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Artigo

^{1}H NMR STUDY OF THE HOST-GUEST CHEMISTRY IN A SUPRAMOLECULAR HELICATE $Fe^{II}_2L_3$ SOLUTION

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A novel $[Fe^{II}_2L_3]^{4+}$ metallo-organic helicate results from subcomponent self-assembly of a C_3-symmetric triamine (4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline), octahedral iron(II) and 2-formyl pyridine in CH_3CN solution. The constitution of this supramolecular helicate was confirmed by ESI-MS and ^{1}H NMR spectra. Different planar aromatic guests were selected to investigate host-guest interactions by shifts of ^{1}H NMR signals. The results show that electron-rich aromatic molecules with matched size and symmetry, such as pyrene, are subject to be bound with the outstretched arms of the helicate ligand via aromatic π–π interactions.

Keywords: self-assembly; helicate complex; iron(II); host-guest chemistry.

INTRODUCTION

The supramolecular self-assembly strategies and principals of metallo-organic complexes through the formation of dynamic-covalent (C=N) and coordinative (N→M) bonds have been investigated detailly during the past decade.[1-3] Among this tremendously expanding family, helicate complex is generally regarded as the intermediate product of the steady state of the final thermodynamic product formation.[4] Nevertheless, comparing to the well established building processes of helicate architectures,[5-8] the non-covalent interactions with guest molecules of these spiral species are less studied due to the limited inner cavity. However, the host still contains potentially active groups such as amino or phenyl groups, which could offer supramolecular interactions, including hydrogen bonding, donor–acceptor interaction or aromatic (π–π) interaction.[9-12]

NMR spectroscopy is a uniquely powerful tool for the study of structure, geometry and kinetics in almost every aspect in chemistry. Without perturbing the system it can provide detailed mechanistic and kinetic information about reactions that are occurring in equilibrium mixtures. It's especially suitable for real time study of the dynamic non-covalent interactions in solution, where the exchange rate may be slower than 10^{-2} or faster than 10^8 s^{-1}, just among the NMR time scale.[13]

In this paper, a novel $[Fe^{II}_2L_3]^{4+}$ helicate was obtained in a single overall process by self-assembly of subcomponents. Then, the interactions between the host and selected aromatic guests were studied by ^{1}H NMR spectroscopy, so as to better understand the supramolecular behaviors of the helicate in solution.

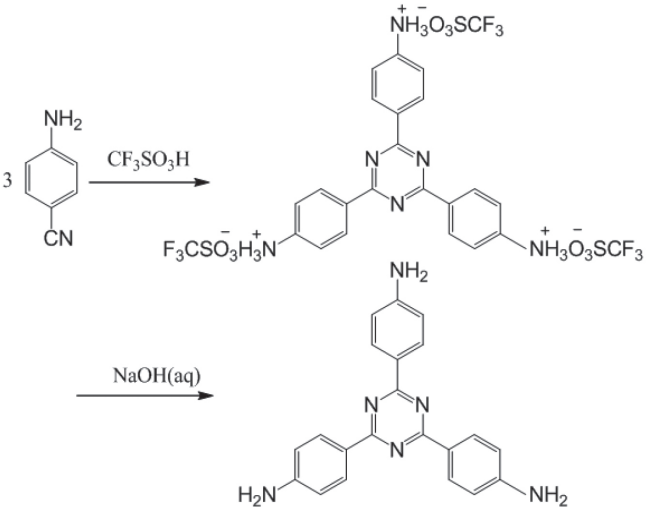
EXPERIMENTAL

Materials and apparatus

All reagents were of commercial origin and used without further purification, except otherwise stated. ^{1}H NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer. The following acquisition parameters were employed: NS (number of scans) = 16, P1 (90° pulse) = 12.28 μs, TD (size of fid) =65536, D1 (relaxation delay) = 5 s, AQ (acquisition time) = 51 s and T (temperature) = 293 K. Electrospray ionisation mass spectrometry (ESI-MS) was recorded with a Micromass Quattro LC instrument (cone voltage 10-30 eV; desolvation temp. 313 K; ionization temp. 313 K), infused at a rate of 10 μL per minute.

Synthesis of the subcomponent triamine

The trifluoromethanesulfonic acid (4 mL, 44.4 mmol) was added slowly to a solution of 3-aminobenzonitrile (1180 mg, 10 mmol) in 20 mL of dichloromethane under 0 °C. The reaction mixture was stirred under N_2 atmosphere at room temperature for 12 h. After the reaction, the upper yellow layer was separated. Distilled water (20 mL) and 2 mol L^{-1} NaOH were added slowly until pH = 12-13 to give a pale yellow solid (Scheme 1). The desired product was collected by filtration, washed twice with distilled water and dried under vacuum. Yield 85.0%, m.p. 381-382 °C; ^{1}H NMR (400 MHz, DMSO) δ8.38 (d, J = 8.5 Hz, 6H, Benzene-H), 6.71 (d, J = 8.5 Hz, 6H, Benzene-H), 5.90 (s, 6H, NH_2).



Scheme 1. *Synthesis of subcomponent triamine*

Self-assembly of helicate 1

The triamine (106.3 mg, 0.3 mmol), iron(II) trifluoromethanesulfonate ($Fe(OTf)_2$, 70.8 mg, 0.2 mmol) and 2-formylpyridine (64.27 mg, 0.6 mmol) in CH_3CN (5 mL) were

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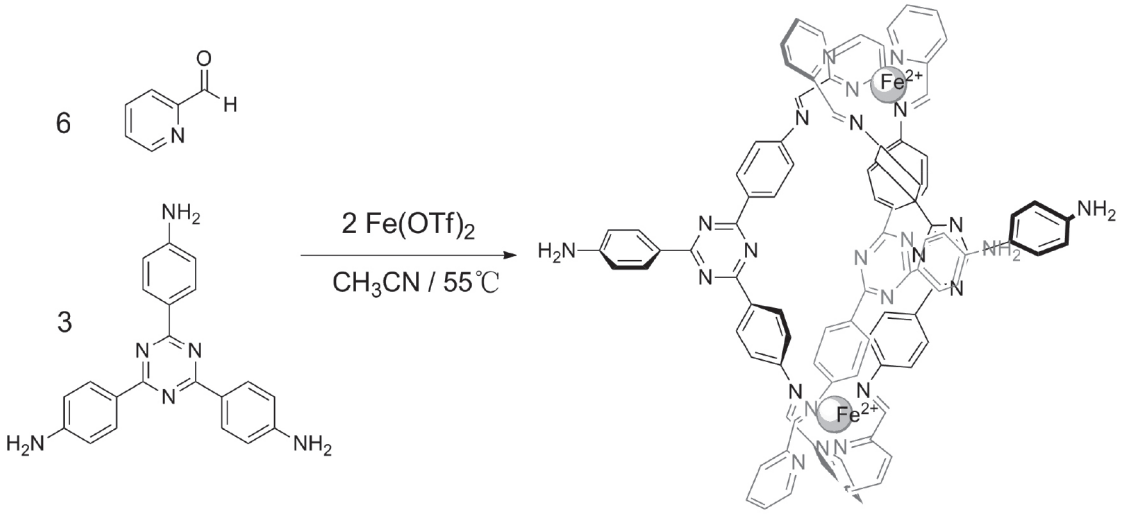
combined under N_2 atmosphere and stirred at 55 °C for 12 h. After the reaction, the solution was cooled to room temperature and Et_2O (10 mL) was added. The salt of helicate **1** ($[Fe^{II}_2L_3]$)·$(OTf)_4$ was precipitated and collected by filtration to give a dark purple solid (Scheme 2). Yield: 57.3%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.98 (s, 1He), 8.69 (d, J = 6.5 Hz, 1Hg'), 8.63 (d, J = 6.4 Hz, 1Hd), 8.44-8.50 (m, 1Hg&1Hh&1Hc), 7.82 (t, 1Hb), 7.44 (d, J = 4.5 Hz, 1Ha), 6.78 (d, J = 7.9 Hz, 1Hi), 6.00 (d, J = 6.4 Hz, 1Hf'), 4.96 (s, 1H, amine), 4.68 (d, J = 7.5 Hz, 1Hf). ESI-MS: m/z 427.58.

RESULT AND DISCUSSION

Structural features of the helicate

The constitution of helicate **1** was confirmed by ^{1}H NMR and ESI-MS (Figure 1 and Figure 2). Simply one set of ligand signals not only proves the achievement of self-assembly but also suggests the presence of high symmetry in the architecture. Both the peak of helicate **1** (m/z 427.4, Figure 2) and protonated triamine fragment (m/z 355.2, Figure 2) were found in the ESI-MS spectrum. As the crystal of **1** suitable for X-ray determination has not been achieved yet, a *MM2*-optimized molecular model[14] based on the crystal structures of similar Fe_2L_3 helicate series with different C_3-symmetric triamines[7] is used to discuss the structure of helicate **1**.

The *MM2* model of helicate **1** (Figure 3) is depicted with the entire complex which contains three schiffbase ligands *L* linked by two iron (II) centers through coordinative bonds. Both iron (II) cations adopt octahedral coordination, and the distance between them is 14.04 Å. There is an open space in this complex kernel, about 5.72 Å × 4.17 Å intersecting area. A counter ion of OTf^- could be bound here, which explains the m/z peak of 619.5 (Figure 2). At the same time, there are three outstretched arms in the complex, containing



Scheme 2. *Self-assembly of the helicate **1***

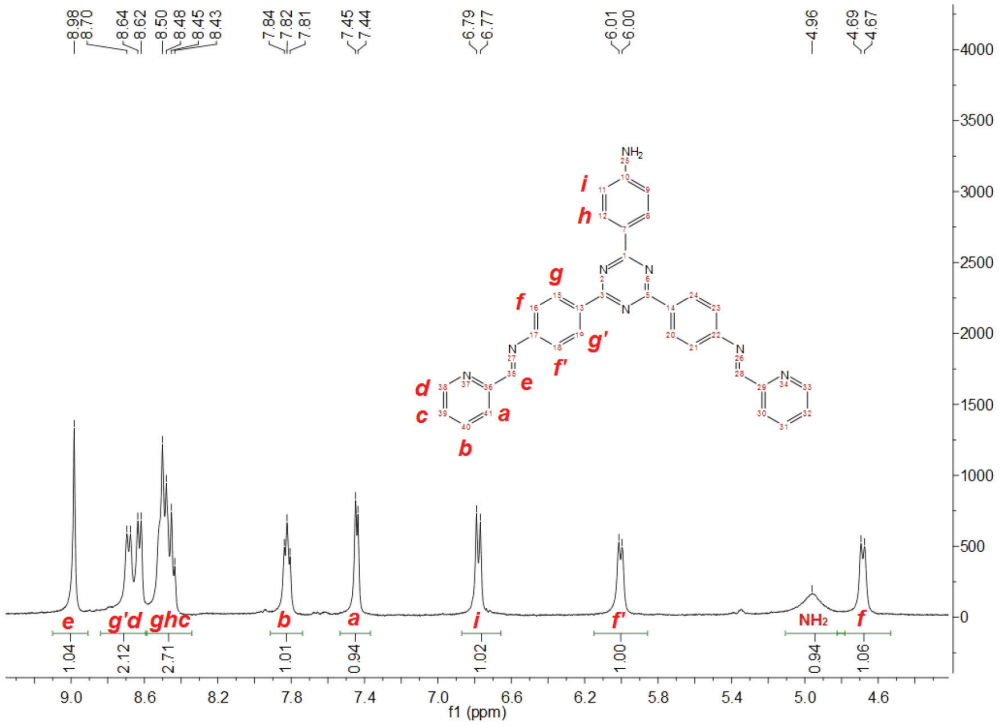


Figure 1. *Assignment of H atoms in helicate **1***

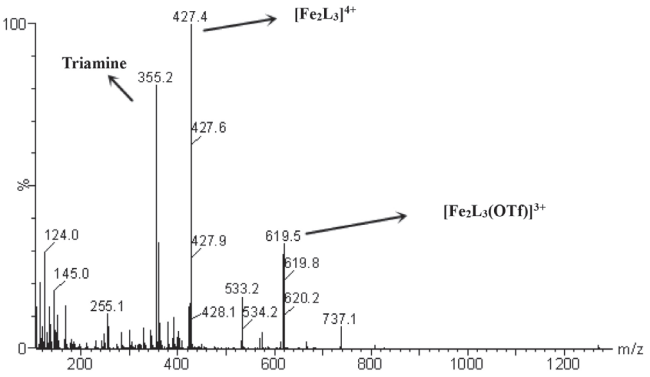


Figure 2. *ESI-MS peaks of helicate **1** in CH_3CN solution*

amine penyl-rings and triazine groups, which could provide potential non-covalent interactions, such as hydrogen bonding, aromatic (π–π) and cation–π interactions.

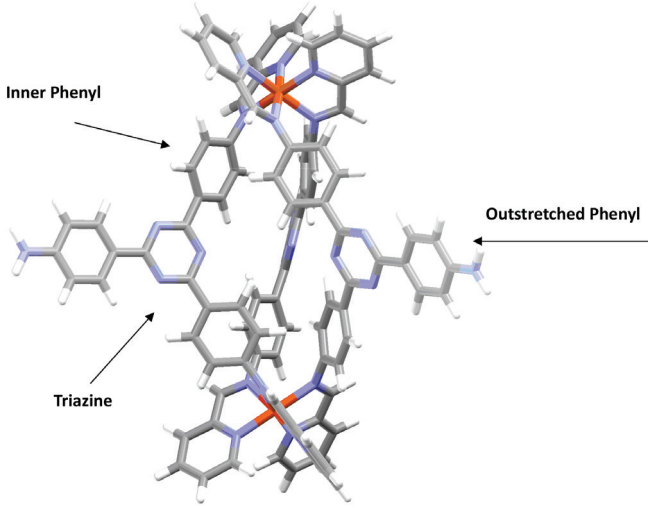


Figure 3. *Front view of the MM2 model of helicate **1***

^{1}H NMR studies of host-guest chemistry

Eight planar aromatic guests (Scheme 3) were selected to research the interactions with helicate **1** through ^{1}H NMR spectrometry. To a stirred solution of the host helicate **1** (0.010 mmol, 1 eq) in 1.0 mL CD_3CN was added slowly one of the chosen guest molecules (0.10 mmol, 10 eq) respectively. Once all guest molecules had been added, the mixture was stirred at least for 2 h. Analyzed by the ^{1}H NMR spectrometry, the data of interactions between the host and guests were obtained.

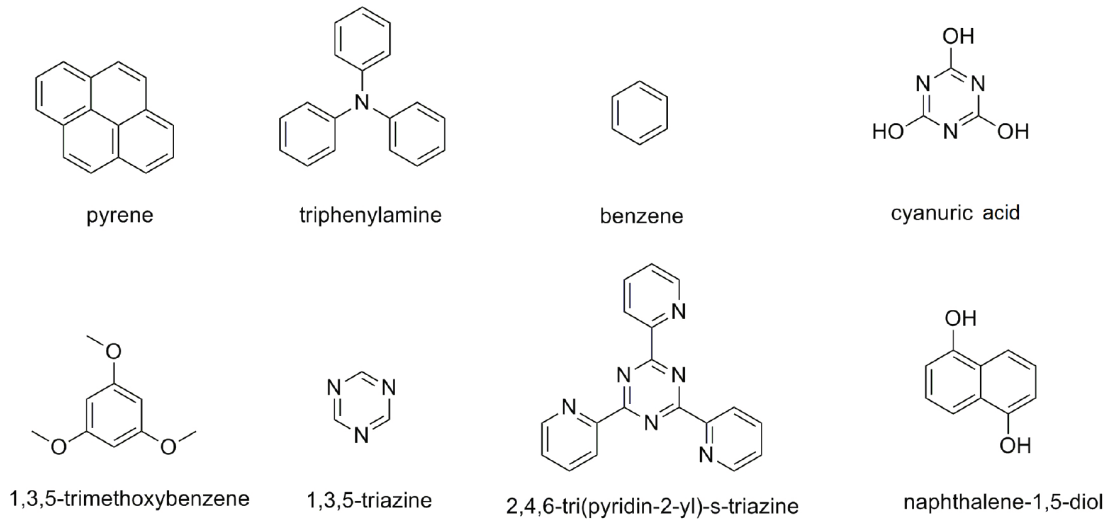
The ^{1}H NMR spectra show that, after adding the molecules of each guest, the changes in the signals of host and guest protons were quiet different. The signals attributed to the guest molecules were kept in one set and changed slightly in comparison with the ^{1}H NMR of free guests ($\Delta\delta < 0.02$ ppm), which reflects the rapidly exchange mode between the free and bound states of guests on the NMR time scale.[15] Meanwhile signals corresponding to helicate **1** were changed more or less after the addition of each guest molecule (Table 1).

The resonance of the protons shifted upfield ($\Delta\delta<0$) in the conjugated host ligand is related to the increasing of the electron shielding, which may be attributed to the host-guest interactions with electron-rich molecules.[16] When the pyrene molecules were added to the host solution, the significant shifts occurred. This is a strong evidence to support our deduction. Various equivalents of pyrene guest were added into the host solution of helicate **1** to obtain the titration curve (Figure 4), which clearly exhibited the influence of guest molecules on the ^{1}H NMR signals of host.

The most significantly shifted signals in helicate **1** were found from the protons adjacent to triazine ring ($H_h/H_f/H_{f'}/H_{g'}$), which infers the occurrence of π-π interactions around here (Figure 6a). However even H_h recorded a maximum shift ($\Delta\delta$ = -0.57) in the 14 eq guest solution, the δ values of H_h were overlapped with the guest resonances and thus covered by much stronger pyrene signals in the 6 eq ~ 10 eq guest solutions (Figure 4). So the secondary shifted signal which is from proton H_f would be tracked instead in later analysis.

A triangular double helicate which was also self-assembled by triazine based ligand could bind pyrene guests more stably than any other guests, suggesting the pyrene is perfectly matched with the central triazine core of the helicate.[17] The guest naphthalene-1,5-diol also contains electron-rich planar structure, while the most down shifts ($\Delta\delta$ = -0.06~-0.08 ppm) of naphthalene-1,5-diol are much smaller than those of pyrene. It's inferred that the symmetrical characteristic is unmatched between host and guest geometry.

The ^{1}H NMR signals of others guests moved even more slightly. Cyanuric acid is almost insoluble in CD_3CN and thus caused none impact on host molecules. 1,3,5-trizaine containing election-deficient N atoms is not a good donor for π-π interaction. There is



Scheme 3. *Guest molecules tested with helicate **1***

Table 1. Summary changes of chemical shift value of protons in helicate ligand during the host-guest (1:10 eq) interaction

δ / ppm		Host only	Host + pyrene	Host + naphtha-lene-1,5-diol	Host + 1,3,5-triazine	Host + 1,3,5-tri-methoxy benzene	Host + triphenyl amine	Host + cyanuric acid	Host + Benzene	Host + 2,4,6-tripyr-idinyl-triazine
pyridyl H	**a**	7.44	7.43(-0.01)	7.42 (-0.02)	7.46(0.02)	7.45(0.01)	7.45 (0.01)	7.45(0.01)	7.45 (0.01)	Disassembly of the helicate observed
	b	7.82	7.83 (0.01)	7.80 (-0.02)	7.83(0.01)	7.83 (0.01)	7.83 (0.01)	7.83(0.01)	7.82 (0.00)	
	c	8.44	8.45 (0.01)	8.42 (-0.02)	8.44(0.00)	8.44(0.00)	8.44 (0.00)	8.44(0.00)	8.44 (0.00)	
	d	8.63	8.64 (0.01)	8.60 (-0.03)	8.64(0.01)	8.63(0.00)	8.63 (0.00)	8.63(0.00)	8.63 (0.00)	
Imine H	**e**	8.98	8.88(-0.10)	8.92(-0.00)	9.00(0.02)	8.99(0.01)	8.97(-0.01)	8.99(0.01)	8.98(0.00)	
Inner phenyl H	**f**	4.68	4.44(-0.24)	4.62(-0.06)	4.70(0.02)	4.68(0.00)	4.68 (0.00)	4.69(0.01)	4.68 (0.00)	
	f'	6.01	5.90(-0.10)	5.96(-0.04)	6.02(0.02)	6.00(0.00)	6.00 (0.00)	6.01(0.01)	6.00(0.00)	
	g	8.50	8.47(-0.03)	8.52(0.02)	8.52(0.02)	8.50 (0.00)	8.49(-0.01)	8.50(0.00)	8.50 (0.00)	
	g'	8.69	8.59(-0.10)	8.67 (-0.02)	8.69 (0.00)	8.69(0.00)	8.68(-0.01)	8.69(0.00)	8.69(0.00)	
Outstretched phenyl H	**h**	8.48	Covered	8.42(-0.06)	8.48(0.00)	8.46(-0.02)	8.47(-0.01)	8.47(-0.01)	8.48(0.00)	
	i	6.78	6.82 (0.04)	6.79(0.01)	6.78(0.00)	6.77(-0.01)	6.87(-0.01)	6.78(0.00)	6.78(0.00)	
amino H		4.96	broadening	broadening	4.95(-0.01)	broadening	broadening	broadening	broadening	

All signals were calibrated base on the CH_3CN solution peak δ = 1.94 ppm. Covered= signals covered by the peaks of guest, cannot be recognized clearly.

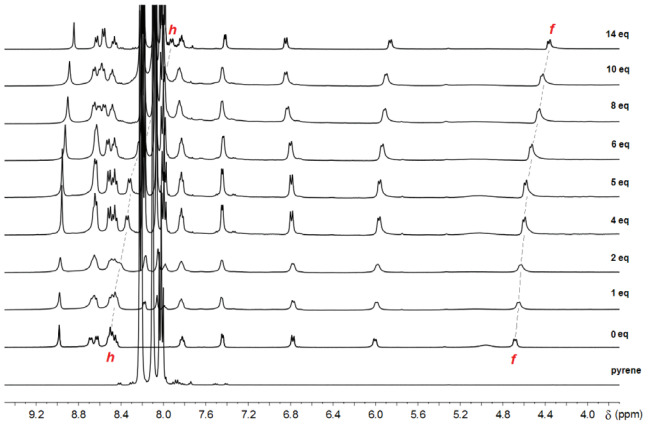


Figure 4. *^{1}H NMR titration of pyrene guest into a solution of helicate **1** in CD_3CN (equivalents of guest are labeled on individual spectra)*

also an N atom at the center of triphenylamine, which separates the phenyl conjugation in the molecule and reduces the supramolecular interaction ability. 1,3,5- trimethoxy benzene not only contains electron withdrawing O atoms but also is not strictly flat, which explains the slight displacement of host NMR signals. The benzene maybe is just too small to adhere the hosts. At last, although 2,4,6-tripyridinyl-triazine is a relatively large conjugated aromatic molecule, it's also a strong terdentate ligand, which makes the helicate disassembled according to the NMR spectrum.

The binding stoichiometry between helicate **1** and pyrene was determined by Job's method of continuous variations by ^{1}H NMR spectrometry.[17,18] Stock solutions of helicate **1** and pyrene were prepared both in 0.010 mM CD_3CN solution. By stepwise addition of varying amounts of pyrene solution to the NMR tube, the total concentration of the host and guest was kept constant (0.010 mM) while the molar fraction between the two was varied. After each addition, a ^{1}H NMR spectrum was recorded (Table 2).

Table 2. Data from the Job plot determination between helicate **1** and pyrene performed by ^{1}H NMR titration in CD_3CN at 298 K

No.	V_1/mL	V_{pyrene}/mL	$C_1/10^{-5}$ M	$C_{pyrene}/10^{-5}$ M	$C_{1+Pyrene}/10^{-5}$ M	χ_1	δHf [ppm]	$-\Delta\delta H_f$ [ppm]	$-\chi_1*\Delta\delta H_f$ [ppm]
1	0.50	0.00	1.00	0.00	1.00	1.00	4.68	0.00	0.000
2	0.50	0.075	0.87	0.13	1.00	0.87	4.67	0.01	0.0087
3	0.50	0.30	0.625	0.375	1.00	0.625	4.65	0.03	0.01825
4	0.50	0.50	0.50	0.50	1.00	0.50	4.63	0.05	0.025
5	0.25	0.375	0.40	0.60	1.00	0.40	4.60	0.08	0.032
6	0.25	0.50	0.33	0.67	1.00	0.33	4.57	0.11	0.0363
7	0.30	0.70	0.30	0.70	1.00	0.30	4.55	0.13	0.0390
8	0.25	0.75	0.25	0.75	1.00	0.25	4.52	0.17	0.0425
9	0.25	1.00	0.20	0.80	1.00	0.20	4.50	0.18	0.0360
10	0.25	1.25	0.167	0.833	1.00	0.167	4.49	0.19	0.0317
11	0.125	0.75	0.143	0.857	1.00	0.143	4.48	0.20	0.0286
12	0.125	1.00	0.111	0.889	1.00	0.111	4.46	0.22	0.0244
13	0.125	1.25	0.091	0.909	1.00	0.091	4.44	0.24	0.0218
14	0.125	1.75	0.067	0.933	1.00	0.0667	4.42	0.26	0.0173
15	0	0.50	0	1.00	1.00	0	-	-	0

As shown in Table 1, the signal of the proton H_f in helicate **1** was shifted upfield as the mole fraction of pyrene was increased. The change in chemical shifts ($\Delta\delta$) was multiplied by the molar fraction of **1** (χ_1) and plotted against χ_1 to obtain the Job plot (Figure 5). A maximum of $-\chi_1*\Delta\delta_{Hf} = 0.425$ ppm at $\chi_1 = 0.25$ was obtained, as it's the value of the *x* axis that indicates the 1:3 stoichiometry between helicate **1** and pyrene.

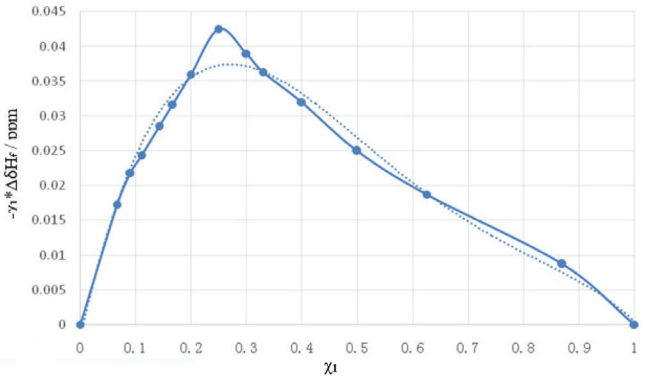


Figure 5. *Job plot between helicate **1** and pyrene showing a maximum of 0.425 at the 1:3 binding ratio*

According to the changes in the protons signals of host ligand (Figure 6a) and the host-guest binding ratio, a *MM2* model containing both host and guests is built (Figure 6b). It suggests that each outstretched arm of helicate cooperates with one pyrene molecule via aromatic π-π interactions. The electron-rich pyrene served as electron donor leans close to the electron-poor triazine-ring, offering the donation of electron density from the guest to the host. The overall up field shifts of host ^{1}H signals around the triazine were thus observed.

CONCLUSION

To sum up, a novel helicate $[Fe^{II}_2L_3]^{4+}$ with potential supramolecular interactions has been synthesized and a host-guest studying method based on the displacement of ^{1}H NMR signals has been attempted. The size and symmetry of the guest molecules impacted the patterns of the host-guest dynamic process significantly. The electron-rich aromatic molecules, such as pyrene, were more inclined to be bound with the flat part around the electron-poor triazine ring in the helicate ligand via aromatic π-π interactions. A job's plot titration analysis suggests the ratio between helicate host and pyrene guest is 1:3, which coincides with above mentioned supramolecular interaction mode.

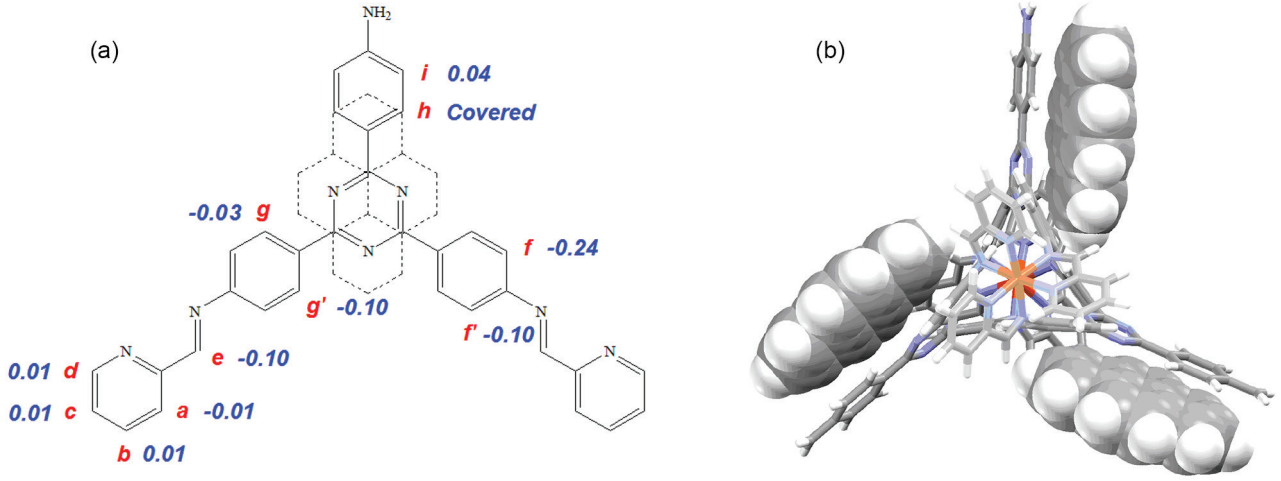


Figure 6. ***(a)*** *The host-guest interaction pattern between helicate ligand and pyrene (dotted line, 10eq) with the shifting of corresponding ^{1}H NMR signals;* ***(b)*** *top view of a MM2 model of helicate **1** binding three pyrene molecules*

SUPPLEMENTARY MATERIAL

Figures 1S to 17S (^{1}H NMR spectra) are freely available at http://quimicanova.sbq.org.br, in PDF format.

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