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A New Water-Soluble Supramolecular Container for Efficient Separation and Storage of Gasoline Components

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Abstract: This study explores the development of a low-energy, low-pollution, and efficient gasoline fraction separation technology using a water-soluble organometallic supramolecular cage. With the growing demand for petroleum and the environmental challenges posed by traditional extraction methods, this research aims to improve the efficiency of gasoline extraction from crude oil. A hybrid metal-organic cage was synthesized using a ligation-driven self-assembly strategy, featuring a specific cavity that selectively screens gasoline fractions based on molecular size and shape. The experimental process involved separating simulated gasoline, commercial gasoline, and crude oil, demonstrating the cage's potential for selective extraction. The findings contribute to advancements in separation technologies for the petrochemical industry and offer a pathway toward more sustainable petroleum refining processes.

1. Introduction

As a non-renewable fossil energy, petroleum has been playing a vital role in the development of human society. The transportation industry is developing rapidly, the number of industrial plants is increasing, and the number of cars is rapidly climbing.

This not only promotes the shortage of oil resources, but also produces serious environmental pollution and climate change problems. Therefore, it is necessary to improve the production mode of petroleum products, improve the utilization rate of petroleum resources, and explore the low-carbon development mode of petrochemical industry to ensure global energy security. According to statistics, the energy consumption for product separation and purification in the petrochemical industry accounts for about 10%-15% of the global total energy consumption [1].Among them, gasoline extracted from petroleum fractionation as fuel plays an indispensable role in transportation, aerospace, industry and other fields. In recent years, the global annual consumption of gasoline is about 3.5 billion tons, but the traditional gasoline fraction extraction technology still has low efficiency, high energy consumption, environmental pollution and other problems, so the research and development of low energy consumption, low pollution, low cost, high efficiency gasoline fraction separation technology is one of the core contents of promoting energy saving technology in the chemical industry. Coordination supramolecular cage compounds have specific cavities and can be used as molecular containers to selectively envelop guest molecules with specific sizes, shapes, functional groups and electronic effects [2]. This property lays a theoretical foundation for their application in the development of new separation technologies.

1.1 Construction strategies of supramolecular coordination compounds

There are many self-assembly methods to choose when constructing supramolecular metal-organic polyhedral complexes, all of which follow the same idea, that is, to design suitable ligand modules and metal elements to ensure the polymerization direction, and to synthesize supramolecular complexes with limited structure, lowest energy and the most stable physical and chemical properties. In the process of ligation-driven supramolecular self-assembly, the main strategies followed are: directional bonding, symmetry matching, molecular panels, weak bonding and subcomponent self-assembly [3].

1.2 Metal-organic supramolecular cage

Metal-organic cage, also known as metal-organic polyhedron, is an important model used in biomimetic synthesis to study enzyme catalytic processes in organisms. These compounds are three-dimensional discrete supramolecular assemblies formed by coordination self-assembly of ligands and metal ions or metal clusters, with cavities of various sizes and different geometric shapes. Because of its persistent porosity, good physicochemical stability, good solubility and other characteristics, it has a good application prospect in recognition, separation, catalysis, drug loading and so on, which has been widely concerned by scholars in many research fields.

1.2.1 Geometric types of metal-organic cages

The structure and function of organometallic cage compounds depend on the selected ligands and metal nodes. With the continuous development of supramolecular coordination chemistry, the available ligands are not only diversified in size, geometry, coordination mode, physical and chemical properties, but also the metal nodes can be expanded from mononuclear metal ions with different coordination modes to binary or multi-nuclear metal clusters. Therefore, more and more metal-organic cage compounds with complex structure, rich properties and specific cavities have been synthesized [4]. As shown in Figure 1, the geometry of these supramolecular complexes can be divided into the following two categories: the "Platonic" polyhedron formed by the Mosaic of one regular polygonal panel, and the "Archimedes" polyhedron formed by two or more regular polygonal panels.

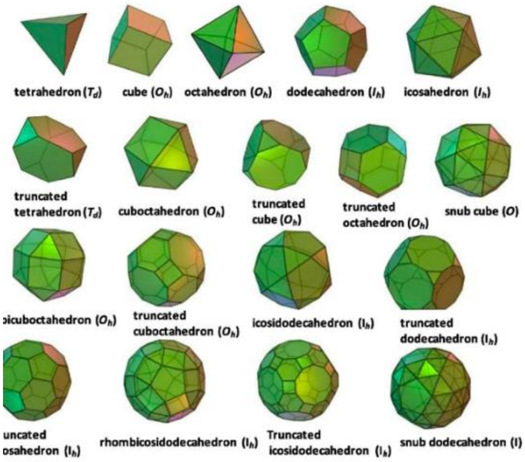

Figure 1: Geometry of common organometallic cage compounds

1.2.2 Application of metal-organic cages in separation

In 2022, Professor Mukherjee's research group constructed a water-soluble ship-shaped complex with novel structure, which can be used as an extractant to achieve the separation of isomers of thick ring aromatic hydrocarbons, as shown in Figure 2 (a). The molecular ship is formed by self-assembly of a flexible tetrapyridine ligand with a cis-formed 90 ° ethylenediamine Pd(II) metal precursor in a 1:2 molar ratio.Although the coordination orientation of the flexible ligands may be different, only the molecular ship configuration products are obtained after the coordination self-assembly, and no other by-products are generated. Due to the flexibility of the ligand main chain, the cavity of the molecular ship has certain adaptability, and based on the adaptability of its hydrophobic cavity, several hydrophobic aromatic hydrocarbons are enclosed [5]. The single crystal structure of the host-guest inclusion complex of the molecular ship and pyrene was obtained by X-ray single crystal diffraction analysis, as shown in Figure 2 (b). In addition, the difference of affinity between phenanthrene and anthracene was used to achieve the efficient separation of phenanthrene isomers, and the purity of phenanthrene was higher than 98%.

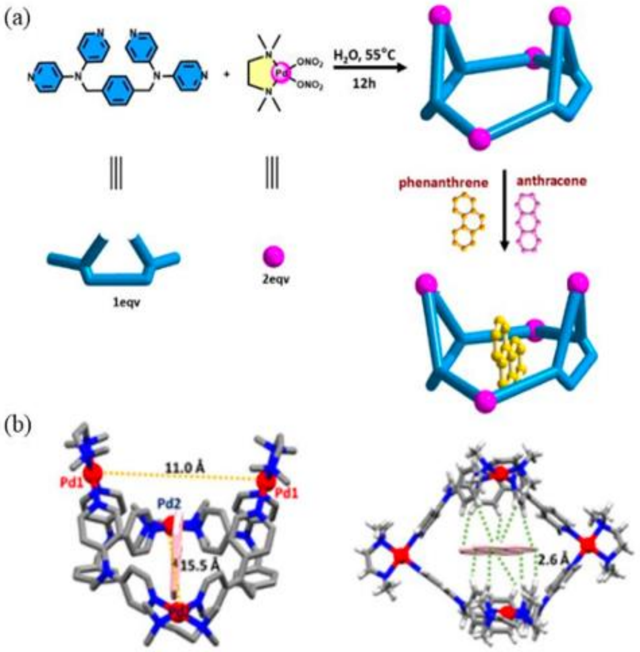

Figure 2: (a) Synthesis and selective recognition of molecular ships; (b) Single crystal structure of the host-guest complex

1.3 Materials and Methods

This paper aims to develop a crude oil separation technology with low energy consumption, low pollution, low cost and high efficiency. A water-soluble organometrics supramolecular cage with a specific cavity was synthesized by using a ligation-driven self-assembly construction strategy. By separating simulated gasoline, commercial gasoline and crude oil in the water phase, whether the molecular cage can play a selective screening role in the process of extracting gasoline fractions from crude oil was explored [6].

2. Materials and Methods

2.1 Preparation of metal-organic supramolecular cages

2.1.1 Synthesis of tripod thione ligand L

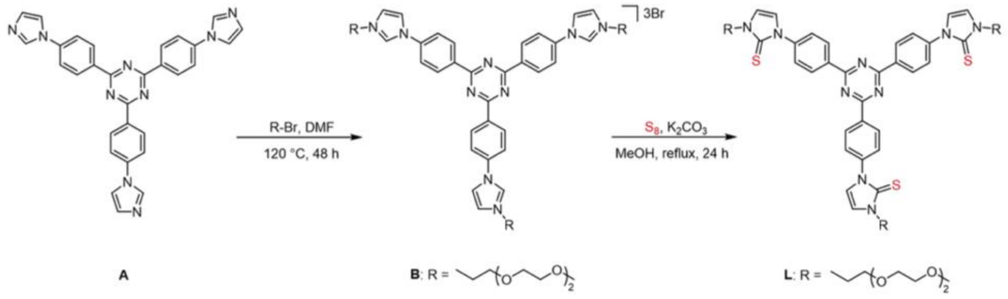

Figure 3: Synthesis route of organic ligand L

(1) Synthesis of compound B

Compound A (304 mg, 0.6 mmol), 1-bromo-3,6,9, 12-tetraoxatridecane (976 mg, 3.6 mmol), and 6 mL N, n-dimethylformamide were added sequentially in a 50 mL Shrek tube. Stir at 120 ℃ for 48 h, cool to room temperature, add 35 mL ethyl acetate. Then centrifuge and collect the underlying black oil and wash it with ethyl acetate (2 × 5 mL). After vacuum drying, 697 mg of black oil B was obtained with a yield of 88% (Figure 3).

(2) Synthesis of compound L

B (396 mg, 0.3 mmol), sulfur powder (57 mg,1.8 mmol), potassium carbonate (248 mg,1.8 mmol), and 150 mL methanol were added successively in a 100 mL round-bottomed flask with branches. Stir reflux at 80 ℃ for 48 h, cool to room temperature, spin evaporation to remove solvent. Then 30 mL of dichloromethane was added, the filtrate was filtered and collected [7], and washed with water (3 × 50 mL). After drying, magnesium sulfate was distilled and purified by column chromatography (SiO2, EtOAc). 144 mg yellow oil L was obtained with a yield of 41%.

2.1.2 Synthesis of water-soluble tetrahedral metal-organic supramolecular cages

(1) Synthesis of compound C

Weigh $AgNO_3$ (152 mg, 0.9 mmol) and dissolve in 1.5 mL water to obtain a colorless solution. Then $(Tr_2Pd_3Cl_3)$ PPh4 (284 mg, 0.3 mmol) was added to the above solution, stirred at room temperature for 5min and filtered. After distillation, the filtrate was concentrated to about 0.5 mL, and 7 mL ethyl ether and 3mL ethanol were added successively to precipitate a large amount of reddish-brown precipitate [8]. After filtration, the obtained reddish-brown solid was dissolved in acetonitrile and slowly diffused into the clear solution with ether to obtain 180 mg reddish-brown strip crystal C with 90% yield.

(2) The compound of $[(Tr_2Pd_3)_4(L1)_4](NO_3)_8$ (1)

Compound $[Tr_2Pd_3(CH_3CN)][NO_3]_2$ (10 mg, 0.015 mmol), (10 mg, 0.015 mmol), ligand L (17.6 mg, 0.015 mmol), and 1 mL water were added successively in a 10 mL nightshade bottle. The dark red reaction liquid was stirred at room temperature for 3 min and then filtered. After the filtration solution was spun and steamed to remove the dissolvant, 27.3 mg red-brown solid powder $[(Tr_2Pd_3)_4(L)_4](NO_3)_8$ (1) was obtained with a yield of 99% (Figure 3).

2.2 Study on host-guest properties of water-soluble tetrahedral metal-organic supramolecular cage 1

Whereas the main components of gasoline fractions in crude oil are C5−C10 normal alkanes, single rings and a small number of double rings.

Naphthenes, such as kerosene, diesel, lubricating oil and other fractions are mainly composed of hydrocarbons with carbon number greater than 10. Therefore, the specific hydrophobic cavity of coordination cage 1 is used to selectively screen alkanes of different shapes and sizes, in an attempt to establish a separation model for extracting gasoline from crude oil, and develop a green and efficient gasoline separation technology [9]. Therefore, we designed the following series of experiments to verify the extraction of simulated gasoline components, commercially available gasoline and crude oil components (as shown in Figure 4) by coordination cage 1.

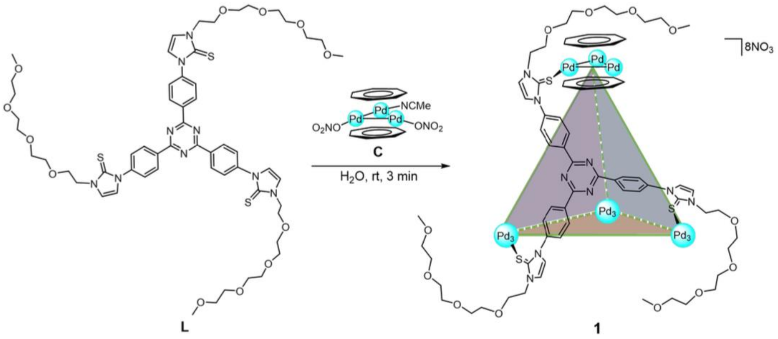

Figure 4: Synthesis route of water-soluble tetrahedral cage 1

Verification experiment 1: Equal equivalent n-pentane, n-hexane, n-heptane, n-octane, n-nonane, methylcyclopentane, cyclohexane, cycloheptane, cyclooctane, cis-decaphthalene, trans-decaphthalene and cyclododecane compounds were uniformly combined to simulate the main components of gasoline (as shown in Figure 5). The main cage 1 (86.4 mg,0.012 mmol) was weighed and added to the 10 mL reaction tube, then 1 mL deuterium water was added, and the reaction tube was shaken to dissolve the main cage 1 completely. Then, a slightly excessive amount of simulated gasoline is added to the above reaction tubes, stirred at room temperature for 3 hours, and the clear liquid is taken for nuclear magnetic test. By analyzing the nuclear magnetic spectrum, it can be found that a new proton signal peak appears in the region of 0.1-1.5 ppm after the interaction between the main cage 1 and the simulated gasoline components.

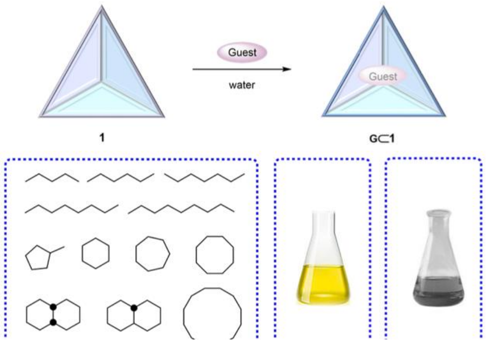

Figure 5: Schematic diagram of subject-object interaction between body cage 1 and simulated gasoline, commercially available gasoline and commercially available crude oil

Verification experiment 2: Purchase a small amount of gasoline from the market for the package verification of gasoline components. The main cage 1 (86.4 mg, 0.012 mmol) was weighed and added to the 10 mL reaction tube, then 1 mL deuterium water was added, and the reaction tube was shaken to dissolve the main cage 1 completely. Then, a slightly excessive amount of commercially available gasoline is added to the above reaction tube, stirring at room temperature for 3 hours. After separating the water and oil, the clear liquid is taken for nuclear magnetic test [10]. Finally, the organic layer was collected after the aqueous phase was extracted with ether for gas chromatography test.

Validation Experiment 3: Purchase a small amount of crude oil from the market to verify whether gasoline fractions can be separated from crude oil. The main cage 1 (86.4 mg, 0.012 mmol) was weighed and added to the 10 mL reaction tube, then 1 mL deuterium water was added, and the reaction tube was shaken to dissolve the main cage 1 completely. Then, a slightly excessive amount of commercially available crude oil is added to the above reaction tubes respectively and stirred at room temperature for 3 hours. After separating the water and oil, the clear liquid is taken for nuclear magnetic test [11]. Finally, the organic layer was collected after the aqueous phase was extracted with ether for gas chromatography test.

3. Discussion

The aqueous solution of the main cage 1 was mixed with an appropriate amount of commercially available gasoline and the clear liquid was used for nuclear magnetic hydrogen spectroscopy characterization. As can be seen from Figure 6, a new proton signal peak appeared in the 1H NMR spectrum of Caged 1 after interaction with commercially available gasoline in the region of 0.1-1.5ppm. Compared with the previous experimental results, a series of new peaks could be attributed to saturated aliphatic hydrocarbons. Therefore, we speculated that gasoline components were extracted into the water phase under the action of Caged 1. The result of this experiment gives us inspiration for further attempts to extract gasoline fractions from more complex crude oil [12].

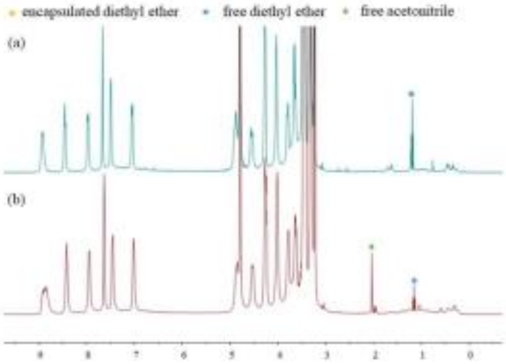

Figure 6: (a) and (b) are 1H NMR spectra of gasoline, crude oil and 1 (400 MHz, D2O), respectively.

In order to verify this conjecture, we further carried out verification experiment 3.After the aqueous solution of main cage 1 was mixed with an appropriate amount of commercially available crude oil, the clear liquid was used for nuclear magnetic hydrogen spectroscopy characterization, as shown in Figure 6. From the nuclear magnetic contrast diagram of the two, it can be seen that the new proton signal peaks appear in the same region. The water phase obtained above was extracted with appropriate organic solvent and characterized by 1H NMR spectroscopy (Figure 6) and gas chromatography (Figure 7), respectively [13]. The data results showed that the components extracted by Cage 1 from crude oil were mainly light oil with boiling point less than 200℃. At the same time, the experimental results show that organic cage 1 can be used as a model molecule for extracting crude oil in mixed phase, providing theoretical support for green and efficient extraction of gasoline[14] (Figure 8).

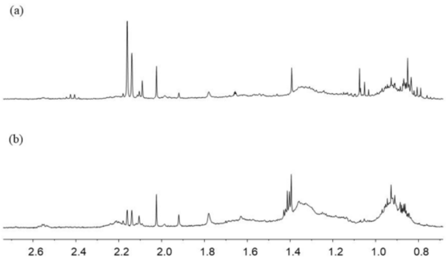

Figure 7: (a) and (b) are 1H NMR spectra of extracts from gasoline and crude oil of Cage 1 (400 MHz, C6D6), respectively.

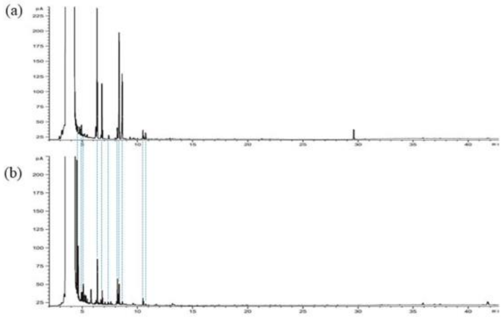

Figure 8: (a) and (b) are the GC spectra of extracts from gasoline and crude oil of Cage 1, respectively

4. Conclusion

We constructed a stable water-soluble tetrahedral coordination molecular cage with sandwich trinuclear palladium organometallic elements as nodes. By using the supramolecular cage with good water solubility, high stability and special hydrophobic cavity, the efficient extraction of gasoline from crude oil was realized, and the green extraction model of gasoline was established. The establishment of this model provides a research idea for the development of new separation materials and a new method for the green separation and purification process of industrial hydrocarbons.

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