

SYNTHESIS OF TETRACATIONIC ORGANIC SALT FROM 4,4'-BIPYRIDINE

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(Received November 18, 2016; Revised December 20, 2017; Accepted December 21, 2017)

ABSTRACT. This report describes the synthesis of a tetracationic organic salt from 4,4'-bipyridine and 1-bromooctane using 1,3-dibromopropane as a spacer just in three simple steps. A careful monoacylation of one of the nitrogen atoms of 4,4'-bipyridine using 1-bromooctane followed by the dimerization using 1,3-dibromopropane as a linker resulted a tetracationic organic salt of formula $[C_8H_6(C_8Bipyr)_2]Br_4$. 1H and ^{13}C NMR, and CHN elemental analysis as well as ultra high vacuum spectroscopic technique (XPS) were employed to confirm the synthesis and the purity of this compound. This compound has demonstrated molar conductivity of $4320 S cm^2 mol^{-1}$ unexpected from a salt with 1:4 cation to anion ratio. It is expected that this salt would have potential applications in materials such as for low-molecular-weight gelators and the preparation of solid films for organic electronic applications.

KEY WORDS: 4,4'-Bipyridine, Tetracationic, 1,3-bis(N-octyl-4,4'-bipyridine)propanium

INTRODUCTION

4,4'-Bipyridine is an ideal connector between any units having Lewis acidic sites (atoms) for network formation. This is because of its two potential binding nitrogen atoms with lone pair of electrons which are arranged in a divergent fashion as well as its rigid structure. Furthermore, it is convenient enough to create predictable molecular dimensions upon the formation of the networks. Even though the pyridine groups of 4,4'-bipyridine freely rotate along a central C–C bond, it does not affect the mutual orientation of the two lone pairs. Therefore, 4,4'-bipyridine can be regarded as rigid and a prototypical bridging heteromolecule [1].

The synthesis and applications of polycationic organic salts has become one of the research directions of pure chemistry and material science. The chemistry and applications of monocationic organic salts has been the starting points for this progress. The majority of the later compounds are known as ionic liquids. Ionic liquids (ILs) are low temperature melting salts (below 100 °C) [2, 3]. These have been widely used as alternative reaction media to conventional organic solvents [4-6] and in electrochemistry [7, 8]. Evolved from the latter, di-, tri- and tetracationic organic salts have become ideal materials in solving several problems [9]. This is due to the potential to change their structural features simply by: varying the nature of the cation and/or the anion; tuning them by introducing small structural changes in the constituting ions, or of the spacers separating them provides the opportunity to obtain materials with sets of desired properties suitable for different applications. They have been applied as a chemical anchorage on a solid support [10], starting materials for the synthesis of molecular devices [11, 12], reaction media or catalysts, immobilization of catalysts [9], reaction media for high-temperature organic reactions [13, 14], catalysts [15], receptors for anion recognition [16], low-molecular-weight gelators [17], fluorescent organic salts [18,19], energetic materials [20, 21], for use in the preparation of solid films for organic electronic applications [22] and electrowetting materials [23]. Heteromolecules including imidazole, 1,10-phenanthroline, pyridine and others have been used as the starting materials for the synthesis of polycationic organic salts. 4,4'-bipyridine has a convenient structure to serve as a precursor for the synthesis

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of polycharged organic salts. Several reports appeared in literature describing the synthesis and applications of organic salts derived from 4,4'-bipyridine [3, 24-29]. In this regard, tetracationic salts derived from 4,4'-bipyridine have been reported using ethylbromide as primary quaternizing and $X(\text{CH}_2)_nX$, $n = 4-10$ as spacers [30-32]. The nature and compositions of the first quaternizing and the spacer alkyl chain significantly influence the characteristics of the polycharged salt. In this report, therefore, we demonstrate the synthesis and characterizations of a new tetracationic organic salt using 4,4'-bipyridine, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Br}$ as a primary quaternizing molecule and $\text{Br}(\text{CH}_2)_3\text{Br}$ as a linker with bromide as a counter anion. The latter is responsible for the high solubility of the salt in water and other polar solvents such as methanol and acetonitrile.

The primary step, which is important to acquire the target tetracationic organic salt, relies up on the successful quaternization of one of the equally active nitrogen atoms in 4,4'-bipyridine by $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Br}$. This gives a monocationic N-octyl-4,4'-bipyridinium bromide as a product [3]. The symmetry of 4,4'-bipyridine is reduced following the quaternization of only one of its nitrogen atoms and this new characteristic feature helps in the identification of the new monocationic organic salt as new peaks appear in both the ^1H and ^{13}C NMR spectra. The careful 1:2 molar ratio treatment of this product with 1,3-dibromopropane yielded bis(N-octyl-4,4'-bipyridine)propanium bromide.

EXPERIMENTAL

Materials and methods

All chemicals used in the present work, *viz.*, 4,4'-bipyridine (99%), 1-bromooctane, 1,3-dibromopropane (99%), 1,4-dioxane, acetonitrile are all from Sigma-Aldrich and are used as received.

The structures of the prepared compounds were confirmed by their ^1H NMR, and ^{13}C NMR using a Bruker AM-270 (270 MHz) spectrometer dissolving in deuterated dimethyl sulfoxide. CHN elemental analysis was done using 5E-CHN2200 Elemental Analyzer taking 15 mg sample. Bromide estimation was conducted taking 1 mg sample dissolved in 20 mL distilled water. Excess AgNO_3 solution was added for the formation of silver bromide (AgBr) precipitate. Then the cruddy white precipitate formed was filtered, dried in an oven and the amount of bromide was calculated from the weight difference. The electronic environment of the component atoms of the cation, $[\text{C}_3\text{H}_6(\text{C}_8\text{Bipyr})_2]^{4+}$ and the anion, bromide, (Br^-) were investigated using ultra-high vacuum (UHV) characterization using X-ray photoelectron spectroscopy, XPS. The X-ray photoelectron spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al K α source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, hemispherical analyzer and a multi-channel plate and delay line detector (DLD) with an X-ray incident angle of 0° (relative to the surface normal). The spectrum was processed without charge correction. Its conductivity for 10^{-4} M solution in deionized water was also investigated using JENWAY 4200 conductivity meter at room temperature with cell constant of 0.96.

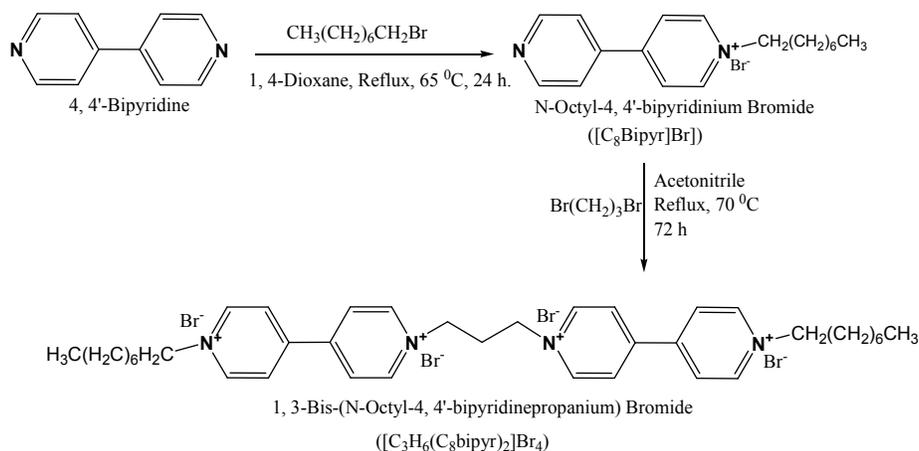
Synthesis of N-octyl-4,4'-bipyridinium bromide, $[\text{C}_8\text{Bipyr}]\text{Br}$

5 g (0.032 mol) of 4,4'-bipyridine was dissolved in 30 mL dry 1,4-dioxane in a two necked 100 mL round bottomed flask fitted with a condenser. 6.20 g (0.032 mol, 5.55 mL) of 1-bromooctane dissolved in 10 mL dry 1,4-dioxane was added drop wise from a dropping funnel and the mixture was allowed to stir at 65°C . After 24 h, a pale yellow precipitate was filtered from the reaction medium and characterized by ^1H and ^{13}C NMR spectroscopy. The result revealed that the product contained a mixture of monoalkylated and dialkylated 4,4'-bipyridinium bromides. 50 mL chloroform was used to extract the dialkylated product from the

mixture. After filtration the chloroform was removed by evaporation in vacuo and the resulting solid dried under high vacuum for 4 hours. A white powder $[C_8\text{Bipyr}]\text{Br}$ was collected (yield 8.56 g, 76.5% [3]).

Synthesis of 1,3-Bis-(N-Octyl-4,4'-bipyridinium bromide), $[C_3H_6(C_8\text{Bipyr})_2]Br_4$

2 g (0.0057 mol) of $[C_8\text{Bipyr}]\text{Br}$ was dissolved in 50 mL dry acetonitrile in a two necked 250 mL round bottomed flask fitted with a condenser. 0.605 g (0.003 mol, 306 μL , slightly excess) of 1,3-dibromopropane ($\text{Br}(\text{CH}_2)_3\text{Br}$) dissolved in 20 mL acetonitrile was added from a dropping funnel and the mixture was allowed to stir at 70 $^\circ\text{C}$. After 72 hours bright yellow precipitate was filtered from the reaction medium and washed three times in 20 mL acetonitrile each and dried under high vacuum for 4 hours (yield 4.44 g, 86%). The reaction path is indicated in Scheme 1.



Scheme 1. The synthetic strategy of $[C_3H_6(C_8\text{Bipyr})_2]Br_4$.

RESULTS AND DISCUSSION

Characterization of N-Octyl-4,4'-bipyridinium bromide, $[C_8\text{Bipyr}]\text{Br}$

^1H NMR (270 MHz, $\text{DMSO-}d_6$) δ ppm 0.78-0.87 (m, 3H), 1.16-1.35 (m, 10H), 1.96 (d, $J = 5.92$ Hz, 2H), 4.70 (t, $J = 7.44$ Hz, 2H), 8.05-8.11 (m, 2H), 8.67-8.72 (m, 2H), 8.82-8.88 (m, 2H), 9.35 (d, $J = 7.02$ Hz, 2H). ^{13}C NMR (68 MHz, $\text{DMSO-}d_6$) δ ppm 14.50 (s, 1C), 22.61 (s, 1C), 25.99 (s, 1C), 29.00 (d, 2C), 31.28-31.79 (m, 2C), 60.80 (s, 1C), 121.82 (s, 1C), 122.50 (s, 2C), 125.94 (s, 1C), 141.37 (s, 1C), 145.91 (s, 1C), 148.22-154.23 (m, 2C), 149.90-156.39 (m, 2C), (CHN elemental analysis: found(calculated), C, 61.86(61.89), H, 7.15(7.16), N, 7.96(8.02), Br, 22.88(22.92).

Characterization of $[C_3H_6(C_8\text{Bipyr})_2]Br_4$

^1H NMR (270 MHz, $\text{DMSO-}d_6$) δ ppm 0.82-0.90 (m, 6H), 0.83-0.88 (m, 6 H), 1.19-1.41 (m, 18H), 1.99 (s, $J = 0.28$ Hz, 6H), 2.77-2.90 (m, 3H), 2.80-2.89 (m, 3H), 4.72 (t, $J = 7.23$ Hz, 6H), 4.95 (t, $J = 7.02$ Hz, 4H), 8.90 (dd, $J = 14.60, 6.89$ Hz, 12H), 9.42-9.61 (m, 12H) (Figure 1). ^{13}C

NMR (68 MHz, DMSO- d_6) δ ppm 14.53 (s, 2C), 22.63 (s, 2C), 26.03 (s, 2C), 29.00 (d, 4C) 31.31-31.75 (m, 3C), 127.20 (d, 4C), 146.55 (d, 3C), 148.92-149.33 (m, 1C) (Figure 2).

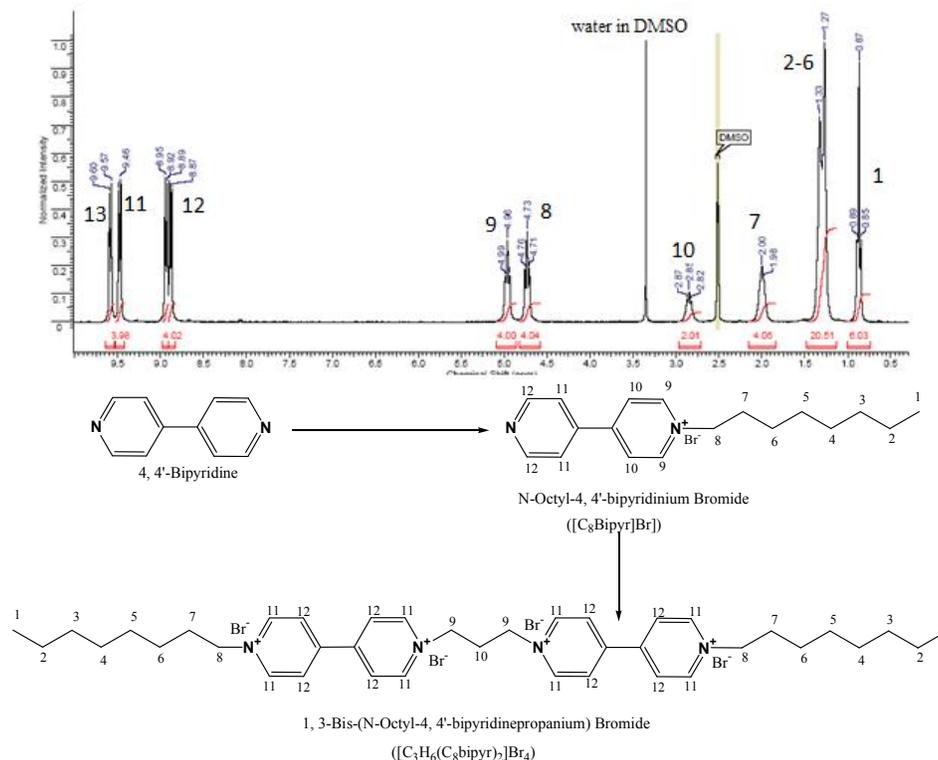


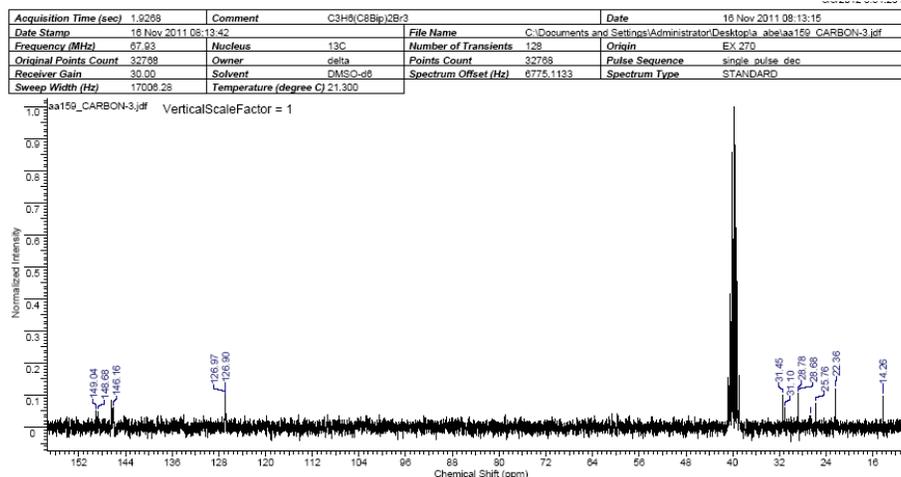
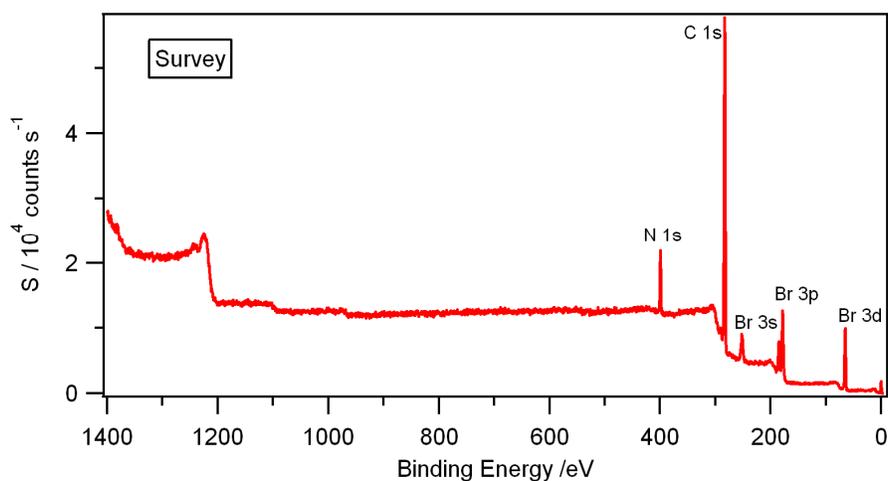
Figure 1. ^1H NMR spectrum of $[\text{C}_3\text{H}_6(\text{C}_8\text{Bipyr})_2]\text{Br}_4$ with the corresponding assignment of the chemical shift.

CHN elemental analysis

Element, found(calculated), C, 51.96(52.00), H, 6.15(6.22), N, 6.10(6.22), Br, 35.50(35.56). The composition and purity of the compound were established by the measurement of XP survey (Figure 3) and high-resolution spectra (Figures 4-6).

The electronic environments of the component atoms in eV: 284.929 for C1s of the fourteen carbons from the octane residues, 286.835 for C1s of the carbons linked to the ring nitrogens, 285.601 for C1s of ring carbons not attached to nitrogen, 285.625 for C1s of the middle carbon in the spacer (Figure 3 and 4), 286.835 for N1s (Figure 3 and 5). For bromine, 67.3275 and 68.376 for 3d $_{5/2}$ and 3d $_{3/2}$, respectively) (Figures 3 and 6).

The dimerization of the $(\text{C}_8\text{Bipyr})\text{Br}$ using $\text{Br}(\text{CH}_2)_3\text{Br}$ as a spacer to $[\text{C}_3\text{H}_6(\text{C}_8\text{Bipyr})_2]\text{Br}_4$ is evident in the ^1H NMR from the appearance of two new peaks centered at δ ppm = 4.95 (t) and 2.85 (m) with peak area equivalent to four and two protons, respectively. Moreover, those peaks observed in the precursor monoalkylated organic salt also are found peak areas doubled in the final compound (Figure 1). Similar confirmations are obtained in the ^{13}C NMR (Figure 2).

Figure 2. ¹³C NMR spectrum of [C₃H₆(C₈Bip)₂]Br₄Figure 3. XP survey spectrum of [C₃H₆(C₈Bip)₂]Br₄.

The survey of spectrum from the XPS showed the purity of the compound which compounded the evidence from the CHN elemental analysis. From the XPS spectra, the electronic environments identified were, only one for all the nitrogens resonated at 401.788 eV, four for carbons and one for bromide. All the carbons linked to the ring nitrogens formed the same electronic environment with a binding energy of 286.835 eV. The remaining ring carbons constituted the second electronic environment with binding energy of 285.601 eV. The middle carbon in the spacer showed a different electronic environment resonating at 285.625 eV where as the fourteen carbons from the octane residues formed the fourth electronic environment with binding energy of 284.929 eV. The maximum molar conductivity of a salt with 1:4 cation to anion or *vice versa* in water at 298 K is 736 S cm² mol⁻¹ [33]. However, this salt demonstrated

attractive molar conductivity ($4320 \text{ S cm}^2 \text{ mol}^{-1}$). This is attributed to the high speed of mobility of the ions due to the nature of the cation. This is a consequence of the very long dimeric, rod-like cation contained relatively long hydrophobic alkyl chain; its positive charge is highly delocalized throughout the aromatic ring portion; subsequently, become amphiphilic [30]. This reduces the drifting (counter directional) speed due to the interaction with the solvent cavity surrounding the cation.

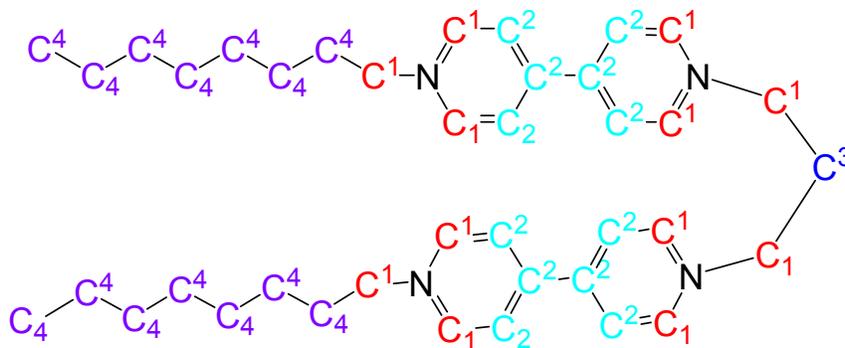
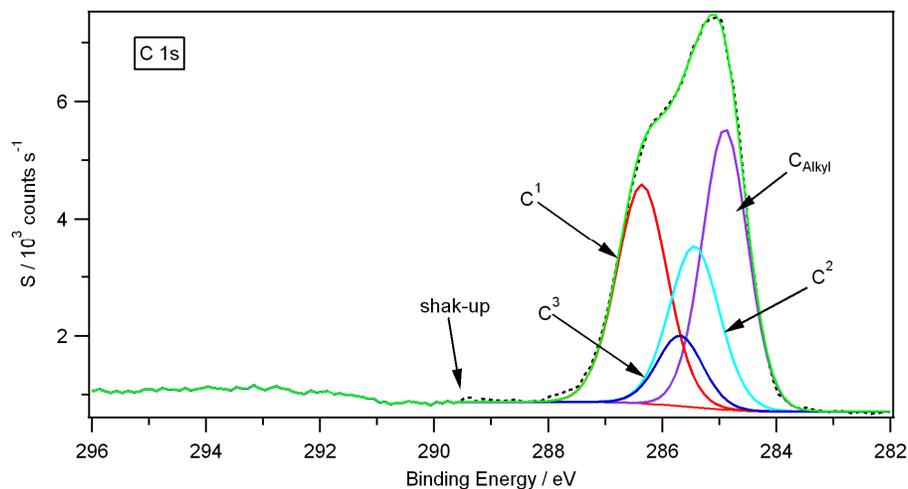


Figure 4. C1s XP spectrum with component fittings of $[\text{C}_3\text{H}_6(\text{C}_8\text{Bip})_2]\text{Br}_4$.

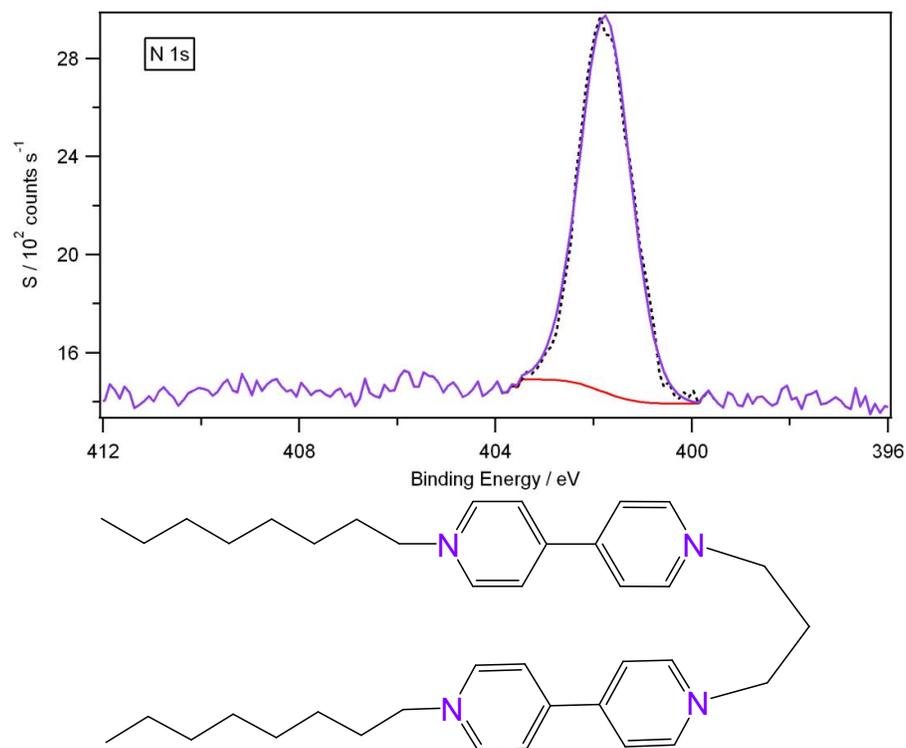


Figure 5. N1s XPS spectrum with component fittings of $C_3H_6(C_8Bip)_2Br_4$.

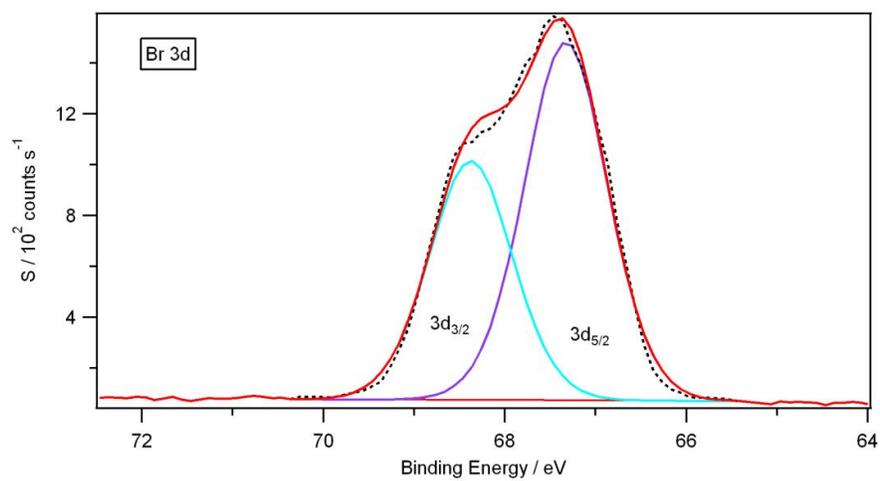


Figure 6. Br $3d_{5/2}$ and $3d_{3/2}$ XPS spectrum with component fittings of $[C_3H_6(C_8Bip)_2]Br_4$.

CONCLUSION

A new tetra cationic organic salt is synthesized from new moieties following techniques that ensure purity as well as acceptable yield. The result increases the number and type of polycationic organic salts at least by one. This creates opportunities to the scientific community to investigate its applications in different areas such as catalysts receptors, for anion recognition, low-molecular-weight gelators, as energetic materials, for use in the preparation of solid films for organic electronic applications to mention a few.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Bahir Dar University, Ethiopia for funding this research. We are indebted to Dr. Emily Smith from the School of Chemistry, University of Nottingham, UK, for assistance with XPS data collection.

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