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The first study about the relationship between the extractability of thiacalix[4]arene derivatives and the position of the coordination binding sites †

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Three organic ionophores (2 – 4) based on the p-tert-butylthiacalix[4]arene backbone, blocked in the 1,3-alternate conformation, bearing two pyridyl coordinating moieties (ortho for 2, meta for 3 and para for 4), have been synthesized and characterized in the solid state. The solvent extracted experiments of the metal ions showed that the ability of these derivatives to complex with Ag⁺ appeared to be largely dependent on the position of the nitrogen atoms of the pyridyl ring. Two different complexation modes have been confirmed by 1H NMR titration, ionophore 2 armed with two pyridyl, complexed with Ag⁺ cation through N···Ag⁺···S interactions; however, ionophore 3 and ionophore 4, complexed with Ag⁺ through metal-nitrogen (N···Ag⁺) interactions. The DFT computational studies were consistent with the experimental findings. These findings will provide us an important rule to design an appropriate thiacalixarene ionophore in the future. Another studied on the possibility for application of ionophores 2 – 4 to the treatment of waste water containing Cr (VI) and Cr (III), showed that ionophore 3 was meaningful for applying solvent extraction method in selective treatment of waste water containing Cr (VI) and Cr (III) prior to discharge.

Introduction

Thiacalix[4]arene is widely used as a macrocyclic platform for designing and building synthetic receptors toward metal cations. The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms and also upon the conformation of the calix[4]arene moiety. It is found that thiacalix[4]arene has a very high ability to bind transition metal ions, which has been quite unexpected considering the poor binding ability of calix[4]arene. The 1,3-alternate stereoisomer, which shows an allosteric effect in metal cation binding, or offers divergently oriented binding sites, is of special interest. For the synthesis of macrocycles with controlled (switchable) binding sites of metal cations, there is a need for the development of novel approaches to the design of tetrasubstituted thiacalix[4]arenes with various groups with specific conformations. Recently, our lab has reported the regioselective synthesis of distal-bis[(2-pyridylmethyl)oxy]tetra-thiacalix[4]arene in the 1,3-alternate conformation by a protection-deprotection method using benzyl groups as protecting groups. Pyridine derivatives of thiacalix[4]arene can exist as positional isomers which differ by the positions of the nitrogen (N) atom on the pyridyl unit which can be ortho, meta and para to the phenolic oxygen attachment position. The N-hetero atoms can serve as additional coordination sites due to their electron lone pairs and can also undergo facile further modification. Given that the position of the nitrogen atoms of the pyridyl ring can differ in thiacalix[4]arene derivatives, it is interesting to assess what kind of ability these derivatives will provide to interact with metal cations (hard or soft).

Chromium (III) has been reported to be biologically essential to mammals as it maintains effective glucose, lipid, and protein metabolisms. However, chromium (VI) can be toxic, as it can diffuse as Cr₂O₇²⁻ or HCr₂O₇ through cell membranes and oxidize biological molecules. Therefore, selective treatment of waste water containing Cr (VI) and Cr (III) prior to discharge is essential. Solvent extraction is one of the most commonly used treatment methods and employs a selective complexant especially for ions in aqueous solution. Thus, the development of efficient extractants for anions has received considerable attention in recent years. The dichromate (Cr₂O₇²⁻ and HCr₂O₇⁻) ions are anions with oxide functionalities at their periphery. These oxide moieties are potential sites for hydrogen bonding to the complexant or host molecule(s). Thiacalix[4]arene derivatives with nitrogen functionalities such as pyridine, amino, or imino groups on their lower rim have been shown to be capable of interacting with anions by hydrogen bonds as efficient extractants for oxoanions. Thus, the introduction of a pyridyl moiety to thiacalix[4]arene would potentially lead to an effective extractant for dichromate anions.

In this study, a series of 1,3-alternate thiacalix[4]arenes bearing pyridyl moieties (ortho, meta and para) at the lower rim which should have the appropriate encapsulating ionophilic cavity were
targeted for synthesis. The relationship between the position of the nitrogen atoms of the pyridyl ring and the ability of these derivatives to interact with various ionic species were evaluated.

**Results and discussions**

The synthesis of the new thiacalix[4]arene derivatives is given in Scheme 1. For the synthesis of thiacalix[4]arene derivatives based on different functional units (1,3-alternate-2, 1,3-alternate-3 and 1,3-alternate-4), the parent compound (distal-1) was prepared according to published literature procedures. The reaction of bisbenzylated compound distal-1 with 3-(chloromethyl)pyridine in THF-DMF in the presence of Cs$_2$CO$_3$ as base yielded 1,3-alternate-3 in 59% yield. 1,3-alternate-2 and 1,3-alternate-4 were prepared as following a published procedure. All of the structures were confirmed by their $^1$H and $^{13}$C-NMR and IR spectra, MS, elemental analyses and by X-ray crystallography.

The $^1$H NMR spectrum of 1,3-alternate-3 shows two singlets for tert-butyl protons, in which both tert-butyl protons were observed at higher field, at $\delta$ 0.85 and 0.86 ppm due to the ring current effect arising from the two benzyl benzene rings and the two pyridine rings introduced; two singlets for the methylene protons at $\delta$ 5.06 ppm (OCH$_2$Benzyl) and 5.19 ppm (OCH$_2$Pyridyl), respectively, indicating a C$_2$-symmetric structure for the 1,3-alternate-3 (Figure S1). X-ray quality colourless crystals of 1,3-alternate-2, and 1,3-alternate-3 were obtained by recrystallizations from mixed MeOH and CHCl$_3$ solutions. The single crystal X-ray diffraction Ortep (Pluto) representations of 2 and 3 are shown in Figure 1. It is clear that these compounds adopt 1,3-alternate conformations. Interestingly, both of the pyridine nitrogen atoms in 2 are orientated outwards, the distance between them being 9.079 Å. However, the pyridine nitrogen atoms in 3 are orientated inwards, the distance between them being only 3.883 Å. This may be attributed to the distances between the pyridine nitrogen atoms and the oxygen atoms (N1···O1 and N2···O2). In the case of compound 2, the distances between N1···O1 and N2···O2 are shorter; but for 3 the corresponding N1···O1 and N2···O2 distances are longer enough.

The shorter distances and hence, the stronger electron repulsion could therefore be the factors which control the different orientations of the nitrogen atoms toward each other.

Recently, the synthesis of calix[4]arenes bearing pendant pyridine groups at the lower rim as potential ligands for transition metal cations have been reported. A similar investigation has also been conducted using hexahomotrioxacalix[3]arene and homocalix[3]arene-based derivatives. It is well-known that the metal selectivity and extractability of these types of receptors are dependent on the ring size and the nature of the O-alkyl substituents. However, it is still unknown whether the metal extractability can be affected by the position of the coordination binding sites of the substituents themselves. Therefore, it is of importance to assess the

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**Scheme 1** O-Alkylation of distal-1 with (chloromethyl)pyridine in the presence of Cs$_2$CO$_3$.
relationship between the position of the nitrogen atoms of the pyridyl ring and the ability of these derivatives (2–4) to interact with ions. Experiments for solvent extraction of aqueous phase metal ions to the organic phase were therefore undertaken with 2–4. The results showed that the extraction of transition metals by all three receptors 2–4 was higher than for the extraction of alkali metals, especially for Cr(cit)3 and Ag(+) (Fig. 2). The E% values of Cr(cit)3 i.e. 43%, 61% and 52% for 2–4, respectively, showed that a higher Cr(III) affinity exists for these molecules. However, what is surprising is that the extractability for Ag(+) cation through N⋯Ag⋯S interactions, the higher extractability (E%) supported by the stability constants, which follow the same order of magnitude. This hypothesis is thereby confirmed by 1H NMR titration experiments with 1.0 equiv. AgClO4(300 MHz, CDCl3:CD3CN = 10:1, [ionophores 2–4] = 5 × 10⁻³ M), which revealed that the protons in the pyridine moieties of the receptors 2–4 with Ag(+) were shifted dramatically to upfield, with ∆δ = +0.27, +0.21, +0.52 and +0.83 ppm for H 2, H 3, H 4 and H 5, respectively. In contrast, the OCH3 group was shifted to lower field with ∆δ = +0.09, +0.42 and +0.43 ppm for H 6, H 7 and H 8, respectively. In contrast, the OCH3 group protons, respectively. In contrast, the OCH3 group protons, respectively. In contrast, the OCH3 group protons, respectively.

Furthermore, in order to look further into the binding properties of receptors 2–4 with Ag+, 1H NMR titration experiments were carried out in CD2Cl2:CD3CN = 10:1 solution. The chemical shift changes for compound 2–4 on complexation with Ag+ are illustrated in Figure 3 and are summarized in Figure 4. Significant changes were observed for the pyridine ring protons after the complexation of each of 2–4 with 1.0 equiv. Ag+. In the case of 2, the protons in the pyridine rings were shifted to lower field with ∆δ = +0.27, +0.21, +0.52 and +0.83 ppm for H 2, H 3, H 4 and H 5, respectively. In contrast, the OCH3 protons were shifted dramatically to upfield, with ∆δ = −0.53. This may be due to both pyridine nitrogens of 2 close to the diaryl thiaether linkages (N2⋯S1 = 5.333 Å, Fig. 1a). Thus, when 2 complexes with Ag+, the Ag+ is easily captured through N⋯Ag⋯S interactions. As a result, since the pyridine moieties orientated inwards, the ring current shielding effect operating in the two thiacalixarene benzene rings is destroyed, forcing the steric congestion change. This affects the protons H 2, H 3, H 4 and H 5 of the pyridine rings which shift to lower field, due to the deshielding effect. Also, the OCH3 py methyl protons become folded into the thiacalix[4]arene cavity and are thus shifted strongly upfield (∆δ = −0.53 ppm), due to the steric conformation changes.

However, a different phenomenon was observed in the complexation of 3 with Ag+. From the X-ray results, both pyridine nitrogen atoms in 3 were orientated inwards and far from the diaryl thiaether linkages (N2⋯S1 = 6.360 Å and N2⋯S2 = 5.847 Å, Fig. 1b), which is exactly opposite to what is seen with 2. The 1H NMR spectrum of the Ag+ of 3 reveals that the protons in the pyridine rings were shifted to lower field with ∆δ = +0.09, +0.42 and +0.43 ppm for H 2, H 3 and H 4, respectively. In contrast, an remarkable shielding effect experienced by proton H 5 (∆δ = −0.38 ppm).
was observed. This maybe attribute that when 3 complexes with Ag⁺, the Ag⁺ is trapped in the cavity formed by the nitrogen atoms in pyridine, induce the proton H₂ become folded into the π-cavity formed by the two thiacalixarene benzene rings and are thus shifted strongly upfield (-0.38 ppm). Thus, 3 complexes Ag⁺ through the metal-nitrogen interactions and thus, due to the interaction of the nitrogens and the Ag⁺, the H₁, H₂ and H₃ protons of the pyridine rings shift to lower fields.¹⁵

Similar phenomena were observed for the complexation of 4 with Ag⁺; protons H₁ and H₃ in the pyridine rings of 4 shifted to lower field after complexation (+0.05 ppm), which are deshielded due to the N⋯Ag⁺ interactions. Pyridine ring protons H₁ and H₃ in 4 shifted upfield after complexation (-0.06 ppm), which may be attributed to the weaker repulsion between the nitrogen atoms in the pyridine rings.¹⁵

The chemical shift changes of the thiacalixarene benzene protons and benzyl protons may also be attributed to the conformational changes of 2 – 4 upon complexation. The chemical shift changes (Δδ) of 2 – 4 upon complexation are in the order 2 > 3 > 4, which corresponds with the extractability of Ag⁺ which found to be in the same order.

To better understand the binding properties of receptors 2 – 4 with Ag⁺, a computation study were carried out. The molecular geometry of the individual structures in the gas-phase were fully optimized using Gaussian09,²² with the B3LYP level of DFT and the lanl2dz basis set. Significant conformational changes were observed for the pyridine ring protons of 2 – 4 after the complexation with Ag⁺. The conformation changes for 2 on complexation with Ag⁺ ion can be seen in Fig. 5 (See the Supporting Information for details of the computational study, Figure S19–24). Fig. 5 shows the structure (right) of the 2⋯Ag⁺ complex. The optimized molecular geometry suggests that the Ag⁺ binds, in accord with the ¹H NMR complex study, via a N⋯Ag⁺⋯S short contact distance bond, which results in the conformation change. The N⋯N distance between the pyridine ring nitrogens decreases from 8.001 to 3.761 (Å) since the nitrogen atoms move inwards after complexing with the Ag⁺. All four bridge sulphur atoms move roughly the same distance from the Ag⁺ and presumably take an equal part in the coordination bonding.

However, a different phenomenon was observed in the complexation of 3 – 4 with Ag⁺. The N⋯N distance between the pyridine ring nitrogens decreases from 9.305 to 4.234 (Å) for 3 and 10.138 to 3.798 (Å) for 4 after complexing with the Ag⁺. (Figure S19 – S24, Table S1) The optimized molecular geometry suggests that complexation of 3 – 4 with Ag⁺ occurs via a N⋯Ag⁺ interactions. The calculated complexation energies (ΔE kJ/mole) of the Ag⁺ complexes of 2 – 4 are -488.096, -464.022 and -372.966 kJ/mole respectively (Table S2), which is in agreement with the trend observed for the experimentally observed complexation data.

A preliminary evaluation of the anion binding efficiencies of 2 – 4 as potential extractants for the dichromate anion has been carried out by solvent extraction of aqueous solution of K₂Cr₂O₇ into dichloromethane at different pH values according to reported procedure.¹⁵¹⁶ The extraction results summarized in Fig. 6, indicate that 3 showed a higher effective for the extraction of dichromate anions at low pH (pH 1.5) than either 2 and 4. This is also consistent with the solvent extraction results seen with Cr³⁺ (Fig. 2). This could be attributed to the closer (3.883 Å) distance (Fig. 1) between the pyridine nitrogen atoms in 3, which was easily formed an efficient ion-pair (hydrogen bonded) complex in the two-phase extraction.

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**Fig. 4.** Chemical shift changes of 2, 3 and 4 induced in the presence of AgClO₄ + denotes the downfield and – denotes the upfield shift.
system following proton transfer to the nitrogen atoms. As the pH of the solution increased from 1.5 to 2.5 to 5.5 to 7.0, the E% for all three receptor ionophores decreased. This may directly be attributed to decreased proton concentrations in the solution.15 In other words, 3 showed a high extractability with dichromate anions only at lower pH, but another high extractability of Cr(VI) at higher pH. Since, Cr(VI) is highly toxic, carcinogenic and harmful to human beings because it can diffuse as CrO$_4^{2-}$ or HCrO$_4^−$ through cell membranes and oxidize biological molecules,7 whereas Cr(III) is an essential ion for mammalian metabolism.18 Thus, 3 could be a meaningful extractant when applying a solvent extraction method for the selective treatment of waste water containing Cr(VI) and Cr(III) ions prior to discharge.

**Conclusion**

Three 1,3-alternate thiacalix[4]arenes bearing pyridyl moieties (ortho for 2, meta for 3 and para for 4) at the lower rim were regioselectively synthesized. The solvent extraction experiments of the metal ions showed that the ability of these derivatives to complex with Ag$^+$ (95%, 52% and 36% for 2, 3 and 4, respectively) appeared to be largely dependent on the position of the pyridine nitrogen atoms. The mode of binding of the C$_{28}$-symmetrical dipyridyl-substituted thiacalix[4]arenes, 2–4 with Ag$^+$ was elucidated clearly using 1H NMR titration method. Two different complexation modes were observed: 2 armed with two ortho pyridyl groups, complexed with Ag$^+$ via N···Ag$^+$···S interactions whereas 3 and 4, complexed with Ag$^+$ through N···Ag$^+$ interactions. The DFT computational studies were consistent with the experimental findings. These findings will provide us an important rule to design an appropriate thiacalixarene ionophore in the future.

Another studies aimed at the potential for application of these extractants to the treatment of waste water containing Cr(VI) and Cr(III) were initiated. The combination of the two-phase solvent extraction data of Cr$^{3+}$ and the results of the dichromate anion extraction by 3, suggest that 3 could be meaningful for applying a solvent extraction method for the selective treatment of waste water containing Cr(VI) and Cr(III) ions prior to discharge.

**Experimental Section**

**General**

All melting points were determined using a Yanagimoto MP-S1. 1H-NMR spectra were determined at 300 MHz with a Nippon Denshi JEOL FT-300 NMR spectrometer with SiMe$_4$ as an internal reference; J-values are given in Hz. IR spectra were measured as KBr pellets or as liquid films on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by a Shimadzu 240 spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at an ionization energy of 70 eV using a direct inlet system through GLC. Elemental analyses were performed by a Yanaco MT-5.

**Materials**


**O-Alkylation of 1 distal-1 with 3-(chloromethyl)pyridine in the presence of Cs$_2$CO$_3$.**

A mixture of distal-1 (400 mg, 0.44 mmol) and Cs$_2$CO$_3$ (1.60 g, 4.92 mmol) in dry tetrahydrofuran (THF) (8 mL) was heated at reflux for 1 h under N$_2$. A solution of 3-(chloromethyl)pyridine (4.92 mmol) [prepared by neutralization of 3-(chloromethyl)pyridine hydrochloride (807 mg, 4.92 mmol) in DMF (8 mL) with a solution of triethylamine (0.68 mL, 4.92 mmol)] was then added and the mixture heated at reflux for another 24 h. After cooling the reaction mixture to room temperature, it was acidified with 1 M HCl (10 mL) and extracted with CH$_2$Cl$_2$ (100 mL × 2). The combined extracts were washed with water (50 mL × 2), and dried (MgSO$_4$) and condensed under reduced pressure to give a yellow oil. The residue was washed with methanol to give a mixture of tetra-O-alkylated products as a colourless precipitate. The precipitate was washed with ether (5 mL) to give a colourless solid. Recrystallization from MeOH:CHCl$_3$ (1:3) gave 3 as a colourless prisms (280 mg, 59%).

25,27-Dibenzoyloxy-26,28-bis[(3-pyridylmethyl)oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra-thiacalix[4]arene (3): Colourless prisms [MeOH:CHCl$_3$ (1:3)], m.p. 285.4–286.6 °C, IR $\nu_{max}$ (KBr/cm$^{-1}$): 3058, 3030, 2958, 2902, 2868, 1575, 1546 and 1496. 1H NMR (400 MHz, CDCl$_3$) $\delta$ = 0.85 (s, 18H, tBu), 0.86 (s, 18H, tBu), 0.56 (s, 4H, Ar–OCH$_2$Ph), 5.19 (s, 4H, Ar–OCH$_2$Py), 6.92 (d, J = 7.2 Hz, 4H, Ph–H$_2$), 7.02 (t, J = 7.6 Hz, 6H, Ph–H$_3$), 7.07 (s, 4H, Ar–H$_2$), 7.10 (s, 4H, Ar–H$_2$), 7.12 (t, J = 7.6 Hz, 2H, Py–H$_2$), 7.24 (d, J = 8.0 Hz, 2H, Py–H$_2$), 8.22 (s, 2H, Py–H$_2$) and 8.46 (d, J = 4.8 Hz, 2H, Py–H$_2$) ppm. 13C NMR (100 MHz, CDCl$_3$) $\delta$ = 30.77, 30.78, 33.89, 33.90, 67.74, 70.64, 122.99, 126.83, 127.08, 127.18, 127.98, 128.38, 128.42, 128.48, 128.60, 133.20, 134.81, 137.47, 146.31, 146.58, 148.33, 148.92, 155.59 and 156.61 ppm. FABMS: m/z: 1083.30 (M$^+$). Anal. calcld. for C$_{66}$H$_{66}$N$_2$O$_{18}$S$_4$: C 73.16, H 6.51, N 2.59%. Found: C 71.85, H 6.56, N 2.38%.
Preparation of 25,27-Dibenzylxoxy-26,28-bis[2-pyridylmethyl]oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra-thiacalix[4]arene (2) was carried out as following our previous report.6

25,27-Dibenzylxoxy-26,28-bis[2-pyridylmethyl]oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra-thiacalix[4]arene (2): Colourless prisms [MeOH:CHCl3 (1:3), m.p. 274.8–275.5 °C. IR νmax (KBr/cm⁻¹): 3058, 3029, 3008, 2955, 2901, 2866, 1571, 1588, 1546, 1496.1 H NMR (400 MHz, CDCl3) δ = 0.83 (s, 18 H, tBu), 0.85 (s, 18 H, tBu), 5.07 (s, 4 H, Ar–OCH2Ph), 5.20 (s, 4 H, Ar–OCH2Py), 6.66 (d, J = 7.2 Hz, 2 H, Py–H), 6.94 (d, J = 7.01 Hz, 4 H, Ph–H), 7.02 (t, J = 7.5 Hz, 6 H, Ph–H), 7.09 (4 H, s, Ar–H), 7.12 (4 H, s, Ar–H), 7.35 (t, J = 6.9 Hz, 4 H, Py–H), and 8.49 (d, J = 4.8 Hz, 2 H, Py–H), ppm. 13C NMR (100 MHz, CDCl3) δ = 30.73, 30.82, 30.88, 33.88, 70.65, 71.46, 121.99, 126.80, 127.19, 127.99, 128.23, 128.60, 128.71, 137.52, 146.15, 146.35, 148.33, 156.01, 156.67 and 157.70 ppm.

Preparation of 25,27-Dibenzylxoxy-26,28-bis[2-pyridylmethyl]oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra-thiacalix[4]arene (4) was carried out as following our previous report.10

25,27-Dibenzylxoxy-26,28-bis[2-pyridylmethyl]oxy]-5,11,17,23-tetra-tert-butyl-2,8,14,20-tetra-thiacalix[4]arene (4): Colourless prisms [MeOH:CHCl3 (1:3), mp. 283–285 °C. IR νmax (KBr/cm⁻¹): 3055, 3029, 2952, 2921, 2853, 1604, 1572, 1562. 1H NMR (400 MHz, CDCl3) δ = 0.84 (s, 18 H, tBu), 0.86 (s, 18 H, tBu), 5.07 (s, 4 H, Ar–OCH2Ph), 5.12 (s, 4 H, Ar–OCH2Py), 6.90 (d, J = 5.5 Hz, 4 H, Ph–H), 6.94 (d, J = 7.4 Hz, 4 H, Ph–H), 7.04 (t, J = 7.6 Hz, 4 H, Ph–H), 7.10 (4 H, s, Ar–H), 7.12 (4 H, s, Ar–H), 7.13–7.18 (m, 2 H, Ph–H) and 8.40 (d, J = 5.8 Hz, 4 H, Py–H), ppm. 13C NMR (100 MHz, CDCl3) δ = 30.70, 30.73, 33.86, 33.89, 69.10, 70.80, 121.80, 126.90, 127.14, 128.03, 128.26, 128.75, 129.11, 137.35, 146.39, 146.50, 146.71, 149.38, 155.97 and 156.72 ppm. FABMS: m/z: 1083.45 (M⁺).

Extraction experiments and stoichiometry of metal complexation.

Metal picrates (4.0 × 10⁻³ M) were prepared in situ by dissolving the metal hydroxide (0.02 mol) in 4.0 × 10⁻³ M picric acid (1000 mL), triply distilled water was used for all aqueous solutions. Two-phase solvent extraction was carried out between aqueous picrates (10 mL, [metal picrate] = 4.0 × 10⁻³ M) and host (10 mL, [host] = 4 × 10⁻³ M in CH2Cl2). The two phase mixture in a stopped flask was immersed in a thermostated water bath at 25 °C which was shaken at 300 strokes per min for 4 h and then kept at the same temperature for 1 h, allowing the complete separation of the two phases. This was repeated 3 times. The absorbance of each solution was determined by UV spectroscopy (λ = 356 nm). The method of continuous variation was employed to determine the stoichiometry in the complexes involving the host receptors 2, 3 or 4. The molar ratios of both the host and metal picrate were varied from 0 to 1, while the total concentration was kept at several constant levels. Job plots were generated by plotting the extracted [M⁺] versus the mole fraction of metal. We confirmed that this period was sufficient to attain the distribution equilibrium. The extractability was determined spectrophotometrically from the decrease in the absorbance of the picrate ion in the aqueous phase, as described by Pedersen.19

1H-NMR complexation experiments

To a CDCl₃–CH₂CN (10:1, v/v) solution (5 × 10⁻³ M) of 2, 3 or 4 in an NMR tube was added a CD₃CN solution (5 × 10⁻³ M) of AgClO₄. The spectra were recorded after the additions. The temperature of the NMR probe was kept constant at 27 °C. The 1H NMR data of the most-representative complexes are given below:

2: 1H NMR (300 MHz, CHCl₃–CH₂CN, 10:1, v/v): δ = 0.83 (s, 18 H, tBu), 0.85 (s, 18 H, tBu), 5.07 (s, 4 H, CH₂Ph), 5.19 (s, 4 H, CH₂Py), 6.67 (d, J = 7.8 Hz, 2H, Py–H), 6.94 (d, J = 7.6 Hz, 4H, Ph–H), 7.03 (t, J = 6.6 Hz, 6H, Ph–H), 7.10 (s, 4H, Ar–H), 7.13 (s, 4H, Ar–H), 7.36 (t, J = 7.8 Hz, 4H, Py–H), and 8.49 (d, J = 4.7 Hz, 2H, Py–H) ppm.

3: 1H NMR (300 MHz, CHCl₃–CH₂CN, 10:1, v/v): δ = 0.85 (s, 18H, tBu), 0.86 (s, 18H, tBu), 5.06 (4H, CH₂Ph), 5.19 (s, 4H, CH₂Py), 6.93 (d, J = 7.2 Hz, 4H, Ph–H), 7.00–7.05 (m, 6H, Ph–H), 7.08 (s, 4H, Ar–H), 7.10 (s, 4H, Ar–H), 7.13 (2H, Py–H), 7.27 (d, J = 7.8 Hz, 2H, Py–H), 8.20 (2H, Py–H) and 8.46 (d, J = 3.9 Hz, 2H, Py–H) ppm.

3: 1H NMR (300 MHz, CHCl₃–CH₂CN, 10:1, v/v): δ = 0.84 (s, 18H, tBu), 0.91 (s, 18H, tBu), 5.07 (s, 4H, CH₂Ph), 5.19 (s, 4H, CH₂Py), 6.98 (d, J = 7.5 Hz, 4H, Ph–H), 7.07 (s, 4H, Ar–H), 7.08–7.12 (m, 4H, Ph–H), 7.17–7.20 (m, 2H, Ph–H), 7.21 (s, 4H, Ar–H), 7.52–7.57 (m, 2H, Py–H), 7.69 (d, J = 7.9 Hz, 2H, Py–H), 7.82 (2H, Py–H) and 8.55 (d, J = 5.1 Hz, 2H, Py–H) ppm.

4: 1H NMR (300 MHz, CHCl₃–CH₂CN, 10:1, v/v): δ = 0.84 (s, 18 H, tBu), 0.85 (s, 18 H, tBu), 5.07 (s, 4 H, CH₂Ph), 5.13 (4 H, CH₂Py), 6.91 (d, J = 5.5 Hz, 4H, Py–H), 6.94 (d, J = 7.4 Hz, 4H, Ph–H), 7.02–7.07 (m, 4H, Ph–H), 7.11 (s, 4H, Ar–H), 7.13 (s, 4H, Ar–H), 7.14–7.18 (m, 2H, Ph–H) and 8.38 (d, J = 5.9 Hz, 4H, Py–H) ppm.

Crystalllographic analyses of 3

Diffraction data were collected on a Bruker APEX 2 CCD diffractometer equipped with graphite-monochromated Mo-Kα X-ray Cu radiation. Data were processed by the Bruker AXS software package. Crystals were h...
radiation at 150(2) K. Data were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods, on \( F^2 \). H atoms were refined using a riding model except for those on hetero atoms in 3 which were freely refined.

**Crystal data for 3.** \( \text{C}_{66}\text{H}_{70}\text{N}_2\text{O}_4\text{S}_4 \), \( M = 1083.48 \). Orthorhombic, space group \( \text{Pmn} \text{2}_1 \), \( a = 15.1668 \) (6), \( b = 14.7772 \) (7), \( c = 12.7612 \) (6) Å, \( V = 2860.1 \) (2) Å\(^3\). \( Z = 2 \), \( D_c = 1.258 \) g cm\(^{-3}\), \( F(000) = 1152 \), \( T = 100 \) K, \( \mu(\text{Mo-K}) = 0.17 \) mm\(^{-1}\), \( \delta(\text{Mo-K}) = 0.6525 \) Å, colourless crystal of size 0.20 × 0.20 × 0.06 mm\(^3\). The total number of reflections measured, to \( \theta_{\text{max}} = 30.3^\circ \), was 34567 of which 11331 were unique (\( R_{\text{int}} = 0.087 \)); 10920 were ‘observed’ with \( I > 2 \sigma(I) \). For the ‘observed’ data only, \( R_1 = 0.037 \); \( wR_2 = 0.101 \) for all 11331 reflections and 400 parameters. Residual electron density within \( +/− 0.48 \) e Å\(^{-3}\).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 245644 for 3, computational study of 2–4 with Ag\(^+\).

**Supporting information:** \(^1\)H, \(^{13}\)C NMR, MS and IR spectra of 3, computational study of 2–4 with Ag\(^+\).

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**Notes and references**

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6. Electronic Supplementary Information (ESI) available: Details of single-crystal X-ray crystallographic data. For ESI and crystallographic data see CIF see DOI: 10.1039/b000000x/.
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