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# Phenyl and thienyl functionalized imidazolium iodides for highly efficient quasi-solid-state dye-sensitized solar cells

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To enhance the ionic conductivity of imidazolium iodide based ionic conductors, the  $\pi$  conjugation of imidazolium cation is expanded via N-substitution with aromatic groups of phenyl and thienyl. Three ionic conductors (ICs) of MPhII, MT<sub>2</sub>II and MT<sub>3</sub>II are designed and synthesized by linking benzene, 2-thiophene, 3-thiophene to the imidazolium ring, respectively, and their single crystal structures are revealed. Quasi-solid-state electrolytes are prepared by solidifying the IC-contained solutions with SiO<sub>2</sub> nanoparticles for quasi-solid-state dye-sensitized solar cells (QSS-DSSCs). The ionic conductivity of the quasi-solid-state electrolytes depends on the substituent and the substitution position as well, which is well correlated with the distance between adjacent iodides, as revealed by the crystal packing structures. Owing to the highest conductivity among the three electrolytes, the QSS-DSSC with MPhII based quasi-solid-state electrolyte achieves the highest power conversion efficiency of 8.36% under AM 1.5G sunlight (100 mW cm<sup>-2</sup>), which also exhibits good long-term stability under one sun soaking for more than 2000 h.

# Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attention because of their low cost, high efficiency, simple fabrication processes and environmentally friendly features.<sup>1</sup> Key components of a DSSC include dye-sensitized porous TiO<sub>2</sub> film as the working electrode and platinized conductive substrate as the counter electrode. Sandwiched between the two electrodes is the redox couple based electrolyte. The redox shuttle has functions of donating electrons to the oxidized dye for dye regeneration and accepting electrons from the counter electrode for circuit completion.

For practical applications, the DSSCs should not only have high efficiency but also exhibit good long-term stability. Quasisolid-state electrolytes possess both cohesive property of solid materials and good diffusion property of liquid electrolytes.<sup>2</sup> Therefore, quasi-solid-state dye-sensitized solar cells (QSS-DSSCs) are able to achieve good long-term stability at a high efficiency level. Quasi-solid-state electrolytes can be prepared by solidifying organic solvent-based liquid electrolytes<sup>3-13</sup> and ionic liquid based electrolytes<sup>14-20</sup> with polymer gelators or metal oxide nanoparticles.

Recently, we developed functionalized ionic conductors (ICs) through introduction of ester, propargyl and hydroxyethyl groups to the imidazolium ring, respectively, for solid-state  $\ensuremath{\mathsf{DSSCs}}\xspace{\ensuremath{\mathsf{21-24}}\xspace}$  In this work, we designed and synthesized three ICs (MPhII, MT<sub>2</sub>II and MT<sub>3</sub>II, inset in Fig. 1) by linking aromatic ionic conductivity. The IC-contained solutions solidified with SiO<sub>2</sub> nanoparticles can be used as guasi-solid-state electrolytes for QSS-DSSCs. We find that the conductivity of these quasisolid-state electrolytes shows great difference, depending on the substituent and the substitution site. Analysis of singlecrystal structures for the three ICs shows that the distances of adjacent iodides in their crystal packing structures are distinctive, which correlates well with the conductivity sequence. Among them, MPhII possesses the highest conductivity due to the shortest distance between neighboring iodides and the lamellar structure. Interestingly, the conductivity of MT<sub>2</sub>II is much higher than that of MT<sub>3</sub>II due to the different substitution position of thiophene. As a consequence, the QSS-DSSC with MPhII-based quasi-solidstate electrolyte achieves the highest power conversion efficiency (PCE) of 8.36% under global air-mass (AM 1.5G) sunlight (100 mW cm<sup>-2</sup>), with short-circuit photocurrent density  $(J_{sc})$  of 15.22 mA cm<sup>-2</sup>, open-circuit photovoltage  $(V_{oc})$ of 782 mV and fill factor (FF) of 0.70, which also exhibits good long-term stability under one-sun soaking for more than 2000

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groups, such as phenyl or thienyl (position-2 and position-3),

to the imidazolium ring, respectively, for highly efficient and stable QSS-DSSCs. The intention of linking an aromatic group

to the imidazolium ring is to expand the  $\pi$  conjugation,  $^{25\text{-}27}$ 

which can cause strong  $\pi$ - $\pi$  interactions between imidazolium

cations. As a result, the distance between neighboring iodides

can be shortened, which is conductive to promote charge

transfer between adjacent jodides and hence increase the

h.

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## **Experimental**

#### Synthesis of Ionic Conductors

The ICs were synthesized in two steps, as shown in Fig. S1a. Replace the hydrogen atom on one nitrogen atom of imidazole with phenyl<sup>28</sup> or thienyl<sup>29</sup> first, and then quaternize the other nitrogen atom with methyl iodide. Specific steps are as follows:

## Synthesis of Intermediates.

1-phenyl-1H-imidazole:<sup>28</sup> A mixture of iodobenzene (1 mmol), imidazole (1.5 mmol), KOH (2.0 mmol), DMSO (1.5 mL) and Cul (0.2 mmol) were charged into a 100 mL two-necked flask under a nitrogen atmosphere and stirred at 120 °C for 24 h. The cooled mixture was diluted with H<sub>2</sub>O and extracted with ethyl acetate. After dried over MgSO<sub>4</sub>, the solvent was removed by rotary evaporation until viscous oil remained. Silica gel chromatography with petroleum ether/ethyl acetate (10/1, v/v) as the eluent afforded the pure product as a viscous yellow oil (yield, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 7.85 (s, 1H), 7.49-7.43 (m, 2H), 7.37-7.33 (m, 3H), 7.27 (s, 1H), 7.21 (s, 1H).

1-(2-thienyl)-1H-imidazole:<sup>29</sup> This compound was obtained with the same procedures for 1-phenyl-1H-imidazole except that the starting materials iodobenzene, KOH and Cul were replaced with 2-bromothiophene, CsCO<sub>3</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, respectively. The yield was 66%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 7.71 (s, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.09 (dd, J = 5.1, 1.5 Hz, 1H), 6.94 (dd, J = 7.9, 2.6 Hz, 2H).

1-(3-thienyl)-1H-imidazole:<sup>29</sup> This compound was obtained with the same procedures for 1-(2-thienyl)-1H-imidazole except that the starting material 2-bromothiophene was replaced with 3-bromothiophene. The yield was 62%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 7.82 (s, 1H), 7.43 (dd, J = 5.2, 3.2 Hz, 1H), 7.24 (d, J = 1.1 Hz, 1H), 7.21 (dd, J = 3.2, 1.4 Hz, 1H), 7.18 (dd, J = 5.2, 1.4 Hz, 2H).

#### Synthesis of the Ionic Conductors.

One of the above compound (0.02 mol), 10 mL of tetrahydrofuran, and iodomethane (0.04 mol) were charged into a 50 mL three-necked flask equipped with a condensing tube and stirred at 50 °C for 48 h. Then, the reaction mixture was precipitated to produce the ICs of MPhII,  $MT_2II$  and  $MT_3II$  as white powders (Fig. S1b) with yield greater than 90%. The sketching vibration peaks of phenyl and thienyl groups appear at 1600-1400 cm<sup>-1</sup> and 1639 cm<sup>-1</sup>, while the peaks at 3055 cm<sup>-1</sup> and 3138 cm<sup>-1</sup> are identified as the C-H stretching vibration of the aryl lateral group (Fig. S2).

3-methyl-1-phenylimidazolium iodide (MPhII): <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  ppm: 9.76 (s, 1H), 8.31 (s, 1H), 7.96 (s, 1H), 7.77 (d, J = 7.9 Hz, 2H), 7.68 (t, J = 7.7 Hz, 2H), 7.60 (t, J = 6.9 Hz, 1H), 3.95 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  ppm: 136.60 (s), 135.39 (s), 130.90 (s), 130.43 (s), 125.11 (s), 122.50 (s), 121.61 (s), 36.95 (s). ESI-HRMS (*m*/*z*): Calcd. for C<sub>10</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup>, 159.0917; found 159.0908.

3-methyl-1-(2-thienyl) imidazolium iodide (MT<sub>2</sub>II): <sup>1</sup>H NMR (500 MHz, DMSO) δ ppm: 9.70 (s, 1H), 8.21 (t, J = 1.8 Hz, 1H), 7.95 (t, J = 1.7 Hz, 1H), 7.69 (dd, J = 5.5, 1.5 Hz, 1H), 7.55 (dd, J = 3.8, 1.5 Hz, 1H), 7.19 (dd, J = 5.4, 3.8 Hz, 1H), 3.92 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO) δ ppm: 137.57 (s), 135.73 (s), 127.28 (s), 126.22 (s), 124.91 (s), 123.21 (d, J = 3.6 Hz), 36.66 (s), 36.66 (s). ESI-HRMS (m/z): Calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>S<sup>+</sup>, 165.0481; found 165.0469.

3-methyl-1-(3-thienyl) imidazolium iodide (MT<sub>3</sub>II): <sup>1</sup>H NMR (500 MHz, DMSO) δ ppm: 9.75 (d, J = 0.4 Hz, 1H), 8.27 (t, J =1.9 Hz, 1H), 8.10 (dd, J = 3.2, 1.5 Hz, 1H), 7.93 (t, J = 1.7 Hz, 1H), 7.89 (dd, J = 5.3, 3.2 Hz, 1H), 7.59 (dd, J = 5.3, 1.5 Hz, 1H), 3.94 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO) δ ppm: 136.30 (s), 133.45 (s), 129.74 (d, J = 2.9 Hz), 124.75 (s), 121.55 (dd, J = 13.1, 3.7 Hz), 117.72 (d, J = 6.3 Hz), 36.61 (s). ESI-HRMS (m/z): Calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>S<sup>+</sup>, 165.0481; found 165.0476.

# Preparation of quasi-solid-state electrolyte and fabrication of QSS-DSSCs

The mixtures of IC, I<sub>2</sub>, LiI, TBP at molar ratio of 12:1:2:10, were first dissolved in a mixed solvent of acetonitrile and methanol (1/1, v/v), and then the liquid electrolytes were solidified by adding 4 wt% SiO<sub>2</sub> to the system. Finally, the mass ratio of the solvent in the quasi-solid-state electrolyte is about 18%. The quasi-solid-state electrolytes containing different ICs are indicated as QSS-IC, such as QSS-MPhII, QSS-MT<sub>2</sub>II, and QSS-MT<sub>3</sub>II. For comparison, the IC is replaced with 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII) to prepare the reference quasi-solid-state electrolyte (QSS-DMPII) at the same ratios.

15  $\mu$ m-thick TiO<sub>2</sub> films on the FTO substrates were obtained with a screen-printing method. The films were sintered at 500 °C for 1 h with a rising rate of 10 °C min<sup>-1</sup>. The above films were then treated with TiCl<sub>4</sub> (0.05 M) aqueous solution at 70  $^{\circ}$ C for 30 min followed by calcinations at 450  $^{\circ}$ C for 30 min. When cooled down to around 120  $^{\circ}$ C, the TiO<sub>2</sub> electrodes were immersed into the N719 dye solutions (0.3 mM) for 20 h at room temperature. The dye-loaded TiO<sub>2</sub> film functioning as the working electrode and the Pt-coated FTO as the counter electrode were separated with a hot-melt Surlyn film (30 µm) and sealed together by pressing them under heat. The quasisolid-state electrolyte was injected between the working and counter electrodes at 80 °C from the two holes predrilled on the back of the counter electrode. Finally, the predrilled holes were sealed with a Surlyn film covered with a thin glass slide under heat.

#### Characterizations

ICs were characterized by <sup>1</sup>H NMR (Varian 400 MHz NMR spectrometer and Bruker 500 MHz NMR spectrometer). Mass spectra were obtained on microTOF II-10257 (Bruker Compass Data Analysis 4.0). Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis were performed on a simultaneous thermal analyzer SDT-Q600 system (TA Instruments, America) with nitrogen gas as purge (80 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup> in a temperature range of 20-700 °C. UV-vis absorption spectra were obtained on a UV-vis spectrophotometer (Shimadzu UV-2550) in a transmission mode. Crystal structures of ICs were acquired on a Bruker SMART diffractometer equipped with an APEX(II)-CCD area detector using graphite-monochromatic Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. The current density-voltage (J-V) curves were measured with a Keithley 2420 source meter (A Tektronic Company) under illumination of simulated AM1.5G solar light

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(Newport-94043A). The simulated light was calibrated using a standard Si solar cell (Oriel PN 91150 V) equipped with a KG5 filter. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were recorded using an SM-250 Hyper Mono-Light system (Bunkoh-Keiki, Japan). The intensity of monochromatic light was measured with a Si detector (S1337-1010BQ). The electrolytes were sandwiched in dummy cells between two platinized FTO electrochemical impedance spectroscopy (EIS) in a frequency range from 100 mHz to 100 kHz and for Tafel polarization measurement at a scanning rate of 50 mV s<sup>-1</sup> with an electrochemical workstation (Zahner CIMPS-1, Germany).

## **Results and Discussion**

The single crystals of ICs can grow from the solutions in mixed solvents of methanol and diethyl ether in a fridge. The three single crystals are transparent and colorless. Crystal structure analyses (Table S1-S3) reveal that MPHII (CCDC 1523312) crystallize in the monoclinic space group P2(1)/c while the MT<sub>3</sub>II (CCDC 1517957) and MT<sub>2</sub>II (CCDC 1523955) crystals belong to the orthorhombic space group of Pca21 and Pna21, respectively. Fig. 1 shows the single crystal structures of the three ICs. For MPHII, the phenyl ring and the imidazolium ring are approximately coplanar with a dihedral angle of  $10.51^{\circ}$  (Fig. S3a). However, the thiophene ring and the imidazolium ring form a larger dihedral angle of  $36.84^{\circ}$  (Fig. S3b) for MT<sub>2</sub>II, which results from the repulsive interaction

between the S and N atoms. When the substitution site is changed from position-2 to position-3, that is from  $MT_2II$  to  $MT_3II$ , the repulsion between the S atom and the N atom diminishes due to the increased distance between them, leading to weakened torsion tension between the thiophene ring and the imidazolium ring. As a result, the dihedral angle decreases from  $36.84^\circ$  for  $MT_2II$  (Fig. S3b) to  $10.31^\circ$  for  $MT_3II$  (Fig. S3c). The coplanarity between the imidazolium ring and the thiophene ring is influenced by the substitution position of thiophene.



Fig. 1 Single crystal structures of (a) MPhII, (b)  $MT_2II$ , and (c)  $MT_3II$ . I (purple), N (blue), S (yellow), C (gray), H (white). The inset in (b) shows the chemical structures of ICs.



Fig. 2 Packing diagrams viewed along (a) the b axis for MPhII; (b) the a axis for MT<sub>2</sub>II and (c) the a axis for MT<sub>3</sub>II. I (purple), N (blue), S (yellow), C (gray).

The packing configurations of the three ICs are distinct, as shown in Fig. 2, which shows the packing orientation of imidazolium cation and the location of iodide. The neighboring cations (that is the coplanar phenyl imidazolium) in the MPhII crystal are stacked together in parallel, forming a lamellar structure (Fig. 2a). For  $MT_2II$ , the nonplanar 2-thienyl imidazolium cations are arranged with the neighboring imidazolium rings in parallel but the neighboring thiophene rings in a cross arrangement (Fig. 2b), due to the interaction between the S atoms in the thiophene ring. However, the adjacent coplanar 3-thienyl imidazolium cations in the  $MT_3II$  crystal are arranged in a V-shape orientation (Fig. 2c), attributed to the interaction between S atoms in the thiophene ring again. The packing structures suggest that the  $\pi$ - $\pi$  interactions increase in the order of MT<sub>3</sub>II < MT<sub>2</sub>II < MPHII. The shortest path of electron transfer between adjacent iodides, which is indicated with green labels in Fig. 2, increases in the order of MPHII (5.3 and 6.4 Å) < MT<sub>2</sub>II (6.3 Å) < MT<sub>3</sub>II (7.9 Å). This implies that strong  $\pi$ - $\pi$  interaction is favorable for reducing the distance between neighboring iodides in the shortest path. The electron transfer rate is expected to

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increase with decreasing the distance between neighboring iodides.



TG and DSC measurements were carried out to determine the thermal properties of the three ICs. Fig. 3a shows the TG curves for the three ICs. The temperature at 2% weight loss is regarded as the decomposition temperature  $(T_d)$ , which is determined to be 222, 227 and 234 °C for MT<sub>2</sub>II, MPhII and MT<sub>3</sub>II, respectively. As the three ICs have the same anion, the thermal stability depends on the imidazolium cation, which is affected by the substituent. For MPhII and MT<sub>3</sub>II, which have comparable dihedral angles (Figure S3) between the imidazolium and phenyl (or thienyl) rings, the positive charge on the imidazolium ring is a major factor on the thermal stability. Compared to the phenyl substitution, the S atom with two free electrons in MT<sub>3</sub>II reduces the positive charge of imidazolium cation, which is likely responsible for the higher decomposition temperature (or higher thermal stability) for MT<sub>3</sub>II. As for MT<sub>2</sub>II, the strong torsional strain between thienyl ring and imidazolium ring, as revealed by its larger dihedral angle (Figure S3), decreases the thermal stability. Therefore, the decomposition temperature of MT<sub>2</sub>II is lower than MT<sub>3</sub>II and even lower than MPhII. The high decomposition temperatures ensure that these ICs do not decompose for outdoor applications, in which the maximum temperature is usually 80 °C.

Fig. 3b displays the DSC curves of the three ICs, where two endothermic peaks are observed for each IC. The left peak is attributed to the phase transition from solid to liquid while the right one is due to the decomposition of matter. Melting points determined from the left DSC peak are 117, 158 and 166 °C for MPhII, MT<sub>2</sub>II and MT<sub>3</sub>II, respectively. The difference of melting points for the three ICs is likely attributed to their different unit cell volumes.<sup>2</sup> Usually, a smaller unit cell volume brings about a higher melting point for similar compounds. Since the unit cell volume decreases in the order of MPhII (4477.1 Å<sup>3</sup>) > MT<sub>2</sub>II (2141.3 Å<sup>3</sup>) > MT<sub>3</sub>II (2100.1 Å<sup>3</sup>), as shown in Table S1-S3, it is reasonable that the melting point increases in the order of MPHII (117 °C)  $\leq$  MT<sub>2</sub>II (158 °C)  $\leq$  MT<sub>3</sub>II (166 °C).<sup>30</sup>

The ionic conductivity of the three IC-based quasi-solid-state electrolytes (QSS-MPhII, QSS-MT<sub>2</sub>II, QSS-MT<sub>3</sub>II) was determined through EIS analysis on the dummy cells with the FTO/Pt/electrolyte/Pt/FTO configuration. Fig. 4a shows the Nyquist plots of the three quasi-solid-state electrolytes, which can be explained by the equivalent circuit shown in the inset of Fig. 4a, according to the literature.<sup>31</sup> The series resistance  $(R_s)$ is determined by the real axis intercept in the high frequency region. The left semicircle located at the high-frequency region represents the charge-transfer resistance (R<sub>ct</sub> for one electrode and 2  $R_{ct}$  for two electrodes) at the electrode/electrolyte interface and the corresponding constant phase angle element (CPE). The right semicircle at the low-frequency region corresponds to the Nernst diffusion impedance  $(Z_N)$  of the  $I/I_3$ redox couple in the electrolyte.<sup>32</sup> The electrochemical parameters for each electrolyte are obtained by fitting the EIS spectra, which are shown in Table 1. The  $R_s$  is same for all the three electrolytes because the same electrodes are used for the EIS measurements. The ionic conductivity ( $\sigma$ ) of electrolyte can be calculated from the  $Z_N$  following equation:  $\sigma = d/(Z_N \times A)$ , where d is the distance between the two electrodes (here 30  $\mu$ m) and A is the active area (here 0.36 cm<sup>2</sup>) of the quasi-solidstate electrolyte. QSS-MPhII has the smallest  $Z_N$  (1.0  $\Omega$ ), corresponding to the highest conductivity of 8.3 mS cm<sup>-1</sup> among the three QSS-IC electrolytes. For the two isomers, QSS-MT<sub>2</sub>II shows a lower  $Z_N$  (1.3  $\Omega$ ) than QSS-MT<sub>3</sub>II (2.0  $\Omega$ ), indicating that the former exhibits higher conductivity (6.4 mS cm<sup>-1</sup>) than the latter (4.2 mS cm<sup>-1</sup>). On the basis of these results we conclude that benzene substituted imidazolium iodide is better than the thiophene substituted imidazolium iodide, and the second position substitution is better than the third substitution of thiophene in terms of conductivity. For comparison, the conductivity for QSS-DMPII is determined to be 3.0 mS cm<sup>-1</sup> (Fig. S4a), which is lower than those for the QSS-ICs.

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The main contribution to the ionic conductivity of imidazolium iodide based quasi-solid-state electrolytes comes from the charge transfer along the polyiodide chain according to the relay-type Grotthuss mechanism.<sup>33</sup> The Grotthuss charge exchange is influenced by the distance between adjacent iodides, which can be revealed by the packing structures of single crystal<sup>22,23</sup> (Fig. 2). The shortest charge transfer path between iodine atoms in MPhII is carried out in a zigzag, where the transfer distance is 5.3 and 6.4 Å alternately (Fig. 2). Similarly, the distance in the shortest charge transfer path is 6.3 and 7.9 Å for MT<sub>2</sub>II and MT<sub>3</sub>II, respectively. As the Grotthuss charge transfer rate is inversely correlated with the I-I distance, the conductivity thus increases in the order of QSS-MT<sub>3</sub>II < QSS-MT<sub>2</sub>II < QSS-MPhII. On the other hand, the lamellar structure of MPhII cation (Fig. 2) is also favorable for stronger  $\pi$ - $\pi$  interactions, which can promote faster charge transfer.<sup>34</sup> Interestingly, the conductivity of QSS-MT<sub>2</sub>II is about 50% higher than that of QSS-MT<sub>3</sub>II due to the different I<sup>-</sup>-I<sup>-</sup> distance arising from the different substitution position.

The temperature dependence of the ionic conductivity is shown in Fig. 4b. The conductivity ( $\sigma$ ) increases with the temperature following the Arrhenius equation:  $\sigma = \sigma_0 \exp(-\frac{1}{2})$  $E_a/RT$ ), where  $\sigma_0$  is a constant,  $E_a$  is the activation energy, R is the ideal gas constant, and T is the absolute temperature.<sup>35</sup> The linear dependence of  $\ln\sigma$  on 1/T indicates that these ICbased electrolytes is ionic conductive, which is attributed to the charge transfer along the polyiodide chain according to the relay-type Grotthuss mechanism.<sup>33</sup> A lower slope of the linear dependence of  $\ln\sigma$  on 1/T represents a smaller  $E_a$  that the energy barrier must be overcome for charge transfer. According to the literature report,<sup>36</sup> shorter distance between iodide/polyiodide species can promote Grotthuss bond exchange  $(I^{-} + I_{3}^{-} = I_{3}^{-} + I^{-})$  and thus leads to efficient charge transfer. As the distance between adjacent iodide/polyiodide species decreases in the order of  $MT_3II > MT_2II > MPhII$  (Fig. 2), the charge transfer becomes more efficient in the sequence of  $MT_3II < MT_2II < MPhII$ . For this reason, the obtained  $E_3$  (16.7 kJ mol<sup>-1</sup>) for QSS-MT<sub>3</sub>II is larger than that for QSS-MT<sub>2</sub>II (11.3 kJ mol<sup>-1</sup>), and the latter is larger than that for QSS-MPhII (8.1 kJ

 $mol^{-1}$ ). The sequence of ionic conductivity at RT is QSS-MT<sub>3</sub>II < QSS-MT<sub>2</sub>II < QSS-MPhII for the same reason.



Fig. 5 Tafel polarization curves of the quasi-solid-state electrolytes containing IC,  $I_2$ , LiI, TBP (12/1/2/10) and 4wt% SiO<sub>2</sub> with 18% solvent of acetonitrile and methanol (1/1, v/v).

Tafel polarization is a convincing electrochemical characterization method to test the diffusion rate of electrolyte. Fig. 5 shows the Tafel polarization curves of the three QSS-IC electrolytes, where the limiting diffusion of I<sub>3</sub> takes place in the high-potential region. The limiting current densities  $(J_{lim})$ , which are summarized in Table 1, decrease in the order of QSS-MPhII (178 mA  $\text{cm}^{-2}$ ) > QSS-MT<sub>2</sub>II (142 mA  $cm^{-2}$ ) > QSS-MT<sub>3</sub>II (89 mA cm<sup>-2</sup>). The J<sub>lim</sub> is proportional to the diffusion coefficient of  $I_3^{-}$ ,  $D(I_3^{-})$ , according to equation:  $J_{lim} =$  $2ne_0D(I_3)c(I_3)N_A/d$ , where n is the number of exchanged electrons,  $e_0$  is the elementary charge,  $c(I_3)$  is the triiodide concentration,  $N_A$  is the Avogadro number and d is the distance between the two electrodes.<sup>31</sup> The  $D(I_3^{-3})$ , calculated from equation (3), is  $2.8 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>,  $2.3 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, and  $1.4 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for QSS-MPhII, QSS-MT<sub>2</sub>II, and QSS-MT<sub>3</sub>II, respectively (Table 1). As the concentrations of ICs and other additives are the same in the three QSS-IC electrolytes, the difference of  $D(I_3)$  is believed to arise from the their different

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crystal structures (Fig. 2). The larger  $D(I_3^{-})$  stems from the shorter distance between the neighboring iodides. Because the distance between neighboring iodides decreases in the order of MT<sub>3</sub>II, MT<sub>2</sub>II, MPhII, the  $D(I_3^{-})$  increases in the same order. The electrolyte based on phenyl substituted imidazolium iodide shows the highest ionic conductivity as a result of its highest  $D(I_3^{-})$ . For comparison, the QSS-DMPII shows  $J_{\text{lim}}$  of 72 mA cm<sup>-2</sup> and  $D(I_3^{-})$  of 1.2 ×10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup> (Fig. S4b), which are respectively lower than those of QSS-ICs.

The Tafel curve also provides information of the exchange current density  $(J_0)$  from the slope in the middle potential region.<sup>37</sup> Here,  $J_0$  represents the reduction rate of  $I_3^-$ . QSS-MPhII and QSS-MT<sub>2</sub>II show a larger slope than QSS-MT<sub>3</sub>II according to Fig. 5, indicating that the interfacial reaction  $I_3^-$ +2e<sup>-</sup> $\rightarrow$ 3I<sup>-</sup> occurs at a faster rate for QSS-MPhII and QSS-MT<sub>2</sub>II than for QSS-MT<sub>3</sub>II. More  $I_3^-$  species for QSS-MPhII and QSS-MT<sub>2</sub>II can move to the interface between the counter

electrode and the electrolyte than for QSS-MT<sub>3</sub>II due to the higher  $D(I_3)$  for the former two electrolytes, accounting for the larger  $J_0$  for the former two electrolytes. We can conclude that the charge transfer at the counter-electrode/electrolyte interface is more effective for QSS-MPhII and QSS-MT<sub>2</sub>II than for QSS-MT<sub>3</sub>II. The result is consistent with the  $R_{\rm ct}$  data that also reflects the interfacial charge transfer behavior.

Table 1 . EIS and conductivity performances of QS-IC electrolytes.

QS-IC	R <sub>s</sub> /Ω	R <sub>ct</sub> /Ω	Z <sub>N</sub> / Ω	σ/mS cm <sup>-1</sup>	J <sub>lim</sub> /mA cm⁻²	<i>D</i> (I <sub>3</sub> <sup>-</sup> )/10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup>
MPhII	4.9	0.9	1.0	8.3	178	2.8
MT <sub>2</sub> II	4.9	0.8	1.3	6.4	142	2.3
MT₃II	4.9	1.1	2.0	4.2	89	1.4



Photocurrent density-voltage curves of the three QSS-ICsbased DSSCs are shown in Fig. 6a, and the corresponding photovoltaic performance parameters are summarized in Table 2. The QSS-MPhII based DSSCs produced a  $J_{sc}$  of 15.22 mA cm<sup>-2</sup>, a  $V_{oc}$  of 782 mV, and an FF of 0.70, corresponding to a PCE of 8.36%. Under the same conditions, the QSS-MT<sub>2</sub>II and QSS-MT<sub>3</sub>II based DSSCs produced efficiencies of 7.92% ( $J_{sc}$  = 14.95 mA cm<sup>-2</sup>,  $V_{oc}$  = 779 mV, FF = 0.69) and 6.81% ( $J_{sc}$  = 14.16 mA cm<sup>-2</sup>,  $V_{oc}$  = 750 mV, FF = 0.64), respectively. Evidently, the substituent group on the imidazolium ring exerts a significant effect on the photovoltaic performance. By comparison, the phenyl substitution is able to yield higher  $J_{sc}$  and PCE than the thienyl substitution. For the thienyl-substituted isomers, the position-2 substitution is better than the position-3 substitution in terms of all photovoltaic performance parameters. The difference of J<sub>sc</sub> among the three quasi-solidstate electrolytes is attributed to their different ionic conductivities. The QSS-MT<sub>3</sub>II electrolyte shows the lowest FF as a result of its largest  $R_{\rm ct}$ . The lowest  $V_{\rm oc}$  is the result of its lowest  $J_{sc}$ . Owing to the highest conductivity and lowest  $R_{ct}$ , the QSS-MPhII electrolyte produces the highest PCE and FF among the three electrolytes.

For comparison, the photovoltaic data for the reported quasi-solid-state electrolytes gelated with SiO<sub>2</sub> nanoparticles in combination with the N719 dye is also included in Table 2. The ethanol solution of Lil, I2 and TBP solidified with SiO2 nanoparticles yielded PCE of 6.1% at illumination of 91.3 mW cm<sup>-2</sup>.<sup>38</sup> The propylene carbonate based gel electrolyte containing 1-methyl-3-propylimidazolium iodide (MPII), iodine, N-methylbenzimidazole (NMBI) and Triton X-100 and SiO<sub>2</sub> nanoparticles showed PCE of 5.4%.<sup>39</sup> The ionic gel electrolyte with SiO<sub>2</sub> nanoparticles containing LiI, I<sub>2</sub>, NMBI, MPII dissolved in 3-methoxy propionitrile generated PCE of 6.71%.<sup>40</sup> By comparison, the QSS-MPhII evidently demonstrates an improvement over the reported SiO<sub>2</sub> based guasi-solid-state electrolytes.<sup>37-40</sup> As compared to other quasi-solid-state electrolytes, such as polymer gel,<sup>12,13,16,41</sup> graphene tailored polymer gel<sup>42</sup> and Al(III)-TBP based metal-organic gel,<sup>43</sup> the QSS-MPhII shows better or comparable PCE using the same dye sensitizer. At the same conditions, the DSSC with the QSS-DMPII electrolyte produces PCE of 6.51% (Fig. S5). Direct comparison reveals that the QSS-MPhII gel developed from this work demonstrates advantage over the QSS-DMPII and

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most reported gel electrolytes and is a promising quasi-solid state electrolyte for highly efficient QSS-DSSCs.

 Table 2. Photovoltaic Performance Parameters of DSSCs based on three QSS-IC electrolytes

QSS-IC	V <sub>oc</sub> /mV	J <sub>sc</sub> /mA cm <sup>-2</sup>	FF	η/%
MPhII	782	15.22	0.70	8.36
MT <sub>2</sub> II	779	14.95	0.69	7.92
MT <sub>3</sub> II	750	14.16	0.64	6.81
DMPII	742	13.12	0.67	6.51
Ref38	619	16.50	0.55	6.1
Ref39	650	12.90	0.62	5.40
Ref40	670	14.40	0.69	6.71
Ref12	760	17.4	0.61	8.00
Ref16	764	13.97	0.67	7.15
Ref41	730	13.99	0.71	6.73
Ref42	742	17.80	0.69	9.10
Ref43	704	17.08	0.70	8.25

Fig. 6b shows IPCE as a function of wavelength. The IPCE value in the visible region reflects dye regeneration rate in different IC-based DSSCs. The IPCE increases in the order of  $MT_3II < MT_2II < MPHII$ , which is consistent with the  $J_{sc}$  tendency. Significantly, the highest IPCE for the QSS-MPHII based DSSCs reaches 83%, which echoes the highest conductivity of QSS-MPHII.

To detect the long-term stability, the QSS-DSSC based on QSS-MPhII was soaked under one-sun illumination for 2012 h. In the light soaking period, the J-V curves of the QSS-DSSC based on QSS-MPhII were frequently recorded under AM 1.5G illumination, and the photovoltaic performance parameters are plotted against time, as shown in Fig. 7. At the initial illumination for 100 h, the  $J_{sc}$ ,  $V_{oc}$  and FF increased to some extent, resulting in increment of PCE in this period, because aging of the QSS-DSSC is favorable for the infiltration of quasisolid-state electrolyte into the photoanode for improved interfacial contact. After the initial 100 h, the  $V_{\rm oc}$  and FF remained unchanged basically up to 2012 h while the  $J_{sc}$  first decreased from 100 to 300 h followed a plateau up to 2012 h. As a consequence, the PCE gradually increased at the initial 100 h, presented a decline until 300 h, and then kept almost constant up to 2012 h. After light soaking for 2012 h the PCE was still 7.62%, which remained 97% of the initial value (7.84%). In a word, all the four photovoltaic performance parameters remained nearly constant from 300 to 2012 h, confirming that the DSSCs based on QSS-MPhII had good longterm stability.



Fig. 7 Evolutions of photovoltaic performance parameters under 1 sun soaking for the DSSCs based on QSS-MPhII and N719 dye sensitizer.

## Conclusions

We have synthesized three imidazole-based ICs by linking aromatic groups to the imidazolium ring and obtained their single crystal structures. When applied as quasi-solid-state electrolytes, the QSS-DSSCs exhibit different photovoltaic performance due to the different ionic conductivity of the electrolyte. The difference of ionic conductivity arises from the different crystal packing structures. The smallest distance between adjacent iodides and approximately planar structure of MPhII are favorable for efficient charge exchange along the polyiodide chain, which endues QSS-MPhII with higher conductivity than thienyl substituted imidazolium iodides. The substitution position of thienyl group can also affect the conductivity. MT<sub>2</sub>II possess higher conductivity than MT<sub>3</sub>II because the former has a shorter distance of adjacent iodides than the latter. Owing to the highest conductivity among the three QSS-IC electrolytes, QSS-MPhII-based DSSCs exhibit the highest PCE of 8.36%. Interestingly, the PCE of QSS-DSSCs increased by 16.3% from 6.81% to 7.92% when the substitution position of thienyl group was changed from position-3 to position-2. The experimental results indicate that the conductivity of the quasi-solid-state electrolyte and the corresponding photovoltaic performance depend largely on the substituent and the substitution position. Importantly, the QSS-MPhII-based DSSC presents good long-term stability under one-sun soaking for 2012 h. These findings may introduce an effective strategy to design ionic conductors with high conductivity for application in highly efficient and stable QSS-DSSCs.

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# **Graphical abstract**

The photovoltaic performance of quasi-solid-state DSSCs depends on the substituent and the substitution site of imidazolium ring as well.

