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Gamma radiolysis of the highly selective ligands $CyMe_4BTBP$ and $CyMe_4BTPhen$: Qualitative and quantitative investigation of radiolysis products

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Abstract

The highly selective nitrogen donor ligands $CyMe_4BTBP$ and $CyMe_4BTPhen$ where γ-irradiated under identical experimental conditions in 1-octanol with and without contact to nitric acid solution. Subsequently, solvent extraction experiments were carried out to evaluate the stability of the extractants against γ-radiation monitoring Am(III) and Eu(III) distribution ratios. Generally, decreasing distribution ratios with increasing absorbed dose were detected for both molecules. Furthermore, qualitative mass spectrometric analyses were performed and ligand concentrations were determined by HPLC-DAD after irradiation to investigate the radiolysis mechanism. An exponential decrease with increasing absorbed dose was observed for both ligands with a faster rate for $CyMe_4BTPhen$. Main radiolysis products indicated the addition of one or more diluent molecules (1-octanol) to the ligand via prior production of α-hydroxyoctyl radicals from diluent radiolysis. The addition of nitric acid during the irradiation lead to a remarkable stabilization of the system, as the extraction of Am(III) and Eu(III) did not change significantly over the whole examined dose range. Quantification of the remaining ligand concentration on the other hand showed decreasing concentrations with increasing absorbed dose. The stabilization of D values is therefore explained by the formation of 1-octanol addition products which are also able to extract the studied metal ions.

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1. Introduction

Within the past and current European research on the development of new separation processes for the partitioning of minor actinides (MA: Np, Am and Cm) from highly active nuclear waste solutions, the group of BTBPs was developed and found to be very efficient. Especially the separation of the trivalent actinides Am(III) and Cm(III) from trivalent lanthanides (Ln(III)) is crucial. Therefore, the group of soft nitrogen donor ligands such as BTBPs is very promising, since it also fulfills the CHON principle.[1] Radiolytic as well as chemical stability are important aspects for a potential ligand application in industrial partitioning processes. The annulated 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands appeared to be more stable against radiolytic degradation than the tetra-*n*-alkyl substituted derivatives such as C5-BTBP.[2-4] The $CyMe_4BTBP$ (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-[2,2']-bipyridine) ligand (Fig. 1a) was successfully studied and finally chosen as European reference molecule for MA partitioning.[3, 5-8] Due to rather slow extraction rates of $CyMe_4BTBP$, a derivative, $CyMe_4BTPhen$ (2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-1,10-phenan-throline) (Fig. 1b), was invented. This new ligand showed faster extraction kinetics, which is caused by its rigidity and the juxtaposition of the N-donor atoms in *cis* conformation that leads to a faster as well as thermodynamically favored complex formation.[9-11]

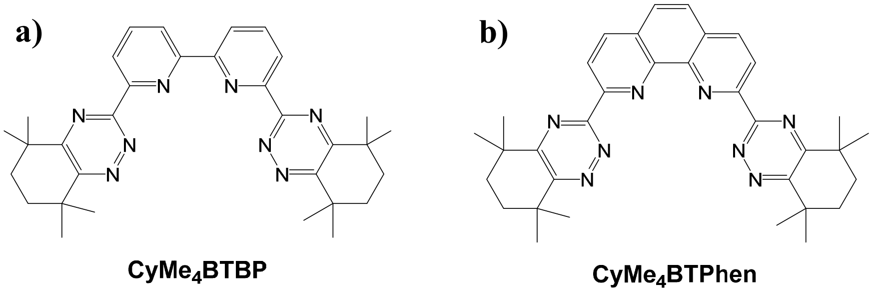

Fig. 1: Investigated ligand molecules $CyMe_4BTBP$ (a) and $CyMe_4BTPhen$ (b), which were irradiated as 10 mmol/L solutions in 1-octanol.

In this paper, we will study and compare the radiolytic stability of the before mentioned ligands $CyMe_4BTBP$ and $CyMe_4BTPhen$ and its influence on the actinide/lanthanide extraction. Therefore, radiolysis experiments were conducted at the Department of Chemical and Biochemical Engineering at the Chalmers University of Technology in Gothenburg, Sweden. A description of the gamma radiolysis experiments as well as liquid-liquid extraction can be found in our previous work.[12] Furthermore, quantitative and qualitative analyses were performed and the influence of nitric acid contact during irradiation was investigated. These measurements were done at the Institute of Inorganic Chemistry, Academy of Sciences, Husinec-Rež, Czech Republic.[12-13]

2. Results and Discussion

$CyMe_4BTBP$ and $CyMe_4BTPhen$ were irradiated in parallel (^{60}Co, dose rate ~9.5 kGy/h) in 1-octanol solution (10 mmol/L) with and without contact to 1.0 mol/L nitric acid. Liquid-liquid extraction studies were performed and distribution ratios of ^{241}Am and ^{152}Eu were measured. For both ligands, decreasing Am(III)/Eu(III) D-values were observed with increasing absorbed dose, while $CyMe_4BTPhen$ started at higher initial distribution ratios (Fig. 2, filled symbols). This effect did not occur when the organic phase was irradiated in contact with a 1.0 mol/L nitric acid solution (Fig. 2, open symbols). Under these conditions, distribution ratios for both nuclides remained high. For $CyMe_4BTPhen$ in contact with nitric acid, an increasing/ decreasing behavior in the low-dose area for D_{Am} was observed. This phenomenon could be attributed to a radiolytic buildup of extracting species (increasing D-values), which are prone to radiolysis themselves with increasing absorbed dose (decreasing D-values).

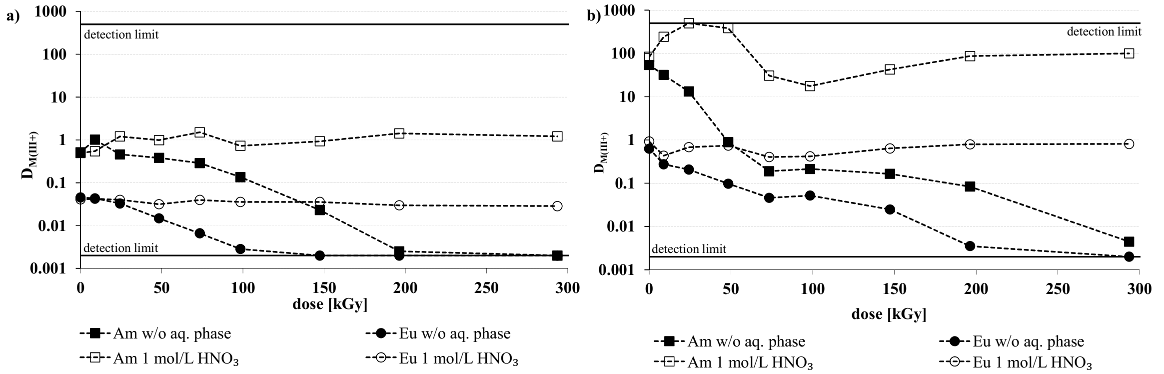

Fig. 2: Distribution ratios of ^{241}Am and ^{152}Eu as function of absorbed dose. Extraction experiment after γ- radiolysis of 10 mmol/L $CyMe_4BTBP$ (a, left) and $CyMe_4BTPhen$ (b, right) in 1-octanol. Irradiation was conducted as pure organic solution (filled symbols) and as organic solution in contact to 1.0 mol/L HNO_3 (open symbols).

Additional to solvent extraction studies, we conducted mass spectrometric measurements of the irradiated samples. Results for the $CyMe_4BTBP$ ligand can be found in Fig. 3 and data for the $CyMe_4BTPhen$ ligand are presented in Fig. 4 (with M = $CyMe_4BTBP$/ $CyMe_4BTPhen$ and X = α-hydroxyoctyl moiety, RC•HOH). Irradiation experiments of both ligands in contact with 1.0 mol/L nitric acid led to less different radiolysis products (Fig. 3b, Fig. 4b). Detected m/z ratios correspond mainly to addition products of the organic diluent, 1-octanol on the ligand molecules (X). These species (M+X, M+2X, M+3X) were also present in organic samples irradiated without nitric acid contact, but especially the M+X species could only be found in lower intensities.

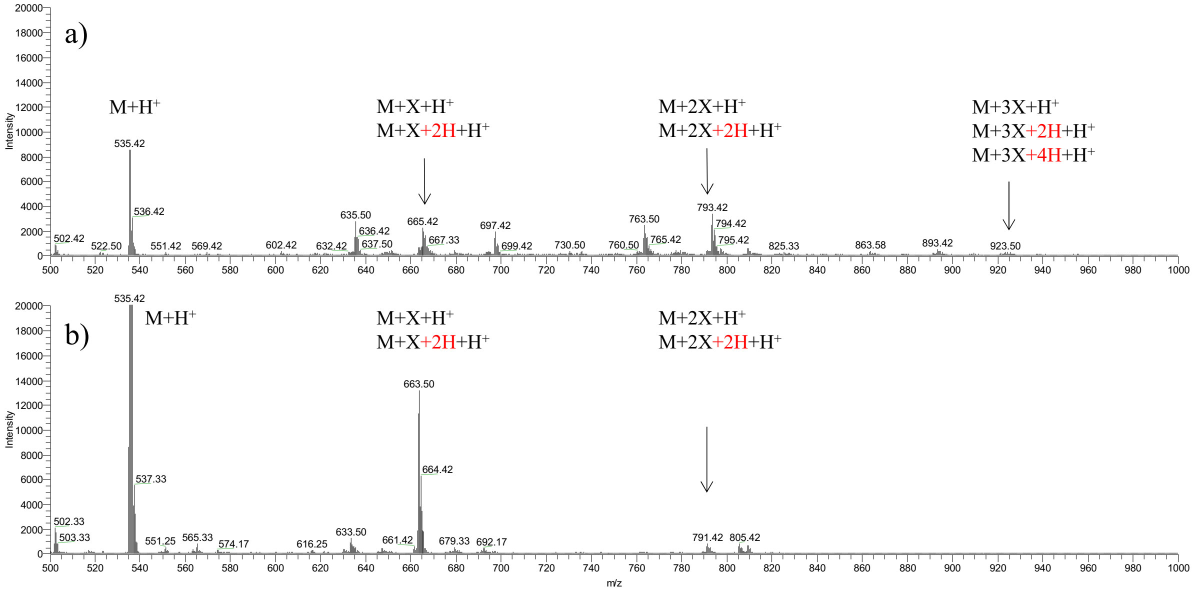

Fig. 3: Mass spectra of 10 mmol/L <u>$CyMe_4BTBP$</u> in 1-octanol irradiated as organic solution without a) and with b) contact to 1.0 mol/L HNO_3. Absorbed dose: 100 kGy. (Data were presented before)[12]

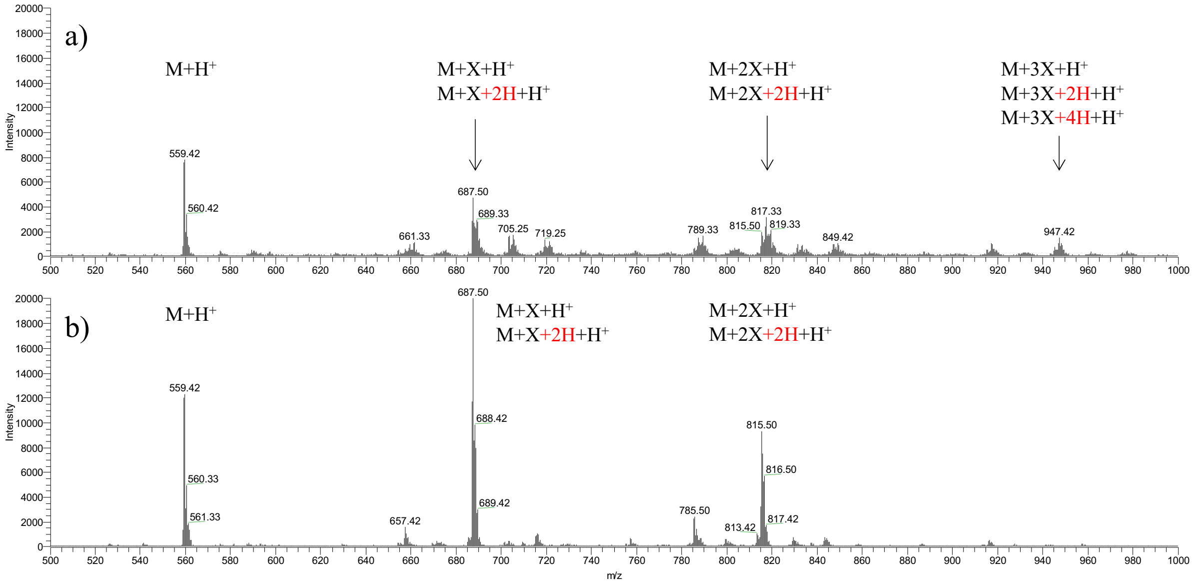

Fig. 4: Mass spectra of 10 mmol/L CyMe$_4$BTPhen in 1-octanol irradiated as organic solution without a) and with b) contact to 1.0 mol/L HNO$_3$. Absorbed dose: 100 kGy.

Furthermore, in irradiated solvents without nitric acid contact (Fig. 3b, Fig. 4b), the 1-octanol addition products were mainly formed with +2 and +4 higher mass units than the predicted molar masses (m/z ratio, z= 1) of 1-octanol addition products. These products could also be found in irradiated organic solutions in contact with nitric acid, but in contrast, the “pure” M+X, M+2X and M+3X species were the dominant products here. The mechanism of alcohol radiolysis was described before:[14-17]

$$\mathrm{RCH_2OH} + \gamma \rightarrow [\mathrm{RCH_2OH}]^{*} \tag{1}$$

$$[\mathrm{RCH_2OH}]^{*} \rightarrow \mathrm{e^{-}_{solv}} + [\mathrm{RCH_2OH}]^{\bullet +} \tag{2}$$

$$\mathrm{e^{-}_{solv}} + \mathrm{RCH_2OH} \rightarrow \mathrm{RCH_2O^{-}} + \mathrm{H^{\bullet}} \tag{3}$$

$$[\mathrm{RCH_2OH}]^{\bullet +} \rightarrow \mathrm{RC^{\bullet}HOH} + \mathrm{H^{+}} \tag{4}$$

$$[\mathrm{RCH_2OH}]^{\bullet +} + \mathrm{RCH_2OH} \rightarrow \mathrm{RC^{\bullet}HOH} + \mathrm{RCH_2OH_2}^{+} \tag{5}$$

Following equations (1) and (2), a solvated electron and the octanol radical cation are formed during alcohol radiolysis. The solvated electron is able to react with new alcohol molecules resulting in hydrogen radicals (3) that are able to attack unsaturated bonds of the ligand molecules. This saturation leads to products with two mass units higher molar weight per saturated bond. When organic phases were irradiated in contact with nitric acid, hydrogen radicals and other reactive species were probably scavenged by $NO_2^{\bullet}$ and $NO_3^{\bullet}$ radicals that were formed during nitric acid radiolysis.[18] This scavenging reactions prevent double bonds from being saturated, in contrast to organic solutions irradiated without contact to nitric acid.

Equations (4) and (5) illustrate the formation of α-hydroxyoctyl radicals, which can further react with the extractants to form 1-octanol addition products observed in the MS spectra (Fig. 3 and Fig. 4). This observation of 1-octanol molecule addition to N-donor ligands was made before by Wilden *et al.*[17] For both ligands, not only addition products of one 1-octanol molecule were found, but also two- and three-fold addition products were detected (M+X, M+2X and M+3X), while the M+3X addition product was only found in irradiated samples of pure organic phase without contact to a nitric acid phase. The formation of those addition products has no adverse effect on extraction, since distribution ratios remained constantly high. Therefore, we predict the addition of 1-octanol radicals (X) takes place somewhere in the outer periphery of the molecules, as the nitrogen donor site binds to the metal ions. For sterical reasons, the pyridine moieties and the additional bond between those two in the CyMe₄BTPhen molecule should be the preferred addition positions. New simulation results from Koubský *et al.* indicate the meta position of the pyridine moiety as the most probable position in the CyMe₄BTBP molecule.[19]

Quantitative analyses were carried out to confirm this observation. Results can be found in Fig. 5, which shows decreasing concentrations for both ligands with increasing absorbed dose. After 196 kGy absorbed dose, nearly no ligand is left in both cases (CyMe₄BTBP: 1%, CyMe₄BTPhen: 0.5%). Irradiated samples in contact with nitric acid showed also decreasing ligand concentrations for both ligands, although the degradation was less severe. Especially CyMe₄BTBP was protected even at higher doses. After 293 kGy absorbed dose, 53% of the initial concentration were left, whereas only 7% CyMe₄BTPhen were remaining. This is in clear contrast to the results from solvent extraction (Fig. 2), which lets us conclude, that at least one of the new formed species is also able to extract Am(III) and Eu(III) to the organic phase.

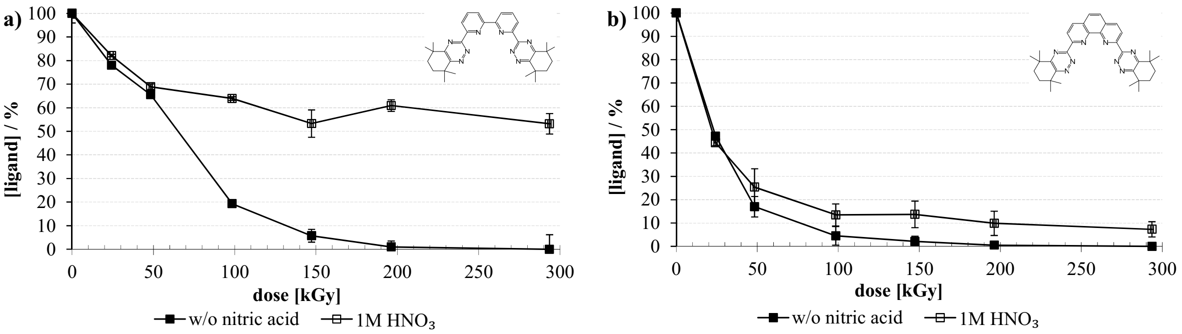

Fig. 5: Quantitative analysis of a) CyMe$_4$BTBP and b) CyMe$_4$BTPhen. Shown are irradiation experiments of neat organic solution (10 mmol/L ligand in 1-octanol) as filled symbols and organic solution in contact with 1.0 mol/L nitric acid as open symbols.

Conclusion

The highly selective soft N-donor ligands CyMe₄BTBP and CyMe₄BTPhen where compared and studied under identical conditions for their radiolytic stability. A significant protective effect when irradiated in contact with nitric acid was found for both ligand molecules, especially with regard to distribution ratios, which remained nearly constant. Mass spectrometric analyses showed mainly the formation of 1-octanol addition products. A partial hydrogenation of those addition products was observed, which is attributed to the formation of hydrogen, hydrogen atoms and other reducing species through diluent radiolysis. Quantification of the ligand species itself showed a higher stability of the CyMe₄BTBP ligand when irradiated in contact with acid in comparison to CyMe₄BTPhen, for which the protective effect was much smaller. This acid protecting effect could also be seen in mass spectrometric measurements in which much higher intensities of the addition products in comparison to pure ligand molecules were detected.

Acknowledgements

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References

1. Panak, P.J.; Geist, A. Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands. Chem. Rev. 2013, 113 (2), 1199-1236.
2. Hill, C.; Berthon, L.; Madic, C. Study of the stability of BTP extractants under radiolysis, Proceedings of GLOBAL 2005 2005, Tsukuba, Japan, 9-13 October, p 283.
3. Retegan, T.; Ekberg, C.; Englund, S.; Fermvik, A.; Foreman, M.R.S.; Skarnemark, G. The behaviour of organic solvents containing C5-BTBP and CyMe4-BTBP at low irradiation doses. Radiochim. Acta 2007, 95 (11), 637-642.
4. Fermvik, A.; Berthon, L.; Ekberg, C.; Englund, S.; Retegan, T.; Zorz, N. Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate. Dalton Trans. 2009,(32), 6421-6430.
5. Geist, A.; Hill, C.; Modolo, G.; Foreman, M.R.S.J.; Weigl, M.; Gompper, K.; Hudson, M.J.; Madic, C. 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine, an effective extracting agent for the separation of americium(III) and curium(III) from the lanthanides. Solvent Extr. Ion Exch. 2006, 24 (4), 463-483.
6. Magnusson, D.; Christiansen, B.; Foreman, M.R.S.; Geist, A.; Glatz, J.P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel, C. Demonstration of a SANEX Process in Centrifugal Contactors using the CyMe4-BTBP Molecule on a Genuine Fuel Solution. Solvent Extr. Ion Exch. 2009, 27 (2), 97-106.
7. Foreman, M.R.S.; Hudson, M.J.; Drew, M.G.B.; Hill, C.; Madic, C. Complexes formed between the quadridentate, heterocyclic molecules 6,6'-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III). Dalton Trans. 2006,(13), 1645-1653.
8. Retegan, T.; Ekberg, C.; Dubois, I.; Fermvik, A.; Skarnemark, G.; Wass, T.J. Extraction of Actinides with Different 6,6'-Bis(5,6-Dialkyl-[1,2,4]-Triazin-3-yl)-[2,2']-Bipyridines (BTBPs). Solvent Extr. Ion Exch. 2007, 25 (4), 417-431.
9. Lewis, F.W.; Harwood, L.M.; Hudson, M.J.; Drew, M.G.B.; Wilden, A.; Sypula, M.; Modolo, G.; Vu, T.-H.; Simonin, J.-P.; Vidick, G.; Bouslimani, N.; Desreux, J.F. From BTBPs to BTPhens: The Effect of Ligand Pre-Organization on the Extraction Properties of Quadridentate Bis-Triazine Ligands. Proc. Chem. 2012, 7, 231-238.
10. Lewis, F.W.; Harwood, L.M.; Hudson, M.J.; Drew, M.G.B.; Hubscher-Bruder, V.; Videva, V.; Arnaud-Neu, F.; Stamberg, K.; Vyas, S. BTBPs versus BTPhens: some reasons for their differences in properties concerning the partitioning of minor actinides and the advantages of BTPhens. Inorg. Chem. 2013, 52 (9), 4993-5005.
11. Lewis, F.W.; Harwood, L.M.; Hudson, M.J.; Drew, M.G.B.; Desreux, J.F.; Vidick, G.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.-H.; Simonin, J.-P. Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-triazine Ligand. J. Am. Chem. Soc. 2011, 133 (33), 13093-13102.
12. Schmidt, H.; Wilden, A.; Modolo, G.; Svehla, J.; Grüner, B.; Ekberg, C. Gamma radiolytic stability of CyMe4BTBP and effect of nitric acid. Nukleonika 2015, 60 (4), 879-884.
13. Fermvik, A.; Grüner, B.; Kvíčalová, M.; Ekberg, C. Semi-quantitative and quantitative studies on the gamma radiolysis of C5-BTBP. Radiochim. Acta 2011, 99 (2), 113-119.
14. Mincher, B.J.; Arbon, R.E.; Knighton, W.B.; Meikrantz, D.H. Gamma-ray-induced degradation of PCBs in neutral isopropanol using spent reactor-fuel. Appl. Radiat. Isot. 1994, 45 (8), 879-887.
15. Freeman, G.R. Radiolysis of alcohols. Actions Chim. Biol. Radiat. 1970, 14, 73-134.
16. Swallow, A.J. Radiation Chemistry of the Liquid State: (2) Organic Liquids. Chap. 11 in Radiation Chemistry - Principles and Applications, Farhataziz; Rodgers, M.A.J., VCH Verlagsgesellschaft mbH: Weinheim, Germany, pp 351-375, 1987.
17. Wilden, A.; Modolo, G.; Hupert, M.; Santiago-Schübel, B.; Löfström-Engdahl, E.; Halleröd, J.; Ekberg, C.; Mincher, B.J.; Mezyk, S.P. Gamma-radiolytic stability of solvents containing C5-BPP (2,6-Bis(5-(2,2-dimethylpropyl)-1H-pyrazol-3-yl)pyridine) for actinide(III)/lanthanide(III) separation. Solvent Extr. Ion Exch. 2016, 34 (1), 1-12.
18. Katsumura, Y. NO2• and NO3• Radicals in Radiolysis of Nitric Acid Solutions. Chap. 12 in The Chemistry of Free Radicals: N-Centered Radicals, Alfassi, Z.B., Wiley: Weinheim, pp 393-412, 1998.
19. Koubsky, T.; Schmidt, H.; Modolo, G.; Kalvoda, L. Simulation of UV/vis spectra of CyMe4-BTBP and some of its degradation products. Proc. Chem. 2016, same issue.