Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting Information for

A Study of the pH Dependence of Electronically Excited Guanosine Compounds by Picosecond Time-resolved Infrared Spectroscopy

David A. McGovern,[a] Gerard W. Doorley,[a] Aine M. Whelan,[a] Anthony W. Parker,[b] Michael Towrie,[b] John M. Kelly*[a] and Susan J. Quinn*[a]

[a] *School of Chemistry and Centre for Chemical Synthesis and Chemical Biology, Trinity College, Dublin 2, Ireland.* E-mail: jmkelly@tcd.ie, quinnsu@tcd.ie
[b] *Central Laser Facility, Facility, Science & Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX, UK.*

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Fig. 2 ps-TRIR kinetics over the range 35 – 1500 ps of 10 mM 5'-H_2GMP in unbuffered D_2O recorded at the carbonyl and ring bleach and associated transient positions 1690 cm^{-1} (◆), 1635 cm^{-1} (■), 1611 cm^{-1} (●), 1584 cm^{-1} (▼) and 1517 cm^{-1} (▲).

Fig. 3: ps-TRIR spectra of 10 mM 5`-Na_2GMP in 50 mM sodium hydrogen phosphate in D_2O pH 8.5. recorded at delays of -25 ps, 2, 3, 4, 6.5, 10, 15, 35, 50, 100, 500 and 1000 ps after excitation at 267 nm. FTIR in Blue.

Fig 4: Kinetic traces of 10 mM 5`-Na_2GMP in 50 mM sodium hydrogen phosphate in D_2O at pH 8.5 recorded at the carbonyl and ring bleach and associated transient positions 1678 cm^{-1}(▲), 1627 cm^{-1}(▼),1581cm^{-1}(■) and 1544 cm^{-1} (●).

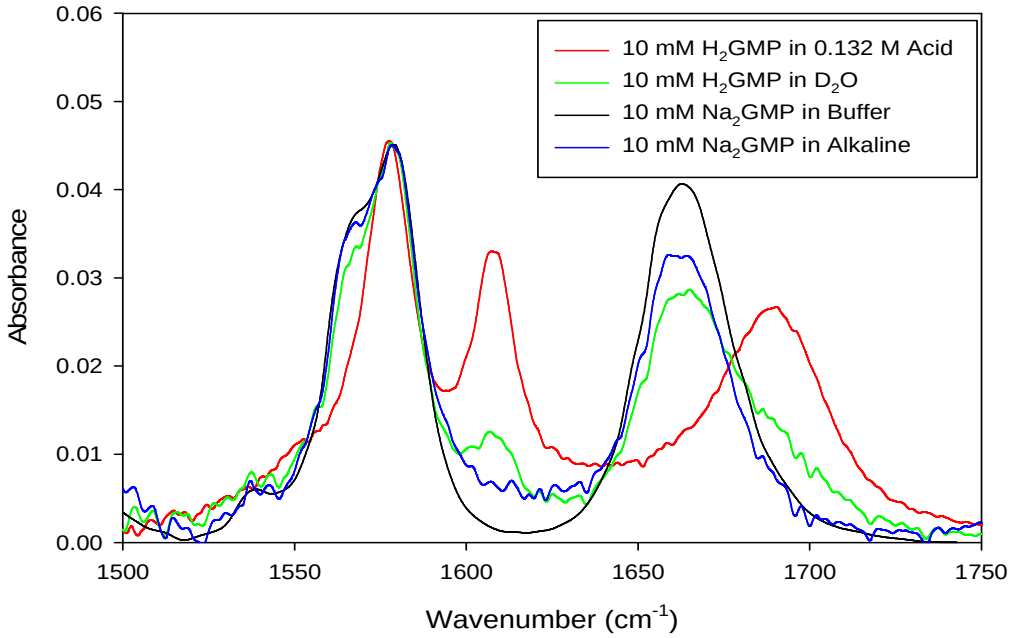
Method for ps-TRIR measurements:

Measurements were performed at the PIRATE ultrafast infrared absorption facility at the Rutherford Appleton Laboratory, Chilton which has been described in detail elsewhere.[1] Briefly, the sample was excited with 267 nm, 200 fs pulses with 2 μJ of energy at 0.5 kHz repetition rate, generated from the third harmonic of part of the output from a 1 kHz, 800 nm, 200 fs, 1 mJ regenerative amplifier (Spectra Physics Tsunami/Spitfire) and probed with 150 cm^{-1} FWHM broadband infrared pulses generated by difference frequency mixing the signal and idler outputs of a BBO (β-BaB_2O_4) optical parametric amplifier, pumped with some residual 800 nm, in $AgGaS_2$ at 1 kHz. The spot size was 200 μm and 150 μm diameter for the pump and the probe beam, respectively. The difference signal pump-on minus pump-off was normalized on a shot-by-shot basis and typically accumulated for four successive rounds of 30 s data integration for a single time delay. The infrared beams were dispersed by 150 l/mm, 4000 nm blaze, gold grating monochromators and imaged onto 64 element MCT array. The data were collected in a number of 150 cm^{-1} spectral windows centred at approximately 1625 and 1565 cm^{-1} using the delay line for optical delays between 2 ps and 1.5 ns, normally at 2, 3, 4, 5, 6.5, 8, 10, 12.5, 15, 20, 35, 50, 100, 150, 200, 500, 1000 and 1500 ps. The difference signal was calibrated using water lines present in the probe spectrum, and the spectral windows were interleaved after scaling using overlapping transients recorded at the same delay time. The sample was raster scanned in *x*- and *y*- directions at an approximate rate of 100 mm/ms.

1. M. Towrie, D. C. Grills, J. Dyer, J. A. Weinstein, P. Matousek, R. Barton, P. D. Bailey, N. Subramaniam, W. M. Kwok, C. S. Ma, D. Phillips, A. W. Parker and M. W. George, *Applied Spectroscopy*, 2003, **57**, 367.

Sample Preparation:

All measurements were preformed in a Harrick demountable liquid cell in which the liquid sample is placed between two 25 mm CaF_2 plates separated by 12 μm Teflon spacers in the case of low concentration experiments and without the use of Teflon spacers in high concentration experiments. Samples were prepared by weighing out an amount of the nucleotide base or polynucleotide into an eppendorf followed by the addition of a known amount of D_2O or buffer solution. Concentrations were determined by UV/vis spectroscopy. The mixtures were homogenised by vortexing the sample for approximately 2 minutes but in some cases longer agitation was required for complete dissolution. 50 -70 μl aliquots of each sample were placed centrally onto the CaF_2 plates for analysis by ps-TRIR, UV/vis and FTIR (Fig. 1) spectroscopies.



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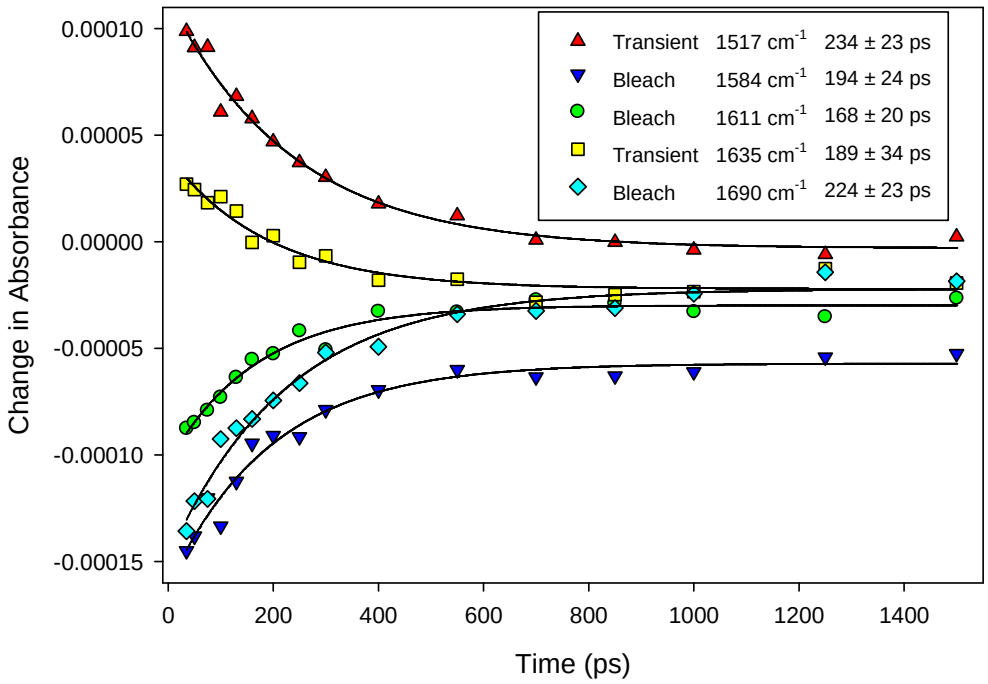

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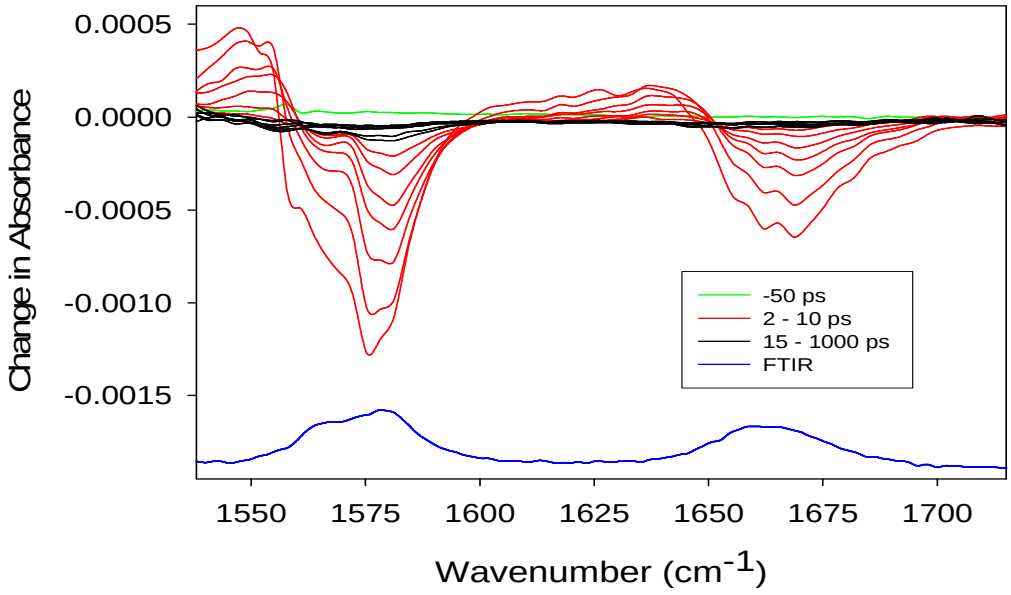

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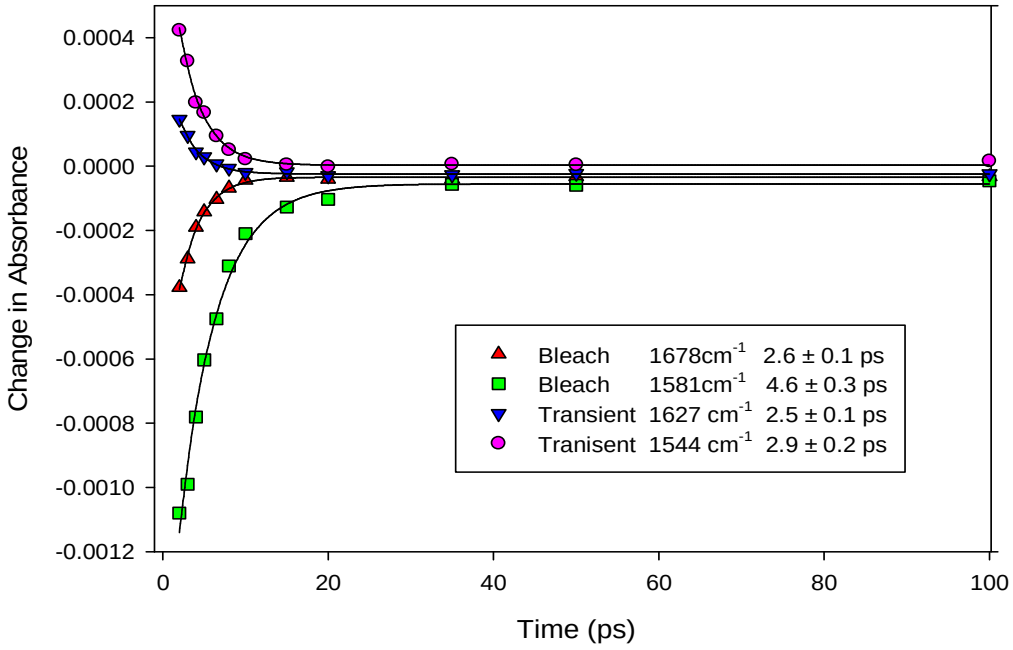

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