

A New Type of Deaggregators, the Bolaamphiphilic DeAgrs. Observations of the Dependence of Deaggregating Ability on Aggregator Concentration and Solvent Aggregating Power

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Four new amphiphilic molecules, *i. e.*, the bolaamphiphiles ω -trimethylamino *n*-hexadecanoate (deAgr 16), *n*-dodecanoate (deAgr 12), *n*-undecanoate (deAgr 11), and *n*-octanoate (deAgr 8) were synthesized. Their ability as deaggregators to break up the aggregating systems of hexadecyl β -naphthoate (A16) and dodecyl β -naphthoate (A12) in dioxane-water binary solvent systems was investigated in a number of solvent systems and at different A16 and A12 concentrations. The results reveal that this new type of bolaamphiphilic molecules appears to be one of the most efficient deaggregators reported, which, at very low concentrations, can effectively break up the aggregating systems of highly concentrated A16 and A12. It is also found that bolaamphiphiles with longer aliphatic chains possess greater deaggregating ability. However, when the overall concentrations of A16 and A12 are very low but still above their critical aggregating concentration, these bolaamphiphilic molecules lose their deaggregating power and tend to coaggregate with the aggregated A16 or A12 molecules. The quite efficient deaggregating ability of the long-chain bolaamphiphiles (deAgr 16 and deAgr 12), as compared to the short-chain deAgr 8, has been ascribed to their dynamic switch-on/switch-off behavior involving coiled-up and uncoiled conformations of their long aliphatic chains.

Keywords deaggregation, bolaamphiphile, aggregation, solvent aggregating power

Introduction

Aggregation is a common phenomenon for many sim-

ple organic molecules as well as complex molecules with important biological activity. Formation of aggregates may be driven by different non-covalent interactions, such as hydrogen bonding,¹ electrostatic interaction,² or hydrophobic-lipophilic interaction (HLI).³ For example, neutral organic molecules with at least one hydrocarbon chain of more than eight carbons tend to form simple aggregates (Agrs)⁴ or coaggregates (CoAgrs)⁵ in solvents with "solvent aggregating power" (SAgrP) because of the HLI driving force.⁶ We and Tung *et al.* have established solid evidence for such HLI-driven aggregation⁴⁻⁷ and extensively investigated the effects of various factors, such as molecular structure and shape,⁸ medium, temperature⁹ and electrostatic interaction,¹⁰ on the aggregating and coaggregating tendency of organic molecules. We also found that one of the inherent properties of fatty molecules such as cholesteryl esters and triglycerides, which makes them behave as culprits of atherosclerosis, might be their coaggregating tendency,^{6,11} although the disease is actually caused by much more complicated combination of many interacting factors and causes. The present work explores the possible existence of yet another type of deAgrs, which behave as deAgrs because they make use of both HLI and electrostatic interactions.

Studies by Menger and others indicate that positively and negatively charged surfactants may break up Agrs at relatively high concentration by their hydrophilicity or micelle formation.^{12,13} Previously, we also found that sugar

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derivatives with long alkyl chains can also act as deAgrs at high concentrations.¹⁴ In search for new and even more efficient deAgrs, we have investigated the deaggregating behaviour of four bolaamphiphilic compounds, *i. e.*, ω -trimethylamino *n*-hexadecanoate (**deAgr 16**), *n*-dodecanoate (**deAgr 12**), *n*-undecanoate (**deAgr 11**), and *n*-octanoate (**deAgr 8**), with oppositely charged terminal groups as shown in Scheme 1. As deAgr's, they turn out to be more effective than those reported before.¹²⁻¹⁴

Scheme 1

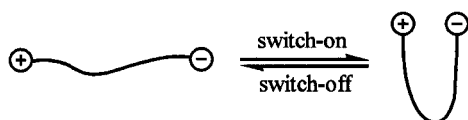


deAgr 16: $n = 16$; **deAgr 12:** $n = 12$

deAgr 11: $n = 11$; **deAgr 8:** $n = 8$

Long chain organic molecules possessing $-(\text{CH}_2)_n-$ chains with $n > 10$ tend to self-coil in solvents of high polarity or SAgP.¹⁵ We reckoned that the roughly 5.0 kJ/mol per ion pair electrostatic attraction¹⁶ in bolaamphiphiles with two oppositely charged head groups can overpower the hydrophilicity of the charged end groups and cause the methylene chain to coil up. Thus we visualized that a combination of electrostatic attraction and self-coiling of bolaamphiphilic molecules would provide these molecules with an effective "switch on/ switch-off" ability (Scheme 2) if these molecules have methylene chains longer than 10–12 carbons. Furthermore, we figured that oppositely charged molecules with shorter chains could not possess enough HLI to overpower the hydrophilicity of their charged end groups and consequently would not switch-on effectively. We hypothesized that a very fast switching-on and -off feature or mechanism might give them the ability to deaggregate Agr more effectively than the simply charged ordinary amphiphiles. The present work attempts to explore this possibility. Thus four new bolaamphiphilic compounds, *i. e.*, **deAgrs 16, 12, 11** and **8** were synthesized and their deaggregating effects on naphthalene-derived Agr systems were investigated.

Scheme 2



Experimental

Instruments and methods

Melting points are uncorrected. ¹H NMR spectra were carried out on a Varian EM 390 or DPX 300 instrument. IR spectra were recorded on a Shimadzu IR-440 instrument. Mass spectra were obtained on an HP 5958A spectrometer. Microanalysis was measured at the SIOC analytical and measurement center. Fluorescence spectra were run on a Perkin-Elmer LS55 Fluorescence spectrometer. Surface tension was measured on a JZHY1-180 surface tension apparatus.

Materials

β -Naphthoic acid dodecyl ester and β -naphthoic acid hexadecyl ester were prepared according to reported methods.¹⁷ After column chromatography (*n*-hexane/ethyl acetate 100:1), the esters were recrystallized twice from dried ethanol. Water and dioxane were purified according to standard methods.

β -Naphthoic acid dodecyl ester

White solid, m. p. 27.5–28.5 °C; ¹H NMR (CDCl₃) δ : 1.05–2.51 (m, 23H), 4.66 (t, 2H), 7.52–8.88 (m, 7H); IR (KBr) ν : 1714 cm⁻¹. Anal. calcd for C₂₃H₃₂O₂: C 81.13, H 9.47; found C 81.07, H 9.63.

β -Naphthoic acid hexadecyl ester

White solid, m. p. 44–46 °C; ¹H NMR (CDCl₃) δ : 1.13–2.00 (m, 31H), 4.70 (t, $J = 6.7$ Hz, 2H), 7.76–8.90 (m, 7H); IR (KBr) ν : 1718 cm⁻¹; Anal. calcd for C₂₇H₄₀O₂: C 81.77, H 10.17; found C 81.59, H 10.07.

(11-(Hydroxycarbonyl)undecyl) trimethylammonium bromide (**DeAgr 12**)

ω -Bromododecanoic acid (2.64 g, 10.0 mmol), trimethyl amine (1.01 g, 10.0 mmol) and benzene (25 mL) were added to a three-necked flask (100 mL). The solution was stirred at room temperature for two days. The reaction mixture was filtered and the white solid was

washed twice with anhydrous ether. The crude product was washed thoroughly with ether. The pure title compound was obtained as a white solid in 80% yield. M. p. 204—206 °C; ^1H NMR (CD_3OD) δ : 1.37—1.68 (m, 16H), 1.68—1.86 (m, 2H), 1.86—2.04 (m, 2H), 2.45 (s, 2H), 3.28 (s, 9H), 3.50 (t, $J = 6.5$ Hz, 2H); IR (KBr) ν : 1721 (C = O) cm^{-1} ; MS (ESI) m/z : 258 (M - Br) $^+$. Anal. calcd for $\text{C}_{15}\text{H}_{32}\text{BrNO}_2$: C 53.25, H 9.53, N 4.14; found C 53.07, H 9.48, N 4.03.

The following compounds were prepared by using a similar procedure as described above for (11-(hydroxycarbonyl)undecyl)trimethylammonium bromide.

(15-(Hydroxycarbonyl) pentadecyl) trimethylammonium bromide (**DeAgr 16**)

The crude compound was recrystallized from dioxane/water (2:3), to afford the title compound as a white solid in 75% yield. M. p. 210—212 °C; ^1H NMR ($\text{DMSO}-d_6/\text{D}_2\text{O}$ 4:1) δ : 1.05—1.36 (m, 22H), 1.39—1.58 (m, 2H), 1.58—1.79 (m, 2H), 2.25 (t, $J = 6.5$ Hz, 2H), 3.03 (s, 9H), 3.23 (t, $J = 6.5$ Hz, 2H); IR (KBr) ν : 1721 (C = O) cm^{-1} ; MS (ESI) m/z : 314 (M - Br) $^+$. Anal. calcd for $\text{C}_{19}\text{H}_{40}\text{BrNO}_2$: C 57.86, H 10.22, N 3.55; found C 57.46, H 9.91, N 3.76.

(10-(Hydroxycarbonyl) decyl) trimethylammonium bromide (**DeAgr 11**)

Yield 80%, white solid, m. p. 209—210 °C; ^1H NMR (CD_3OD) δ : 1.20—1.43 (m, 6H), 1.70—1.78 (m, 10H), 2.30 (t, $J = 7.0$ Hz, 2H), 3.18 (s, 9H), 3.53 (t, $J = 7.0$ Hz, 2H); IR (KBr) ν : 1724 (C = O) cm^{-1} ; MS (ESI) m/z : 244 (M - Br) $^+$. Anal. calcd for $\text{C}_{14}\text{H}_{30}\text{BrNO}_2$: C 51.85, H 9.32, N 4.32; found C 51.50, H 9.28, N 4.28.

(7-(Hydroxycarbonyl) heptyl) trimethylammonium bromide (**DeAgr 8**)

White solid, m. p. 182—183.5 °C; ^1H NMR (CD_3OD) δ : 1.45—1.69 (m, 6H), 1.69—1.89 (m, 2H), 1.89—2.08 (m, 2H), 2.48 (s, 2H), 3.12 (s, 9H), 3.48 (t, $J = 6.4$ Hz, 2H); IR (KBr) ν : 1722 (C = O) cm^{-1} ; MS (ESI) m/z : 202 (M - Br) $^+$.

Anal. calcd for $\text{C}_{11}\text{H}_{24}\text{BrNO}_2$: C 46.81, H 8.57, N 4.96; found C 46.90, H 8.59, N 5.08.

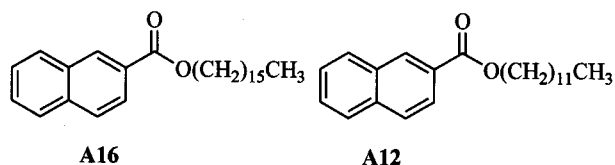
Fluorescence measurement

All the fluorescence spectra were recorded on a Perkin-Elmer LS55 instrument at the excitation wavelength of 284 nm at 35 °C in the dioxane (DX)- H_2O aquio-organo systems of different Φ values (Φ is the volume fraction of dioxane of the solvent mixture), the monomer emission intensity was recorded at 370 nm. All the data reported are the average value of two repeated experiments. The experimental uncertainty is $\pm 5\%$. All the solutions contain 0.34 mol/L of sodium chloride.

Results

Fluorescence method has been used to investigate the deaggregating ability of these bolaamphiphilic molecules.¹⁴ Hexadecyl β -naphthoate (**A16**) and dodecyl β -naphthoate (**A12**) were used as fluorescence probes (Scheme 3). The monomeric emission spectra of the fluorescent probes were measured in the absence or presence of the bolaamphiphiles in various binary DX- H_2O solvent systems. As previously described, I_0 represents the monomer fluorescence intensity in the absence of deAgrs, while I represents the monomer fluorescence intensity in the presence of deAgrs.^{5,13} When I/I_0 is equal to or less than 1, the bolaamphiphilic additives have no deaggregating effect. If I/I_0 is remarkably greater than 1, they are considered to behave as deaggregators. I/I_0 values and plots of I/I_0 vs. [deAgr] are used to assess the deaggregating effectiveness of the deAgr additives.^{14,18} In order to exclude the possible salt effect brought about by the excess of polar bolaamphiphilic additives and also for the sake of comparison with reported results, all the results were obtained in solvent systems containing 0.34 mol/L NaCl. Since this concentration is substantially higher than the greatest additive concentration (0.01 mol/L), it is reasonable to assume that the salt effect of the additives is negligible.¹⁴

Scheme 3



The critical aggregating concentrations (CAGCs) were determined to be 9.8×10^{-7} mol/L ($\Phi = 0.30$), 2.8×10^{-6} mol/L ($\Phi = 0.35$), and 1.0×10^{-5} mol/L ($\Phi = 0.40$) for **A12** and to be 1.3×10^{-6} mol/L ($\Phi = 0.40$), and 7.8×10^{-6} mol/L ($\Phi = 0.45$) for **A16** in the DX-H₂O solvent systems according to the method established in our laboratory.^{4,14,18} The CAGCs values were obtained based on the breaking points of the plots of the I_e/I_m values versus the aggregator concentration, where I_e and I_m represent the excimer and monomer emission intensity, respectively. As expected, **A16** with a longer aliphatic chain affords a lower CAGC value, as compared to **A12** ($\Phi = 0.40$), indicating that the former has a greater aggregating tendency.

Fig. 1 illustrates the effects of all four bolaamphiphiles on the I/I_0 ratios of **A16** ($[\text{A16}] = 1.0 \times 10^{-4}$ mol/L) in the $\Phi = 0.40$ solvent system. The inset represents the plot of I/I_0 vs. $[\text{deAgr 16}]$ ($\Phi = 0.40$) with a narrower concentration range of **deAgr 16** because of its limited solubility. The results obtained for the systems of **deAgrs 12** and **A16** in the $\Phi = 0.45$ DX-H₂O solvent are also included in the figure.

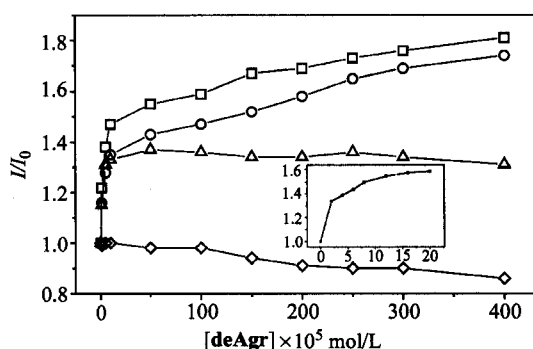


Fig. 1 Plots of the monomer I/I_0 values of **A16** at 1.0×10^{-4} mol/L vs. $[\text{deAgr 12}]$ (\square), $[\text{deAgr 11}]$ (\circ), $[\text{deAgr 8}]$ (\triangle) in the $\Phi = 0.40$ DX-H₂O solvent system, and vs. $[\text{deAgr 12}]$ (\diamond) in the $\Phi = 0.45$ DX-H₂O solvent system. The inset represents the plot of the monomer I/I_0 values of **A16** at 1.0×10^{-4} mol/L vs. $[\text{deAgr 16}]$ (within a narrower concentration range) in the $\Phi = 0.4$ DX-H₂O solvent system. All experiments were carried out at 35 °C.

Fig. 2 lists the effects of the deAgrs on the monomer fluorescence intensity of **A16** at the lower concentration of 2.0×10^{-5} mol/L in the $\Phi = 0.40$ solvent system. Ow-

ing to the lower solubility of the deAgr, the plot for the results of **deAgr 16** vs. **A16** is included as an inset.

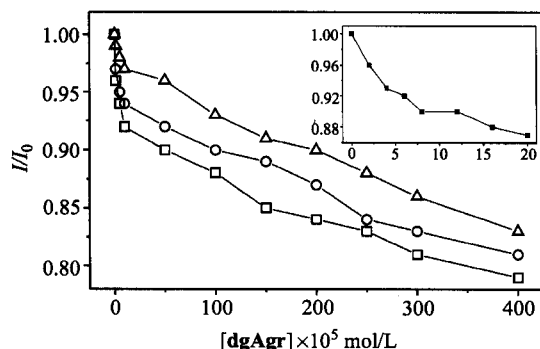


Fig. 2 Plots of the monomer I/I_0 values of **A16** at 2.0×10^{-5} mol/L vs. $[\text{deAgr 12}]$ (\square), $[\text{deAgr 11}]$ (\circ), $[\text{deAgr 8}]$ (\triangle), and $[\text{deAgr 16}]$ (inset, within a narrower concentration range) in the $\Phi = 0.40$ DX-H₂O solvent system at 35 °C.

The influences of **deAgr 12** with changing concentrations on the monomer emission intensity of **A16** at different concentrations in the $\Phi = 0.40$ DX-H₂O solvent system were also investigated and the corresponding results are shown in Fig. 3. The data obtained for **A16** at the concentrations of 1.0×10^{-4} mol/L (Fig. 1) and 2.0×10^{-5} mol/L (Fig. 2) are also included in the figure for the sake of comparison.

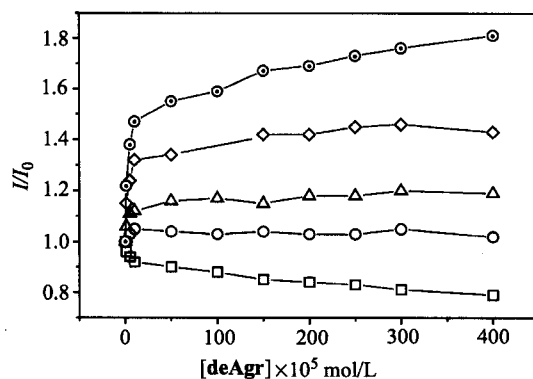


Fig. 3 Plots of the monomer I/I_0 values of **A16** at 2.0×10^{-5} mol/L (\square), 4.0×10^{-5} mol/L (\circ), 6.0×10^{-5} mol/L (\triangle), 8.0×10^{-5} mol/L (\diamond), and 1.0×10^{-4} mol/L (\odot) vs. $[\text{deAgr 12}]$ in the $\Phi = 0.40$ DX-H₂O solvent system at 35 °C. The results obtained for **A16** at 2.0×10^{-5} mol/L (Fig. 2) and 1.0×10^{-4} mol/L (Fig. 1) are included for comparison.

Fig. 4 illustrates the effects of the addition of different bolaamphiphiles on the monomer fluorescence intensity of **A12** at 1.0×10^{-4} mol/L in $\Phi = 0.30$ DX-H₂O solvent system. This solvent system with a lower Φ value and therefore greater aggregating power was used because **A12** possesses a lower aggregating tendency.

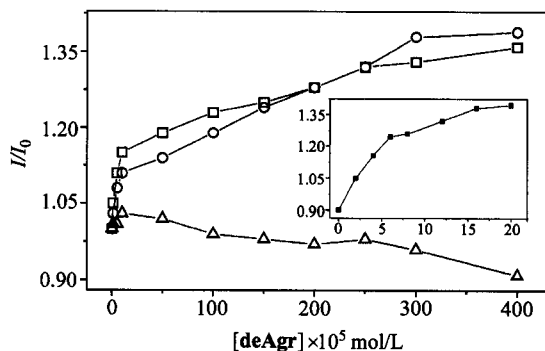


Fig. 4 Plots of the monomer I/I_0 values of **A12** at 1.0×10^{-4} mol/L vs. [**deAgr 12**] (\square), [**deAgr 11**] (\circ), [**deAgr 8**] (\triangle), and [**deAgr 16**] (within narrower concentration range, inset) in the $\Phi = 0.30$ DX-H₂O solvent system at 35 °C.

The results obtained for the effects of the bolaamphiphiles on the monomer emission intensity of **A12** at the lower concentration of 2.0×10^{-5} mol/L in the same solvent system is shown in Fig. 5. The data obtained for **deAgr 16** are not presented since no substantial change was observed for the I/I_0 values ($< 5\%$) of **A12** in the narrower concentration range of $(1.0\text{--}20.0) \times 10^{-5}$ mol/L of **deAgr 16**.

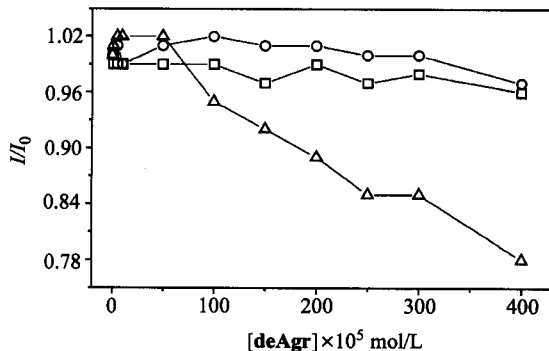
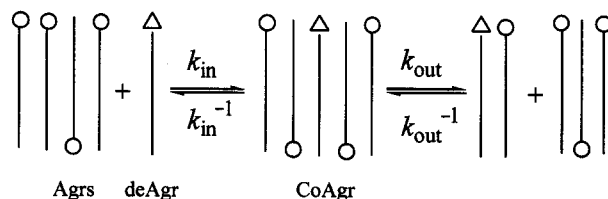


Fig. 5 Plots of the monomer I/I_0 values of **A12** at 2.0×10^{-5} mol/L vs. [**deAgr 12**] (\square), [**deAgr 11**] (\circ), and [**deAgr 8**] (\triangle) in the $\Phi = 0.30$ DX-H₂O solvent system at 35 °C.

Discussion

The extremely complicated processes of aggregation, coaggregation, and deaggregation of all kinds of molecular, supramolecular and conformational species defy exact kinetic description. However, we may still try to visualize or partly understand them through a very crude and simplistic presentation, as shown in Scheme 4.^{7,14} For practicality purpose, the present work is the exploration of a new possible type of deAgr, namely, the “bolaamphiphiles” (**deAgr *n***), which acts by virtue of their switch on/switch off mechanism or capability. For theoretical interest, we wished for the finding of unforeseen experimental observations, which could lead to new studies. Both of these objectives have now been partly achieved.

Scheme 4



In the present study, three kinds of phenomena have been observed for the effects of the added bolaamphiphiles on the monomer fluorescence emission of **A16** and **A12**. (i) At the high aggregation concentrations of **A16** and **A12** (Figs. 1, 3, and 5), addition of the bolaamphiphilic molecules enhances the monomer emission intensity of the aggregators ($I/I_0 > 1$). (ii) Whereas at the lower **A16** and **A12** aggregation concentrations (Figs. 2 and 5), the monomer emission intensity of the aggregating compounds decreases with the addition of the bolaamphiphiles ($I/I_0 < 1$). (iii) In some other cases, the bolaamphiphilic additives have no important influence on the monomer emission intensity of the aggregators ($I/I_0 \approx 1$) (Figs. 3 and 5).

Previous studies have shown that, for naphthalene-derived aggregators, the monomer emission intensity will increase if the aggregates are broken up or reduced in size by a deAgr.¹⁴ Therefore, the I/I_0 value has been used as one parameter to evaluate the effect of the additives. If the I/I_0 value is clearly greater than 1, the additive can be considered to act as deAgr. On the other hand, if the

monomer emission intensity decreases with the increasing concentration of the additives, the additives would be considered to have coaggregated with the Agr's.^{14,19}

It has been found that addition of the excessive bolaamphiphilic compounds does not quench or strengthen the monomer emission of **A12** and **A16** when their concentrations are less than their CAgC's in the solvent systems used in this study. Surface tension measurement in the $\Phi = 0.40$ DX-H₂O solvent system reveals that the micelles of the bolaamphiphilic compounds do not form at the concentration range of the deAgr's used in this study. Therefore, the emission intensity strengthening is not the result of the interaction of micelles.¹⁴ Since all the data were obtained in the DX-H₂O binary systems containing high concentration of NaCl (0.34 mol/L), the possible salt effect of the bolaamphiphiles can also be excluded.²⁰ It appears reasonable to attribute the strengthening of the monomer emission intensity of **A16** (Fig. 1, [**A16**] = 1.0×10^{-4} mol/L, $\Phi = 0.40$) as the result of the breaking-up or size reduction of the corresponding aggregating systems. That is, the result reflects that all the four bolaamphiphilic compounds **deAgrs 16, 12, 11** and **8** can behave as deAgrs for the **A16** aggregating systems. The greater change brought about by the addition of the longer bolaamphiphiles **deAgrs 16, 12** and **11** reflects their greater deaggregating ability.

Interestingly, an unforeseen opposite tendency was displayed for the monomer emission intensity of **A16** at the lower **A16** concentration of 2.0×10^{-5} mol/L in the same solvent system for all the four added bolaamphiphilic compounds (Fig. 2). That is, the addition of all the four bolaamphiphiles decreases the intensity of the monomer emission ($I/I_0 < 1$). We attribute this phenomenon to the result of the formation of CoAgs between the Agrs and the bolaamphiphiles. The result indicates that, at the low concentration of **A16** (still above the CAgC), the bolaamphiphiles can not act as deAgrs, but rather as coaggregators.

In order to see if this unexpected concentration dependence of the effects of the bolaamphiphiles on the naphthalene Agrs is a general phenomenon, a plot of the I/I_0 values of **A16** at changing concentration vs. [**deAgr 12**] was performed, as shown in Fig. 3. It can be seen that at the 4.0×10^{-5} mol/L concentration of **A16**, no important change was observed for the emission intensity with the addition of **deAgr 12**. At lower **A16** concentrations, the deAgrs lose their deaggregating ability and tend

to coaggregate with the aggregating systems of **A16**. Previously, we and Tung *et al.* found that some hydrophobic additives can coaggregate with naphthalene-derived aggregating systems, which lead to the reduction of the monomer emission intensity.^{14,19} However, the phenomenon that the effects of additives on the aggregating systems depend on the concentration of the aggregating systems has not been observed before. The result reflects the unique feature of the new bolaamphiphilic molecules as deAgrs, although we are hard put to provide a decent rationalization for this interesting phenomenon.

In the $\Phi = 0.45$ solvent system, addition of **deAgr 12** does not strengthen the monomer emission of **A16**, as observed in the $\Phi = 0.40$ solvent system. Instead, **deAgr 12** considerably quenches the monomer emission as shown in Fig. 1. The result indicates that the SAgP of the solvent can also substantially affect the balance of the bolaamphiphilic compounds acting as deAgrs or CoAgs. To our knowledge, such changing solvent effect has not been observed in previous studies on aggregation of simple organic molecules.^{6,9}

The effects of the bolaamphiphiles **deAgrs 16, 12** and **11** on the monomer emission of **A12** in the $\Phi = 0.30$ solvent system was also investigated. This solvent system of greater SAgP (smaller Φ value) was chosen for comparison with that at the lower **A12** concentration of 2.0×10^{-5} mol/L (vide infra). The $\Phi = 0.40$ solvent system of smaller SAgP was not used since **A12** displayed smaller aggregating tendency than **A16** and the corresponding data could not be obtained in that solvent system.⁶ The investigation reveals a similar tendency as that observed for **A16** in the $\Phi = 0.40$ solvent system (Figs. 1 and 4). The result indicates that these bolaamphiphilic additives can also break up the aggregation of **A12**. However, instead of strengthening the monomer emission, **deAgr 8** displays a considerable quenching effect ($I/I_0 < 1$), suggesting that this additive has a weak deaggregating ability (if any) and tends to coaggregate with **A12**.

A similar study for **A12** at the lower concentration of 2.0×10^{-5} mol/L in the $\Phi = 0.30$ solvent system reveals very different effects imposed by the bolaamphiphilic additives. As shown in Fig. 5, addition of excessive **deAgrs 12** and **11** to the **A12** aggregating system has no important effect on the monomer emission intensity of **A12**. Since the above study (Fig. 4) has revealed that the bolaamphiphilic additives can insert and/or grab and bring out the Agr molecules from the aggregating state, this re-

sult may indicate that **deAgrs 12** and **11** display both coaggregating and deaggregating effects, which are closely comparable and thus may counteract each other under certain circumstances. The bolaamphiphile **deAgr 16** also exhibits similar effect, albeit only in a narrow concentration range, which is not included in Fig. 5. Fig. 5 also shows that the bolaamphiphile **deAgr 8** displays the similar monomer emission quenching effect on **A12** here as observed for **A12** at the concentration of 1.0×10^{-4} mol/L (Fig. 4), although the fluorescent quenching efficiency is higher at the lower **A12** concentration.

Figs. 1, 3 and 4 also reveal that, in the cases of deaggregating systems, although the monomer emission intensity of the aggregated **A16** and **A12** can be strengthened by addition of excessive bolaamphiphiles, especially **deAgrs 16, 12** and **11**, at all concentrations, the emission strengthening is affected most clearly at the initial stage of concentration increase (1–15 times of [**A16**] or [**A12**]). Further increase of the bolaamphiphile concentration only slowly increases the emission strengthening. In other words, the long-chain bolaamphiphilic additives, at very low concentrations, can effectively deaggregate the naphthalene-derived aggregating systems. Previously reported ionic deaggregators can achieve the deaggregation purpose only at much higher concentrations,¹² therefore the present bolaamphiphilic compounds also might be one of the most efficient kind of deaggregating reagents. The very great deaggregating ability of this new kind of bolaamphiphilic molecules may result from the coiled structure of the long aliphatic chains, which should be more efficient to grab and bring out the aggregated molecules to the medium than simple uncoiled aliphatic chains.^{13,14} It is also an intriguing fact that the new kind of bolaamphiphilic molecules impose two different effects, *i. e.*, a strengthening as well as a weakening of the monomer emission intensity of the aggregating probe molecules. In addition, The present results could not answer such questions: Are the numbers of molecules in the aggregating species are different? How many molecules does one aggregating species have on the average?²⁰

In summary, we have reported a new kind of bolaamphiphilic deaggregators for naphthalene-derived aggregating systems. The deaggregating effects are strongly dependent on the concentration of the aggregating systems, solvent aggregating power, and chain length of the deaggregating bolaamphiphiles. Long chain-containing bolaamphiphiles **deAgrs 16** and **12** usually exhibit stronger

deaggregating ability. The deaggregating ability of the bolaamphiphiles decreases or even vanishes with the decrease of the concentration of the aggregated systems. **DeAgrs 16** and **12** turn out to behave as coaggregators but not deaggregators when the concentration of the aggregated systems is very low. The very effective deaggregating ability of the long-chain bolaamphiphiles has been mostly attributed to the existence of the coiled conformations of their long aliphatic chains. The fact that the short-chain bolaamphiphile **deAgr 8** fails to deaggregate aggregated **A16** and **A12** may serve as a direct demonstration of the switch-on/switch-off concept or mechanism because the short-chain deAgrs cannot coil up and thus fail to deaggregate. Notably, concepts made use of in the present work are related to our studies on the electrostatically stabilized aggregates (ESAgrs).²¹

References and notes

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- 20 Molecular modeling might provide further insight for these questions. We thank one referee for this suggestion.
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