Supplementary Material (ESI) for Chemical Communications

Supporting information

for

First time-resolved EPR observation of Nafion photochemistry

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Instrumentation

TR-EPR measurements.

The experimental setup used for TR-EPR measurements comprises a conventional X-band EPR spectrometer (Bruker ER 200 D) equipped with a nitrogen flow cryostat for temperature control. For optical excitation, the third harmonic (λ = 355 nm) of a Nd/YAG pulsed solid-state laser (Brilliant Quantel) was used (5ns pulse width, 20 Hz repetition rate, and 5mJ energy per pulse). The EPR transient signals, generated by the laser pulses, were recorded without field modulation, with a preamplifier (bandwidth: 20 Hz - 6.5 MHz) and a digital oscilloscope (LeCroy LT344) that averages them.
A two-dimensional surface where the EPR signal is recorded vs. time and magnetic field B (2D TR-EPR spectrum) is obtained by sweeping B in a selected interval and collecting EPR transient signals at each field position. To correct the EPR data for the cavity response to the laser perturbation, an off-resonance signal is subtracted from the averaged transient signals recorded at all the field positions of the 2D TR-EPR surface.

UV-Vis measurements.

Electronic absorption spectra were recorded using a UV-Vis spectrophotometer (Perkin Elmer Lambda 2)

Materials and Sample preparation

Nafion 117 [1] was purchased from Ion Power, Inc. and purified as described in ref. [2]
For EPR experiments a solid film was prepared on the inner wall of an EPR tube as follows. Ca. 10 mm^2 of a purified Nafion 117 membrane were dissolved in 5 mL of N,N-dimethylformamide. The mixture was warmed up in an oil bath until the temperature of 350 K was reached. Then, approximately 0.3 mL of the final solution were transferred into the EPR quartz tube (3 mm inner diameter). The solvent was removed at a pressure of 10^{-3} Torr and the tube was sealed under vacuum (10^{-5} Torr).
Algoflon polytetrafluoroethylene (PTFE) was purchased from Solvay. The film for EPR experiments was prepared transferring the Algoflon PTFE dispersion in an EPR tube and pumping out the solvent. The tube was sealed under the vacuum of a diffusion pump.
Trifluoromethanesulfonic acid 98+% was purchased from Alfa Aesar.

References

[1] R. Borup, J. Meyer, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K. Kimijima, and N. Iwashita, *Chem. Rev.*, 2007, **107**, 3904.

[2] (a) V. Di Noto, R. Gliubizzi, E. Negro, M. Vittadello and G. Pace, *Electrochim. Acta*, 2007, **53**, 1618; (b) V. Di Noto, M. Piga, L. Piga, S. Polizzi and E. Negro, *J. Power Sources*, 2008, **178**, 561.