

Tetra- β -(2-(diethylamino)ethoxy) nickel phthalocyanine: synthesis and inclusion in MCM-41

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Abstract In order to include phthalocyanine macromolecule in MCM-41 molecular sieve, a inclusion-suitable phthalocyanine derivative tetra- β -(2-(diethylamino)ethoxy) nickel phthalocyanine was synthesized, in two steps, from 4-nitrophthalonitrile and 2-(diethylamino)ethanol, and characterized by mass spectra, ^1H nuclear magnetic resonance spectroscopy, ultraviolet visible spectroscopy, infrared spectroscopy and elemental analysis, which confirmed the proposed molecular structure. The inclusion of synthesized phthalocyanine compound in MCM-41 was carried out by the in situ synthesis method using cetyltrimethyl ammonium bromide as structure template and tetraethyl orthosilicate as silica source in presence of this phthalocyanine compound. The inclusion material was studied by means of X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, nitrogen adsorption isotherm measurements, etc. Results showed that the macromolecular compound was successfully included into MCM-41, the obtained inclusion material displayed mainly prisms and globes, and the material was a kind of mesoporous materials with regularly hexagonal honeycomb array of uniform cylindrical pores and high surface area.

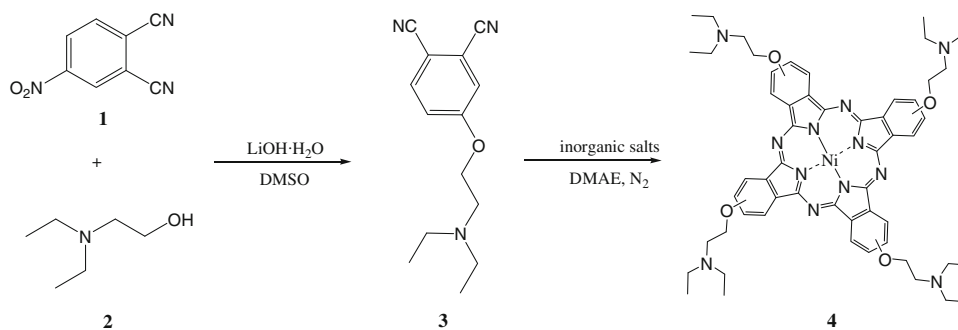
Keywords Synthesis · Characterization · MCM-41 · Phthalocyanine · Inclusion

Introduction

Phthalocyanine (Pc) compounds were a type of organic macromolecules with high chemical stability and diversely functional properties, especially catalysis [1–3]. Those Pc derivatives with catalytic potential were usually included in some materials as carriers, e.g. MCM-41, for used convenience and losing reduction in catalysis [4–6]. MCM-41 is a kind of mesoporous materials with regularly hexagonal honeycomb array of uniform cylindrical pores and high surface area, having many potential applications in material science fields [7, 8]. In MCM-41, many Pc molecules could be loaded by various methods such as encapsulation [9], immobilization [10], or in situ synthesis [11], etc., based on different molecular structures. The in situ synthetic strategy was more suitable for preparation of host/guest molecular sieves if Pc derivatives have appropriate substituents around periphery of Pc ring to cause them with excellent solubility in synthetic system [12]. Thus, a inclusion-suitable tetra- β -(2-(diethylamino)ethoxy) nickel phthalocyanine **4** was imagined and synthesized (Scheme 1). And the synthetic compound were characterized by mass spectra (MS), ^1H nuclear magnetic resonance spectroscopy (^1H NMR), ultraviolet visible spectroscopy (UV–vis), infrared spectroscopy (IR) and elemental analysis, and further a MCM-41-type molecular sieve doped with **4** was prepared by the in situ synthetic method, and characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (TEM), nitrogen adsorption isotherm measurements (NAI), etc.

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Scheme 1 Synthesis of **4**

Experimental

Synthesis of **3**

8.7 g 4-nitrobenzene-1,2-dinitrile (50 mmol) and 6.5 mL 2-(diethylamino)ethanol (50 mmol) were added to 50 mL DMSO at r.t. The reaction mixture was stirred and 2.8 g LiOH·H₂O was interfused over a 2 h period and the mixture was then stirred for 48 h. The mixture was then poured into 200 mL water and then extracted twice with 200 mL chloroform. Organic phase was dried with anhydrous sodium sulfate and evaporated under reduced pressure, the crude product was purified by silica gel chromatography (ethyl ether–ethyl acetate, 10:1) to obtain light yellow adhered liquid 4-(2-(diethylamino)ethoxy)benzene-1,2-dinitrile **3**, 10.0 g, yield: 82%; ¹H NMR (500 MHz, CDCl₃): δ 1.05 (t, 6H, 2CH₃), 2.61 (f, 4H, 2CH₂), 2.88 (t, 2H, NCH₂), 4.10 (t, 2H, CH₂O), 7.19 (f, 1H, ArH), 7.27 (d, 1H, ArH), 7.68 (d, 1H, ArH); MS (CH₃Cl): *m/z* calcd for [M + Na⁺]: 266.8, found: 266.4 (an isotopic cluster peak) [M + Na⁺]; IR (KBr): 2230 cm⁻¹ (C≡N), 1240 cm⁻¹ (C–O–C); UV–vis (CH₃Cl): λ_{max} = 269, 297, 306 nm.

Synthesis of **4**

2.1 g 4-(2-(diethylamino)ethoxy)benzene-1,2-dinitrile (8.0 mmol) and 0.24 g NiCl₂·6H₂O (2.0 mmol) were added under stirring to DMAE (20 mL) in a 50 mL one-neck round-bottomed flask equipped with an air condenser. The mixture was stirred and heated at 135 °C under N₂ for 24 h. After cooling under N₂, the black cyan solution was poured into ice water mixture, stirred and collected by vacuum filtration to afford the crude product. After dried, it was purified by column chromatography with chloroform–methanol (12:1) as the mobile phase to give pure blue–green solid **4** 2.31 g, yield: 26%; ¹H NMR (500 MHz, CDCl₃): δ 1.3 (s, broad, 24H, 8CH₃), 2.8 (s, broad, 16H, 8CH₂), 3.2 (s, broad, 8H, 4NCH₂), 4.3 (s, broad, 8H, 4CH₂O), 7.1–8.5 (m, broad, 12H, ArH); MS (CH₃OH): *m/z* calcd for [M]: 1030.3, found: 1031.5 [M]; IR (KBr): 1,240 cm⁻¹ (COC); Anal. Calcd for C₅₆H₆₈N₁₂O₄Ni

(1,030.3): C 65.18, H 6.64, N 16.29, Found: C 64.78, H 6.54, N 15.82. UV/Vis (CH₃OH): λ_{max} = 289, 338, 617, 682 nm.

Preparation of MCM-41 included with **4**

To a solution of 0.012 g **4** in 2 mL methanol, 0.182 g cetyltrimethyl ammonium bromide (CTMAB, 99%, Shanghai Chemical Reagents Company) was diffused with little deionized water and then added. In the mixture, some additional deionized water was poured and agitated to get 10 mL clear micelle solution. In a solution of 0.025 g NaOH in 5 mL deionized water, 5 mL micelle solution and 0.56 mL tetraethyl orthosilicate (TEOS, 99%, Shanghai Chemical Reagents Company) was dropped and then stirred at 70 °C for 0.5 h, respectively. The resulting mixture with molar composition: 0.00116 **4**:0.5 CTMAB:1.23 NaOH:5 TEOS:50 CH₃OH:1,000 H₂O, was transferred to a Teflon-lined stainless steel autoclave for hydration at 110 °C for 48 h. After filtration, washing and drying, the hydration product was further washed to be colorless with methanol/chloroform (v/v, 1:1) by Soxhlet extraction. The remnant template CTMAB was removed from mesopores by extraction with 150 mL solution of 1 N HCl/ethanol (v/v, 1:2) for 2 h. And after filtration, washing and drying again, the sample was extracted with methanol/chloroform (v/v, 1:1) for 2 h and then dried. In the end, the obtained material was designated PcMCM-41.

Apparatus and methods

Characterization on 4: High-resolution ¹H NMR spectra were recorded on a Varian Unity 500 spectrometer. IR spectra were measured on a Magna 560 FT-IR spectrometer. UV/Vis spectra were taken on a Cary 500 UV–VIS spectrophotometer. MS spectra were obtained on a LDI-1700-TOF mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyzer.

Characterization on PcMCM-41: XRD measurements were performed on a Rigaku A/max-IIB X-ray diffractometer using Ni-filtered Cu Kα radiation operated at

40 kV and 20 mA and in 2θ angle range of 0.8° – 10° with step of $0.02^\circ/0.5$ s. High-resolution transmission electron microscopy (TEM) analysis was taken from a JEOL JEM-2010 transmission electron microscope operated at 300 kV with 0.2 nm point resolution. Field emission scanning electron microscope (SEM) measurements were performed on a Holand XL 30 scanning electron microscope operated at 10 kV with 1.5 nm point resolution. Nitrogen adsorption measurements were performed at -196°C on a Quantachrome instrument NOVA 1000 Surface Area & Pore Size analyzer. Prior to the measurements, 0.10–0.15 g PcMCM-41 was degassed at 90°C for 5 h. Solid-state Fourier transform infrared spectroscopy were characterized on a Magna 560 FT-IR spectrometer by using an in situ FT-IR cell equipped with CaF_2 windows and scanning six times from 4,000 to 400 cm^{-1} with 4 cm^{-1} resolution. Solid-state ultraviolet/visible spectroscopy of power samples were taken on a Cary 500 UV–Vis spectrophotometer by scanning in a wavelength range of 200–2,000 nm and comparing with BaSO_4 power.

Results and discussion

Synthesis and characterization of **4**

Pc derivative **4** have four bulky substituents around its periphery, which would favor not only solubility, but also inclusion of **4** in MCM-41 due to formation of hydrogen bond between silica hydroxyl in MCM-41 and nitrogen or oxygen atom in four 2-(diethylamino)ethoxy groups around Pc ring (Scheme 1). It was synthesized by a modified procedure based on the literature [13]. The substrate **3** was firstly synthesized by an aromatic nucleophilic substitution reaction between 4-nitrophthalonitrile **1** and a suitable oxygen nucleophile 2-(diethylamino)ethanol **2**. The resultant **3** was adhered liquid, so it was extracted out from the reaction mixtures with chloroform and then purified by flash column chromatography. Pc **4** was synthesized by cyclo-tetramerization of phthalonitrile **3** upon treatment with NiCl_2 in DMAE under nitrogen at 135°C , and purified by flash column chromatography with chloroform as mobile phase. TOF–MS showed that the peaks of impurities hardly could be found, which meant **4** with high purity (Fig. 1). However the ^1H NMR displayed several broad bands for that the paramagnetic nature of Ni (II) in a planar environment [14] and the impact of oxygen and nitrogen atoms in 2-(diethylamino)ethoxy groups. The UV–vis spectra exhibited that **4** in methanol had the characteristic B band at 338 nm and Q band at 682 nm as well as shoulder peak at 617 nm (Fig. 2). IR absorption at $1,235\text{ cm}^{-1}$ (COC) revealed the bond between 2-(diethylamino)ethoxy group and Pc ring (Fig. 3b). The experiments on solubility of

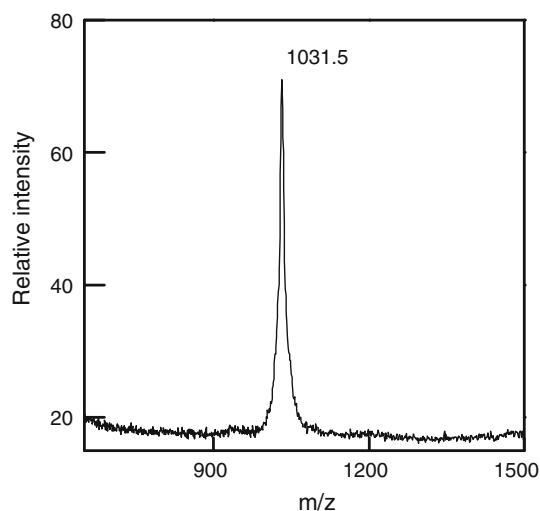


Fig. 1 MS of **4**

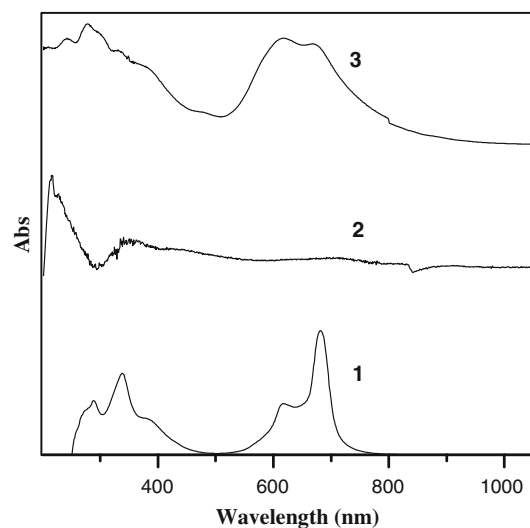


Fig. 2 UV–vis spectra of **4** in methanol (1.0×10^{-4} mol/L) (**1**), MCM-41 (**2**) and PcMCM-41 (**3**)

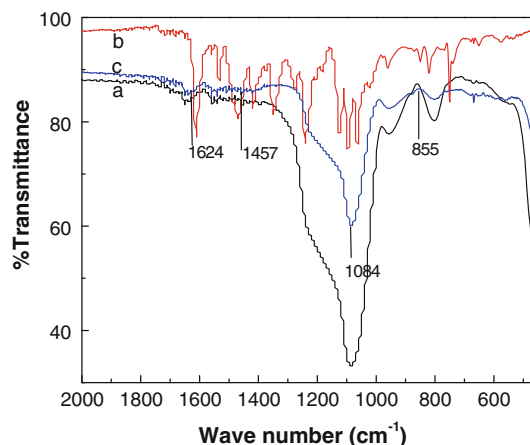


Fig. 3 IR spectra of MCM-41 (**a**), Pc **4** (**b**) and PcMCM-41 (**c**)

4 confirmed that it could be dissolved in chloroform, dichloromethane, acetone, ethanol and methanol, etc., which would facilitate the further inclusion of **4** in MCM-41.

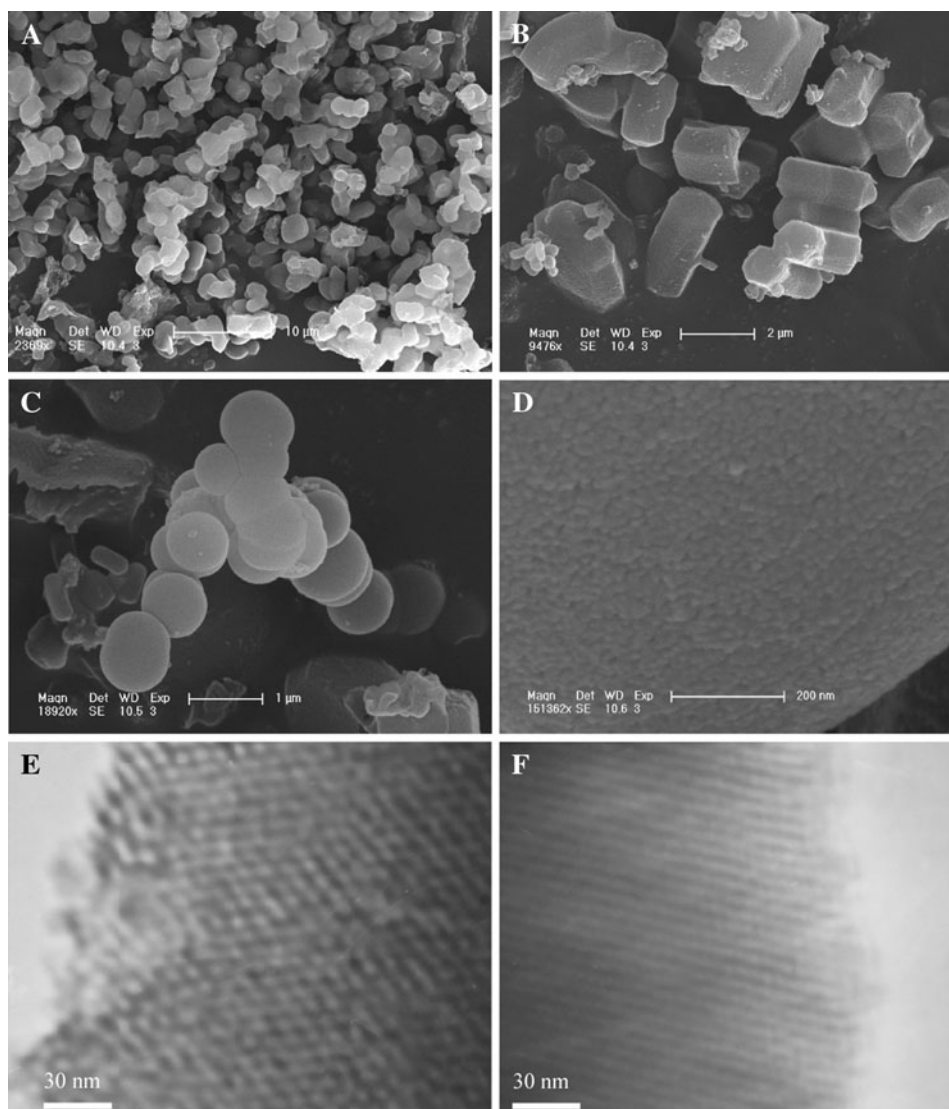
Preparation of molecular sieve PcMCM-41

The solution of **4** in methanol was used to prepare PcMCM-41 by the in situ synthesis method as described in “Preparation of MCM-41 included with **4**” section. During the course of preparation, as we all know that the MCM-41-type molecular sieves usually are calcined to remove the organic template from the pores after synthesis [15]. But it is not suitable in our study for that the complexes had been burned as well. Hence the repetitious exaction was employed to wash the material to be colorless for eluting liquid so as to remove the hydrophilic/lipophilic molecules and mesopore-outside **4** completely. The characteristic

results confirmed that the extraction not only gave no harm on host materials, but also didn't remove the well loaded **4** from pores. Because it was found that PcMCM-41 had the characteristic absorption of **4**, namely a broad Q band at 680 nm, an increased shoulder peak at 620 nm and a broad B band around 310 nm (Fig. 2). Otherwise the MCM-41 without **4** hadn't the characteristic absorption of Pc compound. As for the aforesaid change of Q band and shoulder peak, it resulted from aggregation of Pc molecules in solid state [16]. The IR of PcMCM-41 showed there were vibration absorptions of Pc framework at 855, 1084, 1457 and 1624 cm^{-1} (Fig. 3c) [17], but the IR bands were weak due to low concentration of **4** in MCM-41.

The aforementioned results implied that the Pc **4** was successfully included in PcMCM-41. The desired inclusion might be attributed to three reasons: one was the finer dispersion of **4** in synthetic system for its excellent solubility, another was the severely hindered diffusion of bulky

Fig. 4 FESEM images of PcMCM-41 (a–d) and TEM images of PcMCM-41 (e, highly ordered, long-ranged hexagonal array; f, mesopore system)



molecules of **4** in the relatively narrow pores of PcMCM-41, and the third was the strong action of hydrogen bond of the silica hydroxyl in mesopores with the nitrogen and oxygen atom in 2-(diethylamino)ethoxyl groups.

Characterization on the structures of PcMCM-41

The FESEM images of PcMCM-41 showed that they were mainly prisms and some globed particles, which sizes were from 0.5 to 2 μm (Fig. 4a–c). All of them had a kind of order surface even if the shapes were different (Fig. 4d). The order property was discovered by the TEM images, which gave an apparently long-ranged order of hexagonal array (Fig. 4e, f). This just was the textural features of highly ordered MCM-41 molecular sieves [18].

Further the XRD patterns of PcMCM-41 exhibited three characteristic reflections on (100), (110) and (200) planes of mesoporous molecular sieves with hexagonal symmetry [7] (Fig. 5). The nitrogen adsorption isotherm of PcMCM-41 was a quasi-IV-type isotherm resulted from mesoporous framework [19] (Fig. 6). The adsorption at low relative pressure ($P/P^0 < 0.35$) was derived from monolayer coverage of pore walls by nitrogen. With P/P^0 ranging from 0.35 to 0.40, a sharp inflection in adsorption isotherms appeared, indicating the capillary condensation in primary mesopores [20]. Here, the sharper inflection of the isotherms meant abundant and size-uniform mesopores existing in PcMCM-41 [21]. Namely it had great inner superficial area. Table 1 showed that PcMCM-41 had increased BET surface area and pore volume, but decreased pore diameter relative to MCM-41. The reason might be that the four large 2-(diethylamino)ethoxy groups around Pc **4** compel molecular plates curling to tubes in mesopores and forming a tube-in-the-tube structure [22] (Fig. 6), which structure endowed the material with great inner superficial area. The relatively small hysteresis loop appearing between 0.35 and 0.5 (P/P^0), for the filling of nitrogen in the textural mesopores [23], further suggested high uniform for mesopores in PcMCM-41 and much less for amorphous silica in it. The final increase for absorbed nitrogen at $P/P^0 > 0.8$ was the filling in inter-space of particles at high relative pressures. Further investigation showed that the concentration of Pc **4** in preparation of PcMCM-41 gave no obvious help to its nitrogen adsorption isotherm.

Conclusions

In order to obtain the Pc derivative suitably included in MCM-41, we selected phthalonitrile **3** as the substrate to synthesize **4**, which structure was confirmed by means of MS, ^1H NMR, UV–vis, IR and elemental analysis.

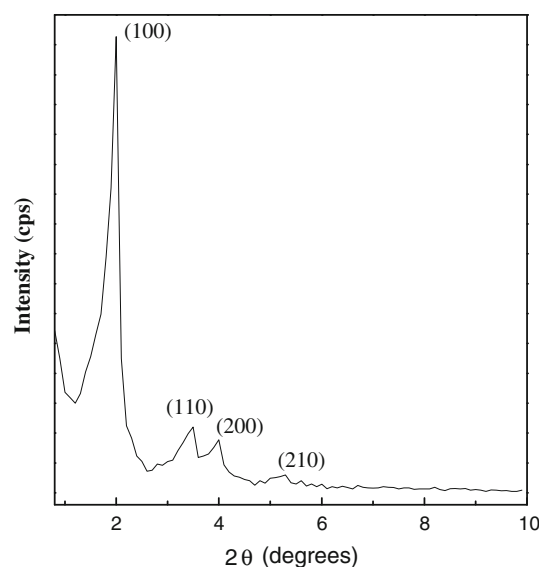


Fig. 5 XRD of PcMCM-41

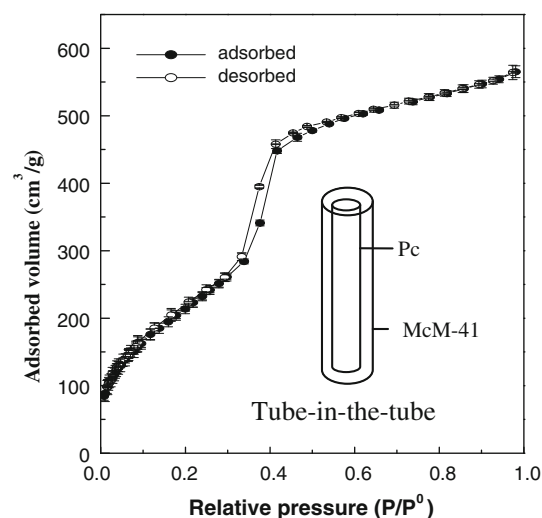


Fig. 6 Nitrogen adsorption isotherms of PcMCM-41 and the tube-in-the-tube structure of mesopore

Table 1 BET surface area, pore volume and pore diameter

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
MCM-41	436.4	0.51	4.67
PcMCM-41	822.1	0.87	4.25

The dissolubility of **4** in methanol caused it suitable to be used to prepare the PcMCM-41 by the in situ synthetic method. The results of characterization by XRD, FESEM, TEM and NAI, etc., displayed: (1) **4** had been successfully doped in PcMCM-41 and couldn't be easily removed from mesopores via extraction; (2) PcMCM-41 displayed structural characters of MCM-41 molecular

sieve; (3) The crystal phases of PcMCM-41 mainly were prisms and global particles.

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