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Preparation and Properties of Poly[9-hexadecyl-3-phenyl-6-(4-vinylphenyl)-9*H*-carbazole]

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Abstract—Preparation of new carbazole-containing polymer, poly[9-hexadecyl-3-phenyl-6-(4-vinylphenyl)-9*H*-carbazole], is reported. The optical properties of the product have been studied in comparison with those of the starting compounds. Electrochemical properties of the polymer solution and its thin film have been investigated. The polymer film images were obtained by atomic force and scanning tunneling microscopy. Thermogravimetric analysis has shown high thermal stability of the obtained polymer.

Keywords: carbazole, Gilch reaction, poly(phenylenevinylene), electrochemical oxidation, thermogravimetry, thin film

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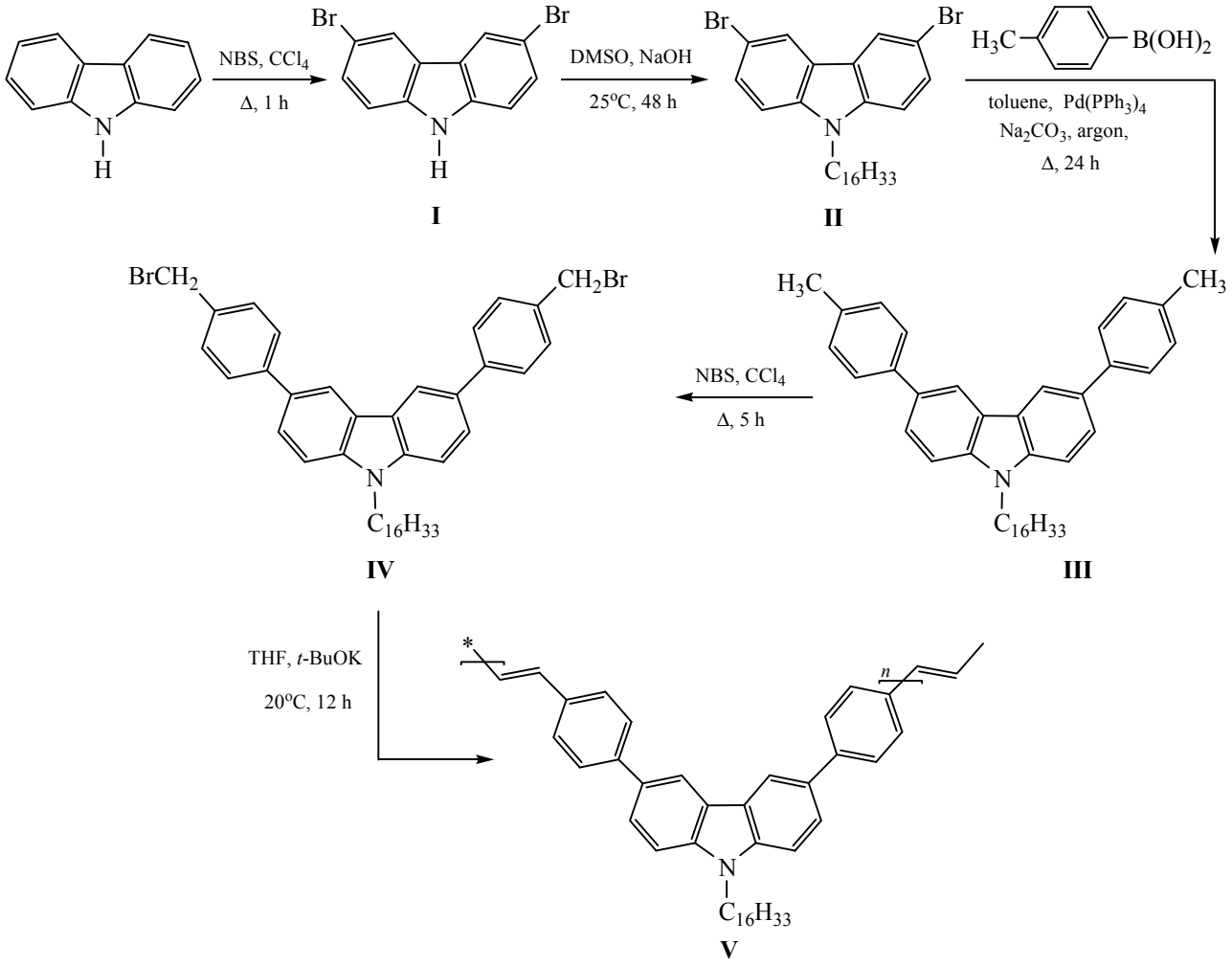
Development and preparation of π-conjugated polymers is an important field of chemistry due to their numerous possible applications in industry and technology: for instance, as materials for organic light emitting diodes, organic field-effect transistors, polymer solar cells, biosensors, and electroluminescent devices [1–6]. Conjugated polymers based on carbazole are of special interest [7–12]: such polymers bear unique combination of high π-type conductivity [13–15], easy processability [16], relatively low cost [17], ability to form thin flexible films [18], and other outstanding properties including thermal stability and optical characteristics [20–22]. The carbazole-based polymers can be further modified at positions 3(6), 2(7), and 9 of the carbazole ring. Here we report on preparation and properties of a new carbazole-containing polymer, readily soluble in common organic solvents.

In particular, bromination of carbazole with *N*-bromosuccinimide NBS at reflux in CCl_4 gave 3,6-dibromocarbazole **I** [23]; subsequent alkylation of the latter with 1-bromohexadecane in DMSO at room temperature in the presence of sodium hydroxide resulted in the formation of 3,6-dibromo-9-hexadecyl-9*H*-carbazole **II**, readily soluble in common organic solvents and easily purified by recrystallization from methanol (Scheme 1).

An extended conjugated system containing carbazole ring as the central part may be obtained via the introduction of additional aromatic fragments adjacent to the carbazole fragment. To do so, we applied the Suzuki reaction: refluxing of compound **II** in toluene with *p*-tolylboronic acid (prepared in turn from *p*-bromotoluene and trimethylborate under argon [24]) yielded 3,6-di(4-tolyl)-9-hexadecyl-9*H*-carbazole **III**. The bromination at methyl groups of the latter with NBS gave pale-yellow amorphous 3,6-di(4-bromomethylphenyl)-9-hexadecyl-9*H*-carbazole **IV** (Scheme 1).

Poly(phenylenevinylenes) were the first polymers used for fabrication of organic light emitting diodes [1]. One of the methods for the preparation of such polymers is the Gilch approach, treating of the monomer containing chloro- or bromomethyl groups with strong base like *t*-BuOK in tetrahydrofuran medium [25, 26]. The method is relatively easy, and the suitable monomers can be prepared easily as well [27]; the reaction usually gives high-molecular products. Using the described method, compound **IV** was converted into pale-yellow oily polymer **V**.

Scheme 1.



Thermal stability of the prepared compounds was studied by TGA measurements. In particular, compound **III** possessed a distinct melting point at 91°C and high thermal stability. Its decomposition started at 280°C (0.11 mg/min at 5 deg/min), and the highest decomposition rate was found at 463°C. Compound **IV** was less stable, being decomposed in four steps. The weight loss in the first stage (167–194°C) was of 7%, the second stage (194–301°C) was accompanied with the loss of 17% of the initial mass at 0.09 mg/min, whereas the third stage of decomposition (301–394°C) showed the weight loss of 18%. The highest decomposition rate of 0.14 mg/min was detected at the last stage of the process 394–481°C.

Polymer **V** was more thermally stable as compared with compounds **III** and **IV**. 10% of the initial mass of polymer **V** was lost at 353°C. The first stage of decomposition, resulting in 37% weight loss, occurred at 350–410°C. The highest decomposition rate of 0.06 mg/min was observed at 383°C. In the second stage of the process (410–520°C) the decomposition was roughly twice slower, the weight loss being 28%. The high-temperature residual mass (600°C) was 32.2%.

Optical properties of the prepared compounds were studied in chloroform solutions by UV absorption and fluorescence spectroscopy techniques. The collected spectral data are given in the table.

Absorption spectra of compounds **III** and **IV** were similar, with two absorption peaks around at 290–330 nm (Fig. 1). Introduction of bromine atoms (compound **IV**) led to a small red shift of the absorption bands, by 13–15 nm, and to the sharp enhancement of the bands (hyperchromic effect). Absorption spectrum of the polymer revealed weakening of the absorption bands as compared with the spectrum of starting carbazole

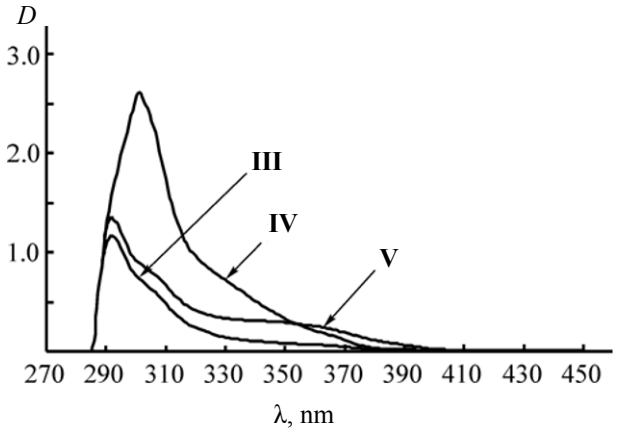


Fig. 1. UV absorption spectra of compounds **III–V**.

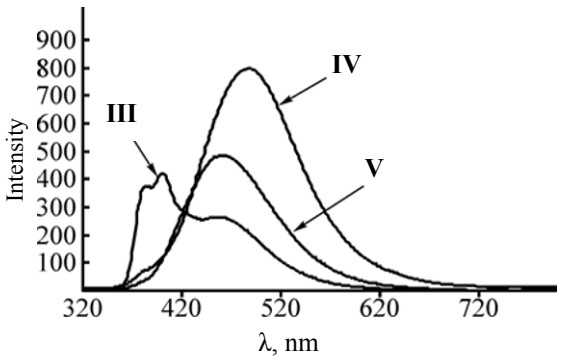


Fig. 2. Fluorescence spectra of compounds **III–V**.

III. Furthermore, the longwave absorption band appeared in the polymer spectrum at 360–365 nm. From the absorption spectrum of polymer **V**, its optical width of the forbidden band-gap was calculated: E_g^{opt} = 1240/λ_{onset} = 3.12 eV (λ_{onset} = 397 nm).

Figure 2 displays the fluorescence spectra of the studied compounds. The spectrum of compound **III** was somewhat different, possessing the lowest Stokes shift. Compounds **IV** and **V** showed the unusually high Stokes shifts of 192 and 172 nm, respectively; the pale-yellow solutions of these compounds emitted bright green light upon UV irradiation. he so high value of the Stokes shift in the case of diarylethylenes without any functional groups is generally explained either by steric hindrance arising in their molecules thus producing reconfiguration in their excited states or by the possible structural changes resulting in the noticeable reduction of the lowest excited state energy [28]. For comparison, absorption and fluorescence spectra of polymer **V** are given in Fig. 3.

Cyclic voltammetry experiment resulted in the formation of wine-colored film on the ITO electrode surface at the electrochemical oxidation of polymer **V** in solution; the redox process occurred likely at the unsubstituted positions 2/7 of carbazole ring. The cyclic voltammogram contained one peak corresponding to reversible redox process at relatively high potential (E_{ox} = 1255 mV and E_{red} = 1124 mV) (Fig. 4).

In order to study electrochemical stability of polymer **V** its film was deposed from methylene chloride solution on the ITO electrode surface using spin-coating technique [29]. The film morphology as visualized by atomic force microscopy is shown in Fig. 5. The polymer film was almost uniform containing some small inclusions smaller than 100 nm. The film fine structure and conductive properties were studied by scanning tunneling microscopy (Fig. 6); the polymer fragments of about 7 × 7 nm, enabling conductivity of the film can be seen in the image.

Cyclic voltammogram of the film so prepared (acetonitrile medium, the non-solvent for the polymer **V**) demonstrateded a single irreversible oxidation peak at E_{ox} = 1250 mV (Fig. 7). After five cycles of measurement the film was completely destroyed, demonstrating the film redox instability under the experiment conditions.

EXPERIMENTAL

^{1}H NMR spectra were recorded with the Varian Mercury plus 300 spectrometer (hexamethyldisiloxane as internal reference). Mass spectra were measured with the Agilent GC 6890N MSD 5975B chromato-mass spectrometer (EI, 70 eV). Electron absorption spectra of the solutions in chloroform were recorded using the SF-2000 spectrometer (l = 1 cm). Fluorescence spectra of the solutions in chloroform

UV absorption and fluorescence spectral data of compounds **III–V**

Comp. no.	λ_{max}^{1abs}, nm	λ_{max}^{2abs}, nm	λ_{max}^{3abs},, nm	λ_{max}^{1em}, nm	λ_{max}^{2em}, nm	λ_{max}^{3em}, nm	Stokes shift Δ, nm
III	291	304	–	382	400	466	103
IV	302	330	–			493	192
V	291	309	362	–	–	465	172

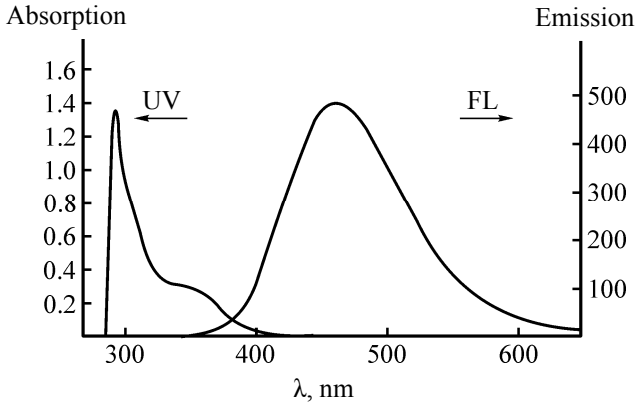


Fig. 3. Comparison of UV absorption and fluorescence spectra of polymer **V**.

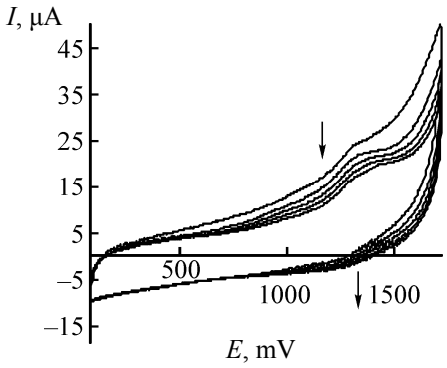


Fig. 4. Voltammogram of polymer **V** solution. E_{ox} = 1255 mV, E_{red} = 1124 mV, ITO electrode, CH_2Cl_2/MeCN, 5 cycles.

were recorded with the Shimadzu RF-5301 spectrofluorimeter (excitation wavelength 220 nm, 1 × 1 cm cell). The reactions course and the products purity were monitored by TLC (Silufol, Kavalier). Isolation of the products was performed at the silica gel column (Lancaster, Silica gel 60, 0.060–0.2 nm).

Thermogravimetry analysis was performed with the NETSCH STA 449F7 Jupiter instrument: the DSC/TG pan Al_2O_3 crucible, 35–700°C, nitrogen atmosphere, heating rate 5 deg/min (compounds **III** and **IV**) or 2 deg/min (compound **V**).

Electrochemical tests of the solutions were performed using the P-8 potentiostat with the Modul EM-04 detector [$c = 10^{-3}$ mol/L, CH_3CN–CH_2Cl_2 1 : 1 as solvent, 0.1 mol/L of $(C_2H_5)_4N^+ClO_4^-$ as background electrolyte, room temperature; three-electrode cell: glassy carbon or ITO on glass as working electrode, Pt wire as auxiliary electrode, Ag|AgCl as reference electrode; 50–100 mV/s].

Spin coating of the polymer film was performed with the Spin 12000 device at linear rate increase up to 1000 rmp, spinning time 20 s.

The film surface morphology was studied with the NTegro–Prima atomic force microscope in the semicontact mode with 1 μm probe and the NSG–10 cantilever, at resonance frequency of 170 kHz. Scan-

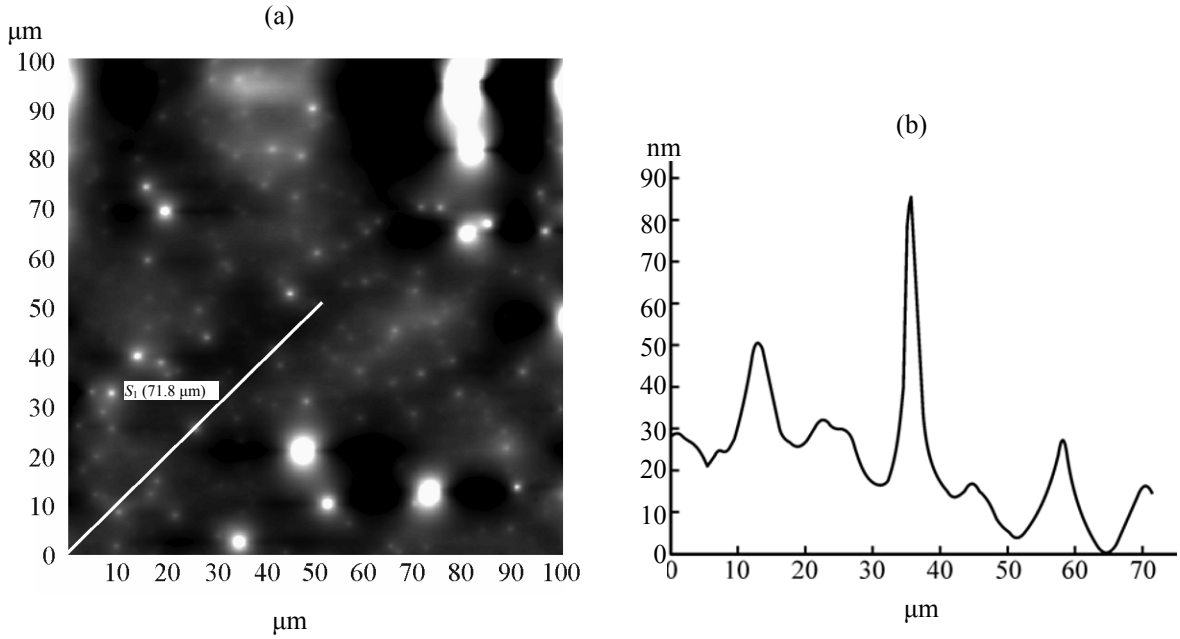


Fig. 5. 2D-ACM image of polymer **V** film (100 μm × 100 μm) (a) and the profile along the specified direction (b).

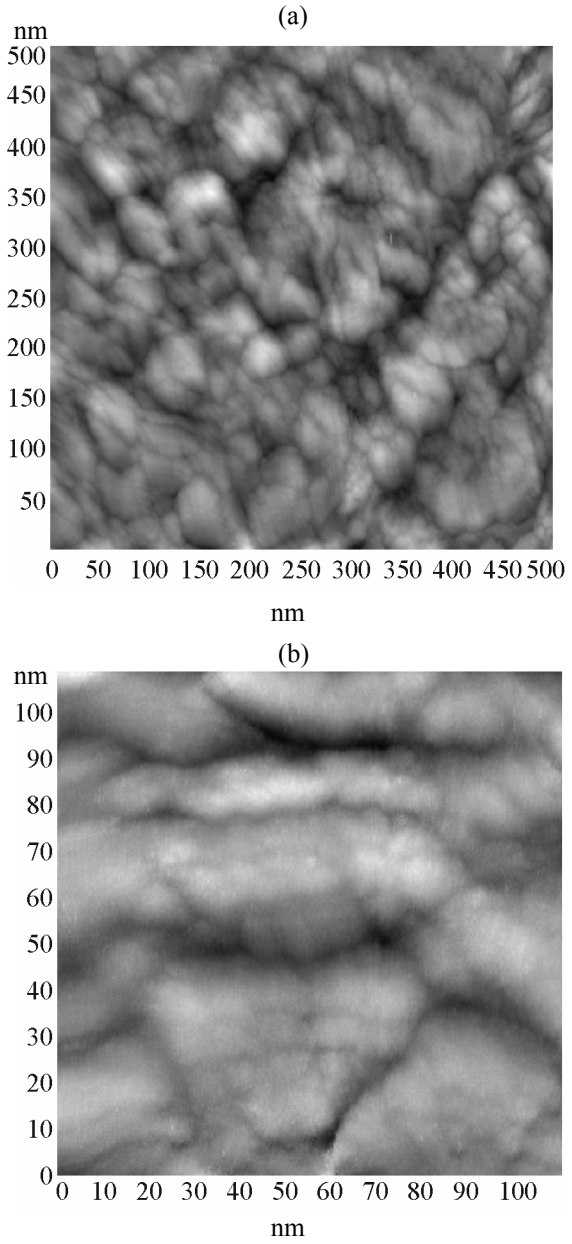


Fig. 6. 2D-STM image of polymer **V** film. (a) 500 nm × 500 nm and (b) 100 nm × 100 nm.

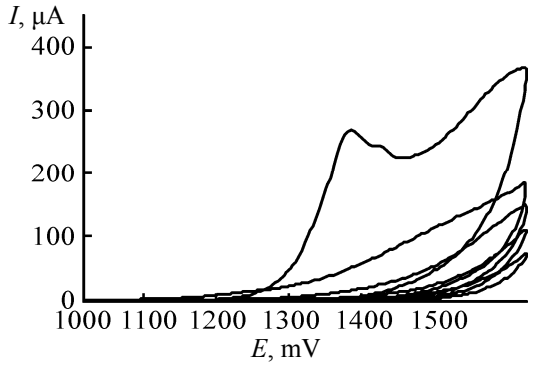


Fig. 7. Voltammogram of polymer **V** film. E_{ox} = 1372 mV, ITO working electrode, MeCN, 5 cycles.

ning tunneling microscopy study was performed by applying 0.1 V voltage at the palladium wire probe with constant current of 0.5 nA.

***N*-Hexadecyl-3,6-dibromocarbazole (II).** 20 g (0.5 mol) of NaOH was added to a mixture of 6.6 g (0.02 mol) of 3,6-dibromocarbazole **I** and 6.09 g (0.02 mol) of 1-bromohexadecane in 65 mL of DMSO. The reaction mixture was stirred during 48 h at room temperature, poured into cold water, and extracted with methylene chloride (the aqueous layer was acidified and extracted repeatedly). The combined organic layers were washed with water to remove DMSO, the solvent was evaporated, and the residue was recrystallized from methanol. Yield 92%, colorless crystals, mp 102–104°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_3, *J* 7.6 Hz), 1.23 m (26H, $13CH_3$), 1.81 m ($\underline{CH_2}CH_2N$), 4.23 t (2H, CH_2N, *J* 7.6 Hz), 7.25 d (2H, carbazole, *J* 9.6 Hz), 7.55 d (2H, carbazole, *J* 9.6 Hz), 7.54 d.d (2H, carbazole, *J* 9.6 Hz, *J* 9.6 Hz), 8.13 s (2H, carbazole). Mass spectrum, *m*/*z* (I_{rel}, %): 549.15 (100) $[M]^+$, 550.2 (16.88) $[M + H]^+$, 551.15 (29.02) $[M + 2H]^+$, 548.2 (9.05) $[M - H]^+$, 547.2 (29.14) $[M - 2H]^+$, 339.85 (46.41), 338.9 (13.57), 337.9 (100), 335.9 (47.98), 260 (26.33), 258.9 (22.67), 258 (28.16), 257 (18.69), 180 (19.98), 179.1 (9.08), 178 (11.58), 151 (11.65), 69.05 (19.65), 57.1 (10.65), 57.1 (19.73), 55.05 (22.39), 43.05 (52.38), 41.05 (29.57).

3,6-Di(4-methylphenyl)-9-hexadecyl-9*H*-carbazole (III). Mixture of 10.98 g (0.02 mol) of compound **II** and 5.42 g (0.04 mol) of *p*-tolylboric acid was refluxed with 20 mL of toluene during 24 h under argon in the presence of 3 mol % of $Pd(PPh_3)_4$ and 10 mL of aqueous Na_2CO_3 (2 mol/L). The reaction completion was confirmed by TLC. After the reaction was completed, the reaction mixture was cooled, the organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were washed with water, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane as eluent, chloranil in benzene as developer). Yield 46%, mp 90.8°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_3, *J* 6.9 Hz), 1.23 m (26H, $13CH_2$), 1.90 m (2H, $\underline{CH_2}CH_2N$), 2.41 s (3H, CH_3), 4.32 t (2H, CH_2N, *J* 6.9 Hz), 7.28 d (4H, 2Ph, *J* 8.1 Hz), 7.45 d (2H,

carbazole, *J* 8.4 Hz), 7.62 d (4H, 2Ph, *J* 7.8 Hz), 7.69 d (2H, carbazole, *J* 8.4 Hz), 8.32 s (2H, carbazole). Mass spectrum, *m*/*z* (I_{rel}, %): 572.45 (100) $[M]^+$, 572.45 (46.29) $[M + H]^+$, 429.1 (4.26) $[M - H]^+$, 377.05 (10.24), 361.15 (30.30), 360.15 (96.78), 347.1 (11.32), 346.1 (12.95), 344.1 (17.27), 331.05 (11.10), 254 (11.05), 253 (38.41), 251.05 (36.06), 208 (15.58), 207 (16.80), 204.9 (10.42), 158.1 (29.08), 96 (17.57), 54.95 (13.04), 43.05 (35.60), 41.05 (11.10). UV absorption and fluorescence spectral features are given in the table.

3,6-Di(4-bromomethylphenyl)-9-hexadecyl-9*H*-carbazole (IV). A mixture of 10.9 g (0.02 mol) of compound **III** and catalytic amount of benzoyl peroxide in 60 mL of CCl_4 was stirred during 30 min. Then 7.1 g (0.04 mol) of NBS was added in portions, and the mixture was refluxed during 5 h. The solvent was then distilled off, and the residue was purified by column chromatography (silica gel, hexane–CH_2Cl_2, 2 : 1, as eluent, chloranil in benzene as developer). Yield 15%, pale-yellow amorphous substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_3, *J* 5.3 Hz), 1.24 m (26H, $13CH_2$), 1.90 m (2H, $\underline{CH_2}CH_2N$), 4.32 t (2H, CH_2N, *J* 6.9 Hz), 4.57 s (3H, CH_3), 7.28 d (4H, 2Ph, *J* 8.1 Hz), 7.46 d (2H, carbazole, *J* 8.4 Hz), 7.62 d (4H, 2Ph, *J* 7.8 Hz), 7.69 d (2H, carbazole, *J* 8.4 Hz), 8.32 s (2H, carbazole). UV absorption and fluorescence spectral features are given in the table.

Poly(9-hexadecyl-3-phenyl-6-(4-vinylphenyl)-9*H*-carbazole (V). A slurry of 0.19 g (0.64 mmol) of compound **IV** and 1.12 g (0.01 mol) of *t*-BuOK in 40 mL of anhydrous THF was stirred during 12 h at room temperature. Pale-yellow precipitate was formed immediately after mixing. After stirring, the solvent was distilled off, the residue was washed with water, dried, and treated with methanol. The product was viscous yellow oil, soluble in $CHCl_3$, CH_2Cl_2, acetone, hexane, benzene, toluene, DMF, and DMSO; poorly soluble in ethanol; insoluble in methanol and acetonitrile. IR spectrum ($CHCl_3$), ν, cm^{-1}: 852, 872, 887, 964, 1012, 1027 (sh.), 1053, 1073 (sh.), 1113, 1150, 1289, 1312, 1351, 1378, 1481, 1470 (sh.), 1517, 1544, 1599, 1627, 1649, 1689. UV absorption and fluorescence spectral features are given in the table.

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