Gel electrolyte materials formed from a series of novel low molecular mass organogelators for stable quasi-solid-state dye-sensitized solar cells†

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Electrolyte materials are the key components in dye-sensitized solar cells (DSCs) and are very crucial to the performance and long-term stability of DSCs. We developed a series of diamide derivatives as novel low molecular mass organogelators (LMOGs) for DSCs. These LMOGs contain different numbers (2, 6, 5 and 9) of methylene groups (–CH2–) between the two amide carbonyl groups and exhibit distinctive self-assembly behaviors. The gel electrolytes prepared by these LMOGs possess high gel-to-solution transition temperatures (over 100 °C) and the stability of DSCs is largely enhanced. More importantly, the parity of the number of –CH2– and their special molecular arrangements have a remarkable influence on the self-assembly of the gelators resulting in a significantly different morphology, and further influence the photovoltaic performances of DSCs. It is found that the LMOGs containing odd-numbered –CH2– lead to a much better charge transport of the gel electrolytes, inducing a longer electron lifetime and higher incident photon-to-electron conversion efficiency compared with the LMOGs containing even-numbered –CH2–. Finally, a superior quasi-solid-state DSC based on the gelator containing five –CH2– is obtained, which exhibits a photoelectric conversion efficiency of 7.53% and excellent thermal and light-soaking stabilities during accelerated aging tests.

Introduction

Over the last few decades, solar energy has emerged as the most practical and long lasting alternative to conventional fossil-fuel based energy sources. To utilize solar energy for a variety of applications one would need to convert it into electricity using photovoltaic cells. Among various kinds of photovoltaic devices, dye-sensitized solar cells (DSCs) have been regarded as a promising candidate for next generation solar cells and aroused intensive interest over the past decade owing to their low cost, low energy consumption, environmentally friendly materials, simple fabrication process and comparatively high power conversion efficiency.1 Many strategies have been reported to enhance the efficiency of the DSC. One approach is to broaden the photoresponse and maximize the light-harvesting efficiency. For example, the hyperbranched titania architectures in the photoanode for DSCs have been investigated by Kuang et al.2,3 and a significant enhancement in power conversion efficiency (11.01%) was obtained.4 Another important way to improve the photovoltaic performance of DSCs is to develop novel electrolytes. The best photoelectric conversion efficiency of DSCs based on the liquid electrolyte has achieved 13%.5 However, it is clear that stability is a prerequisite for the application of any photovoltaic technology and the extent of application is limited by the level of stability that can ultimately be achieved.6,7 In order to improve the stability of liquid electrolyte based DSCs, many strategies have emerged, such as room-temperature molten ionic salts (ILs), p-type semiconductors, and organic and inorganic hole conductors.8–12 ILs possess many unique properties including low vapor pressure, broad electrochemical windows and non-flammability. Recently, the efficiency of DSCs based on the eutectic melt-based ionic liquid electrolytes reached over 8%.13 Despite this, the fluidity of ILs can still lead to leakage of DSCs. Therefore, the quasi-solid-state electrolytes based on low molecular mass organogelators (LMOGs) have attracted much attention in recent years. LMOGs can finely disperse as anisotropic aggregates within the organic solvent resulting in a three-dimensional structure to effectively gelate the liquid electrolyte to form a quasi-solid-state electrolyte. The key factor in gel
formation is the self-assembly process of LMOGs driven by non-covalent interactions, including hydrogen bonding, π–π interactions, metal–ligand coordination, van der Waals forces, hydrophobic effects and so on. More importantly, the gel electrolyte based on LMOGs has good ionic conductivity and pore-filling property, which are similar to the liquid electrolyte, and the network of the gel can reduce the leakage of the liquid electrolyte effectively to improve the long-term stability of DSCs. Many compounds, such as 12-hydroxystearic acid, cyclonexanecarboxylic acid-[4-(3-octadecylureido)phenyl]amide, 1-ethyl-3-methylimidazolium thiocyanate, and tetradoxy- lammonium bromide, have been developed as LMOGs and applied in DSCs, respectively. These literature reports studied the influences of the additive LMOGs in the liquid electrolyte on the gel to the solution transition temperature ($T_{gel}$) of the gel electrolyte and photovoltaic performances of the DSCs. In addition, other researchers generally discussed the gelation capability of different LMOGs or demonstrated the difference in the $I_1/I_3$ redox transport property between the liquid and gel electrolytes. However, little research on the relationship of the gel morphology with the charge transport property of the gel electrolyte and the kinetic processes of electron transport/combination in the quasi-solid-state dye sensitized solar cells (QS-DSCs). Different from other studies, in this paper, we synthesized a series of didodecanoylamides of $\omega$-$\omega$-alkylidenediamines as LMOGs to gelate the 3-methoxypropionitrile (MePN) based liquid electrolytes. Depending on the even- or odd-numbered $-\text{CH}_2-\text{CH}_2-$ in the molecular structure of LMOGs, these LMOGs exhibit intriguingly changeable self-assembly behaviors in electrolytes, which results in quite different microscopic structures of the gel networks. We systematically studied how the molecular structures of the gelators influence the self-assembled 3D network structures of the gels, and how these different microstructures influence the electrochemical properties of the gel electrolytes, the photovoltaic performances and stabilities of the QS-DSCs. By using the polarized optical light microscopy, it is found that the self-assembly behavior of the LMOGs containing odd-numbered $-\text{CH}_2-\text{CH}_2-$ between the two amide carbonyl groups in the molecules of the gelators is quite different from those containing even-numbered $-\text{CH}_2-\text{CH}_2$- and $-\text{CH}_2-$ and not surprisingly, these different self-assembly modes influence the morphologies of the 3D network structures of the gel electrolytes. Furthermore, it is very important that the electrochemical characteristics and photovoltaic performance of QS-DSCs were significantly changed with these different self-assembly behaviors. Therefore, it seems reasonable and important for both fundamental research and practical application of photovoltaic devices to investigate and understand the relationships of the LMOGs molecular structures, microscopic structures of gel electrolytes, photovoltaic performances and stabilities of QS-DSCs.

**Experimental section**

**Synthesis of LMOGs**

$N,N'-1,2$-Ethanediybis-dodecanamide (gelator A); $N,N'-1,6$-hexanediylbis-dodecanamide (gelator B), $N,N'-1,5$-pentanediylbis-dodecanamide (gelator C) and $N,N'-1,9$-nonanediybis-dodecanamide (gelator D) were synthesized by reacting lauric acid with di-$n$-dodecanamide (gelator B), di-$n$-dodecanamide (gelator A); $N,N'-1,2$-Ethanediybis-dodecanamide (gelator A); $N,N'-1,6$-hexanediylbis-dodecanamide (gelator B), $N,N'-1,5$-pentanediylbis-dodecanamide (gelator C) and $N,N'-1,9$-nonanediybis-

**Electrolyte preparation**

1,2-Methyl-3-propylimidazoliumiodide (DMPII) was prepared as reported previously. The liquid electrolyte for DSCs was composed of 0.1 mol L$^{-1}$ iodine (I$_2$: 99%, Aldrich), 0.1 mol L$^{-1}$ anhydrous lithium iodide (LiI: 99%, Aldrich), 0.5 mol L$^{-1}$ N-methylbenzimidazole (NMBI: 99%, Aldrich), and 1 mol L$^{-1}$ DMPII in 3-methoxypropionitrile (MePN: 99%, Fluka). The gel electrolyte was prepared by adding an 8 wt% (vs liquid electrolyte) gelator into the liquid electrolyte and heated to 120 °C under stirring until the gelator was dissolved. After cooling to room temperature (25 °C), the gel electrolytes A, B, C and D with gelators A, B, C and D were respectively formed and used in DSCs.

**Fabrication of dye-sensitized solar cells**

The colloidal TiO$_2$ microspheres were prepared by hydrolysis of titanium tetraisopropoxide as shown in the previous literature. Nanocrystalline electrodes about 11.3 μm thickness were obtained by screen-printing TiO$_2$ paste on FTO glass (TEC-8, LOF). After sintering at 450 °C for 30 min in air then cooling to about 120 °C, the nanoporous TiO$_2$ photoelectrode was immersed in an ethanol solution of 0.5 mM cis-dioxygenate-$N,N$-bis-(4-carboxylate-tetraethylammoniumcarboxylate-2,2-bipyridine) ruthenium$[\text{u}](N719$ dye) for 14 h. The platinized counter electrodes were obtained by spraying H$_2$PtCl$_6$ solution to FTO glass followed by heating at 410 °C for 20 min. DSCs were assembled by sealing the dyed nanoporous TiO$_2$ photoelectrode and the counter electrode with thermal adhesive films (Surlyn 1702, Dupont, USA). The liquid electrolyte was injected into the internal space between two electrodes through the hole on the counter electrode, which was later sealed by a cover glass and thermal adhesive films. The gel electrolytes were heated to 120 °C under stirring until the gel transforms into a liquid completely. Then, the electrolyte (hot solution) was rapidly injected into the cell and the cell was sealed similar to the liquid electrolyte. After cooling to room temperature, a uniform motionless gel layer was formed in the cell.

**Polarized optical light microscopy**

For optical microscopic investigations, a piece of the gel (8 wt% of LMOGs in MePN) was placed onto a glass slide and protected with a cover slip. The sample was heated to 120 °C at a rate of 10 °C min$^{-1}$ and the micrographs were obtained during cooling.
between crossed polarizers using a microscope (DM2500P, Leica, Germany) equipped with a hot-stage (LTSE-420, Linkam, UK) and a camera (Micropublisher 5.0 RTV, Qimaging, Canada) at a rate of 1 °C min⁻¹.

**Differential scanning calorimetry**

The gel to solution transition temperature ($T_{gel}$) of the gel electrolyte was determined by using a differential scanning calorimeter (DSC-Q2000, TA, USA). Approximately 5–7 mg of each sample was weighed and sealed in an aluminum pan and heated at a rate of 10 °C min⁻¹ under nitrogen flow from 25 to 135 °C for DSC measurement.

**Conductivity measurements**

The ionic conductivities of the liquid and gel electrolytes were determined by two electrode thin-layer cells with two platinum black electrodes and an ac impedance technique on an electrochemical workstation (IM6e, Zahner, Germany) over a frequency range of 50 MHz to 1000 kHz with a voltage amplitude of 10 mV at 0 V bias.

**Voltammetric measurements**

Steady-state voltamograms were recorded on a electrochemical workstation (Autolab 320, Metrohrom, Switzerland) at 25 °C in two-electrode mode of the DSC equipped with a 5.0 μm platinum ultramicroelectrode (CHI107, CH Instruments Inc., USA) as the working electrode, a 1 mm radius platinum disk electrode (CHI102, CH Instruments Inc., USA) as the counter electrode and the reference electrode. The steady-state current–voltage curves were obtained at a scan rate of 5 mV s⁻¹.

**FT-IR spectrophotometry measurements**

To confirm the formation of the lithium bond between the gelator and LiI, we prepared four samples: (a) the MePN solvent, (b) solution of LiI (0.1 M) dissolving in the MePN solvent, (c) the gel based on MePN and gelator C (8 wt%) without LiI and (d) the gel based on MePN and gelator C with LiI (the ratio of the molar concentration of gelator C and LiI is 1.7 : 1). These samples were put into the polyethylene cell for measurement and analyzed in a range of 800 to 3200 cm⁻¹ with 16 scans at a resolution of 2 cm⁻¹. IR spectra for all the samples were measured by using KBr pellets and acquired using a FT-IR spectrometer (NICOLET8700, Thermo Fisher Scientific Inc., USA).

**IMVS/IMPS and electrochemical impedance measurements**

The experimental setup for intensity-modulated photocurrent and photovoltage spectroscopy (IMPS and IMVS) measurements has been described elsewhere. Intensity-modulated measurements were carried out by using an electrochemical workstation (IM6e, Zahner, Germany) with light emitting diodes (λ = 610 nm) driven by export (Zahner, Germany). Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Autolab 320, Metrohrom, Switzerland), at a perturbation amplitude of 10 mV within the frequency range from 1 MHz to 10 mHz in the dark.

**Characterization of incident photon-to-electron conversion efficiency (IPCE)**

The photocurrent action spectra were recorded using a QE/IPCE measurement kit consisting of a 300 W xenon lamp (69911, Newport, USA), a 1/4 m monochromator (74125 Oriel Cornerstone 260, Newport, USA), a dual channel power meter (2931-C, Newport, USA) and the calibrated UV silicon photodetector (71675, Newport, USA).

**Photovoltaic characterization and stability tests**

The photovoltaic performance of DSCs with the active area of 0.16 cm² with a black mask was measured by using a Keithley 2420 digital source meter (Keithley, USA), and controlled using Test point software under a 450 W xenon lamp (Oriel, USA) with a filter (AM 1.5, 100 mW cm⁻²). The incident light intensity was calibrated with a standard crystalline silicon solar cell before each experiment.

Hermetically sealed cells were used for long-term stability tests. The cells were stored in the oven at 60 °C for thermal stress experiment. Furthermore, the successive one sun light soaking experiment was also carried out. DSCs covered with a UV cut off filter (up to 394 nm) were irradiated with an open circuit under AM1.5, (XQ3000, 100 mW cm⁻², Shanghai B.R. Science Instrument Co., Ltd, China) and the air temperature was set to 50 °C during the light soaking experiment. $J$–$V$ measurements were carried out at room temperature after allowing these cells to cool down and equilibrate for 30 min.

**Results and discussion**

**Gelation study of the gel electrolytes**

The molecular structure has an important influence on the molecular self-assembly and microscopic 3D network of the gel electrolyte. In addition, the dodecanoyl moiety of all these gelators favorably interact with each other within van der Waals forces. These different self-assemblies respectively result in ribbon and woven 3D networks of the gels containing even-numbered –CH₂– (gelators A and B) and odd-numbered –CH₃– (gelators C and D), which can be further confirmed by polarized optical micrographs.
The \textit{in situ} gelation process of gelator B \((n = 6)\) and gelator D \((n = 9)\) in the MePN solvent was investigated using polarized optical light microscopy in the same area of each sample. Firstly, the gels were heated up to 130 °C at a rate of 10 °C min\(^{-1}\) to ensure complete dissolution of the gelators in MePN. Subsequently, these hot solutions were cooled to 30 °C at a rate of 1 °C min\(^{-1}\). The photographs of Fig. 2(a)–(d) were taken during the cooling process at 110 °C, 108 °C, 103 °C and 30 °C, respectively, which show the formation process of the self-assembly gel network of gelator B. Fig. 2(e)–(h) were obtained at 100 °C, 97 °C, 95 °C and 30 °C, respectively, and show the formation process of self-assembled gel network of gelator D. It is noteworthy that gelator B and gelator D show the remarkable differences in the crosslinking modes, which can be clearly seen from the circular areas of Fig. 2. As predicted, gelator B forms a ribbon network, on the other hand, gelator D forms a woven network. These different characteristics of the gel network could lead to different thermodynamic and electrochemical properties of gel electrolytes.\(^{34,35}\) Since the woven network has a much smaller fibril size than that of the ribbon network, we presume that the ions can move more easily in the woven network than in the ribbon network.

The thermodynamic properties of gelators A–D in MePN based electrolytes were investigated by using a differential scanning calorimeter and the transition temperature \((T_{\text{gel}})\) from the gel state to the liquid state were obtained. The photo of gel electrolytes is shown in Fig. 3. As can be seen, the \(T_{\text{gel}}\) values depend on the parity of the number of \(-\text{CH}_2-\) groups between the two amide carbonyl groups and the length of the carbon chain. The \(T_{\text{gel}}\) values of gel A and gel B are 112.2 °C and 115.4 °C, respectively, which are higher than those of gel C (100.2 °C) and gel D (106.8 °C). It indicated that the gelators containing even-numbered \(-\text{CH}_2-\) groups can construct a more stable network structure than those containing odd-numbered \(-\text{CH}_2-\) groups. In addition, four more \(-\text{CH}_2-\) groups were increased in the molecule of gelator B than that of gelator A; therefore, the \(T_{\text{gel}}\) is also increased with the increase of the length of the carbon chain. This is because the longer carbon chains could increase the van der Waals forces between the molecules of gelators. This phenomenon is also observed in gelator C and gelator D. Furthermore, all the four gel electrolytes exhibited high \(T_{\text{gel}}\) (over 100 °C) which ensures the gel state of the electrolytes at the operating temperature of the solar cell.

\textbf{Electrochemical characteristics of the gel electrolytes}

The Arrhenius equation was used to describe the conductivity-temperature behavior of the liquid and gel electrolytes. The
temperature dependence shows a classical Arrhenius behavior obeying the eqn (1):

$$\sigma = A \exp\left(-\frac{E_\text{A}}{kT}\right)$$  \hspace{1cm} (1)

where $\sigma$ is the conductivity, $A$ is the pre-exponential factor, $E_\text{A}$ is the activation energy, and $k$ is Boltzmann’s constant. Fig. 4(a) shows the ionic conductivity–temperature plot of liquid and gel electrolytes. Table 1 lists the values of the activation energy of the gel electrolytes with different gelators. As can be seen in Fig. 4(a) and Table 1, the activation energy values of the gel electrolytes are changed around the $T_{\text{gel}}$ of gel electrolytes. When the temperature is below $T_{\text{gel}}$, the gel electrolytes show higher activation energy values than liquid electrolytes (10 kJ mol$^{-1}$). However, when the temperature is above $T_{\text{gel}}$, the activation energy values of the gel electrolytes are almost equal to that of the liquid electrolytes. This result suggested that the 3D network of the gel could obstruct the physical diffusion of the charges in the electrolytes, which leads to a lower ionic conductivity than that of the liquid electrolyte. Moreover, when the temperature is below the $T_{\text{gel}}$, the activation energy values of gel A and gel B are higher than those of gel C and gel D. This is due to the completely different fibril sizes and types of the microstructures of the gels caused by different self-assemblies of gelators.

The diffusion of redox species ($\Gamma^-/I^-_3$) is associated with the conductivity which provides information of the mobility of the ions in the electrolyte. Moreover, it is well known that the diffusion coefficient of $I^-_3$ plays an important role in increasing the short circuit photocurrent density ($J_{\text{sc}}$) and reducing the dark reaction at the TiO$_2$ photoelectrode/electrolyte interface in the QS-DSCs. Steady-state cyclic voltammetric analysis was carried out in order to understand the charge transport mechanism in the liquid and gel electrolyte system. Fig. 4(b) shows the comparative steady-state voltammograms of the liquid electrolyte and gel electrolytes at 25 °C. The apparent diffusion coefficients ($D_{\text{app}}$) of redox species ($\Gamma^-$ and $I^-_3$) were calculated from the anodic and cathodic steady-state currents ($I_{\text{ss}}$) using the following equation.

$$I_{\text{ss}} = 4nrcFD_{\text{app}}$$  \hspace{1cm} (2)

where $n$ is the electron number in the electrode reaction, $F$ is the Faraday constant, and $c$ is the bulk concentration of electroactive species, $D_{\text{app}}$ is the apparent diffusion coefficient, and $r$ is the radius of the Pt ultramicroelectrode. As shown in Fig. 4(b) and Table 2, the $D_{\text{app}}$ values of $\Gamma^-$ and $I^-_3$ of gel C are slightly lower than those of the liquid electrolyte. And the $D_{\text{app}}$ values of

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Below $T_{\text{gel}}$</th>
<th>Above $T_{\text{gel}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel A ($n = 2$)</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>Gel B ($n = 6$)</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Gel C ($n = 5$)</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>Gel D ($n = 9$)</td>
<td>14</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 1 The values of activation energy of gel electrolytes A–D at around the $T_{\text{gel}}$.
\(I^-\) and \(I_3^-\) of gel C and gel D are much higher than those of gel A and gel B. Due to the distinctive self-assembly, the gelators containing odd-numbered \(-\text{CH}_2-\) groups form woven 3D networks and provide much better channels for charge diffusion. Therefore, the redox ions can still diffuse smoothly in the gel electrolytes based on woven 3D networks despite the high viscosity of the gel electrolytes. Moreover, the increased \(D_{\text{app}}\) can accelerate the supply of \(I_3^-\) to the Pt counter electrode and increase the \(J_{\text{sc}}\) of QS-DSCs.\(^{39}\) Therefore, due to the larger \(D_{\text{app}}\), the QS-DSCs based on gel electrolytes containing odd-numbered \(-\text{CH}_2-\) groups probably have higher \(J_{\text{sc}}\) than the QS-DSCs based on gel electrolytes containing even-numbered \(-\text{CH}_2-\) groups.

From the above analysis we can conclude that the methylene units between the two amide carbonyl groups in the gelator molecule is the key in the self-assemble behavior. The special molecular arrangement creates different morphologies, types and sizes of the microscopic 3D network of the gel electrolyte. The type and size of the gel microstructures can directly influence the charge transport properties of the gel electrolytes.

### Table 2

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(I_{\text{ss}} (I_3^-)) (10(^{-7}) A)</th>
<th>(I_{\text{ss}} (I^-)) (10(^{-7}) A)</th>
<th>(D_{\text{app}} (I_3^-)) (10(^{-6}) cm(^2) s(^{-1}))</th>
<th>(D_{\text{app}} (I^-)) (10(^{-6}) cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1.45</td>
<td>5.98</td>
<td>3.76</td>
<td>4.20</td>
</tr>
<tr>
<td>Gel A ((n = 2))</td>
<td>0.30</td>
<td>1.39</td>
<td>0.78</td>
<td>0.98</td>
</tr>
<tr>
<td>Gel B ((n = 6))</td>
<td>0.23</td>
<td>0.98</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>Gel C ((n = 5))</td>
<td>0.99</td>
<td>4.15</td>
<td>2.55</td>
<td>2.92</td>
</tr>
<tr>
<td>Gel D ((n = 9))</td>
<td>0.67</td>
<td>2.76</td>
<td>1.73</td>
<td>1.94</td>
</tr>
</tbody>
</table>

### The influences of gelation on the kinetic processes of electron transport and recombination

Importantly, the amide carbonyl groups of gelators A–D can interact with \(\text{Li}^+\).\(^{40,41}\) As a result, the different morphologies of the microstructures of the gels probably cause different \(\text{Li}^+\) adsorption behaviors on the surface of the mesoporous TiO\(_2\) film, therefore, the kinetic processes of the electron transport and recombination can probably be changed in the devices based on the different gel electrolytes, which should be discussed in detail. In the gel electrolytes, the interaction between the amide carbonyl groups of the LMOGs and \(\text{Li}^+\) can be investigated by IR spectra and the results are shown in Scheme 1(A). It is accepted that the shift of the stretching vibration absorption band (1680 cm\(^{-1}\) to 1630 cm\(^{-1}\)) of the carbonyl group \((\nu_{C=O})\) in amide is considered to be an important information to confirm the interaction mentioned above.\(^{41}\) Scheme 1A(a) and A(b) show the IR spectra of the pure MePN solvent and solution of LiI dissolving in the MePN solvent, respectively, and there is no change in these two samples. Scheme 1A(c) shows the IR spectra of the MePN based gel without LiI, and the \(\nu_{C=O}\) is observed at 1648 cm\(^{-1}\). However, the \(\nu_{C=O}\) in the spectra of the MePN based gel with LiI (as shown in Scheme 1A(d)) shifts to the much lower frequency region and is observed at 1633 cm\(^{-1}\). This obvious shift reveals the interaction between the C=O of the gelator molecule and \(\text{Li}^+\). As is known that the \(\text{Li}^+\) can adsorb on the surface of the mesoporous TiO\(_2\) film and intercalate into the TiO\(_2\) lattice as shown in Scheme 1B(a). The interaction between the carbonyl groups and \(\text{Li}^+\) can results in a decreased adsorption of \(\text{Li}^+\) on the surface of the mesoporous TiO\(_2\) film as shown in Scheme 1B(b), this phenomenon can

![Scheme 1](image)
The photoinduced charge (Q) in the mesoporous TiO2 films was detected by IMPS/IMVS measurements. The dependence of the open circuit potential (Voc) on ln Q is shown in Fig. 5. For a given Q, the increase in Voc is attributed to an upward shift of the TiO2 conduction band edge. In contrast, the decrease in Voc is attributed to a downward shift of the TiO2 conduction band edge. As shown in Fig. 5, the conduction band edge of the TiO2 film in the QS-DSCs based on gel electrolytes shifts towards negative potentials compared with the liquid electrolyte based DSC. Generally, adsorption of Li+ ions from the electrolyte to the surface of the mesoporous TiO2 film increases the charge injection from the excited state dye due to the change in the conduction band edge to more positive potentials. In the gel electrolytes, the interaction between the amide carbonyl groups and Li+ results in a decreased adsorption of Li+ on the surface of the mesoporous TiO2 film. The decreased Li+ adsorption causes the conduction band edge of the TiO2 film in the QS-DSCs to shift upward. The ribbon 3D networks of gel electrolytes based on the LMOGs containing even-numbered –CH2– groups (gelator A and B) exhibit stronger steric hindrance effects on the Li+ adsorption than the woven 3D networks of gel electrolytes based on the LMOGs containing odd-numbered –CH2– groups (gelators C and D) due to bigger fibril sizes and more compact microstructures of the ribbon 3D networks. Therefore, the conduction band edges of the TiO2 film in the DSCs with gelators C and D are more positive than those with gelators A and B. In addition, the steric hindrance effects are increased with the increase of the alkyl chain length of the gelator, and the stronger steric hindrance effects decrease the adsorption amount of Li+ on the surface of the mesoporous TiO2 film. As a result, the conduction band edge of the TiO2 film in the DSCs with gelator B (n = 6) is more negative than that in the DSCs with gelator A (n = 2). This result can also be obtained between gelator D (n = 9) and gelator C (n = 5). Furthermore, the TiO2 conduction band edge movement is one of the decisive factors for the change of the open circuit potential. Generally, the increase in Voc could be caused by the negative shift of the TiO2 conduction band edge. On the other hand, if the conduction band edge moves to the positive potential, it could lead to a decreased Voc.

The gelation can also influence the kinetic processes of electron transport and recombination. Fig. 6 presents the comparison of the electron transport time (τd) and the electron recombination lifetime (τn) calculated by τd = 1/2πfimp and τn = 1/2πfinvs, where the fimp and finvs are the frequencies of the lowest imaginary component in the IMPS and IMVS plot, respectively. In addition, the electron collection efficiency (ηcoll) is determined by the competition between the transport of electrons through the TiO2 film and the recombination of photoinjected electrons with the redox electrolyte or oxidized dye, which could be evaluated by ηcoll = 1 − τd/τn (ref. 48) as shown in Fig. 6(c). Due to the different influences of the steric hindrance effect of the gel microstructures and lengths of alkyl chains of the gelators on the Li+ absorption, the decreased adsorption and intercalation of Li+ can reduce the amount of trap states and shallow the surface state energy distribution on the surface of mesoporous TiO2 films. Consequently, the electron transportation should be accelerated, and the order of τd is gel B < gel A < gel D < gel C as can be seen in Fig. 6(a). Furthermore, the process of electron recombination can be reflected by recombination current density (Jr), which depends on the rate constant for back electron transfer k, the concentration of the oxidized half of the redox couple c_ox and the electron density n, as shown in eqn (3).

\[ J_r = k c_\text{ox} n^2 \]

Fig. 5 Voc as a function of ln Q in the DSCs based on the liquid electrolyte and gel electrolytes.

Fig. 6 Light intensity dependence of (a) electron transport time (τd), (b) electron recombination lifetime (τn) and (c) electron collection efficiency (ηcoll) in DSCs based on the liquid electrolyte and gel electrolytes.
where exponent $\gamma$ has typical values of 2–3 (ref. 51 and 52) but can be larger. $^{44}$ Compared with the liquid electrolyte, the crosslinked 3D networks of gel electrolytes obstruct the diffusion of $I^-$ and $I_3^-$, resulting in an increased $c_{nk}$ in the TiO$_2$/electrolyte interface, and the $J_f$ is increased and the electron lifetime is shortened. As can be seen in Fig. 6(b), the $\tau_n$ of the liquid electrolyte based DSC is longer than that of the gel electrolyte based DSCs. And owing to the more obstructed ribbon 3D networks for charge diffusion than the woven 3D networks and the increased steric hindrance effect with the long length of the carbon chains, the $\tau_n$ is decreased in the QS-DSCs based on gelators C, D, A and B in sequence, which also indicates that the electron recombination in the TiO$_2$/electrolyte interface is accelerated with the decreased $\tau_n$ in the gel based DSCs, and further lead to a decreased $V_{oc}$.

Photovoltaic performances and stabilities of quasi-solid-state dye-sensitized solar cells fabricated based on LMOGs

Fig. 7 shows a typical photocurrent density–voltage curve at AM 1.5 (100 mW cm$^{-2}$), the dark current–voltage curve and IPCE spectra for the DSCs based on the liquid electrolyte and gel electrolytes A–D. The photovoltaic performances of the short circuit photocurrent density ($J_{sc}$), open circuit potential ($V_{oc}$) and photoelectric conversion efficiency ($\eta$) are listed in Table 3. It is well known that the IPCE value is the ratio of the observed photocurrent divided by the incident photon flux. $^{53}$

$$\text{IPCE} = \eta_{lh}\eta_{inj}\eta_{coll}$$

(4)

where $\eta_{lh}$ is the product of the light-harvesting efficiency of the dye, $\eta_{inj}$ is electron injection efficiency and $\eta_{coll}$ is the electron collection efficiency. The $\eta_{lh}$, which is determined by the loading and extinction coefficient of the dye, is considered to be the same for all the DSCs in this article due to the equal adsorption capacity of N719 on the TiO$_2$ electrode. $^{44}$ Therefore, according to the eqn (4), it can be confirmed that the change of IPCE is the same as the order of $\eta_{inj}$ and $\eta_{coll}$ as concluded above (liquid $>$ gel C $>$ gel D $>$ gel A $>$ gel B). As shown in Table 3, the $J_{sc}$ of the QS-DSCs based on gelators C and D is higher than those of the QS-DSCs based on gelators A and B, which results from the higher IPCE and $D_{app}$. Fig. 7 also shows that the dark current increased after the liquid electrolyte was gelated, which results from the aggravated electron recombination in the TiO$_2$ photoelectrode/electrolyte interface by gelation. Moreover, the order of the dark currents for these DSCs is gel B $>$ gel A $>$ gel D $>$ gel C $>$ liquid, which indicated that the recombination is slower in the woven-shaped 3D network based QS-DSCs than those in the ribbon 3D network based QS-DSCs.

The TiO$_2$ conduction band edges of DSCs based on the gel electrolytes were shifted to a more negative potential compared with the DSC based on the liquid electrolyte, which would contribute to the $V_{oc}$. However, on the other hand, the $V_{oc}$ is also influenced by the electron recombination in the TiO$_2$ photoelectrode/electrolyte interface. $^{55,56}$ Therefore, it can be concluded that the lower $V_{oc}$ of QS-DSCs is mainly caused by the increased electron recombination. Finally, compared with the DSCs based on the gels A, B and D, due to the faster diffusion of ions, higher electron injection efficiency and lower electron recombination, a superior QS-DSC based on the gelator containing five –CH$_2$– groups (gel C) was obtained. Although this device has the slightly lower $J_{sc}$ and $V_{oc}$ than those of the DSC based on the liquid electrolyte, the $\eta$ (7.53%) of this QS-DSC is very close to that of the DSC based on the liquid electrolyte (7.93%).

Importantly, although the photovoltaic performances of QS-DSCs based on LMOGs are slightly lower than the corresponding liquid based DSC, they exhibit excellent long-term stability. As is shown in Fig. 8, the photoelectric conversion efficiencies of all QS-DSCs could retain 85–93% of their initial values after 60 °C thermal stress for 1000 h, but the liquid electrolyte based DSC retained only 76%. Moreover, during successive one sun light soaking for 1000 h, the photoelectric conversion efficiency of the liquid electrolyte based DSC retained 83% of its initial value, while the photoelectric conversion efficiencies of QS-DSCs retained 95–97% of their initial values, which indicates that the network of the gel electrolyte could hinder the leakage of the liquid electrolyte effectively. These accelerated aging results revealed that the QS-DSCs are more stable than the liquid based DSC, which is caused by the good intrinsic stability of the LMOGs and the high $T_{gel}$ of the gel electrolytes.

![Fig. 7 J–V curves at AM 1.5 (100 mW cm$^{-2}$) and dark conditions for the DSCs based on the liquid electrolyte and gel electrolytes. The inset shows the IPCE spectra for these DSCs.](image-url)
Conclusions

In summary, a series of didodecanoylamides of \( \alpha, \omega \)-alkylidenediamines containing different numbers of \( -\text{CH}_2- \) groups between the two amide carbonyl groups were synthesized and successfully introduced into a MePN based liquid electrolyte. The different molecular structures of the LMOGs cause different molecular self-assemblies of the gelators and result in different types of 3D networks. The gels with LMOGs containing even-numbered \( -\text{CH}_2- \) groups (gelators A and B) and odd-numbered \( -\text{CH}_2- \) groups (gelators C and D) exhibit ribbon and woven networks, respectively. The much smaller fibril size and less compact network of the woven network lead to the higher diffusion of redox species (\( \text{I}^- \) and \( \text{I}_3^- \)) and conductivity compared with the ribbon network, which results in the reduced dark reaction and contributes to the \( J_{sc} \) and \( V_{oc} \) of the QS-DSCs. Because of the positive shift of the conduction band edge which results from the increased adsorption of \( \text{Li}^+ \) on the surface of the mesoporous TiO\(_2\) films, the QS-DSCs based on the gelators containing odd-numbered \( -\text{CH}_2- \) groups have much higher \( \eta_{maj} \) and IPCE than those containing even-numbered \( -\text{CH}_2- \) groups, which also lead to the higher \( J_{sc} \) of the QS-DSCs based on the gelators containing odd-numbered \( -\text{CH}_2- \). Finally, a superior QS-DSC based on the gelator containing five \( -\text{CH}_2- \) groups was obtained. This device exhibited a higher photoelectric conversion efficiency of 7.53% similar to the corresponding liquid based DSC (7.93%). Importantly, due to the good intrinsic stability of the LMOGs and the high \( T_{gel} \) (over 100 °C) of the gel electrolytes, the network of the gels can reduce the volatilization and leakage of the liquid electrolyte effectively and all the QS-DSCs exhibit excellent thermal and light-soaking stabilities during the accelerated aging test. The excellent photovoltaic performance and good long-term stability of QS-DSCs are important for their application and commercialization. Furthermore, this work demonstrates an important strategy to obtain QS-DSCs with high efficiency and excellent stability using the functional gel electrolytes by designing the molecular structures of LMOGs at the molecular level.

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References
