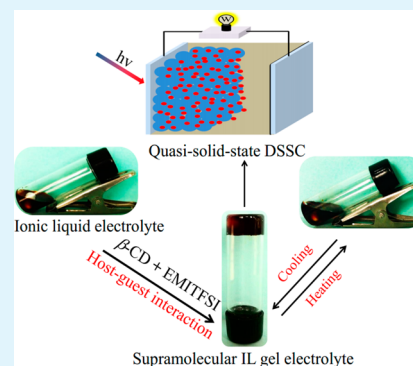


Supramolecular Ionic Liquid Gels for Quasi-Solid-State Dye-Sensitized Solar Cells

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ABSTRACT: A 1-propyl-3-methylimidazolium iodide based supramolecular ionic liquid gel was prepared through the host–guest interactions between a host of β -cyclodextrin and a room temperature ionic liquid type guest, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, which contains bis((trifluoromethyl)sulfonyl)imide as the guest group. The gel-to-sol phase transition temperature of the prepared supramolecular ionic liquid gel could be tuned by the ratio of host to guest. The synthesized supramolecular ionic liquid gel was further applied in quasi-solid-state electrolyte dye-sensitized solar cells, which showed a power conversion efficiency of 4.79% under the simulated air mass 1.5 solar spectrum illumination at 100 mW cm^{-2} and excellent long-term stability.



KEYWORDS: supramolecular gel, ionic liquid, β -cyclodextrin, host–guest, dye-sensitized solar cells

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted a great deal of academic and industrial attention because of their low cost and high efficiency.^{1,2} Recently, a photoelectric conversion efficiency exceeding 12% has been achieved based on an organic solvent electrolyte.³ However, there are still several drawbacks, such as the leakage and volatilization of organic solvent, dye degradation and limited long-term performance, which increase the difficulty of device fabrication and inhibiting the outdoor widespread application.⁴ To overcome the drawbacks, *p*-type semiconductors,^{5,6} organic and inorganic hole transportation materials^{7–9} and inorganic filler and polymer based gel^{10–14} have been applied as alternatives to liquid electrolytes.

Ionic liquids (ILs) are room temperature molten salts with negligible vapor pressure, high thermal stability and ionic conductivity, and the ability to dissolve organic and inorganic solutes as well as tunable solvent properties.^{15–18} They have been widely used to replace traditional volatile organic solvents in DSSCs due to their low volatility and high ionic conductivity.^{19–22} However, devices based on room temperature IL electrolytes are still demonstrating leakage problems in practical use.^{23,24}

Supramolecular self-assembly has been considered as one of the most dynamic and interdisciplinary areas of science, with great application potentials for a wide range of fields.^{25–27} Among the self-assembly strategies studied, supramolecular host–guest chemistry that employs well-established non-covalent interactions for achieving stimulus-responsive functional materials has attracted great attention. Macrocyclic hosts, including cyclodextrins (CDs),²⁸ crown ethers,²⁹ pillar[n]-arenes,³⁰ and cucurbit[n]urils^{31,32} have promoted the growth of the supramolecular structures (such as gels) and materials.³³

Here, we report the synthesis of IL gels via supramolecular host–guest recognition in room temperature ILs. A room temperature IL, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMITFSI), which contains bis((trifluoromethyl)sulfonyl)imide (TFSI[−]) was chosen as the guest, whereas β -cyclodextrin (CD) was used as the host compound. A proper ratio of β -CD and EMITFSI in a hydrophilic IL, 1-propyl-3-methylimidazolium iodide (PMII), yielded the transparent supramolecular IL gels. The resultant supramolecular IL gels show high conductivity, which is comparable to that of the pure room temperature ILs. The gel-to-sol phase transition temperature of formed supramolecular IL gels could be tuned by the ratio of host to guest. The prepared supramolecular IL gels with the melting temperature above $45 \text{ }^\circ\text{C}$ were further applied as the quasi-solid-state electrolytes for DSSCs, which show a power conversion efficiency of 4.79% and excellent long-term stability.

EXPERIMENTAL SECTION

Materials. 1-Iodoethane, 1-iodopropane, iodine (I_2), β -cyclodextrin (β -CD), 4-*tert*-butylpyridine (TBP) and guanidinium thiocyanate were purchased from Alfa Aesar. 1-Propyl-3-methylimidazolium iodide (PMII)/1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMITFSI) were synthesized according to the previous reports.³⁴ Lithium bis((trifluoromethanesulfonyl)imide) (LiTFSI) was kindly provided by Rhodia and used as received. *cis*-Bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) ($[\text{RuL}_2(\text{NCS})_2]$) (dye N719) was purchased from Solaronix SA (Switzerland) and used without further

Received: March 13, 2014

Accepted: April 29, 2014

Published: April 29, 2014

purification. TiCl_4 and H_2PtCl_6 were purchased from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide overlayer (FTO) glass electrodes ($7 \Omega/\text{Sq}$), luries containing 20 nm-sized mesoporous and 200 nm-diameter light-scattering TiO_2 colloidal were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd. (China).

Preparation of Electrolytes. The ionic liquid electrolyte was prepared by stirring of a mixture of PMII, 0.5 M I_2 , 0.1M guanidinium thiocyanate and 0.5 M TBP at 60 °C for 8 h. The supramolecular IL gel electrolyte was prepared by the addition of $\beta\text{-CD}$ (20 wt %) and EMITFSI ($\beta\text{-CD}:\text{EMITFSI} = 1:4$ molar ratio) into the prepared ionic liquid electrolyte with an elevated temperature under continuous stirring and be dried under vacuum at room temperature for 24 h before the characterization and fabrication of DSSCs.

Fabrication of the DSSCs.^{35,36} The cleaned FTO glass was covered with perforated adhesive tape to control the thickness and the area of mesoporous TiO_2 film (the area of TiO_2 film is about 0.283 cm^2). The FTO glass was immersed into a 40 mM aqueous TiCl_4 solution at 60 °C for 30 min and washed with water and ethanol. Then two layers of TiO_2 particles were deposited onto cleaned FTO glass and used as photoelectrodes. A 5 μm thick film of 20 nm-sized TiO_2 particles was deposited onto the FTO glass electrode by the doctor-blade technique. The film was dried at 125 °C for 5 min. Then, a second 3 μm thick layer of 200 nm light-scattering anatase particles were coated on the top of the first TiO_2 layer. The resulting TiO_2 films were annealed at 500 °C for 30 min. The two-layer TiO_2 film was further treated with 40 mM aqueous TiCl_4 solution, and then rinsed with water and ethanol and sintered at 500 °C for 30 min. After cooling to 80 °C, the obtained TiO_2 electrode was immersed in 0.5 mM solution of N719 in acetonitrile and *tert*-butyl alcohol (v:v = 1:1) at room temperature for 24 h. Then the dye-coated TiO_2 electrode was washed with anhydrous ethanol and dried with nitrogen stream. For the preparation of the Pt counter electrode, two drops of 2 mM H_2PtCl_6 in ethanol was placed onto the cleaned FTO glass substrate, followed by drying and annealing at 400 °C for 15 min.

DSSCs were fabricated by sandwiching electrolytes between a dye-sensitized TiO_2 electrode and a Pt counter electrode, which were separated by a 25 μm thick hot melt ring (Surlyn, Dupont) and sealed by heating. The cell was filled with electrolytes via vacuum backfilling at a temperature of 50 °C, which is above the gel-to-sol phase transition temperature of supramolecular IL gels. The electrolyte injection hole on the thermally platinized FTO counter electrode was finally sealed with a Surlyn sheet and a thin glass by heating.

Characterization and Photovoltaic Measurements. The supramolecular gel with a gel-to-sol phase transition temperature ($T_{\text{gel-sol}}$) was determined by a Q200 differential scanning calorimeter at a scanning rate of $10 \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. Steady-state voltammetry was tested in a conventional photoelectrochemical cell equipped with a 5.0 mm radius platinum ultramicroelectrode (CHI107) as the working electrode and a platinum foil as the counter electrode. The conductivity of the electrolytes was characterized in an ordinary cell composed of Teflon tube and two identical stainless steel electrodes (diameter of 1 cm) on a CHI660c electrochemical workstation at room temperature, using the AC impedance method over the frequency range 1 Hz – 1 MHz. The conductivity was calculated using the following equation:

$$\sigma = \frac{l}{RS}$$

where σ is the conductivity in S cm^{-1} , R is the ohmic resistance of the electrolyte, l is the distance between the two electrodes and S is the area of the electrodes.³⁷

The electrochemical impedance spectra (EIS) of the devices were tested using a CHI660c electrochemical workstation using the AC impedance method at the forward bias voltage for the impedance measurement was -0.7 V and the frequency ranged from 0.01 to 105 Hz under dark conditions and the amplitude was 5 mV. The photocurrent density–voltage ($J\text{-}V$) curves of the assembled DSSCs shielded by an aluminum foil mask with an aperture area of 0.1 cm^2 were measured with a digital source meter (Keithley, model 2612) under simulated air mass (AM) 1.5 solar spectrum illumination at 15,

50, and 100 mW cm^{-2} , respectively. Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength was recorded on a Keithley 1612 source meter under the irradiation of a xenon lamp with a monochromator (Oriol Cornerstone 260 1/4).

RESULTS AND DISCUSSION

Preparation and Characterization of the Supramolecular Ionic Liquid Gel. Figure 1 depicts the synthetic

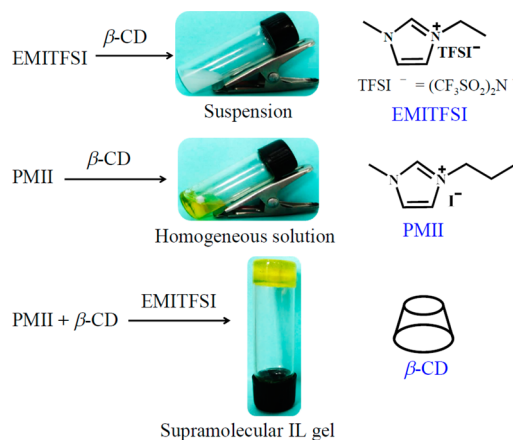


Figure 1. Schematic representation for the synthesis of supramolecular IL gels.

route of supramolecular IL gels. $\beta\text{-CD}$, one of the most common CDs with a hydrophobic cavity, was chosen as the host, whereas a hydrophobic room temperature IL, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide (EMITFSI) was chosen as the guest because TFSI^- anions could be encapsulated into the cavity of $\beta\text{-CD}$ through host–guest interactions.³⁸ Unfortunately, the mixture of $\beta\text{-CD}$ with EMITFSI only formed a turbid white suspension (Figure 1, top), indicating that $\beta\text{-CD}$ cannot be well dissolved in EMITFSI, even after being heated at 50 °C for 10 min. However, the dissolve of $\beta\text{-CD}$ (20 wt %) in a hydrophilic IL, 1-propyl-3-methylimidazolium iodide (PMII), yielded a transparent solution (Figure 1, middle), indicating that PMII could be a good solvent for $\beta\text{-CD}$. It is worth noting that a transparent and stable IL gel was obtained upon the addition of EMITFSI to a $\beta\text{-CD}/\text{PMII}$ solution (Figure 1, bottom). Therefore, it can be concluded that PMII is a good solvent for both $\beta\text{-CD}$ and EMITFSI, which is necessary for the supramolecular IL gelation.

The mechanism of the supramolecular IL gel formation is still not clear. The presence of both $\beta\text{-CD}$ and TFSI^- in the IL mixture may form the inclusion complexes and then decrease the fluidity of ionic liquids. However, we envisioned that only the host–guest interaction could not form the supramolecular IL gels because the TFSI^- anions could be encapsulated into the cavity of $\beta\text{-CD}$ through host–guest interactions,³⁹ which reduced the number of anions and thus positively charged the ILs surrounding the $\beta\text{-CD}$ s. As the driving force, the electrostatic repulsions between the imidazolium cations show higher ionic strengths than the surrounding IL solutions, which would expect it to take up more ILs to maintain osmotic equilibrium. In addition, there are hydrogen-bond networks formed among the hydroxyl groups of CDs and imidazolium cations.^{40–42} Therefore, it is assumed that both the hydrogen-bond networks and electrostatic repulsive force induced by

inclusion complexes between β -CD and TFSI⁻ play a key role for the supramolecular IL gelation. Furthermore, other factors, including hydrophobicity, van der Waals interactions, changes in solvent–surface tensions and the release of the CD ring strain may also play a role.⁴³ However, the gelation mechanism behind our observations is still under exploration.

Previous studies have already recognized that the complex between a TFSI⁻ anion and β -CD increases the distance between a TFSI⁻ anion and imidazolium cation, which leads to a reversible thermoresponsive complexation–dissociation effect at relatively low temperatures.⁴⁴ Here, it was found that the gel-to-sol phase transition temperature increased gradually with the rising amount of EMITFSI and then slightly decreased with further addition (Figure 2). For example, the gel-to-sol

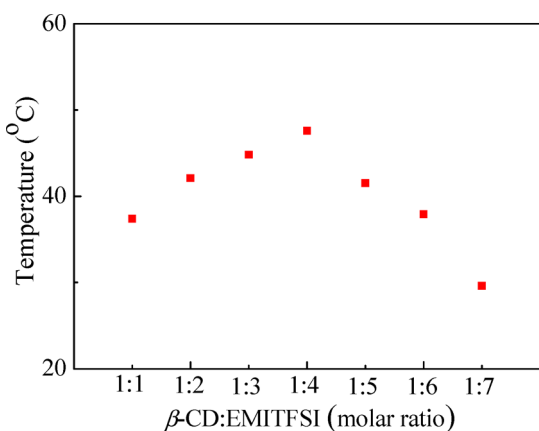


Figure 2. Dependence of the T_{gel} with 20 wt % β -CD as a function of the ratio of β -CD and EMITFSI in PMIL.

phase transition temperature increased from 36.5 to 47.6 °C with the increase of EMITFSI to β -CD ratio from 1:1 to 4:1, due to the enhanced host–guest interactions. Further increases in EMITFSI content decreasing the gel-to-sol phase transition temperature might due to the diluted host–guest inclusion complexes. The formation of supramolecular IL gels was also investigated by detailed ¹⁹F NMR analysis (Figure 3). As the

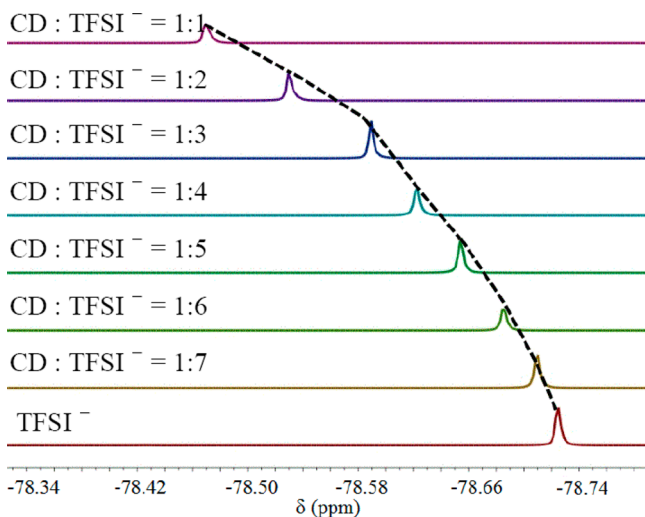


Figure 3. ¹⁹F NMR spectra (using NaF as an internal reference) for various molar ratios of β -CD/EMITFSI and pure EMITFSI. All the samples were dissolved in D₂O.

ratio of β -CD/EMITFSI changed, clear upfield shifts of fluorine signal were observed. The results of ¹⁹F NMR further confirmed the interactions between β -CD and the TFSI⁻ anion.

Characterization of DSSCs. A supramolecular IL gel with a gel-to-sol phase transition temperature at 47.6 °C was further applied as the quasi-solid-state electrolyte for DSSCs, as shown in Figure 4. It should be noted that addition of other

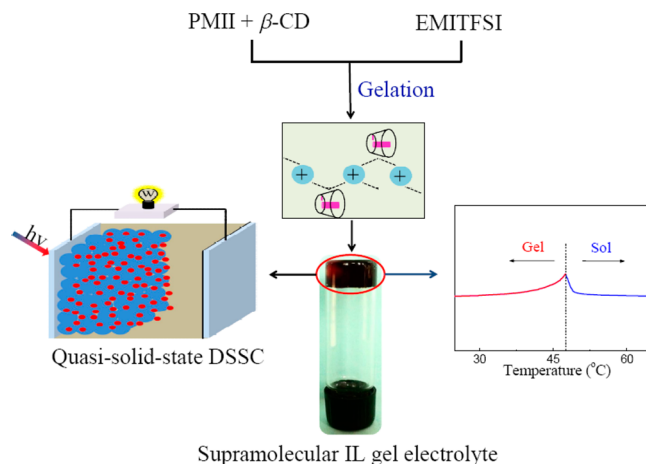


Figure 4. Photographs of supramolecular quasi-solid-state gel electrolyte for DSSCs and possible mechanism of gel formation. The supramolecular gel electrolyte was prepared by adding a mixture of β -CD/EMITFSI (1:4, molar ratio) (20 wt %) into the prepared ionic liquid electrolyte containing PMII, 0.5 M I₂, 0.1 M guanidinium thiocyanate and 0.5 M TBP.

components (such as 4-*tert*-butylpyridine (TBP) and I₂) into the electrolytes does not change the gelation behavior of the supramolecular IL gels. Compared to polymer or hybrid gels reported, the thermoreversible feature of the supramolecular IL gels provides a great convenience for filling gel electrolytes.

Figure 5 shows the steady-state voltammograms of the IL and supramolecular IL gel electrolytes. The coefficient values of

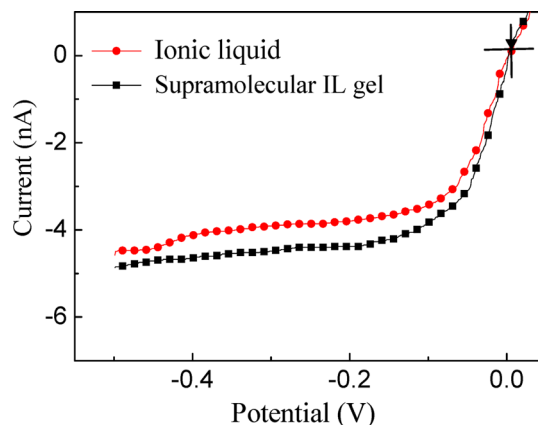


Figure 5. Steady-state voltammograms of ionic liquid and supramolecular IL gel electrolytes.

I₃⁻ are calculated through the anodic and cathodic steady-state I_{ss} according the following equation:⁴⁵

$$I_{ss} = 4nrFCDapp$$

where n is the number of electrons per molecule, F is the Faraday constant, r is the radius of the ultramicroelectrode and

Table 1. Parameters of DSSCs with Ionic Liquid and Supramolecular IL Gel Electrolytes^a

electrolyte	σ (1×10^{-4} S cm ⁻¹)	D (cm ² s ⁻¹ I ₃ ⁻ /10 ⁻⁸)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF (%)	η (%)
ionic liquid	7.73	12.7	592(±5)	13.7(±0.2)	67.0(±0.5)	5.41(±0.12)
supramolecular IL gel	6.54	8.8	567(±4)	12.7(±0.3)	66.5(±0.5)	4.79(±0.14)

^aAverage of three cells.

C is the bulk concentration of the electroactive species. The calculated ion conductivity and diffusion coefficient values are summarized in Table 1. The calculated diffusion coefficients of triiodide in the IL electrolyte and supramolecular IL gel electrolyte were 1.27×10^{-7} and 8.8×10^{-8} cm² s⁻¹, respectively, indicating that the formation of supramolecular IL gel has little effect on the ion transport properties of the electrolytes. Similar results were observed for the values of the conductivity.

Figure 6a shows the J - V curves of the fabricated DSSCs based on ionic liquid and supramolecular IL gel electrolytes,

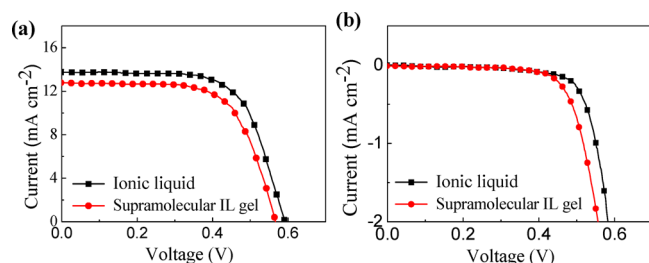


Figure 6. J - V curves of DSSCs consisting ionic liquid and supramolecular IL gel electrolytes (a) under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} and (b) under dark conditions. Cell area was tested with a mask (area: 0.1 cm^2).

respectively. The photovoltaic parameters containing open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and the photoelectric conversion efficiency (η) of DSSCs are summarized in Table 1. It can be seen that the ionic liquid electrolyte exhibited a J_{sc} of 13.7 mA cm^{-2} , V_{oc} of 592 mV, FF of 66.7% and yielded an overall power conversion efficiency (η) of 5.41%. With the addition of β -CD and EMITFSI, the corresponding photovoltaic parameters (J_{sc} , V_{oc} , FF and η) of the supramolecular gel electrolyte are 12.7 mA cm^{-2} , 567 mV, 66.4%, and 4.79%, respectively, indicating that the addition of host-guest compounds have only a little adverse effect on the power conversion efficiency of the device. The lower dark current can result in a higher V_{oc} value and a lower rate of recombination at TiO_2 /electrolyte interface, as shown in Figure 6b, which could reflect on the device performance.⁴⁶ It is noted that the dark current is negatively shifted by approximately 26 mV from the ionic liquid to supramolecular IL gel electrolyte, which is consistent with the resultants of V_{oc} and overall power conversion efficiency.

The incident photon-to-current conversion efficiency (IPCE) spectra (Figure 7) shows a maximum value of 69.39% and 64.4% at 530 nm for IL and supramolecular IL gels, respectively. The IPCE values are consistent with above studies about J_{sc} and power conversion efficiency. The photovoltaic performance parameters of the devices under different light intensity illumination are also tested and summarized in Table 2.

Electrochemical impedance spectroscopy (EIS) was then studied to investigate the kinetics of the electrochemical and photoelectrochemical processes, such as the interpretation of

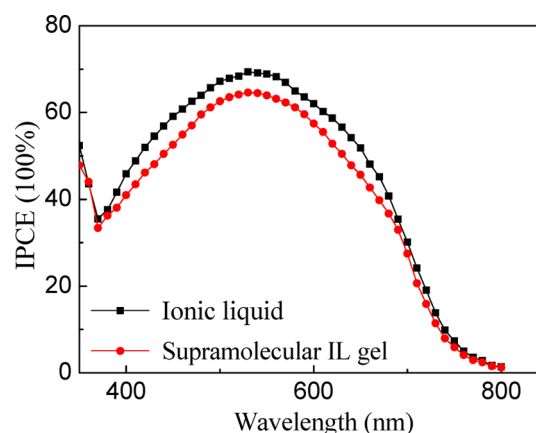


Figure 7. IPCE curves of DSSCs based on IL and IL gel electrolytes.

Table 2. PCE Values of DSSCs Based on Different Electrolytes under Simulated AM 1.5 Solar Irradiation^a

electrolyte	PCE under different incident light intensities irradiation (%)		
	1.0 sun	0.5 sun	0.15 sun
ionic liquid	5.41(±0.12)	5.86(±0.13)	5.43(±0.11)
supramolecular IL gel	4.79(±0.14)	5.21(±0.14)	4.83(±0.12)

^aAverage of three cells.

obvious electronic and ionic processes in DSSCs. Figure 8a shows the EIS spectra measured at -0.7 V bias in a dark

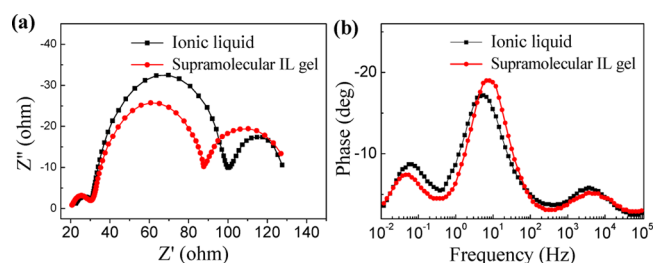


Figure 8. EIS Nyquist plots (a) and Bode phase plots (b) in dark for different electrolytes.

environment. In general, the EIS spectra of a DSSC consist of three semicircles from high to low frequency, R_1 , R_2 and R_3 , they represent the resistance of Pt counter electrode/electrolyte interface, TiO_2 film/electrolyte interface, and the Nernst diffusion in electrolyte, respectively. The bigger the semicircle in the intermediate-frequency region, the slighter the charge recombination at the photoelectrode/electrolyte interface. It can be seen that the addition of β -CD and EMITFSI reduced the resistance of the charge-transfer elements at the TiO_2 photoelectrode/electrolyte interface and leading to an increase recombination. The result is in agreement with our test about dark current and V_{oc} . In addition, compared with the IL electrolyte, the value of R_3 increases in the gel electrolyte, indicating a decrease of diffusion coefficients of triiodide and J_{sc} .

These results further support the determined $J-V$ results of the device. Figure 8b shows the Bode phase plots of EIS spectra, which display the characteristic frequency peaks of the charge transfer process for all cells. The effective lifetime of electrons (τ_e) before recombination in TiO_2 photoelectrode can be related to the inverse of the characteristic frequency and estimated by the following equation:⁴⁷

$$\tau_e = \frac{1}{\omega_{\max}} = \frac{1}{2\pi f_{\max}}$$

where f_{\max} is the maximum frequency of the low-frequency peak. The electron lifetime of recombination (τ_e) for ionic liquid and supramolecular IL gel electrolyte is 30.7 and 21.2 ms, respectively. The value of supramolecular IL gel electrolyte is enough to favor electron transport through a longer distance with less diffusive hindrance, and finally leads to enhanced photoconversion efficiency.

To investigate the long-term stability of the fabricated devices, the cells fabricated with the ionic liquid and supramolecular IL gel electrolytes are stored under ambient conditions without further sealing. The PCE of the cells is measured every 7 days and the total efficiencies are normalized to the values measured on the first day (Figure 9). During the

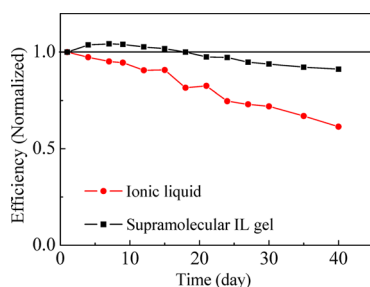


Figure 9. PCEs of DSSCs containing ionic liquid and supramolecular IL gel electrolytes as a function of time.

first 7 days, the efficiency of gel electrolyte was enhanced because of the increase of the dye re-generation rate, and thus increased the J_{sc} value. In the case of the ionic liquid electrolyte, the efficiency decrease gradually possibly due to the electrolyte leakage. It should be noted that the cell containing gel electrolyte still maintains a high efficiency of 91 % after 40-day test, indicating that devices based on this type of gel electrolyte have excellent practical stability.

CONCLUSIONS

In conclusion, a host-guest recognition-induced supramolecular ionic liquid gel was synthesized and successfully employed for quasi-solid-state dye-sensitized solar cells. DSSCs based on the supramolecular IL gel electrolyte shows an excellent long-term stability and an efficiency of 4.79%, which is close to that of the ionic liquid electrolyte. The supramolecular IL gel electrolytes prepared in this work could overcome the leakage problem of liquid electrolytes and demonstrate a feasible approach for quasi-solid-state DSSCs in the practical applications.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of China (No. 21274101), National Basic Research Program of China (973 Program, No. 2012CB825800) and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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