Construction of barrier heterostructures based on carbon and organometallic compounds

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Abstract. This paper presents the results of using hybrid-organic zinc complex C_{24}H_{24}N_6O_3Zn as a component for creating fullerene C_{60}-based heterostructures. The synthesis technique of the complex compound, the microscopy of the film surfaces obtained, their optical and luminescence properties are described in the paper. The introduction of zinc complex to fullerene shows that there occurs a potential barrier at the active layer interface. The obtained thin-film structures have rectifying light volt-ampere characteristics.

1. Introduction

Organic molecules and complex compounds based on them have aroused great interest in researchers for the past decades, largely due to their possible application in the development of high-performance organic light emitting diodes (OLEDs) [1–2], as well as all kinds of optical and photovoltaic devices (lasers, sensors, etc.) [3–4]. Among a wide range of different classes of luminescent materials, hybrid organometallic compounds containing functional emissive ligands represent a new class of luminescent materials [5–6], which are of particular interest because of their accessibility, low manufacturing cost and low toxicity [7]. Schiff-based hybrid organic Zn (II) complexes have been acknowledged as materials with strong photoluminescent properties with high brightness of ~1000 cd/m² [8]. On the other hand, fullerene has proven to be a relatively strong acceptor [9], whose use as a carrier layer can improve the electrical performance of organic light emitting diodes (OLEDs) [10].

There being little and insufficient information on the use of zinc complexes based on Schiff ethylenediamine for organocarbon heterostructures in literature sources, we decided to make an attempt at creating a barrier heterostructure based on fullerene C_{60} and zinc compounds N,N’-ethylaminebis[1-phenyl-3-methyl-4-formylimino-2-pyrazoline-5-ol] - PMFP (C_{24}H_{24}N_6O_3Zn).

2. Synthesis and application

The synthesis of the coordination compound was carried out according to the procedure similar to the one described in [11–12]. 1,2-ethylenediamine (120 mg, 2 mmol) was added dropwise during 10 min to 30 ml of ethanol solution of 4-methyl-1-phenyl-4-formylpyrazol-5-one (808 mg, 4 mmol). The resulting mixture was stirred and heated to 120 °C for 1 hour. Then, zinc acetate dehydrate (438 mg, 2 mmol) was added, and the reaction mixture was heated for 2 h. The resulting solution was cooled to room temperature. The white precipitate was filtered off and washed with EtOH (2 × 5 mL). The washed product was recrystallized from
methanol to form colourless small crystals. [Yield: 522 mg (51%) based on 1,2-ethylenediamine]. The chemical formulae of the ligand and PMFP are shown in the insertions in figure 2(a).

The formation of film structures from starting powders of PMFP and C₆₀ was carried out by the method of irrigation from solution onto substrates [13–14]. Chloroform (CHCl₃) was used as a solvent for the hybrid material, and for the fullerene we used the following solvents: non-aromatic: dichloromethane (CH₂Cl₂), chloroform (CHCl₃), tetrachloromethane (CCl₄), and aromatic: toluene (C₆H₅CH₃), benzene (C₆H₆). The concentration of the starting substance in the solution was 0.5 mg/ml. After thorough mixing and observing the residence time of at least 48 h at room temperature, the obtained suspensions were applied on dielectric and conductive substrates. The volume of the applied solutions was fixed at 1 ml. Cover glasses with dimensions of 18×18 mm were used as dielectric substrates. Indium tin oxide (ITO), with resistivity of 16-18 Ω/sq, and aluminium thin films, obtained by vacuum deposition on sitall, with high homogeneity, low roughness with resistivity equal to 20 Ω/sq were used as a contact group to measure conductivity characteristics. The geometric parameters of the conductive substrates were 10×10 mm.

3. Surface microscopy
The surface topography and volumetric inhomogeneities of the organic thin-film compounds under study were analysed by transmission and reflection microscopy using a LOMO Mii-4M microinterferometer (figure 1).

![Figure 1](image)

*Figure 1.* Microscopy of organic ligand thin films – (a); organometallic PMFP – (b); C₆₀ in toluene – (c); C₆₀ in benzene – (d); C₆₀ in dichloromethane – (e); C₆₀ in chloroform – (f); C₆₀ in tetrachloromethane – (g).

Primary analysis of the film surfaces showed a variety of shapes and objects formed during the self-assembly process. For example, on the surface of the ligand film (figure 1(a)), cells with diameters from 5 to 30 μm were found. The thickness of the film itself was about 2-4 μm. The introduction of Zn to the original organic ligand structure made it possible to obtain more uniform films with a thickness of ~ 5-6 microns (figure 1(b)). Carbon films obtained using toluene (C₆H₅CH₃) are characterized by "branched" formations up to 38 μm long. At the same time the thickness does not exceed 500 nm (figure 1(c)). The use
of benzene (C₆H₆) as a solvent for C₆₀ resulted in rectangular microstructures of a uniform shape. The average length of the microstructures was 46 μm, their widths ranging from 5.7 to 9.8 μm and heights being about 3 μm. It is also worth noting that the film was characterized by the low degree of surface homogeneity (figure 1(d)). The fullerene film deposited using dichloromethane (CH₂Cl₂) was characterized by surface inhomogeneity and the presence of "star-like" structures formed by self-assembly. The length of some sides of the "stars" reached 43 μm at a height of about 2-3 μm (figure 1(e)). The next group of samples obtained using chloroform (CHCl₃) as a solvent was distinguished by the presence of "diamond-shaped" structures and a low degree of film surface homogeneity. Diameters of individual formations averaged 12.5 μm, and the area of the largest microstructures reached 96 μm² at a height of about 6 μm (figure 1(f)). On the other hand, samples deposited using carbon tetrachloride (CCl₄) show relative homogeneity. However, it is worth noting the presence of agglomerations measuring 23.6 μm. The thickness of such films was approximately 6 μm (figure 1(g)).

Based on all of the above mentioned, we can conclude that the nature of the solvent significantly affects the morphology of carbon films.

4. Optics and luminescence

Luminescence spectra of the organic ligand and PMFP were analysed using the "FluoroMax-4" instrument. To identify the optimum maximum value of excitation radiation, the standard technique of pulsed excitation, in which multiple irradiations of the working layers of organic film structures are performed, was used. Considering the parameters of excitation maxima, luminescence spectra were measured [15]. Extremes of PMFP luminescence spectra were recorded in the range of 390-400 nm, in contrast to the original organic ligand, where the maxima of luminescence spectra were not recorded at all (figure 2(a)).

![Figure 2](image-url)

Figure 2. Luminescence spectra (a), optical absorption spectra (b) and optical bandgap width (inset, figure b) of hybrid organic films, where (1) - PMFP, (2) - organic ligand.

The electrodynamics, transmission, reflection and absorption coefficients in the visible range were determined using a GBC Cintra 4040 spectrophotometer. A distinctive feature of this instrument is the presence of a dual monochromator in the Czerny-Turner configuration. A tungsten lamp and a deuterium
lamp were used as radiation sources. This resulted in an incident light range of 190 to 900 nm, with the slit width of 0.1-2 nm. A blank substrate was used as a normalising basis (figure 2(b)). The analysis of the absorption spectra showed the presence of a double peak at 320-350 nm for the organic ligand. PMFP samples had a discernable absorption peak at 300-320 nm. With further increase in wavelengths from the blue 440 nm to the red spectral range a general drop in the absorption coefficient is traced, the spectral dependence is linear.

Taking into account the similarity of the optical range frequency dependences, we should assume the existence of an optical slit in the experimental samples. Assuming that the main transitions between the valence and conduction bands are indirect resolved transitions, according to the Tauc formula, we take the power factor m equal to two [15, 16]:

\[
\alpha \sim \frac{1}{h\nu}(h\nu - E_g)^m,
\]

where \(\alpha\) is the absorption coefficient; \(h\nu\) is the energy of an optical quantum; \(E_g\) is the bandgap width of the material. In this case, the optical bandgap width of the organic ligand is 3.03 eV; of PMFP – 2.85 eV (inset, figure 2(b)).

5. Electrical characteristics

The electrical characteristics of the film structures of the organic ligand, the PMFP-zinc compound as well as the ITO-PMFP-C\(_{60}\)-Al heterostructures were studied by analyzing the volt-ampere characteristics. The use of indium tin oxide as a transparent contact is accounted for by the fact that the electronic work function in ITO is comparable to that of polymers, providing an ohmic contact with organics. All measurements were carried out in the voltage range from -5 to 5 V.

The ligand films showed a non-linear but symmetrical volt-ampere characteristics (VAC) at reverse currents of -3.8 pA and forward currents of 4 pA, in its turn, the zinc complex was characterised by a non-linear and non-symmetrical VAC, with a maximum current of 1.79 nA (figure 3(a)). No change in the conductive properties of the ligand and PMFP was observed when exposed to electromagnetic radiation in the optical range.

To form the heterojunction, the zinc PMFP complex was deposited on ITO, and fullerene C\(_{60}\) was deposited on an aluminum substrate. Due to the variety of solvent types used for the initial fullerene solutions, five modifications of PMFP- and C\(_{60}\)-based heterostructures were formed. After a series of measurements of the dark characteristics, all the barrier samples were irradiated with the LED matrix. Figure 3(b - f) shows the dark and light volt-ampere characteristics of ITO-PMFP-C\(_{60}\)-Al heterostructures.
Figure 3. (a) Volt-ampere characteristics of PMFP (1) and organic ligand (2) as well as light (3) and dark (4) VAC of ITO- PMFP-C60-Al heterostructures where fullerene films were obtained using: (b) toluene, (c) benzene, (d) dichloromethane, (e) chloroform, (f) tetrachloromethane.

The maximum increase in conducting properties during irradiation of heterostructures is observed in the sample whose fullerene film was obtained from C60 solution in dichloromethane. Thus, with a dark current of 44.9 nA and irradiation of the structure with 0.12 μA, the current increase was 2.76-fold. For a heterostructure based on fullerene dissolved in tetrachloromethane, the current increase was 2.08-fold. For modifications based on fullerene dissolved in chloroform, there was less than 1.5 times the current increase and for toluene and benzene, the current increase was less than 1.2 times.

6. Conclusion
Thus, the spectral characteristics of the optical range, as well as luminescent and conductive properties of the obtained samples have been considered. The analysis of the surface of carbon films shows a variety of morphologies of self-assembled structures under the influence of different solvents. Maximum absorption in the optical range for the PMFP compound is observed in the range of 300-320 nm. The resulting coordination compound has luminescent properties and over-emits in the range of 390-400 nm, unlike the original organic ligand. As a result of the calculation of the optical bandgap width, it has been shown that the change in the molecular structure of the original ligand by doping with a zinc molecule is accompanied by a decrease in this parameter by 0.18 eV. A potential barrier resulted from the addition of the PMFP coordination compound to the thin film structure of fullerene C60 only in the case when the latter was deposited using dichloromethane which allowed changes in the yield work, the potential barrier giving non-linearity of the I-V characteristics. Nowadays there are a lot of interpretations of the conductivity mechanisms in organic structures. One of the most acceptable one, in our opinion, is the hopping nature of the charge carrier transfer, but this issue requires additional research.

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References

[1] De Bettencourt-Dias A 2007 *Dalton Transactions* **22** 2229

[2] Kim S, Bae H J, Park S, Kim W, Kim J, Kim J S, Jung Y, Sul S, Ihn S-G, Noh C et al 2018 *Nature Communications* **9**(1) 1211

[3] Amgar D, Aharon S and Etgar L 2016 *Advanced Functional Material* **26**(47) 8576–93

[4] Pashaei B, Karimi S, Shahroosvand H, Abbasi P, Pilkington M, Bartolotta A, Fresta E, Fernandez-Cestau J, Costa R D and Bonaccorso F 2019 *Chemical Society Reviews* **48** 5033–139

[5] Wang S 2001 *Coordination Chemistry Reviews* **215**(1) 79–98

[6] Xu H, Chen R, Sun Q, Lai W, Su Q, Huang W and Liu X 2014 *Chemical Society Reviews* **43**(10) 3259–302

[7] Minei P, Fanizza E, Rodríguez A M, Muñoz-García A B, Cimino P, Pavone M and Pucci A 2016 *RSC Advances* **6**(21) 17474–82

[8] Gusev A N, Kiskin M A, Braga E V, Chapran M, Wiosna-Salyga G, Baryshnikov G V, Minaev B F, Ivaniuk K and Stakhira P et al 2019 *The Journal of Physical Chemistry C* **123**(18) 11850–59

[9] Gusev A N, Mazinov A S, Shevchenko A I, Tyutyunik A S, Gurchenko V S and Braga E V 2019 *Technical Physics Letters* **45**(10) 997–1000

[10] Mazinov A S, Tyutyunik A S, Gurchenko V S and Ilyina V Yu 2020 *Rensit* **12**(3) 361–8

[11] Gusev A, Shul'gin V, Braga E, Zamnius E, Kryukova M and Linert W 2020 *Dyes and Pigments* **183** 108626

[12] Gusev A, Braga E, Tyutyunik A, Gurchenko V, Berezovskaya M, Kryukova M, Kiskin M and Linert W 2020 *Materials* **13**(24) 5698

[13] Gusev A N, Mazinov A S, Tyutyunik A S and Gurchenko V S 2019 *Rensit* **11**(3) 331–6

[14] Mazinov A S, Tyutyunik A S and Gurchenko V S 2020 *Applied Physics* **2** 64

[15] Gusev A N, Mazinov A S, Tyutyunik A S, Fitaev I Sh, Gurchenko V S and Braga E V 2021 *Technical Physics* **66**(1) 84–92

[16] Tan S T, Chen B J, Sun X W, Fan W J, Kwok H S, Zhang X H and Chua S J 2005 *Journal of Applied Physics* **98** 013505