

Supporting Information

Perylene diimide functionalized polynorbornene: a macromolecular scaffold for supramolecular self-assembly

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Synthetic Details

General Methods

Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Solvents were dried using a double-column anhydrous solvent system (Innovative Technologies, Newburyport, MA) and further degassed via nitrogen purge prior to use. Column chromatography was carried out on Silicycle® SiliaFlash® F60, 40-63 μm 60Å. Visualization of TLCs involving non-fluorescent/non-quenching molecules was done in an I_2 chamber or through a potassium permanganate dip. ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra were obtained on a Varian Unity+ 300 and were referenced to the residual solvent peaks. Low- and high-resolution mass spectrometry was carried out by Thermo Finnigan TSQ 700 and Waters Autospec Ultima, respectively. The compounds 9-aminoheptadecane¹, 6-chloro-1-hexyl *p*-toluenesulfonate², *exo*-5-norbornene-2-ol (**1**)³, and *N*-(1-octylnonyl)perylene-3,4,9,10-tetracarboxy-3,4-anhydride-9-10-imide (**5**)⁴ were prepared according to literature procedures. All other chemicals were purchased from commercial suppliers and were used as received.

6-chloro-1-(*exo*-5-norbornene-2-oxy)hexane (**2**)

In an inert atmosphere glovebox, **1** (1.02 g, 9.09 mmol) was weighed into a 100 mL Schlenk flask. THF (50 mL) was added, and the solution was stirred while oil free Na metal (300 mg, 13.04 mmol) was added. The reaction was then refluxed under inert atmosphere for 12 hours and allowed to cool to room temperature. In a separate 100 mL flask, 6-chloro-1-hexyl *p*-toluenesulfonate (2.51 g, 8.62 mmol) was dissolved in dry THF. The cooled solution of deprotonated **1**, was then cannula transferred to the 6-chloro-1-hexyl *p*-toluenesulfonate solution. The new mixture was then refluxed for an additional 12 hours. Upon cooling, the mixture was poured into ether and washed with H_2O , 0.1 M NaOH, 1.0 M HCl, and brine. The organic layer was then dried over magnesium sulfate, filtered, and concentrated under vacuum. Chromatography (silica gel, 30% CH_2Cl_2 in hexanes) gave pale yellow oil (yield = 1.55 g, 79%). ^1H NMR δ (CDCl_3) 6.15 (1H, dd, J = 5.7, 2.8 Hz), 5.94 (1H, dd, J = 5.8, 3.2 Hz), 3.51 (2H, t, J = 6.7 Hz), 3.47-3.31 (3H, m),

2.84 (1H, br s), 2.76 (1H, br s), 1.77 (2H, p, $J = 6.8$ Hz), 1.68-1.22 (10H, m). ^{13}C $\{^1\text{H}\}$ NMR δ (CDCl_3) 140.5, 133.2, 80.2, 68.9, 46.3, 45.9, 45.0, 40.3, 34.4, 32.5, 29.8, 26.6, 25.6. LRMS (CI^+ m/z) (%): Calc. 228, Found 228.

6-amino-1-(*exo*-5-norbornene-2-oxy)hexane (3)

To a Schlenk flask, **2** (0.672 g, 2.95 mmol) and potassium phthalimide (0.602 g, 3.25 mmol) were added. The flask was placed under an inert atmosphere and degassed DMF (40 mL) was added. The flask was equipped with a condenser and the reaction was heated at 100 °C for 24 hours. Upon cooling, the mixture was poured into water and extracted with ether (3x). The organic fractions were collected, washed with water (4x) and brine, dried over magnesium sulfate and filtered. The solvent was removed under vacuum. Chromatography (silica gel, 30% CH_2Cl_2 in hexanes) gave a clear liquid, 2-[6-bicyclo[2.2.1]hept-5-en-2-*exo*-yloxy]hexyl]-1*H*-isoindole-1,3(2*H*)-dione as the isolatable intermediate **2a** (yield = 0.912 mg, 91%). ^1H NMR δ (CDCl_3) 7.80 (2H, m), 7.65 (2H, m), 6.12 (1H, dd, $J = 5.8, 2.8$ Hz), 5.86 (1H, dd, $J = 5.8, 3.1$ Hz), 3.62 (2H, t, $J = 6.6$ Hz), 3.49-3.27 (3H, m), 2.81 (1H, br s), 2.76 (1H, br s), 1.78-1.19 (12H, m). ^{13}C $\{^1\text{H}\}$ NMR δ (CDCl_3) 168.1, 140.3, 133.6, 133.0, 13.9, 122.9, 79.9, 68.8, 46.1, 45.7, 40.1, 37.7, 34.2, 29.6, 28.3, 26.5, 25.7. LRMS (CI^+ m/z) (%): Calc. 339, Found 339.

2a (905 mg) was added into a Schlenk flask under inert atmosphere. Degassed EtOH (40 mL) was added via cannula, followed by an injection of hydrazine monohydrate (1.0 mL). After equipping with a reflux condenser the mixture was heated at 60 °C for 8 h under inert atmosphere. Upon cooling, the mixture was poured into water and the ethanol removed through vacuum. Concentrated HCl (5 mL) was added to the solution while cooled in an ice bath. The resulting white precipitate was removed and the filtrate was extracted with diethyl ether (3x, ~200 mL total volume). The organic fractions were collected and washed with water and brine, then dried over magnesium sulfate and filtered. The solvent was removed under vacuum to give **3** as a clear liquid (yield: 0.491 g, 54%). ^1H NMR δ (CDCl_3) 6.19 (1H, dd, $J = 6.0, 2.9$ Hz), 5.65 (1H, dd, $J = 5.9, 3.1$ Hz), 3.42-3.27 (3H, m), 2.81 (1H, br s), 2.72 (1H, br s), 2.61 (2H, t, $J = 6.8$ Hz), 1.62-1.18 (14H, m). ^{13}C $\{^1\text{H}\}$ NMR δ (CDCl_3) 140.3, 133.0, 80.0, 69.0, 46.2, 45.7, 41.9, 40.1, 34.2, 33.5, 29.8, 26.5, 26.0. LRMS (CI^+ m/z) (%): Calc. 209, Found 209.

N,N'-Bis(1-octylnonyl)-perylene-3,4,9,10-tetracarboxylic diimide (4)

A mixture of 3,4,9,10-Perylenetetracarboxylic acid dianhydride (9.012 g, 22.9 mmol), 9-aminoheptadecane (13.115 g, 50.9 mmol), and imidazole (45 g) was heated with stirring for 2 h at 160 °C. Upon cooling, hexanes was added to the mixture and the entire flask was sonicated. Extraction of the soluble alkylated species continued with additional hexanes until no additional color is seen when fresh hexanes is sonicated. The remaining solid is dissolved in the minimal amount of ethanol. This solution was then poured into an excess of 2N HCl. The resulting precipitate is filtered and combined with the residue remaining after removing the hexanes under vacuum. Chromatography (silica gel, CHCl_3) gave the lead fraction as a red solid (yield = 15.23 g, 76%). ^1H NMR δ (CDCl_3) 8.68-8.45 (8H, br m), 5.16 (2H, m), 2.24 (4H, m), 1.83 (4H, m), 1.39-1.17 (48H, m), 0.79 (12H, t, $J = 6.6$ Hz). ^{13}C $\{^1\text{H}\}$ NMR δ (CDCl_3) 164.5, 163.4, 134.3, 131.7, 131.0, 129.5,

126.3, 123.9, 122.9, 54.7, 32.3, 31.8, 29.5, 29.2, 27.0, 22.6, 14.0. LRMS (Cl^+ m/z) (%):
Calc. 866, Found 866.

***N*-(1-octylnonyl)perylene-3,4,9,10-tetracarboxy-3,4-anhydride-9-10-imide (5)**

4 (5.109 g, 5.90 mmol) and KOH (0.410 g, 7.32 mmol) were added to *t*-BuOH (60 mL). The mixture was refluxed for 30 min. If at 30 min starting material was visible through TLC analysis, small amount of additional KOH was added. Upon disappearance of starting material, the reaction was allowed to cool and was poured into 2M HCl (50 mL) with 50 mL AcOH and stirring. The resulting precipitate was filtered and rinsed with water until neutral. Chromatography (silica gel, CHCl_3) gave a reddish-brown powder (yield = 1.536 g, 41%). ^1H NMR δ (CDCl_3) 8.65 (8H, m), 5.20 (1H, m), 2.25 (2H, m), 1.88 (2H, m), 1.33-1.22 (24H, m), 0.85 (6H, t, J = 6.6 Hz). ^{13}C { ^1H } NMR δ (CDCl_3) 164.4, 163.3, 135.3, 133.8, 131.9, 129.6, 126.5, 126.3, 124.3, 123.9, 123.0, 55.0, 32.5, 32.1, 29.7, 29.4, 27.1, 22.8, 14.1. LRMS (Cl^+ m/z) (%): Calc. 629, Found 629.

Perylene containing monomer (6)

5 (102 mg, 0.16 mmol) and **3** (135 mg, 0.645 mmol) were placed into a Schlenk flask with toluene (7 mL). The reaction was brought to reflux for 2 h, or until TLC showed the disappearance of starting material **5**. Upon cooling the solvent was evaporated to leave crude product. Chromatography (silica gel, 75% CHCl_3 in hexanes) gave red crystals (yield = 111 mg, 83%). ^1H NMR δ (CDCl_3) 8.62-8.21 (8H, br m), 6.12 (1H, dd, J = 5.6, 2.9 Hz), 5.88 (1H, dd, J = 5.7, 3.2 Hz), 5.16 (1H, m), 4.15 (2H, t, J = 7.5 Hz), 3.41 (3H, m), 2.84 (1H, br s), 2.74 (1H, br s), 2.25 (2H, m), 1.89 (2H, m), 1.78-1.12 (36H, m) 0.82 (6H, t, J = 6.7 Hz). ^{13}C { ^1H } NMR δ (CDCl_3) 163.0, 140.5, 134.1, 133.2, 130.9, 80.1, 69.1, 54.8, 46.4, 45.9, 40.3, 34.4, 32.3, 31.8, 30.0, 29.6, 29.3, 28.0, 27.0, 26.1, 22.6, 14.1. UV-Vis (CHCl_3) λ_{max} (ϵ): 525 nm ($84,600 \pm 500 \text{ M}^{-1}\text{cm}^{-1}$) Φ_{F} 487 nm (CHCl_3): 0.99 ± 0.04 vs. *N,N'*-Di(9-octylnonyl)-perylene-3,4,9,10-bis(dicarboximide). LRMS (Cl^+ m/z) (%): Calc. 822, Found 822. HRMS (Cl^+ CH_4) calcd. 821.4893, Found 821.4894.

Polymerization of 6 (poly-PDI)

$\text{Cl}_2\text{Ru}(\text{PCy}_3)_2=\text{CHPh}$, 1st generation Grubbs' catalyst, (11 mg, 0.012 mmol) was dissolved in CHCl_3 (1 mL) in an inert atmosphere glove box. This was added to a CHCl_3 solution (2 mL) of **6** (220 mg, 0.268 mmol) with stirring. After 2 h, TLC showed the disappearance of **6**. The reaction was then quenched with addition of ethyl vinyl ether (1 mL) and allowed to stir for an additional 30 minutes. The solution was then poured into excess MeOH to precipitate the red polymer. The polymer was washed successively with MeOH (3x) and hexanes until washings were colorless to yield poly-PDI (yield = 195 mg, 89%).

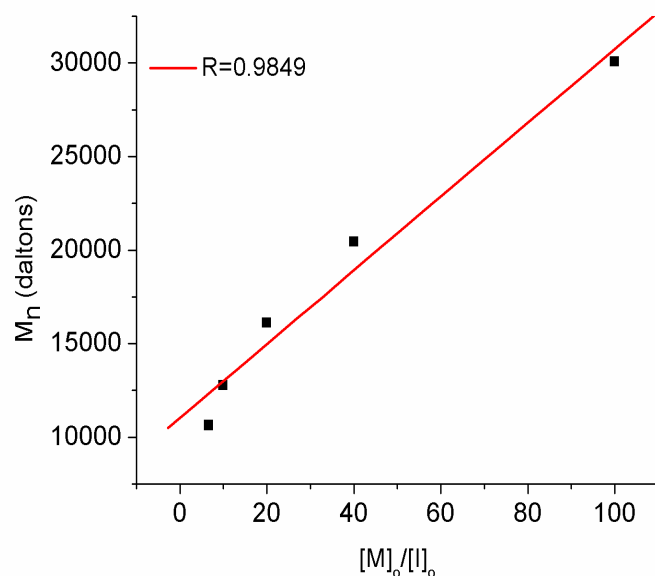


Figure S1: Initial monomer to catalyst ratio vs. molecular weight for five separate polymerization trials.

Figure S2 shows the concentration dependence of PPDI in hexane, ODCB, and toluene for three dilutions. The absorption changes linearly for concentrations with an optical density between 0.01 and 0.5. The plots below, illustrate the ratio of the 0-0 to the 0-1 peak are not changing over an order of magnitude.

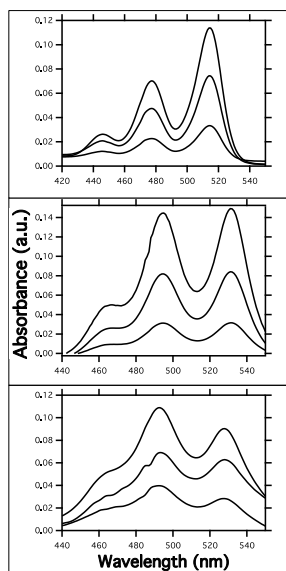


Figure S2: Concentration dependence of PPDI in (A) Hexane, (B) ODCB, and (C) Toluene.

The fluorescence correlation spectroscopy in Figure S3 shows the fluorescence fluctuation vs time. The correlation, G , describes the inverse of the number molecules in the spot of the laser beam. As there is no significant change in the G , there is no reason to believe there is any aggregation between polymer chains.

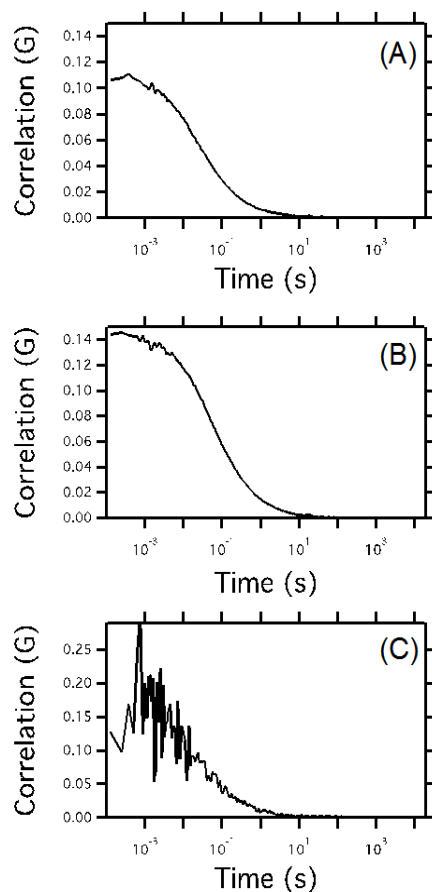


Figure S3: Fluorescence correlation spectroscopy of dilute PPDI in (A) Toluene, (B) ODCB and (C) Hexanes.

In Figure S4, we show the subtracted monomer spectrum from the aggregated spectra of PPDI in ODCB and toluene. The monomer spectrum was obtained from the 3D photoluminescence plots shown in Figure 4 of the paper. In both the toluene and ODCB samples, the fluorescence of the excimer is featureless and greatly red shifted from the monomer spectrum. This was used to calculate the relative quantum yield of ODCB and toluene.

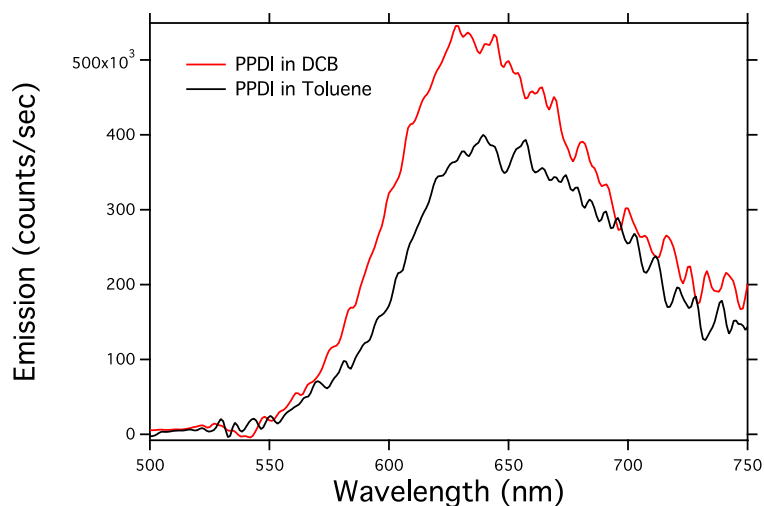


Figure S4: Fluorescence of PPDI in ODCB and toluene with the monomer spectrum subtracted. These plots were used to calculate the relative quantum yield.

References

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