Supporting Information

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SI Text

Absorbance spectra of the 10 mM solutions of 2′-deoxyadenosine monophosphate (A), 2′-deoxyguanosine monophosphate (G), 2′-deoxy-5-methylcytidine (mC), and uridine monophosphate (U) in 50 mM D_2O phosphate buffer are shown in Fig. S1. The spectra were recorded with a UV-visible spectrometer (Lambda 750; PerkinElmer) with a path length of 100 μm. The red-shifted absorbance spectra of mC and G allow us to construct oligonucleotides with selective excitation of mC or G at 295 nm (arrow).

Vibrational spectra were simulated for all involved nucleobases and their corresponding radical states with density functional methods (Fig. S2). The Becke3Lyp 6-311G** functional with the solvent model PCM was used to calculate the harmonic vibrational frequencies. Gaussian 03 software (1) was used for calculations. For simplicity, all calculations were done for the 1-methyl–substituted nucleobases, where all exchangeable hydrogen atoms in the structure were substituted with deuterium. Each vibrational frequency analysis was preceded by a geometry optimization. The frequencies were scaled with a factor of 0.9669 (2). The experimental absorbance spectra (Fig. S2, first row of upper and lower graphs) are very well reproduced by the calculation with this method apart from a spectral shift (second row). For all bases, the cation (third row), and anion (fourth row) spectra were calculated. The marker bands used to characterize the charge-transfer states are colored.

1. Frisch MJ, et al. (2004) *Gaussian 03*. Revision D.01 (Gaussian, Inc., Wallingford CT).

2. Irikura KK, Johnson RD, 3rd, Kacker RN (2005) Uncertainties in scaling factors for ab initio vibrational frequencies. *J Phys Chem A* 109(37):8430–8437.

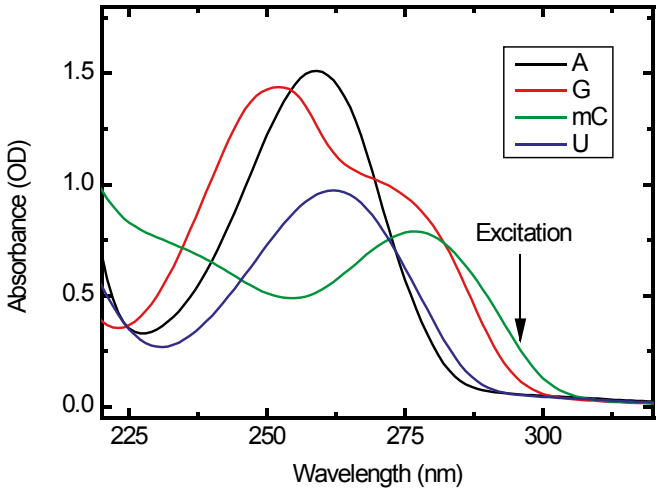

Fig. S1. Absorbance spectra of A, G, mC, and U.

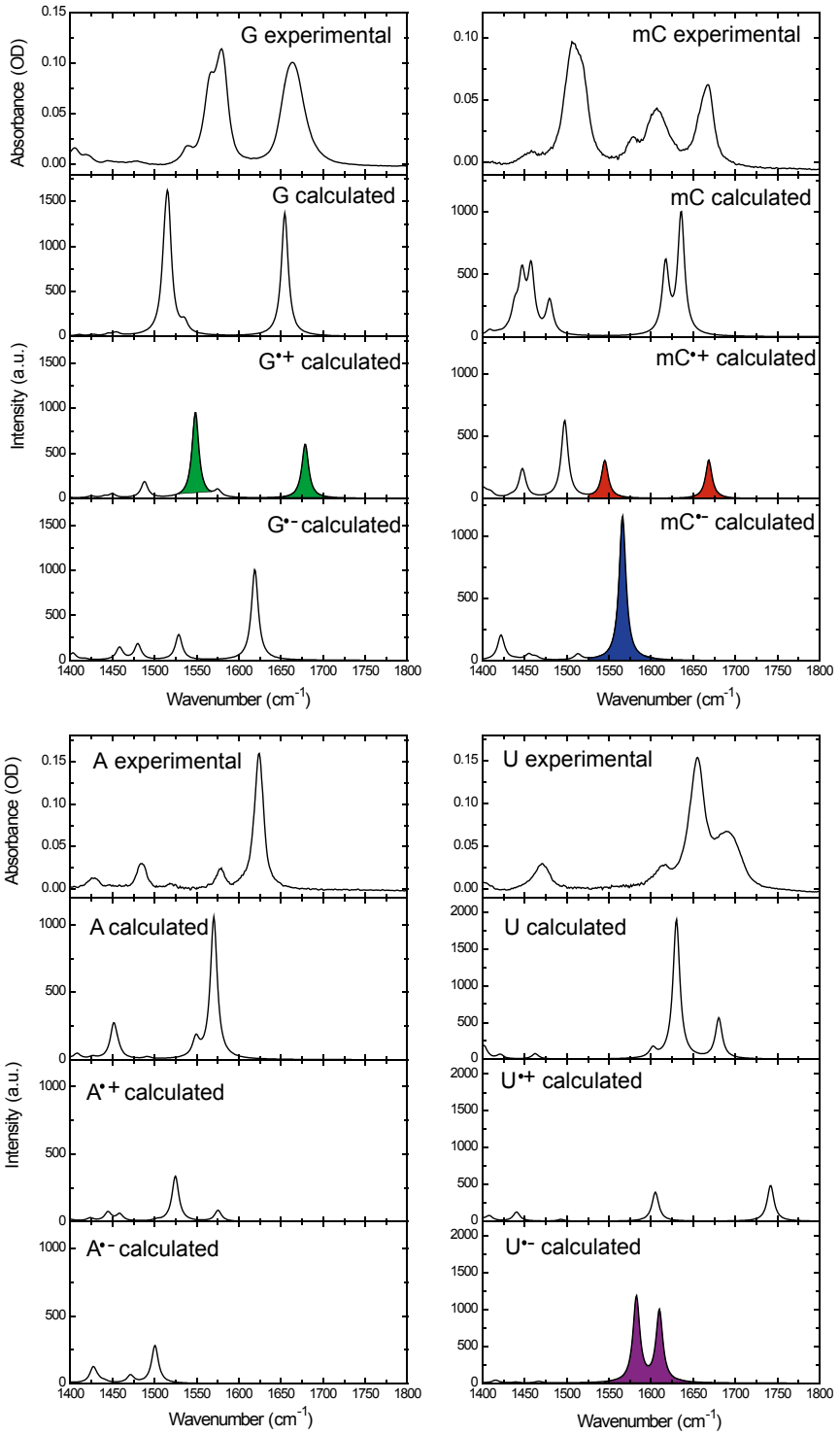

Fig. S2. Theoretical absorbance spectra.