

Effects of Molecular Conformations on Spontaneous Orientation Polarization and Their Control through Intramolecular Interactions

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Spontaneous orientation polarization (SOP) is a phenomenon in which change of the electrostatic potential at the surface is spontaneously formed in the thermal evaporated films of polar organic molecules such as 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi). The SOP can be attributed to accumulated permanent dipole moment of each molecule with a slight orientational preference in the films. The change of the surface potential is proportional to the thickness of the films with the slope of +77.3 mV/nm for TPBi. However, the relationship between the molecular structures and the SOP effect is not clear. In this study, three isomeric derivatives of TPBi were synthesized by introducing ethyl groups on the *N*-phenyl moieties. Packing and orientation of the molecules in the films were analyzed by spectral ellipsometry and 2D grazing-incidence wide-angle X-ray scattering. Density functional theory calculations and single-crystal structure analysis suggest that the intramolecular interactions between the ethyl groups lead to the change of the stable molecular conformation from C_1 to C_3 symmetry (Figure). The surface potential change of the three TPBi derivatives films were enhanced significantly. Especially, the film of *p*-ethyl-TPBi exhibited largest surface potential change of up to 1.8 times that for TPBi which is also the largest reported SOP effect to date (+141.0 mV/nm). Comparing to C_1 symmetry, the permanent dipole moment of TPBi derivatives in C_3 symmetry is vertical to the molecular plane (the plane of central benzene ring) which could be ascribed to the observed enhancement of SOP.

