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Macrocyclic bis(amidonaphthol)s for anion sensing: tunable selectivity by ring size in proton transfer process

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ABSTRACT

The investigation on anion sensing properties for a series of macrocyclic bis(amidonaphthol)s **3a**–**3c** reveals the significant effects of macrocyclic ring size. Among them, macrocycle **3c** with the largest ring size shows F^- ion selectivity by causing clear red shift (24 nm) in fluorescence emission after complexation with F^-, which results in significant color change of fluorescence from blue to green. This excellent selectivity toward F^- ion might be attributed to the fitness between the acidity of –OH group and the basicity of F^- ion. Further exploration indicates that the acidity of –OH group can be tuned by ring size to give it the capability to discriminate the subtle difference in the affinity of F^-, CH_3COO^-, and $H_2PO_4^-$ to –OH proton.

1. Introduction

Considerable attention has been focused on the design and synthesis of effective receptors for anions on account of the importance of detection and recognition of anions in many disciplines, such as biological, medical, catalytic, and environmental sciences.[1] Among anion receptors, colorimetric and/or fluorescent chemosensors are particularly important owing to their high sensitivity for detection and convenience for monitoring the anion recognition.[2] As the smallest and most electronegative atom, fluoride ion has unique chemical properties and plays an important role in the dental care and the treatment of osteoporosis, etc.[3] In this regard, searching for efficient colorimetric and/or fluorescent chemosensor toward fluoride ion has attracted growing attention in recent years.[4]

Up to date, most of the reported fluoride chemosensors are based on flexible acyclic receptors, instead of utilizing relatively rigid macrocyclic molecules.[4] Although in virtually every case studied, macrocyclic anion receptors performed better than their acyclic counterparts owing to their well-preorganized topology.[5] On the other hand, from the viewpoint of signaling mechanism, excited state proton transfer (ESPT) mechanism has been widely utilized as the foundation in the design of efficient colorimetric and fluorescent sensors for anions,[6] and the proton transferring ability of the ligand controls the sensitivity and selectivity. Although some excellent ESPT mechanism-based fluoride ion chemosensors have been reported recently,[4a,7] few of them are endowed with the tunable proton transferring ability.

Herein, we report a new type of fluorescent chemosensor for fluoride ion based on macrocyclic receptor, which has two hydroxyl and two amide groups as the binding sites and naphthalene moieties as the signaling units. More significantly, it was found that the proton transferring ability of –OH group could be tuned by the ring size of the macrocycles to realize fluoride ion selective sensing.

2. Results and discussion

Macrocyclic receptors **3a**, **3b**, and **3c** were synthesized readily based on our recently reported novel synthetic method,[8] and the representative synthetic route is shown in Scheme 1.

Under normal conditions (that means no high-dilution was used), the condensation of di(acid chloride) **1** with diamine derivatives gave macrocyclic polyether compounds **2** in good yields. Then, by tandem Claisen rearrangement, two hydroxyl groups were readily introduced into the cavity of macrocyclic polyethers **2** to yield target macrocycles **3** quantitatively. Compared to the well-studied amide and/or amine N–H hydrogen-bonding motifs, anion receptors based on hydroxyl groups are surprisingly less investigated.[9,10] In fact, many naturally occurring anion-binding processes involve the cooperative work of the amide N–H and hydroxyl groups.[11] Therefore, it is expected that with the cooperative functions of two hydroxyl and two amide groups, as well as the accompanying naphthalene as signaling sites, the macrocyclic receptors **3** would exhibit potential for anion sensing. Furthermore, the different ring size of macrocyclic receptors **3** might play an important role on the anion sensing properties.

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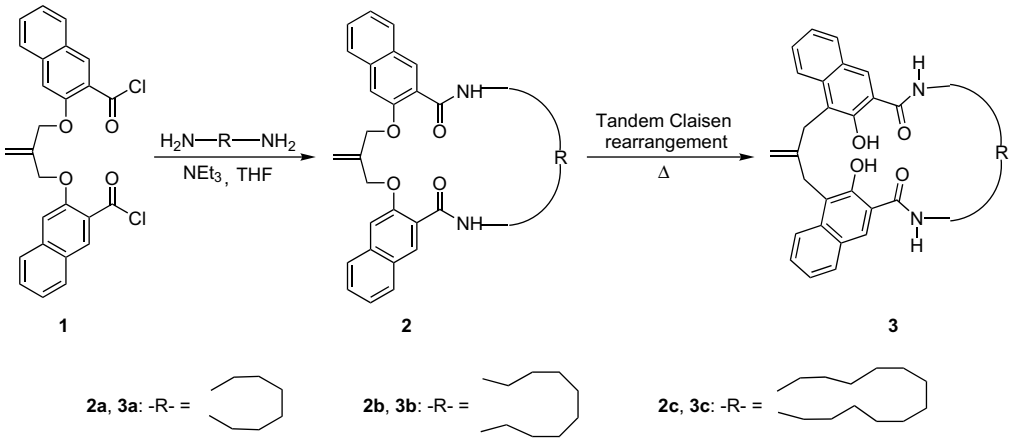
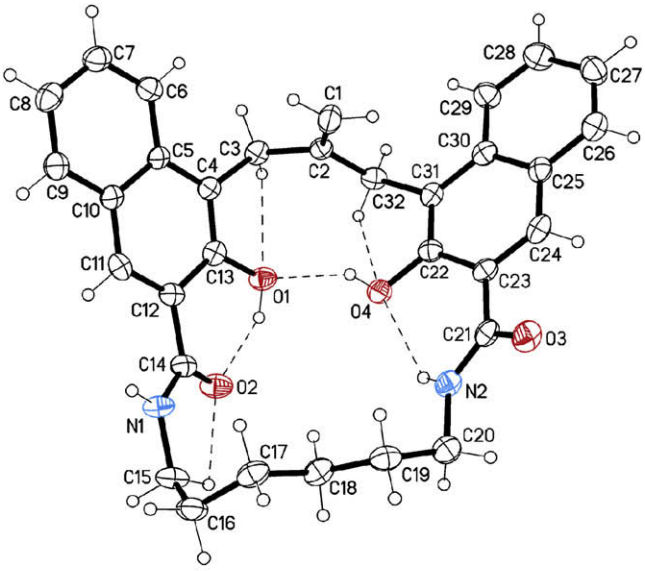


Scheme 1. Synthetic route to macrocyclic receptors of **3a**, **3b**, and **3c**.



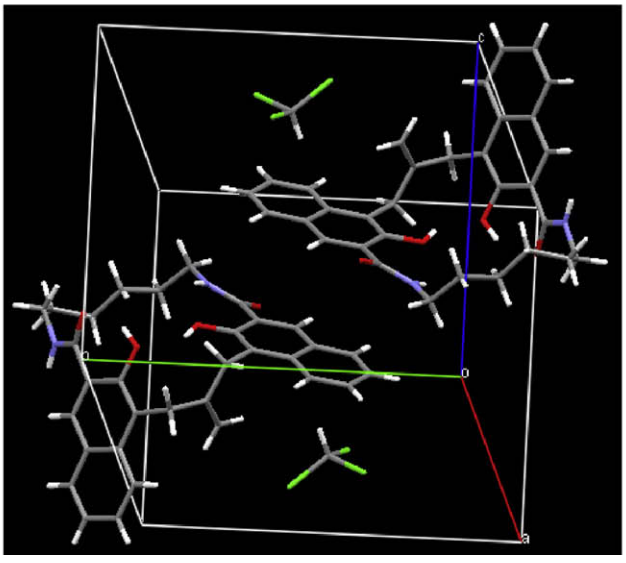


Figure 1. Single crystal structure (upper) and packing mode (below) of receptor **3a**.

Single crystal of **3a** suitable for an X-ray diffraction analysis was grown by slow vapor diffusion of hexane into the chloroform solution containing **3a**.[12] In the crystal structure shown in Figure 1, it was clear that receptor **3a** adopted a bowl-like twisted conformation plausibly owing to ring strain, and two hydroxyl groups directed outside of the cavity. The isobutenylene unit is not long enough as a linker to allow the two hydroxyl groups to become coplanar.[13] It was also clearly estimated that there are continuous intramolecular hydrogen bondings within this macrocycle and no intermolecular interactions were observed from the packing structure of receptor **3a**. Unfortunately, we failed to obtain the single crystals of **3b** and **3c** via the same method due to the worse solubility of them in $CHCl_3$ compared to **3a**. However, it can be predicted that **3b** and **3c** also adopted the twisted conformations on account of the presence of the same bis(hydroxynaphthoic amide) units.

However, from the ^{1}H NMR spectra of receptors **3a**, **3b**, and **3c** shown in Figure 2, no indication of such twisted conformation in solution has been observed, probably due to the flexibility of isobutenylene unit allowing rapid conformational change at room temperature. Moreover, the ^{1}H NMR signals for the –OH protons in these three receptors in CD_3CN were strongly downfield (the magnetic field lower than 11 ppm), consistent with involvement of intramolecular hydrogen bonding even in solution.

Significantly, it was worth noting from these ^{1}H NMR spectra that, with increasing the ring size of these macrocycles, the chemical shifts for phenolic –OH protons move to progressively downfield (δ from 11.82 to 12.06 to 12.42), indicating the corresponding enhancement of their acidity. Herein, acidity represents the hydrogen donating ability of –OH groups. This phenomenon revealed that increasing the ring size of these macrocycles resulted in the enhancement of hydrogen donating ability of their phenolic

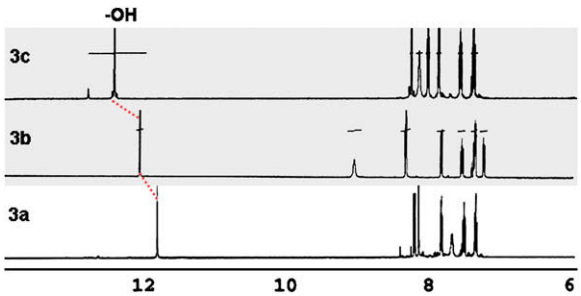


Figure 2. ^{1}H NMR spectra of **3a**, **3b**, and **3c** in CD_3CN.

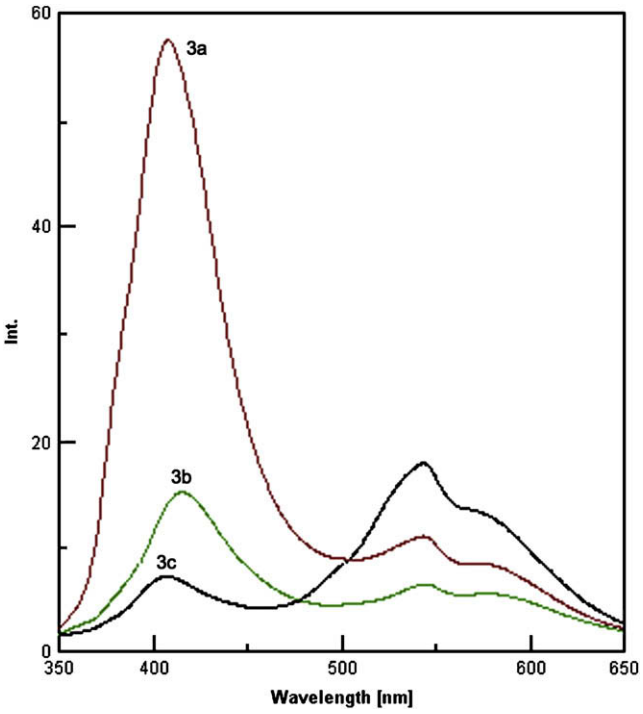


Figure 3. Fluorescence spectra of receptors **3a**, **3b**, and **3c** in CH_3CN.

–OH groups. The reason might be attributed to the formation of better intramolecular hydrogen bonding between –OH and carbonyl groups by enlargement of the ring size. The original fluorescent spectra of receptors **3a**, **3b**, and **3c** in solution provided further proof (Fig. 3). All of the fluorescence spectra exhibited two emission bands at around λ_{max}=400 nm and 550 nm. The longer wavelength is typical of intramolecular ESPT emission bands (I_2)[14] and the shorter one is due to the characteristic emission (I_1) of naphthalene moieties. The ratio of fluorescent intensity between I_2 and I_1 (i.e., I_2/I_1) represents the proton transferring potential (the same meaning as proton donating ability mentioned above) of the receptors at excited state. Accordingly, it was clearly seen from Figure 3 that, with increasing the ring size of macrocycles from **3a** to **3c**, the ratio of I_2/I_1 increases from 0.18 to 0.41 to 2.88, indicating the corresponding enhancement of their proton transferring potential. Therefore, it was concluded from the experimental data from both ^{1}H NMR and fluorescence spectra that, the proton donating ability of –OH groups of this type of macrocyclic receptors could be tuned by changing their ring size.

Just as well known, for anion sensing agents based on ESPT mechanism, their proton transferring ability controls the sensitivity and selectivity.[6] Accordingly, in the case of the macrocyclic receptors we report herein, it can be predicted that, the tunable proton transferring ability by changing their ring size would be advantageous to realize such control of sensitivity and selectivity for anion sensing.

With this aim in mind, anion recognition properties of these macrocyclic receptors **3a**, **3b**, and **3c** were investigated by using fluorescence spectroscopy and ^{1}H NMR method. Figure 4 shows the fluorescence changes of these three receptors upon addition of various anions having tetrabutylammonium as the countercation. After addition of F^-, CH_3COO^-, and $H_2PO_4^-$ anions, respectively, they exhibit significant fluorescence changes with appearence of a new emission peaks as well as the drastic increase of fluorescent intensity. On the basis of previously reported similar cases, the appearance of these new peaks are just due to the formation of intermolecular excited state proton transfer (ESPT) in the sensor–anion complexes by weakening the intramolecular hydrogen bonding between –OH and carbonyl groups.[6,7] In contrast, other anions, such as Cl^-, Br^-, I^-, HSO_4^-, did not induce any fluorescence spectra response, which implied that their relatively lower basicity cannot compete with aforementioned intramolecular hydrogen bonding. Those results clarified that this amidecrownophane-type receptor had the potential as the sensing agent for anions due to the unique change of their fluorescence upon binding certain anions via ESPT mechanism. For example, among halide anions, all of these receptors exhibit F^- ion selectivity. Significantly, we found with great interest from Figure 4 that, only for receptor **3c** having the largest ring size, only the complexation with F^- ion (over 1 equiv) induced clear red shift in its fluorescence emission compared to complexation of AcO^- or $H_2PO_4^-$ ions.

Figure 5 displays the detailed fluorescence titration results of receptor **3c** upon addition of various molar ratios of F^- ions. When the ratio between F^- and receptor **3c** is less than 1, a new fluorescent peak due to intermolecular proton transfer from –OH groups to F^- ion was observed. This phenomenon also occurred when CH_3COO^- and $H_2PO_4^-$ ions were added into receptor **3c** solution (Fig. 4). In contrast, when excess F^- ion (more than 1 equiv) was added, it was clearly found from Figure 5 that the fluorescence emission experienced remarkably red shift from 470 nm to 494 nm (from 1 equiv to 3 equiv of F^- ions), which induced the significant color change in fluorescence from blue to green accordingly.

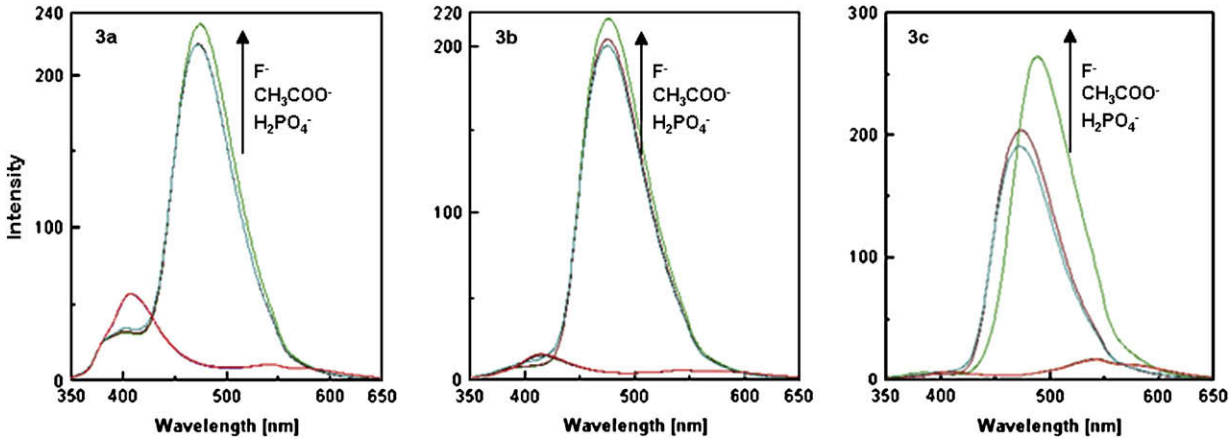


Figure 4. Changes in fluorescence spectra of receptors **3a**, **3b**, and **3c** upon addition of 3 equiv various anions in CH_3CN.

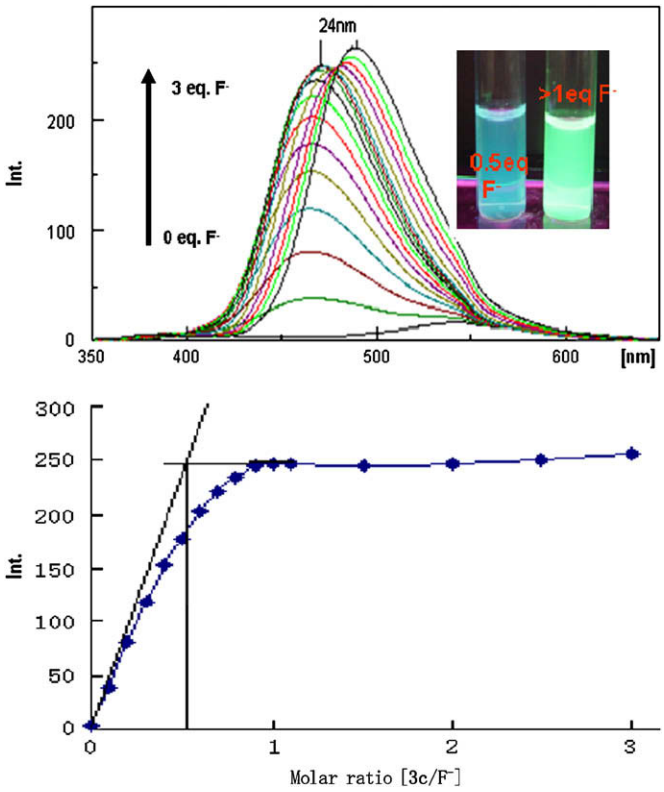


Figure 5. Fluorescence titration of **3c** (2×10^{-4} M) with F^- in MeCN (excitation at 340 nm, inserted spectra indicated the fluorescent color change upon addition different molar ratio F^-).

Fluorescent titration directly pointed to 2:1 stoichiometry between receptor **3c** and F^- ion. This unique binding behavior might be ascribed to the twisted bowl-like conformation of receptor **3c**, which tended to form sandwich-type complex with F^- ion.

In contrast, no such kind of red-shift phenomena was observed upon addition of more than 1 equiv AcO^- and $H_2PO_4^-$ ions into the solution, which demonstrated that receptor **3c** had the capability to discriminate F^- ion from CH_3COO^- and $H_2PO_4^-$ ions to some extend. Moreover, as for receptors **3a** and **3b**, with shorter ring size compared to **3c**, they did not exhibit such kind of ability either (Fig. 6). This result supported our previous prediction that the tunable proton transferring ability of –OH group induced by ring size controlled their anion sensing selectivity.

In order to understand more about the binding characteristics of receptor **3c** with F^- ion, ^{1}H NMR investigation was carried out in CD_3CN solution by monitoring the amide and hydroxy protons of **3c**, which initially appeared at 8.13 and 12.42 ppm, respectively. Figure 7 displays the chemical shifts of receptor **3c** upon addition of various molar ratios of F^- ion. It was clear that, upon addition of 0.25 equiv of F^- ion, the amide proton shifted downfield as a broad signal at about 8.8 ppm, and hydroxy proton disappeared completely. This result proved the formation of complex between receptor **3c** and F^- ion via multiple hydrogen-bonding interactions. Excess F^- (0.5–3 equiv) caused further changes, with the appearance of a new signal at 13.5 ppm after about 3.0 equiv accompanying significant changes in all the proton signals indicating the occurrence of deprotonation from hydroxy group to F^- ion to form HF_2^-. Similar phenomenon was observed in our previously reported case and other references.[15]

In summary, we developed herewith a new type of amide-crownophane with the potential as anion sensing agent. The most significant discovery for them was that the proton transferring ability of hydroxy group could be tuned by ring size to realize sensitive discrimination for various anions having different basicity. The excellent F^- ion sensing selectivity of receptor **3c** with the largest ring size was attributed to the fitness between the acidity of –OH group and the basicity of F^- ion. To the best of our knowledge, this is the first anion sensor that was endowed with the capability of ring size tuned selectivity in proton transfer process.

3. Experimental

3.1. General information

All commercial-grade chemicals and solvents were used without further purification. Tetra-*n*-butylammonium salts were dried under vacuum prior to use. ^{1}H NMR spectra were recorded on a Varian spectrometer operating at 500 MHz. Elemental analyses were obtained on a Fisons EA1108 CHNS-O. MS were measured on Bruker MALDI-TOF-MS apparatus. The fluorescence data were measured on a JASCO FP-6500 fluorescence spectrophotometer.

3.2. Synthesis of macrocyclic receptors 3a, 3b, and 3c

Macrocyclic receptors **3a**, **3b**, and **3c** were synthesized based on our previously reported procedure.[8] Among these, **2b** and **3b** are new compounds and their structures were conformed by NMR, MS, and elemental analyses.

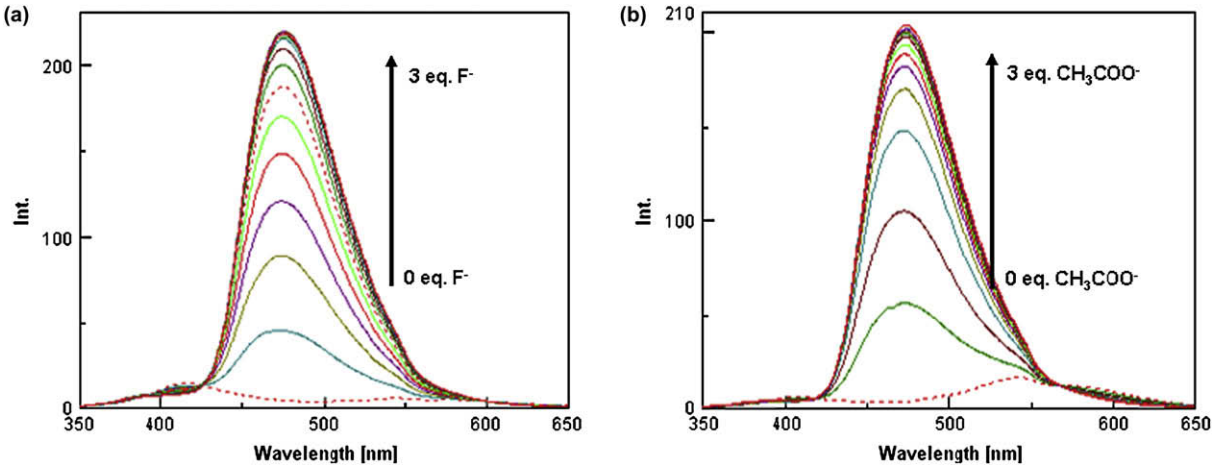


Figure 6. (a) Fluorescence titration of **3b** (2×10^{-4} M) with F^- in CH_3CN (excitation at 340 nm). (b) Fluorescence titration of **3c** (2×10^{-4} M) with CH_3COO^- in CH_3CN (excitation at 340 nm).

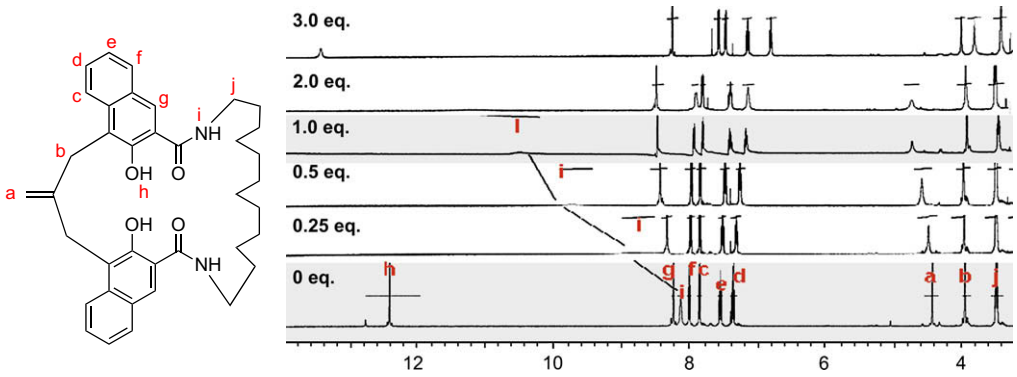


Figure 7. Stack plot of ^{1}H NMRs of **3c** with F^- (0–3 equiv, CD_3CN, 500 MHz).

3.2.1. Compound ***2b***

White solid; yield 69%; ^{1}H NMR (500 MHz, $CDCl_3$) 1.42–1.44 (m, 8H, $-CH_2-CH_2-$), 1.63–1.66 (m, 4H, $-CH_2-CH_2-$), 3.57 (m, 4H, $CONH-CH_2-$), 4.97(s, 4H, $-O-CH_2-$), 5.63 (s, 2H, $CH_2=C-$), 7.26 (s, 2H, naphthyl), 7.42–7.45 (dd, 2H, naphthyl), 7.52–7.55 (dd, 2H, naphthyl), 7.73 (d, J=8 Hz, 2H, naphthyl), 7.85 (br, 2H, NH), 7.92 (d, J=8 Hz, 2H, naphthyl), 8.76 (s, 2H, naphthyl) ppm; TOF-MS (cationic mode), 537.1(M+H). Anal. Calcd for $C_{34}H_{36}N_2O_4\cdot 0.9CHCl_3$: C, 65.07; H, 5.78; N, 4.36. Found: C, 64.83; H, 5.72; N, 4.31.

3.2.2. Compound ***3b***

Tandem Claisen rearrangement was carried out in solution of *N*-methyl-2-pyrrolidinone (NMP), under 160 °C for 40 min, and receptor **3b** was obtained quantitatively. Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) 1.52–1.58 (m, 8H, $-CH_2-CH_2-$), 3.84 (s, 2H, $CH_2=C-$), 4.66–4.67(m, 4H, $-CONH-CH_2-$), 5.28(s, 4H, $-O-CH_2-$), 7.16–7.18 (m, 2H, naphthyl), 7.31–7.33(br, 2H, NH–), 7.50–7.53 (m, 2H, naphthyl), 7.74 (d, J=8 Hz, 2H, naphthyl), 7.99 (s, 2H, naphthyl), 8.24 (d, J=8 Hz, 2H, naphthyl), 10.89 (s, 2H, –OH) ppm; TOF-MS (anionic mode), 535.3(M−H). Anal. Calcd for $C_{34}H_{36}N_2O_4\cdot 0.5CHCl_3$: C, 69.48; H, 6.17; N, 4.70. Found: C, 69.59; H, 6.23; N, 4.73.

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