Clays as a Host Matrix in the Synthesis of Organic Macrocycles

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Abstract: A new approach for the synthesis of amide macrocycles, based on the use of organo-clay derivatives as controlling template, is proposed as an alternative to the rotaxane method. Dications of *p*-xylylene diamine inserted in the clay interlayer space act as molding pillars around which neutral diamine molecules are erected via hydrogen bonding and $\pi-\pi$ interactions to form supramolecular arrays. Condensation of diamines in the supramolecular arrays with diacetyl dichlorides yields various tetramide macrocycles in good yields. Shape, aromaticity and dimensions of the reactants are factors affecting the condensation reaction.

Keywords: clays · intercalations · macrocycles · supramolecular chemistry · template synthesis

Introduction

Smectite clays define a class of layered aluminosilicate minerals that are widely used in many different fields of high interest.[1] This is mainly due to their easy reconstruction to various derivatives by soft physicochemical treatments, including diverse ion-exchange and intercalation reactions at ambient conditions, while their structure remains stable over a wide pH range. These features endow clays with new properties, as in the case of organoclays, pillared clays and clay–polymer composites.[2] As a result, restructuring of smectites attracts numerous research and development efforts nowadays in view of a wide range of applications. Preparative organic chemistry constitutes one such area of mainstream efforts where clays are used as heterogeneous catalysts for a wide variety of organic reactions.[3] In this direction, clays play the role of inorganic solid supports where reagents are deposited. The main advantages of these supported reagents over conventional homogeneous solution techniques are: a) easier experimental set-up and work up, b) mild conditions and c) often substantial improvement of yields and/or selectivity.

In addition, clays and possibly other microporous materials can provide functional and structural microenvironments for the spontaneous organisation of reactive substrates for the purpose of tailoring the architecture of macromolecular and supramolecular arrays. In particular, the predetermined architectures of microporous materials can be effectively used to hold reactive substrates in a manner which controls the subsequent geometry of the macromolecular and supramolecular product, as for example, to control the degree and type of branching in a linear polymer or to determine the shape and coordination of a supramolecular system. The final product can be removed from the clay framework or the clay can be chemically degradated to release the intercalated product.[4, 5]

Recently, we have demonstrated that clay surfaces are efficient templates for the synthesis of nitrogen based macrocycles. In one study, the interlayer synthesis of cyclobis (paraquat-*o*-phenylene) was accomplished by one electron redox process, in which the electron, donated by the clay surfaces, plays the intriguing role of the template for the π-electron deficient bipyridinium moieties.[6] In another study, an organo-pillared clay, derived from the insertion of protonated *p*-xylylenediamine to the clay layers, was shown to act as an active template for the self-assembly of neutral diamine molecules in the clay interlayers to form unique supramolecular arrays. In these arrays the diamine molecules possess the right orientation and alignment for the cyclization reaction with isophthaloyl dichloride molecules. The result is the formation around the organic pillar of a cyclic tetramide macrocycle as shown in Scheme 1. The tetramide was then easily removed from the clay by treatment with a lithium salt in DMSO, whereupon the Li^+ cation dislodge the pillar and DMSO dissolves the macrocycle.[7]

In the present work we have extended this strategy to prepare a series of tetramide macrocycles. Two different diamines and four acid dichlorides were used for the

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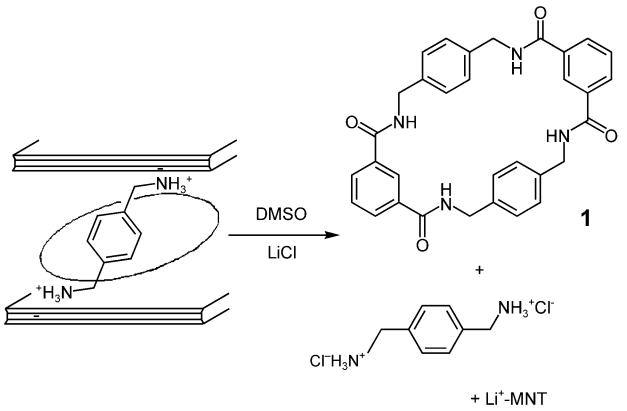


Scheme 1. Tetramer locked in the clay interlayers and its extraction.

successful synthesis of eight cyclic tetramides, thus establishing the general application of the method for amide cyclization reactions. The availability and low cost of clays, the easy handling, the high macrocycle yields and feasibility to study the interesting chemistry in the interlayer space of clays are some of the advantages of the present organo-clay template method.

Results and Discussion

The reaction of *p*-xylylenediamine and isophtaloyl dichloride in chloroform at high dilution leads to a mixture of amide oligomers; among those is the interesting [2]catenane molecule formed by two macrocyclic interlocked rings in low yield.[8] The independent macrocycle can be generated by the so-called rotaxane method, in which a molecular thread is used as a template to form the macrocycle around it by a process driven by intermolecular forces.[9]

As mentioned in the Introduction, the interlamellar space of reconstructured smectite clays offers the necessary architectural conditions for building the cycloamidic skeleton. In the present clay based preparative strategy, two different diamines, designated **a** and **b**, and four acid dichlorides, designated **c**, **d**, **e**, **f**, were used to prepare macrocycles **1**–**8**, all shown in Scheme 2. The synthesis of the amidic macrocycles comprises four steps: i) preparation of a pillared organo-clay precursor obtained from intercalation of the dihydrochloride salt of *p*-xylylenediamine, ii) insertion of the appropriate neutral diamine a or b into the common pillared precursor from i), iii) reaction of the neutral diamine in the layers with the various acid dichlorides and formation of the corresponding tetramide macrocycles, and iv) extraction of the macrocycles product from the clay surfaces.

The amino pillared clay precursor, derived by replacing the interlayer Na^+ cations with *p*-xylylene diamine dications, gave an XRD pattern with a d_{001} basal spacing value of 13.0 Å (see Figure 1a); this indicates an interlayer separation of 3.4 Å (13.0 – 9.6 Å = 3.4 Å, where 9.6 Å measures the thickness of the clay layer). This distance suggests that the dicationic pillars obtain an inclined position in the intergallery space,[9] as depicted in Scheme 3. The consequent introduction of neutral *p*-xylylene diamine molecules into the pillared structure induced an increase in the basal spacing to 15.1 Å (Figure 1b).

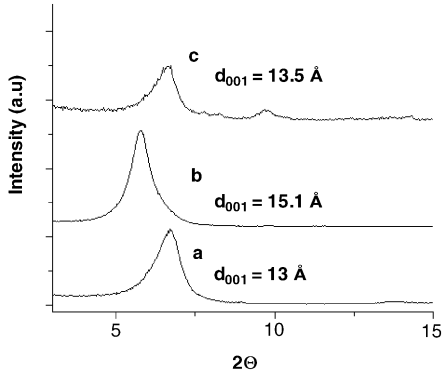
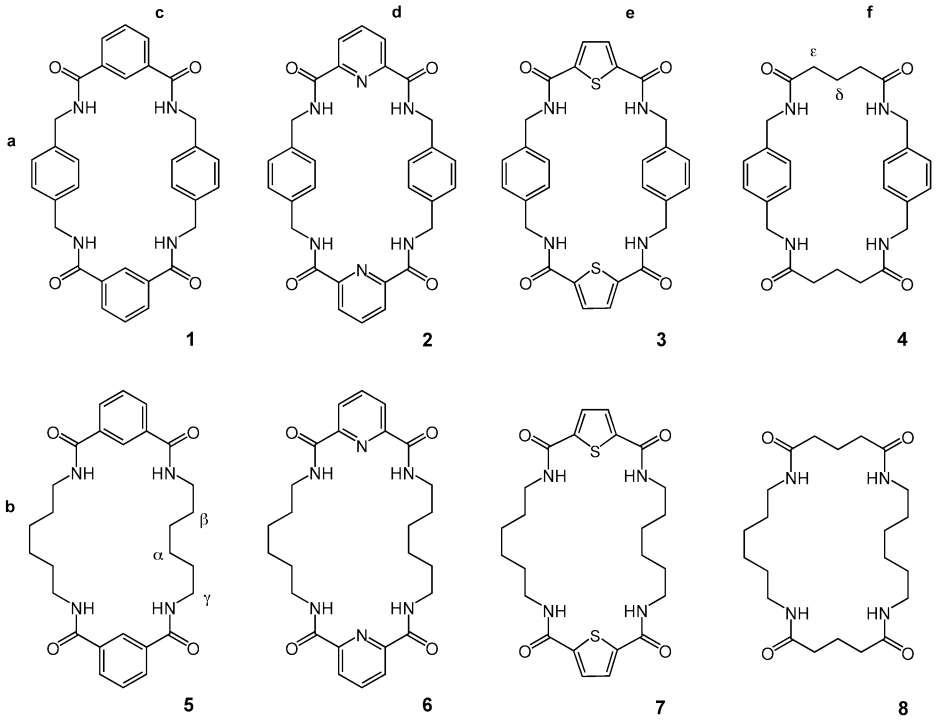
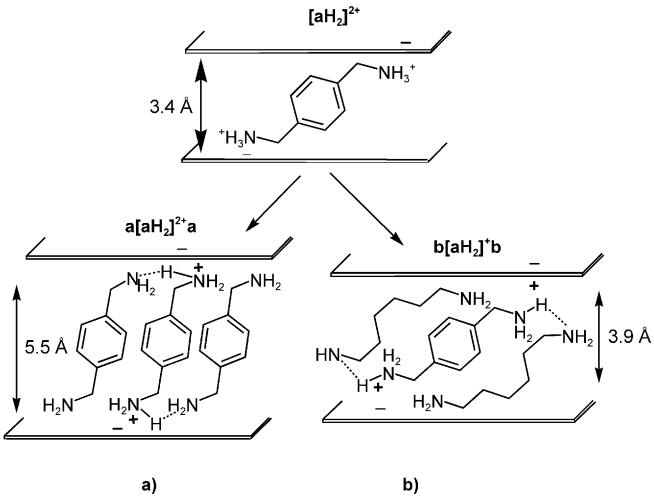


Figure 1. XRD patterns from: a) the clay-*p*-xylylene diamine precursor; b) the clay aggregate after the insertion of neutral *p*-xylylene diamine in the organo clay precursor; c) the clay aggregate after the insertion of neutral 2,6-hexanediamine to the organo clay precursor.



Scheme 2. Tetramide macrocycles (**1**–**8**). Diamines are denoted by **a** and **b** and diacetyl dichloride by **c**, **d**, **e** and **f**.

To explain the observed pillar lifting of 2.1 Å, we propose that neutral *p*-xylylene diamine molecules are pinned to the existing organo pillars by combined hydrogen-bonding interactions between the amino groups and π-stacking interactions between aromatic rings, as depicted in Scheme 3a. Such



Scheme 3. Interlayer arrangement of a) *p*-xylene diamine and b) 1,6-hexanediamine molecules, for cyclic condensation.

interactions can lead to supramolecular associations in the clay galleries, which we denote as $\mathbf{a}[\mathbf{aH_2}]^{2+}\mathbf{a}$. Analogous supramolecular aggregates have been reported in the literature on clays and the term hemisalt aggregates was coined to describe them.[10] However, similar lifting of the *p*-xylylene pillars was not observed when neutral 1,6-hexanediamine was loaded into the clay galleries to form the corresponding $\mathbf{b}[\mathbf{aH_2}]^{2+}\mathbf{b}$ interactions. The d_{001} remained at almost the same 13.5 Å value (see Figure 1c). It seems that the lack of π–π interactions, between *p*-xylylene and 1,6-hexanediamine, prevents the lifting of the electrostatically bound to the layers *p*-xylylene diamine dication pillars. In this case, the neutral aliphatic diamine molecules can be accommodated in the empty space among the electrostatically bound *p*-xylylene diamine pillars via hydrogen-bonding interactions, as illustrated in Scheme 3b. Similar hydrogen-bonding interactions have been proposed to explain the intercalation of excess ethylenediamine in smectite clays.[11]

Further evidence for the association of diamine **a** and **b** in the interlayer clay space arises from the corresponding FT-IR spectra (see Figure 2). The relatively sharp absorptions around 3000 cm^{-1}, in Figure 2a are assigned to the electrostatically bound to the clay layers *p*-xylylene dications. Contrarily, the amine supramolecular associations $\mathbf{a}[\mathbf{aH_2}]^{2+}\mathbf{a}$ and $\mathbf{b}[\mathbf{aH_2}]^{2+}\mathbf{b}$ (see Figure 2b, c) show quite broad bands as a result of the corresponding hydrogen-bonded structures. For the same reasons, the spectra of the clay derivatives are quite different in the 1600 cm^{-1} region, where -NH_2 absorption bands appear.

Because of the favorable positions of the diamine molecules on both sides of the pillars, the condensation reactions that follow the insertion of the different diacetyl dichlorides in the interlayer space, can lead to directed construction of

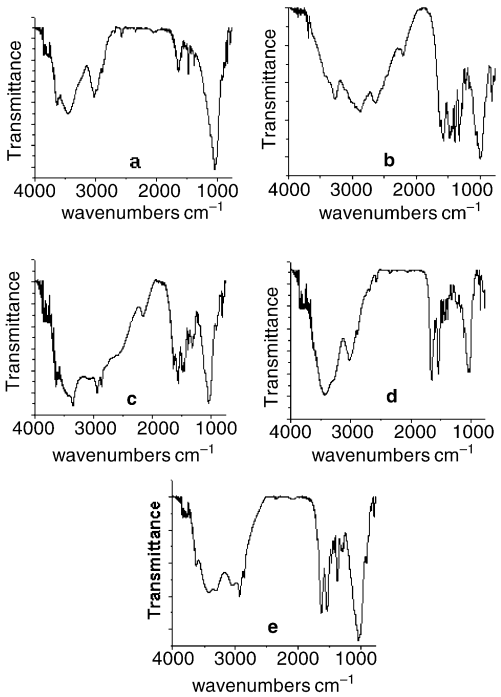
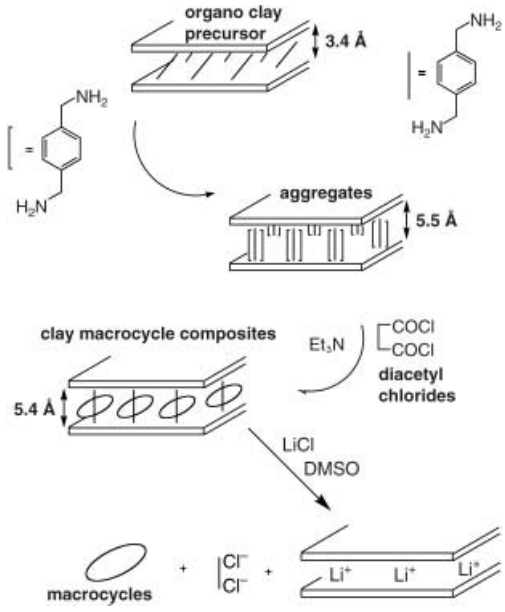


Figure 2. IR spectra of a) the clay *p*-xylylene diamine precursor; b) the interlayer associations $\mathbf{a}[\mathbf{aH_2}]^{2+}\mathbf{a}$; c) the interlayer associations $\mathbf{b}[\mathbf{aH_2}]^{2+}\mathbf{b}$; d) the interlayer formed macrocycle **2**; and e) the interlayer formed macrocycle **5**.

tetramide macrocycles, as for example the tetramide **1** in Scheme 1, trapped by the dicationic pillars. Scheme 4 illustrates the three steps structural reactions in the formation of amidic macrocycles.



Scheme 4. Schematic illustration of the reaction.

Formation of the amide bonds is detected in the FT-IR spectra of the clay bound products, from the characteristic bands around 1530 and 1635 cm^{-1}, (see Figure 2d and e). Furthermore, the relative sharp band near 3000 cm^{-1} unveils

that the electrostatically bound dicationic species are still preserved in these arrays and, by acting as stoppers, prevent the release of the cyclic macrocycles. Finally, the quite different profile in spectra **b** and **c** versus **d** and **e** demonstrate clearly the destruction of the hydrogen bonded amine associations during cyclization.

The ^{1}H NMR spectra of the clay-macrocyclic composite provide further evidence for the cyclization reaction. Recording of the spectra was made possible through the use of laponite, a synthetic clay free of paramagnetic centers in its structure and with platelets small enough to remain in suspension for sufficient time to record the spectrum.[7] Amine–laponite derivatives as cyclic tetramide directing templates afforded all tetramers in good yields. Furthermore, the XRD and FTIR characteristic of the amine derivatives were similar to those from natural montmorillonite implying similar interlayer structural units in both clays.

The last part of the synthetic procedure involved the release of the cyclization products from the clay surfaces. This was accomplished by using solutions of LiCl in DMSO. The Li^+ cations replace the *p*-xylylene dications from the clay surfaces and then the formed macrocycles are released into the DMSO solution together with diamine salt. Addition of acetone to the DMSO solutions precipitates the two products. Finally, the diamine salt is easily solubilized, as neutral amine, by treatment with dilute aqueous Na_2CO_3 solution leaving behind the tetramide as a pure solid.

Using different acid dichlorides, such as pyridyl (**d**) and thiophenyl (**e**) dichlorides, tetramide macrocycles **2** and **3** (see Scheme 2) were obtained in good yield (see Experimental Section). These two diacid dichlorides with aromatic rings in their framework are structurally similar to isophthaloyl dichloride (**c**), and therefore, a similar behavior is anticipated. We have also found that aliphatic diacetyl dichlorides are effective in these cyclization reactions in proper combination with aromatic or aliphatic diamines. In gloutaric dichloride (**f**) the distance between the reactive chlorine atoms is similar to that in isophthaloyl dichloride. The dichloride was found quite reactive in the cyclization reaction with the **a**[**aH$_2$**]$^{2+}$**a** interlayer associations and afforded macrocycle **4**. The IR spectra showed the characteristic bands of the amide formation, while the ^{1}H NMR spectra, were also typical of the cyclic tetraamide macrocycle (see Figure 3).

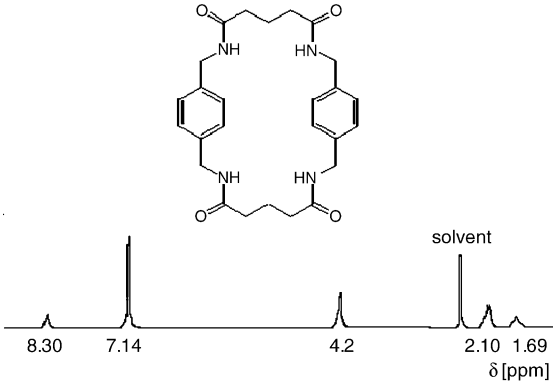


Figure 3. NMR spectra of the macrocycle **4**.

The above paradigms demonstrate that clay interlayer reactions comprise effective routes for amide cyclization, providing that the participating components possess the right dimensions. Successful results were obtained with *p*-xylylenediamine and the aliphatic 2,6-hexanediamine of similar length. A characteristic property of the latter is the flexibility of its skeleton, in contrast with the rigid *p*-xylylene diamine. In spite the fact that the intermolecular association of neutral 2,6-hexanediamine molecules with the clay/*p*-xylylene diamine derivative did not cause any significant change in the layers separation, the condensations that followed the introduction of isophthaloyl, pyridyl or thiophenyl diacetyl diclorides into the clay layers led to the formation of macrocycles **5**, **6** and **7**. Similarly, the combination of 2,6-hexanediamine and gloutaric diacetyl dichloride led to the aliphatic macrocycle **8**. Even though the yields with the aliphatic diamine were low (see Experimental Section), the successful cyclizations proved nonetheless that the interlayer reactions can be further advanced to include other aliphatic diamines. The prime importance of the size factor was demonstrated by using smaller aliphatic diamines, such as 1,3-propyl diamine. In this instance, the amide bonds were formed, but the final solid was a mixture of oligomeric amides with no signs from cyclization products.

The present results clearly demonstrate that amine based organo-clays can act as efficient scaffolds to synthesize a series of amidic macrocycles. The method affords the macrocycles in free form and very good yield without the use of a cyclization directing agent necessary in the classical solution synthesis. The formation of supramolecular structures formed between protonated diamine organoclays and neutral diamine molecule seems to be the crucial factor influencing the final result. An equally important factor for successful cyclization is the right combination of participating molecules with respect to the necessary geometrical conditions.

Experimental Section

Materials: The clay used in this study was a natural Wyoming sodium montmorillonite SWy-1, obtained from the Source Clay Minerals Repository at the University of Missouri, Columbia. It was purified following well established procedures in clay science. The cationic exchange capacity (CEC), as determined by the cobalt method,[12] was equal to 80 mequiv per 100 g clay. For the NMR measurements the synthetic clay laponite (from Laporte Industries Ltd) was used. Laponite is a trioctahedral hectorite with structural formula: $Na_{0.8}[Mg_{5.4}Li_{0.4}]Si_8O_{20}(OH)_4$. It is free of paramagnetic centers and has a cation exchange capacity (CEC) of 48.1 mequiv per 100 g clay. *p*-Xylylene diamine, 1,6-hexanediamine, pyridine 2,6-dicarboxylic dichloride, thiophene 2,5-dicarboxylic dichloride, gloutaric dichloride and isophthaloyl dichloride reagents were obtained from Aldrich Chemicals.

Preparation of *p*-xylylene diamine organo-clay: A solution of the *p*-xylylenediamine dihydrochloride salt (125 mg) in water (20 mL, 0.6 mmol, 1.5 × CEC) was added to a stirred clay suspension of Na^+-MNT (1 g) in water (20 mL). The mixture was stirred for 1 h, centrifuged, washed with water three times and air-dried.

Synthesis of macrocycles in the clay intergalleries: For the synthesis of macrocycles (**1**–**8**) different diamines and dichlorides were used as described below. The dry powder of the *p*-xylylene diamine organo-clay was dispersed in water (30 mL) and to this mixture, a solution of the appropriate diamine (0.8 mmol, 2 × CEC) in water (40 mL) was added. The mixture was stirred for 1 h, and the solid collected by centrifugation without washing and air-dried. The dry powder was dispersed into CH_3CN

(20 mL) and an additional CH_3CN solution (20 mL), containing the corresponding diacetyl dichloride (2.4 mmol) and Et_3N (2.4 mmol), was added and the mixture was stirred for 24 h at room temperature. The resulted clay composites were collected by centrifugation and washed with CH_3CN (20 mL).

Extraction of products from the clay: The clay composites were dispersed in LiCl/DMSO solution (20 mL) in order to remove the organic components from the clay. After stirring for 2 h, the clay was removed by centrifugation and acetone (50–70 mL) was added to precipitate the amide tetramer and the *p*-xylylenediamine dihydrochloride salt. The solid mixture was treated with a diluted Na_2CO_3 solution (5%) to convert the diamine salt into the water soluble neutral diamine, leaving behind the tetramide as pure solid. The yields of the reactions are listed below.

Characterization: The X-ray powder diffraction patterns were collected on a D8 Advance Bruker diffractometer by using CuK_α (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2θ (2Θ) range from 2 to 80°, in steps of 0.02° and counting time 2 s per step. IR spectra were measured with a Bruker Equinox 55S IR spectrometer, in the region of 400–4000 cm^{-1}, equipped with a DTGS detector. Each spectrum was the average of 200 scans collected at 2 cm^{-1} resolution. Samples were in the form of KBr pellets containing ca. 2 wt% sample. ^1H NMR spectra were obtained in [D_6]DMSO with a Bruker AC250 spectrometer operating at 250 MHz. Mass spectra were recorded with a Finnigan Mat GCQ. Elemental analyses were performed in duplicate with a CARLO-ERBA CHNS-O EA-1108 elemental analyzer.

Macrocycle 2: Macrocycle **2**[8b] was prepared in 60% yield, using *p*-xylylene diamine and pyridine 2,6-dicarboxylic dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 4.40$ (s, 8H, CH_2), 7.24 (s, 8H, *p*-xylyl H), 8.16 (m, 6H, pyridyl H), 10.10 (t, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1658, 1537 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{30}H_{26}N_6O_4$ (534): C 67.40, H 4.90, N 15.72, O 11.97; found: C 67.43, H 4.90, N 15.69, O 11.98; m.p. 296–298 °C; EI-MS: *m*/*z*: 534 [M^+].

Macrocycle 3: Macrocycle[8b] **3** was prepared in 63% yield, using *p*-xylylene diamine and thiophene 2,5-dicarboxylic dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 4.40$ (s, 8H, CH_2), 7.21 (s, 8H, *p*-xylyl H), 7.72 (s, 4H, thiophenyl H), 9.16 (t, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1632, 1553 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{28}H_{24}N_4O_4S_4$ (544) C 61.75, H 4.44, N 10.29, O 11.75, S 11.77; found: C 61.78 H 4.45, N 10.32, O 11.73 S 11.72; m.p. 300 °C (decomp); EI-MS: *m*/*z*: 544 [M^+].

Macrocycle 4: Macrocycle **4** was prepared in 65% yield, using *p*-xylylene diamine and gloutaric dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta =$ 1.69 (m, 4H$_\delta$, CH_2), 2.10 (m, 8H$_\varepsilon$, CH_2), 4.2 (d, 8H, CH_2), 7.14 (s, 8H, *p*-xylyl H), 8.30 (t, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1640, 1549 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{26}H_{32}N_4O_4$ (464): C 67.22, H 6.94, N 12.06, O 13.78; found: C 67.27, H 6.89, N 12.12, O 13.72; m.p. 238–240 °C; EI-MS: *m*/*z*: 464 [M^+].

Macrocycle 5: Macrocycle **5** was prepared in 35% yield, using 1,6-hexanediamine and isophthaloyl dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 1.30$ (m, 8H$_\alpha$, CH_2), 1.49 (m, 8H$_\beta$, CH_2), 3.20 (s, 8H$_\gamma$, CH_2), 7.46 (t, 2H, isophthaloyl 5-H), 7.90 (d, 4H, isophthaloyl 4-H and 6-H), 8.36 (s, 2H, isophthaloyl 2-H), 8.67 (t, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1639, 1532 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{28}H_{36}N_4O_{40}$ (492): C 68.27, H 7.37, N 11.37, O 12.99; found: C 68.30, H 7.35, N 11.35, O 13.00; m.p. 176–178 °C; EI-MS: *m*/*z*: 492 [M^+].

Macrocycle 6: Macrocycle **6** was prepared in 30% yield, using 1,6-hexanediamine and pyridine 2,6-dicarboxylic dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 1.17$ (m, 8H$_\alpha$, CH_2), 1.40 (m, 8H$_\beta$, CH_2), 3.20 (s, 8H$_\gamma$, CH_2), 8.12 (m, 6H, pyridyl), 9.40 (m, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1640, 1560 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{26}H_{34}N_6O_4$ (494): C 63.14, H 6.93, N 16.99, O 12.94; found: C 63.18, H 6.90, N 17.05, O 12.87; m.p. 280 °C (decomp); EI-MS: *m*/*z*: 494 [M^+].

Macrocycle 7: Macrocycle **7** was prepared in 32% yield, using 1,6-hexanediamine and thiophene 2,5-dicarboxylic dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 1.05$ (m, 8H$_\alpha$, CH_2), 1.25 (m, 8H$_\beta$, CH_2), 3.00 (s, 8H$_\gamma$, CH_2), 7.30 (s, 4H, thiophenyl), 8.30 (m, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1638, 1558 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{24}H_{32}N_4O_4S_2$ (504): C 57.12, H 6.39, N 11.10, O 12.68, S 12.71; found: C 57.15, H 6.42, N 11.15, O 12.62, S 12.66; m.p. 252–254 °C; EI-MS: *m*/*z*: 504 [M^+].

Macrocycle 8: Macrocycle **8** was prepared in 30% yield, using 1,6-hexanediamine and gloutaric dichloride. ^1H NMR (200 MHz, DMSO, 18 °C): $\delta = 1.20$ (m, 8H$_\alpha$, CH_2), 1.30 (m, 8H$_\beta$, CH_2), 1.65 (m, 2H$_\gamma$, CH_2), 2.01 (m, 2H$_\delta$, CH_2), 2.90 (s, 8H$_\varepsilon$, CH_2), 7.90 (s, 4H, CONH); FT-IR (KBr): $\tilde{\nu}$: 1628, 1550 cm^{-1} (CONH); elemental analysis (%) calcd for $C_{22}H_{40}N_4O_4$ (464) C 67.22, H 6.94, N 12.06, O 13.78; found: C 67.20, H 6.90, N 12.10, O 13.80; m.p. 194–196 °C; EI-MS: *m*/*z*: 464 [M^+].

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