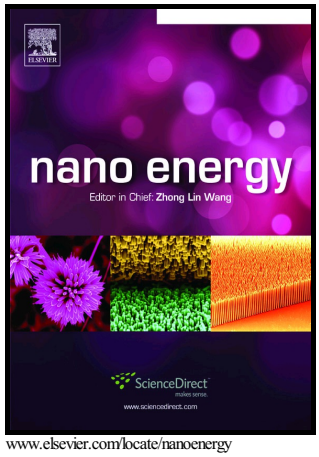

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Abstract

Perovskite solar cells (PSCs) have attracted significant interest and hole transporting materials (HTMs) play important roles in achieving high efficiency. Here, we report additive free ionic type HTMs that are based on 2-ethylhexyloxy substituted benzodithiophene (BDT) core unit. With the ionization of end-capping pyridine units, the hole mobility and conductivity of molecular materials are greatly improved. Applied in PSCs, ionic molecular material **M7-TFSI** exhibits the highest efficiency of 17.4% in the absence of additives [lithium bis(trifluoromethanesulfonyl)imide and 4-tert-butylpyridine]. The high efficiency is attributed to a deep highest occupied molecular orbital (HOMO) energy level, high hole mobility and high conductivity of **M7-TFSI**. Moreover, due to the higher hydrophobicity of **M7-TFSI**, the corresponding PSCs showed better stability than that of Spiro-OMeTAD based ones. In