Acceptor and donor substituted alkoxy(phenyleneethynylenes) (Alkopy-PEs): Synthesis, thermal, linear and nonlinear optical properties


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A series of acceptor and donor substituted bis(alkoxy)phenyl ethynyl oligomers 4,4'-(2,5-alkoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(nitrobenzene) (alkyl = C$_4$H$_9$ 3a; C$_8$H$_{17}$ 3b and C$_{12}$H$_{25}$ 3c) and 4,4'-(2,5-alkoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis(methylbenzene) (alkyl = C$_6$H$_5$ 4a; C$_8$H$_{17}$ 4b and C$_{12}$H$_{25}$ 4c) has been synthesized by the palladium catalyzed cross coupling reaction of 1,4-dialkoxy-2,5-diiodobenzene with appropriate alkynes. The newly synthesized products were characterized by UV-Vis, IR and multinuclear NMR spectroscopic techniques as well as elemental analyses. All the synthesized bis-(alkoxy)phenyl ethynyl derivatives exhibit good thermal stability (T$_g$ = 329–347 °C) as evident by thermo gravimetric analysis. In nitrophenyl substituted 3a-c, emission is observed in the green region, while in tolyl substituted 4a-c, emission is observed in the blue region of the electromagnetic radiation. Continuous wave (CW) closed aperture Z-scan technique reveals the signature of third-order nonlinearity in the materials that are thermal in nature.

1. Introduction

For the last two decades, there have been tremendous efforts in the development of conjugated small molecules, oligomers and polymers for their applications in field-effect transistors, photodectors, photovoltaics and electroluminescence devices [1–5]. These materials are composed of unsaturated units that have extended π-orbitals, thus enabling optical absorption and proper charge transport [6–8]. The extent of conjugation/interaction between these units determines the solution/solid state electronic structure, which in turn controls key material properties such as optical absorption/emission, frontier molecular orbital energy levels (HOMO and LUMO) and redox characteristics [1a]. The π-conjugated system can possess an extremely high optical nonlinearity due to the fact that the π electrons in this kind of material tend to be delocalized more easily and the value of linear and third-order nonlinear polarizabilities can be related to the number of electrons per unit length [9].

Among the conjugated polymers, poly(p-phenyleneethynylenes) (PPEs) are promising for their ease of preparation, solution processability and wide range of materials properties [10]. Palladium is an efficient catalyst for the coupling reaction of bis-(alkynyl)arenes with dihaloarenes to synthesize PPEs [10–12]. However, initial efforts to form PPEs resulted in low-molecular-weight oligomers with poor solubility [13–15]. To overcome these problems, researchers have utilized long-chain alkyl or alkoxy substituted arenes as monomers which gave high molecular weight rigid-rod polymers with good solubility [10a,16]. Though, PPEs are strong candidates for the fabrication of optoelectronic devices [10b,17], they usually do not have well-defined structures, and are often polydisperse, which affect the optical properties [17b]. As an alternative, π-conjugated small molecules and oligomers are attractive due to their exact molecular weight, high purities and defect-free structures [18]. To cite examples of this class of materials, arylene ethynylene [19] (e.g. phenylene, fluorene, pyrene, carbazole) with high fluorescence quantum yield have been studied for OLED device fabrication [19b–c]. The device fabrication and operational lifetime of these materials depend on their good thermal and morphological stability [20].

Oligo- and poly-phenyleneethynylenes, oligo-phenylenevinylene and hybrid poly-phenyleneethylenylene/phenylenevinylene have been extensively studied for third-order nonlinear optics (NLO) [21a–d]. These types of conjugated organic oligomers and polymers and other organic conjugated dyies [21e–k] gained importance as NLO materials.
because of low cost, ease in processing, enhanced properties and biodegradable qualities. The materials exhibiting high optical non-linearities have potential of being a suitable candidate for high density optical data storage, photodynamic therapy and optical limiters [9,29a].

In this study, we report the synthesis and characterization of a new series of substituted bis-(alkoxy)phenyleneethynylenes and investigations of their thermal, linear (absorption and photoluminescence) and nonlinear (third-order) optical properties.

2. Experimental details

2.1. Materials and techniques

All the reactions were performed under nitrogen atmosphere with special Schlenk techniques [22]. Solvents were dried, and freshly distilled from appropriate drying agents [22]. All chemical reagents were special Schlenk techniques [22]. Solvents were dried, and freshly distilled from appropriate drying agents and HC\textsubscript{12}O\textsubscript{16} [24], and HC\textsubscript{25}C\textsubscript{12}O\textsubscript{4} [24] were prepared following published literature methods. NMR spectra were measured with Bruker 400FT NMR spectrometer in CDCl\textsubscript{3} solvent. 1H NMR spectra were referenced to solvents resonances. Infrared spectra were undertaken on a Shimadzu FTIR prestige 21 spectrometer (nitrobenzene) (C\textsubscript{6}H\textsubscript{5}I\textsubscript{2}) was obtained by using TGA-50 thermogravimetric analyzer under silica column chromatography, using hexane and dichloromethane (2:1), to remove 3a as a bright yellow solid in 55% (0.059 g) yield. IR (solid state, KBr): ν 3047, 2962 (C–H str.), 2205 (C=O str.), 1317 (C–O str.) cm\textsuperscript{-1}; 1H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.10 (t, 6H, CH\textsubscript{3}), 1.57 (s, 4H, CH\textsubscript{2}), 1.84 (q, 4H, CH\textsubscript{2}), 4.05 (t, J = 6.4 Hz, 4H, OCH\textsubscript{2}), 7.03 (s, 2H, (RO)\textsubscript{2}Ar-H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ 130.87, 125.19, 31.31, 69.34, 91.21, 93.38, 113.86, 116.83, 123.72, 130.29, 132.21, 147.06, 153.97; Anal. Calc. for C\textsubscript{30}H\textsubscript{21}N\textsubscript{2}O\textsubscript{4}C\textsubscript{16}: C, 70.30; H, 5.51; N, 5.47%. Found: C, 69.83; H, 5.52; N, 5.33%

2.2. Syntheses of substituted bis(alkoxy)ethynylarylethynyl derivatives (3 and 4)

2.2.1. 4,4′′-(2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis (nitrobenzene) (3a)

To a mixture of 1,4-dibutoxy-2,5-diiodobenzene (1a) (0.1 g, 0.21 mmol) and p-nitrophenylacetylene (2a) (0.077 g, 0.53 mmol) in presence of Pd[PPh\textsubscript{3}]\textsubscript{2}Cl\textsubscript{2} (0.003 g, 2% mmol), CuI (0.008 g, 2% mmol) and PPh\textsubscript{3} (0.002 g, 4% mmol) in diisopropylamine (20 mL) was degassed with nitrogen atmosphere, and the resulting mixture was stirred for 18 h at 65 °C. After completion of the reaction, diethylether was added to the reaction mixture, and the precipitate was removed by filtration. The solvent was removed under vacuum, and the solid residue was redissolved in diethylether, and the resulting solution was washed with 10% HCl acid followed by brine solution, and dried over anhydrous magnesium sulfate. After that, the solvent was removed under reduced pressure, and the solid residue was purified on silica gel column chromatography, using hexane and dichloromethane (2:1), to obtain 3a as a bright yellow solid in 55% (0.059 g) yield. IR (solid state, KBr): ν 3047, 2962 (C–H str.), 2205 (C=O str.), 1317 (C–O str.) cm\textsuperscript{-1}; 1H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.10 (t, 6H, CH\textsubscript{3}), 1.57 (s, 4H, CH\textsubscript{2}), 1.84 (q, 4H, CH\textsubscript{2}), 4.05 (t, J = 6.4 Hz, 4H, OCH\textsubscript{2}), 7.03 (s, 2H, (RO)\textsubscript{2}Ar-H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ 130.87, 125.19, 31.31, 69.34, 91.21, 93.38, 113.86, 116.83, 123.72, 130.29, 132.21, 147.06, 153.97; Anal. Calc. for C\textsubscript{30}H\textsubscript{21}N\textsubscript{2}O\textsubscript{4}C\textsubscript{16}: C, 70.30; H, 5.51; N, 5.47%. Found: C, 69.83; H, 5.52; N, 5.33%

2.2.2. 4,4′′-(2,5-dioctyloxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis (nitrobenzene) (3b)

The compound 3b was synthesized using similar procedure as described above for 3a by using 1,4-dioctyloxy-2,5-diiodobenzene (1b) instead of 1,4-dibutoxy-2,5-diiodobenzene (1a). The compound 3b obtained as a yellow solid in yield 60% (0.064 g). IR (solid state, KBr): ν 3078, 2922 (C–H str.), 2205(C=O str.), 1224 (C–O str.) cm\textsuperscript{-1}; 1H NMR (400 MHz, CDCl\textsubscript{3}): δ 0.85 (bt, 6H, CH\textsubscript{3}), 1.24-1.39 (m, 20H, CH\textsubscript{2}), 1.85 (q, 4H, CH\textsubscript{2}), 4.04 (t, J = 6.0 Hz, 4H, OCH\textsubscript{2}), 7.02 (s, 2H, (RO)\textsubscript{2}Ar-H); 13C NMR (100 MHz, CDCl\textsubscript{3}): δ 14.10, 22.69, 28.95, 29.29, 29.35, 31.83, 69.62, 91.92, 92.99, 133.84, 116.80, 123.70, 130.28, 132.22, 147.05, 153.96; Anal. Calc. for C\textsubscript{38}H\textsubscript{37}N\textsubscript{2}O\textsubscript{4}C\textsubscript{16}: C, 73.05; H, 7.10; N, 4.48%. Found: C, 72.63; H, 7.28; N, 3.99%

2.2.3. 4,4′′-(2,5-didodecyloxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis (nitrobenzene) (3c)

The compound 3c was synthesized utilizing similar procedure as described above for 3a, using 1,4-didodecyloxy-2,5-diiodobenzene (1c) instead of 1,4-dibutoxy-2,5-diiodobenzene (1a). The compound 3c was obtained as a yellow solid in 90% yield (0.095 g). Spectroscopic data are in accord with the reported 3c [25a].

2.2.4. 4,4′′-(2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl)bis (methylbenzene) (4a)

A mixture of 1,4-dibutoxy-2,5-diiodobenzene (1a) (0.1 g, 0.21 mmol) and p-tolylacetylene (2b) (0.06 g, 0.53 mmol) in presence of Pd[PPh\textsubscript{3}]\textsubscript{2}Cl\textsubscript{2} (0.015 g, 10% mmol), CuI (0.004 g, 10% mmol) and PPh\textsubscript{3} (0.011 g, 20% mmol) in diisopropylamine (20 mL) was added to a small double-neck flask and degassed with nitrogen atmosphere, and, then, the resulting mixture was stirred for 18 h at 82 °C. The completion of the reaction was determined by TLC and IR. After completion of the reaction, diethylether was added to the reaction mixture, and the precipitate was removed by filtration. The solvent was removed under vacuum, and the solid residue was redissolved in diethylether. Then, the resulting solution was washed with 10% HCl acid followed by brine solution, and dried over anhydrous magnesium sulfate. After that, the solvent was removed under reduced pressure, and the solid residue was...
purified by column chromatography on silica gel eluting with hexane and dichloromethane (3:1). The title compound 4a was obtained as a pale yellow solid in 52% (0.049 g) yield. Spectroscopic data are in accord with the reported 4a [25b].

2.2.5. 4,4’-((2,5-diocyatoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(methylene benzene) (4b)

The same procedure as for compound 4a was followed for the synthesis of 4b by using 1,4-diocyatoxy-2,5-diiodobenzene (1b) instead of 1,4-dibutoxy-2,5-diiodobenzene (1a). The compound 4b obtained as a pale yellow solid in yield 55% (0.065 g). IR (solid state, KBr): ν = 3028, 2922 (C–H str.), 1216 (C–O str.) cm⁻¹. 1H NMR (400 MHz, CDCl₃): δ = 8.87 (t, 6H, Ar-CH₃), 2.36 (s, 6H, Ar-CH₃), 4.01 (t, 3J = 6.4 Hz, 4H, OCH₂), 1.83 (m, 4H, CH₂), 2.36 (s, 6H, Ar-CH₃), 4.01 (t, 3J = 6.4 Hz) is assigned to the OCH₂ proton of the acceptor groups, and 2.5-diiodobenzene (3J = 6.4 Hz) is assigned to the OCH₂ proton of the donor groups. 

The 1H NMR spectrum of 4a displays doublets at 7.65 and 8.22 ppm and its 13C NMR spectrum displays two doublets at 129.09 and 129.34 ppm corresponding to the acceptor and donor end groups. The compound 4b displays a single absorption band at 2205 cm⁻¹, confirming the stretching vibration of C≡C, in the IR spectrum, is diagnostic to the characterization of the ethynyl compounds. The absence of acetylenic hydrogen, υ(C≡H) vibration gives evidence of the desired cross-coupling reaction (RC≡CR). For example, 3a displays a single absorption band at 2205 cm⁻¹, confirming the stretching vibration of the ethynyl group (C≡C), but it did not exhibit absorption band in the range of 3200–3300 cm⁻¹, which suggests that the terminal acetylenic group (≡CH) of p-nitrophenylethynylene (2a) undergoes the coupling with 1,4-dibutoxy-2,5-diiodobenzene (1a). Similarly, compound 3b, 3c, 4a, 4b and 4c display characteristic IR peaks in the expected regions (Table 2).

3.2. Characterization

All the products provided satisfactory elemental analysis. The chemical structures of the products 3a-b and 4b-c have been confirmed by IR and 1H and 13C NMR spectroscopic analyses (Table 2). The stretching vibration of υ(C≡C), in the IR spectrum, is diagnostic to the characterization of the ethynyl compounds. The absence of acetylenic hydrogen, υ(C≡H) vibration gives evidence of the desired cross-coupling reaction (RC≡CR). For example, 3a displays a single absorption band at 2205 cm⁻¹, confirming the stretching vibration of the ethynyl group (C≡C), but it did not exhibit absorption band in the range of 3200–3300 cm⁻¹, which suggests that the terminal acetylenic group (≡CH) of p-nitrophenylethynylene (2a) undergoes the coupling with 1,4-dibutoxy-2,5-diiodobenzene (1a). Similarly, compound 3b, 3c, 4a, 4b and 4c display characteristic IR peaks in the expected regions (Table 2).

The 1H NMR spectrum of 3a displays doublets at 7.65 and 8.22 ppm with coupling constant 3J = 8.8 Hz which confirms the presence of para-substituted benzene ring in the molecule (Fig. 2). A sharp singlet at 7.03 ppm is assigned to the bulky substituted phenyl ring, and the triplet at 4.05 ppm (3J = 6.4 Hz) is assigned to the OCH₂ proton of the butoxy chain. The positions of all other NMR signals and their integration ratio are fully consistent with the structure of the molecule (Fig. 2). Similarly, the alkyl, aryl and phenyl protons of compound 3b and 4b, 4c display 1H NMR peaks in the desired region of spectra (Table 2).

In the 13C NMR spectra, compound 3a displays a strong characteristic peak at 69.34 ppm for –OCH₂ carbon, and peaks at 91.21 and 93.38 ppm for acetylcarbons. The alkyl and phenyl carbons display peaks in the desired positions. Similarly, compounds 3b, 4b, and 4c were isolated as bright yellow solids in 60 and 90% yield, respectively (Table 1, entry 2 and 3), and compounds 4a, 4b, and 4c were isolated as pale yellow solids in 52, 55, and 67% yield, respectively (Table 1, entry 4, 5 and 6). Recently, an oxygen free two-chamber reaction system has been developed, which gives 1,4- and 1,3-octyloxy phenyl ethynyl derivatives (benzene, nitrobenzene 3c, naphthalene, ferrocene etc) and 1,3-azulene ethynyl derivatives (benzene and naphthalene) in high yield [25a] (Pd cat. 0.4 mol%, RT, 9 days). On the other hand, we used conventional Sonogashira coupling reaction to form 3c in 90% (Table 1, entry 3) using mild reaction conditions (2 mol % Pd cat., at 65 °C, 18 h). Compound 4a has also been reported previously [25b] in three steps reaction starting from diiodobutylbenzene to bis-trimethylsilylacetylene derivative, then to bis-terminal acetylene derivative, and finally to product 4a. However, we used straight forward Sonogashira coupling reaction of 1,4-dibutoxyphenyl-2,5-diiodide with commercially available tolyl acetylene to form the product 4a, though the yield of the reaction is low with low catalyst loading. The synthesized coupling products 3a-c and 4a-c display in good solubility in common organic solvents, but are insoluble in hexane. So, these compounds are solution processable, which is an essential criterion for low cost device fabrication.
3.3. Thermal stability

Electronic device fabrication and their performance (life time and durability) depend on the thermal stability of materials [26a,19b]. Thermal stability of 3a-c and 4a-c (Fig. 3) was evaluated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. Nitrogen substituted alkoxynaphthalene ethynlenes 3a-c displays good thermal stability (Table 3), and their stabilities do not significantly depend on the alkoy side chain (T$_d$ 329 °C for 3a, T$_d$ 326 °C for 3b, T$_d$ 321 °C for 3c).

Table 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>1,4-diakloxy-2,5-diiodobenzene, 1 (0.21 mmol)</th>
<th>Arylacetylene, 2 (0.53 mmol)</th>
<th>Pd[PPh$_3$]$_2$Cl$_2$ (% mmol)</th>
<th>Cul (% mmol)</th>
<th>Product</th>
<th>Isolated Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>2</td>
<td>2</td>
<td>3a$^b$</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
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<td>2</td>
<td>2</td>
<td>3b$^a$</td>
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<tr>
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<td>1c</td>
<td>2a</td>
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<td>2</td>
<td>3c$^a$</td>
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<td>1a</td>
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<td>10</td>
<td>4a$^b$</td>
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</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>2b</td>
<td>10</td>
<td>10</td>
<td>4b$^b$</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>2b</td>
<td>10</td>
<td>10</td>
<td>4c$^b$</td>
<td>67</td>
</tr>
</tbody>
</table>

$^a$ The coupling reactions were performed in disopropylamine (20 mL) under nitrogen atmosphere for 18 h.

$^b$ Reactions were carried out at 65 °C.

Tables 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>IR (cm$^{-1}$)</th>
<th>$^1$H NMR (ppm)$^a$</th>
<th>$^{13}$C NMR (ppm)</th>
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<tr>
<td>3a</td>
<td>2205</td>
<td>4.05 ($^3$J = 6.4 Hz, 4H, OC$_3$H$_7$), 7.03 (s, 2H, (RO)$_2$Ar-$H$), 7.65 (d, $^3$J = 8.80 Hz, 4H, C$_6$H$_5$Ar-$H$), 8.22 (d, $^3$J = 8.80 Hz, 4H, C$_6$H$_5$Ar-$H$)</td>
<td>69.34 (OC$_2$H$_5$), 91.21 and 93.38 (C$_6$H$_5$C)</td>
</tr>
<tr>
<td>3b</td>
<td>2205</td>
<td>4.04 ($^3$J = 6.0 Hz, 4H, OC$_3$H$_7$), 7.02 (s, 2H, (RO)$_2$Ar-$H$), 7.65 (d, $^3$J = 8.00 Hz, 4H, C$_6$H$_5$Ar-$H$), 8.22 (d, $^3$J = 7.60 Hz, 4H, C$_6$H$_5$Ar-$H$)</td>
<td>69.62 (OC$_2$H$_5$), 91.22 and 93.38 (C$_6$H$_5$C)</td>
</tr>
<tr>
<td>4b</td>
<td>2206</td>
<td>2.55 (s, 6H, Ar-CHO$_2$), 4.01 (t, $^3$J = 6.4 Hz, 4H, OC$_3$H$_7$), 6.98 (s, 2H, (RO)$_2$Ar-$H$), 7.14 (d, $^3$J = 7.60 Hz, 4H, C$_6$H$_5$Ar-$H$)</td>
<td>69.72 (OC$_2$H$_5$), 85.35 and 95.00 (C$_6$H$_5$C)</td>
</tr>
<tr>
<td>4c</td>
<td>2212</td>
<td>2.36 (s, 6H, Ar-CHO$_2$), 4.01 (t, $^3$J = 6.0 Hz, 4H, OC$_3$H$_7$), 6.99 (s, 2H, (RO)$_2$Ar-$H$), 7.14 (d, $^3$J = 7.60 Hz, 4H, C$_6$H$_5$Ar-$H$)</td>
<td>69.71 (OC$_2$H$_5$), 85.37 and 95.00 (C$_6$H$_5$C)</td>
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</tbody>
</table>

$^a$ $^1$H NMR spectra were referenced to residual solvent (CDCl$_3$) resonances.

display peaks in the desired positions of the $^{13}$C NMR spectra. It is to be noted that compound 3c and 4a were reported in earlier [25].

3.4. Optical absorption and emission properties

Compounds 3a-c displays two bands at 339 and 410 nm in the UV–Vis spectra (Fig. 4). The phenylethynyl π system of the compounds is modified by the oxygen lone pair of alkoy side chain leading to the formation of two HOMO systems: HOMO-1 and HOMO-2, and transitions from these orbitals to the LUMO results two separate bands (Table 5) [27]. These absorption bands are unaffected with the variation of alkoy chain from OC$_2$H$_5$ to O$_2$C$_3$H$_7$ then O$_2$C$_5$H$_9$. However, if the electron withdrawing nitro phenyl group is replaced by electron donating tolyl group as in 4a-c, the absorption band is blue shifted to 309 and 368 nm. This observation suggests that in 3a-c, electron withdrawing NO$_2$ groups delocalizes H-electron on the whole molecule to stabilize quinoid structure [1a] thus lowering the absorption energy [19c].

The room temperature photoluminescence spectra, in dichloromethane, for compounds 3a-c and 4a-c were recorded under excitation at 410 and 370 nm, respectively (Table 5). The spectra are shown in Fig. 5 and Fig. 6. Compounds with electron withdrawing NO$_2$, 3a-b displays emission band peaking at 555 nm, whereas that with electron donating CH$_3$, 4a-c exhibit peaks at 403 nm (Table 5).

‘Acceptor-donor-acceptor’ (A-D-A) type trimers 3a-c emit at a wide region of wavelengths: blue-green whereas ‘donor-donor-acceptor’ (D-D-D) type trimers 4a-c show emission in the blue region. This observation is consistent with previous reports of conjugated ethynyl oligomers [19]. Stokes’ shift of 3a-b is 145 nm which is larger than that for 4a-c (35 nm). It has been reported in the literature that ethynyl oligomers with donor-acceptor end groups give larger Stokes shift [19c]. However, in this study, ethynyl bridged trimers with acceptor-donor-acceptor type aromatic compounds 3a-c gives larger shift than their congeners with donor-donor–donor type aromatic compounds 4a-c. The large stokes shift may be associated with the emission from the intramolecular charge transfer states (delocalized LUMO levels) of the A-D-A type materials [19d–e]. Compounds with small shift are prone to
self-quenching, so large stokes shift is a useful feature for new materials which could be used as laser dyes and molecular imaging [19e].

3.5. Third-order nonlinear optical property

The most commonly used method for measuring the optical non-linearity is the Z-scan method of Bahae [28a]. The method involves the transmission of a focused Gaussian beam of laser light through a sample. A convex lens is used for focusing the beam. The sample is translated along the z-axis. The transmitted light intensity is measured...
in the far field as the sample translation takes place within the focal point of the convex lens (Fig. 1). The refractive index of the sample changes according to

\[ n = n_0 + n_2 I \]

where \( n_0 \) is the linear refractive index, \( n_2 \) is the nonlinear refractive index and \( I \) is the intensity of incident light. When \( n_2 \) is positive, it gives rise to a positive lensing effect in the sample. \( n_2 \) is related to the nonlinear phase shift \( \Delta \phi \) by

\[ \Delta \phi = n_2 k L_{\text{eff}} \]

where \( L_{\text{eff}} = \frac{1-e^{-\alpha L}}{\alpha} \), \( L \) being the width of the sample and \( \alpha \) be the linear absorption co-efficient.

A transmittance vs position plot obtained from the experimental data gives a peak-valley or valley-peak curve which is a signature of third-order nonlinearity: a peak-valley curve gives negative \( n_2 \) value and valley-peak gives positive \( n_2 \) value [28a]. Fig. 7 shows the closed aperture Z-scan traces for compound 3a-c. The curves show a poor fit with the theoretical model in the positive \( z \) positions mainly due to the nonlocal effect produced by the incident laser beam [28b]. The thermal lens that is formed due to the incident laser is retained for relatively longer times so the fractional intensity change becomes slower. The transmittance traces of 3a-c and 4a-c show a prefocal peak followed by a post-focal valley which imply that the nonlinear refractive index are negative (\( n_2 < 0 \)) suggesting self defocusing [29a]. The calculated peak-valley difference \( \Delta T_d \) is found to be \( \approx 1.8 \) times the Rayleigh range \( Z_0 \) reveals the nonlinearity is thermal in nature [29b]. Light absorption by the materials creates heat, and focusing and defocusing effect is observed due to the variation of refractive index with temperature where the material itself act as a thermal lens [29c–d].

In the A-D-A series 3a-c, the \( n_2 \) values increase with increasing alkoxy chain length suggesting the interaction of alkoxy chains with intense laser light. In contrast, the variation of alkoxy chain shows no effect in the UV–Vis light (Fig. 4). The D-D–D series 4a-c follows the same trend except that 4b with OC8H17 gives abnormally high value at lower concentration. The third-order NLO properties of poly(3-alkoxythiophene) also show a strong dependence on the alkoxy side chains [29c].

The NLO response increases with increase of concentration (Fig. 8) attributed to the increasing number of thermally agitated molecules that enhances the nonlinear refractive index value. A similar measurement technique on a phenothiazine system [29a] yields an \( n_2 \) value of the order of \( 10^{-7} \) cm\(^2\)/W. This is comparable to the value reported in this work (Table 6). However, literature shows that NLO properties of pi conjugated systems have also been investigated by femto second (pulse) lasers, \( \gamma \) values and nonlinear susceptibility \( \chi^{(3)} \) were calculated [20e,29f] which are of the order of \( 10^{-23} \) cm\(^2\)/W. The resonance effects and other local effects come into play when ultra fast (femto second) nonlinearity is in consideration.

4. Conclusions

A series of acceptor and donor substituted bis(alkoxy)phenylethenynes has been prepared and characterized. Thermal studies by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere demonstrate good thermal stability of the compounds. Acceptor substituted 3a-c absorb longer wavelength in the UV–Vis spectra than that of donor substituted 4a-c. In the emission spectra, 3a-c emit in the green whereas 4a-c emit in the blue region of
Material | $\Delta \phi \times 10^{-4}$ | $n_2 \times 10^{-8}$ (cm$^2$/W) \\
--- | --- | --- \\
3a | 25 | $-0.97 \pm 0.08$ \\
3b | 23 | $-1.15 \pm 0.10$ \\
3c | 47 | $-2.34 \pm 0.26$ \\
4a | 11 | $-0.66 \pm 0.08$ \\
4b | 31 | $-1.67 \pm 0.33$ \\
4c | 16 | $-0.88 \pm 0.08$ \\

$\Delta \phi$: nonlinear phase shift of the incident beam. Measurements were carried out at $1 \times 10^{-3}$ M concentration.

the electromagnetic radiation. The closed aperture Z-scan technique suggests that the materials have third-order nonlinearity which varies with the acceptor and donor substituents as well as alkoxy chain length.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.synthmet.2017.06.005.

The IR and NMR ($^1$H and $^{13}$C) spectra of all new compounds, and selected TGA and DSC thermograms are available.

References