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Correlation between the Photophysical Properties and Structural Changes of Thianthrene-Containing Imide Compound and Polyimide Generated by High Pressure

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[Introduction] Our group has been reporting highly fluorescent (FL) and phosphorescent (PH) imide compounds and polyimides (PIs). It is important to investigate the correlation between the conformation and photophysical processes of them. It was reported that thianthrene (TA) having a bent structure with a sulfur-containing heterocyclic ring exhibits adjustable FL and PH depending on its conformation.[1] Therefore, it is expected that the conformational changes induced by applying pressure on TA-containing imide compounds and PIs may affect their photoluminescence (PL) properties significantly.[2] In this study, we investigated the PL properties of TA-containing imide compounds and PIs at elevated pressures to explore the relationship between the photophysical properties and conformational changes.

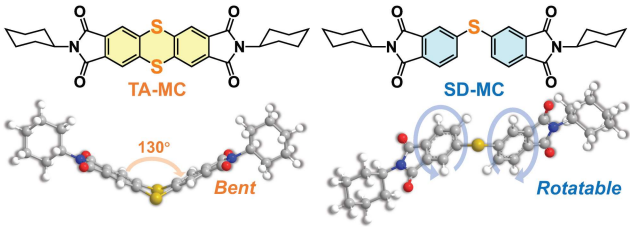

Fig. 1. Chemical and 3D-structures of **TA-MC** and **SD-MC**.

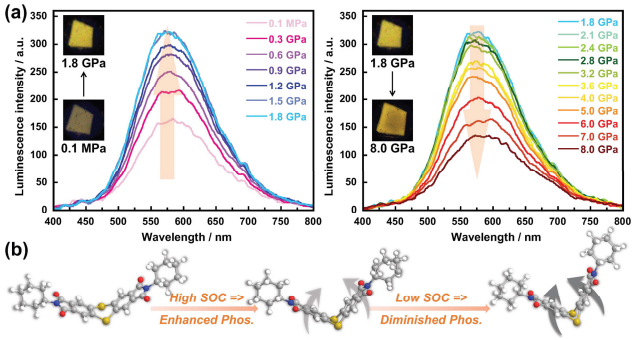

Fig. 2. (a) Pressure dependent PL spectra and (b) possible conformational changes of **TA-MC** in PMMA film.

[Experiment] As shown in **Fig. 1**, TA-containing imide compound (**TA-MC**) and another sulfur-containing imide compound (**SD-MC**) were synthesized and dispersed in PMMA films at 1 wt%. PL spectra at elevated pressures were measured using a diamond anvil cell (DAC) with ruby particles as the indicator of the inside pressure.

[Result and discussion] The **TA-MC**/PMMA film displayed yellowish PL under UV irradiation and exhibited PH at 575 nm (**Fig. 2a**). The PH intensity increased up to 1.8 GPa by 2.2 times as high as that at ambient pressure (0.1 MPa) and decreases at the higher pressures. It suggests that, below 1.8 GPa, the non-radiative deactivation induced by local molecular motion is suppressed by pressure and the more folded conformation in **TA-MC** enhances the spin-orbit coefficient (SOC) which are beneficial for PH (**Fig. 2b**).[1] Whereas, at higher pressures, the excited energy transfer that enhances non-radiative deactivation becomes significant, and the conformation of **TA-MC** becomes more folded with a decrease in SOC, which causes the decrease in PH intensity. In case of **SD-MC** having a rotatable diphenyl-thioether (ϕ-S-Ph) structure, the **SD-MC**/PMMA film displayed bluish PL under UV irradiation and exhibited FL at 430 nm (**Fig. 3a**). The FL intensity increases up to 1.5 GPa by1.2 times as high as that at ambient pressure and kept stable at the higher pressures. The FL spectra also exhibited gradual red shifts with increasing pressure. The increases in intensity and red shift of FL spectra suggests a structural planarization at the rotatable Ph-S-Ph structure in **SD-MC**. However, our previous study showed that the conformation of **SD-MC** is close to planar at ambient pressure (**Fig.3b**); therefore, it is hard to induce a significant conformational change with applying pressure, leading to the slight increase in FL intensity. Meanwhile, the subsequent increase in PH intensity at 510 nm at higher pressures indicates the suppression of molecular motion and the restriction of non-radiative deactivation.

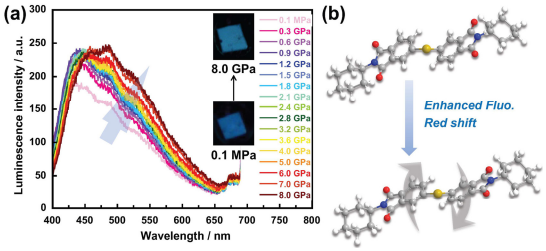

Fig. 3. (a) Pressure dependent PL spectra and (b) a possible conformational change in **SD-MC**/PMMA film.

[Reference] [1] Z. Yang *et al.*, *Chem. Sci.* **2023**, *14*, 2640; [2] S. Ando *et al.*, *Polymer Preprints*, **2023**, *72(1)*, 1G11.