Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Conformational changes underlying variation in the structural dynamics of the materials confined at the nanometric scale.

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EXPERIMENTAL SECTION AMPLIFICATION

Raman measurements details

All Raman data were manipulated by performing a baseline correction and cosmic ray removal. The difference Raman spectrum was obtained by mathematic calculation taking into account difference between the first spectrum obtained after sample quenching and last spectrum collected after sample equilibration. The spectrometer's monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}).

Theoretical computations description in details

Quantum mechanical calculations were applied to resolve the problem of band assignments observed during the Raman experiment. The initial geometry of Ben-IBU in *cis*-configuration was optimized using the molecular modeling method implemented in the Gaussian09 software package.[1] Then, energy barriers for conformational motions of benzene ring at different torsion angles (Φ, φ) were followed. The dihedral angle (Φ or φ) was changed continuously by 10° in the whole range of 360°. Energy barriers were obtained by subtraction of all nonthermal energy (sum of electronic and zero-point vibrational energy) of the transition state from the nonthermal energy of minimum state. These calculations were performed using density functional theory (DFT) in the gas phase[2,3,4] at B3LYP functional[5,6,7] and split-valence 6-31+G(d, p) basis sets with diffuse *s* as well as *p* functions for nonhydrogen atoms due to the presence of lone pairs on oxygen. The optimized transition states (*cis*, *trans* and intermediate) were optimized by the use of eigenvector following method at the same level of theory and used as input files for vibrational harmonic calculations. All conformers had positive harmonic vibrations proving a true energy minimum.[6] Crucial is to note that the theoretical methods overestimate vibrational frequencies due to neglecting the anharmonicity, incomplete incorporation of the electron correlation and the use of finite basis sets in the theoretical treatment. Therefore, the spectra were adjusted by a scale factor of 0.967.[8] Theoretical Raman intensities (I_i) were additionally obtained from the calculated Raman scattering activities (S_i) taken into account experimental temperatures, based on the expression:

$$I_i = \frac{10^{-12}(v_0 - v_i)^4 S_i}{v_i B_i}, \tag{1}$$

where B_i is a temperature factor, which accounts for the intensity contribution of excited vibrational states and is represented by the Boltzmann distribution:

$$B_i = 1 - \exp\left[\frac{(-hv_i c)}{(kT)}\right], \tag{2}$$

where h, k, c, and T are Planck and Boltzmann constants, a speed of light and temperature in Kelvin, respectively; v_0 is the frequency of the laser excitation line ($v_0 = 1/\lambda_0$ where λ_0 is the laser wavelength), v_i is the frequency of normal mode.[9,10]

COMPREHENSIVE RAMAN SPECTRA ANALYSIS

The bands centered below 1000 cm^{-1} (809, 834, 956 cm^{-1}) are linked to the CH ring stretching, CC ring deformation, CC vibration within trimethyl moieties, as well as methyl deformation modes. Five bands located around 1002, 1032, 1117, 1185, 1203 cm^{-1} result from the in-plane CC ring deformation (aryl and para-xylene), CH_3 and CH_2 deformation as well as in-plane CH ring bending modes. Low intense bands at 1283, 1339, 1378, 1445 cm^{-1} originate from the CC ring stretching, in-plane CH ring bending, or CH_3 and CH_2 deformation. In turn, well-visible bands at 1589 and 1616 cm^{-1} correspond to the vibrations involving the carbon and hydrogen atoms of the ring of Ben-IBU. Such bands are overlapping with bands originated from the vibration of the para-xylene ring. Finally, the low-intensity band at 1735 cm^{-1} is associated with the vibration of the carboxylic C=O group, while the bands between 2800 and 3100 cm^{-1} with the CH ring stretching at the aryl and para-xylene rings as well as symmetric and asymmetric stretching vibration of $\nu(CH_2)$ and $\nu(CH_3)$ groups.

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