

Effect of dehydrogenation/hydrogenation on the linear and nonlinear optical properties of Li@porphyrins

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Abstract In the present work, Li@porphyrins and their derivatives were designed in order to explore the effect of dehydrogenation/hydrogenation on linear and nonlinear optical properties. Their stable structures were obtained by the M06-2X method. Moreover, the M06-2X method showed that dehydrogenation/hydrogenation has greatly influences polarizabilities (α_0 values) and hyperpolarizabilities (β_{tot} and γ_{tot} values): α_0 values ranged from 331 to 389 au, β_{tot} values from 0 to 2465 au, and γ_{tot} values from -21.2×10^4 to 21.4×10^4 au. This new knowledge of the effect of dehydrogenation/hydrogenation on nonlinear optical properties may prove beneficial to the design and development of high-performance porphyrin materials.

Keywords Li@porphyrins · Dehydrogenation/hydrogenation effect · Linear and nonlinear optical properties · High-performance NLO materials · M06-2X method

Introduction

Nonlinear optical materials have been extensively explored over the past few decades due to their potential applications in optical and electro-optical devices [1–7]. Both experimental and theoretical studies have been carried out to search for methods of enhancing the nonlinear optical responses of materials [8–35]. Such methods include increasing the length of the π -conjugated chain, enhancing

the combination of the donor and acceptor strength, increasing push–pull effects, utilizing twisted π -electron systems, and doping the ligand metal into organic compounds. In particular, Li-doped systems have systematically been explored by Li's group [3, 8, 9, 11, 12, 16, 17, 20, 24] and, intriguingly, they found that electriles possess rather large first hyperpolarizabilities. This result stimulated our curiosity.

Electrides [36, 37] were first proposed by Dye. In electriles, anionic sites are occupied by loosely bound excess electrons. The central premise for the formation of stable electriles is that alkali metal atoms can be captured by a nonreducible cryptand complexant. Unfortunately, most conventional organic electriles are sensitive to temperature and air [38, 39] due to the reductive rupture of oxygen–carbon bonds in oxygen-based cryptand complexants. Hence, Dye put forward a practical way to search for thermally stable organic electriles: replace oxygen with nitrogen.

In light of the issues and results discussed above, Li's group chose a novel class of organic electriles as the focus of their research. Calix[4]pyrrole [8, 9] with a cone conformation [40] was employed as the cryptand complexant, and an alkali lithium atom was trapped in the calix[4]pyrrole. However, to the best of our knowledge, the calix[4]pyrrole framework consists of four separate pyrrole subunits. This leads to an interesting question: how do the four conjugated pyrrole subunits interact with alkali atoms?

In order to uncover the answer to this question, we investigated the linear and nonlinear optical properties of Li@porphyrins and their derivatives (seen in Fig. 1), and the results of this investigation are provided in this paper. **1** is obtained by removing one of the H atoms connected to an N atoms in **2a/2b**, and **0** is obtained by removing another H atom from **1**; this is called the dehydrogenation effect [41].

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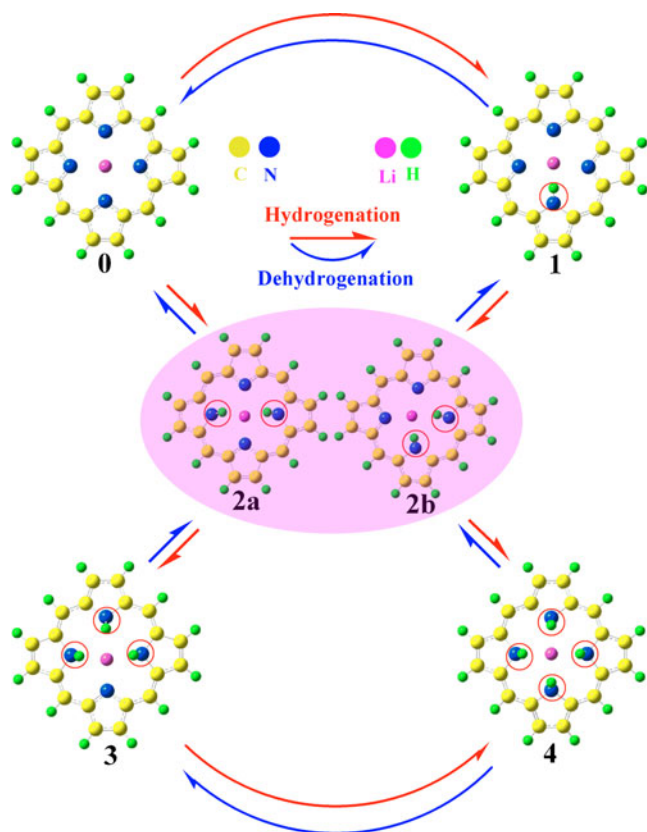


Fig. 1 The stable geometrical structures of **0**, **1**, **2a**, **2b**, **3**, and **4**, all with real frequencies, which were obtained using the M06-2X/6-31G(d) method

On the other hand, **3** is obtained by introducing one H atom onto one of the N atoms that does not have any H atoms in **2a** /**2b**. Then **4** is obtained by introducing an H atom onto an N atom that does not have an H atom in **3**; this is called the hydrogenation effect [42]. It is worth mentioning that the differences among **0**, **1**, **2a**, **2b**, **3**, and **4** are the positions that undergo dehydrogenation/hydrogenation and the number of H atoms. Thus, **0**, **1**/**2a**, **2b**/**3**, and **4** were investigated in order to get a comprehensive

Table 1 Geometrical parameters for **0**, **1**, **2a**, **2b**, **3**, and **4**, as calculated at the M06-2x/6-31G(d) level. The bond lengths (Å) of the four N–Li bonds are listed. NBO charges on Li⁺ in **0**, **1**, **2a**, **2b**, **3**, and **4** were calculated at the M06-2x/6-31G(d) Level

	0	1	2a	2b	3	4
N ₁ –Li	2.043	2.040	2.081	2.573	2.592	2.225
N ₂ –Li	2.043	2.448	2.241	2.343	2.203	2.237
N ₃ –Li	2.043	2.040	2.081	1.940	1.948	2.225
N ₄ –Li	2.043	1.904	2.304	1.979	2.191	2.237
N–Li ^a	2.043	2.108	2.177	2.209	2.233	2.231
Li ⁺	0.611	0.641	0.729	0.737	0.782	0.827

^a Mean (Å) of the N₁–Li, N₂–Li, N₃–Li, and N₄–Li bond lengths

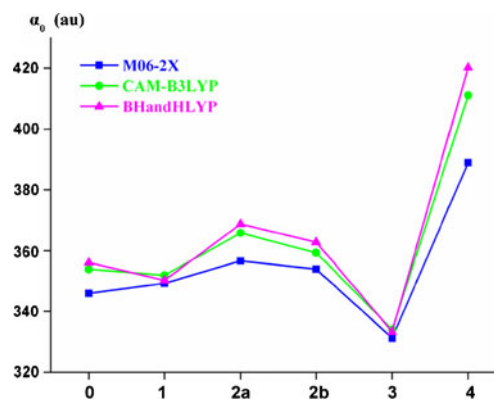


Fig. 2 The α_0 values of **0**, **1**, **2a**, **2b**, **3**, and **4**, as calculated by three DFT methods

understanding of how the dehydrogenation/hydrogenation influences the linear and nonlinear optical properties of these materials. Additionally, we hope that our work will provide a new strategy for designing and synthesizing novel NLO materials via the dehydrogenation/hydrogenation effect.

Theoretical methodologies

According to our previous work [43], structural optimization by the novel hybrid meta exchange correlation functional M06-2X, as proposed by Zhao and co-workers [44, 45], yields good results, and the basis set 6-31G(d) also performs well. Thus, in this work, the stable geometrical structures of **0**, **1**, **2a**, **2b**, **3**, and **4**, all with real frequencies, were obtained using the M06-2X/6-31G(d) method. Natural bond order (NBO) charges of Li⁺ were calculated at the M06-2X/6-31G(d) level of theory. To the best of our knowledge, it is very important to use an accurate method of calculating polarizabilities and first hyperpolarizabilities. However, most conventional methods of doing this have been reported to give inaccurate values for the (hyper)polarizability [46]. Fortunately, three new DFT exchange correlation functionals (M06-2X [44, 45], CAM-B3LYP [47], and BHandHLYP [48]) that possess a good balance between quality and efficiency have been shown to lead to more accurate values for the (hyper)polarizabilities of π -conjugated systems than other methods [49–51]. Hence, in this work, these three different DFT exchange correlation functionals were adopted in order to explore the linear and nonlinear properties of the materials of interest. The 6-31+G(d) basis set was employed for C, N, H, and Li atoms.

The polarizability was defined as follows:

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (1)$$

Table 2 The α_0 (au) and β_{tot} (au) values of **0**, **1**, **2a**, **2b**, **3**, **4**, as calculated by the M06-2X, CAM-B3LYP, and BHandHLYP methods. ΔE (eV) and f_0 were calculated at the M06-2X/6-31+G(d) level. The γ_{tot} (au) values were calculated at the M06-2X/6-31+G(d) level

		0	1	2a	2b	3	4
M06-2X	α_0	346	349	357	354	331	389
	β_x	0	-101	25	611	2452	-1
	β_y	0	4	-126	795	250	2
	β_z	0	24	21	41	48	221
	β_{tot}	0	104	130	1004	2465	221
CAM-B3LYP	α_0	354	352	366	359	334	411
	β_x	0	-113	96	981	2267	4
	β_y	0	1	-122	704	231	-3
	β_z	0	32	39	25	73	270
	β_{tot}	0	117	160	1208	2280	270
BHandHLYP	α_0	356	350	369	363	333	420
	β_x	0	-115	227	1542	2066	6
	β_y	0	4	-110	-459	210	-7
	β_z	0	33	76	-46	81	305
	β_{tot}	0	119	264	1609	2079	305
M06-2X	ΔE	3.9400	3.6034	3.5601	3.5289	3.3727	3.5843
	f_0	0.1371	1.1243	0.4506	0.3366	0.4358	1.1566
M06-2X	$\gamma_{\text{tot}} \times 10^4$	2.3	9.0	9.6	14.0	21.4	-21.2

The first hyperpolarizability was obtained as

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \quad (2)$$

where

$$\beta_i = \beta_{\text{iii}} + \beta_{\text{ijj}} + \beta_{\text{ikk}}, \quad i, j, k = x, y, z. \quad (3)$$

The second hyperpolarizability was calculated at the M06-2X/6-31+G(d) level of theory as

$$\gamma_{\text{tot}} = \frac{1}{5}(\gamma_{\text{xxxx}} + \gamma_{\text{yyyy}} + \gamma_{\text{zzzz}}) + \frac{2}{5} \times (\gamma_{\text{xyxy}} + \gamma_{\text{xzzz}} + \gamma_{\text{yyzz}}). \quad (4)$$

Furthermore, frequency-dependent NLO properties were evaluated using the coupled perturbed Kohn–Sham method

[52]. The frequency-dependent β was calculated as

$$\bar{\beta}(\omega) = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \quad (5)$$

where

$$\beta_i = \beta_{\text{iii}}(-2\omega; \omega, \omega) + \beta_{\text{ijj}}(-2\omega; \omega, \omega) + \beta_{\text{ikk}}(-2\omega; \omega, \omega) \quad (6)$$

for the second-harmonic generation values and

$$\beta_i = \beta_{\text{iii}}(-\omega; \omega, 0) + \beta_{\text{ijj}}(-\omega; \omega, 0) + \beta_{\text{ikk}}(-\omega; \omega, 0) \quad (7)$$

for the electro-optical Pockels effect values.

All of the calculations were performed with the Gaussian 09W software package [53].

Results and discussion

Geometrical parameters

The optimized structures of the Li@porphyrins and their derivatives are given in Fig. 1. From Fig. 1, it is apparent that the two hydrogen atoms bonded to the inwardly orientated nitrogen atoms in **2a** are opposite to each other, whereas they are positioned ortho to each other in **2b**. The important structural parameters and NBO charges are collected together in Table 1. Interestingly, due to the dehydrogenation effect, the mean N–Li bond lengths in **0** and **1** are smaller than that in **2a/2b**. On the other hand, **3** and **4**, which

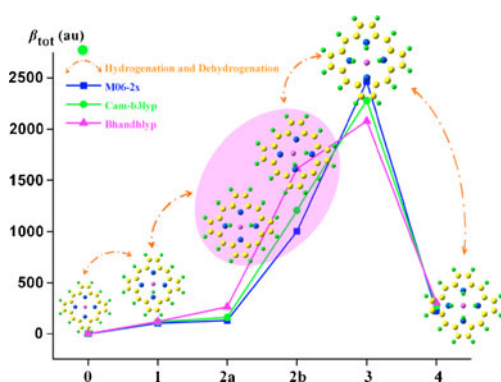


Fig. 3 The β_{tot} values of **0**, **1**, **2a**, **2b**, **3**, and **4**, as calculated by three DFT methods

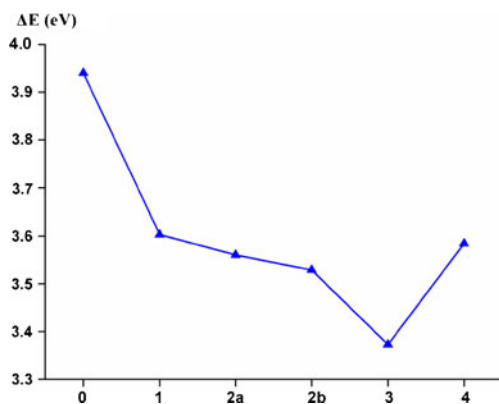


Fig. 4 ΔE values of **0**, **1**, **2a**, **2b**, **3**, and **4**, as calculated by TD-DFT/M06-2X method

form via the hydrogenation effect, have longer mean N–Li bonds than **2a/2b**. The mean length of the N–Li bond increases in the order **0** (2.043 Å) < **1** (2.108 Å) < **2a** (2.177 Å) < **2b** (2.209 Å) < **4** (2.231 Å) < **3** (2.233 Å). Thus, **3** has the largest mean N–Li bond length. According to natural bond orbital (NBO) analysis, this indicates that the charge on Li in the six molecules increases as the number of H atoms increases: **0** (0.611) < **1** (0.641) < **2a** (0.729) < **2b** (0.737) < **3** (0.782) < **4** (0.827), meaning that electrons transfer from the Li atom to the ligands.

According to the above analysis, the Li@porphyrin **3**, which is formed through the hydrogenation of **2a/2b**, and has the largest mean N–Li bond length, is special. Thus, we could not help but wonder how modifying the geometric structures of **2a/2b** via the dehydrogenation/hydrogenation effect changes the linear and nonlinear optical properties of these molecules?

Linear and nonlinear optical properties

Polarizability (α_0)

The α_0 values of **0**, **1**, **2a**, **2b**, **3**, and **4** were calculated by the M06-2X, CAM-B3LYP, and BHandHLYP methods, and these values are collected in Fig. 2 and Table 2. It is clear that the results calculated using M06-2X (which range from 331 to 389 au), CAM-B3LYP (334–411 au), and BHandHLYP (333–420 au) are very similar. For systems **0** and **1**, different trends are observed in the results obtained using CAM-B3LYP, BHandHLYP, and M06-2X, but the values are similar whichever method is used, so we chose to use the M06-2X results to shed light on the changes in α_0 . The α_0

values of **2a** (357 au) and **2b** (354 au) are also very close. Compared to **2a/2b**, the α_0 value of **1** (formed via the dehydrogenation effect) is slightly lower at 349 au (M06-2X). The α_0 value of **0** (346 au), obtained by dehydrogenating **1**, is very similar to the value for **1**. Moreover, if we consider the sequence of hydrogenation (**0** → **1** → **2a/2b** → **3** → **4**), Fig. 2 shows that the value of α_0 dips significantly for **3** to 331 au. This interesting result may relate to the special structure of **3**. Upon hydrogenating **3**, we find that the α_0 value of **4** increases sharply to 389 au, which is the largest value among all of the Li@porphyrins considered here.

Static first hyperpolarizability (β_{tot})

Figure 3 presents the β_{tot} values of the six molecules obtained by three different methods. The trend in the β_{tot} values of the molecules was virtually the same whichever method was used. Very recently, an important work was published in which calculations of linear and nonlinear optical properties using several exchange-correlation functionals were performed [54]. The results showed that the M06-HF and ω B97 exchange-correlation functionals provided a better linear correlation with experimental results. Thus, we calculated the β_{tot} value of **3** using the M06-HF and ω B97 methods. The β_{tot} value calculated by the M06-2X method (2465 au) was very similar to that given by the M06-HF (2420 au) and ω B97 (2345 au) methods. Thus, we looked more closely at the M06-2X results in an attempt to qualitatively understand the β_{tot} values. **2a** and **2b** differ in the relative positions of the two H atoms bonded with the inwardly orientated N atoms. We wanted to know whether this structural difference leads to differences in the β_{tot} value. Figure 3 shows that the β_{tot} value of **2a** (130 au) is distinctly smaller than that of **2b** (1004 au). The β_{tot} value of **1**, formed by the dehydrogenation of **2a/2b**, is slightly lower at 104 au. When **1** is subjected to dehydrogenation, **0** is obtained, and the β_{tot} value of **0** is approximately zero due to its centrosymmetric structure. To our surprise, when we considered the β_{tot} values along the sequence of hydrogenation (**0** → **1** → **2a/2b** → **3** → **4**), we noticed that there was a peak that reached its maximum at **3** (2465 au). Interestingly, **4**, formed by the hydrogenation of **3**, shows a sharply reduced β_{tot} value of 221 au compared to **3**. We found that **3** shows particular linear optical properties due to its special structure. By carefully inspecting the molecular structure of **3**, we elucidated that, under the action of the three H atoms

Table 3 The estimated coupled perturbed Kohn–Sham values of the frequency-dependent first hyperpolarizabilities of **3** (in au)

Frequency	0.0000	0.0050	0.0100	0.0200	0.0239	0.0400	0.0428
$\beta(-\omega, \omega, 0)$	2465	2500	2560	2842	3043	6052	8307
$\beta(-2\omega, \omega, \omega)$	2465	2518	2823	3220	3783	10168	14783

bonded to N atoms, the Li atom is pushed away from the central location, which leads to the largest mean N–Li bond length. As we all know, the structure of a molecule largely determines its chemical properties. Hence, the fact that the largest β_{tot} value is exhibited by **3** may relate to its interesting chemical structure.

Investigating further, the transition energy (ΔE) and the oscillator strength (f_0) of each molecule calculated at the TD-M06-2X/6-31+G(d) level are listed in Table 2. According to the two-level model [55, 56], f_0 is inversely proportional to the first hyperpolarizability, but the third power of ΔE is inversely proportional to the first hyperpolarizability. These results show that the trend in f_0 is unclear. Thus, the variation in β_{tot} cannot be explained by f_0 . Figure 4 shows that **0** has the largest ΔE value among the molecules (3.9400 eV). The ΔE values of **1**, **2a**, and **2b** are clearly lower than that of **0**, ranging from 3.5289 eV to 3.6034 eV. **3** yields the smallest ΔE value (3.3727 eV). Hydrogenating **3** leads to **4**, and the ΔE of **4** is higher at 3.5843 eV than that of **3**. Hence, the variation in ΔE seen in Fig. 4 is opposite to the trend noticed for β_{tot} , suggesting that the trend in ΔE provides a good explanation for the variation in β_{tot} .

Static second hyperpolarizability (γ_{tot})

The second hyperpolarizabilities of the six molecules are collected in Table 2. The γ_{tot} value of **2a** is 9.6×10^4 au, whereas that of **2b** is 14.0×10^4 au, which is about 1.5 times greater than that of **2a**. The different γ_{tot} values of **2a** and **2b** indicate that the relative locations of the H atoms bonded to N atoms have a major influence on the γ_{tot} values. Upon dehydrogenating **2a/2b**, the γ_{tot} value decreases to 9.6×10^4 au (**1**). With further dehydrogenation, the γ_{tot} value decreases to 2.3×10^4 au (**0**). However, upon hydrogenating **2a/2b**, the γ_{tot} value increases to 21.4×10^4 au (**3**), and then to -21.2×10^4 au (**4**). Thus, the dehydrogenation/hydrogenation effect also had a major influence on the γ_{tot} values calculated in our work.

Frequency-dependent NLO properties

Studies of azo-enaminone isomers [57–59] indicate that the dynamic first hyperpolarizabilities are also very important. Thus, we investigated the frequency-dependent first hyperpolarizabilities of **3** using the coupled perturbed Kohn–Sham method. The results listed in Table 3 include second harmonic generation (SHG) $\beta(-2\omega, \omega, \omega)$ and the electro-optical Pockels effect (EOPE) $\beta(-\omega, \omega, 0)$, for which $\omega = 0.0000, 0.0050, 0.0010, 0.0200, 0.0239, 0.0400,$ and 0.0428 au. The results show that the values of $\beta(-2\omega, \omega, \omega)$ and $\beta(-\omega, \omega, 0)$ are larger than the corresponding static β_{tot} values, and the values of $\beta(-2\omega, \omega, \omega)$ and $\beta(-\omega, \omega, 0)$ increase with increasing frequency (ω) from 0.0000 to 0.0428 au. Also, the values of $\beta(-2\omega, \omega, \omega)$ are all larger than the

corresponding values of $\beta(-\omega, \omega, 0)$ at $\omega = 0.0239$ au ($\lambda = 1907$ nm) and $\omega = 0.0428$ au ($\lambda = 1064$ nm), which shows that the frequency-dependent effects on $\beta(-2\omega, \omega, \omega)$ are stronger than those on $\beta(-\omega, \omega, 0)$ of **3**. In addition, the largest value of $\beta(-2\omega, \omega, \omega)$ is 14783 au, which is about six times the static β_{tot} value.

Conclusions

In this paper, the stable structures (all with real frequencies) of the Li@porphyrins **0**, **1** and **3**, **4**, obtained by the dehydrogenation and hydrogenation of **2a/2b**, were obtained using the M06-2X/6-31G(d) method. The natural bond orbital (NBO) charge of Li^+ indicated that electrons transfer from the Li atom to the ligands. Among the Li@porphyrins studied, **3**, which had the largest mean N–Li bond length, is special: the α_0 value of **3** calculated by M06-2X (331 au), CAM-B3LYP (334 au), and BHandHLYP (333 au) was the smallest, and the β_{tot} value of **3** calculated by M06-2X (2465 au), CAM-B3LYP (2280 au), and BHandHLYP (2079 au) was the largest. In addition, the γ_{tot} value of **3** was the largest. The variation in ΔE across the molecules, as calculated by the TD-DFT/M06-2X method, is opposite to the variation in β_{tot} , so the trend in ΔE explains the trend in β_{tot} .

The results of our study enhance our understanding of the structural sensitivity of nonlinear optical properties, and should encourage scientists to consider the dehydrogenation/hydrogenation effect when designing high-performance NLO materials.

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Highlights

The Li@porphyrins **2a** and **2b** and their derivatives **0**, **1** and **3**, **4** were designed based on the dehydrogenation /hydrogenation effect.

The charge on Li in the six molecules ranged from 0.611 to 0.827, which indicates that electrons transfer from the Li atom to the ligands.

3 was found to have the smallest α_0 value as well as the largest β_{tot} value and γ_{tot} value.

The interesting variation in the β_{tot} values of the Li@porphyrins observed in this work should encourage the consideration of the dehydrogenation/hydrogenation effect when designing high-performance NLO materials