Fluorescence and Phosphorescence Properties of Sulfur-containing Polyimides having Adamantyl Skeletal Structure in the Main Chain

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[Introduction] Highly fluorescent polyimides (PIs) are expected to be applied to solar spectrum down-convertors owing to their excellent optical properties such as high transparency and tunable fluorescent colors, as well as outstanding physical properties such as thermal stability, chemical stability, and mechanical strength originated from their rigid and polar primary structures [1]. Efficient wavelength down-convertors require high optical transparency in the visible region as well as large Stokes-shifted (*SS*) emission. In general, phosphorescence exhibits larger *SS* than fluorescence owing to the intersystem crossing (ISC) process. It is well known that ISC can be enhanced by introducing of heavy atoms which enlarge spin-orbit couplings[2]. Our group has recently reported that the PIs containing thioether (−S−) linkage in the main chain exhibit efficient ISC than those containing ether linkage (−O−) [3]. Moreover, we have clarified that the non-radiative deactivation process in PIs is strongly influenced by the molecular mobility at the diamine moiety. Therefore, a higher quantum yield is achievable by introducing diamines having restricted conformational freedom [4]. In this study, we investigated the photoluminescent properties of newly synthesized sulfur-containing PIs (S-PIs) having rigid adamantane-1,3-diamine (1,3-Adm) or *trans*-1,4-cyclohexanediamine (1,4-*t*DACH) skeletal units in the main chain.

[Experimental] An alicyclic diamine (1,4-*t*DACH or 1,3-Adm) and an aromatic dianhydeide (4,4′-thiodiphthalic anhydride (SDPA), 4,4′-[*p*-phenylenebis(thio)]diphthalic anhydride (2SDEA) or 4,4′-[*p*-thiobis(phenylenesulfanyl)]diphthalic anhydride (3SDEA)) was reacted in *N*,*N*-dimethylacetamide (DMAc) for 1 day to give a poly(amic acid) (PAA) precursor solution. The PAA solution was spin-coated onto a fused silica substrate, followed by soft-baking at 70 °C for 50 min and subsequent thermal imidization at 220°C for 1.5 h to obtain PI thin films. Abbreviation and chemical structure of each PI are presented in **Fig. 1**. The excitation and emission spectra, quantum yields, and emission lifetime were analyzed for these S-PIs.

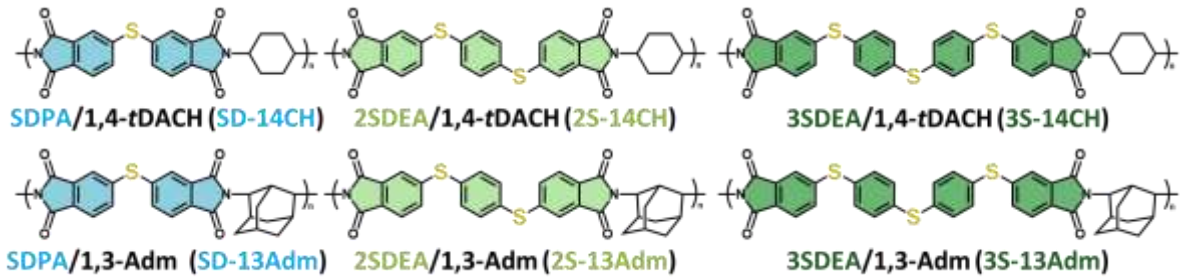

Fig.1 Chemical structures of photoluminescent polyimides.