Photoresponsive organogels consisting of dithienylethenes having urea groups

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Supporting Information

1. Synthesis

The structures of diarylethene derivatives we synthesized are shown below.

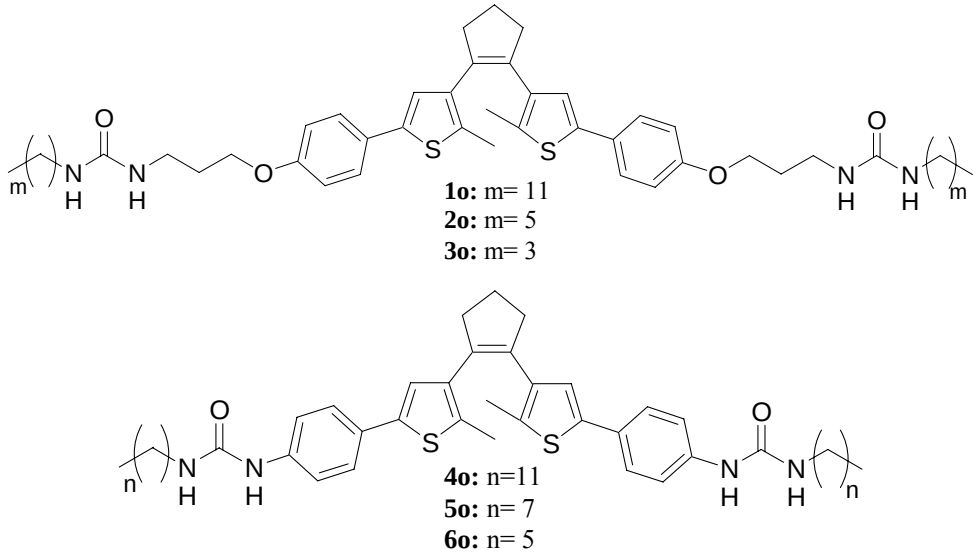
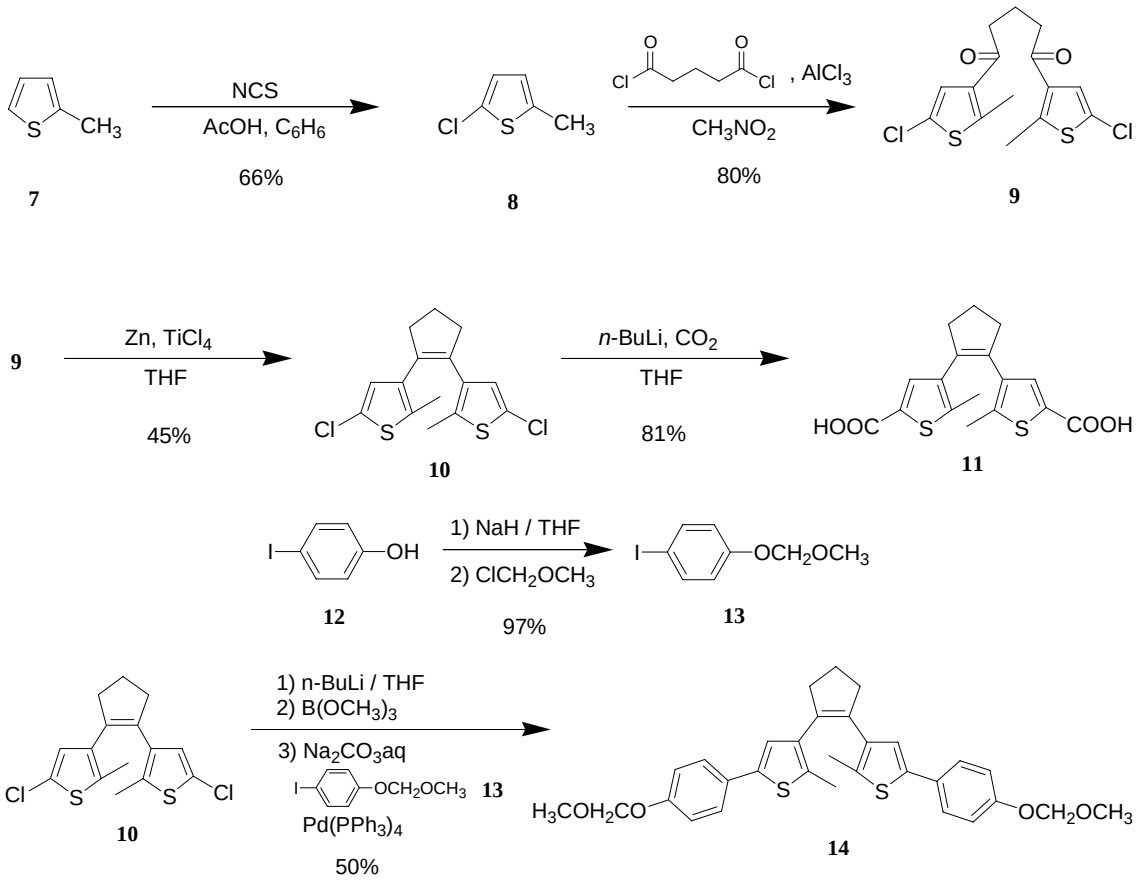
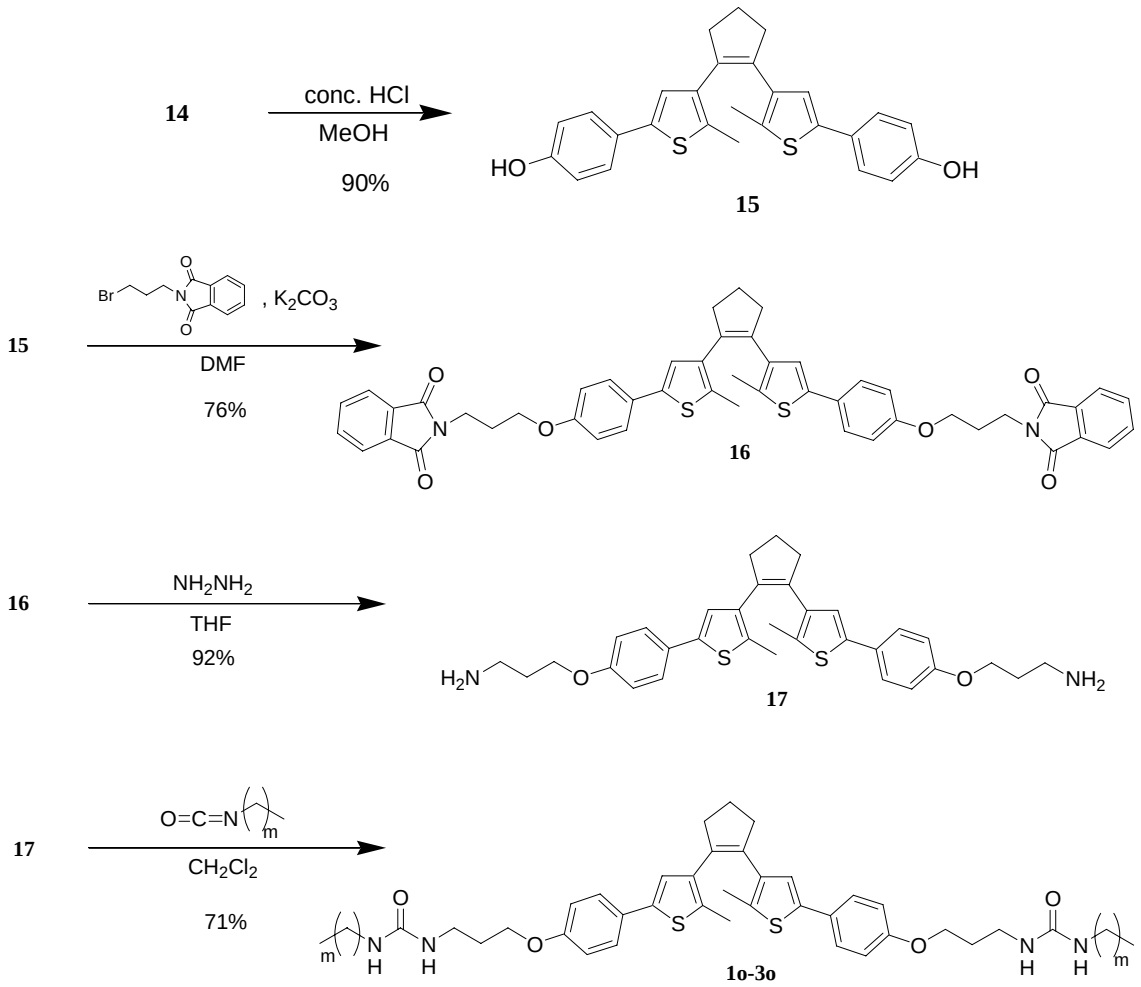


Figure S1 Diarylethenes having urea groups **1o-6o**

Synthetic Route of Diarylethenes **1o-3o** is shown in Scheme S1.





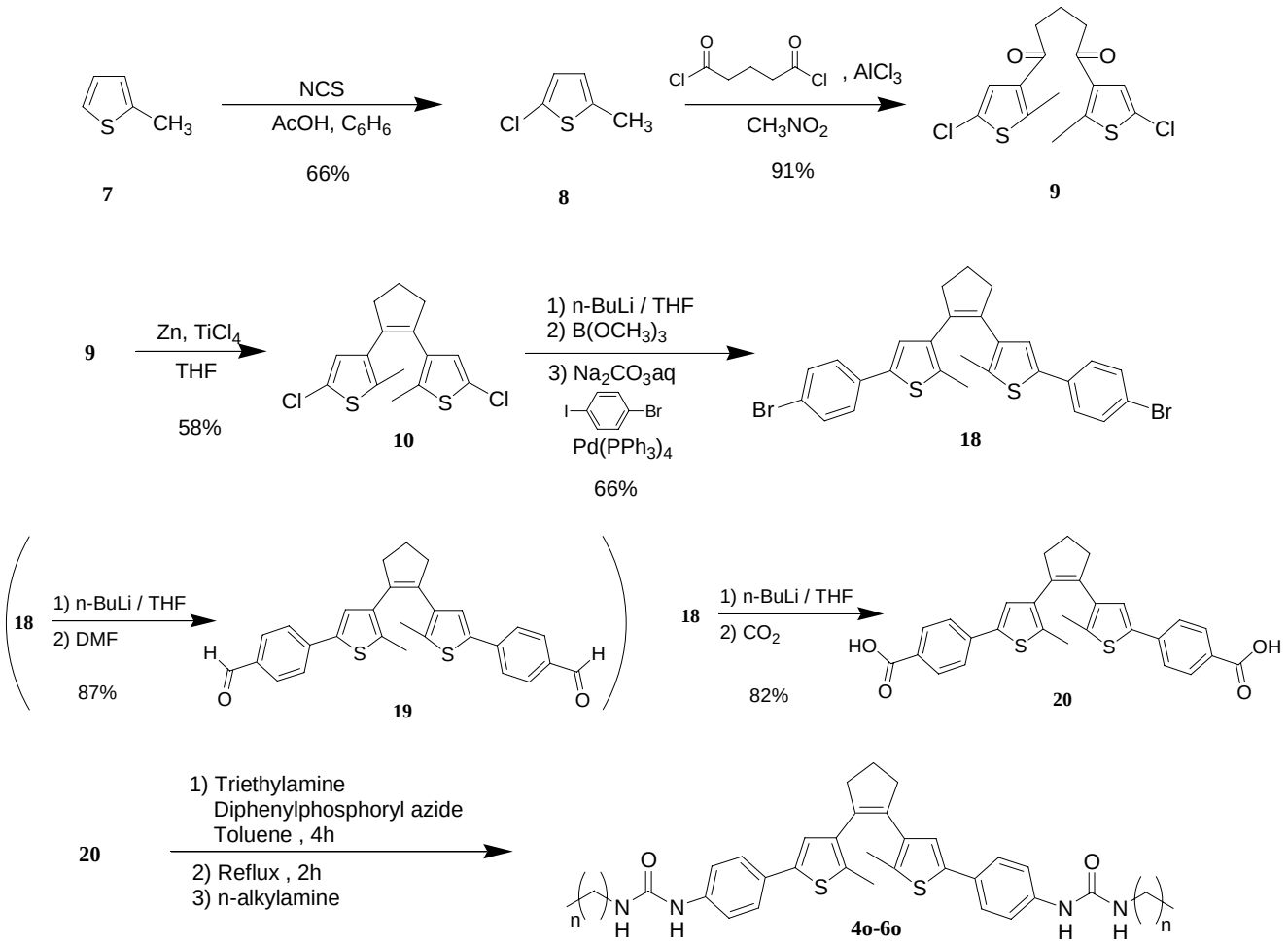
Scheme S1 Synthetic Route of Diarylethenes having Urea groups **1o**-**3o**

As shown in **Scheme S1,** 2-methylthiophene (**7**) was chlorinated by *N*-chlorosuccinimide in benzene – acetic acid mixture to form 2-chloro-5-methylthiophene (**8**) in 66% yield. **8** was acylated with glutalyl chloride in a Friedel-Crafts reaction using $AlCl_3$ in nitrobenzene solution to form 1,5-bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (**9**) in 80% yield. Under argon gas atmosphere, McMurry coupling of **9** was carried out by using Zinc powder and $TiCl_4$ in THF anhydrous to form 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (**10**) in 45% yield. Compound **10** was lithiated by addition of 1.6 N *n*-BuLi hexane solution in THF anhydrous followed by addition of dry ice to form 1,2-bis(5-carboxy-2-methylthien-3-yl)cyclopentene (**11**) in 81% yield.

In order to protect the OH group of *p*-iodophenol (**12**), NaH (60% purity) was added to the THF solution of **12** followed by the addition of chloromethyl methyl ether to obtain *p*-iodophenyl methoxymethyl ether (**13**) in 97% yield. Under Ar gas atmosphere, 1.6 N *n*-BuLi hexane solution was added to THF anhydrous solution of **10** followed by addition of trimethyl borate to obtain boric acid intermediate. The solution was warmed up to room temperature, compound **13**, 20 wt% Na_2CO_3 aqueous solution, and tetrakis(triphenylphosphine) Pd(0) were added to the reaction mixtures, and heated at 60°C with vigorous stirring, and 1,2-bis[2-methyl-5-[*p*-(2-oxapropoxy)phenyl]-3-thienyl]cyclopentene (**14**) was obtained in 50% yield. By refluxing the methanol solution of **14,** the protecting group was removed to yield 1,2-bis[2-methyl-5-(*p*-hydroxyphenyl)-3-thienyl]cyclopentene (**15**) in 90% yield. The obtained **15** was used for Williamson ether synthesis. In argon gas atmosphere, **15**, (3-bromopropyl)phthalimide, and K_2CO_3anhydrous was dissolved in DMF

anhydrous, and heated to obtain 1,2-bis[2-methyl-5-[*p*-[4-(3-phthalimide)propoxy]phenyl]-3-thienyl]cyclopentene (**16).** The yield was 76% after the purification by GPC. **16** was dissolved into THF anhydrous containing large excess amount of hydrazine anhydrous and heated with stirring under argon gas atmosphere. THF solution layer was separated by separating funnel and the solvent was evaporated to obtain 1,2-bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**) in 92% yield. To a dichloromethane solution of **17,** dodecylisocyanate was added to form 1,2-bis[2-methyl-5-[*p*-[3-(3-*N*-dodecylureido)propoxy]phenyl]-3-thienyl]cyclopentene (**1**) in 71%.

General synthetic route is shown in Scheme S2.

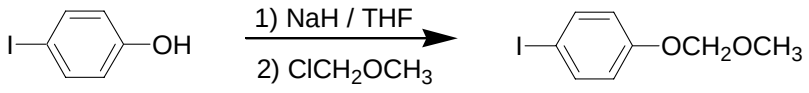


Scheme S2 Synthetic route for Diarylethenes **4o-6o**

As shown in **Scheme S2, 7** was dissolved into the mixture of benzene and acetic acid, and chlorinated by addition of *N*-chlorosuccinimide and heated to give 2-chloro-5-methylthiophene (**8**) in 66% yield. **8** was acylated with glutalyl chloride using $AlCl_3$ in nitromethane solution to form 1,5-bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (**9**) in 91% yield. **U**nder the argon gas atmosphere, McMurry coupling of **9** was carried out by using Zinc powder and $TiCl_4$ in THF anhydrous to form 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (**10**) in 58% yield. **10** Compound **10** was lithiated by addition of 1.6 N *n*-BuLi hexane solution in THF anhydrous followed by addition of *p*-bromoiodobenzene, 20 wt% Na_2CO_3 aqueous solution, and tetrakis(triphenylphosphine) Pd(0), and heated at 60^{o}C with vigorous stirring to form 1,2-bis[2-methyl-(*p*-bromophenyl)-3-thienyl]cyclopentene (**18**) in 66% yield.

Under the argon gas atmosphere, **18** was lithiated by addition of 1.6 N *n*-BuLi hexane solution in THF anhydrous, followed by addition of DMF to yield 1,2-bis[2-methyl-5-(4-formylphenyl)-3thienyl]cyclopentene (**19**) in 87% yield. The yield of oxidation of **19** to **20** by silver oxide was very low. Therefore, **18** was lithiated by addition of 1.6 N *n*-BuLi hexane solution in THF anhydrous under argon gas atmosphere, followed by addition of dry ice to form 1,2-bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**) in 80% yield. **20** was converted to **4o-6o** by refluxing (2 h) after addition of triethylamine and diphenylphosphoryl azide in toluene anhydrous under argon gas atmosphere followed by addition of alkyl amines.

_p_-Iodophenyl methoxymethyl ether (**13**)



FW:220.01
25 g, 113.6 mmol

97%

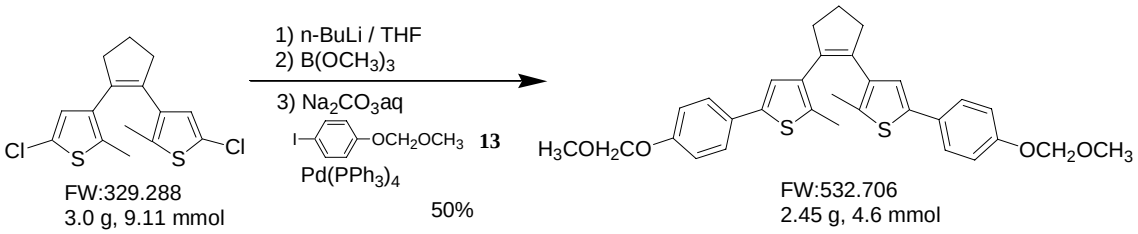
FW:264.06
29.18 g, 110.5 mmol

12 **13**

To a reaction flask (100 ml, three neck flask), *p*-iodophenol (**12**) (25 g, 113.6 mmol) and 150 ml of THF anhydrous were added. And 4.55g (113.6 mmol) of NaH (60% content) was added, and the mixture was stirred at 10 °C till the NaH powder dissolved. Then 8.63 ml (113.6 mmol) of chloromethyl methyl ether was added and stirred for 2.5 hrs. The reaction mixture was extracted with ether (3 x 80 ml), and the combined ether solution was washed with saturated $NaHCO_3$ aqueous solution (3 x 50 ml), followed by 2N NaOH solution (5 x 50 ml). The ether solution was dried over $MgSO_4$ and the solvent was evaporated to obtain *p*-iodophenyl methoxymethyl ether (**13**) (29.18 g, 110.5 mmol) as a brownish oil in 97% yield.

^{1}H-NMR(400 MHz, $CDCl_3$)δ=3.46 (s, 3H), 5.14 (s, 2H), 6.82 (d, 2H, *J*=9.0 Hz), 7.56 ppm(d, 2H, *J*=9.0 Hz) ; ^{13}C-NMR(400 MHz, $CDCl_3$)δ=56.1, 84.4, 94.4, 118.7, 138.4, 157.2 ppm

1,2-Bis[2-methyl-5-[*p*-(2-oxapropoxy)phenyl]-3-thienyl]cyclopentene (**14**)



FW:329.288
3.0 g, 9.11 mmol

50%

FW:532.706
2.45 g, 4.6 mmol

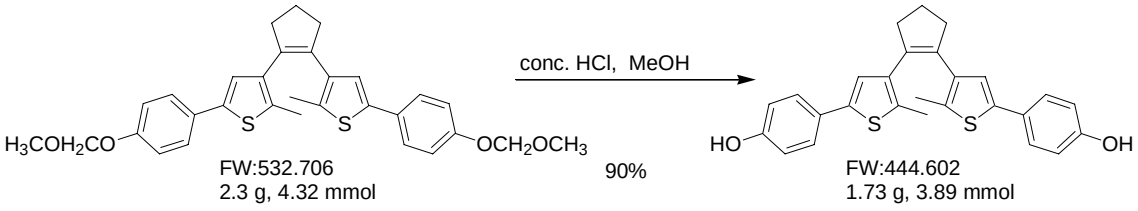
10 **14**

To a reaction flask (500 ml, three neck flask), 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (**10**) (3.0 g, 9.11 mmol) and 150 ml of THF anhydrous were added. To the solution, 1.6 N *n*-BuLi (12 ml, 18.2 mmol) was gradually added followed by stirring for 1 h at room temperature. Then 3.13 ml (28 mmol) of $B(OCH_3)_3$ was added and stirred for 1 h, followed by addition of *p*-Iodophenyl methoxymethyl ether (**13**) (3.61 g, 13.7 mmol) and 60 ml of 20% Na_2CO_3 aqueous solution. To the reaction mixture, $[(C_6H_5)_3P]_4Pd(0)$ (0.08 g, 0.0692mmol) was added and heated (refluxing at 60 °C) for 3 h with stirring vigorously. Then additional 0.08 g (0.0692 mmol) of $[(C_6H_5)_3P]_4Pd(0)$ was added and continued heating with stirring for another 3h. The reaction mixture was cooled

down to room temperature, and extracted with ether (3 x 50 ml). The ether extract was dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by silicagel-chromatography by using the solvent mixture (Hexane : ethyl acetate = 9:1) as the eluent to give 1,2-bis[2-methyl-5-[*p*-(2-oxapropoxy)phenyl]-3-thienyl]cyclopentene (**14**) (2.45 g, 4.6 mmol, 50%) as a brownish crystal.

^{1}H-NMR(400 MHz, $CDCl_3$)δ=1.98 (s, 6H), 2.08 (quin, 2H, *J*=7.4 Hz), 2.84 (t, 4H, *J*=7.4 Hz), 3.48 (s, 6H), 5.18 (s, 4H), 6.92 (s, 2H), 7.01 (d, 4H, *J*=8.9 Hz), 7.41 ppm(d, 4H, *J*=8.9 Hz) ; FAB-MS(NBA)m/z 532(M, 100)

1,2-Bis[2-methyl-5-(*p*-hydroxyphenyl)-3-thienyl]cyclopentene (**15**)

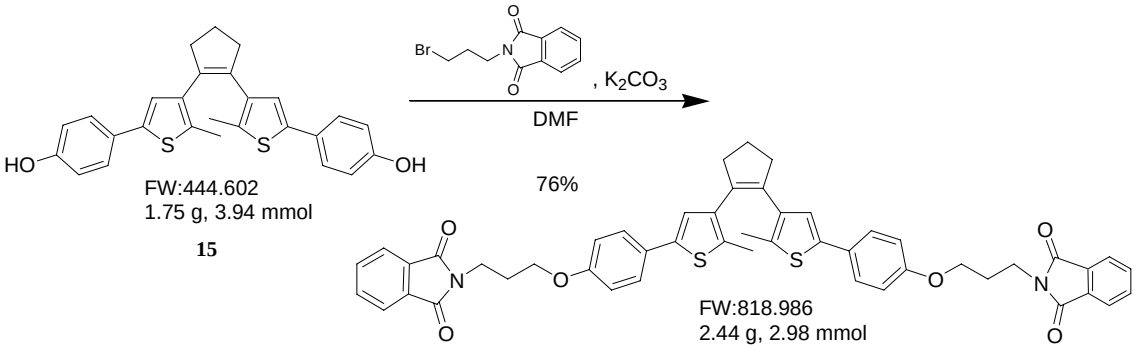


14 **15**

To a reaction flask (200 ml, three neck flask), 1,2-bis[2-methyl-5-[*p*-(2-oxapropoxy)phenyl]-3-thienyl]cyclopentene (**14**) (2.3 g, 4.32 mmol) and methanol (150 ml) were added and refluxed at 62 °C. The reaction was monitored by TLC with adding 3 drops of conc. HCl in every ten minutes. After adding 35 drops of HCl, the reaction was completed. (If addition of excess amount of HCl at once, methoxy groups are formed.) The reaction mixture was extracted with ether (3 x 50 ml), the combined extracts were dried over $MgSO_4$, and the solvent was removed in vacuo. to obtain 1.73 g (3.89 mmol) of 1,2-bis[2-methyl-5-(*p*-hydroxyphenyl)-3-thienyl]cyclopentene (**15**) as a brownish crystal in 90% yield.

^{1}H-NMR(400 MHz, $CDCl_3$)δ=1.98 (s, 6H), 2.07 (quin, 2H, *J*=7.5 Hz), 2.83 (t, 4H, *J*=7.5 Hz), 5.10 (s, 2H), 6.80 (d, 4H, *J*=8.6 Hz), 6.90 (s. 2H), 7.37 ppm (d, 4H, *J*=8.6 Hz)

1,2-Bis[2-methyl-5-[*p*-[4-(3-phthalimide)propoxy]phenyl]-3-thienyl]cyclopentene (**16**)



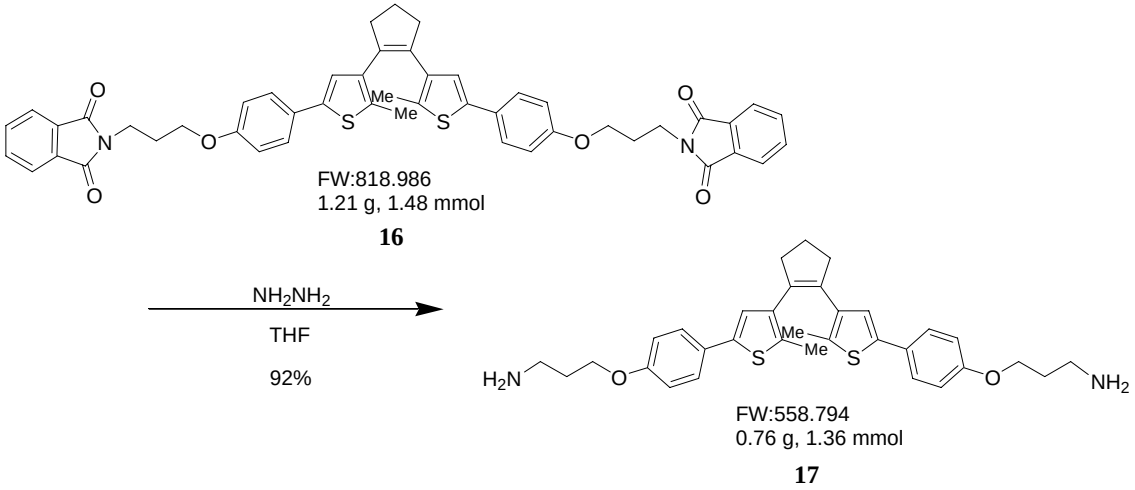
15 **16**

To a reaction flask (50 ml, two neck flask), 1.75 g (3.94 mmol) of 1,2-bis[2-methyl-5-[*p*-(2-hydroxy)phenyl]-3-thienyl]cyclopentene(**15**), K_2CO_3 anhydrous (1.42 g, 10.24 mmol)(dried in oven (130 °C) during overnight), and (3-bromopropyl)phthalimide (2.11 g, 7.88 mmol) were introduced followed by addition of 7 ml of DMF anhydrous, and heated at 65°C for 5 hrs. The reaction mixture was extracted with chloroform, the combined extracts were washed with 30 ml of 5% NaOH aquous solution, water (3 x 10 ml), and brine(30 ml), succesively. And the solution was dried over $MgSO_4$, and the solvent was removed in vacuo. The reaction mixture was

purified by silicagel chromathography (using chloroform: ethyl acetate = 49 : 1 mixture as the eluent) to obtain 2.84 g (3.47 mmol) of white crystal as a crude product in 88% yield. By purification by using preparative GPC (eluent: chloroform, v = 3.8 ml / min, monitoring wavelength: 300 nm) to obtain 1,2-bis[2-methyl-5-[*p*-[4-(3-phthalimide)propoxy]phenyl]-3-thienyl]cyclopentene (**16**) (2.44 g, 2.98 mmol, 76%) as a white crystal.

m.p. 170.3-172.0 °C; ^{1}H-NMR(400 MHz, $CDCl_3$)δ=1.97 (s, 6H), 2.06 (quin, 2H, *J*=7.5 Hz), 2.19 (quin, 4H, *J*=6.3 Hz), 2.82 (t, 4H, *J*=7.5 Hz), 3.91 (t, 4H, *J*=6.3 Hz), 4.04 (t, 4H, *J*=6.3 Hz), 6.76 (d, 4H, *J*=8.8 Hz), 6.89 (s. 2H), 7.36 (d, 4H, *J*=8.8 Hz), 7.71 (dd, 4H, *J*=3.0, 5.3 Hz), 7.84 (dd, 4H, *J*=3.0, 5.3 Hz) ; ^{13}C-NMR(400 MHz, $CDCl_3$)δ=14.42, 23.07, 28.35, 35.55, 38.53, 65.83, 114.81, 123.02, 123.32, 126.57, 127.63, 132.22, 133.47, 133.99, 134.61, 136.60, 139.55, 158.01, 168.44 ppm ; FAB-MS(NBA) m/z 819 (M^+, 2) ; IR (KBr) 1709 cm^{-1}(C=O)

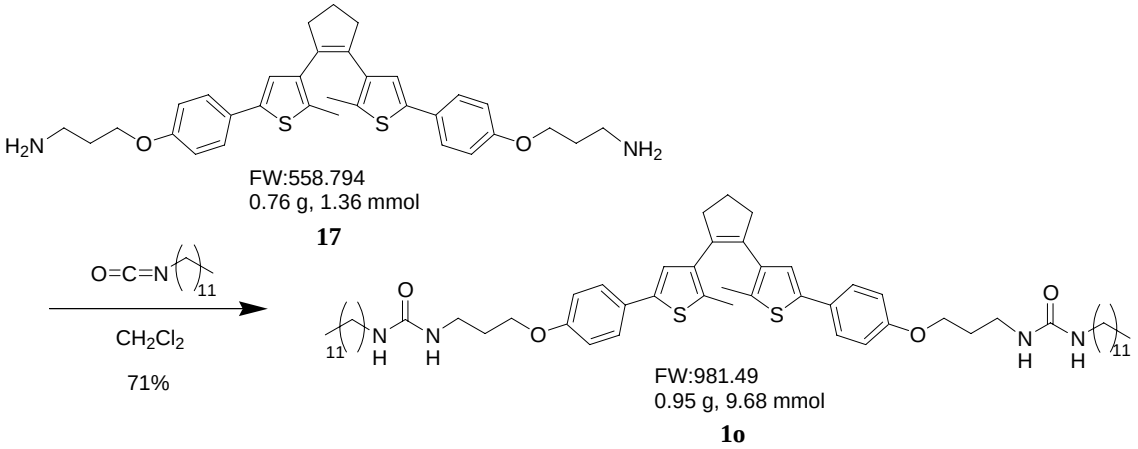
1,2-Bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**)



To a reaction flask (200 ml, two neck flask), 1,2-bis[2-methyl-5-[*p*-[4-(3-phthalimide)propoxy] phenyl]-3-thienyl]cyclopentene (**16**)1.21 g (1.48 mmol), and THF(30 ml) were introduced and heated at 60 °C followed by addition of 70 ml of hydrazine 70 ml and heated for 4 hrs at the temperature, and allowed to cool to room temperature. The lower colorless layer was discarded, and the upper THF layer was collected and evaporated under reduced pressure. The obtained green solid was disslved in 3 N HCl (400 ml) and stirred for 1 h at room temperature. The precipitate was by addition of 3 N NaOH aquous solution. The precipitate was collected by flirtation and it was dissolved into chloroform (dissolution was assisted by the introduction of a few drops of MeOH). The organic layer was washed with 3 N NaOH(30 ml), brine (30 ml), and water(30 ml), successively, and dried over $MgSO_4$, and the solvent was removed in vacuo. to obtain 0.76 g (1.36 mmol) of 1,2-bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**) in 92% yield.

^{1}H-NMR(400 MHz, $CDCl_3$)δ=1.93 (quin, 4H, *J*=6.5 Hz, $CH_2CH_2CH_2$), 1.98 (s, 6H), 2.07 (quin, 2H, *J*=7.5 Hz), 2.83 (t, 4H, *J*=7.5 Hz), 2.91 (t, 4H, *J*=6.5 Hz, NCH_2), 4.06 (t, 4H, *J*=6.5 Hz, OCH_2), 6.86 (d, 4H, *J*=8.9 Hz), 6.91 (s, 2H), 7.40 ppm(d, 4H, *J*=8.9 Hz) ; ^{13}C-NMR(400 MHz, $CDCl_3$)δ=14.49, 23.15, 33.21, 38.59, 39.38, 66.11, 114.90, 123.10, 126.70, 127.61, 133.56, 134.72, 136.69 ppm ; FAB-MS(NBA) m/z 560 (M^+, 50) ; IR (KBr) 3356, 3375 cm^{-1} (-NH_2)

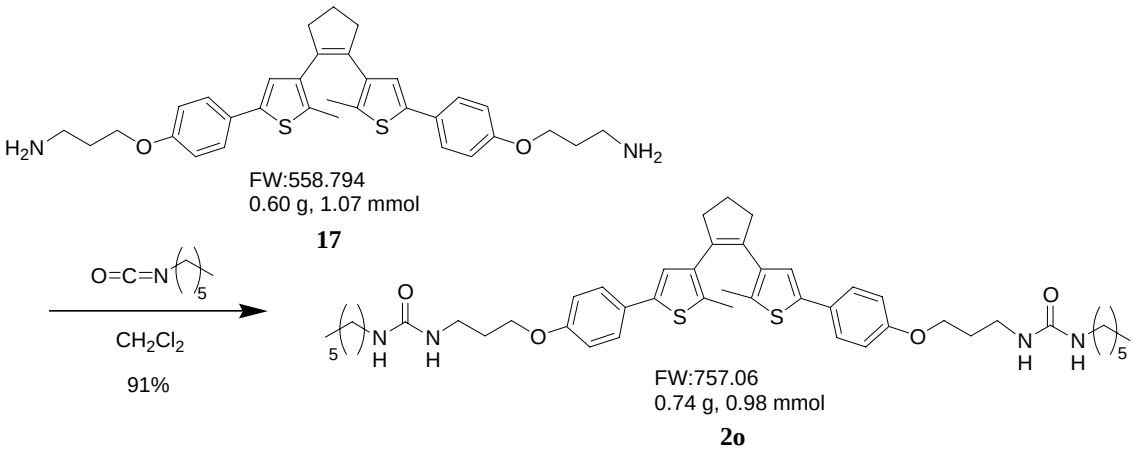
1,2-Bis[2-methyl-5-[*p*-[3-(3-*N*-dodecylureido)propoxy]phenyl]-3-thienyl]cyclopentene (**1o**)



To a reaction flask (200 ml, three neck flask), 1,2-bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**) 0.76 g (1.36 mmol) and dichloromethne anhydrous (30 ml) were introduced and followed by addition of DCM anhydrous solution containing dodecylisocyanate 0.57 g (2.72 mmol), and then stirred overnight at room temperature. Evaporation of the solvent by rotary evaporator caused the gelation, therefore hexane was added for the aim of the crystallization. However, no crystallization occurred, DCM was added and after flirtation the reaction mixture was purified with silica gel chromatography by using the solvent mixture (DCM: MeOH: triethylamine = 4.5: 0.4: 0.1) as the eluent. Ether was added (because gelation does not occure), and evaporated. The formed crystal was dried under vacuum overnight, to give 0.95 g (9.68 mmol) of 1,2-bis[2-methyl-5-[*p*-[3-(3-*N*-dodecylureido)propoxy]phenyl]-3-thienyl]cyclopentene (**1o**) in 71% yield.

m.p. 140.0-140.7°C ; ^{1}H-NMR(400 MHz, $CDCl_3$)δ=0.88 (t, 6H), 1.18-1.31 (m, 36H), 1.44 (t, 4H), 1.99 (quin, 4H), 2.00 (s, 6H), 2.07 (quin, 2H), 2.83 (t, 4H, *J*=7.5 Hz), 3.15 (quar, 4H), 3.38 (quar, 4H), 4.04 (t, 4H, *J*=5.8 Hz), 4.35 (t, 2H, *J*=5.8 Hz), 4.59 (t, 2H, *J*=5.8 Hz), 6.84 (d, 4H, *J*=8.8 Hz), 7.26 (s, 2H), 7.39 ppm(d, 4H, *J*=8.8 Hz) **;** FAB-MS(NBA) m/z 981 (M^+, 30) ; HRMS (FAB) m/z 980.6235 ([M+]), calcd. for $C_{59}H_{88}N_9O_4S_2$ 980.6247.

1,2-Bis[2-methyl-5-[*p*-[3-(3-*N*-hexylureido)propoxy]phenyl]-3-thienyl]cyclopentene (**2o**)

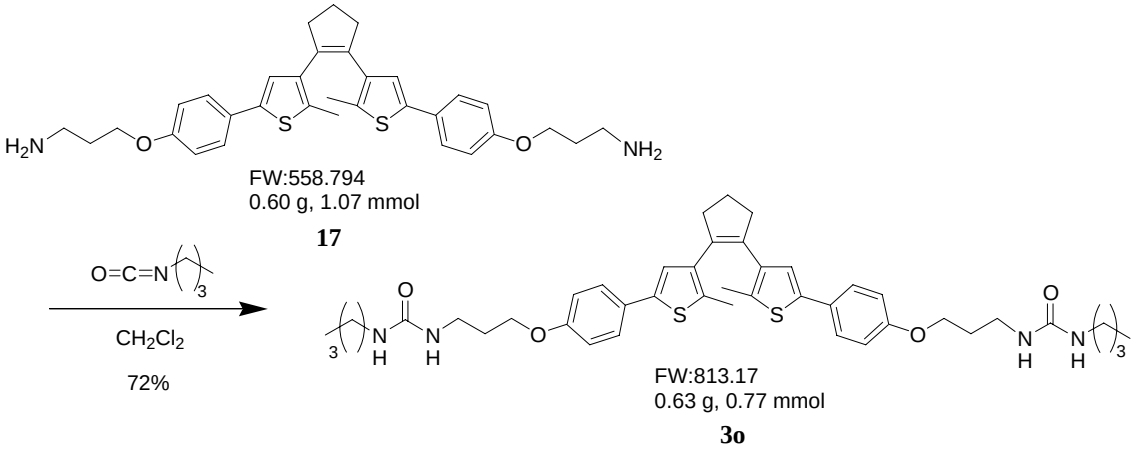


To a reaction flask (200 ml, three neck flask), 1,2-bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**)0.60 g (1.07 mmol) and DCM anhydrous (50 ml) were introduced, and followed by

addition of DCM anhydrous solution containing hexylisocyanate 0.243 ml (2.14 mmol) and then stirred overnight at room temperature. Solvent was removed in vacuo followed by purification by use of silica gel chromatography by using the solvent mixture (DCM: MeOH: triethylamine = 4.5: 0.4: 0.1) as the eluent. After the solvent were evaporated, ether was added (because gelation does not occure), and evaporated. The formed crystal was dried under vacuum overnight, to give 1,2-bis[2-methyl-5-[*p*-[3-(3-*N*-hexylureido)propoxy]phenyl]-3-thienyl] cyclopentene (**2o**) (0.74 g, 0.98 mmol, 91%).

m.p. 76.9-78.1 °C; ^{1}H-NMR(400 MHz, $CDCl_3$)δ=0.89 (t, 6H, *J*=7.3 Hz), 1.31 (m, 4H), 1.43 (m, 4H), 1.97 (quin, 4H, *J*=6.1 Hz), 2.01 (s, 6H), 2.07 (quin, 2H, *J*=7.5 Hz), 2.83 (t, 4H, *J*=7.5 Hz), 3.11 (td, 4H, *J*=1.2, 5.8 Hz), 3.37 (q, 4H, *J*=6.1 Hz), 4.03 (t, 4H, *J*=6.1 Hz), 4.43 (t, 2H, *J*=5.5 Hz), 4.66 (t, 2H, *J*=5.8 Hz), 6.83 (d, 4H, *J*=8.7 Hz), 6.88 (s, 2H), 7.39 ppm(d, 4H, *J*=8.7 Hz); $C_{43}H_{56}N_4O_4S_2$(757.06): calcd. C 68.22, H 7.46, N 7.40; found C 67.67, H 7.47, N 7.29.

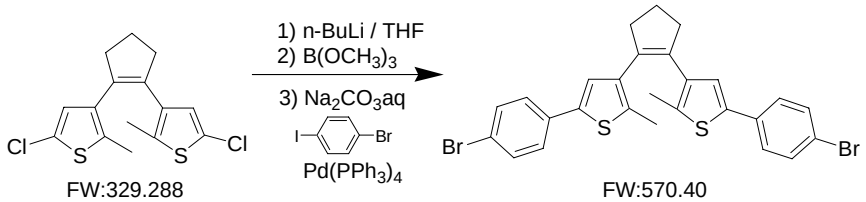
1,2-Bis[2-methyl-5-[*p*-[3-(3-*N*-butylureido)propoxy]phenyl]-3-thienyl]cyclopentene (**3o**)



To a reaction flask (200 ml, three neck flask), 1,2-bis[2-methyl-5-[*p*-(3-aminopropoxy)phenyl]-3-thienyl]cyclopentene (**17**)0.60 g (1.07 mmol) and DCM anhydrous (50 ml) were introduced, and followed by addition of DCM anhydrous solution containing butylisocyanate 0.312 ml (2.14 mmol), and then stirred overnight at room temperature. Solvent was removed in vacuo followed by purification by use of silica gel chromatography by using the solvent mixture (DCM: MeOH: triethylamine = 4.5: 0.4: 0.1) as the eluent. After the solvent were evaporated, ether was added (because gelation does not occur), and evaporated. The formed crystal was dried under vacuum overnight, to give 1,2-bis[2-methyl-5-[*p*-[3-(3-*N*-butylureido)propoxy]phenyl]-3-thienyl] cyclopentene (**3o**)(0.63 g, 0.77 mmol, 72%).

m.p. 133.9-134.6 °C; ^{1}H-NMR(400 MHz, $CDCl_3$)δ=0.89 (t, 6H, *J*=7.3 Hz), 1.31 (m, 4H), 1.43 (m, 4H), 1.97 (quin, 4H, *J*=6.2 Hz), 2.00 (s, 6H), 2.07 (quin, 2H, *J*=7.5 Hz), 2.83 (t, 4H, *J*=7.5 Hz), 3.11 (q, 4H, *J*=6.3 Hz), 3.36 (q, 4H, *J*=6.3 Hz), 4.02 (t, 4H, *J*=5.9 Hz), 4.48 (t, 2H, *J*=5.5 Hz), 4.72 (t, 2H, *J*=5.5 Hz), 6.83 (d, 4H, *J*=8.9 Hz), 6.88 (s, 2H), 7.38 ppm(d, 4H, *J*=8.9 Hz); $C_{47}H_{64}N_4O_4S_2$(813.17): calcd. C 69.42, H 7.93, N 6.89; found C 69.28, H 7.90, N 6.82.

1,2-Bis[2-methyl-(*p*-bromophenyl)-3-thienyl]cyclopentene (**18**)

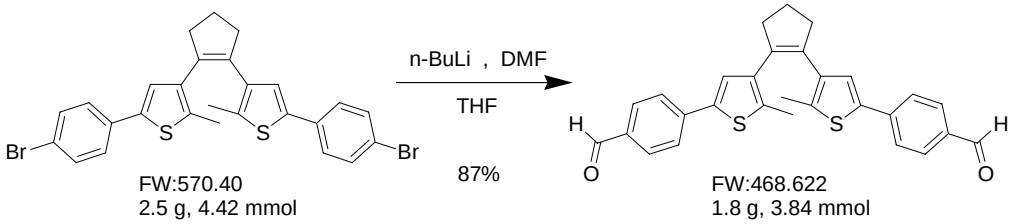


10 **18**

To a reaction flask (500 ml, three neck flask), 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene(**10**) (4.0 g, 12.1 mmol) and THF anhydrous (100 ml) were introduced. To the solution 1.6 N *n*-BuLi hexane solution (18.2 ml, 29.2 mmol) was gradually added at room temperature and stirred for 1 h at the temperature. Then $B(OCH_3)_3$(trimethyl borate)(4.11 ml, 36.91 mmol) was added and stirred for 1h, followed by addition of 4-bromoiodobenzene (6.0 g, 21.18 mmol), 100 ml of 20% Na_2CO_3 aqueous solution, and $[(C_6H_5)_3P]_4Pd(0)$ (0.13 g, 1.12 x 10^{-4} mmol) and refluxed (60 °C) for 3 hr with vigorous stirring. The reaction mixture was extracted with ether (3 x 100 ml), the combined extracts were dried over $MgSO_4$ anhydrous, and the solvent was evaporated. Solvent was removed in vacuo followed by purification by use of silica gel chromatography by using the hexane as the eluent to give 1,2-bis[2-methyl-(*p*-bromophenyl)-3-thienyl]cyclopentene (**18**) (4.53 g, 7.94 mmol) in 66% yield as the white crystal.

m.p. 136.5-137.9 °C ; ^{1}H-NMR(400 MHz, $CDCl_3$)δ=1.99 (s, 6H), 2.08 (quin, 2H, *J*=7.5 Hz), 2.83 (t, 4H,*J*=7.5 Hz), 7.00 (s, 2H), 7.34 (d, 4H, *J*=8.5 Hz), 8.60 ppm (d, 4H, *J*=8.5 Hz) ; $C_{27}H_{22}S_2Br_2$(570.40): calcd. C 56.85, H 3.89; found C 56.95, H 3.89.

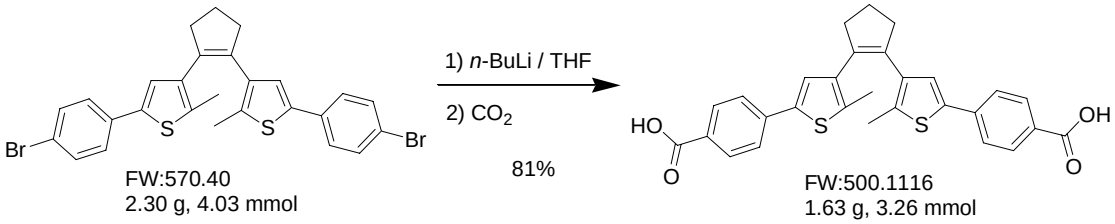
1,2-Bis[2-methyl-5-(4-formylphenyl)-3-thienyl]cyclopentene (**19**)



18 **19**

To a reaction flask (100 ml, four neck flask), 1,2-bis[2-methyl-5-(4-bromophenyl)-3-thienyl]cyclopentene (**18**) (2.5 g , 4.42 mmol) and THF anhydrous (35 ml) were introduced, and cooled down to -60 °C. To the mixture, 1.6 N n-BuLi hexane solution (6.08 ml, 9.72 mmol) was added followed by stirring for 1 hr at the temperature. Then 0.68 ml (8.84 mmol) of DMF was added and stirred for 1 hr at the temperature. The reaction mixture was extracted with ether (50 ml x 3), the combined extracts were dried over $MgSO_4$ anhydrous, and the solvent was evaporated. The obtained crude was purified by silica gel chromatography by using the solvent mixture (hexane: ethyl acetate = 9 : 1) as the eluent to give 1,2-bis[2-methyl-5-(4-formylphenyl)-3-thienyl]cyclopentene (**19**) (1.8 g, 3.48 mmol) in 87% yield.

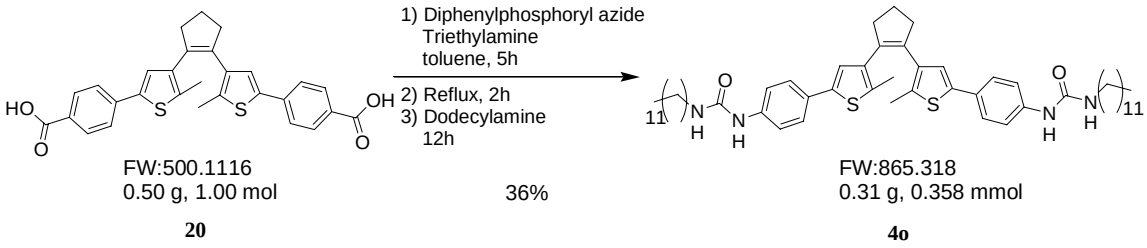
1,2-Bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**)



To a reaction flask (300 ml, three neck flask), 1,2-bis[2-methyl-(*p*-bromophenyl)-3-thienyl]cyclopentene (**18**) 2.30 g (4.03 mmol) and THF anhydrous was introduced and cooled down to -55 °C. To the solution, 1.6 N *n*-BuLi hexane solution (7.56 ml, 12.1 mmol) was added and stirred at the temperature for 1 h. After addition of dryice followed stirred for 1.5 h. 30 ml of water was added the reaction mixture, and 3 N HCl was added to acidify to pH=1. The reaction mixture was extracted with ether (80 ml x 3), the combined extracts were dried over $MgSO_4$ anhydrous, and the solvent was evaporated to obtain 1,2-bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**) (1.63 g, 3.26 mmol) as a white crystal in 81% yield.

m.p. 293 °C (dec.)

1,2-Bis[2-methyl-5-(*p*-*N*-dodecylureidophenyl)-3-thienyl]cyclopentene (**4o**)



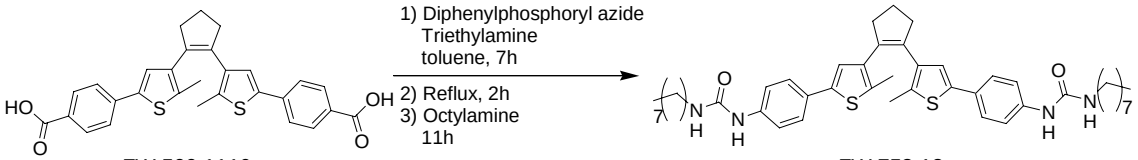
To a reaction flask (50 ml, three neck flask), 1,2-bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**) 0.50 g (1.00 mmol), toluene anhydrous 80 ml, triethylamine (0.293 ml, 2.10 mmol), and diphenylphosphoryl azide (0.453 ml, 2.10 mmol) were added and stirred for 5 h at room temperature, followed by hating (refluxing) at 107 °C for 2 h. The reaction mixture was cooled down to room temperature, followed by addition of dodecylamine (0.389 g, 2.10 mmol) and stirred overnight (12 h). After the solvents were evaporated in vacuo, ethyl acetate (400 ml) and water (200 ml) were added, and the mixture was extracted with ethyl acetate (80 ml x 2), the combined extracts were washed with 1 M HCl (100 ml), water (100 ml), saturated $NaHCO_3$ aqueous solution (100 ml), and brine (100 ml) and dried over Na_2SO_4 anhydrous, and the solvent was evaporated. The reaction mixture was purified by column chromatography (by using a mixture of DCM: THF = 4: 1), followed by recrystallization from ether - ethanol (ethanol: good solvent, ether : poor solvent) mixture to obtain 1,2-bis[2-methyl-5-(*p*-*N*-dodecylureidophenyl)-3- thienyl]cyclopentene (**4o**) (0.31 g, 0.358 mmol) in 36% yield.

^{1}H-NMR(400 MHz, $CDCl_3$: CD_3OD=1:1)δ=0.89 (t, 6H, *J*=7.0 Hz), 1.22-1.37 (m, 18H), 1.49-1.56 (m, 4H), 1.98 (s, 6H), 2.09 (quin, 2H, *J*=7.5 Hz), 2.85 (t, 4H,*J*=7.5 Hz), 3.20 (t, 4H, *J*=7.0 Hz), 6.95 (s, 2H), 7.32 (d, 4H, *J*=8.8 Hz), 7.39 ppm(d, 4H, *J*=8.8 Hz)

^{13}C-NMR(400 MHz, $CDCl_3$: CD_3OD=1:1)δ=15.4, 15.7, 19.2, 24.26, 24.28, 24.6, 28.6, 30.99, 31.0, 31.25, 31.28,

31.29, 31.7, 33.6, 40.0, 41.5, 59.1, 120.8, 124.8, 127.4, 130.5, 135.2, 136.4, 138.4, 140.4, 141.3, 158.5 ppm
FAB-MS(NBA)m/z 868(M+4, 5)

1,2-Bis[2-methyl-5-(*p*-*N*-hexylureidophenyl)-3-thienyl]cyclopentene (**5o**)



FW:500.1116
0.74 g, 1.48 mol

52%

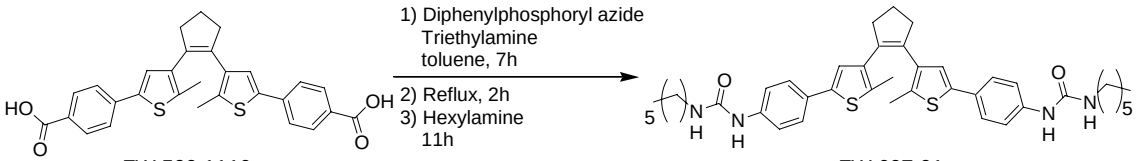
FW:753.12
0.58 g, 0.77 mmol

20 **5o**

To a reaction flask (50 ml, three neck flask), 1,2-bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**) 0.74 g (1.48 mmol), toluene anhydrous 80 ml, triethylamine (0.41 ml, 2.96 mmol), and diphenylphosphoryl azide (0.70 ml, 3.26 mmol) were introduced and stirred for 7 hr at room temperature. After the stirring, reaction mixture was heated (refluxing) at (107 °C) for 2 hr, and after cooling it to room temperature, *n*-octylamine (0.54 ml, 3.26 mmol) was added and stirred overnight (11 hr). After the solvents were evaporated in vacuo, ethyl acetate (400 ml) and water (200 ml) were added, and the mixture was extracted with ethyl acetate (80 ml x 2), the combined extracts were washed with 1 M HCl (100 ml), water (100 ml), saturated $NaHCO_3$ aqueous solution (100 ml), and brine (100 ml) and dried over Na_2SO_4 anhydrous, and the solvent was evaporated. The reaction mixture was purified by column chromatography (by using a mixture of DCM: THF = 4: 1), followed by recrystallization from ether - ethanol (ethanol: good solvent, ether : poor solvent) mixture to obtain 1,2-bis[2-methyl-5-(*p*-*N*- hexylureidophenyl)-3-thienyl]cyclopentene (**5o**) (0.58 g, 0.77 mmol) in 52% yield.

m.p. 192.2-193.3 °C ; FAB-MS(NBA) m/z 753 (M, 20); $C_{45}H_{60}N_4O_2S_2$(753.12): calcd. C 71.77, H 8.03, N 7.44; found C 71.26, H 7.68, N 7.23.

1,2-Bis[2-methyl-5-(*p*-*N*-hexylureidophenyl)-3-thienyl]cyclopentene (**6o**)



FW:500.1116
0.50 g, 1.00 mol

55%

FW:697.01
0.38 g, 0.545 mmol

20 **6o**

To a reaction flask (50 ml, three neck flask), 1,2-bis[2-methyl-5-(4-carboxylphenyl)-3-thienyl]cyclopentene (**20**) 0.50 g (1.00 mmol), toluene anhydrous 80 ml, triethylamine (0.293 ml, 2.10 mmol), and diphenylphosphoryl azide (0.453 ml, 2.10 mmol) were introduced and stirred for 7 hrs. After the stirring was over, reaction mixture was heated (refluxing) at (107 °C) for 2 hr, and after cooling it to room temperature, hexylamine (0.277 ml, 2.10 mmol) was added and stirred overnight (11 hr). After the solvents were evaporated in vacuo, ethyl acetate (400 ml) and water (200 ml) were added, and the mixture was extracted with ethyl acetate (80 ml x 2), the combined extracts were washed with 1 M HCl (100 ml), water (100 ml), saturated $NaHCO_3$ aqueous solution (100 ml), and brine (100 ml) and dried over Na_2SO_4 anhydrous, and the solvent was evaporated. The reaction mixture

was purified by column chromatography (by using a mixture of DCM: THF = 4: 1), followed by recrystallization from ether-ethanol (ethanol: good solvent, ether : poor solvent) mixture to obtain 1,2-bis[2-methyl-5-(*p*-*N*-hexylureidophenyl)-3-thienyl]cyclopentene (**6o**) (0.38 g, 0.545 mmol) in 55% yield.

^{1}H-NMR(400 MHz, $CDCl_3$: CD_3OD=1:1)δ=0.90 (t, 6H, *J*=7.0 Hz), 1.29-1.40 (m, 12H), 1.52 (quin, 4H, *J*=7.0 Hz), 1.98 (s, 6H), 2.08 (quin, 2H, *J*=7.5 Hz), 2.84 (t, 4H,*J*=7.5 Hz), 3.20 (t, 4H, *J*=7.0 Hz), 7.00 (s, 2H), 7.32 (d, 4H, *J*=8.7 Hz), 7.39 ppm(d, 4H, *J*=8.7 Hz) ; ^{13}C-NMR(400 MHz, $CDCl_3$: CD_3OD=1:1)δ=15.4, 15.7, 19.2, 24.2, 24.6, 28.2, 31.7, 33.2, 40.0, 41.4, 59.1, 120.7, 124.7, 127.4, 130.4, 135.2, 136.4, 138.3, 140.4, 141.3, 158.6 ppm ; FAB-MS(NBA) m/z 700(M+4, 40)

2. DSC-curves obtained for *o*-dichlorobenzene gels of 4o

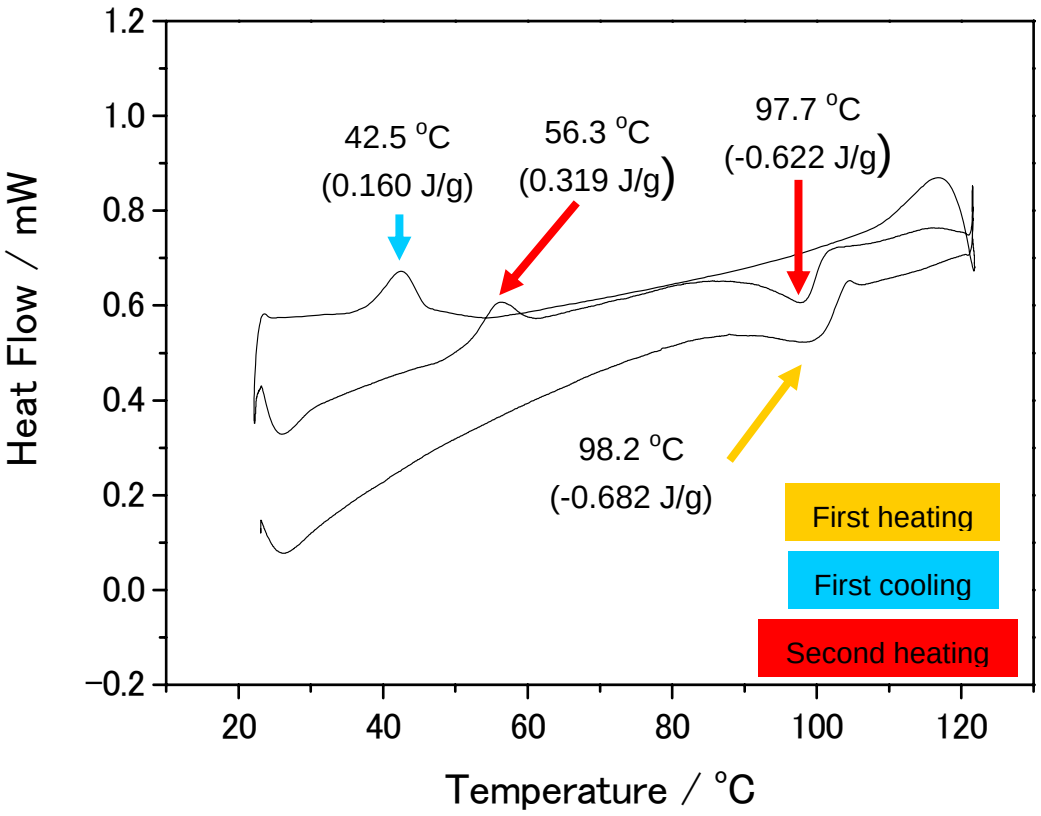


Figure S1. DSC-trace obtained for gels of **4o** in *o*-dichlorobenzene at 12.5 mg/ml concentration, and heated at 120 °C (heating rate of 5 °C/min) for 5 min, followed by cooling to 25 °C (cooling rate of 10 °C/min). After aging for 5 min, heating were recorded from 25 °C up to 120 °C at a scan rate of 5 °C/min.

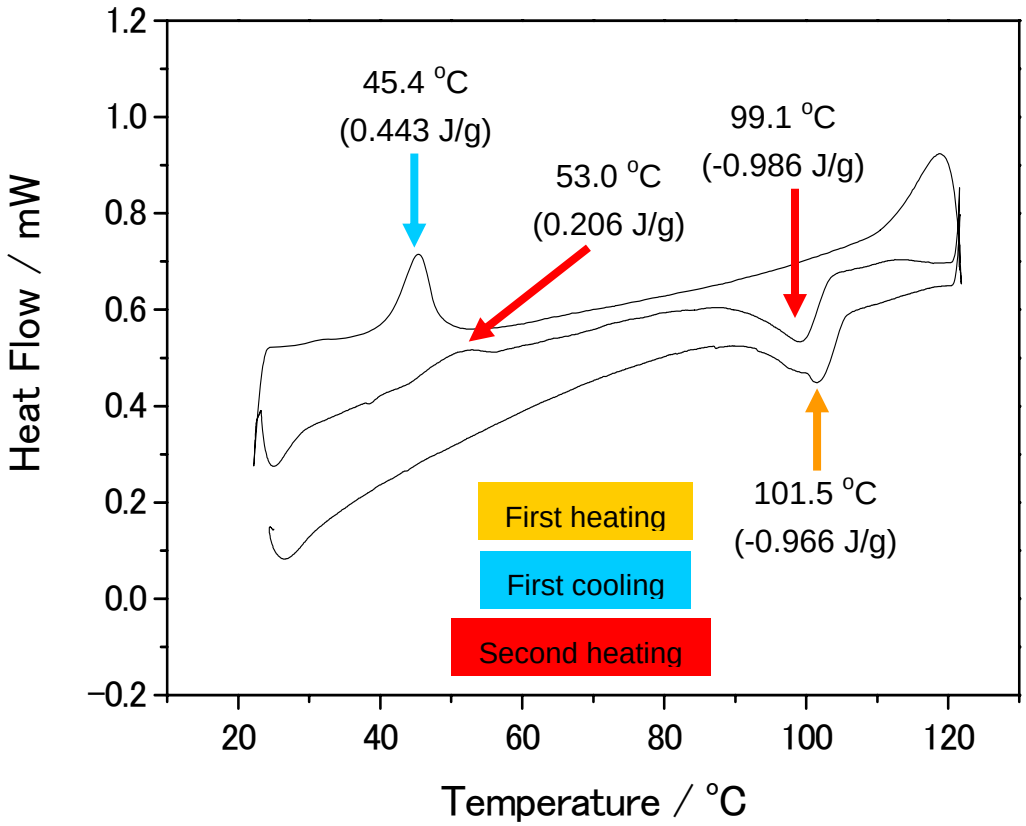


Figure S2. DSC-trace obtained for gels of **4o** in *o*-dichlorobenzene at 25.0 mg/ml concentration, and heated at 120 °C (heating rate of 5 °C/min) for 5 min, followed by cooling to 25 °C (cooling rate of 10 °C/min). After aging for 5 min, heating were recorded from 25 °C up to 120 °C at a scan rate of 5 °C/min.

3. Spectral changes upon prolonged UV irradiation to 1o and 4o

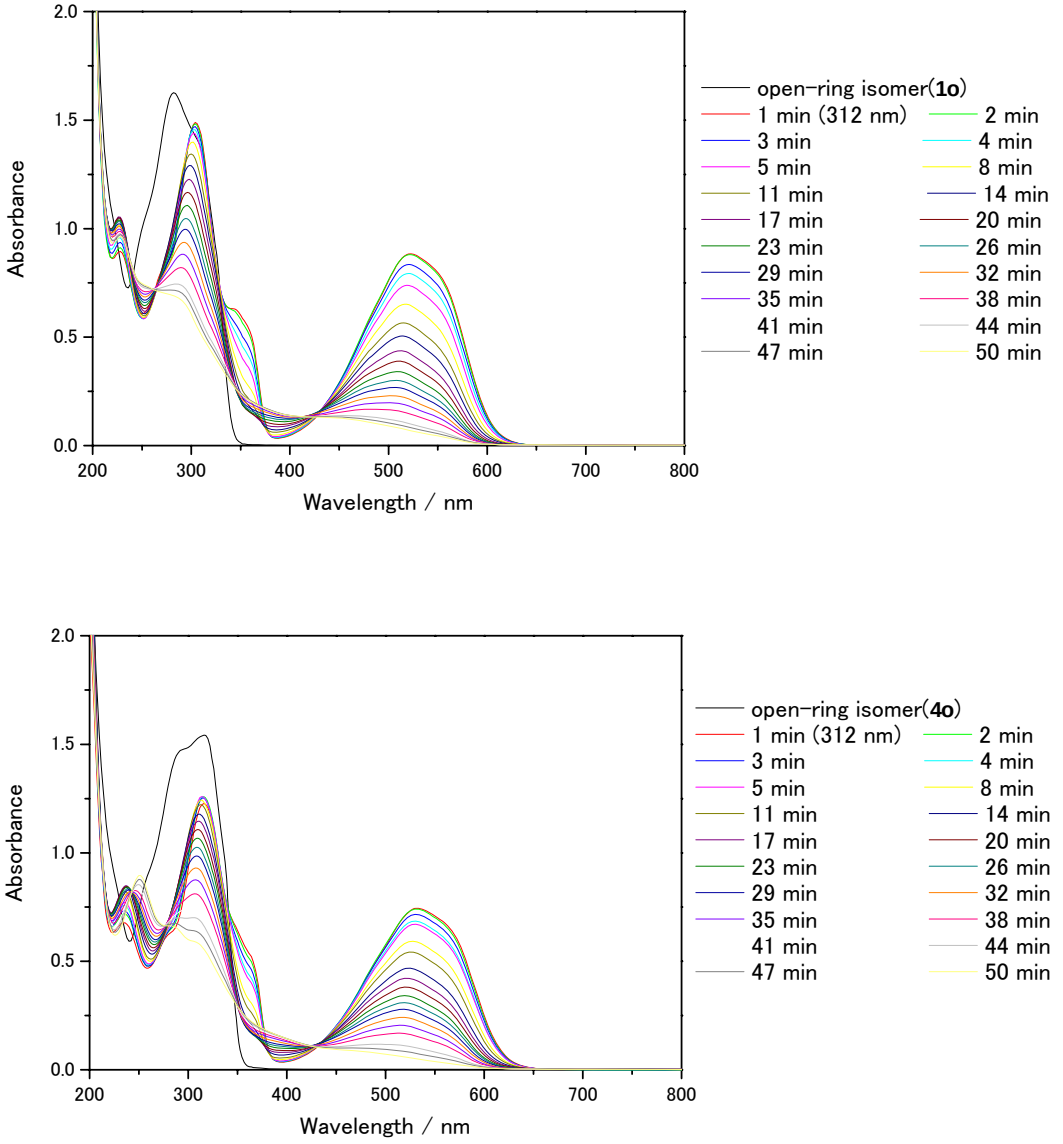


Figure S3 Absorption spectral changes of **1o** upon irradiation with UV (313 nm) light in ethanol solution (a), and Absorption spectral changes of **4o** upon irradiation with UV (313 nm) light in ethanol solution (b).

Figure S3 shows the absorption spectral changes upon irradiation with UV (313 nm) light in ethanol solution. The numbers besides the lines are irradiation period of 313 nm light. After 1 min irradiation, the spectrum (red lines 1) shows the closed-ring isomer formation, however prolonged irradiation with UV light, all bands corrupted. After 50 min irradiation, spectrum turned into flat line (yellow line 50) indicating compound **1** and **4** were decomposed or converted other product. The data show these switchable gelators are not sufficiently stable to UV light.

4. TEM images of the *o*-dichlorobenzene gels of 4o

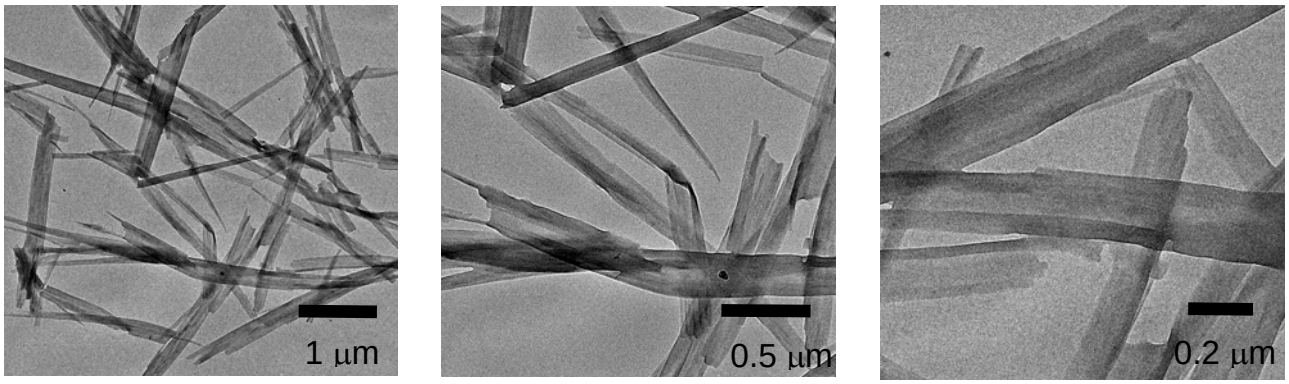
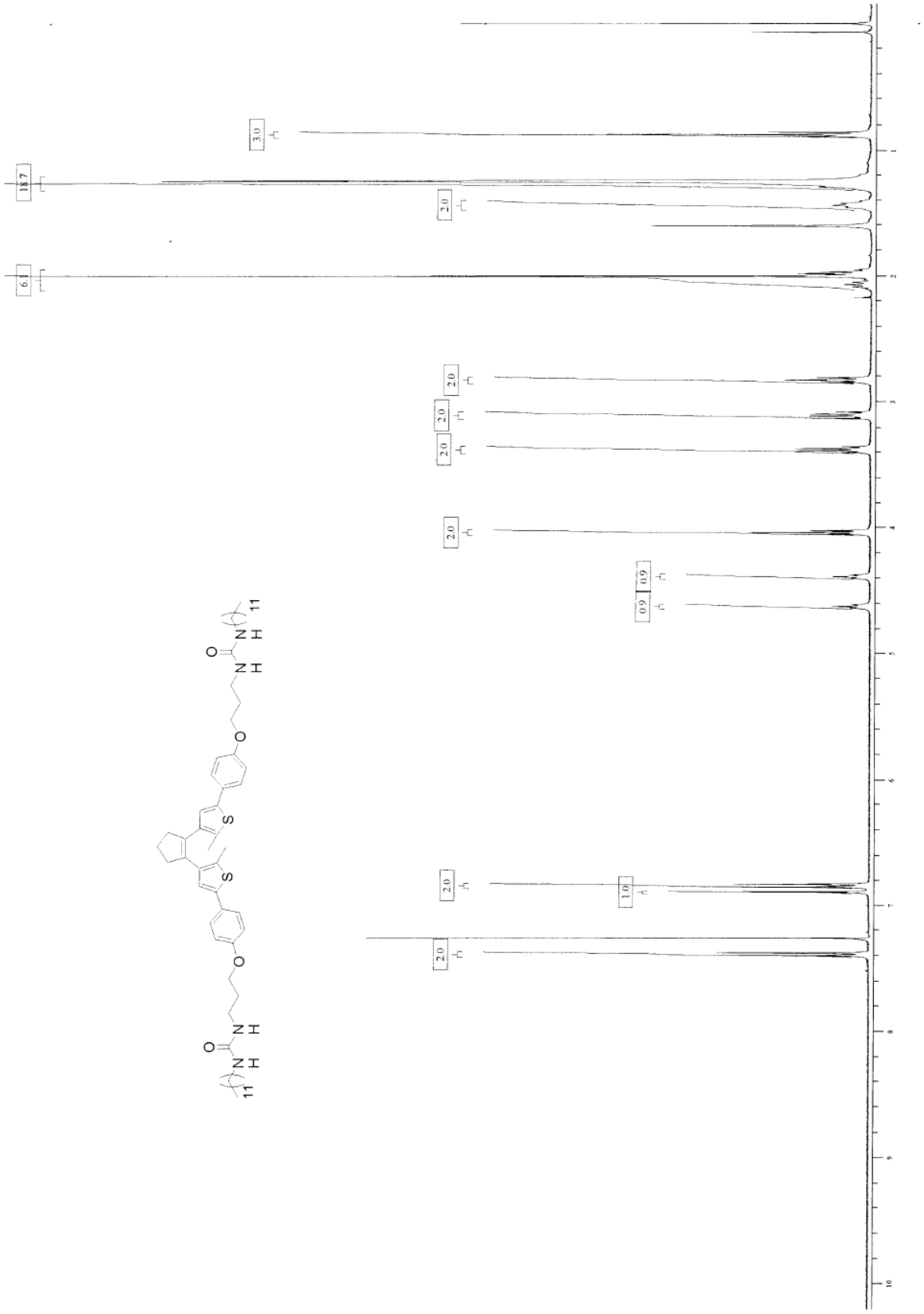
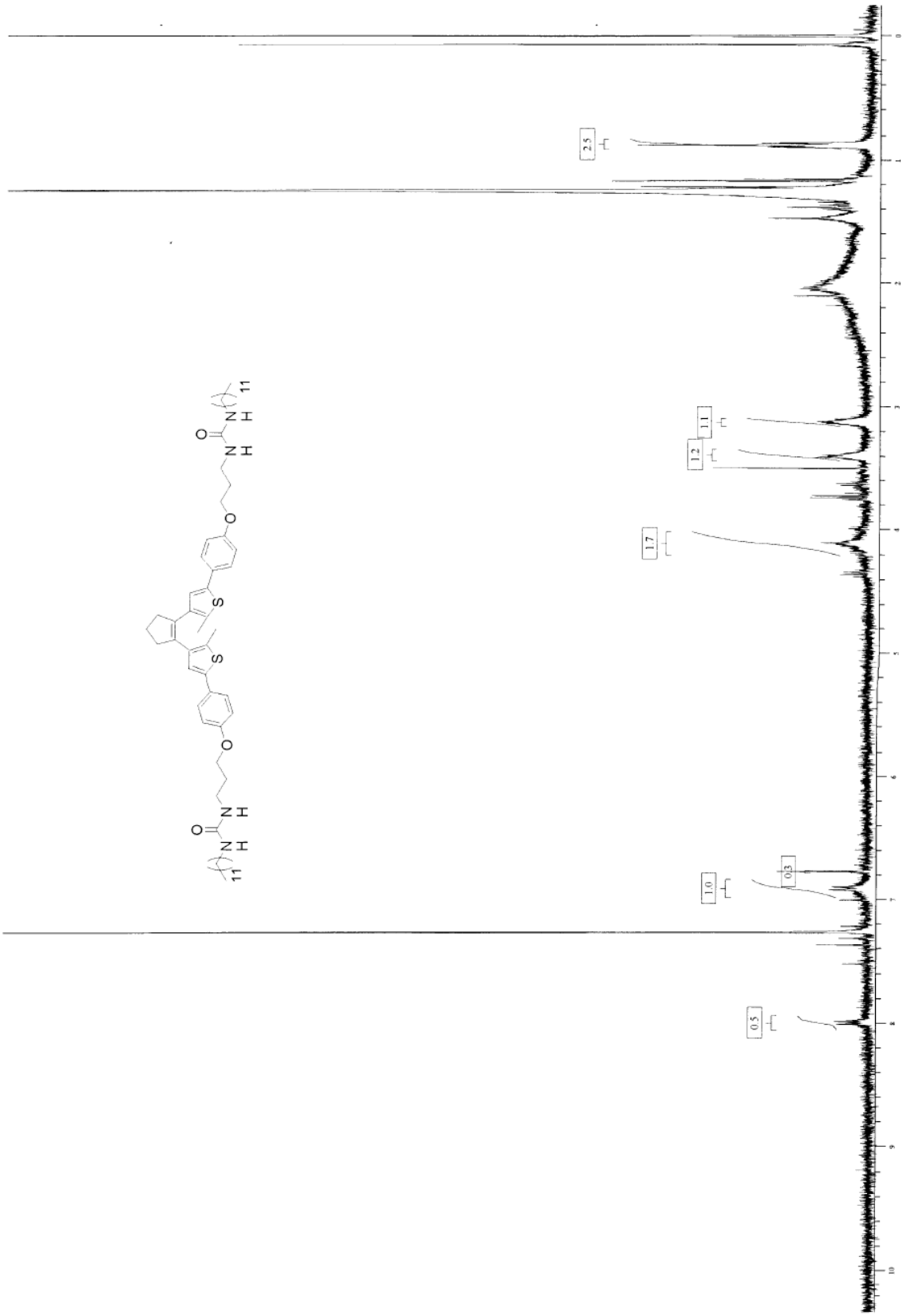


Figure S4 TEM images of the *o*-dichlorobenzene gels of **4o**

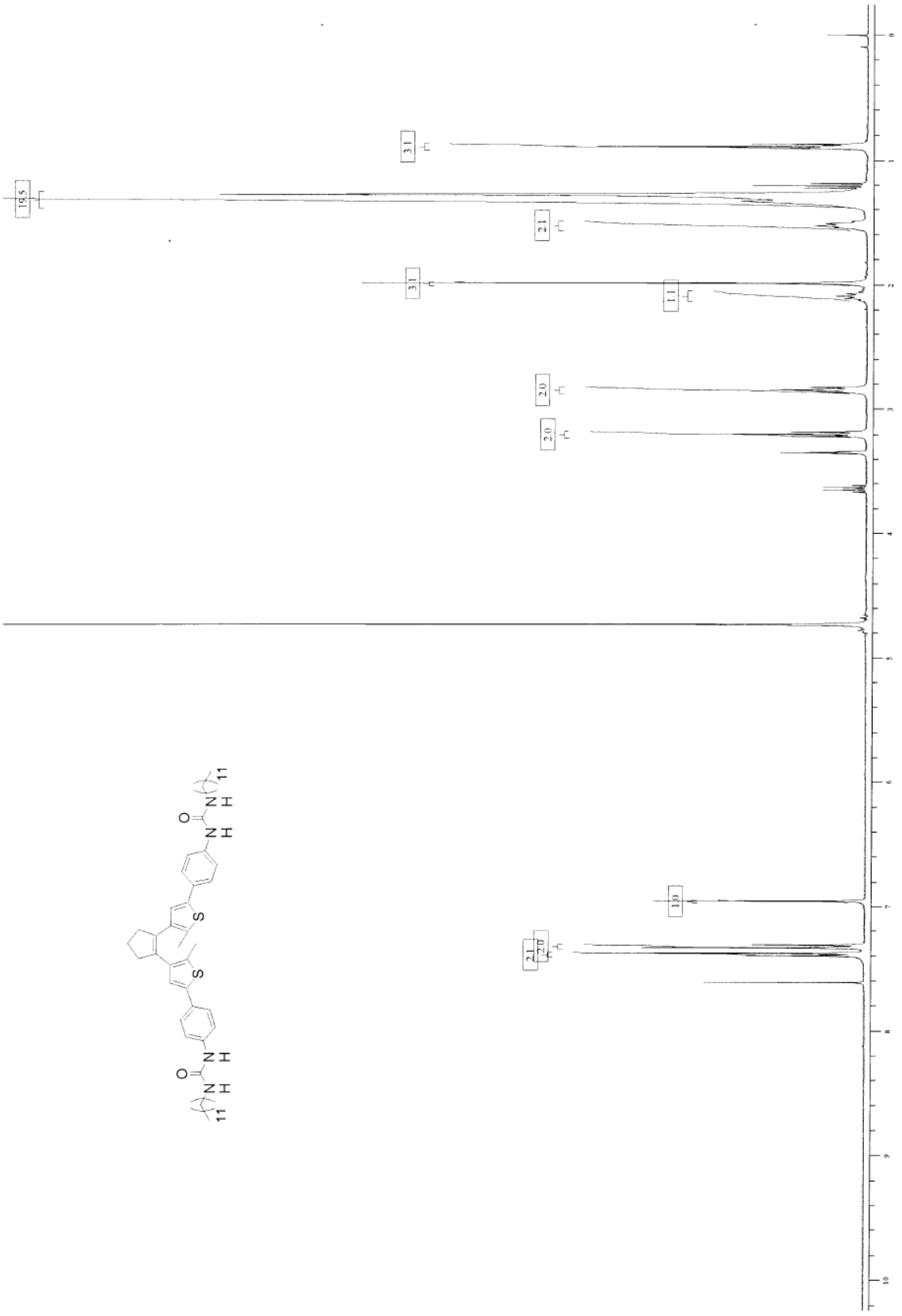
○ ^{1}H-NMR spectrum of **1o** ($CDCl_3$)



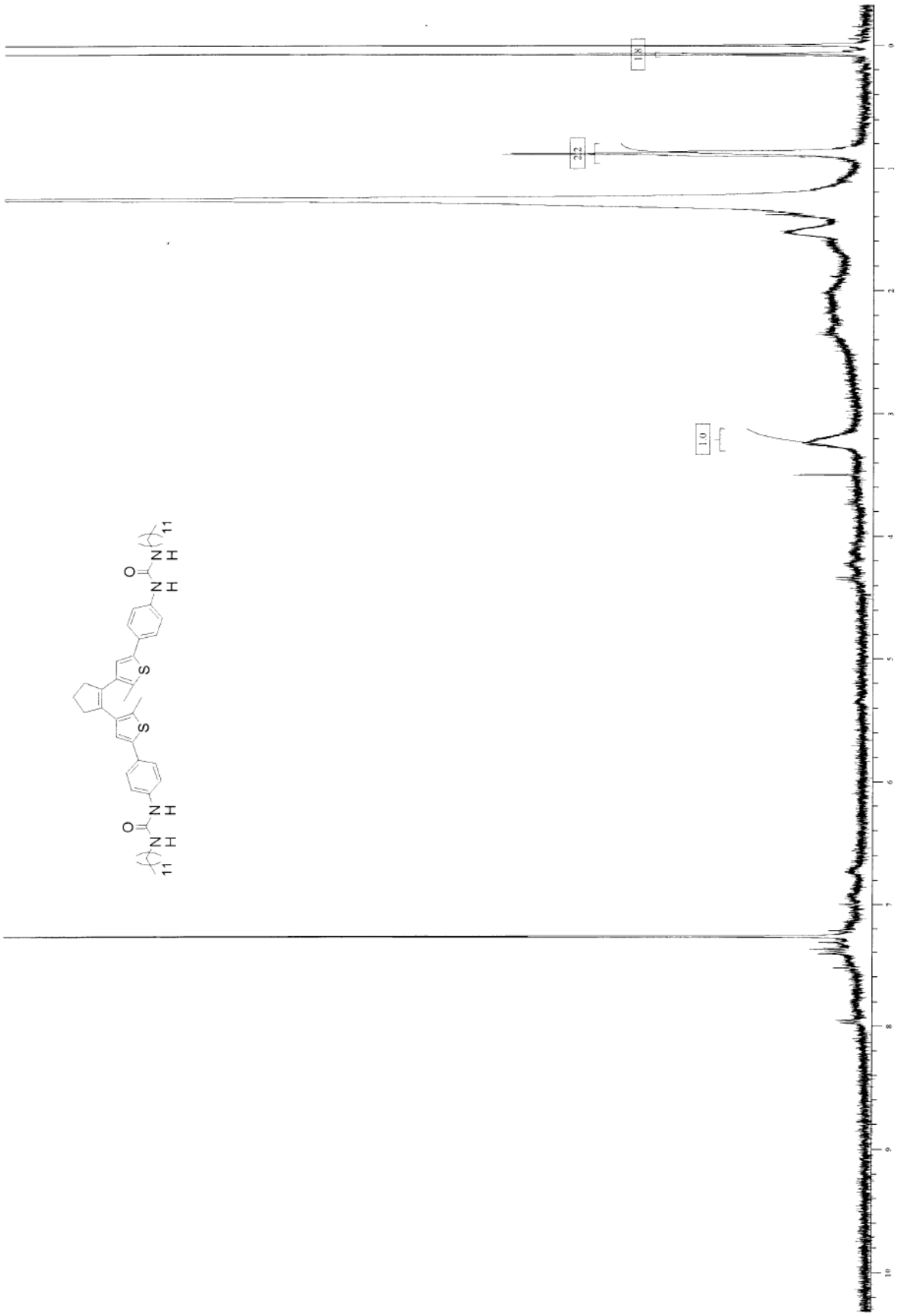
○ ^{1}H-NMR spectrum of decomposition products from **1** ($CDCl_3$)



○ ^{1}H-NMR spectrum of **4o** ($CDCl_3$:CD_3OD=1:1)



○ ^{1}H-NMR spectrum of decomposition products from **4** ($CDCl_3$)



IR Spectrum of gel 4o

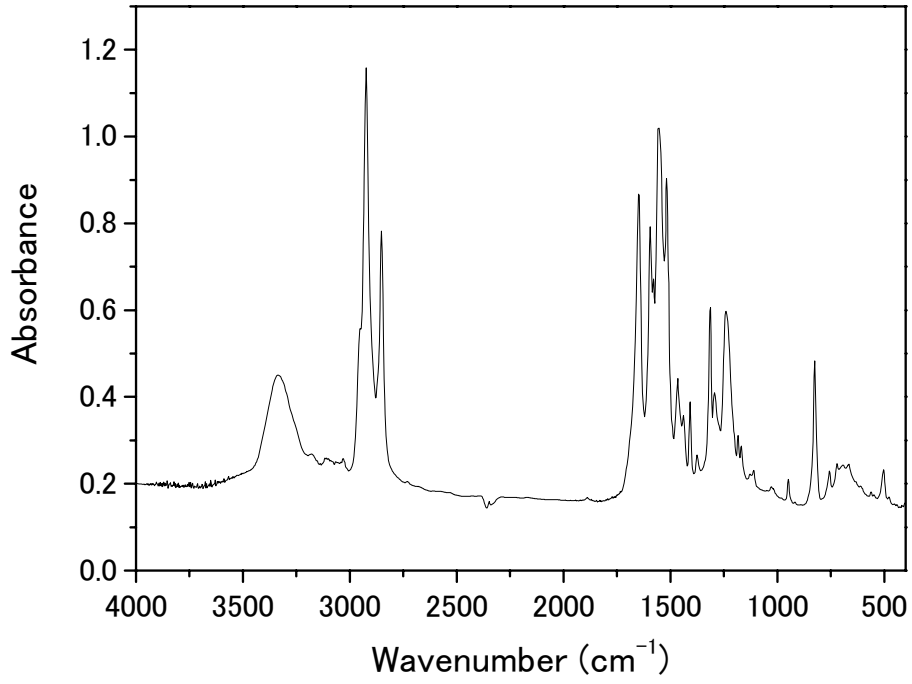


Figure S5 IR spectrum of Xerogel of **4o** obtained from dichloromethane gel

Xerogel of **4o** was prepared by evaporation of solvent under reduced pressure from CH_2Cl_2 gel (2.5 mg of **4o** in 100 μl of CH_2Cl_2). IR bands were observed at 3336 (N-H), and 1648 (C=O) cm^{-1}.
Comparing the following reference, hydrogen-bonding interaction of the amide group of **4o** is not remarkable.

Ref) S. Yagai, T. Karatsu, and A. Kitamura, *Langmuir*, 2005, **21**, 11048-11052.

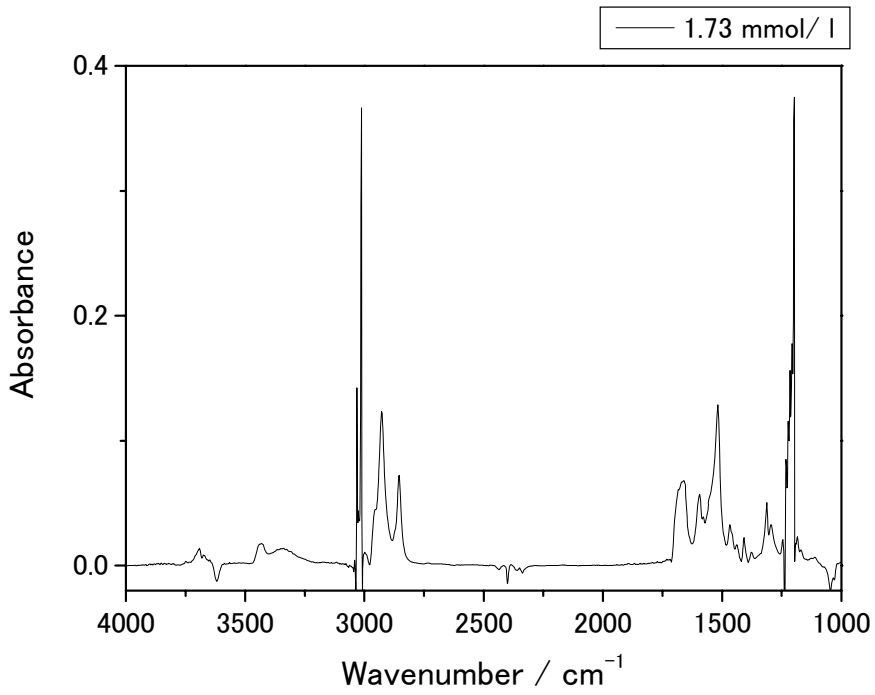


Figure S6 IR spectrum of **4o** in chloroform solution (1.73 mmol/l)

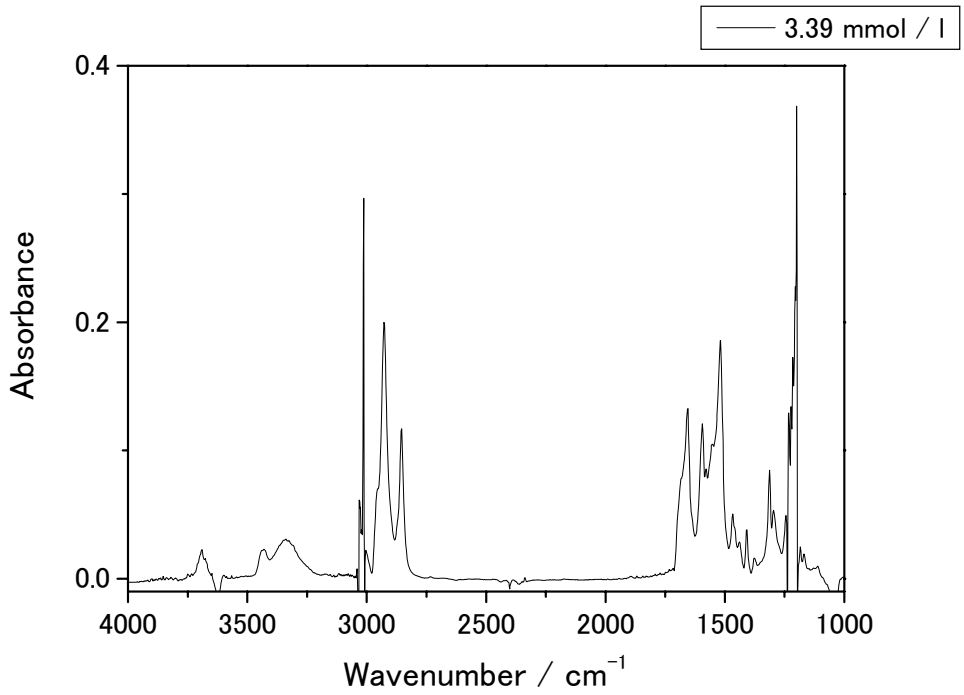


Figure S7 IR spectrum of **4o** in chloroform solution (3.39 mmol/l)

IR bands were observed at 3430 and 3338 (N-H), and 1654 (C=O) cm^{-1}. Wavenumbers of these bands were not shifted up to the concentration.