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Metal-Crown Ether-Porphyrin Decorated Gold Nanoparticles as High Sensitive Raman Ion Probe

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A kind of gold nanoparticles modified with metal crown ether porphyrin (GNPs-CP) was synthesized and characterized. The surface of the resulting gold particles was partially covered by metal crown ether porphyrin molecules through strong covalent Au–S bond. Based on the coupling effect of metal porphyrin and crown ether, the resulting composite gold nanoparticles can serve as a kind of ion probe. Raman and UV-Vis spectra were utilized to evaluate the ion recognition of the system, both of which changed dramatically when meeting metal ion corresponding to ligand of crown ether. Compared with UV-Vis spectra, Raman spectra of the composites are more sensitive and the limit of detection (LOD) can reach 1×10^{-8} g/mL. The study provides a candidate with higher sensitivity to replace current UV-Vis spectrum based evaluation tool for ion recognition.

Keywords: Crown Ether, Porphyrin, Raman, Ion Probe, Sensitivity.

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1. INTRODUCTION

Porphyrin is a kind of important functional molecule and its derivatives have been successfully utilized across a wide range of research fields such as photodynamic therapy of cancer, solar cells, molecular self-assemble, specific sensing of ions etc.¹⁻⁶ Recently, considerable efforts have been devoted to bifunctional porphyrin compounds owing to their diverse and distinct properties. In particular, porphyrin appended crown ether (CP) has been proven very promising for ion sensor mainly relying on the structure of porphyrin, size of crown ether ring and connection form of the two functional rings.7-9 Furthermore, in the case of porphyrin-crown ether donor-acceptor macromolecular systems, both intra- and intermolecular type interactions play an important role in governing the sensitivity corresponding to the out stimulus. Different types of coupling between porphyrin and crown ether ring presented some distinct properties.^{10–12} Along this line of consideration, a variety of crown ether porphyrins were synthesized over the last two decades.^{13–15}

Currently, surface enhanced Raman scattering (SERS) techniques based on noble metals such as gold nanoparticles (GNPs) have further advanced their utility for molecular diagnostics, and they can allow ultrasensitive levels of detection.^{16–20} Due to this feature, considerable studies have been focused on the fabrication of SERS probes for molecular detection. Especially, the SERS probes based on GNPs show low toxicity and can be functionalized with targeting moieties to facilitate *in vivo* imaging.^{21–26} Raman active molecules commonly contain symmetrical conjugate moieties, such as porphyrin which has strong Raman signals originating from the highly polarizable double bonds.^{27–32} To date, several classes of SERS probes based on porphyrins have been applied to *in vitro* and *in vivo* imaging sensing.^{33–37} Inspired by these ideas, a novel ion SERS probe based on crown porphyrin derivatives with special ion recognition ability was proposed.

In fact, ion recognition based on porphyrin-crown ether has previously been developed, but evaluation tool mainly relied on UV-Vis spectra and the sensitivity is unsatisfactory. In this paper, we describe the design and synthesis of a kind of metal crown ether porphyrin immobilized to surface of gold nanoparticles (GNPs-CP) as shown in Scheme 1. Based on the coupling of metal porphyrin and crown ether ring, the resulting composite nanoparticles can serve as a kind of ion SERS probe. Compared with UV-Vis spectra, detection limit of the probe based on Raman spectra can reach 1×10^{-8} g/mL. The study can provide a candidate with higher sensitivity to replace current UV-Vis spectrum based evaluation tool for ion recognition.

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Scheme 1. Synthesis route and plausible structure of GNPs-CP-Hg²⁺.

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2. EXPERIMENT SECTION

Benzaldehyde, propionic acid, TFA, hydrochloric acid, DMSO and EtOH were purchased from Sinopharm Chemical Reagent Co., Ltd. Dichloromethane, Pd (η^3 -1-PhC₃H₄) $(\eta^5$ -C₅H₅), Pd₂dba₃, XPhos, tin(II) chloride and thiol butyrolactone were purchased from Aladdin reagent Co., Ltd. High-purity water from a Milli-Q Academic water purification system (Millipore Corp., Billerica, MA, USA) was used in all experiments. All reagents and solvents are of analytical grade and further purification and drying by standard method were employed. Gold nanoparticles (GNPs) with diameter between $30 \sim 50$ nm were laboratory synthesized. ¹H-NMR spectra were recorded by a Bruker AV-500 spectrometer (Bruker, Germany). UV-Vis spectra were recorded on an UV-3600 spectrometer (Shimadzu, Japan). SERS spectra were recorded on a Micro-Raman spectrometer (Ranishaw, England) with laser wavelength at 786 nm. Morphologies of GNPs were observed via Ziess, Ultra plus FE-SEM with voltage of 5 kV.

2.1. Synthesis of 5,10,15-Triphenyl-20-(4-bromophenyl) Porphyrin

A mixture of benzaldehyde (3.18 g, 30 mmol), 4-brombenzaldehyde (1.84 g, 10 mmol) and freshly distilled pyrrole (2.68 g, 40.0 mmol) in propionic acid (140 mL) was refluxed for 3 h. After completion of the reaction monitored by TLC, the mixture was cooled in an ice-water bath and the crude product was filtered and washed thoroughly with methanol (100 mL) and dichloromethane (30 mL), respectively. The resulting purple product was dried and purified by column chromatography (silica gel, DCM/*n*-hexane: 1/5 V/V),^{38–40} then recrystallization from ethanol gave pure products (0.6 g, 13%) *mp* > 300 °C. ¹H NMR (500 MHz, DMSO) : δ = 7.82 (*d*, *J* = 7 Hz, 8H), 8.21 (*d*, *J* = 6 Hz, 6H), 8.33 (*d*, *J* = 9 Hz, 3H), 8.35 (*d*, *J* = 9 Hz, 2H), 8.83 (*s*, 8H).

2.2. Synthesis of 5,15-biphenyl-10-(4-nitrophenyl)-20-(4-bromophenyl) Porphyrin

To a solution of 5,10,15-Triphenyl-20-(4-bromophenyl) porphyrin (160 mg, 0.261 mmol) in TFA (10 mL) was added sodium nitrite (660 mg, 9.57 mmol). After stirring at 25 °C for 50 min, the reaction was quenched with water (100 mL) and the mixture was extracted with dichloromethane (6 × 25 mL). The organic layers were washed with saturated aqueous NaHCO₃ and then dried by anhydrous Na₂SO₄. Recrystallization from dichloromethane gave 120 mg (62%) of 5,15-biphenyl-10-(4-nitrophenyl)-20-(4-bromophenyl) porphyrin. *Mp* > 300°C. ¹H NMR (500 MHz, DMSO) : $\delta = 7.82$ (*d*, *J* = 7 Hz, 8H), 8.21 (*d*, *J* = 6 Hz, 5H), 8.33 (*d*, *J* = 9 Hz, 3H), 8.35 (*d*, *J* = 9 Hz, 2H), 8.83 (*s*, 8H).

2.3. Synthesis of 5,15-biphenyl-10-(4-nitrophenyl)-20-(4-aminophenyl-benzo-15-crown-5) Porphyrin

To 50 mL three-neck flask was added Pd $(\eta^3-1-PhC_3H_4)$ $(\eta^{5}-C_{5}H_{5})$ or Pd₂dba₂ (0.5–4 mol%), XPhos (1–8 mol%, Pd : L = 1 : 2) and degassed toluene (2 mL) followed by air replacement with argon. Then the mixture was stirred at 70 °C for 15 min. Then 5,15-biphenyl-10-(4-nitrophenyl)-20-(4-bromophenyl)porphyrin (1 mmol), 3-amine-15-crown-5 (1.1 mmol) and NaO^t Bu (1.4 mmol) were added successively and the reaction mixture was kept at $70 \sim 100$ °C. After completion of reaction monitored by TLC, the mixture was cooled and filtered, the precipitate was purified by column chromatography (silica gel, Hexanes/EtOAc:1/3 v/v) to give 223 mg (52%) 5,15-biphenyl-10-(4-nitrophenyl)-20-(4aminophenyl-benzo-15-crown-5)porphyrin. mp > 300 °C. ¹HNMR (500 MHz, DMSO) : $\delta = 3.75$ (t, J = 6 Hz, 8H), 3.92 (t, J = 7 Hz, 4H), 4.15 (t, J = 6 Hz, 4H), 6.89 (d, J =7 Hz, 3H), 7.82 (d, J = 7 Hz, 8H), 8.21 (d, J = 6 Hz, 5H), 8.33 (d, J = 9 Hz, 3H), 8.35 (d, J = 9 Hz, 2H), 8.83 (s, 8H).

2.4. Synthesis of 5,15-biphenyl-10-(4-aminophenyl)-20-(4-aminophenyl-benzo-15-crown-5) Porphyrin

5,15-biphenyl-10-(4-nitrophenyl)-20-(4-aminophenylbenzo-15-crown-5)porphyrin (80 mg, 0.025 mmol) was dissolved in concentrated hydrochloric acid (10 mL), then tin(II) chloride (220 mg, 0.975 mmol) was carefully added under stirring. The final mixture was heated and kept at 65 °C for 1 h under argon followed by being poured into cold water (100 mL). The aqueous solution was neutralized by ammonium hydroxide and then extracted with dichloromethane until colorless. The combined organic phase was concentrated under reduced pressure and the resulting residue was purified by alumina column using dichloromethane for elution. The final product was recrystallized from methanol (55.3 mg yield 54%), mp > 300 °C. ¹H NMR (500 MHz, DMSO) : $\delta = 3.75$ (t, J = 6 Hz, 8H), 3.92 (t, J = 5 Hz, 4H), 4.15 (t, J = 7 Hz, 4H), 6.89 (d, J = 7 Hz, 3H), 7.82 (d, J = 7 Hz, 8H), 8.21 (d, J = 6 Hz, 5H), 8.33 (d, J = 9 Hz, 3H), 8.35 (d, J = 9 Hz, 2H), 8.83 (s, 8H).

2.5. Synthesis of 5,15-biphenyl-10-(4-thiolbutanephenyl)-20-(4-aminophenyl-benzo-15-crown-5) Porphyrin

To a three-neck flask was added 5,15-biphenyl-10-(4aminophenyl)-20-(4-aminophenyl-benzo-15-crown-5) porphyrin (0.3 g, 0.33 mmol) and DMSO (20 mL), then thiol butyrolactone (0.10 g, 0.33 mmol) was added followed by air replacement with argon. The reaction mixture was stirred at 110 °C for 3 h and then cooled to room temperature. After filtered, the precipitate was purified by column chromatography (Hexanes/EtOAc) to give the product (0.21 g, 48%), mp > 300 °C. ¹H NMR (500 MHz, DMSO)

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Figure 1. UV-Vis spectra of GNPs-CP and GNPs-CP-Hg²⁺ with concentration of 1×10^{-6} g/mL in H₂O–EtOH (1:5).

: $\delta = 2.73$ (t, J = 6 Hz, 2H), 3.34 (t, J = 7 Hz, 2H), 3.51 (t, J = 6 Hz, 2H), 3.7 (t, J = 5 Hz, 8H), 3.92 (t, J = 7 Hz, 4H), 4.15 (t, J = 6 Hz, 4H), 6.89 (d, J = 7 Hz, 3H), 7.82 (d, J = 7 Hz, 8H), 8.21 (d, J = 6 Hz, 5H), 8.33 (d, J = 9 Hz, 3H), 8.35 (d, J = 9 Hz, 2H), 8.83 (s, 8H).

¹³C NMR (CDCl3) : $\delta = 26.18$ (CH₂-2'), 26.62 (CH₂-3'), 30.79 (CH₂-1'), 77.42 (C-1), 76.58 (C-2), 77.00 (C-3), 120.20 (C-9), 125.90 (C-7), 126.04 (C-Ph), 129.25 (C-Ph), 129.78 (C-6), 131.71 (C-Ph), 131.85 (C-Ph), 133.50 (C-8), 133.63 (C-5), 136.02 (C-Ph) 145.29 (C-Ph), 145.82 (C-Ph), 147.64 (C-Ph), 164.85 (C-4), 173.63 (C=O). ES-MS: m/z: 1009 (-SH + Na + H)⁺.

2.6. Synthesis of GNPs-CP and GNPs-CP-Hg²⁺

To a three-neck flask was added 5,15-biphenyl-10-(4-thiolbutanephenyl)-20-(4-aminophenyl-benzo-15-crown-5) porphyrin (1 mg, 0.001 mmol) and EtOH (10 mL), then aqueous solution of gold nanoparticles (1 mL, $C_{\rm GNP} = 0.12$ nM) was added under stirring. The final



Figure 2. UV-Vis spectra of GNPs-CP-Hg²⁺ and GNPs-CP-Hg²⁺-NaNO₂ with concentration of 1×10^{-6} g/mL in H₂O–EtOH (1:5).

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Figure 3. Raman spectra of GNPs-CP-Hg²⁺ and GNPs-CP-Hg²⁺-NaNO₂ with concentration of 1×10^{-6} g/mL in H₂O–EtOH (1:5).

mixture reacted under ultrasound for 20 min to synthesize gold nanoparticles modified by crown ether porphyrin (GNPs-CP). On the basis, to a three-neck flask was added the resulting GNPs-CP solution (10 mL), then aqueous solution of HgSO₄ (1 mL, 0.01 mol/L) was added under stirring. The final mixture reacted under ultrasound for 30 min to synthesize GNPs-CP-Hg²⁺.

3. RESULTS AND DISCUSSION

In recent years, the simultaneous complexation of cationic and anionic guest species by ditopic receptors is a rapidly growing area of supramolecular chemistry due to their diverse applications in sensor and selective extraction.⁴¹ Among them, metal-crown ether-porphyrins have been extensively studied by UV-Vis spectroscopy, and many efforts have been devoted to ion recognition. Inspired by our previous researches in the field of gold nanoparticles and its applications in surface enhanced Raman spectroscopy,⁴² we propose the novel strategy to fabricate higher sensitive ion probe based on Raman spectra. To the



Figure 4. Plausible mechanism of separating of the crown ether ring from mercury porphyrin induced by Na^+ .



Figure 5. SEM images of GNPs-CP-Hg²⁺ and GNPs-CP-Hg²⁺-NaNO₂.

best of our knowledge, the similar method has not been mentioned.

3.1. UV-Vis Analysis

Usually, ion recognition of porphyrin derivatives can be detected with UV-Vis spectra. Figure 1 shows the UV-Vis spectra of the GNPs-CP and its corresponding mercury

porphyrin derivative. The inset shows the UV-Vis spectrum of pure gold nanoparticles, which partly overlaps with the Q-band of porphyrin. As for GNPs-CP, a strong absorption peak was found around 417 nm, which is assigned to the soret band of porphyrin. When Hg²⁺ was added in the solution, a new peak around 446 nm occurred, which was accompanied with the decrease in peak intensity around 417 nm simultaneously. Moreover, the number of Q band of porphyrin reduced and an enhanced peak around 680 nm appeared, these data suggested the formation of mercury porphyrin as well as axial coordination between mercury porphyrin and crown ether ring.

When adding NaNO₂ to the solution of GNPs-CP-Hg²⁺, the peak of UV-Vis spectra decreased significantly at 417 nm, which accompanied with a weak blue shift as



Figure 6. SERS spectra (A) and UV-Vis spectra (B) of GNPs-CP-Hg²⁺ and GNPs-CP-Hg²⁺-NaNO₂ measured using 568.2 nm excitation line.
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shown in Figure 2. At the same time, the peak around 680 nm disappeared. The experimental results indicated that the interaction between Na^+ ion and crown ether led to breaking away of crown ether ring from porphyrin molecule. The similar mechanism has played a key role for detecting ion of alkali metal and alkaline earth metal based on UV spectra.⁴¹

3.2. Raman Spectra Analysis

Although the method of ion detection by UV spectra is easy and sensitive, its detection limit cannot reach our requirements. So here, inspired by SERS, we proposed the new ion probe based on crown ether porphyrin. Figure 3 shows the Raman spectra of GNPs-CP-Hg²⁺ and corresponding change with the addition of sodium ion. As in the Raman case of GNPs-CP-Hg²⁺, some large ring stretching vibrations of porphyrin are observed in the low energy region between 200 and 500 cm⁻¹. The strong peak at 880 cm⁻¹ is assigned to C_a - C_M - C_a angular vibration. The peak at 1060 cm⁻¹ corresponds to C_a - C_N stretching vibration, and the peaks at 1100 cm⁻¹, 1280 cm⁻¹ and 1480 cm⁻¹ are assigned to C_M - C_{phenyl} , C_a - C_β and C_β - C_β stretching vibration respectively.

Interestingly, when sodium ion was added to the solution, the Raman spectra underwent a significant change. The peak around 1480 cm⁻¹ was enhanced whereas other region was inhibited. The possible mechanism was described in Figure 4. Without Na⁺ ion, the crown ether ring will undergo an axial coordination with Hg²⁺ ion in another porphyrin ring that resulted in some changes of aggregation state and electron density of porphyrin.⁴³⁻⁴⁷ In contrast, when sodium ion as ligand was added in the solution, the Na⁺ ion will embed in the crown ether ring and decrease the nucleophilic ability of crown ether molecule, which leads to separating of the crown ether ring from mercury porphyrin.

3.3. SEM Analysis

Figure 5 is the corresponding SEM images of GNPs-CP- Hg^{2+} in the above process. Experimental results showed that, without addition of NaNO₂, rod-like or dendritic self-assembled morphology of GNPs-CP- Hg^{2+} were formed. The phenomenon was due to the dominant axial coordination of metal porphyrin unit and crown ether unit. The intermolecular interaction further induced the gold nanoparticles to form rod-like or dendritic morphology. But after addition of NaNO₂, the complexation between Na⁺ and crown ether ring resulted in separation of GNPs-CP- Hg^{2+} as shown in Figure 4, and accordingly, aggregate nature of the GNPs-CP- Hg^{2+} turned to cluster. So the mechanism proposed by us is credible.

3.4. SERS Spectra and UV Spectra Analysis

Figure 6 shows the ion response sensitivity of GNPs-CP-Hg²⁺ based on Raman and UV-Vis spectra respectively

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with three kinds of concentration of NaNO₂, which is 1×10^{-6} g/mL, 1×10^{-7} g/mL and 1×10^{-8} g/mL. The results showed that, when concentration of Na⁺ decreased from 1×10^{-6} g/mL to 1×10^{-8} g/mL, the intensity of Raman signal decreased from 2500 to 1000 and showed a good linear relationship with the concentration of Na⁺, whereas the intensity of UV signal decreased from 0.2 to 0.003 close to the background noise. These results indicated that the ion response based on Raman signals exhibited higher sensitivity than the UV spectra.

4. CONCLUSIONS

In summary, we have prepared a kind of gold nanoparticles modified with metal crown ether porphyrin (CP-GNPs) Based on the coupling effect of metal porphyrin and crown ether, we proposed a novel ion probe with high sensitivity detected by Raman spectra. Compared with traditional detection methods by UV-Vis spectra, when meeting metal ion corresponding to ligand of crown ether, both spectra changed dramatically, but Raman spectra of the composite particles is more sensitive and the limit of detection (LOD) can reach 1×10^{-8} g/mL.

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