

# The first D- $\pi$ -A octupolar cryptand molecule to exhibit bulk non-linearity

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## The cryptand derivative has H-bond mediated trigonal network structure that leads to octupolar bulk nonlinearity

Optically nonlinear organic materials are of paramount importance for applications in optical signal processing and telecommunications.<sup>1</sup> We present here a new strategy for obtaining molecules with bulk optical nonlinearity by derivatizing a cryptand with three D- $\pi$ -A units related by a 3-fold rotational symmetry. Thus, compound **1** (Scheme 1) is engineered with the ultimate aim of a trigonal network necessary for bulk octupolar nonlinearity. The classical molecular requirements for second-order nonlinear optical (NLO) effects have led to the development of strongly conjugated materials asymmetricized by interacting donor and acceptor groups.<sup>2</sup> Even though these molecules exhibit large hyperpolarizability, major drawbacks arise due to their anisotropic dipolar character, *e.g.* a high tendency towards unfavorable aggregation, difficult non-centrosymmetric crystallization, and small off-diagonal tensor components. To alleviate such problems, isotropic molecules with attached octupolar nonlinearities have been proposed, on the basis of group-theoretical and quantum-mechanical calculations.<sup>3</sup> Solution-phase studies by Hyper-Rayleigh Scattering (HRS) technique on crystal violet and tris(4-methoxyphenyl)cyclopropenyl bromide as octupoles have been reported.<sup>4</sup> However, assembly of octupolar molecules into an

acentric bulk presents an arduous task. To-date, only 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) (3  $\times$  urea),<sup>5</sup> substituted triazines (0.1  $\times$  urea)<sup>6</sup> and cyclohexane-1,3,5-triamide derivative (0.06  $\times$  urea),<sup>7</sup> are the only octupolar organic materials reported to exhibit bulk NLO properties.

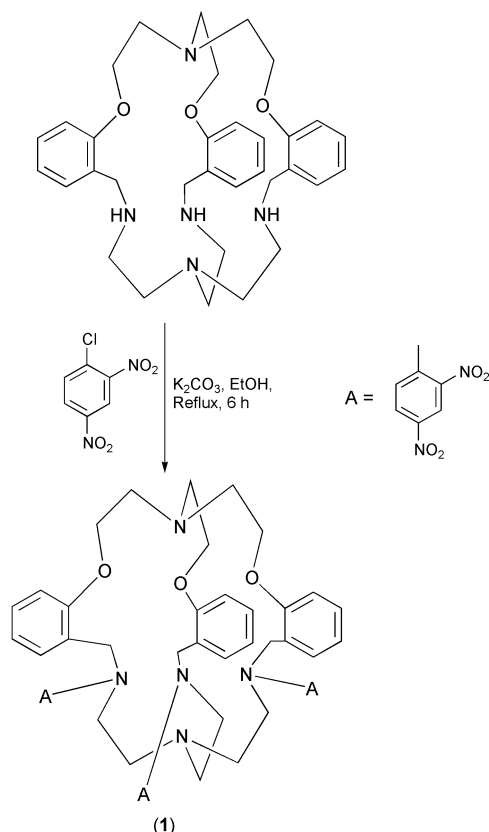
No cryptand-based octupolar molecule having bulk NLO properties has been reported in the literature although cryptands are an important class of molecules having a 3-D cavity with proven recognition properties through supramolecular interactions.<sup>8</sup> Our principal motivation to use the cryptand as a central core stems from the following three assets: (i) a 3-fold rotational symmetry passing through the two bridgehead nitrogen atoms of the cryptand molecule, (ii) three phenyl rings as rigid segments would favor ordered structures and (iii) three easily functionalizable secondary nitrogen atoms would assist in grafting acceptor molecules of choice. We have chosen 2,4-dinitrobenzene as it has been shown to have adequate electronic asymmetry in methyl 2-(2,4-dinitroanilino)propanoate (MAP).<sup>9</sup> Besides, the nitro substitution at the *ortho* position would provide a more rounded-off shape to the molecules (Scheme 1), which would ease their packing in the crystal lattice.

Compound **1** was synthesized (Scheme 1) by refluxing the cryptand<sup>10</sup> with 3 equiv. of 2,4-dinitrochlorobenzene and anhydrous K<sub>2</sub>CO<sub>3</sub> for 6 h in dry EtOH under N<sub>2</sub>. The yellow-orange tri-substituted product was isolated in 92% yield.

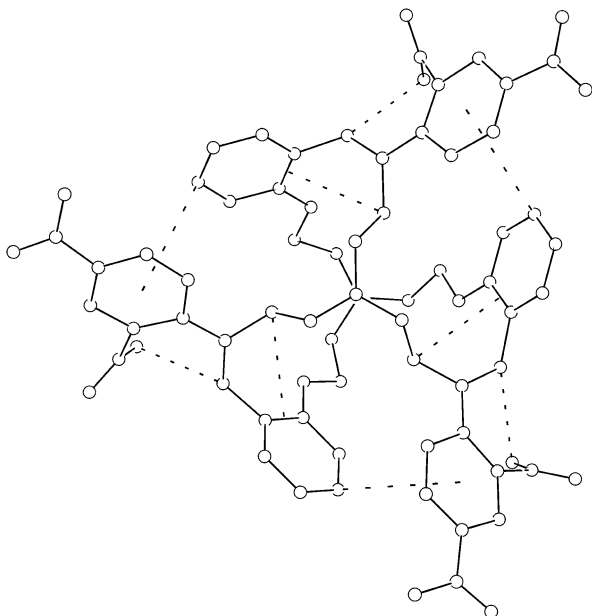
Single crystals suitable for X-ray diffraction were grown by slow evaporation from pyridine solution. The compound afforded very large triangular crystals (~5 mm each side) in just two days. It crystallizes<sup>†</sup> in the desired non-centrosymmetric trigonal space group *P*3, containing three strands in the asymmetric unit. The C<sub>3</sub> symmetry generates the donor-acceptor substituted cryptand molecules **A**, **B** and **C** with the symmetry axis passing through the bridgehead nitrogens which also coincides with the triad axes of the lattice. Supramolecular assembly of these C<sub>3</sub> symmetric cryptand molecules generates an octupolar trigonal network. The molecules **A**, **B** and **C** vary considerably in their conformation. Three different forms of intramolecular forces are operational in the D- $\pi$ -A substituted cryptand molecule: (i) aromatic  $\pi$ -stacking between the phenyl ring of one strand with the dinitro-substituted ring of the symmetry related strand in an edge-to-face fashion with a distance of 3.923 Å, (ii) CH $\cdots$  $\pi$  interaction within the same strand of the molecule with a distance of 3.355 Å, and (iii) CH $\cdots$ O hydrogen bonding between the carbon atom of the benzylic amino group and the oxygen atom of the *ortho*-nitro group with a distance of 2.92 Å (Fig. 1).

The intermolecular interactions leading to the trigonal network structure involve each phenyl ring of the cryptand **B** stacked face-to-face<sup>11</sup> (3.328 Å) with a dinitrobenzene moiety of cryptand **C** while at the same time interacting with a phenyl ring of cryptand **C** in edge-to-face (3.585 Å) manner (Fig. 2). The intermolecular interactions also involve anti-parallel stacking of the dinitro-substituted rings of neighboring cryptands at a distance that ranges between 4.425–4.665 Å and that attenuates the bulk non-linear efficiency of **1** to some extent.

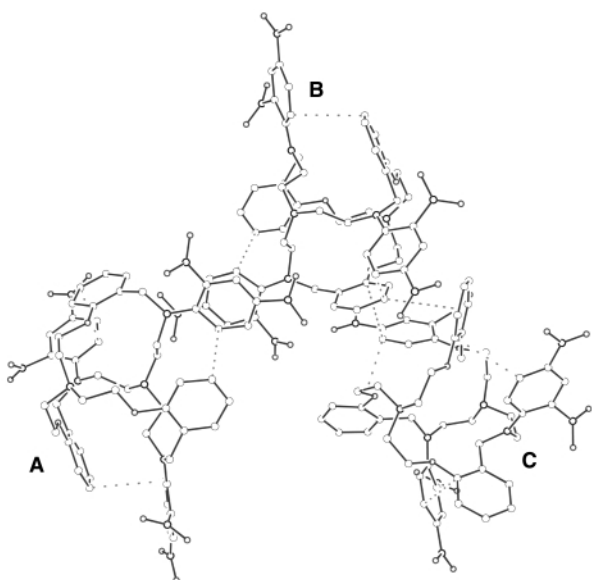
We performed Kurtz powder second-harmonic generation (SHG) measurements<sup>12</sup> on compound **1**. The non-centrosymmetric nature was confirmed by a visible SHG powder signal at



Scheme 1 Synthetic scheme for compound **1**.



**Fig. 1** A perspective view of one cryptand molecule showing the intramolecular H-bonding interactions.



**Fig. 2** A perspective view of A, B and C cryptand molecules showing both intra- and intermolecular H-bonding interactions.

1.064  $\mu\text{m}$  of the order of  $0.6 \times$  urea and represents the first cryptand-based NLO-active bulk molecule. The non-linear

$\sqrt{\langle \beta^2 \rangle}$  coefficient of **1** was determined by HRS technique<sup>13</sup> at 1.064  $\mu\text{m}$  in  $\text{CHCl}_3$  and gave a value of  $16 \times 10^{-30}$  esu. The corresponding  $\sqrt{\langle \beta^2 \rangle(0)}$  static value was found to be  $11 \times 10^{-30}$  esu, which is comparable<sup>6</sup> to that of the classical dipolar PNA molecule under the same measurement conditions. Although powder efficiency of compound **1** is modest, it has a good transparency at the visible region of the spectrum ( $\lambda_{\text{max}} \sim 370$  nm in  $\text{CHCl}_3$ ). Most strikingly, compound **1** by virtue of its strong intermolecular interactions has a mp of 215  $^\circ\text{C}$ , which is the highest among all of the nitroaniline-based compounds reported<sup>14</sup> to have bulk NLO properties. This will make it potentially useful for further device applications. Furthermore, this work presents ample scope for modulating the NLO property through recognition of different metal ions in the cavity of the cryptand as well as by functionalizing the three amino groups with stronger acceptor units.

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## Notes and references

† *Crystal data for 1*:  $\text{C}_{51}\text{H}_{51}\text{N}_{11}\text{O}_{15}$ ,  $M = 1137.133$ , trigonal, space group  $P3$ ,  $a = 16.63(5)$ ,  $b = 16.62(9)$ ,  $c = 16.01(3)$   $\text{\AA}$ ,  $V = 3829(9)$   $\text{\AA}^3$ ,  $Z = 3$ ,  $T = 293$  K,  $\lambda = 0.71073$   $\text{\AA}$ ,  $\mu = 0.11$   $\text{mm}^{-1}$ , 3753 independent reflections,  $R = 0.045$ ,  $wR_2 = 0.103$ . Satisfactory elemental analyses (C, H, N) were obtained for **1**.

CCDC 182/1747. See <http://www.rsc.org/suppdata/cc/b0/b004679p/> for crystallographic files in .cif format.

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