

PHOTOPHYSICAL PROPERTIES OF THIANTHRENE-CONTAINING POLYIMIDES UNDER HIGH PRESSURE UP TO 8 GPa

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Abstract

Thianthrene (TA) having a bent structure with a sulfur-containing heterocyclic ring was reported to exhibit adjustable fluorescence (FL) and phosphorescence (PH) according to its conformation¹. In this study, TA-containing imide compounds (MCs) and polyimides (PIs) (**Fig. 1a**) were synthesized, and high pressure up to 8 GPa was applied using a diamond anvil cell (DAC) to measure their photoluminescence (PL) properties².

TA-MC dispersed in polymethyl methacrylate (PMMA) film exhibited yellowish PH emission in DAC, and its intensity increased up to 1.8 GPa and then decreased (**Fig. 1b**). This suggests that the non-radiative deactivation of PH was reduced by suppression of local molecular motion. In contrast, above 1.8 GPa, the intermolecular energy transfer (IET) became significant, leading to a decrease in PH intensity. TA-PI film with condensed TA moieties exhibited only yellowish FL, and its intensity constantly decreased with a prominent red-shift, followed by quenching at 8.0 GPa (**Fig. 1c**). This indicates that the IET among TA moieties was enhanced by the decreased intermolecular distance. To avoid the aggregation of TA moieties, a copolymer of TA with 6FDA (FCoPI-05) was prepared. This film exhibited pressure-enhanced PL below 1.2 GPa (**Fig. 1d**), which indicates that the dilution of TA moiety suppressed IET, leading to the enhanced PL intensity at relatively low pressures. To further suppress aggregation of TA moieties, 2STA-PI was designed by introducing thioether bonds to provide it with high rotational freedom. 2STA-PI showed only green FL under atmospheric pressure, but yellow PH was newly observed and enhanced up to 0.9 GPa (**Fig. 1e**). These results demonstrate that pressure-induced PL enhancement was realized by suppressions of molecular motion and aggregation of TA moieties.

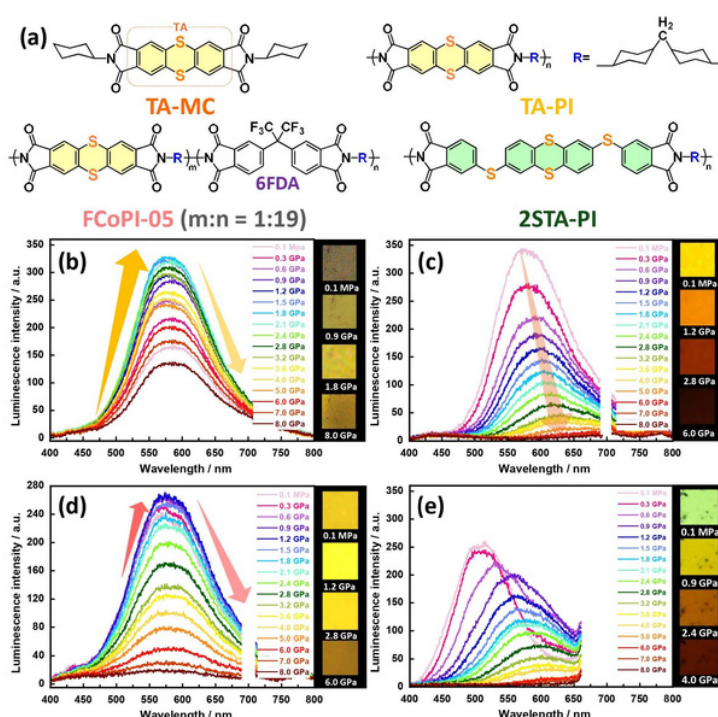


Fig. 1 (a) Chemical structures of TA-MC, TA-PI, FCoPI-05, and 2STA-PI, Pressure-dependent emission spectra of (b) TA-MC, (c) TA-PI, (d) FCoPI-05, and (e) 2STA-PI.

¹ H. Liu *et al.*, *Mater. Chem. Front.* **2018**, 2, 1853.

² H. Liu, R. Isoda, M. Doi, K. Muto, S. Ando, *J. Phys. Chem. B.* **2024**, 128, 7690.