Supporting Information

Supramolecular Assemblies of Ferrocene-Hinged Naphthalenediimides: Multiple Conformational Changes in Film States

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Table of Contents

1.	Synthesis and Characterization	Page S2
2.	Suporting Data (Figures S1–S8)	Page S5
3.	Pertinent XRD Data (Tables S1–S3)	Page S15
4.	¹ H and ¹³ C NMR Spectra	Page S17
5.	References	Page S22

1. Synthesis and Characterization

The synthetic methods and characterization data for a series of naphthalenediimide compounds presented in this study are shown below. The NMR spectra (in CDCl₃ at 25 °C) are shown in the last pages.



NDI. This compound was synthesized from 3,4,5-tridodecyloxyaniline and 1,4,5,8-naphthalenetetracarboxylic dianhydride in DMF (95 °C, 14 h) under argon. The crude product was purified by silica-gel chromatography (CHCl₃), gel permeation chromatography (CHCl₃), and reprecipitated from CHCl₃/MeOH (1:9) to give a pale-yellow solid (84%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.87 (m, 18H), 1.25–1.35 (m, 96H), 1.47 (m, 12H), 1.80 (m, 12H), 3.95 (t, *J* = 6.5 Hz, 8H), 4.04 (t, *J* = 6.6 Hz, 4H), 6.50 (s, 4H), 8.84 (s, 4H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 14.28, 14.29, 22.85, 22.87, 26.25, 26.30, 29.46, 29.52, 29.55, 29.57, 29.79, 29.81, 29.85, 29.87, 29.92, 29.94, 30.56, 32.08, 32.11, 69.26, 73.69, 106.79, 127.18, 127.25, 129.50, 131.58, 138.72, 153.94, 163.14. Elemental analysis (calc. for C₉₈H₁₅₈N₂O₁₀: C, 77.22; H, 10.45; N, 1.84): found C, 77.01; H, 10.02; N, 1.81.



N-(3,4,5-tridodecyloxyphenyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride. 1,4,5,8-naphthalenetetracarboxylic dianhydride was heated for 20 min at 100 °C in DMF under argon. The DMF/THF (1:1) solution of 3,4,5-tridodecyloxyaniline was added dropwise slowly (12 h). The reaction mixture was stirred another 4 h at 100 °C and cooled to room temperature. The solvents were removed under reduced pressure, and the crude was dissolved in CHCl₃. The insoluble species were filtrated off, and the filtrate was evaporated to yield a sticky orange solid. The solid was purified by reprecipitation from CHCl₃/MeOH (1:9) and gel permeation chromatography (CHCl₃) to give a pale-yellow solid (62%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.88 (m, 9H), 1.25–1.55 (m, 54H), 1.78 (m, 6H), 3.94 (t, *J* = 6.5 Hz, 4H), 4.03 (t, *J* = 6.6 Hz, 2H), 6.47 (s, 2H), 8.86 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 14.28, 22.85, 22.87, 26.25, 26.29, 29.44, 29.52, 29.55, 29.57, 29.79, 29.81, 29.85, 29.87, 29.92, 29.94, 30.55, 32.08, 32.11, 69.25, 73.70, 106.63, 123.23, 127.27, 128.19, 129.09, 129.19, 131.75, 133.39, 138.76, 153.96, 158.92, 162.57. The analytical data are in good accordance with those previously reported.^{S1}



NDI-Fc. This compound synthesized from was aminoferrocene and N-(3.4,5-tridodecvloxyphenyl)-1.4,5,8- naphthalenetetracarboxylic monoanhydride in DMF (90 °C, 6 h) under argon. The crude product was purified by silica-gel chromatography $(CHCl_3/MeOH = 98:2)$, gel permeation chromatography $(CHCl_3)$, and reprecipitated from CHCl₃/MeOH (1:9) to give a light-green solid (87%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.87 (m, 9H), 1.25-1.41 (m, 48H), 1.48 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 1.79 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (m, 6H), 3.95 (t, J = 6.5 Hz, 4H), 4.04 (t, J = 6.5 Hz, 4H), 4.04(t, J = 6.6 Hz, 2H), 4.29 (s, 5H), 4.34 (t, J = 2.0 Hz, 2H), 4.75 (t, J = 2.0 Hz, 2H), 6.50 (s, 2H),8.81 (d, J = 7.6 Hz, 2H), 8.84 (d, J = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 14.28, 22.84, 22.87, 26.25, 26.30, 29.46, 29.51, 29.55, 29.57, 29.79, 29.81, 29.85, 29.87, 29.92, 29.94, 30.56, 32.07, 32.11, 65.83, 67.38, 69.24, 70.05, 73.68, 90.17, 106.78, 126.69, 126.72, 127.09, 127.40, 129.57, 131.26, 131.58, 138.66, 153.92, 162.68, 163.23. Elemental analysis (calc. for C₆₆H₉₀FeN₂O₇: C, 73.45; H, 8.41; N, 2.60): found C, 73.33; H, 8.35; N, 2.90.



NDI–Fc–NDI. This compound was synthesized from diaminoferrocene and *N*-(3,4,5-tridodecyloxyphenyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride in DMF (90 °C, 16 h) under argon. The crude product was purified by silica-gel chromatography (CHCl₃/MeOH = 97:3), gel permeation chromatography (CHCl₃), and reprecipitated from CHCl₃/MeOH (1:9) to give a dark-green solid (36%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.88 (m, 18H), 1.24–1.55 (m, 108H), 1.70 (m, 8H), 1.80 (m, 4H), 3.60 (t, *J* = 6.6 Hz, 8H), 4.05 (t, *J* = 6.5 Hz, 4H), 4.47 (t, *J* = 2.0 Hz, 4H), 5.01 (t, *J* = 2.0 Hz, 4H), 6.47 (s, 4H), 8.22 (d, *J* = 7.6 Hz, 4H), 8.29 (d, *J* = 7.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 14.27, 14.29, 22.85, 22.89, 26.28, 26.43, 29.49, 29.56, 29.63, 29.76, 29.88, 29.92, 29.94, 29.96, 30.03, 30.05, 30.08, 30.11, 30.88, 32.10, 32.15, 66.47, 68.85, 69.26, 73.51, 91.72, 106.53, 126.08, 126.40, 126.44, 126.71, 128.95, 130.28, 130.48, 138.41, 153.65, 161.94, 162.58. Elemental analysis (calc. for C₁₂₂H₁₇₀FeN₄O₁₄: C, 74.29; H, 8.69; N, 2.84): found C, 74.38; H, 8.97; N, 2.91.



NDI–Bu–NDI. This compound was synthesized from 1,4-diaminobutane and *N*-(3,4,5-tridodecyloxyphenyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride in DMF (95 °C, 5 h) under argon. The crude product was purified by silica-gel chromatography (CHCl₃), gel permeation chromatography (CHCl₃) and reprecipitated from CHCl₃/MeOH (1:9) to give a pale-orange solid (79%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 0.87 (m, 18H), 1.25–1.55 (m, 108H), 1.79 (m, 12H), 1.97 (m, 4H), 3.93 (t, *J* = 6.5 Hz, 8H), 4.03 (t, *J* = 6.6 Hz, 4H), 4.31 (m, 4H), 6.49 (s, 4H), 8.74 (d, *J* = 7.6 Hz, 4H), 8.77 (d, *J* = 7.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 14.28, 22.84, 22.87, 25.80, 26.24, 26.30, 29.45, 29.52, 29.56, 29.57, 29.79, 29.81, 29.85, 29.88, 29.93, 29.94, 29.95, 30.57, 32.07, 32.11, 69.22, 73.67, 100.06, 106.73, 126.89, 126.94, 127.06, 129.50, 131.20, 131.42, 138.64, 153.91, 162.98, 163.11. Elemental analysis (calc. for C₁₁₆H₁₇₀N₄O₁₄: C, 75.53; H, 9.29; N, 3.04): found C, 75.66; H, 9.12; N, 3.12.

2. Supporting Data



Figure S1. TGA thermograms of (a) **NDI–Fc–NDI**, (b) **NDI–Bu–NDI**, (c) **NDI–Fc**, and (d) **NDI** under flowing argon gas. The arrow indicates the temperature where 3% of the sample weight is reduced.



Figure S2. (a) Open and closed forms of **NDI–Fc–NDI** associated with the rotational motion of the Fc unit. (b) Optimized structures and molecular orbitals of **NDI–Fc–NDI** calculated by DFT B3LYP/6-31G* basis set: the open form (left) and the closed form (right). Dodecyl groups ($C_{12}H_{25}$) are replaced by ethyl groups ($C_{2}H_{5}$) for simplicity. Hydrogen atoms are omitted for clarity. In the closed form, which is slightly more stable than the open form by 7.2 kJ/mol, the mean-plane distance and the slip angle between the NDI π -planes are 3.7 Å and 8.5°, respectively.



Figure S3. Variable-temperature ¹H NMR spectra of NDI–Fc–NDI (1×10^{-3} M) in CDCl₃.



Figure S4. Optimized structure and molecular orbitals of **NDI–Bu–NDI** calculated by DFT B3LYP/6-31G* basis set. The LUMO+1 (top) and LUMO (bottom) are localized in one NDI unit, respectively. Dodecyl groups ($C_{12}H_{25}$) are replaced by ethyl groups ($C_{2}H_{5}$) for simplicity. Hydrogen atoms are omitted for clarity.



Figure S5. The absorbance changes at 358 nm of an MCH solution of NDI–Fc–NDI (5 × 10^{-5} M) at various temperatures upon cooling (1 °C/min), fitted with a cooperative model (solid blue line) and an isodesmic model (dashed red line).^{S2} The cooperative model with an R^2 value of 0.999 fits better than the isodesmic model with an R^2 value of 0.986. The reliable data fitting with the cooperative model leads to the elongation temperature ($T_e = 309$ K = 36 °C), below which the non-sigmoidal transition occurs, and the enthalpy change during the supramolecular polymer elongation ($\Delta H = -1.61 \times 10^2$ kJ mol⁻¹).



Figure S6. UV–vis absorption spectra of **NDI–Fc–NDI** spin-coated films annealed at different temperatures: 25 °C (red line), 180 °C (green line), and 210 °C (blue line). The substrates are quartz plates. The absorption spectrum at 25 °C is fairly similar to that in MCH at 25 °C (black line).



Figure S7. Photoelectron yield spectra of **NDI–Fc–NDI** drop-casting films annealed at different temperatures: (a) 25 °C (red line), (b) 180 °C (green line), and (c) 210 °C (blue line). The substrates are ITO-coated glasses.



Figure S8. XRD patterns of **NDI–Fc–NDI** solid samples obtained by (a) drop-casting from an MCH solution, (b) drop-casting from a CHCl₃ solution, and (c) reprecipitation from CHCl₃/MeOH at 25 °C.





Figure S10. Schematic illustration of energy landscapes of (a) conventional rigid π -system and (b) directionally flexible π -system like **NDI**–**Fc**–**NDI**.

3. Pertinent XRD Data

q, nm ⁻¹	$d_{\rm obs}$, nm	$d_{\rm calc}$, nm	hkl
1.55	4.05	4.04	001
3.09	2.03	2.02	002
4.64	1.36	1.35	003
6.27	1.00	1.01	004
7.75	0.81	0.81	005
11.18	0.56	_	
13.80	0.46	_	halo
17.53	0.36	_	π -stacking

 Table S1. XRD Data for an NDI-Fc Solid Sample at 100 °C upon Cooling from the Isotropic

 Melt

Table S2. XRD Data for an NDI–Bu–NDI Solid Sample at 150 °C upon Cooling from the Isotropic Melt

q, nm ⁻¹	$d_{\rm obs}$, nm	$d_{\rm calc}$, nm	hkl
1.67	3.77	3.77	100
2.90	2.17	2.17	110
3.33	1.89	1.88	200
4.42	1.42	1.42	210
5.01	1.26	1.26	300
6.00	1.05	1.05	310
7.99	0.79	_	
9.47	0.66	_	
13.76	0.46	_	halo
16.67	0.38	_	π -stacking

temperature, °C	helical pitch, nm	column diameter, nm
30	10.82	4.40
100	10.74	4.20
150	11.70	4.05
170	11.63	3.81
180	11.27	3.70

 Table S3.
 Helical Pitch and Column Diameter of the NDI-Fc-NDI Supramolecular

 Assembly at Each Temperature

4. ¹H and ¹³C NMR Spectra



¹H NMR (top) and ¹³C NMR (bottom) spectra of N-(3,4,5-tridodecyloxyphenyl)-1,4,5,8-naphthalenetetracarboxylic monoanhydride in CDCl₃ at 25 °C.



 ^1H NMR (top) and ^{13}C NMR (bottom) spectra of NDI in CDCl3 at 25 °C.



¹H NMR (top) and ¹³C NMR (bottom) spectra of **NDI–Fc** in CDCl₃ at 25 °C.



¹H NMR (top) and ¹³C NMR (bottom) spectra of **NDI–Fc–NDI** in CDCl₃ at 25 °C.



¹H NMR (top) and ¹³C NMR (bottom) spectra of **NDI–Bu–NDI** in CDCl₃ at 25 °C.

5. References

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