Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Towards understanding the color change of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide during gamma irradiation: an experimental and theoretical study

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ATR-IR and ^{1}H NMR spectra of [BMIm][NTf_2] before and after irradiation showed no discernible changes at a dose of 400 kGy (Fig. S1), indicating that less than 1% of [BMIm][NTf_2] underwent radiolysis.[1,2] The same phenomena were found for [BMPyrr][NTf_2] by comparison of corresponding ATR-IR and ^{1}H NMR spectra recorded before and after irradiation (Fig. S2). Consequently, it is concluded that both aromatic and aliphatic RTILs are relatively radiation resistant.

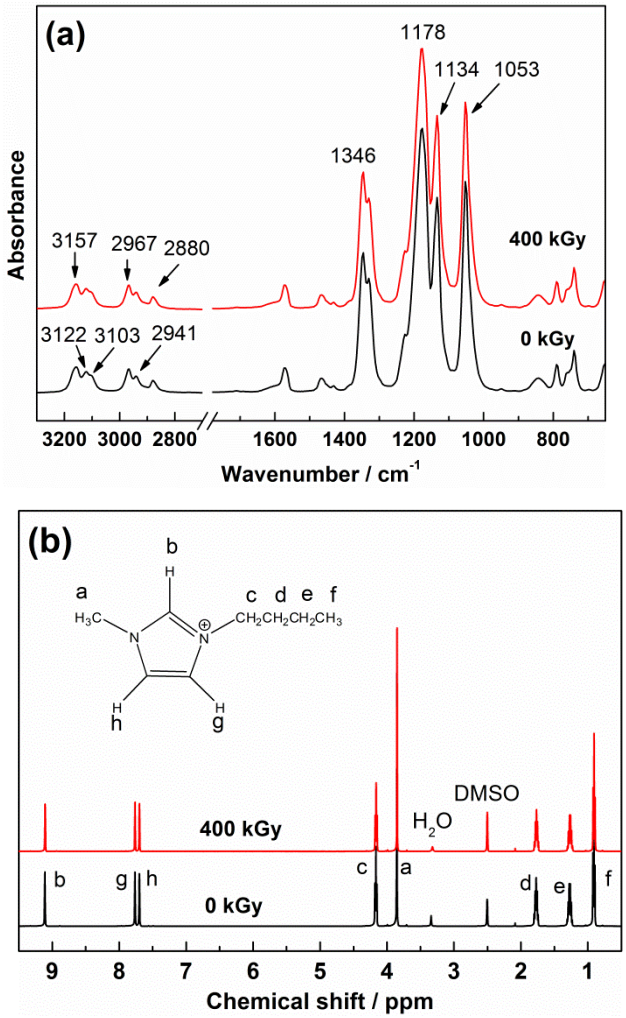

Fig. S1 (a) ATR-IR spectra and (b) ^{1}H NMR spectra of [BMIm][NTf_2] before and after γ-irradiation at 400 kGy under argon atmosphere.

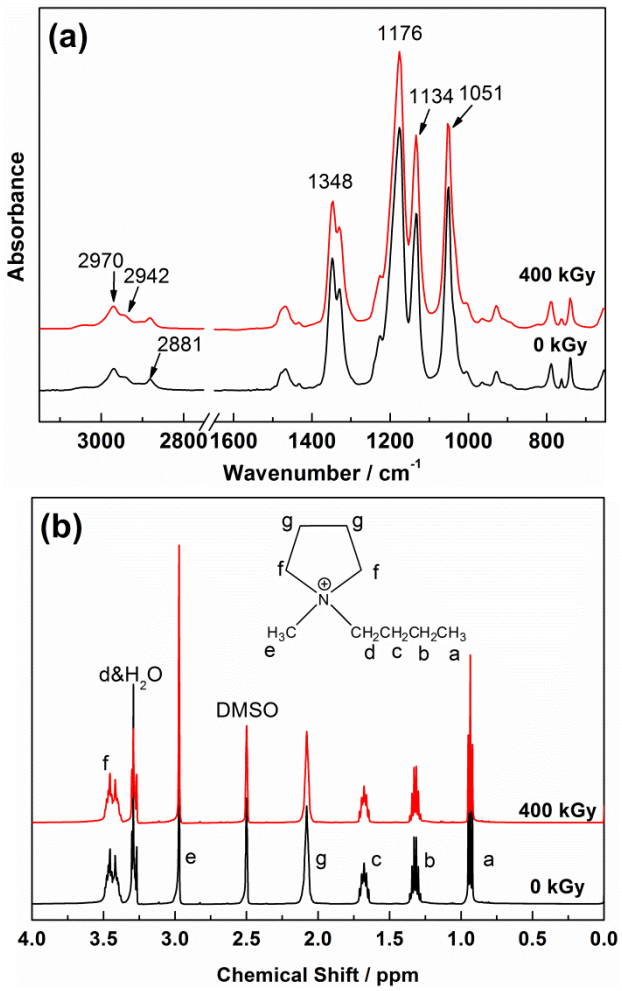

Fig. S2 (a) ATR-IR spectra and (b) ^{1}H NMR spectra of [BMPyrr][NTf_2] before and after γ-irradiation at 400 kGy under argon atmosphere.

Owing to oxidization of "colored products" by HNO_3,[3,4] during HNO_3 treatment the lightening of the irradiated [BMIm][NTf_2] was observed (Fig. S3a). The intensity of broad absorption band decreased markedly after HNO_3 oxidation, accompanied by the disappearance of absorption peak at 290 nm. Decoloration of irradiated [BMPyrr][NTf_2] can also be realized after HNO_3 treatment (Fig. S3b). [BMIm][NTf_2] and [BMPyrr][NTf_2] became slightly cloudy after contacting with HNO_3 aqueous solution, which originates from formation of emulsion when hydrophobic RTILs are in contact with water.[5]

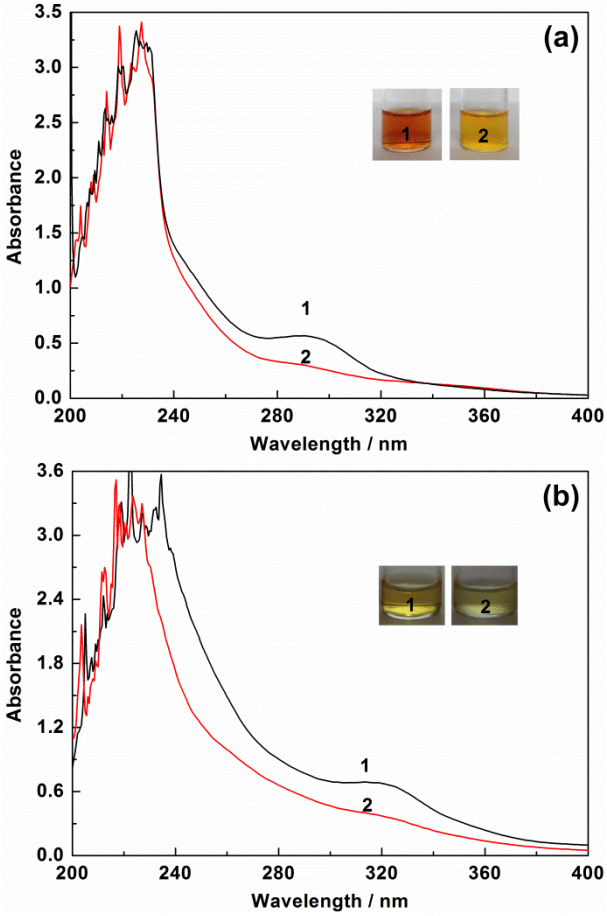

Fig. S3 (a) UV–Vis spectra of irradiated [BMIm][NTf_2] with a dilution factor of 300 before (1) and after (2) contacting with HNO_3 solution (3 mol L^{-1}) for 16 h. (b) UV–Vis spectra of irradiated [BMPyrr][NTf_2] with a dilution factor of 25 before (1) and after (2) contacting with HNO_3 solution (3 mol L^{-1}) for 16 h. Inset of each figure shows the color of corresponding samples.

^{1}H NMR spectrum of irradiated [BMIm][NTf_2] after HNO_3 treatment was similar to that of [BMIm][NTf_2] before decoloration (Fig. S4), indicating that HNO_3 does not oxidize [BMIm][NTf_2] itself. After HNO_3 treatment, the peak of water broadens and shifts to lower field in the ^{1}H NMR spectrum of [BMIm][NTf_2], which is ascribed to the addition of nitric acid.[6] After O_3 treatment for decoloration, some small peaks were observed in the ^{1}H NMR spectrum. Further study reveals that these peaks originate from slight destruction of [BMIm][NTf_2] itself rather than destruction of radiolysis products during O_3 oxidation.

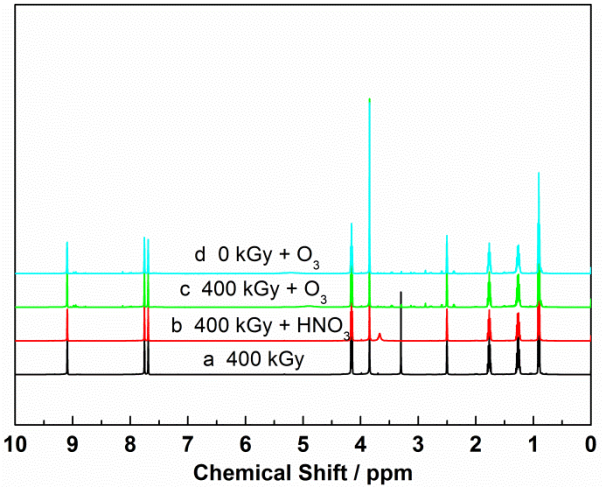

Fig. S4 ^{1}H NMR spectra of [BMIm][NTf_2] (a) after irradiation at 400 kGy; (b) after irradiation at 400 kGy and HNO_3 treatment; (c) after irradiation at 400 kGy and O_3 treatment; (d) after O_3 treatment.

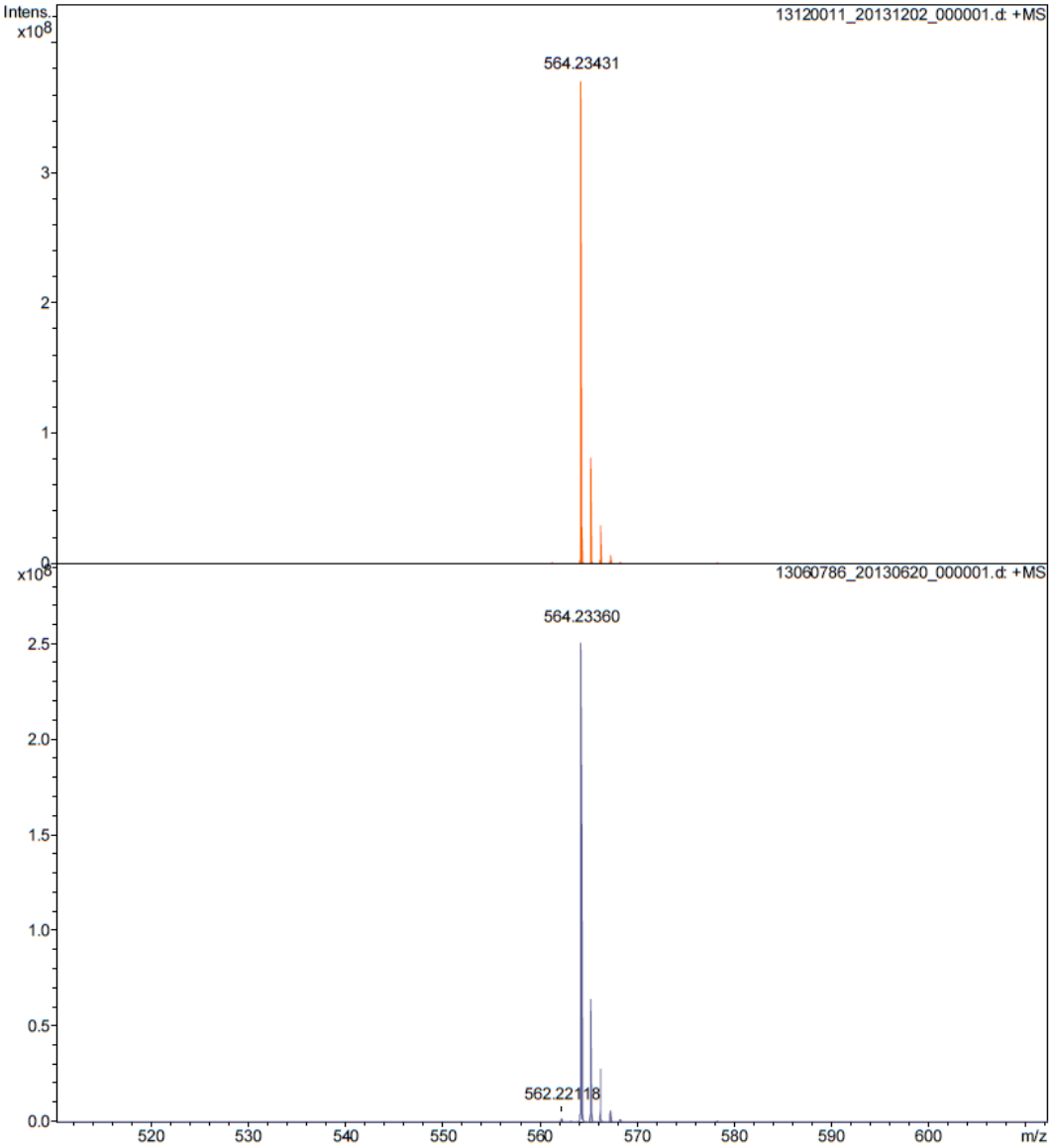

Fig. S5 ESI-MS spectra of [BMPyrr][NTf_2] before (top) and after (bottom) irradiation at 400 kGy in the range of *m/z* =510–612. The peak at *m/z* =562 attributed to the formation of double bonds appears in the ESI-MS spectrum of irradiated [BMPyrr][NTf_2].

[BMIm][NTf_2] samples at different concentrations before and after irradiation at 400 kGy were observed when a beam of light passes through them. Fig. S6 exhibits the typical photographs. Un-irradiated [BMIm][NTf_2] shows almost no visible path of light, while obvious Tyndall effect is observed for [BMIm][NTf_2] after irradiation.

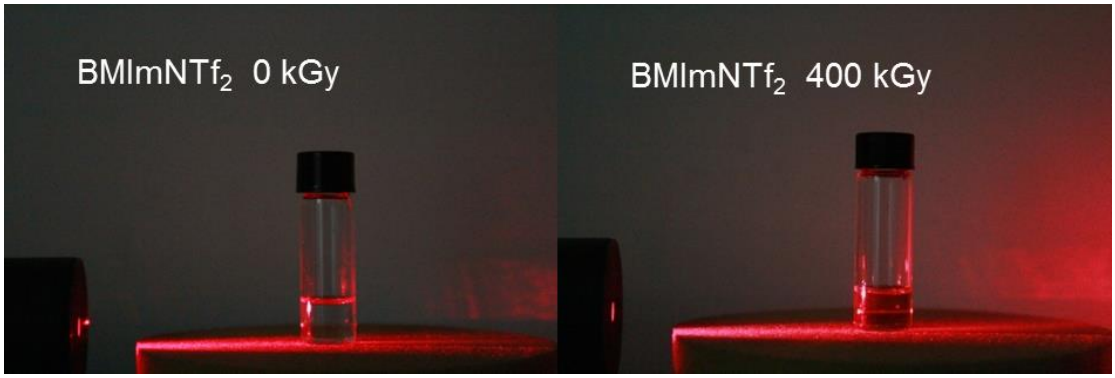

Fig. S6 Typical photographs of [BMIm][NTf_2] before and after irradiation at 400 kGy when a beam of light (632 nm) passes through the RTIL samples.

References

1 D. Allen, G. Baston, A. E. Bradley, T. Gorman, A. Haile, I. Hamblett, J. E. Hatter, M. J. F. Healey, B. Hodgson, R. Lewin, K. V. Lovell, B. Newton, W. R. Pitner, D. W. Rooney, D. Sanders, K. R. Seddon, H. E. Sims and R. C. Thied, *Green. Chem.*, 2002, **4**, 152-158.

2 L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz and P. Moisy, *Dalton Trans.*, 2006, 2526-2534.

3 L. Y. Yuan, J. Peng, L. Xu, M. L. Zhai, J. Q. Li and G. S. Wei, *Radiat. Phys. Chem.*, 2009, **78**, 1133-1136.

4 L. Y. Yuan, J. Peng, M. L. Zhai, J. Q. Li and G. S. Wei, *Radiat. Phys. Chem.*, 2009, **78**, 737-739.

5 S. E. Howett, J. M. Joseph, J. J. Noel and J. C. Wren, *J. Colloid Interf. Sci.*, 2011, **361**, 338-350.

6 L. Y. Yuan, J. Peng, L. Xu, M. L. Zhai, J. Q. Li and G. S. Wei, *Dalton Trans.*, 2008, 6358-6360.