Radiolytic stability of pillar[5]arene-based diglycolamides

Abstract: Radiolytic stability of pillar[5]arene-based diglycolamides (P5DGAs) against gamma irradiation up to 1000 kGy adsorbed dose was studied. The results reveal the increase of radiation damage degree on P5DGAs with dose. The radiolysis products of P5DGAs including the gaseous and solid products were fully characterized by 1H NMR, HR-ESI-MS, GC, and HPLC techniques. It was found that the main radiolytic gas products of P5DGAs under argon are H2, N2, CO and gaseous hydrocarbons. The solid degradation products contain phenolic hydroxyl groups and secondary amine groups. In addition, solvent extraction toward Eu(III) was performed with P5DGAs, in which about 50% decrease in Am(III) partitioning in 1-octanol from aqueous acidic solution. The distribution coefficients (D_{Eu}) of three P5DGAs ligands ([L] = 10^{-7} \text{ M}) with different spacer lengths in 1 M HNO_{3} reach 25.7–127. Greater extraction efficiency of these ligands was observed in ionic liquid (C_{8}minNTf_{2}) system. At 1 M HNO_{3}, the D_{Eu} values of the three P5DGAs ([L] = 5 \times 10^{-7} \text{ M}) in C_{8}minNTf_{2} are 865–7803, which are 36–61 times higher than those in 1-octanol system [26, 27]. These results demonstrate the great potential of P5DGAs as promising candidates for nuclear waste remediation.

1 Introduction

Pillararenes, a new intriguing class of macrocycles discovered in 2008 by Ogoshi et al., have been the focus of considerable researches because of their facile synthesis, unique structural architectures, efficiency in metal ion separation and host-guest chemistry [1–5]. Pillar[5]arenes are made up of dialkoxybenzene units linked by methylene bridges at the 2,5-positions, which resemble calixarenes in structural unit but have symmetric pillar conformation. Benefiting from their relatively rigid structure and diverse functionalization on each portal, pillararenes have been recognized as ideal molecular platform to pre-organize metal chelating groups, making them as promising candidates for metal ion separation [6, 7]. In recent years, it has been reported that pillar[5]arenes functionalized with phosphine oxides (PO) [8], carbamoylmethylphosphine oxides (CMPO) [9] and N,N-dimethyldithiocarbamoyl modified pillar[5]arenes [10] present excellent performance as extractants for lanthanide/actinide separation or Mercury removal.

Diglycolamides (DGAs) as multidentate extractants are considered to be one of the most efficient extractants for the separation of trivalent lanthanides and actinides from PUREX high active raffinates or dissolved spent nuclear fuel [11–15]. A series of diglycolamide-functionalized extractants such as DGA-functionalized task specific ionic liquids [16, 17], tripodal DGA (T-DGA) [18–20] and DGA-functionalized calix[4]arenes [21–23] have been extensively studied for Ln(III)/Am(III) separation from acidic feeds. Inspired by the finding that pillar[5]arenes serve as an excellent preorganization platform for metal complexation [8, 9] and the outstanding performance of DGAs in Ln(III)/Am(III) separation [24, 25], our group synthesized pillar[5]arene-based diglycolamides, where 10 DGAs moieties were introduced onto the pillar[5]arene framework in 2014. Notably, P5DGAs exhibit highly efficient extraction and separation ability for Eu(III) and Am(III) partitioning in 1-octanol from aqueous acidic solution. The distribution coefficients (D_{Eu}) of three P5DGAs ligands ([L] = 10^{-7} \text{ M}) with different spacer lengths in 1 M HNO_{3} reach 25.7–127. Greater extraction efficiency of these ligands was observed in ionic liquid (C_{8}minNTf_{2}) system. At 1 M HNO_{3}, the D_{Eu} values of the three P5DGAs ([L] = 5 \times 10^{-7} \text{ M}) in C_{8}minNTf_{2} are 865–7803, which are 36–61 times higher than those in 1-octanol system [26, 27]. These results demonstrate the great potential of P5DGAs as promising candidates for nuclear waste remediation.

In the actual post-treatment for nuclear waste based solvent extraction, the extractant ligand is dissolved in organic diluents and contacted with spent nuclear fuel dissolved in an
aqueous acidic solution to extract desirable elements. The extractants will inevitably be exposed to radiation field generated by radionuclides decay [28]. Radiation on organic phase may result in radiolytic degradation of extractants, giving lower metals mass-transfer coefficients, reduced distribution ratios and separation factor due to the generation of unwanted complexing products, as well as deterioration of solvent performance. In view of this, study on the radiolytic stability of P5DGAs is important to assess their application feasibility in nuclear fuel recycle [13, 29–32].

Recently, we found that the skeleton of the alkylated pillar[5]arenes and phosphine oxide functionalized pillar[5]arenes was stable to a great extent when the dose of electron beam was lower than 100 kGy, indicating that the excellent radiation stability of pillar[5]arene [32, 33]. Although the radiolytic stability of P5DGAs in ionic liquids was reported by Arijit et al., they only investigated the effect of gamma irradiation on the Pu$^{4+}$ extraction ability of P5DGAs/C$8$mimNTf$_2$ systems. It was found that the P5DGAs/C$8$mimNTf$_2$ systems are radiolytically stable for the extraction of Pu$^{4+}$ and the extraction efficiency decreased by 51% at most after irradiation at a dose of 1000 kGy. To the best of our knowledge, no systematic study on radiolytic stability of neat P5DGAs or solutions of P5DGAs in molecular diluent 1-octanol has been reported, and the corresponding radiolysis mechanism still remains unknown [30]. Thus, it is necessary to explore radiolytic behavior of P5DGAs and the possible changes in the extraction behavior upon gamma irradiation.

In this work, we report on the results of radiation stability of three P5DGAs 1a–c (Figure 1) irradiated by $^{60}$Co source to a dose ranging from 0 to 1000 kGy. Since the P5DGAs contain five repeating units, the acyclic analog of P5DGAs (2a), serving as a control compound, was also assessed for its radiation stability under the same condition. The radiolytic degradation rate of P5DGAs under different dose was investigated by HPLC and $^1$H NMR spectroscopy, and the main resulting radiolytic products were identified by high-resolution ESI-MS and GC. Extrac-

![Figure 1: Chemical structures of pillar[5]arene-based diglycolamides (P5DGAs) 1a–c and control compound 2a.](image)

2 Experimental

2.1 Materials

Compounds 1a, 1b and 1c were prepared as previously reported [26]. Compound 2a was synthesized as a control compound. The molecular structures of these compounds were confirmed by $^1$H NMR and ESI-MS spectroscopy. 1a was chosen as the representative compound for radiolytic degradation study. Deuterated solvents including CDCl$_3$ and CD$_3$OD were purchased from Cambridge Isotope Laboratories (CIL). The organic reagents used in the synthesis and analysis were purchased from Energy Chemical, China. Solvents used in the optical spectroscopic studies were HPLC grade. Ultrapure nitric acid and ultrapure water were used for preparing nitric acid solutions. All other solvents were analytical-grade reagent and used without further purification.

2.2 Irradiation

The samples were irradiated (298 ± 4 K) using a $^{60}$Co source with an average dose rate of ca. 50 Gy/min (Irradiation Preservation Technology Key Laboratory of Sichuan Province, Sichuan Institute of Atomic Energy, Chengdu 610101, China). The dose rate was calibrated by potassium (silver) dichromate dosimeter. Radiolytic degradation experiments involved the irradiation of samples, composed of (1) neat 1a in an air or argon atmosphere (2) neat control compound 2a in an air or argon atmosphere (3) a 0.1 M solution of 1a/1-octanol, 1b/1-octanol and 1c/1-octanol in an air atmosphere. The dose of irradiated samples was accumulated to 50, 100, 200, 500, 800, and 1000 kGy, respectively.

2.3 Characterization

The $^1$H NMR spectra were measured with a Bruker AVANCE AV II-400 MHz spectrometer at a constant temperature of 298 K. High resolution electrospray ionization-mass spectrometry (HRESI-MS) data
were obtained by WATERS Q-TOF Premier. Mass analysis was performed in positive ionization mode (70 eV). Weighed quantities of 1a and 2a were subjected to thermogravimetric analysis (TGA) using a DTG–60(H) instrument, and the samples were heated from room temperature to 800 °C with 10 degrees per minute under an air atmosphere. The samples were analyzed on high-performance liquid chromatography system (HPLC, SPD-20A, Japan) with a positive phase silica gel column (Hypersil GOLD Slica Dim, 5 µm, 250 × 4.6 mm). A mixture of dichloromethane and methanol at a ratio of 92:8 for one was used as mobile phase with a flow rate of 1.0 mL/min. Detection was performed with a UV–Vis diode array detector at the wavelength of 285 nm. Samples were diluted by dichloromethane and the injection volume was 10 µL. The data from three injections were averaged. The radiolytic gas products of irradiated samples were analyzed on GC2002 gas chromatography. A thermal conductivity detector (TCD) and a TDX-13 × 5A column were used to measure H2 and N2 concentrations. A flame ionization detector (FID), TDX-01 column and Al2O3 capillary column were used to measure CO, CO2, CH4, C2H4 and C2H6, respectively. The carrier gas was high purity argon with the flow rate of 500 mL/min. Inductively coupled plasma optical emission spectroscopy (ICP/OES, PerkinElmer ICP optima 8000) was used to determine the europium ion concentrations of the aqueous phase.

2.4 Extraction studies

Solvent extraction procedure follows the reported work [34]. The organic phase contains ligand 1a–1c (5 × 10⁻⁴ M) in 1-octanol. All organic phases were pre-equilibrated by mixing with an equal volume of nitric acid solution (1.0 M) with continuously shaking for 2.5 h before extraction. The aqueous phase contains Eu³⁺ (5 × 10⁻⁵ M) at 1.0 M nitric acid. A 1 mL aliquot of each phase was thoroughly mixed by mechanically shaking in a stoppered glass tube at (25 ± 1) °C for 4 h, which has been proven to be long enough to reach the extraction equilibrium [26]. After equilibration, the tubes were centrifuged at 2000 rpm for 5 min. 0.5 mL aliquot of aqueous phase was removed into a volumetric flask using micro syringe and was then diluted to 5 mL for ICP-OES test (with a detection limit below 0.01 ppm). The distribution ratio (D) values could be calculated from the concentration of the aqueous phase before and after:

\[ D = \frac{C_i - C_f}{C_f} \]

where, \( C_i \) and \( C_f \) are the initial and final concentration in the aqueous phases. All the experiments were carried out in triplicate.

3 Results and discussion

3.1 Thermogravimetric analysis

Thermal stability of irradiated extractants could be used to reflect the degradation under irradiation condition [33]. Thus, the thermal stability of irradiated 1a was probed by TGA, and the result was compared with that of unirradiated 1a.

As shown in Figure 2, the degradation processes of all samples mainly present two stages. The first distinct thermal weight loss of unirradiated 1a and irradiated 1a in the TG curves is observed at 200–420 and 150–420 °C, respectively. In this stage, the weight loss reaches 64.13% for original 1a, 64.17% for irradiated 1a in argon, and 65.43% for irradiated 1a in air, which is close to the theoretical value 65.23% calculated by the formula weight of 10 diglycolamide groups. Thus, the first distinct thermal weight loss could be a result of the degradation of diglycolamide groups on P5DGAs. The second weight loss occurs between 420 and 580 °C due to the breakage of the P5DGAs skeleton, which is similar to our previous observation on irradiated phosphine oxide functionalized pillar [5]arenes [33]. The thermal degradation rate of the three samples follows the order of unirradiated 1a > irradiated 1a in argon > irradiated 1a in air, indicating that gamma irradiation lowers the thermal stability of P5DGAs.

3.2 Analysis of radiolytic degradation products

The structures of different organic species present in the radiolysis products of pillar[5]arene-based diglycolamides were subject to several characterization techniques including ¹H NMR, ESI-MS, GC and HPLC.

![Figure 2: TG curves of unirradiated neat 1a and irradiated ones under different atmosphere.](image)
3.2.1 Proton NMR analysis

The NMR experiments of irradiated 1a at different dose were performed. The 1H NMR spectra are presented in Figure 3a. Almost no chemical shift is witnessed at the dose below 200 kGy. As the dose is over 200 kGy, several new small signals show up at 9.41, 8.20, 8.12, and 4.77 ppm, respectively, and the intensity increases along with the increase of dose. The results above indicate a remarkable structure change of ligand 1a after irradiation. The signal at 9.41 ppm is assigned as phenolic hydroxyl groups [35–37]. The other two new signals at 8.20 and 8.12 ppm are ascribed to -NH groups [21], which are generated by 1a losing isopropyl groups. Because the degradation products containing –NH groups, which are produced by removing one isopropyl group from each side chain, account for a small portion in the total radiolytic degradation products of 1a, only the signals of very low intensity at 8.20 and 8.12 ppm are observed. The strong signal at 7.96 ppm before irradiation corresponds to the –NH of the amide groups close to the portal of the pillar[5]arene. After irradiation, a small part of 1a degrades to the species containing –NH(CH(CH3)2) group which resonates at a lower field (8.20 and 8.12 ppm), thereby leading to the different chemical shifts of –NH groups in 1a before and after irradiation. Furthermore, the assignment of phenolic hydroxyl and secondary amine signals was confirmed by methanol-d4 (CD3OD) exchange experiments. All the three new signals disappear with the addition of CD3OD (Figure 3b). In contrast, the signal at 4.77 ppm remains unchanged with the addition of CD3OD, indicating that the hydrogen at 4.77 ppm is not an active hydrogen and is assigned as alkoxy groups according to its chemical shift. The addition of deuterated methanol gives rise to the enhancement of solvent polarity and the formation of hydrogen bond between deuterated methanol and –NH group [38], which leads to a considerable downfield shift of –NH signal (7.96–8.13 ppm, see Figure 3b). Based on the NMR spectroscopy analysis, the radiolytic products containing phenolic hydroxyl and secondary amine groups are formed during irradiation, which implies the breakage of pillar[5]arenes-based diglycolamides skeleton to some extent under high-dose irradiation.

3.2.2 GC analysis

Due to the less radiolysis degradation of 1a and 2a at low irradiation dose, it is difficult to qualitative and quantitative analyses of the trace gaseous radiolytic products. Therefore, the gaseous radiolytic products of 1a under air are CO, CH4, C2H4 and C2H6 except for the undetected hydrogen and nitrogen, while those under argon are H2, N2, CO, CH4, C2H4, C2H6 without CO2. Heller and Gordon [39, 40] reported that isopropyl radical rearrangement can form gaseous hydrocarbons such as C2H6 and C3H6. Thus, the formation of gaseous hydrocarbons of ligand 1a and 2a is mainly due to the rearrangement of isopropyl radicals. In addition, the type of radiolytic gas products of 1a is identical to that of 2a, suggesting that the similarity of the degradation pathway of these two ligands.

Table 1 lists the amount of gas radiolytic products produced by irradiated samples at 1000 kGy in this study. The amounts of CH4, C2H4 and C2H6 produced by irradiated 1a in argon are 10.2, 11.6 and 2.5 times those of the gas radiolytic products in air, respectively. The amounts of gaseous hydrocarbons produced by irradiated 1a in argon are much more than those of in air. The similar phenomenon is also observed in irradiated 2a. During the irradiation process,
oxygen could easily produce oxidizing free radicals and ozone \([41, 42]\), which will affect the radiolysis pathway of extractants. The oxygen in the air will impede the radiolysis pathway of P5DGAs, leading to the less generation of gaseous hydrocarbons. It is concluded that irradiation atmosphere plays a vital role in the radiolysis of 1a.

3.2.3 Quantitative analysis by HPLC

Three irradiated ligands 1a–c are employed for high performance liquid chromatography analysis of the extent of degradation to which radiolytic decomposition proceeds. The HPLC chromatograms of irradiated solution of 1b/1-octanol with a dose range from 0 to 1000 kGy are shown in Figure 5. The first peak with the shortest retention time (ca. 3.8 min) represents the P5DGAs (1b) molecule. Compared with the chromatogram of unirradiated 1b, a new peak (ca. 6.4 min) appears in the chromatogram of irradiated 1b/1-octanol at 50 kGy. The peak area of the new peak gradually increases with dose. It implies that the degradation degree of P5DGAs increases with dose. It is consistent with result from \(^1\)H NMR experiment.

In order to assess the degradation rate quantitatively, the ratio of ligands 1a–c concentration before and after irradiation as a function of dose was measured by HPLC using external standard method. Figure 6 shows the degradation trend of ligands 1a–1c against the radiation dose. At the dose range of 0–1000 kGy, the residual of ligands 1a–1c decreases with dose and the degradation rate gradually slows down. Degradation rates of 1a–1c exhibit a few different at the low dose. However, the radiation resistance of each irradiated samples is obviously different at the dose exceeds 200 kGy. In the case of a 27% gap appears between solution of 1a/1-octanol and 1c/1-octanol at 1000 kGy. The longer chain is inclined to result in easy breakage of pillararene framework with dose. This phenomenon is in agreement with the irradiated alkylated pillar[5]arene and phosphine oxide functionalized pillar[5]arenes \([32, 33]\). An 18% gap is also observed between neat 1a and solution of 1a/1-octanol at 1000 kGy, indicating that the presence of 1-octanol affects negatively the stability of 1a. This could be ascribed to the sensitization

![Figure 4: GC analysis of gas radiolytic products from neat 1a and 2a irradiated at 1000 kGy. (a) Gas chromatography of CO and CO\(_2\); (b) Gas chromatography of H\(_2\), N\(_2\), CH\(_4\), C\(_2\)H\(_4\), and C\(_2\)H\(_6\).](image)

![Figure 5: HPLC chromatograms of irradiated ligand solution of 1b/1-octanol in air at different doses.](image)

Table 1: Amount of gas radiolytic products of neat 1a and 2a after gamma irradiation at a dose of 1000 kGy in different atmospheres.

| Samples | Atmosphere | H\(_2\) mmol/L | N\(_2\) mmol/L | CO mmol/L | CO\(_2\) mmol/L | CH\(_4\) mmol/L | C\(_2\)H\(_4\) mmol/L | C\(_2\)H\(_6\) mmol/L |
|---------|------------|----------------|---------------|-----------|----------------|----------------|------------------------|------------------------|
| 1a      | Air        | Not determined | Not determined | 1.656     | 3.155          | 2.080          | 0.592                  | 0.115                  |
|         | Argon      | 1.409          | 10.985        | 1.206     | 0              | 21.115         | 7.020                  | 0.292                  |
| 2a      | Air        | Not determined | Not determined | 1.299     | 2.872          | 1.199          | 0.375                  | 0                      |
|         | Argon      | 1.533          | 10.329        | 1.263     | 0              | 29.525         | 8.078                  | 0.347                  |
effect of 1-octanol on the radiolysis of 1a [43–45]. It should be noted that these ligands still remain more than 30% even 57% when the dose is up to 500 kGy, viz., pillar[5]arene-based diglycolamides exhibit good radiation stability at dose less than 500 kGy.

3.2.4 Qualitative analysis by ESI-MS

Electrospray ionization mass spectrometry (ESI-MS) was chosen as the measurement technique to identify degradation products of irradiated samples. To avoid the complexity of pillar[5]arenes in mass spectra, compound 2a, which is similar to 1a in constitutional structures, was tested to elucidate a possible pathway of the degradation.

As shown in Figure 7, three intense signals (m/z = 633.33, m/z = 617.35 and m/z = 595.37) of irradiated 2a are assigned to [2a + K]^+ (theoretical m/z = 633.33), [2a + Na]^+ (theoretical m/z = 617.35) and [2a + H]^+ (theoretical m/z = 595.37), respectively. For most of these radiolytic degradation products, reasonable structures are inferred based on simple homolytic cleavage of the parent structure, followed by capping of the resultant radical [46].

The rupture of the chemical bond between amide and alkyl on 2a gives rise to products A, B, B', D and E. Species A (m/z = 553.33) is generated by the cleavage of one C_isopropyl–N bond of 2a. It should be noted that the different species B (m/z = 511.28) and B' (m/z = 511.28) with the identical mass-to-charge ratio could be obtained by the losing of two isopropyl groups from same side chain and different side chain in 2a, respectively. The peak at m/z = 396.25 is assigned to the species D formed from the C_carbonyl–N breakage of the initial molecule. Species E (m/z = 354.20) is produced by the above two bond cleavage modes. Besides, the cleavage of C_carbonyl–CH2 bond should generates the species C (m/z = 424.21). With the information retrieved from m/z values of the major fragments, the degradation product pathway of 2a was given in Figure 8.

As illustrated in Figure 9a, three intense signals of irradiated 1a correspond to multi-charged ions, all of which are
attributable to an adduct of the molecule with protons and alkali cations. Peaks at $m/z = 1536.40$, $m/z = 1528.41$ and $m/z = 1517.42$ are assigned to $[\text{1a} + \text{H} + \text{K}]^+$ (theoretical $m/z = 1536.40$), $[\text{1a} + \text{H} + \text{Na}]^+$ (theoretical $m/z = 1528.41$) and $[\text{1a} + 2\text{H}]^+$ (theoretical $m/z = 1517.42$), respectively. Previous reports reveal that the main ruptures of diglycolamide-based compounds (such as $N,N',N'$-tetraoctyl diglycolamide, TODGA) take place in Oether–CH$_2$ and C carbonyl–N bonds under irradiation [44, 45, 47]. Indeed, Species 1 ($m/z = 1465.84$) and 2 ($m/z = 1457.83$) are formed by the cleavage of Oether–CH$_2$ bond. Peaks at $m/z = 1417.84$ and $m/z = 1347.29$ are assigned to species 4 and 7. These two species are formed from the cleavage of C carbonyl–N bond. Species 5 ($m/z = 1396.34$) is produced by the breakage of one of the 10 appending arms attached to the pillararene framework. Synchronous cleavage C carbonyl–N and C isopropyl–N, C carbonyl–N and Oether–CH$_2$, from either one of two rims of pillar[5]arene framework results in the original molecule to yield a fragment ions of $m/z = 1446.86$ (species 3) and $m/z = 1366.29$ (species 6), respectively. In addition, species 8 ($m/z = 1317.79$) is generated by the loss of one of 10 arms accompanied by the cleavage of Oether–CH$_2$. The result of species 5 and 8 containing phenolic hydroxyl groups is consistent with the result of $^1$H NMR experiments. The signal of degradation products produced by the rupture of two C isopropyl–N bonds was not found in the mass spectrum of irradiated 1a (Figure 9), indicating that this degradation product was scarcely formed in the radiolysis of 1a. With the information retrieved from $m/z$ values of several major fragments, the schematic representation of the radiolytic degradation of 1a was proposed accordingly (Figure 10). Similar to the cleavage sites in irradiated TODGA [47], the major sites for radiolytic attack are also Oether–CH$_2$, C isopropyl–N and C carbonyl–N bonds in P5DGAs molecules. Generally, radiolytic degradation of the P5DGAs leads to the formation of fragments such as the pillar[5]arene skeleton, de-alkylation, de-amination, and ether linkage cleaved products.

3.3 Solvent extraction studies

To evaluate the effect of gamma irradiation on the extraction ability of extractants, the $D_{\text{Eu}}$ values under different dose were investigated by solvent extraction experiment. As shown in Figure 11, the distribution ratios of Eu(III) decrease with the increase of dose, indicating that the radiolytic degradation of 1a–1c increases with dose. The $D_{\text{Eu}}$ values of unirradiated ligands 1a–1c are 8.31, 16.12 and 20.51, which are similar to the result that we reported before [26]. When the dose up to 500 kGy, the $D_{\text{Eu}}$ values of 1a/1-octanol, 1b/1-octanol and 1c/1-octanol decrease to 1.40, 1.47 and 0.99, respectively. Compared with the $D_{\text{Eu}}$ values of irradiated samples 1a/1-octanol and 1b/1-octanol, the $D_{\text{Eu}}$ values of irradiated 1c/1-octanol are higher at dose ranging from 0 to 500 kGy, which may be attributed to the radiolytic products of 1c having better affinity towards Eu(III). The extraction ability of solutions 1a–1c/1-octanol is almost lost with the dose up to 1000 kGy. In contrast, only 20–50% decrease in the...
Extraction efficiency towards Pu$^{4+}$ is observed for solution 1a–1c/C$_8$mimNTf$_2$ at 1000 kGy [30]. This indicates that the radiolytic stability of solvent system P5DGAs/C$_8$mimNTf$_2$ is better than that of P5DGAs/1-octanol. It is noteworthy that when the dose is up to 500 kGy, the pillar[5]arene-based diglycolamides still show about 50% efficiency towards Eu$^{3+}$. The maximum radiation dose during actinide partitioning from actual high-level nuclear waste depends on the design of the contactor and the flow rates of the aqueous and organic streams and may not exceed a few hundred kGy in each cycle [15]. It suggested that the extractants pillar[5]arene-based diglycolamides hold potential practical application for spent fuel reprocessing in a few cycles of continuous use.

Figure 9: Expanded HRESI-MS spectra of irradiated neat 1a at 1000 kGy. (a) Magnification of the m/z = 1400–1560 region; (b) Magnification of the m/z = 1310–1405 region (the peak intensity in the top figure is magnified four times).
Figure 10: Proposed pathway for the radiolytic degradation of 1a. (a) Generation of species 1, 2, and 8; (b) Generation of species 3, 6, and 7; (c) Generation of species 4 and 5.
4 Conclusion

In conclusion, the radiolytic stability and thermal stability of three pillar[5]arene-based diglycolamides (neat 1a and 1a–1c in molecular diluent) were investigated by various techniques including $^1$H NMR, TG, GC, HPLC and ESI-MS. Owing to the sensitization effect of 1-octanol on P5DGAs radiolysis, the P5DGAs dissolved in 1-octanol present a worse radiolytic stability in comparison with the neat P5DGAs. Based on the analysis by both high-resolution ESI-MS and $^1$H NMR, dealkylation of the isopropyl chain and breakage of amide or ether linkage on P5DGAs lead to the formation of radiolytic products containing secondary amine and phenolic hydroxyl groups. Additionally, the gas radiolytic products of P5DGAs were confirmed to be H$_2$, N$_2$, CO and gaseous hydrocarbons. The amount of gaseous hydrocarbons for P5DGAs in an argon atmosphere is much higher than that in an air atmosphere. Based on the analysis of the radiolytic products of P5DGAs and control compound 2a, the possible pathway of their radiolytic and chemical degradations was proposed, from which the degradation is speculated to occur at the most vulnerable bonds associated with ether and amide moieties of the diglycolamide functional groups, including $O_{ether}$–CH$_2$, $C_{carbonyl}$–N, and $C_{isopropyl}$–N bonds. Results from the solvent extraction experiments reveal that P5DGAs still show about 50% efficiency towards Eu$^{3+}$ at 500 kGy. The present study provides useful information for understanding the mechanism of irradiation-induced degradation of P5DGAs, which is helpful for designing new extractant with excellent radiation stability for spent fuel reprocessing.

Acknowledgments: We are grateful to the National Natural Science Foundation of China (No. 21876121), Open Project of Key Laboratory for Radiation Physics and Technology of Ministry of Education (2018SCURPT11) and Sichuan Institute of Atomic Energy for providing the Cobalt-60 gamma-irradiation facility.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: We are grateful to the National Natural Science Foundation of China (No. 21876121), Open Project of Key Laboratory for Radiation Physics and Technology of Ministry of Education (2018SCURPT11) and Sichuan Institute of Atomic Energy for providing the Cobalt-60 gamma-irradiation facility.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Zhang H. C., Liu Z. N., Zhao Y. L. Pillararene-based self-assembled amphiphiles. Chem. Soc. Rev. 2018, 47, 5491–5528.
2. Kakuta T., Yamagishi T. A., Ogoshi T. Stimuli-responsive supramolecular assemblies constructed from pillar[n]arenes. Acc. Chem. Res. 2018, 51, 1656–1666.
3. Liu Z. C., Nalluri S. K. M., Stoddart J. F. Surveying macrocyclic chemistry: from flexible crown ethers to rigid cyclophanes. Chem. Soc. Rev. 2017, 46, 2459–2478.
4. Wu X., Duan Q. P., Ni M. F., Hu X. Y, Wang L. Y. Recent advances of (pseudo) rotaxanes constructed by pillar[n]arenes. Chin. J. Org. Chem. 2014, 34, 437–449.
5. Cao D. Y., Kou Y. H., Liang J. Q., Chen Z. Z., Wang L. Y., Meier H. A facile and efficient preparation of pillararenes and a pillarcyclonine. Angew. Chem. Int. Ed. 2009, 48, 9721–9723.
6. Chen L. X., Cai Y. M., Feng W., Yuan L. H. Pillararenes as macrocyclic hosts: a rising star in metal ion separation. Chem. Commun. 2019, 55, 7883–7898.
7. Ogoshi T., Kanai S., Fujinami S., Yamagishi T. A., Nakamoto K. Para-bridged symmetrical pillar[5]arenes: their Lewis acid catalyzed synthesis and host-guest property. J. Am. Chem. Soc. 2008, 130, 5022–5023.
8. Fang Y. Y., Wu L., Liao J. L., Chen L., Yang Y. C., Liu N., He L. T., Zou S. L., Feng W., Yuan L. H. Pillar[5]arene-based phosphine oxides: novel ionophores for solvent extraction separation of f-block elements from acidic media. RSC Adv. 2013, 3, 12376–12383.
9. Fang Y. Y., Yuan X. Y., Wu L., Peng Z. Y., Feng W., Liu N., Xu D. G., Li S. I, Sengupta A., Mohapatra P. K., et al. Ditopic CMPO-pillar[5]arenes as unique receptors for efficient separation of americium(III) and europium(III). Chem. Commun. 2015, 51, 4263–4266.
10. Chen L. X., Wang Y., Wan Y. S., Cai Y. M., Xiong Y. Q., Fan Z. W., Conradson S. D., Fu H. Y., Yuan L. H., Feng W. Highly efficient and selective pillararene-based organic materials for Hg$^{2+}$ and CH$_3$Hg$^+$ extraction from aqueous solution. Chem. Eng. J. 2020, 387, 124087.
11. Daniel W., Andreas G., Giuseppe M., Robin T., Mark S., Andreas W. Applications of diglycolamide based solvent extraction processes in spent nuclear fuel reprocessing, part 1: TODGA. Solvent Extr. Ion Exch. 2018, 36, 223–256.

12. Sinharoy P., Khan P. N., Nair D., Jagasia P., Anitha M., Dhami P. S., Sharma J. N., Kaushik C. P., Banerjee K. Separation of americium (III) and strontium (II) using TEHDDGA and 18-crown-6. Radiochim. Acta 2017, 105, 265–273.

13. Sengupta A., Mohapatra P. K., Patil A. B., Kadam R. M., Verboom W. Radiation stability of diglycolamide functionalized calix[4] arenes in ionic liquid: solvent extraction, EPR and GC-MS studies. Separ. Purif. Technol. 2016, 162, 77–83.

14. Ravi J., Venkatesan K. A., Antony M. P., Srinivasan T. G., Vasudeva Rao P. R. New unsymmetrical diglycolamide ligands for trivalent actinide separation. Radiochim. Acta 2014, 102, 609–618.

15. Ansari S. A., Pathak P., Mohapatra P. K., Manchanda V. K. Chemistry of diglycolamides: promising extractants for actinide partitioning. Chem. Rev. 2012, 112, 1751–1772.

16. Sengupta A., Mohapatra P. K., Iqbal M., Huskens J., Verboom W. A diglycolamide-functionalized task specific ionic liquid (TSIL) for actinide extraction: solvent extraction, thermodynamics and radiolytic stability studies. Separ. Purif. Technol. 2013, 118, 264–270.

17. Wu Y., Zhang Y. W., Fan F. Y., Luo H. M., Hu P. Z., Shen Y. L. Synthesis of task-specific ionic liquids with grafted diglycolamide moiety. Complexation and stripping of lanthanides. J. Radioanal. Nucl. Chem. 2013, 299, 1213–1218.

18. Jańczewski D., Reinhoudt D. N., Verboom W., Hill C., Allignol C., Duchesne M. T. Tripodal diglycolamides as highly efficient extractants for f-elements. New J. Chem. 2008, 32, 490–495.

19. Leoncini A., Ansari S. A., Mohapatra P. K., Boda A., Mashuraf Ali S., Sengupta A., Huskens J., Verboom W. Benzene-centered tripod diglycolamide synthesis, metal ion extraction, luminescence spectroscopy, and DFT studies. Dalton Trans. 2017, 46, 1431–1438.

20. Ansari S. A., Mohapatra P. K., Leoncini A., Huskens J., Verboom W., Ali S. M. Highly efficient N-pivot tripodal diglycolamide ligands for trivalent f-cations: synthesis, extraction, spectroscopy, and density functional theory studies. Inorg. Chem. 2019, 58, 8633–8644.

21. Huang H., Ding S. D., Liu N., Wu Y. X., Su D. P., Huang S. Extraction of trivalent americium and europium from nitric acid solution with a calixarene-based diglycolamide. Separ. Purif. Technol. 2014, 123, 235–240.

22. Ali S. M. Enhanced free energy of extraction of Eu³⁺ and Am³⁺ ions towards diglycolamide appended calix[4]arene: insights from DFT-D3 and COSMO-RS solvation models. Dalton Trans. 2017, 46, 10886–10898.

23. Wehbie M., Arracht G., Arrambide C. C., Karame I., Ghannam L., Pellet-Rostaing S. Organization of diglycolamides on resorcinarene cavitation and its effect on the selective extraction and separation of HREES. Separ. Purif. Technol. 2017, 187, 311–318.

24. Sasaki Y., Sugo Y., Suzuki S., Tachimori S. The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO₃-n-dodecane system. Solvent Extr. Ion Exch. 2001, 19, 91–103.

25. Modolo G., Asp H., Schreinemachers C., Vijgen H. Development of a TODGA based process for partitioning of actinides from a PUREX raffinate part I: batch extraction optimization studies and stability tests. Solvent Extr. Ion Exch. 2007, 25, 703–721.

26. Wu L., Fang Y. Y., Jia Y. M., Yang Y. Y., Liao J. L., Liu N., Yang X. S., Feng W., Ming J. L., Yuan L. H. Pillar[5]arene-based diglycolamides for highly efficient separation of americium(III) and europium(III). Dalton Trans. 2014, 43, 3835–3838.

27. Li C. X., Wu L., Chen X. Y., Yuan X. Y., Cai Y. M., Feng W., Liu N., Ren Y., Sengupta A., Murali M. S., et al. Highly efficient extraction of actinides with pillar[5]arene-derived diglycolamides in ionic liquids via a unique mechanism involving competitive host-guest interactions. Dalton Trans. 2016, 45, 19299–19310.

28. Horne G. P., Gregson C. R., Sims H. M., Orr R. M., Taylor R. J., Pimblott S. M. Plutonium and americium alpha radiolysis of nitric acid solutions. J. Phys. Chem. B 2017, 121, 883–889.

29. Ao Y. Y., Peng J., Zhang Y. W., Yuan L. Y., Yu C. H., Li J. Q., Zhai M. L. The radiolytic behavior and mechanism of calixarene crown ether under γ-irradiation. Chin. Sci. Bull. 2013, 58, 1663–1669.

30. Sengupta A., Yuan X. Y., Feng W., Gupta N. K., Yuan L. H. Highly efficient extraction of tetra- and hexavalent plutonium using DGA functionalized pillar[5]arene in RTIL: understanding speciation, thermodynamics and radiolytic stability. Separa. Sci. Technol. 2017, 52, 2767–2776.

31. Drader J. A., Boubals N., Cames B., Guillamont D., Guilbaud P., Saint-Louis G., Berthon L. Radiolytic stability of N,N-diakyl amide: effect on Pu(IV) complexes in solution. Dalton Trans. 2018, 47, 251–263.

32. Geng J. S., Wang Y., Yang B., Yuan L. H., Feng W. Radiation stability of alkylated pillar[5]arenes. Radiat. Phys. Chem. 2019, 161, 1–8.

33. Geng J. S., Wang Y., Cai Y. M., Yang B., Yuan L. H., Feng W. Radiation stability of phosphine oxide functionalized pillar[5]arene. Radiochim. Acta 2019, 107, 713–724.

34. Chen L. X., Wang Y., Yuan X. Y., Ren Y., Liu N., Yuan L. H., Feng W. Highly selective extraction of uranium from nitric acid medium with phosphine oxide functionalized pillar[5]arenes in room temperature ionic liquid. Separ. Purif. Technol. 2018, 192, 152–159.

35. Li H., Chen D. X., Sun Y. L., Zheng Y. B., Tan L. L., Weiss P. S., Yang Y. W. Viologen-mediated assembly of and sensing with carboxylatopillar[5]arene-modified gold nanoparticles. J. Am. Chem. Soc. 2013, 135, 1570–1576.

36. Al-Azemi T. F., Vinodh M., Alipour F. H., Mohamod A. A. An alternative route for the synthesis of hydroxylated pillar[5]arene-based amphiphiles. Org. Biomol. Chem. 2018, 16, 7513–7517.

37. Ao Y. Y., Yuan W. J., Pan Q., Wang Y., Chen J., Zhao L., Li J. Q., Zhai M. L. Radiolysis of alkyl substituted tridentate 2,6-bis(1,2,4-triazine-3-yl)pyridines: an experimental study with DFT validation. New J. Chem. 2018, 42, 18395–18401.

38. Dalterio R., Huang X. H., Yu K. L. Infrared and nuclear magnetic resonance spectroscopic study of secondary amide hydrogen bonding in benzoyl PABA derivatives (retinoids). Appl. Spectrosc. 2007, 61, 603–607.

39. Heller C. A., Gordon A. S. Isopropyl radical reactions. I. Photolysis of diisopropyl ketone. J. Phys. Chem. 1956, 60, 1315–1318.

40. Heller C. A., Gordon A. S. Isopropyl radical reactions. III. Reactions with hydrogen atoms. J. Phys. Chem. 1960, 64, 390–394.

41. Shi J. C., Barker J. R. Odd oxygen formation in the laser irradiation of O₂ at 248 nm: evidence for reactions of O₂ in the Herzberg states with ground state O₂. J. Geophys. Res. 1992, 97, 13039–13050.
42. Ao Y. Y., Wang Q., Peng J., Huang W., Zhai M. L., Long X. G. Influence of atmosphere on the radiolysis products of BPC6 under γ-irradiation. *Acta Phys. Chim. Sin.* 2013, 29, 418–422.
43. Sugo Y., Izumi Y., Yoshida Y., Nishijima S., Sasaki Y., Kimura T., Sekine T., Kudo H. Influence of diluent on radiolysis of amides in organic solution. *Radiat. Phys. Chem.* 2007, 76, 794–800.
44. Galán H., Nunez A., Espartero A. G., Sedano R., Durana A., De Mendoza J. Radiolytic stability of TODGA: characterization of degraded samples under different experimental conditions. *Procedia Chem.* 2012, 7, 195–201.
45. Sugo Y., Sasaki Y., Tachimori S. Studies on hydrolysis and radiolysis of N,N,N,N-tetraoctyl-3-oxapentane-1,5-diamide. *Radiochim. Acta* 2002, 90, 161–165.
46. Galán H., Zarzana C. A., Wilden A., Núñez A., Schmidt H., Egberink R. J. M., Leoncini A., Cobos J., Verboom W., Modolo G., et al. Gamma-radiolytic stability of new methylated TODGA derivatives for minor actinide recycling. *Dalton Trans.* 2015, 44, 18049–18056.
47. Zarzana C. A., Groenewold G. S., Mincher B. J., Mezyk S. P., Wilden A., Schmidt H., Modolo G., Wishart J. F., Cook A. R. A comparison of the γ-radiolysis of TODGA and T(EH)DGA using UHPLC-ESI-MS analysis. *Solvent Extr. Ion Exch.* 2015, 33, 431–447.

**Supplementary material:** Supplementary material to this article can be found online at [https://doi.org/10.1515/ract-2020-0049](https://doi.org/10.1515/ract-2020-0049).