Electronic Supplementary Information

Thermodynamic insights into the entropically driven self-assembly of amphiphilic dyes in water

Pradeep P.N. Syamala, Bartolome Soberats, Daniel Görl, Stephan Gekle*, Frank Würthner*

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1. Materials and methods

General: Reagents were purchased from commercial suppliers and used as received without further purification. Solvents were distilled and dried according to standard procedures. Gravity column chromatography was performed with commercial glass columns using silica gel 60M (particle size 0.04-0.063 mm) as stationary phase, whereas flash coloumn chromatrography was carried out with PuriFlash 420 system from *Interchim* using commercially available silica gel columns from *Interchim* (PF-30SIHP-F0025). NMR spectra were recorded on an Avance III HD (400 MHz or 600 MHz) from Bruker at 295 K. The spectra were calibrated to the residual protic solvent peak and the chemical shifts (δ) are recorded in parts per million (ppm). Multiplicities for proton signals are abbreviated as s, t, quint and m for singlet, triplet, quintet and multiplet, respectively. High resolution mass spectra (HRMS) were recorded with microTOF focus (Bruker Daltonics, Germany).

Sample Preparation: Samples were prepared in either MilliQ-water or D_2O (99.95%, Deutero) which was first filtered using a 0.45 μ m syringe filter (Rotilabo, Carl Roth). The required amount of NBI derivative was weighed and the corresponding solvent was added to it to obtain the desired concentration. These were dissolved first by sonication, followed by vortexing. To ensure complete dissolution, all the samples were stored in a refrigerator at 4 °C for several hours and equilibrated afterwards to the required temperature before the measurements.

UV-vis spectroscopy: UV-vis absorption spectra were recorded using a Perkin-Elmer Lambda 40P and JASCO V-770 spectrophotometer. The measurements were carried out in quartz cuvettes using either spectroscopic grade chloroform or deionized water prepared by water purification system PURELAB classic (ELGA, France). Temperature control was accomplished by Perkin Elmer PTP-1+1 and JASCO PAC-743R Peltier systems. Extinction coefficients were calculated from Lambert-Beer's law and are density corrected in the case of temperature-dependent measurements.

Cloud points were determined by temperature-dependent transmittance measurements at 800 nm using JASCO V-770 spectrophotometer and is referred to the temperature at which the transmittance is 90% of the initial transmittance. Heating rate was 0.1 °C/min.

Isothermal titration calorimetry (ITC): ITC measurements were performed using MicroCal VP-ITC (GE Healthcare, USA). Stirring rate was 307 rpm and the injection volume was 5 μ L. The stock solutions as well as solvent (water) was degassed by applying vacuum before the measurements. The temperature of the sample solutions and water was adjusted to respective temperature prior to the measurement using a MicroCal ThermoVac (GE Healthcare, USA). The enthalpograms were derived by integrating the raw heat signals and were fitted with I2-ITC package.^{1, 2}

Atomic force microscopy (AFM): AFM measurements were performed under ambient conditions using a Bruker Multimode 8 SPM system operating in tapping mode in air. Silica cantilevers (OMCL-AC200TS, Olympus) with a resonance frequency of ~150 kHz and a spring constant of ~10 N m⁻¹ were used. The samples were prepared by spin-coating of aqueous NBI solutions onto silicon wafer with 2000 rpm.

Dynamic light scattering (DLS): DLS measurements were performed at room temperature on a Beckman Coulter N5 submicron particle analyzer equipped with a 25mW Helium-Neon Laser (632.8 nm) using 10 mm Hellma quartz cuvettes.

2. Determination of thermodynamic parameters

Isodesmic model

In isodesmic model, one dimensional aggregation is assumed to proceed via same binding constant and free energy of aggregation for each monomer added to the growing chain.³ The equilibrium between monomer and aggregate for such a system can be denoted as,

$$M + M \stackrel{K_2}{\rightleftharpoons} M_2$$
$$M_2 + M \stackrel{K_3}{\rightleftharpoons} M_3$$
$$\dots$$
$$M_{n-1} + M \stackrel{K_n}{\rightleftharpoons} M_n$$

For isodesmic model, $K_2 = K_3 = \cdots K_n$.

The molar fraction of aggregated species (α_{agg}) for such a system can be denoted as,

$$\alpha_{\rm agg} = 1 - \frac{2Kc_{\rm T} + 1 - \sqrt{4Kc_{\rm T} + 1}}{2K^2 c_{\rm T}^2} \tag{1}$$

where K is the aggregation constant and $c_{\rm T}$ is the total concentration of molecules. $\alpha_{\rm agg}$ can be expressed in terms of apparent extinction coefficient at a given dye concentration ($\bar{\epsilon}(c_{\rm T})$) as

$$\alpha_{\text{agg}} = \frac{\bar{\varepsilon}(c_{\text{T}}) - \varepsilon_{\text{mon}}}{\varepsilon_{\text{agg}} - \varepsilon_{\text{mon}}}$$
(2)

where $\varepsilon_{\rm mon}$ and $\varepsilon_{\rm agg}$ are the extinction coefficients of the aggregated and monomeric species, respectively. Combining eqn (1) and (3), the apparent extinction coefficient at a given dye concentration, $\bar{\varepsilon}(c_{\rm T})$, can be expressed as,

$$\bar{\varepsilon}(c_{\rm T}) = \varepsilon_{\rm agg} + (\varepsilon_{\rm mon} - \varepsilon_{\rm agg}) \frac{2Kc_{\rm T} + 1 - \sqrt{4Kc_{\rm T} + 1}}{2K^2 c_{\rm T}^2}$$
(3)

S3

By fitting plot of $\bar{\varepsilon}(c_{\rm T})$ at a specific wavelength with respect to concentration $c_{\rm T}$ using eqn (3), corresponding binding constant at a particular temperature can be determined. The Gibbs free energy of association, $\Delta G_{\rm ass}$ is computed using the following equation.

$$\Delta G_{\rm ass} = -R \mathrm{Tln} K_{\rm ass} \tag{4}$$

where R is the universal gas constant, T is the temperature and K_{ass} , the association constant.

Goldstein-Stryer model

The anti-cooperativity process is described using the Goldstein-Stryer model, which combines the formation of a nucleus with size 's' and further aggregation into larger structures.⁴ The cooperativity factor σ is defined as the ratio of binding constants for nucleus formation (K_s) and further elongation (K_e).

$$\sigma = \frac{K_{\rm s}}{K_{\rm e}} \tag{5}$$

For $\sigma = 1$, the process is considered as isodesmic, for $\sigma < 1$ cooperative and $\sigma > 1$ anti-cooperative. An anti-cooperative process can be evaluated via the Goldstein-Stryer model using the following equation.

$$K_{e}c_{T} = \sum_{n=1}^{s} n\sigma^{n-1} (K_{e}c_{1})^{n} + \sum_{s=1}^{\infty} n\sigma^{s-1} (K_{e}c_{1})^{n} = \frac{s(K_{e}c_{1})^{s}\sigma^{s-1}}{1-K_{e}c_{1}} + \frac{(K_{e}c_{1})^{s+1}\sigma^{s-1}}{(1-K_{e}c_{1})^{2}} + \frac{K_{e}c_{1}(s(\sigma K_{e}c_{1})^{s-1}-1)}{\sigma K_{e}c_{1}-1} - \frac{s(K_{e}c_{1})^{2}\sigma^{s-1}((\sigma K_{e}c_{1})^{s-1}-1)}{(\sigma K_{e}c_{1}-1)^{2}}$$
(6)

where K_e is the elongation constant, σ is the cooperativity factor, c_1 is the monomeric concentration and c_T , the total concentration of dye molecules. Degree of aggregation, α_{agg} , can be expressed in terms of elongation constant, K_e , monomeric concentration, c_1 , and the total concentration of dye molecules, c_T , as

$$\alpha_{agg} = 1 - \alpha_{\rm mon} = 1 - \frac{K_{\rm e}c_1}{K_{\rm e}c_{\rm T}} \tag{7}$$

The Gibbs free energy of association, ΔG_{ass} , is computed using the following equation.

$$\Delta G_{\rm ass} = -R {\rm Tln} K_{\rm e} \tag{8}$$

where R is the universal gas constant, T is the temperature and K_e , the elongation constant.

3. Molecular Dynamics (MD) calculations

Force field creation

Force fields were derived based on the GROMOS 54A7 parameter set.⁵ Topology files for **NBI 1** and **NBI 3** were created using the Automated Topology Builder⁶ and are publicly available under the molecule IDs #246516 and #246528, respectively. Two additional dihedrals between the core and the attached phenyl rings were added manually so as to match the molecular potential energy during rotation of the dihedral with the DFT-derived values for a biphenyl system.⁷

Simulation procedure

Simulations were carried out using GROMACS⁸ in the NPT ensemble using a Nosé-Hoover thermostat and a Parrinello-Rahman barostat. Temperature was set to 300 K and pressure was maintained at 1 atmosphere. The time step was 1fs, electrostatic interactions were calculated using Particle-Mesh-Ewald summation. The box contained 4008 water molecules for the **NBI 1** monomer in Fig. 6b; 13998 water molecules for the **NBI 1** dimer in Fig. 6c; 3950 water molecules for the **NBI 3** monomer in Fig. 6e and 23705 water molecules for the **NBI 3** dimer in Fig. 6f. The SPC/E water model was used.

Density plots were averaged over 500ns for Fig. 6b; 210ns for Fig. 6c; 500ns for Fig. 6e and 150 ns for Fig. 6f.

Data analysis

To illustrate back-folding of the side chains, the time-averaged density of all carbon atoms in the side chains was determined in a body-fitted coordinate system centered around the naphthalene core (illustrated by the red circles in the density plots). To compute the stacking distance in Fig. S15, first the distance vector between the geometric centres of the two naphthalene cores was determined. In a stacked configuration, the two naphthalene cores are typically arranged parallel to each other such that this vector is almost, but not exactly, parallel to the normal vector with respect to either of the naphthalene planes. Fig. S15 shows the projection of the distance vector onto the normal vector to the first naphthalene plane. To compute the angle in Fig. S16, first the connection vector between the two nitrogen atoms of each naphthalene core was determined. Taking the scalar product between the two connecting vectors leads to the tilt angle shown in Fig. S16.

4. Synthetic procedures

NBI 1-3 were prepared according to the synthetic route depicted in Scheme S1. 2-Bromo-1,3-diiodo-5-nitrobenzene (**1**)⁹, 2,5,8,11-tetraoxatetradec-13-yne (**2**)¹⁰, 3,4,5-tri(3-(2-(2-methoxyethoxy)ethoxy) propyl)aniline (**4a**)¹¹ as well as 3,4,5-tri(2,5,8,11,14-pentaoxaheptadecan-17-yl)aniline (**4c**)¹² were synthesized according to literature procedures.



Scheme S1: Synthetic route to NBI 1-3.

14,14',14"-(5-Nitrobenzene-1,2,3-triyl) tris(2,5,8,11-tetraoxatetradec-13-yne) (3)

2-Bromo-1,3-diiodo-5-nitrobenzene (**1**, 7.0 g, 15.4 mmol) was dissolved in triethylamine (100 mL) and flushed with nitrogen for 10 minutes. Bis(triphenylphosphine)-palladium(II)-dichloride (1.05 g, 1.5 mmol) and copper(I) iodide (285 mg, 1.5 mmol) were added into the solution and flushed with nitrogen for another half hour. Compound **2** (8.0 g, 39.5 mmol) was then slowly added into the reaction mixture and stirred for 8 hours at room temperature. After the completion of reaction (monitored by TLC), another aliquot of bis(triphenylphosphine)-palladium(II)-dichloride (1.05 g, 1.5 mmol) and copper(I) iodide (285 mg, 1.5 mmol) were added into the reaction mixture and flushed with nitrogen for half hour, followed by the slow addition of **2** (4.5 g, 22.2 mmol). The reaction mixture was heated to 75 °C for one hour, and cooled down to room temperature and concentrated by rotary evaporation under reduced pressure. Subsequently, it was filtered through a silica plug by washing with ethyl acetate and methanol. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography, first with methanol (3%)/ethyl acetate and then with methanol (1.5%)/ dichloromethane to yield **3** as a dark viscous oil (3.7 g, 5.11 mmol, 33%).

¹H NMR (400 MHz, CDCl₃): δ = 8.18 (s, 2H), 4.51 (s, 2H), 4.45 (s, 4H), 3.80-3.73 (m, 6H), 3.69-3.60 (m, 28H), 3.53-3.50 (m, 6H), 3.348 (s, 6H), 3.346 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 146.3, 133.1,

127.1, 126.2, 98.8, 92.3, 82.8, 82.7, 71.9, 70.7, 70.65, 70.63, 70.60, 70.49, 70.46, 69.4, 69.3, 59.13, 59.11, 59.0 ppm. HRMS (ESI, positive, ACN/CHCl₃): *m/z* calcd for C₃₆H₅₃NO₁₄Na: 746.3363; found: 746.3382 [M+Na]⁺.

3,4,5-Tri(2,5,8,11-tetraoxatetradecan-14-yl)aniline (4b)

Compound **3** (1.10 g, 1.52 mmol) was dissolved in ethyl acetate (10 mL) and was transferred into an autoclave. Argon was purged through the solution for a minute and 1 g 10% Pd/C was added to the above solution. The reaction mixture was again purged with argon and then by hydrogen. The mixture was allowed to stir at room temperature for 4 days under H₂ atmosphere (10 bar). The reaction mixture was filtered over celite and washed with ethyl acetate and a few drops of methanol. The solution was concentrated by rotatory evaporation and the residue was purified by flash column chromatography (methanol (1%)/ ethyl acetate) to afford **4b** as a yellow oil (459 mg, 0.65 mmol, 42%).

¹H NMR (400 MHz, CDCl₃): δ = 6.40 (s, 2H), 6.68-3.46 (m, 42H), 3.37 (s, 9H), 2.59-2.51 (m, 6H), 1.86-1.79 (m, 4H), 1.73-1.66 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =144.0, 141.1, 128.0, 114.3, 71.9, 71.1, 70.7, 70.6, 70.5, 70.4, 70.1, 70.0, 59.0, 31.3, 31.0, 29.2, 24.2 ppm. HRMS (ESI, positive, MeOH/CHCl₃): *m/z* calcd for C₃₆H₆₈NO₁₂: 706.4742; found: 706.4755 [M+H]⁺.

N,*N*'-[3,4,5-Tris(3-(2-(2-methoxyethoxy)ethoxy)propyl)phenyl] naphthalene-1,4,5,8tetracarboxylic acid bisimide (NBI 1)

1,4,5,8-Naphthalenetetracarboxylic dianhydride (**5**, 31 mg, 0.11 mmol), 3,4,5-tris(3-(2-(2-methoxy)ethoxy)propyl)aniline (**4a**, 169 mg, 0.29 mmol) and acetic acid (5 mL) were charged into a pressure tube and heated at 110 °C for 12 h under nitrogen. After cooling to room temperature, the residue was extracted with water and DCM. The organic phase was washed with saturated sodium bicarbonate solution and brine, and dried with anhydrous sodium sulphate. The solvent was evaporated under vacuum and the residue was purified first by flash column chromatography (methanol (0.5%)/chloroform) and then by GPC to obtain **NBI 1** as a greenish yellow solid (55 mg, 0.04 mmol, 35%).

¹H NMR (400 MHz, CDCl₃): δ = 8.82 (s, 4H), 7.00 (s, 4H), 3.71-3.50 (m, 60 H), 3.40 (s, 6H), 3.34 (s, 12H), 2.77 (t, ³*J* = 7.6 Hz, 12H), 1.92 (quint, 8H, ³*J* = 7.0 Hz), 1.87-1.80 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.2, 141.7, 139.3, 132.1, 131.4, 127.28, 127.22, 126.7, 72.1, 72.0, 71.3, 70.87, 70.79, 70.78, 70.68, 70.65, 70.4, 70.2, 59.2, 59.1, 30.8, 30.7, 29.3, 25.2 ppm. HRMS (ESI, positive, ACN/CHCl₃): *m/z* calcd for C₇₄H₁₁₀N₂O₂₂Na: 1401.7447; found: 1401.7437 [M+Na]⁺. UV-vis (CHCl₃): λ_{max} = 381 nm (ε = 25800 M⁻¹ cm⁻¹), 361 nm (ε = 24500 M⁻¹ cm⁻¹).

N,*N*'-[3,4,5-Tri(2,5,8,11-tetraoxatetradecan-14-yl)phenyl] naphthalene-1,4,5,8tetracarboxylic acid bisimide (NBI 2)

NBI 2 was synthesized according to the procedure used for **NBI 1** by employing 29 mg (0.108 mmol) of **5** and 211 mg of aniline derivative **4b** (0.29 mmol). The crude product was purified first by flash column chromatography (methanol (1%)/chloroform) and then by GPC to obtain **NBI 2** as a yellow viscous oil (59 mg, 0.03 mmol, 33%).

¹H NMR (400 MHz, CDCl₃): δ = 8.80 (s, 4H), 6.97 (s, 4H), 3.70–3.48 (m, 84 H), 3.36 (s, 6H), 3.33 (s, 12H), 2.74 (t, ³*J* = 7.6 Hz, 12H), 1.90 (quint, 8H, ³*J* = 7.0 Hz), 1.85-1.77 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.0, 141.6, 139.2, 132.0, 131.3, 127.17, 127.11, 126.6, 71.98, 71.93, 71.1, 70.7, 70.69, 70.63, 70.61, 70.58, 70.53, 70.2, 70.1, 59.0, 30.7, 30.6, 29.2, 25.1 ppm. HRMS (ESI, positive, ACN/CHCl₃): *m/z* calcd for C₈₆H₁₃₄N₂O₂₈Na: 1665.9020; found: 1665.9020 [M+Na]⁺. UV-vis (CHCl₃): λ_{max} = 381 nm (ε = 26400 M⁻¹ cm⁻¹), 361 nm (ε = 25100 M⁻¹ cm⁻¹).

N,*N*'-[3,4,5-Tri(2,5,8,11,14-pentaoxaheptadecan-17-yl)phenyl] naphthalene-1,4,5,8tetracarboxylic acid bisimide (NBI 3)

NBI 3 was synthesized according to the procedure used for **NBI 1** by employing 27 mg (0.100 mmol) of **5** and 211 mg of aniline derivative **4c** (0.25 mmol). The crude product was purified first by flash column chromatography (methanol (1.5%)/chloroform) and then by GPC to obtain **NBI 3** as a yellow viscous oil (61 mg, 0.03 mmol, 32%).

¹H NMR (400 MHz, CDCl₃): δ = 8.81 (s, 4H), 6.99 (s, 4H), 3.69–3.51 (m, 108 H), 3.38 (s, 6H), 3.36 (s, 12H), 2.76 (t, ³*J* = 7.6 Hz, 12H), 1.92 (quint, 8H, ³*J* = 7.0 Hz), 1.85-1.80 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 163.1, 141.7, 139.2, 132.1, 131.4, 127.2, 127.1, 126.7, 72.02, 72.00, 71.2, 70.75, 70.70, 70.66, 70.63, 70.5, 70.3, 70. 1, 59.15, 59.13, 30.8, 30.6, 29.2, 25.2 ppm. HRMS (ESI, positive, ACN/CHCl₃): *m/z* calcd for C₉₈H₁₅₈N₂O₃₄Na: 1930.0593; found: 1930.0593 [M+Na]⁺. UV-vis (CHCl₃): λ_{max} = 381 nm (ε = 25900 M⁻¹ cm⁻¹), 361 nm (ε = 24500 M⁻¹ cm⁻¹).

5. Monomer UV-vis spectra



Fig. S1 UV-vis absorption spectra of monomeric NBIs in CHCl₃ at 25 °C: (a) **NBI 1** ($c = 3.1 \times 10^{-5}$ M), (b) **NBI 2** ($c = 6.6 \times 10^{-5}$ M) and (c) **NBI 3** ($c = 2.4 \times 10^{-5}$ M).



6. Temperature-dependent UV-vis experiments

Fig. S2 Temperature-dependent UV-vis spectra (density corrected) of (a) **NBI 2** ($c = 2.5 \times 10^{-4}$ M) and **NBI 3** ($c = 2.5 \times 10^{-4}$ M) in water. Arrows indicate spectral changes upon heating.

7. Dynamic light scattering (DLS)



Fig. S3 Unimodal size distribution from CONTIN analysis of the autocorrelation function of (a) **NBI 1** ($c = 1.0 \times 10^{-3}$ M), (b) **NBI 2** ($c = 1.0 \times 10^{-3}$ M) and (c) **NBI 3** ($c = 1.0 \times 10^{-3}$ M) in water at 25 °C from DLS experiments.

8. Atomic force microscopy (AFM)



Fig. S4 AFM height image of **NBI 2** (a, b) in water ($c = 1.6 \times 10^{-3}$ M) and corresponding cross-section analysis from the dashed green line in image (c). AFM height image of **NBI 3** (d, e) in water ($c = 1.6 \times 10^{-3}$ M) and corresponding cross-section analysis from the dashed green line in image (f).



9. Variable temperature concentration-dependent UV-vis experiments

Fig. S5 Concentration-dependent UV-vis spectra of **NBI 1** in water (density corrected) at (a) 10 °C, (b) 20 °C, (c) 30 °C, (d) 40 °C, and (e) 50 °C. Inset: Corresponding plot of fraction of aggregated species, α_{agg} , against concentration and analysis of the data based on the isodesmic model.



Fig. S6 Concentration-dependent UV-vis spectra of **NBI 2** in water (density corrected) at (a) 10 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C, (e) 40 °C, and (f) 50 °C. Inset: Corresponding plot of fraction of aggregated species, α_{agg} , against dimensionless product c (**NBI 2**) K_e and analysis of the data based on the Goldstein-Stryer model ($\sigma = 2$).



Fig. S7 Concentration-dependent UV-vis spectra of **NBI 3** in water (density corrected) at (a) 10 °C, (b) 20 °C, (c) 25 °C, (d) 30 °C, (e) 40 °C, and (f) 50 °C. Inset: Corresponding plot of fraction of aggregated species, α_{agg} , against dimensionless product c (**NBI 3**) K_e and analysis of the data based on the Goldstein-Stryer model (σ = 3).



Fig. S8 Plot of natural logarithm of association constant (ln K_{ass}) for (a) **NBI 2** and (b) **NBI 3** against reciprocal of temperature and corresponding fit according to Clarke-Glew equation.



Fig. S9 Determination of critical aggregation concentration (CAC) for (a) **NBI 1**, (b) **NBI 2** and (c) **NBI 3** from concentration-dependent UV-vis studies of the corresponding derivative (**NBI 1**: Fig. 3a, **NBI 2**: Fig. S6 c, and **NBI 3**: Fig. S7 c) at 25 °C in water. The inflection point corresponds to the CAC.

10. Isothermal titration calorimetry (ITC)



Fig. S10 Determination of critical aggregation concentration (CAC) for **NBI 1** from ITC dilution experiment at 25 °C in water. The inflection point corresponds to the CAC.

Table S1: Heat of dilution for ITC experiments of NBI 1 at different temperatures.

Temperature (°C)	10	20	25	30	40	50
∆H°_{dil}	0.18	-0.14	-0.45	-0.70	-1.27	-1.57
(kJ mol ^{−1})						



Fig. S11 Evolution of heat per injection of **NBI 1** in water at (a) 10 °C, (c) 20 °C, (e) 30 °C, (g) 40 °C, and (i) 50 °C. Corresponding enthalpograms at (b) 10 °C, (d) 20 °C, (f) 30 °C, (h) 40 °C, (j) 50 °C and fit according to isodesmic model (red line).



Fig. S12 (a) Evolution of heat per injection of **NBI 2** in water at 25 °C. (b) Corresponding enthalpogram and fit according to isodesmic model (red line).



Fig. S13 (a) Evolution of heat per injection of **NBI 3** in water at 25 °C. (b) Corresponding enthalpogram and fit according to isodesmic model (red line).

11. Molecular Dynamics (MD) studies



Fig. S14 Snapshot showing back-folding of glycol chains for (a) **NBI 1** and (b) **NBI 3** in stacked state from MD simulations (water molecules are omitted for clarity).



Fig. S15 Trajectory of stacking distance for NBI 1 (a) and NBI 3 (b).



Fig. S16 Tilt angle between naphthalene cores in the stacked state for NBI 1 (a) and NBI 3 (b) in water.

12. NMR studies



Fig. S17 (a) Relevant sections of ¹H NMR spectrum of **NBI 2** monomer in CDCl₃ ($c = 12.0 \times 10^{-3}$ M) (black) and in aggregated state in D₂O ($c = 4.9 \times 10^{-3}$ M) (blue) at 295 K. (b) Chemical structure of **NBI 2** with the significant protons assigned. Selected region of superposed ROESY-NMR and COSY-NMR spectra of **NBI 2** showing NOEs between glycol chains and naphthalene core (c) and phenyl protons and naphthalene core (d) in D₂O ($c = 4.9 \times 10^{-3}$ M) (circles).



Fig. S18 (a) Relevant sections of ¹H NMR spectrum of **NBI 3** monomer in $CDCI_3$ ($c = 10.0 \times 10^{-3}$ M) (black) and in aggregated state in D₂O ($c = 4.9 \times 10^{-3}$ M) (blue) at 295 K. (b) Chemical structure of **NBI 3** with the significant protons assigned. Selected region of superposed ROESY-NMR and COSY-NMR spectra of **NBI 3** showing NOEs between glycol chains and naphthalene core (c) and phenyl protons and naphthalene core (d) in D₂O ($c = 4.9 \times 10^{-3}$ M) (circles).





Fig. S20 1 H NMR (400 MHz, top) and 13 C spectra (100 MHz, bottom) of NBI 2 in CDCl₃ at 295 K.



Fig. S21 1 H NMR (400 MHz, top) and 13 C spectra (100 MHz, bottom) of NBI 3 in CDCl₃ at 295 K.

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