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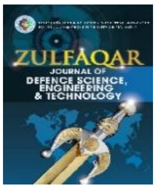

RECENT STUDIES ON ORGANIC DIPOLAR BASED ELECTRONIC AND ELECTRO-OPTIC MATERIAL

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ABSTRACT

The advancement of sensor technologies, optical computing, communication, and signal processing with ultra-broadband at GHz-THz bandwidths relies heavily on high-performance electro-optic (EO) modulators. Significant advancements have been made in silicon-organic hybrid (SOH) and plasmonic-organic hybrid (POH) technologies over the past ten years, enabling devices with higher bandwidth, improved energy efficiency, reduced footprints, and significantly lessen the π-voltage-length product. Modern SOH and POH technologies take advantage of the fundamental of EO activity of organic chromophores as well as the improved electrical and optical field overlap that can be achieved in nanophotonic devices. To achieve ground-breaking performance, synergistic innovation is required from the engineering of devices to the logical design of organic EO materials. It is acknowledged that the forthcoming of information technology depends on the chip-scale integration of electronics and photonics as well as the use of the greatest features of plasmonics, photonics, and electronics to accomplish this goal. However, there are still many obstacles to overcome, such as matching the sizes of the electrical and photonic circuits, accomplishing low-loss transitions across the three fields of electronics, photonics, and plasmonics, and creating and integrating novel materials. This review concentrates on the advancement and innovations of material design of different structures of organic dipolar chromophores that highlight the importance and influence of their structures on electrical and EO properties.

1.0 INTRODUCTION

Organic based materials play a critical role in the sustainable development of electrical and electro-optic (EO) materials for these applications. Compared with inorganic materials, organic materials have unique characteristics such as the ability to form intricate molecular structures, flexibility, and decreased density. By using the femtosecond (30 fs) reaction periods of the conjugated π-electron systems of organic chromophores to time-varying electric fields, organic EO materials have the potential to enable terahertz (THz) device bandwidths. In addition, organic EO materials are promising to exhibit extraordinarily high EO activity due to the considerable charge redistribution brought on by electric fields in extensive π-conjugated systems, provided that dipolar chromophores are rightly coordinated in an acentric order, one might achieve values higher than 1000 pm/V. Moreover, organic EO materials offer outstanding processability and versatility, high optical damage threshold, fast response speed, high bandwidth, low dielectric constant and very affordable when chromophores are manufactured in mass production [1-4]. In the last ten years, improvements to in-device EO activity have frequently been hampered by trade-offs among molecular hyperpolarizability (β), electric field poling-induced acentric order ($\cos3\ \theta$), optical loss

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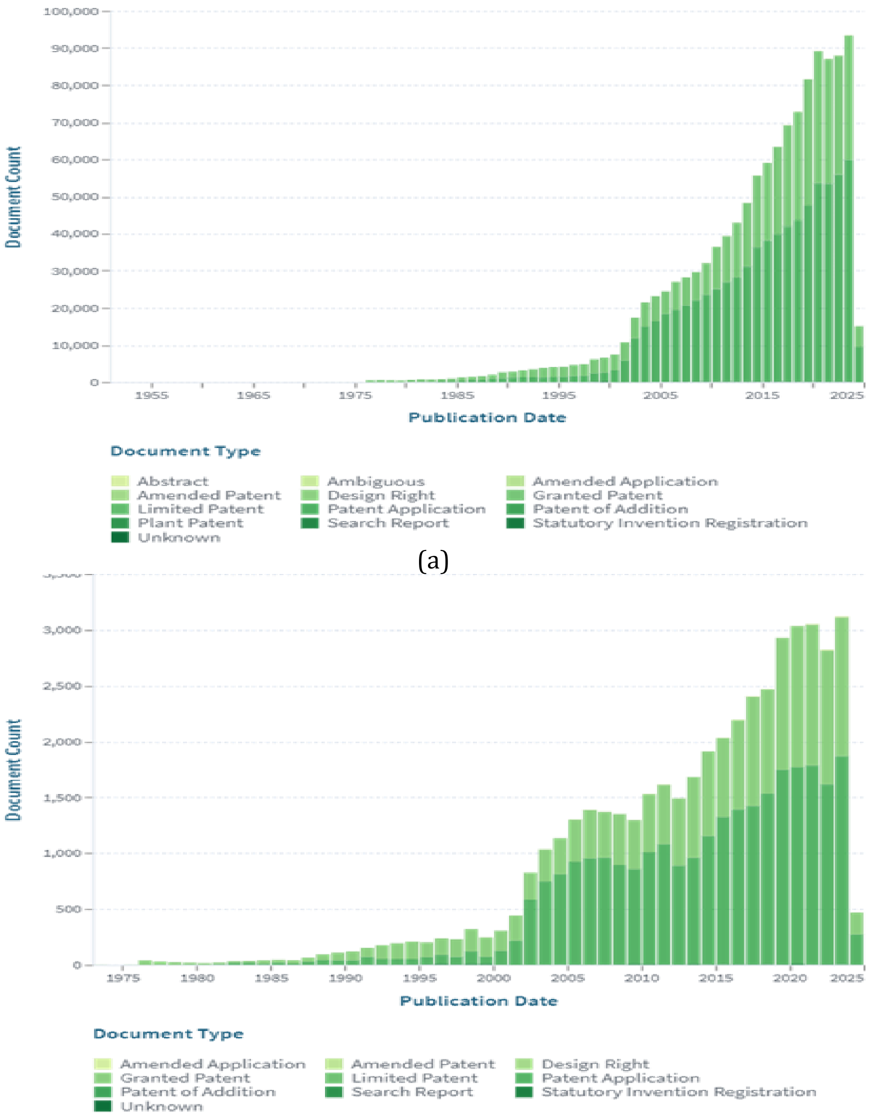
and number density (ρN) of organic EO chromophores [5]. In essence, improving one of these factors often compromises another such as increasing the number density of chromophores may enhance β but also lead to higher optical losses. These trade-offs have hindered progress in optimizing EO activity in devices.

Most of the earlier research on the design of organic EO chromophores has been concentrated on enhancing ordering by side-chain engineering or chromophore mixing, as well as boosting chromophore number density. Nowadays, many calculations such as time-dependent density-functional theory (TD-DFT) and density-functional theory (DFT) calculations using statistical and quantum mechanical methods have been employed to create a new class of organic EO materials that enable target optimization by assessing the predicted band gaps, hyperpolarizabilities (β), and dipole moments (μ). The majority of big β chromophores have been developed using conjugated "push-pull" system compounds that have been optimized which composed of electron-donating (D) and electron-withdrawing or acceptor (A) end groups that interact via a π-conjugated bridge (D-π-A) to produce an intramolecular charge transfer (ICT) transition. The β values of dipolar chromophores are influenced by the strength of the donor and acceptor groups, as well as the type and length of the π-conjugated bridges. The search in finding novel and potent heterocyclic acceptors has been one of the primary strategies for enhancing the molecular hyperpolarizability of dipolar chromophores. The directional bias of π-electrons that are loosely held along the conjugating bridge is the source of the ground-state polarization of dipolar chromophores [6]. In today's technologies and custom solutions for varied applications, materials engineering is crucial.



(a)

(b)

Figure 1. Patent documents over time from lens.org; with (a) keywords of 'organic' and 'electronic' and (b) keywords of 'organic' and 'electro-optic'

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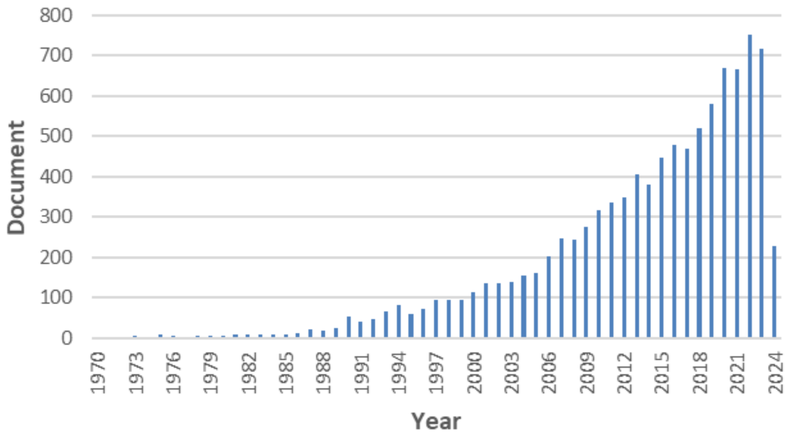


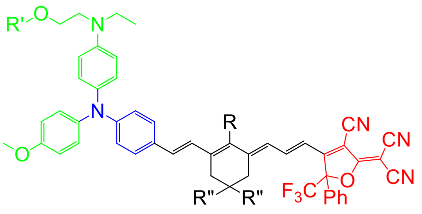
Figure 2. Publication documents over time from Scopus (www.scopus.com)

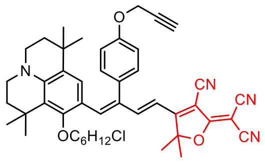
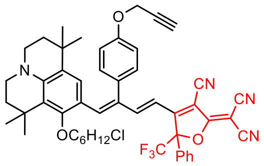
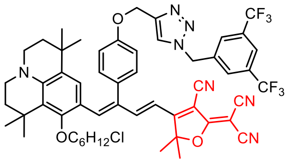
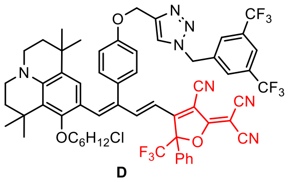
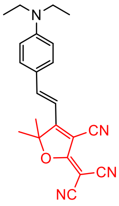
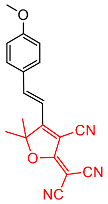
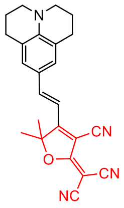
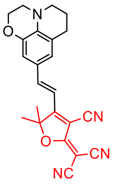
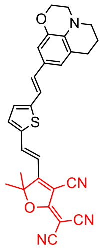
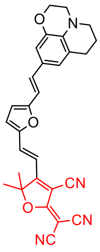
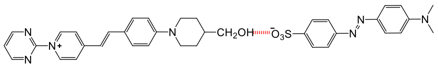
In the years following the beginning of the 21st century, there has been a noticeable rise in patent filings (Figure 1) and publications (Figure 2) concerning organic-based electronic and EO materials. This trend reflects growing interest and investment in the development of organic materials for various applications, including displays, lighting, sensors, photovoltaics, and optoelectronic devices. The increasing demand for energy-efficient, lightweight, and flexible electronic devices has fuelled interest in organic-based materials as alternatives to traditional inorganic semiconductors. Ongoing research efforts have led to the discovery and synthesis of novel organic materials with enhanced optoelectronic properties, such as improved charge transport, higher efficiency, and greater stability. These advancements drive innovation and the emergence of new fabrication techniques, device architectures, and manufacturing processes has enabled the realization of organic-based electronic and EO devices with improved performance and functionality.

2.0 DIPOLAR ORGANIC CHROMOPHORES FOR ELECTRICAL AND ELECTRO-OPTIC (EO) APPLICATIONS

Dipolar chromophores are conjugated "push-pull" system compounds that have been optimized by varying electron-donating (D) and electron-withdrawing or acceptor (A) end groups that interact via a π-conjugated bridge (D-π-A). There were many studies on these by investigating the best combination of D with A and π-conjugated system with the idea the more polar D-π-A system should promote an improved intramolecular charge transfer (ICT) transition in general. Much research has demonstrated the broad practical potential of organic second-order nonlinear chromophores to develop a 500 GHz EO modulator, terahertz field detectors, and other optoelectronic devices [2]. Table 1 lists some recent studies on different potential dipolar organic chromophores as prospective electronic and EO materials.

Table 1. Recent studies on various dipolar organic chromophores as potential electronic and electro-optic (EO) materials

No	Chromophore	Potential Application	Computational/Experimental data	Ref
1	 BAH13	Hyper Rayleigh Scattering (HRS) second-order nonlinear optics (NLO); modulator	HRS > 2-fold in β value; neat BAH13 devices with poling efficiencies = 11.6 ± 0.7 $nm^2 V^{-2}$, max r_{33} value = 1100 ± 100 pm V^{-1} at 1310 nm on HfO_2, BAH13 tested in POH modulator device produced high r_{33} = 208 pm V^{-1} at 1550 nm.	[5]

No	Chromophore	Potential Application	Computational/Experimental data	Ref
2	 A  B  C  D	NLO applications	Chromophore D • the macroscopic EO = 54 pm.V^{-1} (at 1310 nm) • reasonable r_{33} value • good thermal stability • good chromophore yield	[7]
3	 Ref1  Ref2  Ref3  J1  JS  JO	balance nonlinearity and transparency trade-off in second-order NLO materials	• DFT calculations, r_{33} = 9.6 pm V^{-1} of J1/APC = 27% higher than that of Ref1/APC (7.5 pm V^{-1}) • JS-doped film displayed blue-shift in λ_{max} relative to FTC. • thermal decomposition T > 260°C; notable solvatochromic from dioxane to dichloromethane (DCM).	[8]
4	 PMPR	NLO applications and THz photonics	• first hyperpolarizability = 335 × 10^{-30} esu. • ultrathin PMPR crystal with thickness ≈10 µm • exceptional THz wave generation • broadband THz wave generation • wide flat-spectral-band in 0.7–3.4 THz • generation efficiency (producing THz amplitude	[9]

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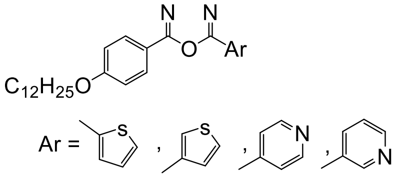
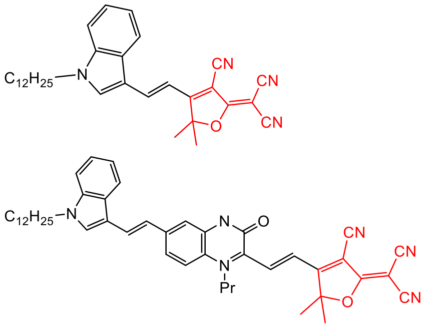
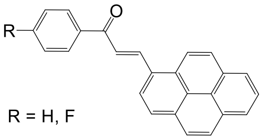
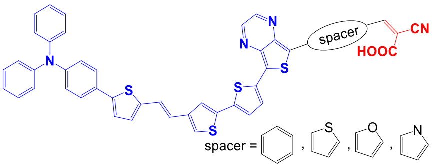
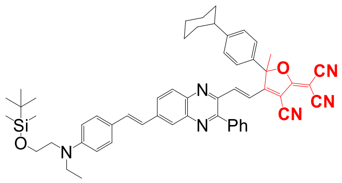
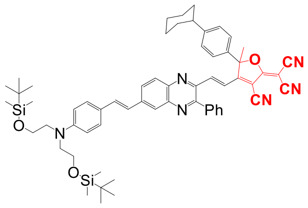
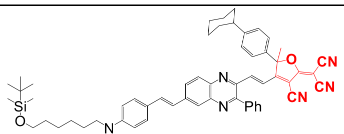
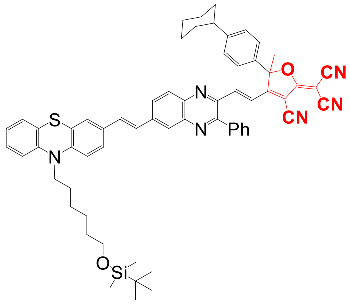
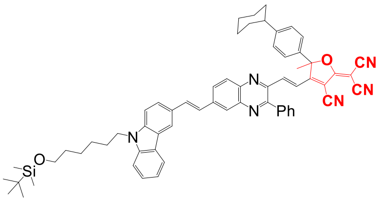
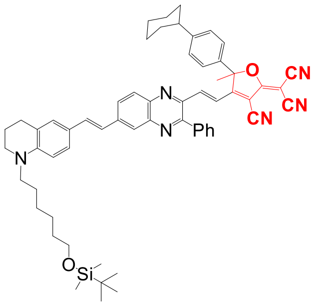
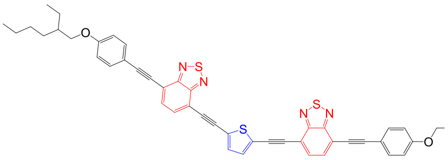
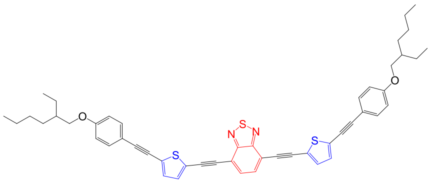
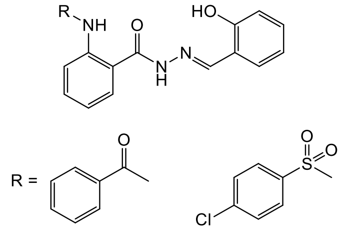
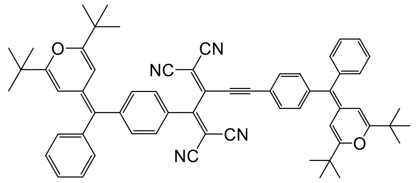
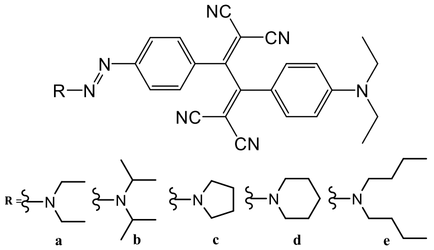
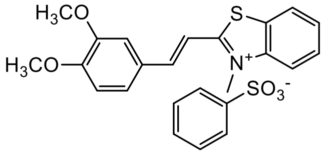
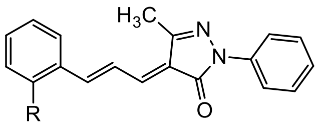
No	Chromophore	Potential Application	Computational/Experimental data	Ref
			five times higher than a ZnTe crystal of mm-scale thickness)	
5		NLO applications	Compound with 4-pyridyl end group give the highest β_o (Oxa-4-Py = β_o 24.0 × 10^{-30} esu)	[10]
6		EO devices functioning within the shortwave infrared (IR) spectrum	• Ind-VQonV-TCF has large µβ value (~13068 x 10^{-48}esu) • optical transparency at a wavelength of 850 nm	[11]
7		Electrode materials, semiconductor, organic light emitting diodes (OLED) devices	PC2 exhibits a specific capacitance of 220 Fg^{-1} at a scan rate of 10 $mV.s^{-1}$	[12]
8		Potential as photosensitizers in dye-sensitized solar cells	• HOMO/LUMO energy levels of D1, D2, D3, D4 = -5.09/-3.36 eV, -5.06/-3.26 eV, -5.10/-3.43 eV, and -5.10/-3.41 eV, respectively. • Calculated energy bandgap D1, D2, D3, D4 = 1.73 eV, 1.78 eV, 1.67 eV, 1.69 eV, respectively. HOMO energy levels < redox couple level I-/I-3 (-4.8 eV), LUMO energy levels > semiconductor conduction band (-4.0 eV).	[13]
9	 Chr-An1  Chr-An2	Second harmonic generation (SHG)	• β = 937 × 10^{-30} esu • NLO coefficient, d_{33}, which was found to be as high as 52 pm/V.	[14]

No	Chromophore	Potential Application	Computational/Experimental data	Ref
	 Chr-An3  Chr-PT  Chr-Car  Chr-TQ			
10	 BSB  SBS	Third-order NLO applications	second-order hyperpolarizability, γ of SBS = 4.4×10^{-28} esu	[15]

No	Chromophore	Potential Application	Computational/Experimental data	Ref
11	 **NHBPB** **CN-BHP**	NLO applications	NHBPB • Red-shifted UV-Vis (297.894 nm at M06-2X & 311.594 nm at M06) • Lower transition energy (4.162 eV at M06-2X & 3.979 at M06) • Higher second hyperpolarizability = 2.749 ×10^5 at M06-2X & 1.945 × 10^5 a.u at M06 functional	[16]
12	 TCBD-5	Second-order NLO, electrochemical	• 2 oxidation waves & 1 reduction wave • $\mu\beta_{EFISH}$ up to 5700 ×10^{-48} esu	[17]
13		Second order NLO	λ_{max} = 454 – 692 nm EFISHG NLO responses with $\mu\beta$ values = 850 × 10^{-48} esu to 6050 × 10^{-48} esu	[18]
14	 DOBS	SHG	• SHG = 1.8 times > standard KDP • DFT: β_{max} = 107.7 × 10^{-30} esu • T_m = 251.5°C (high thermal stability) • low dielectric constant (ε_r = 5.2 ± 0.1) • optical transmittance = 65 % • optical band gap = 2.02 eV • strong green radiation at 560 nm	[19]
15	 R = H (PYR) = OCH_3 (PYROMe)	all-optical modulators, generators of SHG and THG signals	• *trans* isomer has higher CT excited-state dipole moment than *cis* isomer. • $\Delta\mu_{GS}^{(trans\text{-}cis)}$ (*GP gas to water phase*) for PYROMe, the dipole moment increases from 1.84 D to 3.20 D, while for the PYR, increases from 1.75 D to 2.87 D • Theoretical NLO of *trans* PYROMe in water β_{vec} was the highest (8675.02 au) and β_{TOT} was the highest (14458.37 au). • PYR (A ~ 1.6 V) demonstrated a slightly	[20]

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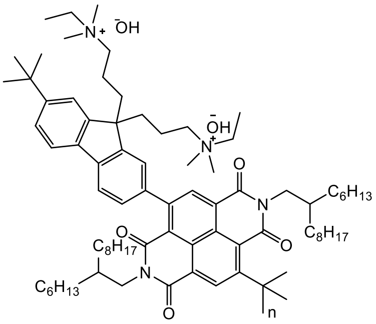
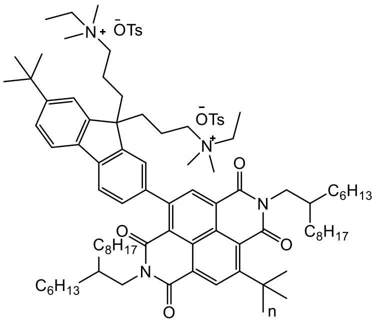
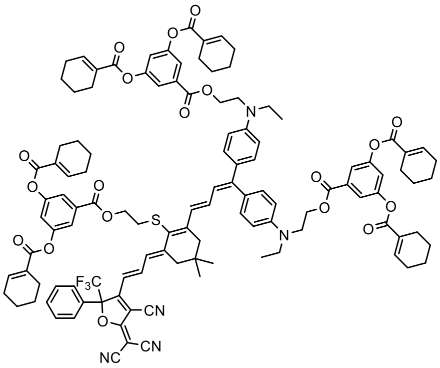
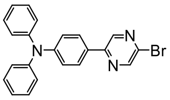
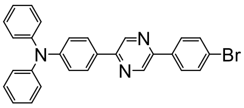
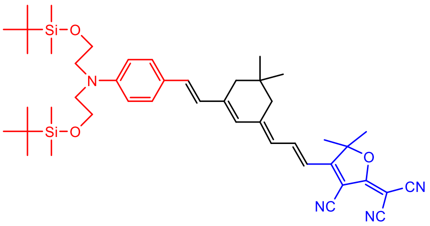
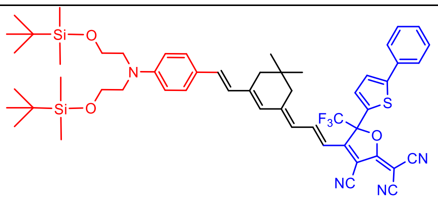
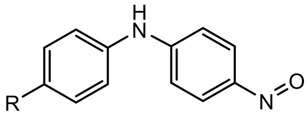
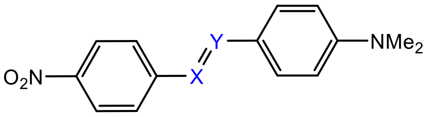
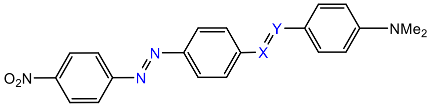
No	Chromophore	Potential Application	Computational/Experimental data	Ref
			higher NLO signal than that of PYROMe (A ~ 1.2 V)	
16	 PFN-NDI-OH  PFN-NDI-OTs	solar cells	improved power conversion efficiencies (PCE) over the ZnO-only based device: • PFN-NDI-OH up to 8.91 %, • PFN-NDI-OTs up to 9.41 %	[21]
17	 AR-1	EO materials	• BLD-1 λ_{max} = 891 nm, β_{tot} = 1722 × 10^{-30} esu, μ (D) = 27.79 • BLD-3 λ_{max} = 905 nm, β_{tot} = 1732 × 10^{-30} esu, μ (D) = 28.58 • AR-1 λ_{max} = 802 nm, β_{tot} = 1353 × 10^{-30} esu, μ (D) = 20.97 AR-1 resulted in smaller μ, one of parameter for excellent choice in manufacturing EO devices.	[22]
18	 PP-1  PP-2	fluorescent sensors	PP-1 and PP-2 demonstrated two wide absorption peaks in the range of 281–298 nm and 380–405 nm (with extinction coefficients of 13194–60014 and 29504–59383 $M^{-1} \cdot cm^{-1}$, correspondingly)	[23]
19	 CLD-1	EO modulators	• Mach–Zehnder architecture • second-order NLO host-guest polymer i.e. PMMA and a CLD-1 chromophore • modulation depth of 0.637 dB • a reduced Vπ of 1.6 V • a loss of 1.7 dB at 1550 nm	[24]

No	Chromophore	Potential Application	Computational/Experimental data	Ref
20	 CLD	EO modulator	• γ_{33} = 63 pm/V • 410° phase shift range achieved over 8 GHz to 26 GHz with < 38 mW of power consumption.	[25]
21	 CNO-DPA	Photonic, EO materials	• order of substituent effect on NLO properties: Me < OCH$_3$ < OEt < NH$_2$ < N(CH$_3$)$_2$ CNO-pN(CH$_3$)$_2$-DPA: • calc. μ.β$_0$ = 570 × 10^{-30} Debye.esu • calc. β$_0$ = 57.46 × 10^{-30} esu	[26]
22	Type-I  X=Y : N=N (PS-1); CH=N (PS-2); CH=CH (PS-3) Type-II  X=Y : N=N (AB-1); CH=N (AB-2); CH=CH (AB-3)	optical frequency converters	The best results were from sample AB-3 • β_{HRS} ~ 1400 × 10^{-30} cm^4·statvolt^{-1} (4 times higher than KDP) at 1064 nm. • β_{HRS} = 631 × 10^{-30} cm^4·statvolt^{-1} at 1310 nm. • β_{HRS} = 456 × 10^{-30} cm^4·statvolt^{-1}, at 1550 nm.	[27]

A dipolar chromophores containing (diarylamino)phenyl electron donating group and tricyanofuran moieties as electron acceptor group were synthesized and labelled as BAH. When compared to common chromophores like JRD1 from their Hyper-Rayleigh scattering (HRS) experiment, BAH demonstrated greater than 2-fold improvement in β value. These values are closer to that of recent BAY and BTP chromophore types. BAH chromophores improved the EO performance in bulk devices by increasing r_{33} values and poling efficiency. BAY1 and neat BAH13 had equivalent EO coefficients (r_{33}) values of 1100 ± 100 pm V^{-1} at 1310 nm, but neat BAH13 showed much improved absorption coefficient of 11.6 ± 0.7 nm^2 V^{-2} thus it is feasible for application in EO modulators exhibiting significantly enhanced r_{33} and poling efficiencies (r_{33} /E_p) as compared to complex chromophores such as JRD1. A decreased poling efficiency of 6.7 ± 0.3 nm^2 V^{-2} and significantly lowered absorbance were observed for blends of 3:1 of BAH-FD: BAH13, which is important to the modulator's performance. On the other hand, 1:1 of BAH-BB:BAH13 blends exhibited higher poling efficiency of 8.4 ± 0.4 nm^2 V^{-2} with an enhanced T$_g$ of 100 ± 41°C. BAH13 was tested in POH modulators and was able to achieve $V_\pi L$ < 50 V μm in slots that were notably wider than those of earlier record devices. BAH13 significantly outperformed earlier chromophores tested in comparable device topologies, exhibiting great r_{33} values of 208 pm V^{-1} at 1550 nm in these modulators. The bulk devices and POH modulators exhibited increased hyperpolarizabilities and EO activities without unfavourable effects on processibility or loss, and proving the trade-off between hyperpolarizability, loss, and processibility is not unmanageable and may be successfully handled by theory-guided design [5].

Another current studies that included tricyanofuran (TCF) were four novel NLO chromophores (labelled as A, B, C, D) which have been synthesized using the julolidinyl as donor group, and TCF and CF$_3$-tricyanofuran (CF$_3$-Ph-TCF) as acceptor groups; and in two of chromophores (C & D), the 3,5-bis(trifluoromethyl)benzene analogue group have been included in the bridge, have demonstrated decomposition at temperatures of above 220 °C which is considered as excellent thermal stability. Energy gaps between the ground state and the excited state as well as the first-order hyperpolarizability (β), were examined using UV–Vis absorption spectroscopy (Figure 3) and DFT calculations; while macroscopic EO was determined by a simple reflection method. At 1310 nm, the 35 wt% of chromophore D poled films with

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a flexible hindrance group, doped in amorphous polycarbonate has resulted in the highest EO coefficient of 54 pm/V, which demonstrating the dipole–dipole interaction of chromophores has been reduced by the 3,5-bis(trifluoromethyl)benzene group. Their potential use in NLO applications is promising based on their overall performance i. e. good yield in synthesis, excellent thermal stability and average r_{33} value [7]. The results showed that CF_3-Ph-TCF had excellent electron-withdrawing ability compared to typical TCF acceptors, and thus its macroscopic EO and microscopic hyperpolarizability (β) were improved. The adequate values of r_{33} and thermal stability show significant potential for diverse device applications for these novel NLO chromophores.

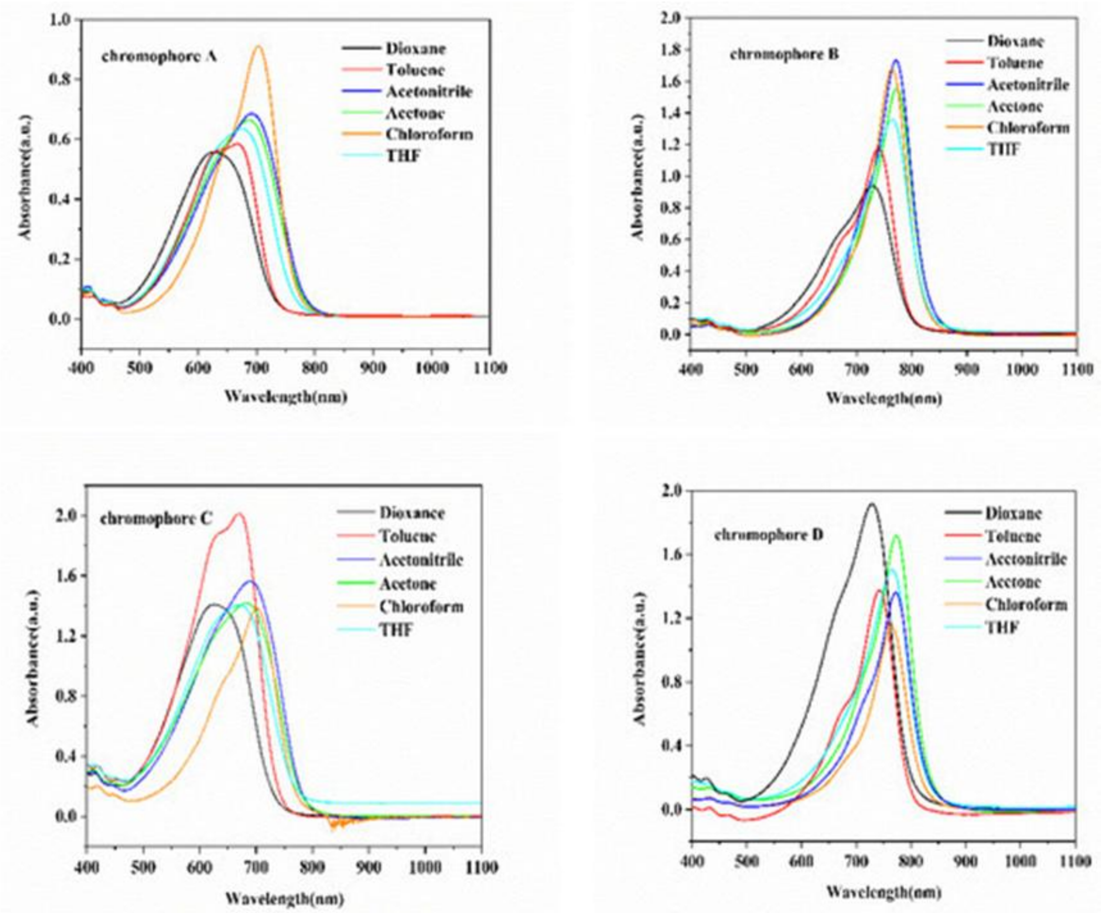

Figure 3. Absorbance spectra of chromophores A, B, C, D in UV-vis range in different types of solvents [7]

A novel NLO chromophores comprising 1-oxajulolidine as donor was studied as second-order NLO molecules was found to enhance the EO performance by introducing 1-oxajulolidine, a polycyclic structure which contains nitrogen and oxygen, the two electron-rich atoms. According to DFT results, the r_{33} value (9.6 pm V^{-1}) of J1/APC is 27% greater than Ref1/APC, indicating better EO performance. Furthermore, JS showed a higher EO coefficient than FTC, having the same acceptor and conjugate bridge at the same doping concentration. Additionally, when doped in film, JS showed a blue-shift in blue-shift in λ_{max} compared to FTC, which has the potential as NLO materials as these chromophores could balance second-order nonlinearity and transparency trade-off. These novel chromophores also have thermal decomposition temperatures above are greater than 260°C and demonstrate notable solvatochromic behavior when shifting from dioxane to dichloromethane [8]. Kim et al. has developed a novel type of NLO organic crystals, which address the limitation in organic NLO caused by the fact that enhancing the molecular optical nonlinearity of chromophores typically leads to zero macroscopic NLO in organic π-conjugated crystals. The new class crystals feature a specially designed chromophore, 4-(4-(4-(hydroxymethyl) piperidin-1-yl) styryl)-1-(pyrimidin-2-yl) pyridin-1-ium (PMPR). Incorporating a head-to-tail cation-anion O⋯H⋯O H-bonding synthon and various optimal molecular anions, the PMPR chromophore was found to have an effective first hyperpolarizability value of 335 × 10^{-30} esu. Contrary to previously reported analogous crystals with zero effective first hyperpolarizability, the ultrathin PMPR crystal, with a thickness of approximately 10 μm, exhibits remarkable THz wave generation capabilities, showcasing both broadband THz wave generation across a wide flat-spectral-band spanning from 0.7 to 3.4 THz and high-generation efficiency (yielding THz amplitudes five times higher than those of a ZnTe crystal with a thickness in the millimeter scale). Thus, these novel PMPR chromophores hold considerable potential for a variety of applications in THz photonics such as in communications, medical imaging, and security and NLO applications (Kim et al., 2023).

The PP-1 and PP-2 linear pyrazine derivatives based on TPA were prepared by following the reaction of common Suzuki cross-linking. Photo-physical studies were conducted on these derivatives in aprotic solvent (Hexane to DMF). The shift towards longer wavelengths (red-shift) was observed in polar solvents, and the emission intensity was progressively lowered. Linear pyrazine compounds with DMF/water demonstarted red-shifted and a common aggregation-caused quenching (ACQ) effect when the fraction of water (fw) was elevated from 0 to 40%. However, as the water fraction (fw) was increased further to 90% from 50%, a mild aggregation-induced emission (AIE) effect with blue-shift were observed. The acidochromic properties of PP-1 and PP-2 in TFA acid was also investigated. It revealed a gradual reduction in emission and absorption strength as concentration of TFA acid increased with new peaks appearing red-shifted [23]. Development of new organic chromophores incorporating the 1,3,4-oxadiazole group have been successfully done by connecting oxadiazole groups to a phenylene bridge with aliphatic tail, whereas the other end with aromatic groups (pyridine or thiophene), and one derivative had an additional phenylene with oxadiazole group dividing the core from thiophene positioned at the other end. The calculated excitation energy and first hyperpolarizability (β_0) by DFT calculation showed a similar trend as observed in their UV-Vis absorbance spectra. Replacing thiophene groups with pyridine groups and expanding the π-conjugated bridge have significantly increased the calculated values of β_0. This might be explained by the decrease in excitation energy and bandgap, however, suitable end group is vital as it could defeat the effect of expanding π-conjugation system. In this work, oxadiazole groups with the 4-pyridyl end group (Oxa-4-Py) was found to have the greatest β_0 i. e. 24.0×10^{-30} esu. These findings indicate that substituted oxadiazoles, such as those presented in this study, hold great promise for NLO applications [10].

A multi-step procedure was employed to synthesize two novel D—π—A chromophores containing indole donor and tricyanofuranyl acceptors linked by vinylene bridge (Ind-V-TCF) and divinyl quinoxalinone π-conjugated bridge (Ind-VQonV-TCF), which showed positive solvatochromism, ICT absorption band in the visible region, and transparency at 850 nm. The chromophore based on indole, featuring a divinylquinoxalinone π-conjugated bridge, demonstrates a significant μβ value of $\sim 13000 \times 10^{-48}$ esu, and the incorporation of the vinyl quinoxalinone unit significantly increased the values of the first hyperpolarizability. The extension of the π-bridge through the inclusion of a vinylquinoxalinone unit results in a by 6–8 times substantial increase in the first hyperpolarizability and an even more pronounced increase in the μβ value by 8-10 times [11]. The Ind-VQonV-TCF chromophore, with a large μβ value ($\sim 13068 \times 10^{-48}$ esu) and optical transparency at a wavelength of 850 nm, shows great potential for further research in developing EO devices for operation in the shortwave infrared window.

Kagatikar et al. (2023) conducted studies on the electrical and optical properties of pyrene-based chalcones, which are n-type small molecule semiconductors for electron transport [12]. The pyrene-based chalcones, designated as PC1 and PC2, were successfully synthesized through the Claisen-Schmidt condensation reaction. These two compounds demonstrated n-type semiconducting behavior with a wide bandgap, and improved charge carrier concentration together with their dielectric constant. They also demonstrated good thermal stability. The computational studies together with experimental results shown by fluorescence measurements, and their morphology, advocated that the ICT and aggregation-induced has increased the emission properties of the molecules. The study also demonstrated that PC1 and PC2 could be used to fabricate a diode and function as an electrode-material in a super capacitor. The dielectric properties and AC impedance of PC1 and PC2 were determined at varying frequencies. PC2, which contains a fluorine atom, exhibited better redox behavior than PC1 as confirmed by quasi-rectangular cyclic voltammogram behavior and AC impedance measurements. The researchers also investigated the performance of PC2 as a material for capacitors by creating symmetric supercapacitor that demonstrated 220 Fg^{-1} specific capacitance at 10 mV s^{-1} scan rate which showed promising potential as n-type semiconducters. Their compatibility with other n/p-type materials in OLED devices, high charge carrier concentration and thermal stability made PC1 and PC2 as potential dopants in host materials for OLEDs application [11]. PC1 and PC2 were active as orange-red emitters with ICT and AIEE properties, as confirmed by fluorescence spectroscopy, morphology and particle size measurements. These compounds also were found to show quasi-reversible redox electrochemical properties and great thermal stability up to 300°C.

New D-π-A organic dyes incorporating triphenylamine as the core (thiophene and thieno[3,4-b]pyrazine served as donor groups, while cyanoacrylic acid functioned as the acceptor), were computationally examined utilizing quantum chemical methods, including DFT and TD-DFT [13]. The acceptor groups were linked by four conjugated spacers: furan, thiophene, pyrrole, and phenyl. The DFT/B3LYP/6-311G(d,p) method optimized the ground-state geometry and electronic properties of the dyes. The HOMO and LUMO energy levels of the dyes D1, D2, D3, and D4 were found to be -5.09/-3.36 eV, -5.06/-3.26 eV, -5.10/-3.43 eV, and -5.10/-3.41 eV, respectively, with corresponding energy bandgap values of 1.73 eV, 1.78 eV, 1.67 eV, and 1.69 eV. These results suggest that these dyes are well-suited as photosensitizers in dye-sensitized solar cells, given their appropriate HOMO and LUMO levels relative to the redox couple I-/I3- (-4.8 eV) and the semiconductor conduction band (-4.0 eV). Modifying the acceptor moiety enhanced the dyes' photovoltaic properties by altering the HOMO and LUMO levels, reducing the bandgap energy (Eg), increasing geometrical planarity, and improving electron injection and dye regeneration. The LUMO levels of the dyes were above the conduction band (CB) of TiO2, facilitating efficient electron transfer. The dyes exhibited Voc values ranging from 0.57 to 0.72 V, indicating effective electron injection capabilities. The absorption wavelengths (λmax) for D1, D2, D3, and D4 were 557.70 nm, 590.14 nm, 593.59 nm, and 574.64 nm, respectively. The study concluded that dyes with small bandgaps, broad absorption wavelengths, suitable FMO levels, high LHE and ΔG_{inj} values, and low λ_{tot} are optimal for photovoltaic applications, making these dyes suitable electron donors in dye-sensitized solar cells.

Novel analogues of D-π-A′-π-A chromophores were synthesized through an eight-to-nine-step process. These chromophores featured quinoxaline as core to act as supporting acceptors and numerous donor groups such as aniline, tetrahydroquinoline, carbazole, and phenothiazine. These donors incorporated large tert-butyldimethylsilyloxy (TBDMSO) groups and TCF acceptors with large cyclohexylphenyl groups. DFT calculations were performed to determine the first hyperpolarizabilities of the chromophores at the M06-2X/aug-cc-pVDZ level. The calculations revealed that the TBDMSO group had an insignificant influence on the donor component, as it was not connected to the π-conjugated system of the chromophore. Atomistic modeling indicated that the bulky substituents in the donor group prevented significant accumulation of the chromophores, despite high chromophore concentration (40 wt.%). Chromophores with a tetrahydroquinoline donor demonstrated the highest first hyperpolarizability among the analogues studied, with a value of 937×10^{-30} esu. The SHG NLO coefficient, d_{33} of guest–host materials containing 25 and 40 wt.% of the proposed chromophore was found to be as high as 52 pm/V [14]. BSB (A-π-D-π-A) and SBS (D-π-A-π-D), synthesized with thiophene as donor, 2,1,3-benzothiadiazole (BTD) as acceptor, and ethylene as π-bridge groups, were studied for their third-order NLO properties. Z-scan experiments at 532 nm revealed their transition from saturable to reverse saturable absorption with self-defocusing effects under varied pulse durations. SBS, with a second-order hyperpolarizability of 4.4×10^{-28} esu, outperformed BSB by a factor of ten due to its alternating D-A modes. Quantum chemical analysis showed stronger symmetrical ICT in SBS, validated by S0-S1 hole-electron examination. These results offer valuable insights for the development of efficient NLO materials, particularly those with extended conjugation or multi-branched EO chromophores [15].

(E)-N-(2-(2-(2-hydroxybenzylidene)hydrazine-carbonyl)-phenyl) benzamide (NHBPB) and (E)-4-chloro-N-(2-(2-(2-hydroxybenzylidene)hydrazine-carbonyl) phenyl)benzene sulfonamide (CNHBP) have been successfully synthesized. The starting materials used were N-4-chlorobenzenesulfonylated analogous of anthranilic acid and N-benzoylated which were reacted with 2-hydroxybenzaldehyde through a condensation reaction. The NLO properties of the compounds were studied using quantum chemical computations with functional of M06 and M06-2X and basis set of 6-311G (d,p). Geometrical parameters of XRD and DFT calculations were compared by doing comparative analysis. NHBPB exhibited a red-shifted UV-Vis trend (297.894 nm at M06-2X ; 311.594 nm at M06) resulted from its narrower HOMO/LUMO energy gap as observed after frontier molecular orbital (FMO) analysis, in comparison to that of CNHBP. From Global Reactivity Parameters (GRPs) calculation, NHBPB also found to have reduce ionization potential and hardness with larger softness, indicating the larger polarizability in NHBPB as compared to CNHBP. These results are in line with their experimental second hyperpolarizability response in which NHBPB with 2.749 ×105 a.u at M06-2X and 1.945×105 a.u at M006 functional, is showing greater second hyperpolarizability values than that of CNHBP. Hydrazide-based compounds could be concluded as having exceedingly high linear and nonlinear polarizabilities as compared to other synthesized molecules by Kausar et al., 2023 [16].

Another novel type of chromophore 1,1,4,4-tetracyanobutadienes (TCBDs) containing γ-pyranylidene as donor group were synthesized using [2 + 2] cycloaddition-retroelectrocyclizations method. TCBDs 1a-

1j displayed two typical reversible reduction waves and two oxidation waves from the γ-pyranylidene groups. TCBD chromophores with many TCBD and/or γ-pyranylidene units revealed more complicated redox waves. TCBDs containing γ-pyranylidene exhibited panchromatic absorption characteristics. Some chromophores also absorbed in the near infrared (NIR) region. The ICT of the push-pull chromophores were altered accordingly with the vary in molecule types around the TCBD units. TD-DFT calculations also supported that TCBDs containing γ-pyranylidene were hypothetical suitable as NLO chromophores. All chromophores showed significant second-order NLO properties, with TCBD-5 showing the highest $\mu\beta_{EFISH}$ value of $5700\ 10^{-48}$ esu [17]. Thirteen triazene-substituted alkyne groups synthesized by Sonogashira cross-coupling reactions have been reported with very high yields i. e. 95 – 99 % and 92 – 99% for one with TCNE and TCNQ, respectively. [2 + 2] cycloaddition-retroelectrocyclizations happened with the use of diethylaniline-substituted substrates. Computational studies have shown the potential of synthesized push-pull compounds as NLO materials, and in line with their λ_{max} observed in the range of 454 – 692 nm. These computational results are also supported by the data from EFISHG measurements i. e. $\mu\beta$ values in the range of $850 \times 10^{-48} - 6050 \times 10^{-48}$ esu, considered as great NLO responses [18]. New benzothiazolium molecule, a triclinic and chiral crystal (DOBS) was synthesized and was found to have the maximum first-order hyperpolarizability (β_{max}) of 107.7×10^{-30} esu. The introduction of two methoxyl groups on the benzene ring facilitates hydrogen bond formation, resulting in the parallel arrangement of cations. Additionally, DOBS exhibited higher thermal stability (T_m = 251.5°C), a lower dielectric constant ($\varepsilon_r = 5.2 \pm 0.1$), optical transmittance of 65%, a smaller optical band gap of 2.02 eV, and strong green radiation at 560 nm which have potential as a SHG material [19].

Organic chromophores based on pyrazolone exhibited distinct spectroscopic response even though with slightly different structures, one with -H and another one with $-OCH_3$. These pyrazolone-based systems demonstrated sensitivity and effectiveness as all-optical modulators and generators of SHG and THG signals. The presence or absence of a small methoxy group in the chromophore structure significantly influenced the kinetics and magnification of photo-induced birefringence, and the modulation of higher harmonics under experimental polarization spatial conditions. The *trans* isomer exhibits a higher charge-transfer (CT) excited-state dipole moment compared to the *cis* isomer and $\Delta\mu_{GS}^{(trans\text{-}cis)}$ (*GP gas to water phase*) for the PYROMe derivative, the dipole moment increases from 1.84 D to 3.20 D, while for the PYR derivative, it increases from 1.75 D to 2.87 D (Szukalski et al., 2023). Theoretical NLO of *trans* PYROMe in water β_{vec} was the highest (8675.02 au) and β_{TOT} was the highest (14458.37 au). Upon analyzing the collected multiple NLO responses and assessing their stability and repeatability, one can be concluded that these two organic systems operate within a comparable range. The amplitude of the output was recorded at intervals of 50 seconds, corresponding to the "ON" and "OFF" states of the UV laser, respectively. The stability of the observed optical Kerr effect (OKE) signal is characterized by deviations of 25% and 28% for the systems based on PYROMe and PYR, correspondingly. The variations in the acquired signal are attributed to the dynamic nature of the investigated phenomenon. Each cycle of light-driven induced (photo-ordering) is intricately linked to various parameters, including the availability of molecular free volume near the active site of the stilbene group, energy resulted from the probability of absorption of photon by singular molecules, localized dye density, and other factors such as reflections and re-absorption phenomena and light losses. Yet, in both instances, the NLO response demonstrates repeatability and reversibility, making these materials promising options for constructing fully organic, bi-component all-optical switches or sensors. Notably, PYR ($A \sim 1.6$ V) demonstrated a slightly higher NLO signal than that of PYROMe ($A \sim 1.2$ V) [20].

Polyelectrolytes based on naphthalene diimide (NDI) were prepared through a simple anion exchange and utilized as a cathode interlayer in organic solar cells (OSCs) [21]. With ionic side chains, these polyelectrolytes readily dissolve in alcohols and generate a favorable interface dipole. The device with PFN-NDI-OH as the interlayer exhibited a PCE improvement from 8.79% to 8.91%, due to the strong adhesion layer formed between the organic active layer and the inorganic metal oxide. Furthermore, the device with PFN-NDI-OTs displayed a PCE increase to 9.41%, with the larger tosylate anion contributing to an enhanced short-circuit current (Jsc). The findings suggest that these polyelectrolytes, synthesized via a straightforward anion exchange method without the need for lengthy purification procedures, are excellent candidates for cathode interlayers in OSCs. By modifying the work function of the ZnO surface, they enhance interfacial properties and facilitate a transition from a Schottky to an Ohmic contact. Incorporation of bulky cyclic alkene groups on the donor and bridge of a chromophore sample, AR-1 has been shown to lower the calculated dipole moments (μ (D) = 20.97) and increase $\beta_{tot} = 1353 \times 10^{-30}$ esu in comparison to conventional chromophores, JRD1 and YLD124 [22]. This type of chromophore has the potential to achieve a high EO coefficient because the bulky groups can prevent self-assembly. Preventing the chromophores from anti-parallel packing directly increases the macroscopic EO coefficient. Chromophore with a smaller dipole moment is an excellent choice for manufacturing EO devices, in which AR-1 sample has smaller calculated dipole moments than its silicon derivatives, BLD-1 and BLD-3 eventhough its β_{tot} is smaller.

Araújo et al. (2023) studied various derivatives of pseudo-stilbene and azobenzene with dimethylamine as donating group and nitro as acceptor group, found that compound AB-3, that contaning azobenzene, at the +G(2d,p) level of theory, exhibited a β_{HRS} value of approximately 1400 × 10^{-30} cm^4·$statvolt^{-1}$ [23]. This value is four orders of magnitude higher than that of KDP which is 0. 2 × 10^{-30} cm^4·$statvolt^{-1}$, which serves as a reference in SHG experiments at 1064 nm. At the same level of theory and in the same solvent, the highest calculated β_{HRS} values at 1310 nm and 1550 nm were 631 × 10^{-30} cm^4·$statvolt^{-1}$ and 456 × 10^{-30} cm^4·$statvolt^{-1}$, respectively, as shown in Figure 4. Among the substituents Me, OMe, OEt, NH_2, and NMe_2 at the para position of C-nitroso compounds, NMe_2 showed the highest hyperpolarizability (β_0) value of 57.46 × 10^{-30} esu, with a molecular hyperpolarizability ($\mu.\beta_0$) of 570 × 10^{-30} Debye·esu for both N- and C-nitroso. These β_0 values are significantly higher compared to diphenylamine, urea, and p-nitroaniline, with increases of 155.29-fold, 73.69-fold, and 13.12-fold, correspondingly. The order of β_0 values has increased with substitution in the order of H < Me < OMe < OEt < NH_2 < NMe_2 for N-nitroso; while for C-nitroso, the order was H < Me < OMe < NH_2 < OEt < NMe_2 [26].

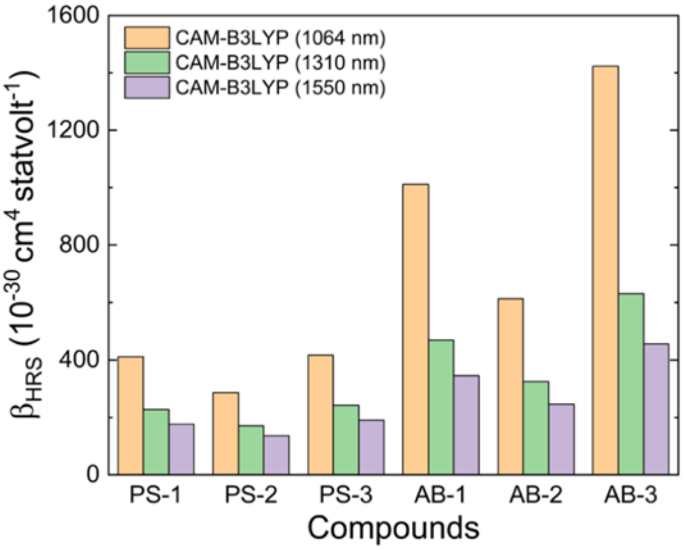

Figure 4. The dynamic first-order molecular hyperpolarizability (βHRS) of the investigated compounds was calculated in DMSO as a solvent medium at 1064 nm, 1310 nm, and 1550 nm incident wavelengths by using the CAM-B3LYP/6–311++G(2d,p) method [23]

A novel push-pull polymer EO modulator with 1.28 V·cm has been developed, demonstrating the capability to accurately detect electrocardiogram (ECG) signals comparable to commercial ECG devices [24]. Built on a Mach–Zehnder modulator (MZM) architecture, the device utilizes a second-order NLO host-guest polymer comprising PMMA and a CLD-1 chromophore that resulted in a modulation depth of 0.637 dB, a reduced Vπ of 1.6 V, and a loss of 1.7 dB at 1550 nm. The two bulky *t*-butyldimethylsilyl groups in CLD-1 minimized the interchromophore interactions during the poling process, thus enhancing poling efficiency and reducing the Vπ. Another study by Zhou et al. (2023) explored a silicon-organic hybrid (SOH) MZM incorporating a CLD-based chromophore, as depicted in Figure 5 [25]. This modulator achieved a half-wave voltage-length product of 0.26 V·cm and a 3 dB EO response bandwidth of 50 GHz, enabled by its high EO coefficient (γ_{33} = 63 pm/V). Additionally, a photonic radiofrequency (RF) phase shifter utilizing the SOH dual parallel MZM demonstrated a phase shift range of 410° across 8 GHz to 26 GHz with less than 38 mW of power consumption. The molecular structure of the CLD chromophore incorporates additional groups in the TCF, enhancing its electron-accepting properties and improving its EO performance. Furthermore, the inclusion of isophorone in the conjugated π-electron bridge enhances electron transport capacity, resulting in excellent overall performance of the structure.

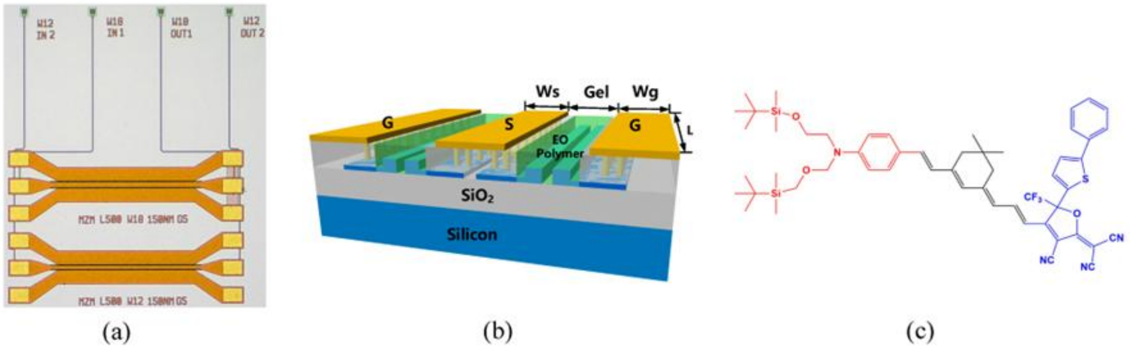

Figure 5. (a) The Mach–Zehnder modulator (MZM)'s micrograph; (b) the SOH MZM's 3D figure;
(c) EO organic molecular structure (CLD chromophore) [25]

3.0 CONCLUSION

A brief overview of recent dipolar organic electronic and EO materials with some of their possible applications has been described. There were many electron-donating and electron-withdrawing groups have been explored, and from this current recent brief review, we believe tricyanofuran (TCF) to be one of the most promising groups that has attracted the attention of many researchers in electronic and EO area. The dipolar materials leverage the molecular dipoles' alignment under an electric field to exhibit strong NLO properties such as Pockels effect. Dipolar EO materials typically have high first-order hyperpolarizability (β), leading to efficient second-order NLO effects which enables high-speed and low-power modulation in optical devices.

4.0 CHALLENGES AND FUTURE RECOMMENDATIONS

Recent research on organic-based electronic and EO materials has shown significant advancements, but they also encounter various challenges and present opportunities for future growth. Some of these materials face issues with stability when exposed to operational conditions like moisture, oxygen, or light, leading to performance degradation over time [2]. Additionally, scaling up production while maintaining consistency and reproducibility poses challenges, impacting their commercial feasibility and hindering large-scale manufacturing. Moreover, the synthesis of organic-based materials often involves intricate routes and specialized processing techniques, resulting in higher production costs compared to inorganic alternatives. Organic materials also characteristically have lower charge carrier mobility compared to inorganic semiconductors.

Therefore, for future recommendations, continued research into the design and synthesis of novel organic materials with improved stability, efficiency, and processability is essential. Advancements in device engineering, including interface modification, encapsulation techniques, and device architectures, can address stability and efficiency issues, leading to more reliable and long-lasting organic-based devices. Developing scalable and cost-effective manufacturing processes for organic electronic and EO devices, such as printing-based methods and roll-to-roll processing, will enable large-scale production and commercialization. However, it is imperative to substitute the conventional toxic and chlorinated solvents, commonly employed in processing conjugated polymers, with less harmful alternatives. In the long run, a critical aspect of high throughput production will be its minimal impact on the environment. To tackle interdisciplinary challenges and accelerate the translation of research findings into practical applications, collaboration between materials scientists, physicists, chemists, engineers, and industry partners should be fostered.

5.0 CONFLICT OF INTEREST

The authors declare no conflicts of interest.

6.0 AUTHORS CONTRIBUTION

Ahmad Shah, N. A. (Conceptualisation; Methodology; Validation; Writing - original draft; Writing - review & editing; Funding acquisition; Supervision)
Abdullah, N. (Writing - original draft; Writing - review & editing; Funding acquisition)

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Jamal, S. H. (Supervision)
Mohd Kasim, N. A. (Methodology; ValidationSupervision)
Wan Yusof, W. Y. (Writing - original draft; Writing - review & editing)

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