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The design of second-order nonlinear optical chromophores exhibiting blue-shifted absorption and large nonlinearities: the role of the combined conjugation bridge†

Jingdong Luo,[a] Jianli Hua,[a] Jingui Qin,*[a] Jiqi Cheng,[b] Yaochun Shen,[b] Zuhong Lu,[b] Peng Wang[c] and Cheng Ye[c]

[a] *Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China. E-mail: jgqin@whu.edu.cn; Tel: +86-27-87684117; Fax: +86-27-87647617*
[b] *National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, P.R. China*
[c] *Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China*

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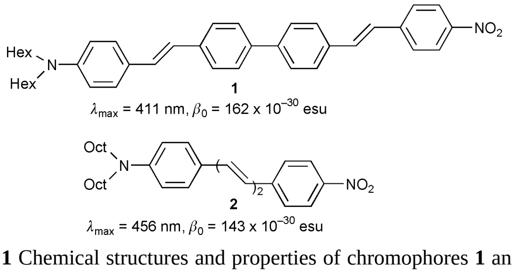
Two new extended chromophoric systems, in which a 4-aminoazobenzene moiety is linked to a cyclo-bridged hexatriene electron withdrawing group, have been synthesized, and show large optical nonlinearities and unexpected blue-shifted absorption in comparison with shorter chain analogues.

Organic and polymeric second-order nonlinear optical (NLO) materials have been extensively studied for their potential applications involving optical signal processing and telecommunications.[1] One of the major challenges in this area of research is to design and synthesize second-order NLO chromophores simultaneously exhibiting large first molecular hyperpolarizability (β), high chemical and thermal stability, and good optical transparency.[2,3] Most attempts to design molecules with large β since the 1980s have been based upon 'push–pull' compounds,[4] in which a π-conjugated bridge is endcapped with an electron donor group and an electron acceptor group. From the two-level model,[5] the β value of this type of chromophore is a strong function of the absorption maximum (λ_{max}), leading to the so-called nonlinearity–transparency tradeoff.

Among all the attempts to solve this kind of trade-off, it has been proved that the nature of π-conjugated bridge of chromophores is one of the crucial factors in determining the linear and nonlinear optical properties of the chromophores. For example, Alain *et al*. recently reported[6] that chromophore **1** (Fig. 1), in which a biphenyl moiety is present between the diphenylpolyene unit, exhibits a 45 nm (2400 cm^{-1}) blue-shifted absorption and similar optical nonlinearity compared with its all diphenylpolyenic analogue (chromophore **2**, Fig. 1), though the conjugation bridge of **1** is much longer. It seems a worthwhile job to study further the linear and nonlinear optical properties of the chromophores by using a combination of different types of conjugation bridges.

Therefore, we have recently designed two new chromophores (**I** and **II** in Fig. 2)† in which the conjugation bridge of isophorone-protected triene with the terminal acceptors is linked to a donor-substituted azo benzene bridge.

The first molecular hyperpolarizabilities of chromophores **I** and **II** were measured by Hyper-Rayleigh Scattering (HRS) in methanol using the fundamental excitation wavelength of 1064 nm; *p*-nitroaniline (PNA) was used as the external reference. The β values of **I** and **II** were found to be 2890×10^{-30} esu and 3490×10^{-30} esu, respectively, and by using the two-level approximation model, the zero-frequency hyperpolarizabilities β_0 of **I** and **II** were extrapolated to be 337×10^{-30} esu and 198×10^{-30} esu, respectively.



1

λ_{max} = 411 nm, β_0 = 162 x 10^{-30} esu

2

λ_{max} = 456 nm, β_0 = 143 x 10^{-30} esu

Fig. 1 Chemical structures and properties of chromophores **1** and **2**.

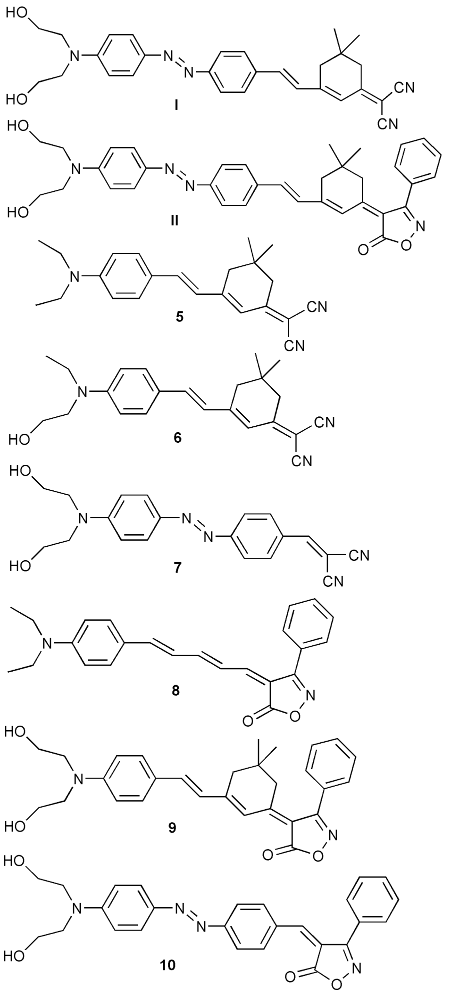


Fig. 2 Chemical structures of chromophores **I**, **II** and their corresponding triene-only and azo-only analogues (chromophores **5**–**10**).

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† Electronic supplementary information (ESI) available: synthesis and structural characterization of several new compounds of this work. See http://www.rsc.org/suppdata/cc/b0/b007653h/

Table 1 The linear and nonlinear properties of chromophore **I**, **II** and **5–10**

	Solvatochromism data[a] (λ_{max}/nm)				Theoretical investigation[7]		Experimental results	
	$CHCl_3$	AcOEt	DMF	NMP	β_0[b]	f[c]	β^0_{HRS}[d]	f^2
I	490	492	511	519	52.6	2.3302	337	1.0
5	519	504	527	535	46.8	1.5646	—	0.72
6	—	—	—	534	—	—	60[e]	—
7	508	505	525	533	42.5	1.4965	55[e]	0.86
II	510	507	517	533	—	—	198	1.1
8	562	—	—	—	—	—	90[e]	—
9	568	—	—	—	—	—	27[e,13]	—
10	516	524	545	553	—	—	—	0.82

[a] AcOEt: ethyl acetate, DMF: dimethylformamide, NMP: *N*-methylpyrrolidone. [b] AM1/FF results, in units of 10^{-30} esu. [c] ZINDO/S-CI results. [d] Dispersion-corrected β values (in units of 10^{-30} esu) of **I** and **II** were calculated by using an approximate two-level model. [e] β^0_{HRS} values are estimated from the data of β^0_{EFISH} previously reported[8] according to the following equation: $\beta^0_{HRS} = (6/35)^{1/2}\beta^0_{EFISH}$.

Besides the target chromophores **I** and **II**, the other six chromophores (**5–10**, see Fig. 2), which are the azo-only or triene-only analogues of **I** and **II**, respectively, will also be discussed below.[8,9]

The linear and the nonlinear properties of these chromophores are summarized in Table 1. It can be seen that **I** and **II**, two chromophores employing the combination of azo benzene and conjugated triene as their conjugation bridge, display unexpectedly blue-shifted absorption compared with the corresponding azo-only or triene-only analogues, although the length of their conjugation bridge is much longer. For instance, the absorption maxima of **I** is about 15 nm (500 cm^{-1}) blue-shifted compared with **5**, **6**, and **7** in different organic solvents. And as shown in Fig. 3, there is no significant broadening of the main absorption band for **I**, if another absorption band around 400 nm in their UV-Vis spectrum is taken into account, and this is also the case for **II**. All these results show that for **I** and **II**, the electron transmission process between donor and acceptor groups is affected, and the intramolecular charge transfer (ICT) efficiency is reduced. This reduction may occur through using different types of bridge with different energy orbitals other than the most efficiently conjugated bridge possible.

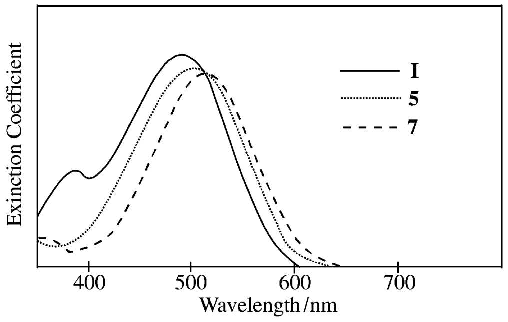

Fig. 3 Comparison of the absorption spectra of chromophores **I**, **5**, and **7** in methanol.

Although the π-electron delocalization efficiency of **I** and **II** is somewhat reduced, it should be noted that the β_0 values of **I** and **II** are quite competitive with those of their corresponding analogues from the theoretical investigation and the experimental results**.** This appears to be at variance with the predictions of the two-level model. However, besides the nonlinearity–transparency trade-off mentioned above, the two-level model also adduces that the β value is a strong function of the oscillator strengths (*f*) and $\Delta\mu$, the change of dipole moment upon excitation. Thus it can be phenomenologically deduced that the reduction of the ICT efficiency of chromophores **I** and **II** does not accompany a decrease in their *f* and/or $\Delta\mu$ values, and this has been partially verified by the experimental results. As shown in Table 1, the oscillator strengths (*f*) of **I** and **II**, respectively determined to be 1.0 and 1.1, are significantly higher than those of the corresponding azo-only or triene-only analogues. It seems that the larger oscillator strengths of **I** and **II** may be one of the major points for counterbalancing the effects of blue shifts. Further study is needed for a full interpretation.

In summary, we have explored two new NLO chromophores with combined conjugation bridges and found that they possess blue-shifted absorption and large molecular nonlinearities. Experimental results indicate that the combined conjugation bridge tunes the linear and nonlinear properties of the chromophores in a different style from those of common homologous chromophores. We expect this methodology to build up new molecular engineering, thereby providing a new opportunity for defeating the ‘nonlinearity-transparency trade-off’. Design and synthesis of further chromophores with different types of combined conjugation bridge, and a detailed investigation of the origin of this new effect are currently in progress.

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