Synthesis and study of 2-alkoxy(2-alkylsulfanyl)-4,6-distyrylpyrimidines containing a terminal carbazole group

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We report the synthesis of new 4,6-distyrylpyrimidines containing an unsubstituted carbazole ring linked with the pyrimidine moiety by a flexible aliphatic seven-membered $-O(CH_2)_6$ - or $-S(CH_2)_6$ - bridge. The electrochemical and spectral properties of the synthesized compounds were studied; optical band gaps were calculated from the relevant UV absorption onsets and were found to be equal to 2.55 and 2.54 eV, respectively. A thin film based on the derivative with sulfur-containing bridge ($-S(CH_2)_6$ -) was deposited on a conductive material and demonstrated to have a smooth surface and hole conductivity.

Keywords: carbazole, pyrimidine, styrylpyrimidines, solvatochromic effect, thin films.

Small molecules, oligomers, and polymers with conjugated systems containing various electron-donating and electron-withdrawing heterocycles have been widely used over the last 20 years as materials for designing organic electronic devices. Such structures serve as the basis for creating organic light emitting diodes (OLED), organic field-effect transistors (OFET), photovoltaic cells, luminescence sensors, as well as nonlinear optical devices.^{1–5} Substituted pyrimidine is one of the important electronwithdrawing building blocks used in the synthesis of conjugated structures. For example, halo-substituted pyrimidines have been used as starting compounds in crosscoupling reactions,^{6–8} while the condensation of aromatic heteroaromatic aldehydes and with monoand dimethylpyrimidines was used for the preparation of substituted vinylpyrimidines.⁹⁻¹² At the same time, one of the most important electron-donating heterocycles used as structural moieties in mixed donor-acceptor systems is carbazole. Derivatives of carbazole and also di- and polycarbazoles possess hole conductivity with high carrier

mobility, enabling the use of these compounds as hole transport layers in organic electronic devices. Carbazole derivatives have high thermal and photochemical stability and are stable emitters of blue light. The molecule of carbazole can be easily modified at positions 3, 6, and 9, providing ways to design compounds with a wide range of electrophysical and optical properties.^{13,14}

Previously we have synthesized and described pyrimidine derivatives containing carbazole, thiophene, *N*-phenylcarbazole, and ferrocene moieties (Fig. 1).^{15–18} Pyrimidines bearing carbazole rings with unsubstituted 3C and 6C positions were found to undergo electrochemical polymerization, forming a polymer film on the surface of electrodes.

We have synthesized new pyrimidine derivatives in which the unsubstituted carbazole ring is linked to 4,6-distyrylpyrimidine by a flexible aliphatic $-O(CH_2)_6$ - bridge (compound 1) or $-S(CH_2)_6$ - bridge (compound 2, Scheme 1). In the first step, the π -conjugated pyrimidines 3, 4 were obtained by condensation of 2-hydroxy(mercapto)-4,6-dimethylpyrimidines 6, 7 with a twofold excess of *p*-tolyl-



Figure 1. Examples of the synthesized Y-shaped pyrimidine structures.

Scheme 1



aldehyde in ethanol in the presence of concd. HCl, followed by the treatment with aqueous alcohol solution of K₂CO₃. The necessary starting material 9-(6-bromohexyl)-9H-carbazole (5) was obtained by N-alkylation of carbazole with excess of 1.6-dibromohexane, using a phase-transfer catalyst.¹⁹ The next step involved an interaction of 9-(bromohexyl)carbazole 5 with 2-hydroxy(mercapto)-4,6disubstituted pyrimidines 3, 4 in DMF in the presence of K₂CO₃, providing the target products, N-substituted carbazoles 1, 2, which were isolated and purified by silica gel column chromatography (eluent CH₂Cl₂). The heterocycles 1, 2 were isolated as light-yellow powders, soluble in chloroform, dichloromethane, acetone, toluene, DMF, and ethyl acetate, but insoluble in hexane, ethanol, and acetonitrile. These compounds can be used as monomers for chemical polymerization initiated by anhydrous ferric chloride²⁰ and for electrochemical polymerization as well.

The electronic absorption spectra of compounds 1, 2 (Fig. 2a,b) were complicated due to the structural features of these compounds, because the long and flexible sevenmembered aliphatic linker in these molecules enables both intramolecular and intermolecular interactions between the terminal electron-donating carbazole moiety and the electron-withdrawing pyrimidine ring. The existence of such interactions affects the character of conjugation, leading to redistribution of electron density within the molecule, manifested in the optical spectra of these compounds. It was observed from the absorption spectra of pyrimidine 1 that changing from a less polar solvent (CHCl₃) to a more polar solvent (EtOAc or DMF) resulted in hypsochromic shift of absorption band maxima (Fig. 2a, Table 1), i.e., produced the effect known as negative solvatochromism. $^{21,22}\,$

Based on the long wavelength absorption edge (λ_{onset}^{abs}) for compounds **1**, **2**, we calculated the band gap values (E_g), which were 2.55 and 2.54 eV, respectively. These values are close to the E_g values of such known organic semiconductors as poly(*p*-phenylene vinylene) (PPV) and poly(*p*-phenylene) (PPP), - 2.4 and 3.0 eV, respectively.²³ Emission band shifts dependent on the solvent polarity were also observed in the fluorescence spectra (Fig. 3*a*,*b*).

Cyclic voltammetry experiments showed that during the first scan cycle of a potential sweep the formation of the radical cations took place at 1.5 V due to oxidation of carbazole moieties of compounds **1**, **2** (Fig. 4*a*,*b*). According to the proposed polymerization mechanisms,^{24,25} the most likely next step was dimerization at the carbazole ring positions 3 or 6. A decrease of current and smoothing of oxidation peaks were observed during the further repetitive voltage cycling, pointing to the absence of additional polymerization processes.

A conductive thin film was prepared from compound **2** by the spin coating method, and its structure was studied by scanning tunneling microscopy (STM).

Images of the obtained film are presented in Figure 5, showing that the molecules tend to form macrostructures with the average size of 200 nm. The voltammetric properties of the obtained film are shown in Figure 6, indicating that this film has hole conductivity, which is higher during the reverse voltage scan.

Thus, we have synthesized 2-alkoxy(alkylsulfanyl)-4,6distyrylpyrimidines containing a terminal carbazole moiety. The study of optical properties of the synthesized

Table 1.	The	optical	characteristics	of compour	1ds 1,	2 in	solutions
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Compound	Solution	λ_{\max}^{abs} , nm	$\lambda_{onset}{}^{abs},nm$	λ_{max}^{em} , nm	$\Delta v^*, \operatorname{cm}^{-1}(\operatorname{nm})$
1	DMF	295, 347, 364, 381 **	408	440	3520 (59)
	Acetone	344, 361, 378	403	418	2532 (40)
	EtOAc	263, 293, 345, 360, 378, 403	475	495	4611 (92)
	CHCl ₃	249, 265, 295, 347, 368, 415	485	485	3478 (70)
	CH_2Cl_2	298, 346, 363, 379, 413	476	430	958 (17)
2	DMF	295, 323, 373, 392	415	440	2783 (48)
	Acetone	333, 345, 370, 388	412	430	2518 (42)
	EtOAc	328, 345, 369, 388	480	482	5027 (94)
	CHCl ₃	266, 295, 346, 375, 396, 420, 436	487	493	2652 (57)
	CH_2Cl_2	330, 346, 371, 390	460	435	2653 (45)

* Stokes shift.

** The absorption band maxima used for the calculation of Stokes shift are marked with semibold font.



Figure 2. Electronic absorption spectra of compounds 1 (a) and 2 (b) in various solvents.

compounds showed a negative solvatochromic effect. The band gap values were determined experimentally. It was shown that dimerization of the carbazole moiety occurred under the conditions of cyclic voltammetry without further polymerization, thus no polymer film formation was observed on the surface of the ITO electrode. The synthesized compounds were found to have good film-forming properties. A thin film of 2-[6-(9*H*-carbazol-9-yl)hexylsulfanyl]-4,6di[2-(4-methylphenyl)ethenyl]pyrimidine was obtained. The investigation of this film has highlighted the homogeneity of its surface and the hole type of conductivity.

Experimental

IR spectra were recorded on a Specord 751R spectrophotometer in KBr pellets. UV spectra were recorded on a Shimadzu UV-2600 UV-VIS spectrophotometer, the concentration of solutions was 10^{-4} mol/l. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer (excitation wavelength 220 nm, cuvette size 10×10 mm, the concentration of solutions was 10^{-3} mol/l). ¹H and ¹³C NMR spectra were acquired on a Varian Mercury Plus 300 MHz spectrometer (300 and



Figure 3. The fluorescence spectra of compounds 1 (a) and 2 (b) in various solvents.



Figure 4. Cyclic voltammograms (10 cycles) of compounds 1 (a) and 2 (b) (indium tin oxide electrode, $Et_4N^+ClO_4^-$, V_{scan} 50 mV/s).



Figure 5. 2D-STM image $(1 \times 1 \ \mu m)$ of the compound 2 thin film.

75 MHz, respectively) in CDCl₃ (compounds 1, 2) or DMSO- d_6 (compound 4), internal standard HMDS (0.04 ppm). Elemental analysis was performed on a LECO CHNS-932 elemental analyzer. The reaction progress and purity of the obtained compounds were controlled by TLC on Sorbfil PTSH-AF-A plates. The target products were purified by silica gel column chromatography (Lancaster, Silica gel 60, 0.060–0.200 mm). Commercially available *p*-tolyl aldehyde, 1,6-dibromohexane, and solvents were used (Alfa Aesar). Compounds 3^{26} , 6^{26} , and 5^{19} were obtained and described by us previously.

Electrochemical measurements were performed in MeCN solution, background electrolyte $Et_4N^+ClO_4^-$, scan rate 50 mV/s, by using a Gamry Interface 1000 Potentiostat/Galvanostat/ZRA equipped with a three-electrode cell: a silver chloride reference electrode (EVL-1M4), a platinum wire auxiliary electrode, and the working electrode – a plate coated with a layer of ITO (R_s 8–12 Sigma-Aldrich).

The coating of thin film was performed in an airtight PlasLabs nitrogen glove box under argon atmosphere with a SPIN 12000 spin coater. The structure of film surface was studied on an NTEGRA Prima scanning probe tunneling microscope. The obtained data were processed with the NOVA 1.0.26 software.



Figure 6. Voltammetric characterization of thin film of compound 2.

2-Mercapto-4,6-di(2-(4-methylphenyl)ethenyl)pyrimidine (4).²⁶ Concd. HCl (7.5 ml) was added to a mixture of 2-mercapto-4,6-dimethylpyrimidine hydrochloride (7)(6.02 g, 37.5 mmol) and *p*-tolylaldehyde (8.84 ml, 75.0 mmol) in EtOH (100 ml). The reaction mixture was refluxed for 5 h, cooled, the obtained precipitate of bright-red hydrochloride of compound 4 was filtered off and washed with acetone. In order to convert the salt to free base, the obtained brightred precipitate was treated with 10% solution of K₂CO₃ in aqueous alcohol. The obtained yellow precipitate was filtered off and air-dried. Yield 10.90 g (85%), yellow powder, mp >250°C. IR spectrum, v, cm⁻¹: 3455, 3148, 3020, 1628, 1590, 1453, 1212. ¹H NMR spectrum, δ, ppm (J, Hz): 3.42 (6H, s, 2CH₃); 4.27 (1H, s, SH); 7.00 (2H, d, J = 15.6) and 7.46 (2H, d, J = 15.6, 2CH = CH - Ar); 7.15 (4H, d, *J* = 8.1, H Ar); 7.30 (1H, s, H-5); 7.49 (4H, d, *J* = 8.1, H Ar). Found, %: C 76.60; H 5.79; N 8.02; S 9.16. C₂₂H₂₀N₂S. Calculated, %: C 76.71; H 5.85; N 8.13; S 9.31.

Synthesis of pyrimidines 1, 2 (General method). 9-(6-Bromohexyl)-9*H*-carbazole (5) (11.0 g, 7 mmol) and K_2CO_3 (9.6 g, 70 mmol) were added to a solution of 2-hydroxy- (3) or 2-mercapto-4,6-di(2-(4-methylphenyl)ethenyl)pyrimidine (4) (7 mmol) in DMF (100 ml). The reaction mixture was refluxed for 6 h, then cooled to room temperature, poured on crushed ice, the precipitate that formed was filtered off, air-dried, and purified by column chromatography (eluent CH_2Cl_2).

2-(6-(9H-Carbazol-9-yl)hexyloxy)-4,6-di(2-(4-methylphenyl)ethenyl)pyrimidine (1). Yield 2.8 g (70%), light-yellow powder, mp 84–85°C. ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.24-1.43 (2H, m, CH₂CH₂CH₂N); 1.49-1.65 (2H, m, OCH₂CH₂CH₂); 1.90–1.97 (2H, m, CH₂CH₂N); 2.10–2.16 (2H, m, OCH₂CH₂); 2.37 (6H, s, 2CH₃); 4.21 (2H, t, J = 6.9, CH₂N); 4.45 (2H, t, J = 7.2, OCH₂); 6.96 (2H, d, J = 15.9) and 7.47 (2H, d, J = 15.3, 2CH=CH); 6.99 (1H, s, H-5); 7.18-7.21 (6H, m, H-3,6 carbazole, H-3,3',5,5' Ar); 7.26-7.29 (4H, m, H-2,2',6,6' Ar); 7.49-7.53 (2H, m, H-2,7 carbazole); 7.83-7.88 (2H, m, H-1,8 carbazole); 8.09 (2H, d, J = 7.8, H-4,5 carbazole). ¹³C NMR spectrum, δ , ppm: 21.3; 23.7; 25.8; 26.8; 29.6; 38.7; 42.7; 66.7; 108.7; 110.9; 118.7; 120.3; 122.8; 124.8; 125.6; 127.6; 129.5; 133.0; 136.7; 139.4; 140.4; 165.1. Found, %: C 83.04; H 6.74; N 7.16. C₄₀H₃₉N₃O. Calculated, %: C 83.15; H 6.80; N 7.27.

2-(6-(9H-Carbazol-9-yl)hexylsulfanyl)-4,6-di(2-(4-methylphenyl)ethenyl)pyrimidine (2). Yield 3.1 g (75%), light-yellow powder, mp 150–151°C. ¹H NMR spectrum, δ, ppm (J, Hz): 1.24–1.32 (2H, m, CH₂CH₂CH₂N); 1.53– 1.59 (2H, m, SCH₂CH₂CH₂); 1.88–1.97 (2H, m, CH₂CH₂N); 2.07-2.16 (2H, m, SCH₂CH₂); 2.37 (6H, s, 2CH₃); 3.29 $(2H, t, J = 6.9, SCH_2); 4.38 (2H, t, J = 7.2, J = 6.9, CH_2N);$ 6.95 (2H, d, *J* = 15.6) and 7.85 (2H, d, *J* = 15.9, 2CH=CH); 6.98 (1H, s, H-5); 7.17-7.23 (6H, m, H-3,6 carbazole, H-3,3',5,5' Ar); 7.40-7.41 (4H, m, H-2,2',6,6' Ar); 7.44-7.53 (4H, m, H-1,2,7,8 carbazole); 8.09 (2H, d, J = 8.1, H-4,5 carbazole). ¹³C NMR spectrum, δ, ppm: 21.3; 23.8; 27.1; 28.1; 30.4; 35.5; 42.5; 108.5; 111.8; 118.7; 120.2; 122.7; 124.6; 125.6; 127.5; 129.5; 132.9; 136.8; 139.4; 140.2; 162.8; 171.1. Found, %: C 80.79; H 6.56; N 6.97; S 5.25. C₄₀H₃₉N₃S. Calculated, %: C 80.90; H 6.62; N 7.08; S 5.40.

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