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Near-field Raman dichroism of azo-polymers exposed to nanoscale dc electrical and optical poling

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Abstract

© 2016 The Royal Society of Chemistry.Azobenzene-functionalized polymer films are functional materials, where the (planar vs. homeotropic) orientation of azo-dyes can be used for storing data. In order to characterize the nanoscale 3D orientation of the pigments in sub-10 nm thick polymer films we use two complementary techniques: polarization-controlled tip-enhanced Raman scattering (TERS) microscopy and contact scanning capacity microscopy. We demonstrate that the homeotropic and planar orientations of the azo-dyes are produced by applying a local dc electrical field and a resonant longitudinal optical near-field, respectively. For a non-destructive probe of the azo-dye orientation we apply a non-resonant optical near-field and compare the intensities of the Raman-active vibrational modes. We show that near-field Raman dichroism, a characteristic similar to the absorption dichroism used in far-field optics, can be a quantitative indicator of the 3D molecular orientation of the azo-dye at the nanoscale. This study directly benefits the further development of photochromic near-field optical memory that can lead to ultrahigh density information storage.

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