# Supramolecular Polymerization of Permanently Dipolar Perylene Diimidebased Diazacoronenes

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#### **Supporting Information**

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#### A. Materials and Methods Materials

All materials were purchased from Fisher Scientific, Sigma Aldrich, or Ambeed unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All chemicals were used as purchased unless otherwise noted. Reactions were performed under inert reaction atmosphere and in flame-dried round-bottom flasks unless otherwise specified.

## **Methods and Instrumentation**

**Nuclear Magnetic Resonance Spectroscopy.** All <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a Bruker 400 MHz spectrometer at 298 K. Chemical shifts were calibrated using residual NMR solvent as an internal reference (CDCl3 7.26 ppm for 1H NMR, 77.00 ppm for <sup>13</sup>C NMR spectra).

**Fourier-Transform Infrared (FTIR) Spectroscopy.** Fourier-transform infrared (FTIR) spectroscopy was performed using a Cary 630 FTIR spectrometer with a diamond attenuated total reflection (ATR) attachment with 1 cm<sup>-1</sup> resolution in ambient atmosphere on neat samples. All spectra are shown with atmospheric background correction applied

**UV-Visible (UV-Vis) Spectroscopy.** UV-Vis spectroscopy, except for heated UV-Vis experiments, was performed using a Cary 5500 instrument from 300-800 nm with a resolution of 0.1 nm. All spectra are baseline corrected and have solvent background subtracted.

**Heated UV-Visible Spectroscopy (Heated UV-Vis).** Heated UV-Vis spectroscopy was performed using a Cary 100 Bio instrument and was heated with a Cary dual cell Peltier accessory from 25° to 60°C in 2° increments while being stirred. Samples were measured from 300-800 nm with a resolution of 0.1 nm. All spectra are baseline corrected and have solvent background subtracted.

**Cyclic Voltammetry (CV).** Cyclic voltammetry was carried out on a Bio-Logic SP-50e/150e potentiostat with a three-electrode setup, using a 2 mm Pt disk as a working electrode, an Ag wire as a reference electrode, and a Pt wire as a counter electrode. Samples (0.5 mM) were dissolved in  $CH_2Cl_2$  with 0.1 M  $nBu_4NPF_6$  as supporting electrolyte, and ferrocene as an internal reference after initial measurements. CVs were then referenced to the ferrocene/ferrocenium redox couple. Measurements were carried out at a scan rate of 200 mV/s with an initial reductive sweep under N<sub>2</sub> at room temperature.

**Steady-state Photoluminescence (PL) Spectroscopy.** Steady-state PL spectroscopy for the 0.01 mM PDAC chloroform solutions was collected using a 405 nm continuous wave laser (LDH-D-C-405, PicoQuant) at a power density of 30 mW cm<sup>-2</sup> where a 425 nm long-pass filter (Chroma Tech) was used to isolate sample emission and remove excess laser scatter.

**Mass Spectrometry (MS).** All mass spectrometry measurements were acquired with a Bruker autoflex maX MALDI Time-Of-Flight (TOF) spectrometer. Samples were solubilized in CHCl<sub>3</sub> and mixed (1:1 vol) with a matrix of 2,5-dihydroxybenzoic acid (DHB) in MeCN:H<sub>2</sub>O (7:3 vol) with TFA (0.1% vol). Spectrometry was performed by the University of Florida Mass Spectrometry Research and Education Center. Funding from NIH S10 OD021758-01A1 and S10 OD030250-01A1

**Time-resolved Photoluminescence (PL) Spectroscopy.** Time-resolved photoluminescence (PL) dynamics for the 0.01 mM PDAC derivative chloroform solutions were collected *via* time-correlated single photon counting (TCSPC) where a 405 nm picosecond pulsed laser (LDH-D-C-405, PicoQuant) at a 1 MHz repetition frequency and power density of 4.93 mW cm<sup>-2</sup> was used. A 425 nm long-pass (Chroma Tech) was used to remove laser scatter and isolate sample emission. Photon arrival times were determined using a single-photon avalanche photodiode (Micro Photon Devices) coupled to a MultiHarp 150 event timer

(PicoQuant). A silicon power meter (ThorLabs PM100-D) was used to measure incident laser powers, and all laser spot sizes were measured using the razor blade method (90:10).

**Quantum Yields.** Quantum yield measurements were performed using a Hamamatsu C11347 Quantaurus-QY spectrometer equipped with a 150 W Xenon arc lamp source. All samples were measured at 3 mM in chloroform. Samples measured were excited under a 350 nm light using a CCD detector.

Abbreviations and symbols: Permanent ground state dipole ( $\mu_g$ ), highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), permanently dipolar diazacoronenes (PDACs), perylene diimide (PDI), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), lowest energy absorption maxima ( $\lambda_{max, absorption}$ ), largest emission maxima ( $\lambda_{max, emission}$ ), photoluminescence quantum yield ( $\Phi_{PL}$ ), monomeric lifetimes ( $\tau_m$ ), assembly lifetimes ( $\tau_a$ )

**B.** Synthetic Methods



**Compound 2**: Procedure adapted from literature.<sup>1</sup> To a flask, perylenetetracaboxylic dianhydride (Compound 1) (4 g, 1 equiv), potassium iodide (846 mg, 0.5 equiv) and dried acetonitrile (400 mL) were added. The mixture was placed under nitrogen, heated to 70 °C and stirred for 30 minutes. To the mixture, 1-bromobutane (6.55 mL, 6 equiv), 1-butanol (5.6 mL, 6 equiv) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (12.17 mL, 8 equiv) were added. The mixture was heated at 82 °C for 18 hours. The solution was allowed to cool to 23 °C and the solvent was removed under reduced pressure. The resulting residue was extracted with ethyl acetate (200 mL). The solution was washed with water (100 mL, 2×) and brine (100 mL, 1×). The resulting organic layers were combined and dried. The crude product was purified by filtering through a silica plug (SiO<sub>2</sub>, 150 mL) with CH<sub>2</sub>Cl<sub>2</sub> (300 mL) to yield Compound 2 as a bright orange solid (6.5 g, 97% yield). <sup>1</sup>H NMR was consistent with previous report.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, J = 8.0 Hz, 4H), 7.96 (d, J = 7.9 Hz, 4H), 4.34 (t, J = 6.8 Hz, 8H), 1.79 (t, J = 1.6 Hz, 8H), 1.55 – 1.40 (m, 8H), 1.00 (t, J = 7.4 Hz, 12H) ppm.

**Compound 3**: Procedure adapted from literature with some modifications.<sup>2</sup> Compound 2 (6.5 g, 1 equiv) was added to a 250 mL round-bottom flask with dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (70 mL). Fuming nitric acid (4 mL) was added to the solution via a Pasteur pipette. The flask was sealed and stirred at 23 °C for 4 hours. The solution was quenched with triethylamine (3 mL) dropwise. The resulting solution was filtered through a silica plug (SiO<sub>2</sub>, 150 mL). The silica plug was thoroughly washed with CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The resulting

solution was dried under vacuum. The product was recrystallized twice in acetonitrile to produce Compound 3 as a red solid (4.4 g, 51% yield). <sup>1</sup>H NMR was consistent with previous report.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (s, 2H), 8.05 (d, J = 2.0 Hz, 4H), 4.36 (q, J = 6.7 Hz, 8H), 1.85 – 1.73 (m, 8H), 1.56 – 1.42 (m, 8H), 1.00 (td, J = 7.4, 1.1 Hz, 12H) ppm.

**Compound 4:** Procedure adapted from literature with some modifications.<sup>2</sup> To a flask, Compound 3 (3.3 g, 1 equiv.) was added with a Teflon-coated stir bar. Chlorosulfonic acid (25 mL) was added to the flask, and the solution was left to stir at 23 °C for 30 minutes. The reaction was quenched by pouring the solution into an ice bath (1000 mL) and allowing the resulting solution to stir for 30 minutes. The solution was filtered and washed with water and hexanes to yield Compound 4 as a highly insoluble dark red solid. (2.13 g, 99% yield). <sup>1</sup>H NMR was consistent with previous report.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 (s, 2H), 8.78 (d, J = 8.0 Hz, 2H), 8.43 (d, J = 8.1 Hz, 2H) ppm.

**2-(2-octyldodecyl) isoindoline-1,3-dione:** Procedure was modified from literature.<sup>3</sup> Potassium phthalimide (5.64 g, 1.1 equiv) was added to the solution of 2-octyl dodecyl bromide (10 g, 1 equiv) in anhydrous DMF. The reaction mixture was sparged with N<sub>2</sub> and then stirred at 90 °C for 18 hours. The reaction mixture was removed from heat, poured into water (150 mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL,  $3\times$ ). The combined organic layer was washed with 0.2 N KOH (100 mL,  $1\times$ ), water (100 mL,  $1\times$ ), saturated NH<sub>4</sub>Cl (100 mL,  $1\times$ ), and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated under reduced pressure after filtration. The crude mixture was purified by filtering through a silica plug (SiO<sub>2</sub>, 150 mL) with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was evaporated under reduced pressure to yield 2-(2-octyldodecyl) isoindoline-1,3-dione (10 g, 85%) as a pale-yellow oil. The product was used in the next reaction without further purification or characterization.

**2-Octyldodecylamine:** 2-(2-Octyldodecyl) isoindoline-1,3-dione (10 g, 1 equiv) and hydrazine hydrate (5 mL, 5 equiv) were placed in a flask with methanol (50 mL). The solution was sparged with N<sub>2</sub>, then stirred at 70 °C for 5 hours. The mixture was allowed to cool to 23 °C. If any methanol remained, it was removed under reduced pressure. The residue was diluted with a 10% KOH solution (100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and extracted. The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL, 3×). The combined organic layers were washed with brine (100 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to yield 2-octyldodecylamine as a yellow oil (6.60g, 95% yield). <sup>1</sup>H NMR was consistent with previous reports.<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.57 (d, J = 4.8 Hz, 2H), 1.26 – 1.22 (m, 35H), 0.92 – 0.80 (m, 6H).

**Compound 5:** Procedure adapted from literature with some modifications.<sup>2</sup> Compound 4 (1.7 g, 1 equiv) was added to a flask. Toluene (45 mL) was added to the vial and sparged under N<sub>2</sub>. 2-Octyldodecylamine (2.1 g, 2.1 equiv) was added via needle. The mixture was stirred and heated at 100 °C for 18 hours. The solution was allowed to cool to 23 °C and then the solvent was removed under reduced pressure. The crude material was purified via flash column chromatography (SiO<sub>2</sub>, 1:1 vol CH<sub>2</sub>Cl<sub>2</sub>:Hexanes) to yield Compound 5 (1.9 g, 83% yield). <sup>1</sup>H NMR was consistent with previous report.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (d, J = 1.2 Hz, 2H), 8.67 (dd, J = 8.1, 1.2 Hz, 2H), 8.33 (dd, J = 8.1, 1.2 Hz, 2H), 4.14 (t, J = 6.5 Hz, 4H), 1.98 (s, 2H), 1.24 (d, J = 7.7 Hz, 68H), 0.94 – 0.70 (m, 12H) ppm.

**Compound 6:** Procedure adapted from literature with some modifications.<sup>2</sup> Pd/C (100 mg) and N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (5 mL) were added to a solution of Compound 5 (0.7 g) in THF (100 mL) under N<sub>2</sub>. The resulting mixture was stirred for 18 hours at 60 °C. The solution was allowed to cool to 23 °C and then filtered through a pad of Celite® (250 mL). The Celite® was washed with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1 vol, 150 mL). The solvent was evaporated under reduced pressure, and the crude material was purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to afford Compound 6 (0.65 g, 98%) as a blue solid. <sup>1</sup>H NMR was consistent with previous report.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.69 (d, J = 8.2 Hz, 2H), 8.59 (d, J = 8.1 Hz, 2H), 7.88 (s, 2H), 5.06 (s, 4H), 4.10 (dd, J = 18.2, 7.3 Hz, 4H), 1.99 (s, 2H), 1.39 – 1.18 (m, 68H), 0.88 – 0.80 (m, 12H) ppm.

#### **PDAC Syntheses**



Scheme S1. Synthetic Scheme for PDAC-CN

**PDAC-CN**. Compound 6 (116 mg, 1 equiv) was placed in a vial with 4-formylnitrile (31 mg, 2 equiv), CH<sub>2</sub>Cl<sub>2</sub> (3.48 mL), and TFA (0.6 mL). The solution was mixed and then distributed into NMR tubes. The tubes were placed into a water bath (42 °C) for 2 hours. The tubes were then irradiated with white LED light (500 W) for 2 hours. DDQ was added to each tube and inverted to mix and irradiated for an additional hour. The mixtures in each of these NMR tubes were combined into a vial, and the solvent was removed under reduced pressure. The crude solid was washed with acetone (100 mL) over a vacuum filter under the solution was clear. The filter cake was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with a K<sub>2</sub>CO<sub>3</sub> solution (2 M, 50 mL, 1×), water (50 mL, 1×), and brine (50 mL, 1×) in a separatory funnel. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated under reduced pressure. The crude was purified by column chromatography without pressure (SiO<sub>2</sub>, 99:1 vol CH<sub>2</sub>Cl<sub>2</sub>:MeOH) to yield PDAC-CN as a green solid (73 mg, 51%).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.09 (s, 2H), 9.80 (s, 2H), 8.38 (d, J = 8.4 Hz, 4H), 8.15 (d, J = 8.4 Hz, 4H), 4.39 (d, J = 7.3 Hz, 2H), 4.27 (d, J = 7.4 Hz, 2H), 1.28 – 1.04 (m, 68H), 0.86 – 0.51 (m, 12H) ppm.

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>) *δ* 163.5, 162.8, 160.7, 142.5, 142.2, 133.0, 132.0, 131.4, 131.0, 130.9, 126.7, 126.4, 124.2, 123.1, 121.4, 121.2, 118.4, 118.3, 118.1, 116.0, 114.4, 32.0, 31.8, 30.3, 30.2, 29.8, 29.8, 29.7, 29.5, 26.8, 26.8, 26.6, 22.8, 14.2 ppm.

FT-IR (Diamond-ATR, neat, cm<sup>-1</sup>): 2953, 2920, 2851, 1707, 1662, 1449, 1377, 1257, 1080, 1017, 801

MS (MALDI-TOF): calc [M+H]<sup>+</sup>: 1203.73 found [M+H]<sup>+</sup>: 1203.691



Scheme S2. Synthetic Scheme for PDAC-Me

**PDAC-Me**. Compound 6 (96.5 mg, 1 equiv) was placed in a vial with tolualdehyde (23.63 mg, 2 equiv) with  $CH_2Cl_2$  (5 mL) and TFA (0.6 mL). The solution was mixed and then distributed into NMR tubes. The tubes were placed into a water bath (42 °C) for 2 hours. The tubes were then irradiated with white LED light (500 W) for 2 hours. DDQ was added to each tube and inverted to mix and were irradiated for an additional hour. The mixtures in each of these NMR tubes were combined into a vial and the solvent was removed under reduced pressure. The crude solid was washed with acetone over a vacuum filter under the solution was clear. The filter cake was dissolved in  $CH_2Cl_2$  (50 mL) and washed with a  $K_2CO_3$  solution (2 M, 50 mL, 1×), water (50 mL, 1×), and brine (50 mL, 1×) in a separatory funnel. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated under reduced pressure. The crude was purified by column chromatography without pressure (SiO<sub>2</sub>, 99:1 vol  $CH_2Cl_2$ :MeOH) to yield PDAC-Me as a green solid (60 mg, 51.64%)

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.79 (s, 2H), 9.56 (s, 2H), 8.08 (d, J = 8.0 Hz, 4H), 7.62 (d, J = 7.6 Hz, 4H), 4.35 (d, J = 7.3 Hz, 2H), 4.24 (d, J = 7.4 Hz, 2H), 2.68 (s, 6H), 1.60 (s, 4H), 1.43 – 1.09 (m, 68H), 0.79 (q, J = 6.8 Hz, 12H) ppm.

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.7, 163.6, 162.6, 142.9, 140.4, 135.3, 132.0, 131.3, 131.0, 130.1, 126.4, 126.0, 124.5, 121.8, 121.3, 115.9, 77.4, 37.1, 36.9, 32.0, 31.9, 30.3, 29.9, 29.8, 29.5, 29.5, 26.8, 26.7, 22.8, 22.8, 21.8, 14.2 ppm.

**FT-IR** (Diamond-ATR, neat, cm<sup>-1</sup>): 2953, 2920, 2853, 1785, 1701, 1664, 1610, 1449, 1304, 1224, 1149, 810

**MS** (MALDI-TOF): calc: [M+H]<sup>+</sup> 1181.77 found: [M+H]<sup>+</sup> 1181.772

A note on the use of NMR tubes in the synthesis of PDACs: Photocyclizations require great optical penetration in order for efficient reactions to occur. There is a direct tradeoff between the width of a reaction vessel and the efficiency of a photochemical reaction. This problem compounds when working with colored solutions. Typically, photoreactors are used to perform photocyclizations on aromatic molecules that suffer from this issue, as the thin tubes allow for optimal light perforation. However, we found similar results doing the reaction in NMR tubes as the thin borosilicate glass tubes have a small diameter that is able to facilitate the Mallory photocyclizations of PDACs.



Scheme S3. Synthetic Scheme for PDAC-OMe

**PDAC-OMe** Compound 6 (100 mg, 1 equiv) was placed in a vial with anisaldehyde (27.74 mg, 2 equiv) with TFA (0.5 mL) and CH<sub>2</sub>Cl<sub>2</sub>. The solution was mixed and heated in the vial at 45 °C for 2 hours. The solvent was removed under reduced pressure. DDQ (100 mg, 5 equiv) was added to the vial with the dried crude solid with CH<sub>2</sub>Cl<sub>2</sub>. The mixture was then distributed into NMR tubes. The tubes were then irradiated with white LED light (500 W) for 2 hours. DDQ was added to each tube and inverted to mix and irradiated for an additional hour. The mixtures in each of these NMR tubes were combined into a vial, and the solvent was removed under reduced pressure. The crude solid was washed with acetone over a vacuum filter under the solution was clear. The filter cake was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with a K<sub>2</sub>CO<sub>3</sub> solution (2 M, 50 mL, 1×), water (50 mL, 1×), and brine (50 mL, 1×) in a separatory funnel. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated under reduced pressure to yield PDAC-OMe as an orange solid (127 mg, 97% yield).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.66 (s, 2H), 9.47 (s, 2H), 8.14 (d, J = 8.6 Hz, 4H), 7.32 (d, J = 8.7 Hz, 4H), 4.34 (d, J = 7.3 Hz, 2H), 4.24 (d, J = 7.3 Hz, 4H), 4.11 (s, 6H), 2.09 (s, 2H), 1.49 – 1.06 (m, 68H), 0.83 – 0.74 (m, 12H) ppm.

<sup>13</sup>**C-NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.3, 161.5, 142.5, 133.0, 131.4, 130.3, 125.7, 121.2, 120.7, 117.8, 114.9, 55.7, 45.6, 45.2, 37.1, 37.0, 32.0, 32.0, 32.0, 31.9, 30.4, 29.9, 29.8, 29.5, 29.5, 26.8, 26.7, 22.8, 22.8, 14.2 ppm.

**FT-IR** (Diamond-ATR, neat, cm<sup>-1</sup>): 2939, 2916, 2849, 1735, 1701, 1667, 1604, 1448, 1254, 1092, 1015, 795

MS (MALDI-TOF): calc: [M+H]<sup>+</sup> 1213.76 found: [M+H]<sup>+</sup> 1213.416



Scheme S4. Synthetic Scheme for PDAC-NMe<sub>2</sub>

**PDAC-NMe**<sub>2</sub>. Compound 6 (200 mg, 1 equiv) was placed in a vial with para-dimethylaminobenzaldehyde (62 mg, 2 equiv) with  $CH_2Cl_2$  (15 mL) and TFA (0.75 mL). The solution was mixed and heated in the vial at 42 °C for 1.5 hours. The mixture was then distributed into NMR tubes. The tubes were then irradiated with white LED light (500 W) for 2 hours. DDQ was added to each tube and inverted to mix and irradiated for an additional hour. The mixtures in each of these NMR tubes were combined into a vial, and the solvent was removed under reduced pressure. The crude solid was washed with acetone over a vacuum filter under the solution was clear. The filter cake was dissolved in  $CH_2Cl_2$  (50 mL) and washed with a K<sub>2</sub>CO<sub>3</sub> solution (2 M, 50 mL, 1×), water (50 mL, 1×), and brine (50 mL, 1×) in a separatory funnel. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated under reduced pressure. The crude was purified by column chromatography without pressure (SiO<sub>2</sub>, 99:1 vol  $CH_2Cl_2$ :MeOH to 95:5 vol  $CH_2Cl_2$ :MeOH) to yield PDAC-NMe<sub>2</sub> as a red solid (124 mg, 62%).

<sup>1</sup>**H-NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.87 (s, 2H), 9.56 (s, 2H), 8.13 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.6 Hz, 4H), 4.33 (dd, J = 25.0, 7.3 Hz, 4H), 3.24 (s, 12H), 2.13 (s, 2H), 1.51 – 0.96 (m, 68H), 0.81 – 0.74 (m, 12H) ppm.

<sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) *δ* 163.9, 162.4, 151.8, 143.5, 132.9, 132.3, 130.6, 127.0, 126.0, 124.5, 121.2, 115.6, 112.8, 77.5, 77.4, 77.2, 76.8, 40.6, 37.0, 32.0, 30.3, 29.9, 29.8, 29.5, 26.8, 22.8, 14.2 ppm.

FT-IR (Diamond-ATR, neat, cm<sup>-1</sup>): 2957, 2922, 2851, 1701, 1662, 1602, 1451, 1361, 1092, 1017, 792

MS (MALDI-TOF): calc: [M+H]<sup>+</sup> 1239.38 found: [M+H]<sup>+</sup> 1239.836

## C. Spectroscopic and Electrochemical Characterization of PDACs

|  | PDAC-CN    | PDAC-Me | PDAC-OMe | PDAC-NMe <sub>2</sub> |
|--|------------|---------|----------|-----------------------|
| Dipole Moment (Debye)*                                 | 1.0185     | 4.0268  | 4.8293   | 5.9898                |
| $\lambda_{	ext{max, absorption}} (	ext{nm})^{\dagger}$ | 477        | 484     | 498      | 456, 557%             |
| $\lambda_{max, emission} (nm)^{\delta}$                | 483        | 498     | 533      | 505, 723 <sup>%</sup> |
| $\Phi_{	extsf{PL}}$ **                                 | 20%        | 10%     | 20%      | 1%                    |
| $\tau_{m} (ns)^{\delta}$                               | 9.5        | 5.9     | 3.6      | $1.8^{\#}$            |
| $\tau_{a} (ns)^{\$}$                                   | $7.8^{\#}$ | 6.6#    | 5.0#     | 5.1#                  |
| $E_{1/2} 1 (V)^+$                                      | -0.96      | -1.21   | -1.52    | -1.27                 |
| $E_{1/2} 2 (V)^+$                                      | -1.17      | -1.34   | -1.68    | -1.53                 |
| $E_{1/2}$ 3 (V) <sup>+</sup>                           | -1.43      | -1.53   | -1.84    | n/a                   |

Table S1. Spectroscopic and electrochemical data of PDACs

\*Calculated Value

 $^{\dagger}$  measured in chloroform at 0.01 mM

<sup>8</sup> measured in chloroform at 0.01 mM, excited at 405 nm

<sup>\$</sup> measured in 95:5 hexanes:chloroform at 0.01 mM, excited at 405 nm

<sup>#</sup> average weighted lifetime based on a biexponential fit

<sup>%</sup> charge-transfer state

\*\* measured in chloroform at 0.03 mM, excited at 350 nm

<sup>+</sup> measured in dichloromethane at 0.5 mM with 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> electrolyte (vs. Fc/Fc<sup>+</sup>)



**Figure S1.** Absorption/emission spectra of PDAC-CN in the monomer state (0.1 mM, CHCl<sub>3</sub>,  $\lambda_{exc} = 405$  nm)



**Figure S2.** Absorption/emission spectra of PDAC-Me in the monomer state (0.1 mM, CHCl<sub>3</sub>,  $\lambda_{exc} = 405$  nm)



**Figure S3.** Absorption/emission spectra of PDAC-OMe in the monomer state (0.1 mM, CHCl<sub>3</sub>,  $\lambda_{exc} = 405$  nm)



**Figure S4.** Absorption/emission spectra of PDAC-NMe<sub>2</sub> in the monomer state (0.1 mM, CHCl<sub>3</sub>,  $\lambda_{exc} = 405$  nm)



Figure S5. Molar absorptivity profile of PDAC molecules (10 µM, CHCl<sub>3</sub>).



Figure S6. Emission spectra of PDACs in chloroform (10 µM, CHCl<sub>3</sub>).



**Figure S7.** Absorption spectra of PDAC-NMe<sub>2</sub> in the monomer state in chloroform and dichloromethane (0.5 mM)



**Figure S8**. Randles-Sevcik ( $i_p$  vs  $v^{1/2}$ ) plot derived from PDAC-NMe<sub>2</sub> CVs



**Figure S9.** Randles-Sevcik ( $i_p$  vs  $v^{1/2}$ ) plot derived from PDAC-OMe CVs



**Figure S10.** Randles-Sevcik  $(i_p \text{ vs } v^{1/2})$  plot derived from PDAC-Me CVs



**Figure S11.** Randles-Sevcik ( $i_p$  vs v<sup>1/2</sup>) plot derived from PDAC-CN CVs



Figure S12. Solvent-dependent assembly of PDACs.



Figure S13. Concentration-dependent assembly for PDACs in 95:5 vol hexanes:chloroform mix

#### D. PDAC Assembly Studies

The mechanism of supramolecular polymerization was studied via variable-temperature UV-Vis spectroscopy. The following equations were utilized to characterize the mechanism of assembly and fit using Origin 8.5 software.

$$\alpha_{agg}(T) = 1 - \frac{\varepsilon(T) - \varepsilon_{agg}}{\varepsilon_{mon} - \varepsilon_{agg}}$$

**Equation S1**. Degree of aggregation from temperature-dependent UV-Vis spectroscopy. Where  $\varepsilon_{mon}$  is the molar absorptivity at 334K and  $\varepsilon_{agg}$  is the molar absorptivity at 298 K

$$\alpha_{agg}(T) = \frac{1}{1 + e^{-0.908\Delta H \frac{T - T_m}{R T_m^2}}}$$

**Equation S2.** Isodesmic assembly prediction model Where  $T_m = \alpha_{agg}(T) = 0.5$ , R is the ideal gas constant, and  $\Delta H$  is the enthalpy release

$$K_e = \frac{(\frac{1}{\sqrt{1 - \alpha_{agg}(T)}} - \frac{1}{2})^2}{C_T} - 1$$

**Equation S3.** Equilibration constant for isodesmic assembly Where  $C_T$  is the concentration of the sample

$$a_{agg}(T) = a_{SAT}(1 - \exp\left[\frac{-\Delta H_e}{RT_e^2}(T - T_e)\right])$$

Equation S4. Prediction model for the elongation regime of cooperative assembly.

Where  $\Delta H_e$  is the enthalpy of elongation, R is the ideal gas constant,  $T_e$  is the elongation temperature, and  $\alpha_{sat}$  is a mathematical parameter to ensure  $\alpha_{agg}/\alpha_{sat}$  does not exceed unity.

$$K_e = \exp\left[\Delta H_e \frac{(T - T_e)}{RT_e^2}\right]$$

**Equation S5.** Equilibration constant for elongation process of cooperative assembly R is the ideal gas constant;  $T_e$  is the elongation temperature.



**Figure S14**. Left. Temperature-dependent UV-Vis experiments of PDAC-NMe<sub>2</sub> (92:8 vol hexanes:chloroform, 0.5 mM) between 298 K and 335 K. **Right.** Plot of  $\alpha_{agg}$  at 400 nm against temperature (K) (red circles) with data fit obtained from nucleation-elongation model (black line).

**Table S2**. Thermodynamic parameters obtained from temperature-dependent UV-Vis experiments based on the cooperative model for PDAC-NMe<sub>2</sub>

| $1.14 \pm 0.002 \qquad 333.97 \pm 0.17 \qquad -63.27 \pm 2.76$ | -20.31 | $1.00 \ge 10^{1}$ |
|--|--------|-------------------|

\*\* Measured at 300 K

Due the limited solvents the molecules were soluble in, we were not able to take measurements past 335K. As calculated, the nucleation regime of the material was beyond the boiling point of the solvents measured in and was not able to be calculated. As such we were only able to model the elongation regime of PDAC-NMe<sub>2</sub>.



**Figure S15**. Left. Temperature-dependent UV-Vis experiments of PDAC-OMe (95:5 vol hexanes:chloroform, 0.5 mM) between 298 K and 335 K. Right. Plot of  $\alpha_{agg}$  at 430 nm against temperature (K).

The plotted degree of aggregation of PDAC-OMe could not be fit to any standard supramolecular assembly profiles. We hypothesize that this observation may be due to there being multiple types of stacking motifs emerging as they undergo assembly. These competitive interactions could be attributed to the apparent two-stage assembly motif observed.



**Figure S16. Left.** Temperature-dependent UV-Vis experiments of PDAC-Me (hexanes, 2 mM) between 298 K and 335 K. **Right.** Plot of  $\alpha_{agg}$  at 400 nm against temperature (K).

The plotted degree of aggregation of PDAC-Me could not be fit to any supramolecular assembly fits. This is likely due to the limited conditions available to observe assembly, as the PDAC molecules were soluble in a limited number of solvents.



**Figure S17. Left.** Temperature-dependent UV-Vis experiments of PDAC-CN (85:15 vol hexanes:chloroform, 0.5 mM) between 298 K and 335 K. **Right.** Plot of  $\alpha_{agg}$  at 385 nm against temperature (K) (green circles) with data fit obtained from isodesmic model (black line).

**Table S3.** Thermodynamic parameters obtained from temperature-dependent UV-Vis experiments based on isodesmic model for PDAC-CN

| $T_{m}(K)$         | $\Delta H (kJ mol^{-1})$ | $\Delta S (J \text{ mol}^{-1} \text{ K}^{-1})$ | K <sub>e</sub> (M <sup>-1</sup> )** |
|--------------------|--------------------------|--|-------------------------------------|
| $315.65 \pm 0.244$ | $-163.2 \pm 6.47$        | -7.56  | 1.2 x 10 <sup>5</sup>               |

\*\* Measured at 300 K



**Figure S18.** Zoomed in regions of isosbestic points of temperature-dependent UV-Vis experiments of PDAC-CN, PDAC-Me, PDAC-OMe, and PDAC-NMe<sub>2</sub> (0.25 mM 85:15 vol hexanes:chloroform, 2 mM hexanes, 0.5 mM 95:5 vol hexanes:chloroform, 0.5 mM 92:8 vol hexanes:chloroform, respectively) between 298 K and 335 K



**Figure S19. Left.** Temperature-dependent UV-Vis experiments of PDAC-NMe<sub>2</sub> (92:8 vol hexanes:chloroform, 0.5 mM) between 335 K K and 298 K. **Right.** Plot of heated (filled circle) and cooled (open circles)  $\alpha_{agg}$  at 400 nm against temperature (K).



**Figure S20. Left.** Temperature-dependent UV-Vis experiments of PDAC-OMe (95:5 vol hexanes:chloroform, 0.5 mM) between 335 K and 298 K. **Right.** Plot of heated (filled circle) and cooled (open circle)  $\alpha_{agg}$  at 430 nm against temperature (K).



**Figure S21. Left.** Temperature-dependent UV-Vis experiments of PDAC-Me (hexanes, 2 mM) between 335 K and 298 K .**Right.** Plot of heated (filled circle) and cooled (open circle)  $\alpha_{agg}$  at 400 nm against temperature (K).



**Figure S22.** Left. Temperature-dependent UV-Vis experiments of PDAC-CN (85:15 vol hexanes:chloroform, 0.5 mM) between 335 K and 298 K. Right. Plot of heated (filled circle) and cooled (open circle)  $\alpha_{agg}$  at 385 nm against temperature (K).



Figure S23. PDI branched arm model compound absorbance in chloroform to hexanes at 0.01mM

We made a branched PDI compound to investigate whether the branched alkyl tail influences the assembly of the PDACs. Here we observe a small hypsochromic shift with increasing non-polarity, which is the opposite trend we observed with the PDACs.



**Figure S24. Left.** Photoluminescence spectra for the PDAC-NMe<sub>2</sub> for the monomer (chloroform, pink), partially assembled (50:50 vol hexanes:chloroform, yellow), and assembled (95:5 vol hexanes:chloroform, blue) solutions. Here, the low energy charge-transfer feature appears for the partially assembled (690 nm) and assembled (620 nm). All solutions were collected under 405 nm excitation at 10 uM. **Right.** Spectrally separated fluorescence decays for the PDAC-NMe<sub>2</sub> solutions (monomer in chloroform (light pink), partially assembled 50:50 vol hexanes:chloroform(light yellow), and assembled 95:5 vol hexanes:chloroform (light blue)). A 650 nm long-pass (LP) and 550 nm LP filter were used to isolate the charge transfer state for the partially assembled and assembled solutions, respectively. All decays were collected under pulsed 405 nm excitation at 1 MHz.

### E. Calculations

The equilibrium geometries of PDAC and its derivatives in the ground state ( $S_0$ ) were calculated using the density functional theory (DFT at the M06-2X/6-31G(d,p) level).<sup>4,5</sup> The absorption spectrum and excitation energy ( $S_0$ - $S_1$ ) were calculated using the Time-dependent DFT (TDDFT) method at the TD-M06-2X/6-31G(d,p) level. The integral equation formalism polarizable continuum model (IEFPCM) was used (chloroform solvent).<sup>6</sup> The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were visualized and were also calculated at the M06-2X/6-31G(d,p) level. The dipole moment was calculated using Multiwfn program.<sup>7</sup> All DFT calculations were carried out using the Gaussian 16 program and TDDFT calculations.<sup>8</sup> To investigate the self-assembly behavior of PDAC derivatives in assembly conditions (hexanes), molecular dynamics (MD) simulations of 15 PDAC derivatives and 300 hexane molecules were performed using the Dreiding<sup>9</sup> force field at 300 K and 1 atm for 10 ns. The MD simulations were carried out using the commercial software Materials Studio.<sup>10</sup>

|  | PDAC-NMe <sub>2</sub>   | PDAC-OMe                | PDAC-Me                 | PDAC-CN                 |
|--|-------------------------|-------------------------|-------------------------|-------------------------|
| Experimental $\lambda_{max, absorption}$<br>(nm) | 456,557nm               | 498nm                   | 484 nm                  | 477 nm                  |
| Calculated Value $\lambda_{max, absorption}$     | 447nm                   | 396 nm                  | 388 nm                  | 381 nm                  |
| Calculated Value $\lambda_{max, absorption}$ **  | 494nm                   | 468nm                   | 460 nm                  | 441 nm                  |
| Oscillator strength*                             | 0.2982                  | 0.1500                  | 0.1145                  | 0.0678                  |
| Transition*                                      | H→L                     | H-1→L                   | H-1→L                   | H-1→L                   |
|  | $(S_0 \rightarrow S_1)$ | $(S_0 \rightarrow S_1)$ | $(S_0 \rightarrow S_1)$ | $(S_0 \rightarrow S_1)$ |
| Experimental $\lambda_{max, absorption}$<br>(eV) | 2.23 eV                 | 2.49 eV                 | 2.56 eV                 | 2.60 eV                 |
| Excitation energy $(S_0 \rightarrow S_1)^*$      | 2.78 eV                 | 3.13 eV                 | 3.19 eV                 | 3.26 eV                 |
| Excitation energy $(S_0 \rightarrow S_1)^{**}$   | 2.51 eV                 | 2.65 eV                 | 2.70 eV                 | 2.81 eV                 |
| HOMO-LUMO gap*                                   | 4.04 eV                 | 4.75 eV                 | 4.92 eV                 | 5.05 eV                 |

Table S4. Experimental and calculated maximum absorbance wavelength and excitation energies

\* Calculated value with model PDAC compound (no side chains)

\*\* Calculated value with full PDAC molecules (side chains)



Figure S25. Calculations for ground state HOMO LUMO of model PDAC compounds



Figure S26. Ground state dipole moment for PDAC model compounds



Figure S27. Calculated absorbance spectra for model PDAC compounds in chloroform





Figure S28. Calculated absorbance spectra for model PDAC-NMe<sub>2</sub> monomers and calculated dimers, seen on the right.



Figure S29. Calculated absorbance spectra for model PDAC-OMe monomers and calculated dimers, seen on the right.



Figure S30. Calculated absorbance spectra for model PDAC-Me monomers and calculated dimers, seen on the right.



Figure S31. Calculated absorbance spectra for model PDAC-CN monomers and calculated dimers, seen on the right.

| Dimer Type        | PDAC-CN     | PDAC-Me      | PDAC-OMe            | PDAC-NMe <sub>2</sub> |
|-------------------|-------------|--------------|---------------------|-----------------------|
| Head-to-head      | 1 (7.600 Å) | 0            | 1 (3.598 Å)         | 0                     |
| Head-to-tail      | 0           | 0            | 1 (3.407 Å)         | 0                     |
| Rotational offset | 0           | 1 (10.124 Å) | 2 (3.572 Å, 3.232Å) | 2 (3.369 Å, 5.586 Å)  |
| Total             | 1           | 1            | 4                   | 2                     |

 Table S5.
 Simulated PDAC assembly dimer summary



Figure S32. Extracted conformations of PDAC-NMe2 in hexanes



Figure S33. Extracted conformations of PDAC-OMe in hexanes



Figure S34. Extracted conformations of PDAC-Me in hexanes



Figure S35. Extracted conformations of PDAC-CN in hexanes



Figure S36. PDAC-NMe<sub>2</sub> rotation-offset dimer A) top B) front C) side view observed in simulated assembly



Figure S37. PDAC-NMe<sub>2</sub> rotation-offset dimer A) top B) front C) side view observed in simulated assembly



Figure S38. PDAC-OMe rotation-offset dimer A) top B) front C) side view observed in simulated assembly



Figure S39. PDAC-OMe rotation-offset dimer A) top B) front C) side view observed in simulated assembly



Figure S40. PDAC-OMe head-to-tail dimer A) top B) front C) side view observed in simulated assembly



Figure S41. PDAC-OMe head-to-head dimer A) top B) front C) side view observed in simulated assembly



Figure S42. PDAC-Me rotational offset dimer A) top B) front C) side view observed in simulated assembly



Figure S43. PDAC-CN head-to-head dimer A) top B) front C) side view observed in simulated assembly

## F. <sup>1</sup>H and <sup>13</sup>C NMR



Figure S44. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of Compound 2



Figure S45. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of Compound 3



Figure S46. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of Compound 4



Figure S47. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of Compound 5



Figure S48. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of Compound 6



Figure S49. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of octyldodecylamine



Figure S50. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of PDAC-CN



Figure S51. <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of PDAC-CN



Figure S52. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of PDAC-Me



Figure S53. <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of PDAC-Me



Figure S54. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of PDAC-OMe



Figure S55. <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of PDAC-OMe



Figure S56. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of PDAC-NMe<sub>2</sub>



Figure S57. <sup>13</sup>C-NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of PDAC-NMe<sub>2</sub>



Figure S58. FT-IR of PDACs

## G. Mass spectrrometry



Figure S59. PDAC-CN MALDI mass spectrum



Figure S60. PDAC-Me MALDI mass spectrum



Figure S61. PDAC-OMe MALDI mass spectrum



Figure S62. PDAC-NMe2 MALDI mass spectrum

## H. Supporting References

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