Theoretical Study of Nonlinear Optical Properties of "Parallel Connection" Chromophores Containing Parallel Nonconjugated D-π-A units

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Chromophores containing two parallel nonconjugated D-π-A units are effective chromophores with high hyperpolarizability and good optical transparency. It provides a method for the design and synthesis of effective chromophores. The semiempirical method ZINDO was employed to study the relationship between enhancement of the static first hyperpolarizabilities (β_0) per D-π-A unit and the number of parallel nonconjugated D-π-A units in a chromophore. The results show that the chromophores containing two parallel nonconjugated D-π-A units would exhibit higher β_0 values than two times the β_0 value of the corresponding reference chromophore containing a D-π-A unit. The chromophore containing three parallel nonconjugated D-π-A units exhibits the highest enhancement of β_0 per D-π-A unit, which is 10.1 times the β_0 value of the corresponding reference chromophore. However, the β_0 value of the chromophore containing four parallel nonconjugated D-π-A units is very small, and the enhancement of β_0 value per D-π-A unit decreases sharply, from 10.1 to 0.3, with increasing the number of parallel D-π-A units in a chromophore from 3 to 4. It could give a useful suggestion for designing chromophores containing parallel nonconjugated D-π-A units.

Introduction

Organic and polymeric second-order nonlinear optical (NLO) materials have attracted much attention in the past two decades due to their potential applications in the fields of telecommunications, optical data storage, and optical information processing.[1] Generally, high performance electro-optic elements, especially those for frequency doubling applications, require both high nonlinearities and low optical loss (high transparency). The first hyperpolarizability β of a molecule increases with increasing length of the conjugated π system and increasing strength of the donor and/or acceptor based on the two-state model.[2] However, an increase in the β value is accompanied by a bathochromic shift due to a larger π-conjugated length and/or stronger donor and acceptor ability.[2] Therefore, there is always a trade-off between nonlinearity and transparency.[2−4] To resolve this problem, we had recently designed and synthesized a series of H-typed second-order nonlinear optical chromophores with two parallel and nonconjugated D-π-A units, in which a 9,10-dihydroanthracene was employed as molecular backbone (Scheme 1).[5,6]

The results of hyper-Rayleigh scattering (HRS) and UV−vis spectra show that the first molecular hyperpolarizability (β) values of H-typed chromophores are remarkably increased compared with the corresponding mono-D-π-A unit reference compounds (enhancement of static first hyperpolarizabilities (β_0) per D-π-A unit from 1.1 to 1.9 is observed), without causing a large shift of the absorption band to longer wavelength.[5−7] It suggests an available way of solving the trade-off between nonlinearity and transparency in designing NLO chromophores, i.e., design of chromophore with parallel and nonconjugated multi-D-π-A units.

The relationship between NLO properties and a π-conjugated length in a "series connection" chromophore is an interesting subject and has been investigated comprehensively in theoretical and experimental areas.[2a,8] Similarly, it would be very interesting that the relationship between the enhancements of β_0 per D-π-A unit and the number of parallel nonconjugated D-π-A units in a "parallel connection" chromophore would be investigated. *p*-Nitrophenol (*p*NP) usually is used as a reference chromophore for investigation and determination of NLO properties of chromophores.[9] Therefore, a series of chromophores with two or multiple parallel and nonconjugated *p*NP units was designed, and their static first hyperpolarizabilities (β_0) were given from quantum chemistry calculations for studying the relationship between the enhancements of β_0 per D-π-A unit and the number of parallel nonconjugated D-π-A units in a parallel connection chromophore (Scheme 2).

Results and Discussion

NLO Properties and Optical Transparency of H-Typed Chromophores Containing Two Parallel Nonconjugated D-π-A Units. Nonlinear optical properties of chromophores containing two parallel nonconjugated D-π-A units were determined via the HRS method.[10]

An external reference method (EFM) was utilized in these HRS experiments by choosing *p*-nitroaniline (*p*NA) as standard.[11] A popular two-level model could be used to estimate their static first hyperpolarizabilities (β_0) which reflect the intrinsic polarizations of the molecules at zero frequency. The two-level model could be expressed as eq 1[11]

$$\beta(\omega) = \frac{\lambda^4}{[(\lambda^2 - \lambda_{ge}^2)(\lambda^2 - 4\lambda_{ge}^2)]}\beta_0 \qquad (1)$$

where λ_{ge} is wavelength corresponding to the transition between the ground and the first excited state, which can be estimated

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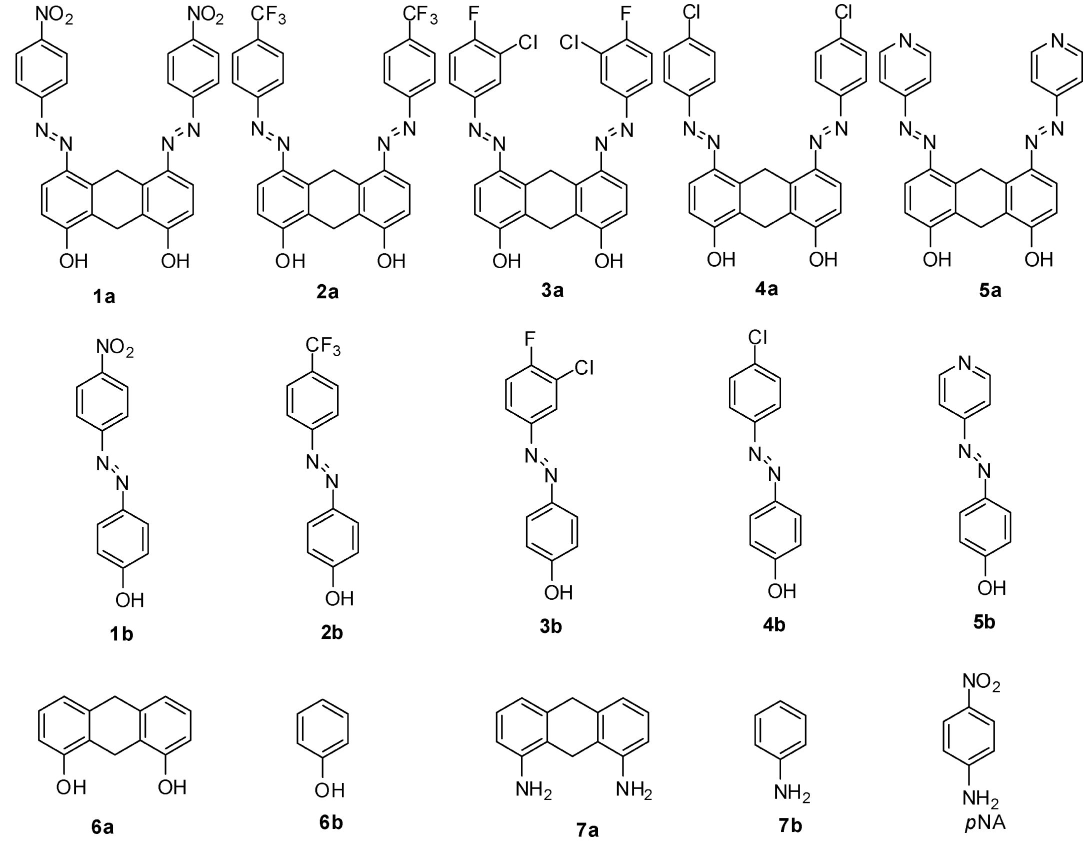
SCHEME 1: H-Typed Chromophores (1a−7a) with Two Parallel Nonconjugated Units and Their Corresponding Reference Compounds (1b−7b) and *p*NA



SCHEME 2: Structures of Parallel Connection Chromophores with Nonconjugated *p*NP Units

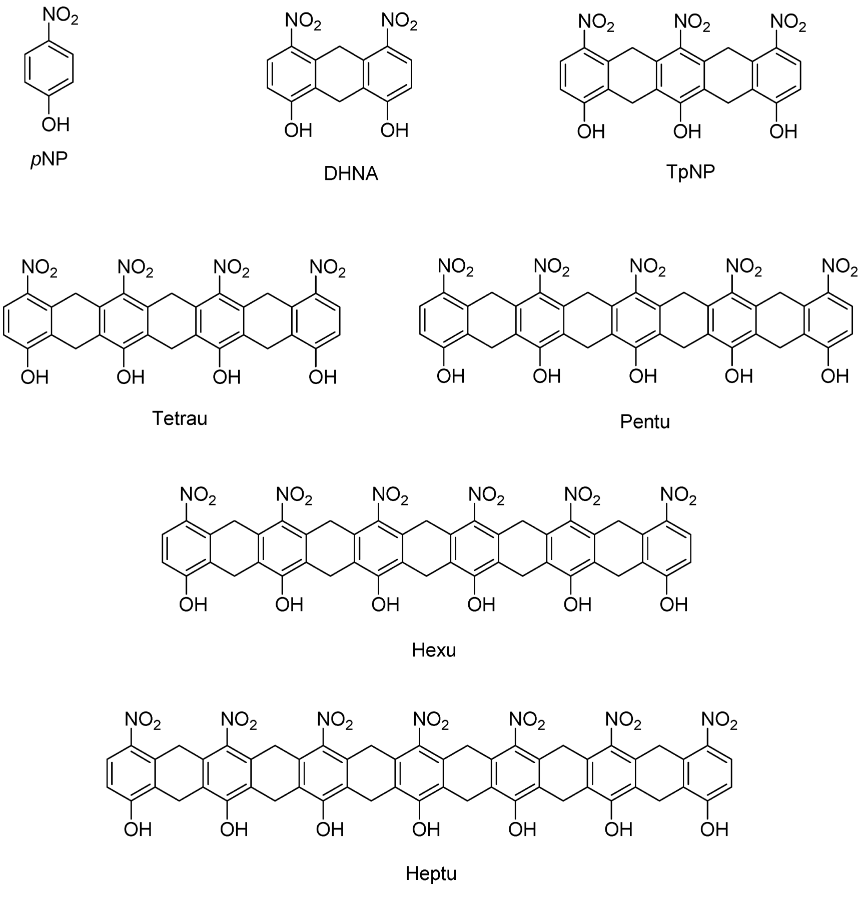


TABLE 1: Values of First Hyperpolarizabilities (β) and Static First Hyperpolarizabilities (β_0)

chromophore	λ_{max}[a] (nm) in THF	red shift[b] (nm) in THF	β[c] (10^{-30} esu)	β_0[d] (10^{-30} esu)	β_0 enhancement[e] per D-π-A unit
1a	398	10	277	105	1.9
1b	388		70	28	
2a	367	10	252	117	1.1
2b	357		108	52	
3a	365	10	185	86	1.2
3b	355		72	35	
4a	366	11	142	66	1.4
4b	355		50	24	
5a	383	21	227	96	1.3
5b	362		80	38	
6a	261	−14	85	40	
6b	275				
7a	289	−4	118	77	
7b	293				

[a] Maximal UV−vis absorption wavelengths (λ_{max}) of compounds were determined in tetrahydrofuran (THF). [b] Red shift of λ_{max} is a variation of λ_{max} in THF between H-typed chromophores **1a, 2a, 3a, 4a, 5a, 6a**, and **7a** and the corresponding monomer reference compounds **1b, 2b, 3b, 4b**, **5b**, **6b**, and **7b**. [c] Data of hyperpolarizabilities (β) were determined with concentration 10^{-4}−10^{-3} mol L^{-1} of compounds at a wavelength of 1064 nm in tetrahydrofuran medium by hyper-Rayleigh scattering (HRS). [d] Static first hyperpolarizabilities (β_0). [e] The values of static first hyperpolarizabilities (β_0) enhancement of each D-π-A unit were calculated according to the following method: (β_0 of H-typed chromophores **1a**, **2a**, **3a**, **4a**, **5a**)/(2 × β_0 of the corresponding monomer **1b, 2b, 3b, 4b, 5b**).

from the peak wavelength λ_{max} in the UV−visible absorption spectra; λ is the wavelength of incident light. β and β_0 values of the samples are shown in Table 1.

It can be seen that the static first hyperpolarizabilities (β_0) of the chromophores (**1a**−**5a**) with two nonconjugated D-π-A units are remarkably increased compared with the corresponding mono-D-π-A unit reference compounds (**1b**−**5b**). The enhancement of β_0 per D-π-A unit from 1.1 to 1.9 is observed. Di Bella et al.[12] reported a theoretical analysis of the NLO response for hypothetical *p*NA dimer based on a two-state model. According to their report, the NLO response would have a sharp increase, when two D-π-A units of a hypothetical *p*NA dimer are arranged in the same direction and the distance between them was shorter than 3.0 Å. In the present case, the two D-π-A units in a single molecule are nearly arranged in the same direction, and the limited distance (R) in the 9,10-dihydroanthracene moiety is 2.531 Å from the crystal structure data of **3a** or shorter than 3.0 Å from calculations of other H-typed chromophore compounds. It implies that these novel H-typed chromophores can exhibit large second-order NLO responses because the close contact between two π-conjugated units in a molecule induces the strong dipole−dipole interaction between two D-π-A units. It suggests that chromophores containing multiple parallel nonconjugated D-π-A units could be effective chromophores with high hyperpolarizability and good optical transparency.[5] It would suggest a method for design and synthesis of effective chromophores.

Theoretical Calculation for Studying NLO Properties of Parallel Connection Chromophores. In order to further study the NLO properties of chromophores containing multiple parallel nonconjugated D-π-A units, the NLO properties of these chromophores were also given based on theoretical calculations. The structure geometries of all chromophore compounds were optimized by the density functional theory (DFT) calculations using Gaussian03 software at the B3LYP/6-31G(d) level.[13,14] Then, the semiempirical method ZINDO was used to calculate their first hyperpolarizabilities.[15]

$$\beta^{\text{two-state}} = \underset{\text{static factor}}{\frac{3\mu_{eg}^2\Delta\mu_{eg}}{E_{eg}^2}} \times \underset{\text{dispersion factor}}{\frac{\omega_{eg}^2}{(1-4\omega^2/\omega_{eg}^2)(\omega_{eg}^2-\omega^2)}} \qquad (2)$$

where μ_{eg} is the transition dipole moment between the ground state $|g\rangle$ and the charge-transfer excited state $|e\rangle$, $\Delta\mu_{eg}$ is the difference in dipole moment, and E_{eg} is the transition energy.

The time-dependent Hatree−Fork (TDHF)[16] is also used to calculate their first hyperpolarizabilities with the semiempirical methods AM1, PM3, and MNDO, respectively. The TDHF calculations were performed using the Gamess program.[17] The determined and calculated values of these chromophores are shown in Table 2.

In a HRS experiment,[15] one measures average $\langle\beta^2\rangle$ for any molecule, where

$$\langle\beta_{HRS}^2\rangle = \langle\beta_{ZZZ}^2\rangle + \langle\beta_{XZZ}^2\rangle \qquad (3)$$

For a molecule of C_{2v} symmetry, $\langle\beta_{zzz}^2\rangle$ and $\langle\beta_{xzz}^2\rangle$ can be given by

$$\langle\beta_{zzz}^2\rangle = \frac{1}{7}\beta_{333}^2 + \frac{6}{35}\beta_{333}\beta_{322} + \frac{9}{35}\beta_{322}^2 \qquad (4)$$

$$\langle\beta_{xzz}^2\rangle = \frac{1}{35}\beta_{333}^2 - \frac{2}{105}\beta_{333}\beta_{322} + \frac{11}{105}\beta_{322}^2 \qquad (5)$$

The letter indices refer to the laboratory frame and the number indices to the molecular frame.

All H-shaped chromophores (**1a**−**7a**) are assumed to have C_{2v} symmetry.[15k] For simplicity, we have assumed that the tensor components in the plane of the molecule (such as **1b**−**7b** and *p*NA) are dominant and that Kleinman symmetry is valid.[15j] The depolarization ratio is defined as

$$\rho = \frac{\langle\beta_{zzz}^2\rangle}{\langle\beta_{xzz}^2\rangle} \qquad (6)$$

Therefore, the following eq 7 would be deduced.

$$\langle\beta_{HRS}^2\rangle = \left(1 + \frac{1}{\rho}\right)\langle\beta_{ZZZ}^2\rangle \qquad (7)$$

Actually, β_{333} is only one dominating tensor component ($\beta_{333} \gg \beta_{322}$). Therefore, enhancement values of β_0 per D-π-A unit in H-shaped chromophores (compared with β_0 of reference chromophores) that were given from calculation would be close to the enhancement values that were given from HRS.

Table 2 shows that enhancement of β_0 per D-π-A unit in H-shaped chromophores which are given from these methods, AM1, MNDO, and PM3, are quite different from experimental values. The reason could be that the interaction between two D-π-A units is ignored when the first hyperpolarizabilities are given from the semiempirical methods AM1, PM3, and MNDO. Therefore, these methods would be unsuitable for studying the

TABLE 2: Nonlinear Optical Properties of H-Typed Chromophores and Their Corresponding Reference Chromophores

	calculation values (β_{vec} (10^{-30} esu) and enhancement per D-π-A unit)								experimental values	
no.	AM1	E^a	MNDO	E^a	PM3	E^a	ZINDO	E^a	β_0 (10^{-30} esu)	E^a
1a	184	0.7	201	0.7	175	0.7	190	4.2	105	1.9
1b	128		138		119		23		28	
2a							165	1.2	117	1.1
2b							70		52	
3a	60	0.8	82	1.0	62	0.8	20	4.0	86	1.2
3b	39		41		41		3		35	
4a	49	0.7	62	0.7	23	0.7	116	40.3	66	1.4
4b	33		44		17		1.4		24	
5a	89	0.7	96	0.7	90	0.8	146	1.2	96	1.3
5b	61		65		60		59		38	
6a							37	1.3	40	
6b							14			
7a							60	1.7	77	
7b							18			
pNA	33		36		38		16		21	

[a] Enhancement of β_{vec} or β_0 per D-π-A unit.

effects of the number of parallel D-π-A units in a chromophore on the NLO properties. The semiempirical method ZINDO would be a suitable method for calculating the enhancements per D-π-A unit when electronic acceptors are strong electron-withdrawing groups, such as NO_2, CF_3, etc. The computational values of enhancement per D-π-A unit are close to the experimental values when electron-withdrawing groups are strong ones due to the interaction between two D-π-A units being taken into account, when the ZINDO method is used for calculating the first hyperpolarizabilities. Therefore, the semiempirical method ZINDO should be employed to study the effect of the number of parallel D-π-A units in a chromophore on its NLO properties when the strong electron-withdrawing group NO_2 is employed as an electronic acceptor. NLO properties of H-typed chromophores, their reference chromophores, and the designed parallel connection chromophores that are calculated by the ZINDO method are shown in Table 3.

β_0 values that are given from the two-state model (eq 2) depend on the differences of energy between the ground and the first excited states (E_{eg}), the transition dipole moment between the ground state $|g\rangle$ and the charge-transfer excited state $|e\rangle$ (μ_{eg}), and the difference in dipole moment ($\Delta\mu_{eg}$). Table 3 clearly shows that all chromophores containing two parallel nonconjugated D-π-A units would exhibit higher β_0 values than two times the β_0 value of the corresponding reference chromophore containing a D-π-A unit. These results given by the ZINDO method are in agreement with the experimental results. The chromophore T*p*NP containing 3 *p*NP units exhibits the highest value of β_0 enhancement per *p*NP unit, which is 10.1 times the β_0 value of *p*NP. However, the β_0 value of Tetrau is very small, and its enhancement of β_0 per *p*NP unit is 0.3 times the β_0 value of *p*NP. Enhancements of β_0 value per *p*NP unit in Pentu, Hexu, and Heptu are 2.2, 2.4, and 1.6 times the β_0 value of *p*NP, respectively.

The time-dependent density functional theory (TDDFF)[15] and the semiempirical method AM1 are also used to calculate their first hyperpolarizabilities of *p*NP, DHNA, T*p*NP, Tetrau, Pentu, Hexu, and Heptu, respectively. The calculated values of these chromophores are shown in Table 4.

TABLE 3: Effects of the Number of Parallel D-π-A Units in a Chromophore on the NLO Properties[a]

no.	$\Delta\mu_{eg}$ (D)	μ_{eg} (D)	λ_{max} (nm)	E_{eg} (ev)	$\beta_0^{\text{two-state}}$ (10^{-30} esu)	enhancement
1a	13.54	13.39	368.00	3.37	190.4	4.2
1b	−2.02	10.10	378.70	3.27	−22.5	
2a	11.29	11.63	376.89	3.29	165.1	1.2
2b	8.81	9.10	355.22	3.49	69.9	
3a	5.89	5.89	355.46	3.49	19.7	3.8
3b	2.66	3.16	357.26	3.47	2.6	
4a	10.56	10.56	359.61	3.45	115.8	40.3
4b	0.84	4.92	333.91	4.92	1.4	
5a	11.69	11.69	345.98	3.58	145.5	1.2
5b	8.46	8.73	345.99	3.58	58.6	
6a	7.36	11.75	205.05	5.64	37.3	1.3
6b	6.34	8.46	220.56	6.10	14.2	
7a	11.65	11.77	203.32	5.62	59.7	1.7
7b	7.94	8.32	219.77	6.05	17.6	
*p*NA	7.04	8.38	203.73	6.09	16.0	
*p*NP	3.05	4.49	206.12	6.02	2.4	
DHNA	−5.93	6.01	322.99	3.84	−17.1	3.6
T*p*NP	9.70	9.74	322.24	3.85	73.0	10.1
Tetrau	2.67	3.69	321.73	3.85	2.9	0.3
Pentu	6.83	6.94	321.18	3.86	25.8	2.2
Hexu	7.55	7.56	320.99	3.86	33.9	2.4
Heptu	6.87	7.12	320.38	3.87	27.2	1.6

[a] *p*NA, *p*-nitroanline; *p*NP, *p*-nitrophenol; DHNA; 1,8-dihydroxy-4,5-dinitro-9,10-dihydroanthracene; T*p*NP, the parallel connection chromophore with 3 parallel *p*NP units connected by 4 methylene; Tetrau, the parallel connection chromophore with 4 parallel *p*NP units connected by 6 methylene; Pentu, the parallel connection chromophore with 5 parallel *p*NP units connected by 8 methylene; Hexu, the parallel connection chromophore with 6 parallel *p*NP units connected by 10 methylene; Heptu, the parallel connection chromophore with 7 parallel *p*NP units connected by 12 methylene.

In Table 4, the calculated values given by ZINDO show clearly that T*p*NP exhibits the largest enhancement values of β and β_0 per *p*NP unit. The β value per *p*NP unit in T*p*NP is 14.6 times the β value of *p*NP, and the β_0 value per *p*NP unit in T*p*NP is 10.1 times the β_0 value of *p*NP. However, both β_0 (2.9×10^{-30} esu) and β (5.0×10^{-30} esu) of Tetrau are very small. β_0 and β per *p*NP are 0.3 and 0.4 times that of *p*NP, respectively. β_0 and β values of Pentu ($\beta_0 = 25.8 \times 10^{-30}$ esu, $\beta = 44.7 \times 10^{-30}$ esu), Hexu ($\beta_0 = 33.9 \times 10^{-30}$ esu, $\beta = 58.6 \times 10^{-30}$ esu), and Heptu ($\beta_0 = 27.2 \times 10^{-30}$ esu, $\beta = 46.9 \times 10^{-30}$ esu) are smaller than that of T*p*NP ($\beta_0 = 73.0 \times 10^{-30}$ esu, $\beta = 126.9 \times 10^{-30}$ esu). β_0 and β enhancement values of Pentu, Hexu, and Heptu are 2.2, 2.4 and 1.6, and 3.1, 3.4 and 2.3, respectively.

The calculated values given by TDDFT show that T*p*NP has the largest β_0 value and the highest β_0 enhancement per *p*NP unit among the seven chromopores. The calculated values given by AM1 show that T*p*NP has the highest enhancement value of β_0 per *p*NP unit among the seven chromopores. It suggests

TABLE 4: First Hyperpolarizabilities and Their Enhancement Compared with *p*NP

	AM1			TDDFT			ZINDO					
no.	β_0[a] (10^{-30} esu)	E[b]	E[c] per unit	β_0 (10^{-30} esu)	E	E per unit	β_0 (10^{-30} esu)	E	E per unit	β[d] (10^{-30} esu)	E	E per unit
*p*NP	0.5	1.0	1.0	0.5	1.0	1.0	2.4	1.0	1.0	2.9	1.0	1.0
DHNA	8.8	19.2	9.6	1.2	2.4	1.2	17.1	7.1	3.6	29.8	10.3	5.1
T*p*NP	10.7	23.3	7.8	6.9	13.8	4.6	73.0	30.4	10.1	126.9	43.8	14.6
Tetrau	12.2	26.5	6.6	2.0	4.0	1.0	2.9	1.2	0.3	5.0	1.7	0.4
Pentu	12.8	27.9	5.6	−0.7	1.4	0.3	25.8	10.8	2.2	44.7	15.4	3.1
Hexu	14.9	32.3	5.4	1.9	3.8	0.6	33.9	14.1	2.4	58.6	20.2	3.4
Heptu	16.5	35.8	5.1	1.4	2.8	0.4	27.2	11.3	1.6	46.9	16.2	2.3

[a] Static first hyperpolarizability. [b] Enhancement values of first hyperpolarizability compared with *p*NP were calculated according to the following methods: (β_0 (or β) of chromophore containing *p*NP units)/(β_0 (or β) of *p*NP). [c] Enhancements of first hyperpolarizability per *p*NP unit compared with *p*NP were calculated according to the following methods: (β_0 (or β) of chromophore containing *p*NP units)/(β_0 (or β) of *p*NP × number of *p*NP units). [d] Dynamic first hyperpolarizability given from ZINDO (the wavelength of incident light is 1064 nm).

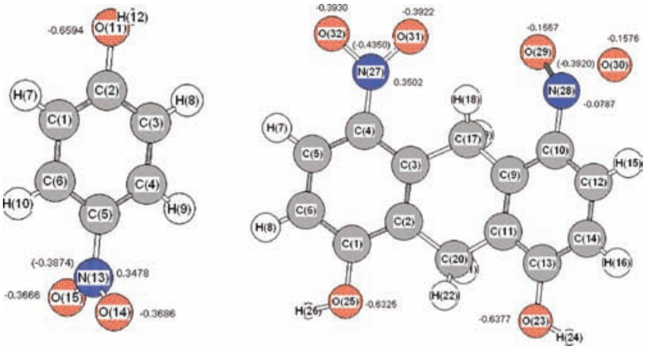


Figure 1. Structures of *p*NP and DHNA optimized by DFT and atomic charges (unit: atomic unit) of N, O atoms (the numbers in brackets are charges of nitro groups).

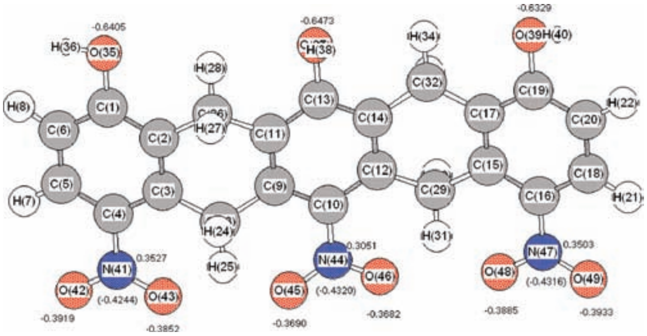


Figure 2. Structures of T*p*NP optimized by DFT and atomic charges (unit: atomic unit) of N, O atoms (the numbers in brackets are charges of nitro groups).

that design of chromophores containing two or three parallel nonconjugated D-π-A units would be an effective strategy in designing NLO chromophores.

Figure 1 shows clearly that nitro group and benzene ring in *p*NP are noncoplanar. However, two benzene rings and their respective substituted nitro group are close to coplanar in a 1,8-dihydroxy-4,5-dinitro-9,10-dihydroanthracene (DHNA) molecule due to hydrogen bonds between atoms H and atoms O. Therefore, π electrons would be better delocalized in the whole *p*NP unit so that the *p*NP unit would exhibit higher first hyperpolarizability than a *p*NP molecule. Another reason is that the first molecular hyperpolarizability of DHNA, as an H-typed chromophore, is higher than the sum of the two independent D-π-A units.[5] This is because the NLO response would have a sharp increase, when two *p*NP units are arranged in the same direction and the distance between them is shorter than 3.0 Å. In the present case, the two *p*NP units in a single molecule are nearly arranged at the same direction, and the limited distance in the 9,10-dihydroanthracene moiety is 2.518 Å (C2−C11) from calculations of DHNA. It implies that the DHMA can exhibit large second-order NLO responses because the close contact between two π-conjugated units in a molecule induces the strong dipole−dipole interaction between two *p*NP units. Generally, a HOMO energy level and a LUMO energy level depend on the electron-donating strength of donor and the electron-withdrawing strength of acceptor, respectively.[18] From the structure of DHNA, the transition from ground to excited state would result in increasing the charge of a nitro group containing atoms N27, O31, and O32. The charge of another nitro group containing atoms N28, O29, and O30 would decrease due to electrostatic repulsion between O31 and O29 atoms when the π electron is excited. The electrostatic repulsion would result in the benzene ring and their respective substituted nitro group containing atoms N28, O29, and O30 being noncoplanar in a *p*NP unit and further reducing the dipole at the excited state. Therefore, the $\Delta\mu_{eg}$ value of DHNA is a negative value. According to the two-state model,[15] values of μ_{eg}^2 and E_{eg}^2 are positive. The $\Delta\mu_{eg}$ value being a negative value would result in the β value of DHNA being negative.

Similarly, Figure 2 shows clearly that all three benzene rings and their respective substituted nitro groups are coplanar as well in a TpNP molecule due to hydrogen bonds between atoms H and atoms O. Therefore, π electrons would be better delocalized in the whole *p*NP unit so that static first hyperpolarizability of the *p*NP unit in T*p*NP would be much larger than that of a *p*NP molecule. Another reason is that the first molecular hyperpolarizability value of T*p*NP is higher than that of the sum of the three independent *p*NP units. Based on a two-state model, Di Bella et al.[12] estimated that the NLO response of hypothetical *p*NA (*p*-nitroaniline) trimer would have a sharp increase, when three *p*NA molecules were arranged in the same direction and the distance between two adjacent *p*NA molecules was shorter than 3.0 Å. The NLO response of the trimer would be higher than that of the sum of the three independent *p*NA molecules when the distance between two adjacent *p*NA units is shorter than 2.7 nm. In the present case, the three *p*NP units in a single molecule are nearly arranged in the same direction and the limited distances between two adjacent *p*NP units are 2.5394 Å (C2−C11) and 2.5214 Å (C14−C17), respectively, from calculations of T*p*NP. Therefore, it implies that the T*p*NP can exhibit large second-order NLO responses because close contact among three π-conjugated units in a molecule induces the strong dipole−dipole interaction among three *p*NP units.

From the structure of T*p*NP, the probability of transition from ground to excited state in the *p*NP unit containing atom O39 would be the biggest due to stability of the excited state in spite of the charge of the nitro group containing atoms N44, O45, and O46 being a little lower than the charge of nitro group

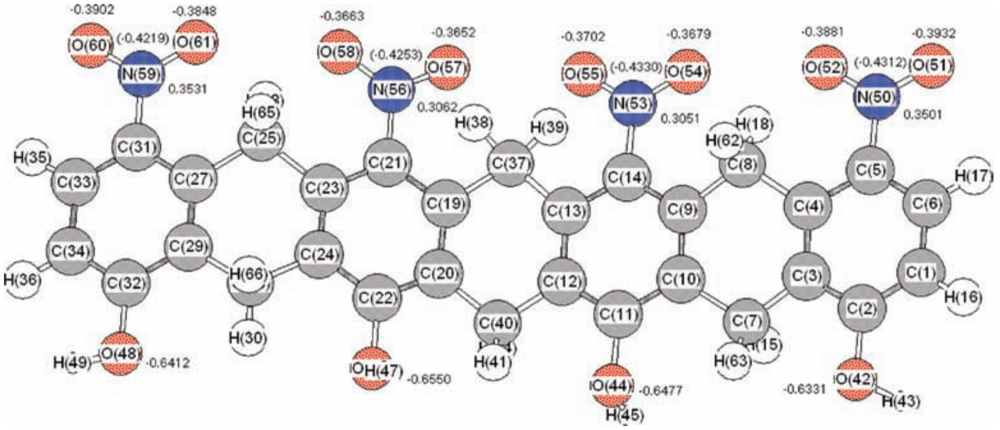


Figure 3. Structures of Tetrau optimized by DFT and atomic charges (unit: atomic unit) of N, O atoms (the numbers in brackets are charges of nitro groups).

containing atoms N47, O48, and O49. Because electrostatic repulsions between O46 and O48 atoms and between O43 and O45 atoms would increase if transition from ground to excited state in the *p*NP unit containing atom O38 took place, the excited state structure would be less stable. The transition from ground to excited state would result in an increase in the charge of a nitro group containing atoms N47, O48, and O49. As a result, the charge of a nitro group containing atoms N44, O45, and O46 would decrease due to electrostatic repulsion between O46 and O48 atoms when the π electron is excited. The electrostatic repulsion would further result in the benzene ring and its respective substituted nitro group containing atoms N44, O45, and O46 being noncoplanar in a *p*NP unit and further reducing the dipole at the excited state. However, the charge of a nitro group containing atoms N41, O42, and O43 would increase due to decreasing electrostatic repulsion between O43 and O45 atoms when the π electron was excited. The decreasing electrostatic repulsion would enhance coplanarity of the *p*NP unit containing atom O35. Therefore, increases of excited dipoles of two *p*NP units and decrease of an excited dipole of *p*NP unit would induce increase of the $\Delta\mu_{eg}$ value of T*p*NP.

Similarly, Figure 3 shows clearly that all four benzene rings and their respective substituted nitro groups are also close to coplanar in a Tetrau molecule due to hydrogen bonds between H atoms and O atoms. Therefore, π electrons would be better delocalized in the whole *p*NP unit so that the *p*NP unit would exhibit much higher first hyperpolarizability than a *p*NP molecule. However, the first molecular hyperpolarizability values of Tetrau would depend on the interactions among four π-conjugated units in a molecule, which induces the strong dipole−dipole interaction among four *p*NP units, rather than a sum of four *p*NP units. Here the local field corrections due to interactions among four *p*NP units begin to play a large role in determining the first molecular hyperpolarizability.[19]

In the present case, the four *p*NP units in a single molecule are nearly arranged in the same direction, and the limited distances between two adjacent *p*NP units are 2.5204 Å (C3−C10), 2.5389 Å (C12−C20), and 2.5369 Å (C24−C29), respectively, from calculations of Tetrau. From the structure of Tetrau, the probability of transition from ground to excited state in the *p*NP unit containing atom O44 would be the biggest. The transition from ground to excited state would result in increasing the charge of a nitro group containing atoms N53, O54, and O55. The charges of two nitro groups containing atoms N50, O51, and O52, and containing atoms N56, O57, and O58 would decrease due to electrostatic repulsion between O52 and O54 atoms and electrostatic repulsion between O55 and O57 atoms when π electrons were excited. The electrostatic repulsion would result in the benzene rings and their respective substituted nitro groups being noncoplanar in a *p*NP unit and further reducing the dipole at the excited state. However, the charge of a nitro group containing atoms N59, O60, and O61 would increase due to decreasing electrostatic repulsion between O58 and O61 atoms when the π electron is excited. The decreasing electrostatic repulsion would enhance coplanarity of the *p*NP unit containing O48 atom. Therefore, increases of excited dipoles of two *p*NP units and decreases of two excited dipoles of *p*NP units would induce a slight increase of the $\Delta\mu_{eg}$ value of Tetrau. Therefore, Tetrau would exhibit a small enhancement value of static first hyperpolarizability per *p*NP unit. Ray et al.[15] reported a theoretical analysis of the NLO response for J-type aggregates of merocyanines. According to their investigation, the increment of the first hyperpolarizability of the J-type aggregate is due to two factors, and those are (1) the red shift of the absorption maxima and (2) the increase of $\Delta\mu_{eg}$ values. In the present case, the $\Delta\mu_{eg}$ value of Tetrau is smaller than that of T*p*NP and close to that of *p*NP. The λ_{max} value of Tetrau is longer than that of *p*NP and close to that of T*p*NP. Therefore, the first hyperpolarizability of Tetrau is slightly larger than that of *p*NP and smaller than that of T*p*NP.

Similarly, Figure 4 shows clearly that all benzene rings and their respective substituted nitro groups are also close to coplanar in Pentu, Hexu, and Heptu due to hydrogen bonds between H atoms and O atoms. Therefore, π electrons would be delocalized well in the whole *p*NP unit so that the *p*NP unit in Pentu, Hexu, and Heptu would exhibit much higher first hyperpolarizability than a *p*NP molecule. However, the first molecular hyperpolarizability values of Pentu, Hexu, and Heptu would depend on interactions among *p*NP units in a chromophore. Here the local field corrections due to interactions among *p*NP units begin to play a large role in determining the first molecular hyperpolarizability.[19]

From the structure of Pentu, the probability of transition from ground to excited state in the *p*NP unit containing atom O78 would be biggest. The transition from ground to excited state would induce increase of excited dipoles of three *p*NP units and decrease of two excited dipole of *p*NP units, which would result in an increase of the $\Delta\mu_{eg}$ value of Pentu. Therefore, Pentu would exhibit a large β_0 value compared with that of *p*NP. Similarly, Hexu and Heptu would also exhibit a large β_0 value compared with that of *p*NP.

Figure 5 shows clearly that from calculated results by ZINDO, enhancement of β (and β_0) values increases sharply from 1.0 to 43.8 (and from 1.0 to 30.4) with increasing the number of

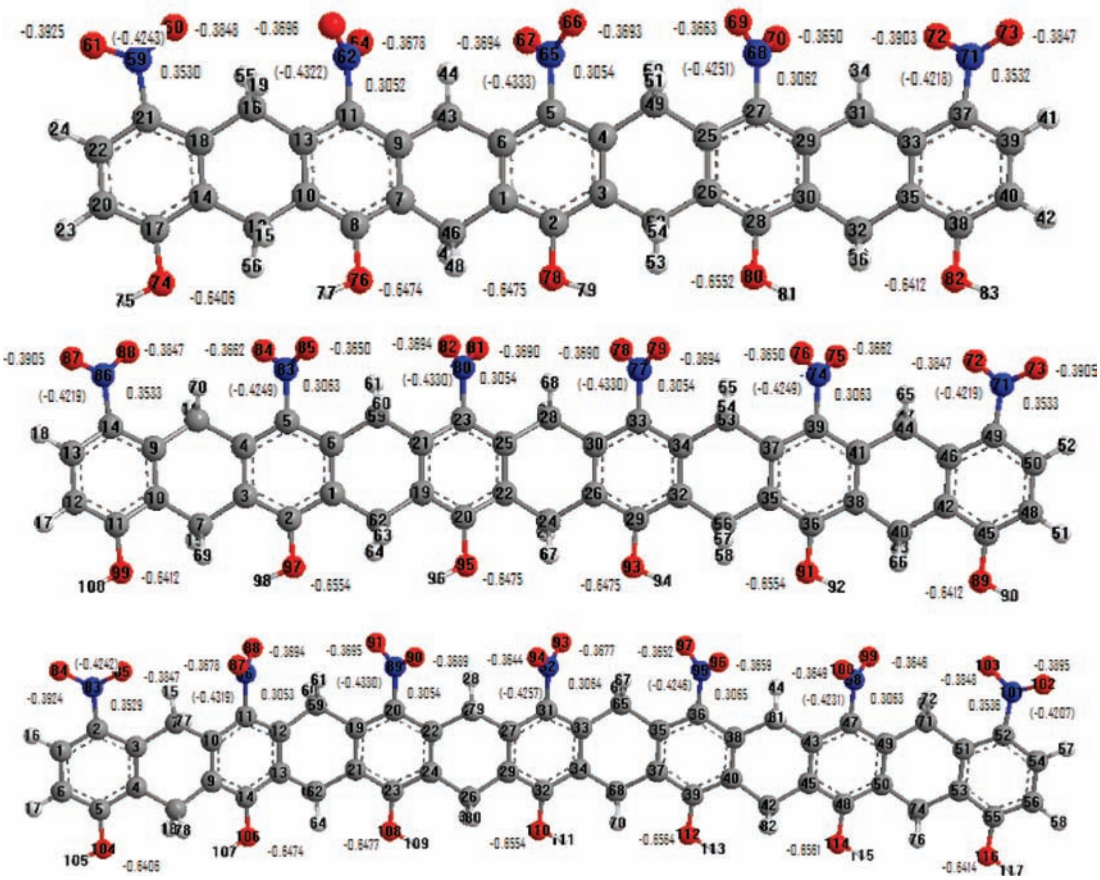


Figure 4. Structures of Pentu, Hexu, and Heptu optimized by DFT and atomic charges (unit: atomic unit) of N, O atoms (the numbers in brackets are charges of nitro groups).

parallel and nonconjugated *p*NP units in a chromophore from 1 to 3. Then the enhancement of β (and β_0) values decreases rapidly from 43.8 to 1.7 (from 30.4 to 1.2), with increasing the number of *p*NP units in a chromophore from 3 to 4. At last, the enhancement of β (and β_0) changes slightly (which lie in the range 20.2−15.4 (and 14.1−10.8)) with increasing *p*NP units in a chromophore from 5 to 7. The enhancements of β (and β_0) per *p*NP unit increase sharply from 1.0 to 14.6 (and from 1 to 10.1), with increasing the number of *p*NP units in a chromophore from 1 to 3. However, the β and β_0 values of Tetrau are very small and the enhancement of β (and β_0) values decreases sharply, from 14.6 to 0.4 (and from 10.1 to 0.3), with increasing the number of *p*NP units in a chromophore from 3 to 4. Lastly, the enhancement of β (and the β_0) per *p*NP unit changes slightly (which lie in the range 3.4−2.3 (and 2.4−1.6)), with increasing *p*NP units in a chromophore from 5 to 7. Calculated results by AM1 and TDDFT give similar graphs of β_0 enhancement and β_0 enhancement per *p*NP unit. It suggests that design of chromophores containing two or three parallel nonconjugated D-π-A units would be an effective strategy for increasing the first molecular hyperpolarizability in designing NLO chromophores. This paper could give a suggestion for designing effective chromophores containing parallel nonconjugated D-π-A units.

Conclusion

The semiempirical method ZINDO was employed to study the relationship between enhancements of static first hyperpolarizabilities (β_0) per D-π-A unit and the number of parallel nonconjugated D-π-A units in a chromophore. The results show that the chromophores DHNA containing two parallel nonconjugated D-π-A units would exhibit higher β_0 values than two times the β_0 value of the corresponding reference chromophore containing a D-π-A unit. The chromophore T*p*NP containing 3 parallel nonconjugated *p*NP units exhibits the highest enhancement of β_0 per *p*NP unit, which is 10.1 times that of *p*NP. The computational results show that the enhancements of β_0 per *p*NP unit increases sharply from 1 to 10.1 (the enhancement of β_0 per *p*NP unit of DHNA is 3.6.), with increasing the number of *p*NP units in a chromophore from 1 to 3. However, the β_0 value of the chromophore Tetrau containing 4 *p*NP units is very small, and the enhancement of β_0 per *p*NP unit decreases sharply, from 10.1 to 0.3, with increasing the number of *p*NP units in a chromophore from 3 to 4. The β_0 enhancement per *p*NP unit changes slightly (which lies in the range 2.4−1.6), with increasing *p*NP units in a chromophore from 5 to 7. It suggests that design of chromophores containing two or three parallel nonconjugated D-π-A units would be an effective strategy in designing NLO chromophores with large first molecular hyperpolarizabilities and good transparency. Designed chromophores with more than three parallel nonconjugated D-π-A units could not exhibit good second-order optical properties.

Computational Details

The transition energy E_{eg} is calculated from λ_{max}, which is given according to the following equation[15a]

$$\lambda_{max} = \frac{\lambda_1 f_1 + \lambda_2 f_2}{(f_1 + f_2)} \tag{8}$$

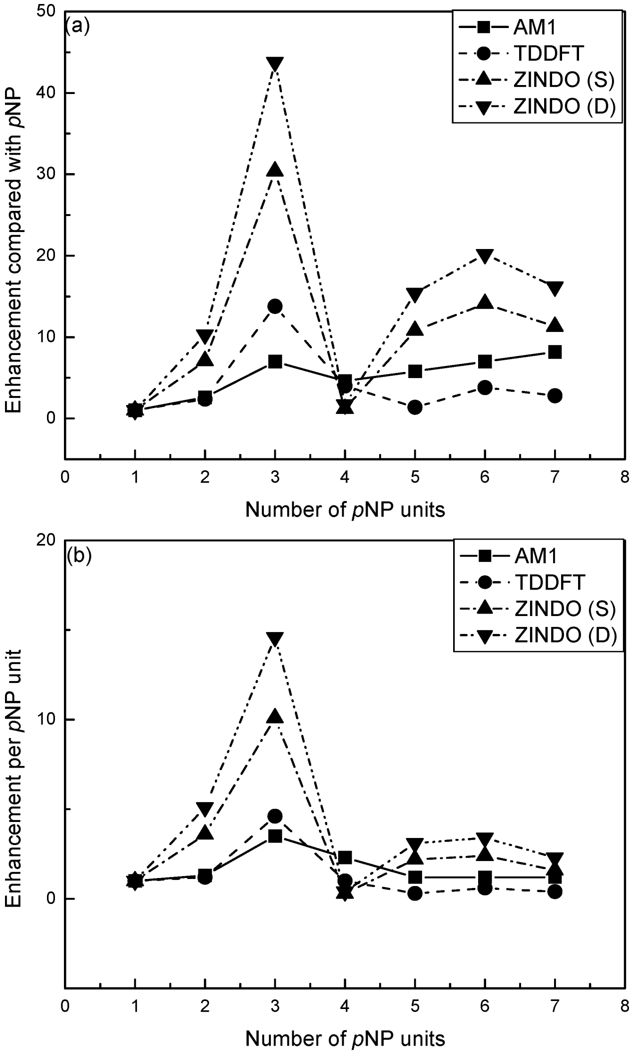


Figure 5. Relationship between enhancement of first hyperpolarizability and the number of *p*NP units in a chromophore: (a) enhancement of first hyperpolarizability versus the number of *p*NP units in a chromophore; (b) enhancement of first hyperpolarizability per *p*NP unit versus the number of *p*NP units in a chromophore.

TABLE 5: Calculations of λ_{max}, E_{eg}, and f

no.	λ_1 (nm)	f_1	λ_2 (nm)	f_2	λ_{max} (nm)	f	E_{eg} (ev)
6a	225.71	1.47	215.55	1.51	220.56	2.98	5.62
6b	204.75	0.85	205.39	0.76	205.05	1.61	6.05
7a	214.06	1.55	226.07	1.40	219.77	2.95	5.64
7b	203.99	0.79	202.71	0.88	203.32	1.67	6.10
*p*NA	203.99	0.73	203.43	0.62	203.73	1.36	6.09
*p*NP	204.97	0.88	207.45	0.76	206.12	1.63	6.02
T*p*NP	322.52	0.46	321.48	0.17	322.24	0.64	3.85
Tetrau	321.64	0.36	321.12	0.27	321.80	0.72	3.85
	$\lambda_3 = 324.24$ nm		$f_3 = 0.10$				

where λ_1 and λ_2 are wavelengths of the two maxima and f_1 and f_2 are the corresponding oscillator strengths.

Table 5 shows that the difference between the two calculated maxima wavelengths is so small that they overlap, so a weighting average should be defined to reflect the absorption maximum wavelength as in eq 8. The transition energy E_{eg} is further acquired.

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