

Synthesis and NLO properties of chromophores with calix[4] arene and ring-locked trienes

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The new chromophore molecules with nonlinear optical (NLO) properties were prepared by Knoevenagel condensation from diformyl calix[4]arene and isophorone derivatives in the presence of piperidine and acetic acid, respectively. In these chromophore calix[4]arenes, the ring-locked trienes were employed as the conjugation bridge and electron acceptor in D- π -A units. Nuclear magnetic resonance (NMR) spectra indicate that the non-conjugated D- π -A units can be oriented at nearly the same direction. Hyper-Rayleigh Scattering (HRS) measurements and ultraviolet (UV) spectra indicate that they have higher first hyperpolarizability β values than the corresponding reference compounds and are not accompanied with a large shift (> 25 nm) of the absorption band to longer wavelengths.

OCIS codes: 160.4890, 160.4330, 190.0190, 000.1570.

Organic compounds with second-order nonlinear optical (NLO) properties have various potential in the development of materials for applications such as frequency doubling and optical switching^[1,2]. Traditional organic NLO materials are organic molecules that contain electron-donating and electron-accepting groups connected via a conjugated π system, i.e. so called D- π -A structure. Generally, the first hyperpolarizability β of a molecule increases with increasing length of the conjugated π system and increasing strength of the donor and acceptor^[3]. Unfortunately, an increase in the β value is accompanied by a red shift in the absorption spectra due to a larger π -conjugated length and/or stronger donor and acceptor substituents, i.e., there is a tradeoff between nonlinearity and transparency^[4]. To resolve this problem, we designed and synthesized new NLO chromophores which the calix[4]arene is used as backbone. Hyper-Rayleigh Scattering (HRS) measurements have demonstrated that they have higher first hyperpolarizability β values than the corresponding reference compound without a large red shift of the charge transfer band. This methodology may provide a new opportunity for defeating the nonlinearity-transparency tradeoff. Calixarenes are a cyclic oligomers having phenolic units linked by methylene groups^[5]. When calix[4] arene exists in the cone conformation, the non-conjugated D- π -A units are oriented nearly at the same direction. Therefore, this system can increase nonlinear optical activity and is not accompanied with an unfavorable shift of absorption to longer wavelengths. The synthetic pathway of new chromophore molecules **4** and **5** is shown in Fig. 1. In order to obtain non-conjugated D- π -A units oriented nearly at the same direction, the conformation of calix[4] arene must be fixed as cone form. Therefore two octyl groups were introduced into the lower rim of calix[4]arene **1** by the selective O-octylation of with *n*-octyl bromide to give 26, 28-dioctyloxy-25, 27-dihydroxy calix[4]arene **2**. As to our knowledge, the configuration-locked triene unit in chromophors can result in higher NLO activity^[6,7], so it was introduced at upper rim of calix[4]arene by Knoevenagel condensation from calix[4]arene dialdehyde **3** and isophorone derivatives under the catalysis of piperidine and acetic acid. The yields are about 35%–45%.

The chromophore molecules **4** and **5** are red or purple crystals, melting point is 193–195° and 164–166°, respectively. The chromophore molecules **4** and **5** gave ¹H NMR, MS and Elemental analysis data in accord with the assigned structures.

HRS technique at 1064 nm is employed to measure the first hyperpolarizabilities β . The excitation source was a Q-switched Nd:YAG laser system (continuum precision II 8010) producing ~ 8 ns-duration, ~ 1 cm⁻¹ spectral-width laser output with a repetition rate of 10 Hz. *p*-Nitroaniline (PNA) was used as the external reference. The charge-transfer band was determined by UV-240 ultraviolet-visible spectrophotometer. The first hyperpolarizability β values, the static first hyperpolarizabilities β_0 and the absorption maximum of the charge-transfer band are summarized in Table 1. It can be seen from Table 1 that the compounds **4** and **5** with two D- π -A moieties have higher first hyperpolarizability β values

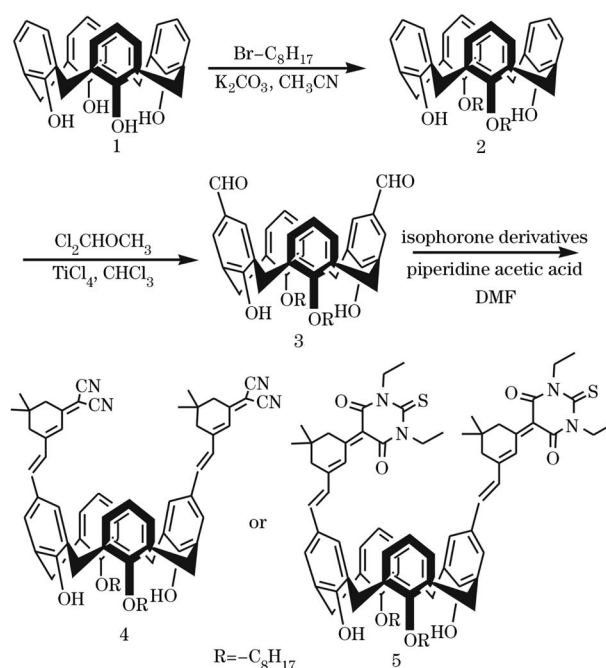


Fig. 1. Synthetic pathway of chromophore molecules **4** and **5**.

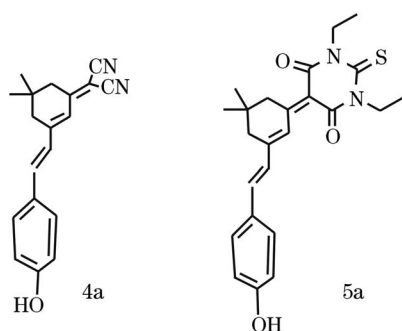


Fig. 2. Molecule structure of reference compounds **4a** and **5a**.

Table 1. First Hyperpolarizability Values β , Static First Hyperpolarizabilities β_0 and Absorption Maximum (λ_{\max}) of the Charge-Transfer Band of the Chromophores and Reference Compounds (at 1064 nm in CHCl_3)

Compounds	$\beta (\times 10^{-30} \text{ esu})$	$\beta_0 (\times 10^{-30} \text{ esu})$	$\lambda_{\max} (\text{nm})$
4a	226	64.3	432.0
4	847	205.4	448.0
5a	583	108.1	494.0
5	1061	44.4	517.5

p-nitroaniline (PNA) was used as the external reference, $\beta = 21.1 \times 10^{-30} \text{ esu}$.

than the corresponding reference compounds **4a** and **5a** with only one D- π -A unit, respectively, the molecule structure of compounds **4a** and **5a** is shown in Fig.2, whereas only a small shift ($< 25 \text{ nm}$) of the absorption band to longer wavelengths is accompanied. Especially, β value of **4** is 3.7 times the value of the reference compound **4a**, and with only slight red shift (16 nm) of

the charge transfer band. Therefore, calix[4]arenes with the non-conjugated and pre-organized D- π -A units can provide a new opportunity for solving the nonlinearity-transparency tradeoff.

In conclusion, the new NLO chromophores **4** and **5** have higher first hyperpolarizability β values than the corresponding reference compounds, and are not accompanied with a large shift ($> 25 \text{ nm}$) of the absorption band to longer wavelengths. Therefore, calix[4]arenes with NLO-active moieties are promising and interesting building blocks for designing organic NLO materials with both high β value and good transparency.

This work was supported by the Science Foundation of JiangSu Province in China (No. BK2004085), and the National Natural Science Foundation of China (No. 90101018). G. Lu is the author to whom the correspondence should be addressed, his e-mail address is lugyuan@nju.edu.cn.

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