Stabilization of Triplet Nitrenes in Nafion Polymer at Room Temperature

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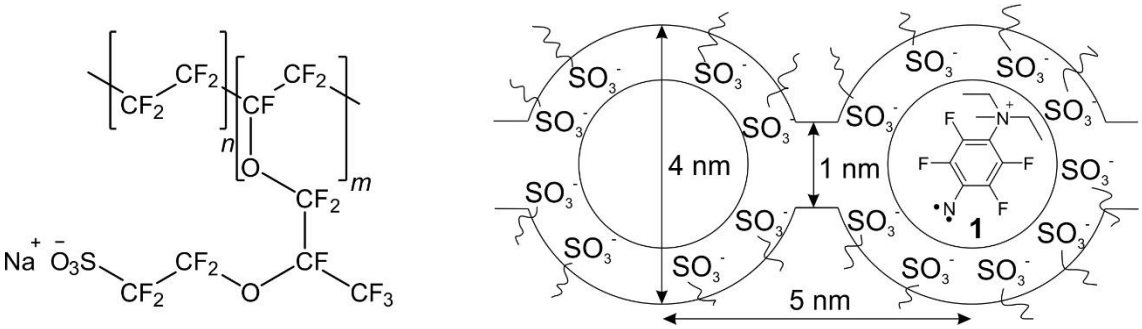
Organic magnets possess properties (e.g. flexibility or transparency) that outcome those of conventional magnets. Triplet nitrenes exhibit strong magnetic properties and are of considerable interest as models for molecular magnets.[1] However, nitrenes are typically very short lived under ambient conditions so are usually trapped in low-temperature matrices.[2,3] Hence, the aim of this work is to generate persistent nitrenes at ambient conditions.



Nafion polymer was chosen as confinement media as its perfluorinated backbone would prevent undesired H-abstraction by nitrenes. Cationic ammonium groups were inserted into nitrene precursors such as 2,3,5,6-tetrafluorophenyl azide to facilitate the attachment to Nafion. Irradiation with UV light of cationic azides embedded into Nafion^{-}Na^{+} affords the corresponding nitrene in high yields. Typical byproducts such as azirines or ketenimines were not detected during photolysis or annealing. The nitrene stability was monitored by UV–vis, IR and EPR spectroscopy at different temperatures. Nitrene **1** is fully persistent in Nafion up to 200 K and survived for several days at RT. The decay of nitrene **1** was observed to follow second-order kinetics, suggesting that dimerization is the main deactivation channel in correspondence with the spectroscopic data. Persistent nitrenes at room temperature could be great candidates as building blocks for organic magnets.

[1] Lahti, P.M. *Magnetic Properties of Organic Materials*, Marcel Dekker, New York **1999**.

[2] Gritsan, N.P.; Zhu, Z; Hadad, C.M.; Platz, M.S. Laser Flash Photolysis and Computational Study of Singlet Phenylnitrene. *J. Am. Chem. Soc.* **1999**, *121*, 1202.

[3] Gritsam, N.P.; Gudmundsdottir, A.D.; Tigelaar, D.; Zhu, Z.; Karney, W.L. Hadad, C.M.; Platz, M.S.; A Laser Flash Photolysis and Quantum Chemical Study of the Fluorinated Derivatives of Singlet Phenylnitrene. *J. Am. Chem. Soc.* **2001**, *123*, 1951.