Electronic Supplementary Information (ESI)

Novel multi-stimuli responsive molecules based on photochromic bithienylethenes containing tetrathiafulvalene unit

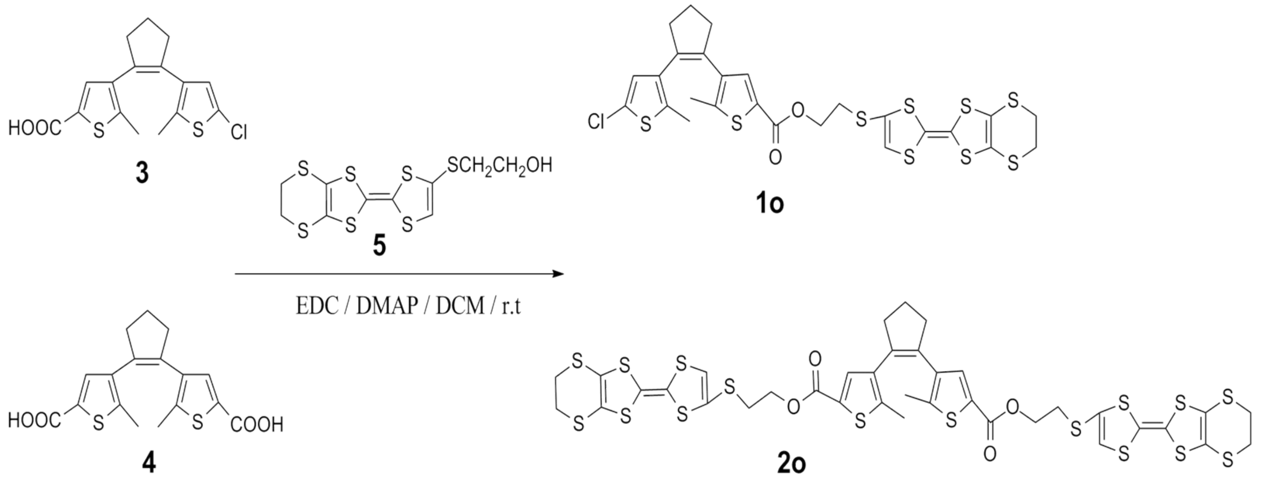
Jingyi Zhang, Bingbing Sun, Qiaochun Wang and Lei Zou*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, China

E-mail: zoulei@ecust.edu.cn ;

Fax: +86 21-642527588; Tel: +86-21-64252758

Scheme S1. Synthetic route of compounds **1o** and **2o**



Experimental

General methods 4-(2-Hydroxyethylthio)-4’,5’-(ethylenedithio)tetrathiafulvalene **5** 、 1-(2-methyl-5-carboxyl-3-thienyl)-2-(2-methyl-5-chloro-3-thienyl) **3** and 1,2-bis(2-methyl-5-carboxyl-3-thienyl) cyclopentene **4** were synthesized according to the literature.[1,2] Other reagents were commercially available and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in CDCl$_3$ solution using tetramethylsilane as the internal standard. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions. (ESI, 70eV)

UV-vis absorption spectra were measured on a Varian Cary 500 UV-vis spectrophotometer. The photochromic reaction was induced in situ by continuous irradiation using an Hg/Xe lamp (Hamamatsu, LC8 Lightningcure, 200 W) equipped with a narrow band interference filter (Shenyang HB optical Technology) for λ_{irr} = 313 nm, a broad-band interference filter (Shenyang HB optical Technology) for λ_{irr}>470 nm, or a monochromator (Monoscan 2000, OceanOptics) for λ_{irr} = 517 nm. The photochromic reaction quantum yields were evaluated by the standard procedures using BTF6 (1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluoro-cyclopentene) as the references for photocyclization and cycloreversion. The rates of isomerization in the initial stage of the reaction (0–5%) were compared with references whose Φo-c (35%) and Φc-o (35%) in hexane are known, which brought forth 5% uncertainties on the calculations of quantum yields. Electrochemical Characterization was performed by Versa Star II Electrochemical analyzer in CH_2Cl_2 (distilled over CaH_2 prior to use) containing 0.1M Tetrabutylammonium hexafluorophosphate （n-Bu4NPF$_6$） as supporting electrolyte. A platinum filament as counter electrode (CE), and an Ag/AgCl wire as reference electrode. Cyclic voltammetry measurements were carried out at a platinum electrode as work electrode (WE). Spectroelectrochemical experiments were carried out using a platinum plate as working electrode (WE).

Synthesis of compound 1o

At room temperature, a mixture of 0.1 g (0.3 mmol) product **3**, 0.074 g (0.2 mmol) product **5**, catalyst 4-dimethylaminopyridine (DMAP) 0.02 g, and water-absorbing agent 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) 0.076 g dissolved in dichloromethane (DCM) 15 mL and stirred for 10h in dark conditions. Then the solvent was evaporated by rotary evaporator. The crude product was purified through column chromatography on silica using dichloromethane/petroleum ether (1:1.5) as the eluent. Compound **1o** was separated in 58% yield as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1H), 6.57 (s, 1H), 6.46 (s, 1H), 4.43 (t, *J* = 6.2 Hz, 2H), 3.29 (s, 4H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.76 (dd, *J* = 15.8, 8.1 Hz, 4H), 2.04 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.97

(s, 3H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):δ 160.74, 142.45, 135.75, 133.89, 133.72, 133.22, 132.25, 127.55, 125.61, 124.76, 124.72, 124.32, 122.78, 116.33, 112.90, 112.87, 105.87, 62.26, 37.54, 33.21, 29.19, 28.68, 21.83, 13.84, 13.23. ESI-HRMS (*m/z*): Calcd. for $C_{26}H_{23}O_2S_9Cl$ ($[M]^+$): 689.8873; Found: 689.8876.

Synthesis of compound 2o

Compound **2o** was prepared by an analogous method to that used for compound **1o** and obtained as a brownish red solid in a yield of 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 2H), 6.45 (s, 2H), 4.43 (t, J = 6.1 Hz, 4H), 3.29 (s, 8H), 3.05 (t, J = 6.1 Hz, 4H), 2.80 (t, J = 7.2 Hz, 4H), 2.13 – 2.02 (m, 2H), 1.93 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.73, 143.42, 136.68, 134.87, 134.79, 128.74, 125.80, 123.82, 117.39, 113.95, 113.91, 106.91, 63.33, 38.67, 34.27, 30.23, 22.89, 14.94. ESI-HRMS (*m/z*): Calcd. for $C_{37}H_{32}O_4S_{16}$ ($[M]^+$): 1051.7832; Found: 1051.7833.

Preparation of PMMA films with 2wt% 1 and 2-loaded PMMA

Compound **1** or **2** (2 mg) was dissolved in 4 mL of $CHCl_3$. The solution was filtered using membranes attached to a Teflon syringe, and then PMMA (200mg) was added to the solution standing until the PMMA was resolved. The solution was coated on a spin-coater with a spin rate of 1000—2000 r/min. The coated film was dried at room temperature for 12 h in a vacuum oven to give a transparent and homogeneous film.[3]

Table S1 Photochromic parameters of compounds **1** and **2** in CH_2Cl_2

Compd	$\lambda_{max}{}^{a}$/nm	$\lambda_{max}{}^{b}$/nm	Φ^{c}		$\alpha_{pss}{}^{d}$(313nm)/%
	$\varepsilon\times10^{3}$ $M^{-1}\cdot cm^{-1}$	$\varepsilon\times10^{3}$ $M^{-1}\cdot cm^{-1}$	$\Phi_{o\text{-}c}$	$\Phi_{c\text{-}o}$	
1	249(37.1)	515（9.15）	0.06	0.022	11
2	260（46.4）	550（8.65）	0.07	0.007	58

[a] Absorption maxima of open-ring forms;

[b] Absorption maxima of closed ring forms;

[c]Quantum yields of photocyclization at 313 nm and photocycloreversion at 517 nm, with uncertainty around ±5% and ±0.5%, respectively;

[d]Conversion yield at photostationary state (PSS) upon irradiation at 313 nm.

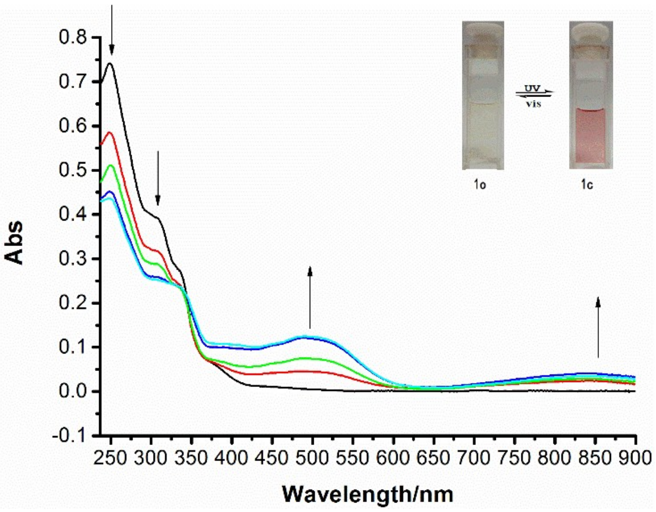


Fig. S1 UV-vis spectrum /color changes of compound **1o** in CH_2Cl_2（2.0×10^{-5} mol·L^{-1}）

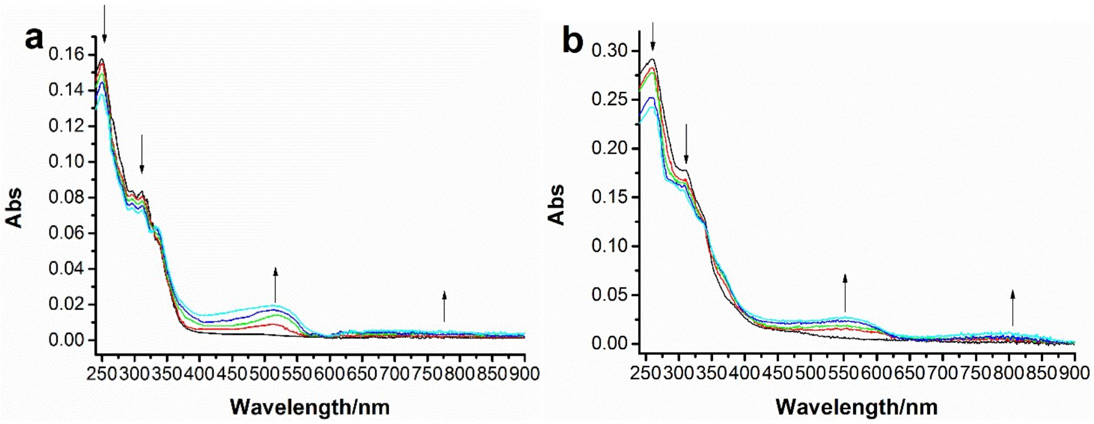


Fig. S2 UV-Vis absorption spectrum changes of 2 wt% **1** (a) and 2 wt% **2** (b) loaded PMMA film at 298 K upon irradiation with UV light.

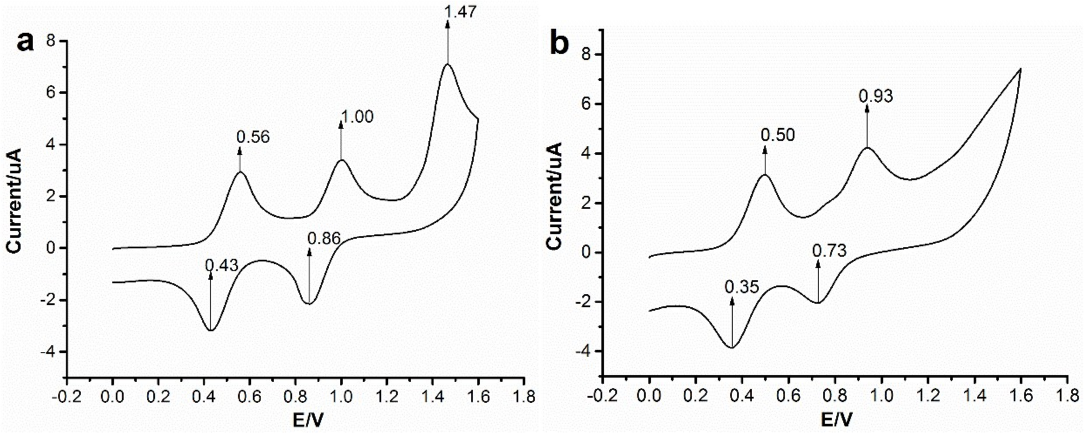


Fig. S3 Cyclic voltammograms of compound 1 in CH_2Cl_2: **1o** (a), **1c** (b). 0.1M tetrabutylammonium hexafluorophosphate as support electrolyte, with a scan rate of 50mV/s

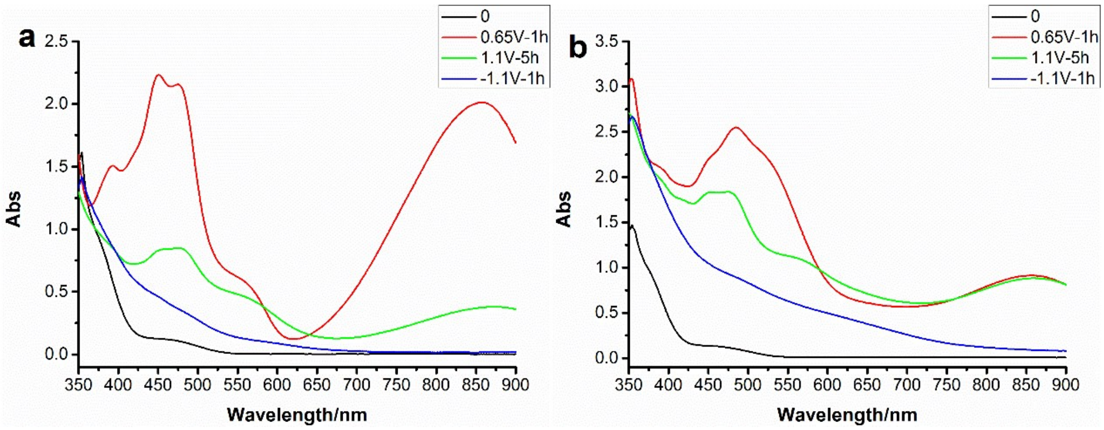


Fig. S4 Absorption spectra of **1o** (a) and **1c** (b) in CH_2Cl_2 (2.5×10^{-4} mol·L^{-1}) after applying different potentials.

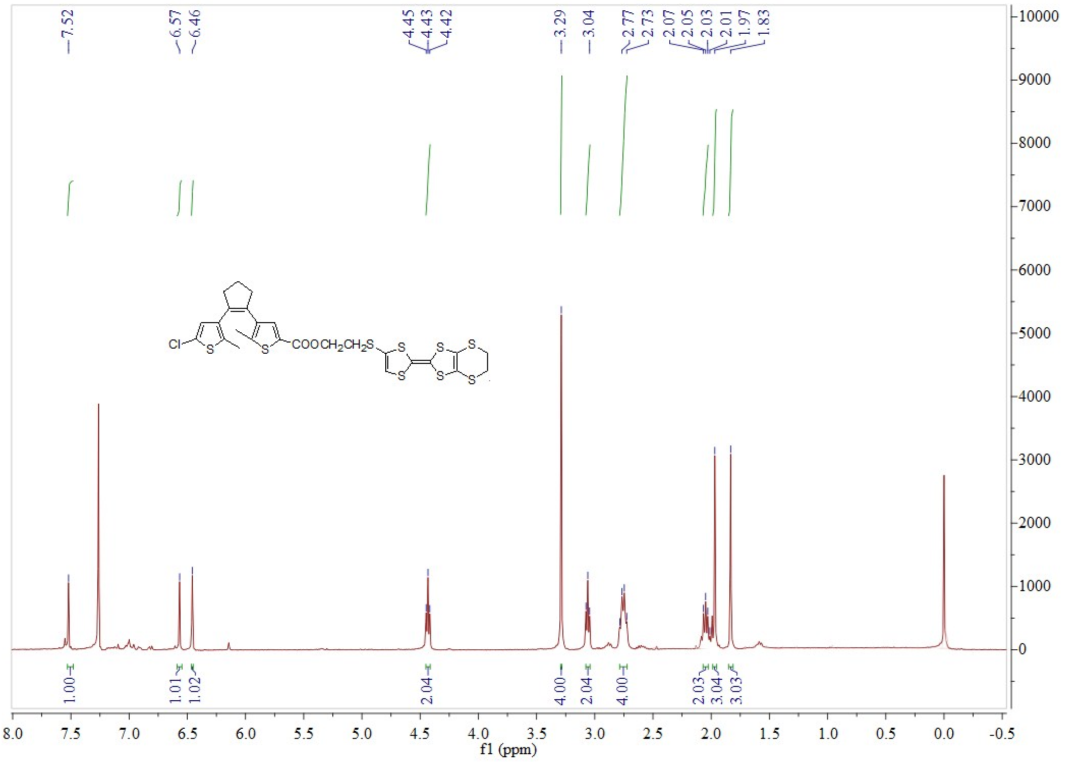


Fig. S5 ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of compound **1o**

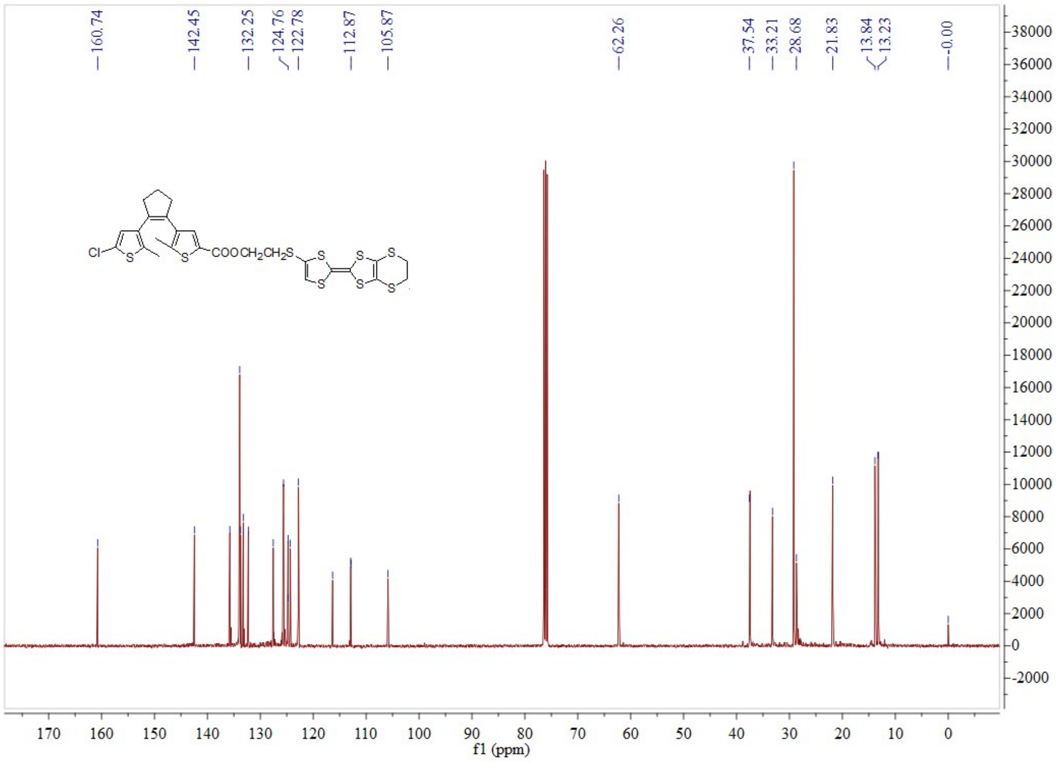
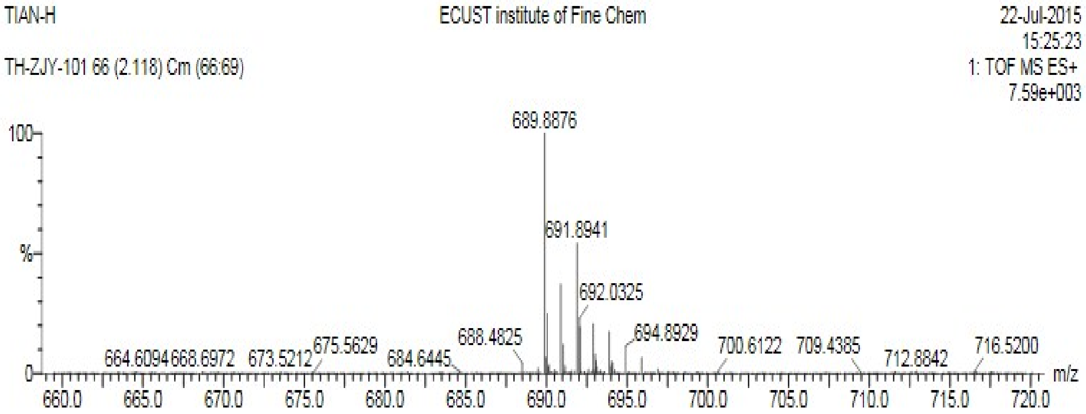


Fig. S6 ^{13}C NMR (CDCl$_3$, 100 MHz) spectrum of compound **1o**



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Minimum:                             -1.5
Maximum:               300.0   50.0   100.0

Mass       Calc. Mass  mDa     PPM    DBE     i-FIT     i-FIT (Norm) Formula

689.8876   689.8873    0.3     0.4    15.0    164.3     0.0          C26  H23  O2  S9  Cl
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Fig. S7 High Resolution Mass spectra of compound **1o**

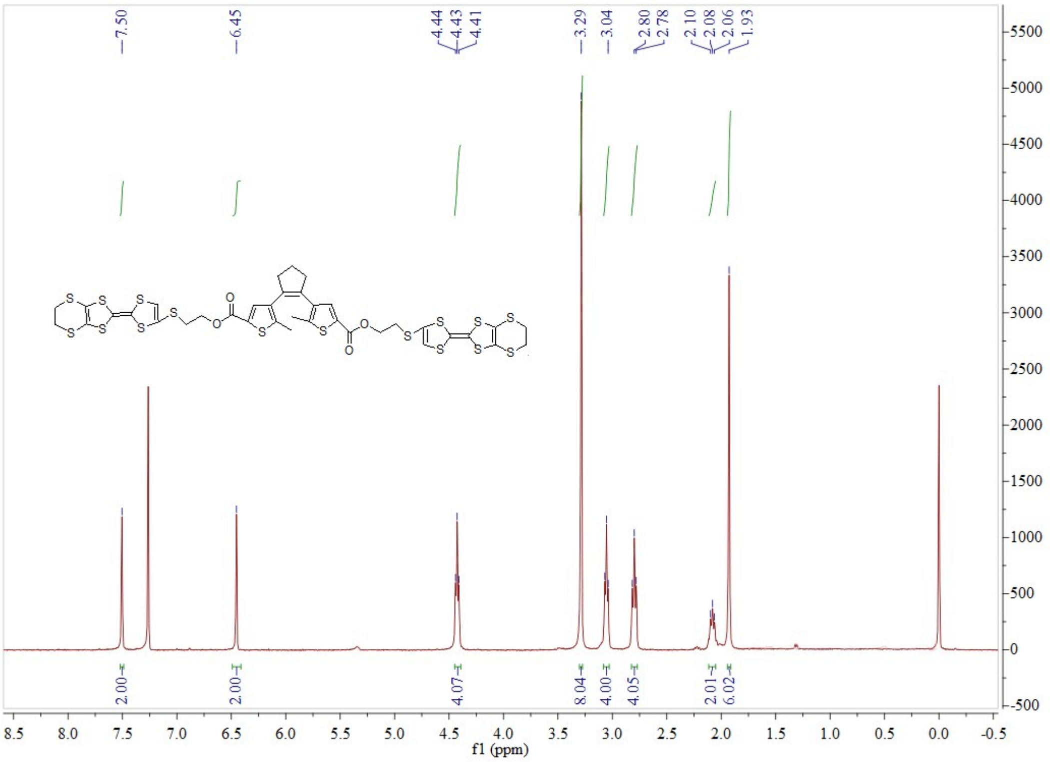


Fig. S8 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **2o**

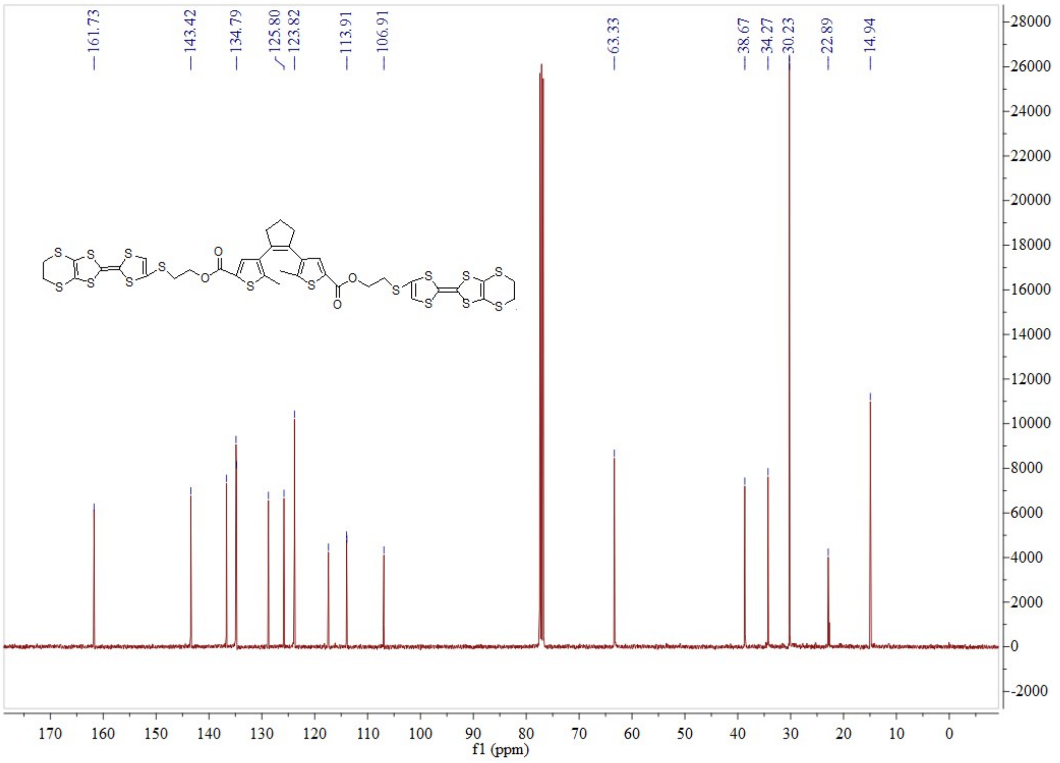
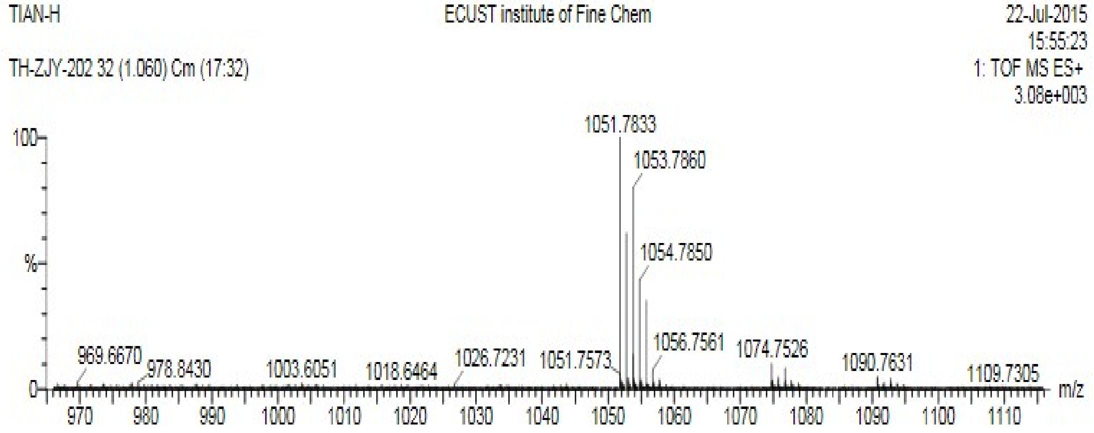


Fig. S9 ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **2o**



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Minimum:                       -1.5
Maximum:          300.0  50.0  100.0

Mass       Calc. Mass  mDa   PPM   DBE   i-FIT  i-FIT (Norm) Formula

1051.7833  1051.7832   0.1   0.1   22.0  178.1  0.0          C37  H32  O4  S16
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Fig. S10 High Resolution Mass spectra of compound **2o**

References

1. L. Zou, W. Xu, X. Shao, D. Zhang, Q. Wang and D. Zhu, *Org. Biomol. Chem.*,

2003, **1**, 2157;

2. A. J. Myles and N. R. Branda, *Macromolecules*, 2003, **36**, 298;
3. J. Jin and L. Zou, *Chin. J. Chem.*, 2011, **29**, 2445.