

1B3b

Supramolecular cross-linking of [60]fullerene-tagged poly(phenylacetylene) by host-guest interaction of calix[5]arene and [60]fullerene

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We have reported the noncovalent synthesis of fullerene-containing supramolecular polymeric networks formed by the iterative host-guest interaction of [60]fullerene and calix[5]arene. In this session, the supramolecular cross-linking of the fullerene-tagged poly(phenylacetylene) via the host-guest interaction of [60]fullerene and calix[5]arene will be presented (Figure 1).

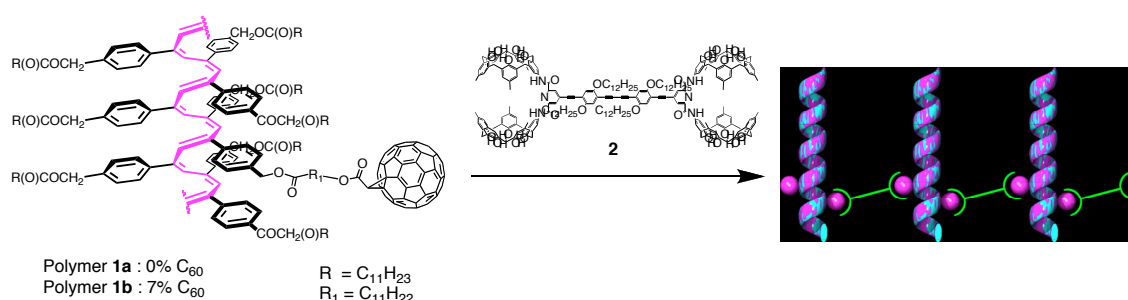


Figure 1. Schematic representation of the supramolecular cross-linking of the [60]fullerene-tagged polymer.

Poly(phenylacetylene) **1a** and [60]fullerene-tagged poly(phenylacetylene) **1b** were synthesized by [Rh(nbd)Cl]₂ catalyzed polymerization (**1a**: Mn = 100000, Mw = 560000, Mw/Mn = 5.6, **1b**: Mn = 13000, Mw = 28000, Mw/Mn = 2.2). The fluorescence spectrum of **2** in toluene showed intense emission at 464 nm. The emission was quenched by the addition of **1a** or **1b**. Stern-volmer plots gave linear correlations (**1a**: $K_{sv} = 3.4 \times 10^5 \text{ M}^{-1}$, **1b**: $K_{sv} = 2.6 \times 10^6 \text{ M}^{-1}$). **1b** quenched the emission more effectively than **1a**, suggesting that the [60]fullerene units of **1b** is encapsulated within the cavity of the double-calix[5]arene units of **2**. The GPC traces of **1b** (a) without or (b) with **2** are presented in Figure 2. The GPC trace of **1b** with **2** gave a higher molecular weight fraction than that of **1b** (a: Mn = 13000, Mw = 28000, Mw/Mn = 2.2, b: Mn = 75000, Mw = 320000, Mw/Mn = 4.3). It is clear that the [60]fullerene-tagged polymer is linked by the host-guest interaction to bring about the higher molecular weight polymers.

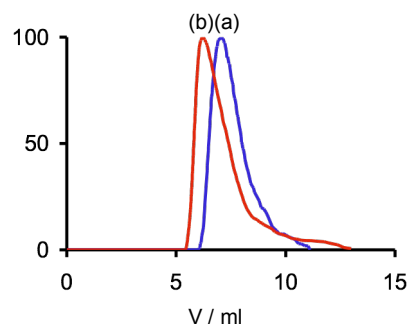


Figure 2. GPC curves of (a) **1b** and (b) **1b** + **2** using toluene as an eluent with linear PS standards. [**1b**] = 1 mg/ml.