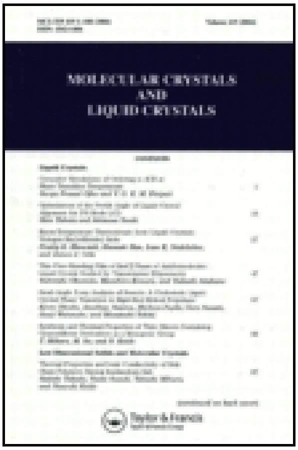

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Charles W. Spangler , Mingqian He , Eric G. Nickel , Joyce Laquindanum , Larry R. Dalton , Nansheng Tang & Robert Hellwarth (1994): The Design of New Organic Materials with Enhanced Nonlinear Optical Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 240:1, 17-23

To link to this article: http://dx.doi.org/10.1080/10587259408029711

Mol. Cryst. Liq. Cryst. 1994, Vol. 240, pp. 17–23
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Printed in the United States of America

THE DESIGN OF NEW ORGANIC MATERIALS WITH ENHANCED NONLINEAR OPTICAL PROPERTIES

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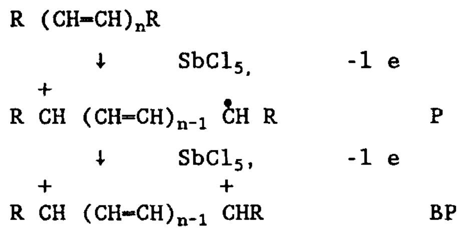
Abstract Bis-anthracenyl and bis-thienyl polyenes have been synthesized using Wittig methodology. These polyenes can be oxidatively doped with $SbCl_5$ to yield bipolaron-like charge states that can be cast as thin film composites. $\chi^{(3)}$ measurements performed by degenerate four wave mixing on neutral and doped polyenes indicate significant enhancement of $\chi^{(3)}$ by bipolaron charge state generation. In the bis-thienyl polyene series, dramatic increases in solubility and processibility have been achieved by multiple alkyl group substitution thus allowing synthesis and characterization of long polyene sequences as oligomeric models of polyacetylene.

INTRODUCTION

During the past five years, considerable progress has been made in the oligomeric modeling of polaronic and bipolaronic charge state formation in electroactive polymers and oligomeric model compounds. Oligomeric polyacetylene segments can be end-capped with a variety of substituents, however good thermal stability is most readily achieved by using aromatic end caps. We have previously demonstrated the formation of both polaron-like and bipolaron-like species in both diphenyl[1,2] and bis-thienyl polyenes[3] by oxidative doping with $SbCl_5$. In these cases, however, lack of polyene solubility precluded spectroscopic study of charge state formation beyond the hexaene. This is illustrated below in Figure 1. In most cases the bipolarons formed



$$\begin{array}{lll} R\,(CH{=}CH)_nR & & \\ \quad\downarrow \quad SbCl_5, & -1\ e & \\ R\,\overset{+}{C}H\,(CH{=}CH)_{n-1}\,\dot{C}H\,R & & P \\ \quad\downarrow \quad SbCl_5, & -1\ e & \\ R\,\overset{+}{C}H\,(CH{=}CH)_{n-1}\,\overset{+}{C}HR & & BP \end{array}$$

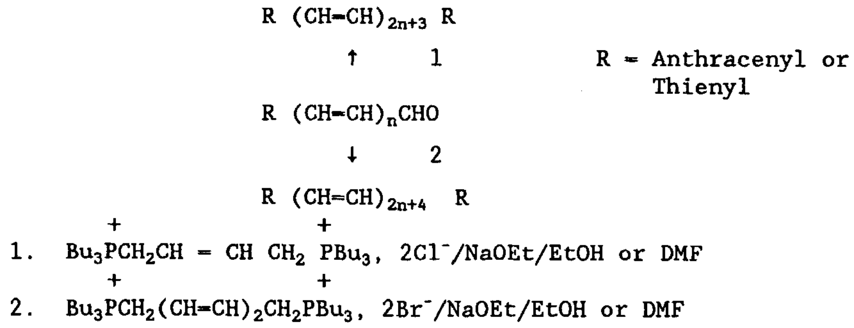
Figure 1 Oxidative doping of polyenes

from the polyenes were stable for several days in contact with air.

Large third order nonlinear optical (NLO) responses have been obtained from a number of electroactive polymers[4], however, their lack of processibility and broad absorption limits their potential use in photonics applications. Recent theoretical[5,6] as well as experimental[7] studies have indicated that long conjugation sequences may not be necessary for large $\chi^{(3)}$ response. In addition, DeMelo and Silbey[8,9] have calculated that charge state incorporation in polyene sequences should lead to large increases in γ_{xxxx}, a result confirmed by more recent calculations by Birge and coworkers[10]. With these results in mind, we have been examining the effect of bipolaron formation upon the third-order NLO properties of bis-anthracenyl and thienyl polyenes with well defined conjugation lengths and absorption characteristics.

SYNTHESIS OF BIS-ANTHRACENYL AND BIS-THIENYL POLYENES

The polyenes reported in this paper were synthesized utilizing Wittig methodology developed in our laboratory[3,11,12] and illustrated below in Figure 2. Anthacenyl polyenes were chosen due

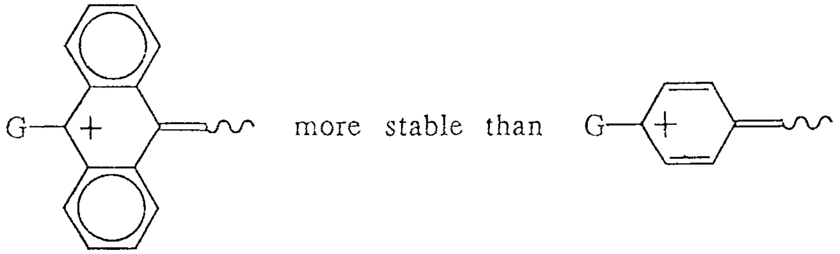


$$\begin{array}{ll} R\,(CH{=}CH)_{2n+3}\,R & \\ \quad\uparrow \quad 1 & R = \text{Anthracenyl or Thienyl} \\ R\,(CH{=}CH)_nCHO & \\ \quad\downarrow \quad 2 & \\ R\,(CH{=}CH)_{2n+4}\ R & \end{array}$$

1. $Bu_3\overset{+}{P}CH_2CH = CH\ CH_2\ \overset{+}{P}Bu_3,\ 2Cl^-/NaOEt/EtOH$ or DMF
2. $Bu_3\overset{+}{P}CH_2(CH{=}CH)_2CH_2\overset{+}{P}Bu_3,\ 2Br^-/NaOEt/EtOH$ or DMF

Figure 2. Synthesis of bis-aromatic polyenes

to the increased benzenoid stabilization of the quinoidal bipolaron versus phenyl. This increased stabilization results in very stable bipolaronic species which can be cast from solution as polycarbonate films which are stable for several months with no decline in optical properties. Associated with the change in oxidation state is a large red shift from the original π-π^* transition to yield absorption maxima in the NIR. However, the solubility characteristics of these materials are less than ideal, yielding only dilute solutions in a variety of solvents.



Noting the increased solubility achieved in poly (3-alkylthiophenes) by inclusion of alkyl side chains in the conjugation sequence, we have also synthesized a bis-thienyl polyene series with butyl substituents in the 3 and 4 positions of each thiophene ring. This substitution dramatically improves the solubility of the polyene series allowing the study of bipolaron formation to the decaene level.

THIRD ORDER NLO PROPERTIES OF NEUTRAL AND DOPED POLYENES

$\chi^{(3)}$ measurements were performed by degenerate four wave mixing (DFWM) at 1064 nm utilizing 5-6 picosecond pulse widths (0.4 mJ/pulse) in a conventional back beam geometry. Bis-anthracenyl polyenes with both hexyl and decylthio substituents were chosen for study because their bipolaron-like cations have minimal absorption (band-edge) at this wavelength. The $\chi^{(3)}$ values, shown in Table 1, were obtained for saturated solutions of the polyenes in CH_2Cl_2 and referenced to CS_2 ($\chi^{(3)} = 8.6 \times 10^{-13}$ esu). Absorption characteristics of neutral and doped species are shown in Table 1.

Table 1 Absorption characteristics of neutral and doped polyenes

$G\text{-}An\text{-}(c{=}c)_n\text{-}An\text{-}G$

G	n	Neutral λ_{max}(nm) CH_2Cl_2 solution	Neutral λ_{max}(nm) composite film	Bipolaron λ_{max}(nm) CH_2Cl_2 solution	Bipolaron λ_{max}(nm) composite film
H'	4	423	435	940	924
	5	428	443	978	950
	6	438	447	1000	934
$C_{10}H_{21}S$	3	435	439	832	848
	4	444	447	886	935
C_6H_{13}	3	429	--	--	--
	4	438	--	--	--

Absorption characteristics of the neutral and doped bis-(3,4-dibutyl-2-thienyl) polyene series is shown in Table 3. DFWM studies for this series is still in progress, however selected values obtained for $\chi^{(3)}$ at 532 nm are included for the neutral species.

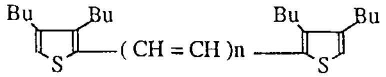
Table 2 $\chi^{(3)}$ values for neutral and doped anthracenyl polyenes

$G\text{-}An\text{-}(C{=}C)_n\text{-}An\text{-}G$

G	n	wt%	λ(nm)	$\chi_{1111}^{(3)}$ $(-\omega;\omega,\omega,-\omega)$(esu) neutral	$\chi_{1111}^{(3)}$ $(-\omega;\omega,\omega,-\omega)$(esu) bipolaron
$C_{10}H_{21}S$	3	0.17	1064	$7\text{x}10^{-14a}$	$1.9\text{x}10^{-13}$
$C_{10}H_{21}S$	4	0.21	1064	$7\text{x}10^{-14}$	$67 \text{ x } 10^{-13}$
C_6H_{13}	3	0.14	1064	$7\text{x}10^{-14}$	$13\text{x}10^{-13}$
C_6H_{13}	3	0.14	532	$2.3\text{x}10^{-14}$	$3.1\text{x}10^{-13}$

[a] Same order of magnitude as solvent (CH_2Cl_2)

Table 3 Absorption characteristics of neutral and doped bis-thienyl polyenes



n	Neutral λ_{max}(nm)	Bipolaron λ_{max}(nm)	$\chi_{1111}^{(3)}$ $(10^{-13}$esu$)^a$
3	432, 399, 380	655, 593	--
4	443, 418, 396	661, 600	--
5	462, 435, 412	715, 679	2.7
6	480, 450, 426	809, 719	--
7	496, 464, 439	849, 790	43.0
8	510, 477, 450	914, 855	258.0
9	521, 489, 461	971, 892	--
10	534, 499, 471	1022, 950	--

[a] 10^{-3} M solution in CH_2Cl_2

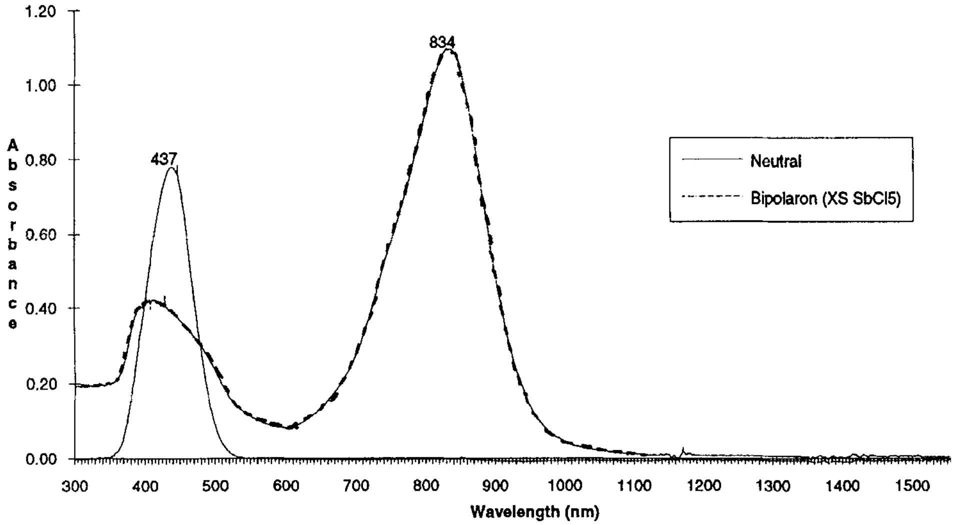


Figure 3. Absorption spectra of neutral and doped bis-decylthioanthracenyl triene

DESIGN OF COPOLYMERS CONTAINING ANTHRACENYL OR THIENYL POLYENE REPEAT UNITS

Extrapolation of $\chi^{(3)}$ to 100% concentration for the above polyenes lead to predicted $\chi^{(3)}$ values of ca. 3 x10 $^{-9}$ esu when doped to a bipolaronic state. This concentration enhancement can be realized by incorporation into a formal copolymer as we have previously outlined[13]. These copolymer syntheses are currently being actively pursued in our laboratory.

CONCLUSIONS

We have presented a new approach to the design of third order materials by incorporating bipolaronic charge states in the conjugation sequence. We have also shown how to solubilize polyene sequences so that longer bipolaron delocalization lengths can be synthesized. Even if the $\chi^{(3)}$ values for the doped species are slightly resonance enhanced, they represent some of the largest third order responses yet measured for small organic molecules. At the present time polyene sequences containing 12-16 double bonds appear to be synthetically accessible without catastrophic loss of processibility. This would allow bipolaron delocalization lengths of more than 30 atoms, and thus even larger $\chi^{(3)}$ values.

ACKNOWLEDGEMENTS

This research was supported in part by the Air Force Office of Scientific Research Grant #AFOSR 90-0060, and partial support is also acknowledged to the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

REFERENCES

1. C.W. Spangler, L.S. Sapochak and B.D. Gates, in Organic Materials for Non-Linear Optics, edited by R. Hann and D. Bloor (Royal Society of Chemistry, London, 1989), pp. 57-62.

2. C.W. Spangler and K.O. Havelka, in Materials for Nonlinear Optics, edited by S. Marder, J. Sohn and G. Stucky (American Chemical Society, Washington, 1991), Chap. 44, pp. 661-671.

3. C.W. Spangler, P.-K. Liu, A. Dembek and K.O. Havelka, J. Chem. Soc. Perkin Trans., 799 (1991).

4. P.N. Prasad and D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers (John Wiley & Sons, New York, 1991), Chap. 10, pp. 222-251.

5. D.N. Beratan, J.N. Onuchic and J.W. Perry, J. Phys. Chem., 91, 2696 (1987).

6. G.J.B. Hurst, M. Duplis and E. Clementi, J. Chem. Phys., 89, 385 (1988).

7. P.N. Prasad and B.A. Reinhardt, Chem. Mater., 2, 660 (1990).

8. C.P. DeMelo and R. Silbey, Chem. Phys. Lett., 140, 537 (1987).

9. C.P. DeMelo and R. Silbey, J. Chem. Phys., 88, 2567 (1988).

10. J.R. Tallent, R.R. Birge, C.W. Spangler and K.O. Havelka, Molecular Electronics - Science and Technology, edited by A. Aviram (American Institute of Physics, New York, 1992), pp. 191-203.

11. C.W. Spangler, P.-K. Liu and K.O. Havelka, J. Chem. Soc. Perkin Trans. 2, 1207 (1992).

12. C.W. Spangler and P.-K. Liu, J. Chem. Soc. Perkin Trans. 2, 1959 (1992).

13. E.G. Nickel, C.W. Spangler, N. Tang, R. Hellwarth and L.R. Dalton, Nonlinear Optics (1993) (In press).