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SHORT COMMUNICATION

Meso-functional calix[4]pyrrole: a solution phase study of anion directed self-assembly

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Abstract The 5,10,10,15,15,20,20-heptamethyl-5(4′-phenylcarboxylate) calix[4]pyrrole allocates dimer formation in solution. The pattern of dimeric self-assembly was recognized by a combination of ^{1}H NMR and mass spectrometry. The addition of F^{-} perturbed this assembly pattern, owing to the selective formation of calixpyrrole–F^{-} complex. Moreover, the spectroscopic findings revealed that calixpyrrole–F^{-} complex further chelates to the pyrrolic core of other OMCP through carboxylate hook, serving as a secondary binding site.

Keywords Meso-functional calix[4]pyrroles · Supramolecular chemistry · Anion directed self-assembly · Hydrogen bonds · Mass spectrometry

Introduction

The use of anionic components to direct self-assembly is a relatively new area of supramolecular chemistry but one which is expanding the available non-covalent and coordinate bonding motifs for the construction of interlocked materials and new non-covalently linked molecular architectures [1, 2]. Many of the structural motifs discovered previously have been used primarily for the production of the functioning structures including non-covalent dimers and dendrimers [3–6], nano-tubes forming cyclic peptides [7, 8], and oligonucleotide based on supramolecular assemblies [9]. Nevertheless, in recent years the templating influence of anions has been widely explored in the synthesis of supramolecular architectures [10–16].

Calix[4]pyrroles (CPs) as a representative class of neutral macrocycle receptors, first reported by Sessler and co-workers [17], are capable of selective binding of anions and neutral substrates both in the solution and the solid states [18, 19]. As major binding contributions, multiple H-bonding interactions between pyrrolic NHs of CP and substrate have been identified and has spawned constant efforts to design and synthesize new homologues as documented by several reports [20–24]. Nevertheless, in despite of rich anion complexation chemistry of CP, there are but few self-assembled CP based supramolecular architectures that are predicated on anion chelation or tempalation. These include self-assembled calix[6]pyrrole capsules that encapsulate different organic guests as well as solvent molecules [25], β-functional CP mono carboxylate that forms 2:1 assembly with bis-amidium calix[4]arene [26], CP-resorcinarene hybrid that forms molecular assembly with TMACl in the solid state [27] and cytosine substituted CP that acts as ditopic receptor and bind both the phosphate ''head'' and purine ''tail'' of 5′-GMP in a ''two-point'' like fashion [28]. More recently, H-bonding interactions have successfully been used to encapsulate one molecule of bis-N-oxide, utilizing self-assembled dimeric tetraurea CP capsules [29]. In an elegant work, Sessler and co-workers have demonstrated that CPs containing appended carboxylate groups at *meso*-position form anionic dimer [30]. Indeed, such findings of great interest provoked us to explore the chemistry of novel CP in solution phase.

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In continuation of our interest in self-assembly [31–33] and non-covalent interactions [34–39] of macrocycles, herein we report the synthesis of 5,10,10,15,15,20,20-heptamethyl-5(4′-phenylcarboxylate) CP **1** and its application in formation of anion mediated homo and hetero-composite self-assembly through meso-carboxylate hook and pyrrolic NH core.

Experimental

General

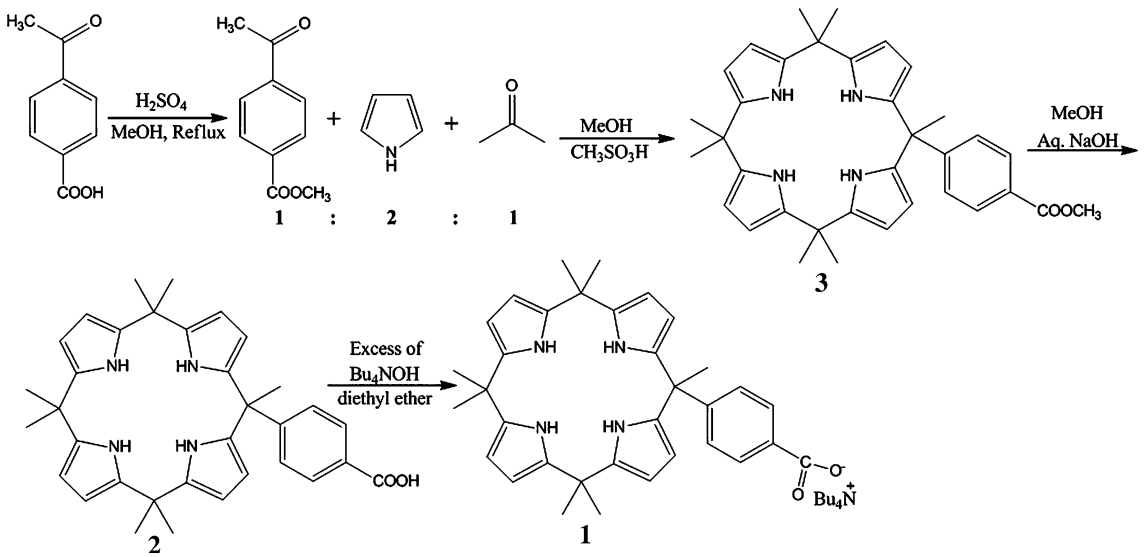
The IR spectra were recorded on Perkin-Elmer spectrum FT-2000 spectrometer and ν_{max} are expressed in cm^{-1}. High resolution mass spectra (ES-HRMS) were recorded on a VG-Fisions 'Autospec' spectrometer. The ^1H NMR and ^{13}C NMR were recorded on Bruker Avance-300 (300 MHz, 75 MHz) spectrometer using tetramethylsilane (TMS) and residual solvent signal (DMSO-d_6, δ 2.49; $CDCl_3$, δ 7.29) as internal standard and chemical shifts (δ) are expressed in ppm. ESI–MS spectra were recorded on KC ESI 455-TOF mass spectrometer of waters (Micromass, Manchester, UK). Column chromatography was carried out using silica gel (60–120 mesh and 230–400 mesh) of Spectrochem Pvt. Ltd. The 4-acetylbenzoic acid and Bu_4NF were purchased from Aldrich and stored in dry box before use. Pyrrole was distilled immediately prior to use. The solvents used were of analytical grade.

Synthesis

The typical experimental procedure is outlined in Scheme 1. Methyl-4-acetyl benzoate was synthesized in presence of conc. Sulfuric acid following the standard protocol. Colorless oil; Yield: 10 mL, 85%; IR $\nu_{max,}$ (Nujol)/cm^{-1}: 2941, 2985, 1729 (C=O), 1646, 1469, 1448, 1394, 1369, 1300, 1261, 1155, 1036(C–O), 980, 776, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 8.10$ (*d*, $J = 8.5$ Hz, 2H, o-Ar), 7.89 (*d*, $J = 8.7$ Hz, 2H, m-Ar), 3.88 (*s*, 3H, $-OCH_3$), 2.35 (*s*, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 196.7$ (C=O), 167.8 (C=O), 143.5 C, 134.9 C, 129.6 CH, 128.5 CH, 52.3 (OCH_3), 23.4 CH_3; ES-HRMS for $C_{10}H_{10}O_3Na$ $[M + Na]^+$: Calcd: 201.0528, Found 201.0525.

Synthesis of 5,10,10,15,15,20,20-hepta methyl-5-(4-phenylmethyl carboxylate)CP **3**: The compound was synthesized by following mixed condensation approach as reported previously [30]. White solid; Yield: 145 mg, 12%; IR $\nu_{max,}$ (Nujol)/cm^{-1}: 3440 (–NH), 3030, 2856, 1733, 1445, 1370, 1302, 1259, 1155, 1034 (C–O), 977, 774, 667 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6, 298 K): $\delta = 9.28$ (*s*, 2H, NH), 8.89 (*s*, 2H, NH), 8.08 (*d*, $J = 7.8$ Hz, 2H, Ar), 7.60 (*d*, $J = 7.8$ Hz, 2H, Ar), 5.45–5.82 (*m*, 8H, β-pyrrolic), 3.69 (*s*, 3H, $-OCH_3$), 1.75 (*s*, 3H, CH_3), 1.32–1.43 (*m*, 18H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): $\delta = 169.9$ (C=O), 138.7 C, 137.6 C, 137.4 C, 136.9 C, 128.7 CH, 127.9 CH, 106.7 CH, 105.4 CH, 104.5 CH, 104.9 CH, 53.1 OCH_3, 36.8 C, 36.2 C, 35.8 C, 35.3 C, 30.4 CH_3, 28.5 CH_3, 27.9 CH_3, 27.1 CH_3, 26.8 CH_3, 26.2 CH_3, 25.9 CH_3, 25.6 CH_3; ES-HRMS for $C_{35}H_{39}N_4O_2$ $[M–H]^-$: Calcd: 547.3073, Found: 547.3078; for $C_{35}H_{40}N_4O_2Cl$ $[M + Cl]^-$: Calcd: 583.2840, Found: 583.2842.

Preparation of 5,10,10,15,15,20,20-heptamethyl-5-(4′-phenylcarboxylic acid)CP **2**: the basic hydrolysis of **3** afforded corresponding acid in 85% yield. ^1H NMR (300 MHz, DMSO-d_6, 298 K): $\delta = 9.16$ (*bs*, 2H, NH),



Scheme 1 Schemetic representation of synthesis of *meso*-hooked calix[4]pyrroles

8.82 (*bs*, 2H, NH), 8.10 (*d*, $J = 8.7$ Hz, 2H, Ar), 7.71 (*d*, $J = 8.9$ Hz, 2H, Ar), 5.45–5.78 (*m*, 8H, *β*-pyrrolic), 1.67 (*s*, 3H, CH_3), 1.32–1.42 (*m*, 18H, CH_3); ES-HRMS for $C_{34}H_{38}N_4O_2Na$ $[M + Na]^+$: Calcd: 557.2892, Found: 557.2885.

Preparation of tetrabutylammonium 5,10,10,15,15,20,20-heptamethyl-5-(4′-phenylcarboxylate)CP **1**: The reaction of **2** with two equiv of Bu_4NOH in diethyl ether afforded corresponding salt. Creamy solid; ^1H NMR (300 MHz, DMSO-d_6, 298 K): $\delta = 10.18$ (*s*, 2H, NH), 9.86 (*s*, 2H, NH), 8.0 (*d*, $J = 7.8$ Hz, 2H, Ar), 7.6 (*d*, $J = 6.9$ Hz, 2H, Ar), 5.52–5.41 (*m*, 8H, *β*-pyrrolic), 3.0 (*m*, 8H, $NCH_2CH_2CH_2CH_3$), 1.75 (*s*, 3H, *meso*-CH_3), 1.03–1.44 (*m*, 34H, *meso*-CH_3 and $NCH_2CH_2CH_2CH_3$), 0.87 (*t*, 12H, $NCH_2CH_2CH_2CH_3$). ES-HRMS for $C_{50}H_{72}N_5O_2[M–H]^-$: Calcd: 774.5686, Found: 774.5680; for $C_{34}H_{37}N_4O_2$ $[M–(Bu)_4N]^-$: Calcd: 533.2920, Found: 533.2923.

Results and discussion

Solution phase studies of assembly formation

Homo-composite dimeric self-assembly

Initial evidence for facile self-assembly in solution phase came from ^1H NMR spectroscopy. Unfortunately, owing to intense broadening of NHs in CD_2Cl_2, the solvent of choice was DMSO-d_6. An assessment of NH resonances in the ^1H NMR spectra of **3** and **1** revealed that **1** exists in the dimer form in solution. For instance, in the ^1H NMR spectrum of **3** in DMSO-d_6, the NH resonances appeared at δ 8.89 and 9.28 ppm while the signals of NH protons of **1** underwent a significant downfield shift ($\Delta\delta_{\text{pyrrole NH}} \sim 1.0$ ppm) and appeared at 9.86 and 10.1 ppm, respectively. This significant downfield shifting was supposed to be as a consequence of H-bonding interactions since the free carboxylate spacer in **1** is capable to form dimer or some higher homologues. From this viewpoint, we decided to go with mass spectrometry in non polar solvent. The HR-ES mass spectra of **1** (2.0×10^{-4} mol L^{-1}) in DCM: CH_3CN (1:1,v/v) gave doubly charged complexation peaks at 1066.5840 Da for **1.1** along with a monomer peak at 533.2923 Da (Fig. 1). The rational intensities of monomer and dimer peaks observed were 100% and >20%, respectively. Interestingly, such peaks were not recognized in case of **3** which suggested that the presence of unprotected carboxylate group in the molecule is essential for self-assembly processes and ruled out the possibility of dimer formation due to simple Vander Waals or hydrophobic interactions.

Perturbation of dimer formation: fluoride effect

It is well established and quite reasonable that due to its high electro-negativity and small size (more basicity), F^- binds to CPs most effectively and selectively. Taking this

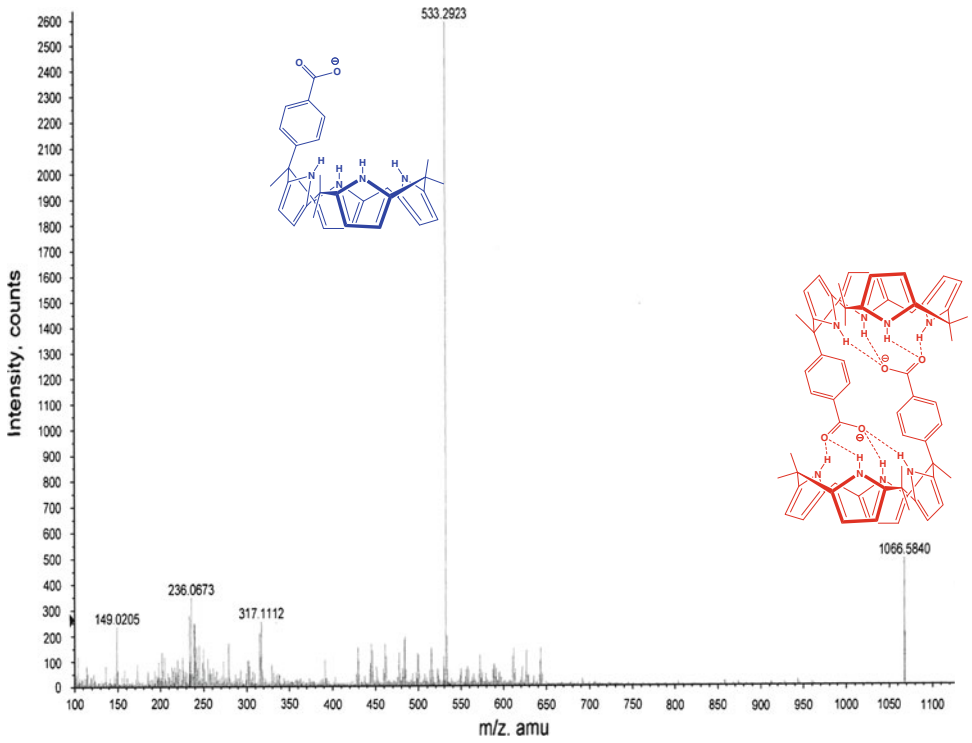


Fig. 1 ES-Mass spectrum of **1** (2.0×10^{-4} mol L^{-1}) in DCM:CH_3CN (1:1, v/v) at 298 K

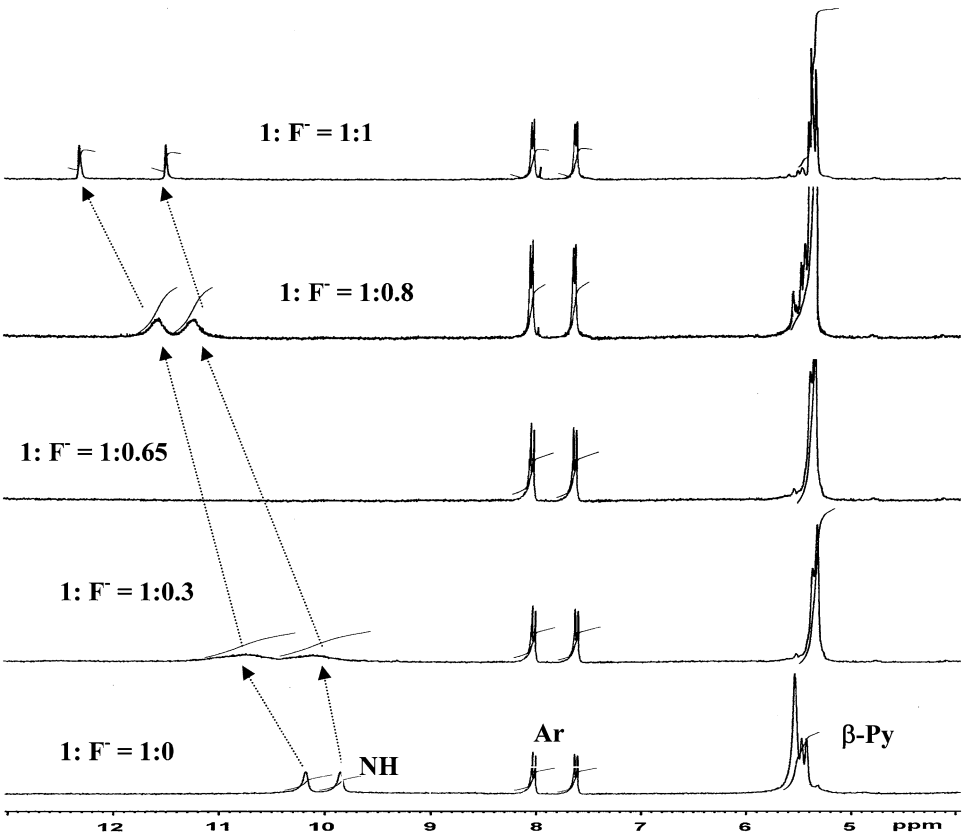
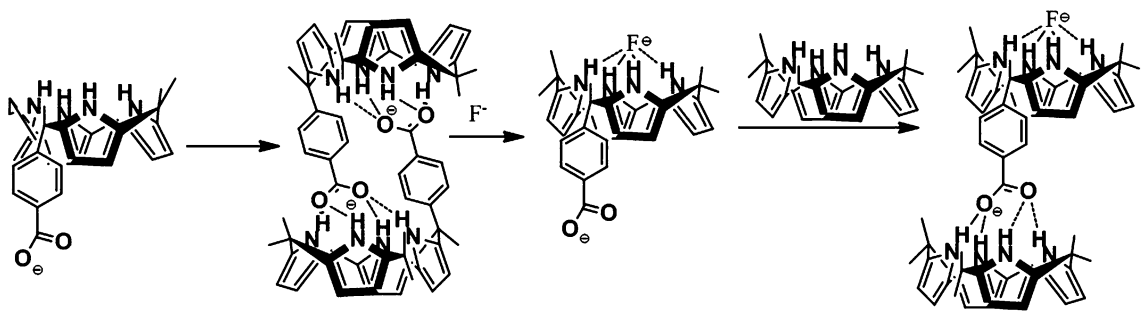


Fig. 2 ^{1}H NMR titration profile of **1** (0.01 M) with F^- (0.1 M) in DMSO-d_6-0.5% water at 298 K: perturbation of dimer formation

into account, ^{1}H NMR titrations of **1** were performed with F^- in DMSO-d_6 water (Fig. 2). Upon addition of 0.2 equiv of F^- (0.1 M) to the solution of **1** (0.01 M), the pyrrolic NH experienced a dramatic effect and two NH resonances shifted downfield with significant broadening from δ 9.86 and 10.1 ppm to δ 10.1 and 10.8 ppm, respectively, indicative of NH–F^- complexation. On further addition of 0.35 equiv of F^- (total 0.65 equiv), the NH resonances completely disappeared, a case which is frequently encountered during titrations of chromophoric CPs with F^- [36, 40]. A new set of resonances was recognized at δ 11.2 and 11.6 ppm on addition of 0.80 equiv of F^- and finally two NHs appeared at δ 11.5 and 12.3 ppm on administration of 1.0 equiv of F^-. Further addition of F^- caused no changes in the proton NMR spectra. Titrations were stopped at this point. Such large shift changes for NHs ($\Delta\delta_{NH} = 1.64$ ppm, $\Delta\delta_{NH} = 2.2$ ppm) were assumed due to selective and effective complexation of F^- with **1** i.e. F^- inhibits the dimer formation (Scheme 2). Indeed, it proved to be the case when the original dimer peak at 1066.5840 Da in **1** disappeared completely on addition of F^- to the DCM solution of **1**. The mass spectrum showed exclusively **1**.F^- complexation peak at 552.6810 Da with 100% intensity. In addition, monomer and chlorinated peaks were also observed at 533.2925 and 568.2605 Da.

The NMR data proved the 1:1 stoichiometry of resulting CP–F^- complex. Moreover, the β-pyrrolic protons were simplified after titration, an indication for transition from



Scheme 2 Carboxylate directed homo and hetero-composite self-assembly

1,3-alternate ($\delta = 5.59$, d, $J = 2.1$ Hz) to symmetrical cone conformation ($\delta = 5.31$, s). The resulting CP–F^- complex still has its carboxylate tail at meso-position, capable to bind through multiple H-bonds. These findings are important because a single molecule provides a two point binding platform for complexation.

Hetero-composite self-assembly

In order to utilize, the second binding site, a carboxylate pendent arm, the titrations of CP–F^- complex were performed with OMCP in DMSO-d_6 water solution at 298 K. For this purpose, the solution of CP–F^- complex was used as analyte while OMCP as host. In the absence of analyte, the ^{1}H NMR spectrum of OMCP in DMSO-d_6 showed three resonances at δ 9.18 (4H), 5.59 (8H) and 1.42 (24H) ppm for NHs, β-pyrrolic CH and *meso*-CH_3 protons respectively. Upon addition of 0.70 equiv of CP–F^- to the solution of OMCP, the pyrrolic NHs were broadened and shifted downfield from δ 9.18 to δ 9.7 ppm significantly and finally appeared at 10.6 ppm after complete addition ($\sim$1 equiv) of CP–F^- (Fig. 3). The NMR findings clearly reveal the chelation of carboxylate hook of CP–F^- with NH core of OMCP (Scheme 2). Further, the chelation of same was also monitored by mass spectroscopy. The mixing of CP–F^- and OMCP in 1:1 M ratio, showed a dimer peak at 980.5849 Da along with peaks at 552.6809 and 428.0373 Da which were recognized for CP–F^- complex and OMCP (Fig. 4).The appearance of a dimer peak clearly indicated that *meso*-hooked CP with carboxylate hook effectively binds with pyrrole core of the second molecule, while the pyrrole core of former interacts with F^-.

Conclusions

In summary, we have explored the potential application of novel meso-functional CP in anion mediated self-assembly in solution phase. The spectroscopic findings suggest the formation of CP–F^- and CP-carboxylate, dual complex, in solution. Undoubtedly, the present protocol may offer the advantage to recognize the precise functioning of non-covalent interactions of Uroporphyrinogen decarboxylate and Coproporphyrinogen oxidase, the essential enzymes in the heme biosynthetic pathway, which in turn will be prolific in understanding the mechanism of natural life pigments.

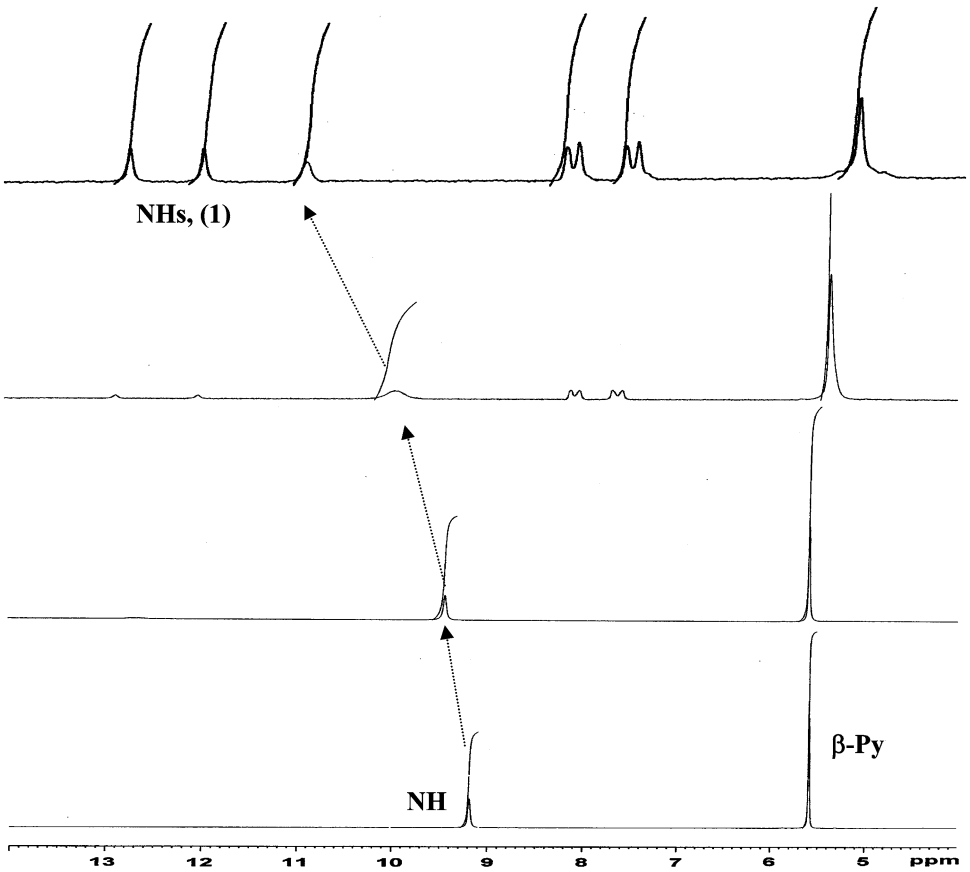


Fig. 3 ^{1}H NMR titration profile of CP-F^- complex (0.05) with OMCP (0.05 M)

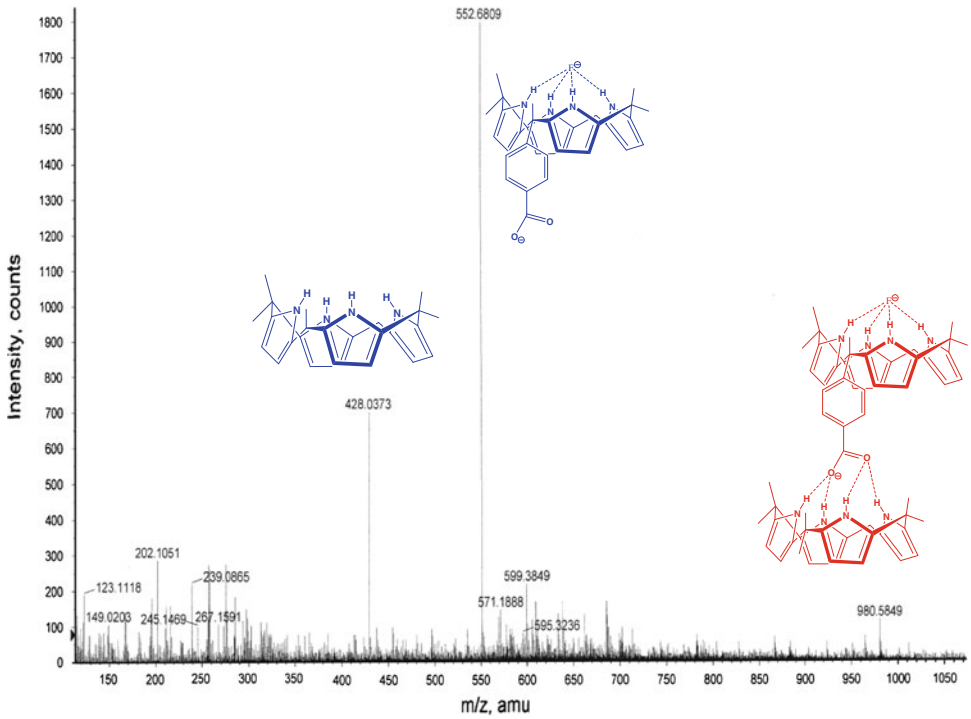


Fig. 4 ES-Mass spectrum of 1:1 CP-F^- complex and OMCP: hetero-composite self-assembly

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