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Spontaneous Counterion-Induced Vesicle Formation: Multivalent Binding to Europium(III) for a Wide-Range Optical pH Sensor

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A counterion-directed molecular design strategy is described for the spontaneous formation of stable vesicles via readily available imidazolium salts with the EDTA counterion in aqueous media. The counteranion is employed to adjust the balance between hydrophobic and hydrophilic parts, which satisfies the requirement of packing parameter for vesicle formation. The counterion-induced vesicles (CIVs) feature spontaneous formation, simple preparation, and easy availability of surfactants. Importantly, the unusual counterion-induced vesicle-like sphere aggregates can further chelate europium(III) ions to enhance the europium-centered emission in aqueous media and make it viable for an optical pH sensor, which exhibits a linear response in a wide range of pH values from 3 to 11. To the best of our knowledge, this constitutes one of the widest ranges of Eu-based pH sensors reported so far. This design concept has offered a new avenue for the preparation of functional vesicles.

1. Introduction

Vesicles, which contain a bilayer membranous structure with an inner aqueous void volume, have been a hot subject of research because of their potential for applications in models of biological membranes,[1] as agents for drug/gene delivery,[2] and as microreactors for the production of inorganic materials.[3] Generally, vesicles are constituted by amphiphiles bearing polar head groups and double flexible apolar tails (e.g., phospholipids) under external stimuli such as sonication or extrusion (**Figure 1**a).[4] The amphiphiles employed in these studies are usually either not easily available or expensive and require multi-step synthesis. Given that most surfactants are single-tailed, an effective method based on mixed cationic/anionic (called "catanioinc") surfactants has been developed to construct vesicles (Figure 1b).[5] The further fusion of formed vesicles can be initiated by multivalent anions.[5b] When a cationic surfactant and an anionic surfactant are simply mixed at an appropriate ratio, the strong reduction in the area per headgroup triggered by ion pairing may induce the formation of thermodynamically stable molecular bilayers at a low concentration. Compared with vesicles formed from phospholipids and other double-chained amphiphiles, the catanionic vesicles feature readily available structure, excellent stability, and convenience in production. Since Kaler et al. reported the first spontaneous vesicle formation in the cetyltrimethylammonium tosylate and sodium dodecylbenzene sulfonate system,[6] a great deal of excellent work about the vesicle phases that occur in cationic–anionic surfactant mixtures has been done.[7] These methods are certainly attractive, but multiple surfactants (at least two) are required and in most cases, one of the surfactants has to be in excess, otherwise the resulting vesicles may tend to precipitate out due to the lack of electrostatic repulsion, which would lead to difficulties for further application.[5,8]

Imidazolium salts typically bearing two alkyl groups at the two nitrogen atoms of the imidazolium core, as one of the most common type of ionic liquids, have been used as the components of catanionic surfactants to synthesize vesicles.[9] Following our long-term interest in the development of imidazolium-based materials,[10,11] we herein demonstrate a new method for vesicle preparation called "counterion-induced vesicle (CIV) formation". It is known that vesicle formation from micelle can be accomplished mainly by adjusting the packing parameters between hydrophilic heads and hydrophobic tails

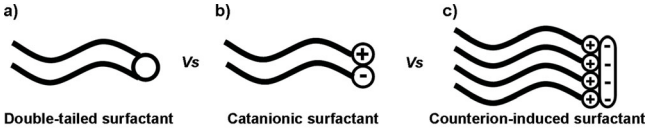

Figure 1. Comparison of three different methods to prepare vesicles: a) a method based on double-tailed surfactant; b) a method based on mixed cationic/anionic (called "catanionic") surfactants; and, c) the counterion-induced surfactant method reported herein.

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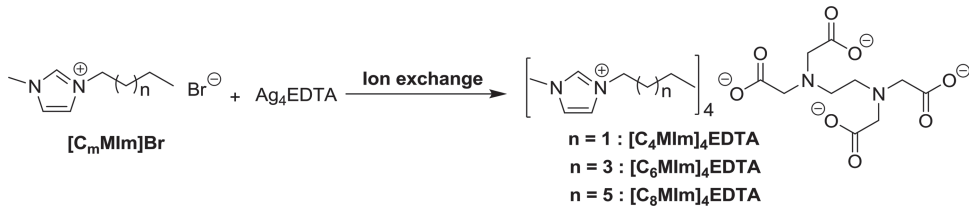

Scheme 1. Preparation of functional 1-alkyl-3-methylimidazolium salts with the EDTA counterion.

of amphiphiles. In the method of double-tailed surfactant (Figure 1a), two hydrophobic tails are covalently attached to a polar headgroup, while the method of the mixed cationic/anionic surfactant takes advantage of the electrostatic interactions between cationic and anionic surfactants (Figure 1b). In the current method, the counterion described here is used to adjust the balance between hydrophobic and hydrophilic parts to meet the requirement of packing parameter for vesicle formation (Figure 1c).[12] To illustrate this new strategy, a series of imidazolium salts with the anion of ethylenediaminetetraacetic acid (EDTA) as the counterion have been designed. In each imidazolium salt four identical imidazolium cations share one EDTA anion. The experiment results show that the imidazolium salts with the EDTA anion as the counterion are capable of spontaneously forming stable vesicles with controllable size in aqueous media, whereas the corresponding imidazolium salts with bromide counteranion cannot form any significant assemblies. This method not only offers a new avenue for the preparation of vesicles, but also brings a potential for vesicle applications through the introduction of counterions. As an example, the vesicle-like sphere aggregate has been developed for enhancement of the europium-centered emission in aqueous media by virtue of multivalent binding of EDTA with europium(III) ions. More importantly, the Eu-centered emission exhibits a nice linear response in a range of pH values from 3 to 11, which would serve as a good candidate for a wide range optical pH sensor.

2. Results and Discussions

The EDTA anion was chosen as the counterion mainly based on the following considerations: first of all and most importantly, the EDTA anion contains multi-electric charges, which facilitates the adjustment of the areas between hydrophobic and hydrophilic parts; and, secondly, as a polydentate ligand containing four carboxylic anions, the EDTA has strong chelating ability with metal ions, which provides the possibility for further applications. In this work, three 1-alkyl-3-methylimidazolium salts with the EDTA anion ($[C_mMIm]_4EDTA$) were synthesized through a simple ion-exchange process (**Scheme 1**), which involved the reaction of 1-alkyl-3-methylimidazolium bromide $[C_mMIm]Br$ with silver EDTA (Ag_4EDTA), followed by washing with acetone to give analytically pure $[C_mMIm]_4EDTA$ with high yields. The chemical compositions of these compounds were characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (see the Supporting Information).

With these compounds in hand, their self-assembly behaviors in aqueous solution were investigated first by dynamic light scattering (DLS) measurement. All three compounds are readily soluble in water and give rise to optically transparent solutions at room temperature. The light-scattering experiments indicated that no assemblies were monitored for $[C_4MIm]_4EDTA$. To our delight, nanoparticles with a hydrodynamic diameter of approximately 200 nm were obtained when $[C_6MIm]_4EDTA$ was employed (**Figure 2**a). With continuously increasing the hydrophobic chain to eight carbons ($[C_8MIm]_4EDTA$), larger nanoparticles with a size of approximately 450 nm were formed (Figure 2b). The critical aggregation concentrations (CACs) of $[C_6MIm]_4EDTA$ and $[C_8MIm]_4EDTA$ were about 35.0 and 20.0 mM, respectively (Figure S1). It is noteworthy that the

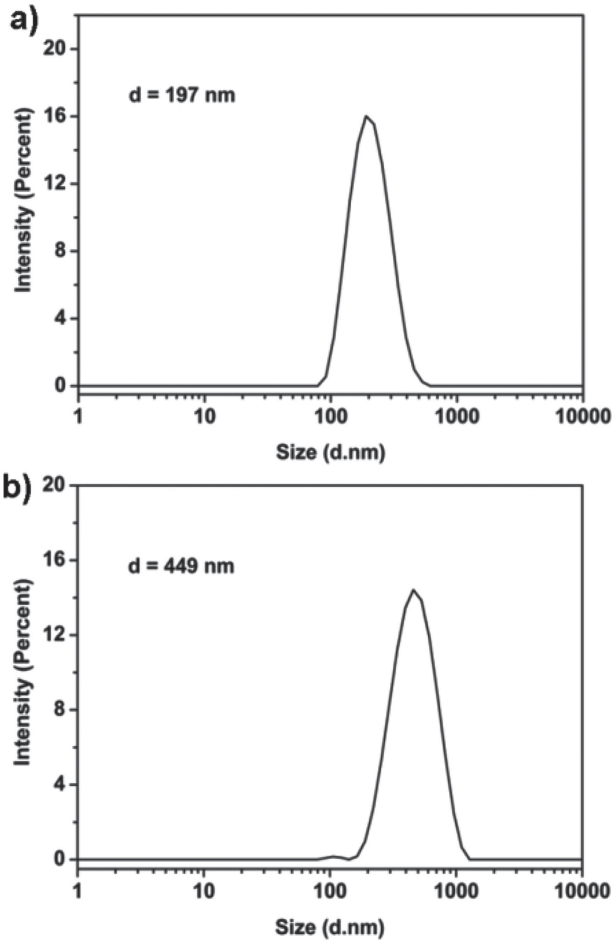

Figure 2. Distribution of the hydrodynamic diameters of CIVs formed by: a) $[C_6MIm]_4EDTA$ (40 mM), and, b) $[C_8MIm]_4EDTA$ (40 mM) determined by DLS.

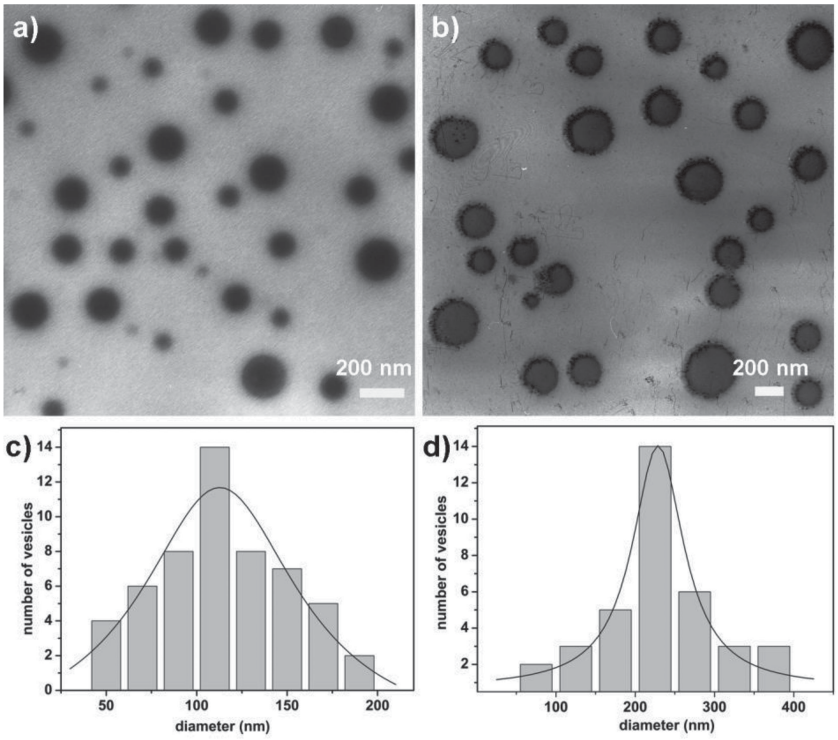

Figure 3. a) TEM micrograph of counterion-induced vesicles (CIVs) formed by $[C_6MIm]_4EDTA$ in aqueous solution (100 mM) on a carbon-coated copper grid. b) TEM micrograph of CIVs formed by $[C_6MIm]_4EDTA$ (40 mM), stained with an aqueous solution of europium chloride. c, d) The corresponding histograms (Lorentzian fit) of vesicles in a and b, respectively.

vesicles could maintain stability for a period of several months at ambient temperature with a negligible decrease of size.

Transmission electron microscopy (TEM) allowed us to directly visualize these vesicles. The TEM specimens were prepared by dipping a carbon-coated copper grid into aqueous solutions of the samples. The TEM grid was dried for 0.5 h at room temperature, and then subjected to TEM observation. As illustrated in **Figure 3**a, the TEM image obtained from the sample of $[C_6MIm]_4EDTA$ showed the formation of distinct spherical aggregates with a mean diameter of around 110 nm (Figure 3c). Very interestingly, from the sample stained with europium chloride one could see an obvious contrast between the inner and periphery of the spherical structure (Figure 3b). We rationalized that this contrast was generated by the heavy Eu^{3+} ions, which coordinated with the EDTA counterions distributed in the periphery of vesicles. In addition, the TEM image of the $[C_8MIm]_4EDTA$ sample exhibited a more uniform size distribution than that of the $[C_6MIm]_4EDTA$ dispersion (Figure S2 in the Supporting Information). The particle size determined from TEM is smaller than that from DLS. It is reasonable to assume that the DLS assay determines the hydrodynamic diameter with fully hydrated vesicles in solution while the TEM assay measures the dry samples in the collapsed state.

As we know, one of the important characteristics of vesicles is their ability to trap hydrophilic molecules. We then tested the entrapment ability of the counterion-induced vesicles by the glucose leakage assay, a widely used technology for liposome encapsulation.[13] Once there is any glucose entrapped inside the vesicles, the addition of detergent (e.g., Triton X-100) causes glucose leakage from the disrupted vesicles. The escaped glucose is then phosphorylated and oxidized in the presence of enzymes while nicotinamide adenine dinudeotide phosphate (NADP) is reduced to NADPH, which shows a typical peak at 340 nm in absorbance. Since the enzyme-catalyzed process is very fast, an increase in the absorbance intensity at 340 nm normally correlates directly with the amount of glucose efflux. Thus, one can monitor the release of entrapped glucose as well as the trapping efficiency of the vesicles.

We here chose the CIVs of $[C_6MIm]_4EDTA$ as the model to perform the entrapping experiment. Glucose-loaded CIVs were prepared in a 300.0 mM glucose aqueous solution instead of pure water according to a slightly modified procedure of CIVs synthesis. After the external glucose was removed by gel filtration, hexokinase, glucose-6-phosphate dehydrogenase, NADP, and ATP were added into the vesicle solution. At this stage, the absorbance at 340 nm is very weak (**Figure 4**a). Triton X-100 was then added into the sample and vortexed for 5 min to make sure that the vesicles were disrupted and all entrapped contents were released, which leads to an absorbance increase at 340 nm. This observation demonstrated that a substantial amount of glucose was efficiently entrapped inside the CIVs. It is noteworthy that the entrapped content had a long-term stability, and the release of glucose was less than 20% even after 2 weeks (Figure 4b), while most phospholipid vesicles usually spend only a very few days for total release. The long-term stability of CIVs is also comparable with that of documented catanionic vesicles.[14] Thus, the CIVs have enough stability and would be promising candidates for high-efficiency capture and long-term encapsulation of hydrophilic solutes.

Monitoring of pH is one of the most important tasks in environmental and biological systems. In recent years, many efforts have been made to develop lanthanide-based pH sensors due to their unique luminescence properties.[15] However, their applications are hampered by inherent limitation of energy losses to OH oscillators of nearby or coordinated water molecules in aqueous media, especially for Eu-centered emission.[16] To eliminate the undesirable quenching, a combination of organic ligand and/or co-ligand is usually required.[17] However, multistep synthetic procedure and tedious screening for ligands have restricted further applications to some extent. In the counterion-induced vesicles, a number of EDTA anions are located at the periphery of the spherical structure. Therefore, the CIVs are particularly suited for multivalent binding with metal ions to induce luminescence enhancement. Indeed, the addition of europium chloride into the CIVs of $[C_8MIm]_4EDTA$ led to a bright pink color under UV irradiation. Subsequently, we further investigated the luminescence of $EuCl_3$ with different EDTA salts in aqueous solutions. As

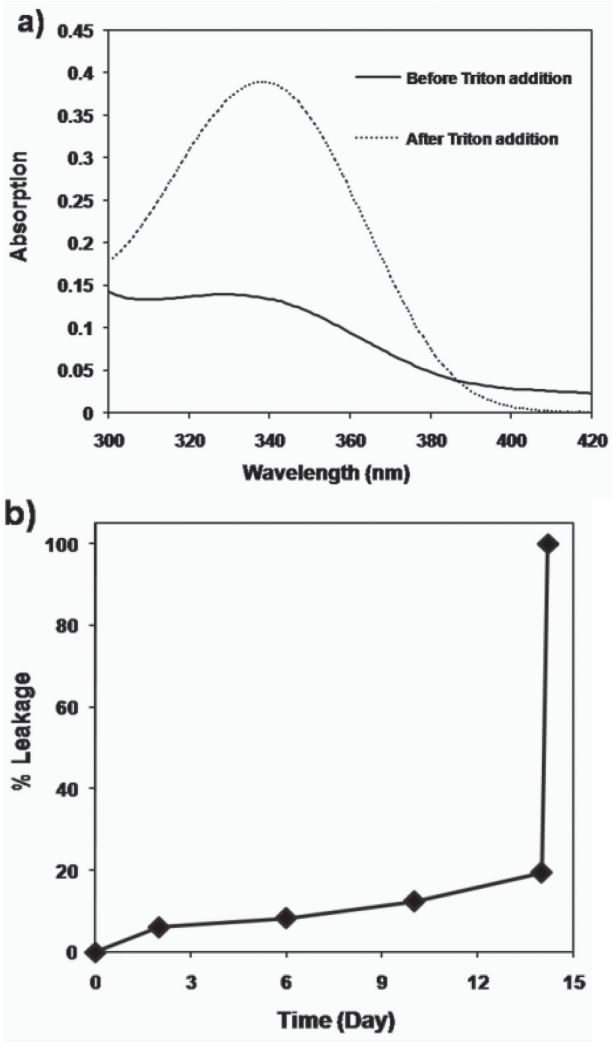

Figure 4. a) Comparison of the absorbance spectra of glucose-loaded CIVs before and after adding Triton X-100 (5% v/v), [[C_6MIm]$_4$EDTA] = 12.5 mM. b) Percent leakage of glucose from CIVs over time. The vesicles were lysed at the 14th day upon addition of Triton X-100.

shown in **Figure 5**, the Eu-centered emission was enhanced with the increase of the alkyl chain length of imidazolium salts and an aqueous [C_8MIm]$_4$EDTA solution gave an approximately three-fold luminescence emission enhancement, as compared to an aqueous Na_2MgEDTA solution. Thus, our system overcomes the obstacles encountered in the previously reported organic ligand-assisted systems. We hypothesized that the luminescence enhancement might be attributed to a synergistic effect of the following two aspects: i) the simultaneous binding of Eu with multiple EDTA ions surrounding the surface of the CIVs leads to the emission enhancement; and, ii) the local coordination environment of europium is protected by the hydrophobic micro-environment derived from the vesicle-like sphere structure, reducing the quenching effect of water, which was confirmed by measurement of water coordination number using luminescence decay of the Eu^{3+}. The water-coordination number of Eu^{3+} ion decreased from 2.74 for the Eu/Na_2MgEDTA system to 0.80 for the Eu/[C_6MIm]$_4$EDTA system

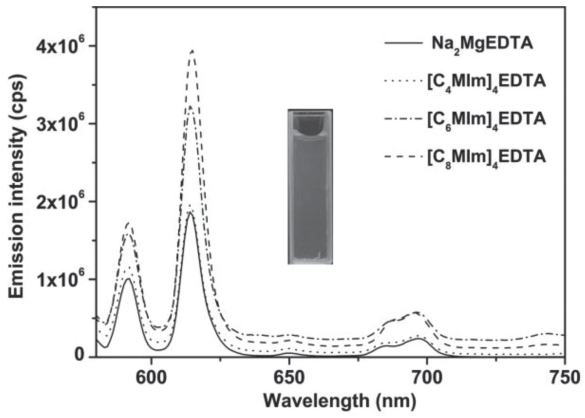

Figure 5. Spectra of Eu-centered emission with different EDTA salts (40.0 mM) in aqueous solutions, excited at 395 nm ([Eu]/[EDTA] = 1:1, pH = 8.5). Inset: photograph of Eu/[C_8MIm]$_4$EDTA in aqueous solution under UV irradiation at 365 nm.

(Table S1 in the Supporting Information). Notably, the emission of Eu/[C_4MIm]$_4$EDTA was almost identical to that of Eu/Na_2MgEDTA. We rationalized that [C_4MIm]$_4$EDTA could not undergo significant self-assembly, leading to nearly the same

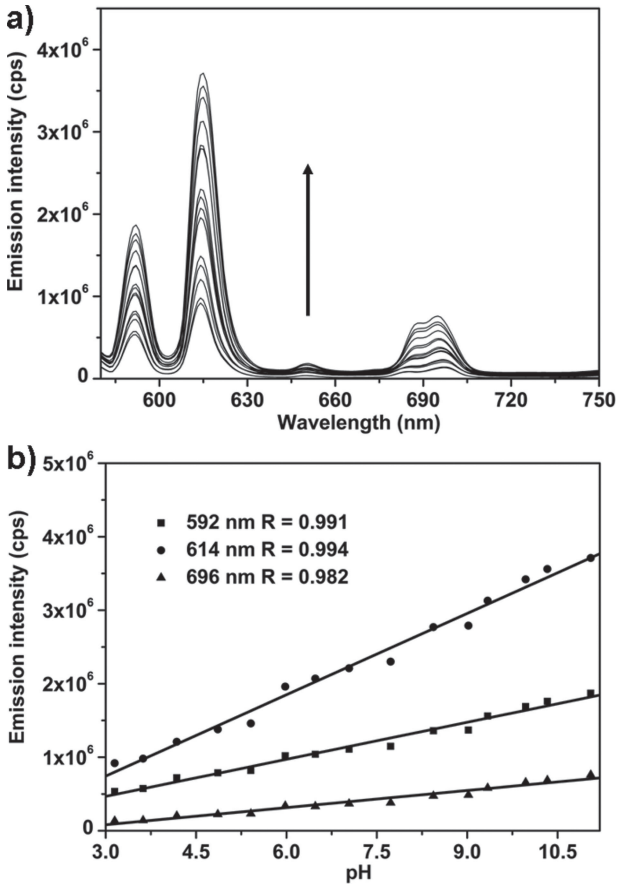

Figure 6. a) pH Dependence of the Eu-centered emission spectra in an aqueous [C_6MIm]$_4$EDTA solution (40.0 mM, [Eu]/[EDTA] = 0.5), excited at 395 nm. The pH values from bottom to top correspond to 3.15, 3.62, 4.18, 4.86, 5.41, 5.98, 6.48, 7.04, 7.73, 8.41, 9.02, 9.34, 9.98, 10.33, and 11.05. b) Linear fits between pH values and the intensities of the Eu-centered emission at 592, 614, and 696 nm.

local Eu coordination environment as that in $Na_2MgEDTA$ solution. It should be noted that the enhanced Eu-centered emitting level in aqueous solution was stable in air and under light irradiation (Figure S4 in the Supporting Information).

It is known that the EDTA anion is sensitive to pH and a stepwise protonation of the carboxylic groups can occur during the decrease of local pH, which could lead to the change of coordination mode of Eu^{3+} and further influence the emission intensity of Eu^{3+}. To our delight, the Eu/$[C_6MIm]_4EDTA$ system is capable of serving as an optical pH sensor. **Figure 6** illustrated the emission intensity of Eu^{3+} increased gradually with the increase of pH value and a linear response was observed in a wide pH range from 3 to 11. It is noted that no obvious changes of the Eu^{3+} emission could be observed in the Eu/$Na_2MgEDTA$ system in the same pH range (Figure S5 in the Supporting Information). When the pH value was more than 11, the emission intensity of Eu^{3+} ion became weaker probably due to the decomposition of imidazoium cation and partial formation of europium hydroxide. When the pH value was less than 3, a small quantity of the protonated EDTA anion might precipitate out of the system. It is worth noting that this pH sensor, to the best of our knowledge, constitutes one of the widest ranges of Eu-based pH sensors reported so far.[15c]

3. Conclusions

We have demonstrated a new strategy for the spontaneous formation of stable vesicles by readily available imidazolium salts with the EDTA anion in aqueous media. The formation of the counterion-induced vesicles mainly relies on a selection of multi-electric charged counterion to adjust the balance between hydrophobic and hydrophilic parts. The unusual counterion-induced vesicle-like sphere aggregates can further chelate europium(III) ions to enhance the Eu-centered emission in aqueous media and make it viable for an optical pH sensor, which exhibits a linear response in a wide range of pH values (3–11). The easy availability of couterion-induced surfactants and the simple preparation of vesicles would make this method highly attractive for the synthesis of advanced functional vesicles. Further work will be directed toward exploring other combinations of counterions and surfactants to give birth to a general methodology.

4. Experimental Section

General Remarks: NMR spectra were obtained on a Bruker AV II-400. The ^1H NMR spectroscopy chemical shifts were measured relative to $CDCl_3$ or D_2O-d_2 as the internal reference ($CDCl_3$: δ = 7.26 ppm; D_2O-d_2: δ = 4.79 ppm). The ^{13}C NMR spectroscopy chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). Fluorescence spectra of Eu-centered emission were obtained using a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer. Glucose leakage assay was monitored on a Cary 50 Bio UV–vis spectrophotometer. TEM studies were carried out using a HITACHI H-600 instrument, operating at 75 kV. The ESI-TOF mass spectra were recorded with a Waters Q-Tof premier instrument. DLS experiments were recorded using a Malvern Zetasizer Nano ZS particle analyser instrument. The excited state lifetimes were determined on a HORIBA TEMPRO-01 instrument. Elemental analyses were performed by using a Flash EA 1112 instrument. The critical aggregation concentration (CAC) of $[C_mMIm]_4EDTA$ was determined by using the fluorescence method by monitoring I_3/I_1 of pyrene at different concentrations of $[C_mMIm]_4EDTA$ according to the reported literatures.[18] The photostability of the sample was tested according to the reported literature.[19]

Chemicals: Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The syntheses of Ag_4EDTA, dialkylimidazolium bromide, and dialkylimidazolium salts with the EDTA anion are reported in the Supporting Information.

Typical Preparation of Counterion-Induced Vesicles: $[C_6MIm]_4EDTA$ (383.0 mg, 0.4 mmol) was added into 10.0 mL of deionized water at room temperature. The resulting solution was then left to stand and the vesicles formed spontaneously within minutes. The corresponding vesicles of europium(III) complex could be prepared by adding $EuCl_3{\cdot}6H_2O$ into the aqueous solution of $[C_6MIm]_4EDTA$.

Glucose-Leakage Assay: Glucose-containing vesicles were prepared by adding $[C_6MIm]_4EDTA$ into 300.0 mM of D-(+)-glucose in 50.0 mM Tris buffer (0.5 mL, pH = 7.5). The resultant solution was then vortexed at room temperature for 3 h. A portion (0.5 mL) of the vesicle solution was passed through a column of Sephadex G-50 by using Tris buffer (50.0 mM Tris, 150.0 mM NaCl, pH = 7.5) as the eluent to remove the extravesicular glucose. The liposome fractions were combined and diluted to 5.0 mL with the Tris buffer. The concentration of $[C_6MIm]_4EDTA$ in the stock solution was 100.0 mM. Glucose released from the liposomes was measured by a slightly modified literature procedure.[20] An aliquot of the above vesicle solution (250.0 μL), Tris buffer (750.0 μL, 50.0 mM Tris, pH = 7.5, 145.0 mM NaCl, 3.5 mM $MgCl_2$, and 0.15 mM $CaCl_2$), the enzyme solution (500.0 μL, 10 units per mL of hexokinase/glucose-6-phosphoate dehydrogenase and 2.0 mM ATP dissolved in the above Tris buffer), and NADP solution (500.0 μL, 1.0 mM dissolved in the above Tris buffer) were placed in a cuvette. The absorbance of NADPH at 340 nm was monitored. Subsequently, the vesicles were lysed by the addition of 100.0 μL of Triton X-100 (5% v/v) and the absorbance at 340 nm (A_{max}) was used to calculate the percent leakage as $(A_t - A_0)/(A_{max} - A_0) \times 100$, where A_0 and A_t are the initial and intermediate absorbance, respectively.

Measurement of the Coordination Number of Water Bound to the Eu^{3+} Ion: The number of coordinated water (q) bound to the Eu^{3+} ion is determined by the following equation:[16c]

$$q = 1.2 \times (\tau_{H_2O^{-1}} - \tau_{D_2O^{-1}} - 0.25) \quad (1)$$

where τ_{H2O} and τ_{D2O} are the lifetimes of the Eu^{3+} complexes in H_2O and D_2O, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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