A New Type of Inverted Supramolecular Amphiphile which Self-Assembles into Vesicular Networks based on Ion Pairing and Aromatic Stacking Interactions **

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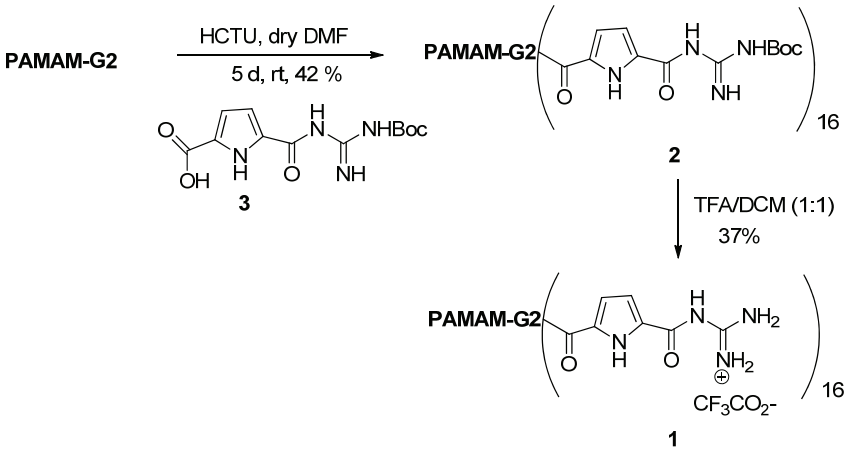
1. General Remarks

Determination of pH values was carried out with a pH-Meter 766 Calimatic from *Knick*. Fluorescence spectra were obtained with a *Varian* Cary Eclipse spectrometer. AFM imaging was carried out with an Innova Scanning Prope Microscope from *Veeco* and *Olympus* N-type silicon cantilevers AC-160TS in tapping mode on freshly cleaved mica surface from *Plano GmbH*. The analysis was done utilizing the software Gwyddion (Vers. 2.19). Dynamic Light Scattering (DLS) experiments were performed using a Zetasizer-Nano ZS from *Malvern* equipped with a 4 mW He-Nelaser (633 nm wavelength) at a fixed detector angle of 173° with an avalanche photodiode detector. All viscosity data were measured by using a Lovis 2000 M/ME microviskometer, device softwear version 2.21.

2. Synthetic procedure



For detailed experimental procedures and characterization, follow reference [1]

3. Dynamic light scattering (DLS) experiments

First stock solution of the individual compounds **1** and NDIDC were prepared in 10% H_2O/DMSO respectively and fixed the pH (6.80 ± 0.01) for **1** and pH (6.90 ± 0.01) for NDIDC adding either acid or base. The two solutions were mixed by equal volume (v/v = 50/50) in (1:8) ratio. All measurements were carried out at 25° C in UV-transparent microcuvettes (1 cm) equipped with a stopper. The solution was filtered prior to measure *via* 0.20 µm nylon filters. The autocorrelation functions of the backscattered light fluctuations were analyzed with the DTS 6.20 software from *Malvern* providing the hydrodynamic diameter (Z-average), polydispersity and size distribution (NNLS analysis).

Individual compounds, con. and time-dependent DLS study

Sample name	Z-average (d.nm)	Size (d.nm) (%)	PDI
Compound **1**	111.3	0.658 (100)	0.882
NDIDC, 1 mM	37.79	0.686 (100)	0.389
(1:8)mix., 25 µM	1780	0.702 (100)	0.860
(1:8)mix., 40 µM	1011	0.666 (65), 1.54 (35)	0.810
(1:8)mix., 50 µM	313.6	294 (100)	0.050
Same mix., 1 h	325.5	303.2 (100)	0.050
Same mix., 24 h	1549	685.1 (100)	0.719

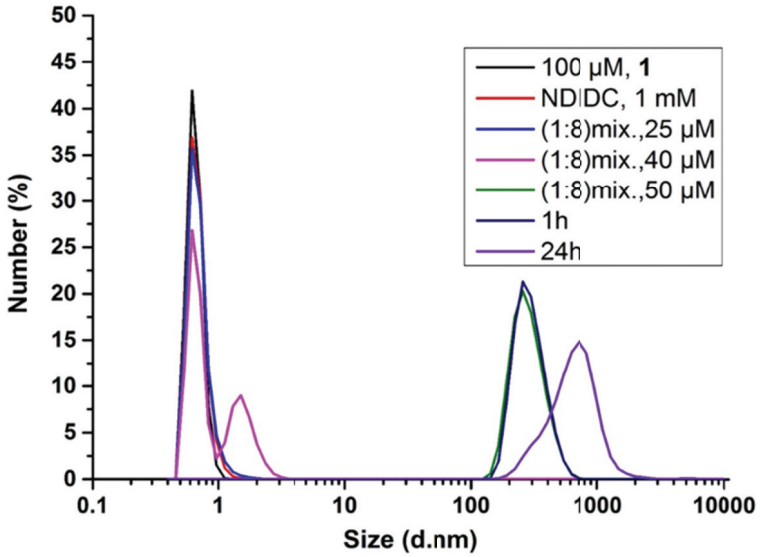


Figure S1: DLS study in 10% H_2O/ DMSO, the above mentioned concentrations for (1:8) mixture w.r.t **1**.

*The size of the polymer increased significantly with time (294 d.nm to 685 d.nm). But, the process is slow, indicating the dynamic morphological changes occurred in the solution. In addition, at least (c = 50 µM) concentration of **1** was required for the supramolecular polymerization.*

pH dependent DLS study

Sample name	Z-average (d.nm)	Size (d.nm) (%)	PDI
(1:8) mix., pH 3.85	126.4	0.668 (100)	0.475
(1:8) mix., pH 9.91	7460	4.848 (100)	0.375
(1:8) mix., pH 6.42	3431	493 (100)	0.693
Same mix., 24 h	6850	1026 (100)	0.466
Same mix., 72 h	6543	2088 (100)	0.336

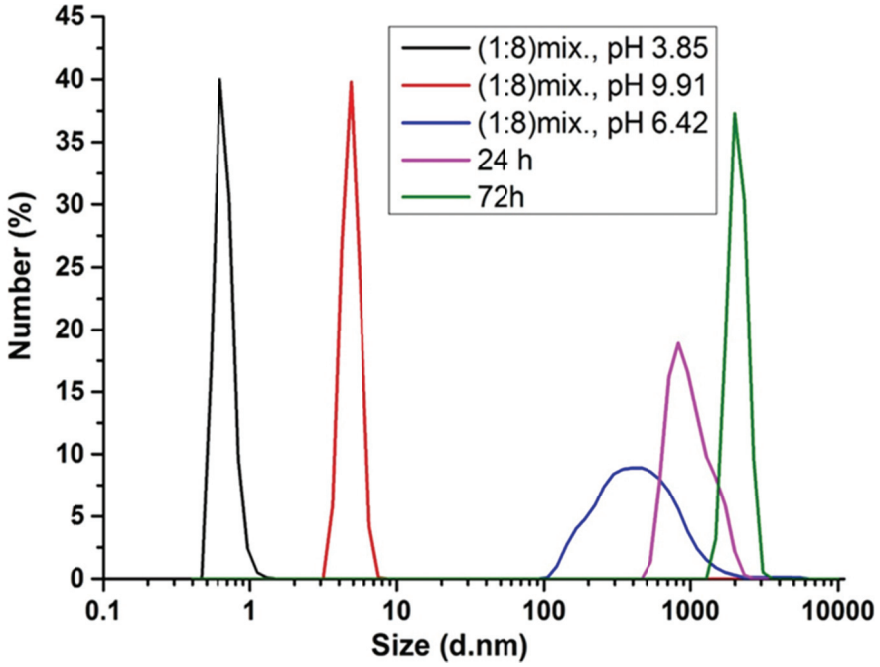


Figure S2: pH dependent DLS study in 10% H_2O/ DMSO, *c* = 125 µM w.r.t **1**.

The polymer can be switched between the monomers and polymer reversibly using external stimuli like pH-alteration.

DLS study of (1:8) mixtures of 1 with glutaric acid and compound 2

Sample concentration	Z-average (d.nm)	Size (d.nm) (%)	PDI
250 µM, **1** + bicyclic com. **3** (1:8) mix.	93.27	4.835 (100)	0.508
250 µM, **1** + glutaric acid (1:8) mix.	342.4	4.369 (100)	0.800

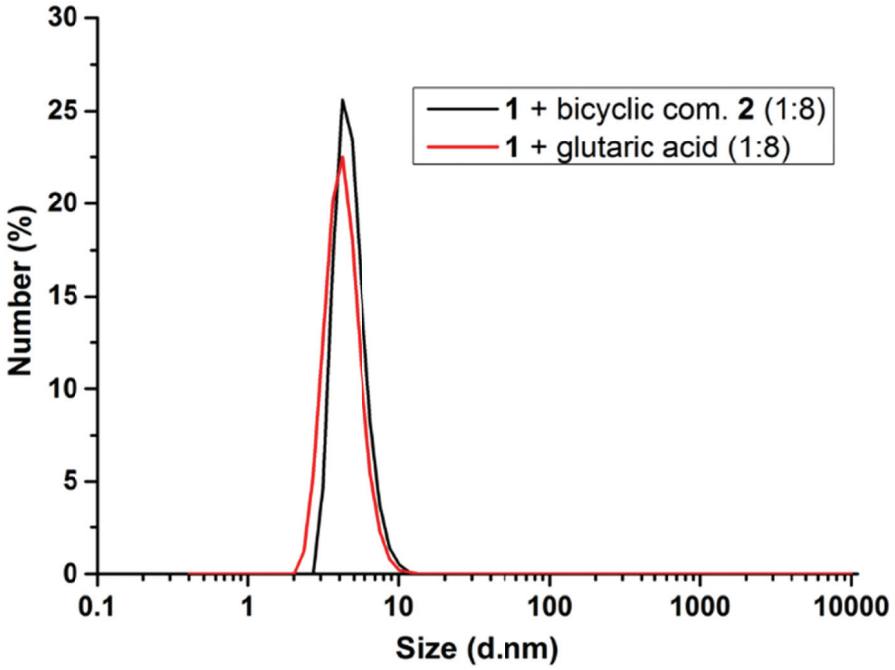


Figure S3: (a) DLS study of (1:8) mixture of **1** with glutaric acid (v/v = 50/50), and bicyclic bridge compound **3** (v/v = 50/50), c= 250 µM in 10% H_2O/DMSO at neutral pH. The above mentioned concentrations w.r.t **1**.

4. Fluorescence Titration

Fluorescence titration of **1** (c = 300 μM) with NDIDC (c = 18.6 mM) in aqueous DMSO. The samples were each excited at the wavelength λ = 297 nm appropriate for the fluorescence of pyrrole. The slit widths were set to 10 nm for excitation and emission. The emission at 362 nm was monitored during titrations.

Calculation

Vol. added	con (mM)	con (M)	1/con.	Intensity	Δ FI	1/ΔFI
0				117.96	0	#DIV/0!
4	0.210169	0.000210169	4758.064516	115.65	2.31	0.432900433
8	0.415642	0.000415642	2405.913978	103.65	14.31	0.069881202
12	0.616575	0.000616575	1621.863799	99.77	18.19	0.054975261
16	0.813115	0.000813115	1229.83871	90.18	27.78	0.03599712
20	1.005405	0.001005405	994.6236559	78.64	39.32	0.02543235
24	1.193583	0.001193583	837.8136201	64.23	53.73	0.018611576
28	1.377778	0.001377778	725.8064516	57.91	60.05	0.016652789
32	1.558115	0.001558115	641.8010753	45.97	71.99	0.013890818
36	1.734715	0.001734715	576.4635603	37.67	80.29	0.012454851
40	1.907692	0.001907692	524.1935484	14.05	103.91	0.009623713
44	2.077157	0.002077157	481.427175	10.33	107.63	0.00929109
48	2.243216	0.002243216	445.7885305	10	107.96	0.00926269
52	2.40597	0.00240597	415.6327543	7.68	110.28	0.009067827
56	2.565517	0.002565517	389.7849462	9.61	108.35	0.009229349
60	2.721951	0.002721951	367.3835125	9.24	108.72	0.00919794
64	2.875362	0.002875362	347.7822581	3.91	114.05	0.008768084

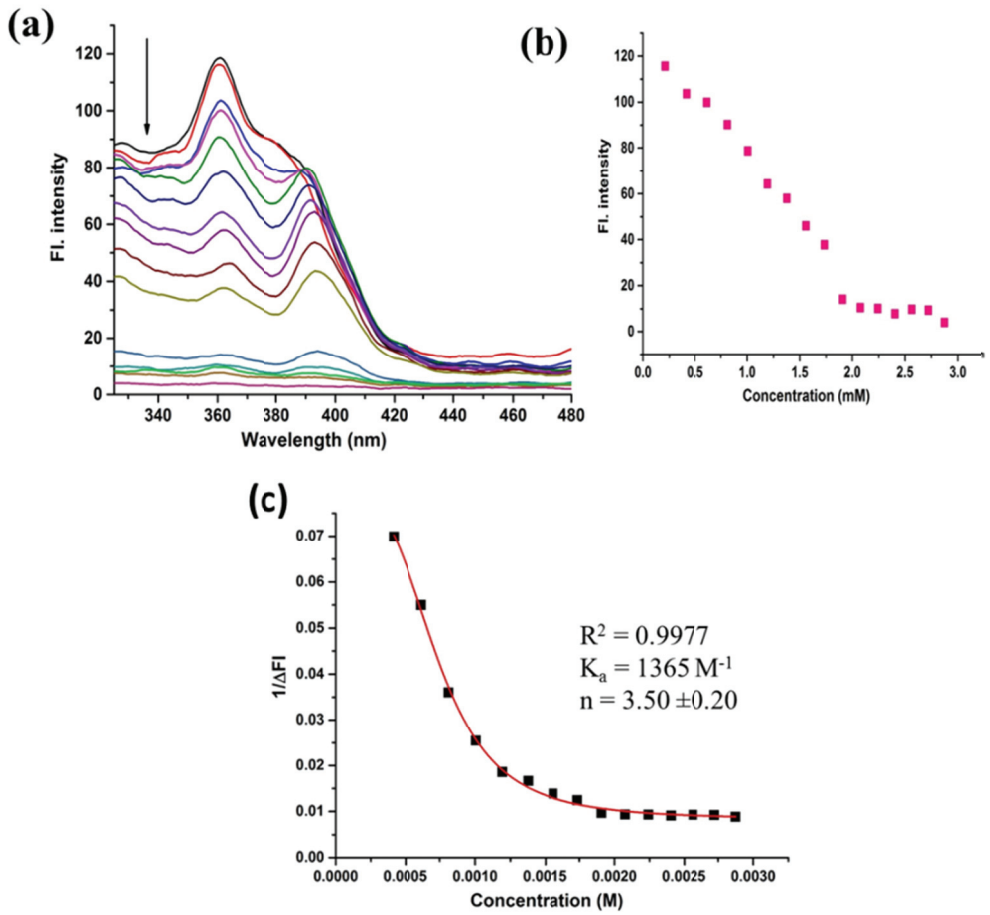


Figure S4: (a) Fluorescence intensity decreased during titrations; (b) Binding isotherm at λ = 362 nm; (c) A binding constant ca. 10^3 M^{-1} was calculated from the nonlinear model (Hill 1).

6. AFM images

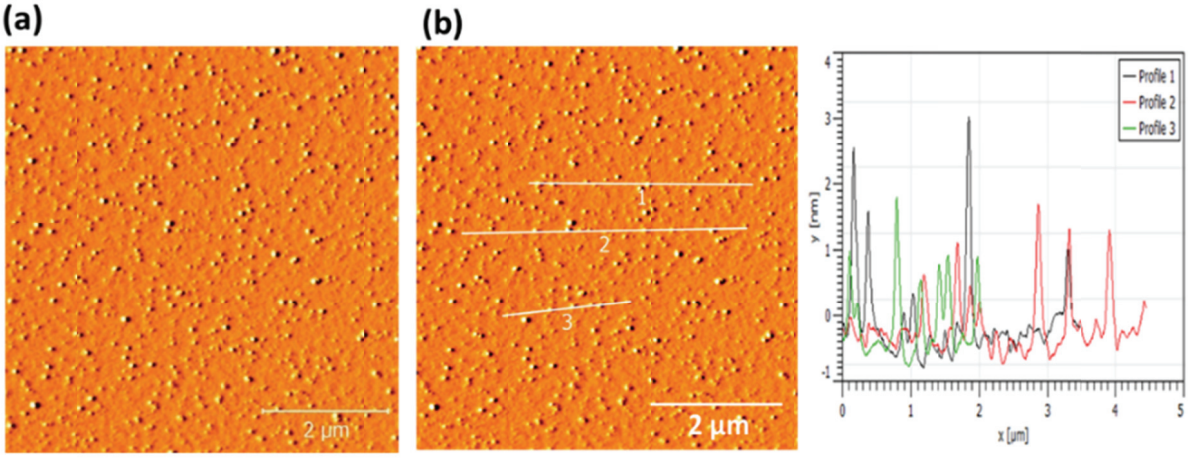


Figure S10: (A) Image of **1** (*c*=500 µM) alone, at pH 6.85; (B) Height image of **1.**

Dynamic morphologies change upon aging of the (1:8) mixture of 1 and NDIDC at neutral pH.

Within 0-1 h:

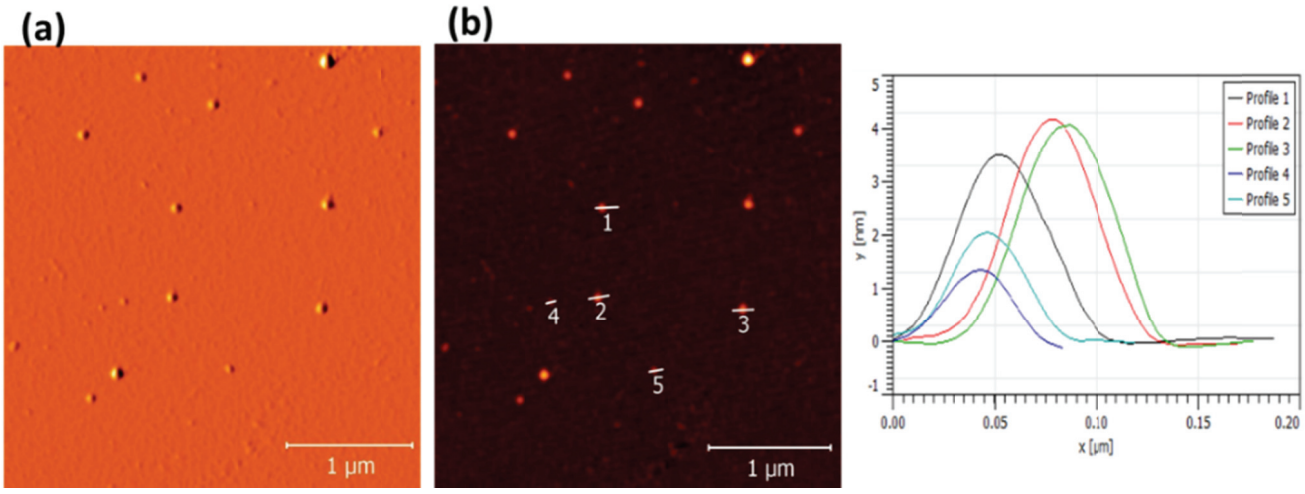


Figure S5: (a) Spherical aggregates or reverse micellar aggregates; (b) Height image, at 125 µM.

5 h:

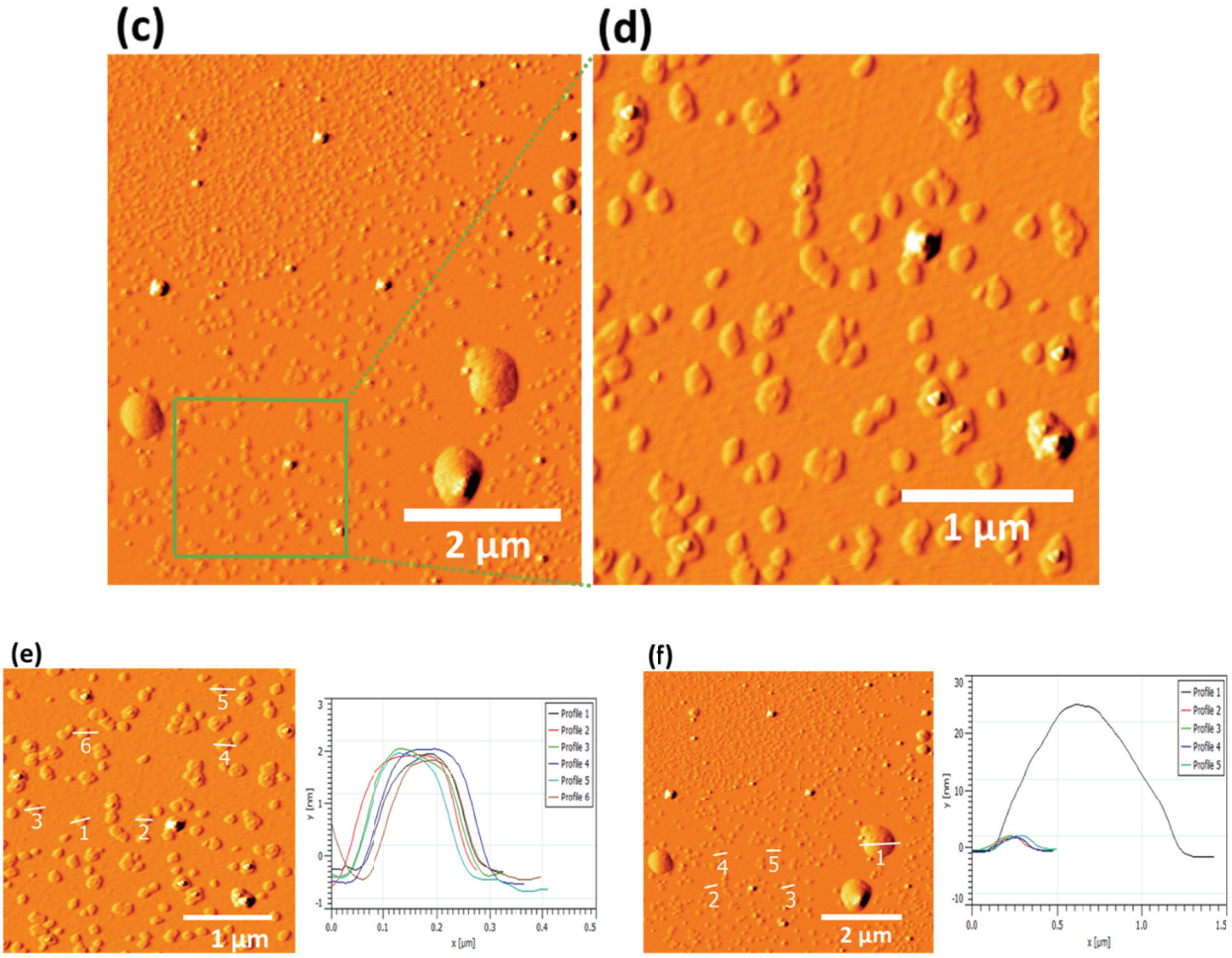


Figure S6: (c) Image at 5 h; (d) Zooming image, disk shape; (e, f) Height images, at 125 µM.

Small disk shape morphology changed further into reverse big vesicles through fusion to each other.

17 h:

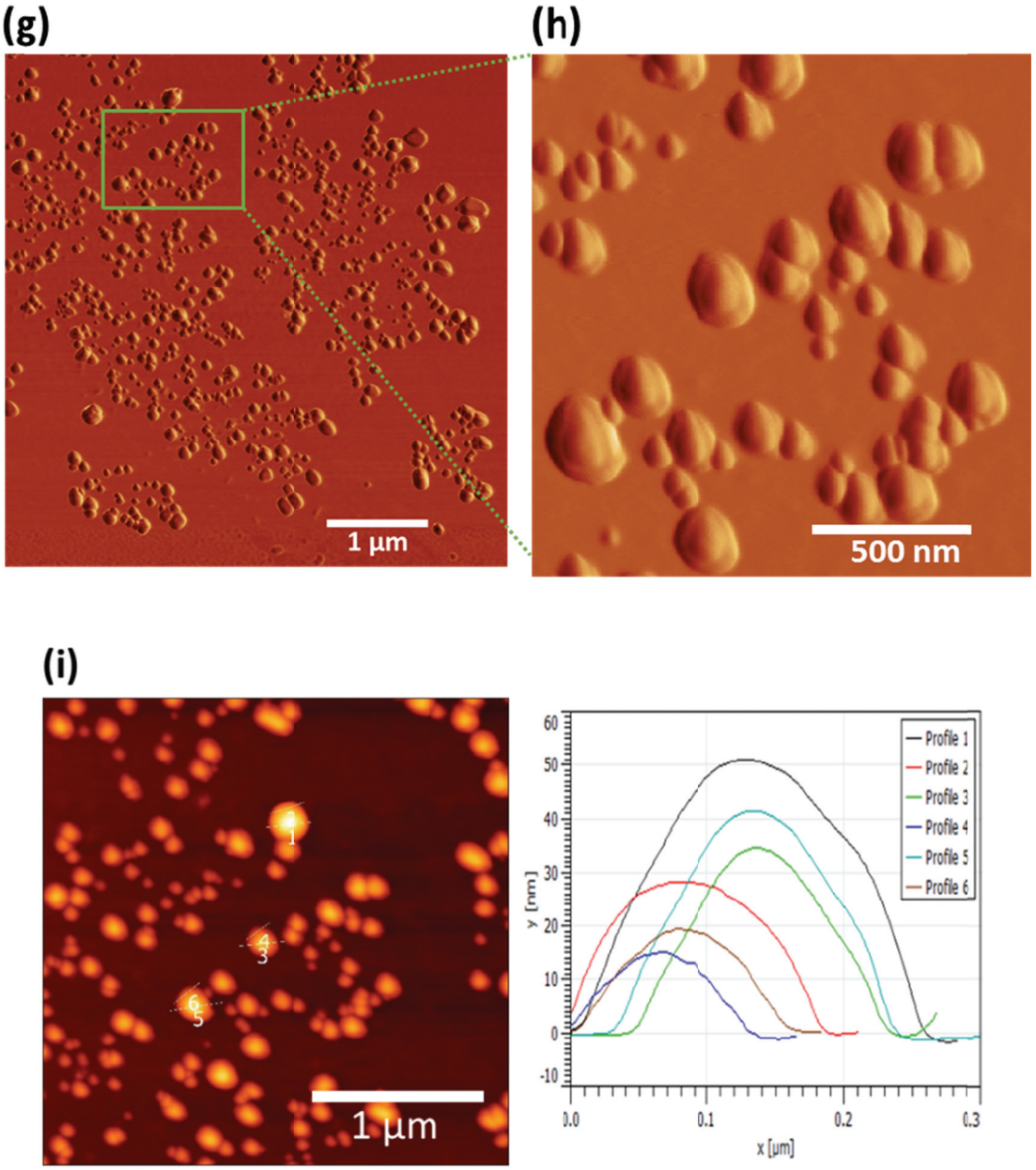
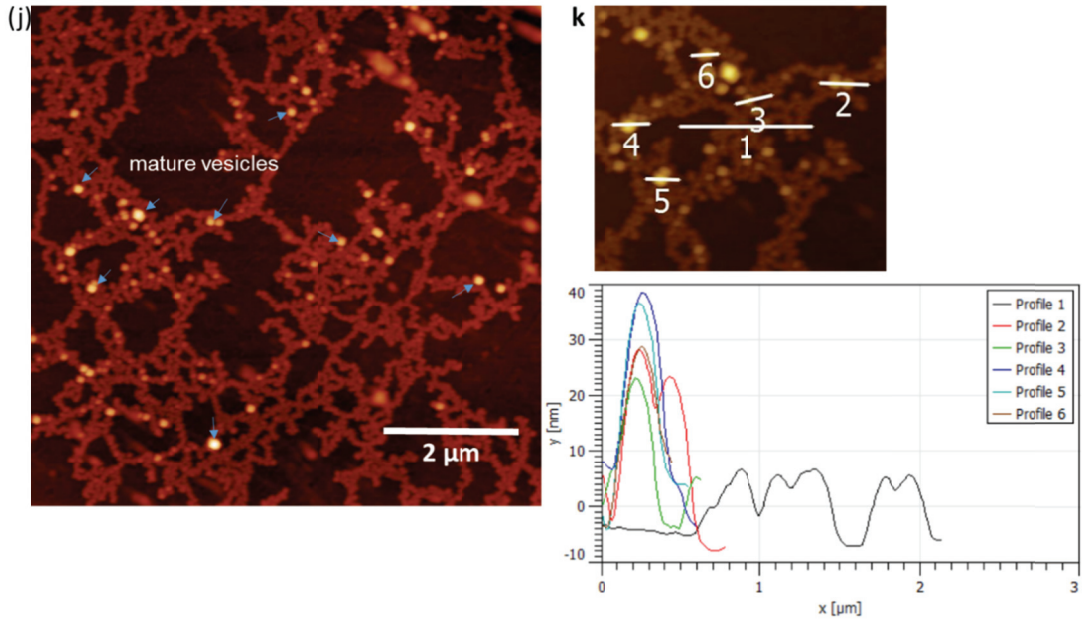
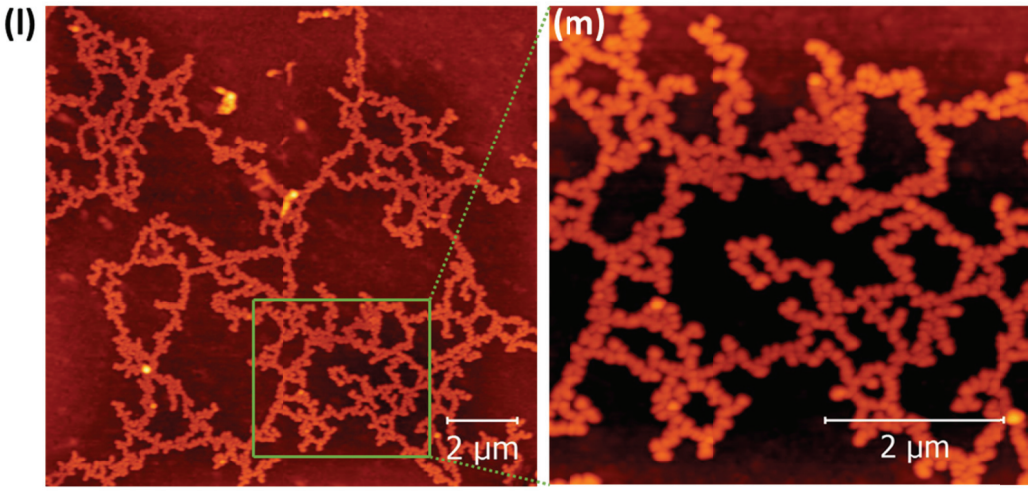
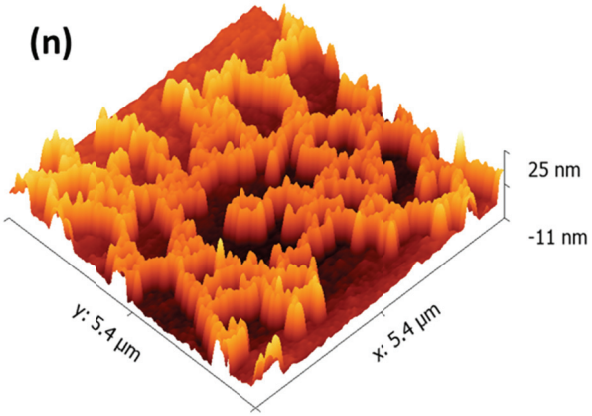


Figure S7: (g) Image at 17 h; (h) Zooming image, reverse vesicles with double layers; (i) Height image, at 125 µM.

24 h:


(j)
mature vesicles
2 µm
k
6
3
2
4
1
5
Profile 1
Profile 2
Profile 3
Profile 4
Profile 5
Profile 6
y [nm]
x [µm]


(l)
2 µm
(m)
2 µm


(n)
25 nm
-11 nm
y: 5.4 µm
x: 5.4 µm

o

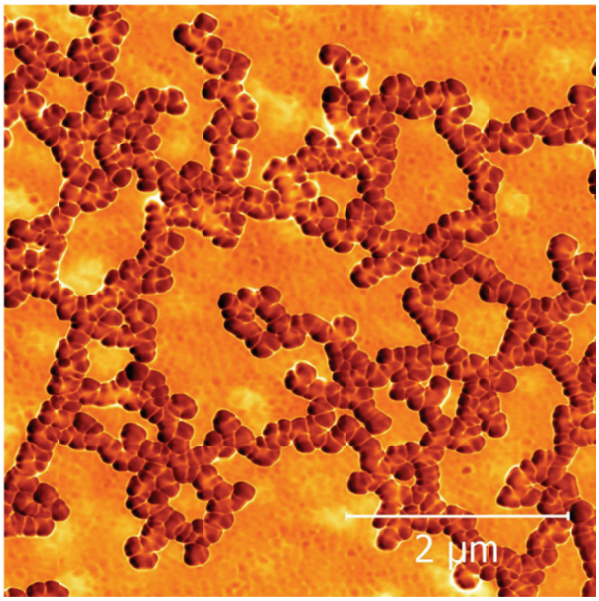


Figure S8: (j, l) Large networks; (m) Zooming image, vesicles networks; (n, k) Height images; (O) Zooming image, vesicles networks, tapping phase, at 125 µM.

8. TEM images

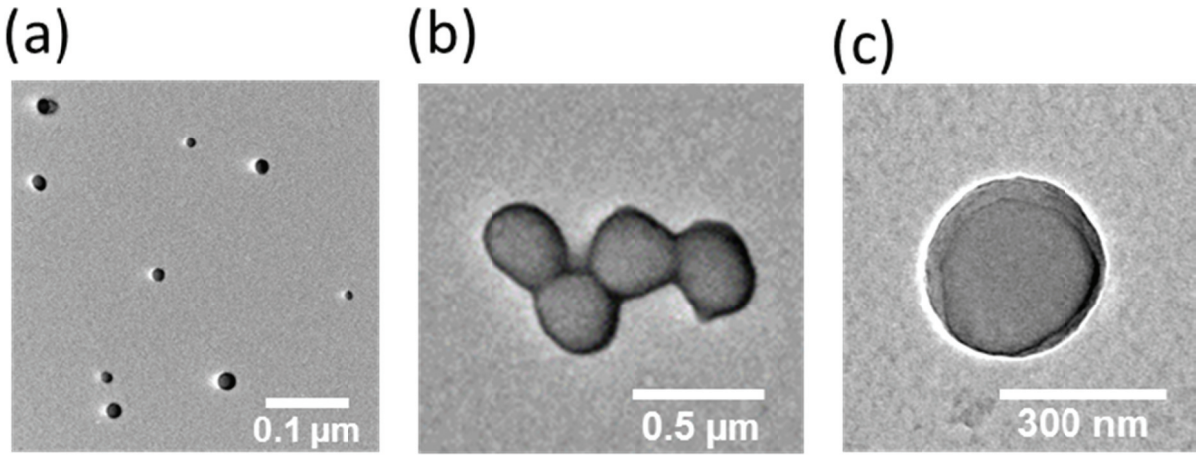
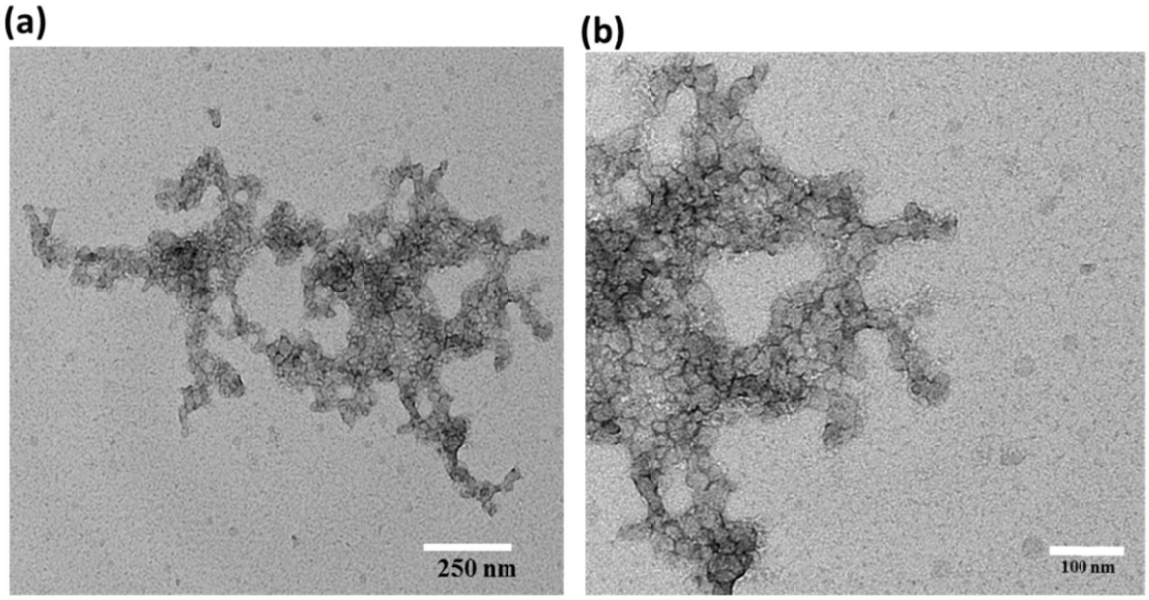


Figure S9: TEM images, Reverse micellar aggregates within (0-1h) (a); Fusion of disk shape aggregates, 5 h (b); reverse vesicle with double layer, 12 h (c).

Large vesicle networks in 24 h.



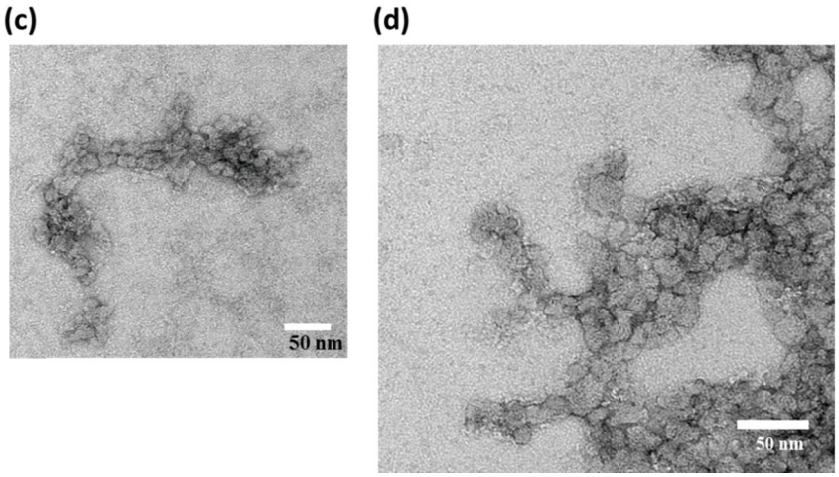


Figure S10: (a) Large vesicle networks; (b, c, and d) zooming images at 125 μM.

All individual vesicles are held to one another through π-surface interaction.

9. Viscosity

All viscosity data were measured using a Lovis 2000 M/ME microviskometer, device softwear version 2.21. at 25 °C and at neutral pH. All measurements were carried out in 10% H_2O/DMSO solvent system.

Sample	Kinetic vis.	Relative vis.	Sample	Kinetic vis.	Relative vis.
10% H_2O/DMSO	2.3669		10% H_2O/DMSO	2.3669	
50 µM, **1**	2.5858	1.09248384	50 µM, NDIDC	2.5962	1.09687777
100 µM, **1**	2.6318	1.111918543	100 µM, NDIDC	2.6025	1.09953948
200 µM, **1**	2.6952	1.138704635	200 µM, NDIDC	2.6035	1.09996198
300 µM, **1**	2.739	1.157209853	300 µM, NDIDC	2.6144	1.10456716
400 µM, **1**	2.8076	1.186192911	400 µM, NDIDC	2.62	1.10693312

Sample	Kinetic vis.	Relative vis.
10% H_2O/DMSO	2.3669	
50 µM, (1:8) mix	2.9024	1.2262453
100 µM, (1:8) mix	3.1142	1.315729435
200 µM, (1:8) mix	3.7207	1.571971777
300 µM, (1:8) mix	4.5008	1.901559001
400 µM, (1:8) mix	6.2758	2.651485065

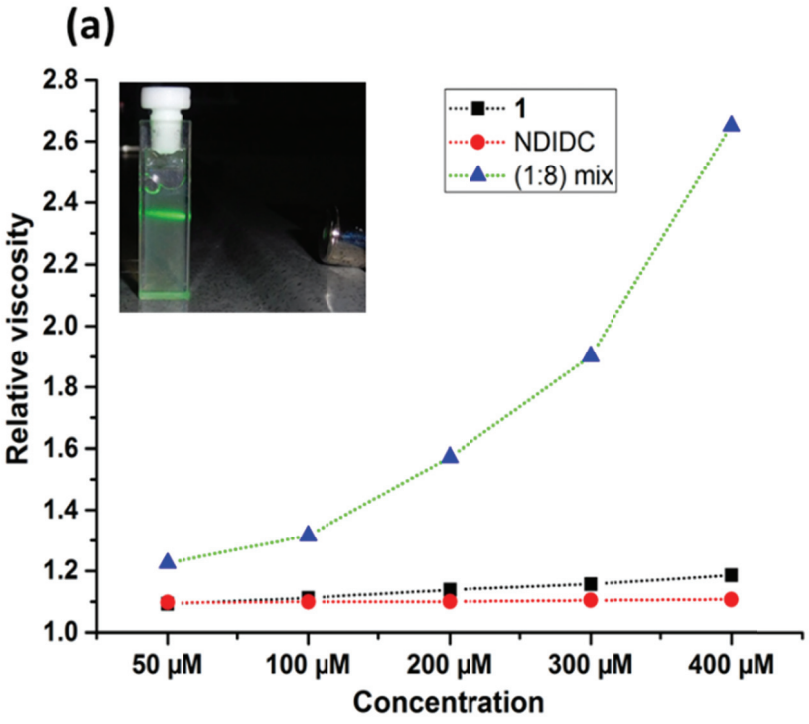


Figure S11: (a) Relative viscosity of **1**, NDIDC and (1:8) mixture.

10. Pulsed field gradient (PFG) NMR experiments

This method is based on the combination of a stimulated echo sequence with a set of two field gradient pulses. The gradient strength G as well as the spacing Δ between the gradient pulses is systematically varied, leading to a set of echo decay patterns. The latter are analyzed by a numeric analysis based on a molecular exchange process between two domains with different self-diffusion characteristics.[2]

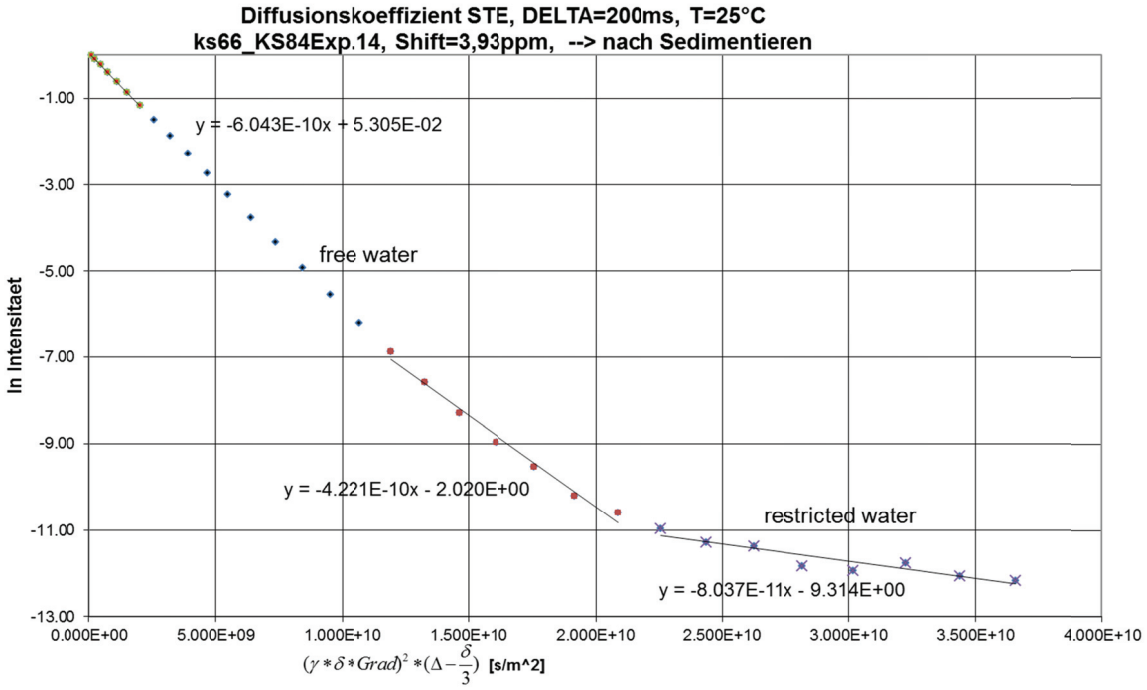


Figure S12: Logarithmic plot of the relative echo signal intensity of H_2O **(**with the vesicles, c= 50 μM) as a function of the pulse spacing Δ (200 ms).

11. Zeta Potential

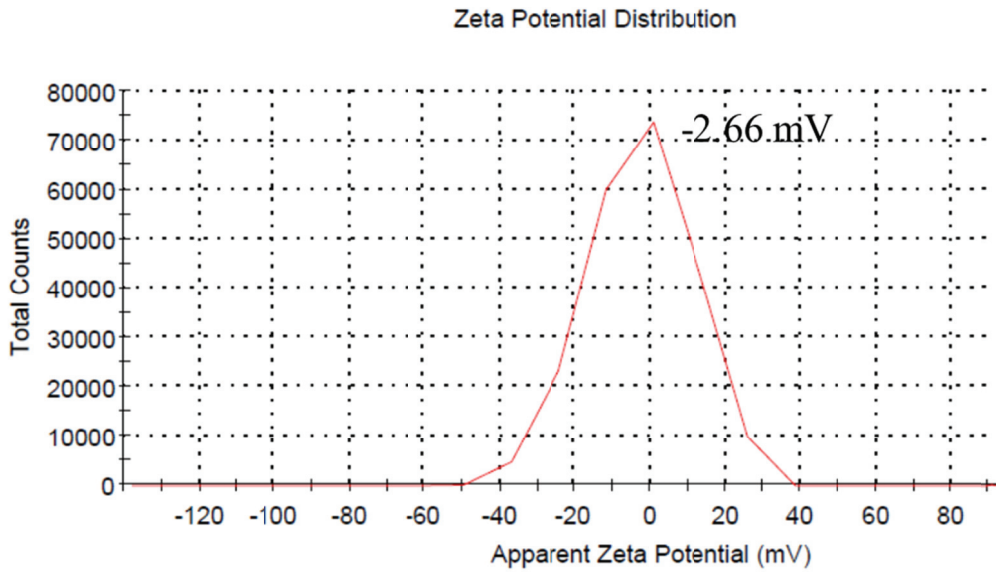


Figure S13: Zeta potential of the reverse vesicle (*c*= 125 µM).

Reference: (1) K. Samanta, P. Jana, S. Bäcker, S. Knauer and C. Schmuck *Chem. Commun.* **2016**, DOI:10.1002/chem.201603944.

(2) a) A. Rumplecker, S. Förster, M. Zähres, C. Mayer, *J. Chem. Phys.* **2004**, *120*, 8740; b) A. Bauer, S. Hauschild, M. Stolzenburg, S. Förster, C. Mayer, *Chem. Phys. Lett.* **2006**, *419*, 430.