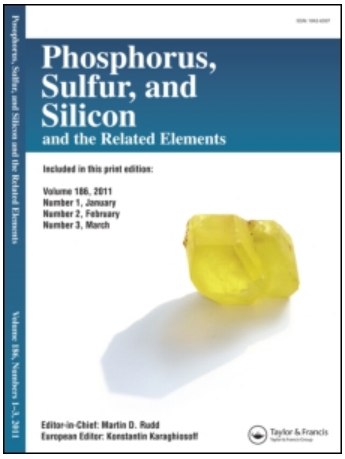

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Functionalized Phenothiazine and Carbazole Chromophores: Synthesis and Characterization

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To cite this Article Doskocz, Jacek , Sołoducho, Jadwiga , Cabaj, Joanna , Nowakowska, Anna and Roszak, Szczepan(2009) 'Functionalized Phenothiazine and Carbazole Chromophores: Synthesis and Characterization', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 5, 1257 — 1268
To link to this Article: DOI: 10.1080/10426500902856354
URL: http://dx.doi.org/10.1080/10426500902856354

Phosphorus, Sulfur, and Silicon, 184:1257–1268, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902856354

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Functionalized Phenothiazine and Carbazole Chromophores: Synthesis and Characterization

Jacek Doskocz,[1] Jadwiga Sołoducho,[1] Joanna Cabaj,[1] Anna Nowakowska,[1] and Szczepan Roszak[2]
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Synthesis, characterization, and photophysical properties for a few optical chromophores are reported. Phenothiazine and carbazole units played an important role to contribute high electron donability and connect the resonance pathway via conjugate effect in the cyclized ring besides the aromatic ring. Theoretical calculations and an absorption spectroscopic study gave useful information about the energy states and structures of chromophores.

Keywords Chalcone derivatives; LB technique; photoluminescence; theoretical study; Vilsmeier method

INTRODUCTION

Organic electronics, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), photovoltaic cells, and organic spintronics have progressed enormously in recent years in device fabrication as well as in the underlying chemistry, physics, and materials sciences.

It is well known that efficiencies of small molecule and polymeric OLEDs have reached close to their respective theoretical maxima, for

Received 8 January 2008; accepted 21 January 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

Financial support from the PBZ-KBN Grant No. 098/T09/2003/01 and financial support from the Wrocław University of Technology, Grant No 332093, is gratefully acknowledged. We would like also to thank the Wroclaw Centre for Networking and Supercomputing (WCSS) for the generous allocation of computer time.

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example external quantum efficiencies of >10% (photons/electrons) and luminous efficiencies of 200 lm/W.[1] However, still several problems need to be solved, such as carrier injection, interfaces, morphology, quenching of electroluminescence processes, theory, and modeling.

Phenothiazine and carbazole used in this study are electron donating groups that can facilitate the charge transport of the carrier. On the other hand, carbazole derivatives have attracted much attention in OLED device fabrication due to their fine hole transporting capability and high photochemical stability.[1]

Quite early it was recognized that the low oxidation potentials of this class of tricyclic nitrogen-sulfur heterocycles and their propensity to form stable radical cations play a key role in their physiological activities. More recently, due to their reversible oxidation mechanism, phenothiazine derivatives have become attractive motifs for supramolecular and materials science.[2]

Here we report the synthesis and the microscopic nonlinear optical properties of two different types of the heterocyclic chromophores. We can show that the electron rich phenothiazine and carbazole rings are excellent molecular building blocks for obtaining optical materials.

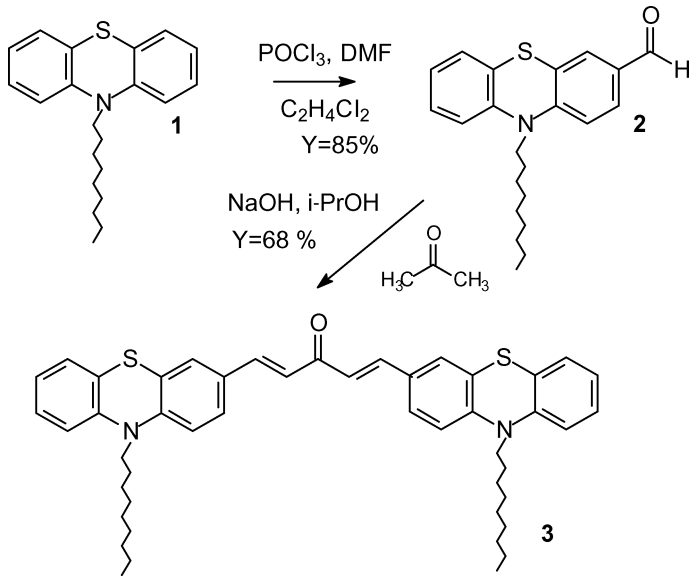
RESULTS AND DISCUSSION

Syntheses

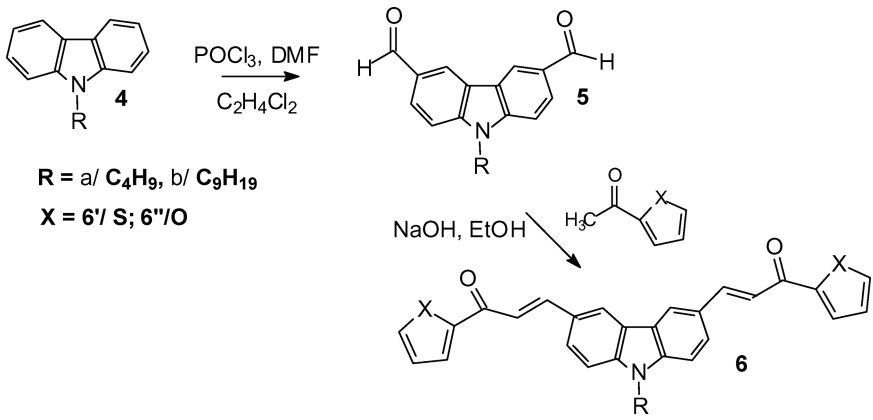
The synthetic procedure for chromophores is illustrated in Schemes 1 and 2. All chromophores were synthesized based on the heterocyclic donor units and contain an electron acceptor. Compound **1** was prepared by the alkylation of commercially available phenothiazine with alkyl bromide. Then, *N*−nonyl-3-formylphenothiazine (**2**) was synthesized via Vilsmeier formylation of compound **1**.[4] Finally, chalcone **3** was obtained by condensation of compound **2** with acetone. By the same method we synthesized *N*-alkyl-3,6-diformylcarbazoles (**5**, Scheme 2).

Based on the synthetic procedure for the phenothiazine chromophores, we followed a similar route to synthesize the carbazole-based derivatives. The synthetic procedure for preparation of derivatives based on carbazole compounds is illustrated in Scheme 2. Compounds **5** were prepared from *N*-alkylcarbazole (**4**) by Vilsmeier formylation.[4] *N*-alkyl- 3,6-bis(1′-oxy-3′-thiophene-2-propenyl)carbazole (**6′**) and *N*-alkyl-3,6-bis(1′-oxy-3′-furane-2-propenyl)carbazole (**6′a**) were obtained in good yield using the condensation of aldehydes (**5**) with acetothiophene or -furane derivatives.[5]

All the synthesized compounds were identified by ^{1}H NMR, ^{13}C NMR, and UV-Vis spectroscopy.



SCHEME 1



SCHEME 2

Optical Absorption and Fluorescence Properties of Materials Based on Phenothiazine and Carbazole

Some compounds that contain both electron-donor and electron-acceptor moieties exhibit intermolecular charge transfer absorbance and fluorescence behavior. In such donor–acceptor molecules (D–A),

very large changes in charge distribution can be induced in the excited state upon absorption of light photons. Recently these organic D–A compounds have been of increasing interest and have been used as fluorescent probe to study microenvironments. The microenvironments of the binding sites of these intermolecular charge transfer chalcones are expected to be complex in nature and should influence their photophysical properties. A series of substituted chalcones show strong intermolecular charge transfer behavior in various aprotic solvents.

The normalized absorption spectrum of **3** in solvents of different polarity is shown in Figure 1. The absorption spectrum of the phenothiazine derivative in different solvents undergoes a red shift with increasing polarity. This absorption band should be attributed to the charge transfer between the keto fragments and the phenothiazine *N*-alkyl units in the structure. Furthermore, charge transfer direction comes from the observed blue shift of the absorption maximum in strongly hydrogen bonding solvents (MeOH). Such behavior is consistent with the restriction of charge transfer process from phenothiazine *N*-alkyl group due to hydrogen bonding interactions between solvent molecules and the electrons on the donor group. Compound **3** is sensitive to solvent polarity due to intermolecular charge transfer.

Quantifying phenothiazine derivatives at very low limits of detection in the nanomolar range using fluorescence detection with simple and

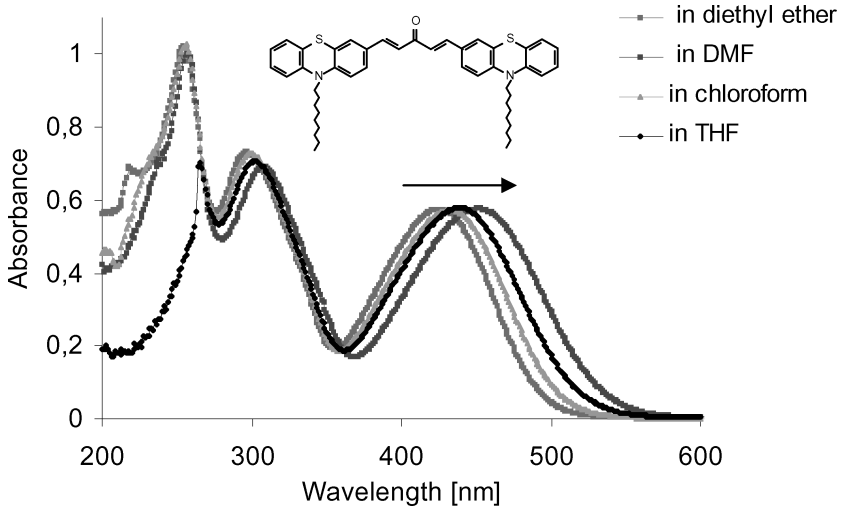


FIGURE 1 Normalized absorption spectrum of chalcone derivative **3** in various solvents ($c = 10^{-5}$ mol/dm^3). The arrow direction indicates increasing solvent polarity.

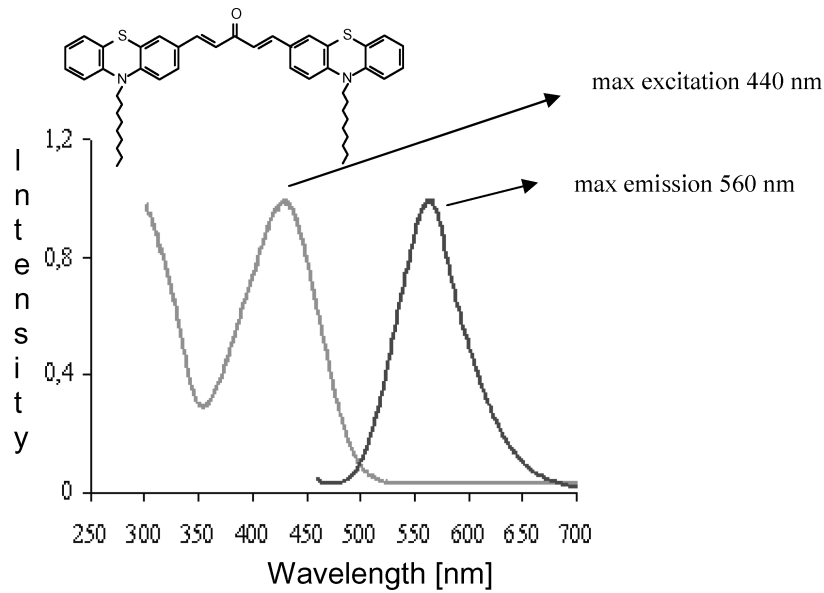


FIGURE 2 The fluorescence spectrum of compound **3**.

available instrumentation gives further possibilities to analyze real samples as blood or urine.[6]

The normalized photoluminescence (PL) emission-excitation spectra of phenothiazine monomer in diethyl ether $c = 10^{-5}$ mol/dm^3 are shown in Figure 2. The fluorescence spectra of **3** exhibit a broad and structured emission band with at least one distinct maximum and a pronounced shoulder. These relativity high values in the range near 560 nm are characteristic for conjugated phenothiazine derivatives and are due to a large structural difference between the non-excited ground state and corresponding excited state.[7] In this case of phenothiazine oligomers, the ground state is characterized by a prevalent aromatic structure, whereas the excited state has a predominant quinoidic character.

The fluorescence technique informs us about the form of occurring phenothiazine derivatives and their interactions with their surroundings. The almost planar phenothiazine ring is a good building block to obtained materials with fluorescence properties.

The fluorescence of the compound is connected with luminescence of the crystal—maximum of emission of yellow-green fluorescence is at 560 nm, maximum of excitation is at 440 nm. In case of solution with concentration near 10^{-5} M fluorescence is connected with monomers.

In accordance with the corresponding absorption properties, the emission behavior of compound **3** leads us to the conclusion that this material consist of largely conjugated systems, which are fully delocalized over the phenothiazine core.

Chalcone derivative of carbazole (**6″a**) is sensitive and decomposed under daylight; it probably is dimerized.

In summary, linear systems consisting of phenothizine units show characteristic bands. However, not all optical properties are enhanced in this manner, and it seems to be important to create a large fully π-conjugated system for maximizing quantum yields and overall absorptivity.

Theoretical Geometry Study of Phenothiazine and Carbazole Derivatives

Bis(thiophene)derivatives of phenothiazine have an almost planar, butterfly-like structure not dependent on chain length, which determines luminescence characteristics. From our previous experience and theoretical calculations,[7–9] we know that chalcone derivatives usually have planar structures, in opposition to bis(thiophene) phenothiazine derivatives.

One of the main results of the theoretical study was to find the isomer with the lowest energy. We also found, according to the Boltzmann method, that this isomer represents 77% of the population (Figure 3).

For structure **3**, we calculated the electronic spectra using the ZINDO method. This study revealed that $S_{0-} > S_1$state is at 349.9 nm (oscillator force $f = 1.5148$). This transition is mainly connected with the transition from the HOMO to the LUMO orbital (Figure 4).

Properties of Langmuir—Blodgett Films Built of Chalcone Derivative of Carbazole (6′b)

Traditionally, continuing our previous work connected with surface chemistry, we carried out a few LB experiments. The

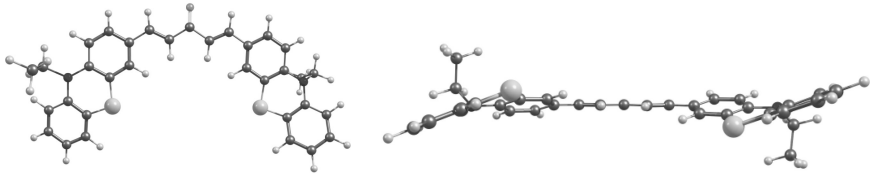


FIGURE 3 View of the structure of isomer **3**.

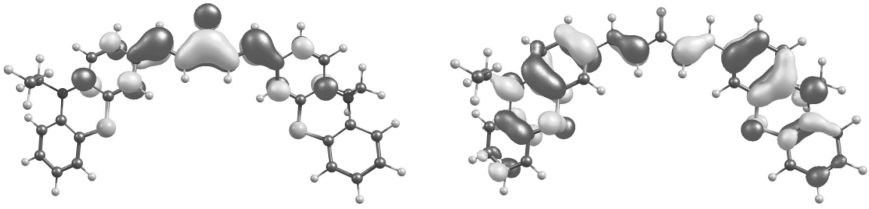


FIGURE 4 HOMO-LUMO orbitals of bis-1,5-(N-butyl-3-phenothiazine)-3-carbonyl-penta-1,4-diene.

chalcone derivative obtained—*N*-nonyl-3,6-bis(1′-oxy-3′-thiophene-2-propenyl)carbazole—was dissolved in an organic solvent (chloroform) and was spread on water; subsequently the organic layers were deposited by LB technique onto quartz substrate. All initially unmeasured under water, films were deposited at the velocity lower than the draining rate of film of carboxylic acids, i.e., 1.3 mm/min. After deposition, films were stored in vacuum desiccators prior to use.

The thermal properties of the films were evaluated by thermogravimetric analysis (TGA). TGA revealed that the onset decomposition temperature of the films under nitrogen was 360°C.

Langmuir monomolecular films of chalcone derivative **6′b** were spread from $CHCl_3$ solution on high purity water at room temperature. Langmuir–Blodgett deposition was carried out with a KSV System 5000 LB at a surface pressure of around 30 mN/m. The preparation of sample processing was carried out at ca. 23°C. The transference of LB film was of Y-type in first deposition and of Z-type in the following depositions. The relationship between absorbance and number of layers and constant transfer ratio during the deposition indicates the constant architecture of LB film layers. The absorption spectrum of chalcone derivative deposited film confirms also the formation of homogenous films in good yield (Figure 5).

LB film built of *N*-nonyl-3,6-bis(1′-oxy-3′-thiophene-2-propenyl) carbazole (15 layers) after 15 min exposure at 294 nm (UV lamp) is characterized by a lower absorbance value (Figure 4). It can be observed also by a small shift to longer wavelengths; this fact is probably connected with the formation of dimers on the surface of the LB substrate.

The UV-VIS absorption spectra of the LB film (Figure 5) showed maximum absorption corresponding to the π-π^* transition with charge transfer character at 420 nm.

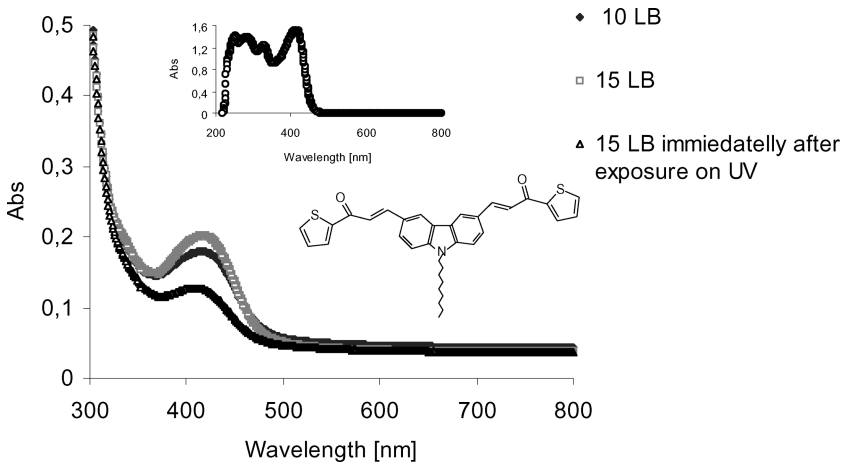


FIGURE 5 Absorption spectrum of LB films obtained from *N*-nonyl-3,6-bis(1′-oxy-3′-thiophene-2-propenyl)carbazole, the spectrum of a chloroform solution of *N*-nonyl-3,6-bis(1′-oxy-3′-thiophene-2-propenyl)carbazole is shown as a kink in the figure.

CONCLUSION

We successfully synthesized phenothiazine- and carbazole-based chromophores and investigated their potential for optical application. The films of the compounds showed good thermal stability and good temporal stability. In addition, the chalcones obtained have good optical absorption properties in the UV spectral region, ensuring efficient light absorption from most UV-curing tools. Additionally, the maximum luminescence was 560 nm (emission). All these properties suggest that phenothiazine and carbazole chalcones may be used in a variety of practical optical applications.

EXPERIMENTAL

Commercially available reagents were used without further purification unless otherwise started. All reactions were monitored by thin-layer chromatography (TLC) with Merck precoated glass plates. Compounds were visualized with UV-light irradiation at 254 and 365 nm. NMR spectra were measured in appropriate deuterated solvents with a Bruker 300 spectrometer. For ^{1}H and ^{13}C NMR data, chemical shifts are quoted relative to the internal standard tetramethylsilane. Melting points were determined with a melting points measurement instrument. Fluorescence spectra were recorded with a Hitachi F-4500

fluorescence spectrophotometer at room temperature. UV-Vis spectra were measured with a CARY BIO VARIAN 100 instrument.

N-Nonyl-3-formylphenothiazine (2)

To a round-bottom flask equipped with a condenser and a magnetic stirring bar, dimethylformamide (1.50 g, 20.0 mmol) in 50 mL of dichloroethane was added. Keeping the temperature at 0°C, phosphorus oxychloride (3.10 g, 20 mmol) was added dropwise. To this Vilsmeier reagent after 30 min, a solution of *N*-nonylphenothiazine (5.0 g, 15.4 mmol) in dichloroethane (15 mL) was added. The mixture was stirred for 48 h at 85–95°C. Subsequently the mixture was cooled to room temperature, the organic layer was separated, and the water layer was extracted three times with ethyl acetate. The combined organic extracts were washed with an aqueous solution of $NaHCO_3$ and with water and then dried over $MgSO_4$. The crude product was purified by silica gel column chromatography using ethyl acetate:hexane (1:2 v/v) as eluent; green oil, (6.0 g, 85%). ^{1}H NMR ($CDCl_3$): $\delta = 9.77$ (s, 1H, -C(=O)H), 7.58 (dd, $J = 8.4$ Hz, $J = 2.1$ Hz, 1H), 7.30 (br. d, $J = 1.8$ Hz, 1H), 7.16–7.05 (m, 2H), 6.95–6.90 (m, 1H), 6.86–6.83 (m, 2H), 3.91 (t, $J = 7.0$ Hz, 2H), 1.85 (dd, $J = 7.2$ Hz, $J = 7.0$ Hz, 2H), 1.50–1.47 (m, 2H), 1.39–1.35 (m, 10H), 0.98 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 189.9$, 152.1, 145.1, 132.0, 130.0, 128.4, 127.5, 123.5, 115.9, 114.8, 51.3, 32.1, 29.7, 29.5, 29.4, 28.3, 27.0, 26.9, 22.8. Anal. Calcd. for $C_{22}H_{27}NOS$: C, 74.74; H, 7.70; N, 3.96. Found: C, 74.55; H, 7.59; N, 3.75%.

Bis-1,5-(*N*-nonyl-3-phenothiazine)-3-carbonyl-penta-1,4-diene (3)

To a solution of sodium hydroxide (1.10 g, 28 mmol) in isopropanole (30 mL), *N*-nonyl-3-formylphenothiazine (1.9 g, 2.8 mmol) and acetone (0.16 g, 2.7 mmol) were added. The reaction mixture was stirred for 12 h at room temperature; during this time the color of the mixture changed from dark green to red. Subsequently the reaction mixture was cooled with ice, the organic layer was separated, and the water layer was extracted three times with ethyl acetate. The combined organic extracts were washed with water and then dried over $MgSO_4$. The crude product was purified by silica gel column chromatography using toluene:chloroform (3:1 v/v) as eluent; red oil, (68%, 0.7 g); ^{1}H NMR ($CDCl_3$): δ =7.57 (d, $J = 15.8$ Hz, 2H), 7.34 (br. s, 2H), 7.32 (br. d, $J = 7.1$ Hz, 2H), 7.13 (br. dd, $J = 7.0$ Hz,$J = 5.9$ Hz, 2H), 7.09 (br. d, $J = 8.1$ Hz, 2H), 6.90 (dd, $J = 7.2$ Hz, $J = 7.0$ Hz, 2H), 6.88 (d, $J = 15.9$ Hz, 2H), 6.86

(d, $J = 8.5$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 3.82 (t, $J = 7.0$ Hz, 4H), 1.78 (tt, $J = 7.2$ Hz, $J = 7.0$ Hz, 4H), 1.50–1.47 (m, 4H), 1.39–1.35 (m, 20H), 0.83 (t, $J = 6.4$ Hz, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 189.5$, 149.1, 147.2, 144.1, 141.8, 129.1, 128.5, 127.4, 126.5, 125.0, 123.8, 123.5, 122.8, 115.5, 115.2, 47.7, 31.7, 29.4, 29.1, 26.7, 22.6. Anal. Calcd. for $C_{47}H_{56}N_2OS_2$: C, 77.43; H, 7.74; N, 3.84. Found: C, 77.28; H, 7.59; N, 3.75%.

N-Alkyl-3,6-diformylcarbazoles (5): General Procedure

To a round-bottom flask equipped with a condenser and a magnetic stirring bar, dimethylformamide (15.0 g, 200.0 mmol) in 120 mL of dichloroethane was added. Keeping the temperature at 0°C, phosphorus oxychloride (31.0 g, 200 mmol) was added dropwise. To this Vilsmeier reagent after 40 min, a solution of *N*-butylcarbazole (8.90 g, 40 mmol) in dichloroethane (30 mL) was added. The mixture was stirred for 75 h at the temperature 95–105°C. Subsequently the mixture was cooled to room temperature, the organic layer was separated, and the water layer was extracted three times with ethyl acetate. The combined organic extracts were washed with an aqueous solution of $NaHCO_3$ and with water and then dried over $MgSO_4$. The crude product was recrystallized from ethyl alcohol.

5a: An ivory colored powder of the product was isolated with a yield of 78% (8.70 g), mp 150–153°C (lit. 153–156°C).[3] ^{1}H NMR ($CDCl_3$): $\delta = 10.1$ (s, 2H, CHO), 8.63 (d, $J = 1.2$ Hz, 2H, arom-H), 8.05 (dd, $J = 8.5$ Hz, $J = 1.3$ Hz, 2H, arom-H), 7.51 (d, $J = 8.6$ Hz, 2H, arom-H), 4.36 (t, $J = 7.2$ Hz, 2H, CH_2), 1.90 (q, $J = 7.3$ Hz, 2H, CH_2), 1.47–1.35 (m, 2H, CH_2), 0.96 (t, $J = 6.5$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 191.3$, 144.8, 129.7, 127.8, 124.2, 123.2, 109.7, 43.5, 31.0, 20.4, 13.7. Anal. Calcd. For $C_{18}H_{17}NO_2$: C, 74.74; H, 7.70; N, 3.96. Found: C, 74.55; H, 7.59; N, 3.75%.

5b: Cream powder, 81% (5.4 g), mp 130°C; ^{1}H NMR ($CDCl_3$): $\delta = 10.10$ (s, 2H), 8.62 (d, $J = 1.3$ Hz, 2H), 8.05 (dd, $J = 8.6$ Hz, $J = 1.6$ Hz, 2H), 7.51 (d, $J = 8.6$ Hz, 2H), 4.34 (t, $J = 7.3$ Hz, 2H), 1.87 (q, $J = 7.2$ Hz, 2H), 1.32–1.20 (m, 12H), 0.82 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 191.5$, 144.7, 129.6, 127.8, 124.2, 123.1, 109.7, 43.8, 31.2, 29.3, 29.2, 29.1, 28.9, 27.2, 22.6, 14.0. Anal. Calcd. for $C_{23}H_{27}NO_2$: C, 79.05; H, 7.79; N, 4.01. Found: C, 78.95; H, 7.59; N, 3.85%.

N-Alkyl-3,6-bis(1′-oxy-3′-thiophene-2-propenyl)carbazoles (6′): General Procedure

To a solution of sodium hydroxide (2.20 g, 56 mmol) in ethanol (30 mL), *N*-butyl-3,6-diformylcarbazole (1.40 g, 5.0 mmol) and acetothiophene

(0.76 g, 5.5 mmol) were added. The reaction mixture was stirred for 20 h at room temperature; during this time the color of mixture changed from cream to intensive yellow. The product was filtered, washed with ethanol, and recrystallized from ethanol.

6′a: Yellow powder, 78% (1.70 g), mp 136°C; ^{1}H NMR ($CDCl_3$): δ =8.40 (s, 2H), 8.07 (d, J = 15.5 Hz, 2H, arom-H), 7.91 (d, J = 3.4 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 4.8 Hz, 2H), 7.48 (d, J = 15.4 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H) 7.21–18 (m, 2H), 4.29 (t, J = 7.1 Hz, 2H, CH_2), 1.86–1.83 (m, 2H, CH_2), 1.47–1.21 (m, 2H, CH_2), 0.82 (t, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 182.2, 145,2, 133.5, 131.4, 128.2, 127.1, 126.6, 121.4, 119.1, 109.6, 43.5, 31.7, 29.3, 29.1, 29.0, 27.3, 22.6, 14.1. Anal. Calcd. for $C_{30}H_{25}NO_2S_2$: C, 72.70; H,5.08; N,2.83. Found: C, 72.52; H, 4.89; N, 2.75%.

6′b: Yellow powder, mp 165°C, yield 95% (3.08 g); ^{1}H NMR ($CDCl_3$): δ = 8.32 (s, 2H); 8.02 (d, J = 15.4 Hz, 2H); 7.90 (dd, J = 3.0 Hz,J = 0.8 Hz, 2H); 7.72 (d, J = 8.6 Hz, 2H); 7.64 (d, J = 4.9 Hz, 2H); 7.45 (d, J = 15.4 Hz, 2H); 7.35 (d, J = 8.5 Hz, 2H); 7.18–7.15 (m, 2H); 4.22 (t, J = 7,1 Hz, 2H); 1.83–1.80 (m, 2H); 1.30–120 (m, 12H); 0.83 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 182.0, 145.9, 145.1, 142.4, 133.4, 131.5, 128.2, 127.1, 126.5, 123.2, 121.4, 119.0, 109.5, 43.5, 31.7, 29.4, 29.3, 29.2, 28.9, 27.2, 22.6, 14.1; Anal. Calcd. for $C_{35}H_{35}NO_2S_2$: C, 74.30; H, 6.24; N, 2.48. Found: C, 74.25; H, 6.09; N, 2.25%.

N-Butyl-3,6-bis(1′-oxy-3′-furane-2-propenyl)carbazole (6″a)

To a solution of sodium hydroxide (2.20 g, 56 mmol) in ethanole (30 mL) was added *N*-butyl-3,6-diformylcarbazole (1.40 g, 5.0 mmol) and acetofurane (0.69 g, 5.5 mmol). The reaction mixture was stirred for 20 h at room temperature; during this time the color of the reaction mixture changed from cream to intensive yellow. The product was filtered, washed with ethanol, and recrystallized from ethanol; Yellow-orange crystals, 41%, (0.95 g), mp 120°C. ^{1}H NMR ($CDCl_3$): δ = 8.36 (s, 2H), 8.05 (d, J = 15.7 Hz, 2H, arom-H), 7.74 (d, J = 8.4 Hz, 2H), 7.65 (s, 2H), 7.50 (d, J = 15.7 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.35 (br. s, 2H), 6.59 (d, J = 1.6 Hz, 2H), 4.24 (t, J = 7.2 Hz, 2H, CH_2), 1.83 (q, J = 7.3 Hz, 2H, CH_2), 1.47–1.35 (m, 2H, CH_2), 0.82 (t, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 178.1, 154.0, 146.2, 145.0, 142.4, 127.3, 126.6, 123.3, 121.4, 118.6, 117.0, 112.5, 109.5, 43.5, 31.7, 29.25, 29.0, 28.9, 27.2, 22.5, 14.0. Anal. Calcd. for $C_{30}H_{25}NO_4$: C, 77.73; H, 5.44; N, 3.02. Found: C, 77.55; H, 5.26; N, 2.85%.

REFERENCES

[1] Z. V. Vardeny, A. J. Heeger, and A. Dodabalapur, *Synth. Met.*, **148,** 1 (2005).
[2] C. S. Kramer, K. Zeitler, and T. J. Muller, *J. Org. Lett*., **2,** 3723 (2000).
[3] L. Su, C. Bao, R. Lu, Y. Chen, T. Xu, D. Song, C. Tan, T. Shi, and Y. Zhao, *Org. Biomol. Chem*., **4,** 2591 (2006).
[4] Y. Liu, C. Di. Y. Xin, G. Yu, Y. Liu, Q. He, F. Bai, S. Xu, and S. Cao, *Synth. Met.,* **156,** 824 (2006).
[5] N. R. El-Rayyes, *J. Heterocycl. Chem.*, **19,** 415 (1982).
[6] H. Hayen and U. Karst, *Anal. Chem*., **75,** 4833 (2003).
[7] J. Doskocz, J. Sołoducho, J. Cabaj, M. Łapkowski, S. Golba, and K. Palewska, *Electroanalysis*, **19,** 1394 (2007).
[8] J. Sołoducho, J. Doskocz, J. Cabaj, and S. Roszak, *Tetrahedron*, **59,** 4761 (2003).
[9] J. Doskocz, M. Doskocz, S. Roszak, J. Sołoducho, and J. Leszczynski, *J. Phys. Chem. A*, **110,** 1398 (2006).