

Scientific paper

Electronic Absorption Spectra and Nonlinear Optical Properties of Ruthenium Acetylide Complexes: A DFT Study Toward the Designing of New High NLO Response Compounds

Muhammad Ramzan Saeed Ashraf Janjua,^{1,2,*} Asif Mahmood,²
Muhammad Faizan Nazar,³ Zhihua Yang¹ and Shilie Pan^{1,*}

¹ Key Laboratory of Functional Materials and Devices for Special Environments of CAS, Xinjiang Technical Institute of physics & Chemistry of CAS, Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40–1 South Beijing Road, Urumqi 830011, China

² Department of Chemistry, University of Sargodha, Sargodha, Pakistan

³ Department of chemistry, University of Gujrat, Gujrat, Pakistan

* Corresponding author: E-mail: Janjua@uos.edu.pk, slpan@ms.xjb.ac.cn

Received: 12-07-2013

Paper based on a presentation at the 4th RSE-SEE 2013 Symposium on Electrochemistry in Ljubljana, Slovenia

Abstract

In this study we have used density functional theory (DFT) to calculate nonlinear optical properties and simulate the UV-VIS absorption spectra of ruthenium acetylide complexes. Among the studied systems, system 4 has shown highest non-linear optical properties ($\alpha = 72.92 \times 10^{-24}$ esu and $\beta = 76.32 \times 10^{-30}$ esu). New compounds have been theoretically designed by the extension of conjugation length and substitution of electron withdrawing atom/groups as acceptor on system 4. All designed compounds show intense band due to metal-to-ligand charge transfer (MLCT). Second-order polarizability of new design compounds was remarkably high as compared to system 4 (123.35×10^{-30} to 360.23×10^{-30} esu). Effect of acceptors was more prominent than pi-spacers. Results of theoretical investigation indicate that all systems should be excellent non-linear optical materials.

Keywords: Ruthenium acetylide, density functional theory (DFT), Non-linear optics

1. Introduction

Non-linear optics (NLO) is the study of interaction of electromagnetic radiations with matter, resulting new electromagnetic radiations with change frequency, phase or other physical properties.¹ Atomic, molecular, solid-state physics, surfaces interface sciences, materials science, medicine, chemical dynamics and biophysics are diverse disciplines in which nonlinear optical materials have been used. In recent years, due to advances in laser technology Non-linear optics (NLO) become a field of major study.²

Acoustic-optic conversions, optical computing, Optical signal processing and optoelectronics are important technical areas in which nonlinear optical materials are used. The development of non-linear optical materials

with better response is very important. Theoretical understanding of factors which control the non-linear optical properties is very important to develop materials with enhanced non-linear optical properties.²

Great efforts have been devoted to obtain highly efficient NLO materials. It is well-known that the molecular second-order NLO properties can be manipulated by modifying the donor and acceptor capacity and extending the π -conjugated bridge. The first hyperpolarizability and, hence, the second-order NLO response is related to an electronic intramolecular charge transfer (ICT) of the molecule.³⁻¹² Thus, in most cases, the D- π -A structure is designed to enhance the CT transitions.

NLO activity can be found in organic compounds and inorganic crystals such as LiNbO₃, and also in orga-

nometallic complexes.^{13,14} Organic materials have low energy transitions in the UV–vis region which enhanced the NLO efficiency, but result in a tradeoff between nonlinear efficiency and optical transparency and they may have low thermal stability.¹⁵ Inorganic crystals have several drawbacks: high quality single crystals are difficult to grow, are expensive, and are not easy to incorporate into electronic devices.¹⁴ However, organometallic complexes offer greater scope for creation of multifunctional NLO materials by virtue of their greater design flexibility, low energy, and intense electronic transitions.^{15–17}

Both theoretical and experimental studies have shown that large hyperpolarizabilities generally arise from amalgamation of a strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path. However, the structure–property relationship indicates that the β value also increases with π -conjugating length.^{18,19}

Recently organo-metallic complexes have attained significant attention due to high nonlinear optical (NLO) properties.²⁰ Ruthenium compounds have been studied intensively for both their second order and third order behavior.²¹

Metal acetylide complexes have been intensely studied for decades.²² In early works much attention had focused on synthetic and structural issues. Later on extensive work has been done on electronic, magnetic properties, optical and non-linear optical of these compounds.²² Recently, acetylidemetal complexes of ruthenium have become promising candidates for NLO materials.²³

Designing, development and search of NLO materials become very important during recent years due to potential applications in optical limiting devices, optical bistability, high-speed all optical switches, optical signal processing and computing.²⁴ Criterion of large hyperpolarizability is being applied in the search of NLO metal complexes.²⁵

In this study we have studied the non-linear optical properties of ruthenium acetylide complexes. Structures of studied compounds are shown in Fig. 1. Best of our knowledge no study has been done to explore NLO properties of these compounds. New compounds have been designed by modification of pi-spacer and acceptor. ($\text{—C}\equiv\text{C—}$) groups are added to system 4 to enlarge the conjugation length. Three electron withdrawing atoms/groups (F, CF_3 and CN) are substituted to anthracene of system 4. This theoretical study is not only important for interpretation of NLO properties but also for designing new NLO materials with high NLO response. In this research work absorption spectra, polarizability (α) and first hyperpolarizability (β) were calculated using density functional theory. This work may provide a useful means in designing the new polymeric NLO materials.

2. Computational Details

2.1. Theoretical Methodology

When a molecule is placed in a uniform static electric field, its electronic energy can be written as a series

involving coefficients identified as permanent multipole moments and polarizabilities (Eq. 1).²⁶

$$E^P = E^0 - \mu_a F_a - \left(\frac{1}{2}\right) \alpha_{\alpha\beta} F_\alpha F_\beta - \left(\frac{1}{6}\right) \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \left(\frac{1}{24}\right) \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta \quad (1)$$

Where F_α , F_β , etc. denote the field at the origin. E^0 and μ_α are the energy and the permanent dipole moment, respectively. The quantities $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ are the dipole polarizability, the first and the second dipole hyperpolarizabilities, respectively. The subscripts represent the Cartesian coordinates.

2.2. Computational Procedure

Gaussian 09 program package was used to perform all calculations.²⁷ All systems were optimized using density functional theory.^{28–32} Cam-b3lyp functional was used for geometry optimization, calculation of non-linear optical properties and UV/Vis spectra. The 6-311+g(d) basis set for S and 6-31g(d) basis set for other nonmetal atoms were adopted. The Stuttgart/Dresden double- ζ (SDD)^{33,34} basis set was used for Ru atom. It is a relativistic effective core potential (ECP), which replaces the inner core 28 electrons, leaving the outer core 14 electrons ($4s^2 4p^6 4d^6$) as the valence electrons for Ru(II).³⁵ This computational approach successfully used to study the non-linear optical properties of metallic complexes.^{33–38}

Absorption spectra of dyes simulated by using TDDFT calculations with CAM-B3LYP. 10 lowest singlet–singlet excitation energies were computed. Symmetry constraints are not considered in all calculations.

Following formulas are used to calculate average polarizability and hyperpolarizability.²⁵

$$\alpha = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2 \right]^{1/2} \quad (3)$$

3. Results and Discussion

3.1. Non-linear Optical Properties

Understanding of nonlinear optical properties is very important in the designing of materials for signal processing, communication technology, optical memory devices and optical switches.

Values of average polarizability of four systems are given in Table 1. Order of average polarizability of four systems is: syst4 > syst3 > syst2 > syst1. Polarizability of system 4 was 72.92×10^{-24} esu. Polarizability of a molecule depends upon the energy gap between HOMO and LUMO. For a molecule to be polarizable small energy gap is

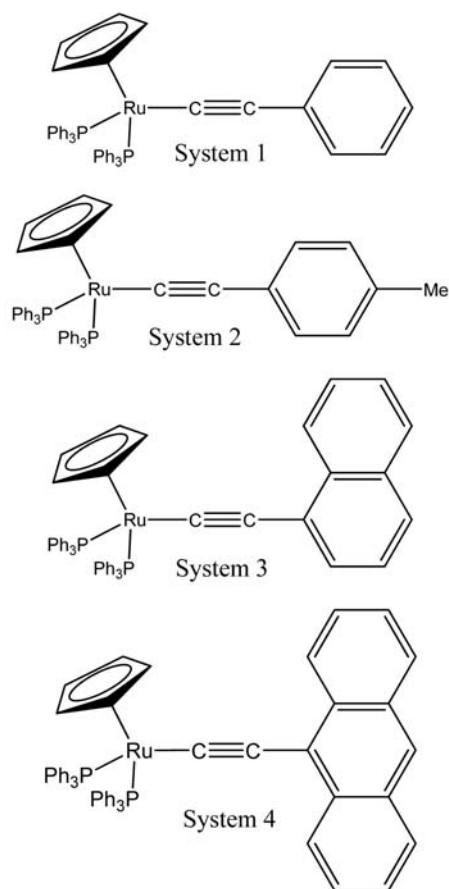


Figure 1. Structure of systems 1–4.

required. Generally, a large linear polarizability is required to obtain large hyperpolarizabilities.³⁹

Hyperpolarizabilities were calculated by using CAM-B3LYP method. The computed β_{tot} values of systems 1–4 are given in Table 1. They are reported as 10^{-30} esu. Order β_{tot} of four systems is: syst 4 > syst 3 > syst 2 > syst 1. System 4 has longer conjugation as compared to other systems. Delocalization of π -electrons increases the hyperpolarizability. Delocalization of π -electrons stabilizes the molecule and decreases the HOMO-LUMO energy gap. Molecules become more polarizable. β_{tot} of system 4 was 76.32×10^{-30} esu. Relationship between HOMO-LUMO energy gap and hyperpolarizability (β_{tot}) is depicted in Fig. 2. From figure it is clear that system with low energy gap has high hyperpolarizability (β_{tot}).

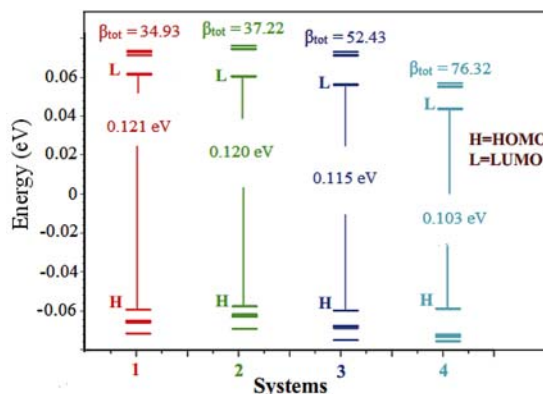


Figure 2. Molecular orbital energy diagram, HOMO-LUMO energy gaps and β_{tot} ($\times 10^{-30}$ esu) values of systems 1–4.

3. 2. Optical Absorption Studies

The quantum chemical calculations are a easy and efficient way to stimulate the absorption spectra. Simulation of Spectra is very important because they provide the range of absorbance of NLO material. The wide absorbance range increases the practical use of nonlinear optical material.

Electronic spectra were simulated with TDDFT/CAM-B3LYP method using optimized geometries. In TD-DFT calculations, the first 10 spin-allowed singlet-singlet excitations were calculated. The percentage contributions of molecular orbitals to formation of the bands were obtained by using gaussian 2.2.4 Program.⁴⁰

TDDFT calculations have been performed to understand electronic transitions of all the studied systems. Transition energy, maximum wavelengths, oscillator strength, main configurations, and transition character are presented in Table 1.

To understand the origin of the second-order NLO properties of the studied compounds, a better elucidation of a structure-property relationship is required. From the sum-overstates (SOS) approach, a two-state model linked between β and a low-lying charge-transfer transition has been recognized.⁴¹ In the static case, the following model expression is employed to estimate β_{CT} :

$$\beta_{\text{CT}} \propto \frac{\Delta\mu_{\text{gm}} f_{\text{gm}}}{E_{\text{gm}}^3} \quad (4)$$

Table 1. Polarizability α (1×10^{-24} esu), hyperpolarizability β_{tot} (1×10^{-30} esu), excitation energy (nm; eV), oscillator strengths (f_{gm}) and transition moment (M_x^{gm} a.u.) of system 1–4.

System	α	β_{tot}	λ_{max}	E_{gm}	f_{gm}	M_x^{gm}	MO transtion
1	58.83	34.93	401	3.09	0.024	0.236	H-2 \rightarrow L (70%)
2	60.38	37.22	403	3.08	0.023	0.284	H-2 \rightarrow L (69%)
3	65.06	52.43	454	2.73	0.028	0.484	H \rightarrow L (91%)
4	72.92	76.32	471	2.63	0.309	2.150	H-1 \rightarrow L (38%)

where $\Delta\mu_{gm}$ is the change of dipole moment between the ground and m^{th} excited state, f_{gm} is the oscillator strength of the transition from the ground state (g) to the m^{th} excited state (m), and E_{gm} is transition energy. In the framework of two-state model expression, the hyperpolarizability is proportional to the product of the transition dipole moments and oscillating strength and is inversely proportional to the cube of the transition energy.

Therefore, well-performing NLO material must possess a low-energy CT excited state with large oscillator strength.⁴² These factors ($\Delta\mu_{gm}$, f_{gm} , and E_{gm}) are closely related with each other and are governed by choice/strength of the donor/acceptor along with the conjugated bridge. The most favourable combination of these factors can provide a larger β value. All the studied systems possess the same general skeleton, and thus there is not much difference in the $\Delta\mu_{gm}$ value. That's why $\Delta\mu_{gm}$ is considered as constant. Therefore, the first hyperpolarizabilities for our studied systems are mainly proportional to f_{gm} and inversely proportional to the cube of E_{gm} .

For maximum capturing of solar radiation molecule should absorb photons in visible.⁴³ All compounds have shown absorbance in visible region. The maximum absorption wavelength is an approximate measure of the transparency achievable.⁴⁴ System 4 is red shifted as compare to other systems due to better conjugation. Major absorption peaks of all systems exit between 401 and 471 nm. HOMO-2 to LUMO transition is most probable and low energy transition of system 1 and 2. For system 3 HOMO to LUMO transition is most probable and low energy transition. But for system 4 HOMO-1 to LUMO transition is most probable and low energy transition. For all systems very low transition energy is required (3.09–2.63eV). Low transition energy results the large β . Order of transition energy was opposite the order of hyperpolarizability. Transition energy decrease in the following order: syst1 > syst2 > syst 3 > syst 4, whereas the NLO response increases accordingly as follows: syst1 < syst2 < syst 3 < syst 4.

Oscillating strength (f_{gm}) is directly related to length of conjugation.⁴⁵ Oscillating strength (f) of system 1, 2, 3 and 4 was in following order: syst 4 > syst 3 > syst 1 > syst 2. Higher oscillating strength of system 4 was due to better conjugation. From Table 2 and 3 it is clear that strong oscillating strength and small transition energy are responsible for large β_{tot} values. The oscillator strength can be directly obtained from the TDDFT calculations. The computed M_x^{gm} values increase from system 1 to 4 in accordance with the β_{tot} values.

3. 3. Theoretical Designing of High Response NLO Compounds

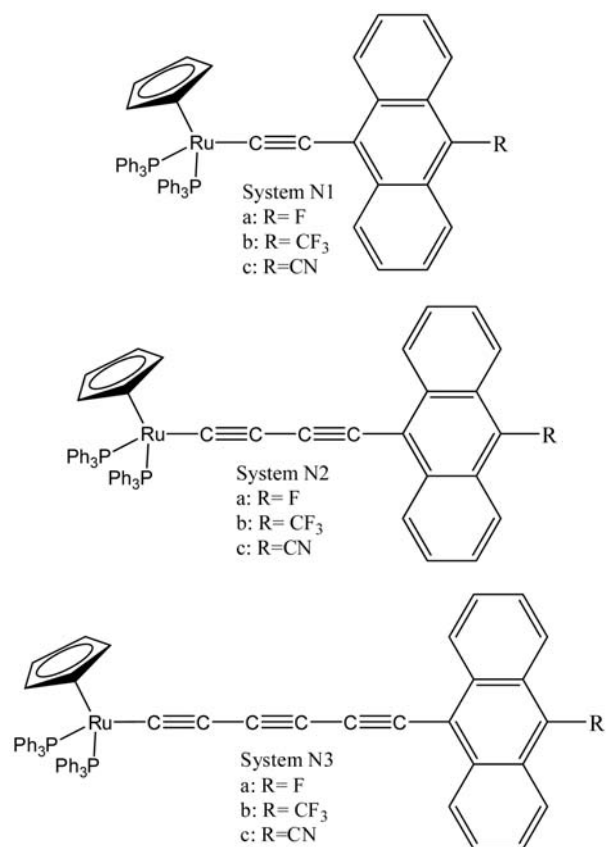
Compounds which show NLO response mostly consist of donor-conjugation-acceptor (D- π -A) configuration. Different methodologies are used to enhance the NLO response. NLO response can be tuned by the modification

of the donor/acceptor and the length of pi-spacer. In most of studies all, two or one component has been changed.

In the present study we have decided to study the effect of pi-spacer and acceptor. Among the studied systems non-linear response of system 4 was high. Therefore system 4 is selected for the designing of new compounds. All systems have very good donor. Electron-rich d^6 ruthenium (II) centres are especially well-suited for incorporation into NLO chromophores because their highly polarizable d orbitals can cause effective π -electron-donating properties when coordinated to ligands with low-lying π^* orbitals.²¹

β value is strongly conjugation length dependent. It increases with the increase p-conjugating length.^{18,19} The bridge mediated donor-acceptor electron interaction is large enough to maximize the strength of the transition matrix element (associated with the oscillator strength) of the charge-transfer transition. ($\text{—C}\equiv\text{C—}$) groups are added in system 4 along the already existing ($\text{—C}\equiv\text{C—}$) group to extend the conjugation.

Three electron withdrawing atom/groups (F, CF_3 and CN) have been used. The positive role of these electrons withdrawing atom/groups as acceptors to enhance the NLO response is already demonstrated in literature.^{46–53} In the designing of compounds of series N1, three electron withdrawing atom/groups (F, CF_3 and CN) are alternatively add to anthracene of system 4. For the design-



ning of compounds of N2 and N3 series, one and two ($\text{—C}\equiv\text{C—}$) groups are added along ($\text{—C}\equiv\text{C—}$) group of systems of series N1 respectively. Structures of designed compounds are shown in Figure 3. Non-linear optical properties and time dependent density functional theory (TDDFT) calculations' results are given in Table 2. From the table it is clear that the second-order polarizability has been significantly increased by the introduction of different electron withdrawing atom/groups (F, CF_3 and CN). Second-order polarizability is also increase due to extension of conjugation length by addition of ($\text{—C}\equiv\text{C—}$) groups from system N1 series to N3 series. Graphical comparison of hyperpolarizabilities of already existing and designed compounds is depicted in Figure 4. From figure it is clear that introduction of different electron withdrawing atom/groups (F, CF_3 and CN) has remarkably increase the hyperpolarizability as compared to extension of conjugation length. A similar trend was observed for polarizability. But increase in polarizability was lower. Substitution effect of acceptors on second-order polarizability is found in following order: $\text{CN} > \text{CF}_3 > \text{F}$.

From Table 2 it is can be noted that no clear effect of pi-spacer and acceptor change is observed on λ_{max} . Energy of most probable transition was decrease in designed systems as compared to system 4. Trend of transition energy is opposite to the trend of hyperpolarizability. It means low energy transitions may be responsible for higher

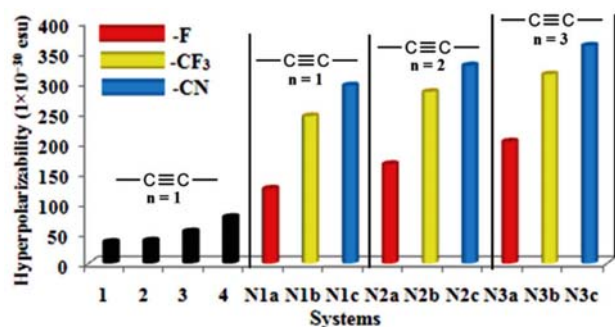


Figure 4: Comparison of hyperpolarizabilities of already existing and designed compounds.

hyperpolarizability. Transition dipole moment of designed systems was also greater than system 4. From Table 2 it is clear that oscillator strength has increased due to the introduction of electron withdrawing atom/group as acceptor and increase of conjugation. Transition dipole moment of new designed compounds was greater than the system 4.

The HOMOs and LUMO composition of designed compounds is shown in Fig. 5. Most systems have different HOMO and LUMO composition. This indicates the significant charge transfer.

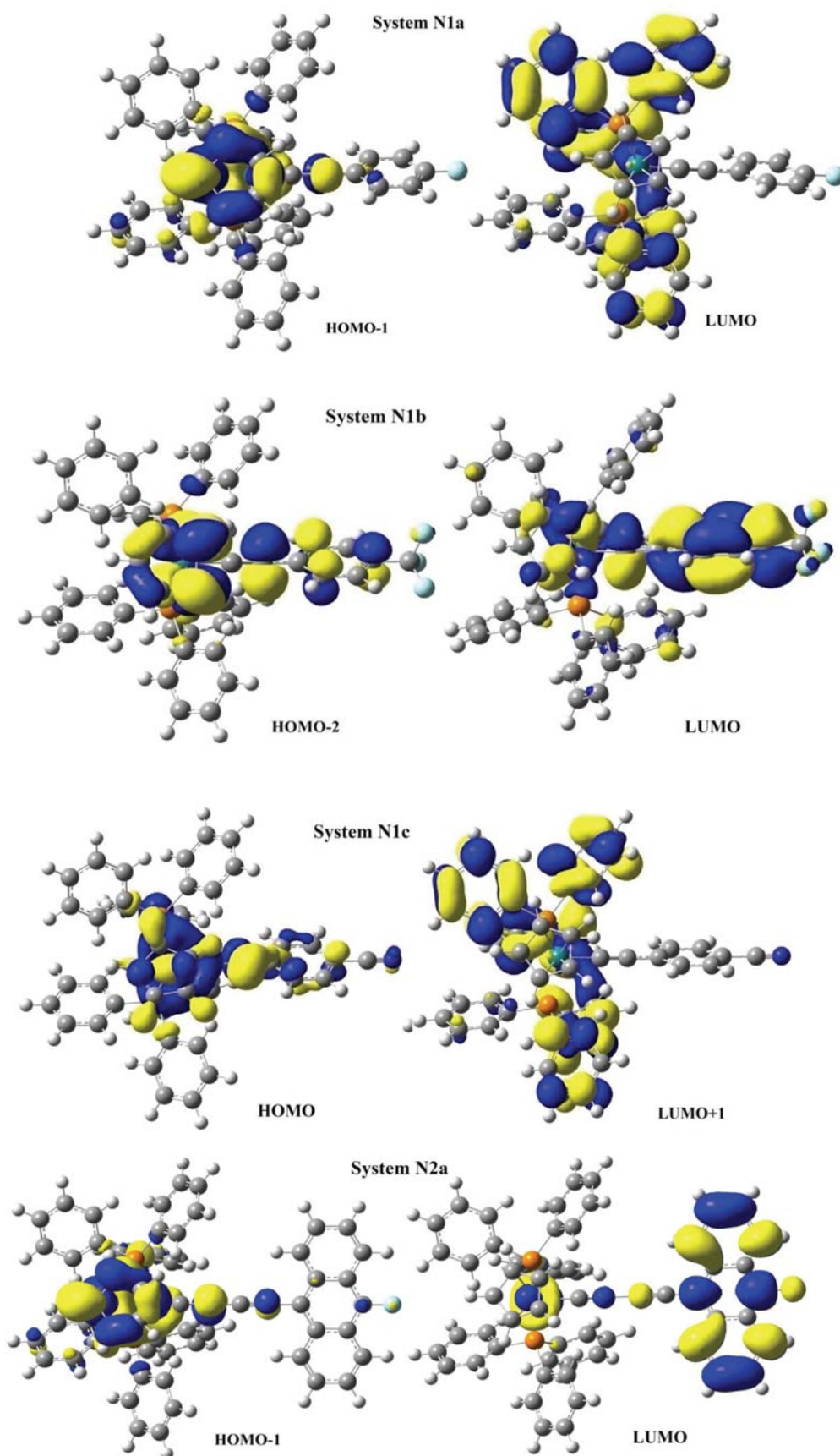
The present investigation provides insight into the NLO properties of ruthenium acetylide complexes. These compounds can become excellent material in the second order NLO field. For the better utilization of these compounds further research is required. This study is an initiative in this regard. This study will catch the attention of scientists for the development of better NLO materials.

4. Conclusion

The present theoretical investigation gives insight into the NLO properties of ruthenium acetylide complexes. All systems display large second-order NLO properties. All studied systems have good non-linear optical properties. Among the studied systems, system 4 has shown highest non-linear optical properties ($\alpha = 72.92 \times 10^{-24}$ esu and $\beta = 76.32 \times 10^{-30}$ esu). All studied systems show absorbance in visible region. All systems show high oscillating strength, light harvesting efficient efficiency and transition moment. Transition energy of all systems was low. Nine new compounds have been designed by the alternate introduction of three acceptors (F, CF_3 and CN) and extension of conjugation length. Second-order NLO response of designed compounds was high than the system 4 due to the increase of the charge transfer. The second-order polarizabilities of compounds that contain CN were larger than those that have F and CF_3 . Effect of pi-spacer was more prominent the effect of acceptors. The present calculations give a theoretical framework in which the CT and NLO properties may be understood and provide new ways for experimentalists to design high-performance NLO materials.

Table 2. Polarizability α (1×10^{-24} esu), hyperpolarizability β_{tot} (1×10^{-30} esu), excitation energy (nm; eV), oscillator strengths (f_{gm}) and transition moment (M_x^{gm} a.u.) of new designed systems.

System	α	β_{tot}	λ_{max}	E_{gm}	f_{gm}	M_x^{gm}	MO transition
N1a	80.08	123.35	479	2.41	0.485	2.901	H-1 \rightarrow L (89%)
N1b	92.35	243.46	484	2.26	0.606	3.205	H-2 \rightarrow L (73%)
N1c	103.89	294.32	495	2.11	0.734	3.506	H \rightarrow L+1 (91%)
N2a	94.32	163.90	490	2.32	0.567	3.012	H-1 \rightarrow L (93%)
N2b	99.78	283.56	487	2.15	0.667	3.562	H-2 \rightarrow L (73%)
N2c	111.56	327.45	498	1.89	0.750	3.856	H \rightarrow L+1 (87%)
N3a	102.34	201.23	506	2.23	0.599	3.230	H-2 \rightarrow L (84%)
N3b	112.72	312.56	501	1.88	0.723	3.982	H \rightarrow L (83%)
N3c	115.34	360.23	497	1.81	0.798	4.089	H \rightarrow L+1 (71%)



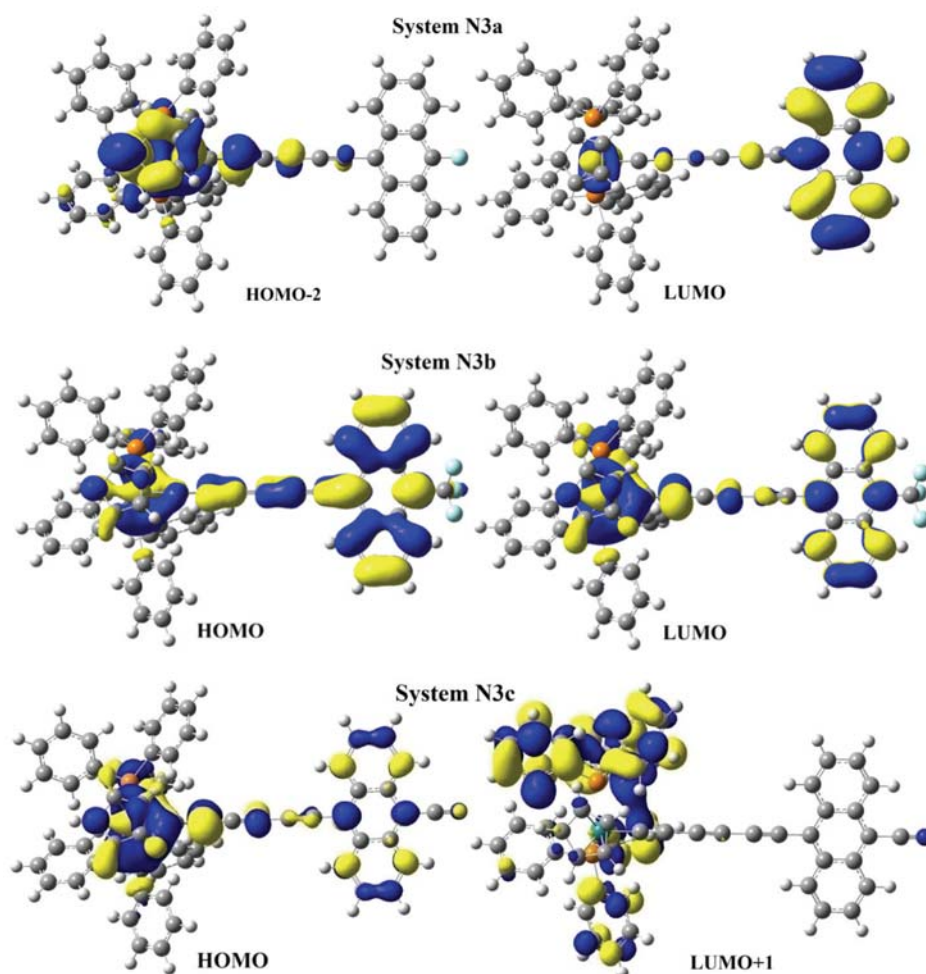


Figure 5. HOMO and LUMO composition of designed systems.

5. Acknowledgement

This work is supported by CAS Visiting Fellowship for Researchers From Developing Counties (Grant No. 2014FFGB0001), 973 Program of China Grant Nos. 2014CB648400, 2012CB626803), the National Natural Science Foundation of China (Grant Nos. U1129301, 51172277), the Recruitment Program of Global Experts (1000 Talent Plan, Xinjiang Special Program), Main Direction Program of Knowledge Innovation of CAS (Grant No. KJCX2-EW-H03-03), the Funds for Creative Cross & Cooperation Teams of CAS, Major Program of Xinjiang Uygur Autonomous Region of China during the 12th Five-Year Plan Period (Grant No. 201130111).

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Povzetek

Z uporabo gostotne funkcionalne teorije (DFT) smo izračunali nelinearne optične lastnosti in ponazorili UV-VIS absorpcijske spektre kompleksov rutenijevega acetilida. Izmed proučevanih kompleksov sistem 4 kaže najvišje nelinearne optične lastnosti ($\alpha = 72.92 \times 10^{-24}$ esu in $\beta = 76.32 \times 10^{-30}$ esu). S podaljšanjem konjugirane dolžine ter vpeljavo različnih elektron akceptorskih atomov/skupin smo na sistemu 4 ustvarili več teoretičnih modelov spojin, ki vse kažejo močno absorpcijo zaradi prenosa naboja kovina-ligand (MLCT). Rezultati teoretičnih raziskav kažejo, da vsi proučevan