OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 4, April 2009, p. 364 - 370

Synthesis, characterization, thermal stability and nonlinear optical properties of push-pull chromophores containing ferrocene donor group

A. M. ASIRI[*], G. A. BAGHAFFAR[a], M. S. AL-AMOUDI[b], A. G. AL-SEHEMI[c]
Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21413, P.O. Box 80203, Saudi Arabia
[a]*Department of Chemistry, Hadhramout University of Science and Technology, P.O.Box 50512, Mukalla, Republic of Yemen*
[b]*Chemistry Department, College of Science, Taif University, Taif, Saudi Arabia*
[c]*Chemistry Department, Faculty of Science, King Khalid University, Abha, Saudi Arabia*

Two organo-metallic chalcones as second-order nonlinear optical (SONLO) material, were synthesized via Knovoenagel reactions of ferrocene carboxaldehyde and two active methylene compounds and evaluated. The ferrocenyl chalcones prepared have shown a bathochromic shift and thermal stability in polymeric films. On heating the dyes films up to 90 ºC, the extent of degradation reaches up to 56.68 % and very small amounts of degradation were observed at 60 ºC for 40 and 60 min. These compounds have UV-Vis bathochromic shift, enabling them to be used as Second Order Nonlinear Optical materials in the blue domain as well as dyes.

Received December 21, 2008; accepted April 23, 2009)

Keywords: Ferrocene, Second order nonlinear, Optical materials, Thermal stability

1. Introduction

Mankind was interested in light and its interaction with matter since ancient times. In our modern society light is not limited to the scientific society but has grown immensely to encompass many kinds of applications, such as optical communication, medical surgery and diagnostics using optical tools and techniques. With advent of laser, the search for new nonlinear materials started a new race. The ability to manipulate frequency, phase, polarization or path of light has an important utilization such as production of tuneable laser light, data storage and solar protection. Currently research is devoted to organic and organomettalic materials that exhibit nonlinear optical (NLO) effects, especially second harmonic generation (SHG) which causes doubling in the frequency of light [1-6]. For constructing SHG devices with large (β) hyperpolarizability, the molecule must be noncentrosymmetric so that their NLO properties do not cancel out. Moreover is needed small energy gap [6].

"Push-pull" compounds with ferrocenyl (Fc) donor group linked to a conjugated polyenic chain capped by an acceptor moiety A, (Fc-π-A), have shown to be a good candidates as second-order nonlinear optical (NLO) chromophores [7]. We have recently synthesized and characterized NLO materials contain ferrocenyl as a donor and barbituric and thiobarbituric acids as acceptor with conjugated moieties and with moderate solubility in polar organic solvents [8, 9]. In this article, we report our study of "push-pull" compounds containing ferrocenyl (Fc) donor group bound to a conjugated chain capped by an acceptor ketone moiety A, of the forms (Fc-π-A) and (Fc-π-A-π-Fc). During the last two decades organomettalic compounds have shown to be good candidates for NLO especially SHG [10]. For example compounds **A** with 3-dicyanomethylidene-2, 3-dihydrobenzothiophene-1, 1-dioxide as acceptor have $\mu\beta$ values of ($11200 \mathrm{x} 10^{-48}$ esu) [11,12] and **B** with 1,3-bis(dicyanomethylidene)indane as acceptor was (8720×10^{-48} esu) [13] as determined with EFISH technique. In these types of compounds one expects additional behavior to mixing with the metal states. Thus a methyl substituted at the cyclopentadienyl ring should increase the dipole moment as well nonlinearity by making the donor component electron rich.

2. Experimental

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disks on a Nicolet Magna 520 FTIR spectrometer. NMR spectra were obtained with a Bruker DPX 400 (400MHz) spectrometer using $CDCl_3$ solutions. Microanalysis was carried out using a Perkin Elmer 240B analyzer. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for films of dyes doped in PMMA polymer at room temperature, 60°C for different intervals of time, and 90°C for 3 hrs.

Thermal analysis measurements, thermogravimetry (TG) and differential thermal analysis (DTA) were carried out by a Shimadzu DT-60 thermal analyzer. All experiments were performed in a dynamic nitrogen atmosphere (30 ml /min). Highly sintered α – Al_2O_3 powder (Shimadzu) was used as a reference material for DTA measurements.

2.1 Materials

Ferrocene carboxaldehyde, 3-Acetylthiophene and the 4-methoxy acetopheneone and solvents were all supplied by Aldrich chemicals Co.

2.2 General procedure for the preparation of compounds 1 and 2

To a well-stirred solution of Fc-CHO (10 mmol) and the appropriate ketone (10 mmol) in ethanol (30ml) was added drop wise to a solution of NaOH (30 ml, 10%) at 60°C over a period of 20 min. After the addition was completed the solution was left to stir at room temperature for 12 hrs, then poured into ice-cold water (200 ml) and stirred for 2 hrs., The precipitated chalcone was filtered off and washed with copious amounts of water until the wash was neutral; then it was washed with cold ethanol and dried. The solid products were recrystallized from ethanol.

2.2.1 3-Ferrocenyl-1-(3-thienyl)propenone (1)

Red crystals, yield 70%; m.p. 135-140° C. Anal. Found: C, 63.23; H, 4.28. Cal. For $C_{17}H_{14}FeOS$: C, 63.35; H, 4.35%, ν_{max} (KBr/cm^{-1}) 1652 (C=O),1600 (C=C), 1103, 998, 806. ^{1}H NMR: δ 8.13 (d, 1H); 7.38 (d, 1H); 9.98 (s, 1H); 4.62 (s, 2H, -CH=C); 4.50 (s, 2H, -CH=C); 7.16 (d, 1H, J = 15.32 Hz); 7.76 (d, 1H); 4.20 (s, 5H, C_5H_5).

2.2.2 3-Ferrocenyl-1-(4-methoxyPhenyl)propenone (2)

Red crystals, yield 70%; m.p. 145-155° C. Anal. Found: C, 69.20; H, 5.41. Cal. For $C_{20}H_{18}FeO_2$: C, 69.38; H, 5.20%, ν_{max} (KBr/cm^{-1}) 1648 (C=O),1600 (C=C), 1103, 999, 808. ^{1}H NMR: δ 7.00 (d, 2H, *J* = 8.68 Hz,); 8.02 (d, 2H, j = 8.72 Hz); 7.76 (d, 1H, J =15 Hz); 7.16 (d, 1H, *J* = 15 Hz); 4.62 (s, 2H, -CH=C); 4.50 (s, 2H, -CH=C); 4.20 (s, 5H, C_5H_5); 3.91 (s, 3H, CH_3O).

3. Results and discussion

3.1 Synthesis of ferrocene 1 and 2

Ferrocene 1 and 2 were prepared by Aldol condensation of Ferrocenecarboxaldehyde and 3-Acetylthiophen and 4-methoxyacetophenone respectively.

3.2 Electronic structure and solvatochromism

The absorption maxima for compounds 1 and 2 measured in different solvents of increasing polarity are given in Table 1. There are two bands at 230-255 nm and at 495-505 nm for dye **1**, and at 225-255 nm and at 495-505 nm for dye 2. These bands are assigned to π→π* at shorter wavelength and MLCT (M-A) at longer wavelength. The assignment is based on theoretical results proposed by Barlow [14] and other experimental results [15-18]. The visible absorption band gives them their distinct colors, red for both 1 and 2, in their solid form as well as in solutions. Both transitions have different maxima for the two compounds. Absorption maxima (λ_{max}), were obtained in a series of solvents with different polarities and are summarized in Table 1. The absorption maxima of the two compounds (1and 2**)** show a large solvent dependence. Furthermore, the absorption maxima of the two compounds are always hypsochromicaly shifted.

Table 1. Absorption of dyes at λ_{max} in PMMA, $CHCl_3$, CH_3CN and ethanol for the transitions π→π and MLCT (M→A) at room temperature.*

	PMMA		$CHCl_3$		C_2H_5OH		CH_3CN	
	Π → Π*	MLCT	Π → Π*	MLCT	Π → Π*	MLCT	Π →Π*	MLCT
Dye 1	330	505	255	490	230	505	235	495
Dye 2	330	510	255	495	230	505	225	495

The negative bathochromic shifts are due to the mesomeric form of the molecules in their ground states with a dipole moment opposite in sign to that of excited state but the charge transfer is in the same direction as for other charged molecules in a similar compound [14,9]. These properties are important for designing second-order nonlinear optical (SONLO) devices in the blue domain.

3.3 Hyperpolarizabilities of 1 and 2

The nonlinear optical second-order polararizability (β) includes two parts in a donor-л-acceptor molecule (D-л-A): one is the yperpolarizability from charge separation induced by the high field (β_{add}) and the other is the hyperpolarizability from the contribution of charge transfer state (β_{CT}). β_{CT} is usually the main part of β, and can be used to describe the nonlinear optical property of the donator-л-acceptor molecule with an intensive intramolecular electron transfer structure [26]. Here, the $\beta_{CT}\mu_g$ was approximately determined by the solvatochromic method in two different solvents [27,28,29,30] :

$$\beta_{CT}\mu_g = 4.612x10^{-5} F(\lambda)\, \varepsilon \Delta\nu_{½} \frac{\alpha^3}{\Delta F(D)} \qquad (1)$$

in which F(λ) = $\lambda^3\lambda_v^4 / [(\lambda_v^{2-}4\,\lambda^2)(\lambda_v^{2-}\lambda^2)]$, F(D) = 2(D-1)/(2D+1), μ_g is the permanent dipole moment of ground state, ε the molar extinction coefficient of the solution, $\Delta\nu_{1/2}$ the width at half-height of the absorption peak (л→л*) of the dye, Δν the shift of frequency of the absorption peak in the two different solvents, α the semidiameter of the dye, D the dielectric constant of the solvent, λ the absorption wave-length of the excited state of the dye and λ_v is the wavelength of the fundamental laser. The parameter α which is of critical importance for the magnitude of Δμ can be estimated for these compounds by assuming a cylindrical symmetry and calculate the radius from the length L and diameter D of the cylinder [31.32].

$$\alpha = \left({}^{3}\!/_{16} LD^{2}\right)^{1/3} \tag{2}$$

Using length 18 Å and diameter 6.8 Å derived from chemical model a radius of 5.38 Å for all donor-acceptor substituted compounds is obtained.

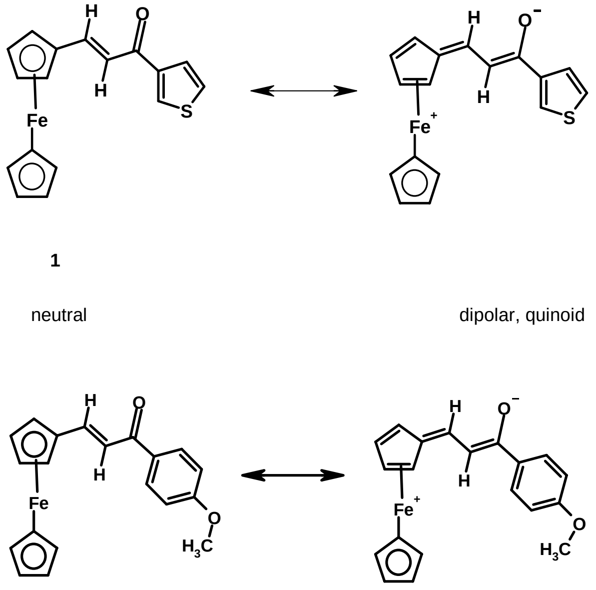
The measurements were performed in both ethanol and chloroform. The D of ethanol is 34 and that of chloroform is 4.81 D. The function F (D) in the these two solvents is $\Delta F(D) = F(D)_{EtOH} - F(D)_{CHCl3}$ 0.2. We took λ_v = 1064 nm as the fundamental light. The $\beta_{CT}.\mu_g$ values of dyes 1 and 2 at wavelength of 1064 nm are listed in Table 6.

Table 6. Spectrum data, first hyperpolarizabilities of dye 1 and 2.

Dye no	Eth OH			$CHCl_3$			
	λ (nm)	ε	$\Delta\nu_{1/2}$ cm^{-1}	λ (nm)	Δν/ cm^{-1}	α (nm)	$\beta_{CT}\mu$ x10^{-30}esu)
1	515	2184	3870	500	384	0.538	468
2	505	2371	3870	500	198	0.538	99

Table 7. Oscillator strength (f) and transition dipole moment (μ).

Dye no	EthOH			$CHCl_3$			
	λ (nm)	ε	$\Delta\nu_{1/2}$ cm^{-1}	λ (nm)	Δν/ cm^{-1}	μ (D)	
1	515	2184	3870	500	583	1.998	0.37
2	505	2371	3870	500	607	2.062	0.39



1

2

Scheme 1. Structure of dyes 1 and 2.

It can be found that the values of are 468 × 10^{-30} esu and 99 x10^{-30} esu, respectively. Comparing with Azo dyes of hexafluoroisopropylidene derivatives [33], the newly synthesized dyes showed increased hyperpolarizabilities , which can be attributed to the ferrocene which have shown good SHG [34-39]. The higher hyperpolarizability of dye 1 can be explained on theoretical and experimental studies which demonstrated that λ-excessive and λ-deficient heterocycles can efficiently function as primary [40] and/ or auxiliary [41] donor and acceptor groups in push-pull dyes; furthermore, the reduced ring aromaticity relative to benzene of the five-membered heterocycles leads both to an increased transition moment and to change in dipole moment [42,43]. The oscillator strength (f) which is a dimensionless quantity used to express the transition state probability of the charge transfer band [15] and the transition dipole (μ) of the charge transfer [16] , Table 7 have been calculated from the following equation [17] :

$$f = 4.32 \times 10^{-9} [\varepsilon_{max}\Delta\nu_{1/2}],$$

$$\mu = 0.0958 [\varepsilon_{max}\Delta\nu_{1/2} / \nu_{max}]^{1/2}$$

where $\Delta\nu_{1/2}$ is the band width at half absorbance, ε_{max} and ν_{max} the extinction coefficient and wavenumber at the absorption maximum, respectively. The values of (f) indicate the difference of interaction between the donor-acceptor chromophores,. The negatively charged oxygen (see quinoid form) in the bridge obstructs the donation of electron density from the ferrocene group to the end of the molecule. This rationalizes the transition dipole moment μ_{ge}, which corresponds to the shift of charge during an electronic transition, is small.

3.4 Optical properties of ferrocene derivatives 1 and 2 in PMMA thin films

The absorption maxima for compounds 1and 2 measured at RT, 60°C (20, 40, and 60 min.), and 90°C for 3 hrs. in PMMA polymer films are given in Table 2.

Table 2. Absorption of dyes 1 and 2 at λ_{max} in PMMA, for the transitions $\pi \rightarrow \pi$.

	Dye **1**		Dye **2**	
	$\Pi \rightarrow \Pi^*$	MLCT	$\Pi \rightarrow \Pi^*$	MLCT
RT	330	505	330	510
60°C/20min	335	505	330	505
60°C/40min	335	505	330	505
60°C/60min	335	505	325	505
90°C/3hrs	335	503	330	505

* and MLCT (M→A) at room temperature

The absorption bands in PMMA films are between 330 – 335 nm and 503 -505 nm for compound 1, while for compound 2 they are between 325 – 330 nm and 505 – 510 nm. The proximity of the molecules in the film induces intermolecular interaction that affects both ground and excited state energies [19]. Similar changes in absorption spectra (hypsochromic shift) have been observed in *trnans*-stilbene containing non polar groups [20, 21] or p-donor and p'-acceptor substituents [19, 20, 22] as reported for 4-octadecyaamino-4'-nitro stilbene [23] (Table 1).

3.5 Thermal stability

We studied Dyes 1 and 2 for their thermal stability at 60°C for various times and at 90°C for 3 hrs. in PMMA matrix. Thin films of poly(methyl methacrylate)(PMMA) doped with dyes 1 and 2 were prepared from a solution of polymer and the chalcone in chloroform (chalcone contents around 3%), then the mixture of the above two solutions was casted on glass substrates and dried at room temperature while protected from light. The absorption spectra were measured for nonannealed films (at room temperature), and annealed films at 60°C for various intervals of time, and 90°C for 3 hrs. (Figs. 1 and 2) . The purpose of heating the matrix is to get rid of the chloroform solvent from the film. Heating has quite obvious effect to the kinetics and relates to many mechanisms that also control the properties of the films. There is a fluctuation in absorbance with time i.e. decrease or increase. This behavior is either due to the molecule decomposition or the interface/phase of the matrix might be modified. Moreover, the fluxional process causes internal rotation in the ferrocene moiety and is similar to the process in ethane which may also cause the absorbance fluctuation [24]. We prefer the fluxional process as an explanation to this variation in absorbance since no new peaks are observed. The extents of degradation of dyes 1 and 2 on heating at different temperature of polymethyl metha acrylate thin films are summarized in Tables 3 and 4.

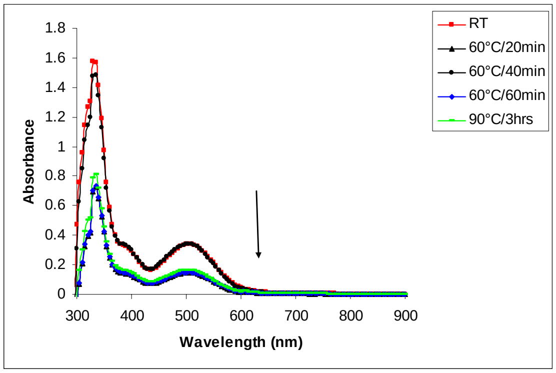


Fig. 1. Effect of annealing time and temperatures on Dye 1. The arrow direction indicates the decrease of absorbance with exposure annealing time and temperature.

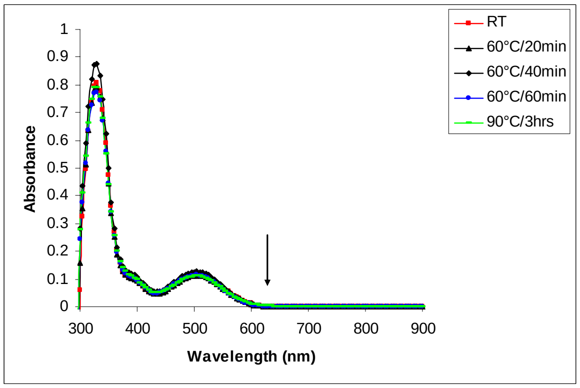


Fig. 2. Effect of annealing time and temperatures on Dye 2. The arrow direction indicates the decrease of absorbance with exposure annealing time and temperature.

Table 3. Extents of degradation of dye 1 at various temperatures and different intervals of time.

	λ_{max}	Degradation %
RT	505	0
60°C/20min	505	57.01
60°C/40min	505	0.41
60°C/60min	505	55.95
90°C/3hrs	503	52.13

Table 4. Extents of degradation of dye 2 at various temperatures and different intervals of time.

	λ_{max}	Degradation %
RT	510	0
60°C/20min	505	2.02
60°C/40min	505	-10.61
60°C/60min	505	0.17
90°C/3hrs	505	3.33

Fig. 6 and Fig. 7 show DTA-TG curves, recorded at heating rate of 10°C min^{-1} up to 800 °C in air for the thermal decomposition of compounds 1 and 2.

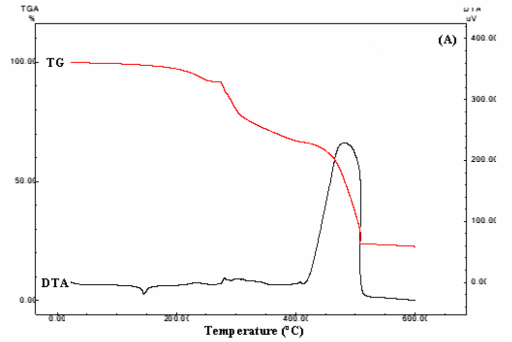


Fig. 6. DTA-TG curves at heating rate of 10 °C for dye (1).

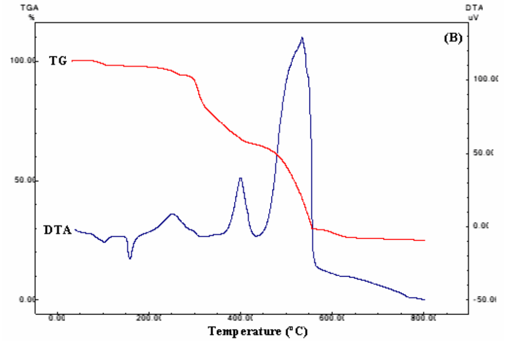


Fig. 7. DTA-TG curves at heating rate of 10 °C for dye (2).

The TG curves show that the compound 1 begins to decompose at about 200°C, while compound 2 starts to decompose at 70°C, showing a very small weight loss amounts to about 1.5 %. The TG curves also show that the pyrolytic decomposition for compounds 1 and 2 occurs through several steps and finished at 520 and 630°C, respectively, where a thermal stability for both compounds was obtained. The obtained weight losses for both compounds indicate the complete decomposition of the organic ligands with the formation of iron (III) oxide.

The DTA curves show peaks which are closely corresponding to the weight losses obtained in the TG curves. The decomposition in both compounds after 200°C, are obviously exothermic in nature. The compound 2 shows an endothermic DTA peak in the temperature range from 70 to 120°C which can be assigned to the evaporation of adsorbed water molecules. According to melting point measurements, the endothermic DTA peak appeared at 140 and 153°C for compounds 1 and 2, respectively, can be assigned to the melting of compounds.

3.6 Kinetics of the thermal decomposition of Ferrocene Dyes 1 and 2

From Fig. 3, it is clear that the rate constant of photocoloration reaction for dye 1 is somewhat higher than that for dye 2. Table 5 summarizes the values of rate constants and half-live of both dyes 1 and 2.

Table 5. Rate constants and half-time for thermal degradiation of Dyes 1 and 2 at 60 °C for different intervals of time.

	k (s^{-1})	$t_{1/2}$ (min)
Dye 1	6.0x10^{-4}	19.25
Dye 2	5.0x10^{-4}	23.11

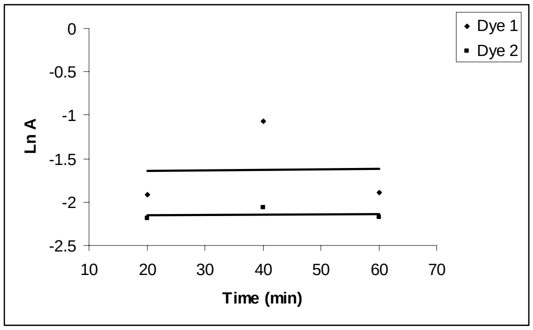


Fig. 3. First-order plot of Dyes 1 and 2 at 60 °C for different intervals of time.

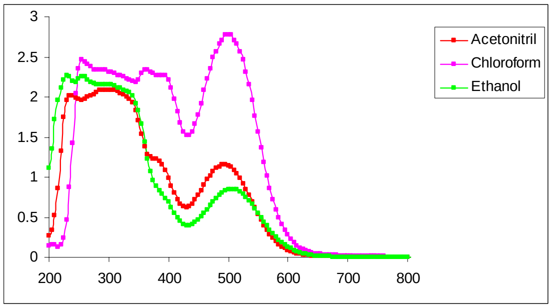


Fig. 4. Effect of solvent's polarity on absorbance of Dye 1.

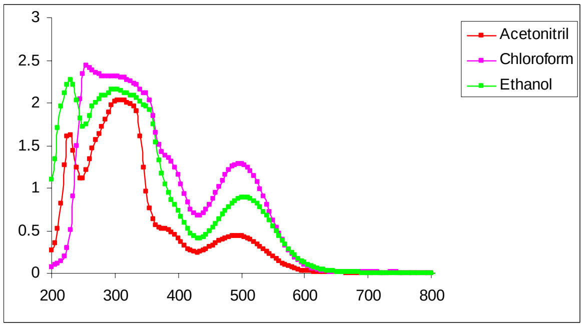


Fig. 5. Effect of solvent's polarity on absorbance of Dye 2.

4. Conclusions

It can be concluded that ferrocene derivative of different ketones are unique molecules for various applications owing to their blue shift and good thermal stability in different matrixes.

Acknowledgments

The authors thank King Abdul Aziz University for the financial support of this research.

References

[1] D. M. Burland, Chem. Rev. **94**, 1 (1994).
[2] D. S. Chemla, J. Zyss, Eds., Nonlinear Optical Properties of Organic molecules and Crystals, Academic Press, FL, USA (1987).
[3] D. J. Williams, Nonlinear Optical Properties of Organic and polymeric Materials, ACS Symposium Series 233, American Chemical Society, Washington, DC, (1985).
[4] J. Zyss, Ed., Molecular Nonlinear Optics, Materials, Physics and devices, Academic Press, San Diego, USA, (1994).
[5] A. M. Asiri, M. I. Iqbal, K. A. Al-Amry, N. A. Fatani, Dyes and Pigments **67**, 11 (2005).
[6] N. J. Long, Angew. Chem. Int. Ed. Engl. **34**, 2 (1995).
[7] S. Di Bella, Chem. Soc. Rev. **30**, 355 (2001).
[8] A. M. Asiri, Appl. Organomet. Chem. **15**, 907 (2001).
[9] A. M. Asiri, M. S. Al-Amoudi, Pigment & Resin Technology **35**, 270 (2006).
[10] M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, Nature (London) **330**, 360 (1987).
[11] V. Alain, M. Blanchard-Desce, C. T. Chen, S. R. Marder, A. Fort, M. Barzoukas, Synt. Met. **81**, 133 (1996).
[12] V. Alain, A. Fort, M. Barzuokas, C. T. Chen, M. Blanchard-Desce, S. R. Marder, J. W. Perry, Inorg. Chem. Acta **242**, 43 (1996).
[13] I. Janowska, J. Zakrzewski, K. Nakatani, J. Delaire, M. Palusiak, M. Walak, H. Scholl, J. Organomet. Chem. **675**, 35 (2006).
[14] S. Barlow, J. Am. Chem. Soc. **122**, 3715 (1999).
[15] J. A. Mata, J. Orgaomet. Chem. **562**, 197 (1998).
[16] J. C. Calobresse, T. C. Lap, C. G. Jennifer, S. R. Marder, T. Wilson, J. Am. Chem. Soc. **113**, 19, 7227 (1991).
[17] A. Houlton, J. R. Miller, J. Silver, N. Jassim, M. J. Ahmet, T. L. Axon, D. Bloor, G. H. Cross, Inorg. Chem. Acta. **205**, 67 (1993).
[18] J. S. Schumm, D. L. Pearson, J. M. Tour, Angew. Chem. Int. Ed. Engl. **33**, 1360 (1994).
[19] M. Kasha, H. R. Rawls, A. El-Bayyoumi, Pure Appl. Chem. **11**, 371 (1965).
[20] E. M. Koswer, Physical Organic Chemistry, Wiley, New York (1968).
[21] I. Furman, H. C. Geiger, D. G. Whitten, T. L. Penner, A. Ulman, Langmuir **10**, 837 (1994)..
[22] W. F. Mooney, D. G. Whitten, J. Am. Chem. Soc. **108**, 19, 571 (1986).
[23] M. E. Lippitsch, S. Draxler, E. Koller, Thin Solid Films 217, 161 (1992).
[24] D. F. Shriver, P. W. Atkins, Inorganic Chemistry, 3rd Ed., Oxford, 569 (1999).
[25] Z. Sekkat, W. Knoll, Photo reactive organic thin films, Academic Press, 184 (2002).
[26] K. D. Singer, J. E. Sohn, S. L. Lalama, Appl. Phys. Lett. **49**, 248 (1986).
[27] L. Chen, Q. Zhong, Y. Cui, G. Qian, M. Wang; Dyes and Pigments **76**, 195 (2008).
[28] J. Kabatac, B. Osmialowski, J. Paczkowski. Spectrochimica Acta Part A **63**, 524 (2006).
[29] X. Huang, S. Zhong, X. Yan, X. Ke, N. Srisanit, M. R. Wang, Synthetic Metals **140**, 79 (2004).
[30] M. S. Paley, J. M. Harris, J. Org. Chem. **54**, 3774 (1989).
[31] A. Immirzi, B. Perini, Acta Cryst. **A33**, 216 (1977).
[32] C. A. Van Walree, O. Franssen, A. W. Marsman, M. C. Flipse, L. W. Jenneskens, J. Chem. Soc., Perkin Trans. **2**, 799 (1997).
[33] C. Z. Zhang, J. Zhu, H. Yang, C. Lu, C-Y. Lu, Y. Cui; Dyes and Pigments **76**, 765 (2008).
[34] C. C. Frazier, M. A. Harvey, M. P. Cockerham, E. A. Chauchard, C. H. J. Lee, J. Phys. Chem. **90**, 5703 (1986).
[35] D. F. Eaton, A.G. Anderson, W. Tam, Y. Yang, J. Am. Chem. Soc. **133**, 1886 (1987).
[36] W. Tam, J. C. Calabrese, Chem. Phys. Letts. **133**, 244 (1987).
[37] M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, Nature **330**, 360 (1987).
[38] A. G. Anderson, J. C. Calabrese, W. Tam, I. D. Williams, Chem. Phys. Lett. **134**, 392 (1987).
[39] W. Tam, J. C. Calabrese, I. D. Williams, Y. Yang, A. G. Anderson, Chem. Mat. **1**, 128 (1989).
[40] S. Bradamante, A. Facchetti, G. A. Pagani, J. Phys. Org. Chem. **10**, 514 (1997).
[41] I. D. L. Albert, T. J. Marks, M. A. Ratner, *J.* Am. Chem. Soc. **119**, 6575 (1997).

[42] C. W. Dirk, H. E. Katz, M. L. Schilling, L. A. King, Chem. Mater. **2**, 700 (1990).
[43] K. Y. Wong, A. K.-Y. Jen, V. P. Rao, Phys. Rev. A **49**, 3077 (1994).
[44] A. B. P. Lever, Inorganic Electronic Spectroscopy, Second Ed., Elsevier, Amsterdam, 161 (1985).
[45] H. Tsubmora, R. Lang, J. Am. Chem. Soc. **86**, 3930 (1964).
[46] R. Rathone, S. V. Lindeman, J. K. Kochi, J. Am. Chem. Soc. **119**, 9393 (1997).

---

*Corresponding author: aasiri2@kau.edu.sa