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Triphenylamine derived coumarin chalcones and their red emitting OBO difluoride complexes: Synthesis, photophysical and NLO property study

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ABSTRACT

The auxiliary methoxy aided triphenylamine donors derived coumarin chalcones and their OBO complexes with branched donor-pi-acceptor systems are synthesized and characterized. Their photophysical properties are extensively studied in solvents of different polarity. They show strong emission solvatochromism and have quantum yields up to 0.87. The BF_2-complexation of coumarin chalcones enhanced the quantum efficiency by approximately 1.4 times compared to the uncomplexed chalcones. Frontier molecular orbital analysis and Generalised Mulliken Hush analysis revealed a strong intramolecular charge transfer character of these chromophores. The first, second and third order polarizability of these chromophores are evaluated by the solvatochromic method and supported by Density Functional Theory calculations using CAM-B3LYP/6-31g(d) method. The third order nonlinear optical susceptibilities of these chromophores obtained by Z-scan analysis showed very less values of the imaginary part. Replacement of N-ethyl donors by aryl amine groups provided branched push-pull systems with enhanced thermal stability and nonlinear optical response.

1. Introduction

Since a photon has replaced the electron as information carrier the field of design of nonlinear optical (NLO) materials, investigation of their properties and application are tremendously growing [1]. Inorganic materials are relatively more stable than the organic materials but usually accompanied with poor amplitudes of hyperpolarizability [2]. Inorganic materials are also associated with difficulties in obtaining high purity crystals and in device fabrication [2]. Organic NLOphores provide a diversity of structures, ease of fabrication and low synthetic cost combined with large amplitudes of hyperpolarizability [3,4]. As far as the quadratic hyperpolarizability is concerned, organic molecules are versatile NLOphores [4–6]. Organic NLO materials are widely used for NLO devices and applications like optical switches, optical sensors, integrated optical circuits for telecommunications, optical computing, optical poling, phase modulators of optical signal and devices for frequency mixing processes [5,7–9]. The organic π-conjugated systems have widely been investigated as efficient NLO materials due to strong charge transfer in the system as these compounds generally show a high degree of nonlinearity, faster optical response high damage resistance and high nonlinear optical susceptibilities compared to conventional materials [10–14]. Among the organic NLOphores, the chalcones are the promising ones with good NLO efficiency and transparency [15]. By virtue of their design, NLOphoric structures are largely of the push-pull type with donor and acceptor groups separated by π-conjugated framework [16–19]. The bulk nonlinear properties of such systems are crucially dependent on the molecular hyperpolarizability and dipole moment of the molecule [11,20]. Several amino substituted coumarins with the donor-acceptor framework and styryl coumarins have been emphasized for their NLO properties using different methods [21,22]. Understanding the molecular origins of the NLO properties of chromophores provides rational guidelines to synthesize better-performing architecture [23]. Oudar's two level

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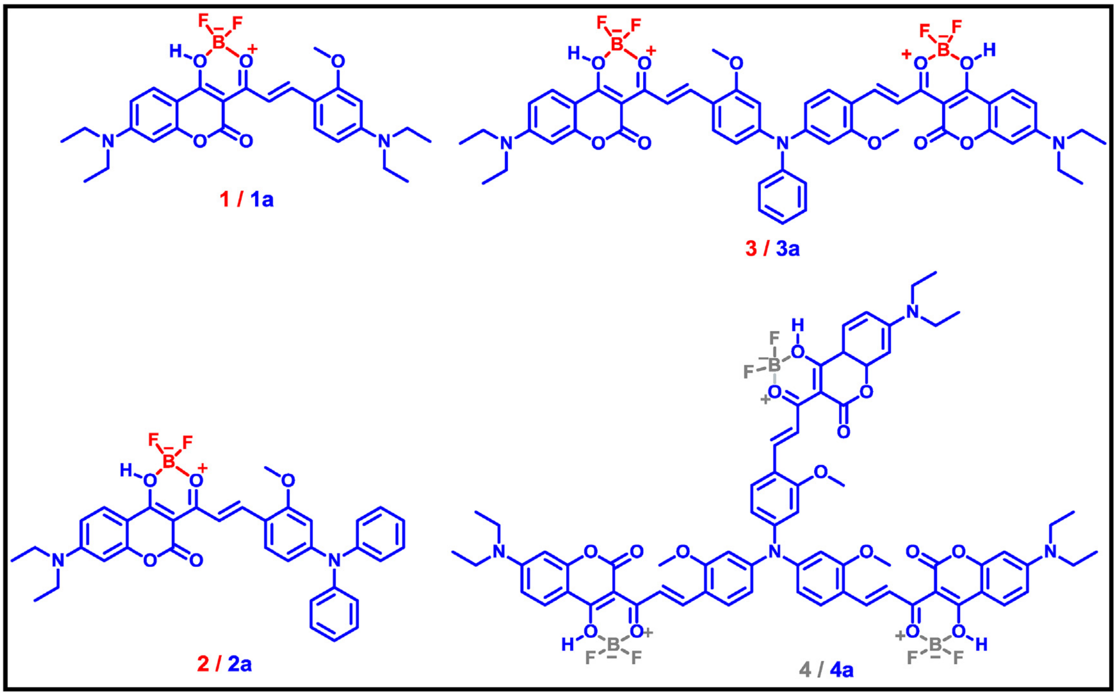
model (eq. (1)) is the tool to provide the basis for designing organic NLO molecules with large first order hyperpolarizability (β) [24,25]. (see Fig. 1)

$$\beta \propto \frac{\mu_{ge}\Delta\mu_{ge}}{(\Delta E_{eg})^3} \qquad (1)$$

The first order hyperpolarizability β is proportional to the product of excess dipole moment ($\Delta\mu_{ge}$), the difference in dipole moments between the ground (μ_g) and excited states (μ_e) and the transition dipole moment (μ_{ge}). Also, β is inversely proportional to the energy gap (ΔE_{eg}) between these two states. Increase in the value of product $\mu_{ge}.\Delta\mu_{ge}$ and a decrease in ΔE_{eg} value lead to maximization of the β value. Highly delocalized acentric π-electron systems interacting with suitably substituted electron donor and electron acceptor group are known to exhibit a large value of the first hyperpolarizability (β) and second hyperpolarizability (γ) [26]. Thus NLO properties of organic molecules can be engineered by tuning their HOMO-LUMO energy gap (HLG. For a π-conjugated system like chalcones, an extension of the conjugation can lead to a decrease in the HLG to a certain extent [27]. Considering the undesirable degradation of most of the organic molecules when excited by high energy optical beams, chalcones are the better candidates to enhance the NLO responses to avoid possible damage of matrix [28–34]. Some simple coumarins are reported to show significant NLO properties [11,26,35]. Further solid state emissive D-A-D coumarin chalcones are reported to possess promising NLO characteristics [33,36]. So in this study, we have investigated the solvatochromism and NLO properties of newly designed D-A-D type coumarin chalcones. From Oudar's formula, it is clear that β is intrinsically related to the charge-transfer excited states i.e ICT [4]. In coumarin chalcones, the ICT can be assisted by lowering HLG [37] which can be achieved by electron donating group at the 7 position and/or an electron withdrawing group either at the 3 position via resonance and inductive effects [38]. A donor at 7 position and acceptor at 3 position resulting in the "push-pull" effect align more closely with the direction of the ICT from the 7 position to lactone carbonyl [38]. To exhibit such a strong ICT, 7 position is substituted with N, N-diethyl donor group and 3 position by an acetyl group. The formation of intramolecular hydrogen bonding with the acceptor unit in D-A compounds is an effective way to lower the bandgap. In that context, OH group is deployed at 4 position of coumarin moiety for betterment of NLO response. The acetyl moiety is further extended to a chalcone by substituting with differently substituted phenyl and triphenylamine as strong donors by Claisen-Schimidt condensation to achieve highly efficient D-A-D (D-π-A-π-D) NLOphoric system. The electronic property of the substituents on the aromatic compounds can greatly affect the electronic state of the entire molecule [39] hence phenyl and triphenylamine donor part of coumarin chalcones are substituted with methoxy group as an auxiliary donors which further helps to improve solubility. This overall design strategy makes the coumarin chalcones as a rich π-conjugated system with asymmetric distribution of electronic charge to realize large molecular hyperpolarizability values. The further red shift in absorption may lead to manifestation of enhanced hyperpolarizability characteristics which can be achieved by BF_2 complexation of coumarin chalcones [40–42]. BF_2 complexation of coumarin and dipyrromethane moiety is often utilised to enhance its fluorescence characteristics and photochemical stability [43–47]. Also BF_2 complexation of such type of ligands results into red shifted absorption and emissive entities with enhanced NLO responses [42,48–50]. OBO difluoride complexes are known to possess good solvatochromic properties [45,51–53]. The crucial role of the B(III) is to stabilize the ligand by coordination and to make the π-system planar to enhance the conjugation and charge transfer along the molecular axis. This is expected to furnish more efficient ICT for enhancement of NLO properties of D-A-D coumarins. Thus synthesized chalcones and their red shifted BF_2 complexes were studied for their NLO properties by solvatochromic measurement and computations. Theoretical investigation of ground and excited state geometries and energies, dipole moment, polarizability and hyperpolarizability are


1 / **1a**

3 / **3a**

2 / **2a**

4 / **4a**

Fig. 1. Structures of dyes **1** to **3** and **1a** to **4a**.