Abstract

The design and development of novel ambipolar semiconductors is very crucial to advance various optoelectronic technologies including organic complementary (CMOS) integrated circuits. Although numerous high-performance ambipolar polymers have been realized to date, small molecules have been unable to provide high ambipolar performance in combination with ambient-stability and solution-processibility. In this study, by implementing highly π-electron deficient, ladder-type **IFDK/IFDM** acceptor cores with bithiophene donor units in D–A–D π-architectures, two novel small molecules, **2OD-TTIFDK** and **2OD-TTIFDM**, were designed, synthesized and characterized in order to achieve ultralow band-gap (1.21–1.65 eV) semiconductors with sufficiently balanced molecular energetics for ambipolarity. The HOMO/LUMO energies of the new semiconductors are found to be −5.47/−3.61 and −5.49/−4.23 eV, respectively. Bottom-gate/top-contact OFETs fabricated *via* solution-shearing of **2OD-TTIFDM** yield perfectly ambient stable ambipolar devices with reasonably balanced electron and hole mobilities of 0.13 $cm^2\ V^{-1}\ s^{-1}$ and 0.01 $cm^2\ V^{-1}\ s^{-1}$, respectively with I_{on}/I_{off} ratios of $\sim 10^3$–10^4, and **2OD-TTIFDK**-based OFETs exhibit ambipolarity under vacuum with highly balanced ($\mu_e/\mu_h \sim 2$) electron and hole mobilities of 0.02 $cm^2\ V^{-1}\ s^{-1}$ and 0.01 $cm^2\ V^{-1}\ s^{-1}$, respectively with I_{on}/I_{off} ratios of $\sim 10^5$–10^6. Furthermore, complementary-like inverter circuits were demonstrated with the current ambipolar semiconductors resulting in high voltage gains of up to 80. Our findings clearly indicate that ambient-stability of ambipolar semiconductors is a function of molecular orbital energetics without being directly related to a bulk π-backbone structure. To the best of our knowledge, considering the processing, charge-transport and inverter characteristics, the current semiconductors stand out among the best performing ambipolar small molecules in the OFET and CMOS-like circuit literature. Our results provide an efficient approach in designing ultralow band-gap ambipolar small molecules with good solution-processibility and ambient-stability for various optoelectronic technologies, including CMOS-like integrated circuits.