

Article

Macrocyclic Azopyrrole: Synthesis, Structure and Fluoride Recognition

Ying An, Ying Sun and Zhenming Yin * 

Tianjin Key Laboratory of Structure and Performance for Functional Molecule, College of Chemistry, Tianjin Normal University, Tianjin 300387, China; anyingtjnu@163.com (Y.A.); sunying990909@163.com (Y.S.)

* Correspondence: tjyinzm@aliyun.com

Abstract: A macrocyclic receptor based on azopyrrole and polyether was synthesized, and its structure was characterized by NMR (^1H and ^{13}C), HRMS and X-ray crystallography. In the solid state, the macrocyclic molecules could bind methanol through a pair of N-H...O hydrogen bonds and further self-assembled into tubular structures through C-H...N hydrogen bonds. This revealed that the crystal could still keep its porous properties after the included molecules were removed. The UV–Vis titration indicates that the macrocyclic receptor can chromogenically and selectively sense fluoride ion in DMSO solution, and the sensing mechanism was rationalized by ^1H NMR.

Keywords: macrocyclic; azopyrrole; synthesis; structure; fluoride detection

1. Introduction

Azo dyes, compounds containing N=N double bond, are widely used in many fields for their reversible *trans-cis* isomerization ability and ease of synthesis [1]. Compared to azobenzene-analogous, heterocyclic azo dyes, in which the N=N group connects at least one heterocyclic substituent, have higher color brilliance and strength as well as better color fastness, and have been increasingly studied recently [2,3]. Among the various types of heterocyclic azo dyes, azopyrroles have received much attention for the design of advanced materials and devices because of their promising absorption properties. For examples, most azopyrroles can reversibly convert from the thermodynamically stable *E*-isomer to a *Z*-isomer, which can be used as photoswitches [4–7]. Lee et al. found that azopyrrole has multiple Brønsted basic sites and can be used in three-stage binary switching [8]. 2,5-Bisazopyrroles and their BF_2 complexes are near-infrared absorbing azo dyes [9] and can be applied to fabricate bulk heterojunction organic solar cells and photovoltaic devices [10,11]. Previously, we found that 5,5'-bisdiazo-dipyrromethane compounds commonly formed hydrogen-bonded interlocked dimers through quadruple N-H...N hydrogen bonds [12].

On the other hand, anions are ubiquitous in nature and play important roles in the fields of chemistry, biology, and the environment. As result, studies on anion recognition have attracted great attention in the recent years [13–16]. Colorimetric and fluorescent receptors, which have a high sensitivity, fast response and technical simplicity, are especially desirable [17,18]. Artificial colorimetric and fluorescent anion sensor are always made up of two parts, binding sites and covalently linked signaling units. The pyrrole group is a commonly used binding site in the design of anion receptors because it can form a strong hydrogen bonding interaction with anions [19]. Calixpyrrole, dipyrrolequinoxaline, dipyrromethane, and pyrrolic amide are all well-known receptors [20–28]. The azo



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N=N group, as a signal unit, has already been used in the design of colorimetric anion sensors [29–33]. Azopyrrole, which contains the binding site pyrrole group and signal part azo group, can be used as a colorimetric anion sensor. Chauhan et al. have proved that 1-aryldiazo-5,5-dimethyl dipyrromethanes are versatile chromogenic probes for anions [34]. Recently, we also found that some azopyrroles have anion-sensing ability in DMSO solution [35,36]. At present, the anion sensors based on azopyrroles are acyclic and their anion binding ability is moderate. Macrocyclic hosts always have enhanced affinity and selectivity for target guests due to their highly pre-organized binding cavities [37–41]. With these facts in mind, herein, a macrocyclic compound (**2**), which consists of azopyrrole and polyether groups, was synthesized and its structure was characterized by X-ray crystallography. The anions sensing property of compound **2** was studied in a UV–Vis titration experiment and rationalized by ^1H NMR.

2. Materials and Methods

2.1. Materials and Apparatuses

^1H NMR and ^{13}C NMR spectra were recorded in $\text{DMSO-}d_6$, with TMS as an internal standard, on a BRUKER AV-400 spectrometer at 400 MHz and 100 MHz, respectively. HR-MS analyses were performed on a Thermo Scientific LTQ Orbitrap XL spectrometer equipped with an ESI source. TGA were carried out using TGA Q500 instrument. The Powder X-ray diffraction patterns were recorded on a D8 ADVANCE X-Ray diffractometer. UV–Vis spectra were recorded on the SHIMADZU UV-2550 spectrometer. Melting points (mp) were recorded on an electro-thermal digital melting point apparatus and uncorrected. 5,5'-bis(3-hydroxyphenyldiazo)-dipyrromethane (**1**) was prepared according to the procedure in [42]. (Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) and other reagents are commercially available and were used without further purification.

2.2. Preparation of Compound 2

5,5'-bis(3-hydroxyphenyldiazo)-dipyrromethane (**1**) 0.422 g (1 mmol), 0.275 g (2 mmol) K_2CO_3 and 30 mL acetonitrile were mixed and refluxed. A solution of (ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) 0.458 g (1 mmol) in 10 mL acetonitrile was added 30 min later, and the mixture was refluxed. The reaction progress was monitored by TLC. After 12 h, the reaction was complete, and the solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/petroleum ether ($v:v = 1:3$), affording the compound **2**, orange powder, 43%, m.p. = 268 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 0.85 (t, 6H, $J = 7.2$ Hz, $-\text{CH}_3$), 2.29 (q, 4H, $J = 7.2$ Hz, $-\text{CH}_2-$), 3.65 (s, 4H, $-\text{CH}_2-$), 3.79 (t, 4H, $J = 5.2$ Hz, $-\text{CH}_2-$), 4.18 (t, 4H, $J = 5.2$ Hz, $-\text{CH}_2-$), 6.28 (d, 2H, $J = 3.6$ Hz, PyCH), 6.80 (d, 2H, $J = 4.0$ Hz, PyCH), 6.97–6.99 (m, 2H, ArCH), 7.26–7.28 (m, 2H, ArCH), 7.32 (t, 2H, $J = 1.6$ Hz, ArCH), 7.39 (t, 2H, $J = 8.0$ Hz, ArCH), 11.65 (s, 2H, PyNH); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 8.0, 25.0, 42.9, 67.1, 68.5, 69.9, 109.4, 114.9, 130.1, 142.7, 145.8, 154.1, 159.1; HRESI-MS: Calcd $[\text{M}+1]^+$ 557.2798, Found $[\text{M}+1]^+$ 557.2877.

2.3. X-Ray Crystallography

The single crystal of compound **2** suitable for X-ray crystallographic study was grown by slowly evaporating its methanol solution. Diffraction data were measured on a BRUKER SMART APEX II CCD diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) by scan mode at 150(2) K. The SADABS program [43] was implemented for semi-empirical multi-scan attenuation correction. The structure was confirmed by a direct routine and refined with the full-matrix least-squares technique using the SHELXT [44] and SHELXL [45] programs through the OLEX-2 [46] interface. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms

on F^2 . Crystallographic data and refinement parameters of the crystal are summarized in Table 1.

Table 1. Crystal data of compound **2**.

Crystal	2
CCDC No.	2117984
Empirical formula	$C_{64}H_{82}N_{12}O_{11}$
Formula weight	1195.41
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a(Å)	7.6407(17)
b(Å)	14.487(3)
c(Å)	28.857(6)
$\alpha(^{\circ})$	90
$\beta(^{\circ})$	90
$\gamma(^{\circ})$	90
V(Å ³)	3194.2(12)
Z	2
Dcalc.(g/cm ³)	1.243
$\mu(\text{mm}^{-1})$	0.086
F(000)	1276.0
Reflections collected	16356
Independent reflections	5539 [$R_{\text{int}} = 0.0676$, $R_{\text{sigma}} = 0.0865$]
R_1/wR_2 [$I > 2\sigma(I)$]	0.0752/0.1930
R_1/wR_2 (all data)	0.01550/0.2431
GoF on F^2	0.946

2.4. Titration Studies

The Job's plot method [47] was applied to determine the stoichiometry of the complex formed between the macrocycle **2** and the fluoride. Two stock solutions of **2** (1×10^{-5} mol/L) and the fluoride (1×10^{-5} mol/L) in DMSO were mixed in different proportions from 1:0 to 0:1, keeping the total concentration of [**2** + F^-] constant at 1×10^{-5} mol/L. The UV–Vis spectra of the solutions were measured. The Job's plot was generated by Origin as a function of $\chi\Delta A$ Vs χ , where χ is the molar fraction of **2** and $\Delta A = A - A_0$.

To study the fluoride (as tetrabutylammonium salts) binding ability of the macrocycle **2**, an increasing fluoride were added to a constant concentration (2.5×10^{-5} mol/L) DMSO solution of the **2** and the UV–Vis spectra were recorded. According to the spectra change, the association constants (K_a) of **2** with fluoride was calculated by non-linear least-square analysis using the equation for the 1:1 type host–guest complex [48],

$$\Delta A = \frac{1}{2} \left\{ \Delta \epsilon ([H]_0 + [G] + 1/K_a) - \sqrt{\Delta \epsilon^2 ([H]_0 + [G] + 1/K_a)^2 - 4\Delta \epsilon [H]_0 [G]} \right\}$$

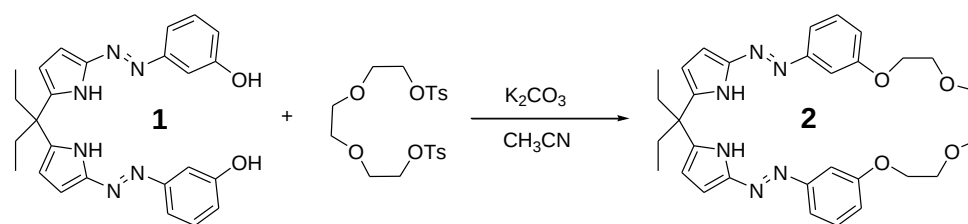
where $[H]_0$ denotes the concentration of host **2** and $[G]$ refers to the concentration of fluoride, and ΔA is the change in absorbance.

^1H NMR titration experiments were measured on 400 MHz NMR spectrometers. Small aliquots of Bu_4NF in $\text{DMSO}-d_6$ (1 mol/L) were introduced to 0.4 mL $\text{DMSO}-d_6$ solution of **2** (5×10^{-3} mol/L) in an incremental fashion (corresponding to 0, 0.25, 0.5, 1.0 and 4.0 equiv of fluoride), and their corresponding spectra were recorded.

3. Results

3.1. The Synthesis of Compound 2

The macrocyclic compound **2** was synthesized by the condensation reaction between 5,5'-bis(3-hydroxyphenyldiazo)-dipyrromethane and (ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) in a diluted solution of acetonitrile with moderate yield (Scheme 1). The structure of compound **2** was characterized by ^1H , ^{13}C NMR, HR-MS (S1-S3) and single-crystal X-ray diffraction analysis. Notably, no photochromic property or *E/Z* isomerization of compound **2** in DMSO solution was observed. This is potentially because of azo-hydrazone tautomerism [49,50].



Scheme 1. Synthesis of compound **2**.

3.2. The Crystal Structure of Compound 2

Compound **2** crystallizes in the orthorhombic space group, $P2_12_12_1$, with one molecule of **2**, as well as one methanol and half water molecule in the asymmetric unit. The structure of compound **2** is shown in Figure 1, in which both $\text{N}=\text{N}$ bonds adopt an *E* configuration identical to the previous azopyrrole compounds [42,51,52]. The selected bond distances and torsion angles are listed in Table 2. The $\text{N}(2)\text{--N}(3)$ and $\text{N}(5)\text{--N}(6)$ bond distances are 1.240 (8) and 1.208 (8) Å, respectively, which are slight shorter than previous results (1.239–1.292 Å) [42,51,52]. The dihedral angles of O3--C21--C20--O4 , O2--C23--C22--O3 , and O2--C24--C25--O1 are 66.0° , -67.4° , and -175.5° , respectively. In the crystal of compound **2**, the two pyrrole NH groups point to the same side of the molecule, and the angle between them is 63.6° . It is quietly different with bis-diaryldiazo-dipyrromethanes, in which the two pyrrole rings point in the opposite direction [42,51,52]. The reason should be the methanol binding through a pair of $\text{N--H}\cdots\text{O}$ ($\text{N1--H1}\cdots\text{O5}$: $\text{H}\cdots\text{O} = 2.15$ Å, $\text{N}\cdots\text{O} = 3.001$ Å, $\angle\text{N--H}\cdots\text{O} = 169^\circ$ and $\text{N4--H4}\cdots\text{O5}$: $\text{H}\cdots\text{O} = 2.14$ Å, $\text{N}\cdots\text{O} = 2.917$ Å, $\angle\text{N--H}\cdots\text{O} = 149^\circ$) hydrogen bonds (Figure 2). In the crystal, bridged by methanol through aforesaid $\text{N--H}\cdots\text{O}$ and $\text{O5--H5}\cdots\text{O3}$ ($\text{O5--H5}\cdots\text{O3}$: $\text{H}\cdots\text{O} = 1.95$ Å, $\text{O}\cdots\text{O} = 2.758$ Å, $\angle\text{O--H}\cdots\text{O} = 166^\circ$) hydrogen bonds, molecules of compound **2** assemble into tubular structure along an axis (Figure 2). The tubular is also stabilized by $\text{C21--H21B}\cdots\text{N6}$ ($\text{C21--H21B}\cdots\text{N6}$: $\text{H}\cdots\text{N} = 2.61$ Å, $\text{C}\cdots\text{N} = 3.314$ Å, $\angle\text{C--H}\cdots\text{N} = 129^\circ$) hydrogen bonds between two neighboring **2** molecules. The included water molecule donates its two hydrogen atoms and connects with crown ether part of **2** molecule through pair of $\text{O--H}\cdots\text{O}$ ($\text{O6--H6A}\cdots\text{O2}$: $\text{H}\cdots\text{O} = 2.31$ Å, $\text{O}\cdots\text{O} = 2.957$ Å, $\angle\text{O--H}\cdots\text{O} = 133^\circ$ and $\text{O6--H6A}\cdots\text{O4}$: $\text{H}\cdots\text{O} = 2.36$ Å, $\text{O}\cdots\text{O} = 2.917$ Å, $\angle\text{O--H}\cdots\text{O} = 127^\circ$) hydrogen bonds (Figure 2). The parameters of the hydrogen bonds were also listed in Table 3. After remove the solvents, the cavity is about 10.0% of the total volume of the crystal, as calculated using the program PLATON [53]. The tubes are packed with each other through Van der Waals interactions (Figure 3).

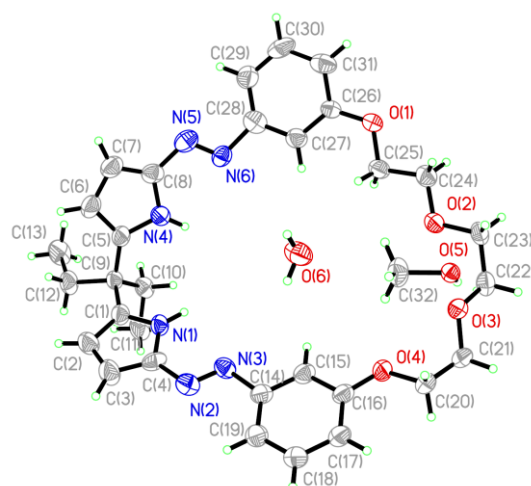


Figure 1. ORTEP diagram of compound **2** showing 30% probability of displaced ellipsoids.

Table 2. Selected bond lengths (Å) and torsion angles (°) of compound **2**.

Bonds	Length (Å)	Torsion Angles	Degree (°)
N2–N3	1.240(8)	N1–C4–N2–N3	0.2(11)
N5–N6	1.208(8)	C3–C4–N2–N3	179.4(8)
N1–C1	1.366(8)	C4–N2–N3–C14	179.5(6)
N1–C4	1.364(8)	C19–C14–N3–N2	6.1(11)
C1–C2	1.391(10)	C15–C14–N3–N2	172.5(7)
C2–C3	1.383(11)	N4–C8–N5–N6	3.5(11)
C3–C4	1.385(11)	C7–C8–N5–N6	174.3(8)
N2–C4	1.403(9)	C8–N5–N6–C28	174.4(6)
N3–C14	1.473(9)	C29–C28–N6–N5	21.5(10)
N4–C5	1.353(8)	C27–C28–N6–N5	155.9(7)
N4–C8	1.399(10)	C20–O4–C16–C17	12.3(11)
C5–C6	1.381(11)	O4–C20–C21–O3	66.0(8)
C6–C7	1.424(13)	O3–C22–C23–O2	67.4(7)
C7–C8	1.294(12)	O2–C24–C25–O1	175.5(6)
N5–C8	1.426(11)	C25–O1–C26–C27	8.0(11)
N6–C28	1.535(10)	N1–C1–C9–C10	51.6(9)
C16–O4	1.359(8)	N1–C1–C9–C5	71.3(9)
C26–O1	1.362(8)	N4–C5–C9–C10	34.7(9)
O4–C20	1.439(8)	N4–C5–C9–C1	87.7(8)
O1–C25	1.409(8)		

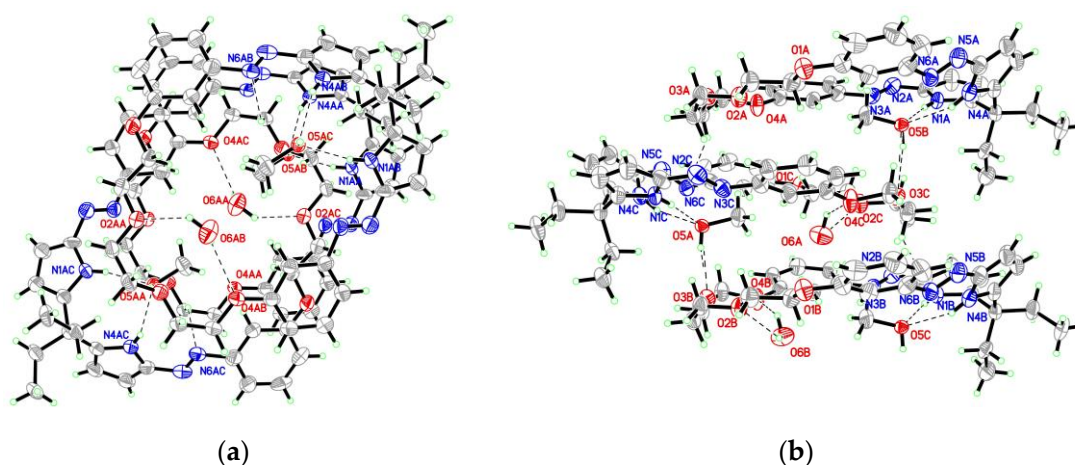
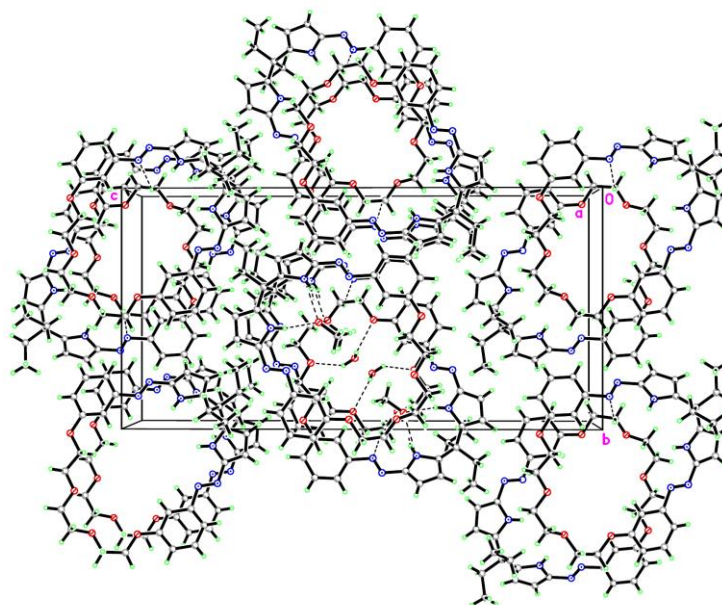


Figure 2. (a) Top view and (b) side view of tube structure self-assembled by hydrogen bonds in the crystal.

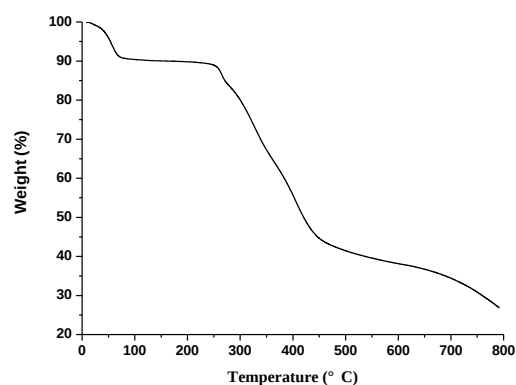
Table 3. Hydrogen bond parameters in the crystal of **2**.

D-H...A	D...A (Å)	H...A (Å)	∠D-H...A (°)
N1-H1...O5 ⁱ	3.001 (8)	2.15	169
N4-H4...O5 ⁱ	2.917 (8)	2.14	149
O5-H5...O3	2.758 (8)	1.95	166
O6-H6A...O2 ⁱⁱ	2.957 (13)	2.31	133
O6-H6A...O4 ⁱⁱ	2.951 (13)	2.36	127
C21-H21B...N6 ⁱ	3.314 (11)	2.61	129

Symmetry code i: $1/2 + x, 3/2 - y, 1 - z$; ii: $-1/2 + x, 3/2 - y, 1 - z$.

**Figure 3.** Crystal packing diagram of crystal of **2** (only one channel was filled with solvents for clarity).

To study the stability of the crystal, thermogravimetric analysis (TGA) was carried out. The TGA curve of the crystal of **2** is shown in Figure 4. It clearly shows a gradual weight loss of 9.0% before 70 °C, corresponding to the release of methanol and water molecules (calc. 8.3% for the crystal structure). The TGA curve also demonstrates that compound **2** starts to decompose after 250 °C, which indicates that compound **2** is stable to heat. It is consistent with other azopyrrole compounds [54]. The powder X-ray diffraction plots of crystal of **2** before and after heat at 100 °C for 6 h were shown in Figure 5. The two plots are almost the same. It means that the tubular structure of the crystal is unaffected after removing of the solvents.

**Figure 4.** The TGA curve of the crystal of **2**.

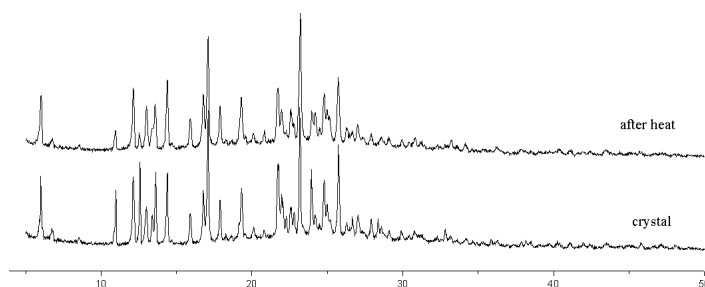


Figure 5. Powder X-ray diffraction plots of crystal of **2** before (below) and after heat (top).

3.3. The Anions Recognition of Compound **2**

The anions binding of macrocycle **2** with common anions such as F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- , and NO_3^- were studied in DMSO solution using a UV–Vis titration method. As shown in Figure 6A, only fluoride caused the UV–Vis spectrum change in compound **2** after the addition of 100 equivalent anions. Fluoride also caused the solution color to change from orange to red, whereas other anions did not. This indicates that compound **2** can selectively sense fluoride in DMSO solution. The UV–Vis spectra changes of compound **2** with the addition of fluoride are shown in Figure 6B. In DMSO solution, the λ_{max} of compound **2** is at 380 nm, which can be assigned to the absorption of the azopyrrole group and consistent with other azopyrroles [35]. Upon the gradual addition of fluoride, the intensity of the peak at 380 nm decreases, and the intensity of a new peak at 500 nm increases (Figure 6C). This is why the solution color changes. A linear response for fluoride was observed in the 1.25×10^{-5} – 2.5×10^{-4} M range. The limit of detection was 3.5×10^{-6} M in DMSO solution. The Job's plot analysis at 500 nm suggests that compound **2** formed a 1:1 complex with fluoride (Figure 6D). Calculated by non-linear least-square analysis [48], the association constant $K_a = 1846 \text{ M}^{-1}$, which is slightly higher than previous acyclic azopyrrole receptor [36].

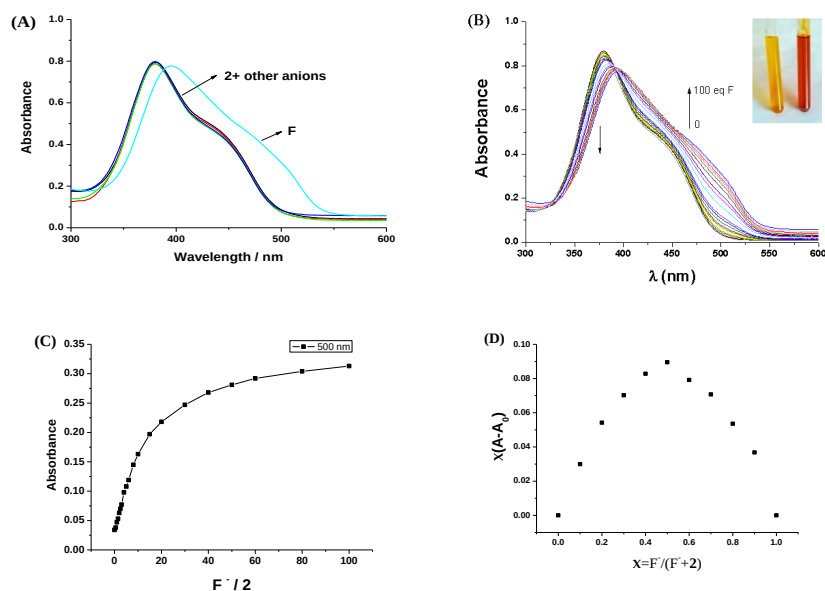


Figure 6. (A) UV–Vis spectral changes in **2** in DMSO (2.5×10^{-5} M) after the addition of 100 equivalent anions; (B) UV–Vis spectra change in compound **2** in DMSO solution (2.5×10^{-5} M) with the addition of fluoride (inset: color change of the solution); (C) changes observed at 500 nm with the addition of fluoride ions; and (D) the stoichiometry analysis of complex formation by Job's plot analysis at 500 nm ($[2] + [F^-] = 1 \times 10^{-5}$ M).

To interpret F^- sensing mechanism of probe **2**, ^1H NMR titration experiments were performed in $DMSO-d_6$. The ^1H NMR spectra changes in probe **2** upon gradual addition of fluoride ion are shown in Figure 7. The signals of pyrrole NH moved downfield and became broader upon the addition of only 0.25–1 equivalent of F^- ion. No solution color change was observed. This implies that probe **2** first interacted with fluoride ion through the hydrogen bonds. When four equivalents of F^- were added, the resonance signal of the N-H proton disappeared and peaks at 16.1 ppm for HF_2^- appeared, and the solution color changed from orange to red (Figure 6B inset). It indicates that more fluoride ions caused the deprotonation of the pyrrole NH. The deprotonation of pyrrole NH proton was also evident in the upfield shifts of aromatic protons of azopyrrole. According to the ^1H NMR spectra changes, the possible binding mode of probe **2** with fluoride is shown in Scheme 2.

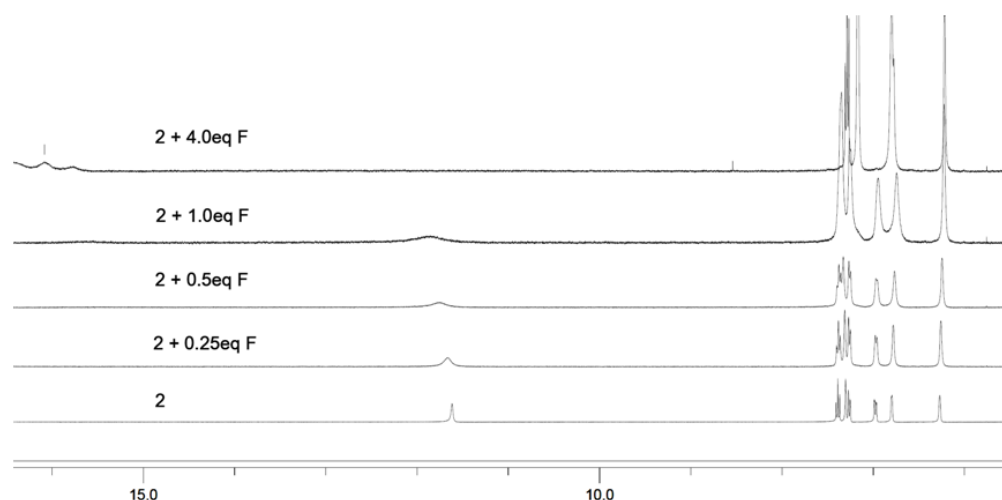
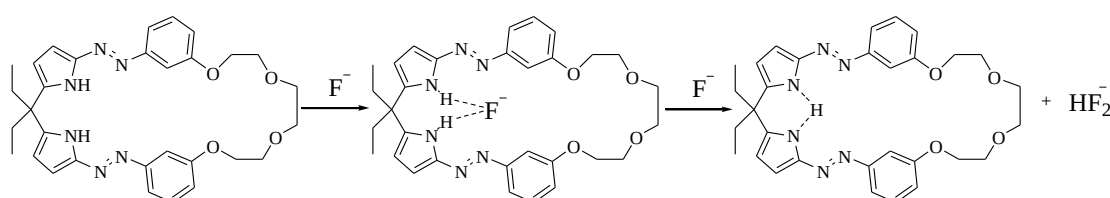


Figure 7. Partial ^1H NMR spectrum of **2** in $DMSO-d_6$ with the addition of different equivalents of fluoride.



Scheme 2. Proposed binding mode of receptor **2** with fluoride.

4. Conclusions

The synthesis and structural characterization of a macrocyclic compound **2**, which consist of bis-azopyrroles and polyether parts, was described. The structure of macrocycle **2** was confirmed by X-ray crystallography. The macrocycle **2** can bind methanol via pyrrole NH groups through a pair of N-H...O hydrogen bonds, and further self-assembled into tubular structures through C-H...N hydrogen bonds. It revealed that the crystal of macrocycle **2** can still maintain its porous properties after removing the included methanol molecules by heating. UV-Vis titration experiments suggested that macrocycle **2** can selectively sense fluoride in DMSO solution. The ^1H NMR titration experiments indicate that compound **2** firstly bound fluoride through hydrogen bonds and then was deprotonated with more fluoride. The polyether may has the ability to interact with cations, such as Li^+ and Na^+ . The ion-pair recognition of compound **2** to inorganic fluoride is under study.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/org6020025/s1>, Figure S1: ^1H NMR spectrum of compound **2** in DMSO- d_6 solution; Figure S2: ^{13}C NMR spectrum of compound **2** in DMSO- d_6 solution; Figure S3: The HR-MS spectrum of compound **2**. Crystallographic data for compound **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2117984. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Author Contributions: Y.A. and Z.Y. wrote the main manuscript text; Y.A. and Y.S. prepared the compound, and did other experiments. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All data generated or analyzed during this study are included in this published article and its supplementary information file.

Conflicts of Interest: The authors declare no conflicts of interest.

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