Summary of Doctoral Dissertation

Degree requested Doctor of Soft Matter Science Applicant's name Xiao Zheng

Clarification for Molecular Structure-Physical Property Correlation of Alkyl-π Functional Molecular Liquids
（アルキル-π 機能性分子液体の分子構造-物性相関の解明）

This dissertation focuses on revealing the molecular structure-physical property correlation of alkyl-π functional molecular liquids (FMLs), which is mainly constituted by two categories: substitution pattern-physical property relationship of alkyl-distyrylbenzene (DSB) liquids in Chapter 2 and molecular conformation-physical property relevance of alkyl-diphenylanthracene (DPA) liquids in Chapter 3. Those two complementary studies have provided a deeper insight to construct FMLs with superior properties for soft optoelectronic applications, such as lower viscosity, intrinsic optoelectronic properties of π-conjugated unit, good thermal- and photo-stabilities as a practically stable liquid at room temperature.

The substitution pattern-physical property relationship was clarified by utilizing a series of alky-DSB derivatives with different substituent positions and alkyl chain lengths. Namely, 2-octydodecyl (C_8C_{12}) chains were attached at various substituent positions of the terminal phenyl units of DSB core, including (2,4-), (2,5-), (2,6-) and (3,5-). The 2-hexyldecyl (C_6C_{10}), 2-decyltetradecyl ($C_{10}C_{14}$), 2-dodecylhexadecyl ($C_{12}C_{16}$), as well as C_8C_{12} chains were attached at (2,5-) substituent position. Results showed attaching 2-decyltetradecyl chains at the (2,5-) substituent position of appending phenyl units can create a superior alkyl-DSB liquid with the lowest viscosity, intrinsic optical properties of DSB moiety, good phase-, thermal-, and photo-stabilities as a solvent-free liquid. The most essential factors contributing to lower viscosity of alkyl-DSB liquids was thoroughly uncovered as smaller molecular size, faster molecular motion, and larger fractional free volume. Their various optical properties of the electronic structure were studied by the synergy of UV-vis absorption, fluorescence, Raman spectroscopy and DFT calculation. More importantly, the superior 2,5-$C_{10}C_{14}$ substitution pattern applied to construct an alkyl-dicyanostyrylbenzene liquid with comparable liquid physical and optical superiorities.

The molecular conformation-physical property correlation was revealed by using a twin of *anti*- and *syn*- alkyl-DPA liquids with the 2-hexyldecyl (C_6C_{10}) attached at (2,4-) substituent position of appending phenyl units. The *anti*- and *syn*-2,4-C_6C_{10}-DPA atropisomers were successfully synthesized in moderate yield and accurately assigned by 1D/2D-NMR spectroscopy and single-crystal XRD analysis of simplified 2,4-isobutyl-DPA isomers. The thermal, liquid physical, and optical properties of single pure *anti*- or *syn*- 2,4-C_6C_{10}-DPA atropisomer were unambiguously investigated. The orientation of C_6C_{10} chains significantly varies their T_g, viscosity, phase- and photo-stabilities in the solvent-free liquid state, which was vitally contributed by the different coverage of anthracene moiety. Temperature-dependent isomerization between *anti*- and *syn*-2,4-C_6C_{10}-DPA provided the rotational barrier ($\Delta G^{\ddagger}$) and *Gibbs* free energy difference (ΔG), which indicated both atropisomers are conformationally-stable, and *anti*-isomer was a more thermodynamically favorable compound. Furthermore, physically mixing *anti*- and *syn*-atropisomers with different molar ratios can create solvent-free liquid materials with distinct T_g, viscosity, and phase stability, which was recognized as a valuable strategy to achieve the desired physical properties for alkyl-π FMLs.

In summary, the molecular structure-physical property correlation of alkyl-π FMLs has been comprehensively elucidated from two viewpoints: substitution pattern and molecular conformation. When we

design and apply the alkyl-π FMLs with optoelectronic properties as an active component into the flowable and deformable devices, first and foremost, it is more vital to attach the superior substitution pattern on the π-conjugated moiety for achieving lower viscosity, intrinsic optical properties of the π-conjugated unit, and good phase-, thermal-, and photo-stabilities. Secondly, if alkyl-π FMLs contain separable atropisomers, it is suggested that each component ought to be separated and analyzed individually, because the properties of atropisomers are significantly altered by molecular conformation. While for the most non-separable atropisomers, treating alkyl-π FMLs as atropisomers mixture show many advantages, such as, distinct physical properties compared with individual component, and simultaneously the challenge and cost of purification, structural assignment, and dynamic interconversion for atropisomers can be reduced. These two correlations between the molecular structures and liquid physical properties pave the development of alkyl-π FMLs with optoelectronic properties into flowable and stretchable devices.