Supporting Information

Disclosing chirality in consecutive supramolecular polymerizations. Chiral induction by light in N-annulated perylenetetracarboxamides

Elisa E. Greciano,a Rafael Rodríguez,b Katsuhiro Maeda,b,c Luis Sánchez*,a

aDepartamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, E-28040 Madrid (Spain).
bWPI Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan
cGraduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

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1. Experimental section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 (\(^{1}H: 300\) MHz; \(^{13}C: 75\) MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (\(J\)) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. Multiplicities are denoted as follows: \(s = \text{singlet}\), \(d = \text{doublet}\), \(t = \text{triplet}\), \(m = \text{multiplet}\), \(br = \text{broad}\). FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded on a Varian Cary 50 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a FTMS Bruker APEX Q IV spectrometer. Circular dichroism (CD) measurements were performed on a JASCO-1500 dichrograph equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 700 and 200 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm. A 1 cm path-length quartz cuvette (Hellma) was used. VCD spectra were recorded in a JASCO FVS-6000 over an average of 6000 scans using a cell equipped with BaF\(_2\) lens and a Teflon spacer generating a 150 \(\mu\)m path length. CPL spectra were recorded on a JASCO CPL-300 at a scanning rate of 100 nm/min over an average of 5 scans, using a 10 mm quartz cell. CPL irradiation was performed with a JASCO CPL irradiation instrument equipped with a 500 W Deep UV lamp and a Babinet-Soleil Compensator using a 10 mm quartz cell.

Preparation of Aggl and Aggll species. In good agreement with our previous results on achiral compound \(3^{51}\) a stock solution of chiral \(1\) and \(2\) in MCH as solvent and at \(c_T = 500\ \mu\text{M}\) is initially prepared. A dilution of this stock solution is carried out to attain the desired final concentration (10 \(\mu\text{M}\)). Registering the UV-Vis spectra of this diluted solution results in the broad absorption spectrum shown in Figure 2a that coincides with that reported for Aggll species of achiral \(3\) (reference 10 of the manuscript). Heating this 10 \(\mu\text{M}\) solutions of \(1\) or \(2\) to 90 °C, yields a heating curve with two clear transitions ascribable to Aggl and the monomeric species. Once the initial solution is completely disassembled to the monomeric species, a further cooling of this solution to 20 °C allows the reassembly of this monomeric species to form Aggl species, as demonstrate the UV-Vis spectra shown in Figure 2b. A similar strategy is followed for the solutions in which Tol is utilized as solvent. However, in this case, only more concentrated solutions of \(1\) and \(2\) (\(c_T = 100\ \mu\text{M}\) or higher) allows detecting the formation of Aggll. In good correlation with that reported for achiral \(3\), the UV-Vis spectra of diluted solutions of \(1\) and \(2\) (\(c_T = 20\ \mu\text{M}\)) yields Aggl species as the only aggregated state, as demonstrates the identical absorption pattern to that registered for the MCH solution upon applying the heating/cooling cycle mentioned above.
2. Synthetic details and characterization

Scheme S1. Synthesis of the reported N-annulated tricarboxamides 1-3.

Compounds 4-12 were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.\(^{52,53}\)

4-(2-(3,4,5-tris((S)-3-methyloctyloxy)benzamido)ethylcarbamoyl)phenylboronic acid (13)

4-(Dihydroxyboryl)benzoic acid (0.18 g, 1.06 mmol) was dissolved in dry DMSO (2 mL) and in dry methylene chloride (17 mL) under Argon atmosphere. The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.14 g, 1.17 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (0.22 g, 1.17 mmol) were slowly added. The mixture was stirred for 30 minutes. After that, compound 11 (0.74 g, 1.17 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 66 hours. The organic layer was washed with water, HCl 1 M, dried over MgSO\(_4\) and evaporation of the solvent under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/methanol 10/1) affording compound 13 as a white solid (0.65 g, 78 %). \(^1\)H NMR (DMSO-\(d_6\), 500 MHz, 328 K) \(\delta\) 8.61 (1H, \(H_e\), br), 8.51 (1H, \(H_x\), br), 8.18 (2H, \(H_a\), s), 7.85 (2H, \(H_2\), d, \(J=8.1\) Hz), 7.80 (2H, \(H_1\), d, \(J=8.1\) Hz).
Hz), 7.13 (2H, H₃, s), 4.03 (4H, Hᵣ, m), 3.93 (2H, Hᵣ, m), 3.46 (4H, Hₑᵥₛ, br), 1.77 (3H, Hₘ, m), 1.70 (3H, Hₘ, br), 1.51 (6H, Hₜₔ, m), 1.33–1.14 (18H, Hᵢₖₙ, br), 0.92 (6H, Hₜ, d, J=6.6 Hz), 0.89 (3H, Hᵣ, d, J=6.6 Hz), 0.85 (18H, Hᵣ, d, J=6.6 Hz); ¹³C NMR (DMSO-d₆, 125 MHz, 328 K) δ 166.6, 165.9, 152.0, 139.8, 135.6, 133.6, 129.3, 125.7, 105.9, 70.5, 66.7, 38.5, 38.4, 36.6, 36.6, 36.5, 35.7, 29.0, 28.9, 27.1, 23.9, 23.8, 22.2, 22.1, 19.2, 19.1; FTIR (neat) 715, 761, 858, 1016, 1045, 1115, 1231, 1337, 1365, 1380, 1427, 1465, 1497, 1542, 1580, 1636, 2870, 2926, 2954, 3317 cm⁻¹. HRMS (MALDI-TOF) calcd. for C₄₆H₇₈BN₂O₇ [M+H]⁺, 781.590; found, 781.358.

4-(2-(3,4,5-tris((R)-3-methyloctyloxy)benzamido)ethylcarbamoyl)phenylboronic acid (14)

4-(Dihydroxyboryl)benzoic acid (0.19 g, 1.12 mmol) was dissolved in dry DMSO (1 mL) and in dry methylene chloride (14 mL) under Argon atmosphere. The solution was cooled to 0 °C and 4-dimethylaminopyridine (0.15 g, 1.23 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (0.24 g, 1.23 mmol) were slowly added. The mixture was stirred for 30 minutes. After that, compound 12 (0.78 g, 1.23 mmol) was dissolved in dry methylene chloride (4mL) and added portionwise. The reaction mixture was stirred at room temperature for 44 hours. The organic layer was washed with water, HCl 1 M, dried over MgSO₄ and evaporation of the solvent under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform/methanol 10/1) affording compound 14 as a white solid (0.76 g, 86 %). ¹H NMR (DMSO-d₆, 300 MHz, 328 K) δ 8.44 (1H, Hₑ, br), 8.34 (1H, Hᵢ, br), 7.94 (2H, Hₐ, s), 7.85 (2H, H₂, d, J=8.1 Hz), 7.80 (2H, H₁, d, J=8.1 Hz), 7.13 (2H, H₃, s), 4.03 (4H, Hᵣ, m), 3.94 (2H, Hᵣ, m), 3.46 (4H, Hₑᵥₛ, br), 1.72 (6H, Hₘₙ, br), 1.51 (6H, Hₜₔ, m), 1.32–1.14 (18H, Hᵢₖₙ, br), 0.92 (9H, Hₜ, d, J=6.6 Hz), 0.85 (18H, Hᵣ, d, J=6.6 Hz); ¹³C NMR (DMSO-d₆, 75 MHz, 328 K) δ 166.7, 166.0, 152.2, 139.5, 135.7, 133.9, 129.5, 126.1, 105.6, 70.6, 66.5, 36.8, 36.8, 36.7, 35.9, 29.1, 29.0, 27.4, 24.2, 24.1, 22.5, 22.5, 22.4, 19.4, 19.3; FTIR (neat) 668, 718, 762, 858, 997, 1017, 1047, 1115, 1230, 1337, 1365, 1402, 1427, 1465, 1497, 1540, 1580, 1635, 2870, 2926, 2954, 3320 cm⁻¹. HRMS (MALDI-TOF) calcd. for C₄₆H₇₈BN₂O₇ [M+H]⁺, 781.590; found, 781.530.
(S,S,S)-N,N’-(((4,4’-(1-decyl-1H-phenanthro[1,10,9,8-cdefg]carbazole-3,10-diyl)bis(benzoyl))bis(azanediyl))bis(ethane-2,1-diyl))bis(3,4,5-tris(((S)-3,7-dimethyloctyl)-oxy)benzamide) (1)

Compound 4 (111 mg, 0.20 mmol), compound 13 (340 mg, 0.44 mmol), tetrakis(triphenylphosphine) palladium(0) (23 mg, 0.02 mmol) were dissolved in dry THF (42 mL). K2CO3 (137 mg, 0.99 mmol) was dissolved in water (2.3 mL) and added to the solution under Argon atmosphere. The reaction mixture was heated at reflux for 26 hours. After evaporation of the solvent under reduced pressure, the residue was washed with water, extracted with chloroform, dried over MgSO4 and evaporation of the solvent under reduced pressure. After that, the residue was purified by column chromatography (silica gel, chloroform/methanol 10/0.05) affording compound 1 as a yellow solid (145 mg, 39 %). 1H NMR (CDCl3, 300 MHz, 298 K) δ 8.62 (2H, H1, d, J=7.7 Hz), 8.03 (4H, H3+6, m), 7.72 (6H, H2+5, m), 7.62 (2H, H4, s), 7.52 (2H, Ha, br), 7.42 (2H, Hd, br), 7.12 (4H, H7, s), 4.43 (2H, Hn, t, J=7.2 Hz), 4.06 (12H, H6, m), 3.81 (8H, Hbc, br), 1.96 (2H, Hm, quin, J=7.2 Hz), 1.85 (6H, H2, m), 1.63 (6H, H5, br), 1.49 (14H, Hbr, m), 1.30–1.11 (48H, Hk,l,m,n,o,p,q,r,s,t,u,v,w,x,y,z); 13C NMR (CDCl3, 175 MHz, 313 K) δ 168.7, 168.7, 153.2, 145.6, 141.3, 136.4, 132.5, 131.9, 130.6, 130.5, 128.8, 127.3, 124.8, 123.9, 121.1, 117.1, 114.1, 105.8, 71.7, 67.7, 45.8, 41.5, 41.1, 39.4, 39.3, 37.5, 37.4, 37.4, 36.4, 35.4, 32.0, 31.8, 31.2, 29.9, 29.7, 29.7, 29.4, 29.3, 29.2, 28.2, 28.0, 27.9, 27.1, 24.7, 24.7, 22.7, 22.6, 22.6, 22.5, 19.6, 14.1, 14.0; FTIR (neat) 668, 718, 760, 802, 851, 1116, 1232, 1303, 1342, 1380, 1430, 1466, 1500, 1543, 1581, 1634, 2860, 2925, 2953, 3289 cm⁻¹. HRMS (MALDI-TOF, exact mass) calcd. for C122H179N5O10 [M], 1874.3652; found, 1874.3656.
(R,R,R)-N,N'-(((4,4'-{(1-decyl-1H-phenanthro[1,10,9,8-cdefg]carbazole-3,10-diyl)bis(benzoyl)})bis(azanediyl))bis(ethane-2,1-diyl))bis(3,4,5-tris((R)-3,7-dimethyloctyl)-oxy)benzamide) (2)

Compound 4 (115 mg, 0.20 mmol), compound 14 (350 mg, 0.45 mmol), tetrakis-(triphenylphosphine) palladium(0) (24 mg, 0.02 mmol) were dissolved in dry THF (43 mL). K$_2$CO$_3$ (141 mg, 1.02 mmol) was dissolved in water (2.4 mL) and added to the solution under Argon atmosphere. The reaction mixture was heated at reflux for 72 hours. After evaporation of the solvent under reduced pressure, the residue was washed with water, extracted with chloroform, dried over MgSO$_4$ and evaporation of the solvent under reduced pressure. After that, the residue was purified by column chromatography (silica gel, chloroform/methanol 10/0.05) affording compound 2 as a yellow solid (170 mg, 45 %). $^1$H NMR (CDCl$_3$, 700 MHz, 298 K) $\delta$ 8.63 (2H, H$_1$, d, $J$=7.7 Hz), 8.05 (2H, H$_3$, d, $J$=8.2 Hz), 8.02 (4H, H$_6$, d, $J$=7.7 Hz), 7.74 (6H, H$_2$+$t$, m), 7.64 (2H, H$_{4}$, s), 7.47 (2H, H$_{8}$, br), 7.37 (2H, H$_{8}$, br), 7.12 (4H, H$_7$, s), 4.48 (2H, H$_{n}$, t, $J$=7.2 Hz), 4.04 (12H, H$_e$, m), 3.83 (4H, H$_{b\ or\ c}$, br), 3.78 (4H, H$_{b\ or\ c}$, br), 1.97 (2H, H$_o$, quin, $J$=7.2 Hz), 1.87 (4H, H$_m$, m), 1.82 (2H, H$_l$, m), 1.69 (6H, H$_{ip}$, br), 1.59 (6H, H$_{ip}$, br), 1.49 (8H, H$_i$, m), 1.31–1.10 (48H, H$_{ij+k+q+rs+tv}$, br), 0.91 (18H, H$_w$, d, $J$=6.5 Hz), 0.85 (12H, H$_m$, d, $J$=6.5 Hz), 0.82 (24H, H$_n$, d, $J$=6.5 Hz), 0.80 (3H, H$_w$, t, $J$=7.2 Hz); $^{13}$C NMR (CDCl$_3$, 175 MHz, 298 K) $\delta$ 168.9, 168.8, 153.3, 145.7, 141.2, 136.5, 132.6, 131.9, 130.7, 128.9, 127.4, 125.0, 124.9, 124.0, 121.3, 117.2, 114.2, 105.6, 71.8, 67.6, 45.8, 41.5, 41.1, 39.5, 39.4, 37.7, 37.5, 37.5, 36.5, 31.9, 31.3, 30.0, 29.8, 29.6, 29.4, 28.1, 28.1, 27.3, 24.9, 22.9, 22.8, 22.8, 22.7, 19.7, 14.2; FTIR (neat) 736, 802, 851, 1060, 1117, 1232, 1303, 1343, 1382, 1429, 1465, 1501, 1543, 1581, 1634, 2854, 2925, 2955, 3291 cm$^{-1}$. HRMS (MALDI-TOF, exact mass) calcd. for C$_{122}$H$_{179}$N$_5$O$_{10}$ [M], 1874.3652; found, 1874.3680.
3. Collection of spectra

\[ ^1H \text{ NMR (DMSO-}d_6, 500 MHz, 328 K) \text{ of compound 13.} \]

\[ ^{13}C \text{ NMR (DMSO-}d_6, 125 MHz, 328 K) \text{ of compound 13.} \]
$^1$H,$^{13}$C-HMQC spectrum (DMSO-$d_6$, 328 K) of compound 13.
\(^1\)H NMR (DMSO-\(d_6\), 300 MHz, 328 K) of compound 14.

\(^{13}\)C NMR (DMSO-\(d_6\), 75 MHz, 328 K) of compound 14.
$\text{H, C}$-HMQC spectrum (DMSO-d6, 328 K) of compound 14.
$\text{H NMR (CDCl}_3$, 300 MHz, 298 K) of compound 1.

$\text{C NMR (CDCl}_3$, 175 MHz, 313 K) of compound 1.
\(^1\)H,\(^13\)C-HMQC spectrum (CDCl\(_3\), 313 K) of compound 1.
$^1$H NMR (CDCl$_3$, 700 MHz, 298 K) of compound 2.

$^{13}$C NMR (CDCl$_3$, 175 MHz, 298 K) of compound 2.
$^{1}H,^{13}C$-HMOC spectrum (CDCl$_3$, 298 K) of compound 2.
4. Supplementary Figures and Tables

**Figure S1.** UV-Vis spectra of 1 (a) and 2 (c) in MCH, at $c_T = 5 \mu M$, at different temperatures and as-prepared or upon applying a heating/cooling (h/c) cycle. Heating and cooling curves of 1 (b) and 2 (d) in MCH, at $c_T = 10 \mu M$ utilizing a heating and a cooling rate of 1 °C/min.

**Figure S2.** (a) UV-Vis spectra of 1 in MCH, at $c_T = 10 \mu M$, at different temperatures and as-prepared or upon applying a heating/cooling (h/c) cycle. (b) Heating and cooling curves of 1 in MCH at $c_T = 10 \mu M$ utilizing a heating and a cooling rate of 1 °C/min.
Figure S3. (a) UV-Vis (bottom) and CD (top) spectra of the AggII species formed from 1 and 2. Comparison of the UV-Vis (b, bottom), CD (b, top) fluorescence (c, bottom) and CPL (c, top) spectra of Aggl and AggII formed from the self-assembly of 1. Experimental conditions: MCH, \(c_T = 20 \mu M\), \(\lambda_{exc} = 380\) nm, 20 °C.

Figure S4. LD spectra of chiral 1 and 2 for both the AggII (a) and Aggl (b) species obtained in MCH and Tol, respectively. Experimental conditions: \(c_T = 20 \mu M\), 20 °C.

Figure S5. (a) UV-Vis (a,bottom), CD (b, top), fluorescence (b, bottom) and CPL (b, top) spectra of the Aggl species formed from 1 and 2 in Tol. Experimental conditions: \(c_T = 20 \mu M\), \(\lambda_{exc} = 380\) nm, 20 °C.
Figure S6. UV-Vis spectra of 2 at $c_T = 500 \mu$M in MCH and Tol, 20 °C.
References