

# Stabilization of Triplet Arylnitrenes in Nafion Polymer at Room Temperature

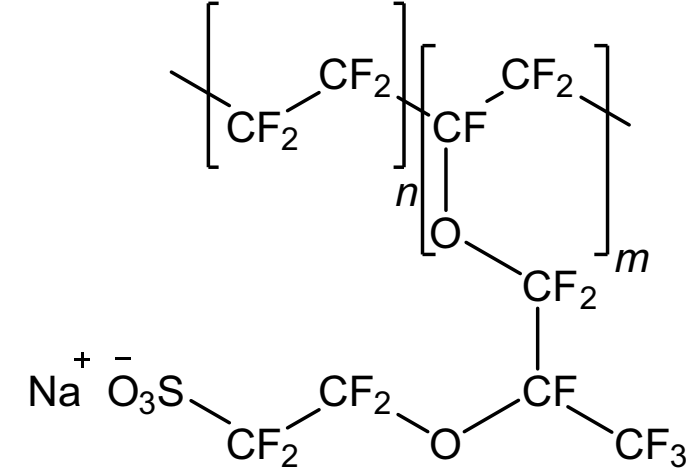
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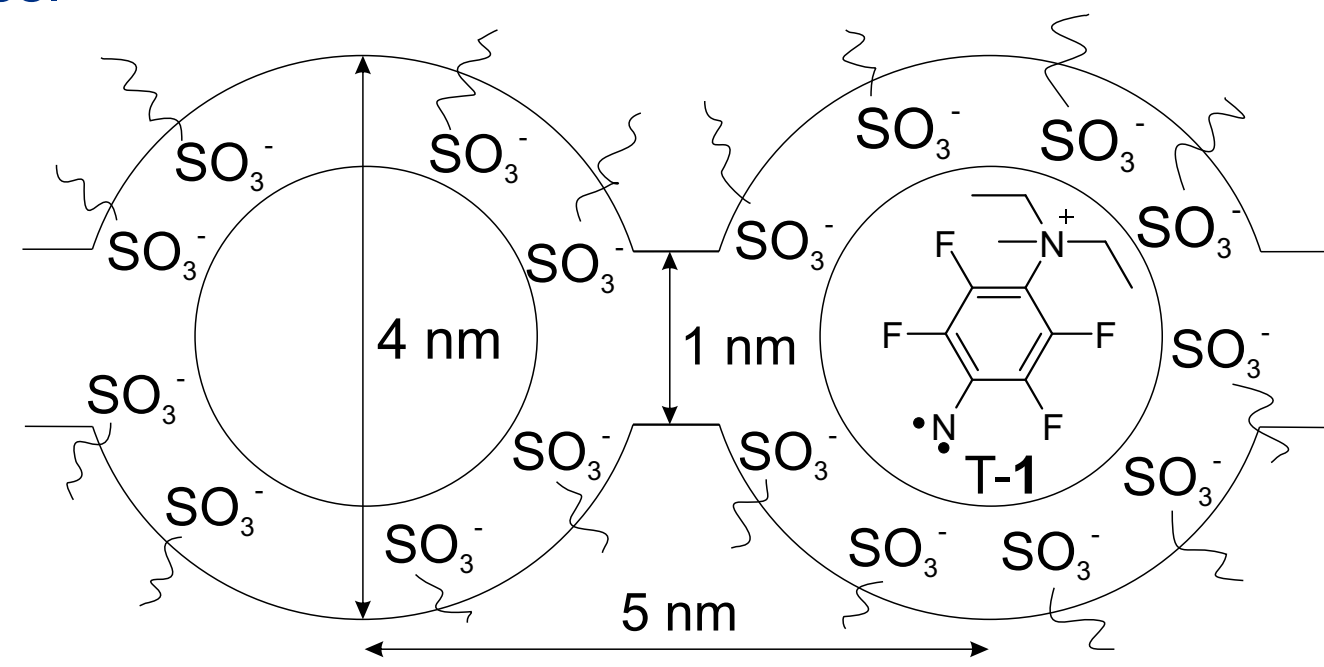
## Introduction

Organic magnets have properties (e.g. flexibility or transparency) that outcome those of traditional magnets. Nitrenes exhibit the strongest magnetic properties among all known organic polyradicals, which makes them great candidates as building blocks for organic magnets. However, nitrenes are very short lived species at room temperature and their study is usually limited to cryogenic temperatures (e.g. matrix isolation).

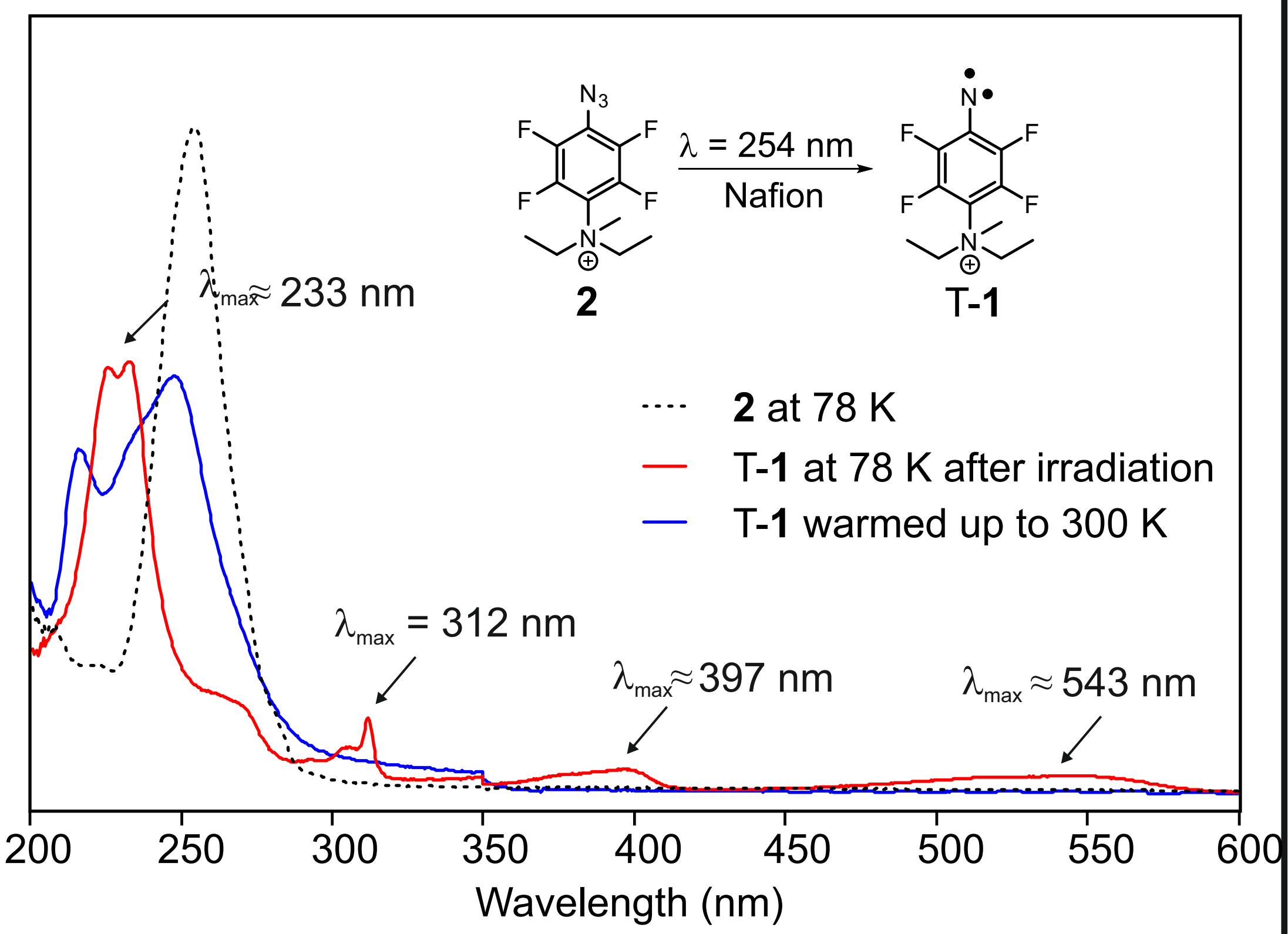
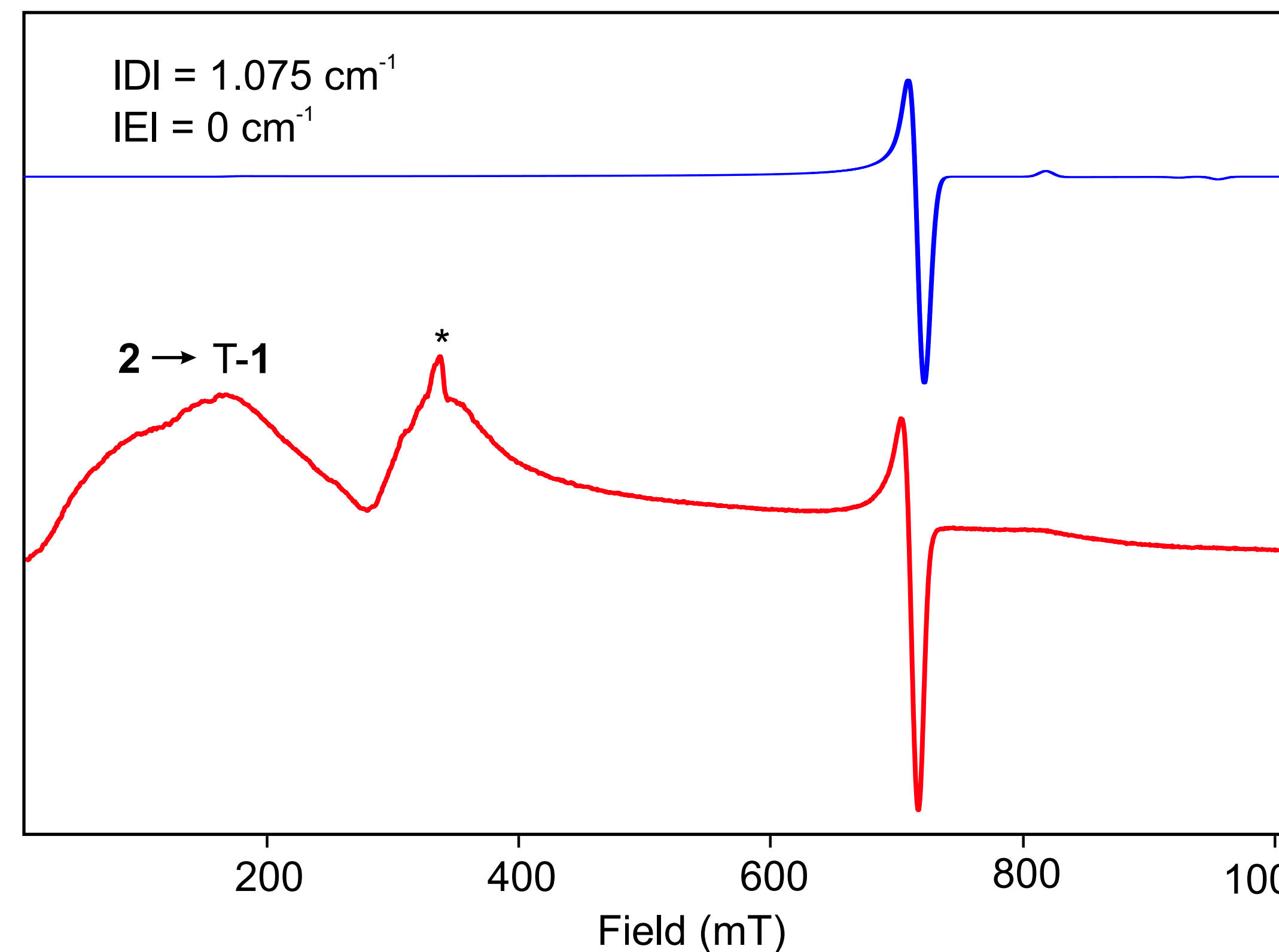
Nafion polymer was chosen as the confining media due to its perfluorinated backbone that avoids undesired reactions with the nitrene as insertions in C-H bonds.



The transparency of Nafion in the UV-vis region allows the characterization of the desired nitrenes using this technique. The acidic protons are exchanged with sodium so that the azide can be embedded by cationic exchange, avoiding the diffusion of the molecules inside of Nafion due to electrostatic forces.



## Nitrene T-1 observed at low temperatures

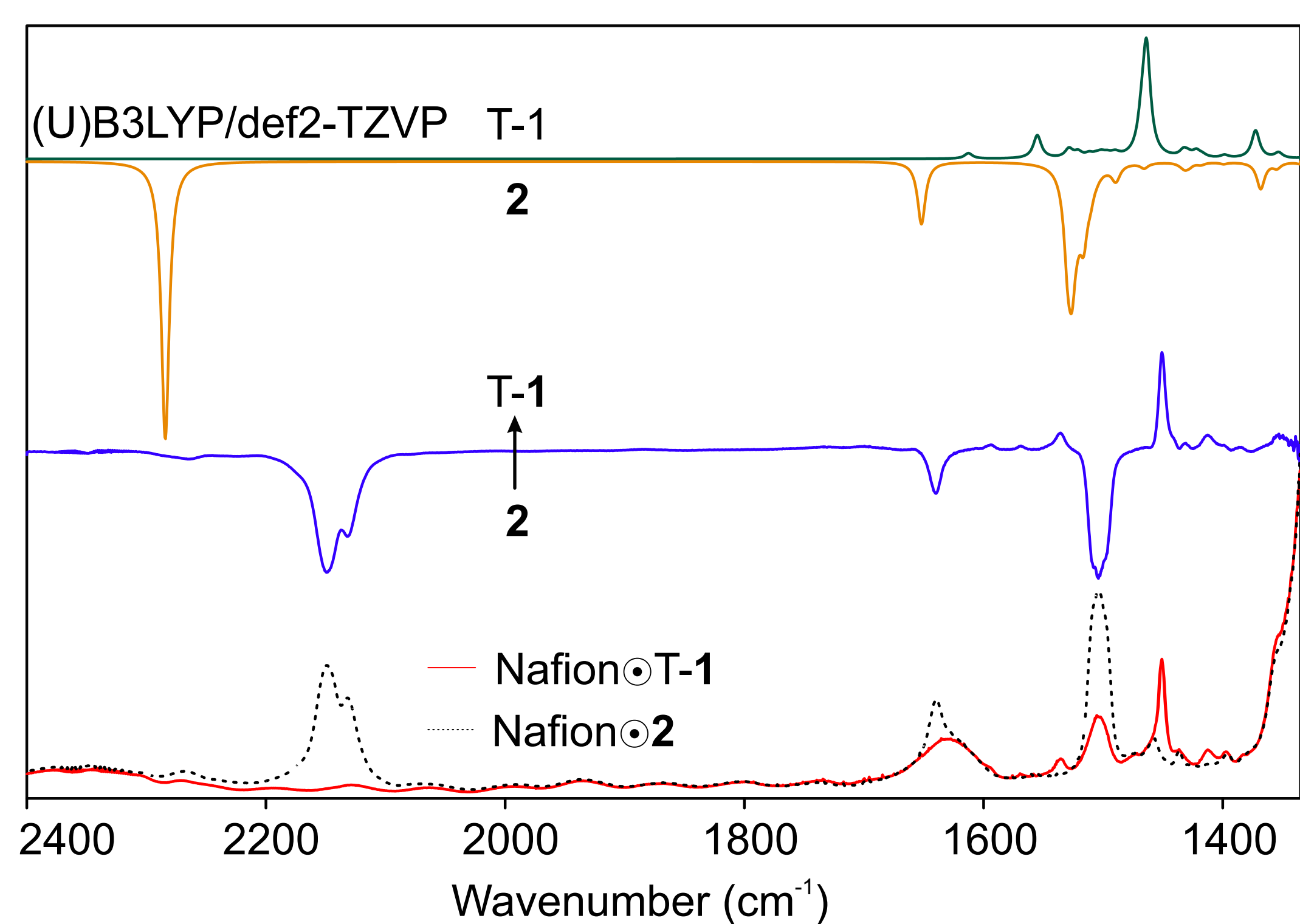


- > Irradiation of **2** with  $\lambda = 254$  nm light produces T-1 inside of Nafion at 5 K as shown by the very characteristic triplet nitrene EPR spectrum obtained.
- > Annealing of the sample shows that the sample maintains stable (applying the Curie correction) up to nearly 200 K.

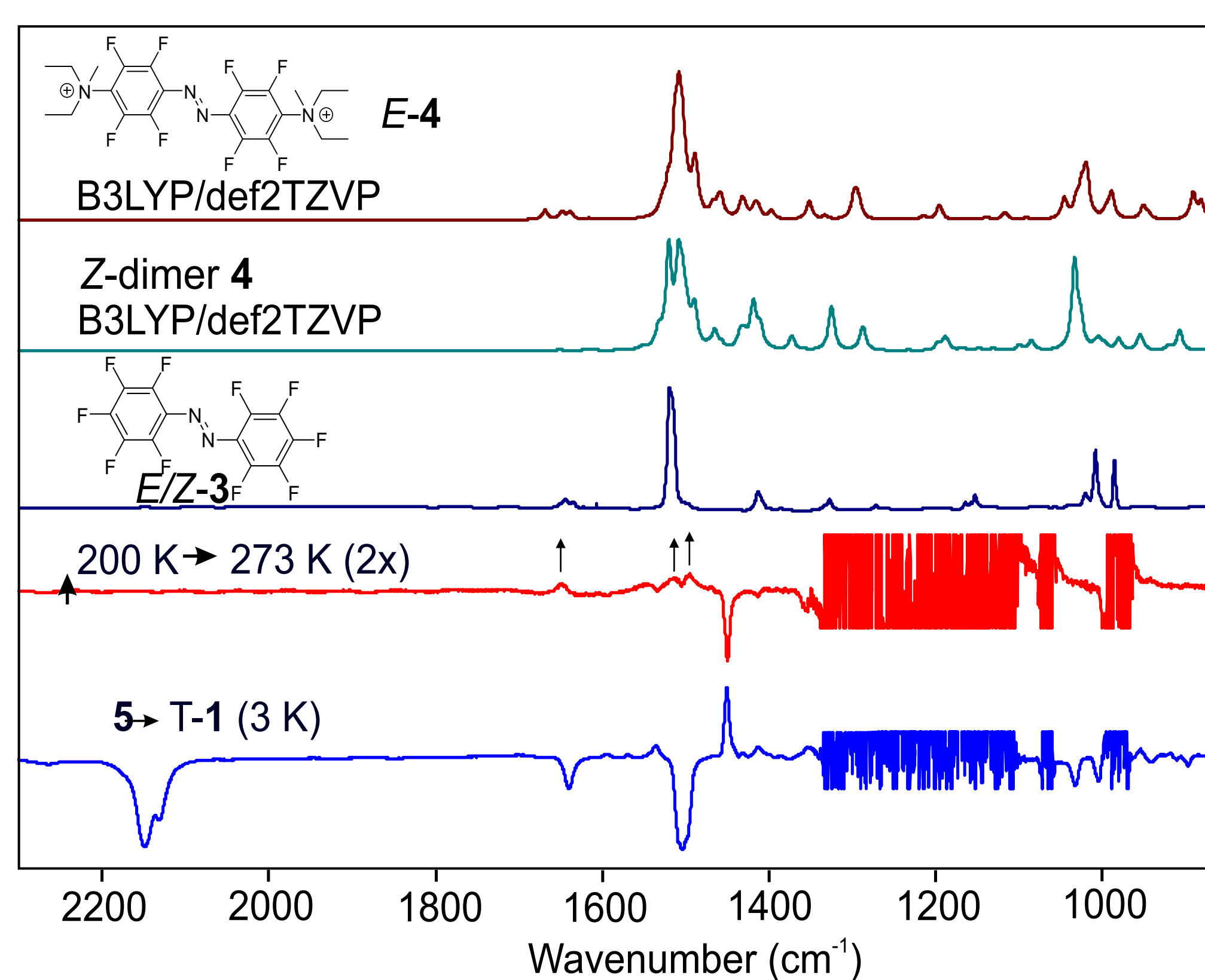
- > UV-vis experiments also show that T-1 is produced at 78 K and all the bands detected can be assigned solely to T-1 based on literature.
- > Annealing experiments show a very slight decrease of intensity at around 190 K.

> N. P. Gritsan, Z. D. Zhu, C. M. Hadad, M. S. Platz; *J. Am. Chem. Soc.*, 1999, 121, 1202-1207.

## IR spectroscopy

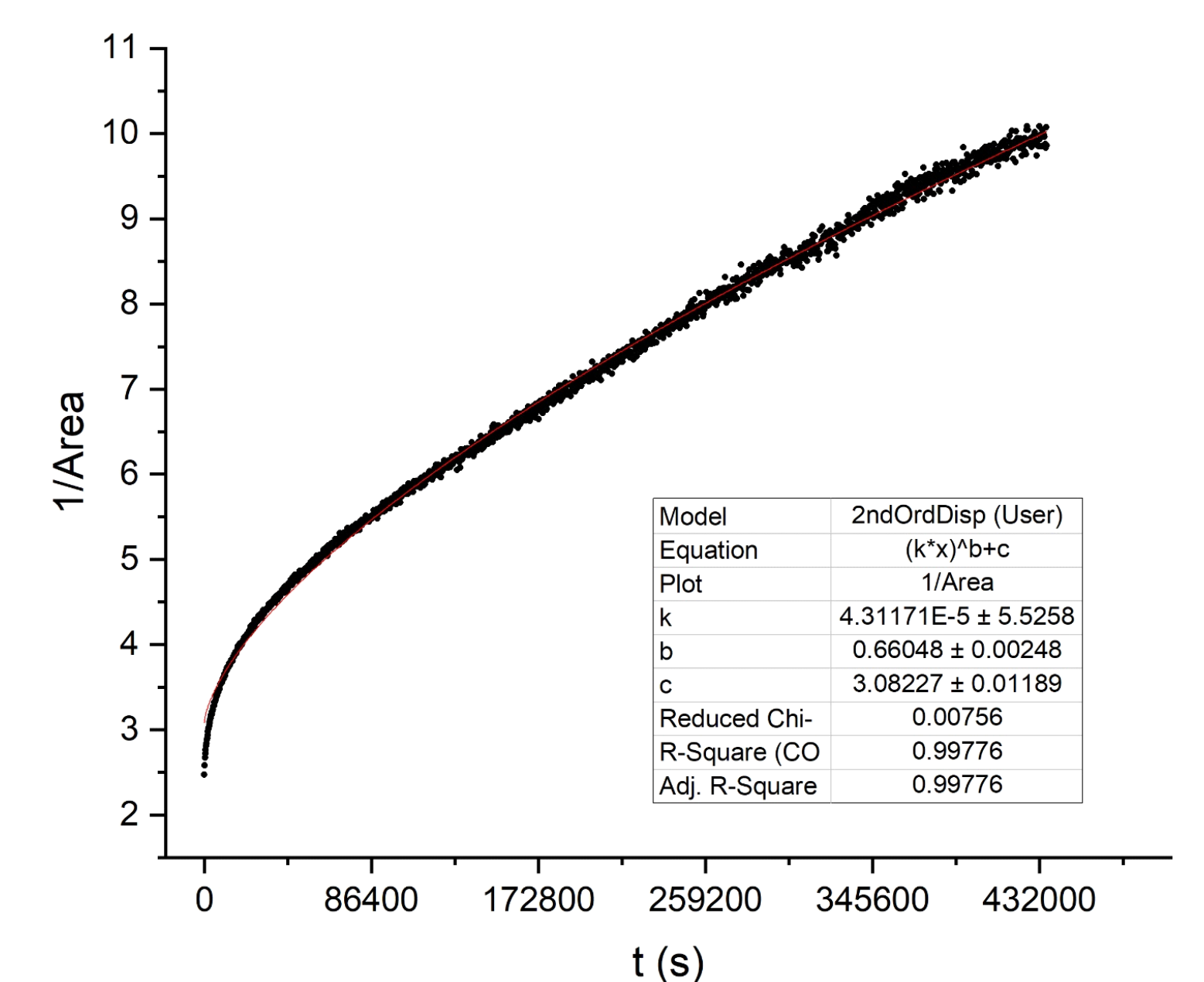


- > Despite the Nafion bands, nitrene T-1 could also be characterized by IR spectroscopy in good agreement with calculations.
- > IR spectroscopy also confirms that T-1 is produced quantitatively from **2** and insertion products are not observed.



- > The bands of the product formed upon annealing show a good agreement with those of dimer **4**.

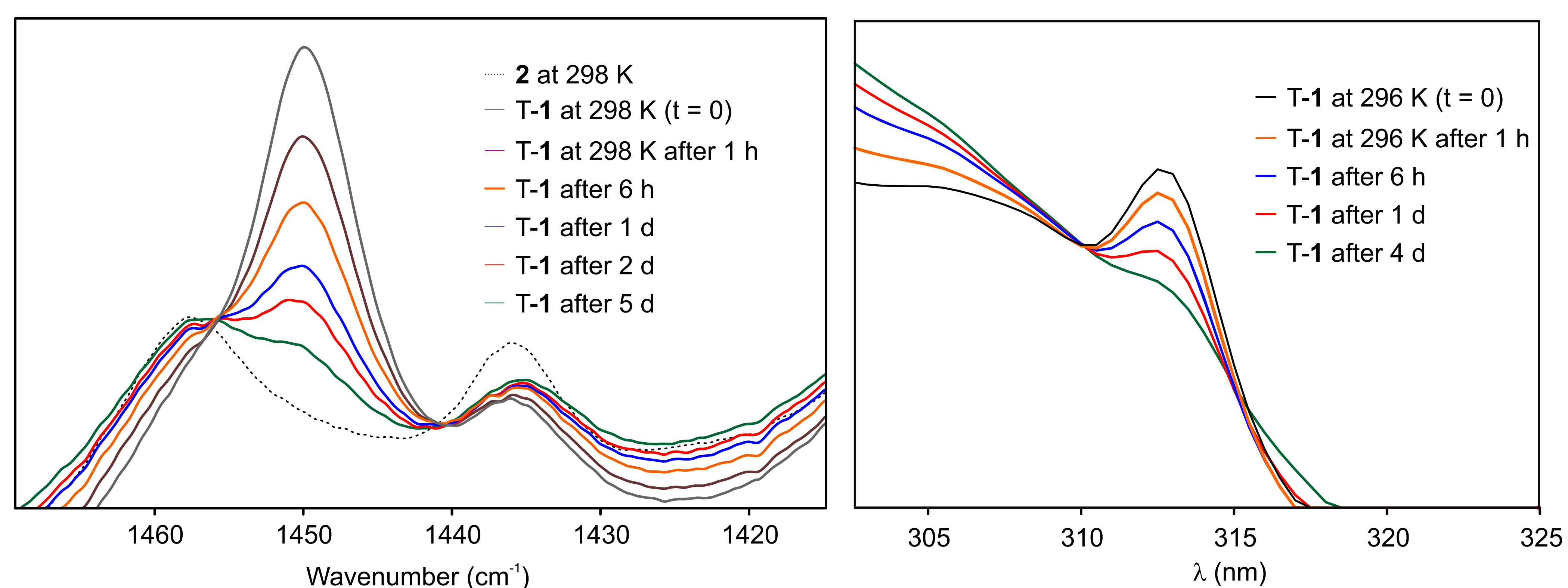
## Kinetic experiments



Decay of T-1 at 298 K followed by IR spectroscopy based on its 1450 cm<sup>-1</sup> feature.

- > T-1 decays linearly against the inverse concentration showing second order kinetics. The initial part can be matched through the dispersive kinetics approach.

## Decay at room temperature



- > The decay of T-1 was followed by its characteristic feature by both IR and UV-vis spectroscopy.
- > T-1 can still be clearly detectable after several days.

## Conclusions

- > Nafion was proven to be an adequate host for aryl nitrenes and no reaction between them was detected.
- > T-1 was observed to be stable up to 190-200 K.
- > Nitrenes could be characterized and observed at room temperature by different techniques.
- > The lifetime of aryl nitrenes at room temperature was increased from ns in solution to days in Nafion polymer.
- > Despite the electrostatic interaction with Nafion, nitrene molecules slowly diffuse affording dimer.
- > Further improvements could lead to increase stability.
- > The increase of the stability of triplet aryl nitrenes show that their use as organic magnets could be achieved.