Selective inclusion of regioisomers of disubstituted aromatic compounds with crystals of *p-tert*-butylcalix[4]arene: Mechanistic consideration for guest selectivity and application for separation

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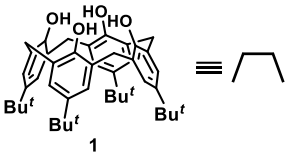

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The development of solid materials that can strictly discriminate the size and shape of organic molecules and selectively collect them is important in the separation and purification processes. We have been studying the selective inclusion of organic compounds with crystals of calixarenes. Although crystals of *p-tert*-butylcalix[4]arene (**1**) exhibit almost no inclusion selectivity toward chain alcohols and alkanes with flexible structures, the crystals included rigid regioisomers of disubstituted benzenes with high selectivities.[1] However, the discussions about quantitativity are not enough. In this study, we investigated the quantitativity of the inclusion with the intention of developing a practical method for the separation of regioisomeric disubstituted benzenes.

Inclusion experiments were performed by suspending crystals of **1** in decane solutions containing three regioisomers of disubstituted benzenes (1 or 0.5 molar equiv each to **1**). The resulting crystals were collected by filtration, dried in vacuo, and analyzed by ^{1}H NMR. Several disubstituted benzenes gave inclusion crystals with high selectivity and quantitativity. For example, the crystals of **1** included *p*-nitrotoluene and *p*-xylene, giving inclusion crystals formulated as **1**·*p*-nitrotoluene and **1**$_2$·*p*-xylene, respectively (Fig. 1). The guests could be recovered from the crystals by guest exchange. For example, suspending **1**·*p*-nitrotoluene in hexane gave crystals including only hexane. Isomerically pure *p*-Nitrotoluene was recovered from the filtrate in 84% yield. Mechanisms to realize the guest selectivities are also reported.

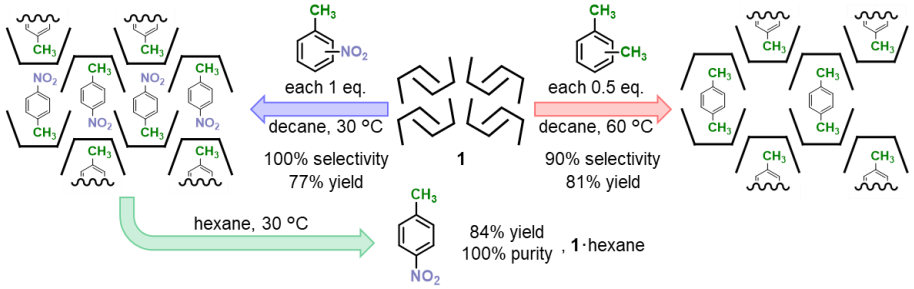

Figure 1. Selective inclusion of disubstituted benzenes with the crystals of **1**.

1) Morohashi, N.; Tonosaki, A.; Kitagawa, T.; Sasaki, T.; Ebata, K.; Hattori, T. *Cryst. Growth Des.* **2017**, *17*, 5038.