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Propeller-shaped molecules with giant off-resonance optical nonlinearities

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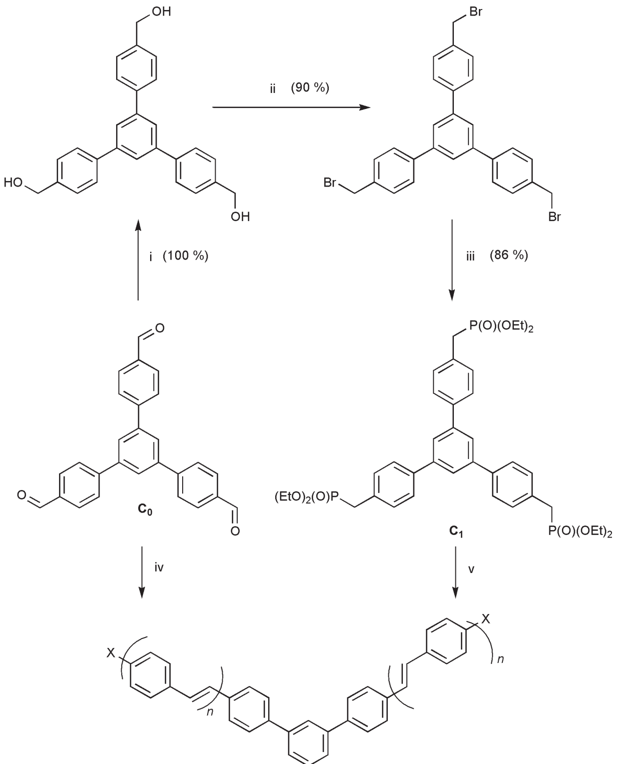
Propeller-shaped molecules based on a triphenylbenzene crux bearing three oligomeric phenylenevinylene branches have been designed; very large first-order hyperpolarisabilities (up to $\|\beta\| = 800\ 10^{-30}$ esu) were obtained while maintaining wide transparency in the visible region by taking advantage and boosting of intramolecular charge transfer between the centre and the periphery.

Molecular nonlinear optics (NLO) has attracted increasing interest over the past twenty years,[1] owing to numerous applications in various fields such as telecommunications, optical data storage and information processing.[2] A substantial effort has been devoted to the design of molecules with enhanced NLO responses. Molecular engineering of conjugated one-dimensional (1D) compounds has been particularly successful, leading to push–pull compounds displaying giant off-resonance first-order (β)[3] and/or second-order (γ)[4] hyperpolarisabilities. Yet it became increasingly clear over recent years that multidimensional and multipolar structures offer challenging possibilities.[5] Lehn, Zyss and coworkers have opened a pioneering route towards octupolar molecules.[6] Such 2D or 3D structures take benefit from the tensorial nature of β, and potentially lead to very large β[7] and γ[8] values but most often at the expense of significantly reduced transparency in the visible region.[9] In order to achieve an improved nonlinearity–transparency trade-off, we have prepared nanoscale propeller-shaped molecules whose design is based on the grafting of three extended blades bearing an electron-withdrawing or an electron-releasing tip on a triphenylbenzene crux (Scheme 1). Oligomeric phenylenevinylene rods were selected to ensure effective electronic conjugation and preserve transparency. The triphenylbenzene core maintains a large distance between the conjugated branches, thus preventing sterical hindrances.

Based on this strategy, we have prepared homologous molecules with radius varying between 1.4 and 2.5 nm. The first generation (n = 1) was prepared from 1,3,5-tris(4-formylphenyl)benzene (**C$_0$**[10]) *via* either a triple Wittig or Wittig–Horner–Emmons reaction whereas the second generation (n = 2) was obtained from **C$_1$** *via* a triple Wittig–Horner–Emmons condensation with extended conjugated aldehydes X–Ph–CH=CH–Ph–CHO. The key reagent **C$_1$** was synthesized from **C$_0$** in a three-step procedure (Scheme 1). The conjugated aldehydes were primarily prepared in nearly quantitative yield by reacting terephthalaldehyde mono(diethyl acetal) with one equivalent of phosphonium salt X–Ph–CH$_2$–P(Ph)$_3$I (X = N(nC$_6$H$_{13}$)$_2$,[4b] or X = OnC$_8$H$_{17}$) or of diethyl 4-(methylsulfonyl)benzyl phosphonate (X = SO$_2$CH$_3$) followed by acid-catalysed hydrolysis. Molecules **1–6** were characterised by NMR spectroscopy, elemental analysis and/or high-resolution mass spectra, in agreement with the assigned structures.

All molecules show good transparency in a wide range of the visible region and an intense absorption in the near UV–blue visible region whose position is dependent on both the nature of the peripheral groups and the length of the transmitter system (Table 1). As expected, a red shift of the absorption band is observed with increasing electron-withdrawing or electron-releasing strength of the end groups. Interestingly, a bathochromic shift of the absorption band is obtained with increasing solvent polarity (Fig. 1a) and a noticeably more pronounced positive solvatochromism is observed in emission (Fig. 1b), indicative of a polar excited state. Such characteristic behaviour hints to significant charge redistribution taking place upon excitation, consistent with a multidimensional intramolecular charge transfer (MDICT) occurring between the core and the peripheral groups. The large Stokes shift values (4050



Scheme 1 *Reagents and conditions*: i: KBH$_4$ (1 equiv.), EtOH, 4 h, rt; ii: HBr conc. (10 equiv.), 5 h, reflux; iii: P(OEt)$_3$ (5 equiv.), 24 h, reflux; iv: compounds **1** and **2**: X–Ph–CH$_2$–P(Ph)$_3$I (3.3 equiv.), KOtBu (3.5 equiv.), CH$_2$Cl$_2$, 4 h, rt; compounds **3** and **4**: X–Ph–CH$_2$–P(O)(OEt)$_2$ (3.3 equiv.), NaH (3.5 equiv.), THF, 4 h, rt; v: compounds **5** and **6**: X–Ph–CH=CH–Ph–CHO (3.3 equiv.), KOtBu (3.5 equiv.), CH$_2$Cl$_2$, 5 h, rt.

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Table 1 Linear and nonlinear optical properties of nanoscale propeller-shaped molecules derived from triphenylbenzene

	$\lambda_{\max}$(abs)^a /nm	$\Delta\tilde{\nu}^b$/cm^{-1}	λ_{HLS}/nm	$\beta_{\mathrm{HLS}}{}^a$/ 10^{-30} esu	$\lVert\beta\rVert^c$/ 10^{-30} esu	$\lVert\beta(0)\rVert^d$/ 10^{-30} esu
1	344	170	1064	5	16	8
2	387	790	1064	29	94	50
3	342	510	1064	30	97	51
4^e	385^e	1060	1340	70	227	140
5	407	—	1340	150	486	278
6	377	1830	1340	250	810	510
***p*NA**	348	—	1064	10	32	12

^{a} In chloroform. ^{b} Absorption solvatochromic shift = $1/\lambda_{\max}$(toluene) $-1/\lambda_{\max}$(DMSO). ^{c} The modulus $\lVert\beta\rVert = \sqrt{\sum_{ijk}\beta_{ijk}^2}$ is derived from β_{HLS} according to $\lVert\beta\rVert = \sqrt{\frac{21}{2}}\,\beta_{\mathrm{HLS}}$ for molecules with C_{3h} symmetry, and to $\lVert\beta\rVert = \beta_{zzz} = \sqrt{\frac{35}{6}}\,\beta_{\mathrm{HLS}}$ for 1D dipolar chromophores such as *p*-nitroaniline (*p*NA). ^{d} Static values are calculated using a two-level dispersion factor.[6b] ^{e} In DMSO.

cm^{-1} for molecule **2** in chloroform, and 8500 cm^{-1} for molecule **4** in DMSO) corroborate that important nuclear reorganisation is taking place after excitation, prior to emission as a result of significant electronic redistribution.

The first hyperpolarisabilities β have been determined by performing harmonic light scattering (HLS) experiments which yield the HLS molecular averaged hyperpolarisability $\sqrt{\langle\beta^2\rangle} = \beta_{\mathrm{HLS}}$.[11] HLS experiments were performed at 1.064 or 1.34 µm in order to locate the second harmonic signal in the transparency region of the chromophores and to avoid contamination by two-photon fluorescence.[12] Comparison of homologous molecules bearing electron-releasing (**1**,**2**) or electron-withdrawing (**3**,**4**) end groups clearly shows that increasing the donating or accepting strength of the three terminal substituents results in a significant enhancement of β (Table 1), providing evidence that MDICT strongly influences the nonlinear responses. Following this observation, increasing the distance between the core and the periphery appeared as a rational way to boost the nonlinear responses. This strategy proved particularly successful: molecule **5** was found to exhibit a $\lVert\beta(0)\rVert$ value about six times larger than molecule **2**, whereas molecule **6** exhibits a first-order hyperpolarisability *one order of magnitude larger* than its shorter analogue **3**, while increasing by no more than 36% in weight and maintaining suitable transparency in the visible region. This is particularly advantageous in terms of efficiency-transparency trade-off: molecule **6** exhibits a $\lVert\beta(0)\rVert$ value about forty times larger than the prototypical push–pull compound *p*-nitroaniline (*p*NA), with a molecular weight no more than eight times larger.

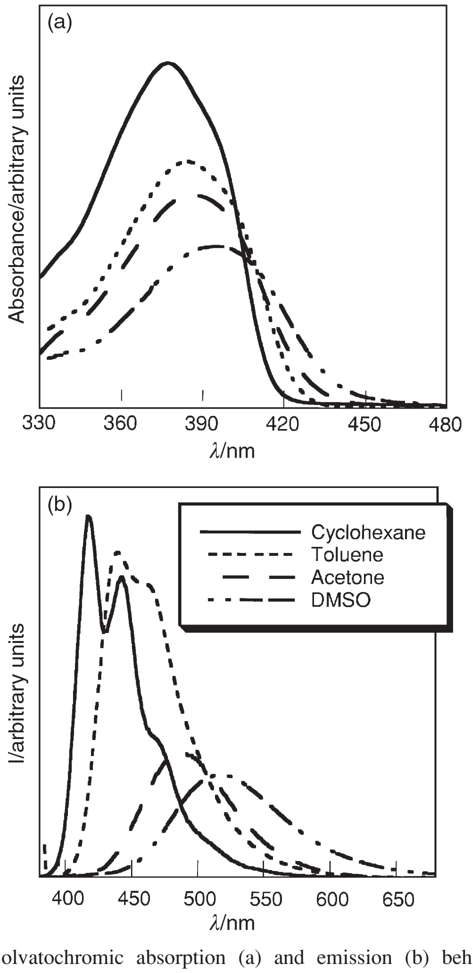

Fig. 1 Solvatochromic absorption (a) and emission (b) behaviour of molecule **2**.

Finally, by grafting either electron-donating or electron-withdrawing groups on the edges of conjugated blades branched on a triphenylbenzene crux, propeller-shaped molecules exhibiting high NLO properties and wide transparency in the visible range have been designed. Optimization leads to compounds presenting an improved transparency–nonlinearity trade-off ($\lVert\beta(0)\rVert$ = 500 10^{-30} esu, $\lambda_{\max}$ = 377 nm) as compared to tris-donor tris-acceptor octupolar 2D molecules. In addition, the superlinear dependence of β on size and their particular concave shape makes elongated analogues attractive candidates for incorporation in polymeric materials.

Notes and references

1 See for instance the special issue of *Chemical Physics* devoted to molecular nonlinear optics: *Chem. Phys.*, 1999, 245, for current trends in molecular NLO.

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