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Synthesis and Photophophysical Properties of a Novel [13]aneN$_4$ with Chromophoric Groups

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Abstract

In this work, a new ligand [13]aneN$_4$ with anthracene, pyrene and naphthalene was synthesized and characterized by mass spectrometry, NMR, UV-Vis and fluorescence spectroscopies. The fluorescence quantum yield of the ligands is significantly less than the chromophore group alone. This low value can be explained by the presence of a photoinduced electron transfer of the free doublet from the nitrogen atom of the functional group to chromophore group. The fluorescence studies were also performed in order to study the influence of pH on the photoinduced electron transfer. The fluorescence intensity of the fluorophore group excited at acidic pH shows an increase. Therefore, the inhibition of photoinduced electron transfer from the nitrogen atom doublet of the amine protons from the side chain to the chromophore group is responsible for this. The amine's deprotonation causes electron transfer at a basic pH, resulting in a decrease in fluorescence intensity.

Subject Areas

Inorganic Chemistry

Keywords

Synthesis, Spectroscopy, X-Ray Diffraction, Single Crystal Structure, Tetraazacyclo-Alkanes, Fluorescence, Photoinduced Electron Transfer, Anthracene, Pyrene, Naphthalene

1. Introduction

Nitrogen-containing macrocycles called tetraazacyclo-alkanes and their derivatives are known for their ability to form complexes with transition metals and heavy metals. Their applications are diverse, including liquid purification [1] [2],

medical imaging [3], biomedical application [4], fluorescence probe [5], medical [6], neuroprotective or agents to cure Alzheimer's disease [7] and development of agents for biotechnology [8]…

The use of anthracene and its derivatives, known as fluorescent fluorophores, has been implemented in different applications such as pH sensing, organic molecules with small molecules, metal ions, and simple inorganic anions, due to their ease of processing, unique properties, and commercial availability. [9]

To examine their photophysical properties, we thought of creating new fluorescent chemosensors by incorporating a chromophore group (anthracene, pyrene, or naphthalene) into the primary amine function of compound [10].

Efforts have been made to study fluorescent chemosensors and switches in recent years due to their high sensitivity and rapid response. Two fundamental principles guide the design of them: photoinduced electron transfer (PET) and internal charge transfer (ICT). [10] [11] The most prevalent way to design fluorescent sensors and switches is by using PET with the "fluorophores-spacer-receptor" format. [12] [13] The components were selected to ensure that the fluorescence of the system is quenched by PET from the receptor, usually an amino group, to the fluorophores.

2. Synthesis and Characterization

1) Synthesis of cis-(9b,9c-Dimethyldecahydro-2a,4a,7a,9a-tetraazacyclopenta[cd]-phenylen-1-yl)methanamine (Ligand 1) [14] [15]

A solution of 2,3-butanedione (27.45 g, 0.319 mol) in acetonitrile (10 mL) was added to a solution of N,N-bis(aminoethyl)propane-1,3-diamine (51.1 g, 0.319 mmol) in acetonitrile (1.5 L) at 0˚C. The mixture was stirred at this temperature for 2 h. Benzotriazole (38.1 g, 1 equiv.) and K_2CO_3 (88.2 g, 2 equiv.) were added. A solution of 50% chloroacetaldehyde in water (50.1 g, 0.319 mol) was slowly added at 0˚C and the resulting mixture was stirred overnight at room temperature. Then the solution was filtered through Celite and washed with acetonitrile (100 mL). The filtrate was evaporated. The resulting solid was dissolved in CH_2Cl_2 (500 mL). After filtration, the organic phase was washed with a 3 M NaOH solution (200 mL). After extraction, the organic phase was dried with $MgSO_4$ and the solvent was evaporated. The residual brown solid was purified by aluminium oxide chromatography (eluent: CH_2Cl_2). A solution of this compound (40.73 g, 0.156 mol) in dry THF (50 mL) was slowly added to a suspension of $LiAlH_4$ (11.8 g, 0.31 mol) in THF (200 mL) under nitrogen at −78˚C. The resulting mixture was stirred overnight. Ethyl acetate (100 mL) and then water (25 mL) were carefully added. After removal of the solvent, the residual white-grey solid was taken up in chloroform (2 × 200 mL) and insoluble products were eliminated by filtration. Compound 1 was obtained as a colorless oil (yield 32.16 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 1.04 (s, 3 H), 1.12 (s, 3 H), 1.27 (s, 2.9 H), 1.28 (s, 2.9 H), 1.76 (m, 1.3 H), 2.2 - 3.6 (m, 26.6 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300 K): δ = 11.9, 12.3 (×2), 13.4 (CH_3),

18.7, 25.8 (CH_2-β), 44.8, 44.9, 45.7, 45.9, 46.5, 46.6, 47.2 (×2), 48.0, 48.3, 48.4, 49.4, 50.0, 50.1, 51.0, 51.1 (CH_2-α), 61.8, 68.1 (C-H), 73.2, 73.4, 79.3, 80.5 (N-C-N) ppm. MS (MALDI-TOF): m/z = 265.82 $[M]^+$.

2) Synthesis of (1,4,7,10-Tetraazacyclotridecan-5-yl)methanamine (Ligand 2) [14] [15]

A solution of 35% hydrochloric acid (107 mL, 1.2 mol) was added to a solution of 1 (32.16 g, 0.12 mol) in ethanol (200 mL). The resulting mixture was heated at reflux for 4 h. After cooling, the solution was filtered and washed with ethanol (50 mL) and then diethyl ether (100 mL). The solid was dissolved in a saturated 15 M NaOH solution (10 mL). After extraction with chloroform (2 × 150 mL), the organic phase was dried with $MgSO_4$ and the solvent was evaporated. Compound **2** was obtained as a white solid; yield 11.02 g, 42%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (m, 2 H), 1.87 (s, 6 H), 2.67 - 2.76 (m, 17 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 28.9 (CH_2-β), 44.3, 46.2, 47.7, 49.0, 49.0, 49.7, 49.8, 50.8 (CH_2-α), 59.0 (CH) ppm. MS (MALDI-TOF): m/z = 215.68 $[M]^+$. $C_{10}H_{25}N_5 \cdot 0.2H_2O$ (221.62): calculated. C 54.86, H 11.69, N 31.99; found C 55, H 11.57, N 31.81.

3) Synthesis of N-((1,4,7,10-Tetraazacyclotridecan-5yl)methyl)-1-(anthracen-9-yl)methanamine (3b):

To a solution of 350 mg (1.6 mmol) of ligand **2** in 50 mL of ethanol is added 411 mg (1.6 mmol) of 9-bromoanthracene. The mixture is stirred at ambient temperature for 4 h. $NaBH_4$ (0.6 g, 16 mmol, 10 equivalents) is then added and the mixture is brought to reflux. After 24 h, the solvent is evaporated off and the solid is dissolved in 50 mL of chloroform and then filtered. After evaporation of the solvent, the solid is dissolved in 50 mL of cyclohexane and then filtered and the solvent is evaporated off. Compound **3b** is obtained in the form of yellow oil (486 mg, 1.2 mmol, Yield = 75%). MALDI-TOF: m/z = 405.86 $[M]^{+\bullet}$, 405.25 calculated for $C_{25}H_{35}N_5$. UV-vis. (CH_3OH): λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$) = 385 (9135). ^{1}H NMR ($CDCl_3$, 300 MHz): 8.18 (m, 3H), 7.78 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8,3 Hz, 1H), 7.35 (m, 4H), 4.72 (s, 2H), 2.45 (m, 22H), 1.69 (m, 2H). RMN $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz): 142.8, 135.1, 132.4, 128.9, 125.2, 125.2, 124.8, 124.4, 123.3, 120.5, 57.6, 53.2, 51.1, 49.8, 49.6, 49.0, 48.8, 47.4, 46.2, 28.4.

4. Synthesis of N-((1,4,7,10-Tetraazacyclotridecan-5-yl)methyl)-1-(pyren-2-yl)methanamine (4b):

To a solution of 350 mg (1.6 mmol) of compound **2** in 50 mL of ethanol is added 450 mg (1.6 mmol) of 2-bromopyrene. The mixture is stirred at ambient temperature for 4 h. $NaBH_4$ (0.6 g, 16 mmol, 10 equivalents) is then added and the mixture is brought to reflux. After 24 h, the solvent is evaporated off and the solid is dissolved in 50 mL of chloroform and then filtered. After evaporation of the solvent, the solid is dissolved in 50 mL of cyclohexane and then filtered and the solvent is evaporated off. Compound **4b** is obtained in the form of a yellow oil (515 mg, 1.2 mmol, Yield = 75%). MALDI-TOF: m/z = 429.88 $[M]^{+\bullet}$, 429.27

calculated for $C_{27}H_{35}N_5$. UV-vis. (CH_3OH): λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$) = 341 (35185). ^1H NMR ($CDCl_3$, 300 MHz): 8.40 (m, 1H), 7.92 (m, 8H), 4.42 (s, 2H), 3.54 – 1.92 (m, 22H), 1.60 (m, 2H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$, 75.4 MHz): 130.8, 126.8, 126.3, 125.8, 124.7, 123.5, 123.4, 123.1, 122.9, 121.2, 120.0, 119.6, 118.1, 117.5, 51.8, 49.7, 48.9, 48.6, 48.4, 48.1, 47.7, 47.6, 47.3, 27,9.

5) Synthesis of N-((1,4,7,10-tetraazacyclotridecan-5-yl)methyl)-1-(naphthalen-1-yl)methanamine (5b):

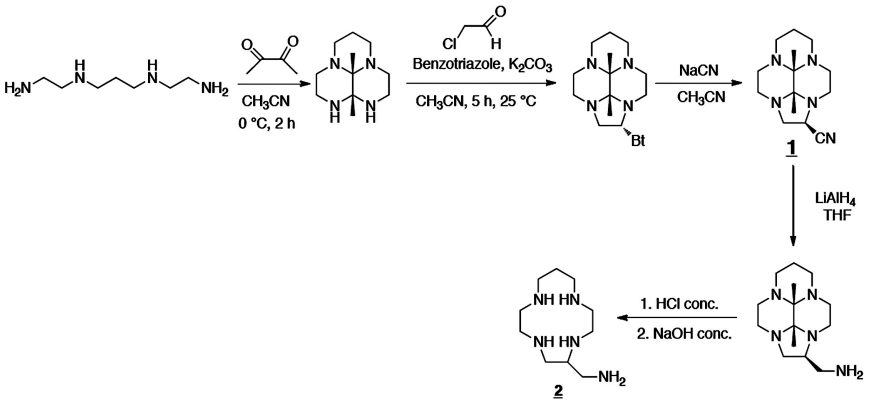
To a solution of 350 mg (1.6 mmol) of compound **2** in 50 mL of ethanol is added 250 mg (1.6 mmol) of 1-naphthaldehyde. The mixture is stirred at ambient temperature for 4 h. $NaBH_4$ (0.6 g, 16 mmol, 10 equivalents) is then added and the mixture is brought to reflux. After 24 h, the solvent is evaporated off and the solid is dissolved in 50 mL of chloroform and then filtered. After evaporation of the solvent, the solid is dissolved in 50 mL of cyclohexane and then filtered and the solvent is evaporated off. Compound **5b** is obtained in the form of yellow oil (512 mg, 1.44 mmol, Yield = 90%). MALDI-TOF: m/z = 355.88 $[M]^{+\bullet}$; 355.27 calculated for $C_{21}H_{33}N_5$. UV-vis. (CH_3OH): λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$) = 283 (6746). ^1H NMR ($CDCl_3$, 300 MHz): 8.10 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.43 (m, 4H), 4.9 (s, 2H), 2.63 (m, 22H), 1.69 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): 135.1, 132.9, 130.9,127.7, 126.8, 125.2, 125.0, 124.7, 124.4, 122.9, 56.0, 51.4, 51.2, 50.2, 48.7, 48.6, 48.2, 47.5, 46.5, 45.0, 27.3.

3. Results and Discussion

3.1. Synthesis of the Ligands

We considered synthesizing new fluoroionophores by adding a chromophore group (anthracene, pyrene and naphthalene) on the primary amine function of the compound 5-aminomethyl [13]aneN_4 in order to study their photophysical properties in the presence of metallic cations.

The synthesis of these macrocycles was carried out initially by the synthesis of 5-aminomethyl-[13]aneN_4 [1] [2] (Scheme 1).



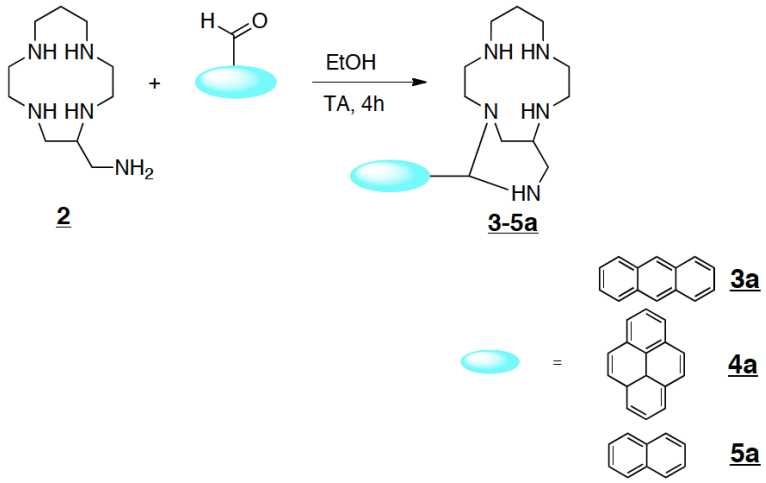
Scheme 1. Synthesis of 5-aminomethyl [13]ane N_4 (Ligand 2).

Then, the compounds were made by condensing the primary amine function of ligand **2** onto the chromophore group. The corresponding imine was created by condensation of the primary amine function onto the chromophore group with an aldehyde function. Aldehyde's action does not result in the formation of an imine, but rather an exocyclic amine function (compounds **3a**, **4a** and **5a** of Scheme 2).

The formation of the amine was confirmed by the structure of compounds **3a** and **4a** determined by X-ray diffraction. Figure 1 represents the ORTEP view of the crystallographic structure of compound **4a**. Based on these results, we can assume that compound **5a** also forms a six-membered ring.

The reduction of the exocyclic amine of compounds **3a**, **4a**, and **5a** is carried out by adding sodium borohydride to ethanol at reflux for 12 hours. The isolation of compounds **3b** and **4b** yielded 75%, while compound **5b** yielded 90% (Scheme 3).

The successful synthesis of these three ligands is well characterized in the experimental section, we report an example of the characterization of compound **5b**



Scheme 2. Synthesis of ligands **3a**, **4a** and **5a**.

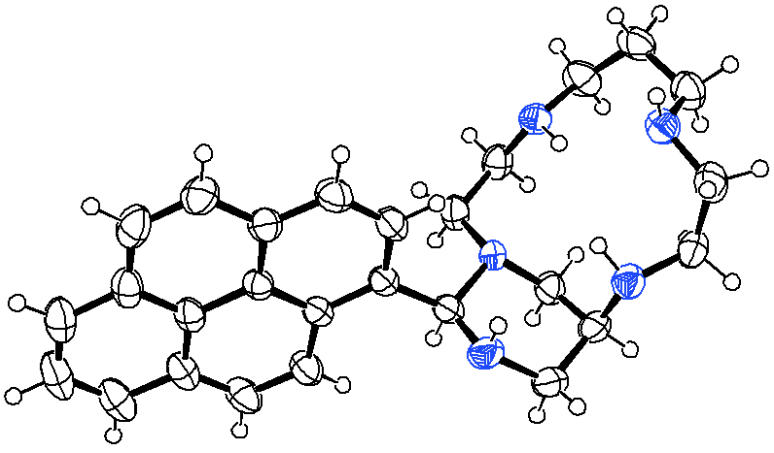
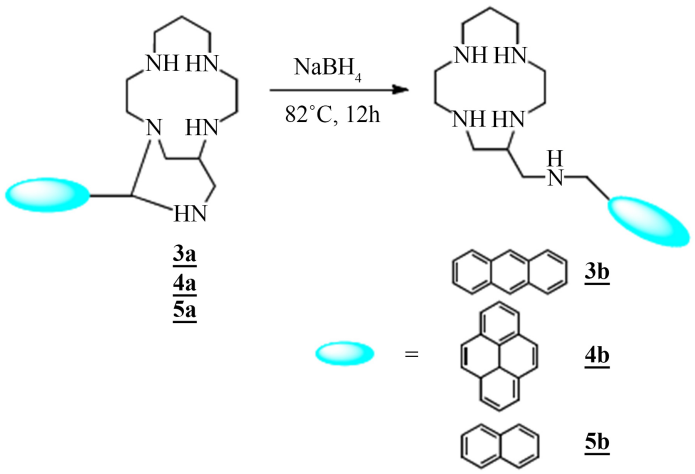


Figure 1. ORTEP view of compound **4a**. Ellipsoids are shown at the 50% probability level.

that was first characterized by mass spectrometry MALDI-TOF (Figure 2). The spectrum of this mass compound exact 355.27 Daltons and of experimental mass equals to 355.91 g·mol^{-1}, therefore, let us observe a good correlation between the obtained mass and the calculated mass.

The ^{1}H NMR spectrum (300 MHz) of compound **5b** was recorded in chloroform at ambient temperature (Figure 3). This spectrum is in agreement with the structure of the compound, we were able to attribute the different signals of the different hydrogen nucleus of the molecule. The protons of β-CH_2 (Ha, Hb) of the macrocycle appear as massive at 1.68 ppm. The strong field signal mass



Scheme 3. Synthesis of ligands **3b**, **4b** and **5b**.

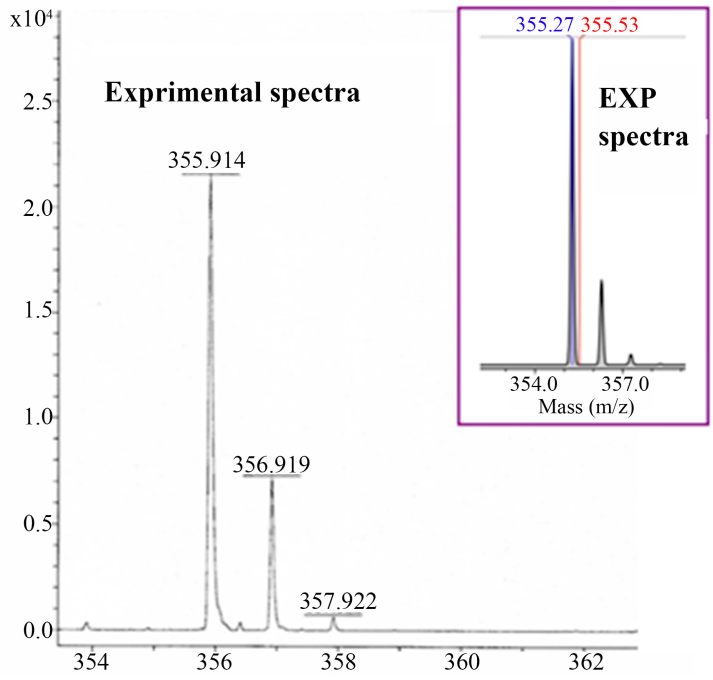


Figure 2. Correlation between the MALDI-TOF spectrum of compound **5b** and its exact calculated mass.

(2.5 - 3 ppm) corresponds to the atoms hydrogen of the macrocycle. The signal at 4.2 ppm is attributed to the two protons of CH_2 bound to the Naphthalene (Hc and Hd). Finally, the nucleus of the naphthalene group resonate at low field between 7.4 and 8.1 ppm (Figure 3).

3.2. Study of the Photophysical Properties of the Ligands

3.2.1. Absorption and Emission Spectra

We recorded the fluorescence absorption and emission spectra of compounds **3b**, **4b** and **5b** in methanol at room temperature. The spectra obtained with compound **3b** are shown in Figure 4.

The absorption spectrum of compound **3b** shows the presence of an absorption band centered at a wavelength of 385 nm. This band is attributed to the $S_0 \rightarrow S_1$ transition of anthracene [16].

The fluorescence spectrum was recorded after excitation at $\lambda = 345$ nm at ambient temperature. This compound has a fluorescence emission band between

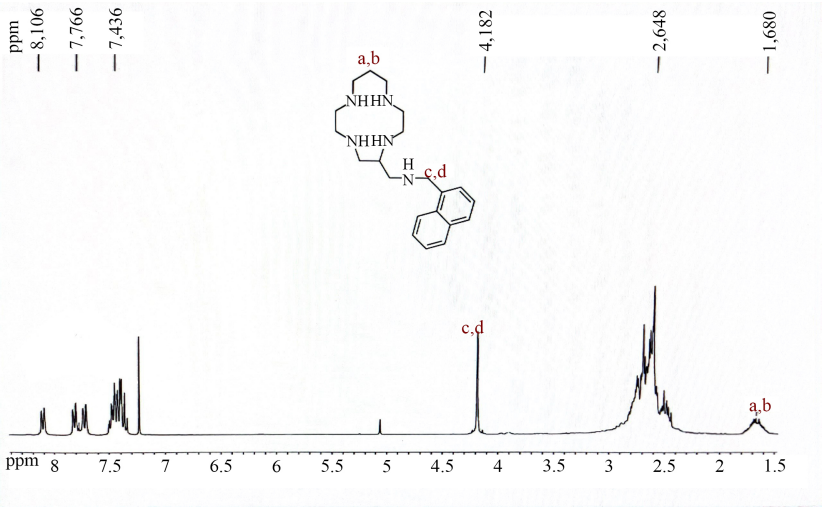


Figure 3. ^{1}H NMR spectrum (300 MHz) of compound 5b in $CDCl_3$.

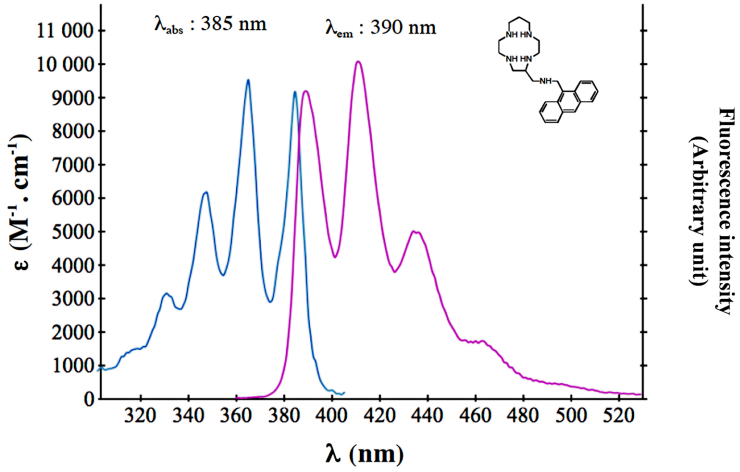


Figure 4. Absorption and emission spectra of compound 3b in methanol [10^{-5} M].

380 and 500 nm. The fluorescence quantum yield is of the order of 4%, it is lower than the quantum yield of anthracene alone (φ = 0.27) [17]. This low value can be explained by a photoinduced electron transfer from the nitrogen atom doublet of the amine from the side chain to the anthracene group [18].

The absorption and emission spectra of compound **4b** in methanol are shown in Figure 5.

On the absorption spectrum of compound **4b**, the $\pi \rightarrow \pi^*$ transitions of pyrene give occur at absorption bands centered at 341 nm and 270 nm.

The fluorescence emission band is observed between 360 and 480 nm with a maximum at λ = 375 nm after excitation at 340 nm. The fluorescence quantum yield has a low value (0.01) compared to that of pyrene alone (φ = 0.65) [19]. This low value can be explained by the presence of a photoinduced electron transfer of the doublet free from the nitrogen atom of the functional group to pyrene [18].

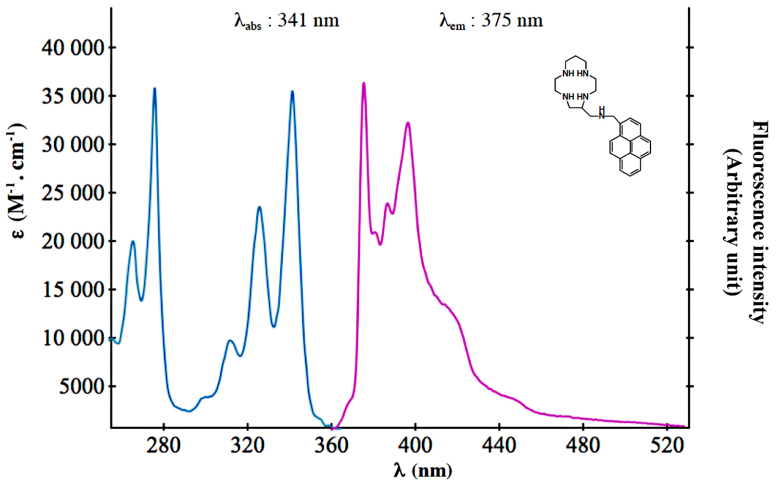


Figure 5. Absorption and emission spectra of compound 4b in methanol [10^{-6} M].

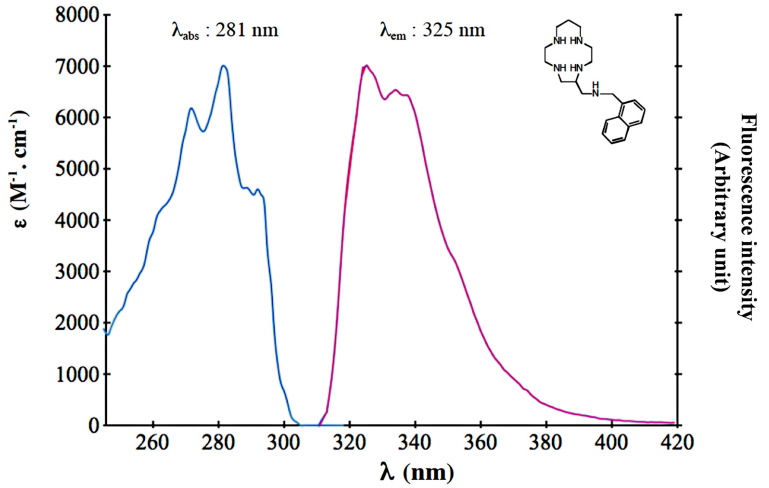


Figure 6. Absorption and emission spectra of compound 5b in methanol [10^{-5} M].

The absorption and emission spectra of compound **5b** in methanol are shown in Figure 6.

The absorption spectrum of compound **5b** has an absorption band at λ = 281 nm due to the $S_0 \rightarrow S_2$ transition of the naphthalene group [16].

In the emission spectrum, a band is centered at a wavelength of 325 nm with a low quantum yield of 0.05 compared to that of naphthalene alone (φ = 0.21) [17]. Therefore, this compound has a behavior similar to the two previous ligands.

3.2.2. Study of the Fluorescence of Ligands in Water as a Function of pH

In order to study the influence of fluorescence on compounds **3b**, **4b** and **5b**, the emission spectra of the latter were recorded in H_2O (KCl: 0.1 M) by modifying the pH base addition (NaOH: 0.1 M) and acid (HCl: 0.1 M). The superposition of this spectrum is shown in Figure 7.

The superposition of the emission spectra of compound **3b** shows that the intensity of fluorescence is very high at pH3. By adding base, the fluorescence intensity of the anthracene group decreases until stabilization at pH 11 corresponding to a decrease of about 83%. This decrease in fluorescence is illustrated in Figure 8.

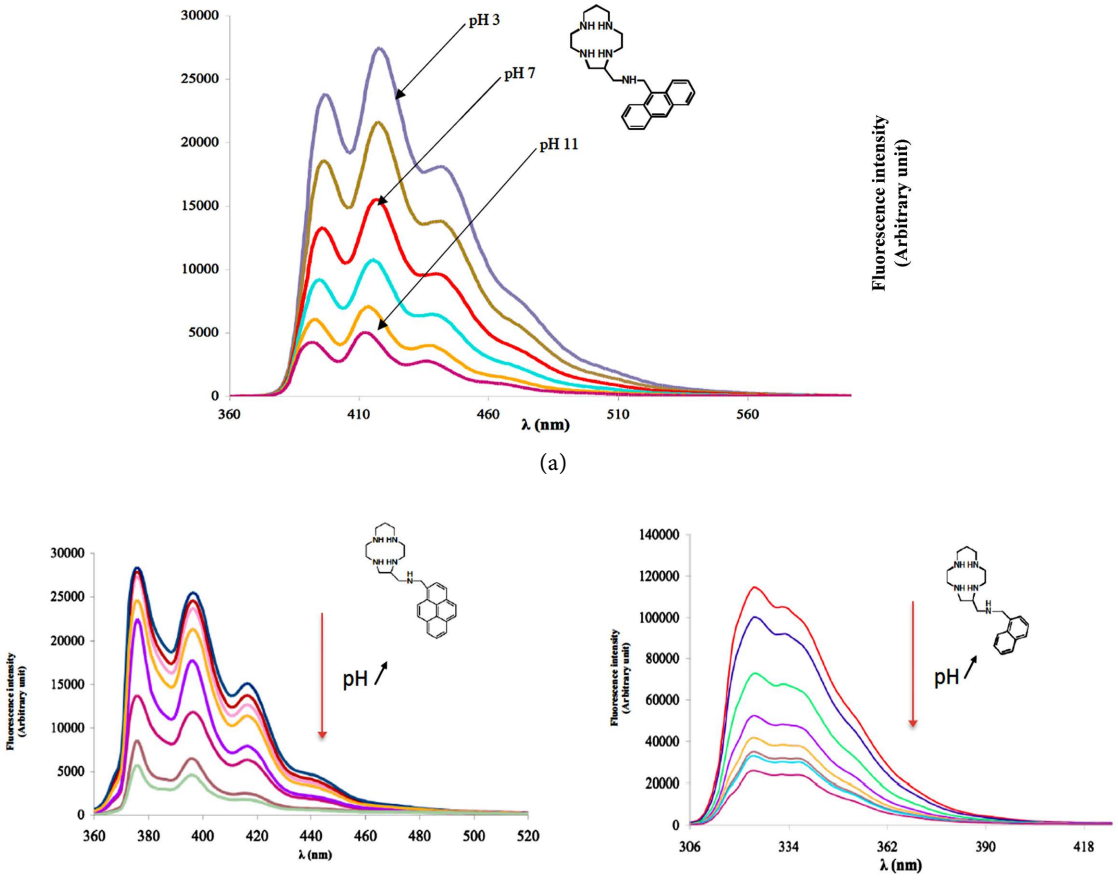


Figure 7. Evolution of the emission spectrum as a function of the pH in H_2O, KCl (0.1 M) of compound: (a) 3b (λ_{ex} = 345 nm), (b) 4b (λ_{ex} = 340 nm), (c) 5b (λ_{ex} = 281 nm).

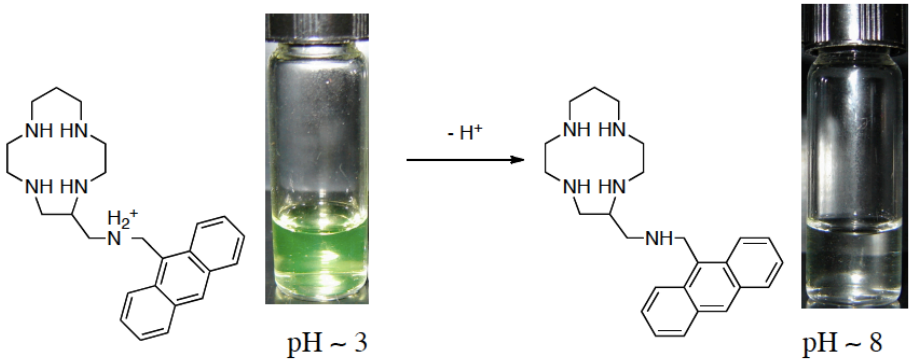


Figure 8. Evolution of the fluorescence of compound 3b as a function of the pH.

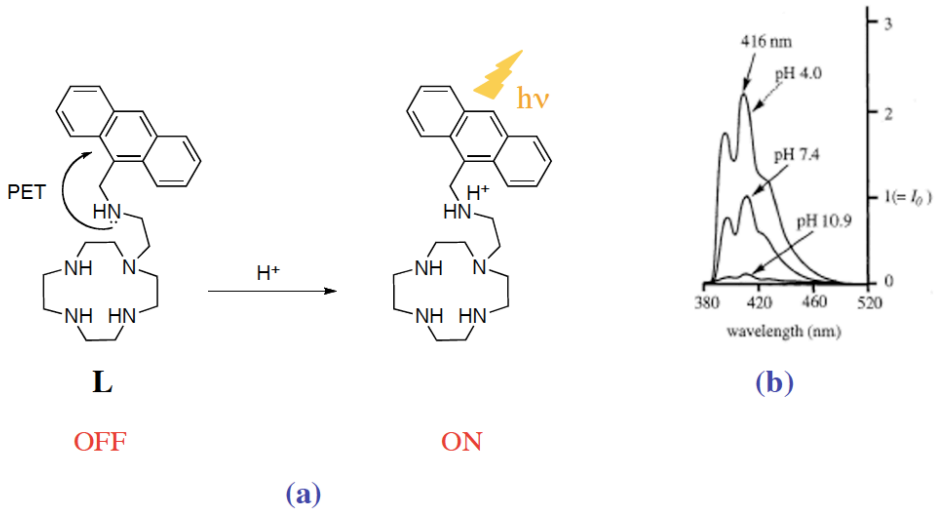


Figure 9. (a): Disturbance of fluorescence of N-(anthracen-9-ylmethyl)-2-(1,4,7,10-tetraazacyclododecan-1-yl) ethanamine (L) as a function of pH, (b): Emission spectra of fluorescence of L as a function of pH.

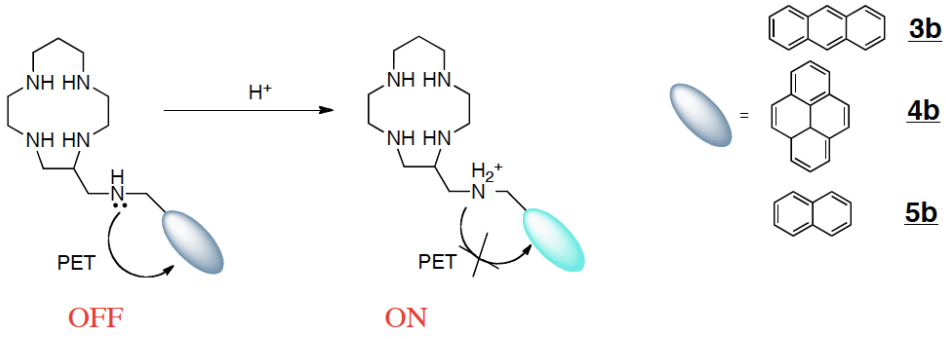


Figure 10. ON-OFF type of photoinduced electron transfer.

Similar results were observed for compounds **4b** and **5b** (**Figure 7**).

To explain this phenomenon, we referred to the work of Kimura and Co. [18], who performed a spectrofluorimetric titration of an N-functionalized cyclene by an anthracenyl amino-methyl group (L, **Figure 9**). Their results show an increase in fluorescence intensity of the fluorophore group excited at acidic pH (4 -

5) due to the inhibition of photoinduced electron transfer from the nitrogen atom doublet of the amine protonated from the side chain to the chromophore group. On the other hand, at basic pH, the amine is deprotonated and electron transfer reappears, resulting in a decrease in fluorescence intensity (**Figure 9**).

Therefore, we can explain the variation in the fluorescence intensity of compounds **3b**, **4b** and **5b** depending on the pH by the same phenomenon of photoinduced electron transfer observed by Kimura and Co. [18] (**Figure 10**).

4. Conclusion

In this work, we focused on the synthesis of 5-aminomethyl [13]aneN_4 derivatives with fluorophore groups (anthracene, pyrene, and naphthalene) with the aim of designing new fluoroionophores and investigate their use as metal detectors. After synthesizing these macrocycles, we were able to characterize them using ^{1}H NMR and MALDI-TOF. A study of the photophysical properties of the ligands shows a photoinduced electron transfer from the nitrogen atom doublet of the amine from the side chain to the anthracene, pyrene and naphthalene groups. Then we tried to study the effect of pH on the fluorescence of these macrocycles. We have observed that the intensity of fluorescence rises when the pH is acidic, which can be explained by the inhibition of photoinduced electron transfer from the nitrogen atom doublet of the amine protonated from the side chain to the chromophore group. On the other hand, at basic pH, the amine is deprotonated, and electron transfer reappears, resulting in a decrease in fluorescence intensity.

Conflicts of Interest

The authors declare no conflicts of interest.

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