

Nondipolar Structures with Threefold Symmetry for Nonlinear Optics

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Abstract: The second-order polarizabilities $\beta(-2\omega; \omega, \omega)$ of six nondipolar NLO chromophores—1,3,5-tris(isopropylamino)-2,4,6-trinitrobenzene (**1**), 1,3,5-tris(isopropylamino)-2,4,6-tris(trifluoromethylsulfonyl)benzene (**2**), tris(dimethyl-*imonomethyl*)methide diperchlorate (**3**), 2,4,6-tris[4-(*N,N*-diethylamino)phenylethynyl]-1,3,5-triazine (**4**), 2,4,6-tris[4-(*N,N*-diethylamino)phenyl]-1,3,5-triazine (**5**), and tris(2-dimethylaminoethenyl)-

methinium perchlorate (**6**)—were studied by polarized hyper-Rayleigh scattering (HRS). The NLO activity of these two-dimensional NLO chromophores is attributed to three-level contributions to the

β values, for which different optimization strategies are investigated. Exceptionally large second-order polarizabilities were observed for the conjugationally elongated structures: the β value of triazine **4** is 15 times larger than that of the one-dimensional two-level chromophore 4-nitroaniline. Results obtained with the polarized HRS experiment are discussed with respect to local field corrections, calibration, and systematic sources of error.

Keywords

aluminium · gallium · hydrolyses · Si ligands · structure elucidation

Introduction

Organic materials for nonlinear optics (NLO) offer a number of advantages over inorganic solids.^[1] They are not only relatively easy to synthesize and to integrate into polymeric structures, but also have high optical nonlinearities and their response is fast. Since their bulk properties, to a first approximation, may be determined by the summation of molecular contributions, strategies for the rational optimization of organic materials must begin at the molecular level. Until recently it has been a universally held view that extended π systems with a considerable molecular dipole (e.g., stilbenes substituted with donors and acceptors in *para* positions) show the greatest promise as second-order NLO materials.^[1] Molecules devised on the basis of this concept are close in chemical structure and frequently belong to known classes of dyes (e.g., the merocyanines). In these molecules, only the component β_{zzz} of the second-order polarizability tensor parallel to the dipole axis z is relevant and can be optimized. Owing to the lack of significant off-diagonal

components, β may be termed “one-dimensional” (1D). In the two-level model^[2, 3] β is associated with only one HOMO–LUMO electronic transition of charge-transfer (CT) character. The two-level contributions to β are given by Equation (1), where

$$\beta^{(aa)}(-2\omega; \omega, \omega) = \Delta\mu^{ag}(\mu^{ag})^2 \frac{6\omega_{ag}^2}{\hbar^2(\omega_{ag}^2 - \omega^2)(\omega_{ag}^2 - 4\omega^2)} \quad (1)$$

$\Delta\mu^{ag}$ denotes the dipole change associated with the transition from the electronic ground state g to the excited state a , μ^{ag} the corresponding transition dipole, and ω_{ag} the circular frequency of the transition. As in previous work,^[4] we adopt the Taylor-series convention for β .^[5]

While there has been great progress in devising chemical structures based on the two-level approach,^[6, 7] it has become apparent that some problems in NLO cannot be effectively solved in this way. One of these problems is the efficiency–transparency trade-off, which is of crucial importance for second-harmonic generation (SHG).^[11, 8] The efficiency of the energy conversion must be high, but reabsorption of the converted light low—a condition that is difficult to fulfill with classic π systems, because the desirable increase in second-order polarizability is accompanied by a bathochromic shift of the electronic transition.^[8] Alternative concepts for the design of NLO chromophores are therefore needed.

One new approach is based on molecules with a two-dimensional (2D) character of β . It was shown previously^[3] that off-diagonal tensor components of β can become significant in dipolar molecules with C_{2v} symmetry where the direction of the transition dipole is perpendicular to the C_2 axis. This causes

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interesting phenomena such as deviations from Kleinman symmetry^[9] and could be useful in circumventing the efficiency–transparency trade-off.^[3,4] A series of C_{2v} symmetric NLO chromophores with large off-diagonal components of β and remarkable transparency properties was recently reported.^[4]

This paper deals with a second class of molecules with 2D character of β , which has been suggested by Ledoux and Zyss.^[10] By a formal analysis of β it was shown^[10a] that, in certain point groups with threefold rotation symmetry, molecules without a dipole can display NLO activity. It was argued from model calculations that trisdonor–trisacceptor substituted benzenes of D_{3h} symmetry, which have four significant components of β , may combine constant UV/Vis absorption with larger values of β . In terms of chemical concepts, the origin of the improved second-order polarizabilities is based on the degenerate LUMO found for π systems of minimum symmetry C_3 . The second-order polarizability may now be approximated as being proportional to the product of transition dipoles between three levels (HOMO and 2 LUMO's).^[10a] The three-level contributions arising from the ground state, g , and two—not necessarily degenerate—excited states, a and b , are of the general form given in Equation (2),^[10a] where, for reasons of simplicity,

$$\beta^{(gab)}(-2\omega; \omega, \omega) = \mu^{ga}\mu^{ab}\mu^{bg} \frac{12\omega_{ag}^2}{\hbar^2(\omega_{ag}^2 - \omega^2)(\omega_{ag}^2 - 4\omega^2)} \quad (2)$$

degeneracy of states a and b , $\omega_{ag} = \omega_{bg}$, was assumed. A complete perturbation theoretical expression for β in terms of two-level and three-level contributions $\beta^{(ga)}$ and $\beta^{(gab)}$ was given previously.^[4]

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was the first prototype molecule with D_{3h} symmetry for which second-order NLO effects in the solid state could be demonstrated.^[10f] The origin of this NLO activity was controversially discussed in the literature^[10f, 11] and could only recently be interpreted in terms of the presence of two polymorphic forms in samples used to evaluate powder efficiencies.^[11e] Considerable second-order polarizabilities were also observed for trinitrophenol and 1,3,5-tris(isopropylamino)-2,4,6-trinitrobenzene (**1**).^[12] The

method of choice for studying such nondipolar NLO chromophores is hyper-Rayleigh scattering (HRS).^[13] Since this experimental technique relies on incoherent frequency doubling, no poling of the solution is required, as is necessary with the electric field induced second harmonic generation (EFISH) method.^[14, 3] Thus nondipolar and even ionic species can be studied by HRS. Several nondipolar 2D NLO chromophores were investigated by HRS in the recent literature.^[10, 15] The exceptionally high β values initially reported for organometallic (ruthenium) complexes^[16a, b] have been brought into question or proven much lower.^[16c] Transiently noncentrosymmetric structures were studied by optical poling techniques.^[17]

In this work, we have followed three different strategies to optimize second-order polarizabilities of nondipolar NLO chromophores with threefold symmetry. Figure 1 summarizes the

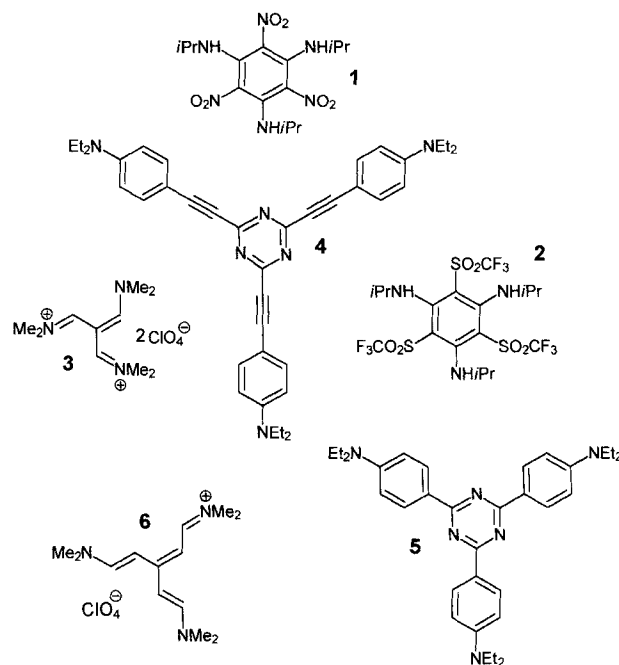


Figure 1. Nondipolar NLO chromophores with threefold symmetry investigated in this work.

Abstract in German: Die Polarisierbarkeiten zweiter Ordnung $\beta(-2\omega; \omega, \omega)$ der nichtdipolaren NLO-Chromophore 1,3,5-Tris(isopropylamino)-2,4,6-trinitrobenzol (**1**), 1,3,5-Tris(isopropylamino)-2,4,6-tris(trifluoromethylsulfonyl)benzol (**2**), Tris(dimethylmoniomethyl)methid-diperchlorat (**3**), 2,4,6-Tris[4-(*N,N*-diethylamino)phenylethynyl]-1,3,5-triazin (**4**), 2,4,6-Tris[4-(*N,N*-diethylamino)phenyl]-1,3,5-triazin (**5**) und Tris(2-dimethylaminoethenyl)methinium-perchlorat (**6**) wurden durch polarisiert detektierte Hyper-Rayleigh-Streuung (HRS) bestimmt. Die NLO-Aktivität dieser zweidimensionalen NLO-Chromophore wird auf Dreineiveau-Beiträge zu β zurückgeführt, für die mehrere Optimierungsstrategien untersucht werden. Ungewöhnlich große Polarisierbarkeiten zweiter Ordnung treten bei Strukturen mit vergrößerter Konjugationslänge auf. Der β -Wert von **4** ist 15mal größer als der des eindimensionalen Zweineiveau-Chromophors 4-Nitroanilin. Die durch polarisiert detektierte HRS erhaltenen Resultate werden im Hinblick auf lokale Feldkorrekturen, Kalibrierung und systematische Fehlerquellen diskutiert.

investigated structures. In the hope that increased electronic polarization would lead to enhanced second-order polarizabilities, we first replaced the nitro groups in **1** with the stronger acceptor trifluoromethylsulfonyl^[18] to give **2**. Since benzene derivatives of type **1** and **2** adopt conformations with nonplanar rings and decreased conjugation in comparison to hypothetical planar structures,^[19] we sought to construct molecules with decreased steric hindrance, as in the symmetric triazines **4** and **5**. In **4**, the π system was also considerably enlarged in comparison to **1** or **2**. In general, the extension of a π system leads to an increase in the magnitude of the transition dipole,^[20] which is a prerequisite for large second-order polarizabilities [cf. Eqs. (1) and (2)]. The third approach is exemplified by the branched C_{3h} symmetric cyanines **3** and **6**. Cyanines are known to have the highest linear polarizabilities of conjugated organic π systems,^[21] but owing to their centrosymmetry do not display second-order polarizabilities. Branching removes the center of inversion and gives rise to a nonvanishing β , as has been demonstrated by Stadler et al. for **3**.^[15e] In general, organic salts

may present advantages over neutral compounds in optimization of crystalline bulk structures.^[1d] Exchange of counterions of NLO-active molecular ions may allow much more rapid and facile screening of crystal structures than tedious chemical modifications of the NLO chromophore itself. In this paper, we present the characterization of the nondipolar 2D NLO chromophores **1–6** by polarized HRS experiments and report the syntheses of **2**, **4**, and **5**. We also address some possible sources of inaccuracies that may arise when the HRS technique is used to evaluate second-order polarizabilities.

Theory

Hyper-Rayleigh Scattering: The phenomenon of incoherent frequency doubling (hyper-Rayleigh scattering, HRS) by liquids was first observed by Terhune et al.^[23] in 1965. It was recently established as a new method for the determination of second-order polarizabilities of molecules in solution by Clays and Persoons.^[13, 24] HRS is an alternative to the electric field induced second harmonic generation (EFISH) method commonly applied for dipolar molecules and is the only available technique that enables measurement of β for nondipolar or ionic molecules. The experimentally detected HRS signal $S_{2\omega}$ is a quadratic

$$S_{2\omega} = C I_{\omega}^2 \quad (3)$$

function of the incident intensity I_{ω} , where C is a quadratic fit coefficient that can be expressed in terms of the number densities of solvent and solute and the rotational averages $\langle \beta^2 \rangle$ of their second-order polarizabilities.^[24] Solvent and solute contributions can be separated by investigating a concentration series. A general protocol for the determination of molecular quantities from measurements on macroscopic systems of two constituents was described previously.^[25, 3, 4]

With suitable calibration of the HRS apparatus, the averages $\langle \beta^2 \rangle$ can be derived from the results of polarized HRS measurements. For molecules with C_{3h} symmetry, there are eight nonvanishing tensor components of which two are independent. The nonzero components are $\beta_{zzz} = -\beta_{zyy} = -\beta_{yzy} = -\beta_{yyz}$, and $\beta_{yyy} = -\beta_{yzz} = -\beta_{zyz} = -\beta_{zzy}$, where x, y, z indicate Cartesian tensor components in the molecule-fixed frame. The rotational averages for parallel (ZZ) and perpendicular (ZX) polarization of the scattered 2ω photons relative to the polarization of the incident laser light can be calculated by standard techniques.^[26] The results are given in Equations (4) and (5). The same rela-

$$\langle \beta^2 \rangle_{zz} = \frac{48}{210} (\beta_{zzz}^2 + \beta_{yyy}^2) \quad (4)$$

$$\langle \beta^2 \rangle_{zx} = \frac{32}{210} (\beta_{zzz}^2 + \beta_{yyy}^2) \quad (5)$$

tionships hold for D_{3h} molecules with $\beta_{zzz} = -\beta_{zyy} = -\beta_{yzy} = -\beta_{yyz}$ ^[27] and $\beta_{yyy} = 0$. For both D_{3h} and C_{3h} NLO chromophores, the depolarization ratio is expected to be $\rho = \langle \beta^2 \rangle_{zz} / \langle \beta^2 \rangle_{zx} = 1.5$.

For molecules with symmetry C_{2v} , β has seven nonvanishing tensor components of which five are independent. The nonzero components are $\beta_{xxz} = \beta_{zxx}$, $\beta_{yyz} = \beta_{zyy}$, $\beta_{zxx} = \beta_{zyy}$, and β_{zzz} where z is the C_2 axis. The components containing transition dipoles

perpendicular to the molecular plane $\beta_{xxz} = \beta_{zxx}$ and β_{zzx} are usually negligible.^[3] The rotational averages of the remaining four components are given by Equations (6) and (7).^[4] For

$$\langle \beta^2 \rangle_{zz} = \frac{1}{210} (30\beta_{zzz}^2 + 12\beta_{zzz}\beta_{zyy} + 24\beta_{zzz}\beta_{yzy} + 24\beta_{zyy}\beta_{yzy} + 24\beta_{yzy}^2 + 6\beta_{zyy}^2) \quad (6)$$

$$\langle \beta^2 \rangle_{zx} = \frac{1}{210} (6\beta_{zzz}^2 + 8\beta_{zzz}\beta_{zyy} - 12\beta_{zzz}\beta_{yzy} - 12\beta_{zyy}\beta_{yzy} + 16\beta_{yzy}^2 + 18\beta_{zyy}^2) \quad (7)$$

dipolar 1D NLO chromophores with only one significant component β_{zzz} , the depolarization ratio is expected to be $\rho = 5$. Details of the calibration of the HRS apparatus and the determination of depolarization ratios are described in the Experimental Section.

Local field corrections: The local field acting on a molecule in solution differs from the applied macroscopic field in the medium. This difference has to be taken into account in the quantitative evaluation of linear and nonlinear optical experiments on condensed systems. In practice, only models based on classical electrodynamics and continuum approaches to the solvent environment, the Lorentz and Onsager corrections, have been used. Within Onsager's reaction field model^[28] the solute molecules are considered as polarizable point dipoles in the center of a spherical or ellipsoidal cavity in the solvent. The solvent itself is treated as a homogeneous and isotropic dielectric. Recently, a consistent extension of the reaction field model to second harmonic generation (SHG) was presented.^[3, 4] Assuming spherical cavities and equal polarizability volumes of solvent and solute molecules, the general relations^[3] reduce to the approximate expression (8) for the effective second-order polarizability in

$$\beta_{\text{eff}}(-2\omega; \omega, \omega; E^{R0}) = \frac{(\epsilon^{2\omega} + 2)(2\epsilon^{2\omega} + 1)}{9\epsilon^{2\omega}} \frac{(\epsilon^{\omega} + 2)^2}{9} \beta(-2\omega; \omega, \omega; E^{R0}) \quad (8)$$

solution, where $\epsilon^{2\omega}$ and ϵ^{ω} are relative permittivities of the solvent at the respective frequencies. Note that Lorentz type local field factors, $(\epsilon^{\omega} + 2)/3$, occur only for the fundamental frequency ω but not for 2ω .^[3, 4] β as obtained from Equation (8) is usually quoted as the experimental result of EFISH or HRS measurements in solution. It does not, however, represent the second-order polarizability of the free molecule. In the Onsager model, it still contains a component that is induced by the static reaction field E^{R0} , which is associated with the permanent dipole moment μ of the solute molecule. Applying the same approximations as in Equation (8) and assuming a spherical cavity of radius a , E^{R0} can be represented by Equation (9).

$$E^{R0} = \frac{(\epsilon^0 - 1)(\epsilon^{\infty} + 2)}{6\pi\epsilon_0 a^3 (2\epsilon^0 + \epsilon^{\infty})} \mu \quad (9)$$

where ϵ^0 is the static relative permittivity of the solvent, ϵ^{∞} the optical permittivity extrapolated to infinite wavelength,^[29] and ϵ_0 the permittivity of free space. The reaction field gives rise to an induced contribution to the second-order polarizability according to Equation (10). The induced contribution γE^{R0} can

$$\beta(-2\omega; \omega, \omega; E^{R0}) = \beta(-2\omega; \omega, \omega) + \gamma(-2\omega; \omega, \omega, 0) E^{R0} \quad (10)$$

be significant for polar molecules and may lead to a strong dependence of β on the solvent polarity.^[24, 29] For 4-nitroaniline (pNA) this effect has been studied quantitatively by experiment^[29] and quantum chemical calculations.^[30] It should be noted that the reaction field also causes solvent effects on the position and intensity of optical absorption bands.^[31] The absence of reaction field induced bathochromic shifts of the absorption bands for nondipolar 2D NLO chromophores is a major advantage of these compounds compared to dipolar 1D NLO chromophores.

Results and Discussion

The UV/Vis spectra of NLO chromophores 1–6 are displayed in Figure 2. The spectra of 3–6 are characterized by intense transitions at low energies, which are a prerequisite for large

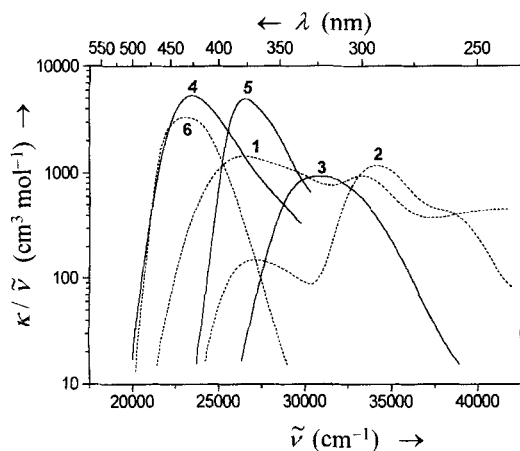


Figure 2. Absorption spectra of NLO chromophores 1–6. κ is the molar decadic absorption coefficient ($T = 298\text{ K}$; solvents as listed in Table 1).

nonlinearities. The absorptions of 1 and 2 are less intense and exhibit more structure, possibly indicating conformational distortions. All NLO chromophores are essentially transparent at 532 nm (18800 cm^{-1}), enabling nonresonant HRS measurements at $\lambda = 1064\text{ nm}$. The HRS measurements for 1 and 2 were carried out in dioxane solution. For reasons of solubility, 4 and 5 were studied in acetone, and the cyanine salts 3 and 6 in acetonitrile. Typical results illustrating the quadratic dependence of the harmonic signal $S_{2\omega}$ on the fundamental intensity I_ω according to Equation (3) and the linear dependence of the quadratic fit coefficient C on the mass fraction w of the solute are displayed in Figures 3 and 4, respectively. Concentrated solutions of 6 showed a weak absorption at 532 nm, probably caused by the low-energy tail of the main absorption band. This led to absorption losses in the HRS signal and to deviations from the linear dependence of C on the mass fraction w , which were taken into account by applying Beer's law. The HRS signals of all NLO chromophores except 4 and 5 were confirmed to be free of background fluorescence. Probable sources for the fluorescence of 4 and 5 are multiphoton processes, such as two-photon absorption, three-photon absorption, or reabsorption

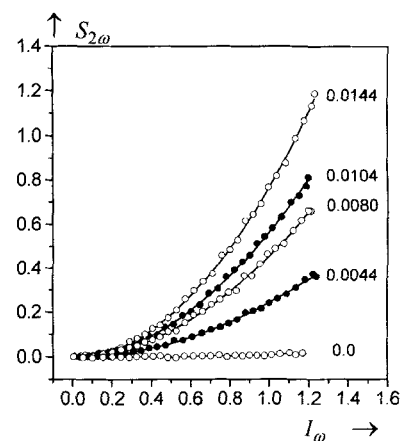


Figure 3. HRS signal $S_{2\omega}$ (arb. units) as a function of the fundamental laser intensity I_ω (arb. units) for dioxane solutions of 1 with mass fractions $w = 0.0, 0.0044, 0.0080, 0.0104$, and 0.0144 . Each point represents an average over 300 laser pulses. The solid lines are quadratic fits.

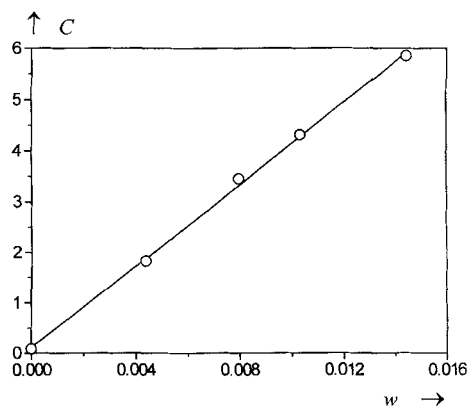


Figure 4. Quadratic fit coefficient C (arb. units) as a function of the mass fraction w of 1 in dioxane solution. The straight line is a linear fit.

of an internally generated third harmonic. The true HRS coefficients of 4 and 5 were extrapolated from results obtained with interference filters of varying bandwidth, as described in the Experimental Section below. The HRS apparatus was externally calibrated against a pNA standard. Local field corrections of the second-order polarizabilities were carried out by use of the modified Lorentz expression Equation (8). More refined corrections within the ellipsoidal Onsager model yielded only slightly different results; differences are typically on the order of 10% or less.^[32] Significant nonlinearities were observed for all NLO chromophores; the results are listed in Table 1.

The second-order polarizability β of the nondipolar 2D NLO chromophore 1 is found to be significantly lower than β of the 1D NLO chromophore pNA in the same solvent (cf. Table 2 below). It should be noted, however, that β of pNA in solution is strongly enhanced by reaction field induced contributions^[29] [cf. Eq. (10)]. Quantum chemical calculations for the isolated molecules indicate similar values for pNA and the related NLO chromophore 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).^[10d] Compound 1 has been studied previously^[12] in chloroform and nitromethane with comparable results for β . Here we compare NLO chromophore 1 with 2, in which the nitro groups have

Table 1. Results of hyper-Rayleigh-scattering measurements on NLO chromophores **1–6** ($\lambda = 1064$ nm, $T = 298$ K).

	pNA	1	2	3	4	5	6
solvent	dioxane	dioxane	dioxane	acetonitrile	acetone	acetone	acetonitrile
$\lambda_{\max}$ (nm)	354	375	290	320	425	375	430
$\kappa_{\max}$ (m ² mol ⁻¹)	1590	3850	4040	2710	12 600	13 300	7750
M (g mol ⁻¹)	138.13	384.39	645.60	382.20	594.81	522.74	321.80
ρ	5.0 ± 0.2	1.59 ± 0.03	1.5 ± 0.4	—	1.70 ± 0.04	1.1 ± 0.4	—
$\beta(-2\omega; \omega, \omega)$ [a] (10^{-50} C m ³ V ⁻²)	27.4 ± 2.8 [b]	18.4 ± 1.2 [b]	7.1 ± 0.3 [b]	8.7 ± 1.4 [c]	404 ± 10 [b]	162 ± 12 [b]	102 ± 6 [c]
β_0 [d] (10^{-50} C m ³ V ⁻²)	13.5	8.1	4.6	5.0	123	71	30

[a] Second-order polarizabilities are given in Taylor series convention [5]. [b] $\beta = \beta_{zzz}$; the approximate symmetry is D_{3h} . [c] $\beta = (\beta_{zzz}^2 + \beta_{yyy}^2)^{1/2}$; the approximate symmetry is C_{3h} . [d] $\beta_0 = \beta(0; 0, 0)$ determined by extrapolating of $\omega \rightarrow 0$ in Equation (2).

been replaced by the stronger acceptor trifluoromethylsulfonyl. The substitution leads to a pronounced blue-shift of the main absorption maximum $\lambda_{\max}$ from 375 to 290 nm, but also to a significantly lowered β value (Table 1). This result suggests that trifluoromethylsulfonyl is a weaker π acceptor than nitro, although in general comparable nonlinearities have been observed for 1D NLO chromophores substituted with fluorinated sulfone and nitro groups.^[18] Distortions occurring in the sterically crowded system **2** could also contribute to the lower β value.

The results for cyanine salts **3** and **6** are interesting in a number of ways. Compound **3** is nonabsorbing in the whole visible region (see Figure 1). The transparency is even higher than for **2**, although the absorption maximum of **3** is more bathochromic by 30 nm. The second-order polarizability of **3** observed here based on a careful external calibration of the HRS apparatus is significantly lower than the value published by Stadler et al.^[15e] for **3** in aqueous solution. Nevertheless, β of **3** is remarkably high for such a small chromophore and comparable to β of the tricyanomethanide anion reported by Verbiest et al.^[27] Increasing the conjugation length, however, leads to much larger second-order polarizabilities; β of the next higher homologue cyanine **6** is about twelve times larger than that of **3**. At the same time, the absorption is red-shifted to 430 nm.

The most promising results were obtained for the trisdonor-substituted triazines **4** and **5**. Symmetrically substituted triazines have been investigated previously by Ray and Das,^[33] who demonstrated the superiority of the triazine over the benzene ring as a central unit in nondipolar NLO chromophores with threefold symmetry. The most efficient donors studied in reference [33] were methoxy and phenyl. In the triazines presented here, we introduce substituents with stronger donor properties (diethylaminophenyl in **5**) and elongated conjugation (diethylaminophenylethynyl in **4**). In this way threefold donor–acceptor structures with exceptional second-order polarizabilities are created. The $\beta(-2\omega; \omega, \omega)$ of **5** is six times and that of **4** even fifteen times larger than that of pNA in dioxane (Tables 1 and 2). An approximate measure of nonlinear efficiency is the ratio of second-order polarizability and molar mass β/M . The value of β/M for the triazine **4** reported here is among the highest observed so far for a nondipolar NLO chromophore, especially in view of the rather short-wavelength absorption maximum.

We finally comment on the observed HRS depolarization ratios ρ (Table 1). All ratios were found to be close to the ideal value of 1.5 expected for D_{3h} and C_{3h} symmetry [cf. Eqs. (4)

and (5)]. The ρ values of the cyanine salts **3** and **6** were not measured, and ρ of **2** and **5** could only be determined with a relatively large error because of experimental difficulties such as small signals, background fluorescence, and absorption. Small but experimentally significant deviations of ρ from 1.5 were observed for **1** and **4**. These deviations are probably caused by symmetry-lowering distortions of the molecules or conformational distributions. Distortions of the benzene ring in hexasubstituted aromatics have been studied previously.^[35] In **5** the phenyl substituents may rotate out of the plane of conjugation. Any deviation from D_{3h} symmetry introduces dipolar contributions to the second-order polarizability. This usually leads to an increase of the observed depolarization ratio because ρ for a 1D dipolar chromophore is 5 [cf. Eqs. (6) and (7)].

Conclusion

New nondipolar NLO chromophores were synthesized and studied by the hyper-Rayleigh scattering (HRS) technique. The HRS experiment was performed with polarized detection. Effects of finite aperture on the depolarization ratio were discussed and suitably corrected. The fluorescence background observed in some experiments was eliminated by the use of interference filters with varying bandwidth.

Two 1,3,5-trisubstituted 2,4,6-tris(isopropylamino)-benzenes **1** and **2** were studied to compare the effects of the nitro and the trifluoromethylsulfonyl acceptor in nondipolar chromophores with threefold symmetry. It was found that the trifluoromethylsulfonyl derivative **2** was inferior in its nonlinear efficiency, but superior in its short-wavelength transparency. Highly polarizable cyanine salts **3** and **6** were investigated as prototypes of NLO chromophores with cross-conjugated structures. The large β values of **4** and **5** demonstrate the high potential of 2,4,6-trisdonor-substituted *s*-triazines as interesting new NLO chromophores that combine large second-order polarizabilities with good transparency properties. The absence of exocyclic acceptor groups in these NLO chromophores reduces steric interactions and enables the introduction of large and effective donors, opening a field for further optimization. Increasing the conjugation length was demonstrated to be an efficient strategy to maximize three-level contributions to β and achieve high nonlinearities in nondipolar NLO chromophores with threefold symmetry.

Experimental Section

Solvents: Spectrograde acetone was purchased from Merck and used as received. Dioxane was purified according to a previously described procedure.^[3] Acetonitrile was distilled from P_4O_{10} and the procedure was repeated until the P_4O_{10} residue was found to remain colorless. The distilled acetonitrile was further purified by percolation through 3 Å molecular sieves followed by distillation from P_4O_{10} .

HRS Apparatus: The experimental set-up for HRS is an extension of the EFISH-apparatus described previously^[3] and similar to the one described by Clays et al.^[13b] The pulses of the Nd:YAG-Laser ($\lambda = 1064$ nm) were focused into a cell containing the liquid sample. The incoherently scattered 2ω photons were collected orthogonal to the laser beam by a condenser system containing an aspheric lens and a concave retroreflection mirror. After passage through a rotatable dichroic sheet polarizer and an interference filter, the signal was focused onto the cathode of a photomultiplier (Burle C31034-02). Measurements with three different 532 nm interference filters (1, 3, and 10 nm fwhm) were performed to check the 2ω signal for fluorescence. When a fluorescence background was present, the true HRS signal was separated by extrapolating to zero bandwidth. In this procedure, the carefully measured transmission characteristics of the filters and the fluorescence bandshapes were taken into account. We found that this method yields reliable results as long as the fluorescence contribution does not exceed about 65% of the signal with the 10 nm filter. For **4** the fluorescence contribution was less than 40%. The photomultiplier was placed in a cooled housing (Products for Research Inc.: TE-104RF) and operated at -30°C . Cooling lowered the dark current and increased the sensitivity of the photocathode.^[3b] The ratio of the SHG signal generated in the sample and in a reference crystal, respectively, was recorded with a boxcar averager. The fundamental energy in the sample beam was varied by rotating a half-wave plate in a motorized rotation stage (OWIS controller 200) followed by a fixed Glan laser polarizer. In both the reference and the sample beam, the energy of the laser pulses was monitored by a dual energy meter (Laser Precision Rm 6600). Finally, the output signals of the energy meter and the boxcar were transferred via an IEEE interface to a personal computer for storage and subsequent manipulation. Absorption spectra were recorded on a Perkin-Elmer UV/340 spectrophotometer using Suprasil quartz cells.

HRS Calibration: It has frequently been suggested^[13, 23, 24] that the nonlinearity of the solvent can be used as an internal standard in the calibration of HRS measurements. The main disadvantage of this method is that it is applicable only when the nonlinearity of the solvent is known and large enough to be measured with sufficient accuracy. In general, the solute contribution to the HRS signal is much larger than that of the solvent. Hence internal calibration of the slope (solute contribution) by the intercept (solvent contribution) in the linear regression analysis of concentration dependent HRS measurements introduces an unnecessarily large statistical error. Therefore we preferred to calibrate the HRS device by measuring solutions of 4-nitroaniline (pNA) with several concentrations. The same solvent was used in the reference measurement with pNA and the chromophore under study. Because the second-order polarizability of pNA is known to be strongly solvent dependent,^[3,7] pNA was characterized in each solvent by electric field induced second harmonic generation (EFISH).^[3] The results are summarized for three different solvents in Table 2. This calibration method ensures consistency of second-order polarizabilities measured by HRS or EFISH and relates them to the same nonlinear standard (quartz, $d_{11}(1064\text{ nm}) = 0.5\text{ pm V}^{-1}$).^[3]

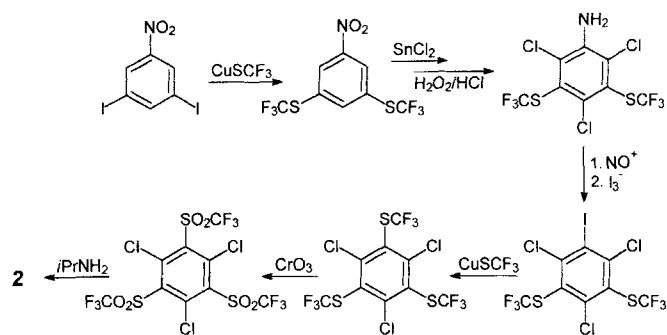
Table 2. Second-order polarizability $\beta_{zzz}(-2\omega; \omega, \omega)$ of pNA in different solvents obtained by EFISH ($\lambda = 1064$ nm, $T = 298$ K).

Solvent	λ_{max} (nm)	β_{zzz} ($10^{-50}\text{ C m}^3\text{ V}^{-2}$)
dioxane	354	27.4 ± 2.8
acetonitrile	364	49.6 ± 4.0
acetone	366	54.7 ± 4.1

Measurement of the HRS depolarization ratio: Another important aspect of the calibration is related to the depolarization ratio ρ . The theoretical depolarization ratio of a dipolar 1D NLO chromophore is $\rho = 5$ [cf. Eqs. (6)

and (7)]. Usually, the measured depolarization ratio ρ is strongly dependent on the detection aperture. The correct result for orthogonal detection geometry is obtained only by extrapolating ρ to vanishing aperture. This yields $\rho = 5.0 \pm 0.2$ for pNA in dioxane, in excellent agreement with theory and larger than the value obtained by Heesink et al.^[38] who carried out the experiment with a fixed aperture. ρ of pNA was confirmed to be independent of the solvent within experimental error. In general, the aperture dependence of the second harmonic intensity is a function of ρ . This implies that it is necessary to determine ρ when 2D NLO chromophores are measured relative to the 1D pNA standard. To minimize statistical errors, we measured ρ at high concentration and performed the concentration dependent HRS measurements using vertical polarization (ZZ) and large aperture.

Compounds: 1,3,5-Tris(isopropylamino)-2,4,6-trinitrobenzene (**1**)^[19] and tris(dimethyliminomethyl)methide diperchlorate (**3**)^[39] were obtained according to previously published procedures. The syntheses of compounds **2** and **4** are shown in Schemes 1 and 2, respectively. Solvents for the syntheses were dried and purified according to standard procedures. For reactions under inert gas, the Schlenk technique was used. Melting points (hotstage microscope) are given uncorrected.



Scheme 1. Synthesis of **2**.

3,5-Bis(trifluoromethylthio)nitrobenzene was synthesized by reaction of 3,5-dinitrobenzoic acid^[40] with CuSCF_3 in DMF under argon.^[41a] We found a reaction temperature of 100°C (lower than used previously) applied for 3 h to give much improved yields. Since the preparation of the reagent is either hazardous and inconvenient,^[41d] or very expensive,^[42] it is important to note that only 1.5 instead of 2 equiv of CuSCF_3 per iodine atom are necessary to effect the conversion in the modified procedure. At higher temperatures, the reagent decomposes^[43] to give Cu_2S which also reacts with the substrate. The thioether was purified by silica gel chromatography (3/97 Et_2O /light petroleum), 93% yield. $^1\text{H NMR}$ (CDCl_3 , 200 MHz): $\delta = 8.26$ (t, $J = 1.5$ Hz, 1H), 8.61 (d, $J = 1.6$ Hz, 2H). $^{13}\text{C NMR}$ (CDCl_3 , 50.3 MHz): $\delta = 128.37$ (q, $J = 2.3$ Hz), 128.71 (q, $J = 309.4$ Hz), 132.53, 148.01, 148.68.

3,5-Bis(trifluoromethylthio)aniline: To a solution of 3,5-bis-trifluoromethyl-nitrobenzene (3.923 g, 12.14 mmol) in ethanol (20 mL), a solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (11.0 g, 48.6 mmol) in concentrated HCl (20 mL) was added slowly. After the exothermic reaction had subsided, the mixture was heated to reflux for 1 h. The ethanol was distilled in vacuo, and the residue cooled with ice and made strongly alkaline with a concentrated solution of KOH. It was extracted with Et_2O (3×30 mL). The extracts were washed with water, saturated brine, and dried with Na_2SO_4 . The solvent was removed, and the residue distilled in a Kugelrohr oven at $125^\circ\text{C}/1$ mm. Colorless crystals were collected (3.339 g, 11.39 mmol, 93.8%), m.p. $53-54^\circ\text{C}$ ($59^\circ\text{C}^{[41b]}$). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 3.95$ (s, 2H), 7.03 (d, $J = 1.3$ Hz, 2H), 7.30 (t, 1H, coupling not resolved). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): $\delta = 123.80$ (m, $J = 0.8$ Hz), 126.36 (q, $J = 2.1$ Hz), 129.39 (q, $J = 308.3$ Hz), 132.14 (m, $J = 0.8$ Hz), 147.92.

2,4,6-Trichloro-3,5-bis(trifluoromethylthio)aniline: The literature procedure^[41c] was followed except that the reaction mixture had to be stirred for 30 min after appearance of the turbidity; otherwise, considerable amounts of a dichlorinated product were also observed. Crude yield, 91%; from heptane at -25°C , 89%; m. p. $93-96^\circ\text{C}$ ($96-97^\circ\text{C}^{[41c]}$). $^1\text{H NMR}$ (CDCl_3 ,

300 MHz): $\delta = 4.93$ (s). ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 123.57$ (q, $J = 2.3$ Hz), 128.86 (q, $J = 311.9$ Hz), 130.58 (m, $J \approx 0.8$ Hz), 138.38 (m, $J \approx 0.7$ –0.8 Hz), 141.39.

1,3,5-Trichloro-2-iodo-4,6-bis(trifluoromethylthio)benzene: Within 15 min, a solution of the above trichloroaniline (1.769 g, 4.461 mmol) in glacial acid (10 mL) was added at 0 °C to nitrosyl sulfuric acid (335 mg NaNO_2 and 10 mL conc. H_2SO_4) with vigorous stirring. After 20 min, the mixture was slowly poured into a vigorously stirred solution of KI (1.60 g) and iodine (1.60 g) in water (25 mL); gas was evolved. The mixture was then briefly heated to 80 °C. After 15 min, the mixture was cooled, iodine removed by addition of Na_2SO_3 , and the mixture extracted with ether (3 $\times$ 30 mL). The extracts were washed with water, neutralized with aqueous sodium carbonate, and dried with Na_2SO_4 . The solvent was removed and the residue (2.243 g) chromatographed on silica gel with pentane to give colorless crystals (2.206 g, 4.347 mmol, 97.4%), m.p. 92–95 °C. An analytical sample was further purified by crystallization from a minimum amount of pentane to give colorless prisms, m.p. 95.5–96.5 °C. ^1H NMR (CDCl_3 , 300 MHz): no signal. ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 104.92$, 123.87 (q, $J = 2.3$ Hz), 128.75 (q, $J = 312.3$ Hz), 152.08 (m, $J = 0.9$ Hz), 152.89 (m, $J \approx 0.9$ Hz). Anal. calcd for $\text{C}_8\text{Cl}_3\text{F}_6\text{I}_2\text{S}_2$ (507.47): C, 18.93; H, 0.00; Cl 20.96; I, 25.01; S, 12.64. Found: C, 18.98; H, 0.00; Cl, 20.57; I, 24.85; S, 12.69.

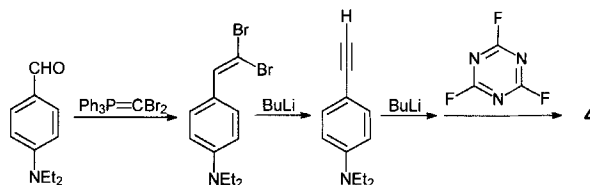
1,3,5-Trichloro-2,4,6-tris(trifluoromethylthio)benzene: The above iodide (2.290 g, 4.513 mmol) was stirred with a 2M solution of CuSCF_3 (10 mmol) in DMF under argon at 90 °C for 21 h. The mixture was cooled and stirred with diethyl ether (50 mL), and the ether was decanted. The residue was washed again with ether (50 mL). The combined ethereal phases were washed with water (3 $\times$ 30 mL) and saturated brine. After drying (Na_2SO_4), the solvent was removed and the residue (2.118 g) chromatographed on silica gel with light petroleum. The trithioether was obtained as semi-solid diamond-shaped colorless plates, m.p. ≈ 27 –35 °C (1.833 g, 3.806 mmol, 84.3%), slightly contaminated by a reduction product (3%, GC), see below. For analysis, a sample was recrystallized from methanol at –20 °C to give colorless plates of the same habit, m.p. 39.5–40.5 °C. ^1H NMR (CDCl_3 , 300 MHz): no signal. ^{13}C NMR (CDCl_3 , 50.3 MHz): $\delta = 126.41$ (q, $J = 2.3$ Hz), 128.66 (q, $J = 312.3$ Hz), 156.21 (br m). Anal. calcd for $\text{C}_6\text{Cl}_3\text{F}_9\text{S}_3$ (481.64): C, 22.44; Cl 22.08; S, 19.97. Found C, 22.43; H, 0.00; Cl, 21.80; S, 20.15.

Higher reaction temperatures (120 °C), as used previously^[41a, d] for Ullmann reactions with CuSCF_3 , led to appreciable decomposition of the reagent, and gave low yields of mixtures of approximately equal amounts of the trisether and a reduction product, 1,3,5-trichloro-2,4-bis(trifluoromethylthio)benzene, separable only by analytical GC. Data for the latter: ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.79$ (s). ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 124.60$, (q, $J = 2.3$ Hz), 128.72 (q, $J = 312.0$ Hz), 130.38, 147.37 (m, $J \approx 0.6$ Hz), 153.04 (m, $J \approx 0.6$ Hz). MS (EI): 380 (M^+ for $^{35}\text{Cl}_3$).

In addition, bis[(2,4,6-trichloro-3,5-bis(trifluoromethylthio)phenyl] sulfide was isolated in 11% yield at these high reaction temperatures. It possibly arises from the reaction of $\text{Cu}_2\text{S}^{[42]}$ with the starting material; large prisms from *n*-heptane, m.p. 120–121.5 °C. ^1H NMR (CDCl_3 , 300 MHz): no signal. ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 126.13$, 128.59 (q, $J = 312.3$ Hz), 134.39, 150.46, 152.28. MS (EI): 790 (55%, M^+ for $^{35}\text{Cl}_6$; isotope cluster in accordance with $\text{C}_{16}\text{Cl}_6\text{F}_{12}\text{S}_2$).

1,3,5-Trichloro-2,4,6-tris(trifluoromethylsulfonyl)benzene: A mixture of the trithioether (738 mg, 1.53 mmol), concentrated sulfuric (20 mL), and trifluoroacetic anhydride (10 mL) was stirred for 20 min at RT. It was cooled to 0 °C, and finely powdered chromium trioxide (1.8 g, 18 mmol) was added with vigorous stirring. The mixture was left stirring in the ice bath for 20 h at RT. It was poured on ice, and the precipitate filtered and washed with water. The crude product was dried (790 mg), and recrystallized from toluene to give colorless needles, m.p. 193–194 °C (closed capillary; 528 mg, 0.914 mmol, 59.7%). ^1H NMR (CD_3CN , 200 MHz): no signal. ^{13}C NMR (CD_3CN , 50.3 MHz): $\delta = 120.75$ (q, $J = 328.2$ Hz), 137.18 (q, $J = 2.9$ Hz), 152.95. Anal. calcd for $\text{C}_9\text{Cl}_3\text{F}_9\text{O}_6\text{S}_3$ (577.64): C, 18.71; Cl, 18.41; S, 16.65. Found: C, 18.57; H, 0.00; Cl, 18.53; S, 16.78. MS (EI): 576 (2%, M^+ for $^{35}\text{Cl}_3$; isotope cluster in accordance with $\text{C}_9\text{Cl}_3\text{F}_9\text{O}_6\text{S}_3$).

1,3,5-Tris(isopropylamino)-2,4,6-tris(trifluoromethylsulfonyl)benzene (2): A mixture of the above trichloride (330 mg, 0.519 mmol), excess isopropylamine (1 mL), and dry DMSO (10 mL), was heated to 100 °C for 16 h under argon. It was then diluted with water (59 mL), and acidified with hydrochloric acid. It was extracted with diethyl ether (3 $\times$ 30 mL), and the ethereal layers were washed with water (3 $\times$ 30 mL) and brine, and dried. The residue left behind after evaporation of the solvent (320 mg) was chromatographed on silica gel with light petroleum/diethyl ether (94/6) as eluent to give a pale yellow oil, which was crystallized from absolute methanol at –20 °C to give triangular plates, m.p. 111.5–114 °C (194 mg, 0.30 mmol, 57.9%). ^1H NMR (CD_2Cl_2 , 300 MHz): all signals are broadened; $\delta = 1.11$ –1.41 (m, 18 H), 4.34–4.69 (m, 3 H), 7.39 (brd, $J \approx 8.1$ Hz, 1 H), ca. 7.58 (brs, 1 H), 7.85 (brd, $J \approx 7$ Hz, 1 H), ca. 8.05 (brs, 1 H), 8.70 (brd, $J \approx 8$ Hz, 1 H), 8.78 (brd, $J \approx 8.3$ Hz, 1 H). ^{13}C NMR (CD_2Cl_2 , 75.5 MHz): all signals are broadened to different extents due to conformational dynamics; $\delta = 21.42$, 21.65, ca. 22.1, ca. 22.7, 23.04, 23.26, 23.61, 23.98, 53.93, 56.44, 72.68, 73.05, 79.58, 91.98, 121.21 (q, $J = 329$ Hz), 121.78 (q, $J = 331$ Hz), 160.02, 162.98, 163.65, 164.26. Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{F}_9\text{N}_3\text{O}_6\text{S}_3$ (645.59): C, 33.49; H, 3.75; N, 6.51; S, 14.90. Found: C, 33.65; H, 3.86; N, 6.69; S, 15.11.



Scheme 2. Synthesis of 4.

***N,N*-Diethyl-4-ethynylaniline:** Previously published procedures^[44] proved cumbersome and gave the desired alkyne in low yields. We found the two-step sequence given below, which is modified from the protocol by Corey–Fuchs,^[45] to be much more convenient. Alternatively, it was obtained by Pd-mediated cross-coupling of *N,N*-diethyl-4-iodoaniline with the zinc salt of acetylene or with TMS acetylene, followed by removal of the TMS group with base.^[46]

1,1-Dibromo-2-(4-*N,N*-diethylaminophenyl)ethene: Under argon, a mixture of zinc (4.9 g, 75 mmol), triphenylphosphine (19.67 g, 74.99 mmol), and carbon tetrabromide (24.87 g, 74.99 mmol) in dry dichloromethane (250 mL) was sonicated in a standard laboratory ultrasonic cleaning bath for 2 h with cooling. The reagent precipitated as a greyish solid. 4-*N,N*-diethylaminobenzaldehyde (5.30 g, 29.9 mmol) was then added, and the mixture stirred overnight, whereupon the precipitate dissolved to give an orange-brown solution. The mixture was concentrated, and light petroleum (500 mL) was added, whereupon a tarry precipitate was formed. It was washed twice with 1/1 CH_2Cl_2 /light petroleum (100 mL each). The combined organic phases were concentrated, and the residue was chromatographed on silica gel (150 g), eluting with 1/1 CH_2Cl_2 /light petroleum to give the bromoalkene as a yellow oil (5.187 g, 15.57 mmol, 52.1%). ^1H NMR (CDCl_3 , 300 MHz): $\delta = 1.18$ (t, $J = 7.1$ Hz, 6H), 3.37 (q, $J = 7.1$ Hz, 4H), 6.63 (pseudo-d, $J = 8.9$ Hz, 2H), 7.33 (s, 1H), 7.49 (d, $J = 8.9$ Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 12.6$, 44.3, 83.5, 110.8, 121.9, 129.9, 136.6, 147.7.

***N,N*-Diethyl-4-ethynylaniline:** *n*-Butyllithium (1.6M in hexanes, 41.0 mL, 65.7 mmol) was added dropwise via syringe to a stirred solution of the dibromoalkene (9.503 g, 28.53 mmol) in dry THF (190 mL) under argon at –78 °C. After the addition had been completed, the mixture was stirred for 45 min at this temperature, and then for 1 h at RT. Water (20 mL) was added cautiously, and the organic layer was decanted. The solvent was removed, and the residue taken up in diethyl ether. It was then washed with water (50 mL) and saturated brine, and dried over Na_2SO_4 . The ether was removed, and the residue was distilled in a Kugelrohr oven at 110 °C/0.1 mm to give a very pale yellow oil (4.149 g, 23.95 mmol, 83.9%); colorless needles from pentane, m.p. 20 °C (colorless oil^[44]). ^1H NMR: identical to lit.^[44c] ^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 12.46$, 44.25, 74.39, 85.01, 107.63, 111.03, 133.37, 147.79.

2,4,6-Tris[4-(*N,N*-diethylamino)phenylethynyl]-1,3,5-triazine (4): Under argon, *n*-butyllithium (1.6M in hexanes, 4.2 mL, 6.7 mmol) was added dropwise

via syringe to a stirred solution of the alkyne (1.17 g, 6.75 mmol) in dry THF (20 mL), cooled to -78°C . The cooling bath was removed after 1 h, and the solution stirred for another 20 min at RT. It was then cooled again to -78°C , and a solution of cyanuric fluoride (260 mg, 1.93 mmol) in dry THF (2 mL) was added dropwise. The mixture was warmed to RT, and stirred for 2 h. CH_2Cl_2 (20 mL) and water (20 mL) was added, the phases separated, and the aqueous phase extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with saturated brine, and dried (Na_2SO_4). The solvent was removed, and the residue chromatographed (basic alumina, act. III; 1/1 diethyl ether/light petroleum) to give small yellow leaflets, m.p. 235°C (430 mg, 0.723 mmol, 37.5%). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.18$ (t, $J = 7.0$ Hz, 18H), 3.37 (q, $J = 7.1$ Hz, 12H), 6.61 (pseudo-d, $J = 9.0$ Hz, 6H), 7.55 (pseudo-d, $J = 8.9$ Hz, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): $\delta = 12.48, 44.41, 87.07, 96.89, 105.51, 110.97, 135.22, 149.17, 160.33$. MS (EI): 594 (100, M^+). Anal. calcd for $\text{C}_{39}\text{H}_{42}\text{N}_6$ (594.81): C, 78.74; H, 7.12; N, 14.14. Found: C, 77.92; H, 7.15; N, 14.39.

2,4,6-Tris(4-diethylaminophenyl)-1,3,5-triazine (5) was obtained by addition of a solution of 4-lithio-*N,N*-diethylaniline (from 4-bromo-*N,N*-diethylaniline and *n*BuLi at -60°C) in THF to a stirred solution of cyanuric chloride in the same solvent under Ar, first at -70°C and then at RT for 2 d. Purification by chromatography (silica gel, CH_2Cl_2); 20% yield; yellow prisms from toluene, m.p. $286-290^{\circ}\text{C}$. 2-chloro-4,6-bis(4-diethylaminophenyl)-1,3,5-triazine was also isolated (50% yield). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.26$ (t, $J = 7.1$ Hz, 18H), 3.49 (q, $J = 7.1$ Hz, 12H), 6.83 (AA' part of AA'MM' system; m, 6H), 8.69 (MM' part of AA'MM' system; m, 6H). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): $\delta = 12.54, 44.39, 110.70, 123.84, 130.37, 150.40, 170.23$. Anal. calcd. for $\text{C}_{33}\text{H}_{42}\text{N}_6$ (522.74): C, 75.82; H, 8.10; N, 16.08. Found: C, 75.66; H, 8.12; N, 16.10. MS (EI): 522 (M^+ , 100); 507 ($M^+ - \text{CH}_3$, 85).

Tris(2-dimethylaminoethenyl)methinium perchlorate (6) was obtained according to ref. [47], but with a reaction time of 3 h instead of 16 h; orange needles from EtOH/MeCN; m.p. 190°C (decomp.), lit.: red needles m.p. $214-215^{\circ}\text{C}$ (EtOH/MeCN), NMR data as reported in ref. [47].

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