Enhanced photoluminescence and the self-assembled fibrillar nanostructure of 5-(cholesteryloxy)methyl-8-hydroxyquinoline lithium in a gel state

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Soluble 5-(cholesteryloxy)methyl-8-hydroxyquinoline lithium(I) (LiChQ) was synthesized through the modification of 8-hydroxyquinoline lithium (LiQ) with cholesterol, and showed about 3 times more enhanced luminescence than pristine LiQ. When increasing the concentration of LiChQ up to 1 wt% in non-protic solvents, nanoscale fibers of 30–100 nm diameter were formed through self-assembly in a super-gel state. There was a red shift in the absorption of the gel in comparison to the solution, which indicates that LiChQ tends to form a J-aggregate in the gel state. We also investigated the gelation process of LiChQ using the Lippert–Mataga equation. We suggest that LiChQ has potential applications in luminescent devices and/or as a template for nanostructured optoelectronic materials.

Introduction

Recently, organometallic nanostructures have been intensively investigated due to their diverse applications, including in optoelectronic devices and sensors.[1–8] These nanostructures are usually formed by the self-assembling of functional molecular materials *via* various non-covalent intermolecular interactions. The introduction of gelation ligands in metal complexes makes them easy to self-assemble into various shapes of nanostructure, each with unique optical and optoelectronic properties. These complexes and their resultant assembled nanostructures are of interest in the fields of optoelectronic devices and sensors.[9,10]

Shinkai and co-workers[9] have reported phosphorescent gelator 8-hydroxyquinoline heavy metal (*e.g.*, Pd, Pt) complexes by using 3,4,5-tris(alkoxy)phenyl substituents as gelation functional groups. Columnar stacking structures were formed by self-assembly *via* hydrogen bond-associated π–π stacking. The attractive phenomenon observed was the long-lived phosphorescence of triplet states, which was attributed to the inhibition by the gel state of oxygen quenching. However, the long-lived triplet states resulted in low efficiency luminescence that might not be suitable for luminescent devices. Metal complexes of 8-hydroxyquinoline are highly efficient fluorescent materials that are widely used in organic light-emitting devices (OLEDs).[11] We have previously used tri(8-hydroxyquinoline) aluminium(III) (Alq_3) and 8-hydroxyquinoline lithium(I) (LiQ) as highly efficient emitters and electron transporting materials.[12] However, their low solubility in organic solvents limits their applications in solution-based processes.

To further investigate the assembly mechanism of organometallic gelators and to integrate gelation with FL, we have changed the heavy metal ions to other ions (*e.g.*, Li(I)) in this contribution. In addition, a cholesterol group (widely used as a functional group to form gelators with nanowire structures), which possesses significant potential applications in the field of optoelectronic devices (*e.g.*, organic photovoltaic cells), was chosen to modify the insoluble LiQ. The resultant complex was more readily dissolved in common organic solvents than the pristine LiQ complex and showed significantly enhanced luminescence with increasing concentration in dilute solution. A typical nanofiber structure of 30–100 nm diameter was formed in the gel state as well. It is likely that this material has potential applications in luminescent devices and/or as a template for nanostructured optoelectronic materials.

Experimental section

General

8-Hydroxyquinoline, the 37% formaldehyde solution, cholesterol, sodium bicarbonate, aqueous ammonia and lithium hydroxide were all purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. and used as received. ^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) NMR spectrometer. Mass spectra were recorded on a Bruker Apex IV FTMS instrument. FT-IR spectra were acquired on a Nicolet Magna IR-750 spectrometer. UV-vis absorption and photoluminescence (PL) measurements were carried out by an Agilent 8453E UV-vis spectroscope system and a Hitachi F-2500 fluorescence spectrophotometer, respectively. The quantum yield of the fluorescence was measured in tetrahydrofuran (THF) and calculated using dye C152 in ethanol as the standard. The spectra of gel samples were measured

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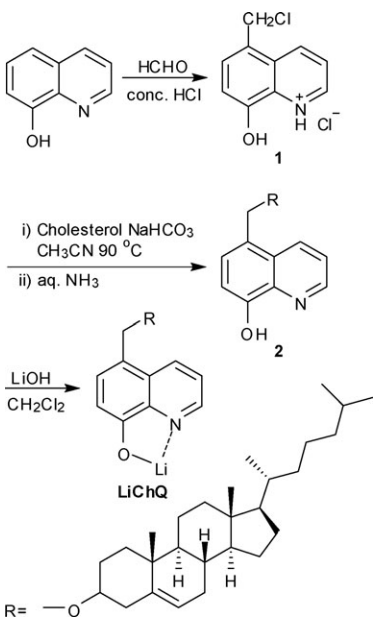
between two quartz plates. X-Ray diffraction (XRD) data was obtained using a Rigaku Dmax/2400 X-ray diffractometer on a xerogel of LiChQ in toluene. Transmission electron microscope (TEM) images were obtained from a sample of LiChQ neat gel placed on a carbon-coated copper grid (230 mesh), dried in a vacuum ($<10^{-2}$ Pa) overnight and then examined under a JECL CX200 transmission electron microscope at 160 kV.

Synthesis

The modification of insoluble LiQ by cholesterol to form LiChQ is shown in Scheme 1. To graft the cholesterol group onto 8-hydroxyquinoline, the chloromethylation of 8-hydroxyquinoline was carried out by reacting it with formaldehyde and concentrated hydrochloric acid to yield **1** as a hydrochloride salt. This was followed by reacting cholesterol with compound **1** to give modified ligand **2**, in which the cholesteryl group was connected to the C5-position of 8-hydroxyquinoline through a $–CH_2O–$ linkage. Finally, soluble LiChQ was obtained by the reaction of ligand **2** with lithium hydroxide.

Synthesis of 5-chloromethyl-8-hydroxyquinoline hydrochloride (1). Compound **1** was synthesized according to a literature procedure, as shown in Scheme 1.[13] A mixture of 8-hydroxyquinoline (7.30 g, 50 mmol), concentrated hydrochloric acid (60 mL) and 37% formaldehyde (8 mL, 50 mmol) was treated with HCl gas for 10 h. The yellow solid was collected by a filter, washed with acetone three times and then dried to give 10.00 g of **1** (yield 87%). ^{1}H NMR (D_2O, δ/ppm): 9.18 (d, J = 8.8 Hz, 1H), 8.94 (d, J = 5.2 Hz, 1H), 8.02 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H) and 5.00 (s, 2H).

Synthesis of 5-(cholesteryloxy)methyl-8-hydroxyquinoline (2). Compound **2** was synthesized using a modified version of a procedure already described in the literature.[14] To a suspension of compound **1** (2.00 g, 8.7 mmol) in acetonitrile were added cholesterol (4.04 g, 10.4 mmol) and sodium bicarbonate (0.73 g, 8.7 mmol). The mixture was stirred under reflux for 72 h. After cooling to room temperature, the yellow residue was filtered and then treated with dilute ammonia. The white solid that formed was dried and recrystallized twice from tetrahydrofuran–ethanol to yield 1.40 g of **2** as colorless crystals (yield 30%). ^{1}H NMR ($CDCl_3$, δ/ppm): 8.80 (d, J = 5.8 Hz, 1H), 8.51 (d, J = 10.0 Hz, 1H), 7.50 (m, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 5.34 (d, J = 5.3 Hz, 1H), 4.84 (s, 2H), 3.30 (m, 1H), 1.85–2.40 (m, 7H) and 0.67–1.53 (m, 36H).



Scheme 1 Synthetic route to LiChQ.

Synthesis of 5-(cholesteryloxy)methyl-8-hydroxyquinoline lithium(I) (LiChQ). Compound **2** (0.489 g, 0.9 mmol) and lithium hydroxide (0.038 g, 0.9 mmol) were added to 40 mL of dichloromethane in a single-necked flask. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the solvent was removed by rotary evaporation. Reprecipitation using THF–methanol was then repeated several times. The crude product was further purified by recrystallization from petroleum ether to give 0.10 g of yellow powder (yield 20%). ^{1}H NMR ($CDCl_3$, δ/ppm): 8.46 (s, 1H), 8.35 (s, 1H), 7.26 (s, 3H), 6.79 (s, 1H), 5.33 (s, 1H), 4.78 (m, 2H), 3.30 (m, 1H), 1.82–2.40 (m, 7H) and 0.67–1.55 (m, 36H). MS (m/z) = 1093.8 ($Li(ChQ)_2$; calc. 1092.6), 568.4 ($LiChQ{\cdot}H_2O$; calc. 568.4) and 550.4 (LiChQ [M^+]; calc. 549.8). FT-IR (cm^{-1}) = 2929, 2866, 1571, 1507, 1465, 1379, 1324, 1285, 1246, 1168, 1149, 1084, 1024, 956, 884, 830, 778 and 716.

Results and discussion

Optical properties

The resultant complex, LiChQ, is more readily dissolved in common organic solvents than pristine complex LiQ. To obtain insight into the optical properties of LiChQ, UV-vis absorption spectra were obtained. There are two characteristic absorption peaks in solution for the hydroxyquinoline component, as previously reported.[15] As shown in Fig. 1, one of the absorption peaks for LiChQ in 1,2-dichloroethane (6×10^{-5} M) at around 325 nm, resulting from a π–π* transition, shifts to a longer wavelength of 333 nm with increasing concentration (5×10^{-4} M). The other absorption peak, located around 370 nm, is a shoulder originating from an intraligand charge transition (ILCT). Unlike the former peak, this peak blue-shifts with increasing concentration. However, an obvious absorption peak rather than a shoulder peak was observed at 393 nm in THF. This may be due to the interaction of the oxygen atom in THF with the Li(I) ion. An absorption peak of LiChQ in the gel state was also observed at 333 nm, with the absorption band at around 370 nm disappearing. This observation is different from the results reported by Shinkai.[9] In the previous examples, there were two quinoline moieties coordinated to Pt(II) or Pd(II), while there is only one quinoline coordinated to Li(I) here. Considering the shift of the absorption peak resulting from a π–π* transition (red shift), related to one of the driving forces for gelation, *i.e.*, π–π interactions between ligands, a J-aggregate could be deduced as the aggregation mode of LiChQ.[9a,16] However,

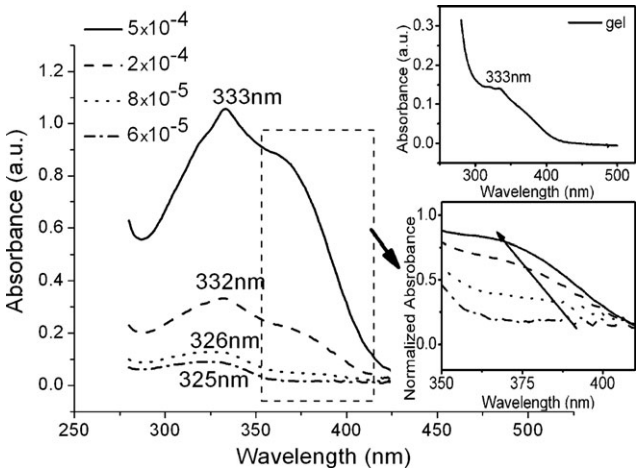


Fig. 1 UV-vis absorption spectra of LiChQ in solution (1,2-dichloroethane) at different concentrations. Top inset: UV-vis absorption spectrum of LiChQ in the gel state (1,2-dichloroethane). Bottom inset: normalized absorption of LiChQ at around 370 nm.

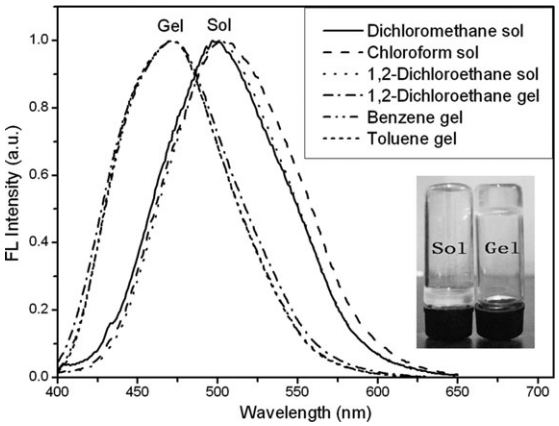


Fig. 3 FL spectra of LiChQ in different solutions and gel states. Inset: photograph of luminescent LiChQ in solution (1,2-dichloroethane) and in a gel under UV radiation.

why does the other absorption band blue-shift? As discussed later, the intermolecular dipole–dipole interaction between LiQ moieties is an essential driving force for gelation, which results in a weakening of the intramolecular interaction between the central Li(I) ion and the ligand, disrupting ILCT. Therefore, the ILCT absorption band at around 370 nm is suppressed and blue-shifts in the aggregated state.

The fluorescence (FL) peak (excited at 370 nm) in the gel state was blue-shifted from that in dilute solution. The FL peak in 1,2-dichloroethane solution (5×10^{-5} M) was located at 503 nm, shifting to 499 nm when the concentration was increased, as shown in Fig. 2. The FL peak in the gel phase from 1,2-dichloroethane was observed at 493 nm. Upon aggregation in the gel state, the intermolecular interaction was enhanced, resulting in disruption of the intramolecular interaction, *i.e.*, ILCT; thus, a blue-shift of the FL peak in the gel state was induced. It should be noted that there was little difference among the solvents in the FL of LiChQ in solution (503 nm), and little change was observed for its FL in the gel state (493 nm) either (Fig. 3). This observation indicates that solvents scarcely effect the aggregation mode. Because the FL and the absorption at around 370 nm both result from ILCT, a blue-shift is observed in the FL.

The FL of LiChQ in a THF solution (5×10^{-5} M) was shifted to 518 nm from the 485 nm of pristine complex LiQ owing to the introduction of the cholesterol component. The quantum yield of LiChQ was dramatically increased to 32.6%, much larger than that of LiQ (12%) in THF. The high quantum yield of the luminescence of LiChQ also supports J-aggregation, in which transitions to lower excited states are dominant. In addition, when cyclohexane was added into a THF solution of LiChQ, almost 100% enhancement of the FL intensity was observed (Fig. 4). The emission peak of LiChQ blue-shifted from 518 nm in THF to 503 nm in a mixture of 1 : 4 (v/v) THF : cyclohexane when the cyclohexane was added. Since cyclohexane is a poor solvent for LiChQ, the molecules aggregate with increasing cyclohexane concentration. This enhanced emission due to the poorer solvent might be due to an aggregation-induced emission (AIE), as first reported by Tang *et al.*[17] It is supposed that the restricted vibration and rotation of the cholesterol group in the aggregate state of LiChQ reduced non-emissive relaxation, thus endowing it with enhanced emission. Considering the blue shift of the FL

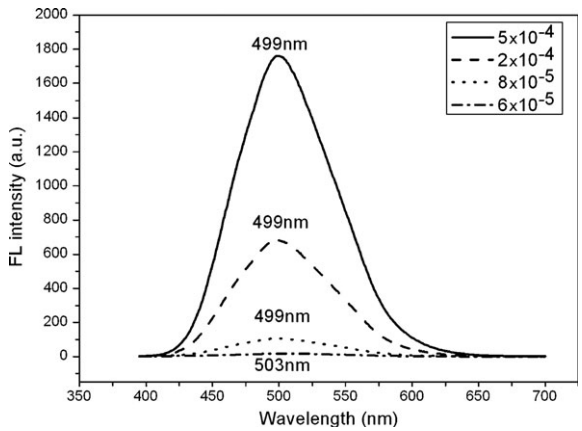


Fig. 2 FL spectra of LiChQ in 1,2-dichloroethane at different concentrations.

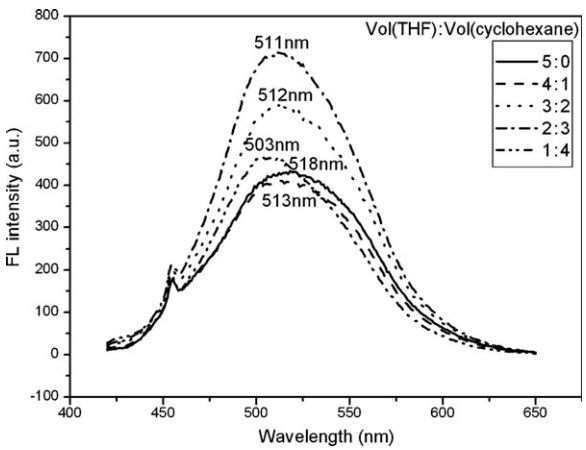


Fig. 4 FL spectra of LiChQ (5×10^{-5} mol L^{-1}) in different ratio THF : cyclohexane mixtures.

spectra and the highly enhanced intensity in the aggregated state, the material has potential applications in luminescent materials and optoelectronic devices.

Aggregation behavior

When the concentration of LiChQ was increased to 1 wt% (about 10^{-2} M), it formed nano-scaled fibers by self-assembly in common organic non-protic solvents, including non-polar solvents (*e.g.*, benzene), polar solvents (*e.g.*, toluene, chlorobenzene, dichloromethane and 1,2-dichloroethane), and showed supergelation behavior.[18] However, it could not be dissolved in common protic solvents (*e.g.*, methanol and ethanol). The ability for self-assembled gelation was tested in different non-protic solvents, as listed in Table 1. A capped test bottle containing LiChQ in a solvent was heated until the LiChQ dissolved, and the resultant solution was then cooled down to room temperature. Gel formation was confirmed by simply inverting the bottle and observing the flow quality of the samples. As summarized in Table 1, LiChQ formed a supergel in a variety of organic solvents at a concentration as low as 1.0 wt%. Light yellow translucent or transparent gels were formed in chlorobenzene, toluene and dichloromethane. When the concentration increased to 2.0 wt%, a stable gel also formed in chloroform, but not in THF or 1,4-dioxane, even when the concentration was much higher. However, no gelation occurred in the case of compound **2**, with a similar chemical structure to LiChQ. Moreover, the complexes of Zn(II) or Al (III) with compound **2** showed no gelation either. These results indicate that the Li(I) ion might play a key role in the gelation of LiChQ.[5–8] Due to the low electronegativity of lithium, dipole–dipole interactions between the Li(I) ion and the ligand should be an essential driving force for gelation, unlike the reported 8-hydroxyquinoline/Pt (II) complex, which has hydrogen bonds provided by amide groups. Moreover, the Li(I) ion readily forms dimers, as previously reported.[12] Actually, we did observe the dimer peak in the mass spectrum of LiChQ. In addition, van der Waals interactions between the cholesterol groups and π–π stacking of the quinoline moieties are also necessary for LiChQ to form a gel. Therefore, it is supposed that the 8-hydroxyquinoline lithium(I) moieties are aggregated *via* strong dipole–dipole interactions and π–π stacking. The cholesterol components here are aggregated *via* van der Waals interactions.[19] The proposed aggregation mode is showed in Fig. 5. LiChQ is favorable to have a large slippage to form a J-aggregate. Therefore, fibers can be expected to be obtained *via* this aggregation mode.

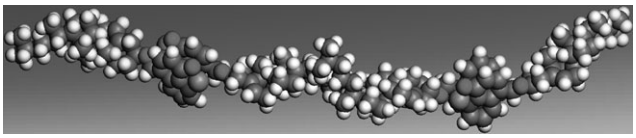


Fig. 5 Proposed aggregation mode for LiChQ in the gel state (the simulation was carried out by the DMol3 software package; shown here is the assembly behavior of four LiChQ molecules).

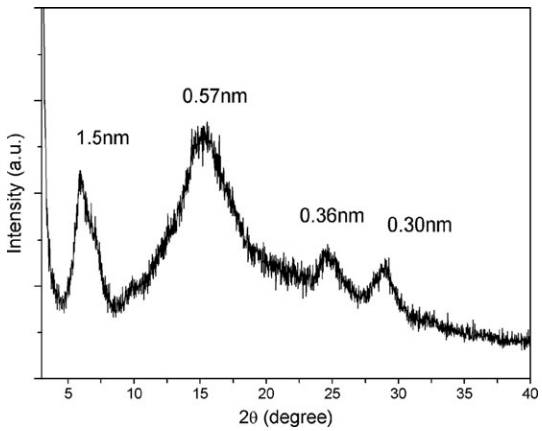


Fig. 6 The XRD pattern of a xerogel of LiChQ from toluene.

To confirm this, the XRD pattern of the LiChQ xerogel was measured. As shown in Fig. 6, a diffraction peak was found at $2\theta = 5.9^\circ$, corresponding to $d = 1.50$ nm, which is shorter than the calculated molecular length (2.41 nm). This might be due to the molecules being packed with a slippage, as presented in the proposed aggregation mode. Another strong diffraction signal is located at around $2\theta = 15.5^\circ$ (0.57 nm), which is close to the width of a LiChQ molecule (*ca.* 0.61 nm). Two peaks were found at around $2\theta = 24.7^\circ$ (0.36 nm) and $2\theta = 29.3^\circ$ (0.30 nm). The former is a typical π–π stacking distance[20] and the latter might be assigned to the dimer of LiChQ.

To determine the aggregation behavior of LiChQ in different solvents, the conventional solvent effect described by the Lippert–Mataga equation[21] can be considered:

$$\nu_a - \nu_{fl} = \frac{2}{hc}\frac{(\mu_e - \mu_g)^2}{a^3}\Delta f + \text{constant} \quad (1)$$

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) \quad (2)$$

Table 1 Absorption, FL and gelation properties of LiChQ in organic solvents[a]

Solvent	n	ε	Δf	λ_a/nm	λ_{fl}/nm	$\nu_a - \nu_{fl}$/cm^{-1}	Gelation properties
Toluene	1.496	2.38	0.0135	333	493	9746	G
Chlorobenzene	1.524	5.69	0.1445	334	498	9860	G
Chloroform	1.446	4.81	0.1483	333	500	10030	G
Dichloromethane	1.424	8.93	0.2172	331	501	10251	G
1,2-Dichloroethane	1.442	10.42	0.2221	333	500	10030	G
THF	1.405	7.52	0.2097	338, 393	516	6196	S
1,4-Dioxane	1.422	4.25	0.1413	325	399	5706	S

[a] n: refractive index of the solvent; ε: static dielectric constant; Δf: orientation polarizability; λ_a: wavelength of the absorption; λ_{fl}: wavelength of the fluorescence; $\nu_a - \nu_{fl}$: Stokes shift; G: gelation; S: solution.

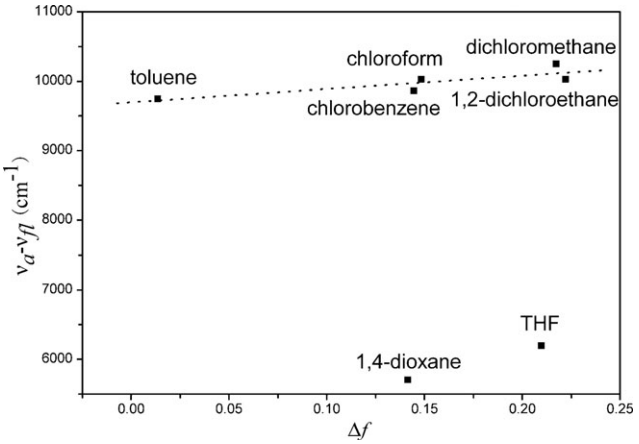


Fig. 7 Lippert–Mataga plot for LiChQ in different solvents.

where h is Planck's constant (6.6256×10^{-27} g cm^2 s^{-2}), c is the speed of light (2.9979×10^{10} cm s^{-1}), a is the radius of the cavity in which the fluorophore resides, ν_a and ν_{fl} are the wavenumbers (/cm^{-1}) of the absorption and FL, μ_e and μ_g are the dipolar moments of the excited and ground state, and ε and n are the static dielectric constant and refractive index of the solvent, respectively.[22]

The Lippert–Mataga plot of the Stokes shifts $\nu_a - \nu_{fl}$ *vs.* the orientation polarizability Δf is shown in Fig. 7. The data generated from toluene, chlorobenzene, chloroform, dichloromethane and 1,2-dichloroethane show an almost linear behavior, indicating a general solvent effect on the spectral shifts.[22] Gelation is also observed in these solvents. However, the data obtained for THF and 1,4-dioxane are far from the linear region. This difference might originate from the coordination of the oxygen atom of the solvents to the Li(I) ion. The packing mode of the molecules then changes due to this coordination, as supported by the obvious absorption peak rather than a shoulder peak at 393 nm in THF solution. As a result, the gelation is suppressed and only a solution can be formed.

The TEM images of gels prepared from benzene and toluene are shown in Fig. 8. In these supermolecular gels, LiChQ forms nanofibers (30–100 nm in diameters) whose entanglements create a three-dimensional network. Similar images are observed for both a benzene gel and a toluene gel. This result is consistent with the conclusions made from the Lippert–Mataga theory and the FL spectra of the gels in different solvents, *i.e.*, the solvent scarcely affects the aggregation mode.

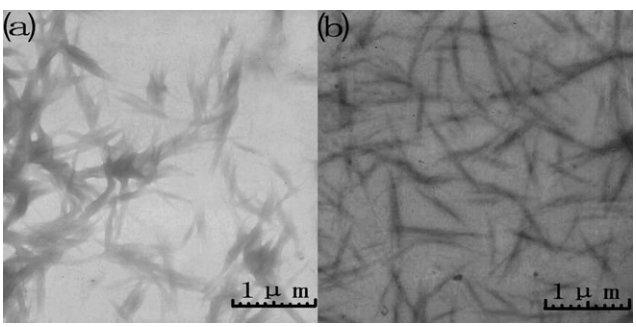


Fig. 8 TEM images of LiChQ xerogels derived from (a) benzene and (b) toluene.

Conclusions

In summary, we have obtained a soluble, highly efficient, fluorescent organometallic gelator, LiChQ, through the modification of insoluble LiQ with cholesterol. A supergel was formed with the resultant complex in non-protic organic solvents. A red-shift was observed for the absorption peak of LiChQ in gel states in comparison to its solutions, which indicates that LiChQ tends to form J-aggregates in gel states. It was also shown that aggregation can induce the enhancement of FL emission. van der Waals interactions between the cholesterol groups, π–π stacking of quinoline moieties, together with dipole–dipole interactions between 8-hydroxyquinoline lithium(I) moieties might be responsible for the aggregation of LiChQ. TEM images showed that LiChQ assembled into fibrillar nanostructures of 30–100 nm diameter. These structures have potential applications in optoelectronic devices and/or templates for nanostructured optoelectronic materials.

Acknowledgements

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References

1 (*a*) Y. Gao, X. Zhang, C. Ma, X. Li and J. Z. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 17044; (*b*) G. Lu, Y. Chen, Y. Zhang, M. Bao, Y. Bian, X. Li and J. Z. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 11623.
2 T. Takami, T. Ye, D. P. Arnold, K.-I. Sugiura, R. Wang, J. Z. Jiang and P. S. Weiss, *J. Phys. Chem. C*, 2007, **111**, 2077.
3 (*a*) N. Satoh, J.-S. Cho, M. Higuchi and K. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 8104; (*b*) K. Albrecht, A. Kimoto, J.-S. Cho, Y. Matsuura and K. Yamamoto, *J. Photopolym. Sci. Technol.*, 2008, **21**, 181; (*c*) T. Nakashima, N. Satoh, K. Albrecht and K. Yamamoto, *Chem. Mater.*, 2008, **20**, 2538.
4 C.-P. Cho and T.-P. Perng, *J. Nanosci. Nanotechnol.*, 2008, **8**, 69.
5 T. Klawonn, A. Gansäuer, I. Winkler, T. Lauterbach, D. Franke, R. J. M. Nolte, M. C. Feiters, H. Börner, J. Hentschel and K. H. Dötz, *Chem. Commun.*, 2007, 1894.
6 G. Bühler, M. C. Feiters, R. J. M. Nolte and K. H. Dötz, *Angew. Chem., Int. Ed.*, 2003, **42**, 2494.
7 T. Tu, W. Assenmacher, H. Peterlik, H. R. Weisbarth, M. Nieger and K. H. Dötz, *Angew. Chem., Int. Ed.*, 2007, **46**, 6368.
8 P. Sahoo, D. Krishna Kumar, D. R. Trivedi and P. Dastidar, *Tetrahedron Lett.*, 2008, **49**, 3052.
9 (*a*) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, M. Ojima, A. Fujii, M. Ozaki and S. Shinkai, *Chem.–Eur. J.*, 2007, **13**, 4155; (*b*) M. Shirakawa, N. Fujita, T. Tani, K. Kanekob and S. Shinkai, *Chem. Commun.*, 2005, 4149.
10 A. Kishimura, T. Yamashita and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 179.
11 (*a*) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (*b*) C. Schmitz, H.-W. Schmidt and M. Thelakkat, *Chem. Mater.*, 2000, **12**, 3012.
12 (*a*) J. Luo, L. Xiao, Z. Chen and Q. Gong, *Appl. Phys. Lett.*, 2008, **93**, 133301; (*b*) B. Qu, Z. Chen, F. Xu, H. Cao, Z. Lan, Z. Wang and Q. Gong, *Org. Electron.*, 2007, **8**, 529.
13 J. H. Burckhalter and R. I. Leib, *J. Org. Chem.*, 1961, **26**, 4078.
14 A. Mishra, P. K. Nayak and N. Periasamy, *Tetrahedron Lett.*, 2004, **45**, 6265.
15 M. Shirakawa, S.-i. Kawano, N. Fujita, K. Sada and S. Shinkai, *J. Org. Chem.*, 2003, **68**, 5037.
16 (*a*) N. C. Maiti, S. Mazumdar and N. Periasamy, *J. Phys. Chem. B*, 1998, **102**, 1528; (*b*) X. D. Song, J. Perlstein and D. G. Whitten, *J. Am. Chem. Soc.*, 1997, **119**, 9144.

17 (*a*) G. Yu, S. W. Yin, Y. Q. Liu, J. S. Chen, X. J. Xu, X. B. Sun, D. G. Ma, X. W. Zhan, Q. Peng, Z. G. Shuai, B. Z. Tang, D. B. Zhu, W. H. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335; (*b*) H. Tong, Y. Hong, Y. Dong, M. Häussler, J. W. Y. Lam, Z. Li, Z. F. Guo, Z. H. Guo and B. Z. Tang, *Chem. Commun.*, 2006, 3705.
18 (*a*) H. Bouas-Laurent and J.-P. Desvergne, in *Molecular Gels: Materials With Self-Assembled Fibrillar Networks*, ed. R. G. Weiss and P. Terech, Springer, Dordrecht, The Netherlands, 2006, ch. 12, pp. 363; (*b*) F. Würthner, C. Bauer, V. Stepanenko and S. Yagai, *Adv. Mater.*, 2008, **20**, 1695.
19 F. Fages, *Angew. Chem., Int. Ed.*, 2006, **45**, 1680.
20 G. Palui and A. Banerjee, *J. Phys. Chem. B*, 2008, **112**, 10107.
21 (*a*) E. Z. Von Lippert, *Electrochem*, 1957, **61**, 962; (*b*) N. Mataga, Y. Kaifu and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 1956, **29**, 465.
22 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, Taylor and Francis, Boca Raton, FL, 87th edn, 2007, ch. 8.

