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New Class of Ionic Liquids for Dye-Sensitized Solar Cells

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1. Introduction

1.1. Dye-Sensitized Solar Cells (DSSCs)

Nowadays, the raising consumption of fossil fuel illustrates the urgent needs for alternative energy resources. Considering the variable environmental issues, renewable clean energy resources is the most reliable replacement for the sustainable usage in the future due to their unlimited energy input onto the earth. Among various kinds of renewable clean energy, solar energy is the only external energy source derived from outer space. Solar energy is nominated for its clean, non-hazardous, sufficient, and infinite power supply, and it is remarkable that a mere 10 min of solar irradiation onto the earth's surface is equal to the total yearly human energy consumption [1]. Thereby, solar energy can be considered as the most promising renewable power supplement without limitation in the next generation. Solar energy conversion can be divided into three parts: solar-to-electricity conversion, solar-to-chemical conversion, and solar-to-thermal conversion. For the case of solar-to-electricity conversion, plenty of solar cells have been widely explored for decades; the most common solar cell is the inorganic solid-state junction devices, including GaAs or CdTe tandem cells, crystalline or amorphous silicon solar cells, and CIGS or CZTS solar cells. However, the expensive, energy-intensive, high-temperature, and high-vacuum processes is needed for the fabrication of inorganic solid-state junction devices, thereby the extremely high cost of those solar cells limits their usages and applications. Therefore, the third generation solar cells are designed to cost down and are based on the cheap, simple, and easy fabrication process.

In recent years, dye-sensitized solar cells (DSSCs) have been extensively investigated and wildly developed due to its outstanding advantages, *i.e.*, low-cost production, large-scale fabrication, and good conversion efficiency. In 1991, Professor M. Grätzel introduced the

nanoporous films as the dye-derived wide-band semiconductor and made the breakthrough in the solar-to-chemical conversion efficiency of DSSCs [2]. In 2014, by incorporating the novel porphyrin dye (SM315), the DSSC containing the cobalt complex redox electrolyte reached the highest efficiency record of 13.00% [3], which encouraged lots of explorations of new organic materials for higher efficiency. As shown in Figure 1, a DSSC device is in a sandwich-like construction, which is composed of three adjacent thin layers [4]: (1) working electrode contains a high band-gap nanocrystalline semiconductor-based mesoporous film adsorbed with dye molecules; (2) the electrolyte contains a redox mediator and several additives; (3) counter electrode contains a electrocatalytic film. Generally, for a working electrode, the titanium dioxide (TiO_2) semiconductor is used for the mesoporous film, and the ruthenium bipyridyl derivatives (N3, N719, Z907 or black dye, *etc.*) are employed for the dye sensitizers. For the counter electrode, the platinum thin film is usually applied for collecting electrons and triggering the redox reaction of the electrolyte. The electrolyte mostly contains iodide/triiodide (I/I_3^-) redox couple, which is obtained by the mixing of iodine (I_2) and inorganic or organic salts with iodide anion in suitable non-aqueous solvents.

The solar-to-electricity conversion mechanism of the DSSCs [4-5] is motivated from the solar illumination as shown in Figure 2. Upon absorption of light, a photo-induced electron is injected from a metal-to-ligand charge transfer excited state of the dye into the conduction band of the TiO_2 film. The rate of this electron injection reaction is ultrafast, typically occurring on the order of hundreds of femtoseconds to tens of picoseconds. The injected electron transports through the TiO_2 film via a "hopping" mechanism, which is driven by a chemical diffusion gradient (rather than an electric field), and is collected at a transparent conductive substrate of fluorine doped tin oxide glass. After passing through an external circuit, the electron is reintroduced into the solar cell at the platinum counter electrode, where triiodide ion is reduced to iodide ion. The iodide then regenerates the oxidized dye, thereby completing the circuit without net chemical change. Among a DSSC, the electrolyte is a key part to determine the cell performance, because it provides the necessary ionic conductivity in the bulk of the electrolyte solution and sets the proper potential barrier for the energy conversion. In addition, it offers a reduction reaction at the counter electrode and helps for the dye regeneration by the charge-transfer reaction with the dye molecules. However, the DSSCs encounter two virtual problems induced by using the conventional liquid electrolytes: (i) limited conversion efficiency and (ii) poor long term stability. The limited conversion efficiency is mainly caused by some unfavorable reactions, including the recombination between the photo-induced electrons and I_3^- ions, and the delayed dye regeneration due to the low diffusivity and ionic conductivity of the electrolyte, *etc.* The poor long term stability is attributed to the evaporation and leakage of organic solvent in the liquid electrolyte; also, the permeation of oxygen and water and their corresponding side reactions with the electrolyte can damage the stability. To solve these two problems, ionic liquids (ILs) can be considered to be most attractive for replacing the conventional electrolytes due to their low melting points (below 100 °C), good chemical and electrochemical stability, high thermal stability, non-toxic, non-flammability, negligible vapor pressure, and high ionic conductivity [6-8].

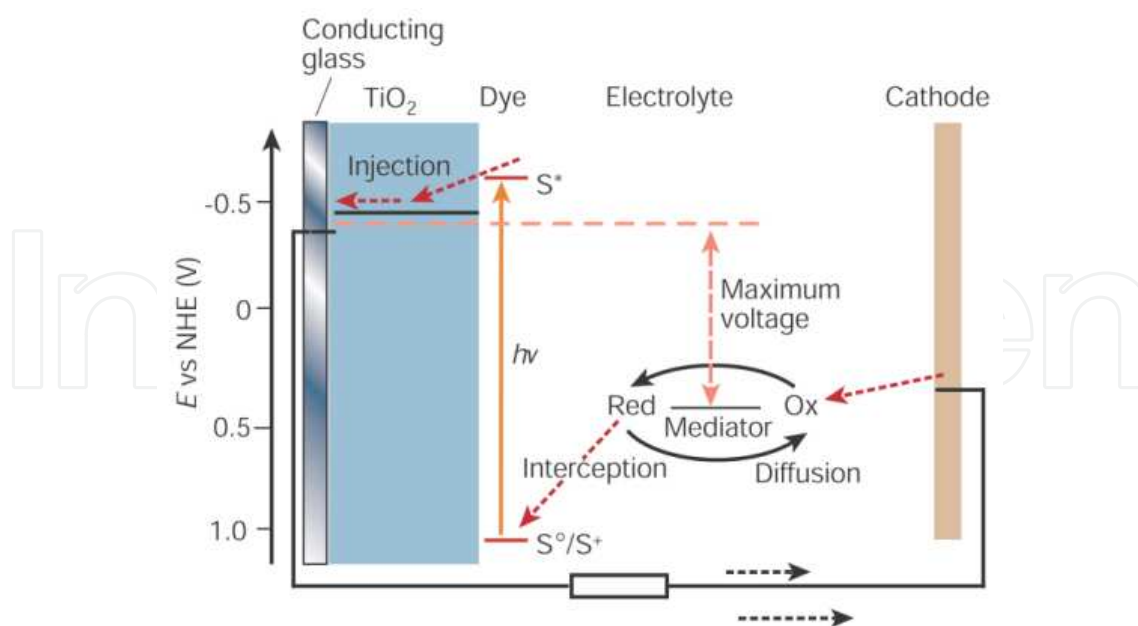


Figure 1. The construction of dye-sensitized solar cells (DSSCs) [4].

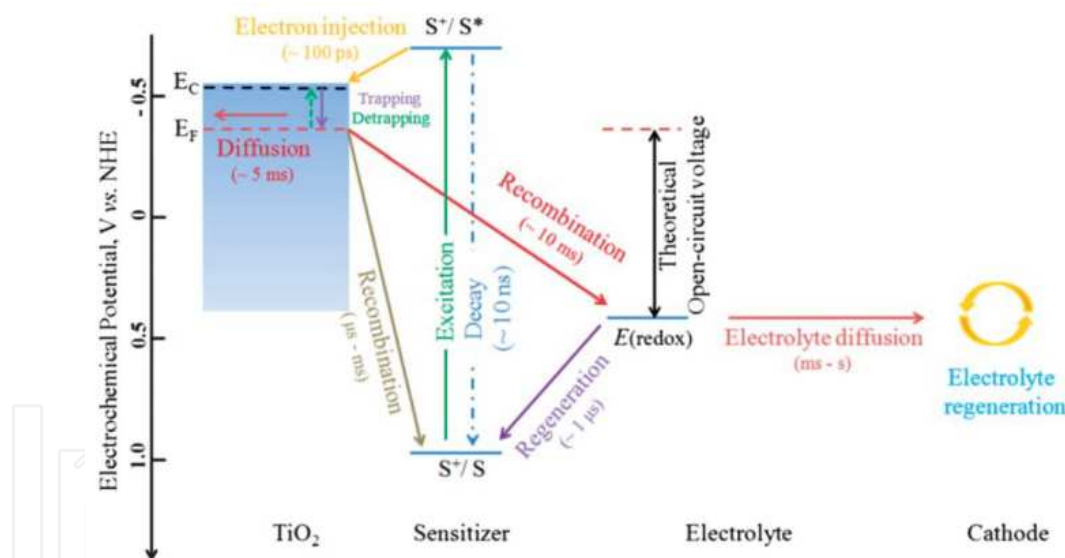


Figure 2. The energy diagram of the kinetics of DSSC function [5].

1.2. Ionic liquids as the mediator for DSSCs

Traditional ILs are composed by only ions and are characterized by the weak interactions between the large cations and a charge-delocalized anions. Therefore, the ILs are in a low tendency to crystallize due to the flexibility caused by the anions and the dissymmetry caused by the cations. ILs are basically composed of organic cations and anions [6-8]; the cations include imidazolium, N-substituted imidazolium, benzimidazolium, pyridinium, pyrrolidi-

nium, alkylammonium, alkylphosphonium, guanidinium, alkylpyrrolidinium, and alkylsulfonium groups, *etc.*, and the anions include chloride (Cl⁻), iodide (I⁻), bromide (Br⁻), tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, bis(trifluoromethylsulfonyl)imide, bis(fluorosulphonyl)imide groups, *etc.* The versatility of ILs, in terms of molecular structure, conductivity, hydrophobicity, melting point, viscosity, solubility, *etc.*, can be varied by altering the substitutive group on the cation part, or the combined anion type. Various kinds of salts can be used to design the ILs with the desired properties for the specific applications.

For the use as the “mediator” in the DSSCs, a specific group of ILs containing the redox species (Cl⁻, I⁻, Br⁻, S²⁻, CN⁻, *etc.*) as the anions has been highlighted. Lee *et al.* [9] employed two iodide-based ILs, 1-ethyl-3-methylimidazolium iodide (EMII) and 1-methyl-3-propyl imidazolium iodide (PMII), as the redox mediator. The binary IL electrolyte rendered a cell efficiency of 3.49% to its all-solid-state DSSC. Chen *et al.* [10] applied two kinds of IL mediators, 1-butyl-3-methylimidazolium iodide (BMII) and 1-butyl-3-methylimidazolium thiocyanate (BMISCN) for the electrolyte of DSSCs. In the binary electrolyte, the BMISCN was used to lower the viscosity, enhance the ionic conductivity, and reduce the interfacial charge transfer resistance of the electrolyte. The pertinent cell efficiency of 5.55% was obtained by using the binary IL electrolyte containing BMII, BMISCN, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Chi *et al.* [11] synthesized two solid-state iodide-based ILs, 1-[(4-ethenylphenyl)methyl]-3-butyl-imidazolium iodide (EBII) with a single aliphatic C=C bond and 1-[(4-ethenylphenyl)methyl]-3-vinyl-imidazolium iodide (EVII) with two aliphatic C=C bonds. The EBII exhibited weaker π - π stacking interactions, longer d-spacing, and a lower melting temperature. Therefore, the solid-state EBII-based DSSC reached higher efficiency of 4.7% than that of the EVII-based DSSC (3.8%) due to its facile charge transport and lower electron recombination. Hsu *et al.* [12] synthesized four kinds of iodide-based ILs, 1-allyl-3-ethylimidazolium iodide (AEII), 1-allyl-3-propylimidazolium iodide (APII), 1-3-diallylimidazolium iodide (DAII), and 1-methyl-3-propylimidazolium iodide (MPII), as the mediators in the novel agarose gel electrolytes. The agarose gel electrolyte containing AEII exhibited the highest I₃⁻ diffusion coefficient of $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and thereby gave the best DSSC efficiency of 5.89%. Liu *et al.* [13] synthesized two kinds of sulfide-based ILs, tetra-methylammonium sulfide (TMAS) and 1-propyl-2,3-dimethylimidazolium sulfide (DMPIS), as the sulfide/polysulfide mediators. In their research, several iodide-based ILs (EMII, 1,3-dimethylimidazolium iodide (DMII) or PMII,) were applied as another kind of the mediators. The electrolyte containing TMAS, EMI and DMII as the IL mediators can provide its DSSC a cell efficiency of 6.40%, while the electrolyte containing DMPIS and PMII as the IL mediators can provide its DSSC a cell efficiency of 6.20% under 100 mW cm⁻² illumination and a higher cell efficiency of 6.60% under 10 mW cm⁻² illumination. Furthermore, by controlling the concentration of TMAS, the electrolyte containing TMAS and 1,2-dimethyl-3-propylimidazolium iodide (DMPII) as the IL mediators can provide its DSSC a cell efficiency of 9.10% [14].

Except for the anions, the cations of IL mediators also play important roles in determining the conversion efficiency of the DSSCs. For example, the imidazolium cations were reported as the efficient functional group to retard the charge recombination at the working electrode/electrolyte interface [15]. And the alkyl chain-substituted imidazolium cations were de-

signed for prolonging the electron lifetime within a DSSC[16]. Therefore, different functional group-substituted cations of the IL mediators can be designed for compensating the defaults of the DSSCs with traditional electrolyte. Recently, the development of new classes of functional group-substituted IL mediators has been demonstrated as a promising strategy to further enhance the efficiency and the long-term stability of DSSCs. This chapter mainly reviewed the recent researches on the topic of new classes of ILs used as the electrolyte in DSSCs. Here the new classes of ILs employed in the electrolytes of DSSCs can be divided into two sections: (i) the applications in liquid electrolytes in DSSCs and (ii) the applications in quasi/all-solid-state electrolytes in DSSCs.

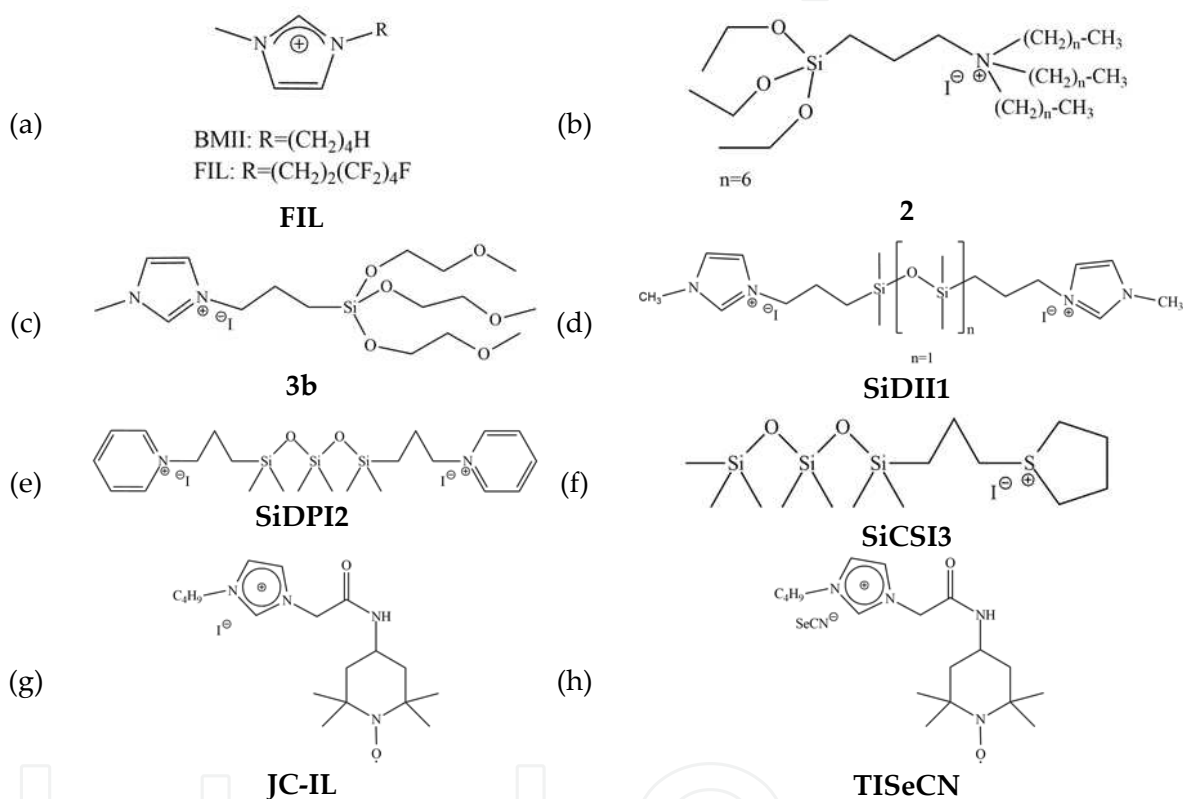


Figure 3. A partial literature review of the molecular structure of novel functional IL mediators for the application for the liquid electrolytes in DSSCs.

2. New class of ionic liquids

2.1. Applications in liquid electrolytes in DSSCs

To improve the conversion efficiency of the IL-based DSSCs, novel functional IL mediators were investigated by incorporating versatile organic functional groups into the traditional IL mediators. Those organic functional groups on the newly synthesized ILs were designed for enhancing the ionic conductivity, lowering viscosity, or speeding up the redox reaction of the

pristine ILs. Abate *et al.* [17] synthesized a polyfluorinated IL, 1-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)imidazolium iodide (FIL, Figure 3a). The high electronegative 3,3,4,4,5,5,6,6,6-nonafluorohexyl functional group is designed for making FIL to improve the dye regeneration and facilitate the charge transport by providing a microphase separation (fluorophobic effect) between the long alkyl chains of the amphiphilic dye and the fluoruous environment in the electrolyte. Therefore, a cell efficiency (η) of 5.10% was obtained with an open-circuit voltage (V_{OC}) of 610 mV, short-circuit current (J_{SC}) of 11.50 mA cm⁻², and fill factor (FF) of 0.73. Cerneaux *et al.* [18] synthesized three new triethoxysilanes bearing quaternary ammonium alkyl iodides ILs, N,N,N-triethyl-3-(triethoxysilyl)propan-1-aminium iodide (1), N,N,N-triheptyl-3-(triethoxysilyl)propan-1-aminium iodide (2), and N,N,N-tridodecyl-3-(triethoxysilyl)propan-1-aminium iodide (3). The alkylsilane functional group were introduced due to their benefits to the solubility and electron transfer of the electrolytes. By adjusting the compositions of IL-based liquid electrolyte containing 2 (Figure 3b), the pertinent DSSC showed the best efficiency of 5.00% under 100 mW cm⁻² and provided a very high efficiency of 8.1% under 10 mW cm⁻². Zalas *et al.* [19] synthesized three Si-tripodand-functionalized ILs by using the polyoxaethylene chains with different lengths to attach to the central silicon atom, namely 1-methyl-3-(3-(trimethoxysilyl)propyl)imidazolium iodide (3a), 1-methyl-3-(3-(tris(2-methoxyethoxy)silyl)propyl)imidazolium iodide (3b), and 1-methyl-3-(3-(tris(2-(2-methoxyethoxy)ethoxy)silyl)propyl)imidazolium iodide (3c). Those Si-tripodand-functionalized ILs are thermally stable (decomposition temperatures, $T_d \approx 270$ °C) and electrochemically stable. The 3b (Figure 3c) exhibited specific conductivity adequate for DSSCs, and thereby the pertinent electrolyte possessed a very high conductivity approaching 10⁻² S cm⁻¹ at ambient temperature. And the DSSC containing 3b showed a η of 5.10% with V_{OC} of 688 mV, J_{SC} of 14.30 mA cm⁻², and FF of 0.52. In 2013, Lee *et al.* introduced three novel classes of siloxane-functionalized ILs, including (i) siloxane diimidazolium iodides [20], (ii) siloxane pyridinium iodides [21], and (iii) siloxane cyclic sulfonium iodides [22], as the liquid electrolytes for DSSCs. Siloxane chains possessed highly thermal stability (up to 350 °C), relatively low permittivity, excellent flexibility and good amphiphilicity. Additionally, oxygens of siloxane were expected to have a complex with TiO₂ and capturing effect of cation, which could enhance the stability of the electrolytes and possibly be advantageous to the transportation of anionic species in the cell. The three types of the siloxane-functionalized ILs are depicted as the follows:

- i. For the case of siloxane diimidazolium iodides (SiDII) ILs [20], three siloxane moieties with different chain lengths were separately incorporated between two imidazolium cations to form three different SiDII ILs (SiDII1, SiDII2, and SiDII3). The synthesized SiDII were viscous liquids with different color and with good thermal stability (decomposition temperatures, $T_d \approx 380$ °C). With an increase in the siloxane chain lengths, the flexibilities and diffusion coefficients of the SiDII ILs increased, but the viscosities and conductivities decreased; the unusual decrease in their viscosities was attributed to that the amphiphilic siloxane chains could make SiDII ILs reduce the surface tension of both water and organic solvents. Among the SiDII-based DSSCs, the cell containing SiDII1 (Figure 3d) in the electrolyte showed a maximum conver-

sion efficiency (η) of 6.20% with an open-circuit voltage (V_{OC}) of 721 mV, short-circuit current (J_{SC}) of 12.90 mA cm⁻², and fill factor (FF) of 0.67. In addition, SiDII1-based DSSC showed better long-term stability than the DSSC with other conventional liquid type electrolytes.

- ii. For the case of siloxane pyridinium iodides (SiDPI) ILs [21], three siloxane moieties with different chain lengths were separately incorporated between two pyridinium cations to form three different SiDPI ILs (SiDPI1, SiDPI2, and SiDPI3). All SiDPI ILs showed good thermal stability ($T_d \approx 300$ °C). The solid-state SiDPI1 with short chain length was brown. The gel-state SiDPI2 and SiDPI3 with long chain length were shown as the highly viscous ILs. The DSSC containing SiDPI2 (Figure 3e) in the electrolyte achieved the highest η of 6.80% with V_{OC} of 703 mV, J_{SC} of 15.85 mA cm⁻², and FF of 0.61, which could be attributed to the reason that SiDPI2 had the relative low viscosity and the largest diffusion coefficient.
- iii. For the case of siloxane cyclic sulfonium iodides (SiCSI) ILs [22], two siloxane moieties with different chain length were separately incorporated between two cyclic sulfonium cations to form SiCSI1 and SiCSI2 ILs, and the SiCSI3 IL is constructed by a siloxane chain sited as the terminal group of one cyclic sulfonium cation. The thermooxidative stabilities of SiCSI ILs were lower than those of SiDII ILs because the bond strength of S⁺-C in sulfonium was lower than that of N⁺-C in imidazolium. The bis-sulfonium electrolytes (SiCSI1 and SiCSI2) were solid due to their high molecular weight and large size of sulfur element even though they had siloxane group; meanwhile, they were with relative low thermal stability ($T_d \approx 260$ °C). The mono-sulfonium (SiCSI3) electrolyte maintains gel state owing to its low molecular weight and free siloxane functional group; thereby SiCSI3 (Figure 3f) possesses the best thermal stability ($T_d \approx 300$ °C), highest ionic conductivity, and the largest diffusion coefficient than those values of SiCSI1 and SiCSI2 ILs. The SiCSI3-based liquid electrolyte renders its DSSC the highest η of 7.30% with V_{OC} of 689 mV, J_{SC} of 18.03 mA cm⁻², and FF of 0.59.

Among all the functional IL mediators for the liquid electrolyte in DSSCs, a novel class of free radical-substituted IL mediators brings the brand new level and broadens the horizons of the ILs applications recently. A free radical-substituted IL mediator can provide double redox channels: one is the free radical-substituted cation, and the other is the anion. The free radical-substituted IL mediator was designed to largely improve the redox potential, ionic conductivity, diffusion coefficient, and the intrinsic redox reaction of the liquid electrolytes for DSSCs. In 2014, our group (Chu *et al.* [23]) synthesized a new IL mediator, 1-butyl-3-(2-oxo-2-((2,2,6,6-tetramethyl-piperidin-1-oxyl-4-yl)amino)ethyl)-1H-imidazol-3-ium iodide (JC-IL, Figure 3g). The synthetic pathway to JC-IL was depicted in Figure 4a. The 2,2,6,6-tetra-methylpiperidin-N-oxyl (TEMPO) functional group could provide a nitroxide free radical (N-O.), which was notable for its simple one-electron redox reaction, extremely fast charge transfer ability, high redox potential, and large diffusion coefficient. Therefore, the JC-IL possessed dual redox channels, the TEMPO-substituted imidazolium cation and the iodide anion, which made the

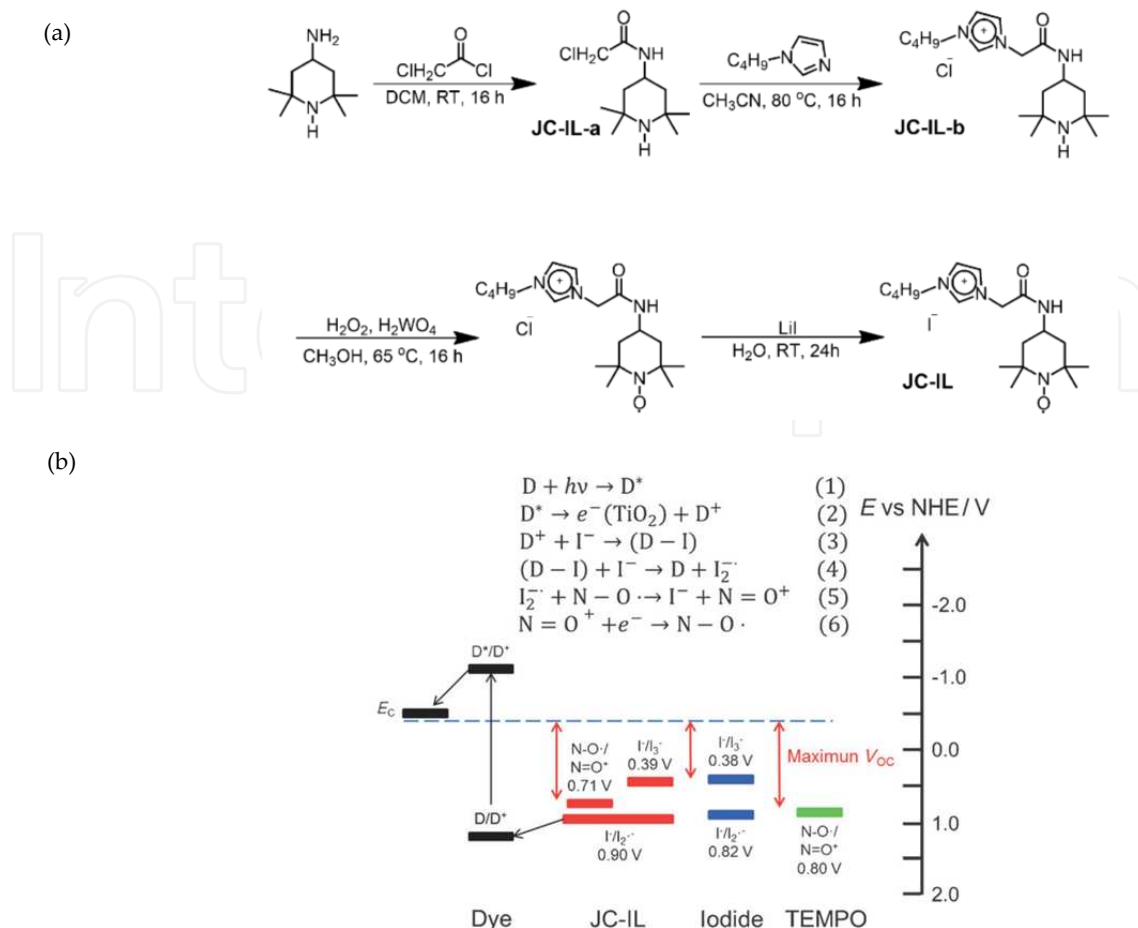


Figure 4. (a) The synthetic pathway to JC-IL. (b) Mechanism for the function of JC-IL, iodide, and TEMPO in DSSCs; energy levels of these charge mediators and those of the dye at ground and excited states are also shown [23].

JC-IL to exhibit three electron transfer redox reaction, high distinct redox potential (Figure 4b), large diffusion coefficient, and rapid intrinsic heterogeneous electron-transfer rate. The DSSC with JC-IL electrolyte showed a good cell efficiency of 8.12% with remarkably high V_{oc} of 858 mV, J_{sc} of 13.70 mA cm⁻², and FF of 0.69. The high open-circuit voltage of DSSCs with JC-IL was over 850 mV, which was approximately 150 mV higher than that of the DSSCs with a standard iodide-based liquid electrolyte. Currently, we further exchanged the iodide (I⁻) to another redox anion, selenocyanate (SeCN⁻), to synthesize a novel iodide-free IL mediator, 1-butyl-3-(2-oxo-2-((2,2,6,6-tetramethyl-piperidin-1-oxyl-4-yl)amino)ethyl)-1H-imidazol-3-ium selenocyanate (TISECN, Figure 3h). Since the selenocyanate was beneficial for faster kinetic electron transfer for redox reaction accompanying with a high redox potential, the TISECN electrolyte could facilitate the charge transportation within the electrolyte and thus greatly reduced the energy loss in the cell. Thus, a DSSC with TISECN-based liquid electrolyte showed a good cell efficiency of 8.38% with a high V_{oc} value of 854.3 mV, J_{sc} of 14.70 mA cm⁻², and FF of 0.67 [24].

Table 1 is a partial list of the DSSCs' performance containing above novel functional IL mediators in the liquid electrolytes.

ILs	Liquid electrolytes	Dye	η (%)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF	Ref.
FIL	0.6 M FIL, 0.03 M I ₂ , 0.1 M GuSCN, 0.5 M TBP in ACN/VN (v/v = 85/15)	Z907	5.10	610	11.50	0.73	[17]
2	1.5 M 2, 0.08 M I ₂ , 0.1 M GuSCN, 0.5 M TBP in ACN	Z907	4.40	769	13.50	0.42	[18]
3b	0.6 M 3b, 0.03 M I ₂ , 0.1 M GuSCN, 0.5 M TBP in ACN	N3	5.10	688	14.30	0.52	[19]
SiDIII1	0.5M SiDIII1, 0.05M I ₂ , 0.1 M GuSCN, 0.5 M TBP in MPN	N719	6.20	721	12.90	0.67	[20]
SiDPI2	0.6 M SiDPI2, 0.05M I ₂ , 0.1 M GuSCN, 0.5 M TBP in MPN	N719	6.80	703	15.85	0.61	[21]
SiCSI3	0.6 M SiCSI3, 0.05M I ₂ , 0.1 M GuSCN, 0.5 M TBP in MPN	N719	7.30	689	18.03	0.59	[22]
JC-IL	0.4 M JC-IL, 0.04 M NOBF ₄ in ACN	CR147	8.12	858	13.70	0.69	[23]
TiSeCN	0.2 M TiSeCN and 0.05 M (SeCN) ₂ in ACN.	CR147	8.38	854	14.70	0.67	[24]

Note: Guanidinium thiocyanate (GuSCN), tert-butylpyridine (TBP), acetonitrile (ACN), valeronitrile (VN), 3-methoxypropionitrile (MPN), nitrosyl tetrafluoroborate (NOBF₄)

Table 1. A partial literature review of the DSSCs' performance containing the novel functional IL mediators in the liquid electrolytes.

2.2. Applications in quasi/all-solid-state electrolytes in DSSCs

To further enhance the long-term stability of the IL-based DSSCs, several classes of functional IL mediators are designed in the quasi-solid-state or all-solid-state to prevent the leakage and volatilization of the electrolyte. Various organic functional groups were designed for enhancing the ionic conductivity, charge transfer ability, and mechanical stability of the newly synthesized ILs.

First, conductive IL mediators were introduced to enhance the conductivity of electrolyte and thereby improved the electron/hole transfer ability within a quasi/all-solid-state DSSC. Midya *et al.* [25] synthesized three solid-state conductive IL mediators, namely SD1 (Figure 5a), SD2 (Figure 5b), and SD3, which all contained carbazole-substituted imidazolium cations. Considering the iodide species as the redox couple, two carbazole-imidazolium iodide (CBZ-IMDZ-I) ILs, SD2 and SD3, were composed of an iodide (I⁻) anion and a carbazole-substituted imidazolium cation, which were the 1-carbazole-3-methyl-imidazolium and 1-carbazole-3-hexyl-imidazolium, respectively. In the presence of iodine (I₂), the LUMO-state dye was regenerated by oxidizing an I⁻ into the triiodide (I₃⁻) ion, and the I₃⁻ ion was subsequently reduced to I⁻ by the cation of CBZ-IMDZ-I because it could transport the holes to the counter electrode via a hole hopping mechanism (Figure 6a). Moreover, the hole hopping mechanism in the CBZ-IMDZ-I might assist the traditional Grotthuss-type exchange mechanism or work in parallel, leading to a fast I₃⁻ diffusion in the electrolyte. In a CBZ-IMDZ-I IL conductor, the carbazole functional group worked as the hole conductor to facilitate the dye regeneration via a hole hopping mechanism (Figure 6a) and to transport the iodine radical to the counter electrode via a Grotthuss-type mechanism (Figure 6b). Therefore, the solid-state electrolyte

containing SD2 can provide dual channels for hole/iodide transportation, and thereby could render its solid-state DSSC a cell efficiency of 2.85% with V_{OC} of 718 mV, J_{SC} of 6.23 mA cm⁻², and FF of 0.64. Furthermore, the SD1 contained a 1-carbazole-3-hexyl-imidazolium cation with a thiocyanate (SCN⁻) anion, and thereby the pertinent solid-state DSSC reached a cell efficiency of 1.43% with V_{OC} of 726 mV, J_{SC} of 3.10 mA cm⁻², and FF of 0.64. Wang *et al.* [26] synthesized two conductive IL mediators, namely propargyl-substituted imidazolium iodide (PMIm) and propargyl-functionalized piperidinium (PMPi). The pendent propargyl group possessed a lamellar structure, which was favorable for charge transfer and was expected to yield high conductivity. As compared to the alkyl-substituted imidazolium iodide, the introduction of unsaturated propargyl group to the imidazolium ring enhanced the conductivity by more than 4 orders. The newly synthesized propargyl-functionalized IL were in the solid state below 80 °C and had good thermal stability ($T_d \approx 330$ °C); they were also with good solubility in common organic solvents such as methanol and ethanol, which was advantageous to solution processing for pore-filling of the solid-state electrolyte in the DSSCs. Moreover, the PMIm and PMPi could be used directly as the single-component solid-state electrolyte for the DSSCs, which could perform efficiently without any additives in the electrolyte and any post-treatments on the dye-loaded TiO₂ films. By coupling an organic sensitizer (MK2), the DSSC with solely PMIm (Figure 5c) as the solid-state electrolyte achieved cell efficiency of 6.30% with V_{OC} of 710 mV, J_{SC} of 12.65 mA cm⁻², and FF of 0.70, and exhibited good long-term stability under continuous 1 sun illumination for 1,500 h. Besides, they also synthesized five kinds of ester-substituted IL mediators [27], 1-(2-methoxy-2-oxylethyl)-3-alkyl imidazolium iodide, containing different alkyl chain (methyl, ethyl, propyl, hexyl, dodecyl). The ester functional group possessed advantages over inorganic and organic hole conductors. First, the ester-substituted IL can form a three-dimensional (3D) ionic channel of iodides, which was advantageous for fast movement of iodides and charge transfer along the polyiodide chain. Secondly, the coordination interactions between esters and Li⁺ ions (typically used cations in the electrolyte of DSSCs) could form dimers of conductor molecules, and thus the distance of adjacent polyiodides was reduced, resulting in faster charge transfer and higher conductivity. In addition, the molecular size of the ester-substituted IL permitted a deep penetration of the electrolytes into the porous TiO₂ films, which facilitated the reduction of the oxidized dye molecules and favored high photocurrent generation. Among their five ester-substituted IL mediators, the 1-(2-methoxy-2-oxylethyl)-3-methyl imidazolium iodide (1, Figure 5d) showed the best conductivity of 5.76 mS cm⁻¹ because of the formation of ionic channels and the interaction of Li⁺ with the oxygen in the ester group, which resulted in fast charge transfer along the polyiodide chain. Thus, the pertinent DSSC exhibited a cell conversion efficiency as high as 6.63% with V_{OC} of 660 mV, J_{SC} of 13.77 mA cm⁻², and FF of 0.73, and exhibited excellent long-term stability remained at 100% of the initial value after continuous light soaking for 1,000 h. Li *et al.* [28] synthesized a novel solid-state conductive IL mediator, hydroxyethyl and ester co-substituted imidazolium iodide (HEII, Figure 5e). The ester functional group could significantly enhance the ionic conductivity of the IL electrolyte and thus to remarkably improve DSSC performance. The oxygen and hydrogen atoms within the hydroxyethyl functional group were designed to participate in hydrogen bonding, which was favorable to form a closely packed structure towards high conductivity. The solid-state HEII started to decompose at 150 °C and had a melting point of 79 °C. By coupling an organic sensitizer (MK2), the DSSC with HEII in the solid-state electrolyte achieved cell efficiency of 7.45% with a V_{OC}

of 733 mV, J_{SC} of 14.66 mA cm⁻², and FF of 0.69. Under continuous 1 sun illumination for 1,000 h, the cell efficiency maintained 96% and exhibited good long-term stability. Additionally, they synthesized a double-ester-substituted imidazolium iodide, 1,3-di(2-methoxy-2-oxoethyl)imidazolium iodide (DEII, Figure 5f) to act as the electron donor [29]. The donor (DEII) was deposited in the photoanode for efficient dye regeneration preceded by electron injection from the excited dye to the conduction band of TiO₂, while the acceptor (mixture of DEII and iodine) was deposited on the counter electrode surface for efficient electron relay for circuit completion. The counter electrode was placed on top of the photoanode to form a close contact between the donor and acceptor, which was then sealed into a solid device. As compared to the redox mixture electrolyte based device A (Figure 7), separating the electron donor and acceptor of a redox couple in device B (Figure 7) could significantly retard charge recombination because of the absence of I₃⁻ in the photoanode. Device A produced a cell efficiency of 2.41% (with a V_{OC} of 562 mV, J_{SC} of 7.02 mA cm⁻², and FF of 0.61), while device B produced a cell efficiency of 6.50% (with a V_{OC} of 633 mV, J_{SC} of 16.29 mA cm⁻², and FF of 0.63). Briefly, with the new device structure, the DSSC performance could be further improved by increasing the ionic conductivity of IL mediator through molecular design. Upon separation of the donor and acceptor of the IL mediator, the new device structure opened up a new way for optimization of the solar cell performance. Miao *et al.* [30] synthesized a novel solid-state conductive IL mediator, namely ILMC (Figure 5g), which was composed of the carboxyl-substituted imidazolium-europium (Eu) complex as the cation and the bromide as the anion. ILMC was synthesized through a green route by simply adding europium oxide into the carboxyl-substituted imidazolium IL, and the component, Eu, was selected as the metal center due to its excellent photophysical properties of the corresponding complexes. Thus, ILMC possessed the advantages of an easy and green preparation process, simple composition, light color, high conductivity, superior stability as well as the most important property of high efficiency. The solid-state DSSC with ILMC in the solid-state electrolyte achieved cell efficiency of 6.99% with a V_{OC} of 640 mV, J_{SC} of 15.28 mA cm⁻², and FF of 0.72. Xu *et al.* [31] synthesized a pyridylheptyl-substituted IL, N-butyl-N-(4-pyridylheptyl)imidazolium bromide ([BuPyIm]Br, Figure 5h). The pyridylheptyl functional group gave [BuPyIm]Br the good thermal stability ($T_d \approx 360$ °C) and a good solubility in aqueous solution. The DSSC containing [BuPyIm]Br in the electrolyte exhibited higher V_{OC} than the cell without [BuPyIm]Br. The enhanced V_{OC} of cell could be assigned from the suppression of the charge recombination at the TiO₂/electrolyte interface, and it was attributed to that the nitrogen-containing pyridylheptyl functional group anchored on the free areas of the dye-coated TiO₂ surface. Besides, the iodine could form anion complexes with some anions such as I₂Br⁻, and the imidazolium rings could interact strongly with I₂Br⁻ because the bigger anions had a lower charge density. Therefore, these anion complexes could also reduce the recombination between the photo-induced electrons and I₃⁻, thus enhanced the V_{OC} of the DSSC. However, the electrolyte containing [BuPyIm]Br provided the smaller values of both ionic conductivity and diffusion coefficient than those of the electrolyte without [BuPyIm]Br. Under the optimized condition with the addition of 0.1 M [BuPyIm]Br in the electrolyte, the highest conversion efficiency is 5.67 % under 100 mW cm⁻² and 6.69% under 15 mW cm⁻². The pertinent [BuPyIm]Br-based DSSC maintained almost 95% of its initial efficiency after 60 days long-term test under 80 °C, and thereby the [BuPyIm]Br IL could render a promising stability to its DSSC.

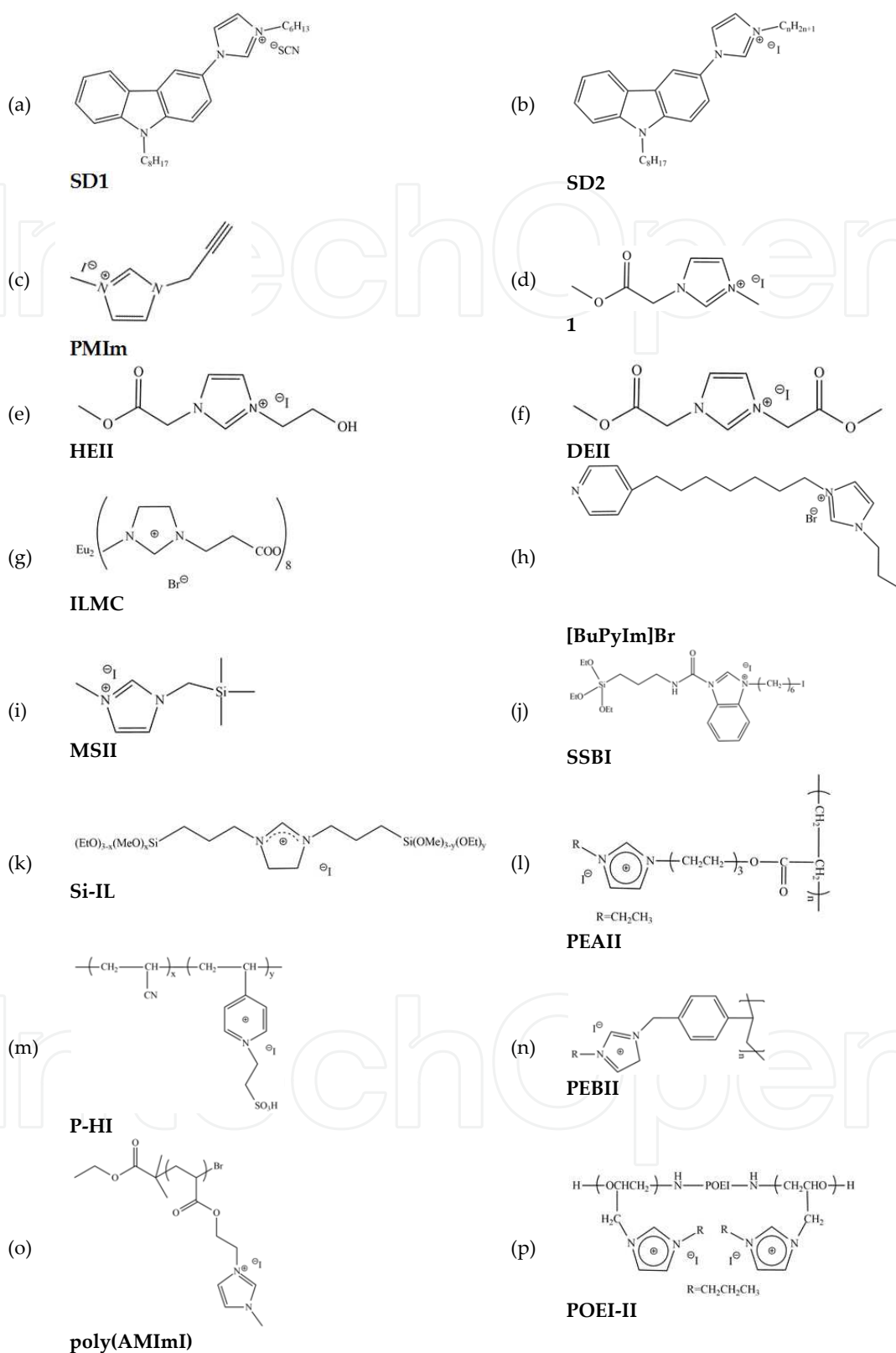


Figure 5. A partial literature review of the molecular structure of novel functional IL mediators for the application for the quasi/all-solid-state electrolytes in DSSCs.

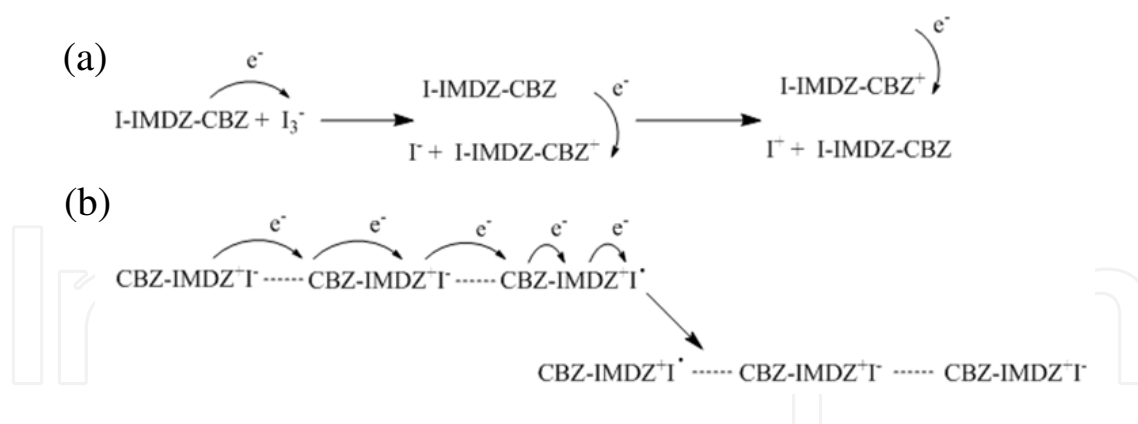


Figure 6. Schematic illustration of charge transfer phenomenon of the CBZ-IMDZ solid state IL conductor via (a) hole hopping mechanism and (b) Grotthuss-type mechanism [25].

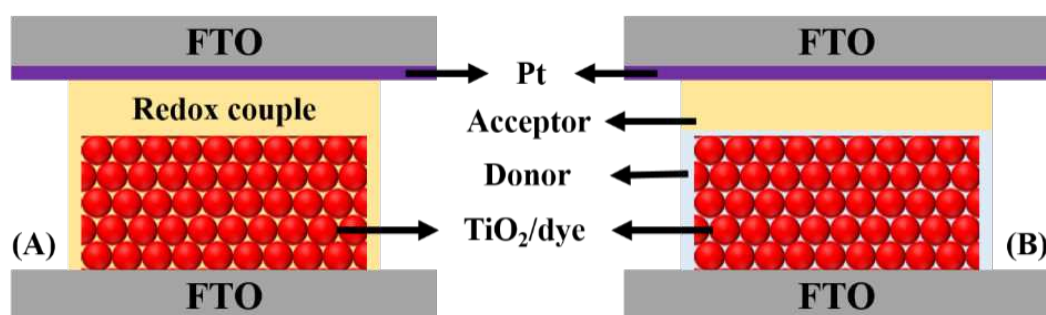


Figure 7. The device structures for device A and device B. A redox-couple mixture is used as the solid-state electrolyte in device A while the electron donor and acceptor of the redox-couple are separated in device B: the donor is in the photoanode layer but the acceptor (the mixture of donor and acceptor) is on top of the photoanode in contact with the counter electrode [29].

Second, quasi/all-solid-state alkylsilane-substituted IL mediators were also studied for their benefits of electron transfer within the electrolytes. Wu *et al.* [32] synthesized a room temperature (RT) IL, 1-methyl-3-(trimethylsilyl)methyl-imidazolium iodide (MSII, Figure 5i). The trimethylsilyl functional group was designed to reduce the viscosity and to enhance the conductivity of the IL. The DSSCs with a MSII-based quasi-solid-state IL electrolyte showed the largely decreased electron transfer resistance (R_{ct}) and increased electron lifetime (τ_e); thereby a cell efficiency (η) of 3.23% is provided with an open-circuit voltage (V_{OC}) of 600 mV, short-circuit current (J_{SC}) of 8.97 mA cm⁻², and fill factor (FF) of 0.61. Lee *et al.* [33] synthesized a novel quasi-solid-state alkylsilane-substituted IL, 3-(iodohexyl)-1-(3-(triethoxysilyl)propyl-carbamoyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (SSBI, Figure 5j) by using the 1,6-diiodohexane and the silane-substituted benzimidazole (SSB), N-[3-(triethoxy-4-silyl)propyl]-1*H*-benzimidazole-1-carboxamide, as the reagents. The quasi-solid-state SSBI was prepared through the in-situ gelation, which was induced by the reaction of 1,6-diiodohexane and SSB in a DSSC cell heated at 60 °C for 30 min. The SSBI presumably formed a three-dimensional network due to the formation of hydrogen bonds among the amide groups of the silane-substituted benzimidazolium and the van der Waals force between the two iodohexyl moieties. Therefore,

the SSBI was able to immobilize the cations and facilitate the anionic transport in the quasi-solid-state DSSC, which showed a cell efficiency of 5.0 % with a V_{OC} of 710 mV, J_{SC} of 11.20 mA cm^{-2} , and FF of 0.63. The DSSC with quasi-solid-state SSBI-based electrolyte decreased to 52% of its initial value, while the cell with liquid electrolyte decreased to 79% of its initial value. Fontaine *et al.* [34] synthesized a novel alkylsilane-substituted IL, 1,3-(3-propyltriethoxysilane, 3-propyltrimethoxysilane)-4,5-dihydroimidazolium iodide (Si-IL, Figure 5k), which was used to form a hybrid ionogel containing silica-based matrix and imidazolium iodide redox mediator as shown in Figure 8. In the ionogel with 3-D architecture, ILs were immobilized through covalent bonds with silane groups. The Si-IL ionogel constructed multiple ion channels to facilitate the transport of iodide ions; thus the charge transfer at the electrode/electrolyte interfaces would be enhanced and then the reaction with the hole and the iodide would be facilitated, avoiding electron/hole recombination. The DSSC coupled with solely Si-IL as the ionogel electrolyte showed an efficiency of 1.25% with a V_{OC} of 680 mV, J_{SC} of 2.80 mA cm^{-2} , and FF of 0.65. The presence of covalent bonds between silica and ILs might avoid leakage or volatilization of ILs and prevent electrolyte from leaking. These conditions were more favorable for long-term performances and the flexible applications.

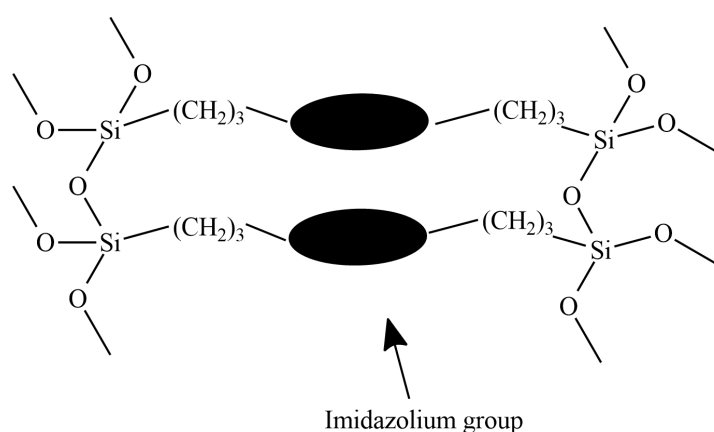


Figure 8. Schematic of the organization of the imidazolium groups into the silica network [34].

Third, polymeric IL mediators were designed by incorporating the polymer chain into the ILs as the gelator for the solidification of ILs-based electrolytes. Wang *et al.* [35-37] synthesized a group of solid-state IL polymers, poly(1-alkyl-3-(acryloyloxy)hexylimidazolium iodide) (PAAII) with four different alkyl side chains (methyl, ethyl, propyl, and butyl). The PAAII was synthesized by a thermal bulk polymerization of IL monomers, 1-alkyl-3-(acryloyloxy)hexylimidazolium iodide; thereby, multiple comb-like imidazolium iodide ILs were fixed onto the main chain of PAAII containing three ethylene units. The PAAII was a flexible solid with good ionic conductivity and good thermal stability ($T_d \approx 380$ °C) due to its specific functions, including charge transport of target ions, specific polar environment, and mechanical strength. Among all the PAAII ILs, the one with an ethyl side chain, namely poly(1-ethyl-3-(acryloyloxy)hexylimidazolium iodide) (PEAII, Figure 5l), showed the highest ionic conductivity (3.63×10^{-4} S cm^{-1}) and good charge transport ability. Due to the conjugation effect of imidazolium ring and the steric hindrance of polymer backbone, the attraction between the cation and the

iodide anion was weak, resulting in easy diffusion of iodide anions in PEAI. A π -stacked imidazolium chain in PEAI can provide the favorable channel for holes transport from the photoanode to the counter electrode. The electron was fast transported from the counter electrode to the dye by diffusion of I⁻. Therefore, without the presence of iodine (I₂), the DSSC assembled with solid-state PEAI electrolyte reached the good cell efficiency of 5.29% with a V_{OC} of 838 mV, J_{SC} of 9.75 mA cm⁻², and FF of 0.65. Under long-term stability test for 1,000 h, the DSSC assembled with PEAI electrolyte maintained about 85% of their initial efficiency after 1,000 h without sealing. Fang *et al.* [38] synthesized an acidic IL polymer, P[(3-(4-vinylpyridine) propanesulfonic acid) iodide)-co-(acrylonitrile)] (P-HI, Figure 5m), which was composed of a co-polymer chain (polyethylene and polyacrylonitrile) and a sulfonic acid group. The sulfonic acid group possessed strong electronegativity, which was beneficial to form the homogeneous and continuous framework of ILs polymer for enhancing transportation of redox couples in the electrolyte. Without the addition of I₂, the DSSC containing P-HI in the solid-state electrolyte achieved the cell efficiency of 6.95% with a V_{OC} of 643 mV, J_{SC} of 15.10 mA cm⁻², and FF of 0.72. Chi *et al.* [39] designed and synthesized a polymerized IL, poly((1-(4-ethenylphenyl)methyl)-3-butyl-imidazolium iodide) (PEBII, Figure 5n). An (4-ethenylphenyl)methyl functional group was anchored on 1-butylimidazolium iodide IL and served as the self-polymerization site and rendered high conductivity (2.0×10^{-4} S cm⁻¹ at 25 °C) to the PEBII due to the strong π - π stacking interaction between the benzene groups. For the application of iodine-free solid-state electrolyte in DSSCs, the solid-state PEBII was able to deeply penetrate into mesoporous TiO₂ film, perfectly fill the nanopores between the TiO₂ nanoparticles, and prevent the formation of cavities during solvent evaporation. Therefore, the charge transfer at the electrode/electrolyte interface and the electron lifetime within the pertinent cell were significantly improved, and the conversion efficiency of the solid-state DSSC with PEBII electrolyte reached 5.93%, measured at 100 mW cm⁻². Furthermore, by coupling a photoanode containing double layer mesoporous TiO₂ beads, the PEBII electrolyte rendered its DSSC an enhanced cell efficiency up to 6.70% with a V_{OC} of 760 mV, J_{SC} of 16.60 mA cm⁻², and FF of 0.53 [40]. Chang *et al.* [41] synthesized a novel polymeric IL, poly(1-(2-acryloyloxyethyl)-3-methyl-imidazol-1-ium iodide) (poly(AMImI), Figure 5o), by using an atom transfer radical polymerization (ATRP) method. The monomeric IL, 1-(2-acryloyloxyethyl)-3-methyl-imidazol-1-ium iodide (AMImI), possessed a 2-acryloyloxyethyl functional group anchoring on 1-methylimidazolium iodide IL. The 2-acryloyloxyethyl functional group served as the self-polymerization site. The solid-state DSSC with poly(AMImI)-based electrolyte reached the 1.16%. By adding multi-wall carbon nanotubes (MWCNTs) into the poly(AMImI)-based electrolyte, the pertinent DSSC achieved 3.55% with a V_{OC} of 646 mV, J_{SC} of 8.51 mA cm⁻², and FF of 0.64.

Recently, our group (Chang *et al.* [42]) synthesized a novel polymeric IL, poly(oxyethylene)-imide imidazolium iodide (POEI-II, Figure 5p). The synthetic pathway to POEI-II was depicted in Figure 9. A poly(oxyethylene)-segmented oligo(imide) (POEI) functional group incorporated with two 1-butylimidazolium iodide ILs at both ends of POEI. The POEI possessed aromatic imides and hydrophilic POE segments with multiple dipole-dipole interaction sites, which rendered POEI-II a high solubility in aqueous solutions as well as in organic solvents. The POE segment in the POEI-II could chelate lithium cations (Li⁺) within

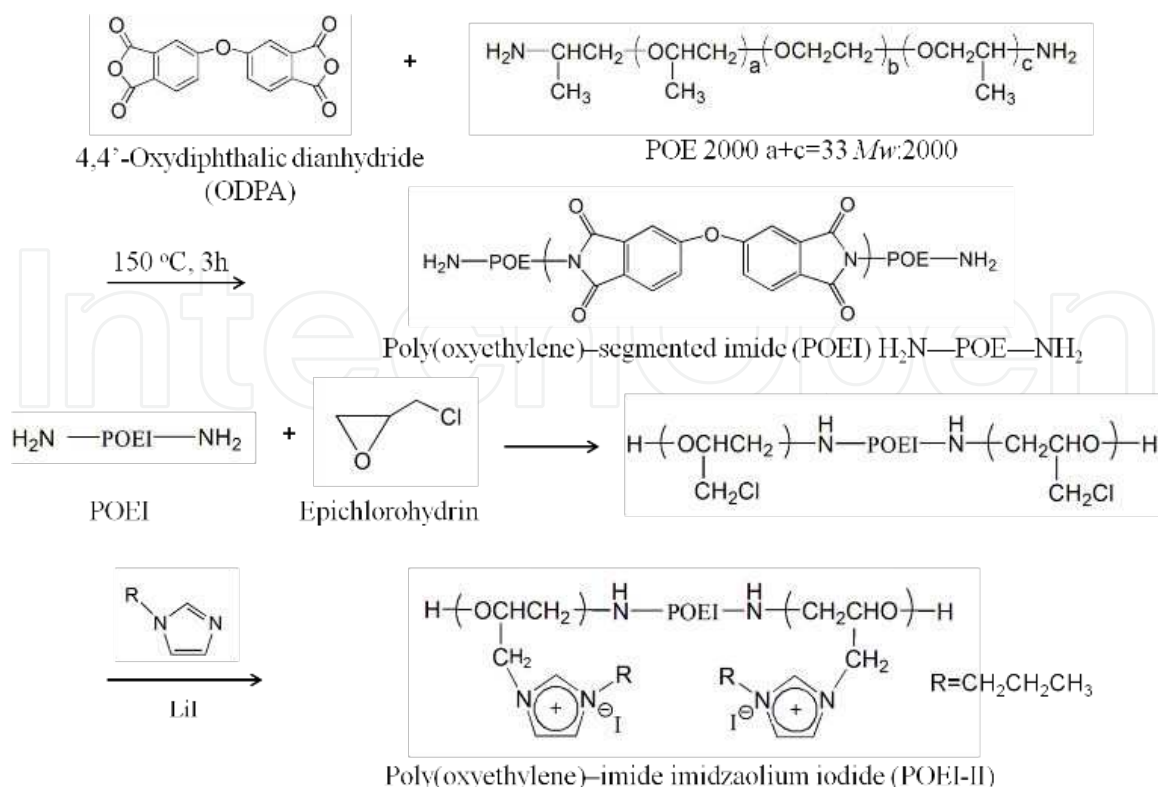


Figure 9. Synthetic pathway to poly(oxyethylene)-imide imidazolium iodide (POEI-II) [42].

the electrolyte to improve the V_{OC} value of a DSSC and enable the strong inner π - π and long-pair- π electron interactions to enhance the ionic conductivity and the diffusivity of POEI-II. Consequently, the quasi-solid-state DSSC with POEI-II gel electrolyte reached a high cell efficiency of 7.19%. In addition, MWCNTs were incorporated into POEI-II gel electrolyte (Figure 10) as the extended electron transfer material (EETM) to facilitate charge transfer from counter electrode to redox mediator, which benefited the dye regeneration more efficiently. Meanwhile, the POE segments on POEI-II could prevent the MWCNTs from aggregation, which made the well dispersed MWCNTs to largely expose to I^-/I_3^- redox mediators and thereby gave more charge transfer active sites. The highest cell efficiency of 7.65% was achieved by using the MWCNTs/POEI-II gel electrolyte and showed an unflinching durability of greater than 1,000 h under $50\text{ }^\circ\text{C}$ as shown in Figure 11.

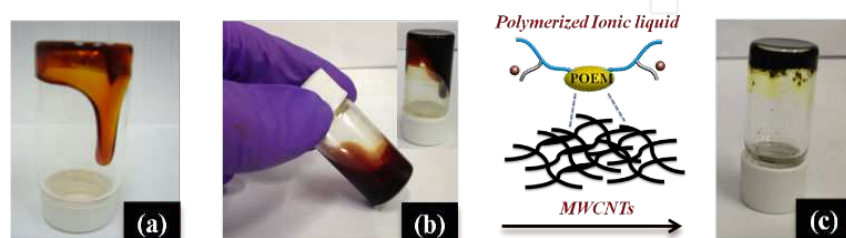


Figure 10. Photographs of the (a) pristine POEI-II, (b) POEI-II gel electrolyte, and (c) POEI-II/MWCNTs gel electrolyte [42].

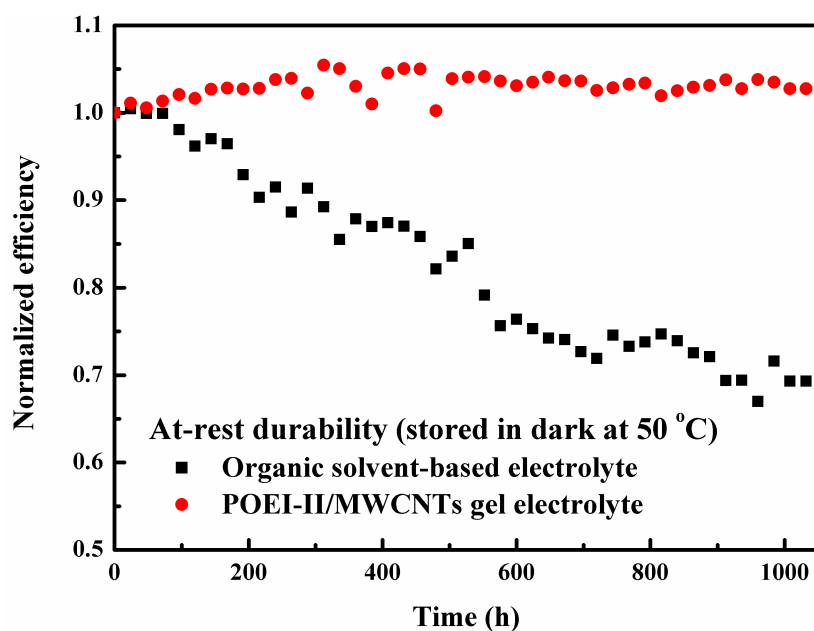


Figure 11. At-rest durability data of the DSSCs (stored in dark at 50 °C) with POEI-II/MWCNTs gel electrolyte and with an organic solvent electrolyte [42].

Table 2 is a partial list of the DSSCs' performance containing above novel functional IL mediators in the quasi/all-solid-state electrolytes.

ILs	Quasi/All-solid-state Electrolytes	Dye	η (%)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF	Durability (% to the initial η)	Ref.
SD1	0.12 M SD1, 0.03 M I ₂ , 0.1 M TBP, 0.12 M LiTFSI, 0.012 M EMIB(CN) ₄	N719	1.43	726	3.10	0.64	N.A.	[25]
SD2	0.12 M SD2, 0.03 M I ₂ , 0.1 M TBP, 0.12 M LiTFSI, 0.012 M EMIB(CN) ₄	N719	2.85	718	6.23	0.64	84% (after 1 month)	[25]
PMIm	PMIm	MK2	6.30	710	12.65	0.70	100% (after 1500 h)	[26]
1	1/I ₂ /LiI/EMIBF ₄ = 5/1/1.25/0.25	MK2	6.63	660	13.77	0.73	100% (after 1000 h)	[27]
HEII	HEII/I ₂ /LiI/NMBI/MPII = 12:1:3:10:0.5	MK2	7.45	733	14.66	0.69	96% (after 1500 h)	[28]
DEII	For WE: DEII; For CE: DEII/I ₂ = 6:1	FNE29	6.50	633	16.29	0.63	N.A.	[29]
ILMC	0.1 M I ₂ , 0.1 M LiI in PMII/ILMC (v/v = 3/1)	N719	6.99	640	15.28	0.72	100% (after 1000 h)	[30]

ILs	Quasi/All-solid-state Electrolytes	Dye	η (%)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF	Durability (% to the initial η)	Ref.
[BuPyIm]Br	0.1 M [BuPyIm]Br, 0.2 M I ₂ , 0.14 M GuSCN in PMII/EMISCN (v/v = 13/7)	Z907	5.67	640	13.60	0.66	96% (after 60 days)	[31]
MSII	MSII/I ₂ /BI/GuSCN (24/2/2/0.4)	DPP-I	3.23	600	8.97	0.61	N.A.	[32]
SSBI	0.05 M I ₂ , 0.1 M LiI, 0.5 M TBP, 0.053 M SSB, 0.22 M diiodoalkane in MPN	N719	5.00	710	11.20	0.63	52% (after 1000 h)[33]	
Si-IL	Si-IL	D5	1.25	680	2.80	0.65	N.A.	[34]
PEAII	PEAII	N3	5.29	838	9.75	0.65	85% (after 1000 h)[35-37]	
P-HI	20 wt% of P-HI in HMII/AMII/NMBI/GuSCN (8/8/1.2/1.2)	N3	6.95	643	15.10	0.72	N.A.	[38]
PEBII	PEBII	N719	6.70	760	16.60	0.53	N.A.	[39-40]
poly (AMImI)	0.5 wt% MWCNT/AMBIImI, 0.05 M I ₂ , 0.17 M NMBI, 0.013 M GuSCN, and 1 g poly(AMImI) in ACN	N3	3.55	646	8.51	0.64	N.A.	[41]
POEI-II	5 wt% MWCNTs, 0.1 M LiI, 0.05 M I ₂ , 0.5 M TBP, and 0.3 M POEI-II in N719 ACN/MPN (v/v = 1/1).	N719	7.65	784	14.50	0.67	100% (after 1000 h)	[42]

Note: 1-ethyl-3-methylimidazolium tetracyanoborate (EMIB(CN)₄), ethanol (EtOH), 1-methyl-3-ethyl-imidazolium tetrafluoroborate (EMIBF₄), 1-methylbenzimidazole (NMBI), 1-Ethyl-3-methyl-imidazolium thiocyanate (EMISCN), benzimidazole (BI), 1-hexyl-3-methylimidazolium iodide (HMII), 1-allyl-3-methylimidazolium iodide (AMII), 1-(2-acryloyloxy-ethyl)-3-methyl-benzoimidazol-1-ium iodide (AMBIImI)

Table 2. A partial literature review of the DSSCs' performance containing the novel functional IL mediators in the quasi/all-solid-state electrolytes.

3. Summary and future prospects

Traditional ILs are organic salts basically composed of variable cation-anion unions that exhibit low volatility accompanying with high thermal stability, excellent electrochemical stability, and high ionic conductivity. These characteristics of ILs create the possibility of designing ideal electrolytes for DSSCs. Recently, the development of new classes of functional group-substituted ILs, *i.e.* conductive ILs, dual redox mediators-based ILs, and polymeric ILs, etc., has been demonstrated as a promising strategy to further enhance the efficiency and the long-term stability of ILs electrolyte-based DSSCs. In this chapter, we mainly review the recent researches on the topic of new classes of ILs used as the electrolyte in DSSCs, and our last relevant works

are also introduced for comparison. The new classes of ILs employed in the electrolytes of DSSCs are divided into two sections: (i) the applications in liquid electrolytes in DSSCs and (ii) the applications in quasi/all-solid-state electrolytes in DSSCs.

Among section (i), our group synthesized a novel IL with TEMPO-imidazole complex coupling with I⁻, namely JC-IL, for preparing the liquid electrolyte for DSSCs. Due to its dual redox mediators of nitroxide radical (N-O \cdot) and I⁻, this kind of electrolyte exhibited not only faster regeneration rate toward oxidized dye but also the more positive redox potential in DSSCs than the traditional electrolyte containing only I⁻ redox mediator. As a result, the DSSC with JC-IL-based liquid electrolyte showed a good cell efficiency of 8.12% with remarkably high V_{OC} of 858 mV. Based on the structure of JC-IL, we further exchanged I⁻ to SeCN⁻ for synthesizing an iodide-free IL mediator coded as TISECN. The combination of the dual charge transfer mediators, *i.e.* N-O \cdot and SeCN⁻, in the TISECN-based liquid electrolyte could facilitate the charge transportation within the electrolyte and greatly reduced the energy loss in the cell, such as charge recombination, usually occurring in a DSSC with I⁻/I₃⁻ redox couple. An impressive cell efficiency of 8.38% with a high V_{OC} of 854 mV, J_{SC} of 14.70 mA cm⁻², and FF of 0.67 was achieved for the iodide-free DSSC by using the TISECN-based liquid electrolyte.

In section (ii), an polymeric IL, POEI-imidazole complex coupling with I⁻ (coded as POEIII), was synthesized for preparing the gel electrolyte for quasi-solid-state DSSCs. Herein, POEIII, which acted simultaneously as a redox mediator for dye regeneration and a gelator for the solidification of organic solvent-based electrolyte, was used to improve cell durability. The presence of the POE segment in the POEIII could chelate lithium cations (Li⁺) within the electrolyte to improve the V_{OC} of a DSSC and enable the strong inner π - π and long-pair- π electron interactions to enhance the ionic conductivity and the diffusivity of redox couple within the gel electrolyte. Consequently, the quasi-solid-state DSSC with POEIII gel electrolyte reached a high cell efficiency of 7.19%. In addition, appropriate amount of MWCNTs were incorporated into POEIII gel electrolyte as the extended electron transfer materials to facilitate charge transfer from counter electrode to redox mediator, which benefited the dye regeneration more efficiently. Meanwhile, the POE segments in POEIII could prevent the MWCNTs from aggregation, which made the well dispersed MWCNTs to largely exposed to I⁻/I₃⁻ redox mediators. The highest cell efficiency of 7.65% was achieved by using the MWCNTs/POEIII gel electrolyte and showed a unflinching durability of greater than 1,000 h under 50 °C.

Up to now, most quasi/all-solid state DSSCs with IL electrolyte achieved relatively low cell efficiency as compared to the traditional DSSCs with liquid electrolyte. Despite the former system which showed superior durability than that of the latter, the cell efficiency indeed needs to be further improved because both stability and solar-to-electricity efficiency are the two essential criteria for a good DSSC. Besides, iodine-free electrolyte is desirable for developing flexible DSSCs where a metal substrate is prone to corrosion by iodine. Accordingly, in the future, we can synthesize a novel IL with TEMPO-Imidazole-POEI complex coupling with SeCN⁻ for preparing an iodine-free and quasi-solid state electrolyte for DSSCs. This kind of multi-functional ILs could potentially provide dual channels for charge transportation within the DSSCs, and simultaneously acts as a gelator for the solidification of organic solvent-based electrolyte. This idea would be a key issue for future study.

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