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9,9'-Bifluorenylidene derivatives as novel hole-transporting materials for potential photovoltaic applications

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Abstract: Novel 9,9'-bifluorenylidene derivatives were designed to study the effect of alkyl chain length on selected physical properties. The structure of the synthesized compounds was confirmed by using NMR spectroscopy (¹H, ¹³C, H-H COSY, H-C HMQC, H-C HMBC) and elemental analysis. They showed high thermal stability and undergo decomposition in the range of 388-400°C. As was revealed by DSC investigations, they can be converted from crystalline to amorphous materials with relatively high glass transition temperature. The replacement of the alkyl chains from ethyl to butyl resulted in a significant negative impact on melting and glass transition temperatures. The synthesized derivatives undergo reversible electrochemical oxidation and reduction and showed a very low energy band gap (1.47 and 1.79 eV). They intensively absorb the light up 550 nm and also exhibited a week absorption band in the range of 550-750 nm. Their hole transporting ability was tested in perovskite solar cells. Additionally, the effect of the doping concentration of Li⁺ on photovoltaic device performance for these compounds was investigated. It should be stressed found that 9,9'bifluorenylidene derivative substituted with ethyl units applied as hole transporting materials in perovskite solar cells demonstrated the highest device efficiency of 7.33 % higher than of the spiro-OMeTAD utilized for preparation of the reference cell (4.40 %).

Keywords: 9,9'-bifluorenylidene derivatives, Buchwald-Hardwig reaction, electrochemistry, holes transporting materials, perovskite solar cells (PSC)

1. Introduction

Intensive technological development in the world causes a rapid increase in demand for electricity. The result is an increase in electricity prices, which affects many aspects of human life. Nowadays, most of the methods used to generate electricity are based on scarce natural resources (coal, gas and oil). These methods largely expose the natural environment to overexploitation and pollution. On the other hand, nuclear energy raises concerns of people living in the vicinity of the power plant. That is why renewable energy sources are an extremely interesting alternative. Among them, new generation photovoltaic (PV) cells deserve special attention. They allow the production of electricity without significant interference in the natural environment. Examples of such devices are perovskite (PSC) [1-10] and dye-sensitized solar cells (DSSC) [11-20]. In recent years, these types of PV devices have achieved high power conversion efficiency (PCE) and PCE of PSC and DSSC has reached 24% [2] and 14% [17], respectively. However, in their case, further, development is necessary for the field of materials creating the active layers of cells. Many examples of inorganic [9,12,16,21-23] and organic [3,6,8-10,12-13,16-17,19] chemical compounds investigated in the aspect of materials used to construct cells have been described in the literature. Special attention is paid for low molecular weight organic compounds due to many advantages such as efficient and repeatable synthesis, high purity even in industrial conditions, the welldefined structure that can be confirmed by many methods and possibility to modify properties (optical, electrochemical and even solubility) by changing functional groups or replacement of substituents [3,6,8,10,12-13,17]. Among them, organic molecules that possess hole transportation ability - p-type organic semiconductors, so called hole transporting materials (HTMs) receive much attention for applications in PV technology. They play a significant role in the regeneration of the oxidized state light absorbers and transportation of the holes to the counter-electrode both in DSSC and PCS [24-25]. Thus, HTMs can be applied as solidstate electrolyte instead of the liquid electrolyte used in the DSSC which can generate potential leakage problems limited to this technology. In 1998, first time, p-type 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'semiconductor, that is spirobifluorene known as Spiro-OMeTAD successfully replaced the conventional liquid electrolyte as the hole-transporting conductor [26]. In turn, in 2012, Spiro-OMeTAD was utilized with the perovskite resulted in a great breakthrough in PCE of PSC [27-28]. To date, Spiro-OMeTAD is the most popular organic HTM used in PSC [6-10,29] and DSSC technology [24,30]. Unfortunately, it requires a multi-step synthesis [29,31], which significantly affects its price (about 1g/\$450), and thus the cost of photovoltaic devices. Thus,

many research groups focus on the development of the new HTMs. As a cheaper alternative to Spiro-OMeTAD, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-bifluorenylidene has been presented [32]. PSC cells with such compound used as HTM exhibited high power conversion efficiency (PCE) 17.8%. Inspired by this result we have undertaken a synthesis and investigation of two new 9,9'-bifluorenylidene derivatives, such as 2,2',7,7'-tetrakis(N,Ndi-p-ethoxyphenylamine)-9,9'-bifluorenylidene (**M**-1) and 2,2',7,7'-tetrakis(N,N-di-pbutoxyphenylamine)-9,9'-bifluorenylidene (M-2) toward the replacement of the popular spiro-OMeTAD. The compounds were designed to meet general HTM requirements such as appropriate energy level in relation to the light absorber, good stability, solution processability, smooth thin layer forming capacity and low-cost and environment-friendly synthesis. The designed compounds comprising a 9,9'-bifluorenylidene core with bis(4alkoxyphenyl)amines were obtained in the Buchwald-Hartwig reaction, and their structure was confirmed by NMR spectroscopy (¹H, ¹³C, H-H COSY, H-C HMQC, H-C HMBC) and elemental analysis. Then, their thermal, electrochemical and absorption properties, from the point of view of the alkyl chains length effect, were discussed and compared with reported 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-bifluorenylidene [32]. Finally, the prepared novel 9,9'-bifluorenylidene derivatives were tested as HTM in the perovskite solar cells.

2. Experimental Section

2.1. Materials

All starting materials and chemicals were commercially available and were used without further purification. Materials, measurements and methods are available in Supporting information. 2,2',7,7'-Tetrabromo-9,9'-bifluorenylidene (**3**) was prepared according to the literature [32].

2.2. Typical procedure for the synthesis of 1-bromo-4-alkoxybenzenes (1-A and 1-B)

A mixture of 4-bromophenol (7,78 g, 45,00 mmol), potassium carbonate (31,10 g, 225,00 mmol) and 360 ml acetone stirred for 10 minutes. Next, bromoalkane (58,50 mmol) (bromoethane or 1-bromobutane) was added and the mixture was heated at reflux for 24h, under argon atmosphere. After the post-reaction mixture was filtered and the solvents were evaporated from the filtrate using a rotary evaporator. Crude product was purified using column chromatography.

1-bromo-4-ethoxybenzene (A-1)

After purification by silica gel column chromatography (hexane : ethyl acetate, 10:1), product **1-A** was obtained as colorless oil with **86**% yield. ¹**H NMR** (**400 MHz**, **CDCl**₃) δ 7.36 (d, J = 8.6 Hz, 2H, **H**^{B2}), 6.77 (d, J = 8.6 Hz, 2H, **H**^{B3}), 4.00 (q, J = 6.9 Hz, 2H, **H**^{B5}), 1.40 (t, J = 6.9 Hz, 3H, **H**^{B6}). ¹³**C NMR** (**100 MHz**, **CDCl**₃) δ 158.16 (C^{B4}), 132.30 (C^{B2}), 116.38 (C^{B3}), 112.71 (C^{B1}), 63.77 (C^{B5}), 14.83 (C^{B6}).

1-bromo-4-butoxybenzene (A-2)

After purification by silica gel column chromatography (hexane : ethyl acetate, 5:1), product **1-A** was obtained as colorless oil with **92**% yield. ¹**H NMR** (**400 MHz**, **CDCl**₃) δ 7.37 (d, J =8.5 Hz, 2H, **H**^{B2}), 6.78 (d, J = 8.4 Hz, 2H, **H**^{B3}), 3.92 (t, J = 6.4 Hz, 2H, **H**^{B5}), 1.80 – 1.73 (m, 2H, **H**^{B6}), 1.54 – 1.45 (m, 2H, **H**^{B7}), 0.99 (t, J = 7.4 Hz, 3H, **H**^{B8}). ¹³**C NMR** (**100 MHz**, **CDCl**₃) δ 158.40 (C^{B4}), 132.29 (C^{B2}), 116.42 (C^{B3}), 112.66 (C^{B1}), 68.05 (C^{B5}), 31.35 (C^{B6}), 19.33 (C^{B7}), 13.94 (C^{B8}).

2.3. Typical procedure for the synthesis of bis(4-alkoxyphenyl)amines (2-A and 2-B)

A mixture of 1-bromo-4-alkoxybenzene (40,00 mmol) (1-bromo-4-ethoxybenzene (**A-1**) or 1-bromo-4-butoxybenzene (**A-2**)), 4-alkoxyaniline (32,00 mmol) (4-ethoxyaniline or 4-butoxyaniline), potassium carbonate (14.72 g, 12.80 mmol), L-proline (1.62 g, 12.80 mmol), copper iodide (1.22 g, 6.40 mmol) and 50 ml DMSO was stirred and heated at 100° C for 48h, under argon atmosphere. After then the post-reaction mixture was quenched with distilled water and extracted with ethyl acetate. The organic phase was collected and the solvent was evaporated using a rotary evaporator. Crude product was purified using column chromatography.

bis(4-ethoxyphenyl)amine (B-1)

After purification by silica gel column chromatography (hexane : ethyl acetate, 3:1), product **2-A** was obtained as beige solid with **45**% yield. ¹H NMR (**400 MHz, DMSO**) δ 7.48 (s, 1H, H^{B0}), 6.89 (d, *J* = 8.9 Hz, 4H, H^{B2}), 6.79 (d, *J* = 8.9 Hz, 4H, H^{B3}), 3.93 (q, *J* = 7.0 Hz, 4H, H^{B5}), 1.29 (t, *J* = 7.0 Hz, 6H, H^{B6}). ¹³C NMR (**100 MHz, DMSO**) δ 152.03 (C^{B4}), 137.98 (C^{B1}), 118.02 (C^{B2}), 115.19 (C^{B3}), 63.18 (C^{B5}), 14.78 (C^{B6}).

bis(4-butoxyphenyl)amine (B-2)

After purification by silica gel column chromatography (hexane : ethyl acetate, 5:1), product **2-B** was obtained as pale brown solid with **39**% yield. ¹H NMR (**400** MHz, DMSO) δ 7.47 (s, 1H, H^{B0}), 6.89 (d, *J* = 8.9 Hz, 4H, H^{B2}), 6.79 (d, *J* = 8.9 Hz, 4H, H^{B3}), 3.87 (t, *J* = 6.5 Hz,

4H, $\mathbf{H^{B5}}$), 1.69 – 1.62 (m, 4H, $\mathbf{H^{B6}}$), 1.47 – 1.37 (m, 4H, $\mathbf{H^{B7}}$), 0.92 (t, J = 7.4 Hz, 6H, $\mathbf{H^{B8}}$). ¹³C NMR (100 MHz, DMSO) δ 152.25 (C^{B4}), 138.00 (C^{B1}), 118.04 (C^{B2}), 115.24 (C^{B3}), 67.44 (C^{B5}), 30.94 (C^{B6}), 18.78 (C^{B7}), 13.72 (C^{B8}).

2.4. Typical procedure for the synthesis of 2,2',7,7'-tetrakis(N,N-di-palkoxyphenylamine)-9,9'-bifluorenylidene (M-1 and M-2)

A mixture of bis(4-alkoxyphenyl)amine (4,00 mmol) (bis(4-ethoxyphenyl)amine (**B-1**) or bis(4-butoxyphenyl)amine (**B-2**)), 2,2',7,7'-tetrabromo-9,9'-bifluorenylidene (0,78 mmol,0,50 g), *t*-BuONa (4.60 mmol, 0,45 g) and 20 ml toluene stirred for 20 minutes, under argon atmosphere. Next, $[Pd_2dba_3]$ (0.11 mmol, 0,10 g) and Xphos (0.21 mmol, 0,10 g) were added and the mixture was heated at reflux for 24h also under argon atmosphere. After the post-reaction mixture was diluted with THF and flashed through a plug of MgSO₄. The organic phase was collected and the solvent was evaporated using a rotary evaporator. Crude product was purified using column chromatography.

2,2',7,7'-tetrakis(N,N-di-p-ethoxyphenylamine)-9,9'-bifluorenylidene (M-1)

After purification by silica gel column chromatography (hexane : THF, 5:1), isolated compound was dissolved in THF and dropped into MeOH, precipitate was collected by filtration, washed with MeOH and dried. **M-1** was obtained as pale brown solid with **59**% yield. ¹H NMR (400 MHz, THF) δ 8.02 (s, 4H, H^{A3}), 7.27 (d, *J* = 8.2 Hz, 4H, H^{A6}), 6.82 (d, *J* = 9.0 Hz, 16H, H^{B2}), 6.76 – 6.72 (m, 20H, H^{A5+B3}), 3.94 (q, *J* = 6.9 Hz, 16H, H^{B5}), 1.34 (t, *J* = 7.0 Hz, 24H, H^{B6}). ¹³C NMR (100 MHz, THF) δ 156.00 (C^{B4}), 148.16 (C^{A7}), 142.34 (C^{B1}), 140.02 (C^{A4}), 136.25 (C^{A2}), 126.62 (C^{B2}), 125.54 (C^{A1}), 121.73 (C^{A3}), 120.25 (C^{A6}), 116.08 (C^{B3+A5}), 64.28 (C^{B5}), 15.44 (C^{B6}). HRMS (ESI): calcd. for C₉₀H₈₄N₄O₈ [M]⁺ 1348.6284, found 1348.6289.

2,2',7,7'-tetrakis(N,N-di-p-butoxyphenylamine)-9,9'-bifluorenylidene (M-2)

After purification by silica gel column chromatography (toluene), isolated compound was dissolved in THF and dropped into EtOH, precipitate was collected by filtration, washed with EtOH and dried. **M-1** was obtained as brown solid with **53**% yield. ¹H NMR (**400 MHz**, **THF**) δ 8.02 (s, 4H, H^{A3}), 7.27 (d, *J* = 8.2 Hz, 4H, H^{A6}), 6.82 (d, *J* = 8.9 Hz, 16H, H^{B2}), 6.76 – 6.73 (m, 20H, H^{A5+B3}), 3.89 (t, *J* = 6.4 Hz, 16H, H^{B5}), 1.77 – 1.68 (m, 16H, H^{B6}), 1.54 – 1.45 (m, 16H, H^{B7}), 0.97 (t, *J* = 7.4 Hz, 24H, H^{B8}). ¹³C NMR (**100 MHz, THF**) δ 156.18 (C^{B4}), 148.20 (C^{A7}), 142.39 (C^{B1}), 140.06 (C^{A4}), 136.32 (C^{A2}), 126.56 (C^{B2}), 125.71 (C^{A1}), 121.97 (C^{A3}), 120.37 (C^{A6}), 116.09 (C^{B3+A5}), 68.57 (C^{B5}), 32.67 (C^{B6}), 20.34 (C^{B7}), 14.39 (C^{B8}). **HRMS** (ESI): calcd. for C₁₀₆H₁₁₆N₄O₈ [M]⁺ 1572.8788, found 1572.8767.

3. Result and discussion

3.1. Synthesis and structural characterization

The synthesis of two new 9,9'-bifluorenylidene derivatives, that is, 2,2',7,7'-tetrakis(N,Ndi-p-ethoxyphenylamine)-9,9'-bifluorenylidene and 2,2',7,7'-tetrakis(N,N-di-pbutoxyphenylamine)-9,9'-bifluorenylidene denoted as M-1 and M-2 started from preparation of the necessary substrates (Fig. 1). First, 1-bromo-4-alkoxybenzenes (A-1 and A-2) were synthesized in the reactions 4-bromophenol with bromoalkanes (bromoethane or 1bromobutane) based on the procedure described in the literature [33]. Both of these syntheses were carried out with the potassium carbonate. Acetone was used as the solvent, which is much cheaper and easier to evaporate than recommended by literature DMF [34-35] or DMSO [36-37]. The synthesized 1-bromo-4-alkoxybenzenes (A-1 and A-2) were purified by column chromatography and used in further reactions without additional purification. The procedure used proved to be extremely simple and efficient giving the yield equal 86 and 92% for A-1 and A-2, respectively. Then, bis(4-alkoxyphenyl)amines (B-1 and B-2) were obtained in reactions 1-bromo-4-alkoxybenzenes (A-1 or A-2) with 4-alkoxyanilines (4-ethoxyaniline or 4-butoxyaniline) analogous to the procedures described in the literature [33, 38]. Syntheses were carried out in the presence of potassium carbonate, L-proline and copper iodide. The use of the mentioned reagents allowed for a reduction of the reaction costs compared to the catalysts recommended in the literature [39-40]. DMSO was used as the solvent. The synthesized compounds also were purified by column chromatography. As a result of the reactions bis(4-alkoxyphenyl)amines (B-1 and B-2) were obtained with yield 45 and 39% for 2-A and 2-B, respectively.

Finally, 9,9'-bifluorenylidene derivatives (**M-1** and **M-2**) were obtained by Buchwald-Hardwig reactions bis(4-alkoxyphenyl)amines (**B-1** and **B-2**) with 2,2',7,7'-tetrabromo-9,9'bifluorenylidene (**3**) (Fig. 1). The syntheses were carried out based on the procedure described in the literature [32]. Xphos, *t*-BuONa and [Pd₂dba₃] were used as the catalytic system. The use of Xpos turned out to be easier and safer than the popular tritert-butylphosphine [41-42]. Toluene was used as a reaction medium. The reaction products were purified by column chromatography and precipitation from an alcohol solution (**M-1** – methanol, **M-2** – ethanol). In summary, synthesized derivatives were obtained with good yield (59 and 53% for **M-1** and **M-2**).



Fig. 1. The synthesis route and chemical structures of all prepared compounds

In order to better understand the structure of the 9,9'-bifluorenylidene derivatives (M-1 and M-2), they were analyzed by NMR spectroscopy (¹H, ¹³C, H-H COSY, H-C HMQC and H-C HMBC). All analyzes for M-1 and M-2 were performed in THF-d8 as solvent. NMR spectra are shown in supporting information. Signals from atoms in the core of the molecule are assigned the letter A, while atoms in substituents are assigned the letter B. In the case of ¹H NMR spectra (for both compounds), in aromatic zone we observed: singlet (8.02 ppm) from A3 protons, doublet (7.27 ppm) from A6 hydrogens, doublet (6.82 ppm) from B2 hydrogens and multiplet (6.76 – 6.72 ppm) formed as a result of overlapping signals from A5 and B3 protons. In the aliphatic zone for M-1 we can notice a quartet (3.94 ppm) from B5 hydrogen and a triplet (1.34 ppm) from B6 protons. In turn, for M-2 we observe a triplet (3.89 ppm) from B5 hydrogen, two multiplets (in the range 1.77 - 1.68 ppm and 1.54 - 1.45 ppm) from B6 and B7 hydrogen and a triplet (0.97 ppm) from B8 protons respectively. On the other hand, on the ¹³C NMR spectra, we observe a series of signals in the range from 116.08 -156.18 ppm. They are come from carbon atoms in the 9,9'-bifluorenylidene core and from carbon atoms in the phenyl rings of substituents. Moreover in the range of 14.39 - 68.57 ppm we can see signals to carbon atoms in aliphatic chains. Interestingly, the analysis of the H-C HMQC and H-C HMBC spectra allowed for a detailed assignment of the obtained signals to carbon atoms in M-1 and M-2 structures (Fig. 2). This made it possible to understand the structure of synthesized compounds given their high degree of symmetry.



3.2. Thermal studies

The thermal properties of the synthesized 9,9'-bifluorenylidene derivatives (M-1 and M-2) were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The obtained results were summarized in Table 1. The representative DSC traces during two heating scans for M-1 (in DSC measurements) are shown in Fig. 3. Upon the first heating scan, M-1 exhibited melting endotherm indicating its crystalline nature. In the case of 9,9'-bifluorenylidene derivative with butyl substituents (M-2) in DSC thermograms registered during first heating scan the glass transition temperature (Tg) before melting point was seen confirms its semicrystalline character (Fig. S2). The second heating scan, when the isotropic liquid was rapid cooled, revealed the glass transition temperature (T_g) and for M-1 exothermic crystallization (T_c) which let to obtain new crystal which melted at 268 °C. Thus, they showed behaviour typical for molecular glasses, which can provide uniform, transparent amorphous thin films contrary to low molecular weight compounds with a strong tendency for crystallization. It could be observed that modification of the alkyl chains from ethyl (M-1) to butyl (M-2) causes a significant lowering of T_m (from 288°C to 95°C) and T_g (from 132°C to 95°C). However, the replacement of ethyl with butyl group let to favour amorphous phase formation. On the other hand, the length of the alkyl chains only slightly affects the thermal

stability of the tested derivatives. The beginning of thermal decomposition determined as the temperature of 5% weight loss (T_5) was detected above 400°C with the difference between **M-1** and **M-2** being only 13°C (Fig. S3). As was mentioned similar to **M-1** and **M-2**, 9,9'-bifluorenylidene derivative with methoxy substituents, that is, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-bifluorenylidene denoted as KR216 has been reported [32]. Its thermal properties were added to Table 1 for comparison with M-1 and M-2. However, note that experiential conditions of DSC and TGA measurements are not the same. It is seen that the presence of methoxy units (KR216) increases T_m , T_g , Tc and T_5 .

In summary, it is worth emphasizing that both compounds exhibited melting point (T_m) significantly below T_5 . However, taking into account the operating temperature of devices, the presence of ethyl chains in 9,9'-bifluorenylidene derivative (**M-1**) is beneficial to obtain better thermal properties, that is higher T_m and T_g . Considering the thermal properties of the new 9,9'-bifluorenylidene derivatives it can be pointed out that compound with ethyl substituents (M-1) showed slightly higher T_5 and T_m and lower T_g compare to typical HTM spiro-OMeTAD (T_5 =388, T_m =248 and T_g =167°C [41]).

Table 1. Thermal Properties of M-1 and M-2

Cada	DSC			TGA			
Code	T _m ^a [°C]	T _g ^b [°C]	T _c ^b [°C]	T ₅ ^c [°C]	T ₁₀ ^c [°C]	T _{max} ^d [°C]	
M-1	288	132	212	401	428	445, 691	
M-2	95	89	_	388	414	435, 709	
KR216 ^[32]	309	157	228	417	-	-	

^a registered in I heating run ^b registered in II heating run,

 $^{c}T_{5}$ and T_{10} temperature of 5% and 10% weight loss, respectively.

^d Temperature of maximum decomposition rate.



Fig 3. DSC thermograms of M-1 registered in the first and second heating run

3.3. Redox behavior

It is worth remembering that before organic materials as HTMs can be used in PV devices they have to exhibit compatible energy levels. Its oxidation potential should be lower than that of the light harvester, that is, perovskite in PSC or dye sensitizer in DSSC. In view of the above fact, obtained compounds were tested using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which are a useful technique to study redox behavior and to get information about ionization potential (IP) and electron affinity (EA) being closely related to HOMO and LUMO energy, respectively. The research was carried out in CH_2Cl_2 solution in 0.1 M Bu_4NPF_6 as the supporting electrolyte. The electrochemical oxidation and reduction onset potentials were used for estimation of the IP and EA energies of the 9,9'bifluorenylidene derivatives (assuming that IP of ferrocene equals – 5.1 eV) [43]. The obtained results are gathered in Table 2, whereas their CV voltammograms are depicted in Fig. 4.

Та	ble 2.	Redox	potentials	, IP and	EA ener	gies and	lelectro	chemical	band ga	aps (E _g)
	Code	E _{1re}	d E _{2red}	E _{10x}	E _{20x}	E _{30x}	E _{40x}	$IP_{(CV)}^{a}$	EA _(CV) ^b	E _{g(CV)} ^c

Code	E _{1red}	E _{2red}	E _{1ox}	E _{20x}	E _{30x}	E _{4ox}	$IP_{(CV)}^{a}$	EA _(CV) ^b	E _{g(CV)} ^c
	[V]	[V]	[V]	[V]	[V]	[V]	[eV]	[eV]	[eV]
M 1	-1.44	-1.76	0.03	0.2	0.39	1.03	5 12	266	1 47
IVI-1	$(-1.35)^{d}$	$(-1.65)^{d}$	$(0.03)^{d}$	$(0.18)^{d}$	$(0.35)^{d}$	$(1.01)^{d}$	-3.15	-3.00	1.4/
мэ	-1.55	-1.89	-0.10	0.07	0.24	0.89	5.00	2 21	1 70
IVI-2	$(-1.52)^{d}$	$(-2.86)^{d}$	$(-0.18)^{d}$	$(0.01)^{d}$	$(0.15)^{d}$	$(0.74)^{d}$	-5.00	-3.21	1.79
${}^{a}\mathbf{D} = 51 \mathbf{E} \cdot {}^{b}\mathbf{E}\Lambda = 51 \mathbf{E} \cdot {}^{c}\mathbf{E}\mathbf{g}_{max} = \mathbf{E}$									

Both compounds are characterized by two-stage reversible reduction (Fig. 4) contrary to similar compound KR216, for which no reduction potential was observed in the CV voltammograms [32]. The first reduction process (-1.44 V for M-1 and -1.55 V for M-2) most likely corresponds to the reduction on the core 9.9'-bifluorenylidene [44-45]. The obtained values of the cathode peak potentials allowed determination of EA, which were -3.66 eV and - 3.21 eV in the case of M-1 and M2, respectively. In the next step, an oxidation process was performed. It was found that the tested compounds undergo multi-stage oxidation. The first three peaks were reversible and the last was irreversible (Fig. 4-b). In the case of both compounds (**M-1** and **M-2**) the oxidation is due to the formation of cations first M⁺, than M²⁺, next M³⁺ and finally M⁴⁺ similar as was described in the literature for spiro-OMeTAD [46]. The IP values for **M-1** and **M-2** is -5.13 eV and -5.00 eV, respectively, which classifies them as good HTM for PSC because are located above the valence band of perovskite CH₃NH₃PbI₃ (-5.44 eV) [47]. Thus, the smooth hole extraction can be expected. The IP values are similar

to the HOMO energy level of spiro-OMeTAD 5.20 eV or 5.04 eV reported in the literature [41] and [32], respectively. The ionization potential of the reported 9.9'-bifluorenylidene with methoxy groups (KB216 [32]) was 5.09 eV was between IP value of compound containing ethoxy (M-1) and butoxy (M-2) units. The prepared 9,9'-bifluorenylidene derivatives showed higher EA level than the conduction band (CB) of perovskite which may prevent charge recombination [48]. In the case of spiro-OMeTAD reduction process was not observed [41]. What is very important, these derivatives have small energy gaps. Take into account the discussed processes, the introduction of longer alkyl chains into the compound structure resulted in a shift towards more negative values of both reduction and oxidation process.



Fig. 4. CV spectra of M-1 and M-2 derivatives (reduction (a) and oxidation (b)

processes)

3.4. UV-vis absorption spectroscopy

The optical properties of obtained 9,9'-bifluorenylidene derivatives (**M-1** and **M-2**) were studied in solution and the solid-state as a thin film on the glass substrate. Three solvents, THF, chlorobenzene and dichloromethane were applied for UV-Vis measurements. Moreover, the thin films of studied compounds without and with a dopant (4-tBP with different amount of Li-TFSI) were prepared. Such additives were applied as p-type dopants in the next step of investigations concerns of testing of the prepared 9,9'-bifluorenylidene derivatives as HTM in PCSs. As chemical doping is a powerful tool to improve the charge carrier transport and the electrical conductivity of organic semiconductors. The representative UV-Vis absorption spectra were shown in Fig. 5 and the optical parameters were collected in Table S1.



Figure 5. The absorption spectra of (a) **M-1** and (b) **M-2** in the solid state and in chlorobenzene solution (c = $5 \times 10^{-6} \text{ mol/L}$)

The synthesized **M-1** and **M-2** exhibited three (chlorobenzene) or four (CH₂Cl₂, THF) strong absorption bands and a weak and broadband around 650 nm. As can be expected a lack of impact of 9,9'-bifluorenylidene derivatives (**M-1** and **M-2**) chemical structure on UV-vis spectra were observed. As shown in the Table S1 the solvent polarity has no effects on the position of absorption bands maximum (λ_{max}) and molar absorption coefficient of investigated compounds. The presented in literature spiro-OMeTAD showed in dichloromethane, THF and chlorobenzene three or two absorption bands with λ_{max} around 300, 400 and 625 nm, about 300 and 378 nm and at 380 and 530 nm, respectively [32, 49-51]. The molecules **M-1** and **M-2** showed almost the same absorption band in the visible region with λ_{max} at 463 as similar reported KB216 [32]. However, in the case of **M-1** and **M-2** additional weak absorption band located at 682 nm was detracted. Compare electronic absorption properties of the 9,9'-bifluorenylidene derivatives in solution and the solid-state it was found that they exhibited similar position of λ_{max} , which suggest a lack of strong intermolecular π - π stacking of 9,9'-bifluorenylidene derivatives in the thin-film state. Moreover, no influence of increasing the amount of dopant in a film on UV-vis spectra was found.

3.5. AFM measurements

Keep in mind that the HTMs should form the high quality of smooth thin layer, the prepared films were characterized by atomic force microscopy (AFM) by determination of its roughness and thickness. The AFM micrographs of the selected films are depicted in Fig. 6. The AFM measurements indicate that the film surfaces were quite planar with root-mean-square (RMS) roughness low values estimated from 1.7 to 9.2 nm (cf. Table S2). It was found that neat films prepared from both 9,9'-bifluorenylidene derivatives exhibited the same RMS value. In the case of **M-1** addition of Li-TFSI resulted in the soothing of film surface and

reduction of RMS from 5.8 to 1.7 nm was seen. The correlation between the RMS values and the amount of Li-TFSI was not observed. The prepared films were characterized by thicknesses in the range of 123 - 248 nm. The film obtained from **M-1** are slightly thicker compare to **M-2** films. In both cases, the thickness increasing together with higher amount of Li-TFSI.



Figure 6. The AFM micrographs of the prepared films (a) a neat M-1, (b) M-1 with 8.75 μL of Li-TFSI, (c) M-1 with 15.5 μL of Li-TFSI and (d) M-1 with 35 μL of Li-TFSI

3.6. Photovoltaic investigations

To investigate the effect of a new 9,9'-bifluorenylidene derivatives on the performance of perovskite cells, the devices with the structure FTO/b-TiO₂/m-TiO₂/perovskite/Au and FTO/b-TiO₂/m-TiO₂/perovskite/HTM/Au were constructed (cf. Fig. 7-a) and detailed fabrication process is given in Supplementary Materials). Additionally, except for 9,9'-bifluorenylidene derivatives as HTM spiro-MeOTAD was applied. FTO was applied as

cathode (the electron collecting electrode), whereas Au was used as anode (the hole collecting electrode). Perovskite layer was prepared by two step method. The photovoltaic tests were done for non-encapsulated devices. The measurements were carried out in Standard Test Conditions (STC). The representative current–voltage (I–V) characteristics of the studied devices are given in Fig. 7-b, whereas photovoltaic parameters are collected in Table 3.





In the first step of study, the device without HTM was prepared. As can be seen from Table 3 such device without HTM yielded the low PV parameters giving low PCE. Next, the cells with 9,9'-bifluorenylidene derivatives (**M-1** and **M-2**) doped with 4-tBP and Li-TFSI were fabricated. It should be stressed that different HTMs may need different doping concentration of Li⁺. In our investigations, the impact of Li⁺ concentration was tested for both 9,9'-bifluorenylidene derivatives. Considering this effect on device performance, it was found that the dopant additive in value of 17.5 μ L let to obtain off the highest PCE for both tested new HTMs (cf. Table 3). Thus, for reference cell based on commercially available spiro-MeOTAD also the 17.5 μ L of Li-TFSI was applied. The highest device performance exhibited

cell with synthesized M-1. Because the device with M-1 showed the highest value of PCE in previous tests it was decided that only M-1 and spiro-MeOTAD was used for subsequent studies concern preparation of devices without dopant. As can be expected the Li-TFSI is essential to render a low series resistances and to facilitate photocurrent generation. The utilization of dopant resulted in increase of PCE from 2.40 to 4.40, from 4.53 to 7.33 and from 2.63 to 4.13% for cell with spiro-MeOTAD, M-1 and M-2, respectively. Surprisingly, the PSC based on spiro-MeOTAD without dopant exhibited a lower value of PCE compare to device without HTM. The low efficiency resulted from the low value of open circuit voltage (V_{oc}), which may be a consequence of incomplete covering of perovskite with spiro-MeOTAD. Considering the PV parameters of the constructed devices given in Table 3, it was seen that the best PV performance showed device based on 9,9'-bifluorenylidene derivative substituted with ethyl units (M-1) Similar results, that is, shorter alkyl chains in HTMs improved perovskite solar cells parameters have been recently reported for spiro-bifluorene derivatives [41]. The different alkoxy chains effect on oxidation potential (cf. Table 2) and may lead to different molecular packing in solid-state, which can be reflected in device efficiency. It can be noticed that device based on M-1 showed higher PV parameters than that of PSC based on the standard spiro-OMeTAD. One of the reason may be the amount of dopant, which Li⁺ concentration was adjusted to investigated 9,9'-bifluorenylidene derivatives. On the other hand, it seems that the M-1 displayed higher absorption in the visible region compare to spiro-OMeTAD. For an explanation of the observed phenomenon, additionally study covering hole mobility measurements, which are out of scope of the presented work, are necessary.

Device of structure	V _{Li-TFSI} [µL]	J _{sc} [mA/cm ²]	V _{oc} [mV]	FF [-]	PCE [%]
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/Au	-	12.2	631	0.36	2.90
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/spiro-MeOTAD/Au	0.00	13.6	482	0.35	2.40
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/spiro-MeOTAD/Au	17.50	14.2	691	0.43	4.40
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-1/Au	0.00	15.8	752	0.36	4.53
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-1/Au	8.75	15.2	713	0.39	4.50
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-1/Au	17.50	16.7	823	0.51	7.33
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-1/Au	35.00	13.3	776	0.59	6.40
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-2/Au	8.75	12.0	667	0.31	2.63
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-2/Au	17.50	12.0	769	0.42	4.13
FTO/b-TiO ₂ /m-TiO ₂ /perovskite/M-2/Au	35.00	10.8	628	0.48	3.40

Table 3. Photovoltaic properties of fabricated perovskite solar cells

 $V_{\text{Li-TFSI}}$ - volume of additive of solution Li-TFSI;

 $J_{sc} \text{ - short-circuit current; } V_{oc} \text{ - open-circuit voltage; } FF \text{ - fill factor; } PCE \text{ - power conversion efficiency; }$

- without HTM.

The cell based on the reported 9,9'-bifluorenylidene derivative with methoxy units (KR216) exhibited better PV parameters (J_{sc} =22.3 mAcm-1, V_{oc} =1023 mV, FF= 77 and PCE=17.8%) [32]. Moreover, presented in [32] device with spiro-MeOTAD showed better performance compared to our PCS. However, it should be stressed that the structure of both cells, that is, presented herein and reported [32] are significant differences. Thus, a direct comparison of the effect of utilization of KR216 and M-1 or M-2 as HTM is impossible.

4. Conclusions

Summarizing, it can be pointed out that:

- new HTM materials with 9,9'-bifluorenylidene core and different alkoxy chains (ethyl or butyl) substituted to the *para* position of diphenylamine were synthesized with good yield,
- the presence of butyl units: significantly lowered T_m, T_g and to a lesser extent impacts on thermal stability, does not effect on UV-vis absorption range and shifted IP and EA to slightly higher value,
- device with a neat compound bearing ethoxy units gave significant PCE = 4.53 %,
- using of doped 9,9'-bifluorenylidene derivative with shorted alkoxy substituent lead to the highest PCE value of 7.33 % of PSC being higher than that obtained for reference cell based on spiro-OMeTAD,
- the obtained results indicate that 9,9'-bifluorenylidene derivative with ethoxy groups is promising hole transport compounds, which may lead to the development of highly efficient solar cells. In our further study it will be tested as solid electrolyte in DSSC.

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Supporting Information

9,9'-Bifluorenylidene derivatives as novel hole-transporting materials for potential photovoltaic applications

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1. Materials

4-Bromophenol (98%, TCI), potassium carbonate (anhydrous pure p.a., Chempur), bromoethane (98%, Sigma-Aldrich), 1-bromobutane (98%, TCI), 4-ethoxyaniline (98%, TCI), 4-butoxyaniline (98%, TCI), 1-proline (99%, TCI), Sodium tert-butoxide (t-BuONa, 97%, Sigma-Aldrich), tris(dibenzylideneacetone)dipalladium(0) ([Pd₂dba₃], 99%, Fluorochem), Xphos (97%, Sigma-Aldrich), Magnesium sulfate (MgSO₄, pure p.a., Chempur), CDCl₃ (99.8 atom % D, Sigma-Aldrich), DMSO-d6 (99.9 atom % D, Sigma-Aldrich), THF-d8 (≥99.5 atom % D, Sigma-Aldrich), hexane (95% pure, Chempur), ethyl acetate (pure, Chempur), acetone (pure, Chempur), dimethyl sulfoxide (DMSO, pure p.a., Chempur), toluene (pure p.a., Chempur), tetrahydrofuran (THF, pure p.a., Chempur), methanol (MeOH, pure p.a., Chempur), ethanol (EtOH, 96% pure p.a., Chempur or POCH), hydrochloric acid (HCl, 36-38%, Chempur). All reactions were carried out under argon atmosphere. Thin layer chromatography (TLC) was carried out on silica gel (Merck TLC Silica Gel 60 F₂₅₄). Silica gel from Merck was used for column chromatography. Surfactant (Hellmanex III, Hellma Analytics), fluorine doped tin oxide coated glass slides (FTOs, 7 Ω /sq, Sigma-Aldrich), tetraethyl orthotitanate ((C_2H_5O)₄Ti, assay \geq 95% Merck), paste Ti-Nanoxide T600/SP $(PbI_2,$ assay 99%. Sigma-Aldrich), (Solaronix), lead iodide anhydrous N.Ndimethylformamide (DMF, assay 99.8%, Sigma-Aldrich), methylammonium iodide (MAI, Solaronix), isopropanol (IPA, POCH), chlorobenzene (C_6H_5Cl , POCH). 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD), 4-tert-butyl pyridine (TBP), lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI), acetonitrile (99.8%, Sigma-Aldrich).

2. General methods - measurements

Bruker Avance 400 MHz instrument used to record the NMR spectra in CDCl₃, DMSOd₆ and THF-d₈ (as solvent). The HRMS measurements were performed using QTOF Maxis Impact Bruker mass spectrometer equipped with an electrospray (ESI) ion source and q-TOF type mass analyzer. The recorded data were processed using Data Analylis 4.1 software package. The analyzed samples were dissolved in a mixture of MeCN/CHCl₃/HCOOH. Differential Scanning Calorimetry (DSC) was performed by TA-DSC 2010 apparatus, under nitrogen atmosphere with heating/cooling rate of 20 °C/min and using aluminum sample pans. Thermogravimetric analysis was performed on Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA at a heating rate of 15 °C/min under nitrogen. Eco Chemie Autolab PGSTAT128n potentiostat was used to the electrochemical measurements. Researches were

carried out using glassy carbon electrode (diam. 2 mm), platinum coil and silver wire as working, auxiliary and reference electrode, respectively. Potentials are referenced with respect to internal standard (ferrocene (Fc)). Differential pulse voltammetry and cyclic voltammetry experiments were conducted in a standard one-compartment cell, in dichloromethane, under argon. As the supporting electrolyte was used 0.1M Bu₄NPF₆ (Aldrich, 99%). The concentration of compounds was equal $1.0 \cdot 10^{-4}$ mol/dm³. Deaeration of the solution was achieved by argon bubbling through the solution for about 10 min before measurement. All electrochemical experiments were carried out under ambient conditions and an argon atmosphere was maintained over the solution during measurements. UV-Vis spectra were recorded in dichloromethane, tetrahydrofuran and chlorobenzene solution as the concentration of 5*10⁻⁶ mol/L using the Evolution 220 Thermo Scientific UV-Vis Spectrophotometer and UV-Vis-NIR Jasco-V-570 Spectrophotometer. AFM micrographs were obtained using a TopoMetrix Explorer, working in the contact mode in the air, in the constant force regime.

Fabrication of perovskite solar cells (PSCs)

The solar cells of structures: **FTO/b-TiO₂/m-TiO₂/perovskite/Au** and **FTO/b-TiO₂/m-TiO₂/perovskite/compound/Au** without and with various amount of Li-TFSI additive were prepared. The fluorine doped tin oxide coated glass slides (FTOs, 2 x 2 cm) were first cleaned with warm deionised water with Hellmanex III (1 % solution) for 5 minutes in an ultrasonic bath. Subsequently, the FTOs were rinsing in hot deionised water (~100 °C) twice. Further step was that FTOs were put into isopropanol in an ultrasonic bath for 5 minutes and again rinsing in hot deionised water. The next step was prepared a blocking layer b-TiO₂ on FTO (1.14 g tetraethyl orthotitanate in 10 mL EtOH and 0.2 mL HCl) [1]. The fresh solution was spin coated on the surface of FTO at 2000 r.p.m. for 15 seconds and dried at 200 °C for 10 minutes. Then samples were annealed at 500 °C for 30 minutes in air to calcination. Then mesoporous m-TiO₂ layer was screen-printed on FTO/b-TiO₂ and was also dried at 200 °C for 10 minutes. Finally samples were annealed at 500 °C for 30 minutes in air.

Perovskite preparation

A two-step method was used to prepare perovskite layer. In the first step was made solutions of PbI₂ (1.39 g) in anhydrous DMF (3.5 mL) and MAI (0.1 g) in isopropanol (11 mL). The solution PbI₂ in DMF was first stirring at room temperature for a few minutes, next at 70 °C for 30 minutes and was spin coated on the hot FTO with TiO₂ layers at 2000 r.p.m. for 30 seconds, next were dried at 70 °C for 3 minutes and 90 °C for 5 minutes. The second

step of method was dipping in solution of MAI in IPA for 15 minutes and after samples were dried at 90 °C for 30 minutes. Before dipping every samples were pre-wetting by IPA.

Hole-transporting material (HTM) preparation

M-1, M-2 and spiro-MeOTAD solutions were prepared according to the description included in the publication [2]. The composition of HTM solution was 72.3 mg of the HTM in 1 mL of chlorobenzene, 28.8 μ l of 4-tert-butyl pyridine and 8.75 μ l or 17.5 μ l or 35 μ l of lithium bis(trifluoromethanesulfonyl)imide (0.002 mol/mL). The prepared solution was spin coated on the perovskite layer at 4.000 r.p.m. for 30 seconds. Finally, the gold electrode was deposited by thermal evaporation (~ 10⁻⁶ mbar) on the devices.

Measurements of photovoltaic cells

Current–voltage (I–V) characteristics of the prepared devices were measured using the PET Photo Emission Tech Inc. Model SS 200AAA class solar simulator in STC (Standard Test Conditions) conditions (temperature of the cell 25 °C, solar irradiance – 1000 W/m², air mass 1.5 spectrum – AM1.5). Active area of the tested cells was 0.25 cm².



3. Thermal characteristics (DSC and TGA)

Fig S1. DSC thermograms of M-1



Fig. S3. TGA thermograms of M-1 and M-2 recorded at a heating rate of 15°C min⁻¹

4. Redox behavior



Fig. S4. DPV voltamogramms of M-1 and M-2

5. Photographs



Fig. S5. Photographs of HTM-1 (a) and HTM-2 (b) in solid state under visible light.

6. UV-vis spectra

Table S1. UV-Vis spectroscopic data of obtained M-1 and M-2 in solution and in the solid

Code	Solution λ_{max} [nm] (ϵ ·10 ⁵) ^a			Film			
			A neat	With Li-TFSI			
	$CH_2Cl_2^{\ b}$	chlorobenzene ^b	THF ^b		(8.75 µL)	(17.5 μL)	(35 µL)
M-1	289(1.51)	-	288(1.39)	-	-	-	-
	314(1.63)	317(1.46)	311(1.47)	311	315	314	316
	387(1.43)	390(1.29)	387(1.31)	389	389	389	389
	466(0.46)	468(0.44)	463(0.42)	471	471	471	471
	697(0.04)	691(0.03)	682(0.04)				
M-2	287(1.43)	-	287(1.60)	-	-	-	-
	315(1.54)	317(1.62)	313(1.68)	311	315	314	314
	386(1.19)	390(1.29)	385(1.34)	389	389	390	390
	466(0.43)	467(0.51)	463(0.50)	471	472	471	472
	703(0.02)	690(0.04)	698(0.04)				
^a ϵ – molar absorp	tion coefficient, [o	$\operatorname{Im}^{3} \cdot \operatorname{mol}^{-1} \cdot \operatorname{cm}^{-1}].^{\mathrm{b}} \mathrm{c} = 5$	$*10^{-6}$ mol/dm ³				

state

7. RMS data

Structure of layer	RMS [nm]	Thickness [nm]
M-1	5.8	156
M-1:TBP:Li-TFSI (8.75 µL)	2.1	195
M-1:TBP:Li-TFSI (17.5 μL)	2.9	211
M-1:TBP:Li-TFSI (35 µL)	1.7	248
M-2	5.8	123
M-2:TBP:Li-TFSI (8.75 µL)	3.1	134
M-2:TBP:Li-TFSI (17.5 µL)	6.0	135
M-2:TBP:Li-TFSI (35 µL)	9.2	151

Table S2. Collected values of RMS and thickness of prepared layers

8. ¹H NMR and ¹³C NMR spectra























H-C HMQC of 1-bromo-4-butoxybenzene (A-2)



H-C HMBC of 1-bromo-4-butoxybenzene (A-2)



¹H NMR of bis(4-ethoxyphenyl)amine (B-1)



¹³C NMR of bis(4-ethoxyphenyl)amine (B-1)



H-C HMBC of bis(4-ethoxyphenyl)amine (B-1)



35



















H-C HMBC of M-1









H-C HMBC of M-2

9. HRMS spectra

(a)







Fig. S6. HRMS spectra of M-1 (a) and M-2 (b)

10. Literature

[1] Gawlińska-Nęcek K, Starowicz Z, Tavgeniene D, Krucaite G, Grigalevicius S, Schab-Balcerzak E, Lipiński M. Opto-Electron Rev 2019;27:137-142.

[2] Im JH, Jang IH, Pellet N, Grätzel M, Park NG, Nat nanotechnol 2014;9:927.

Novel 9,9'-bifluorenylidene derivatives were synthesized and characterized.

The effect of alkoxy substituent on thermal, UV-vis and electrochemical properties was studied. They were tested as HTMs in perovskite solar cells.

Application of moiety with ethoxy groups in cell gave the highest PCE 7.33 %.

This value was higher than that obtained for reference cell based on spiro-OMeTAD (4.40%).

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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