Supplementary Information

Bio-Inspired Design Strategy: Molecular Interactions Induced Organization of Tryptophan Appended Naphthalenediimide into Well Defined Architectures

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Experimental section

Materials and methods

All the solvents and reagents were obtained from Sigma-Aldrich and used as received unless otherwise mentioned. ¹H and ¹³C NMR were measured on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in CDCl₃/CD₃CN/DMSO-*d*₆, Tetramethylsilane as internal standard). Mass spectra were obtained from Shimadzu 2020 LC-MS. UV-vis spectra were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer. Circular dichroism (CD) measurements were carried out on a Jasco J-810 spectropolarimeter. FESEM measurements were performed by using FEI Nova nanoSEM-600 equipped with field emission gun operating at 15 kV. AFM measurements were performed using Innova (Veeco) atomic force microscope. For FESEM and AFM measurements sample was taken on a fresh, ultra clean Si (111) substrate. TEM micrographs were obtained on a 200 mesh holey carbon supported copper grids. Elemental analysis was carried out on ThermoScientific FLASH 2000 Organic Element Analyzer. IR spectra were recorded on a Bruker IFS 66/V spectrometer on a sodium chloride crystal.

Synthesis of tryptophan appended naphthalenetetracarboxylicdiimide (NDI 1): A modified procedure of Sanders and coworkers¹ has been employed to synthesize NDI 1. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (200 mg, 0.746 mmol) and L-tryptophan (305 mg, 1.491 mmol) were suspended in DMF (20 mL) in a 250 mL Erlenmeyer flask. To this suspension was added 0.2 mL of triethylamine. The suspension was sonicated until the mixture became homogeneous. The reaction mixture was heated under microwave irradiation at full power for 3 min. in steps of 30 sec. and with 30 sec interval. The resulting dark brown oil was taken up into methanol (400 mL). The solution was added under stirring to 600 mL of 1N HCl. The resulting suspension was allowed to coagulate overnight and then filtered through a sintered glass funnel. The solid was then washed with 200 mL deionized water and dried in vacuo to obtain a brown solid of NDI **1**. Yield 90%. ¹H NMR: (400 MHz, DMSO- d_6) δ_{ppm} 3.46–3.52, (dd, 2H, CH₂, J = 8 Hz, 8 Hz); 3.65-3.71 (dd, 2H, CH₂, J = 8 Hz, 8 Hz); 5.84-5.87 (dd, 2H, α CH, J = 4 Hz, 4 Hz); 6.78-6.82 (m, 2H, ArH); 6.92-6.96 (m, 2H, ArH); 7.04-7.05 (d, 2H, ArH, J = 4 Hz); 7.19-7.21 (d, 2H, ArH, J = 8 Hz); 7.46-7.48 (d, 2H, ArH, J = 8 Hz); 8.61 (s, 4H, ArH); 10.64-10.65 (d, 2H, COOH, J = 4 Hz); 12.99 (br, 2H, NH). ¹³C NMR: (400 MHz, DMSO-d₆) δ_{ppm} 24.0, 54.2, 110.1, 111.2, 117.9, 118.2, 120.7, 123.6, 125.7, 125.9, 127.0, 131.1, 135.9, 162.0, 170.4. MS (EI): $m/z = 641.16 [M+H]^+$ for $C_{36}H_{24}N_4O_8$. Elemental analysis: Found: C, 67.35; H, 3.88; N, 8.72; Calcd: C, 67.39; H, 3.84; N, 8.75 for $C_{36}H_{24}N_4O_8$.

Synthesis of tryptophan methyl ester appended naphthalenetetracarboxylicdiimide (NDI 2): Synthesis of L-Tryptophan methyl ester hydrochloride: Anhydrous methanol (50 mL) was taken in a 100 mL 2-necked round bottom flask fitted with a reflux condenser and an additional dropping funnel and cooled to ice temperature. Acetyl chloride (3 mL) was added drop wise through the dropping funnel. After 15 min, L-tryptophan (3 g) was added and the reaction mixture was refluxed at 70 °C for 6 h. The reaction mixture was vacuo dried to obtain L-tryptophan methyl ester hydrochloride in quantitative yield and used for further reaction without purification.

1,4,5,8-Naphthalenetetracarboxylic dianhydride (200 mg, 0.746 mmol) and L-tryptophan methyl ester hydrochloride (380 mg 1.491 mmol) were suspended in 20 mL of DMF in a 100 mL round bottom flask. To this suspension was added 0.5 mL of triethylamine under inert atmosphere. The reaction mixture was refluxed at 65 °C for 21 h. Solvent was evaporated under vacuo and the residue was purified by column chromatography (15 % methanol in chloroform) to obtain NDI **2** in good yield. Yield 86%. ¹H NMR: (400 MHz, CDCl₃-CF₃COOH) δ_{ppm} 3.64–3.70, (dd, 2H, CH₂, *J* = 8 Hz, 8 Hz); 3.78-3.84, (dd, 2H, CH₂, *J* = 8 Hz, 8 Hz); 3.90 (s, 6H, CH₃); 6.12-6.16 (dd, 2H, α CH, *J* = 8 Hz, 4 Hz); 6.86-7.02 (m, 6H, ArH); 7.13-7.15 (d, 2H, ArH, *J* = 8 Hz); 7.46-7.48 (d, 2H, ArH, *J* = 8 Hz); 8.57 (s, 4H, ArH). ¹³C NMR: (400 MHz, CDCl₃-CF₃COOH) δ_{ppm} 24.5, 53.9, 55.1, 110.2, 110.4, 118.6, 119.8, 122.4, 123.2, 126.1, 126.6, 127.2, 131.8, 136.1, 163.0, 172.5. MS (EI): m/z = 668.19 [M]⁺ for C₃₈H₂₈N₄O₈. Elemental analysis: Found: C, 68.23; H, 4.25; N, 8.35; Calcd: C, 68.26; H, 4.22; N, 8.38 for C₃₈H₂₈N₄O₈.

¹H NMR spectrum of NDI 1 (*DMSO-d*₆)



¹³C NMR spectrum of NDI 1 (*DMSO-d*₆)



¹H NMR of NDI 2 (*CDCl*₃ + *CF3COOH*)



¹³C NMR of NDI 2 (*CDCl*₃ + *CF3COOH*)





Fig. S1 IR spectra of NDI 1 obtained from acetonitrile and 90% aqueous acetonitrile.



Fig. S2 IR spectra of NDI 2 obtained from acetonitrile and 60% aqueous acetonitrile.



Fig. S3 (a) and (b) FESEM; (c) and (d) TEM micrographs of NDI 1 nanospheres self-assembled from acetonitrile solution.



Fig. S4 (a), (b), (c) and (d) FESEM micrographs of NDI **2** fibers (bundle of nanobelts) assembled from 60% aqueous acetonitrile solution.



Fig. S5 (a) and (b) FESEM micrographs of NDI 2 assembled from 1 mM acetonitrile solution.



Fig. S6 (a) and (b) FESEM micrographs of NDI 1 fractals formed from 10% aqueous acetonitrile containing with 2 equiv of NaOH.



Fig. S7 EDAX spectrum of NDI **1** fractals obtained from 10% aqueous acetonitrile with 2 equiv of NaOH measured on a Si(111) substrate (measurement was performed in the marked region of Fig. S6b).



Fig. S8 FESEM micrographs of NDI **1** obtained from 10% aqueous acetonitrile containing (a) 10 and (b) 100 equiv of NaOH. (c) FESEM micrograph of 1 mM NDI **1**. (d) Corresponding high magnification micrograph of (c).



Fig. S9 AFM images (**a-d**) of NDI **2** showing the structural transition from nanospheres to nanobelts and in turn into microfibers (60% aqueous acetonitrile).



Fig. S10 AFM images of (a) NDI **2** microfiber (nanobelt bundle) assembled from 60% aqueous acetonitrile and (b) NDI **1** particle assembled from 90% aqueous acetonitrile. (c) and (d) The corresponding height profiles of (a) and (b) respectively.

Reference

1 P. Pengo, G. D. Pantos, S. Otto and J. K. M. Sanders, J. Org. Chem., 2006, 71, 7063.