

Supporting Information:

New Violet to Yellow Light Sensitive Diketo Pyrrolo-Pyrrole Photoinitiators: High Performance Systems with Unusual Bleaching Properties and Solubility in Water

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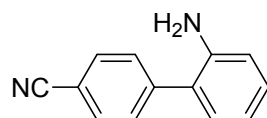
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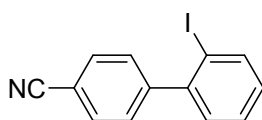
Synthesis of DKPPs

General

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy and NMR were recorded at the Aix-Marseille University' Spectropole. The HRMS mass spectral analyses were performed with a SYNAPT G2 HDMS (Waters) mass spectrometer. ¹H and ¹³C NMR were recorded at room temperature in 5 mm o.d. tubes on a Bruker AC 400 spectrometer: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak DMSO (2.50 ppm), CDCl₃ (7.26 ppm). The ¹³C chemical shifts were determined by ¹³C-APT experiment and are referenced to the solvent peak DMSO (39.5 ppm), CDCl₃ (77 ppm). Chromatography on atmospheric pressure column was performed on silica gel 60 with particle size of 40-63 nm (Merck). Eluents were specified for each operation. All the products were prepared with analytical purity up to accepted standards for new organic compounds (> 98%); their purity was checked by high field NMR analysis.

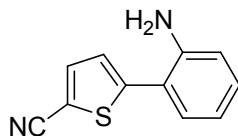


2'-Aminobiphenyl-4-carbonitrile (1a). 2-Iodoaniline (1.42 g, 6.48 mmol) and 4-cyanobenzeneboronic acid (1.0 g, 6.8 mmol, 1.05 eq.) were introduced in a melt of toluene (27 mL), ethanol (13 mL) and K₂CO₃ (2 M, 13 mL). Pd(PPh₃)₄ (449.5 mg, 0.39 mmol, 0.06 eq.) was added and the mixture was stirred at 80 °C for 4 h. The obtained solution was cooled at room temperature then diluted with water. The product was extracted with ethyl acetate. The combined organic layers were washed with water, dried over MgSO₄ and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography on silica gel (CH₂Cl₂) to provide a brown oil (1.01 g, 5.2 mmol, 80 % yield). ¹H NMR (CDCl₃) δ(ppm): 3.80 (br s, 2H), 6.80 (dd, 1H, ³J = 8.0 Hz, ⁴J = 0.7 Hz), 6.87 (td, 1H, ³J = 7.5 Hz, ⁴J = 1.0 Hz), 7.11 (dd, 1 H, ³J = 7.6 Hz, ⁴J = 1.5 Hz), 7.22 (td, 1 H, ³J = 7.7 Hz, ⁴J = 1.4 Hz), 7.61 (d, 2H, J = 8.2 Hz), 7.74 (d, 2H, J = 8.4 Hz); ¹³C NMR (CDCl₃) δ(ppm): 110.9 (C_q), 116.1 (CH), 118.8 (C≡N), 119.1 (CH), 125.5 (C_q), 129.6 (CH), 129.8 (CH), 130.2 (CH), 132.6 (CH), 143.2 (C_q), 144.5 (C_q); HRMS (ESI MS) m/z: theor: 195.0917 found: 195.0918 ((M+H)⁺ detected).

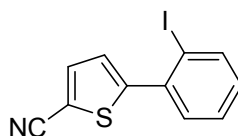


2'-Iodobiphenyl-4-carbonitrile (2a). 2'-Aminobiphenyl-4-carbonitrile (1.0 g, 5.15 mmol) and HCl (4 M, 14 mL) were introduced in THF (14 mL) then cooled in an ice bath. A solution of NaNO₂ (426.3 mg, 6.18 mmol, 1.2 eq.) in water (6 mL) was added dropwise and the mixture was stirred for 20 min. A solution of KI (2.05 g, 12.36 mmol, 2.4 eq.) in water (9 mL) was added and the mixture was stirred at 0 °C for 10 min and at room temperature for 1 h. Then, a solution of Na₂S₂O₃ (1 M) was added dropwise until the stabilization of the color of the solution. The organic and the aqueous layers were separated and the latter was further washed with ethyl acetate. The combined organic layers were washed with water, dried over MgSO₄ and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography on silica gel (pentane/AcOEt: 9.5/0.5) to provide a white solid (1.33 g, 4.36 mmol, 85 % yield). ¹H NMR (CDCl₃) δ(ppm): 7.10 (td, 1 H, ³J = 7.6 Hz, ⁴J = 1.7 Hz), 7.28 (dd, 1 H, ³J = 7.6 Hz, ⁴J = 1.7 Hz), 7.44 (td, 1 H, ³J = 7.5 Hz, ⁴J = 1.2 Hz), 7.47 (d, 2H, J = 8.6 Hz), 7.73 (d, 2H, J = 8.6 Hz), 7.98 (dd, 1H, ³J = 8.0 Hz, ⁴J = 1.0 Hz); ¹³C NMR (CDCl₃) δ(ppm): 97.4 (C_q), 111.6 (C_q), 118.7 (C≡N), 128.4 (CH),

129.7 (CH), 129.8 (CH), 130.2 (CH), 131.9 (CH), 139.8 (CH), 144.7 (C_q), 148.5 (C_q); **HRMS** (**ESI MS**) *m/z*: theor: 323.0040 found: 323.0041 ((M+NH₄)⁺ detected).

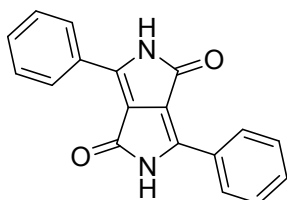


5-(2-Aminophenyl)thiophene-2-carbonitrile (1b). 5-Cyanothiopheneboronic acid (1.0 g, 6.54 mmol) and 2-iodoaniline (2.15 g, 9.81 mmol, 1.5 eq.), 13 mL of DME and 13 mL of K₂CO₃ (2 M) were stirred at room temperature for 30 min under argon atmosphere. PdCl₂(PPh₃)₂ (138.5 mg, 0.26 mmol, 0.04 eq.) was added and the mixture was stirred at 80 °C for 16 h. The obtained solution was allowed to reach room temperature then ethyl acetate was added. The organic layer was washed with water, dried over MgSO₄ and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/pentane: 8/2) to provide a brown solid (360 mg, 1.80 mmol, 27 % yield). **¹H NMR (CDCl₃) δ(ppm):** 3.99 (br s, 2H), 6.82 (m, 2H), 7.24 (m, 3H), 7.64 (d, 1H, J = 3.8 Hz); **¹³C NMR (CDCl₃) δ(ppm):** 108.8 (C_q), 114.2 (C≡N), 116.5 (CH), 117.6 (C_q), 119.0 (CH), 125.9 (CH), 130.5 (CH), 130.8 (CH), 137.9 (CH), 144.1 (C_q), 149.1 (C_q); **HRMS (ESI MS) *m/z*:** theor: 201.0481 found: 201.0480 ((M+H)⁺ detected).

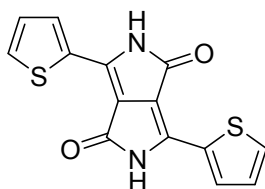


5-(2-Iodophenyl)thiophene-2-carbonitrile (2b). 5-(2-Aminophenyl)thiophene-2-carbonitrile (0.58 g, 2.90 mmol) and HCl (4 M, 8 mL) were introduced in THF (8 mL) then cooled in an ice bath. A solution of NaNO₂ (239.8 mg, 3.48 mmol, 1.2 eq.) in water (3.4 mL) was added dropwise and the mixture was stirred for 20 min. A solution of KI (1.15 g, 6.95 mmol, 2.4 eq.) in water (5.1 mL) was added and the mixture was stirred at 0 °C for 10 min and at room temperature for 1 h. Then, a solution of Na₂S₂O₃ (1 M) was added dropwise until the stabilization of the color of the solution. The organic and the aqueous layers were separated and the latter was further washed with ethyl acetate. The combined organic layers were washed with water, dried over MgSO₄ and the solvent was removed under reduced pressure using a rotary evaporator. The combined organic layers were washed with water, dried over MgSO₄ and the solvent was removed under reduced pressure using a rotary evaporator. The

crude product was purified by column chromatography on silica gel (pentane/CH₂Cl₂: 6/4) to provide a white solid (730 mg, 2.35 mmol, 81 % yield). ¹H NMR (CDCl₃) δ(ppm): 7.12 (m, 1H), 7.17 (d, 1H, J = 3.9 Hz), 7.42 (m, 2H), 7.62 (d, 1H, J = 3.9 Hz), 8.00 (d, 1H, J = 8.1 Hz); ¹³C NMR (CDCl₃) δ(ppm): 98.6 (C_q), 109.9 (C_q), 114.1 (C≡N), 128.1 (CH), 128.4 (CH), 130.7 (CH), 131.2 (CH), 137.0 (C_q), 137.1 (CH), 140.3 (CH), 152.2 (C_q); HRMS (ESI MS) m/z: theor: 328.9604 found: 328.9605 ((M+NH₄)⁺ detected).

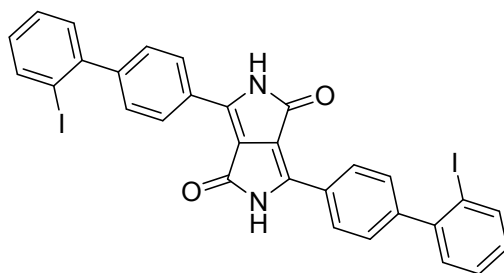


3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3). *Tert*-amyl alcohol (40 mL), sodium (1.15 g, 50.0 mmol, 5 eq.) and a catalytic amount of iron (III) chloride were introduced in a three-neck round bottom flask under an argon atmosphere then the mixture was refluxed until sodium was completely reacted. The reaction was cooled to 90 °C and benzonitrile (2.37 mL, 23.0 mmol, 2.3 eq.) was added with a syringe. The mixture was heated to 110 °C and diisopropyl succinate (2.1 mL, 10.0 mmol) was added dropwise. After 16 h of reaction at 110 °C, the mixture was cooled at room temperature and a solution of water/methanol/acetic acid (1/1/1) (100 mL) was added. The resulting suspension was refluxed for few minutes then cooled to 30 °C. The obtained solid precipitate was filtered, washed several times with hot water and methanol and dried under vacuum to provide a red solid (1.44 g, 4.99 mmol, 50 % yield). ¹H NMR (DMSO-*d*₆) δ(ppm): 7.58 (m, 6H), 8.49 (m, 4H), 11.35 (s, 2H); ¹³C NMR (DMSO-*d*₆) δ(ppm): 110.7 (C_q), 127.7 (C_q), 127.7 (CH), 129.1 (CH), 131.9 (CH), 144.1 (C_q), 162.5 (C=O); HRMS (ESI MS) m/z: theor C₁₈H₁₃N₂O₂: 289.0972 found: 289.0973 ((M+H)⁺ detected).



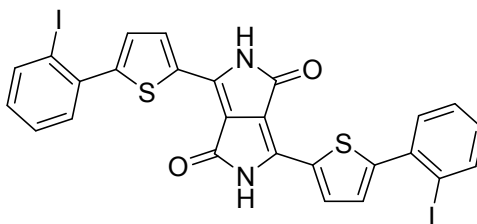
3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4). *Tert*-amyl alcohol (40 mL), sodium (1.15 g, 50.0 mmol, 5 eq.) and a catalytic amount of iron (III) chloride were introduced in a three-neck round bottom flask under argon atmosphere then the mixture was

refluxed until sodium was completely reacted. The reaction was cooled to 90 °C and thiophene-2-carbonitrile (2.14 mL, 23.0 mmol, 2.3 eq.) was added with a syringe. The mixture was heated to 110 °C and diisopropyl succinate (2.1 mL, 10.0 mmol) was added dropwise. After 16 h of reaction at 110 °C, the mixture was cooled at room temperature and a solution of water/methanol/acetic acid (1/1/1) (100 mL) was added. The resulting suspension was refluxed for few minutes then cooled to 30 °C. The obtained solid precipitate was filtered, washed several times with hot water and methanol and dried under vacuum to provide a dark red solid (2.71 g, 9.02 mmol, 90 % yield). **¹H NMR (DMSO-*d*₆) δ(ppm)**: 7.30 (t, 2H, J = 4.4 Hz), 7.96 (d, 2H, J = 5.0 Hz), 8.21 (d, 2H, J = 3.8 Hz), 11.24 (s, 2H); **¹³C NMR (DMSO-*d*₆) δ(ppm)**: 108.5 (C_q), 128.7 (CH), 130.8 (C_q), 131.3 (CH), 132.7 (CH), 136.1 (C_q), 161.6 (C=O); **HRMS (ESI MS) *m/z***: theor C₁₄H₉N₂O₂S₂: 301.0100 found: 301.0101 ((M+H)⁺ detected).

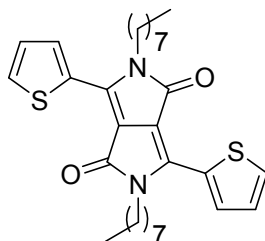


3,6-Bis(2'-iodobiphenyl-4-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (5). *Tert*-amyl alcohol (7 mL), sodium (196.7 mg, 8.55 mmol, 5 eq.) and a catalytic amount of iron (III) chloride were introduced in a three-neck round bottom flask under argon atmosphere then the mixture was refluxed until sodium was completely reacted. The reaction was cooled to 90 °C and 2'-iodobiphenyl-4-carbonitrile (1.2 g, 3.93 mmol, 2.3 eq.) was added. The mixture was heated to 110 °C and diisopropyl succinate (0.35 mL, 1.71 mmol) was added dropwise. After 16 h of reaction at 110 °C, the mixture was cooled at room temperature and a mixture of water/methanol/acetic acid (1/1/1) (18 mL) was added. The resulting suspension was refluxed for few minutes then cooled to 30 °C. The obtained solid precipitate was filtered, washed several times with hot water and methanol and dried under vacuum to provide a dark red solid (600 mg, 0.87 mmol, 51 % yield). **¹H NMR (DMSO-*d*₆) δ(ppm)**: 7.18 (t, 2H, J = 7.5 Hz), 7.41 (d, 2H, J = 7.3 Hz), 7.52 (t, 2H, J = 7.2 Hz), 7.56 (d, 4H, J = 8.3 Hz), 8.03 (d, 2H, J = 7.8 Hz), 8.57 (d, 4H, J = 8.3 Hz), 11.5 (br s, 2H); **¹³C NMR (DMSO-*d*₆) δ(ppm)**: 98.3 (C_q), 111.1 (C_q), 127.0 (C_q), 127.5 (CH), 128.6 (CH), 129.7 (CH), 129.9 (CH), 130.1 (CH), 139.4 (CH), 143.7

(C_q), 145.0 (C_q), 146.8 (C_q), 162.5 (C=O); **HRMS (ESI MS) *m/z***: theor: 692.9531 found: 692.9535 ((M+H)⁺ detected).

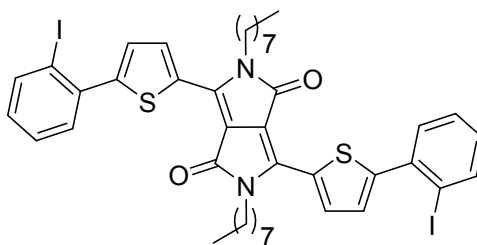


3,6-Bis(5-(2-iodophenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (6). *Tert*-amyl alcohol (4 mL), sodium (112.5 mg, 4.89 mmol, 5 eq.) and a catalytic amount of iron (III) chloride were introduced in a three-neck round bottom flask under argon atmosphere then the mixture was refluxed until sodium was completely reacted. The reaction was cooled to 90 °C and 5-(2-iodophenyl)thiophene-2-carbonitrile (700 mg, 2.25 mmol, 2.3 eq.) was added. The mixture was heated to 110 °C and diisopropyl succinate (0.2 mL, 0.98 mmol) was added dropwise. After 16 h of reaction at 110 °C, the mixture was cooled at room temperature and a mixture of water/methanol/acetic acid (1/1/1) (10 mL) was added. The resulting suspension was refluxed for few minutes then cooled to 30 °C. The obtained solid precipitate was filtered, washed several times with hot water and methanol and dried under vacuum to provide a dark purple solid (440 mg, 0.62 mmol, 64 % yield). **¹H NMR (DMSO-*d*₆) δ (ppm)**: 7.41 (m, 1H), 7.51 (m, 2H), 7.76 (m, 2H), 8.21 (d, 1H, *J* = 3.9 Hz); **HRMS (ESI MS) *m/z***: theor: 704.8659 found: 704.8665 ((M+H)⁺ detected).



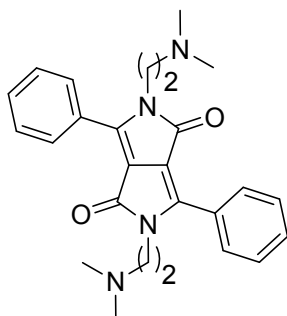
2,5-Dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP4). 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **4** (2.0 g, 6.66 mmol) was dissolved in anhydrous DMF (70 mL) under argon atmosphere. NaH (60% in mineral oil, 665.9 mg, 16.7 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 1-Bromooctane (2.9 mL, 16.7 mmol, 2.5 eq.) was added dropwise and the mixture was stirred at 140 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under

vacuum. The obtained residue was diluted with CH₂Cl₂ then washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/pentane: 8/2) to provide a dark purple solid (2.27 g, 4.33 mmol, 65 % yield). ¹H NMR (CDCl₃) δ(ppm): 0.88 (t, 6H, J = 6.7 Hz), 1.27 (m, 16H), 1.42 (quint, 4H, J = 7.0 Hz), 1.75 (quint, 4H, J = 7.6 Hz), 4.08 (t, 4H, J = 7.9 Hz), 7.29 (dd, 2H, J = 5.0 Hz, J = 4.1 Hz), 7.65 (dd, 2H, ³J = 5.0 Hz, ⁴J = 0.9 Hz), 8.93 (dd, 2H, ³J = 3.9 Hz, ⁴J = 0.9 Hz); ¹³C NMR (CDCl₃) δ(ppm): 14.1 (CH₃), 22.6 (CH₂), 26.9 (CH₂), 29.17 (CH₂), 29.19 (CH₂), 29.9 (CH₂), 31.8 (CH₂), 42.2 (CH₂), 107.7 (C_q), 128.6 (CH), 129.8 (C_q), 130.6 (CH), 135.2 (CH), 140.0 (C_q), 161.4 (C=O); HRMS (ESI MS) m/z: theor: 525.2604 found: 525.2603 ((M+H)⁺ detected).

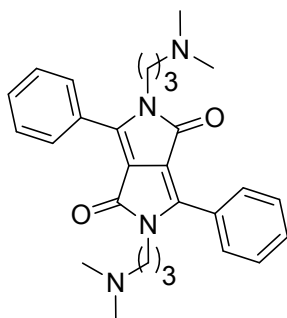


3,6-Bis(5-(2-iodophenyl)thiophen-2-yl)-2,5-diocetylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP9). 3,6-Bis(5-(2-iodophenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **6** (0.4 g, 0.57 mmol) was dissolved in anhydrous DMF (15 mL) under argon atmosphere. NaH (60% in mineral oil, 56.8 mg, 1.42 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 1-Bromooctane (0.49 mL, 2.84 mmol, 5 eq.) was added dropwise and the mixture was heated at 140 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The residue was diluted with CH₂Cl₂ then washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/pentane: 6/4) to provide a dark purple solid (140 mg, 0.15 mmol, 27 % yield). ¹H NMR (CDCl₃) δ(ppm): 0.86 (t, 6H, J = 5.9 Hz), 1.27 (m, 16H), 1.45 (quint, 4H, J = 6.7 Hz), 1.81 (quint, 4H, J = 7.5 Hz), 4.12 (t, 4H, J = 7.8 Hz), 7.10 (td, 2H, ³J = 7.6 Hz, ⁴J = 1.6 Hz), 7.38 (d, 2H, J = 4.2 Hz), 7.43 (td, 2H, ³J = 7.5 Hz, ⁴J = 1.0 Hz), 7.50 (dd, 2H, ³J = 7.7 Hz, ⁴J = 1.6 Hz), 8.02 (dd, 2H, ³J = 7.8 Hz, ⁴J = 0.7 Hz), 9.00 (d, 2H, J = 4.2 Hz); ¹³C NMR (CDCl₃) δ(ppm): 14.1 (CH₃), 22.6 (CH₂), 26.9 (CH₂), 29.2 (CH₂), 29.3

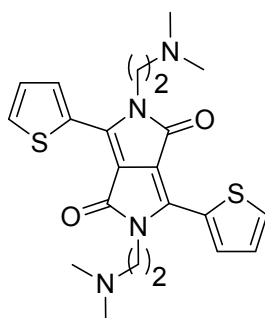
(CH₂), 30.0 (CH₂), 31.8 (CH₂), 42.4 (CH₂), 98.7 (C_q), 108.1 (C_q), 128.3 (CH), 129.4 (CH), 130.1 (C_q), 130.2 (CH), 131.3 (CH), 135.4 (CH), 138.0 (C_q), 139.7 (C_q), 140.4 (CH), 150.2 (C_q), 161.4 (C=O); **HRMS (ESI MS) *m/z***: theor: 929.1163 found: 929.1164 ((M+H)⁺ detected).



2,5-Bis(2-(dimethylamino)ethyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DKPP6). 3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione **3** (0.25 g, 0.87 mmol) was dissolved in anhydrous DMF (8 mL) under argon atmosphere. NaH (60 % in mineral oil, 173.4 mg, 4.3 mmol, 5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). The mixture was cooled with an ice/water bath then 2-chloro-*N,N*-dimethylethylamine hydrochloride (312.3 mg, 2.16 mmol, 2.5 eq.) was added dropwise followed by KI (36 mg, 0.22 mmol, 0.25 eq.). The mixture was heated at 60 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/EtOH/NEt₃: 9.5/0.5/0.1) to provide a red/orange solid (80 mg, 0.19 mmol, 21 % yield). **¹H NMR (CDCl₃) δ (ppm)**: 2.17 (s, 12H), 2.51 (t, 4H, J = 6.8 Hz), 3.88 (t, 4H, J = 6.8 Hz), 7.52 (m, 6H), 7.82 (m, 4H); **¹³C NMR (CDCl₃) δ (ppm)**: 40.0 (CH₂), 45.6 (CH₃), 57.9 (CH₂), 109.9 (C_q), 128.3 (C_q), 128.9 (CH), 129.1 (CH), 131.3 (CH), 148.8 (C_q), 162.9 (C=O); **HRMS (ESI MS) *m/z***: theor: 431.2442 found: 431.2441 ((M+H)⁺ detected).

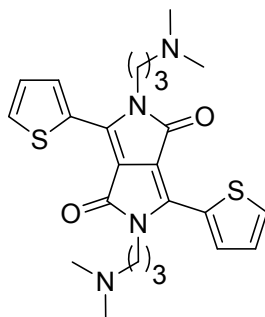


2,5-Bis(3-(dimethylamino)propyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP5). 3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **3** (1.5 g, 5.2 mmol) was dissolved in anhydrous DMF (50 mL) under argon atmosphere. NaH (60% in mineral oil, 520 mg, 13 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 3-Chloro-*N,N*-dimethylpropylamine (1.69 mL, 13 mmol, 2.5 eq.) was added dropwise followed by KI (216 mg, 1.3 mmol, 0.25 eq.). The mixture was heated at 140 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/EtOH/NEt₃: 9/1/0.1) to provide a red solid (1.1 g, 2.40 mmol, 46 % yield). ¹H NMR (CDCl₃) δ(ppm): 1.78 (quint, 4H, J = 7.4 Hz), 2.14 (s, 12H), 2.26 (t, 4H, J = 7.1 Hz), 3.81 (t, 4H, J = 7.6 Hz), 7.53 (m, 6H), 7.81 (m, 4H); ¹³C NMR (CDCl₃) δ(ppm): 27.4 (CH₂), 40.2 (CH₂), 45.2 (CH₃), 56.8 (CH₂), 109.7 (C_q), 128.1 (C_q), 128.7 (CH), 128.9 (CH), 131.2 (CH), 148.5 (C_q), 162.7 (C=O); **HRMS (ESI MS)** *m/z*: theor: 459.2755 found: 459.2754 ((M+H)⁺ detected).



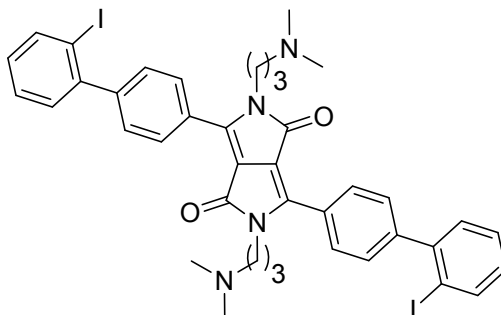
2,5-Bis(2-(dimethylamino)ethyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP2). 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **4** (0.5 g, 1.66 mmol) was dissolved in anhydrous DMF (16 mL) under argon atmosphere. NaH (60 % in

mineral oil, 499.4 mg, 12.5 mmol, 7.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). The mixture was cooled with an ice/water bath then 2-chloro-*N,N*-dimethylethylamine hydrochloride (1.2 g, 8.32 mmol, 5 eq.) was added dropwise followed by KI (69.1 mg, 0.42 mmol, 0.25 eq.). The solution was heated at 60 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/EtOH/NEt₃: 9.5/0.5/0.1) to provide a dark purple solid (329 mg, 0.74 mmol, 45 % yield). ¹H NMR (CDCl₃) δ(ppm): 2.36 (s, 12H), 2.65 (t, 4H, J = 7.8 Hz), 4.24 (t, 4H, J = 7.8 Hz), 7.30 (dd, 2H, J = 4.9 Hz, J = 4.0 Hz), 7.66 (dd, 2H, ³J = 5.0 Hz, ⁴J = 0.9 Hz), 8.86 (dd, 2H, ³J = 3.9 Hz, ⁴J = 1.0 Hz); ¹³C NMR (CDCl₃) δ(ppm): 40.3 (CH₂), 45.7 (CH₃), 57.9 (CH₂), 107.8 (C_q), 128.7(CH), 129.5 (C_q), 130.8 (CH), 135.1 (CH), 140.0 (C_q), 161.3 (C=O); HRMS (ESI MS) m/z: theor: 453.1570 found: 453.1571 ((M+H)⁺ detected).



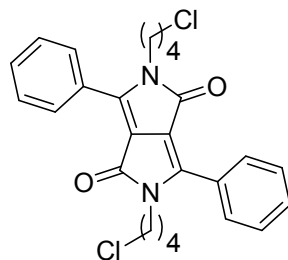
2,5-Bis(3-(dimethylamino)propyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP1). 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **4** (1.0 g, 3.33 mmol) was dissolved in anhydrous DMF (34 mL) under argon atmosphere. NaH (60% in mineral oil, 333 mg, 8.32 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 3-Chloro-*N,N*-dimethylpropylamine (1.08 mL, 8.32 mmol, 2.5 eq.) was added dropwise followed by KI (138.2 mg, 0.83 mmol, 0.25 eq.). The mixture was heated at 140 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on

silica gel (CH₂Cl₂/EtOH/NEt₃: 9/1/0.1) to provide a dark purple solid (473 mg, 1.0 mmol, 30 % yield). **¹H NMR (CDCl₃) δ(ppm)**: 1.95 (quint, 4H, J = 7.5 Hz), 2.27 (s, 12H), 2.45 (t, 4H, J = 7.3 Hz), 4.15 (t, 4H, J = 7.7 Hz), 7.29 (dd, 2H, J = 5.0 Hz, J = 4.0 Hz), 7.65 (dd, 2H, ³J = 5.0 Hz, ⁴J = 1.0 Hz), 8.89 (dd, 2H, ³J = 3.9 Hz, ⁴J = 1.0 Hz); **¹³C NMR (CDCl₃) δ(ppm)**: 27.9 (CH₂), 40.4 (CH₂), 45.4 (CH₃), 56.9 (CH₂), 107.7 (C_q), 128.7 (CH), 129.6 (C_q), 130.8 (CH), 135.2 (CH), 140.0 (C_q), 161.4 (C=O); **HRMS (ESI MS) m/z**: theor: 471.1883 found: 471.1884 ((M+H)⁺ detected).

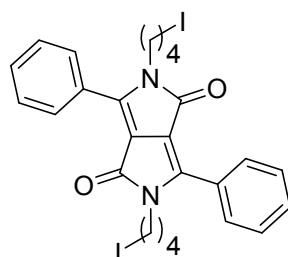


2,5-Bis(3-(dimethylamino)propyl)-3,6-bis(2'-iodobiphenyl-4-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP8). 3,6-Bis(2'-iodobiphenyl-4-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **5** (0.23 g, 0.33 mmol) was dissolved in anhydrous DMF (8 mL) under argon atmosphere. NaH (60% in mineral oil, 33.2 mg, 0.83 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 3-Chloro-N,N-dimethylpropylamine (0.22 mL, 1.66 mmol, 5 eq.) was added dropwise followed by KI (18 mg, 0.08 mmol, 0.25 eq., 166 g/mol). The mixture was heated at 140 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/EtOH/NEt₃: 9/0.5/0.1) to provide an orange solid (100 mg, 0.12 mmol, 35 % yield). **¹H NMR (CDCl₃) δ(ppm)**: 1.93 (quint, 4H, J = 6.8 Hz), 2.26 (s, 12H), 2.44 (t, 4H, J = 6.5 Hz), 3.93 (t, 4H, J = 7.5 Hz), 7.09 (td, 2H, ³J = 7.6 Hz, ⁴J = 1.6 Hz), 7.35 (dd, 2H, ³J = 7.6 Hz, ⁴J = 1.6 Hz), 7.45 (td, 2H, ³J = 7.4 Hz, ⁴J = 1.2 Hz), 7.56 (d, 4H, J = 8.3 Hz), 7.94 (d, 4H, J = 8.3 Hz), 8.00 (dd, 2H, ³J = 7.9 Hz, ⁴J = 0.8 Hz); **¹³C NMR (CDCl₃) δ(ppm)**: 27.1 (CH₂), 40.2 (CH₂), 45.0 (CH₃), 56.7 (CH₂), 97.9 (C_q), 110.0 (C_q), 127.2 (C_q), 128.3 (CH), 128.4 (CH), 129.3 (CH), 129.4 (CH), 130.0 (CH), 139.7 (CH), 145.5 (C_q), 146.9

(C_q), 148.2 (C_q), 162.8 (C=O); **HRMS (ESI MS) *m/z***: theor: 863.1314 found: 863.1319 ((M+H)⁺ detected).

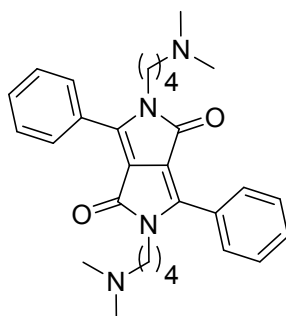


2,5-Bis(4-chlorobutyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (7a). 3,6-Diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione **3** (0.5 g, 1.73 mmol) was dissolved in anhydrous DMF (20 mL) under argon atmosphere. NaH (60% in mineral oil, 173.4 mg, 4.34 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 1-Chloro-4-iodobutane (0.53 mL, 4.34 mmol, 2.5 eq.) was added dropwise and all the mixture was heated at 60 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂) to provide an orange solid (388 mg, 0.83 mmol, 48 % yield). **¹H NMR (CDCl₃) δ (ppm)**: 1.75 (m, 8H), 3.47 (t, 4H, J = 6.1 Hz), 3.81 (t, 4H, J = 6.9 Hz), 7.55 (m, 6H), 7.81 (m, 4H); **¹³C NMR (CDCl₃) δ (ppm)**: 26.7 (CH₂), 29.6 (CH₂), 40.9 (CH₂), 44.2 (CH₂), 109.7 (C_q), 128.0 (C_q), 128.6 (CH), 129.0 (CH), 131.3 (CH), 148.4 (C_q), 162.6 (C=O); **HRMS (ESI MS) *m/z***: theor: 469.1444 found: 469.1443 ((M+H)⁺ detected).

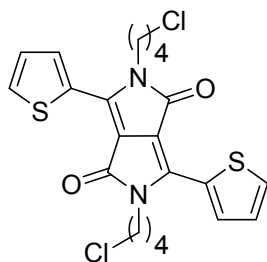


2,5-Bis(4-iodobutyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (7b). A mixture of 2,5-bis(4-chlorobutyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione **7a** (0.5 g, 1.07 mmol) and NaI (1.6 g, 10.65 mmol, 10 eq.) in acetone (10 mL) was heated at reflux temperature for 24 h. The resulting solution was cooled at room temperature and the solvent

was removed using a rotary evaporator under vacuum. The obtained residue was diluted with CH_2Cl_2 then washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ and water. The organic layer was dried over MgSO_4 and the solvent was removed using a rotary evaporator under vacuum to provide the pure product as a red solid (589 mg, 0.9 mmol, 85 % yield). $^1\text{H NMR (CDCl}_3)$ $\delta(\text{ppm})$: 1.75 (m, 8H), 3.11 (t, 4H, $J = 6.5$ Hz), 3.80 (t, 4H, $J = 7.0$ Hz), 7.55 (m, 6H), 7.81 (m, 4H); $^{13}\text{C NMR (CDCl}_3)$ $\delta(\text{ppm})$: 5.6 (CH_2), 30.2 (CH_2), 30.5 (CH_2), 40.6 (CH_2), 109.7 (C_q), 128.0 (C_q), 128.6 (CH), 129.1 (CH), 131.3 (CH), 148.4 (C_q), 162.6 (C=O); **HRMS (ESI MS)** m/z : theor: 653.0157 found: 653.0161 ($(\text{M}+\text{H})^+$ detected).

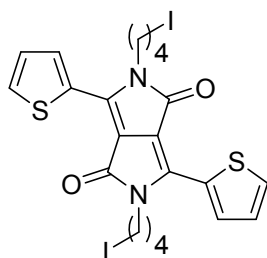


2,5-Bis(4-(dimethylamino)butyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP7). In a sealed flask, 2,5-bis(4-iodobutyl)-3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **7b** (0.5 g, 0.77 mmol) was dissolved in anhydrous THF (10 mL) under argon atmosphere. Dimethylamine (2 M in THF, 1.91 mL, 3.83 mmol, 5 eq.) was added then the mixture was heated at 60 °C for 4 h. The solution was cooled at room temperature and a second fraction of dimethylamine (2 M in THF) (1.91 mL, 3.83 mmol, 5 eq.) was added. The mixture was heated at 60 °C for 2 h. The resulting solution was cooled at room temperature and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel ($\text{CHCl}_3/\text{MeOH}$: 9/1 to $\text{CHCl}_3/\text{MeOH}/\text{NEt}_3$: 9/1/0.1) to provide an orange solid (160 mg, 0.33 mmol, 43 % yield). $^1\text{H NMR (CDCl}_3)$ $\delta(\text{ppm})$: 1.41 (quint, 4H, $J = 7.5$ Hz), 1.62 (quint, 4H, $J = 7.6$ Hz), 2.15 (s, 12H), 2.18 (t, 4H, $J = 7.6$ Hz), 3.79 (t, 4H, $J = 7.5$ Hz), 7.53 (m, 6H), 7.82 (m, 4H); $^{13}\text{C NMR (CDCl}_3)$ $\delta(\text{ppm})$: 24.9 (CH_2), 27.3 (CH_2), 41.7 (CH_2), 45.4 (CH_3), 59.0 (CH_2), 109.8 (C_q), 128.2 (C_q), 128.7 (CH), 128.9 (CH), 131.1 (CH), 148.4 (C_q), 162.7 (C=O); **HRMS (ESI MS)** m/z : theor: 487.3068 found: 487.3064 ($(\text{M}+\text{H})^+$ detected).



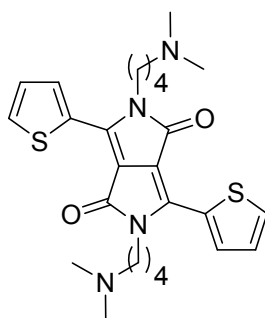
2,5-Bis(4-chlorobutyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (8a**).**

3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione **4** (1.5 g, 4.99 mmol) was dissolved in anhydrous DMF (50 mL) under argon atmosphere. NaH (60% in mineral oil, 499.4 mg, 12.49 mmol, 2.5 eq.) was added in small fractions then the mixture was stirred until the extinction of boiling (15 min). 1-Chloro-4-iodobutane (1.53 mL, 12.49 mmol, 2.5 eq.) was added dropwise and the mixture was heated at 60 °C for 16 h. The resulting solution was cooled at room temperature and a maximum of DMF was removed using a rotary evaporator under vacuum. The residue was poured onto water. The obtained precipitate was collected by filtration and washed with water, few milliliters of cold ethanol and pentane to afford a dark purple powder. The crude product was purified by column chromatography on silica gel (CHCl₃) to provide a dark purple solid (1.8 g, 3.74 mmol, 75 % yield). ¹H NMR (CDCl₃) δ(ppm): 1.93 (m, 8H), 3.59 (t, 4H, J = 5.9 Hz), 4.15 (t, 4H, J = 6.9 Hz), 7.31 (dd, 2H, J = 5.0 Hz, J = 4.1 Hz), 7.67 (dd, 2H, ³J = 5.0 Hz, ⁴J = 1.0 Hz), 8.91 (dd, 2H, ³J = 3.9 Hz, ⁴J = 0.9 Hz); ¹³C NMR (CDCl₃) δ(ppm): 27.5 (CH₂), 29.8 (CH₂), 41.2 (CH₂), 44.4 (CH₂), 107.7 (C_q), 128.8 (CH), 129.5 (C_q), 130.9 (CH), 135.4 (CH), 140.0 (C_q), 161.4 (C=O); HRMS (ESI MS) m/z: theor: 481.0573 found: 481.0569 ((M+H)⁺ detected).

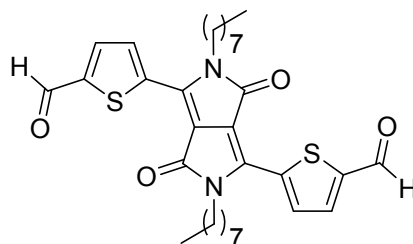


2,5-Bis(4-iodobutyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (8b**).** A mixture of 2,5-bis(4-chlorobutyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione **8a** (1.0 g, 2.08 mmol) and NaI (3.11 g, 20.8 mmol, 10 eq.) in a mixture acetone/chloroform (2/1) (150 mL) was heated at reflux temperature for 5 days. The resulting solution was cooled at room temperature and the solvent was removed using a rotary

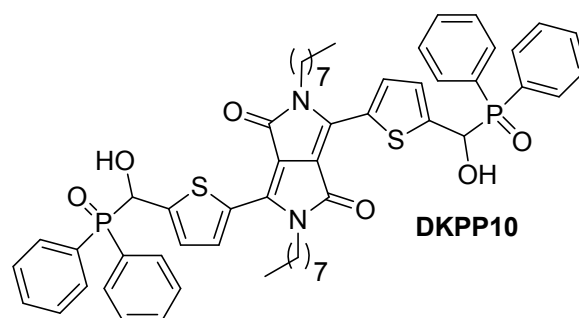
evaporator under vacuum. The obtained residue was diluted with CH₂Cl₂ then washed with saturated Na₂S₂O₃ and water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum to provide the pure product as a purple solid (1.087 g, 1.64 mmol, 79 % yield). ¹H NMR (CDCl₃) δ(ppm): 1.93 (m, 8H), 3.24 (t, 4H, J = 6.7 Hz), 4.14 (t, 4H, J = 7.2 Hz), 7.31 (dd, 2H, J = 4.7 Hz, J = 4.2 Hz), 7.67 (dd, 2H, ³J = 5.0 Hz, ⁴J = 0.8 Hz), 8.91 (dd, 2H, ³J = 3.8 Hz, ⁴J = 0.9 Hz); ¹³C NMR (CDCl₃) δ(ppm): 5.6 (CH₂), 30.7 (CH₂), 30.9 (CH₂), 40.9 (CH₂), 107.7 (C_q), 128.8 (CH), 129.5 (C_q), 130.9 (CH), 135.4 (CH), 140.0 (C_q), 161.3 (C=O); HRMS (ESI MS) m/z: theor: 664.9285 found: 664.9293 ((M+H)⁺ detected).



2,5-Bis(4-(dimethylamino)butyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP3). In a sealed flask, 2,5-bis(4-iodobutyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **8b** (1.0 g, 1.51 mmol) was dissolved in anhydrous THF (20 mL) under argon atmosphere. Dimethylamine (2 M in THF, 3.76 mL, 7.53 mmol, 5 eq.) was added then the mixture was heated at 60 °C for 4 h. The solution was cooled at room temperature and a second fraction of dimethylamine (2 M in THF, 3.76 mL, 7.53 mmol, 5 eq.) was added. The mixture was heated at 60 °C for 2 h. The resulting solution was cooled at room temperature and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/MeOH/NEt₃: 9/1/0.1) to provide a dark purple solid (457 mg, 0.92 mmol, 61 % yield). ¹H NMR (CDCl₃) δ(ppm): 1.61 (quint, 4H, J = 7.5 Hz), 1.79 (quint, 4H, J = 7.7 Hz), 2.24 (s, 12H), 2.35 (t, 4H, J = 7.5 Hz), 4.12 (t, 4H, J = 7.7 Hz), 7.29 (dd, 2H, J = 5.0 Hz, J = 3.9 Hz), 7.65 (dd, 2H, ³J = 5.0 Hz, ⁴J = 1.1 Hz), 8.91 (dd, 2H, ³J = 3.9 Hz, ⁴J = 1.1 Hz); ¹³C NMR (CDCl₃) δ(ppm): 24.8 (CH₂), 27.9 (CH₂), 41.9 (CH₂), 45.3 (CH₃), 59.1 (CH₂), 107.7 (C_q), 128.6 (CH), 129.7 (C_q), 130.7 (CH), 135.2 (CH), 140.0 (C_q), 161.4 (C=O); HRMS (ESI MS) m/z: theor: 499.2196 found: 499.2195 ((M+H)⁺ detected).

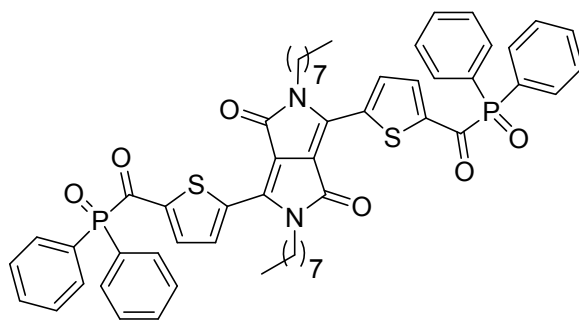


5,5'-(2,5-Dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dithiophene-2-carbaldehyde (10**).** In a 250 mL two-neck round bottom flask, 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione DKPP4 (2.0 g, 3.81 mmol) was dissolved in THF (100 mL) under argon atmosphere. The mixture was cooled at -20 °C. Lithium diisopropylamide (2 M in THF, 4.0 mL, 8.0 mmol, 2.1 eq.) was added dropwise then the mixture was warmed up to 0 °C and stirred for 1h. After this time, 1-formylpiperidine (0.89 mL, 8.0 mmol, 2.1 eq.) was added dropwise then the mixture was stirred at 0 °C for 2 h. HCl 0.5 M (130 mL) was added to the resulting solution. The mixture was extracted with CH₂Cl₂. The latter organic fraction was further washed with water. The organic layer was dried over MgSO₄ and the solvent was removed using a rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel (CHCl₃) to provide a dark purple solid (1.06 g, 1.83 mmol, 48 % yield). ¹H NMR (CDCl₃) δ(ppm): 0.88 (t, 6H, J = 6.7 Hz), 1.27 (m, 16H), 1.43 (quint, 4H, J = 6.6 Hz), 1.75 (quint, 4H, J = 7.5 Hz), 4.12 (t, 4H, J = 7.7 Hz), 7.89 (d, 2H, J = 4.0 Hz), 9.10 (d, 2H, J = 3.9 Hz), 10.04 (s, 2H); ¹³C NMR (CDCl₃) δ(ppm): 14.1 (CH₃), 22.6 (CH₂), 26.8 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 30.1 (CH₂), 31.7 (CH₂), 42.5 (CH₂), 110.8 (C_q), 136.1 (CH), 136.6 (C_q), 140.1 (C_q), 146.6 (C_q), 161.0 (C=O), 182.8 (CHO); HRMS (ESI MS) m/z: theor: 581.2502 found: 581.2501 ((M+H)⁺ detected).



3,6-Bis(5-((diphenylphosphoryl)(hydroxy)methyl)thiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DKPP10). 5,5'-(2,5-Dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo- [3,4-c]pyrrole-1,4-diyl)dithiophene-2-carbaldehyde **10** (0.4 g, 0.69 mmol)

and diphenylphosphine oxide (348.1 mg, 1.72 mmol, 2.5 eq.) was introduced in THF (8 mL). Triethylamine (0.24 mL, 1.72 mmol, 2.5 eq.) was added dropwise then the mixture was stirred at room temperature for 3 h 30. The solvent was removed using a rotary evaporator under vacuum then, the obtained residue was washed with acetonitrile and pentane to provide the pure product as a purple/pink solid (0.5 g, 0.51 mmol, 74 % yield). **¹H NMR (CDCl₃/TFA-d: 4/1) δ(ppm):** 0.89 (t, 6H, J = 6.5 Hz), 1.28 (m, 20H), 1.57 (br s, 4H), 3.88 (t, 4H, J = 7.6 Hz), 6.12 (d, 2H, J = 5.5 Hz), 7.01 (br s, 2H), 7.52 (m, 4H), 7.59 (m, 4H), 7.69 (m, 10H), 7.83 (m, 4H), 8.45 (d, 2H, J = 3.3 Hz); **³¹P NMR (CDCl₃/TFA-d: 4/1) δ(ppm):** 37.77 (s); **¹³C NMR (CDCl₃/TFA-d: 4/1) δ(ppm):** 14.0 (CH₃), 22.6 (CH₂), 26.6 (CH₂), 29.08 (CH₂), 29.09 (CH₂), 29.7 (CH₂), 31.7 (CH₂), 42.6 (CH₂), 70.1 (CH), 107.9 (C_q), 125.6 (m, C_q), 129.1 (m, CH), 129.6 (d, C_q, J = 2.9 Hz), 132.0 (d, CH, J = 9.5 Hz), 132.2 (d, CH, J = 10.3 Hz), 133.8 (m, CH), 135.8 (CH), 141.3 (C_q), 145.3 (d, C_q, J = 5.9 Hz), 161.8 (C=O); **HRMS (ESI MS) m/z:** theor: 985.3597 found: 985.3598 ((M+H)⁺ detected).



3,6-bis(5-((diphenylphosphoryl)carbonyl)thiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DKPP11). A mixture of 3,6-bis(5-((diphenylphosphoryl)(hydroxy)methyl)-thiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione DKPP10 (0.3 g, 0.3 mmol) and manganese dioxide (1.059 g, 12.18 mmol, 40 eq.) in CH₂Cl₂ (15 mL) was stirred at room temperature for 16 h. The obtained solution was filtered on celite and the solvent was removed using a rotary evaporator under vacuum. The residue was dissolved in diethyl ether and pentane was added to provoke the crystallization of the pure product as blue solid. The product was recovered by filtration (130 mg, 0.13 mmol, 44 % yield). **¹H NMR (CDCl₃) δ(ppm):** 0.86 (t, 6H, J = 6.7 Hz), 1.25 (m, 16H), 1.39 (quint, 4H, J = 7.3 Hz), 1.70 (quint, 4H, J = 7.5 Hz), 4.07 (t, 4H, J = 7.7 Hz), 7.53 (m, 8H), 7.61 (m, 4H), 7.93 (m, 8H), 8.95 (d, 2H, J = 4.4 Hz), 8.96 (d, 2H, J = 4.4 Hz); **³¹P NMR (CDCl₃) δ(ppm):** 20.70 (s); **¹³C NMR (CDCl₃) δ(ppm):** 14.1 (CH₃), 22.6 (CH₂), 26.7 (CH₂), 29.09 (CH₂), 29.10 (CH₂), 30.0 (CH₂), 31.7 (CH₂), 42.5 (CH₂), 111.4 (C_q), 128.8 (CH,

$J = 11.7$ Hz), 129.7 (C_q), 131.9 (d, CH, $J = 9.5$ Hz), 132.8 (d, CH, $J = 2.2$ Hz), 136.7 (CH), 138.4 (C_q), 138.8 (CH), 140.2 (C_q), 146.4 (d, C_q , $J = 58.7$ Hz), 160.9 (C=O), 196.7 (d, C=O, $J = 86.6$ Hz); **HRMS (ESI MS) m/z** : theor: 1003.3104 found: 1003.3116 ($(M+Na)^+$ detected).

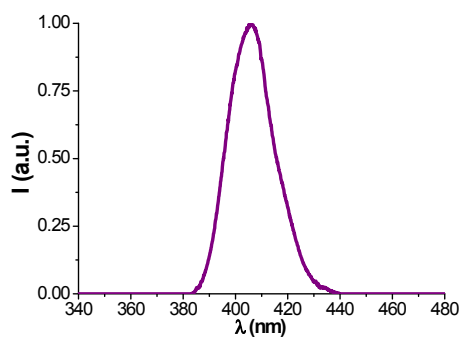


Figure S11. The emission spectrum of the LED centered at 405 nm.

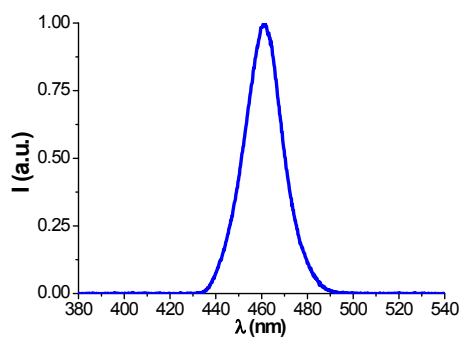


Figure S12. The emission spectrum of the blue LED centered at 470 nm.

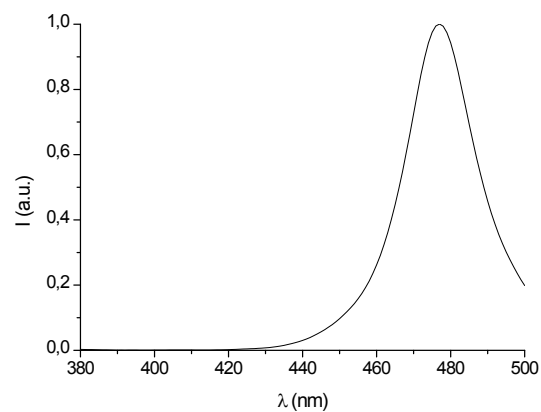


Figure S13. Emission spectrum of the blue LED centered at 477 nm

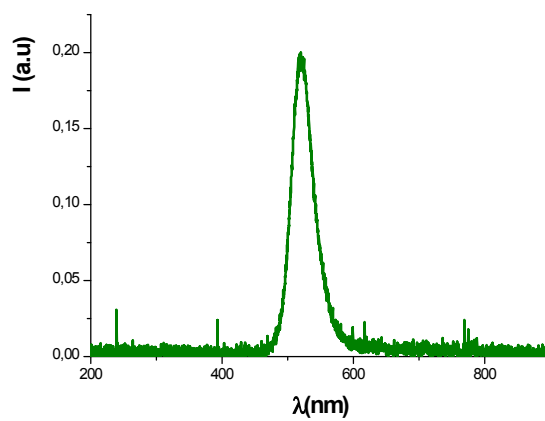


Figure S14. The emission spectrum of the green LED centered at 520 nm.

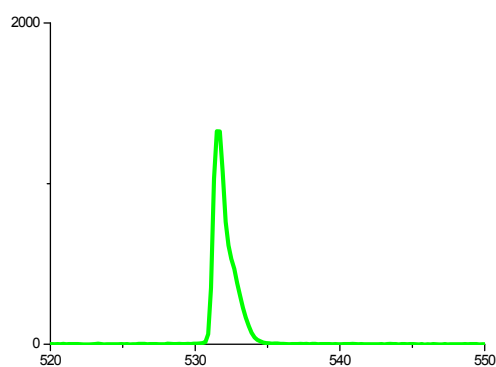


Figure S15. The emission spectrum of the laser diode at 532 nm.

*For Figures S1, S2, S3, S4 and S5, the nominal wavelengths indicate the wavelengths at which the LEDs appear brightest to the human eye. This may not correspond to the peak wavelength as measured by a spectrograph. (from <http://www.thorlabs.de/>)

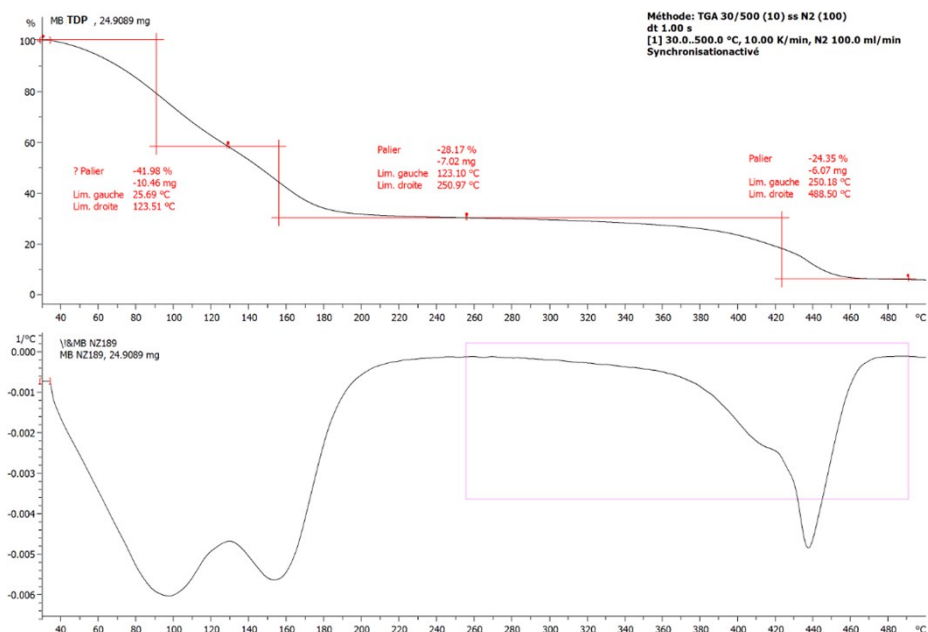


Figure S16. TGA results of TDKPP1/MDEA in HEA/H2O.