



Synthesis of julolidine-containing nonlinear optical chromophores: Achieving excellent electro-optic activity by optimizing the bridges and acceptors



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ABSTRACT

Two series of highly efficient nonlinear optical chromophores A1-C1 and A2-C2 based on the julolidinyl donors and tricyanofuran or phenyl-trifluoromethyl-tricyanofuran acceptors (CF₃-Ph-TCF) linked together via π -conjugation through thiophene or pyrrole or tetraene moieties as the bridges, have been synthesized and investigated. The ultraviolet absorption, solvatochromic, thermal stabilities and electro-optic activities of these chromophores were systematically studied to illustrate structure-performance relationships within the six chromophores. All the chromophores exhibited good thermal stabilities with the decomposition temperatures (T_d) higher than 200 °C. Appropriate combination of the π -conjugated bridge, electron-donor and electron-acceptor as well as the isolated group in the chromophores plays an important role in achieving larger electro-optic activities. Exemplified by the chromophore A2 with CF₃-Ph-TCF acceptor, it gave a very large r_{33} value of 223 pmV⁻¹ at 1310 nm at the doping concentration of 25 wt%.

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1. Introduction

Organic electro-optic (OEO) materials have been developed over the last three decades because they can be used in optical switches, high-speed and broadband information technology and telecommunications [1–8]. One of the major component in such materials is the second-order nonlinear optical (NLO) chromophore contain an electron donor-acceptor functionality connected to a π -conjugated bridge [9,10]. To meet the stringent requirements for the using of devices, NLO chromophores should exhibit good properties such as high thermal and chemical stabilities, large nonlinearity, and good transparency, as well as easy syntheses [11]. Bulk second-order EO coefficient (r_{33}) requires non-centrosymmetric arrays of chromophores with high molecular first hyperpolarizability (β) [12]. Rational design and synthesis of dipolar NLO chromophores with high β and robust thermal stability

still represents one of the most critical challenges, optimization of the π -conjugated bridge, electron-donor and electron-acceptor characteristics of the substituents is needed in achieving higher β [12,13]. Strong chromophores, are characterized by a large dipole moment (μ) and large first-order hyperpolarizability (β), but unfortunately tend to lower the NLO response at higher chromophore loading levels due to aggregation effects. In molecular optimization, introducing a large steric hindrance group to isolate chromophores is the most popular and easy way to attenuate the dipole–dipole interactions of chromophores [14,15].

Among all of the materials studied, most of the high-performance organic EO materials developed generally include a primary class of high first-order hyperpolarizability (β) chromophores containing 4-(dialkylamino)phenyl groups or triarylamino groups as a donating group, the tricyanovinylidihydrofuran (TCF) or phenyl-trifluoromethyl-tricyanofuran acceptors (CF₃-Ph-TCF) acceptors, and ring-locked tetraene (CLD) or 2,5-divinylthienyl (FTC) bridges [16–20]. There remains strong continued interest in improving the properties of these materials as well as the synthetic strategies for their preparation. Further enhancement of NLO activity of such structures can be achieved by fine-tuning the strength

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of bridge, donor and acceptor groups as well as considering the additional molecular characteristics of chromophores [21].

Previously, many papers had compared the julolidinyl-derived donors with a traditional diethylamine donor [22–24]. The results showed that the julolidinyl-derived chromophores showed much higher electro-optic (EO) activities because of its strong electron donating ability. The ring-fused aminophenyl structures in julolidinyl donors facilitate the overlap of the p-orbital of the amino atom with the phenyl ring thus providing a good mechanism to increase the electron-donating strength [22]. Meanwhile, the julolidinyl donor contains electron rich heteroatom oxygen thus increase the electron-donating ability furthermore. They focus on using a thiophene bridge and a TCF acceptor or CLD bridge and a CF₃-Ph-TCF acceptor [22,25]. However, there is no study conducted using a thiophene or pyrrole-based bridge and a CF₃-Ph-TCF acceptor.

So, in this study we want to compare the structure-property relationship between the six second-order chromophores with julolidinyl-based donors, but with different electron acceptors and bridges. The bridges studied here including thiophene, pyrrole and CLD-based groups, and the acceptors including TCF and CF₃-Ph-TCF groups (Chart 1). The UV–Vis, solvatochromic behavior, thermal stabilities and EO activities of these chromophores were systematically studied and compared to understand their structure-property relationships.

2. Experimental

2.1. Materials and instrument

All chemicals are commercially available and are used without further purification unless otherwise stated. *N,N*-dimethylformamide (DMF), Phosphorus oxychloride (POCl₃), tetrahydrofuran (THF) and ether were distilled over calcium hydride and stored over molecular sieves (pore size 3 Å). Compound **2a** was synthesized according to literature [26]. Compounds **2b** and **3b** were synthesized according to literature [27]. Compounds **2c**, **3a**, **4a** and chromophore A1 were synthesized according to literature [28,29]. TLC analyses were carried out on 0.25 mm thick pre-coated silica plates and spots were visualized under UV light. Chromatography on silica gel was carried out on Kieselgel (200–300 mesh).

¹H NMR spectra were determined on an Advance Bruker 400 M (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). The MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEXIII (Broker Inc.,) spectrometer. The UV–Vis spectra were performed on Cary 5000 photo spectrometer. The TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C min⁻¹ under the protection of nitrogen.

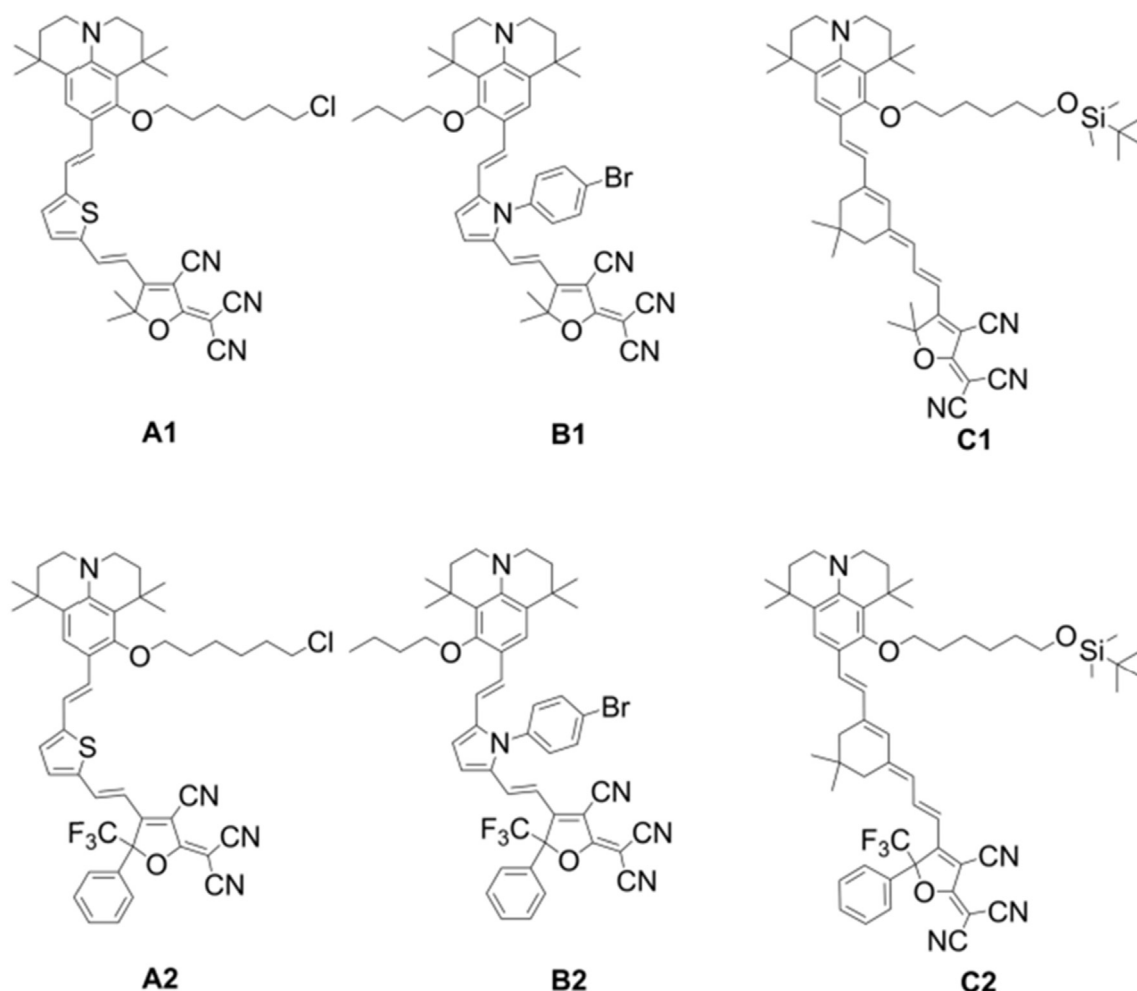


Chart 1. Chemical structures for chromophores A1–C1 and A2–C2.

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