



Near-room-temperature phase-change fluorescent molecular rotor and its hybrids

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ABSTRACT

A unique molecular rotor consisting of a tetraphenylethylene derivative with a paraffin wax-like long alkyl chain (TPE18) is synthesized and compared to other derivatives containing shorter alkyl chains. In differential scanning calorimetry, TPE18 shows an endothermic peak (enthalpy of fusion, $\Delta H_{\text{fus}} = 55.3 \text{ J g}^{-1}$) at 45 °C during the heating process and an exothermic peak at 38.6 °C during the cooling process. TPE18 exhibits critical changes in the fluorescence intensity and color during the crystal–melt phase change. TPE18 can be dissolved by an octadecane melt and then absorbed by filter paper. When the waxed paper is exposed to the heat sources of an IR laser or a finger, high-resolution fluorescence images of the characters and fingerprints appear on the paper. TPE18 also serves as a host matrix in a melt state that was easily mixed with the guest fluorophores of Alq3 and rubrene. Homogeneous hybrid solids with defined features are obtained without any significant segregation after cooling to room temperature. Fluorescence images with various colors are drawn onto the surfaces of glass slides or papers using the hybrids as crayons.

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1. Introduction

Organic fluorophores have recently become ubiquitous as high-tech materials for applications such as optoelectronic device materials, (bio) sensors, and image probes [1–9]. These functional active materials will be more intelligent if the fluorescence emission can be varied in response to external stimuli, such as heat, light, electric fields, and chemicals [10–18]. A thorough understanding of the static and dynamic fluorescence emission behaviors is essential to design such materials [19]. Since most fluorophores are π -conjugated systems with planar geometry, an intermolecular (in solid phase) or intramolecular (in liquid phase) stack structure has the most significant influence on static fluorescence quenching. As the degree of stacking between the fluorophore molecules increases, the probability of the occurrence of an excimer that exhibits remarkable fluorescence attenuation will increase. Conversely, if the stack structure is relaxed in an ambient environment, the excimer will be removed, and significant fluorescence enhancement will take place. In this case, fluorescence behavior associated with molecular dynamics should be carefully considered. Molecular fluctuation according to the internal and external environment is a primary factor that influences the dynamic fluorescence quenching. As vibrational relaxation and collisional quenching in the process of heating (or solvation) increases, non-radiative fluorescence decay becomes dominant. The

thermo- or hydrodynamically induced fluorescence attenuation should be pronounced in the melt (or solution). These static and dynamic fluorescence quenching processes always compete with each other [20].

Using this knowledge, we aim to develop highly advanced functional materials that exhibit unique thermodynamic fluorescence emission behavior. The target materials were designed to be more emissive in the crystal state than in the melt state and to undergo reversible crystal-to-melt phase changes near room temperature. Nakanishi et al. recently developed highly emissive liquid fluorophores by covalently connecting branched long alkyl chains to typical crystalline π -conjugated core systems [21–23]. In a bulk state, the intermolecular π - π stacking of the rigid core with a planar geometry was completely avoided due to randomly arranged alkyl chains. The original crystallinity was disrupted and led to highly emissive liquid phase at room temperature. The bulk liquid served as fluorescent matrices for other components in composite systems to result in white-light emission at appropriate composition ratios. Although Nakanishi's finding was promising in the development of softened bulk fluorophores with high fluorescence quantum efficiency, the practical application was limited because the materials exist in a permanent liquid state around room temperature [24]. Therefore, development of liquid fluorophores that can be readily converted into solid phase near room temperature with significant fluorescence enhancement is greatly desired.

Organic compounds that exhibit stronger fluorescence emission in the solid state than in the solution state have been extensively developed by Tang's research group with a well-established mechanism

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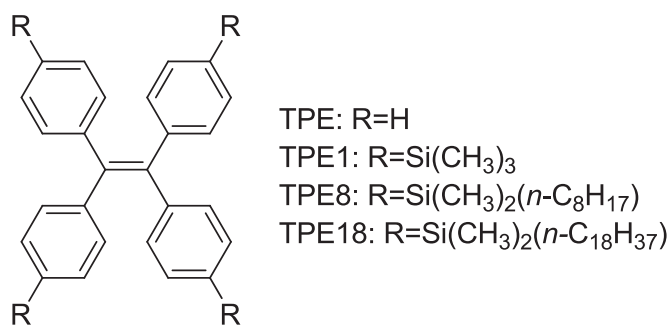


Fig. 1. Chemical structures of TPE derivatives.

[25–28]. These compounds, often called molecular rotors, exhibit very weak fluorescence in solution, but the emission is remarkably enhanced by an aggregation process induced by the non-solvent. Some molecular rotors react with carbon dioxide and biomolecules in solution to show significant fluorescence enhancement due to the formation of nano-sized aggregate complexes [29–34]. This phenomenon is termed aggregation-induced emission enhancement (AIEE) and is intrinsically based on the restriction of intramolecular rotation (RIR) [35–37]. Increasing the ambient medium (solvent) viscosity or substantially lowering the ambient temperature may also be effective strategies to intensify the RIR activity [38]. Similar to the case of solutions, the degree of RIR will significantly change during the crystal–melt phase change in the bulk state with an associated change in fluorescence emission. However, since molecular rotors are highly crystalline compounds with full

aromaticity, the thermodynamic phase transition temperatures are often >100 °C. This property may limit the processability and practical uses. Therefore, by using simple molecular design to lower the phase transition temperature near room temperature, a material with a reversible crystal–melt phase change and dramatic fluorescence change can be developed for advanced functions and extensive applications.

We synthesized a novel molecular rotor containing a paraffin wax-like long alkyl chain via a simple substitution reaction. We found that this material underwent a critical phase change near room temperature and showed remarkable simultaneous changes in fluorescence intensity and color. This material was also readily hybridized with other fluorophores in the melt state that became highly emissive solids after cooling to room temperature. Fluorescence images with various colors, including visible wavelengths of blue, green, orange, and even white, could be drawn on the surfaces of glass slides or paper by using the solid hybrids as crayons. The material was also readily dissolved in paraffin wax melts and absorbed into filter papers. When the fluorescent waxed paper was brought into contact with heat sources, high-resolution fluorescence images appeared on the paper.

2. Results and discussion

Tetraphenylethylene (TPE) derivatives with different-length alkyl side chains were synthesized by a substitution reaction between four-armed lithiated TPE and the corresponding alkyldimethylchlorosilanes (TPE1, TPE8, and TPE18 in Fig. 1 and Scheme S1). The thermodynamic properties of the TPE derivatives were examined using differential scanning calorimetry (DSC). Fig. 2 shows the DSC curves of the TPE derivatives and the results are summarized in Table 1. TPE18 did not show

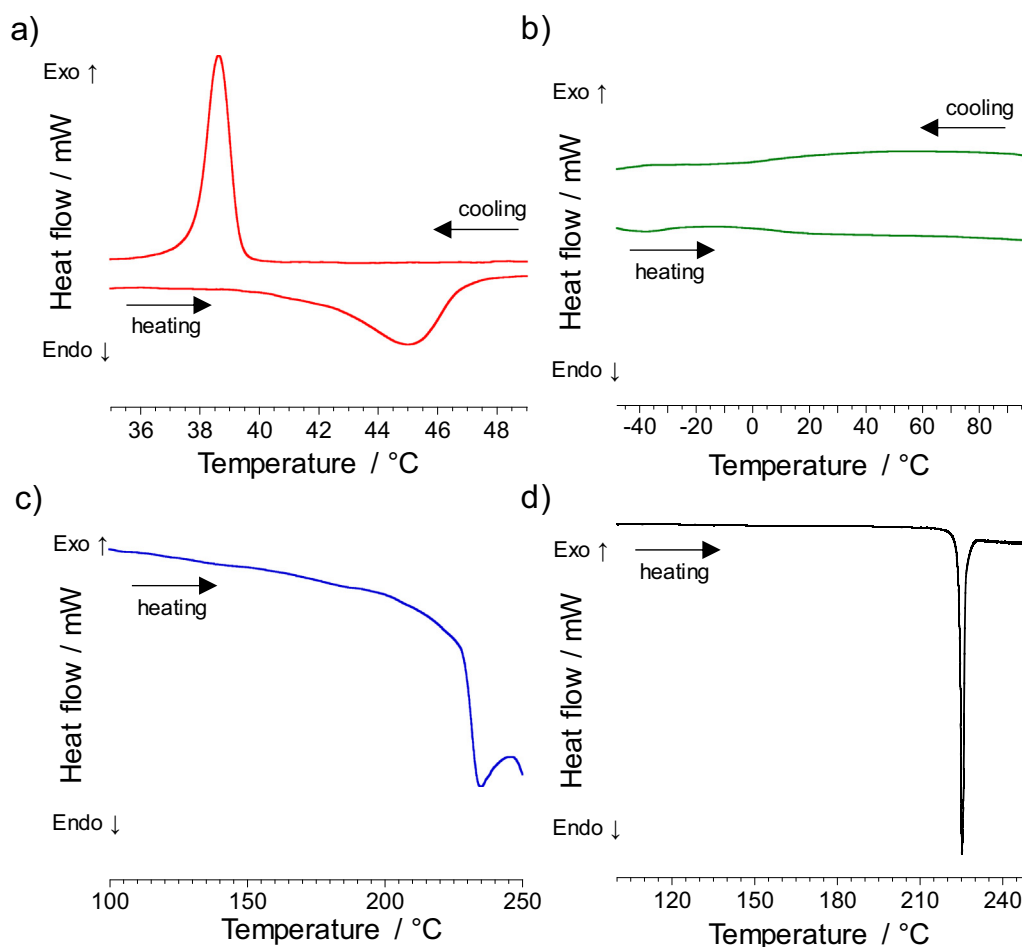


Fig. 2. DSC thermograms of a) TPE18 (heating rate: 0.1 °C min^{-1} in N_2 atmosphere), b) TPE8, c) TPE1 and d) TPE (heating rate: 5 °C min^{-1}).

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