Electronic Supplementary Information (ESI)

Reversible photocontrollable gels based on bisthienylethene-doped lecithin micelles

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Contents:

Experimental section

Materials

The synthesis of **3** 1-(5-chloro-2-methyl-3-thienyl)-2-(5-formyl-2-methyl -3- thienyl) cyclopentene and **5** N-(4-bromophenyl)-aza-15-crown-5-ether were based on the literature method[1,2]. Soybean lecithin (95% purity) was purchased from Lipoid. n-Decane (at least >99% purity) were purchased from Adamas. All purchased chemicals and reagents were of high commercially available grade. Solvents were purified by standard procedures.

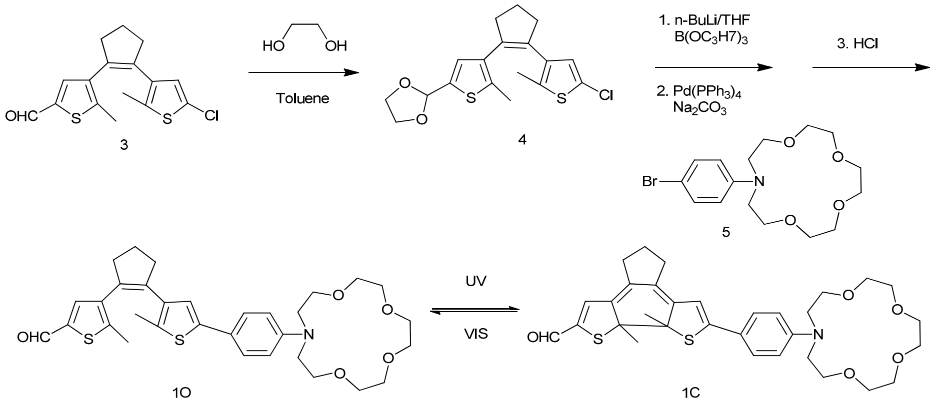
Sample preparation

Ground lecithin was dried in a vacuum oven at least for 48 h to remove residual water. Lecithin and anhydrous $CaCl_2$ (molar ratio=3/1) were mixed together in n-decane. The solutions became transparent and homogeneous by stirring and heating at 60°C. When it was cooled to room temperature, the original gel sample was obtained. The photocontrollable gel sample was obtained by adding 1mg 1O to 1mL original gel. The mixture was heated and stirred at 60°C for ca. 10 minutes till it became transparent and homogeneous. When it was cooled to room temperature, the fluid which could be stimulated by light was obtained.

Instrumentations

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer in $CDCl_3$ solutions using tetramethylsilane as the internal standard (chemical shifts in departs per million). High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70eV). All UV-Vis absorption spectrum were recorded with a Varian Cray 500. Dynamic rheological experiments were performed on an Anton-Paar physica MCR101 rheometer.

Scheme S1 Synthetic route of compounds **1O** and **1C**.



Synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-(1, 3-dioxolane)-2-methyl-3-thienyl) cyclopentene (**4**)

3 (0.45g, 1.36mmol), ethylene glycol (0.5mL, 8.98mmol) and p-toluenesulfonic acid (10mg) in toluene (15mL) was added in a 50mL flask with the Dean-Stark apparatus. Then the mixture was refluxed for overnight. After cooling, the reaction mixture was poured into 10% NaOH aqueous solution (30 mL). The resulting mixture was extracted by dichloromethane (3 times), and the combined organic extracts were dried with anhydrous Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, Ethyl Acetate/ petroleum ether 1:3) to give the compound **4** (0.43g, 86.5%) as a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 6.58 (s, 1H), 5.97 (s, 1H), 4.12 – 4.07 (m, 2H), 4.01 – 3.97 (m, 2H), 2.68 – 2.78 (m, 4H), 2.05 – 1.99 (m, 2H), 1.96 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 137.15, 136.02, 135.15, 134.86, 133.74, 133.22, 127.40, 126.77, 124.99, 100.35, 65.11, 38.35, 22.86, 14.43, 14.12. HRMS (ESI) calcd for $C_{18}H_{20}O_2S_2Cl$ (M+H) 367.0593, found 367.0588.

Synthesis of 1-(5-(4-aza-15-crown-5-phenyl)-2-methyl-3-thienyl)-2-(5-(1, 3-dioxolane)-2-methyl-3-thienyl) cyclopentene (**1O**)

To a stirred solution of 4 (0.42 g, 1.15 mmol) in THF (10 ml) at -78 ºC under Ar_2 in the absence of light was added dropwise 2.4 M *n*-BuLi in hexane (0.72, 1.72 mmol), and the reaction mixture was stirred at -78 ºC for further 30 min. Then triisopropyl borate (0.42 mL, 1.8 mmol) was quickly added in one portion. This reaction mixture was stirred for 1 h at room temperature, and was then used in the Suzuki coupling reaction.

A mixture of 5 (0.43 g, 1.15 mmol) and the catalyst Pd $(PPh_3)_4$ in 20 ml THF under Ar_2 was stirred for 15 min at room temperature. Then aqueous Na_2CO_3 (20 mL, 2 M) was added. The reactive mixture was heated at a temperature of 60 ºC, and the solution of boronic esters prepared from 4 was added dropwise via a syringe. Subsequently, the mixture was refluxed for 12 h and cooled to room temperature. The reactive mixture was poured into water and extracted with ether, and the organic layer was collected and dried with anhydrous $MgSO_4$.

After filtration and concentration, the mixture was dissolved in THF (10 ml), and then concentrated hydrochloric acid (10mL) was added dropwise. After stirred at room temperature for 2 hours, the resulting mixture was extracted by dichloromethane (3 times) and the organic solvent was washed with saturated $NaHCO_3$ aqueous, dried with anhydrous Na_2SO_4, and removed in vacuum. The residue was purified by column chromatography (silica gel, Ethyl Acetate/ petroleum ether 2:1) to give the compound **1O** (0.305g, 45.7%) as a colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.48 (s, 1H), 7.32 (d, J = 8.8 Hz, 2H), 6.77 (s, 1H), 6.62 (d, J = 8.9 Hz, 2H), 3.76 (t, J = 6.2 Hz, 4H), 3.70 – 3.58 (m, 16H), 2.90 – 2.76 (m, 4H), 2.08 – 2.12 (m, 2H), 2.08 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.70, 146.78, 141.02, 139.65, 138.33, 137.94, 136.90, 135.68, 132.61, 132.13, 126.52, 122.11, 121.08, 111.53, 71.34, 70.17, 68.47, 52.56, 38.37, 22.97, 15.51, 14.29; HRMS (ESI) calcd for $C_{32}H_{40}NO_5S_2$ (M+H) 582.2348, found 582.2348.

Synthesis of ring-closed isomer **1C**

1O (100mg) was dissolved in CH_2Cl_2 (50 ml), then irradiated with 365nm UV light till the color of the solutions would not become deeper. After solvent was removed in vacuum, the residue was purified by column chromatography (silica gel, Ethyl Acetate/ petroleum ether 2:1) to give the compound **1C** (71g, 71%) as a blue solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.38 (d, J = 8.9 Hz, 2H), 6.74 (s, 1H), 6.63 (d, J = 9.0 Hz, 2H), 6.22 (s, 1H), 3.76 (t, J = 6.1 Hz, 4H), 3.70 – 3.60 (m, 16H), 2.50 (m, 4H), 2.01 (s, 3H), 1.97 (s, 3H), 1.95 – 1.89 (m, 2H).

Crystallography

Single crystals of **1O** suitable for X-ray analyses were obtained by recrystallization in the ethanol solutions.

Crystal data for **1O**: C32 H39 N O5 S2, Mw=581.76 g·mol^{-1}, 0.20 x 0.16 x 0.12 mm^3, Orthorhombic, Pca2(1), a = 14.249(3), b = 15.131(3), c = 14.177(3) Å, β= 90°, V=3056.6(10) Å^3, F(000)=1240, ρ_{calcd}=1.264 Mg/m^3, $\mu(MoK\alpha)$=0.214 mm^{-1}, T=140(2) K, 29544 data were measured on a Bruker SMART Apex diffractometer, of which 8916 were uinque (R_{int}=0.1465); 363 parameters were refined against Fo^2 (all data), final wR_2=0.1147, S=1.056, $R_1(I>2\sigma(I))$=0.0711, largest final difference peak/hole= +0.984/-0.935 eÅ^{-3}. Structure solution by direct methods and full-matrix least-squares refinement against F^2 (all data) using SHELXTL.

Conversion at photostationary state

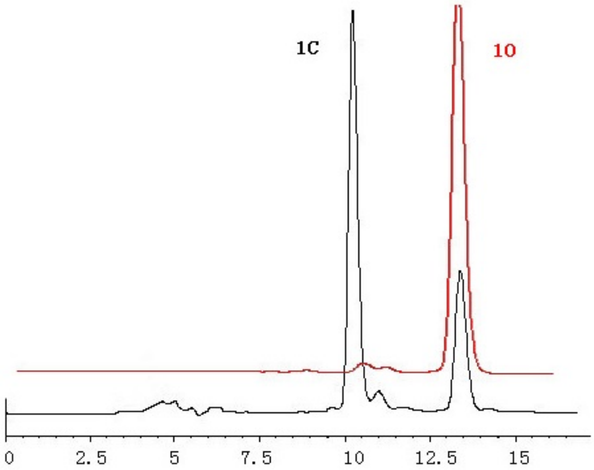


Fig. S1 The photoconversion ratios of diarylethene **1** at photostationary state in methanol analyzed by HPLC method.

Association constant

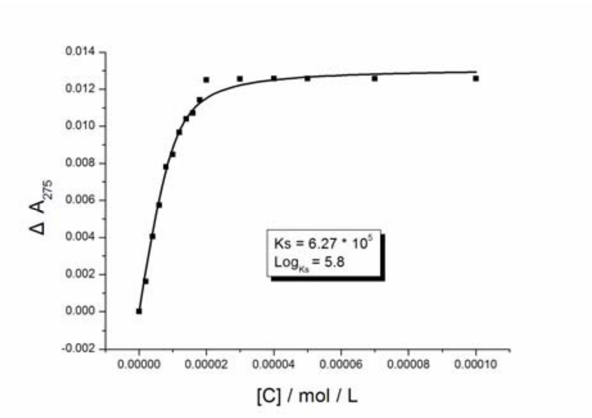


Fig. S2 Association constant of **1O** with Ca^{2+}.

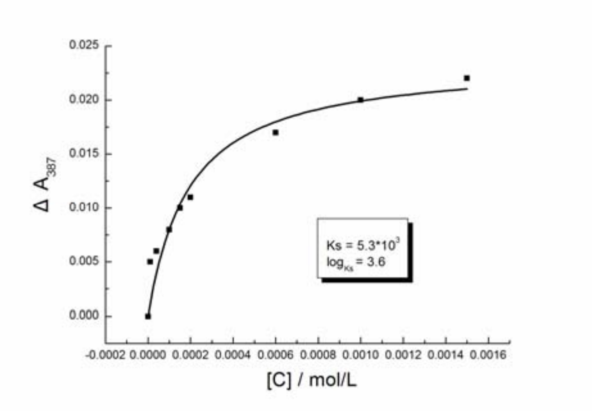


Fig. S3 Association constant of **1C** with Ca^{2+}.

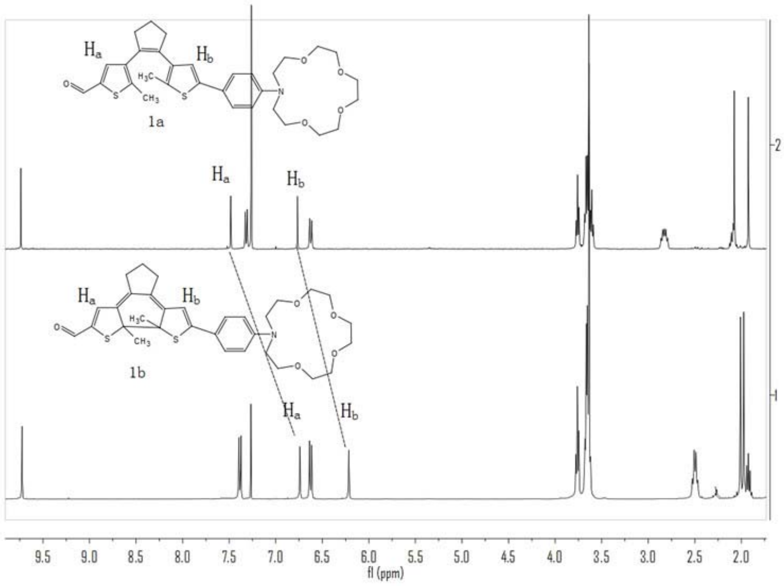


Fig. S4 ^{1}H NMR ($CDCl_3$, 400 MHz) spectral changes of **1O** and **1C**.

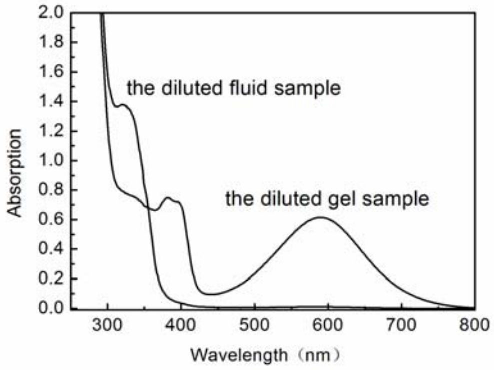


Figure S5 Absorption spectra of the diluted samples containing 2.5 mM lecithin, 0.83 mM $CaCl_2$ and 0.17mM **1** in n-decane at 25 °C.

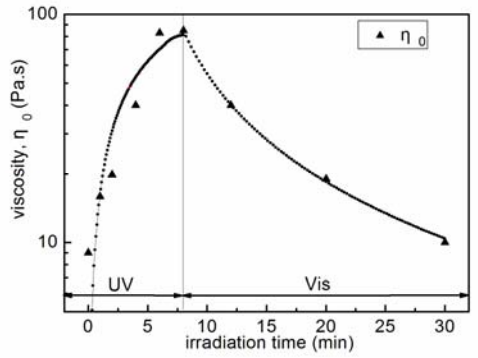


Fig. S6 Changes of the zero shear viscosity η_0 of the sample in n-decane containing 25mM lecithin, 8.3mM $CaCl_2$ and 1.7mM **1O** at room tempurature. Before irradiation, the fluid has a low viscosity. Upon UV irradiation for 8 min, the viscosity increases 10-fold relative to its initial value, and the sample is gel-like. Upon visible light irradiation for 22 min, the viscosity almost recovers to its initial value.

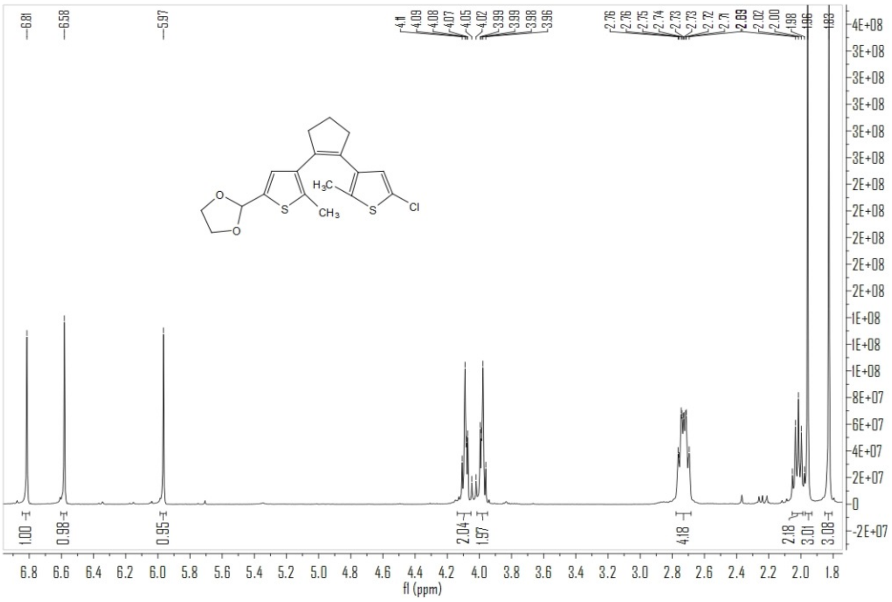


Fig. S7 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **4**.

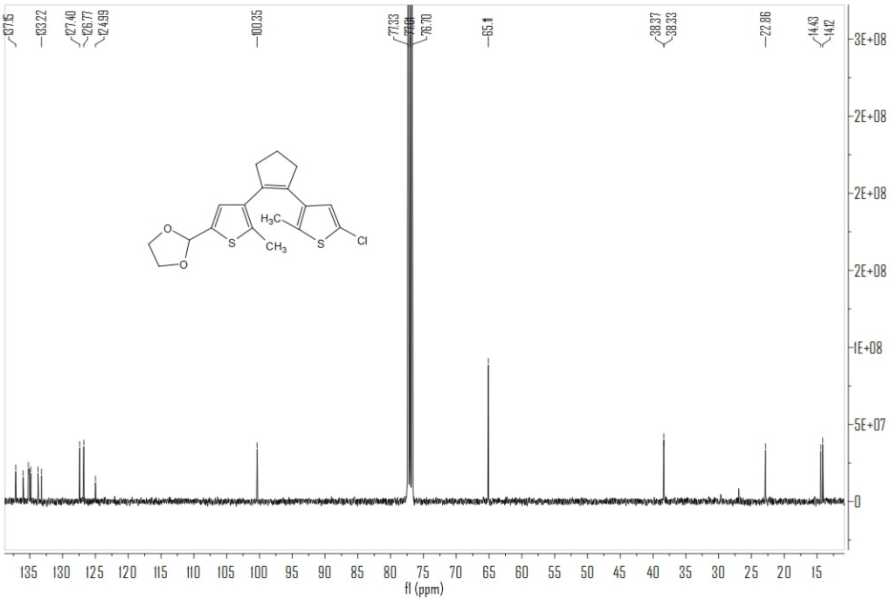
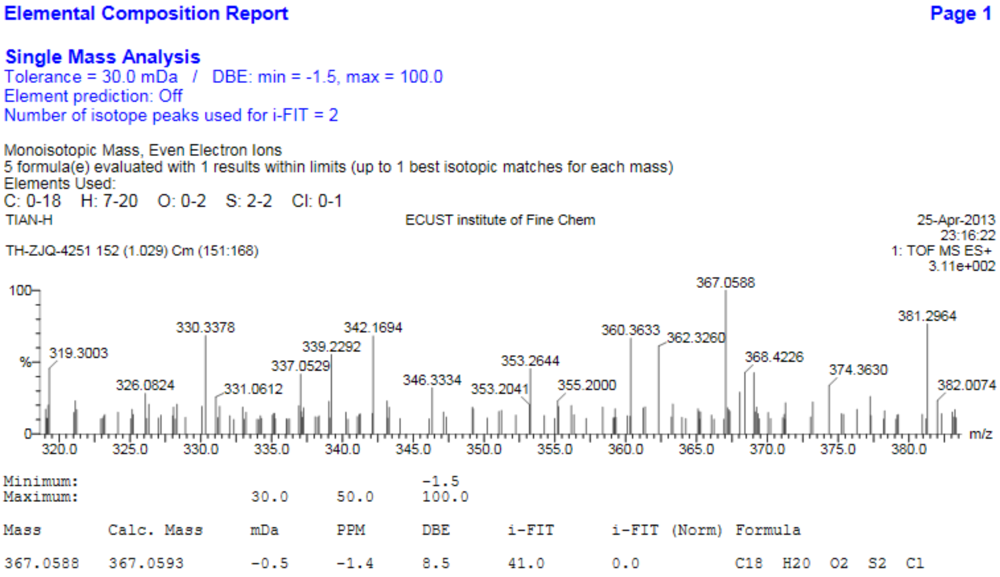


Fig. S8 ^{13}C NMR (CDCl$_3$, 100 MHz) spectrum of **4**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-18 H: 7-20 O: 0-2 S: 2-2 Cl: 0-1
TIAN-H ECUST institute of Fine Chem 25-Apr-2013
23:16:22
TH-ZJQ-4251 152 (1.029) Cm (151:168) 1: TOF MS ES+
3.11e+002

```
Minimum:                                   -1.5
Maximum:                  30.0      50.0      100.0

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

367.0588    367.0593      -0.5     -1.4     8.5      41.0       0.0          C18  H20  O2  S2  Cl
```

Fig. S9 HRMS (ESI) spectrum of compound **4**.

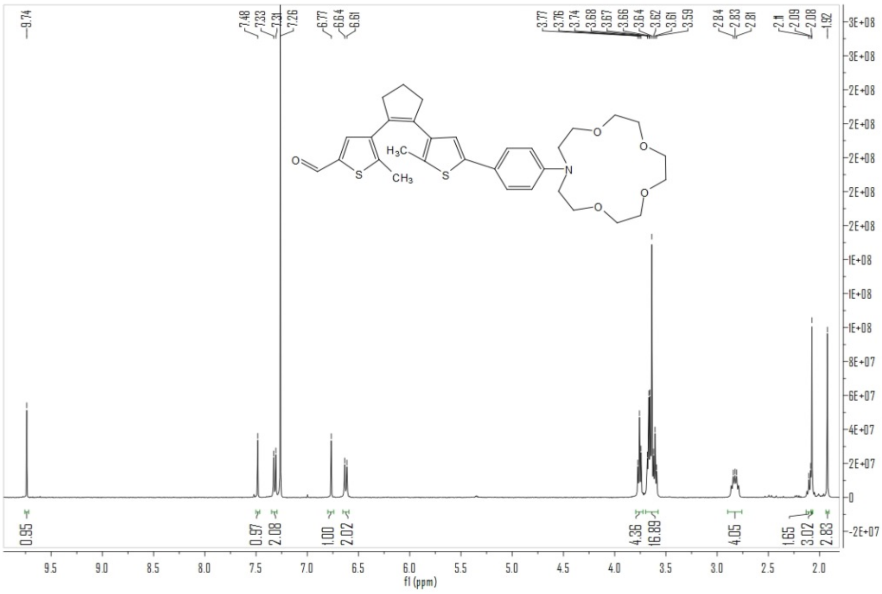


Fig. S10 ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of **1O**.

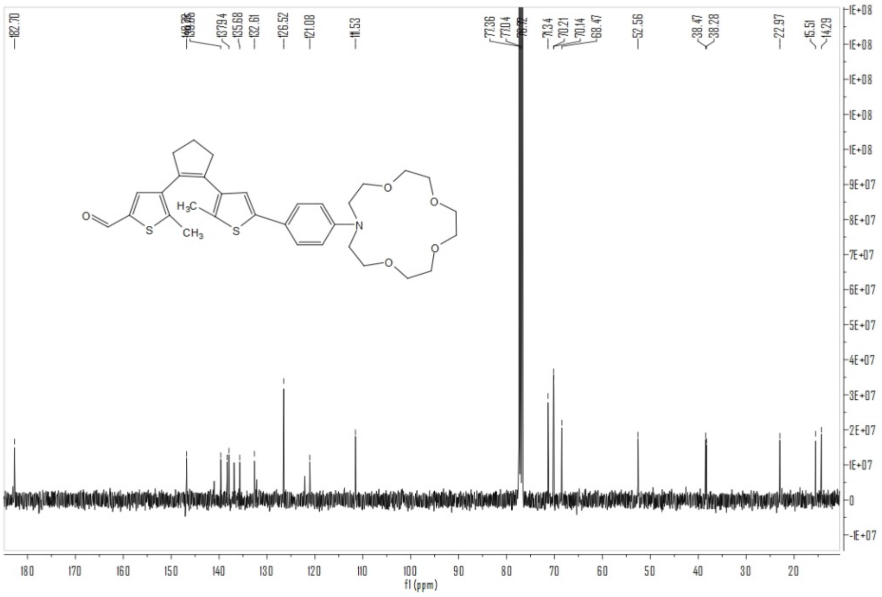
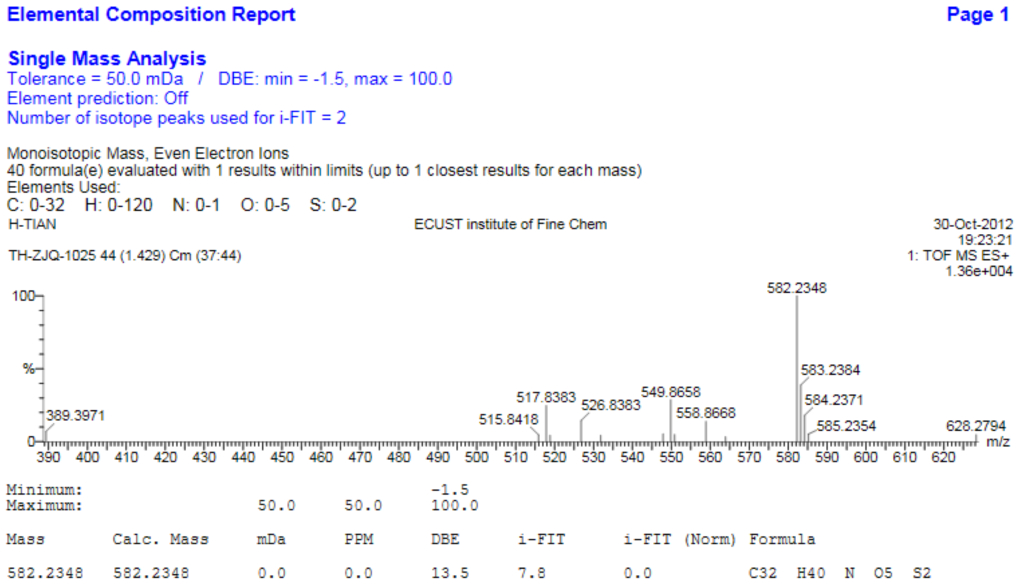


Fig. S11 ^{13}C NMR (CDCl$_3$, 100 MHz) spectrum of **1O**.



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-32 H: 0-120 N: 0-1 O: 0-5 S: 0-2

```
Minimum:                                    -1.5
Maximum:                 50.0      50.0     100.0

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

582.2348    582.2348     0.0       0.0      13.5      7.8        0.0          C32  H40  N  O5  S2
```

Fig. S12 HRMS (ESI) spectrum of compound **1O**.

References

1. Q. Zou, J. Y. Jin, B. Xu, L. Ding, H. Tian, *Tetrahedron*, 2011, **67**, 915-921.
2. A. Khazaei, M. A. Zolfigol, E. Kolvari, N. Koukabi, H. Soltani, F. Komaki, *Synthesis*, 2009, **21**, 3672 – 3676.