

New Synthetic Routes to Z-shape Functionalized Perylenes

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Supporting Material A

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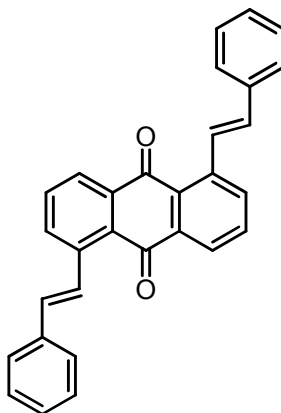
1. Instruments and General Experimental Set-ups:

Nuclear magnetic resonance spectra were taken on Bruker AMX-400 (400 MHz), Bruker AV-400 (400 MHz) or Bruker AV-500 (500 MHz) spectrometer. Chemical shifts were reported as delta scale in ppm relative to CDCl_3 ($\delta = 7.24$) or $\text{DMSO}-d_6$ ($\delta = 2.5$) for ^1H NMR, CDCl_3 ($\delta = 77.0$) or $\text{DMSO}-d_6$ ($\delta = 39.5$) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, coupling constant (Hz). Infrared spectrum data were measured on a Thermo Nicolet Avatar 360 E.S.P. FT-IR spectrometer. Samples were pressed into KBr tablets or deposited on KBr pellets from CH_2Cl_2 solutions. High resolution mass spectra were taken on JEOL JMS-700 10kV. Ultraviolet-visible electronic absorption spectra were recorded on a Hewlett–Packard 8453 diode array spectrophotometer. The samples were dissolved in dichloromethane and placed in a 1 cm quartz cell. The absorptions were monitored between 300–700 nm. Photoluminescence (PL) spectra were recorded on a Hitachi F-4500 spectrometer. Fluorescence quantum yields were determined using the integrating sphere method as described by de Mello et al.¹. X-ray crystallography was performed on Bruker Ninium X8APEX. Cyclic voltammetry samples were prepared in dichloromethane solution with TBAPF_6 as the supporting electrolyte. The measurements were carried out on Bio analytical system BAS1008 with a scan-rate of 100–150 mV/sec.

All reactions were performed under 1 atmosphere of dried nitrogen and well mixed with magnetic stirring devices. Reagent grade chemicals and solvents were used in all reactions. Reaction vessels were dried in oven before use. All reactions were monitored by TLC or ^1H NMR. Analytical thin layer chromatography was performed on 250 μM silica gel 60 F_{254} plates. Detection was performed by illumination with a UV lamp (254 nm), staining with I_2 , or PMA. Solvents for extraction, washing and chromatography were HPLC grade. Diethyl ether and tetrahydrofuran were distilled over metallic sodium with benzophenone radical anion as the indicator. Dichloromethane were distilled from CaH_2 . Flash column chromatography was performed with Merck silica gel 60 (1.11567.9025, 0.040–0.063 mm) as the stationary phase. All ratios of reported mixed eluents were based on volume. Compound 1,5-diiodo-anthraquinone² was synthesized according to a known method.

2. Synthetic procedures and characterization data:

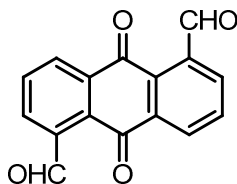
1,5-Distryryl anthraquinone:



A mixture of 1,5-diiodo-anthraquinone (1.00 g, 2.17 mmol), styrene (1.12 mL, 10.85 mmol), $(\text{MeCN})_2\text{PdCl}_2$ (0.11 g, 0.43 mmol), tetrabutylammonium bromide (1.74 g, 5.42 mmol) and triethylamine (2.0 mL) in dry toluene (20.0 mL) was heated at 100 °C under nitrogen for 24 h. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (silica gel; CH_2Cl_2 : hexane = 1:1) to give yellow solid product (520 mg, 64 %).

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2959, 2872, 1662, 1578, 1463, 1320, 1272, 748; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 8.34 (d, 2H, $J = 16.3$ Hz), 8.26 (d, 2H, $J = 7.8$ Hz), 7.96 (d, 2H, $J = 7.8$ Hz), 7.74 (dd, 2H, $J = 7.8$ Hz, 7.8 Hz), 7.63 (d, 4H, $J = 7.5$ Hz), 7.39 (dd, 4H, $J = 7.5$ Hz, 7.5 Hz), 7.30 (dd, 2H, $J = 7.5$ Hz, 7.5 Hz), 7.05 (d, 2H, $J = 16.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 185.30, 140.31, 137.26, 136.27, 133.48, 133.12, 132.86, 129.23, 128.75, 128.56, 128.14, 127.24, 127.09; HR-EI-MS. (M^+), $\text{C}_{30}\text{H}_{20}\text{O}_2$, Calc.: 412.1463; Found: 412.1470

Anthraquinone-1,5-dicarbaldehyde (5):



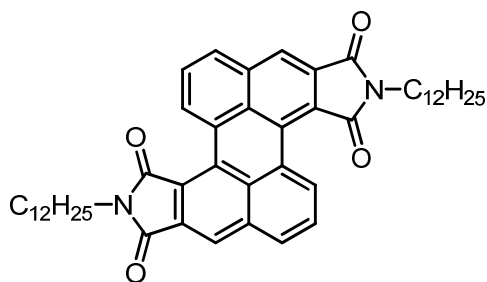
1, 5-distyryl anthraquinone (1.00 g, 2.42 mmol) was dissolved in dichloromethane (200 mL) and cooled to -78 °C. O₃/O₂ gas was bubbled through the solution for 10 minutes at -78 °C. Then nitrogen was bubbled through the solution for further 5 minutes to remove excess ozone before the reaction was quenched with dimethyl sulfide (3.0 mL). The reaction was warmed to room temperature over the course of 1 h and stirring was continued for 12 h. The solution was concentrated at reduced pressure. The crude product obtained was washed with methanol (10.0 mL) and a precipitation started to form. The solid was filtered to give brown colored product (0.50 g, 78 %) which was used in the subsequent steps without further purification.

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2870, 1791, 1665, 1570, 1322, 1287, 1238, 820; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.81 (s, 2H), 8.52 (dd, 2H, *J* = 1.5 Hz, 7.8 Hz), 8.15 (dd, 2H, *J* = 1.5 Hz, 7.8 Hz), 7.94 (dd, 2H, *J* = 7.8 Hz, 7.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 192.17, 183.70, 138.83, 134.59, 134.32, 134.08, 132.51, 131.55; HR-EI-MS. (M⁺), C₁₆H₈O₄, Calc.: 264.0423; Found: 264.0430

General procedure A for perylene ring formation reactions:

Electron deficient olefins (fumaronitrile, diethyl maleate, or N-dodecyl maleimide, 2.35 mmol) were dissolved in dry dichloromethane (2.0 mL) and the solutions were cooled to 0 °C. Triethyl phosphine (1.0 M in THF, 2.0 mL, 2.00 mmol) was slowly added at this temperature. The reaction mixture was stirred at the same temperature for 10 min. To this solution, anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) in dry dichloromethane (10.0 mL) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled again to 0 °C, and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU, 2.35 mmol) was slowly added. The reaction was then warmed back to room temperature and stirred for 2 h before quenched with cold water. The organic layer was separated and aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic phases was dried over MgSO₄. After concentrated in vacuum, the crude product was purified by silica gel column to give the desired perylene products.

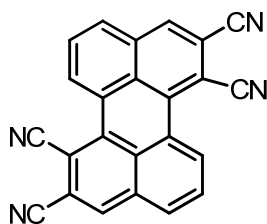
Perylene-1,2,7,8-bis(1'-dodecyl-1*H*-pyrrole-2'5'-dione) (1a):



General procedure A was followed by using N-dodecyl-maleimide (0.62 g, 2.35 mmol) and anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) as substrates. The crude product was purified by flash column chromatography (silica gel; CH₂Cl₂: hexane = 2: 3) to furnish the perylene bisimide (440 mg, 65 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 3784, 2920, 2850, 1752, 1696, 1101, 802, 750; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.16 (d, 2H, *J* = 7.4 Hz), 8.32 (s, 2H), 8.09 (d, 2H, *J* = 7.4 Hz), 7.83 (dd, 2H, *J* = 7.4 Hz, 7.4 Hz), 3.78 (t, 4H, *J* = 7.6 Hz), 1.76-1.69 (m, 4H), 1.34-1.22 (m, 36H), 0.84 (t, 6H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 168.35, 167.20, 134.74, 133.31, 132.70, 132.58, 132.11, 130.49, 128.71, 128.68, 123.91, 123.17, 38.78, 31.89, 29.69, 29.61, 29.56, 29.50, 29.32, 29.23, 28.51, 27.00, 22.66, 14.08; UV/Vis (CH₂Cl₂): λ_{max} = 420, 452 and 482 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 482 nm): λ_{em} = 500, 533 and 577 nm, Φ_{F} = 0.36; HR-EI-MS. (*M*⁺), C₄₈H₅₈N₂O₄, Calc.: 726.4397; Found: 726.4400

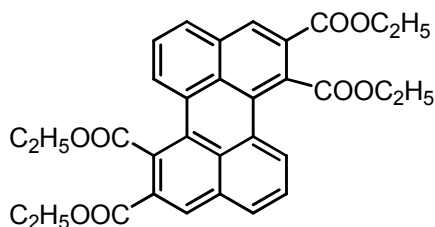
Perylene-1,2,7,8-tetracarbonitrile (**1b**):



General procedure A was followed by using fumaronitrile (0.18 g, 2.35 mmol) and anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) as the substrates. The crude product was purified by flash column chromatography (silica gel; CH₂Cl₂) to furnish the desired compound (135 mg, 40 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2920, 2850, 2215, 1718, 1580, 1260, 899, 799; ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): 9.24 (d, 2H, J = 8.0 Hz), 8.98 (s, 2H), 8.39 (d, 2H, J = 8.0 Hz), 8.17 (dd, 2H, J = 8.0 Hz, 8.0 Hz); ¹³C NMR (125 MHz, DMSO-d₆, the spectrum is poor quality due to low solubility) δ (ppm): 136.11, 135.57, 134.99, 132.97, 132.00, 130.68, 130.55, 128.56, 126.88, 117.97, 116.34, 113.36; UV/Vis (CH₂Cl₂): λ_{max} = 406, 430 and 457 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 457 nm): λ_{em} = 475, 503 and 542 nm, Φ_{F} = 0.38; HR-EI-MS. (M⁺), C₂₄H₈N₄, Calc.: 352.0749; Found: 352.0748

Tetraethyl perylene-1,2,7,8-tetracarboxylate (1c):



General procedure A was followed by using diethyl maleate (0.40 mL, 2.35 mmol) and anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) as the substrates. The crude product was purified by flash column chromatography (silica gel; CH₂Cl₂) to furnish the desired compound (101 mg, 23 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2981, 1723, 1370, 1264, 1194, 1154, 1026, 751; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.43 (s, 2H), 8.14 (d, 2H, J = 8.0 Hz), 7.90 (d, 2H, J = 8.0 Hz), 7.60 (dd, 2H, J = 8.0 Hz, 8.0 Hz), 4.45-4.38 (m, 8H), 1.43 (t, 6H, J = 7.3 Hz), 1.26 (t, 6H, J = 7.3 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 170.59, 166.30, 132.17, 130.99, 130.75, 129.65, 129.23, 129.20, 128.72, 128.55, 128.33, 127.58, 62.08, 61.79, 14.23, 13.71; UV/Vis (CH₂Cl₂): λ_{max} = 385, 406 and 429 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 429 nm): λ_{em} = 486 nm, Φ_{F} = 0.07; HR-ESI-MS. (M+Na)⁺, (C₃₂H₂₈O₈Na)⁺, Calc.: 563.1682; Found: 563.1646

General procedure B for perylene ring formation reactions:

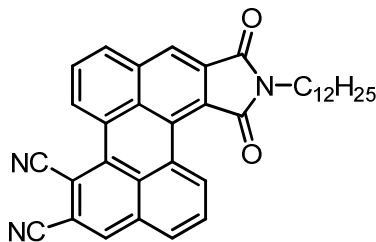
Three reactions were merged into a one pot procedure. Initially, the first electron deficient olefin (0.94 mmol) was dissolved in dry dichloromethane (2.0 mL) and the solution was cooled to 0 °C. Triethyl phosphine (1.0 M in THF, 1.0 mL, 1.00 mmol) was slowly added at this

temperature. The reaction mixture was stirred at the same temperature for 10 min. To this solution, anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) in dry dichloromethane (10.0 mL) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h.

A second electron deficient olefin (0.94 mmol) was likewise dissolved in dry dichloromethane (2.0 mL) and treated with triethyl phosphine (1.0 M in THF, 1.0 mL, 1.00 mmol) at 0 °C. This was stirred at the same temperature for 10 min. This reaction solution was slowly added to the above reaction mixture at 0 °C. The reaction mixture was again warmed back to room temperature and stirred for another 2 h.

The reaction mixture was again cooled to 0 °C and DBU (2.35 mmol) was then slowly added. The reaction was again warmed back to room temperature and stirred for 2 h before quenched with cold water. The organic layer was separated and aqueous layer was further extracted with dichloromethane (3 x 50 mL). The combined organic phases was dried over MgSO₄. After concentrated in vacuum, the crude product was purified by silica gel column to give the desired perylene compound.

Perylene-7,8-dicarbonitrile-1,2-(1'-dodecyl-1*H*-pyrrole-2'5'-dione) (1d):

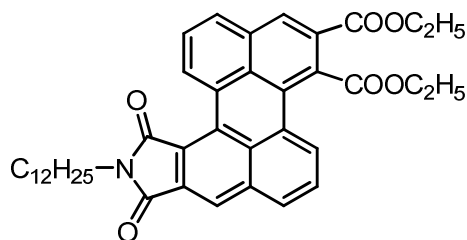


General procedure B was followed by using the N-dodecyl-maleimide (0.25 g, 0.94 mmol) as the first electron deficient olefin and fumaronitrile (0.07 g, 0.94 mmol) as the second. The crude product was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 2: 3) to furnish the desired compound (122 mg, 23 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 3077, 2920, 2853, 2224, 1752, 1700, 800, 755; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.32 (d, 1H, *J* = 7.8 Hz), 9.20 (d, 1H, *J* = 8.0 Hz), 8.37 (s, 1H), 8.30 (s, 1H), 8.16 (d, 1H, *J* = 7.8 Hz), 8.03 (d, 1H, *J* = 8.0 Hz), 7.93 (dd, 1H, *J* = 7.8 Hz), 7.89 (dd, 1H, *J* = 8.0

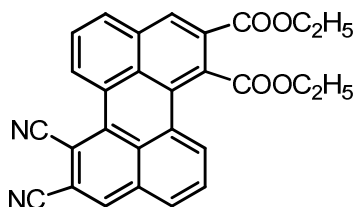
Hz), 3.78 (t, 2H, $J = 7.1$ Hz), 1.73-1.70 (m, 2H), 1.33-1.22 (m, 18H), 0.84 (t, 3H, 7.1 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 168.04, 166.81, 137.01, 135.18, 134.83, 134.57, 133.01, 132.92, 132.16, 131.51, 131.01, 130.61, 130.21, 129.79, 129.62, 129.43, 128.87, 127.53, 124.39, 124.08, 117.93, 116.06, 114.09, 105.37, 38.91, 31.89, 29.69, 29.61, 29.55, 29.48, 29.32, 29.21, 28.45, 26.97, 22.66, 14.09; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 416, 441$ and 468 nm, Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 468$ nm): $\lambda_{\text{em}} = 487, 517$ and 561 nm, $\Phi_{\text{F}} = 0.55$; HR-FAB-MS. ($\text{M}+\text{H}^+$), $\text{C}_{36}\text{H}_{34}\text{N}_3\text{O}_2$, Calc.: 540.2651; Found: 540.2645

Diethyl-7,8-(1'-dodecyl-1H-pyrrole-2',5'-dione)perylene-1,2-dicarboxylate (1e):



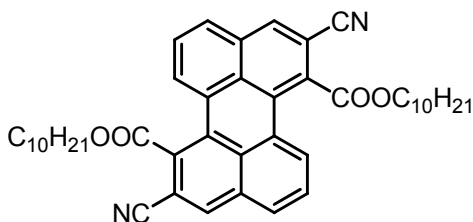
General procedure B was followed by using diethyl maleate (0.15 mL, 0.94 mmol) as the first olefin and N-dodecyl-maleimide (0.25 g, 0.94 mmol) as the second. The crude product was purified by column chromatography (silica gel; CH_2Cl_2 : hexane = 2: 3) to furnish the desired compound (106 mg, 18 %).

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2922, 2853, 1754, 1722, 1702, 1260, 1026, 800, 755; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 9.15 (d, 1H, $J = 7.8$ Hz), 8.47 (s, 1H), 8.25 (s, 1H), 8.18 (d, 1H, $J = 7.8$ Hz), 8.02 (d, 1H, $J = 8.2$ Hz), 7.96 (d, 1H, $J = 8.2$ Hz), 7.77 (dd, 1H, $J = 8.2$ Hz), 7.65 (dd, 1H, $J = 7.8$ Hz, 7.8 Hz), 4.46-4.40 (m, 4H), 3.77 (t, 2H, $J = 7.2$ Hz), 1.73-1.68 (m, 2H), 1.44 (t, 3H, $J = 7.2$ Hz), 1.40-1.22 (m, 21H), 0.84 (t, 3H, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 170.50, 168.33, 167.34, 166.25, 135.13, 133.31, 133.00, 132.87, 131.83, 131.47, 131.39, 131.28, 130.71, 130.55, 130.19, 129.97, 128.71, 128.60, 128.54, 128.46, 127.58, 126.97, 123.35, 122.33, 62.22, 61.89, 38.70, 31.89, 29.61, 29.59, 29.56, 29.50, 29.32, 29.24, 28.50, 26.99, 22.66, 14.25, 14.10, 13.74; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 411, 437$ and 463 nm, Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 463$ nm): $\lambda_{\text{em}} = 497$ and 522 nm, $\Phi_{\text{F}} = 0.18$; HR-FAB-MS. (M^+), $\text{C}_{40}\text{H}_{43}\text{NO}_6$, Calc.: 633.3090; Found: 633.3084

Diethyl 7,8-dicyanoperylene-1,2-dicarboxylate (1f):

General procedure B was followed by using diethyl maleate (0.15 mL, 0.94 mmol) as the first olefin and fumaronitrile (0.07 g, 0.94 mmol) the second. The crude product was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to furnish the desired compound (93 mg, 22 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2969, 2883, 2219, 1723, 1264, 1202, 842, 759; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.17 (d, 1H, *J* = 7.5 Hz), 8.53 (s, 1H), 8.28 (d, 1H, *J* = 7.5 Hz), 8.24 (s, 1H), 8.09 (d, 1H, *J* = 8.0 Hz), 7.90 (d, 1H, *J* = 8.0 Hz), 7.82 (dd, 1H, *J* = 7.5 Hz, 7.5 Hz), 7.75 (dd, 1H, *J* = 8.0 Hz, 8.0 Hz), 4.44 (q, 4H, *J* = 7.3 Hz), 1.45 (t, 3H, *J* = 7.3 Hz), 1.31 (t, 3H, *J* = 7.3 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 170.09, 165.80, 137.29, 134.34, 134.32, 133.34, 132.26, 132.23, 131.94, 130.93, 130.36, 130.25, 130.08, 129.68, 129.59, 129.16, 128.77, 128.25, 127.42, 127.19, 118.03, 116.13, 114.11, 104.65, 62.43, 62.09, 14.25, 13.72; UV/Vis (CH₂Cl₂): λ_{max} = 401, 427 and 451 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 451 nm): λ_{em} = 504 nm, Φ_F = 0.35; HR-FAB-MS. (M⁺), C₂₈H₁₈N₂O₄, Calc.: 446.1267; Found: 446.1260

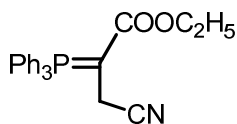
Didecyl 2,8-dicyanoperylene-1,7-dicarboxylate (1g):

General procedure A was followed by using (E)-decyl 3-cyanoacrylate (0.55 g, 2.35 mmol) and anthraquinone-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) as the substrate. The crude product was purified by flash column chromatography (silica gel; CH₂Cl₂: hexane = 4: 1) to furnish the

desired compound (330 mg, 52 %).

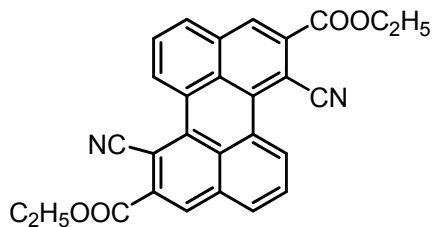
IR (CH₂Cl₂, cast) ν (cm⁻¹): 2925, 2229, 1723, 1464, 1268, 1165, 1127, 800; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.26 (s, 2H), 8.06 (d, 2H, J = 7.5 Hz), 7.93 (d, 2H, J = 7.5 Hz), 7.69 (dd, 2H, J = 7.5 Hz, 7.5 Hz), 4.40 (t, 4H, J = 6.9 Hz), 1.69-1.67 (m, 4H), 1.26-1.20 (m, 28H), 0.85 (t, 6H, J = 6.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 168.42, 134.44, 132.21, 130.17, 129.79, 129.71, 129.52, 129.42, 128.79, 128.51, 116.67, 110.48, 67.29, 31.82, 29.42, 29.23, 29.12, 28.05, 25.87, 22.62, 14.05; UV/Vis (CH₂Cl₂): λ_{max} = 413, 433 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 433 nm): λ_{em} = 486 nm, Φ_F = 0.17; HR-FAB-MS. (M⁺), C₄₄H₅₀N₂O₄, Calc.: 670.3771; Found: 670.3744

Ethyl 3-cyano-2-(triphenylphosphoranylidene)propanoate:



To a solution of ethyl 2-(triphenylphosphoranylidene)acetate (1.20 g, 3.44 mmol) dissolved in ethyl acetate (20.0 mL) was added, under nitrogen, potassium carbonate (0.94 g, 6.88 mmol) followed by bromoacetonitrile (0.36 mL, 5.16 mmol). The solution was refluxed for 4 h. After being cooled back to room temperature, the reaction was quenched with water (20 mL). The water layer was washed twice with ethyl acetate (50 mL). The combined organic phase was dried over MgSO₄ and concentrated. The crude product was purified by column chromatography (silica gel; EtOAc: hexane = 1: 4). The mixture thus obtained (670 mg, 50 %) is used in the next step without further purification.

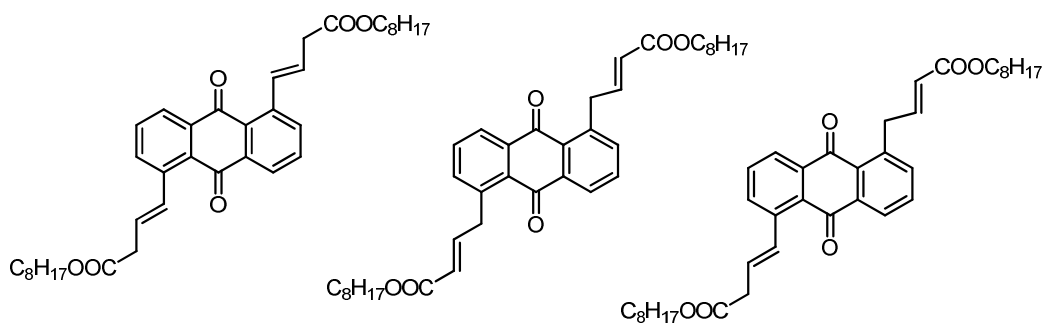
Diethyl 1,7-dicyanoperylene-2,8-dicarboxylate (1h):



3-cyano-2-(triphenyl- λ^2 -phosphanylidene)-propionic acid ethyl ester (0.91 g, 2.35 mmol) was dissolved in dry dichloromethane (10.0 mL) and the solution was cooled to 0 °C. Anthraquinone 1,5-dicarbaldehyde (0.25 g, 0.94 mmol) in dry dichloromethane (10.0 mL) was slowly added during 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was cooled again to 0 °C and DBU (0.35 mL, 2.35 mmol) was slowly added. The reaction was then warmed back to room temperature and stirred for another 2 h before quenched with cold water. The organic layer was separated and aqueous layer was further extracted with dichloromethane (3 x 50 mL). The combined organic extracts was dried over MgSO₄ and concentrated. The crude product was purified by column chromatography (silica gel; CH₂Cl₂) to furnish the desired compound (97 mg, 23 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2923, 2852, 2219, 1731, 1371, 1282, 801, 702; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.26 (d, 2H, *J* = 7.8 Hz), 8.54 (s, 2H), 8.06 (d, 2H, *J* = 7.8 Hz), 7.88 (dd, 2H, *J* = 7.8 Hz, 7.8 Hz), 4.57-4.53 (q, 4H, *J* = 7.3 Hz), 1.50 (t, 6H, *J* = 7.3 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 164.75, 136.68, 133.14, 131.84, 131.52, 131.21, 130.59, 130.02, 129.76, 128.07, 118.91, 104.40, 62.55, 14.19; UV/Vis (CH₂Cl₂): λ_{max} = 409, 432 and 459 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 459 nm): λ_{em} = 480, 505 nm, Φ_F = 0.67; HR-EI-MS. (*M*⁺), C₂₈H₁₈N₂O₄, Calc.: 446.1267; Found: 446.1269

1,5-Dialkenyl anthraquinone (6):

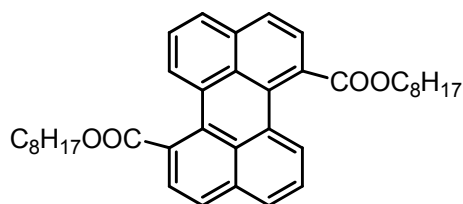


A mixture of 1,5-diiodo-anthraquinone (1.00 g, 2.17 mmol), octyl 3-butenate (2.14 g, 10.85 mmol), (MeCN)₂PdCl₂ (0.11 g, 0.43 mmol), tetrabutylammonium bromide (1.74 g, 5.42 mmol) and triethylamine (2.0 mL) in dry toluene (20.0 mL) was heated at 100 °C for 24 h under nitrogen. The solvent was removed under reduced pressure. The crude product was purified by

flash chromatography (silica gel; CH₂Cl₂: hexane = 8: 2) to give yellowish mixture of alkene regioisomers (770 mg, 59 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2926, 2855, 1731, 1668, 1319, 1269, 1162, 1024, 712; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.22-8.18 (m), 7.81-7.79 (m), 7.69-7.66 (m), 7.61 (d, *J* = 16 Hz), 7.53-7.50 (m), 7.22-7.17 (m), 6.26-6.23 (m), 5.76 (d, *J* = 16.0 Hz), 4.16-4.10 (m), 4.06 (t, *J* = 7.0 Hz), 3.38-3.37 (m), 1.66-1.58 (m), 1.35-1.24 (m), 0.86-0.82 (m); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 185.13, 185.04, 184.82, 184.73, 171.57, 166.54, 146.62, 140.46, 139.75, 137.07, 137.00, 136.58, 135.91, 135.85, 133.87, 133.81, 133.66, 133.46, 133.05, 130.32, 129.05, 127.28, 127.19, 127.14, 127.03, 126.14, 126.09, 122.40, 65.06, 64.52, 38.45, 37.47, 31.76, 29.20, 29.18, 29.13, 28.61, 25.92, 22.61, 14.05; HR-ESI-MS. (M+Na)⁺, C₃₈H₄₈O₆Na, Calc.: 623.3349; Found: 623.3339

Diethyl perylene-1,7-dicarboxylate (2):

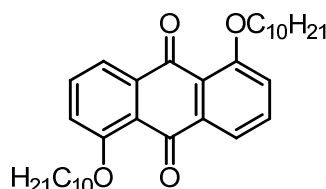


To a solution of diethyl perylene-1,7-dicarboxylate (100 mg, 0.16 mmol) in t-butanol (5.0 mL) was added sodium tert-butoxide (0.038 g, 0.4 mmol) in t-butanol (5.0 mL) at room temperature. The reaction mixture was stirred for 60 minutes before quenched with saturated NH₄Cl solution. The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 50 mL). The combined organic extracts was dried over MgSO₄ and concentrated. The crude product was purified by flash column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to give yellow solid product (24 mg, 26 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2925, 2854, 1712, 1463, 1266, 1121, 836, 755; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.80 (d, 2H, *J* = 8.5 Hz); 7.79 (d, 2H, *J* = 7.8 Hz); 7.75 (d, 2H, *J* = 7.8 Hz), 7.69 (d, 2H, *J* = 8.5 Hz), 7.53 (dd, 2H, *J* = 7.8 Hz, 7.8 Hz), 4.26 (t, 4H, *J* = 6.9 Hz), 1.58~1.54 (m, 8H); 1.23~1.15 (m, 16H), 0.83 (t, 6H, *J* = 6.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 172.07, 133.99, 129.98, 129.80, 129.40, 128.85, 128.06, 127.76, 127.33, 127.23, 126.95, 66.07, 31.70,

29.17, 29.09, 28.20, 25.98, 22.61, 14.05; UV/Vis (CH₂Cl₂): λ_{max} = 419 and 440 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 440 nm): λ_{em} = 503 nm, Φ_{F} = 0.24; HR-EI-MS. (M⁺), C₃₈H₄₄O₄, Calc.: 564.3240; Found: 564.3246

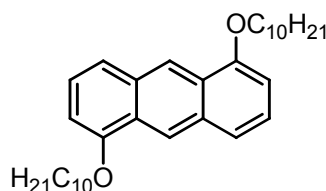
1,5-Bis(decyloxy)anthraquinone:



A suspension of 1,5-dihydroxy anthraquinone (5.00 g, 20.83 mmol) and K₂CO₃ (10.00 g, 72.90 mmol) in anhydrous DMF (100 mL) was heated at 100 °C under N₂. Then, 1-iododecane (11.1 mL, 52.07 mmol) was added dropwise and the mixture was stirred overnight at 100 °C. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (200 mL) and washed with 10 % HCl (100 mL) followed by H₂O (2 x 100 mL). The organic layer was dried over MgSO₄ and concentrated to give the alkylated compound (7.8 g, 72 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2951, 2921, 2849, 1665, 1584, 1446, 1273, 1260; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86 (dd, 2H, J = 0.8 Hz, 8.1 Hz), 7.63 (dd, 2H, J = 8.1 Hz, 8.1 Hz), 7.22 (dd, 2H, J = 0.8 Hz, 8.1 Hz), 4.12 (t, 4H, J = 6.5 Hz), 1.96-1.89 (m, 4H), 1.57-1.50 (m, 4H), 1.39-1.30 (m, 24H), 0.85 (t, 6H, J = 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 182.56, 159.36, 137.50, 134.77, 121.07, 119.48, 117.77, 69.64, 31.90, 29.54, 29.33, 29.32, 29.10, 25.91, 22.67, 14.10; HR-EI-MS. (M⁺), C₃₄H₄₈O₄, Calc.: 520.3553; Found: 520.3546

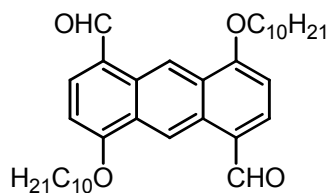
1,5-Bis(decyloxy)-anthracene:



1,5-bis(decyloxy)anthraquinone (1.00 g, 1.92 mmol) was dissolved in n-BuOH (20.0 mL). NaBH₄ (1.42 g, 38.4 mmol) was added to the reaction mixture and stirred at 100 °C for 12 h under nitrogen. The reaction was cooled before excess hydride was decomposed by 1N HCl (50.0 mL, added slowly). The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 100 mL). Combined organic extracts was washed with water (2 x 100 mL) followed by brine (50 mL). The organic layer was dried over MgSO₄ and evaporated in vacuo. The crude product was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 4) to give the desired compound (620 mg, 64 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2918, 2847, 1632, 1541, 1458, 1257, 1175, 1112; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.76 (s, 2H), 7.59 (d, 2H, *J* = 8 Hz), 7.31 (dd, 2H, *J* = 8 Hz, 8 Hz), 6.70 (d, 2H, *J* = 8 Hz), 4.18 (t, 4H, *J* = 6.5 Hz), 2.00-1.96 (m, 4H), 1.61-1.56 (m, 4H), 1.44-1.27 (m, 24H), 0.86 (t, 6H, *J* = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 154.81, 132.20, 125.46, 124.98, 120.83, 120.46, 102.59, 68.22, 31.92, 29.63, 29.60, 29.48, 29.35, 29.32, 26.34, 22.69, 14.10; HR-EI-MS. (M⁺), C₃₄H₅₀O₂, Calc.: 490.3811; Found: 490.3803

4,8-Bis(decyloxy)- 1,5-dicarbaldehyde anthracene (7):

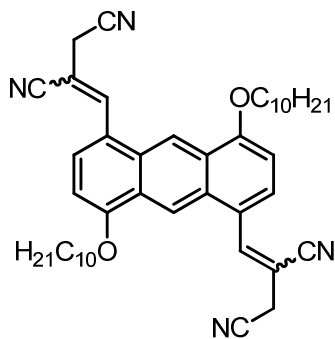


To distilled POCl₃ (0.28 mL, 3.05 mmol) at 0 °C, N-methy formanilide (0.45 mL, 3.66 mmol) was added and stirred for 10 minutes. The Vilsmeier reagent formed was added to a solution of 1,5-bis(decyloxy)anthracene (0.60 g, 1.22 mmol) in o-dichlorobenzene (10.0 mL) slowly at 0 °C. The reaction mixture was heated at 100 °C for 2 h under nitrogen. The reaction mixture was then cooled in an ice-salt bath and neutralized with sodium acetate solution. Diluted with more water, the reaction mixture was allowed to stand at 0 °C for 2 h. Dichloromethane (50 mL) was added to the reaction mixture and separated the organic layer. Aqueous phase was again extracted with dichloromethane (2 x 100 mL). The combined organic extracts was dried over MgSO₄ and evaporated in vacuo. The crude product was purified by column chromatography (silica gel;

CH₂Cl₂: hexane = 1: 1) to furnish the dialdehyde product (480 mg, 73 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2918, 2851, 2731, 1674, 1543, 1198, 1113, 1071; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.36 (s, 2H), 10.25 (s, 2H), 7.95 (d, 2H, *J* = 7.8 Hz), 6.89 (d, 2H, *J* = 7.8 Hz), 4.31 (t, 4H, *J* = 6.5 Hz), 2.09-2.04 (m, 4H), 1.67-1.63 (m, 4H), 1.47-1.29 (m, 24H), 0.84 (t, 6H, *J* = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 191.84, 161.00, 141.39, 128.73, 126.55, 125.13, 119.76, 102.65, 69.05, 31.89, 29.61, 29.58, 29.37, 29.31, 28.95, 26.07, 22.67, 14.10; HR-EI-MS. (M⁺), C₃₆H₅₀O₄, Calc.: 546.3709; Found: 546.3703

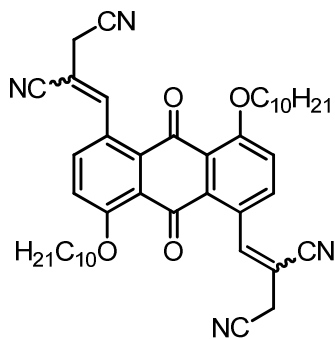
2,2'-(anthracene-4,8-didecyloxyl -1,5-diylbis(methan-1-yl-1-ylidene))disuccinonitrile (8):



Fumaronitrile (0.18 g, 2.35 mmol) was dissolved in dry dichloromethane (2.0 mL) and the solution was cooled to 0 °C. Triethyl phosphine (1.0 M in THF, 2.5 mL, 2.5 mmol) was slowly added at this temperature. The reaction mixture was stirred at the same temperature for 10 min. To this solution, 4,8-bis(decyloxy)-anthracene-1,5-dicarbaldehyde (0.25 g, 0.94 mmol) in dry dichloromethane (10.0 mL) was slowly added. The reaction mixture was refluxed for 12 h. The reaction mixture was brought to room temperature before poured into cold water. The organic layer was separated and aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic phases were dried over MgSO₄. After concentrated in vacuum, the residue was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to furnish the desired compound (167 mg, 55 %). At least three E/Z isomers can be distinguished in ¹H NMR spectrum. This mixture was taken in the subsequent transformation without further purification. IR (CH₂Cl₂, cast) ν (cm⁻¹): 2924, 2854, 2212, 1655, 1611, 1546, 1416, 1322, 1259, 1194, 1109, 1054, 879, 822, 746, 537; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.90 (s), 8.73 (s), 8.19 (s); 8.14-8.05 (m), 7.40-7.38 (m), 6.88-6.83 (m), 4.31-4.25 (m), 3.65 (s), 3.51 (s), 2.75 (s), 2.05-2.00 (m),

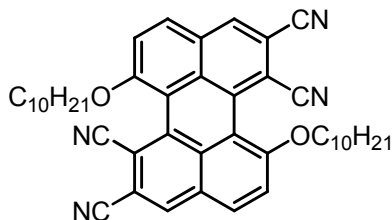
1.59-1.56 (m), 1.49-1.43 (m), 1.36-1.25 (m), 0.85 (t, $J = 6.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 157.45, 157.37, 157.24, 157.16, 147.35, 147.25, 144.49, 144.42, 129.86, 129.63, 129.57, 129.35, 129.00, 128.95, 128.80, 128.69, 125.42, 125.33, 125.25, 125.16, 121.70, 121.39, 118.16, 118.10, 118.04, 117.20, 117.12, 117.04, 115.21, 115.12, 114.73, 114.68, 104.34, 104.13, 103.04, 102.83, 102.61, 100.59, 100.32, 69.03, 68.96, 68.90, 68.82, 31.88, 29.65, 29.60, 29.56, 29.32, 28.95, 28.89, 26.22, 23.77, 22.65, 19.91, 14.08; HR-EI-MS. (M^+), $\text{C}_{44}\text{H}_{54}\text{N}_4\text{O}_2$, Calc.: 670.4247; Found: 670.4247

2,2'-(anthraquinone-4,8-didecyloxyl -1,5-diylbis(methan-1-yl-1-ylidene))disuccinonitrile (9):



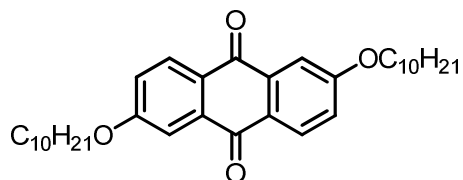
The mixed Wittig product from last step, (600 mg, 0.895 mmol) was suspended in a mixed solvent (40.0 mL HOAc, 4.0 mL H_2O , and 20.0 mL acetone). To this suspension was added a solution of CrO_3 (0.89 g, 8.95 mmol) in HOAc (20.0 mL) and H_2O (8.0 mL) at room temperature. The mixture was stirred for 24 h before quenched with isopropyl alcohol (5.0 mL). Stirring was continued for further 30 min. The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 100 mL). The combined organic phases was dried over MgSO_4 and concentrated to furnish the desired compound (330 mg, 53 %). At least three diastereomers can be distinguished in ^1H NMR spectrum. This compound was used in the next step without further purification.

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2924, 2854, 2253, 2216, 1663, 1582, 1553, 1426; ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.99-7.85 (m), 7.48-7.45 (m), 7.33-7.29 (m), 4.19-4.16 (m), 3.56 (s), 3.25 (s), 1.95-1.90 (m), 1.70-1.36 (m), 0.85 (t, $J = 6.8$ Hz); HR-FAB-MS. ($\text{M}+\text{H}^+$), $\text{C}_{44}\text{H}_{53}\text{N}_4\text{O}_4$, Calc.: 701.4067; Found: 701.4069

6,12-Bis(decyloxy)perylene-1,2,7,8-tetracarbonitrile (3a):

The anthraquinone derivative from last step (300 mg, 0.42 mmol) was dissolved in dry dichloromethane (10.0 mL) and the solution was cooled to 0 °C. To this chilled solution, DBU (640 mg, 4.20 mmol, 10 equivalents) was added. The reaction was then warmed to room temperature and stirred for 2 h before being added with cold water. The organic layer was separated and aqueous layer was further extracted with dichloromethane (3 x 50 mL). The combined organic extracts was dried over MgSO₄ and concentrated. The crude product was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to furnish the desired compound as red colored power (0.13 g, 46 %).

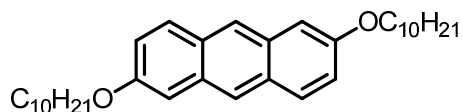
IR (CH₂Cl₂, cast) ν (cm⁻¹): 2924, 2854, 2226, 1587, 1486, 1464, 1268, 1113; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.16 (s, 2H), 8.00 (d, 2H, J = 9.0 Hz), 7.61 (d, 2H, J = 9.0 Hz); 4.41-4.01 (br, 4H), 2.10-1.95 (m, 4H), 1.42-1.21 (m, 28H), 0.85 (t, 6H, J = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 159.07, 133.04, 132.95, 132.29, 132.01, 126.75, 117.15, 116.36, 116.26, 113.58, 110.57, 109.31, 69.25, 31.87, 29.49, 29.47, 29.26, 29.24, 28.70, 25.89, 22.65, 14.10; UV/Vis (CH₂Cl₂): λ_{max} = 489 and 516 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 489 nm): λ_{em} = 552 and 592 nm, Φ_{F} = 0.83; HR-EI-MS. (M⁺), C₄₄H₄₈N₄O₂, Calc.: 664.3777; Found: 664.3783

2,6-Bis(decyloxy)anthracquinone:

A suspension of 2,6-dihydroxy anthraquinone (5.00 g, 20.83 mmol) and K_2CO_3 (10.00 g, 72.90 mmol) in anhydrous DMF (100 mL) was heated at 100 °C under N_2 . Then, 1-iododecane (11.1 mL, 52.07 mmol) was slowly added and the mixture was stirred overnight at 100 °C. After cooled to room temperature, the mixture was concentrated under reduced pressure. The residue was dissolved in dichloromethane (200 mL) and washed with 10 % HCl (100 mL) followed by H_2O (2 x 100 mL). The organic layer was dried over $MgSO_4$ and concentrated to give the desired compound (7.8 g, 72 %).

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2920, 2851, 1664, 1587, 1331, 1318, 884, 746; 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.20 (d, 2H, $J = 9.0$ Hz), 7.68 (d, 2H, $J = 2.5$ Hz), 7.19 (dd, 2H, $J = 2.5$ Hz, 9.0 Hz), 4.12 (t, 4H, $J = 6.5$ Hz), 1.85-1.79 (m, 4H), 1.49-1.43 (m, 4H), 1.35-1.26 (m, 24 H), 0.86 (t, 6H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 182.30, 164.07, 135.87, 129.64, 127.00, 120.89, 110.57, 68.83, 31.89, 29.54, 29.32, 29.31, 29.03, 25.95, 22.67, 14.09; HR-FAB-MS. $(M+H)^+$, $C_{34}H_{49}O_4$, Calc.: 521.3631; Found: 521.3629

2,6-Bis(decyloxy)anthracene:

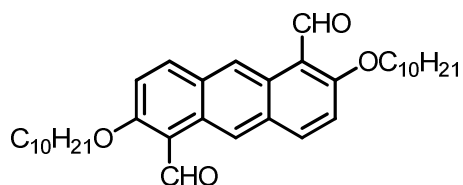


$NaBH_4$ (1.42 g, 38.4 mmol) was added to a suspension of 2,6-bis(decyloxy)anthraquinone (1.00 g, 1.92 mmol) in n -BuOH (20.0 mL). The reaction was stirred at 100 °C for 12 h under nitrogen. After the reaction mixture was cooled to room temperature, the excess hydride was decomposed by 1N HCl (50 mL). The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 100 mL). Combined organic extracts were washed with water (2 x 100 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography (silica gel; CH_2Cl_2 : hexane = 1: 4) to give the desired compound (620 mg, 64 %).

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2918, 2850, 1612, 1464, 1207, 1019, 886, 803; 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.15 (s, 2H), 7.81 (d, 2H, $J = 9.0$ Hz), 7.13 (s, 2H), 7.12 (d, 2H, $J = 9.0$ Hz), 4.08 (t, 4H, $J = 6.8$ Hz), 1.88-1.82 (m, 4H), 1.53-1.47 (m, 4H), 1.39-1.27 (m, 24H), 0.87 (t, 6H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 155.91, 131.20, 129.05, 128.63, 124.05,

120.71, 104.57, 67.92, 31.85, 29.55, 29.52, 29.39, 29.27, 29.21, 26.11, 22.62, 14.04; HR-EI-MS. (M^+), $C_{34}H_{50}O_2$, Calc.: 490.3811; Found: 490.3809

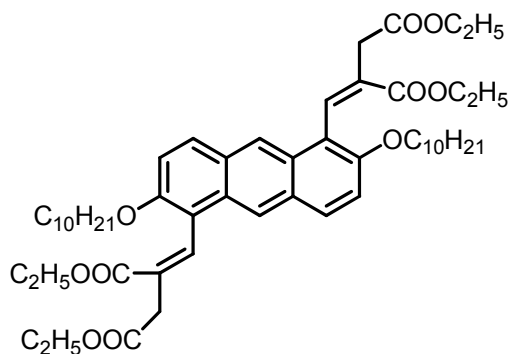
2,6-Bis(decyloxy)anthracene-1,5-dicarbaldehyde (10):



2,6-bis(decyloxy)-anthracene (0.60 g, 1.22 mmol) was dissolved in o-dichlorobenzene (10.0 mL). N-methy formanilide (0.45 mL, 3.66 mmol) and distilled $POCl_3$ (0.28 mL, 3.05 mmol) were added. The reaction mixture was heated to 80 °C for 50 minutes. The reaction mixture was then cooled in an ice-salt bath and neutralized with sodium acetate solution. After diluted with water, the reaction mixture was allowed to stand at 0 °C for another 2 h. Dichloromethane (50 mL) was added to the reaction mixture and the organic layer was separated. Aqueous phase was extracted with dichloromethane (2 x 100 mL). The combined organic extracts was dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography (silica gel; CH_2Cl_2 : hexane = 2: 3) to furnish the dialdehyde product (300 mg, 45 %) along with the by-product 2,6-bis(decyloxy)anthracene-9-carbaldehyde (222 mg, 35 %).

IR (CH_2Cl_2 , cast) ν (cm^{-1}): 2919, 2849, 1656, 1461, 1155, 1085, 887, 805; 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 10.94 (s, 2H), 9.86 (s, 2H), 8.29 (d, 2H, $J = 9.5$ Hz), 7.36 (d, 2H, $J = 9.5$ Hz), 4.27 (t, 4H, $J = 6.3$ Hz), 1.92-1.86 (m, 4H), 1.51-1.48 (m, 4H), 1.37-1.26 (m, 24 H), 0.86 (t, 6H, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 191.70, 164.66, 139.51, 129.97, 127.54, 125.05, 115.42, 69.89, 31.87, 29.69, 29.54, 29.40, 29.33, 29.29, 26.05, 22.66, 14.08; HR-MALDI-MS. ($M+H$) $^+$, $C_{36}H_{51}O_4$, Calc.: 547.3787; Found: 547.3808

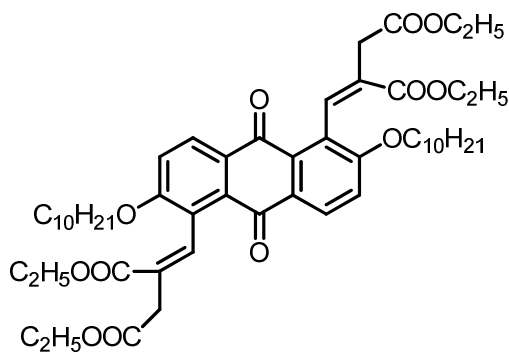
(2Z,2'Z)-Tetraethyl2,2'-((2,6-bis(decyloxy)anthracene-1,5-diyl)bis(methanylylidene))disuccinate (11):



Bis(2,2,2-trifluoroethyl)phosphite (0.53 g, 2.16 mmol) was added slowly to a stirred suspension of sodium hydride [NaH (60 %), 0.086 g, 2.16 mmol] in THF (20.0 mL) at 20 °C under nitrogen. The reaction mixture was stirred for 0.5 h at 20 °C and diethyl maleate (0.37 g, 2.16 mmol) was slowly added. The mixture was further stirred for 0.5 h and the 2,6-bis(decyloxy)anthracene-1,5-dicarbaldehyde (0.30 g, 0.54 mmol in 30.0 mL THF) was added. After the addition, the mixture was refluxed for 24 h before the reaction was quenched with HCl (2.0 M, 30 mL). The reaction mixture was extracted with dichloromethane (3 x 50 mL). The combined organic layer was washed with brine (20 mL) and dried over anhydrous MgSO₄. After the volatiles were removed in vacuo, the residue was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to furnish the Wittig-Horner product (0.29 g, 62 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2926, 2857, 1735, 1714, 1610, 1462, 1260, 1178, 1090; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.28 (s, 2H), 8.09 (s, 2H), 7.95 (d, 2H, *J* = 9.5 Hz), 7.29 (d, 2H, *J* = 9.5 Hz), 4.35 (q, 4H, *J* = 7.0 Hz), 4.09 (t, 4H, *J* = 7.0 Hz), 3.98 (q, 4H, *J* = 7.0 Hz), 3.23 (s, 4H), 1.77-1.72 (m, 4H), 1.42-1.22 (m, 34H), 1.08 (t, 6H, *J* = 7.0 Hz), 0.85 (t, 6H, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 171.07, 167.14, 152.66, 136.70, 130.91, 130.02, 128.99, 128.58, 123.29, 116.67, 116.52, 69.98, 60.97, 60.42, 34.87, 31.87, 29.59, 29.55, 29.35, 29.30, 25.95, 22.66, 14.28, 14.06, 14.03; HR-FAB-MS. (M⁺), C₅₂H₇₄O₁₀, Calc.: 858.5282; Found: 858.5278

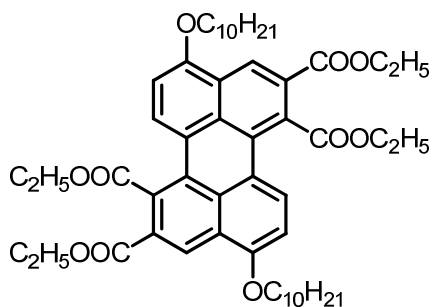
(2Z,2'Z)-Tetraethyl-2,2'-((2,6-bis(decyloxy)-anthraquinone-1,5-diyl)bis(methanylylidene))disuccinate (12):



To a suspension of the Wittig-Horner product from last step, (300 mg, 0.34 mmol in 20.0 mL HOAc, 2.0 mL H₂O, and 10.0 mL acetone) was added a solution of CrO₃ (0.34 g, 3.40 mmol in 10.0 mL HOAc and 4.0 mL H₂O) at room temperature. The mixture was stirred for 6 h before quenched with isopropyl alcohol (2.5 mL). Stirring was continued for further 30 min. The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 100 mL). The combined organic phases was dried over MgSO₄ and concentrated to furnish the desired compound (250 mg, 81 %).

IR (CH₂Cl₂, cast) ν (cm⁻¹): 2926, 2853, 1740, 1666, 1567, 1275, 1032, 847, 744; ¹H NMR (500 MHz, acetone-d₆) δ (ppm): 8.24 (d, 2H, *J* = 9.0 Hz), 8.01 (s, 2H), 7.56 (d, 2H, *J* = 9.0 Hz), 4.29 (q, 4H, *J* = 7.0 Hz), 4.21 (t, 4H, *J* = 6.5 Hz), 3.90 (q, 4H, *J* = 7.0 Hz), 3.07 (s, 4H), 1.83-1.78 (m, 4H), 1.48-1.28 (m, 34H), 1.05 (t, 6H, *J* = 7.0 Hz), 0.87 (t, 6H, *J* = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 182.74, 170.50, 166.93, 160.08, 138.18, 132.18, 130.47, 128.15, 126.51, 124.89, 116.20, 69.36, 60.92, 60.37, 34.33, 31.84, 29.51, 29.49, 29.26, 29.23, 28.76, 25.80, 22.64, 14.27, 14.05, 14.02; HR-EI-MS. (M⁺), C₅₂H₇₂O₁₂, Calc.: 888.5024; Found: 888.5018

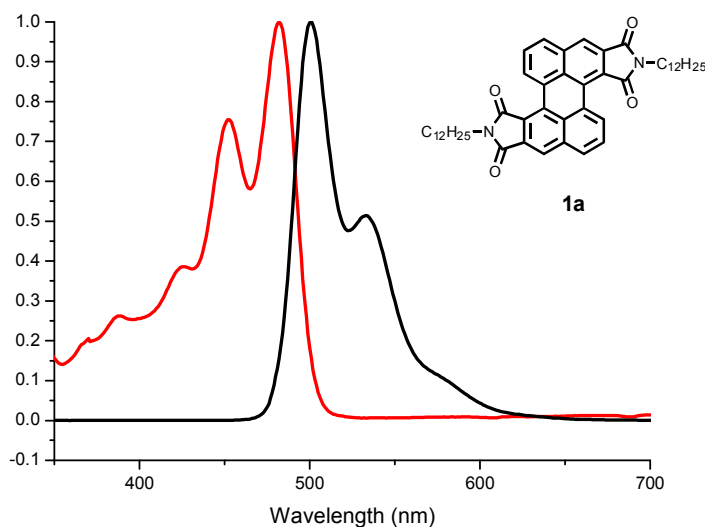
Tetraethyl 4,10-bis(decyloxy)-7,8-bis(propionyloxy)perylene-1,2,7,8-tetracarboxylate (3b):



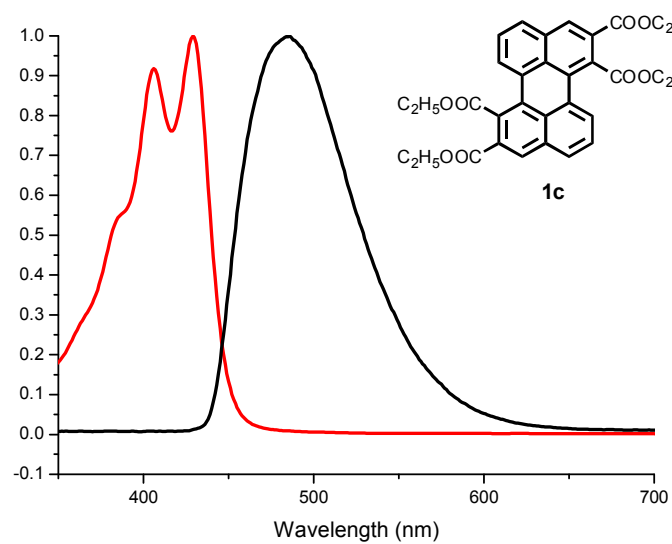
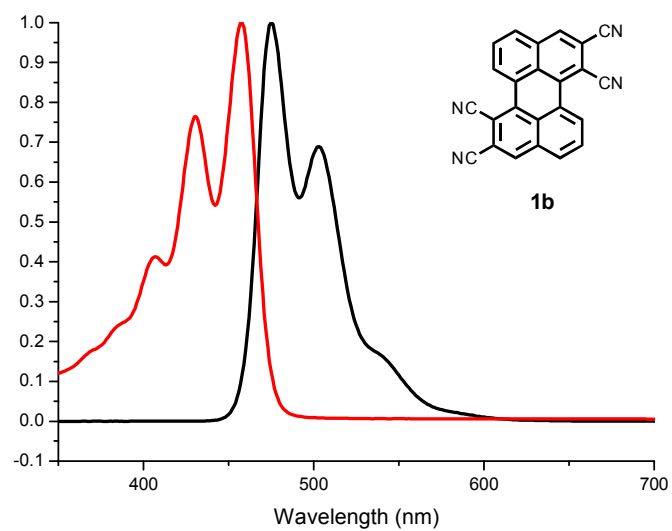
The crude anthraquinone product from last step (250 mg, 0.28 mmol) was dissolved in dry toluene (10.0 mL) and the solution was cooled to 0 °C. To this chilled solution was added DBU (0.42 mL, 2.80 mmol) and the reaction was then refluxed for 12 h. The volatiles were removed in vacuo and the residue was extracted with dichloromethane (3 x 100 mL). The combined organic extracts were dried over MgSO₄ and concentrated. The crude product was purified by column chromatography (silica gel; CH₂Cl₂: hexane = 1: 1) to furnish the desired compound as a yellow solid (170 mg, 71 %).

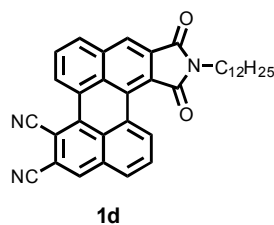
IR (CH₂Cl₂, cast) ν (cm⁻¹): 2927, 2855, 1721, 1584, 1468, 1262, 1129, 1025; ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.68 (s, 2H), 7.92 (d, 2H, *J* = 8.5 Hz), 6.85 (d, 2H, *J* = 8.5 Hz), 4.43-4.36 (m, 8H), 4.19 (t, 4H, *J* = 6.5 Hz), 1.99-1.93 (m, 4H), 1.59-1.53 (m, 4H), 1.42-1.23 (m, 36H), 0.86 (t, 6H, *J* = 6.8 Hz); ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 171.03, 166.81, 155.63, 131.89, 129.08, 129.03, 128.01, 127.74, 124.13, 123.84, 121.91, 106.67, 68.78, 61.79, 61.53, 31.89, 29.64, 29.58, 29.45, 29.33, 29.11, 26.18, 22.67, 14.23, 14.09, 13.84; UV/Vis (CH₂Cl₂): λ_{max} = 435 and 459 nm, Fluorescence (CH₂Cl₂, λ_{ex} = 489 nm): λ_{em} = 550 nm, Φ_{F} = 0.54; HR-FAB-MS. (M⁺), C₅₂H₆₈O₁₀, Calc.: 852.4812; Found: 852.4820

3. UV/Vis Absorption and Fluorescence Spectra:

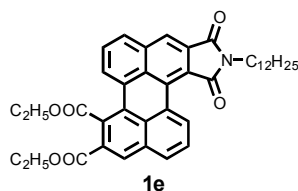


UV and PL spectrum of perylene-1,2,7,8-bis(1'-dodecyl-1H-pyrrole-2,5'-dione) (**1a**)

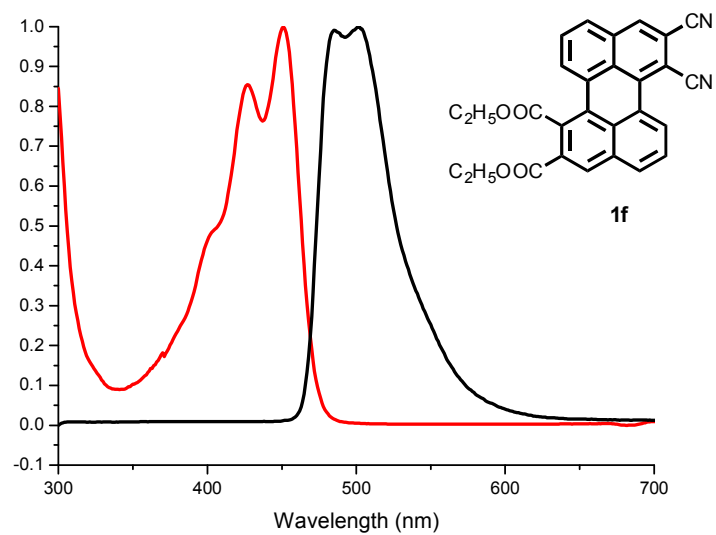




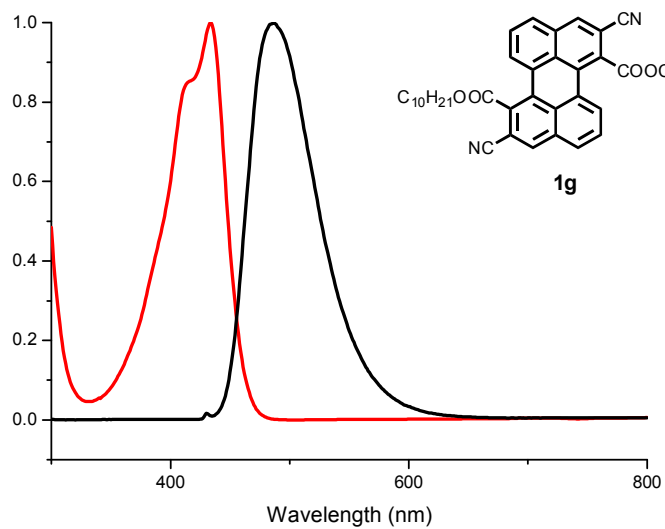
UV and PL spectrum of perylene-7,8-dicarbonitrile1,2-(1'-dodecyl-1H-pyrrole-2',5-dione) (**1d**)



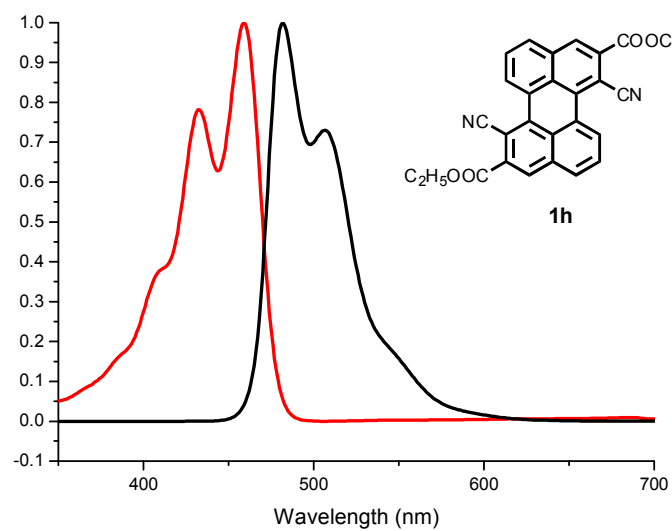
UV and PL spectrum of diethyl 7,8-(1'-dodecyl-1H-pyrrole-2',5'-dione)-1,2-dicarboxylate (**1e**)



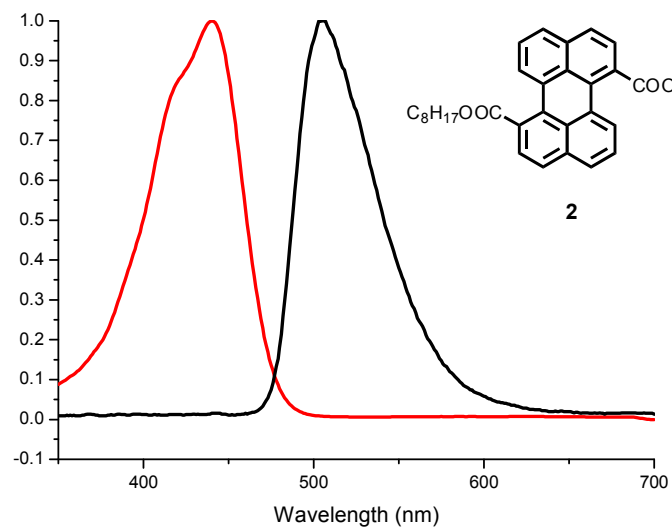
UV and PL spectrum of diethyl 7,8-dicyanoperylene-1,2-dicarboxylate (**1f**)



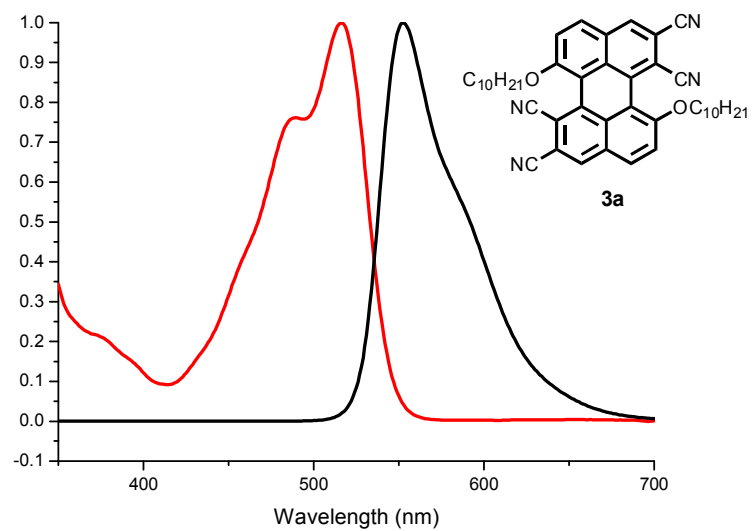
UV and PL spectrum of didecyl 2,8-dicyanoperylene-1,7-dicarboxylate (**1g**)



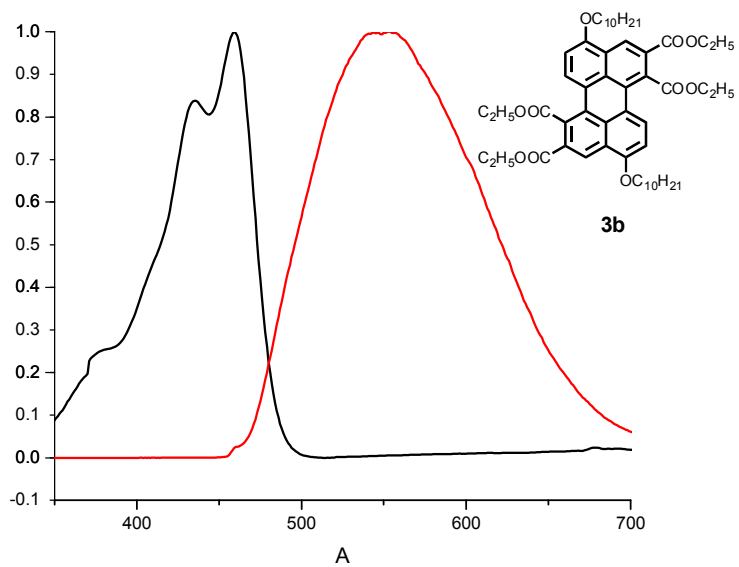
UV and PL spectrum of diethyl 1,7-dicyanoperylene-2,8-dicarboxylate (**1h**)



UV and PL spectrum of dioctyl perylene-1,7-dicarboxylate (**2**)

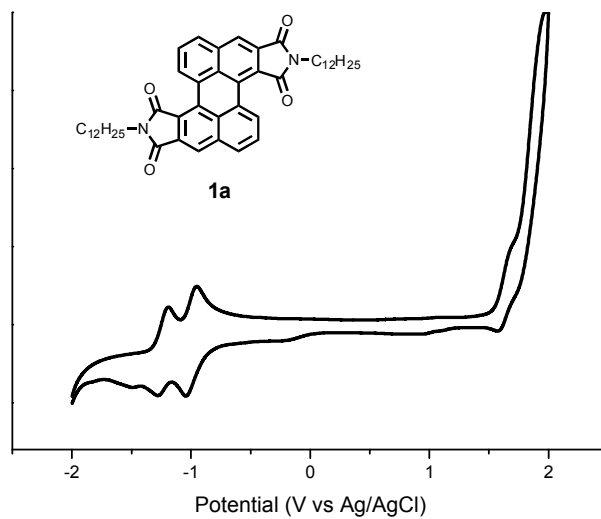


UV and PL spectrum of 6,12-bis(decyloxy)perylen-12,7,8-tetracyanonitrile (**3a**)

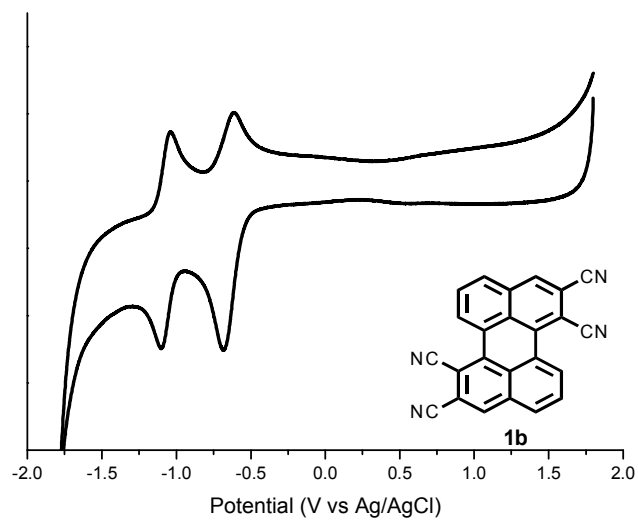


UV and PL spectrum of diethyl 4,10-bis(decyloxy)-7,8-bis(propionyloxy)perylen-1,2-dicarboxylate (**3b**)

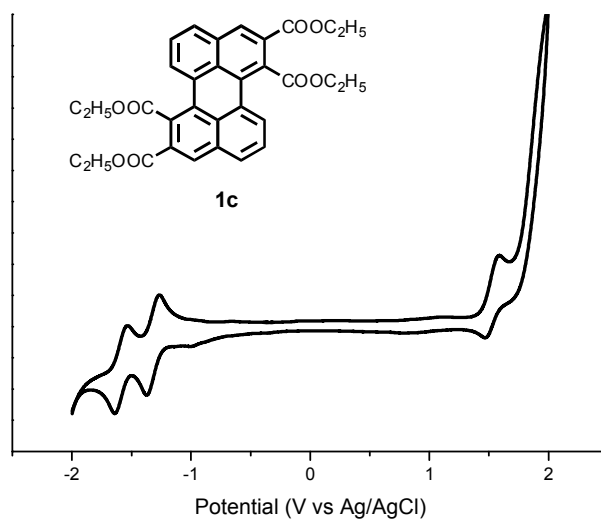
4. Electrochemical Analysis:



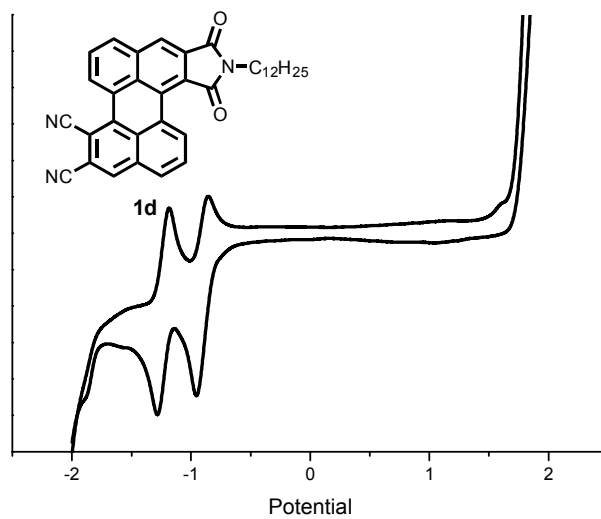
Cyclic voltammogram of perylene-1,2,7,8-bis(1'-dodecyl-1H-pyrrole-2,5'-dione) (**1a**)



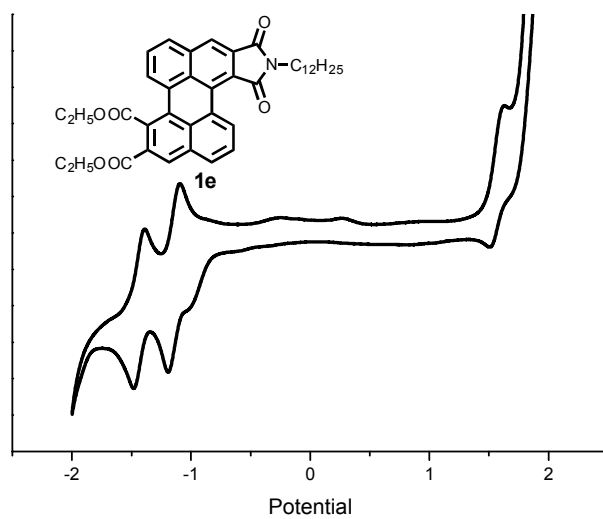
Cyclic voltammogram of perylene-1,2,7,8-tetracarbonitrile (**1b**)

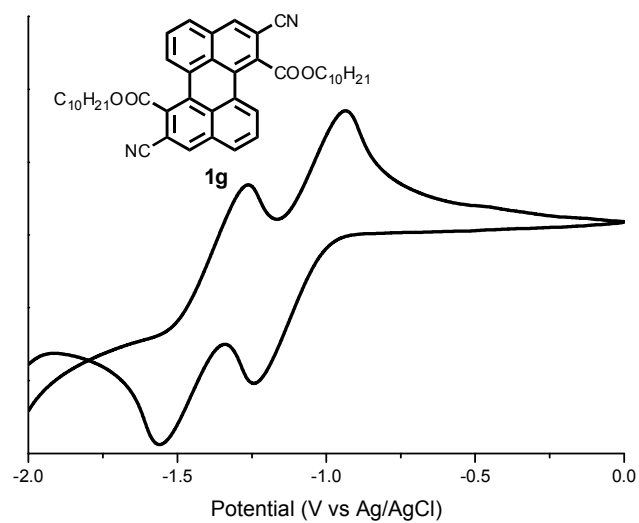


Cyclic voltammogram of tetraethyl perylene-1,2,7,8-tetracarboxylate (**1c**)

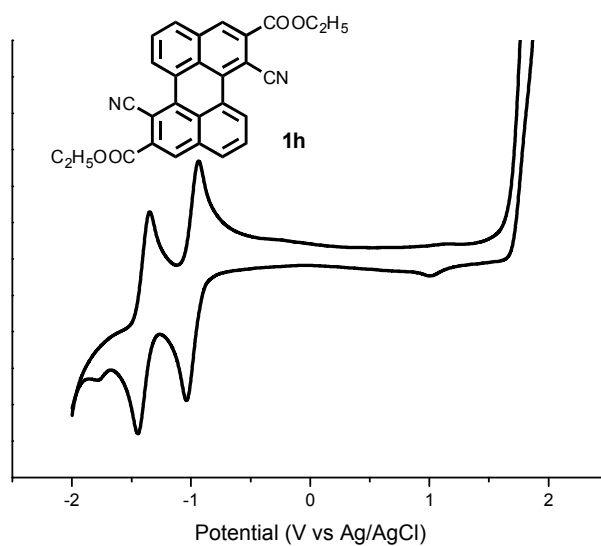


Cyclic voltammogram of perylene-7,8-dicarbonitrile1,2-(1'-dodecyl-1H-pyrrole-2',5-dione) (**1d**)

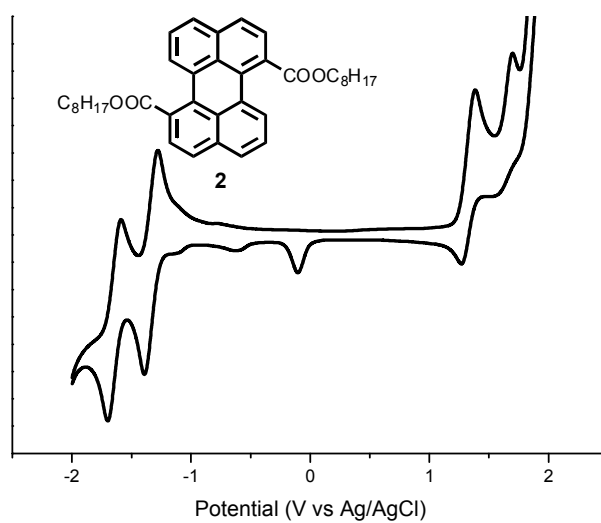




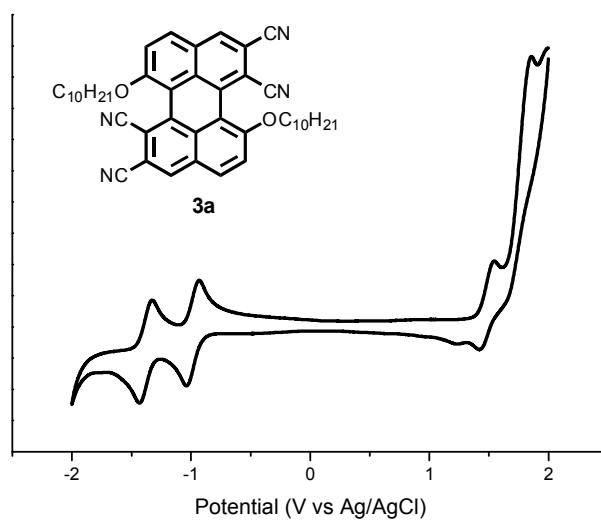
Cyclic voltammogram of didecyl 2,8-dicyanoperylene-1,7-dicarboxylate (**1g**)



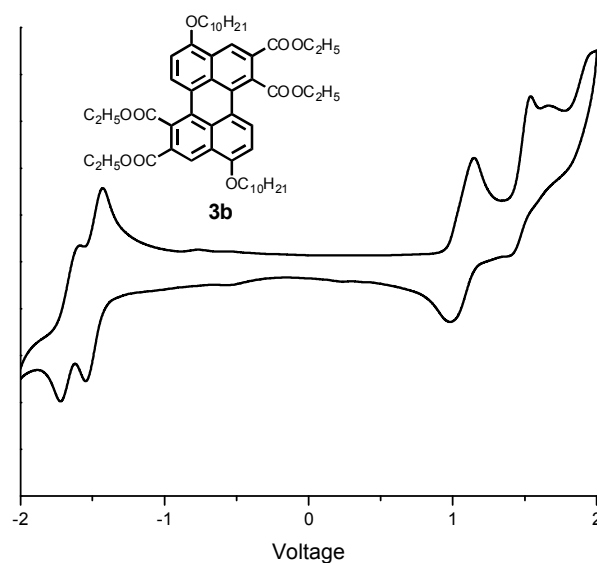
Cyclic voltammogram of diethyl 1,7-dicyanoperylene-2,8-dicarboxylate (**1h**)



Cyclic voltammogram of dioctyl perylene-1,7-dicarboxylate (**2**)



Cyclic voltammogram of 6,12-bis(decyloxy)perylen-12,7,8-tetracarbonitrile (**3a**)



Cyclic voltammogram of diethyl 4,10-bis(decyloxy)-7,8-bis(propionyloxy)perylene-1,2-dicarboxylate (**3b**)

Table 1.

Compound	UV (nm)	PL (nm)	E _{red} (V)	E _{ox} (V)	Quantum Yield	LUMO (eV)	HOMO (eV)	E _{gop} (eV)
1a	482	500	-0.998	1.625	0.36	-3.326	-5.925	2.44
1b	457	475	-0.648	--	0.38	-3.556	-6.136	2.58
1c	429	486	-1.319	1.52	0.07	-3.005	-5.827	2.75
1d	468	487	-0.905	--	0.55	-3.408	-5.928	2.52
1e	463	497	-1.143	1.570	0.18	-3.170	-5.869	2.53
1f	451	504	-1.043	--	0.35	-3.270	-5.880	2.61
1g	433	486	-1.088	--	0.17	-3.236	-5.876	2.64
1h	459	480	-0.987	--	0.67	-3.312	-5.882	2.57
2	440	503	-1.335	1.326	0.24	-2.964	-5.625	2.56
3a	516	552	-0.974	1.472	0.83	-3.361	-5.771	2.26
3b	459	550	-1.487	1.067	0.54	-2.859	-5.377	2.55

Conditions: Potentials versus Fc/Fc⁺, Working electrode: C, Counter electrode: Pt, Reference electrode: Ag/AgCl (for compound 1, Ag/AgNO₃), Scan rate 100 mV/sec. Measure in 0.1 M Bu₄NPF₆ CH₂Cl₂ solution.

Crystallographic information (X-ray crystal packing structure of 3a):

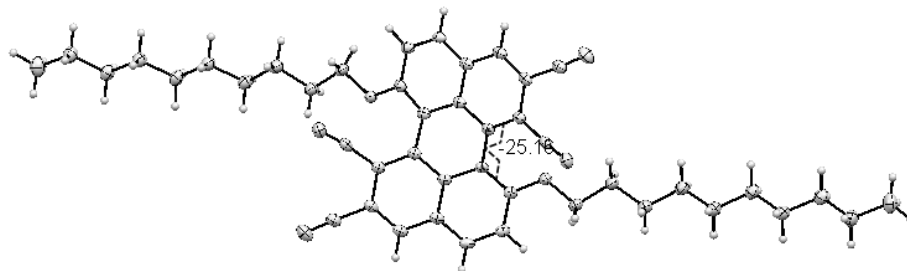


Figure 1. Single-crystal structure of **3a**

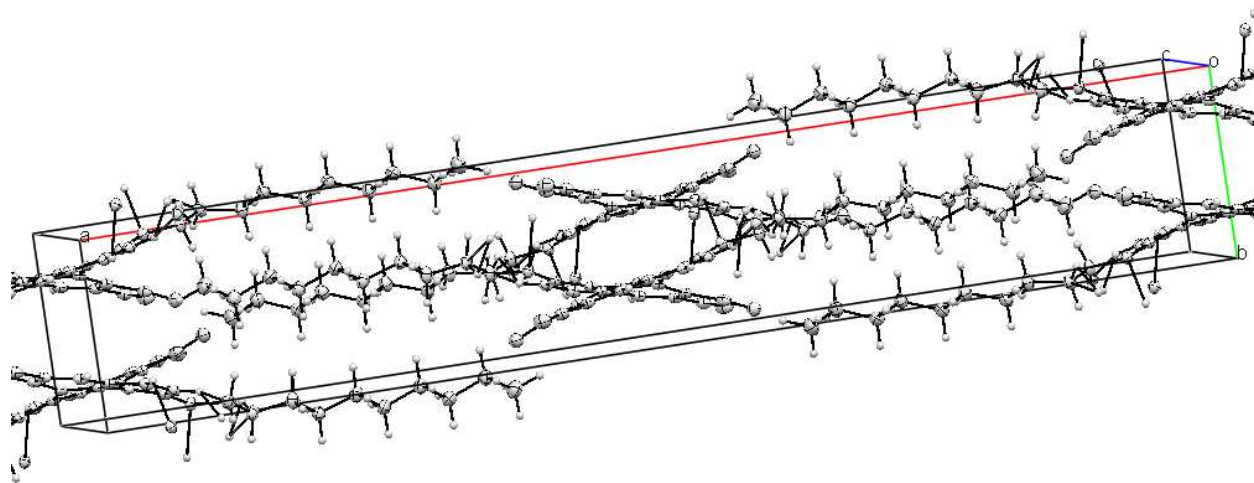


Figure 2. Crystal packing of **3a**

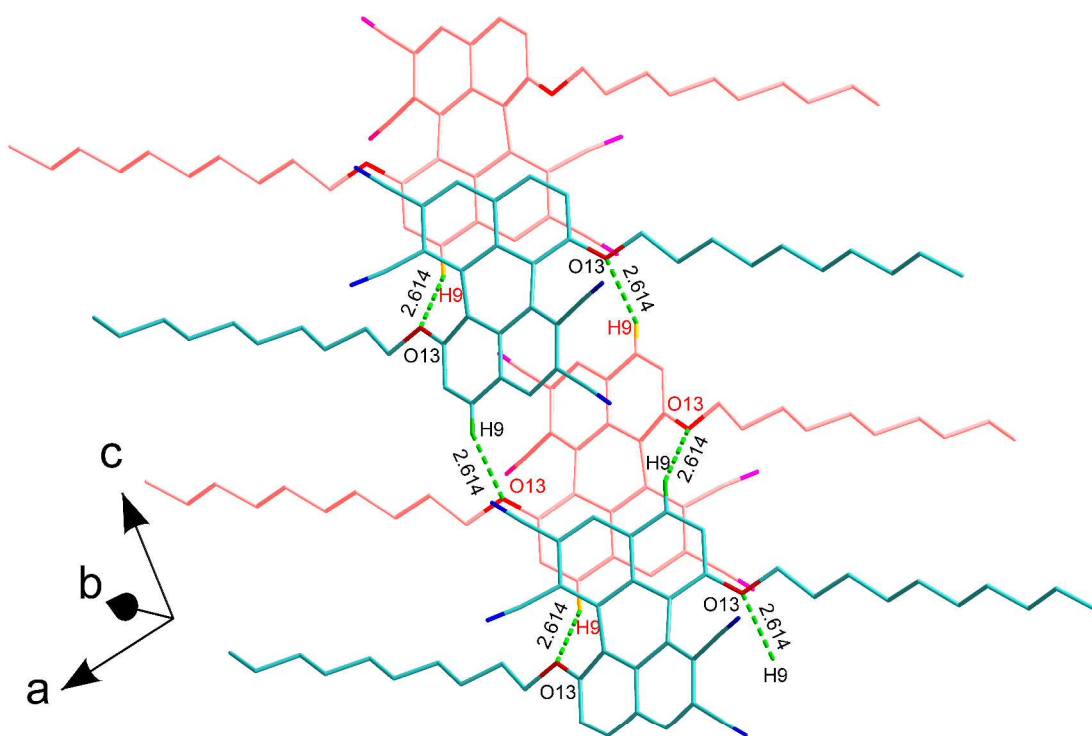


Figure 3. Hydrogen bonded network

Table 2.

	1
Empirical Formula	C44 H48 N4 O2
Formula weight	664.86
Temperature (K)	100.0(1) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> , Å	41.6679(13)
<i>b</i> , Å	6.9812(2)
<i>c</i> , Å	12.1463(3)
α (°)	90.00
β (°)	92.385(2)
γ (°)	90.00
<i>V</i> , Å ³	3530.20(17)
<i>Z</i>	4
ρ_{calc} Mg/m ³	1.251
μ , mm ⁻¹	0.077
<i>F</i> (000)	1424
<i>T</i> (min.)	0.7454
<i>T</i> (max.)	0.6974
Data / parameter	3121/ 323
Reflection (Unique)	3121
GOOF on <i>F</i> ²	1.111
<i>R</i> _{Final} <i>R</i> 1 =	0.0426
<i>I</i> > 2 σ (<i>I</i>) <i>wR</i> 2 =	0.1089
<i>R</i> _{all} <i>R</i> 1 =	0.0548
(all data) <i>wR</i> 2 =	0.1248

References:

- (1) de Mello, J.C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.
(2) Kendall, J. K.; Shechter, H. *J. Org. Chem.* **2001**, *66*, 6643.