Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Effect of electrolyte constituents on the motion of ionic species and recombination kinetics in dye-sensitized solar cells

Shota Kuwahara, Soichiro Taya, Naoya Osada, Qing Shen, Taro Toyoda and Kenji Katayama

Electronic Supplementary Information (ESI):

HD-TG and TA responses for a DSSC under open circuit condition (Fig. S1, Fig. S2)

The HD-TG and TA responses under open circuit condition were shown in Fig. S1 and Fig. S2. Figure S1 shows the I_2 concentration dependence, and Fig. S2 shows the I^- concentration dependences, respectively. The HD-TG responses were measured at 635 nm of the probe light, while the wavelength of the probe light for the TA measurements was changed to 785 nm. For the measurements under the open-circuit condition, the working and counter electrodes were disconnected.

As shown in Fig. S1(a), the HD-TG responses had 3 exponential components, and the rise of the $A_{rearrange}$ component was delayed as the I_2 concentration increased (The time constant increased from 5 to 7 μs.), while the decay of the $A_{e/electrolyte}$ component was accelerated (The time constant decreased from 6 to 4 ms.). This is the same tendency as the I_2 concentration dependence under short-circuit condition. The TA responses (Fig. S1(b)) had a decaying component in the time region of 10^{-4} to 1 s corresponding to electron loss by recombination processes, and the obtained result was same as the TA measurements at 635 nm under the short circuit condition.

The responses of the $A_{rearrange}$ component did not depend on the I^- concentration (Fig. S2(a)). From the intensity dependence of the $A_{e/electrolyte}$ shown in Fig. S2(a), the electron/electrolyte recombination was not observed for the concentration lower than 30 mM of the I^- concentration, same as the results obtained under the short-circuit condition (Fig. 2(a)). The TA responses monitored at 785 nm probe light shown in Fig. S2(b) had a decay component in the time region from 10^{-6} to 10^{-3} s except for 300 mM of the I^- concentration and a slower decay component in 10^{-3} to 1 s for all the concentrations. The probe wavelength (λ = 785 nm) is in the region where the dye cation and electrons in TiO_2 have absorption, and it is considered that the first decay component in time region 10^{-6} to 10^{-3} s corresponds to the slower regeneration of the dye cations as we discussed in the result of TA responses for the lower I^- concentration under the short-circuit condition. The slower decay component in 10^{-3} to 1 s corresponds to the electron loss by recombination processes as discussed in I_2 concentration. The conclusion given from the TA for the different probe wavelengths

(635 and 785 nm) and the different electrical condition (open and short) was same.

Cation dependence on the HD-TG responses under the open circuit condition (Fig. S3)

The HD-TG responses under the open circuit condition for a DSSC in various cation species were shown in Fig. S3. The response of the $A_{rearrange}$ component for Li^+ was faster than those for $DMPI^+$ and TBA^+. The intensity of the $A_{e/electrolyte}$ component also depended on the cation species, and decreased in the order of Li^+, $DMPI^+$, TBA^+, which is the same tendency as the cation dependence under the short-circuit condition.

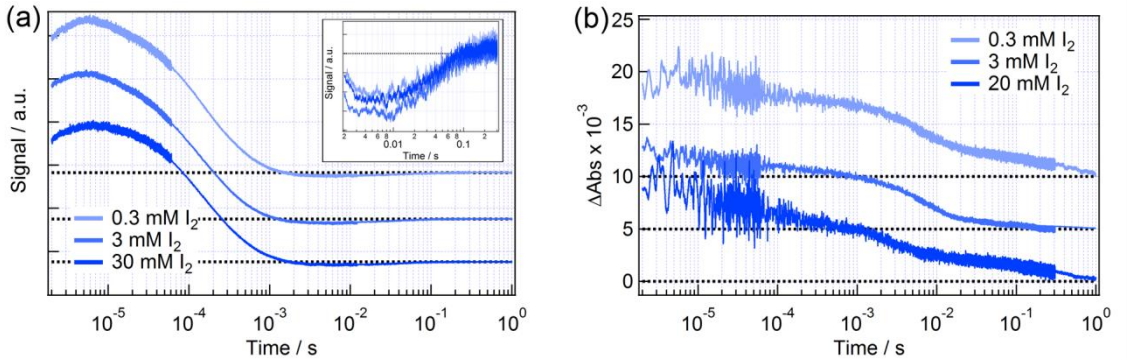

Fig.S1 (a) HD-TG and (b) TA responses for a DSSC with 300 mM LiI/ACN in the presence of 0.3, 3.0, 30 mM I_2 under the open circuit condition. The TA responses were monitored at the wavelength of 785 nm of the probe light, while it was 635 nm for the HD-TG measurements. The horizontal axis was plotted on a logarithmic scale. Each horizontal black dot line shows the background level of the signals, which were vertically displaced for clarity. The HD-TG responses were normalized at the maximum signal intensity.

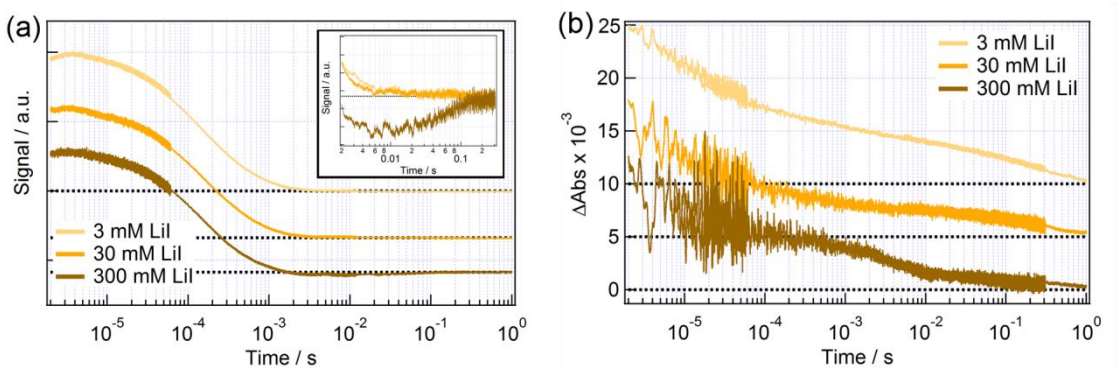

Fig. S2 (a) HD-TG and (b) TA responses for a DSSC with 30 mM I_2/ACN in the presence of 3, 30, 300 mM LiI under the open circuit condition. A $LiClO_4$/acetonitrile solution was added as a supporting electrolyte to maintain the ionic strength and the cation concentration almost equal. TA responses were monitored at the wavelength of 785 nm of the probe light, while it was 635 nm for the HD-TG measurements. The horizontal axis was plotted on a logarithmic scale. Each horizontal black dot line shows the background of the signals, which were vertically displaced for clarity. The HD-TG responses were normalized at the maximum signal intensity. The inset in (a) enlarges the TG responses in the time region of 10^{-3} to 10^{-1} s.

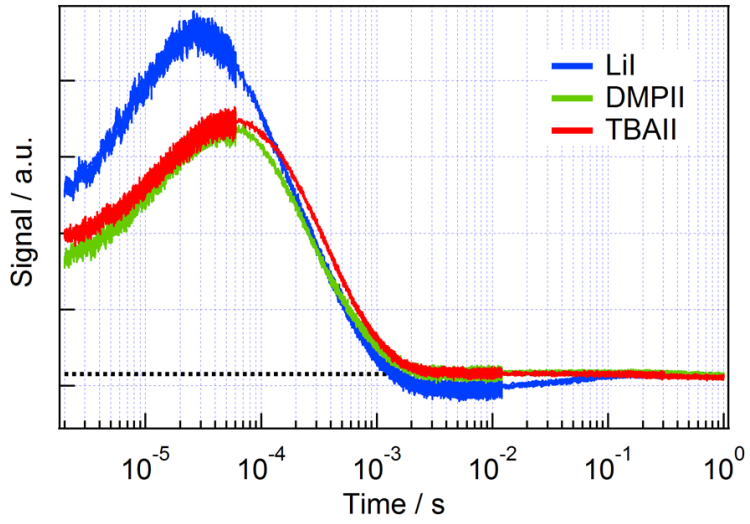

Fig. S3 HD-TG responses for a DSSC with 30 mM I_2/ACN in the presence of 300 mM LiI, DMPII, TBAI under the open circuit condition. The horizontal axis was plotted on a logarithmic scale. Each horizontal black dot line shows the background level of signals.