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Constructing a Mixed π-Conjugated Bridge to Effectively Enhance the Nonlinear Optical Response in the Möbius Cyclacene-Based Systems

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Abstract:

By the density functional theory computations, employing the concept of mixed π-conjugated bridge can effectively improve the first hyperpolarizability (β_0) of Möbius cyclacene (MC)-based systems with D−π−A framework. This mixed π-conjugated bridge is constructed through applying $–(CH{=}CH)_x–NH_2$ or $–(CH{=}CH)_x–NO_2$ chain to modify [8]MC, which can lead to the considerable β_0 value (*e.g.* $[8]MC–(CH{=}CH)_{12}–NO_2$ (9.87×10^5 au) with only a certain chain length), much larger than the sole [8]MC (261 au) and the corresponding NH_2/NO_2-modified polyethylene chain with the same π-conjugated length. It is revealed that the substituent sites and the chain length can play a crucial role in improving β_0 values of these MC−chain systems, where the β_0 value can monotonically increase with increasing the $–(CH{=}CH)_x–$ length, and the substituent electron-withdrawing $–(CH{=}CH)_x–NO_2$ chain is superior to the parallel electron-donating $–(CH{=}CH)_x–NH_2$. These appealing findings can provide valuable insights into the design of novel NLO materials based on MC.

Keywords: Nonlinear optical (NLO) response; Möbius cyclacene; Polyacetylene chain; First hyperpolarizability; Mixed π-conjugated bridge.

1. Introduction

Nonlinear optics (NLO)[1-4] has developed very quickly in the past several decades. Various types of novel high-performance materials with considerable NLO responses have been extensively designed and investigated in experiment and theory, in view of the potential applications in a variety of important technological processes, such as, electro-optical devices and optical data processing technologies.[5-7] Different strategies[8-29] have been proposed to achieve new types of excellent NLO materials. One of the most effective approaches is to design the Donor−π conjugated bridge−Acceptor (D−π−A) [8,11-13,15,16,19] motif, which can usually exhibit low-lying intramolecular charge transfer (ICT) and give rise to the large hyperpolarizability. This merit has been confirmed extensively by many investigations, especially suitable for the organic NLO materials[8,12-18,24,25] with the easy fabrication and modification.

Under the D−π−A scheme, selecting an appropriate π-conjugated bridge can play a crucial role in enhancing the NLO response of system. Therefore, developing the new type of π-conjugated bridge can be an effective strategy to realize the excellent NLO materials. In earlier reports, the π-conjugated bridge was only restricted to the simple conjugated chain, for example, linear polyacetylene,[24] aromatic polyfuran and polyphenyl,[25] and the correlative D−π−A systems can exhibit considerable NLO responses (over 10^4 au). Further, the employed π-bridge has been extended to complex π-conjugated systems with more electron-delocalized, such as, the ladder-type polydiacetylene (PDA) derivatives consisting of double carbon chains with alternant single-double bonds, where both of chains are linked with −C≡C− triple bonds. It has been reported that a significantly increasing β_0 value (over 10^5 au) can be achieved by decorating the π-conjugated PDA chain with donor/acceptor (NH_2/NO_2) pairs.[18]

With the development of nanotechnology, the low-dimensional nanomaterials, such as, graphene nanoribbons (GNRs),[30] carbon nanocones (CNC)[31] and carbon nanotubes (CNT),[32] have been realized in experiment, and aroused great concern in the field of NLO materials, since their huge delocalized backbones with abundant π electrons can provide strong support to make them as the excellent π-conjugated bridge. For example, when employing the donor/acceptor pair (NH_2/NO_2) to decorate GNR, the obtained NH_2–GNR–NO_2 species with D−π−A framework can display considerable β_0 value (even up to 2.5×10^6 au).[13] Similarly, the large β_0 value (in the range of $4.46 \times 10^3 \sim 8.86 \times 10^3$ au) can also be observed in the NH_2/NO_2 pair modifying CNC systems, in which the modified donor/acceptor groups are located at the corresponding end/top of CNC, respectively.[15] Additionally, when the NH_2/NO_2 pair is used to modify the opposite end of CNT (6, 0) to construct the D−π−A scheme, the achieved NO_2−CNT–NH_2 can display large β_0 value as 3.8×10^4 au. Further, when CNT is substituted with only an electron-donating NH_2 group, the β_0 value can be significantly enhanced to 1.3×10^5

au,[12] where the carbon nanotube plays a dual role serving as not only the π-conjugated bridge but also acceptor.

Besides, a new concept of mixed π-conjugated bridge[8] was proposed by our group very recently, which is identified to significantly improve the NLO properties of CNT-based systems with D−π−A framework. It was revealed that series of CNT systems end-substituted with a $–(CH=CH)_x–NH_2$ chain (denoted as $CNT–(CH=CH)_x–NH_2$, where both the CNT and $–(CH=CH)_x–$ chain can collaboratively serve as the mixed π-conjugated bridge), can display considerable β_0 values (over 10^6 au), much larger than the corresponding NH_2-directly-modified CNTs systems with same conjugated length. It is shown that employing the mixed π-conjugated bridge can effectively overcome the bottleneck encountered with pure CNT serving as the π-conjugated bridge, that is, further extending the CNT will not produce any positive effect on improving their first hyperpolarizabilities in $CNT–NH_2$ configurations once the CNT reaches a certain length. And it is highly expected that through constructing a mixed π-conjugated bridge can be an effective strategy for significantly improving the NLO responses of π-conjugated systems.

Recently, the fascinating Möbius strip has been attracting considerable attention, which is an intriguing closed strip with a knot, and was named after the German mathematician who mathematically investigated it in the late nineteenth century.

Extensive theoretical[19-23,33-38] and experimental efforts[39-45] have been made on the systems based on nonorientable Möbius strips with the only single-side and single-edge, where the Möbius topological character,[33,34] the aromatic[36,37,41] and magnetic properties,[33] and the selection rule of pericyclic reaction,[36,40] *etc*. have been investigated. Especially, the considerable endeavors have been made on NLO properties of Möbius-based systems,[19-23] where different approaches have been proposed to effectively enhance the NLO response. For instance, Xu *et al.* theoretically studied the effects of the shape and number of knots on β_0 values of the nitrogen-substituted Möbius cyclacenes.[20,21] It was revealed for the N-substituted [7]Möbius system with the smaller diameter,[20] through opening the knot to form normal cyclacene can bring an increase of β_0 value from original 393 to 1049 au, and further enhancement of the β_0 value (about three times) from 1049 to 2814 au can be also caused by opening the normal cyclacene to form the corresponding linear strip. However, in the N-substituted [15]Möbius system with the larger diameter,[21] the β_0 values corresponding to one knot (60845 au) and three knots (24519 au), with the former superior to the latter, can be much larger than that of the according normal cyclacene (4693 au). Furthermore, a novel framework of Möbius basket molecule[23] has been focused, and it was found that the twisting effect can effectively increase the β_0 value (3773 au) of system, by making a comparison with the corresponding normal basket without any knot (2836 au). Besides, the intriguing Möbius strip has been employed as a π-bridge to construct the excellent NLO system under the D–π–A framework, where the Möbius ring possesses the *4n* π electrons and is aromatic, different from the traditional Hückel aromaticity.[36,37] For example, when alkali Li atom is used as the donor group to monosubstitute the H atom of [7]Möbius molecule,[22] the β_0 value of doped systems can be increased to the range of 352 ~ 1019 au, compared with undoped [7]Möbius (250 au). Moreover, by means of linking the electron donor ($-NH_2$) and acceptor ($-NO_2$) groups to construct a D–π–A framework,[19] the β_0 values of [8]Möbius strip can be significantly improved (even up to 12467 au), which are much larger than that of sole [8]MC (only 261 au).

Although some progress has been made on the NLO investigations of systems based on the Möbius cyclacene, the concept of constructing a mixed π-conjugated bridge to improve the NLO property of Möbius cyclacene has not been considered under the D–π–A framework. In view of the case that this strategy could be rather effective (as discussed above), in this work we intend to perform the first attempt to employ the approach of mixed π-conjugated bridge to improve the β_0 values of the intriguing Möbius cyclacene (MC)-based systems. We take the [8]MC as an example, and propose a new type of mixed π-conjugated bridge by combining Möbius cyclacene and a $-(CH{=}CH)_x-$ chain, where the end of $-(CH{=}CH)_x-$ chain is decorated by the sampled donor NH_2 or acceptor NO_2 group. These novel MC–chain motifs can be also viewed as the [8]MC decorated by the –$(CH{=}CH)_x$–NH_2 or –$(CH{=}CH)_x$–NO_2 chain, which can be denoted as [8]MC–$(CH{=}CH)_x$–NH_2 and [8]MC–$(CH{=}CH)_x$–NO_2, respectively. Here, we perform detailed computations to investigate the first hyperpolarizabilities of these systems based on the MC–chain, and mainly address the following issues: (1) Can the proposed mixed π-conjugated bridge composed of Möbius cyclacene together with –$(CH{=}CH)_x$– chain significantly improve the first hyperpolarizabilties (β_0) of these MC-based systems, even larger than the corresponding H–$(CH{=}CH)_{x+2}$–$NH_2(NO_2)$ with the equal π-conjugated length? (2) How will increasing the length of –$(CH{=}CH)_x$–$NH_2(NO_2)$ chain affect the β_0 values of these MC–chain systems? (3) Can employing the –$(CH{=}CH)_x$– chain decorated by electron-donating NH_2 or electron-withdrawing NO_2 group endow these systems based on the MC–chain motif with the larger β_0 values? By addressing them, this work can provide valuable insights for the design of the novel high-performance NLO materials based on the Möbius cyclacene. It is worth mentioning that employing the concept of the mixed π-conjugated bridge can be an effective strategy to significantly improve the NLO properties of MC-based systems, for example, our computed results revealed that a dramatic 3782-fold increase can be achieved for the β_0 value of [8]MC–$(CH{=}CH)_{12}$–NO_2 (9.87×10^5 au) with only a certain –$(CH{=}CH)_x$– chain length ($x = 12$), compared with the sole [8]Möbius cyclacene (261 au).

2. Computational Methods

The total energy of a molecular system in the presence of a homogeneous electric field can be expressed as:[46,47]

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \cdots\cdots \tag{1}$$

where E^0 is the molecular total energy in the absence of the external electric field, F_α is the electric field component along the α direction, μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the dipole moment, polarizability, and the first hyperpolarizability, respectively.

The average of the polarizability (α) is calculated via:

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

The first hyperpolarizability (β_0) is defined as

$$\beta_0 = (\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2)^{1/2} \tag{3}$$

in which

$$\beta_i = \frac{3}{5}(\beta_{ixx} + \beta_{iyy} + \beta_{izz}) \qquad (i = x, y \text{ and } z) \tag{4}$$

The popular hybrid non-local density functional theory (DFT) method, the B3LYP approach, has been widely employed for structural optimization of many systems[8,9,12-16,18-23,48-51] involving the Möbius-based structures[19-23] in previous studies. Following the convention, we performed the geometry optimization with all real frequencies at the B3LYP level in this work. Further, on the basis of the equilibrium geometries, the polarizabilities (α) and first hyperpolarizabilities (β_0) of all the studied systems were computed at the BHandHLYP level via a finite-field approach, considering that the BHandHLYP method involves more percentages of HF exchange than the B3LYP approach, and can usually achieve a credible estimation for the (hyper)polarizability, which has been proved to be very close to the corresponding result from MP2 level.[22,48] Particularly, it is worth mentioning that the good performance of the BHandHLYP for computing the first hyperpolarizability can be further supported by the recent fascinating report,[52] that is, of all the used DFT methods, the BHandHLYP approach performs best and the BHandHLYP-related results can be close to MP4, even more sophisticated CCSD(T) method. Indeed, the BHandHLYP approach has been widely applied to predict the hyperpolarizabilities for different systems,[19,21-23,49-51] including Möbius-based system,[19,21-23] due to the good compromise between the computational accuracy and efficiency.

Moreover, we know the calculation of hyperpolarizability is basis-set-sensitive,[53-56] however, considering that the size of the studied system is considerably large, we adopted the basis sets 6-31G(d) and 6-31+G(d) to perform the computations on the geometry optimization and the NLO response, respectively, which usually can provide a qualitative trend to extract valuable NLO prediction for the studied systems[19-23,57] including the reported Möbius-based structures.[19-23] Bear in mind that the main focus of this study is to propose an effective strategy through constructing a mixed π-conjugated bridge under

D–π–A scheme to significantly improve the first hyperpolarizabilities of systems based on the intriguing Möbius cyclacenes with unique structure. For this purpose, the chosen basis set can provide a qualitative description of the NLO responses of studied systems, especially their relative trend, and achieve a good compromise between computational accuracy and resource consumption.

In addition, for the related systems, the time dependent density functional (TD-DFT) calculations were also carried out at the BHandHLYP level with 6-31+G(d) basis set to get the crucial transition energy (ΔE), the oscillator strength (f_0), the difference of dipole moment ($\Delta\mu$) between the ground state and the crucial excited state.

All of the calculations in this work were performed by the Gaussian 09 program package.[58]

3. Results and discussions

3.1 The NLO properties of [8]Möbius cyclacene modified by $-CH=CH-NH_2$ and $-CH=CH-NO_2$ at the different sites

The optimized geometric structure of the sampled [8]Möbius cyclacene (MC) with a knot is shown in Figure 1a, in which [8] represents the number of eight benzo rings. It can be easily found that the sixteen H atoms of [8]MC can be differentiated from each other (Figure 1a), due to the unique one-sided and one-edged structure of MC. Here, we can construct the [8]MC−chain motifs through substituting all the possible H atoms by $-(CH{=}CH)_x-NH_2$ or $-(CH{=}CH)_x-NO_2$, where the [8]MC combining with $-(CH{=}CH)_x-$ chain can serve as a novel mixed π-conjugated bridge (Figure 1). For convenience, all of these [8]MC−chain motifs under this study are named as [8]MC–n–$(CH{=}CH)_x-NH_2$ and [8]MC–n–$(CH{=}CH)_x-NO_2$ ($n = 1 \sim 16$), respectively, where n and x represent the possible substituted sites of [8]MC, and the number of vinyl units in the polyacetylene $-(CH{=}CH)_x-$ chain, respectively. Note that the substituted site corresponding to the Arabic number "8" in Möbius cyclacene cannot be involved (Figure 1a), due to the existence of space steric hindrance.

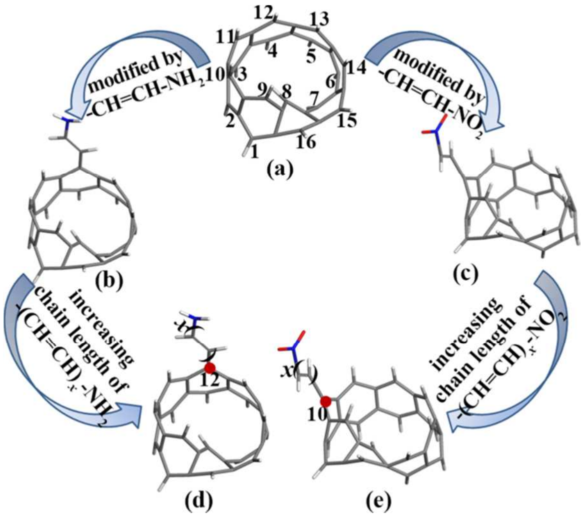

Figure 1. The geometry structures of the studied systems: the sole [8]Möbius cyclacene ([8]MC) with sixteen different H atoms (a), the [8]MC-based systems modified by the shortest $-CH{=}CH-NH_2$ (b) and $-CH{=}CH-NO_2$ (c) at all the possible substituent sites, as well as with the increasing chain length of $-(CH{=}CH)_x-NH_2$ at the optimum 12-site of [8]MC (d), and

–$(CH=CH)_x$–NO_2 at 10-site (e), respectively.

Table 1. The polarizabilities (α) and first hyperpolarizabilities (β_0) of [8]MC–*n*–CH=CH–NH_2 and [8]MC–*n*–CH=CH–NO_2 ($n = 1 \sim 16$, $n \neq 8$) systems with the different substituent sites.

n	[8]MC–*n*–CH=CH–NH_2		[8]MC–*n*–CH=CH–NO_2	
	α (au)	β_0 (au)	α (au)	β_0 (au)
1	491	1307	515	5054
2	487	1172	498	2296
3	492	1253	504	3236
4	508	1566	528	4705
5	532	1298	567	3920
6	552	1043	608	4357
7	505	1019	556	2762
9	518	784	550	3453
10	550	499	600	5400
11	534	1789	572	2948
12	510	1967	537	3627
13	471	751	516	3739
14	488	1304	502	2437
15	490	1089	505	2438
16	483	802	491	1317

Initially, we constructed [8]MC–chain motifs by employing the shortest –CH=CH–NH_2 and –CH=CH–NO_2 chains to decorate the end of [8]MC. Upon examination of all the possible modifications (Figures 1b and 1c), we wonder whether the end-substitution through the –CH=CH–NH_2(NO_2) chain can effectively enhance the NLO response of [8]MC system, and find out the most appropriate substituent position for –CH=CH–NH_2 and –CH=CH–NO_2, respectively.

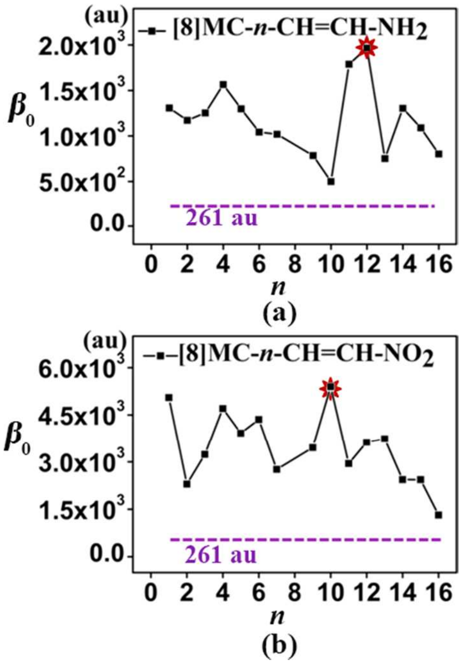

Figure 2. The first hyperpolarizabilities of (a) [8]MC–*n*–CH=CH–NH_2 and (b) [8]MC–*n*–CH=CH–NO_2 ($n = 1 \sim 16$, $n \neq 8$) with the shortest –CH=CH–NH_2(NO_2) chain at the different substituted sites. Note that the purple dotted line presents the β_0 value (only 261 au) of sole [8]Möbius cyclacene.

As shown in Table 1 and Figure 2, we have systematically investigated the polarizabilities and first hyperpolarizabilities of [8]MC–*n*–CH=CH–NH_2 and [8]MC–*n*–CH=CH–NO_2 ($n = 1 \sim 16$) series. The computed results show that for the [8]MC–*n*–CH=CH–NH_2 series with electron-donating group, the polarizabilities (α) and first hyperpolarizabilities (β_0) are in the range of 471 ~ 550 au and 499 ~ 1967 au, respectively (Table 1), which are larger than the corresponding α (439 au) and β_0 (261 au) values of the sole [8]MC. Moreover, it can be found that among these fifteen MC-based systems decorated by $–CH=CH–NH_2$ chain, [8]MC–12–$CH=CH–NH_2$ can exhibit the largest β_0 value (1967 au), which is about eight times as large as that of sole [8]MC (261 au), indicating that the optimum substitution, for the modified $–CH=CH–NH_2$ chain with the electron-donating characteristic, should be at the corresponding site to the Arabic number "12" (denoted as 12-site) in Möbius cyclacene.

Similarly, when the shortest electron-withdrawing chain $–CH=CH–NO_2$ is employed, not only the polarizabilities but also the first hyperpolarizabilities of modified [8]MC-based systems can be also effectively enhanced. As shown in Table 1, compared with the sole [8]MC (261 au), the α and β_0 values of these [8]MC–*n*–$CH=CH–NO_2$ systems are in the range of 491 ~ 608 au and 1317 ~ 5400 au, respectively, along with the variation of substituted site, where the 10-site in [8]MC is indicated to be the optimum substituent position for achieving the largest β_0 value (5400 au). Moreover, we can find that, at the same substituted site in [8]MC, the modified systems with $–CH=CH–NO_2$ ([8]MC–$CH=CH–NO_2$) can present larger β_0 values than the corresponding those with $–CH=CH–NH_2$ ([8]MC–$CH=CH–NH_2$), suggesting that employing the electron-withdrawing chain to construct MC−chain motif can be more effectively than the parallel electron-donating chain to improve the NLO properties of these MC-based systems.

Clearly, constructing a mixed π-conjugated bridge by linking the

–CH=CH–NH_2(NO_2) chain under D−π−A motif can be an efficient approach to enhance the NLO responses of Möbius-based systems, where the substituent site can play an important role in increasing the β_0 value.

3.2 The NLO properties of [8]MC−12−(CH=CH)$_x$−NH_2 (x = 1, 2, 3, 5, 6, 9 and 12)

Based on the discussion above, we know that the donor –NH_2 group linked to [8]MC through the shortest –CH=CH– chain to form the [8]MC−chain motif with a mixed π-bridge can effectively enhance the first hyperpolarizability of the [8]MC-based system, compared with the β_0 value of sole [8]MC (only 261 au). Subsequently, we wonder how lengthening –(CH=CH)$_x$–NH_2 chain will affect the β_0 value of these Möbius−chain motifs. Considering that the modified [8]MC structure by the shortest chain –CH=CH–NH_2 at the optimum 12-site can achieve the largest β_0 value among the [8]MC–n−CH=CH–NH_2 (n = 1 ~ 16) systems, we have investigated the polarizabilities and first hyperpolarizabilities of [8]MC–12–(CH=CH)$_x$–NH_2 (x = 2, 3, 5, 6, 9 and 12) series (Table 2 and Figure 3a), in which the 12-site in [8]MC is selected as the substituent position for the longer –(CH=CH)$_x$–NH_2 chain. For the purpose of comparison, the corresponding NH_2-substitued polyacetylene chain series with the same conjugated length have also investigated, as presented in Table 3 and Figure 3. For the comparison convenience, these corresponding NH_2-modified polyacetylene can be labeled as

H–(CH=CH)$_{x+2}$–NH$_2$ (x = 1, 2, 3, 5, 6, 9 and 12), in view of the [8]MC consisting of two zigzag carbon chains in the parallel [8]MC–12–(CH=CH)$_x$–NH$_2$ systems.

Table 2. The polarizabilities (α), the first hyperpolarizabilities (β_0), the transition energy (ΔE), the oscillator strength (f_0) corresponding to the crucial transition state, the difference of dipole moment between the ground state and the crucial excited state ($\Delta\mu$), the estimated β_0 value ($\Delta\mu \cdot f_0/\Delta E^3$) under the two-level expression, and the compositions of the crucial transition state (CTS) for the [8]MC–12–(CH=CH)$_x$–NH$_2$ series (x = 1, 2, 3, 5, 6, 9 and 12).

		[8]MC–12–(CH=CH)$_x$–NH$_2$						
Properties	x =	1	2	3	5	6	9	12
α (au)		510	591	693	943	1088	1562	2107
β_0 (au)		1.97×10^3	4.48×10^3	8.54×10^3	2.23×10^4	3.22×10^4	7.05×10^4	1.17×10^5
ΔE (eV)		3.791	3.609	3.462	2.720	2.628	1.819	1.780
f_0		0.1980	0.3690	0.4459	0.6483	0.8778	1.3757	2.1847
$\Delta\mu$ (au)		0.341	0.330	0.719	0.311	0.406	0.771	1.007
$\Delta\mu \cdot f_0/\Delta E^3$		25	52	155	202	395	3546	8393
CTS[a]		H-2→L+1	H-1→L+2	H-1→L+2	H-2→L	H-2→L	H-1→L	H-1→L

[a] H and L mean the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

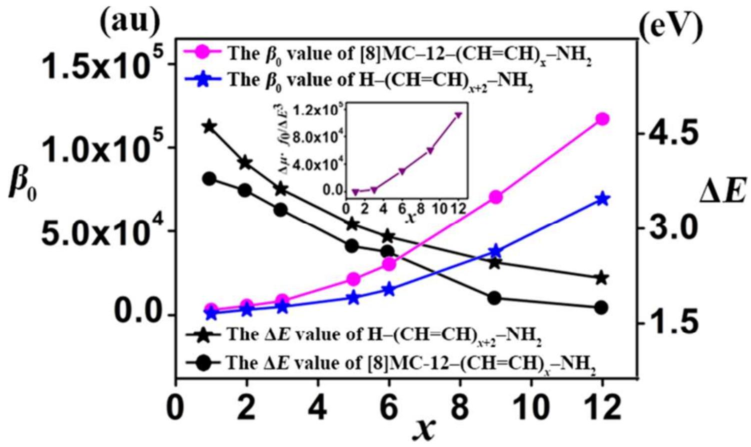

Figure 3. The relationship of the computed β_0 values or the transition energies (ΔE) versus x values for [8]MC–12–(CH=CH)$_x$–NH$_2$ series (x = 1, 2, 3, 5, 6, 9, 12) and the corresponding H–(CH=CH)$_{x+2}$–NH$_2$ series with the same π-conjugated chain length. Note that the inset picture shows the relationship between the estimated β_0 ($\Delta\mu{\cdot}f_0/\Delta E^3$) under the two-level state and x values for the [8]MC–12–(CH=CH)$_x$–NH$_2$ series.

Table 3. The polarizabilities (α), the first hyperpolarizabilities (β_0), the transition energy (ΔE), the oscillator strength (f_0) , and the compositions of the crucial transition state (CTS) of H–(CH=CH)$_{x+2}$–NH$_2$ series (x = 1, 2, 3, 5, 6, 9 and 12).

	H–(CH=CH)$_{x+2}$–NH$_2$						
Properties x =	1	2	3	5	6	9	12
α (au)	107	158	221	378	472	809	1217
β_0 (au)	1.06×10^3	2.18×10^3	3.98×10^3	1.04×10^4	1.53×10^4	3.79×10^4	6.95×10^4
ΔE (eV)	4.613	4.044	3.631	3.070	2.872	2.465	2.217
f_0	1.0070	1.7661	2.2145	3.0931	3.5267	4.8128	6.0882
CTS[a]	H→L	H→L	H→L	H→L	H→L	H→L	H→L

[a] H and L represent the HOMO and LUMO, respectively.

From Table 2 and Figure 3, we can find that all the [8]MC-based systems ([8]MC–12–(CH=CH)$_x$–NH$_2$) decorated with longer –(CH=CH)$_x$–NH$_2$ chains (x = 2, 3, 5, 6, 9 and 12) can exhibit considerable β_0 value in the range of $4.48 \times 10^3 \sim 1.17 \times 10^5$ au, much larger than the corresponding shortest [8]MC−chain motif of [8]MC–12–CH=CH–NH$_2$ (1.97×10^3 au). Moreover, the β_0 value for [8]MC–12–(CH=CH)$_x$–NH$_2$ can increase significantly with increasing x value (β_0 = 1.97

× 10^3, 4.48 × 10^3, 8.54 × 10^3, 2.23 × 10^4, 3.22 × 10^4, 7.05 × 10^4, 1.17 × 10^5 au for x = 1, 2, 3, 5, 6, 9, 12, respectively), for instance, a significant 59-fold increase for the β_0 value can be achieved when enlarging x from 1 to 12 in the [8]MC–12–$(CH{=}CH)_x$–NH_2 motifs (Table 2 and Figure 3). And these β_0 values of [8]MC–12–$(CH{=}CH)_x$–NH_2 series are much larger than those of the corresponding NH_2-modified polyacetylene chain (H–$(CH{=}CH)_{x+2}$–NH_2) series with the same conjugated length (β_0 = 1.06 × 10^3, 2.18 × 10^3, 3.98 × 10^3, 1.04 × 10^4, 1.53 × 10^4, 3.79 × 10^4, 6.95 × 10^4 au for x = 1, 2, 3, 5, 6, 9, 12, respectively), as shown in Table 3 and Figure 3. Particularly, it can be found that the difference of β_0 values between the [8]MC–12–$(CH{=}CH)_x$–NH_2 and H–$(CH{=}CH)_{x+2}$–NH_2 series can also increase with increasing x value (Figure 3). Obviously, elongating the –$(CH{=}CH)_x$–NH_2 chain can be an effective approach to improve the first hyperpolarizabilities of these [8]MC–chain motifs with a mixed π-conjugated bridge.

To qualitatively understand the monotonic increase for the β_0 values of [8]MC–12–$(CH{=}CH)_x$–NH_2 series with increasing x value, and the reason for the much larger β_0 values than the corresponding H–$(CH{=}CH)_{x+2}$–NH_2 with the same π-conjugated length, we may employ the following two-level expression:[59-61]

$$\beta_0 \propto \frac{\Delta\mu \times f_0}{\Delta E^3}$$

in which ΔE, f_0 and $\Delta\mu$ are the transition energy, the oscillator strength, and the difference of the dipole moment between the ground state and the crucial excited state, respectively. Note that the β_0 value is inversely proportional to the third power of the transition energy (ΔE). Therefore, the low transition energy can usually be a decisive factor in determining the large first hyperpolarizability.

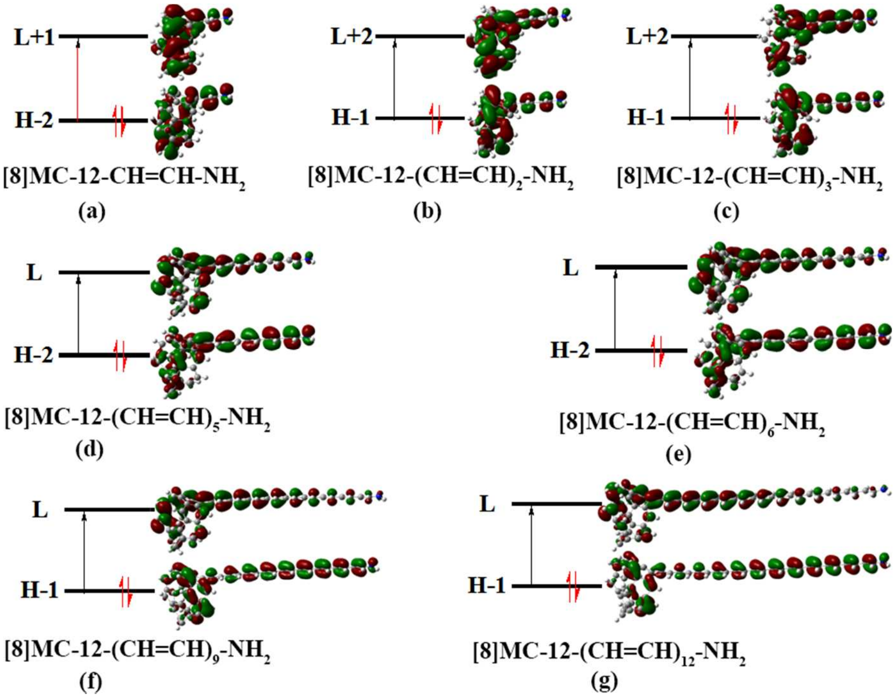

Figure 4. The crucial transition states of [8]MC–12–(CH=CH)$_x$–NH$_2$ series (x = 1, 2, 3, 5, 6, 9 and 12). The H and L mean the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

Here, we performed the TD-DFT computations for [8]MC–12–(CH=CH)$_x$–NH$_2$ and H–(CH=CH)$_{x+2}$–NH$_2$ (x = 1, 2, 3, 5, 6, 9 and 12) series to achieve their crucial excited states, as shown in Figures 3 and 4. From Figure 3, we can find that for the [8]MC–12–(CH=CH)$_x$–NH$_2$ systems, their transition energies (ΔE) related to the crucial excited state decrease monotonously (from 3.791 to 1.780 eV) with lengthening the –(CH=CH)$_x$–NH$_2$ chain from $x = 1$ to 12, which can lead to the continuous increase of the β_0 value in the [8]MC–12–(CH=CH)$_x$–NH$_2$ series according to the two-level expression. It is worth mentioning when the corresponding oscillator strength (f_0) and the difference of the dipole moment ($\Delta\mu$) between the ground state and the crucial excited state are also considered, their estimated β_0 values (inset in Figure 3) by using the correlative ΔE, f_0 and $\Delta\mu$ terms under the two-level expression can exhibit the similar increasing trend to the corresponding computed β_0 values (Figure 3).

Moreover, we can also find that the ΔE values of the [8]MC–12–(CH=CH)$_x$–NH$_2$ systems (3.791, 3.609, 3.462, 2.720, 2.628, 1.819, 1.780 eV for $x = 1, 2, 3, 5, 6, 9$ and 12, respectively) are much smaller than those of the parallel H–(CH=CH)$_{x+2}$–NH$_2$ systems (4.613, 4.044, 3.631, 3.070, 2.872, 2.465, 2.217 eV for $x = 1, 2, 3, 5, 6, 9$ and 12, respectively), as shown in Table 3 and Figure 3. This can be responsible for the much larger β_0 values of [8]MC–12–(CH=CH)$_x$–NH$_2$ than the corresponding H–(CH=CH)$_{x+2}$–NH$_2$ systems with the same π-conjugated chain length.

Further, from the Figure 4 illustrating the crucial excited states of [8]MC–12–(CH=CH)$_x$–NH$_2$ series, it can be found that the electron cloud in their related occupied orbitals (HOMO-1 or HOMO-2) can be distributed on the [8]MC ring and the –(CH=CH)$_x$–NH$_2$ chain, in which the closer to the NH$_2$-end, the more electron cloud.

However, the opposite trend can be observed in the correlative unoccupied orbitals (LUMO、LUMO+1 or LUMO+2), namely, farther away from the NH_2-end, the electron cloud gradually becomes stronger. Particularly, this distribution in these related occupied and unoccupied orbitals of [8]MC–12–$(CH{=}CH)_x$–NH_2 is strongly dependent on the length of the –$(CH{=}CH)_x$–NH_2 chain: when lengthening the substituted –$(CH{=}CH)_x$–NH_2 chain, this inclination can become more prominent. Obviously, the greatly opposite trend of electron cloud distribution between the correlative occupied and unoccupied orbitals can significantly enhance the degree of charge transfer in the process of the transitions, and the longer –$(CH{=}CH)_x$–NH_2 chain, the larger charge transfer occurs, which can further rationalize the monotonous increase of the first hyperpolarizability with extending the –$(CH{=}CH)_x$–NH_2 length. In addition, by analyzing these correlative occupied and unoccupied orbitals for the [8]MC–12–$(CH{=}CH)_x$–NH_2 series, we can also find that the [8]MC serves as not only the acceptor but also the π-conjugated bridge together with the substituted –$(CH{=}CH)_x$– chain, indicating the existence of a mixed π-conjugated bridge in the studied MC−chain framework.

3.3 The NLO properties of [8]MC–10–$(CH{=}CH)_x$–NO_2 (x = 1, 3, 6, 9 and 12)

Based on the results above, we can understand that extending the –$(CH{=}CH)_x$– chain decorated by the donor NH_2 group can effectively increase the β_0 value of

[8]MC–12–$(CH{=}CH)_x$–NH_2 series with a mixed π-conjugated bridge, which can exhibit much larger β_0 value than the corresponding polyacetylene chains linked with NH_2 group (H–$(CH{=}CH)_{x+2}$–NH_2). In view of the case that the modified [8]MC by the shortest chain –CH=CH–NO_2 at the optimum 10-site (5400 au for [8]MC–10–CH=CH–NO_2) displays much larger β_0 value than the decorated [8]MC with –CH=CH–NH_2 at the optimum 12-site (1967 au for [8]MC–12–CH=CH–NH_2), naturally, we intend to know whether elongating the chain length of –$(CH{=}CH)_x$–, linked with the electron-withdrawing NO_2 group, can more significantly enhance the β_0 values of these MC–chain systems ([8]MC–10–$(CH{=}CH)_x$–NO_2) with the –$(CH{=}CH)_x$–NO_2 chain at the 10-site, and whether their β_0 values can be significantly larger than the corresponding those of H–$(CH{=}CH)_{x+2}$–NO_2 series with the same π-conjugated chain length, even the parallel [8]MC–chain systems ([8]MC–12–$(CH{=}CH)_x$–NH_2) modified by the electron-donating group (NH_2).

Here, we performed the computations on the polarizabilities and first hyperpolarizabilities of the [8]MC–10–$(CH{=}CH)_x$–NO_2 and H–$(CH{=}CH)_{x+2}$–NO_2 series (x = 1, 3, 6, 9 and 12). The computed results show that the β_0 values of [8]MC–10–$(CH{=}CH)_x$–NO_2 systems can increase significantly with increasing x value, namely, 5.4×10^3 ($x = 1$) < 1.07×10^4 ($x = 3$) < 1.12×10^5 ($x = 6$) < 3.28×10^5 ($x = 9$) < 9.87×10^5 au ($x = 12$) (Table 4 and Figure 5a), which is in good agreement with the decreasing trend of the calculated Δ*E* value: 1.291 ($x = 1$) > 1.124 ($x = 3$) > 0.975 ($x = 6$) > 0.898 ($x = 9$) > 0.829 eV ($x = 12$), according to the two-level approach. Obviously, extending $–(CH{=}CH)_x–NO_2$ chain can greatly enhance the β_0 values of these [8]MC−chain motifs by effectively decreasing the Δ*E* value, such as, when enlarging *x* from 1 to 12, a dramatic 183-fold increase of the β_0 value can be achieved along with the decrease of Δ*E* from 1.291 to 0.829 eV. Note that for the $[8]MC–10–(CH{=}CH)_x–NO_2$ systems, the estimated β_0 values by considering the correlative Δ*E*, f_0 and $\Delta\mu$ under the two-level expression can exhibit a similar increasing trend to the corresponding computed β_0 values (inset in Figure 5a).

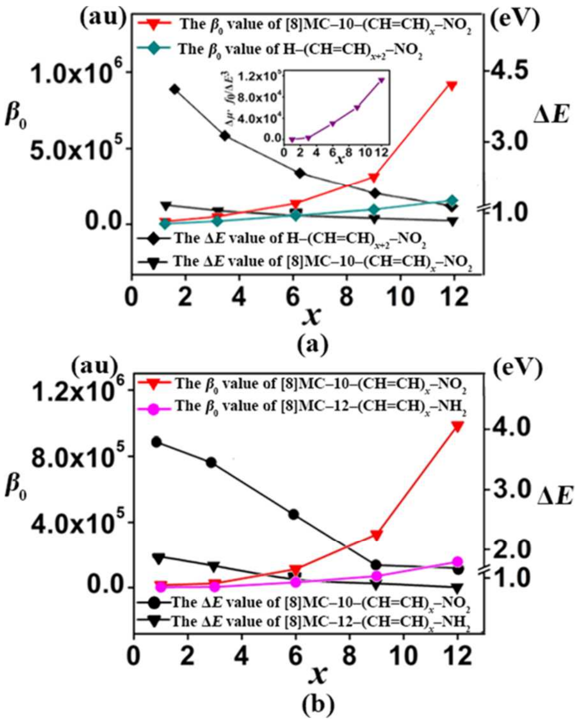

Figure 5. (a) The relationship of the computed β_0 values or the transition energies (ΔE) versus x values for [8]MC–10–(CH=CH)$_x$–NO$_2$ series (x = 1, 3, 6, 9 and 12) and the parallel H–(CH=CH)$_{x+2}$–NO$_2$ series with the same π-conjugated chain length, and the inset picture shows the relationship between the estimated β_0 ($\Delta\mu\cdot f_0/\Delta E^3$) under the two-level state and x values for the [8]MC–10–(CH=CH)$_x$–NO$_2$ series. (b) The relationship of the computed β_0 values or the transition energies (ΔE) versus x values for the [8]MC–10–(CH=CH)$_x$–NO$_2$ series and the corresponding [8]MC–12–(CH=CH)$_x$–NH$_2$ series with the same π-conjugated length.

Table 4. The polarizabilities (α), the first hyperpolarizabilities (β_0), the transition energy (ΔE), the oscillator strength (f_0) corresponding to the crucial transition state, the difference of dipole moment between the ground state and the crucial excited state ($\Delta\mu$), the estimated β_0 value ($\Delta\mu\cdot f_0/\Delta E^3$) under the two-level expression, and the compositions of the crucial transition state (CTS) for [8]MC–10–(CH=CH)$_x$–NO$_2$ series (x = 1, 3, 6, 9 and 12).

		[8]MC–10–(CH=CH)$_x$–NO$_2$				
Properties	x =	1	3	6	9	12
α (au)		600	971	1791	2798	4176
β_0 (au)		5.40×10^3	1.07×10^4	1.12×10^5	3.28×10^5	9.87×10^5
ΔE (eV)		1.291	1.124	0.975	0.898	0.829
f_0		0.3387	0.6819	1.2403	1.8097	2.3479
$\Delta\mu$ (au)		0.026	0.341	1.121	1.198	1.352
$\Delta\mu\cdot f_0/\Delta E^3$		82	3295	30187	60248	112124
CTS[a]		H→L	H→L	H→L+3	H-1→L	H→L

[a] H and L represent the HOMO and LUMO, respectively.

In addition, the β_0 values of [8]MC–10–(CH=CH)$_x$–NO$_2$ series (5.4×10^3, 1.07×10^4, 1.12×10^5, 3.28×10^5, 9.87×10^5 au for $x = 1, 3, 6, 9, 12$) are much larger than those of the corresponding H−(CH=CH)$_{x+2}$−NO$_2$ with the equal conjugated chain length ($\beta_0 = 1.28 \times 10^3$, 6.33×10^3, 2.79×10^4, 7.31×10^4, 1.43×10^5 au for $x = 1, 3, 6, 9, 12$, respectively), which is consistent with the order of ΔE values between the two series, that is , the ΔE values of [8]MC–10–(CH=CH)$_x$–NO$_2$ series (1.291, 1.124, 0.975, 0.898, 0.829 eV for $x = 1, 3, 6, 9, 12$) are much smaller than the corresponding those of H−(CH=CH)$_{x+2}$−NO$_2$ series (4.163, 3.350, 2.694, 2.335, 2.116 eV for $x = 1, 3, 6, 9, 12$, respectively), as shown in Table 5 and Figure 5a. Moreover, we can find the ΔE values of [8]MC–10–(CH=CH)$_x$–NO$_2$ series modified with the acceptor –NO$_2$ group (1.291, 1.124, 0.975, 0.898, 0.829 eV for $x = 1, 3, 6, 9, 12$) are also much smaller than the corresponding those of [8]MC–12–(CH=CH)$_x$–NH$_2$ series modified with the donor –NH$_2$ group (3.791, 3.462, 2.628, 1.819, 1.780 eV for $x = 1, 3, 6, 9, 12$, respectively) (Figure 5b), which can lead to much larger β_0 values of [8]MC−10−(CH=CH)$_x$–NO$_2$ series (5.4×10^3, 1.07×10^4, 1.12×10^5, 3.28×10^5, 9.87×10^5 au for $x = 1, 3, 6, 9, 12$) than the parallel [8]MC–12–(CH=CH)$_x$–NH$_2$ ($\beta_0 = 1.97 \times 10^3$, 8.54×10^3, 3.22×10^4, 7.05×10^4, 1.17×10^5 au for $x = 1, 3, 6, 9, 12$, respectively) (Figure 5b). Obviously, employing the −(CH=CH)$_x$− chains with the certain length, linked with the electron-withdrawing NO$_2$ group, to modify the [8]MC system can more effectively improve the β_0 values of

MC−chain motifs than the corresponding electron-donating NH_2 group, where increasing the $-(CH{=}CH)_x-$ chain length can play a crucial role in enhancing the β_0 values of MC-based systems.

Table 5. The polarizabilities (α), the first hyperpolarizabilities (β_0), the transition energy (ΔE), the oscillator strength (f_0), and the compositions of the crucial transition state (CTS) of $H-(CH{=}CH)_{x+2}-NO_2$ series (x = 1, 3, 6, 9 and 12).

	$H-(CH{=}CH)_{x+2}-NO_2$				
Properties x =	1	3	6	9	12
α (au)	118	241	513	874	1307
β_0 (au)	1.28×10^3	6.33×10^3	2.79×10^4	7.31×10^4	1.43×10^5
ΔE (eV)	4.163	3.350	2.694	2.335	2.116
f_0	1.0722	2.0030	3.3343	4.6136	5.8823
CTS[a]	H→L	H→L	H→L	H→L	H→L

[a] H and L represent the HOMO and LUMO, respectively.

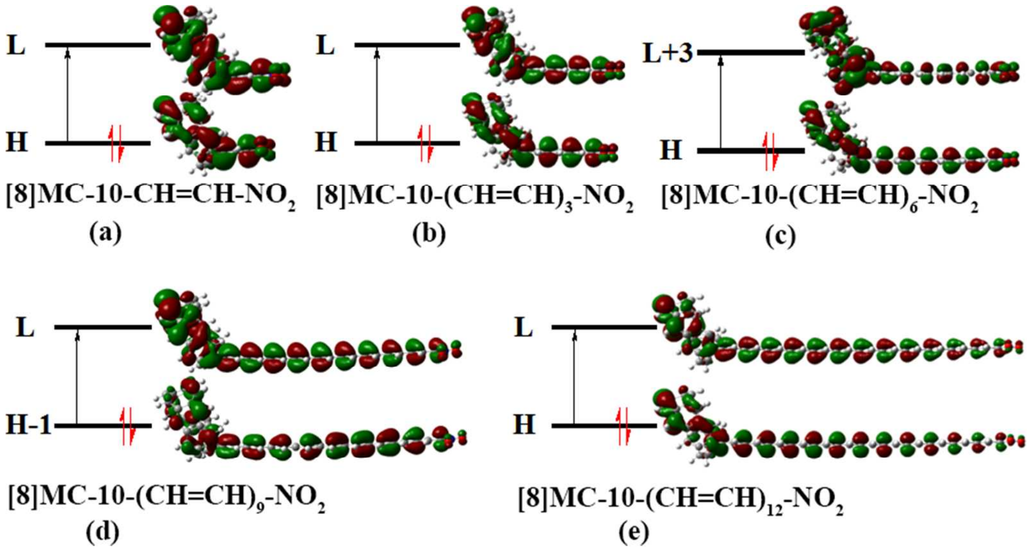

Figure 6. The crucial transition states of [8]MC–10–$(CH=CH)_x$–NO_2 series (x = 1, 3, 6, 9 and 12). The H and L mean the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

Further, the transition diagrams of crucial excited states for [8]MC–10–$(CH=CH)_x$–NO_2 systems have been depicted in Figure 6. We can find that the electron cloud in the related occupied orbitals (HOMO or HOMO-1) is distributed on the [8]MC ring and the –$(CH=CH)_x$– chain, where the more electron cloud can be observed along with farther away from the NO_2-end. However, compared with these occupied orbitals, the electron cloud can exhibit the flowing trend from the MC ring to the NO_2-end in the correlative unoccupied orbitals (LUMO or LUMO+3). In particular, this distribution trend of electron cloud in the related occupied and unoccupied orbitals can become more prominent with elongating the substituent –$(CH=CH)_x$–NO_2 chain. Clearly, the evident charge transfer occurs in the process of the transitions, where the longer substituent –$(CH=CH)_x$–NO_2 chain, the more charge transfer. This can be responsible for the significant improvement of NLO properties for [8]MC–10–$(CH=CH)_x$–NO_2 systems with the monotonic increase of β_0 value as increasing the –$(CH=CH)_x$–NO_2 length.

Undoubtedly, constructing a mixed π-conjugated bridge through the –$(CH=CH)_x$– chain to decorate the Möbius cyclacene can be an effective approach to significantly enhance the NLO response of MC-based systems. This can be further demonstrated by making a comparison with the reported MC-based systems,[19,22,23] for example, under this study, the β_0 value of [8]MC−10−(CH=CH)$_{12}$−NO$_2$ system, with only a certain chain length (x = 12), can present as large as 9.87×10^5 au, which is much larger than those of the previously studied MC-based systems, such as, 3773 au for the Möbius basket molecule,[23] 12467 au for the NH$_2$–[8]MC–NO$_2$ system with fascinating spiral charge transfer,[19] and 352 ~ 1019 au for the Li-atom monosubstituted [7]Möbius systems,[22] respectively.

4. Conclusions

In this study, we can find that employing the concept of mixed π-conjugated bridge through constructing a Möbius cyclacene (MC)−chain motif can significantly increase the first hyperpolarizabilities of MC-based systems under D−π−A framework, by investigating a series of [8]MC systems decorated by a π-conjugated –(CH=CH)$_x$– chain linked with the donor NH$_2$ or acceptor NO$_2$ group. Specifically, the following intriguing findings can be achieved:

(1) Employing the shortest –CH=CH–NH$_2$ and –CH=CH–NO$_2$ chains to modify [8]MC can effectively enhance the β_0 values of these [8]MC−chain motifs ([8]MC–CH=CH–NH$_2$ and [8]MC–CH=CH–NO$_2$) with a mixed π-conjugated bridge in the range of 499 ~ 1967 and 1317 ~ 5400 au, respectively, which are much larger than the

corresponding values (261 au) of sole [8]MC. Particularly, the substituent site of the modified chain can play a crucial role in increasing the β_0 values of these [8]MC–chain motifs, where the 12-site is the most appropriate for the modification of $–CH=CH–NH_2$ to get the largest β_0 value (1967 au) among the fifteen possible isomers, while the 10-site for the decorated $–CH=CH–NO_2$ chain to obtain the largest β_0 value (5400 au).

(2) When employing the longer substituent $–(CH=CH)_x–$ ($x = 2 \sim 12$) chains linked with the donor NH_2 group, the β_0 values of the corresponding [8]MC-based systems $[8]MC–12–(CH=CH)_x–NH_2$ ($x = 2 \sim 12$) can be significantly enhanced in the range of $4.48 \times 10^3 \sim 1.17 \times 10^5$ au, with the monotonic increase of β_0 value as increasing the $–(CH=CH)_x–NH_2$ length, which are much larger than those ($2.18 \times 10^3 \sim 6.95 \times 10^4$ au) of the corresponding NH_2-modified polyacetylene chain ($H–(CH=CH)_{x+2}–NH_2$) series with the same π-conjugated length. Obviously, elongating the $–(CH=CH)_x–NH_2$ chain with the electron-donating characteristic can be an effective approach to improve the first hyperpolarizabilies of these MC–chain motifs with a mixed π-conjugated bridge.

(3) Similarly, for the modified [8]MC-based systems by the longer electron-withdrawing $–(CH=CH)_x–NO_2$ chain, namely, $[8]MC–10–(CH=CH)_x–NO_2$ ($x = 3 \sim 12$) series, their β_0 values can significantly increase monotonously as elongating the $–(CH=CH)_x–NO_2$ chain (in the range of $1.07 \times 10^4 \sim 9.87 \times 10^5$ au), which are much larger than the corresponding those ($6.33 \times 10^3 \sim 1.43 \times 10^5$ au) of $H–(CH=CH)_{x+2}–NO_2$

series with the same π-conjugated length, even the parallel [8]MC–12–$(CH=CH)_x$–NH_2 series ($8.54 \times 10^3 \sim 1.17 \times 10^5$). Clearly, the employing the electron-withdrawing –$(CH=CH)_x$–NO_2 chain can more effectively enhance the β_0 values of these [8]MC-based systems with a mixed π-bridge than the parallel electron-donating –$(CH=CH)_x$–NH_2 chain, where increasing the –$(CH=CH)_x$– chain length can also play a crucial role in enhancing the β_0 value.

Undoubtedly, these fascinating findings may deliver immensely valuable insights for the design of novel high-performance NLO materials based on the intriguing Möbius cyclacene with unique structure.

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