Computational Simulation and Prediction to the Protonated Uranyl-Salophen Coordination with Cyclohexenone

Wenbo Lan¹, Yanbin Meng², Huiwen Zeng¹, Xiaofeng Wang¹*, Liping He¹, Bin Tan¹, Jianhuang Li³, Liping Wang¹, Ying He¹, Hui Zeng¹, Lei Wang¹
¹School of Public Health, Xiangnan University, Chenzhou, Hunan, 423043, China
²Basic Medical School, Xiangnan University, Chenzhou, Hunan, 423043, China
³Office of Network Information Technolog, Xiangnan University, Chenzhou, Hunan, 423043, China
*Corresponding author’s e-mail: wangxf2016@xnu.edu.cn

Abstract: In this study, computer simulation prediction technology was used to establish an interaction model between cyclohexene and protonated small molecules modified uranyl-Salophen. Theoretical simulation research the compounds using Uranyl-Salophen modified by methyl, vinyl and carboxyl-propenyl, with the cyclohexene complexes in vacuum condition, were performed by using density functional theory (DFT) at level with the B3LYP/6-311G* basis set. All of the combination structure is carried out under the same base group, in optimization, infrared spectrum, the binding energy, and the calculation of molecular orbital energy level. The results showed that the capacity and stability of complexes whose Uranyl-Salophen modified by carboxyl-propenyl was strongest, the vinyl followed, and the methyl weakest, and methyl modified even reduce the compounds combining ability.

1. Introduction
Uranium atoms have a special atomic structure and valence layer electron arrangement, and their 5f and 6d orbital energy levels are very close[1], therefore, its 5f can also participate in the formation of bonds with the ability to form multiple coordination bonds. Urany ions can form complexes with a four-twisted plane configuration with Salophen[2], in which uranium atoms can also coordinate with other atoms or groups[3-6]. Because the Uranyl-Salophen complex has a special rigid cavity structure, it produces a special molecular recognition function[7]. Some related studies have found that the association constant and catalytic recognition energy of salophen with one-sided benzene ring substituted by cyclohexone are higher than those of unsubstituted Uranyl-Salophen to cyclohexene[6, 7]. The association constant and catalytic recognition ability of ketene are large, and the most affected modification site of Uranyl-Salophen is located at the position corresponding to the substitution of the benzene ring. With the development of computational chemistry, the calculation accuracy of the density functional theory (DFT)[8, 9] of the B3LYP/6-311G* method has reached a fairly high-precision calculation level[10, 11], which was confirmed on the Uranyl-Salophen complex. According to related reports, computer simulation can replace some routine experiments, reducing the exploration of synthesis conditions and unnecessary reagents and manpower investment[12]. The accuracy of quantum chemistry calculations makes it instructive for experiments[13]. In this paper, the B3LYP/6-311G* method is used to optimize the structure, infrared spectra, binding energy and molecular orbital energy levels of the various possible coordination configurations shown in figure 1.
2. Research methods and content
Using Gaussian 09 quantum chemistry calculation software[14], using the B3LYP method in density functional theory (DFT)[15-17]. Therelativistic effects were taken into account by using small nuclear Relativistic pseudopotential ECP60MWB[18] for U atom, the 6-311G* basis set was used for atoms of C O and H. Various complexes formed by methyl, vinyl, and carboxypropenyl substituted Uranyl-Salophen and cyclohexenone were subjected to molecular simulations and theoretical calculations, and the structure was optimized under vacuum conditions, and the optimized complexes structural parameters, infrared spectroscopy, binding energy and molecular orbital energy levels are compared and analyzed.

3. Results and discussion

3.1. Configuration
The configuration of each complex formed by Uranyl-Salophen and cyclohexenone modified with methyl, vinyl, and carboxypropylene substrates was fully optimized under vacuum, and the structure was obtained as shown in figure 2. The basis for the substitution of each complex is shown in table 1.

| complexes    | Substituent type | complexes    | Substituent type                  |
|--------------|------------------|--------------|-----------------------------------|
| complex 0    | --               | complex ab   | methyl+vinyl                      |
| complex a    | methyl           | complex ac   | methyl+carboxypropenyl           |
| complex b    | vinyl            | complex bb   | vinyl+vinyl                       |
| complex c    | carboxypropenyl  | complex bc   | vinyl+carboxypropenyl            |
| complex aa   | methyl+methyl    | complex cc   | carboxypropenyl+carboxypropenyl  |

Table 1  Mulliken charge distribution of some atoms in three phenolic compounds
3.2. Infrared spectroscopy

The infrared spectrum of each complex is shown in figure 3. The frequency of each protonated modified Uranyl-Salophen and cyclohexenone complexes was calculated. The results show that there are no false frequencies in the normal vibration mode. This shows that after the molecular structure is fully optimized, each complex can exist stably[19]. It also shows that the geometric configurations of all Uranyl-
Salophen-cyclohexenone complexes are at the minimum point on the potential energy surface after optimization.

Figure 3  Infrared spectrum for complexes

It can be seen from the infrared data in the figure that the modification of the methyl group significantly reduces the conjugation of the C=O double bond and the C=C double bond. At the same time, the coordination ability between the O atom of cyclohexenone and U atom are weakened. While, the substitution of vinyl and carboxypropenyl is just the opposite, and the substitution of carboxypropenyl has more obvious effects on Uranyl-alophen to cyclohexenone. At the same time, the infrared data of Uranyl-Salophen and unmodified Uranyl-Salophen complexes were compared by comparing the infrared data of vinyl and carboxyl propylene substrates. Obviously, the formation of Uranyl-Salophen and cyclohexenone complex makes the original C=N double bond of Uranyl-Salophen and the stretching vibration of the aromatic ring skeleton move in the direction of large wave numbers, which indicates the interaction of Uranyl-Salophen and cyclohexyl ketene and its derivatives activates cyclohexenone and its complexes.

3.3. Molecular orbital energy

Table 3 shows the frontier molecular orbital energy $E_{HOMO}$, $E_{HOMO}$ and energy gap $\Delta E_{H-L}$ ($\Delta E_{H-L}$ is the absolute value of the difference between $E_{HOMO}$ and $E_{HOMO}$) of each complex. From the data in the table, we can see that the complex formed by Uranyl-Salophen modified by carboxypropenyl and cyclohexenone has a higher energy gap value than the corresponding complexes of vinyl and methyl modified Uranyl-Salophen. The energy gap of Uranyl-Salohen modified with propenyl group is larger than that of Uranyl-Salophen modified with monocarboxypropenyl group, and the energy gap of Uranyl-Salophen modified with divinyl group is higher than that of monovinyl-modified Uranyl-Salophen. The larger the energy gap, the more difficult it is for the outermost electrons to transition and the more stable the corresponding compound. From this analysis, we can see that the stability of each complex: complex c>complex b>complex a, and complex cc>complex c, complex bb >complex b.
### Table 3  The energy of $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $\Delta E_{\text{H-L}}$ for complexes.

| complexes | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $\Delta E_{\text{H-L}}$ | complexes | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $\Delta E_{\text{H-L}}$ |
|-----------|-----------------|-----------------|-----------------|-----------|-----------------|-----------------|-----------------|
| complex 0 | -5.5296         | -2.4487         | 3.0809          | complex ab| -5.4327         | -2.5089         | 2.9238          |
| complex a | -5.4621         | -2.5317         | 2.9304          | complex ac| -5.6178         | -2.7843         | 2.8335          |
| complex b | -5.4183         | -2.5101         | 2.9082          | complex bb| -5.4246         | -2.3475         | 3.0771          |
| complex c | -5.4836         | -2.3660         | 3.1176          | complex bc| -5.5887         | -2.6324         | 2.9563          |
| complex aa| -5.4466         | -2.4752         | 2.9714          | complex cc| -5.4521         | -2.3070         | 3.1451          |

#### 3.4. Binding energy

### Table 4  The binding energy of the complexes (kJ/mol)

| complexes | binding energy | complexes | binding energy |
|-----------|----------------|-----------|----------------|
| complex 0 | -69.31         | complex ab| -68.80         |
| complex a | -69.01         | complex ac| -77.49         |
| complex b | -70.08         | complex bb| -72.51         |
| complex c | -75.87         | complex bc| -75.74         |
| complex aa| -66.84         | complex cc| -85.31         |

Table 4 shows the binding energy values of protonated Uranyl-Salophen and cyclohexenone in each combination under the same base group. From the calculations in the table, it can be seen that when the protonation modification group is carboxypropyl or vinyl, the binding ability of Uranyl-Salophen and cyclohexenone is improved, and the increase of carboxypropyl is larger than that of vinyl. The more carboxypropyl or vinyl groups, the greater the increase in binding energy. However, when the protonated group is a methyl group, the binding ability of Uranyl-Salophen and cyclohexenone is weakened. And Uranyl-Salophen modified by dimethyl protonation has stronger binding ability to cyclohexenone than Uranyl-Salophen modified by monomethyl protonation.

### 4. Conclusion

The carboxenyl modified Uranyl-Salophen and cyclohexenone have the strongest ability and stability to form a complex, followed by vinyl, and the weakest methyl group, and the substitution of methyl groups even reduces the Uranyl-Salophen and cyclohexenone. The more carboxypropyl or vinyl groups, the greater the increase in binding energy and in molecular stability.

### Acknowledgments:

This work was supported by National Natural Science Foundation and National Social Science Foundation Key cultivation projects of Xiannan University [grant number 2020XJ08] and the Chenzhou City Heavy Metal Pollution Health Risk Assessment Technology Research and Development Center, and the Chenzhou City Science and Technology Innovation Ability Cultivation Project [zdyf201912].

### References

[1] Reis, R.D., Veiga, L.S.I., Escanhoela, C.A., Lang, J.C., Joly, Y., Gandra, F.G., Haskel, D., Souza-Neto, N.M. (2017) Unraveling 5f-6d hybridization in uranium compounds via spin-resolved L-edge spectroscopy. Nat. Commun., 8:1203.
[2] He, Y., Liao, L., Xu, C., Wu, R., Li, S., Yang, Y. (2015) Determination of ATP by resonance light scattering using a binuclear Uranyl complex and aptamer modified gold nanoparticles as optical probes. Microchim. Acta., 182:419-426.

[3] Lan, W., Gao, S., Lin, Y.W., Liao, L.F., Wang, X.F., Nie, C.M. (2016) Computational insight into complex structures of thorium coordination with N, N'-bis(3-allyl salicylidene) -o-phenylenediamine. J. Mol. Model., 22:224.

[4] Carugo, O. (2018) Structural features of uranium-protein complexes. J. Inorg. Biochem., 189:1-6.

[5] Ming, X., Frelon, S., Simon, O., Lobinski, R., Mounicou, S. (2014) Non-denaturing isoelectric focusing gel electrophoresis for uranium-protein complexes quantitative analysis with LA-ICP MS. Anal. Bioanal. Chem., 406:1063-1072.

[6] Warner, B.P., Scott, B.L., Burns, C.J., (2010) A Simple Preparative Route to Bis(imido)uranium(VI) Complexes by the Direct Reductions of Diazenes and Azides. Angew. Chem. Int. Ed. Engl., 37:959-960.

[7] Takao, K., Ikeda, Y. (2007) Structural characterization and reactivity of UO$_2$(salophen)L and [UO$_2$(salophen)]$: dimerization of UO$_2$(salophen) fragments in noncoordinating solvents (salophen=N,N' -disalicylidene-o- phenylenediaminate, L=N,N-dimethyl formamide, dimethyl sulfoxide). Inorg. Chem., 46:1550-62.

[8] Zhao, M., Liao, L., Wu, M., Li, Y., Xiao, X., Nie, C. (2012) Double-receptor sandwich supramolecule sensing method for the determination of ATP based on Uranyl-salophen complex and aptamer. Biosens. Bioelectron., 34:106-111.

[9] Szilagyi, R.K., Winslow, M.A. (2010) On the accuracy of density functional theory for iron-sulfur clusters. J. Comput. Chem., 27:1385-1397.

[10] Trickey, S.B., Alford, J.A., Boetgger, J.C. (2004) Chapter Methods and Implementation of Robust, High-Precision Gaussian Basis DFT Calculations for Periodic Systems: the GTOFF Code. J. Theor. Comput. Chem., 15:171-228.

[11] Glushkov, V.N. (2006) Optimum basis sets of spherical Gaussian functions and their structure for high-precision calculations of the energies of molecules in the Hartree-Fock approximation. Optics. Spectrosc., 100:807-817.

[12] Kim, S.J., Lee, C.S., Yeo, H.J., Cho, J.Y. (2002) Direct Numerical Simulation of Composite Structures. J. Compos. Mater., 36:2765-2785.

[13] Matlashov, A.N., Schultz, L.J., Espy, M.A., Kraus, R.H., Savukov, I.M., Volegov, P.L., Wurden, C.J. (2011) SQUIDs vs. Induction Coils for Ultra-Low Field Nuclear Magnetic Resonance: Experimental and Simulation Comparison. IEEE T. Appl. Supercon., 21:465-468.

[14] Malli, G. (1979) Spherical gaussian basis sets in relativistic quantum chemistry. Chem. Phys. Lett., 68:529-531.

[15] Perdew, J.P. (1986) Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys. Rev. B. Condens. Matter, 33: 8822-8824.

[16] Pan, Q.J., Schreckenbach, G., Arnold, P.L., Love, J.B. (2011) Theoretical predictions of cofacial bis(actiny1) complexes of a stretched Schiff-base calixpyrrole ligand. Chem. Commun., 47: 5720-5722.

[17] Pan, Q.J., Schreckenbach, G. (2010) Binuclear hexa- and pentavalent uranium complexes with a polypyrrolic ligand: a density functional study of water- and hydronium-induced reactions. Inorg. Chem., 49: 6509-17.

[18] Devlin, F.J., Stephens, P.J. (1994) Ab Initio Calculation of Vibrational Circular Dichroism Spectra of Chiral Natural Products Using MP2 Force Fields: Camphor. J. Am. Chem. Soc., 116:5003-5004.

[19] Pradhan, M., Basu, M., Sarkar, S., Pal, T. (2011) Solvent effect on the optical property of Uranyl acetylacetone monohydrate. Spectrochim. Acta A., 78: 205-210.