

Exciplex Enhancement as a Tool to Increase OLED Device Efficiency.

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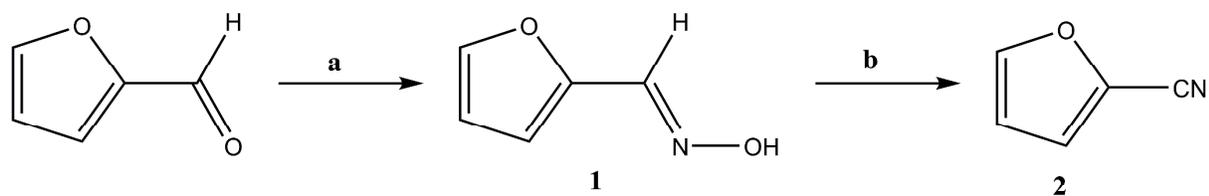
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1. Materials

Materials for the syntheses were purchased from Acros Organics, Sigma-Aldrich or POCH SA. Furfural was purified by vacuum distillation under nitrogen atmosphere, *N,N*-dimethylformamide was distilled under reduced pressure and dried over 4A molecular sieves, thionyl chloride was purified by distillation with linseed oil. Other materials were used without special purifications.

Melting points (not corrected) were determined in an open capillary [**OC**] or using a Boetius HMK apparatus [**B**];. ¹H and ¹³C NMR spectra were recorded on a Varian 600 MHz System (600 MHz for ¹H, 150 MHz for ¹³C), in specified solvent and with tetramethylsilane as the internal reference. The chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) in Hertz. Chemical shifts in *2,5-dialkyl-3,6-diarylpyrrolo[3,4-c]pyrrole-*

1,4(2H,5H)-diones (DADPPs) are described as follows: sign " " is used to denote atoms in the alkyl chains, the sign ' ' is used to denote atoms in aromatic rings.



a - NaOH, HONH₂*HCl
b - SOCl₂, pyridine, ice cooling

Scheme S1. Synthesis of furan based substrates.

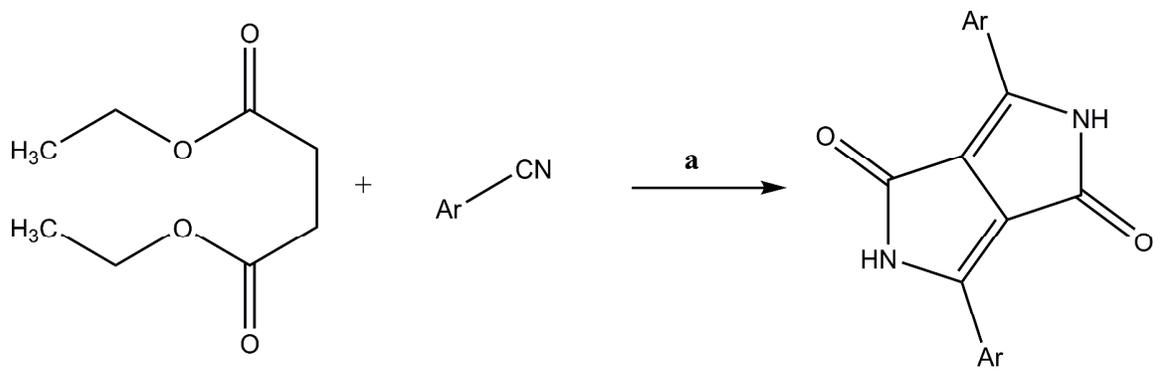
Furan-2-carbaldehyde oxime (1)

Freshly vacuum distilled under nitrogen atmosphere furfural (9.6 g, 0.1X mol) was added to a solution of sodium hydroxide (5.9 g, 0.13 mol) in water (40 mL). To this mixture hydroxylamine hydrochloride (8.7 g, 0.13 mol) was added portion-wise during 30 min and stirred overnight. The reaction mixture was then extracted with diethyl ether (3×30 mL). The combined organic layers were dried over anhydrous magnesium sulfate and next evaporated to dryness. Furan-2-carbaldehyde oxime (9.3 g 0.08 mol) was obtained as a creamy semisolid. Yield 84% m.p.: 45-48 °C [OC] (lit.: 82-84 °C^{S1}). ¹H NMR (Acetone-d₆), δ (ppm): 6.59-6.60 (dd, 1H, *J*=3.6 Hz, *J*=1.8 Hz, H-4); 7.28 (d, 1H, *J*=3.6 Hz, H-3); 7.43 (s, 1H, N=C-H); 7.61 (d, 1H, *J*=1.8 Hz, H-5), 10.88 (s, 1H, -OH). ¹³C NMR (CDCl₃), δ (ppm): 112.78 (1C, C-3); 117.48 (1C, C-4); 136.62 (1C, C-2); 143.74 (1C, C-5); 146.61 (1C, -C=N).

Furan-2-carbonitrile (2)

(S1) Langa, F.; de la Cruz, P.; Espildora, E.; Gonz ales-Cort ez, A.; de la Hoz, A.; L opez-Arza, V. Synthesis and Properties of Isoxazolo[60]fullerene–Donor Dyads. *J. Org. Chem.* **2000**, *65*, 8675–8684.

This compound was prepared through the modification of the procedure described in literature^{S2}. Freshly distilled thionyl chloride (1.8 mL 0.02 mol) was added to an ice-cooled stirred solution of pyridine (1.8 mL, 0.02 mol) in dichloromethane (90 mL). After 20 min. to this solution *furan-2-carbaldehyde oxime* (**1**) (2.0 g, 0.02 mol) was added portion-wise followed by addition of the next portion of pyridine (1.8 mL 0.02 mol). Stirring was continued overnight at room temperature and the reaction mixture was washed with water (3×30 mL), dried over anhydrous magnesium sulfate, filtered and the solvent evaporated on a rotary evaporator (bath temperature 30 °C). Furan-2-carbonitrile (1.0 g, 0.01 mol) was obtained as an oil pure enough for further use. Yield, 61%. ¹H NMR (CDCl₃), δ (ppm): 6.55 (dd, 1H, *J*=3.3 Hz, *J*=1.8 Hz, H-4); 7.12 (dd, 1H, *J*=3.3 Hz, *J*=0.6 Hz, H-3); 8.92 (dd, 1H, *J*=1.8 Hz, *J*=0.6 Hz, H-5) ¹³C NMR (CDCl₃), δ (ppm): 111.38 (-CN); 111.42 (C-3); 121.95 (C-4); 126.30 (C-2); 147.3 (C-5).



Ar - thiophen-2-yl (Th), furan-2-yl (Fu), phenyl (Ph)

a - N₂ atmosphere, *tert*-amyl alcohol, potassium *tert*-butoxide, heating

DPP

Scheme S2. Synthesis of DPP substrates

Synthesis of 3,6-diaryl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-diones [DPPs]

(S2) Arrietta, A.; Palomo, C. Reagents and Synthetic Methods; 22. 1-Chlorosulfinyl-4-dimethylaminopyridinium Chloride as a New Reagent for the Dehydration of Aldoximes to Nitriles. *Synthesis* **1983**, 6, 472–474.

Those compounds were prepared through the modification of the procedure described in literature.^{S3}

General procedure

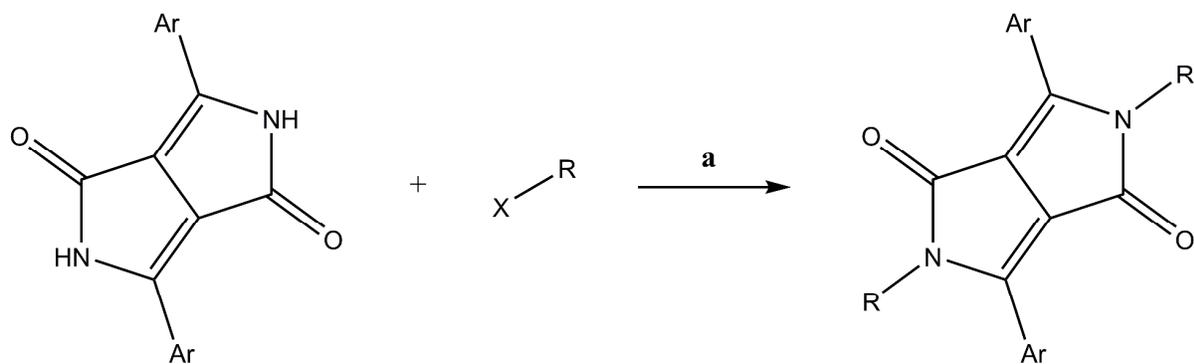
The appropriate nitrile derivative (14 mmol) was introduced under a nitrogen atmosphere to the three times nitrogen degassed stirred solution of potassium *tert*-butoxide (15 mmol) in *tert*-amyl alcohol (30 mL). Diethyl succinate (7 mmol) was added dropwise to this mixture. After addition of the whole amount of diester, the heating was started and the mixture was stirred and heated under reflux for 16 to 24 h and next poured onto a solution of methanol (30 mL) and concentrated hydrochloric acid (3.5 mL). The precipitate was filtered off, washed with cold methanol and dried in a vacuum desiccator.

3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (3)

Reaction time 20 hours, Yield: 80%, m.p.: over 360 °C [B] (lit.: over 300 °C^{S4}). **¹H NMR** (DMSO-d₆), δ (ppm): 7.31 (dd, 2H, *J*=4.8 Hz, *J*=3.9 Hz, H-4'); 7.97 (dd, 2H, *J*=4.8 Hz, *J*=1.2 Hz, H-3'); 8.23 (dd, 2H, *J*=3.9 Hz, *J*=1.2 Hz, H-5'); 11.25 (s, 2H, N-H). **¹³C NMR** (DMSO-d₆), δ (ppm): 108.46; 128.62; 130.71; 131.21; 132.58; 136.10; 161.53.

(S3) Sonar, P.; Ng, G.-M.; Lin, T. T.; Dodabalapur, A.; Chen, Z.-K. Solution Processable Low Bandgap Diketopyrrolopyrrole (DPP) Based Derivatives: Novel Acceptors for Organic Solar Cells. *J. Mater. Chem.* **2010**, *20*, 3626–3636.

(S4) Stas, S.; Sergeyev, S.; Geerts, Y. Synthesis of Diketopyrrolopyrrole (DPP) Derivatives Comprising Bithiophene Moieties. *Tetrahedron* **2010**, *66*, 1837–1845.



Ar - thiophen-2-yl (Th), furan-2-yl (Fu), phenyl (Ph)

R - butyl, hexyl, octyl, decyl, dodecyl

X - Br, I

a - N₂ atmosphere, DMF, K₂CO₃, heating

Scheme S3. Synthesis of investigated compounds.

3,6-di(furan-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4)

Reaction time 20 hours. Yield: 46%, m.p.: over 360 °C [**B**]. ¹H NMR, (DMSO-d₆), δ (ppm): 6.85 (dd, 2H, *J*=3.6 Hz, *J*=1.8 Hz, H-4'); 7.68 (d, 2H, *J*=3.6 Hz, H-3'); 8.05 (d, 2H, *J*=1.8 Hz, H-5'); 11.20 (s, 2H, NH) ¹³C NMR, (DMSO-d₆), δ (ppm): 107.50; 113.60; 116.69; 131.18; 143.68; 146.80; 161.08.

3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5)

Reaction time 16 hours. Yield: 78%, m.p.: over 360 °C [**B**] (lit.: 383 °C, sublimation^{S5}). ¹H NMR, (DMSO-d₆), δ (ppm): 7.56-7.60 (m, 6H, H-Ar), 8.47-8.49 (m, 4H, H-Ar), 11.28 (s_B, 2H, NH). ¹³C NMR, (DMSO-d₆), δ (ppm): 110.59; 127.64; 128.57; 128.94; 131.74; 143.99; 162.39.

Synthesis of 2,5-dialkyl-3,6-diarylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione

(S5) Luňák Jr., S.; Havel, L.; Vyňuchal, J.; Horáková, P.; Kučerík, J.; Weiter, M.; Hrdina, R. The Geometry and Absorption of Diketo-Pyrrolo-Pyrroles Substituted with Various Aryls. *Dyes Pigments* **2010**, *85*, 27–36.

General procedure

Anhydrous potassium carbonate (2.5 mmol) was added under nitrogen to the three times nitrogen degassed stirred mixture of *N,N*-dimethylformamide (8.5 mL) and appropriate 3,6-*aryl*-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (0.83 mmol). The mixture was stirred for 1 hour at 90 °C, followed by dropwise addition of the alkyl halide (2.08 mol). Stirring and heating was continued 24 hours. After this time, the reaction mixture was poured onto ice (50 g) and after melting off ice was extracted with ethyl acetate (5×15 mL). The combined organic layers were washed with cold water, dried over anhydrous magnesium sulfate, filtered off and evaporated to dryness. The crude product was purified by column chromatography.

2,5-dibutyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (6)

Yield: 19%, m.p.: 165-168 °C [B]. ¹H NMR (CDCl₃), δ (ppm): 0.97 (t, 6H, *J*'=7.5 Hz, H-4''); 1.45-XX (m, 4H, H-3''); 1.71-1.76 (m, 4H, H-2''); 4.07-4.1 (m, 4H, H-1''); 7.28 (dd, 2H, *J*=4.8 Hz, *J*=3.9 Hz, H-4'); 7.63 (dd, 2H, *J*=4.8 Hz, *J*=1.2 Hz, H-3'); 8.93 (dd, 2H, *J*=3.9 Hz, *J*=1.2 Hz, H-5'). ¹³C NMR (CDCl₃), δ (ppm): 13.72; 20.18; 32.02; 41.98; 107.72; 128.6X; 129.8X; 130.66 ; 135.26; 140,06; 161.41.

2,5-dihexyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (7)

Yield: 12%, m.p.: 169-172 °C (lit.: 174 °C^{S6}). ¹H NMR (CDCl₃), δ (ppm): 0.88-XX (m, 6H, H-6''); 1.28-1.46 (m, 12H, H-5'' - 3''); 1.72-1.77 (m, 4H, H-2''); 4.05-4.08 (m, 4H, H-1''); 7.28 (dd, 2H, *J*=4.8 Hz, *J*=3.6 Hz, H-4'); 7.63 (dd, 2H, *J*=4.8 Hz, *J*=1.2 Hz, H-3'); 8.92 (dd, 2H, *J*=3.6

(S6) Tamayo, A. B.; Tantiwiwat, M.; Walker, B.; Nguyen, T.-Q. A Low Band Gap, Solution Processable Oligothiophene with a Diketopyrrolopyrrole Core for Use in Organic Solar Cells. *J. Phys. Chem. C* **2008**, *112*, 15543–15552.

Hz, $J=1.2$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 14.00; 22.55; 26.54; 29.91; 31.41; 42.22; 107.70; 128.60; 129.79; 130.65; 135.25; 140.01; 161.36.

2,5-dioctyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (8)

Yield: 7%, m.p.: 130-133 °C (lit.: 139-143 °C^{S7}). ^1H NMR (CDCl_3), δ (ppm): 0.87 (t, 6H, $J=7.0$ Hz, H-8''); 1.24-1.36 (m, 16H, H-7'' - 4''); 1.39-1.44 (m, 4H, H-3''); 1.74 (m, 4H, [H-1''-H-2''-H-3''], H-2''); 4.05-4.09 (m, 4H, H-1''); 7.28 (dd, 2H, $J=5.0$ Hz, $J=4.0$ Hz, H-4'); 7.63 (dd, 2H, $J=5.0$ Hz, $J=1.0$ Hz, H-3'); 8.92 (dd, 2H, $J=3.9$ Hz, $J=1.0$ Hz, H-5') ^{13}C NMR (CDCl_3), δ (ppm): 16.72; 25.27; 29.52; 31.83; 31.85; 32.60; 34.41; 44.87; 110.35; 131.23; 132.43; 133.28; 137.87; 142.65; 164.01.

2,5-dibutyl-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (9)

Yield: 69%, m.p.: 155-157 °C. ^1H NMR (CDCl_3), δ (ppm): 0.96 (t, 6H, $J=7.4$ Hz, H-4''); 1.42-XX (m, 4H, H-3''); 1.66-1.17 (m, 4H, H-2''); 4.11-4.13 (m, 4H, H-1''); 6.69 (dd, 2H, $J=3.6$ Hz, $J=1.8$ Hz, H-4'); 7.64 (dd, 2H, $J=1.8$ Hz, $J=0.6$ Hz, H-3'); XX (dd, 2H, $J=3.6$ Hz, $J=0.6$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 13.81; 20.11; 32.34; 42.16; 106.44; 113.45; 120.12; 133.66; 144.69; 145.18; 160.90.

3,6-di(furan-2-yl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (10)

Yield: 39%, m.p.: 125-127 °C. ^1H NMR (CDCl_3), δ (ppm): 0.86-0.90 (m, 6H, H-6''); 1.28-1.35 (m, 8H, H-5'' - 4''); 1.37-1.42 (m, 4H, H-3''); 1.67-1.72 (m, 4H, H-2''); 4.09-4.12 (m, 4H, H-

(S7) Zhang, L.; Zeng, S.; Yin, L.; Ji, C.; Li, K.; Li, Y.; Wang, Y. The Synthesis and Photovoltaic Properties of A-D-A-Type Small Molecules Containing Diketopyrrolopyrrole Terminal Units. *New J. Chem.* **2013**, *37*, 632–639.

1''); 6.69 (dd, 2H, $J=3.6$ Hz, $J=1.8$ Hz, H-4'), 7.63 (dd, 2H, $J=1.8$ Hz, $J=1.2$ Hz, H-3'); 8.30 (dd, 2H, $J=3.6$ Hz, $J=1.2$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 14.03; 22.54; 26.51; 30.17; 31.47; 42.41; 106.45; 113.45; 120.09; 133.64; 144.69; 145.15; 160.86.

3,6-di(furan-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (11)

Yield: 24%, m.p.: 120-122 °C. ^1H NMR (CDCl_3), δ (ppm): 0.87 (t, 6H, $J=6.9$ Hz, H-8''); 1.22-1.41 (m, 20H, H-7'' - 3''); 1.67-1.72 (m, 4H, H-2''); 4.09-4.12 (m, 4H, H-1''); 6.69 (dd, 2H, $J=3.6$ Hz, $J=1.8$ Hz, H-4'); 7.63 (dd, 2H, $J=1.8$ Hz, $J=0.6$ Hz, H-3'); 8.30 (dd, 2H, $J=3.6$ Hz, $J=0.6$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 14.09; 22.65; 26.86; 29.20; 29.26; 30.22; 31.81; 42.43; 106.46; 113.45; 120.10; 133.66; 144.69; 145.15; 160.87.

2,5-didecyl-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (12)

Yield: 22%, m.p.: 118-120 °C. ^1H NMR (CDCl_3), δ (ppm): 0.87 (t, 6H, $J=6.9$ Hz, H-10''), 1.25-1.41 (m, 28H, H-9'' - 3''); 1.67-1.72 (m, 4H, H-2''), 4.09-4.12 (m, 4H, H-1''); 6.69 (dd, 2H, $J=3.6$ Hz, $J=1.8$ Hz, H-4'); 7.63 (dd, 2H, $J=1.8$ Hz, $J=0.6$ Hz, H-3'); 8.30 (dd, 2H, $J=3.6$ Hz, $J=0.6$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 14.12; 22.68; 26.86; 29.30; 29.54; 29.55; 30.22; 31.90 (4C); 42.43; 106.46; 113.46; 120.11; 133.67; 144.70; 145.15; 160.89.

2,5-didodecyl-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (13)

Yield: 20%, m.p.: 117-118 °C. ^1H NMR (CDCl_3), δ (ppm): 0.87 (t, 6H, $J=7.2$ Hz, H-12''); 1.25-1.41 (m, 36H, H-11'' - 3''); 1.67-1.72 (m, 4H, H-2''); 4.09-4.12 (m, 4H, H-1''); 6.69 (dd, 2H, $J=3.6$ Hz, $J=1.8$ Hz, H-4'); 7.63 (dd, 2H, $J=1.8$ Hz, $J=0.6$ Hz, H-3'); 8.30 (dd, 2H, $J=3.6$ Hz,

$J=0.6$ Hz, H-5'). ^{13}C NMR (CDCl_3), δ (ppm): 14.12; 22.68; 26.86; 29.31(4C); 29.54(4C); 29.55 (4C); 30.22; 31.90; 42.42; 106.46; 113.45; 120.10; 133.66; 144.70; 145.15; 160.87.

2,5-dibutyl-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (14)

Yield: 15%, m.p.: 123-126 °C (lit.: 120 °C from DSC^{S8}). ^1H NMR (CDCl_3): 0.84 (t, 6H, $J=7.2$ Hz, H-4''), 1.23-1.30 (m, 4H, H-3''), 1.55-1.61 (m, 4H, H-2''), 3.75-3.77 (m, 4H, H-1''), 7.51-7.55 (m, 6H, $\underline{\text{H}}'$ -Ar), 7.80-7.82 (m, 4H, $\underline{\text{H}}'$ -Ar), ^{13}C NMR (CDCl_3), δ (ppm): 13.58; 19.99; 31.57; 41.68; 109.75; 128.31; 128.70 (4C); 128.89 (4C); 131.10; 148.52; 162.73.

2,5-dihexyl-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (15)

Yield: 6%, m.p.: 120-123 °C. ^1H NMR (CDCl_3), δ (ppm): 0.82 (t, 6H, $J=7.2$ Hz, H-6''); 1.17-1.26 (m, 12H, H-5'' - 3''), 1.56-1.61 (m, 4H, H-2''); 3.73-3.76 (m, 4H, H-1''), 7.49-7.55 (m, 3H, $\underline{\text{H}}'$ -Ar), 7.79-7.82 (m, 2H, $\underline{\text{H}}'$ -Ar). ^{13}C NMR (CDCl_3), δ (ppm): 13.92; 22.43; 26.37; 29.38; 31.19; 41.89; 109.75; 128.31; 128.68; 128.87; 131.06; 148.49; 162.70.

2,5-dioctyl-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (16)

Yield: 8%, m.p.: 116-119 °C. ^1H NMR (CDCl_3), δ (ppm): 0.85 (t, 6H, $J=7.2$ Hz, H-8'') 1.18-1.26 (m, 20H, H-7'' - 3''), 1.56-1.61 (m, 4H, H-2''), 3.73-3.76 (m, 4H, H-1''), 7.51-7.56 (m, 6H, $\underline{\text{H}}'$ -Ar), 7.80-7.82 (m, 4H, $\underline{\text{H}}'$ -Ar). ^{13}C NMR (CDCl_3), δ (ppm): 14.07; 22.50; 26.70; 28.99; 29.08; 29.41; 31.71; 41.90; 109.75; 128.31; 128.69; 128.87; 131.08; 148.49; 162.71.

(S 8) David, J.; Weiter, M.; Vala, M.; Vyňuchal, J.; Kučerík, J. Stability and Structural Aspects of Diketopyrrolopyrrole Pigment and Its N-Alkyl Derivatives. *Dyes Pigments* **2011**, *89*, 137–143.

2,5-didodecyl-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (17)

Yield: 5%, m.p.: 106-112 °C. ¹H NMR (CDCl₃), δ (ppm): 0.88 (t, 6H, *J*=7.2 Hz, H-12''), 1.19-1.30 (m, 36H, H-11'' - 3''), 1.56-1.61 (m, 4H, H-2''), 3.76-3.73 (m, 4H, H-1''), 7.51-7.55 (m, 6H, H'-Ar), 7.80-7.82 (m, 4-H, H'-Ar). ¹³C NMR (CDCl₃), δ (ppm): 14.12; 22.69; 26.72; 29.04; 29.34; 29.43 (2C); 29.52; 29.61 (2C); 31.91; 41.91; 109.76; 18.31; 128.70; 128.89; 131.09; 148.51; 162.72.

2. Experimental

2.1 Electrochemistry

The solutions of investigated compounds with the concentration of 1 mM were used for electrochemical measurements. All these studies were carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Sigma-Aldrich 98%) in dichloromethane (Sigma-Aldrich ≥99.9%), which served as supporting electrolyte. An Ecochemie AUTOLAB potentiostat-galvanostat model PGSTAT20 was used for electrochemical characterization. The resulting data were collected and analyzed using GPES software (General Purpose Electrochemical System). Cyclic voltammetry (CV) was the main method used for investigating of the redox behavior of studied compounds. The typical three-electrode cell was employed. The working electrode was a platinum disk electrode with 1 mm diameter of working area. A platinum coil served as the auxiliary electrode. Silver wire calibrated versus a ferrocene/ferrocenium redox couple was used as a pseudo reference electrode. All cyclic voltammetry measurements were performed at a scan rate 100 mV s⁻¹. The solutions were purged with argon to eliminate any interaction with oxygen.

2.2 Photoluminescence

Photoluminescence spectra of investigated monomers were obtained on a Hitachi F-2500 spectrofluorometer. Fluorescence excitation spectra were recorded in relation to the emission maximum, and fluorescence emission spectra were recorded at the excitation maximum. All measurements were completed in pure dichloromethane. The quantum yield of DPP derivatives was estimated by comparison with a quantum yield standard (Rhodamine 6G, Rhodamine 101 and Sulforhodamine 101), using the comparative method.^{S9,S10}

2.3 Spectroelectrochemistry

UV-vis-NIR spectroelectrochemical investigations were carried out using Ocean Optics QE65000 and NIRquest 512 spectrometers, connected to a DH-BAL200 light source with optical fiber. The UV-vis-NIR spectra were obtained in a 2 mm quartz cuvette using ITO covered glass as a working electrode, a platinum wire as a counter electrode and Ag wire as a pseudo-reference electrode.

A JEOL JES-FA200 spectrometer was used for EPR spectroelectrochemical experiments. For these experiments, solutions were placed in custom made quartz spectroelectrochemical cell. A platinum wire and coil served as a working and auxiliary electrode, respectively. A silver electrode was used as a quasi-reference electrode. Radicals were generated by applying the appropriate potential and maintaining it throughout the measurement. Microwave power and

(S9) Allen, M. W. Measurement of Fluorescence Quantum Yields, Thermo Fisher Scientific technical note 52019, Madison, WI, USA.

(S10) Williams, A. T. R.; Winfield, S. A.; Miller, J. N. Relative Fluorescence Quantum Yields Using a Computer-Controlled Luminescence Spectrometer. *Analyst* **1983**, *108*, 1067–1071.

modulation amplitude were adjusted to record properly the hyperfine structure of radicals. EPR spectra of radicals were fitted using WinSim software.^{S 11} Solutions used in spectroelectrochemical investigations were identical to those used in electrochemical experiments.

2.4 OLED fabrication and characterization

All organic evaporated compounds were purified by Creaphys organic sublimation system, BCP - bathocuproine (Sigma Aldrich), CBP - 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (Sigma Aldrich), NPB - *N,N'*-Di-1-naphthyl-*N,N'*-diphenylbenzidine (TCI-Europe), TAPC - 4,4'-Cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (Sigma Aldrich), TPBi - 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (LUMTEC), LiF (99.995%, Sigma Aldrich), Aluminium wire (99.9995%, Alfa Aesar). OLED devices were fabricated using pre-cleaned indium-tin-oxide (ITO) coated glass substrates purchased from Ossila with a sheet resistance of 20 Ω/cm^2 and ITO thickness of 100 nm. The formed OLED devices had a pixel size of 2 mm by 1.5 mm. The small molecule and cathode layers were thermally evaporated using Kurt J. Lesker Spectros II deposition at 10^{-6} mbar. All organic materials and aluminum were deposited at a rate of 1 $\text{\AA}\text{s}^{-1}$, and the LiF layer was deposited at 0.1 $\text{\AA}\text{s}^{-1}$. IV characteristic of OLED devices was conducted in 10 inches integrating sphere (Labsphere) connected to a Source Meter Unit.

(S11) Duling, D. R. Simulation of Multiple Isotropic Spin-Trap EPR Spectra. *J. Magn. Reson. Ser. B.* **1994**, *104*, 105–110.

2.5 DFT calculations

Calculations were performed with Gaussian 09 revision B.01 software [G]. All geometry optimizations in this work were conducted with Density Functional Theory (DFT), using B3LYP^{S12,S13,S14} global hybrid functional (as implemented in Gaussian software) with a 6-31G(d) basis set. Single point calculations were carried at a higher 6-311+(d,p) basis set to increase the accuracy of calculations of orbital positions. For all molecules, alkyl chains were reduced to C2 while the point group was set to Ci (see Supporting Information fig. S1 and comment below for more details). For molecules in a neutral state, charge and multiplicity were set to 0 and 1, respectively. In case of charged species, the charge of the molecules was set to -1 (anion radical); +1 (cation radical) or +2 (dication), maintaining multiplicity at 2 for radicals and 1 for dications. Following geometry optimization, frequency calculations were carried out in order to determine if the obtained structure corresponded to a local minimum. In all cases, no imaginary frequencies were found. Optical transitions were calculated with Time Dependent Density Functional Theory (TDDFT) TDDFT/CAM-B3LYP/6-31+(d).^{S15} All calculations in this work were carried out using

(S12) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(S13) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(S14) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of The Electron Density. *Phys. Rev. B.* **1988**, *37*, 785–789.

(S15) Yanai, T. Tew, D.P. Handy, N.C. A New Hybrid Exchange–Correlation Functional Using The Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.

a Polarizable Continuum model (dichloromethane), as implemented in Gaussian software. Input files, orbital, and spin density plots were prepared with Gabedit software.^{S16}

3. Additional results

3.1 Electrochemical measurements

All of investigated compounds underwent two-step oxidation at the potential range from 0.43 V to 0.74 V for the first step, and from 0.81 to 1.08 V for the second step of oxidation. The first step is reversible for all molecules while the second step is reversible for thiophene derivatives only. Reduction proceeds as a two-step process. The first step occurs at a potential lying in the range from -1.88 V to -1.72 V and is reversible in each case, while the second step is irreversible for all of investigated molecules and occurs from -2.52 V to -2.36 V.

Electrochemical measurements were also used for estimating the value of the band gap energy (**Table S1**)

Table S1. Electrochemical data.

	E_{Ox} (V) ^a	E_{Red} (V) ^b	IP (eV) ^c	EA (eV) ^d	E_{G}^{el} (eV) ^e
DPPPhC4	0.563	-1.762	-5.663	-3.338	2.325
DPPPhC6	0.613	-1.714	-5.713	-3.386	2.327
DPPPhC8	0.624	-1.692	-5.724	-3.408	2.316
DPPPhC12	0.609	-1.709	-5.709	-3.391	2.318
DPPhThC4	0.315	-1.692	-5.415	-3.408	2.007
DPPhThC8	0.418	-1.602	-5.518	-3.498	2.020
DPPFuC4	0.396	-1.648	-5.496	-3.452	2.044

(S16) Allouche, A.-R. Gabedit--a Graphical User Interface for Computational Chemistry Softwares. *J. Comput. Chem.* **2011**, *32*, 174–82.

DPPFuC6	0.392	-1.641	-5.492	-3.459	2.033
DPPFuC8	0.394	-1.663	-5.494	-3.437	2.057
DPPFuC10	0.402	-1.646	-5.502	-3.454	2.048
DPPFuC12	0.392	-1.663	-5.492	-3.437	2.055

[a] First oxidation potentials of compounds from CV measurements; [b] First reduction potentials of monomers from CV measurements; [c] Ionization potential energy calculated from $E_{IP} = - (E_p + 5.1)$, where E_p is onset of CV oxidation potential versus Fc/Fc^+ ; [d] Electron Affinity energy calculated from $E_{EA} = - (E_n + 5.1)$, where E_n is onset of CV reduction potential versus Fc/Fc^+ ; [e] Energy of band-gap calculated from the difference between Energy of IP and EA energies;

3.2 Spectroscopic measurements

Table S2. Optical results of DPP derivatives dissolved in dichloromethane, together with data from TDDFT simulations

	λ_{max}	Optical Eg (eV) ^b	Absorption peaks				λ_{max} TDDFT
	(nm) ^a		(nm)				(nm) ^c
DPPPhC4	467	2.39	467	289	267		448
DPPFuC4	538	2.23	538	498	339	277	519
DPPTThC4	549	2.18	549	510	339	291	527

^aabsorption maxima; ^bThe energy of the onset of the first absorption signal in experimental data: HOMO and LUMO levels; ^cabsorption maxima of first excited state calculated at CAM-B3LYP/6-31G+(d) level of theory.

Table S3. Experimental values for excitation wavelengths λ_{ex} , luminescence λ_{em} peak maximums, Stokes shift $\Delta\lambda_{\text{Stokes}}$ and fluorescence quantum yield ϕ_{F}

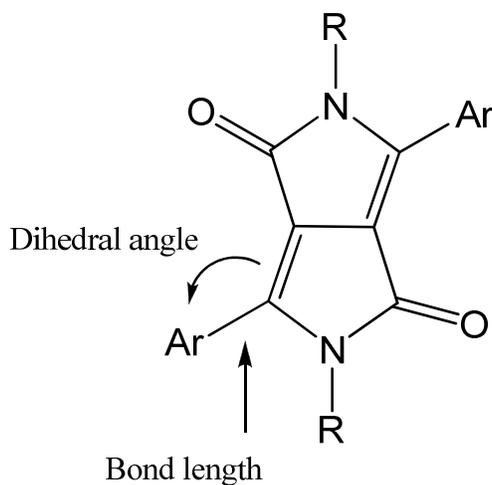
	λ_{ex}	λ_{em}	$\Delta\lambda_{\text{Stokes}}$		ϕ_{F}
	(nm)	(nm)	(nm)		
DPPPhC4	520	467	526	59	0.69
DPPFuC4	538	545	591	7	0.79
DPPTThC4	549	560	610	11	0.74

Table S4. Influence of alkyl chain to fluorescence quantum yield.

	ϕ_{F}
DPPPhC4	0.69
DPPPhC6	0.77
DPPPhC8	0.77
DPPPhC12	0.79
DPPTThC4	0.74
DPPTThC8	0.76
DPPFuC4	0.79
DPPFuC6	0.79
DPPFuC8	0.80
DPPFuC10	0.81
DPPFuC12	0.82

3.3 DFT calculations

The geometry of investigated compounds was simulated with Density Functional Theorem. In case of all molecules, alkyl chains were reduced to C2 and restricted to a Ci point group to speed up the calculation.



Scheme S4. Structure of simulated molecule.

We also tried to simulate molecules with alkyl chain reduced to C1, this, however, resulted in fully planar geometry with C_{2v} point group for compounds with thienyl and furyl substituents. This kind of geometry (fully planar) was found not to be a ground state for simulations with longer alkyl chains. Thus, we concluded that placing methyl group in place of alkyl chain could be an oversimplification.

Table S5. Dihedral angles and bond lengths between central DPP-C2 unit and aryl substituent in neutral and charged forms, calculated at (u)B3LYP/6-31G(d)/DCM level of theory. The figure above presents the designated dihedral angle and bond length. Table Caption.

	Neutral		Radical cation		Dication		Radical anion	
	Dihedral angle (°)	Bond length (Å)						
DPPFu	1.53	1.43	1.53	1.41	1.78	1.39	1.19	1.42
DPPTTh	1.80	1.44	1.44	1.43	1.03	1.39	1.45	1.43
DPPPh	41.86	1.47	39.09	1.45	29.87	1.43	20.39	1.45

Simultaneously, simulations with longer alkyl chains gave results very similar to C2 alkyl chain (the ground state was found with the same dihedral angle and point group). This has convinced us that model compounds with C2 alkyl chains are appropriate model compounds for our study.

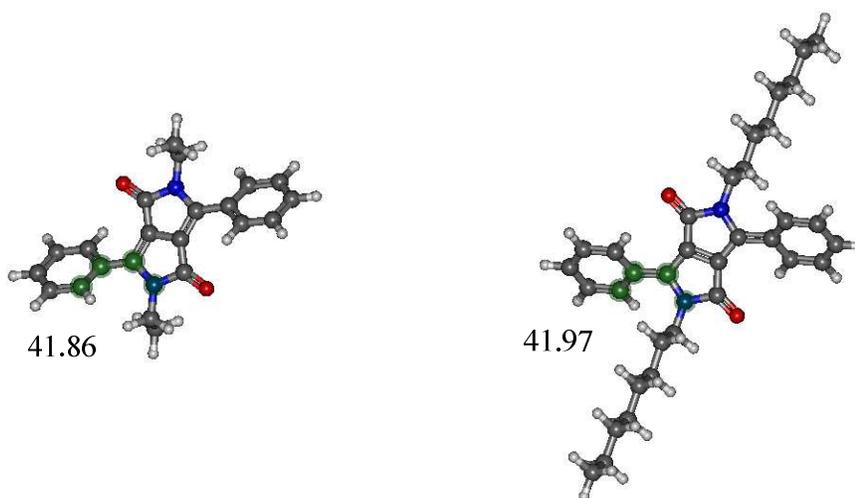


Figure S1. Differences between ground state geometry between molecules with C2 and Cx alkyl chain. Both geometries were free of imaginary frequencies.

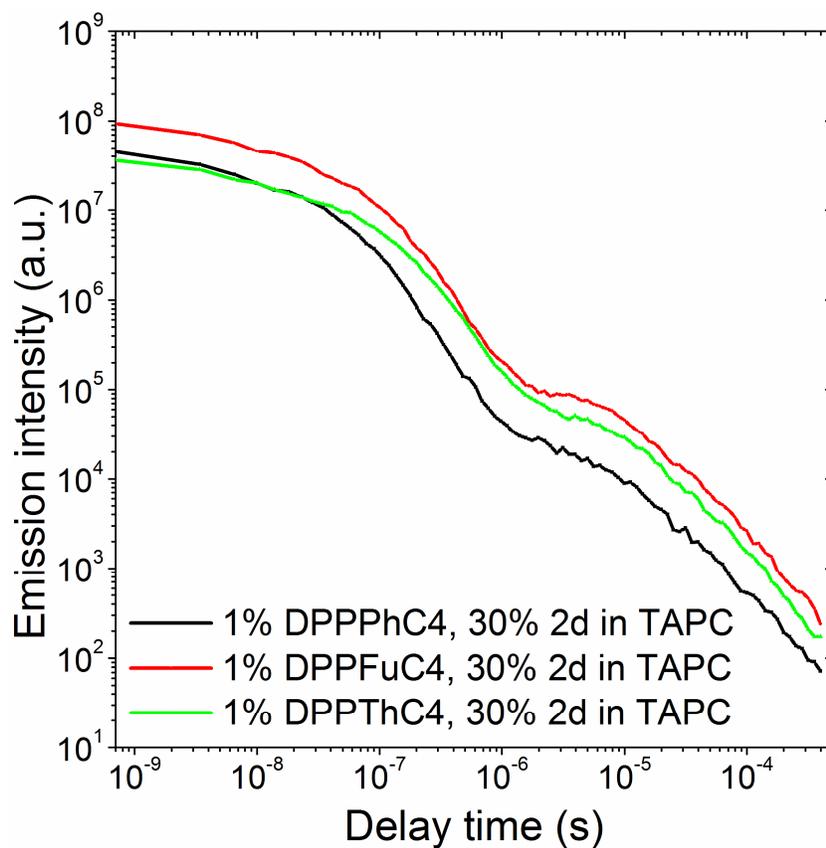


Figure S2. Plot of the exciplex enhanced diketopyrrolopyrroles in 2d:TAPC layer emission intensity over a time interval.