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Proton-sensitive fluorescent organogels †

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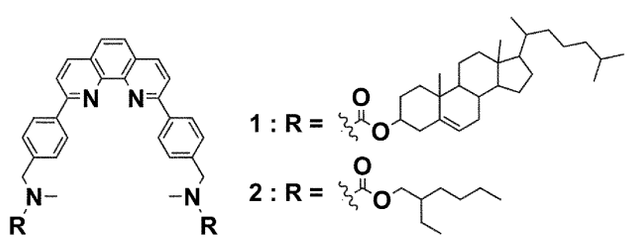
Received 8th November 2002, Accepted 15th January 2003
First published as an Advance Article on the web 11th February 2003

A 1,10-phenanthroline-appended cholesterol-based gelator (**1**) and its nongelling reference compound (**2**) were synthesized. Among 19 solvents tested herein, gelator **1** could gelate 11 solvents including alcohols, dipolar aprotic solvents, organic acids and a base (triethylamine), indicating that **1** acts as a versatile gelator. The TEM observation gave a visual image showing that fibrillar aggregates are entangled in the three-dimensional network structure. In the fluorescence measurements, most gels afforded an emission maximum at 394 nm (purple emission), whereas only the acetic acid gel afforded an emission maximum at 522 nm (yellow emission). Thus, the influence of protonation of the 1,10-phenanthroline nitrogens (by trifluoroacetic acid) on the fluorescence properties in the gel phase was investigated in detail. The results have established that the fluorescence intensity of **1**·H^+ becomes particularly strong in the gel phase, presumably because of the energy transfer from neutral **1*** to protonated **1**·H^+ and the restriction of the **1**·H^+ molecular motion. The finding suggests the possibility that the gel system would be useful not only as a new proton-sensitive fluorescence system but also as a new medium for designing efficient energy transfer systems.

Introduction

Motivated by the numerous applications for gels formed by dilute solutions of polymers, proteins and inorganic substances,[1] development of new low molecular weight gelators for organic solvents, and the investigation of their particular self-assembly properties, have recently received much attention. They not only gelate various organic solvents but also create novel networks with fibrous superstructures that can be characterized by scanning electron microscopy (SEM) pictures of xerogels.[2–13] The one-dimensional (1D) self-assembly of these gelling agents with fiber-like structures, that entangle to form a three-dimensional (3D) network, is able to prevent the solvent from flowing, in a similar way to their macromolecular and inorganic counterparts.[14] Such low molecular weight gelators have been classified according to their driving forces for molecular aggregation into two categories: non-hydrogen-bond-based gelators and hydrogen-bond-based gelators. Cholesterol derivatives[7–10] are typical examples of the former group whereas aliphatic amide and urea derivatives[2–5] and saccharide-containing gelators[9,15–18] are the main representatives of the latter group.

The main research interest in the organogel system has been focused, so far, on the variety of supramolecular structures constructed in the gels. In addition, one would also expect that they show the characteristic absorption and fluorescence spectroscopic properties arising from their difference in the aggregation mode. Taking their structural variety into consideration, the spectral variety would make it possible to utilize the gels as potential candidates for memory systems, devices, sensors, molecular imprinting, *etc*. To the best of our knowledge, however, such functional applications of the spectroscopic properties have been very limited. For example, Weiss *et al.* and Desvergne *et al.* synthesized anthracene-containing gelators and measured the fluorescence spectra.[19] Maitra *et al.* deposited a dye molecule in the gel system to evaluate the microenvironmental effect.[20] We also designed azonaphthol- and azobenzene-containing gelators and estimated the aggregation mode and the microenvironmental effect by spectroscopic methods.[8,21] Other groups reported on fluorescent chromophore containing organogelators.[22] To develop a further, interesting, spectroscopically functionalized gelator we designed compound **1** which consists of two gel-forming cholesterol moieties and one fluorescent 1,10-phenanthroline moiety (Scheme 1). Since the 1,10-phenanthroline skeleton changes its fluorescence properties by protonation and aggregation, one may be able to develop a proton-sensitive organogel system. Compound **2** was used as a nongelling reference compound.



Scheme 1 Structure of cholesterol-based 1,10-phenanthroline gelator (**1**) and its nongelling reference compound (**2**): 2-carbon in the 2-ethylhexyl group is racemic.

Results and discussion

Gelation properties

The gelation properties of 19 different solvents were tested.[23] The gelation test was carried out as follows: the gelator was mixed in a closed capped test tube with the appropriate amount of solvent and the mixture was heated until the solid was dissolved. By this procedure the solvent′s bp becomes higher than that under standard atmospheric pressure. The sample vial was cooled in air to 25 °C unless otherwise stated, left for 1 h at this temperature and then turned upside down. If the gelator formed a clear or slightly opaque gel by immobilizing the solvent at this stage, it was denoted by a 'G' mark in Table 1.

† Electronic supplementary information (ESI) available: excitation spectrum of **1**·H^+ and fluorescence spectrum of **1** in 1-propanol at 25 °C. See http://www.rsc.org/suppdata/ob/b2/b210968a/

DOI: 10.1039/b210968a

Table 1 Organic solvents tested for gelation with **1** and CGC

Entry	Solvent	Phase[a] at 3.0 wt%	CGC[b]/wt% (mmol dm^{-3})
1	Ethanol	I	—
2	1-Propanol	G	0.2 (1.6)[c]
3	2-Propanol	G	0.3 (2.4)[c]
4	1-Butanol	I	—
5	Hexane	I	—
6	Cyclohexane	G	1.0 (8.0)
7	Methylcyclohexane	G	0.5 (4.0)[c]
8	Benzene	S	—
9	Toluene	S	—
10	Pyridine	S	—
11	Chloroform	S	—
12	Ethyl acetate	G	0.3 (2.4)[c]
13	Acetonitrile	I	—
14	Acetone	G	0.3 (2.4)[c]
15	Dimethylformamide	G	3.0 (24.0)[c]
16	Dimethylsulfoxide	G	0.5 (4.0)
17	Acetic acid	G	1.0 (8.0)
18	Propionic acid	G	3.0 (24.0)[c]
19	Triethylamine	G	0.2 (1.6)[c]

[a] The solution was warmed until **1** was dissolved and then cooled to 25 °C to grow the gel: G = gel, S = solution, I = insoluble. [b] Critical gelation concentration: this denotes the minimum concentration necessary for gelation of solvents. [c] Cooled to 4 °C.

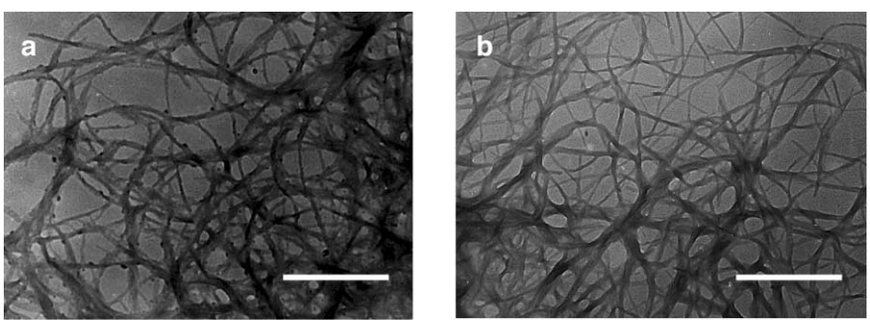


Fig. 1 TEM pictures of the xerogels prepared from (a) the **1** (0.3 wt%: 2.4 mmol dm^{-3}) + 1-propanol gel and (b) the **1** (0.3 wt%: 2.4 mmol dm^{-3}) + TFA (4.8 mmol dm^{-3}) + 1-propanol gel: the scale bar length is 500 nm.

It is seen from Table 1 that **1** is capable of gelating 11 out of the 19 solvents tested herein. The results indicate that **1** acts as a versatile gelator not only for alcohols and dipolar aprotic solvents (DMF and DMSO) but also for organic acids and a base (triethylamine). The CGC (critical gelation concentration), at which the solvent is gelated with the minimum amount of gelator, was estimated for several solvents (Table 1). In most cases, the CGC values range from ~0.2–1.0 wt%, indicating that **1** is a so-called 'super-gelator'. The lowest CGC value (0.2 wt%) was observed for 1-propanol and triethylamine. The T_{gel} (gel–sol phase transition temperature) for the 1-propanol gel (0.3 wt%) was estimated to be 82–88 °C. The result indicates that **1** can provide a thermally stable gel.

To obtain a visual image of the aggregation mode in the gel phase, we took the pictures of the xerogels with a transmission electron micrograph (TEM).[24] As shown in Fig. 1a, plenty of fibrillar aggregates with ~20–100 nm diameters were observed, which were entangled with each other to give the 3D network structure. We added trifluoroacetic acid (TFA) to protonate the 1,10-phenanthroline nitrogens, but the TEM image was scarcely changed (Fig. 1b). Furthermore, the CD spectrum of the **1** gel was quite similar to that of **1** with TFA gel (not shown). These results indicate that the gelation mode is scarcely affected by proton addition not only at the macroscopic level but also at the molecular level. Indeed, both **1** gels in the absence and in the presence of TFA have good stability for at least several weeks.

Spectroscopic properties

The fluorescence spectra are frequently affected by the microenvironment and the microviscosity around the fluorescent probe. We thus measured the fluorescence spectra of **1** in both the gel and the sol phase. In the gel phase of most solvents, the emission maximum appeared at 394 nm (purple), which is very close to that of **2** in homogeneous solutions (Fig. 2). On the other hand, in the gel phase of acetic acid the emission maximum was unusually shifted to a longer wavelength (522 nm; yellow). A similar longer wavelength shift, the origin of the yellow light emission, was also induced by the addition of TFA to the **1** + 1-propanol gel or to the homogeneous 1-propanol solution of **2**: however, the fluorescence change in the **1** + 1-propanol gel was much more sensitive to the TFA concentration than the homogeneous **2** solution was. According to Sauvage *et al.*,[25] the red shift of the emission maximum is generally observed for 1,10-phenanthroline derivatives. This is because the lowest $^1\pi\pi^*$ level is stabilized by protonation of the phenanthroline nitrogens. In the present gel system, it should be emphasized that the emission colour change is particularly conspicuous in the gel phase of **1**, indicating that **1** acts as a proton-sensitive fluorescent gelator. We thus investigated the fluorescence properties of **1** and **2** more in detail.

To find the wavelength suitable for fluorescence excitation, the UV/VIS absorption spectra of **1** were measured at the typical spectroscopic concentration ([**1**] = 1.6×10^{-5} mol dm^{-3}) as a function of the TFA concentration (Fig. 3). At such a low concentration, **1** is discretely soluble in 1-propanol in a monomeric form as confirmed by UV/VIS spectrum. It is seen from Fig. 3 that the absorption maxima at 268 and 310 nm decrease with increasing TFA concentration and the broad band at 330–400 nm increases. Since a tight isosbestic point is observed at 285 nm, this wavelength was used as the excitation wavelength for the subsequent fluorescence measurements.

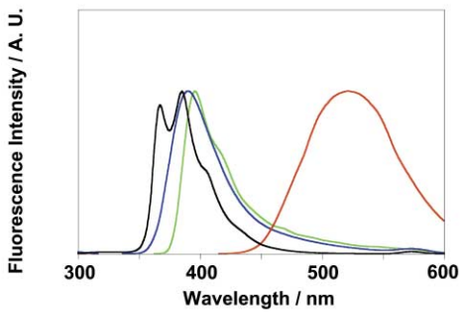


Fig. 2 Fluorescence spectra of monomeric **1** (1.6×10^{-5} mol dm^{-3}) in 1-propanol (black), **1** (0.3 wt%: 2.4 mmol dm^{-3}) in gelated 1-propanol (green), **2** (2.4 mmol dm^{-3}) in 1-propanol (blue) and **1** (8.0 mmol dm^{-3}) in gelated acetic acid (red).

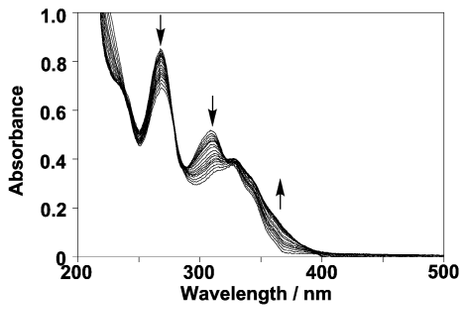


Fig. 3 Absorption spectral change in monomeric **1** (1.6×10^{-5} mol dm^{-3}) induced by the TFA addition: 1-propanol, 25 °C, [TFA] = 0–15 mmol dm^{-3}.

The fluorescence spectral change of **1** (1.6×10^{-5} mol dm^{-3}) in the absence and in the presence of TFA is shown in Fig. 4. With increasing TFA concentration, the emission maxima at 367 and 386 nm assignable to neutral **1** decrease, while the longer wavelength band at 493 nm assignable to protonated **1** (**1**·H$^+$) increases. FI_{493} (fluorescence intensity at 493 nm) plotted against TFA concentration (Fig. 5) gradually increases but is not saturated even at 15 mmol dm^{-3}. As expected, the shorter wavelength emission bands assignable to neutral **1** are still observable even in the presence of excess TFA (Fig. 4). When the fluorescence measurements of **1** were carried out in CH_2Cl_2 under similar conditions, the shorter wavelength emission bands disappeared entirely (red line in Fig. 4) and the plot was saturated at [TFA] = 1.1 mmol dm^{-3} (Fig. 5). It is known that in the excited state of 1,10-phenanthroline derivatives, protonation and deprotonation processes can hardly compete with the relatively fast excited-state decay.[25] In CH_2Cl_2, therefore, **1**·H$^+$ is excited and simply emits the longer wavelength light. In 1-propanol, on the other hand, the solvent molecules can act as a proton acceptor and it is energetically difficult to fully protonate the 1,10-phenanthroline nitrogens in the ground state. In addition, protonation and deprotonation processes may compete with the excited-state decay to some extent. Thus, one can still observe the shorter wavelength emission from neutral **1***, even in the presence of excess TFA. Similar spectral properties were also observed for **2** at [**2**] = 1.6×10^{-5} mol dm^{-3}.

Now, our major interest is to examine how these photochemical processes are affected by the sol–gel phase transition in the mmol dm^{-3} order region. The concentration effect expected from the concentration increase from 1.6×10^{-5} mol dm^{-3} to 2.4 mmol dm^{-3} was examined using a nongelling reference compound **2**. As shown in Fig. 6b, the emission maximum of neutral **2** (2.4 mmol dm^{-3}) in 1-propanol appeared as a single, broad peak at 390 nm. When 4.8 mmol dm^{-3} of TFA (2.0 equivalents with respect to **2**) were added, a new, longer wavelength band assignable to protonated **2** (**2**·H$^+$) appeared at 493 nm with a slight shift of the shorter wavelength band to 409 nm.

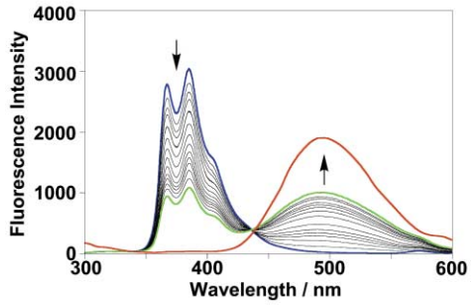


Fig. 4 Fluorescence spectral change in monomeric **1** (1.6×10^{-5} mol dm^{-3}) induced by TFA addition: 1-propanol, 25 °C, [TFA] = 0–15 mmol dm^{-3} (blue to green), λ_{ex} = 285 nm. The red line indicates a fluorescence spectrum of **1** (1.6×10^{-5} mol dm^{-3}) in CH_2Cl_2 at 25 °C: [TFA] = 1.3 mmol dm^{-3}, λ_{ex} = 294 nm (an isosbestic point in the UV/VIS absorption spectra in CH_2Cl_2).

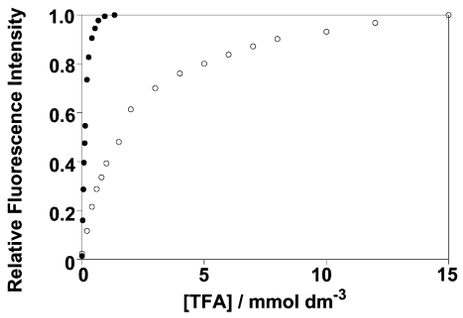


Fig. 5 Fluorescence intensity at 493 nm plotted against TFA concentration: in 1-propanol; open circles, in CH_2Cl_2; filled circles.

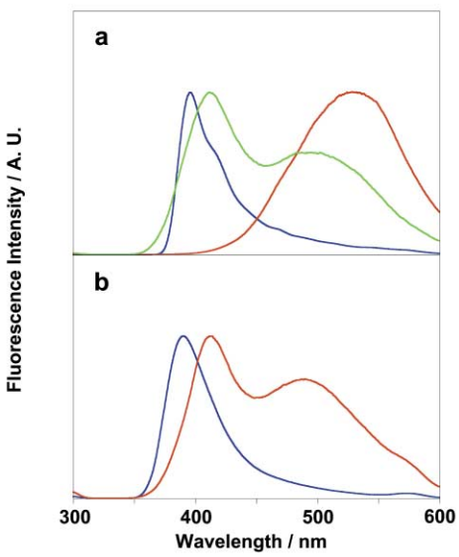


Fig. 6 Fluorescence spectra of (a) **1** (0.3 wt%: 2.4 mmol dm^{-3}) in the gel phase at 25 °C without TFA (blue), in the gel phase at 25 °C with TFA (2.0 equivalents) (red) and in the sol phase at 90 °C with TFA (2.0 equivalents) (green); (b) **2** (2.4 mmol dm^{-3}) in the sol phase at 25 °C without TFA (blue) and with TFA (2.0 equivalents) (red).

In the gel phase of **1**, the fluorescence maximum appeared at 396 nm, a slightly longer wavelength than that for **2** (390 nm) (Fig. 6a). Very interestingly, when only 2.0 equivalents (with respect to **1**) of TFA were added, the 396 nm peak assignable to emission from neutral **1*** entirely disappeared and a broad longer wavelength band assignable to emission from (**1**·H$^+$)* appeared at 530 nm. Peak-top difference between 493 nm in Fig. 4 and 530 nm in Fig. 6a (red line) is probably due to the molecular stack through gelation. When this gel was converted to the sol at 90 °C, in the presence of TFA, the fluorescence

spectrum with the bimodal emission maxima, similar to that of **2** in the presence of 2.0 equivalents of TFA, appeared. One can conclude, therefore, that the fluorescence intensity at longer wavelengths is sensitive to the proton addition only in the gel phase.

The foregoing findings suggest that energy transfer from **1*** to **1**·H^+ is taking place in the gel phase, which is corroborated by the following two experiments. Firstly, the fluorescence intensities at 396 nm (assignable to emission from neutral **1***) and 530 nm (assignable to emission from (**1**·H^+)*) are plotted against TFA concentration (Fig. 7a). The fluorescence intensity at 396 nm totally disappears at [TFA]/[**1**] = 0.2, indicating that even though neutral **1** still exists, the emission band is no longer observable. On the other hand, the 530 nm band subsequently increases up to 2.0 equivalents with increasing TFA concentration. At the same gelator concentration (2.4 mmol dm^{-3}), the **1** + 1-propanol gel (without addition of TFA) gives a strong emission band at 396 nm. Furthermore, when the same experiment was carried out in a homogeneous solution of **2**, the fluorescence decrease in the 390 nm band (assignable to emission from neutral **2***) is synchronized with the fluorescence increase in the 493 nm band (assignable to emission from (**2**·H^+)*). Hence, the rapid decrease in the 396 nm band in the gel phase (Fig. 7a) is rationalized in terms of energy transfer. In fact, the fluorescence spectrum of **1** and the excitation spectrum of **1**·H^+ overlap in the ~350–400 nm region (Fig. S1†), which should facilitate energy transfer from **1*** to **1**·H^+. Secondly, the gel growth process of the **1** + 1-propanol + TFA system was monitored by a fluorescence spectroscopic method (Fig. 8). The mixture was first heated to 100 °C to obtain the sol phase, and then the cuvette containing this solution was left in a thermostatic (25 °C) cell holder. The fluorescence spectra were measured as a function of the medium temperature. It is seen from Fig. 8 that the fluorescence intensity at 530 nm increases with the decrease in the medium temperature. Interestingly, once gelation occurs at around 400 s, the fluorescence intensity from (**1**·H^+)* rapidly increases and that from **1*** decreases. Although the rigidification effect which frequently enhances the fluorescence intensity cannot be ruled out in this experiment, the finding can be raised as supporting evidence for energy transfer in the gel phase. As a summary of the foregoing findings, one may conclude that the energy transfer from neutral **1*** to **1**·H^+ can take place particularly in the gel phase and the fluorescence emission from (**1**·H^+)* is intensified.

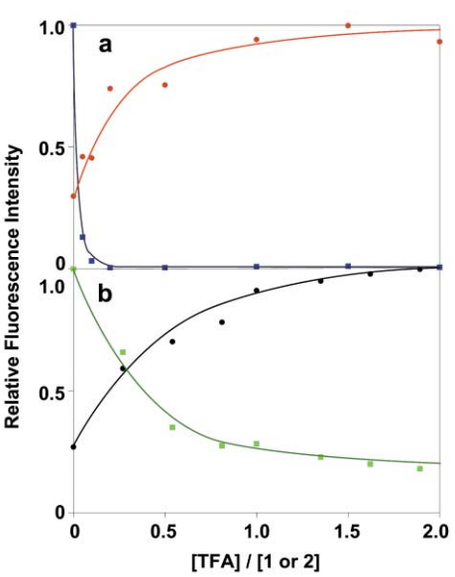


Fig. 7 Plots of the fluorescence intensities for (a) **1** (at 396 nm) (blue) and (**1**·H^+) (at 530 nm) (red) in the gel phase and (b) **2** (390 nm) (green) and (**2**·H^+) (at 493 nm) (black).

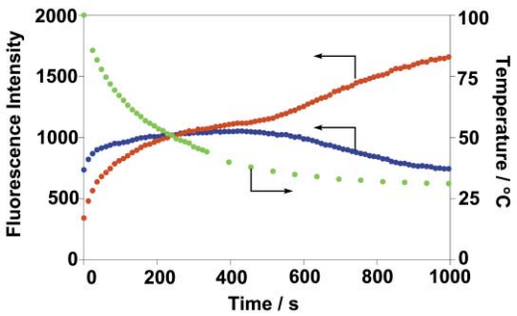


Fig. 8 Time dependence of the fluorescence intensity at 409 nm (blue), at 530 nm (red) and medium temperature (green).

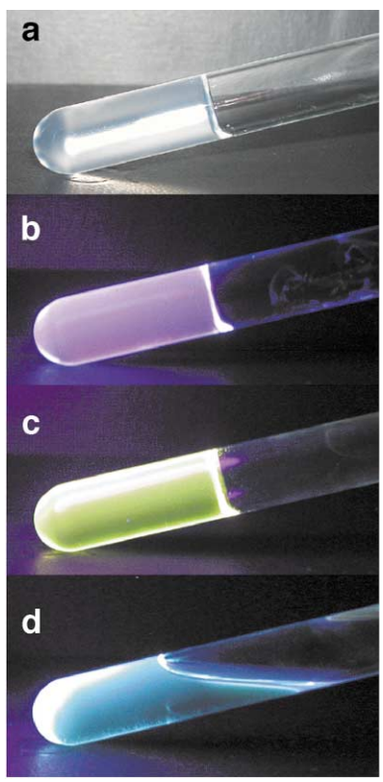


Fig. 9 Pictures of (a) **1**+1-propanol gel, (b) **1**+1-propanol gel under UV light (365 nm), (c) **1**+1-propanol gel in the presence of 2.0 equivalents of TFA and (d) the (c) gel was heated at 90 °C.

The colour pictures taken at each treatment step are shown in Fig. 9. It is visually seen in Fig. 9 that the colourless **1** + 1-propanol gel (Fig. 9a) shows a purple colour under UV light irradiation (Fig. 9b). Addition of TFA changes its fluorescence colour to greenish yellow (Fig. 9c). When this **1** + 1-propanol + TFA gel was converted to the sol phase by heating, the colour was changed to light blue. One may propose, therefore, that the present organogel is sensitive to proton and temperature.

Conclusion

The present study showed the gelation properties as well as the spectroscopic properties of 1,10-phenanthroline-appended cholesterol-based gelator **1**. The first harvest obtained from this study is the finding that **1** acts as a relatively versatile gelator of organic solvents. The more important second harvest is the unexpected finding that the gel which is constructed from densely π–π-stacked 1,10-phenanthroline groups is useful for designing a proton-sensitive gel system and energy transfer system. We consider that these characteristics are due to the crystal-like nature of the gel system.[6,8,10,12] We believe that the present findings will lead to the exploitation of new functions inherent to the organogel system.

Experimental

Equipment

^{1}H NMR spectra were measured on a Bruker DMX 600 spectrometer. *J* values are given in Hz. IR spectra were obtained using a Shimadzu FT-IR 8700 spectrometer. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer. UV/VIS and fluorescence spectra were measured on a Shimadzu UV-2500PC spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively.

TEM measurements

For transmission electron microscopy (TEM) a piece of the gel was placed on a carbon-coated copper grid and removed after 1 min, leaving some small patches of the gel on the grid. After specimens had been dried at low pressure, they were stained with one drop of phosphotungstic acid aqueous solution (2.0 wt%). They were then dried for 1 h at low pressure. The specimens were examined with a Hitachi H-600 transmission electron microscope.

Materials

2,9-Bis(*p*-methylaminomethylphenyl)-1,10-phenanthroline was prepared according to the literature reported previously and identified by IR and ^{1}H NMR spectral evidence and elemental analysis.[26]

Synthesis of compound 1

To a CH_2Cl_2 solution (30 ml) of 2,9-bis(*p*-methylaminomethylphenyl)-1,10-phenanthroline (0.56 g, 1.34 mmol) and triethylamine (10 ml) was added portionwise cholesteryl chloroformate (1.8 g, 4.0 mmol) for 30 min at 0 °C under a nitrogen atmosphere. The solution was stirred at room temperature for 15 h. The reaction mixture was washed with aqueous 5% $NaHCO_3$ solution and then dried over $MgSO_4$. The solution was concentrated to dryness, the solid residue being further purified through chromatography [silica gel, CH_2Cl_2–MeOH = 50 : 1 (v/v)] to give **1** (1.36 g, 82%); mp 73.5–75.0 °C; δ_H (600 MHz; $CDCl_3$; Me_4Si) 0.67–2.44 (m, cholesteryl, 86H), 2.87, 2.95 (s, NCH_3, 6H), 4.58 (s, OC*H*, 2H, benzyl CH_2, 4H), 5.40 (s, C*H*, 2H), 7.44, 7.49 (br, PhCH_2, 4H), 7.80 (s, Ph-*H*, 2H), 8.14 (d, Ph-*H*, *J* = 8.3, 2H), 8.32 (d, Ph-*H*, *J* = 8.3, 2H), 8.42 (br, Ph-*H*, 4H); IR: ν_{max}/cm^{-1} 1701 (CO); MS [dithranol] *m*/*z*: 1244.4 [*M* + H]$^+$; Anal. Calcd for $C_{84}H_{114}N_4O_4$·1.5 H_2O: C, 79.67; H, 9.27; N, 4.42. Found C, 79.52; H, 9.06; N, 4.50%.

Synthesis of compound 2

Compound **2** was obtained as colourless oil by the method similar to the synthesis of compound **1** from 2,9-bis(*p*-methylaminomethylphenyl)-1,10-phenanthroline and chloroformic acid 2-ethylhexyl ester; δ_H (600 MHz; $CDCl_3$; Me_4Si) 0.90–1.6 (m, 2-ethylhexyl, 28H), 1.61 (br, C*H*, 2H), 2.89–2.98 (s, NCH_3, 6H), 4.10 (d, OCH_2, *J* = 5.49, 4H), 4.60 (s, PhCH_2, 4H), 7.46 (m, Ph-*H*, 4H), 7.79 (s, Ph-*H*, 2H), 8.13 (d, Ph-*H*, *J* = 8.42, 2H), 8.31 (d, Ph-*H*, *J* = 8.43, 2H), 8.39 (d, Ph-*H*, *J* = 8.14, 4H); IR: ν_{max}/cm^{-1} 1701 (CO); MS [dithranol] *m*/*z*: 731.6 [*M* + H]$^+$; Anal. Calcd for $C_{46}H_{58}N_4O_4$·0.25 H_2O: C, 75.12; H, 8.02; N, 7.62. Found C, 75.03; H, 8.01; N, 7.45%.

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