Controlling Energy of π-Conjugated Systems with Hypervalent Bond and Application to Polymer Materials

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A hypervalent compound is a class of molecules where a main-group element has more than nine electrons in its valence shell beyond the limits of the Lewis octet rule. I proved electronic contribution of hypervalent bonds originating from three-center four-electron (3c-4e) bonds to π-conjugated systems through distorted trigonal bipyramidal structure of hypervalent tin-fused azobenzene (TAz) complexes.[1] I showed examples of the compounds exhibiting near-infrared (NIR) emission despite small molecules with germanium-fused azobenzene (GAz) complexes.[2] Furthermore, it was found that expanded π-conjugation with polymerization synergically improved optoelectronic properties of the π-conjugated system including the hypervalent moleclues.[3] Herein, I will explain my research on basic concepts of the hypervalent compounds and their allocations to polymer materials.

Figure 1 shows structures and NIR emission behaviors of π-conjugated polymers including TAz and GAz compounds in the polymer main-chain. The π-conjugated systems were well expanded via nitrogen–nitrogen (N=N) double bonds and the optical properties were dependent on the elements. The GAz polymers had more bathochromic-shifted luminescence wavelengths (λ_{PL}s) than the TAz ones, whereas absolute photoluminescence quantum yields (Φ_{PL}s) of the GAz polymers were smaller than those of the TAz one in the same monomers. The results suggest the potentiality that π-conjugated polymers including hypervalent compounds enable fine tuning of optical properties even in the NIR region.

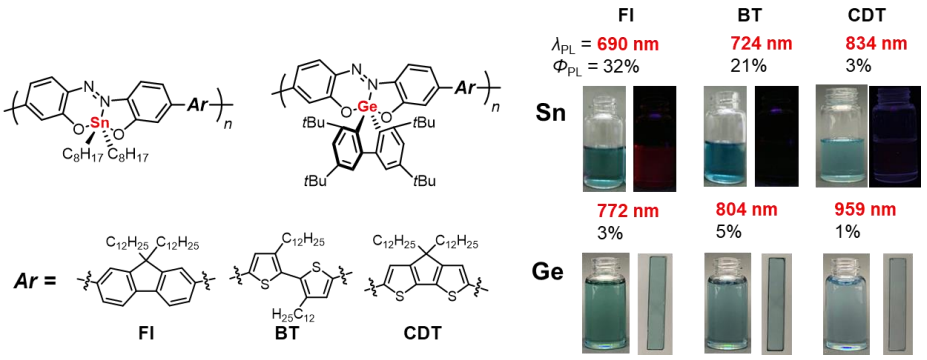

Figure 1. Structures and NIR emissions of TAz and GAz polymers in diluted toluene.

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