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Article

A Straightforward Strategy for Constructing Zirconium Metallocavitands

Shunfu Du, Xuying Yu, Guoliang Liu, Mi Zhou, EI-Sayed M. El-Sayed, Zhanfeng Ju, Kongzhao Su, and Daqiang Yuan*



ABSTRACT: Metallocavitands (MCs), a new burgeoning class of functional multimetallic molecules with specific cavities, are considered as promising materials in many fields. However, designing and constructing metallocavitands with compatibility and tunability from simple ligands is highly challenging. In this work, a series of Zr-based MCs with three distinct structural types have been prepared based on in situ generated trinuclear zirconocene (Cp₃Zr₃) secondary building blocks (SBBs) and Vshaped dicarboxylic linkers. First, a novel window-shaped Zr-based MC, namely **ZrMC-1**, has been constructed based on four Cp₃Zr₃



SBBs and six simple isophthalate linkers. Its window size and environment could be easily modified by different functional groups, including nitro $(-NO_2)$ and amino $(-NH_2)$. Interestingly, the amino-functionalized one, **ZrMC-1-NH**₂, can serve as a robust heterogeneous cascade catalyst to effectively catalyze the one-pot tandem deacetalization—Knoevenagel condensation reactions. Second, with the introduction of a sulfonic $(-SO_3H)$ group, an unprecedented bowel-like Zr-based MC, namely **ZrMC-2**, comprising three Cp_3Zr_3 SBBs and four 5-sulfoisophthalate ligands, has been obtained. Unexpectedly, one sulfonic group of the ligand coordinates to the Cp_3Zr_3 SBB, forming the base of **ZrMC-2**. Finally, an unexpected zigzag-shaped MC denoted as **ZrMC-3** has been prepared by using 2,5-thiophenedicarboxylic acids, featuring a larger bend angle than that of the isophthalate-type one. Specifically, **ZrMC-3** contains two Zr-based prisms with three Cp_3Zr_3 SBBs and four 2,5-thiophenedicarboxylate linkers; the bottoms of these two prisms are bridged by another 2,5-thiophenedicarboxylate linker. These results highly suggest that Cp_3Zr_3 can be an excellent SBB to construct MCs with fascinating architectures and properties by merely varying the organic linkers.

1. INTRODUCTION

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Metallocavitands (MCs), an emerging class of functional cavernous compounds, have attracted considerable interest in the past decades due to their structural beauty and their promising applications in chemical sensing, separation, hostguest chemistry, molecular reactors, and so on.¹⁻⁴ Varieties of MCs based on different metal ions/clusters and organic linkers have been well developed.⁵⁻⁹ These MCs can be specifically divided into six categories based on either a macrocycletemplating or self-assembly strategy, including flexible macrocycle-templated, Schiff base macrocycle-templated, noble metal N-donor assembled, paddlewheel, miscellaneous metallacrown, and organometallic half-sandwich MCs.¹ In particular, the organometallic half-sandwich MCs with distinct structural characteristics, in which metal centers were blocked by cyclopentadienyl (Cp), pentamethylcyclo-pentadienyl (Cp^{*}), or arene (C_nH_m) ligands,^{10–12} are amenable to form discrete structures. To date, several organometallic half-sandwich MCs, assembled from Ru^{II}-C_nH_n, Rh^{III}-Cp*, Ir^{III}-Cp*, Zr^{IV-}Cp, and Ta^V-Cp* half-sandwich complexes, have been reported.¹³⁻¹⁷ However, such MCs require a tightly designed ligand with high compatibility. Therefore, it is highly desirable

to construct stable organometallic half-sandwich MCs from simple and readily accessible ligands for their practical applications.

It has been found that the sandwich complex, bis-(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂), can be slowly hydrolyzed in water and carboxylic acid simultaneously, forming near- C_3 -symmetric Cp₃Zr₃ clusters, whose one side is blocked by three Cp ligands, and the other side is coordinated by three carboxylate ligands.¹⁸ With this in mind, our group initially reported that Cp₃Zr₃ clusters could be excellent secondary building blocks (SBBs) in the construction of Zrbased tetrahedrons by using rigid linear dicarboxylate and trigonal tricarboxylate linkers.¹⁹ Notably, we have also corroborated that these Zr-based tetrahedrons show excellent stability in neutral, acidic, and even weak basic aqueous

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environments.²⁰ Since then, numerous Zr-based polyhedrons, including tetrahedron, hexahedron, lantern-shaped, and cigar-like cages built from Cp_3Zr_3 SBBs, have been developed (Scheme 1a)²¹⁻²⁶ and exhibited potential applications in many

Scheme 1. (a) Molecular Topology of the Reported Coordination Polyhedra, Including Tetrahedron, Lantern, Cigar, And Hexahedron, Based on Cp₃Zr₃ SBBs; (b) Molecular Topology of Zr-Based MCs, Including Window-Shaped, Bowel-Like, And Zigzag-Shaped Structures, in This Work^a



^aColor code: Cp₃Zr₃ SBBs, red; linker, blue; sullfonate, yellow.

fields, such as gas storage, catalysis, guest encapsulation, energy storage, and so on.^{27–35} However, the reported types of Cp_3Zr_3 -based coordination complexes are limited to the above-mentioned polyhedrons based on ditopic and tritopic ligands. Thus, there is much room to create Cp_3Zr_3 -based complexes with different architectures by choosing ligands with different shapes.

In this work, five novel Zr-based MCs with three distinct structural types, including three window-shaped, bowel-like, and zigzag-shaped structures, have been developed based on in situ generated Cp_3Zr_3 SBBs and V-shaped dicarboxylate linkers (Scheme 1b). To the best of our knowledge, most of the reported Zr-based MCs are bowel-shaped and constructed by using one Cp_3Zr_3 SBB as a base and three monocarboxylate ligands as a wall.^{36,37} Besides, there is only one triangularshaped Zr-based MC based on the geometrically frustrated tetramethyl terephthalate,³² which prevents the formation of the previously reported tetrahedral structure. However, the systematic preparation, characterization, and applications of Cp_3Zr_3 -based MCs by using linkers with specific shapes have not been reported.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. All solvents, including N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), carbon tetrachloride (CCl₄), methanol (MeOH), reagent Cp₂ZrCl₂, isophthalic acid (H2BDC), 5-nitroisophthalic acid (H2BDC-NO2), 5aminoisophthalic acid (H₂BDC-NH₂), sodium 3,5-dicarboxybenzenesulfonate (H2BDC-SO3Na), and thiophene-2,5-dicarboxylic acid (H₂TDB), were provided by commercial sources and used without further purification. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO elemental analyzer. Fourier transform infrared (FT-IR) spectra of the samples were recorded on KBr pellets in the 4000-400 cm⁻¹ range using a PerkinElmer Spectrum One FT-IR spectrometer. The powder X-ray diffraction (PXRD) patterns are collected by a Rigaku DMAX 2500 X-ray diffractometer using Cu K α radiation ($\lambda = 0.154$ nm). All gas sorption isotherm measurements were performed by using automatic volumetric adsorption equipment (BeiShiDe 3H-2000PS1).

2.2. Synthesis. *ZrMC-1*. Excess Cp_2ZrCl_2 (0.015 g) and H_2BDC (0.005 g) were dissolved in a mixture of 1 mL of DMF and 3 drops of distilled water, and the mixture was then heated at 45 °C for 10 h. After the mixture slowly cooled down to room temperature, colorless block crystals were obtained. IR (KBr pellet, cm⁻¹): 3350, 1609, 1550, 1456, 1408, 1274, 1072, 1018, 815, 746, 709, 615, 474. Elemental analysis (%): calculated for $ZrMC-1\cdot18DMA\cdot3H_2O$ ($Zr_{12}C_{180}N_{18}O_{61}H_{264}Cl_4$): C, 38.39; H, 5.41; N, 5.17. Found: C, 38.33; H, 5.45; N, 5.1.

*ZrMC-1-NO*₂. Excess Cp₂ZrCl₂ (0.015 g) and H₂BDC–NO₂ (0.005 g) were dissolved in a mixture of 1 mL of DMF, 1 mL of MeOH, and 3 drops of distilled water, and the mixture was then heated at 45 °C for 10 h. After the mixture slowly cooled down to room temperature, colorless block crystals were obtained. IR (KBr pellet, cm⁻¹): 3350, 1654, 1610, 1566, 1465, 1388, 1348, 1082, 1016, 815, 785, 723, 711, 609, 513, 476. Elemental analysis (%): calculated for **ZrMC-1-NO**₂. 11DMF·CH₃OH·H₂O (Zr₁₂C₁₄₂N₁₇O₆₅ H₁₇₃Cl₄): C, 38.9; H, 3.9; N, 5.4. Found: C, 37.5; H, 3.9; N, 5.4.

ZrMC-1- NH_2 . Excess Cp_2ZrCl_2 (0.015 g) and H_2BDC - NH_2 (0.005 g) were dissolved in a mixture of 0.25 mL of DMA, 0.25 mL of CCl₄, and 8 drops of distilled water, and the mixture was then heated at 45 °C for 10 h. After the mixture slowly cooled down to room temperature, yellow block crystals were obtained. IR (KBr pellet,



Figure 1. Assembly strategy of ZrT-2 and ZrMC-1-X (X = NO₂, NH₂). The coordination environment of Cp₃Zr₃ SBB in ZrT-2 (a) and ZrMC-1 (b).



Figure 2. (a) Molecular structure of ZrMC-2. (b) Comparison of the coordination environment of Cp_3Zr_3 SBBs in ZrMC-2 (b, c). Color code: S, yellow. H atoms are omitted for clarity.

 $\rm cm^{-1}):$ 3350, 1606, 1546, 1462, 1400, 1020, 817, 773, 713, 617, 478. Elemental analysis (%): calculated for $\rm ZrMC-1-NH_2\cdot12DMA\cdot4CCl_4\cdot3H_2O~(Zr_{12}C_{160}N_{18}O_{55}H_{216}Cl_8):$ C, 37.9; H, 4.2; N, 4.9. Found: C, 37.32; H, 4.66; N, 4.51.

ZrMC-2. Excess Cp₂ZrCl₂ (0.015 g) and H₂BDC–SO₃Na (0.005 g) were dissolved in 1 mL of CH₃CN and 3 drops of distilled water, and the mixture was then heated at 65 °C for 10 h. After the mixture slowly cooled down to room temperature, colorless block crystals were obtained. IR (KBr pellet, cm⁻¹): 3350, 1608, 1556, 1452, 1382, 1127, 1190, 1113, 1045, 1018, 997, 819, 771, 713, 623, 480. ZrMC-2: CH₃CN·NaCl·50H₂O (Zr₁₈C₁₅₆NO₁₃₀H₂₀₆ClNaS₈): C, 30.56; H, 3.38; N, 0.23. Found: C, 30.57; H, 3.42; N, <0.3.

ZrMC-3. Excess Cp_2ZrCl_2 (0.015 g) and thiophene-2,5-dicarboxylic acid (0.005 g) were dissolved in 1 mL of MeOH and 3 drops of distilled water, and the mixture was then heated at 45 °C for 10 h. After the mixture slowly cooled down to room temperature, colorless block crystals were obtained. IR (KBr pellet, cm⁻¹): 3350, 1552, 1531, 1390, 1018, 817, 769, 684, 599, 515, 470. **ZrMC-3**·48H₂O (Zr₁₈C₁₄₄O₁₀₈H₂₂₂S₉Cl₆): C, 29.68; H, 3.84; N, 0. Found: C, 29.15; H, 3.30; N, <0.3.

Deacetalization–Knoevenagel Condensation Reactions. The catalytic reactions were performed with 1 mmol of each substrate in $CDCl_3$ (2 mL), and the catalyst (1.2 mmol %) was then added, followed by continuous stirring at 50 °C for 48 h. To follow up the tandem reaction process, ¹H NMR spectroscopy was utilized, and the yields were calculated by the integration of benzylic protons at the end of the reaction.

3. RESULTS AND DISCUSSION

The reaction between Cp_2ZrCl_2 and H_2BDC in a mixture of DMF and H₂O resulted in the isolation of colorless crystals with a formula of { $[Cp_3Zr_3(\mu_3-O)(\mu_2-OH)_3]_4(BDC)_6$ }4Cl·nS (ZrMC-1, S = guest solvent molecule). Single-crystal X-ray diffraction analysis revealed that ZrMC-1 crystallizes in the space group $P\overline{1}$, featuring a cationic window-shaped container topology (Figure 1b), whose charge is balanced by four Clcounteranions. In this structure, four approximately vertical benzene rings of the BDC act as the wall, and two benzene rings function as the bottom of MC. The window size of **ZrMC-1** is about 9.3×9.9 Å², and the optimized intrinsic void diameter and void volume of this MC are 6.65 and 153.76 Å³, respectively. Although both ZrMC-1 and the classical Zr-based tetrahedron, ZrT-2, are composed of four trinuclear Cp₃Zr₃ SBBs and six ligands, their structures are completely different (Figure 1). Notably, in response to using lower C_2 -symmetric V-shaped BDC compared to C3-symmetric 1,3,5-benzenetricarboxylic acid (H₃BTC), a reduction in the symmetry of Cp₃Zr₃ SBBs was realized. After careful analysis and comparison of these two structures, it was found that, in the ZrT-2 structure, the neighboring Zr centers of Cp₃Zr₃ SBB are

in the same coordination environment with three BTC linkers with the same orientation (Figure 1a); whereas in ZrMC-1, two BDC ligands are in the same orientation, and the other is in the opposite orientation (Figure 1b). In other words, the carboxylate-bridged Cp₃Zr₃ SBBs in ZrT-2 are symmetric, while those in ZrMC-1 are asymmetric. This reveals that symmetry breaking in carboxylate-bridged Cp₃Zr₃ SBB could be an effective strategy to develop low-symmetric Zr-based MCs.

To validate this strategy, H2BDC-NO2 and H2BDC-NH2 were used to replace the mBDC in ZrMC-1, which unsurprisingly resulted in two new window-shaped Zr-based MCs, denoted as ZrMC-1-NO2 and ZrMC-1-NH2, respectively. Notably, these two substituents in the 5-position of the isophthalic acid do not affect their main structures relative to ZrMC-1 but influence window sizes, environments, and cavity volumes. The introduction of substituent causes the four benzene rings of the wall to turn inward, leading to a reduction in window size. Specifically, the window size and cavity volumes of ZrMC-1-NO2 and ZrMC-1-NH2 are reduced to 5.7×9.7 Å² and 4.7×8.8 Å², and 117.7 Å³ and 83.53 Å³, respectively. Moreover, both electron-acceptor -NO2 and electron-donor -NH2 groups located at the outer edge and bottom of MCs may serve as additional binding sites to substrates with different electrical properties.

In the course of continuous exploration, we further introduced the H2BDC-SO3Na with sulfonate group in the 5-position of the isophthalic acid to determine how this group affects the resulting structure. Unexpectedly, an unprecedented bowel-like Zr-based MC with a formula of {[$Cp_3Zr_3(\mu_3-O)(\mu_2 OH_{3}_{3}(BDC-SO_{3})_{4}$ Cl·Na·nS, abbreviated as ZrMC-2, built from three Cp₃Zr₃ SBBs and four BDC-SO₃H linkers, has been produced (Figure 2a). In the structure of ZrMC-2, three BDC-SO₃ ligands are connected with three Cp₃Zr₃ SBBs, forming a triangular prism core. Interestingly, it has been found that the other deprotonated BDC-SO₃ ligand functions as a tridentate ligand to occupy the remaining uncoordinated sites of the three Cp₃Zr₃ SBBs. Since only one sulfonate on the ligand is coordinated, there are two distinct Cp₃Zr₃ SBBs in ZrMC-2. Specifically, two Cp₃Zr₃ SBBs in this structure are all coordinated by three carboxylates (Figure 2c), while the remaining one is coordinated by two carboxylates and one sulfonate (Figure 2b). To our knowledge, this is the first Cp₃Zr₃-based coordination compound in which sulfonate is involved in coordination. This implies that new Cp₃Zr₃-based coordination complexes can be built by using other heterotopic ligands with both sulfonate and carboxylate sites, disulfonate,



Figure 3. (a) Structure of ZrMC-3. (b, c) Coordination environment of Cp₃Zr₃ SBBs in this structure. H atoms are omitted for clarity.

or trisulfonate ligands. Compared with ZrMC-1, the coordination of sulfonate forces the structure to become more compact. The optimized intrinsic void diameter and void volume of this MC is 5.11 and 69.7 Å³, respectively.

Regarding the diversity and adjustability of Cp₃Zr₃ SBB in ZrMC-1 and ZrMC-2, H₂TDB, another type of V-shaped ligand but with a larger bend angle than that of isophthalatetype, is used, affording an unexpected zigzag-shaped MC, **ZrMC-3**, with a formula of $\{[Cp_3Zr_3(\mu_3-O)(\mu_2 OH_{3}_{6}(TDB)_{9}$ ·6Cl·nS (Figure 3a). This structure contains two parallel bowl-like prisms, whose bottoms are linked by one TDB ligand. It should be noted that each bowl-like prism is interconnected by three Cp₃Zr₃ SBBs and three TDB linkers, which are similar to ZrMC-2. However, the remaining Zr coordination sites at the bottom of this prism are sealed by three carboxylates from two different TDB ligands, which are very different from those in ZrMC-2. With a closer look at the structure of ZrMC-3, it was found that while all Cp₃Zr₃ SBBs are coordinated by carboxylate groups from TDB ligands, they can be divided into two different types based on their opening difference, resulting from the difference in dihedral angles between the TDB square and Zr₃ triangle face. Specifically, the dihedral angles in two Cp₃Zr₃ SBBs bridged by TDB ligands are about 79.043°, 82.001°, and 53.068°, respectively (Figures 3c and S1a), while those in type II are 49.010°, 69.938°, and 67.261°, respectively (Figures 3b and S1b).

Unfortunately, the nitrogen gas uptakes for the ZrMC-1 series and ZrMC-3 are negligible. This might be ascribed to the fact that they are hydrogen-bonded frameworks, which are built from Cl⁻ anions and μ_2 -OH groups of the cationic Zrbased MCs. Such hydrogen bonding interaction is weak, resulting in their framework collapse during activation as determined by PXRD (Figures S2-S4). In contrast, ZrMC-2 maintains its framework intact after activation (Figure S3b), showing better N₂ adsorption performance and demonstrating a fully reversible type I isotherm with a Brunauer-Emmett-Teller (BET) surface area of 249 m² g⁻¹ (Figure 4). The porosity and desirable aperture of ZrMC-2 encouraged us to investigate its absorption capacities for other gas further. As shown in Figures S5 and S6, they demonstrated that ZrMC-2 could adsorb significant amounts of CO_2 (34.84 cm³ g⁻¹ under 293 K), H₂ (68.23 cm³ g⁻¹ under 77 K), olefins (31.46 and 40.36 cm³ g⁻¹ for C_2H_4 and C_3H_6 under 293 K, respectively), and alkynes (45.70 and 58.90 cm³ g⁻¹ for C_2H_2 and C_3H_4 under 293 K, respectively).



Figure 4. N₂ adsorption at 77 K for ZrMC-2.

In recent years, there has been a growing interest in the design and synthesis of bifunctional heterogeneous cascade catalysts with both Lewis acid and basic sites to effectively catalyze the tandem one-pot deacetalization-Knoevenagel reaction, because of less waste, lower cost, and fewer purification steps.³⁸⁻⁴² Notably, the deacetalization-Knoevenagel condensation reaction comprises two catalytic steps. In the first step, deacetalization of dimethoxymethylbenzene is carried out to generate benzaldehyde by acid sites, while, in the second step, Knoevenagel reaction between benzaldehyde and malononitrile is performed to obtain benzylidene malononitrile by base sites. With these in mind, we believed that ZrMC-1- NH_2 , combining acidic Zr^{4+} sites and basic $-NH_2$ sites, could be a suitable catalyst to the aforementioned reaction. In order to prove this point, ZrMC-1 and ZrMC-1-NO₂ were used to explore their catalytic activity for tandem deacetalization-Knoevenagel condensation reaction. As shown in Table 1, the yield of the corresponding benzylidenemalononitrile product catalyzed by ZrMC-1-NH₂ reaches 93.2%. This finding is much higher than yields of ZrMC-1 (21.3%) and ZrMC-1- NO_2 (25.4%) when benzaldehyde dimethyl acetal is utilized as a substrate. Notably, this tandem catalytic performance based on 1-(dimethoxymethyl)-4-methoxybenzene substrate displayed the same trend by the three MC catalysts described above. These results highly demonstrate that the existence of

Table 1. Reaction of Deacetalization-Knoevenagel Condensation

Reactant	Entry	Yield (%)
R = H	No catalyst	trace
	ZrMC-1	21.9
	ZrMC-1-NO ₂	25.4
	ZrMC-1-NH ₂	93.2
$R = OCH_3$	No catalyst	trace
	ZrMC-1	29.1
	ZrMC-1-NO ₂	28.6
	ZrMC-1-NH ₂	97.8

both Lewis acid and base catalyst sites is necessary for the promotion of the tandem deacetalization-Knoevenagel condensation reaction.

4. CONCLUSIONS

In conclusion, we have constructed three types of Zr-based MCs, including three window-shaped, bowel-like, and zigzagshaped structures, by using simple V-shaped dicarboxylic ligands and Cp₃Zr₃ SBBs. Specifically, the window-shaped ZrMC-1 provides an excellent platform for window environment modification in MCs by introducing functional groups such as $-NO_{21}$, $-NH_{21}$, and so on. The respective MCs, based on these groups, especially ZrMC-1-NH₂, showed improved performance in practical applications, such as a tandem deacetalization-Knoevenagel condensation reaction. To the best of our knowledge, bowel-like ZrMC-2 presents the first Cp₃Zr₃-based coordination compound in which sulfonate is involved in coordination. Moreover, the supramolecular framework of ZrMC-2 is retained after vacuum activation and can therefore adsorb considerable amounts of N2 as well as other gases. ZrMC-3 has a rare zigzag-shaped structure, which bridges two prism-shaped MCs parallel to each other through TDB linkers. This example prefigures that Zr-based MCs could be promising supramolecular building blocks to construct hierarchical coordination nanostructures. All the aforementioned results indicate that Cp₃Zr₃ SBBs have great potential in the construction of MCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge athttps://pubs.acs.org/doi/10.1021/acs.cgd.0c01561.

Crystallographic data and additional figures (PDF)

Accession Codes

CCDC 2027347–2027351 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Daqiang Yuan – Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; ⊙ orcid.org/0000-0003-4627-072X; Email: ydq@fjirsm.ac.cn

Authors

- Shunfu Du College of Chemistry, Fuzhou University, Fuzhou 350108, China; Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China
- Xuying Yu College of Chemistry, Fuzhou University, Fuzhou 350108, China; Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China
- **Guoliang Liu** Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; o orcid.org/0000-0001-7418-5659
- Mi Zhou Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; © orcid.org/0000-0002-0752-1488
- EI-Sayed M. El-Sayed Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; University of the Chinese Academy of Sciences, Beijing, P. R. China; Chemical Refining Laboratory, Refining Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt
- Zhanfeng Ju Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; ⊙ orcid.org/0000-0002-5081-4032
- Kongzhao Su Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 50002, China; © orcid.org/0000-0001-9557-6982

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.0c01561

Notes

The authors declare no competing financial interest.

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