>MgBr in diethyl ether (27.4 mL, 54.8 mmol) was added into a solution of **1** (4 g, 13.7 mmol) and Ni(dppp)Cl<sub>2</sub> (520 mg, 0.96 mmol) in dry diethyl ether (60 mL) at 0 °C under N<sub>2</sub> and the reaction mixture was stirred and refluxed for 10 h. The resulting solution was then allowed to reach room temperature and was stirred overnight. The mixture was quenched with water at 0 °C, extracted with diethyl ether and HCl (10 mL, 1 M), dried (MgSO<sub>4</sub>), and evaporated. Flash column chromatography (silica gel, hexane) yielded **2F-2C<sub>6</sub>** as a colorless oil (3.2 g, 77% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.37 (d, J = 1.8 Hz, 1H), 6.36 (d, J =

1.8 Hz, 1H), 2.69–2.59 (t, J=7.5, 2H), 1.66–1.52 (t, J=7.5, 2H), 1.38–1.26 (m, 6H), 0.90 (t, J = 6.0, 5.0 Hz, 3H).



**2**

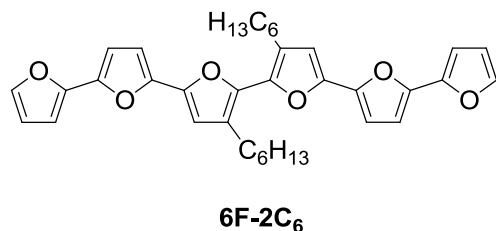
**5,5'-dibromo-3,3'-dihexyl-2,2'-bifuran.** N-Bromosuccinimide (NBS; 3.1 g, 15.5 mmol) was added into a solution of **2F-2C<sub>6</sub>** (2.3 g, 7.6 mmol) in benzene (70 mL) and the reaction mixture was stirred at room temperature for 20 min. Triethylamine (5 mL) was then added and the solvent was evaporated. The product was further purified by flash column chromatography (silica gel, hexane) to yield compound **2** (2.5 g, 71.6% yield) as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.26 (s, 2H), 2.66–2.42 (m, 4H), 1.56 (dd, J = 10.6, 4.3 Hz, 4H), 1.30 (dd, J = 5.7, 1.3 Hz, 12H), 0.90 (dt, J = 7.6, 4.4 Hz, 6H) ppm.



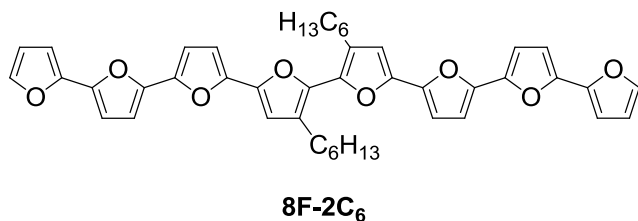
**4F-2C<sub>6</sub>**

**3'',4''-dihexyl-2,2':5',2'':5'',2'''-quaterfuran.** Pd(PPh<sub>3</sub>)<sub>4</sub> (597 mg, 0.517 mmol) was added into a solution of compound **2** (1.7 g, 3.69 mmol) and 2-tributyltinfuran (3.16 g, 7.36 mmol) in dry toluene (200 mL) and the reaction mixture was refluxed under N<sub>2</sub> for 20 h. The solvent was then evaporated and saturated KF solution (40 mL) and hexane (20 mL) were added. The resulting solution was filtered, extracted with hexane, dried (MgSO<sub>4</sub>), and evaporated. Flash column chromatography (silica gel, hexane) yielded compound **4F-2C<sub>6</sub>** (958 mg, 59.5% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.44–7.38 (m, 2H), 6.55–6.51 (m, 4H), 6.47 (dd, J = 3.3, 1.8 Hz, 2H), 2.83–2.65 (t, J=7.5, 4H),

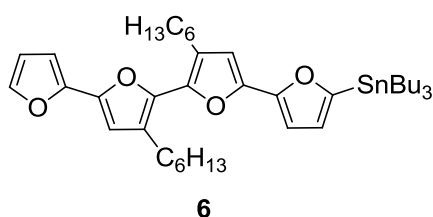
1.65 (t,  $J = 7.5, 6.9$  Hz, 4H), 1.50–1.21 (m, 12H), 0.89 (t,  $J = 6.0$ , 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.7, 144.7, 141.7, 141.5, 124.5, 111.5, 108.6, 104.8, 31.8, 30.2, 29.2, 25.3, 22.7, 14.1. HRMS (FD):  $m/z$  calcd for  $\text{C}_{28}\text{H}_{34}\text{O}_4$ : 434.2457; found: 434.2442. UV/Vis (dioxane):  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) 368 nm (27400).



**3''',4''-dihexyl-2,2':5'',2''':5''',2''''':5''''',2''''-sexifuran.** Pd ( $\text{PPh}_3$ )<sub>4</sub> (191 mg, 0.165 mmol) was added into a solution of compound **2** (1.08 g, 2.35 mmol) and 2-(tributylstannyl)-2,2'-bifuran (2.0 g, 4.73 mmol) in dry toluene (220 mL) and the reaction mixture was refluxed under  $\text{N}_2$  for 16 h. The solvent was then evaporated and saturated KF solution (40 mL) and hexane (30 mL) were added. The resulting solution was filtered, extracted with hexane, dried ( $\text{MgSO}_4$ ), and evaporated. Flash column chromatography on basified ( $\text{NEt}_3$ ) silica using hexane as eluent yielded **6F-2C<sub>6</sub>** (550 mg, 41.4 % yield).  $^1\text{H}$  NMR (300 MHz, DMSO):  $\delta$  7.79–7.76 (m, 2H), 6.86 (dd,  $J = 10.7, 4.5$  Hz, 4H), 6.78 (dd,  $J = 8.0, 3.5$  Hz, 4H), 6.65 (dd,  $J = 3.4, 1.8$  Hz, 2H), 2.72 (t,  $J = 7.5$  Hz, 4H), 1.62 (t,  $J = 7.5$  Hz, 4H), 1.48–1.13 (m, 12H), 0.81 (t,  $J = 6.0$  Hz, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  146.2, 145.7, 145.7, 144.4, 142.1, 141.8, 125.0, 111.5, 109.0, 107.0, 106.8, 105.4, 31.7, 30.2, 29.2, 25.2, 22.6, 13.8. HRMS (FD):  $m/z$  calcd for  $\text{C}_{36}\text{H}_{38}\text{O}_6$ : 566.2668; found: 566.2675. UV/Vis (dioxane):  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) 409 nm (52000).



**3'''',4'''-dihexyl-2,2':5',2'':5'',2''':5''',2''':5''',2''':5''',2''':5''',2''':5''',2''':5'''-octifuran.**

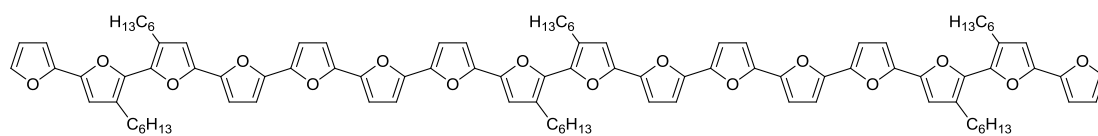


**2-(tributylstannyl)-3'',4'-dihexyl-2,2':5',2'':5'',2'''-quaterfuran.** A 2.5 M solution of n-BuLi in hexane (2 mL, 5 mmol) was added dropwise into a solution of **4F-2C<sub>6</sub>** (580 mg, 1.33 mmol) in dry THF (50 mL) at -78 °C under N<sub>2</sub>. The reaction mixture was stirred for 20 min at -78 °C. Bu<sub>3</sub>SnCl (0.4 mL, 1.5 mmol) was then added dropwise and the reaction was stirred for another 2 h under the same conditions. The mixture was quenched with water, extracted with hexane, dried (MgSO<sub>4</sub>), and evaporated. Repetitive flash chromatography on basified (NEt<sub>3</sub>) silica using hexane as eluent gave



BrC1=CC=C2C=C1OC2c3cc4cc(OC4=CC=C5C(=C3)OC(=C5)C6=CC=C(C(=C6)OC7=CC=C(C(=C7)OC8=CC=C(C(=C8)Br)OC9=CC=C(C(=C9)OC10=CC=C(C(=C10)OC11=CC=C(C(=C11)OC12=CC=C(C(=C12)OC13=CC=C(C(=C13)OC14=CC=C(C(=C14)OC15=CC=C(C(=C15)OC16=CC=C(C(=C16)OC17=CC=C(C(=C17)OC18=CC=C(C(=C18)OC19=CC=C(C(=C19)OC20=CC=C(C(=C20)OC21=CC=C(C(=C21)OC22=CC=C(C(=C22)OC23=CC=C(C(=C23)OC24=CC=C(C(=C24)OC25=CC=C(C(=C25)OC26=CC=C(C(=C26)OC27=CC=C(C(=C27)OC28=CC=C(C(=C28)OC29=CC=C(C(=C29)OC30=CC=C(C(=C30)OC31=CC=C(C(=C31)OC32=CC=C(C(=C32)OC33=CC=C(C(=C33)OC34=CC=C(C(=C34)OC35=CC=C(C(=C35)OC36=CC=C(C(=C36)OC37=CC=C(C(=C37)OC38=CC=C(C(=C38)OC39=CC=C(C(=C39)OC40=CC=C(C(=C40)OC41=CC=C(C(=C41)OC42=CC=C(C(=C42)OC43=CC=C(C(=C43)OC44=CC=C(C(=C44)OC45=CC=C(C(=C45)OC46=CC=C(C(=C46)OC47=CC=C(C(=C47)OC48=CC=C(C(=C48)OC49=CC=C(C(=C49)OC50=CC=C(C(=C50)OC51=CC=C(C(=C51)OC52=CC=C(C(=C52)OC53=CC=C(C(=C53)OC54=CC=C(C(=C54)OC55=CC=C(C(=C55)OC56=CC=C(C(=C56)OC57=CC=C(C(=C57)OC58=CC=C(C(=C58)OC59=CC=C(C(=C59)OC60=CC=C(C(=C60)OC61=CC=C(C(=C61)OC62=CC=C(C(=C62)OC63=CC=C(C(=C63)OC64=CC=C(C(=C64)OC65=CC=C(C(=C65)OC66=CC=C(C(=C66)OC67=CC=C(C(=C67)OC68=CC=C(C(=C68)OC69=CC=C(C(=C69)OC70=CC=C(C(=C70)OC71=CC=C(C(=C71)OC72=CC=C(C(=C72)OC73=CC=C(C(=C73)OC74=CC=C(C(=C74)OC75=CC=C(C(=C75)OC76=CC=C(C(=C76)OC77=CC=C(C(=C77)OC78=CC=C(C(=C78)OC79=CC=C(C(=C79)OC80=CC=C(C(=C80)OC81=CC=C(C(=C81)OC82=CC=C(C(=C82)OC83=CC=C(C(=C83)OC84=CC=C(C(=C84)OC85=CC=C(C(=C85)OC86=CC=C(C(=C86)OC87=CC=C(C(=C87)OC88=CC=C(C(=C88)OC89=CC=C(C(=C89)OC90=CC=C(C(=C90)OC91=CC=C(C(=C91)OC92=CC=C(C(=C92)OC93=CC=C(C(=C93)OC94=CC=C(C(=C94)OC95=CC=C(C(=C95)OC96=CC=C(C(=C96)OC97=CC=C(C(=C97)OC98=CC=C(C(=C98)OC99=CC=C(C(=C99)OC100=CC=C(C(=C100)OC101=CC=C(C(=C101)OC102=CC=C(C(=C102)OC103=CC=C(C(=C103)OC104=CC=C(C(=C104)OC105=CC=C(C(=C105)OC106=CC=C(C(=C106)OC107=CC=C(C(=C107)OC108=CC=C(C(=C108)OC109=CC=C(C(=C109)OC110=CC=C(C(=C110)OC111=CC=C(C(=C111)OC112=CC=C(C(=C112)OC113=CC=C(C(=C113)OC114=CC=C(C(=C114)OC115=CC=C(C(=C115)OC116=CC=C(C(=C116)OC117=CC=C(C(=C117)OC118=CC=C(C(=C118)OC119=CC=C(C(=C119)OC120=CC=C(C(=C120)OC121=CC=C(C(=C121)OC122=CC=C(C(=C122)OC123=CC=C(C(=C123)OC124=CC=C(C(=C124)OC125=CC=C(C(=C125)OC126=CC=C(C(=C126)OC127=CC=C(C(=C127)OC128=CC=C(C(=C128)OC129=CC=C(C(=C129)OC130=CC=C(C(=C130)OC131=CC=C(C(=C131)OC132=CC=C(C(=C132)OC133=CC=C(C(=C133)OC134=CC=C(C(=C134)OC135=CC=C(C(=C135)OC136=CC=C(C(=C136)OC137=CC=C(C(=C137)OC138=CC=C(C(=C138)OC139=CC=C(C(=C139)OC140=CC=C(C(=C140)OC141=CC=C(C(=C141)OC142=CC=C(C(=C142)OC143=CC=C(C(=C143)OC144=CC=C(C(=C144)OC145=CC=C(C(=C145)OC146=CC=C(C(=C146)OC147=CC=C(C(=C147)OC148=CC=C(C(=C148)OC149=CC=C(C(=C149)OC150=CC=C(C(=C150)OC151=CC=C(C(=C151)OC152=CC=C(C(=C152)OC153=CC=C(C(=C153)OC154=CC=C(C(=C154)OC155=CC=C(C(=C155)OC156=CC=C(C(=C156)OC157=CC=C(C(=C157)OC158=CC=C(C(=C158)OC159=CC=C(C(=C159)OC160=CC=C(C(=C160)OC161=CC=C(C(=C161)OC162=CC=C(C(=C162)OC163=CC=C(C(=C163)OC164=CC=C(C(=C164)OC165=CC=C(C(=C165)OC166=CC=C(C(=C166)OC167=CC=C(C(=C167)OC168=CC=C(C(=C168)OC169=CC=C(C(=C169)OC170=CC=C(C(=C170)OC171=CC=C(C(=C171)OC172=CC=C(C(=C172)OC173=CC=C(C(=C173)OC174=CC=C(C(=C174)OC175=CC=C(C(=C175)OC176=CC=C(C(=C176)OC177=CC=C(C(=C177)OC178=CC=C(C(=C178)OC179=CC=C(C(=C179)OC180=CC=C(C(=C180)OC181=CC=C(C(=C181)OC182=CC=C(C(=C182)OC183=CC=C(C(=C183)OC184=CC=C(C(=C184)OC185=CC=C(C(=C185)OC186=CC=C(C(=C186)OC187=CC=C(C(=C187)OC188=CC=C(C(=C188)OC189=CC=C(C(=C189)OC190=CC=C(C(=C190)OC191=CC=C(C(=C191)OC192=CC=C(C(=C192)OC193=CC=C(C(=C193)OC194=CC=C(C(=C194)OC195=CC=C(C(=C195)OC196=CC=C(C(=C196)OC197=CC=C(C(=C197)OC198=CC=C(C(=C198)OC199=CC=C(C(=C199)OC200=CC=C(C(=C200)OC201=CC=C(C(=C201)OC202=CC=C(C(=C202)OC203=CC=C(C(=C203)OC204=CC=C(C(=C204)OC205=CC=C(C(=C205)OC206=CC=C(C(=C206)OC207=CC=C(C(=C207)OC208=CC=C(C(=C208)OC209=CC=C(C(=C209)OC210=CC=C(C(=C210)OC211=CC=C(C(=C211)OC212=CC=C(C(=C212)OC213=CC=C(C(=C213)OC214=CC=C(C(=C214)OC215=CC=C(C(=C215)OC216=CC=C(C(=C216)OC217=CC=C(C(=C217)OC218=CC=C(C(=C218)OC219=CC=C(C(=C219)OC220=CC=C(C(=C220)OC221=CC=C(C(=C221)OC222=CC=C(C(=C222)OC223=CC=C(C(=C223)OC224=CC=C(C(=C224)OC225=CC=C(C(=C225)OC226=CC=C(C(=C226)OC227=CC=C(C(=C227)OC228=CC=C(C(=C228)OC229=CC=C(C(=C229)OC230=CC=C(C(=C230)OC231=CC=C(C(=C231)OC232=CC=C(C(=C232)OC233=CC=C(C(=C233)OC234=CC=C(C(=C234)OC235=CC=C(C(=C235)OC236=CC=C(C(=C236)OC237=CC=C(C(=C237)OC238=CC=C(C(=C238)OC239=CC=C(C(=C239)OC240=CC=C(C(=C240)OC241=CC=C(C(=C241)OC242=CC=C(C(=C242)OC243=CC=C(C(=C243)OC244=CC=C(C(=C244)OC245=CC=C(C(=C245)OC246=CC=C(C(=C246)OC247=CC=C(C(=C247)OC248=CC=C(C(=C248)OC249=CC=C(C(=C249)OC250=CC=C(C(=C250)OC251=CC=C(C(=C251)OC252=CC=C(C(=C252)OC253=CC=C(C(=C253)OC254=CC=C(C(=C254)OC255=CC=C(C(=C255)OC256=CC=C(C(=C256)OC257=CC=C(C(=C257)OC258=CC=C(C(=C258)OC259=CC=C(C(=C259)OC260=CC=C(C(=C260)OC261=CC=C(C(=C261)OC262=CC=C(C(=C262)OC263=CC=C(C(=C263)OC264=CC=C(C(=C264)OC265=CC=C(C(=C265)OC266=CC=C(C(=C266)OC267=CC=C(C(=C267)OC268=CC=C(C(=C268)OC269=CC=C(C(=C269)OC270=CC=C(C(=C270)OC271=CC=C(C(=C271)OC272=CC=C(C(=C272)OC273=CC=C(C(=C273)OC274=CC=C(C(=C274)OC275=CC=C(C(=C275)OC276=CC=C(C(=C276)OC277=CC=C(C(=C277)OC278=CC=C(C(=C278)OC279=CC=C(C(=C279)OC280=CC=C(C(=C280)OC281=CC=C(C(=C281)OC282=CC=C(C(=C282)OC283=CC=C(C(=C283)OC284=CC=C(C(=C284)OC285=CC=C(C(=C285)OC286=CC=C(C(=C286)OC287=CC=C(C(=C287)OC288=CC=C(C(=C288)OC289=CC

**5,5'-dibromo-3,4'-dihexyl-2,2':5',2'':5'',2''':5''',2''':5''',2''':5''',2''':5'''-octifuran.** NBS (55.9 mg, 0.28 mmol) was slowly added into a solution of **8F-2C<sub>6</sub>** (100 mg, 0.14 mmol) in benzene (60 mL) in an ice/water bath. The reaction mixture was then stirred at room temperature for 20 min. Triethylamine (7 mL) was then added and the solvent was evaporated. The product was further purified by repetitive flash column chromatography on basified (NEt<sub>3</sub>) silica using hexane/ethyl acetate (1:10) as eluent to give **7** as an orange powder (102 mg, 83 % yield). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.8–6.57 (m, 12H), 6.45 (d, J = 3.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 4H), 1.69 (t, J = 7.5 Hz, 4H), 1.52–1.23 (m, 12H), 0.93–0.79 (t, J = 6.0, 6H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 147.96, 146.02, 145.70, 145.12, 144.67, 144.23, 141.85, 125.06, 121.60, 113.38, 109.31, 107.76, 107.72, 107.70, 107.21, 106.94, 31.81, 30.26, 29.21, 25.29, 22.70, 13.89. HRMS (FD): m/z calcd for C<sub>44</sub>H<sub>40</sub>Br<sub>2</sub>O<sub>8</sub>; 856.1075; found: 856.0954.

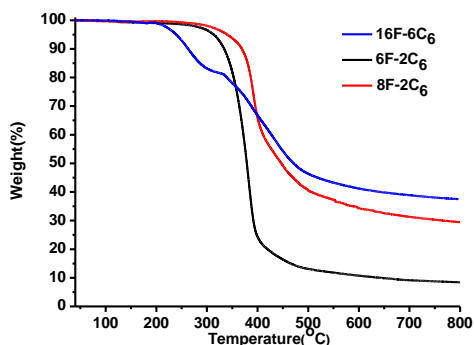


S9

**16F-6C<sub>6</sub>**. Pd (PPh<sub>3</sub>)<sub>4</sub> (75 mg, 0.065 mmol) was added into a solution of compound **6** (783 mg, 1.08 mmol) and compound **7** (200 mg, 0.23 mmol) in dry toluene (150 mL) and the reaction mixture was refluxed under N<sub>2</sub> for 18 h. The solvent was then evaporated and KF solution (300 mg KF in 40 mL H<sub>2</sub>O) and diethyl ether (40 mL) were added. The resulting solution was stirred for 20 min, filtered, extracted with ether, dried (MgSO<sub>4</sub>), and evaporated. Flash column chromatography on basified (NEt<sub>3</sub>) silica using hexane/ethyl acetate (7:3) as eluent yielded **16F-6C<sub>6</sub>** (205 mg crude product). The pure compound was obtained by repeated flash column chromatography of the crude product using hexane/ethyl acetate (hexane from 100% to 70%) as eluent (115 mg, 32 % yield). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.45 (s, 2H), 6.85 – 6.60 (m, 20H), 6.57 (d, J = 4.1 Hz, 4H), 6.50 (dd, J = 3.3, 1.8 Hz, 2H), 2.90 – 2.68 (t, J = 7.5, 12H), 1.76 – 1.64 (t, J = 7.5, 12H), 1.41 – 1.28 (m, 36H), 0.88 (t, J = 6.0 Hz, 18H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 146.58, 146.03, 145.70, 145.52, 145.28, 144.86, 144.26, 141.97, 141.47, 131.58, 131.48, 128.62, 128.49, 124.96, 111.50, 109.22, 108.63, 107.65, 107.45, 106.97, 105.00, 31.78, 31.76, 31.75, 31.70, 30.25, 30.24, 29.69, 29.23, 29.20, 29.15, 25.27, 25.24, 22.69, 13.87. HRMS (FD): m/z calcd for C<sub>100</sub>H<sub>106</sub>O<sub>16</sub> ([M+H]<sup>+</sup>): 1564.7593; found: 1564.7548. UV/Vis (dioxane): λ<sub>max</sub> (ε/ M<sup>-1</sup>cm<sup>-1</sup>) 451 nm (124000).

### Thermal properties

The thermal properties of the **nF-2C<sub>6</sub>** (n = 4, 6, 8) series and **16F-6C<sub>6</sub>** were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The resulting TGA curves showed the **nF-2C<sub>6</sub>** series to be stable in the solid state, with stability similar to that of unsubstituted oligofurans **nF** (n = 4, 6, 8). For example, **8F-2C<sub>6</sub>** is stable up to 260 °C under a nitrogen atmosphere compared with 250 °C for 8F. The decomposition temperature of the 16-mer **16F-6C<sub>6</sub>** is slightly lower than that of the shorter **nF-2C<sub>6</sub>** (n = 4, 6, 8) series, but it is still stable up to 180 °C under a nitrogen atmosphere (Figure 1a), which suggests that it can satisfy the stability requirements for applications in organic electronic devices.

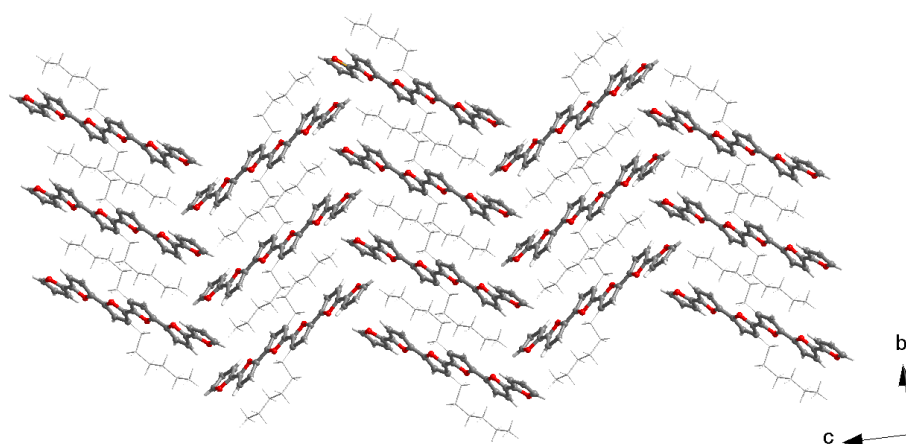


**Figure S1:** Thermogravimetric analysis (TGA) of **6F-2C<sub>6</sub>**, **8F-2C<sub>6</sub>** and **16F-6C<sub>6</sub>**.

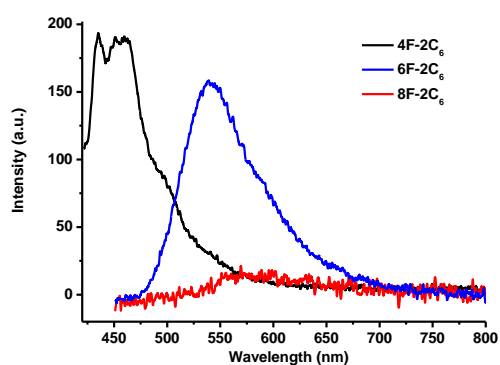
### General X-ray Procedures:

X-ray diffraction data for **6F-2C<sub>6</sub>** were collected on a Bruker KappaAPEX II CCD diffractometer, MoK $\alpha$  ( $\lambda = 0.71073$  Å), graphite monochromator,  $-9 < h < 9$ ,  $-7 < k < 8$ ,  $-30 < l < 30$ ,  $2\theta_{\max} = 50.7$ , frame scan width =  $0.5^\circ$ , scan speed  $1.0^\circ$  per 60 sec,  $T = 100(2)$  K. The structure was solved with Bruker Autostucture and refined by full matrix least-squares based on  $F^2$  with SHELXL-97.

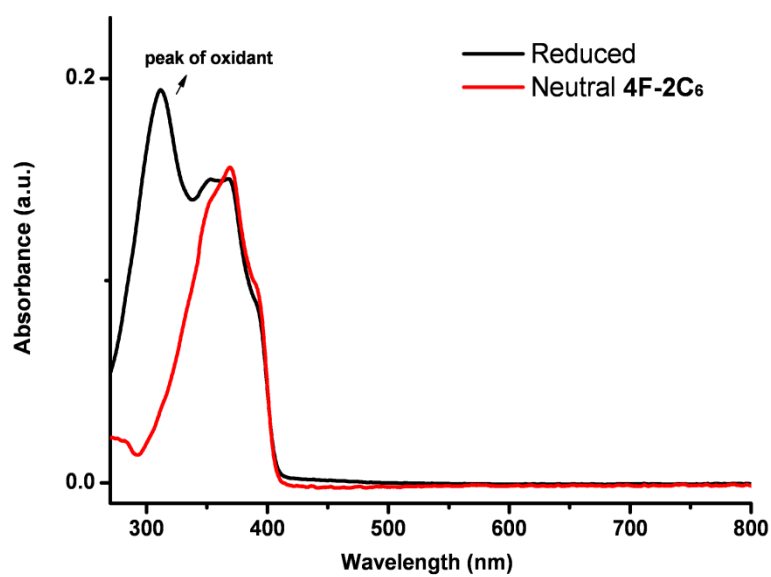
$C_{36}H_{38}O_6$ , yellow plate,  $0.20 \times 0.16 \times 0.03$  mm<sup>3</sup>, triclinic, P-1,  $a = 8.2211(9)$  Å,  $b = 7.3440(8)$  Å,  $c = 25.041(3)$  Å,  $\alpha = 90.015(4)^\circ$ ,  $\beta = 94.660(3)^\circ$ ,  $\gamma = 90.010(4)^\circ$ ,  $Z = 2$ ,  $F_w = 566.66$ ,  $D_c = 1.249$  Mg·m<sup>-3</sup>,  $\mu = 0.084$  mm<sup>-1</sup>, 19329 reflections collected, 5429 independent reflections ( $R_{\text{int}} = 0.051$ ), final  $R_1 = 0.0697$  (based on  $F^2$ ) for data with  $I > 2\sigma(I)$  and  $R_1 = 0.886$  on 5429 reflections, goodness-of-fit on  $F^2 = 1.073$ , largest density peak  $0.286$  e Å<sup>-3</sup>, largest hole  $-0.313$  e Å<sup>-3</sup>.

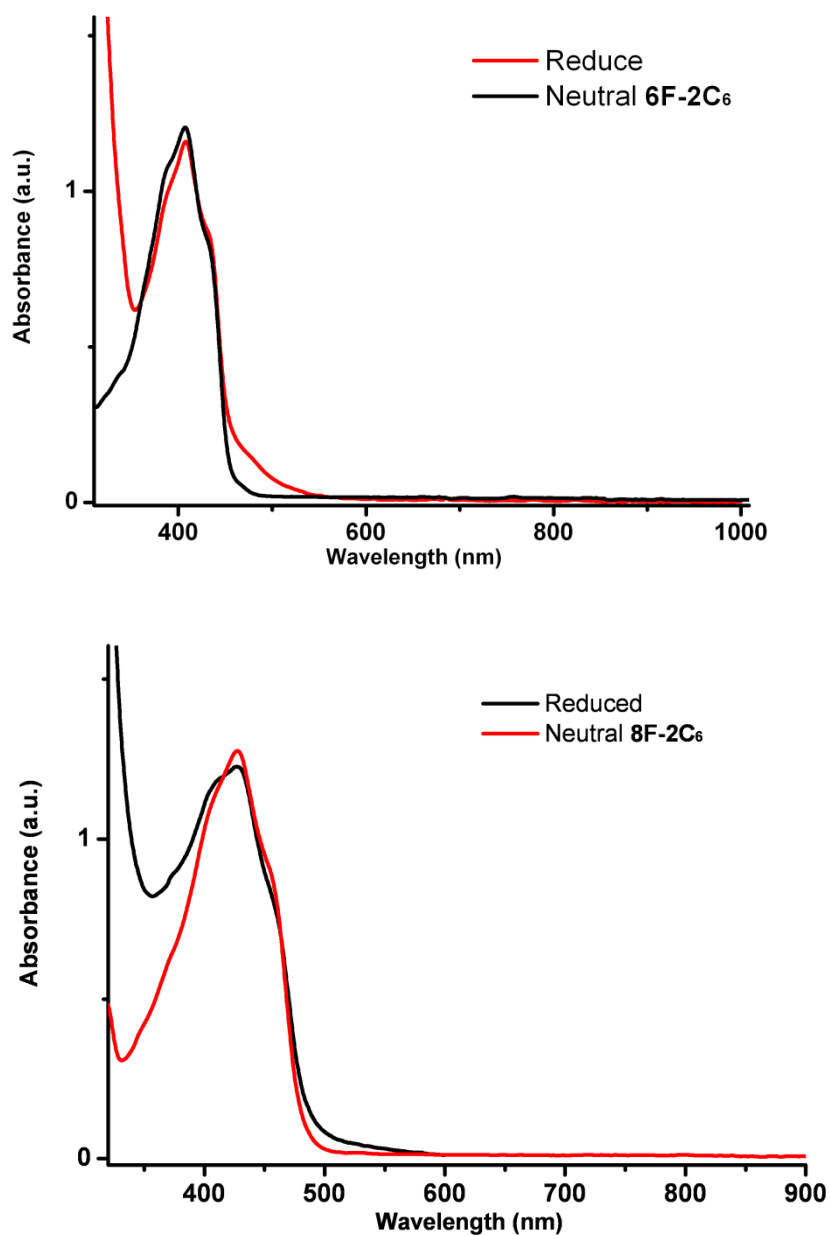


**Figure S2:** Herringbone structure of **6F-2C<sub>6</sub>**. Partial alky side chains are deleted for clarity.

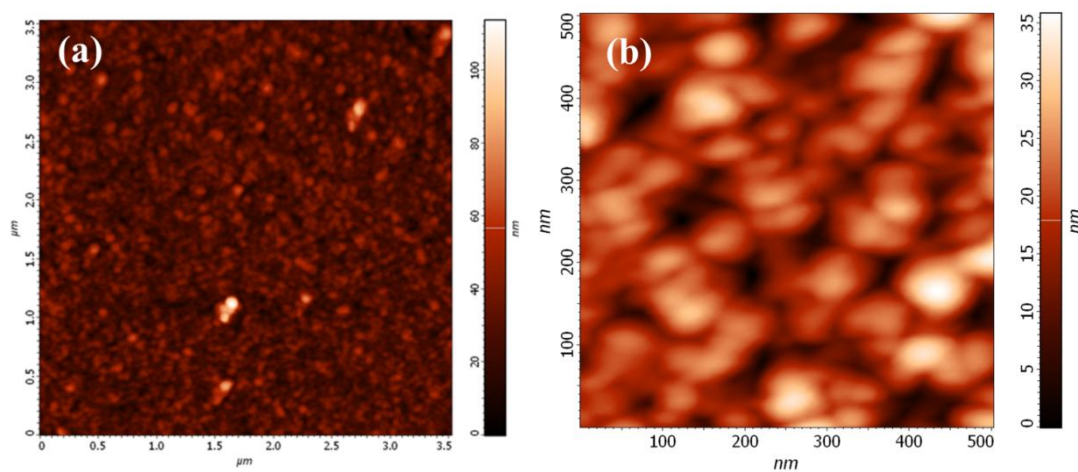


**Figure S3:** Fluorescence spectra of **nF-2C<sub>6</sub>** ( $n = 4, 6, 8$ ) in the solid state (powder). Insert: photograph of powders (from left to right: **4F-2C<sub>6</sub>**, **6F-2C<sub>6</sub>**, **8F-2C<sub>6</sub>**, **16F-6C<sub>6</sub>**) under ambient light (left) and UV light (right) at a wavelength of 365 nm.

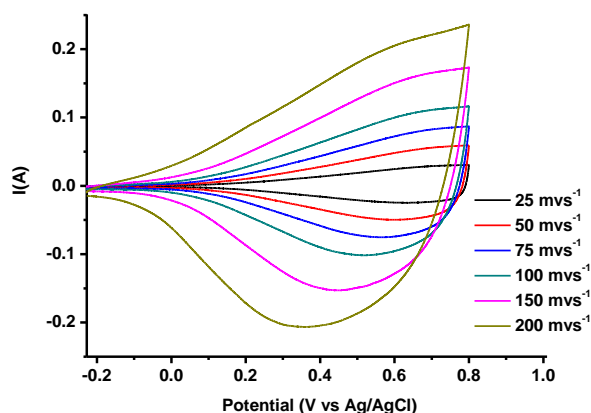




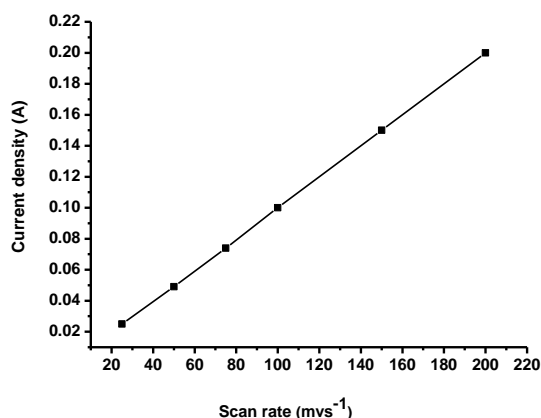
**Figure S4:** Absorption spectra of  $nF-2C_6$  ( $n = 4, 6, 8$ ) in neutral states and their corresponding reduced spectra of radical cations using hydrazine as a reducing agent.



**Figure S5.** AFM height images of the topography of polyfuran film prepared from **16F-6C<sub>6</sub>** on an ITO-coated glass surface by electrochemical polymerization. (a)  $3.5 \times 3.5 \mu\text{m}$  square with RMS of 8.6 nm. (b)  $500 \times 500 \text{ nm}$  square with RMS of 5.8 nm.



**Figure S6.** CV of poly(**16F-6C<sub>6</sub>**) thin film on ITO glass in DCE with 0.1 M TBABF<sub>4</sub> at different scan speeds.

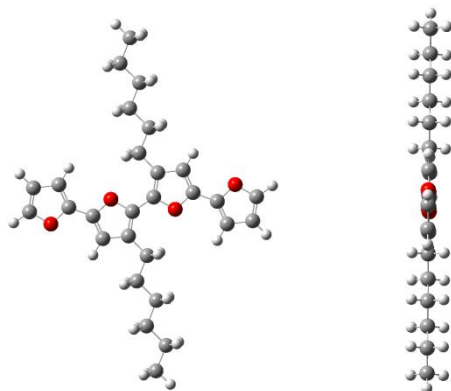


**Figure S7.** Plots of the current density against the scan speed for poly(**16F-6C<sub>6</sub>**) thin film in DCE with 0.1 M TBABF<sub>4</sub>.

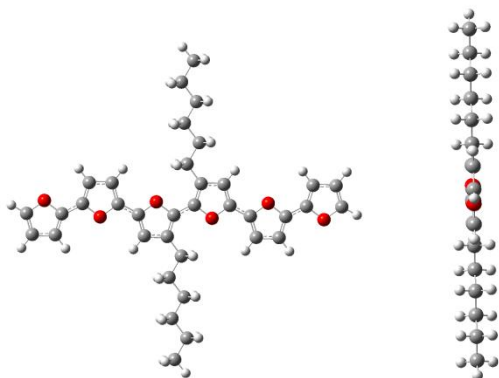
### Details of computations.

All calculations were performed using the Gaussian 09<sup>4</sup> series of programs. The commonly used Becke's three parameter exchange functional combined with the LYP correlation functional (B3LYP) was used for the calculations. The geometries of **nF-2C<sub>6</sub>** ( $n = 4, 6, 8$ ) and **16F-6C<sub>6</sub>** were fully optimized using the 6-31G (d) basis set (B3LYP/6-31G (d)). The optimized geometries of **nF-2C<sub>6</sub>** ( $n = 4, 6, 8$ ) were further

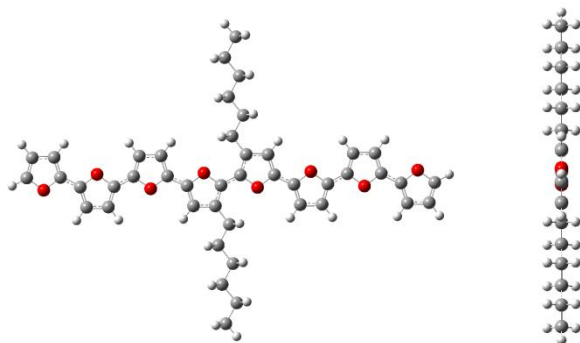
confirmed as minima by carrying out frequency calculations. No symmetry constraints were applied during geometry optimization. TD-DFT calculations of **nF-2C<sub>6</sub>** (n = 4, 6, 8) and **16F-6C<sub>6</sub>** for UV and fluorescence spectra were performed at the B3LYP/6-31G(d) level. Geometry optimization at the TD/B3LYP/6-31G(d) level was performed to calculate the first excited state. These geometries were used for calculations of fluorescence spectra.



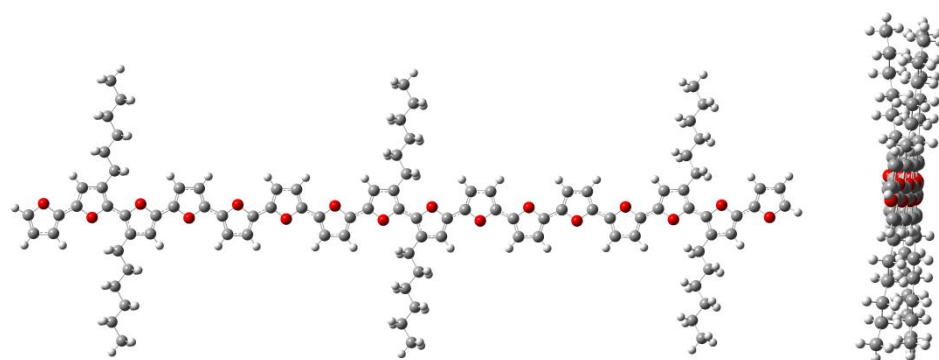
**4F-2C<sub>6</sub>** (-1388.312174 a.u.)



**6F-2C<sub>6</sub>** (-1845.993251 a.u.)

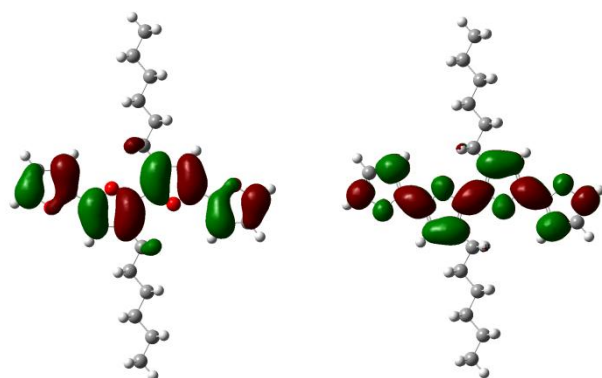


**8F-2C<sub>6</sub>** (-2203.674072 a.u.)

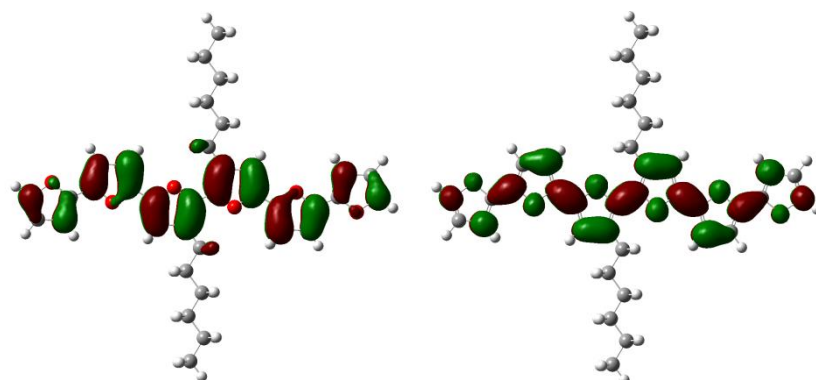


**16F-6C<sub>6</sub>** (-5077.940991 a.u.)

**Figure S8.** Optimized structures of **nF-2C<sub>6</sub>** (n = 4, 6, 8) and **16F-6C<sub>6</sub>** and their side views at the B3LYP/6-31G(d) level. The absolute energy for each compound is given in parentheses.

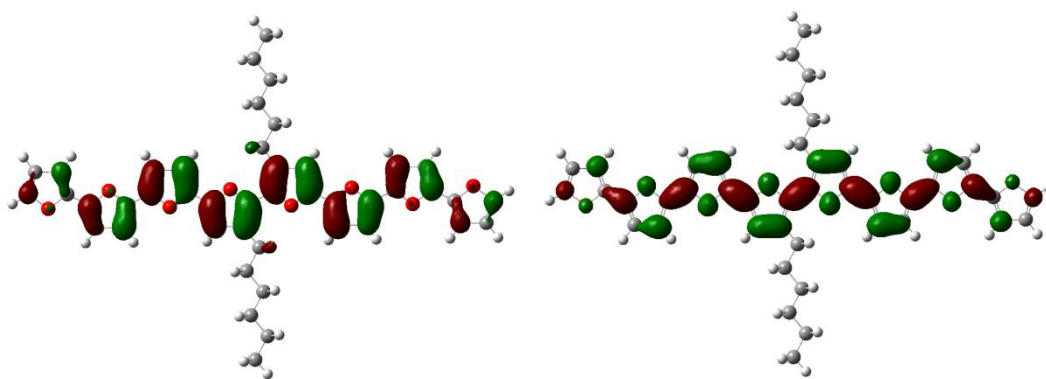


HOMO (left) and LUMO (right) of **4F-2C<sub>6</sub>**

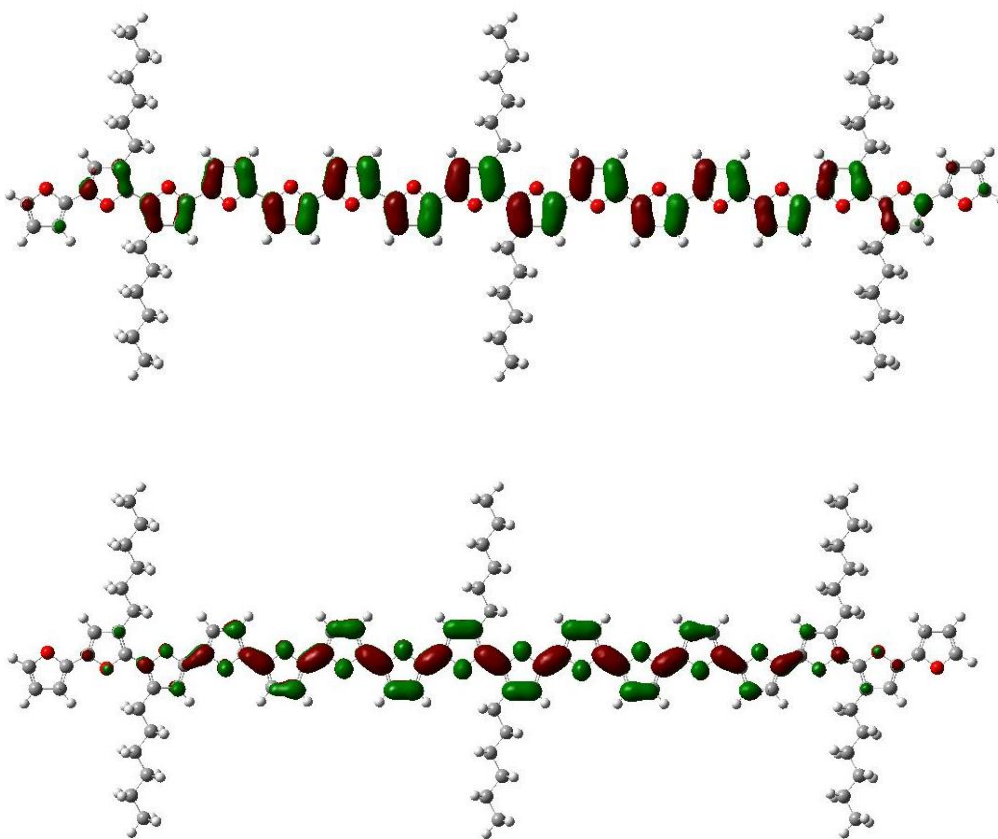


HOMO (left) and LUMO (right) of **6F-2C<sub>6</sub>**





HOMO (left) and LUMO (right) of **8F-2C<sub>6</sub>**



HOMO (upper panel) and LUMO (lower panel) of **16F-6C<sub>6</sub>**.

**Figure S9.** Frontier orbitals of representative **nF-2C<sub>6</sub>** ( $n = 4, 6, 8$ ) and **16F-6C<sub>6</sub>** at the B3LYP/6-31G(d) level.

**Table S1.** Calculated (at the TD-B3LYP/6-31G (d) level of theory) and experimental absorption and emission spectra of **nF-2C<sub>6</sub>** (n = 4, 6, 8) and **16F-6C<sub>6</sub>**.

	Total energy, a.u	E <sub>HOMO</sub> eV	E <sub>LUMO</sub> eV	UV-Absorption			Emission	
				Exp, nm	Calc, nm ( <i>f<sub>ex</sub></i> )	Orbitals involved in electronic transition	Exp, nm (0-0')	Calc, nm ( <i>f<sub>em</sub></i> )
<b>4F-2C<sub>6</sub></b>	-1388.312174	-4.50	-1.19	368	395 (1.06)	HOMO→LUMO (100%)	402	443 (1.13)
<b>6F-2C<sub>6</sub></b>	-1845.993251	-4.38	-1.47	409	466 (1.76)	HOMO→LUMO (100%)	450	527 (1.91)
<b>8F-2C<sub>6</sub></b>	-2203.674072	-4.33	-1.62	428	512 (2.37)	HOMO→LUMO (100%)	473	585 (2.59)
<b>16F-6C<sub>6</sub></b>	-5077.940991	-4.23	-1.77	451	591 (4.80)	HOMO→LUMO (87%) HOMO-1→LUMO+1 (8%)	499	682 (4.91)

*f<sub>ex</sub>* and *f<sub>em</sub>* are the calculated oscillator strength for absorption and emission transition respectively and are given in parentheses along with the corresponding wavelength of absorption or emission.

#### Calculation of twisting energy for **4F-2C<sub>6</sub>**, **4T-2C<sub>6</sub>**, **16F-6C<sub>6</sub>** and **16T-6C<sub>6</sub>**.

The geometry was optimized, setting the dihedral angles between the carbon atoms of adjacent rings and the dihedral angle between the four external carbons of the two external rings to constant values (see table S2 and S3).

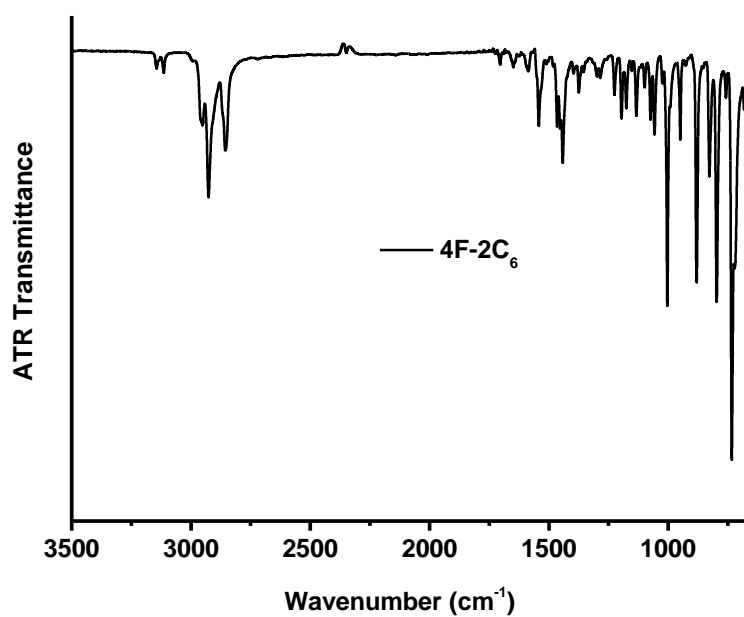
**Table S2:** Values for twisting energy of **4F-2C<sub>6</sub>** and **4T-2C<sub>6</sub>** calculated at B3LYP/6-31G(d).

Twist angew	energy <b>4F-2C<sub>6</sub></b>	ΔE <sub>4F-2C<sub>6</sub></sub> (kcal/mol)	energy <b>4T-2C<sub>6</sub></b>	ΔE <sub>4T-2C<sub>6</sub></sub> (kcal/mol)
0	-1388.312174	0	-2680.209767	2.240394
10	-1388.311297	0.549959	-2680.210285	1.915788
20	-1388.310445	1.084349	-2680.211436	1.194110
30	-1388.306090	3.814742	-2680.213050	0.182072
40	-1388.301794	6.508294	-2680.213340	0

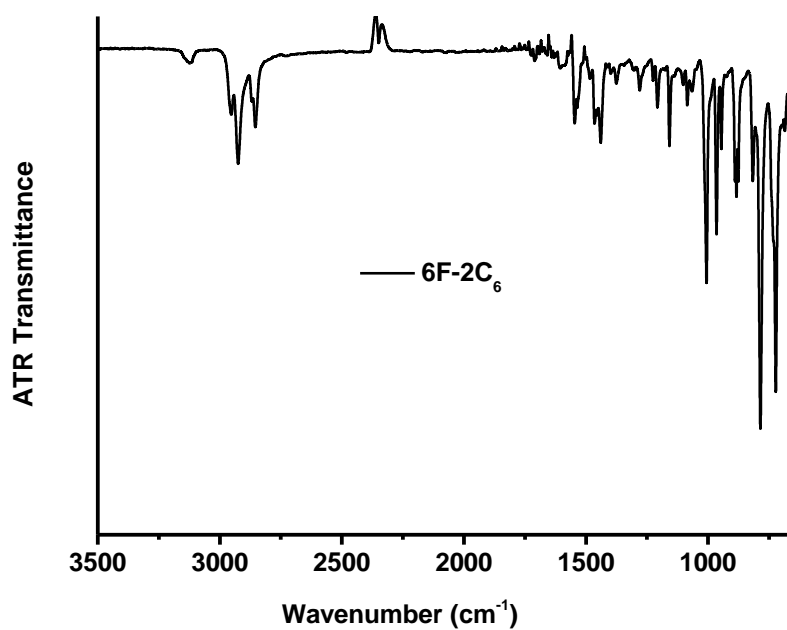
**Table S3:** Values for twisting energy of **16F-6C<sub>6</sub>** and **16T-6C<sub>6</sub>** calculated at B3LYP/6-31G(d).

Twist angew	energy <b>16F-6C<sub>6</sub></b>	$\Delta E_{16F-6C_6}$ (kcal/mol)	energy <b>16T-6C<sub>6</sub></b>	$\Delta E_{16T-6C_6}$ (kcal/mol)
0	-5077.940986	0	-10245.519526	2.484764
10	-5077.940059	0.5810886	-10245.521523	1.232225
15	-5077.935098	3.6912251	-10245.522475	0.635768
20	-5077.929206	7.3857545	-10245.523184	0.190793
25	-5077.924114	10.578246	-10245.523489	0

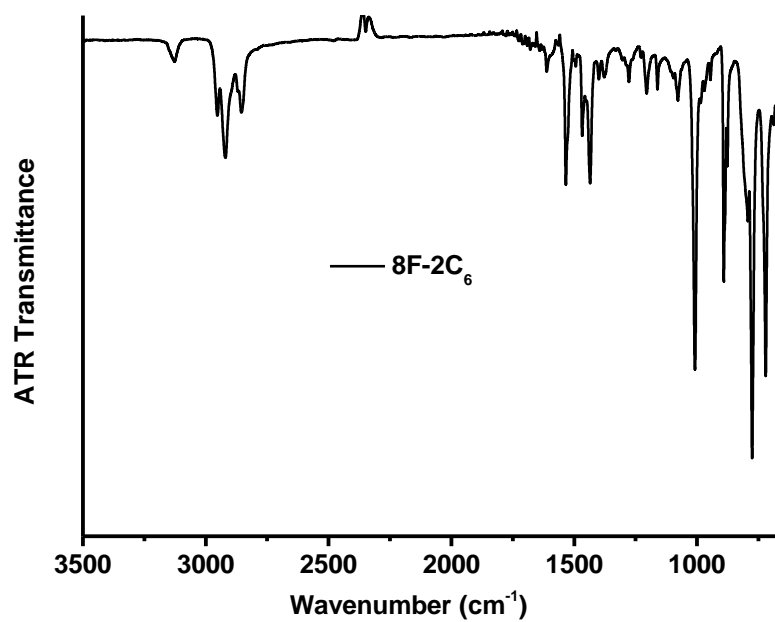
**FTIR-ATR spectra**



**Figure S10.** FTIR-ATR spectra of **4F-2C<sub>6</sub>**.



**Figure S11** FTIR-ATR spectra of 6F-2C<sub>6</sub>.



**Figure S12.** FTIR-ATR spectra of 8F-2C<sub>6</sub>.

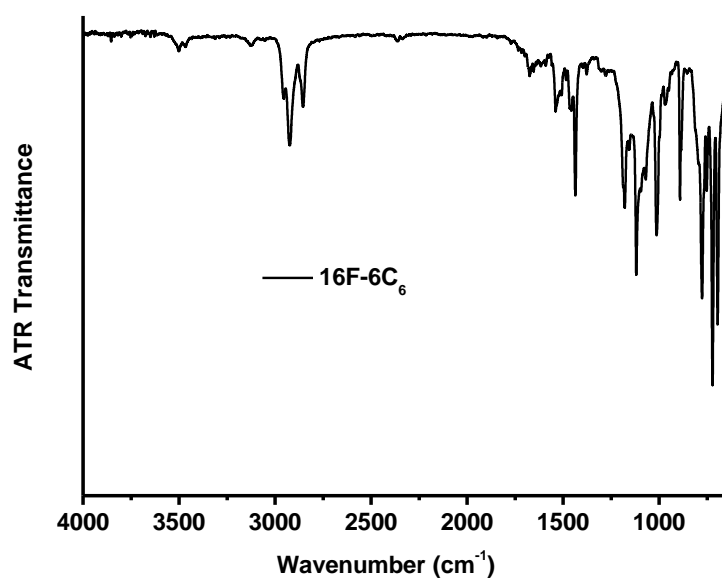
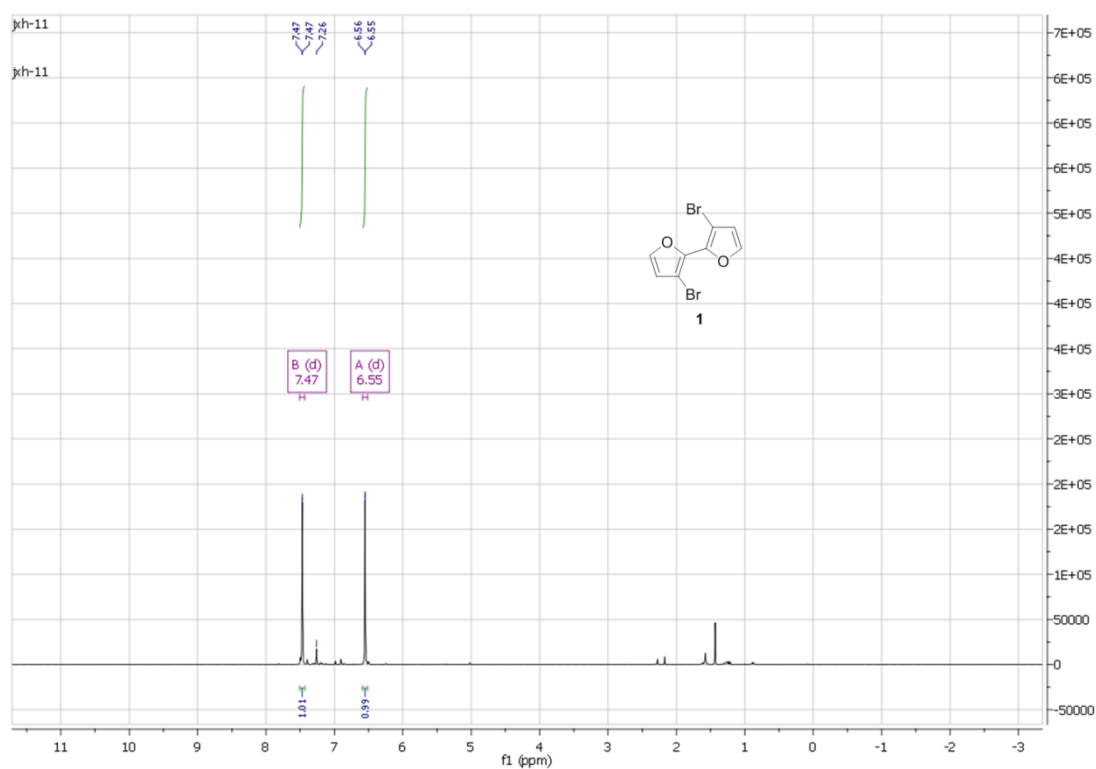
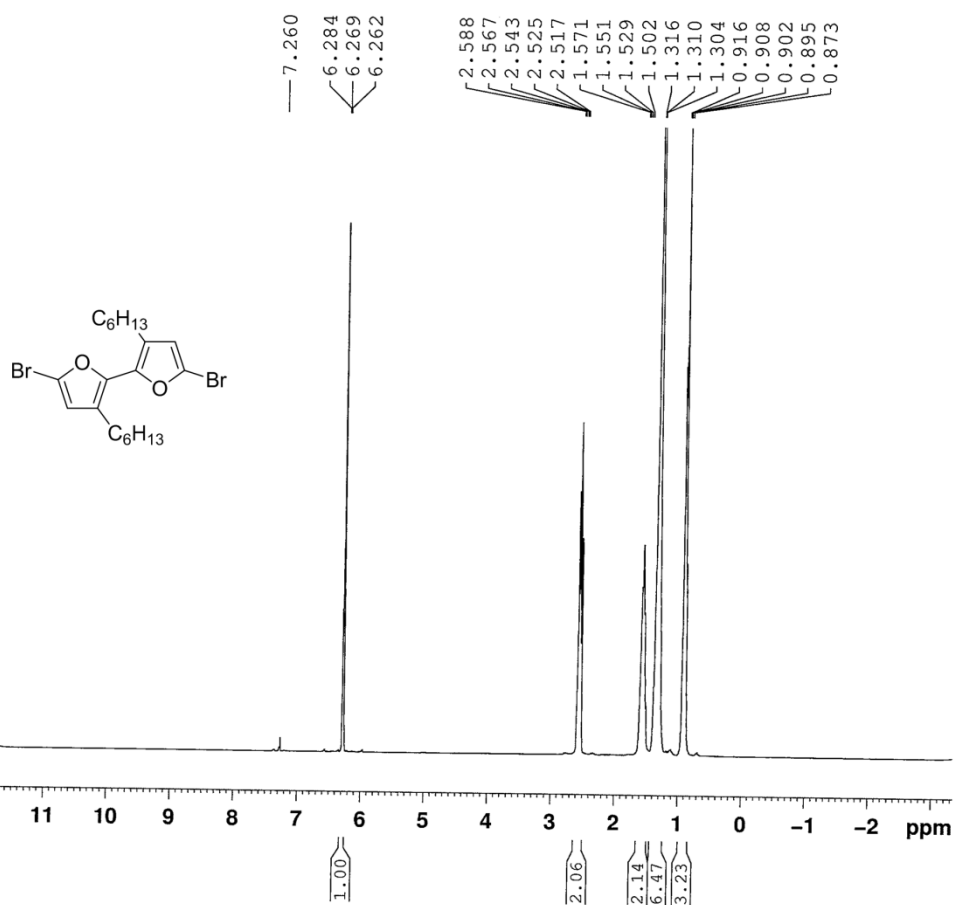
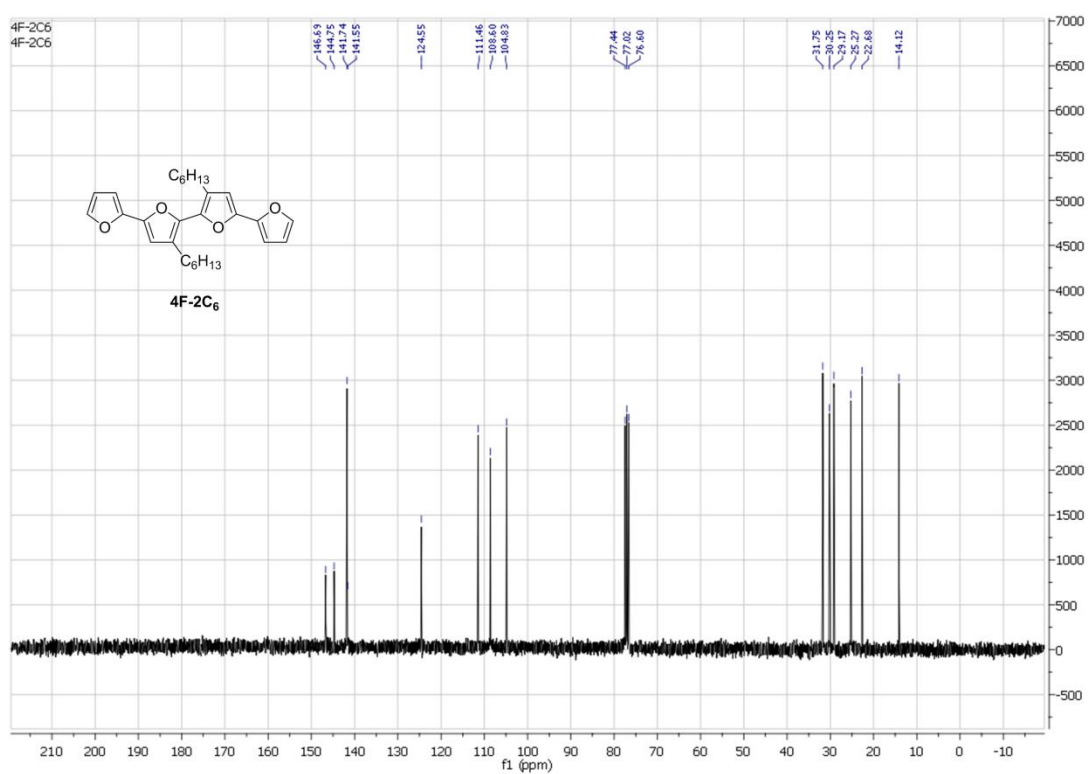
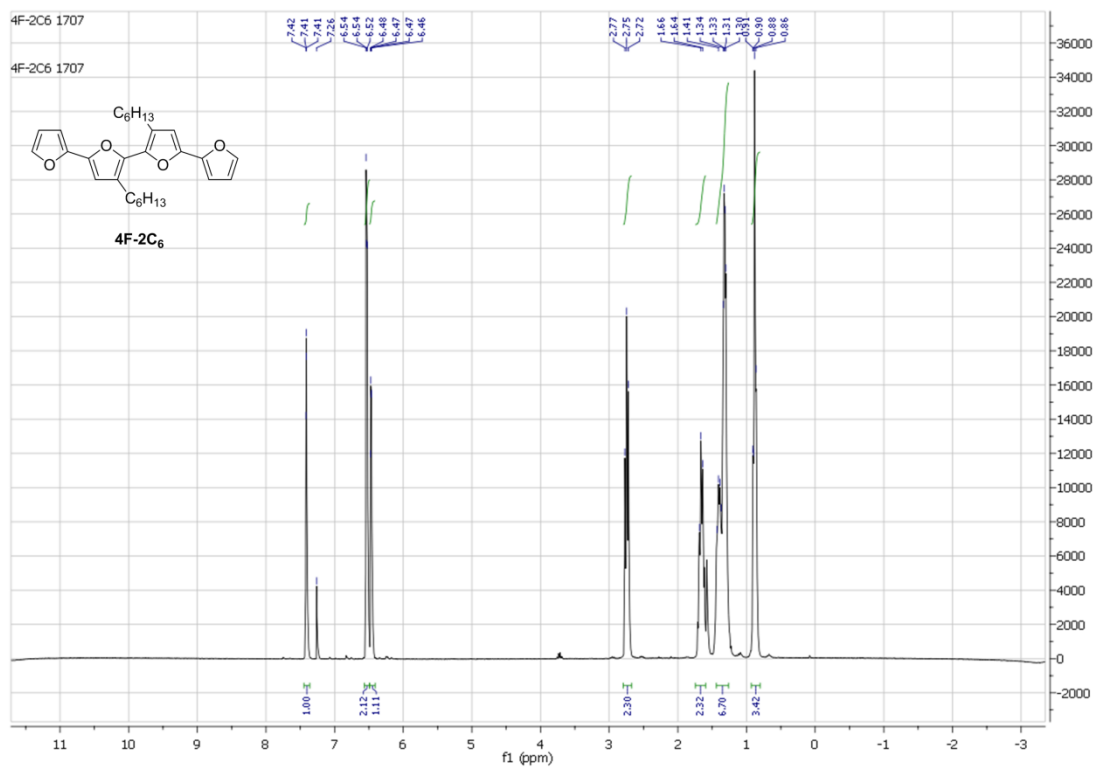


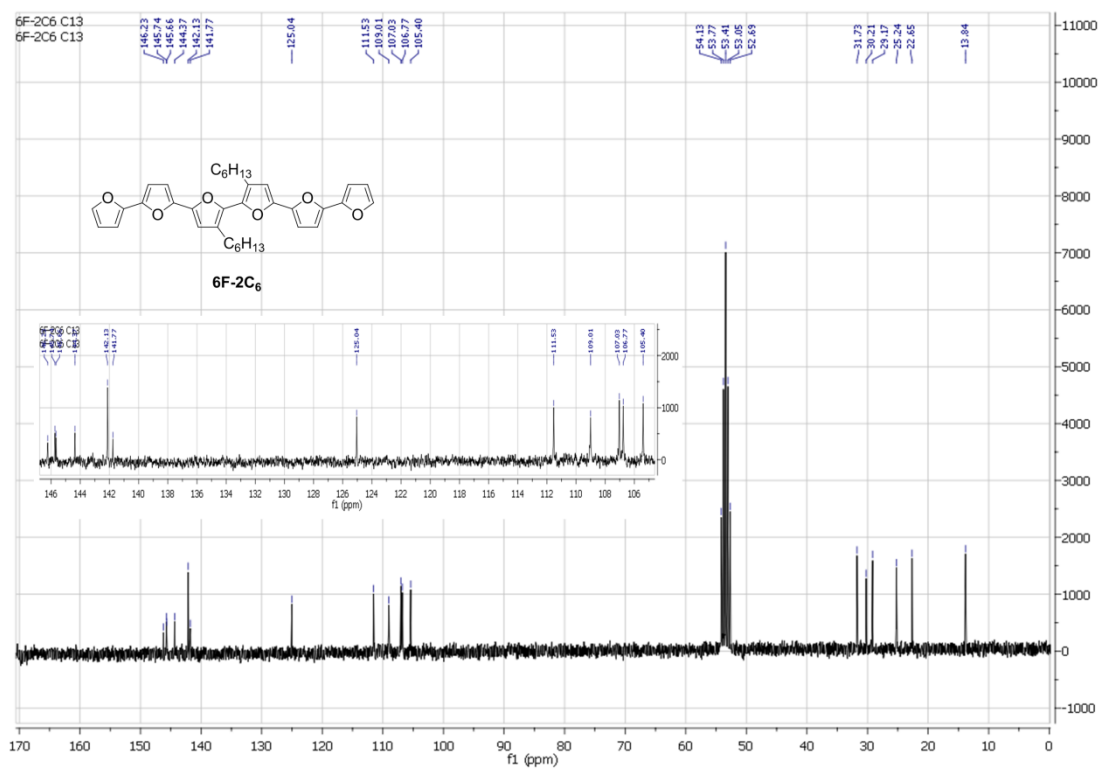
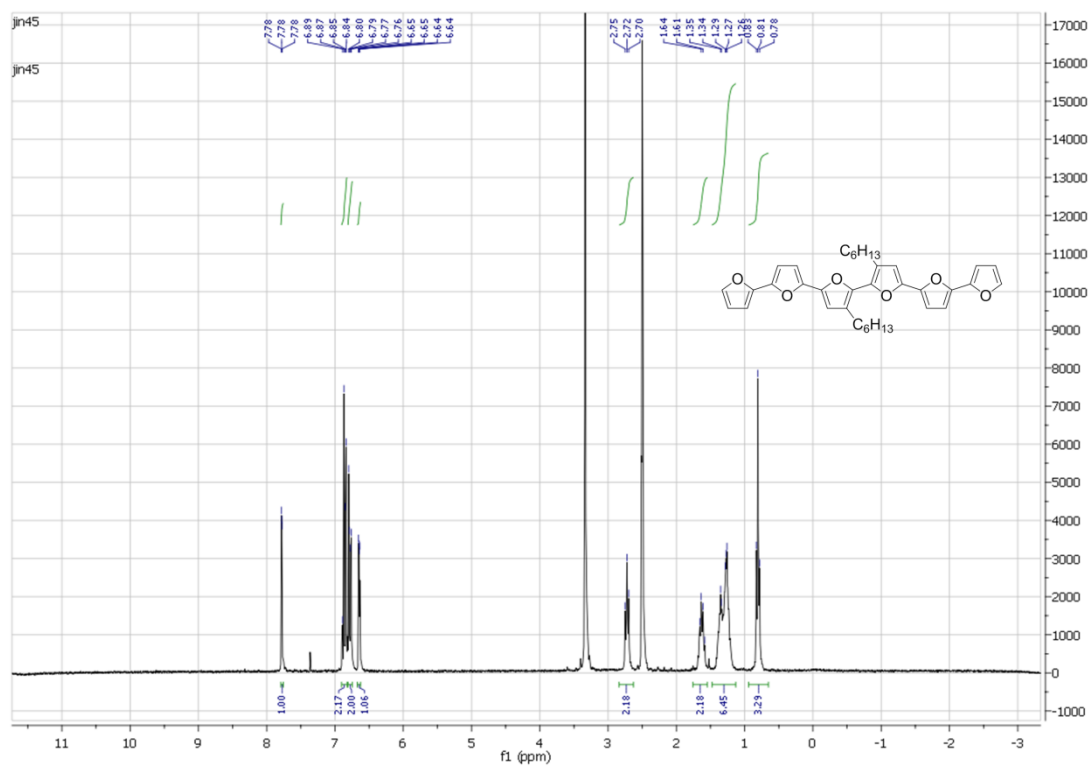
Figure S13. FTIR-ATR spectra of 16F-6C<sub>6</sub>.

### <sup>1</sup>H and <sup>13</sup>C NMR spectra

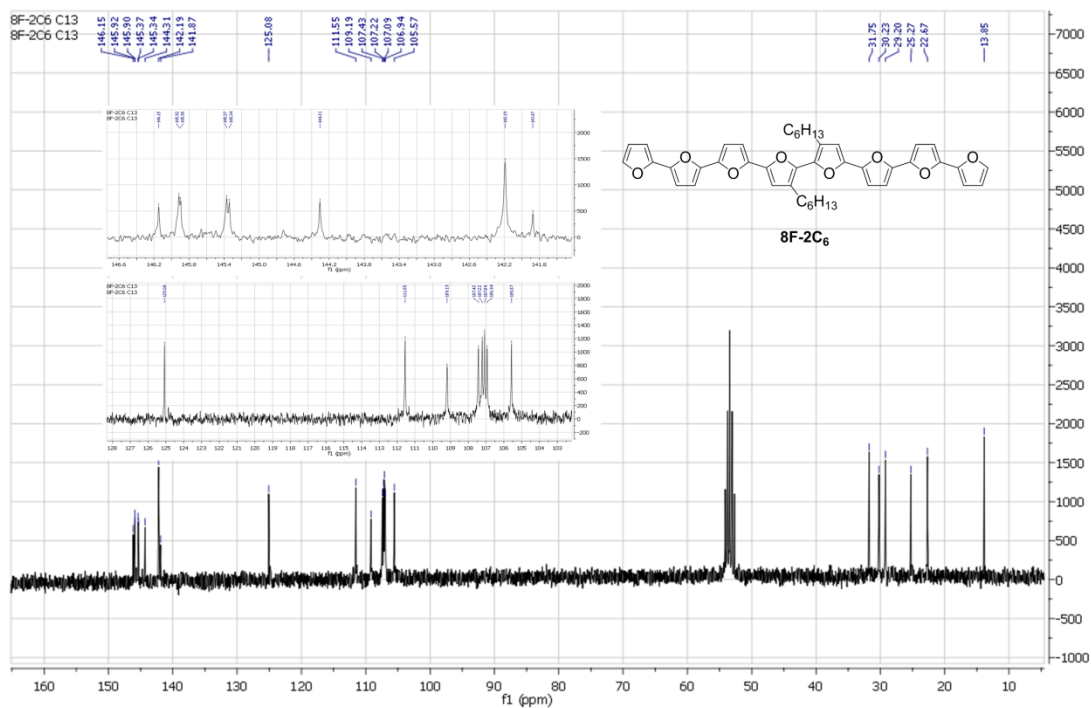
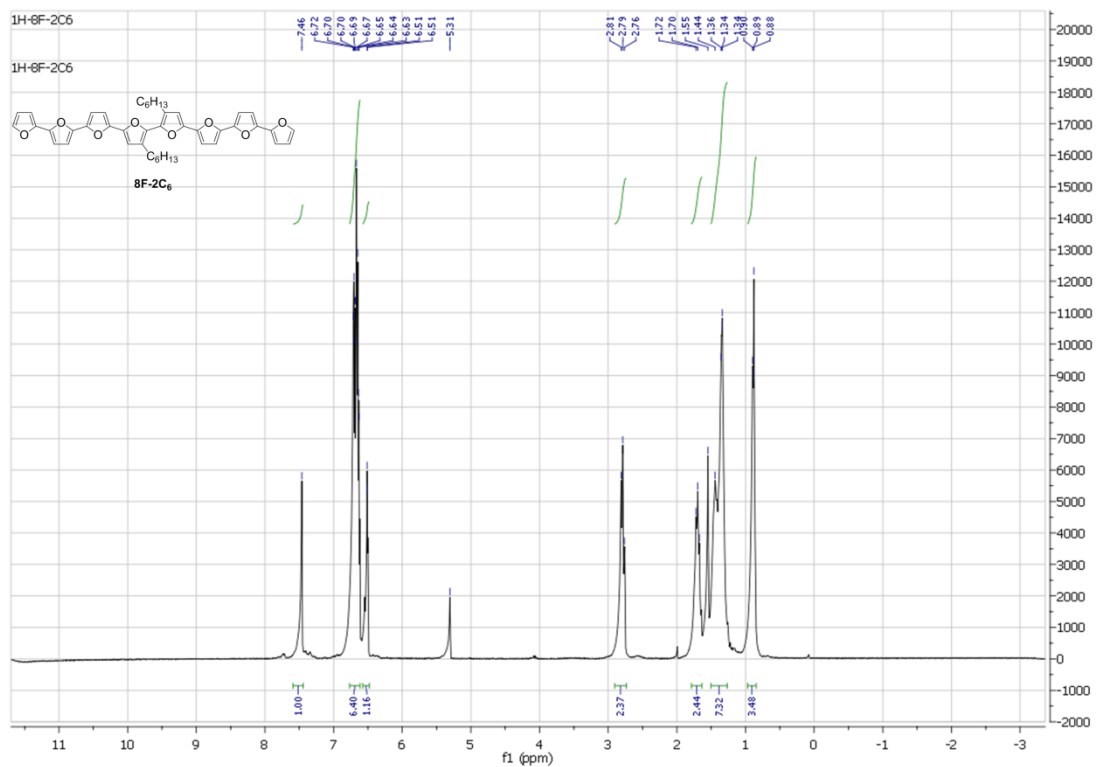


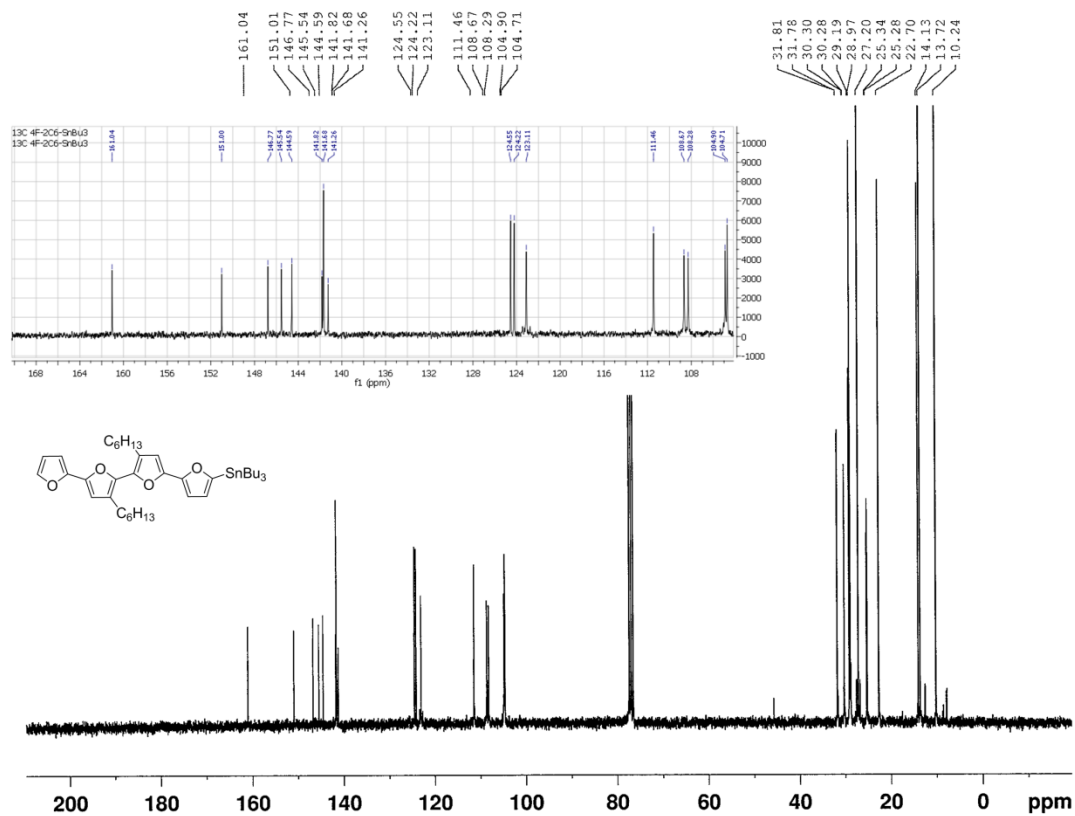
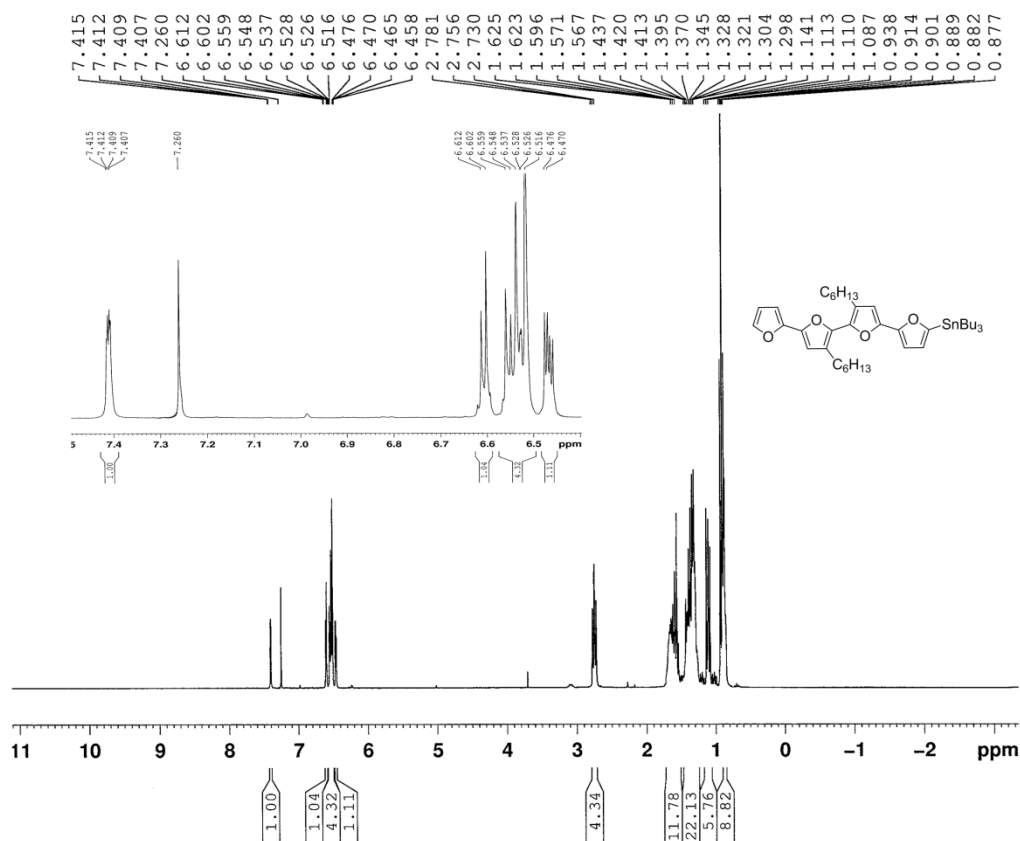


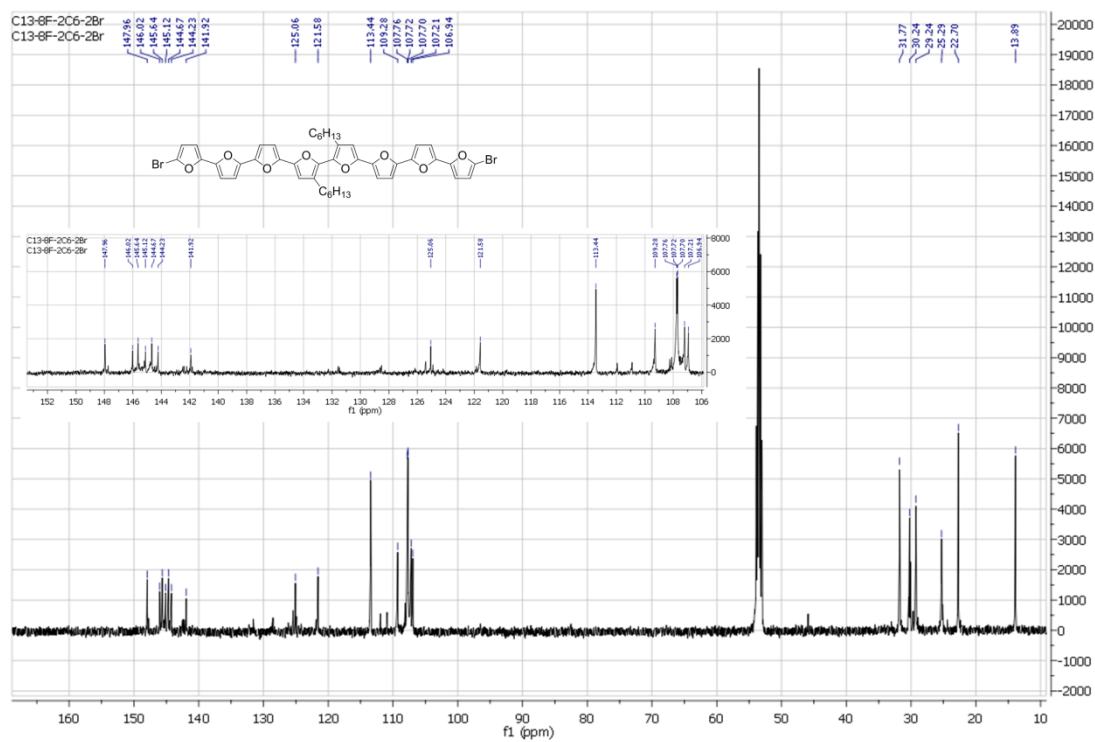
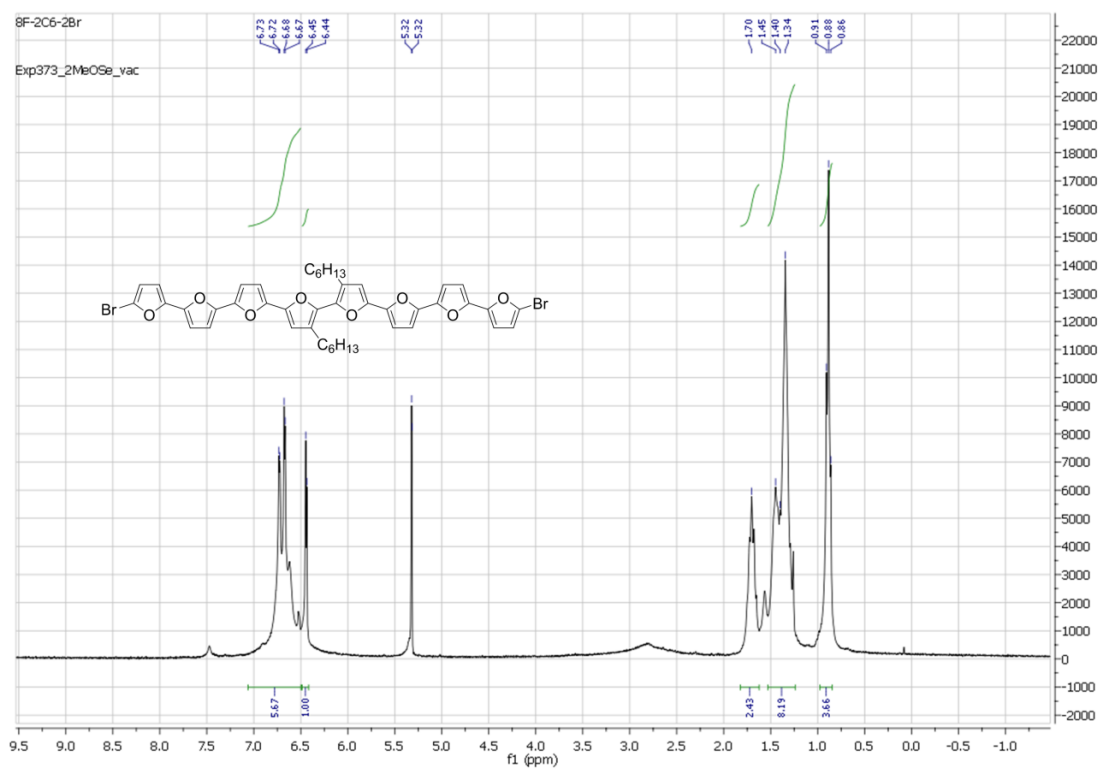


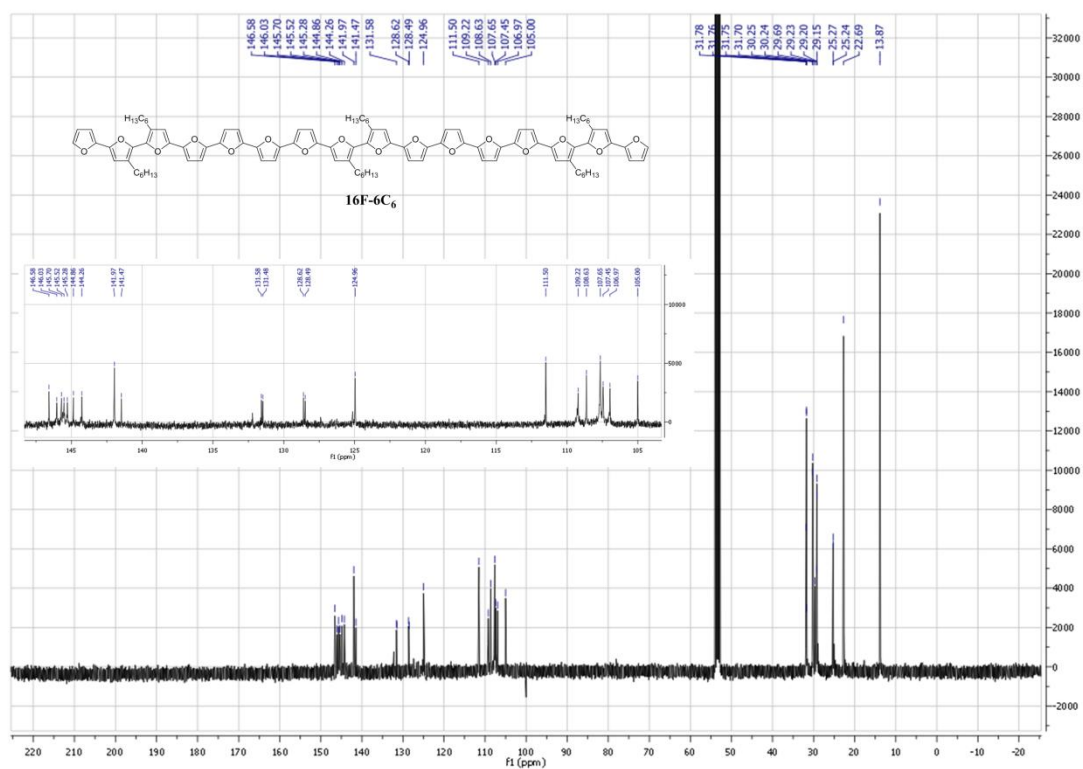
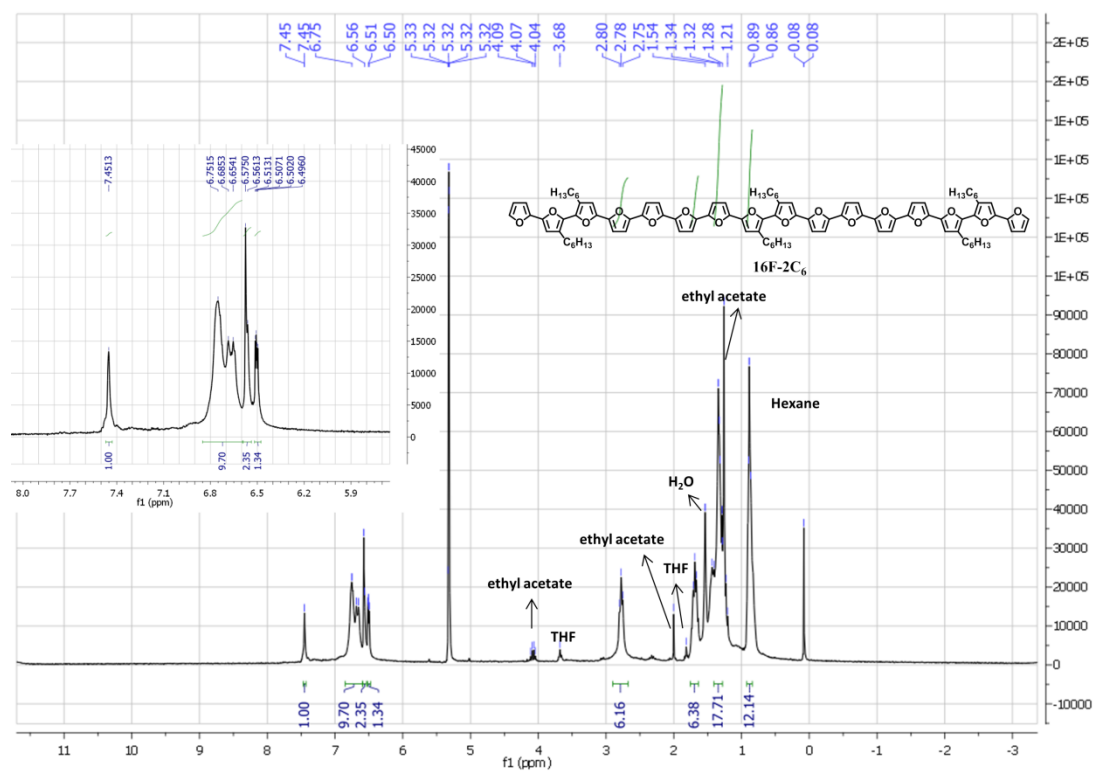




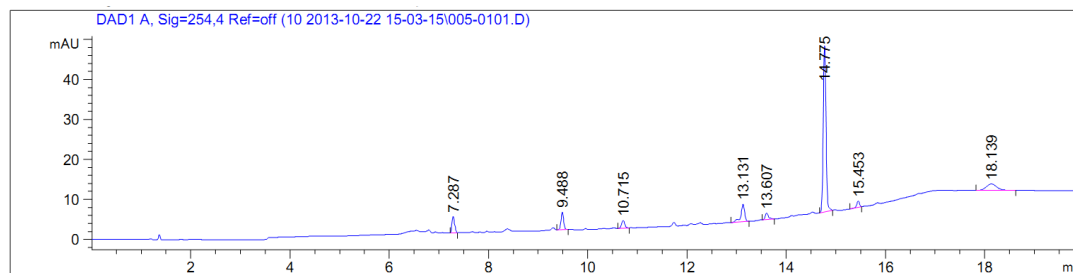








## HPLC trace of 16F-6C<sub>6</sub>



- <sup>1</sup> *Principles of Fluorescence spectroscopy*. 2nd ed.; Lakowicz, J. R., Eds.; Kluwer Academic/Plenum: New York, 1999.
- <sup>2</sup> Jones, G.; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.
- <sup>3</sup> Gidron, O.; Diskin-Posner, Y.; Bendikov, M. *J. Am. Chem. Soc.* **2010**, *132*, 2148.
- <sup>4</sup> Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.