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Preparation and photophysical properties of benzimidazole-based gels

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Abstract

Two kinds of benzimidazole-based compounds, pyridinium salts (**1a**–**3b**) and amides (**4a**, **4b**), which consist of long alkyl chains and benzimidazole moiety, were designed as blue colour fluorescent gelators. The pyridinium salts **1a**–**3b** were synthesized using the simple and economical microwave-assisted method. The gelation ability of **1a**–**2b** in a variety of organic solvents was higher than that of **3a**–**4b**. The SEM of the gels showed fibrous, spherical and filmlike morphologies depending on the gelators and the solvents. Red shift of fluorescence spectra and blue shift of absorption spectra from solution to gel state was observed in the organic solvent tested. The fluorescence intensity of the gel and the solution state increased with the increase of the solvent polarity. The fluorescence quantum yields of the gels were found to be considerably lower by one or two orders of magnitude than those of the solutions.

Keywords: Benzimidazoles; Gels; Fluorescence; Microstructures

1. Introduction

Within a very short period organogels have developed from a chemical and physical curiosity to a highly promising new area of research [1–3]. Their well-defined structure, the coexistence of highly ordered fibers with a liquid phase, the large interfacial area, and the possibility to entrain solutes within the network pores make organogels very attractive materials. Many organogels have been used for sensors, molecular recognition as well as in industrial fields such as cosmetics, health care and textiles [4–8]. For these applications, the development of organogelators that can be cheaply, simply, and effectively synthesized is important. Most organogelators have been found by serendipity rather than design, and many aspects of gels induced by small organic molecules are still poorly understood. Organogelators containing chromophore group would show the characteristic absorption and fluorescence spectroscopic properties arising from their difference in the aggregation mode, the spectral variety would make it possible to utilize the organogels as potential candidates for memory systems, sensors, molecular imprinting, etc., however, such researches on the spectroscopic properties of organogels have been very limited [9–12].

In continuation of our studies on organogels [13], we designed the spectroscopically functionalized organogelators, pyridinium salts **1a**–**3b** and amides **4a**–**4b**, which consists of long alkyl chains and benzimidazole moiety (Scheme 1). The benzimidazole part can act as fluorescence chromophore. Salts with long alkyl chains usually have the trend to form gel [14,15]. We now describe the easy and effective synthesis of new organogelators and their organogelation properties. The new gelators can confine a variety of organic solvents under mild condition. We have demonstrated that the fluorescence properties of the gels depend on the solvents, which were entrained and immobilized inside the gels.

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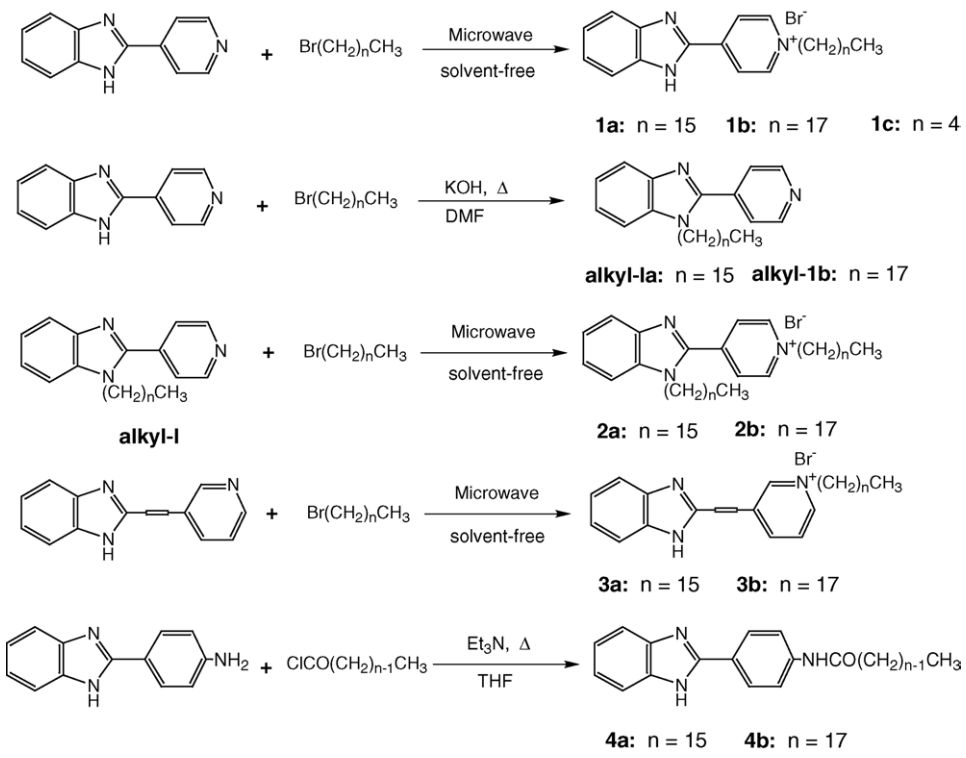

Scheme 1. Synthesis of compounds **1a**–**4b**.

2. Experimental details

2.1. General procedures

^{1}H NMR spectra were measured on a JEOL JNM-GSX270 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-300E spectrophotometer. Melting points were not corrected. Mass spectra were carried out with a Perkin-Elmer ELAN 600. The solvents for gelation experiments were of analytical grade. 2-(4′-Pyridyl)benzimidazole, 2-[2-(3-pyridyl)vinyl]-1*H*-benzimidazole and 4-(1*H*-benzimidazol-2-yl)aniline were prepared by a published procedure [16]. All the reagents were commercially available and were used without further purification.

2.2. Synthesis of the gelators

*Synthesis of 2-[4′-(N-hexadecylpyridinylium)]benzimidazole bromide (**1a**)*. 2-(4′-Pyridyl)benzimidazole (2 mmol), 1-bromohexadecane (5 mmol) were introduced in a breaker (50 ml) and completely mixed using ultrasonic bath. The so-obtained mixture was irradiated intermittently (2 min irradiation with 30 s mixing) in a household MW oven at 200 W for 10 min. After irradiation, the mixture was cooled, washed with ether (3 ml × 5 ml), dried and purified by column chromatography (silica gel, $CH_3COOC_2H_5$/CH_3OH 10:1). Gelator **1a** was obtained as pale yellow solid in 96% yield; mp 75–77 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.10 (d, 2H, J = 7.1 Hz), 8.66 (d, 2H, J = 7.0 Hz), 7.75 (m, 2H), 7.41 (m, 2H), 4.65 (t, 2H, J = 7.7 Hz), 2.05 (m, 2H), 1.28 (m, 26H), 0.89 (t, 3H, J = 6.6 Hz); IR (KBr) 3394, 3065, 2922, 1561, 1467 cm^{-1}; MS (FAB), m/z 420 ([M − Br]$^+$, 100).

*Synthesis of 2-[4′-(N-octadecylpyridinylium)]benzimidazole bromide (**1b**)*. Compound **1b** was obtained in 94% yield from 2-(4′-pyridyl)benzimidazole and 1-bromooctadecane as a pale yellow solid after purification by column chromatography according to the same procedure as above. mp 76–78 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.09 (d, 2H, J = 7.1 Hz), 8.65 (d, 2H, J = 6.9 Hz), 7.75 (m, 2H), 7.41 (m, 2H), 4.64 (t, 2H, J = 7.3 Hz), 2.07 (m, 2H), 1.27 (m, 30H), 0.89 (t, 3H, J = 6.6 Hz); IR (KBr) 3386, 3073, 2902, 1581, 1465 cm^{-1}. MS (FAB), m/z 448 ([M − Br]$^+$, 100).

*Synthesis of 2-[4′-(N-pentylpyridinylium)]benzimidazole bromide (**1c**)*. Compound **1c** was obtained in 90% yield from 2-(4′-pyridyl)benzimidazole and 1-bromopentane as a pale yellow solid after purification by column chromatography according to the same procedure as above. mp 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ: 9.14 (d, 2H, J = 6.0 Hz), 8.90 (d, 2H, J = 6.4 Hz), 7.83 (m, 2H), 7.37 (m, 2H), 4.80 (t, 2H, J = 7.1 Hz), 2.04 (m, 2H), 1.39 (m, 4H), 0.90 (t, 3H, J = 6.7 Hz); IR (KBr) 3390, 3078, 2902, 1571, 1465 cm^{-1}. MS (FAB), m/z 266 ([M − Br]$^+$, 100).

*Synthesis of 1-hexadecyl-2-(4′-pyridyl)benzimidazole (alkyl-**Ia**)*. 2-(4′-Pyridyl)benzimidazole (4 mmol), 1-bromohexadecane (9 mmol) was dissolved in a mixture of 30 ml of DMF and 10 ml of THF. Solid KOH (100 mmol) was added and the reaction mixture stirred for 12 h at 100 °C.

The precipitate was filtered off, washed with THF. The organic layers were combined. After removal of the solvent, the mixture was dried and chromatographed over silica gel (eluted with ethyl acetate) to give the product (alkyl-**Ia**) in 87% yield as a colourless solid. mp 66–67 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 8.78 (d, 2H, J = 6.2 Hz), 7.81 (d, 2H, J = 6.2 Hz), 7.73 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 7.5 Hz), 7.42–7.34 (m, 2H), 4.40 (t, 2H, J = 7.3 Hz), 1.76 (m, 2H), 1.27 (m, 26H), 0.89 (t, 3H, J = 6.8 Hz); IR (KBr) 3404, 2919, 2852, 1604, 1466, 1413 cm^{-1}; MS (FAB), m/z 419 (M^+, 100).

*Synthesis of 1-octadecyl-2-(4′-pyridyl)benzimidazole (alkyl-**Ib**)*. Compound alkyl-**Ib** was obtained in 85% yield from 2-(4′-pyridyl)benzimidazole and 1-bromooctadecane as a colourless solid after purification by column chromatography according the same procedure as above. mp 71–72 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 8.78 (d, 2H, J = 6.2 Hz), 7.81 (d, 2H, J = 6.2 Hz), 7.73 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 7.5 Hz), 7.42–7.34 (m, 2H), 4.40 (t, 2H, J = 7.3 Hz), 1.76 (m, 2H), 1.27 (m, 30H), 0.89 (t, 3H, J = 6.8 Hz); IR (KBr) 3404, 2919, 2852, 1604, 1466, 1413 cm^{-1}; MS (FAB), m/z 447 (M^+, 100).

*Synthesis of 1-hexadecyl-2-[4′-(N-hexadecylpyridinylium)]benzimidazole bromide (**2a**)*. Compound **2a** was obtained in 82% yield from compound alkyl-**Ia** and 1-bromohexadecane as a pale yellow solid after purification by column chromatography according to the same procedure as **1a**. mp 62–64 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.18 (d, 2H, J = 6.9 Hz), 8.54 (d, 2H, J = 6.7 Hz), 7.81 (d, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 8.2 Hz), 7.52–7.39 (m, 2H), 4.72 (t, 2H, J = 7.5 Hz) 4.56 (t, 2H, J = 7.5 Hz), 2.10 (m, 2H), 1.85 (m, 2H), 1.27 (m, 52H), 0.89 (m, 6H); IR (KBr) 3441, 2920, 2850, 1641, 1465 cm^{-1}; MS (FAB), m/z 645 ([M − Br]$^+$, 100).

*Synthesis of 1-octadecyl-2-[4′-(N-octadecylpyridinylium)]benzimidazole bromide (**2b**)*. Compound **2b** was obtained in 78% yield from compound alkyl-**Ib** and 1-bromooctadecane as a pale yellow solid after purification by column chromatography according to the same procedure as **1a**. mp 62–64 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.17 (d, 2H, J = 6.9 Hz), 8.54 (d, 2H, J = 6.8 Hz), 7.81 (d, 1H, J = 7.8 Hz), 7.71 (d, 1H, J = 8.0 Hz), 7.52–7.39 (m, 2H), 4.71 (t, 2H, J = 7.5 Hz), 4.55 (t, 2H, J = 7.5 Hz), 2.09 (m, 2H), 1.85 (m, 2H), 1.27 (m, 60H), 0.90–0.86 (m, 6H); IR (KBr) 3411, 2927, 2847, 1634, 1465 cm^{-1}; MS (FAB), m/z 701 ([M − Br]$^+$, 100).

*Synthesis of 1-hexadecyl-3-[2-(1H-benzimidazol-2-yl) vinyl]pyridinium bromide (**3a**)*. Compound **3a** was obtained in 44% yield from compound 2-[2-(3-pyridyl)vinyl]-1*H*-benzimidazole and 1-bromohexadecane as a pale yellow solid after purification by column chromatography according to the same procedure as **1a**. mp 61–63 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.56 (s, 1H), 8.32 (d, 1H, J = 8.1 Hz), 8.09 (d, 1H, J = 6.0 Hz), 7.81 (d, 1H, J = 16.4 Hz), 7.71 (d, 1H, J = 16.5 Hz), 7.57–7.54 (m, 2H), 7.41 (t, 1H, J = 6.3 Hz), 7.19–7.16 (m, 2H), 4.61 (t, 2H, J = 7.2 Hz), 1.92 (m, 2H), 1.24 (m, 26H), 0.87 (t, 3H, J = 6.9 Hz); IR (KBr) 3424, 2927, 2852, 1626, 1465, 1428 cm^{-1}. MS (FAB), m/z 447 ([M − Br]$^+$, 100).

*Synthesis of 1-octadecyl-3-[2-(1H-benzimidazol-2-yl)-vinyl]pyridinium bromide (**3b**)*. Compound **3b** was obtained in 31% yield from compound 2-[2-(3-pyridyl)vinyl]-1*H*-benzimidazole and 1-bromooctadecane as a pale yellow solid after purification by column chromatography according to the same procedure as **1a**. mp 74–75 °C; ^{1}H NMR (300 MHz, CD_3OD), δ: 9.59 (s, 1H), 8.29 (d, 1H, J = 8.4 Hz), 7.96 (d, 1H, J = 6.0 Hz), 7.79 (d, 1H, J = 16.6 Hz), 7.71 (d, 1H, J = 16.5 Hz), 7.58–7.55 (m, 2H), 7.35 (t, 1H, J = 6.3 Hz), 7.20–7.17 (m, 2H), 4.61 (t, 2H, J = 7.2 Hz), 1.85 (m, 2H), 1.24 (m, 30H), 0.87 (t, 3H, J = 6.9 Hz); IR (KBr) 3399, 2918, 2851, 1739, 1646, 1469, 1428 cm^{-1}; MS (FAB), m/z 475 ([M − Br]$^+$, 100).

*Synthesis of 4-(1H-benzimidazol-2-yl)palmitanilide (**4a**)*. To a stirred solution of 4-(1*H*-benzimidazol-2-yl)aniline (3 mmol) and triethylamine (3 mmol) in 30 ml dry THF was added palmitoyl chloride (3 mmol) in 20 ml of dry THF at 0 °C over 10 min. The reaction mixture was stirred at room temperature for 25 h. The precipitate formed was collected on a filter rinsed with methanol, dried in vacuum to give **4a** (yield 37%). mp 233–235 °C; ^{1}H NMR (300 MHz, DMSO-d_6), δ: 10.09 (s, 1H), 8.09 (d, 2H, J = 8.7 Hz), 7.76 (d, 2H, J = 8.7 Hz), 7.55 (m, 2H), 7.18 (m, 2H), 2.34 (t, 2H, J = 7.2 Hz), 1.22 (m, 26H), 0.84 (t, 3H, J = 6.0 Hz); IR (KBr) 3326, 1669, 1601, 1535 cm^{-1}; MS (EI), m/z 447 (M^+).

*Synthesis of 4-(1H-benzimidazol-2-yl)stearanilide (**4b**)*. Compound **4b** was obtained in 56% yield from compound 4-(1*H*-benzimidazol-2-yl)aniline and stearoyl chloride according to the same procedure as **4a**. mp 239–241 °C; ^{1}H NMR (300 MHz, DMSO-d_6), δ: 12.75 (s, 1H), 10.08 (s, 1H), 8.08 (d, 2H, J = 8.7 Hz), 7.75 (d, 2H, J = 8.7 Hz), 7.55 (m, 2H), 7.16 (m, 2H), 2.32 (t, 2H, J = 7.2 Hz), 1.20 (m, 30H), 0.83 (t, 3H, J = 6.9 Hz); IR (KBr) 3264, 1669, 1604, 1543 cm^{-1}; MS (EI), m/z 475 (M^+).

2.3. Gelation test

A gelator (3.0 mg) and appropriate solvent (0.1 ml) were mixed in a closed-capped test tube and the mixture was heated until the solid was dissolved. The solution was subsequently cooled in air to room temperature. When the gelator formed a clear or slightly opaque gel by immobilizing the solvent at this stage, it was denoted by a “G” in Table 1.

2.4. Electron microscopy

A piece of a gel was placed on a scanning electron microscope (SEM) stub with a carbon tape, dried, coated with Au, and observed on the stage of JEOL JSM-5300 scanning electron microscope using a 15–20 kV accelerating voltage.

Table 1
Gelation test with various organic solvents[a]

Entry	Solvent	States[b]							
		1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
1	*n*-Hexane	I	I	I	G	I	I	I	I
2	Cyclohexane	I	I	G	G	G	G	I	P
3	Benzene	G	G	G	G	Gp	P	I	P
4	Toluene	G	G	G	G	Gp	P	Gp	P
5	Chlorobenzene	P	P	S	S	Gp	P	Gp	P
6	Cumene	G	G	S	G	Gp	P	P	P
7	Carbon tetrachloride	G	G	Gp	G	Gp	P	G	G
8	Dichloromethane	Gp	G	S	Gp	S	S	I	I
9	1,4-Dioxane	Gp	Gp	S	G	Gp	P	P	P
10	Ethyl ether	I	I	I	G	G	P	I	I
11	THF	S	S	S	G	P	P	P	P
12	Triethylamine	I	I	I	G	P	P	P	P
13	Acetonitrile	G	G	G	P	P	P	P	P
14	DMF	S	S	S	S	S	S	P	P
15	Cyclohexanone	P	P	S	S	Gp	P	P	P
16	Acetone	Gp	G	S	P	G	P	P	P
17	Ethyl acetate ($10\,g\,l^{-1}$)	G	G	G	P	P	P	P	P
18	Methanol	G	G	S	G	S	S	P	P
19	Ethanol	G	G	S	G	S	S	P	P
20	1-Propanol	G	Gp	S	S	S	S	P	P
21	2-Propanol	Gp	Gp	S	S	P	S	P	P
22	*n*-Hexyl alcohol	Gp	Gp	S	P	S	S	P	S
23	Benzyl alcohol	S	S	S	S	S	S	P	S
24	Ethylene glycol ($10\,g\,l^{-1}$)	G	G	G	G	S	P	Gp	G
25	Diethylene glycol ($10\,g\,l^{-1}$)	Gp	G	Gp	G	S	S	G	G
26	Glycerol ($10\,g\,l^{-1}$)	G	G	G	G	G	G	G	G

[a] Minimum gelator concentration (MGC) is $30\,g\,l^{-1}$ (gelator/organic solvent) at 25 °C unless specified otherwise.
[b] G: gel; Gp: partial gel; P: precipitation; S: solution; I: insoluble.

2.5. X-ray diffraction

For X-ray diffraction measurements, gel prepared in a vessel was dried and mounted on a glass plate. X-ray diffractograms (PXD) were taken on a Rigaku RINT2000 powder diffractometer using Cu $K\alpha_1/K\alpha_2$ radiation (1.54060 and 1.54439 Å).

2.6. Spectroscopic measurements

Absorption spectra were acquired using a Hitachi U-4000 spectrophotometer and emission spectra were obtained on a Hitachi F-4500 spectrofluorimeter. Absorption and fluorescence spectra of gels were measured with a sample gel sandwiched by two quartz plates, one of which had 1 mm concavity. Fluorescence quantum yields in gel and solution were estimated using anthracene in ethanol ($\Phi_{fl} = 0.27$) as a standard, employing the methodology of literature [17,18].

3. Results and discussion

3.1. Synthesis

A series of alkylpyridinylium benzimidazole derivatives **1** and several analogues were designed. In **2** alkyl chains replaced the 1-H of benzimidazole. In **3** alkylpyridinylium was connected to the benzimidazole through the C=C double bond at the position 3 of the pyridine ring. In **4** alkylpyridinylium was replaced by palmitanilide or stearanilide connected to the benzimidazole directly.

We have developed the simple and economical synthesis of alkylpyridinium compounds **1a**–**3b** that occurs fast under solvent-free conditions in a household microwave oven with high yields. The reaction via conventional heating method in refluxing solvents requires more than 16 h to afford reasonable yield and at the same time need a large excess of alkyl halides.

3.2. Gelation properties

Gelation properties of the compounds **1a**–**4b** were tested in a variety of solvents, and the results are collected in Table 1. Mono-alkyl derivatives **1a** and **1b** formed gels with not only low polar solvents (entries 3, 4, 6, 7) but also high polar solvents such as alcohols (entries 18–17, 24–26). Compound **1c** with a short alkyl group ($n = 4$) cannot gelate any solvent investigated in this study (the data were not shown in Table 1). Bis-alkyl derivative **2b** dissolved in all solvents investigated including hexane and cyclohexane upon heating. Moreover, upon cooling of hot solutions gels were formed with most solvents investigated (entries 1–4, 6, 7, 9–12, 18, 19 and 24–26).

Compound **2a** was less effective than **2b**. In this study, the compound **2b** showed the best gelation properties among all of the mono- and bis-alkyl derivatives.

Compounds **3a** and **3b** were much too soluble in alcohols to form gels (S: entries 18–25). Compound **3a** can form gels in cyclohexane, ethyl ether, acetone, glycerol (entries 2, 10, 16 and 26) and partial gels in carbon tetrachloride, 1,4-dioxane, cyclohexanone (Gp: entries 7, 9 and 15). Compound **3b** is almost insoluble in most other organic solvents at room temperature, but upon heating it gradually dissolves. Upon cooling to room temperature, **3b** precipitated from most solvents (P: entries 3–7, 9–13, 15–17 and 24), only formed gels with cyclohexane and glycerol (entries 2 and 26).

Amide gels were observed only in carbon tetrachloride, diethylene glycol and glycerol for the compound **4a**, while **4b** formed gel in ethylene glycol besides these solvents (entries 7 and 24–26). This indicates that the compounds **4a** and **4b** are also poor gelators like **3b** in the solvents investigated.

The gelation ability of the organogelators discussed in this paper significantly depends on the alkyl chains and the positively charged pyridinylium group. The π–π interactions between the adjacent heterocyclic moieties and the electrostatic interactions may be largely responsible for the gelling properties of the pyridinium **1**–**3**. Longer alkyl chains strengthen the gelation due to greater London dispersion forces. However, the structural difference in aromatic moieties of compounds **3** compared with **1** and **2** disturb significantly the π–π interactions between the adjacent aromatic moieties that contribute significantly to the assembly of the gel, leading to poorer gelation properties. The compounds **4** were also poor gelators in most of the solvents mentioned, because **4** which have amide group on the aromatic ring and lack of pyridinium moieties can undergo stronger hydrogen bonding than the other compounds and lead to precipitation rather than gel formation.

3.3. Morphology studies

To obtain a visual insight into the morphologies of the aggregation mode, the morphology of gels in various solvents was investigated by scanning electron microscopy (SEM). The gelators **1a**–**4b** in this investigation gave rise to gels of widely differing morphologies, from fibers, sheets to spherical structures.

Fig. 1 shows several examples of SEM photographs of gels formed by **1a**–**4b** in some solvents. Comparison between the morphology of mono-alkyl and corresponding bis-alkyl derivative revealed that **1b** and **2b** had very different appearances with the corresponding mono-alkyl derivative **1a** and **2a**. Ethyl acetate gel **1a** was able to aggregate into long, intertwining bundles of fibers, which were occasionally split up and fused, with other fiber bundles. The elongated shape of the fibers most likely results from a strongly anisotropic growth process, and indicates that the intermolecular interactions are highly directional [19]. Compound **2a** and **3a** also formed fiberlike structure in carbon tetrachloride and cyclohexane, respectively, but they had a little different appearance. Enormous very thin fibers could be distinguished on the micrographs. Morphologies of the glycerol gel **2b** and **4b** revealed globular structures with globules of 1–8 μm diameter. Ethanol gel of **1b**, cyclohexane gel of **3b** and carbon tetrachloride gel of **4a** revealed the filmlike lamellar structures; these filmlike lamellae observed in this stage are the genuine structures in swollen gels, and not collapsed network induced by drying processes.

The different morphologies should originate from differences in interfacial free energy or attachment energies in the various solvents. However the available data at present do not allow us to suggest a clear correlation between the aggregate morphology and solvent properties and how the units could possibly assemble to generate the macroscopic morphology structures seen in SEM.

3.4. X-ray diffraction

X-ray powder diffraction (XRD) has great potential for elucidating the molecular structure of organogels. The X-ray diffraction patterns of the xerogels **1b** prepared from ethanol showed a broad peak in the range $2\theta = 15–35^\circ$ ($d = 5.9–2.6$ Å) and two sharp peaks at 16.7° (5.30 Å), 23.0° (3.86 Å) (Fig. 2a). The broad diffraction peak suggests a lower molecular packing order arising as a consequence of the weaker intermolecular interactions in the gel state (Fig. 1b, SEM image of ethanol gel of **1b**). Crystal structures of related molecules can provide information about molecular order in the gelled state. The short chain derivative **1c** could not gel any solvents. Although our attempts at preparing single crystals of the short chain derivative **1c** suitable for X-ray analysis have been unsuccessful, we obtained the very fine crystals of **1c** from methanol solution. The XRD pattern of the crystalline powder of **1c** revealed a number of sharp peaks in the same range $2\theta = 15–35^\circ$ ($d = 5.9–2.6$ Å) (Fig. 2b), suggesting that the crystal of **1c** and the gel of **1b** maybe have common fundamental interactions at the molecular level.

3.5. Spectroscopic properties

Gel formation can be easily monitored by recording absorption and fluorescence spectra of the pyridylbenzimidazole chromophore, which displays changes along the sol–gel transition. The electronic absorption and fluorescence spectra of **1b** gel and solution are shown in Fig. 3. The gel phase of **1b** in glycerol exhibited a blue shift from 365 to 331 nm in the absorption spectrum compared with that in solution. The blue shift of the absorption maximum can be usually assigned to parallel interaction modes “H-aggregation” of the benzimidazole chromophores [20]. However, the broaden absorption band of **1b** in gel may be due to a coexistence of different aggregate type besides H-aggregation and a combination of factors that includes aggregate sizes, aggregation modes, and solubility. The molar extinction coefficient of

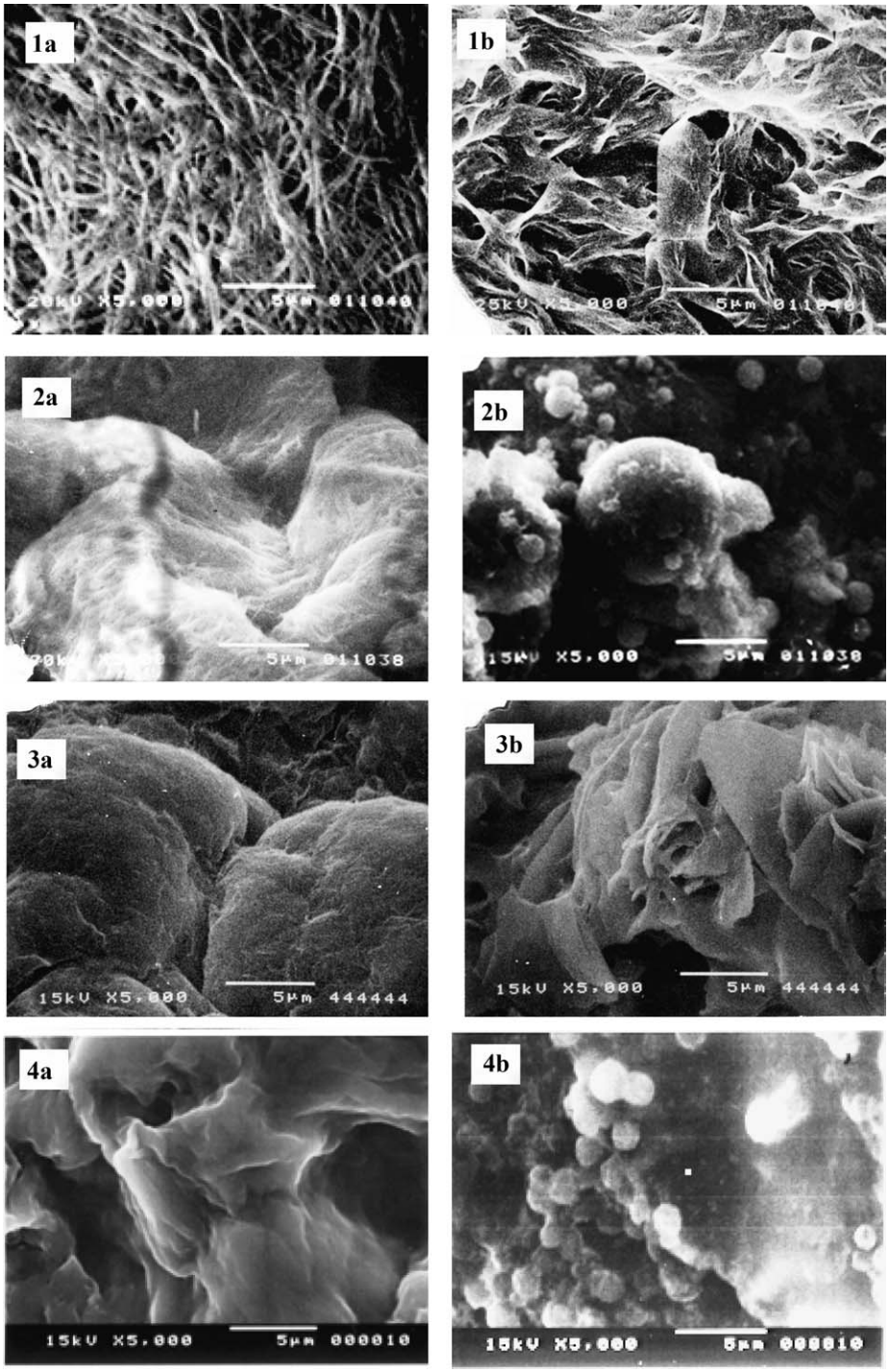

Fig. 1. SEM of the gels of (1a) ethyl acetate with **1a**; (1b) ethanol with **1b**; (2a) carbon tetrachloride with **2a**; (2b) glycerol with **2b**; (3a) cyclohexane with **3a**; (3b) cyclohexane with **3b**; (4a) carbon tetrachloride with **4a**; (4b) glycerol with **4b**.

1b gel in glycerol (ε, $9.1 \times 10\,M^{-1}\,cm^{-1}$) is much smaller than that in the solution phase (ε, $1.6 \times 10^4\,M^{-1}\,cm^{-1}$) (Table 2).

The fluorescence maximum of **1b** gel in glycerol was red shifted from 467 nm of the solution to 492 nm (Fig. 3). It also suggests that the lowest $\pi\pi^*$ level in the "H" aggregate is stabilized by the intermolecular π–π interaction of the benzimidazole chromophores at the molecular level [21]. The other pyridinium compounds **1a**–**3b** exhibited similar trends in all the tested gels and solutions on their absorption and fluorescence spectra; some of the results are summarized in Table 2. Similar blue shift of absorption and red shift of fluorescence of gel phase were also reported with other organogelators [22].

Table 2
Absorption and fluorescence properties of the gelators in the solutions and the gels[a]

Gelator	Solvent	Cyclohexane		CCl_4		Ethanol		Ethylene glycol		Diethylene glycol		Glycerol	
	State	S	G	S	G	S	G	S	G	S	G	S	G
1b	λ^{ab}_{max} (nm)			380	338	373	360	364	364	364	363	365	331
	ε (M^{-1} cm^{-1})			5.0×10^3	3.1×10	1.8×10^4	1.8×10^2	2.4×10^4	3.3×10^2	2.1×10^4	4.7×10^2	1.6×10^4	9.1×10
	λ^{fl}_{max} (nm)			451	468	468	493	472	504	471	507	467	492
	Φ_{fl}			1.6×10^{-3}		4.1×10^{-2}	7.8×10^{-3}	8.3×10^{-2}	2.0×10^{-2}	8.8×10^{-2}	1.7×10^{-2}	9.5×10^{-2}	6.0×10^{-3}
2b	λ^{ab}_{max} (nm)	331	322	364	331	359	353	351	351	353	352	349	364
	ε (M^{-1} cm^{-1})	4.7×10^3	2.3×10^2	1.3×10^4	7.6×10	1.3×10^4	1.7×10^2	8.5×10^3	1.9×10	8.8×10^3	4.6×10	2.7×10^4	9.1×10
	λ^{fl}_{max} (nm)	431	455	439	451	493	503	502	492	502	512	489	493
	Φ_{fl}	2.0×10^{-5}	2.8×10^{-5}	2.3×10^{-4}		2.4×10^{-2}		2.2×10^{-2}	2.6×10^{-3}	1.3×10^{-2}	6.7×10^{-4}	6.7×10^{-2}	5.0×10^{-4}
3b	λ^{ab}_{max} (nm)											355	327
	ε (M^{-1} cm^{-1})											1.1×10^4	2.7×10^2
	λ^{fl}_{max} (nm)											463	497
	Φ_{fl}											0.54	1.7×10^{-3}
4b	λ^{ab}_{max} (nm)			326	303			320	288	321	319		
	ε (M^{-1} cm^{-1})			6.5×10^3	1.3×10^2			2.3×10^4	6.1×10	2.2×10^4	6.2×10		
	λ^{fl}_{max} (nm)			414	432			376	390	361	364		
	Φ_{fl}			4.2×10^{-2}				0.87	5.7×10^{-3}	0.44	5.6×10^{-3}		

[a] λ^{fl}_{max} excited at λ^{ab}_{max}.

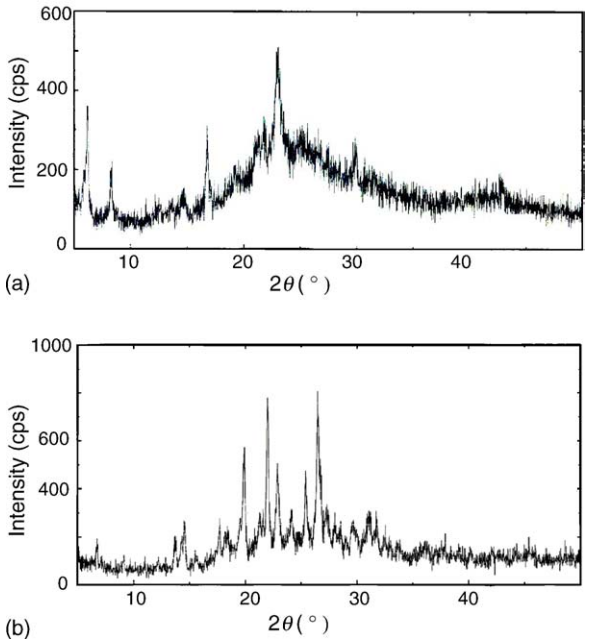

Fig. 2. X-ray diffractograms of (a) the xerogel of **1b** and (b) the crystalline powder of **1c**.

In the case of amide compounds **4a** and **4b**, the absorption and fluorescence spectra appeared at shorter wavelengths either in gel or solution phase than those of the pyridinium compounds **1a**–**3b**, due to the neutral molecules (Table 2). Fig. 4 shows the absorption and fluorescence spectra of **4b** gel and solution in ethylene glycol. The absorption blue shift from 320 to 288 nm and the fluorescence red shift from 376 to 390 nm of **4b** gel were observed in comparison to those in ethylene glycol solution. It also suggests the H-aggregation of the benzimidazole chromophores in the **4d** gel.

The absorption and fluorescence maximum of all the gels and solutions were affected by a change in the solvent, depending on the polarity and hydrogen bonding capacity of the solvents (Table 2). The magnitudes of molar extinction coefficient of the gels are smaller by about two orders than those in the solution phase. The fluorescence intensity in the gels and solutions increased with increase of the sol-

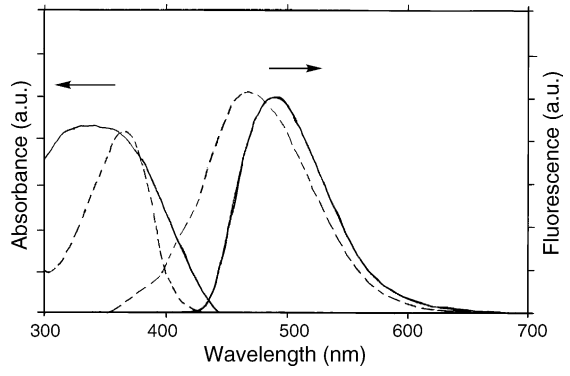

Fig. 3. Absorption and fluorescence spectra of **1b** in different states of glycerol: (—) gel; (- - -) solution.

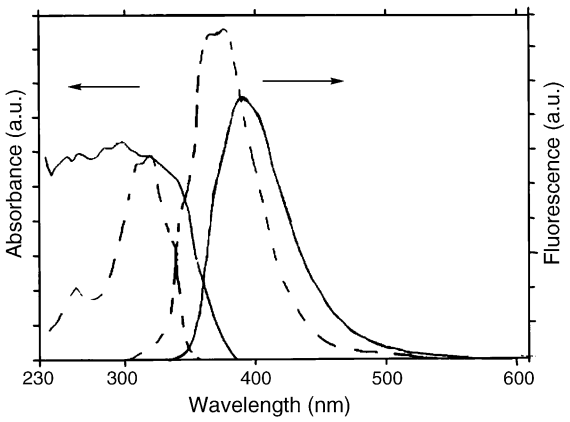

Fig. 4. Absorption and fluorescence spectra of **4b** in different states of ethylene glycol: (—) gel; (- - -) solution.

vent polarity, by a great deal in protic solvents like ethanol, ethylene glycol, diethylene glycol and glycerol. Fluorescence was very weak in non-polar solvents, almost not observed. The hydrogen bonding in the excited state maybe contribute to the stabilization of a much more planar geometry of these molecules and thus will decrease the non-radiative decay rate in solution.

Finally, we measured fluorescence quantum yield (Φ_{fl}) in the gel and solution phase (Table 2). Upon gelation, the fluorescence quantum yields became markedly lower by one or two orders of magnitude than those of solution. For instance, the Φ_{fl} values for **1b** solution and gel in glycerol were 0.095 and 0.006, respectively, and those for **4b** solution and gel in ethylene glycol 0.87 and 0.0057. Although the some inaccurate calculation that is caused by the measurement of absorption maximum of opaque gel cannot be ruled out in this experiment, the finding can be raised as supporting evidence for energy transfer in the gel phase. Internal conversion becomes important as a deactivation route when low concentration solution is changed to high concentration gel, showing that the interactions, most probably between the benzimidazole or pyridine group, act as a bridge for non-radiative deactivation. Namely, the interactions including self-quenching reduced the importance of fluorescence as a deactivation route. The intermolecular structural reorganization and the solvent–solute dipole–dipole reorientation usually play a major role on the photophysical parameters of these molecules.

4. Conclusion

We have designed and synthesized two kinds of benzimidazole-based compounds, pyridinium salts **1a**–**3b** and amide **4a**–**4b**, as fluorescent gelators using the simple and economical method. Various microstructures of the gels were formed in fibrous, spherical and filmlike morphologies depending on the structure of the gelators and the solvent. Red shift of fluorescence maxima and blue shift of absorption maxima from solution to gel state were found. The distinct spectroscopic changes accompanying gel formation offer an excellent tool to investigate the mechanism of gelation by spectroscopic methods. Further investigation in this area is a must to better understand the detailed structures and photophysical properties of the gels.

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