Two-Dimensional Supramolecular Nanoarchitectures of Polypseudorotaxanes Based on Cucurbit[8]uril for Highly Efficient Electrochemical Nitrogen Reduction

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ABSTRACT: Supramolecular assemblies with two-dimensional (2D) topology have drawn great attraction in the development of functional materials through a modular approach. Herein, a novel organic 2D polypseudorotaxane has been constructed on the basis of cucurbit[8]uril (CB[8]) through host-stabilized charge-transfer (CT) interactions of naphthol-modified porphyrin (TPP-Np) and viologen derivatives (DMV). Interestingly, the 2D polypseudorotaxanes could serve as a platform for preparation of ultrathin Pt nanowires with favorable and homogeneous dispersion through a simple self-metalized process, leading to the formation of supramolecular hybrid materials (PtNPs@CB[8]/DMV/TPP-Np). Surprisingly, the PtNPs@CB[8]/DMV/TPP-Np could be applied to efficient electrochemical nitrogen reduction reaction, with a \( \text{NH}_3 \) yield rate up to 23.2 \( \text{µmol} \cdot \text{h}^{-1} \cdot \text{mg}_{\text{Pt}}^{-1} \) at \(-0.2 \text{ V} \) versus a reversible hydrogen electrode under ambient conditions. Notably, our results not only demonstrate the feasible construction of 2D polypseudorotaxanes but also deepen the understanding of structure–activity relationships in supramolecular nanoarchitectures, as well as pave an effective and low-energy input strategy for artificial nitrogen fixation.

INTRODUCTION

Two-dimensional (2D) nanoarchitectures have drawn a great deal of attention in nanotechnology and materials science because of their fascinating physical and chemical properties as well as potential application in catalysis, electronics, sensing, separation, and other related fields.\(^1\)–\(^3\) To date, numerous efforts have been devoted to the formation and development of 2D nanoarchitectures. Among these various structures, organic 2D nanomaterials constructed through noncovalent interactions or supramolecular assembly were considered remarkable because of their flexible design routes, potential additional functionality, and highly modular nature.\(^4\)–\(^7\) Significantly, taking advantage of the host–guest interactions for the formation of stable (pseudo)rotaxanes or poly(pseudo)rotaxanes, a series of 2D nanoarchitectures with a single-layer arrangement and high structural regularity were constructed. For instance, Li and Zhao reported remarkable results using mild conditions for the construction of 2D supramolecular organic frameworks (SOFs) in solution.\(^8\) Moreover, Feng et al. utilized interface synthesis to obtain the large-area freestanding monolayers by host–guest enhanced donor–acceptor interactions.\(^9\) In addition, our group designed photocontrolled and interconvertible 2D/1D supramolecular nanostructures with different fluorescence enhancement effects for Nile Red.\(^10\) Recently, Scherman and Barrio reported platelet-like aggregates and 2D nanofibers undergo a stepwise self-assembly process.\(^11\) Although the design and construct of 2D supramolecular nanoarchitectures of (pseudo)rotaxanes or poly(pseudo)rotaxanes have been explored using diverse methods, their potential as reactors has rarely been studied, despite the fact that the 2D nanostructures have highly accessible active sites, homogeneous features, and large surface areas, which can provide a well-defined platform for substance formation and exchange.

On the other hand, integrating building blocks with special features into 2D nanoarchitectures to realize the generation of functional materials is becoming of widespread interest and general concern. In artificial systems, supramolecular assembly strategies using various noncovalent interactions provide the possibility to achieve optimal performance from simple elements under mild conditions, which is particularly important for the discussion of structure–activity relationships.\(^12\) Porphyrin and its derivatives with unique physical, chemical, biological, and catalytic properties have attracted growing interest in the fields of nanotechnology and materials...
ions and ultimately give TPP-Np in yields of 60%.21 Another nitrogen environment with 2-(2-bromoethoxy)-naphthalene. starting with 1,5-naphthalenediamine, which was reacted with shown in the Supporting Information. Characteristics for the solid. The detailed synthesis route of TPP-Np and DMV is fl to form a 1:1:1 ternary complex with high association and an electron-rich guest by host-stabilized CT interactions. cucurbit[8]uril, possessing a large cavity, is capable of significantly shifting upfield by addition of 2 equiv of CB[8]. This phenomenon provided evidence for the formation of a 2:1 inclusion complex between CB[8] and DMV, in which the viologen units were located in the cavity of the host and influenced by the shielding effect of CB[8]. The Job’s plot was employed to find the binding stoichiometry of DMV and CB[8]. The top point of the curve appeared at the molar fraction $X_{\text{guest}} = 0.33$, indicating the 2:1 binding stoichiometry between CB[8] and DMV (Figure S13), which corresponds to the result of $^1$H NMR experiments. Furthermore, the association constant ($K_a$) of DMV and CB[8] was calculated as $K_a = 2.59 \times 10^4 \text{ M}^{-1}$, $K_2 = 2.12 \times 10^4 \text{ M}^{-1}$ according to the result of UV/vis spectroscopic titrations (Figure S14). $^1$H NMR experiments were utilized to collect information about the polypseudorotaxanes. With the addition of TPP-Np to a solution of CB[8]/DMV (Figure S12c), the signals of viologen units of DMV were further shifted upfield and broadened, meaning that a higher-level supramolecular assembly was formed. However, when the same operation was handled in D$_2$O solution of DMV alone, neither chemical shifts of the protons on DMV nor TPP-Np displayed, indicating that there was no obvious interaction between TPP-Np and DMV in the absence of CB[8] (Figure S15). According to the above experiment results, we believe that CB[8] can be employed as the module of the “molecular handcuff” to combine the two guest molecules together to form network-like polypseudorotaxanes.24

More detailed information on the polypseudorotaxanes was investigated by spectroscopy experiments. As shown in Figure 1, a remarkable intensity decrease was observed at peaks at 219 and 267 nm in the UV/vis spectra of CB[8]/DMV/TPP-Np compared to that of the individual components, which are attributed to the naphthalene units and viologen units, respectively. Moreover, there was an increase in the range of 450–700 nm, exhibiting the formation of the proposed polypseudorotaxanes via host-stabilized CT interactions. Fluorescence spectra provided further insight into the interactions between each part of the building blocks in the supramolecular nanoarchitectures. The peaks centered at 680 and 720 nm displayed a slight decline with the formation of polypseudorotaxanes, also suggesting cucurbit[8]uril is capable of drawing close the two guest molecules so that photoinduced electron transfer arises from the porphyrin moieties of TPP-Np to the viologen units of DMV (Figure S16).25

Dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM) were subsequently utilized to identify the size and morphology of the 2D polypseudorotaxanes. The data from the DLS experiments indicate that the large size of CB[8]/DMV/TPP-Np formed indeed via CB[8]-mediated host–guest complexations, whereas there were no detectable signals in the solution of TPP-Np or CB[8]/DMV (Figures S17 and S18). TEM is an
Figure 1. UV/vis spectra of TPP-Np ([TPP-Np] = 5 × 10^{-5} M, blank line), DMV ([DMV] = 1 × 10^{-4} M, red line), CB[8]/DMV/TPP-Np (CB[8]:DMV:TPP-Np = 2:1:0.5, [TPP-Np] = 5 × 10^{-5} M, blue line) and TPP-Np + DMV (TPP-Np:DMV = 0.5:1, [TPP-Np] = 5 × 10^{-5} M, purple line) in aqueous solution (light path = 1 mm).

A simple and efficacious method to intuitively characterize the morphology of the supramolecular assembly. As expected, the TEM images of CB[8]/DMV/TPP-Np indicate the formation of filmlike structures with some wrinkles, on account of the flexible structure between porphyrin and naphthalene units in TPP-Np (Figure 2A). The thickness of the nanomaterial is a very important parameter to evaluate the 2D nanostructures. Therefore, the as-prepared solution of CB[8]/DMV/TPP-Np was dropped onto a mica wafer and then investigated by tapping-mode AFM. As can be seen in Figure 2C, the graphene-like nanostructure of CB[8]/DMV/TPP-Np was observed by AFM. Cross-section analysis indicated that the height of the 2D supramolecular nanoarchitectures was symmetrical and uniform. The height of CB[8]/DMV/TPP-Np was measured to be ∼2.2 nm at different positions, approaching the outer diameter of CB[8], strongly suggesting that the formation of single-layer 2D nanostructures resulted from a cross-link by CB[8].26 Meanwhile, the CB[8] macrocycles effectively prevent the interlayer packing, leading to the 2D polysuperoxidrotaxanes remaining as single-layer films with a lateral size. Moreover, for characterization of the fine microstructure arrangement inside the CB[8]/DMV/TPP-Np, grazing incidence small-angle X-ray diffraction (GI-SAXS) experiments were carried out. A sharp scattering peak corresponding to a d spacing of 4.1 nm is observed in Figure S19, which is assigned to the spacing of the quadrangular pores in the molecular model of the 2D polysuperoxidrotaxanes, which is consistent with the proposed supramolecular assembly mode (Scheme 1).

Preparation and Characterization of PtNPs@CB[8]/DMV/TPP-Np. Size-controlled and confined growth of such ultrafine metal nanoparticles have attracted extensive research interests because of excellent properties for applications in heterogeneous catalysis and electrocatalysis.27,28 The porphyrin-based and well-defined 2D supramolecular nanoarchitectures have potential in the preparation of ultrafine Pt nanoparticles through a succession of light harvesting and photochemical cycles (Scheme S3).29,30 First of all, platinum(II) solution was prepared by dissolving K2PtCl4 in ultrapure water under ambient conditions and was aged at least 24 h in the dark. The photoinduced reduction of platinum salts by CB[8]/DMV/TPP-Np was accomplished in the case of ascorbic acid as an electron donor under visible-light irradiation. Scanning electron microscope (SEM) images and TEM images show that the Pt nanoparticles were generated with uniform size (approximately 3 nm) and fine dispersion (Figure 3 and Figure S20). The high-resolution TEM image and selected area electron diffraction pattern exhibit the polycrystalline nature and characteristic diffraction rings of Pt nanoparticles. TEM-EDS also illustrated that Pt nanoparticles were prepared successfully (Figure S21). In addition, the Pt content in PtNPs@CB[8]/DMV/TPP-Np was estimated to be about 4.17 wt % based on ICP-AES measurement, which is consistent with the theoretical amount. As shown in FTIR spectra (Figure S22), the absorption at 3368 cm⁻¹ assigned to the N-H stretching vibration in porphyrin units was obviously attenuated; meanwhile, the peak at 1722 cm⁻¹ corresponding to C=O of cucurbit[8]uril stretching vibration shifted to 1715 cm⁻¹, suggesting that the Pt nanoparticles were immobilized by 2D polysuperoxidrotaxanes. Furthermore, the Pt nanoparticles were characterized via X-ray photoelectron spectroscopy (XPS). The spectrum in the Pt 4f region showed peaks centered at 70.9 eV for Pt 4f7/2 and 74.2 eV for Pt 4f5/2, which could be assigned to Pt(0) (Figure S23).31 However, no Pt nanoparticles were observed in the absence of the CB[8]/DMV/TPP-Np or without light irradiation. On the another hand, the obtained Pt nanoparticles were large in size and easy to reunite in the case of TPP-Np operating alone. The above control experiments demonstrated that the photoactivity of the porphyrin and the two-dimensional configuration of the CB[8]/DMV/TPP-Np are both critical for the development of functional supramolecular nanostructures.

Electrochemical Nitrogen Reduction Performance of PtNPs@CB[8]/DMV/TPP-Np. Recently, the electrochemical nitrogen reduction reaction (NRR) to produce ammonia...
(NH₃) at atmospheric pressure and moderate temperature powered by renewable electricity has been an attractive subject of intense research. Different from the current industrial Haber-Bosch process, which produces NH₃ from N₂ and H₂,
catalyzed by iron-based catalysts under high temperature (350−550 °C) and high pressure (150−350 atm), the electrochemical NRR is considered a sustainable and promising approach for NH₃ production. Recent reports illustrated that various materials including noble metals showed favorable activity for NH₃ production. Significantly, we found that the Pt-based catalysts, which were thought to not be appropriate for NRR, could be efficient NRR catalysts. Inspired by previous results and PtNPs@(CB[8]/DMV/TPP-Np) with high-density and finely dispersed Pt nanoparticles, extensive explorations and investigations toward the catalytic reactivity of hybrid materials for electrochemical NRR were conducted. To the best of our knowledge, there was no prior work based on supramolecular nanoarchitectures for nitrogen fixation, which is challenging but potentially valuable research.

The N₂ reduction activity of PtNPs@(CB[8]/DMV/TPP-Np) was carried out at room temperature and atmospheric pressure in an H-shaped electrochemical cell, which was separated by a Nafion membrane at room temperature and atmospheric pressure. The NRR activity of the electrode was evaluated using controlled potential electrolysis with N₂-saturated electrolytes. All potentials mentioned in this work were converted as the value versus RHE unless specified otherwise. The linear sweep voltammetry (LSV) curves of PtNPs@(CB[8]/DMV/TPP-Np) exhibited different current densities in the range from 0 to −0.70 V in 0.1 M K₂SO₄ solution with Ar-saturated and N₂-saturated electrolytes, respectively (Figure S24). The current density in N₂-saturated electrolyte is higher than that in Ar-saturated electrolyte, indicating that PtNPs@(CB[8]/DMV/TPP-Np) possesses catalytic activity toward N₂ electrochemical reduction.

The NH₃ yield rate was normalized on the basis of the weight of Pt loading. The produced NH₃ and N₂H₄ were measured according to the reported indophenol blue method and Watt and Chrisp method, respectively (the corresponding calibration curves are shown in Figures S25 and S26). The production of hydrazine was below the detection limit, indicating high selectivity for NH₃ over PtNPs@(CB[8]/DMV/TPP-Np) (Figure S27). The NH₃ yield increased with more negative potential until −0.2 V, where the maximum value of the NH₃ yield was calculated as 23.2 μg h⁻¹ mgPt⁻¹, and the Faradaic efficiency displayed the highest value of 10.39% at −0.1 V and then decreased gradually, which was ascribed to the competitive selectivity toward the hydrogen evolution reaction (HER). For determination of the active sites of PtNPs@(CB[8]/DMV/TPP-Np) for electrocatalytic NRR, bare Pt nanoparticles and 2D polypseudorotaxanes as the controlled samples were also studied at the same catalytic potential (Figure S28). The results confirmed that the Pt nanoparticles with high density and fine dispersion in PtNPs@(CB[8]/DMV/TPP-Np) was an efficient catalyst for the fixation of inert N₂ molecules into valuable NH₃. As shown in Figure 4a, the NH₃ yield increased with more negative potential until −0.2 V, where the maximum value of the NH₃ yield was calculated as 23.2 μg h⁻¹ mgPt⁻¹, and the Faradaic efficiency displayed the highest value of 10.39% at −0.1 V and then decreased gradually, which was ascribed to the competitive selectivity toward the hydrogen evolution reaction (HER). For determination of the active sites of PtNPs@(CB[8]/DMV/TPP-Np) for electrocatalytic NRR, bare Pt nanoparticles and 2D polypseudorotaxanes as the controlled samples were also studied at the same catalytic potential (Figure S28). The results confirmed that the Pt nanoparticles with high density and fine dispersion in PtNPs@(CB[8]/DMV/TPP-Np) was the actual active sites for electroreduction of N₂ under ambient conditions. According to a previous report, Pt nanoparticles were stabilized by oxygen atoms at the edge of macrocycle structures of CB[8] and displayed positive charge, which can favorably chemisorb and activate the N₂. In addition, macrocycle structures of CB[8] provided locally hydrophobic sites, which is unfavorable to the HER process. As shown in Figure 4c, the findings of the electrocatalytic behaviors of PtNPs@(CB[8]/DMV/TPP-Np) was confirmed by the NMR spectra for the postelectrolysis 0.1 M K₂SO₄ electrolytes with ¹⁵N₂ and ¹⁴N₂ as the feeding gases. Also shown are the spectra for ¹⁵NH₄⁺ and ¹⁴NH₄⁺ standard samples.

**Figure 4.** Electrocatalytic NRR activity of PtNPs@(CB[8]/DMV/TPP-Np). (a) Chronoamperometric curves at various potentials in N₂-saturated 0.1 M K₂SO₄. (b) NH₃ yields (left axis) and Faradaic efficiencies (FEs) (right axis) of PtNPs@(CB[8]/DMV/TPP-Np) at each given potential in 0.1 M K₂SO₄. The error bars correspond to the standard deviations of measurements over three separately prepared samples under the same conditions. (c) Corresponding NH₃ yield rates and Faradaic efficiencies in the three electrolytes at −0.2 V. (d) ¹⁵N isotope labeling experiment. ¹H NMR spectra for the postelectrolysis 0.1 M K₂SO₄ electrolytes with ¹⁵N₂ and ¹⁴N₂ as the feeding gases. Also shown are the spectra for ¹⁵NH₄⁺ and ¹⁴NH₄⁺ standard samples.
DMV/TPP-Np) in different N2-saturated electrolytes reveal that, compared with that in neutral electrolyte (0.1 M K2SO4, pH 7) at −0.2 V, the NH3 yield and the Faradaic efficiency of PtNPs@([CB][8]/DMV/TPP-Np) were much lower than those in acid (0.05 M H2SO4, pH 1) and basic electrolytes (0.1 M KOH, pH 14), indicating that K2SO4 should be a promising electrolyte for electrochemical NRR because of its effective suppression of HER (Figure S29). Therefore, all of the following NRR experiments were conducted in 0.1 M K2SO4.

To confirm the origin of the produced NH3, we carefully examined the nitrogen source through control experiments. First, the PtNPs@([CB][8]/DMV/TPP-Np) was immersed in a N2-saturated electrolyte without applied potentials, and no NH3 was detected using the indophenol blue method. Furthermore, the control experiments were carried out in Ar-saturated electrolyte at −0.2 V in 0.1 M K2SO4 solution, and only negligible NH3 could be detected (Figure S30). And the pristine carbon paper was used as a working electrode in N2-saturated electrolyte at −0.2 V in 0.1 M K2SO4 solution; no NH3 was detected. The above experiment results suggest that the NH3 was produced from electroreduction of N2 by PtNPs@([CB][8]/DMV/TPP-Np). In addition, 15N (99 atom % 15N) isotopic labeling experiment was executed as an alternative method to verify the nitrogen source of the produced NH3 generated in our experimental conditions.36 As shown in Figure 4d, the standard samples illustrated a triplet coupling for 14NH4+ and a doublet coupling for 15NH4+ in 1H NMR spectra. When 14N2 or 15N2 was supplied as the feeding gas, 14NH4+ or 15NH4+ could be detected, respectively, suggesting that the produced NH3 originated from the electroreduction of N2 instead of decomposition of catalysts or other contaminations.

The stability of the PtNPs@([CB][8]/DMV/TPP-Np) for electrochemical NRR was assessed by consecutive recycling electrolysis at −0.2 V. Under sustained N2 gas flow, no obvious change in current density could be observed during electrolysis within 8 h. Furthermore, the catalytic activity displayed only a slight decrease in NH3 yields and Faradaic efficiencies during eight consecutive cycles (Figure 5), suggesting that PtNPs@([CB][8]/DMV/TPP-Np) maintained satisfactory electrocatalytic activity. According to the high-resolution Pt XPS spectrum, the Pt chemical state of PtNPs@([CB][8]/DMV/TPP-Np) almost remained unchanged after electrocatalysis for NRR (Figure S31). The good stability of PtNPs@([CB][8]/DMV/TPP-Np) may be attributed to the strong host–guest interactions.

For investigation of the activation of N2 on the surface of PtNPs@([CB][8]/DMV/TPP-Np) in our work, in situ time-resolved Fourier transform infrared (FTIR) spectroscopy was employed to demonstrate time-dependent changes of the N contained after injection of N2. As shown in Figure 6a, the absorption band that can be assigned to N2H4 intermediates gradually enhanced, exhibiting that N2 can be efficiently adsorbed and activated on the surface of the PtNPs@([CB][8]/DMV/TPP-Np). More concretely, absorption bands appearing in the range from 1050 to 1500 cm−1 can be assigned to H−...
N–H bending (1450 cm\(^{-1}\)), –NH\(_2\) wagging (1301 cm\(^{-1}\)), adsorbed NH\(_3\) (1200 cm\(^{-1}\)), and N–N stretching (1070 cm\(^{-1}\)) models of –N\(_2\)H\(_3\) intermediates, respectively. The in situ time-resolved FTIR data provide strong evidence that the nitrogen reduction reaction on PtNPs@(CB\([8]\)/DMV/TPP-Np) surfaces follows an associative mechanism.\(^{43}\) Specifically, the possible NRR process over PtNPs@(CB\([8]\)/DMV/TPP-Np) cathode can be reasonably deduced, as shown in Figure 6b. N\(_2\) molecules were first adsorbed on the surface, and then the adsorbed N\(_2\) reacted with the dissociated proton (H\(^+\)) from the electrolyte to form intermediates, resulting in the facilitation of dissociation of N≡N triple bonds.

### CONCLUSIONS

In conclusion, novel 2D polypseudorotaxanes have been constructed by host-stabilized charge-transfer interactions by CB\([8]\). The functional and structural features allow the 2D supramolecular nanomaterial to be used as a platform for preparation of ultrafine Pt nanoparticles, which has been proven to pave a new way for electrochemical ammonia synthesis from nitrogen under ambient conditions with high yield and favorable stability. To the best of our knowledge, this is the first construction to realize artificial nitrogen fixation through supramolecular assembly strategy. As it is convenient, facile, and effective, the modular supramolecular assembly approach exhibits great potential for designing and constructing various functional 2D nanomaterials, which could give rise to new opportunities for electrochemical nitrogen reduction reaction and lead to various other applications.

### EXPERIMENTAL SECTION

#### Preparation of PtNPs@CB\([8]\)/DMV/TPP-Np

Platinum(II) solution was prepared by dissolving K\(_2\)PtCl\(_4\) in water under ambient conditions and was aged 24 h before use; 125 μL of aqueous K\(_2\)PtCl\(_4\) (20 mM), 10 mL solution of CB\([8]\)/DMV/TPP-Np (0.05 mM of TPP-Np), and 125 μL of aqueous ascorbic acid (200 mM) were added into a glass vial together. The samples were irradiated by visible light through a 400 nm cutoff filter from a 300 W Xe lamp for 10 min.

#### Calculation of NH\(_3\) Faradaic Efficiency (FE), NH\(_3\) Yield Rate

The ammonia synthesis rate was calculated using the following equation:

\[
\nu_{\text{NH}_3} = \frac{V_{\text{NH}_3}}{m_{\text{tot}}} 
\]

FE was calculated according to the following equation:

\[
\text{FE} = \frac{3F\eta_{\text{NH}_3}}{Q} 
\]

where \(V\) is the volume of the electrolyte, \(C_{\text{NH}_3}\) is the NH\(_3\) concentration, \(t\) is the reduction reaction time, \(A\) is the geometric area of the cathode, \(F\) is the Faraday constant, \(m_{\text{tot}}\) is the loading mass of the catalyst, and \(Q\) is the quantity of applied electricity.

#### Isotope-Labeled Experiments

The \(^{14}\text{N}\) and \(^{15}\text{N}\) isotopic labeling experiments were conducted using \(^{14}\text{N}_2\) and \(^{15}\text{N}_2\) as the feeding gases (99% enrichment of \(^{15}\text{N}_2\) in \(^{15}\text{N}_2\), supplied by Beijing Yinuokai Technology Co., Ltd.). Before the test was started, labeled \(^{15}\text{N}_2\) gas was passed by alkaline solution (pH 14, KOH aqueous solution) and acid solution (pH 1, H\(_2\)SO\(_4\) aqueous solution) to remove any N contamination before purging into the electrolyte solution. Because of the high price and small volume of \(^{15}\text{N}_2\) gas bottles, we used a circulation setup in which \(^{15}\text{N}_2\) gas was continuously cycled and resupplied to the electrode surface. Before flowing of \(^{14}\text{N}_2\) gas, Ar gas was first flowed through the whole setup for 30 min to remove any \(^{15}\text{N}_2\) gas that was present in the system, and then \(^{15}\text{N}_2\) was flowed for 15 min. The NRR experiment was conducted at –0.2 V vs RHE for 6 h in 10 mL of 0.1 M K\(_2\)SO\(_4\) aqueous solution in a circulation setup. Then 0.5 mL of the above solution mixed with 0.05 mL of \(d_x\)-DMSO was used for \(^1\text{H}\) nuclear magnetic resonance (NMR) spectroscopy measurement (Bruker AVANCE III 600 MHz).

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### REFERENCES


