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Title of Doctoral Dissertation

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)

Liquid with excellent fluidity and processability are an inherently soft matter. To meet the requirement as a promising functional component in the soft and stretchable electronics, versatile functional liquid materials with excellent optical, electronic, and catalytic characteristics have been developed, such as liquid metals and ionic liquids. In addition, molecular liquids, such as porous liquids, cyclic liquids, and alkyl- π functional molecular liquids (FMLs), have appeared as new liquid forms with comparable or enhanced functions, which were constituted by functional organic molecules with regulated intra-/inter- molecular interactions. Achieving controllable design and construction of these functional molecular liquids is always challenging, because their precise molecular structure-property relationship has not been clarified yet.

Alkyl- π FMLs is facilely constructed by attaching bulky yet flexible branched alkyl chains on the periphery of the optoelectronically-active π -conjugated unit to achieve a solvent-free liquid at room temperature. In the last decade, various types of alkyl- π FMLs with extraordinary optical and electronic properties have been achieved, for instance, luminescent and macrocycle liquids. Some have been applied as active components in microfluidic organic light-emitting diodes (OLEDs) and mechanoelectric generators (MEGs). Nevertheless, the molecular structure-physical property relationship of alkyl- π FMLs has not been precisely uncovered, so rational design/creation of alkyl- π FMLs with superior physical properties were hard to achieve for the promising application in the flowable and stretchable devices.

It has been argued that the viscosity of alkyl- π FMLs with larger π -conjugated moiety, such as fullerene and porphyrin, has a relatively higher viscosity than that of smaller alkyl-tetrazine and -naphthalene liquids, that is mainly contributed by their larger molecular size/weight (Stokes-Einstein equation). However, the molecular structure-viscosity relevance of alkyl- π FMLs is not always monomerically changed on various π -conjugated moiety and substitution patterns; we have not yet identified the most crucial factors that contribute to the lowering viscosity. Apart from that, the effect of substitution patterns on the thermal, optical properties, phase-, thermal-, and photo- stabilities of alkyl- π FMLs has not been fully understood. Another essential argument is that most alkyl- π FMLs exist as an atropisomers mixture in the bulk liquid state, which resulted from the different orientations of the branched alkyl chains at the asymmetric substituent position relative to the π -conjugated plane. Those atropisomers that appeared in previous alkyl-pyrene and -porphyrin liquids were difficult to be separated at ambient conditions due to the many different atropisomers and/or low rational energy barrier of the single $C(sp^2)-C(sp^2)$ bond. The conformational differences resulted in different dipole moment, molecular size, π - π , and van der Waals interactions, further reflected in the liquid physical properties. Therefore, it is essential to know whether and why different atropisomers exhibit different physical properties and how individual atropisomers contribute to the physical properties of atropisomers mixture.

In my doctoral studies, we clarified (i) the substitution pattern-physical property relationship by utilizing alkyl-distyrylbenzene (DSB) liquids in Chapter 2 and (ii) the molecular conformation-physical property relationship by investigating alkyl-diphenylanthracene (DPA) liquids in Chapter 3. The substitution pattern has been specified as two viewpoints. The effects of substituent positions were rigorously investigated for four regioisomers by attaching 2-octyldodecyl (C_8C_{12}) chains at different (2,4-), (2,5-), (2,6-), and (3,5-) substituent position of the peripheral phenyl units of DSB moiety. After comprehensive studies on their thermal, liquid physical, and optical properties by employing TGA, DSC, Rheology, UV-Vis absorption, fluorescence, and Raman, etc., the (2,5-) was identified as a superior substituent position. Then, the effect of alkyl chain length was investigated by attaching 2-hexyldecyl (C_6C_{10}), 2-decyltetradecyl ($C_{10}C_{14}$), 2-dodecylhexadecyl ($C_{12}C_{16}$)

as well as C₈C₁₂ chains at (2,5-) substituent position. Attaching the 2,5-C₁₀C₁₄ substitution pattern can construct an alkyl-DSB liquid with superior physical properties, such as the lower complex viscosity ($|\eta^*|$) of 1.65 Pa s at 25 °C, intrinsic optical properties of DSB core, good thermal- and photo- stabilities as a practically stable liquid at room temperature. The significant contributions to the lower viscosity of alkyl-DSB liquids were revealed as smaller molecular size by gel permeation chromatography, faster molecular motion by solid-state nuclear magnetic resonance, and larger fractional free volume by positron surface analysis. Moreover, the 2,5-C₁₀C₁₄ substitution pattern applied to an alkyl-dicyanostyrylbenzene liquid with comparable liquid physical properties to 2,5-C₁₀C₁₄-DSB liquid, e.g., 1.59 Pa s of $|\eta^*|$ at 25 °C. Therefore, the 2,5-C₁₀C₁₄ is the superior substitution pattern to constructing functional liquid materials with the aforementioned physical properties.

To reveal the molecular conformation-physical properties relationship, we focused on a pair of *anti*- and *syn*- alkyl-diphenylanthracene (DPA) liquids attached with branched 2-hexyldecyl (C₆C₁₀) chains at (2,4-) substituent position on the two appending phenyl units. The *anti*- and *syn*- 2,4-C₆C₁₀-DPA atropisomers were synthesized, and stepwise separated by preparative liquid chromatography. The combined 1D/2D NMR measurements and single-crystal X-ray diffraction analysis of simplified *anti*- and *syn*- 2,4-DPA atropisomers with shorter isobutyl (C₁C₃) chains accurately achieved structural assignment. Through careful analysis of their physical properties by several techniques, such as DSC, rheology, and photoirradiation experiment, we observed *anti*-2,4-C₆C₁₀-DPA atropisomer had 5 °C lower $T_{g, offset}$ and metastable SCL character, half viscosity at 25 °C, and 13.5 times better photostability than those of the *syn*- atropisomer. The fragility obtained by Angell plots may explain these differences. For liquid fragility, the crucial factors in the current system could be the protection of π -conjugated moieties from the chain orientation and the dipole from the symmetry of the molecule. While, their optical properties, including UV-Vis absorption, fluorescence, and fluorescence quantum yield were almost indistinguishable in the solvent-free liquid state and the solution, which can be explained by their similar π -conjugation tendency. The exact single-crystal structure of *anti*- and *syn*- 2,4-C₁C₃-DPA atropisomers and their energy-minimized structures by DFT calculation at B3LYP/6-31g(d,p) level both proved the alike orthogonal orientation between the anthracene core and appending phenyl units. The *anti*-/*syn*- 2,4-C₆C₁₀-DPA atropisomers mixtures with different molar ratios were also studied, including the thermodynamically stable equilibrium [70/30] determined by the thermal isomerization. The results show their physical properties distinctly differ from individual *anti*- or *syn*- component. This behavior is similarly known for reported binary polymers or ionic liquid mixtures. More specifically, the $T_{g, offset}$ of atropisomers mixture exhibited a sigmoidal relationship against the relative molar ratio, the phase stability was not determined by the major *anti*- component, and the viscosity was contributed more by the dominant *anti*- atropisomer with lower viscosity. Therefore, the distinct physical properties of atropisomers mixture was contributed unequally from the individual components.

In conclusion, the molecular structure-physical property correlation of alkyl- π FMLs has been clarified from two complementary categories; the substitution pattern-physical property of alkyl-DSB liquids and the molecular conformation-physical property of alkyl-DPA liquids. Firstly, it is more prominent to attach the superior 2,5-C₁₀C₁₄ substitution pattern on the π -conjugated moiety to construct an alkyl- π FMLs processing lower viscosity, intrinsic optical properties of π -conjugated unit, good thermal-, and photo- stabilities as a practically stable liquid at room temperature. Secondly, the conformational effect was significant on the thermal and liquid physical properties, while almost no distinguishable on the optical properties of individual atropisomer. The physical mixing atropisomers with different molar ratios was also vital on the physical properties, which was not simply determined by the major constituent. If alkyl- π FMLs contains separable atropisomers as 2,4-C₆C₁₀-DPA liquids, it is suggested to isolated and individually characterized. While the tradeoff challenges of purification, structural assignment, and interconversion of individual atropisomers should be considered. For the most alkyl- π FMLs includes non-separable atropisomers, such as alkyl-pyrene and alkyl-porphyrin liquids, as long as the physical properties were precisely characterized, it is not a detrimental issue for exploiting their optical and electronical properties. The substitution pattern- and molecular conformation- physical property correlations are beneficial to create functional liquid materials with superior physical properties, such as lower viscosity, intrinsic optical properties of the π -conjugated unit, excellent stabilities in phase, heat and photo conditions, which can pave the application of alkyl- π FMLs into flowable and deformable optoelectronic devices, and other soft electronics.