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Synthesis and Nonlinear Optical Properties of 1,3,5-Methoxy-2,4,6-tris(styryl)benzene Derivatives[†]

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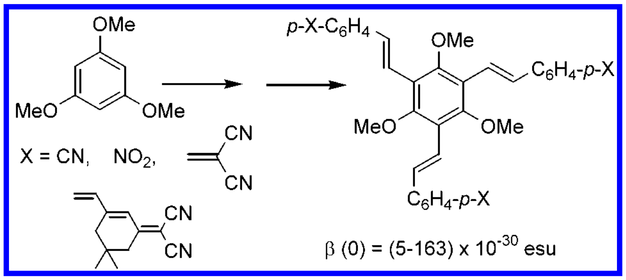
ABSTRACT



Novel two-dimensional octupoles containing donors at the core and acceptors at the edge of peripheral groups were synthesized by Horner–Wittig reactions. These chromophores show very large first hyperpolarizability and good thermal stability and are attractive candidates for nonlinear optical materials.

There is much research effort to develop octupolar nonlinear optical (NLO) molecules for possible applications in optical and optoelectronic devices.[1,2] An advantage of such molecules in comparison to the more conventional dipolar NLO molecules is that the second harmonic response of octupoles does not depend on the polarization of the incident light because they are more isotropic than the dipolar NLO molecules.[1d] We are particularly interested in the two-dimensional octupoles because there exists a design strategy for such molecules with large β values.[3] Theoretical studies predicted and experimental results confirmed that the first hyperpolarizability of the two-dimensional octupoles such as crystal violet, subphthalocyanine, 1,3,5-tricyano-2,4,6-tris(ethynyl)benzene, triphenylamine, 1,3,5-tricyano-2,4,6-tris(styryl)benzene, and 1,3,5-tris[(*p*-styryl)phenyl]benzene derivatives increases with the extent of charge transfer.[2,3]

[†] This paper is dedicated to Prof. Jung-Il Jin of Korea University, Seoul, Korea, on the occasion of his 60th birthday.

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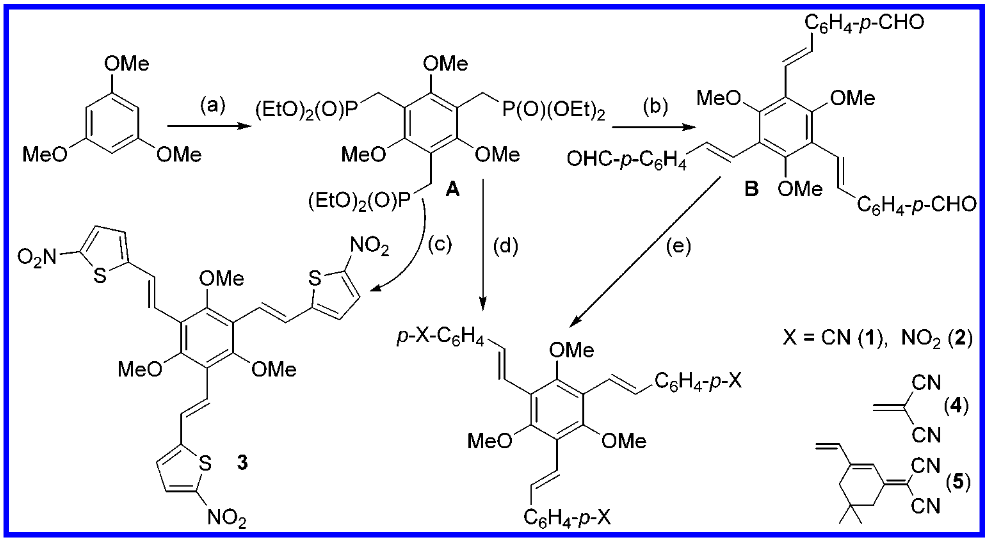
Scheme 1[a]



[a] Reagents and condition: (a) (i) HCHO/HBr/AcOH, 60−70 °C, 3 h; (ii) $P(OEt)_3$, 120 °C, 3 h, 80%. (b) (i) LDA/THF, 0 °C, 1 h; (ii) p-CNC_6H_4CHO, 12 h, rt; (iii) DIBAL-H/THF, −40 °C, 3 h, 65%. (c) (i) LDA/THF, 0 °C, 1 h, (ii) 4-O_2N-thiophene-2-CHO, 12 h, rt, 34 %. (d) (i) LDA/THF, 0 °C, 1 h; (ii) p-$O_2NC_6H_4CHO$, 12 h, rt, 30%; (e) H_2A/DMF, 80 °C, 2−3 h, 68−80%.

Hence, to obtain octupoles with a maximum β value, one should simultaneously increase the π orbital energy, conjugation length, and donor−acceptor strength. For practical application of the NLO molecules, they must be arranged noncentrosymmetrically in the solid state to exhibit significant second harmonic generation (SHG). In case of dipolar molecules, noncentrosymmetric alignment of the chromophores is usually achieved by electrical poling.[4] Although there has been a major breakthrough in the development of electro-optic modulators by using this approach, the very high voltage required for the electric poling has been a serious problem in device fabrication.[4b] In addition, because the dipoles favor antiparallel pairing, there is a relaxation problem.[4a] An ideal solution to these problems would be spontaneous formation of noncentrosymmetric NLO materials that do not undergo relaxation. Two-dimensional octupoles are of particular interest in this respect. It was predicted that the octupolar molecules may favor the formation of noncentrosymmetric crystals as a result of the lack of ground-state dipole moment.[2b,g] The prediction was experimentally confirmed in a few cases, where the octupoles have been shown to assemble noncentrosymmetric crystals and exhibit significant second harmonic generation (SHG).[2b,i,j] Moreover, the octupolar crystals and thin films could find useful applications as SHG and optical waveguide materials if the molecules are arranged noncentrosymmetrically in the bulk state. Therefore, it is worthwhile to develop octupolar molecules for NLO applications.

The first step in obtaining efficient organic NLO materials is to synthesize molecules with high nonresonant molecular hyperpolarizabilities. We have previously reported the synthesis and NLO properties of 1,3,5-trinitro- and 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives.[2i,j] The maximum β value was obtained from 1,3,5-tricyano-2,4,6-tris(p-diphenylaminostyryl)benzene having the donor−acceptor pair at the edges of 1,4-bis(styryl)benzene moieties. To further enhance β values, it is essential to use stronger donor−acceptor pairs, while maintaining the conjugation bridge to the optimum length. However, change of the acceptors to other than a nitro or cyano group at the core is difficult for synthetic reasons. Also, a bulky acceptor is expected to cause a steric hindrance, which would in turn distort the planarity to decrease β.[2i] In this work, we have synthesized a series of 1,3,5-trimethoxy-2,4,6-tris(styryl)benzene derivatives, in which the donors are attached to the central phenyl group and the acceptors are varied (Scheme 1). A variety of strong acceptors have now been introduced at the peripheral phenyl groups. We have determined the first hyperpolarizability and thermal stability of these octupoles. The structure−property relationship is established.

Synthesis of the octupoles (**1**−**5**) is shown in Scheme 1. 1,3,5-Trimethoxy-2,4,6-tris[(diethoxyphosphoryl)methyl]-benzene (**A**) was synthesized by the bromomethylation of 1,3,5-trimethoxybenzene followed by the phosphorylation with $P(OEt)_3$. Horner−Wittig reactions between **A** and substituted benzaldehyde or 5-nitro-2-thiophenecarbaldehyde afforded compounds **1**−**3** in modest to high yields. Compounds **4** and **5** were prepared by DIBAL reduction of **1** to afford 1,3,5-trimethoxy-2,4,6-tris(p-formylstyryl)benzene (**B**), followed by the condensation with appropriate carbon acids.[5]

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The structure of **1**−**5** was unambiguously confirmed by ^{1}H and ^{13}C NMR, IR, and elemental analysis.

Figure 1 shows the absorption and emission spectra of **1**−**5**. As expected, a red shift of the absorption band is observed with increasing electron-withdrawing ability and conjugation length. Except for **2**, which did not emit fluorescence, all of the compounds show relatively large Stokes shifts ranging from 3000 to 6100 cm^{-1}. This indicates that the nuclear reorganization is taking place after excitation prior to emission as a result of significant electronic redistribution. For a given donor−acceptor pair, the Stokes shift increases with the conjugation length (**4** and **5**). However, it is much smaller for a compound with a thienyl group in the conjugation bridge (**3**), probably because of the shorter conjugation length. It also decreases significantly when there are additional cyano groups as the acceptor (**1** and **4**). This result could be attributed to the additional site for the electron redistribution, which may reduce the excited-state nuclear reorganization.[9]

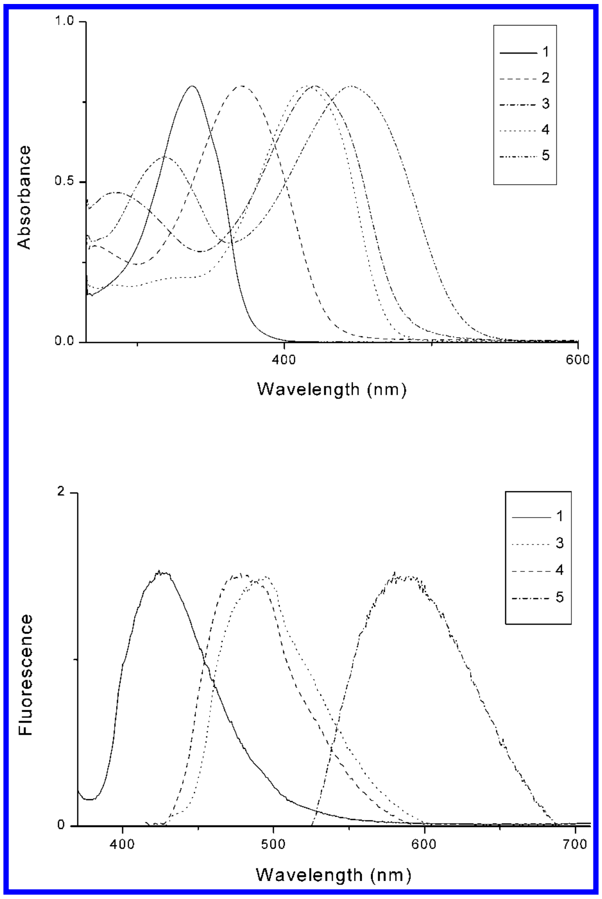

Figure 1. Absorption and emission spectra of **1**−**5** in CHCl$_3$.

The β values of the octupoles were measured by the hyper-Rayleigh scattering (HRS) method.[3,6] To avoid complications due to the self-absorption and multiphoton excitation, the fundamental wavelength was shifted to 1360 nm with the OPO laser (Continuum Surelite OPO, 5 ns pulses), which was pumped by the 355-nm third harmonic of the Nd:YAG laser (Continuum SL-II-10, Q-switched, 10 Hz).[7] HRS measurements of **1**−**5** were carried out in dilute CHCl$_3$ solution (1×10^{-4} to 1×10^{-2} M) by a normalized internal reference method.[3,6] As shown in Figure 1, **1**−**5** showed neither absorption nor emission band at 680 nm, where we collect the HRS signal. This result indicates the reliability of the HRS measurement, as it is neither underestimated by absorption nor overestimated by the multiphoton fluorescence.[8]

The linear and nonlinear optical data and the thermal stability of **1**−**5** are summarized in Table 1. For comparison, the data for closely related 1,3,5-tricyano-2,4,6-tris(*p*-diphenylaminostyryl)benzene and the β value of the most efficient dipolar NLO chromophore, julodinyl-(CH═CH)$_3$-A, where A is *N*,*N*′-diethylthiobarbituric acid, are included.[3j,10] Interestingly, both λ_{max} and $\beta(0)$ increase as the acceptor strength and the conjugation length increase. The parallel increase in these values is consistent with the theoretical prediction that the β value of the two-dimensional octupoles should increase with the extent of charge transfer.[3] For a given acceptor, the absorption maximum and the $\beta(0)$ increase as the conjugation bridge is changed from phenyl to a thienyl group (**2** and **3**). This is again due to the increased charge transfer. Because the thienyl group has smaller aromatic resonance energy than the phenyl group, it should facilitate the charge transfer from the donor to the acceptor to stabilize the excited state. This would in turn increase λ_{max} and β, as observed. Similar results were previously reported for the dipolar NLO chromophores.[11] The most important

Table 1. Linear and Nonlinear Optical Data and Thermal Stabilities of 1,3,5-Trimethoxy-2,4,6-tris(styryl)benzene Derivatives

compd	$\lambda_{max}{}^{a}$	$\lambda_{cut-off}{}^{b}$	$\Delta\tilde{\nu}^{c}$	$\beta^{d,e}$	$\beta(0)^{e,f}$	T_d^{ig}
1	337	388	6088	7.1	5.2	363
2	370	444		16	11	305
3	420	498	3062	34	20	309
4	415	480	3853	56	35	354
5	445	534	5522	319	163	377
TCTB[h]	488	568		223	124	422
JDA[i]	686			2169	911	

[a] In nm. [b] Wavelength at which the transmittance is 95%. [c] Stokes shift in cm^{-1}. [d] Determined at 1360 nm. [e] 10^{-30} esu. [f] Corrected at $\lambda \rightarrow \infty$ using a three-level model.[1a] [g] Initial decomposition temperature (°C) determined by thermal gravimetric analysis (TGA). [h] 1,3,5-Tricyano-2,4,6-tris[4-(*p*-diphenylaminostyryl)benzene.[3j] [i] Julodinyl-(CH═CH)$_3$-A, where A is *N*,*N*′-diethylbarbituric acid.[10]

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result of the present study is that **5** exhibits a $\beta(0)$ value of 163×10^{-30} esu, which is larger than that of closely related 1,3,5-tricyano-2,4,6-tris(*p*-diphenylaminostyryl)benzene, despite the modest electron-donating ability of the methoxy group (Table 1).[3j,12] This underlines the importance of grafting strong acceptors at the edge of peripheral groups to obtain a large β value. Also, this result suggests an interesting possibility that the β value of such molecules could be further increased if a stronger donor is introduced in the core. Furthermore, **5** shows improved transparency/nonlinearity trade-off in comparison to the latter. Finally, these octupoles show very high thermal stability as indicated by their initial decomposition temperatures (T_d^i) ranging from 305 to 377 °C.

In conclusion, we have synthesized a series of two-dimensional octupoles with large first hyperpolarizability and good thermal stability by grafting modest donors at the core and strong acceptors at the edge of the peripheral groups. Optimization has led to compounds with among the largest nonresonant hyperpolarizability ($\beta(0) = 163 \times 10^{-30}$ esu). The large first hyperpolarizability and good thermal stability make them attractive candidates for nonlinear optical materials.

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Supporting Information Available: Synthesis of **1**−**5** and determination of β values by hyper-Rayleigh scattering. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The most efficient octupoles are 4,4′-bis(dibutylaminostryl)-[2,2′]-bipyridine Ru(III) complex ($\lambda_{max} = 509$ nm, $\beta(0) = 240 \times 10^{-30}$ esu);[1c] 1,3,5-tricyano-2,4,6-tris[4-(*p*-diethylaminophenylethynyl)benzene ($\lambda_{max} = 476$ nm, $\beta(0) = 428 \times 10^{-50}$ Cm^3 V^{-2});[3e] 1,3,5-tris(methylsufonylbistryl)-benzene ($\lambda_{max} = 377$ nm, $\beta(0) = 510 \times 10^{-30}$ esu).[2c]