[Article]

doi: 10.3866/PKU.WHXB201504291

www.whxb.pku.edu.cn

采用 12 种密度泛函理论方法表征三种三价铀复合物

丁万见^{1,*} 方维海¹ 柴之芳^{2,3} 王东琪^{2,*}

(¹北京师范大学化学学院, 理论及计算光化学教育部重点实验室, 北京 100875; ²中国科学院高能物理研究所, 中国科学院核辐射与核能技术重点实验室, 北京 100049; ³苏州大学核药物与交叉科学学院, 江苏 苏州 215123)

摘要: 比较了 BP86、PBE、B3LYP、B3PW91、BHandHLYP、PBE0、X3LYP、CAM-B3LYP、TPSS、M06L、M06 和 M06-2X 等 12 种采用了广义梯度近似(GGA、hybrid GGA、*meta*-GGA 和 hybrid *meta*-GGA)的密度泛函理论(DFT)方法在三个三价铀复合物表征中的应用. 研究模型采用铀复合物催化 CO₂ 和 CS₂ 官能团化反应中的三个中间体 (Tp*)₂U-η¹-CH₂Ph (Cpd2), (Tp*)₂U-κ²-O₂CCH₂Ph (Cpd3) 和 (Tp*)₂U-κ²-S₂CCH₂Ph (Cpd4). 研究发现, B3LYP 和 B3PW91 在几何结构和电子结构方面优于其它方法. 基于分子轨道理论的 MP2 方法在 Cpd2 和 Cpd3 的表征中给出与 DFT 方法相近的结果, 而在 Cpd4 的表征中表现出较大的差异. 这可能是由于同样是单参考态方法的 MP2 捕捉到了与 DFT 方法不同的电子结构. 同时, 通过对比分别采用小核赝势(5f-in-valence)和大核赝势(5f-in-core)基组处理铀原子的计算结果, 发现对测试的模型体系, 两种处理方法可获得相近的热力学能量. 与以往主要关注高价态铀系复合物的处理方法的评估工作不同, 本项工作适应逐渐增加的对低价态铀系分子体系的研究的需求, 对 12 种常用的密度泛函理论方法在低价态铀系复合物研究中的应用进行了评估, 期望为处理类似体系的研究工作提供参考.

关键词: 密度泛函理论; 三价铀复合物; 铀系计算化学; QTAIM

中图分类号: O641

Performance of Twelve Density Functional Theory Methods in the Characterization of Three Trivalent Uranium Complexes

DING Wan-Jian^{1,*} FANG Wei-Hai¹ CHAI Zhi-Fang^{2,3} WANG Dong-Qi^{2,*}

(¹Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China; ²CAS Key Laboratory of Nuclear Radiation and Nuclear Energy Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R. China; ³School of Radiation Medicine and Interdisciplinary Sciences (RAD-X), Soochow University, Suzhou 215123, Jiangsu Province, P. R. China)

Abstract: We report a comparative study on the characterization of three trivalent uranium complexes using 12 density functional theory (DFT) methods, i.e., BP86, PBE, B3LYP, B3PW91, BHandHLYP, PBE0, X3LYP, CAM-B3LYP, TPSS, M06L, M06, and M06-2X, representing (*meta*-)GGA and hybrid (*meta*-)GGA levels of treatment of molecular systems. The MP2 method was used in single-point calculations to provide an *ab initio* view of the electronic structure. Three model systems in the experimental work on the activation of CO₂ and CS₂ by a trivalent uranium complex (Tp*)₂U-η¹-CH₂Ph (Cpd2) were used i.e., (Tp*)₂U-η¹-CH₂Ph (Cpd2), (Tp*)₂U-κ²-O₂CCH₂Ph (Cpd3), and (Tp*)₂U-κ²-S₂CCH₂Ph (Cpd4) (Tp=hydrotris(3,5-dimethylpyrazolyl)borate). The hybrid functionals, B3LYP and B3PW91, displayed good performance in view of both the geometrical and electronic

Received: January 7, 2015; Revised: April 29, 2015; Published on Web: April 29, 2015.

*Corresponding authors. DING Wan-Jian, Email: dingwanjian@bnu.edu.cn; Tel: +86-10-58804232. WANG Dong-Qi, Email: dwang@ihep.ac.cn; Tel: +86-10-88236606.

The project was supported by the National Natural Science Foundation of China (21073013, 91026000, 91226105) and Chinese Academy of Sciences Hundred Talent Program (Y2291810S3).

国家自然科学基金(21073013, 91026000, 91226105)和中国科学院“百人计划”(Y2291810S3)资助项目

作者强烈要求保留长度单位“Å”和能量单位“cal”, 其与国家法定计量单位的换算关系为: 1 Å=0.1 nm, 1 cal=4.184 J.

© Editorial office of Acta Physico-Chimica Sinica

structures. The MP2 method generated consistent results as DFT methods for Cpd2 and Cpd3, while provided an odd picture of the electronic structure of Cpd4 that may be due to its single determinant feature, leading to its capture of an electronic configuration of Cpd4 different from the one with the DFT methods. The use of a quasi-relativistic 5*f*-in-core ECP (LPP) treatment for U(III) in the thermodynamic calculations was supported by the calculations with a small-core ECP treatment (SPP) for U. Owing to increasing interests in low-valent actinide molecular systems, this work complements previous comparative studies, which mainly focus on high-valent actinide complexes, and provides timely information on the performance of 12 widely used DFT methods in studying low-valent actinide systems. It is expected to contribute to a more sensible selection of DFT methods in the study of low-valent actinide molecular systems.

Key Words: Density functional theory; Trivalent uranium complex; Computational actinide chemistry; QTAIM

1 Introduction

Actinides (actinoids in IUPAC convention) are unique in the sense of their fissile or fertile property¹ and their propensity to form novel type of chemical bonds with the participation of their 5*f* orbitals.^{2–11} These specific features, together with their radioactivity, some with short half-lifetime while others long, make the study of actinide chemistry a compelling need in nuclear fuel development, nuclear waste management,^{12–14} and homogeneous catalysis.^{15–18} To enrich our knowledge on the origin of their behavior, which may lead to the discovery of fundamental theories and the development of new applications, both experimental and computational scientists have walked into the field of actinide chemistry.

A key to master the actinide chemistry is to precisely understand the electronic structures and the bonding properties of actinides, which largely govern the behavior of actinides. To probe the electronic structures of actinide-containing molecular systems, advanced experimental techniques such as fluorescence^{19,20} and multi-photon ionization spectroscopy^{21,22} have been adopted and applied,²³ and this has significantly contributed to our deeper understanding on the chemical properties of actinides. However, due to the limit of size and time scale, and the extreme experimental conditions required in some cases, experimental techniques are not always able to provide sufficient information. On the other hand, theoretical and computational tools gain more and more attention for their obvious advantages in exploring the vast unknown fields where experiment studies are difficult, in many cases also dangerous to be conducted, and their applications in studying actinide-containing molecular systems have been reviewed.^{24–31} Compared to experimental tools, theoretical and computational methods, which stem from strict mathematical formulation, may pave a road with relatively higher efficiency in view of cost.

A precise understanding of the electronic properties of actinides relies on an accurate description of the electronic structures of the model systems containing actinides. Over the years, thanks to the continuous endeavors of pioneer scientists, significant progress in the development of new theoretical methods and their applications in organometallic chemistry has been witnessed. Among these methods, density functional theory (DFT) is increasingly applied

for the sake of its acceptable accuracy and affordable computational cost, if used properly, and its application in organometallics has been reviewed by, for example, Cramer and Truhlar.³²

The great success of DFT in studying chemistry does not eliminate the necessity to benchmark the functionals to be used on molecular systems with new types of interactions. As reported before,^{33–35} functionals of local spin-density approximation (LSDA) or generalized gradient approximation (GGA) are based on the localized model exchange correlation holes, which are actually fully nonlocal, and the successful case studies of DFT are in general believed to have a cancellation of errors between the exchange and the correlation. This raises an alarm on un-validated model systems where benchmark should be carefully carried out to avoid erroneous results due to incomplete cancellation of errors.

In recent years, many groups have conducted comparative studies^{36–43} in order to evaluate the performance of DFT methods on the description of actinide molecular systems. In an evaluation of several wave function based methods, including CASPT2, CCSD, and CCSD(T), and several DFT methods, Gagliardi *et al.*⁴¹ showed that MPW3LYP, B3LYP, M05, and M06 gave mean unsigned errors similar to CASPT2, CCSD, and CCSD(T) for actinide-oxygen bond energies and for ionization potentials of actinide oxides and their cations.

In the latest benchmark of the relativistic time-dependent DFT (TDDFT) on uranyl systems including UO_2^{2+} , NUO^+ , and NUN , Tecmer *et al.*⁴³ examined the performance of local density approximation (LDA), GGA (PBE, BLYP), *meta*-GGA (M06L), hybrid GGA (B3LYP, PBE0), hybrid *meta*-GGA (M06, M06-2X), range-separated hybrid GGA (CAM-B3LYP) functionals, and model potentials (SAOP), and concluded that by taking the CASPT2 and the intermediate Hamiltonian Fock-space coupled cluster (IHFSCC) results as the references, both the hybrid GGA and hybrid *meta*-GGA functionals outperform the others, suggesting the importance of Hartree-Fock (HF) exchange.

The above benchmark work suggests that in general hybrid density functional theory methods are better choice towards descriptions of actinide molecular systems and give results more consistent with experimental data. There are reports^{36–38} that pure density functionals, such as PBE, are better than hybrid functionals when studying metal diatomic molecular systems, and was

used to study endohedral and exohedral $U_2@C_n$ ($n=60, 70, 84$).¹⁰

These somewhat model-dependent choices of functionals imply that there is no universal functional that is always superior over other ones, and for a rarely investigated system, it is necessary to compare possible choices to identify the one mostly applicable on a specific model system.

Note that the previous benchmark work of DFT mainly concentrates on high valent actinide molecular systems. As one element of major actinides, U has an electronic configuration of $[Rn] 7s^2 5f^3 6d^1$, and its most stable oxidation state is +6. In its low valence state, it shows rather strong reducing activity, and requires coordination to one or several bulky ligands for stabilization.^{44–48} The rational design of ligands relies on sufficient knowledge on the interaction mode between low valent U and the ligand subject to various chemical environment, e.g., polarity and ionic strength.

In recent years, as an alternative choice in the activation of small molecules, low valent uranium molecular systems have been used. Due to the unique properties of actinide rising from the participation of $5f$ -orbitals in its bonding interaction, the application of actinide molecular systems in homogeneous catalysis is an attractive issue towards the activation of strong bonds that are believed to be extremely stable under ambient conditions. Available work has covered a broad area towards the activation of small molecules.^{49,50} Taking CO_2 and CS_2 as examples, studies have been reported on, but not limited to, the reduction of CO_2 ,^{51–53} and the insertion of CO_2 into a U–C bond,^{48,54–58} a U–N bond,^{59,60} and a U–S bond.⁶¹ The experimental work on the application of low valent uranium complex in CO_2 activation and functionalization has been reviewed recently.⁶²

The growing promising application of low valent uranium in homogeneous catalysis puts forward a compelling need to evaluate the performance of easily reachable methods in the description of low valent uranium complexes and to propose one or several methods of choice to assist the evaluation and the development of new type low valent uranium catalysts.

Recently Bart and coworkers⁴⁸ reported a new trivalent uranium complex in which the U(III) was stabilized by hydrotris(3,5-di-

methylpyrazolyl)borate (TP^*). This complex showed reactivity towards the functionalization of small compounds such as CO_2 and CS_2 ⁴⁸ but not acetone.⁶³

For the insertion reaction of CO_2 and CS_2 ,⁴⁸ the intermediates (Cpd2) and products (Cpd3 and Cpd4) have been isolated (Fig.1). In a recent paper we reported a density functional theory mechanistic study⁶⁴ on the prototype molecular systems in the experimental work⁴⁸ to understand the nature of the functionalization of CO_2 and CS_2 promoted by trivalent uranium complex, and proposed that the higher reactivity of CO_2 functionalization than that of CS_2 is mainly due to the stronger electronegativity of O than that of S, while U(III) does not behave as a reducing agent during the reaction. This provides an atomic scale understanding on the reaction mechanisms.

During that work, we noted the importance to make a sensible choice on the methods, and had thus carried out a comparative study to investigate the performance of twelve widely used methods in the treatment of trivalent uranium molecular systems, representing the levels of GGA (BP86^{65–67} and PBE^{68,69}), hybrid GGA (PBE0,^{68–70} B3LYP,^{71,72} BHandHLYP,^{71,72} B3PW91,^{71,73} and X3LYP⁷⁴), and range-separated hybrid GGA (CAM-B3LYP⁷⁵), *meta*- and hybrid *meta*-GGA (TPSS,⁷⁶ M06L,⁷⁷ M06,⁷⁸ and M06-2X⁷⁸), see Table 1, in order to find an appropriate choice for the study of trivalent uranium molecular systems which show potentials to be used in the functionalization of CO_2 , and thus may contribute to the development of C_1 chemistry.⁷⁹

2 Computational details

2.1 Brief description of methods tested

2.1.1 Functionals

In an earlier paper, Scuseria and Staroverov⁸⁰ reviewed strategies to design density functionals, including local spin density approximation (LSDA), density-gradient expansion, constraint satisfaction, modeling the exchange-correlation hole, empirical fits, or mixing Hartree-Fock and approximate DFT exchange, and the development of new functionals in general fulfils one or

Fig.1 A schematic elucidation of the three model systems

Only non-hydrogen atoms are shown for simplicity. The numbering of key atoms is also shown.

Table 1 Compositions of the DFT methods employed in this work

Functional	Exchange	Correlation	$E_{\text{ex}}^{\text{HF}}/\%$ ^a	Type ^b	Ref.
BP86	S+B88	VWN+P86	0	GGA	65–67
PBE	S+PBE(X)	PW+PBE(C)	0	GGA	68,69
B3LYP	0.8S+0.72B88+0.2HF	0.19VWN+0.81LYP	20	hGGA	71,72
B3PW91	0.20HF+0.80S+0.72B88	PW91local+0.81PW91nonl	20	hGGA	71,73
BHandHLYP	0.5(S+B88)+0.5HF	LYP	50	hGGA	71,72
PBE0	0.75(S+PBE(X))+0.25HF	PW+PBE(C)	25	hGGA	68–70
X3LYP	0.782S+0.542B88+0.167PW91+0.218HF	0.129VWN+0.871LYP	21.8	hGGA	74
CAM-B3LYP ^c	0.19HF+0.81B88SR+0.65HF+0.35B88LR	0.19VWN+0.81LYP	19	rhGGA	75
TPSS	S+TPSS(X)	PW+TPSS(C)	0	mGGA	76
M06L	M06L	M06L	0	mGGA	77
M06	M06	M06	27	hmGGA	78
M06-2X	M06-2X	M06-2X	54	hmGGA	78

^apercentage of HF exchange. ^bGGA: generalized gradient approximation; hGGA: hybrid GGA; rhGGA: range-separated hybrid GGA;

mGGA: meta-GGA; hmGGA: hybrid meta-GGA. ^cSR: short-range; LR: long-range

several of them. Among the large amount of available functionals, twelve widely used ones were evaluated here, and the type and compositions, i.e. the exchange and correlation, of each method are tabulated in Table 1. For more details about these methods, please refer to the original literature.

In the hierarchy of density functional theory, the so-called LDA method lies at the bottom level. In LDA the exchange energy per particle in each spatial point is taken as the exchange energy per particle from a uniform electron gas with a density equivalent to the density in this same point, and originally the correlation part uses the Wigner correlation. Rooted from the density functional theory, uniform electron gas limit has been shown to be important in studying bulk metallic systems.⁸¹ The introduction of gradient of density correction gives the GGA class of functionals. BP86^{65–67} belongs to this class, and was recommended by Ahlrichs *et al.*⁸² for general applications in chemistry. It combines Becke's 1988 exchange functional (B88)⁶⁵ and Perdew's 1986 correlation functional (P86),^{66,67} and VWN of Vosko *et al.*⁸³ is used to construct the local spin density part of the correlation functional and the P86 for the non-local part. This functional is available in some known quantum packages such as ADF⁸⁴ (Becke-Perdew), Gaussian⁸⁵ (BVP86), and Turbomole⁸⁶ (BP86) which use the functional form of VWN5 (functional V). Note that in Gaussian program the official version of the BP86 functional adopts VWN3 (functional III) of Vosko *et al.*,⁸³ which was used in this work.

The B3LYP,^{71,72} B3PW91,^{71,73} and BHandHLYP^{71,72} hybrid functionals represent three of the most widely used functionals for their well verified ability in the prediction of the thermodynamic properties of a chemical system with acceptable accuracy. Both of the former two use Becke's 3-parameter hybrid treatment to construct the exchange term, and differ in the composition of the correlation term, with B3LYP using VWN3 of Vosko *et al.*⁸³ and LYP^{72,87} for the local part, and LYP for the non-local part of the correlation functional, while B3PW91 using VWN3 for the local part and Perdew/Wang91 (PW91) for the non-local part of the correlation functional, i.e., $(1-c)E_c^{\text{VWN}}+cE_c^{\text{LYP}}$ for B3LYP and $E_c^{\text{VWN}}+cE_c^{\text{PW91}}$ for B3PW91.

These two functionals are featured with 20% Hartree-Fock exchange and the gradient contribution to both exchange and correlation being adjusted. Note that VWN3 of Vosko *et al.*⁸³ rather than VWN5 was used in this work to construct the local part of the correlation function, as implemented in Gaussian program.⁸⁵ We note that B3LYP was shown to have good performance in the studies of molecular properties and reaction energies of actinide complexes.^{27,88–93} In a recent comparative study⁹⁴ of C–H bond activation barriers catalyzed by pincer complexes of the late platinum group transition metals (Rh, Pd, Ir, Pt) using corrective LCCSD(T) results as the reference, B3LYP method was also reported to give values closest to those obtained from corrective LCCSD(T) calculations, and it is followed by B2GP-PLYP, B2-PLYP, and PBE0. That work⁹⁴ also shows that empirical dispersion correction (DFT-D3) has little effect on barrier height. In addition, B3LYP was also recommended by Truhlar *et al.*,⁴⁰ together with M05, M06, and M06L, for application in catalysis, including the evaluation of bond energies (metal–metal bonds, metal–ligand bonds, alkyl bond dissociation energies, and atomization energies of small main group molecules) and barriers.

To improve the deficiency in long range behavior of B3LYP, such as in describing charge transfer excitation energies, CAM-B3LYP⁷⁵ was developed via a “Coulomb-attenuating method (CAM)”, which introduced a form of $1/r_{ij}$ as

$$\frac{1}{r_{ij}} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\mu r_{ij})]}{r_{ij}} + \frac{\alpha + \beta \cdot \text{erf}(\mu r_{ij})}{r_{ij}} \quad (1)$$

where the first term accounts for the short-range interaction and the second term for the long range interaction, and the two parameters α and β satisfy the relations $0 \leq \alpha + \beta \leq 1$, $0 \leq \alpha \leq 1$, $0 \leq \beta \leq 1$. This range-separated functional was shown in a recent study⁹⁵ to predict the electron density distribution of insulin much closer to the MP2 results than that with the standard B3LYP, which stresses the importance for a proper treatment of long range interaction.

As discussed,⁹⁵ compared to MP2 calculations, a common problem of DFT methods is their overestimation of charge delocalization, leading to a too small electrostatic potential (ESP) difference between the anionic and the cationic sites, and an in-

crease of exact exchange could systematically improve the results. The good performance of range-separated density functional CAM-B3LYP is attributed to the elimination of self-interaction errors at long distance when the range-separator value is appropriately chosen. The use of range-separated density functionals is recommended, especially in the cases when the anionic and cationic sites are separated by more than 10 Å and in proteins where multiple charged sites exist.

The X3LYP functional of Xu and Goddard⁷⁴ was derived with the exchange energy density part in a form (Eq.(2)) that a density decays in Gaussian-like manner at long range toward an improved description of hydrogen-bonded and van der Waals (vdW) complexes, heats of formation, ionization potentials, electron affinities, total atomic energies, dipole moments, polarizabilities, and accurate excitation energies from *s* to *d* orbitals for transition metal atoms and ions. This functional was shown to be useful for predicting ligand binding in proteins and DNA.

$$F^X(s)=1+\alpha_{x1}(F^{B88}(s)-1)+\alpha_{x2}(F^{PW91}(s)-1) \quad (2)$$

where *s* is a dimensionless gradient, $F^X(s)$ is the extended exchange functional, F^{B88} and F^{PW91} are the B88 and PW91 functionals, α_{x1} and α_{x2} are the parameters determined through a least-square fitting procedure to physical properties related to the chemistry of the first- and the second-row elements.

Meta-GGA (mGGA) is essentially an extension of the GGA in which the non-interacting kinetic energy density $\tau_s(\mathbf{r})$, the electron density $\rho(\mathbf{r})$ and its gradient $\nabla\rho(\mathbf{r})$ are used as input to the functional, and the spin-independent form of this functional is

$$E_{xc}^{mGGA}[\rho]=\int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau_s(\mathbf{r})] \\ \text{with } \tau_s(\mathbf{r})=\frac{1}{2}\sum|\phi_{ik}(\mathbf{r})|^2 \quad (3)$$

Several mGGA functionals have been developed, and among the widely used are TPSS⁷⁶ and the M06 suite of complementary density functionals.^{77,78,96,97} TPSS⁷⁶ was designed to satisfy a chosen set of constraints and improve the equilibrium geometries of molecules, and the three functionals of the M06 suite, the M06L local functional,⁷⁷ the M06,⁷⁸ and the M06-2X,⁷⁸ were developed by empirically fitting their parameters while constraining to the uniform electron gas model, and are complementary to each other in terms of the composition and the property of model systems. A recent comparative study⁷⁸ of the M06 suite recommends the use of the M06-2X functional in calculating main-group thermochemistry, kinetics, non-covalent interactions, and electronic excitation energies to valence and Rydberg states, and the use of the M06 functional in studying organometallic and inorganometallic chemistry and for non-covalent interactions.

2.1.2 Dispersion correction

To evaluate the influence of dispersion interaction, an empirical correction according to Grimme *et al.*⁹⁸ is taken into account to PBE and PBE0 functionals, representing GGA and hybrid GGA, respectively. According to the DFT-D3 scheme proposed by Grimme *et al.*, the total energy of the model system is obtained as $E=E_{DFT}-E_{disp}$. The dispersion correction energy E_{disp} contains the contributions of two- and three-body energies.

The two-body term in general dominates, while the three-body

contribution plays a minor role, and is not recommended due to the unverified three-body behavior of most density functionals in overlapping density regions. In our calculations, the implementation in the program Turbomole⁸⁶ was used.

2.1.3 Basis set and treatment of relativistic effect

We note that the choice of basis set and the treatment of relativistic effect, particularly for heavy atoms, are also crucial to obtain reasonable results, especially for transition metal complexes,⁹⁹ and proper use of basis set is important to make a computational study meaningful, as emphasized in an earlier study¹⁰⁰ of the interactions between trivalent actinide atoms (An(III)) and ligands. In general, a small-core ECP, which treats the *5f* orbitals as valence shell, performs better than a large-core treatment which defines the *5f* orbitals with pseudopotential. However, there are exceptions,^{91,101} and in some cases the inclusion of core-polarization potentials (CPP)^{102–104} in a large-core treatment may produce comparable results. Previous work⁵³ also proposed that the *5f*-electrons were found to be not active in reactions, and a large-core treatment of actinide atoms may give qualitatively correct description of the reactivity of organoactinide, which may be further improved with the inclusion of core-polarization potentials (CPP).

In the present work, both *5f*-in-core (ECP81MWB,¹⁰⁵ LPP) treatment, which defines 81 electrons in the core region and allows for a partial occupation in the *5f* orbitals to adapt to the situation where *5f* orbitals may participate in chemical bonding interactions, and *5f*-in-valence (ECP60MWB,^{106–108} SPP) treatment, which contains 60 electrons in the core region, were used for U(III), in combination with their corresponding optimized aVDZ¹⁰⁵ ((7s6p5d)/[4s3p3d]) basis set or segmented^{107,108} ((14s13p10d8f6g)/[10s9p5d4f3g]) basis set for the valence shells of U. For the other atoms, two double- ζ quality basis sets, 6-31G(*d*)^{109,110} and def2-SVP,¹¹¹ were used. This gives four different combinations of basis sets, as shown in Table 2.

Note that the quasi-relativistic treatments of U(III) do not take into account of spin-orbit coupling (SOC). For an open-shell model system, it is in general necessary to verify whether the

Table 2 Combinations of basis sets used in this work^a

	Basis set		Model size ^b		
	U	C, H, N, B, O, S	Cpd2	Cpd3	Cpd4
BS1	ECP60MWB-SEG ^c	6-31G(<i>d</i>)	933/1915	975/1999	983/2047
BS2	ECP60MWB-SEG	def2-SVP	1086/1915	1128/1990	1136/2014
BS3	ECP81MWB-aVDZ	6-31G(<i>d</i>)	844/1687	886/1771	894/1819
BS4	ECP81MWB-aVDZ	def2-SVP	997/1687	1039/1762	1047/1786

^aThe total number of electrons is: 459 in Cpd2 (103 atoms), 481 in Cpd3 (106 atoms), and 497 in Cpd4 (106 atoms). ^bThe size of each model system, *i/j*, where *i* is the number of basis functionals contracted from *j* Gaussian primitives. ^cThe

name of the basis set for U atom is in the format of ECP_nMWB-*x*, where *n* represents the number of electrons in core treated with pseudopotential, MWB is the generation of pseudopotential based on the reference data of neutral U atom obtained at a quasi-relativistic level (Wood-Boring *ab initio* model potential), *x* is

the basis set optimized for the valence shell, which includes the

5s²5p⁶6s²5d¹⁰6p⁷7s²5f⁶6d¹ in BS1 and BS2, and 6s²6p⁶7s²6d¹ in BS3 and BS4.

contribution of SOC is significant in the calculation of a model system. In order to evaluate the potential influence of SOC on the model systems under study, the Cpd2 complex was re-optimized at the level of B3PW91/ECP60MDF(U)¹¹²U6-31G(*d*)(C, H, N, B), i.e., the U atom was treated with fully relativistic pseudopotential and the corresponding basis set for the valence shells.

2.2 Models

The three trivalent uranium complexes crystallized by Bart *et al.*,⁴⁸ as shown in Fig.1, were used as the model systems in the present calculations, with a stoichiometry of C₃₇H₅₁B₂N₁₂U for Cpd2, C₃₈H₅₁B₂N₁₂O₂U for Cpd3, and C₃₈H₅₁B₂N₁₂S₂U for Cpd4, respectively.

In all of the three complexes, the oxidation state of U is +3, and the coordination numbers of U atom are 7, 8, and 8, respectively. In its first coordination sphere, besides the six N atoms of the two Tp* ligands, an additional methylene, carboxyl or thiocarboxyl group is present respectively, and interacts with U atom *via* η^1 , κ^2 , or κ^2 mode, respectively. A schematic elucidation of the three compounds is given in Fig.1.

All stationary points reported here were fully optimized, followed by a vibrational frequency analysis to confirm its nature as a minimum and to obtain the zero point energy correction.

The Gaussian 09 package⁸⁵ was employed to carry out the calculations. The calculations with dispersion correction included were done with Turbomole.⁸⁶

3 Results and discussion

3.1 Spin states

Uranium atom holds an electronic configuration of [Rn] 7s²5f³6d¹. Considering its oxidation state of +3 in the model systems studied here, it is possible for the model compounds to take a doublet (*S*=1/2) or a quartet (*S*=3/2) spin state. In the three model systems, as seen in Fig.1, the U atom is surrounded by two bulky ligands Tp*, leaving limited space for the access of other ligands to U atom which results in different coordination numbers of U atom in the three compounds as 7, 8, and 8, respectively, differing in the coordination mode of U to the benzyl and the chalcogen atoms. These distinct coordination environments do not change the formal charge of U atom, but may modulate the interaction modes between U and ligands.

Due to the multi-configurational character of the *S*=1/2 states of the three complexes, in order to pin down the electronic structure of the *S*=1/2 states, one should in principle employ multi-configurational methods, which is however beyond our reach concerning the enormous computational power demanded by the calculations of the three bulky complexes studied here. For this reason, in this work we focus mainly on the characterization of high spin quartet state of the complexes, and the calculation of the *S*=1/2 state is simply to provide an estimate on the energy difference between the quartet and the *S*=1/2 states. Due to the complexity of the *S*=1/2 state, in order to make a proper comparison, the Kohn-Sham orbitals of quartet state were used as the initial guess to optimize the corresponding *S*=1/2 states, and the

spin contamination was monitored to be negligible. In Fig.2, the energy difference between quartet and doublet states obtained at DFT/BS1 and DFT/BS2 levels is plotted. For all three complexes, Cpd2, Cpd3, and Cpd4, calculations at different levels give consistent result that the quartet state is more stable than the doublet state by more than 10 kcal·mol⁻¹. The hybrid functionals, both for GGAs and mGGAs, predict a larger energy gap than the GGA ones.

At BS1 level, the hybrid functionals, both at the GGA and mGGA levels, give similar energy difference for Cpd3 and Cpd4 between their quartet and doublet states, while the pure DFT methods predict a larger energy difference for Cpd3 than for Cpd4. This correlates to a larger spin density on U atom in Cpd4 in its doublet state given by pure DFT methods than by hybrid ones, which will be discussed later in Section 3.4.1. Using a moderately larger basis set, BS2, changes the behavior of PBE, BHandHLYP, CAM-B3LYP, M06L, and M06-2X, but shows little influence on the other functionals.

To evaluate the influence of dispersion correction, the geometries of Cpd3 and Cpd4 were re-optimized with PBE and PBE0 functionals using Turbomole program with and without the correction taken into account. As seen in Table 3, the inclusion of dispersion correction in a semi-empirical way according to Grimme *et al.*⁹⁸ does not change much the energy gap between the doublet and the quartet states of the compounds.

The above discussion is made within the scalar relativistic

Fig.2 Relative energies between quartet and doublet states of Cpd2, Cpd3, and Cpd4 from DFT/SPP calculations

Table 3 Influence of dispersion interaction on the energy gap (kcal·mol⁻¹) between doublet and quartet states of Cpd2, Cpd3, and Cpd4 at DFT/BS2 level^a

Compound	Energy gap/(kcal·mol ⁻¹)				
	PBE	PBE-D3	PBE0	PBE0-D3	B3LYP-D3 ^b
Cpd2	-13.2(-13.0)	-12.7	-17.3(-17.9)	-17.2	-15.5(-16.4 ^c)
Cpd3	-12.4(-13.7)	-13.1	-17.1(-17.0)	-16.0	-16.6(-16.4 ^c)
Cpd4	-12.7(-12.6)	-13.0	-17.2(-16.4)	-17.4	-16.3(-16.1 ^c)

^aFor fair comparison, all structures were re-optimized using Turbomole and the data are zero-point-energy corrected. The values obtained from Gaussian program calculations are given in parentheses. ^bVWN5 was used to construct the local exchange, as implemented in Turbomole. ^cThe values in parentheses were obtained using the standard version of B3LYP functional in Gaussian program without dispersion correction.

approximation. To evaluate the effect of SOC, Cpd2 was re-optimized at the level of B3PW91/ECP60MDF(U)U6-31G(*d*)(C, H, N, B) and analyzed. The calculations give essentially same description of the complex as the calculations with a quasi-relativistic treatment of U in its geometry, orbital occupation, and relative energy between quartet and doublet states.

Fig.3 Sample standard deviation of key geometric parameters of Cpd2, Cpd3, and Cpd4 in their quartet states from calculations with a small-core treatment of U atom

filled bar: BS1; open bar: BS2. The sample standard deviations for Cpd3 and Cpd4 were derived from key geometrical parameters including 11 bonds (6 U—N, 2 U—E, 2 E—C⁹, 1 C⁹—C⁸) and 4 angles (∠E¹⁰—C⁹—E¹¹, ∠E¹⁰—U—E¹¹, ∠U—E¹⁰—C⁹, ∠U—E¹¹—C⁹). For Cpd2, only six U—N and one U—C⁸ bonds were considered.

3.2 Geometry

Key geometrical parameters of fully optimized structures of Cpd2, Cpd3, and Cpd4 were chosen to evaluate the performance of tested functionals by compared to the crystal structures.⁴⁸ These parameters for Cpd3 and Cpd4 cover 11 bonds, including six U—N, two U—E, two E—C⁹, one C⁹—C⁸, and four angles, including ∠E¹⁰—C⁹—E¹¹, ∠E¹⁰—U—E¹¹, ∠U—E¹⁰—C⁹, and ∠U—E¹¹—C⁹. For Cpd2, only six U—N and one U—C⁸ bonds were considered. The sample standard deviation (SD) of each set of data consisting of *M* geometrical parameters was calculated as

$$SD = \sqrt{\frac{\sum_{i=1}^M (A_i - A_i^{\text{exp}})^2}{M-1}} \quad (4)$$

where *A_i* is the *i*-th calculated geometrical parameter, and *A_i*^{exp} is the corresponding experimental value. The results are plotted in Figs.3 and 4.

With a small-core treatment of U and 6-31G(*d*) of the other atoms (BS1), the deviation of bonds is in general smaller than 0.04 Å for BP86, PBE, PBE0, and TPSS for Cpd2, as seen in Fig.3, with the three pure DFT methods giving the smallest deviation away from the crystal structure for the selected parameters

Fig.4 Sample standard deviation of key geometric parameters of Cpd2, Cpd3, and Cpd4 in their quartet states from calculations with a large-core treatment of U atom

filled bar: BS3; open bar: BS4. The sample standard deviations for Cpd3 and Cpd4 were derived from key geometrical parameters including 11 bonds (6 U—N, 2 U—E, 2 E—C⁹, 1 C⁹—C⁸) and 4 angles (∠E¹⁰—C⁹—E¹¹, ∠E¹⁰—U—E¹¹, ∠U—E¹⁰—C⁹, ∠U—E¹¹—C⁹). For Cpd2, only six U—N and one U—C⁸ bonds were considered.

Fig.5 Superimposition of optimized structures at DFT/BS1 level on the X-ray crystal structures

Cpd2 (left), Cpd3 (middle), and Cpd4 (right). The crystal structures are shown in ball-and-stick, and the optimized ones are in stick. The optimized structures are distinguished by colors (see web version), BP86: red; PBE: gray; TPSS: orange; B3LYP: yellow; B3PW91: tan; BHandHLYP: silver; PBE0: green; M06: iceblue; M06-2X: pink; X3LYP: magenta; CAM-B3LYP: purple; M06L: lime

by around 0.03 Å. This is followed by B3PW91 and M06 with which the deviation is around 0.05 Å.

For Cpd3, the smallest deviation was obtained when using TPSS, M06, and M06L methods with a value smaller than 0.03 Å, while for Cpd4, B3PW91, PBE0, CAM-B3LYP, and M06 outperform the other methods with a deviation value less than 0.04 Å. We note that for Cpd3 the deviation value obtained by using the GGA functionals, B3PW91, PBE0, M06-2X, is around 0.03 Å, suggesting that they are among the methods of choice when optimizing the geometry of Cpd3. For bond angles analyzed here, the hybrid GGA functionals perform marginally better than the other functionals.

Using another double- ζ quality basis set for the atoms other than U, def2-SVP (BS2), does not show much difference from the BS1 treatment.

With a large-core description of U atom (Fig.4), the deviations of selected parameters away from their corresponding experimental values become larger, but are still in the range as that with a small-core treatment of U atom. Meanwhile, the differences in the standard deviations of selected bonds and angles optimized by tested functionals diminish.

In Fig.5, all of the optimized structures obtained at the level of DFT/BS1 in their quartet states are superimposed to the corresponding X-ray crystallographic structure with respect to the coordinates of U and twelve N atoms. The atoms in the neighborhood of U atom fit very well, while one pyrazolyl group of each of the bulky Tp* ligands and the phenyl ring of the benzyl group display high flexibility.

Atomic positional root-mean-square deviations (RMSD) of two sets of specified atoms were also calculated as indicators on the agreement between the optimized geometries and the experimental ones based on the above superimposition. The first set covers U and twelve N atoms. The second set takes into account of all non-hydrogen atoms, i.e., U, N (12), C (37) and B (2) atoms. For Cpd3 and Cpd4, the two chalcogen atoms, O or S, and one additional C atom were also included. The calculated RMSD values are plotted in Fig.6.

According to the analysis, for Cpd2, the RMSD values of the structures optimized by using M06-2X and M06L are around 0.2

Å for the first set of atoms and above 0.5 Å for the second set of atoms. These values are significantly larger than those obtained using the other methods. M06 functional shows a moderate improvement, and all the other functionals display a better agreement with an RMSD of around 0.1 Å and 0.2–0.3 Å respectively for the two sets of atoms.

The performance of these functionals remains in presence of chalcogen atoms, except for a significant improvement of M06 functional when working on Cpd3. By using M06 functional,

Fig.6 Atomic root-mean-square deviation (RMSD) of Cpd2, Cpd3, and Cpd4 in their quartet states from calculations at DFT/BS1 level with corresponding coordinates of X-ray structure as the reference

All structures are aligned with respect to the atomic positions of U and N atoms.

Fig.7 Reaction energies for the insertion reactions of CO_2 and CS_2 to form Cpd3 (a, c) and Cpd4 (b, d) in their quartet states (a, b) BS1 (filled) and BS2 (open); (c, d) BS3 (filled) and BS4 (open)

Fig.8 Atomic spin density on U atom in Cpd2 , Cpd3 , and Cpd4 in their doublet (upper panels) and quartet (lower panels) states from Mulliken population analysis (MPA, left) and natural bond orbital (NBO, right) analysis at DFT/BS1 level

according to our calculations, the atomic RMSD of the first set atom of Cpd3 is 0.08 Å and for the second set 0.31 Å. While for Cpd4, B3LYP, B3PW91, BHandHLYP, X3LYP, and CAM-B3LYP display smaller RMSD values, and the three *meta* functionals, TPSS, M06L, and M06-2X give the largest RMSD values.

3.3 Reaction energies

For reactions

and

we have calculated the reaction energies using the functionals tested here, and the results at the quartet state are plotted in Fig. 7.

In the present study, both the *5f*-in-core (LPP) and *5f*-in-valence (SPP) ECPs have been used for the treatment of U atom. In previous work,⁶⁴ the two types of treatments were found to give almost identical relative energies with B3PW91 functional for the two reactions. This statement still holds according to the results in the present comparative study where several other functionals were also used, which qualifies the application of LPP treatment for U atom in current model systems when calculating reaction energies in the quartet electronic state.

Regarding to the influence of functionals, for the formation of Cpd3, the reaction was calculated to be exothermic by more than 50 kcal·mol⁻¹ with most of the functionals tested here, with CAM-B3LYP predicting the most exothermicity of 64.4 kcal·mol⁻¹ at BS1 level. One exception is M06L, which gives a value of 47.1 kcal·mol⁻¹. For the formation of Cpd4, all methods show that the reaction is less exothermic than the formation of Cpd3, which is reasonable concerning the weaker electroaffinity of S than O atom. The treatment of U by LPP or the treatment of lighter atoms by def2-SVP basis set does not change the results much.

3.4 Electronic structures

3.4.1 Electronic configuration

Both Mulliken population analysis (MPA) and natural bond orbital (NBO) analysis were carried out to understand the bond feature between U and the atoms in its first coordination shell. In Figs. 8–10 the spin density residing on U atom, the natural atomic charges of selected atoms, and the populations in the *5f* and *6d* orbitals of U atom are plotted.

In doublet states, for Cpd2 and Cpd3, all methods predict a spin density of 1.0–1.2 on U atom by Mulliken population analysis. For Cpd4, this is still true except for the four pure density functionals which predict a spin density on U of 1.3–1.4. This suggests that in the absence of HF exchange, DFT methods may favor a more uniform distribution of electrons in the (near-)degenerate orbitals than hybrid functionals. In their quartet states, for Cpd2 and Cpd3, all methods predict a spin density on U atom of 3.0–3.1 by MPA except for M06 and M06-2X. For Cpd4, the spin density on U was calculated to be 3.0–3.1 by most of the methods except for BP86, PBE, and TPSS which give lower values of 2.90–2.95, and M06 and M06-2X which give higher values of 3.2–3.3. In general, the pure DFT methods favor a moderately lower spin density distribution on U than the hybrid

Fig.9 Natural atomic charges on U (top, q_U), the six N atoms coordinated to U (middle, $\langle q_N \rangle$) and the other atoms coordinated to U (bottom, q_X) of Cpd2, Cpd3, and Cpd4 in their quartet states from natural population analysis at DFT/BS1 level

The $\langle q_N \rangle$ is calculated by averaging the atomic charges of the six N atoms that are coordinated to U atom, $\langle q_N \rangle = \frac{1}{6} \sum_i q_N^i$, and the standard deviation of each data set is also shown.

functionals do. The NBO analysis gives similar results but with a little smaller values.

The influence of the HF exchange on the electronic configurations of the three complexes is also reflected by the natural atomic charges, as seen in Fig. 9, where pure DFT methods suggest a more delocalized charge distribution than the hybrid ones, i.e., less positive charge on U and less negative charge on the atoms in the first coordination shell of U.

In view of the natural populations in the *5f* and *6d* orbitals of U atom, which are shown in Fig. 10, in both of the doublet and quartet states of the three complexes, the population in *5f* orbital is in the range of 3.1–3.3, while that in *6d* orbital is in the range of 0.7–0.9 for Cpd2 and Cpd3, and of 0.9–1.3 for Cpd4.

In their quartet states, the population in *5f* is larger in Cpd3 and Cpd4 than that in Cpd2 with exceptions of BP86, PBE, TPSS, and M06-2X. Furthermore, in their doublet states, the population in *5f* orbitals of Cpd4 is larger than that of Cpd2 by hybrid functionals while opposite results were observed when using pure DFT methods.

For the population in *6d* orbitals, all methods give consistent results. The values of Cpd3 are similar to those of Cpd2, and those

Fig.10 Natural population in the $5f$ and $6d$ orbitals of U atom in Cpd2, Cpd3, and Cpd4 in their doublet and quartet states from natural population analysis at DFT/BS1 level

Fig.11 Net spin density ($\alpha-\beta$) in the $5f$ and $6d$ orbitals of U atom in Cpd2, Cpd3, and Cpd4 in their doublet and quartet states from natural population analysis at DFT/BS1 level

Fig.12 Mayer bond order of key bonds of Cpd2 (left), Cpd3 (middle), and Cpd4 (right) in their quartet states from calculations at DFT/BS1 level

These bonds include six U—N, one U—C⁸, two U—E (E=O, S), one C⁸—C¹² or C⁸—C⁹, and two C⁹—E bonds.

of Cpd4 are significantly larger, especially with pure DFT methods. This suggests that the involvement of *6d* orbitals of U in the bonding interaction with benzyl group (Cpd2) is similar to that of U with the carboxylate group in Cpd3. The much larger values for Cpd4 indicate a heavier involvement of *6d* orbital when U is coordinated to the “softer” basic S atom.

The net spin densities in *5f* and *6d* orbitals of U are also ana-

lyzed by subtracting β spin density from α one (Fig.11). For *5f* orbitals, in general, (*meta*-)GGA methods give larger values in the doublet of the three complexes, especially in the case of Cpd4, while lower for the quartet states. This again indicates the influence of HF exchange on the electronic structure of the complexes. For *6d* orbitals, in both doublet and quartet states, the *6d* net spin density is small and less than 0.08 by all methods.

Fig.13 Electrostatic potential difference between CAM-B3LYP and selected methods X (CAMB3LYP-X) on the CAM-B3LYP optimized geometries of Cpd2 (a–e), Cpd3 (f–j), and Cpd4 (k–o)

The isovalues for the surfaces are 0.006, 0.006, and 0.01 a.u. respectively for Cpd2, Cpd3, and Cpd4. Note that for (o) the isovalue is 0.02 a.u., and color map is -0.02 – 0.02 a.u.

Fig.14 Electron density difference between CAM-B3LYP and selected methods X (CAMB3LYP-X) on the CAM-B3LYP optimized geometries of Cpd2 (a-e), Cpd3 (f-j), and Cpd4 (k-o)

The isovalues are 0.003, 0.003, and 0.006 a.u. respectively for Cpd2, Cpd3, and Cpd4.

3.4.2 Bonding mode between U and ligand atoms

Mayer bond order¹¹³ was used as an indicator of the bond strength. This analysis covers the key bonds of U—N, C⁸—C¹², and U—C⁸ of Cpd2, and additionally C⁸—C⁹, U—E^{10/11}, and C⁹—E^{10/11} of Cpd3 and Cpd4. As seen in Fig.12, all functionals show similar performance on the characterization of the C⁸—C¹² or C⁸—C⁹ bond in the three complexes.

Regarding to the U—X (X=N, C, O, S) bond, in general, BHandHLYP predicts a smaller bond order than the other functionals do. This may be due to a relatively larger proportion of HF exchange in BHandHLYP functional which does not favor a covalent bonding interaction of the highly polarized U—X bond. However, the difference is not significant.

The most significant difference is found in the U—S and C—S bonds in Cpd4, where the pure DFT methods, BP86, PBE, and TPSS, give a larger value than the other functional by about 0.2 for U—S bond, which may be relevant to the behavior of pure DFT methods in which they describe a model system with more significant delocalization than the hybrid functionals. M06L does not display this feature in the present study.

In addition, different from the other functionals in a description

of qualitatively nearly equivalent six U—N bonds in the three complexes and two U—S bonds in Cpd4, M06-2X shows that large difference may exist in these bonds. However, concerning the relatively larger deviation in the geometries of the complexes optimized by using M06-2X method from the crystal structure (Figs.4 and 6), it lacks convincing ground to justify the messages above delivered by M06-2X and further qualification is needed in order to use M06-2X to optimize the complexes.

In spite of the difference mentioned above, all methods give qualitatively consistent description in the covalency of U—C, U—O, and U—S bonds. As observed in Fig.12, the bond order of the three types of bonds vary in the order of U—C>U—S>U—O. This may be a consequence due to the co-play of the distinct electronegativities^{114,115} of C (2.55 in Pauli scale), S (2.58) and O (3.44), and their different ionic radii.

3.4.3 Electrostatic potential and electron density

In a recent work, Jakobsen *et al.*⁹⁵ proposed that CAM-B3LYP may reproduce the electrostatic potential (ESP) of insulin molecule calculated by MP2 while B3LYP does not, which stresses the importance for a range-separated treatment of the electronic interactions. On the other hand, the usage of MP2 method in

Fig.15 Mulliken population analysis with the methods tested here based on the CAM-B3LYP optimized geometry

(a) atomic charge of U atom; (b) (averaged) atomic charge of C* (Cpd2), O (Cpd3), and S (Cpd4); (c) spin density of U atom; (d) molecular dipole moments.

The symbol "x" in red (color on web version) in (c, d) highlighted the odd value given by MP2 method for Cpd4. 1 debye= 3.3356×10^{-30} C·m

studying the set of uranium fluorides and oxofluorides, e.g., UF_6 and UO_2F_2 , was questioned in an earlier study by Schreckenbach and Shamov,²⁷ where MP2 was shown to behave somewhat erratically for the set of model systems, and GGA functionals may be the methods of choice in view of their geometries and frequencies, and when energetics are concerned, hybrid GGA methods appear to be better choices. This is the case for the high valent uranium molecular complexes constituted of the so-called "hard-base" (O, F atoms) and "hard-acid" (U(VI)) components.

In this work, as mentioned above, a series of DFT methods representing GGA, hGGA, mGGA, and hmGGA were tested on the characterization of trivalent uranium complexes. As we are not able to afford the full optimization of the model complexes by MP2 or the single point calculation by CCSD(T) or other higher level post-HF methods, we chose the structures optimized by using CAM-B3LYP functional, then did single point calculations using MP2 and the other DFT methods tested here to identify how MP2 behaves on the low valent uranium molecular systems in terms of electrostatic potential and electronic density. The data of CAM-B3LYP were used as the reference for the comparison.

By its definition, the molecular electrostatic potential may be used as a qualitative representation of the polarity of a molecule derived from the interaction between the various gridded parts of the molecule and a test positive unit charge. In this sense, a negative potential value corresponds to an attractive interaction

and a positive value to a repulsive interaction.

In Fig.13 the electrostatic potential difference, and in Fig.14 the electron density difference, between the values of selected methods, i.e., TPSS, B3PW91, PBE0, M06, and MP2, and those of CAM-B3LYP are plotted based on $90 \times 79 \times 72 = 511920$ (Cpd2, Fig.13(a–e)), $92 \times 81 \times 69 = 514188$ (Cpd3, Fig.13(f–j)), and $93 \times 81 \times 68 = 512244$ (Cpd4, Fig.13(k–o)) grid points. For the data of the other DFT methods, please refer to Supporting Information (Figs. S1–S6). The data of B3LYP and X3LYP methods are not shown because of only negligible difference from those of CAM-B3LYP.

As seen in Fig.13, besides B3LYP and X3LYP, B3PW91 gives electrostatic potential closest to CAM-B3LYP than the other methods. We can also see that the difference between CAM-B3LYP and the other DFT methods mainly rises in the vicinity of U atom, while that between CAM-B3LYP and MP2 is global, though the absolute value is not big for Cpd2 and Cpd3.

In the case of Cpd4, the difference becomes much more significant. The distinct behaviors of DFT and MP2 methods may root from their propensities in describing the bonding interactions between the central U atom and the ligands. The analysis of electron density difference gives consistent result (Fig.14).

In Fig.15, we plotted the atomic charges of U, C* (Cpd2), O (Cpd3), and S (Cpd4) atoms, the net spin density on U atom, and the molecular dipole moments of the three compounds to analyze the polarization of the model systems described by the methods

Fig.16 Electron density ρ_b and its Laplacian $\nabla^2\rho_b$, the electron energy density $H_b(r)$ at a bond critical point (BCP), and the delocalization index $DI(A, B)$ between two atoms A and B of $U-X$ ($X=C, O, S$) and $E-C^9$ ($E=O, S$) bonds in Cpd2, Cpd3, and Cpd4 at DFT/BS1 level

tested here. The U atom is more positively charged in Cpd2 and Cpd3 than in Cpd4, suggesting a weaker electron-withdrawing ability of thiocarboxyl group than the benzyl and the carboxyl groups. This is consistent with the less negatively charged feature of S atom than C^8 (Cpd2) and O (Cpd3), as seen in Fig.15b. It is also clear that for all of the three compounds, the charge distributions on U and the atoms bound to it (C, O, S) are more discretized when using MP2 method than when using DFT methods. This agrees with the behaviors of density functionals and HF exchanges in the description of molecular systems.

The odd behavior of MP2 is found in the calculations of atomic spin density of U atom (Fig.15c) and molecular dipole moments

(Fig.15d). In the model systems of Cpd2 and Cpd3, MP2 does not deviate away much the values of DFT methods, while in Cpd4, MP2 favors much lower net spin density on U atom, suggesting a significant counting of the contribution of “dynamic” correlation in MP2 calculations. However, with the complicated electronic structure of U atom in the presence of $5f$ and $6d$ orbitals, it may bring severe concern on the “non-dynamic” correlation which MP2, as a single-determinant based method, does not secure.

3.4.4 Topological analysis

The four quantities in the framework of quantum theory of atom in molecule (QTAIM) technique,¹¹⁶ the electron density ρ_b and its Laplacian $\nabla^2\rho_b$, the total electron energy density $H_b(r)$ at a bond

critical point (BCP), and the delocalization index $DI(A, B)$ between two atoms A and B were used to characterize the bonding interactions between U and the atoms coordinated to it. The analysis was done at the level of DFT/BS1, and the results were plotted in Fig.16 and tabulated in Table S5 (Supporting Information).

In view of electron density ρ_b , the value of U—C bond is larger than those of U—O and U—S bonds with marginal difference, and the values of all of the three bonds are smaller than $0.07 e \cdot \text{bohr}^{-3}$. As proposed,¹¹⁶ the value of $0.2 e \cdot \text{bohr}^{-3}$ of ρ_b may be looked as a lower bound of a covalent bond and a value of $0.1 e \cdot \text{bohr}^{-3}$ as an upper bound for closed-shell interactions, e.g., ionic interactions and vdW interactions. This means that all of the three types of bonds are of mainly ionic feature with U—C bond close to the upper bound of an ionic bond due to the weaker electron withdrawing ability of the terminal C atom of the benzyl group compared to those of O and S atoms.

As electron density may accumulate at the BCP of a covalent bond, but experience a depletion for a closed-shell bond, the Laplacian of electron density, $\nabla^2 \rho_b$, appears with different signs for these bonds, i.e., positive for an ionic bond while negative for a single covalent bond. According to our calculations, the $\nabla^2 \rho_b$ is positive for all of the three types of bonds, with a larger value for the U—O bonds than for the U—C and U—S bonds, suggesting a stronger ionic feature for the former than for the latter. This is also supported by the value of H_b , which is more negative for U—C bond than for U—O and U—S bonds, and the value of U—O bond is closer to 0.0. Regarding to the E—C⁹ (E=O, S) bonds, both have negative values of $\nabla^2 \rho_b$ with that of O—C⁹ closer to 0, which suggests that both bonds are covalent bonds, with O—C bond weaker covalency.

The delocalization index, $DI(A, B)$, which integrates the electron density ρ_b in the bonding region between two atoms A and B, may be used as a measure of the bond order. In view of $DI(A, B)$, for both U—C and U—O bonds, the employed DFT methods give a value of around 1.0, while for U—S bonds, the three pure DFT methods, BP86, PBE, and TPSS, suggest a value of 1.15–1.20 which is larger than the other methods. This shows that the three methods tend to give a description with stronger covalency of U—S bond than the hybrid functionals.

4 Conclusions

In this work a comparative study of twelve widely used DFT methods is reported to evaluate their performance on the characterization of three trivalent uranium complexes in order to qualify their proper use in studying low valent actinide molecular systems.

With a small-core ECP treatment of U atom, the relative energies of the doublet and the quartet states of the three complexes were calculated, and all methods support a more stable quartet electronic state than a doublet state, suggesting that all tested methods are qualitatively consistent in characterizing the ground state of the three complexes, and the replacement of the methylene

of the benzyl group in Cpd2 by the carboxyl group in Cpd3 or the thiocarboxyl group in Cpd4 does not invoke spin flip of the electronic ground states of the trivalent uranium complex.

In view of geometry, taking the X-ray crystallographic coordinates⁴⁸ as the reference, for the bonding interactions between U and the atoms in its first coordination shell, PBE and TPSS give the smallest deviation for Cpd2, and M06 and M06L methods for Cpd3. For Cpd4, B3PW91, PBE0, CAM-B3LYP, and M06 outperform the others. The analysis of atomic positional RMSD of non-hydrogen atoms shows that B3LYP and B3PW91 display good performance in optimizing the geometries of the three compounds, and can be recommended in the optimization of trivalent uranium model systems, while M06-2X and M06L should be used with caution.

According to the analysis of electronic structures, DFT methods are in general able to provide consistent description of the populations and bonding mode for the interactions between U atom and the ligand atoms in the first coordination shell, but the inclusion of HF-exchange does matter in characterizing the participation of 5f and 6d orbitals of U atom. For the three types U—X (X=C⁸, O, S) bonds, the bond order varies in the order of U—C>U—S>U—O, which is confirmed by AIM topological analysis.

In summary, B3LYP and B3PW91 functionals seem to perform better in both geometry and electronic structure calculations, while M06-2X and M06L give larger geometrical deviations with respect to crystal structures. The electronic structure calculation using MP2 method based on CAM-B3LYP optimized structures gives a similar picture to DFT methods for Cpd2 and Cpd3, while seems to behave in an odd way in the calculation of Cpd4, suggesting the complexity of U—S bond. This observation is tentatively attributed to the “imbalanced” account of “dynamic” and “non-dynamic” correlation due to the participation of 5f orbital in the bonding interaction.

Acknowledgment: Calculations were done on the computational grids in the College of Chemistry, Beijing Normal University (BNU), in the Institute of High Energy Physics (IHEP), in the Supercomputing Center of Chinese Academy of Sciences (SCCAS) and in the National Supercomputing Center in Tianjin (NSCC-TJ).

Supporting Information: Full citation of Gaussian 09 program, relative energies between the quartet and the doublet states, deviation of key geometric parameters with respect to X-ray crystallographic structures, reaction energies at quartet and doublet states, QTAIM topological analysis of selected bonds, electrostatic potential and electron density surfaces calculated by 12 methods have been included. This information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

References

- (1) Morss, L. R.; Edelstein, N. M.; Fuger, J.; Katz, J. J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.;

- Springer: Dordrecht, The Netherlands, 2008.
- (2) Streitwieser, A., Jr.; Mueller-Westerhoff, U. *J. Am. Chem. Soc.* **1968**, *90*, 7364.
 - (3) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500. doi: 10.1021/ja00189a022
 - (4) Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 11456. doi: 10.1021/ja9821145
 - (5) Seyferth, D. *Organometallics* **2004**, *23*, 3562. doi: 10.1021/om0400705
 - (6) Gagliardi, L.; Roos, B. O. *Nature* **2005**, *433*, 848. doi: 10.1038/nature03249
 - (7) Roos, B. O.; Malmqvist, P.; Gagliardi, L. *J. Am. Chem. Soc.* **2006**, *128*, 17000. doi: 10.1021/ja066615z
 - (8) Gagliardi, L.; Roos, B. O. *Chem. Soc. Rev.* **2007**, *36*, 893. doi: 10.1039/b601115m
 - (9) Wu, X.; Lu, X. *J. Am. Chem. Soc.* **2007**, *129*, 2171. doi: 10.1021/ja067281g
 - (10) Infante, I.; Gagliardi, L.; Scuseria, G. E. *J. Am. Chem. Soc.* **2008**, *130*, 7459. doi: 10.1021/ja800847j
 - (11) Hu, H. S.; Qiu, Y. H.; Xiong, X. G.; Schwarz, W. H. E.; Li, J. *Chem. Sci.* **2012**, *3*, 2786. doi: 10.1039/c2sc20329d
 - (12) Haschke, J. M.; Stakebake, J. L. *The Chemistry of the Actinide and Transactinide Elements*, Vol. 5; Morss, L. R., Edelstein, N. M., Fuger, N. M., Katz, J. J. Eds.; Springer: Dordrecht, 2008; pp 3199–3272.
 - (13) Choppin, G. R.; Jensen, M. P. *The Chemistry of the Actinide and Transactinide Elements*, Vol. 4; Morss, L. R., Edelstein, N. M., Fuger, N. M., Katz, J. J. Eds.; Springer: Dordrecht, 2008; pp 2524–2621.
 - (14) Choppin, G. R. *J. Radioanal. Nucl. Chem.* **2007**, *273*, 695. doi: 10.1007/s10967-007-0933-3
 - (15) Colmenares, C. A. *Prog. Solid State Chem.* **1984**, *15*, 257. doi: 10.1016/0079-6786(84)90003-7
 - (16) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855. doi: 10.1016/j.ccr.2005.12.007
 - (17) de Almeida, K. J.; Cesar, A. *Organometallics* **2006**, *25*, 3407. doi: 10.1021/om060112k
 - (18) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 4253. doi: 10.1021/ja0665444
 - (19) Field, R. W. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 771. doi: 10.1002/bbpc.19820860903
 - (20) Demtroder, W. *Laser Spectroscopy: Basic Concepts and Instrumentation*, 3rd ed.; Springer-Verlag: Berlin, Heidelberg, New York, 2003.
 - (21) Schlag, E. W. *ZEKE Spectroscopy*; Cambridge University Press: Cambridge, UK, 1998.
 - (22) Softley, T. P. *Int. Rev. Phys. Chem.* **2004**, *23*, 1. doi: 10.1080/01442350310001652940
 - (23) Heaven, M. C. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4497. doi: 10.1039/b607486c
 - (24) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *J. Comput. Chem.* **1999**, *20*, 70.
 - (25) Kaltsoyannis, N. *Chem. Soc. Rev.* **2003**, *32*, 9. doi: 10.1039/b204253n
 - (26) Kaltsoyannis, N.; Hay, P. J.; Li, J.; Blaudau, J. P.; Bursten, B. E. *The Chemistry of The Actinide and Transactinide Elements*, Vol. 3; Morss, L. R., Edelstein, N. M., Fuger, N. M., Katz, J. J. Eds.; Springer: Dordrecht, The Netherlands, 2008; pp 1893–2012.
 - (27) Schreckenbach, G.; Shamov, G. A. *Accoutns Chem. Res.* **2010**, *43*, 19. doi: 10.1021/ar800271r
 - (28) Buehl, M.; Wipff, G. *ChemPhysChem* **2011**, *12*, 3095. doi: 10.1002/cphc.201100458
 - (29) Lan, J. H.; Shi, W. Q.; Yuan, L. Y.; Li, J.; Zhao, Y. L.; Chai, Z. F. *Coord. Chem. Rev.* **2012**, *256*, 1406. doi: 10.1016/j.ccr.2012.04.002
 - (30) D'Angelo, P.; Spezia, R. *Chem. -Eur. J.* **2012**, *18*, 11162. doi: 10.1002/chem.v18.36
 - (31) Wang, D.; van Gunsteren, W. F.; Chai, Z. *Chem. Soc. Rev.* **2012**, *41*, 5836. doi: 10.1039/c2cs15354h
 - (32) Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757. doi: 10.1039/b907148b
 - (33) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
 - (34) Dreizler, R. M.; Gross, E. K. U. *Density Functional Theory: An Approach to the Quantum Many-Body Problem*; Springer-Verlag: Berlin, Heidelberg, 1990.
 - (35) Chai, J. D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *128*, 084106. doi: 10.1063/1.2834918
 - (36) Yanagisawa, S.; Tsuneda, T.; Hirao, K. *J. Chem. Phys.* **2000**, *112*, 545. doi: 10.1063/1.480546
 - (37) Barden, C. J.; Rienstra-Kiracofe, J. C.; Schaefer, H. F., III. *J. Chem. Phys.* **2000**, *113*, 690. doi: 10.1063/1.481916
 - (38) Gutsev, G. L.; Bauschlicher, C. W., Jr. *J. Phys. Chem. A* **2003**, *107*, 4755. doi: 10.1021/jp030146v
 - (39) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127. doi: 10.1021/jp0539223
 - (40) Yang, K.; Zheng, J.; Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2010**, *132*, 164117. doi: 10.1063/1.3382342
 - (41) Averkiev, B. B.; Mantina, M.; Valero, R.; Infante, I.; Kovacs, A.; Truhlar, D. G.; Gagliardi, L. *Theor. Chem. Acc.* **2011**, *129*, 657. doi: 10.1007/s00214-011-0913-0
 - (42) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670. doi: 10.1039/c0cp02984j
 - (43) Tecmer, P.; Gomes, A. S. P.; Ekstroem, U.; Visscher, L. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6249. doi: 10.1039/c0cp02534h
 - (44) Antunes, M. A.; Ferrence, G. M.; Domingos, A.; McDonald, R.; Burns, C. J.; Takats, J.; Marques, N. *Inorg. Chem.* **2004**, *43*, 6640. doi: 10.1021/ic049204x
 - (45) Antunes, M. A.; Domingos, A.; dos Santos, I. C.; Marques, N.; Takats, J. *Polyhedron* **2005**, *24*, 3038. doi: 10.1016/j.poly.2005.06.025

- (46) Korobkov, I.; Gorelsky, S.; Gambarotta, S. *J. Am. Chem. Soc.* **2009**, *131*, 10406. doi: 10.1021/ja9002525
- (47) Duhović, S.; Khan, S.; Diaconescu, P. L. *Chem. Commun.* **2010**, *46*, 3390. doi: 10.1039/b927264j
- (48) Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C. *J. Am. Chem. Soc.* **2011**, *133*, 4948. doi: 10.1021/ja110158s
- (49) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341. doi: 10.1038/nature07372
- (50) Arnold, P. L. *Chem. Commun.* **2011**, *47*, 9005. doi: 10.1039/c1cc10834d
- (51) Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2005**, *127*, 11242. doi: 10.1021/ja053497r
- (52) Lam, O. P.; Bart, S. C.; Kameo, H.; Heinemann, F. W.; Meyer, K. *Chem. Commun.* **2010**, *46*, 3137. doi: 10.1039/b927142b
- (53) Castro, L.; Lam, O. P.; Bart, S. C.; Meyer, K.; Maron, L. *Organometallics* **2010**, *29*, 5504. doi: 10.1021/om100479r
- (54) Moloy, K. G.; Marks, T. J. *Inorg. Chim. Acta* **1985**, *110*, 127. doi: 10.1016/S0020-1693(00)84568-5
- (55) Domingos, A.; Marcalo, J.; Marques, N.; de Matos, A. P. *Polyhedron* **1992**, *11*, 501. doi: 10.1016/S0277-5387(00)83295-7
- (56) Evans, W. J.; Walensky, J. R.; Ziller, J. W. *Organometallics* **2010**, *29*, 945. doi: 10.1021/om901006t
- (57) Evans, W. J.; Walensky, J. R.; Ziller, J. W. *Inorg. Chem.* **2010**, *49*, 1743. doi: 10.1021/ic902141f
- (58) Evans, W. J.; Siladke, N. A.; Ziller, J. W. *C. R. Chimie* **2010**, *13*, 775. doi: 10.1016/j.crci.2010.02.003
- (59) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536. doi: 10.1021/ja804263w
- (60) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9036. doi: 10.1021/ja2019492
- (61) Lescop, C.; Arliguie, T.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Organomet. Chem.* **1999**, *580*, 137. doi: 10.1016/S0022-328X(98)01139-5
- (62) Lam, O. P.; Meyer, K. *Polyhedron* **2012**, *32*, 1. doi: 10.1016/j.poly.2011.07.015
- (63) Matson, E. M.; Fanwick, P. E.; Bart, S. C. *Organometallics* **2011**, *30*, 5753. doi: 10.1021/om200612h
- (64) Ding, W.; Fang, W.; Chai, Z.; Wang, D. *J. Chem. Theory Comput.* **2012**, *8*, 3605. doi: 10.1021/ct300075n
- (65) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. doi: 10.1103/PhysRevA.38.3098
- (66) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. doi: 10.1103/PhysRevB.33.8822
- (67) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.
- (68) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. doi: 10.1103/PhysRevLett.77.3865
- (69) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
- (70) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158. doi: 10.1063/1.478522
- (71) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. doi: 10.1063/1.464304
- (72) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. doi: 10.1103/PhysRevB.37.785
- (73) Perdew, J. P. *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H. Eds.; Akademie Verlag, Berlin, 1991; pp 11–20.
- (74) Xu, X.; Goddard, W. A., III. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 2673. doi: 10.1073/pnas.0308730100
- (75) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51. doi: 10.1016/j.cplett.2004.06.011
- (76) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401. doi: 10.1103/PhysRevLett.91.146401
- (77) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101. doi: 10.1063/1.2370993
- (78) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. doi: 10.1007/s00214-007-0310-x
- (79) Keim, W. *Pure & Appl. Chem.* **1986**, *58*, 825.
- (80) Scuseria, G. E.; Staroverov, V. N. *Theory and Application of Computational Chemistry: the First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E. Eds.; Elsevier: Amsterdam, 2005; pp 669–724.
- (81) Paier, J.; Marsman, M.; Kresse, G. *J. Chem. Phys.* **2007**, *127*, 024103. doi: 10.1063/1.2747249
- (82) Ahlrichs, R.; Furche, F.; Grimme, S. *Chem. Phys. Lett.* **2000**, *325*, 317. doi: 10.1016/S0009-2614(00)00654-0
- (83) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. doi: 10.1139/p80-159
- (84) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
- (85) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 09*, Revision C.01; Gaussian Inc.: Wallingford, CT, 2009.
- (86) TURBOMOLE V6.5 2013, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007. TURBOMOLE GmbH since 2007; available from <http://www.turbomole.com>.
- (87) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. doi: 10.1016/0009-2614(89)87234-3
- (88) de Jong, W. A.; Harrison, R. J.; Nichols, J. A.; Dixon, D. A. *Theor. Chem. Acc.* **2001**, *107*, 22. doi: 10.1007/s002140100293
- (89) Shamov, G. A.; Schreckenbach, G. *J. Phys. Chem. A* **2005**, *109*, 10961. Erratum. *J. Phys. Chem. A* **2006**, *110*, 12072. doi: 10.1021/jp053522f
- (90) Shamov, G. A.; Schreckenbach, G.; Vo, T. N. *Chem. -Eur. J.* **2007**, *13*, 4932.
- (91) Odoh, S. O.; Schreckenbach, G. *J. Phys. Chem. A* **2010**, *114*, 1957. doi: 10.1021/jp909576w
- (92) Odoh, S. O.; Schreckenbach, G. *J. Phys. Chem. A* **2011**, *115*, 14110. doi: 10.1021/jp207556b

- (93) Odoh, S. O.; Walker, S. M.; Meier, M.; Stetefeld, J.; Schreckenbach, G. *Inorg. Chem.* **2011**, *50*, 3141. doi: 10.1021/ic2001706
- (94) Lai, W.; Yao, J.; Shaik, S.; Chen, H. *J. Chem. Theory Comput.* **2012**, *8*, 2991. doi: 10.1021/ct3005936
- (95) Jakobsen, S.; Kristensen, K.; Jensen, F. *J. Chem. Theory Comput.* **2013**, *9*, 3978. doi: 10.1021/ct400452f
- (96) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 5121. doi: 10.1021/jp060231d
- (97) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 13126. doi: 10.1021/jp066479k
- (98) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104. doi: 10.1063/1.3382344
- (99) Vanquickenborne, L. G.; Verhulst, J.; Coussens, B.; Hendrickx, M.; Pierloot, K. *J. Mol. Struct. -Theochem* **1987**, *153*, 227. doi: 10.1016/0166-1280(87)80006-4
- (100) Banik, N. L.; Schimmelpfennig, B.; Marquardt, C. M.; Brendebach, B.; Geist, A.; Denecke, M. A. *Dalton Trans.* **2010**, *39*, 5117. doi: 10.1039/b927016g
- (101) Iché-Tarrat, N.; Marsden, C. J. *J. Phys. Chem. A* **2008**, *112*, 7632. doi: 10.1021/jp801124u
- (102) Migdalek, J.; Baylis, W. E. *Can. J. Phys.* **1982**, *60*, 1317. doi: 10.1139/p82-178
- (103) Müller, W.; Flesch, J.; Meyer, W. *J. Chem. Phys.* **1984**, *80*, 3297. doi: 10.1063/1.447083
- (104) Foucrault, M.; Millie, P.; Daudey, J. P. *J. Chem. Phys.* **1992**, *96*, 1257.
- (105) Moritz, A.; Cao, X.; Dolg, M. *Theor. Chem. Acc.* **2007**, *117*, 473. doi: 10.1007/s00214-006-0180-7
- (106) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, *100*, 7535. doi: 10.1063/1.466847
- (107) Cao, X.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2003**, *118*, 487. doi: 10.1063/1.1521431
- (108) Cao, X.; Dolg, M. *J. Molec. Struct. -Theochem* **2004**, *673*, 203. doi: 10.1016/j.theochem.2003.12.015
- (109) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. doi: 10.1063/1.1677527
- (110) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. doi: 10.1063/1.444267
- (111) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. doi: 10.1063/1.463096
- (112) Dolg, M.; Cao, X. *J. Phys. Chem. A* **2009**, *113*, 12573. doi: 10.1021/jp9044594
- (113) Mayer, I. *Int. J. Quantum Chem.* **1984**, *26*, 151.
- (114) Pauling, L. *Nature of the Chemistry Bond*; Cornell University Press: Ithaca, United States, 1960; pp 88–107.
- (115) Lide, D. R. *CRC Handbook of Chemistry and Physics*, Internet Version. <http://www.hbcpnetbase.com>; CRC Press: Boca Raton, FL, 2005.
- (116) Matta, C. F.; Boyd, R. J. *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*; WILEY-VCH: Weinham, 2007.

采用 12 种密度泛函理论方法表征三种三价铀复合物

丁万见^{1,*} 方维海¹ 柴之芳^{2,3} 王东琪^{2,*}

(¹北京师范大学化学学院, 理论及计算光化学教育部重点实验室, 北京 100875; ²中国科学院高能物理研究所, 中国科学院核辐射与核能技术重点实验室, 北京 100049; ³苏州大学核药物与交叉科学学院, 江苏苏州 215123)

Performance of Twelve Density Functional Theory Methods in the Characterization of Three Trivalent Uranium Complexes

DING Wan-Jian^{1,*} FANG Wei-Hai¹ CHAI Zhi-Fang^{2,3} WANG Dong-Qi^{2,*}

(¹Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China; ²CAS Key Laboratory of Nuclear Radiation and Nuclear Energy Techniques, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, P. R. China; ³School of Radiation Medicine and Interdisciplinary Sciences (RAD-X), Soochow University, Suzhou 215123, Jiangsu Province, P. R. China)

*Corresponding authors. DINGWan-Jian, Email: dingwanjian@bnu.edu.cn; Tel: +86-10-58804232.

WANG Dong-Qi, Email: dwang@ihep.ac.cn; Tel: +86-10-88236606.

1 Full citation of Gaussian 09

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.

2 Relative energies between the quartet and the doublet

Table S1 Relative energies between the quartet and the doublet^a

Functional	Cpd2				Cpd3				Cpd4			
	$\Delta E^{d/q}$	$\Delta G^{d/q}$	$\Delta H^{d/q}$	$\Delta S^{d/q}$	$\Delta E^{d/q}$	$\Delta G^{d/q}$	$\Delta H^{d/q}$	$\Delta S^{d/q}$	$\Delta E^{d/q}$	$\Delta G^{d/q}$	$\Delta H^{d/q}$	$\Delta S^{d/q}$
BS1: SC-6-31G(d)												
BP86	-13.1	-12.7	-13.1	-1.3	-13.3	-14.0	-13.3	2.4	-10.6	-11.7	-10.7	3.3
PBE	-12.3	-12.5	-12.4	0.3	-13.6	-13.8	-13.5	0.9	-10.8	-11.1	-11.0	0.3
B3LYP	-16.4	-16.6	-16.4	0.7	-16.4	-17.2	-16.4	2.6	-16.2	-16.7	-16.2	1.8
B3PW91	-16.4	-16.5	-16.4	0.2	-16.6	-16.3	-16.7	-1.2	-16.0	-16.8	-16.0	2.9
BHandHLYP	-19.6	-19.6	-19.7	-0.6	-18.6	-19.3	-18.5	2.8	-19.4	-20.2	-19.4	3.0
PBE0	-17.6	-18.1	-17.5	1.7	-16.8	-17.1	-16.8	1.0	-16.5	-16.6	-16.5	0.3
X3LYP	-16.7	-18.0	-16.6	4.7	-16.3	-17.7	-16.1	5.5	-16.4	-17.1	-16.4	2.3
CAM-B3LYP	-17.6	-17.1	-17.7	-1.9	-17.0	-17.8	-16.9	2.9	-16.8	-17.0	-16.8	0.8
TPSS	-15.9	-15.6	-16.0	-1.2	-16.2	-15.4	-16.3	-3.1	-13.4	-14.3	-13.4	3.2
M06L	-20.9	-27.9	-20.9	0.8	-21.0	-21.0	-21.1	-0.5	-19.5	-21.0	-19.4	5.6
M06	-16.5	-16.8	-16.5	1.0	-17.0	-18.5	-16.8	5.5	-16.2	-16.2	-16.2	-0.3
M06-2X	-21.1	-21.4	-21.0	1.3	-19.1	-18.6	-19.1	-1.4	-18.3	-19.8	-18.2	5.3
BS2: SC-Def2-SVP												
BP86	-12.5	-12.3	-12.6	-1.0	-13.2	-13.7	-13.2	1.5	-10.6	-11.7	-10.5	4.0
PBE	-13.0	-13.7	-13.0	2.3	-13.7	-14.4	-13.6	2.6	-12.6	-12.1	-12.7	-2.0
B3LYP	-16.4	-16.1	-16.5	-1.5	-16.4	-16.9	-16.4	1.6	-16.1	-17.3	-15.9	4.9
B3PW91	-17.1	-16.5	-17.3	-2.7	-16.4	-16.9	-16.4	1.8	-16.1	-17.7	-15.9	6.1
BHandHLYP	-19.7	-20.1	-19.8	0.9	-21.4	-21.3	-21.5	-0.5	-19.4	-18.8	-19.5	-2.4
PBE0	-17.9	-18.7	-17.9	2.7	-17.0	-18.1	-16.9	4.1	-16.4	-16.7	-16.4	1.2
X3LYP	-17.4	-18.0	-17.3	2.2	-17.9	-17.7	-18.0	-1.0	-17.5	-19.0	-17.2	5.8
CAM-B3LYP	-16.8	-18.0	-16.7	4.4	-17.8	-18.7	-17.8	3.2	-15.5	-16.4	-15.3	3.7
TPSS	-15.9	-16.0	-16.0	0.2	-16.3	-16.4	-16.3	0.4	-12.7	-13.1	-12.8	1.0
M06L	-21.1	-22.4	-20.9	5.0	-22.4	-22.3	-22.4	-0.4	-19.4	-20.5	-19.3	4.2
M06	-16.7	-17.3	-16.6	2.3	-16.9	-16.8	-16.9	-0.5	-16.3	-17.1	-16.3	2.5

M06-2X	-18.9	-18.4	-19.0	-1.9	-20.2	-23.4	-19.6	12.5	-18.9	-21.0	-18.5	8.4
--------	-------	-------	-------	------	-------	-------	-------	------	-------	-------	-------	-----

^a $\Delta A^{d \rightarrow q} = A^q - A^d$, where A is the total electronic energy E (kcal mol⁻¹), Gibbs free energy G (kcal mol⁻¹), enthalpy H (kcal mol⁻¹), or entropy S (J mol⁻¹ K⁻¹).

3 Deviation of key geometric parameters

Table S2 Deviation of key geometric parameters (distance d in Å, angle A in degree) in quartet state from calculations with small-core (BS1 & BS2) and large-core (BS3 & BS4) treatments of U^a

Functional	BS1					BS2				
	Cpd2	Cpd3		Cpd4		Cpd2	Cpd3		Cpd4	
	d	d	A	d	A	d	d	A	d	A
BP86	0.03	0.03	1.54	0.05	2.18	0.03	0.03	1.11	0.05	1.87
PBE	0.03	0.03	1.67	0.05	1.88	0.03	0.03	1.24	0.05	1.86
B3LYP	0.08	0.05	1.02	0.05	0.72	0.08	0.05	0.67	0.05	0.64
B3PW91	0.05	0.04	1.24	0.03	0.57	0.05	0.04	0.79	0.03	0.30
BHandHLYP	0.07	0.05	0.95	0.06	1.13	0.07	0.05	0.75	0.06	1.34
PBE0	0.04	0.03	1.44	0.04	0.73	0.04	0.04	0.99	0.04	0.74
X3LYP	0.07	0.06	1.09	0.05	0.59	0.07	0.05	0.71	0.05	0.63
CAM-B3LYP	0.06	0.05	1.07	0.04	0.69	0.06	0.04	0.78	0.04	0.82
TPSS	0.03	0.03	1.65	0.05	1.65	0.03	0.03	1.21	0.04	1.62
M06L	0.06	0.03	1.93	0.04	2.14	0.05	0.03	1.47	0.03	1.57
M06	0.05	0.03	1.70	0.04	1.11	0.04	0.02	1.32	0.04	1.18
M06-2X	0.06	0.03	2.06	0.05	1.84	0.05	0.02	1.60	0.05	1.97
	BS3					BS4				
BP86	0.14	0.09	1.24	0.10	1.37	0.13	0.09	1.00	0.09	1.16
PBE	0.13	0.09	1.33	0.09	1.39	0.13	0.09	1.10	0.09	1.26
B3LYP	0.15	0.10	0.98	0.11	1.81	0.15	0.10	0.99	0.11	1.65
B3PW91	0.13	0.09	1.04	0.09	1.52	0.13	0.09	0.96	0.09	1.39
BHandHLYP	0.13	0.09	1.04	0.10	2.02	0.13	0.09	1.12	0.10	1.87
PBE0	0.12	0.08	1.24	0.08	1.55	0.12	0.08	1.06	0.08	1.45
TPSS	0.13	0.09	1.18	0.09	1.31	0.13	0.09	0.96	0.09	1.23
M06	0.12	0.08	1.57	0.08	1.69	0.11	0.07	1.44	0.08	1.81

^a The standard deviation of the M geometrical parameters from their corresponding experimental value.

4 Reaction energies at quartet and doublet states

Table S3 Reaction energies (in kcal/mol) at the quartet state

Functional	Cpd2 + CO ₂ →			Cpd2 + CS ₂ →			Cpd2 + CO ₂ →			Cpd2 + CS ₂ →		
	Cpd3			Cpd4			Cpd3			Cpd4		
	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH
BS1						BS2						
BP86	-52.	-42.	-53.	-45.	-33.	-46.	-50.	-40.	-51.	-46.	-36.	-47.
	6	2	5	4	3	1	3	8	1	8	0	2
PBE	-55.	-46.	-56.	-49.	-37.	-50.	-52.	-43.	-53.	-50.	-39.	-50.
	4	0	0	6	5	3	4	1	1	4	0	9
B3LYP	-57.	-48.	-58.	-44.	-33.	-45.	-55.	-45.	-55.	-45.	-34.	-45.
	5	7	1	6	2	0	1	9	7	4	8	7
B3PW91	-55.	-47.	-56.	-48.	-37.	-48.	-53.	-43.	-54.	-49.	-39.	-50.
	7	1	4	2	0	7	4	8	2	8	2	2
BHandHLYP	-62.	-53.	-63.	-52.	-40.	-52.	-60.	-51.	-61.	-53.	-41.	-54.
	7	4	4	1	9	6	7	4	3	7	8	2
PBE0	-59.	-49.	-59.	-54.	-42.	-54.	-56.	-47.	-57.	-55.	-43.	-55.
	0	3	7	0	7	4	9	5	6	2	1	9
X3LYP	-58.	-48.	-59.	-46.	-34.	-46.	-56.	-47.	-57.	-47.	-36.	-47.
	7	8	4	4	8	9	6	2	2	2	8	5
CAM-B3LYP	-64.	-55.	-65.	-52.	-41.	-52.	-61.	-52.	-62.	-49.	-38.	-50.
	4	2	0	2	8	7	9	4	6	7	2	4
TPSS	-53.	-44.	-54.	-46.	-36.	-47.	-51.	-42.	-52.	-48.	-37.	-49.
	8	1	5	9	3	1	5	0	1	9	2	4
M06L	-47.	-35.	-47.	-48.	-36.	-48.	-48.	-36.	-48.	-50.	-38.	-50.
	1	5	9	3	6	8	1	9	8	2	3	6
M06	-55.	-44.	-55.	-54.	-43.	-54.	-52.	-40.	-52.	-53.	-42.	-53.
	1	7	5	7	5	5	1	7	9	4	2	6
M06-2X	-56.	-44.	-57.	-54.	-43.	-54.	-56.	-47.	-57.	-59.	-48.	-60.
	0	5	0	4	9	9	3	5	0	9	7	5
BS3						BS4						
BP86	-52.	-43.	-53.	-44.	-32.	-45.	-50.	-41.	-51.	-46.	-37.	-47.
	8	4	6	7	2	3	8	4	5	7	1	0
PBE	-55.	-46.	-55.	-47.	-36.	-48.	-52.	-43.	-53.	-49.	-38.	-50.
	0	2	5	9	3	3	9	9	5	9	3	4
B3LYP	-57.	-47.	-57.	-45.	-33.	-45.	-55.	-45.	-56.	-47.	-35.	-47.
	3	9	9	2	7	6	3	9	0	0	8	4
B3PW91	-55.	-46.	-56.	-48.	-36.	-49.	-53.	-44.	-54.	-51.	-40.	-51.
	5	0	2	4	1	0	8	9	4	1	0	6
BHandHLYP	-62.	-53.	-63.	-52.	-41.	-53.	-61.	-51.	-61.	-55.	-43.	-55.
	9	7	5	9	5	3	0	9	7	1	5	6
PBE0	-59.	-49.	-59.	-53.	-42.	-54.	-57.	-48.	-57.	-56.	-44.	-57.
	1	5	7	9	0	4	2	2	8	4	6	0

TPSS	-53.	-44.	-54.	-45.	-33.	-46.	-51.	-43.	-52.	-49.	-38.	-49.
	7	3	3	7	3	3	6	0	2	1	7	5
M06	-55.	-46.	-55.	-54.	-42.	-54.	-51.	-39.	-52.	-54.	-40.	-54.
	1	0	5	3	4	7	7	8	6	1	4	9

Table S4 Reaction energies (in kcal mol⁻¹) at the doublet state^a

	Cpd2 + CO ₂ → Cpd3			Cpd2 + CS ₂ → Cpd4			Cpd2 + CO ₂ → Cpd3			Cpd2 + CS ₂ → Cpd4		
functional	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH	ΔE	ΔG	ΔH
	BS1						BS2					
BP86	-52.4	-40.9	-53.3	-47.8	-34.3	-48.5	-49.6	-39.4	-50.4	-48.7	-36.6	-49.3
PBE	-54.1	-44.7	-54.9	-51.1	-38.9	-51.7	-51.8	-42.4	-52.5	-50.9	-40.6	-51.3
B3LYP	-57.4	-48.2	-58.1	-44.7	-33.1	-45.2	-55.1	-45.1	-55.8	-45.6	-33.5	-46.3
B3PW91	-55.5	-47.3	-56.1	-48.6	-36.6	-49.2	-54.1	-43.3	-55.0	-50.8	-37.9	-51.6
BHandHLYP	-63.8	-53.7	-64.6	-52.3	-40.2	-52.9	-59.0	-50.1	-59.6	-54.0	-43.1	-54.5
PBE0	-59.7	-50.3	-60.4	-55.0	-44.1	-55.5	-57.8	-48.1	-58.6	-56.8	-45.0	-57.3
X3LYP	-59.1	-49.0	-59.9	-46.6	-35.7	-47.0	-56.0	-47.5	-56.6	-47.1	-35.8	-47.6
CAM-B3LYP	-65.0	-54.5	-65.8	-53.1	-41.9	-53.5	-60.9	-51.6	-61.5	-51.1	-39.8	-51.8
TPSS	-53.5	-44.4	-54.2	-49.4	-37.6	-49.8	-51.1	-41.6	-51.8	-52.2	-40.1	-52.6
M06L	-46.9	-35.7	-47.7	-49.6	-36.7	-50.4	-46.8	-37.0	-47.3	-51.8	-40.2	-52.2
M06	-54.5	-43.1	-55.2	-55.0	-44.1	-54.8	-51.9	-41.2	-52.6	-53.8	-42.5	-53.9
M06-2X	-58.0	-47.3	-59.0	-57.1	-45.5	-57.8	-55.1	-42.6	-56.3	-59.9	-46.2	-61.0

$$^a \Delta A_{\text{Cpd3}}^{\text{d}} = A_{\text{Cpd3}}^{\text{d}} - (A_{\text{Cpd2}}^{\text{d}} + A_{\text{CO2}}), \Delta A_{\text{Cpd4}}^{\text{d}} = A_{\text{Cpd4}}^{\text{d}} - (A_{\text{Cpd2}}^{\text{d}} + A_{\text{CS2}}).$$

5 QTAIM topological analysis of selected bonds

Table S5 QTAIM topological analysis of U-X (X=C, O, S) and E-C⁹ (E=O, S) bonds in Cpd2, Cpd3 and Cpd4

	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	DI	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	DI
Cpd2	U-C ⁸				C ⁸ -C ¹²			
BP86	0.070	0.075	-0.019	1.055	0.261	-0.596	-0.223	1.153
PBE	0.068	0.079	-0.018	1.050	0.262	-0.596	-0.224	1.151
B3LYP	0.065	0.075	-0.016	1.038	0.264	-0.630	-0.230	1.144
B3PW91	0.069	0.077	-0.018	1.052	0.265	-0.631	-0.232	1.146
BHandHLYP	0.064	0.079	-0.016	1.032	0.270	-0.684	-0.243	1.134
PBE0	0.068	0.077	-0.018	1.040	0.266	-0.640	-0.235	1.144
X3LYP	0.065	0.074	-0.016	1.033	0.265	-0.635	-0.231	1.143
CAM-B3LYP	0.065	0.079	-0.016	1.041	0.266	-0.643	-0.233	1.134
TPSS	0.067	0.077	-0.017	1.032	0.262	-0.609	-0.226	1.147
M06L	0.060	0.079	-0.013	0.985	0.270	-0.649	-0.241	1.154
M06	0.064	0.081	-0.016	1.025	0.268	-0.639	-0.236	1.145
M06-2X	0.061	0.085	-0.014	1.016	0.263	-0.620	-0.229	1.131
Cpd3	U-O ¹⁰				U-O ¹¹			
BP86	0.054	0.180	-0.003	1.050	0.055	0.181	-0.003	1.049
PBE	0.055	0.184	-0.003	1.057	0.054	0.178	-0.003	1.045
B3LYP	0.051	0.179	-0.002	1.018	0.051	0.174	-0.002	1.005
B3PW91	0.053	0.187	-0.003	1.034	0.054	0.185	-0.003	1.026
BHandHLYP	0.050	0.190	-0.002	1.008	0.050	0.179	-0.002	0.983
PBE0	0.054	0.191	-0.003	1.032	0.053	0.185	-0.003	1.022
X3LYP	0.051	0.177	-0.002	1.011	0.050	0.175	-0.002	1.005
CAM-B3LYP	0.052	0.184	-0.003	1.018	0.051	0.184	-0.002	1.011
TPSS	0.055	0.191	-0.003	1.062	0.055	0.185	-0.003	1.046
M06L	0.049	0.177	-0.001	0.993	0.051	0.188	-0.001	1.026
M06	0.049	0.181	-0.001	0.999	0.050	0.185	-0.002	1.015
M06-2X	0.049	0.187	-0.002	0.990	0.056	0.204	-0.003	1.076

to be continued

The unit of ρ_{BCP} is e bohr⁻³, and that of $\nabla^2\rho_{BCP}$ is e bohr⁻⁵. H_{BCP} represents the total electron energy density at a bond critical point (BCP), and $DI(A;B)$ the delocalization index between two atoms A and B.

continued

	ρ_{BCP}	$\nabla^2 \rho_{BCP}$	H_{BCP}	DI	ρ_{BCP}	$\nabla^2 \rho_{BCP}$	H_{BCP}	DI
Cpd3	$O^{10} - C^9$				$O^{11} - C^9$			
BP86	0.350	-0.268	-0.580	1.488	0.353	-0.251	-0.587	1.508
PBE	0.350	-0.263	-0.580	1.484	0.355	-0.232	-0.590	1.515
B3LYP	0.361	-0.207	-0.604	1.502	0.365	-0.184	-0.612	1.528
B3PW91	0.362	-0.157	-0.604	1.500	0.366	-0.135	-0.612	1.524
BHandHLYP	0.373	-0.078	-0.627	1.504	0.379	-0.051	-0.638	1.539
PBE0	0.364	-0.126	-0.607	1.502	0.368	-0.114	-0.616	1.524
X3LYP	0.362	-0.204	-0.606	1.506	0.365	-0.183	-0.612	1.526
CAM-B3LYP	0.366	-0.196	-0.615	1.507	0.369	-0.164	-0.620	1.527
TPSS	0.349	-0.210	-0.575	1.482	0.353	-0.184	-0.584	1.509
M06L	0.359	-0.046	-0.591	1.524	0.358	-0.052	-0.589	1.501
M06	0.364	-0.178	-0.608	1.521	0.365	-0.174	-0.611	1.513
M06-2X	0.366	-0.031	-0.606	1.538	0.359	-0.079	-0.593	1.477
Cpd4	$U-S^{10}$				$U-S^{11}$			
BP86	0.046	0.084	-0.008	1.199	0.046	0.083	-0.008	1.197
PBE	0.046	0.084	-0.008	1.190	0.045	0.082	-0.007	1.182
B3LYP	0.033	0.071	-0.003	0.982	0.033	0.067	-0.003	0.974
B3PW91	0.037	0.079	-0.005	1.029	0.037	0.076	-0.005	1.021
BHandHLYP	0.032	0.072	-0.003	0.951	0.032	0.067	-0.003	0.945
PBE0	0.037	0.076	-0.005	1.005	0.037	0.079	-0.004	1.021
X3LYP	0.034	0.072	-0.003	0.985	0.033	0.067	-0.003	0.973
CAM-B3LYP	0.034	0.075	-0.003	0.976	0.034	0.071	-0.004	0.969
TPSS	0.043	0.086	-0.006	1.153	0.043	0.084	-0.006	1.147
M06L	0.036	0.082	-0.004	1.032	0.038	0.087	-0.004	1.062
M06	0.035	0.075	-0.004	0.997	0.035	0.074	-0.004	0.997
M06-2X	0.034	0.073	-0.004	0.969	0.035	0.076	-0.004	0.991
Cpd4	$S^{10} - C^9$				$S^{11} - C^9$			
BP86	0.206	-0.387	-0.184	1.336	0.208	-0.399	-0.192	1.357
PBE	0.209	-0.402	-0.193	1.359	0.208	-0.397	-0.190	1.352
B3LYP	0.215	-0.395	-0.241	1.427	0.215	-0.380	-0.244	1.429
B3PW91	0.216	-0.376	-0.248	1.417	0.216	-0.356	-0.251	1.417
BHandHLYP	0.219	-0.180	-0.267	1.437	0.219	-0.184	-0.266	1.429
PBE0	0.217	-0.316	-0.257	1.425	0.216	-0.331	-0.255	1.416
X3LYP	0.215	-0.374	-0.247	1.433	0.214	-0.377	-0.244	1.424
CAM-B3LYP	0.218	-0.282	-0.261	1.429	0.218	-0.269	-0.261	1.432
TPSS	0.208	-0.407	-0.199	1.360	0.209	-0.411	-0.207	1.372
M06L	0.210	-0.335	-0.235	1.404	0.210	-0.346	-0.231	1.388
M06	0.212	-0.374	-0.228	1.429	0.210	-0.378	-0.222	1.411
M06-2X	0.216	-0.263	-0.258	1.442	0.213	-0.305	-0.250	1.405

6 Electrostatic potential and electron density

Fig.S1 The ESP difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd2
The isovalue for the surfaces is 0.006.

Fig.2 ESP difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd3
The isovalue for the surfaces is 0.006.

Fig.S3 ESP difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd4

The isovalue for the surfaces is 0.01.

Fig.S4 The electron density difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd2

The isovalue for the surfaces is 0.003.

Fig.S5 The electron density difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd3
The isovalue for the surfaces is 0.003.

Fig.S6 The electron density difference between CAM-B3LYP and other methods on the CAM-B3LYP optimized geometries of Cpd4
The isovalue for the surfaces is 0.006.