Theoretical Framework of 1,3-Thiazolium-5-Thiolates Mesoionic Compounds: Exploring the Nature of Photophysical Properties and Molecular Nonlinearity

Zeyu Liu,*† Shugui Hua,§ Tian Lu,§ and Ziqi Tian¶

†College of Biotechnology, Jiangsu University of Science and Technology, Zhenjiang 212018, People’s Republic of China
‡College of Life Science and Chemistry, Jiangsu Key Laboratory of Biological Functional Molecules, Jiangsu Second Normal University, Nanjing 210013, People’s Republic of China
§Beijing Kein Research Center for Natural Sciences, Beijing 100022, People’s Republic of China
¶Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People’s Republic of China

*Email: liuzy@just.edu.cn. Phone: +86 511 85638328.
Abstract

Inspired by a previous experimental study on the first-order hyperpolarizabilities of 1,3-thiazolium-5-thiolates mesoionic compounds using Hyper-Rayleigh scattering technique, we theoretically investigated the UV-Vis absorption spectra and every order polarizabilities of these mesoionic molecules. Based on the fact that the photophysical and nonlinear properties observed in the experiment can be perfectly replicated, our theoretical calculations explored the essential characteristics of the optical properties of the mesoionic compounds with different electron-donating groups at the level of electronic structures through various wave function analysis methods. The influence of the electron-donating ability of the donor on the optical properties of the molecules and the contribution of the mesoionic ring moiety to their optical nonlinearity are clarified, which have not been reported by any research so far. This work will help people understand the nature of optical properties of mesoionic-based molecules and provide guidance for the rational design of molecules with excellent photoelectric performance in the future.

TOC Graphic:
1. Introduction

For a long time, one of the hotspots in optical nonlinearity research has been the design and development of new compounds with enhanced (hyper)polarizability for telecommunications, data storage, sensor protection, and imaging. So far, a variety of molecules exhibiting nonlinear optical (NLO) response, including inorganic semiconductors, organic dyes, metal clusters, and metal-doped electrides, have been synthesized and applied in the field of materials. Among them, the electronic push-pull organic chromophores formed by connecting the two ends of the π-conjugated linker (Rπ) with the electron-donating unit (RD) and electron-accepting group (RA), respectively, so it is also called D-π-A type structures, have always been the most popular molecules. Generally, a D-π-A molecule with excellent NLO properties can be assembled by rationally adjusting or modifying its three components.

According to the characteristics of the π-conjugated linker, the chromophores can be further differentiated into various species. Mesoionic rings are planar five- or six-membered heterocyclic betaines with at least one side-chain whose α-atom is also in the ring plane. These structures were described as “cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of electrons in association with the atoms comprising the ring”. Since Baker and Ollis proposed the concept of mesoionic in 1949, it has been almost universally recognized in heterocyclic chemistry. Because the mesoionic rings can provide mobile electrons, molecules that use them as efficient asymmetric bridges, which are often called the mesoionic compounds, have been considered to be promising candidates for practical applications in optical material. Early computational study demonstrated, for example, that compounds with a mesoionic ring as the π-conjugated bridge exhibit exciting optical nonlinearity, and their second-order NLO responses were observed to be comparable to that of symmetric polyenic bridges containing more than seven conjugated double bonds.

Recently, Barbosa-Silva et al. measured the first-order hyperpolarizabilities of the mesoionic compounds 2-(4-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazole-5-thiolate, 2-(4-chlorophenyl)-3-methyl-4-(4-methylphenyl)-1,3-thiazole-5-thiolate, and (2-(4-chlorophenyl)-3-methyl-4-(4-methoxyphenyl)-1,3-thiazole-5-thiolate) through Hyper-Rayleigh scattering (HRS) experiments at the 1180 nm fundamental wavelength for the first time and then extrapolated their intrinsic molecular hyperpolarizabilities at
the zero-frequency limit. However, in general, it is difficult to reveal the nature and origin of the optical properties of molecules by experimental observation alone, and meanwhile, most of the previous theoretical studies on such molecules only focused on the numerical value of their first-order hyperpolarizability. Therefore, in view of the fact that the optical properties of mesoionic compounds can be controlled through structural tailoring and continuing our consistent interest in the molecules with abnormal structures, we have conducted detailed studies on the photophysical and nonlinear properties of these experimental molecules.

2. Computational Details

The structure optimizations of three mesoionic compounds were performed with hybrid density functional theory (DFT) at the PBE0/def-TZVP level. Vibrational frequency analyses were then carried out on optimized geometries to determine the natures of them. The excitation energies and oscillator strengths of the low-lying singlet states of the mesoionic compounds were calculated with the time-dependent DFT (TD-DFT) at the PBE0/def2-TZVP level. The molecular (hyper)polarizabilities and (hyper)polarizability densities were evaluated using analytic derivatives of the system energy (namely, coupled-perturbed Kohn-Sham method, CPKS) at the CAM-B3LYP/aug-cc-pVTZ(-f,-d) level, where aug-cc-pVTZ(-f,-d) is a reduced version of the aug-cc-pVTZ basis set with the removal of f-type polarization functions of non-hydrogen atoms and d-type polarization functions of hydrogen atoms. The selections of long-range corrected CAM-B3LYP functional in calculations of molecular nonlinearity were based on previous benchmark works on the response property of some organic molecules. The decompositions of the overall (hyper)polarizability into each structural unit were obtained by numerical integrations of the (hyper)polarizability density in the space of every atom partitioned by Becke’s method. The solvation model of density (SMD) approach was applied to consider solvent effects of dimethyl sulfoxide (DMSO) molecules on molecular structure and optical properties.

The dipolar direction of the mesoionic compounds followed along the z axis of the coordinate system, and the original point was set at the center of mass of the molecules. For the formulas of the (hyper)polarizability and (hyper)polarizability density, please refer to the detailed descriptions in the Supporting Information.
All (TD-)DFT calculations were performed with the Gaussian 16 program. The wave function analyses were carried out by Multiwfn 3.7(dev) code, and the visualizations of the isosurface maps were realized with VMD software.

3. Results and Discussion

In the present work, we theoretically investigated the optical properties of three mesoionic compounds related to the 1,3-thiazolium-5-thiolates group. For the convenience of the comparative discussion, the same naming method as in reference 24 is used to name the molecules studied, as shown in Scheme 1. The Cartesian coordinates for ground-state mesoionic compounds are listed in Table S1.

Scheme 1. Structure of the mesoionic compounds studied in this work

![Scheme 1](image)

Also shown is the Cartesian axis. Atom color code: white, H; grey, C; blue, N; yellow, S; green, Cl.

3.1. Perfectly Replicated Absorption Spectra and the Natures of Electronic Transitions

Absorption bands in the UV-green region of 370-550 nm for current mesoionic compounds obtained from theoretical simulations are shown in Figure 1. The strongest absorption peaks are observed to be centered at about 448 nm. One can see that although they have different electron-donating groups, the absorption bands in visible region of the three mesoionic compounds are very similar. However, the spectral differences of the three molecules in the near UV region are obvious. Specifically, the UV-Vis absorption spectra of the studied systems reported in experiment can be perfectly reproduced by our DFT calculations. Compared with the experimental values, the calculated maximum absorption wavelengths have a
systematic error of only 13 nm. This lends confidence for us to analyze the excitation characteristics of these molecules below.

Figure 1. Optical absorbance spectra for the studied mesoionic compounds. A Gaussian function has been employed for broadening with a full width at half-maximum of 2000 cm\(^{-1}\). The inset shows dominant natural transition orbital pairs (isovalue = 0.03 au) involved in maximum absorptions. The numbers on the inset denote the associated eigenvalues for the transitions.

The natural transition orbital (NTO) analyses,\(^{46}\) which can provide straightforward images for exploring the orbital character involved in electronic transitions, were implemented for the strongest absorptions and the isosurfaces of NTO pairs were schematically illustrated in the inset of Figure 1. The low-energy absorption features for all mesoionic compounds are assigned to transitions from lone-pair orbitals, \(n\), of S atoms and \(\pi\)-bonding orbitals at mesoionic rings to \(\pi^*\)-antibonding orbitals located at the mesoionic rings and benzene units connected to the electron acceptors, namely, \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) electronic excitations on molecular skeletons. Electron-donating and electron-accepting moieties at the terminals of the molecules are barely participated in this process. So it is not difficult to understand why different molecules show extremely similar UV-Vis absorption spectra to each other.

The frontier molecular orbitals (FMOs), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), involved in the maximum absorption for studied mesoionic compounds are displayed in Figure S1. It can be seen that the HOMO-LUMO transition, which contributes 99.0\% to the total
absorption, plays a decisive role of the maximum absorption peak. Based on this fact, the NTO pair associated with molecular maximum absorption is almost identical with the molecular FMOs.

3.2. HRS-Derived First-Order Hyperpolarizabilities: Dipolar/Octupolar Contributions to the Second-Order NLO Activity

In order to compare with the experimental data, we calculated the molecular first-order hyperpolarizabilities corresponding to the HRS measurement, \( \beta_{\text{HRS}}(-2\omega,\omega,\omega) \) [abbreviated \( \beta_{\text{HRS}}(\lambda) \), where \( \lambda \) denotes the incident wavelength], of the studied molecules at the 1180 and 99999 nm fundamental wavelengths and the zero-frequency limit. The \( \beta_{\text{HRS}}(\lambda) \) values of the mesoionic compounds are summarized in Table 1.

Table 1. First-Order Hyperpolarizabilities Related to HRS Experiment [\( \beta_{\text{HRS}}(\lambda), \lambda = 1180, 99999, \text{ and } \infty \text{ nm, in } 10^{-30} \text{ esu} ] \) of the Studied Mesoionic Compounds

<table>
<thead>
<tr>
<th>compound</th>
<th>( \beta_{\text{HRS}}(1180 \text{ nm}) )</th>
<th>( \beta_{\text{HRS}}(\infty \text{ nm}) )</th>
<th>( \beta_{\text{HRS}}(99999 \text{ nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>expt.(^a)</td>
<td>calc.(^b)</td>
<td>expt.(^a)</td>
</tr>
<tr>
<td>MIC-1</td>
<td>30.2</td>
<td>28.2</td>
<td>10.1</td>
</tr>
<tr>
<td>MIC-2</td>
<td>26.4</td>
<td>31.5</td>
<td>8.7</td>
</tr>
<tr>
<td>MIC-3</td>
<td>31.7</td>
<td>33.7</td>
<td>10.4</td>
</tr>
</tbody>
</table>

\(^a\)Values taken from reference 24. \(^b\)Results of current work. \(^c\)Values taken from reference 19.

It can be seen that our calculated \( \beta_{\text{HRS}}(1180 \text{ nm}) \) values are in good agreement with the experimental data, while there are some differences in the zero-frequency hyperpolarizabilities, \( \beta_{\text{HRS}}(\infty \text{ nm}) \), between our calculations and experimental extrapolations. Moreover, the previously calculated \( \beta_{\text{HRS}}(\infty \text{ nm}) \) values at the static field limit for the three mesoionic compounds by Lyra et al. are even larger than our results.\(^{19}\) The most likely reason for the discrepancy was that their calculations employed the semi-empirical time-dependent Hartree-Fock (AM1-TDHF) method and did not take into account the solvation effect. In particular, we have calculated the NLO properties of the mesoionic compounds at some large wavelengths of incident
light. The results show that when the fundamental wavelength reaches thousands of nanometers, each calculated (hyper)polarizability will converge to a specific value. Generally, we may think that it is the zero-frequency (hyper)polarizability of the molecule. However, the first-order hyperpolarizability listed in Table 1 at an incident wavelength of 99999 nm, $\beta_{\text{HRS}(99999 \text{ nm})}$, is obviously smaller than the static one of the molecule (the molecular dipole moment, polarizability, and second-order hyperpolarizability also show the same characteristics) and coincides with the experimental zero-frequency extrapolation.

In our DFT calculations, the first-order hyperpolarizability calculated at the 1180 nm and zero frequency ($\infty$ nm) increases with the donating ability of the electron donor in the molecule and follow the order: $\beta_{\text{HRS}}^{\text{MIC-1}}(\lambda) < \beta_{\text{HRS}}^{\text{MIC-2}}(\lambda) < \beta_{\text{HRS}}^{\text{MIC-3}}(\lambda)$ ($\lambda = 1180$ and $\infty$ nm). Moreover, we can see that the frequency-dependent $\beta_{\text{HRS}}(1180 \text{ nm})$ values are higher than the zero-frequency $\beta_{\text{HRS}}(\infty \text{ nm})$. It reveals a resonance effect caused at the 1180 nm fundamental in the HRS study.

The polarization scan of the HRS intensity was performed for further exploring the dipolar/octupolar contributions to the second-order NLO activity of these mesoionic compounds. As can be inferred from the $\tilde{T}_V^{3\nu} = \nu$ schemes in Figure 2, all studied compounds belong to intermediate molecule with almost equal dipolar and octupolar characteristics. More detailed analysis shows that, with the enhancement of the electron donating ability in the order of MIC-1 < MIC-2 < MIC-3, the HRS intensity of the molecule gradually increases at any polarization angle $\Psi$ and more dipolar characteristics are displayed either at frequency-dependent field or at zero-frequency limit, as reflected by the calculated nonlinear anisotropy parameter ($\rho$) and depolarization ratio ($DR$) in Table S2. The HRS intensity enhances significantly and the dipolar characteristic slightly increases for each molecule at a fundamental wavelength of 1180 nm relative to those displayed at static field limit.
Figure 2. Harmonic light intensity for the studied mesoionic compounds as a function of the polarization angle Ψ by polar representation. The inset shows the calculated nonlinear anisotropy parameters (ρ) at the 1180 nm fundamental wavelength and the zero-frequency limit for every molecule.

3.3. EFISHG-Derived Every Order Polarizabilities: the Essential Research

To evaluate the potential applications in nonlinear response of the title molecules, we have calculated their every order polarizabilities, α(−ω,ω), β(−2ω,ω,ω), and γ(−2ω,ω,ω,0) [abbreviated α(λ), β(λ), and γ(λ), respectively, where λ denotes the incident wavelength], related to the electric-field-induced second-harmonic generation (EFISHG) technique by CPKS method. The (hyper)polarizability density analyses and (hyper)polarizability contribution decompositions by numerical integration were then carried out to make a further insight into the origination of molecular nonlinearity.

3.3.1. Molecular (Hyper)Polarizabilities

The selected components of (hyper)polarizabilities of the mesoionic compounds studied at the zero-frequency field and 1180 nm fundamental wavelength are arranged in Table S3. The variation trend of the total first-order hyperpolarizability determined by EFISHG is the same as that obtained by HRS method, that is, both the static and the dynamic β_{in}(λ) values increase with the ability of the electron-donating group in the molecule. The first-order hyperpolarizability of the same order of magnitude is given by the two methods.

Since the molecules were oriented in such a way that their dipolar vectors coincide with the Cartesian z axis, it can be determined that the most meaningful component of the response properties is the diagonal element in z direction. Also, we can see that
the $x$ component of the (hyper)polarizability significantly contributes to the total, which is even larger than that in the $z$ direction in most cases. In contrast, the $y$ components of molecular (hyper)polarizability, especially for the first- and second-order hyperpolarizabilities, are negligibly small.

The $z$ components of every order polarizabilities are schematically shown in Figure 3. It can be seen that the three mesoionic compounds show almost the same polarizability. However, with the increase in the strength of the electron donor, the first-order hyperpolarizability component $\beta_{zzz}(\infty \text{ nm})$ of the molecules decreases, which is contrary to the change of the total hyperpolarizability $[\beta_{tot}(\infty \text{ nm})]$. The conflicting trend between the total hyperpolarizability and its $z$ component must derive from the influence of the component in $x$ direction. In fact, it can be seen from Figure S2 that the $x$ component of the first-order hyperpolarizability increases with the enhancement of the electron-donating ability of the donor in the molecules, which is the same trend as that of the total amount. Therefore, in the current coordinate system, the effect of the $x$ component of molecular response property on the total amount of the system is even greater than that of the component in the dipolar direction ($z$ axis). It can also be inferred that this is why the studied systems show the characteristic of intermediate molecule rather than the apparent dipolar species, as we discussed in previous section. The second-order hyperpolarizability of the molecules shows the same trend as the first-order hyperpolarizability, and the reason is self-evident.

![Figure 3](image_url)

Figure 3. Diagrams of calculated polarizabilities $[\alpha_{zz}(\lambda)]$, first-order hyperpolarizabilities $[\beta_{zzz}(\lambda)]$, and second-order hyperpolarizabilities $[\gamma_{zzzz}(\lambda)]$ of the
studied mesoionic compounds: (a) at the zero-frequency limit ($\lambda = \infty$ nm) and (b) at the 1180 nm fundamental.

The change of the frequency-dependent (hyper)polarizability with the electron donor capacity is the same as that in the static limit case. In contrast, the polarizability $\alpha_{\infty}(1180 \text{ nm})$ of the mesoionic molecules under the external field is slightly smaller than that at zero frequency [$\alpha_{\infty}(\infty \text{ nm})$], which seems to be somewhat abnormal (see Section 3.2 for a related discussion). The dynamic hyperpolarizabilities [$\beta_{zz}(1180 \text{ nm})$ and $\gamma_{zzz}(1180 \text{ nm})$] are substantially higher than the static ones [$\beta_{zz}(\infty \text{ nm})$ and $\gamma_{zzz}(\infty \text{ nm})$], indicating that the frequency-dispersion of molecular hyperpolarizability is clearly appeared in the studied systems. Moreover, the order of (hyper)polarizabilities of the mesoionic compounds induced by external field of 1180 nm are the same as those in electrostatic field.

3.3.2. (Hyper)Polarizability Density Analyses

The analysis of (hyper)polarizability density is helpful in understanding the physical essence of molecular (hyper)polarizability. The integrand functions of the (hyper)polarizability densities, that is, the local contributions of the (hyper)polarizability, in $z$ direction $[-z\rho^{(1)}_{zz}(\vec{r}), -z\rho^{(2)}_{zz}(\vec{r}),$ and $-z\rho^{(3)}_{zz}(\vec{r})]$ of the studied molecules under the zero-frequency field are rendered in Figure 4.

It was observed that except for the distinguishable differences near the electron-donating group, the $-z\rho^{(1)}_{zz}(\vec{r})$ functions show an almost invisible decline with the increase of the electron donating ability of electron donors. For all studied molecules, the positive contribution in the isosurface map occupies larger area compared with the negative part leading to a positive $\alpha_{\infty}(\infty \text{ nm})$ value of them. For the first-order hyperpolarizability density $[-z\rho^{(1)}_{zz}(\vec{r})]$, in addition to the still existing difference around the electron donor, either positive or negative distribution seems to decrease slightly in other parts of the molecular skeletons with increasing of the strength of electron-donating group. However, it is difficult to distinguish the size of positive and negative parts of the first-order hyperpolarizability density through intuitive observation from the isosurfaces. There is no population of the second-order hyperpolarizability density $-z\rho^{(3)}_{zz}(\vec{r})$ on the electron-donating group of the molecules.
The positive contribution region of the $-z\rho_{zz}^{(3)}(\vec{r})$ function is significantly greater than the negative part in every molecule, thereby explaining the source of their much larger second-order hyperpolarizability, $\gamma_{zzz}(\infty \text{ nm})$. Comparatively speaking, increasing the strength of electron-donating group causes more reduction in the positive contribution, which makes the $\gamma_{zzz}(\infty \text{ nm})$ value weaken in turn.

![Figure 4](image)

**Figure 4.** Plots of local contribution functions of every order polarizabilities of the studied mesoionic compounds under the zero-frequency field: (a) $-z\rho_{zz}^{(1)}(\vec{r})$ for the polarizability (isovalue = 0.5 au), (b) $-z\rho_{zz}^{(2)}(\vec{r})$ for the first-order hyperpolarizability (isovalue = 5.0 au), and (c) $-z\rho_{zz}^{(3)}(\vec{r})$ for the second-order hyperpolarizability (isovalue = 50.0 au). Blue and red colors depict positive and negative contributions, respectively.

Displayed in Figure S4 are the local contribution functions of the molecular (hyper)polarizability in $x$ axis of the studied mesoionic compounds under the zero-frequency field. It can be clearly seen that in the isosurface of every order local contributions of the (hyper)polarizability, both the positive and the negative contributions increase with the electron-donating capacity within the molecule.
What's more obvious is that the positive contribution areas of the molecular polarizability and second-order hyperpolarizability isosurfaces occupy an overwhelming share, while on the contrary, the negative region of the first-order hyperpolarizability density isosurface accounts for the dominant area. These features of the hyperpolarizability density isosurface in x direction well explain the observations of the x components of molecular hyperpolarizability discussed above.

Compared with the components in the above two directions (z and x axes), the y component of the molecular (hyper)polarizability density is very inconspicuous, as shown in Figure S5, and hence leads to the negligible value of the (hyper)polarizability related to the y axis.

3.3.3. (Hyper)Polarizability Contribution Decompositions

The decomposition of the overall (hyper)polarizability of a molecule into the contribution of its constituent units is conducive to the investigation of the structural sources of the response properties.\textsuperscript{25,26} This is particularly useful for exploring how to tailor and modify the structure of organic molecules to improve their response activity. Here, we integrated the (hyper)polarizability density functions $-i\rho_i^{(1)}(\vec{r})$, $-i\rho_i^{(2)}(\vec{r})$, and $-i\rho_{ii}^{(3)}(\vec{r})$, $i = x, y, \text{and } z$ in the domain of every atom to quantitatively study the contribution of fragments to overall molecular (hyper)polarizability. By comparing Table S4 with Table S3, we can see that the overall diagonal elements of (hyper)polarizabilities of the mesoionic compounds estimated by the numerical integration are very consistent with those calculated via CPKS method which ensures the reliability of our study on (hyper)polarizability decompositions.

As plotted in the z components decomposition of (hyper)polarizabilities in Figure 5, we can see intuitively that almost all (hyper)polarizability contributions offered by a specific structural unit of the molecules decrease gradually in the order of molecule from MIC-1 to MIC-2 and then to MIC-3. This is the structural cause why the overall (hyper)polarizability components of the mesoionic compounds in z axis show the same trend, as mentioned above. Specifically, mesoionic ring (B\textsuperscript{M}) of each molecule exhibits an overwhelming (hyper)polarizability value relative to other subunits. The electron-accepting group (R\textsuperscript{A}) and the benzene ring (B\textsuperscript{A}) connected to it also make a considerable contribution to the overall (hyper)polarizability of the molecule. By
comparison, the electron-donating unit (R^D) and adjacent benzene ring (B^D) account for a very small proportion of the direct contribution to the molecular (hyper)polarizability in z direction. Nonetheless, the electron donor affects the electronic structure of other parts in the molecules, resulting in a significant change in the contribution of response properties of other structural units. This can be seen from the difference z component value of their (hyper)polarizabilities of groups B^M, B^A, and R^A in different compounds.

Figure 5. Decomposition of the z components of (a) polarizabilities \( \alpha_{zz}^{NI}(\infty \text{ nm}) \), (b) first-order hyperpolarizabilities \( \beta_{zzz}^{NI}(\infty \text{ nm}) \), and (c) second-order hyperpolarizabilities \( \gamma_{zzzz}^{NI}(\infty \text{ nm}) \) into each constituent unit by integrating the (hyper)polarizability density functions. Capital letters shown on the horizontal axis denote the units that make up the molecules, as designated in Scheme 1.

In terms of the x component of every order polarizabilities of the molecule in Figure S6, except that the BD group shows the opposite trend in the contribution to the (hyper)polarizability, the (hyper)polarizability values of other groups in the molecule increase in varying degrees with the increase of the donating ability of the electron donor. It is worth noting that each structural unit of the molecules has a significant contribution to the x component of their (hyper)polarizability. This shows that the electron-donating group can not only indirectly affects the (hyper)polarizability of the mesoionic compounds studied by changing the electronic structure of other parts of the molecule, as discussed in its contribution to the z component of molecular (hyper)polarizability, but also can directly contributes to the
overall (hyper)polarizability by modifying its $x$ component.

Due to the (hyper)polarizability component of the molecule in the $y$ direction has an insignificant contribution to the total (hyper)polarizability, the (hyper)polarizability decomposition diagram drawn in Figure S7 is not discussed here.

4. Conclusion

The optical properties of experimental mesoionic compounds were studied theoretically by using (TD-)DFT method. The absorption spectra of the studied molecules obtained by theoretical simulation are in good agreement with those observed in experiment. The NTO analysis shows that the contribution to the maximum absorption of molecules comes from the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the $\pi$-linker in molecular skeleton. Calculated HRS-derived response parameters indicate that all studied compounds belong to intermediate molecule with almost equal dipolar and octupolar characteristics. The diagonal tensor components of the hyperpolarizability in the dipole direction decrease with the increasing in the ability of the electron-donating group in the molecule. However, the (hyper)polarizability component perpendicular to the molecular dipole greatly contributes to the total nonlinearity of the molecule, and eventually leads to an increase in the total (hyper)polarizability of the molecule as its electron donor capability enhanced. The causes of the changes in the (hyper)polarizability of different molecules are clarified from the perspectives of the physical origin and structural origin by (hyper)polarizability density analysis and (hyper)polarizability contribution decomposition, respectively. The results show the electron-donating group in the mesoionic compound can not only indirectly affects molecular total (hyper)polarizability by changing the electronic structure of molecular skeleton, but also can directly contributes to the total (hyper)polarizability by offering a certain components of (hyper)polarizability. In addition, the every order polarizabilities of the molecules show obvious chromatic dispersion under the external electric field with frequency. This work provides a physical perspective for understanding the underlying causes of optical properties for mesoionic compounds, which will be helpful for the synthesis of related molecules with more excellent performances.

Supporting Information Available:
Detailed formulas for molecular NLO properties; optimized Cartesian coordinates; critical FMOs involved in the maximum absorption; selected parameters related to the HRS study; values and diagrams of total (hyper)polarizabilities and their components related to the EFISHG technique; plots of local contribution functions of (hyper)polarizabilities; diagonal tensor components of the (hyper)polarizability of the constituent units; decomposition of the components of the (hyper)polarizability into each constituent unit.

Acknowledgments
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References


(19) Lyra, B. F.; de Morais, S. A.; Rocha, G. B.; Miller, J.; Moura, G. L. C.; Simas, A. M.; Peppe, C.; de Athayde-Filho, P. F. 1, 3-Thiazolium-5-Thiolates Mesoionic


