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SELF-ASSEMBLY AND HOST-GUEST BEHAVIORS OF A SUPRAMOLECULAR HELICATE $\mathrm{FE}^{II}_2\mathrm{L}_3$

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A novel helicate complex $[\mathrm{Fe}^{II}_2\mathrm{L}_3]^{4+}$ resulted from subcomponent self-assembly of a C_3-symmetric triamine, 2-formylpyridine and octahedral iron(II) in CH_3CN, which was confirmed by ESI-MS measurement. After the addition of selected planar aromatic molecules in CD_3CN solution, shifts of ^{1}H NMR signals of the helicate were investigated. The results revealed that the size, functional group and symmetry of guest molecules remarkably influence the interaction patterns.

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

INTRODUCTION

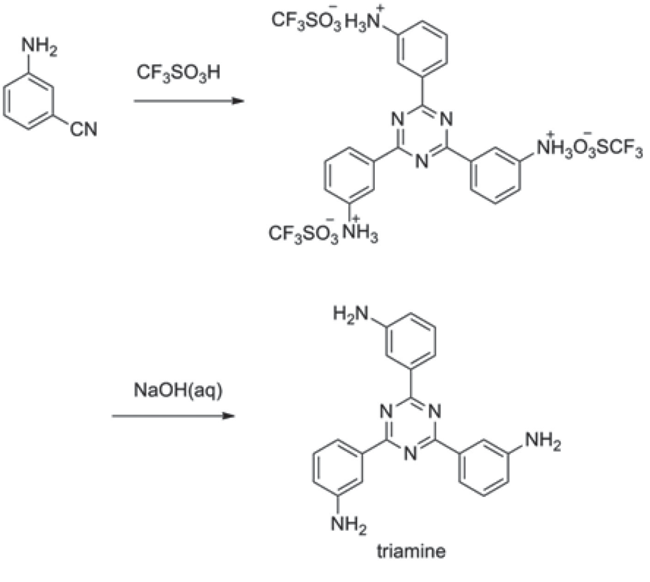
Supramolecular chemistry is"the chemistry beyond the molecule", the science of non-covalent interactions, which are weak but enormously important in chemistry and biology.[1] The supramolecular self-assembly strategies and principals of metal-organic complexes have been a topic of great interest in recent years due to its design maneuverability and regulation possibility.[2] Such subcomponent self-assembly molecules which are condensed by simple building blocks through the formation of dynamic-covalent(C=N) and coordinative (N→M) bonds[3,4] have affluent figures such as rotaxanes,[5] catenans,[6,7] grids,[8,9] tetrahedra,[10-12] cubes,[13] etc. They all have profound application prospects in the field of molecular recognition and separation,[14,15] chemical sensors[16] and specific catalysis.[17,18] Among these, helicates are often regarded as metastable intermediates from the forming process of final thermodynamic product.[19] The building of helical architectures is well established,[20-23] helping our understanding of self-assembly processes. Yet the non-covalent interactions of the helicate complexes are less investigated, as their constructions are reported to be spiral with limited space in central cores, which may not encapsulate even small molecules. However these hosts still are excellent candidates for incorporation into supramolecular networks to explore complex and stimuliresponsive behaviors[24-27] due to their potential non-covalent interaction abilities, such as hydrogen bonding, aromatic (π–π) and cation–π interactions. Investigating of these common and propound species in the nature[28] that may allow for new functions to be designed beyond single host-guest systems should never be ignored.

In this paper, a novel $[\mathrm{Fe}^{II}_2\mathrm{L}_3]^{4+}$ helicate **1** (L = (NE,N'E) -3,3'- (6-(3-aminophenyl) -1,3,5-triazine-2,4-diyl) bis (N-(pyridin-2-ylmethylene)aniline)) has been prepared from self-assembly of subcomponents: C_3-symmetric triamine (3,3',3''- (1,3,5-triazine-2,4,6-triyl) trianiline), Iron(II) trifluoromethanesulfonate ($\mathrm{Fe(CF_3SO_3)_2}$) and 2-formylpyridine. Then the host-guest interactions with selected aromatic guests were investigated by ^{1}H NMR and UV-Vis spectra to better understand the supramolecular mechanism of the helicates in CD_3CN solution.

EXPERIMENTAL

Materials and apparatus

Unless otherwise specified, all starting materials were purchased from commercial sources and used as supplied. Manipulations were performed under normal atmospheric conditions unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker Avance DPX400 spectrometer; ESI-MS was performed on a Micromass Quattro LC instrument. Electronic absorbance spectra were measured in acetonitrile with a Perkin Elmer Lambda 750 UV−Vis NIR spectrometer.



Scheme 1. *Synthesis of subcomponent triamine*

Synthesis of the subcomponent triamine

A typical synthesis (Scheme 1) of the subcomponent triamine (3,3',3''- (1,3,5-triazine-2,4,6-triyl) trianiline) follows the procedure below. A solution of 3-aminobenzonitrile (827 mg, 7 mmol) in 30 mL of dichloromethane was stirred in an ice bath to maintain the temperature below -5 °C. Trifluoromethanesulfonic acid (3 ml, 33.3 mmol) was added dropwise and the resulting mixture was stirred under N_2 atmosphere for 16 h.[29] After the reaction, the yellow layer

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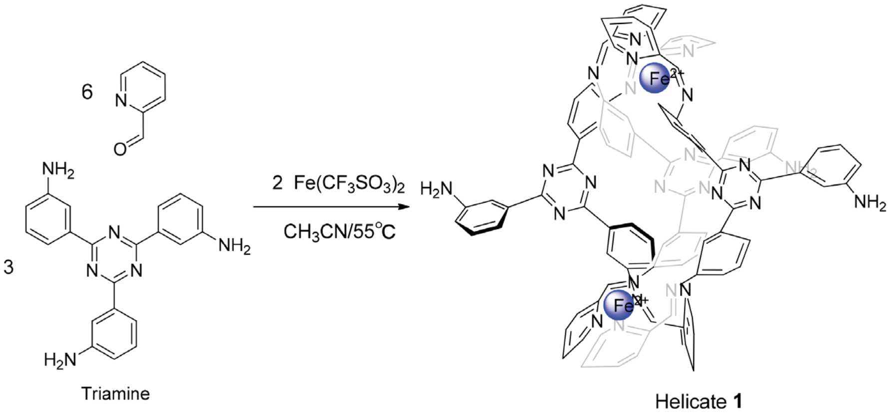
was separated. Distilled water (50 mL) and 2M NaOH solution were added until pH = 13-14 to afford a pale yellow precipitate. The crude product was filtered, washed twice with distilled water and purified by recrystallization in acetone. Yield 60%. ^{1}H NMR (400 MHz, CD_3CN) (Figure 1S): 8.06 (m, 3H), 8.03 (m, 3H), 7.32 (dd, J = 9.8, 5.8 Hz, 3H), 6.93 (ddd, J = 7.9, 2.4, 0.9 Hz, 3H), 4.43 (s, NH_2). Found: C, 71.15; H, 5.13; N, 23.70. Calcd. for $C_{21}H_{18}N_6$: C, 71.17; H, 5.12; N, 23.71.

Scheme 2 shows the self-assembly of the helicate **1**. The triamine (106.3 mg, 0.3 mmol), $Fe(CF_3SO_3)_2$ (70.8 mg, 0.2 mmol) and 2-formylpyridine (64.27 mg, 0.6 mmol) were mixed in CH_3CN (10 mL) and heated to 55 °C under N_2 atmosphere for 12 h. After the reaction, the solution was allowed to cool down to indoor temperature (15 °C). The $[Fe^{II}_2L_3](CF_3SO_3)_4$ was precipitated as a dark purple solid by the addition of Et_2O (10 mL). Yield: 72.3%. ^{1}H NMR (400 MHz, CD_3CN) (Figure 1): 9.07 (s, $2H_e$), 8.72 (d, J = 7.0 Hz, $2H_a$), 8.48 (t, J = 7.4 Hz, $2H_b$), 8.21 (m, $1H_m$&$1H_j$), 7.82(m, $2H_c$), 7.71 (s, $2H_g$&$2H_h$), 7.51 (t, J = 7.5 Hz, $1H_k$), 7.42 (d, J = 5.3 Hz, $2H_d$), 7.03 (d, J = 7.1 Hz, $1H_l$), 6.03 (s, $2H_f$), 5.96 (s, $2H_i$), 4.65 (s, $2H_n$). MS: m/z 427.58 ($[Fe^{II}_2L_3]^{4+}$ peak). Elemental analysis of $[Fe^{II}_2L_3](CF_3SO_3)_4$ (%): Calcd for $C_{103}H_{72}F_{12}Fe_2N_{24}O_{12}S_4$: C, 53.65; H, 3.15; N, 14.58. Found: C, 53.54; H, 3.50; N, 14.51.

RESULT AND DISCUSSION

Structural features of the helicate

The presence of helicate **1** was confirmed by ESI-MS and ^{1}H NMR measurements (Figures 1 & 2). The simple ^{1}H NMR spectrum, displaying only one set of ligand signals reflects the high symmetry of 1. ESI-MS spectrum not only gives the peak of helicate **1** (m/z 427.4, isotope peaks pattern shown in Table 1S and Figure 20S), but also offers the evidence of the protonated ligand (m/z 533.2, isotope peaks pattern shown in Table 2S and Figure 21S). As the crystal of **1** suitable for X-ray determination has not been achieved yet under



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

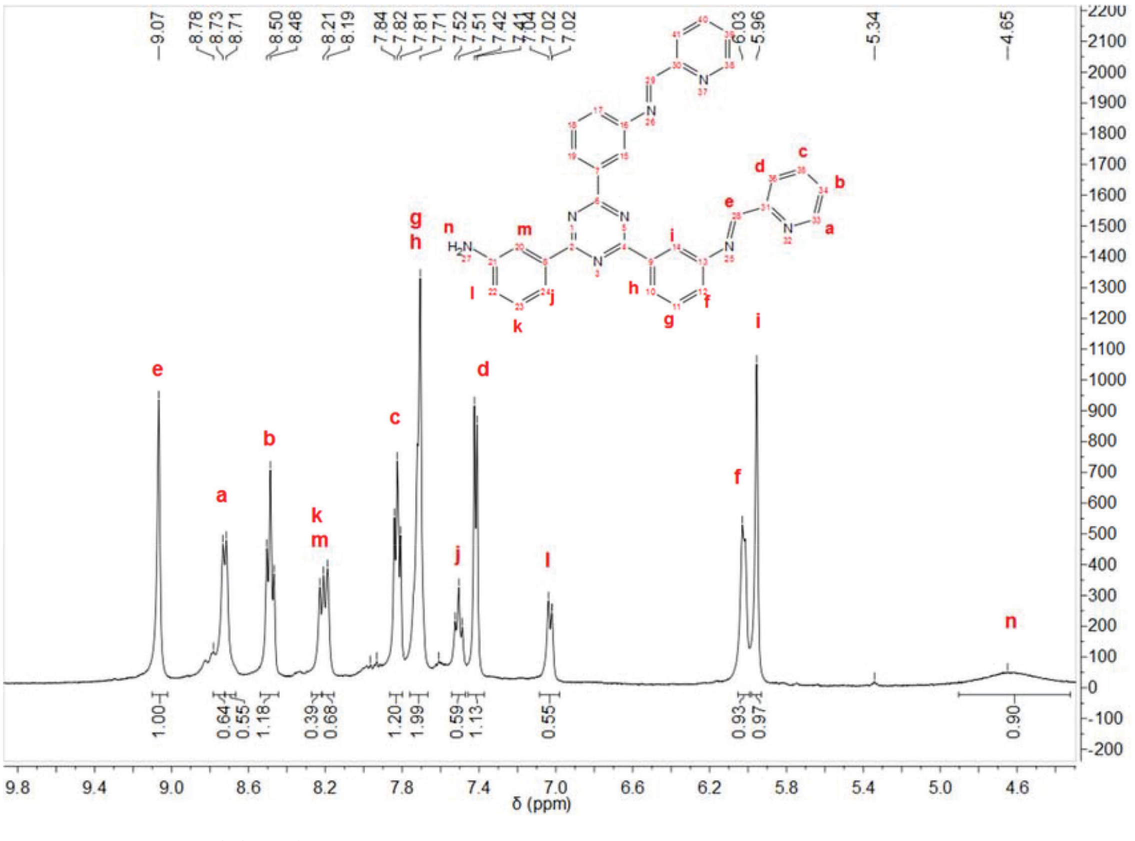


Figure 1. *Assignment of H atoms in helicate* ***1***

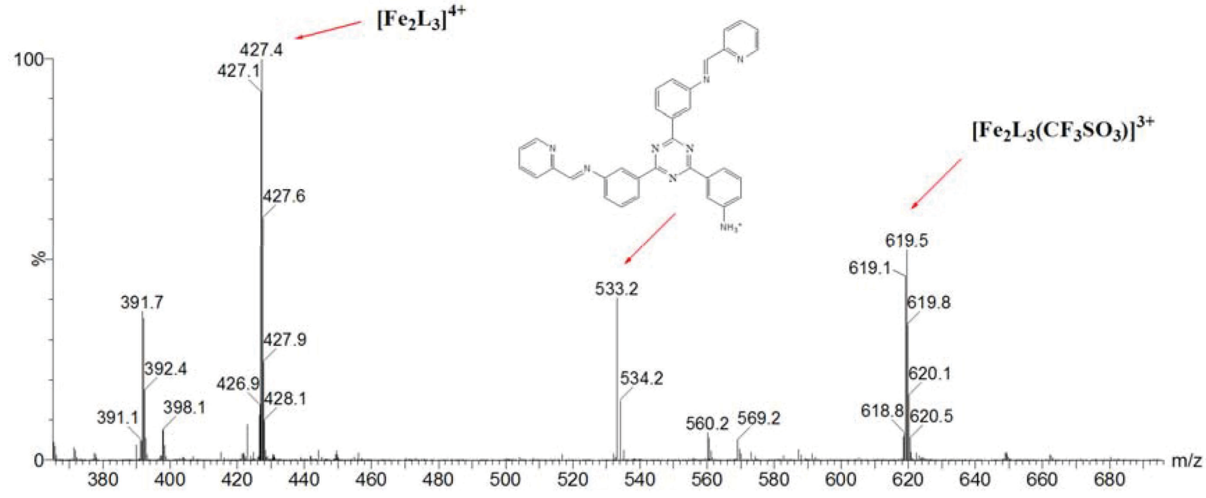


***Figure 2.** ESI-MS peaks of helicate **1** in CH_3CN solution*

all efforts tried, the structure of the helicate is optimized with *MM2* force field[30] based on the crystal structures of a similar Fe_2L_3 helicate series,[22] where different C_3-symmetric triamines have been applied.

The *MM2* model of helicate **1** shows that the whole molecular contains three schiffbase ligands and two Fe(II) ions through the formation of dynamic-covalent (C=N) and the coordinative (N→M) bonds. The coordination configuration of each Fe (II) ion is octahedral, and the distance between two ions is 11.9 Å. There is a hole in the kernel of the complex with approximate size of 5.72 Å×4.17 Å. A counter ion of $CF_3SO_3^-$ could be bound here, which explains the *m/z* peak of 619.5 (isotope peaks pattern shown in Table 3S and Figure 22S). The central part of each ligand is a triazine ring which is subject to bind planar aromatic guest molecules by π-π interaction. Also both the inner and outstretched phenyl groups are opened to electron-rich aromatic guests.

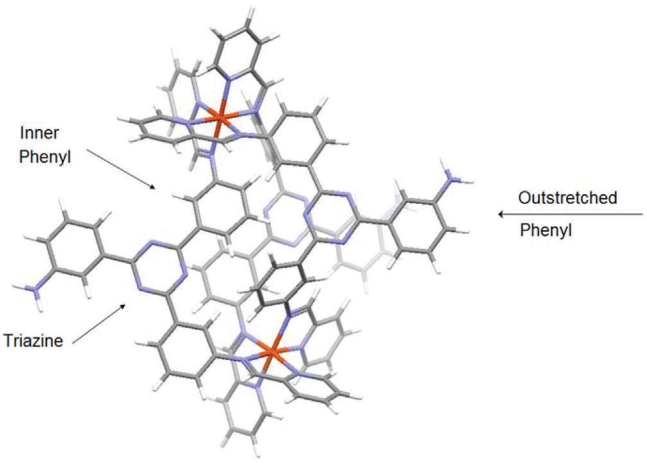


Figure 3.** Front view of the MM2 model of helicate **1

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

Seven planar aromatic guests (Table 1) of high symmetry were selected as the testing guests in the solution ^{1}H NMR investigations. The host helicate **1** (0.01 mmol, 1 eq) was dissolved in CD_3CN and then into which was added one of the chosen guest molecules (0.1 mmol, 10 eq) respectively. After the process of stirring reaction (at least for 2 h), the whole system was analyzed by ^{1}H NMR to obtain the data of host-guest interaction (Figure 2S to 15S).

From the ^{1}H NMR comparison between host helicate **1** and host-guest mixture, it shows that the signal corresponding to helicate **1** was changed more or less after the addition of each guest molecular. While the signals attributed to the excessive guest molecules were kept in one set and changed only slightly in comparison with the ^{1}H NMR of free guests ($\Delta < 0.02$ ppm), which coincide the rapidly exchange mode between free and bound states of guests on the NMR time scale.[31]

According to general knowledge, the up field shifts in the host NMR signals are associated with the increasing of electron density in the conjugated system of ligand, which could be attributed to the π-π stacking interaction with the electron-rich guests.[32] The most up field shift (Δ = -0.15 ppm of H_h) occurred when adding pyrene molecules into the host solution, which is a strong evidence to support our deducing. Also the most shifted signals were from the inner phenyl protons (H_f - H_i), which infers the host-guest π-π stacking are taken place here (Figure 4a). Another guest molecule causing the most significant shifts to the down field (Δ = 0.13 ppm of H_l) is naphthalene-1, 5-diol (Figure 4b). The two hydroxyl groups are supposed to form the strong hydrogen bonds with the amino group in the outstretched phenyl or the N atom from the triazine part, which are responsible for the electron-deficient phenomenon in the outstretched phenyl group of the ligand. A third guest of pyren-1-ol was selected deliberately to verify our theory, which not only contain the polycyclic aromatic part to serve as the π-π interaction guest, but also has the ability to be a hydrogen donor. ^{1}H NMR spectrum did show the combination of the two opposite interaction: π-π interaction causes the up field shifts of inner phenyl protons, while hydrogen bond results in the down field changing of outstretched phenyl (Figure 4c). However the most down shift (Δ = 0.08 ppm of H_l) is smaller than that of naphthalene-1,5-diol, which may due to the presence of only one hydrogen bond donor group (-OH) here. And the up shift (Δ = -0.05 ppm of H_h) is also not so obvious compared to pyrene guest, which could be explained by the away from the inner phenyl after the hydrogen bonding to the amino group in outer phenyl.

The others guests' ^{1}H NMR signals even move more slightly. 1,3,5-trizaine molecular couldn't be a good π-π interaction donor, which contains electron withdrawing nitrogen atoms. Triphenylamine also contains an electron withdrawing N atom in the center of the molecule and separate the electron conjugation of the molecule, further reducing the π-π interactions with host helicate. There are electron withdrawing oxygen atoms in 1,3,5-trimethoxy benzene and the molecule is not strictly flat, explaining the slight shifts of the helicate ^{1}H NMR signals. At last, 5'-phenyl-1,1':3',1''-terphenyl is a relatively large conjugated aromatic molecule, but may be a little

Table 1. Summary changes of chemical shift value of protons in helicate ligand during the host-guest interaction

		Host only	Host + pyrene	Host + naphthalene-1,5-diol	Host + pyren-1-ol	Host + 1,3,5-trizaine	Host + 1,3,5-trimethoxy-benzene	Host + triphenylamine	Host + 5'-phenyl-1,1':3',1''-terphenyl
Pyridyl H	**a**	8.72	8.69(-0.03)	8.68(-0.04)	8.65(-0.07)	8.72(0)	8.72(0)	8.71(-0.01)	8.70(-0.02)
	b	8.48	8.47(-0.01)	8.46(-0.02)	8.45(-0.03)	8.49(0.01)	8.48(0)	8.48(0)	8.48(0)
	c	7.82	7.80(-0.02)	7.79(-0.03)	7.79(-0.03)	7.83(0.01)	7.82(0)	7.82(0)	covered
	d	7.42	7.39(-0.03)	7.39(-0.03)	7.39(-0.03)	7.43(0.01)	7.41(-0.01)	7.42(0)	covered
Imine H	**e**	9.07	8.98(-0.09)	9.03(-0.04)	9.00(-0.07)	9.08(0.01)	9.06(-0.01)	9.07(0)	9.06(-0.01)
Inner phenyl H	**f**	6.03	5.94(-0.09)	6.01(-0.02)	5.96(-0.01)	6.04(0.01)	6.03(0)	6.03(0)	6.02(-0.01)
	g&h	7.71	g 7.64(-0.07) h 7.56(-0.15)	7.71(0)	7.66(-0.05)	7.73(0.02)	7.71(0)	7.74(0.03)	7.73(0.02)
	i	5.96	5.86 (-0.10)	5.95(-0.01)	5.90(-0.06)	5.98(0.02)	5.96(0)	6.98(0.02)	5.97(0.01)
Outstretched phenyl H	**j&m**	8.21	Covered**	j 8.33(0.12) m 8.30(0.09)	8.23(0.02)	8.23(0.02)	8.25(0.04)	8.24(0.03)	8.24(0.03)
	k	7.51	7.52(0.01)	covered	Covered**	7.52(0.01)	7.53(0.02)	7.53(0.02)	Covered**
	l	7.03	7.07(0.04)	7.16(0.13)	7.11(0.08)	7.06(0.03)	7.07(0.04)	7.02(-0.01)	7.07(0.04)
Amino H	**n**	4.65	4.66(0.01)	Not observed	4.65(0)	4.65(0)	Not observed	4.66(0.01)	4.68(0.03)

* All signals were calibrated base on the CD_3CN solution peak δ = 1.94 ppm. ** Covered= signals covered by the peaks of guest, can not be recognized clearly.

large for the ligand of helicate, which makes the binding to the host unstable.

UV- Vis studies of host-guest chemistry

Further UV- Vis studies were conducted to seek the detailed evidence of host-guest π-π interaction. The host concentration was kept in the range of 1×10^{-6} mol L^{-1}, while the guest concentrations were kept in 10 times of host. The helicate complex showed two absorptions from 200 to 700 nm. One at 244 nm originates from π–π^* transition, while the other at 278 nm is assigned to n–π^* transition (Figure 5). When the guests applied to the host solution, the electronic absorptions were all changed obviously. However, the absorptions of host and guests are overlapped somewhat during the UV-Vis band. It's hard to draw the conclusion that the spectrum changes reflect the host-guest interaction. So the absorption value of merely host and guest were added to obtain the calculated mixture absorption value of a host-guest complex. The result is compared with the actual mixture of host and guest, which shows no significant changes in all test samples. The spectrograms of naphthalene-1,5-diol as the guest are shown in Figures 5 and 6, while the data of pyrene or pyren-1-ol as guest are available in supplementary information file. No significant changing in the UV–Vis spectroscopy of the complex after guests applied is in accord with the rapid guests exchange between the free states and the binding states.

CONCLUSION

In summary, we have synthesized a novel helicate complex $[Fe^{II}_2L_3]^{4+}$ by the self-assembly of a C_3-symmetric triamine,

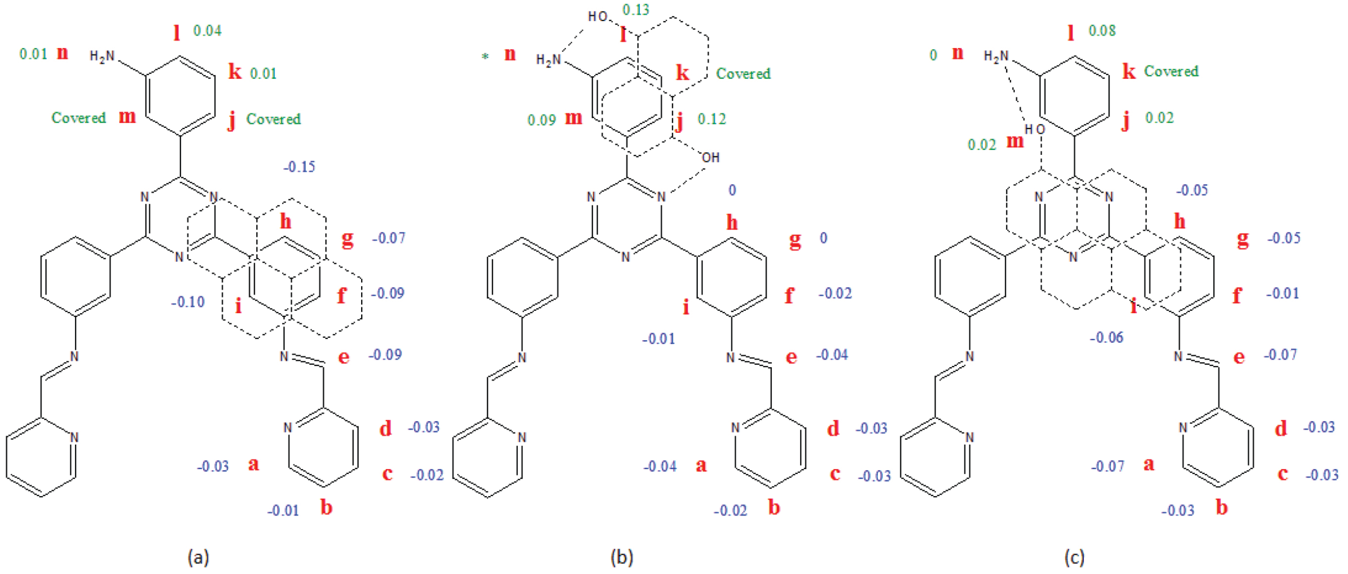


Figure 4. *The host-guest interaction patterns of helicate **1** with pyrene **(a)**, naphthalene-1, 5-diol **(b)** and pyren-1-ol **(c)** with the shifting of corresponding* ^{1}*H NMR signals*

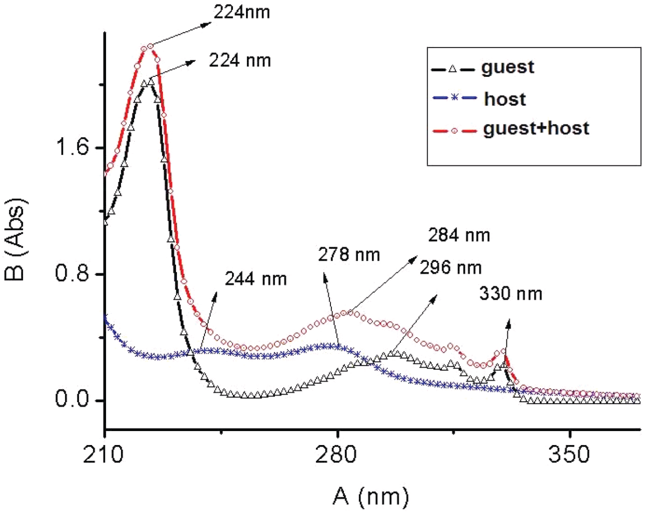


Figure 5. *UV–Vis spectra of host (helicate* ***1****), guest (naphthalene-1,5-diol) and the mixture of host and guest*

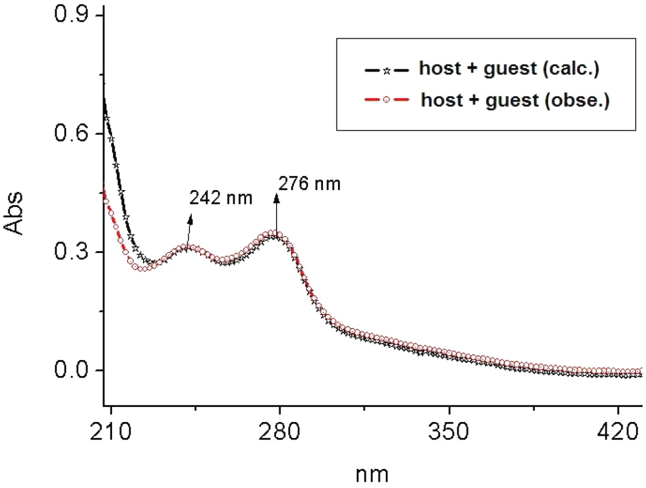


Figure 6. *UV–Vis absorption of host-guest complex (helicate* ***1*** *+ naphthalene-1,5-diol) compared with observed and calculated value*

2-formylpyridine and octahedral iron(II). Then the solution behaviors of the helicate while interacted with different aromatic guests were studied by ^{1}H NMR and UV-Vis spectrometry. Electron-rich aromatic molecules such like pyrene prefer to be bound with the relatively inner part of helicate ligand by the ϖ-ϖ stacking interaction, while the similar molecule with hydroxyl group is ready to be bound with the outstretched part of the ligand via additional O-H…N hydrogen forces. The size, functional group and symmetry of the guest molecule decide the patterns of the host-guest dynamic process in solution. Both ^{1}H NMR spectrum and UV-Vis spectrum confirm rapid guests exchange between equivalent binding sites.

SUPPLEMENTARY MATERIAL

Supporting information is available for download at http://quimicanova.sbq.org.br in pdf format, with free access.

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