Low-frequency vibrations due to biomolecular recognition of duplex DNA enhanced by solvent

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The bis-benzimidazole dye Hoechst 33258 binds to A:T-rich regions in the minor groove of duplex DNA. Low-frequency oscillations of such recognition sites, when several phosphodiester residues move coherently, were not observed until now in aqueous solutions. They are reported here as depending on solvent. Following optical excitation of the ligand, we monitor its entire fluorescence band with 80 fs time resolution using broadband fluorescence upconversion and, independently, broadband stimulated emission. Weak oscillations of the dynamic Stokes shift reflect supramolecular vibrational modes, as determined by molecular dynamics simulations. Oscillations are stronger in (aqueous) ethylene glycol compared to water. The THz dielectric loss band of water offers frictional forces which dampen out coherent oscillations of the biopolymer in that frequency range. If it is reduced by a cosolvent, low-frequency vibrational spectroscopy of DNA becomes possible even in aqueous solutions.