



Cite this: *New J. Chem.*, 2019, **43**, 10948

Second-order nonlinear optical properties of eight-membered centrosymmetric cyclic borasiloxanes†

Mohan Gopalakrishnan,^{‡,ab} Thamodharan Viswanathan,^{id} ‡^a Ezhumalai David,^{id} ^a Krishnan Thirumoorthy,^{id} ^a Nattamai S. P. Bhuvanesh^c and Nallasamy Palanisami^{id} ^{*a}

In an efficient 2+2 cyclocondensation reaction, electron-withdrawing arylboronic acids with diphenylsilanediol were converted to eight-membered cyclic borasiloxanes [(RPhBO)(PhSiO)]₂ [R = F (**1**), 2,4-F (**2**), CF₃ (**3**), CN (**4**), NO₂ (**5**)]. All these compounds were characterized by elemental analysis, FT-IR, and NMR (¹H, ¹³C, ¹⁹F, ²⁹Si and ¹¹B) and structurally confirmed by single-crystal X-ray diffraction studies. Compounds **1–5** crystallized in the centrosymmetric space group, revealing an eight-membered ring (B₂O₄Si₂) configuration with organic substitutions, which occupied axial and equatorial positions. Compounds **1** and **2** feature 2D network hydrogen bonding whereas compound **3** has a solid-state 3D supramolecular architecture. The other two compounds **4** and **5** exhibit only C–H...π interactions which lead to a 1D polymeric structure and these intermolecular interactions influence crystal packing. Photophysical properties were studied by UV-visible and fluorescence spectroscopic techniques. In addition, the optical band gaps (*E_g*) of compounds **1–5** were determined by diffuse reflectance spectra and compound **5** has a lower band gap value than the others, due to the strong electron-withdrawing nitro group in compound **5**. The thermal behaviour of compounds **4** and **5** has been investigated using thermogravimetric analysis and differential thermal analysis, both compounds being stable up to 250 °C. The nonlinear optical response of the crystalline powdered borasiloxanes by Q-switched Nd-YAG laser and second harmonic generation (SHG) efficiency of borasiloxanes **4** and **5** were found very similar to those of potassium dihydrogen phosphate. The SHG efficiency of the centrosymmetric borasiloxanes mainly arises from the distorted silicon atom and non-covalent interactions which preclude the dipoles in the antiparallel arrangement in crystal packing. Further, optical and nonlinear properties of the borasiloxanes were investigated by density functional theory calculations.

Received 28th March 2019,
Accepted 12th June 2019

DOI: 10.1039/c9nj01611b

rsc.li/njc

Introduction

Inorganic-organic hybrid nonlinear optical (NLO) materials are interesting in research owing to their wide applications, such as electro-conductive, optical, structural and industrial developments.¹ The major typical design of molecules with second-order NLO

properties consists of strong electron donor and acceptor connected by a π-conjugated system (D–π–A). In these types of molecules, the π-conjugation contributes a pathway for the redistribution of electronic charge under the influence of an electric field. The phenyl rings incorporated in a π-conjugated system concurrently enhance the thermal and chemical stabilities as well as make the molecule nonlinear.^{2,3} In particular, the second harmonic generation (SHG) properties require high molecular hyperpolarizability and an optimal arrangement of those molecules in a crystal, which is the macroscopic equivalent.⁴ The shape of a molecule, its atomic arrangement and the mobility to modify a variety of packing states to a great extent may determine the packing of molecules in the crystalline medium and concomitantly the space group.⁵

Borasiloxane (B–O–Si) rings have attracted considerable attention owing to potential applications arising out of their interest in structural and materials science.^{6–9} Cyclo-borasiloxanes are well represented by six-, eight- and ten-membered ring

^a Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632 014, Tamil Nadu, India.

E-mail: palanisami.n@gmail.com; Tel: +91 98426 39776

^b Department of Chemistry, Karpagam Academy of Higher Education, Coimbatore-641021, Tamil Nadu, India

^c X-ray Diffraction Lab, Department of Chemistry, Texas A&M University, College Station, TX 77842, USA

† Electronic supplementary information (ESI) available: Optimized structures, UV-vis, fluorescence, DRS, TGA and all NMR spectra are available. CCDC 1046949, 1046953, 1402889–1402891. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9nj01611b

‡ These authors contributed equally to this work.