Contact Ion-Pairing of LiOCN Under Multiple Solvent Conditions Enabled by Interfacing Microfluidics with 2D IR Spectroscopy

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We present the interfacing of IR compatible microfluidics with 2D IR spectroscopy to examine the solvatochromic pseudo-halide anion, cyanate (OCN⁻) in cosolvent environments. 2D IR spectra are collected laterally across the device to capture the vibrational dynamics of OCN⁻ in methanol/dimethyl formamide cosolvent environments.

Coupling high repetition rate 2D IR spectroscopy with the use of thin polydimethylsiloxane (PDMS) IR transparent microfluidic devices as a sample cell [1] allows for the creation of reproducible heterogeneous environments across sample cells. The fast gradient generators used in this work are capable of mixing on microsecond time scales and produce stable, tunable gradients on millisecond timescales. These devices allow for a reduction in the number of samples that must be created as a single device can be sampled in multiple locations giving different mixing ratios of the outer and inner fluids. It is also possible to take advantage of the precision control in mixing to observe reaction kinetics at different points along the channel.

Here we are utilizing IR transparent microfluidic devices (Fig. 1a) to examine the pseudohalide anion, cyanate, in multiple cosolvent conditions of methanol and dimethylformamide (DMF). The cosolvent conditions produced in the device are mapped in Figs. 1b and c. We are able to sample OCN⁻ in these cosolvent conditions using 2D IR spectroscopy by collecting spectra at several points laterally in the microfluidic channel. Thus, we can probe the dynamics associated with KOCN in mixed solvent environments and the interchange of the cyanate ion with different cations including lithium. The microfluidic devices employed here can be interfaced with any 2D IR spectrometer. However, in this work we employ a 100 kHz 2D IR spectrometer built based on a mid-IR OPCPA laser source developed in our lab [2]. This laser technology will also be discussed given the impact it will have on nonlinear vibrational imaging technology.



Fig.1 (a) Bright-field image of the 500 μ m wide IR transparent microfluidic device. IR chemical map of the channel integrated for the peak associated with (b) 30 mM KOCN in methanol and (c) 30 mM KOCN in DMF. (d) Experimental 2D IR spectra collected at points across the microfluidic channel in 40 μ m steps.

[1] M. V. Barich, *et al.*, Anal. Chem., **85**, 10000–10003 (2013)

[2] B. M. Luther, et al., Opt. Express 24, 4117-4127 (2016)