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Fullerene recognition by 5-nitro-11,17,23,29-tetramethylcalix[5]arene

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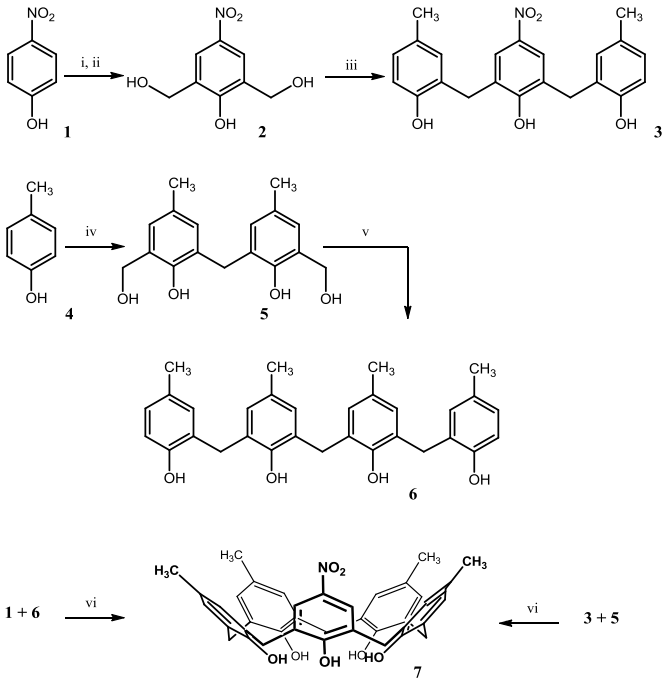
ABSTRACT

The condensation of different building blocks allows the synthesis of an electrochemically active 5-nitro-11,17,23,29-tetramethylcalix[5]arene that was designed to study fullerene complexation using cyclic voltammetry. Although this method was ultimately unsuccessful, the formation of complexes between the calix[5]arene derivative and C_{60} or C_{70} fullerenes in solution was proved by mass spectrometry. Moreover, the solid state structure of the complex with fullerene C_{60} was confirmed by X-ray crystallography.

Calix[n]arenes are cavity-shaped macrocycles[1] consisting of electron-rich aromatic (phenolic) subunits making them suitable hosts for electron-deficient guests such as various ammonium salts, soft metal cations or fullerenes that can be held by cation-π or π-π interactions.[2] Unfortunately, calix[4]arene in the *cone* conformation is too small to accommodate fullerenes inside its cavity. Furthermore, larger macrocycles such as calix[6]arene or calix[8]arene also suffer from several drawbacks, which include conformational mobility and the absence of selective derivatization techniques. Hence, calix[5]arene seems to be the best choice as the size of the cavity perfectly corresponds to the diameter of the most common fullerenes, C_{60} and C_{70}. Moreover, matching of the fullerene curvature with a bowl-shaped calixarene (concave–convex principle) leads to attractive interactions between both systems via additional van der Waals (dispersion) forces.[2] The perfect size and shape complementarity of both systems has also been confirmed from the crystal structures of fullerene-calix[5]arene complexes,[3] leading to the development of several highly efficient hosts, which has enabled UV-Vis or fluorescence detection of the complexation phenomenon in solution.[4] A recent electrochemical study of nitrocalixarenes[5] led us to the idea of introducing this redox marker into the calix[5]arene host and to study the complexation of fullerene via electrochemical methods.

From a synthetic point of view, the introduction of only one nitro group to the upper rim was desirable to maintain the good solubility of the host and to preserve its complexation ability. Since selective mononitration of calix[5]arene requires alkylation of the lower rim,[6] direct synthesis of the macrocycle from suitable oligomers was chosen. As the corresponding building blocks are easily obtainable and known compounds, we studied



Scheme 1. Reagents and conditions: (i) CH_2=O, AcOH, H_2SO_4, 60 °C, 35 h; (ii) aq. HCl, reflux overnight; (iii) **4**, HCl, 130 °C, 10 h; (iv) CH_2=O, KOH, 0 to 40 °C, 4 d; (v) **4**, HCl, 130 °C, overnight; (vi) xylene, reflux, 3 d.

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