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CARBOXYLATE LIGANDS CONTAINING PYRIDINIUM GROUPS – VERSATILE LINKERS IN CONSTRUCTION OF NEW MOFs: ONE-POT SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

A general straightforward synthesis of an original class of flexible ligands containing pyridinium groups and an increasing number of coordinating sites has been developed, 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride 1, 1,1',1''-(benzene-1,3,5-triyl)-tris(methylene)tris(4-carboxypyridinium) tribromide 2 and 1,1',1'',1'''-(benzene-1,2,4,5-tetrayl)-tetrakis(methylene)tetrakis(4-carboxypyridinium) tetrabromide 3. All three ligands were fully characterized by ^{1}H, ^{13}C NMR, mass and IR spectra.

I - INTRODUCTION

Single-crystal structure research on metal-organic frameworks (MOFs) [1] is rapidly expanding because of their original structural motifs [2] and their promising applications in various technical areas such as catalysis [3], gas storage [4], molecular adsorption and selective separation [5].

The design and construction of new MOFs structure is controlled by many factors such as the fixed coordination geometry of the metal centers and their organic linkers, as well as the synthetic method [6]. Among these factors, organic linkers play crucial roles thanks to the flexibility of their symmetry, molecular backbone, bridging units and conformational preference [7]. The aromatic multicarboxylate ligand precursors such as 1,4-bezenedicarboxylic acid; 1,3,5-benzenetricarboxylic acid; 1,2,4,5-benzentetracarboxylic acid and biphenyldicarboxylic acid have been widely used in the construction of MOFs with various topologies [1, 8]. These rigid ligands are either commercially available or easy to synthesize but the construction of unprecedented frameworks with original topologies and properties requires more flexible or tunable ligands.

In an attempt to developing new MOFs materials and studying the roles of ligand conformations in the structure of the coordination networks, we designed and synthesized, in one-pot method, an original class of carboxylate ligands containing pyridinium groups and an increasing number of coordinating sites, the 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride **1** [9]; the 1,1',1''-(benzene-1,3,5-triyl)-tris(methylene)tris(4-carboxypyridinium) tribromide **2** and the 1,1',1'',1'''-(benzene-1,2,4,5-tetrayl)-tetrakis(methylene)tetrakis(4-carboxypyridinium) tetrabromide **3**. To the best of our knowledge, the synthesis of ligands **2** and

3 were not reported in the literature. The presence of a benzyl group may increase the flexibility of the molecular skeleton. The introduction of positively charges from pyridinium groups in the ligand backbone can lead to electrostatic repulsion which is helpful to avoid the interpenetration in the construction of MOFs. Furthermore, the steric structure of these ligands can be easily tuned by choosing appropriate precursors.

II - EXPERIMENTAL

1. Materials and instrumentation

Chemicals were purchased from Sigma-Aldrich, Acros and Merck, and used as received without further purification. NMR spectra were recorded with a Brucker AV 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C are referenced to residual solvent resonances used as an internal standard and reported relative to TMS. Mass spectra were recorded with a Thermo Finigan TSQ 7000 mass spectrometer. Infrared spectra were performed in KBr pellets with a Bruker Vector 22 spectrometer.

2. Synthesis of ligand 1

The ligand **1** was synthesized according to the procedure described in the literature [9]. A mixture of 4,4′-bipyridine (0.062 g, 0.400 mmol) and 4-(chloromethyl)benzoic acid (0.136 g, 0.800 mmol) in DMF (5 mL) was stirred 12h at 120 °C. The reaction mixture was then cooled to room temperature. The resulting precipitate was filtered off, washed with DMF and Et_2O and then dried in a vacuum for 4h to give **1** as a white powder in 30% yield (0.057g, 0.120 mmol). FT-IR (KBr, pellet): ν = 3437 (O–H), 1688 (C=O), 1636 (C=N) cm^{-1}. ^{1}H NMR (500,1 MHz, D_2O): δ = 9.09 (d, $^{3}J_{HH}$ = 6.5 Hz, 4H, C*H*-2,6$_{Py}$), 8.46 (d, $^{3}J_{HH}$ = 6.5 Hz, 4H, C*H*-3,5$_{Py}$), 7.96 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, C*H*$_{Ph}$), 7.48 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, C*H*$_{Ph}$), 5.91 (s, 4H, CH_2N^+) ppm. ^{13}C NMR (125.8 MHz, D_2O): δ = 169.8 (s, *C*=O), 150.4 (s, *C*H-4$_{Py}$), 145.8 (s, *C*H-2,6$_{Py}$), 137.3 (s, *i*-CH_2C_{Ph}), 131.4 (s, *C*H$_{Ph}$), 130.6 (s, *C*H$_{Ph}$), 129.2 (s, *i*-CO*C*$_{Ph}$), 127.2 (s, *C*H-3,5$_{Py}$), 64.1 (s, CH_2N^+) ppm. ESI MS: *m/z* = 425 $[M\text{-}2Cl\text{-}H]^+$.

3. Synthesis of ligand 2

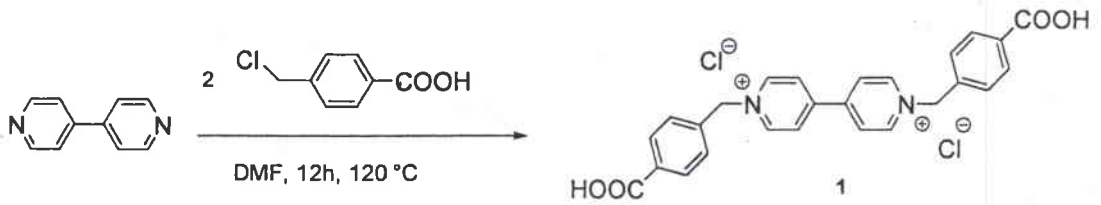
1,3,5-Tris(bromomethyl)benzene (0.500 g, 1.400 mmol) and isonicotinic acid (0.517 g, 4.200 mmol) were dissolved in DMF (70 mL). The reaction mixture was stirred for 48h at room temperature until a white precipitate appeared. After filtration, the precipitate was washed with Et_2O (3 × 10 mL) and dried in a vacuum for 4h to give **2** as a pale white powder in 59% (0.590 g, 0.800 mmol). FT-IR (KBr, pellet): ν = 3401 (O–H), 1726 (C=O), 1641 (C=N) cm^{-1}. ^{1}H NMR (500,1 MHz, DMSO-d_6): δ = 9.38 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C*H*-2,6$_{Py}$), 8.51 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, C*H*-3,5$_{Py}$), 7.75 (s, 3H, C*H*$_{Ph}$), 6.00 (s, 6H, CH_2N^+) ppm. ^{13}C NMR (125,8 MHz, DMSO-d_6): δ = 163.5 (s, *C*=O), 146.4 (s, *C*H-2,6$_{Py}$), 146.1 (s, *i*-CO*C*$_{Ph}$), 135.6 (s, *i*-CH_2C_{Ph}), 130.1 (s, *C*H$_{Ph}$), 127.6 (s, *C*H-3,5$_{Py}$), 62.6 (s, CH_2N^+) ppm. ESI MS: *m/z* = 724 $[M\text{-}H]^-$, 484 $[M\text{-}3Br\text{-}2H]^+$.

4. Synthesis of ligand 3

1,2,4,5-Tetrakis(bromomethyl)benzene (0.074 g, 0.156 mmol) and isonicotinic acid (0.078 g, 0.624 mmol) were dissolved in DMF (10 mL). The reaction mixture was stirred for 48h at room temperature. Et_2O was then added to form a precipitate. After filtration, the precipitate was washed with Et_2O (3 × 10 mL) and dried in a vacuum for 4h to give **3** as a pale green powder in 67% (0.098 g, 0.104 mmol). FT-IR (KBr, pellet): ν = 3383 (O–H), 1727 (C=O), 1643 (C=N) cm^{-1}. ^{1}H NMR (500.1 MHz, D_2O): δ = 8.94 (d, $^{3}J_{HH}$ = 5.8 Hz, 8H, C*H*-2,6$_{Py}$), 8.37 (d, $^{3}J_{HH}$ = 5.8 Hz, 8H, C*H*-3,5$_{Py}$), 6.82 (s, 2H, C*H*$_{Ph}$), 6.08 (s, 8H, CH_2N^+) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 165.2 (s, *C*=O), 148.7 (s, *i*-CO*C*$_{Ph}$), 146.2 (s, *C*H-2,6$_{Py}$), 134.3 (s, *i*-CH_2C_{Ph}), 131.3 (s, *C*H$_{Ph}$), 128.2 (s, *C*H-3,5$_{Py}$), 60.6 (s, CH_2N^+) ppm. ESI MS: the molecular peak was not observed.

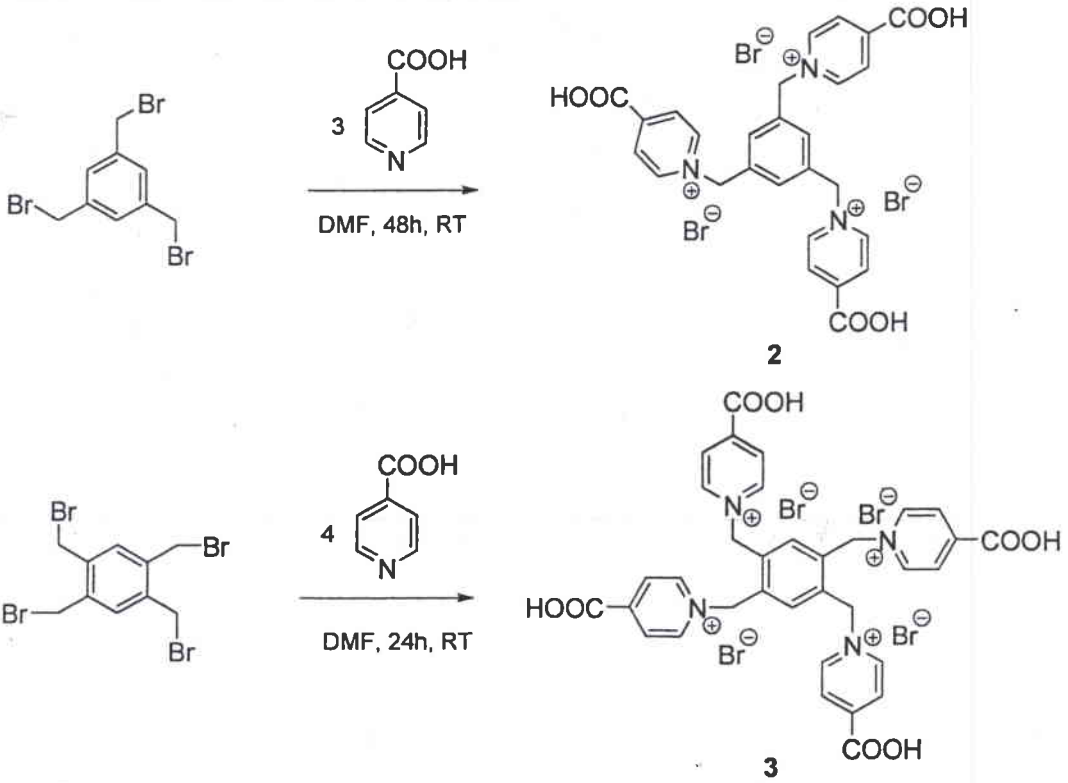
III - RESULTS AND DISCUSSION

The ditopic ligand **1** was prepared by the reaction of 4,4′-bipyridine with 2 equivalents of 4-(chloromethyl)benzoic acid in DMF at 120 °C (Scheme 1) [9]. The yield after purification is 30%, comparable to that described by Sun and al. [9].



Scheme 1: Synthesis of ligand **1**

The reaction of 1,3,5-tris(bromomethyl)benzene or 1,2,4,5-tetrakis(bromomethyl)benzene with appropriate equivalents of isonicotinic acid in DMF at room temperature afforded the tritopic ligand **2** (59% yield after purification) or tetratopic ligand **3** (67% yield after purification) respectively (scheme 2).



Scheme 2: Synthesis of ligands **2, 3**

Ligands **1-3** were fully characterized by ^{1}H, ^{13}C NMR, mass and IR spectroscopies. It is noteworthy that although the ligand **1** was synthesized firstly by Sun and al. [9], the NMR and mass spectra of this compound have never been reported.

Mass spectroscopic analyses allowed us to identify the molecular peak $[M\text{-}2Cl\text{-}H]^+$ and $[M\text{-}3Br\text{-}2H]^+$ for the ligand **1** and **2** respectively. In the case of ligand **3**, the molecular peak was not observed, due to the instability of this compound during the ionization process.

FT-IR spectra of compounds **1 - 3** displayed a broad band in the region of 3383 - 3437 cm^{-1} corresponding to the stretching vibration of the O-H group. The strong band between 1688 and 1727 cm^{-1} can be attributed to the characteristic C=O stretching vibration of carboxylic acid. The typical C=N stretching vibrations of the pyridinium groups appear as strong bands in the region of 1636 - 1643 cm^{-1}.

The most characteristic chemical shifts in ^1H and ^{13}C NMR for ligands **1 - 3** are presented in the Table 1. ^1H NMR spectra of these compounds are very simple suggesting that ligands **1**, **2** and **3** have C_2, C_3 and C_4 symmetries respectively. The formation of pyridinium groups in compounds **1-3** is evidenced in their ^1H NMR spectra by the downfield shift of the protons on the pyridine ring (8.74 and 7.53 ppm for 4,4'-bipyridine [10] versus 9.09 and 8.46 ppm for **1**; 8.79 and 7.83 ppm for isonicotinic acid [10] versus 9.38, 8.51 ppm for **2** and 8.94, 8.37 ppm for **3**). The dramatic deshielding effects observed for the protons CH_2N^+ (δ in the region of 5.91-6.08 ppm) is characteristic for the methylene group directly connected to the nitrogen atom of pyridinium group [11].

Moreover, HMBC experiment monitored on ligand **2** (figure 1) showed the correlation between the protons CH_2N^+ (δ ^1H 6.00 ppm) and the carbon atoms $CH\text{-}2,6_{Py}$ (δ ^{13}C 146.4 ppm) confirmed definitely the connection of methylene group to the nitrogen atom of the pyridine ring. The signal of proton of carboxylic group in compounds **1-3** was not observed in ^1H NMR spectra.

Table 1: The most characteristic chemical shifts in ^1H and ^{13}C NMR for ligands **1-3**

Ligands	δ ^1H (CH-2,6$_{Py}$, $^3J_{HH}$)	δ ^1H (CH-3,5$_{Py}$, $^3J_{HH}$)	δ ^1H (CH_2N^+)	δ ^{13}C (C=O)	δ ^{13}C (CH_2N^+)
1	9.09 (6.5)	8.46 (6.5)	5.91	169.8	64.1
2	9.38 (6.8)	8.51 (6.8)	6.00	163.5	62.6
3	8.94 (5.8)	8.37 (5.8)	6.08	165.2	60.6

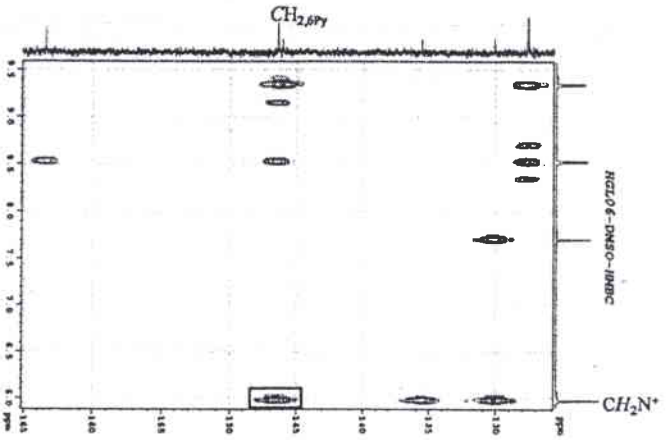


Figure 1: HMBC spectrum of ligand **2**

The ^{13}C NMR spectra of ligands **1-3** exhibited a singlet in the region of 163.5-169.8 ppm and a singlet in the region of 60.6-64.1 ppm respectively assigned to the carbon of the carboxylic group and the carbon of the CH_2N^+ moiety.

IV - CONCLUSION

In summary, we have developed a general straightforward synthesis of an original class of carboxylate ligands incorporating pyridinium groups. The method of synthesis allowed us to vary the number of coordinating sites as well as the geometry of ligands. All obtained compounds were fully characterized by ^1H, ^{13}C NMR, mass and IR spectroscopies. Since the electronic and steric properties of these ligands can be finely and easily tuned, studies to evaluate the potential uses of these compounds in the synthesis of new MOFs materials are under active investigation.

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