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Pressure-induced Conformational Changes and Photophysical Properties of Thianthrene-Containing Imide Compounds and Polyimides

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INTRODUCTION

Our group has been reporting highly fluorescent (FL) [1] and phosphorescent (PH) [2] imide compounds and polyimides (PIs) and investigating the correlation between PIs structures and photoluminescence (PL) processes under very high pressure.[3] Thianthrene (TA) having a bent structure with a sulfur-containing heterocyclic ring was reported to exhibit adjustable FL and PH according to its dihedral angle.[4] Therefore, applying very high pressure is expected to induce conformational changes for TA-containing imide compounds and PIs, which would significantly affect their PL properties.[5] However, a PI (**TA-PI**) derived from TA-containing anhydride (TADA) didn't exhibit PH due to its non-radiative deactivation through strong intermolecular excitation energy transfer (IEET) between the aggregated TA moieties. A copolymerization utilizing TADA with non-emissive dianhydrides is expected to reduce the formation of aggregated states. In this study, the TA-containing imide compounds and PIs were synthesized, and their PL properties under high pressure were investigated to explore the relationship between photophysical properties and conformational changes induced by pressure.

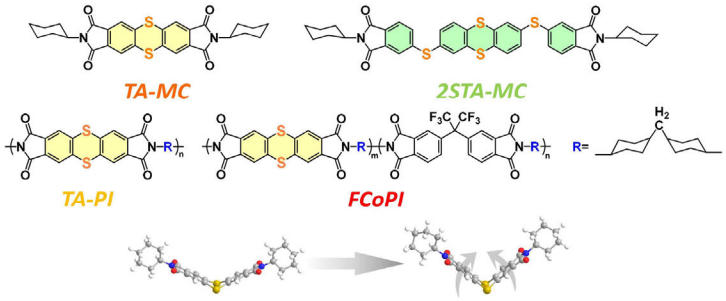

Fig. 1. Chemical structures of **TA-MC, 2STA-MC, TA-PI** and **FCoPI** (m:n = 1:4) and a possible conformational change of **TA-MC** induced by pressure.

EXPERIMENTAL

As shown in **Fig. 1**, imide compounds containing TA core (**TA-MC** and **2STA-MC**) were synthesized and dispersed in poly(methyl methacrylate) (PMMA) films, in which the weight fraction was set to 1 wt%. A homo-polyimide of **TA-PI** from TADA and 4,4'-diaminodicyclohexylmethane, as well as its copolyimide (**FCoPI**) with 4,4'-(hexafluoro isopropylidene) diphthalic anhydride, were prepared by the conventional two-step thermal imidization method. High-pressure photo-luminescence spectra were measured using a diamond anvil cell with a hydraulic medium and ruby particles as the indicator of pressure.[3]

RESULTS AND DISCUSSION

TA-MC dispersed in PMMA film exhibited yellowish PH emission at 575 nm (**Fig. 2**). With increasing pressure, the PH intensity increased up to 1.8 GPa, which was 2.2 times as high as that at ambient pressure (0.1 MPa) and then decreased above 1.8 GPa. This suggests that, below 1.8 GPa, the TA unit adopted a more folded conformation with enhanced spin-orbit coupling (SOC), which is beneficial for PH [2], in addition to the suppression of non-radiative deactivation caused by local molecular motion. In contrast, above 1.8 GPa, the non-radiative deactivation *via* IEET became significant, and more folded conformations of **TA**

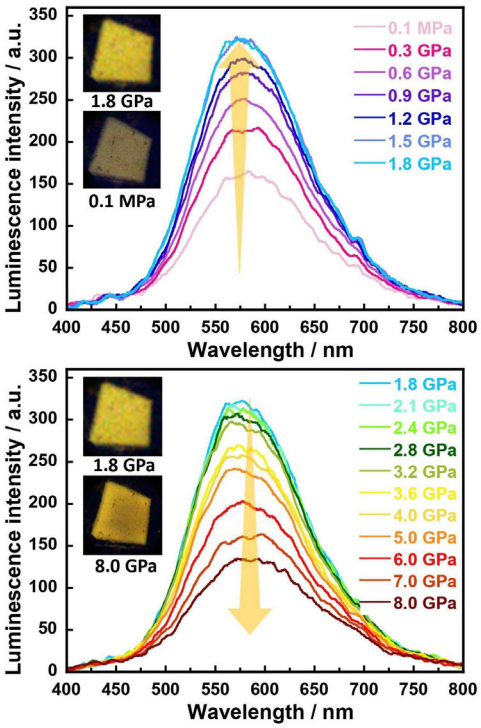

Fig. 2. Pressure-dependent PL spectra of **TA-MC**/PMMA film at 0.1 MPa to 1.8 GPa (top) and from 1.8 to 8.0 GPa (bottom).

moieties reduced the SOC, leading to a decrease in PH intensity.

2STA-MC dispersed in PMMA film displayed a green color FL and PH at 515 nm under UV irradiation at 430 nm. With applying pressure, the intensity of both FL and PH decreased accompanied by a gradual red-shift. This caused a color change of PL to yellowish (**Fig. 3**), which suggests the absence of enhanced SOC in the folded conformation, which differs from **TA-MC**. Instead, the rate constant of non-radiation deactivation increased in 2STA-MC due to its IEET.

To inhibit IEET, **2STA-MC**/PMMA film with a lower concentration of 0.2 wt% was prepared, and PL spectra were measured. Under ambient conditions, the PH intensity was lower than 1.0 wt% film. This suggests that **2STA-MC**s were well dispersed, which led to vigorous molecular motion and weak PH emission. With applying pressure, the PH intensity of 0.2 wt% film exhibited only a slight enhancement, and the emission color changed from blue to green, unlike the 1 wt% film. This change indicates that IEET was effectively suppressed at the lower concentration. The well-dispersed **2STA-MC** and the restricted molecular motion under high pressure led to a weak enhancement in PH intensity.

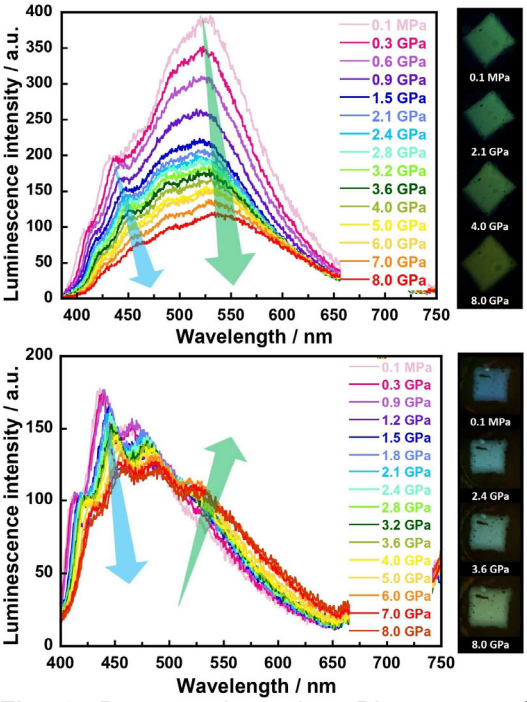

Fig. 3. Pressure-dependent PL spectra of **2STA-MC**/PMMA film with 1.0 wt% (top) and 0.2 wt% (bottom).

TA-PI film with concentrated TA moieties exhibited only yellowish FL at 580 nm (**Fig. 4**). With increasing pressure, the FL intensity constantly decreased with a prominent red-shift and was almost quenched at 8.0 GPa. This indicates that IEET among the concentrated TA moieties became significantly stronger due to the shortened intermolecular distance by pressure. To decrease the concentration of the TA moieties and inhibit IEET, a copolymer of TA with 6FDA (**FCoPI**) was prepared and measured. The **FCoPI** film, which exhibits yellowish FL emission at 570 nm, still showed a decrease in FL intensity under high pressure due to IEET (**Fig. 4**), which indicates that TA moieties were still concentrated. Notably, **FCoPI** didn't exhibit an obvious red-shift under high pressure like **TA-PI**, which suggests that the variations of their absorption spectra under pressure are different. Accordingly, to further reduce the formation of aggregated states of TA moieties, a copolymer with an even lower TA concentration (n:m = 1:>15) would be prepared and analyzed.

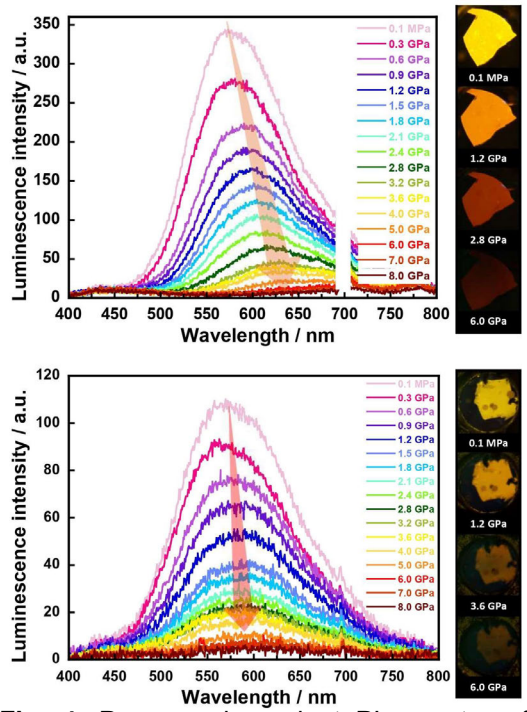

Fig. 4. Pressure-dependent PL spectra of **TA-PI** (top) and **FCoPI** (bottom).

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