4-vinylpyridine derivatives: Protonation, methylation and silver(I) coordination chemistry

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Abstract

(E)-4-[2-(Pyridin-4-yl)vinyl]benzaldehyde, containing both a 4-vinylpyridine and an aldehyde functionality, is utilized to develop new, highly conjugated chalcone compounds and a bis-Schiff base azine compound. The chalcone-containing compounds are further explored for their protonation, methylation and silver(I) coordination chemistry using the pyridine moiety. In parallel, a cyano-containing analogue, (E)-4-[2-(pyridin-4-yl)vinyl]benzonitrile is also synthesized and studied for its silver(I) coordination chemistry. These new compounds are fully characterized by mass spectrometry, elemental analysis and spectroscopic techniques. The methylated product of (E)-1-(9-anthryl)-3-[4-[2-(pyridin-4-yl)vinyl]phenyl]prop-2-en-1-one and a silver complex of (E)-4-[2-(pyridin-4-yl)vinyl]benzonitrile are structurally determined by X-ray crystallography.

Keywords
4-Vinylpyridine, chalcones, methylation, protonation, silver complexes

Introduction

4-Vinylpyridine (VP) has long been known as an essential building block in polymer chemistry. In 1984, Frechet and de Meftahi published a brief review article entitled ‘Poly(vinylpyridine): Simple Reactive Polymers with Multiple Applications’. Since then, a significant increase in research efforts has been dedicated to the structural modification and materials applications related to poly(4-vinylpyridine)s (PVP). While being structurally similar to the polymer, polystyrene (PS), PVP is particularly attractive with regard to its unique functionality because of the presence of nitrogen atoms within the aromatic pendant. Pyridine is one of the important structural units in metal coordination chemistry and is a hydrogen-bonding acceptor in supramolecular chemistry due to its strong electron-donating ability; it also provides scope for rich chemical modifications on the nitrogen atom. Thus, the incorporation of pyridyl units in polymer materials will certainly bring versatile physical and chemical properties along with applications in optical, electronic, magnetic, catalytic, conductive and chemosensing materials. Remarkable recent progress in PVP chemistry includes applications in solar cells, organic–inorganic hybrid functional materials, catalysis/electrocatalysis, heavy metal absorption/removal and environmental sensors.

In addition to its main applications in polymer materials, 4-VP is also an important synthon in organic synthetic chemistry as well as in small molecular materials. Assuming that studies on the synthesis and modification of small molecules derived from 4-VP could be helpful for understanding the properties and behaviour in the polymeric state, we were interested in the synthesis of novel organic compounds derived from 4-VP and further studying the derivatization and coordination chemistry utilizing the pyridine functionality. In particular, the incorporation of an additional important chromophores, such as chalcone and anthracene, into 4-VP would extend the conjugation and may result in interesting photonic and electronic properties. Herein, we report the synthesis and derivatization of an aldehyde-containing 4-VP with chalcone, anthracene, and imine functionalities and further modification through protonation, methylation and silver coordination. A novel silver coordination complex of cyano-derived 4-VP was also synthesized and structurally characterized (Scheme 1).
Results and discussion

Synthesis of 4-PV derivatives 3-5

The benzaldehyde-containing 4-PV (1), prepared according to a published procedure,25 allows facile derivatization by condensation with ketones or amines. Thus, we first conducted the reactions of 1 with acetophenone and 9-acetylanthracene in order to prepare chalcones, (E)-1-phenyl-3-[4-[2-(pyridin-4-yl)vinyl]phenyl]prop-2-en-1-one (3) and (E)-1-(9-anthryl)-3-[4-[2-(pyridin-4-yl)vinyl]phenyl]prop-2-en-1-one (4), respectively. Mixing a solution of equimolar acetophenone and 1 in ethanol with an aqueous solution of potassium hydroxide (1.3 equiv.) at room temperature for 18 h afforded 3 as a yellow crystalline product in 90% isolated yield after filtration. Likewise, yellow solid 4 was prepared in 86% yield by the same procedure, except using 9-acetylanthracene as the ketone. The compounds were fully characterized by IR, MS, elemental analysis and 2D nuclear magnetic resonance (NMR) spectroscopic techniques. Although the photophysical and photochemical properties of compound 3 were reported in 1988,26 its synthesis and characterization had not been reported. The electrospray ionization mass spectrum (ESI-MS) of 3 shows the base peak at 334.1 and another peak at 645.3, corresponding to the molecular species as well.

In addition, we studied the reaction of 1 with hydrazine in order to prepare the azine, 4-[2-(pyridin-4-yl)vinyl]benzaldazine (5), which was isolated as a yellow precipitate in 73% yield. Compound 5 displays a high melting point (>275°C) and is poorly soluble in common organic solvents. It was characterized by IR, MS and elemental analysis, even though no appreciable NMR data can be obtained due to its poor solubility in common deuterated solvents. The imine bond formation of 5 was confirmed by the strong absorption at 1617 cm⁻¹ in the IR spectrum. The ESI-MS gave a base peak at 415.2 corresponding to the molecular ion [M + Na]⁺. The peak with the highest m/z value at 437.2 indicates the presence of an [M + Na]⁺ species as well.

Protonation, methylation and metalation of compounds 3 and 4

Next, we explored the modification of new chalcone-containing 4-VP 3 with HCl, MeI and silver salts, respectively (Scheme 1). Protonation of a solution of 3 in MeOH/CH₃CN (2:2:1) with an excess amount of aqueous HCl (6 N) resulted in the formation of a yellow microcrystalline compound of (3-H)⁺Cl⁻ after evaporation of the solvent over 5 days. Compound (3-H)⁺Cl⁻ was isolated in 88% yield and fully characterized by IR, MS, elemental analysis and NMR spectroscopy. The ESI-MS spectrum revealed the base peak at 312.1 assigned to the species [3 + H]⁺. The characteristic N-H proton was observed at 3.16 ppm as a broad peak in the ¹H NMR spectrum in DMSO-d₆.

Furthermore, the reactions of 3 with silver nitrate and trifluoroacetate salts were studied. Thus, reacting 3 with AgNO₃ or AgCF₃CO₂ (0.5 equiv.) in a solution of CH₂Cl₂-MeOH gave Ag(3)₂(NO₃) and Ag(3)₂(CF₃CO₂) as yellow solids in good yields, the compositions of which were identified by elemental analysis. Their structures were further characterized by IR, MS, ultraviolet (UV)-Vis and NMR spectroscopy. It is believed that in both structures the silver centers coordinate with two N atoms of the ligand and are surrounded with the counter anions, which should be similar to the related X-ray structure of Ag(2)₂(ClO₄), which will be discussed in detail below. The ESI-MS spectrum of Ag(3)₂(NO₃) recorded in CH₃CN/MeOH reveals a base peak at 731.2 assigned to [Ag(3)⁺]⁺ (calcd. 731.2), which also appears to be the peak with the highest m/z value, while other relevant species with weaker signals were detected. In contrast, the fast atom bombardment (FAB)-MS spectrum of Ag(3)₂(CF₃CO₂) shows the peak with the highest m/z value at 731.3 for [Ag(3)⁺]⁺, yet the base peak was found at 312.2, corresponding to a decomposed form, [3 + H]⁺ (calcd. 312.1).

While we were unable to isolate pure product from the protonation of compound 4, the metalation of 4 with AgNO₃ was realized by the procedure similar to that used for Ag(3)₂(NO₃). Thus, compound Ag(4)₂(NO₃) was isolated in 77% yield as a yellow solid. Its structure was characterized by IR, MS, elemental analysis, UV-Vis and NMR spectroscopy. The FAB-MS revealed the peak with the highest m/z value at 929.2 assigned to [Ag(4)⁺]⁺ (calcd. 929.2). In addition, the base peak was found at 412.2 for the decomposed [4 + H]⁺ species (calcd. 412.2) and another peak at 518.2 [3 + Ag]⁺ due to a mono-ligand component was also detected (calcd. 518.1). In the next step, methylation of 4 was readily achieved by adding 2.0 equivalent of methyl iodide to a CH₂Cl₂/CH₃CN solution of 4 at room temperature. The product was isolated as orange crystals in 74% yield after slow evaporation of the filtrate. This compound was identified as (4-Me)⁺Cl⁻ and was fully characterized by spectroscopic methods as well as by single-crystal X-ray diffraction analysis. Its melting point was dramatically higher than that of 4 and the ESI-MS spectrum revealed a single peak appearing at 426.2 that assigned to [4-Me]⁺Cl⁻ (calcd. 426.2). X-ray structural analysis unambiguously determined its solid state structure and an ORTEP drawing of the molecule (4-Me)⁺Cl⁻ is shown in Figure 1. (4-Me)⁺Cl⁻ crystallizes in the monoclinic space group P2₁/c and there exist four (4-Me)⁺Cl⁻ molecules in the asymmetric unit. The conjugated 4-PV and chalcone units are coplanar, and there exist four (4-Me)⁺Cl⁻ molecules in the asymmetric unit. The conjugated 4-PV and chalcone units are coplanar. Furthermore, the reactions of 3 with silver nitrate and trifluoroacetate salts were studied. Thus, reacting 3 with AgNO₃ or AgCF₃CO₂ (0.5 equiv.) in a solution of CH₂Cl₂-MeOH gave Ag(3)₂(NO₃) and Ag(3)₂(CF₃CO₂) as yellow solids in good yields, the compositions of which were identified by elemental analysis. Their structures were further characterized by IR, MS, ultraviolet (UV)-Vis and NMR spectroscopy. It is believed that in both structures the silver centers coordinate with two N atoms of the ligand and are surrounded with the counter anions, which should be similar to the related X-ray structure of Ag(2)₂(ClO₄), which will be discussed in detail below. The ESI-MS spectrum of Ag(3)₂(NO₃) recorded in CH₃CN/MeOH reveals a base peak at 731.2 assigned to [Ag(3)⁺]⁺ (calcd. 731.2), which also appears to be the peak with the highest m/z value, while other relevant species with weaker signals were detected. In contrast, the fast atom bombardment (FAB)-MS spectrum of Ag(3)₂(CF₃CO₂) shows the peak with the highest m/z value at 731.3 for [Ag(3)⁺]⁺, yet the base peak was found at 312.2, corresponding to a decomposed form, [3 + H]⁺ (calcd. 312.1).

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Synthesis and crystal structure of Ag(2)₂(ClO₄)

The silver coordination chemistry of the 4-PV ligand was further explored using the related compound 2 bearing a nitrite group (see Scheme 1). The synthesis of Ag(2)₂(ClO₄)
was thus carried out following the same procedure as that used for the preparation of the aforementioned silver complexes of 3 and 4, while using a AgClO₄ salt instead. Single crystals of Ag(2)₂(ClO₄) were isolated from a CH₂Cl₂/CH₃CN/MeOH solution in 66% yield and were fully characterized. The molecular structure was further determined by X-ray diffraction analysis. The complex crystallizes in a monoclinic P2₁/c space group and a molecule of Ag(2)(ClO₄) is shown in Figure 2(a). The half of an independent molecule of Ag(2)(ClO₄) is present in the asymmetric unit and the other half was generated by the symmetry operation (I = −x, −y, −z). There is also a solvate acetonitrile molecule co-crystallized in the unit cell. It is clear that the silver ion is coordinated to two ligand molecules via the pyridine-N atoms and the complex adopts a linear geometry as the N-Ag-N angle is perfectly 180.00(8)°. The disordered counter anion ClO₄⁻ was not coordinated to the silver centre. The ligand molecule is found to be coplanar and the torsion angle between the planes of 4-PV and benzonitrile is only about 6.03°. The Ag1-N1 bond length is 2.1434(17) Å falling in the range of a typical Ag-N distance of 2.1–2.4 Å,²⁷ indicating a strong coordination bond. Further inspection of the structure indicates the presence of weak Ag⋯N contact between the silver ion and nitrile-N atom with a Ag⋯N distance of 2.941 (3) Å and N⋯Ag–N angle of 180.00(8)°. The disordered counter anion ClO₄⁻ was not coordinated to the silver centre. The ligand molecule is found to be coplanar and the torsion angle between the planes of 4-PV and benzonitrile is only about 6.03°. The Ag1-N1 bond length is 2.1434(17) Å falling in the range of a typical Ag-N distance of 2.1–2.4 Å,²⁷ indicating a strong coordination bond. Further inspection of the structure indicates the presence of weak Ag⋯N contact between the silver ion and nitrile-N atom with a Ag⋯N distance of 2.941 (3) Å and N⋯Ag–N angle of 180.00(8)°. The disordered counter anion ClO₄⁻ was not coordinated to the silver centre. The ligand molecule is found to be coplanar and the torsion angle between the planes of 4-PV and benzonitrile is only about 6.03°. The Ag1-N1 bond length is 2.1434(17) Å falling in the range of a typical Ag-N distance of 2.1–2.4 Å,²⁷ indicating a strong coordination bond. Further inspection of the structure indicates the presence of weak Ag⋯N contact between the silver ion and nitrile-N atom with a Ag⋯N distance of 2.941 (3) Å and N⋯Ag–N angle of 180.00(8)°. The disordered counter anion ClO₄⁻ was not coordinated to the silver centre. The ligand molecule is found to be coplanar and the torsion angle between the planes of 4-PV and benzonitrile is only about 6.03°. The Ag1-N1 bond length is 2.1434(17) Å falling in the range of a typical Ag-N distance of 2.1–2.4 Å,²⁷ indicating a strong coordination bond. Further inspection of the structure indicates the presence of weak Ag⋯N contact between the silver ion and nitrile-N atom with a Ag⋯N distance of 2.941 (3) Å and N⋯Ag–N angle of 180.00(8)°. The disordered counter anion ClO₄⁻ was not coordinated to the silver centre. The ligand molecule is found to be coplanar and the torsion angle between the planes of 4-PV and benzonitrile is only about 6.03°. The Ag1-N1 bond length is 2.1434(17) Å falling in the range of a typical Ag-N distance of 2.1–2.4 Å,²⁷ indicating a strong coordination bond.

Conclusion
In summary, we report the derivatization of an aldehyde-containing 4-VP with chalcone and imine functionalities and have further investigated the reactions of chalcone-based 4-PVs in protonation, methylation and silver coordination chemistry. The new compounds were synthesized in good yields and fully characterized by IR, MS, elemental analysis and 2D NMR spectroscopy. The methylated product was also structurally determined by single-crystal X-ray diffraction. In addition, an analogue of a silver complex with a related cyano-based 4-PV ligand was synthesized and structurally characterized by X-ray crystallography, revealing the coordination mode of this complex as a mononuclear bis-ligand complex. The newly synthesized derivatives of 4-VP are anticipated to be utilized as potential candidates for photocyclodimerization and polymerization for preparing new PVP materials. The additional chalcone moiety included in the 4-VP structures may give rise to opportunities for regioselective olefin polymerization.

Experimental
Solvents and reagents were purchased from Fisher Scientific or Sigma-Aldrich. All reactions were performed under ambient conditions in air. Fourier transform infrared (FTIR) spectra were measured on a Shimadzu 8400S instrument with solid samples using a Golden Gate ATR accessory. ¹H and ¹³C NMR and 2D NMR spectra were obtained at room temperature on a Bruker III 500 MHz
spectrometer. Electrospray ionization mass spectra were recorded using a Finnigan MAT LCQ mass spectrometer. UV-Vis electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. (E)-4-[2-(Pyridin-4-yl)vinyl]benzaldehyde (1)\textsuperscript{25} and (E)-4-[2-(pyridin-4-yl)vinyl]benzonitrile (2)\textsuperscript{29} were prepared following procedures reported in the literature.

**Synthesis of (E)-1-phenyl-3-(4-(2-(pyridin-4-yl)vinyl)phenyl)prop-2-en-1-one (3)**

Acetophenone (0.600 g, 5.00 mmol) and (E)-4-[2-(pyridin-4-yl)vinyl]benzaldehyde (1) (1.05 g, 5.00 mmol) were dissolved in ethanol (30 mL), and then aqueous KOH (0.364 g, 6.50 mmol in 4.0 mL H\textsubscript{2}O) was added with stirring. The resulting mixture was stirred at room temperature for 18 h, during which time a yellow solid formed. The solid was collected by filtration, washed with ethanol and diethyl ether and then dried in vacuo. Yield: 1.40 g (90%). M.p.: 179–181°C. FTIR (solid, cm\textsuperscript{-1}): 3030(w), 1740(s), 1652(s), 1586(s), 1570(s), 1412(m), 1337(m), 1298(w), 1276(w), 1217(s), 1178(w), 1032(w), 1014(m), 986(m), 972(s), 958(m), 871(w), 828(s), 779(s), 741(m), 722(m), 697(s), 667(s), 612(s). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 8.58 (dd, J = 4.5, 1.5 Hz, 2H, H\textsuperscript{A2}), 8.03 (dd, J = 8.5, 1.5 Hz, 2H, H\textsuperscript{C2}), 7.81 (d, J = 15.5 Hz, 1H, H\textsuperscript{E}), 7.67 (d, J = 8.5 Hz, 2H, H\textsuperscript{H1}), 7.61–7.57 (m, overlapping, 3H, H\textsuperscript{H2}–H\textsuperscript{E}), 7.55–7.49 (m, overlapping, 3H, H\textsuperscript{H1}), 7.38 (dd, J = 1.5, 4.5 Hz, 2H, H\textsuperscript{A3}), 7.30 (d, J = 16.5 Hz, 1H, H\textsuperscript{B}), 7.09 (d, J = 16.5 Hz, 1H, H\textsuperscript{A}), 13C NMR (126 MHz, CDCl\textsubscript{3}): δ: 190.6 (C C=O), 150.5 (C A2), 144.4 (C A3), 144.1 (C), 138.5 (C\textsuperscript{B1}), 138.4 (C\textsuperscript{A4}), 135.4 (C\textsuperscript{B4}), 133.1 (C\textsuperscript{C}), 132.4 (C\textsuperscript{C1}), 129.2 (C\textsuperscript{C2}), 128.9 (C\textsuperscript{C1}), 128.7 (C\textsuperscript{C2}), 127.7 (C\textsuperscript{B2}), 127.6 (C\textsuperscript{B3}), 122.4 (C\textsuperscript{C3}), 121.1 (C\textsuperscript{A3}). ESI-MS (CH\textsubscript{3}Cl\textsubscript{2}/MeOH): m/z 312.3 [M + H\textsuperscript{+}] (calcd. 312.1), 334.1 [M + Na\textsuperscript{+}] (calcd. 334.1), 645.2 [2M + Na\textsuperscript{+}] (calcd. 645.3). Anal. Calcd. for C\textsubscript{22}H\textsubscript{17}NO\textsubscript{0.2}H\textsubscript{2}O: C 83.89, H 5.57, N 4.45%. Found: C 83.88, H 5.58, N 4.43.

**Synthesis of (E)-1-(9-anthryl)-3-(4-(2-(pyridin-4-yl)vinyl)phenyl)prop-2-en-1-one (4)**

9-Acetylanthracene (1.10 g, 5.00 mmol) and 1 (1.05 g, 5.00 mmol) were dissolved in ethanol (40 mL), the mixture was stirred as aqueous KOH (0.364 g, 6.50 mmol in 4.0 mL H\textsubscript{2}O) was added with stirring. The mixture was stirred at room temperature for 6 h. During which time, yellow precipitate had formed, which was collected by filtration, washed with ethanol and diethyl ether and then dried in vacuo. Yield: 1.77 g (86%). M.p.:
Synthesis of Ag(3)$_2$(NO$_3$)$_3$

Ligand (31.1 mg, 0.100 mmol) was dissolved in CH$_3$Cl$_2$ (8 mL) and a solution of AgNO$_3$ (8.45 mg, 0.0500 mmol) in MeOH (5 mL) was added. The reaction mixture was stirred at room temperature for 10 min and then filtered. The filtrate was left to evaporate slowly at room temperature for 1 week. During which time, yellow solid formed. The solid was collected by decanting the solvent, washed with MeOH and dried in air. Yield: 30.0 mg (76%). FTIR (solid, cm$^{-1}$): 1733 (m), 1652 (s), 1587 (m), 1557 (s), 1333 (m), 1299 (m), 1217 (s), 1177 (w), 1033 (w), 1017 (m), 965 (m), 951 (m), 826 (s), 776 (m), 738 (m), 720 (m), 700 (s), 668 (s). 1H NMR (500 MHz, DMSO-d$_6$): 8.84 (dd, D, 3.5, 4.5 Hz, 4H, H$_A2$), 7.96 (d, overlapping, D, 16.5 Hz, 2H, H$_H$), 7.77 (d, overlapping, D, 15.5 Hz, 2H, H$_D$), 7.69 (m, 2H, H$_I$), 7.65 (overlapping, D, 15.5 Hz, 2H, H$_C$), 7.41 (d, overlapping, D, 15.5 Hz, 2H, H$_F$), 7.19 (d, overlapping, D, 16.5 Hz, 2H, H$_B$). 1H NMR (500 MHz, CH$_3$CN): 8.17 (m, D, 15.5 Hz, 2H, H$_H$), 7.77 (d, overlapping, D, 8.5 Hz, 4H, H$_E$), 7.77 (d, overlapping, D, 15.5 Hz, 2H, H$_D$), 7.69 (m, 2H, H$_I$), 7.65 (overlapping, D, 15.5 Hz, 2H, H$_C$), 7.41 (d, overlapping, D, 16.5 Hz, 2H, H$_F$), 7.19 (d, overlapping, D, 16.5 Hz, 2H, H$_B$). 1H NMR (500 MHz, DMSO-d$_6$): 189.1 (C=O), 152.8 (C$_I$), 143.1 (C$_G$), 142.2 (C$_A2$), 138.7 (C$_E$), 137.5 (C$_F$), 137.4 (C$_H$), 136.2 (C$_B2$), 133.3 (C$_C$), 129.6 (C$_B1$), 128.9 (C$_C$), 128.6 (C$_C$), 128.5 (C$_B2$), 125.3 (C$_A3$), 123.3 (C$_J$), 122.9 (C$_F$), 121.6 (C$_B4$), 120.8 (C$_I$), 120.4 (C$_A2$), 120.1 (C$_A3$), 118.7 (C$_K$), 118.3 (C$_J$), 117.1 (C$_G$), 116.7 (C$_G$), 116.3 (C$_F$), 115.9 (C$_H$), 115.8 (C$_E$), 113.3 (C$_D$), 110.7 (C$_I$), 110.2 (C$_H$), 109.5 (C$_G$), 109.1 (C$_F$), 108.8 (C$_E$), 108.3 (C$_D$).

Synthesis of 4-[2-(pyridin-4-yl)vinyl]-benzaldehyde (5)

To a stirred solution of 1 (0.418 g, 2.00 mmol) in ethanol (10 mL) was added dropwise hydrazine monohydrate (0.050 g, 1.00 mmol) at room temperature. The resulting yellow suspension was stirred for 2 h, then filtered, and the obtained yellow precipitate was washed with ethanol and dried in vacuo. Yield: 0.360 g (73%). M.p.: 275–277 °C. FTIR (solid, cm$^{-1}$): 3448 (br), 3424 (br), 3341 (br), 3282, 3262 (w), 3242 (m), 3222 (s), 3160 (s), 2928 (w), 2858 (w), 1686 (m), 1641 (m), 1585 (s), 1484 (m), 1326 (w), 1060 (s), 997 (m), 970 (s), 856 (m), 829 (s), 802 (w). No appreciable NMR spectra could be recorded due to the poor solubility. ESI-MS (CH$_3$Cl$_2$/MeOH): m/z 412.2 [M + Na$^+$] (calcd. 412.2), 434.2 [M + Na$^+$] (calcd. 434.2), 450.1 [M + K$^+$] (calcd. 450.1), 845.4 [2M + Na$^+$] (calcd. 845.3). Anal. Calcd. for C$_{30}$H$_{21}$NO: C 77.75, H 5.58, N 12.95%. Found: C 77.75, H 5.58, N 13.06.

Synthesis of (3-H)$_+Cl^-$

To a stirred solution of the ligand 3 (31.1 mg, 0.100 mmol) in a mixture of MeOH/CH$_2$Cl$_2$/CH$_3$CN (10 mL, 2:2:1, v/v) was added 6 N aqueous HCl (0.4 mL) at room temperature. The resulting clear yellow solution was allowed to stand and evaporate slowly over a period of 5 days, during which time, a yellow crystalline product was collected by filtration, washed with methanol and dried in air. Yield: 30.5 g (88%). M.p.: 280 °C (decomp.). FTIR (solid, cm$^{-1}$): 3037 (m), 1650 (s), 1623 (w), 1590 (m), 1505 (m), 1418 (m), 1368 (s), 1293 (w), 1217 (s), 966 (s), 848 (m), 874 (w), 828 (s), 785 (s), 733 (s), 714 (s), 703 (s). 1H NMR (500 MHz, DMSO-d$_6$): 8.84 (d, D, 6.5 Hz, 2H, H$_D$), 8.19–8.16 (overlapping, m, 4H, H$_B2$), 8.03 (overlapping, d, D, 15.5 Hz, 1H, H$_E$), 8.02 (overlapping, d, D, 8.5 Hz, 2H, H$_B3$), 8.01 (overlapping, d, D, 16.5 Hz, 1H, H$_F$), 7.84 (d, D, 8.5 Hz, 2H, H$_B4$), 7.77 (d, D, 15.5 Hz, 1H, H$_G$), 7.69 (t, D, 7.5 Hz, 1H, H$_H$), 7.65 (d, D, 16.5 Hz, 1H, H$_I$), 7.59 (t, D, 7.5 Hz, 2H, H$_C$), 3.5 (br, 1H, H$_N$). 13C NMR (126 MHz, DMSO-d$_6$): 189.1 (C=O), 152.8 (C$_A4$), 143.1 (C$_G$), 142.2 (C$_A2$), 138.7 (C$_E$), 137.5 (C$_F$), 137.4 (C$_H$), 136.2 (C$_B2$), 133.3 (C$_C$), 129.6 (C$_B1$), 128.9 (C$_C$), 128.6 (C$_C$), 128.5 (C$_B2$), 125.3 (C$_A3$), 123.3 (C$_J$), 122.9 (C$_F$), 121.6 (C$_B4$), 120.8 (C$_I$), 120.4 (C$_A2$), 120.1 (C$_A3$), 118.7 (C$_K$), 118.3 (C$_J$), 117.1 (C$_G$), 116.7 (C$_G$), 116.3 (C$_F$), 115.9 (C$_H$), 115.8 (C$_E$), 113.3 (C$_D$), 110.7 (C$_I$), 110.2 (C$_H$), 109.5 (C$_G$), 109.1 (C$_F$), 108.8 (C$_E$), 108.3 (C$_D$).
129.5 (C(B1)), 128.9 (C(C3)), 128.6 (C(C2)), 127.7 (C(B2)), 127.2 (C(C1)), 122.2 (C(4)), 121.3 (C(C4)), FAB-MS (NBA) m/z 731.3 [M – CF\textsubscript{3}CO\textsubscript{2}]\textsuperscript{+} (calcd. 731.2), 418.0 [3 + Ag\textsuperscript{+}]\textsuperscript{+} (calcd. 418.0), 312.2 [3 + H\textsuperscript{+}]\textsuperscript{+} (calcd. 312.1). The isotope peaks matched those simulated. Anal. Calcd. for C\textsubscript{46}H\textsubscript{34}AgF\textsubscript{3}N\textsubscript{2}O\textsubscript{4}: C 69.23, H 4.48, N 8.60%. Found: C 53.01, H 3.35, N 8.87.

**Synthesis of (4-Me)\textsuperscript{1}I**

Ligand 4 (20.6 mg, 0.0500 mmol) was dissolved in a mixture of CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}CN (10 mL, 4:1, v/v) at room temperature, then CH\textsubscript{2}I\textsubscript{2} (14.2 mg, 0.100 mmol) was added. The resulting orange solution was stirred at room temperature for 10 min and then filtered. The filtrate was left to evaporate slowly at room temperature for 2 weeks during which time, a yellow crystalline product had formed, which were collected by decanting the solvent, washing with MeOH and drying in air. Yield: 20.5 mg (74%). M.p.: >300 °C. FT-IR (solid, cm\textsuperscript{-1}): 2985(w), 1603(s), 1354(m), 1292(m), 1262(w), 1178(m), 1169(m), 1105(m), 985(s), 824(s), 732(s). 1H NMR (500 MHz, DMSO-\textsubscript{d6}): 8.74 (d, J = 8.5 Hz, 2H, H\textsubscript{a}), 8.05 (d, J = 6.0 Hz, 2H, H\textsubscript{b}), 7.98 (d, J = 16.5 Hz, 2H, H\textsubscript{c}), 7.32 (d, J = 6.5 Hz, 2H, H\textsubscript{d}). 13C NMR (126 MHz, DMSO-\textsubscript{d6}): 152.0 (CH\textsubscript{B}), 146.1 (CH\textsubscript{C}), 145.2 (CH\textsubscript{D}), 139.3 (C\textsubscript{4}), 137.6 (C\textsubscript{B}), 133.5 (C\textsubscript{C}), 130.7 (C\textsubscript{D}), 129.9 (C\textsubscript{2}), 129.7 (C\textsubscript{B}), 128.8 (C\textsubscript{C}), 128.5 (C\textsubscript{D}), 128.4 (C\textsubscript{C}), 127.6 (C\textsubscript{C}), 127.6 (C\textsubscript{B}), 127.0 (C\textsubscript{D}), 125.7 (C\textsubscript{C}), 124.9 (C\textsubscript{2}), 124.7 (C\textsubscript{C}), 123.7 (C\textsubscript{A}), 47.1 (C\textsubscript{C}). ESI-MS (CH\textsubscript{3}CN/MeOH): m/z 519.1 [Ag(2\textsubscript{+})\textsubscript{2}]\textsuperscript{+} (calcd. 519.1), 207.1 [2 + H\textsuperscript{+}]\textsuperscript{+} (calcd. 207.1). The isotope peaks matched those simulated. Anal. Calcd. for C\textsubscript{46}H\textsubscript{34}AgCl\textsubscript{2}N\textsubscript{2}O\textsubscript{4}: C 69.23, H 4.48, N 8.60%. Found: C 53.01, H 3.35, N 8.87.

**X-ray structural determinations**

Suitable crystals of compounds (4-Me)\textsuperscript{1}I and Ag(2\textsubscript{+})\textsubscript{2}(ClO\textsubscript{4})\textsubscript{2} were mounted on Cryoloops with Paratone-N oil. Data were collected with a Bruker APEX II CCD using Mo-K\textsubscript{α} radiation and corrected for absorption with SADABS. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F\textsuperscript{2}. Hydrogen atoms were found from Fourier difference maps and refined isotropically, otherwise they were placed in calculated positions with appropriate riding parameters. The relevant structural refinement parameters are summarized in Table 1. Crystal structures and packing figures were drawn with the programme Mercury v. 2.4.

**Declaration of conflicting interests**

The author declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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Table 1. structural refinement data for (4-Me)\(^+\)I\(^-\) and Ag(2)\(_2\)(ClO\(_4\)).

| Compound | (4-Me)\(^+\)I\(^-\) | Ag(2)\(_2\)(ClO\(_4\))·2CH\(_3\)CN |
|----------|------------------|----------------------------------|
| Formula  | C\(_{17}\)H\(_{21}\)INO | C\(_{32}\)H\(_{26}\)AgCl\(_2\)N\(_6\)O\(_8\) |
| Formula weight | 553.41 | 801.36 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2(1)/c | P2(1)/c |
| a/Å | 9.3662(6) | 4.7780(9) |
| b/Å | 23.7992(18) | 18.821(5) |
| c/Å | 11.1408(7) | 17.980(4) |
| α/º | 90 | 90 |
| β/º | 103.976(5) | 91.017(16) |
| γ/º | 90 | 90 |
| U/Å\(^3\) | 2409.9(3) | 1616.7(6) |
| D\(_c\)/Mg m\(^-3\) | 1.525 | 1.646 |
| Z | 4 | 2 |
| μ/mm\(^-1\) | 1.353 | 0.851 |
| T/K | 173(2) | 173(2) |
| Reflections/unique | 62,765/6932 | 28,786/4085 |
| Parameters | 308 | 261 |
| R\(_1\), wR\(_2\) [I > 2σ(I)] | 0.0232, 0.0605 | 0.0643, 0.1728 |
| R\(_1\), wR\(_2\) (all data) | 0.0242, 0.0612 | 0.0697, 0.1792 |
| GOF | 1.124 | 1.105 |

\(^1\)R\(_1\) = (F\(_o\) – F\(_c\))/F\(_o\). \(^2\)wR\(_2\) = [(w(F\(_o\)^2 – F\(_c\)^2)²)/w(F\(_o\)^2)]\(^{1/2}\).

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**Supplemental material**

CCDC 1980771 and 1980772 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2020.xx.xxxx.

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