

## Design and synthesis of hyperstructured molecules based on cyclophosphazene core for multiphoton absorption



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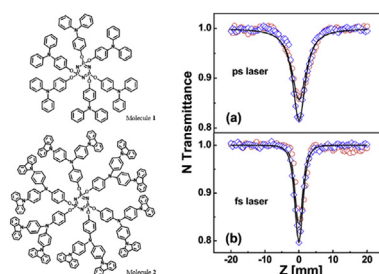
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### HIGHLIGHTS

- Two hyperstructured molecules based on cyclophosphazene core are designed for multiphoton absorption.
- NLO properties are measured using Z-scan technique at 532 nm and 800 nm wavelengths.
- The molecules were tested for the optical limiting applications at 532 nm and 800 nm laser pulses.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Cyclophosphazene based hyperstructured molecules were synthesized through simple nucleophilic substitution reactions. All these molecules were characterized by multinuclear NMR, MALDI and HRMS spectral data. Third order nonlinear optical properties of the hyperstructured molecules were measured using Z-scan technique with 532 nm, picosecond (ps) laser and 800 nm, femtosecond (fs) laser pulses. The molecules showed reverse saturable absorption on excitation at both 532 nm and 800 nm, which could be attributed to the two-photon absorption (2 PA) and three-photon absorption (3 PA), respectively. The 2 PA and 3 PA cross section values exhibited by the molecules based on cyclophosphazene are as high as 527 GM and  $1.86 \times 10^{-76} \text{ cm}^{-6} \text{ s}^2 \text{ photon}^{-1}$ , respectively. The 2PA, 3PA coefficients and optical limiting properties make them suitable candidates for nonlinear optical devices in the visible and near IR range.

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### 1. Introduction

Multiphoton absorption is defined as the electronic excitation of molecule induced by a simultaneous absorption of two or more photons of same or different energy [1]. Over recent years, there is substantial interest in multiphoton absorption particularly two-photon absorption (2 PA) and three-photon absorption (3 PA) because of the demand for their wide variety of applications. The

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application area includes two-photon excited fluorescence microscopy, optical limiting, optical data storage, memory based devices, photodynamic therapy and recently, multiphoton absorption in nanowaveguides have been reported for broadband light generation in semiconductor nanostructures [2]. Therefore, substantial interest is on designing molecules with large two-photon and three-photon absorption cross-sections [1]. In this context, hyperstructured molecules based on inorganic-organic hybrid systems could provide a new class of nonlinear optical (NLO) materials [3,4]. These hyperstructured molecules potentially combine the properties of both small molecules and oligomers and hence find applications in various fields.

Many strategies have been developed to increase the performance of two-photon absorption by increasing the  $\pi$ -conjugation length, introducing electron donor and  $\pi$ -acceptor system, using multipolar and dendritic structures. Consequently, the NLO properties of many hyperstructured molecules produced using aromatic conjugated systems including triaryl amines and carbazole moieties are studied. The cyclophosphazene are robust inorganic heterocyclic molecules with partially delocalized cyclic ring systems. Unlike regular organic aromatic compounds, two different atoms (P and N) construct these conjugated rings thus they are expected to influence the NLO properties. Several researchers have exploited the use of hexachlorocyclophosphazene ( $N_3P_3Cl_6$ ) as a starting material for the dendrimer synthesis since the six labile chlorines can be substituted with the desired group by a simple chemistry [5].

The substituent groups influence the delocalization and planarity that influence the property of the cyclophosphazene derivative. Due to the projection of substituent groups above and below the plane of phosphazene ring, the complete substitution would create a rigid spherical like structure. The rigid spheres like three-dimensional architecture minimize the aggregation and introduce the amorphous property to the material that is important for nonlinear optics. Albeit the cyclophosphazene based dendrimers are known for decades, their NLO properties are virtually unexplored [6,7]. Therefore, the present work highlights our synthesis of hyperstructured molecules constructed on cyclophosphazene core where the building blocks are triarylamine and carbazole moieties and their NLO properties studied with femtosecond (fs) and picosecond (ps) laser pulses. These dendrons are substituted by simple nucleophilic substitution reaction on hexachlorocyclophosphazene.

## 2. Experimental section

### 2.1. Materials and instrumentation

Commercially available reagents like hexachlorocyclophosphazene, carbazole, diphenylamine, methoxy iodomethane, copper powder, triethylene glycol dimethylether, potassium iodide, potassium iodate, cyanuric chloride were purchased from Aldrich. Potassium carbonate, glacial acetic acid and deuterated  $CDCl_3$  were obtained from SRL, India and used as such without any further purification. The precursors, carbophosphazene, diphenyl carbophosphazene, 4,4'-di(carbazol-9-yl)-4''-hydroxy triphenylamine were prepared according to the standard literature procedure [8]. The solvents, tetrahydrofuran and dichloromethane were dried according to standard procedure. The inert atmosphere was maintained throughout the reaction by purging dry nitrogen using standard schlenk techniques. The dendrons, (4-hydroxy)diphenylamine and 4,4-di(carbazol)-4- hydroxytriphenylamine) were purified by using silica gel 60–120 mesh, and the hyperstructured molecule was purified by pure neutral  $Al_2O_3$  column chromatography purchased from SRL company.

$^1H$ ,  $^{13}C$  (400 MHz) and  $^{31}P$  NMR (162 MHz) spectra were recorded on a Bruker Avance-400 MHz NMR spectrometer at room temperature using  $CDCl_3$  as the solvent. All NMR chemical shift are reported in parts per million; downfield shifts are reported as positive values from tetramethylsilane (TMS) as standard at 0.00 ppm. IR spectra were recorded on a JASCOFT/IR-5300 spectrometer with KBr pellets. UV–Vis absorption spectra were recorded using JASCO V-670 UV–Vis–NIR spectrometer. The thickness of the samples used for the absorption measurement was 1 mm thin quartz cell. The fluorescence spectra were recorded on Fluoromax-4 Spectrofluorometer using DCM as the solvent. Elemental analyses were performed on an EA1112, Thermo Finnigan, France. High-resolution mass spectroscopy (HRMS) was performed on a Bruker Maxis HRMS mass spectrometer.

### 2.2. Synthesis of hyperstructured molecule 1

The compound (4-hydroxy)diphenylamine (0.32 g, 1.488 mmol) was dissolved in dry THF (30 ml) and cooled to 0 °C and sodium hydride (0.07 g, 2.96 mmol) was added. The reaction mixture was allowed to warm up to room temperature and then refluxed under nitrogen atmosphere for two hours. Then, hexachlorocyclophosphazene (0.08 g, 0.23 mmol) dissolved in dry THF (20 ml) was added to the reaction mixture at reflux temperature under the protection of dry nitrogen and continued the refluxing for 48 h. Then the reaction mixture was cooled, and the solid was separated via frit, and the filtrate was evaporated. The residue obtained was purified by neutral  $Al_2O_3$  column chromatography (70: 30, HEXANE -DCM) to yield the molecule 1. Yield: 72%. IR(KBr)  $cm^{-1}$ : 3063, 3030, 1583, 1501, 1315, 1271, 1200, 1172, 947, 876, 832, 750, 695, 641, 619. NMR:  $^1H$  (400 MHz,  $CDCl_3$ )  $\delta$  7.15–7.11 (m), 7.02–6.91 (m) ppm;  $^{31}P\{^1H\}$  (162 MHz,  $CDCl_3$ )  $\delta$  9.41 ppm;  $^{13}C$  (100.62 MHz,  $CDCl_3$ )  $\delta$  147.64, 145.88, 144.90, 129.25, 124.92, 124.00, 127.74, 121.93 ppm. HRMS: Exact mass calculated is 1695.5757, experimentally determined is 1696.5626 ( $M+H$ )<sup>+</sup>. Elemental analysis: Calculated for  $C_{108}H_{84}N_9O_6P_3$  is C, 76.45; H, 4.99; N, 7.43%; experimentally determined is C, 76.34; H, 4.92; N, 7.51%.

### 2.3. Synthesis of hyperstructured molecule 2

The compound 4,4-di(carbazole)-4-hydroxytriphenylamine) (0.07 g, 1.18 mmol) was dissolved in dry THF (30 ml) and cooled to 0 °C and sodium hydride (0.05 g, 2.36 mmol) was added. The reaction mixture was allowed to warm up to room temperature and then refluxed under nitrogen atmosphere for two hours. Then, hexachlorocyclophosphazene (0.06 g, 0.19 mmol) dissolved in dry THF (20 ml) was added to the reaction mixture at reflux temperature under the protection of dry nitrogen and continued the refluxing for 72 h. Then the reaction mixture was cooled, and the solid was separated via frit, and the filtrate was evaporated. The residue obtained was purified by neutral  $Al_2O_3$  column chromatography (70: 30, HEXANE -DCM) to yield the molecule 2. Yield: 72%. IR (KBr)  $cm^{-1}$ : 3463, 3042, 2959, 2356, 1625, 1597, 1562, 1507, 1451, 1333, 1263, 1228, 1174, 1102, 1014. NMR:  $^1H$  (400 MHz,  $CDCl_3$ )  $\delta$  8.10–8.06 (m), 7.32–7.18 (m) ppm;  $^{31}P\{^1H\}$  (162 MHz,  $CDCl_3$ )  $\delta$  9.30 ppm;  $^{13}C$  (100.62 MHz,  $CDCl_3$ )  $\delta$  146.23, 140.81, 132.44, 129.54, 128.01, 125.86, 124.62, 123.27, 122.38, 122.12, 120.31, 119.90, 109.62 ppm. HRMS: HRMS: Exact mass calculated is 3676.2699, experimentally determined is 3677.610 ( $M+H$ )<sup>+</sup>. Elemental analysis: Calculated for  $C_{252}H_{168}N_{21}O_6P_3$  is C, 82.27; H, 4.60; N, 7.99%; experimentally determined is C, 82.16; H, 4.71; N, 7.85%.

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