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Improved transparency-nonlinearity trade-off with boroxine-based octupolar molecules†

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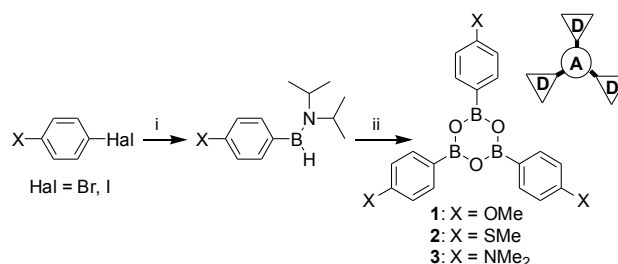
A series of octupolar molecules derived from the boroxine framework were designed and their optical nonlinearities were investigated by performing harmonic light scattering experiments in solution; the molecules were found to combine excellent transparency in the near UV-visible region ($\lambda_{\text{max}} \leq 280$ nm) and significant first-order hyperpolarisabilities (up to $\beta(0) = 56 \cdot 10^{-30}$ esu).

The field of molecular nonlinear optics (NLO) has attracted increasing interest over the past twenty years, owing to its connection with fundamental issues such as charge transfer, higher order polarisabilities or conjugation, as well as to numerous applications in various fields such as telecommunications,¹ optical data storage,² microfabrication, biological imaging... Within this framework, organic chromophores have received major attention owing to their chemical flexibility. For instance, molecular engineering of "push-pull" compounds has proven particularly successful leading to chromophores displaying record first (β) and second (γ) hyperpolarisabilities. Yet, these chromophores are plagued by an intense absorption in the near-UV-visible region that significantly restricts their transparency range. Novel strategies were thus needed for optimising the efficiency-transparency trade-off.

Octupolar molecules, with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as the prototypical structure, provide an interesting alternative for this purpose.³ Following this approach, a variety of organic molecules with a two-dimensional (2D) character of β^4 as well as several 3D octupolar molecules⁵ have been designed and investigated in recent years.⁶ Within this context, we have investigated a series of original and transparent octupolar molecules built from the boroxine ring. Their molecular design is based on the symmetrical grafting of three donating appendices on the electron-deficient boroxine core (Scheme 1). The boroxine ring usually leads to quasi planar structures,⁷ a common feature with triazines whose octupolar derivatives have been widely studied.^{4b,d-f} In contrast, boroxine shows much lower aromatic character.⁸ We emphasize that although boron inorganic derivatives have long been known to display interesting NLO properties,[‡] the potentialities of organic boroxine derivatives for NLO have not been considered yet.

Phenyl units were used as rigid links between the electron-releasing substituents and the boroxine core. Peripheral groups with increasing donating character were used with the aim of tuning the optical properties. Triarylboroxine derivatives are usually obtained from the corresponding boronic acids via a cyclocondensation reaction leading to the cyclic trimeric

anhydride. We have implemented an innovative route that allows



Scheme 1 Reagents and conditions: i, *i*-Pr₂NBH₂ (2 equiv.), Et₃N (5 equiv.), Pd⁰ (5 mol%), dioxane, 15h, 78 °C; ii, H₂O (1.5 equiv.), 16h, rt.

an efficient and versatile preparation of triarylboroxines *via* the borylation/hydrolysis sequence of *p*-substituted aryl halides⁹ (Scheme 1). The presence of electron-donating substituents has been reported to increase the stability of triorganoboroxine derivatives towards hydrolysis.¹⁰ All the derivatives investigated in the present study have been fully characterized by NMR, HRMS and elemental analysis prior to their optical study. X-Ray diffraction from single crystals of **1** shows that this molecule is quasi planar with the three phenyl rings lying approximately in the plane of the boroxine ring (Fig. 1).§

The absorption characteristics of the series of derivatives **1-3** are gathered in Table 1. The molecules show an intense

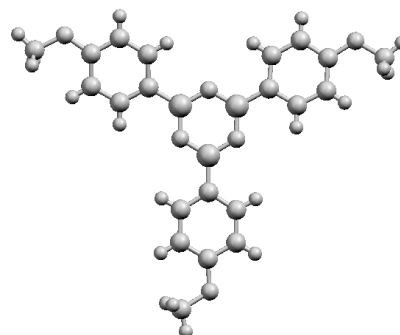


Fig. 1 X-Ray structure of boroxine derivative **1**.

absorption band in the UV region but maintain full transparency in the near UV-visible region. A slight positive solvatochromism is observed, indicative of a larger stabilisation of the excited state as compared to the ground state by a polar solvent. Increasing the donating strength of the substituents leads to a broadening and a bathochromic and hyperchromic shift of the absorption band and to a more pronounced solvatochromism.

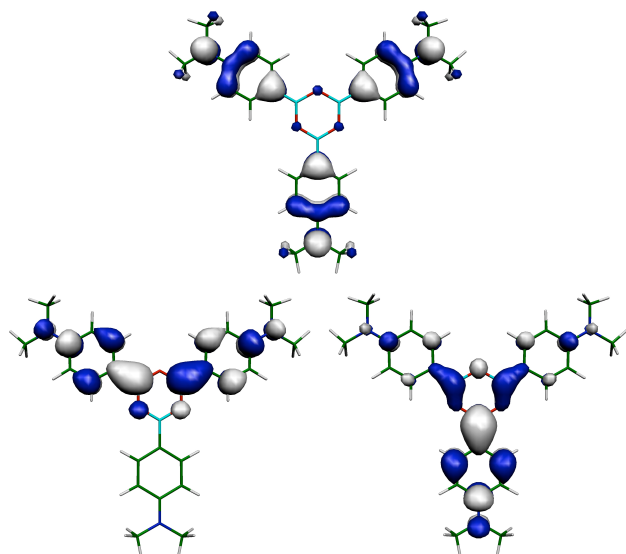
Table 1 Absorption and nonlinear properties of molecules **1–3** in chloroform

Comp d	λ_{\max} (nm)	ϵ_{\max} (M ⁻¹ cm ⁻¹)	FWHM ^a (cm ⁻¹)	$\lambda_{\text{cut-of}}$ (nm)	$\Delta\nu^b$ (cm ⁻¹)	β_{HLS} (10 ⁻³⁰ esu)	$\beta_{\text{HLS}}(0)$ (10 ⁻³⁰ esu)
1	241	4.0 10 ⁴	1750	286	-	47	35
2	270	4.6 10 ⁴	3360	301	69	45	31
3	281	5.8 10 ⁴	4350	326	450	83	56
TIATB	375					10	4.4

^aHalfbandwidth. ^b Solvatochromic shift = $1/\lambda_{\max}(\text{CHCl}_3) - 1/\lambda_{\max}(\text{DMSO})$.

Interestingly, HOMO-LUMO calculations[¶] reveal an intramolecular charge density shift from the donating appendices towards the boron atoms (Fig. 2).

The first hyperpolarisabilities β have been determined by

**Fig. 2** Contour surfaces of HOMO (up) and degenerated LUMO, LUMO+1 (down) of organoboroxine **3**.

performing harmonic light scattering (HLS) experiments in solution, which yield the HLS molecular averaged hyperpolarisability $\sqrt{\langle\beta^2\rangle} = \beta_{\text{HLS}}$.¹¹ HLS experiments were performed at 1.064 μm locating the second harmonic signal in the transparency region.[#] The corresponding static values $\beta_{\text{HLS}}(0)$ are calculated using a degenerated three-level dispersion factor.^{3b} The experimental values are compared to those reported for TIATB,^{4a} a soluble analogue of TATB, using the β^x convention.¹²

Examination of the series of molecules indicates that increasing the donating strength of the substituents results in a significant enhancement of β . Molecule **3** which bears the strongest electron-releasing substituents of the series displays a molecular optical nonlinearity nearly twice larger than molecule **1**, providing evidence that intramolecular charge transfer influences the nonlinear responses. We note that such boroxine derivative indeed leads to an improved efficiency-transparency trade-off as compared to triazine or TATB octupolar derivatives: molecule **3** displays a $\beta(0)$ value about one order of magnitude larger than TIATB while remaining blue-shifted by nearly 100 nm and having a molecular weight less than twice larger.

Finally, our study demonstrates that the functionalisation of the boroxine core provides a promising and innovative route for the optimisation of the nonlinearity-transparency trade-off. It also opens the way for further engineering of the optical nonlinearity by boosting the multidimensional intramolecular charge transfer between the core and the peripheral groups.^{4h,i}

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Notes and references

[†] Electronic supplementary information (ESI) available: Characterization data and UV-Visible spectra for compounds **1–3**; computational details. See http://****

[‡] Such as BBO, used in wavelength conversion devices.

[§] Crystal data for **1**: C₂₁H₂₁B₃O₆, M=401.81, monoclinic, space group P2₁/n, $a = 9.0568(2)$, $b = 14.1334(4)$, $c = 16.9564(7)$ Å, $\beta = 104.5710(10)^\circ$, $V = 2100.67(11)$ Å³, $Z = 4$, $T = 293(2)$ K, $D_c = 1.271$ g cm⁻³, $R_1 = 0.0502$, $wR_2 = 0.1184$ for $I > 2\sigma(I)$. See http://**** for crystallographic data.

[¶] The corresponding transition are symmetrically allowed and the calculated energy gaps (242 nm for **1**, 268 nm for **2**, and 269 nm for **3**) show good agreement with the values derived from the absorption spectra for the lowest energy transition (Table 1).

[#] This procedure avoids possible contamination of the HLS signal by two-photon excited fluorescence. In addition, the boroxines **1–3** did not show any detectable fluorescence when excited in their absorption band.

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