

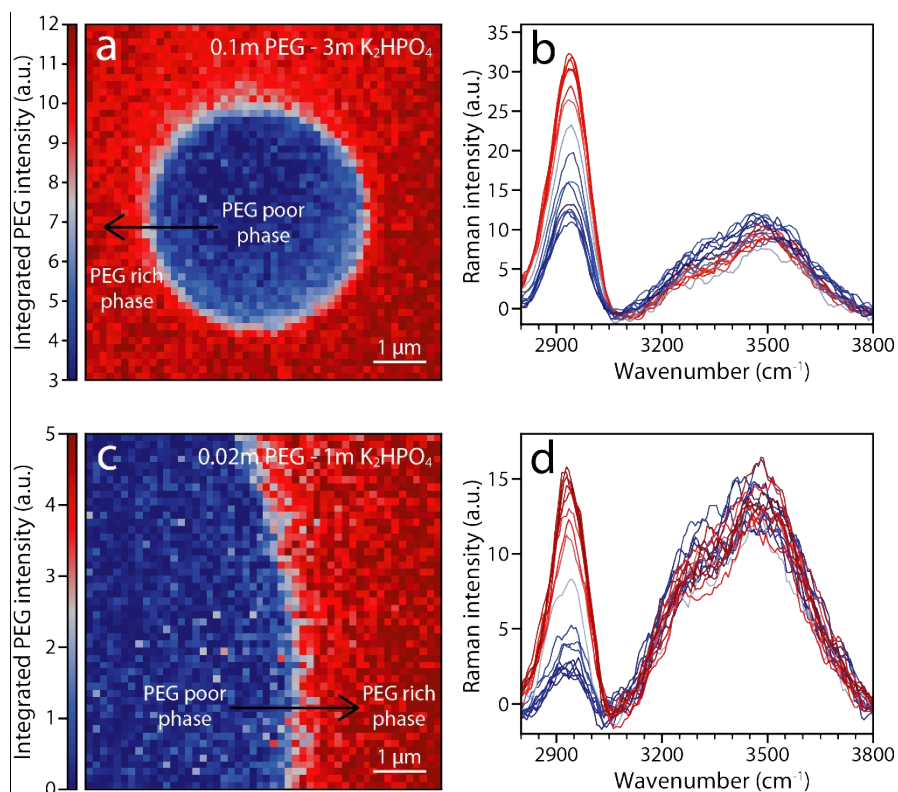
## Supporting Information

Sophie Bonnassieux,<sup>1</sup> Raj Pandya,<sup>2,3,4</sup> Dhyllan Adan Skiba,<sup>5</sup> Damien Degoulange,<sup>6,7</sup> Dorothée

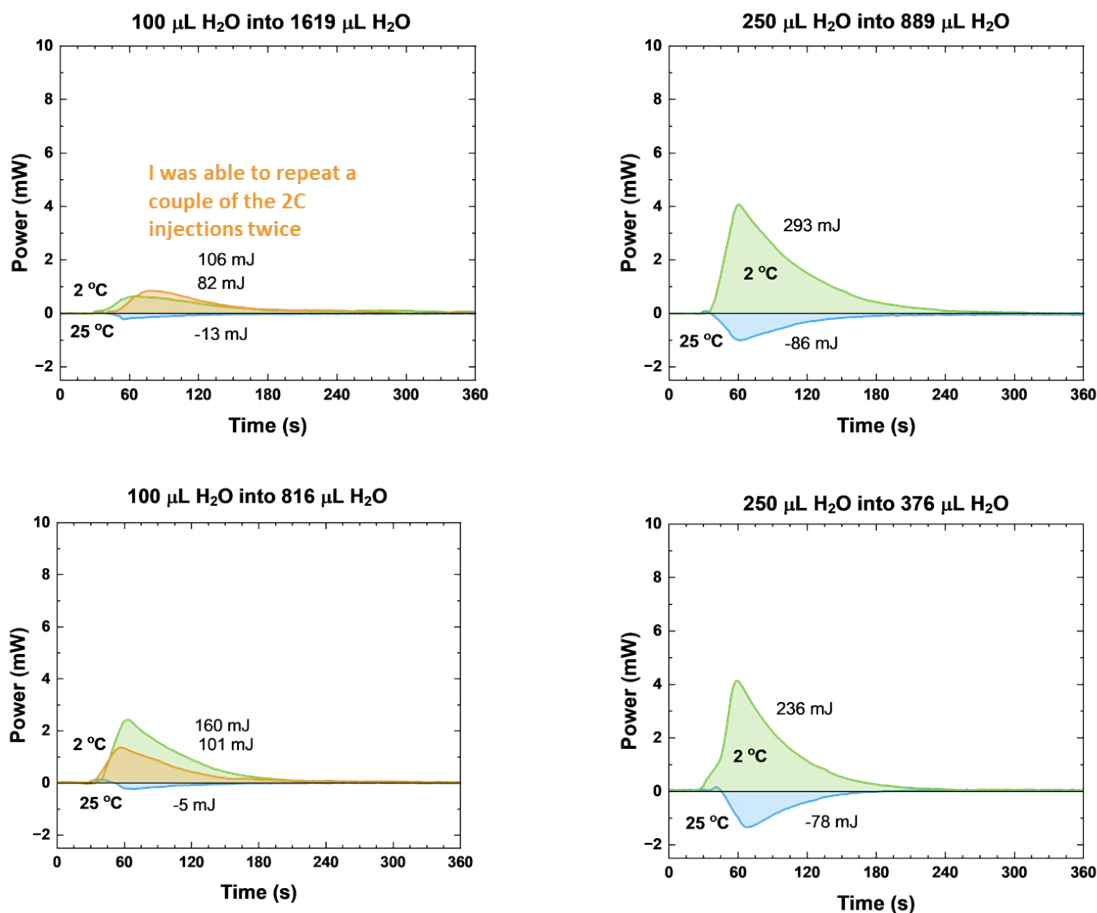
Petit<sup>8</sup>, Peter Seem<sup>8</sup>, Russel P. Cowburn<sup>3,8</sup>, Betar Gallant,<sup>5</sup> Alexis Grimaud<sup>1</sup>

1. Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467, USA
2. Laboratoire Kastler Brossel, ENS-Université PSL, CNRS, Sorbonne Université, Collège de France, 24 rue Lhomond, 75005 Paris, France
3. Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK
4. Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK
5. Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
6. Chimie du Solide et de l'Énergie, Collège de France, UMR 8260, 75231 Paris Cedex 05
7. Sorbonne Université, 75006 Paris, France
8. Durham Magneto Optics Ltd, Church Road, Toft, Cambridge CB23 2RF, UK

**\*Corresponding author:** Alexis Grimaud ([alexis.grimaud@bc.edu](mailto:alexis.grimaud@bc.edu))



**Figure S1. High resolution Raman imaging across the interface of the 0.1mPEG4000/3mK<sub>2</sub>HPO<sub>4</sub> and 0.02mPEG20000/1mK<sub>2</sub>HPO<sub>4</sub> systems.** Raman imaging of the (a) 0.1mPEG4000/3mK<sub>2</sub>HPO<sub>4</sub> and (c) 0.02mPEG20000/1mK<sub>2</sub>HPO<sub>4</sub> system generated by integration of PEG vibrations. Raman spectra collected across the interface for PEG and OH vibrations of the (b) 0.1mPEG4000/3mK<sub>2</sub>HPO<sub>4</sub> and (d) 0.02mPEG20000/1mK<sub>2</sub>HPO<sub>4</sub> system.



**Figure S2. Calorimetry measurements for water injected into water at different temperatures and different volumes.** Measurements with different volumes of water injected into water were carried out to probe the effect of a small temperature gradient existing in the injection syringe. The bottom of the syringe is in thermal equilibrium with the calorimeter, while the top might deviate in temperature by a very small amount. This deviation will be increased when increasing the volume of injectant. The results presented here show that the positive heat measured when mixing pure water with pure water (so perfectly miscible) is non-negligible and reproducible. Comparing the effect of the volume of injectant and the volume of water contained in the calorimeter, we conclude that the volume of injectant is responsible for the non-negligible heat measure upon mixing. This observation, with the heat being greater when injecting 250  $\mu\text{L}$  than 100  $\mu\text{L}$ , while being independent on the volume of water contained in the calorimeter, confirms that a small temperature gradient exists within the syringe. Water injected into water is thus not perfectly at the same temperature, which induces a non-negligible heat to be recorded.