Synthesis and Nonlinear Optical Properties of 1,3,5-Tricyano-2,4,6-tris[2-(thiophen-2-yl)vinyl]benzene Derivatives[†]

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1,3,5-Tricyano-2,4,6-tris[2-(thiophen-2-yl)vinyl]benzene derivatives have been synthesized as a new type of octupolar nonlinear optical molecules and their linear and nonlinear optical properties were determined. The λ_{max} values increased with the conjugation length and as the conjugation bridge was changed from phenyl to thienyl group. For phenyl and thiophene derivatives, the β value increased with conjugation length. In contrast, the b values of the thiophene derivatives were much smaller than the corresponding phenyl derivatives.

Key Words : Nonlinear optics, Octupole, Thiophene

There is on-going research interest to develop organic materials with large second-order nonlinear optical (NLO) properties for possible application in the optical and opto-electronic devices.[1-7] Much effort has been concentrated on the design and synthesis of donor-acceptor dipoles with optimum physical properties acceptable for device fabrication.[1] The results of these studies have shown that the β values of the dipolar NLO molecules increase as the donor-acceptor strength and conjugation length increase.[2] It was also found that the β was significantly larger when hetero-aromatic rings such as thiophene or furan were used as the conjugation bridge in place of the phenyl group.[3] For practical applications, the molecules must be aligned non-centrosymmetrically in the solid state to exhibit significant second harmonic generation (SHG). In case of dipolar molecules, this has been most successfully achieved by electric poling.[1] Although there has been a major breakthrough in the development of polymer based electro-optic devices with huge bandwidth acceptance and low modulation voltage, the high voltage required for the electric poling has been a serious problem in the device fabrication.[1c] In addition, because the dipoles favor anti-parallel pairing, there is a relaxation problem.[1]

A fundamentally different approach to overcoming these difficulties would be to use octupolar molecules as an alternative NLO molecule.[4-7] The advantages of these molecules in comparison to the more conventional dipolar molecules are (i) the molecular hyperpolarizabilities of octupoles increase monotonically with the extent of charge transfer.[6] Hence to obtain octupolar molecules with large β, one only need to increase the donor-acceptor strength, conjugation length, and π orbital energy. (ii) It has been already demonstrated that some of the two-dimensional octupoles produce noncentrosymmetric crystals spontaneously.[7] Moreover, such crystals showed no sign of relaxation for a prolonged period

of time, probably due to the lack of the ground state dipole moment. These results suggest that a new crystal engineering principle could be developed for the production of octupolar materials with large bulk nonlinearity. (iii) The second harmonic response of octupolar molecules does not depend on the polarization compared with the dipolar compounds, which has important implications for applications.[4d]

The first step in obtaining efficient organic NLO materials is to design and synthesize molecules with high nonresonant molecular hyperpolarizability. This requires extensive structure-property relationship studies. We have previously reported such studies on the crystal violet, 1,3,5-trinitro-2,4,6-tris-(styryl)benzene, and 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives.[6,7b,c] As a extension to these works, we have synthesized 1,3,5-tricyano-2,4,6-tris[2-(thiophen-2-yl)vinyl]-benzene derivatives as a new type of octupolar NLO chromophores and measured their first hyperpolarizabilities (Chart 1). We were interested in learning the effects of changing the conjugation moiety from phenyl to thienyl on the NLO property.

Results and Discussion

Synthesis of the octupoles is summarized in Scheme 1. 1,3,5-Tricyanomesitylene (**A**) was synthesized as reported in the literature.[8] This compound could be conveniently isolated in 69% yield when extracted with CH_2Cl_2 after removing the copper salt from the reaction mixture by repeated extraction with ethylenediamine. 1,3,5-Tricyano-2,4,6-tris(bromomethyl)benzene (**B**) was obtained in 90% yield by irradiating the solution of **A** and Br_2 in CCl_4 with a 400 W tungsten lamp for 15 hrs in a photochemical reactor. Reaction of **B** with triethylphosphite in toluene at room temperature afforded 1,3,5-tricyano-2,4,6-tris(diethoxyphosphorylmethyl)benzene (**C**) in 69% yield.[4c] The octupolar compounds **1-3** were obtained in modest to reasonable yields by the Horner-Wittig olefination of **C** with appropriate arylaldehydes.

Chart 1

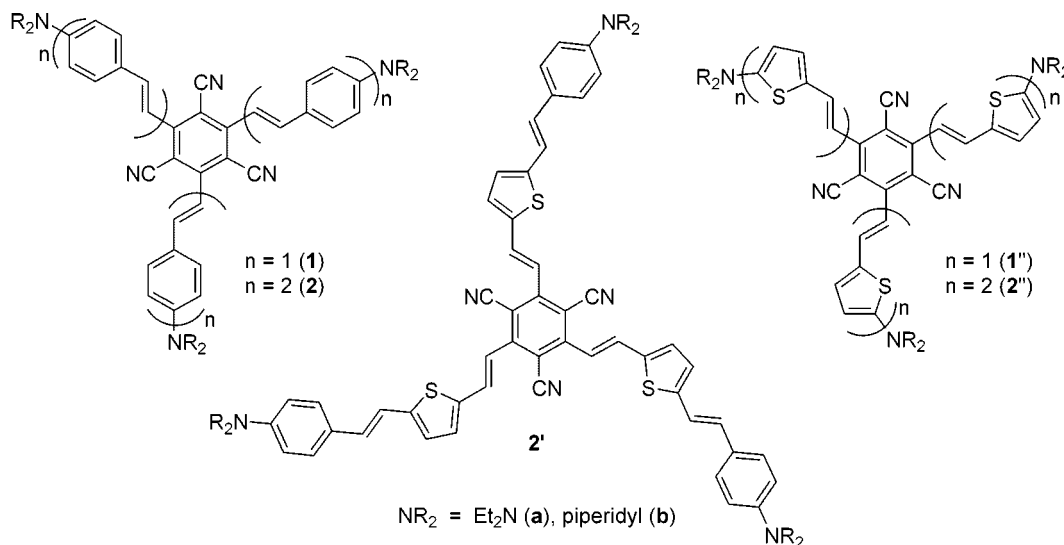The β values of the octupoles were measured at 1560 nm by Hyper-Rayleigh Scattering (HRS) method as previously reported.[4c,9] The $\lambda_{\text{cut-off}}$, the wavelength at which the transmittance is 95%, of all of the compounds is shorter than 780 nm, negating the possible re-absorption of the second-harmonic light by the chromophore. Also, little fluorescence was detected at 780 nm, where we collect the HRS signal. These results indicate the reliability of the HRS measurements as it is neither underestimated by absorption nor overestimated by the multi-photon fluorescence.

Table 1 compares the linear and nonlinear optical properties of the newly synthesized octupoles (**1"**, **2**, **2"**) and 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives (**1** & **2**). It is immediately evident that the λ_{max} of all of the compounds increases with the conjugation length (entries 1 & 5, 2 & 7). Similar increase is also observed by the change in the conjugation moiety from phenyl to thienyl (entries 1 & 2, 3 & 4, 5-7). Note that there is approximately linear increase in the λ_{max} as the thienyl group replaces the phenyl group successively in the conjugation moiety (entries 5-7). This result can readily be explained with the smaller aromatic resonance energy of the thiophene than benzene. As the π-orbital energy is increased by the change in the conjugation bridge, the charge transfer from the donor to the acceptor should be more efficient to decrease the excitation energy.

On the other hand, the change in the β values with the chromophore structure variation cannot be explained as above.

Table 1. Linear and Nonlinear Optical Properties of Octupolar Compounds

entry	Compound	λ_{max} (ε)	$\lambda_{\text{cut off}}$	β	$\beta(0)^a$
1	**1a**[c]	492 (82,200)	560	121	65.0
2	**1a"**[b]	559 (111,760)	617	41.0	17.0
3	**1b**[c]	468 (74,900)	565	118	69.0
4	**1b"**[b]	559 (87,840)	617	28.4	12.0
5	**2a**[c]	499 (82,200)	633	219	116
6	**2a**[b]	560 (107,890)	684	128	54.0
7	**2a"**[b]	613 (101,770)	780	59.4	22.7

[a]Calculated by using the three level model.[10] [b]Reference 19. [c]This work.

The nearly identical β values **1a"** and **1b"** are apparently due to the similar electron donating ability of the substituents (entries 2 & 4). Also, the increase in β with increased conjugation length is consistent with our theoretical model that β of the two-dimensional octupoles should increase with the extent of charge transfer (entries 1 & 5, 2 & 7).[6] In sharp contrast, the value of β for **1a"** is much smaller than that for **1a**, despite the smaller aromatic resonance energy and longer absorption maximum (entries 1 & 2). The same dichotomy is also observed for **1b** and **1b"** (entries 3 & 4). Furthermore, the β decreases monotonically as the thienyl group successively replaces the phenyl group in the conjugation moiety from **2a** to **2a** to **2a"** (entries 5-7). This is opposite to what was observed from donor-acceptor substituted stilbene
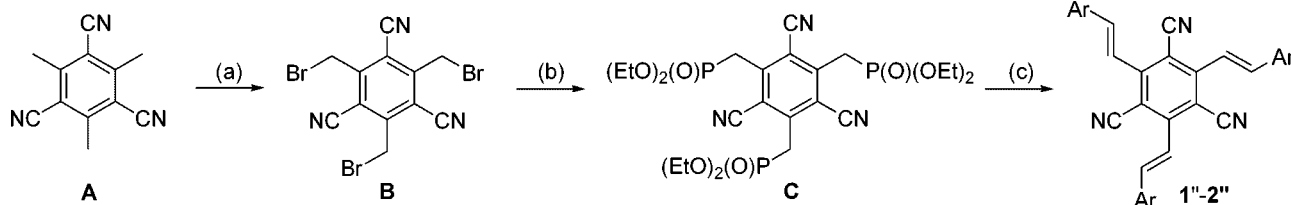
Scheme 1. (a) Br$_2$/CCl$_4$, 400 W Tungsten lamp, 15 hr, 90%. (b) (EtO)$_3$P/toluene, RT, 8 hr, 69%. (c) (i) DA/THF, 0 °C, 30 min, (ii) ArCHO, 48 hrs, 33-85%.

derivatives, in which significant increase in β value was noted by the same variation of the conjugation bridge.[3] The origin of this dichotomy is not clear at present. Nevertheless, this result clearly indicates that the effect of chromophore structure variation on the molecular hyperpolarizability of the octupolar compound could be entirely different from the donor-acceptor dipoles.

In conclusion, we have synthesized a new class of octupolar molecules containing thienyl group in the conjugation bridge. They show longer λ_{max} than the corresponding phenyl derivatives. Both λ_{max} and β of the thienyl derivatives increase with conjugation length. Noteworthy is the dramatic decrease in β with the change of the conjugation bridge from phenyl to thienyl group.

Experimental Section

5-Diethylaminothiophene-2-carbaldehyde and 5-piperidylthiophene-2-carbaldehyde were prepared by the reaction between 5-bromo-2-carbaldehyde and appropriate secondary amine by the literature procedure.[10] 5-[2-(5-Diethylaminothiophen-2yl)vinyl]thiophene-2-carbaldehyde and 5-(*p*-diethylaminostyryl)thiophen-2-carbaldehyde were synthesized by the Wittig olefination of 5-diethylaminothiophen-2-carbaldehyde and *p*-diethylaminobenzaldehyde with diethyl (2-thienylmethyl)phosphonate, followed by the formylation as reported in the literature.[3b] Synthesis of other compounds is described below.

1,3,5-Tricyanomesitylene. CuCN (22 g, 243 mmol), 1,3,5-tribromomesitylene (25 g, 76 mmol), and pyridine (150 mL) were thoroughly mixed in a steel autoclave and heated for 3 hr while maintaining the bath temperature at 240 $^{\circ}$C. After cooling, the mixture was transferred to a 2 L separatory funnel with 500 mL of CH_2Cl_2 and extracted with ethylenediamine/H_2O (1/4) until all of the copper salt was removed. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 layer was dried, evaporated, and the crude product was purified by column chromatography using hexane/CH_2Cl_2 (1/1) as the eluent to obtain 1,3,5-tricyanomesitylene as white solid. Yield, 10 g (68%); mp 172-174 $^{\circ}$C (lit mp 180 $^{\circ}$C)[20]; IR (KBr, cm^{-1}) 2228 (CN); ^{1}H NMR (300 MHz, CDCl$_3$) δ 42.83 (s, 9H).

1,3,5-Tricyano-2,4,6-tris(bromomethyl)benzene. A solution of 1,3,5-tricyanomesitylene (6.0 g, 31 mmol) and Br_2 (17.2 g, 108 mmol) in 350 mL of CCl_4 was irradiated with 400 W tungsten lamp for 15 hr. After removing the excess Br_2 with $Na_2S_2O_3$ (aq), the product was extracted with CH_2Cl_2, and purified by column chromatography with hexane/ethyl acetate (10/1) to obtain 1,3,5-tricyano-2,4,6-tris(bromomethyl)-benzene as white solid. Yield, 12.1 g (90%); mp 120 $^{\circ}$C; IR (KBr, cm^{-1}) 2229 (CN); ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.80 (s, 6H).

1,3,5-Tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]-benzene. A solution of 1,3,5-tricyano-2,4,6-tris(bromomethyl)-benzene (1.0 g, 2.3 mmol) and P(OEt)$_3$ (1.6 g, 14 mmol) in 60 mL of toluene was refluxed for 4 hrs. The solvent was

removed *in vacuo* and the product was purified by column chromatography with ethyl acetate/methanol (30/1) as the eluent to obtain colorless oil. Yield, 1.0 g (69%); IR (KBr, cm^{-1}) 2299 (CN), 1263 (P=O); ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.21 (q, 12H, J = 7.2), 3.73 (d, 6H, J = 22.1), 1.32 (t, 18H, J = 7.2).

Synthesis of 1,3,5-tricyano-2,4,6-tris[(thiophen-2-yl)-vinyl]benzene derivatives. LDA (1.5 M, 2.5 mL) was slowly added to a stirred solution of 1,3,5-tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene (0.70 g, 1.2 mmol) in 100 mL of THF at 0 $^{\circ}$C. The mixture was stirred for 30 minutes. To this solution, appropriate derivative of 5-thiophene-2-carbaldehyde (3.6 mmol) in 5.0 mL of THF was added slowly and stirred for 1 day. The solvent was evaporated and the product was purified by column chromatography. The yield (%), melting point ($^{\circ}$C), IR (KBr, cm^{-1}), ^{1}H NMR (300 MHz, CDCl$_3$), CMR (75 MHz, CDCl$_3$), and combustion analysis data for **1''-2''** are as follows. Chemical shifts are in ppm and J values in Hz.

1,3,5-Tricyano-2,4,6-tris[2-(5-diethylaminothiophen-2-yl)vinyl]benzene (1a''). Yield, 0.70 g (85%); mp 196 $^{\circ}$C; IR 2213 (CN), 1600 (C=C); ^{1}H NMR δ 7.91 (d, 3H, J = 15.6), 7.03 (d, 3H, J = 3.9), 6.66 (d, 3H, J = 15.6), 5.79 (d, 3H, J = 3.9), 3.40 (q, 12H, J = 6.9), 1.25 (t, 18H, J = 6.9). CMR δ δ 160.6, 148.8, 135.2, 134.7, 123.7, 117.6, 112.7, 102.3, 101.8, 47.3, 12.5. Anal. Calcd for $C_{39}H_{42}N_6S_3$: C, 67.79; H, 6.13; N, 12.16; S, 13.92. Found: C, 67.84; H, 6.25; N, 11.99; S, 13.85.

1,3,5-Tricyano-2,4,6-tris[2-(5-piperidylthiophen-2-yl)-vinyl]benzene (1b''). Yield, 0.20 g (33%); mp 260 $^{\circ}$C; IR 2213 (CN), 1610 (C=C); ^{1}H NMR δ 7.89 (d, 3H, J = 15.9 Hz), 7.03 (d, 3H, J = 4.2 Hz), 6.73 (d, 3H, J = 15.9 Hz), 5.97 (d, 3H, J = 4.2 Hz), 3.29 (m, 12H), 1.65 (m, 18H). CNMR δ 162.9, 148.6, 135.3, 134.0, 125.4, 117.3, 113.9, 104.0, 103.2, 51.4, 25.1, 23.8. Anal. Calcd for $C_{42}H_{42}N_6S_3$: C, 69.39; H, 5.82; N, 11.56; S, 13.23. Found: C, 69.27; H, 5.91; N,11.46; S, 13.32.

1,3,5-Tricyano-2,4,6-tris(2-{5-[2-(5-diethylaminothiophen-2-yl)vinyl]thiophen-2-yl}vinyl)benzene (2a''). Yield, 0.20 g (30%); mp 190 $^{\circ}$C; IR 2213 (CN), 1600 (C=C); ^{1}H NMR δ 7.92 (d, 3H, J = 15.9 Hz), 7.14 (d, 3H, J = 3.8 Hz), 7.04 (d, 3H, J = 15.9 Hz), 7.01 (d, 3H, J = 15.3 Hz), 6.82 (d, 3H, J = 3.8 Hz), 6.79 (d, 3H, J = 3.9 Hz), 6.52 (d, 3H, J = 15.3 Hz), 5.72 (d, 3H, J = 3.9 Hz), 4.59 (q, 12H, J = 7.2), 1.25 (t, 18H, J = 7.2). CMR δ 157.5, 148.0, 147.6, 137.4, 134.4, 132.6, 129.9, 125.3, 124.9, 124.8, 118.4, 116.3, 114.2, 105.7, 101.2, 47.09, 12.48. Anal. Calcd for $C_{57}H_{54}N_6S_6$: C, 67.42; H, 5.36; N, 8.28; S, 18.95. Found: C, 67.33; H, 5.41; N, 8.15; S, 19.07.

1,3,5-Tricyano-2,4,6-tris{2-[5-(*p*-diethylaminostyryl)thio-phen-2-yl]vinyl}benzene (2a). Yield, 0.15 g (35%); mp 250 $^{\circ}$C; IR 2213 (CN), 1590 (C=C); ^{1}H NMR δ 7.94 (d, 3H, J = 15.9 Hz), 7.36 (d, 6H, J = 8.7 Hz), 7.19 (d, 3H, J = 3.9 Hz), 7.12 (d, 3H, J = 15.9 Hz), 6.97 (s, 6H), 6.92 (d, 3H, J = 3.9 Hz), 6.65 (d, 6H, J = 8.7 Hz), 4.15 (q, 12H, J = 6.9 Hz), 1.19 (t, 18H, J = 6.9 Hz). CMR δ 148.3, 147.9, 147.8, 137.7, 134.8, 132.5, 131.5, 128.5, 125.5, 123.6, 118.6, 116.2,

116.1, 111.6, 106.2, 44.5, 12.8. Anal. Calcd for $C_{63}H_{60}N_6S_3$: C, 75.87; H, 6.06; N, 8.43; S, 9.64. Found: C, 75.98; H, 5.98; N, 8.36; S, 9.65.

Measurement of first hyperpolarizability (β). The β values of the octupoles were measured at 1560 nm by Hyper-Rayleigh Scattering (HRS) method.[4c,9] To avoid complications due to the multi-photon excitation, the excitation wavelength was shifted to 1560 nm with the OPO laser (Continuum Surelite OPO, 5 ns pulses), which was pumped by 355 nm third harmonic of the Nd:YAG laser (Continuum SL-II-10, Q-switched,10 Hz).

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