Порфиразины
Porphyrazines

Макрогетероциклы
http://macroheterocycles.isuct.ru

Статья
Paper

Multilayer Photovoltaic Structures Based on Tetrathiadiazoloporphyrazine/Subphthalocyanine Heterojunction

Pavel A. Stuzhin,[a] Maxim S. Mikhailov,[a] Vlad V. Travkin,[b] Evgeny Yu. Gudkov,[b] and Georgy L. Pakhomov[b,@]

[a]*Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russia*
[b]*Institute for Physics of Microstructures, Russian Academy of Sciences, 603950 Nizhny Novgorod, Russia*
[@]*Corresponding author E-mail: pakhomov@ipmras.ru*

Multilayered thin-film structures incorporating a planar junction of two molecular semiconductors, subphthalocyanine (SubPc) and iron tetrakis(1,2,5-thiadiazolo)porphyrazine (FeTTDPz) were fabricated using vacuum evaporation technique. Photovoltaic properties of such structures were tested. The open circuit voltage measured under illumination was equal to 0.4 V indicating that FeTTDPz may readily be used in planar heterojunction photovoltaic cell as n-type semiconductor, instead of conventional acceptor fullerene.

Keywords: Tetrathiadiazoloporphyrazine, iron, subphthalocyanine, photovoltaic cell.

Introduction

Progress in molecular electronics is tightly coupled with design of new semiconducting molecular compounds and their introduction in full-organic or hybrid devices, *e.g.*, field-effect transistors (OFET), photovoltaic cells (OPVC), light emitting diodes, *etc*. Tetrakis(1,2,5-thiadiazolo)porphyrazines (TTDPz) are analogs of widely used in molecular electronics phthalocyanines; their synthesis was first reported ~15 years ago by Ercolani and Stuzhin.[1] Despite structural similarity with phthalocyanines, there are important distinctions,[2] that may stimulate a more intensive research on TTDPz complexes as materials for (opto-)electronic applications. Firstly, introduction of π-electron-deficient thiadiazole rings instead of benzene rings leads to downward shift in energy positions of frontier molecular orbitals as compared with phthalocyanine compounds[3] (Figure 1a), which gives rise to negative sign of majority charge carriers.[4,5] Secondly, appearance of large peripheral sulfur atoms causes certain peculiarities in mutual arrangement of molecules in the bulk.[5-8] Third, there are no H-atoms in metallo-TTDPz complexes, so there is no hydrogen bonding, which is responsible for many distinct features of molecular solid.

Very recently, *n*-type conductivity of several TTDPz compounds was proved by measurements in OFET,[5-7] in sandwich cells with different work function electrodes[7] and invertors,[9] theoretical considerations have also been reported.[5] Since phthalocyanine-like compounds are mostly *p*-type, opposite sign is often desired when manufacturing OPVC with planar or bulk *p-n* heterojunctions, as alternative to commonly used acceptor fullerene.[10,11] In this work we report on first, to our knowledge, prototype of OPVC with a planar heterojunction based on TTDPz complex. Corresponding energy level diagram is shown in Figure 1a. For comparison, the HOMO/LUMO values for C_{60}, by various estimates, are in the range of 6.2/3.6 eV (see, literature cited in Refs. [10,11,13-15])
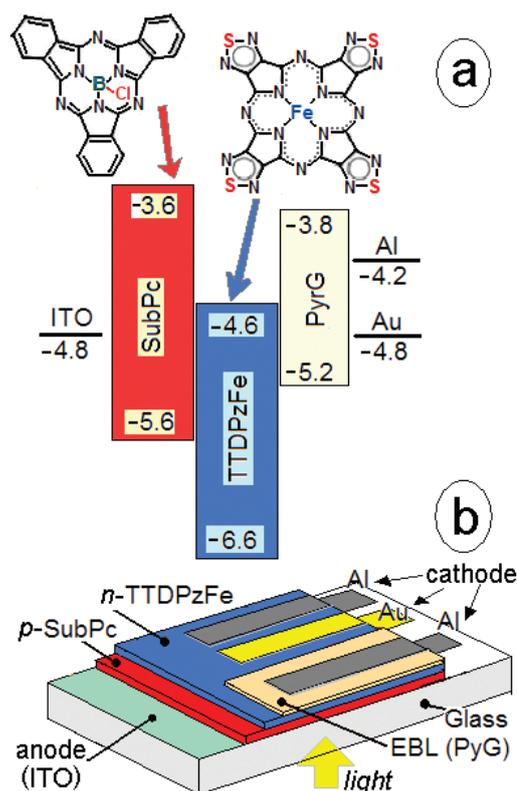
Figure 1. Energy diagram with molecular structures of SubPc and FeTTDPz (a) and schematic of OPVC (b) used in this work. The energy values (HOMO/LUMO levels for molecular and work functions for inorganic materials, in eV) are adopted from Refs.[1,7,10-15]

Experimental

Iron(II) tetrakis(thiadiazolo)porphyrazine (FeTTDPz) was synthesized as described elsewhere.[1b] Boron subphthalocyanine

chloride (SubPc) was purchased from Aldrich and used as received. SubPc was chosen as a *p*-type organic semiconductor[12-15] with appropriate energy band structure (Figure 1a) and optical properties (Figure 2). Its successful application in the planar heterojunction OPVC is described in the literature.[14,15]

The simple non-optimized single junction OPVC were fabricated using standard vacuum evaporation technique by depositing thin layers of SubPc, FeTTDPz and top cathode, in that order, onto pre-cleaned glass/ITO substrate (anode) kept without intentional heating.[12,13] Thickness of layer was 35, 35 and 80 nm, respectively. Schematic of samples is shown in Figure 1b. Three types of cathode materials were tested: Au, Al and Al with pre-deposited 8 nm thick pyronine G (PyG) as exciton blocking layer (EBL) – see, Figure 1b. Details of the sample preparation and testing can be found in Refs.[12,13] (and literature cited therein). The active device area (set by the area of top electrode – Figure 1b) was ~0.03 cm^2.

A non-contact profilometer TalySurf CCI2000 by Taylor&Hobson (white light interferometry) was used to check the uniformity and roughness of molecular layers. The optical spectra in the UV/Vis/NIR domain were measured using a home-made spectrometer based on MRD-41 (LOMO) monochromator inter-faced with a lock-in amplifier and computer. FT-IR spectra were recorded using InfraLum FT-801 (Lumex) spectrometer. X-ray diffraction spectra were obtained with Bruker D8 Discover diffractometer (Cu-Kα irradiation) equipped with Ge (220) mono-chromator, as 2θ scan in grazing incidence geometry (@ 0.5°).

For (photo-)electrical measurements, the samples were placed into a shielded steel chamber filled with pure argon to minimize atmospheric exposure and kept in the dark for at least 12 hrs before testing. Illumination from a 25 W tungsten lamp with deflector provided incident light power on the sample surface P_{in} equal to 25 mW/cm^2 (measured by a broadband IMO-4 detector). Current density-*vs*-voltage (*J-V*) plots were obtained using a Keithley 4200-SCS instrument in the range of DC bias potentials +2 ÷ -2 V for sandwich-type cells and +15 ÷ -15 V for planar cells with interdigitated contact pattern, in dual sweep mode. Sweeping rate was quiet, since we intended to avoid possible hysteresis effects and to maintain a steady-state regime.

Results and Discussion

At first, structural characterization of the vacuum sublimed single-layer FeTTDPz thin films was carried out. When dealing with evaporation of heavy volatile macro-cyclic metal complexes, there is often a risk of partial destruction during high-temperature resistive heating or deposition in strongly nonequilibrium conditions. On the other hand, such vacuum deposited layers may possess some interesting features in arrangement of molecules with respect to each other, or to the substrate.[6,7,13]

Optical absorption measurements confirmed that FeTTDPz can successfully be sublimed under moderate vacuum (<10^{-3} Pa) at temperatures around 500°C forming continuous layers without serious damage of molecular composition. Films are grayish-blue, with relatively smooth surface: RMS roughness (Sq) is equal to 0.8 nm in 1 mm^2 window for a 90 nm thick FeTTDPz film deposited on ITO/glass substrate, which is in ~1 mm^2 window, which is less than typical Sq of phthalocyanine films deposited in similar conditions. This is consistent with observation of other authors[6,7] that TTDPz films have a rather smooth surface.

The Figure 2*A* shows the UV/Vis/NIR spectra of FeTTDPz thin film on a quartz glass substrate (curve *2*, green line). Fundamental π-π* electronic transitions of porphyrazine π-chromophore, such as Soret band (diffused through 330-380 nm) and *Q*-band (peaked at ~660 nm) are clearly seen. Less intensive band at ~500 nm arises from charge transfer transition typical of Fe^{II} porphyrazines. [16] All bands are much broader than for SubPc film (curve *1*, pink line). This broadening can be ascribed to poorly resolved Davydov splitting originating from interaction of molecular chromophores and other specific intermolecular interactions between FeTTDPz molecules, which exist in solid film. It was demonstrated by X-Ray work[8] that FeTTDPz in the crystal state forms coordination polymers due to intermolecular Fe…N(thiadiazole) interaction with considerable π-π-overlap between porphyrazine π-systems in the neighboring chains. Interestingly, that the spectrum of FeTTDPz recorded in a DMF solution (Figure 2*B*, curve *3*, green line) is also characterized by broad absorption bands and is very similar to the spectrum of the thin solid film (Fugure 2*A*, curve *2*, green line). This indicates that similar aggregation effects are observed in thin films and in solution. The spectrum of FeTTDPz in the monomeric form having narrow *Q*-band absorption (Figure 2*B*, curve *4*, blue dashed line) was possible to register only when the sample was first dissolved in one drop of concentrated H$_2$SO$_4$ to destroy intermolecular coordination interactions and then diluted with large amount of DMF.

It should be noted that XRD patterns (not shown here) do not reveal ordering in packaging of FeTTDPz molecules in thin film. This is similar to recently reported data[6] for a cone-shaped VOTTDPz derivative, which also forms amorphous layers during vacuum sublimation. Note, however, that earlier Miyoshi *et al.* obtained highly oriented films for other (planar) TTDPz compounds.[6,7] Generally
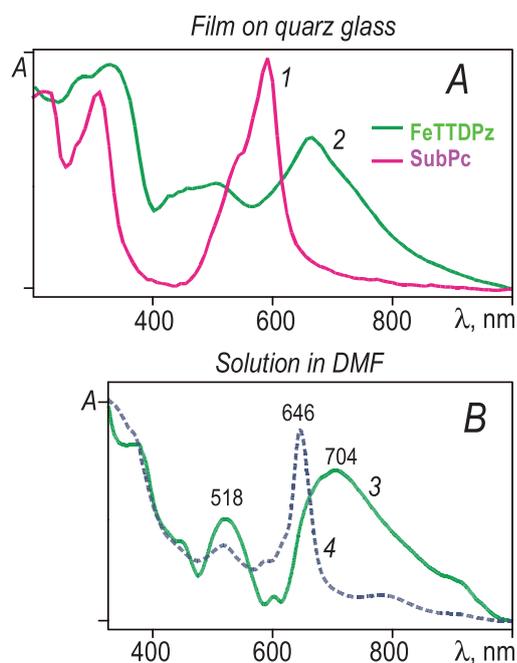
Figure 2. Optical absorption spectra in the UV/Vis/NIR range: *A* - thin (100 nm) vacuum sublimed films of SubPc (*1*, pink line) and FeTTDPz (*2*, green line); *B* – solution of FeTTDPz in DMF – aggregated form (*3*, green line) and monomeric form (*4*, blue dashed line).

speaking, absence of crystallinity in our case may be caused by different deposition rate (here – 0.1 nm/s), substrate material or temperature. Furthermore, freshly made TTDPz crystals may absorb some quantities of water from ambient, so that weakly bound water molecules may modify long-range order of molecules with time.[1b] XRD spectrum of SubPc underlayer also suggests amorphous structure.

FT-IR spectra (500-5000 cm^{-1}) of sublimed film show characteristic vibration bands that conform to those of initial FeTTDPz in KBr pellet – Figure 3. Most intensive bands can be assigned[2] to stretching vibrations: ~1530 ($v_{C=N(meso)}$), ~1334 and 1260-1265 ($v_{C=C}$ and $v_{C=N}$ of thiadiazole), 1114-1120 ($v_{C=N}$ of pyrrole), 770-760 (v_{SN}) cm^{-1}, as well as to the out-of-plane deformation of macrocycle (~685 cm^{-1}).
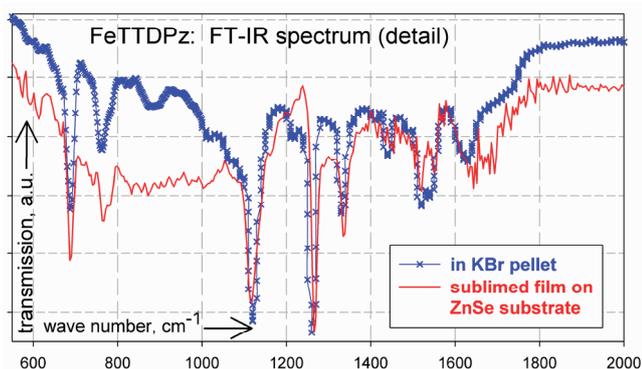

Figure 3. Optical transmission spectra of FeTTDPz in the infrared: thin vacuum sublimed film (red line) and pressed KBr pellet FeTTDPz (blue line with crosses).

Next, FeTTDPz films were deposited on insulating Al_2O_3 substrate with interdigitated Cr contacts to estimate their resistivity and photosensitivity. It was found out that specific conductivity (σ) of FeTTDPz layer is in order of $2 \cdot 10^{-11}$ Ohm$^{-1} \cdot$cm^{-1} (@ 25°C). Thermal activation energy of conductivity E^{act} is equal to 0.7 eV in the range of 360-460 K (calculated from eq.: $\sigma = \sigma_o \cdot \exp(-E^{act}/2kT)$. Ratio of photocurrent to the dark current is fairly low as compared to phthalocyanines, and particularly to SubPc. Thus a minor contribution of photogenerated charge carriers to the photovoltaic effect in OPVC is expected from FeTTDPz side.[4] Additionally, for simple single-layer sandwich cells ITO/FeTTDPz/Metal (Metal=Al,Au), the asymmetry of J-V plots was stronger in the case of Au contact reflecting existence of a Schottky barrier to the n-type FeTTDPz semiconductor. [7]

Finally, the completed multilayer OPVC ITO/SubPc/FeTTDPz/cathode were subjected to (photo-)electrical testing. As follows from Figure 4, diode properties in the dark depend markedly on the cathode material (ITO electrode is positively biased). The best rectification ratio *RR,* that is ratio of currents under forward to reverse bias, was obtained with PyG/Al cathode ($RR > 10^4$ @ 1.5 V), owing to the lower current density in the reverse direction (Figure 4).

When exposed to the light, the cells generate an output electrical power, which manifests itself by displacement of curves from the point of origin on the J-V plot (Figure 4). Basic photovoltaic parameters are collected in Table 1. Here, fill-factor was calculated as $FF = (U_{mpp} \cdot J_{mpp})/(U_{oc} \cdot J_{sc})$, where
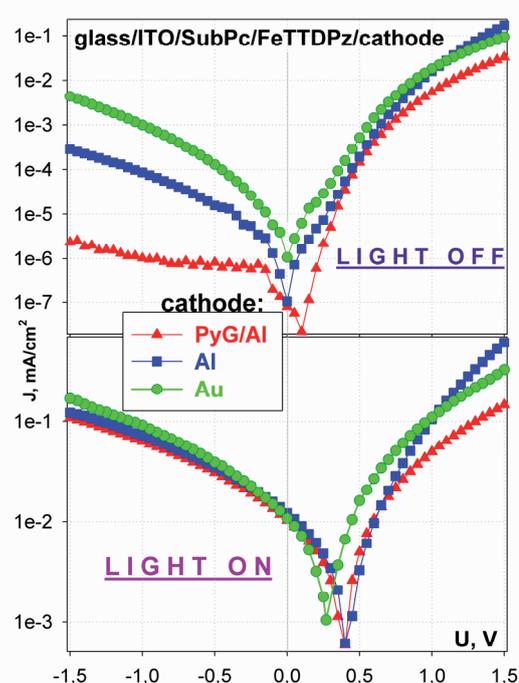
Figure 4. J-V plots for OPVC with different cathodes in the dark (top) and under illumination (bottom).

U_{mpp} and J_{mpp} are the current and the voltage of the maximum power point, respectively. Power conversion efficiency (CPE) was calculated as $CPE = (FF \cdot U_{oc} \cdot J_{sc})/P_{in}$.[10-15]

Table 1. Photovoltaic parameters of OPVC with SubPc/FeTTDPz heterojunction and different cathode materials (see, also Figure 4)

Parameter → Cell ↓	U_{oc} (V)	J_{sc}, (mA/cm^2)	FF	CPE (%)
SubPc/FeTTDPz/Au	0.29	0.010	0.20	0.003
SubPc/FeTTDPz/Al	0.42	0.012	0.25	0.007
SubPc/FeTTDPz/PyG/Al	0.38	0.010	0.26	0.006

As follows from Table 1, better values are achieved with Al cathode, mainly due to greater short circuit current J_{sc}, and open circuit voltage U_{oc}, with almost no effect of PyG interlayer. Lower values of U_{oc} and FF in case of Au may be explained by a barrier at Au/TTDPz contact.[7] Efficiencies (CPE in Table 1) of the thus obtained cells are very low, which is not surprising for OPVC without optimization of the layer thickness, heterojunction morphology, optical scheme *etc*. Optimization of technology in necessary in the future for eliminating parasitic resistances (and thus improving fill-factor) and for increasing J_{sc} values by using appropriate hole and electron transporters, optical spacers *etc*.[10,11]

Though no especial care was taken on maintaining oxygen(water)-free conditions, the cells degraded less notably than their full analogs with SubPc/C_{60} heterojunction. There was very little dispersion of parameters between several OPVC samples in the batch, which implies good reproducibility and stability of devices made with FeTTDPz compound.

Conclusions

In this work we have fabricated and demonstrated the working prototype of thin film OPVC with planar heterojunction employing iron(II) tetrakis(thiadiazolo)-porphyrazine as *n*-type semiconductor for the first time. Introduction of a new class of phthalocyanine-like macroheterocyclic complexes in junction would be an advantage over the well-known fullerenes, since it opens new possibilities in varying the cell's optics, transport properties and heterojunction morphology.

References

1. (a) Stuzhin P.A., Bauer E.M., Ercolani C. *Inorg. Chem.* **1998**, *37*, 1533-1539. (b) Bauer E., Cardarilli D., Ercolani C., Stuzhin P.A., Russo U. *Inorg. Chem.* **1999**, *38*, 6114-6120. (c) Donzello M.P., Agostinetto R., Ivanova S.S., Fujimori M., Suzuki Y., Yoshikawa H., Shen J., Awaga K., Ercolani C., Kadish K.M., Stuzhin P.A. *Inorg. Chem.* **2005**, *44*, 8539-8551. (d) Donzello M. P., Fujimori M., Yasuhito M., Yoshikawa H., Viola E., Awaga K., Ercolani C. *J. Porphyrins Phthalocyanines*, **2010**, *14*, 343.
2. Donzello M.P., Ercolani C., Stuzhin P.A. *Coord. Chem. Rev.* **2006**, *250*, 1530-1561.
3. Donzello M.P., Ercolani C., Kadish K.M., Ricciardi G., Rosa A., Stuzhin P.A. *Inorg. Chem.* **2007**, *46*, 4145-4157.
4. Schlettwein D., Karmann E., Oekermann T., Yanagi H. *Electrochim. Acta*, **2000**, *45*, 4697-4704.
5. Cai X., Zhang Y.-X., Qi D.-D., Jiang J.-Z. *Science in China Series B: Chemistry* **2009**, *52*, 840-848.
6. Miyoshi Y., Takahashi K., Fujimoto T., Yoshikawa H., Matsushita M.M., Ouchi Y., Kepenekian M., Robert V., Donzello M.P., Ercolani C., Awaga K. *Inorg. Chem.* **2012**, *51*, 456-462.
7. Miyoshi Y., Fujimoto T., Yoshikawa H., Matsushita M., Awaga K., Yamada T., Ito H. *Organ. Electron.* **2011**, *12*, 239-243.
8. Suzuki Y., Fujimoto T., Yoshikawa H., Awaga K. *Chem. Eur. J.* **2004**, *10*, 5158-5164.
9. Walzer K., Maennig B., Pfeiffer M., Leo K. *Chem. Rev.* **2007**, *107*, 1233-1271.
10. Mishra A., Bauerle P. *Angew. Chem., Int. Ed.* **2012**, *51*, 2020-2067.
11. Fujimoto T., Miyoshi Y., Matsushita M., Agawa K. *Chem. Commun.* **2011**, *47*, 5837-5839.
12. Pakhomov G., Travkin V., Bogdanova A., Guo T.-F. *J. Porphyrins Phthalocyanines* **2008**, *12*, 1182-1186.
13. Pakhomov G.L., Travkin V.V., Tropanova A.N., Geudkov E.A. *Semiconductors+* **2012**, *accepted*.
14. Pandey R., Gunawan A.A., Mkhoyan K.A., Holmes R.J. *Adv. Func. Mat.* **2012**, *22*, 617-624.
15. (a) Beaumont N., Cho S.W., Sullivan P., Newby D., Smith K.E., Jones T.S. *Adv. Funct. Mater.* **2012**, *22*, 561–566. (b) Gommans H., Cheyns D., Aernouts T., Girotto C., Poortmans J., Heremans P. *Adv. Funct. Mater.* **2007**, *17*, 2653-2658.
16. Stuzhin P. A., Homborg H. *Koord. Khim.* **1997**, *23*, 666-671 (Russ). [*Russ. J. Coord. Chem.* **1997**, *23*, 623-628 (Eng.)]