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Multi-addressable supramolecular gels based on linear amino acid and bisthienylcyclopentene

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ABSTRACT: 1,2-Bisthienylperfluorocyclopentenes covalently linked to two aggregative side-arms derived from 11-aminoundecanoic acid have been designed to self-assemble leading to the formation of supramolecular gels which could be reversibly and independently revealed or suppressed upon acidity, temperature changes and also light irradiation. Copyright © 2007 John Wiley & Sons, Ltd.
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KEYWORDS: photochromism; self-assembly; gelation; photoswitchable; organogel

INTRODUCTION

The reversible organo- and/or hydrogelation phenomenon exhibited by low-molecular weight molecules (LMOGs) is the subject of increasing attention.[1] This class of compounds is able to self-assemble into supramolecular fibrous aggregates that in turn crosslink, thus entrapping solvent molecules within three-dimensional networks. The unique chemical and physical properties of these materials have paved the way to fascinating nanostructured materials such as nanotubules of silica.[2] However, it remains a challenging task to design smart gels whose formation could be simultaneously or alternatively controlled by external stimuli such as heat, acidity, electric fields and/or light. Of external changes, light has the advantage of providing stimulus to specific chromophores in the molecules by selective-wavelength irradiation. In that connection, Zinic *et al*. recently reported an irreversible photochemically induced gelation system based on *cis–trans* photoisomerization of fumaride derivatives.[3] Anthracene-containing binary gelators[4] and naphthopyran-based gelators[5] have also been fruitfully designed as photoresponsive LMOGs, nevertheless for both approaches the gels can only be transformed into sol upon irradiation the back reaction being thermally induced. As diarylethene constitute a peculiar class of molecular photoswitches that can undergo reversible electrocyclization between their colourless ring-open and coloured ring-closed forms when irradiated with appropriate wavelengths of light.[6] Because of excellent fatigue resistance, thermal stability in both isomeric forms, solid-state photoreactivity and high photochemical quantum yield, these molecules constitute obviously powerful candidates to photoswitch in both directions between sol and gel phases.[7] Indeed, the photochromic reactions of 1,2-bis-thienylcyclopentenes functionalized with two amide groups have been reported to largely influence the medium viscosity.[8] Nevertheless incorporation of diarylethene does not guarantee photoswitchable macroscopic phase transition as reported recently in two very elegant studies. In fact these derivatives covalently linked to a chiral moiety have been shown to reversibly control supramolecular chirality switching between different chiral aggregates in the gel phase,[9] and multi-switchable cholesterol-based gelators have been reported to be photochromic without any phase changes.[10] Various compounds based on 11-aminoundecanoic acid, hereafter denoted AUDA, have been shown to act as potent organogelators or hydrogelators, furthermore the presence of a sodium carboxylate has been exploited to alter the self-assembling process and thus to largely modify the gel formation upon acidic conditions.[11] As an attempt to obtain new functional organogelators with multiple-switch applications, we have rationally designed

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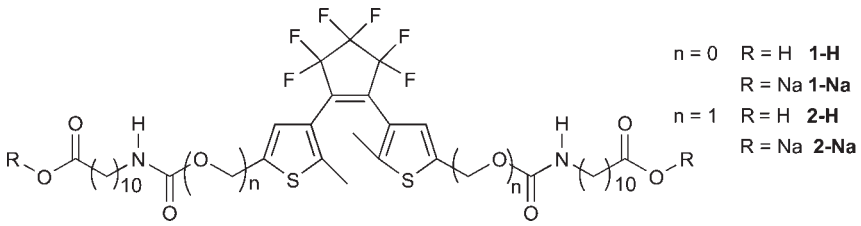


Scheme 1. Rationally designed dithienylethenes substituted by two AUDA arms

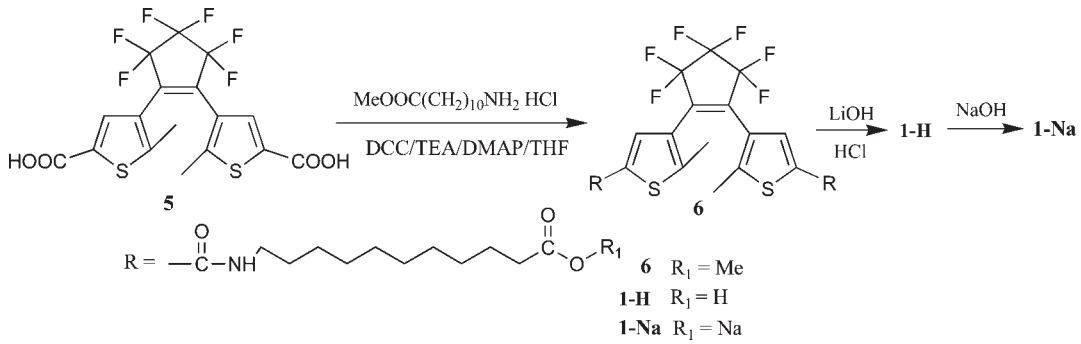
photochromic organogelators based on bis-thienylperfluorocyclopentenes containing two AUDA aggregative side-arms (Scheme 1).

RESULTS AND DISCUSSION

In the present study, amide and urethane groups have been selected as bridging units between the photoresponsive and aggregative parts as these H-bonding groups do not prevent the gel formation when sterically demanding groups are connected to AUDA unit.[10] A classic peptide-coupling procedure using DCC, DMAP and methyl 11-aminoundecanoate was used to synthesize 1,2-bis[5′-(10″-carboxyldecylcarbamoyl)-2′-methylthien-3′-yl] perfluorocyclopentene **1-H** starting from the previously described photochromic compound **5** bearing two carboxylic functions,[12] the resulting ester **6** being subsequently saponified under mild conditions using lithium hydroxide (Scheme 2). Diacid **2-H** was synthesized in a three step-procedure starting from 1,2-bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene **7**.[13] This dialdehyde was reduced with sodium borohydride in corresponding dihydroxymethyl derivative **8** which subsequently condensed with an appropriate isocyanate to yield a urethane derivative **9** which was converted by saponification into 1,2-bis[5-(10-carboxydecylcarbamoyloxymethyl)-2-methylthien-3-yl] perfluorocyclopentene **2-H** (Scheme 3). Compounds **1-H** and **2-H** were obtained, respectively, in 18 and 57% overall yield.

Neutral dicarboxylic derivatives **1-H** and **2-H** failed to gel any investigated fluids, on the contrary their corresponding disodium salts **1-Na** and **2-Na** easily obtained upon basic treatment could be considered as supergelators.[14] Indeed, the gel-to-sol phase transition temperature of DMF gel using a 1% wt/v concentration of **2-Na** (1.08×10^{-2} M) is as high as 120 °C, and millimolar range of concentrations of the prepared organogelators is efficient enough to gelify DMSO and DMF. For instance a 0.095% wt/v (10^{-3} M) **2-Na** DMF gel melts at 30 °C. The gels obtained are translucent and stable for months. These outstanding gelling abilities are restricted to aprotic polar solvents as these disodium salts can be dissolved in various alcohols and water, and are totally insoluble in apolar organic fluids. The minimum gelation concentrations for **1-Na** and **2-Na** are collected in Table 1 and the gel-to-sol phase transition temperatures along concentration variation are depicted on Fig. 1. **1-H** and **2-H** were found to be very soluble in DMF and DMSO at ambient temperature. Upon addition of sodium hydroxide, they rapidly convert to the gel state which can in turn be transformed into sol upon acidic addition. As the targeted AUDA derivatives act as potent LMOG, this cycle can be repeated several times before dilution will dramatically change the macroscopic properties. Gels arising from LMOGs are intrinsically thermoswitchable, here they also respond to environmental variations of acidity by reversibly transcripting the molecular modification to the supramolecular level.

When methanol solutions of **1-Na** and **2-Na** were irradiated with 313 nm light absorption increased, respectively, at 569 nm and 517 nm and reached by 3 min a photostationary state[6] that consisted of a mixture of ring-open and ring-closed forms, respectively, denoted **3-Na** and **4-Na**. When prolongated irradiation time (4 h) were used, any further increase of closed forms was detected, furthermore elucidation of ^{1}H NMR spectrum of



Scheme 2. Synthetic route for **1-H** and **1-Na**

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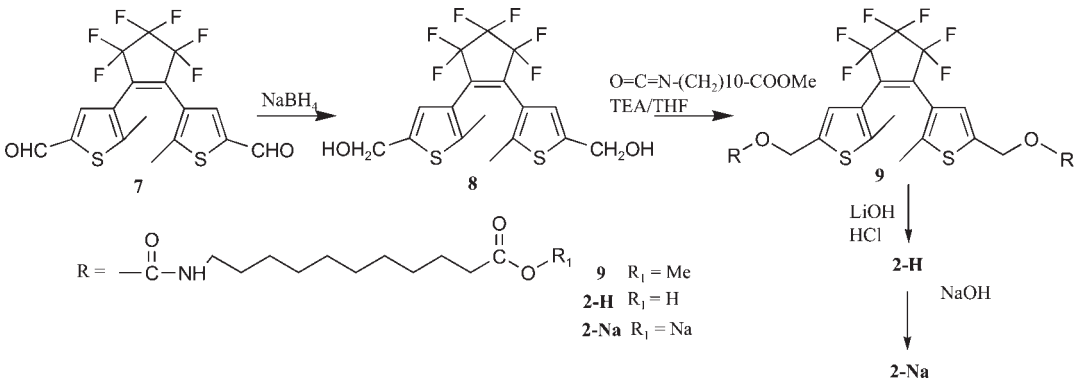


Scheme 3. Synthetic route for **2-H** and **2-Na**

Table 1. Minimum gel concentration[a] at 30 °C

Compounds	DMF	DMSO
1-Na	1.45 (1.7)	7.58 (8.7)
2-Na	0.95 (1)	6.56 (7.1)

[a]In g L^{-1} (gelator/liquid); in parentheses in mM.

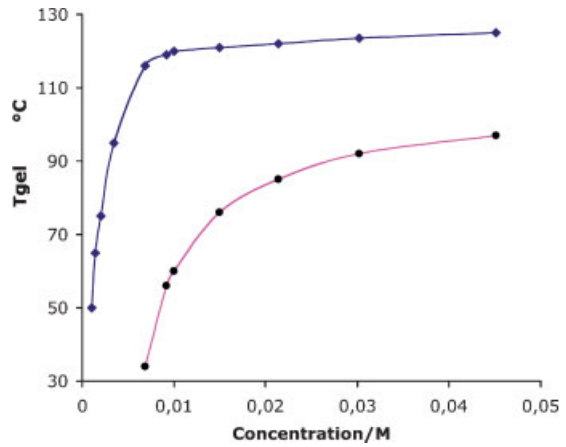
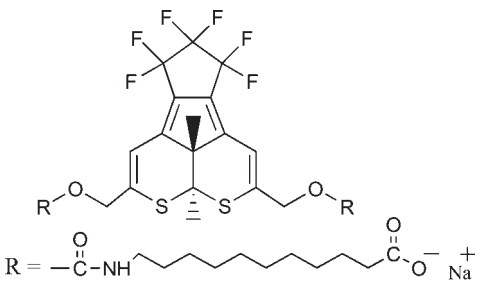


Figure 1. T_{gel} of disalt **2-Na** as a function of organogelator concentration: (◆) in DMF; (●) in DMSO

the resulting mixture showed the presence of **2-Na**, **4-Na** and a tricyclic by-product **10** (Scheme 4) in a 7:2:1 ratio.[15] When diluted DMF and DMSO (0.2 mM) solutions are exposed to UV-light, similar large absorption bands are obtained whose maxima do not exhibit any significant shift. When gels are irradiated, superimposable maxima have been found for DMSO and DMF, and more interestingly this transformation is accompanied by the gel-to-sol phase transition within 3 min. The absorption intensity of the photoinduced sols is noticeably lower in comparison to expected values. This indicates that some photochromic units are still embedded within small remaining aggregates. In both solvents macroscopic gelation could be photodisrupted. For further investigation DMF was chosen because of the excellent stability of the translucent gel and the minimum gelation concentration (*ca* 1 mM). UV-irradiation ($\lambda > 530$ nm) of the photoinduced sols gave rise to the photocycloreversion to reform **2-Na,** which in turn gave birth to the gel phase. This represents one of the rare examples of a gel-to-sol phase transition that could be photoswitched in both directions using appropriate wavelength (Scheme 5). Pictures of the three steps of one cycle is depicted in Fig. 2. Sequential alternating UV/Visible light irradiation have been performed and resulting T_{gel} values have been found to decrease as a function of number of cycles. This phenomenon could not be ascribed neither to photodegradation, as the initial T_{gel} value was recovered by simply heating and then cooling the uncoloured phase, and nor to lowered photochemical electrocyclization process efficiency as totally uncoloured gels are reformed. Visible irradiation leads to a ring-opening process which is only accompanied by a partial reorganization of the network. Total reformation of a three-dimensional network of numerous fibres that composed a physical gel is usually thermally achieved except for thixotropic gels.[16] In that connection, additional experiments based on mixing photochromic gelators and simple-related compounds will be undertaken in an attempt to overcome these limitations. This macroscopic behaviour has also been characterized at the supramolecular level using AFM technique. Non-irradiated sample show the presence of numerous bundle of fibrillar aggregates whereas the area irradiated through a mask with UV light gave typical answer of solvents (Fig. 3). This is an additional evidence that the molecular event induces the supramolecular rearrangement of these promising nanostructured materials.



Scheme 4. Tricyclic by-product **10**

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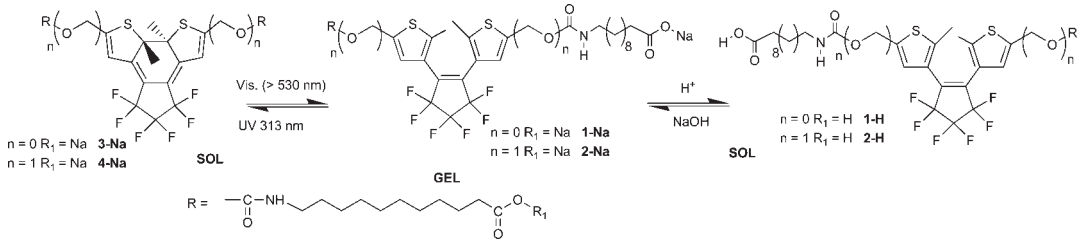

Scheme 5. Self-assembled supramolecular aggregates controlled by molecular changes induced by light and acidity

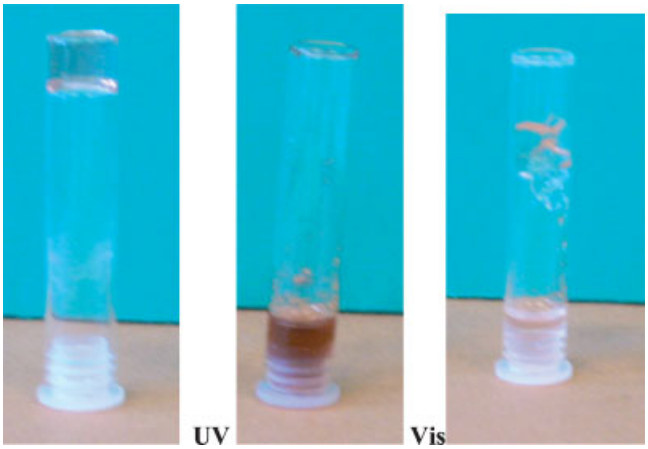

Figure 2. Photocontrolled Gel-to-sol phase transition of **2-Na** DMF gel/**4-Na** sol. (Left: **2-Na** before irradiation, middle: **4-Na** sol and right: photoregenerated **2-Na** DMF gel)

CONCLUSION

In conclusion, we demonstrated that acid- and photo-responsive organogelators can be readily obtained from the combination of a P-type photochromic dithienylethene and a versatile aggregative unit derived from a synthetic amino acid. As expected, the multi-addressable molecular switches operate at supramolecular scale, the phase changes among gel and sol being independently driven by acidity, light and temperature. Of particular interest for organogelator material science are such smart gels which may pave the way to new multi-responsive sensor materials.

EXPERIMENTAL

Photochromic measurements (UV-visible) were performed in methanol, DMF and DMSO solution of spectrometric grade (Aldrich) at 20 °C. The analysis cell (optical pathlength 1 cm) was placed in a thermostated copper block with magnetic stirring inside the sample chamber of a Beckman-DU-7500-diode-array spectrometer. Flash column chromatography was performed on silica gel (Merck 40–63 μm). Melting points were determined on an Electrothermal Eng. Ltd melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 250 NMR spectrometer with $CDCl_3$ or DMSO-d_6 as a solvent and TMS as an internal standard ($\delta = 0$ ppm). UV-visible measurements were performed using a Hitachi U-3300 spectrophotometer. FT-IR measurements were performed using a Perkin Elmer Paragon 1000 instrument. Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. MALDI-MS spectra were recorded in the positive mode by using a 2,5-dihydroxy-benzoic acid in dioxane as matrix. Microanalyses were determined in the microanalytical laboratory at the CNRS, Vernaison. AFM was performed using Tapping Mode (Nanoscope IIa, Digital Instruments, Inc.) with a pyramidal Si_3N_4 tip.

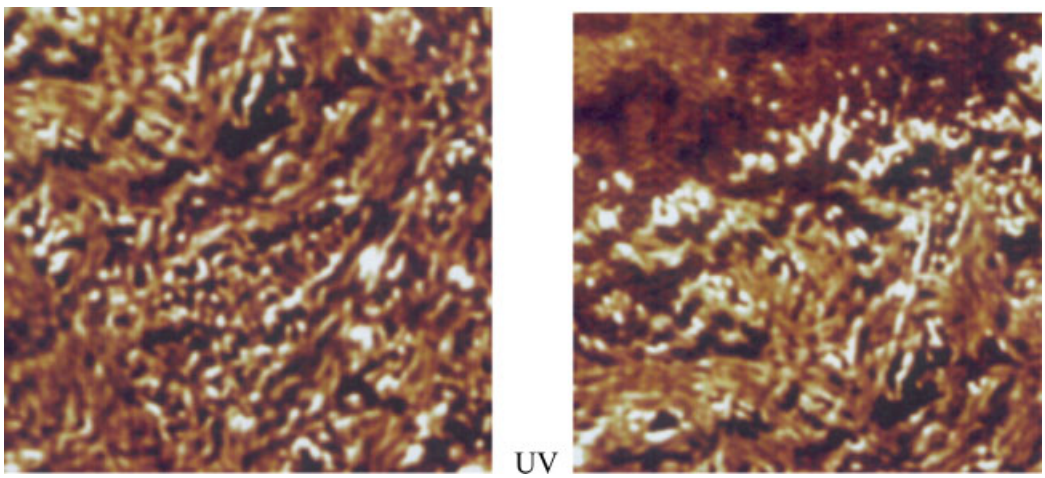

Figure 3. AFM height images of native (left) and partially irradiated (on top) with 313 nm UV light **2-Na** DMF gel (right)

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PREPARATION OF COMPOUNDS

1,2-Bis{5′-[10′′-(methoxycarbonyl)-decylcarbamoyl]-2′-methylthien-3′-yl}perfluorocy-clopentene (6)

A mixture of **(5)** (500 mg, 1.1 mmol) and triethylamine (1.0 g, 9.9 mmol) were dissolved in 30 ml dry THF under nitrogen atmosphere. Then DMAP (50 mg, 0.4 mmol) and DCC (600 mg, 3 mmol) were added. The mixture was stirred at room temperature overnight. *N*,*N*-dicyclohexylurea was collected by filtration, and the filtrate was concentrated under reduced pressure. The residue was then chromatographed on silica gel with dichloromethane/ethyl acetate (10:1) as eluent to afford 364 mg of 1,2-bis{5′-[10′′-(methoxycarbonyl)-decylcarbamoyl]-2′-methylthien-3′-yl}perfluorocyclopentene **(6)** in 35% yield. 6: mp 113.3–115.7 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (s, 2H), 5.98 (s, 2H), 3.66 (s, 6H), 2.05 (q, $J = 6.4$, 7.1 Hz, 4H), 2.30 (t, $J = 7.5$ Hz, 4H), 1.91 (s, 6H), 1.65–1.50 (m, 8H), 1.40–1.20 (m, 24H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 173.4, 159.9, 145.2, 136.8, 126.0, 124.0, 50.4, 39.2, 33.1, 28.6, 28.4, 28.3, 28.2(2C), 28.1, 25.9, 23.9, 13.8; ^{19}F NMR ($CDCl_3$, 200 MHz) δ −110.3, −132.0; MALDI-MS. *m/z* 873.2 [M+Na$^+$].

1,2-Bis[5′-(10′′-carboxy-decylcarbamoyl)-2′-methylthien-3′-yl]perfluorocyclopentene (1-H)

Ester (**6**) (115 mg, 0.13 mmol) was dissolved in 15 ml ethanol and then was added to a solution of lithium hydroxide (37 mg, 1.54 mmol) in 10 ml water. The mixture was stirred at room temperature overnight. The solution was acidified to pH 5 with 1N hydrochloride solution and stirred for 2 h. The product was extracted with dichloromethane and dried over Na_2SO_4 and evaporated in vacuum to yield a light red residue which was subsequently purified by flash column chromatography with 10% methanol in ethyl acetate to afford 56 mg of 1,2-bis[5′-(10′′-carboxy-decylcarbamoyl)-2′-methylthien-3′-yl] perfluorocyclopentene (**1-H**) in 52% yield as a light yellow viscous oil. 1-H: ^{1}H NMR (DMSO-$_{d6}$, 300 MHz) δ 11.99 (br, 2H), 8.62 (s, 2H), 7.83 (s, 2H), 3.20 (m, 4H), 2.21 (m, 4H), 1.87 (s, 6H), 1.55–1.40 (m, 8H), 1.35–1.10 (m, 24H); ^{13}C NMR (DMSO-$_{d6}$, 300 MHz) δ 174.4, 159.9, 146.0, 138.9, 126.6, 124.1, 54.8, 33.6, 28.9 (2C), 28.8, 28.7 (2C), 28.5, 26.4, 24.4, 14.2; ^{19}F NMR (DMSO-$_{d6}$, 200 MHz) δ −109.8, −131.5; MALDI-MS. *m/z* 845.5 [M+Na$^+$].

1,2-Bis[5′-(10′′-carboxy-decylcarbamoyl)-2′-methylthien-3′-yl]perfluorocyclopentene disodium salt (1-Na)

Diacid 1-H (53 mg, 0.064 mmol) dissolved in 5 ml methanol was added to 129 mg of a 1N sodium hydroxide solution. The mixture was stirred at room temperature for 2 h. Then the solvent was removed under vacuum. The product was washed with dichloromethane and diethyl ether and dried to yield 54 mg of the disodium salt (1-Na) in 96% yield as a white solid. 9: mp 232.3(decom.) °C. ^{1}H NMR (CD_3OD, 250 MHz) δ 7.74 (s, 2H), 3.32 (m, 4H), 2.14 (t, $J = 7.5$ Hz, 4H), 1.92 (s, 6H), 1.70–1.50 (m, 8H), 1.40–1.20 (m, 24H); ^{19}F NMR ($CDCl_3$, 200 MHz) δ −112.0, −133.8; FT-IR (KBr-cast): 3315, 2925, 2853, 1628, 1564, 1442, 1420, 1339, 1304, 1275, 1194, 1141, 1113, 1052, 987.

1,2-Bis(5′-hydroxylmethyl-2′-methylthien-3′-yl)perfluorocyclopentene (8)

To a solution of **7** (100 mg, 0.24 mmol) in 20 ml ice-cooled methanol, $NaBH_4$ (18 mg, 0.48 mmol) was added. The mixture was stirred for 2 h, ice water was then added to quench the reaction and the product was extracted with dichloromethane and dried over Na_2SO_4. Removal of the solvent gave a light red crude product which was subsequently purified by flash column chromatography with 10:1 dichloromethane/methanol as eluent to afford 94 mg of 1,2- bis(5′-hydroxylmethyl-2′-methylthien-3′-yl)perfluorocyclopentene (9) in 95% yield as a white powder. 9: mp 132.7–133.7 °C. (reference mp: 125–128 °C) ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.95 (s, 2H), 4.75 (s, 4H), 1.88 (s, 6H); ^{13}C NMR (DMSO-$_{d6}$, 300 MHz) δ 149.7, 145.2, 127.7, 127.3, 62.5, 18.5; ^{19}F NMR ($CDCl_3$, 200 MHz) δ −110.2, −132.0; MALDI-MS. *m/z* 474 [M+2Na$^+$]. Anal. Calcd for $C_{17}H_{14}F_6O_2S_2$: C, 47.66; H, 3.29. Found: C, 47.67; H, 3.37.

1,2-Bis{5′-[10′′-(methoxycarbonyl)-decylcarbamoyloxymethyl]-2′-methylthien-3′-yl}perfluorocyclopentene (9)

A mixture of **8** (0.52 g, 1.2 mmol) and triethylamine (1.0 g, 9.9 mmol) were dissolved in 20 ml dry THF under nitrogen atmosphere. Methyl 11-isocyanatoundecanoate (2.3 g, 9.5 mmol) was added and the reaction mixture was refluxed for 24 h. The solvent was evaporated to give a light red oil residue. The residue was dissolved in 20 ml dichloromethane, then 50 ml of water was added and the mixture was stirred overnight. The water layer was extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4 and concentrated. The product was then chromatographed on flash column with 0.5% methanol in dichloromethane as eluent to afford 864 mg of 1,2-bis{5′-[10′′-(methoxycarbonyl)-decylcarbamoyloxymethyl]-2′-methylthien-3′-yl}perfluorocyclopentene (**9**) in 85% yield. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.00 (s, 2H), 5.12 (s, 4H), 4.75 (m, 2H), 3.67 (s, 6H), 3.17 (m, 4H), 2.30 (t, $J = 7.6$ Hz, 4H), 1.85 (s, 6H), 1.64–1.40 (m, 8H), 1.35–1.2 (m, 24H); ^{13}C NMR

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($CDCl_3$, 400 MHz) δ 174.6, 155.2, 143.4, 137.4, 127.6, 124.6, 60.8, 51.7, 41.4, 34.3, 30.2, 29.7, 29.6, 29.5(2C), 29.4, 26.9, 25.2, 14.6; ^{19}F NMR ($CDCl_3$, 200 MHz) δ −110.3, −132.1; MALDI-MS. *m/z* 933.4 [M+Na^+]. Anal. Calcd for $C_{43}H_{60}F_6N_2O_8S_2$: C, 56.69; H, 6.64; N, 3.07. Found: C, 57.10; H, 6.92; N, 3.23.

1,2-Bis[5′-(10′′-carboxy-decylcarbamoyloxymethyl)-2′-methylthien-3′-yl]perfluoro-cyclopentene (2-H)

Ester **9** (674 mg, 0.74 mmol) was dissolved in 35 ml ethanol, and then was added to a solution of lithium hydroxide (700 mg, 29.2 mmol) in 25 ml water. The mixture was stirred at room temperature overnight. The solution was acidified to pH 5 with 1N hydrochloride solution and stirred for 2 h. The product was extracted with dichloromethane and dried over Na_2SO_4 and evaporated in vacuum to yield a light red residue which was subsequently purified by flash column chromatography with 4% methanol in dichloromethane to afford 460 mg of 1,2-bis[5′-(10′′-carboxy-decylcarbamoyloxy-methyl)-2′-methylthien-3′-yl]perfluorocyclopentene (**2-H**) in 70% yield as a light yellow viscous oil. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.00 (s, 2H), 5.12 (s, 4H), 4.81 (m, 2H), 3.18 (m, 4H), 2.11 (m, 4H), 1.87 (s, 6H), 1.73–1.40 (m, 8H), 1.4–1.2 (m, 24H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 156.4, 143.5, 137.5, 127.7, 124.7, 61.0, 41.5, 30.2, 30.1, 29.7, 29.6, 29.5(2C), 29.3, 27.0, 25.0, 14.7; ^{19}F NMR ($CDCl_3$, 200 MHz) δ −110.3, −132.1; MALDI-MS. *m/z* 905.2 [M+Na^+].

1,2-Bis[5′-(10′′-carboxy-decylcarbamoyloxymethyl)-2′-methylthien-3′-yl]perfluorocy-clopentene disodium salt (2-Na)

Diacid **2-H** (190 mg, 0.21 mmol) dissolved in 10 ml methanol was added to 418 mg of 1N sodium hydroxide solution. The mixture was stirred at room temperature for 2 h. Then the solvent was removed under vacuum. The product was washed with dichloromethane and diethyl ether and dried to yield 192 mg of the disodium salt (2-Na) in 96% yield as a white solid. 2-Na: mp 206.3 °C (decom.). ^1H NMR (CD_3OD, 300 MHz) δ 7.08 (s, 2H), 5.14 (s, 4H), 3.09 (m, 4H), 2.15 (t, $J = 6.3$ Hz, 4H), 1.86 (s, 6H), 1.70–1.40 (m, 8H), 1.40–1.20 (m, 24H); FT-IR (KBr-cast): 3341, 2919, 2840, 1698, 1565, 1462, 1442, 1417, 1339, 1270, 1191, 1157, 1137, 1113, 1049, 985. Anal. Calcd for $C_{41}H_{54}F_6N_2Na_2O_8S_2$: C, 53.12; H, 5.87; N, 3.02; Na, 4.96. Found: C, 52.94; H, 6.03; N, 2.98; Na, 4.64.

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REFERENCES

1. (a) Terech P, Weiss RG. *Chem. Rev.* 1997; **97**: 3133–3159; (b) van Esch J, Feringa BL. *Angew. Chem. Int. Ed.* 2000; **39**: 2263–2266; (c) Estroff LA, Hamilton AD. *Chem. Rev.* 2004; **104**: 1201–1217.
2. Jung JH, Lee SH, Yoo JS, Yoshida K, Shimizu T, Shinkai S. *Chem. Eur. J.* 2003; **9**: 5307–5313.
3. Frkanec L, Jokic M, Makarevic J, Wolsperger K, Zinic M. *J. Am. Chem. Soc.* 2002; **124**: 9716–9717.
4. Ayabe M, Kishida T, Fujita N, Sada K, Name B, Shinkai S. *Org. Biomol. Chem.* 2003; **1**: 2744–2747.
5. Ahmed S, Sallenave X, Fages F, Mieden-Gundert G, Müller WM, Müller U, Vögtle F, Pozzo JL. *Langmuir* 2002; **18**: 7096–7101.
6. Irie M. *Chem. Rev.* 2000; **100**: 1683–1716.
7. Del Guerzo A, Pozzo JL. Chap. 24, *Molecular Gels* Terech P, Weiss RG (eds). Springer: Dordrecht. 2006; 817–856.
8. Lucas LN, van Esch J, Feringa BL, Kellogg RM. *Chem. Comm.* 2001; 759–760.
9. de Jong J, Lucas LN, Kellogg RM, van Esch J, Feringa BL. *Science,* 2004; **304**: 278–281.
10. Wang S, Shen W, Feng Y, Tian H. *Chem. Comm.* 2006; 1497–1499.
11. (a) Mieden-Gundert G, Klein L, Fischer M, Vögtle F, Heuzé K, Pozzo JL, Fages F. *Angew. Chem. Int. Ed.* 2001; **40**: 3164–3166; (b) D'Aléo A, Pozzo JL, Fages F, Schmutz M, Mieden-Gundert G, Vögtle F, Caplar V, Zinic M. *Chem. Comm.* 2004; **35**: 190–191; (c) Caplar V, Zinic M, Pozzo JL, Fages F, Mieden-Gundert G, Vögtle F. *Eur J. O. C.* 2004; **97**: 4048–4059.
12. Myles AJ, Branda N. *Macromolecules* 2003; **36**: 298–303.
13. Osuka A, Fujikane D, Shinmori H, Kobatake S, Irie M. *J. Org. Chem.* 2001; **66**: 3913–3923.
14. Gronwald O, Shinkai S. *Chem. Eur. J.* 2001; **7**: 4329–4333.
15. (a) Irie M, Lifka T, Uchida K, Kobatake S, Shindo Y. *Chem. Comm.* 1999; 747–750; (b) the tricyclic by-product (**10**) gives characteristic ^1H NMR data δ (CH_3) 2.66 and 2.68, δ (CH_2O) 4.97 and δ (CH-thienyl) 6.52 ppm.
16. Terech P, Weiss RG (eds). 2006. *Molecular Gels*. Springer: Dordrecht.

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