BEDO-TTF provides many two-dimensional metallic cation radical salts with various size and shape of counter components, because of their self-assembling ability [1]. To obtain a variety of physical properties, the self-assembling ability would be suppressed by chemical modification. EDO-TTF which have suppressed this ability, affords the cation radical salts with many types of packing motifs. Among them, \((\text{EDO-TTF})_2\text{PF}_6\) salt shows a metal-insulator (MI) transition and an ultra-fast photo-induced phase transition (PIPT) at around room temperature [2]. To explore the materials with various electronic structures, we synthesized vinylogous EDO-TTFs \(\text{1b-d}\) by the phosphite-mediated cross-coupling reactions and \(\text{1a}\) could be obtained by demethoxycarbonylation of \(\text{1d}\) (Fig. 1). Although the TCNQ complexes of \(\text{1b}\) and \(\text{1c}\) show low electrical conductivity due to DDAA-type alternate stacking, the cation radical salt \((\text{1b})_2\text{PF}_6\) shows metallic behavior down to \(T_{\text{MI}} = 185\) K (Fig. 2). Donor packing motif of the \(\text{PF}_6\) salt is resemble in that of \((\text{EDO-TTF})_2\text{PF}_6\) (Fig. 3). Low temperature structure analyses revealed that the phase transition of the \(\text{PF}_6\) salt is originated from the charge disproportionation.

**Fig. 1.** Vinylogous EDO-TTFs.

**Fig. 2.** Temperature dependence of the resistivity of \((\text{1b})_2\text{PF}_6\).

**Fig. 3.** Donor sheet structure of \((\text{1b})_2\text{PF}_6\).