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ARTICLE TYPE

Multifunctional fluorescent material based on metallomicelles trapped in silica nanochannels

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Here we report the self-assembly of metallomicelle/silica nanocomposite with mesoscopic structure using amphiphilic quinoline molecules as both structure-directing agents and ligands. The inorganic host alters the compatibility of the
10 metallorganics to various polymers. The resulting nanocomposite is also a chemical stimulus-response material to fabricate sensors. This material provides sufficient physical integrity to be integrated into devices and microsystems.

Coordination compound with aromatic ligands (CWA) is a kind
15 of important fluorescent materials for optoelectronics, display, imaging, and sensor.[1] Compared with quantum dots (QD) and rare earth oxides (REO), CWA can be easily prepared under mild and nontoxic reactions. Lots of CWA are got through simply mixing reactants in water under room temperature. The excitation
20 and emission wavelengths of CWA are conveniently adjusted by changing ligands or central metal ions.[2] Most importantly, the aromatic ligands can be produced on an industrial-scale, which make it possible to use CWA to manufacture commercial products.
25 Although the above advantages of CWA attracted great interests of chemists, some weaknesses still limit the extensive application of CWA. First, unlike QD or REO, many CWAs usually lack enough compatibility with other solid substrates or good stability in common solvents. It is difficult to fabricate
30 CWA into hybrid fluorescent materials. Then, the micro-morphology of CWA materials is hard to control, so using CWA to assemble micro-nano devices is not facile. Lastly, to maintain the luminescent stability of CWA, the materials are usually sealed in polymers to be isolated from O_2 or H_2O, particularly in
35 optoelectronic device.[3] If CWA is not only stable with its unique chemical performance, but also as operable as QD or REO, it will be an ideal material for fluorescent utilization.

Herein, we report a one-step synthesis of fluorescent material based on trapping CWA micelles in silica nanochannels. The
40 porous structure of silica is guided by self-assembly of amphiphilic quinoline molecules, which subsequently coordinates with aluminum ions. These assembled amphiphilic molecules and their coordination products give hybrid materials distinct and robust optical activity, which can be attributed to the combination
45 of the CWA micelles and silica nanostructures.

So far, it is difficult to directly deposit silica on the surface of CWA with cheap central metal ions to form a fluorescent complex at the molecular scale. As the required interaction between the CWA and the silica source is extremely hard to
50 achieve, our approach is based on the preparation of hybrid mesoporous silica, which is a result of electrostatic interactions between the functional amphiphilic molecules and the silicate during the sol-gel process. [4] It is well known that amphiphilic molecules, such as hexadecyl trimethyl ammonium bromide
55 (CTAB) with hydrophobic alkyl chains, can self-assemble to form micelle with a rod-like molecular arrangement.[5] It can be used as templates for the oriented polymerization of silicates through electrostatic interactions between the positively charged quaternary ammonium heads and the negatively charged silicates.
60 In this work, amphiphilic molecules both served as aromatic ligands and directed the formation of mesoporous silica framework (Scheme 1), which protected the soft CWA micelle and provided a limited space. The multifunctional surfactants played an important role during the construction of hybrid
65 material system. The hydrophobic quinolone tails packed together in the center of micelle. At the same time, the hydrophilic quaternary ammonium salt had an electrostatic force with silicates to guide the fabrication of nanopores. After adsorbing aluminum ion, quinolone tails formed metallorganic complex.
70 Then, the hybrid materials gave a strong blue-green fluorescence. There was no need to remove template molecules, which formed the fluorescent CWA directly. The functionalization procedure was clean, mild and easy, and only the water solution of aluminium chloride was used. Since silica had high compatibility
75 with many other organics, inorganics or even biological tissues, the hybrid material we prepared was applied to different fields like chemosensor, photoluminescence polymer and paint, showing excellent properties.

As shown in Scheme 1, the QC12Et3Br was an amphiphilic
80 version of quinolone ligand. It had a 12-carbon chain between the positively charged head and the ligand tail. Similar to the fabrication of MCM-41, a molar ratio of 1 TEOS/0.12 QC12Et3Br/8 NH3.H2O/114 H2O was established for the sol-gel synthesis of the QC12Et3Br/silica hybrid. The base catalyst
85 (NH3.H2O) was used to ensure the hydrophobicity of the tail in the sol-gel process. Then the hydrophobic unprotonated quinoline groups filled in mesoporous channels. Compared with post-

functionalization of mesoporous silica, this method could make more organic groups be incorporated in the channels. Quinolone was a famous ligand that could further coordinate with different metal ions and showed a strong fluorescence.[6] For example, 8-hydroxyquinoline aluminium (Alq$_3$) was an important
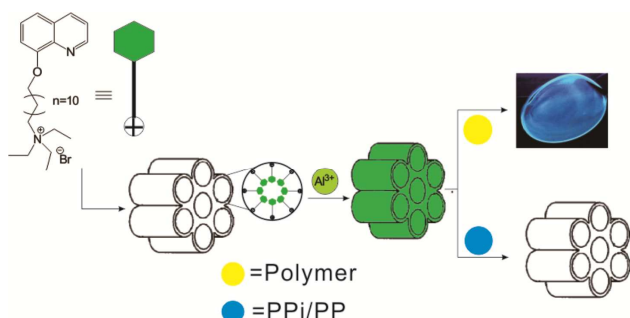
Scheme 1. Schematic illustration of synthetic process of hybrid QC12Et3Br-Al3+/silica complexes, and its application in fluorescent display and ions detection.

fluorescence material for fabricating luminescent device.[7] Metal ions displayed a certain affinity to the donor atoms (such as oxygen and nitrogen) and could coordinate with the quinoline moiety. So the metallic hybrid materials were easily obtained via immersing the as-synthesis QC$_{12}$Et$_3$Br/silica in the aqueous solution of aluminum salt.

The obtained hybrid materials were firstly examined by small-angle X-ray diffraction pattern as shown in Figure 1a to confirm the existence of mesoporous structure. This material showed a strong diffraction peak at a small angle (θ = 2.2°), which was attributed to the diffraction mesoporous structure.[8] Since the peak was broad and no other peaks were found, the mesopores might be worm-like.[9] After coordinated with Al^{3+}, the resultant QC$_{12}$Et$_3$Br-Al^{3+}/silica materials still revealed a well-resolved diffraction peak at 2.0°, which showed the integrity of mesoporous framework during the metallic approach. As shown in Figure 1b, TEM image confirmed the worm-like mesoporous structure. The pore diameter was about 3-5 nm. After removing the metallomicelles from the hybrid material, the mesoporous structure was further characterized by N$_2$ adsorption/desorption (Supporting Information, Figure S1). The porous silica displayed type IV isotherm according to the IUPAC classification. The textural parameters of all samples were given in Figure S1. It was observed that the porous silica using QC$_{12}$Et$_3$Br as structure-directing agent had a large surface area (1069.43 m^2 g^{-1}) and uniform pore diameter (2.43 nm). These structure parameters fully indicated that the inorganic silica frame was in the typical mesoporous form.

In the FT-IR spectra (Supporting Information, Figure S2) of hybrid materials, the band located at 1070 cm^{-1}, which belonged to the vibration of Si-O-Si bonds, evidenced the formation of silica framework. The peaks at 2927, 2854, 1503, 1467, 1385 and 1319 cm^{-1} proved the immobilization of QC$_{12}$Et$_3$Br into the as-synthesized materials. Additionally, after coordinated with Al^{3+}, a new sharp absorption band appeared at 1384 cm^{-1}, which was due

to the C-O stretching mode of the M-O-C, [10] and confirmed Al^{3+} had coordinated with quinoline moiety. Elemental analysis results showed the weight content of N is 1.658%, which proved that the amount of QC$_{12}$Et$_3$Br assembled inside the pore was around 29 wt%. This content was closed to the amount of QC$_{12}$Et$_3$Br (30 wt%) gotten from the template extraction method. In addition, the
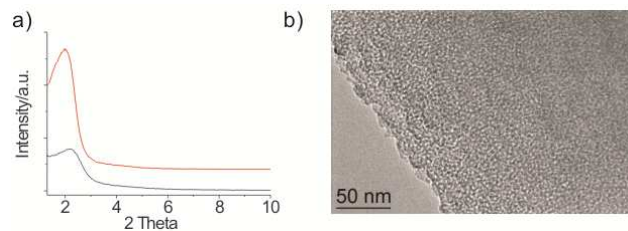
Figure 1. (a) Small-angle XRD patterns of the silica hybrid materials using QC$_{12}$Et$_3$Br as structure-directing agent under 1 TEOS/0.12 QC$_{12}$Et$_3$Br/8 NH$_3$.H$_2$O/114 H$_2$O before (red line) and after (black line) coordination with Al^{3+}; and (b) TEM image of the QC$_{12}$Et$_3$Br/silica
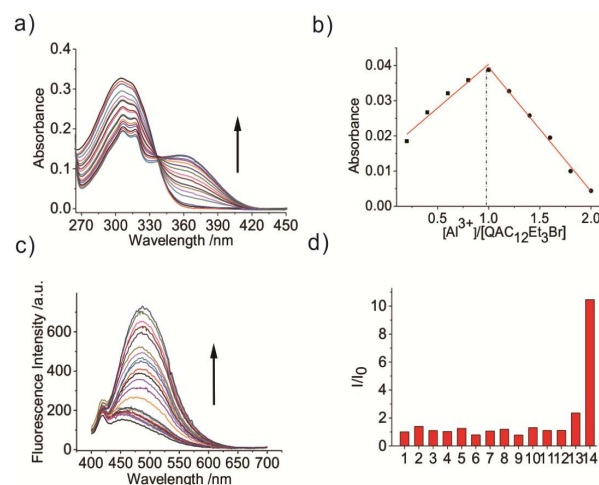

Figure 2. (a) Adsorption spectra of QC$_{12}$Et$_3$Br (10^{-4} M) in water solution when titrated by Al^{3+}; (b) Job's plot of QC$_{12}$Et$_3$Br and Al^{3+} in the same medium according to the absorbance at 365 nm; (c) Fluorescence spectra of QC$_{12}$Et$_3$Br/silica materials (0.02 g/L) in water solution when titrated by Al^{3+}; and (d) Fluorescence response of spectra of QC$_{12}$Et$_3$Br/silica materials (0.02 g/L) in water solution to various cations: 1. none; 2. Zn^{2+}; 3. Hg^{2+}; 4. Cd^{2+}; 5. Cu^{2+}; 6. K$^+$; 7. Fe^{2+}; 8. Mn^{2+}; 9. Ni^{2+}; 10. Pb^{2+}; 11. Mg^{2+}; 12. Na$^+$; 13. Co^{2+}; 14. Al^{3+}. Excitation was at 365 nm, emission was monitored at 493 nm.

atomic ratio of Si: N (1:0.10) was similar to the initial reaction dosage (1:0.12), meaning that most of QC$_{12}$Et$_3$Br was confined into mesopores channels.

The interaction of QC$_{12}$Et$_3$Br with Al^{3+} ion was researched with UV-Vis and fluorescent spectra. (Figure 2a) QC$_{12}$Et$_3$Br in water solution exhibited a strong absorption band at about 307 nm with a shoulder at about 327 nm, which was assigned to the quinolone centered charge transfer.[11] Adding Al^{3+} to the solution of QC$_{12}$Et$_3$Br caused a dramatic decrease of absorption band at 307 nm.Meanwhile, a new absorption band appeared at about 365

nm, and its absorbance gradually increased with the addition of Al^{3+}. The Job's plot at 365 nm (Figure 2b) supported the formation of 1:1 stoichiometry adducts. Remarkable fluorescence enhancement was observed when Al^{3+} was added in to the
5 solution of $QC_{12}Et_3Br$. These changes were due to the coordination of $QC_{12}Et_3Br$ with Al^{3+}, which was ascribed to the metal-to-ligand charge transfer. [12]

QC$_{12}$Et$_3$Br/silica hybrid materials showed the same change when it was dispersed in Al^{3+} solution. The titration of Al^{3+} into
10
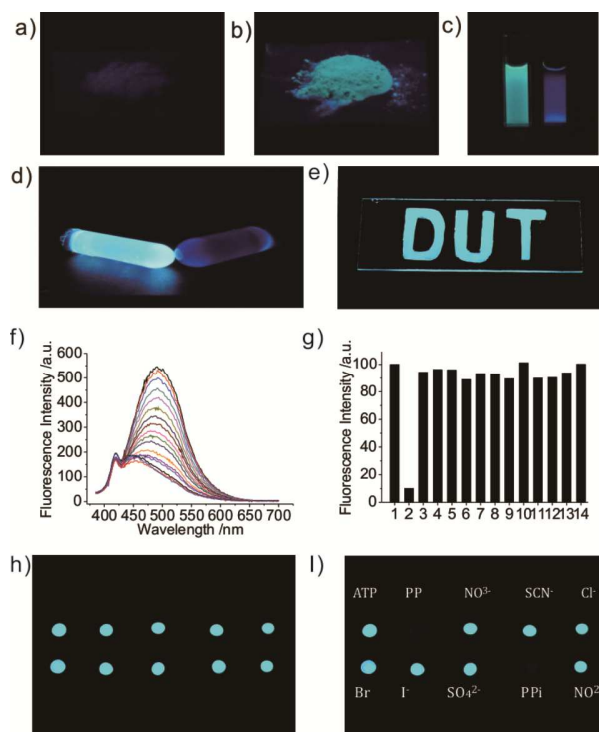
Figure 3. The photographs of (a), (b) were the powdery of the $QC_{12}Et_3Br$-Al^{3+}/silica (a) before and (b) after the UV light irradiation (365nm); (c) the $QC_{12}Et_3Br$/silica materials (right) before and (left) after
15 adsorbing Al^{3+} ions in water; (d) rod-like PMMA materials under UV light irradiation (365 nm); (e) the commercial oil paint, which was mixed with $QC_{12}Et_3Br$-Al^{3+}/silica, was painted on a glass slide; (f) fluorescence spectra of $QC_{12}Et_3Br$-Al^{3+}/silica materials (0.02 g/L) in water solution with the increasing amount of the added PPi; (g) fluorescence response of
20 spectra of $QC_{12}Et_3Br$-Al^{3+}/silica materials (0.02 g/L) in water solution to various anions: 1. none; 2. PPi; 3. ATP; 4. Cl$^-$; 5. Br$^-$; 6. I$^-$; 7. NO$_3^-$; 8. NO$_2^-$; 9. SO$_4^{2-}$; 10. HSO$_3^-$; 11. S$_2$O$_3^{2-}$; 12. ClO$_4^-$; 13. SCN$^-$; 14. ClO$_3^-$. Excitation was at 365 nm, emission was monitored at 493 nm; (h) The fluorescent material was mixed with CMC and painted on glass slide; and
25 (i) it showed the various results after meeting different anion solutions.

QC$_{12}$Et$_3$Br/silica materials dispersion induced a significant enhancement of the luminescence intensity at 493 nm (Figure 2c). Al^{3+} ions were absorbed by the hybrid material. According to
30 inductively coupled plasma atomic emission spectrometry (ICP-AES) result, the adsorption reached equilibrium in 10 minutes. The equilibrium adsorption capacity of $QC_{12}Et_3Br$/silica hybrid material to Al^{3+} was 5.85×10^{-4} mol g^{-1}, so the ratio of $QC_{12}Et_3Br$ to Al^{3+} in hybrid material was approximately 1:1, which was also
35 consistent with the results of UV-Vis and fluorescence spectra titration experiments (Supporting Information, Figure S3 and

Figure S4). Since cationic surfactants in mesoporous materials could be washed out slowly by water, leaching of the amphiphilic quinolone ligand was tested. In 10-minute adsorption process,
40 about 1.9 % of quinolone ligand had leached out (Supporting Information, Figure S5). This meant that nearly all the Al^{3+} ions combined with quinolone ligand in the mesopores. Few free fluorescent compounds formed in water.

Besides Al^{3+} ions, some other common metal ions (such as
45 Zn^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Co^{2+}, Na^+, K^+) were also chosen to interact with $QC_{12}Et_3Br$/silica hybrid material (Figure 2d), but these ions exhibited a very weak fluorescence enhancement performance, and no obvious spectra changes of suspension solution occurred. The $QC_{12}Et_3Br$ had a
50 specific sensing ability to Al^{3+}.

The fluorescence of the $QC_{12}Et_3Br$-Al^{3+}/silica hybrid could be observed clearly by the naked eye (Figure 3a and Figure 3b). It depicted the silica-based $QC_{12}Et_3Br$ materials before and after (Figure 3c) adsorbing Al^{3+} ions. The $QC_{12}Et_3Br$-Al^{3+}/silica
55 powder gave a strong blue-green photoluminescence. $QC_{12}Et_3Br$-Al^{3+}/silica had fine compatibility with many other chemicals. After mixing the fluorescent powder with methyl methacrylate (MMA), the complex was polymerized to film, rod or other shapes. For example, the transparent monolithic polymethyl
60 methacrylate (PMMA) with the regular shape of cylinder was obtained. It gave a bright fluorescence under UV light irradiation, which was quite different from the pure PMMA (Figure 3d). Using this method, fluorescent transparent polystyrene film was also prepared (Scheme 1). When commercial oil paint was mixed
65 with $QC_{12}Et_3Br$-Al^{3+}/silica, it was easily to draw a fluorescent pattern on the substance surface (Figure 3e). According to this property, $QC_{12}Et_3Br$-Al^{3+}/silica was an ideal material to fabricate fluorescent device in different form, such as painting, fibre and coating.
70 Fluorescent materials were widely used in the field of highly sensitive and selective sensors, so the sensory property of $QC_{12}Et_3Br$-Al^{3+}/silica material was explored. It was found that the fluorescence of the hybrid material could be quickly quenched by pyrophosphate (PPi) and phosphate (PP). PPi and
75 PP were important commonly accessed anions for their essential role in metabolic process, [13] so developing a highly efficient method to detect them was meaningful. As shown in Figure 3f, titrating PPi gradually quenched the fluorescence of $QC_{12}Et_3Br$-Al^{3+}/silica. Since Al^{3+} exhibited higher affinity to the oxygen-
80 donor atoms originated from phosphates than that from quinolone moiety,[14] the decrease of fluorescence intensity could be speculated to the coordination of PPi to Al^{3+}. As shown in Figure 3g, only weak fluorescence decrease signals could be detected for anions such as Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, NO$_2^-$, ClO$_3^-$, HSO$_3^-$, ClO$_4^-$, SCN$^-$,
85 SO$_4^{2-}$, S$_2$O$_3^{2-}$ and ATP, even if their addition amount were 10-folds of PPi, when the addition of PPi produced a dramatic decrease in fluorescence intensity. The detection limit of the nanocomposite to PPi was as low as 1.78 ppm, and the linear range is from 10 ppm to 295 ppm (Supporting Information,
90 Figure S6). PP showed the same quenching ability to the fluorescence as PPi. To make the sensory visible, the fluorescent material was mixed with carboxyl methyl cellulose (CMC) and painted on glass slide (shown in Figure 3h). After meeting solution containing different anions, the fluorescent spots showed

various results, which were quickly observed by naked eyes (Figure 3i). These results demonstrated that the present "on-off" fluorescence material was highly selective and sensitive to PPi and PP.

Conclusions

In summary, we have developed an efficient strategy for producing multifunctional fluorescent CWA hybrid based on a confined self-assembly approach. The crucial point of this strategy is the construction of confined nanochannels by ligand-based surfactant for trapping and protecting CWA molecules. The excellent compatibility of CWA hybrid with various polymers makes it facile to be treated into device. The bottom-up approach employed herein has several advantages, such as the mild preparation conditions and the avoidance of hazardous materials. Moreover, the procedure is controllable and can be used to produce fluorescent CWA hybrid materials on hundred grams scale. We believe that our findings represent an important development in the preparation of high-quality fluorescent materials on a large scale, which may significantly facilitate the application of CWA in a wide range of areas.

Acknowledgements

Notes and references

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Multifunctional fluorescent material based on metallomicelles trapped in silica nanochannels

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Multifunctional fluorescent material with a chemical stimulus-response is prepared by trapping metallomicelles in confined silica nanochannels.