

## Changes in Stereo-structures and Optical Properties of Thianthrene-containing Imide and Polyimide Induced by Photoexcitation and High Pressure

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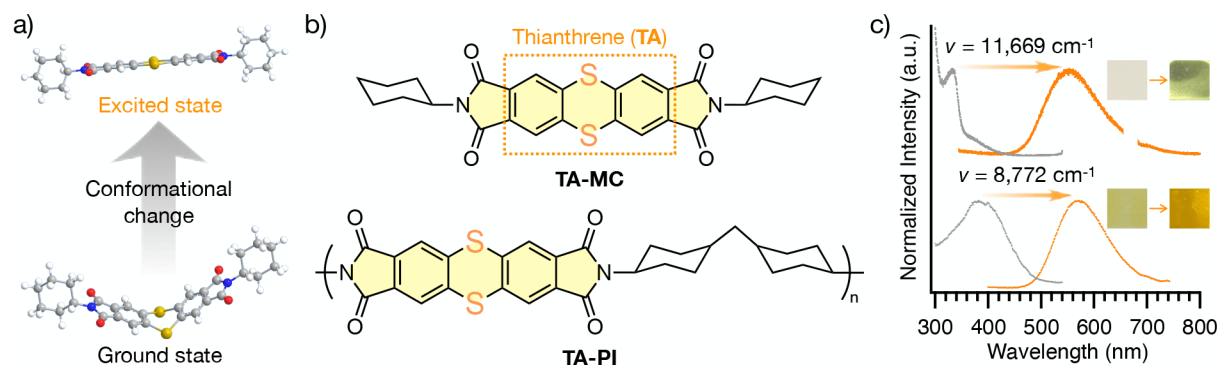
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### INTRODUCTION:

Our group has been focused on developing highly fluorescent and room-temperature phosphorescent imide compounds and polyimides (PIs) [1]. In particular, we have been interested in PI thin films that can convert ultraviolet light to long-wavelength visible light, offering potential applications in spectral conversion for solar cells and crop cultivation. These films require high transparency in the visible region, high luminescent quantum efficiency, and large Stokes shifts (SS) for efficient light emission. Thianthrene (TA), a sulfur-containing heterocycle, has been explored for high refractive index PI and organic light-emitting diodes [2]. TA molecules exhibit a drastic conformational change upon excitation (**Fig. 1a**), leading to adjustable fluorescence (FL) and phosphorescence (PH) emission. By incorporating TA into the PI main chain, it allows us to get insights into the luminescent properties and establish design guidelines for developing new fluorescent and phosphorescent PI materials.

### RESULTS AND DISCUSSION:

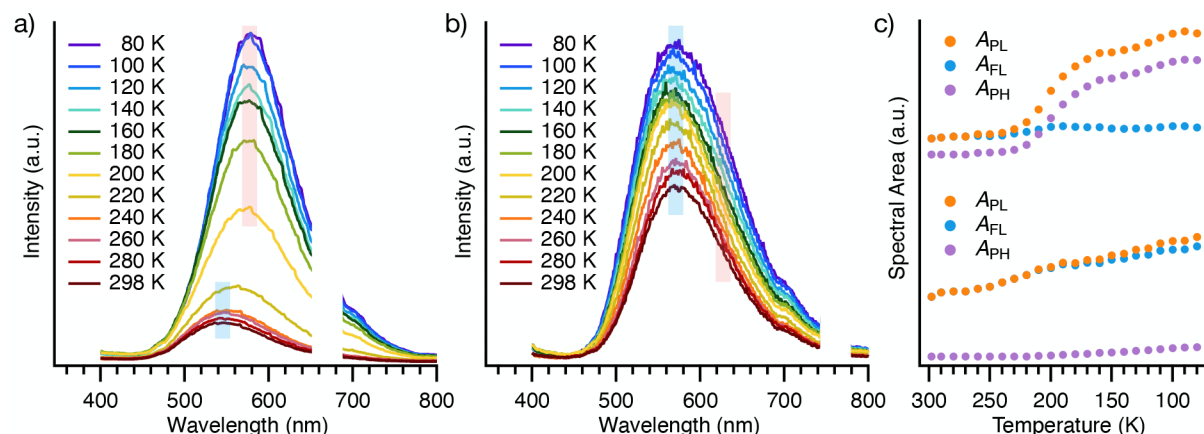
As depicted in **Fig. 1b**, we synthesized an imide compound (**TA-MC**) and polyimide (**TA-PI**) incorporating a TA into their skeletons. Our objective is to investigate the photo-luminescent (PL) properties of these materials under low-temperature and high-pressure conditions. We firstly examined the PL properties of **TA-MC** dispersed in poly(methyl methacrylate) at 1 wt%, referred to as **TA-MC** hereafter. As shown in **Fig. 1c**, the **TA-MC** film demonstrated intense UV absorption and excellent transparency in the visible region. Upon excitation at 335 nm, it emitted yellow PL at 550 nm, which was identified as FL with a short nsec lifetime. The large SS ( $11,669\text{ cm}^{-1}$ ) indicates that the FL was emitted from a planar structure, similar to that observed in chloroform solution ( $13,184\text{ cm}^{-1}$ ). In contrast, **TA-PI** exhibited yellow absorption extending up to 500 nm due to the presence of TA aggregates. Excitation at 380 nm resulted in orange PL at 570 nm, originating from the planar TA moiety and characterized by a short FL lifetime at 15 nsec. The redshift by 20 nm compared to **TA-MC** was attributed to the formation of aggregates and the presence of strong intermolecular  $\pi$ - $\pi$  interactions.



**Fig. 1.** (a) Schematic diagram illustrating the conformational change (from bent to planar) in a TA skeleton. (b) Chemical structures of **TA-MC** and **TA-PI**. (c) UV-vis absorption spectra (gray) and PL spectra (orange) of (top) **TA-MC** and (bottom) **TA-PI**. The Inset shows photographs of the film's appearance before and after UV irradiation ( $\lambda_{\text{ex}} = 365\text{ nm}$ ).

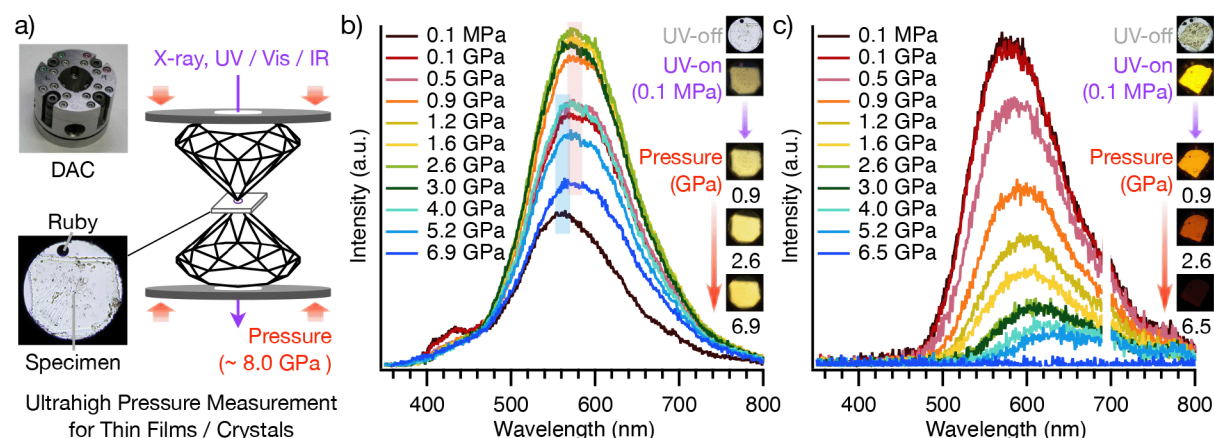
Optical measurements were conducted at 70 K to investigate the relationship between the molecular mobility and the PL properties. **Figs. 2a** and **2b** show the temperature-dependent PL spectra of **TA-MC** and **TA-PI**, respectively. The FL peak of **TA-MC** at around 540 nm was red-shifted to 580 nm between 200 and 260 K. **Fig. 2c** demonstrates the changes in the areas of the separated FL and PH spectra for **TA-MC**. Below 230 K, the contribution of FL remained unchanged, while that of PH significantly

increased, suggesting a pronounced PH emission as molecular motion was suppressed. In **Fig. 2b**, the emission intensity of **TA-PI** also increased with decreasing temperature, and PH was observed below 240 K, with a further increase in intensity. Comparing with **TA-MC**, the increase in emission intensity and longer wavelength shift were limited, indicating a smaller PH fraction and increased nonradiative deactivation of triplet excitons. However, the PH shift in **TA-PI** (45 nm) was larger than that of **TA-MC** (20 nm), likely due to the temperature-dependent  $\pi$ - $\pi$  interactions caused by the rigid PI structure.



**Fig. 2.** Temperature-dependent PL spectra of (a) **TA-MC** and (b) **TA-PI**. (c) Temperature-dependent changes in the spectral areas of FL and PH for (top) **TA-MC** and (bottom) **TA-PI**.

Understanding of the relationship between the aggregated state and their PL properties is crucial for achieving high PL efficiency in polymer materials. To investigate the control of the aggregated state, we conducted static hydraulic pressure experiments using a diamond anvil cell (DAC) as shown in **Fig. 3a** [4]. **Figs. 3b** and **3c** depict the pressure dependence of the emission spectra of **TA-MC** and **TA-PI**, respectively, along with microphotographs under UV irradiation. In case of **TA-MC**, the PH intensity gradually increased up to 2.6 GPa and then decreased at higher pressures. This suggests that the non-radiative deactivation induced by local molecular motion was suppressed below 2.6 GPa, similar to the effect observed at low temperatures. Whereas, at higher pressures, the contribution of energy transfer to the non-radiative deactivation became more significant and exceeded the suppression of molecular motion. For **TA-PI**, the PL spectra exhibited a prominent redshift from 0.1 MPa to 6.5 GPa, accompanied by a constant decrease in intensity, which indicates that the enhanced energy transfer resulting from a more concentrated **TA** moiety under pressure had a greater impact on **TA-PI** compared to **TA-MC**.



**Fig. 3.** (a) Schemes of optical experiments under ultrahigh pressure. Pressure-dependent PL spectra of (b) **TA-MC** and (c) **TA-PI**. The Inset shows photographs of the film's appearance before and after UV irradiation ( $\lambda_{ex} = 360$  nm) and under elevated pressures.

## REFERENCES:

- [1] S. Ando, *et al.*, *J. Phys. Chem. B* **2009**, 113, 15212; *ACS Macro Lett.* **2016**, 5, 1301. [2] Liu. J, *et al.*, *Macromolecules* **2007**, 40, 4614; G. Xie, *et al.*, *Adv. Mater.* **2015**, 28, 181. [3] H. Liu *et al.*, *Mater. Chem. Front.* **2018**, 2, 1853. [4] S. Ando, *Polym. J.* **2023**, 55, 645.