Perovskite solar cells have attracted much attention as a promising printable photovoltaic device with high power conversion efficiency. The performance of perovskite solar cells highly depends on the quality of the perovskite layer, and thus the development of the fabrication technology to obtain a dense and flat perovskite layer is one of crucial issues in this field. We have recently optimized our solution method with solvent engineering using a mixed solvent of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), which gave a high power conversion efficiency (PCE) ~20% even in the cells composed of pure CH$_3$NH$_3$PbI$_3$ perovskite as a photo-absorber. In this method, the higher volatility of DMF relative to DMSO needs a rather narrow process window during spin-coating. For the larger scale devices, the development of fabrication method for perovskite layer with a wider process window and high reproducibility is strongly required.

We found that the perovskite film of CH$_3$NH$_3$PbI$_3$ changes from black to colorless immediately upon exposure of DMF vapor. To confirm the component of the colorless crystalline material, we isolated colorless crystals from a mixture of PbI$_2$ and CH$_3$NH$_3$I in DMF. X-ray structural analysis confirmed that these colorless crystals correspond to the complex of CH$_3$NH$_3$PbI$_3$(dmf), in which a solvent molecule of DMF is intercalated in the perovskite components (Figure 1). This complex shows higher solubility in DMSO (within 10 min, 2.0 M at room temperature) than that of a mixture of PbI$_2$ and CH$_3$NH$_3$I (1:1, 60 min, 1.2 M), suggesting its utility as a highly purified precursor for perovskite layer in the solution method using DMSO with a wider process window.

Our standard devices of perovskite solar cells are composed of FTO-glass / compact-TiO$_2$ / mesoporous-TiO$_2$ / CH$_3$NH$_3$PbI$_3$ / Spiro-OMe-TAD / Au. Whereas the previously optimized our solution process with a mixed solution (3:1) of DMF and DMSO for perovskite layer needs the short spin-coating period within ca. 10 s before toluene addition, the use of DMSO as a solvent allows the elongation of the spin-coating period to 90 s even under dry atmosphere of N$_2$ gas in glove box on account of the lower volatility of DMSO. In the case of using a mixture of PbI$_2$ and CH$_3$NH$_3$I (1:1), the lower saturated concentration (1.2 M) in DMSO limits the concentration of the precursor solution to 1.1 M. The higher saturated concentration of CH$_3$NH$_3$PbI$_3$(dmf) (2.0 M) allowed us to use the higher concentration of 1.4 M in DMSO for spin-coating. Using a 1.1 M DMSO solution of a mixture of PbI$_2$ and CH$_3$NH$_3$I resulted in the formation of thin perovskite with the thickness of ca. 180 nm, which gave the moderate $J_{SC}$ and PCE (Figure 2a blue line; $J_{SC} = 21.8$ mA/cm$^2$, $V_{OC} = 1.15$ V, FF = 0.70, PCE = 17.6%). In contrast, the use of 1.4 M DMSO solution of the complex successfully provided a dense and thicker perovskite layer with the thickness of ca. 350 nm, which improved $J_{SC}$ and PCE (Figure 2a red line; $J_{SC} = 22.7$ mA/cm$^2$, $V_{OC} = 1.15$ V, FF = 0.76, PCE = 19.8%). As a feature of this method with the wide process window, its excellent reproducibility for the fabrication of high performance cells was confirmed for 30 cells (Figure 2b).