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Sol-gel phase transition of brucine-appended porphyrin gelator: a study by vibrational circular dichroism spectroscopy

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Abstract—A novel approach to study the sol-gel phase transition of a brucine–porphyrin based gelator, which uses vibrational circular dichroism (VCD) spectroscopy, is described. The gelation process leading to highly ordered chiral supramolecular assemblies was investigated in various solvents at the different temperatures and concentrations. The VCD spectra sensitively reveal the specific parts of molecule whose configuration is influenced by a sol-gel phase transition and chiral supramolecular aggregation and therefore indicate the parts of the molecule responsible for the chiral self-assembly formation. Temperature stability of the organogel studied is discussed on the basis of the VCD and IR absorption spectra. The scanning electron microscopy was used to visualize the structure of brucine–porphyrin conjugate in the gel phase.

1. Introduction

Owing to numerous applications of sol-gel systems in different fields of chemistry, such as supramolecular chemistry, medicine, oil industry, cosmetics, etc., low molecular mass gelling agents (organogelators) capable of immobilizing a liquid continue to attract considerable attention.[1,2] The gelators are classified into two categories as the hydrogen bond-based and nonhydrogen-bond-based gelators[1] according to the difference in the force driving the molecular aggregation. The common property of most organogelators is their self-assembling into fiber-like structures through highly specific noncovalent interactions, such as hydrogen bonding, van der Waals forces, dipole–dipole interactions, and π-π stacking.

Characterization of the self-assemblies is a challenging problem for current supramolecular chemistry. The fibrous supramolecular structures have been investigated mainly by NMR,[3–5] infrared (IR),[3,4] Raman,[6] fluorescence spectroscopy,[7] scanning (SEM)[3,4] and transmission electron microscopy (TEM).[8] In addition, electronic circular dichroism (ECD)[9] spectroscopy has been utilized as a chiroptical technique to observe the molecular effects accompanying the sol-gel phase transition of the chiral gelators.[8,10]

To the best of our knowledge, herein we report the first use of another chiroptical method, vibrational circular dichroism (VCD)[11–14] spectroscopy, to study the sol-gel phase transition process. VCD is one of the few techniques that reliably reflects the detailed stereochemical information and structural features of chiral small[12,15–20] as well as large[11,13,21–23] molecules and their complexes.[24–27] It is a method that has been already applied to the absolute configuration, the enantiomeric purity determination and the solution conformation study of pharmaceuticals,[12] peptides, and proteins.[22] We have considered this technique as a beneficial tool for sol-gel study because functional groups involved in the chiral aggregation can be clearly followed and evaluated.

In this paper, the gelation abilities and sol-gel phase transition process of the tetrabrucine- and dibrucine–porphyrin conjugates (Fig. 1) were studied by the VCD spectroscopy in the various organic solvents. The temperature stability characterized by the gel-to-sol phase transition temperature T_{gel} at which the gel melts into the sol phase was followed by the VCD. Additionally, we want to explore the potentiality of the VCD spectroscopy to structural study of the supramolecular assemblies.

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2. Results and discussion

2.1. Brucine

Brucine is well soluble in CD_3OD, DMSO-d_6 and $CDCl_3$ and forms the transparent colorless solutions, even after sonication. Concentrations used for spectral measurement and gelation tests are summarized in Table 1. The VCD and IR absorption spectra of brucine are given in Fig. 2. Absorption bands between 1680–1640 cm^{-1} (Fig. 2B) were assigned to ν(C=O) vibration and bands at 1604, 1501, 1467, and 1453 cm^{-1} to the ν(C=C) vibrations. In addition, bands in the 1470–1300 cm^{-1} region involve also the $\delta(CH_3)$, $\delta(CH_2)$ and δ(CH) vibrations.

The maximum of the ν(C=O) absorption band in DMSO-d_6 and $CDCl_3$ is localized at 1659 and 1655 cm^{-1}, respectively. The ν(C=O) band is splitted into absorption maximum at 1646 cm^{-1} and the shoulder at 1672 cm^{-1} in CD_3OD. The frequency shift of the absorption maximum in the CD_3OD solution to values lower than observed in DMSO-d_6 and $CDCl_3$ is explained by the solvent effect accompanied by formation of C=O···D–O bond between the C=O group of brucine and CD_3OD. The same spectrum was obtained in CH_3OH (data not shown), so the deuteration effect does not change the positions and shape of the ν(C=O) bands.

Table 1. Molar concentration of the solutions used in the gelation test by brucine, **1**, **2** and **3**

Organic solvent (v/v)	Molar concentration (mmol L^{-1})			
	Brucine	**1**	**2**	**3**
$CDCl_3$	190, **S**	9, **I**	12, **I**	160, **S**
CD_3OD	190, **S**	9, **G**	22, **I**	160, **S**
CD_3OD/DMSO-d_6 = 4/1		10, **G**	10, **S**	
CD_3OD/DMSO-d_6 = 3/1		10, **S**	10, **S**	
CD_3OD/DMSO-d_6 = 2/1		10, **S**	10, **S**	
CD_3OD/DMSO-d_6 = 1/1		10, **S**	10, **S**	
CD_3OD/DMSO-d_6 = 1/4		10, **S**	10, **S**	
DMSO-d_6	160, **S**	19, **S**	54, **S**	160, **S**

G = gelation; **S** = solubilization; **I** = insolubilization.

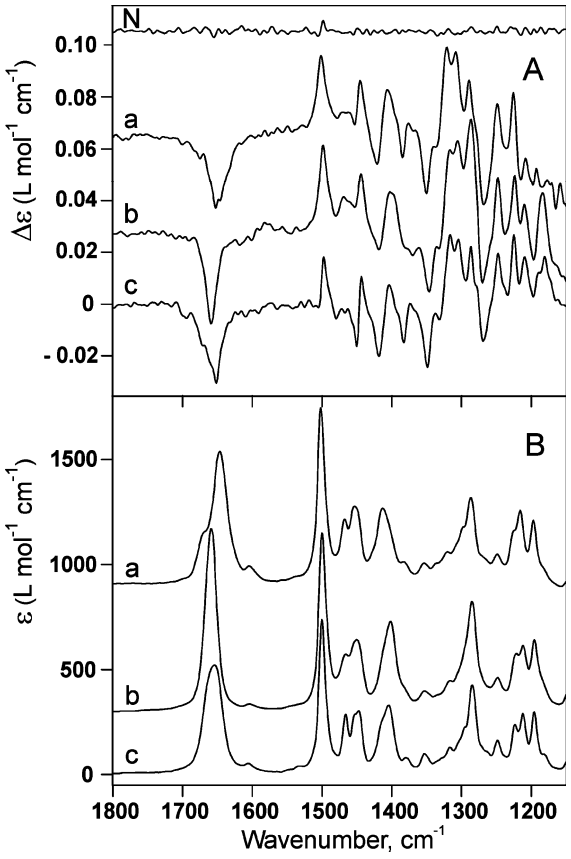

Figure 2. VCD (A) and IR absorption (B) spectra of brucine in CD_3OD (a), DMSO-d_6 (b), $CDCl_3$ (c) and typical noise spectrum (N) (for concentrations see Table 1).

The VCD spectra of brucine shown in Fig. 2A reveal the almost same shape, positions, and intensities of

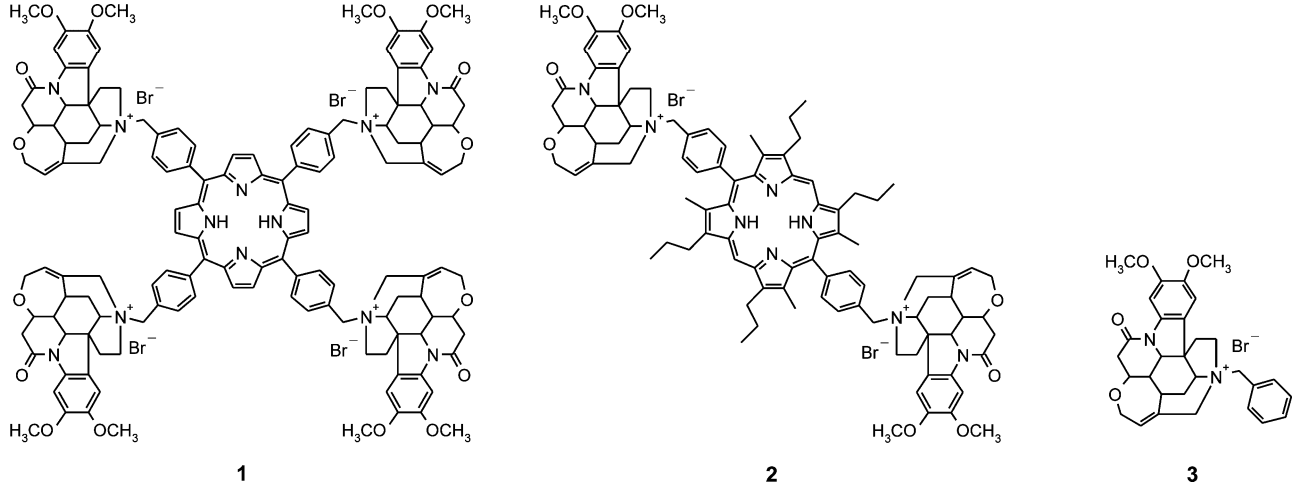

Figure 1. Molecular structures of conjugates studied.

VCD bands independently on the solvent used. The negative sign of the ν(C=O) VCD band was observed in all cases, although the spectral variations in this region were detected in absorption (Fig. 2B). Because VCD spectroscopy sensitively reflects the local arrangement of molecules in the solutions, it is obvious from the similarity in VCD features that the brucine molecule has the considerably rigid conformation in all the solvents used. This fact is in agreement with observation published in previous chiroptical study[28] of alkaloids showing that molecular framework of brucine is a rigid polycyclic structure. Thus, conformational freedom of the brucine is very restricted.

2.2. Porphyrin-based gelators

The conjugates **1** and **2** were tested for the gelation capability of the some organic solvents (for concentrations see Table 1). Conjugate **1** is more soluble in CD_3OD and DMSO-d_6 than **2** and in contrast to **2**, **1** forms under specific conditions a very robust dark red–brown transparent organogel. CD_3OD and CD_3OD/DMSO-d_6 mixed solvents (volume ratio from 1/1 to 15/1) were used for the gelation test of **2**, but no gelation was observed for all studied ratios after sonication. Therefore, attention will be focused on **1** in the following text.

2.2.1. Conjugate 1. Conjugate **1** forms a dark red–brown solution in DMSO-d_6, whereas the homogenous organogel of the same color is produced after sonication of **1** in CD_3OD at concentration of the gelator 2.4 wt%, that is 9.0 mmol L^{-1}. This means that one molecule of **1** entraps about 3000 molecules of CD_3OD and, therefore, **1** has been shown to be excellent gelator of this solvent. The gel prepared in this way in CD_3OD in a 1 cm diameter test-tube can be turned upside down without any flow. The DMSO-d_6 and CD_3OD/DMSO-d_6 mixed solvents (volume ratio of 1/4, 1/3, 1/2, 1/1, 2/1, 3/1 and 4/1) were also investigated for the gelation. The formation of organogel was observed for ratio of CD_3OD/DMSO-$d_6 \geq 4/1$ (v/v).

The VCD and IR absorption spectra of **1** in the ν(C=O) region are given in Fig. 3. The maximum of the C=O absorption band in CD_3OD, mixtures CD_3OD/DMSO-d_6, and DMSO-d_6 (Fig. 3B) has almost the same position contrary to the brucine solutions where solvent effect of CD_3OD is evident from the shift of ν(C=O) to lower frequency (cf. Fig. 2B). This implies that the C=O groups of the gelator in gel phase are not markedly solvated by the solvent molecules, therefore, the C=O group is situated inside the cluster and solvent does not significantly affect neighborhood of this group for all volume ratios studied.

The changes of molecular chirality of **1** induced by the sol-gel phase transition are observable via the VCD spectra (Fig. 3A). It is obvious that the sign of the VCD band in the ν(C=O) region is inverted to positive after the gel formation is accomplished: Conjugate **1** in the DMSO-d_6 provides the characteristic negative VCD signal in ν(C=O) region similar to that observed for pure brucine (Fig. 2A). In the mixed solution up to the ratio CD_3OD/DMSO-d_6<4/1 where the gel phase was not achieved, the negative VCD band of lower intensity in comparison to the pure DMSO-d_6 solution was observed in the ν(C=O) region (Fig. 3A, spectra c and d). For the CD_3OD/DMSO-d_6=4/1 ratio, the gel is formed and the positive signal is observed in the VCD (Fig. 3A, spectrum b). The gel formed in pure CD_3OD showed the positive VCD band of higher intensity (Fig. 3A, spectrum a) and the gel is proved to be more viscous than the one prepared in CD_3OD/DMSO-d_6=4/1.

In the ν(C=O) region, the sign of the VCD band of **1** in DMSO-d_6 is the same as observed for pure brucine. This observation is in the agreement with the fact that in DMSO-d_6, the intermolecular hydrogen bonding is highly unlikely owing to the strongly hydrogen-bond accepting character of DMSO-d_6, which causes the disruption of inter- and intramolecular solute hydrogen bonds and no aggregation of **1** takes place. The positive VCD signal (Fig. 3A, spectra a and b) observed in the gel phase indicate the coupling in the C=O stretching modes,[29] and, therefore, the formation of the highly ordered chiral assemblies.

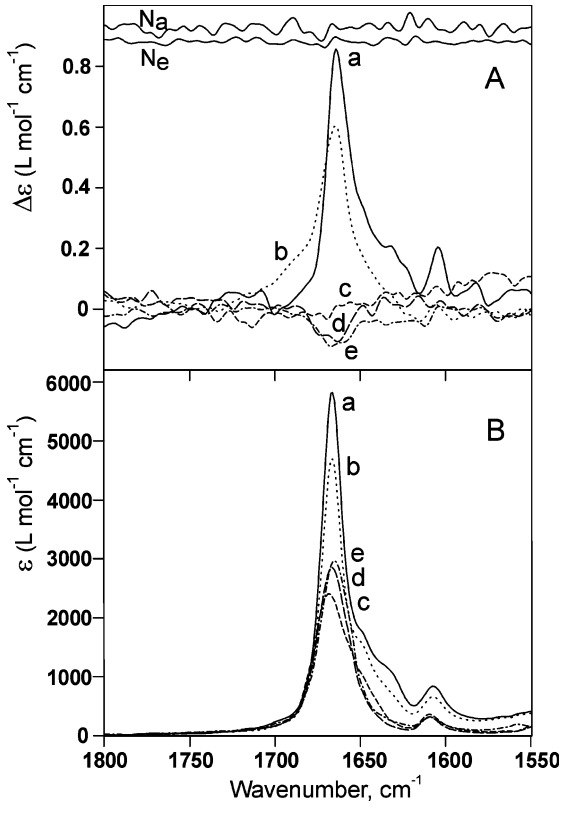

Figure 3. VCD (A) and IR absorption (B) spectra of **1** in CD_3OD (a), DMSO-d_6 (e), and in the CD_3OD/DMSO-d_6 mixture solvent (v/v): 4/1 (b), 1/1 (c), 1/4 (d), noise spectrum for spectrum a (N_a), noise spectrum for spectrum e (N_e).

2.2.2. SEM picture of the xerogel of 1. In order to obtain a visual insight into the aggregation mode, we have prepared a dry sample of organogel from a CD_3OD gel of **1** by the method published.[10] The SEM picture (Fig. 4) showed a supramolecular network consisting of puckered fibrils with 200–250 nm diameter. It can be seen that **1** gives the regular right-handed helical structure at several positions as the arrows indicate. Comparing the fiber diameter with the size of **1** (molecular modeling indicates the size of the monomer approximately 3.7 nm), one may consider that the bundles observed are composed of about 60 incipient, one-dimensionally stacked porphyrin columns. The observation of helical structure by SEM is in accord with the strong VCD intensity of **1** observed in the gel phase (Fig. 3). The structure is disrupted after the phase transition to sol, which is accompanied by observation of the negative VCD signal in the C=O stretching mode.

In order to answer the question whether the porphyrin moieties of the studied conjugates play important role in the gel formation, we also carried out a control experiment with conjugate **3**, in which the porphyrin was replaced by benzyl (Fig. 1). This conjugate provides colorless solution and does not form gel at the same conditions for which the gel was formed by **1**. For **3**, the negative VCD band as in the case of pure brucine was observed (data not shown). Therefore, it follows from our experiments that the presence of the porphyrin skeleton is crucial for the organogel formation. The π-π stacking force among porphyrin moieties seems to be responsible for chiral superstructure formation and indispensable for the organogel formation of **1**. This interpretation is in accord with results on similar porphyrin-based gelators published recently.[30,31] We thus consider that porphyrin moieties primarily constitute the column observed by SEM (Fig. 4). The brucine molecules surrounded this central helically twisted column. As a consequence of the chirality of the peripheral brucine moieties the VCD is observed in both phases, positive in the gel and negative in the sol. In addition, we also found that not only the presence of porphyrin moiety but also the number of brucine units on the periphery of porphyrin as well as geometry of the molecule has a crucial influence on the gelation abilities. This fact can be clearly deduced from the different behavior of the conjugate **1** and **2** under the same experimental conditions under which **2** does not form the organogel and the positive VCD was not observed in the ν(C=O) region although **2** also involves the porphyrin part as conjugate **1**.

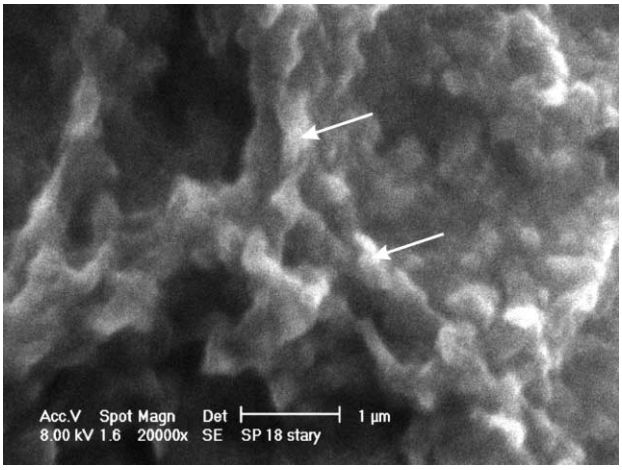

Figure 4. Scanning electron micrograph of a dried gel from a **1** in CD_3OD ($c=9.0$ mmol L^{-1}).

2.2.3. Temperature stability of the organogel 1. The gel-to-sol transition process of **1** is temperature dependent. Therefore, the temperature stability of the organogel was also studied by VCD and IR spectroscopy. The mixed solvent of CD_3OD/DMSO-d_6 = 4/1 was used because pure CD_3OD has a low boiling point (65.4°C) insufficient for this experiment. The VCD patterns obtained for the different temperature are given in Fig. 5. It can be seen that the VCD spectra sensitively reflect the temperature changes. The positive VCD intensity is unchanged in the temperature region of 20–40°C, gradually decreased at 50–60°C, and the sign of VCD signal is even changed to a negative value at 70°C. The dissymmetry factor $\Delta\varepsilon/\varepsilon$ of the ν(C=O) VCD band was calculated from VCD and IR absorption intensities (Fig. 5) and is plotted vs. temperature for two concentrations in Fig. 6. While the $\Delta\varepsilon/\varepsilon$ is

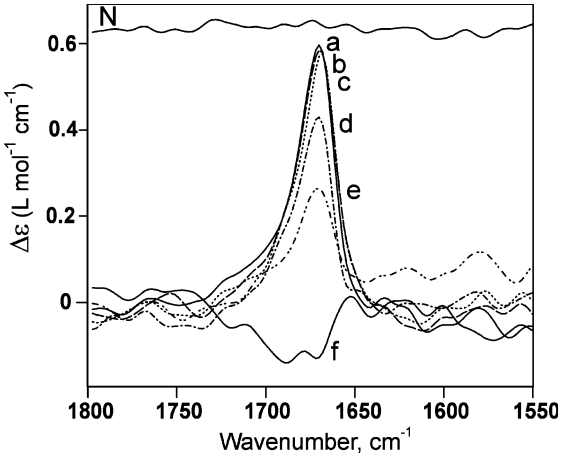

Figure 5. VCD spectra of the gel of **1** ($c=6.0$ mmol L^{-1}) in CD_3OD/DMSO-d_6 = 4/1 (v/v): 20°C (a), 30°C (b), 40°C (c), 50°C (d), 60°C (e), 70°C (f), typical noise spectrum (N).

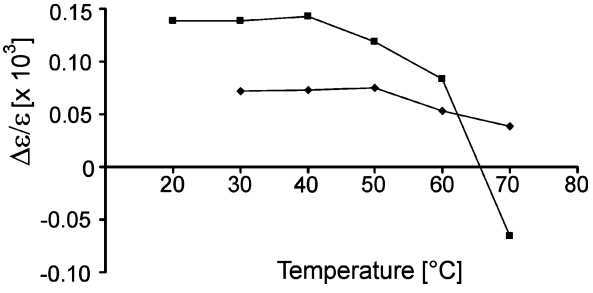

Figure 6. The dissymmetry factor of the ν(C=O) band versus temperature of the gel of **1** in CD_3OD/DMSO-d_6 = 4/1 (v/v). ($c=6.0$ [■] and 10 [◆] mmol L^{-1}).

almost same for temperature in the region 20–50°C and decreased to about 50% of original $\Delta\varepsilon/\varepsilon$ with further increase of temperature to 70°C for $c=10$ mmol L^{-1}, in the case of concentration $c=6.0$ mmol L^{-1} the start of the $\Delta\varepsilon/\varepsilon$ decrease is shifted to lower temperature of about 10°C. The gradual decrease of $\Delta\varepsilon/\varepsilon$ to the negative value is ascribed to structural changes of the gel arrangement in first step, and than to a phase transition to sol at the higher temperature. The negative value of $\Delta\varepsilon/\varepsilon$ indicates the existence of the sol phase. These findings lead to the conclusion that the molecular arrangement of the organogel is already changed at temperatures above 50 and 40°C for concentrations of 10 and 6.0 mmol L^{-1}, respectively. Additional increase of temperature causes the subsequent gel conversion to the isotropic sol phase. For comparison, the test-tube-tilting method, the most common technique,[10] was used to determination of T_{gel} in the same region of concentrations as was used for VCD measurements. It can be seen from Fig. 7 that the T_{gel} values strongly decrease with decreasing concentration of **1**. The gel concentrations 6.0 and 10 mmol L^{-1}, which are consistent with the VCD experiment in CD_3OD/DMSO-d_6=4/1 give T_{gel} at 53 and 74°C, respectively. The lower values of T_{gel} obtained by the test-tube-tilting method than obtained by VCD spectra are probably due to distinct capillary forces in the cell and test-tube. Nevertheless, it can be deduced that VCD represents the powerful technique for the sol-gel studies because sensitively reflects the structural changes of the organogel even at temperature lower than T_{gel}. In addition, the T_{gel} can also be estimate by the VCD. On the contrary, the test-tube-tilting method detects only the T_{gel} without any structural features.

3. Conclusion

We have reported here the novel approach of VCD spectroscopy for the monitoring of sol-gel transition process of chiral compounds, where the other spectral methods can only be used to a limited extent. The results presented demonstrate the potential of the VCD spectroscopy for study of sol-gel transition, open the possibilities for the more extensive sol-gel VCD studies and extend the applicability of the VCD spectroscopy to new areas. The VCD spectra showed remarkable sensitivity to the gel formation and provide valuable information on the involvement of specific parts of molecules in the formation of chiral self-assemblies and sensitively reveal the parts of molecules whose optical activity is influenced by an organogel formation. Thus, proven sensitivity of the VCD spectra to sol-gel phase transition can be conveniently employed in monitoring of such chiral systems.

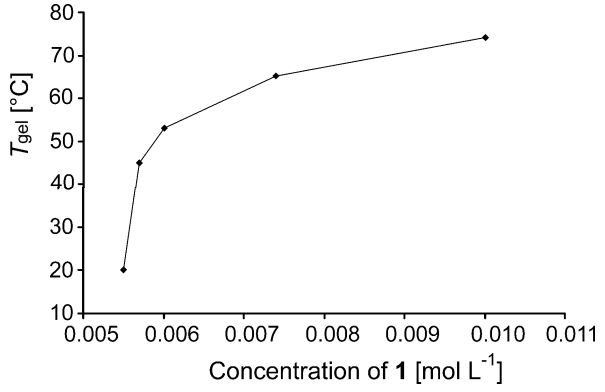

Figure 7. Melting points of a CD_3OD/DMSO-d_6=4/1 (v/v) gel of **1** versus concentration as determined by the test-tube-tilting method.

4. Experimental

The tetrabrucine–porphyrin **1**, dibrucine–porphyrin **2**, and benzyl-brucine **3** conjugates (see Fig. 1) were synthesized[32] at the Institute of Chemical Technology, Prague. Brucine was purchased from Lachema Chemical Company (Czech Republic). Methanol-d_4 (CD_3OD, 99.8% D, Isosar), dimethylsulfoxide-d_6 (DMSO-d_6, 99.8% D, Chemotrade), and deuterochloroform ($CDCl_3$, 99% D, Uvasol, Merck) were used as solvents.

4.1. Gelation test of various solvents

Most of the organogels known have been prepared by heating of the gelator with the solvent until the solid dissolved and then the solution obtained has been cooled. Our samples were prepared by new way, without the heat treatment step. The brucine and its conjugates (**1**, **2** and **3**) were mixed with CD_3OD, DMSO-d_6, $CDCl_3$, and the CD_3OD/DMSO-d_6 solvent of various volume (v/v) ratios to achieve the concentration desired for the VCD measurements given in Table 1. The mixtures were shaken and than sonicated at the ambient temperature. The stable gel formation was classified as 'G' in Table 1. The cases when the solvent was not gelatinized were signed as 'S' and insolubilization of the gelator in molar concentration given in Table 1 was signed as 'I'. The formation of the transparent gel of dark red–brown color was observed only for conjugate **1** after sonication in CD_3OD and CD_3OD/DMSO-$d_6\geq$ 4/1 (v/v) mixtures, whereas in all the other cases, just the sol phase was prepared or the conjugates were insoluble.

4.2. Apparatus

VCD spectra were recorded using a Fourier transform infrared spectrometer IFS-66/S equipped with the VCD/IRRAS module PMA 37 (Bruker, Germany) by procedure, which was described elsewhere.[33] The BaF_2 polarizer, ZnSe photoelastic modulator (Hinds Instruments) and MCT detector (InfraRed Associates) were used. VCD spectra were obtained as an average of 3 block of 3380 scans and measured with spectral resolution of 4 cm^{-1} and the zero filling factor of 4. The vibrational spectra presented were expressed in molar absorptivity ε (L mol^{-1} cm^{-1}). The quality of our VCD measurements is demonstrated by typical noise spectra, which were calculated as a half of difference of two following blocks of scans.

The sol phase samples were measured in a demountable cell A145 (Bruker, Germany) constructed of CaF_2 windows separated by a 50 μm Teflon spacer. The organogels were placed on the CaF_2 window before the cell was assembled and covered by second window separated by a 50 μm spacer. The homogeneity of the samples was proved by similar VCD spectra obtained for the various positions of the cell. Temperature dependent spectra of the organogel were measured for concentration of 6.0 and 10 mmol L^{-1} in CD_3OD/DMSO-d_6=4/1 (v/v) in demountable electric heated cell P/N20500 (Specac, UK) constructed of CaF_2 windows separated also by a 50 μm Teflon spacer. The heated jacket controller 3000 Series (Specac, UK) adjusted the temperature.

A Philips XL30CP Scanning Electron Microscope was used for taking the SEM picture. The gel was firstly cooled in liquid nitrogen and then the solvent was evaporated by a vacuum pump. The dry sample thus obtained was shielded by gold. The accelerating voltage was 8 kV.

The thermostat Lauda RC6CP Edition 2000 (Germany) with thermostatted water-bath was used to determination of T_{gel} by test-tube-tilting method.[10,34] A test-tube containing the gel was immersed upside down in a thermostatted water bath. The temperature was raised at the rate of 0.5°C min^{-1}. The T_{gel} was measured as a function of the gelator concentration.

Acknowledgements

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