

Temperature-Controlled Supramolecular Vesicles Modulated by *p*-Sulfonatocalix[5]arene with Pyrene

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Construction of vesicles is a significant topic of research in the fields of chemistry, biology, and materials science for their various applications.^[1] Recently, more and more research has been focused on “supramolecular amphiphiles”, which have emerged as a smart strategy due to their simplicity, versatility, and especially reversibility. Several kinds of noncovalent interactions have been used to tune the molecular amphiphilicity and self-assembled nanostructures,^[2] including hydrogen-bonding,^[3] charge-transfer,^[4] and $\pi\cdots\pi$ interactions,^[5] among others.^[6] The noncovalent interactions often employed (e.g., hydrogen bonding, coordination, and π stacking) are not always effective for designing supramolecular architectures in aqueous medium, and hence, they lack the necessary biocompatibility for applications in the fields of biotechnology. Macrocyclic receptors, such as cyclodextrins, calixarenes, and cucurbiturils, exhibit particular advantages in building water-soluble supramolecular architectures,^[7] more significantly, the three macrocyclic species are all friendly to organisms.^[8] To the best of our knowledge, supramolecular vesicles formed by host–guest interactions between macrocyclic hosts and guests have been explored less frequently.^[9] Kim et al. reported, for the first time, the spontaneous formation of vesicles triggered by the formation of a stable ternary inclusion complex that behaves as a large supramolecular amphiphile, in which cucurbituril was employed.^[9a] Cyclodextrin is the macrocyclic host used most frequently in building organized amphiphiles, and the first noncovalent vesicle based on a cyclodextrin complex was reported by Chen and co-workers in 2007.^[9b]

Calixarenes,^[10] composed of phenolic units linked by methylene groups, represent a particularly significant class of the host molecules in supramolecular chemistry. Their in-

trinsic cone shape is the prerequisite for high-curvature aggregations of amphiphiles.^[11,12] Their relatively rigid framework can enhance the stability of amphiphilic aggregation.^[13] Consequently, calixarenes have received certain attention in constructing micellar and vesicular aggregations. The vesicles reported are uniformly formed by a covalent approach that modifies calixarenes into amphiphiles by the linkage of lipophilic groups at one rim and hydrophilic groups at the other rim,^[12–15] whereas no supramolecular vesicles based on host–guest complexation have been explored. Recently, García-Río and Basilio found that the complexation of water-soluble calix[6]arene can tune the amphiphilicity of a cationic surfactant.^[16] Blanzat et al. reported the spontaneous formation of vesicles by combining an aminocalix[6]arene with sugar-based surfactants using an acid–base reaction to obtain a catanionic association while this manuscript was under preparation.^[17] Our particular interest herein is to fabricate calixarene-based supramolecular vesicles through host–guest complexation. The most fascinating aspect of supramolecular chemistry is that two or more components can self-assemble into higher-order structures, which exhibit particular properties and functions that the individual component cannot achieve.

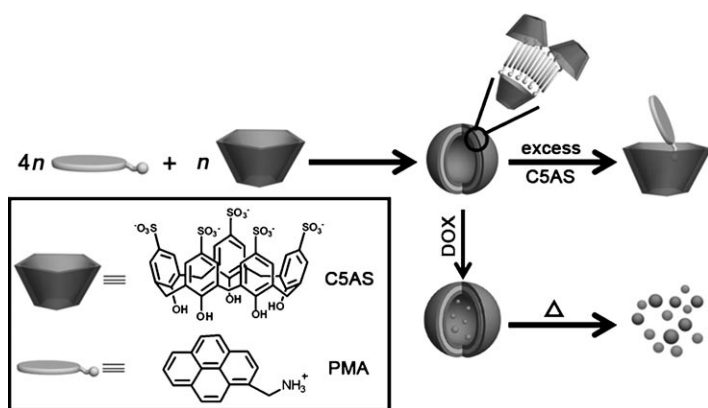
Herein, we report the successful construction of nanoscale supramolecular binary vesicles on the basis of host–guest complex formation between *p*-sulfonatocalix[5]arene (C5AS) and 1-pyrenemethylaminium (PMA) (Scheme 1). Notably, neither free C5AS nor PMA can form nanoscale aggregates themselves. Furthermore, the obtained vesicle shows thermal reversibility and it can disassemble when the temperature increases up to 35–40 °C. This temperature-responsive character makes this kind of vesicle a potential delivery model for special substrates.

A simple mixture of C5AS (0.05 mM) and PMA (0.25 mM) with a charge-matching molar ratio in aqueous solution shows the Tyndall effect, which prompted us to explore the higher hierarchy aggregation based on the host–guest complexation of C5AS with PMA. The critical aggregation concentrations (CAC) of PMA in the absence and presence of C5AS were measured by monitoring the polarity of the sur-

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Scheme 1. Schematic representation of the construction of a supramolecular binary vesicle and its temperature-responsive dye release. The final disassembled products may be C5AS, PMA, C5AS+PMA 1:1 complex, and C5AS+PMA micelle. DOX = doxorubicin hydrochloride.

rounding medium of pyrene (dependence of the fluorescence intensity ratio (I_{395}/I_{375}) of PMA on its concentration).^[18] A moderately appreciable CAC value of 0.27 mM for free PMA was observed (Figure S1a-b in the Supporting Information). Whereas upon addition of C5AS, the concentration-dependent titrations show sharper inflection points, and the CAC values decrease more than 3 times: 0.07 mM at 0.02 mM C5AS, 0.09 mM at 0.05 mM C5AS, and 0.08 mM at 0.08 mM C5AS (Figure S1c-h in the Supporting Information). It is noted that C5AS is without any tendency to self-aggregation in aqueous solution.^[19]

Although different concentrations of C5AS can all decrease the CAC value of PMA pronouncedly, it is still necessary to determine the best molar fraction of C5AS leading to aggregation. I_{395}/I_{375} evolution as a function of C5AS concentration with a fixed PMA concentration at 0.20 mM is shown in Figure 1, which undergoes a pronounced increase and then an inverse decrease upon gradual addition of C5AS. In the left-hand portion of inflexion, C5AS and PMA form a higher-order complex with a tendency toward self-aggregation, whereas in the right-hand portion of inflexion,

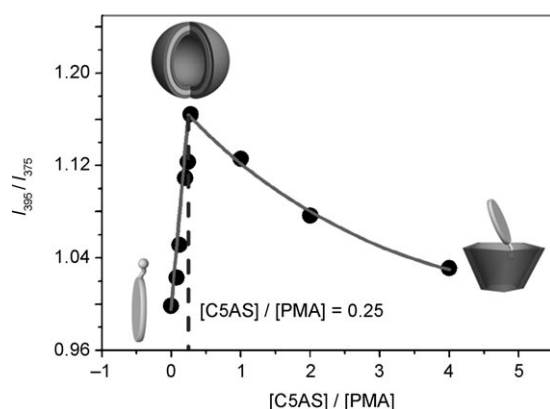


Figure 1. Dependence of the I_{395}/I_{375} value on C5AS concentration with a fixed PMA concentration of 0.20 mM at 25 °C.

excess C5AS leads to the formation of 1:1 inclusion complex, accompanied by the disassembly of the amphiphilic aggregation. The binding stoichiometry between C5AS and PMA was measured to be 1:1 (Figure S2a in the Supporting Information), and its binding affinity is as strong as $7.8 \times 10^4 \text{ M}^{-1}$ (Figure S2b in the Supporting Information) in dilute solution. The ultimate I_{395}/I_{375} value in the presence of excess C5AS is still larger than that of free PMA, mainly arising from the immersion of PMA into the hydrophobic cavity of calixarene. The inflexion appears at the C5AS/PMA molar ratio of 0.25. The same data was also obtained when monitoring the excimer emission of pyrene (I_{483}) (Figure S3a-b in the Supporting Information). That is, in the present C5AS+PMA system, the best mixing ratio for amphiphilic aggregation is 1:4 C5AS to PMA.

We compared the UV/Vis absorption and fluorescence emission spectra of PMA in the presence of C5AS and 4-phenolsulfonic sodium, the building subunit of C5AS, as control experiments (Figure S4a-b in the Supporting Information). Upon the addition of C5AS, a broad absorption appears between 400 and 550 nm, corresponding to the characteristic absorption of the charge-transfer complex,^[4b] and also, the monomer emission diminishes, whereas the excimer emission emerges, accompanied with the evolution from blue to green fluorescence (Figure S5a in the Supporting Information), indicating the aggregation of pyrene segments. However, the excess addition of 4-phenolsulfonic sodium does not cause any appreciable change in both absorption and emission spectra of PMA, which proves undoubtedly the crucial role of host-guest complexation. On the other hand, as can be seen from Figure S5a in the Supporting Information, a solution of C5AS+PMA presents a curved surface due to the decrease of surface tension, and concurrently, exhibits a clear Tyndall effect (Figure S5b in the Supporting Information), indicating the existence of abundant nanoparticles, whereas this effect is not observed for the solution of free PMA even condensed to 1.0 mM (Figure S6b). This phenomenon reveals that free PMA blocks cannot form nanoscale aggregates themselves, although they have a limited stacking capability with respect to the fluorescence spectra (Figure S6a) (they may just form small dimers and oligomers that cannot induce a Tyndall effect). It is also reflected from the surface tension data (Figure S7 in the Supporting Information). In the presence of C5AS, the surface tension of the solution decreases dramatically upon adding PMA at lower concentration until a maximum is reached, and after that C5AS+PMA amphiphiles start to aggregate in aqueous solution. However, in the absence of C5AS, the surface tension decreases at higher concentrations and it still cannot achieve balance with the concentration increasing up to the high-point of PMA.

Furthermore, dynamic laser scattering (DLS) and transmission electron microscopy (TEM) were employed to identify the self-assembled morphology and size of C5AS+PMA amphiphiles. DLS results show that the C5AS+PMA complex forms spectacular aggregates with a narrow size distribution, giving an average diameter of 98.8 nm (Fig-

ure 2a), whereas no signal was observed for free PMA. TEM images show the hollow spherical morphology, indicating convincingly the vesicular structure (Figure 2b). Given

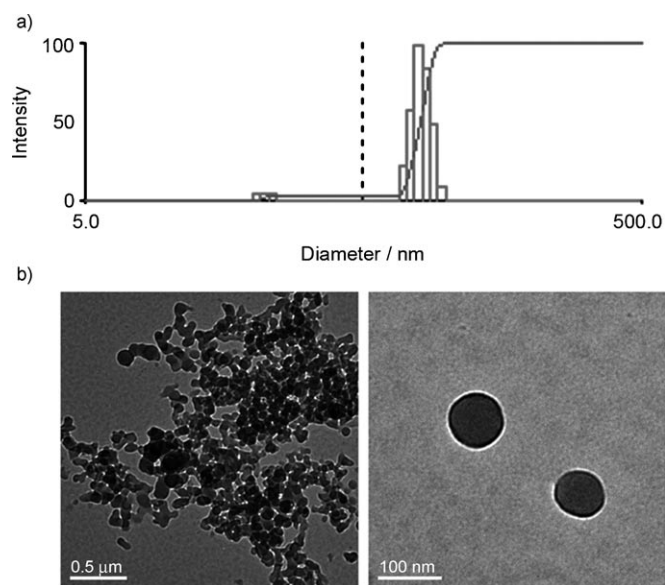


Figure 2. a) DLS data of C5AS+PMA aggregation. b) TEM images of C5AS+PMA aggregation.

these equally distributed spheres, the average diameter was calculated to be 90 nm, which is in accordance with the results obtained from DLS. Such spheres with similar sizes were also found in SEM images (Figure S8 in the Supporting Information). It is well known that structures with sizes in the region of 1–100 nm always exhibit unique properties, called the nanoeffect. Moreover, from the distinguishably dark periphery and light central parts in the TEM images, we obtained the thickness of the bilayer membrane as about 3 nm, which is in the same order of magnitude as the sum of one PMA length (7 Å)^[20] and two C5AS heights (14 Å),^[21] indicating that the vesicle is unilamellar. Combining all of the aforementioned results, we deduced the model of forming supramolecular vesicles as that illustrated in Scheme 1. The hydrophobic pyrene segments are packed together, and the inner- and outer-layer surfaces consist of hydrophilic phenolic hydroxyl groups of C5AS, which are exposed to water. C5AS and PMA are connected together by host-guest interactions.

Another significant point regarding the study of vesicles should be concerned with their capability to respond to external stimuli, such as pH and temperature.^[13,22] We have tested the pH response of the present vesicle, but it failed because of the low water solubility of nonprotonated PMA species. Alternatively, the binary C5AS+PMA vesicle is satisfactorily sensitive to external stimulus of temperature. Compared with other external stimuli, high temperature is one of the best signals in terms of easy and safe medical applications.^[23] As shown in Figure 3a, the excimer emission

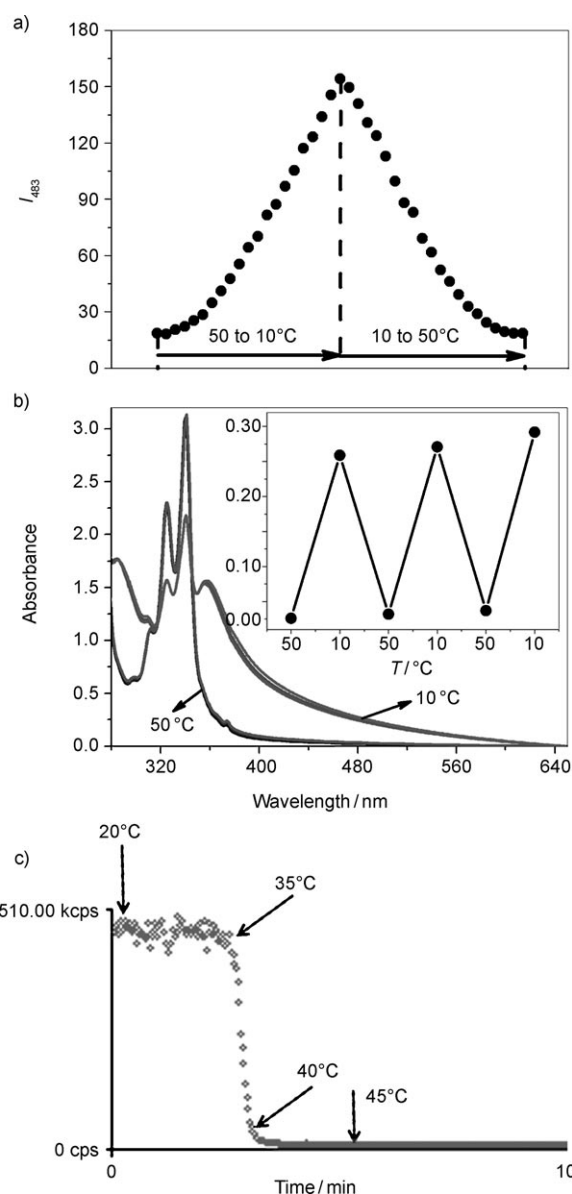


Figure 3. a) Dependence of the I_{483} value on temperature. b) UV/Vis absorption spectra of C5AS+PMA aggregation observed upon several cycles of thermal equilibration at 10 and 50°C. Inset: absorbance changes at 475 nm. c) Evolution of scattering intensity for the C5AS+PMA aggregation as a function of time and temperature.

(I_{483}) increases gradually with temperature descending from 50 to 10°C, and decreases inversely with temperature ascending from 10 to 50°C, which reflects the processes of assembly and disassembly, respectively. The left assembly curve is almost symmetric to the right disassembly one. The same phenomenon was also observed for the I_{395}/I_{375} value (Figure S9 in the Supporting Information). The reversible assembly/disassembly process was further validated by UV/Vis spectra (Figure 3b), which can be modulated repeatedly several times. More powerful evidence for the disassembly of the vesicles comes from the DLS measurements (Figure 3c), showing that the scattering intensity decreases sharply when the temperature increases from 35 to 40°C,

and then gradually becomes steady upon further increasing the temperature. The temperature response of the vesicle is acceptable for both the complexation of sulfonatocalixarenes with organic guests and the $\pi\cdots\pi$ stacking of aromatic pyrenes because they are enthalpy-driven processes, which would be weakened upon warming.^[24] It is mentioned here that the obtained vesicle is stable at room temperature and the vesicular structure can be maintained at least over one week (Figure S10 in the Supporting Information). Moreover, the assembly/disassembly process can be accomplished in the timescale of minutes or even more rapidly with changing temperature, which endows the vesicle with kinetic availability for dye carry/release.

According to the temperature-responsive character of binary C5AS+PMA vesicles, we selected doxorubicin hydrochloride (DOX), one kind of water-soluble fluorescence dye and anticancer drug molecules, to investigate its capability of dye release. After purification by ultracentrifugation and dialysis, DOX was successfully loaded in the vesicle. In comparison with the unloaded vesicle, the absorption from 450 to 550 nm becomes much stronger after loading (Figure 4a), which represents the characteristic absorption of DOX. Moreover, the vesicular solution turns from colorless to light red (Figure S11 in the Supporting Information). The emission of pyrene segments also undergoes obvious change before and after loading DOX (Figure S12), which refers that the binary vesicle is with self-labeled fluorescence signal. More intuitionistically, the loaded vesicle shows a darker interior in TEM observations (Figure 4b and Figure S13 in the Supporting Information), suggesting that DOX molecules are loaded into the vesicular interior under the condition of sample preparation. These loaded vesicle displays larger sizes (127 nm in diameter) than unloaded one (90 nm in diameter), which is consistent with the size increase of vesicles after guest encapsulation reported before.^[5c, 25]

The loaded DOX molecules were successfully released upon warming, together with the disassembly of the vesicles, as proved by detecting the amplification of the fluorescence signal of DOX accompanied with temperature increase (Figure S14 in the Supporting Information). The dye-release process as a function of temperature was recorded and is shown in Figure 4c. Almost no leakage of entrapped DOX was observed when the temperature was fixed at 25 °C for 25 min, however, in another independent experiment, increasing the temperature from 25 to 45 °C (enhancement of 5 °C per 5 min, which is enough time to reach a steady state according to the kinetics of the vesicle proved by DLS) triggers a gradual enhancement for DOX release, reaching 100% at 45 °C. The dye-release process, accompanied with the disassembly of the vesicle, was further reinforced by the control experiment with the addition of Triton X-100, which is known to solubilize vesicles (Figure S14 in the Supporting Information).

For conventional amphiphiles,^[26] such as ionic surfactants, the temperature sensitive vesicle-to-micelle transitions are attributed to the increasing solubility of the counterion

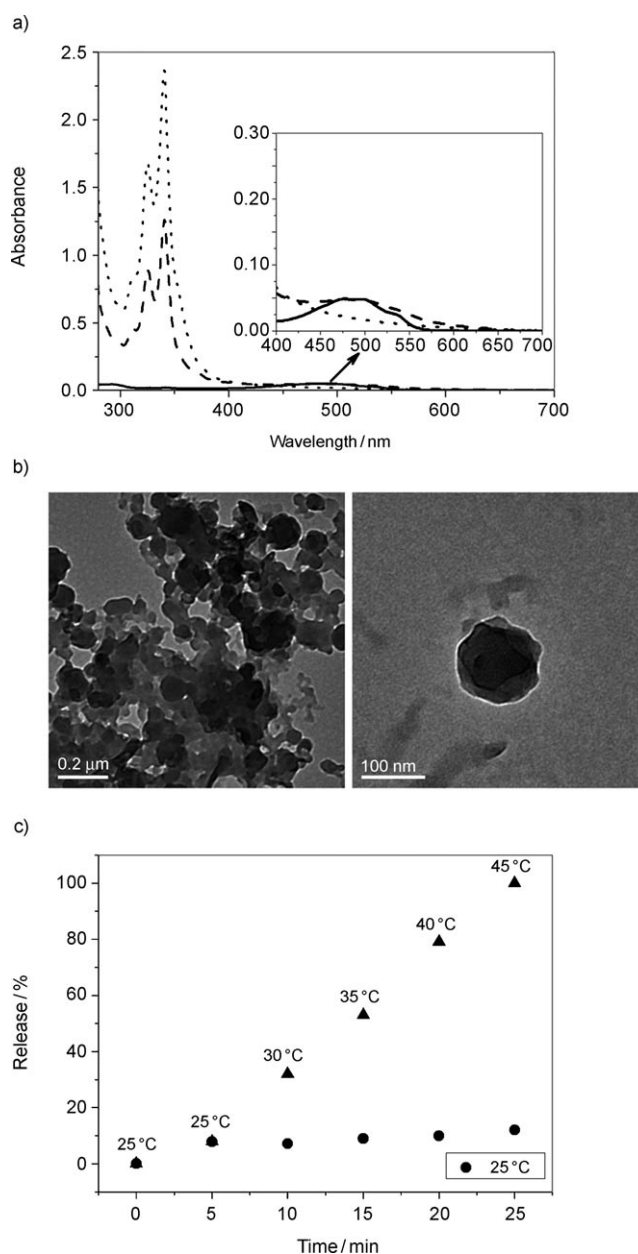


Figure 4. a) UV/Vis spectra of DOX (—), unloaded vesicles (.....), and DOX-loaded vesicles (---) at 25 °C. b) TEM images of DOX-loaded vesicles. c) Release percent of DOX from the loaded vesicle as a function of time and temperature.

upon increasing the temperature. For nonionic surfactants, temperature-induced micelle-to-vesicle transitions are well known, which is attributed to a decrease in head-group hydration upon increasing the temperature. Moreover, the hydrocarbon chains become less ordered upon increasing the temperature. The binary supramolecular vesicle investigated was constructed on the basis of host-guest complex formation. The temperature response is designed mainly from the viewpoint that both the complexation of sulfonatocalixarenes with organic guests and the $\pi\cdots\pi$ stacking of aromatic pyrenes are enthalpy driven, which would be weakened

upon warming. Such supramolecular strategy paves an alternative way to fabricate stimuli-responsive vesicles, showing certain advantages compared with covalent amphiphiles.

In conclusion, we have successfully constructed self-assembled binary supramolecular vesicles based on host-guest interactions, employing C5AS as the host and PMA as the guest, respectively. The present case highlights the fascinating feature of self-assembly that neither of the two individual components possesses typical amphiphilicity and can form nanoscale aggregates themselves. Furthermore, the obtained vesicles exhibit benign water solubility, self-labeled fluorescence, and more importantly, temperature response, which can act as potential delivery model for special substrates. Endeavors to construct supramolecular vesicles based on other water-soluble calixarenes and suitable guests are ongoing, in which of particular interest is exploring species with multistimuli responses and higher responsivity.

Experimental Section

Materials preparation: 1-Pyrenemethylaminium, 4-phenolsulfonic sodium, and doxorubicin hydrochloride were commercially available from Aldrich, Acros, and Aladdin, respectively. All of these were used without further purification. *p*-Sulfonatocalix[5]arene was synthesized and purified according to previously reported procedures^[27] and it was identified by ¹H NMR spectroscopy, performed on a Varian 300 spectrometer, and elemental analysis, performed on a Perkin-Elmer-2400C instrument.

DOX-loaded vesicle: DOX-loaded vesicles were prepared as follows: A certain amount of DOX was added to a solution containing C5AS and PMA, and then some water was added until the volume of the solution reached 25 mL. The ultimate concentrations of DOX, C5AS, and PMA were 0.01, 0.05, and 0.20 mM, respectively. Subsequently, the prepared DOX-loaded vesicles were purified by ultracentrifugation (10000 rpm for 2 min) and dialysis (molecular weight cutoff = 3500) in distilled water.

Temperature-responsive dye release: An excitation wavelength of 500 nm and an emission wavelength of 589 nm were used. The initial fluorescence intensity (F_0) of DOX-loaded vesicles was measured by using a fluorescence spectrometer. And then the fluorescence intensity (F_t) was measured as a function of time. After 25 min, the fluorescence intensity had not changed. In another independent experiment, the temperature was increased from 25 to 45 °C and the fluorescence intensity (F_t) of the DOX-loaded vesicles was measured every 5 °C. To confirm the overall intensity (F_{Triton}), more DOX-loaded vesicles were completely disrupted by adding Triton X-100. The release percentage of DOX-loaded vesicles was calculated by using Equation (1):

$$\text{Release percentage (\%)} = (F_{t(t)} - F_0) / (F_{\text{Triton}} - F_0) \times 100 \quad (1)$$

The fluorescence emission of DOX was quenched in the vesicles not only due to self-quenching originating from its relative high concentration in the vesicles, but also due to photoinduced electron transfer from the oxygen anion at the lower-rim of C5AS to DOX. The pH value for this C5AS+PMA system is 5.02. According to the pK_a values of lower-rim phenolic hydroxyl groups of C5AS (pK_a values = 4.31, 7.63, 10.96)^[27] at least one phenol group is deprotonated at this pH value.

UV/Vis absorption and fluorescence emission spectra: UV/Vis spectra were recorded in a quartz cell (light path 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature.

Surface tension measurements: The static surface tension in aqueous solution was measured by using a QBZY full-automatic surface tensiometer at 25 °C.

TEM and SEM experiments: TEM images were recorded on a Philips Tecnai G2 20S-TWIN microscope operating at an accelerating voltage of 200 keV. The sample for TEM measurements was prepared by dropping the solution onto a copper grid. SEM images were recorded on a Hitachi S-3500N SEM. The concentrations of C5AS and PMA were 0.05 and 0.20 mM, respectively.

DLS measurements: The sample solution for DLS measurements was prepared by filtering solution through a 450 nm Millipore filter into a clean scintillation vial. The samples were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (Turbo Corr.) at a scattering angle of 90°.

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Keywords: aggregation · calixarenes · dyes/pigments · host-guest systems · vesicles

- [1] a) S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe, E. Nakamura, *Science* **2001**, *291*, 1944–1947; b) A. Mueller, D. F. O'Brien, *Chem. Rev.* **2002**, *102*, 727–757; c) D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967–973; d) D. M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev.* **2005**, *105*, 1445–1489; e) T. Kunitake, *Angew. Chem.* **1992**, *104*, 692–710; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 709–726; f) S. Kolesheva, T. Shahal, R. Jelinek, *J. Am. Chem. Soc.* **2000**, *122*, 776–780; g) T. Renkes, H. J. Schäfer, P. M. Siemens, E. Neumann, *Angew. Chem.* **2000**, *112*, 2566–2570; *Angew. Chem. Int. Ed.* **2000**, *39*, 2512–2516; h) B. J. Ravoo, R. Darcy, *Angew. Chem.* **2000**, *112*, 4494–4496; *Angew. Chem. Int. Ed.* **2000**, *39*, 4324–4326; i) M. Brettreich, S. Burghardt, C. Böttcher, T. Bayerl, S. Bayerl, A. Hirsch, *Angew. Chem.* **2000**, *112*, 1915–1918; *Angew. Chem. Int. Ed.* **2000**, *39*, 1845–1848; j) A. M. Cassell, C. L. Asplund, J. M. Tour, *Angew. Chem.* **1999**, *111*, 2565–2568; *Angew. Chem. Int. Ed.* **1999**, *38*, 2403–2405; k) T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem.* **2005**, *117*, 7338–7364; *Angew. Chem. Int. Ed.* **2005**, *44*, 7174–7199.
- [2] Y. Wang, H. Xu, X. Zhang, *Adv. Mater.* **2009**, *21*, 2849–2864.
- [3] a) N. Kimizuka, T. Kawasaki, T. Kunitake, *J. Am. Chem. Soc.* **1993**, *115*, 4387–4388; b) N. Kimizuka, T. Kawasaki, K. Hirata, T. Kunitake, *J. Am. Chem. Soc.* **1998**, *120*, 4094–4104.
- [4] a) W. Pisula, M. Kastler, D. Wasserfallen, J. W. F. Robertson, F. Nolde, C. Kohl, K. Müllen, *Angew. Chem.* **2006**, *118*, 834–838; *Angew. Chem. Int. Ed.* **2006**, *45*, 819–823; *Angew. Chem. Int. Ed.* **2006**, *45*, 819–823; b) C. Wang, S. Yin, S. Chen, H. Xu, Z. Wang, X. Zhang, *Angew. Chem.* **2008**, *120*, 9189–9192; *Angew. Chem. Int. Ed.* **2008**, *47*, 9049–9052; c) A. Okabe, T. Fukushima, K. Ariga, T. Aida, *Angew. Chem.* **2002**, *114*, 3564–3567; *Angew. Chem. Int. Ed.* **2002**, *41*, 3414–3417.
- [5] a) F. Würthner, *Chem. Commun.* **2004**, 1564–1579; b) X. Zhang, Z. Chen, F. Würthner, *J. Am. Chem. Soc.* **2007**, *129*, 4886–4887; c) X. Zhang, S. Rehm, M. M. Safont-Sempere, F. Würthner, *Nat. Chem.* **2009**, *1*, 623–629.
- [6] a) Y. Wang, N. Ma, Z. Wang, X. Zhang, *Angew. Chem.* **2007**, *119*, 2881–2884; *Angew. Chem. Int. Ed.* **2007**, *46*, 2823–2826; b) P. Wan, Y. Jiang, Y. Wang, Z. Wang, X. Zhang, *Chem. Commun.* **2008**, 5710–5712; c) Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* **2007**, 1305–1315; d) K. Kim, W. S. Jeon, J.-K. Kang, J. K.

- Lee, S. Y. Jon, T. Kim, K. Kim, *Angew. Chem.* **2003**, *115*, 2395–2398; *Angew. Chem. Int. Ed.* **2003**, *42*, 2293–2296; e) C. Park, I. H. Lee, S. Lee, Y. Song, M. Rhue, C. Kim, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1199–1203.
- [7] D.-S. Guo, K. Chen, H.-Q. Zhang, Y. Liu, *Chem. Asian J.* **2009**, *4*, 436–445.
- [8] a) F. Perret, A. N. Lazar, A. W. Coleman, *Chem. Commun.* **2006**, 2425–2438; b) A. W. Coleman, S. Jebors, S. Cecillon, P. Perret, D. Garin, D. Marti-Battle, M. Moulin, *New J. Chem.* **2008**, *32*, 780–782; c) K. Wang, D.-S. Guo, H.-Q. Zhang, D. Li, X.-L. Zheng, Y. Liu, *J. Med. Chem.* **2009**, *52*, 6402–6412; d) V. D. Uzunova, C. Cullinane, K. Brix, W. M. Nau, A. I. Day, *Org. Biomol. Chem.* **2010**, *8*, 2037–2042; e) V. J. Stella, R. A. Rajewski, *Pharm. Res.* **1997**, *14*, 556–567; f) K. Uekama, F. Hirayama, T. Irie, *Chem. Rev.* **1998**, *98*, 2045–2076.
- [9] a) Y. J. Jeon, P. K. Bharadwaj, S. W. Choi, J. W. Lee, K. Kim, *Angew. Chem.* **2002**, *114*, 4654–4656; *Angew. Chem. Int. Ed.* **2002**, *41*, 4474–4476; b) B. Jing, X. Chen, X. Wang, C. Yang, Y. Xie, H. Qiu, *Chem. Eur. J.* **2007**, *13*, 9137–9142; c) J. Zeng, K. Shi, Y. Zhang, X. Sun, B. Zhang, *Chem. Commun.* **2008**, 3753–3755.
- [10] A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713–1734.
- [11] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York, **1985**.
- [12] M. Kellermann, W. Bauer, A. Hirsch, B. Schade, K. Ludwig, C. Böttcher, *Angew. Chem.* **2004**, *116*, 3019–3022; *Angew. Chem. Int. Ed.* **2004**, *43*, 2959–2962.
- [13] M. Lee, S.-J. Lee, L.-H. Jiang, *J. Am. Chem. Soc.* **2004**, *126*, 12724–12725.
- [14] a) E.-H. Ryu, Y. Zhao, *Org. Lett.* **2004**, *6*, 3187–3189; b) K. Sugiyama, K. Esumi, Y. Koide, *Langmuir* **1996**, *12*, 6006–6010.
- [15] a) Y. Tanaka, M. Miyachi, Y. Kokube, *Angew. Chem.* **1999**, *111*, 565–567; *Angew. Chem. Int. Ed.* **1999**, *38*, 504–506; b) S. Houmadi, D. Coquière, L. Legrand, M. C. Fauré, M. Goldmann, O. Reinaud, S. Rémita, *Langmuir* **2007**, *23*, 4849–4855; c) N. Micali, V. Villari, G. M. L. Consoli, F. Cunsolo, C. Geraci, *Phys. Rev. E* **2006**, *73*, 051904–051908.
- [16] N. Basilio, L. García-Río, *Chem. Eur. J.* **2009**, *15*, 9315–9319.
- [17] C. Bize, J.-C. Garrigues, M. Blanzat, I. Rico-Lattes, O. Bistri, B. Collasson, O. Reinaud, *Chem. Commun.* **2010**, *46*, 586–588.
- [18] K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **1977**, *99*, 2039–2044.
- [19] M. Rehm, M. Frank, J. Schatz, *Tetrahedron Lett.* **2009**, *50*, 93–96.
- [20] L. D. C. Baldi, E. T. Iamazaki, T. D. Z. Atvars, *Dyes Pigm.* **2008**, *76*, 669–676.
- [21] Y. Liu, D.-S. Guo, H.-Y. Zhang, F. Ding, K. Chen, H.-B. Song, *Chem. Eur. J.* **2007**, *13*, 466–472.
- [22] a) X. Guo, F. C. Szoka, *Acc. Chem. Res.* **2003**, *36*, 335–341; b) F. Chécot, S. Lecommandoux, Y. Gnanou, H.-A. Klok, *Angew. Chem.* **2002**, *114*, 1395–1399; *Angew. Chem. Int. Ed.* **2002**, *41*, 1339–1343; c) Y. Sumida, A. Masuyama, M. Takasu, T. Kida, Y. Nakatsuji, I. Ikeda, M. Nojima, *Langmuir* **2001**, *17*, 609–612; d) M. Johnsson, A. Wagenaar, J. B. F. N. Engberts, *J. Am. Chem. Soc.* **2003**, *125*, 757–760; e) J. Zhu, R. J. Munn, M. H. Nantz, *J. Am. Chem. Soc.* **2000**, *122*, 2645–2646; f) D. C. Drummond, M. Zignani, J.-C. Leroux, *Prog. Lipid Res.* **2000**, *39*, 409–460.
- [23] M. Nakayama, T. Okano, T. Miyazaki, F. Kohori, K. Sakai, M. Yokoyama, *J. Controlled Release* **2006**, *115*, 46–56.
- [24] a) D.-S. Guo, K. Wang, Y. Liu, *J. Inclusion Phenom. Macrocyclic Chem.* **2008**, *62*, 1–21; b) Z. Chen, A. Lohr, C. R. Saha-Möller, F. Würthner, *Chem. Soc. Rev.* **2009**, *38*, 564–584; c) Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P. Marqueand, V. Engel, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 436–449.
- [25] C. Giacomelli, V. Schmidt, R. Borsali, *Macromolecules* **2007**, *40*, 2148–2157.
- [26] a) H. Yin, Z. Zhou, J. Huang, R. Zheng, Y. Zhang, *Angew. Chem.* **2003**, *115*, 2238–2241; *Angew. Chem. Int. Ed.* **2003**, *42*, 2188–2191; b) H. Yin, Y. Lin, J. Huang, J. Ye, *Langmuir* **2007**, *23*, 4225–4230; c) H. Yin, J. Huang, Y. Lin, Y. Zhang, S. Qiu, J. Ye, *J. Phys. Chem. B* **2005**, *109*, 4104–4110; d) R. T. Buwalda, M. C. A. Stuart, J. B. F. N. Engberts, *Langmuir* **2000**, *16*, 6780–6786; e) S. V. G. Menon, C. Manohar, F. Lequeux, *Chem. Phys. Lett.* **1996**, *263*, 727–732; f) D. Otten, L. Löbbecke, K. Beyer, *Biophys. J.* **1995**, *68*, 584–597; g) P. R. Majhi, A. Blump, *J. Phys. Chem. B* **2002**, *106*, 10753–10763; h) K. Bryskhe, S. Bulut, U. Olsson, *J. Phys. Chem. B* **2005**, *109*, 9265–9274; i) P. A. Hassan, B. S. Valaulikar, C. Manohar, F. Kern, L. Bourdieu, S. J. Candau, *Langmuir* **1996**, *12*, 4350–4357; j) K. Tsuchiya, H. Nakanishi, H. Sakai, M. Abe, *Langmuir* **2004**, *20*, 2117–2122; k) H. Yin, J. Huang, Y. Gao, H. Fu, *Langmuir* **2005**, *21*, 2656–2659; l) B. F. B. Silva, E. F. Marques, U. Olsson, *Langmuir* **2008**, *24*, 10746–10754.
- [27] J. W. Steed, C. P. Johnson, C. L. Barnes, R. K. Juneja, J. L. Atwood, S. Reilly, R. L. Hollis, P. H. Smith, D. L. Clark, *J. Am. Chem. Soc.* **1995**, *117*, 11426–11433.

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