Photophysical Properties of Thianthrene-Containing Imide Compounds and Polyimides at Elevated Pressure

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[Abstract]

Thianthrene (TA), having a bent structure with a sulfur-containing heterocyclic ring, is known to exhibit adjustable fluorescence (FL) and phosphorescence (PH) depending on its conformation. We expected that the conformational changes induced by applying pressure on TA-containing imide compounds (MCs) and polyimides (PIs) may affect their photoluminescence (PL) properties significantly. Moreover, the copolyimides (co-PIs) synthesized from luminescent and non-luminescent dianhydrides are expected to exhibit intense PH at elevated pressure owing to the suppression of aggregate formation and intermolecular energy transfer (IEET). Besides, **2STA-PI** was newly synthesized by introducing two thioether (−S−) linkages into **TA-PI** to introduce a significant degree of rotational freedom, which is expected to suppress the aggregation of TA moieties and improve its PL properties under high pressure. In this study, TA-containing MCs and PIs were synthesized to clarify the relationship between pressure-induced structural changes and photophysical properties, expecting the development of novel pressure-induced PL materials.

[Introduction]

Our group has been reporting MCs and PIs with high FL and PH intensities and investigating the correlation between the structures of PIs and PL processes under very high pressure [1−3]. 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 MCs and PIs, significantly affecting their PL properties [5]. However, a PI (**TA-PI**) derived from TA-containing dianhydride (TADA) exhibited no PH due to its significant non-radiative deactivation through strong IEET between the aggregated TA moieties. Copolymerization utilizing TADA with non-emissive dianhydrides is expected to inhibit the formation of aggregated structures. In this study, several TA-containing MCs and PIs were synthesized, and their PL properties at elevated pressure were investigated to explore the relationship between photophysical properties and conformational changes induced by high pressure.

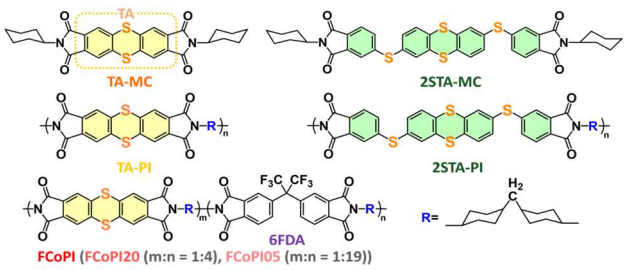

Fig. 1 Chemical structures of **TA-MC**, **TA-PI**, **FCoPI**, **2STA-MC** and **2STA-PI**.

[Experimental]

MCs containing a TA core (**TA-MC** and **2STA-MC**, **Fig. 1**) were synthesized and dispersed

in poly(methyl methacrylate) (PMMA), in which the weight fraction was set to 1.0 wt%. The homo-PIs using TADA (**TA-PI**) and 2STADA (**2STA-PI**) with 4,4'-diaminodicyclo-hexylmethane, as well as the co-PIs (**FCoPI**) using TADA and 4,4'-(hexafluoro-isopropylidene) diphthalic anhydride (6FDA), were prepared by the conventional two-step thermal imidization method (**Fig. 1**). Photo-luminescence spectra under high pressure were measured using a diamond anvil cell with a hydraulic medium (Daphne 7474, Idemitsu Co., Ltd., Japan) and ruby particles as the indicator of pressure.

[Results and Discussion]

PMMA-dispersed film of TA-MC exhibited yellowish FL emission at 550 nm as well as PH emission at 575 nm. Based on the decomposed spectra, the FL intensity decreased with applying pressure, suggesting that the decrease in the intermolecular distance caused enhanced non-radiative deactivation via IEET, whereas the PH intensity significantly 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 (**Fig. 2**). 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 inducing PH, 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 dominant, leading to a decrease in PH intensity. Besides, more folded conformations of **TA-MC** lowered SOC, contributing to the decrease in PH intensity.

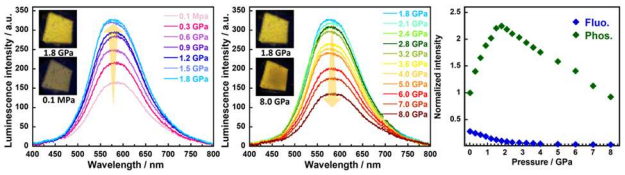

Fig. 2 Pressure-dependent emission spectra of **TA-MC**/PMMA film and emission intensity.

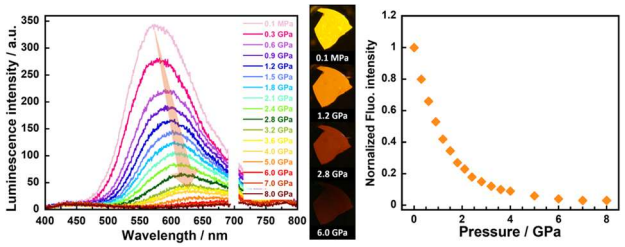

Fig. 3 Pressure-dependent emission spectra and emission intensity of **TA-PI** film.

A TA-PI film with concentrated TA moieties exhibited only yellowish FL at 580 nm (**Fig. 3**). With increasing pressure, the FL intensity gradually decreased with a prominent red-shift, and it was almost quenched at 8.0 GPa. These facts indicate that IEET among the concentrated TA moieties became significant due to the shortened intermolecular distance by pressure. To decrease the concentration of TA moiety and to inhibit IEET, a non-luminescent 6FDA dianhydride can be introduced to prepare co-PIs with TADA to separate the TA moieties and improve their PL properties under high pressure. Thus, TADA was copolymerized with 6FDA to prepare PI films of **FCoPI-20** (TADA:20 mol%) and **FCoPI-05** (TADA:5 mol%). In their PL

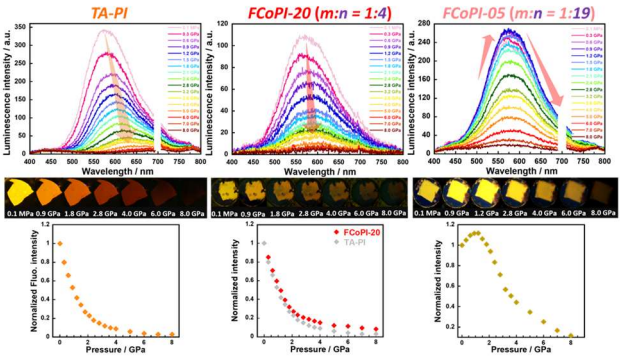

Fig. 4 Pressure-dependent emission spectra and intensity of **TA-PI**, **FCoPI-20** and **FCoPI-05**.

spectra under high pressure (**Fig. 4**), **FCoPI-20** still showed a decrease in PL intensity with applying pressure, but it was slower than **TA-PI**. It suggests that the TA moiety in FCoPI-20 is still concentrated to induce IEET, though TA moieties are rather separated compared to **TA-PI**. Meanwhile, **FCoPI-05** with an even lower concentration of TA moiety showed an obvious increase in PL intensity at pressures below 1.2 GPa. This fact indicates that a sufficient reduction of TA content in **FCoPI-05** effectively suppressed IEET at relatively lower pressure, leading to the PL enhancement.

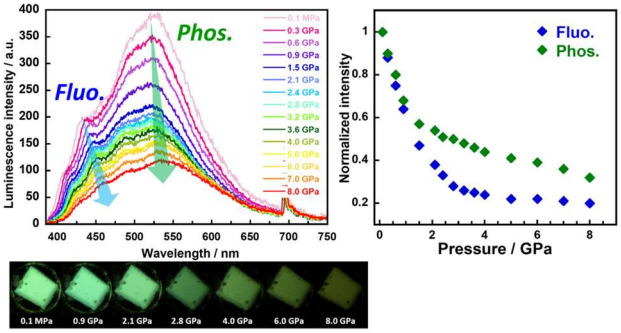

Fig. 5 Pressure-dependent emission spectra and intensity of **2STA-MC**/PMMA film at 1.0 wt%**.**

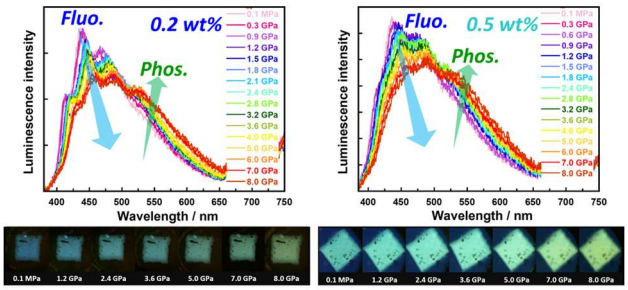

Fig. 6 Pressure-dependent emission spectra of **2STA-MC**/PMMA film at 0.2 wt% and 0.5 wt%.

We considered that the incorporation of a thioether group having a high degree of rotational freedom is benecicial to inhibit the molecular stacking of TA moieties in the PIs. Accordingly, **2STA-MC** and **2STA-PI** were synthesized to promote the PL properties of the TA-containing PIs. A **2STA-MC**/PMMA film at 1.0 wt% concentration of 2STA-MC displayed a green color FL at 430 nm as well as PH at 515 nm under UV (365 nm) irradiation. By applying pressure, the intensity of both FL and PH decreased, accompanied by gradual red-shifts. This caused an apprant change of PL color to yellowish, which suggests that the IEET among **2STA-MC** was enhanced due to the shortened intermolecular distance caused by pressure (**Fig. 5**).

For fortified suppression of IEET by separating **2STA-MC**, PMMA-dispersed films with lowered concentrations of MC at 0.2 and 0.5 wt% were synthesized, and their pressure-dependent PL spectra were measured. With applying pressure, their PH intensity exhibited only a slight enhancement, and the emission color changed from blue to green, unlike the 1.0 wt% film (**Fig. 6**). This color change indicated that the IEET was effectively suppressed at the lower concentrations because **2STA-MC** was homogeneously dispersed, and the molecular motion was restricted under high pressure, resulting in the slight enhancement of the PH intensity.

The PL spectra of **2STA-PI** film were measured under high pressure (**Fig. 7**). **2STA-PI** showed only green FL at ambient pressure (0.1 MPa), but with wwapplying pressure, yellowish PH gradually appeared and became dominant. To clarify the intensity changes of FL and PH with applying pressure, the spectra were decomposed into FL and PH. The FL intensity exhibited a constant decrease

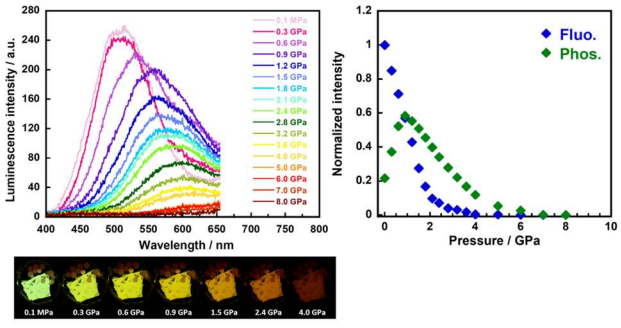

Fig. 7 Pressure-dependent emission spectra and intensity of **2STA-PI** film.

with increasing pressure due to the shortened intermolecular distance with enhanced IEET, whreas the PH intensity increased up to 0.9 GPa. This indicates that the TA stacking and molecular motion in the PI were effectively suppressed at relatively low pressures, induced 'pressure-induced PH' below 0.9 GPa. However, at higher pressures (>0.9 GPa), the effects of shortened intermolecular distance and enhanced IEET became dominant, which leads to a decrease in both FL and PH intensity.

[Conclusion]

TA-MC exhibited enhanced PH at lower pressures (<1.8 GPa) with a folded conformation of TA moiety with a high SOC and restriction of local molecular motion. However, the stacking of TA moiety led to the enhanced IEET and weakened PL properties of TA-PI and FCoPI films under high pressure. Copolymerization with a non-luminescent 6FDA effectively separated TA moieties and suppressed the IEET, leading to the pressure-induced PH in FCoPI-05 at relatively low pressures.

The thioether linkages with high rotation freedom were introduced into the **2STA-MC** and **2STA-PI**. For **2STA-MC**, the aggregation was suppressed in the films with lower concentration at 0.2 and 0.5 wt% compared to the film at 1.0 wt%. Thus, the emission intensity decreased in PMMA film at 1.0 wt%, whereas the PH intensity was enhanced for the films at 0.2 and 0.5 wt% due to the suppression of molecular motion. The rotational freedom of the thioether group also inhibits the PH properties of **2STA-PI** due to strong molecular motion under atmospheric pressure. However, at relatively lower pressure (<0.9 GPa), the **2STA-PI** can exhibit enhanced PH by applying pressure originating from the restriction of TA stacking and molecular motion.

[References]

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