ISSN 0012-5008, Doklady Chemistry, 2014, Vol. 456, Part 1, pp. 65–71. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © M.L. Keshtov, G.D. Sharma, D.Yu. Godovskii, N.M. Belomoina, Yanhou Geng, Yingping Zou, V.S. Kochurov, A.I. Stakhanov, A.R. Khokhlov, 2014, published in Doklady Akademii Nauk, 2014, Vol. 456, No. 1, pp. 49–55.

Novel Electron-Withdrawing π-Conjugated Pyrene-Containing Poly(phenylquinoxaline)s

M. L. Keshtov[a], **G. D. Sharma**[b], **D. Yu. Godovskii**[a],
N. M. Belomoina[a], **Yanhou Geng**[c], **Yingping Zou**[d], **V. S. Kochurov**[e],
A. I. Stakhanov[a], **and Academician A. R. Khokhlov**[a]

Received December 30, 2013

DOI: 10.1134/S0012500814050036

In recent time, conjugated polymers have attracted considerable attention of researchers not only from scientific but also from a practical viewpoint due to their fundamental optoelectronic properties and application as electroactive materials for organic light emitting diodes [1], field-effect transistors [2], and photovoltaic devices [3]. Conjugated polymers are prepared by Stille, Suzuki, and Yamamoto reactions using nickel (Yamamoto) and palladium (Suzuki and Stille) catalysts [4, 5]. However, the high cost of the processes and difficulties of purification from metal catalyst residues, which are undesirable impurities for optoelectronic devices, are considerable drawbacks of these reactions. New noncatalytic methods for the synthesis of high-purity conjugated polymers should be developed to solve these problems. It has also been found that intense electroluminescence and high charge mobility in a polymer require a high electron–hole conduction of a medium due to charge carriers mobility and a balance of injection of carriers of both signs from opposite electrodes into the emission polymer layer. However, the majority of conjugated polymers provide hole transport that causes imbalance of charge injection and a poor quantum yield.

The search for new efficient electron-transport polymers is necessary to improve the characteristics of electrooptical devices, which is provided, in particular, by the introduction of electron-withdrawing fragments—triazole [6], oxodiazole [7], quinoline [8], and quinoxaline [9]—into macromolecules. The latter are the least studied and show higher electron-withdrawing properties due to the presence of four electron-withdrawing heteroatoms. π-Conjugated thiophene-containing poly(phenylquinoxaline)s (PPQs) have been obtained recently. These PPQs behave as excellent electron-transport materials for organic light-emitting diodes [10]. We prepared new conjugated pyrene-containing PPQs as high-purity polymers by noncatalytic polycondensation reaction to provide the balance of the hole and electron conduction. The introduction of flat structures, such as pyrene, into a conjugated polymer is supposed to enhance intermolecular electronic interaction in the solid state and result in formation of π–π stacking structures. In continuation of our studies [11, 12], we prepared and studied new bipolar pyrene-containing PPQs as efficient electron-hole and transport materials and thereby synthesized, previously unknown bis(α-diketone)s **IV** and **VIII**.

RESULTS AND DISCUSSION

Novel pyrene-containing bis(α-diketone)s **IV** and **VIII** were obtained to prepare conjugated PPQs. Compound **IV** was obtained by sequential transformations including pyrene bromination, interaction of compound **I** with a twofold molar amount of trimethylsilylacetylene followed by elimination of trimethylsilyl group, palladium-catalyzed cross coupling of 1,6-diethynylpyrene (**II**) with a twofold molar amount of

---

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*
e-mail: keshtov@ineos.ac.ru
[b] *Jaipur Engineering College, SP 43, RIICO Industrial Area, Delhi Road, Kukas, Jaipur 303101, India*
[c] *Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, No. 5625 Renmin Rd., Changchun, Jilin 130022, China*
[d] *Central South University, Changsha, Hunan, China 410083*
[e] *Moscow State University, Moscow, 119991 Russia*

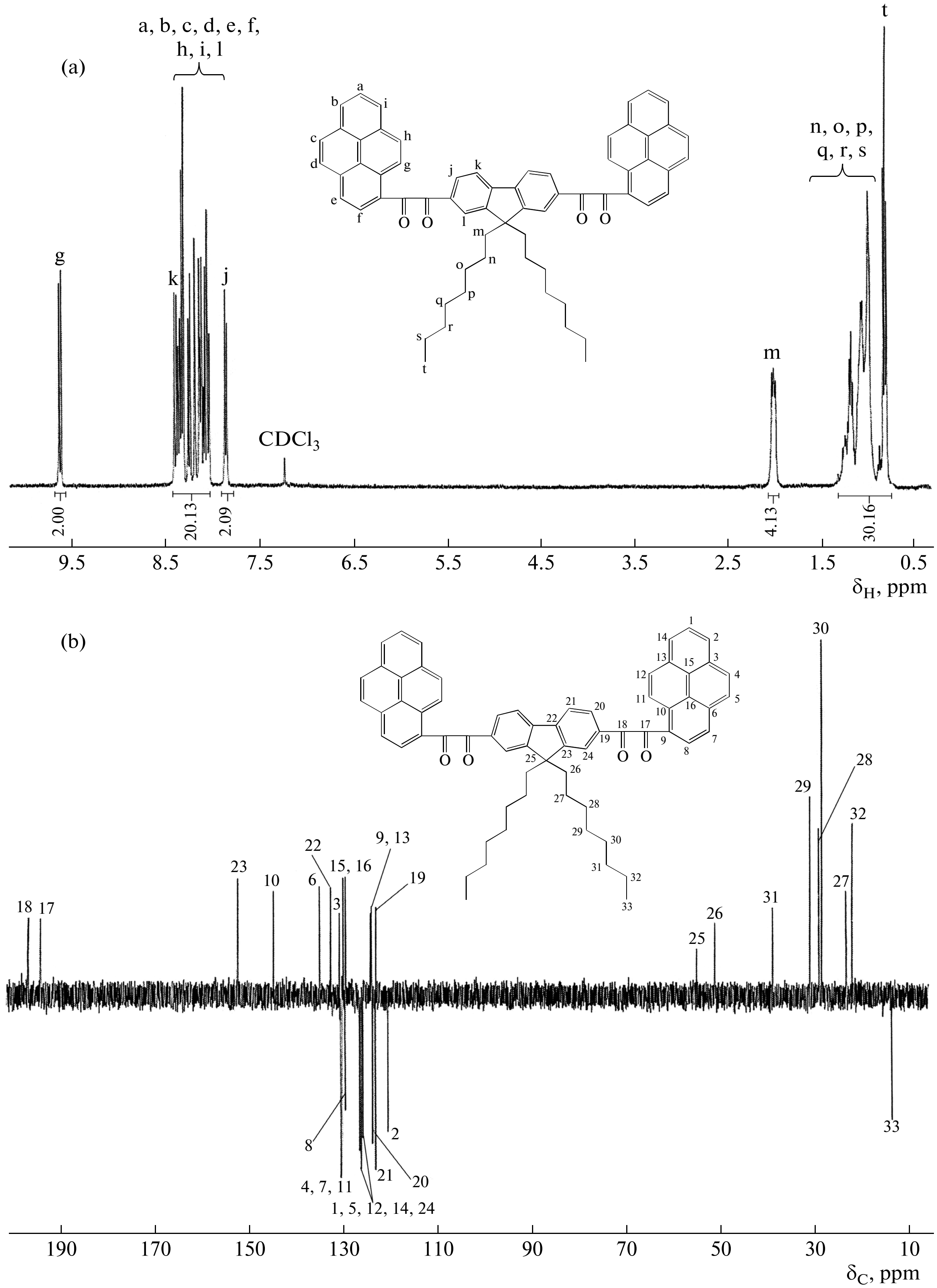
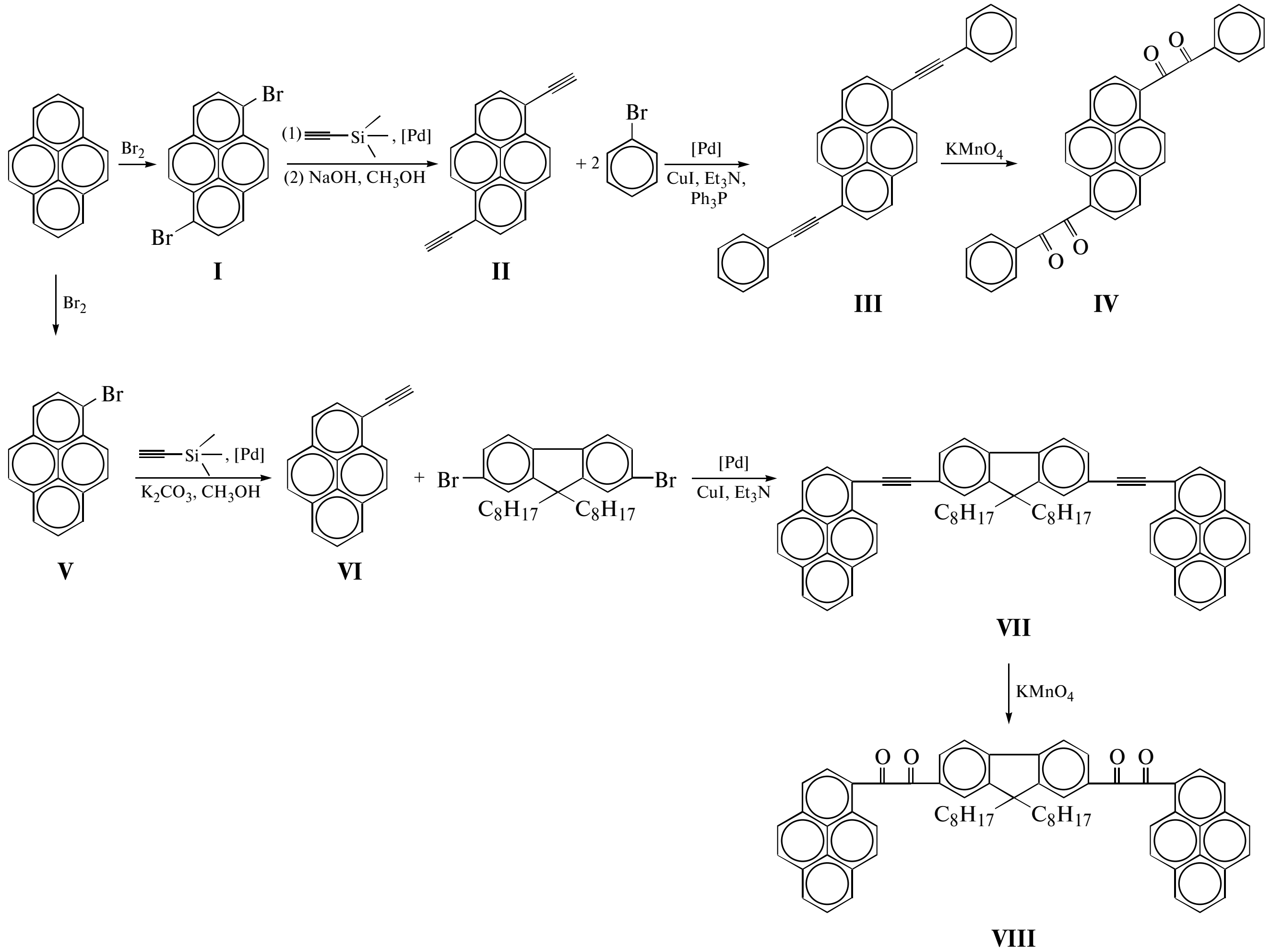


Fig. 1. ^{1}H (a) and ^{13}C (b) NMR spectra of bis(α-diketone) **VIII**.

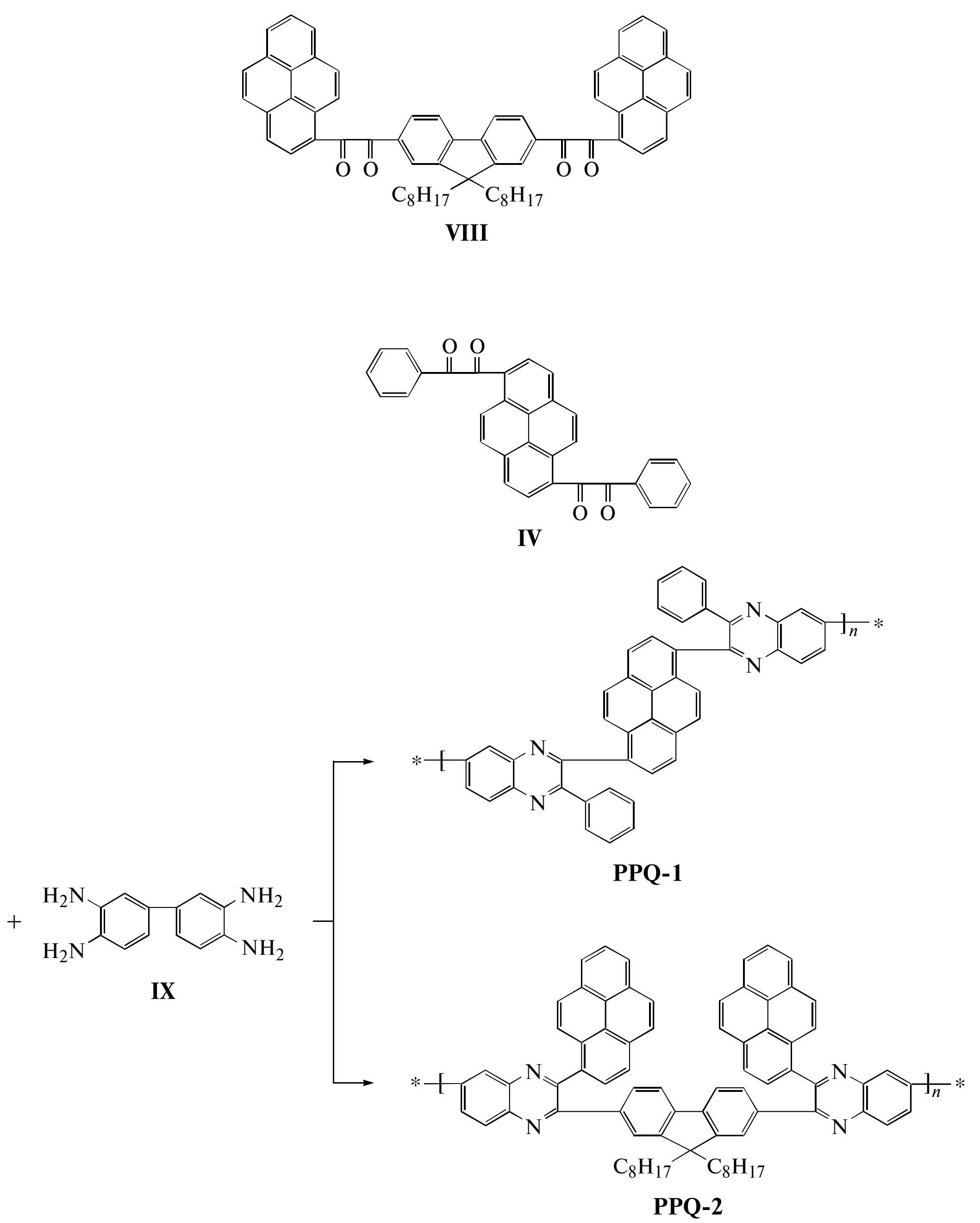
bromobenzene. Thus prepared 1,6-bis(phenylethynyl)pyrene (**III**) was oxidized with potassium permanganate to give the target monomer 1,6-(phenylglyoxalyl)pyrene (**IV**) in a rather high yield (78%). Compound **VIII** was obtained in 73% yield in a similar manner according to Scheme 1.



Scheme 1.

The composition and structure of target compounds **IV** and **VIII** were confirmed by elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR. In particular, the IR spectra of bis(α-diketone)s **IV** and **VIII** show strong absorption bands at 1665 and 1702 cm^{-1}, respectively, typical of the CO group of an α-diketone fragment. The ^1H NMR spectra of compounds **IV** and **VIII** show three multiplets at $\delta = 8.1$–8.3 (4H), 7.7–7.8 (6H), and 7.4–7.58 ppm (4H); one singlet at $\delta = 8.37$ ppm; one doublet at 7.99 ppm (4H, $J = 8.1$ Hz); and three well-resolved triplets at $\delta = 7.64$ (2H), 7.4 (2H), and 7.32 ppm (2H, $J = 7.2$ Hz) (Fig. 1a). Signal assignment in the ^1H NMR spectra was made from the ratio of the integrated intensities of signals and the values of spin–spin coupling constants. The ^{13}C NMR spectra of compound **VIII** display 20 intense signals in the region $\delta = 110$–150 ppm, eight of which pertain to quaternary carbon atoms. A specific feature of the spectra of compound **VIII** is the presence of downfield signals of two different carbonyl groups of the α-diketone fragment at $\delta = 194$ and 193 ppm (Fig. 1b).

The prepared bis(α-diketone)s **IV** and **VIII** were used in the synthesis of PPQs containing pyrene groups in the main and side chains of macromolecules in accordance with Scheme 2.



Scheme 2.

PPQs were obtained by reacting aromatic tetraamine **IX** with bis(α-diketone)s **IV** and **VIII** in an *m*-cresol solution at 190°C for 7 h. The reaction proceeded under homogeneous conditions to lead to polymers with high viscosity characteristics (η = 0.79–0.94 dL/g). The structure of PPQ was confirmed by IR and NMR spectroscopy. The IR spectra of the prepared polymers exhibit the lack of absorption bands at 3200–3400 and 1660–1680 cm^{-1} related to the C=O and NH_2 stretching vibrations of the initial compounds and the presence of absorption bands at 1640 cm^{-1} typical of the C=N bond in quinoxaline rings. This is also confirmed by the ^{13}C NMR spectra of all polymers, which contain no signals in the region δ = 190–195 ppm related to α-diketone fragments. The molecular weights of the polymers determined by GPC vary within (188.3–222.5) $\times 10^3$ (M_w) and (61.8–68.7) $\times 10^3$ (M_n) with dispersity 2.7–3.6, respectively. According to X-ray diffraction analysis, all the polymers are amorphous, which seems to be due to their isomeric heterounit structure, and this feature is responsible for the good solubility of PPQ in a wide

Table 1. Molecular-weight, thermal, and mechanical properties of poly(phenylquinoxaline)s

Polymer	η, dL/g	$M_n \times 10^3$	$M_w \times 10^3$	$\frac{M_n}{M_w}$	T_g, °C	$T_{10\%}$, °C *	Stretching properties of films	
							σ, MPa	ε, %
PPQ-1	0.62	61.8	222.5	3.6	344	492 (515)	86	5.2
PPQ-2	0.71	68.7	188.3	2.7	247	375 (463)	76	6.3

* Temperature of 10% weight loss in air and argon.

Table 2. Optical properties of poly(phenylquinoxaline)s in solutions and films

Polymer	λ^{a}_{max}, nm *1	λ^{fl}_{max}, nm *2		E_{opt}, eV *3	λ_{onset}, nm *4
	solution	solution	film		
PPQ-1	347 (422)	491	525	2.68	463
PPQ-2	359 (397)	478	500	2.81	441

*1 Absorption spectra maximum for polymers.
*2 Fluorescence spectra maximum for polymers.
*3 Optical energy gap width for polymer found from equation $E_{opt} = 1240/\lambda_{onset}$.
*4 λ_{onset} is the absorption spectrum onset in polymers.

range of organic aprotic and chlorinated solvents, such as DMF, DMA, DMSO, chloroform, and dichloroethane.

Thermal properties of PPQ were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the results are given in Table 1. Polymers **PPQ-1** and **PPQ-2** exhibit good thermal stability in air and argon with $T_{10\%}$ 492, 375 and 515, 463°C, respectively. Polymer **PPQ-2** has a lower stability as compared with **PPQ-1** probably because of the presence of an aliphatic fragment. The glass transition temperature of polymers **PPQ-1** and **PPQ-2** is rather high, 344 and 247°C, respectively (Table 1). Both polymers show high viscosity characteristics, which enables the preparation of films with high strength characteristics. The tensile strength and elongation of polymers **PPQ-1** and **PPQ-2** are 86, 76 MPa and 5.2, 6.3%, respectively.

Optical properties of the polymers were studied by UV and photoluminescence spectroscopy in solution and as thin films; selected characteristics are presented in Table 2. Figure 2 shows typical fluorescence curves for solution and solid films. The absorption spectra for polymers **PPQ-1** and **PPQ-2** in chloroform display maxima at 347 (422) and 359 (397) nm, respectively. The PPQs strongly fluoresce in chloroform. They exhibit green emission with fluorescence maxima in solution at 491 and 478 nm, respectively. The polymers in solid films also fluoresce with maxima at 525 and 510 nm, respectively. The optical energy gap width (E_{opt}) found from the absorption spectra of films is 2.68 and 2.81 eV, respectively.

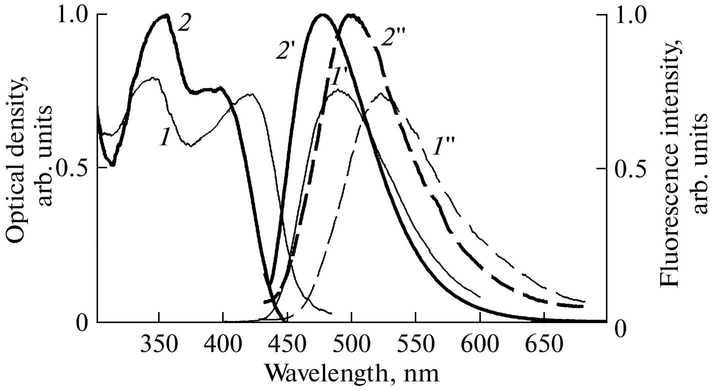


Fig. 2. Absorption spectra of **PPQ-1** (*1*) and **PPQ-2** (*2*) and fluorescence spectra of **PPQ-1** (*1'*) and **PPQ-2** (*2'*) in chloroform solution, fluorescence spectra of **PPQ-1** (*1''*) and **PPQ-2** (*2''*) as films. Excitation wavelength is 350 nm.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra of the initial compounds and polymers were recorded on a Bruker Avance-400 spectrometer operating at 400.13 and 100.62 MHz, respectively. The IR spectra were obtained on a Perkin-Elmer 1720-X IR FT spectrometer. TGA was performed on a Perkin-Elmer TGA-7 instrument at a heating rate of 20 K/min. The molecular weight distribution was analyzed by GPC using a Bruker LC21 liquid chromatograph with refractometric and UV detectors. Chromatography conditions: methylene chloride, 1 mL/min, $\lambda = 390$ nm. Calibration was performed using PS standards. The absorption spectra of thin-layer structures were recorded on a PC2000 fiber-optical spectrophotometer. The fluorescence spectra of the polymers were recorded on a Hitachi 850 spectrofluorimeter.

1,6-Dibromopyrene (I). Twenty grams of pyrene and 500 mL of carbon tetrachloride were placed into a 2-L two-necked flask. A solution of 10 mL of bromine in 500 mL of carbon tetrachloride was added dropwise with vigorous stirring at ambient temperature for 5 h. The mixture was stirred under the same conditions for 12 h. The precipitate was separated by filtration and recrystallized from toluene. Yield, 61%; $T_{\mathrm{mp}} = 220$–222°C (lit.: 221–222°C).

1,6-Diethynylpyrene (II). 1,6-Dibromopyrene (13.8 g, 38.8 mmol), 7.52 g (76.6 mmol) of trimethylsilylacetylene, 0.8 g of a palladium catalyst, 0.48 g of Cu I, 0.5 g of Ph_3P, and 550 mL of triethylamine were placed in a 700-mL three-necked flask equipped with a reflux condenser, a stirrer, and an argon inlet. The reaction mixture was heated at reflux with stirring for 10 h. The precipitate was separated by filtration, the solvent was removed to dryness. The residue was recrystallized from hexane. Yield, 75%; $T_{\mathrm{mp}} = 200$–202°C (lit.: 199–200°C).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.39 (s, 18H), 8.10–8.13, 8.55–8.58 (m, 8H).

A mixture of 2.1 g (5.3 mmol) of the prepared 1,6-bis(trimethylsilylethynyl)pyrene, 300 mL of diethyl ether, 200 mL of methanol, and 100 mL of 1 N aqueous NaOH was stirred at ambient temperature for 6 h. The organic layer was separated and dried with magnesium sulfate. After removal of the solvent, the residue was crystallized from a hexane–benzene mixture. Yield, 48%.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.64 (s, 2H), 8.52 (d, 2H), 8.35–8.32 (m, 4H, Ar), 8.24 (d, 2H).

1,6-Bis(phenylethynyl)pyrene (III). A three-necked 700-mL flask equipped with a reflux condenser, a stirrer, and an argon inlet was charged with 9.7 g (38.8 mmol) of 1,6-diethynylpyrene, 7.8 g (76.6 mmol) of bromobenzene, 0.8 g of a palladium catalyst, 0.48 g of Cu I, 0.5 g of Ph_3P, and 550 mL of triethylamine. The reaction mixture was stirred under reflux for 10 h. The precipitate was separated by filtration, and the solvent was evaporated to dryness. The residue was recrystallized from butyl acetate. Yield, 85%; $T_{\mathrm{mp}} = 193$–194°C.

^{1}H NMR (DMSO, δ, ppm): 8.6 (s, 2H), 8.2–8.5 (m, 6H), 7.8 (s, 4H), 7.5 (s, 6H).

1,6-Bis(phenylglyoxalyl)pyrene (IV). IR (KBr, ν, cm^{-1}): 1668.

^{1}H NMR (DMSO, δ, ppm): 9.49 (d, 2H), 8.60–8.57 (m, 4H), 8.47 (d, 2H), 8.10 (d, 4H), 7.83 (t, 2H), 7.70–7.60 (m, 4H).

1-Bromopyrene (V). A 2-L two-necked flask was charged with 20.225 g (100 mmol) of pyrene and 500 mL of DMF. A solution of 17.779 g (100 mmol) of bromosuccinimide in 500 mL of DMF was added dropwise with vigorous stirring at ambient temperature for 2 h and allowed to stand overnight. The precipitate was separated by filtration and recrystallized from hexane. Yield, 78%; $T_{\mathrm{mp}} = 100$–103°C.

1-Ethynylpyrene (VI). The compound was synthesized similarly to compound **II**. Yield, 95%; $T_{\mathrm{mp}} =$ 110–111°C.

IR (KBr, ν, cm^{-1}): 2097.

^{1}H NMR ($CDCl_3$, δ, ppm): 3.63 (s, 1H), 8.58 (d, 1H), 8.24–8.02 (m, 8H).

2,7-Bis(1-ethynylpyrene)-9,9'-dioctylfluorene (VII). The compound was synthesized similarly to compound **III**. Yield, 65%.

^{1}H NMR ($CDCl_3$, δ, ppm): 0.73 (4H), 0.8 (m, 6H), 1.12 (12H), 1.18–1.21 (m, 4H), 2.10–2.13 (m, 4H), 7.72 (s, 2H), 7.75–7.80 (m, 4H), 8.03–8.13 (m, 6H), 8.16 (d, 2H), 8.21–8.27 (m, 8H), 8.75 (d, 2H).

^{13}C NMR ($CDCl_3$, δ, ppm): 13.97, 22.51, 23.74, 29.21, 29.98, 31.72, 40.38, 55.35, 89.07 (C≡C), 96.19 (C≡C), 117.90, 120.06, 122.21, 124.29, 124.49, 125.53, 125.90, 126.15, 127.17, 128.05, 128.24, 128.85, 129.55, 129.90, 130.89, 131.03, 131.15, 131.20, 131.79, 140.80, 151.25.

2,7-Bis(1-glyoxalylpyrene)-9,9'-dioctylfluorene (VIII) was obtained similarly to compound **IV**.

IR (KBr, ν, cm^{-1}): 1668.

^{1}H NMR ($CDCl_3$, δ, ppm): 9.64–9.62 (d, 2H), 8.41–8.00 (m, 20H), 7.86 (d, 2H), 2.20–0.50 (m, 34H).

^{13}C NMR ($CDCl_3$, δ, ppm): 13.99, 22.49, 23.83, 29.06, 29.70, 31.61, 39.66, 55.82, 121.29, 123.96, 123.99, 124.58, 126.70, 126.98, 127.09, 127.34, 130.39, 131.14, 131.18, 131.33, 123.82, 124.81, 124.99, 130.32, 130.80, 131.58, 133.45, 135.79, 145.53, 152.99, 194.78 (C=O), 197.37 (C=O).

Poly(phenylquinoxaline) PPQ-1. A 25-mL three-necked flask equipped with a mechanical stirrer, a reflux condenser, and an argon inlet was charged with 0.2143 g (1 mmol) of 3,3',4,4'-tetraminodiphenyl, 0.9032 g (1 mmol) of bis(α-diketone) **VIII**, and 2.5 mL of *m*-cresol. The reaction mixture was stirred at ambient temperature for 2 h, next temperature was increased to 170°C and heated under these conditions for 5 h. Then the solution of polymer was cooled and poured into 10-fold excess of acetone. The precipitate of polymer was separated by filtration, washed with alcohol, and dried in a vacuum at 100°C. The reduced viscosity of **PPQ-1** was 0.81 dL/g in *m*-cresol at concentration 0.5 g/dL and 25°C. **PPQ-2** was obtained in similar manner, its characteristics are presented in Table 2.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project GFEN_a no. 12–03–91175, GFEN_a no. 13–03–91166, and IND_a no. 13–03–92709).

REFERENCES

1. Akcelrud, L., *Prog. Polym. Sci.,* 2003, vol. 28, no. 6, pp. 875–962.
2. Wu, Q., Wang, M., Qiao, X., Xiong, Y., Huang, Y., Gao, X., and Li, H., *Macromolecules*, 2013, vol. 46, pp. 3887–3894.
3. Wright, W. and Uddin, A., *Sol. Energ. Mat. Sol. Cells*, 2012, vol. 107, pp. 87–111.
4. Carsten, B., He, F., Son, H., Xu, T., and Yu, L., *Chem. Rev.*, 2011, vol. 111, pp. 1493–1528.
5. Duan, Ch., Zhang, K., Zhong, Ch., Huang, F., and Cao, Y., *Chem. Soc. Rev.*, 2013, vol. 42, pp. 9071–9104.
6. Strukelj, M.J., *J. Am. Chem. Soc.*, 1995, vol. 117, pp. 11976–11983.
7. Zhang, X. and Jenekhe, S., *Mater. Res. Symp. Proc.,* 1998, vol. 488, pp. 539–544.
8. Jenekhe, S., Zhang, X., Chen, X., Choong, V.E., Cao, Y., and Hsieh, B., *Chem. Mat*, 1997, vol. 9, pp. 409–412.
9. Karastatiris, P., Mikroyannidis, J., and Spiliopoulus, K., *Macromolecules*, 2004, vol. 37, pp. 7867–7878.
10. Cui, Y., Zhang, X., and Jenekhe, S., *Macromolecules*, 1999, vol. 32, pp. 3824–3826.
11. Keshtov, M.L., Mal'tsev, E.I., Lypenko, D.A., Brusnetsova, M.A., Sosnovyi, M.A., Vasnev, V.A., Peregudov, A.S., Vannikov, A.V., and Khokhlov, A.R., *Vysokomol. Soedin. Ser. A* 2007, vol. 49, no. 3, pp. 565–570.
12. Keshtov, M.L, Mal'tsev, E.I, Lypenko, D.A., Brusentseva, M.A., Sosnovyi, M.A., Il'ina, M.N., Vasnev, V.A., Peregudov, A.S., Petrovskii, P.V., Vannikov, A.V., and Khokhlov, A.R., *Vysokomol. Soedin. Ser. A,* 2008, vol. 50, no. 1, pp. 25–32.

Translated by I. Kudryavtsev