Supporting information

Competing forces in the self-assembly of amide-functionalized discotic mesogens

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Materials and methods

All solvents employed were reagent grade. Diethyamine, butylamine, and oxalyl chloride were purchased from Aldrich and used without further purification. Dibenzophenazine carboxylic acids were prepared according to a literature procedure.\textsuperscript{1,2} \textsuperscript{1}H NMR were measured at 400 MHz or 500 MHz (Bruker Avance III 400 or 500 spectrometer) and \textsuperscript{13}C NMR were measured at 126 MHz. 2D NMR spectroscopy (HMBC, HSQC, COSY) was also performed for \textbf{HBu(n)} and \textbf{dEt(n)} (n=6-12). Infrared spectroscopy in ATR mode was carried out on a UATR TWO (Perkin Elmer) spectrometer. High resolution mass spectrometry was carried out on a Bruker microTOF (ESI\textsuperscript{+}) using an acetonitrile as the solvent.

Texture analysis was carried out using optical polarizing microscopy on an Olympus BX50 microscope with crossed polarizers using a Linkam LTS350 heating stage. Phase transition temperatures and enthalpies were investigated using differential scanning calorimetry (DSC) on a Perkin Elmer DSC, heating and cooling at a rate of 10 °C min\textsuperscript{-1}. X-ray diffraction studies of liquid crystalline samples were carried out on a Rigaku RAXIS rapid diffractometer using Cu K\textalpha\ radiation, a graphite monochromator and a Fujifilm Co., Ltd curved image plate (460 mm x 256 mm). A 0.1 mm collimator was used and typical irradiation times were of 30 minutes. A home made capillary furnace was used for variable temperature measurements.\textsuperscript{3}

Dynamic light scattering (DLS) experiments were conducted on a Zetasizer Nano ZS ZEN 3600 by Malvern Instruments equipped with a red laser (633 nm). Hydrodynamic diameter measurements of all \textbf{dEt(n)} and \textbf{HBu(n)} series in chloroform (viscosity: 0.05370 cP, refractive index: 1.44) were carried out by dynamic light scattering. All measurements were performed at 25 °C in a glass cuvette. Sample volumes were set to 1 mL. Prepared solutions (10 – 70 mM) were filtered through 0.2 \textmu m Acrodisc CR 13 mm syringe filters with PTFE membranes (Life Sciences). 10-20 scans are performed for each measurement. The equipment determines the scan number automatically. For each compound at each concentration, 5 measurements were performed and averaged. The results of DLS were analyzed as an intensity size distribution (results were not converted to a volume or number size distribution). Two peaks were often observed in the intensity size distribution, since the observed intensity I is proportional to the sixth power of the particle diameter d (I \propto d\textsuperscript{6}). Even an extremely small number of large particles (trace impurities) can result in a large peak in the intensity size distribution. Because of this, only the peak corresponding to a smaller particle size (10 to 30 Å) was considered.
General synthesis of dEt(n) and HBu(n) (n=6-12)

To a flame-dried flask, dry dichloromethane (50 ml), 2,3,6,7-tetakis(alkoxy)dibenzo[a,c]phenazine-11-carboxylic acid (500 mg), N,N'-dimethylformamide (1.0 eq.), and oxalylchloride (1.3 eq.) were successively added. The mixture was heated to 40 °C and stirred for 3 h. After the solvent was removed in vacuo, the solid were dispersed in dichloromethane (50 ml). To this dispersion, an excess amine (1.0–2.0 ml) was added. After the mixture was stirred for additional 1 h, it was extracted by dichloromethane. The combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The crude was subjected to silica gel column chromatography (solvent: dichloromethane~dichloromethane/ethylacetate = 20/1).

N,N-diethyl-2,3,6,7-tetakis(hexyloxy)dibenzo[a,c]phenazine-11-carboxamide (dEt(6)), a yellow solid (41% yield); ¹H NMR (400 MHz, CDCl₃, 54 mM) δ 8.76 (s, 1H), 8.72 (s, 1H), 8.32 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 1.7 Hz, 1H), 7.79 (dd, J = 8.6, 1.8 Hz, 1H), 7.69 (d, J = 5.3 Hz, 2H), 4.34 (q, J = 6.5 Hz, 4H), 4.28 (td, J = 6.5, 2.0 Hz, 4H), 3.66 (s, 2H), 3.41 (s, 2H), 2.05 - 1.90 (m, 8H), 1.67 – 1.54 (m, 8H), 1.50 – 1.12 (m, 22H), 0.95 (t, J = 7.0 Hz, 12H).

¹³C NMR (126 MHz, CDCl₃, 54 mM) δ 170.58, 152.12, 152.07, 149.54, 142.63, 142.57, 141.49, 140.94, 137.49, 129.81, 127.37, 126.89, 126.81, 123.71, 123.63, 108.91, 108.86, 106.46, 69.71, 69.28, 69.25, 31.82, 29.46, 29.40, 25.99, 25.96, 22.81, 22.79, 14.21, 14.19.

HRMS (ESI⁺): calculated for C₄₉H₇₀N₃O₇ 780.5310, found 780.5331.

N,N-diethyl-2,3,6,7-tetakis(octyloxy)dibenzo[a,c]phenazine-11-carboxamide (dEt(8)), a yellow solid (80% yield);

¹H NMR (400 MHz, CDCl₃, 56 mM) δ 8.76 (s, 1H), 8.71 (s, 1H), 8.32 (d, J = 8.7 Hz, 1H), 8.27 (d, J = 1.6 Hz, 1H), 7.79 (dd, J = 8.6, 1.8 Hz, 1H), 7.69 (d, J = 5.3 Hz, 2H), 4.33 (q, J = 6.5 Hz, 4H), 4.27 (td, J = 6.5, 2.1 Hz, 4H), 3.66 (s, 2H), 3.41 (s, 2H), 2.05 – 1.90 (m, 8H), 1.67 – 1.52 (m, 8H), 1.51 – 1.10 (m, 38H), 0.90 (t, J = 6.8 Hz, 12H).

¹³C NMR (126 MHz, CDCl₃, 56 mM) δ 170.58, 152.12, 152.07, 149.54, 142.63, 142.56, 141.48, 140.93, 137.48, 129.80, 127.37, 126.89, 126.79, 123.70, 123.63, 108.93, 108.87, 106.48, 69.72, 69.29, 69.27, 32.01, 32.00, 29.62, 29.52, 29.49, 29.48, 29.46, 26.34, 26.33, 26.31, 22.85, 22.84, 14.27, 14.26.

HRMS (ESI⁺): calculated for C₅₁H₈₆N₃O₅ 892.6562, found 892.6575.
N,N-diethyl-2,3,6,7-tetrakis(decyloxy)dibenzo[a,c]phenazine-11-carboxamide (dEt(10)), a yellow solid (42% yield);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 44 mM) \(\delta\) 8.76 (s, 1H), 8.72 (s, 1H), 8.32 (d, \(J = 8.8\) Hz, 1H), 8.28 (d, \(J = 1.5\) Hz, 1H), 7.79 (dd, \(J = 8.6, 1.8\) Hz, 1H), 7.70 (d, \(J = 4.4\) Hz, 2H), 4.33 (q, \(J = 6.5\) Hz, 4H), 4.28 (td, \(J = 6.5, 1.8\) Hz, 4H), 3.66 (s, 2H), 3.41 (s, 2H), 2.06 – 1.88 (m, 8H), 1.72 – 1.52 (m, 8H), 1.52 – 1.09 (m, 54H), 0.89 (t, \(J = 6.8\) Hz, 12H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 44 mM) \(\delta\) 170.59, 152.13, 152.08, 149.56, 142.64, 142.58, 141.49, 140.94, 137.49, 129.81, 127.38, 126.90, 126.81, 123.71, 123.65, 108.95, 108.89, 106.50, 69.74, 69.30, 69.28, 32.08, 29.85, 29.77, 29.68, 29.66, 29.54, 29.46, 26.32, 22.85, 14.27.

HRMS (ESI\(^+\)): calculated for C\(_{65}\)H\(_{102}\)N\(_3\)O\(_5\) 1004.7814, found 1004.7825.

N,N-diethyl-2,3,6,7-tetrakis(dodecyloxy)dibenzo[a,c]phenazine-11-carboxamide (dEt(12)), a yellow solid (62% yield);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 45 mM) \(\delta\) 8.76 (s, 1H), 8.73 (s, 1H), 8.32 (d, \(J = 8.7\) Hz, 1H), 8.28 (d, \(J = 1.7\) Hz, 1H), 7.79 (dd, \(J = 8.6, 1.8\) Hz, 1H), 7.70 (d, \(J = 4.0\) Hz, 2H), 4.33 (q, \(J = 6.5\) Hz, 4H), 4.28 (td, \(J = 6.4, 1.6\) Hz, 4H), 3.66 (s, 2H), 3.41 (s, 2H), 2.06 – 1.90 (m, 8H), 1.66 – 1.53 (m, 8H), 1.53 – 1.10 (m, 70H), 0.88 (t, \(J = 6.8\) Hz, 12H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 45 mM) \(\delta\) 170.57, 151.97, 151.92, 149.38, 142.55, 142.49, 141.39, 140.85, 137.37, 129.79, 127.33, 126.30, 126.70, 123.55, 123.46, 108.63, 108.57, 106.50, 69.74, 69.30, 69.28, 32.08, 29.85, 29.77, 29.68, 29.66, 29.54, 29.46, 29.41, 26.33, 26.30, 22.85, 14.30.

HRMS (ESI\(^+\)): calculated for C\(_{73}\)H\(_{118}\)N\(_3\)O\(_5\) 1116.9066, found 1116.9044.

N-butyl-2,3,6,7-tetrakis(hexyloxy)dibenzo[a,c]phenazine-11-carboxamide (HBu(6)), a yellow solid (57% yield);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 13 mM) \(\delta\) 8.71 (d, \(J = 4.0\) Hz, 2H), 8.58 (d, \(J = 1.7\) Hz, 1H), 8.33 (d, \(J = 8.8\) Hz, 1H), 8.21 (dd, \(J = 8.8, 1.9\) Hz, 1H), 7.66 (s, 1H), 7.65 (s, 1H), 6.50 (t, \(J = 5.6\) Hz, 1H), 4.40 – 4.19 (m, 8H), 3.59 (q, \(J = 6.7\) Hz, 2H), 2.04 – 1.91 (m, 8H), 1.77 – 1.55 (m, 10H), 1.55 – 1.33 (m, 18H), 1.02 (t, \(J = 7.3\) Hz, 3H), 0.99 – 0.88 (m, 12H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 73 mM) \(\delta\) 167.66, 151.91, 151.70, 149.28, 149.13, 142.48, 142.34, 142.20, 140.35, 135.01, 129.48, 127.53, 127.15, 126.60, 126.41, 123.29, 123.13, 108.47, 108.42, 106.03, 105.78, 69.56, 69.42, 69.12, 69.03, 40.31, 32.02, 31.89, 31.87, 29.54, 29.51, 29.47, 26.06, 26.03, 26.02, 25.99, 22.84, 22.82, 20.46, 14.23, 14.21, 14.02.

HRMS (ESI\(^+\)): calculated for C\(_{49}\)H\(_{70}\)N\(_3\)O\(_5\) 780.5310, found 780.5303.
N-butyl-2,3,6,7-tetrakis(octyloxy)dibenzo[a,c]phenazine-11-carboxamide (HBu(8)), a yellow solid (62% yield);

$^1$H NMR (400 MHz, CDCl$_3$, 49 mM) $\delta$ 8.41 (s, 2H), 8.36 (s, 1H), 8.14 (d, $J = 8.7$ Hz, 1H), 8.11 (dd, $J = 8.8$, 1.6 Hz, 1H), 7.43 (s, 1H), 7.36 (s, 1H), 6.76 (t, $J = 5.6$ Hz, 1H), 4.32 – 4.10 (m, 8H), 3.59 (q, $J = 6.7$ Hz, 2H), 2.07 – 1.88 (m, 8H), 1.82 – 1.68 (m, 2H), 1.67 – 1.26 (m, 42H), 1.04 (t, $J = 7.4$ Hz, 3H), 0.92 (d, $J = 6.8$ Hz, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$, 49 mM) $\delta$ 167.61, 151.97, 151.76, 149.33, 149.19, 142.52, 142.36, 142.24, 140.37, 135.04, 129.50, 127.52, 127.20, 126.66, 126.47, 123.32, 123.17, 108.55, 108.49, 106.12, 105.87, 32.06, 32.03, 29.72, 29.70, 29.59, 29.54, 26.42, 26.38, 26.35, 22.88, 22.86, 20.46, 14.28, 14.27, 14.02.

HRMS (ESI$^+$): calculated for C$_{57}$H$_{86}$N$_3$O$_5$ 892.6562, found 892.6596.

N-butyl-2,3,6,7-tetrakis(decyloxy)dibenzo[a,c]phenazine-11-carboxamide (HBu(10)), a yellow solid (53% yield);

$^1$H NMR (500 MHz, CDCl$_3$, 35 mM) $\delta$ 8.58 (d, $J = 2.8$ Hz, 2H), 8.48 (d, $J = 1.6$ Hz, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 8.17 (dd, $J = 8.8$, 1.8 Hz, 1H), 7.56 (s, 1H), 7.52 (s, 1H), 6.61 (t, $J = 5.6$ Hz, 1H), 4.32 – 4.17 (m, 8H), 3.59 (q, $J = 6.7$ Hz, 2H), 2.05 – 1.89 (m, 8H), 1.73 (dt, $J = 14.9$, 7.4 Hz, 2H), 1.65 – 1.55 (m, 8H), 1.55 – 1.20 (m, 50H), 1.03 (t, $J = 7.4$ Hz, 3H), 0.89 (t, $J = 6.7$ Hz, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$, 35 mM) $\delta$ 167.68, 151.89, 151.67, 149.33, 149.19, 142.43, 142.32, 142.16, 140.33, 135.01, 129.46, 127.53, 127.13, 126.57, 126.38, 123.28, 123.11, 108.46, 108.41, 106.05, 105.75, 69.58, 69.41, 69.12, 69.02, 40.31, 32.11, 32.04, 29.92, 29.84, 29.80, 29.77, 29.63, 29.62, 29.58, 26.44, 26.40, 26.37, 22.86, 20.47, 14.26, 14.03.

HRMS (ESI$^+$): calculated for C$_{65}$H$_{102}$N$_3$O$_5$ 1004.7814, found 1004.7834.

N-butyl-2,3,6,7-tetrakis(dodecyloxy)dibenzo[a,c]phenazine-11-carboxamide (HBu(12)), a yellow solid (71% yield);

$^1$H NMR (400 MHz, CDCl$_3$, 19 mM) $\delta$ 8.58 (d, $J = 4.3$ Hz, 2H), 8.49 (s, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 8.17 (dd, $J = 8.8$, 1.8 Hz, 1H), 7.56 (s, 1H), 7.52 (s, 1H), 6.63 (t, $J = 5.6$ Hz, 1H), 4.25 (ddt, $J = 17.9$, 13.1, 6.5 Hz, 8H), 3.59 (q, $J = 6.7$ Hz, 2H), 2.05 – 1.90 (m, 8H), 1.73 (dd, $J = 8.4$, 6.1 Hz, 2H), 1.67 – 1.20 (m, 74H), 1.03 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 12H).

$^{13}$C NMR (126 MHz, CDCl$_3$, 116 mM) $\delta$ 167.81, 151.76, 151.52, 149.14, 148.94, 142.16, 142.06, 141.86, 140.09, 135.01, 129.26, 127.47, 127.06, 126.41, 126.21, 123.06, 122.85, 108.28, 105.87, 105.50, 69.49, 69.29, 69.04, 68.92, 40.33, 32.10, 32.06, 29.96, 29.94,

HRMS (ESI\(^{+}\)): calculated for \(C_{73}H_{118}N_{3}O_{5}\) 1116.9066, found 1116.9035.

\(^1\text{H}\text{ NMR spectra of dEt(n) and HBu(n)} (n = 6-12)\)

![NMR spectrum image]

**Figure S1.** \(^1\text{H}\) NMR spectrum of dEt(6) measured at 54 mM in CDCl\(_3\).
Figure S2. $^1$H NMR spectrum of dEt(8) measured at 56 mM in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of dEt(10) measured at 44 mM in CDCl$_3$. 
Figure S4. $^1$H NMR spectrum of dEt(12) measured at 45 mM in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of HBu(6) measured at 48 mM in CDCl$_3$. 
Figure S6. $^1$H NMR spectrum of HBu(8) measured at 73 mM in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of HBu(10) measured at 9.6 mM in CDCl$_3$. 
Figure S8. $^1$H NMR spectrum of HBu(12) measured at 19 mM in CDCl$_3$. 
$^{13}$C NMR spectra of dEt(n) and HBu(n) (n =6-12).

Figure S9. $^{13}$C NMR spectrum of dEt(6) measured at 54 mM in CDCl$_3$.

Figure S10. $^{13}$C NMR spectrum of dEt(8) measured at 56 mM in CDCl$_3$. 
Figure S11. $^{13}$C NMR spectrum of dEt(10) measured at 44 mM in CDCl$_3$.

Figure S12. $^{13}$C NMR spectrum of dEt(12) measured at 45 mM in CDCl$_3$. 
Figure S13. $^{13}$C NMR spectrum of HBu(6) measured at 73 mM in CDCl$_3$.

Figure S14. $^{13}$C NMR spectrum of HBu(8) measured at 49 mM in CDCl$_3$. 

Figure S15. $^{13}$C NMR spectrum of HBu(10) measured at 53 mM in CDCl$_3$.

Figure S16. $^{13}$C NMR spectrum of HBu(12) measured at 116 mM in CDCl$_3$. 
Figure S17. Experimental isotropic patterns of dEt(6) (Top two patterns) and theoretical isotopic pattern (bottom) for [C_{49}H_{70}N_{3}O_{5}]^{+} ([dEt(6) + H]^{+}) in the ESI-MS measurement.
Figure S18. Experimental isotropic patterns of dEt(8) (Top two patterns) and theoretical isotopic pattern (bottom) for $[C_{57}H_{86}N_3O_5]^+$ ([dEt(8) + H]$^+$) in the ESI-MS measurement.
Figure S19. Experimental isotropic patterns of dEt(10) (top three patterns) and theoretical isotopic pattern (bottom) for [C_{65}H_{102}N_{3}O_{5}]^{+} ([dEt(10) + H]^{+}) in the ESI-MS measurement.
Figure S20. Experimental isotropic patterns of dEt(12) (top three patterns) and theoretical isotopic pattern (bottom) for [C$_{73}$H$_{118}$N$_3$O$_5$]$^+$ ([dEt(12) + H]$^+$) in the ESI-MS measurement.
Figure S21. Experimental isotropic patterns of HBu(6) (top two patterns) and theoretical isotopic pattern (bottom) for [C_{48}H_{70}N_{3}O_{3}]^{+} ([HBu(6) + H]^{+}) in the ESI-MS measurement.
Figure S22. Experimental isotropic patterns of HBu(8) (top two patterns) and theoretical isotopic pattern (bottom) for $[C_{57}H_{86}N_3O_5]^+$ ([HBu(8) + H]$^+$) in the ESI-MS measurement.
Figure S23. Experimental isotropic patterns of HBu(10) (top three patterns) and theoretical isotopic pattern (bottom) for \([C_{65}H_{102}N_3O_5]^+ ([HBu(10)+H]^+)\) in the ESI-MS measurement.
Figure S24. Experimental isotropic patterns of $\text{HBu(12)}$ (top three patterns) and theoretical isotopic pattern (bottom) for $[C_{73}H_{118}N_{3}O_{5}]^+$ ([$\text{HBu(12)} + \text{H}$]$^+$) in the ESI-MS measurement.
$^1$H NMR spectra of HBu(8) in the presence of triethylamine.

$^1$H NMR spectra of HBu(8) were measured at several concentrations (19, 58, 116 mM) in the presence of three equivalent of triethyl amine. When the aggregation of HBu(8) occurs via impure protons, the presence of triethylamine is expected to change the chemical shifts and shape of the signals at the aromatic regions. However, the spectra at each concentration was almost the same with that measured without triethyl amine, ruling out the possibility that aggregate proceeds via impure protons.

![Figure S25. Aromatic region of the $^1$H NMR spectra of HBu(8) at various concentrations (19, 58, and 116 mM) with 3 equiv. of triethylamine in CDCl$_3$.](image-url)
2D NMR spectroscopy and peak assignments.

Peaks in the aromatic region of the $^1$H NMR spectra of dEt(n) and HBu(n) (n=6-12) were assigned using 2D NMR spectroscopy. $^1$H NMR spectra of dEt(n) were almost identical between 3 and 9 ppm regardless the concentration. For the case of dEt(n) series, a full proton assignment using COSY, HMBC and HSQC spectra was only carried out only for dEt(6) and dEt(8), but it is assumed to apply to the other dEt(n) compounds. Full assignments were carried out for each of HBu(n) series and were found to be identical.

Figure S26. Proton labels for molecules in dEt(n) and HBu(n) series.

Figure S27. Aromatic region of the $^1$H NMR spectra with numbered peaks for a) dEt(6) at 60 mM in CDCl$_3$, b) HBu(8) at 245 mM in CDCl$_3$, and HBu(8) at 49 mM in CDCl$_3$. 
Assignment for dEt(6) at 60 mM

The two broad singlets observed around 3.5 ppm correspond to the two CH\textsubscript{2} groups of the diethyl. Peak 4, the singlet, can be straightforwardly assigned as proton Ha, while the doublet (peak 3) and doublet doublet (peaks 5), are H\textsubscript{b} or H\textsubscript{c}. The four remaining peaks, singlets 1, 2, 6 and 7, correspond to the four protons on the phenanthrene moiety (H\textsubscript{d}, H\textsubscript{e}, H\textsubscript{f} or H\textsubscript{g}). The COSY spectrum shows strong coupling between peak 3 and 4 and weak coupling between peak 3 and 5. It follows that doublet doublet 5 is H\textsubscript{b} and doublet 3 is H\textsubscript{c}, since these H\textsubscript{b} is closer to H\textsubscript{a}. Protons H\textsubscript{c} and H\textsubscript{f} are in a very similar environment, as are protons H\textsubscript{d} and H\textsubscript{g}. Two singlets (peaks 1 and 2) are assigned to H\textsubscript{d} and H\textsubscript{g} from the analogy of the assignment in 3 based on ROESY spectrum. Other two singlets (peaks 6 and 7) are assigned to H\textsubscript{e} and H\textsubscript{f}. HSQC spectrum shows that Peaks 1 and 2 are coupled with two carbons with similar chemical shifts (108.97 and 108.88 ppm), again showing that they are in a very similar environment. In the HMBC spectrum, the carbonyl peak (170.5 ppm) couples with peaks 4 and 5, which confirms their assignment as H\textsubscript{a} and H\textsubscript{b}, respectively. Discrimination between H\textsubscript{e} and H\textsubscript{f} and between H\textsubscript{d} and H\textsubscript{g} was impossible from these experimental results.

Figure S28. COSY spectrum of dEt(6) at 60 mM in CDCl\textsubscript{3}.
Figure S29. HSQC spectrum of dEt(6) at 60 mM in CDCl₃.

Figure S30. HMBC spectrum of dEt(6) at 60 mM in CDCl₃.
Assignment for HBu(8) at 245 mM

The triplet peak 7 can be assigned as the proton on the NH group. Peak 4, the triplet, should be proton H_b, while the doublets 1 and 2 correspond to protons H_a or H_c. Peak 1, the singlet, can be straightforwardly assigned as proton H_a, while the doublet doublet (peak 4) and doublet (peaks 5), are H_b or H_c. The four remaining peaks, singlets 2, 3, 6 and 8, correspond to the four protons on the phenanthrene moiety (H_d, H_e, H_f or H_g). The COSY spectrum shows strong coupling between peak 4 and 5 and weak coupling between peak 1 and 4. It follows that doublet doublet 4 is H_b and doublet 5 is H_c, since these H_b is closer to H_a. Two singlets (peaks 2 and 3) are assigned to H_d and H_g as the cases of HBu(6). Other two singlets (peaks 6 and 7) are assigned to H_e and H_f. In the HSQC spectrum, peak 6 and 8 are coupled with the carbon peaks at 105.7 and 105.2 ppm, respectively. In contrast, peak 2 and 3 are coupled with the carbon peak at 108.0. The results indicates that environmental difference between H_e and H_f are slightly larger than that of H_d and H_g. In the HMBC spectrum, the carbonyl peak (168.0 ppm) couples with peaks 1 and 5, which confirms their assignment as H_a and H_b, respectively. Discrimination between H_e and H_f and between H_d and H_g was impossible from these experimental results.

Figure S31. COSY spectrum of HBu(8) at 245 mM in CDCl_3.
Figure S32. HSQC spectrum of HBu(8) at 245 mM in CDCl₃.

Figure 33. HMBC spectrum of HBu(8) at 245 mM in CDCl₃.
Assignment for HBu(8) at 49 mM

The assignment could be performed similarly with case at 245 mM. Major difference of the spectra at 245 and 49 mM is the position of H_b and H_c. From the $^1$H NMR and COSY spectra, the peaks 4 and 5 are assigned to H_c and H_b, respectively. The coupling between carbonyl peak (167.6 ppm) with peaks 3 and 5 in the HMBC spectrum confirms the assignment of H_a and H_b.

**Figure S34.** COSY spectrum of HBu(8) at 49 mM in CDCl$_3$. 
Figure S35. HSQC spectrum of HBu(8) at 49 mM in CDCl₃.

Figure S36. HMBC spectrum of HBu(8) at 49 mM in CDCl₃.
$^1$H NMR dilution experiments and analysis

Dilution experiments were performed on all molecules in series $\text{dEt}(n = 6-12)$ and $\text{HBu}(n = 6-12)$. A stock solution of the desired compound was prepared in deuterated chloroform (0.045 – 0.056 M for $\text{dEt}(n = 6-12)$, 0.106 – 0.245 M for $\text{HBu}(n = 6-12)$). Samples at various concentrations were prepared by mixing the stock solution with additional deuterated chloroform placed in a vial. $^1$H NMR spectra of $\text{dEt}(n = 6-12)$ show no significant variation with concentration, while those of $\text{HBu}(n = 6-12)$ show explicit upfield shifts with the increase of the concentration.

In order to fit the data to the isodesmic model, the chemical shift of each proton on the monomer had to be estimated. This was done by linear regression on the first two or three data points for each curve. Results were always very close to the values obtained at the lowest measured concentration. Once chemical shifts of the monomer were obtained for $\text{HBu}(n = 6-12)$, the difference in chemical shift ($\delta_M - \delta$) was plotted against concentration. The plots were fitted to the equation (1) using Origin 2019b. Equilibrium constant was set to equal in every proton.

![Figure S37. Aromatic region of the $^1$H spectra of $\text{dEt}(8)$ measured at 56, 19, and 6.2 mM in CDCl$_3$.](image-url)
Figure S38. Aromatic region of the $^1$H spectra of dEt(8) measured at 56, 19, and 6.2 mM in CDCl$_3$.

Figure S39. Aromatic region of the $^1$H spectra of dEt(10) measured at 44, 15, and 5.0 mM in CDCl$_3$. 
Figure S40. Aromatic region of the $^1$H spectra of dEt(12) measured at 45, 15, and 5.0 mM in CDCl$_3$.

Figure S41. Aromatic region of the $^1$H spectra of HBu(6) measured at various concentrations from 0.2 to 222 mM in CDCl$_3$. 
**Figure S42.** Aromatic region of the $^1$H spectra of HBu(8) measured at various concentrations from 0.5 to 245 mM in CDCl$_3$.

**Figure S43.** Aromatic region of the $^1$H spectra of HBu(10) measured at various concentrations from 0.8 to 106 mM in CDCl$_3$. 
Figure S44. Aromatic region of the $^1$H spectra of HBu(12) measured at various concentrations from 0.9 to 116 mM in CDCl$_3$.

Figure S45. Changes in chemical shift versus concentration in CDCl$_3$ for HBu(8). Fitting curves were calculated based on the isodesmic model.
Figure S46. Changes in chemical shift versus concentration in CDCl₃ for HBu(10). Fitting curves were calculated based on the isodesmic model.

Figure S47. Changes in chemical shift versus concentration in CDCl₃ for HBu(12). Fitting curves were calculated based on the isodesmic model.
Table S1. Maximal chemical shifts of aromatic (Hₐ-g) and NH protons for the solute in an aggregate, equilibrium constant ($K_d$), and chi-square obtained from the fitting for HBU(n) (n = 6-12). Letters refer to labels shown in Figure S26.

<table>
<thead>
<tr>
<th></th>
<th>Hₐ</th>
<th>Hₖ</th>
<th>Hₗ</th>
<th>Hₘ</th>
<th>Hₙ</th>
<th>NH</th>
<th>Kₚ</th>
<th>Residual sum of $\chi^2$</th>
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<tr>
<td>HBU(6)</td>
<td>7.11</td>
<td>7.49</td>
<td>7.06</td>
<td>6.77</td>
<td>6.05</td>
<td>5.82</td>
<td>6.77</td>
<td>8.08</td>
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<tr>
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<td>7.72</td>
<td>7.45</td>
<td>7.45</td>
<td>7.45</td>
<td>6.51</td>
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<tr>
<td>HBU(10)</td>
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<td>7.75</td>
<td>7.44</td>
<td>7.63</td>
<td>6.89</td>
<td>6.71</td>
<td>7.62</td>
<td>7.15</td>
</tr>
<tr>
<td>HBU(12)</td>
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<td>7.90</td>
<td>7.68</td>
<td>7.93</td>
<td>7.14</td>
<td>7.00</td>
<td>7.93</td>
<td>6.99</td>
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Single crystal X-ray diffraction study

The crystal structure of dEt(6) was determined by the single-crystal X-ray diffraction method. A Rigaku XtaLAB Synergy-S (Cu-Kα radiation) with a HyPix-6000 area detector was used for the data collection. The structures were solved using the program SHELXT. The refinement and all further calculations were carried out using the program SHELXL via OLEX2. All H atoms were generated geometrically.

<table>
<thead>
<tr>
<th>Table S2</th>
<th>Crystallographic and experimental data for dEt(6).</th>
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<tr>
<td><strong>Compound</strong></td>
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<tr>
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<tr>
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<tr>
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<tr>
<td>b / Å</td>
<td>12.3684(3)</td>
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<tr>
<td>c / Å</td>
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<tr>
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<td>β / °</td>
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<td>T / K</td>
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<tr>
<td>( bW(R_2) ) (all data)</td>
<td>0.1974</td>
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</table>

\[ aR_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad bW(R_2) = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}. \]
**Figure S48.** DSC trace (1st scan) for dEt(6) with a heating and cooling rate of 10 °C min⁻¹.

**Figure S49.** DSC trace (1st scan) for dEt(8) with a heating and cooling rate of 10 °C min⁻¹.
**Figure S50.** DSC trace (1st scan) for dEt(10) with a heating and cooling rate of 10 °C min⁻¹.

**Figure S51.** DSC trace (1st scan) for dEt(12) with a heating and cooling rate of 10 °C min⁻¹.
Figure S52. DSC trace (1st scan) for HBu(6) with a heating and cooling rate of 10 °C min⁻¹.

Figure S53. DSC trace (1st scan) for HBu(8) with a heating and cooling rate of 10 °C min⁻¹.
**Figure S54.** DSC trace (1st scan) for HBu(10) with a heating and cooling rate of 10 °C min⁻¹.

**Figure S55.** DSC trace (2nd scan) for HBu(10) with a heating and cooling rate of 10 °C min⁻¹.
Figure S56. DSC trace (3rd scan) for HBu(10) with a heating and cooling rate of 10 °C min⁻¹.

Figure S57. DSC trace (1st scan) for HBu(12) with a heating and cooling rate of 10 °C min⁻¹.
**Figure S58.** DSC trace (2nd scan) for HBu(12) with a heating and cooling rate of 10 °C min⁻¹.

**Figure S59.** DSC trace (3rd scan) for HBu(12) with a heating and cooling rate of 10 °C min⁻¹.
Figure S60. Representative textures observed by optical microscopy for (1a) dEt(6), (1b) dEt(8), (1c) dEt(10), (1d) dEt(12), (2a) HBu(6), (2b) HBu(8), (2c) HBu(10), (2d) HBu(12) at 1–6 °C below the clearing temperatures on cooling from the isotropic liquid. All images were taken with polarizers uncrossed.
Figure S61. XRD patterns of dibenzophenazines with diethyl amides: dEt(6) measured at 135°C, dEt(8) at 135°C, dEt(10) at 120°C, and dEt(12) at 110°C.
Figure S62. XRD patterns of dibenzophenazines with butyl amides: HBu(6) measured at 120°C, HBu(8) at 115°C, HBu(10) at 115°C, and HBu(12) at 150°C.
References