Electronic Supplementary Information

A photochromic fluorescent switch in organogel system with non-destructive readout ability

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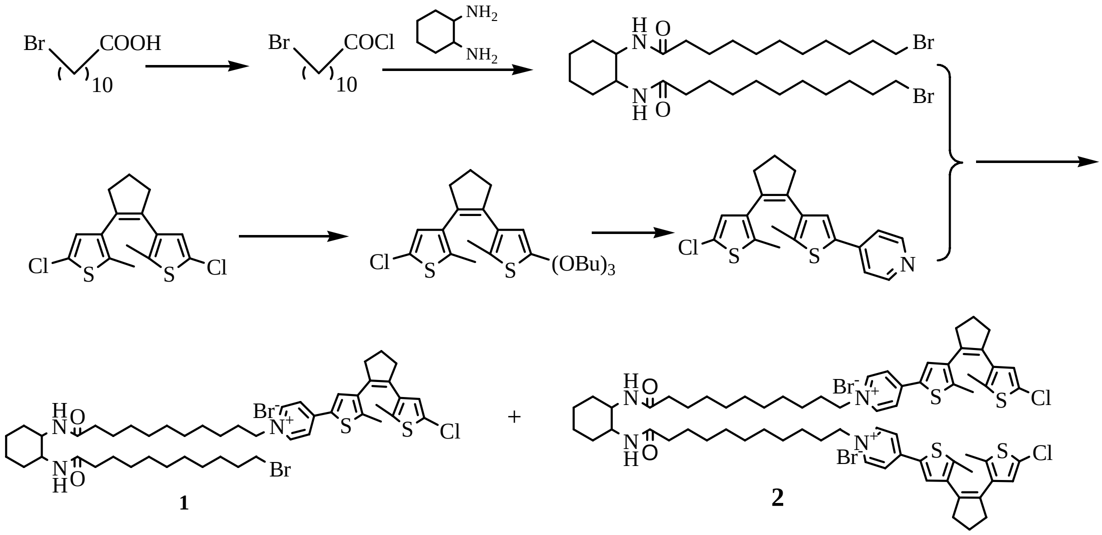
Experimental

All starting materials were obtained from commercial supplies and used as received. (±)-*trans*-Cyclohexanediamine was purchased from Lancaster. 11-Bromodecanoic acid, *n*-butyllithium and tetrakis(triphenylphosphine)palladium were purchased from Sigma-Aldrich. 2-Methylthien, pentanedioic acid, and other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). Column chromatography was carried out on silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercuryplus-Varian instrument (400 MHz). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). MALDI-TOF-MS was recorded on AXIMA-CFRPLVS mass spectroscopy instrument (Shimadzu). Melting points were determined on a hot-plate melting point apparatus XT4-100A without correction. Element analysis was carried out on a VARIOEL3 apparatus (ELEMENTAR). UV-Vis spectra were recorded on UV-Vis 2550 spectroscope (Shimadzu). Fluorescent spectra were measured on Edinburgh Instruments (FLS 900). The UV and visible irradiations were carried out on a CHF-XM550W power system (China) by using suitable band-pass filter (Omega). Confocal fluorescence imaging was performed with an OLYMPUS IX81 laser scanning microscopy with a 60x oil-immersion objective lens. Excitation at 488 nm was carried out with a Multi Ar laser; irradiation with 405 nm was carried out with a semiconductor laser, and emission was collected from 550 to 650 nm. SEM images of the xerogels were obtained using a SSX-550 (Shimadzu) with an accelerating voltage of 15 KV. Samples were prepared by spinning the gels on glass slices and coating with Au. TEM was recorded on a JEOL JEM-2011 apparatus operating at 200 KV. The sample was prepared by putting the gel on a carbon-coated copper grid and staining with phosphotungstic acid (2.0 wt% aqueous solution).



Scheme S1. Synthetic routes of diarylethenes **1** and **2**

Synthesis and characterizations

(±)-1,2-bis(11-bromoundecanoylamino)cyclohexane was synthesized according to reference,[1] using (±) cyclohexanediamine as a starting material. The product obtained as a white solid with 71% yield. M.p: 94 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.98 (s, 2H), 3.65 (t, J=6.4, 2H), 3.41 (t, J=5.2, 4H), 2.12-1.27 (m, 44H).

1-(5-chloro-2-methylthien-3-yl)-2-[2-methyl-5-(pyridine-4-yl)thien-3-yl]cyclopentene: The intermediate of 1-(5-chloro-2-methylthien-3-yl)-2-[5-(dibutoxyboryl)-2-methylthien-3-yl] cyclopentene was prepared according to reference,[2] using 3.0 g 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene. Then the THF solution of prepared compound was added to a flask containing 4-bromopyridine hydrochloride (1.8 g), $Pd(PPh_3)_4$ and 30 mL Na_2CO_3 solution (20 wt %) at 50 ºC. The reaction was refluxed under Ar atmosphere for 6 h. Column chromatograph (chloroform) was carried out to obtain a pale yellow sticky solid (1.8 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.83 (d, J = 5.2, 2H), 7.34 (d, J = 5.6, 2H), 7.18 (s, 1H), 6.60 (s, 1H), 2.79 (m, 4H), 2.06 (m, 2H), 2.03 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 14.42, 14.85, 23.14, 38.59, 38.64, 119.47, 125.47, 126.48, 126.94, 133.49, 134.74, 134.90, 135.13, 136.81, 137.21, 137.51, 141.51, 150.45. EI-ms (m/z): 371.1 (M^+).

11-(4-{5-[2-(5-Chloro-2-methyl-thiophen-3-yl)-cyclopentene]-2-methyl-thiophen-3-yl}-pyridinium)-undecanoic acid [2-(11-bromo-undecanoylamino)-cyclohexyl]-amide (1): 0.74 g (±)-1,2-bis(11-bromoundecanoylamino)cyclohexane (1.2 mmol) and 1.0 g 1-(5-chloro-2-methylthien-3-yl)-2-[2-methyl-5-(pyridine-4-yl)thien-3-yl]cyclopentene (2.7 mmol) was refluxed in acetonitrile for 24 h. The pure product of **1** was obtained as a yellow solid by column chromatograph (dichloromethane : methanol=20:1) with the yield of 36%. M.p: 98 ºC; ^{1}H NMR (400 MHz, CD_3OD): δ = 8.74 (d, J = 6.8, 2H), 8.10 (d, J = 6.8, 2H), 7.90 (s, 1H), 6.68 (s, 1H), 4.48 (t, J = 7.2, 2H), 3.59 (t, J = 4.8, 2H), 3.41 (t, J = 6.8, 2H), 2.84 (m, 4H), 1.17-2.13 (m, 20H), 1.29-1.57 (m, 32H); ^{13}C NMR (100 MHz, CD_3OD): δ = 13.17，13.96，22.77，24.71，25.97，26.04，28.03，28.69，29.00，29.17，29.30，29.33，29.41，31.13，32.14，32.85，33.41，36.26，38.17，52.84，60.56，121.78，125.36，126.93，133.18，133.20，133.66，134.29，135.08，136.14，139.52，144.28，145.03，149.20，174.81; Anal. Calcd (%) for $C_{48}H_{70}Br_2ClN_3O_2S_2$: C 58.80, H 7.20, N 4.29; Found: C 58.04, H 7.15, N 4.68; Maldi-tof (m/z): 899.8 $(M-Br^-)^+$.

Yellow compound **2** was obtained as a by-product with 4% yield. M.p: 119 ºC; ^{1}H NMR (400 MHz, CD_3OD): δ = 8.74 (d, J = 6.8, 4H), 8.10 (d, J = 6.8, 4H), 7.89 (s, 2H), 6.67 (s, 2H), 4.48 (t, J = 7.6, 4H), 3.59 (t, J = 3.2, 2H), 2.84 (m, 8H), 1.91-2.13 (m, 28H), 1.29-1.56 (m, 32H); ^{13}C NMR (100 MHz, CD_3OD): δ= 13.09，13.89，22.75，24.68，25.93，26.02，28.96，29.10，29.24，29.29，31.09，32.10，36.22，38.12，52.83，60.54，121.74，125.36，126.92，133.14，133.19，133.66，134.28，135.07，136.16，136.20，139.52，144.26，145.07， 149.23，174.822; Maldi-tof (m/z): 1188.8 (M-2Br$^-$)$^+$.

Fig. S1. Images of the sol-gel transition and photochromism of **1O** gel.

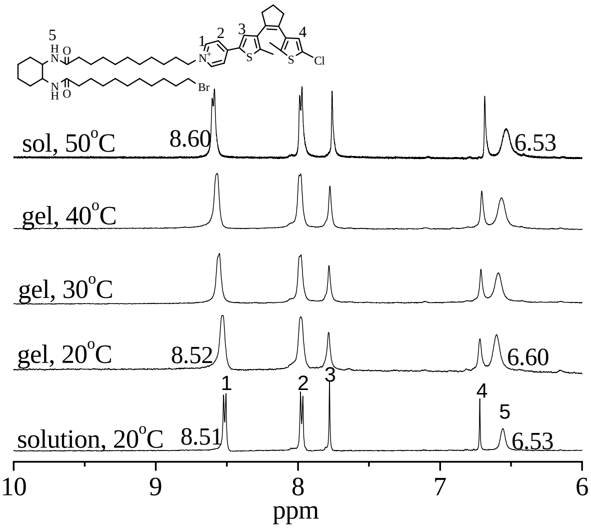


Fig. S2 Concentration and temperature-dependent 1H NMR spectra (solution, 5.0×10^{-3} M; gel, 2.0×10^{-2} M, CD_3CN)

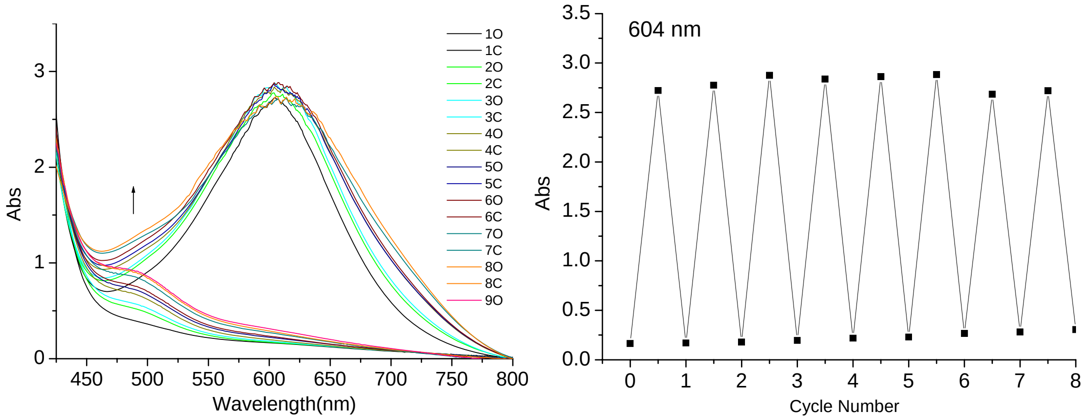


Fig. S3 (A) Absorption spectral change of **1O** gel (1.5×10^{-2} M in 1 mm quartz vessel) under alternate irradiation of 365 and 620 nm irradiation. (B) Absorption switch cycles upon alternating irradiation of UV (15 min/cycle) and visible light (3.5 hr/cycle) of **1O** gel

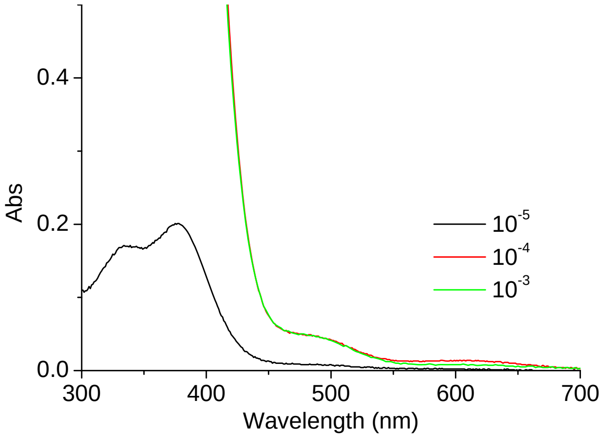


Fig. S4 Absorption spectra of **1O** in acetronitrile with different concentrations. (spectra of 10^{-5} and 10^{-4} M were charactered in 10 mm quartz vessel, and spectrum of 10^{-3} M was measured in 1 mm quartz vessel).

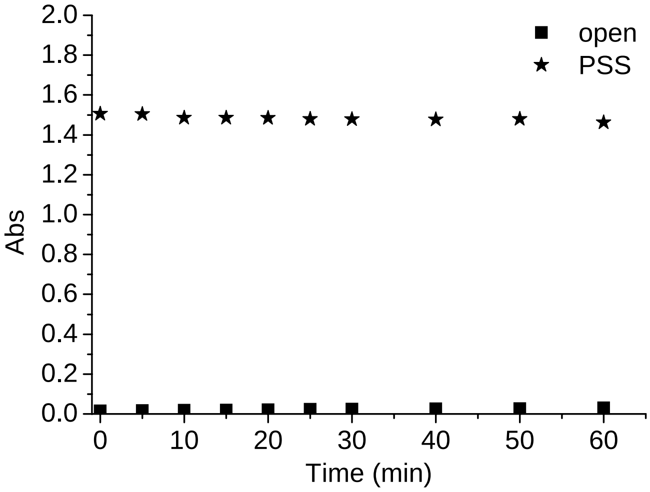
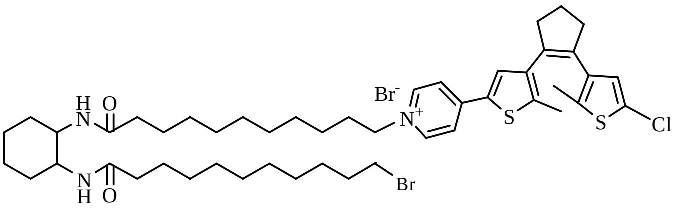
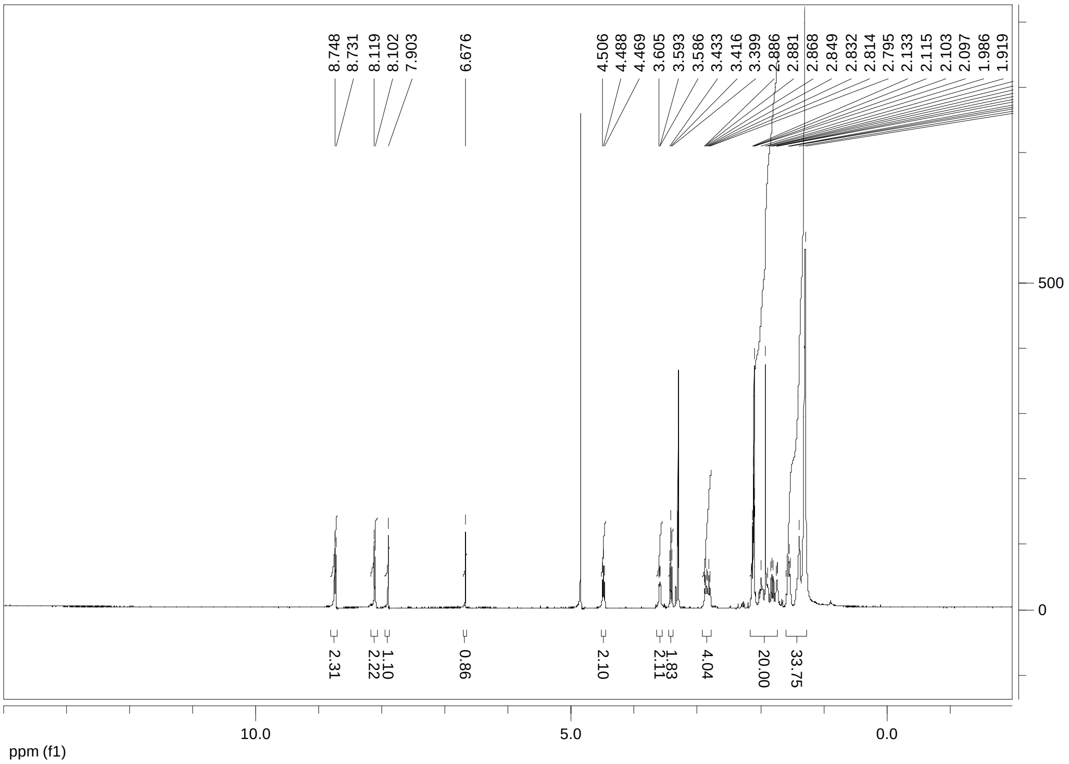
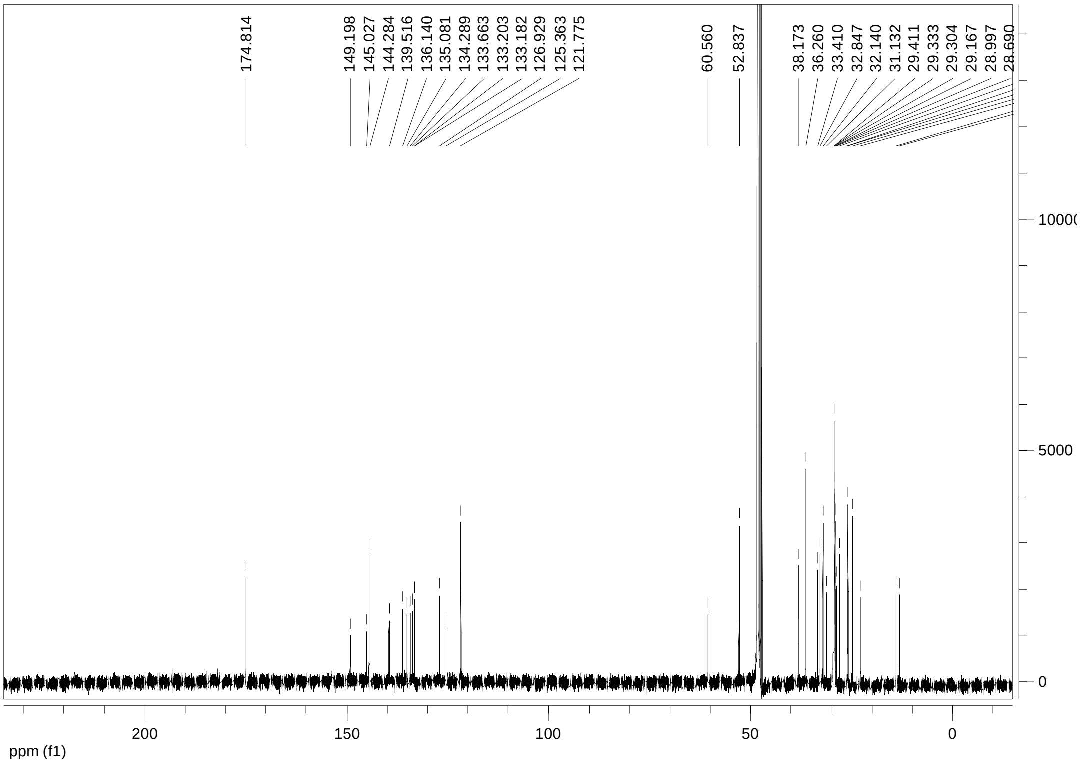


Fig. S5 Absorption change of **1O** (1.0×10^{-3} M in 1 mm quartz vessel) at 610 nm under 470 nm irradiation.


H
N
O
N
H
O
Br-
N+
S
S
Cl
Br


8.748
8.731
8.119
8.102
7.903
6.676
4.506
4.488
4.469
3.605
3.593
3.586
3.433
3.416
3.399
2.886
2.881
2.868
2.849
2.832
2.814
2.795
2.133
2.115
2.103
2.097
1.986
1.919
500
0
2.31
2.22
1.10
0.86
2.10
2.11
1.83
4.04
20.00
33.75
10.0
5.0
0.0
ppm (f1)


174.814
149.198
145.027
144.284
139.516
136.140
135.081
134.289
133.663
133.203
133.182
126.929
125.363
121.775
60.560
52.837
38.173
36.260
33.410
32.847
32.140
31.132
29.411
29.333
29.304
29.167
28.997
28.690
1000
5000
0
200
150
100
50
0
ppm (f1)

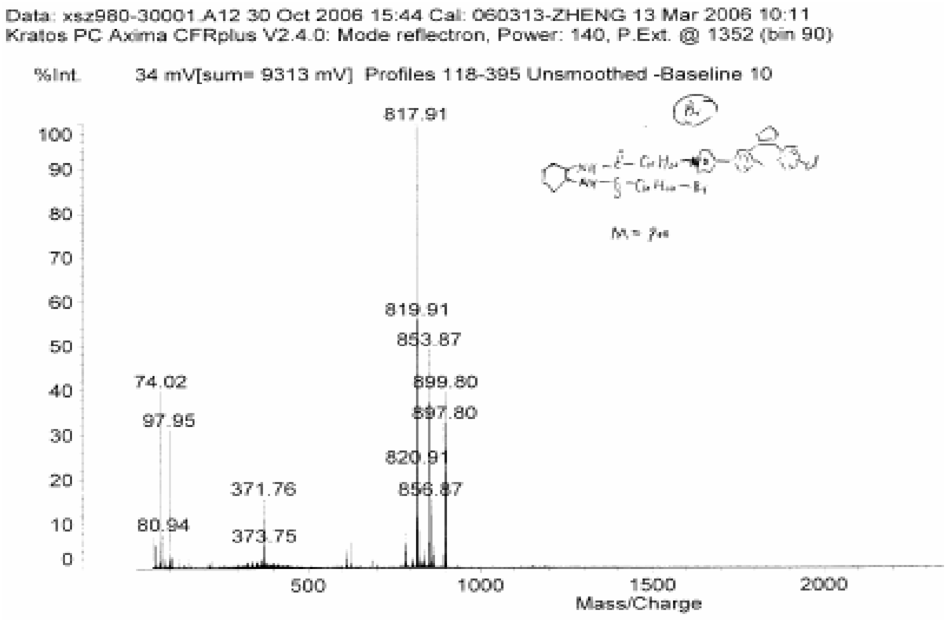
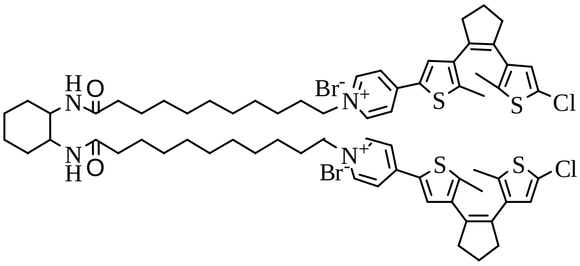
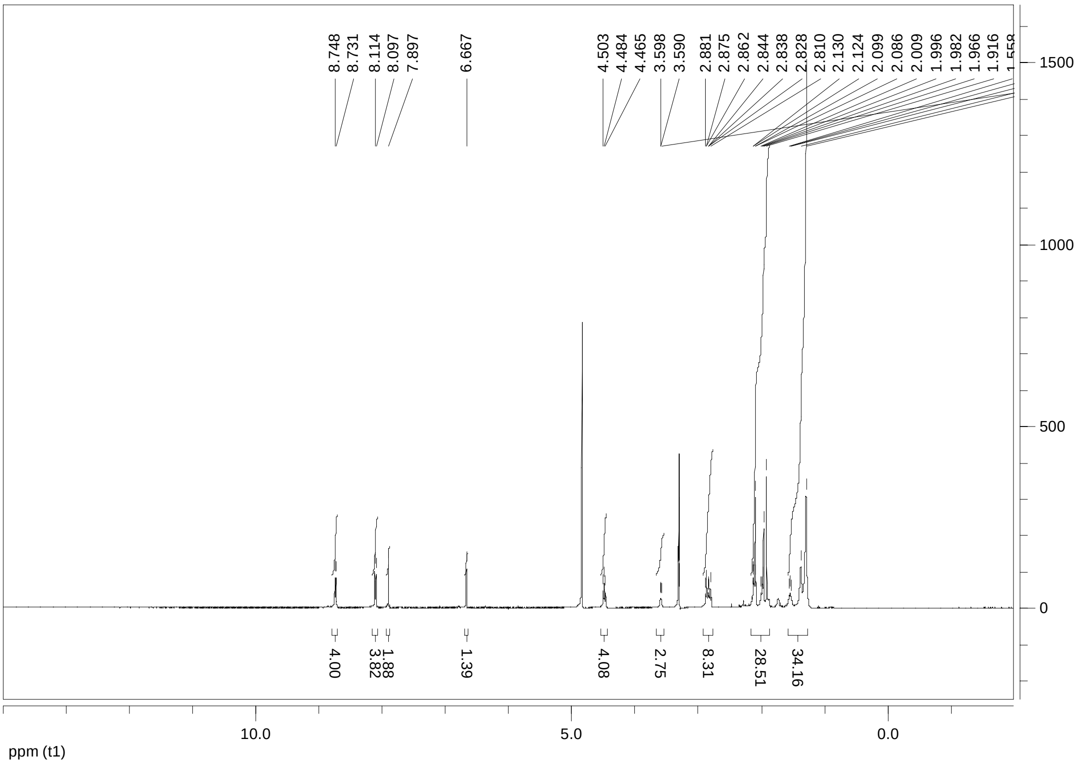


Fig. S6. ^{1}H NMR, ^{13}C NMR and Maldi-tof spectra of compound **1**. (in CD_3OD)





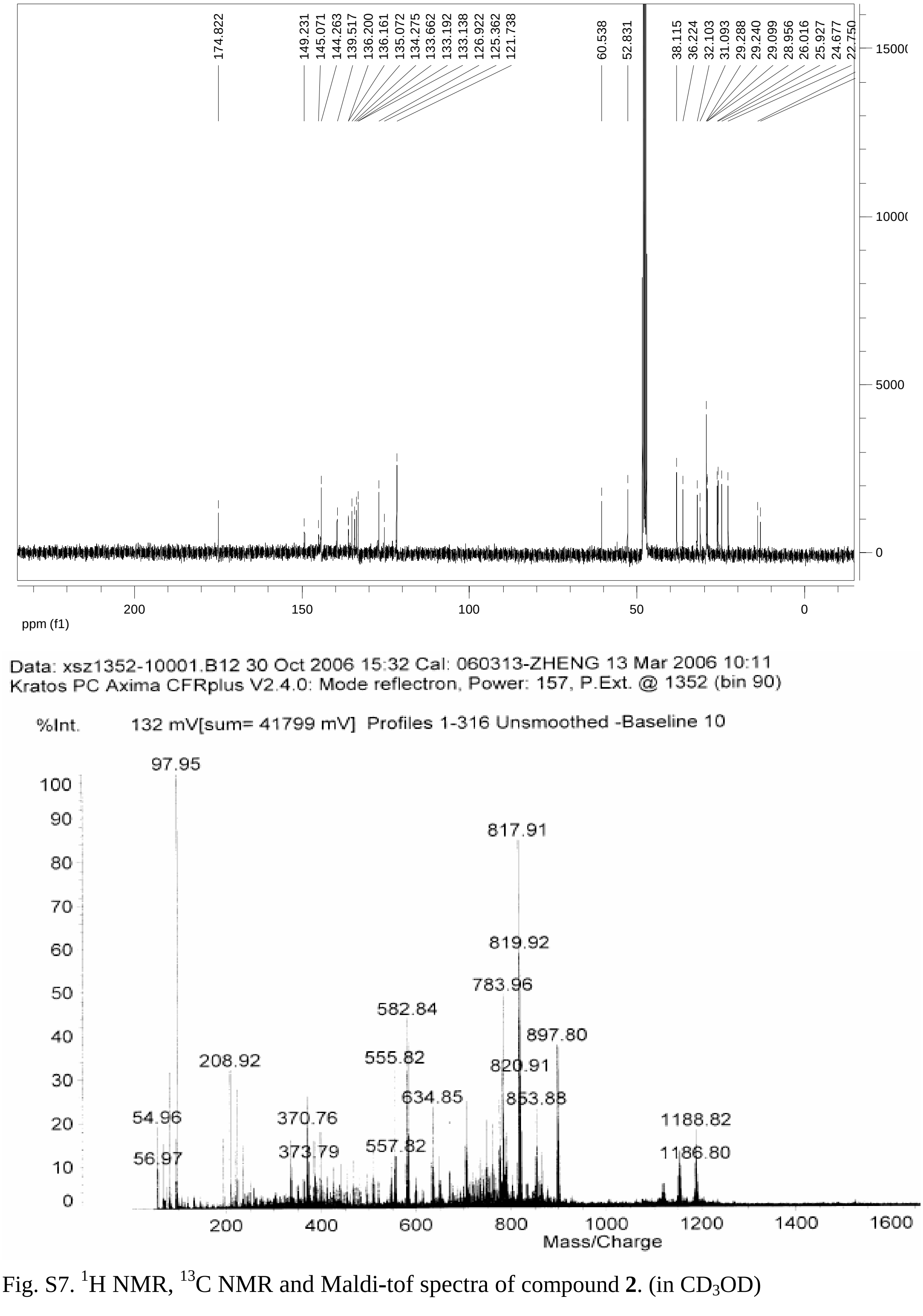


Fig. S7. ^{1}H NMR, ^{13}C NMR and Maldi-tof spectra of compound **2**. (in CD_3OD)

1. (a) Kobayashi, S.; Hanabusa, K.; Hamasaki, N.; Kimura, M.; Shirai, H. *Chem. Mater.*, 2000, 12, 1523-1525; (b) Jung, J. H.; Ono, Y.; Shinkai, S. *Chem. Eur. J.*, 2000, 6, 4552-4557.
2. Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. Eur. J. Org. Chem., 2003, 155-166