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Electronic Supplementary Information (ESI)

Donor-Acceptor Interaction-Driven Self-Assembly of Amphiphilic Rod-

Coil Molecules into Supramolecular Nanoassemblies

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Experimental

Synthetic route of coil-rod-coil molecule **1–3**.



Synthesis 4 and 5. These compounds were synthesized according to the same procedure, a representation example is described for 4. 4-Hydroxy-4'-iodobiphenyl (2.82 g, 9.53 mmol), TsOR (4.0 g, 7.94 mmol) and excess K_2CO_3 (4.3 g, 31.1 mmol) were dissolved in 55 ml acetonitrile. The mixture was refluxed for 24 h. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methylene chloride: ethyl acetate (10:1 v/v) as eluent to yield 4.13 g (82.6%).

Compound 4. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.489–7.566 (m, 6H), 6.990 (d, J = 4.5 Hz, 2H), 4.176 (t, J = 5.1 Hz, 2H), 3.882 (t, J = 5.1 Hz, 2H), 3.529–3.762 (m, 30H), 3.377 (s, 3H).

Compound 5. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.489–7.566 (m, 6H), 6.990 (d, J = 4.5 Hz, 2H), 4.176 (t, J = 5.1 Hz, 2H), 3.882 (t, J = 5.1 Hz, 2H), 3.529–3.762 (m, 72H), 3.377 (s, 3H).

Synthesis of 6. Compound **4** (4.13 g, 6.58 mmol) and Trimethylsilylacetylene (1.42 g, 14.5 mmol) were dissolved in 25 ml tetrahydrofuran and 20ml triethylamine. Degassed and then CuI (0.01 g, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.03 g, 0.03 mmol) were added to the solution. The mixture was heated at reflux for 24 h under nitrogen and keep it away from the light. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) to yield 2.90 g (73.79%).

Synthesis of 7. Compound 6 (2.90 g, 2.91 mmol) and Potassium fluoride (1.65 g, 28.4 mmol) were dissolved in 60 ml ethyl alcohol. The mixture was refluxed for 12 h. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) to yield 2.05 g (76.2%).

Synthesis of 8. Compound 7 (0.4 g, 0.7 mmol) and 4,4'-Diiodobiphenyl (1.23 g, 3.03 mmol) were dissolved in 25 ml tetrahydrofuran and 20 ml triethylamine. Degassed and then CuI (0.01 g, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (0) (0.03 g, 0.03 mmol) were added to the solution. The mixture was heated at reflux for 24 h under nitrogen and keep it away from the light. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was

removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) to yield 0.36 g (60.0%).

Synthesis of 9. 1-bromopyrene (0.54 g, 1.92 mmol) and Trimethylsilylacetylene (0.41 g, 4.18 mmol) were dissolved in 25 ml tetrahydrofuran and 20 ml triethylamine. Degassed and then CuI (0.01 g, 0.05 mmol) and Bis(triphenylphosphine) palladium chloride (0.27 g, 0.30 mmol) were added to the solution. The mixture was heated at reflux for 24 h under nitrogen and keep it away from the light. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using petroleum ether as eluent to yield 0.26 g (45.4%).

Sythesis of 10. Compound **9** (0.26 g, 0.87 mmol) and Potassium fluoride (0.5 g, 8.6 mmol) were dissolved in 60 ml ethyl alcohol. The mixture was refluxed for 12 h. The resulting solution was poured into water and extracted with methylene chloride and ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using petroleum ether as eluent to yield 0.16

g (81.2%). ¹H NMR (300 MHz, CDCl₃, δ, ppm):8.60 (d, J = 9.0 Hz, 1H), 8.017–8.256 (m, 8H), 3.627 (s, 1H).



Fig. S1. ¹H-NMR of molecule 1 in CDCl₃.



Fig. S2. ¹³C-NMR of molecule 1 in CDCl₃.



Fig. S3. ¹H-NMR of molecule **2** in CDCl₃.



Fig. S4. ¹³C-NMR of molecule 2 in CDCl₃.



Fig. S5. ¹H-NMR of molecule $\mathbf{3}$ in CDCl₃.



Fig. S6. ¹³C-NMR of molecule **3** in CDCl₃.



Fig. S7. MALDI-TOF mass spectra of (a) molecule 1, (b) molecule 2, (c) molecule 3.

Small-angle X-ray diffraction data

Table S1. Small-angle X-ray diffraction data for 2-D columnar structure for molecule 1 (measured at 80°C).

q obsd	q calcd	h	k	Ι	
1.092	1.097		1	0	0
1.780	1.780		0	1	0
1.873	1.866		2	1	0
2.182	2.179		2	0	0

qobsd and qcalcd are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S2. Small-angle X-ray diffraction data forhexagonal columnar structure for molecule **2** (measured at 50°C).

q _{obsd}	q _{calcd}	h k l
1.227	1.225	1 0 0
2.121	2.122	1 1 0
2.451	2.449	2 0 0

Table S3. Small-angle X-ray diffraction data for 2-D columnar structure formolecule 3(measured at 220°C).

q _{obsd}	q _{calcd}	h k l
0.919	0.926	1 0 0
1.419	1.424	0 1 0
1.811	1.809	2 1 0

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda = 0.154$ nm).

Table S4. Small-angle X-ray diffraction data for 2-D columnar structure

for molecule 2 with 1.0 equivTNF(measured at 30 °C).

q _{obsd}	q _{calcd}	h k l	-
0.782	0.783	1 0 0	
0.916	0.911	0 1 0	
1.563	1.566	2 0 0	

 q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections ($\lambda =$

0.154 nm).



Fig. S8. Absorption spectra (dash) and emission spectra (solid) of 2 (0.01 wt%) in CH₂Cl₂ (black) and in an aqueous solution (red).



Fig. S9. Absorption spectra (dash) and emission spectra (solid) of **3** (0.01 wt%) in CH_2Cl_2 (black) and in an aqueous solution (red).



Fig. S10. Size distribution graphs of **1-3** in aqueous solution (0.01 wt%).



Fig. S11. Molecular dynamic simulations result of (a) 1, (b) 2, (c) 3 in a water environment.



Fig. S12. (a) Fluorescence spectra and (b) absorption spectra of 2 upon the addition of TNF in aqueous solution (0.01 wt%). (0 eq (equiv) means without addition of the TNF in aqueous solution of molecule 2).



Fig. S13. (a) Fluorescence spectra and (b) absorption spectra of **3** upon the addition of TNF in aqueous solution (0.01 wt%). (0 eq (equiv) means without addition of the TNF in aqueous solution of molecule **3**).



Fig. S14. Size distribution graphs of **1-3** (0.01 wt%) with 1.0 equiv TNF in aqueous solution.