Improved crystallinity of the asymmetrical diketopyrrolopyrrole derivatives by the adamantane substitution

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Graphical abstract



	Journal Pre-proof
1	Improved crystallinity of the asymmetrical diketopyrrolopyrrole
2	derivatives by the adamantane substitution
3	
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10	ABSTRACT
11	Alkylation of diketopyrrolopyrroles (DPPs) is a powerful tool for increasing the solubility and
12	processability of these pigments. Moreover, alkylation contributes to solid state packing and
13	structural ordering of DPPs. In this study, the influence of the alkylation and solubilization
14	side group engineering to DPPs on the thermal and optical properties was systematically
15	investigated. Two series (each containing 3 derivatives: N,N'-, N,O'- and O,O'-substituted
16	examples) of alkylated DPPs by 2-ethylhexyl and ethyladamantyl substituents were
17	synthesized. Separation of all formed DPP derivatives was accomplished in order to perform
18	an in-depth study of their physicochemical properties. DSC measurements revealed that the
19	O-substitution caused a decrease in the thermal stability of DPP derivatives. On the contrary,
20	an ethyladamantyl side chain, as a rigid alicyclic substituent, contributed very effectively to
21	the increase of the melting point and thermal stability. The new results provide insights into
22	the development of DPP-alkylated regioisomers and their thermal and optical properties.
23	
24	1. INTRODUCTION
25	In the past few decades, soluble organic semiconductors have found a number of applications

26 in various fields of organic electronics, mainly due to their convenient processability using

27	common organic solvents and lower production costs compared to their conventional
28	inorganic counterparts [1]. Organic semiconducting materials, suitable for applications in
29	organic electronics should exhibit high absorption coefficients [2], high thermal and chemical
30	stability [2] and good charge transport properties [3]. One of the most attractive groups of
31	organic pigments are derivatives of 2,5-dihydropyrrolo[4,3-c]pyrrolo-1,4-dione (DPP) [4].
32	They have a considerable application potential for low-cost solution processable electronic
33	devices [5]. The fundamental DPP structure can be modified by conventional chemical
34	pathways, producing various derivatives exhibiting desired chemical and physical properties
35	[6]. Currently, there are a number of scientific reports showing examples of successful
36	application of DPP derivatives as functional high-performance materials in dye-sensitized [7]
37	and bulk heterojunction solar cells [8], organic field-effect transistors [9]-[13], organic light-
38	emitting diodes [14],[15], sensors [16] and biosensors [17], fluorescence imaging [18].
39	In general, in order to achieve high performance in the above-mentioned applications, the
40	conjugated length of the molecule has to be extended, which is possible either by
41	polymerization via direct arylation [19][20] or by the cross-coupling reactions on the side
42	aromatic rings of the DPP core [21],[22]. Most commonly, DPP derivatives are substituted by
43	thiophene-2-yl [23] groups at the 3 and 6 positions. The N,N'-unsubstituted DPP derivatives
44	have good thermal stability and photostability [2],[25], but on the other hand they also are
45	poorly soluble in most common organic solvents due to the strong intermolecular hydrogen
46	bonding between neighboring carbonyl-oxygen and lactam-nitrogen atoms [2]. Therefore, to
47	achieve high solubility of DPP derivatives, the N,N' -positions can be substituted with linear or
48	branched alkyl chains, which interrupt intermolecular hydrogen-bonds [26]. N,N'-alkylation
49	ranks among the most important and common methods of DPP substitution, which has
50	resulted in broader applications in the previously-mentioned areas of organic electronics [6].
51	However, the disadvantage of alkylation of DPPs is poor regioselectivity, which results in

52 isolation of O-alkylated side products in moderate yields [27]. Alkylation is performed through base-catalyzed nucleophilic substitution reactions. The influence of the bases, 53 54 solvents and reaction conditions used on the alkylation progress and regioselectivity has been 55 studied only rarely [28], [29]. However, two competitive anions O^- and N^- on the lactam core 56 contribute to a drop in the regioselectivity of N_{N} '-substitutions. Stas et al. [28] reported that 57 substitution of alkyl chains on oxygen atoms is possible alongside with the nitrogen heteroatoms due to the delocalization of the negative charge between the two atoms of a 58 59 lactam group. Frebort et al. [30] already described the formation of O-alkylated by-products, but very few reports so far have investigated the properties of these O-alkylated derivatives 60 [31],[32]. 61

We recently reported [33] synthesis and study of a novel *N*,*N*'-substituted DPP derivative contained bulky ethyladamantyl groups. Substitution had a significant impact on highly ordered adamantane-induced molecular packing, which resulted in exceptional ambipolar charge transport of this new chromophore. Nevertheless, the synthesis of the new aforesaid DPP derivative exhibited very low regioselectivity of *N*,*N*'-alkylation and thus, formation of competitive by-products was largely observed.

68 Herein, to systematically study the effect of branching and bulky substituents on alkylation 69 regioselectivity and their binding position, the optical and thermal properties of all symmetrical (N,N'-; O,O'-) and asymmetrical (N,O'-) DPP products were determined. The 2-70 71 ethylhexyl chain was chosen as a branching substituent for comparison with the aforesaid 72 bulky ethyladamantyl chains. The key was to isolate all these products in quantities enabling the systematic study of optical and thermal properties and to examine both the effect of the 73 74 alkyl chain character and the binding site in the DPP molecule on these properties. Systematic 75 studies showed that asymmetrical derivatives tend to exhibit large Stokes shift which reduces the reabsorption of the emitted luminescence. Moreover, O-substitution causes the 76

disappearance of carbonyl group and the substitution on the highly polar ketone group induces
electron cloud polarization, which is beneficial for e.g. the two-photon absorption [34].
However, *O,O'*- and *N,O'*-substituted DPP derivatives have their drawbacks: substitution on
keto-group disturbs the crystalline organization in the solid state, which causes these materials
to have a paste-like consistency at room temperature [31], and this makes their application in
the field of organic electronics rather doubtful.

- However, O,O'- and asymmetrical N,O'-substituted derivatives can be of interest not only from a fundamental but also from a practical point of view. Therefore, the main challenge of the present paper is to improve the crystallinity and thermal stability of O,O'- and N,O'ethyladamantyl substituted DPP derivatives and investigate in detail their yet unknown optical properties.
- 88

89 2. EXPERIMENTAL SECTION

90 2.1. Materials

2-Thiophenecarbonitrile (99%), sodium, iron(III) chloride (>97%, anhydrous), tert-Amyl 91 92 alcohol (≥99%), N,N-dimethylformamide (DMF, 99.8%, anhydrous), potassium carbonate (99.99%, anhydrous), 2-ethylhexyl bromide (95%) and deuterochloroform (99.96 atom % D) 93 94 were purchased from Sigma-Aldrich (now Merck) and were used as received. Diisopropyl 95 succinate (98%) was purchased from Synthesia, Inc. and also was used as received. 1-(2-96 Bromoethyl)adamantane (98%) was purchased from Provisco CS Ltd. Acetic acid (99%), 97 isopropyl alcohol (p.a.), methanol (p.a.), toluene (p.a.) and chloroform (p.a.) were purchased 98 from PENTA Ltd. and were used as received. Separation by column chromatography was 99 carried out on a Silica Gel 60Å (230–400 mesh, Sigma-Aldrich). All reactions were 100 performed in oven-dried apparatus, under argon atmosphere while magnetically stirred.

102 **2.2. Characterization**

¹H NMR spectra were recorded on a FT-NMR spectrometer Bruker Avance III 300 MHz or 500 MHz in CDCl₃. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS as an internal reference. The melting point was determined on a Kofler apparatus and the temperature was not calibrated. Mass spectra were recorded on a GC–MS spectrometer Thermo Fisher Scientific ITQ 700 (DEP). Elemental analysis was measured with an elemental analyser Flash 2000 CHNS Thermo Fisher Scientific.

109

110 Thermogravimetry (TG) was conducted on a TA Instruments Q5000IR (New Castle,

111 Delaware, USA) to analyze the stability of the derivatives and changes in mass before

112 degradation. A sample was placed on the Pt crucible sample holder and heated at 10 $^{\circ}$ C/min

113 from room temperature to $600 \,^{\circ}$ C under a stream of nitrogen (ultra-high-purity) flow rate

114 40 mL/min. TG was used to analyze the thermal stability of the investigated materials.

Briefly, the TG record (dependence of mass on temperature) was derived and onset of thederivate was determined.

117 Differential Scanning Calorimetry (DSC) was conducted on a TA Instruments Q2500 118 (New Castle, Delaware, USA) equipped with an RCS cooler to analyze the physicochemical 119 properties of derivatives. The samples, typically 3–7 mg, were weighed to aluminum pans 120 (Tzero®), hermetically sealed and measured under a stream of nitrogen flow rate 50 mL/min. 121 The loading temperature was 30 °C. The following temperature program was applied: heating 122 10 °C/min to temperature 50 °C below the degradation temperature determined using TG to 123 delete the thermal history of the sample. The sample was quickly (15 °C/min) cooled to 124 -90 °C and heated again at 10 °C/min. This cycle was used to estimate the physicochemical 125 structure of the sample upon fast cooling. Then, the sample was cooled slowly (3 °C/min) to

-90 °C and heated again at 10 °C/min. This cycle was used to estimate the physicochemical
structure of the sample upon slow cooling.

Both TG and DSC records were evaluated using TRIOS and Universal analysis softwareprovided by TA Instruments.

130

131 Solutions were prepared by diluting materials in anhydrous chloroform. The concentration of materials was 10^{-5} to 10^{-6} mol \cdot dm⁻³. Solutions were characterized in a quartz cuvette 132 133 (Herasil®, Heraeus Quarzglas Co.). Optical measurements of thin films were performed on 134 quartz glass slides (Herasil® 102, Heraeus Quarzglas Co.) which were pre-treated by 135 ultrasonic cleaning in the following baths: 1) Detergent Neodisher (Miele, Inc., NJ, USA) 136 10 min; 2) deionized (Milli-Q) water 20 min; 3) isopropyl alcohol (a. p.) 10 min. Films were 137 deposited by spin-coating. The spin rate was 2000 rpm and the deposed material was 138 dissolved in chloroform. The final thickness of layers was in the range 50–100 nm. Absorption spectra of samples were measured with a Varian Cary Probe 50 UV-VIS 139 140 spectrometer (Agilent Technologies Inc.). The fluorescence spectra were recorded with a 141 Horiba Jobin Yvon Fluorolog. This apparatus equipped with integration sphere was also used 142 to determine the fluorescence quantum yield by absolute method. The fluorescence lifetime 143 was measured with a Horiba Jobin Yvon Fluorocube. 144

145 **2.3. Synthesis**

146 The targeted molecules were synthesized according to the known general procedure [35],[36].

147 The synthetic route and the molecular structures are illustrated in Scheme 1.



Th-DPP-1a: R = 2-ethylhexyl; 41%Th-DPP-1b: R = 2-ethylhexyl; 18%Th-DPP-1c: R = 2-ethylhexyl; 3%148Th-DPP-2a: R = adamantylethyl; 36%Th-DPP-2b: R = adamantylethyl; 20%Th-DPP-2c: R = ethyladamantyl; 6%149Scheme 1. Procedure for the synthesis of the N,N'-; N,O'- and O,O'-alkylated DPP derivatives1502.3.1. Synthesis of 2,5-dihydropyrrolo[4,3-c]pyrrolo-1,4-dione molecules

Sodium (~1.3 equiv., 7.2 g, 313.2 mmol) was dissolved in tert-amyl alcohol (400 mL) heated 152 153 to reflux and with the addition of catalytic amount of iron(III) chloride. After dissolution of 154 all sodium, there was added in one portion 1.0 equiv. of thiophene-2-carbonitrile (26.2 g, 240.0 mmol) and the reaction mixture was stirred for 30 min at reflux. Then, 0.65 equiv. of 155 156 diisopropyl succinate (31.6 g, 156.2 mmol) dissolved in *tert*-amyl alcohol (80 mL) was 157 gradually added dropwise for 4 h and the mixture was stirred at reflux for 18 h. After that, 158 protolysis was performed by addition of diluted acetic acid to the reaction mixture cooled to 159 laboratory temperature. The mixture was refluxed for 6 h and then the heterogenic mixture 160 was filtered while hot and the filter cake was washed with hot water and isopropyl alcohol. 161 The crude product was refluxed in methanol for 1 h and, after that, it was filtered while hot to 162 get a pure product. **Th-DPP**: Dark purple solid (27.5 g, yield 59%). Melting point >400 °C, ¹H NMR (300 MHz, 163

164 DMSO- d_6 , ppm): $\delta = 11.21$ (s, 2H), 8.20 (d, J = 3.01 Hz, 2H), 7.93 (d, J = 3.04 Hz, 2H),

165 7.31–7.27 (m, 2H), Anal. calcd. for $C_{14}H_8N_2O_2S_2$: C 55.98%, H 2.68%, N 9.33%, Found: C

166 55.42%, H 2.37%, N 9.71%.

167

- 168 2.3.2. Synthesis of the alkylated DPP derivatives
- 169 Anhydrous potassium carbonate (~5.3 equiv., 2.4 g, 17.4 mmol) was added to a solution of
- 170 **Th-DPP** (1.0 equiv., 1.0 g, 3.3 mmol in 45 mL of anhydrous DMF) and the mixture was
- 171 heated to 60 °C and stirred for 1 h. Then, 3.50 equiv. (11.6 mmol) of alkyl bromide (**R**–**Br**,

172 2-ethylhexyl bromide: 2.23 g; 1-(2-bromoethyl)adamantane: 2.81 g) dissolved in anhydrous

173 DMF (20 mL) was gradually added dropwise for 30 min. After 20 min, the mixture was

- 174 heated to 105 °C and stirred for 2 h. Then, DMF was distilled off by vacuum distillation, the
- solid material was suspended in methanol and filtered to get a crude product.
- 176 **Th-DPP-1a**: Dark red crystal material (0.71 g, yield 41%) was obtained after purification of
- 177 the crude product by column chromatography on silica gel (toluene, $R_{\rm F} = 0.26$). Melting point
- 178 126 °C, ¹H NMR (300 MHz, CDCl₃, ppm, Fig. S1): δ = 8.88 (dd, J = 5.1, 2.7 Hz, 2H), 7.64
- 179 (dd, *J* = 6.3, 3.9 Hz, 2H), 7.29 (dd, *J* = 7.2, 1.2 Hz, 2H), 4.04 (m, 4H), 1.88 (m, 2H), 1.40–
- 180 1.24 (m, 16H), 0.92–0.85 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 161.79, 140.44,
- 181 135.23, 130.48, 129.86, 128.41, 107.98, 45.89, 39.13, 30.25, 28.39, 23.59, 23.05, 13.99,
- 182 10.50; Anal. calcd. for C₃₀H₄₀N₂O₂S₂: C 68.66%, H 7.68%, N 5.34%, Found: C 68.12%, H
 183 7.47%, N 5.53%.
- 184 **Th-DPP-1b**: Purple waxy material (0.31 g, yield 18%) was obtained after purification of the
- 185 crude product by column chromatography on silica gel (toluene, $R_{\rm F} = 0.36$). Melting point –,
- ¹H NMR (300 MHz, CDCl₃, ppm, Fig. S2): δ = 8.48 (d, J = 3.6 Hz, 1H), 8.19 (d, J = 3.9 Hz,
- 187 1H), 7.68 (dd, *J* = 4.1, 1.6 Hz, 1H), 7.50 (d, *J* = 3.2 Hz, 1H), 7.26 (dd, *J* = 4.3, 1.2 Hz, 1H),
- 188 7.20 (d, *J* = 3.5 Hz, 1H), 4.52 (m, 2H), 3.94 (m, 2H), 1.79 (m, 2H), 1.38–1.23 (m, 16H), 0.91–
- 189 0.85 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 166.38, 161.73, 149.62, 142.46,
- 190 138.73, 134.82, 131.63, 131.49, 130.09, 128.96, 128.23, 127.96, 114.30, 111.15, 72.45, 45.54,
- 191 39.37, 39.13, 31.26, 30.76, 30.29, 29.70, 29.09, 28.40, 24.12, 23.62, 23.03, 14.01, 11.28,

- 192 10.51; Anal. calcd. for $C_{30}H_{40}N_2O_2S_2$: C 68.66%, H 7.68%, N 5.34%, Found: C 68.21%, H
- 193 7.54%, N 5.12%.
- 194 **Th-DPP-1c**: Dark purple waxy material (0.06 g, yield 3%) was obtained after purification of
- the crude product by column chromatography on silica gel (toluene, $R_{\rm F} = 0.68$). Melting point
- 196 –, ¹H NMR (300 MHz, CDCl₃, ppm, Fig. S3): δ = 8.04 (dd, J = 4.9, 2.4 Hz, 2H), 7.55 (dd, J =
- 197 6.3, 3.9 Hz, 2H), 7.18 (dd, *J* = 5.7, 3.3 Hz, 2H), 4.55 (m, 4H), 1.82 (m, 2H), 1.54–1.29 (m,
- 198 16H), 0.98–0.83 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, ppm): δ = 147.72, 147.10, 138.53,
- 199 129.01, 124.49, 123.99, 119.16, 39.51, 31.46, 30.23, 29.71, 29.08, 23.01, 14.08, 11.27; Anal.
- 200 calcd. for $C_{30}H_{40}N_2O_2S_2$: C 68.66%, H 7.68%, N 5.34%, Found: C 68.34%, H 7.93%, N
- 201 5.60%.
- 202 **Th-DPP-2a**: Violet crystal material (0.75 g, yield 36%) was obtained after purification of the
- 203 crude product by column chromatography on silica gel (toluene/chloroform 3/1, $R_F = 0.60$)
- and the following recrystallization in toluene with addition of *n*-heptane. Melting point
- 205 321 °C, ¹H NMR (500 MHz, CDCl₃, ppm, Fig. S4): δ = 8.91 (d, J = 3.8 Hz, 2H), 7.64 (d, J =
- 206 4.9 Hz, 2H), 7.27 (dd, *J* = 6.0, 5.0 Hz, 2H), 4.14–4.11 (m, 4H), 1.99–1.82 (m, 6H), 1.75–1.72
- 207 (m, 7H), 1.68–1.65 (m, 19H), 1.53–1.51 (m, 3H); ¹³C NMR (125 MHz, CDCl₃, ppm): $\delta =$
- 208 161.28, 140.13, 135.23, 130.57, 129.69, 128.57, 107.87, 43.23, 42.30, 37.72, 37.11, 32.22,
- 209 28.63; EI [*m*/*z*] 624.89, Found 624.97, Anal. calcd. for C₃₈H₄₄N₂O₂S₂: C 73.04%, H 7.10%, N
- 210 4.48%, S 10.26%, Found: C 73.15%, H 7.08%, N 4.42%, S 10.38%.
- 211 **Th-DPP-2b**: Dark violet solid material (0.41 g, yield 20%) was obtained after purification of
- the crude product by column chromatography on silica gel (toluene/chloroform 3/1,
- 213 $R_{\rm F} = 0.65$). Melting point 210 °C, ¹H NMR (300 MHz, CDCl₃, ppm, Fig. S6): $\delta = 8.42$ (d, J =
- 214 3.9 Hz, 1H), 8.25 (d, *J* = 3.8 Hz, 1H), 7.69 (dd, *J* = 5.9, 4.1 Hz, 1H), 7.49 (dd, *J* = 5.6, 4.1 Hz,
- 215 1H), 7.27 (d, *J* = 3.2 Hz, 1H), 7.24–7.17 (m, 1H), 4.67–4.63 (t, *J* = 7.8 Hz, 2H), 4.06–4.00 (m,
- 216 2H), 1.98 (m, 6H), 1.75–1.67 (m, 26H), 1.62–1.53 (m, 3H); ¹³C NMR (125 MHz, CDCl₃,

- 217 ppm): δ = 166.15, 161.35, 149.43, 142.41, 138.76, 135.29, 131.65, 131.48, 130.02, 129.78,
- 218 128.91, 128.23, 113.87, 111.44, 66.79, 43.34, 42.93, 42.72, 42.27, 37.43, 37.09, 37.05, 32.20,
- 219 32.01, 28.67, 28.61; Anal. calcd. for C₃₈H₄₄N₂O₂S₂: C 73.04%, H 7.10%, N 4.48%, Found: C
- 220 72.81%, H 7.01%, N 4.57%.
- 221 **Th-DPP-2c**: Dark violet solid material (0.12 g, yield 6%) was obtained after purification of
- the crude product by column chromatography on silica gel (toluene/chloroform 3/1,
- 223 $R_{\rm F} = 0.95$). Melting point 221 °C, ¹H NMR (300 MHz, CDCl₃, ppm, Fig. S7): $\delta = 8.05$ (d, J =
- 4.5 Hz, 2H), 7.55 (d, *J* = 5.5 Hz, 2H), 7.19 (dd, *J* = 8.1, 1.1 Hz, 2H), 4.69–4.65 (m, 4H), 1.98
- 225 (m, 4H), 1.70–1.64 (m, 24H), 1.54 (s, 4H), 1.34–1.26 (m, 2H); ¹³C NMR (125 MHz, CDCl₃,
- 226 ppm): $\delta = 147.52, 146.96, 138.29, 129.09, 124.43, 123.98, 118.92, 42.50, 36.88, 31.89, 31.39,$
- 227 30.05, 28.45; Anal. calcd. for $C_{38}H_{44}N_2O_2S_2$: C 73.04%, H 7.10%, N 4.48%, Found: C
- 228 72.96%, H 6.99%, N 4.51%.
- 229 **3. RESULTS AND DISCUSSION**

230 **3.1. Thermal properties**

231 The TG record of the sample Th-DPP-1a (Fig. S8, Supplementary Information) resulted in a 232 slow mass loss (5%) up to 289 °C, where the degradation processes started accompanied by 233 an intensive mass loss. Consequently, upon both fast and slow cooling, the DSC record (Fig. 234 S8) showed two endothermal peaks, which can be attributed to the melting of crystalline 235 structures. The comparison of lower temperature peaks showed that they had similar onsets 236 around 53 °C, but they differed in the enthalpies, i.e. the slow-cooled sample gave 12 J/g, 237 which was higher than the 10 J/g of the fast-cooled sample. The second peaks were 238 comparable, their enthalpies were around 56 J/g and onsets at 118 °C. This revealed formation 239 of two distinct crystalline structures, while the crystallites melting at lower temperatures were 240 affected by the cooling regime. We assume that the crystallites in sample **Th-DPP-1a** are 241 formed from 2-ethylhexyl chains. Longer linear aliphatic chains have a high tendency to form

242 packed structures, but their substitution may induce formation of several stable forms 243 energetically close to each other (i.e. crystalline structures with similar melting temperatures) 244 [37],[38]. An asymmetric analog to the sample **Th-DPP-1a** is the sample **Th-DPP-1b** which 245 showed slightly lower degradation temperature at 270 °C (Fig. S9). The DSC record showed 246 only step transition after fast and slow cooling around 23 °C which was attributed to the glass 247 transition. However, an endothermal peak with the enthalpy of 40 J/g was observed around 248 30 °C, which started simultaneously with the run (first heating cycle) that is normally used for 249 deleting the thermal history of the sample. The endothermal peak was not observed in the 250 subsequent run. The sample was stored at 20 °C and the experiment was repeated after 9 days, and the peak was observed again, at the same temperature with enthalpy 34 J/g. An attempt to 251 252 induce the crystallization at 10 °C for 30 minutes failed (Fig. S9). This means that the 253 crystallization of sample Th-DPP-1b is a slow process with kinetic constants in order of 254 several days. Unlike the **Th-DPP-1a** sample, **Th-DPP-1b** contains 2-ethylhexyl chains 255 asymmetrically bound to N- and O-atoms, which apparently influence the kinetics of 256 recrystallization. Furthermore, the symmetrically N,N'- substituted sample Th-DPP-1a 257 indicates the presence of two types of crystallites, while the asymmetrically N,O'-substituted 258 Th-DPP-1b revealed only one type of crystals. This indicates that the crystallites are formed 259 predominantly from 2-ethylhexyl bound on the N-atom, while the O-substitution does not 260 support the formation of crystals. Accordingly, the high temperature melting in the sample 261 Th-DPP-1a would be caused by larger crystals of 2-ethylhexyl chains probably composed of 262 chains from adjacent molecules.

The TG record of the *N*,*N'*-ethyladamantyl symmetrically substituted sample **Th-DPP-2a** showed the degradation around 368 °C, but it was preceded by a negligible mass loss of 0.3 % (Fig. S10). The mass loss can be attributed to the residual mass loss of either moisture or the residual content of some ethyladamantyl-based impurity. In the DSC records (Fig. S10), the

fast cooling resulted in a glass transition around 123 °C, followed by cold crystallization at 267 163 °C with enthalpy 36 J/g and melting at 320 °C with enthalpy 76 J/g. This means that fast 268 269 cooling initiated only partial crystallization of the melted sample. The slow cooling resulted in 270 glass transition at 133 °C followed by cold crystallization at 186 °C with enthalpy 30 J/g 271 followed by melting. In this case, however, the melting occurred in two steps, one started at 272 274 °C with enthalpy 13 J/g and the second started at 300 °C with enthalpy 29 J/g. Between 273 these two endothermal peaks no exothermal was observed (recrystallization), therefore the 274 melting corresponded to two distinct crystalline domains in a sample. Hence, the sample 275 Th-DPP-2a responded to a difference in the cooling rate by shifts in the glass transitions and 276 crystallinity degree. The stability of the asymmetrically substituted sample Th-DPP-2b 277 showed degradation at 264 °C (Fig. S11). The DSC record (Fig. S11) showed a glass 278 transition at 113 °C upon fast cooling, which shifted to 110 °C upon slow cooling. The 279 heating segment applied for deleting the thermal history showed an exothermal peak with onset 250 °C, probably corresponding to degradation, while the consequent heating runs did 280 281 not show any melting process in the temperature range used. We conclude that in comparison 282 to the sample **Th-DPP-2a**, asymmetrical substitution hampers the formation of the crystals, 283 and the structure has the tendency to remain in amorphous rather than crystalline form, which 284 is less stable. The TG record of the O,O'-symmetrically substituted sample **Th-DPP-2c** 285 showed a continuous decrease in mass from 100 °C to 250 °C (mass loss around 20%) while above 250 °C the rate of mass decrease accelerated, i.e. the sample was degraded (Fig. S12). 286 287 For this reason, the correct temperature of the degradation could not be determined using TG. The DSC showed an endothermal process, probably melting with onset at 221 °C overlaid by 288 289 an intensive exotherm at 246 °C attributed to degradation of the melt (Fig. S12). We conclude 290 that O,O'-substitution results in formation of significantly less stable derivatives in 291 comparison to *N*.*N*'-substitution.

Compound	DSC	Tg	melting I	enthalpy	melting II	enthalpy	cold crystallization	crystallization	T _{end} DSC	T _G degradation
-		°C	°C	J/g	°C	J/g	°C	°C	°C	°C
	first heating		55	6	118	56			150	289
Th-DPP-1a	after fast cooling		55	10	118	56			150	
	after slow cooling		53	12	118	56			150	
	first heating		30*	40*			×.		180	270
Th-DPP-1b	after fast cooling	23	20	0,04					180	
	after slow cooling	23	22	0,02					180	
	first heating		321	94	330	8	133	6	360	368
Th-DPP-2a	after fast cooling	123	320	76			163	36	360	
	after slow cooling	133	274	13	300	29	186	30	360	
	first heating		210	62					250	264
Th-DPP-2b	after fast cooling	113	207	2			157	1	250	
	after slow cooling	110							250	
	first heating								200**	n.d.
Th-DPP-2c	after fast cooling	36	221**						200	
	after slow cooling	29							200	

292 Table 1 : Summarized thermal properties of the materials under invest	igation.
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**when extended to 300°C melting occurred at 221°C followed by degradation around 246°C *started simultaneously with experiment

3.2. Optical properties

- 295 The optical properties of DPP materials were studied in solution as well as in thin spin-casted
- films to investigate the effects given by the position and the type of solubilization group
- 297 substitution.





Fig. 1. Absorption and fluorescence spectra of studied DPPs dissolved in chloroform.

300

301 **Table 2:** Optical parameters of solutions determined from fluorescence and absorption measurements.

Substitution	λ _{ABS max} [nm]	λ _{ABS edge} [nm]	λ _{PL} [nm]	QY [%]	τ [ns]	$E_{\rm g opt} [{\rm eV}]$
Th-DPP-1a	547	569	563	63 ± 6	6.05 ± 0.01	2.23
Th-DPP-1b	533	602	602	0.8 ± 0.5	0.63 ± 0.02	2.16
Th-DPP-1c	505	598	-	-	0	Not det.
Th-DPP-2a	549	572	562	65 ± 5	6.07 ± 0.01	2.23
Th-DPP-2b	533	602	598	0.7 ± 0.5	0.65 ± 0.02	2.16
Th-DPP-2c	505	598	731	Not det.	0.32 ± 0.05	2.05

³⁰²

306 solubilization groups provided similar spectra in solution. Quantitative parameters describing

³⁰³ Absorption and fluorescence emission spectra are summarized in Fig. 1. We observed that 304 the major influence on the optical properties had the position of the substitution (N,N'-; N,O'-305 and O,O'-) rather than the type of the solubilization group. Ethyladamantyl and 2-ethylhexyl

307the optical properties of solutions are summarized in Table 2. Absorption maximum is shifted308with the change of substitution position: while N,N'-substituted DPPs has a maximum at309approximately 548 nm, N,O'-substituted derivatives has a maximum at 533 nm and O,O'- at310505 nm (see spectra on Fig. 1). These shifts seem to be mainly the consequence of311suppression of electron transition to lower vibration modes in excited state in the case of312N,O'- and O,O'-derivatives (zero phonon transitions are suppressed).

313 The position of the alkyl group also has a major influence on fluorescence emission spectra

314 (see Fig. 1). The emission maximum of N,N'-derivatives was at 563 nm. Emission maximum

315 of *N*,*O*'-derivatives was bathochromically shifted to 600 nm. Emission spectrum of *N*,*O*'-

316 derivative has resolved vibronic structure in contrast to absorption/excitation spectrum. This

317 is probably because the excited molecule is more planar than in the ground state. A clear

318 emission spectrum of *O*,*O*'-substituted derivatives was found only in the case of

319 ethyladamantyl-substituted DPP with a maximum at 730 nm.

The photoluminescence quantum yields (PLQY) drop with substitution in *O*-position dramatically. While *N*,*N'*-derivatives have relatively high fluorescence quantum yields about 60 %, *N*,*O'*-derivatives showed PLQY only of about 1%. The PLQY of *O*,*O'*-derivatives was found to be too small for quantitative evaluation. The fluorescence quantum yield relates to the fluorescence lifetime, which was found for *N*,*N'*-derivatives to be about 6 ns, for *N*,*O'*-

derivatives 0.6 ns and for *O*,*O*'-derivatives only 0.3 ns.

The intersection point of emission and absorption/excitation spectra can be used to provide information about the HOMO-LUMO difference $E_{g opt}$. This quantity was found to be 2.23 eV for *N,N'*-derivatives, 2.16 eV for *N,O'*-derivatives and 2.05 eV for *O,O'*-derivatives, respectively. These values are very close and thus provide other evidence of the abovementioned hypothesis about suppressed electron transitions from the ground state to the excited state with the lowest vibration energy in the case of *O*-substituted derivatives.



Next, thin films from studied DPPs were characterized. Prepared films were annealed at
different temperatures, from 50 to 300 °C with increments of 50 °C. The changes in the
layers' quality (morphological as well as possible degradation) were studied by optical spectra
measurements. Absorption and fluorescence spectra of as-cast and annealed films are
summarized in plots on Fig. 2. The determined optical parameters are summarized in
Table 3. In contrast to solutions, a strong impact of the alkyl substitution position as well as
the kind of substituents on the absorption and emission spectra was observed.









344

Fig. 2. Optical spectra of thin films annealed at different temperatures. The curves marked by 0 are spectra of as-cast films.

	:	as cast film		8	annealed film	
Substitution	λ _{ABS max} [nm]	λ _{ABS edge} [nm]	$\lambda_{\rm PL}$ [nm]	λ_{ABSmax} [nm]	λ _{ABS edge} [nm]	λ PL [nm]
Th-DPP-1a	508	613	696	510	613	695
Th-DPP-1b	518	671	732	562	672	-
Th-DPP-1c	508	622	-	509	621	-
Th-DPP-2a	566	600	691	593	608	588
Th-DPP-2b	541	623	740	547	633	-
Th-DPP-2c	506	730	-	627	≈750	-

345 **Table 3:** Optical parameters of thin films.

346 347 One of the most significant differences between 2-ethylhexyl and ethyladamantyl 348 derivatives is the thermal stability of the layers. The films prepared from 2-ethylhexyl 349 derivatives annealed already at low temperatures lost integrity and over 150 °C vanished from 350 the substrate (evaporated). This is consistent with findings from thermal characterization, 351 which showed that the melting point of 2-ethylhexyl derivatives is up to 120 °C while 352 ethyladamantyl substituted materials were melted at temperatures over 200 °C. Thus films 353 from ethyladamantyl derivatives had better thermal stability. In optical spectra this process 354 was observed as a decrease of signal intensity (see Fig. 2). Layer quality changes were also 355 observed by optical microscopy and the temperature induced changes were documented by 356 photos (see the Supplementary Information: Fig. S13–Fig. S14). 357 The decrease in the fluorescence intensity of the Th-DPP-1a derivative and of both N,O'-358 substituted derivatives (see spectra in Fig. 2) is predominantly a result of the films' integrity losses during annealing, but a contribution of molecular packing changes cannot be excluded. 359 360 The fluorescence intensity of a layer from the **Th-DPP-2a** derivative unequivocally increased 361 after annealing, thus the fluorescence quantum yield was increased. This can be evidence for a

362 longer excitons lifetime as result of higher molecular order.

Thin films from *O*,*O*'-derivatives were not fluorescent as follows from curves in the plot on Fig. 2, which correspond to the background signal from the fluorimeter without the fluorescence signal. This result was expected in the context of the weak fluorescence of solutions.

Looking at the absorption and emission spectra as a whole, we can observe significant
differences between the studied materials' behavior in reaction to thermal annealing. As cast
films from **Th-DPP-1a** shows spectra with significantly lower zero phonon transition
intensity resulting in maximum shifted hypsochromically comparing to the diluted solution.

This shift is typically assigned to H-aggregation. Thermal annealing has little influence to the shape of the spectrum. On the other hand, the absorption of as-cast **Th-DPP-2a** is similar to the diluted solutions but changes dramatically upon annealing. The annealed films showed significant bathochromic shift revealing strong intermolecular interactions induced by the ethyladamantyl *N*-substitution. These interactions can be the reason for high charge carrier mobilities observed in our previous work [33].

377 In the case of both N,O'-substituted derivatives (Th-DPP-1b and Th-DPP-2b) the optical 378 spectra have a shape which at first sight suggests small evidence for J-aggregation. Their as-379 cast films have a very similar position of absorption (≈ 530 nm) and emission (≈ 735 nm) 380 maxima and in the case of the absorption maxima it is practically the same as for the solutions 381 (533 nm). This implies that molecules in films have a rather individual character, without 382 strong interactions. However, the absorption spectrum of film from the **Th-DPP-1b** derivative 383 has an absorption edge at 671 nm, while the film from the Th-DPP-2b derivative has an 384 absorption edge at only 623 nm. The absorption onsets in solution were 600 nm for both 385 derivatives. The extending of the absorption band of films to longer wavelengths is evidence 386 of intermolecular interaction, which seems to be more significant in the case of the 387 2-ethylhexyl derivative **Th-DPP-1b**. Observation of the thin films' structure in optical 388 microscopy (see Fig. 3) revealed that the fresh as-cast layer from the 2-ethylhexyl derivative 389 (Th-DPP-1b) is crystalline, while the layer from the ethyladamantyl derivative (Th-DPP-2b) 390 seems to be amorphous. Intermolecular interaction of molecules in films is also manifested by 391 the emission maxima position, because in the case of films, they are in comparison with the 392 solution bathochromically shifted by approximately 130 nm.

Thermal annealing had practically no effect on the optical spectra shape of films from
ethyladamantyl-substituted derivatives. The rather amorphous character of the Th-DPP-2b
material was also confirmed by thermal characterization. In the case of the Th-DPP-1b

derivative, thermal annealing caused a relative increase of absorption peak intensity at longer
wavelengths, and thus the absorption spectrum after annealing at 150 °C has a more
J-aggregation-like character. The film during annealing at all temperatures was at least
particularly melted according to the picture from microscopy (see the *Supplementary Information*: Fig. S13–Fig. S14). Thus, possible structural changes which can explain the
observed changes in spectra, took place in the melt and during solidification. At temperatures
higher than 150 °C the film was destroyed.

403 The absorption maxima positions of as-cast thin films prepared from O,O'-derivatives are very near to solutions (≈ 505 nm). The presence of $\pi - \pi$ intermolecular interactions in films 404 405 can be deduced only from the bathochromic shift of absorption edges. In the case of 406 Th-DPP-1c derivative, the shift of absorption edge is only weak, but in the case of 407 Th-DPP-2c the absorption edge is even 120 nm shifted in comparison with the solutions. 408 While the overall spectra shape of the 2-ethylhexyl as-cast film suggests that the molecules in 409 the films keep a considerably individual character, the film of the ethyladamantyl derivative 410 seems to be at least partially ordered. The photo from optical microscopy confirms the 411 crystalline structure of the layer from this material (see Fig. 3). It should be noted that the 412 2-ethylhexyl derivative has a waxy character, thus it is rather more liquid than solid (see 413 photos on Fig. 4 and thermal characterization). This explains the observed weak 414 intermolecular interaction in the spectra. The fluorescence emission was not found in both 415 cases as was already reported. Thermal annealing in the case of the 2-ethylhexyl derivative 416 caused only layer destruction which is in good agreement with TGA data. It is a consequence 417 of the degradation of the material and the low melting point (see pictures in the 418 Supplementary Information). In the case of the ethyladamantyl derivative **Th-DPP-2c**, the 419 thermal annealing above 150 °C caused the absorption spectrum to have the J-aggregation 420 character with a maximum at 627 nm. However, with respect to the results from thermal

- 421 characterizations, which show that this derivative has low thermal stability, it cannot be
- 422 guaranteed that the new order of material after annealing is not the result of co-crystallization
- 423 of the original material and degradation products. These changes after annealing at
- 424 temperature above 200 °C are results of re-crystallization from more or less melted matter.





430

Fig. 4. Pictures of the studied materials from optical microscopy. While most of the materials are crystalline, *O*,*O*'-ethylhexyl derivative **Th-DPP-1c** is waxy.

431 432	4. CONCLUSION
433	In summary, we have synthesized and subsequently investigated two series of alkylated DPP
434	derivatives: N,N' -, N,O' - and O,O' -substituted by 2-ethylhexyl and ethyladamantyl chains. It
435	can be summarized that according to the observed optical spectra and the films' pictures from
436	optical microscopy, the 2-ethylhexyl group enhances the films' crystallization, especially in
437	the case of asymmetrical substitution in N,O' -positions. On the other hand, derivatives
438	alkylated by ethyladamantyl chains showed better order if the substitution was symmetrical in
439	O,O'-positions. This observation is in good agreement with the found low glass transition
440	temperatures (20–40 °C) in both cases.
441	Thermal measurements also revealed that substitution in the O-position leads to worse
442	thermal stability of materials. Next, it can be noted that the ethyladamantyl side group gave
443	the materials a higher melting point and better thermal stability than 2-ethylhexyl, as was
444	confirmed by all presented methods (TG and DSC).
445	The used solubilization groups and substitution positions have a significant influence on
446	thin films' consistency and stability. Results from this work can prove valuable especially in
447	the design and fabrication of organic electrical and optoelectrical devices, which requires high
448	molecular order of material as well as structural stability.
449	

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548		





SUPPLEMENTARY INFORMATION









Fig. S5. ¹H–¹⁵N HMBC correlation 2D NMR spectrum of the derivative **Th-DPP-2a**.





2. Thermal analysis





Fig. S9b. The DSC record of the derivative **Th-DPP-1b** after 9 days, melting appeared at 60 °C, after fast cooling appeared a step transition around -18 °C, then was applied annealing at 10 °C for 30 minutes, in consequent heating no melting re-appeared.













Fig. S12b. DSC record of the derivative Th-DPP-2c, thermal deleting run.

615 **3.** Optical properties





Fig. S13. Thin film pictures from optical microscopy after deposition and annealing for 2-ethylhexyl
 substituted DPP derivatives.







Fig. S14. Thin film pictures from optical microscopy after deposition and annealing for ethyladamantyl substituted DPP derivatives.

Highlights

- Two series of asymmetrically substituted DPP derivatives were synthesized.
- Optical properties (both in solution and thin layers) and thermal properties (TGA and DSC analyses) were comprehensively studied for all prepared DPP derivatives.
- Effects of alkyl chain character and binding position in DPP molecule were investigated.
- *O*-substitution caused a significant decrease in the thermal stability of DPP derivatives compared with *N*-alkylated.
- Ethyladamantyl side chain as a rigid alicyclic substituent contributed very effectively to the increase of melting point and thermal stability compared to 2-ethylhexyl substituted DPPs.

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Conflict of interest

This manuscript has not been published and is not under consideration for publication elsewhere. We have no conflicts of interest to disclose.

Please address all correspondence concerning this manuscript to krajcovic@fch.vut.cz.

Jozef Krajcovic

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Dear Professor Heron, dear Editor, dear Referees,

Thank you for reviewing and valuable comments on improving our manuscript. Based on the relatively numerous objections to the language (grammatical) level of the text from both the editor and both reviewers, we have decided to increase the level and especially the clarity of the text to undergo manuscript language correction from a professional certified agency by a native (UK) speaker. As a result of these corrections, there have been done many minor changes in the formulation of sentences beyond your comments. All grammatical and formal objections from the editor and reviewers have also been accepted and corrected. However, all interventions have in no way affected the meaning of sentences, ideas or conclusions arising from the text.

We strongly believe that all made changes have increased the level of our manuscript for accepting by Dyes and Pigments.

Sincerely,

Jozef Krajcovic