ISSN 1392–1320 *MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 3. 2015*

Study of Optical and Electrical Properties of Organic Thin Films for Photovoltaic Applications

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crossref http://dx.doi.org/10.5755/j01.ms.21.3.7278

Received 25 September 2014; accepted 07 February 2015

The paper deals with the study of optical, electrical and dielectric properties of thin film organic materials suitable for the preparation of optoelectronic devices (e.g. photodiodes, phototransistors, photovoltaic cells). As active layers palladium phthalocyanine (PdPc[t-Bu]$_4$), fullerene (acceptor material, PCBM) and their mixture (9 : 5 mass %) were used. Thin films were prepared by two methods: by spin coating (Chemat technology Spin Coater) and by material inkjet printing (Dimatix Materials Printer DMP-2800). UV-VIS spectroscopy and ellipsometry were used to study the optical properties. The paper also presents results of electrical and dielectric measurements. We found out that the properties of all structures prepared by spin coating depend on the rotational speed of spin coater, on the mode of solution casting (static, dynamic) and in the case of material inkjet printing they are too much influenced by the substrate. Samples prepared on the substrate at 60 °C showed a photovoltaic effect with fill factor about 0.25 and the conversion efficiency about 0.2 %.

Keywords: material inkjet printing; spin coating; layer thickness; complex refractive index; DC and AC properties.

1. INTRODUCTION

We have witnessed a rapid development of electrical and dielectric applications of organic semiconductors in recent years [1]. In addition to the traditional fabrication methods such as vacuum evaporation, new wet-coating methods are constantly being introduced (e.g. doctor blade coating, electrophoretic deposition, spray coating and material printing [2 – 5]). Layers prepared by these methods do not yet reach the high quality of vacuum methods, but they will play an important role in the future for their technological simplicity and low cost of production. The key problem of printing materials lies in the different surface energy of substrates (e.g. indium tin oxide (ITO), polyethylene terephthalate (PET), glass) but also in the quality of printed material on its own (e.g. titanium dioxide (TiO_2), diketopyrrolopyrrole (DPP), phthalocyanine (Pc), fullerene PCBM). In particular, the second problem is related to the solubility of the raw materials and their purity, deterioration rates, resp. reliability of the fabricated electronic components. Optical methods for measuring of the thickness and optical homogeneity (e.g. refractive index) can provide information about the reasons for electronic component functionality and quality. Effects of film thickness on optical and electrical properties of similar structures have been investigated recently [6, 7].

Phthalocyanines are phthalocyanine complexes with the central atom (Cu, Pd, Ni, Fe, Zn and so on). Their advantages include their catalytic activity, light stability, heat stability (do not show rapid degradation up to 400 °C) and resistance to solvents. They are used as pigments, and also in gas sensors, catalysts for fuel cells, photosensitizers in photodynamic cancer therapy, magnetic imaging of tumours, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFET), solar cells, spintronics and magnetic switches [8].

For organic semiconductors, charge separation and charge mobility is limited and therefore it is necessary to add an acceptor, such as PCBM, that there was a very rapid photoinduced charge transfer between the donor, acceptor and organic semiconductor. Then, the optimal solution is the mixing of donor and acceptor to form a heterojunction [9].

Thus, the aim of this work is to study optical, electrical and dielectric properties of thin film organic materials, i.e. palladium phthalocyanine PdPc[t-Bu]$_4$ (PdPc), fullerene PCBM and their mixture (9 : 5 mass %), especially the influence of layer preparation on such properties. All these material can be used e.g. in organic photovoltaic devices (organic solar cells have been reviewed [10, 11]).

To study optical properties (e.g. complex refractive index, complex permittivity) the UV-VIS spectroscopy and the ellipsometry were applied, while electrical and dielectric properties were evaluated by using of impedance spectroscopy and measurement of current-voltage (I-V) characteristics.

2. PREPARATION OF LAYERS

Active layers for optical measurements were prepared both by spin coating and by material inkjet printing on the special glass substrate. To prepare the structure of thin film layers for electrical measurements, only the material inkjet printer was used. Printing of active layers, i.e. PCBM, PdPc and their mixture, was carried out on the glass coated with ITO. Last layer of that sample (top Al electrode) was prepared by vacuum evaporation. The sample structure for electrical and dielectric measurement is illustrated in

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Fig. 1. The sample consists of six "identical" sandwich structures (ITO/active layer/Al).

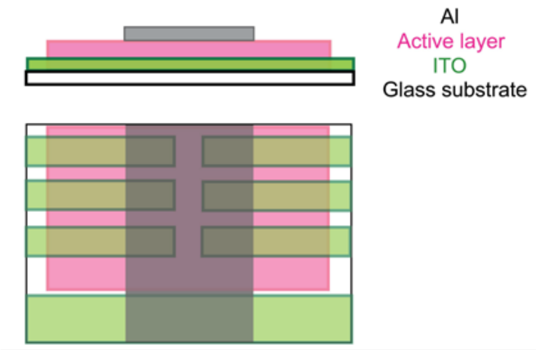


Fig. 1. Sample structure for electrical and dielectric measurement (active surface area of one sandwich structure is 6 mm^2)

The primary focus was to study the effect of preparing thin films on their optical properties, thickness and homogeneity of the surface [7]. For the samples prepared by spin coating the difference between optical properties of thin films prepared in static and dynamic mode was investigated, in the dynamic mode also the influence of rotational speed to the layer thickness and to their structure. For the layers prepared by material inkjet printing, the influence of temperature films on their optical, electrical and dielectric properties was studied (substrate temperature has influence on the formed thin film density, which is responsible for crystallographic, structural and optical properties [12]).

3. OPTICAL PROPERTIES OF LAYERS

3.1. Layer thickness

The thickness of the layers is an important parameter in terms of electrical properties, mainly due to the diffusion length, which affects the optoelectronic properties of all photovoltaic cells. The layer thickness influences the homogeneity and also the functionality of the entire electronic component.

Exciton diffusion length of polymers and pigments (organic materials) is about 10 – 20 nm [13]. Because of the absorption, layer thickness must be at least 100 nm. So, there are recombination losses – electron-hole pair (exciton) does not manage to divide [14]. It is therefore necessary to choose a compromise. The thickness must be large enough to allow it to absorb the radiation, on the other hand, the generated exciton must reach the heterojunction in order to allow the charge separation [15].

It turns out that the layer thickness of the order of tens of nanometers can be printed with a suitable quality for such applications.

The layer thickness was determined in two ways:
- directly, using mechanical profilometer measurements (Profilometer Bruker Dektakt XT) on a groove formed in a thin layer,
- non-contactly, from ellipsometric spectra (Ellipsometer UVISEL 2) based on the interference of light [16, 17].

Results of the ellipsometric measurements for the layers prepared by spin coating and by material inkjet printing are shown in Table 1. The thicknesses determined by the profilometer are given in parentheses. Deviations are caused by method of determining the thickness. Using the profilometer, the thickness of layers is determined in a particular place (see Fig. 2 c), using the ellipsometer, the thickness is averaged from the illuminated and analyzed area (spot) [16, 17].

A comparison of studied layers (PCBM) prepared by spin coating and by material inkjet printing and profile of this printed layer obtained from profilometry is presented in Fig. 2. As we can see, there are inhomogenities and some new domains in printed layer (see Fig. 2 b), which are responsible for worse properties of active layer (homogeneity of layer affects optical properties, such as ellipsometric and UV-VIS spectra – influence of light scattering, and also electrical properties – a problem with charge transfer, the individual domains are substantially greater than the exciton diffusion length).

Table 1. The results for thickness measurements of layers prepared by spin coating (static and dynamic regime) and by material inkjet printing (for different substrate temperatures)

	PdPc (nm)	PCBM (nm)	PdPc/PCBM (nm)
static	36.1 ± 0.1 (28)	20.9 ± 0.1 (16)	61.3 ± 0.3 (72)
dynamic	30.5 ± 0.2 (28)	19.3 ± 0.1 (25)	49.9 ± 0.3 (34)
30 °C	25.3 ± 0.2	16.2 ± 0.1	76.8 ± 0.4
45 °C	23.6 ± 0.2	16.0 ± 0.2	80.8 ± 0.5
60 °C	22.0 ± 0.2	11.7 ± 0.2	30.0 ± 0.2

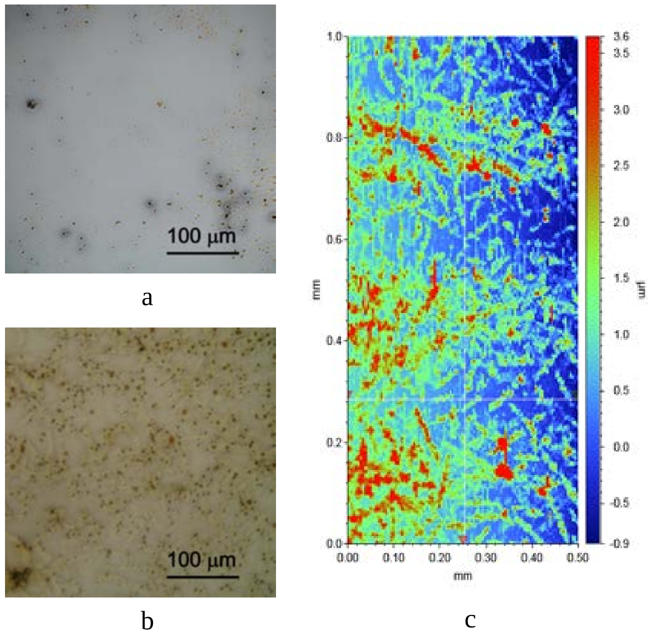
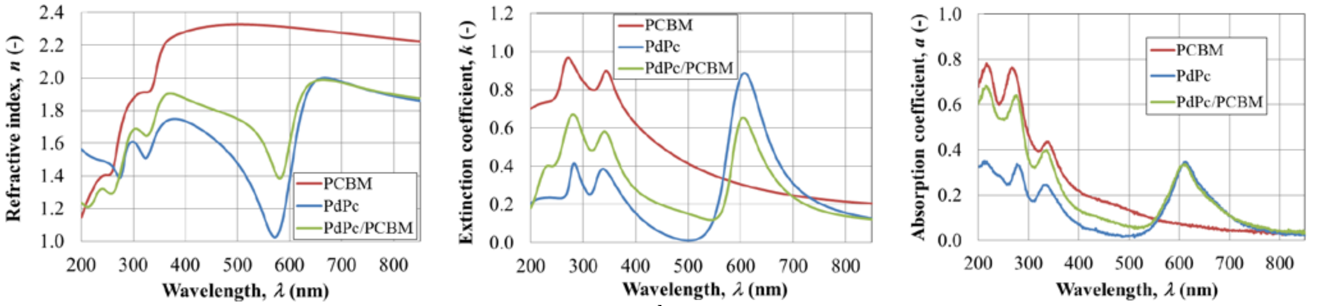


Fig. 2. Microphotography example of studied layers (PCBM) prepared by spin coating (a) and by material printing (b) and profile of this printed layer (c)

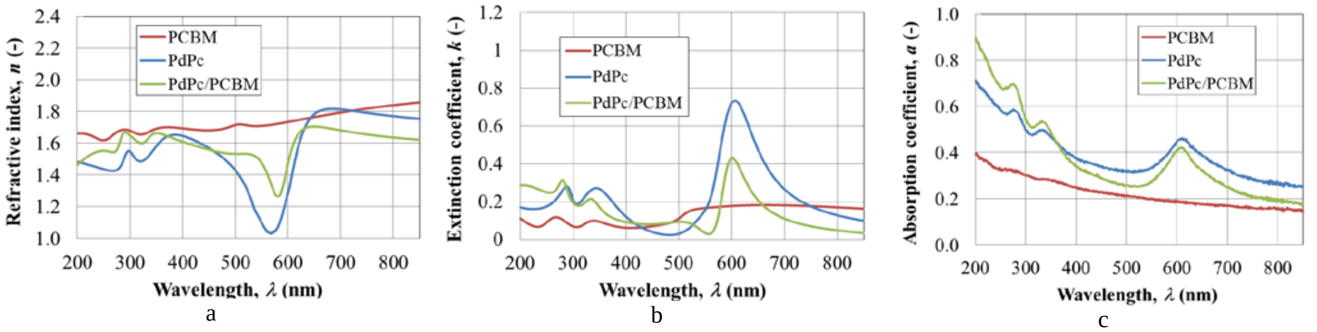
3.2. Ellipsometric and UV-VIS spectra

Ellipsometric and UV-VIS spectra provide information about the absorption edge of all electronic components, i.e. about the conversion efficiency of electromagnetic radiation (sunlight) [17].



a b c

Fig. 3. Dependence of refractive index (a), extinction coefficient (b) and absorption coefficient (c) on wavelength for PCBM, PdPc and mixture PdPc/PCBM prepared by spin coating



a b c

Fig. 4. Dependence of refractive index (a), extinction coefficient (b) and absorption coefficient (c) on wavelength for PCBM, PdPc and mixture PdPc/PCBM prepared by material inkjet printing

Expected ellipsometric model consisted of two layers: 2 mm thick glass substrate (quartz) coated with an active layer of an unknown thickness, surrounded by an optically thinner medium (void). The aim was to determine the thickness, but mainly the disperse dependence of complex refractive index of the active layer. Experimental data of refractive index and extinction coefficient comprise optical properties of all layers (void, glass substrate, active layer) including the interference phenomena in the studied structure. From these spectra the dependences of refractive index and extinction coefficient of all active layers and their thicknesses (see Table 1) were defined (due to the knowledge of optical properties of the glass and the void). Dependences in Fig. 3 represent ellipsometric and UV-VIS spectra (Transmission UV-VIS Spectrometer Varian Cary 50) for the layers prepared by spin coating (see Fig. 3), while Fig. 4 shows the characteristics for the layers prepared by material inkjet printing on the substrate heated to a temperature of 30 °C (see Fig. 4). From a comparison of all images are obvious significant differences for PCBM at which failed to print quality layer [16 – 19].

From UV-VIS spectra is obvious relatively large absorption for a short wavelength and a similar character of dependences of extinction coefficients determined by the ellipsometer, especially in the peak position. Different intensities are related to the fact that absorption spectra depend on the layer thickness, while the extinction coefficients do not. The maximum absorption occurs for both materials (PdPc, PdPc/PCBM) at about 620 nm and the absorption edge is situated at approximately 750 nm (see Fig. 3 c, resp. Fig. 4 c).

4. ELECTRICAL PROPERTIES OF LAYERS

The samples prepared on the glass substrate coated with ITO and equipped with top Al contact were characterized in terms of electrical and photoelectrical properties.

The measurement of I-V characteristics (Electrometer Keithley 6517B) and impedance spectra (Solartron SI 1260 Impedance/Gain-Phase Analyzer with Solartron Dielectric Interface 1296) during light was done under Solar Simulator LOT-Oriel LS0916 with xenon lighting 1 000 W/m^2 [19].

4.1. Current-voltage characteristics

The results for measuring of I-V characteristics in the dark and under illumination are shown in Fig. 5. Similar sample configurations have been investigated recently [20, 21]. The characteristics have a weak diode character for both voltage polarities (both measured in the dark and under illumination). The ratio of photocurrent and dark current (I_{light} /I_{dark}) defines the photoconductive properties of an active layer. From Fig. 6 it is evident that the material is really a photoconductive material (negligibly). All prepared samples showed both photoconductivity (the ratio of photocurrent and dark current is about 1.3, see Fig. 6) and weak photoelectric effect (see Fig. 7, fourth quadrant of I-V characteristic). Table 2 shows the parameters characterizing the properties of photovoltaic cell. It is quite obvious a small fill factor and a small cell performance.

4.2. Impedance spectroscopy

Impedance spectroscopy deals with the study of the frequency response of AC currents and is used to study the dielectric properties of the medium as a function of frequency. The method is widely used to characterize the electrical behaviour of systems, in which the behaviour of a whole is influenced by the amount of closely interlinked processes.

Table 2. Parameters of photovoltaic cell with volume heterojunction of PdPc/PCBM active layer (P_0 = 989 W/m^2)

	I_{light}/I_{dark}	I_{sc} (mA)	V_{oc} (V)	V_{max} (V)	I_{max} (mA)	P_{max} (mW)	FF	η (%)
9e(1)	1.47	0.131	0.2	0.1	0.061	6.06	0.233	0.153
9e(2)	1.19	0.109	0.3	0.1	0.074	7.34	0.226	0.186

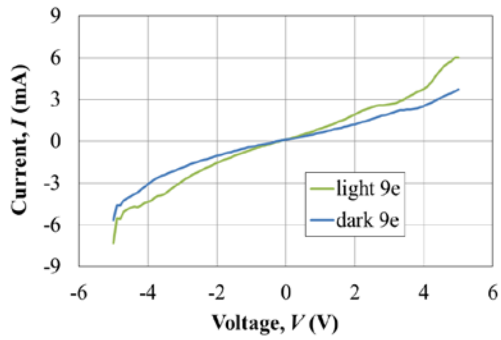


Fig. 5. Dark and light I-V characteristics of photovoltaic cell with PdPc active layer prepared by material inkjet printing

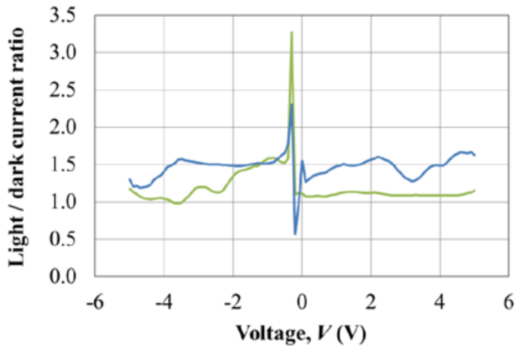


Fig. 6. Light/dark current ratio of the structure with PdPc active layer (for both voltage polarities)

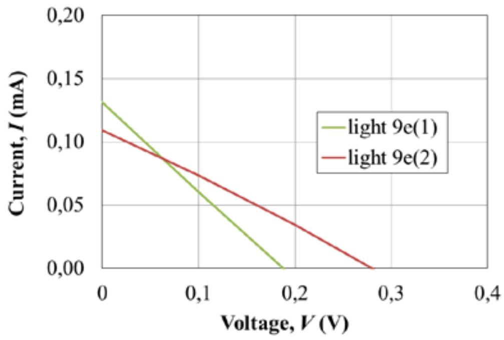


Fig. 7. Fourth quadrant of I-V characteristic of photovoltaic cell with PdPc active layer (two measurements of contact 9e)

The study of dielectric properties is very important source of valuable information about conduction processes since it can be used to understand the origin of the dielectric losses, the electrical and dipolar relaxation time and its activation energy [22].

The impedance characteristics give information about the model of electronic components, which includes both the conductivity of material and heterojunction but also parasitic capacitance, which negatively affects the conversion efficiency of the photovoltaic cell [22].

Results for the measurement of impedance spectra in the dark and under illumination are shown in next figures, the dependences of admittance magnitude (see Fig. 8) and phase shift (see Fig. 9) on frequency defined by relation

$$Y = |Y| \exp(j\varphi) = G + jB, \tag{1}$$

where $|Y| = \sqrt{G^2 + B^2}$ and $\varphi = \arctan(B/G)$, where G and $B = \omega C$ are conductance and susceptance of parallel circuit [23].

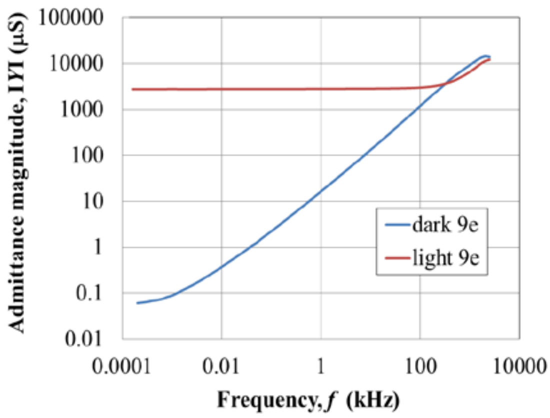


Fig. 8. Dependence of admittance magnitude on frequency for PdPc active layer (dark and light curves)

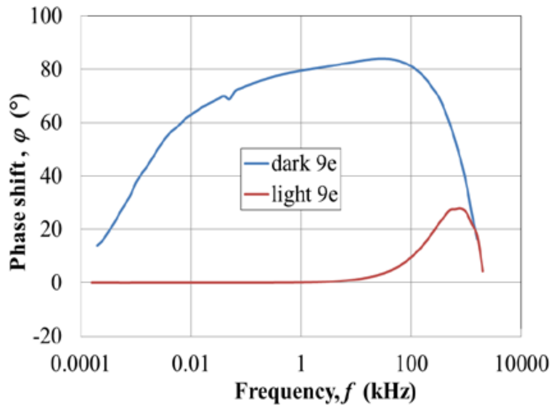


Fig. 9. Dependence of phase shift on frequency for PdPc active layer (dark and light curves)

From Fig. 8 it is evident that for low frequencies the admittance magnitude, when illuminated, is more than four orders of magnitude higher than in the dark (this material is really a photoconductive material). That is, as shown in Fig. 9, due to the changing nature of the material behaviour. While the sample measured in the dark passes from ohmic to capacitive nature since frequency 0.1 Hz (phase shift increases from zero to 90 degrees), when illuminated, it has got ohmic character up to frequency 10 kHz (phase shift is zero) and only then phase shift increases. For frequencies higher than 1 MHz both measurements do the same – phase shift decreases and admittance magnitude is approximately the same.

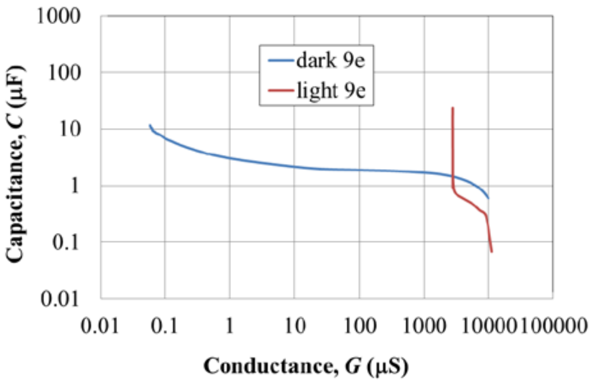


Fig. 10. Modified Cole-Cole diagram, i.e. dependence of parallel capacitance on conductance, for PdPc active layer (dark and light curves)

5. CONCLUSIONS

This complex approach to study the properties of photovoltaic cells allows us to determine all the relevant parameters of solar cells and the influence of technological processes on those qualities (it could lead to the optimization of the manufacturing process).

In the article the results for optical measurements of thin films of PdPc, PCBM and their mixture PdPc/PCBM prepared by spin coating and by material inkjet printing are presented. From these results it is evident that layers prepared using these two methods give different results for PCBM at which failed to print quality layer, while the results for PdPc and for their mixture PdPc/PCBM of both methods are the same. They only differ in the intensity of the absorption peaks. The maximum absorption occurs for both samples (PdPc, PdPc/PCBM) at about 620 nm and the absorption edge is situated at approximately 750 nm. From this perspective, both materials are not so much optimal for photovoltaic applications because the absorption maximum is achieved at relatively short wavelengths. On the contrary, absorption at higher wavelengths (about 800 nm or more) because solar light (incident to the planet surface) contains a large portion of radiation of longer wavelength is preferred.

The presented results indicate that the samples exhibit weak photoconductive behavior (photocurrent is about 1.3 times higher than of the dark current) and weak photoelectric effect (fill factor is about 0.25 and conversion efficiency during lighting 989 W/m^2 is about 0.2). It is clear that photovoltaic properties are not staggering (conversion efficiency is very low), but on the other hand, the advantage of cheap printing and increase in the conversion efficiency of the order of 10 times could lead to potential applications in consumer electronics).

AC characteristics confirm the results of DC measurements. The increase of photocurrent about four orders of magnitude (as shown in Fig. 10), as opposed to the DC measurement, is caused by Schottky barrier (at the interface of metal and semiconductor – the influence of the possible surface oxidation before a deposition of the organic semiconductor layer and metal, as well as formation of barrier inhomogeneities at the metal-semiconductor interface should be taken into account as well, see e.g. [24, 25]), which does not play an important role during AC measurements.

Acknowledgments

Authors thank to Ministry of Education, Youth and Sports of Czech Republic for support by national project COST LD14131 and for support by project Sustainability and Development REG LO1211 addressed to Materials Research Centre at FCH BUT.

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