Electronic Supplementary Material (ESI) for RSC Advances.

Role of lithium and co-existing cations in electrolyte to improve performance of dye-sensitized solar cells

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Electronic Supplementary Information (ESI):

Transient absorption spectra for a DSSC with different cation species (Li^+, $DMPI^+$ and TBA^+) (Fig. S1)

For the transient absorption spectroscopy (TAS) measurement, a xenon flash lamp (Hamamatsu Photonics, K.K.) with a wavelength range, 185 – 2000 nm, with a pulse width less than 1 μs was used for the probe light. The pump pulse source was same as the HD-TG measurement. The probe light was detected by a fiber optic spectrometer (Ocean Optics, Inc., USB2000+) with a wavelength range of 350 – 890 nm.

The TAS spectra were shown in Fig. S1. The bleach recovery of the dye absorption was observed in a wavelength range of 500 – 700 nm, and the absorption of the dye cation was observed in a wavelength range of 700 – 890 nm. The peaks of the dye bleach responses were found at 570 nm for LiI, at 560 nm for DMPII and at 550 nm for TBAI, respectively. On the other hand, the peak of the dye bleach response was found at 530 nm when the TAS spectra were measured in the absence of electrolyte. It was understood that the Stark effect caused the red shift of metal-to-ligand charge transfer (MLCT) absorption. The peak of the dye bleach was supposed to be shifted, when cation species in electrolyte were strongly adsorbed on TiO_2 surface. The order of the adsorbability on TiO_2 is $Li^+ > DMPI^+ > TBA^+$, and the peak of the dye bleach appeared at the longer wavelength as the stronger adsorbability on TiO_2, which indicated that the cations in electrolytes screen the charge on TiO_2 and that the MLCT absorption shifted in the presence of cations in the electrolytes.

The dependence of HD-TG responses on the mixed cation ratio for low concentrations of TBA^+ (0-25 %) (Fig. S2)

Figure S2 shows the HD-TG responses for a DSSC for the lower concentrations of TBA^+ to Li^+ (< 25%). The time constant of the second component gradually increased from 15 to 30 us until 17 % of TBA^+ was added in the electrolyte. The signal intensity of the fourth component also kept constant until 17 % of TBA^+ was added to the electrolyte, and then decreased for larger ration of TBA^+.

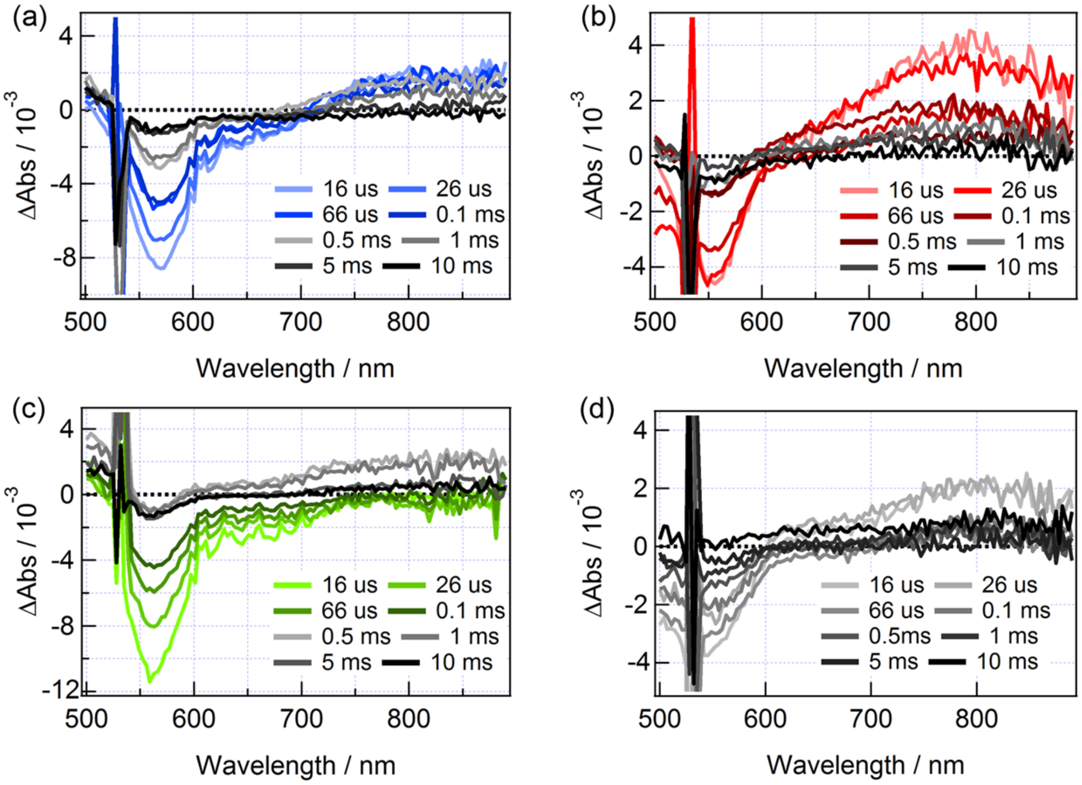

Fig.S1 Transient absorption spectra measured for a DSSC with 30 mM I_2/ACN with 300 mM (a) LiI, (b) TBAI and (c) DMPII. (d) Transient absorption spectra measured for a DSSC in the absence of electrolyte. They were measured under the open-circuit condition. The transient absorption spectra were taken at 16, 26, 66, 100, 500, 10^3, 5 x 10^3 and 10^4 μs, after an excitation pulse at 532 nm.

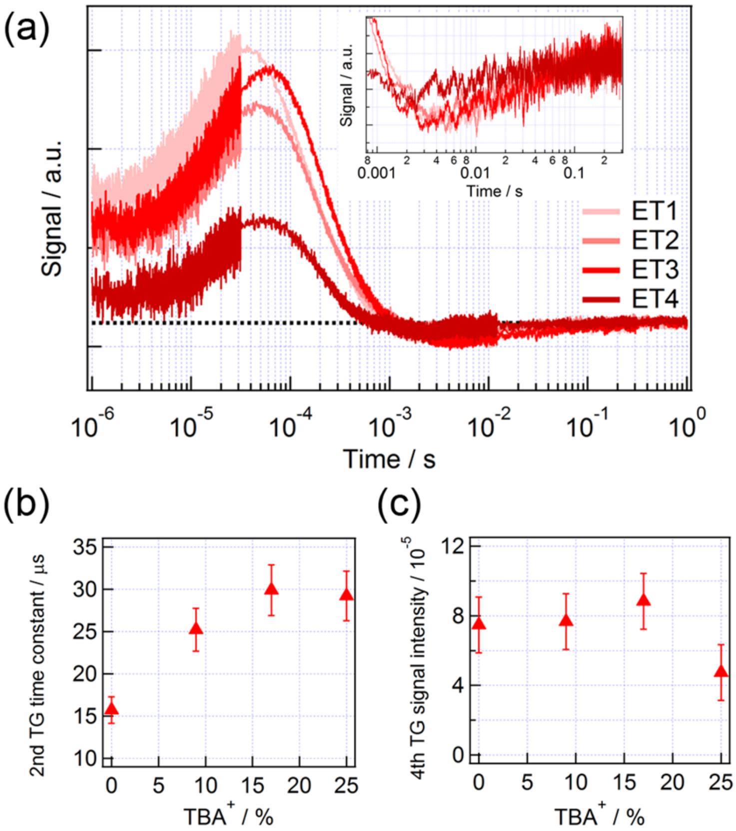

Fig. S2 (a) The HD-TG responses for DSSCs for different mixing ratio of the TBA$^+$ and Li$^+$ cations in the electrolytes. The mixed ratios can be referred to Table 1. The inset in (a) enlarges the HD-TG responses in the time range of 10^{-3} to 0.7 s. (b) Time constant of the second HD-TG component and (c) the signal intensity of the fourth HD-TG component in (a) as a function of the mixed ratio with TBA$^+$. The time constant was analyzed by a hybrid analysis that combines the maximum entropy method with nonlinear least squares fitting, using MemExp software.