Supporting Information

Incorporation of Pyrrole to Oligothiophene-Based Quinoids Endcapped with Dicyanomethylene: a New Class of Solution Processible n-Channel Organic Semiconductors for Air-Stable Organic Field-Effect Transistors

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Table of the Contents

1. TGA data for derivatives 3a-c

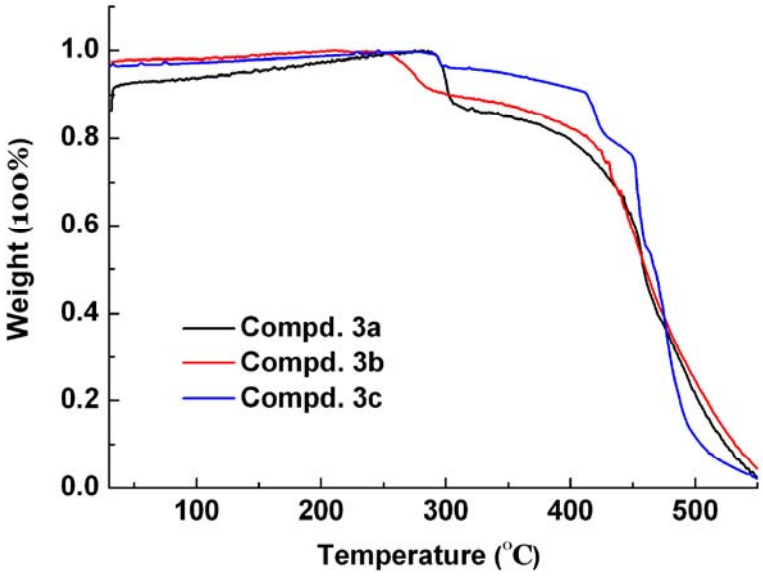

Fig. S1 Thermal gravimetric analysis (TGA) of compounds **3a-c** performed at a heating rate of 10 °C min^{-1} under a N_2 atmosphere with runs recorded from room temperature to 550 °C.

2. DSC data for derivatives 3a-c

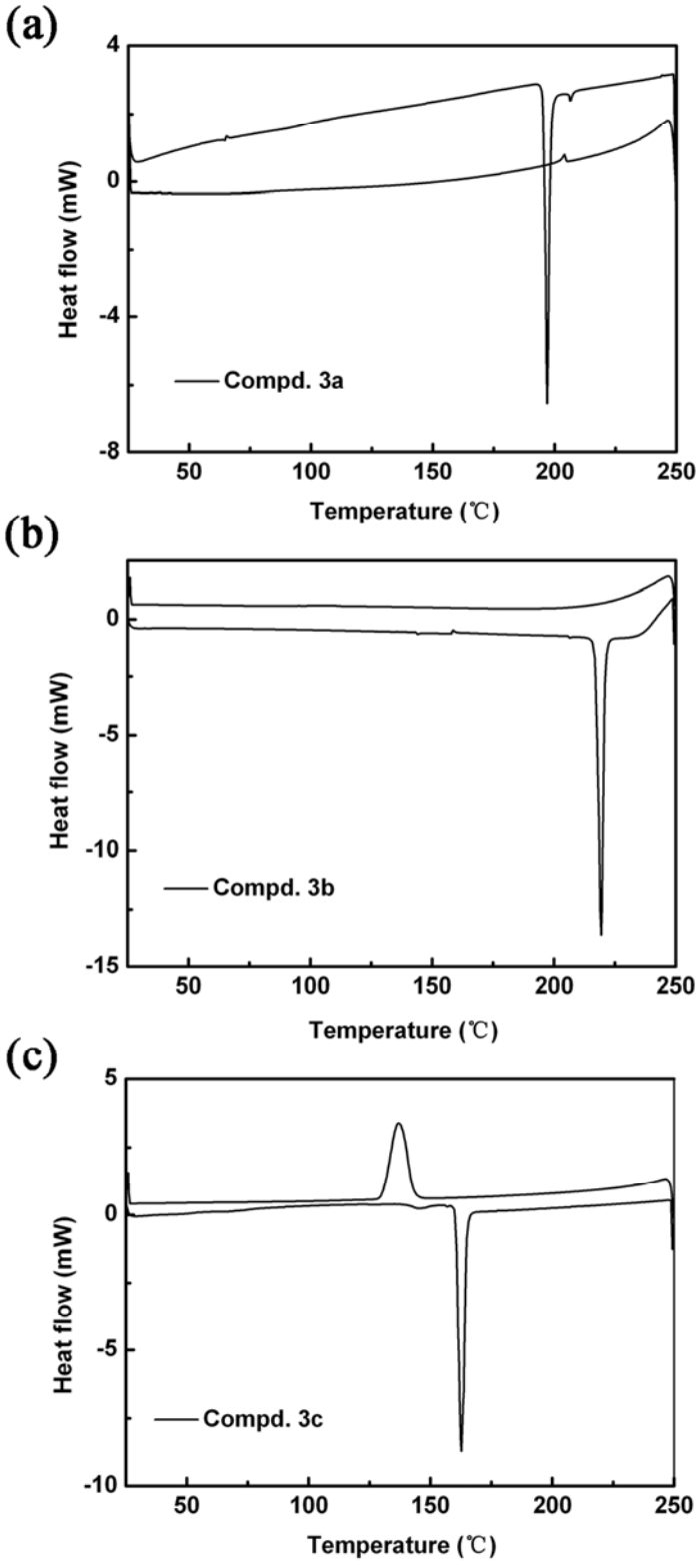

Fig. S2 Differential scanning calorimetry (DSC) curves of powder of compounds **3a-c** performed under a N_2 atmosphere. Upward peaks indicate exothermic processes, while downward peaks indicate endothermic processes. Scan rate: 10 °C min^{-1}.

3. Data of X-ray crystallographic analysis

Table S1. Crystal data and structure refinement for compound **3b**.

Empirical formula	$C_{26}H_{23}N_5S_2$
Formula weight	469.61
T/K	173(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
space group	P-1
a, Å	10.463(2)
b, Å	11.737(2)
c, Å	12.856(3)
α, deg	91.16(3)
β, deg	105.66(3)
γ, deg	114.76(3)
Volume, $Å^3$	1364.3(5)
Z	2
Calculated density, Mg/m^3	1.143
Absorption coefficient, mm^{-1}	0.216
F(000)	492
Crystal size, mm	0.42 × 0.28 × 0.24
θ range, deg	1.66 to 27.46
Limiting indices	-13<=h<=13, -15<=k<=15, -16<=l<=16
Reflections collected / unique	15139 / 6219 [R(int) = 0.0447]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6219 / 0 / 298
Goodness-of-fit on F^2	1.059
Final R indices [I>2σ(I)]	R_1 = 0.0676, wR_2 = 0.1911
R indices (all data)	R_1 = 0.0736, wR_2 = 0.1971
Largest diff. peak and hole, $e.A^{-3}$	1.523 and -0.480

4. UV-vis spectra of thin films

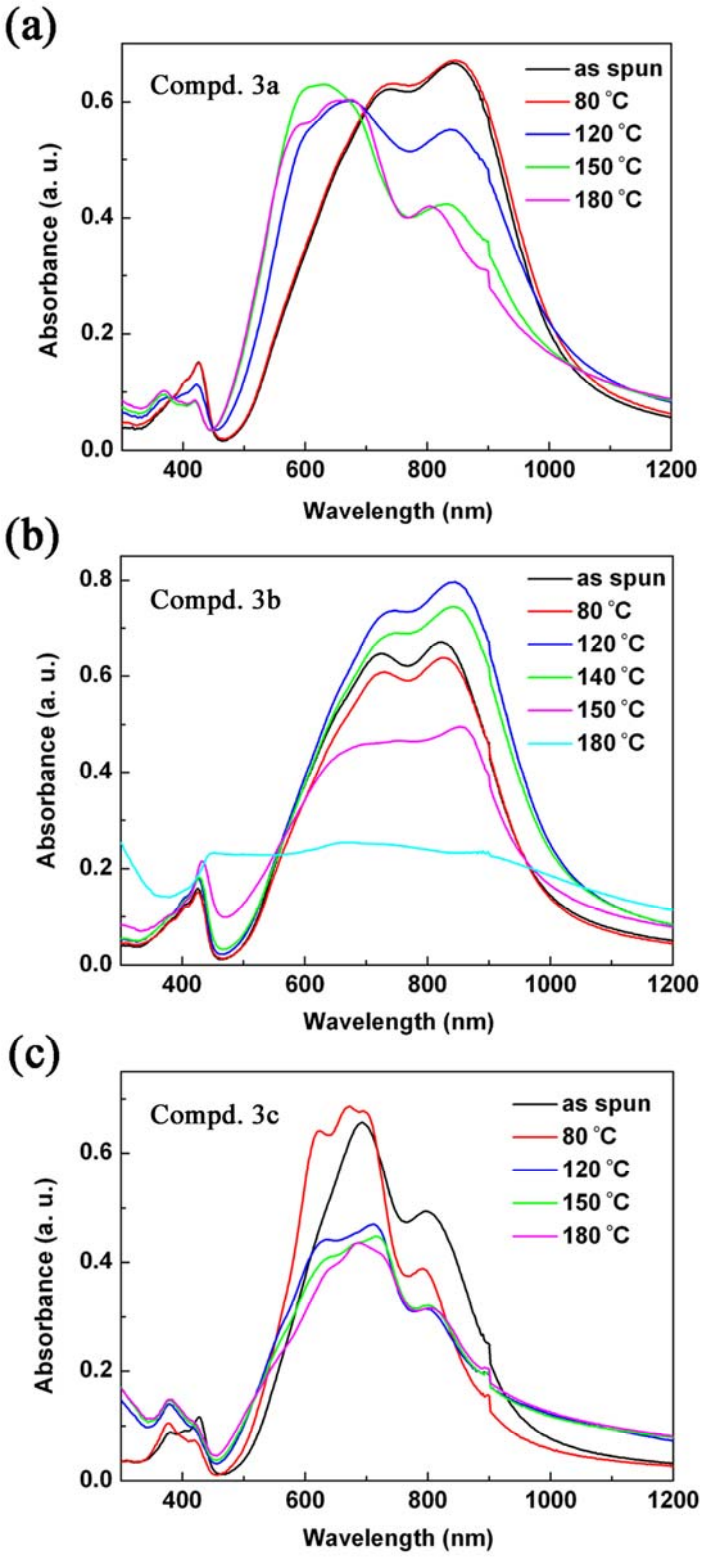

Fig. S3 UV-vis absorption spectra of thin films of compounds **3a-c** spin-coated on quartz substrates and annealed at different temperatures.

5. Structural isomers in solution state

Generally, for oligothiophene-based quinoidal substituted with dicynomethylene, the E/Z isomerism can exist in the thienoquinoidal core parts. Similarly, for our results, we found there are some small ^{1}H NMR signals appearing in the aryl portion, which are seemingly signals for inpurity, taking compound **3b** as a example, see Fig. S4. However, because the compound was purified by repeated recrystallization and its purity was confirmed by elemental analysis (less than 0.3%), we think there might be some configuration isomers (i.e. *cis-cis*, *cis-trans*, *trans-trans* in terms of the double bonds between thiophene and pyrrole rings, see Fig. S5) co-exisiting for **3b** in the solution, although data of X-ray crystallographic analysis for **3b** was successfully obtained and the structure for such pyrrole-containing quinoid displays one configuration (*cis-cis*) in the solid state. In order to confirm our consideration about the isomerization phenomenon, NOESY spectrum analysis was carried out: clear correlated peaks between thiophene *β*-protons $H_{b(b')}$ and methylene protons $H_{d(d')}$ on the first carbon in the alkyl substituent were observed as displayed in Fig. 6 and 7, demonstrating that there are probably two kinds of isomers (eg. *cis-cis* and *cis-trans*) at least co-existing as an equilibrium mixture in the solution.

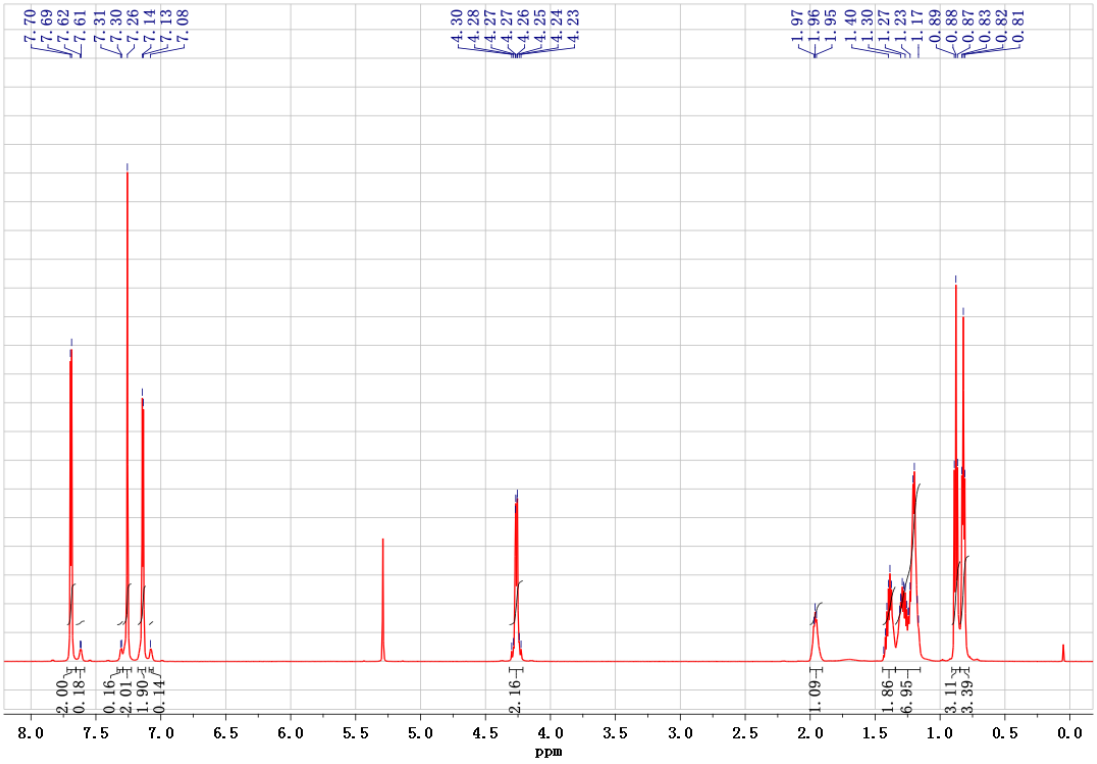

Fig. S4 The ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) at 298 K for **3b**.

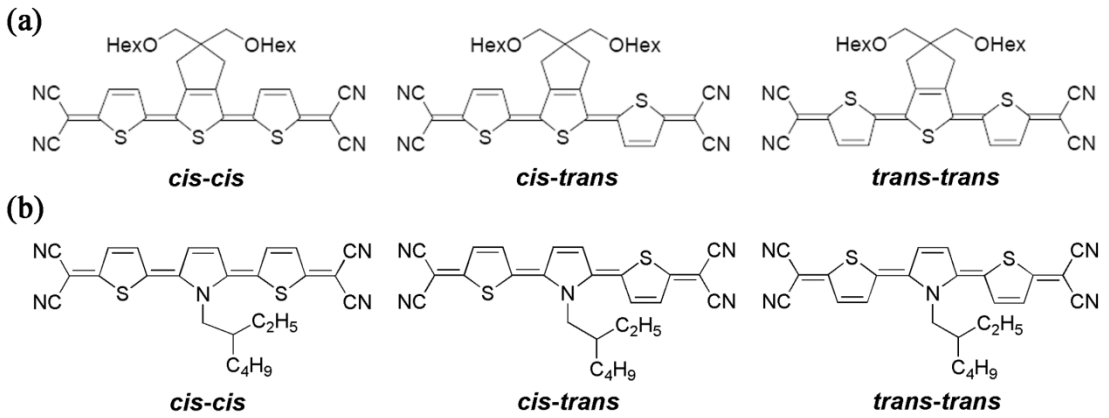

Fig. S5 (a) Three isomers for a terthienoquinoid as reported by Takimiya's group[1], and (b) three possible isomers for **3b** in solution.

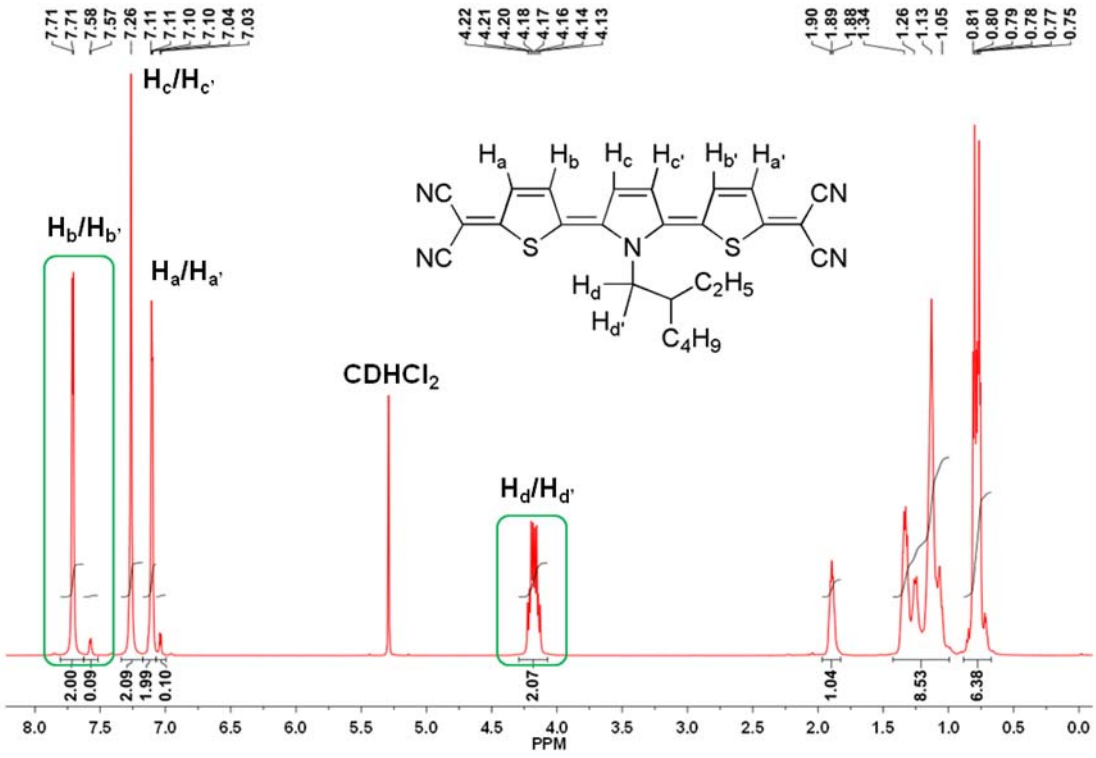

Fig. S6 The ^{1}H NMR spectrum (600 MHz, CD_2Cl_2) at 213 K for **3b**. *Note*: Isomer with larger proportion is called Part A and the one with much smaller proportion is called Part B; and the assignment of some key hydrogen atoms are indicated.

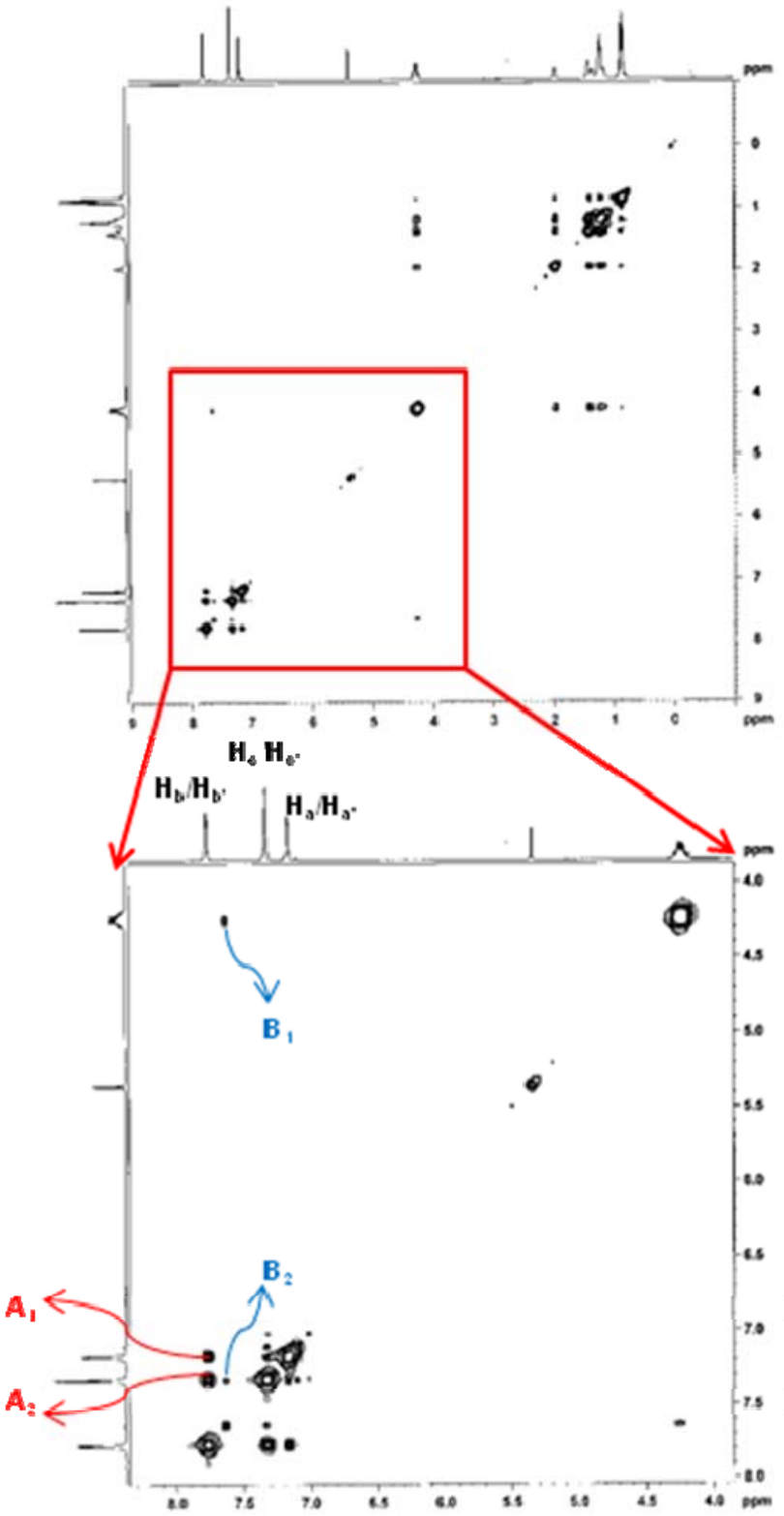

Fig. S7 The NOESY spectrum (600 MHz, CD_2Cl_2) at 213 K for **3b**. *Note*: Correlation peaks A_1 and A_2 indicate Part A exists as a *cis-cis* configuration; Correlation peaks B_1 and B_2 indicate Part B more possibly exists as a *cis-trans* configuration.

6. Copies of ^{1}H NMR and ^{13}C NMR spectra

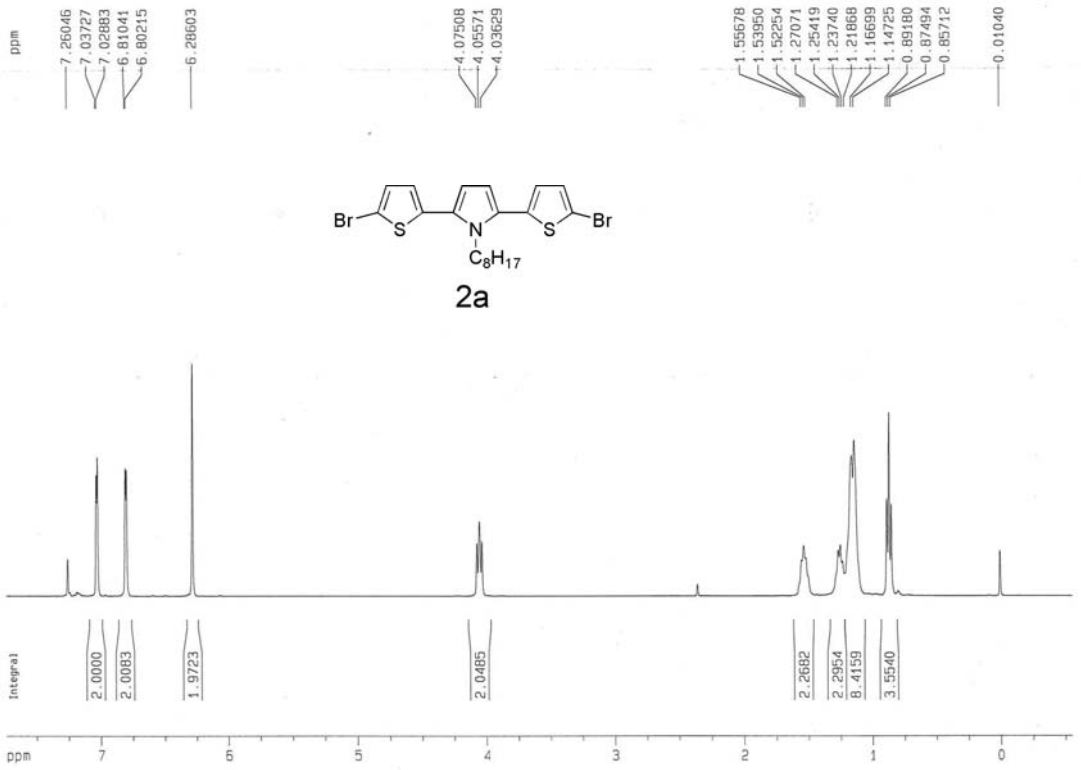

Fig. S8 ^{1}H NMR spectrum of **2a**.

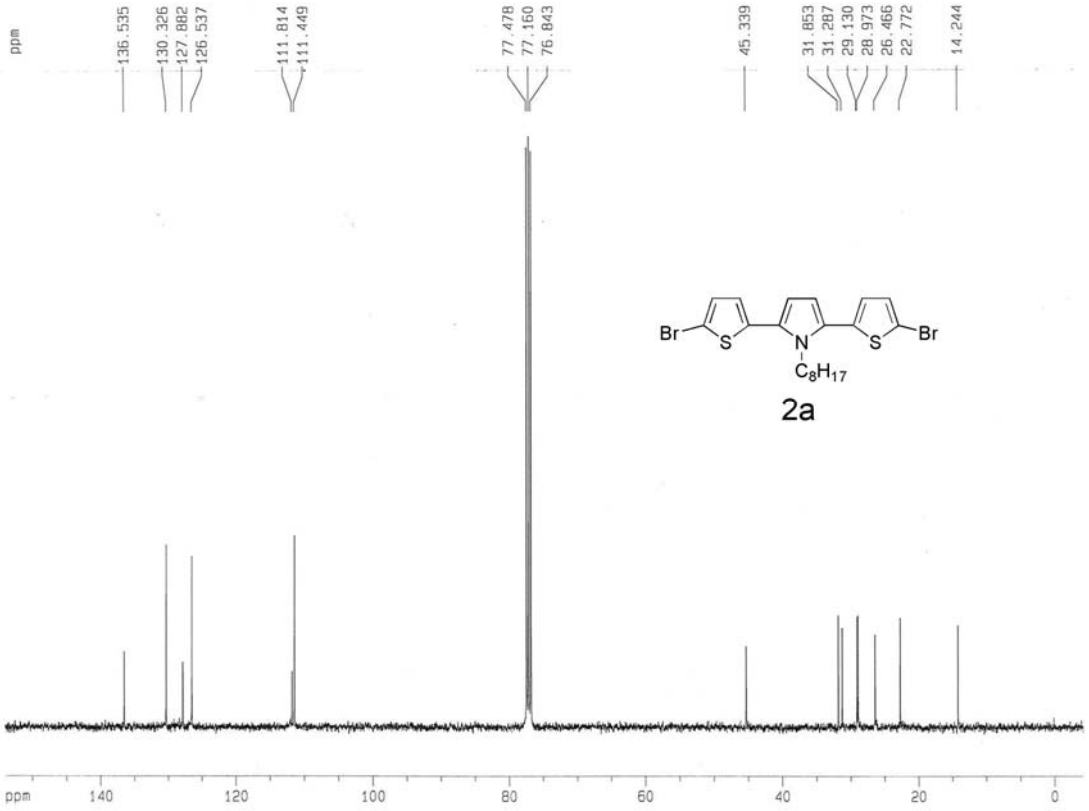

Fig. S9 ^{13}C NMR spectrum of **2a**.

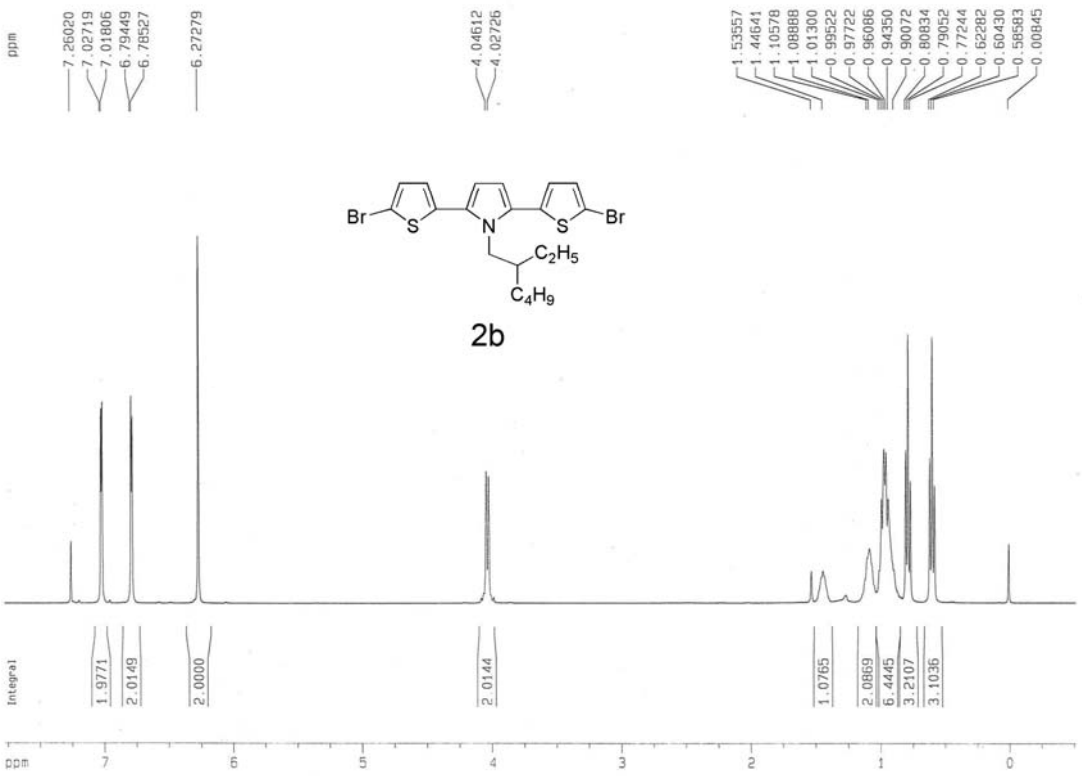

Fig. S10 ^{1}H NMR spectrum of **2b**.

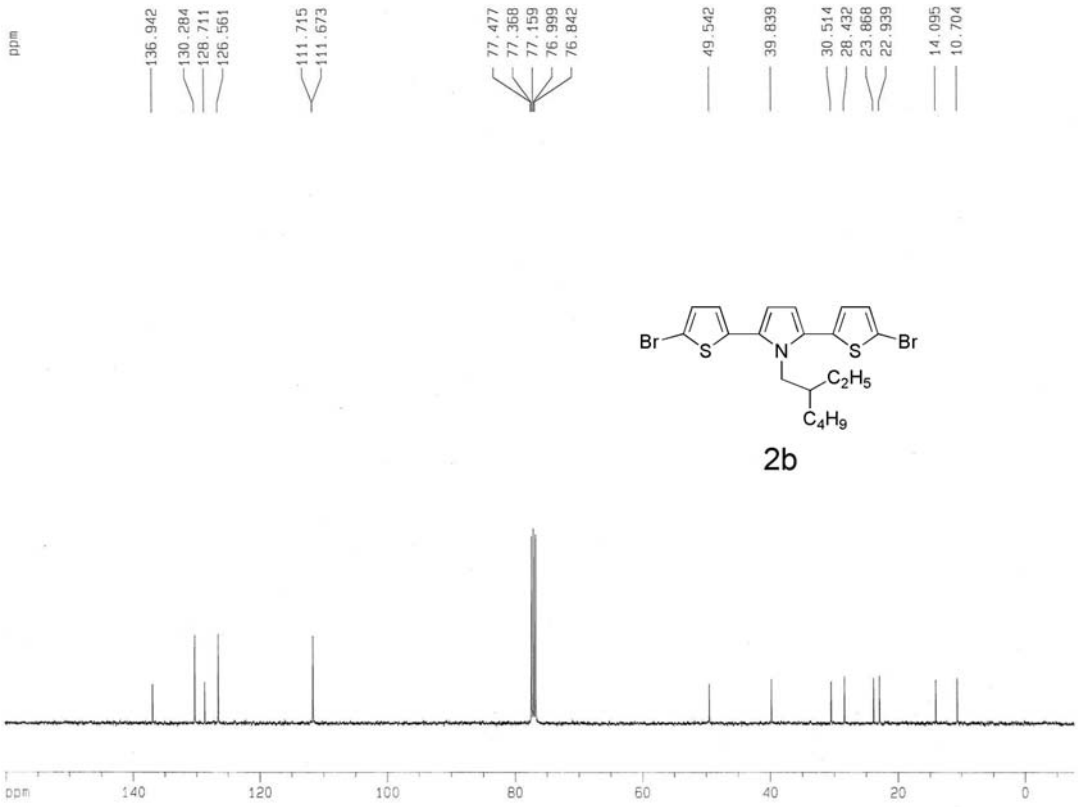

Fig. S11 ^{13}C NMR spectrum of **2b**.

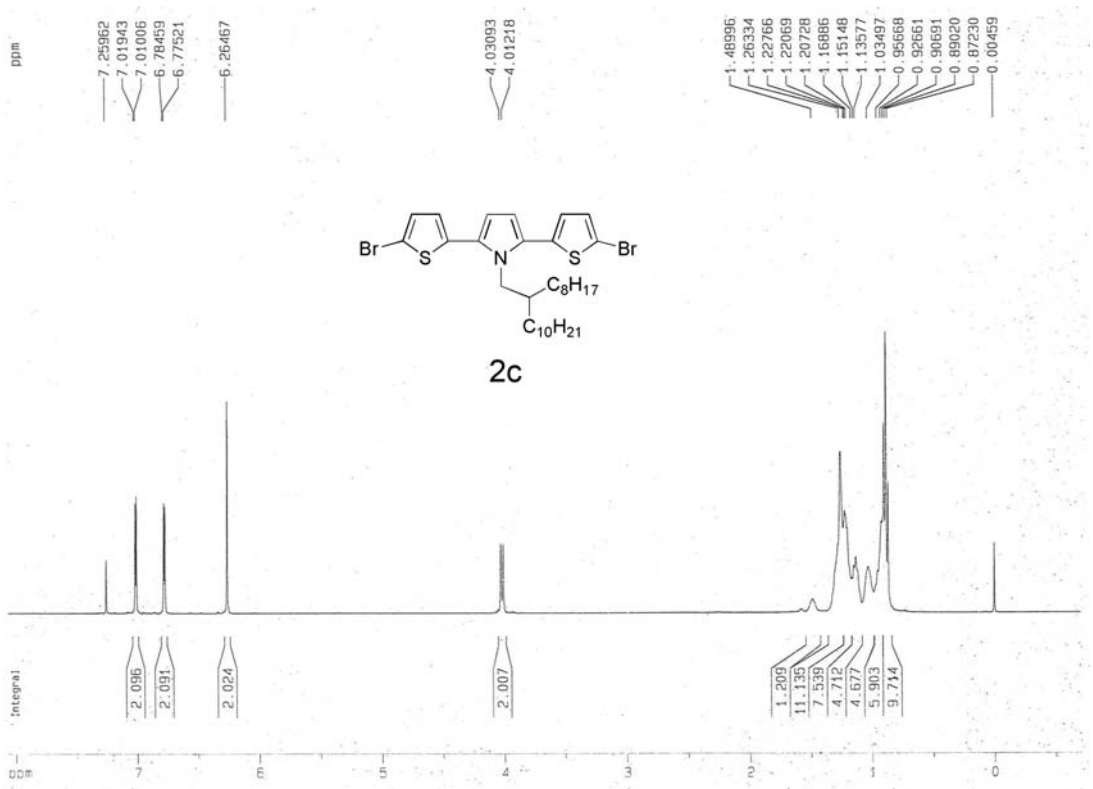

Fig. S12 ^{1}H NMR spectrum of **2c**.

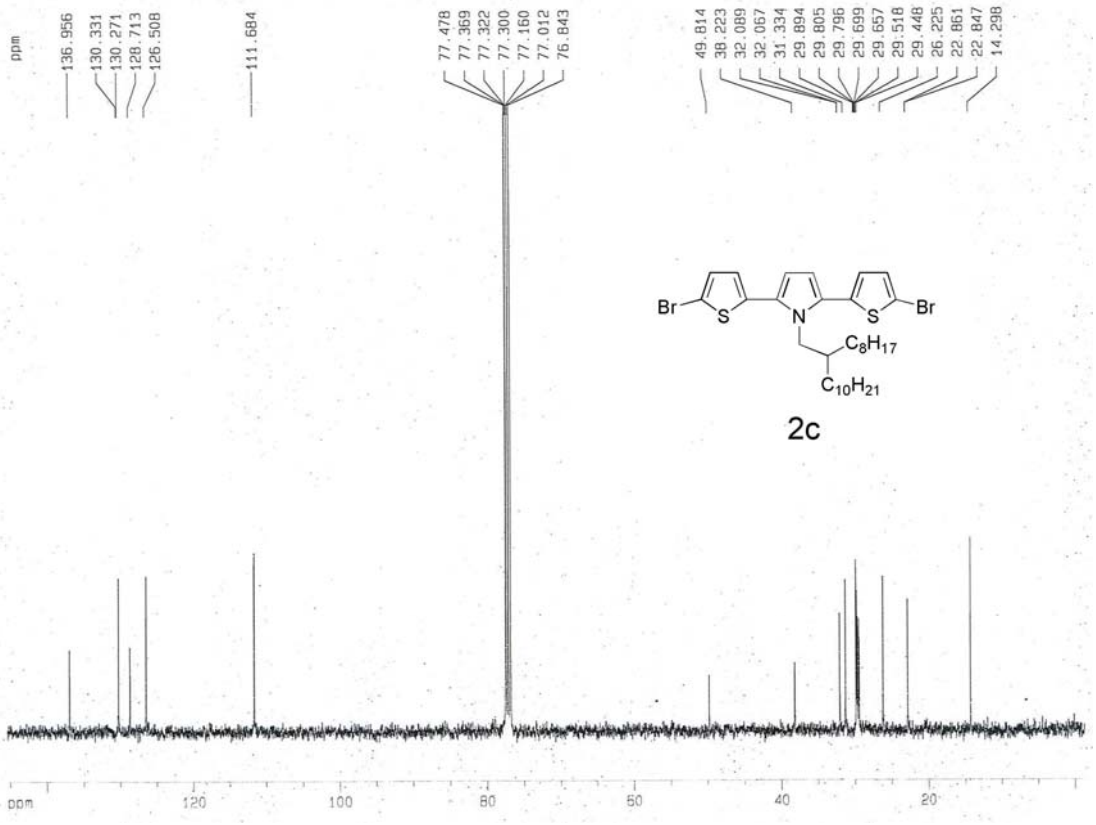

Fig. S13 ^{13}C NMR spectrum of **2c**.

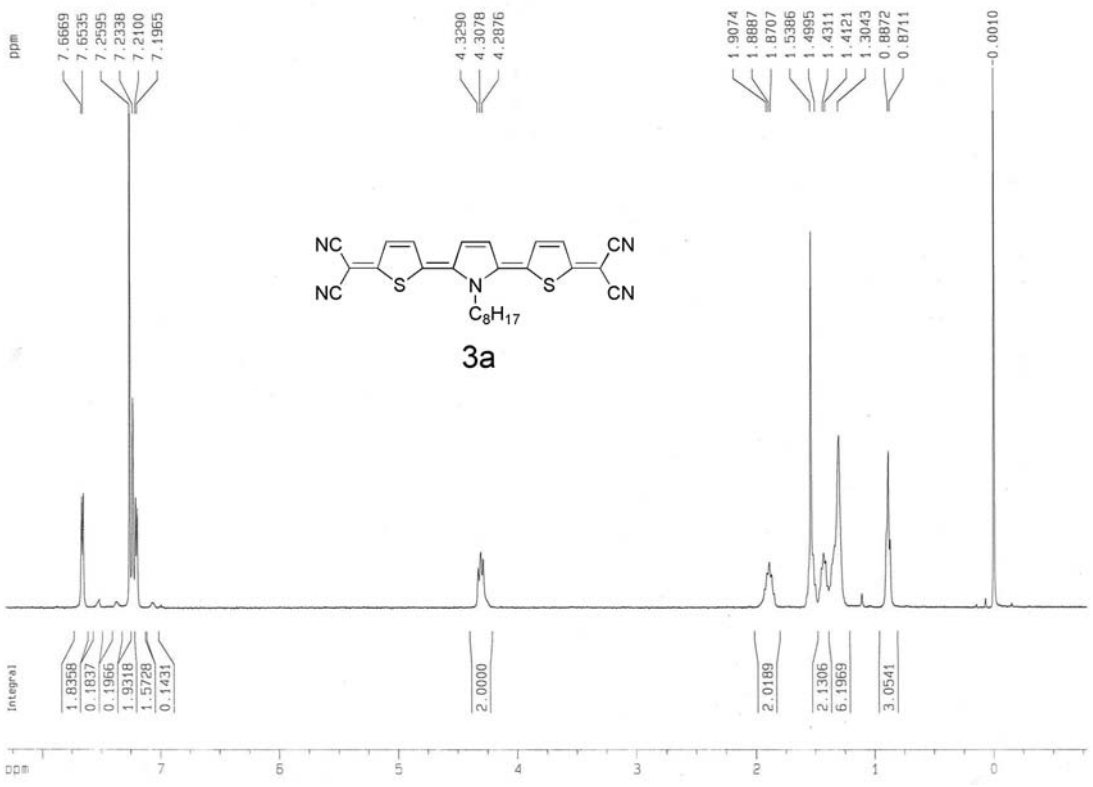

Fig. S14 ^{1}H NMR spectrum of **3a**.

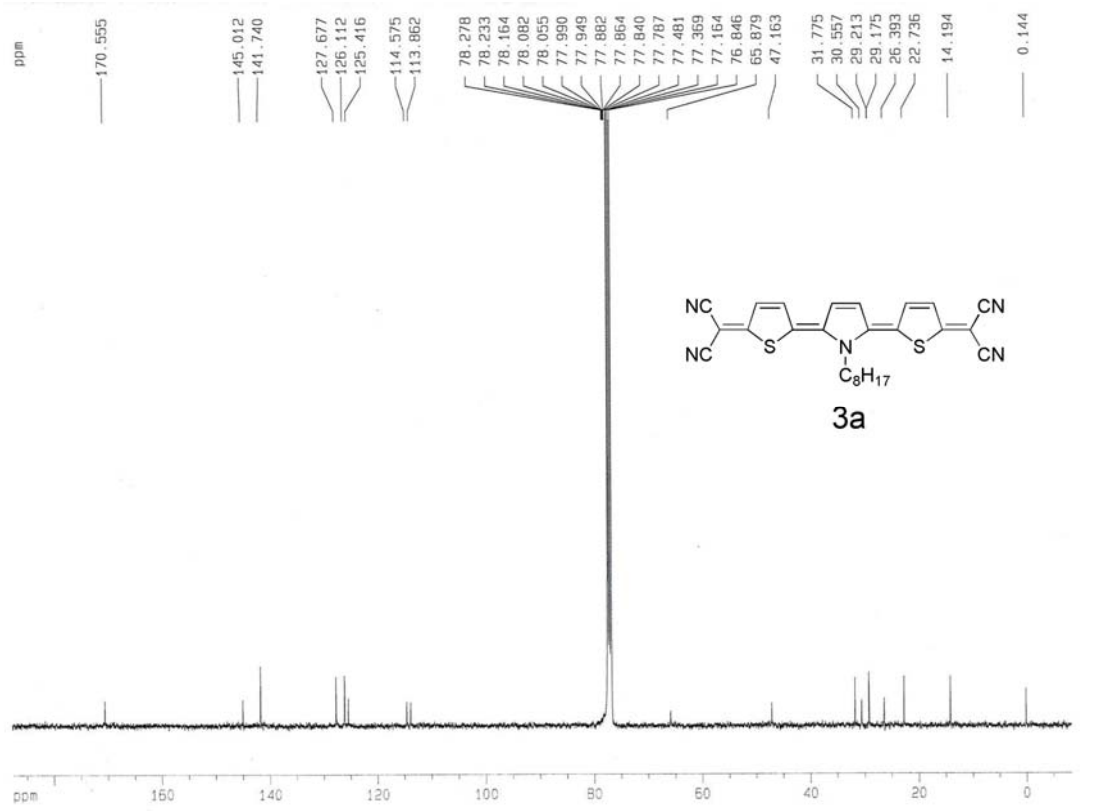

Fig. S15 ^{13}C NMR spectrum of **3a**.

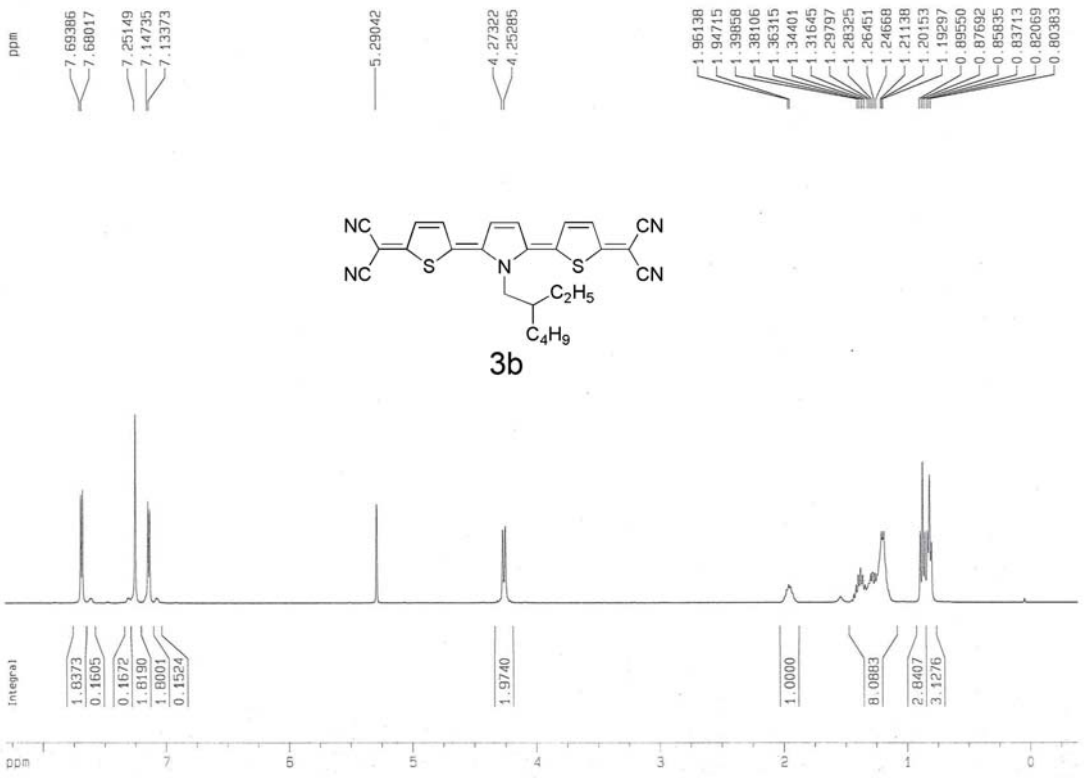

Fig. S16 ^{1}H NMR spectrum of **3b**.

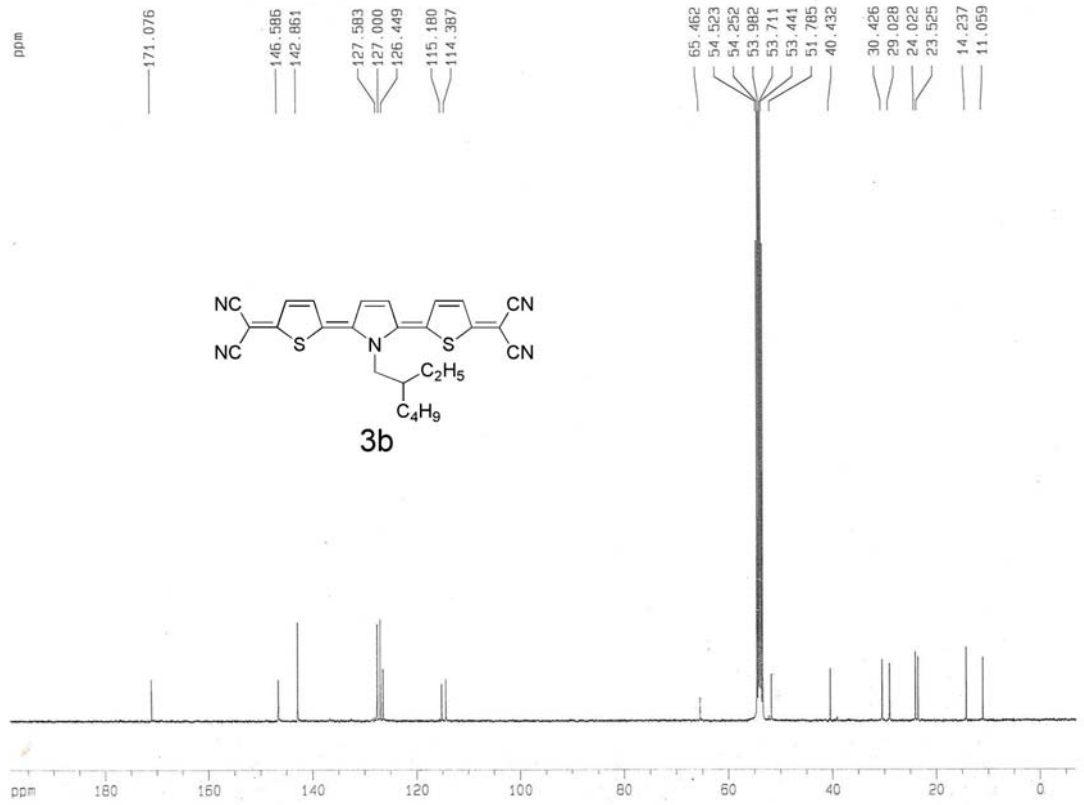

Fig. S17 ^{13}C NMR spectrum of **3b**.

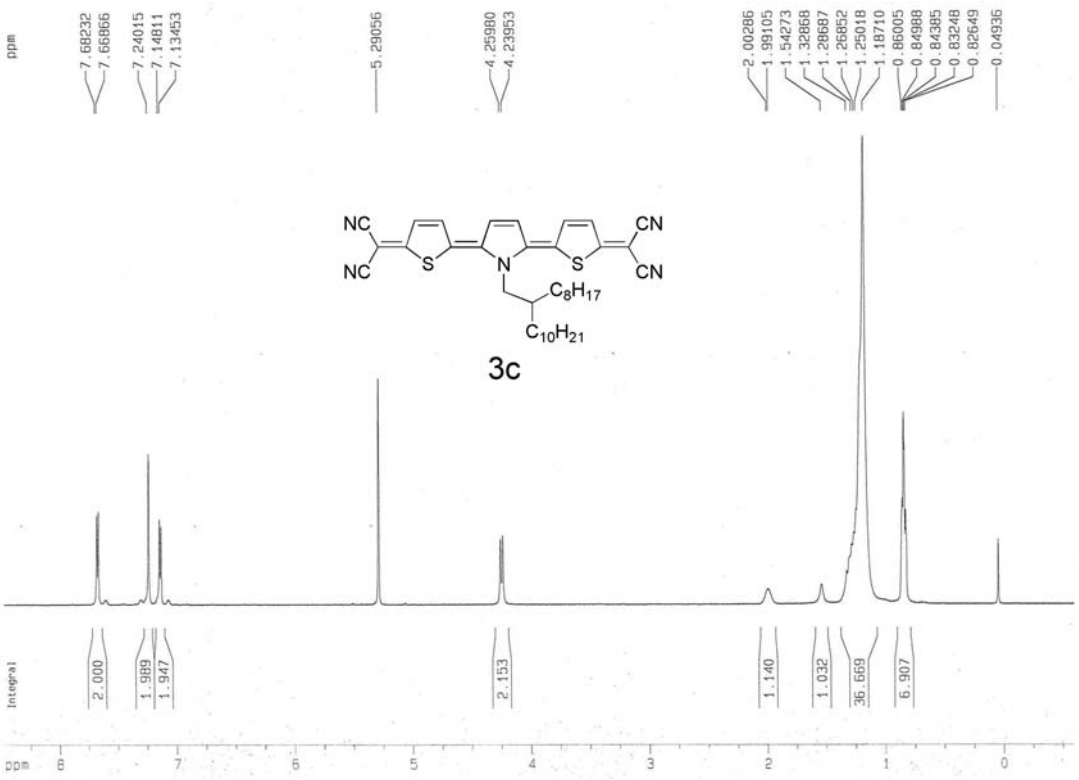

Fig. S18 ^{1}H NMR spectrum of **3c**.

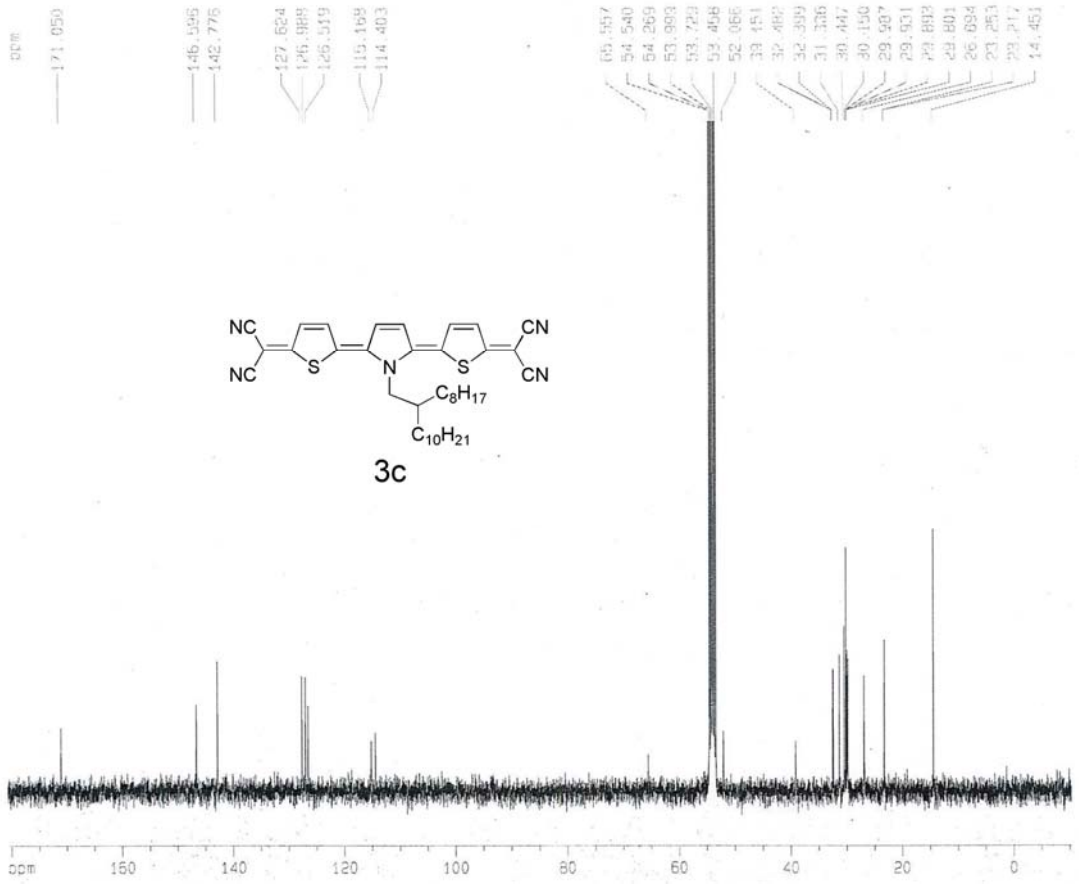

Fig. S19 ^{13}C NMR spectrum of **3c**.

7. References

S1. S. Handa, E. Miyazaki, K. Takimiya and Y. Kunugi, *J. Am. Chem. Soc.*, 2007, **129**, 11684.