Hexasubstituted Donor–Acceptor Benzenes as Nonlinear Optically Active Molecules with Multiple Charge-Transfer Transitions

Boris Traber,[a] J. Jens Wolff,*[a, b] Frank Rominger,[a] Thomas Oeser,[a] Rolf Gleiter,*[a] Mark Goebel,[c] and Rüdiger Wortmann*[c]

Abstract: The synthesis of three novel nonlinear optical (NLO) chromophores with threefold symmetry, namely 1,3,5-tris(4-*N*,*N*-diethylaminophenyl)-2,4,6-tris(4-nitrophenyl)benzene (**3**), 1,3,5-tris(4-*N*,*N*-dihexylaminophenylbutadiynyl)-2,4,6-tris(4-nitrophenyl)benzene (**13**) and 1,3,5-tris(4-*N*,*N*-dihexylaminophenylethynyl)-2,4,6-tris(4-nitrophenylethynyl)benzene (**4b**), is reported. We used the [$Co_2(CO)_8$]-catalysed trimerisation of 4-*N*,*N*-diethylamino-4′-nitrotolane (**5**) to prepare **3**. The trimerisation experiment carried out with 1-(4-*N*,*N*-diethylaminophenyl)-6-(4-*N*,*N*-nitrophenyl)hexatriyne (**6**) and [$Rh(PPh_3)_3Cl$] afforded **13**. A stepwise approach was used to prepare **4b**. 1,3,5-Trichloro-2,4,6-triiodobenzene (**8b**) was coupled with 4-nitrophenyl-acetylene (**14**) under Pd^0 catalysis to yield 1,3,5-trichloro-2,4,6-tris(4-nitrophenylethynyl)benzene (**15**). The coupling reaction of **15** with 4-*N*,*N*-dihexylaminophenylethynyltributylstannane (**21**) led to **4b**. X-ray investigations on **3**, **4b** and **13** confirmed the structural assignments and revealed that the peripheral aryl rings in **4b** are less twisted around the connecting bonds than in **3** and **13**. A large second-order polarisability (β) of **4b** relative to **3** and **13** was determined by hyper-Rayleigh scattering (HRS). Compound **4b** represents an NLO chromophore with second-order polarisabily among the highest obtained so far for two-dimensional nondipolar NLO chromophores.

Keywords: alkynes • cross-coupling • cyclotrimerization • nonlinear optics • UV/Vis spectroscopy

Introduction

The advantages of organic versus inorganic materials for nonlinear optical (NLO) applications include technical aspects like their relative ease of synthesis and integration into polymeric structures but also large optical nonlinearities and fast response.[1–7] To a first approximation, the bulk NLO properties of organic materials result from a tensorial addition of the contributions of the individual molecules, for example their second- or third-order polarisabilities.[6] Most molecules with high second-order polarisability (β) were devised according to a similar design principle, that is an extended, linear π system with a high molecular dipole such as substituted stilbenes with a donor and an acceptor in 4,4′-positions. Chromophores of this type usually exhibit one intense low-lying charge-transfer (CT) transition whose intensity and dipole difference determine the NLO response within a two-level model.[8]

While great progress has been made in the optimisation of such one-dimensional (1D) NLO chromophores, it has become apparent that some problems in nonlinear optics cannot be effectively addressed by this approach. One is the efficiency–transparency trade-off which is of crucial importance for second-harmonic generation (SHG). The efficiency of the energy conversion must be high, but the reabsorption of the converted light low. However, the desirable increase in second-order polarisabilities in more extended π systems is usually accompanied by a bathochromic shift of the CT transition.[6] Furthermore, the strong dispersion of the refractive index makes it difficult to achieve noncritical phase matching between fundamental and frequency-doubled waves in a bulk material or crystal. Alternative design strategies at the molecular level are therefore desirable.

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[a] Dr. B. Traber, Priv.-Doz. Dr. J. J. Wolff, Dr. F. Rominger,
Dr. T. Oeser, Prof. Dr. R. Gleiter
Organisch-Chemisches Institut der Ruprecht-Karls-Universität
Heidelberg
Im Neuenheimer Feld 270
69120 Heidelberg (Germany)
Fax: (+49) 6221-54-4205
E-mail: rolf.gleiter@urz.uni-heidelberg.de

[b] Priv.-Doz. Dr. J. J. Wolff
Deceased

[c] Dipl. Chem. M. Goebel, Prof. Dr. R. Wortmann
Physikalische Chemie der Universität Kaiserslautern
Erwin-Schrödinger-Strasse
67663 Kaiserslautern (Germany)
Fax: (+49) 631-205-2750
E-mail: ruediger.wortmann@chemie.uni-kl.de

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One approach exploits π systems with several donor and acceptor groups.[9–19] The multiple substitution leads to a two-dimensional (2D) character of the tensor $\boldsymbol{\beta}$ in which off-diagonal elements become significant. In particular nondipolar compounds with threefold symmetry (C_{3h}, D_{3h}) have been investigated for which the significant tensor elements are given by $\beta_{zzz}=-\beta_{zyy}=-\beta_{yzy}=-\beta_{yyz}$. A number of reviews on such 2D NLO chromophores[6,20,21] including work on organometallic compounds[22,23] have been published. The second-order polarisabilities of highly symmetric 2D chromophores are usually investigated by hyper-Rayleigh scattering (HRS).[24–26] In contrast to the coherent frequency doubling in the direction of the laser beam used in electric-field-induced second-harmonic generation (EFISHG),[27,28] frequency doubling in the HRS experiment is incoherent and occurs in all directions of space. Far fewer investigations have been carried out on C_{2v}-symmetric dipolar 2D NLO chromophores with multiple donor–acceptor substitution.[6,21] A complete characterisation of chromophores of this symmetry requires a consistent combination of both polarised HRS and EFISHG measurements, sometimes supported by a third technique like electrooptical absorption measurements (EOAM).[8,29] Some of these chromophores exhibit deviations from Kleinman symmetry.[8]

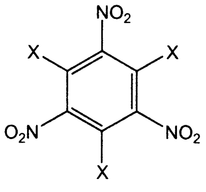
In this work we focused on the optimisation of 2D NLO chromophores with D_3 or D_{3h} symmetry, which have been shown to provide large β values at an improved efficiency/transparency ratio. A systematic study of 2D versus 1D NLO chromophores based on a central *S*-triazine or 1,3,5-tricyanobenzene moiety has demonstrated that these systems may exhibit nonlinear optical properties which compare very well with the best dipolar systems.[30] The systems 1,3,5-tris(diisopropylamino)-2,4,6-trinitrobenzene (**1**) and 1,3,5-trihydroxy-2,4,6-trinitrobenzene (**2**) yielded values for the second-order polarisability (β) comparable to that of *p*-nitroaniline, the prototype of a dipolar aromatic system.[11] In continuation of this work we extended the central π system by synthesising the donor–acceptor-substituted derivates of hexaphenylbenzene **3**, hexaphenylethynylbenzene **4** and the congener **13**, all three of which have approximately D_3 symmetry. Hexaphenylbenzenes have also gained considerable interest in material science owing to their remarkable electron transfer properties[31,32] and their ability to form liquid crystalline mesophases.[33–35] To the best of our knowledge no functionalised hexaphenylethynylbenzenes have been reported to date. Herein we report the synthesis of the novel 2D NLO chromophores **3**, **4** and **13**, their molecular structures and NLO properties.

Synthesis: *Retrosynthetic considerations*: Modern synthetic techniques provide several pathways to achieve our goal. Although low yields are often encountered in cyclotrimerisation processes, this protocol is the method of choice because it gives easy access to these highly substituted benzenes.[36–38] Although this type of reaction is well known,[39] cyclotrimerisation is still the object of current studies.[40–42] The most simple example is the cobalt-catalysed trimerisation of alkynes.[43] In our case, this means the trimerisations of **5** (Scheme 1) and **6** (Scheme 2).

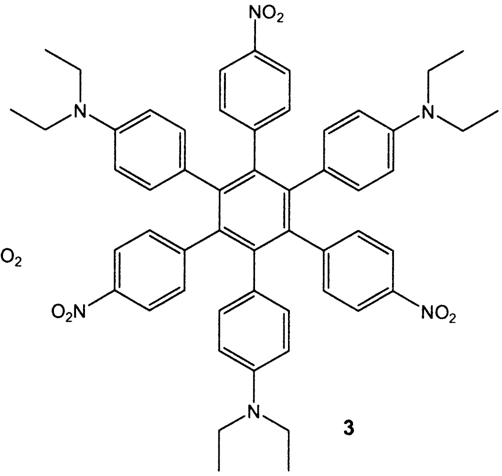
In both cases we face the problem of obtaining regioisomers; however, given the simplicity of the reaction and the availability of the starting materials it was tempting to try these approaches first.

For the synthesis of **4** we also considered a multistep approach using modern coupling procedures. Thus, starting from 1,3,5-trihalogeno-2,4,6-triiodobenzene (**8a**–**8c**), the tris- and hexaphenylethynyl-substituted product seemed to attainable. We planed to perform the step from **8** to **7** with a Sonogashira-type coupling. For the replacement of the chlorine substituents a Stille-type coupling seemed necessary.[44]

Synthesis of 3 and 4: Heating 4-*N*,*N*-diethylamino-4′-nitrotolane (**5**) in dioxane with dicobaltoctacarbonyl at 80–100 °C for 24 h afforded **3** in 9 % yield together with **9** (Scheme 3). Both isomers could be separated by chromatography on



X = N(*i*-C_3H_5) **1**
X = OH **2**



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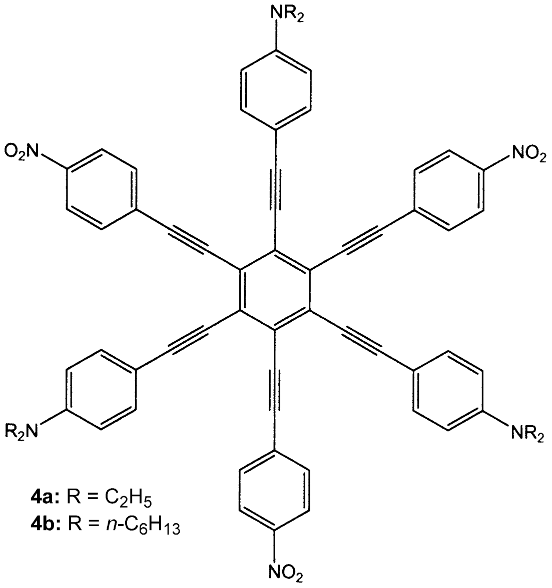
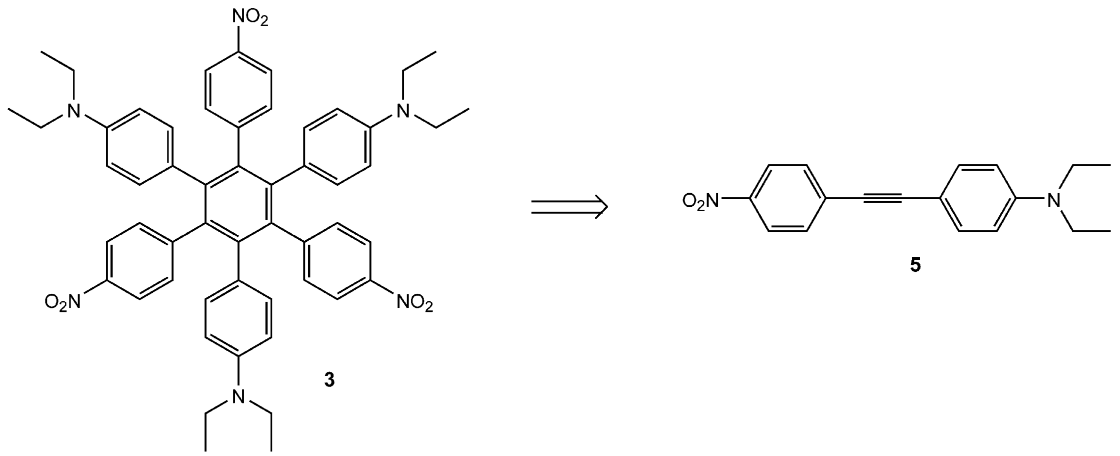
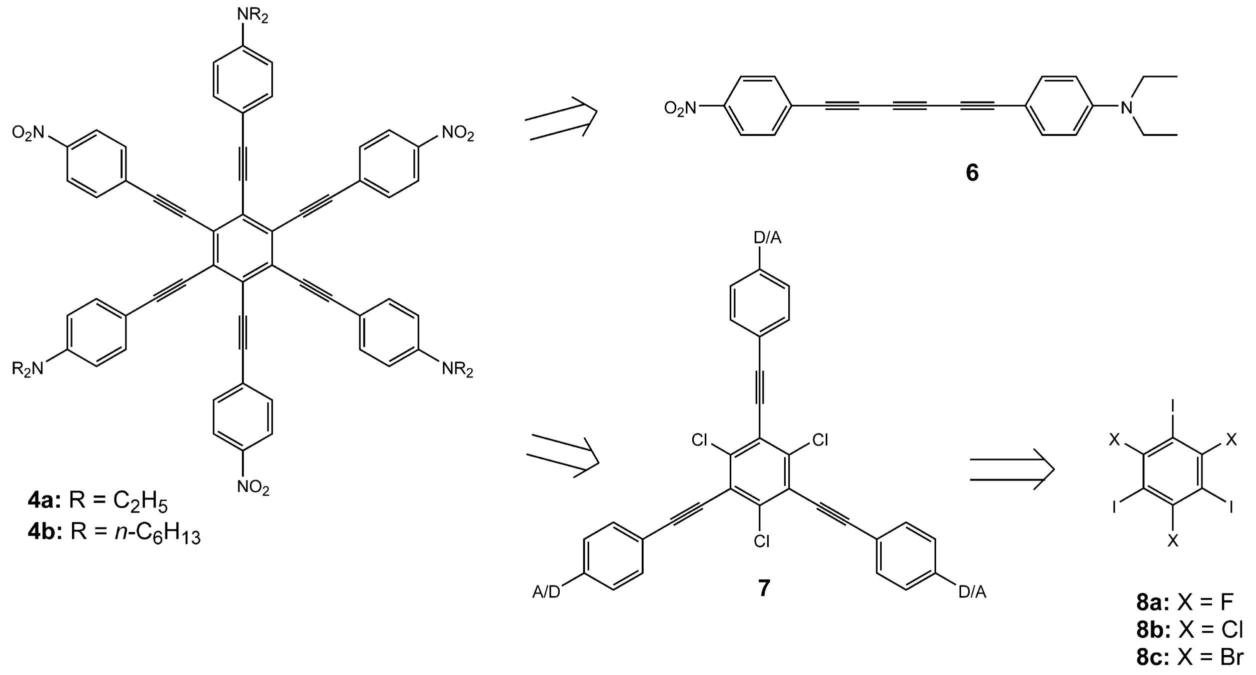


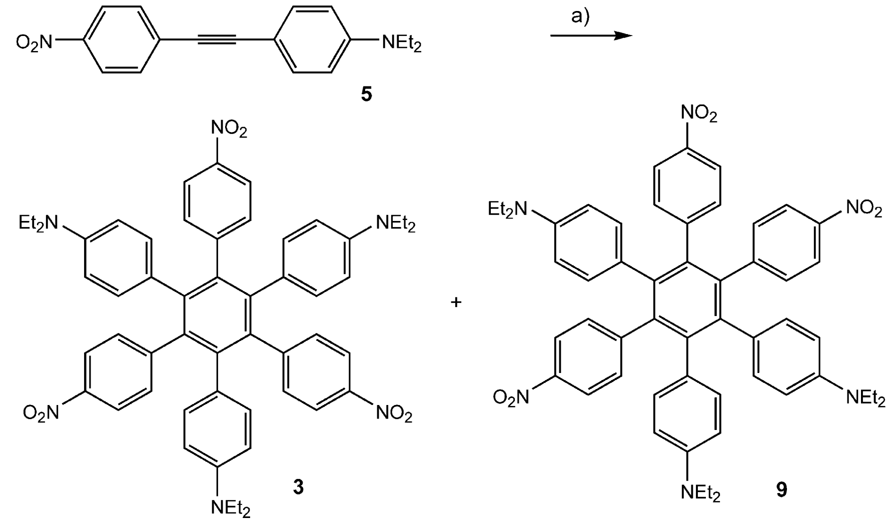
4a: R = C_2H_5
4b: R = *n*-C_6H_{13}



Scheme 1. Retrosynthetic analysis of compound **3**.



Scheme 2. Retrosynthetic analysis of **4**.



Scheme 3. a) $[Co_2(CO)_8]$, dioxane, 100 °C.

silica gel. The tolerance of the catalyst toward the nitro group is surprising.[45]

As a result of the strong twisting of the phenyl rings in **3** (see below) we also tried to synthesize the hexa-*peri*-benzocoronene with methods described in the literature;[46–48] unfortunately, this attempt failed. We therefore focused on the synthesis of **4**. Encouraged by the success of the transition-metal-induced trimerisation of **5** we first tried this pathway. The synthesis of the starting material, 1-(4-*N*,*N*-diethylaminophenyl)-6-(4-nitrophenyl)hexatriyne (**6**), was achieved by a Hay cross-coupling reaction[49] of (4′-nitrophenyl)butadiyne (**10**) with 4-(*N*,*N*-diethylaminophenyl)acetylene (**11**) in 30% yield (Scheme 4).

Initial attempts to cyclotrimerise **6** with catalysts[50–52] such as $[Pd(PhCN)_2Cl_2]$,[53] Me_3SiCl and Pd/C,[54] $[Cp_2ZrCl_2]$[55,56] and $[Co_2(CO)_8]$,[57] failed without any reaction. Ligands with high steric hindrance (1,1′-bis(diphenylphosphino)ferrocene nickel(II) chloride, dichloro-bis(tri-*n*-butylphosphine)nickel-(II)) were also tried without the desired result. Trimerisation of **6** occurs with $Ni(PPh_3)_2(CO)_2$[58–60] as catalyst; however, only 1,2,4-tris(4-*N*,*N*-diethylaminophenylethynyl)-3,5,6-tris-(4-nitrophenylethynyl)benzene (**12**) was detected (Scheme 4), and besides a couple of further trimerisation products, the desired 1,3,5 isomer was not found. Surprisingly, heating **6** with Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$[61] in dioxane afforded small amounts of **13** (Scheme 4). This reaction also occurred with $[Co(PPh_3)_3Cl]$[62] as catalyst, but the conversion was worse. It is noteworthy that the cyclotrimerisation takes place mainly with the alkyne unit at the nitrophenyl ring.

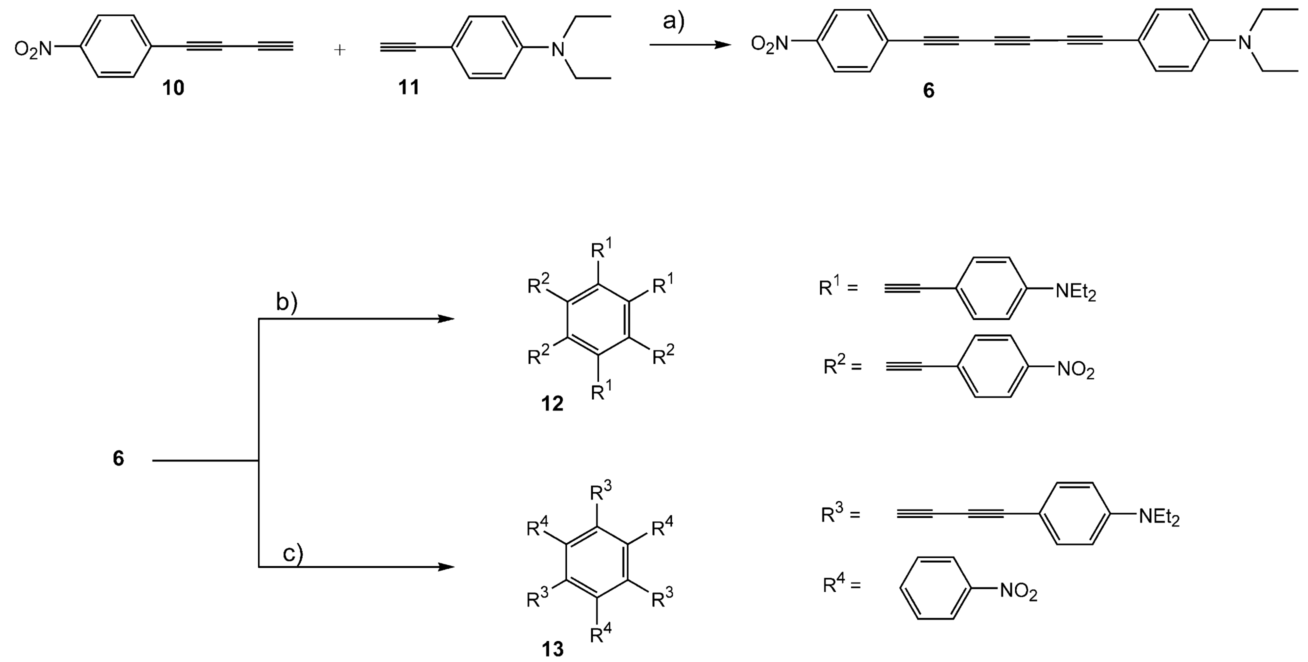
After this failure we examined a stepwise approach as indicated in Scheme 2 by using Pd-catalysed coupling reactions. 1,3,5-Trichloro-2,4,6-triiodobenzene[63] (**8b**), 1,3,5-tribromo-2,4,6-triiodobenzene (**8c**) and 1,3,5-trichloro-2,4,6-trifluorobenzene (**8a**) were coupled with the acceptor unit, 4-nitrophenylacetylene (**14**). However, the Sonogashira protocol[64–69] was only successful with **8b** as starting material to give 1,3,5-trichloro-2,4,6-tris(4-nitrophenylethynyl)benzene (**15**) in 50% yield (Scheme 5). In the cases of **8a** and **8c**, only reduction products were obtained in which an iodine centre was substituted by a hydrogen atom. Attempts to couple the donor unit first failed.

Purification of **15** was difficult as a result of its low solubility in common solvents. It was also not possible to achieve complete conversion in the Stille coupling of **11** to the threefold substituted **4a** with diethyl amino group as donor. In this experiment the main reaction was a twofold substitution. The resulting product was also difficult to purify as a result of its low solubility in common solvents. Therefore, we decided to carry out the originally planned Stille coupling (see above) with 4-*N*,*N*-dihexylaminophenylethynyltributylstannane (**21**) (Scheme 6).

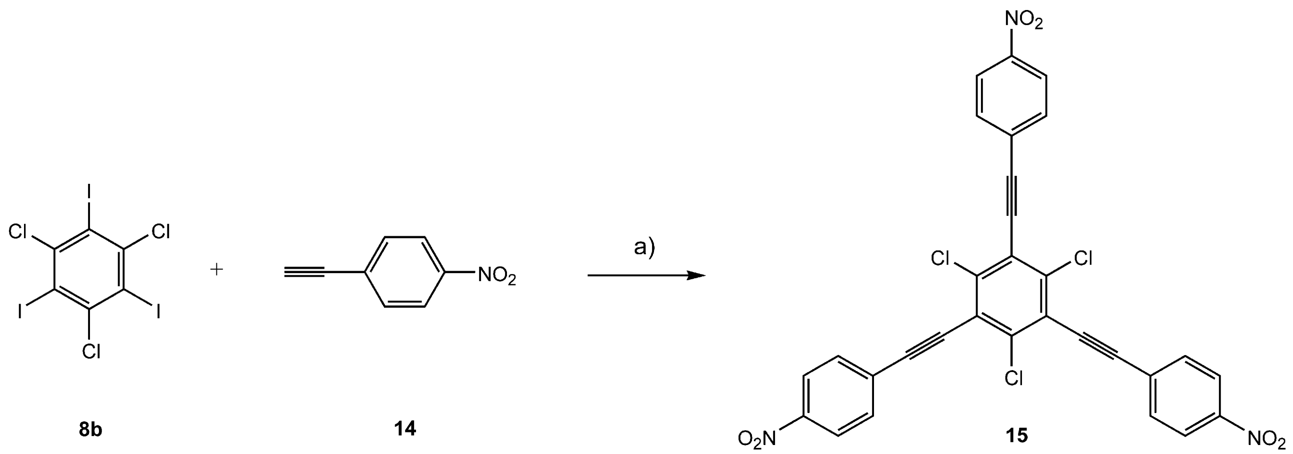
The synthesis of **21** was achieved in a four-step procedure by using conventional means. The readily available 4-iodo-*N*,*N*-dihexylaniline (**18**) was transformed into **19** by a Sonogashira coupling reaction with trimethylsilylacetylene. After removal of the protecting group the alkyne **20** was stannylated to afford **21** in an overall yield of 54% starting from 4-iodoaniline (**16**) and *n*-hexyliodide (**17**).

The final Stille coupling reaction between **15** and **21** afforded **4b** as a red-coloured product in 14% yield (Scheme 7). The product could easily be purified by chromatography owing to the presence of the hexyl groups. Interestingly, the reaction occurred only above 90 °C.

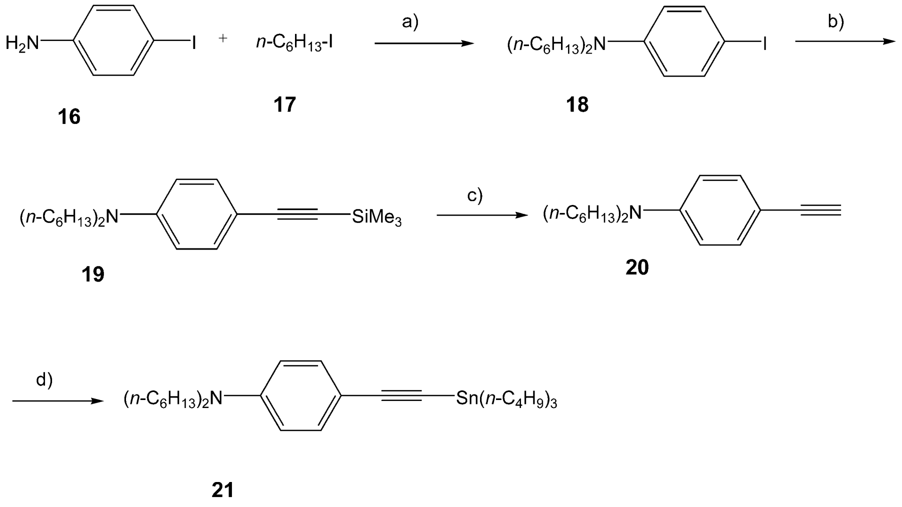
Structural investigations: We were able to grow single crystals of **3**, **4b** and **13** suitable for X-ray investigations and the results are presented in Figures 1–4. Crystals of **3** were obtained from a hexane/CH_2Cl_2 solution. The molecular structure of **3** has a strong torsion of the peripheral rings with re-



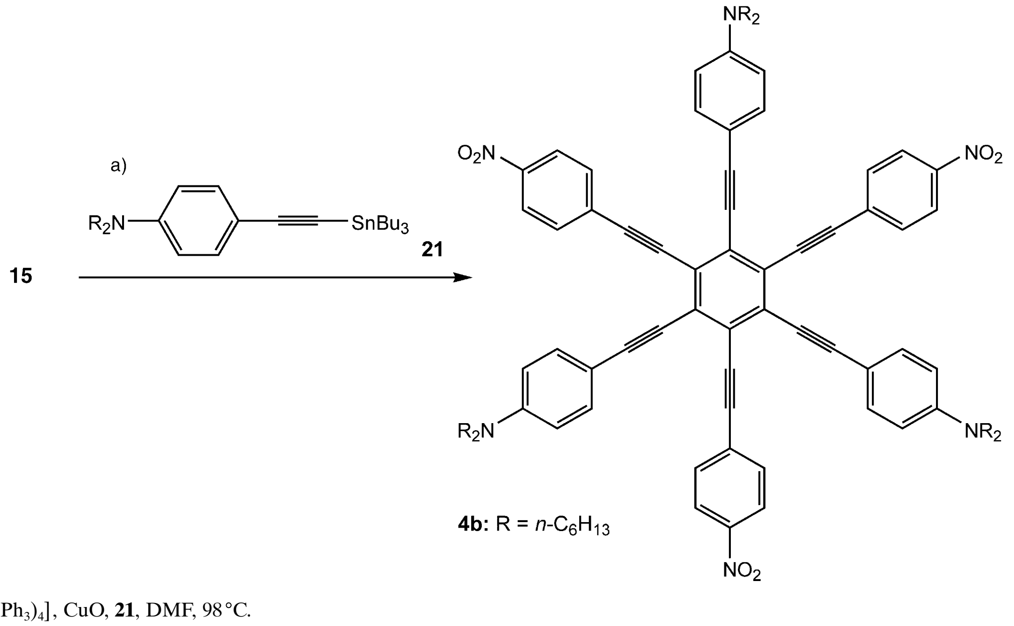
Scheme 4. a) CuCl, TMEDA, O_2; b) $[Ni(PPh_3)_2(CO)_2]$; c) $[Rh(PPh_3)_3Cl]$.



Scheme 5. a) [Pd(PPh$_3$)$_4$], CuI, HN(iC$_3$H$_5$)$_2$, THF.



Scheme 6. a) Na$_2$CO$_3$, DMF, 120 °C, 20 h; b) HC≡C–SiMe$_3$, [Pd(PPh$_3$)$_4$], CuI, HNEt$_2$; c) KOH, H$_2$O/EtOH, d) nBuLi/THF, (nC$_4$H$_9$)$_3$SnCl.



Scheme 7. a) [Pd(PPh$_3$)$_4$], CuO, **21**, DMF, 98 °C.

spect to the central benzene nucleus (Figure 1). The interplanar angles between the peripheral and central phenyl rings vary between 54° and 75°. The nitro and diethylamino groups are nearly oriented coplanar to the adjacent phenyl rings. The bond lengths of the central ring are between 1.40 Å and 1.41 Å and are therefore a little bit longer than the normal value.[70] The bond lengths within the peripheral phenyl rings and between phenyl rings and substituents vary within the usual range. In the solid state we observe a weak interaction between nitro groups of neighbouring ring systems. The close contact distance between the oxygen centre of one NO_2 group and the nitrogen atom of the other is 2.97(4) Å. This value is close to that calculated from the van der Waals radii[71] (N = 1.5 Å, O = 1.4 Å) of both atoms. Interestingly, there is no evidence for a close contact between the amino and nitro groups.

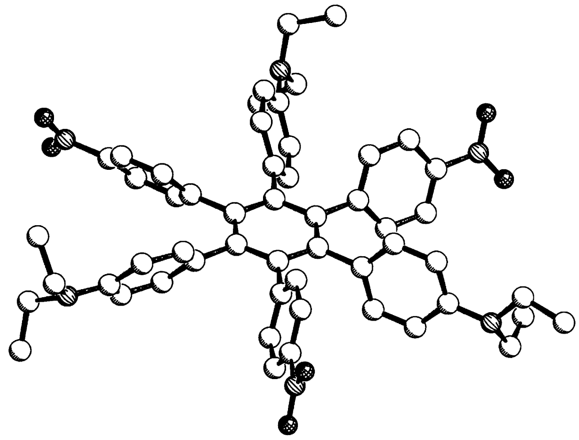


Figure 1. Molecular structure of **3**. Hydrogen atoms were omitted for the sake of clarity; nitrogen and oxygen atoms are hatched.

The molecular structure of **4b** is presented in Figure 2. Crystals of **4b** suitable for X-ray diffraction were obtained from a dioxane solution. The introduction of the alkyne spacer units successfully improves the planarity of the molecule. The interplanar angles between the peripheral and central phenyl rings vary between 1° and 26° (Figure 2). The bond length of the aminophenyl rings has a significant chinoid distortion in the range of 3σ. The nitro and dihexylamino groups are oriented coplanar to the adjacent rings. Similar to the molecular structure of **3**, there is a close contact of 3.24(1) Å between the oxygen centre of one NO_2 group and the nitrogen atom of another. As shown in Figure 3, these nitro groups with close contacts are situated on an axis in the crystal and are involved in the build up of the crystal.

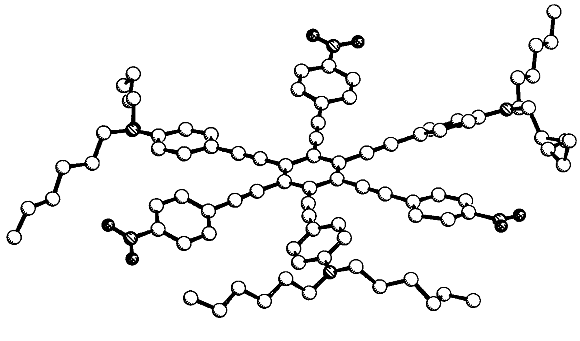


Figure 2. Molecular structure of **4b**. Hydrogen atoms were omitted; nitrogen and oxygen atoms are hatched.

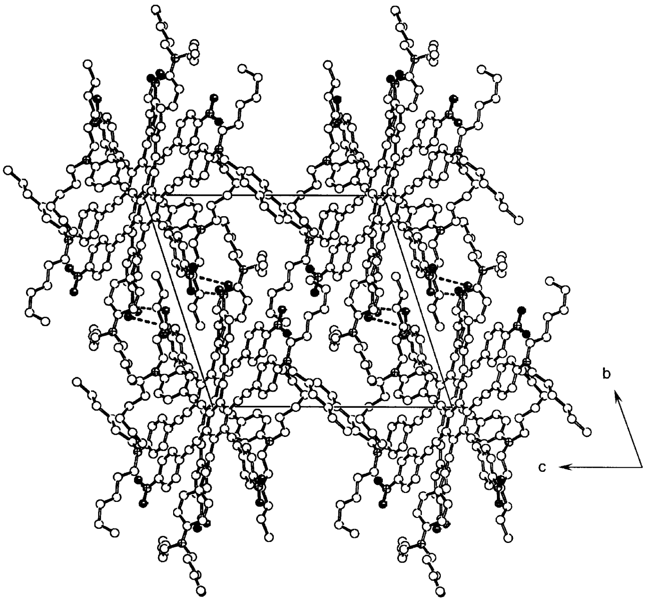


Figure 3. Packing arrangement of **4b**. View along the crystallographic *a* axis. Hydrogen atoms were omitted; nitrogen and oxygen atoms are hatched. Intermolecular N–O contacts are indicated by fragmented lines.

The molecular structure of **13** is presented in Figure 4. Crystals of **13** suitable for X-ray diffraction were obtained from an *n*-heptane/CH_2Cl_2 solution. The interplanar angles between the central ring and the nitrophenyl rings are a little bit reduced (50–67°) relative to those of **3**. The corresponding angles of the diethylaminophenyl rings are not coherent (23–83°). As in the previous cases the donor and acceptor groups are situated in the plane of the adjacent phenyl ring.

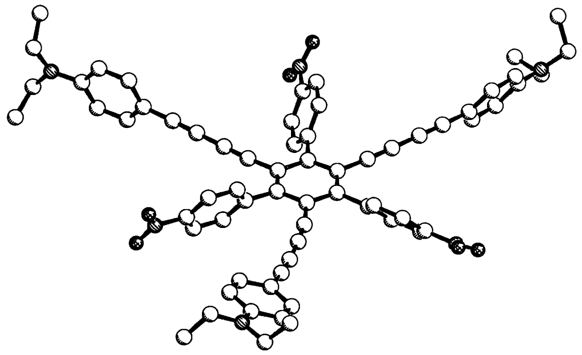


Figure 4. Molecular structure of **13**. Hydrogen atoms and the CH_2Cl_2 molecules included were omitted; nitrogen and oxygen atoms are hatched.

Determination of linear and nonlinear optical properties: The UV/Vis spectra of **3**, **4b** and **13** in 1,4-dioxane are displayed in Figure 5. All chromophores exhibit spectra with an intense absorption below 500 nm. The spectrum of the sterically crowded and distorted hexaphenylbenzene derivative **3** has no clear maximum, which is consistent with its strongly distorted structure (discussed above). On the other hand, owing to reduced steric hindrance, **4b** and **13** have more pronounced CT transition maxima with a transition wavelength of 453 nm and 431 nm, respectively; these are bathochromically shifted with respect to that of **3**.

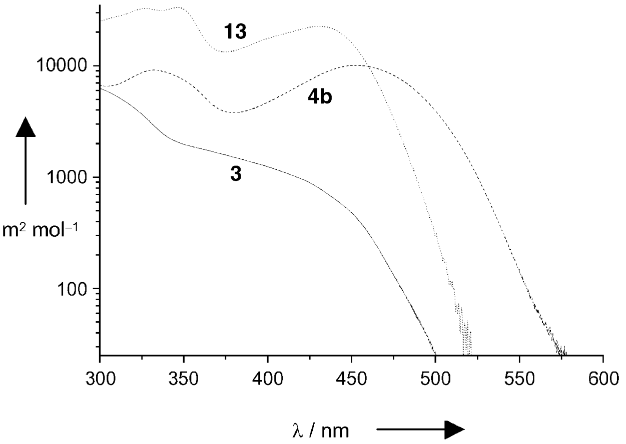


Figure 5. UV/Vis spectra of **3** (full line), **4b** (dashed) and **13** (dotted) in 1,4-dioxane at 298 K.

Since the 2D NLO chromophores **3**, **13** and **4b** have no dipole moment it is not possible to determine their second-order polarisabilities by EFISHG. Instead the HRS method was applied which does not rely on the dipolar alignment of the chromophores in an externally applied electric field. The HRS signal is generated by incoherent scattering caused by fluctuations of the second-order susceptibility of the solution. In contrast to linear Rayleigh scattering at frequency ω, the intensity of the HRS signal ($S^{2\omega}$) at frequency 2ω is quadratically dependent on the irradiance of the fundamental beam (I^{ω}) of the form $S^{2\omega} = C_q(I^{\omega})^2$ where C_q is a quadratic fit parameter related to the number densities of solute and solvent and to rotational averages of their second-order polarisabilities $\langle\beta^2\rangle$.[26,72,73] The fit parameter is usually linearly dependent on the solute concentration, and a suitable regression allows one to separate solute from solvent contributions and to determine β. The HRS signal can be detected under different polarisation conditions (i.e. with parallel (*ZZ*) or perpendicular orientation (*ZX*) relative to the polarisation of the incident light). For the highly symmetrical 2D NLO chromophores in this work measurements under parallel polarisation conditions were sufficient to determine β. The results of the HRS measurements with different concentrations of **3** and **4b** in 1,4-dioxane solution are displayed in Figure 6, and those for **13** are displayed in Figure 7. The HRS signals of **3**, **13** and **4b** are clearly quadratically dependent on the fundamental intensity at low concentrations. Slight deviations from the quadratic behaviour were observed at lower fundamental intensity for higher concentrations only. The quadratic fit parameters (C_q) obtained are plotted against the concentrations of **3**, **13** and **4b** in Figures 8–10 and show a nonlinear dependence on the concentrations in contrast to the expected linear behaviour. The largest deviations are observed for concentrated solutions and are the result of absorption at the second-harmonic wavelength of 532 nm. The absorption losses were taken into account by a correction factor derived from the Lambert–Beer law and final fits in Figures 8–10 were carried out with this correction over the whole concentration range. The slope at vanishing concentration ($c \rightarrow 0$) was determined from the linear part of the fit formula, and β values for **3**, **13** and **4b** were calculated relative to the measured slope of the 4-nitroaniline (*p*NA) reference. The HRS signals were checked for possible fluorescence contributions by using notch filters with different bandwidth or fluorescence quenchers.[11] These additional experiments showed that the observed HRS signals are free from fluorescence. The results of the UV/Vis and the HRS measurements are summarised in Table 1.

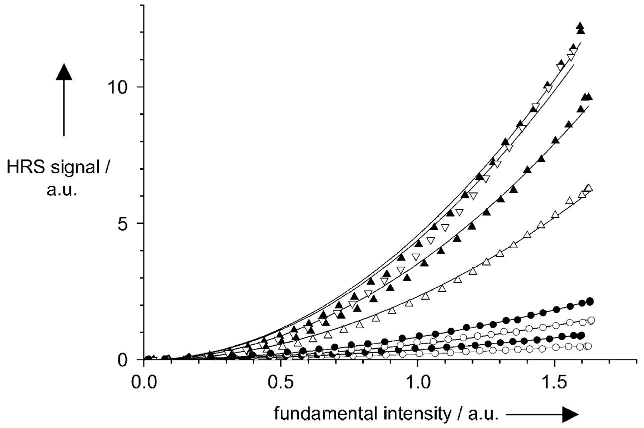


Figure 6. HRS signals $S^{2\omega}$ as a function of the fundamental intensity I^{ω} of **3** (circles, $c = 1.3$, 2.7, 5.4, 11.0 mol m^{-3}) and **4b** (triangles, $c = 0.10$, 0.19, 0.39, 0.80 mol m^{-3}) in 1,4-dioxane for increasing concentration *c*.

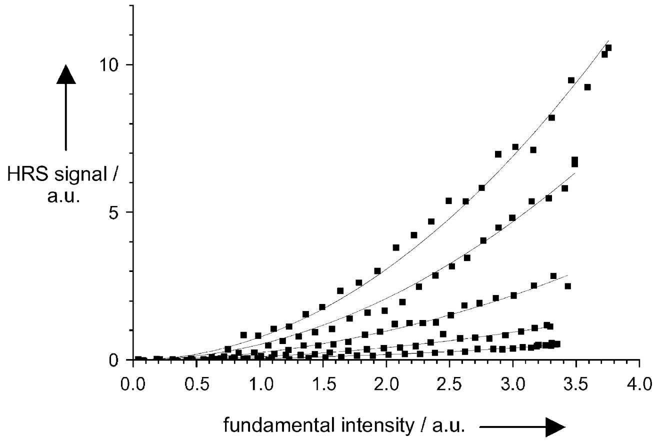


Figure 7. HRS signals $S^{2\omega}$ as function of the fundamental intensity I^{ω} of **13** ($c = 0.03$, 0.06, 0.11, 0.26, 0.40 mol m^{-3}) in dioxane for increasing concentration *c*.

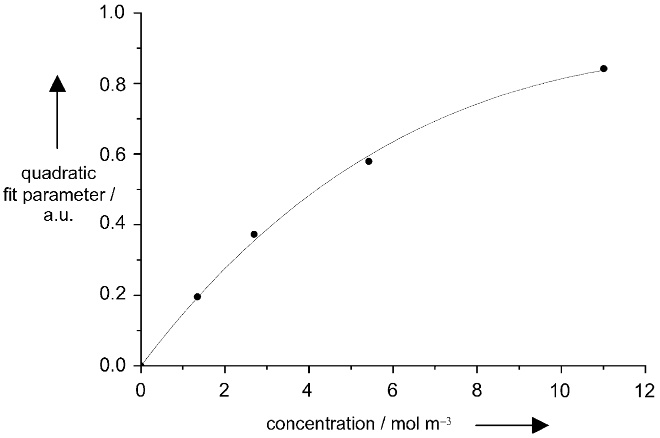


Figure 8. Quadratic fit parameter C_q of the HRS measurements of **3** in 1,4-dioxane.

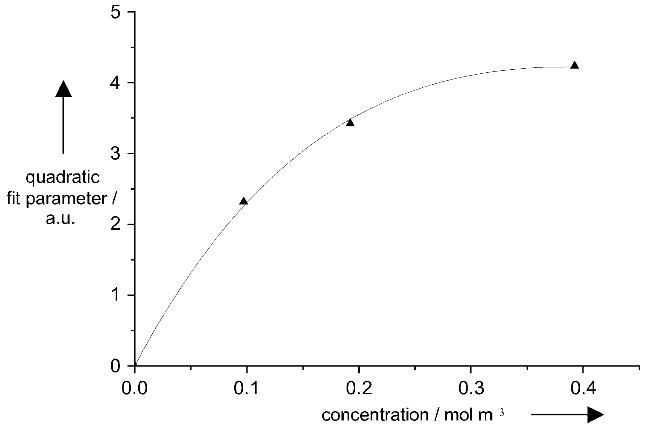


Figure 9. Quadratic fit parameter C_q of the HRS measurements of **4b** in 1,4-dioxane.

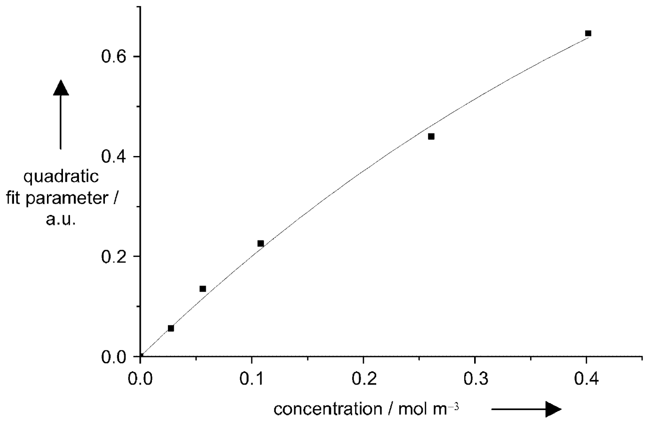


Figure 10. Quadratic fit parameter C_q of the HRS measurements of **13** in 1,4-dioxane.

The most striking point in the comparison of **3**, **13** and **4b** is the dramatic increase of the second-order polarisability (β). According to theory, the value of **13** is larger than for **3** owing to the bisalkyne units which cause reduced steric hindrance, but smaller than **4b**, because the nitrophenyl rings in **13** are still distorted. The value of **4b** is one of the largest second-order polarisabilities reported in the literature for nondipolar 2D NLO chromophores.[30] Compounds **13** and **4b** differ in one main structural feature, the extra acetylene units in the latter. These units increase the conjugation length and efficiently reduce the steric hindrance between the phenyl groups. This allows a more planar conformation and strongly enhances the π conjugation between the donor and acceptor groups of the molecule. Another consequence of the elongated π system is the reduced HOMO–LUMO energy gap which contributes to the higher β value but also leads to a loss of transparency as a result of the bathochromic shift of the absorption band. Nevertheless, the transparency of **4b** is still remarkably good in the observed region, and the absorption losses are only small.

Table 1. Linear and nonlinear optical properties of **3**, **4b** and **13** derived from UV/Vis and HRS measurements.

Substance	**3**	**4b**	**13**
λ_{ag} [nm]	382 (shoulder)	453	431
ε_{max} [m^{2}mol^{-1}]	1480	10100	22613
$\langle\beta^2\rangle^{1/2}_{ZZ}$ [10^{-50} Cm^{3}V^{-2}]	58 ± 9	800 ± 67	258 ± 60
β_{zzz} [10^{-50} Cm^{3}V^{-2}]	120 ± 20	1670 ± 140	537 ± 126

Conclusion

Three donor–acceptor hexasubstituted benzenes were synthesised and successfully characterised by hyper-Rayleigh scattering (HRS) as novel nonlinear optical (NLO) chromophores with threefold symmetry. Steric hindrance in these highly substituted compounds may be efficiently reduced by introduction of acetylene bridges. The concomitant increase of conjugation length led to NLO chromophores with second-order polarisability among the highest obtained so far for two-dimensional (2D) nondipolar NLO chromophores.

Experimental Section

General: Reactions were carried out in oven-dried (120 °C) glassware under argon and with magnetic stirring. THF was dried by distillation over sodium. DMF (Acros) was used as purchased. Starting materials and chemicals were obtained from commercial sources. *p*-Iodoaniline (Aldrich) and tributyltin chloride (Fluka) were used without further purification. Trimethylsilylacetylene,[74] tetrakis(triphenylphosphine)palladium,[75] 1,3,5-trichloro-2,4,6-triiodobenzene,[76] 4-*N*,*N*-diethylamino-4′-nitrotolane,[77] (4-nitrophenyl)butadiyne and diethylaminophenylacetylene[78] were synthesised by literature methods. Schlenk techniques were used for reactions performed under inert gas. Melting points were recorded on a Büchi B-540 and are uncorrected. NMR spectra were measured at 300.133 MHz for ^{1}H and 75.469 MHz for ^{13}C. Microanalyses were performed at the Analytical Laboratory of Heidelberg University.

HRS experiments were carried out in 1,4-dioxane (dried over sodium/potassium alloy and distilled prior to use) following a previously described protocol.[11,29] A 1 % wt solution of 4-nitroaniline (*p*NA) in 1,4-dioxane was used as an external standard, and a value of $\beta_{zzz}=27.4\times10^{-50}$ Cm^{3}V^{-2} was used for *p*NA as determined by EFISHG measurements.[8] Optical absorption spectra were recorded on a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer. The temperature was adjusted to

298 K by a Lauda Ecoline 200 Thermostat. The spectra were recorded in 1-cm quartz cells.

1,3,5-Tris(4-*N*,*N*-diethylaminophenyl)-2,4,6-tris(4-nitrophenyl)benzene (3) and 1,2,4-tris(4-*N*,*N*-diethylaminophenyl)-3,5,6-(4-nitrophenyl)benzene (9): A mixture of 4-*N*,*N*-diethylamino-4′-nitrotolane **5** (1.00 g, 4.00 mmol) and dicobaltoctacarbonyl (370 mg, 1.08 mmol) in dry dioxane (10 mL) was stirred under an atmosphere of argon at 100 °C. The reaction was monitored by TLC (silica gel, toluene/ethyl acetate, 1:1). Two new green spots (probably due to intermediates) were formed and further dicobaltoctacarbonyl was then added in small amounts (50 mg) until these spots disappeared. After 8 h the solvent was removed in vacuo, and the residue was passed through silica gel (toluene/ethyl acetate, 1:1). The isomers were separated by column chromatography (silica gel, toluene/ethyl acetate, 40:1) to yield 1,3,5-tris(4-*N*,*N*-diethylaminophenyl)-2,4,6-tris(4-nitrophenyl)benzene (**3**) (94 mg, 9.3 %) as red–orange crystals and 1,2,4-tris(4-*N*,*N*-diethylaminophenyl)-3,5,6-tris(4-nitrophenyl)benzene (**9**) (120 mg, 12 %) as a red solid. (**3**): M.p. 283 °C; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 272 (58918), 302 nm (67032 $M^{-1}cm^{-1}$); ^1H NMR (300 MHz, CD_2Cl_2): δ = 0.97 (t, ^3J = 7.0 Hz, 18 H), 3.15 (q, ^3J = 7.0 Hz, 12 H), 6.21 (d, ^3J = 8.8 Hz, 6 H), 6.54 (d, ^3J = 8.8 Hz, 6 H), 7.05 (d, ^3J = 8.8 Hz, 6 H), 7.79 ppm (d, ^3J = 8.8 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.07, 44.11, 110.99, 121.84, 125.92, 132.12, 132.50, 139.24, 141.00, 145.36, 146.24, 149.02 ppm; MS (FD$^+$): *m*/*z*: 882.3 ([M^+], 100); elemental analysis calcd (%) for $C_{54}H_{54}N_6O_6$ (883.00): C 73.45, H 6.16, N 9.52; found: C 79.29, H 6.12, N 9.52. (**9**): M.p. 258–264 °C; ^1H NMR (300 MHz, CD_2Cl_2): δ = 0.95–0.99 (18 H, m), 3.09–3.19 (12 H, m), 6.19 (d, ^3J = 8.8 Hz, 2 H), 6.23 (d, ^3J = 8.8 Hz, 2 H), 6.24 (d, ^3J = 8.8 Hz, 2 H), 6.53 (d, ^3J = 8.8 Hz, 2 H), 6.58 (d, ^3J 8.8 Hz, 2 H), 6.59 (d, ^3J = 8.8 Hz, 2 H), 7.02 (d, ^3J = 8.8 Hz, 4 H), 7.04 (d, ^3J = 8.8 Hz, 2 H), 7.76 (d, ^3J = 8.8 Hz, 4 H), 7.77 ppm (d, ^3J = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.09, 12.14, 44.17, 44.11, 111.01, 111.05, 121.84, 122.16, 122.18, 125.65, 126.48, 126.75, 132.14, 132.21, 132.24, 132.31, 132.37, 132.44, 137.93, 139.17, 139.75, 140.47, 140.93, 142.16, 143.35, 145.66, 145.71, 146.03, 146.27, 148.27, 148.51, 149.23 ppm; MS (FD$^+$): *m*/*z*: 882.3 ([M^+], 100); HRMS(FAB$^+$): *m*/*z* calcd for $C_{54}H_{54}N_6O_6$ ([M^+]): 882.4116; found: 882.4116.

1-(4-*N*,*N*-Diethylaminophenyl)-6-(4-nitrophenyl)hexatriyne (6): Cu catalyst [from CuCl (1 g) and TMEDA (0.5 mL) in acetone (20 mL); the formation of the catalyst was finished when the temperature of the stirred suspension decreased] was added to a solution of (4-nitrophenyl)butadiyne (**10**) (1.52 g, 8.88 mmol) and 4-*N*,*N*-diethylaminophenylacetylene (**11**) (2.24 g, 12.9 mmol) in acetone (200 mL) and the mixture was stirred overnight. Water (200 mL) was then added and the mixture was extracted with Et_2O and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel, petroleum ether/toluene/CH_2Cl_2, 9:4:1) to yield 1-(4-*N*,*N*-diethylaminophenyl)-6-(4-nitrophenyl)hexatriyne (**6**) (0.92 g, 30.3 %) as orange crystals. M.p. > 182 °C (decomp); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (45347), 288 (22800), 306 (24067), 324 (32173), 344 (40407), 364 (45473), 386 (36733), 450 nm (22800 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 2973, 2188, 2161, 2093, 1601, 1588, 1521, 1409, 1377, 1194 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.17 (t, ^3J = 7.0 Hz, 6 H), 3.15 (q, ^3J = 7.0 Hz, 4 H), 6.21 (d, ^3J = 8.8 Hz, 2 H), 6.54 (d, ^3J = 8.8 Hz, 2 H), 7.05 (d, ^3J = 8.8 Hz, 2 H), 7.79 ppm (d, ^3J = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.32, 44.52, 65.24, 70.36, 72.50, 76.21, 79.48, 83.31, 104.47, 111.28, 123.72, 128.45, 133.65, 134.93, 147.69, 149.10 ppm; MS (EI$^+$): *m*/*z* (%): 342 (66, [M^+]), 327 (100, [M^+-CH_3]), 312 (10, [$M^+-CH_3-CH_3$]); elemental analysis calcd (%) for $C_{22}H_{18}N_2O_2$ (342.37): C 77.17, H 5.30, N 8.22; found: C 76.91, H 5.25, N 8.18.

1,2,4-Tris(4-*N*,*N*-diethylaminophenylethynyl)-3,5,6-tris(4-nitrophenylethynyl)benzene (12): A solution of 1-(4-*N*,*N*-diethylaminophenyl)-6-(4-nitrophenyl)hexatriyne (**6**) (417 mg, 1.22 mmol) and bis(triphenylphosphine)nickel dicarbonyl (0.205 g, 0.321 mmol) in benzene (15 mL) was heated for 2 h at reflux. After the mixture had been cooled to room temperature, the solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, petroleum ether/CH_2Cl_2, 1:1) to give 1,2,4-tris(4-*N*,*N*-diethylaminophenylethynyl)-3,5,6-tris(4-nitrophenylethynyl)benzene (**12**) (75 mg, 18 %) as a red powder. M.p. > 250 °C (decomp); ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.10–1.17 (m, ^3J = 7.0 Hz, 18 H), 3.30–3.40 (m, ^3J = 7.0 Hz, 12 H), 6.53 (d, ^3J = 8.8 Hz, 2 H), 6.54 (d, ^3J = 8.8 Hz, 2 H), 6.56 (d, ^3J = 8.8 Hz, 2 H), 7.17 (d, ^3J = 8.8 Hz, 2 H), 7.29 (d, ^3J = 8.8 Hz, 2 H), 7.32 (d, ^3J = 8.8 Hz, 2 H), 7.35 (d, ^3J = 8.8 Hz, 2 H), 7.36 (d, ^3J = 8.8 Hz, 2 H), 7.80 (d, ^3J = 8.8 Hz, 2 H), 8.09 (d, ^3J = 8.8 Hz, 2 H), 8.13 (d, ^3J = 8.8 Hz, 2 H), 8.41 ppm (d, ^3J = 8.8 Hz, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.30, 12.34, 44.45, 44.47, 71.16, 71.71, 71.83, 77.16, 77.33, 77.96, 84.85, 86.19, 86.27, 88.21, 88.46, 89.05, 105.22, 105.53, 105.55, 111.15, 111.19 , 111.20, 122.31, 123.21, 123.30, 123.46, 126.35, 126.47, 131.24, 131.48, 134.22, 134.37, 134.39, 144.52, 144.70, 144.71, 146.22, 147.34, 147.39, 148.04, 148.81, 148.83 ppm; MS: (FAB$^+$): *m*/*z* (%): 1026 ([M^+]), 1027 ([M^++H]); HRMS (FAB$^+$): *m*/*z* calcd for $C_{66}H_{54}N_6O_6$ ([M^+]): 1026.4105; found: 1026.4083.

1,3,5-Tris(4-*N*,*N*-diethylaminophenylbutadiynyl)-2,4,6-tris(4-nitrophenyl)benzene(13): A mixture of 1-(4-*N*,*N*-diethylaminophenyl)-6-(4-nitrophenyl)hexatriyne (**6**) (685 mg, 2.00 mmol) and [$Rh(PPh_3)_3Cl$] (140 mg, 0.15 mmol) in dry dioxane (20 mL) was stirred under an atmosphere of argon at 100 °C for three days. During this period some catalyst (50 mg) was added in small amounts. Column chromatography (silica gel, light petroleum ether/CH_2Cl_2, 4:6) gave small amounts of **13** as red crystals. M.p. > 220 °C (decomp); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (53176), 330 (109775), 346 (114568), 430 nm (80334 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 2973, 2927, 2198, 2133, 1738, 1633, 1601, 1521, 1348 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.13 (t, ^3J = 7.1 Hz, 18 H), 3.34 (q, ^3J = 7.0 Hz, 12 H), 6.52 (d, ^3J = 9.1 Hz, 6 H), 7.19 (d, ^3J = 9.1 Hz, 6 H), 7.79 (d, ^3J = 8.8 Hz, 6 H), 8.39 ppm (d, ^3J = 8.8 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 12.59, 44.74, 71.30, 76.83, 85.23, 87.97, 105.47, 111.42, 123.00, 123.67, 131.52, 134.51, 145.22, 146.63, 148.28, 149.07 ppm; MS (FAB$^+$): *m*/*z* (%): 1026 ([M^+], 100), 1011 ([M^+-CH_3], 25); HRMS (FAB$^+$): *m*/*z* calcd for $C_{66}H_{54}N_6O_6$ ([M^+]): 1026.4105; found: 1026.4078.

1,3,5-Trichloro-2,4,6-tris(4-nitrophenylethynyl)benzene (15): A mixture of 4-nitrophenylacetylene (**14**) (4.53 g, 30.78 mmol), 1,3,5-trichloro-2,4,6-triiodobenzene (**8b**) (4.41 g, 7.89 mmol), [$Pd(PPh_3)_4$] (1.23 g, 1.06 mmol), CuI (0.40 g, 2.12 mmol) and diisopropylamine (2.87 g, 28.36 mmol) in dry THF (125 mL) was heated at reflux under argon overnight. The colour of the solution turned to red and a yellow–brown precipitate was formed. After the mixture had been cooled to room temperature, the precipitate was filtered off, washed first with warm water and then with CH_2Cl_2 until the colour of the precipitate was yellow. Repeated recrystallisation in toluene or dioxane yielded **15** (2.61 g, 53.6 %) as colourless needles, which might still have traces of the side product, bis(4-nitrophenyl)butadiyne. M.p. > 320 °C (decomp); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 256 (30363), 336 nm (107520 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 1594, 1520, 1372, 856 cm^{-1}; ^1H NMR (300 MHz, $C_2D_2Cl_4$): δ = 7.83 (d, J = 7.9 Hz, 6 H), 8.30 ppm (d, J = 7.9 Hz, 6 H); ^{13}C NMR (75.5 MHz, $C_2D_2Cl_4$): δ = 97.62, 99.20, 99.78, 122.84, 123.70, 128.59, 132.68, 148.38 ppm; MS (EI$^+$, 70 eV): *m*/*z* (%): 617 (100, [M^+]); 587 (15, [M^+-NO]); elemental analysis calcd (%) for $C_{30}H_{12}N_3O_6Cl_3$ (616.80): C 58.42, H 1.96, N 6.81, Cl 17.24; found: C 58.15, H 2.23, N 6.70, Cl 17.18.

4-Iodo-*N*,*N*-dihexylaniline (18): 1-Iodohexane (**17**) (51.6 mL, 348 mmol) and Na_2CO_3 (19.2 g, 182 mmol) were added to a solution of *p*-iodoaniline (**16**) (23.12 g, 105.56 mmol) in DMF (320 mL) and stirred at 120 °C for 20 h. Further 1-iodohexane (18 mL, 121.38 mmol) was added to the reaction picture and the mixture stirred at 120 °C for an additional 2 h. After the mixture had been cooled to room temperature, the solution was separated from the resulting salts by filtration and the solvent was removed in vacuo. The remainder was dissolved in CH_2Cl_2 and washed with brine (100 mL) and then dried. The residue was purified by chromatography (silica gel, light petroleum ether/CH_2Cl_2, 7:3) to give **18** (28.85 g, 70.5 %) as a clear oil. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 276 (43379), 304 nm (5449 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2926, 2856, 2588, 2552, 1498, 1466, 1370, 1253, 1194, 801 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.4 Hz, 6 H), 1.29 (m, 12 H), 1.50–1.54 (m, 4 H), 3.19 (t, ^3J = 7.7 Hz, 4 H), 6.39 (d, J = 8.9 Hz, 2 H), 7.40 ppm (d, J = 8.9 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.01, 22.65, 26.78, 27.01, 31.69, 51.00, 75.33, 114.03, 137.62, 147.64 ppm; MS (EI$^+$, 70 eV): *m*/*z* (%): 387 (43, [M^+]), 316 (100, [$M^+-C_5H_{11}$]); elemental analysis calcd (%) for $C_{18}H_{30}NI$ (387.34): C 55.81, H 7.81; N 3.62, I 32.76; found: C 55.96, H 7.82, N 3.65, I 32.96.

4-*N*,*N*-Dihexylaminophenyltrimethylsilylacetylene (19): A mixture of **18** (20.00 g, 51.63 mmol), trimethylsilylacetylene (6.59 g, 67.11 mmol), [$Pd(PPh_3)_4$] (577 mg, 0.5 mmol) and CuI (190 mg, 0.1 mmol) in degassed Et_2NH (75 mL) was stirred at 50 °C under argon for 2 h. The formation of two phases was observed. The top phase was decanted and the bottom phase was washed with Et_2O three times. The ether phase was combined with the Et_2NH phase and the solvent was removed. Column chromatography (silica gel, light petroleum ether) gave **19** (15.74 g, 85.2 %) as a yellow oil. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 304 (27952), 312 nm (28560 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 2956, 2928, 2858, 2149, 1607, 1517, 1467, 1370, 1248, 864, 841 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2): δ = 0.22 (s, 9H), 0.90 (t, ^3J = 6.62 Hz, 6H), 1.32 (m, 12H), 1.50–1.54 (m, 4H), 3.26 (t, ^3J = 7.7 Hz, 4H), 6.53 (d, J = 9.2 Hz, 2H), 7.25 ppm (d, J = 9.2 Hz, 2H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 0.29, 14.20, 23.08, 27.14, 27.52, 32.11, 51.25, 91.00, 107.16, 108.73, 111.43, 133.42, 148.64 ppm; MS (EI^+, 70 eV): *m/z* (%): 357 (68, [M^+]), 286 (100, [$M^+ - C_5H_{11}$]); elemental analysis calcd (%) for $C_{23}H_{39}NSi$ (357.65): C 77.24, H 10.99; N 3.92, Si 7.85; found: C 77.27, H 10.98, N 3.95.

4-*N,N*-Dihexylaminophenylacetylene (20): KOH (2.82 g, 50.32 mmol) in H_2O (5 mL) was added to a solution of **19** (15.00 g, 41.94 mmol) in EtOH (90 mL) and the mixture was heated at reflux for 10 min. The solvent was removed and the residue was dissolved in Et_2O. The organic layer was washed with brine (100 mL) and then dried. After evaporation **20** (11.79 g, 98%) was obtained as an orange oil and was used for analysis without further purification. UV/Vis (CH_2Cl_2): λ_{max} (ε): 296 nm (30207 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 3309, 2955, 2928, 2857, 2101, 1609, 1517, 1466, 1370, 1202, 813 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, ^3J = 6.6 Hz, 6H), 1.32 (m, 12H), 1.50–1.54 (m, 4H), 2.98 (s, 1H), 3.27 (t, ^3J = 7.7 Hz, 4H), 6.55 (d, J = 9.2 Hz, 2H), 7.29 ppm (d, J = 9.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.19, 23.07, 27.13, 27.48, 32.11, 51.25, 74.63, 85.34, 107.52, 111.45, 133.57, 148.77 ppm; MS (EI^+, 70 eV): *m/z* (%): 285 (48, M^+), 214 (100, $M^+ - C_5H_{11}$); elemental analysis calcd (%) for $C_{20}H_{31}N$ (285.47): C 84.15, H 10.95; N 4.91; found: C 84.39, H 10.89, N 5.20.

4-*N,N*-Dihexylaminophenylethynyl-*n*-tributylstannane (21): A stirred solution of **20** (5.85 g, 20.49 mmol) in THF (40 mL) at −78 °C under argon was treated with *n*BuLi (1.6 M in *n*-hexane, 12.8 mL, 20.5 mmol), then slowly warmed up to room temperature and cooled again to −78 °C. Tri-*n*-butyltin chloride (6.70 g, 20.49 mmol) was then added and the solution was warmed to room temperature and stirred overnight. The mixture was then diluted with Et_2O (150 mL), quenched with brine (100 mL), dried over $MgSO_4$ and evaporated. Kugelrohr distillation (235 °C, 10^{-5} mbar) yielded **21** (10.45 g, 93%) as pale yellow oil. UV/Vis (CH_2Cl_2): λ_{max} (ε): 298 nm (31214 $M^{-1}cm^{-1}$); IR (neat): $\tilde{\nu}$ = 3310, 2955, 2926, 2855, 2126, 2101, 1608, 1517, 1369, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80–0.96 (m, 15H), 0.96–1.16 (m, 6H), 1.17–1.45 (m, 18H), 1.45–1.77 (m, 10H), 3.25 (t, ^3J = 7.7 Hz, 4H), 6.52 (d, J = 9.0 Hz, 2H), 7.22 ppm (d, J = 9.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.47 (satellites: d, $^1J(^{117}Sn,^{13}C)$ = 183.4 Hz; d, $^1J(^{119}Sn,^{13}C)$ = 191.9 Hz), 13.86, 14.20, 23.09, 27.16, 27.41 (satellites: d, $^2J(^{117}Sn,^{13}C)$ = 28.8 Hz; d, $^2J(^{119}Sn,^{13}C)$ = 30.2 Hz), 27.54, 29.34 (satellites: d, $^3J(^{117}Sn,^{199}Sn–^{13}C)$ = 11.6 Hz), 32.12, 51.28, 89.43, 110.08, 111.46, 111.72, 133.28 (satellites: d, $^4J(^{117}Sn,^{199}Sn–^{13}C)$ = 3.1 Hz), 148.19 ppm; MS (EI^+, 70 eV): *m/z* (%): 575 (26, [M^+]), 518 (46, [$M^+ - C_4H_9$]), 404 (52, [$M^+ - 3\,C_4H_9$]), 284 (32, [$M^+ - 3\,C_4H_9 - Sn$]), 214 (100); elemental analysis calcd (%) for $C_{32}H_{57}NSn$ (574.51): C 66.90, H 10.00; N 2.44; found: C 67.17, H 9.97, N 2.67.

1,3,5-Tris(4-*N,N*-dihexylaminophenylethynyl)-2,4,6-tris(4-nitrophenylethynyl)-benzene (4b): A mixture of 1,3,5-trichloro-2,4,6-tris(4-nitrophenylethinyl)-benzene (**15**) (997 mg, 1.61 mmol), [$Pd(PPh_3)_4$] (373 mg, 0.32 mmol) and powdered CuO (512 mg, 6.43 mmol) in dry DMF (45 mL) was heated at 90 °C under argon for 30 min. 4-*N,N*-Dihexylaminophenylethynyltributylstannane (**21**) (3.54 g, 6.16 mmol) was added dropwise, and the colour of the mixture immediately turned dark red. Heating was continued at 90 °C for 4 h; then further CuO (250 mg 3.14 mmol), [$Pd(PPh_3)_4$] (130 mg, 0.11 mmol) and **21** (1.43 g, 2.49 mmol) were added and the mixture was heated at 98 °C for 3 h. Finally, to complete the reaction, another portion of **21** (0.50 g, 0.87 mmol) was added and the mixture was stirred for a further 1 h. After the mixture was cooled to room temperature, CH_2Cl_2 was added to the mixture and the organic phase was washed twice with aqueous KF, twice with water, then dried and evaporated. Column chromatography (silica gel, light petroleum ether/CH_2Cl_2, 1:1) yielded **4b** (304 mg, 14%) as a red powder. M.p. > 250 °C (decomp); UV/Vis (CH_2Cl_2): λ_{max} (ε): 464 nm (65025 $M^{-1}cm^{-1}$); IR (KBr): $\tilde{\nu}$ = 3453, 2956, 2929, 2856, 2189, 1605, 1524, 1370 cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2): δ = 0.94 (t, ^3J = 6.3 Hz, 18H), 1.36 (m, 36H), 1.50–1.64 (m, 12H), 3.29 (t, ^3J = 7.5 Hz, 12H), 6.49 (d, J = 8.7 Hz, 6H), 7.29 (d, J = 8.7 Hz, 6H), 7.59 (d, J = 8.5 Hz, 6H), 8.01 ppm (d, J = 8.7 Hz, 6H); ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 14.22, 23.12, 27.21, 27.59, 32.13, 51.26, 86.68, 93.89, 96.42, 103.79, 108.33, 111.48, 123.81, 123.83, 130.55, 130.90, 132.63, 133.72, 147.14, 149.24 ppm; MS (FAB^+): *m/z* (%): 1363 ([M^++H]); elemental analysis calcd (%) for $C_{90}H_{102}N_6O_6$ (1363.84): C 79.26, H 7.54, N 6.16; found: C 79.20, H 7.73, N 6.04.

X-ray structural analysis: The measurements were performed with a Siemens CCD diffractometer (for **3**), a Bruker SMART APEX-diffractometer (for **4b**) or a Nonius–Kappa CCD-diffractometer (for **13**) with $Mo_{K\alpha}$ radiation and a graphite monochromator. Intensities were corrected for Lorentz and polarisation effects. A semiempirical absorption correction (SADABS[79]) was performed. All structures were solved by direct methods (SHELXTL[80] for **3** and **4b**, SIR-97[81]). Structural parameters of the non-hydrogen atoms of **3**, **4b** and **13** were refined anisotropically according to a full-matrix least-squares technique (F^2) (Table 2). All hydrogen atoms of **3** were calculated. Several disordered atoms in **3**, **4b** and **13**

Table 2. Crystallographic data and details of the refinement procedure.

Compound	**3**	**13**	**4b**
empirical formula	$C_{54}H_{54}N_6O_6$	$C_{66}H_{54}N_6O_6 \cdot 2.5\,CH_2Cl_2$	$C_{90}H_{102}N_6O_6$
molecular mass [$g\,mol^{-1}$]	883.03	1239.47	1363.78
crystal size [mm]	0.5 × 0.3 × 0.04	0.7 × 0.15 × 0.03	0.32 × 0.19 × 0.10
crystal colour	orange	red	red
crystal shape	lamina	needle	plate
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
crystal system	monoclinic	triclinic	triclinic
a [Å]	10.8747(3)	13.8653(3)	13.431(1)
b [Å]	9.7903(3)	15.4622(3)	17.884(2)
c [Å]	44.880(1)	15.7283(5)	18.402(2)
α [°]	90	78.717(1)	68.746(2)
β [°]	96.432(1)	81.135(1)	75.893(2)
γ [°]	90	70.763(1)	69.328(2)
V [$Å^3$]	4748.2(2)	3107.5(1)	3820.4(7)
ρ_{calcd} [$mg\,m^{-3}$]	1.235	1.32	1.19
λ [Å]	0.71073	0.71073	0.71073
Z	4	2	2
F(000)	1872	1290	1464
T [K]	210(2)	148	100
h_{min}/h_{max}	−12/13	−17/18	−16/17
k_{min}/k_{max}	−11/11	−20/19	−17/23
l_{min}/l_{max}	−53/52	−18/20	−20/24
Θ range [°]	1.83–25.70	1.3–27.8	2.35–28.32
μ [mm^{-1}]	0.081	0.29	0.074
refl. collected	34401	21226	28337
refl. unique	8242	14535	18693
refl. observed [$I > 2\sigma(I)$]	5241	6871	13071
variables	620	1024	1339
$(\Delta/\sigma)_{max}$	0.001	< 0.001	0.001
R	0.072	0.099	0.050
R_w	0.142	0.207	0.118
S (Gof)	1.17	1.02	1.01
$(\Delta\rho)_{max}$ [$e\,Å^{-3}$]	0.26	0.50	0.38
$(\Delta\rho)_{min}$ [$e\,Å^{-3}$]	−0.22	−0.78	−0.27

were found involving nitro groups, hexyl side chains and dichloromethane guest molecules.

The atoms at disordered groups were refined isotropically. In **13**, inclusion of two and a half molecules of dichloromethane per host molecule was found. The hydrogen atoms of **4b** and **13** were refined isotropically with the exception of those involved with disordered molecule fragments. Refinement of all structures was carried out with SHELXTL. CCDC-221726 (**3**), CCDC-221727 (**4b**) and CCDC-221728 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

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