



Title	Miscibility Control of Solvent-free π -Molecular Liquids
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Title of Doctoral Dissertation

Miscibility Control of Solvent-free π -Molecular Liquids
(無溶媒 π 分子液体の混和性制御)

Solvent-free functional π -molecular liquids are optoelectronically functional soft materials at room temperature. They consist of a π -conjugated core covalently bonded to external liquefying components. The liquefying components usually comprise bulky yet flexible side chains, such as branched alkyl chains (Alk), branched triethylene glycol chains (TEG), etc. These bulky yet flexible side chains increase conformational entropy to promote liquefaction at room temperature and sterically isolate the π -core from the environment, enhancing its stability. Due to such a unique structure, π -molecular liquids combine the fluidity of liquids with the optoelectronic properties of π -conjugated systems, offering advantages such as low volatility, thermal and photostability, high flexibility, and so on, towards free-deformable devices. Further functional tuning of π -molecular liquids is crucial for future development, commonly achieved through chemical modification or blending. While chemical modification offers precise control of the intrinsic π -functions, it is often time-consuming and labor-intensive. Blending refers to the process of mixing two or more components by physical methods to form a material with new fusion properties, while miscibility is a key property that describes whether these substances can be uniformly mixed to form a single phase at the molecular level.

The research on π -molecular liquids blending aims to achieve synergistic enhancement of material performance or generate new fusion functions by combining different π -electron systems. The main challenges faced by the research on functional- π liquid blends are the control of component compatibility, characterization, and analysis of phase interfaces. In this dissertation, a series of biphenyl derivatives with different π -cores was developed. By introducing various types of side chains on the phenyl groups on both sides, three representative π -molecular liquids were obtained: hydrophobic Alk- π liquids (containing alkyl side chains), hydrophilic TEG- π liquids (containing TEG side chains), and amphiphilic Am- π liquids (containing both alkyl and TEG chains). The study concentrates on the comparison of the properties of these π -molecular liquids and their blending behaviors.

Chapter 2 of this dissertation focuses on the miscible blending of π -molecular liquids. By introducing bulky Guerbet-type alkyl side chains (octyl-dodecane, C_8C_{12}) and selecting benzothiadiazole (abbreviated as B, acceptor type), benzothiadiazole-dithiophene (abbreviated as TBT, donor-acceptor-donor type), and thiophene (abbreviated as T, donor type) as π functional groups, a series of dialkylated phenyl derivatives (Alk- π liquids): **Alk-TBT**, **Alk-B**, and **Alk-T** were designed and synthesized. Since these Alk- π liquids have similar chemical structures and physical properties, the miscibility of their blends cannot be effectively judged by common methods. In this study, we proposed a method to verify their miscibility using the "time-temperature superposition principle (TTS)" in rheological analysis. According to TTS, if the blend system can form a continuous and smooth rheological master curve, the system is miscible; otherwise, it is immiscible. The experimental results show that the blending systems between the three Alk- π liquids have successfully constructed rheological master curves, verifying their high miscibility and homogeneity. Based on this premise, we further use "luminescent color tuning" as a representative case to demonstrate the feasibility of functional regulation. Due to the Förster resonance energy transfer (FRET) effect, the luminescent color of binary or ternary Alk- π liquid blends can be precisely controlled by adjusting the proportion of components. The obtained luminescent color covers a wide visible light range and changes regularly with the increase of the acceptor ratio. After obtaining a homogeneous and miscible blending system, we noticed a slight shift in the distribution of luminescent colors in the CIE 1931 chromaticity diagram, which may be attributed to the discrepancy in the polarity of each chromophore. Theoretical calculation results (including dipole moment difference analysis, electrostatic potential distribution diagram, and natural transition orbital pair analysis) further support this

explanation.

Chapter 3 of this dissertation studies the immiscible blending of π -molecular liquids. Based on the study presented in Chapter 2, representative **Alk-B** and **Alk-T** molecules were selected, and their Alk chains were replaced with TEG chains without changing their chromophore structures to synthesize the corresponding **TEG-B** and **TEG-T**. Due to the significant polarity difference between the TEG and alkyl chains, the Alk- π liquid and TEG- π liquid exhibited prominent and visible liquid-liquid phase separation behavior after blending. Studies have shown that each component retains its original properties in the phase separation state. For example, two glass transition temperatures can be observed in the **Alk-B/TEG-T** blend, which is $-59\text{ }^{\circ}\text{C}$ and $-65\text{ }^{\circ}\text{C}$, respectively, corresponding to **Alk-B** and **TEG-T**, further confirming the independence of the two phases. Interface analysis (confocal laser scanning microscopy and high-resolution fluorescence intensity mapping) showed that no obvious intermediate transition zone was formed between the two phases, but a clear interface separation was maintained, and the phase separation behavior significantly inhibited the occurrence of the FRET. Due to the density difference between Alk- π liquid (density about $0.90\text{ g}\cdot\text{cm}^{-3}$) and TEG- π liquid (density about $1.10\text{ g}\cdot\text{cm}^{-3}$), the liquid-liquid interface formed after blending is not a simple contact, but there is a certain degree of overlap, in which Alk- π liquid is usually located in the upper layer, and TEG- π liquid is distributed in the lower layer. In addition, since both are fluids, their interface morphology and edge profile will change slowly and continuously over time, showing liquid dynamic behavior.

Chapter 4 of this dissertation focuses on the amphiphilic π -molecular liquids (Am- π liquids). Based on the work of the previous two chapters, two types of chromophores, **B** and **T**, were selected. By introducing Alk chains (C_8C_{12}) and TEG chains on both sides of the molecule, a new type of amphiphilic π -molecular liquids (**Am-B** and **Am-T**) was designed and developed. No liquid materials with similar structures have been reported in the literature. We systematically compared the similarities and differences between Alk- π liquids, TEG- π liquids, and Am- π liquids in terms of morphology, physical properties, surface wettability, photophysical properties, and molecular relaxation behavior. For example, we found that the molecules of the **B** series have a "sidechain-chromism" effect. As the number of TEG chains increases, the luminescent color of the molecule changes from green to yellow-green and then to yellow. The reason may be that the side chain environment of the molecule plays a role similar to that of the solvent. The larger dipole moment of **B** is stabilized in polar solvents, thus causing changes in optical properties. Such research and comparison of the three types of π -molecular liquids not only deepens the understanding of the structure-property relationship of amphiphilic π liquids but also provides new insights for the precise regulation of the miscibility and functionality of π -molecular liquids, which has important guiding significance for the future construction of functional liquid systems with stable phase interfaces.

In summary, we designed and developed three types of representative π -molecular liquids in this dissertation. We conducted in-depth research around their basic properties and blending behaviors, focusing on the structural differences of the three types of systems and their effects on miscibility. The main research content can be divided into the following three parts:

- 1) Uniform and miscible blending behavior of Alk- π liquids (Chapter 2);
- 2) Immiscible blends of Alk- π /TEG- π liquids (Chapter 3);
- 3) Amphiphilic π -molecular liquids containing Alk and TEG chains in the same molecule (Chapter 4).

These three parts constitute a complete research framework. A preliminary relationship model between the structure and compatibility of π -molecular liquids is established, which provides a theoretical basis and practical path for the future realization of functional regulation and miscibility control of such highly functional, solvent-free π -molecular liquid materials.