

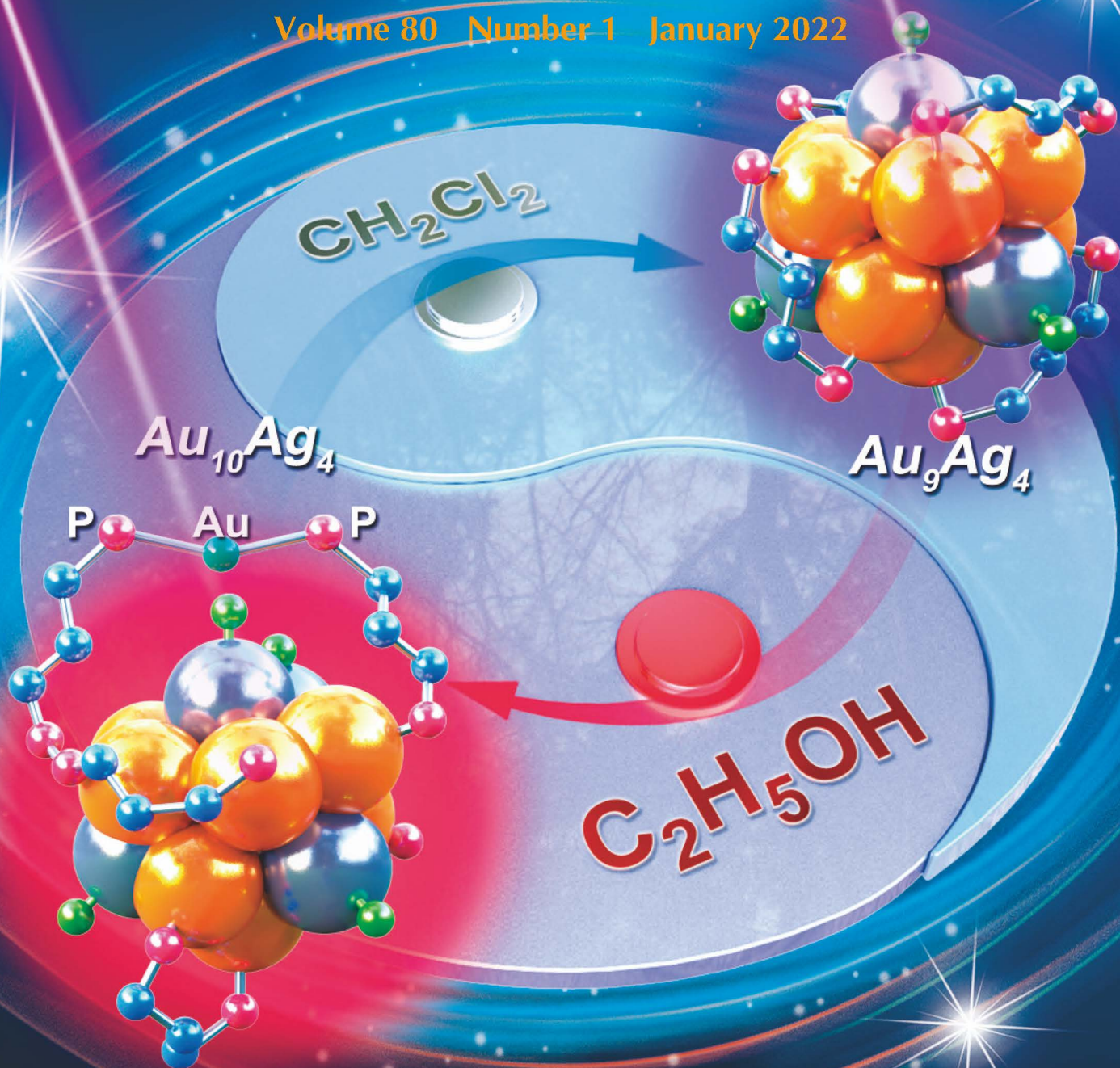


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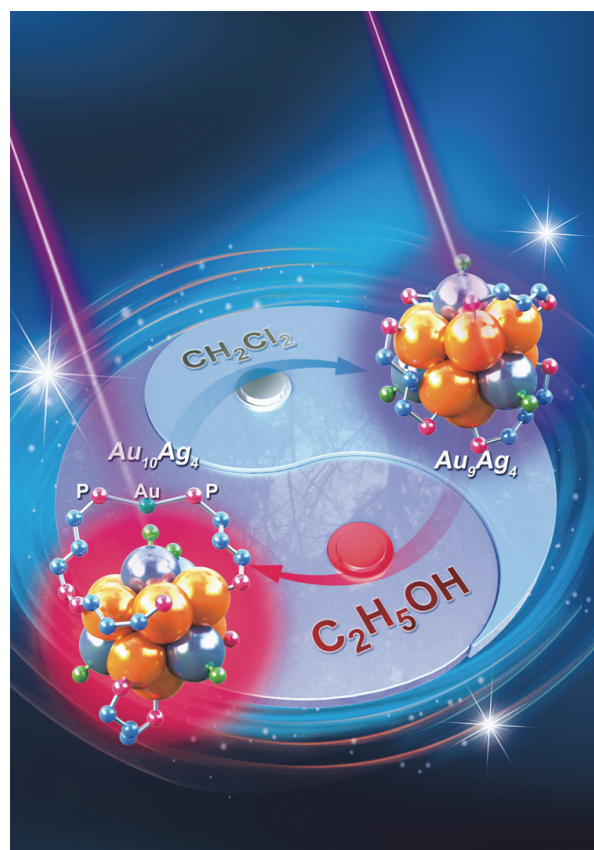
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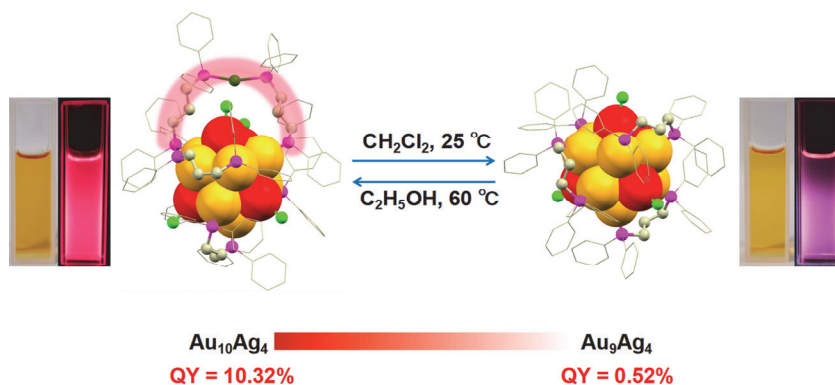
* 通信联系人.

On the cover: A special RP-Au-PR motif is first reported in metal nanoclusters, and it can self-bear and self-vanish in various solvents and thus result in the two-way transformation between $\text{Au}_{10}\text{Ag}_4$ nanocluster and Au_9Ag_4 nanocluster, accompanied by the enhancement and weakening of photoluminescence. [Wu, Zhikun *et al.* on page 1-6.]



Communication

Single, Self-Born RP-Au-PR Motif Boosts 19-Fold Photoluminescence Quantum Yield of Metal Nanocluster

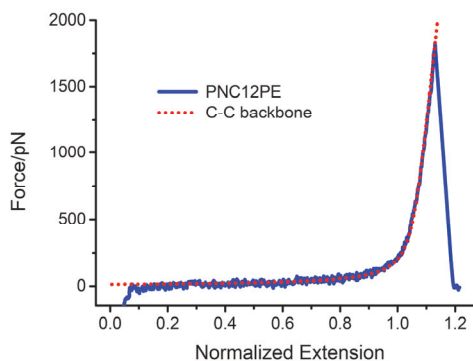


Xu, Daolan; Yang, Ying; Fan, Wentao; He, Zongbing; Zou, Jiafeng; Feng, Lei; Li, Man-Bo*; Wu, Zhikun*

Acta Chim. Sinica **2022**, *80*(1), 1-6

A special RP-Au-PR motif was first reported in nanoclusters, and it can self-bear and self-vanish and thus result in the two-way transformation between $\text{Au}_{10}\text{Ag}_4$ NC and Au_9Ag_4 NC, accompanied by the enhancement and weakening of photoluminescence.

Single-chain Mechanics of Proline-based Polyesters

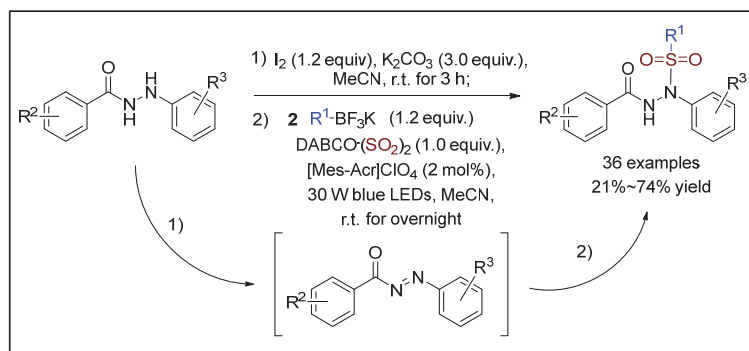


The normalized force-extension (F - E) curve of PNC12PE (a kind of proline-based polyesters), which shows the inherent elasticity of this polymer, is virtually identical to the quantum mechanics-freely rotating chain (QM-FRC) model fitting curve of C—C backbone, indicating that the main chain of PNC12PE is as soft as the common polymers with C—C backbone. In addition, the pyrrolidine rings in the main chain of PNC12PE are mechanically stable ($F < 2200$ pN) during single-molecule force spectroscopy (SMFS) experiment, indicating that PNC12PE is suitable for the applications requiring high mechanical stability.

Gong, Zheng; Zhang, Yi; Lu, Hua*; Cui, Shuxun*

Acta Chim. Sinica **2022**, *80*(1), 7-10

Visible-light Photocatalytic Alkyl-sulfonylation of Aroylhydrazides with Alkylsulfonyl Radicals



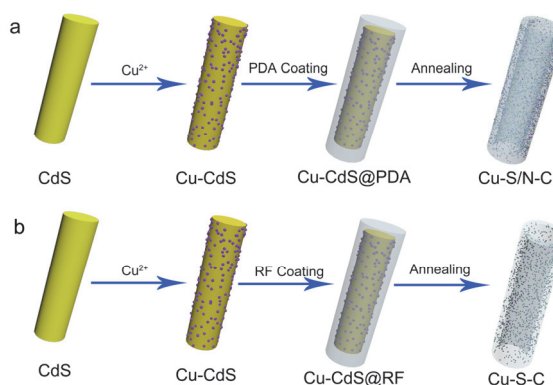
A photoinduced reaction of potassium alkyltrifluoroborates, DABCO•(SO₂)₂ (1,4-Diazabicyclo[2.2.2]octane, DABCO) and aroylhydrazides under visible light irradiation was developed. This reaction works in a green and mild way with a broad substrate scope, which obtained *N*'-acyl-*N*-alkylsulfonylhydrazides in moderate to good yields in one-pot.

Yang, Min; Ye, Baibai; Chen, Jianqiang*; Wu, Jie*

Acta Chim. Sinica **2022**, *80*(1), 11-15

Article

Synthesis of Cu Single Atom with Adjustable Coordination Environment and Its Catalytic Hydrogenation Performance

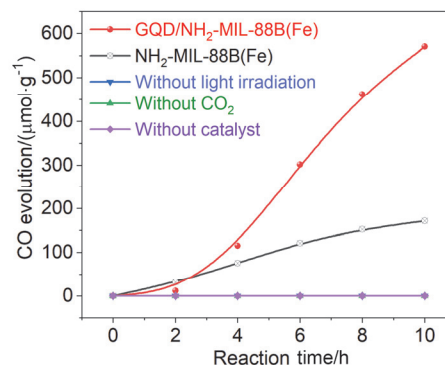
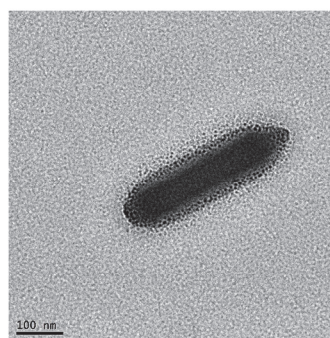


A cation exchange strategy was developed and two Cu single-atom catalytic materials with different coordination structures were synthesized. In these two materials, except for the Cu single-atom coordination environment, the other structures are the same. The experimental results show that the Cu single atom of S and N double-modified metal sites has better nitrobenzene hydrogenation activity than that of only S-modified metal sites.

Li, Lingling; Liu, Yu; Song, Shuyan*; Zhang, Hongjie*

Acta Chim. Sinica **2022**, *80*(1), 16-21

Graphene Quantum Dots Supported on Fe-based Metal-Organic Frameworks for Efficient Photocatalytic CO₂ Reduction

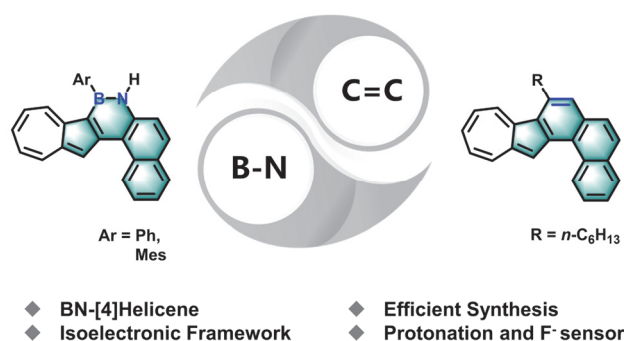


Graphene quantum dots (GQD) supported on the Fe-based nano-sized metal-organic frameworks (MOFs) NH₂-MIL-88B(Fe) were prepared via electrostatic self-assembly strategy to enhance the photoreduction of CO₂. The resulting GQD/NH₂-MIL-88B(Fe) composites showed much enhanced CO production rate (4 times) in comparison with the parent NH₂-MIL-88B(Fe), reaching 590 μmol/g under 10 h visible light irradiation, which benefits from both the high CO₂ adsorption of MOFs and the enhanced separation of photogenerated electrons and holes.

Wang, Xusheng; Yang, Xu; Chen, Chunhui; Li, Hongfang; Huang, Yuanbiao*; Cao, Rong

Acta Chim. Sinica **2022**, *80*(1), 22-28

Design, Synthesis and Properties of Azulene-based BN-[4]Helicenes

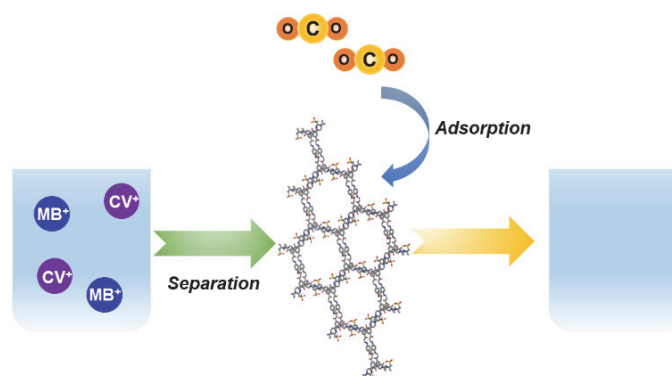


Two types of azulene-based [4]helicene **1a/1b** and **2** that contain isoelectronic B—N and C=C units were synthesized by efficient electrophilic boronation and platinum-catalyzed cycloisomerization. The single crystal structure analysis demonstrates that **1a** has a helically twisted framework and *Plus (P)/Minus (M)* enantiomers. Additionally, **1a** with a phenyl group exhibits the deboronization upon addition of trifluoroacetic acid (TFA) as well as a specific sensing behavior to fluoride ion. **1b** and **2** have a reversible stimuli-responsiveness with acid and base.

Duan, Chao; Zhang, Jianwei; Xiang, Junjun; Yang, Xiaodi*; Gao, Xike*

Acta Chim. Sinica **2022**, *80*(1), 29-36

A New Covalent Organic Framework Modified with Sulfonic Acid for CO₂ Uptake and Selective Dye Adsorption

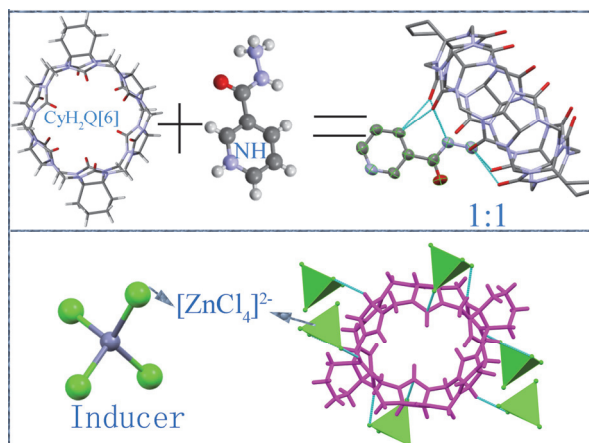


Wang, Zitao; Liu, Yaozu; Wang, Yujie; Fang, Qianrong*

Acta Chim. Sinica **2022**, *80*(1), 37-43

We chose a covalent organic framework (COF) (3-PD) as a template and modulated by adding a sulfonic acid group. Based on this modulation, a new highly crystalline COF (JUC-603) with a pore size of 1.6 nm was successfully prepared. The COF displayed an outstanding performance in the uptake of CO₂ (52 cm³/g at 273 K and 0.1 MPa) and dye adsorption (removal efficiency 98% in 30 min) toward cationic dyes.

Supramolecular Self-assembly of Symmetric Dicyclohexanocucurbit[6]uril and Nicotinic Hydrazide

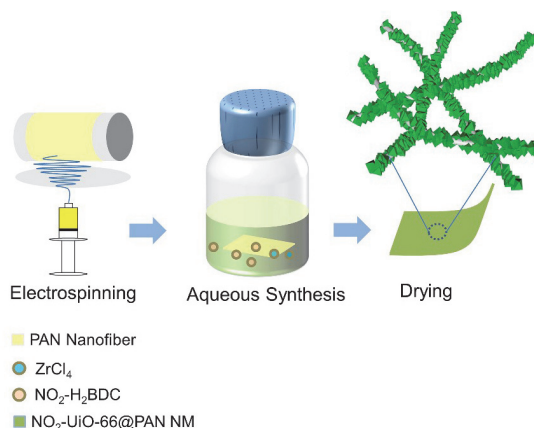


The interaction mode between the symmetric dicyclohexanocucurbit[6]uril (CyH₂Q[6]) as a host and nicotinic hydrazide (NH) as a guest was investigated by nuclear magnetic resonance spectroscopy (¹H NMR), isothermal titration calorimetry (ITC), matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry, and single-crystal X-ray diffraction. The experimental results showed that CyH₂Q[6] formed a stable 1 : 1 exclusion complex with NH in an aqueous solution. The single-crystal structure of the complex showed that there are ion-dipole interactions and hydrogen bonds between the CyH₂Q[6], NH and [ZnCl₄]²⁻. These weak interactions are the driving forces of the multi-dimensional and multi-level supramolecular framework formed by the complex.

Jin, Yanmei*; Meng, Ye; Li, Yuan; Shi, Jianhua; Deng, Lei

Acta Chim. Sinica **2022**, *80*(1), 44-48

Preparation and Performance Characterization of Flexible and Washable Zr-MOFs Composite Nanofiber Membrane

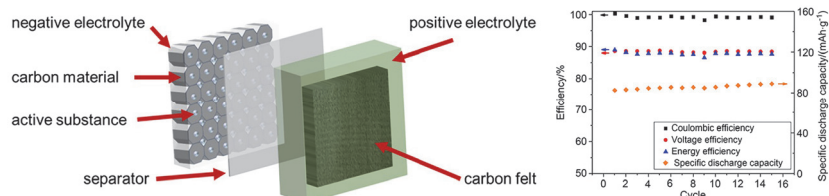


Hao, Xiaoke; Zhai, Zhenyu; Sun, Yaxin; Li, Congju*

Acta Chim. Sinica **2022**, *80*(1), 49-55

NO₂-UiO-66 was successfully produced on a electrospun nanofiber membrane by aqueous synthesis method with water as the solvent and trifluoroacetic acid as a regulator, which prepared a flexible, breathable and excellent physical and chemical stability NO₂-UiO-66@polyacrylonitrile composite nanofiber membrane (NO₂-UiO-66@PAN NM) material.

Research on Iron-Lead Semi-Flow Battery Based on 3D Solid Electrode

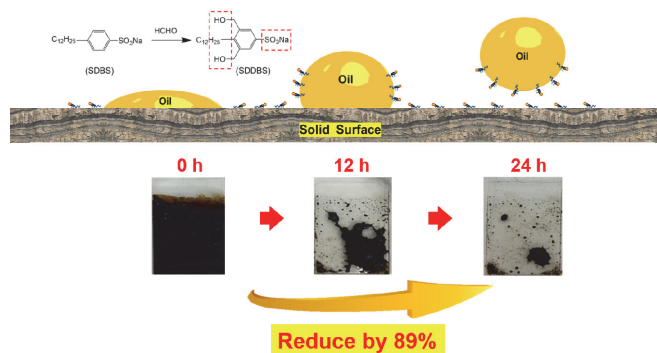


Zhang, Zhuhan; Jiang, Fengjing*; Wu, Keke; Shen, Peng

Acta Chim. Sinica **2022**, *80*(1), 56-62

A new type of energy storage battery is proposed, the positive and negative active materials of which are ferrous sulfate/iron sulfate and lead/lead sulfate respectively. This battery has excellent performance without problems of hydrogen evolution and dendrites.

Synthesis and Performance Evaluation of Polyhydroxy Benzene Sulfonate Oil Displacement Agent Based on Enhanced Interfacial Wettability Control



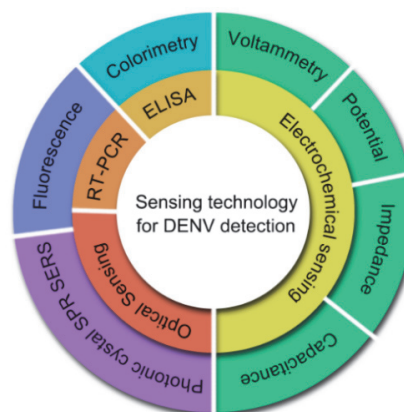
Li, Lin*; Wang, Zizhao; Liu, Jiawei; Chen, Jia; Jin, Xiao; Dai, Caili

Acta Chim. Sinica **2022**, *80*(1), 63-68

An interfacial wettability controlling oil displacement agent sodium dimethyldodecyl benzene sulfonate (SDDBS) was synthesized. By introducing hydrogen bonds to enhance the surface adsorption, SDDBS could regulate the wettability of the oil-wet rock surface to strong hydrophilic state, and peel off oil film with high efficiency.

Account

Biosensing Technology for Dengue Virus Detection



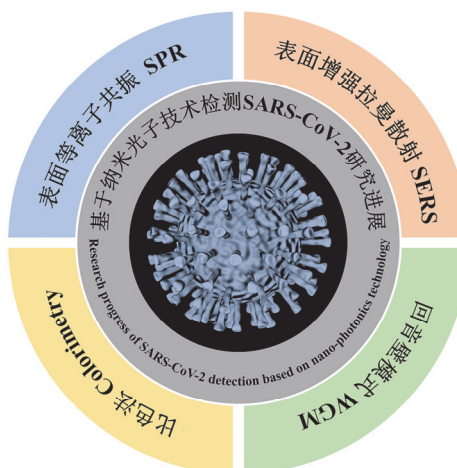
Shi, Yao; Xia, Qianfeng; He, Zhengqing; Ju, Huangxian*

Acta Chim. Sinica **2022**, *80*(1), 69-79

Dengue virus is a single-stranded RNA virus transmitted by mosquitoes, belonging to the flaviviridae. Due to the importance of clinical detection, new methods for detecting Dengue virus have been developed. This review mainly describes the biosensing technologies for the detection of Dengue virus related diagnostic markers, including optical, electrochemical, enzyme-linked immunosorbent assay and other biosensing methods, and comprehensively evaluates the sensitivity, accuracy, concentration range, detection limit and clinical application ability of different detection methods, so as to further improve the detection performance of these technologies, and to promote the development of this field. It will provide references for the early diagnosis of Dengue virus infection.

Review

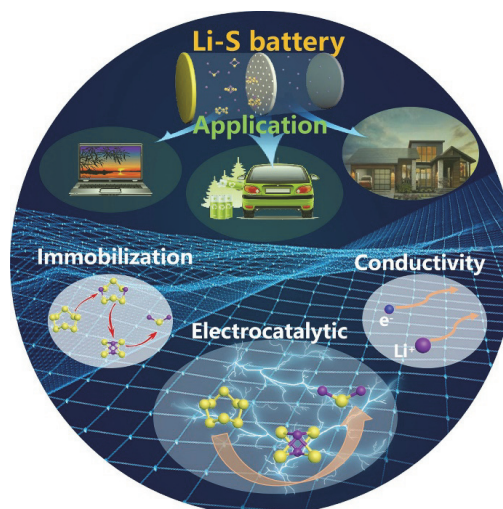
Research Progress on Nano Photonics Technology-based SARS-CoV-2 Detection



Yang, Xu; Zhang, Zeying; Su, Meng*; Song, Yanlin*

Acta Chim. Sinica **2022**, *80*(1), 80-88

Functionalized Carbon-Based Composite Materials for Cathode Application of Lithium-Sulfur Batteries



Liu, Handing; Jia, Guodong; Zhu, Sheng;
Sheng, Jian; Zhang, Zeyao; Li, Yan*

Acta Chim. Sinica **2022**, *80*(1), 89-97

High-performance lithium-sulfur batteries are energy storage technology with great application potential, which can play a key role in portable energy storage, power vehicles and smart grids. However, the sulfur cathode has the problems of non-conductivity, easy loss, and kinetic conversion delay. It is urgent to develop a sulfur cathode carrier with the three functions of conduction, sulfur fixation and catalysis to improve the above problems.

SCI 收录期刊

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对称二环己基取代六元瓜环与 3-吡啶甲酰肼的超分子自组装

金艳梅^{*a} 蒙叶^b 李远^a 史建华^a 邓雷^a^a 贵州省煤炭产品质量监督检验院 六盘水 553001^b 贵州大学精细化工研究开发中心 贵阳 550025

摘要 本工作以对称二环己基取代六元瓜环(CyH₂Q[6])为主体分子, 3-吡啶甲酰肼(NH)为客体分子, 利用核磁共振(¹H NMR)、等温滴定量热(ITC)、基质辅助激光解吸电离飞行时间质谱(MALDI-TOF)研究客体分子与瓜环在水溶液中形成的物质的量比为 1 : 1 的稳定配合物; 用 X-射线单晶衍射可以观察到客体分子通过离子-偶极和氢键与瓜环端口羰基氧相互作用, 以及基于瓜环外壁正电性与无机阴离子之间形成的配合物, 从而形成多维多层次超分子框架的自组装体。

关键词 对称二环己基取代六元瓜环; 3-吡啶甲酰肼; 配合物; 超分子框架; 自组装体

Supramolecular Self-assembly of Symmetric Dicyclohexanocucurbit[6]uril and Nicotinic Hydrazide

Jin, Yanmei^{*a} Meng, Ye^b Li, Yuan^a Shi, Jianhua^a Deng, Lei^a^a Guizhou Coal Product Quality Supervision & Inspection Institute, Liupanshui 553001, China^b Center for Research and Development of Fine Chemicals, Guizhou University, Guiyang 550025, China

Abstract Cucurbit[*n*]uril (Q[*n*]) is a relatively new supramolecular macrocyclic compound, which has a unique structure comprised of a hydrophobic cavity with intermediate potential, two carbonyl portals with negative potential, and an outer surface with positive potential. Cyclohexyl-substituted Q[*n*]s have also attracted a lot of attention as the first member of the Q[*n*] family that can be dissolved in organic solvents and water. In this paper, the interaction modes between the symmetric dicyclohexanocucurbit[6]uril (CyH₂Q[6]) as a host and nicotinic hydrazide (NH) as a guest were investigated by nuclear magnetic resonance spectroscopy (¹H NMR), isothermal titration calorimetry (ITC), matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry, and single-crystal X-ray diffraction. The ¹H NMR spectrum results showed that the proton peaks shift to the downfield, indicating that NH is located at the portal of CyH₂Q[6]. ITC experiment results showed that the binding constant (*K*_a) of NH@CyH₂Q[6] is $(1.019 \pm 0.118) \times 10^3 \text{ L} \cdot \text{mol}^{-1}$, the host-guest binding ratio is 0.954 ± 0.013 , and the enthalpy value is $\Delta H = (-48.21 \pm 0.35) \text{ kJ} \cdot \text{mol}^{-1}$ and entropy value $T\Delta S = (-31.04 \pm 0.52) \text{ kJ} \cdot \text{mol}^{-1}$. The MALDI-TOF mass spectrum also showed that the molecular ion peak *m/z* is 1242.4542 (theoretical value: 1242.1603), which is attributed to [CyH₂Q[6]•HNH]⁺. These experimental results showed that CyH₂Q[6] formed a stable 1 : 1 exclusion complex with NH in an aqueous solution. In addition, the host CyH₂Q[6], ZnCl₂ and the guest NH were added to HCl aqueous solution, and the complex single-crystal structure was obtained by evaporation and standing. The single-crystal structure of the complex showed that there are ion-dipole interactions and hydrogen bonds between the carbonyl oxygen of CyH₂Q[6] and NH, and there are ion-dipole interactions between the outer surface of CyH₂Q[6] and [ZnCl₄]²⁻. These weak interactions are the driving forces of the multi-dimensional and multi-level supramolecular framework formed by the complex.

Keywords symmetric dicyclohexanocucurbit[6]uril; nicotinic hydrazide; complex; supramolecular framework; self-assembly

1 引言

无机材料, 如无机沸石^[1]、金属有机框架化合物^[2-4]以及共价有机框架化合物^[5-7]在多相催化、吸附、纳米技术、储能、离子交换过程等方面具有潜在的应用前景^[8-12]。在过去的几十年里, 瓜环^[13-18](Cucurbit[*n*]urils, Q[*n*]=6, 7, 8)作为超分子化学中一支新兴的主体分支, 其结构高度对称且空腔具有疏水效应能封装一些小客体分子^[19-23], 端口羰基单元周围的区域具有显著的负电势, 使瓜环成为具有多作用位点的有机配体分子,

不同聚合度的瓜环具有不同大小的瓜环端口, 则可提供不同结构特征的配位环境, Q[*n*]与不同金属离子的端口相互作用已被广泛研究, 并构建了各种配位聚合物和金属有机框架。

1981年 Mock 研究组^[24]利用 X-射线单晶衍射技术测定了六元瓜环^[25]是一种由六个昔脲单体通过十二个亚甲基桥联形成的一种中间有着疏水性空腔, 而两端口处有极性的羰基氧原子环状化合物, 2001年 Kim 研究组^[26]报道了能溶于醇-水体系的改性环己基全取代五及

* E-mail: jym2583693@163.com

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六元瓜环. 如图 1 所示, 客体 3-吡啶甲酰胺(NH)主要是化工中间体, 其结构含有氨基与吡啶环, 在酸性条件下容易质子化与瓜环通过端口相互作用构建超分子框架, 主体对称二环己基取代六元瓜环(CyH₂Q[6])是较普通瓜环水溶解性比较好的改性瓜环. 本工作利用核磁共振(¹H NMR)、等温滴定量热(ITC)、基质辅助激光解吸电离飞行时间质谱(MALDI-TOF)研究客体分子与瓜环在水溶液中的主客体相互作用; 用 X-射线单晶衍射技术探究在 ZnCl₂ 为诱导剂得到 NH@CyH₂Q[6]晶体的超分子自组装体.

2 结果与讨论

2.1 ¹H NMR 分析

探究主客体相互作用最常用的手段是核磁共振技术. 由 CyH₂Q[6]的结构(图 1)可看出, 瓜环的内部空腔对被封装的客体的质子具有屏蔽效应, 在瓜环的外表面羰基氧原子附近, 客体的质子会受到去屏蔽效应. 图 2 为 NH 与 CyH₂Q[6]在水溶液中的主客体相互作用的 ¹H NMR 谱图, 可以明显看出, NH 的所有质子共振峰的化学位移都往低场移动. 当 CyH₂Q[6]与 NH 的物质的量比为 0.49 : 1.04 时, H_α、H_β、H_γ 和 H_δ 的质子信号分别向低场位移 δ 0.17、0.12、0.29 和 0.23, 表明 NH 受到了去屏蔽效应. 也就是说, NH 位于 CyH₂Q[6]端口羰基之外, 形成客体在瓜环端口作用的配合物 NH@CyH₂Q[6], 而不是被瓜环腔内包结的配合物^[27].

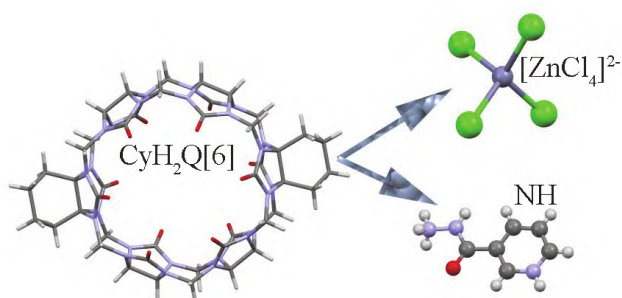


图 1 主体 CyH₂Q[6]、客体 NH 及诱导剂[ZnCl₄]²⁻的分子结构式
Figure 1 The molecular structures of the host CyH₂Q[6], the guest NH and the inducer [ZnCl₄]²⁻

2.2 热力学分析

利用等温滴定量热仪在 298.15 K 来测定 NH@CyH₂Q[6]之间的热力学数据, 并将得到的数据拟合成曲线(图 3), 热力学参数见表 1. 实验结果表明 NH@CyH₂Q[6]的结合常数(*K_a*)为(1.019 ± 0.118) × 10³ L·mol⁻¹, 主客体结合比(*n*)为 0.954 ± 0.013, 说明 NH@CyH₂Q[6]这个体系在水溶液中形成了物质的量比为 1 : 1 的稳定配合物. 另外, 客体与瓜环结合的熵变为负值, 说明熵的变小是由于溶液中自由移动的客体分子变少造成的. 从焓值(Δ*H* = -48.21 ± 0.35 kJ·mol⁻¹)和熵值(*T*Δ*S* = -31.04 ± 0.52 kJ·mol⁻¹)可以看出, 焓变和熵

变均促使了客体和 CyH₂Q[6]的结合.

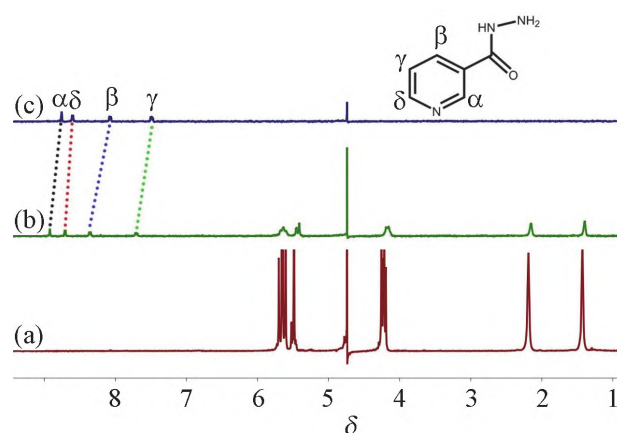


图 2 NH@CyH₂Q[6](D₂O)的 ¹H NMR 谱图: (a) CyH₂Q[6]; (b) *n*(CyH₂Q[6]) : *n*(NH) = 0.49 : 1.04; (c) 客体 NH

Figure 2 ¹H NMR spectra of NH@CyH₂Q[6](D₂O): (a) CyH₂Q[6], (b) *n*(CyH₂Q[6]) : *n*(NH) = 0.49 : 1.04, and (c) guest NH

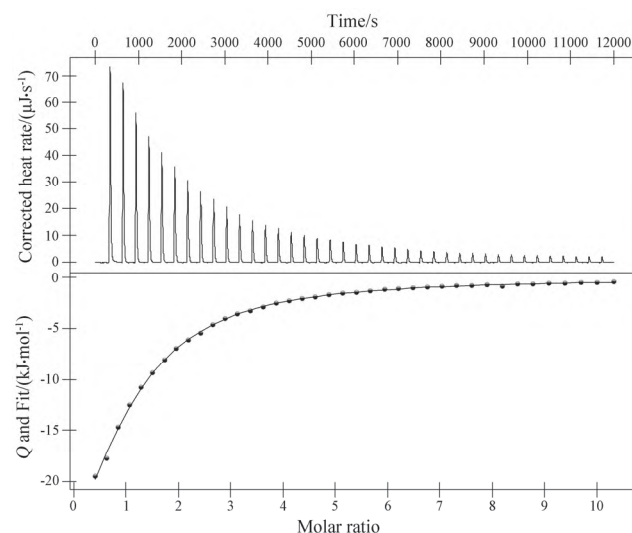


图 3 NH@CyH₂Q[6]在 298.15 K 溶液(去离子水)中结合的 ITC 数据
Figure 3 ITC data for the binding of NH with CyH₂Q[6] in aqueous solution (deionized water) at 298.15 K

表 1 在 298.15 K 下, ITC 测量的 NH 和 CyH₂Q[6]相互作用的热力学
Table 1 ITC measurements of the thermodynamics of NH and CyH₂Q[6] interactions at 298.15 K

Experiment	NH@CyH ₂ Q[6]
Model	Independent
<i>K_a</i> /(L·mol ⁻¹)	(1.019 ± 0.118) × 10 ³
Δ <i>H</i> /(kJ·mol ⁻¹)	-48.21 ± 0.35
<i>n</i>	0.954 ± 0.013
<i>T</i> Δ <i>S</i> /(kJ·mol ⁻¹)	-31.04 ± 0.52

2.3 质谱分析

MALDI-TOF 质谱也用于表征 NH 与 CyH₂Q[6]的结合作用. 图 4 中 *m/z* 有一处明显的分子离子峰 *m/z* 为 1242.4542, 归属于[CyH₂Q[6]·HNH]⁺(理论计算值 *m/z* 为 1242.1603). 这些分子离子峰进一步表明主-客体以 1 : 1 模式结合, 这与上述分析的结果相吻合(注: H 表示客体

被质子化).

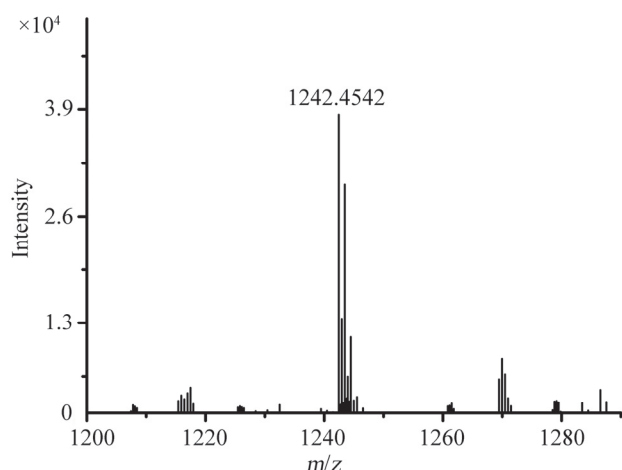


图4 NH@CyH₂Q[6]的MALDI-TOF质谱图

Figure 4 MALDI-TOF mass spectrum of NH@CyH₂Q[6]

2.4 自组装体的晶体结构

在 HCl 水溶液中加入 CyH₂Q[6]、ZnCl₂ 和客体 3-吡啶甲酰胺, 通过蒸发静置得到如图 5 所示的配合物晶体. 晶体结构分析表明, 配合物的不对称单元由一个 CyH₂Q[6]分子、1 个质子化的客体分子和 1 个 [ZnCl₄]²⁻ 阴离子组成^[27](图 5a). 如图 5b 所示, NH 位于 CyH₂Q[6] 主体的端口之外, 即 NH 分子链状这端上的质子化的氮原子(N14, N15)和 CyH₂Q[6]端口羰基氧原子(O1, O2, O3, O4, O6)通过离子-偶极相互作用和氢键连接. N—H…O 的键长在 0.2841~0.3048 nm 范围之内. 而吡啶基上的碳原子(C24)与 CyH₂Q[6]端口发生 C—H… π 作用, 相邻的 CyH₂Q[6]与吡啶基上的其它原子也有弱相互作用, 其键长在 0.2680~0.3162 nm 范围之内. 一个 CyH₂Q[6]外壁上的亚甲基(—CH₂)、次甲基(—CH)则通过离子-偶极和 C—H…Cl 连接 6 个游离的 [ZnCl₄]²⁻, 作用距离在 0.2739~0.3318 nm 之间(图 5c). 部分键长如表 2 所示.

从图 6b、6d 可以观察到, NH 分子通过诱导 [ZnCl₄]²⁻ 阴离子形成一维超分子链, 一维链再通过离子-偶极作用连接 CyH₂Q[6]分子, 进一步构筑三维超分子自组装体. NH 分子通过 N—H…O 与 CyH₂Q[6]分子外壁上的甲基连接, 此处属于外表面相互作用, 在不同方向产生另一个一维链(图 6a); 而链之间的相互作用由 [ZnCl₄]²⁻ 阴离子形成超分子层(图 6c、6e); 这些弱相互作用均属于 CyH₂Q[6]端口相互作用和 CyH₂Q[6]外表面相互作用, 从而促使超分子框架的形成(图 6f).

3 结论

本工作使用 CyH₂Q[6]和 NH 以 [CdCl₄]²⁻ 为结构导向剂构建了超分子框架, 并进行了单晶 X-射线衍射分析.

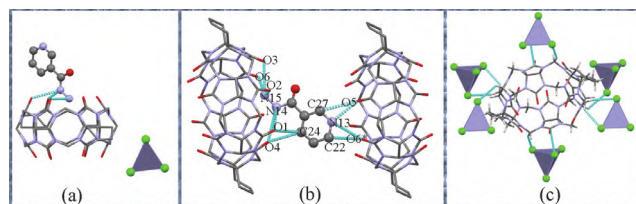


图5 配合物的晶体图: (a, b) 配合物的不对称单元; (c) CyH₂Q[6]与周围 [ZnCl₄]²⁻ 的弱相互作用

Figure 5 Crystal structure of the complex: (a, b) asymmetric unit of the complex; (c) the weak interactions of CyH₂Q[6] with [ZnCl₄]²⁻

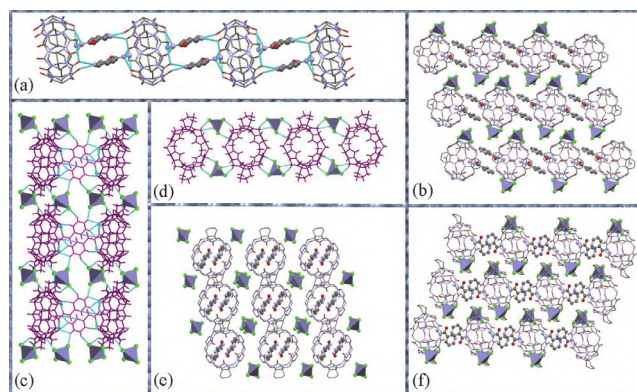


图6 配合物堆积图: (a) NH 与 CyH₂Q[6]超分子链; (b, e, f) 配合物的超分子骨架; (c) 超分子层; (d) [ZnCl₄]²⁻ 与 CyH₂Q[6]超分子链

Figure 6 Packing diagram of the complex: (a) supramolecular chain of CyH₂Q[6] with NH; (b, e, f) supramolecular framework of the complex; (c) supramolecular layer; (d) supramolecular chain of CyH₂Q[6] with [ZnCl₄]²⁻

表2 NH@CyH₂Q[6]主要的键长(nm)和键角数据(°)

Table 2 Data of main bond lengths (nm) and bond angles (°) of NH@CyH₂Q[6]

NH@CyH ₂ Q[6]			
Bond	Length/nm	Bond	Length/nm
N15—O3	0.2841	N13—O5	0.2680
N15—O6	0.2925	N13—O6	0.3009
N15—O2	0.2927	C22—O6	0.2953
N14—O1	0.2990	C10—Cl1	0.3318
N14—O4	0.3048	H13A—Cl6	0.2739
C24—O1	0.3095	H5—Cl3	0.2950
C24—O4	0.3035	H1A—Cl3	0.2782
C27—O5	0.3162	H1B—Cl2	0.2924

同时, 利用 ¹H NMR、ITC 和 MALDI-TOF 研究 NH 分子与瓜环在水溶液中的主客体结合作用. 实验结果表明, 无论是在固态还是在水溶液中, NH 都位于 CyH₂Q[6]端口羰基之外, 形成了一个外表面配合物. 这种超分子框架的构建应归因于端口相互作用(包括氢键、离子-偶极子、N—H…O 和 C—H… π 相互作用)、外表面相互作用(C—H…Cl 相互作用)以及许多其它弱相互作用的结合, 这种超分子框架可能在各种功能材料中有潜在的应用前景.

4 实验部分

4.1 实验仪器与试剂

试剂：自制对称二环己基取代六元瓜环 (CyH₂Q[6]), ZnCl₂, 3-吡啶甲酰肼(NH), 盐酸等均为分析纯, 蒸馏水。

仪器：分析天平, Bruker Smart ApexII X-射线单晶衍射仪(德国 Bruker 公司), Varianinova-400M 核磁共振仪, Agilent6545 Q-TOF 质谱仪。

4.2 ¹H NMR 的测定

先用 D₂O 将 3-吡啶甲酰肼配制成 2.0 × 10⁻³ ~ 2.5 × 10⁻³ mmol·L⁻¹ 的溶液, 滴加到 0.5 ~ 0.7 g 瓜环配成的 D₂O 溶液中, 20 °C 下于 Varianinova-400M 核磁共振仪上进行测试。

4.3 ITC 测试

用等温滴定量热仪(英国马尔文仪器有限公司)测定热力学参数和结合常数(K_a)。先用二次水分别制备客体为 3.0 × 10⁻³ mol·L⁻¹ 的溶液和 CyH₂Q[6] 为 1.0 × 10⁻⁴ mol·L⁻¹ 的溶液, 然后用客体溶液在 25 °C, 每滴客体溶液的体积 8 μL, 时间间隔 300 s, 搅拌速度 250 r·min⁻¹ 下滴定 CyH₂Q[6], 确定体系的热力学系数。

4.4 质谱测试

将样品在二次水中配制成 10 μg·mL⁻¹ 的溶液, 使用 0.22 μm 的水系滤膜过滤纸过滤到色谱进样瓶中, 在 Agilent6545 Q-TOF 型质谱仪上测试质谱数据。

4.5 NH@CyH₂Q[6]的合成

取 15 mg 的 CyH₂Q[6]于烧杯中, 加入 10 mL 稀盐酸 (6 mol·L⁻¹), 使 CyH₂Q[6]溶解, 然后取一定比例的 3-吡啶甲酰肼并加入少量的诱导剂 ZnCl₂ 于 3 mL 蒸馏水中, 加热使其溶解, 将该溶液倒入 CyH₂Q[6]溶液中, 溶液在 30 °C 水浴下加热搅拌 10 min, 冷却至室温并静置。3 周后有适于晶体结构测定的无色单晶析出, 产率为 45.2%。

4.6 晶体测试

选取无裂痕透亮大小合适可测的配合物晶体 (CyH₂Q[6]/Zn²⁺/NH), 用凡士林固定在玻璃丝上, 并装在 Bruker Smart ApexII X-射线单晶衍射仪上采集衍射数据。采用 Mo 靶, Mo 的激发电压为 20 kV, 波长 λ(MoKα)=0.071073 nm。采用 SHELXT-97 程序直接法进行结构解析^[28-29], 以及 SHELXL-97 程序全矩阵最小二乘法进行数据精修, 使用 PLATON 程序的 SQUEEZE 对晶体进行去除部分溶剂分子的处理^[30-31], CCDC: 2115417, 主要晶体结构参数参见表 3。

表 3 配合物的晶体结构数据

Table 3 Data of crystal structure of the complex

NH@CYH ₂ Q[6]			
Empirical formula	C ₅₆ H ₆₆ Zn ₂ Cl ₈ N ₃₀ O ₁₄	Formula weight	1797.72
Crystal system	Triclinic	Space group	P-1
a/nm	1.2304(3)	b/nm	1.3677(3)
c/nm	1.3896(4)	α/(°)	71.692(9)
β/(°)	76.013(7)	γ/(°)	67.789(7)
V/nm ³	2.0352(9)	Z	1
D _{calcd} /(g·cm ⁻³)	1.467	T/K	298
μ/mm ⁻¹	0.927	Parameters	525
R _{int}	0.0994	R[I > 2σ(I)] ^a	0.1458
wR[I > 2σ(I)] ^b	0.3933	R (all data)	0.2284
wR (all data)	0.4437	GOF on F ²	1.352

^a Conventional R on F_{hkl}: Σ||F_o|-|F_c||/Σ|F_o|. ^b Weighted R on |F_{hkl}|²: Σ[w(F_o²-F_c²)]/Σ[w(F_o²)]^{1/2}.

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