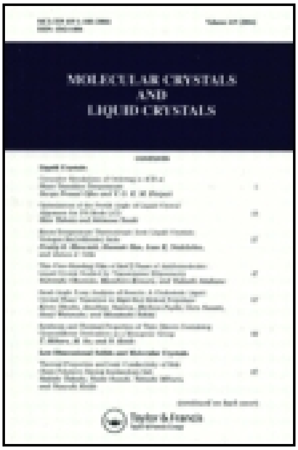

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Formation and Electrical Properties of Metal/Organic Semiconductor/Si Heterostructures Based on Naphthalene Diimide-Based Compounds

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We report on the synthesis of two naphthalene diimide-based organic derivatives: POANT containing electronically isolated 1,4,5,8-naphthalenetetracarboxylic diimide units and FCAND – a low-molar-mass compound with two different (fluorenone and 1,4,5,8-naphthalenetetracarboxylic diimide) electron-accepting units. Initial decomposition temperatures of 305°C and 390°C were indicated for FCAND and POANT, respectively. Organic semiconductor/Si heterostructures have been prepared by using spin coating (POANT, PEPK) and thermal evaporation in vacuum (FCAND). All heterojunctions demonstrated nonlinear I-U *dependences and defined rectifying properties. The Schottky thermoionic emission model has been applied to explain the carrier transport and to estimate the barrier height and the ideality factor* n *of heterojunctions.*

Keywords: naphthalene diimide; organic-inorganic heterostructure; Schottky thermoionic emission

1. INTRODUCTION

Organic semiconductors (OS) provide new promising possibilities for cheap, low-weight, mechanically flexible, chemically interactive, and bottom-up fabricated electronics [1]. During the last decade,

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considerable progress has been made in the fabrication of new electronic and optoelectronic devices containing organic materials and particularly hybrid organic-on-inorganic semiconductor heterojunctions. Optical and electronic properties of such hybrid device structures may be altered either by introducing new combinations of organic and inorganic semiconductors or changing the composition and preparation conditions of OS films. The other advantage of organic materials is the relatively simple and low-temperature processing of their thin films through inexpensive techniques such as thermal evaporation, drop-casting, and spin coating.

A number of hybrid heterojunctions with the thin layer of an organic semiconductor deposited onto the surface of an inorganic semiconductor substrate such as Si and GaAs have been reported recently by various authors. Nonlinear current-voltage characteristics with rectifying property similar to that of the ideal *p*-*n* junction have been demonstrated.

In this work, we report on the synhesis of two organic materials: polymer containing electronically isolated 1,4,5,8-naphthalenetetracarboxylic diimide units and a low-molar-mass compound with two different (fluorenone and 1,4,5,8-naphthalenetetracarboxylic diimide) electron-accepting units, and focus on the preparation and comparative study of metal/organic semiconductor/Si heterostructures based on thin films naphthalene diimide-based organic materials and poly[9-2,3-epoxypropylcarbazole] (PEPK) which is oligomeric *p*-type semiconductor. Highly doped *n*- and *p*-type silicon substrates were used as the inorganic counterpart of heterojunctions.

Current-voltage characteristics of the heterostructures were measured to study the electrical properties of heterojunctions and to check their applicability to the fabrication of novel device structures.

2. EXPERIMENTAL

2.1. Synthesis of the Organic Semiconductors

Poly{N,N′-bis-[2-(oxiran-2-ylmethoxy)-5-tert-amylphenyl]-1,4,5,8 naphtalenetetracarboxylic diimide-alt-4,4′-thiobisbenzenethiol} (POANT) has been obtained via the nucleophilic reaction of bifunctional naphthalene diimide with 4,4′-thiobisbenzenthiol (see Fig. 1). 0.13 ml (0.9 mmole) of triethylamine were slowly added at room temperature to the solution of 1 g (14.2 mmole) of preliminarily synthesized N,N′-bis-[2-(oxiran-2-ylmethoxy)-5-tert-amylphenyl]-1,4,5,8-naphtalenetetracarboxylic diimide **(2)** and 0.357 g (14.2 mmole) of 4,4′-thiobisbenzenethiol in 25 ml of dry THF. Mixture of the reaction

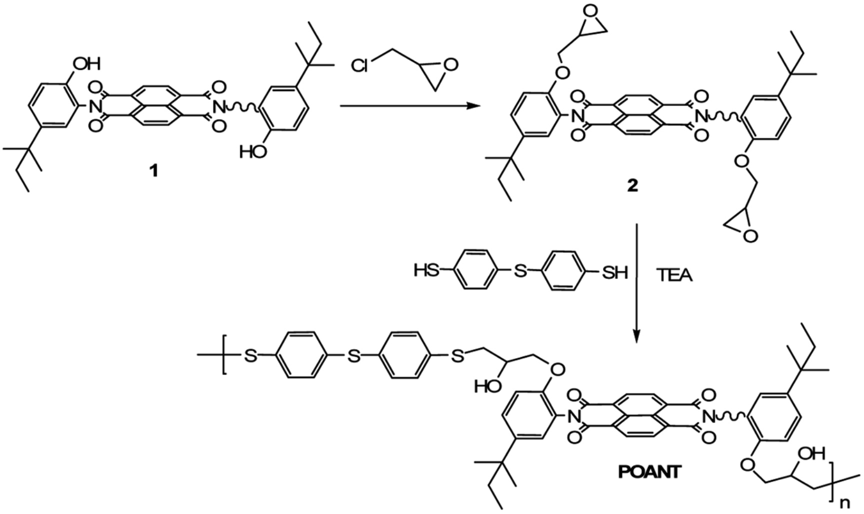

FIGURE 1 Synthetic route to monomer **2** and POANT.

was kept over night at a reflux temperature. The obtained product was isolated by precipitation into diethyl ether. The precipitate was subjected to chromatography (silica gel) using THF as an eluent. Finally, 0.66 g (49%) of brownish powder was obtained.

N,N′-Bis-[2-(oxiran-2-ylmethoxy)-5-tert-amylphenyl]-1,4,5,8 naphtalenetetracarboxylic diimide (**2**) was obtained by the reaction of N,N′-bis-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphtalenetetracarboxylic diimide (**1**) with 3-chloro-1,2-epoxypropane. 7.05 g (0.0127 mole) of N,N′-bis-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphtalenetetracarboxylic diimide (**1**) was dissolved in 130 ml of 3-chloro-1,2-epoxypropane at 120°C. Catalytic amount of benzyltriethylammonium chloride was added to the reaction mixture, and it was stirred for 2 h at a reflux temperature. In following, 3-chloro-1,2-epoxypropane was removed by vacuum distillation, and the crude product was washed with plenty of diethyl ether. Yield of yellowish powder was 6.2 g (69%) (FW = 702 g/mole). A small part of the product was purified by column chromatography (silica gel) using the mixture of diethyl ether/toluene = 1/1 as an eluent (m.p.: 265–266°C).

The other materials, namely, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4′-thiobisbenzenethiol, and 9-fluorenone-4-carbonyl chloride were purchased from “Aldrich” and used as-received without further purification, while N,N′-Bis-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphtalenetetracarboxylic diimide (**1**) was synthesized according to the procedure published by Chong Yong *et al.* [2].

N,N'-bis-[2-(9-fluorenone-4-carboxylate)-5-tert-amylphenyl]-1,4,5,8 naphtalenetetracarboxylic diimide (**FCAND**) was prepared by the reaction of 9-fluorenone-4-carbonyl chloride with N,N′-bis-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphtalenetetracarboxylic diimide (**1**) in the presence of pyridine as a catalyst (Fig. 2). In an oven–dried, 250 mL, two–necked, round–bottomed flask equipped with a magnetic stir bar was placed N,N′-bis-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphtalenetetracarboxylic diimide (**1**) (1.71 g, 2.9 mmole) and pyridine (0.4 g, 5.3 mmole) in 50 ml of dry dioxane in an nitrogen atmosphere. 9-Fluorenone-4-carbonyl chloride (1.6 g, 6.6 mmole) was added to the stirred reaction mixture heated subsequently up to 70°C and stirred for 48 h. The reaction mixture was concentrated, and 200 ml of methyl alcohol was added to the flask. The crude product was precipitated, filtered, and purified by column chromatography (silica gel) using the mixture of diethyl ether/toluene = 1/3. As a result, 0.5 g of yellow crystals (17%) (m.p.: 343–344°C, FW = 1003 g/mole) have been obtained.

The third organic semiconductor, namely, **poly[9-(2,3-epoxypropyl)carbazole] (PEPK)** has been received from Biolar (Latvia). It was prepared by the anionic polymerization of 9-(2,3-epoxypropyl) carbazole and purified by adsorption chromatography [3].

Infrared (IR) spectra of various compounds were recorded using a Perkin Elmer Spectrum GX in KBr pellets. The proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained using a Varrian Unity Inova (300 MHz). All the data are given as chemical shifts in (ppm), integration downfield from $(CH_3)_4$ Si. The mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). Thermogravimetric analysis was carried out using Netzsch STA 409 with a data acquisition system 414/1. All the measurements were performed under a nitrogen gas flow (75 cm^3 min^{-1}) at a heating rate of 10°C/min /min and temperatures ranging from 30 to 650°C. Differential scanning calorimetry was carried out with Perkin–Elmer Diamond DSC, with heating/cooling rates of 10°C/min.

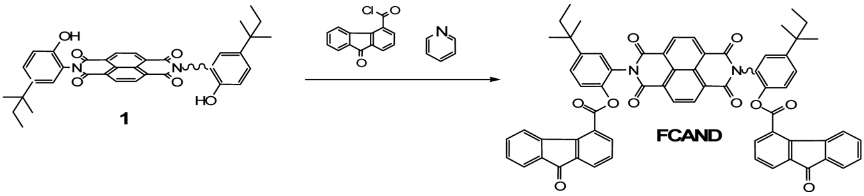

FIGURE 2 Synthetic route to FCAND.

2.2. Preparation of Hybride OS-Si Heterostructures

All the OS-Si heterostructures were formed either on highly doped *n*- and *p*-type Si(111) wafers with a resistivity of about 0.01 Ωcm and 0.05 Ωcm, respectively. The Si substrates were cleaned in an ultrasonic bath using acetone, trichloroethylene, and deionized water. The silicon dioxide layer with a thickness of about 0.2 μm has been grown onto a top of the substrates by wet oxidation. In following, an array of windows with area $2 \times 2\,\mathrm{mm}^2$ was opened in the oxidized substrates by the standard photolithography technique and the subsequent HF etching.

The POANT and PEPK overlayers ($d = 100 \div 500\,\mathrm{nm}$) were prepared onto the patterned substrates by the standard spin coating technique (rotation speed–5000 rpm for 60 s) using 5% and 1.5% chloroform solutions, respectively, followed by drying for 2 h at 60°C in air. Meanwhile the FCAND films ($d = 100 \div 300\,\mathrm{nm}$) were thermally evaporated in vacuum ($p \approx 4 \times 10^{-6}\,\mathrm{Torr}$) onto non-heated Si substrates mounted at a distance of 10 cm from a crucible.

Finally, metallic (Ag or Au) electrodes were thermally evaporated onto the masked polymer films for electrical measurements, one attached to the backside of the silicon substrate being used as a bottom electrode. Typical active area of the as-prepared hybrid organic-on-inorganic semiconductor heterojunction devices was $4\,\mathrm{mm}^2$.

Surface morphology of the prepared OS films was studied by atomic force microscopy (AFM) while their thickness (*d*) was measured by a DECTAC profilometer. Chemical compositions of the films were investigated by X-ray photoelectron spectroscopy method (XPS) employing a KRATOS ANALYTICAL XSAM-800 spectrometer and using nonmonochromatized Al K_α radiation ($h\gamma = 1486.6\,\mathrm{eV}$) as an excitation source. Surface atomic concentrations of the films were calculated using the KRATOS DS800 software from the appropriate peak area. Surface charging effects for all detailed spectra were corrected assuming that the carbon C 1*s* peak is at the 284.75-eV position.

Current-voltage (*I*-*U*) dependences of the prepared heterostructures containing various OS layers were measured at $T = 290\,\mathrm{K}$ to investigate electrical properties of the heterojunctions and to elucidate electrical properties of the organic compounds.

3. RESULTS AND DISCUSSION

The structures of all intermediate organic compounds and the target derivatives were confirmed by ^{1}H NMR, IR spectroscopies. Low–molar–mass compounds were characterized by mass spectrometry. The average molecular weight of the polymers was determined by size exclusion chromatography. The data obtained are summarized in Table 1.

Thermal properties of low and high molar mass compounds have been studied by employing DSC and TGA techniques. The characteristic temperatures of a glass transition (T_g) and the initial decomposition (T_{ID}) of the materials are summarized in Table 2.

It follows from Table 2 that high molar mass derivative POANT shows higher T_g value as compared with that of PEPK. This difference is, probably, caused by the rigidity of naphthalene diimide chromophore. It can be seen from Table 2 that POANT and FCAND are characterized by relatively high initial decomposition temperatures. The highest T_{ID} value of 390°C has been indicated for FCAND. High thermal stability of this compound may be understood taking the presence of rigid ester linkages into account.

AFM surface images of the prepared organic PEPK, POANT, and FCAND films are displayed in Figures 3a–c, respectively. The FCAND films thermally evaporated onto *n*-type Si substrates demonstrated the relatively smooth surface with a uniform grain size of about 30 nm and a surface roughness of about 2.7 nm. At the same time, the POANT and PERK films prepared by spin coating on *p*-type Si showed the unusually smooth surface (surface roughess was of about 0.28 and 0.24 nm, respectively). This difference in surface morphology may be understood taking the amorphous state of both POANT and FCAND films and the crystalline state of PEPK films into account.

Figure 4 shows the wide XPS spectra of POANT, FCAND, and PEPK films. A certain constant number of counts per second was added to the POANT and PEPK spectral data to overcome the overlapping of the data points in the plot.

The surface atomic concentrations of the films are presented in Table 3. A small disagreement between the experimental and theoretical film compositions can be explained by assuming a possible influence of atmospheric contaminants.

The prepared hybrid organic-on-inorganic semiconductor heterojunctions demonstrated nonlinear *I-U* dependences and clearly defined rectifying properties. Figure 5 shows the voltage-current characteristic measured for the heterostructure containing of a *p*-type

TABLE 1 SEC Analysis Data

Polymer	M_n	M_w	M_w/M_n
POANT	5070	18800	3.7
PEPK	1200	1400	1.15

TABLE 2 Thermal Characteristics of Naphthalene Diimide-Based Organic Materials

Compound	T_m, [°C][a]	T_g, [°C][a]	T_{ID}, [°C][b]
PEPK	—	78	300
POANT	—	152	305
FCAND	341	—	390

[a] Determined by DSC, scan rate 10°C/min, N_2 atmosphere.
[b] Onset of decomposition determined by TGA, heating rate 10°C/min.

PEPK layer and the electrically doped Si substrate. Meanwhile, Figure 6 demonstrates *I-U* plots obtained for *n*-(FCAND, POANT)/*p*-Si heterostructures. Linear regions of forward bias *I-U* plots at low voltages ($U < 0.3\,\mathrm{V}$) expressed on the semilogaritmic scale show that the heterojunctions behave like a Schottky (metal/semiconductor) contact. One can expect the existence of a potential barrier between the organic and inorganic semiconductor interface. Thus, we assume that the thermionic emission over the OS/Si interface is the dominating charge transport mechanism at low current densities.

The vertical carrier transport in the heterostructures has been modeled within a model based on Schottky thermoionic emission. The current flowing through the uniform metal–semiconductor interface due to the thermionic emission in the case of the forward bias voltage can be expressed as [4]

$$I = I_0\left[\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1\right], \tag{1}$$

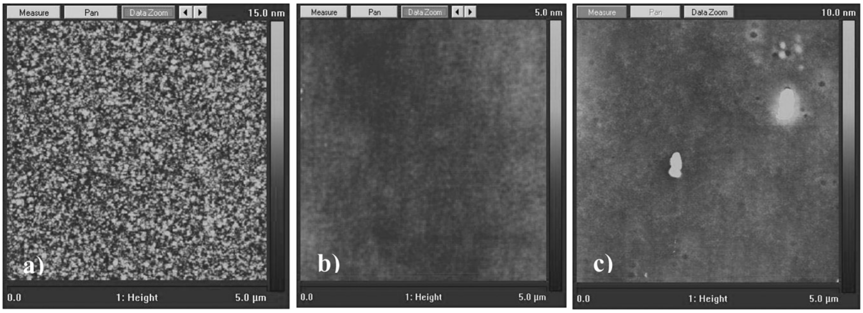

FIGURE 3 Morphology of the AFM surface images of organic films on Si substrates: (a) PEPK film ($d = 0.3\,\mu\mathrm{m}$) prepared by thermal evaporation in vacuum, POANT ($d = 0.3\,\mu\mathrm{m}$) (b) and FCAND ($d = 0.3\,\mu\mathrm{m}$) (c) films prepared by spin coating.

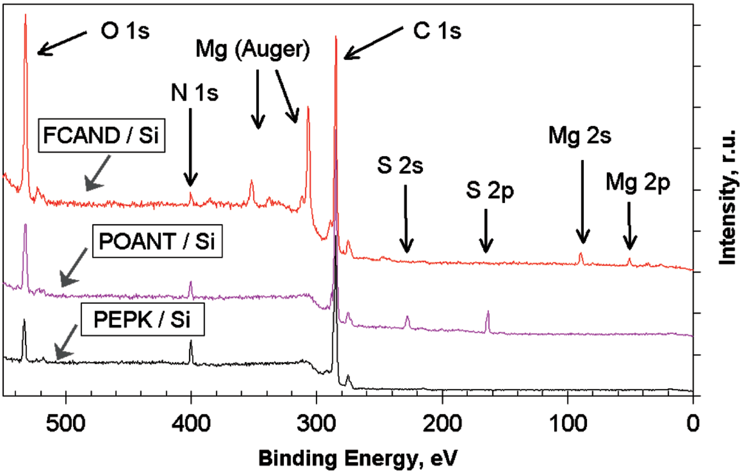

FIGURE 4 Wide XPS spectra of POANT, FCAND and PEPK films on a Si substrate.

where q is the electron charge, U is the forward bias voltage, n is the ideality factor demonstrating a deviation of the experimental I-U data from the ideal thermionic model ($n = 1$ for an ideal contact), T – the absolute temperature, R_s is the series resistance, and I_0 is the saturation current (derived from the straight line intercept of ln I at $U = 0$) expressed by

$$I_0 = AA^*T^2 \exp\left(-\frac{q\Phi_{b0}}{kT}\right), \tag{2}$$

where A is the effective diode area, k is the Boltzmann constant, A^* – the effective Richardson constant ($A^* = 32.0$ and $112\,\mathrm{A\,cm^{-2}\,K^{-2}}$ for

TABLE 3 Atomic Concentrations of the POANT, FCAD and PEPK Films Calculated from the XPS Data. Theoretical Values Corresponding to the Chemical Formula of the Compounds are Displayed in Brackets for Comparison

Element and spectral line	POANT (%)	FCAND (%)	PEPK (%)
O 1s	13.2 (11.59)	25.1 (13.16)	7.7 (5.88)
N 1s	3.2 (2.90)	1.8 (2.63)	6.0 (5.88)
C 1s	81.6 (81.16)	73.1 (84.21)	86.3 (88.24)
S 2p	2.0 (4.35)	–	–

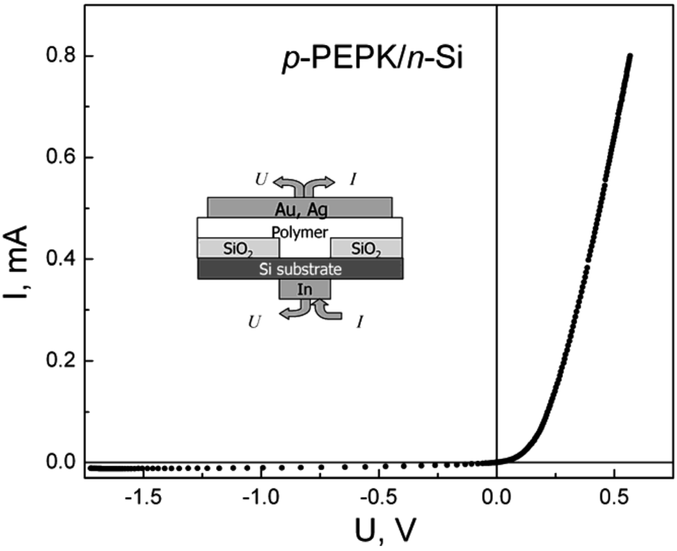

FIGURE 5 Typical current versus voltage dependence measured for a PEPK/n-Si heterojunction at 290 K. Schematic view of the sample is shown in the inset.

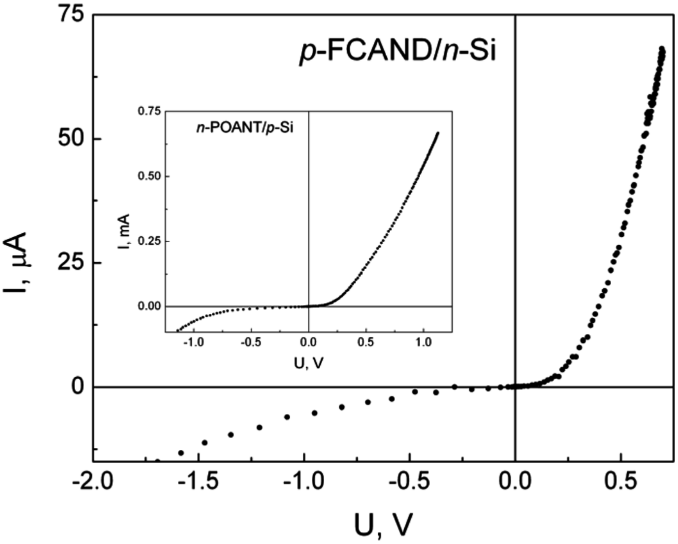

FIGURE 6 Current – voltage characteristics measured at 290 K for the FCAD/p-Si and POANT/p-Si (in the insert) heterojunctions.

TABLE 4 Major Electrical Parameters of the POANT/*p*-Si, FCAND/*p*-Si, and PEPK/*n*-Si Heterostructures Derived from the *I-U* Plots

Organic material	FCAND	POANT	PEPK
Substrate	*p*-Si	*p*-Si	*n*-Si
Thickness, nm	300	120	340
Roughness (rms), nm	2.7	0.28	0.24
Ideality factor *n*	3	2.9	2
Barrier height Φ_{b0}, eV	0.70	0.66	0.60
Saturation current density J_0, A/cm^2	2^*10^{-7}	1^*10^{-6}	2^*10^{-6}

p- and *n*-type Si, respectively), and Φ_{b0} is the activation energy (the zero-bias barrier height).

The experimental values of the barrier height Φ_{b0} and the ideality factor *n* were determined from the intercept and slope of the linear portion from the forward bias ln *I* versus *U* plots. The averaged values of the parametes estimated for various heterojunctions are summarized in Table 4.

In conclusion, we have carried out the synthesis of two naphthalene diimide-based organic derivatives: polymeric POANT containing electronically isolated 1,4,5,8-naphthalenetetracarboxylic diimide units and FCAND – a low-molar-mass compound with two different (fluorenone and 1,4,5,8-naphthalenetetracarboxylic diimide) electron-accepting units. The initial decomposition temperatures of 305°C and 390°C have been indicated for FCAND and POANT, respectively. At the first time, three different organic semiconductor on Si heterostructures have been prepared by using spin coating (POANT/*p*-Si, PEPK/*n*-Si) and thermal evaporation in vacuum (FCAND/p-Si). The prepared heterojunctions demonstrated nonlinear *I-U* dependences and clearly defined rectifying properties. A model based on Schottky thermoionic emission has been applied to explain the carrier transport and to estimate the barrier height, ideality factor *n*, and series resistance of the heterojunctions.

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