Supporting Information

pH triggered self-assembly induced enhanced emission of phosphonic acid appended naphthalenediimide amphiphile

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1. Experimental details

Fourier Transform Infrared (FTIR) Spectroscopy Measurement: All FTIR spectra were collected on a Perkin Elmer FT-IR 400 at ambient temperature. The instrument was continuously purged with CO_2-free dry air. Spectra were recorded between 450- 4000 cm^{-1}.

Differential scanning calorimetry (DSC)*:* Differential scanning calorimetry was carried out by using a DSC Q 100. 20 mg of sample was placed into a large volume capsule (LVC) that was then sealed. The sample LVC pan was placed into the DSC apparatus together with an empty LVC pan as reference. The

pans were cooled to 0 °C, and aged for 30 min at this temperature. Heating scan was then recorded from 0 – 180 °C at a scan rate of 1°C min^{-1}.

Thermal Gravimetric Analysis (TGA): Thermo-gravimetric analysis (TGA) was carried out by using a TGA Q500 thermal analyzer. Measurements were carried out in platinum pans under nitrogen atmosphere (flow rate of 50 mL/ min) with a heating rate of 10 °C/min over a temperature range of 0-700 °C. The temperature calibration of the TGA equipment was carried out by use of the Curie-point calibration technique (Alumel, Ni, Perkalloy, Fe).
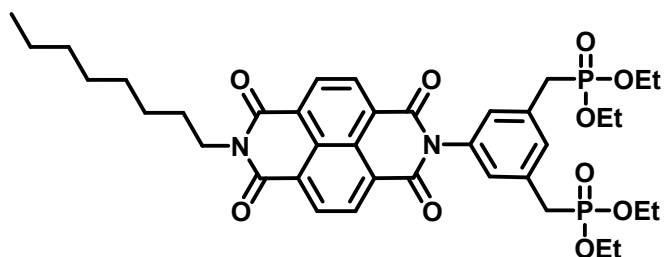
Surface Electron Microscopy (FE-SEM): FE-SEM measurements were performed on an electron microscopy HITACHI S-4800, operating at an accelerating voltage of 15 kV. 0.5 µl of freshly prepared NDI (**1**) (1×10^{-4} M) solution and was dropped onto a carbon tape and the solvent was allowed to evaporate before investigation by SEM and the collection of images.

Dynamic Laser Scattring (DLS): The particle size distribution of the aggregates were studied at various pH between 9 and 3 (stock solution diluted 1:4) solution using dynamic light scattering particle size analyzer (DLS, Brookhaven Instrument Corp., 90Plus Particle Sizer) equipped with a He–Ne laser (632.8 nm, 35 mW) and quartz cuvette. Solution at pH 9 was filtered using cellulose acetate 0.21 µm syringe filter, the DLS measurement showed no a clear solution and no particle was detected, the pH was adjusted using 0.1M HCl to lower pHs down to pH 3.
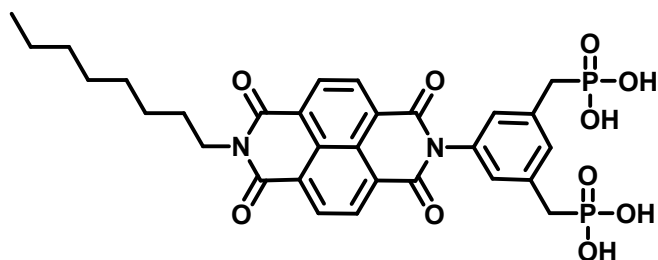
2. Synthetic Procedures and Characterisation data:

N-octyl-naphthalene-1,8-dicarboxyanhydride-4,5-dicarboximide **3** was prepared according to known literature method.[S1]

Synthesis of Dissymmetrical naphthalene diimide derivatives (2):

A substituted phosphonated amine **4** (1.5 equiv.) and monoanhydride **3** (1.9 g, 5.0 mmol, 1.0 equiv.) of were suspended in 20 mL dry *N, N'*-Dimethyl acetamide (DMA) under nitrogen atmosphere. The mixture was heated on magnetic stirrer at 120 °C with vigorously stirring for 12 h. The reaction mixture was cooled at room temperature and poured into cooled 100 mL of 1N aqueous HCl. The resulting suspension was extracted with dichloromethane (2 x 100 ml) and separate organic layer. The organic layer was washed with brine solution (2 x 50ml), dried over anhydrous $MgSO_4$ and evaporated using rotary evaporator. The obtained crude product was purified by column chromatography (silica gel 100-200, using $CHCl_3$: MeOH, 9:1) and further recrystallized with $CHCl_3$: Hexane gives solid product with 73 % yield. ^1H NMR (300 MHz, $CDCl_3$)δ: 0.85 (t, 3H), 1.24 -1.44 (m, 22 H), 1.71- 1.78 (m, 2H), 3.2 (d, 4H, *J*= 21.6 Hz), 4.0- 4.1 (m, 8H), 4.18 (t, 2H), 7.21 (s, 2H), 7.4 (s, 1H), 8.78 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$)δ: 13.7, 16.1, 22.3, 26.7, 27.7, 28.8, 28.9, 31.4, 32.2, 34.1, 40.7, 62.4, 126.3, 126.5, 128.3, 130.6, 130.9, 131.7, 133.1, 134.7, 162.3, 162.4. IR (KBr, ν cm^{-1}): 767, 1023, 1247, 1346, 1580, 1668, 1708, 2854, 2924 and 2956. ESI-MS (*m/z %*): 756 (25 %) $[M + 2H]^+$, 773 (100 %), $[M+H_3O]^+$. HRMS: calculated for $C_{38}H_{48}O_{10}N_2NaP_2$ = 777.2682, Found (ESI$^+$) [M + Na] = 777.2709.

The deprotection of phosphonated NDI Amphiphiles (1):

Compounds **2** (1 equiv.) was dissolved in dry acetonitrile under inert atmosphere and cooled to 0 °C. TMSBr (15 equiv.) was added dropwise to above cooled solution with stirring. The ice bath was removed,

the mixture was stirred at room temperature for 1h and clear solution was stirred at 50 ^{0}C further 8 h. Cool the reaction mixture to room temperature and the volatiles were removed under vacuo. The crude material was suspended in 95% methanol and stirred overnight. Filter the precipitated solid, washed with hot acetonitrile (10 ml) and methanol (10 ml) afforded powdery white solid (0.28 gm, 66 % yield). ^{1}H NMR (300 MHz, DMSO-d_6, 50 $^{\circ}$C)δ: 0.83 (t, 3H), 1.26 -1.33 (m, 10 H), 1.65- 1.73 (m, 2H), 2.95 (d, 4H, J= 21.6 Hz), 4.03 (t, 2H), 7.16 (s, 2H), 7.29 (s, 1H), 8.64- 8.71 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, 50 ^{0}C)δ: 13.8, 22.0, 27.4, 28.5, 28.6, 31.2, 34.7, 35.8, 126.2, 126.3, 126.5, 126.8, 128.4, 129.5, 130.2, 130.4, 133.4, 134.8, 162.5, 162.8. IR (KBr, ν cm^{-1}): 768, 1090, 1250, 1349, 1580, 1663, 1708, 2313, 2852, 2922, 3080 and 3498. ESI-MS (m/z %): 828 (100 %) [M + DMSO + 5Na – 2H]$^+$. HRMS: calculated for $C_{33}H_{33}O_{11}N_2Na_2P_2$ = 705.1356, Found (ESI$^+$) [M + 2Na + H$_2$O] = 705.1392.

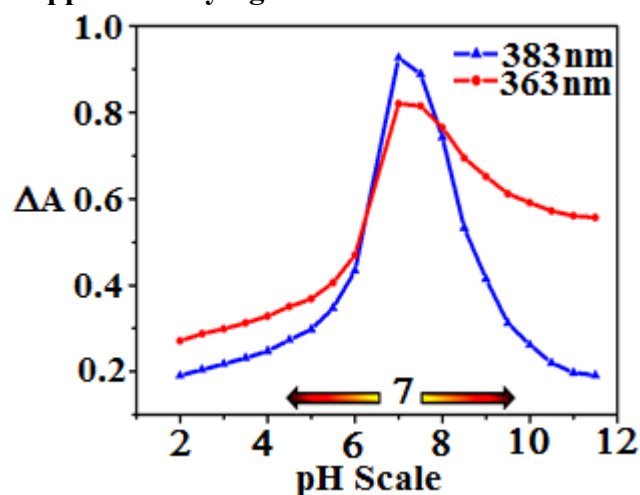**Supplementary figures**

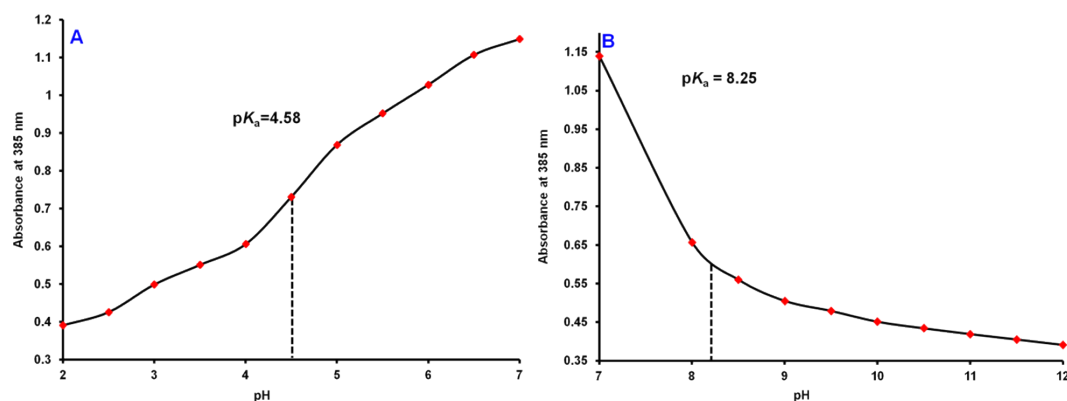**Fig. S1** pH dependent plot of changes in absorbance intensity at 383 nm and 363 nm.

Fig. S2 UV-vis titration of NDI amphiphile 1 (8×10^{-5} M).
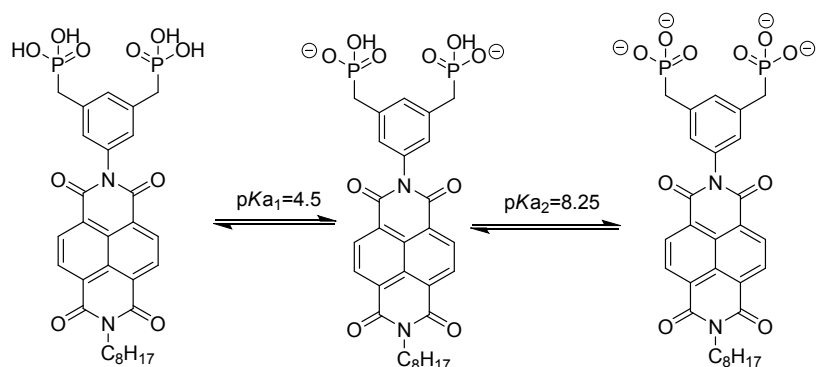
Fig. S3 Acid base equibrilia involving NDI amphiphile **1**. The reported pKa values have been measured by UV-vis spectrophotometric titration at 25 °C
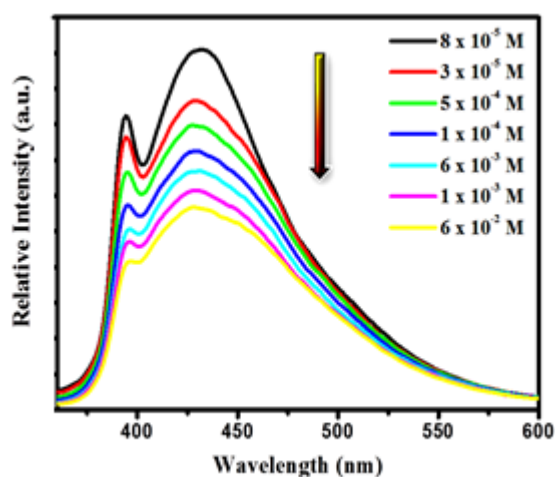

Fig. S4 Fluorescence emission spectra of **1** (8×10^{-5} M, $\lambda_{ex} = 380$ nm) in water with increasing concentration.
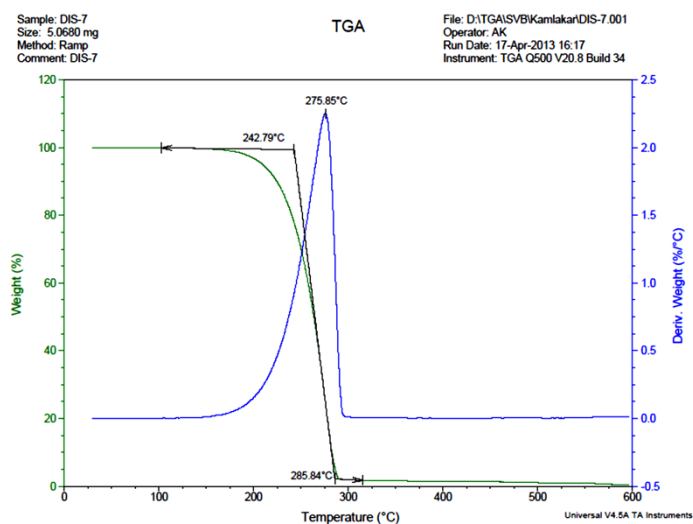

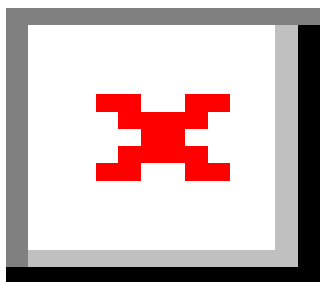**Fig. S5** TGA/DTG thermogram of amphiphile **1**.
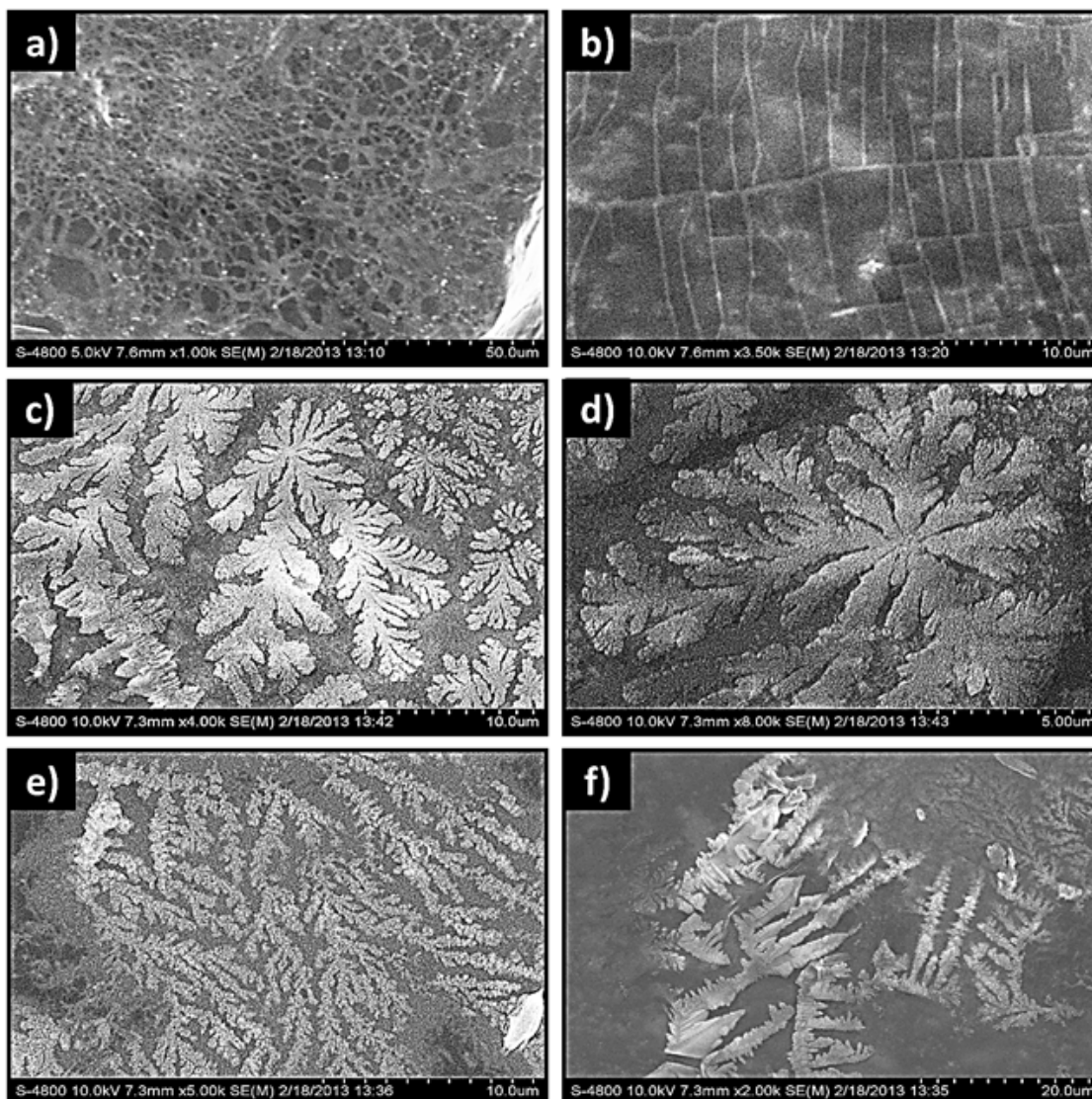
Fig. S6 DSC of amphiphile **1**.

Fig. S7 FE-SEM images of amphiphile **1** at pH (a) 4.5 (b) 7.0, (c) 9.5, (d) 9.0 and (e) 10.3 and (f) 11.6 in water.

The NDI solution equilibrated at acidic pHs resulted in clustered NDI aggregates and total precipitation at pH 3, therefore no particulate aggregates were detected after solvent evaporation of the filtered solutions using SEM technique, very small aggregated were observed at pH 7. At pH 9.5 the phosphonic acid-NDI amphiphiles is completely soluble and large fractal aggregates were produced after solvent evaporation of the filtered solution. However, pH 4.5 upon filtration self-assembled nanostructured filtered off.
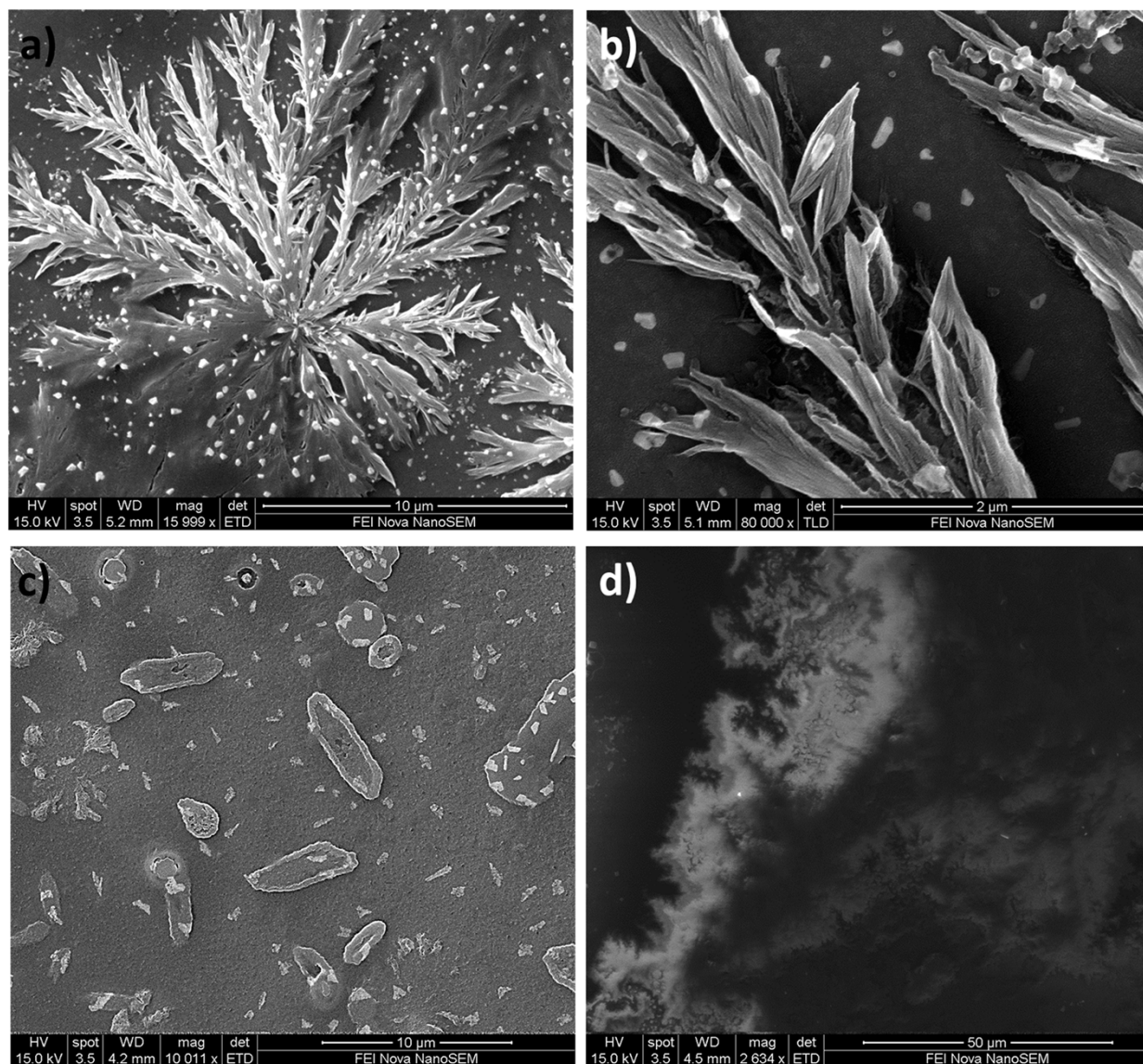

Fig. S8 SEM micrographs of aggregates produced by filtered NDI amphiphile **1** at pH (a,b) 9.5, (c) 7.0 and (d) 4.5 buffered solutions.

Atomic force microscopy (AFM) images were recorded using a Multi-Mode IIIa scanning probe microscope with Entender Module (DigitalInstruments, Inc., Santa Barbara, CA, USA) that was operated in dynamical mode. Olympus etched silicon cantilevers were used with a typical resonance frequency in the range of 200–400 MHz and spring constant of 42 N/m. The sample was first adjusted using optical microscopy (Nano Scope, Optical Viewing System). The microscope was then mounted

on a vibration isolation table (Halcyonics, MOD-1) and under a glass bell for reduction of acoustic noise. Sample of NDI **1** (pH 9.5) was prepared by spin-coating the freshly prepared solution (1.2 x 10^{-4} M) onto silica at 2000 rpm.
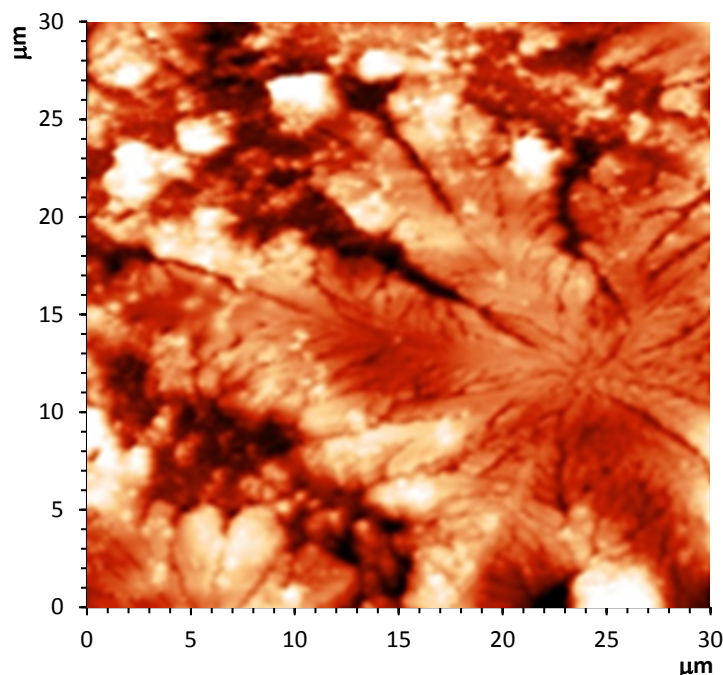

Fig. 9 AFM images of amphiphile **1** at pH 9.5

Dynamic Laser Scattring (DLS): The NDI solution at 1×10^{-4} M at pH 9 produced no detectable particles. When pH was reduced to 8.02 NDI aggregates start becoming detectable at 74 nm mean diameter. The particles continue to grow with further reducing pH, these particles cluster to produce precipitate over few hours that by filtration can be easily removed. Fig.S8 (a) shows the particle growth at increasingly acidic conditions, the numerical valused averaged over 5 measurments are listed in Table S1. When particle size distribution was produced based on mean square displacement, see Fig.S8 (b), the primary NDI aggregates are ~40 nm in diameter as measured at pH 8.02. These aggregates cluster at lower pHs where the phosphonate groups become protonated redusing the solubility of the NDI and the hydration of the agergates making the hydrophobic interactions more prominent in aquoeous environment. The clusters are 270 nm in diameter at pH 7.73. The primary aggregates concentration decreased with decreasing pH and the clusters became larger reaching 1.2 µm diameter at pH 4.82. These cluster produce larger clusters at pH 3.32 with a new peak at 5.8 µm diameter.
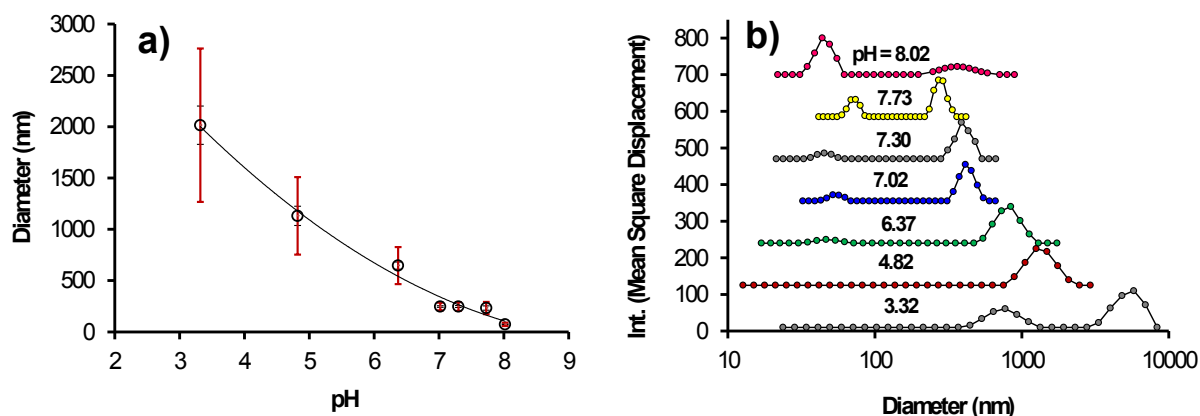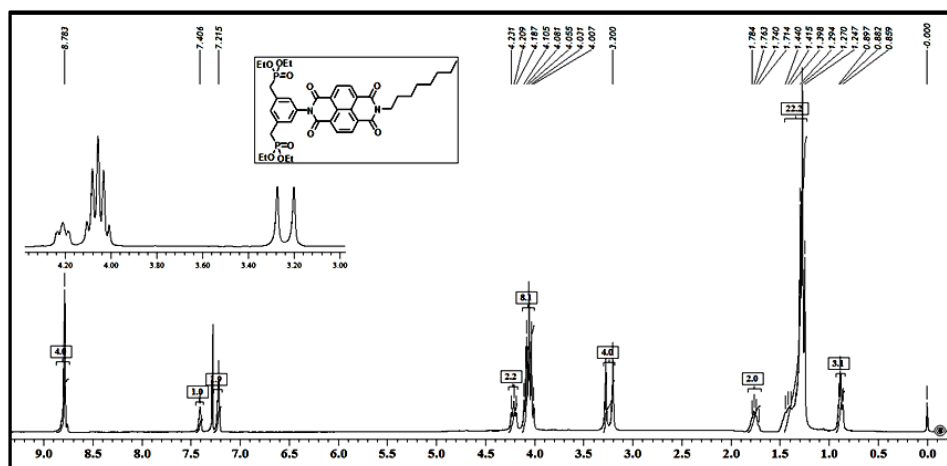
Fig. S10 a) Mean NDI aggregate size, red error bars represent the standard deviation of the distribution and the black error bars represent the standard error of the measurement, b) the mean square displacement as directly measured by DLS technique and various pHs of the NDI solution.

Table S1. Mean particle size (5 scattering measurement) and the peak width represented by standard deviation of distribution at various pHs.
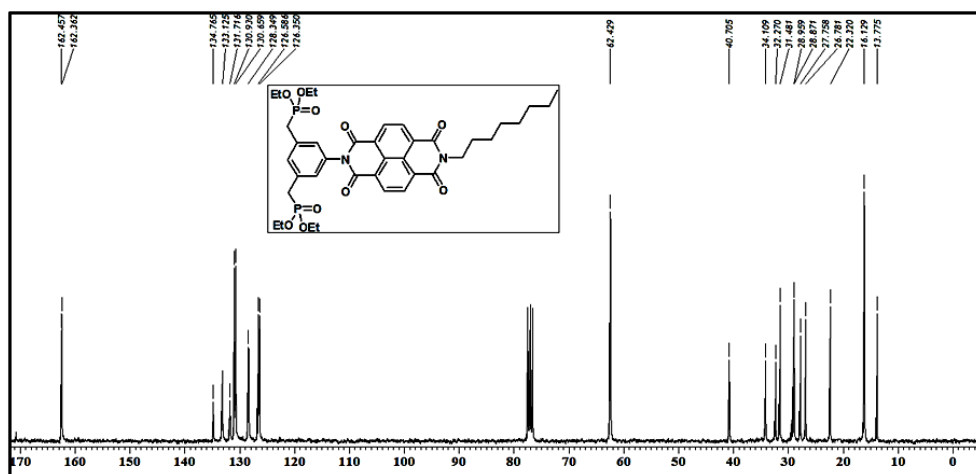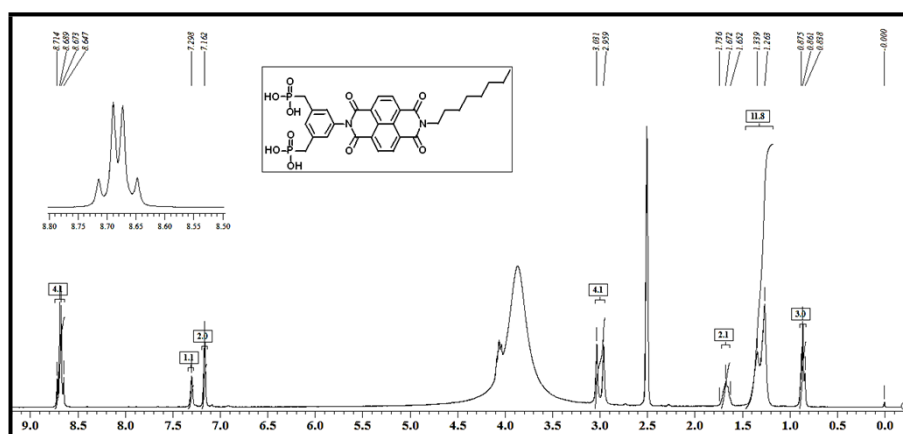
pH	Mean particle size (nm) ± σ	Standard deviation of the size distribution (nm)
3.32	2014 ± 187	747
4.82	1131 ± 94	377
6.37	646 ± 35	181
7.02	247 ± 7	38
7.30	248 ± 10	43
7.73	233 ± 21	60
8.02	74 ± 4	17

^{1}H NMR and ^{13}C NMR spectra's

^{1}H NMR (DMSO-d_6, 50 $^\circ$C) of compound **2**

^{13}C NMR (DMSO-d_6, 50 °C) of compound **2**

^{1}H NMR (DMSO-d_6, 50 °C) of compound **1**

^{13}C NMR (DMSO-d_6, 50 °C) of compound **1**

References

S1. M. E. El-Khouly, J. H. Kim, K.-Y. Kay, C. S. Choi, O.Ito, S. Fukuzumi, *Chem. Eur. J.* **2009**, *15*, 5301–5310.