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Tetrahedron Letters 46 (2005) 3913–3916

Tetrahedron Letters

Synthesis and hyperpolarizabilities of high temperature triarylamine-polyene chromophores

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> Received 23 February 2005; revised 19 March 2005; accepted 21 March 2005 Available online 12 April 2005

Abstract—The synthesis and hyperpolarizabilities of a series of push–pull chromophores containing bis-(4-methoxyphenyl)-amine donor and efficient acceptors bridged with ring locked polyene are presented. The chromophores are readily soluble in common organic solvents and exhibit high thermal decomposition temperatures (highest $T_d = 330$ °C). Molecular hyperpolarizabilities (β) of the chromophores were measured by Hyper Rayleigh Scattering (HRS) at 1604 nm (highest $\beta = 20,000 \times 10^{-30}$ esu). These chromophores can be used to develop electro-optic (EO) materials due to their large optical nonlinearities, good absorption characteristics, high thermal decomposition temperatures, and excellent solubility with organic solvents and polymeric materials. © 2005 Elsevier Ltd. All rights reserved.

Organic nonlinear optical (NLO) chromophores with enhanced thermal and chemical stability and a high hyperpolarizability are of interest for photonic applications.¹ Quantum mechanical calculations have helped to identify polyene and thiophene based chromophores with the highest nonlinearity.² Recently, we have reported the synthesis of heterocyclic bridged triarylamine chromophores with high hyperpolarizability (β).³ Here, we report the synthesis and hyperpolarizabilities of ring locked polyene and polyene–thiophene derived chromophores 7–12 with the same triarylamine donor. The chromophores are soluble in common organic solvents, show good thermal stability, and adequate absorption behavior. The synthesis, thermal, linear, and nonlinear optical properties are discussed.

Ring locked phenyltetraene-bridged chromophores $(CLD)^4$ and analogues in general exhibit high β values and electro-optic (EO) devices derived from them have shown commercial promise. Due to their high ground state dipole moment induced head to tail interactions, noncentrosymmetric alignment remains a challenge.⁵

Keywords: Triarylamine chromophores; Hyperpolarizability.

The rigid isophorone bridge also causes crystallization and solubility problems. Usage of bulky protected donor groups,⁶ attachment of floppy side chains,⁷ attachment of bulky groups to the acceptor,⁸ and use of dendritic structures⁹ are methods sought for minimizing these interactions. It has also been recognized that the addition of aromatic rings in the donor may impose a quinoidal bonding pattern and help prevent unfavorable organization of the chromophores.¹¹ Also the use of diarylamino electron donor substituents in extended donor–acceptor substituted chromophores results in significant improvement in thermal stability compared to the alkyl amino substituted derivatives.^{3,10}

Molecules with 4-(N,N-di-p-anisylamino)phenyl moieties as the electron donor have shown long-lived charge separation and have been used in multiphoton absorbing materials.¹² In the present study, triarylamine donors are bridged to powerful acceptors via ring locked polyenes and polyene linked thiophene moieties to give chromophores 7–12 (Fig. 1). The triarylamine polyene aldehyde **5** was synthesized in five steps as shown in Scheme 1. Ullmann coupling of 4-iodoanisole with aniline yielded N,N-bis(4-methoxyphenyl)-N-phenylamine (1) in 65% yield. A Vilsmeier–Haack reaction of 1 provided 4-[bis-(4-methoxyphenyl)amino]benzaldehyde (2) in 78% yield.³ Condensation of 2 with

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^{0040-4039/\$ -} see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2005.03.140



Figure 1. Triarylamine derived chromophores 7–12.



Scheme 1. Synthesis of parent aldehyde 5. Reagents and conditions: (i) CuI, 4-iodoanisole; (ii) DMF, POCl₃; (iii) isophorone, Na, EtOH; (iv) *n*-BuLi, Di-*iso*-propylcyanomethyl phosphonate; (v) DIBAL-H, CH₂Cl₂.

isophorone in basic conditions produced ketone **3** in 65% yield.¹³ Reaction of **3** with di-*iso*-propyl cyanomethyl phosphonate gave **4** (97%) and successive reduction using DIBAL-H gave aldehyde **5** in 85% yield.¹⁴ Knoevenagel condensation of **5** with different acceptors gave chromophores **7–12** as shown in Scheme 2.¹⁸ Chromophore **11** was synthesized by the condensation of **2** with **13** in basic conditions. Condensation of **5** with diethyl thienylmethyl phosphonate (TMP) followed by lithiation and treatment with DMF gave aldehyde **6** in 80% yield (7:3, *E:Z*). Knoevenagel condensation of **6** with **14** gave chromophore **12** in 66% as shown in Scheme 2. All intermediates and chromophores were isolated as pure compounds as evidenced by ¹H NMR, ¹³C NMR, and high resolution MS or MALDI-TOF. The electron acceptors **13** and **14** were prepared as reported previously.^{15,16} Diethyl thienylmethyl phosphonate was prepared from 2-methylthiophene using a standard procedure.¹⁷ Di-*iso*-propyl cyanomethyl phosphonate was chosen for the synthesis of **4** to favor the formation of the trans isomer from which **5** was isolated with a 8:2, E:Z ratio. The highly conjugated aldehyde **5** was stable at cold temperature over long periods of time.

The electronic absorption and thermal stability of the chromophores are summarized in Table 1. As expected the increase of acceptor strength induces a bathochromic shift of the λ_{max} . For example, the powerful tricy-anofuran (TCF) acceptor (9) resulted in a ~40 nm red shift over the diethylthiobarbiturate acceptor (8). Similarly an increase in conjugation using thiophene (12) has increased the absorption wavelength by 20 nm with the same type of donor-acceptor groups. Chromophore 11 gave the lowest absorption due to the presence of the weak dicyanovinyl electron acceptor.

The decomposition temperature, T_d , of the chromophores was measured by thermal gravimetric analysis (TGA) in N₂, with a heating rate of 10 °C/min. The chromophores exhibit T_d ranging from 179 to 330 °C. Compounds containing the dicyano acceptor have lower T_d values compared to others. An extension of conjugation has decreased the T_d values as expected.

Additional tests on thermal stability for selected chromophores were performed by dispersing them into highly thermally stable perfluorocyclobutyl (PFCB) aromatic ether polymers¹⁹ and heating them at 200 °C for 45 min under N₂ atmosphere. Chromophore **9** exhibited good thermal stability as the UV–visible spectra of the



Scheme 2. Synthesis of chromophores 7–12 (in Fig. 1). Reagents and conditions: (vi) and (viii) acceptor, Et_3N ; (vii) TMP, *t*-BuOK, THF, *n*-BuLi, DMF. Compounds 7–10 were synthesized from 5 [A = CN–CH₂–CN (7), diethyl thiobarbiturate (8), TCF (9), and 13 (10)]. Compound 11 was synthesized from 2 (A = 13). Compound 12 was synthesized from 6 (A = 14).

 Table 1. Thermal, linear, and nonlinear optical properties of 7–12

Chromophore	$\lambda_{max} \ (nm)^a$	$T_{\rm d}$ (°C) ^b	β (10 ⁻³⁰ esu)	$\beta_0 (10^{-30} \operatorname{esu})^c$
7	550	267	_	
8	627	272	_	
9	670	330	20,000	4000
10	585	258	2000	700
11	515	230	700	400
12	690	179	_	

^a λ_{max} measured in CHCl₃.

 $^{\rm b}\,T_d$ is the onset temperature of TGA in N_2 with a scanning rate of 10 °C/min.

^cOudar–Chemla method.

films before and after heating exhibited no significant change. Further, thin-layer chromatography (TLC) of the mixture after heating revealed no new eluted products.

Finally, β values for chromophores 7–12 were evaluated using Hyper Rayleigh Scattering (HRS) at 1604 nm²⁰ and the results are shown in Table 1. All the values were obtained by the external reference method as previously described.³ For chromophore 9, the linear absorption of the second harmonic was corrected using Beer's law.²¹ While the difference in β for chromophore 10 and 11 can be explained by simple conjugation length, the enhancement of β for chromophore 9 over 10 is due to the improved electron withdrawing power of the TCF acceptor. Absence of two-photon induced fluorescence enhancement²¹ was confirmed by analysis of the linear fluorescence spectrum in solution and monitoring the pulse width of the HRS signal.

In summary, we have accomplished the efficient synthesis of a series of chromophores (7-12) based on ring locked polyene-thiophene as electron bridge and dimethoxy triarylene amine as electron donor. The good thermal stability and the solubility of the chromophores are demonstrated. Chromophore 9 exhibited the highest

 β value of 20,000 × 10⁻³⁰ esu placing it among the highest recorded values to date.

Acknowledgements

We thank the Defense Advanced Research Projects Agency (DARPA), D.S. thanks the National Science Foundation (NSF) (CAREER Award DMR-9985160) and South Carolina EPSCoR for financial support. D. W. Smith is a Cottrell Scholar of Research Corporation.

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- 18. Synthesis and characterization of 9: To a stirred solution of aldehyde 5 (1 equiv) in dry CH_2Cl_2 (10 mL/g) was

added TCF (1.2 equiv) and catalytic amount of Et₃N. The dark reaction mixture was heated to reflux for 3 h and monitored by TLC. After complete disappearance of aldehyde, the reaction mixture was cooled to room temperature, poured onto ice cold water, and extracted with excess CH₂Cl₂. The combined organic layer was washed with water, dried (MgSO₄), and concentrated in vacuo. The residue was purified by chromatography (CH₂Cl₂) to afford (65%) green solid. ¹H NMR (300 MHz, CDCl₃) δ 8.08 (t, 16.4 Hz, 1H), 7.39 (d, 2H), 7.08 (d, 4H), 6.86-6.79 (m, 8H), 6.37 (s, 1H), 6.32 (d, 7.7 Hz, 1H), 6.24 (d, 14.6 Hz, 1H), 3.80 (s, 6H), 2.41 (s, 2H), 2.32 (s, 2H), 1.25 (s, 6H), 0.96 (s, 6H). ¹³C NMR (75.5 MHz, CDCl₃) δ 178.0, 174.0, 156.4, 154.0, 151.2, 148.3, 145.1, 140.0, 132.3, 130.8, 128.3, 127.4, 126.1, 119.0, 116.5, 114.7, 113.0, 112.2, 98.7, 96.3, 56.0, 48.1, 41.7, 39.5, 32.0, 29.7, 28.4, 26.5. HR-MS m/z: 660 (M^+) .

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