Crystal Lattices of H_2O-Adsorption n-type Semiconductor of Anionic Naphthalenediimide

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Electrostatic cation – anion Coulomb interaction has been utilizing for fabrication of chemically stable crystal lattice of the organic semiconducting materials.[1-3] Among them, dianionic bis(propionate)-naphthalenediimide ($PCNDI^{2-}$) formed simple 2:1 cation–anion salts of $(M^+)_2(PCNDI^{2-})\bullet(H_2O)_n$ (M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+), which exhibited reversible H_2O adsorption–desorption behavior because of the presence of their electrostatically binding crystal lattices (Fig. 1).[4,5] The maximum H_2O adsorption amounts (n) for M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+ were 0.25, 6.0, 4.0, 6.0, and 2.0, respectively, whereas the reversible gate-opening (gate-closing) H_2O adsorption–desorption isotherms were observed at 273 and 298 K, except for M^+ = Li^+. High ionic conductivities around 10^{-3}–10^{-4} S cm^{-1} were observed in M^+ = Na^+ and K^+ salts, whereas short-range thermal fluctuations occurred in large-sized cations of M^+ = Rb^+ and Cs^+. The change in the electrostatic lattice energy for M^+ = Na^+ and K^+ salts during H_2O adsorption–desorption cycles was significantly larger than those for M^+ = Rb^+ and Cs^+. Therefore, the Na^+ and K^+ salts had a considerably flexible electrostatic crystal lattice with large amplitude of lattice modulation during the H_2O sorption cycle. In contrast, the lattice modulation for M^+ = Rb^+ and Cs^+ salts involved a low magnitude of ion displacements, forming a relatively rigid cation–anion electrostatic crystal lattice. The flash-photolysis time-resolved microwave conductivity and transition absorption spectroscopy results revealed the high electron mobility of H_2O-adsorbed thin films, wherein the crystallized H_2O molecules did not act as electron-trapping sites. The values of electron mobility increased in the order of $Cs^+ \approx Rb^+ > K^+ > Na^+ > Li^+$.

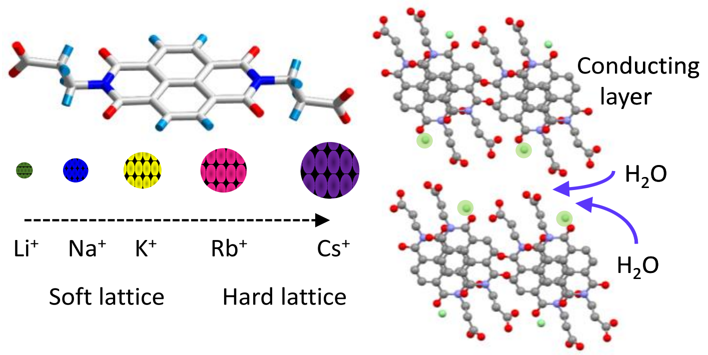

Fig. 1. Electrical conducting cation – anion crystal lattice of $(M^+)_2(PCNDI^{2-})\bullet(H_2O)_n$ (M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+).

References

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