



Photophysical Properties of Thianthrene-Containing Imide Compounds and Polyimides under High Pressure up to 8 GPa

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Abstract: The photoluminescence (PL) properties of thianthrene (TA) characterized by a bent structure with a sulfur-containing heterocyclic ring are known to be adjustable through a change in its dihedral angle.¹ Therefore, the PL properties of TA-containing materials are expected to be altered by conformational changes induced by applying pressure (Fig. 1).² In this study, the relationships between the PL properties and the conformational changes was explored based on the PL spectra of TA-containing imide compounds (TA-MC and 2STA-MC dispersed in PMMA) and polyimide (TA-PI, Fig. 1) under high pressure up to 8 GPa.

For TA-MC which exhibits a single phosphorescence (PH) peak under 575 nm UV radiation,² the PH intensity increased up to 1.8 GPa and then decreased with a further increase in pressure (Fig. 2). Below 1.8 GPa, the local molecular motion was suppressed, and a more folded conformation enhances the spin-orbit coupling (SOC) which is beneficial for PH. In contrast, excited energy transfer becomes dominant at higher pressures due to the reduced intermolecular distances. 2STA-MC, showing both fluorescence (FL) and PH peaks, exhibited decreases in both peak intensities with a gradual red-shift under high pressure (Fig. 3). This suggests an enhancement of the excited energy transfer facilitated by compression in the PMMA matrix. For TA-PI, the FL spectra exhibited a constant decrease in intensity with increasing pressure, coupled with a prominent red-shift with PL quenching at 8.0 GPa (Fig. 4). These behaviors indicate that energy transfer among concentrated TA moieties was enhanced in PI at higher pressures. These results also indicate that applying pressure induces conformation changes at TA moieties as well as enhanced intermolecular interactions, impacting on their PL properties.

Keywords: polyimide, high pressure, thianthrene, fluorescence, phosphorescence

Reference:

- [1] Yang Z, et al., Chem. Sci., 14, 2640-2645 (2023).
[2] S. Ando et al., Polymer Preprints, 72, 1G11 (2023).

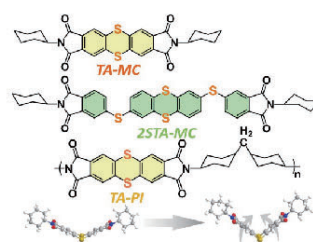


Fig. 1. Chemical structures of TA-MC, 2STA-MC, TA-PI and a possible conformational change of TA-MC.

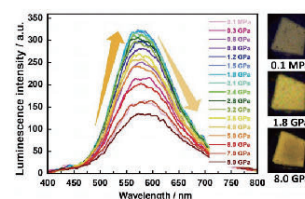


Fig. 2. Pressure-dependent PL spectra of TA-MC

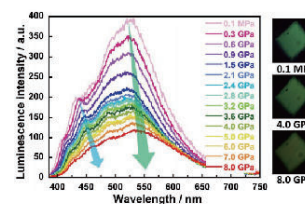


Fig. 3. Pressure-dependent PL spectra of 2STA-MC.

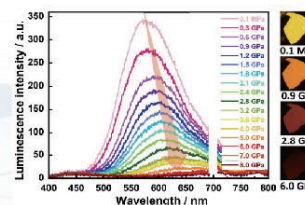


Fig. 4. Pressure-dependent PL spectra of TA-PI.