## Solid-State Synthesis of Indium-Fused Azobenzene Complexes from Indium Oxide

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Rare metals are indispensable for high-tech industries, whereas their uneven distribution and limited reserves have led to a serious depletion of the resources. Among rare metals, indium is used in many devices as a transparent conducting film (ITO, indium tin oxide), and the recovery of indium from its waste is desired. Conventionally, although various recovery techniques have been proposed<sup>1</sup>, simpler and lower-cost recovery methods are required.

From these backgrounds, we focused our attention on solid-state reactions. Solid-state reactions are synthetic methods that minimize the use of solvents, and efficient solvent-free reactions are achieved by the strong mechanical stirring of a ball mill. In fact, Saito *et al.* reported the reduction from ITO to indium metal under a nitrogen atmosphere using Li<sub>3</sub>N as a reducing agent.<sup>2</sup> Furthermore, we has designed typical element complexes by combining elements and azobenzene tridentate ligands to create functional luminescent materials. Recently, we reported the creation of functional complexes by solid-state reactions of azobenzene tridentate ligands with organometallic reagents.<sup>3</sup>

In this study, we aimed at simple recovery of indium from ITO and creation of functional compounds by solid-state synthesis. To achieve our goal, indium oxide (In<sub>2</sub>O<sub>3</sub>) was used as a raw material. As a result, luminescent indium complexes were obtained from In<sub>2</sub>O<sub>3</sub> and the azobenzene tridentate ligands by adding a small amount of concd. HCl as a reactant with ball milling for 1 h (Scheme 1). In the presentation, the synthetic conditions and optical properties of the resulting complexes will be discussed in detail.

$$In_2O_3 + X$$

OH

HO

The pyridine H2O

 $In_2O_3 + X$ 
 $In_2O_3$ 

**Scheme 1**. Solid-state synthesis of indium-fused azobenzene complexes.

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