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## Simulation of UV/vis spectra of CyMe<sub>4</sub>BTBP and some of its degradation products

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### Abstract

Wet extraction and selective separation methods of actinide elements from highly active spent nuclear fuel constitutes a key step in the current waste reprocessing technologies. The quadridentate 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands (BTBPs) form a very promising group of extraction agents investigated at recent. Radiation decay process of one of the BTBPs representatives, CyMe<sub>4</sub>BTBP, is indirectly analyzed by simulating the UV-Visible absorption spectra of the original compound and one proposed possible CyMe<sub>4</sub>BTBP and 1-octanol adduct and comparing the obtained courses with experimentally observed data. Ab-initio TDDFT approach using 6-31++G(d,p) basis set and wB97X, CAM-B3LYP, LC-wPBE functionals is applied. Partial agreement of the simulated and experimental data is found and discussed.

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### 1. Introduction

During several past decades, much effort has been spent on development of wet extraction and selective separation methods of actinide elements from highly active spent nuclear fuel. The latter constitute a key step in the current waste reprocessing technologies.<sup>1</sup>

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One strategy for reducing the radiotoxicity of the remaining waste involves partitioning and transmutation of the long-lived minor actinides into shorter-lived or stable elements by neutron fission. However, it is, at first, necessary to separate the actinides from the lanthanides and other fission products due to the high cross sections of lanthanides for neutron capture. Therefore, separation of the radioactive minor actinides from the lanthanides itself represents one of the main challenges of today's nuclear waste reprocessing.<sup>2</sup>

It has been shown that ligands with soft N-donor atoms can distinguish between the actinides and lanthanides. Among others, the N-heterocyclic ligand class have emerged as a particularly promising one: the quadridentate 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands (BTBPs) with its representative CyMe<sub>4</sub>BTBP (Figure 1). In general, the BTBP ligands can be considered as currently the most suitable ligands for the herein mentioned separation tasks.<sup>3,4</sup>

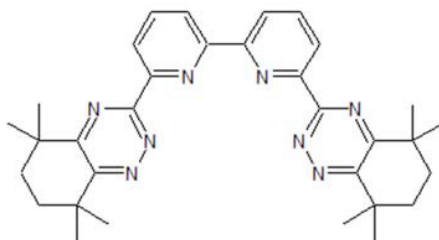


Figure 1: Chemical formula of CyMe<sub>4</sub>BTBP

To evaluate the applicability of extractants for process development, it is necessary to demonstrate not only their good extraction and selective properties, but also their resistance against degradation caused by contact of the extracting phase with highly radioactive solutions and highly concentrated nitric acid. Detailed investigation of the degradation mechanisms of CyMe<sub>4</sub>BTBP and identification of its degradation products is thus very desirable in relation to the further extraction process development.

In this paper, we present results of quantum mechanical simulations of one type of the expected major degradation products. The structure guess was made according to measured mass spectra of CyMe<sub>4</sub>BTBP 1-octanol solution before and after irradiation. Together with that, we present evolution of UV-Visible absorption spectra measured on the same experimental system and compare them with the simulated spectra calculated both for the pure CyMe<sub>4</sub>BTBP and the selected degradation product by several quantum mechanical simulation methods.

## 2. Computational / experimental details

For the geometrical optimizations, the Density Functional Theory (DFT) method was used as implemented in the Gaussian 09 code, with the hybrid exchange-correlation functional B3LYP<sup>5,6,7,8</sup> and the 6-31G(d,p) basis set. The PCM cavity approximation of solvent is used with 1-octanol.<sup>9</sup> For the simulation of UV-Visible absorption spectra, the time-dependent DFT (TDDFT) method was used together with the 6-31++G(d,p) basis and three different long range corrected exchange and correlation functionals: wB97X<sup>10</sup>, CAM-B3LYP<sup>11</sup>, and LC-wPBE<sup>12,13,14</sup>. These three different methods were used in order to evaluate the level of the possible dependence of the calculated electronic excitations on the applied ab-initio theory level. Comparison of the results obtained by the three selected widely used methods provides an estimate of such dependence. The relaxation level of transition state was confirmed by subsequent vibrational analysis.

## 3. Results and discussion

### 3.1. CyMe<sub>4</sub>BTBP molecular structure

As already shown, the free BTBP-type ligands are expected to adopt the 'trans' conformation (the molecule is close to C<sub>2h</sub> symmetry; trans-CyMe<sub>4</sub>BTBP in Figure 2), where the central bond between two pyridine rings comprises the center of symmetry; the 'cis' conformation (C<sub>2v</sub> point group) is less energetically favored.<sup>4,15</sup> The

results calculated for CyMe<sub>4</sub>BTBP confirmed such expectation: the ‘cis’ conformation is 5.7 kcal/mol higher in energy than the ‘trans’ conformation possessing the activation energy 8.1 kcal/mol. Accordingly, we further assume that majority of CyMe<sub>4</sub>BTBP molecules in the solution adopt the ‘trans’ conformation. The further investigation shows that also the torsion angle of the triazine-pyridine bonds plays a role in the total energy of the molecule. Turning of such bond by 180 degrees with respect to the complexing conformation (bond L; trans-CyMe<sub>4</sub>BTBP-L in Figure 2) causes the drop in energy of about 0.3 kcal/mol. Changing the torsion angle of the second triazine-pyridine bond has the same effect (see Table 1)

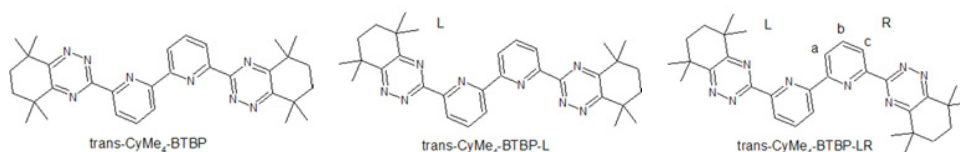


Fig. 2. Chemical conformations of CyMe<sub>4</sub>-BTBP. In the trans-CyMe<sub>4</sub>BTBP-LR structure, the probable position of the C8H<sub>17</sub>O group are marked (a, b, and c).

Table 1. Energy of different CyMe<sub>4</sub>BTBP conformations.

Molecular system	potential energy (kcal/mol)
trans-CyMe <sub>4</sub> BTBP-LR	0.00
trans-CyMe <sub>4</sub> BTBP-L	0.27
trans-CyMe <sub>4</sub> BTBP	0.63
cis-CyMe <sub>4</sub> BTBP	6.30

### 3.2. Prevailing reaction products

The HPLC-MS analysis of irradiated CyMe<sub>4</sub>BTBP solutions in 1-octanol showed that in such case no degradation of the distribution ratios occurs and the resulting solution contains, in addition to the original CyMe<sub>4</sub>BTBP molecules, some adduct of 1-octanol to CyMe<sub>4</sub>BTBP.<sup>16</sup> It is thus plausible to expect that the core structure of the adducts - involving the vicinity of the complexing nitrogen atoms - remains the same as in CyMe<sub>4</sub>BTBP. Based on this assumption, we have selected three positions where the octanol can be attached to the CyMe<sub>4</sub>BTBP molecule (see trans-CyMe<sub>4</sub>BTBP-LR in Figure 2) and optimized the structures (marked A, B, C in figure 3).

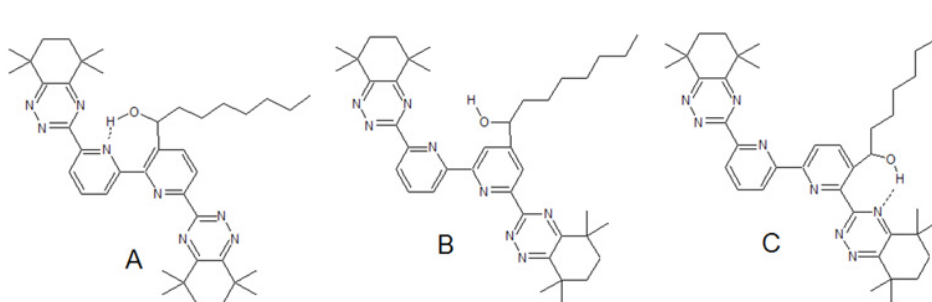


Fig. 3. Chemical structures of the investigated adducts of CyMe<sub>4</sub>BTBP and 1-octanol.

In this case, the role of torsion of the triazine-pyridine bond is further complicated by the interaction of the alpha-hydroxyoctyl function group with the remaining structure. Therefore, the core conformation is not identical in this case with the above described trans-CyMe<sub>4</sub>BTBP-LR conformation, most favorable in case of the original CyMe<sub>4</sub>BTBP molecule. After the geometrical optimization, the energy of formation was calculated and compared

for all three structures. The obtained energetic difference between the structures A, B, C is small, presumably comparable to the energy of thermal vibrations.

Assuming that the attachment of the alpha-hydroxyoctyl group runs through the nucleophilic substitution, the most susceptible position of the reaction should be position 'b' thanks to the inductive effect. Surprisingly, the structure B is not the one showing the lowest energy. On the other hand, in structures A and C, the possibility of an H-bond creation between the alpha-hydroxyoctyl group and the neighboring triazine or pyridine group arises equalizing likely the preference of the 'b' position and causing that the structures A and C can successfully compete with the structure B. The conformations of A, B, and C with the lowest energy are depicted in Figure 3 and their energy is presented in Table 2. Since the energy differences of the structures A, B, and C are small and significantly sensitive to small possible conformation changes, all three structures should be incorporated in further investigations.

Table 2. Energy of formation calculated for the optimized molecular structures.

Molecular system	potential energy (kcal/mol)
product A	0.00
product B	0.64
product C	4.00

### 3.3. UV-Visible absorption spectra

The experimental UV-Visible absorption spectra recorded before and after several different doses of gamma irradiation are presented in figure 4. With the absorbed dose increasing up to 200 kGy, the broad absorption bands between 220 - 300 nm decrease in intensity. Further irradiation results in a slight reversal of the intensity decay in the range of longer wavelengths (~ 240 - 320 nm). The short wavelengths absorption is steadily growing with the absorbed dose. Within a close vicinity of the wavelength point located at ca. 215 nm, the observed spectral courses corresponding to the different irradiation doses are intersecting, suggesting thus the possibility that the observed spectral changes can be interpreted by a chemical transition of the initial CyMe<sub>4</sub>BTBP molecules into a mixture of products characterized (in average) by a stronger extinction in the region at the "left" and a weaker extinction at the "right" from the intersection region. Remarkably, the spectrum measured after irradiation with 300 kGy dose digresses from the previous monotonic spectral evolution both in sense of the red shift of the intersection point and the reversal of the extinction decay in the region of wavelengths longer than 240 nm. Such behavior can suggest that the original CyMe<sub>4</sub>BTBP molecules are already depleted and some next step of the radiation decay starts to proceed.

In order to confirm selection of the representative products A, B, and C, the UV-Visible absorption spectra were simulated for both CyMe<sub>4</sub>BTBP and the chosen degradation products and the results compared with the experimental data. The spectra obtained for original CyMe<sub>4</sub>BTBP molecule are presented in figure 5. The result obtained with the wB97XD functional can be perhaps preferred because of a closer similarity of the calculated spectral course with the experimental one as well as due to the fact that the CAM-B3LYP functional has provided very similar results and supported the reliability of them.

The calculated envelope curves are featuring four absorption maxima within the studied region for LC-wPBE; the short-wavelength maximum predicted by xB97XD (~ 198 nm) is very weak and coincides with the shoulder of the stronger band localized at ca ~ 220 nm in case of the CAM-B3LYP. The spectra obtained with wB97XD and CAM-B3LYP are close to each other in the region of longer wavelengths but differ in the oscillator strength and position of the high energy band. Much weaker absorption of the latter is predicted by CAM-B3LYP. The spectral course calculated using LC-wPBE is comparable in shape to the ones obtained with wB97XD and CAM-B3LYP, but the positions of maxima show all a 15-20 nm blue shift. With exception of the results obtained with CAM-B3LYP functional, the simulated spectra contain the same number of absorption maxima as the experimental courses; however, the calculated band positions show all a significant blue shift (~ -30 nm for the spectra calculated with wB97XD and CAM-B3LYP) compared with the experimental ones. Energetic shift of such extent (0.3-0.4 eV) and direction have been already reported in connection with TDDFT simulations of electronic excitations in small organic molecules.<sup>17</sup>

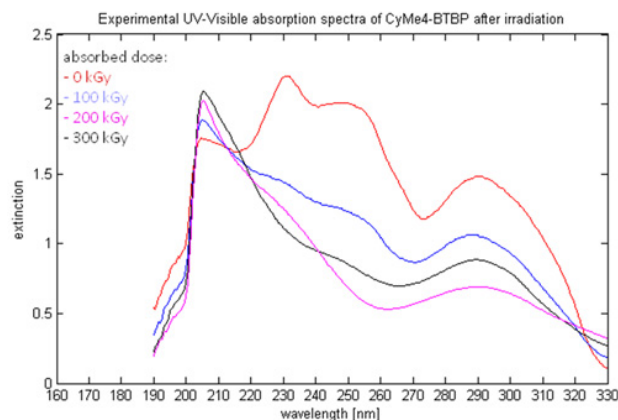


Fig. 4. Experimental absorption spectra of CyMe<sub>4</sub>BTBP in 1-octanol after various absorbed doses with absorption maxima at 205.0 nm, 231.5 nm, and 290.5 nm.

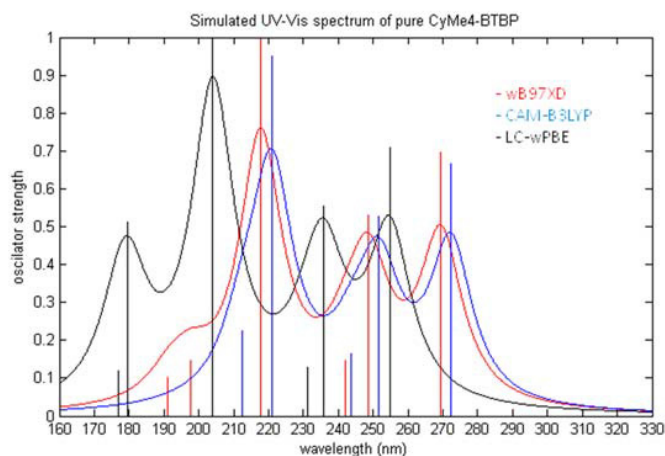


Fig. 5. Simulated absorption spectra of CyMe<sub>4</sub>BTBP by TDDFT / wB97XD, CAM-B3LYP, LC-wPBE.

Spectral positions of electronic transitions calculated for the molecular fragments A, B, and C (figure 6) are similar to those obtained for CyMe<sub>4</sub>BTBP but the computed oscillator strength of the most intense absorption band at ~ 220 nm is remarkably reduced. Again, the spectrum calculated with LC-wPBE is blue-shifted in respect to the two other spectra. The very weak maximum at the blue-side shoulder of the 220 nm band is missing in case of the C-structure and wB97XD and CAM-B3LYP functionals; however, the maximum is preserved in the LC-wPBE spectra. The apparent differences in the intensity and position of the two maxima at ~ 250 nm and ~ 270 nm between A, B, and C are probably linked to the different torsion angles of the triazine-pyridine bonds. The effect appears in the results obtained with all three applied theoretical methods. Taking in account the already mentioned systematic shift in energy between the calculated and experimental spectra, and the fact that the real experimental absorption spectrum is composed from contributions of all thermodynamically feasible molecular structures existing in the solution under test, the simulated spectra qualitatively agree with the observed evolution of the experimental spectra in the spectral region ~ 215-320 nm. On the other hand, the observed increase of extinction in the region of short wavelengths is not copied by the simulated spectra of the compounds A, B, and C. In this regard, the closest match provides the LC-wPBE functional.

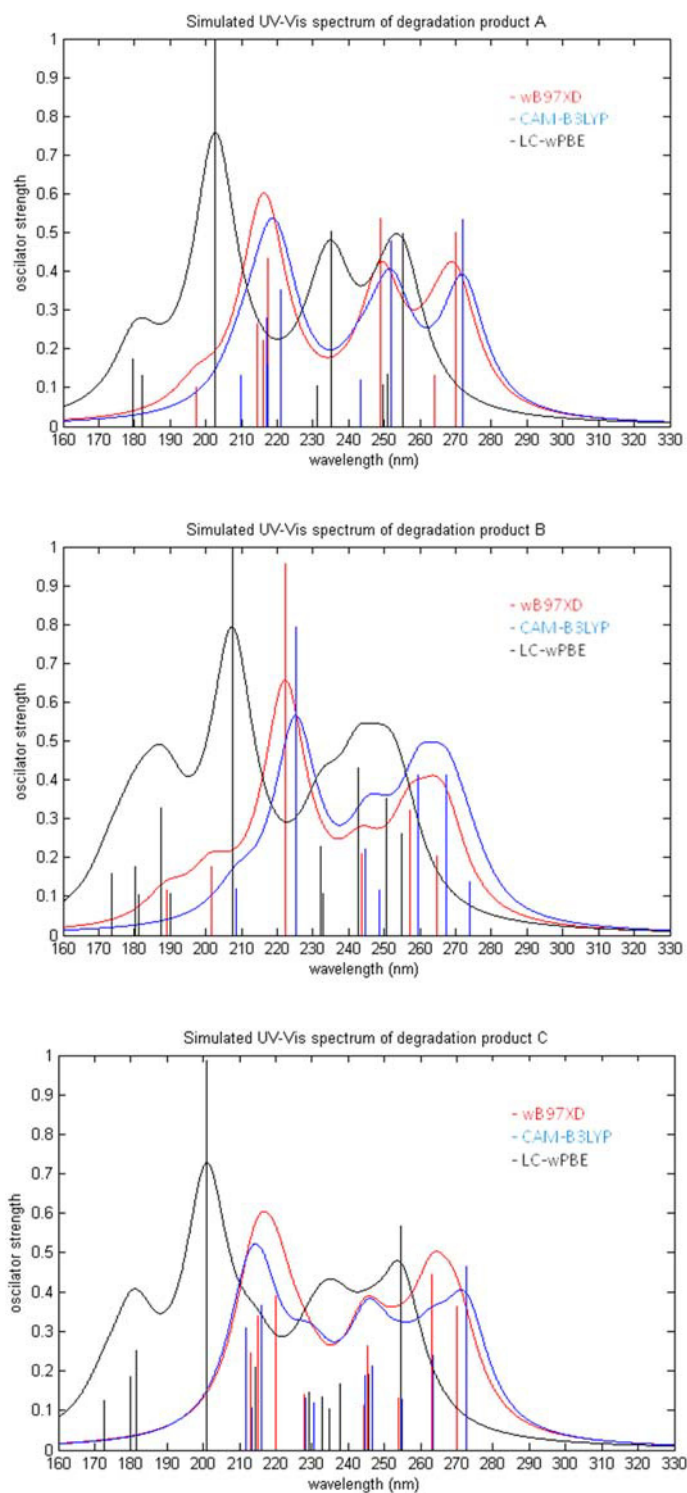


Fig. 6. Simulated absorption spectra of the structures A, B, and C by TDDFT / wB97XD, CAM-B3LYP, LC-wPBE.



Evaluation of the electronic transitions obtained with the wB97XD functional shows that the main excitations occur predominantly between the  $\pi$  orbitals energetically close to the HOMO and the  $\pi^*$  orbitals close to the LUMO (the details are not presented due to the restricted article extend). We furthermore note that because the dominant orbitals involved in the electronic transitions are only weakly affected by the presence of the 1-octanol chain, no substantial change of the UV-Vis. spectra can be expected due to the changing the binding positions 'a', 'b', and 'c'.

#### 4. Conclusions

The molecular structure of CyMe<sub>4</sub>BTBP and three possible degradation products were optimized by the quantum mechanical simulation methods and its molecular structure features were investigated. For the original structure and three probable degradation products selected on the basis of the HPLC-MS analysis, UV-Visible spectra were simulated and compared with the experimental results. The different simulation methods were found to be qualitatively in agreement. The changes in simulated spectra between the original ligand and the products with one 1-octanol group attached correlate at least qualitatively with the observed evolution of the experimental spectra at the longer measured wavelengths. However, the extinction enhancement with the absorbed dose that is observed at the high energy end of the experimental spectra has no adequate counterpart in the simulated results. Thus, a larger group of the possible products of the CyMe<sub>4</sub>BTBP radiation induced transformation must be considered and tested.

The real experimental spectra are measured at thermodynamic conditions allowing for existence of thermally excited molecular conformations contributed thus to the resulting spectral course. Fitting of the experimental spectrum by a simulated course constructed as a weighted average of the selected, most thermodynamically feasible molecular/conformation constituents could provide us with an improved level of the agreement between the experimental and the simulated results. Results obtained with the use of such procedure will be presented in the forthcoming article.

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#### References

1. Madic C. Overview of the Hydrometallurgical and Pyrometallurgical Processes Studied Worldwide for the Partitioning of High Active Nuclear Wastes. Proc. of OCDE-NEA 6th Information Exchange Meeting on P&T: Madrid; 2000, p. 53-6.
2. Mathur JN, Murali MS, Nash KL. Actinide partitioning - A review. *Solvent Extraction and Ion Exchange*. 2001; **19**: 357-390.
3. Geist A, Hill C, Modolo G, Foreman M, Weigl M, Gompfer K, Hudson MJ. 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 Extraction and Ion Exchange*. 2006; **24**: 463-483.
4. Foreman M, Hudson MJ, Drew MGB, 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 Transactions*. 2006; **13**: 1645-1653.
5. Becke AD. Density - functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993; **98**: 5648-5652.
6. Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*. 1988; **37**: 785-789.
7. Vosko SH, Wilk L, Nusair M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys.* 1980; **58**: 1200-1211.
8. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* 1994; **98**: 11623-11627.
9. Tomasi J, Mennucci B, Cammi R. 2005. Quantum mechanical continuum solvation models. *Chemical Review*. 2005; **105**: 2999-3093.
10. Chai JD, Head-Gordon M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* 2008; **128**: 084106.

11. Yanai T, Tew D, Handy N. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* 2004; **393**: 51-57.
12. Vydrov OA, Scuseria GE. Assessment of a long range corrected hybrid functional. *J. Chem. Phys.* 2006; **125**: 234109.
13. Vydrov OA, Heyd J, Krukau A, Scuseria GE. Importance of short-range versus long-range Hartree-Fock exchange for the performance of hybrid density functionals. *J. Chem. Phys.* 2006; **125**: 074106.
14. Vydrov OA, Scuseria GE, Perdew JP. Tests of functionals for systems with fractional electron number. *J. Chem. Phys.* 2007; **126**: 154109.
15. Lewis FW, Harwood LM, Hudson MJ, Drew MGB, 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. *Inorganic Chemistry*. 2013; **52**: 4993-5005.
16. Schmidt H, Wilden A, Modolo G, Švehla J, Grüner B, Ekberg C. Gamma radiolytic stability of CyMe<sub>4</sub>BTBP and the effect of nitric acid. *NUKLEONIKA* 2015; **60**: 879-884.
17. Furche F, Rappoport D. Density functional methods for excited states: equilibrium structure and electronic spectra. *Theoretical and Computational Chemistry*. 2005; **16**: 93–128.