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Conjugated Iron-Doped Heterocyclic Materials with Different Degrees of Conjugation

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Conjugated two-dimensional materials with metal atoms are being actively studied for a number of modern applications, particularly for printed electronics. Our work investigates the synthesis of two-dimensional iron polyphthalocyanines (PPC). Liquid-phase (low-temperature) and solid-phase (high-temperature) approaches are compared. It is shown that in the former case a predominantly mononuclear phthalocyanine is obtained, while in the latter case a polymerized material is obtained. In addition, it is shown that carbonization of two-dimensional iron PPC can yield a graphene-like material strongly doped with iron atoms. For the studied materials of three different classes (mononuclear and polymerized PPC, as well as doped graphene-like material), suspensions were obtained and the bandgap width was estimated by optical absorption and electrophysical measurements.

Keywords: Polyphthalocyanines, 2D polymers, spectroscopy, band gap, semiconducting inks.

Сопряженные гетероциклические материалы с атомами железа с разными масштабами сопряжения

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Сопряженные двумерные материалы с атомами металлов активно изучаются для ряда современных применений, в частности, для печатной электроники. В нашей работе исследуется синтез двумерных полифталоцианинов (ПФц) железа. Сравнивается жидкофазный (низкотемпературный) и твердофазный (высокотемпературный) подходы. Показано, что в первом случае получается преимущественно моноядерный фталоцианин, а во втором – полимеризованный материал. Кроме того, показано, что карбонизацией двумерного ПФц железа можно получить графеноподобный материал, сильно легированный атомами железа. Для изученных материалов трёх разных классов (моноядерный и полимерный Фц, а также легированный графеноподобный материал) получены суспензии и проведена оценка ширины запрещённой зоны по оптическому поглощению и электрофизическим измерениям.

Ключевые слова: Полифталоцианины, двумерные полимеры, спектроскопия, запрещённая зона, полупроводниковые чернила.

Introduction

Two-dimensional (2D) materials are extremely promising in printed electronics. There is quite a large number of works describing prototypes of devices based on such compounds so far: transistors,[1] memristors,[2] and spintronic devices.[3,4] The most reviewed 2D compounds promising for printable microelectronics include graphene and its modifications, various transition metal dichalco-genides, black phosphorus, boron nitride.[5] There is noticeably less information on such application of phthalo-cyanines and their polymeric analogs. In contrast to the above mentioned materials, phthalocyanine compounds are interesting as more flexible in terms of possible applications and tuning of physicochemical properties due to the capabilities of coordinating different types of metal in the macrocycle core. Compared to monomeric forms, polyphthalocyanines (PPC) are characterized by higher thermal and chemical stability and the size of electron density delocalization in macromolecules.[6] Thus the semiconductor properties of the material change significantly with increasing delocalization of electron density in the polymer chain,[7,8] *i.e.* strongly dependent on the polymerization degree. Moreover, it is possible to obtain metal-free PPC[9] that can be doped by various metals later.[10] As recently shown in [11], it is possible to produce graphene-like materials strongly doped with nitrogen and metal atoms by carbonization of organometallic frameworks (MOFs). PPC may well be appropriate for obtaining this type of material.

The choice of synthesis conditions and metal-containing precursors for polymerization is an important issue in the context of the PPC use in printed microelectronics (primarily by ink-jet printing technology). These factors determine the polymers applicability for the creation of stable suspensions used as functional printing inks.[12] Thus, it is reasonable to compare the physicochemical properties of similar compounds that differ by synthesis conditions. Such approach allows to establish the relationship between the material structure, methods of its preparation and final semiconductor properties, which is critical in optimizing the printing process of microelectronic components.

In the current work, we synthesized three types of conjugated 2D materials: oligophthalocyanine (FeOPC), polyphthalocyanine (FePPC), and the graphene-like material based on FePPC. Iron was chosen as the central metal in the macrocycle core since it is an effective coordinating agent and a promising metal for studying spin properties in graphene-like metal-containing materials.[11] We should note that in the present work we use the term "2D material" as a material that is based on flat (or layered) molecules or nanoparticles, and with some degree of arbitrariness herein we apply it to molecular phthalocyanines also.

Earlier it was found that temperature plays an important role in the synthesis of PPC: at temperatures below 350 ºC a low molecular weight fraction (mainly mononuclear phthalocyanine) is formed, while at synthesis conditions above 350 ºC a markedly larger polymerization of tetracyanobenzene occurs with the formation of 2D-polymer.[13] The polymerization reaction proceeds with higher yield by adding a drop of DBU as a catalyst. These circumstances can be used to obtain various degrees of polymerized materials. The solid phase powders were further converted into suspension form. Absorption spectra in the optical and near-infrared ranges can be used as an indicator of electronic coupling.[14,15] By using these spectra it is also possible to obtain more concrete information about semiconductor properties. Thus, the band gap for samples in solution/suspension form can be estimated by analyzing the spectra.[16,17] In addition, absorption in the near-infrared has a special application importance for the infrared dyes.[18,19] Application of solvents and surfactants in the suspension preparation can significantly affect the conductive properties of materials. Therefore, the band gap from the temperature dependences of the powders conductivity was also evaluated separately for solid-phase samples.

Experimental

Materials

Commercial reagents were used for the synthesis: 1,2,4,5-tetracyanobenzene (Sigma-Aldrich), ferrocene (Merck), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Sigma-Aldrich), 1-pentanol (Sigma-Aldrich), Triton X-100 (Sisco Research Lab.), 99.999% argon Ar (Linde gas, Russia). Organic solvents dimethyl sulfoxide DMSO and ethyl alcohol were also purchased from Chimmed (Russia). Hydrogen was obtained using an electrolytic hydrogen generator GVCh-12M1 ("Himelektronika", Moscow, Russia).

Synthesis

Iron phthalocyanine (FeOPC). $8.4\cdot10^{-4}$ mol of tetracyanobenzene and $3.2\cdot10^{-3}$ mol of ferrocene and a drop of DBU (0.05 mL) were mixed in 50 mL of 1-pentanol. The mixture was kept for an hour at 140 °C in microwave reactor "Uwave-2000" (Sineo, China) under ultraviolet irradiation of 365 nm (100 W) and stirring. A dark brown solution was obtained.

Iron polyphthalocyanine (FePPC). $1.7\cdot10^{-3}$ mol of tetracyanobenzene and $6.5\cdot10^{-3}$ mol of ferrocene were mixed in a quartz crucible and placed in the reactor. A couple of drops of DBU (0.1 mL) were added and mixed thoroughly (the mixture becomes red-brown). First, an argon-hydrogen mixture of 1:1 was passed through the reactor at a rate of about 6 L/h, then the rate was reduced to 2 L/h and the reactor was heated to 460 ºC, the crucible with the reaction mixture is maintained at this temperature for 4 h. After cooling, the mixture was washed with hot water, hot DMSO and hot alcohol, dried for a couple of hours at a temperature of 120 ºC. As a result, we obtained a black powder with a shine, insoluble in organic solvents, sulfuric acid, water and stable in air at room temperature. Product yield ~80%. Calculated for $[C_{20}H_4N_8Fe]_n$: C, 58.25%; N, 27.18%; H, 0.98%; Fe, 13.59%. Found (mean value): C, 62%; N, 19%; Fe, 6%.

Graphene-like material (FeGLC). FePPC powder was heated in a quartz crucible with hydrogen gas flow (5 L/h) at 900 ºC for 4 h. Product yield: ~40%. Found (mean value): C, 85%; Fe, 11%.

Suspension preparation. 1.5 g of Triton X-100 and 20 mL of deionized water were added to 150 mg of FePPC or FeGLC. The mixtures were ultrasonicated by 400 W power in an ice-water bath for one hour, followed by 30 min spinning on a centrifuge at 5000 rpm. 10 mL of supernatant was taken as a target suspension.

Methods

Thin film preparation. Thin films were obtained by EZ4 (Zhengzhou TCH Instrument Co., Ltd., China) spin-coater at

1500–2000 rpm for a small amounts of FeOPC solution or FePPC and FeGLC suspensions deposited on 20×10×1 mm quartz plates and subsequent annealing of samples at 300 °C to remove solvents and surfactants. For spin-coating, we used ~1% suspensions for FeOPC, FePPC and FeGLC; about 0.1 mL was added for each coating step. The coating was repeated several times (from 5 to 10) and controlled visually until the pronounced color was observed.

Energy Dispersive X-Ray Spectroscopy (EDX). Spectral measurements. The *EDX* measurements were carried out using the scanning electron microscope JSM 6490 (Jeol) equipped with the Oxford Instruments INCAx-sight energy dispersive system. The beam energy was 20 keV and the beam current about 10^{-10} A. At least three measurements were done for each sample; it was shown that the agreement between the measurements is within 15%.

Optical absorbance was measured on the UV-Vis-NIR spectrophotometer Cary 5000 Varian (AgilentTech).

Raman spectra were measured with Bruker Senterra micro-Raman system under excitation at 532 nm, laser power at sample point was 0.1–1 mW and 50× objective; acquisition was 2×60 s. The samples were either powders or films deposited on a quartz plate (it was checked that the spectra are reproducible and do not depend on the sample form as long as the film is thick enough to exclude the spectrum of the wafer). The spectra shown in Figure 2 are from powders for FePPC and FeGLC and from the film for FeOPC.

IR spectra were recorded with a Bruker Vertex 70v FTIR spectrometer. For bulk samples from liquid-phase synthesis, KBr pellets were used (3 mg polymer per 300 mg KBr), while for thin films IR spectra were recorded via the Bruker Hyperion 2000 FTIR microscope in reflection mode.

Conductivity measurement. Two-piston method was utilized for measuring conductivity. The lab-built set-up resembled that described in reference:[20] it consisted of two cylindrical brass electrodes (5 mm in diameter) housed within a ceramic tube and connected to a Keithley 2000 digital multimeter. Ceramic tube was encased in a spiral coil band heater. Keithley 2000 was used in 4-wire resistance measurement mode (0.008% basic accuracy for resistance). DC voltage was recorded by a separate multimeter AKTACOM AM-1109 (0.06% accuracy for voltage). The samples, in powdered form (100 mg for each sample), were placed between the electrodes. A constant pressure of approximately 0.56 MPa was maintained, while the temperature was varied at a rate of about 5 degrees per minute. The temperature dependencies were recorded both at increasing and decreasing temperature. The dispersity of the samples was not studied in detail; it can be roughly estimated from SEM measurements that the powders consist of particles from hundreds of nm up to tens of microns.

We tested the reproducibility of the conductivity measurements for the same samples obtained in different syntheses (up to 3 attempts); the agreement is within 10%.

Results and Discussion

Polyphthalocyanines were prepared by polymerization of 1,2,4,5-tetracyanobenzene in the presence of ferrocene as an iron source. It was observed that the yield of FePPC is higher in excess of ferrocene, so it was taken in four times excess. To obtain differently polymerized samples, two syntheses were made: synthesis of FeOPC at relatively low temperature 140 ºC (slightly above the boiling point of pentanol), and in the case of FePPC the reagents were sintered at 460 °C in argon-hydrogen atmosphere to avoid oxidation of CN groups (Figure 1). EDX measurements, within precision of the experimental set-up and data analysis, show good agreement with the expected structure. It should be noted that the EDX peaks of carbon and nitrogen nearly superimpose, therefore in addition to the intrinsic sensitivity of the method (~1%), there is a certain uncertainty resulting from the fitting procedure. The nitrogen content therefore should be considered rather approximate. The metal content is lower than stoichiometric, which can be explained by the absence of metal atoms in some of the cells as reported previously in the literature.[21]

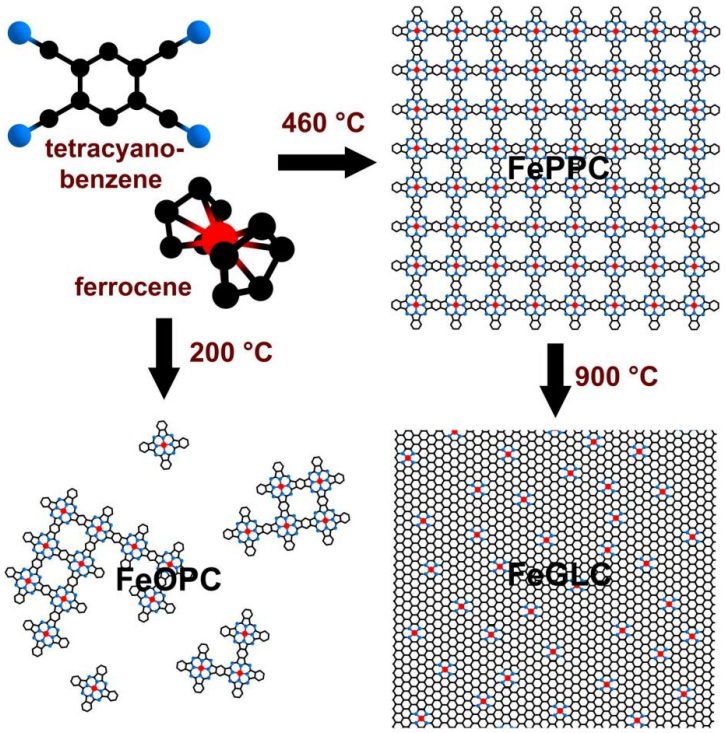

Figure 1. Schematic structures of the studied objects: FeOPC, FePPC, FeGLC. Atom colors: black - C, blue - N, red - Fe, H atoms are not shown.

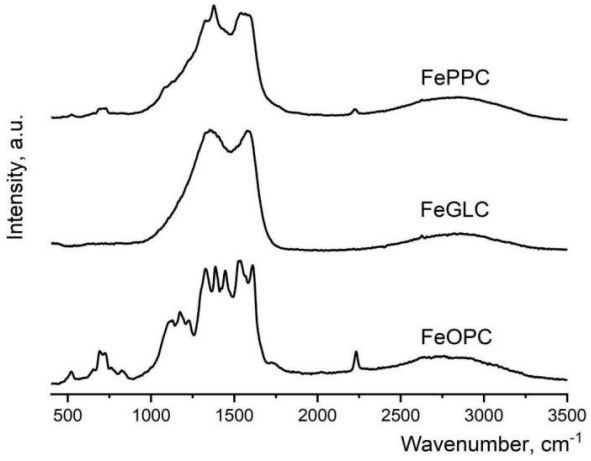

Figure 2. Raman spectra of the three 2D materials: FePPC, FeOPC and FeGLC.

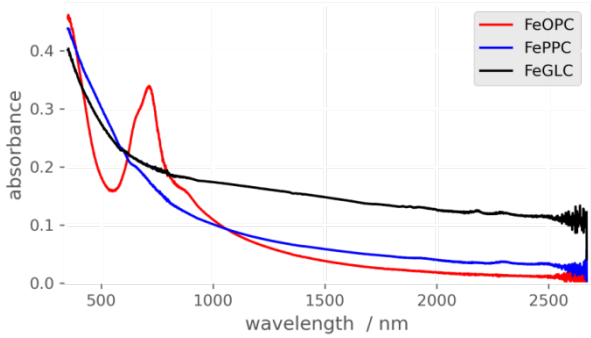

Figure 3. Vis-NIR absorption spectra of three conjugated iron-doped heterocyclic materials

A part of FePPC was further heated to 900 ºC in an inert atmosphere (Ar/H_2) to obtain iron-containing graphene-like material. Nitrogen was not detected by EDX in the carbonized sample (or its content is beyond the sensitivity of the method). The effective concentration of iron therefore increased upon the carbonization.

To create prototypes of functional inks, it would be convenient to obtain concentrated solutions of PPC. Unfortunately, graphene-like materials do not dissolve in any solvents, even in sulfuric acid. Therefore, we have to deal with suspensions, where ultrasonically dispersed nanosheets are stabilized with surfactants and sorted by size by centrifugation at different speeds.[22]

Raman spectra

It is known that the Raman spectra should consist of two intense broad peaks for a well-polymerized PPC resembling D (~1350 cm^{-1}) and G (~1580 cm^{-1}) peaks in defective graphene-like carbon.[13] Significantly more peaks of smaller width should be observed for mononuclear material. This is exactly what we observe in the experimental spectra of the samples obtained (see Figure 2). In addition, the peak intensity for CN bonds (2220 cm^{-1}) is significantly higher for low molecular weight FeOPC, which is also consistent with the notion of a lower degree of polymerization of the low temperature sample. After the carbonization, the narrow peaks from molecular fragments disappear, and the spectrum has typical features of the graphene-like carbon films,[23] *i.e.* broad D- and G-peaks (see Supplementary information, Figure S1).

Optical absorbance

The experimental spectra for all studied samples (FePPC, FeOPC, FeGLC) do not have pronounced peaks in the near infrared region 1000–2750 nm (Figure 3). This is consistent with the concept of the electronic nature of absorption associated with two-dimensional conjugation. The peak at ~750 nm in the visible region refers to the mononuclear/low molecular weight FeOPC, referred to in the Q-band for monomeric analogs.[13,24] The weak bands about 2300 nm are probably related to OH-groups of quarts.[25]

Several studies illustrated the Q-band shift to the near IR region for phthalocyanine derivatives that increased the number of conjugated macrocyclic cores.[7,8] Accordingly, there is a decrease of the band gap. Thus, larger conjugated structures based on phthalocyanines can exhibit additional absorption features extending into the near-infrared region due to enhanced conjugation and intermolecular interactions. For PPCs with larger number of macrocyclic core , the absorption should proceed further into the IR region. For example, in the limiting case (graphene sheet) it should be smooth and continuous up to the far IR range.[26]

Conductivity and band gap

The measurement results of the sample resistivity in the powders form are shown in Figure 4 and Table 1. The FePPC powder resistivity decreases 23 times when the temperature is increased to 410 K (from $1.4 \cdot 10^3$ to $6.2 \cdot 10^1$ Ω·m). The resistivity of the carbonized sample is not significantly affected by heating. However, the carbonized FeGLC sample has ~$2 \cdot 10^5$ and ~$2 \cdot 10^3$ Ω·m times lower resistivity than FePPC for 300 K and 410 K, respectively.

From literature data, it can be assumed that PPCs are *p*-type semiconductors,[27] of a low band gap;[28] computational data show that for the case of infinitely large macromolecules, these materials might have semimetallic properties.[28,29]

To estimate band gaps from UV-IR-NIR spectra, the experimental absorption data were fitted according to the Tauc model using the procedure described in [16]:

$$Abs(\lambda) = B_1 \cdot \lambda \, (1/\lambda - 1/\lambda_g)^m + B_2, \quad (1)$$

where *Abs* – absorbance, B_1 and B_2 – constants, m – index characterizing the nature of electron transition process (2 – direct allowed and 0.5 – indirect allowed). The best fit was obtained for m=2, which is typical for semiconductor materials with significant structural disorder [30,31]. λ_g value was estimated by fitting the NIR part of the absorption spectra with Equation (1). The fit is shown in Figure S2. It is convenient to convert resulting values λ_g to eV units:

$$E_{gap}(eV) = hc/\lambda_g \, , \quad (2)$$

where h is the Planck's constant, c is the speed of light.

Table 1. Resistivities (Ω·m) of powder samples at different temperatures.

	T = 300 K	T = 410 K
FePPC	$1.4 \cdot 10^{3}$	$6.2 \cdot 10^{1}$
FeGLC	$7.1 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$

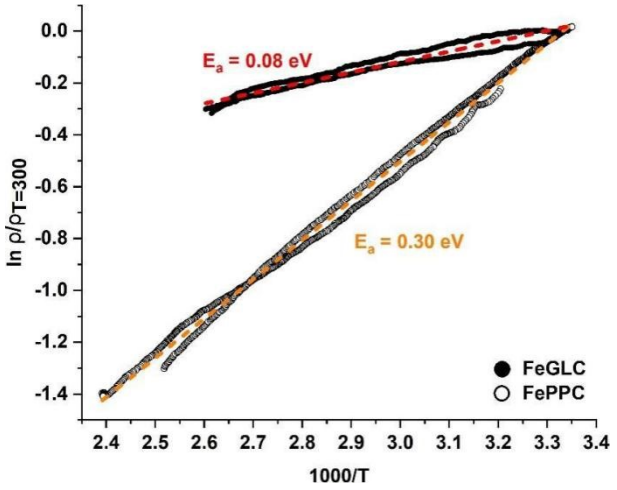

Figure 4. Temperature dependence of electrical resistance of FePPC and FeGLC powders. The points were recorded both during heating and cooling of the samples. The approximation was carried out for all points (dash lines).

Table 2. Band gap energy values (eV) from absorption spectra fitting (for suspension deposited on quartz) and from resistivity measurements (for powders)

	Tauc fitting (film from suspension)	Two-piston (powder)
FePPC	0.28 (water)	0.30 (“water”)
FeOPC	0.50 (pentanol)	----
FeGLC	0.00	0.08

Estimation of band gap by two separate methods confirms the semiconductor nature of FePPC: 0.30 eV from the temperature dependence of the electrical resistance of the sample in powder form (see Figure 4) and 0.28 eV from the absorption spectra in the UV-IR-NIR bands by fitting the experimental data with the Tauc model for samples deposited on quartz glass from suspension (see Figure S2). The band gap of the carbonized sample was close to 0.0 eV. Thus, this material shows transport properties close to metallic type.

The conductivity of conjugated phthalocyanine structures strongly depends on the conditions of their preparation and metal content. Nevertheless, it is noticeable that polymers have almost always several orders of magnitude better conductivity compared to the corresponding oligomers.[32] For example, the resistance of OPC is ~10^2 Ohm/m higher than for PPC.[33] The band gap also decreases markedly, especially for metal-doped compounds. Metal content has a higher impact on the conductivity than on the band gap.

For applications in printable electronics, of special interest are materials with relatively large conjugated macromolecules, such as FePPC and FeGLC. These materials show distinctly different electrophysical properties: FePPC has a pronounced semiconducting conductivity, while FeGLC is close to metal; also, FeGLC has much higher conductivity. Both these materials contain iron atoms, and both of them can be processed into stable aqueous suspensions.

Conclusions

We synthesized three fundamentally different iron-containing types of materials: mononuclear phthalocyanine (FeOPC), polyphthalocyanine (FePPC), and graphene-like material (FeGLC). All of them can be processed into dispersions. The band gaps, estimated from temperature-dependent conductivity measurements, and from optical absorbance, show consistent results: ~0.5 eV for FeOPC, ~0.3 eV for FePPC, and close to 0 eV for Fe-GLC. These 2D materials are promising candidates for printable electronics and spintronic devices.

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