Evaluation of Stimulus Responsiveness by Hypervalent Bismuth Compounds with π-Conjugated Scaffolds

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Organic molecules have been widely used in the development of OLEDs and OPVs. Among them, π-conjugated molecules have attracted much attention due to their high stability, electrical conductivity, and unique optical properties. In addition, they have also been expected to develop the sensing function to visualize stimuli in various environments. Since the sensing function of such π-conjugated polymers is challenging to achieve with only a carbon skeleton, introducing heteroatoms is one of the effective strategies.

This research focuses on hypervalent states of heavy elements to develop new molecular designs and sensing functions for response to various environments. Bismuth, a group 15 element of period 6, has Lewis acidity. We created a new sensing material using the interaction of Lewis acidity with functional groups by combining hypervalent bismuth with π-conjugated molecules.

To investigate stimulus responsiveness, we synthesized bismuth compounds using azobenzene tridentate ligands (Figure 1). We focused on acid responsiveness. In **BiAz**, the absorption spectrum changed in response to the addition of trifluoroacetic acid (TFA) (Figure 2a), and then the addition of triethylamine (Et_3N) recovered its original state. The Lewis acidity of hypervalent bismuth causes it to interact with Lewis basic molecules and to change its interaction with π-conjugated scaffolds. It was found that the response was more acute after the addition of dimethyl sulfoxide (DMSO) than before (Figure 2b). In this presentation, we will discuss the detailed mechanism and evaluation of the response.

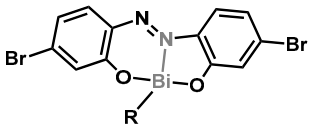

Figure 1. Hypervalent bismuth compounds, **BiAz** (R = Ph).

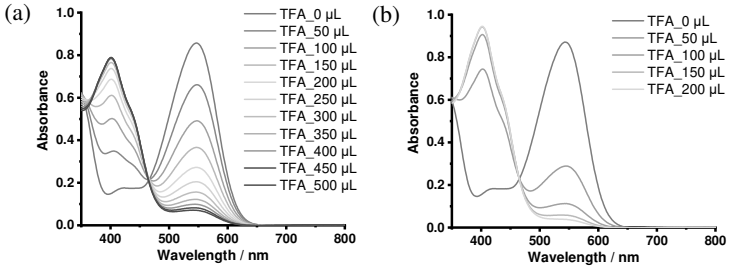

Figure 2. UV–vis absorption spectra of the mixtures containing (a) **BiAz** (5.0×10^{-5} M in THF), and (b) **BiAz** (5.0×10^{-5} M in THF/DMSO = 99/1 v/v) with each amount of TFA solution (1.0×10^{-3} M in THF).