Development of Air-stable, d/π-conjugated Ambipolar Semiconductors Focusing on Molecular Stacking Structures

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Air-stable single component ambipolar organic semiconductors that conduct both holes and electrons are highly desired, but have rarely been realized. d/π-Conjugated nickel bisdithiolene complexes have attracted attention as materials that meet the stringent electronic requirements of shallow HOMO levels and deep LUMO levels for ambipolar semiconductors to work in air (Fig. 1a).[1] However, most nickel bisdithiolene complexes have twisted molecular structure which hinder effective intermolecular interactions required for carrier conduction, limiting their carrier mobility below 10^{-3} $cm^2 V^{-1} s^{-1}$.[2] Herein, we synthesized alkoxy-substituted nickel bisdithiolene analogs (Fig. 1b) with a planar structure that allowed tight packing with effective intermolecular interactions. Remarkably, by slightly extending the methoxy substituents to ethoxy or propoxy groups, the molecular stacking structure dramatically changed from one-dimensional to two-dimensional one (Fig. 1b), while maintaining effective intermolecular interactions. Furthermore, the extension of the substituent chain length overcame a usual trade-off between solubility in organic solvents and single-crystallinity, which enabled us to form highly ordered layers that can be used as semiconducting layers in field-effect transistors by a solution-coating process. The devices based on these compounds exhibit significant ambipolar characteristics in air over several months, and in particular **Ni(4OEt)** and **Ni(4OPr)** achieved high hole and electron mobilities up to 10^{-3} $cm^2 V^{-1} s^{-1}$ and on/off ratios above ~10^4. These values are the highest levels among d/π-conjugated, air-driven single-component ambipolar materials developed to date.

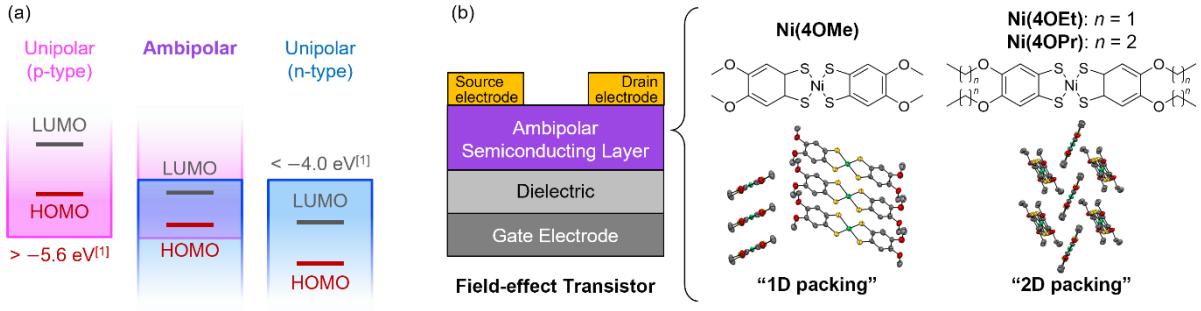

Fig. 1. (a) Electronic requirements for ambipolar semiconductors to work in air. (b) Molecular and packing structures of alkoxy-substituted nickel bisdithiolene complexes used as semiconducting layers in FETs.

References

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