Supporting information for

An efficient and thermally stable dye-sensitized solar cell based on smectic thiolate/disulfide electrolyte and carbon/PEDOT composite nanoparticle electrode

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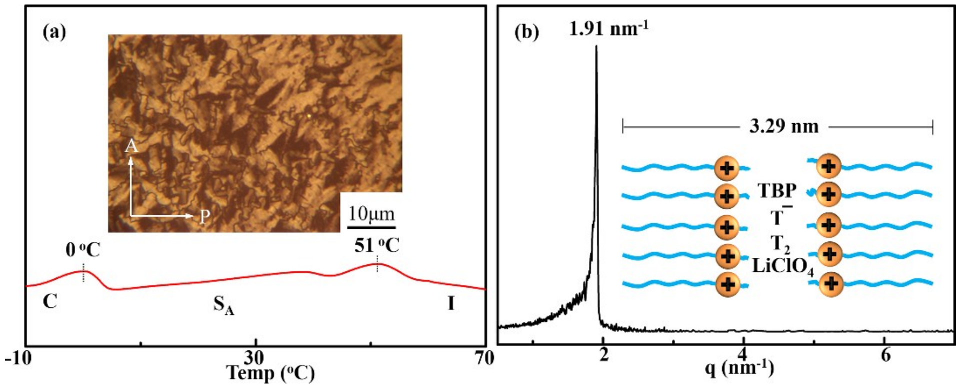
1. Mesomorphic properties of the electrolytes

Mesomorphism of the electrolytes was characterized by differential scanning calorimetry (DSC), polarizing optical microscope (POM) observations and small angle X-ray scattering (SAXS) analyses. Multiple peaks in the DSC traces of $C_{12}T_{add}$ indicated appearance of mesophases (**S-Figure 1a**). Mesophase type was assigned based on the POM textures. The characteristic focal conic textures (inset of **S-Figure 1a**) indicated the S_A liquid crystal phase of $C_{12}T_{add}$.



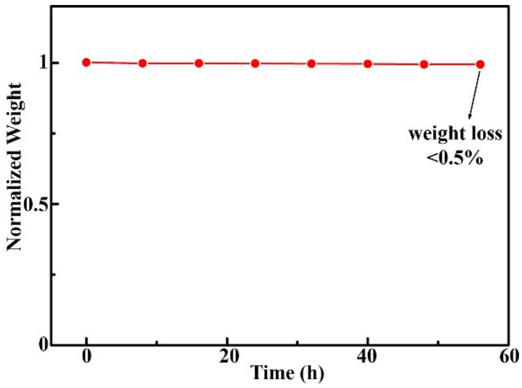
S-Figure 1 (a) DSC traces of $C_{12}T_{add}$ during the second heating process (C: crystal, S_A: smectic A phase, I: isotropic liquid) and POM observation of $C_{12}T_{add}$ at 30 °C; (b) SAXS patterns of $C_{12}T_{add}$ at 30 °C and the proposed molecular arrangement of $C_{12}T_{add}$

Temperature dependent SAXS measurements of $C_{12}T_{add}$ confirmed the presence of the S_A phase. A sharp peak centered at q=1.91 nm^{-1} appeared in the SAXS pattern of $C_{12}T_{add}$ at 30 °C (**S-Figure 1b**), which indicated a lamellar structure with an interlayer spacing of 3.29 nm. As we described previously,[1] the undoped $C_{12}T$ formed a bilayer structure and the interlayer spacing of $C_{12}T$ obtained from SARX measurement was

3.24 nm. The interlayer spacing of smectic $C_{12}T_{add}$ was slightly higher than that of undoped smectic $C_{12}T$. This fact suggested that smectic $C_{12}T_{add}$ also formed a bilayer structure wherein the T_2 and the additives should be intercalated between smectic layers as proposed in the inset of S-Figure 1b. The layered assembly of the T^-/T_2 redox formed ordered pathways for efficient charge transport.

2. Volatility of the electrolytes

The volatility of the electrolytes were determined using a gravimetric method. The electrolytes were placed in a vacuum oven at 40 ^{o}C and weighted at specific time to obtained the weight change. The normalized weight of $C_{12}T_{add}$ as a function of time is shown in **S-Figure 2**. The weight loss of $C_{12}T_{add}$ was less than 0.5% after 55 h at 40 ^{o}C under vacuum, indicating a non-volatile property of the liquid crystal electrolyte.



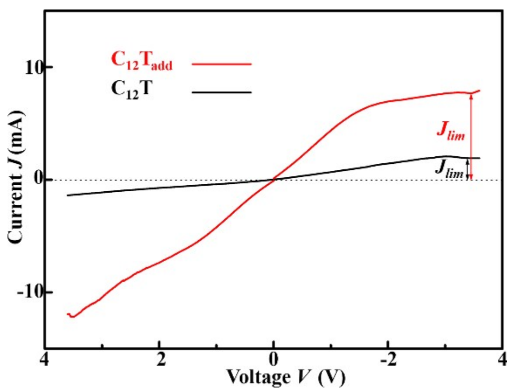
S-Figure 2 Normalized weight of $C_{12}T_{add}$ as a function of time at 40 ^{o}C under vacuum

3. Cyclic voltammograms of the electrolytes

Diffusion coefficient (D) of the electrolyte was determined from the limited current (J_{lim}) obtained by CV measurement (scanning rate: 10 mV s^{-1}) using a symmetric cell as described in the literature[1]. The symmetric cell was prepared by sandwiching the electrolyte between two carbon/PEDOT composite electrodes. Temperature of the symmetric cell was controlled by a hot stage. The measured CV curves of the electrolyte at 30 °C are shown in **S-Figure 3.** The relationship between D and J_{lim} is described by Eq. (S-1).

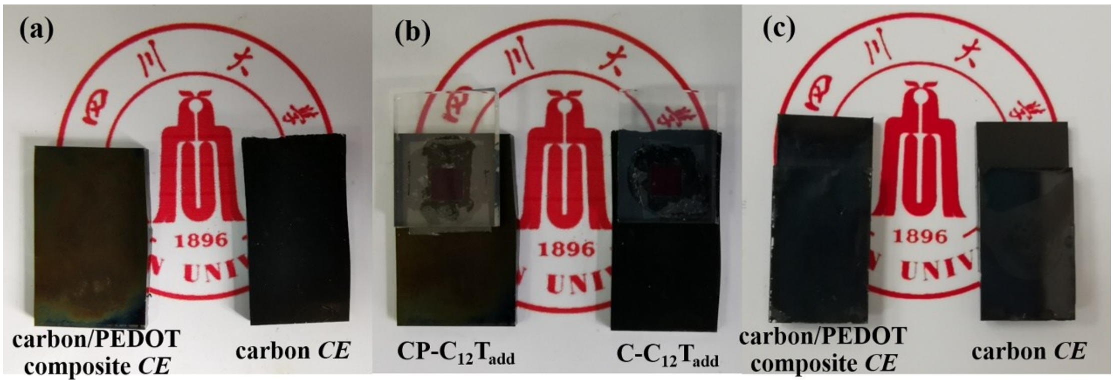
$$J_{\mathrm{lim}} = \frac{2ne_0 DCN_A A}{l} \quad \text{(S-1)}$$

Where n, e_0, C, N_A, l and A denote the number of electrons transferred in the reaction (n=2), the elementary charge (e_0=1.6×10^{-19} C), the charge carrier concentration (mol L^{-1}), the Avogadro constant (N_A=6.02×10^{23} C), the distance between electrodes and the active area of the interface between the electrodes and electrolyte, respectively.



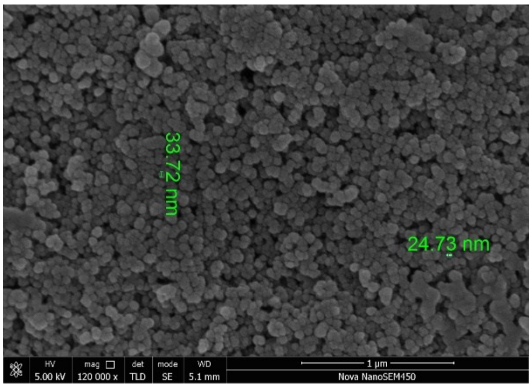
S-Figure 3 Cyclic voltammogram curves of the symmetric cells containing $C_{12}T$ and $C_{12}T_{add}$ at 30 °C

4. The images of the prepared electrode and DSSCs



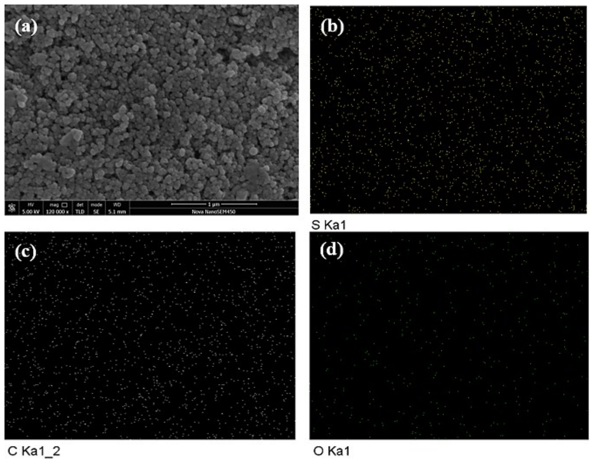
S-Figure 4 images of the prepared electrodes (a), DSSCs (b) and symmetric cells (c) the for the electrochemical measurement

5. The morphology of the carbon electrode



S-Figure 5 SEM image of the top-surface of the carbon electrode

6. EDS measurement



S-Figure 6 SEM image of the top-surface of the carbon/PEDOT electrode (a) and EDS mapping images of sulfur (b), carbon (c) and oxygen (d) elements.

Reference

1 Tan, S.; Zhao, Z.; Wang, S.; Wu. Y. A thiolate/disulfide liquid crystalline electrolyte for dye-sensitized solar cells: Promotion of the Grotthuss-type charge transport through lamellar nanostructures. *Electrochim*. *Acta* **2018**, *288*, 165-172.

2 Berginc, M.; Krašovec, U. O; Jankovec, M.; Topič, M. The effect of temperature on the performance of dye-sensitized solar cells based on a propyl-methyl-imidazolium iodide electrolyte. *Sol*. *Energ*. *Mater*. *Sol*. *C*., **2007**, *91*, 821-828.