Supporting Information

γ-radiation effect on Th^{4+} extraction behaviour of TODGA/$[C_2mim][NTf_2]$: identification and extractability study of radiolytic products

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Characterization part

XPS analysis:the sediment, which appeared after extraction, was collected after centrifuging and purification. The X-ray photoelectron spectra (XPS) ofthe sediment was recorded by an AXIS-Ultra instrument fromKratos Analytical using monochromatic Al Kα radiation andlow energy electron flooding for charge compensation.

Quantitative/semi-quantitative analysis using UPLC-Q-TOF-MS: An equal volume of irradiated/unirradiatedsample 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 MicromassQ-TOFPemier mass spectrometer). UPLC was performed at 45 ^{o}C using an AcquityUPLCBEHC_{18} column (100 mm × 2.1mm, i.d.: 1.7 μm; Waters, Milford, USA), equipped with an AcquityUPLCVanGuardprecolum (5 mm × 2.1 mm, i.d.: 1.7 μm; Waters). The elution gradient used has been shown in Table S1. 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 $L{\cdot}h^{-1}$; collision energy 6.0 eV; scan range m/z 100-2000; scan time 0.3 s; inter-scan time 0.02 s.

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 SolariXFTMS 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 thinfilm of homogeneous crystals. The mass range (m/z)was from 80 to 1000.

Table S1.UPLC mobile phases and gradient elution details

Time(min)	Solvent A (0.2% aqueous formic acid) (%)	Solvent B (0.2% aqueous acetonitrile) (%)
0	95	5
0.2	95	5
2.2	75	25
4.5	70	30
6.0	60	40
12.0	1	99
15.5	1	99
16.5	95	5
19.0	95	5

Table S2.γ-radiation effect on E_{Th} of TODGA extraction system

Dose(kGy)	E_{Th}		
	(a) TODGA/[C2mim][NTf2] $[HNO_3]$=0.01M	(b) TODGA/[C2mim][NTf2] $[HNO_3]$=3M	(c)TODGA/dodecane $[HNO_3]$=3M
0	99.4	88.7	93.0
100	98.8	89.9	89.5
200	99.2	84.7	87.3
300	98.6	84.5	80.2
400	98.9	79.4	60.4
500	98.5	73.4	54.3
800	98.5	59.1	21.9
1000	98.6	54.0	16.3

Table S3.The concentration of TODGA dissolved in $[C_2mim][NTf_2]$ (a) and in dodecane (b) after irradiated.

Dose (kGy)	(a) [TODGA] in $[C_2mim][NTf_2]$ $mmol \cdot L^{-1}$	(b) [TODGA] in dodecane $mmol \cdot L^{-1}$
0	10.00	10.00
10	9.43	-
20	9.39	9.52791
30	8.81	-
50	-	9.35511
80	-	8.76592
100	7.94	8.58093
200	6.88	7.48093
300	5.93	6.99342
400	5.20	5.86319
500	4.51	5.22512
800	3.01481	2.74654
1000	2.1	1.78

-:not measured

Table S4. Theoretical Cartesian coordinates (in Å) for the structure of $[Th(TMDGA)_3]^{4+}$ in the gas-phase using the B3LYPmethod.

Standard orientation:

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	-2.158713	0.033555	0.044631
6	-1.023172	0.973812	-0.353326
1	-0.630939	1.510591	0.519403
1	-1.363740	1.708785	-1.094015
6	1.149625	0.892662	-1.350550
6	2.130606	-0.125746	-1.927160
1	0.855116	1.629593	-2.107940
1	1.591895	1.423108	-0.497360
8	0.002748	0.152785	-0.920394
8	-2.005820	-1.206163	-0.227195
8	1.791747	-1.356921	-1.865400
6	-3.444520	1.940420	0.949743
1	-2.656350	2.568574	0.538030
1	-3.482005	2.073360	2.034956
6	-4.337858	-0.371969	1.056713
1	-4.058791	-1.410604	0.897649
1	-5.232978	-0.126588	0.477466
7	-3.232922	0.511489	0.639889
6	3.692203	1.694550	-2.524044
1	4.694601	1.779376	-2.095765
1	3.022213	2.349649	-1.969674
6	4.225620	-0.672079	-3.045459
1	4.471664	-0.341389	-4.058135
1	3.785201	-1.665616	-3.076309

7	3.266618	0.281285	-2.456856
1	-4.400684	2.254902	0.522584
1	-4.544917	-0.199134	2.116291
1	5.140233	-0.680712	-2.445049
1	3.727229	2.013574	-3.569946
6	-1.932243	-2.087784	-4.068594
6	-2.851436	-3.204234	-3.578268
1	-2.838552	-4.057515	-4.267849
1	-3.885019	-2.847856	-3.480341
6	-3.114476	-4.658277	-1.697274
6	-2.459912	-4.950462	-0.349229
1	-4.1562	-4.338776	-1.570052
1	-3.095807	-5.545909	-2.342891
8	-2.353407	-3.605757	-2.298103
8	-0.994919	-1.721174	-3.280285
8	-1.40028	-4.293968	-0.065107
6	-3.207715	-1.94254	-6.180235
1	-3.914554	-2.626394	-5.713086
1	-2.774929	-2.417837	-7.065535
6	-1.240114	-0.486624	-5.76965
1	-0.397158	-0.352055	-5.096326
1	-1.808536	0.444091	-5.857221
7	-2.124391	-1.549214	-5.25583
6	-4.203002	-6.629515	0.15025
1	-3.989036	-7.687441	0.323936
1	-4.515178	-6.506337	-0.885614
6	-2.39812	-6.132784	1.780234
1	-3.181407	-6.055595	2.539054
1	-1.605143	-5.41964	1.991553
7	-2.989534	-5.845332	0.460078

1	-3.747244	-1.043705	-6.490604
1	-0.882865	-0.776757	-6.7614
1	-2.002436	-7.152836	1.783794
1	-5.015706	-6.320229	0.814316
6	1.545639	-2.830159	1.781242
6	2.309769	-3.960943	1.096096
1	2.182401	-4.90797	1.635081
1	3.381606	-3.731126	1.038316
6	2.388838	-5.099435	-1.005589
6	1.704774	-5.076528	-2.370432
1	3.462762	-4.895548	-1.098945
1	2.257591	-6.073356	-0.516597
8	1.766345	-4.075754	-0.222854
8	0.674943	-2.21085	1.079244
8	0.747026	-4.243922	-2.524345
6	2.815125	-3.212543	3.866984
1	3.407584	-3.91798	3.286752
1	2.320689	-3.743752	4.685585
6	1.06075	-1.462528	3.738577
1	0.243244	-1.110498	3.114249
1	1.746386	-0.640679	3.965747
7	1.797485	-2.532174	3.039982
6	3.200076	-6.875581	-3.168522
1	2.829038	-7.860772	-3.463933
1	3.555911	-6.932551	-2.14112
6	1.484406	-5.880894	-4.659969
1	2.270727	-5.785528	-5.413535
1	0.793286	-5.045131	-4.736969
7	2.108893	-5.891566	-3.323892
1	3.485568	-2.459032	4.28937

1	0.667506	-1.86338	4.676633
1	0.956361	-6.825965	-4.818561
1	4.031487	-6.600348	-3.824142
90	-0.198919	-2.507348	-1.146637

Table S5. Theoretical Cartesian coordinates (in Å) for the structure of $[Th(TMDGA/C2mim)_3]^{5+}$in the gas-phase using the B3LYP method.

Standard orientation:

AtomicNumber	Coordinates (Angstroms)		
	X	Y	Z
6	-2.054750	0.044520	0.631023
6	-1.002391	0.990792	0.063373
1	-0.555866	1.607989	0.848150
1	-1.468917	1.653418	-0.683165
6	1.072537	0.923464	-1.286080
6	1.822673	-0.200411	-2.011305
1	0.598279	1.557082	-2.042703
8	-0.008877	0.176361	-0.567622
8	-2.061646	-1.157299	0.205580
8	1.632707	-1.415356	-1.623082
6	-2.995868	1.902561	1.964731
1	-2.568582	2.583416	1.228716
1	-2.473968	2.011063	2.921352
6	-3.947916	-0.388762	2.108994
1	-3.726041	-1.421285	1.849320
1	-4.945226	-0.117639	1.749242
7	-2.943881	0.501716	1.502647
6	2.940185	1.456337	-3.487007
1	3.917736	1.477492	-3.972849
1	2.961494	2.174902	-2.666955
6	3.363773	-0.970542	-3.748980
1	3.101349	-0.889241	-4.810228
1	3.056257	-1.940255	-3.364900
7	2.693076	0.094247	-2.992456

1	-4.042668	2.179619	2.108121
1	-3.922704	-0.261635	3.195210
1	4.448591	-0.860018	-3.653269
1	2.186357	1.755413	-4.225613
6	-1.781483	-2.324197	-3.929947
6	-2.923892	-3.256759	-3.505188
1	-2.816204	-4.197268	-4.055634
6	-3.405251	-4.526294	-1.438990
6	-2.870071	-4.689336	-0.020007
1	-4.459549	-4.235194	-1.435308
1	-3.304070	-5.479286	-1.982564
8	-2.605055	-3.522809	-2.071201
8	-1.087926	-1.747589	-3.009785
8	-1.717519	-4.210457	0.236861
6	-2.307680	-2.724248	-6.323742
1	-3.372251	-2.776883	-6.092218
1	-1.921444	-3.728243	-6.538275
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1	0.111884	-0.889988	-4.789458
1	-0.802773	-0.398677	-6.242102
7	-1.558040	-2.083950	-5.232724
6	-4.900005	-5.963854	0.590324
1	-4.980219	-6.888991	1.165331
1	-5.001130	-6.217464	-0.464820
6	-3.130988	-5.489167	2.270691
1	-3.943392	-5.192813	2.940551
1	-2.262306	-4.855903	2.435909
7	-3.588998	-5.349409	0.877916
1	-2.193814	-2.118242	-7.224533
1	0.240114	-1.835309	-6.301506

1	-2.877194	-6.534581	2.471628
1	-5.712363	-5.295025	0.893695
6	1.185666	-3.177692	2.131649
6	2.081641	-4.168405	1.395786
1	2.077601	-5.148522	1.880870
1	3.114864	-3.785470	1.380161
6	2.390415	-5.102026	-0.868434
6	1.761469	-4.790307	-2.235805
1	3.415121	-4.715277	-0.873726
8	1.582344	-4.262755	0.057814
8	0.459306	-2.401203	1.428497
8	0.607626	-4.220910	-2.261525
6	2.103804	-3.957351	4.292490
1	2.994848	-4.268033	3.747114
1	1.565072	-4.836719	4.660915
6	0.336492	-2.211148	4.204247
1	-0.403067	-1.784090	3.530611
1	0.929913	-1.414595	4.663641
7	1.220813	-3.120787	3.456408
6	3.713419	-5.792394	-3.404860
1	3.807538	-6.340172	-4.344746
1	3.830311	-6.508008	-2.590899
6	1.835401	-4.803895	-4.680799
1	2.570554	-4.215853	-5.241535
1	0.921566	-4.228845	-4.551609
7	2.389493	-5.153856	-3.365918
1	2.427464	-3.364810	5.151081
1	-0.161775	-2.776595	4.997057
1	1.623227	-5.718082	-5.244492
1	4.515591	-5.045558	-3.363683

90	-0.347564	-2.519052	-0.868267
6	1.849485	1.835909	-0.397020
7	1.752190	3.210353	-0.433700
6	2.713505	3.751786	0.392645
6	0.829962	4.016928	-1.240119
1	2.827503	4.818417	0.521283
1	1.006514	5.068503	-1.012318
1	1.009436	3.863588	-2.308490
1	-0.210158	3.781551	-0.999241
7	2.885512	1.543224	0.454576
6	3.413164	2.721770	0.943938
6	3.361947	0.183998	0.782615
6	4.418410	0.165331	1.883781
1	3.768894	-0.252352	-0.135521
1	2.484028	-0.405584	1.071020
1	4.696854	-0.874255	2.081225
1	5.333306	0.687112	1.588882
1	4.048553	0.595055	2.819675
1	4.239142	2.748602	1.635835
6	-4.328054	-2.797667	-3.722721
7	-5.305985	-3.569357	-4.311353
6	-6.432063	-2.798341	-4.504264
6	-5.201461	-4.970104	-4.734940
1	-7.330421	-3.194146	-4.955453
1	-6.168674	-5.280421	-5.131280
1	-4.454832	-5.083141	-5.526619
1	-4.951069	-5.617426	-3.890414
6	-6.160688	-1.546715	-4.041053
7	-4.864729	-1.544672	-3.564788
6	-4.162036	-0.381283	-2.984771

6	-5.065949	0.832664	-2.789055
1	-3.334865	-0.128887	-3.656414
1	-3.729934	-0.706051	-2.031299
1	-4.475481	1.636087	-2.338440
1	-5.453534	1.218449	-3.736270
1	-5.905450	0.620463	-2.120015
1	-6.790987	-0.672741	-4.021887
6	2.479336	-6.531599	-0.441850
7	3.621409	-7.115408	0.059481
6	3.405600	-8.468218	0.210757
6	4.902522	-6.462432	0.352720
1	4.167366	-9.133825	0.590161
1	5.581188	-7.210683	0.763055
1	5.350891	-6.057077	-0.559172
1	4.776952	-5.667485	1.092502
7	1.565252	-7.541299	-0.603777
6	0.196597	-7.376526	-1.136914
6	-0.636117	-8.653281	-1.065049
1	0.288013	-7.045151	-2.176378
1	-0.276888	-6.567342	-0.569194
1	-1.634443	-8.439141	-1.458300
1	-0.219284	-9.455792	-1.680265
1	-0.752939	-9.013964	-0.038622
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1	1.605628	-9.671525	-0.227779

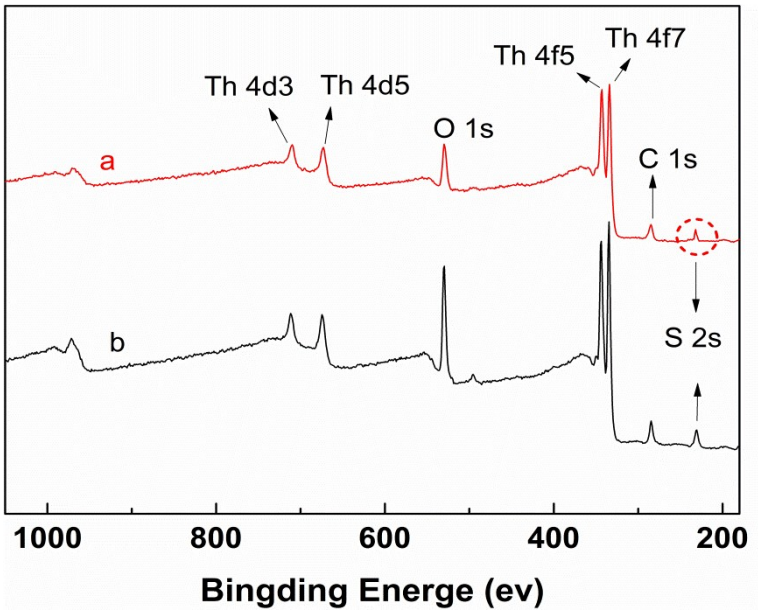

Fig.S1 XPS spectra of the sediment (a) and $Th(SO_3)_2$ (b).

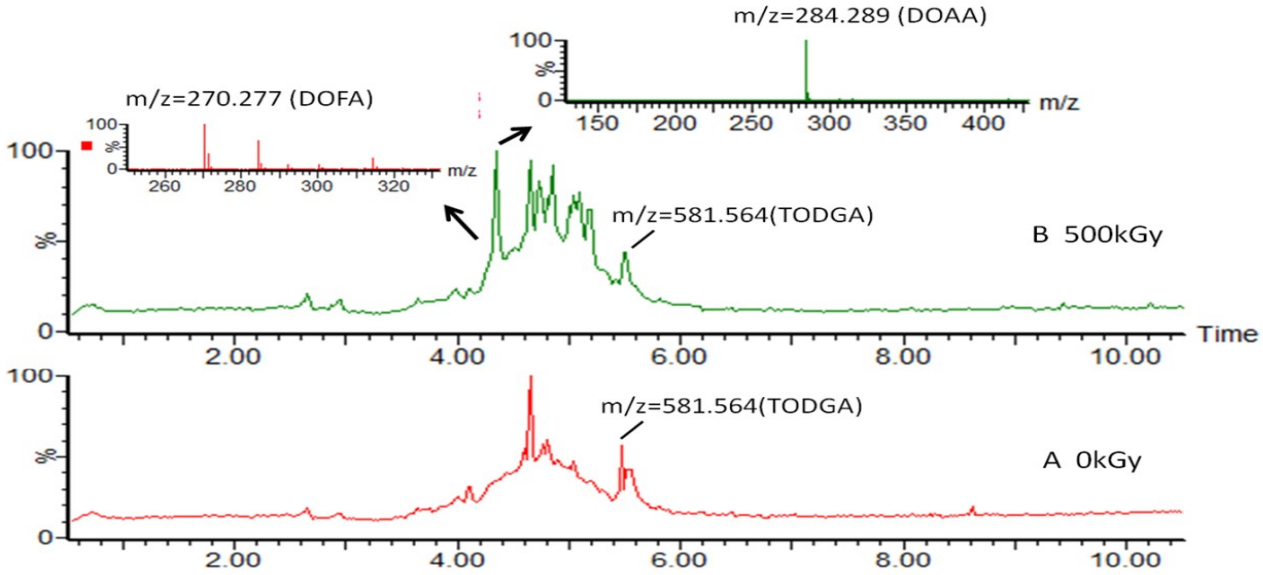

Fig.S2 UPLC/Q-TOF-MS spectra of TODGA/dodecane before (A) and after irradiation (B).

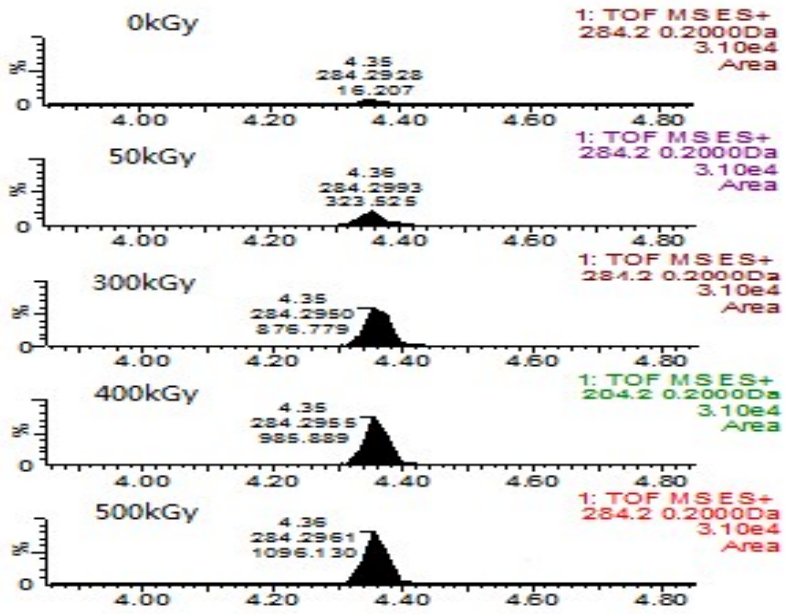

Fig.S3The area of extracted-ion peak of DOAA measured by UPLC/Q-TOF-MS

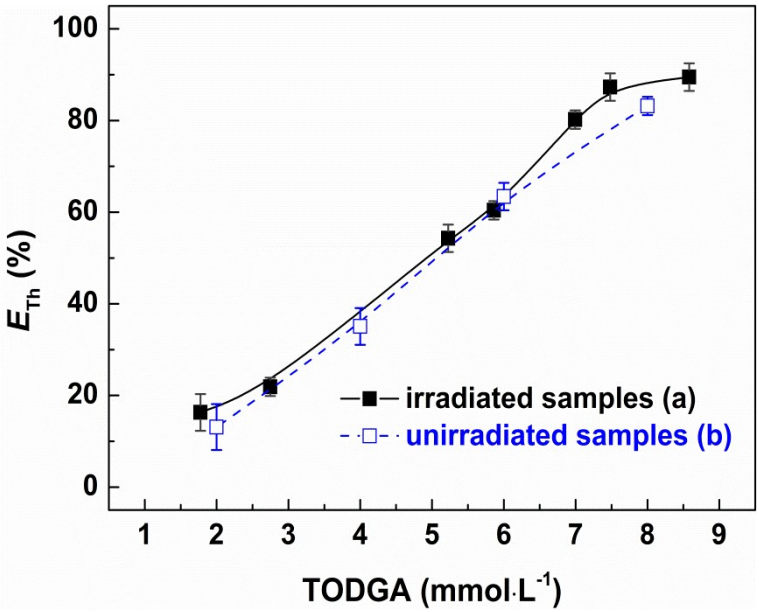

Fig.S4 Extraction of Th^{4+} using irradiated TODGA/dodecane (a) or unirradiated samples (b).

([TODGA] in irradiated TODGA/dodecane was detected by UPLC-Q-TOF-MS)