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Smart Materials

Macroscopic Responsive Liquid Quantum Dots Constructed via Pillar[5]arene-Based Host-Guest Interactions

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Abstract: Liquid quantum dots (QDs) have been used as a fluorescent films sensor. Constructing a macroscopic, responsive, liquid QD system for lysine (Lys) is a challenging task. To achieve a selective macroscopic response towards Lys, herein we present a new strategy for integrating host–guest chemistry into a liquid QD system. Water-soluble pillar[5]arene WP5 was designed and synthesized as a host. WP5 was introduced onto the surface of PEG1810-modified QDs by host–guest interactions to obtain liquid WP5-1810-QDs. The interaction between WP5 and Lys is stronger than that between WP5 and PEG-1810, causing WP5 to be released from the 1810-QDs surface in the presence of Lys, resulting in macroscopic fluorescence quenching. This smart material shows promise in amino acid sensing and separation.

Quantum dots (QDs),[1] with unique photophysical properties and size-controlled fluorescence, have attracted broad interest over the past few decades and have been widely used in applications such as optical sensors,[2] optoelectronics[3] and biological imaging.[4] However, QDs are usually synthesized in solvents that are constraining for applications in many fields. Meanwhile, solid-state QDs are subject to fluorescence quenching. To solve these problems, novel, solvent-free QDs, denoted as liquid QDs, were recently developed.[5–9] A variety of approaches to prepare liquid QDs have been proposed. For instance, Giannelis and coworkers prepared liquid ZnO[10] and PbS[11] QDs by ionic exchanges, but the fluorescent properties of the resultant QDs were undesirable. Xiong et al. used a classic extraction method to produce liquid CdSe QDs with excellent fluorescent properties.[12] More recently, we synthesized multi-emission liquid CdSe QDs based on a hydrogen-bonded assembly.[13] The resulting hydrophobic, liquid QDs displayed tunable optical and structural properties, and could be used as fluorescent-film sensors.[14] As far as we know, liquid QD-based fluorescent-film sensors are largely unexplored and pose a big challenge.[15]

To address this challenge, herein we present a new strategy to construct liquid QDs using host–guest interactions. Pillararenes are a relatively new class of supramolecular host that have received considerable attention because of their novel symmetrical, pillar-shaped architectures, unique host–guest properties, electron-rich cavities and highly tunable functionality.[16] Based on these unique properties, pillararenes can be used as building blocks to construct supramolecular architectures including rotaxane,[17] pseudorotaxanes,[18] and polyrotaxanes.[19] Such adjustability allow pillararenes to display specific responses to different kinds of analytes, such as alkanes,[20] azobenzenes,[21] and viologen derivatives.[22] Thus, pillararenes have been incorporated into various nanomaterials, such as Ag and Au nanoparticles, which have potential applications in chemical and biological sensors.[23,24]

Amino acids are the building blocks of proteins, play vital roles in the metabolic processes of living bodies.[25] In particular, lysine (Lys) is important in protein synthesis, and human growth. A major post-translational modification that plays an important regulatory role in almost every aspect of both eukaryotic and prokaryotic cells involves Lys.[26] Consequently, selective recognition of Lys is crucial in biochemistry and medical science. Designing a selective receptor for Lys and immobilizing this receptor into a liquid QDs system are the two main objectives of this work. To achieve high selectivity for Lys, the carboxyl group was used because it can interact with amino acids via intermolecular hydrogen bonds. The electron-rich cavity of pillar[5]arene can bind amino acids.[27] Herein, we design and synthesize a water-soluble pillar[5]arene modified with carboxylic acid groups (WP5) by a "thiol-ene" click reaction[28] (Figure 1 A). WP5 was introduced onto the surface of 1810-QDs by host–guest interaction and construct a macroscopic Lys responsive liquid QDs system.

First, WP5 was synthesized by the classical "thiol-ene" click reaction (Figure 1 A). The structure of WP5 was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry (Supporting Information, Figures S1–11). The host–guest interaction of WP5 and Lys was then investigated by ^{1}H NMR spectroscopy. As shown in Figure 1 B, when 1.0 equivalent of Lys was added to a solution of WP5, H_1 of Lys exhibited an upfield shift of $\delta_1 = 0.05$ ppm, and the H_a aromatic protons, H_b of WP5 shifted downfield by $\delta_a = 0.28$ ppm, $\delta_b = 0.12$ ppm because of inclusion-induced deshielding effects and hydrophobic interactions. These changes are consistent with the alkyl chain of Lys being inserted into the cavity of WP5 to form a host–guest

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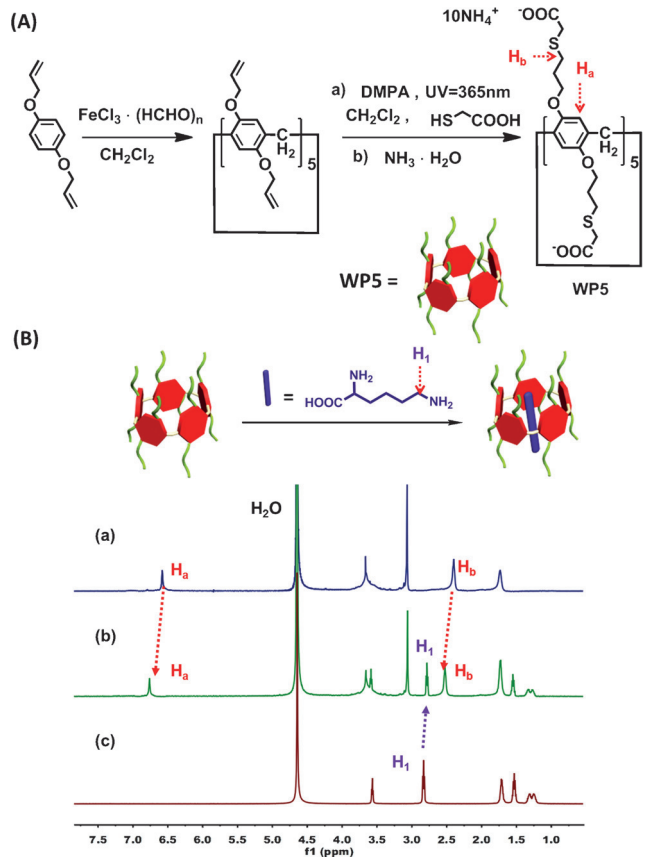

Figure 1. (A) Synthesis of WP5. (B) ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of (a) free WP5 (6 mM), (b) WP5 (6 mM) + Lys (6 mM), and (c) free Lys (6 mM). This indicated that Lys inserts into the cavity of WP5 and that WP5 is a Lys receptor.

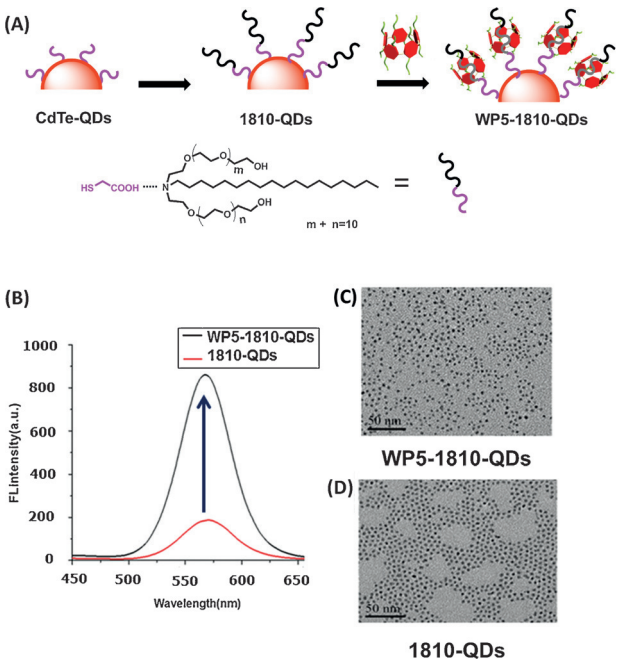

Figure 2. (A) Schematic diagram of the preparation of supramolecular QDs (WP5 −1810-QDs) based on host–guest interactions. (B) Fluorescent spectra of 1810-QDs and WP5-1810-QDs. (C) TEM images of WP5-1810-QDs and (D) 1810-QDs. This indicates the successful modification of WP5 on the surface of 1810-QDs.

complex. Computational calculations at the B3LYP/6-31G (d) level of theory indicated that the formation of this host–guest complex was driven by hydrophobic interactions (Figure S18). These results reveal that WP5 is a good candidate sensor for Lys.

To introduce WP5 to QDs to construct a macroscopic Lys-responsive QDs system, 1810-QDs were synthesized by intermolecular hydrogen bond between mercaptoacetic acid (MAA) capped CdTe-QDs and PEG-1810 [$C_{18}H_{37}N(CH_2CH_2O)_nH$–$(CH_2CH_2O)_mH$ ($n+m=10$)].[13,29] We devised a new strategy to introduce pillar[5]arene to liquid QDs based on host–guest interactions. ^{1}H NMR spectroscopy was performed to investigate the interaction of WP5 and PEG-1810. When 1.0 equivalent of PEG-1810 was added to a solution of WP5, the chemical shifts of some protons of PEG-1810 and WP5 changed (Supporting Information, Figure S13). The H_1 alkyl chain protons of PEG-1810 exhibited upfield shifts of $\delta_1=0.10$ ppm and the H_a aromatic protons of WP5 showed a downfield shift of $\delta_a=0.15$ ppm because of inclusion-induced shielding effects. These shifts are consistent with the alkyl chain of PEG-1810 being inserted into the cavity of WP5 to form a host–guest complex. Then, WP5 was introduced onto the surface of 1810-QDs by self-assembly (Figure 2A). The obtained QDs were designated as WP5-1810-QDs.

As illustrated in Figure 2B and C, WP5-1810-QDs were successfully characterized by fluorescence spectroscopy and transmission electron microscopy (TEM), respectively. The 1810-QDs showed weak fluorescence, which were induced by the strong entangling interactions between the long flexible PEG chains in water. After modification with WP5, the WP5-1810-QDs displayed an obvious increase in fluorescence intensity. This fluorescence intensity increase is attributed to the WP5 restricts the PEG-1810 conformation, enhanced conformational rigidity of the surface inducing a uniform arrangement. Fluorescence enhancement may result from the suppression of the quenching path to the medium by effective core protection and/or from the suppression of a nonradiative process. In addition, the functionalization of QDs was also confirmed by Fourier transform infrared spectroscopy (Supporting Information, Figure S12), which revealed the characteristic peaks of carboxyl and phenyl groups of WP5. All of these results indicate that WP5 was successfully introduced to 1810-QDs by host–guest interactions.

To evaluate the response of the WP5-1810-QDs to Lys, their fluorescent response towards different amino acids was investigated. The response of the WP5-1810-QDs to six amino acids (Glu, Trp, Cys, Arg, His and Lys), including acidic, basic, and neutral examples, was evaluated. As shown in Figure 3A, the WP5-1810-QDs exhibited relatively strong fluorescence quenching only after adding Lys. This result reveals the high fluorescent selectivity of the WP5-1810-QDs for Lys in aqueous solution. Figure 3B displays the changes in fluorescence ratio ($(I_o-I)/I_o$) of the WP5-1810-QDs in the presence of the six amino acids. The possible mechanism of fluorescence quenching in

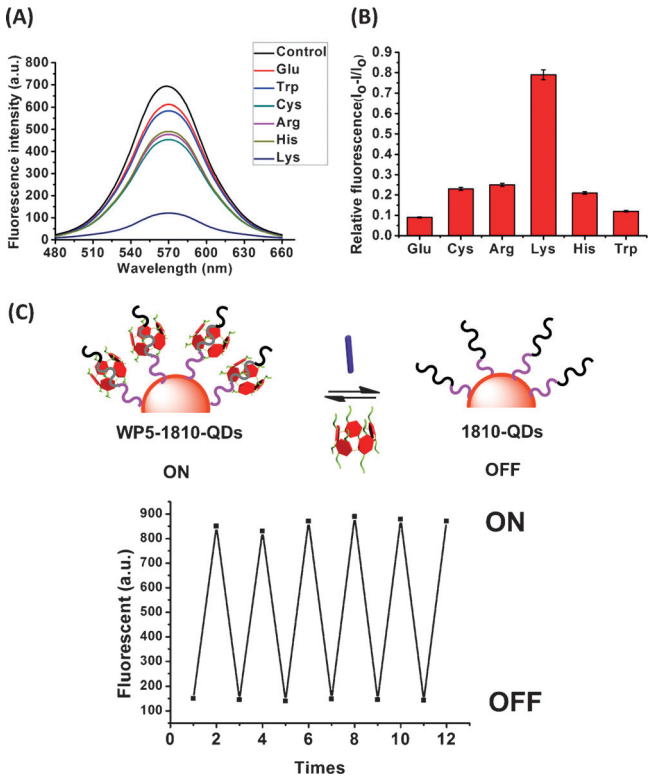

Figure 3. (A) Fluorescence spectra showing the response of the WP5-1810-QDs to six amino acids (control, Glu, Trp, Cys, Arg, His and Lys) in aqueous solution. (B) Relative fluorescence intensity ((I_o-I)/I_o), where I_o and I are the fluorescence intensities without and with an amino acid, respectively. The result shows the high selectivity of WP5-1810-QDs for Lys in aqueous solution. (C) Cycling experiment investigating the fluorescence switching behavior of the WP5-1810-QDs with Lys. The cycling experiment indicates good reversibility.

the presence of Lys may be that when Lys was added to the WP5-1810-QDs, it competed with the QDs binding to WP5, causing the 1810-QDs to release WP5. The ^{1}H NMR spectra indicate that WP5 binds more strongly to Lys than PEG-1810. The H_a aromatic protons of the WP5-Lys complex are shifted downfield ($\delta_a = 0.28$ ppm) compared with that of WP5. In comparison, H_a of WP5 is shifted downfield by $\delta_a = 0.15$ ppm when it interacts with PEG-1810. A cycling experiment to examine the fluorescence switching behavior of the WP5-1810-QDs with Lys was conducted. The results indicate that this system shows good reversibility (Figure 3C). The detection limit of WP5-1810-QDs for Lys is 1.2 μM which calculated by the rules of 3σ IUPAC and the result is shown in Figure S16 (Supporting Information).

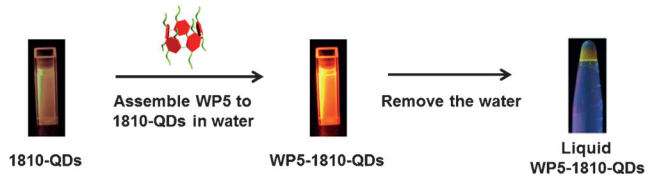

Figure 4. Photographs of liquid WP5-1810-QDs and its precursor solutions.

Liquid WP5-1810-QDs were obtained as a waxy solid through evaporation of an aqueous solution of the WP5-1810-QDs under reduced pressure (Figure 4). The digital photographs in Figure 4 demonstrate that the fluorescent properties of liquid WP5-1810-QDs are retained in the waxy solid state at room temperature.

Compared with non-doped liquid WP5-1810-QDs, the addition of amino acids to the liquid WP5-1810-QDs resulted in poor flow ability and high rheological temperature. However, the rheological temperature of the Lys-doped liquid WP5-1810-QDs indicated good fluidity at 27 °C (Figure 5). Moreover,

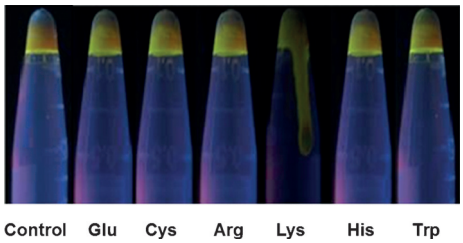

Figure 5. Photograph of liquid WP5-1810-QDs interacting with six different amino acids. The Lys can restoring flow ability compared with other five kinds of amino acid in temperature 27 °C, Lys doped liquid QDs material led to fluorescence quenching of WP5-1810-QDs, which is the closest to the fluorescence of 1810-QDs, showing the high selectivity of Lys interacted with WP5.

in both solid and liquid states, the Lys-doped liquid WP5-1810-QDs displayed distinct fluorescence quenching. In contrast, the fluorescent properties of the liquid WP5-1810-QDs were retained after adding the other amino acids. This is attributed to WP5 being removed from the liquid WP5-1810-QD surface by the strong WP5–Lys interaction. The fluorescent and fluid properties of the liquid WP5-1810-QDs indicate that this system exhibited a selective response towards Lys. It is anticipated that this study will pave the way to construct smart sensors with high specificity.

Because of the temperature response and good fluidity of the liquid WP5-1810-QDs, they can be spread on a support material such as quartz to test surface properties. The high selectivity of the liquid WP5-1810-QDs for Lys was also investigated by fluorescence spectra and contact angle (CA) measurements. As shown in Figure S17 (Supporting Information), the liquid WP5-1810-QDs film also exhibited strong fluorescence quenching only after adding Lys. This result reveals the high fluorescent selectivity of the liquid WP5-1810-QDs for Lys. The CA of liquid WP5-1810-QDs cast on a quartz slide was 79.5°, showing they were hydrophobic. A remarkable decrease of CA to 35.1° was observed after treatment of the liquid WP5-1810-QDs with Lys. Figure 6 shows the change of CA when different amino acids were added to the liquid WP5-1810-QDs, revealing a remarkable selectivity for Lys. A possible mechanism of the wettability response of the liquid WP5-1810-QDs to Lys is that the coordination between WP5 and Lys caused WP5 to be released from the PEG alkyl chains. The quartz surface was therefore covered by unbound WP5, resulting in weaker surface hydrophilicity.

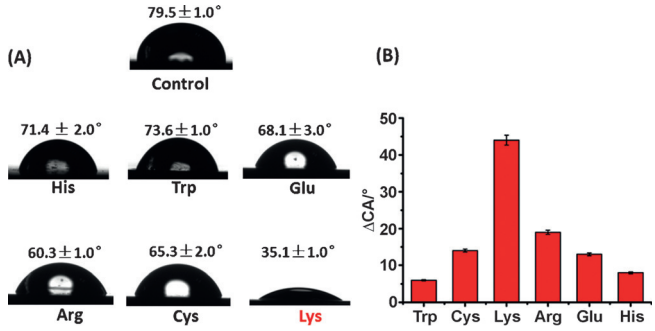

Figure 6. (A) Profiles of water droplets on the liquid WP5-1810-QDs on quartz substrates and treated with amino acids (control, Glu, Trp, Cys, Arg, His and Lys); concentration of amino acids was 10^{-4} M; Lys induced CA change of WP5-1810-QDs from 79.5° to 35.1°. (B) Histogram showing the change of CA ($\Delta CA = CA_{control} - CA_{amino\ acid}$) upon adding different amino acids. It indicates a highly selective wettability response of WP5-1810-QDs towards Lys.

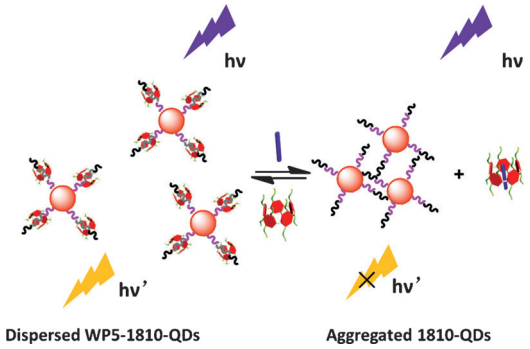

Figure 7. Possible mechanism for the fluorescence quenching of the liquid WP5-1810-QDs in the presence of Lys.

The fluorescence quenching, and change of fluidity and microstructure of the liquid WP5-1810-QDs in the presence of Lys were caused by the stronger interaction between Lys and WP5 than that between WP5 and the PEG alkyl chain. Thus, a possible mechanism for the fluorescence quenching of Lys-doped liquid WP5-1810-QDs is as follows. As described in Figure 7, the quenching of luminescence of the WP5-1810-QDs can be attributed to the ability of Lys molecules to enter the cavity of WP5 and compete with PEG-1810 to form a complex. WP5 was peeled off the surface of the 1810-QDs. It might lead to the generation of 1810-QDs surface distort and the nonradiative process.[30] The reason why the rheological temperature of Lys-doped liquid WP5-1810-QDs was lower than that of the liquid WP5-1810-QDs was because of the release of WP5 from the PEG chains. This increased the freedom of the PEG chains, increasing their flexibility, and resulting in a lower solid–liquid transition temperature.

In summary, we prepared the water-soluble pillar[5]arene WP5 through a "thiol-ene" click reaction. Lys is positively charged under neutral conditions and can form an inclusion complex with WP5. We built a liquid supramolecular QD material modified with PEG-1810 through the host–guest interaction between WP5 and the PEG-modified QDs. Lys bound strongly to WP5, competing with the 1810-QDs. Thus, the modified QDs exhibited a macroscopic selective response to Lys in the solution phase. This film sensor shows promise for applications in biological separation and uptake.

Experimental Section

Preparation of 1810-QDs

Mercaptoacetic acid capped CdTe QDs (MAA CdTe-QDs) were prepared according to the literature.[13] A mixture of PEG-1810[$C_{18}H_{37}N(CH_2CH_2O)_nH$-$(CH_2CH_2O)_mH$, $(n+m=10)$] and MAA-capped CdTe-QDs (10 mL) was stirred at room temperature for 6 h. The resultant 1810-QDs were obtained by washing and centrifugation to remove any excess PEG-1810. After that, the obtained wax-like and viscous QDs were redispersed into doubly distilled water to obtain the 1810-QDs solution.

Modification process

To aqueous solutions of 1810-QDs (40 mL), WP5 (16 mg) was added and the mixture was stirred at room temperature overnight. After that, the solvents were removed under reduced pressure to afford the resultant waxy QDs. After this, the waxy and viscous materials were dispersed into less double-distilled water to test fluorescence, Fourier transform infrared spectroscopy and another property in aqueous solution.

Preparation of the amino acids doped liquid WP5–1810-QDs

Taken the WP5-1810-QDs solution 1.5 mL into seven centrifuge tube, added 0.5 mL double distilled water, 10^{-4} M (Glu, Trp, Cys, Arg, His and Lys) amino acids into the WP5–1810-QDs, respectively. Spectral properties were tested in half an hour. The dopants of amino acid and liquid WP5–1810-QDs were prepared by the aforementioned method and vacuum dried until the solvent was completely removed. The resultant waxy material (the amino-acid-doped liquid WP5–1810-QDs) were acquired and used for the macroscopic response measurements.

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