



Supporting Information

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Tunable Molecular Assembly Codes Direct Reaction Pathways: It's in the Twist**

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Supporting Information

General. Synthesis and characterization for compounds **1** and **4** have previously been reported,^[S1-S2] as have compounds **11-16**.^[S2] Synthesis and characterization of compounds **2-3**, **5-10**, and **18-22** are detailed below. Solvents and reagents were purified where necessary using literature methods. MALDI-TOF mass spectra were obtained with an ABVS-2025 spectrometer. ¹H-, ¹³C-, and ³¹P- NMR spectra were recorded with a Mercury 300 (300 MHz) spectrometer in CDCl₃ (CD₃OD) solutions. Bruker 500 MHz was also used when necessary. TMS was used as a reference for ¹H-NMR; 77.23ppm was adopted as the central line of CDCl₃ for ¹³C-NMR; an 85% H₃PO₄ solution was used as an external reference for ³¹P-NMR. UV-vis spectra were recorded with a Varian Cary 100 spectrophotometer using quartz cuvettes. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F₂₅₄ (EM Science). Column chromatography was performed on silica gel 60 (230-400 mesh, EM Science) or flash silica gel, 32-60um (Dynamic Adsorbents).

Bis-N,N'-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)-1-bromo-3,4,9,10-perylenetetracarboxylic diimide. (2). Perylene-3,4,9,10-tetracarboxylic dianhydride (5g, 12.7 mmol) was dissolved in concentrated H₂SO₄ and heated to 85C. Br₂(l) (0.5ml, 9.7 mmol) was then added and the bromine refluxed; careful monitoring by TLC (CH₂Cl₂) showed formation of the mono-brominated (R_f = 0.2) and di-brominated (R_f = 0.3) compounds. When TLC reported nearly equal amounts of mono-bromo, di-bromo, and unreacted perylene, the reaction was cooled to RT, vented to remove excess bromine, and the mixture slowly poured into 2L of water. The precipitate was filtered and dried in a vacuum oven at 65C. The solid red powder mixture was used for the next step without purification. The mixture, containing mono-bromo-perylene-3,4,9,10-tetracarboxylic dianhydride, (1.0g, ~2 mmol) was dissolved in pyridine (20 ml). 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethanol (0.703g, 3.6 mmol) was added and the reaction mixture was heated to 85C for four hours. Reaction monitoring by TLC (DCM:MeOH 15:1) showed evolution of the desired red colored product (R_f = 0.3) as well as the dibromo product (R_f = 0.35); non-substituted perylene remained mostly unreacted. The reaction mixture was cooled to RT and the solvent removed under reduced pressure. The residue was subject to a silica gel column (DCM:MeOH 15:1) and compound **2**, 0.73 g (0.09 mmol, 4% theoretical yield) was collected as one of the main fractions; compound **3** was also collected for future use. ¹H-NMR(CDCl₃): 9.586 (d, 1H, J=8.1Hz, perylene), 8.699 (s, 1H, perylene), 8.54-8.49 (m, 3H, perylene), 8.37-8.33 (m, 2H, perylene), 4.48-4.41(m, 4H, NCH₂CH₂O), 3.90-3.384 (m, 4H, NCH₂CH₂O), 3.77-3.54 (m, 24H, OCH₂CH₂O, CH₂OH), 2.75 (bs, 2H, CH₂OH). ¹³C-NMR(CDCl₃):163.202, 162.908, 162.780, 161.989, 138.940, 133.239, 132.897, 132.850, 132.616, 130.761, 130.274, 128.323, 127.923, 127.645, 127.449, 126.196, 123.606, 123.261, 123.104, 122.874, 122.767, 122.287, 120.880, 72.746, 70.811, 70.701, 70.688, 70.520, 70.287, 70.256, 68.072, 68.005, 61.886, 39.612, 39.528. MS (MALDI-TOF): m/z 821.19 [M+H]⁺; 843.17 [M+Na]⁺.

Bis- N, N' - (2 - (2 - (2 - (2 - hydroxyethoxy) ethoxy) ethoxy) ethyl) - 1, 7 - dibromo - 3, 4, 9, 10 - perylenetetracarboxylic diimide. (3). 1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhydride was prepared according to literature procedures;^[S3] (2 g, 3.6 mmol) was dissolved in pyridine (20 ml). 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethanol (1.756 g, 9.09 mmol) was added and the reaction mixture was heated to 85C for four hours. Reaction monitoring by TLC (DCM:MeOH 15:1) showed evolution of the desired red colored product (R_f = 0.35). The reaction mixture was cooled to RT and the solvent removed under reduced pressure. The residue was subject to a silica gel column (DCM:MeOH 15:1) and 1.597 g (1.77 mmol, 49% theoretical yield) was collected as the main fraction. ¹H-NMR(CDCl₃): 9.466 (d, 2H, J=8.1Hz, perylene), 8.911 (s, 2H, perylene), 8.689 (d, 2H, J=8.1Hz, perylene), 4.478 (t, 4H, J=5.7Hz, NCH₂CH₂O), 3.869 (t, 4H, J=5.7Hz, NCH₂CH₂O), 3.741-3.542 (m, 24H, OCH₂CH₂O, CH₂OH), 2.53 (bs, 2H, CH₂OH). ¹³C-NMR(CDCl₃): 162.961, 162.463, 138.095, 132.862, 132.732, 130.098, 129.104, 128.516, 126.960, 123.152, 122.707, 120.987, 72.707, 70.913, 70.827, 70.798, 70.531, 70.322, 68.063, 61.907. MS (MALDI-TOF): m/z 900.4 [M]⁺. Note: The dianhydride and the diimide 1,7-dibromo isomers

contain about 10% of the 1,6-dibromo isomer which is not easily separated by column chromatography. Both isomers have similar twist angles and apparently assemble almost interchangeably, as seen in Figures S2 and S5.

Bis-N, N'-(2-(2-(2-(2-(2-cyanoethyl-N,N-diisopropylphosphoramidous)-ethoxy)ethoxy)ethoxy)ethyl)-3,4,9,10-perylenetetracarboxylic diimide. (5). To a solution of bis-N,N'-(2-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)-3,4,9,10-perylenetetracarboxylic diimide (150 mg, 0.20 mmol) in 25 ml dry CH_2Cl_2 was added diisopropylethylamine 0.14 mL (~4eq). Then chloro-N,N-diisopropylaminocynoethoxyphosphane (0.12 mL, 0.56 mmol, ~2.8 eq) was added dropwise at RT under argon. After 20 min of stirring under argon at RT, the reaction mixture was diluted with $\text{CH}_2\text{Cl}_2/\text{Et}_3\text{N}$ (300/15, v/v) 100 mL and the organic phase was washed with a saturated aqueous NaHCO_3 solution and brine. The organic layer was dried over Na_2SO_4 , filtered, and evaporated to dryness. The residue was subject to a silica gel column ($\text{CH}_2\text{Cl}_2/\text{EtOAc}/\text{Et}_3\text{N}$, 3/6/1) to give the title product **5** 184 mg (yield 80%) as a red solid, which is unstable and used for the next step freshly. ^1H NMR (CDCl_3): 8.273 (d, 4H, $J = 7.8$ Hz, perylene), 8.033 (d, 4H, $J = 7.8$ Hz, perylene), 4.392 (t, 4H, $J = 5.7$ Hz, $\text{NCH}_2\text{CH}_2\text{O}$), 3.84-3.58 (m, 36H, $\text{NCH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{OP}$, $\text{OCH}_2\text{CH}_2\text{CN}$, $\text{NCH}(\text{CH}_3)_2$), 2.624 (t, 4H, $J = 6.3$ Hz, $\text{OCH}_2\text{CH}_2\text{CN}$), 1.145-1.103 (m, 24H, $\text{CH}(\text{CH}_3)_2$). ^{13}C -NMR(CDCl_3): 163.004, 133.869, 130.958, 128.843, 125.647, 122.995, 122.841, 117.998, 71.479, 71.381, 70.912, 70.862, 70.807, 70.749, 70.309, 68.114, 62.906, 62.679, 58.914, 58.667, 43.395, 43.230, 39.565, 25.001, 24.931, 24.902, 24.839, 20.712, 20.625. ^{31}P -NMR (CDCl_3): 148.886 (s).

Cyclization of bisphosphoramidite 5 with variously twisted monomers:

Compound 6. The bisphosphoramidite **5** (57 mg, 0.05 mmol) and compound **1** (16 mg, 0.024 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry CH_2Cl_2 (30mL). 3A MS (0.2 g) were added into the solution and the mixture was stirred for 15 min under Argon. Then N-phenyl-imidazolium triflate (N-PhIMT) (44 mg, 0.15 mmol) was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I_2 (1 mL of $\text{CH}_2\text{Cl}_2/\text{Pyridine}/\text{H}_2\text{O}$, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, and then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution and brine and extracted with chloroform. The organic layer was dried over Na_2SO_4 , filtered, and evaporated to dryness. The residue was subject to a silica gel column ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 15/1) to give compound **6**, 9 mg (yield: 27%). ^1H -NMR (CDCl_3): 8.13 (d, 8H, $J = 8.1$ Hz), 7.82 (d, 8H, $J = 8.1$ Hz), 4.36-4.20 (m, 20H), 3.86-3.82 (m, 8H), 3.73-3.61 (m, 40H), 2.85 (t, 4H, $J = 6.3$ Hz). ^{31}P -NMR(CDCl_3): -0.765 (s). MS (MALDI-TOF): m/z 1715.52 [$\text{M}+\text{H}$] $^+$; 1737.50 [$\text{M}+\text{Na}$] $^+$.

Compound 7. The bisphosphoramidite **5** (57 mg, 0.05 mmol) and compound **2** (24 mg, 0.024 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry CH_2Cl_2 (30mL). 3A MS (0.2 g) were added into the solution and the mixture was stirred for 15 min under Argon. Then N-PhIMT (44 mg, 0.15 mmol) was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I_2 (1 ml of $\text{CH}_2\text{Cl}_2/\text{Pyridine}/\text{H}_2\text{O}$, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, and then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution and brine, extracted with chloroform. The organic layer was dried over Na_2SO_4 , filtered, and evaporated to dryness. The residue was subject to a silica gel column ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 15/1) to give compound **7**, 9.8 mg (yield: 27%) ^1H NMR (CDCl_3): 9.37 (d, 1H, $J = 8.4$ Hz), 8.42 (s, 1H), 8.28-8.20 (bt, 7H), 7.98-7.92 (bt, 6H), 4.41-4.24 (m, 20H), 3.90-3.87 (m, 8H), 3.78-3.63 (m, 40H), 2.90 (t, 4H, $J = 6.3$ Hz). ^{31}P -NMR(CDCl_3): -0.606 (s). MS (MALDI-TOF): m/z 1793.43 [$\text{M}+\text{H}$] $^+$; 1815.41 [$\text{M}+\text{Na}$] $^+$.

Compound 8. The bisphosphoramidite **5** (57 mg, 0.05 mmol) and compound **3** (28 mg, 0.024 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry CH_2Cl_2 (30mL). 3A MS (0.2 g) were added into the solution and the mixture was stirred for 15 min under Argon. Then N-PhIMT (44 mg, 0.15 mmol) was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I_2 (1 ml of $\text{CH}_2\text{Cl}_2/\text{Pyridine}/\text{H}_2\text{O}$, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, and then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution and brine, extracted with chloroform. The organic layer was dried over Na_2SO_4 , filtered, and evaporated to dryness. The residue was subject to a silica gel column ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 15/1) to give compound **8**, 2.2 mg (yield: 5.8%) ^1H NMR (CDCl_3): 9.17 (d, 2H, $J = 8.1$ Hz), 8.56 (s, 2H), 8.38 (d, 4H, $J = 8.4$ Hz), 8.35 (d, 2H, $J = 8.1$ Hz), 8.16 (d, 4H, $J = 8.4$ Hz), 4.47-4.22 (m, 20H, $\text{NCH}_2\text{CH}_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{OP}$, $\text{OCH}_2\text{CH}_2\text{CN}$), 3.88-3.82 (m, 8H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.75-3.62 (m, 40H, TEG), 2.86 (t, 4H, $J = 6.3$ Hz). ^{31}P -NMR(CDCl_3): -0.623 (s). MS (MALDI-TOF): m/z 1871.34 [$\text{M}+\text{H}$] $^+$; 1893.32 [$\text{M}+\text{Na}$] $^+$.

Compound 9. Bis-N,N'-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)-1,6,7,12-tetraphenoxy-3,4,9,10-perylenetetracarboxylic diimide was prepared according to literature procedures.^[S4] The tetraphenoxy starting material (81 mg, 0.073 mmol) and bisphosphoramidite **5** (100 mg, 0.087 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry CH_2Cl_2 (30mL). 3A MS (100 mg) were added into the solution and the mixture was stirred for 15 min

under Argon. Then 292 μ L of a 0.45M tetrazole solution in acetonitrile was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I₂ (1 ml of CH₂Cl₂/Pyridine/H₂O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, and then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% Na₂S₂O₃ aqueous solution and brine, and extracted with chloroform. The organic layer was dried over Na₂SO₄, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH₂Cl₂/CH₃OH, 15/1) to give compound **9**, 9 mg (yield: 5.9%). ¹H-NMR (CDCl₃): 8.49 (d, 4H, J=6.9Hz, perylene), 8.38 (d, 4H, J=7.5 Hz, perylene), 7.96 (s, 4H, perylene), 7.26-7.21 (m, 8H, phenoxy), 7.09 (t, 4H, J=7.2Hz, phenoxy), 6.85 (d, 8H, J=7.8Hz, phenoxy) 4.35-4.20 (m, 20H, NCH₂CH₂O, OCH₂CH₂OP, OCH₂CH₂CN), 3.68-3.60 (m, 48H, TEG, NCH₂CH₂O), 2.81 (t, 4H, J=6.3Hz, OCH₂CH₂CN). ¹³C-NMR (CDCl₃): 163.27, 163.00, 134.15, 132.57, 131.37, 130.18, 124.75, 123.31, 122.92, 122.38, 120.60, 120.43, 120.34, 120.12, 119.89, 119.57, 117.12, 70.75, 70.34, 70.17, 68.02, 67.48, 62.26, 39.50, 19.85. ³¹P-NMR(CDCl₃): -0.634 (s).

Compound 10. The bisphosphoramidite **5** (57 mg, 0.05 mmol) and compound **4** (28 mg, 0.024 mmol) were dried at RT in high vacuum for 24 hrs and dissolved in dry CH₂Cl₂ (30mL). 3A MS (0.2 g) were added into the solution and the mixture was stirred for 15 min under Argon. Then N-PhIMT (44 mg, 0.15 mmol) was added into the mixture and after 5 hrs of stirring at RT under argon, a 0.2 M solution of I₂ (1 ml of CH₂Cl₂/Pyridine/H₂O, 1/3/1, v/v/v) was added dropwise into the reaction. The mixture was stirred for 20 min, and then filtered and the residue was washed with chloroform. The filtrate was washed with a 5% Na₂S₂O₃ aqueous solution and brine, extracted with chloroform. The organic layer was dried over Na₂SO₄, filtered, and evaporated to dryness. The residue was subject to a silica gel column (CH₂Cl₂/CH₃OH, 20/1) to give compound **10**, 2.2 mg (yield: 4%). ¹H-NMR (CDCl₃): 8.631-8.538 (m, 12H, perylene), 4.48-4.20 (m, 16H, NCH₂CH₂O, OCH₂CH₂OP), 3.90-3.60 (m, 52H, TEG, OCH₂CH₂CN), 2.85-2.81 (m, 4H, OCH₂CH₂CN).

Bis-N,N'-(2-(2-(2-(2-thioacetyloxy)ethoxy)ethoxy)ethyl)-perlyo[1,12-bcd]thiophene-3,4:9,10-tetracarboxylic diimide (18). To a solution of compound **3** (2 g, 2.22 mmol) in 100 mL dry CH₂Cl₂ (4 Å activated molecular sieves, 3 days) at 0 °C, was added *p*-toluenesulfonyl chloride (2.22 g, 11.65 mmol, 5.2 equiv) and dry triethylamine (NaOH, pellets 3 days) (18.5 ml, 133 mmol). The reaction mixture was then stirred for 2 h at 0 °C, and left overnight at room temperature (RT) under an argon atmosphere. TLC detection showed the completion of the reaction. The solvents were evaporated and the residue was diluted with CHCl₃. The organic phase was washed with 1 N HCl (aq) solution and brine until the aqueous phase is pH ~7-8. The organic layer was dried, concentrated, and the residue was purified by chromatography on a silica gel column eluted with cyclohexane / ethyl acetate (1/1), and intermediate bis-N,N'-(2-(2-(2-(2-tosyloxyethoxy)ethoxy)ethoxy)ethyl)-1,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide was furnished in a yield of 70% (1.9 g). *R*_f 0.23, CH₂Cl₂/MeOH (50/1). (purity 85%, impurity, 1,6-disubstituted): ¹H-NMR (CDCl₃, 300 MHz) δ 9.31 (d, J = 8.1 Hz, 2 H, perylene), 8.75 (s, 2 H, perylene), 8.55 (d, J = 8.1 Hz, 2H, perylene), 7.75 (d, J = 8.1 Hz, 4H, tosyl), 7.32 (d, J = 8.1 Hz, 4 H, tosyl), 4.45 (t, J = 6.0 Hz, 4H, TEG), 4.13 (t, J = 4.8 Hz, 4H, TEG), 3.84 (t, J = 6.0 Hz, 4H, TEG), 3.72-3.58 (m, 12H, TEG), 3.57-3.50 (m, 8 H, TEG), 2.43 (s, 6 H, -CH₃). ¹³C-NMR (CDCl₃, 75.48 MHz) δ 162.9, 162.4, 145.0, 138.0, 133.1, 132.8, 132.7, 130.1, 130.0, 129.1, 128.5, 128.1, 126.9, 123.1, 122.7, 121.0, 70.9, 70.8, 70.7, 70.3, 69.5, 68.9, 68.0, 39.7, 21.9. MS (MALDI): *m/z* 1205.9 [M]⁺. To a solution of this compound (446 mg, 0.37 mmol) in DMF (29 mL) was added potassium thioacetate (0.68 g, 5.8 mmol, 15.6 equiv), and the mixture was stirred at 80 °C under an argon atmosphere overnight. The mixture was then concentrated under reduced pressure and purified by chromatography on a silica gel column eluted with cyclohexane / ethyl acetate (2/3). The title product was obtained in a yield of 19% (70 mg). *R*_f 0.22, CH₂Cl₂/MeOH (30/1). ¹H-NMR(CDCl₃, 300 MHz, ~20 mg/0.5 mL): δ 8.89 (s, 2H, perylene), 8.51(d, J = 7.8 Hz, 2H, perylene), 8.35 (d, J = 7.8 Hz, 2H, perylene), 4.53 (t, J = 5.7 Hz, 4H, TEG), 3.94 (t, J = 5.7 Hz, 4H, TEG), 3.81-3.79 (m, 4H, TEG), 3.71-3.68 (m, 4H, TEG), 3.64-3.61 (m, 4H, TEG), 3.57-3.55 (m, 4H, TEG), 3.54 (t, J = 6.3 Hz, 4H, TEG), 3.03 (t, J = 6.3 Hz, 4H, TEG), 2.30 (s, 6 H, -COCH₃). ¹³C-NMR (CDCl₃, 75.48 MHz): δ 195.8, 163.6, 163.2, 138.0, 132.4, 130.6, 129.3, 127.1, 125.5, 123.2, 122.4, 122.2, 122.0, 70.96, 70.73, 70.49, 70.36, 69.9, 68.2, 39.8, 30.8, 29.0. MS (MALDI-TOF): *m/z* 889.0 [M+H]⁺. Anal. Calcd. For C₄₄H₄₄N₂O₁₂S₃ (889.02): C 59.44, H 4.99, N 3.15, O 21.60, S 10.82. Found: C 58.36, H 4.32, N 2.94, O 22.24, S 11.10.

Disulfide cyclization reactions:

Heterogeneous cyclization of mixture 11 + 12: Compounds **11** and **12** were synthesized as previously described.^[S2, S5] Compound **11** (26 mg, 0.03 mmol) and **12** (30 mg, 0.03 mmol) were dissolved in CH₂Cl₂ (300 mL), where the concentrations of each were 0.1 mM. To the above solution was added NaOMe (2 M in MeOH) dropwise, 15 drops

(9" Pasteur pipette), at RT. The color of the reaction mixture changed from red to dark blue. The reaction was monitored by TLC and then neutralized with Amberlite IR-120 (H^+) resin upon the disappearance of both starting materials. The mixture was filtered and the filtrate concentrated, flash chromatographed (Silica gel, $CH_2Cl_2/MeOH$ 10/1) to analyze the final products. **No new compounds** were detected by either TLC or chromatography (1H -NMR detection after separation) besides those formed in the separate reactions, compounds **13-16**. The reaction was repeated with early and late quenching; no additional compounds were formed.

Homogeneous cyclization of compound 18: Two concentrations, 0.14 mM and 0.55 mM were used separately. Similar to the planar perylene **11**, monomer ring **19**, dimer cyclic ring **20**, and dimer-dimer catenated ring **21** were separated. In the 0.14 mM solution **19** and **20** were the major products, while in the 0.55 mM solution, **20** and **21** were the major products.

Compound 19: R_f 0.41, $CH_2Cl_2/MeOH$ (20/1). 1H NMR ($CDCl_3$, 300 MHz) δ 9.32 (s, 2H, perylene), 8.96 (d, J = 8.1 Hz, 4H, perylene), 8.92 (d, J = 8.1 Hz, 4H, perylene), 4.62 (t, J = 4.8 Hz, 4H, TEG), 3.93 (t, J = 4.8 Hz, 4H, TEG), 3.65-3.59 (m, 4H, TEG), 3.57-3.50 (m, 4H, TEG), 3.30 (t, J = 4.8 Hz, 4H, TEG), 2.87 (t, J = 4.8 Hz, 4H, TEG), 2.79 (t, J = 6.6 Hz, 4H, TEG), 1.90 (t, J = 6.6 Hz, 4H, TEG). ^{13}C -NMR ($CDCl_3$, 150.81 MHz) δ 164.0, 163.6, 138.3, 133.3, 131.6, 129.7, 127.6, 126.1, 123.8, 123.3, 122.8, 122.4, 71.1, 70.5, 70.4, 70.2, 68.8, 68.0, 40.0, 37.1. MS (MALDI-TOF): m/z 803.2 $[M+H]^+$.

Compound 20: R_f 0.38, $CH_2Cl_2/MeOH$ (20/1). 1H NMR ($CDCl_3$, 300 MHz) δ 8.80 (s, 4H, perylene), 8.44 (d, J = 7.8 Hz, 4H, perylene), 8.20 (d, J = 7.8 Hz, 4H, perylene), 4.56 (t, J = 6.0 Hz, 8H, TEG), 4.01 (t, J = 6.0 Hz, 8H, TEG), 3.87-3.82 (m, 8H, TEG), 3.80-3.72 (m, 8H, TEG), 3.70-3.64 (m, 8H, TEG), 3.63 (t, J = 6.6 Hz, 8H, TEG), 3.60-3.55 (m, 8H, TEG), 2.78 (t, J = 6.6 Hz, 8H, TEG). ^{13}C -NMR ($CDCl_3$, 150.81 MHz) δ 163.5, 163.1, 137.8, 132.0, 130.2, 129.1, 126.9, 125.2, 123.0, 122.3, 121.9, 121.7, 71.0, 70.9, 70.64, 70.56, 69.6, 68.3, 39.9, 38.9. MS (MALDI-TOF): m/z 1605.3 $[M+H]^+$.

Compound 21: R_f 0.35, $CH_2Cl_2/MeOH$ (20/1). 1H -NMR ($CDCl_3$, 300 MHz): δ 8.25 (s, 8 H, perylene), 7.89 (d, J = 7.5 Hz, 8 H, perylene), 7.41 (bd, J = 7.5 Hz, 8 H, perylene), 4.45-4.36 (m, 16 H, TEG), 3.99-3.92 (m, 16 H, TEG), 3.90-3.62 (m, 64 H, TEG), 3.80 (t, J = 6.3 Hz, 16 H, TEG), 2.96 (t, J = 6.3 Hz, 16 H, TEG). MS (MALDI-TOF): m/z 3208.7 $[M]^+$.

Heterogeneous cyclization of mixture 12 + 18: Compound **18** (7 mg, 0.007 mmol) and **12** (7 mg, 0.007 mmol) were dissolved in CH_2Cl_2 (60 mL) where the concentrations of each were 0.11 mM. To the above solution was added NaOMe (2 M in MeOH) dropwise, 3 drops (9" Pasteur pipette), at RT. The color of the reaction mixture changed from red to dark blue. The reaction was monitored by TLC and was neutralized with Amberlite IR-120 (H^+) resin upon the disappearance of the starting materials. The mixture was filtered and the filtrate was concentrated, flash chromatographed (SiO_2 , $CH_2Cl_2/MeOH$) to analyze the final products. **No new compounds** could be found by either TLC or column chromatography (1H -NMR detection after separation); only **16** and **19-21**. The reaction was repeated with early and late quenching and no new compounds were detected.

Heterogeneous cyclization of mixture 11 + 18: Compound **18** (7 mg, 0.0069 mmol) and **11** (6 mg, 0.007 mmol) were dissolved in CH_2Cl_2 (60 mL), where the concentrations of each were 0.12 mM. To the above solution was added NaOMe (2 M in MeOH) dropwise, 3 drops (9" Pasteur pipette), at RT. The color of the reaction mixture changed from red to dark blue. The reaction was monitored by TLC and was neutralized with Amberlite IR-120 (H^+) resin once upon the disappearance of both of the starting materials. The mixture was filtered and the filtrate was concentrated, flash chromatographed (SiO_2 , $CH_2Cl_2/MeOH$) to analyze the final products. One new compound, **22**, was obtained by chromatography (1H -NMR detection after separation) besides **13**, **14**, **19** and **20**. The bigger ring structures (as a mixture of concatenated rings) were too complicated to be purified and identified.

Compound 22: R_f 0.34, $CH_2Cl_2/MeOH$ (20/1). 1H -NMR ($CDCl_3$, 500 MHz): δ 8.90 (s, 2H, perylo-thiophene), 8.60 (d, J = 7.5 Hz, 2H, perylo-thiophene), 8.43 (d, J = 7.5 Hz, 2H, perylo-thiophene), 8.19 (d, J = 8.0 Hz, 4H, perylene), 7.80 (d, J = 8.0 Hz, 4H, perylene), 4.55 (t, J = 6.0 Hz, 4H, TEG), 4.47 (t, J = 6.0 Hz, 4H, TEG), 4.00 (t, J = 6.0 Hz, 4H, TEG), 3.96 (t, J = 6.0 Hz, 4H, TEG), 3.84-3.81 (m, 8H, TEG), 3.76-3.73 (m, 8H, TEG), 3.68-3.56 (m, 24H, TEG), 2.82 (t, J = 6.0 Hz, 4H, TEG), 2.81 (t, J = 6.0 Hz, 4H, TEG). ^{13}C -NMR ($CDCl_3$, 150.81 MHz) δ 163.6, 163.3, 163.0, 138.3,

133.0, 132.6, 130.9, 130.7, 129.4, 128.4, 127.1, 125.7, 124.9, 123.6, 122.7, 122.5, 122.4, 122.3, 122.2, 71.0, 70.8, 70.6, 70.5, 69.6, 68.3, 68.1, 39.9, 39.6, 38.7.

Determination of equilibrium constant. The equilibrium constant is determined using the isodesmic equal K (EK) model summarized by Martin.^[S6] Under this model, the π -stacking force is assumed to be the same between the i^{th} and $(i+1)^{\text{th}}$ monomer, and $K_2=K_3=\dots K_\infty = K_{\text{SA}}$. We can determine the properties of the free monomer (P_α), the “end-cap” molecules that are on the ends of the π -stacks (P_λ), and the “sandwiched” molecules within a stack (P_ξ). Consequently, the P_{obs} can be determined from the mole fraction of each molecule type (α , λ , and ξ) according to the following equation:

$$P_{\text{obs}} = \alpha P_\alpha + \lambda P_\lambda + \xi P_\xi$$

This model predicts the observed properties extremely well for our series of planar folded oligomers, much better than a dimerization-only model. P_λ can be described in terms of its fraction between P_α and P_ξ according to the following equation:

$$P_\lambda = (1 - f)P_\alpha + fP_\xi$$

f is commonly assumed to be 0.5. From our known series of linear folded planar oligomers, we determined the end-cap *absorbance* more closely resembled the intra-stack molecular absorbance ($f = 0.7$) while end-cap *chemical shift* tended toward the free molecules ($f = 0.42$); thus we used these f values for the other twisted compounds.

P_α is clearly defined because the monomers are completely free in low concentration and the property approaches a constant maximum, changing no further with additional dilution. P_ξ was determined from synthesized oligomers when available or estimated from high concentration solutions or solid thin film samples where the molecules are arranged into infinitely long π -stacks.

We next applied least squares curve fitting to the experimental data to determine K_{SA} for the series of twisted monomers, using the isodesmic equal K model for both NMR and absorbance data. The experimental data and the best-fit lines for each compound are plotted in Figure 1 while Table S1 summarizes the optimized variables and parameters obtained from fitting.

The K_{SA} values determined for the planar **1** (50 at RT) were nearly identical as previously determined (52) using known oligomer properties.^[S7] Also, the K_{SA} values determined by A^{0-0} / A^{0-1} ratios agreed remarkably well to those determined by NMR. The K_{SA} values were used to calculate ΔG_{SA} for each of the variously twisted perylene species.

Molecular code thermodynamics. To further understand the thermodynamics that tunes the molecular codes, we performed variable temperature experiments to determine the enthalpy and entropy components, ΔH_{SA} and ΔS_{SA} , of ΔG_{SA} for the various twisted perylene monomers using the Van't Hoff analysis (Figure S14). Table S2 reveals these insightful parameters.

Within the experimental error, the ΔG_{SA} values agree remarkably well with the values obtained by variable concentration listed in Table S1, decreasing with increasing twist angle θ .

Solvent-dependent assembly. In addition to concentration and temperature, the solvent composition controls DSA because solvophobicity significantly alters self-assembly behavior. Plotting r_{obs} value against solvent composition for the various twisted monomers demonstrates this apparent principle (Figure S15). Thus, as solvophobicity increases, K_{SA} grows larger and ΔG_{SA} becomes increasingly negative with the least twisted monomers self-assembling first (Table S2).

Variable temperature optical absorption was then used to explore solvent dependent assembly thermodynamics. Compounds **1-4** exhibit dramatic shifts in r_{obs} in a 1:1 MeOH:H₂O mixture as a function of temperature (Figure S16). As temperature decreases, solvophobic assisted self-assembly intensifies and drives the r_{obs} values lower. Despite the large changes in the peak ratio, the λ_{max} values exhibit only small temperature dependent changes in compounds **1-3**, with $\Delta\lambda$ being the largest in the more planar units. Concomitantly, the vibronic peaks broaden. Such characteristics demonstrate expected consistency with a displaced harmonic oscillator model, exhibiting weak *electronic* coupling but large *vibronic* coupling in the stacked assemblies. Greater twisted monomers increasingly resist DSA, until compound **4** apparently achieves an entirely different assembled morphology, evident by the new red-shifted spectra.

Supporting figures.

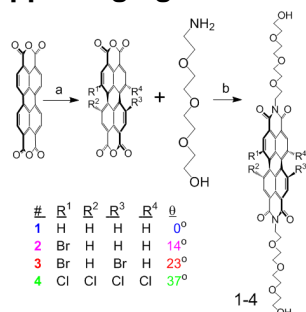


Figure S1. Monomer synthesis. Bay-substituted perylenetetracarboxylic dianhydrides were synthesized by literature procedures^[S3,S8] as were the amino functionalized TEG chains,^[S1] which were attached to both ends of the twisted perylene core as imides to form **1-4**. a) Br₂(l) or Cl₂(g), conc. H₂SO₄, 85C. b) **2-4**: Pyridine, 85C, 4 hours; **1**: DMSO, Et₃N, 4 hours, 150C.

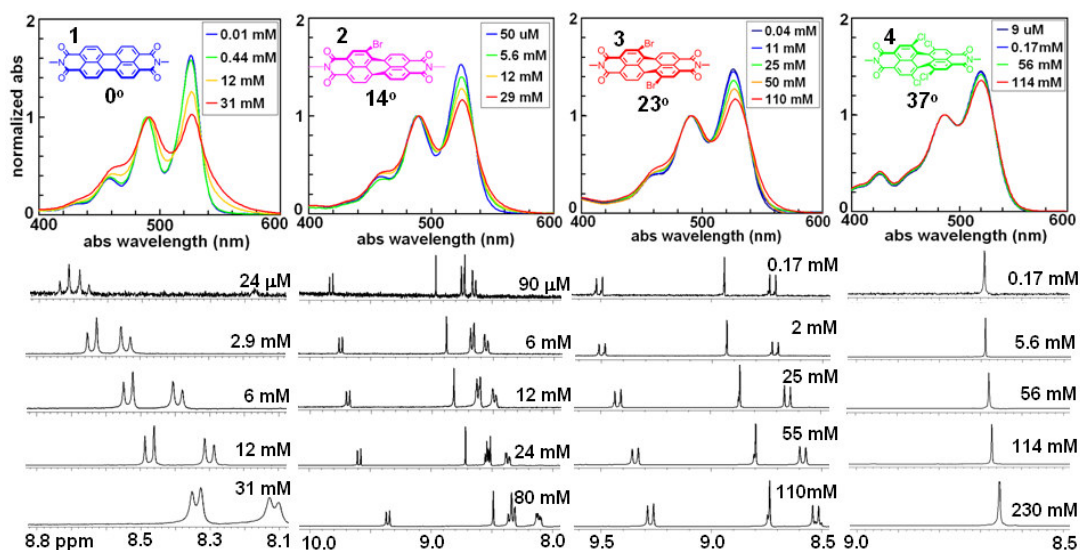


Figure S2. Selected variable concentration absorbance (top) and ¹H-NMR spectra (bottom) from Figure 1, main text, for compounds **1-4** in CHCl₃ / CDCl₃ at RT. The critical concentration increases with twist angle such that more highly twisted units assemble at higher concentrations. Monomers **1-4** exhibit various dihedral angles as depicted; angles for compounds similar to **1,3**, and **4** have been determined by crystal structures.^[S3,S9-S11] The twist angle for compound **2** was calculated as described in figure S3.

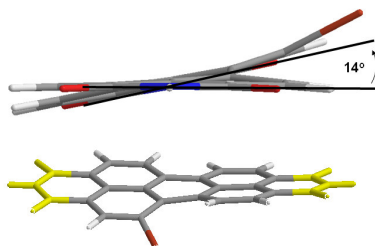


Figure S3. No known crystal structure exists for mono-Br perylene such as compound **2**; the twist angle was calculated by measuring the angle between the imide planes (shown in yellow) from the MMFF94 energy minimized structure. A longitudinal view is also shown to help visualize the angle.

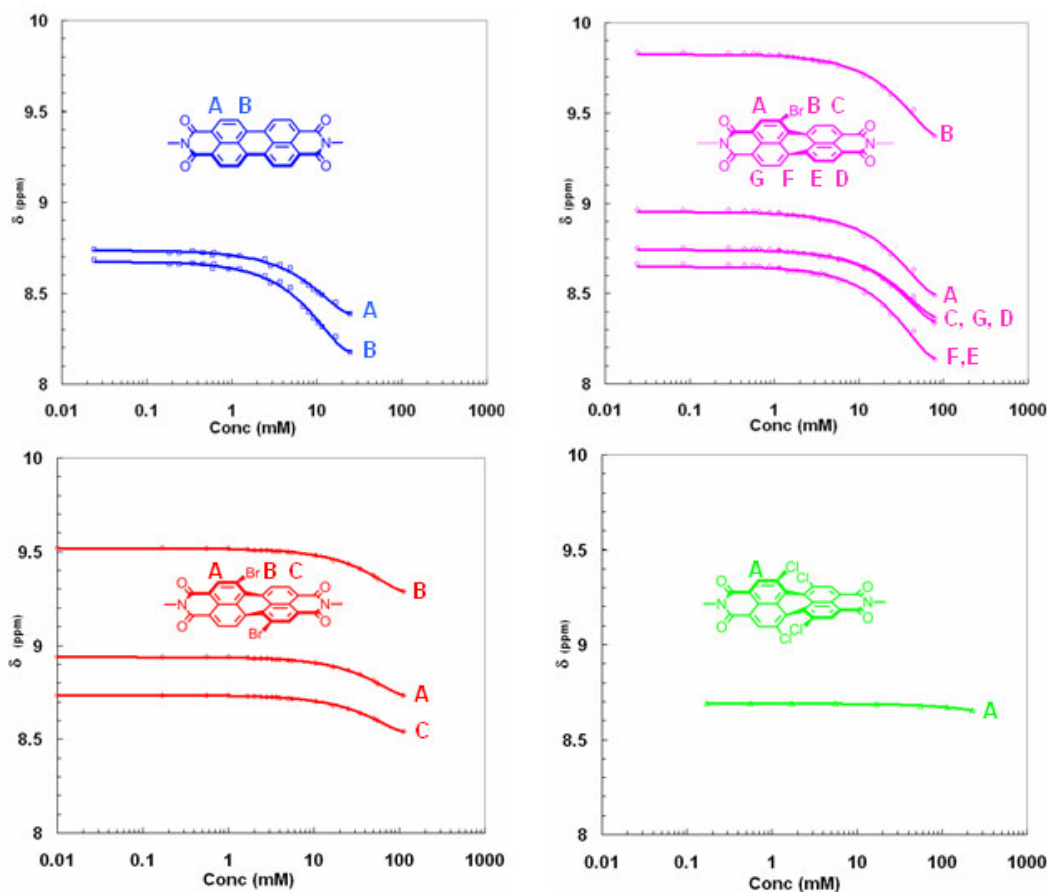


Figure S4. Concentration dependent chemical shifts for compounds **1-4** in CDCl_3 . All perylene aromatic protons experience up-field chemical shifts beyond the critical concentrations, albeit with slightly varying slopes due to varying ring-currents within the stacked configurations. To be as consistent as possible between different twisted compounds, non-bay position protons were selected to compare equilibrium constants in Figure 1 (proton A for **1**, proton G(D) for **2**, proton C for **3**, and proton A for **4**).

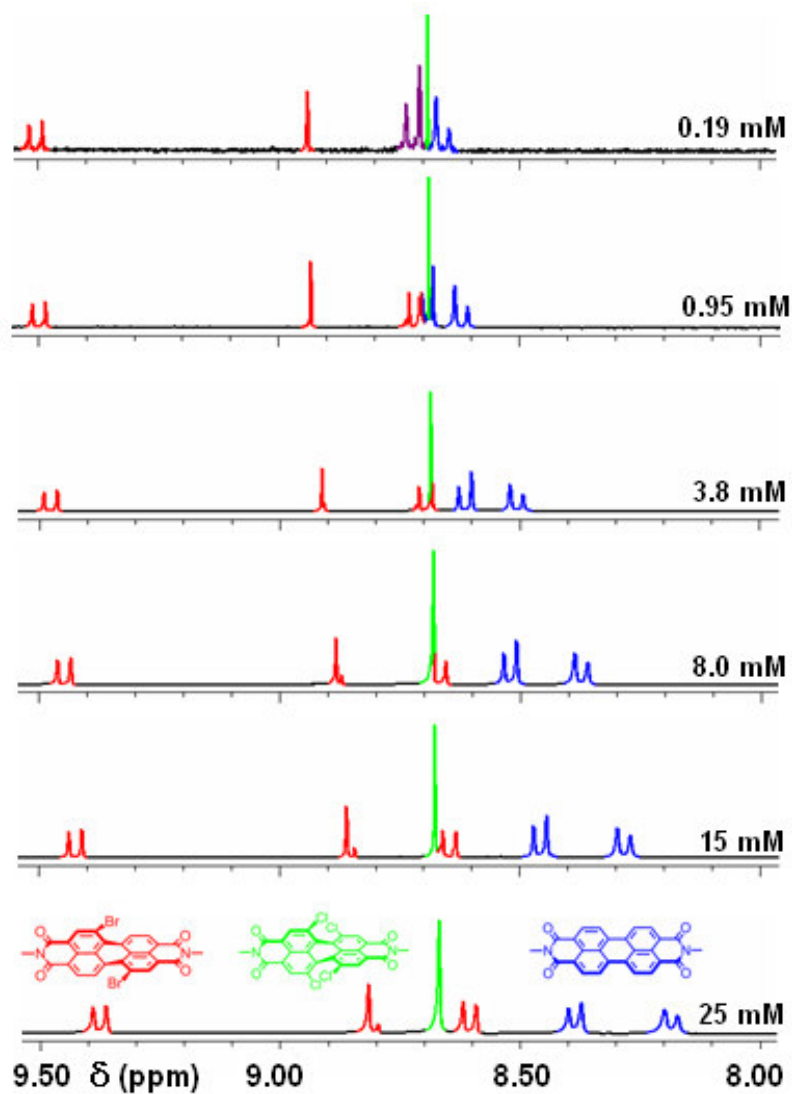


Figure S5. ^1H -NMR (CDCl₃) spectra for a 1:1:1 heterogeneous mixture of compounds **1**, **3**, and **4** displaying the perylene aromatic protons at various concentrations listed for of each spectrum. Planar **1** begins to self-assemble first near 1 mM, evident by the up-field chemical shift, followed by **3** near 8 mM; compound **4** has not yet reached its critical SA concentration by 25 mM. Importantly, the monomers do not cross-assemble significantly, revealing their independent and unique molecular codes.

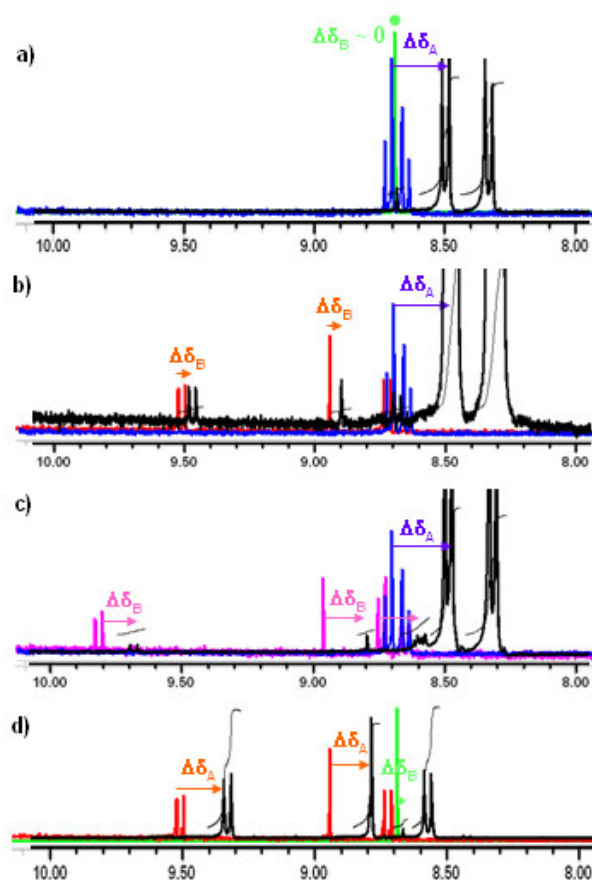


Figure S6. Four example NMR spectra (CDCl_3 , RT) used to calculate χ_{CA} . To a concentrated solution of monomer A ($>$ A's critical concentration) a small amount of monomer B was measured in (\ll B's critical concentration). Monomer B is well below its own critical concentration, and thus $\Delta\delta_{\text{B}}$ results only from cross-assembly with monomer A. Mixture spectra are shown in black; dilute monomer spectra are shown in color: **4**, **3**, **2**, and **1**. a) A=**1**, B=**4**; b) A=**1**, B=**3**; c) A=**1**, B=**2**; d) A=**3**, B=**4**. Integrals show the ratio of A:B and $\delta_{\text{obs,A}}$ reports [A] using figure 1b in the main text. $\chi_{\text{CA}} = (\delta_{\text{B,dil}} - \delta_{\text{B,obs}}) / (\delta_{\text{A,dil}} - \delta_{\text{A,obs}}) = \Delta\delta_{\text{B}} / \Delta\delta_{\text{A}}$. Note that $\Delta\delta_{\text{B}}$ (and χ_{CA}) increases from examples a to c as the codes become more compatible. χ_{CA} is widely invariable to [A] because $\Delta\delta_{\text{B}}$ increases proportionally with $\Delta\delta_{\text{A}}$ over a wide range. χ_{CA} is also invariable to [B] as long as [B] \ll B's critical concentration.

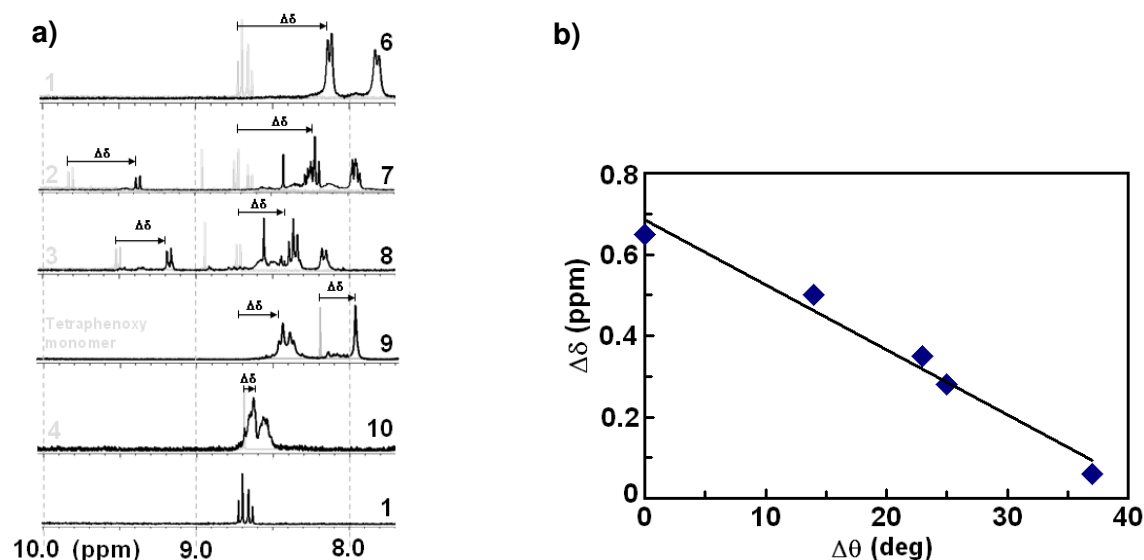


Figure S7. a) ¹H-NMR (CDCl₃) spectra of cyclic compounds **6-10** (black) are contrasted to the corresponding free monomers **1-4** (gray). Matching codes dictate compound **6** folds strongly and the perylene aromatic protons shift 0.6 and 0.8 ppm up-field. As twist angle difference $\Delta\theta$ enlarges, intramolecular assembly codes become more and more incompatible and the structures remain mostly unfolded as evidenced by small $\Delta\delta$ despite restricted cyclic architectures. The twisted components also reveal up-field shifts compared to their “free” state with a similar decrease in $\Delta\delta$ as $\Delta\theta$ increases: notably $\Delta\delta_{\text{planar}} \approx \Delta\delta_{\text{twisted}}$. b) Interestingly, $\Delta\delta$ scales nearly linearly with $\Delta\theta$.

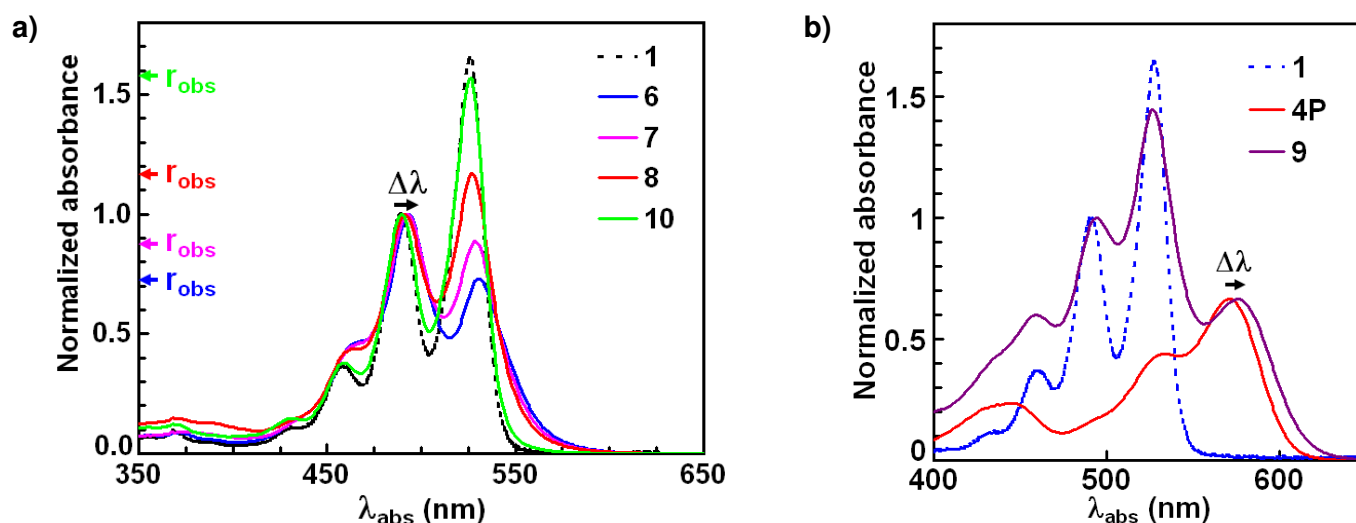


Figure S8. a) Cyclic dimers **6-8** and **10** demonstrate dramatic absorption differences (CH₂Cl₂, RT). Despite constrained cyclic architectures, compounds with decreasing code compatibility (increasing $\Delta\theta$) fold less, exhibiting characteristically larger r_{obs} . Additionally, cyclic dimers with smaller $\Delta\theta$ exhibit larger red-shift ($\Delta\lambda$) in peak wavelength λ_{max} compared to the free monomer. Free planar monomer **1** (black dotted) provides the calibration standard at 100% incompatibility. b) The r_{obs} in **9** is distorted due to overlap with the tetraphenoxy moiety **4P**, although the $\Delta\lambda$ is still apparent.

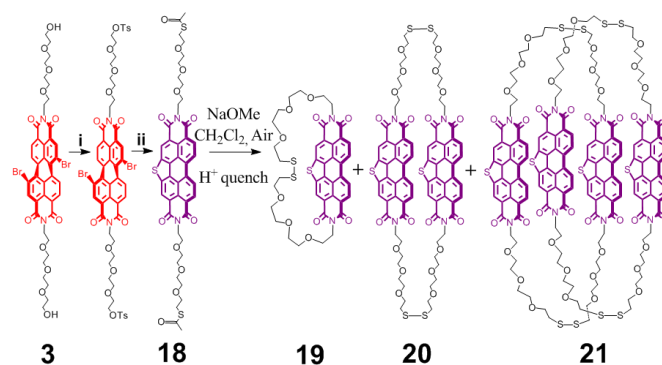


Figure S9. Highly planar mono-sulfur perylene **18** is the major product during dithioacetate functionalization of the dibromo **3**. **18**, highly planar and even more dihedrally rigid, self-assembles even stronger than the unsubstituted planar perylene. Cyclization products **19-21** are similar to those formed by the unsubstituted planar monomer **11**, alluding to similar codes. i) TsCl, Et₃N, CH₂Cl₂ ii) CH₃COSK, DMF.

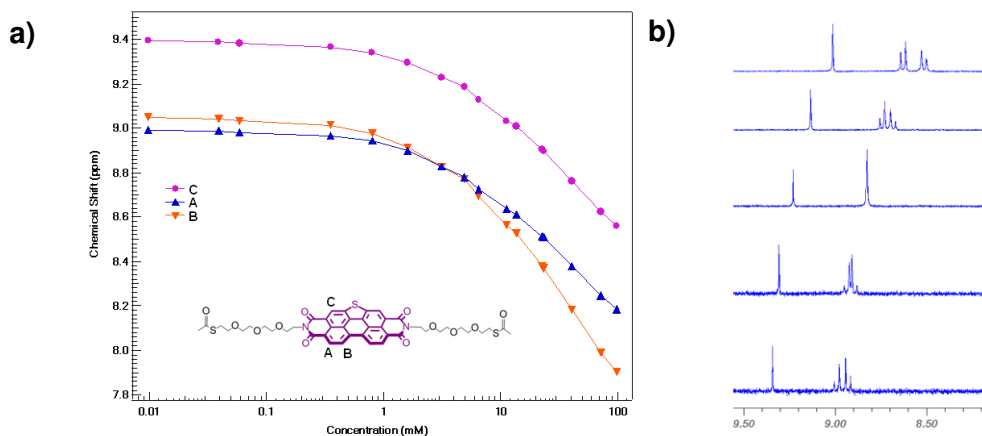


Figure S10. a) Concentration dependent chemical shift for compound **18**. Monosulfur perylene has a slightly lower critical self-assembly concentration than unsubstituted **11**. Interestingly, the “bay” position protons B are initially down-field of the outside protons A; upon assembly, the B protons overtake the A protons due to a larger ring-current upon π -stacking. b) ¹H-NMR(CDCl₃) spectra at selected concentrations.

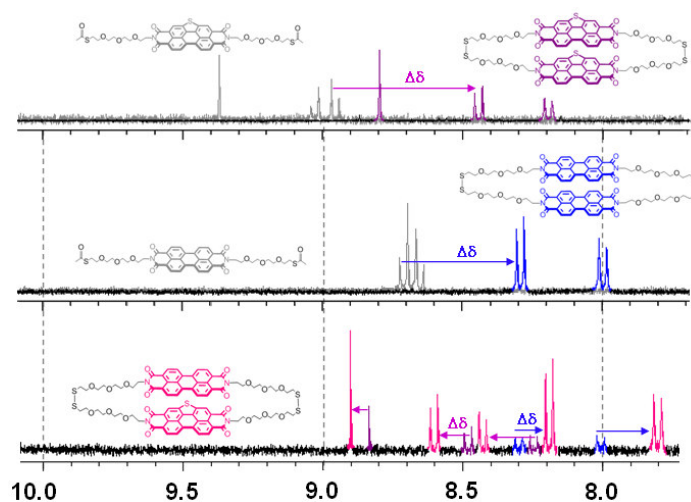


Figure S11. ^1H -NMR (CDCl_3) spectra for cyclic compounds **20** (purple, top) and **14** (blue, middle) compared to spectra for dilute monomers **18** and **11** (gray), respectively. Clearly $\Delta\delta(\mathbf{20}) > \Delta\delta(\mathbf{14})$. Spectrum for a mixture containing compound **22** (pink, bottom) and small amounts of **14** and **20** demonstrates the mono-sulfur component $\Delta\delta$ decreases when compared to **20**, while the unsubstituted component $\Delta\delta$ increases when compared to **14**.

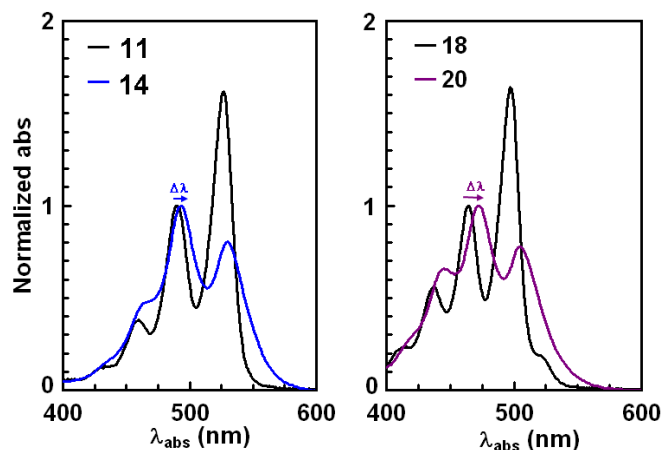


Figure S12. Absorbance spectra for homogeneous cyclic dimers **14** and **20** compared to the free monomers **11** and **18**. **20** ($r_{\text{obs}} = 0.77$) has a larger r_{obs} than **14** ($r_{\text{obs}} = 0.81$) indicating $K_{\text{fold}}(\mathbf{20}) > K_{\text{fold}}(\mathbf{14})$. The red-shift in the vibronic peaks ($\Delta\lambda$) between monomers and cyclic dimers also exhibit larger values for **20** than **14**, corroborating the stronger interaction. (CHCl_3 , RT)

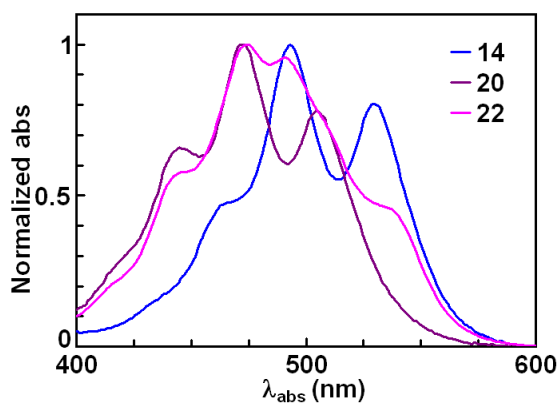


Figure S13. Absorbance spectra for heterochromophoric cyclic dimer **22** compared to homochromophoric dimers **14** and **20**. Similar codes dictate all three are similarly highly folded as evidenced by low r_{obs} values and significant $\Delta\lambda$ for each chromophore. (CHCl_3 , RT).

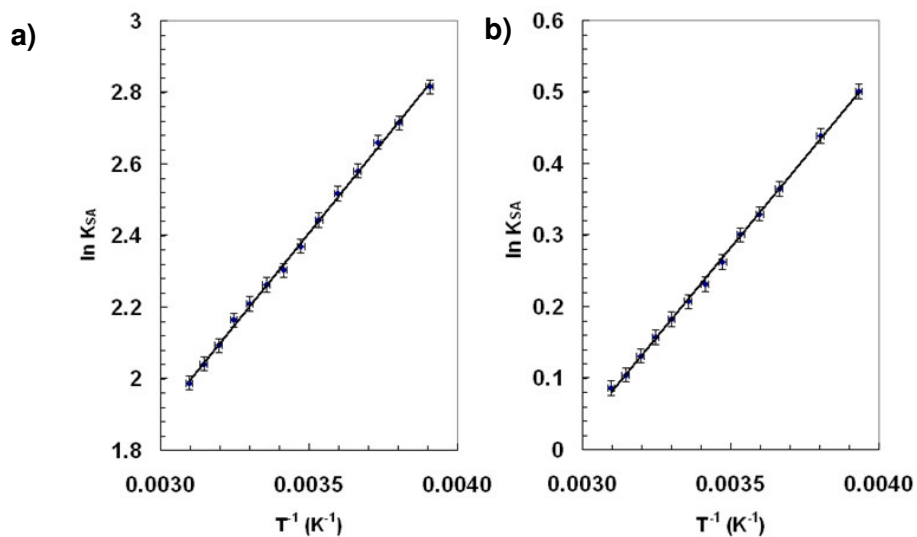


Figure S14. Van't Hoff plots for compounds **3** (a) and **4** (b); equilibrium constants determined by variable temperature ^1H -NMR (CDCl_3).

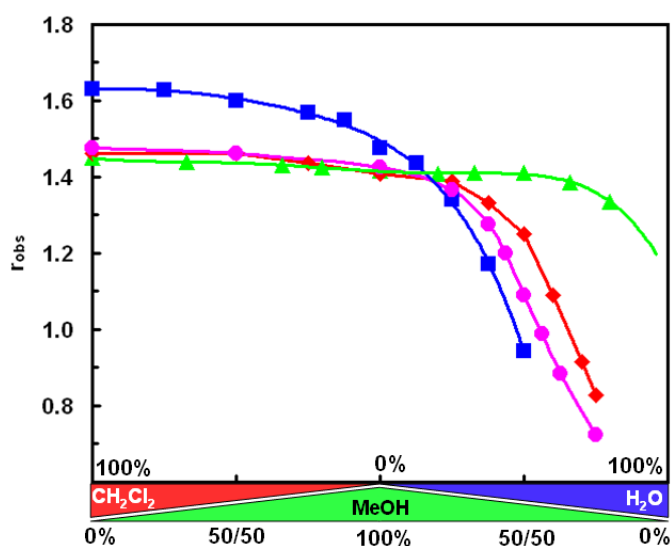


Figure S15. r_{obs} as a function of solvent composition for compounds **1** (blue squares), **2** (pink circles), **3** (red diamonds) and **4** (green triangles) at 5uM (RT). With increasing solvophobicity, all compounds eventually self-assemble, with greater twisted compounds assembling at higher solvophobicity. Lines help visualize the trend in the actual data points (markers).

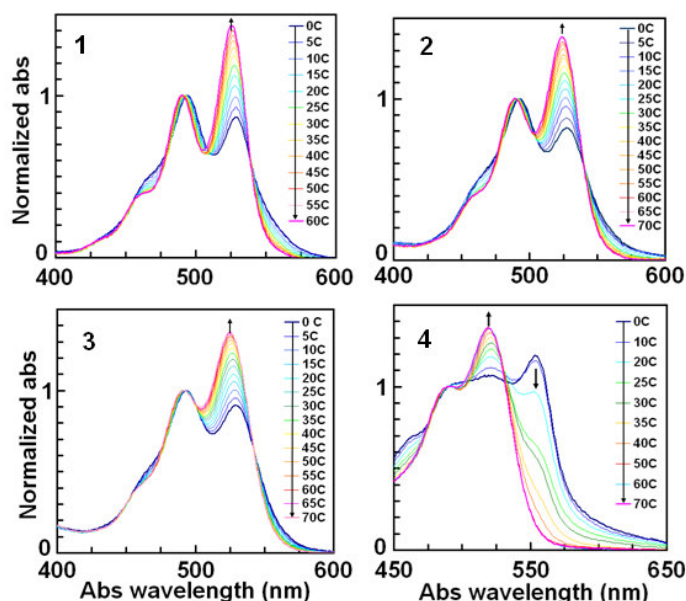


Figure S16. Normalized absorbance spectra for compounds **1-4** in 1:1 MeOH / H₂O solutions as a function of temperature. As the temperature decreases, the r_{obs} decreases due to solvophobic assisted self-assembly; more highly twisted units resist DSA, until **4** achieves a different assembled morphology evident by considerably shifted λ_{max} .

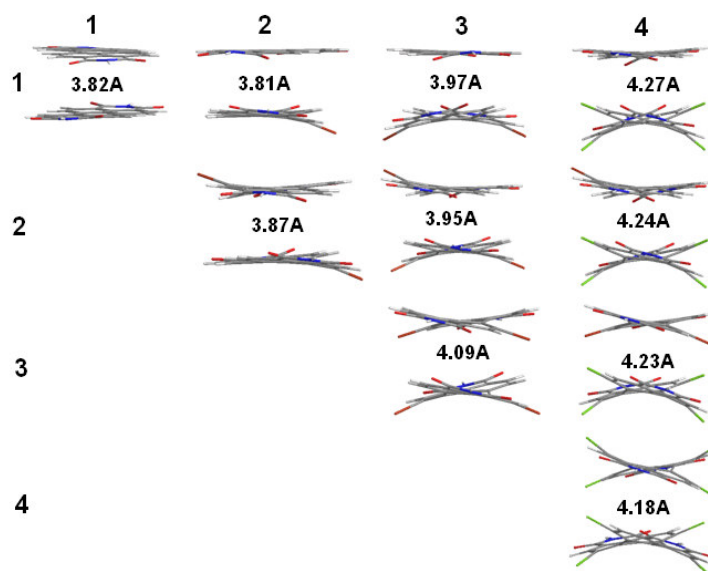


Figure S17. Merck Molecular Force Field (MMFF94) modeling shows energy minimized dimers responsible for molecular coding between compounds **1-4**. θ and $\Delta\theta$ dictate the average interchromophore distance (shown numerically) in the stacked dimers. The interchromophore distance is variable within each dimer and thus the average distance between the 6 central perylene carbons in each dimer was used. Only the perylene core is shown for clarity. While these simple models are only approximate dimer configurations, they provide insight into how molecular shape (twist angle) tunes the π -stacking force and imparts selective molecular coding. More accurate modeling and NOE experiments are in-progress and will be published separately. Note that other encounter configurations are possible such as heterochiral dimers or same-side / opposite side bromine.

Supporting tables.

Table S1. Optimized variables determined by least-squares analysis according to the equal K isodesmic model using both NMR (top) and optical absorbance (bottom) data. Twist angle θ is shown at the bottom.

Compound:	1	2	3	4
<i>NMR</i>				
δ_α (ppm)	8.74	8.75	8.74	8.69
δ_ξ (ppm)	7.8	7.9	8.1	8.3
f	0.42	0.42	0.42	0.42
δ_λ (ppm)	8.34	8.38	8.47	8.60
K_{SA}	50	20	7	1.3
ΔG_{SA} (kcal/mol)	-2.4±0.1	-1.8±0.1	-1.2±0.1	-0.16±0.1
<i>Absorbance</i>				
r_α	1.64	1.54	1.47	1.45
r_ξ	0.6	0.6	0.8	1.0
f	0.7	0.7	0.7	0.7
r_λ	0.91	0.88	1.0	1.13
K_{SA}	50	25	10	1.5
ΔG_{SA} (kcal/mol)	-2.4±0.1	-1.9±0.1	-1.4±0.1	-0.25±0.1
θ (deg)	0	14	23	37

Table S2. Calculated ΔH_{SA} (kcal/mol) and ΔS_{SA} (e.u.) from Van't Hoff analysis for separately coded compounds **1**, **3**, and **4** in $CDCl_3$, determined by variable temperature NMR (Figure S14). MeOH/ H_2O values were determined by UV-Vis (Figure S16).

Compound:	1	3	4
<i>$CDCl_3$</i>			
ΔH_{SA}	-7.4±0.2	-2.1±0.2	-1.0±0.1
ΔS_{SA}	-17.5±0.7	-2.4±0.4	-2.9±0.3
ΔG_{SA}	-2.2±0.2	-1.4±0.2	-0.14±0.1
<i>Methanol: Water 1:1</i>			
ΔG_{SA}	-7.4±0.3	-6.4±0.4	-5.2±0.4

Supporting references.

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