Application of DOSY to Confirm the Obtention of a Novel Crowned Porphyrin

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Abstract: *The extremely rich chemistry of porphyrins and metalloporphyrins has stimulated the application of these compounds in many different areas. When functional groups, like crown ethers, are introduced in the macrocycle, the resultant supramolecular system can associate these characteristics and develop new functions. Diffusion-ordered spectroscopy (DOSY) is a tool to study diffusion coefficients of compounds in mixture by NMR. All NMR signals from the same molecule have the corresponding D.Therefor,e DOSY measurements can be used to confirm a formation of an intermolecular interaction or a chemical reaction. The present work reports the application of DOSY and ^{1}H,^{19}F NMR spectra in the confirmation of the crowned porphyrin H_2(T15C5P) formation and its characterisation. The DOSY spectrum showed the same diffusion coefficients for all H_2(T15C5P) ^{1}H signals and distinct D to the porphyrin precursor. The ^{1}H and ^{19}F NMR spectra were consistent with H_2(T15C5P). The ^{19}F NMR spectrum showed two doublets at δ -142.1 (J=17.43 Hz) and δ -161.8 (J=17.43 Hz) relative to the fluorine atoms in the orto and meta positions of the phenyl substituents. Howeve,r it did not show any signal correspondent to the F_{para} of the parent porphyrin. ^{1}H NMRdata showed a singlet in δ -2.83, a multiplet in δ 3.51-4.14 and a singlet in 8.95 ppm, which were attributed to NH, crown ether and pyrrolic hydrogens, respectively. The DOSY experiment was indispensable to confirm the formation of a new Crowned Porphyrin H_2(T15C5P), a reaction product of H_2(TFPP) with 2-(aminomethyl)-15-crown-5-ether.*

The extremely rich chemistry of porphyrins and metalloporphyrins has stimulated the application of these compounds in many differents areas. When functional groups like molecules or entities, with well-known and specific properties, are introduced in the macrocycle, the resultant supramolecular system can associate these characteristics and develop new functions.[1] An interesting group of compounds used as porphyrin substituents are crown ethers, which form complexes with alkali and alkaline earth metal ions as well as with neutral organic molecules.[2,3]

Diffusion-*o*rdered *s*pectroscop*y* (DOSY) is a tool to study diffusion coefficients of compounds in mixture by NMR. The results are displayed as a 2D spectrum in which signals are dispersed according to chemical shift in one dimension and diffusion coefficients (*D*) in the other. All NMR signals from the same molecule have the corresponding *D*, therefore DOSY measurements can be used to confirm the formation of an intermolecular interaction or a chemical reaction.

The present work reports the application of DOSY and ^{1}H, ^{19}F NMR spectra to confirm unequivocally the product of reaction between porphyrin and crown ether H_2(T15C5P) and its characterization. This new metal-free porphyrin containing four covalently attached 2-aminomethyl-15-crown-5 moieties on the periphery of 5, 10, 15, 20-tetrakis (pentafluorophenyl) porphyrin (Figure 1) was obtained by the reaction of free ligand H_2(TFPP) with 2-(aminomethyl)-15-crown-5-ether.

NMR spectra were recorded on a Bruker DRX400 9.4 Tesla equipment, at 298K, in a 5 mm indirect detection probe equiped with gradient coil in *z* direction (maximum 30 G), using $CDCl_3$ as solvent. TMS and CF_3COOH were used as internal and external references for ^1H, and ^{19}F, respectively.

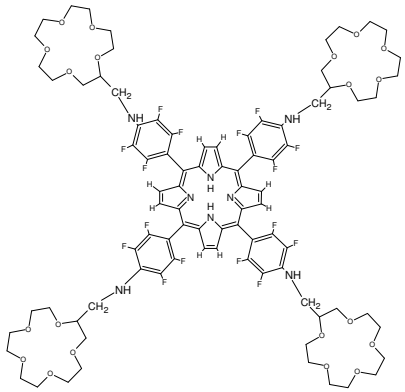

Figure 1. 5, 10, 15, 20 – tetrakis [4'-(1",4",7",10",13"-Pentaoxa-cyclopentadec-2methylamino) 2', 3', 5', 6'-tetrafluoro] phenyl porphyrin, H_2(T15C5P).

The DOSY spectrum (Figure 2) show the same diffusion coefficients for all H_2(T15C5P) ^1H signals. Furthermore, the porphyrin precursor presents distinct *D* in the same acquisition condition, which proves that they are covalently attached.

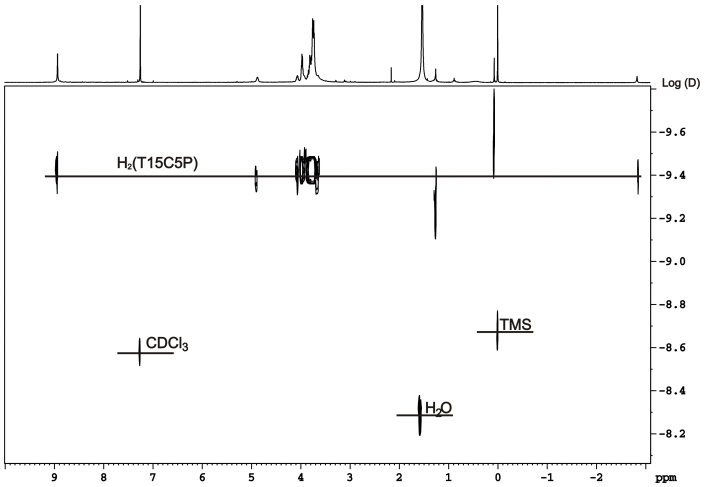

Figure 2. DOSY NMR spectra of H_2(T15C5P), obtained using the BPPLED pulse sequence. The gradient strength of 1.6 ms duration was incremented in 32 steps, with diffusion time Δ of 100 ms and recovery delay τ_R of 5 ms. The *D* (diffusion coefficient) is given in m^2/s.

^{1}H and ^{19}F NMR spectra were consistent with H_2(T15C5P). The ^{19}F NMR spectrum showed two doublets at δ -142.1 (J=17.43 Hz) and δ -161.8 (J=17.43 Hz) relative to the fluorine atoms in the orto and meta positions of the phenyl substituents. However, it did not show any signal correspondent to the F_{para} of the precursor porphyrin, which normally appears at δ -153.6 ppm.

^{1}H NMR data showed a singlet in δ -2.83, a multiplet in δ 3.51-4.14 and a singlet in 8.95 ppm attributed to NH, crown ether and pyrolic hydrogenous, respectively.

The DOSY experiment was indispensable to confirm the formation of a new Crowned Porphyrin H_2(T15C5P), a reaction product of H_2(TFPP) with 2-(aminomethyl)-15-crown-5-ether.

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