PERKIN 2

Cationic π-electron systems with high quadratic hyperpolarisability

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Cationic NLO-chromophores based on tolane π-systems in which conventional electron donors are combined with ionic pyridinio or triorganoammonio and -phosphonio substituents, respectively, perform much better than conventional donor/acceptor-substituted (D/A-substituted) tolanes concerning their hyperpolarisability–transparency trade-off. This effect occurs because ionic acceptors do not enlarge the π-system in contrast to conventional acceptors. The same holds true for benzene-type chromophores. Despite their different electronic nature, the extrapolated maximal high-energy absorption of the ionic chromophore series as well as of the conventional donor/acceptor-tolanes coincide at the absorption energy of unsubstituted tolane. This proves that the maximal blue transparency of a given series of substituted chromophores is governed by the absorption maximum of the unsubstituted parent chromophore. In this way chromophores have been designed with much higher quadratic hyperpolarisability than *e.g. p*-nitroaniline at about the same absorption wavelength. By applying the same concept, a two- and a three-dimensional highly efficient octupolar NLO-chromophore assembly has also been synthesised.

Introduction

Electro-optic modulator devices based on organic materials play a major role in future information transduction technology.[1] Thus, the search for chromophores with optimised second-order nonlinear-optical (NLO) properties is of great importance. Recent achievements in preparing stable high-speed modulator devices with concomitantly low half-wave voltage are very promising.[2] On the other hand, the interest in organic NLO-chromophores for frequency doubling applications of cheap NIR laser diodes has somewhat faded due to the development of blue emitting laser diodes.[3]

The hyperpolarisability of linear (1D) chromophores can be estimated by a two-level model where only the electronic ground state and the first excited charge-transfer (CT) state are considered:[4] From eqn. (1) (where μ_g and μ_e are the dipole

$$\beta^{2\omega}_{zzz} = \frac{1}{\hbar^2}\frac{(\mu_e - \mu_g)\mu_{eg}^2}{\omega_{eg}^2}\frac{\omega_{eg}^4}{(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - \omega^2)} \qquad (1)$$

moments in the ground and in the first excited CT state, respectively, μ_{eg} is the transition moment connecting the ground and the first excited CT state, ω_{eg} is the CT energy and ω is the energy of the incident laser light) it is apparent that a high quadratic hyperpolarisability β arises with bathochromic charge-transfer absorptions. Therefore, a true improvement of the so-called nonlinearity–transparency trade-off is achieved only if the slope of a correlation of β *vs.* $1/\omega_{eg}^2$ of a series of compounds is steeper than that of a reference series.[5] For both applications, electro-optic modulators and frequency doubling, as well as for photorefractive applications, an improvement of the nonlinearity–transparency trade-off is required.

Recently, we were successful in preparing zwitterions in which simple π-systems such as tolane (diphenylacetylene) are substituted by trialkylammonio and trialkylborato substituents (*e.g.* **1**).[6] These zwitterions show high quadratic hyperpolarisabilities and, at the same time, a comparatively hypsochromic CT absorption (high blue transparency). In these zwitterions the trialkylammonio substituent and the trialkylborato substituent serve as ionic electron acceptors and donors, respectively, which polarise the π-electron system by inductive effects rather than by mesomeric resonance effects (the same holds true for phosphonio substituents).[7] The latter effect (as present in *e.g.* conventional donors and acceptors like dialkylamino or nitro substituents) would increase the π-system and lead to bathochromic absorptions, which are circumvented by the use of ionic substituents. However, a closer inspection of the situation shows that trialkylborato substituents donate electron density upon excitation by hyperconjugation: the alkyl groups attached to the boron lose electron density rather than the boron centre itself (see Fig. 1 in ref. 6 and *cf.* ref. 8). Consequently, a trialkylborato substituent might not be superior to a conventional donor acting by resonance effects. This encouraged us to investigate ionic chromophores with cationic acceptors combined with conventional donors because these derivatives do not have the synthetic and stability restraints associated with triorganoborato groups. Thus, we synthesised a set of chromophores derived from tolane with trialkylammonio (**2**), triphenylphosphonio (**3**) and *N*-alkylpyridinio (**4**, **5**) acceptors combined with dianisylamino (**2**, **3** and **4**, anisyl = 4-methoxyphenyl) and triphenylmethyl (**5**) donors. Trialkylammonio and, for comparison, triarylphosphonio substituents have been chosen for the reasons mentioned above. They will be compared with the *N*-alkylpyridinio acceptor, which acts by resonance but does not enlarge the π-system relative to the tolane parent system. A

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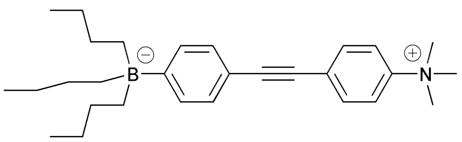

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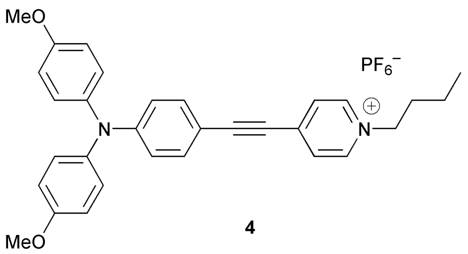

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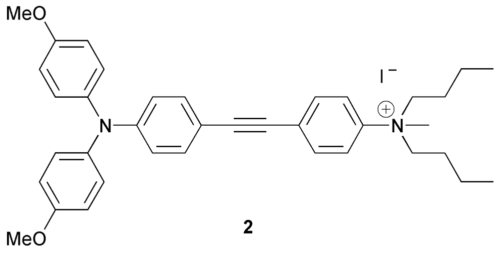

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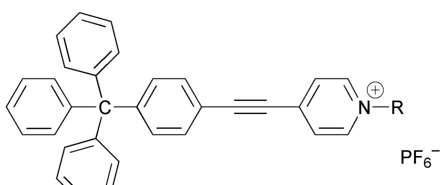

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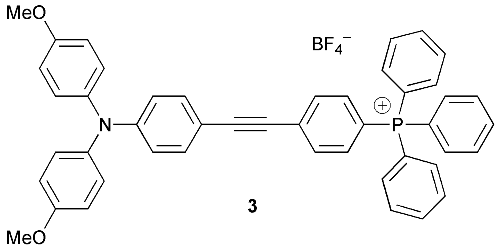

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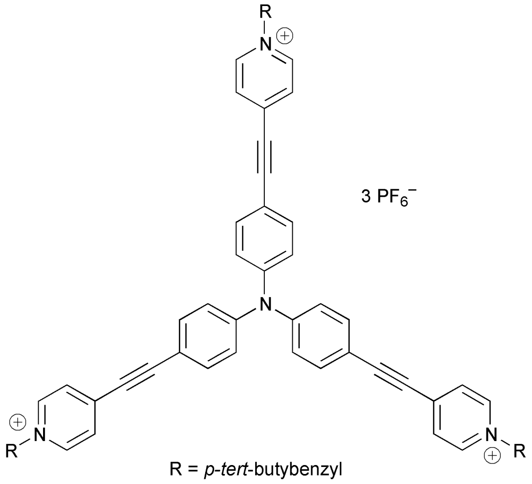

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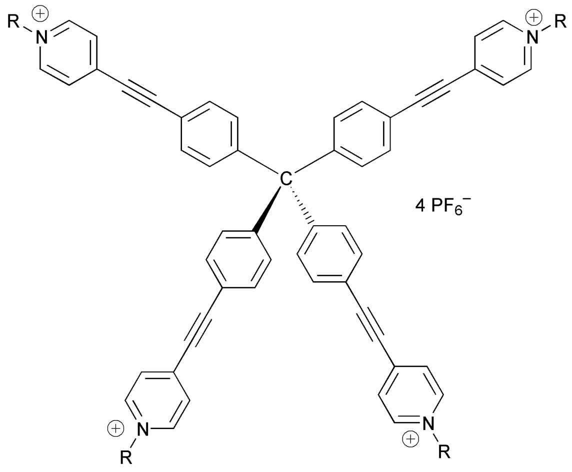

R = *p*-*tert*-butybenzyl

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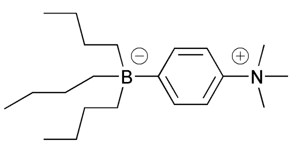
phenylene chromophore with a dianisylamino and a triphenylphosphonio substituent **9** was also synthesised for comparison with a tributylborato- and trimethylammonio-substituted phenylene zwitterion **8**[6] and *p*-amino-*N*-methylpyridinium iodide **10**.[9]

Many ionic NLO-chromophores have been investigated in the past but most of them employ a pyridinium group as this is a very strong electron acceptor. For example, a number of stilbazolium salts have been investigated in the solid state, in solution and theoretically. Nakanishi *et al.*[10] performed hyper-Rayleigh scattering measurements (HRS) on a series of stilbazolium salts, however, these values have recently been re-evaluated by Morrison *et al.*[11] because a wrong internal reference value for the methanol solvent had been used, which subsequently led to significantly too high β values. The group of Grahn *et al.*[12] investigated a number of pyridinium and quinolinium dyes in solution and found favourable nonlinearities compared to conventional systems. Although side chain bound ionic chromophores can be oriented by an electric field,[13] the focus of ionic chromophores is usually on crystalline solid state structures[14] and on structured films.[15] Kondo *et al.*[16] prepared a series of blue-transparent phenylpyridylacetylene salts, some of which displayed high powder SHG (second harmonic generation) intensities in the solid state.

As electron donor substituents, we employed the conventional dianisylamino group because diarylamino groups are known to be good donors with—compared to dialkylamino groups—high thermal stability and often increased quadratic nonlinearity.[17] The triphenylmethyl substituent also has been chosen as it may serve as a neutral and, formally inductive, donor, similar to the anionic trialkylborato substituent.

The use of the triphenylmethyl group as well as the diarylamino substituents opens an easy way to two- and three-dimensional chromophore assemblies such as **6** and **7**. In the past, many groups have investigated these types of so called "octupolar" NLO-chromophores because they might exhibit higher first-order hyperpolarisabilities at the same CT wavelength than their one-dimensional counterparts.[18] The reason for this behaviour is partly due to the lack of a permanent dipole moment, which leads to small solvatochromic shifts of the CT band, and also due to enhanced excited state couplings, which increase the hyperpolarisability.[19] Additionally,



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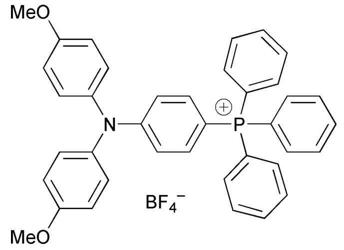

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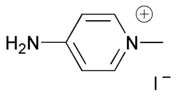

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π-conjugated hydrocarbons with a tetrahedrally branched topology recently stimulated much interest for application in materials, *e.g.* as light emitting components in organic light emitting devices (OLEDs).[20] For these reasons we also synthesised compounds **6** and **7**.

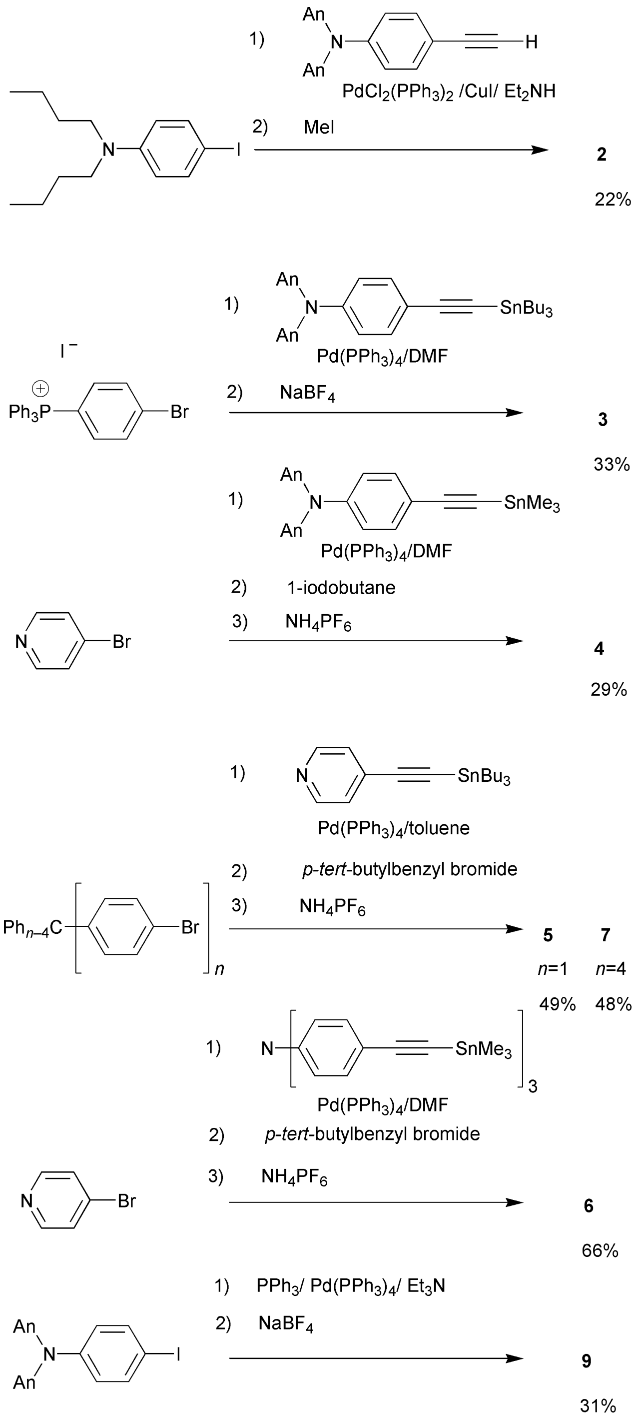
The linear and nonlinear optical properties of compounds **2**–**7** and **9** were investigated. The NLO properties were investigated by hyper-Rayleigh scattering measurements[21] at 1500 nm in MeCN because the EFISH (electric field induced second harmonic generation) method cannot be applied to ion pairs.

Results and discussion

Synthesis

The syntheses of **1** and **8** are outlined in ref. 6 but their detailed experimental procedures are given here in the Experimental. Compounds **2**–**7** were synthesised by conventional palladium(0)-catalysed C–C cross coupling reactions of a terminal alkyne (Hagihara coupling) or of trialkylstannylalkynes (Stille coupling) with the appropriate aromatic halide derivative as outlined in Scheme 1. Quaternisation of the amine or pyridine nitrogen followed for **2**, **4**, **5**, **6** and **7**. For the synthesis of **3**, the already quaternised (bromophenyl)triphenylphosphonium salt was used and coupled with the tin derivative. This procedure was checked in order to provide a general method for the synthesis of substituted tetraphenylphosphonium salts. However, palladium-induced scrambling of the aryl substituents[22] can occur and might be the reason for the low yield. The yields for all the other C–C coupling reactions range between *ca.* 50 and 95% per step. In many cases, the overall yield was decreased considerably by the successive incomplete quaternisation and counter ion exchange steps. The choice of more reactive reagents for quaternisation was limited due to the susceptibility of the tolane C≡C triple bond to electrophilic attack.

The phosphonium ion **9** was directly prepared by palladium-catalysed coupling of triphenylphosphine with the iodoarene derivative. Again, scrambling of the phosphorus substituents might be the reason for the low yield. In general, the purification of the ion pairs proved to be difficult due to extremely broad and overlapping fractions on the chromatography column.



(An = 4-methoxyphenyl)

Scheme 1

Linear and nonlinear optical properties

The UV–Vis spectra of all the compounds **1**–**9** were measured in THF and MeCN in order to estimate the trend of solvatochromism. These solvents proved to be very suitable because they readily dissolve most ion-pairs, they are both aprotic and their polarity in terms of their Dimroth–Reichardt parameters are quite different.[23] In Table 1 the data for the CT bands of **1**–**10** in THF and MeCN are given. The zwitterions **1** and **8** display a pronounced negative solvatochromism, which indicates a large ground state and a small excited state dipole moment. From eqn. (1) it is evident that a large dipole moment difference will increase the hyperpolarisability. However, the solvatochromism of the cations **2**–**4** is distinctly smaller and even absent in **5**–**7**. At first glance one might conclude that the dipole moment difference for **2**–**4** and **5**–**7** is quite small and, consequently, the quadratic hyperpolarisability is small, too. However, it will be explained later, on the basis of semi-empirical calculations, that this conclusion is wrong.

Although in MeCN the D_3 symmetric species **6** absorbs at the same wavelength as its one-dimensional counterpart, **4**, the band width at half-height is somewhat smaller (4140 cm^{-1}) than in the 1D species (4330 cm^{-1}). This leads to a long-wavelength tailing of the CT band of **4** compared to **6**. The same behaviour

Table 1 Linear and nonlinear optical data for *p*-nitroaniline (pNA) and **1**–**10**

	λ_{THF}/ nm	λ_{MeCN}/ nm	ε_{MeCN}/ $cm^{-1} M^{-1}$	$\Delta\tilde{\nu}/cm^{-1}$ [a]	$\lvert\beta^0\rvert/10^{-30}$ esu [b]	M [c]	β/M [c] relative to pNA
pNA [h]	362	366		300	13.6	138.1	≡1
1 [i]	349	329	27100	−1740	19 (18) [g]	417.5	0.47
2	367	360	30000	−530	38	547.3	0.70
3	406	395	31100	−690	87	666.3	1.34
4	463	454	35300	−430	128	558.8	2.34
5	354	354	34100	0	41	463.6	0.90
6	454	454	76200	0	127	990.4	1.31
7	354	354	145000	0	32 [f]	1313.8	0.25 [f]
8 [i]	253	237	7900	−2670	5	317.4	0.16
9	326 (331) [d]	322	20000 [d]	−380	22 [d]	501.5	0.45 [d]
10 [e]		270 [e]	27000 [e]		8 [e]	90.2	0.91 [e]

[a] Energy difference between the absorption maxima in THF and MeCN. [b] Static hyperpolarisability in MeCN, β_{zzz} for **1**–**5**, **8**, **9** and **10**, β_{yyy} for **6**. [c] Molecular mass used of cations only. [d] In $CHCl_3$. [e] In MeOH, see ref. 9. [f] Calculated by tensor addition from the β value of **5**. [g] Value from the two-level model, see footnote ‡. [h] See ref. 31*a*. [i] See ref. 6.

has also been observed in the 1D and 2D species of the *p*-nitrophenyl and the *p*-tricyanovinylphenyl derivatives (instead of the pyridinio acceptor).[24] The ratio of oscillator strength of **4** and **6** is only 1 : 2.04 while a ratio of 1 : 3 would have been expected in the case of negligible interaction between the chromophore branches of **6**. Deviation towards a smaller ratio has also been observed for tricyanovinyl-substituted triphenylamines[19f] and for triarylphosphonium cations.[19c] However, the ratio of the oscillator strengths of species **5** and **7** is *ca.* 1 : 4.3, much closer to the expected ratio of 1 : 4. We conclude that the interaction in the triarylamine branches of **6** is much stronger than in the tetrahedral methane derivative **7**, although the conjugation in **6** is diminished by the propeller-like arrangement of the *N*-phenyl substituents.[25]

The quadratic hyperpolarisability has been measured in MeCN at 1500 nm. The long incident wavelength has been chosen so as to avoid two- and three-photon induced fluorescence which otherwise might interfere with the HRS signal.[21b,c] As the HRS method allows only the square of the hyperpolarisability tensor to be determined, the sign of the hyperpolarisability is unknown but assumed to be negative because of the negative solvatochromism of **1**–**4**, **8** and **9**. For **1**–**5**, **8** and **9** only the β_{zzz} tensor component out of 18 possible components is significant; for **6** it is $\beta_{xxy} = -\beta_{yyy}$. For compound **7** it was impossible to measure the β value because of its poor solubility in MeCN.

The corresponding static hyperpolarisabilities have been calculated by the frequency dependence term of the two-state model [eqn. (1)] and are given together with the linear optical data in Table 1.

In Fig. 1 the quadratic hyperpolarisabilities of **1**–**5** are plotted against the reciprocal square of the CT energy as β should increase with this term according to eqn. (1) as confirmed by Stiegman *et al.*[26] for a series of tolanes substituted with conventional donors and acceptors (D/A-tolanes). For comparison these data are included. Our series of tolane derivatives **1**–**5** also shows an approximate linear correlation *vs.* $1/\omega_{eg}^2$. This means that the $\mu_{eg}^2(\mu_e - \mu_g)$ term in eqn. (1) is fairly constant and that the two-level model is valid for both series of compounds, *i.e.* an increase of β is solely due to an increase in absorption wavelength. However, the slope of series **1**–**5** (11.44×10^{-20}) is much steeper (factor 2.7) than that of the D/A-tolane series (4.30×10^{-20}), *i.e.* **1**–**5** display a much better nonlinearity–transparency trade-off than the D/A-tolane species.† Consequently, the $\mu_{eg}^2(\mu_e - \mu_g)$ term must be higher in the **1**–**5** series than in the D/A-tolanes for a given CT energy. Because μ_{eg}^2 varies approximately in proportion to the molar absorptivity, ε, and the average value for ε is 24700 for the D/A-tolanes and 31500 for **1**–**5**, this difference can only account for a factor of *ca.* 1.3 of the slope. Therefore, the major effect is likely to originate from a higher ($\mu_e - \mu_g$) difference in **1**–**5** compared to the D/A-tolanes.

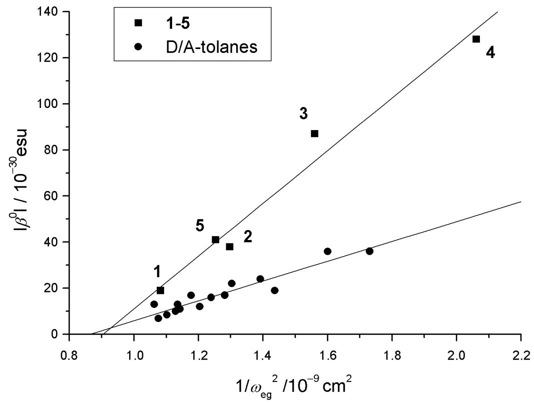


Fig. 1 Hyperpolarisability *vs.* reciprocal square of the CT energy of **1**–**5** (values from Table 1) and a set of tolanes substituted in 4,4′-position with conventional electron donors and acceptors from ref. 26 (measured in $CHCl_3$).

The most important observation is that the intercept of the correlation lines with the *x* axis coincides for both series and is at the absorption wavelength of unsubstituted tolane (300 nm), which, owing to its centrosymmetry, has a vanishing quadratic hyperpolarisability. This is because both series can be regarded as tolane, more or less weakly perturbed by substituents or by replacement of an aromatic CH group by an N^+-alkyl moiety. Therefore, the absorption energy of the unsubstituted parent chromophore dictates the limit of transparency for a series of chromophores. Though trivial we have not seen this point made clear in the literature before.

Analogous plots of our data (see Fig. 2) for species **8**–**10** compared to benzene substituted by conventional donors and acceptors (D/A-benzenes) taken from Cheng *et al.*[27] also show linear correlations. The intercept with the *x* axis is at the energy of the ^1L_b band of benzene (200 nm). Again, the slope of the correlation line for **8**–**10** (3.27×10^{-20}) is much steeper (factor 4) than that of the D/A-benzene series (0.80×10^{-20}) which proves that the (zwitter)ionic chromophores **8**–**10** show a much

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† Because tolanes substituted with conventional donors and acceptors show a positive solvatochromism, these chromophores will likely have somewhat higher β values in dipolar MeCN than in the less polar $CHCl_3$, thus reducing the ratio of the slopes. On the other hand, species **1**–**4** show negative solvatochromism and, consequently will show somewhat higher β values in $CHCl_3$ than in MeCN which would result in a higher ratio of the slopes. Therefore, measurements in solvents in which both series of compounds display their lowest hyperpolarisabilities seem to be a reasonable basis for a fair comparison.

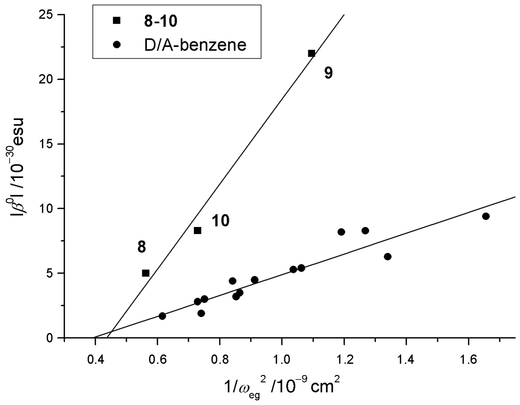


Fig. 2 Hyperpolarisability *vs.* reciprocal square of the CT energy of **8**–**10** (values from Table 1) and a set of benzenes substituted in the 1,4-position with conventional electron donors and acceptors from ref. 27 (measured in dioxane).

better nonlinearity–transparency trade-off than their conventional counterparts. However, compared to both tolane series, the benzene-type chromophores are inferior because of the inherently lower polarisability of benzene compared to tolane. A similar conclusion for stilbenes has been drawn before by Cheng *et al.*[27].

We stress that the linear correlations observed should be confined to systems where the substituents (be they ionic or conventional) induce a weak perturbation in the parent chromophore. In cases where the response to a perturbation is strong, *e.g.* in polyenes, and/or with stronger electron donors or acceptors, cyanine structures may originate from mixing donor and acceptor type states which then show vanishing hyperpolarisability at decreasing CT energies (increasing $1/\omega_{eg}^2$ term). This type of behaviour expresses itself in a reduced bond order alternation and has thoroughly been examined by Marder *et al.*[28] However, the force constant of the C≡C triple bond in tolane and the aromaticity of benzene counteract the electron-donating and -accepting influences of the substituents, which results in only a weak perturbation.

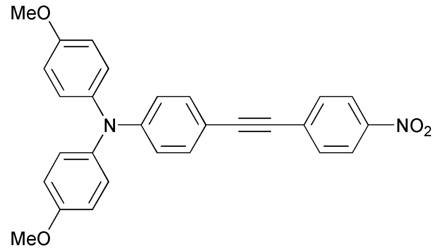
HRS measurement of the two-dimensional chromophore **6** gave a β^0_{yyy} value of 127×10^{-30} esu (Table 1). If one ignores interactions of the tolane subchromophore units in **6**, tensor addition of the β_{zzz} value of three subchromophores in the proper orientation (taken from **4**: 128×10^{-30} esu) results in $0.75 \times \beta_{zzz}(\mathbf{4}) = 96 \times 10^{-30}$ esu. Thus, the observed value of 127×10^{-30} esu is *ca.* $\frac{1}{3}$ higher than expected. We and other groups have observed enhancements of hyperpolarisability in higher-dimensional chromophores compared to their one-dimensional counterparts.[19c,d,f,h] The increases were interpreted in terms of excited state couplings, which is likely also the case for the triarylamine **6** in the present study.

In terms of their hyperpolarisability to molecular weight ratio (β/M, see Table 1), which is often used as a figure of merit, chromophores **3**, **5** and **6**, but especially **4**, perform well compared to *p*-nitroaniline (pNA) as the standard. The value of **6** could be further improved if the *tert*-butylphenyl substituents, which have been introduced for solubility reasons, were replaced by smaller groups.

It is often stated that higher-dimensional NLO-chromophores such as **6** and **7** are inferior to one-dimensional analogues owing to their high molecular mass relative to their β values that are in the range of those of the 1D species. However, this is not true at all: for applications in the crystalline state one has to consider the orientation of the chromophores in the crystal lattice; owing to phase-matching conditions this leads to effective SHG coefficients *d* which are much smaller per molecule than the β value of an isolated chromophore. For example, the maximal possible relative SHG coefficient in the crystal point groups 1 (triclinic), 2, *m* (monoclinic) and *mm*2 (orthorhombic) is $d = 2/(3\sqrt{3}) \cong 0.38$.[29] In other point groups the maximal *d* value is smaller, *e.g.* in 3 (trigonal) it is ¼ and in 4 (tetragonal) it is $1/(3\sqrt{3}) \cong 0.19$.[29] The latter point groups are those which can be adopted by **6** and **7**, respectively. This means—if one presumes additivity for the subchromophore branches in **7**—that a crystal built from **7** (in the tetragonal point group 4) can only show ½ of the *d* value of a crystal built from **5** in the monoclinic point group *m*. However, if one takes the molecular mass (see Table 1) into account, this difference levels completely out because $d_{\mathrm{rel}}(\mathbf{5})/(4 \times 558.8) \cong d_{\mathrm{rel}}(\mathbf{7})/(1313.8)$. This is because four subchromophores in **7** share one "donor" which makes the molecular mass of **7** much smaller than four times the mass of **5**. The same holds true for **4** and **6**. If subchromophore interactions increase the molecular hyperpolarisability compared to its one-dimensional analogue as in *e.g.* **6**, the relative *d* coefficient of a crystal of a higher-dimensional chromophore might be much higher than that of its analogous 1D chromophore.

Semiempirical calculations

In order to get a closer insight into the polarisation mechanism of the tolane chromophores studied in this paper, we performed semiempirical calculations at the NDDO level using the AM1 parametrisation. The excited state properties of species **1**–**5** and of a dianisylamino- and nitro-substituted tolane **11** were calculated at the CISD level with an active window comprising the four highest occupied and the four lowest unoccupied orbitals. The hyperpolarisability tensor was calculated using the time-dependent Hartree–Fock method (TDHF).[30]



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Both the linear and the nonlinear optical properties of dipolar chromophores are usually quite sensitive to the solvent.[31] Although this fact has been known for quite a long time, with some exceptions[32] most quantum chemical calculations on nonlinear optical properties still refer to the gas phase. We modelled the influence of the medium using the COSMO method introduced by Klamt and Schüürmann[33] because this model involves a solvent accessible surface modelled by van der Waals radii rather than a spherical or ellipsoidal cavity. Thus, this model should be more suitable for the rod-like molecules employed in this study.[32e,k]

In Table 2 the AM1 CISD computed absorption energies are given which deviate strongly from the observed ones (Table 1) with an unsigned mean deviation of 4750 cm^{-1}. This error reduces significantly to 2850 cm^{-1} when computing the absorption energies in MeCN. However, the error is still large compared to the rather small range of absorption energies of **1**–**5**. The quadratic hyperpolarisability was computed by two entirely different methods. The first is based on the time-dependent Hartree–Fock theory, *i.e.* the time-dependent response to an oscillating electric field is calculated analytically. The second method is based on the two-level approximation [eqn. (1)] where only the first excited singlet state is used in a truncated sum-over-states expansion. For this purpose we calculated the dipole moments of the ground state, the dipole moment and the energy of the first excited singlet (CT) state as well as the transition dipole moment by a CISD expansion in MeCN. This method has been employed by Zhang *et al.*[34] with

Table 2 AM1 computed linear and nonlinear optical properties of **1**–**5** and **11** in MeCN. Values in italics refer to the gas phase

	λ_{max}/ nm	$\tilde{\nu}_{max}$/ cm^{-1}	f	$\mu_e - \mu_g$/D	β^0_{zzz}(TDHF)[a]/ 10^{-30} esu	β^0_{zzz}(two-level)[b]/ 10^{-30} esu
1	357	28000	0.768	−12.7 (−18)[e]	−30.1	−23.9 (−18)[e]
	503	19900	*0.660*	*−23.4*	*−166.0*	*−106.2*
2	356	28100	0.862	−13.4	−37.7	−28.1
	405	24700	*0.636*	*−22.0*	*−93.8*	*−50.2*
3	338	29600	0.490	−23.0	−51.2	−35.8
	350	28600	*0.612*	*−30.0*	*−95.3*	*−42.5*
4	397	25200	0.721	−18.5	−69.6	−44.9
	520	19200	*0.565*	*−22.0*	*−214.5*	*−94.3*
5	309	32400	0.863	−14.0	−20.2	−19.1
	309	32400	*0.118*	*−39.2*	*−63.3*	*−7.4*
11	353[c]	28300	0.704	21.1	38.6[d]	35.4
	343	29200	*0.993*	*12.6*	*32.7*	*27.2*

[a] Calculated by the AM1 TDHF method. [b] Calculated by the two-level approximation [eqn. (1)] using AM1 CISD computed data. [c] Exp. value 413 nm. [d] Exp. value of diphenylamino derivative in $CHCl_3$: 28.2 × 10^{-30} esu, see ref. 17a. [e] Exp. value, see footnote ‡.

much success. The computed static β_{zzz} values are given in Table 2 together with the dipole moment differences. Although no solvatochromism was observed for **3**–**5** the computed changes of dipole moment upon excitation are quite substantial (see Table 2) and no qualitative difference can be seen between zwitterion, ion-pair and neutral chromophores. Thus, the assumption that the absence of solvatochromism indicates a vanishing dipole moment difference is false, at least for the ion-pairs of this study.

Comparison of the AM1 calculated $\mu_e - \mu_g$ difference of **1** (−12.7) with the experimental one (−18 D) ‡ shows that the computation underestimates the dipole moment difference in MeCN solution but overestimates this difference in the gas phase (−23.4 D). On the other hand, comparison of the experimental $\mu_e - \mu_g$ difference of 4-dimethyamino-4′-nitrotolane (5.7 D)[26] with those of the AM1 calculated value of **11** indicates that the calculation overestimates the $\mu_e - \mu_g$ difference both in MeCN and in the gas phase, with the MeCN value being much higher than the gas phase value. These effects are due to the negative and positive solvatochromism of **1** and **11**, respectively and are also due to the inability of the COSMO procedure to model correctly the solvent influences quantitatively. Thus, it seems likely that the zwitterions and ion-pairs actually show a higher $\mu_e - \mu_g$ difference than conventional D/A-tolanes as anticipated previously.

As can be seen from Fig. 3 there is a fairly good linear correlation of the hyperpolarisability calculated by the TDHF *vs.* the two-level method for **1**–**5** and **11**, the slope being 0.74. Thus, the hyperpolarisability estimated by the two-level model is about $\frac{1}{4}$ smaller than the TDHF values, which indicates that the first excited state does indeed play the dominant role, but higher excited states are necessary for a complete description of the hyperpolarisability. Similar conclusions have been drawn by Marks *et al.* [35] from careful analysis of SOS expansions.

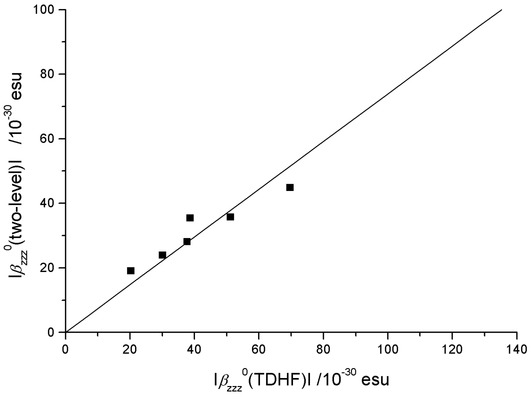

Fig. 3 Hyperpolarisabilities of **1**–**5** and **11** calculated by the two-level approximation *vs.* TDHF calculated values in MeCN. The solid line is a linear correlation through the origin.

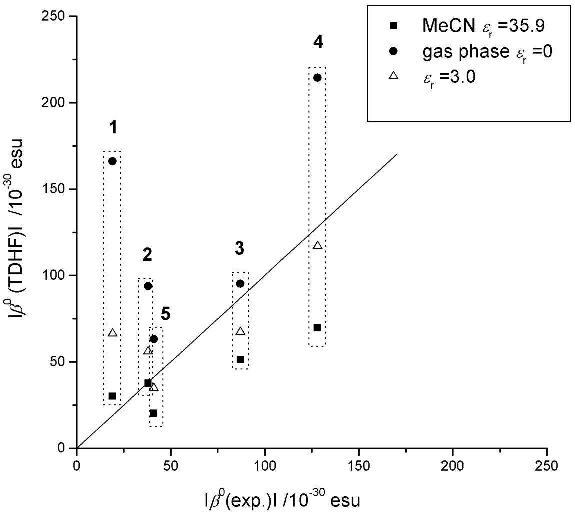

Fig. 4 AM1-TDHF computed hyperpolarisabilities of **1**–**5** in the gas phase, MeCN and in a solvent with with the permittivity ε_r = 3.0 *vs.* experimental values in MeCN. The straight line has a slope = 1.

However, comparison of the TDHF-computed hyperpolarisabilities in the gas phase and in MeCN with the experimental ones in MeCN shows no satisfactory correlation (see Fig. 4). While the theoretical MeCN values (signed mean error

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‡ The ground state dipole moment of **1**, which is $\mu_g = 38 \pm 4$ D, has been determined by dielectric relaxation spectroscopy[43] in MeCN. The excited state dipole moment of **1** has been measured by a solvatochromic method. As the absorption energies of **1** show a very good linear correlation with the Dimroth–Reichardt E^N_T solvent parameters[23] we used these E^N_T values for an empirical solvent characterisation instead of more complicated solvent functions based on the permittivity and/or the index of refraction with $\Delta\tilde{\nu} = K\frac{\mu_g(\mu_e - \mu_g)}{a^3}\Delta E^N_T$.[44] The unknown constant K which absorbs all theoretical inaccuracies is 1.90 × 10^4 and can be evaluated by using μ_g, $\mu_e - \mu_g$ and a (the effective solute diameter) of the Dimroth–Reichardt dye (μ_g = 14.8 D, $\mu_e - \mu_g$ = −8.7 D and a = 6.0 Å).[45] The ratio $\Delta\tilde{\nu}/\Delta E^N_T$ refers to the slope (6.45 × 10^3) of a linear correlation of the absorption energies of **1** in 9 different solvents with the appropriate E^N_T parameters.[46] For a we used the AM1 calculated B–N distance of **1** (12.7 Å). With these values we evaluated $\mu_e - \mu_g$ = −18 D for **1** which lies in between the AM1 computed values for the gas phase and the MeCN solution. Using the two-level approximation [eqn. (1)] with μ_{eg} = 6.0 D (from the integrated absorbance of the CT band) and $\mu_e - \mu_g$ = −18 D we estimated the quadratic hyperpolarisability for **1** to be −18 × 10^{-30} esu in MeCN, which is in excellent agreement with the HRS measurement.

Table 3 AM1 computed linear and nonlinear optical properties of **5** and **12**–**14** in MeCN

	λ_{max}/nm	$\tilde{\nu}_{max}$/cm^{-1}	f	$\mu_e - \mu_g$/D	β^0_{zzz}(TDHF)^a/ 10^{-30} esu	β^0_{zzz}(two-level)^b/ 10^{-30} esu
5	309	32400	0.863	−14.0	−20.2	−19.1
12	297	33700	0.611	−4.3	−12.4	−3.7
13	285	35100	1.119	2.0	1.2	3.0
14	261	38300	0.613	0.0	0.0	0.0

[a] Calculated by the AM1 TDHF method. [b] Calculated by the two-level approximation [eqn. (1)] using AM1 CISD computed data.

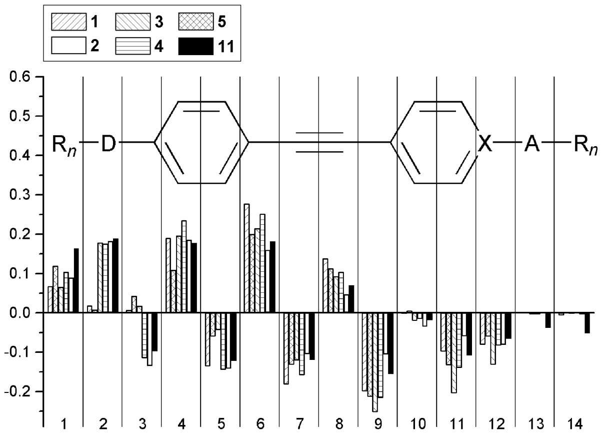


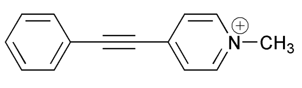
Fig. 5 AM1 CISD computed Coulson charge differences upon excitation for **1**–**5** and **11**. The charge differences refer to the sum of all atoms drawn in each column. A positive charge difference indicates a loss of negative charge upon excitation. X = C for **1**–**3** and X = N for **4** and **5**. The entries in each column are from left to right: **1**, **5**, **3**, **4**, **2**, **11**.

-21×10^{-30} esu, unsigned 25×10^{-30} esu) are close to the experimental ones for **1** and **2**, they appear to be much too small for **3**–**5**. In contrast, the TDHF gas phase values (signed = unsigned error = $+68 \times 10^{-30}$ esu) are much too high for **1**, **2**, **4** and **5** but in good agreement for **3**. In general, the gas phase values are higher than those in MeCN. The good correlation of β(TDHF) *vs.* β(two-level) indicates that the main problem of correct β computations is not the TDHF procedure nor the CISD expansion nor the AM1 parametrisation but the model for the solvent calculation. One way out of this problem might be to parametrise the COSMO model for calculating accurate β values by adjusting the relative permittivity empirically. If, for example, $\varepsilon_r = 3.0$ is used, the signed error reduces to 6×10^{-30} esu but the unsigned error still is 20×10^{-30} esu. Of course, for a reasonable parametrisation, a much larger data set is necessary, which will be the topic of future investigations.

In order to investigate the process of charge transfer upon excitation we plotted the AM1 CISD Coulson charge differences between ground and excited state for **1**–**5** and **11** in Fig. 5. On going from column 2 through column 11, it is apparent that the charge transfer is alternate (negative, positive) upon excitation. The donor substituents (separated into a central atom and its ligands R) as well as the C atoms in columns 4 and 6 lose negative charge upon excitation whereas those at the C atoms in columns 9, 11 and 12 gain charge. The acetylene bridge also shows a strong change of charge density. The change of charge density is marginal at column 10 and, especially, at the "acceptor" side: the triorganoammonio and phosphonio substituents in **1**–**3** stabilise the negative charge density in the adjacent benzene ring but do not accept charge density themselves. In this way, these substituents are electronically very similar to the *N*-alkylpyridinio group in **4** and **5**. In the pyridinio derivatives the electron acceptor of course is confined to the pyridine moiety as the *N*-alkyl group lies in the σ-plane. This permits the *N*-alkylpyridinio and trialkylammonio and -phosphonio derivatives to be regarded as *one class* of tolanes. Much in contrast, the nitro group of **11** gains negative charge upon excitation and, thus, increases the size of the "active" π-electron system, which, consequently, reduces the CT energy leading to a worse nonlinearity–transparency ratio as demonstrated in Fig. 1 for the D/A-substituted tolanes.

In **1** and **5**, the ligands R lose most of the charge density of the donor side, which is due to hyperconjugation whereas in **2**, **3** and **4**, it is the amine nitrogen of the dianisylamino group which loses most of the electron density, which in turn reflects the resonance effect. Although **2**, **3** and **4** possess the same type of donor substituent, the charge density change is quite different at the C-atom next to the donor in column 3. This demonstrates that the acceptor substituent has a strong effect on the change of charge density even far away from its position in the vicinity of the donor!

It is startling to see the triphenylmethyl group in **5** acting as a donor substituent. Its Hammett constant $\sigma_p = 0.02$[36] indicates almost neutral behaviour. We performed AM1 CISD model calculations on three species for comparison: in compound **12**, the triphenylmethyl group in **5** has been replaced by a hydrogen atom, in compound **13** the *N*-methylpyridinium moiety in **5** has been replaced by benzene, and, finally, unsubstituted tolane **14**.



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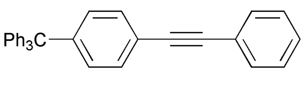
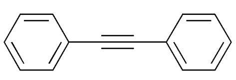


13



14

The calculated linear and nonlinear optical data are collected together with those for **5** in Table 3. From the data in Table 3 one can see that substitution of a hydrogen in tolane **14** by a triphenylmethyl group only results in a quite small β value of the tolane derivative **13**. The dipole moment difference upon excitation also is marginal (2.0 D). In contrast, substituting a hydrogen in the pyridinium compound **12** by a triphenylmethyl group to yield **5** results in a large increase of β and in a quite substantial dipole moment difference (14 D). This shows that the triphenylmethyl group itself is a weak donor, as indicated by its almost vanishing Hammett constant, but readily releases negative charge in combination with a strong acceptor like a pyridinium group. Thus, in **5**, the triphenylmethyl moiety serves as as an electron *source* rather than an electron *donor*.

Conclusions

In this study we were able to prove that cationic NLO-chromophores based on tolane π-electron systems with conventional electron donors combined with ionic pyridinio or triorganoammonio and -phosphonio substituents, respectively, perform much better than conventional D/A-substituted tolanes with respect to their hyperpolarisability–transparency trade-off. This effect is due to the fact that these ionic acceptors do not enlarge the π-system in contrast to conventional acceptors. The same holds true for benzene-type chromophores. Despite their different electronic nature, the extrapolated maximal high-energy absorptions of the ionic chromophore series as well as of the conventional D/A-tolanes coincide at the absorption energy of unsubstituted tolane. This important observation proves that the maximal blue transparency of a given series of substituted chromophores is governed by the absorption maximum of the unsubstituted parent chromophore. In this way, a chromophore such as **5** has been designed that displays a much higher quadratic hyperpolarisability than *e.g.* pNA at about the same absorption wavelength. On the other hand, a chromophore such as **4** has been described which has a much higher β/M ratio than pNA. Both linear chromophores were extended to two- and a three-dimensional chromophore assemblies, **6** and **7**, which shows that by applying the same concept one can also synthesise highly efficient octupolar NLO-chromophores.

Experimental

Synthesis

Commercial grade reagents were used without further purification. Solvents were purified, dried and degassed following standard procedures. All air-sensitive manipulations were carried out using flame-dried glassware and applying Schlenk techniques under a nitrogen atmosphere.

General synthesis for zwitterions 1 and 8

To a solution of bromoarene (1.0 mmol) in THF (10 ml) ^{n}BuLi–hexanes (0.63 ml, 1.0 mmol, 1.6 M solution) was added at −78 °C. The solution was warmed to −40 °C for 10 min and again cooled down to −78 °C. A solution of BBu_3–THF (1.0 ml, 1.0 mmol, 1.0 M solution) was added and the mixture was allowed to warm up within 1 h. The solvent was removed *in vacuo* and replaced by MeCN (5 ml). Iodomethane was added (0.5 ml) and the mixture was stirred for 1 d. The solvent was removed *in vacuo* and the residue was treated with H_2O–CH_2Cl_2. The product precipitated and was filtered off. The crude product was recrystallised from hot acetone–EtOH for **1** and pure EtOH for **8**.

4-Trimethylammoniophenyl-4′-tributylboratophenylacetylene 1. Yield 61%, colourless crystals, mp 219 °C (decomp.) (Found: C, 83.4; H, 10.6; N, 3.4. Calc. for $C_{29}H_{44}BN$: C, 83.2; H, 10.4; N, 3.6%); ν_{max}(Nujol)/cm^{-1} 2220 (C≡C); δ_H(400 MHz, [D$_6$]DMSO) 7.95 (2 H, m, AA′, arom.), 7.71 (2 H, m, BB′, arom.), 7.31 (2 H, m, AA′, arom.), 7.09 (2 H, m, BB′, arom.), 3.59 (9 H, s, Me$_3$N) 1.10 (6 H, m, BCH$_2$CH$_2$C*H*$_2$-), 0.88 (6 H, m, BCH$_2$C*H*$_2$-), 0.75 (9 H, t, *J* 7.3, -CH$_2$C*H*$_3$), 0.13 (6 H, m, br, BC*H*$_2$-); δ_C(100.6 MHz, [D$_6$]DMSO) 176.5 (br, *C*(phenyl)-B), 145.8, 132.9, 132.0, 128.2, 125.7, 120.9, 112.4, 95.3, 84.6, 56.3, 30.1, 27.8, 27.2, 14.7.

1-Trimethylammonio-4-tributylboratobenzene 8. Yield 91%, colourless crystals, mp 202–204 °C (Found: C, 79.5; H, 12.7; N, 4.4. Calc. for $C_{21}H_{40}BN$: C, 79.4; H, 12.5; N, 4.8%); δ_H(250 MHz, [D$_6$]acetone) 7.54 (2 H, m, AA′, arom.), 7.33 (2 H, m, BB′, arom.), 3.71 (9 H, s, Me$_3$N), 1.19 (6 H, m, BCH$_2$CH$_2$C*H*$_2$-), 1.02 (6 H, m, BCH$_2$C*H*$_2$-), 0.81 (9 H, t, ^3J 7.2, -CH$_2$C*H*$_3$), 0.31 (6 H, m, br, BC*H*$_2$-); δ_C(62.9 MHz, [D$_6$]acetone) 177.8 (q, $J_{B,C}$ 45.0, *C*(phenyl)-B), 141.8 (t, $J_{N,C}$ 4.9, *C*(phenyl)-N), 135.1, 115.6, 57.6 (t, $J_{N,C}$ 3.6, Me$_3$N), 31.2, 29.0, 28.3 (q, $J_{B,C}$ 42.0, B*C*H$_2$-), 14.9.

Dibutyl(4-{4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylethynyl}-phenyl)amine 2a

(4-Ethynylphenyl)[bis(4-methoxyphenyl)]amine[19d] (250 mg, 0.759 mmol), *N*,*N*-dibutyl-4-iodophenylamine (270 mg, 0.185 mmol), PdCl$_2$(PPh$_3$)$_2$ (35 mg, 6.5 mol%) and CuI (7 mg, 3.5 mol%) were dissolved in dry diethylamine (25 ml) and stirred at 55 °C for 3 h. The solvent was removed *in vacuo*, water was added and the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography [petroleum ether–CH_2Cl_2 3 : 1] on silica gel. Yield 250 mg (62%) of an air-sensitive yellow oil; δ_H(250 MHz, CDCl$_3$) 7.27 (4 H, AA′-BB′, phenylene), 7.04 (4 H, AA′, methoxyphenyl), 6.82 (2 H AA′, phenylene), 6.82 (4 H, BB′, methoxyphenyl), 6.55 (2 H, BB′, phenylene), 3.79 (6 H, s, MeO-), 3.26 (4 H, m, N-C*H*$_2$), 1.56 (4 H, m, -C*H*$_2$-), 1.34 (4 H m, -C*H*$_2$-), 0.95 (m, 6H, -C*H*$_3$).

Dibutyl(methyl)-4-{4-[*N*,*N*-bis(4-methoxyphenyl)amino]phenylethynyl}phenylammonium iodide 2

Iodomethane (1 ml) was added to a solution of amine **2a** (120 mg, 0.222 mmol) in dry acetone (3 ml) and stirred in a flask closed with a rubber stopper at 50 °C overnight. The solvent was removed *in vacuo*; the residue was purified by flash chromatography (gradient: pure CH_2Cl_2 then CH_2Cl_2–MeOH 100 : 7) on silica gel. The product was dissolved in a small amount of CH_2Cl_2 and precipitated by dropping into hexane. Yield 55 mg (36%), yellow solid, mp 78–85 °C; δ_H(250 MHz, CD$_2$Cl$_2$) 7.66 (4 H, AA′-BB′, phenylene), 7.31 (2 H, AA′, aminophenyl), 7.08 (4 H, AA′, methoxyphenyl), 6.87 (4 H, BB′, methoxyphenyl), 6.79 (2 H, BB′, aminophenyl), 4.30 (2 H, m, N-CH*H*-), 4.00 (2 H, m, N-C*H*H-), 3.79 (6 H, s, MeO-), 3.69 (3 H, s, N-C*H*$_3$), 1.67 (2 H, m, -CH*H*-), 1.38 (4 H, m, -C*H*$_2$-), 1.18 (2 H, m, -C*H*H-), 0.90 (6 H, t, *J* 7.3, -C*H*$_3$); δ_C(62.9 MHz, CD$_2$Cl$_2$) 157.4, 150.2, 140.8, 140.2, 133.6, 133.1, 128.9, 127.2, 122.1, 118.8, 115.4, 112.5, 94.3, 86.0, 69.8, 55.9, 48.4, 25.1, 19.8, 13.8; MS (FAB, high resolution) *m*/*z* found: 547.3335, calc. for $C_{37}H_{43}N_2O_2$: 547.3325.

4-Bromophenyltriphenylphosphonium iodide 3a

A mixture of triphenylphosphine (1.76 g, 6.72 mmol), 4-bromoiodobenzene (1.90 g, 6.72 mmol) and Pd(OAc)$_2$ (75 mg, 0.33 mmol, 5 mol%) in *p*-xylene (40 ml) was stirred at 130–140 °C for 12 h. The yellow solution turned brown and a colourless precipitate formed. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (CH_2Cl_2–MeOH–ethyl acetate 8 : 1 : 1) on silica gel. The bright yellow product was dissolved in boiling water (50 ml)–methanol (20 ml) and decanted from an oily residue. The methanol solvent was removed *in vacuo* and the phosphonium salt was precipitated by adding an excess of NaI. Yield 2.01 g (55%), bright yellow solid, mp 215–218 °C; δ_H(400 MHz, CDCl$_3$) 7.97–7.59 (19H, arom.); δ_P(162 MHz, CDCl$_3$) 23.8.

4-{4-[*N*,*N*-Bis(4-methoxyphenyl)amino]phenylethynyl}phenyltriphenylphosphonium tetrafluoroborate 3

4-(Tributylstannylethynyl)phenylbis(4-methoxyphenyl)-amine[19d] (255 mg, 0.41 mmol), 4-bromophenyltriphenylphosphonium iodide **3a** (225 mg, 0.41 mmol), Pd(PPh$_3$)$_4$ (24 mg, 0.02 mmol, 5 mol%) were dissolved in DMF (10 ml) and stirred at 35 °C for 48 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (CH_2Cl_2–MeOH–ethyl acetate 25 : 1 : 1) on silica gel. The oily product was dissolved in a little CH_2Cl_2 and precipitated by dropping into PE. Counter ion metathesis was performed by dissolving the salt in a saturated $NaBF_4$–MeOH solution, addition of water and extraction of the organic BF_4^- salt with CH_2Cl_2. This procedure was repeated twice. The CH_2Cl_2 solution was dried over Na_2SO_4 and the solvent evaporated. Yield 75 mg (33%), yellow solid, mp 112–113 °C; ν_{max}(KBr)/cm^{-1} 2206 (C≡C); δ_H(400 MHz, CDCl$_3$) 7.97–7.89 (3 H, arom.), 7.86–7.76 (8 H, arom.), 7.72–7.57 (8 H, arom.), 7.33 (2 H, m, AA′, phenylene), 7.08 (4 H, m, AA′, methoxyphenyl), 6.91–6.80 (2 H, m, BB′, phenylene and 4 H, m, BB′, methoxyphenyl), 3.80 (6 H, s, -C*H*$_3$); δ_C(100.6 MHz, CDCl$_3$) 156.6, 149.8, 139.5, 135.8 (d, $J_{C,P}$ 3.1), 134.3 (d, $J_{C,P}$ 10.3), 134.2 (d, $J_{C,P}$ 10.8), 132.9, 132.8 (d, $J_{C,P}$ 13.5), 132.0 (d, $J_{C,P}$ 3.1), 130.9 (d, $J_{C,P}$ 12.6), 127.3, 118.3, 117.3 (d, $J_{C,P}$ 89.8), 115.0 (d, $J_{C,P}$ 91.1), 114.8, 116.6, 97.7, 86.4 (d, $J_{C,P}$

1.8), 55.4; δ_P(162 MHz, $CDCl_3$) 23.6; MS (FAB, high resolution) *m*/*z* found: 666.2547, calc. for $C_{46}H_{37}NO_2P$: 666.2562.

Bis(4-methoxyphenyl)[4-(pyridin-4-ylethynyl)phenyl]amine 4a

4-Bromopyridine hydrochloride (230 mg, 1.20 mmol) was dissolved in aqueous NaOH (2 M, 20 ml); the solution was extracted with toluene (20 ml) and dried over Na_2SO_4. To this solution, bis(4-methoxyphenyl)(4-trimethylstannylethynylphenyl)amine[19d] (440 mg, 0.92 mmol), $Pd(PPh_3)_4$ (110 mg, 10 mol%) and DMF (3 ml) were added and the mixture was degassed by bubbling nitrogen into the solution. The mixture was stirred at 95 °C for 14 h. The solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (CH_2Cl_2–ethyl acetate 1 : 1) on silica gel. Yield 176 mg (47%), orange glassy solid, mp 42–44 °C (Found: C, 79.3; H, 5.6; N, 6.6. Calc. for $C_{27}H_{22}N_2O_2\cdot0.1\ H_2O$: C, 79.4; H, 5.5; N, 6.9%); ν_{max}(KBr)/cm^{-1} 2213 (C≡C); δ_H(250 MHz, $CDCl_3$) 8.55 (2 H, m, AA′, py), 7.29–7.34 (2 H + 2 H, m, BB′, AA′, phenylamine + py), 7.07 (4 H, m, AA′, methoxyphenyl), 6.81–6.89 (4 H + 2 H, m, BB′, BB′, methoxyphenyl and phenylamine), 3.80 (6 H, s, -OC*H*$_3$), 1.8 (s, br, H_2O); δ_C(62.9 MHz, $CDCl_3$) 156.7, 149.7, 149.6, 139.9, 132.8, 132.1, 127.3, 125.4, 118.7, 115.0, 112.4, 95.2, 85.7, 55.5; *m*/*z* 406 (100%, M$^+$).

Bis(4-methoxyphenyl)[4-(*N*-butyl-4-pyridinioethynyl)phenyl]amine hexafluorophosphate 4

Bis(4-methoxyphenyl)[4-(pyridin-4-ylethynyl)phenyl]amine **4a** (176 mg, 0.43 mmol) and iodobutane (1.0 ml, 3.3 mmol) were dissolved in acetone (5 ml) and stirred at 60 °C for 14 h. The solvent was evaporated and the residue was purified by flash chromatography (first acetone, then acetone–water–NH_4PF_6 50 ml–50 ml–1 g) on silica gel. The red product was extracted with CH_2Cl_2; the organic layer was washed three times with saturated aqueous NH_4PF_6 solution and dried over Na_2SO_4. The solution was concentrated and the product crystallised by adding hexane. Yield 160 mg (62%), red crystals, mp 144–146 °C (Found: C, 60.7; H, 5.0; N, 4.5. Calc. for $C_{31}H_{31}F_6N_2O_2P\cdot0.25\ H_2O$: C, 60.7; H, 5.2; N, 4.6%); ν_{max}(KBr)/cm^{-1} 2213, 2178 (C≡C); δ_H(250 MHz, [D_6]acetone) 9.00 (2 H, m, AA′, arom.), 8.13 (2 H, m, BB′, arom.), 7.47 (2 H, m, AA′, arom.), 7.19 (4 H, m, AA′, arom.), 6.99 (4 H, m, BB′, arom.), 6.77 (2 H, m, BB′, arom.), 4.75 (2 H, t, *J* 7.5, N-C*H*$_2$-), 3.82 (6 H, s, -OMe), 2.81 (s, H_2O), 2.16 (2 H, m, -C*H*$_2$-), 1.46 (2 H, m, -C*H*$_2$-), 1.01 (3 H, t, *J* 7.4, -CH$_2$C*H*$_3$); δ_C(62.9 MHz, [D_6]acetone) 158.6, 152.6, 145.0, 141.9, 139.6, 135.0, 129.5, 129.0, 117.7, 116.0, 109.0, 108.1, 86.5, 62.0, 55.8, 33.7, 19.9, 13.6; *m*/*z* 463 (100%, M$^+$).

Tris(4-trimethylstannylethynylphenyl)amine 6b

^{n}BuLi (0.96 ml, 1.54 mmol, 1.6 M solution in hexanes) was rapidly added to a vigorously stirred solution of tris(4-ethynylphenyl)amine[37] (0.148 mg, 0.47 mmol) in THF (5 ml) at −78 °C. A grey suspension formed which was allowed to warm up to RT and was stirred for 30 min. To this suspension trimethyltin chloride (0.38 ml, 1.41 mmol) was added; a yellow solution formed which subsequently became a grey suspension. After 1 h, water was added, the mixture was extracted with CH_2Cl_2 and the organic layer was dried over Na_2SO_4. The solvent was evaporated and a grey solid was obtained. This crude product decomposes on alumina and on silica gel but is sufficiently pure for further reactions. Yield 340 mg (100%), grey solid, mp 107 °C; ν_{max}(KBr)/cm^{-1} 2135 (C≡C); δ_H(250 MHz, $CDCl_3$) 7.35 (6 H, m, AA′, arom.), 6.96 (6 H, m, BB′, arom.), 0.34 (27 H, s, -C*H*$_3$).

Tris[4-(pyridin-4-ylethynyl)phenyl]amine 6a

4-Bromopyridine hydrochloride (500 mg, 4.4 mmol) was dissolved in aqueous NaOH (2 M, 20 ml) and extracted with Et_2O (20 ml). The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The oily residue, tris(4-trimethylstannylethynylphenyl)amine **6b** (250 mg, 0.31 mmol) and $Pd(PPh_3)_4$ (60 mg, 6 mol%) were dissolved in a mixture of toluene (6 ml) and DMF (3 ml). The solution was stirred at 75 °C for 21 h and the solvent was removed *in vacuo*. The residue was purified by flash chromatography (ethyl acetate) on silica gel. The product crystallised from ethyl acetate solution after adding hexane. Yield 148 mg (87%), yellow crystals, mp 202–204 °C (Found: C, 84.8; H, 4.9; N, 10.1. Calc. for $C_{39}H_{24}N_4\cdot0.25\ H_2O$: C, 84.7; H, 4.5; N, 10.1%); ν_{max}(KBr)/cm^{-1} 2218 (C≡C); δ_H(250 MHz, $CDCl_3$) 8.64 (6 H, m, AA′, py), 7.47 (6 H, m, AA′, arom.), 7.36 (6 H, m, BB′, py), 7.11 (6 H, m, BB′, arom.), 2.06 (s, br, H_2O); δ_C(62.9 MHz, $CDCl_3$) 149.8, 147.2, 133.3, 131.5, 125.4, 124.2, 117.2, 93.8, 86.9; *m*/*z* 548 (100%, M$^+$).

Tris{4-[*N*-(4-*tert*-butylbenzyl)-4-pyridinioethynyl]phenyl}amine tris(hexafluorophosphate) 6

Tris[4-(pyridin-4-ylethynyl)phenyl]amine **6a** (78 mg, 0.14 mmol) and 4-*tert*-butylbenzyl bromide (0.3 ml, 1.40 mmol) were dissolved in CH_2Cl_2 (5 ml) and refluxed for 30 h. The precipitated crystals were filtered off and washed with a little CH_2Cl_2. The product was dissolved in ethyl acetate and washed three times with a saturated aqueous NH_4PF_6 solution, the organic phase was dried over Na_2SO_4. Concentrating the solution under reduced pressure and adding Et_2O yielded violet crystals. Yield 152 mg (76%), mp 200 °C (decomp.) (Found: C, 59.7; H, 4.9; N, 3.8. Calc. for $C_{72}H_{69}F_{18}N_4P_3\cdot H_2O$: C, 59.9; H, 5.0; N, 3.9%); ν_{max}(KBr)/cm^{-1} 2217, 2187 (C≡C); δ_H(250 MHz, CD_3CN) 8.66 (6 H, m, AA′, arom.), 7.98 (6 H, m, BB′, arom.), 7.65 (6 H, m, AA′, arom.), 7.53 (6 H, m, AA′, arom.), 7.37 (6 H, m, BB′, arom.), 7.20 (6 H, m, BB′, arom.), 5.63 (6 H, s, -C*H*$_2$-), 2.13 (s, H_2O), 1.32 (27 H, s, ^{t}Bu); δ_C(62.9 MHz, CD_3CN) 154.3, 149.5, 145.0, 141.9, 135.4, 130.9, 130.5, 129.9, 127.5, 125.7, 116.5, 105.5, 86.7, 64.9, 35.4, 31.4; *m*/*z* 1279 (25%, $R_3N^{3+} + 2\ PF_6^-$), 1134 (100, $R_3N^{2+} + 1\ PF_6^-$), 989 (80, R_3N^+).

4-[(4-Triphenylmethylphenyl)ethynyl]pyridine 5a

(4-Bromophenyl)triphenylmethane[38] (399 mg, 1.00 mmol), 4-(tributylstannylethynyl)pyridine (431 mg, 1.10 mmol, prepared from 4-pyridylacetylene[39] with ^{n}BuLi in ether at −78 °C and tributyltin chloride), and $Pd(PPh_3)_4$ (35 mg, 3 mol%) were refluxed in dry toluene (10 ml) for 2 h. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (CH_2Cl_2–MeOH 100 : 2) and subsequent recrystallisation from $CHCl_3$–MeOH. Yield 359 mg (85%), colourless needles, mp 237–238 °C (Found: C, 90.3; H, 5.6; N, 3.1. Calc. for $C_{32}H_{23}N\cdot0.25\ H_2O$: C, 90.2; H, 5.7; N, 3.3%); δ_H(400 MHz, $CDCl_3$) 8.59 (2 H, m, AA′, py), 7.43 (2 H, m, AA′, arom.), 7.36 (2 H, BB′, py), 7.29–7.18 (17 H, m, BB′, phenylene +15 H, C*Ph*$_3$), 1.68 (s, H_2O); δ_C(100.6 MHz, $CDCl_3$) 149.7, 148.3, 146.2, 131.5, 131.3, 131.0, 131.0, 127.6, 126.1, 125.5, 119.6, 93.9, 86.7, 65.0.

N-(4-*tert*-Butylbenzyl)-4-[(4-triphenylmethylphenyl)ethynyl]pyridinium hexafluorophosphate 5

4-[(4-Triphenylmethylphenyl)ethynyl]pyridine **5a** (220 mg, 0.52 mmol) and 4-*tert*-butylbenzyl bromide (0.38 mL, 2.09 mmol) were stirred in dry $CHCl_3$ (10 ml) at 60 °C for 1 d and at RT for 10 d. A brown oil separated. The solvent was decanted and the oily residue was purified by chromatography on silica gel (CH_2Cl_2–MeOH 100 : 6). The product was dissolved in acetone–MeOH; NH_4PF_6 was added in excess and the product was precipitated by the addition of water as an oil. The oil was extracted with CH_2Cl_2 and dried over Na_2SO_4; the solvent was evaporated and the residue was recrystallised from ethyl acetate–EtOH–$CHCl_3$ (1 : 1 : 5). Yield 213 mg (57%), bright yellow hygroscopic powder, mp 220 °C (decomp.) (Found: C, 71.7; H, 5.6; N, 1.8. Calc. for $C_{43}H_{38}NPF_6\cdot 0.5\,H_2O$: C, 71.5; H, 5.4; N, 1.9%); δ_H(250 MHz, CD_3CN) 8.64 (2 H, m, AA′, py), 7.98 (2 H, m, BB′, py), 7.59 (2 H, m, AA′, phenylene), 7.52 (2 H, m, AA′, phenylene), 7.41 (2 H, m, BB′, phenylene), 7.37 (2 H, m, BB′, phenylene), 7.34–7.19 (15 H, C*Ph*$_3$), 5.61 (2 H, s, C*H*$_2$), 2.13 (s, br, H_2O), 1.31 (9 H, s, ^{t}Bu); δ_C(100.6 MHz, CD_3CN) 154.2, 151.7, 147.3, 145.1, 141.8, 132.9, 132.4, 131.7, 130.9, 130.7, 129.9, 128.9, 127.5, 127.2, 118.7, 105.0, 86.1, 66.2, 64.9, 35.4, 31.4.

Tetrakis[4-(pyridin-4-ylethynyl)phenyl]methane 7a

Tetrakis(*p*-bromophenyl)methane[40] (156 mg, 0.25 mmol), 4-(tributylstannylethynyl)pyridine (431 mg, 1.10 mmol, prepared from 4-pyridylacetylene[39] with ^{n}BuLi in ether at −78 °C and tributyltin chloride), and $Pd(PPh_3)_4$ (35 mg, 3 mol%) were refluxed in dry toluene (7 ml) for 5 h. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (CH_2Cl_2–MeOH 100 : 5) and by subsequent recrystallisation from ethyl acetate–CH_2Cl_2–MeOH (5 : 5 : 1). Yield 88 mg (49%), bright yellow needles, mp 250 °C (Found: C, 85.6; H, 4.8; N, 7.1. Calc. for $C_{53}H_{32}N_4\cdot H_2O$: C, 85.7; H, 4.6; N, 7.5%); δ_H(250 MHz, $CDCl_3$) 8.61 (8 H, m, AA′, py), 7.49 (8 H, m, AA′, phenylene), 7.37 (8 H, m, BB′, py), 7.24 (8 H, m, AA′, phenylene), 1.97 (s, H_2O); δ_C(62.9 MHz, $CDCl_3$) 149.9, 146.5, 131.5, 131.2, 130.9, 125.5, 120.6, 93.3, 87.3, 65.1.

Tetrakis{4-[*N*-(4-*tert*-butylbenzyl)-4-pyridinioethynyl]phenyl}-methane tetrakis(hexafluorophosphate) 7

Tetrakis[4-(pyridin-4-ylethynyl)phenyl]methane **7a** (30 mg, 0.041 mmol) and 4-*tert*-butylbenzyl bromide (0.10 ml, 0.55 mmol) were stirred in 3 ml of a mixture of dry MeCN–$CHCl_3$ (1 : 2) at 70 °C for 2 d and at RT for 7 d. The product was precipitated by the addition of ether, filtered off and washed with CH_2Cl_2. The bright yellow product (65 mg, 97%) was dissolved in MeOH–acetone; an excess of NH_4PF_6 was added and the PF_6^- salt was precipitated with water. The product was filtered off and recrystallised from MeOH–acetone–$CHCl_3$. Bright yellow hygroscopic powder, mp 220 °C, (decomp.) (Found: C, 60.5; H, 5.1; N, 3.2. Calc. for $C_{97}H_{92}N_4P_4F_{24}\cdot 2\,H_2O$: C, 60.4; H, 5.0; N, 2.9%); δ_H(250 MHz, CD_3OD) 8.99 (8 H, m, AA′, py), 8.13 (8 H, m, BB′, py), 7.68 (m, AA′, 8 H, arom.), 7.53 (8 H, m, AA′, arom.), 7.44 (8 H, m, BB′, arom.), 7.41 (8 H, m, BB′, arom.), 5.77 (8 H, s, C*H*$_2$), 4.86 (s, H_2O), 1.32 (36 H, s, ^{t}Bu); δ_C(100.6 MHz, CD_3OD) 154.7, 149.5, 145.6, 142.1, 133.7, 132.4, 131.5, 131.0, 130.1, 127.7, 120.3, 104.6, 86.6, 67.1, 65.3, 35.7, 31.6.

{4-[*N*,*N*-Bis(4-methoxyphenyl)amino]phenyl}triphenylphosphonium tetrafluoroborate 9

Bis(4-methoxyphenyl)-4-iodophenylamine (300 mg, 0.696 mmol), triphenylphosphine (500 mg, 1.91 mmol) and $Pd(PPh_3)_4$ (21 mg, 3 mol%) were refluxed in dry triethylamine (10 ml) for 24 h. The solvent was removed *in vacuo*, the residue treated with little water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (first PE–CH_2Cl_2 1 : 1, then pure CH_2Cl_2, then CH_2Cl_2–MeOH 10 : 1) on silica gel. For counter ion exchange, the product was dissolved in a small amount of CH_2Cl_2 and a saturated solution of $NaBF_4$ in MeOH was added. Water was added and the mixture was extracted with CH_2Cl_2. The solvent was evaporated and this procedure was repeated twice. The product was dissolved in pure CH_2Cl_2 and dried over Na_2SO_4. The solution was concentrated and the product was precipitated by dropping into Et_2O. Yield 140 mg (31%), yellow solid, mp 125–130 °C; δ_H(400 MHz, $CDCl_3$) 7.87 (3 H, m, P-Ph), 7.77 (6 H, m, P-Ph), 7.62 (6 H, m, P-Ph), 7.21 (2 H, m, AA′, phenylene), 7.19 (4 H, m, AA′, methoxyphenyl), 6.93 (4 H, m, BB′, methoxyphenyl), 6.92 (2 H, m, BB′, phenylene), 3.89 (6 H, s, MeO-); δ_C(100.6 MHz, $CDCl_3$) 158.0, 154.5 (d, $J_{C,P}$ 2.6), 137.2, 135.3 (d, $J_{C,P}$ 11.7), 135.3 (d, $J_{C,P}$ 3.0), 134.1 (d, $J_{C,P}$ 10.3), 130.6 (d, $J_{C,P}$ 12.8), 128.4, 118.8 (d, $J_{C,P}$ 90.0), 116.7 (d, $J_{C,P}$ 13.8), 115.4, 100.6 (d, $J_{C,P}$ 100.7), 55.5; δ_P(162 MHz, $CDCl_3$) 22.5; MS (FAB, high resolution) *m*/*z* found: 566.2223, calc. for $C_{38}H_{33}NO_2P$: 566.2249.

Hyper-Rayleigh-scattering measurements

The experimental set-up is described in detail in ref. 21*b* and the data evaluation in ref. 19*c*. The 1500 nm output of an optical parametric power oscillator (OPPO) was used as the incident light. This long wavelength was chosen so as to avoid two- or three-photon induced fluorescence contributions to the HRS signal. In addition, the spectral purity of the detected signal was checked by using different filters. All measurements were done in MeCN with exception of those for **9** which were carried out in $CHCl_3$. The reference compound was *p*-dimethylaminocinnamaldehyde ($\beta_{zzz} = 58 \times 10^{-30}$ esu at 1500 nm in MeCN)[19d] under identical experimental conditions. The accuracy of all measurements was estimated to be *ca.* ±15%. The β^{B*} convention of Willets *et al.*[41] was used throughout this paper.

Semiempirical calculations

Calculations were performed with the AM1 Hamiltonian implemented in the MOPAC97 program package.[42] In compounds **1**, **2**, **4** and **5**, longer alkyl chains have been replaced by methyl groups for simplicity. All molecules (cations) were optimised without symmetry constraints in the gas phase. Test optimisations in MeCN with the COSMO method[33] proved the influence of the solvent on the geometries to be negligible. The excited state properties were calculated with a CISD expansion in an active orbital window comprising the four highest occupied and the four lowest unoccupied orbitals. The time-dependent Hartree–Fock[30] method was used to calculate the first-order hyperpolarisability tensor. The CISD and TDHF computations were also performed in MeCN using the COSMO solvent model.

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