



Interlayer Formation of Cyclobis(paraquat-*o*-phenylene) by the Reaction of Laponite-4,4'-bipyridinium Intercalates with α , α' -Dibromo-*o*-xylene: A One Electron Template Synthesis

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Abstract

Cyclobis(paraquat-*o*-phenylene) cyclophane can be synthesised in the form of a free radical within the gallery space of a synthetic aluminosilicate clay mineral. The interlayer formation of the cyclophane was revealed by XRD, IR and optical measurements. The mechanism of its formation is consistent with a one electron redox synthesis in which the electron donated by the clay mineral plays the role of the template towards the π -electron deficient bipyridinium moieties.

Introduction

Cyclobis(paraquat-*o*-phenylene) is a phane tetracation having two 4,4'-bipyridinium moieties linked *via* two *o*-xylene bridges. The bulk preparation of this macrocycle comprises either reaction of the trimer bisparaquat-*o*-phenylene with excess of α , α' -dibromo-*o*-xylene in water and stirring for three weeks at ambient temperature (yield 60%) or aqueous reflux of almost equimolar amounts of 4,4'-bipyridine and the dibromide in water for three hours (yield 25%) [1, 2]. However, no efforts have been made for the template synthesis of this π -electron deficient macrocycle with a π -electron rich donor through π - π interactions as has been implied for the related cyclobis(paraquat-*p*-xylene) analogue [3, 4]. The reason is probably the small cavity of the macrocycle which makes difficult the inclusion of some electron rich aromatic molecules inside the cavity [5]. Here, we wish to report for the first time the formation of the reduced form of cyclobis(paraquat-*o*-phenylene) inside the gallery space of a layered clay mineral through a one electron template mechanism. X-ray diffraction, IR and optical absorbance measurements demonstrate the formation of the macrocycle, while the mechanism of formation was revealed by ESR spectroscopy.

Experimental

A synthetic hectorite under the commercial name Laponite (monovalent cation exchange capacity: CEC = 0.74 meq g⁻¹) obtained from Laporte Industries Ltd. and a natural occurring montmorillonite from the island of Milos, Greece, having the code name Zenith-N (CEC =

0.8 meq g⁻¹), were used. 4,4'-Bipyridine was supplied from Merck-Schuchardt while α , α' -dibromo-*o*-xylene was from Fluka. The synthetic procedures are described below.

Lap-4³⁺: Sodium Laponite (0.32 g) was dispersed in water (2–3 mL) and a solution of 4,4'-bipyridine (85 mg) in ethanol (3 mL) was added. The flocculated slurry was stirred for 10 min followed by centrifugation and washing of the solid once with water and twice with ethanol. The washed product was re-dispersed in a few mL of ethanol and dried on a glass plate (**Lap-1·2H⁺**). To the dried powder (0.3 g) plus α , α' -dibromo-*o*-xylene (**2**) (100 mg), 15 mL of H₂O were added and the mixture was refluxed for 3 h. The green solid obtained was centrifuged, washed once with water and twice with methanol and finally dried in air on a glass plate. Notice that no coloration of the supernatant liquids was observed during centrifugation and washing. Chemical analysis for this clay product revealed a carbon to nitrogen weight ratio of 7.8 which is in close proximity to that theoretically expected for the tetramer cation (7.5).

Lap-3¹⁺·2H⁺: This intermediate product (*vide infra*) was isolated from the reaction mixture after 15 min reaction time in the above preparation by centrifugation, washing and drying.

Lap-4³⁺/R and **Lap-3¹⁺·2H⁺/R:** These reference samples were prepared by the exchange reaction between an aqueous dispersion of sodic Laponite with an aqueous solution of the pre-prepared cations **4⁴⁺** and **3²⁺** added in quantities corresponding to 1 CEC of the clay. Cations **4⁴⁺** and **3²⁺** were obtained according to published procedures. Notice that the insertion of these cationic species into the clay galleries was accompanied by strong coloration of the mineral, indicating their reduction to a free radical form.

X-ray powder diffraction patterns (XRD) were recorded on a D-500 Siemens diffractometer using CuK α radiation.

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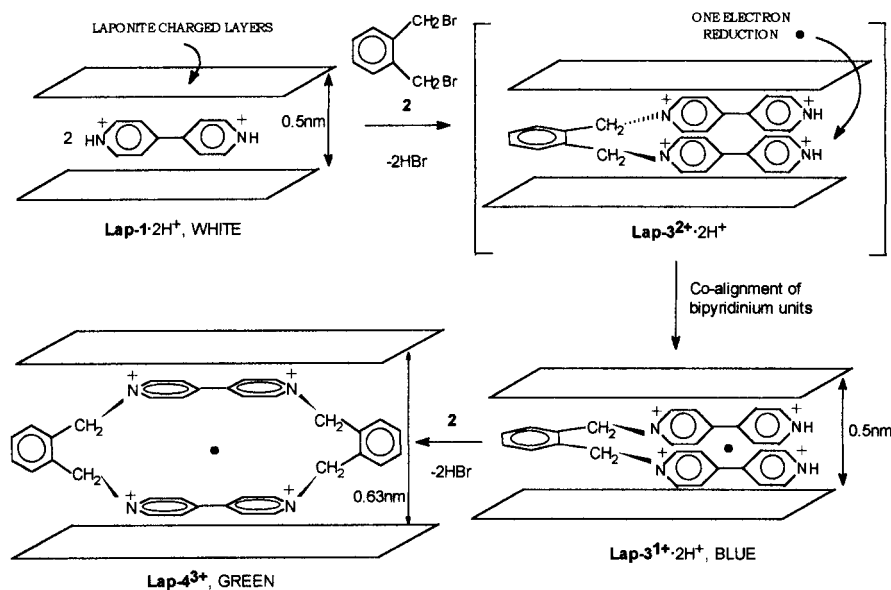


Figure 1. Illustrative model for the interlayer formation of cyclabis(paraquat-*o*-phenylene) via a one electron template mechanism [the interlayer distances depicted in this model have been calculated by subtracting the layer thickness of the platelets (9.6 Å) from the d_{001} distance].

Infrared spectra were recorded with a Bruker, Equinox 55/S FT-IR spectrometer. Electron spin resonance (ESR) measurements were obtained at room temperature on a Bruker 200D-SRC spectrometer with a resonance cavity of 9.4GHz. Optical measurements were carried out with a Shimadzu UV2100 photometer.

Results and discussion

The various steps in the synthesis are illustrated in Figure 1. The synthesis starts with an exchange reaction between the protonated dication of 4,4'-bipyridine and an aqueous dispersion of sodium Laponite to give the intercalated complex **Lap-1·2H⁺**. The complex, after its isolation, was refluxed in aqueous solution in the presence of **2** for three hours. The color of the initial white slurry changed to blue after 15–20 min, and then gradually turned to permanently green. These color changes indicate that the blue product, designated as **Lap-3¹⁺·2H⁺** (**3¹⁺** being the reduced, in the form of a free radical, state of **3²⁺**), is an intermediate product which is transformed to the final product **Lap-4³⁺** (**4³⁺** standing for the reduced, again in the form of a free radical, state of the tetracationic macrocycle **4⁴⁺**). It must be emphasized that the intercalation of either the preformed trimer **3²⁺·2H⁺** or preformed tetramer **4⁴⁺** into Laponite gave similarly a blue or a green product, respectively. These results point to the occurrence of unique intercalative redox reactions, which transform the original trimeric or tetrameric diamagnetic molecular species into paramagnetic free radicals that are stabilized by the host matrix. To distinguish the intercalated solids obtained from reference samples we denote them as **Lap-3¹⁺·2H⁺/R** and **Lap-4³⁺/R**. In the following, all characterizations pertinent to the samples (starting, intermediate and final) were obtained on their dried powder form.

The XRD patterns of dried samples of **Lap-1·2H⁺**, **Lap-3¹⁺·2H⁺**, **Lap-4³⁺** and **Lap-4³⁺/R**, shown in Figure 2, indicate how the basal spacings (d_{001}) change with reaction time. The initial 001 reflection of the Laponite-4,4'-bipyridine intercalate [6] (planes of the two aromatic rings perpendicular to the layers) remained unaltered after 15 min reaction time when the blue intermediate was formed. As discussed later, during this time only a small quantity of the trimeric species was produced, the rest of the interlayer species being non-reacted 4,4'-bipyridine molecules. Therefore, it is not surprising that **Lap-1·2H⁺** and **Lap-3¹⁺·2H⁺** exhibit the same basal spacing. In addition, as the reference sample **Lap-3¹⁺·2H⁺/R** exhibits in its XRD pattern (not shown) a basal spacing of 15 Å, which is in close proximity to that of **Lap-1·2H⁺**, we conclude that the planes of the bipyridinium moieties are perpendicular to the layers while that of the phenyl group are parallel. After refluxing for three hours the XRD pattern of the resulting product changed drastically in position giving a d_{001} spacing of 15.9 Å for the **Lap-4³⁺** green product. In this product we assume that the planes of the bipyridinium and phenyl groups are parallel and perpendicular, respectively, to the layers. A first indication for the interlayer formation of the macrocycle came from comparing the XRD pattern of sample **Lap-4³⁺** with that of the reference **Lap-4³⁺/R**. The identical XRD patterns support the tetramer formation.

The intralaponite formation of the macrocycle **4³⁺** was further explored by IR spectroscopy in the region 1800–1300 cm^{-1} , Figure 3. Upon formation of the intermediate blue product, the IR spectrum of the initial **Lap-1·2H⁺** intercalate changed significantly. Firstly, the main peak at 1600 cm^{-1} in the 4,4'-bipyridinium spectrum lost intensity, whereas the peak at 1638 cm^{-1} gained intensity as the reaction progressed. Secondly, a new band at 1447 cm^{-1} , missing from the bipyridinium spectrum, started to develop with the reaction. For comparison, the spectrum from a ref-

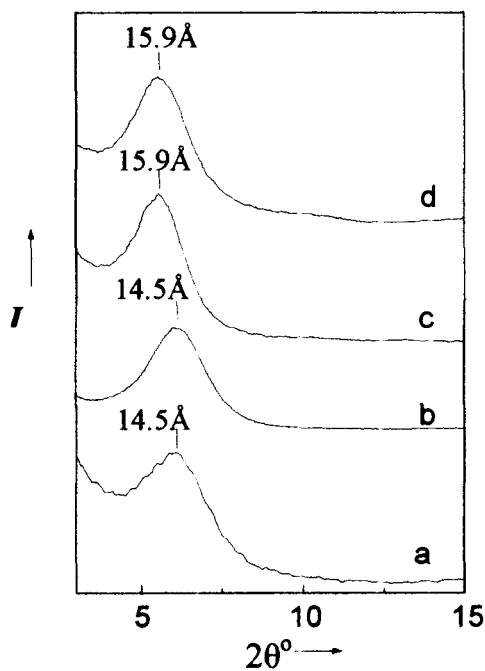


Figure 2. XRD patterns of samples **Lap-1-2H⁺** (a), **Lap-3¹⁺.2H⁺** (b), **Lap-4³⁺** (c) and **Lap-4³⁺/R** (d) (*I*: Intensity in a.u.).

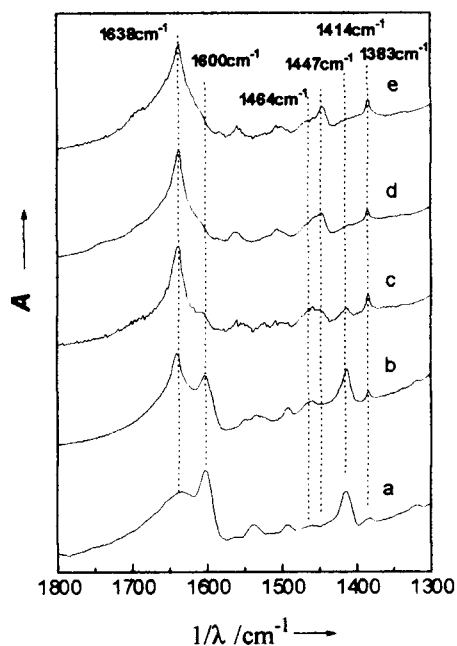


Figure 3. IR spectra of samples **Lap-1-2H⁺** (a), **Lap-3¹⁺.2H⁺** (b), **Lap-3¹⁺.2H⁺/R** (c), **Lap-4³⁺** (d) and **Lap-4³⁺/R** (e) (*A*: Absorbance in a.u.).

reference sample **Lap-3¹⁺.2H⁺/R** was also used. It appeared that the spectrum of the blue intermediate was similar to the reference, although not exactly the same. Therefore, it was concluded that only a small (but IR detectable) portion of the initial intercalated bipyridine molecules was being transformed to the trimeric **3¹⁺.2H⁺** species after a 15 min reaction time. After accomplishment of reaction, the final product **Lap-4³⁺** exhibited an IR spectrum totally different from those of the starting and intermediate materials.

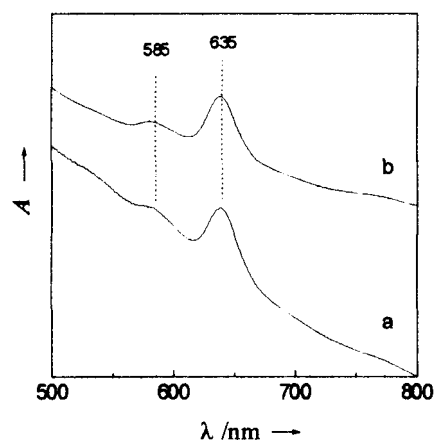


Figure 4. Visible spectra of aqueous dispersions of samples **Lap-4³⁺** (a) and **Lap-4³⁺/R** (b) (*A*: Absorbance in a.u.).

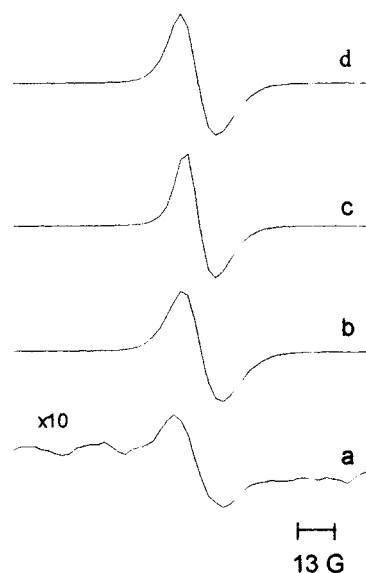


Figure 5. ESR spectra of samples **Lap-3¹⁺.2H⁺** (a), **Lap-3¹⁺.2H⁺/R** (b), **Lap-4³⁺** (c) and **Lap-4³⁺/R** (d), recorded at room temperature.

Now, the bands at 1600 cm^{-1} and 1414 cm^{-1} are suppressed, while a new band at 1447 cm^{-1} with a shoulder at 1464 cm^{-1} appeared. Most importantly, the spectrum of the final product was the same as that of the reference sample **Lap-4³⁺/R**, adding an extra indication for the macrocycle formation. In addition, it was found that due to the small sized platelets of Laponite the derivatives **Lap-4³⁺** and **Lap-4³⁺/R** could form stable colloids in water which enabled the recording of their visible spectra. As shown in Figure 4, the visible spectra of the corresponding colloids are identical in shape and position exhibiting two bands at 585 nm and 635 nm.

So far the X-ray, IR and visible absorption data point to the macrocycle formation in the interlayer space of the aluminosilicate material. However, it must be mentioned that it was a very difficult task to recover by extraction either the in-situ formed or the simply intercalated macrocycle molecule from the clay host matrix for further characterization. Treatments with concentrated solutions of salts such as NH_4PF_6 ,

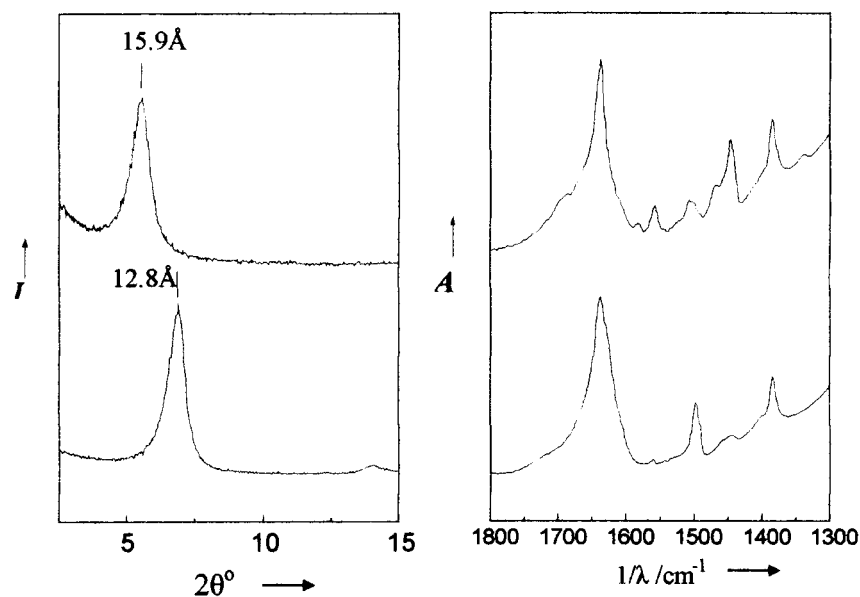


Figure 6. XRD patterns (left) and IR spectra (right) of Zenith-N-4,4'-bipyridine intercalate after reaction with *o*-dibromide (lower) as compared with a reference Zenith-N-tetramer sample (upper) (*I*: Intensity, *A*: Absorbance in a.u.).

LiCl and AlCl₃ under reflux conditions or acid extraction with diluted acids such as HCl, HPF₆ and HBF₄ released only traces of the interlayer species. This was also confirmed by IR spectroscopy on the clay samples after extraction, which showed that a significant portion of the organic matter was still retained by the inorganic support. This indicates that the macrocycle is tightly bound onto the clay surfaces by strong electrostatic and van der Waals forces.

A key question is how the Laponite surfaces affect the macrocycle formation. In order to elucidate the mechanism of the reaction in the presence of Laponite sheets, ESR spectroscopy, which is a powerful technique to detect the presence of paramagnetic centers, was used. After 15 min reaction time, the sample **Lap-3¹⁺·2H⁺** gave an ESR spectrum, Figure 5, with a broad signal at $g \sim 1.99$ implying a free radical formation [7]. A similar signal, but more intense, was also registered from the reference sample **Lap-3¹⁺·2H⁺/R**. The data indicate that the reduced species **3¹⁺·2H⁺** is formed inside the clay galleries. After three hours reaction time, the initial weak ESR signal observed for the intermediate product was considerably amplified to give an intense absorption of the final product **Lap-4³⁺**. The same spectrum (intensity and position) was also obtained from the reference sample **Lap-4³⁺/R**. These results strongly suggest that the clay layers act as a reducing agent for either the fully oxidized form of the intercalated **3²⁺·2H⁺** trimeric or the tetrameric **4⁴⁺** species. In addition, the surfaces provide a stabilizing environment for the generated radicals as has been observed for other clay-radical complexes [8, 9]. The reducing power of the mineral, although it is not well understood, probably relies on two factors: the presence of Mg²⁺ cations as the main constituent of the octahedral layer of the clay (magnesium content $\sim 17\%$ w/w) and also the small size of the clay platelets ($\sim 0.3 \mu\text{m}$). For instance, it has been reported elsewhere that small size MgO particles exhibit strong electron donat-

ing properties [10]. Most importantly, clay substrates with a much lower magnesium content and larger platelet size were found to have no reducing effects upon insertion either of the pre-formed trimeric or tetrameric cationic species. In these cases, the formation of a monoradical was viable only by chemical reduction of the interlayer species with a mild reducing agent e.g., sodium ascorbate. However, the as-formed radicals turned out to be inactive after standing for a few hours in air indicating their weak stabilization by the clay platelets. Furthermore, in order to examine the effect of the reducing power of the mineral for the formation of the macrocycle molecule, the same reactions described in the experimental section were tried using a clay substrate (Zenith-N, magnesium content $\sim 1.7\%$ w/w, platelet size $\sim 0.9 \mu\text{m}$) that does not reduce the intermediate trimeric molecule. Macrocycle formation was not observed in this case as was confirmed by XRD and IR measurements, Figure 6. More specifically, after reaction the basal spacing of 14.9 \AA for the initial Zenith-N-4,4'-bipyridine intercalate decreased to near 13 \AA instead of increasing to the value of 15.9 \AA , while the IR spectrum of the final product was totally different from that of the reference sample. Although, we are not in a position to ascribe in detail the observable changes, we believe that they may originate from the formation of linear oligomeric or polymeric species with their aromatic components lying parallel to the layer. It is known that aromatic molecules lying parallel to the clay sheets give a basal spacing of about 13 \AA (thickness of the aromatic ring $\sim 3 \text{ \AA}$).

Based on these results, we suggest that the macrocycle formation proceeds as shown in Figure 1. The intercalated bipyridine molecules react with the dibromide to first form the disorientated trimer **3²⁺·2H⁺**. The clay layers then donate an electron to the intergallery trimer turning it to its reduced state (blue intermediate). The key step in the synthesis is the uptake of this electron and its entrapment by the trimer. At this point, strong interactions between

the electron deficient bipyridinium units of the trimer and the entrapped electron could lead to a co-alignment of the bipyridinium units *via* donor-acceptor interactions. Once the trimer has attained the appropriate π -shape conformation, another dibromide molecule can react with the trimer to form the reduced cyclophane 4^{3+} .

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