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PAPER

## Self-organized photochromic dithienylcyclopentene organogels

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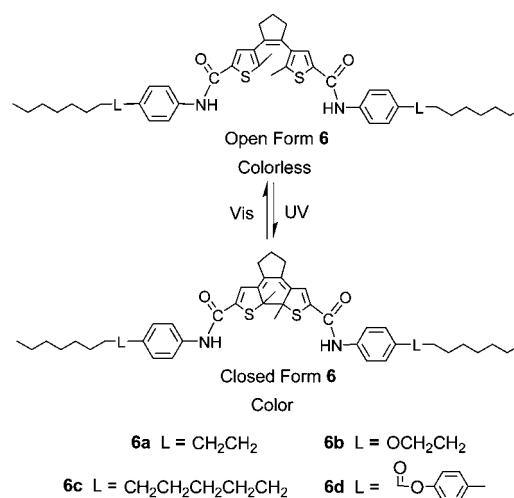
A series of photochromic organogelators based on dithienylcyclopentene amides with a phenylene unit as a bridge between the amide and long alkyl chain were synthesized, their gelation behaviors were characterized by rheology, FT-IR, <sup>1</sup>H NMR, SEM, optical microscopy, UV-Vis and fluorescence spectroscopy. These organogelator molecules were found to be able to induce gelation in apolar solvents such as benzene, toluene and *p*-xylene to form entangled networks driven by intermolecular hydrogen bonding together with  $\pi$ - $\pi$  interactions. Their excellent reversible photochromism with thermal stability in both solution and gel states was observed, and the thermally reversible property in sol-gel transition was exhibited.

## Introduction

Organogelators, *i.e.* functional materials that assemble to macroscopic three-dimensional (3D) networks and immobilize organic solvent molecules in the networks, recently have emerged as a class of fascinating self-organized materials. Self-organization of organogelator molecules acting as low molecular weight gelators (LMWGs) into an entangled supramolecular 3D fibrous network in organic solvents is often driven by weak intermolecular interactions such as electrostatic, dipole-dipole, hydrogen bonding and  $\pi$ - $\pi$  interactions.<sup>1-6</sup> Any variation in the molecular structure of organogelators would affect the corresponding intermolecular interactions, and hence the morphology and properties of the resulting gels. In this context, smart molecular materials, consisting of small molecules responsive to external stimuli, may provide a promising route towards active control over the properties and multi-scale structures of organogels. Compared with stimuli such as electric field, heat, chemical reaction or electrochemical reaction, light is particularly attractive due to its advantages of remote, spatial, and temporal control. The extension to reversible photochromic organogels has drawn increasing attention due to their potential application as sensors, molecular electronics and catalysis.<sup>7</sup> Among all the photochromic organogelators that have been reported to date, dithienylcyclopentenones hold a particular promise because of their unique fatigue resistance, thermal irreversibility and electrical conductivity.<sup>8,9</sup> Colorless open-ring dithienylcyclopentene can be transformed photochemically to the colored closed-ring form upon UV irradiation whereas its reverse process occurs photochemically with visible light. Since the physical and chemical properties of the two forms are different, the photochemically

reversible switching has been the basis for creating new functional materials with applications in photonics, information storage, fluorescent photoswitches, sensors *etc.*<sup>9</sup> However, only minor attention has been paid to the developments of dithienylcyclopentene based LMWG.<sup>3,4,10</sup>

Here we report the design and synthesis of four new photochromic organogelators based on dithienylcyclopentene amides with a phenylene unit as a bridge between the amide and long alkyl chain (Scheme 1). These organogelator molecules were found to be able to induce gelation in apolar solvents to form photochromic entangled networks driven by  $\pi$ - $\pi$  interactions in addition to intermolecular hydrogen bonding between the amide groups. The interest behind the introduction of the phenylene unit between the amide and the long alkyl chain is to enhance aggregation behavior by forming the  $\pi$ - $\pi$  stacking arrangement.



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**Scheme 1** Light-driven open-ring and closed-ring isomerization of photochromic dithienylcyclopentene amides **6a-d**.

**Table 1** Gelation behavior of photochromic dithienylcyclopentene amide **6a–d** in organic solvent. G: gel; P: precipitation; VS: viscous solution; CGC: critical gelation concentration in mg mL<sup>-1</sup> at 20 °C

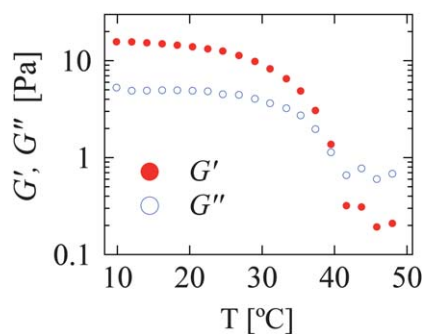
Solvents	<b>6a</b> (CGC)	<b>6b</b> (CGC)	<b>6c</b> (CGC)	<b>6d</b> (CGC)
Toluene	G (2.5)	G (2.0)	G (1.6)	G (3.0)
Benzene	G (3.0)	G (2.0)	G (1.8)	G (3.0)
CH <sub>2</sub> Cl <sub>2</sub> : hexane	G (3.0)	G (2.0)	G (2.0)	G (3.0)
CCl <sub>4</sub>	P	P	G (1.6)	G (3.0)
<i>p</i> -Xylene	G (2.5)	G (1.8)	G (1.6)	G (3.0)
Dodecane	P	P	VS	VS
Ethanol	P	P	P	P

Meanwhile, the terminal alkyl chain would improve the solubility and the gelation ability of gelator molecule.

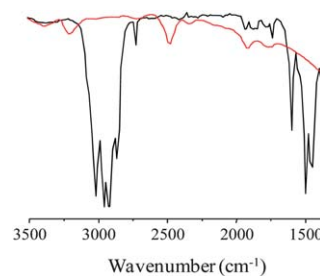
## Results and discussion

The target photochromic dithienylcyclopentene amides **6a–d** (Scheme 1) were thermally and chemically stable, and exhibited the expected reversible photochromic behavior. All the compounds **6a–d** were found to be able to induce gelation in apolar solvents to form entangled networks at ambient temperature (Table 1, in which a test tube inversion method was adopted for testing their gelation behavior).<sup>11</sup> We evaluated the temperature dependence of the sol–gel transition using shear rheometry.<sup>12</sup> Fig. 1 shows the rheology of 2 mg mL<sup>-1</sup> **6b** in toluene. The storage modulus  $G'$  is higher than the loss modulus  $G''$  at lower temperatures, and the sol–gel transition temperature is approximately 40 °C. On cooling to room temperature the solution became gel mainly in apolar solvents and precipitation was found in polar solvents due to limited solubility. All the organogels exhibited remarkable stability at room temperature which were stored even for one year without any decomposition in gelation properties, although the photochromic gels were sensitive to light and alteration of the color indicates the transformation from open form to closed form.

FT-IR experiments were performed to analyze the intermolecular hydrogen bonding motif. For example, FT-IR spectra of the xerogel **6c** showed two strong absorption bands around 3080 and 1610 cm<sup>-1</sup> corresponding to N–H and C=O stretching vibrations, whereas its corresponding organogel, 2 mg mL<sup>-1</sup> in



**Fig. 1** Temperature dependence of the dynamic moduli of 2 mg mL<sup>-1</sup> **6b** solution in toluene. Storage modulus,  $G'$  (●), and loss modulus,  $G''$  (○), were measured at an oscillatory frequency of 1 Hz with an applied strain of 0.05.

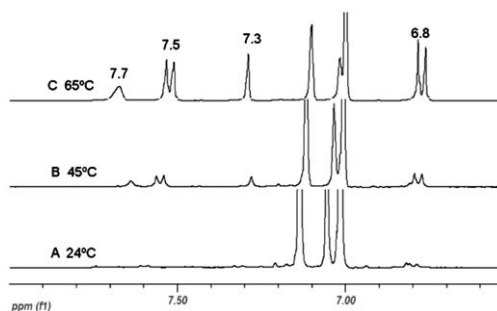


**Fig. 2** IR spectra of **6c** in xerogel (black line) and toluene organogel state (red line).

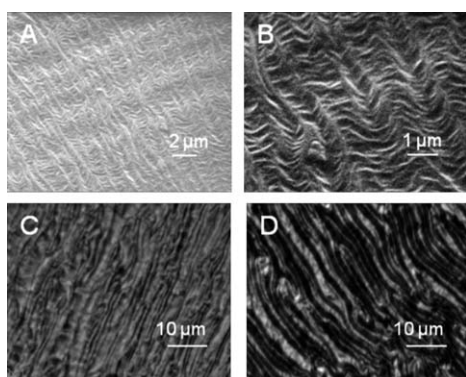
toluene, exhibited weak absorption bands at approximately 3400 cm<sup>-1</sup> and 1680 cm<sup>-1</sup> (Fig. 2). This indicates the existence of the intermolecular hydrogen bonding through two amide moieties in the gel state.<sup>13</sup> To study the driving force of the gel formation, we examined temperature dependence of <sup>1</sup>H NMR spectra. <sup>1</sup>H NMR spectra of 25 mg mL<sup>-1</sup> **6b** in toluene-*d*<sub>8</sub> at 24 °C (gel state), 45 °C (“partial” solution state, gel–sol transition ~40 °C), and 65 °C (solution state) are shown in Fig. 3. On increasing temperature, the aromatic and amide protons of **6b** developed strong signals with slight shifts. The characteristic proton in NH group of amide was observed at 7.7 ppm as a broad singlet peak, while the protons on phenyl group were located at 7.5 ppm and 6.8 ppm as characteristic doublet peaks. The singlet at around 7.3 ppm was assigned to the protons on thiophene moiety. The NMR changes provide clear evidence that hydrogen bond together with  $\pi$ – $\pi$  interactions plays a significant role in the gelation process.<sup>14</sup>

The morphology of the xerogels of **6a–d**, which were prepared by slow evaporation of toluene from the corresponding organogels, was investigated by scanning electron microscopy (SEM) and optical microscopy. The xerogels obtained by drying the corresponding organogels in toluene were found to have fibrous architectures formed by self-organization of the organogelators as shown in Fig. 4. The SEM images provide fine details of the morphology structure, while the optical microscope images exhibit coexistence of the intertwisted fibers and ordered fibers in a larger length scale.

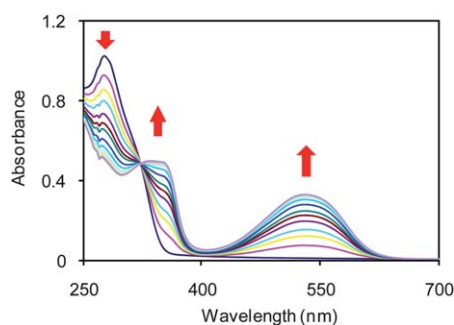
As expected, all the organogelators **6a–d** exhibited the reversible photochromic behavior with thermal stability in both solution and gel states. For example, a solution of **6d** in CHCl<sub>3</sub> is colorless where there is no absorption in the visible region,



**Fig. 3** <sup>1</sup>H NMR spectra of 25 mg mL<sup>-1</sup> **6b** in toluene-*d*<sub>8</sub> at different temperatures 24 °C, 45 °C and 65 °C.

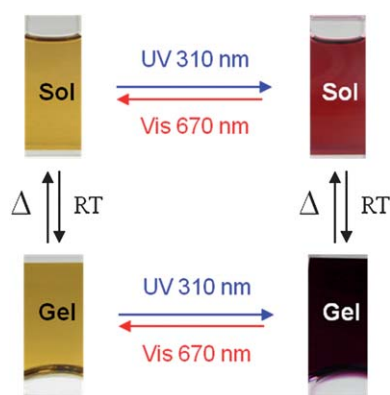


**Fig. 4** SEM images (A for **6c** and B for **6d**) and optical microscope images (C for **6c** and D for **6d**) of xerogels prepared by the evaporation of toluene from the organogels.

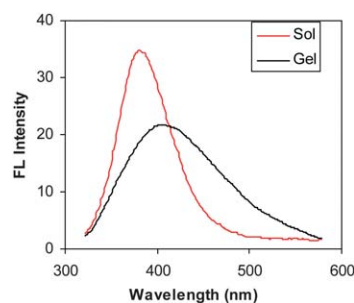


**Fig. 5** UV-Vis spectra of **6d** in chloroform ( $1.4 \times 10^{-5}$  M) under 310 nm irradiation with different times.

corresponding to the open-ring **6d** (Scheme 1). UV irradiation at 310 nm of this solution resulted in a clean photoisomerization to the closed-ring **6d**, as evidenced by a decrease in the absorbance at 288 nm and the appearance of new broad absorption bands at 355 nm and 530 nm with an isosbestic point at 330 nm (Fig. 5). The open-ring **6d** is colorless whereas its closed-ring isomer is colored, which is attributed to the closed-ring form having a larger  $\pi$ -conjugation than its open-ring form. The photostationary state of the open-ring **6d** to its closed-ring **6d** was reached within approximately 140 s upon UV irradiation at 310 nm,



**Fig. 6** Images of **6d** in toluene ( $4 \text{ mg mL}^{-1}$ ) at the gel state and the solution state. Top: open form (left) and closed form (right) in solution. Bottom: open form (left) and closed form (right) in gel.



**Fig. 7** Fluorescence spectra of **6d** in toluene at solution (red line,  $50^\circ\text{C}$ ) and gel state (black line, room temperature).

whereas its reverse process to the open-ring form upon irradiation of visible light at 670 nm takes approximately 300 s. The cycle was repeated many times without fatigue. These organogels also showed reversible photochromic property in the gel state with thermally reversible gel–sol transformation (Fig. 6). Interestingly, the gel and its corresponding solution state exhibited an obvious difference in their fluorescence emission spectra (Fig. 7), *e.g.*, **6d** showed a broad maximum at 400 nm in gel state at room temperature, while a sharp maximum of its solution state at  $50^\circ\text{C}$  is around 380 nm. This result may root in the different intermolecular interactions between organogelator molecules in gel and solution states.

## Conclusions

Four photochromic dithienylcyclopentene amides with a phenylene unit as a bridge between the amide and long alkyl chain, the first of their kind, were synthesized and characterized. They were found to be able to self-organize into reversible photochromic organogels in apolar solvents. SEM and optical microscopy studies of their xerogels showed the typical fibrous networks. Temperature dependence of the sol–gel transition by shear rheology was evaluated. FT-IR,  $^1\text{H}$  NMR, and fluorescence emission spectra indicate that such a fibrous network might result from the cooperation of the hydrogen bonding between the amide groups and the  $\pi$ – $\pi$  interactions between the aromatic moieties. These materials exhibited excellent reversible photochromism in both solution and gel states. The findings that hydrogen bonded networks enhanced by  $\pi$ – $\pi$  interactions through the insertion of a phenylene bridge between the terminal alkyl chain and the center dithienylcyclopentene core would provide insight to design organogels with enhancement of gelation behavior.

## Experimental section

### Materials and methods

All chemicals and solvents were used without further purification. Melting points were uncorrected. The rheology of **6b** organogel in toluene was obtained using a stress-controlled rheometer (HAAKE MARS II, Thermo Scientific) on a Peltier plate with a solvent trap to ensure homogeneous temperature and to prevent solvent evaporation from the organogel solution. Storage and loss moduli are measured by applying shear strain of 0.05 with a cone-and-plate geometry (cone angle =  $4^\circ$ , diameter

= 35 mm) at an oscillatory frequency of 1 Hz, while varying temperature to determine gelation temperature. The temperature is varied from 50 to 10 °C by 2 °C steps with a 2 minute equilibrium time for each temperature step. FTIR spectra were recorded with KBr pellets on Nicolet Instruments. For measuring gels, it is deposited in KBr pellets and dried until complete evaporation under vacuum. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 spectrometer or Varian Gemini 200. Chemical shifts are in δ units (ppm) with the residual solvent peak as internal standard. The coupling constant (*J*) is reported in hertz (Hz). NMR splitting signal are designated as s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60–200 mesh). Elemental analysis was performed by Robertson Microlit Laboratories, Inc. Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. The intertwined fibers were observed by optical microscopy using an Olympus microscope. UV-Vis spectra were recorded using a Perkin-Elmer Lambda spectrophotometer in the range of 200–800 nm. Fluorescence measurements were performed using Varian Cary Eclipse fluorescence spectrophotometer controlled with slit excitation of 5 nm and scan ranges from 300–600 nm. The irradiation studies were carried out using a high-pressure 100 W Xenon lamp (Asahi spectra co Ltd, Japan) with mirror module of UV and visible range of 300–400 and 400–700 nm with respective cutoff filters. SEM images were taken using a JEOL and a Hitachi S–2600 N model with an operating voltage of 20–25 kV. SEM samples were prepared by dropping dilute gels onto a clean wiped glass slide. The slow evaporation of solvent in air for 15 min afforded xerogels. All the samples for SEM experiments were sputtered with gold thin films.

## Gelation

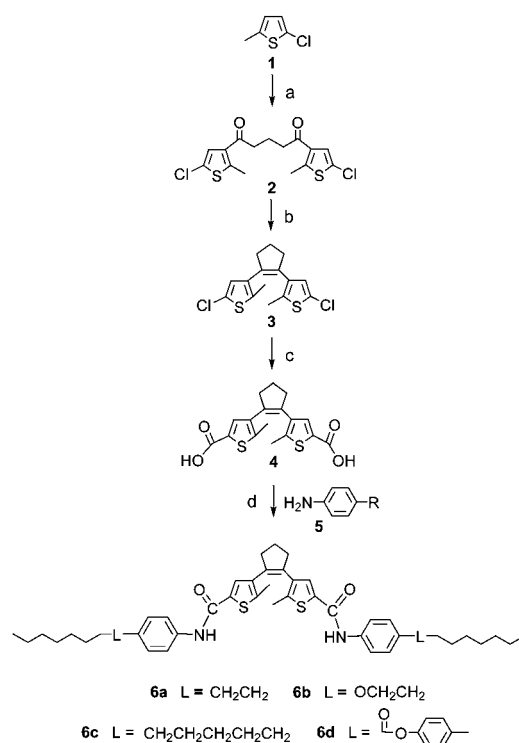
The gelation test was carried out with various solvents using a test tube inversion method. The compound and solvent were added in a septum capped test tube and heated (>85 °C) until the solid dissolved. In order to obtain gels, the sample was cooled to ambient temperature and left for a period of time. No gravitational flow while inverting the test tube of the sample indicates successful gelation.

## Synthesis

The photochromic organogelator molecules **6a–d** were prepared starting from 2-chloro-5-methylthiophene **1** in a facile synthesis following the general procedure as shown in Scheme 2.<sup>15</sup> Their structures were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis and HR-MS.

### Data for 6a

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.3 Hz, 6H), 1.28–1.49 (m, 28H), 1.72 (t, *J* = 7.4 Hz, 4H), 1.95–2.01 (m, 8H), 2.73 (t, *J* = 7.3 Hz, 4H), 6.80 (d, *J* = 8.7 Hz, 4H), 7.30 (s, 2H), 7.44 (d, *J* = 8.8 Hz, 4H), 7.60 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.1, 14.3, 22.5, 25.9, 29.2, 29.1, 29.3, 31.1, 38.1, 113.2, 114.2, 122.0, 129.1, 130.2, 134.7, 134.8, 135.2, 140.1, 155.2, 158.8. TOF MS ES (*m/z*) (M + Na<sup>+</sup>) calcd for C<sub>47</sub>H<sub>62</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Na: 773.4145, found: 773.4140.



**Scheme 2** Synthesis of photochromic dithienylcyclopentene amide **6**. (a) Glutaryl dichloride, AlCl<sub>3</sub>, CS<sub>2</sub>; (b) TiCl<sub>3</sub>(THF)<sub>3</sub>, Zn, THF; (c) *n*-BuLi, THF, solid CO<sub>2</sub>; (d) SOCl<sub>2</sub>, DMF, CH<sub>2</sub>Cl<sub>2</sub>.

Anal. calcd for C<sub>47</sub>H<sub>62</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 75.15, H 8.32, N 3.73, S 8.54; found: C 75.11, H 8.63, N 3.63, S 8.34%.

### Data for 6b

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.3 Hz, 6H), 1.28–1.51 (m, 24H), 1.75 (t, *J* = 7.4 Hz, 4H), 1.99–2.05 (m, 8H), 2.73 (t, *J* = 7.2 Hz, 4H), 3.90 (t, *J* = 6.4 Hz, 4H), 6.83 (d, *J* = 8.8 Hz, 4H), 7.29 (s, 2H), 7.44 (d, *J* = 9.0 Hz, 4H), 7.72 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.1, 14.8, 22.7, 26.0, 29.3, 29.4, 29.5, 31.9, 38.4, 68.3, 114.8, 122.1, 130.0, 130.6, 134.6, 134.9, 136.5, 140.6, 156.2, 159.8. TOF MS ES (*m/z*) (M + Na<sup>+</sup>) calcd for C<sub>47</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>Na: 805.4043; found: 805.4040. Anal. calcd for C<sub>47</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C 72.08, H 7.98, N 3.58, S 8.19; found: C 72.11, H 8.31, N 3.54, S 8.11%.

### Data for 6c

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 7.0 Hz, 6H), 1.25–1.57 (m, 40H), 1.99–2.09 (m, 8H), 2.55 (t, *J* = 7.7 Hz, 4H), 2.76 (t, *J* = 7.9 Hz, 4H), 7.13 (d, *J* = 8.8 Hz, 4H), 7.31 (s, 2H), 7.47 (d, *J* = 8.8 Hz, 4H), 7.63 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 14.1, 14.8, 22.7, 29.2, 29.4, 29.5, 29.7, 31.5, 31.9, 35.3, 38.3, 115.2, 120.1, 128.8, 129.0, 129.9, 134.6, 134.8, 135.2, 136.5, 139.2, 140.7, 159.7. TOF MS ES (*m/z*) (M + Na<sup>+</sup>) calcd for C<sub>53</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Na: 857.5084, found 857.5081. Anal. calcd for C<sub>53</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 76.21, H 8.93, N 3.35; found C 76.41, H 9.28, N 3.40%.

### Data for 6d

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 7.0 Hz, 6H), 1.28–1.33 (m, 16H), 1.58–1.63 (m, 4H), 2.02–2.10 (m, 8H), 2.61 (t, *J* = 7.6 Hz,



4H), 2.78 (t,  $J = 7.2$  Hz, 4H), 7.09 (d,  $J = 8.4$  Hz, 4H), 7.21 (d,  $J = 8.4$  Hz, 4H), 7.37 (s, 2H), 7.74 (d,  $J = 9.2$  Hz, 4H), 7.97 (s, 2H), 8.15 (d,  $J = 8.8$  Hz, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 14.1, 14.9, 22.7, 22.8, 29.1, 29.2, 31.5, 31.8, 35.4, 38.4, 119.2, 121.3, 125.1, 129.3, 139.8, 131.4, 134.0, 134.9, 136.7, 140.6, 141.8, 142.5, 148.8, 160.0, 164.9$ . TOF MS ES ( $m/z$ ) ( $\text{M} + \text{Na}^+$ ) calcd for  $\text{C}_{57}\text{H}_{62}\text{N}_2\text{O}_6\text{S}_2\text{Na}$ : 957.3941, found: 957.3937. Anal. calcd. for  $\text{C}_{57}\text{H}_{62}\text{N}_2\text{O}_6\text{S}_2$ : C 73.20, H 6.68, N 3.00, S 6.86; found C 73.13, H 7.43, N 2.74, S 6.35%.

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