MS15-O4 Molecular rotors in nanoporous periodic architectures

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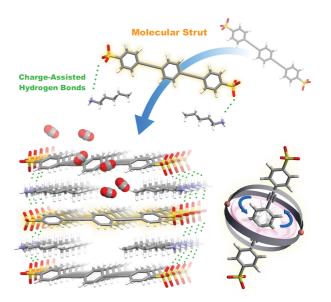
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New mesoporous hybrid covalent frameworks were prepared to realize a periodic architecture of fast molecular rotors containing dynamic C-F dipoles in their structure.[1] The mobile elements, designed on the basis of fluorinated p-divinylbenzene moieties, were integrated into the robust covalent structure through siloxane bonds, and showed not only the rapid dynamics of the aromatic rings (ca. 10^8 Hz at 325 K), as detected by solid-state NMR spectroscopy, but also a dielectric response typical of a fast dipole reorientation under the stimuli of an applied electric field. The nanochannels are open and accessible to diffusing-in gas molecules, and rotor mobility could be individually regulated by I_2 vapors. The iodine enters the channels of the periodic architecture and selectively reacts with the pivotal double bonds of the divinyl-fluoro-phenylene rotors without disrupting the structure, affecting their motion and the dielectric properties. The combination of porosity with rotor dynamics was also discovered in molecular crystals.

Disulfonated rotor-containing molecular rods were self-assembled with alkylammonium salts to fabricate porous supramolecular architectures held together by charge-assisted hydrogen bonds (Figure 1) [2]. The rotors, as fast as 10^8 Hz at 240 K, are exposed to the crystalline channels, which absorb CO₂ and I₂ vapors at low pressure. The rotor dynamics could be switched off and on by I₂ absorption/desorption, showing remarkable change of material dynamics by the interaction with gaseous species and suggesting the use of molecular crystals in sensing and pollutant management.

Moreover, porosity can be switched on/off in molecular crystals based on star-shaped azobenzene tetramers by photoirradiation[3]. Photoinduced trans-cis isomerization of molecules changes intermolecular interactions triggerring the formation of a non porous material which can be reverted to porous crystals by visible light irradiation or thermal treatment.

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Molecular Rotors in Organic Porous Architecture

Figure 1.

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