Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Influence of radiation effect on extractability of *iso*butyl-BTP/ionic liquid system: quantitative analysis and identification of radiolytic products

Weijin Yuan,[a,‡] Yinyong Ao,[b,‡] Long Zhao,[a*] Maolin Zhai,[b*] Jing Peng,[b] Jiuqiang Li,[b] and Yuezhou Wei [a]

[a] Nuclear Chemical Engineering Laboratory, School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

[b] Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory for Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

* Corresponding authors: Tel/Fax: +86-21-34207654, E-mail: ryuuchou@sjtu.edu.cn; Tel/Fax: +86-10-62753794, mlzhai@pku.edu.cn

‡ These authors contributed equally.

Experiment part

1. Extraction of Dy^{3+}: The extraction solution (0.5 mL) contained 20 mmol L^{-1} *iso*butyl-BTP was prepared by dissolving *iso*butyl-BTP in $[C_2mim][NTf_2]$, and the aqueous solution (0.5 mL) with various concentrations of Dy^{3+} (abbreviated as $[Dy^{3+}]$). The extraction experiments were oscillated in a constant temperature water bath at 25 ^oC with a rotating speed of 120 r min^{-1}, then were centrifuged for 2 min to ensure that two phases were completely separated. After phase separation, the aqueous solution was diluted with deionized water, and then the $[Dy^{3+}]$ in the diluted aqueous solution was measured by Prodigy high dispersion inductively coupled plasma atomic emission spectrometer (ICPS-7510, SHIMADZU, JPN). The extraction efficiencies (D_{Dy}) and distribution ratios (E_{Dy}) were calculated from Eqn (1) and Eqn (2), respectively. The subscript "org/aq" is short for organic phase/aqueous phase, while the "i/f" designates the initial/final concentration of Dy^{3+} in the diluted solution.

$$D_{Dy} = \frac{[Dy]_{org}}{[Dy]_{aq}} = \frac{[Dy]_{aq.i} - [Dy]_{aq.f}}{[Dy]_{aq.f}} \quad (1)$$

$$E_{Dy} = \frac{[Dy]_{aq.i} - [Dy]_{aq.f}}{[Dy]_{aq.i}} \quad (2)$$

2. Quantitative analysis using UPLC-Q-TOF-MS: An equal volume of sample was added to 2 mL acetonitrile, followed by mixing for 10 min. The supernatant was obtained by centrifugation at 12,000 rpm for 10 min and was directly used for UPLC-Q-TOF-MS (Waters Micromass Q-TOF Pemier mass spectrometer). UPLC was performed at 45 ^oC using an Acquity UPLC BEH C_{18} column (100 mm × 2.1mm, i.d.: 1.7 μm; Waters, Milford, USA), equipped with an Acquity UPLC VanGuard pre-column (5 mm × 2.1 mm, i.d.: 1.7 μm; Waters). The flow rate was 0.4 mL min^{-1} and the injection volume was 2 μL. MS condition: capillary potential 3.0 kV; sampling cone potential 35.0 V; desolvation gas flow 600.0 L h^{-1}; collision energy 6.0 eV; scan range m/z 100-2000; scan time 0.3 s; inter-scan time 0.02 s. Calibrations were performed using the standards at a series of initial concentration of the *iso*butyl-BTP dissolved in $[C_2mim][NTf_2]$ and 1-octanol.

3. MALDI–FTMS: Matrix Assisted Laser Desorption Ionization/ Fourier Transform Mass spectrometry (MALDI-FTMS) measurements were recorded in positive mode. Experiments were conducted using a 7.0 T SolariX FTMS system equipped with a dual ESI-MALDI

source (Bruker Daltonics). The intensity of MALDI-laser irradiation was 15% with frequency at 1000 Hz. The sample was diluted with acetonitrile by 5 times, 100 mg $\cdot$mL^{-1} of 2,5-dihydroxybenzoic acid matrix was prepared in 50% acetonitrile in water (0.1% Trifluoroacetic acid), and mixed at the ratio of 3:1 with sample, 1 μL of mixture was deposited on the stainless steel target and dried to produce a thin film of homogeneous crystals. The mass range (m/z) was set from 80 to 1000.

Table S1. E_{Dy} and D_{Dy} of *iso*butyl-BTP extraction system

Dose (kGy)	(a) *iso*butyl-BTP at solid		(b) *iso*butyl-BTP in $[C_2mim][NTf_2]$		(c) *iso*butyl-BTP in 1-octanol	
	E_{Dy} (%)	D_{Dy}	E_{Dy} (%)	D_{Dy}	E_{Dy} (%)	D_{Dy}
0	83.0	4.9	83.0	4.9	64.9	2.4
100	75.1	3.0	73.5	2.7	56.7	1.3
200	76.4	3.4	68.1	2.1	34.2	0.5
300	80.5	4.4	57.3	1.3	10.9	0.12
400	79.5	4.3	38.1	0.6	2.1	0.02
500	78.6	4.1	26.8	0.4	0.0	0.0

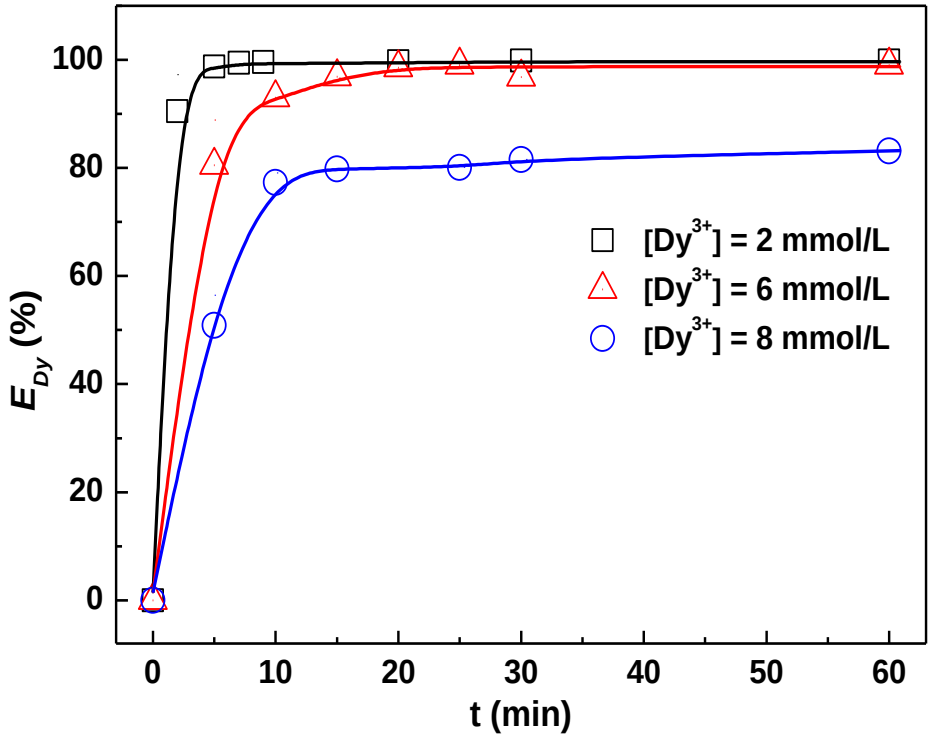

Fig.S1 Dependence of E_{Dy} in *iso*butyl-BTP/[C_2mim][NTf_2] system on oscillation time.

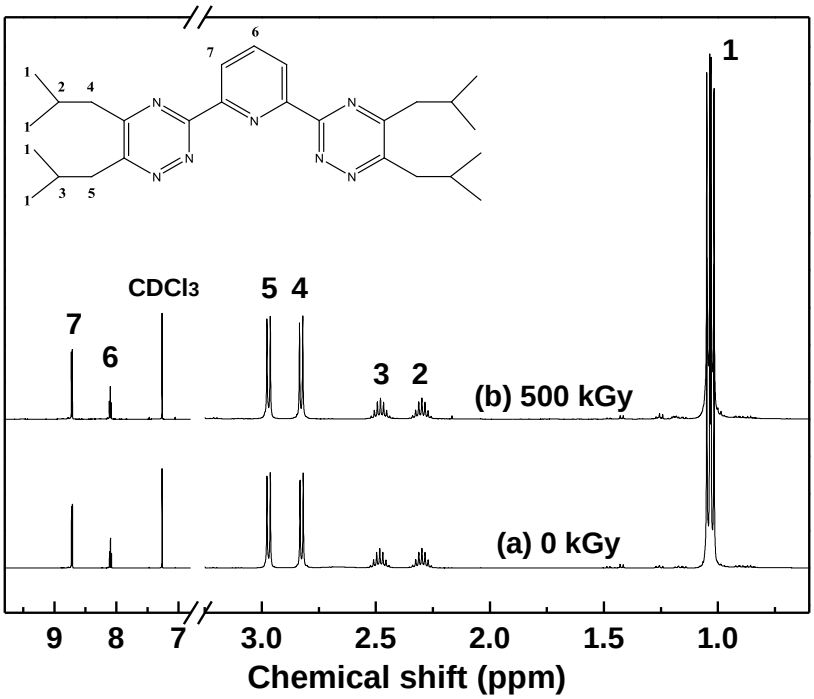

Fig.S2 ^{1}H NMR spectra of *iso*butyl-BTP before and after irradiation at 500 kGy.

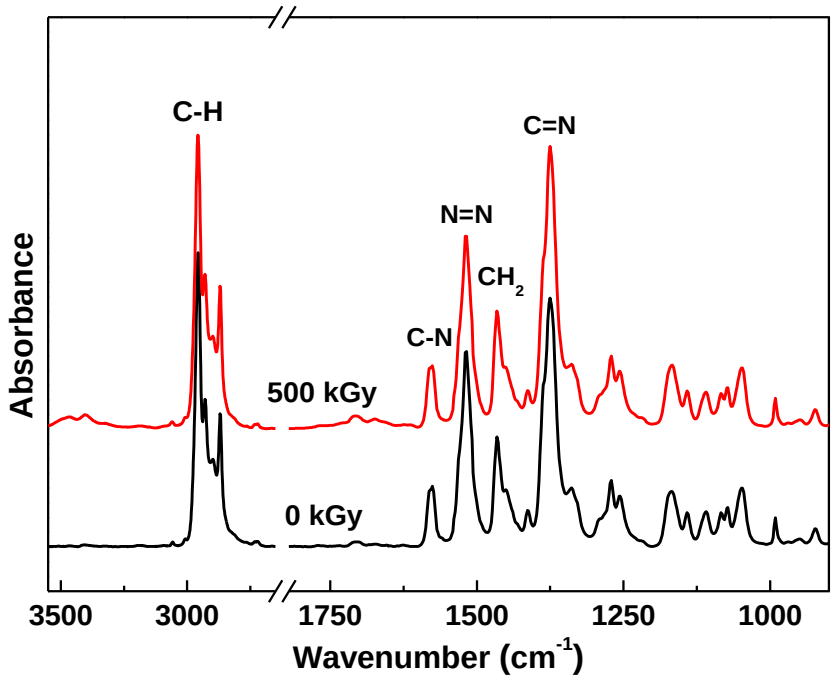

Fig.S3 Micro-FTIR spectra of unirradiated and irradiated *iso*butyl-BTP.

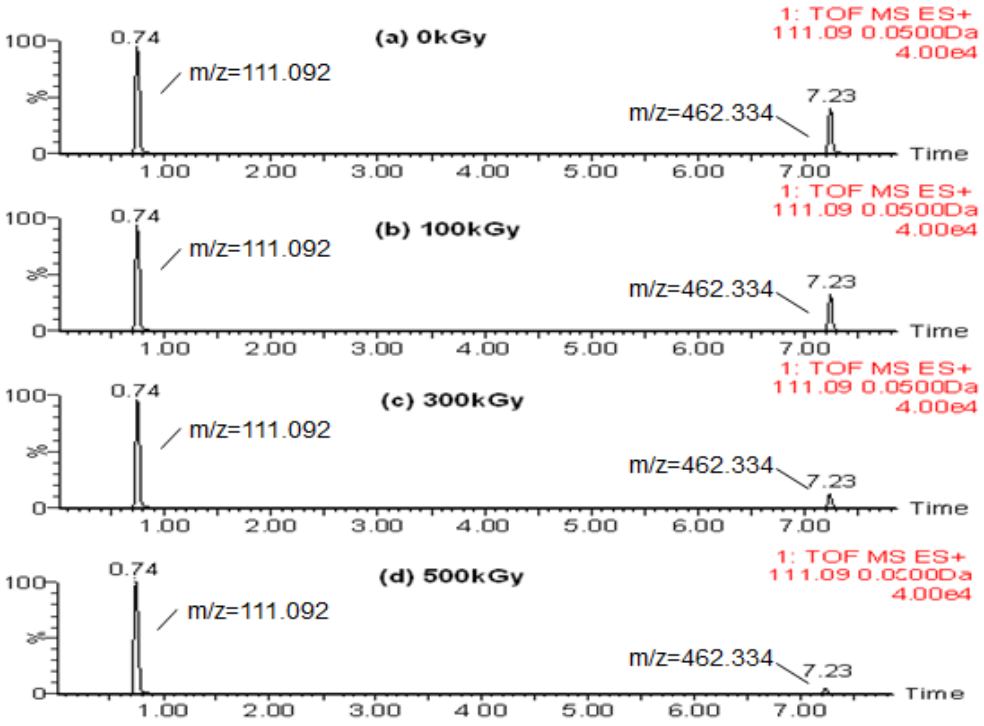

Fig.S4 UPLC/Q-TOF-MS spectra of *iso*butyl-BTP/[C_2mim][NTf_2] (20 mM) before and after irradiation ((a): 0 kGy, (b):100 kGy, (c):300 kGy, (d):500 kGy).

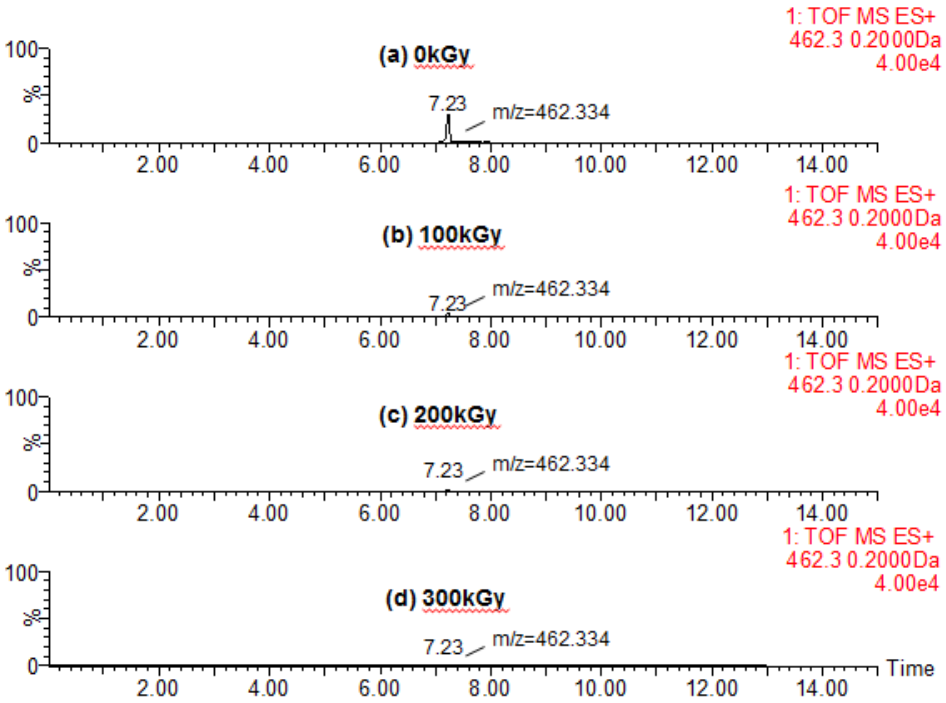

Fig.S5 UPLC/Q-TOF-MS spectra of *iso*butyl-BTP/1-octanol (20 mM) before and after irradiation ((a): 0kGy, (b):100kGy, (c):200kGy, (d):300kGy).

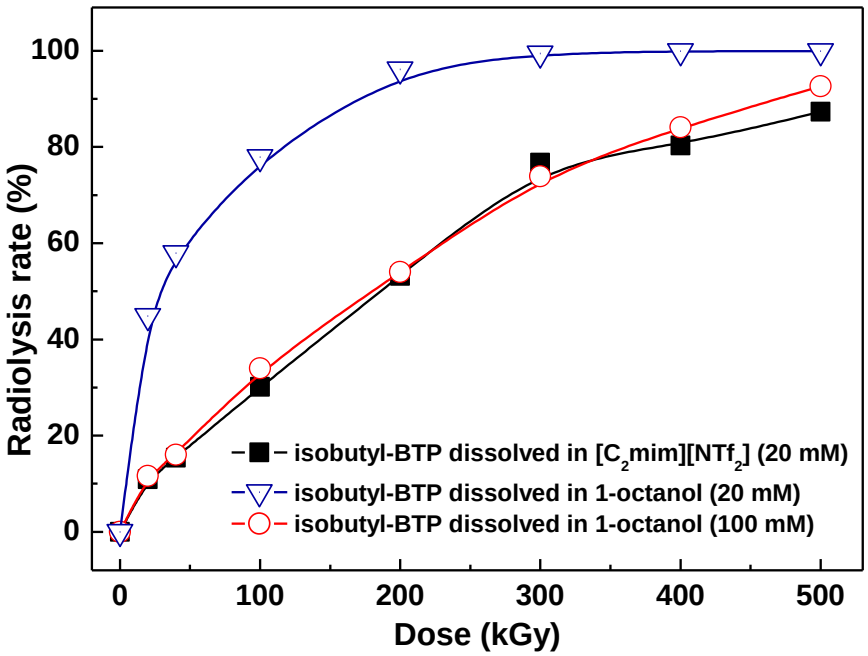

Fig.S6 Radiolysis rate of *iso*butyl-BTP in $[C_2mim][NTf_2]$ and 1-octanol at different doses.