

SELF-ASSEMBLY OF TETRA-O-ALKYLATED P-NITROCALIX[4]ARENE IN SOLID STATE: EFFECT OF THE CHAIN LENGTH

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Tetra-O-alkylated p-nitrocalix[4]arenes are well known and their second-order nonlinear optical properties and potential application for frequency doubling and optical switching have been demonstrated¹. In these molecules an electron-donating alkyl group (D) is connected to electron-accepting nitro group (A) via a π -conjugated system of phenyl ring. These so-called D- π -A units meet thereby the requirement of asymmetric polarizability. The combination of several D- π -A units within one single molecule has the advantages that a high dipole moment is combined with a high hyperpolarizability. In this study, we present self-assembly of tetra-O-alkylated p-nitrocalix[4]arene in the pinched cone conformation (with 8, 12 and 14 carbon atoms in chains) in crystals. Surprisingly, the octylated calix[4]arenes self-assembly resembles rather the behavior of O-propylated p-nitrocalix[4]arenes¹⁻³ ones than those with 4 and 5 carbon atoms in the chains. The calix[4]arene molecules self-assemble into infinite chains along of each coordinate axis of the rhombohedral unit cell in “up-down” manner mainly due to π - π interaction, which is additionally stabilized by the C-H \cdots O contacts. π - π Interactions, C-H \cdots O contacts between adjacent calix[4]arenes of neighbor infinite chains and interactions with solvent molecules force spatial coherence of disordered alkyls chain location and as a result hexagonal distribution of ‘channels’ in calix[4]arene-solvent matrix filled by disordered flexible alkyl chains (Fig. 1).

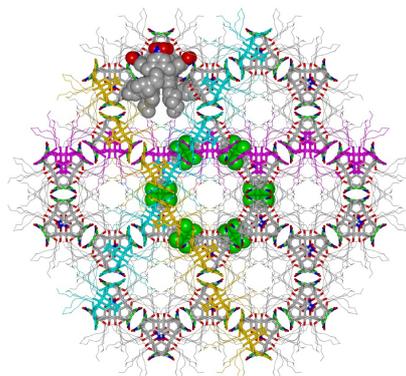


Figure 1. Packing diagram for tetra-O-octylated p-nitrocalix[4]arene monochloroform clathrate.

In spite of elongation of alkyl chains to twelve carbon atoms, crystal structure of tetra-O-dodecylated solvent free p-nitrocalix[4]arene is also kindred with O-propylated p-nitrocalix[4]arenes¹⁻³ and O-octylated ones. Two calix[4]arene molecules with opposite spatial orientation form centrosymmetric dimer via π - π stacking interactions between the conjugated systems of the phenyl rings and nitro groups of the neighbouring calixarenes and two C–H \cdots O bonds between H-atoms of the second methylene groups of the alkyl chains and the nitro group of the adjacent calixarene. The dimers are joined by pairs of C–H \cdots O contacts into infinite chains in ‘up-down’ manner along [110] direction via *meta*-H-atoms of calix-phenyl ring of adjacent calixarenes. However, presence of long hydrophobic alkyl chains forces classical for amphiphile compounds bilayer packing motif with the alkyl chains interdigitated (Fig. 2a).

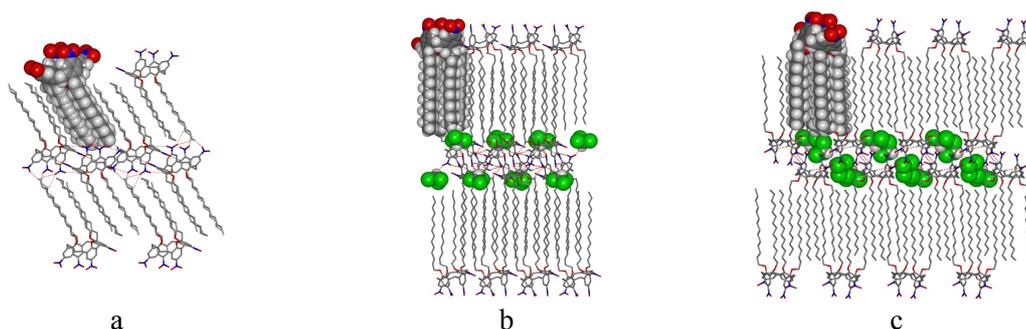


Figure 2. Packing diagram for p-nitrocalix[4]arenes: (a) dodecylated solvent free; (b) tetradecylated monochloroform clathrate; (c) tetradecylated dichloroform clathrate.

Tetra-O-tetradecylated p-nitrocalix[4]arene monochloroform clathrate crystallizes in monoclinic crystal system and is isostructural to p-tert-butylcalix[4]arene monochloroform clathrates with 10, 12 and 14 carbon atoms in the chains and also reveals bilayer packing motif (Fig. 2b). Crystallographic data comparison of these isostructural structures reveals that parameter *a* of unit cells increases with the elongation of the alkyl chains for p-tert-butylated calix[4]arenes (26.9568(6), 29.6303(5), 32.215(1) Å for 10, 12 and 14 carbon atoms in alkyl chains respectively) but it is shorter for the p-nitrocalix[4]arene (30.0091(7) Å) due to interdigitated of the calix[4]arene cores of the neighbor bilayers.

Presence of long alkyl chains in the crystal structure of tetra-O-tetradecylated dichloroform clathrate also results in layered structure formation (Fig. 2c). Higher content of solvent results in richest network of intermolecular interaction. In addition to C–H \cdots O bonding and π - π stacking interactions, there also is a number of close N \cdots O and N \cdots O contacts.

The role chain length, presence of solvent and weak interactions on self-assembly of tetra-O-alkylated p-nitrocalix[4]arenes in their crystal structures will be discussed.

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