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CRYSTAL GROWTH

Growth from Solutions, Structure, and Spectral–Luminescent Properties of Crystalline Films of Di-*n*-hexyl-*para*-quaterphenyl

V. A. Postnikov[a,*], **G. A. Yurasik**[a], **A. A. Kulishov**[a], **M. S. Lyasnikova**[a], **O. V. Borshchev**[b], **E. A. Svidchenko**[b], **and N. M. Surin**[b]

[a] *Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics," Russian Academy of Sciences, Moscow, 119333 Russia*

[b] *Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Moscow, 117393 Russia*

**e-mail: postva@yandex.ru*

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Abstract—The results of studying the growth and structure of crystalline films of *para*-quaterphenyl derivative with terminal *n*-hexyl substituents—di-*n*-hexyl-*para*-quaterphenyl—are reported for the first time. The structure of crystalline films has been investigated using X-ray diffraction. It is found that crystalline films of di-*n*-hexyl-*para*-quaterphenyl, as well as crystals of unsubstituted *para*-quaterphenyl, are prone to outgrowth on a liquid–air interface in the form of a stack of parallel monomolecular layers with a thickness d_{001} = 3.05 nm. The optical absorption and photoluminescence spectra of solutions in *n*-hexane, toluene, and tetrahydrofurane, as well as crystalline samples, have been studied.

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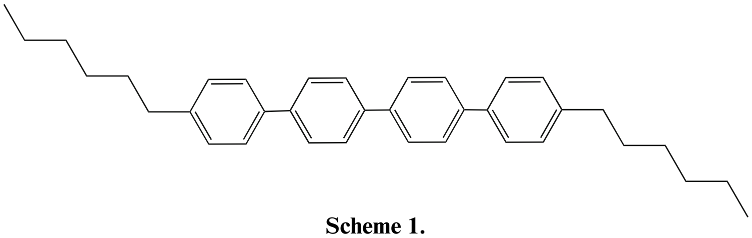
INTRODUCTION

The crystalline films based on organic π-conjugate linear oligomers, obtained by growth from solutions, are of great interest for the development of organic electronics and photonics [1–3]. From the point of view of semiconductor properties, linear molecules with a number of π-conjugate groups $n \geq 4$ are most interesting for electronics. However, because of the dramatic decrease in the solubility of material with an increase in the number of π-conjugate groups in the molecular, the growth of large crystalline films from solutions is a difficult problem even for $n = 4$ and can hardly be implemented at $n \geq 5$ [4–6]. For example, the results on the growth of single-crystal films of *para*-quaterphenyl (4P) (whose structure consists of four conjugate phenyl groups) from solutions were reported in [4]. The growth cycle for thin 4P single crystals with a thickness of ~5 μm and length up to 5 mm on an interface under conditions of precipitant vapor slow diffusion at room temperature amounted to 20 days [4]. It was shown in [7] that, under conditions of slow isothermal evaporation of high-boiling solvent from solution drops on substrates, crystalline 4P films few millimeters long can be formed for several hours. The increase in oligomer solubility due to the introduction of terminal substituent groups into molecular structure may increase the efficiency of crystal growth from solutions. This approach proved to be valid for *para*-quaterphenyl derivatives with terminal trimethylsilyl groups [8]. A positive effect of the presence of long alkyl terminal substituents in the structure of conjugate linear oligomers on the formation of single-crystal films on liquid–air interface was noted in [9–12]. In this paper, we report the results of studying the growth from solutions, structure, and spectral–luminescent properties of crystalline films of *para*-quaterphenyl derivative with terminal *n*-hexyl substituents: di-*n*-hexyl-*para*-quaterphenyl (Hex-4P-Hex).



Scheme 1.

The optical properties of solutions of this compound in 2-methyltetrahydrofuran were reported in [13]. The results of studying the growth and structure of Hex-4P-Hex crystalline films are presented here for the first time.

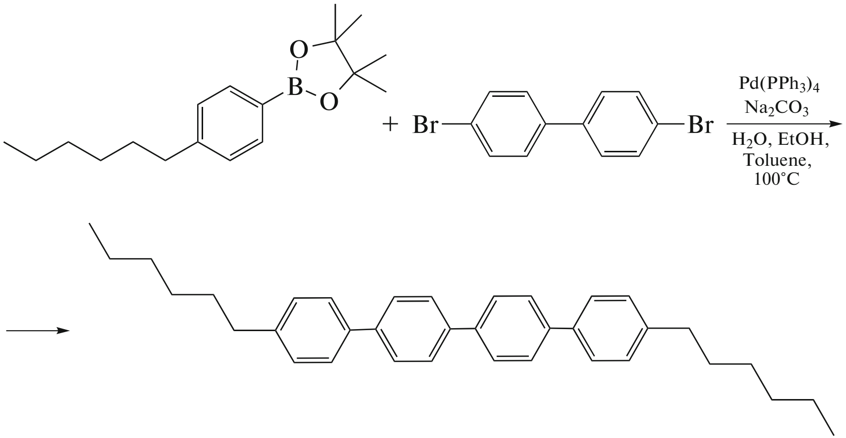
EXPERIMENTAL

Materials

We used sodium carbonate, 4,4'-dibromine-1,1'-biphenyl, and tetrakis(triphenylphosphine) palladium (0) Pd(PPh3)4 of Merck production. 2-(4-hexyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxoborolan was synthesized according to the technique described in [14]. The following solvents were used: *n*-hexane (of special-purity grade), toluene (special-purity grade), tetrahydrofuran (special-purity grade), 1,2,4-trichlorobenzene (reagent grade), isopropyl alcohol (analytical grade), and butanol-1 (special-purity grade).

Synthesis

We used Hex-4P-Hex synthesized according to the scheme



Scheme 2.

To this end, 4,4'-dibromine-1,1'-biphenyl and 2-(4-hexyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxoborolan were involved in the Suzuki reaction of metalorganic synthesis. After 28-h boiling, the precipitate formed in the reaction flask was filtered and recrystallized from toluene. As a result, white Hex-4P-Hex crystals were obtained with a yield of 85%.

The synthesized crystals were investigated using NMR spectroscopy on ^{1}H nuclei (with chloroform $CHCl_3$ as a reference). The chemical shifts δ were found to be 0.86 ppm (triplet, 6H, $J = 6.7$), 1.28 ppm (multiplet, 12H), 1.58 ppm (multiplet, 4H), 2.60 ppm (triplet, 4H, $J = 7.3$), 7.26 ppm (multiplet 4H), 7.56 ppm (multiplet 4H), and 7.62–7.74 ppm (overlapping 8H signals). Concentrations of chemical elements were determined for $C_{36}H_{42}$: 91.78 and 9.03 wt % for C and H, respectively. The calculated values were 91.08 and 8.92 wt %, respectively.

Crystalline Film Growth

The growth of crystalline films from a toluene solution was performed at room temperature (20°C) under conditions of slow isothermal evaporation of solvent and by the solvent precipitation method [3, 4, 6, 8, 12]. Butanol-1 was used as a precipitant (solvophobic liquid). A solution with an initial concentration of 0.45 g/L in a 20-mL glass flask was processed in an ultrasonic bath PSB-2835-05 (Russia) up to complete disappearance of precipitate. Then the processed solution was settled at room temperature for several days, after which sedimentation of a small amount of crystalline precipitate was observed. The thus obtained saturated Hex-4P-Hex solution was filtered using a single polytetrafluoroethylene (PTFE) filter with a pore diameter of 0.45 μm and poured into a 50-mL glass measuring vessel, which was placed in a thermostat within a hermetic glass growth chamber with a precipitant (butanol-1) poured previously on the bottom. Fourteen days after several large crystalline films, with a length up to 20 mm, were found, mainly on the solution surface (Fig. 1a). To grow crystals by the method of slow isothermal solvent evaporation, a filtered solution was poured into a pure 20-mL glass flask and placed in a thermostat loosely closed with a lid. Twenty eight days after several large crystalline Hex-4P-Hex films were observed, mainly on the solution surface.

Crystalline Hex-4P-Hex films were also grown on glass substrates by the sessile drop method [7]. A high-boiling solvent—1,2,4-trichlorobenzene (3CB)— was used to provide conditions of solution drop slow drying. The Hex-4P-Hex solution in 3CB with an initial concentration of 0.45 g/L was prepared according to the above-described technique for the toluene solution. Crystalline films on glass substrates were grown using a saturated solution, diluted by a factor of 4 with pure 3CB. Crystalline Hex-4P-Hex films were obtained as follows: a solution was deposited drop by drop (drop volume 15 μL) on object glasses (Steklopribor, Russia), previously purified with isopropyl alcohol and then dried under a glass hood in a thermostat at 45°C.

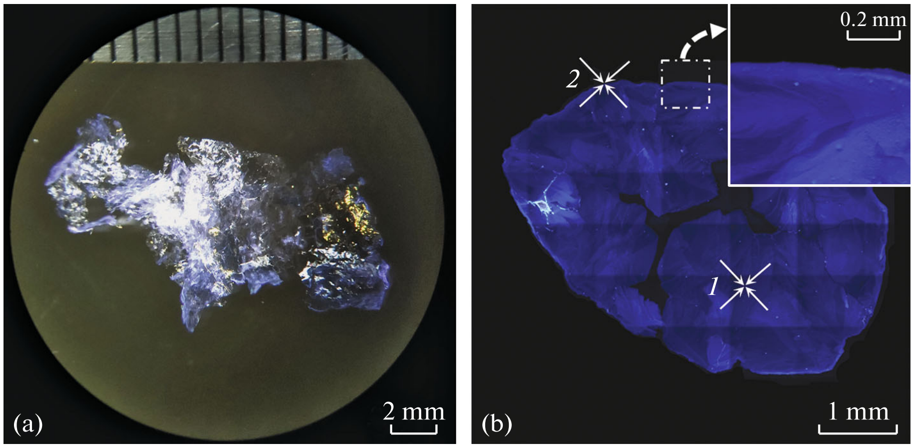


Fig. 1. (a) Crystalline Hex-4P-Hex film grown on a solution–air interface and (b) luminescence image of crystalline Hex-4P-Hex film formed as a result of drying of a 3CB solution drop (the inset in the upper right angle is an enlarged image of the area selected by dash-dotted line).

Optical and Atomic Force Microscopy

The dry substrate surface was analyzed on an Olympus IX81 luminescent microscope (Japan) and an optical long-focal-length microscope MBS-10 (Russia) in polarized light with crossed polarizers. The surface morphology and thickness of crystalline Hex-4P-Hex films grown on glass substrates were investigated using an atomic-force microscope (AFM) Solver BIO (NT-MDT, Russia) in the semicontact mode (NSG01 probe, NT-MDT, hardness 5.1 N/m, tip radius of no more than 10 nm).

X-Ray Diffraction

Structural analysis of a crystalline Hex-4P-Hex film grown from toluene solution, glued to a quartz plate, was performed at room temperature on an X-ray powder diffractometer Miniflex 600 (Rigaku, Japan) with the following characteristics: CuK_α radiation, λ = 1.54178 Å, and collection rate 2 deg/min.

Absorption and Photoluminescence Spectra

Absorption spectra of molecular Hex-4P-Hex solutions in *n*-hexane, toluene, and tetrahydrofuran (THF) were measured on a Shimadzu UV-2501PC spectrophotometer (Japan). Photoluminescence (PL) spectra were recorded on an ALS-1M spectrofluorimeter (developed at the Institute of Synthetic Polymer Materials of the Russian Academy of Sciences (RAS)) in the photon-counting mode on successive time intervals. Standard quartz cells 10 × 10 mm in size were used to measure the luminescence spectra of solutions. The PL spectra of crystalline Hex-4P-Hex films were measured in a Teflon integrating sphere. The PL quantum yield of solutions was determined by comparing with the known quantum yield of references using the method for measuring the fluorescence of optically diluted solutions [15]. When measuring the quantum yield φ of Hex-4P-Hex, a solution of *para*-terphenyl in cyclohexane ($\varphi = 0.91$) was used as a reference [16].

RESULTS AND DISCUSSION

Growth of Crystalline Films and Their Morphology

Crystal growth occurred most intensively on the liquid–air interface. Figure 1a presents one of the largest samples of crystalline Hex-4P-Hex films. Extraction from the solution surface and further drying made films shrunk. As can be seen in Fig. 1a, the thus obtained films are shapeless and have an inhomogeneous surface.

Figure 1b shows a luminescence image of crystalline Hex-4P-Hex film formed as a result of slow drying of 3CB solution drop in a thermostat at 45°C. It was shown previously by an example of unsubstituted *para*-quaterphenyl that this temperature is optimal for the formation of the largest crystalline films from 3CB solution drops [7]. As can be seen in Fig. 1b, a crystalline Hex-4P-Hex film on a glass substrate was formed practically as a single whole, but with a nonuniform thickness (decreasing towards the film center). As well as for the unsubstituted 4P, solution drop contraction towards the central region with 3CB evaporation did not lead to the formation of coffee-ring structures, consisting of a fine-grained precipitate, which indicates a low growth-center formation rate under these conditions [7]. One can observe a polycrystal (Fig. 2) consisting of crystallites up to 1 mm long (the central inset in Fig. 2) in the film images obtained in polarized light with crossed polarizers. Some crystallites have cracks, and, judging from the nonuniform color tone, there is small thickness inhomogeneity.

Figure 3a presents a topographic surface image in the central film area, indicated by arrow 1 in Fig. 1b.

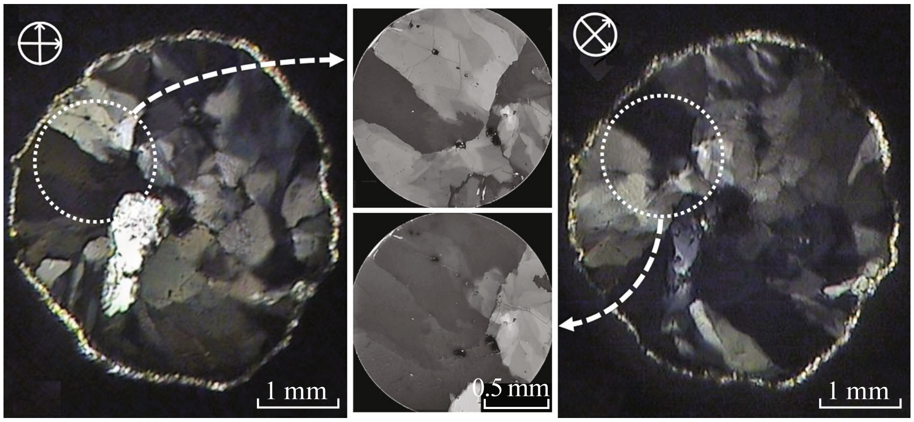


Fig. 2. Optical polarized images of crystalline Hex-4P-Hex film formed from a 3CB solution drop on a substrate, in different positions relative to crossed polarizers. Areas selected by white dotted line in the left and right images are shown in the middle on the enlarged scale.

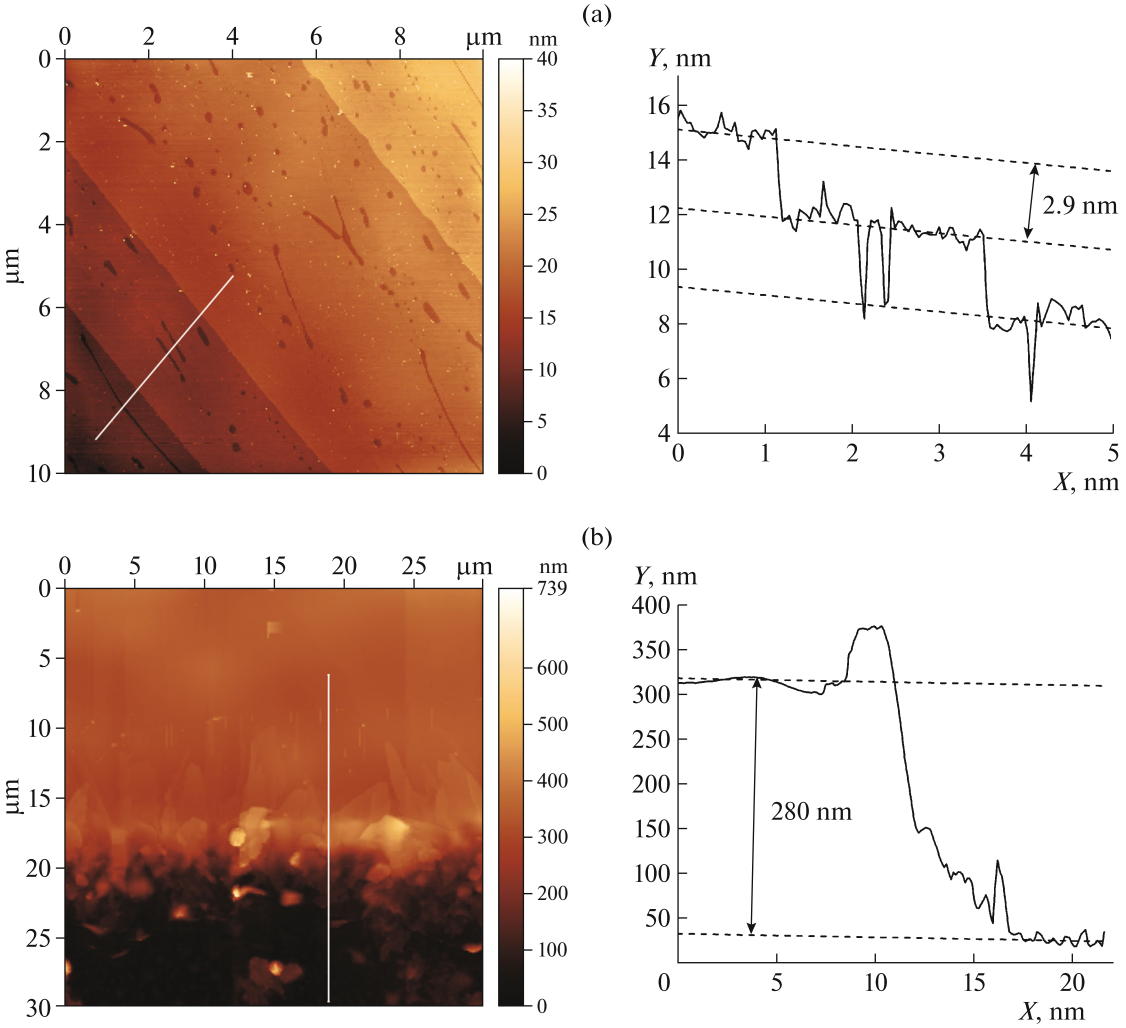


Fig. 3. Topographic surface images of crystalline Hex-4P-Hex film grown from a 3CB solution drop on a substrate, with the corresponding cross-sectional profiles (along the white segment in the images): (a) central and (b) peripheral areas of the film surface.

This surface area exhibits growth steps. According to the profile (on the right) of the surface cross section along the white segment in the topographic image, the step height is 2.9 ± 0.3 nm. An estimation of the length of Hex-4P-Hex molecule as the sum of bond length projections on the axis of conjugate core yields a value $l_0 \approx 3.3$ nm; therefore, the observed growth steps may be elementary. Many pits can be seen between growth steps on terraces; according to the surface cross section profile, the depth of these pits is equal to the step height. Figure 3b shown a topographic surface image of the peripheral region of crystalline film, indicated as 2 in Fig. 1b. One can see that the film edge is loose and coated by a layer of microcrystals. According to the cross section profile (on the right) along the white segment in the topographic image, the crystalline film height above the substrate surface is 280 nm.

X-Ray Diffraction Analysis

Figure 4a shows an X-ray diffraction pattern of a crystalline Hex-4P-Hex film grown from toluene solution. This pattern is a set of narrow peaks. Since collection was started not from zero reference point but from 3°, the position of the first peak was not completely resolved; however, the positions of other peaks are multiple of the angle 2.90° ± 0.05°. The observed diffraction pattern is the result of reflection from a set of parallel monolayers with the closest molecular packing. As in the case of 4P crystals [4, 6], we will assume that this set of planes is characterized by indices (00*l*). A calculation of the interplanar spacing for the first maximum from the Wulf–Bragg equation at $2\theta_{001} = 2.90°$ yields the following value of monomolecular-layer thickness: $d_{001} = 3.05$ nm. Thus, the height of elementary growth step of crystalline Hex-4P-Hex film (Fig. 3a) found from AFM measurements is in agreement with the monolayer thickness d_{001}.

The diffraction pattern of ground crystalline Hex-4P-Hex powder is shown in Fig. 4b. The positions of the strongest maxima (indicated by arrows) correspond to the positions of peaks in the diffraction pattern of crystalline film in Fig. 4a. The observed texture indicates that the crystalline powder is structured basically in the form of scales oriented parallel to the (001) plane.

Therefore, the molecules in the crystal are oriented at an angle of about 68° relative to the monolayer plane (001), as shown schematically in Fig. 5. Thus, the Hex-4P-Hex crystal has a sandwich structure, composed of alternating “soft” (loose) and “rigid” (with the highest packing density) layers, formed, respectively, by groups of alkyl terminal substituents and the central conjugate molecular core. This structural feature explains apparently the fact of most likely cleavage of crystals along the (001) slip plane under mechanical grinding.

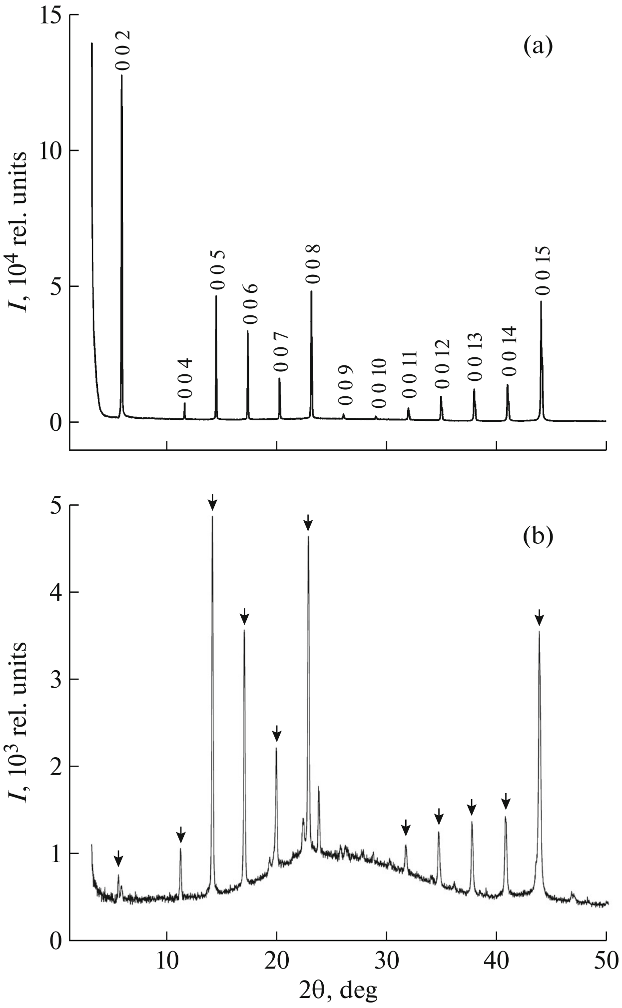


Fig. 4. X-ray diffraction pattern of (a) crystalline Hex-4P-Hex film grown from toluene solution and (b) ground crystalline powder.

Absorption-Luminescent Properties of Solutions and Crystalline Films

The spectral distributions of extinction coefficients of Hex-4P-Hex solutions in *n*-hexane, toluene, and THF are shown in Fig. 6. The properties of Hex-4P-Hex dissolved in these solvents are listed in Table 1. The positions of the maxima of long-wavelength absorption band for toluene and THF solutions coincide, while for the *n*-hexane solution the maximum is slightly blue-shifted. A short-wavelength absorption band (at 204 nm) is observed for only *n*-hexane. Table 1 contains the values of the extinction coefficient ε in the corresponding maximum of long-wavelength absorption band. The extinction coefficient of the short-wavelength band in *n*-hexane is $\varepsilon_{204\text{nm}} = 99000$ L mol^{-1} cm^{-1}, which is larger than that of the long-wavelength band by a factor of 1.9. For all three solvents the long-wavelength absorption band has a Gaussian shape. The absorption spectrum of a thin crystalline film is shown

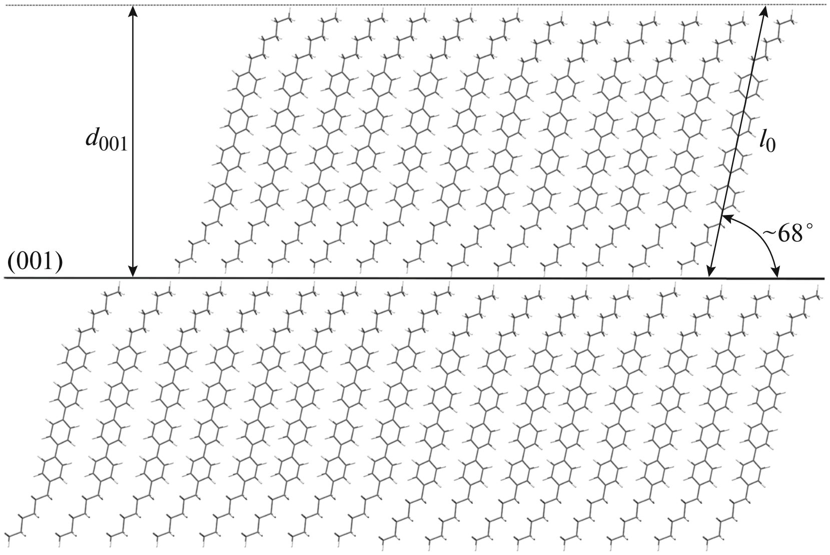


Fig. 5. Schematic model image of a fragment of Hex-4P-Hex crystal structure.

in Fig. 7. It differs significantly from the absorption spectra of the Hex-4P-Hex solutions presented in the same figure. The absorption band of crystalline film in the range of 200–400 nm contains several weak maxima at wavelengths of 202, 232, 278, 307, and 346 nm (Fig. 7). The true absorption intensity corresponding to these wavelengths differs from the observed one, because the investigated Hex-4P-Hex film was significantly inhomogeneous in thickness and rough. Therefore, the absorption profile presented in Fig. 7 should be considered as a "technical" (distorted) spectrum of crystalline film.

Let us compare the luminescence spectra of Hex-4P-Hex solutions and crystalline film (Fig. 7). The luminescence spectra of solutions have a pronounced vibrational structure. The frequency of the 0–0 transition in both THF and toluene is 400 cm^{-1} lower than in *n*-hexane. The frequency of the 0–0 transition in the crystalline film is red-shifted by 2500–2900 cm^{-1} in comparison with that in solutions. The Stokes shift in solutions (6100–6350 cm^{-1}) increases slightly with a decrease in the solvent polarity. As compared with a solution of unsubstituted *para*-quaterphenyl in THF, Hex-4P-Hex exhibits a bathochromic shift of the luminescence spectrum with conservation of its shape; the Stokes shift increases (5040 cm^{-1} for 4P), and the frequency of the 0–0 transition somewhat decreases (29850 cm^{-1} for 4P) [4].

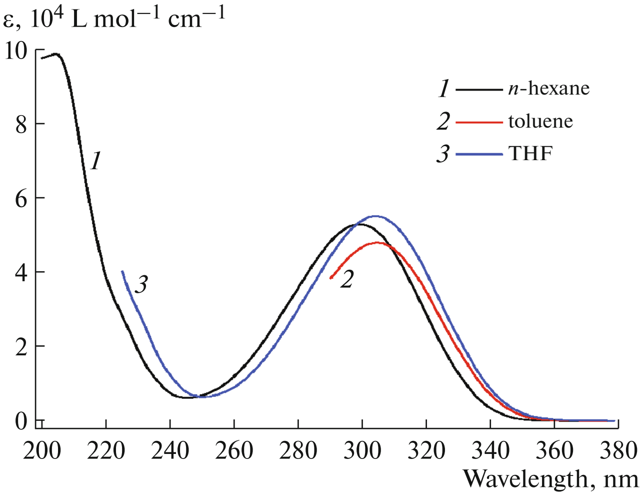


Fig. 6. Extinction coefficient spectra of Hex-4P-Hex in solvents.

Concerning the Stokes shift for a crystalline film, its value depends on the choice of the calculation technique. If the Stokes shift is counted from the maximum of the longest wavelength band in the film absorption spectrum (346 nm), its value is 3800 cm^{-1}. The luminescence quantum yield φ is the same for Hex-4P-Hex solutions in *n*-hexane and toluene; the φ value for the THF solution is somewhat lower (Table 1). Within the measurement error its value for these solvents can be considered as unified and equal to 90 ± 2%, which is somewhat lower than for unsubstituted *para*-quaterphenyl in THF: 94% [4]. The luminescence quantum yield of crystalline film is 95 ± 5%, which exceeds only slightly that of solutions.

CONCLUSIONS

It was shown that, in comparison with unsubstituted *para*-quaterphenyl, the presence of terminal *n*-hexyl substituents in the composition of Hex-4P-Hex molecule increases significantly the outgrowth rate of

Table 1. Properties of Hex-4P-Hex in solvents and in the form of a thin polycrystalline film

Medium	Absorption		Luminescence	0–0 transition, cm^{-1}	Stokes shift, cm^{-1}	φ, %
	$\lambda_{abs/max}$, nm	ε, L mol^{-1} cm^{-1}	$\lambda_{lum/max}$, nm			
n-Hexane	299	53000 ± 1300	369	29700	6350	92 ± 5
Toluene	304	48000 ± 1200	375	29300	6230	92 ± 5
THF	304	55000 ± 1400	373	29300	6090	88 ± 5
Crystal	346*		398	26800	3800	95 ± 5

ε is the extinction coefficient in the maximum of long-wavelength absorption band $\lambda_{abs/max}$ and φ is the luminescence quantum yield.
* Maximum long-wavelength absorption peak.

crystalline films from a solution on the liquid–air interface at an insignificant increase in solubility. According to the obtained X-ray diffraction data, Hex-4P-Hex crystals, as well as unsubstituted 4P crystals [4], are formed as stacks of plane-parallel monolayers. The presence of terminal *n*-hexyl substituents in the composition of molecule gives rise to specific structural features of crystals: formation of a sandwich regular structure composed of alternating "soft" (formed from alkyl groups $-C_6H_{13}$) and "rigid" (formed from conjugate cores –4P–) layers. However, this layered structure of Hex-4P-Hex crystal apparently negatively affects the long-range order of molecules in it, which explains the low structural quality of grown crystalline samples. The crystalline films formed on the interface are polycrystalline aggregates, consisting of crystallites up to 1 mm long, misoriented in the film plane (Fig. 2). The quality of the surface morphology of crystalline Hex-4P-Hex films forming on a substrate by the sessile drop method is higher than that of separate crystalline films grown from a large-volume solution. As compared with spectral-luminescent properties of unsubstituted *para*-quaterphenyl in a THF solution, the presence of terminal *n*-hexyl substituents leads to a bathochromic luminescence shift, increases the Stokes shift, and reduces insignificantly the 0–0 transition frequency with conservation of the spectral shape. The luminescence quantum yield in Hex-4P-Hex solutions is few percent below than for unsubstituted 4P.

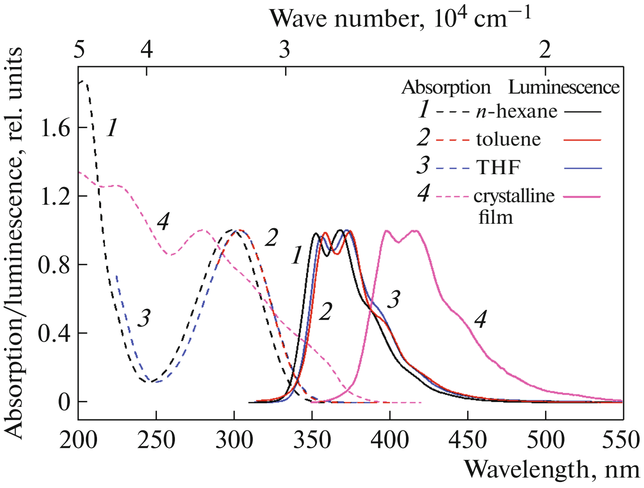


Fig. 7. Absorption and luminescence spectra (normalized to peak intensities) of Hex-4P-Hex in *n*-hexane (λ_{exc} = 300 nm), in toluene and THF (λ_{exc} = 304 nm), and in the form of thin crystalline film (λ_{exc} = 310 nm).

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