



Organosilatranes

Organosilatranes with Acylthiourea Derivatives – Metal-Ion Binding, Substituent-Dependent Sensitivity, and Prospects for the Fabrication of Magnetic Hybrids

Gurjaspreet Singh*^[a] and Sunita Rani^[a]

Abstract: A variety of topologically interesting acylthioureatethered organosilatranes (AcTu-OS) were prepared, and their function as metal-ion binding sites was investigated. The prepared compounds have been characterized by elemental analysis; FTIR, UV/Vis and NMR (¹H and ¹³C) spectroscopy; and mass spectrometry. The organosilicon complexes **4a–4e** possess diverse coordination abilities for the surveyed metal ions (Cu²⁺, Cd²⁺, Hg²⁺ and Pb²⁺), as was appraised by the corresponding absorption shifts in the UV/Vis spectra. In addition, a facile preparatory route for the covalent grafting of the most efficient receptor **4e** onto a silica-encrusted magnetic nanosupport was implemented. The resultant organic–inorganic hybrid nanoparticles (H-NPs) were characterized by physicochemical techniques such as FTIR spectroscopy, XRD, thermogravimetric analysis (TGA), TEM, field-emission SEM (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX). The grafting of the sensory module afforded active sites for the adsorption of metal ions from the aqueous solution which is outlined using the Langmuir adsorption isotherm. The potential in sensing, sorbent properties and facile magnetic recovery of the hybrid evinces the separation process practical to undertake environmental issues.

Introduction

In today's technology-driven society, the recognition of cations in aqueous or nonaqueous media is an imperative research direction, as their 'surplus value' induces lethal health afflictions.^[1] Considering the heavy- and transition-metal (HTM) ions, mercury and its derivatives (Hg⁰, Hg₂²⁺ and MeHg⁺) are highly deleterious, carcinogenic and notorious environmental pollutants, which cause a sequence of disorders such as headaches, nerve pain, nose bleeds, brain damage and splanchnic damage.^[2] On the other hand, Cu²⁺ ions play vital roles in numerous biological systems including metalloenzymes, metalloproteins, haemoglobin, superoxide dismutase and cytochrome c oxidase.^[3] Nevertheless, irregular levels of free Cu²⁺ ions may lead to colon cancer, Indian childhood cirrhosis and gastrointestinal, kidney and neurodegenerative diseases.^[4] Similar consequences are encountered for Cd²⁺, Zn²⁺ and Pb²⁺ ions, and for all these reasons, the recognition and proficient removal of HTM ions even at low concentrations are strongly desirable.^[5] In this context, various approaches including electrochemical methods, atomic absorption, and chromatography have been developed.^[6-8] However, highly sophisticated and pricey instrumentation, time-consuming and tedious experimentation and unsuitability for on-site monitoring are some of the major constraints. Accordingly, the desire for simple molecular chemosensors that respond through modifications to their optical signals upon specific binding with a guest analyte is constantly mounting.^[9]

Urea and its derivatives are considered as "privileged groups" in both organic and inorganic chemistry owing to their multifarious traits.^[10] In particular, the N-acylated thiourea derivatives (AcTu) are receiving attention in the fields of heterocyclic chemistry, polymer chemistry and optoelectronics and have displayed an array of pharmacological activities.^[11,12] Furthermore, on account of its structural framework comprising multiple ligating sites, namely, C=O, C=S and N-H, the AcTu group is the most prominent chelating ionophore for HTM ions.^[13] Its inbuilt coordinative fondness for both soft and hard metal ions supports the architectural versatility of these AcTu ligands. In the present scenario, acylthiourea binding units have been appended onto heterocyclic chromophores, for instance, furan, thiophene, pyridine and pyrazine. The rationale behind the selection of these heterocycles is that they contain one or more heteroatoms with an unshared pair of electrons to provide sensible scaffolds for cogent coordination with metal ions.^[14] Furthermore, these rings may boast differential sensory aptitudes towards particular metal ions.

On the other hand, silatranes $[RSi(O^1CH_2CH_2)_3N^1(O^1-N^1)]$ are intramolecularly caged pentacoordinate silicon complexes that can be fabricated readily by the reactions of precursor alkoxysilanes with triethanolamine.^[15] The variably functionalized organosilatranes have important applications in organic synthesis, medicine and agriculture.^[16] Recently, the modification of metal oxide solid surfaces (SiO₂, TiO₂, Al₂O₃Fe₃O₄, etc.) with silatrane through Si–O covalent tethering was explored.^[17] If silatranes

 [[]a] Department of Chemistry, Panjab University, Chandigarh, 160014, India E-mail: gjpsingh@pu.ac.in http://chemistry.puchd.ac.in/show-biodata.php?qstrempid= 139&qstrempdesigcode=9

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are applied as the organic precursor, much better coating results with greater ease are produced, in comparison with those with conventional alkoxysilanes. This can be attributed to the reduced propensity of silatranes towards hydrolysis, which leads to the smooth coating of the metal oxide surface.^[18] As a result, the silatrane-coated silica nanohybrids have found some amazing applications in materials science, catalysis, chemosensing, drug design, atomic force microscopy and so forth.^[19] However, the tedious separation of the hybrid somewhat hinders its practical utility as an advanced nanocomposite. To alleviate this issue and move towards the goal of an ideal nanomaterial, the encapsulation of a magnetic Fe_3O_4 core into a silica matrix is an emerging trend.^[20] The silicified magnetic nanoparticles obtained with such core-shell hierarchical architecture have synergistic contributions from both materials that result in high robustness, stability and magnetic retrievability, whereas the potential of the silica template for further conjugation with organic moieties is conserved.[21]

In this paper, the UV/Vis absorption spectral behaviour of a series of organosilatrane derivatives upon interaction with HTM ions is investigated. In addition, to the best of our knowledge, the successful immobilization of a heterocyclic-ring-appended acylthiourea moiety onto the surface of magnetic silica is reported here for the first time. It is envisioned that such grafting might provide an easy pathway for the effective recognition and removal of transition-metal ions.

Results and Discussion

Synthetic Approach

In the present work, a simple methodology was selected to tether carboxylic acids to silatrane through acylthiourea linkers to generate acylthiourea-tethered organosilatranes (AcTu-OS, Scheme 1). Firstly, (3-aminopropyl)silatrane (APS) was prepared from (3-aminopropyl)trimethoxysilane (APTMS) and attached to the carboxylic acid derivatives; this route was used instead of using APTMS for the condensation reaction each time and then reacting each condensation product with triethanolamine, as it would be more time-consuming and tedious. In the next step, the carboxylic acids were derivatized into more reactive acyl chlorides by treatment with excess thionyl chloride, and the acyl chlorides generated acyl isothiocyanates on substitution with KNCS.

The acyl isothiocyanates can undergo condensation reactions with functional groups that feature a labile H atom such as amines, alcohols, thiols, phenols and amino acids.^[22] The addition or condensation reactions of acyl isothiocyanates are a little more complex than the corresponding reactions of isothiocyanates. During the reactions of the acyl isothiocyanates with the amine, in addition to the expected addition product, a simple substitution at C=O can also lead to the formation of the corresponding amide derivative (Scheme 2). The formation of the substituted product can be vastly suppressed only in nonprotonic solvents such as acetonitrile or acetone. In addition, proper care must be taken during the drying of the solvent, because even a slight amount of moisture will favour the substitution rather than the addition. In our case, screening both of these solvents independently for the addition reaction of 3a with APS revealed that a significant yield could be obtained only with acetonitrile as the solvent. We noticed that APS is only sparingly soluble in acetonitrile, whereas it dissolved readily in acyl isothiocyanate.^[23] Therefore, in a further attempt to improve the yield, the optimized molar ratio of acid chloride and APS was determined to be 1:0.8, and the excess acyl isothiocyanate helps with solvation and prompts the generation of a highly pure product in a shorter time.



Scheme 2. Possible reaction profile of primary amines with acyl isothiocyanates.

Spectroscopic Characterization

IR spectroscopy is one of the most widely used techniques for the characterization of acylthiourea derivatives. Quantum mechanical studies on such compounds established that the two N–H groups are in different environments and, hence, their IR bands should be observed at different frequencies.^[24] This



Scheme 1. Synthesis of AcTu-OS derivatives 4a-4e.



trend was observed for the present set of compounds. For instance, the N–H group attached to the carbonyl group is observed at $\tilde{v} = 3223-3403 \text{ cm}^{-1}$, which is akin to the position of the band for an amidic NH group. On the other hand, the N–H group attached to the C=S group behaves differently, and its IR bands are observed at $\tilde{v} = 3170-3183 \text{ cm}^{-1}$, which provides compelling evidence for the intramolecular H bonding of this N–H group with the O atom of the C=O group. Another affirmation of this H bonding stems from the lowered absorption frequencies of the C=O group ($\tilde{v} = 1642-1654 \text{ cm}^{-1}$). The formation of an atranyl cage is established by the N \rightarrow Si stretching vibrations in the range $\tilde{v} = 581-592 \text{ cm}^{-1}$ for all AcTu-OS derivatives.^[25]

The ¹H and ¹³C NMR spectra of the compounds are consistent with the respective structures. In the ¹H NMR spectra, the signal for the CH₂NH protons splits into a multiplet, and a shift occurs in its position from δ = 2.62 (APS) to 3.37–3.68 ppm (for 4a-4e). This shift supports the derivatization of the amine group. Secondly, the chemical shifts of the N-H protons of the AcTu group are significantly different ($\delta = 9.03-10.81$ and 10.29–11.10 ppm) owing to the aforementioned intramolecular H bonding. The peaks corresponding to the OCH₂ and NCH₂ protons of the silatranyl fragment appear as triplets in the ranges δ = 2.76–2.83 and 3.70–3.77 ppm, respectively. The corresponding peaks of the ring carbon atoms (NCH₂ and OCH₂) are present in the ranges δ = 50.14–52.76 and 56.78–57.71 ppm, respectively, in the ¹³C NMR spectra. Collectively, the ¹³C NMR resonances ascribed to the C=O (δ = 156.44–163.56 ppm) and C=S (δ = 178.62–180.83 ppm) carbon atoms substantiate the product formation. The mass spectra of all AcTu-OS derivatives coincide with the projected structures and have successfully depicted the respective molecular-ion peaks with the addition of H⁺, Na⁺ or K⁺ ions.

UV/Vis Absorption Study

All AcTu-OS derivatives possess major absorption bands in the region $\lambda = 248-292$ nm, which confirm the $\pi - \pi^*$ electronic transitions in the conjugated system. The normalized UV/Vis spectra are presented in Figure 1, and the salient absorption features are listed in Table 1. The spectral characteristics of any chromophore depend on its electronic environment and the degree of conjugation encircling it, which can together allow a systematic fine-tuning. In the context of UV/Vis absorption (Figure 1), as



the acyl thiourea unit is prevalent in all derivatives, one can safely surmise that it is the incorporation of different aromatic rings that affects the absorption maxima so significantly. For instance, amongst all of the derivatives, compound **4a** with a furan unit absorbs at the lowest value of $\lambda_{max} = 248$ nm. The replacement of the O atom (**4a**) in the heterocyclic ring by a S atom (**4b**) instigates a pronounced redshift of 7 nm in the absorption spectra, which highlights the fact that the thiophene ring has more-delocalized π electrons than the furan ring.^[26]



Figure 1. Normalized UV/Vis spectra of 4a-4e.

On switching from five- to six-membered heterocycles, higher λ_{max} values are obtained (Table 1, Entries 3–5). We infer that this phenomenon is caused by the overall larger conjugation imparted by the six-membered rings compared with the analogous five-membered rings. Further, **4d** exhibits a lower absorption maxima than **4c**, and this can be attributed to the electron-withdrawing inductive effect of the extra N atom introduced into the ring. On the other hand, compound **4e**, containing a pyridine ring conjugated with bis(acylthiourea) moieties on both sides of the central plane, absorbs at the highest λ_{max} value; this highlights the effect of conjugation length in the UV/ Vis absorption study of the present set of compounds.

Recognition Studies Involving Cations

All of the recognition studies were performed at 25 °C, and ample time was provided for the solutions to become consistent before the spectra were recorded. The sensing abilities of all of the compounds were scrutinized through the addition of Na⁺, K⁺, Mg²⁺, Al³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Pb²⁺

Table 1. Observed yields, UV/Vis absorption data and chemosensing parameters of 4a-4e.

Entry	AcTu-OS derivative	Synthetic yield ^[a] [%]	λ _{max} ^[b] [nm]	$\epsilon_{max}{}^{[c]}\times10^4$ [L mol ⁻¹ cm ⁻¹]	Detected M ²⁺ ion	Spectral behaviour Stoichiometry (AcTu-OS/M ²⁺)	Association constant (K_a)
1	4a	78	249	3.5714	Cu ²⁺	2:1	$1.41 \times 10^2 \text{ M}^{-1/2}$
					Cd ²⁺	2:1	1.57 × 10 ⁴ м ^{-1/2}
2	4b	80	256	3.125	Cu ²⁺	2:1	$1.62 \times 10^2 \text{ M}^{-1/2}$
					Cd ²⁺	2:1	$1.64 \times 10^4 \text{ m}^{-1/2}$
					Hg ²⁺	1:1	$3.05 \times 10^5 \text{ m}^{-1}$
3	4c	82	270	2.560	Cu ²⁺	2:1	1.76 × 10 ² м ^{-1/2}
4	4d	84	266	1.776	Cu ²⁺	2:1	$1.45 \times 10^2 \text{ M}^{-1/2}$
5	4e	85	281	4.450	Cu ²⁺	1:1	5.97 × 10 ⁵ м ⁻¹
					Pb ²⁺	1:1	7.29 × 10 ⁵ м ⁻¹

[a] Isolated yield. [b] Maximum absorption wavelength. [c] Molar absorption coefficient at the maximum absorption wavelength.





cations (up to 20 equiv.) to CH_3CN solutions of each receptor (1 μ m; Figures S1–S5).

In the metal complexes of thiourea-containing ligands, coordination can occur through the N or S atom separately or both simultaneously.^[27] The incorporation of the acyl fragment into the thiourea core increases the complexity of the binding system. Depending on the dihedral angles between the acyl N atom and the adjacent N-C bond, several feasible confirmations can be categorized into four main forms, as outlined in Scheme 3, in which the capital letters indicate the positions of the C=O and C=S bonds with respect to the N-H bond. Quantum mechanical calculations on a library of acylthiourea derivatives indicated the prevalence of the S and U forms only.^[28] Further, in the complexes of monosubstituted derivatives, the S form with an opposite orientation between the C=O and C=S bonds is dominant; in this geometry, the C=O bond and H atom of the adjacent N-H group form a pseudo-six-membered cavity. When this intramolecular H bonding is prevented, as for disub-



Scheme 3. Possible conformations around the -C(O)NHC(S)N- moiety.

stituted analogues, the anticlinal conformation (archlike shape, U) is favoured. In addition to these fundamental rearrangements, the orientation of the donor site is highly affected by the appending sites to which the acylthiourea unit is attached (R group in Scheme 3).

The UV/Vis titration experiments disclosed that all of the receptors 4a-4e possess an approximately identical response toward copper ions (Figure 2). Specifically, the injection of Cu²⁺ ions into the receptor solution resulted in the enhancement of the absorption intensity and a simultaneous bathochromic shift in the wavelength maxima. This trend may arise because increased conjugation on complexation with copper ions leads to a decrease in the π - π * transition-energy difference. During the titrations, the absorption changes occurred in the UV region only (below 400 nm); therefore, colour changes could not be observed. As all of the compounds showed identical perturbations in the presence of copper ions, we envisaged that the heterocyclic ring might not be involved in the bonding, otherwise radically different absorption patterns would have been observed. To ascertain the exact role of the heterocyclic ring in Cu²⁺ complexation, a model compound (MC) devoid of any heteroatoms in the aromatic ring was prepared from benzoic acid as the precursor. To our delight, the UV/Vis titration plot of MC with Cu2+ ions was akin to that of the heterocyclic-cored receptors (Figure S6); this strongly suggests that the heterocyclic rings do not participate in Cu²⁺ recognition.



Figure 2. Series of UV/Vis spectra recorded in the course of the titrations of (i) **4a**, (ii) **4b**, (iii) **4c**, (iv) **4d** and (v) **4e** (1 μ M in CH₃CN) with Cu²⁺ ions (0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6.0, 6.4, 6.8, 7.2, 7.6, 8.0, 8.4, 8.8, 9.2, 9.6, and 10.0 equiv.). Insets: the B–H plots for 2:1 complexation between the receptors and Cu²⁺ ions (1:1 for **4e**).





As the actual binding site, that is, the acylthiourea unit embodies S, N and O donor atoms, it can act as a monodentate S donor, a bidentate O,S donor, or a bidentate O,N donor.^[13] To further deduce the most pertinent coordination mode, the IR spectra of the pure receptor (**4a**) and the receptor in the presence of copper ions were compared (Figure S7). A close inspection unveils the absence of the broad peak ascribed to the N–H group upon complexation and, therefore, indicates that the N–H group is deprotonated (Figure S7B). This increases the electron density over the adjacent double bonds, as shown in Figure 3, and chelation is favoured. As a result, the characteristic peaks of the C=O and C=S bonds are redshifted by 25 and 10 cm⁻¹, respectively, which indicates that the ligand adopts the monobasic bidentate (O,S) chelation (in the U-shaped confirmation) with Cu²⁺ ions, as shown in Figure 3.

On the other hand, when the receptors were titrated with Hg^{2+} ions, the expected shifts in the absorption spectra were observed for **4b** only [Figure 4 (i)], whereas the spectra of the other compounds remained unchanged even with an excess of Hg^{2+} ions (Figures S1–S5). This observation firmly rules out the formation of a binding cavity similar to that for copper ions. If the chelation occurred through an O,S-donor system, then even better binding results would be expected, as the highly thio-

philic mercuric ions would coordinate strongly with either the S atom alone or the O and S donor atoms, according to the Pearson hard and soft acid and base (HSAB) principle.^[29] Therefore, some preorganization of the ligating sites of the molecular platform must occur in the presence of Hg²⁺ ions to produce different complexation behaviour.

The recognition of Hg²⁺ ions by **4b** is in accord with the HSAB principle, and the coordination with the S atom of the thiophene ring and the O atom of the adjacent C=O group is the expected outcome (Figure 3). Further, the recognition mechanism is confirmed by the IR spectra of **4b**, which reveals a 36 cm⁻¹ decrease in the frequency of the band of the C=O group in the presence of Hg²⁺ ions, whereas the peaks ascribed to rest of the acylthiourea moiety were only affected minimally (Figure S8).

The binding behaviour of the receptors towards Cd^{2+} ions was also studied by UV/Vis spectroscopy. The data reveal that only the spectra of **4a** and **4b** showed prominent changes (Figure 5), whereas those of the other compounds **4c–4e** remained unperturbed. This is in accord with previous reports, in which furan-based acylthiourea ligands formed stable complexes with Cd^{2+} ions through coordination with the S atom of the C=S group by rearranging into the "S" conformer (Figure 3).^[30] Strik-



Figure 3. Proposed binding modes of the compounds with different ions.



Figure 4. Series of UV/Vis spectra recorded over the course of the titrations of (i) **4b** (1 μ m in CH₃CN) with Hg²⁺ ions and (ii) **4e** (1 μ m in CH₃CN) with Pb²⁺ ions. The insets show the corresponding linear B–H plots between the receptors and ions.







Figure 5. Series of UV/Vis spectra recorded over the course of the titrations of (i) **4a** (1 μ m in CH₃CN) with Cd²⁺ ions and (ii) **4b** (1 μ m in CH₃CN) with Cd²⁺ ions. The insets show the corresponding B–H plots for 2:1 complexation between the receptors and ions.

ingly, only silatranes containing five-membered rings showed sensitivity with Cd^{2+} ions to form the pseudocavities, whereas the substitution of the furan/thiophene ring in the OS derivatives by larger six-membered moieties caused poor association with Cd^{2+} ions; therefore, the steric encumbrance by the aromatic ring over the whole molecular skeleton leads to the interruption of the chelation process.

Similar screening experiments were performed for lead ions, and only the spectrum of 4e showed clear divergence. Many research groups have established that pyridine-2,6-dicarboxylic acid and its derivatives form a burgeoning class of ligand scaffolds for numerous metal ions. This is because of the generation of an optimum cleftlike cavity for the metal ions through the rearrangement of the carbonyl groups with the coplanar pyridine ring.^[31] As a consequence, only receptor **4e** could recognize Pb²⁺ ions by entrapping them in the cavity, and the binding results are shown in the UV/Vis spectra [Figure 4 (ii)]. Decisively, even the spectrum of 4c, which is a close analogue of 4e, did not show noticeable change even with an excess of Pb²⁺ ions (Figure S3). This emphasizes the worth of a suitable cavity for the complexation with lead ions, as a higher number of binding atoms and their orientation flexibility increases the stability of the complex formed with Pb²⁺ ions.

Benesi-Hildebrand Plots, Association Constants and Stoichiometry Calculations for Receptor-Cation Complexation

As the cation-recognition properties of receptors **4a–4e** had been explored by examining UV/Vis spectral changes upon the addition of different cations, the altered absorbance data could be evaluated further through the modified Benesi–Hildebrand (B–H) equation to gauge the comparative strength of different receptors towards the tested ions.^[32] In general, the B–H relationship is used to determine the stoichiometry of complexation as well as the association constant (K_a), a measure of the strength of the interaction between the receptor and the metal ions in a complex.

As the UV/Vis absorption plots (Figure 2) revealed the binding of all of the chemoreceptors with copper ions, we first measured the stoichiometry of the complexation in each case. From the assessment of the titration data, a linear regression for the plot of $(A - A_0)^{-1}$ versus $[Cu^{2+}]^{-1}$ could be obtained for 4e only, and the plots for the other compounds showed sigmoid shapes. Alternatively, graphs of $(A - A_0)^{-1}$ versus $[Cu^{2+}]^{-0.5}$ were plotted to attain the required linearity. Therefore, in all cases except 4e, the stoichiometry of the complex with copper ions is 2:1; this suggests that two acylthiourea moieties are required to form a stable complex with copper ions, as shown in Figure 3. The observation wavelengths for the B-H plots of 4a-4e with Cu²⁺ ions were 284, 292, 285, 307 and 305 nm, respectively. As discussed earlier, the heterocyclic ring is not directly involved in the binding with copper ions; however, it significantly affects the strength of the resultant complex. For instance, amongst all of the derivatives, 4e exhibits the most prominent binding, as indicated by the highest K_a value, which was calculated from the slope of the linear fit of the corresponding B-H graph. This is on account of its geometrical features, through which two copper ions can be entrapped by the acylthiourea ligands present on both sides of the central pyridine ring to form a 1:1 complex. A comparison of the K_a values of silatranes 4a and 4b with five-membered rings discloses that **4b** emerges as a better chelator for Cu²⁺ ions (Table 1). This can be explained by the fact that thiophene is superior electron donor than furan and leads to higher electron density at the binding unit, which facilitates the coordination with copper ions. On a similar basis, among the monosubstituted six-membered derivatives, compound 4c containing a pyridine ring showed better binding than that of the pyrazine-containing compound 4d, as the electron-withdrawing nature of the additional N atom in 4d disfavours the chelation process (Table 1, Entries 3 and 4).

For the Hg²⁺ binding system (**4b**), the heterocyclic ring is actually included in the chelation and is not just an extension to the absorbing chromophore (on the basis of the FTIR spectroscopy results). On the stepwise addition of Hg²⁺ ions to a solution of **4b**, the absorbance intensity increased, and saturation was observed when 10 equiv. Hg²⁺ ions had been added. From the Benesi–Hildebrand plot (wavelength 291 nm), it was deduced that a 1:1 stoichiometry fits better for the complex of **4b** with Hg²⁺ ions, and the association constant was determined to be $3.05 \times 10^5 \text{ m}^{-1}$ (Table 1, Entry 2).

On the other hand, the B–H plots obtained for the addition of Cd^{2+} ions to **4a** (wavelength 297 nm) and **4b** (wavelength 284 nm) involved 2:1 stoichiometries, and the binding constants are comparable (Table 1, Entries 1 and 2). The enhanced





selectivity shown by **4b** can be attributed to the electron-releasing effect of the thiophene ring. Furthermore, **4e** showed sensitivity towards Pb²⁺ ions, and the corresponding complex is formed in 1:1 stoichiometry with $K_a = 7.29 \times 10^5 \text{ m}^{-1}$. A comparison of the K_a values of the complexes of **4e** with Cu²⁺ and Pb²⁺ ions reveals that a more stable complex is formed with Pb²⁺ ions. This can be explained on the basis of the higher ionic radius of Pb²⁺ (0.98 Å) compared with that of Cu²⁺ (0.57 Å) and suggests that the cavity size of this cleft-shaped molecule is more suitable for larger cations.^[33]

Characterization of the Hybrid Nanomaterial

An imperative technique to provide information about the attachment of organic groups to an inorganic structure is the FTIR spectrum of the material in the solid state.^[34] The FTIR spectrum of pristine Fe₃O₄ nanoparticles displays an intense band at $\tilde{v} = 1396 \text{ cm}^{-1}$, which corresponds to the stretching vibrations of the Fe–O bonds (Figure 6, A). The broad band centred at $\tilde{v} = 3007 \text{ cm}^{-1}$ is attributed to O–H stretching. In the IR spectrum of silica-encapsulated Fe₃O₄ nanoparticles (Figure 6, B), the strongest peak corresponds to the characteristic peak of Si– O bonds at $\tilde{v} = 1061 \text{ cm}^{-1}$. Importantly, the intensity of the previously observed Fe–O peak is largely reduced, which authenticates the modification of the Fe₃O₄ cores. The final attachment of the organic moiety (**4e**) by immobilization on the siliceous magnetic matrix is confirmed by the intense peak corresponding to the aromatic functionality ($\tilde{v} = 1410 \text{ cm}^{-1}$); therefore, the coating procedure was successful (Figure 6, C). The peak at $\tilde{v} = 1627 \text{ cm}^{-1}$ corresponds to the bending vibration of adsorbed water molecules.

The composition and arrangement of the proposed coreshell architecture were elucidated by powder XRD. The XRD pattern of the hybrid nanomaterial (Figure 7, A) matches very well with that of standard Fe₃O₄ crystals with a cubic spinel structure (Figure S9). This confirms the validity of the synthetic procedure for the magnetite nanoparticles as well as their preservation under the modification conditions.^[35] In addition, a broad peak at $2\theta = 23^{\circ}$ (Figure 7, A) validates the existence of amorphous silica in the final hybrid. The important point that needs to be highlighted is that no changes to the inherent properties of the silica and Fe₃O₄ occur even after their modification to form the core–shell arrangement.



Figure 6. FTIR spectra of (A) Fe₃O₄, (B) Fe₃O₄@SiO₂ and (C) Fe₃O₄@SiO₂-silatrane.



Figure 7. XRD pattern (A) and (B) TGA and DTA profiles of the hybrid composite.





Further, to probe the thermal stability of the hybrid material, thermogravimetric analysis (TGA) was employed under a flow of N₂. The corresponding TGA and differential thermal analysis (DTA) curves of the $Fe_3O_4@SiO_2$ -silatrane are depicted in Figure 7 (B).

During the thermal analysis of silatrane immobilized on Fe₃O₄@SiO₂ particles, the weight loss (13.6 %) corresponding to the initial heating stage (25-200 °C range) was attributable to the thermodesorption of physically adsorbed water or solvent molecules and indicates that these nanoparticles have hydrophilic surfaces.^[36a] Moreover, above 240 °C, the decomposition of the attached organic moiety to form gases occurs, as specified by the weight loss of ca. 33.4 % in the TGA graph. As the loss is much greater than that observed for the bare Fe₃O₄@SiO₂ (Figure S10), the presence of organic material over the core-shell matrix is confirmed. The DTA curve shows that exothermic transitions commence during the decay of the hybrid.^[36b] It is worth mentioning here that the inorganic templates did not decompose up to the studied temperature, which indicates the stability of the hybrid nanoparticles (H-NPs, Figure 7, B), and the analysis revealed that the hybrid is composed of 48 % core-shell unit, whereas the organic contents comprise 33.4 % of the hybrid. It is fascinating that the organic content in the present nanocomposite is 0.905 mmol/g, which is greater than that predicted on the basis of previous reports and can be credited to the appliance of a silatrane as the coupling agent. This feature can be highly advantageous for the adsorption of metal ions, as discussed in the next section.

The morphology, particle size and composition of the grafted nanohybrid were appraised by TEM. The sample was dispersed in absolute ethanol and ultrasonicated for 2 h before the analysis, and the resultant micrographs at different magnifications are presented in Figure 8 (A and B). A completely uni-

form silica coating over tiny agglomerated magnetic cores can be visualized (Figure 8, A). The closer view elucidates the fact that the dense Fe_3O_4 particles have been strongly encompassed by the silica shell rather than simply adhering physically or blending into the silica.^[37] The aggregation of the Fe_3O_4 nanoparticles (which occurred before the coating procedure) led to the imprisonment of more than one magnetic nanoparticle into the silica shell, as shown in Figure 8 (B), and this could be beneficial during the magnetic separation of the H-NPs.

Insights into the surface morphology and topography of the silatrane-grafted magnetic nanoparticles were pursued by fieldemission SEM (FE-SEM) analysis, and the corresponding images recorded at different magnifications are shown in Figure 8 (C– E). From the surface analysis, one can conclude that the particles possess well-defined large spherical shapes with smooth surfaces and are uniformly distributed. During the preparation of the hybrid nanoreceptor, a series of chemical reactions were performed, but apparently no clogging occurred between the particles, and the particles maintained a regular spherical shape, which implies that their inherent mechanical strength is preserved.^[38]

For the quantitative interpretation of the composition of the hybrid nanomaterial, energy-dispersive X-ray spectroscopy (EDX) was employed. The elemental mapping of the uncovered $Fe_3O_4@SiO_2$ nanoparticles is shown in Figure 9a, and discernible peaks can be indexed to Fe, Si and O atoms; therefore, the EDX results provide evidence for the encapsulation of iron oxide by the silica shell. On the other hand, the EDX spectra of the covalently grafted nanoreceptor (Figure 9, b) possess some additional peaks for the C, N and S atoms of the organic precursor, and the original peaks corresponding to core–shell architecture remained intact. This confirms the successful surface tailoring of the organosilica unit over the Fe_3O_4 nanoparticles.



Figure 8. (A and B) TEM and (C-E) FE-SEM micrographs of Fe₃O₄@SiO₂-silatrane at different magnifications.







Figure 9. EDX spectra of (a) Fe₃O₄@SiO₂ and (b) Fe₃O₄@SiO₂@silatrane.

Metal-Ion Adsorption Study

Owing to the lethal side-effects of HTM ions, various advanced techniques have been formulated for their separation and removal from water, including ion exchange, coagulation, chemical precipitation, solvent extraction, complexion, distillation and reverse osmosis.^[39] Currently, almost all of these techniques are associated with impediments such as partial removal efficiency, high cost, complicated sample preparation, non-recyclability and the generation of toxic waste. The liquid-solid phase adsorption stimulated by the immobilization of metal-ion-receptive sites onto inorganic materials possessing magnetic separability has been a favoured pursuit in this regard.^[40] The immobilization process is necessary for the spontaneous adsorption, because bare inorganic nanoparticles cannot be used directly as a lack of potential binding sites would largely inhibit the adsorption process. Therefore, in the present work, a hybrid inorganic sorbent, which has been tailored to the analysis and efficacious removal of heavy-metal ions, is utilized for the adsorption purpose. This particular assembly of a chelating dipicolinic acid derivatized ligand (4e) anchored onto the magnetic core-shell matrix (H-NPs) is deemed to be a versatile nanoreceptor for HTM ions.

As the precursor organosilatrane (**4e**) has shown binding with copper and lead ions (Table 1), both of these ions were tested for their adsorptive removal. For this, the H-NPs (0.025 g) were added into aqueous solutions (10 mL) of Cu^{2+} and Pb^{2+} ions of concentrations 0.5–2.5 mmol/L. The adsorption kinetics was explored by UV/Vis spectroscopy, as the absorbance is directly proportional to the concentration of metal ions. The nanoadsorbent was first reacted with the ions for an adequate time, after which the nanoparticles were separated by the application of an external magnet, and the concentration of ions in the supernatant was measured by UV/Vis spectroscopy. For both ions, the adsorption increased with reaction time from 1 to 120 min and remained invariable for a reaction time of more than 2 h. Therefore, the nanoadsorbent was treated with the ions for 2 h before further analysis. The amount of metal ions adsorbed by the hybrid adsorbent at equilibrium can be determined with Equation (1).

$$Q_{\rm e} = \frac{(C_{\rm i} - C_{\rm e})V}{M} \tag{1}$$

 $Q_{\rm e}$ is the amount of ions adsorbed per unit mass of adsorbent at equilibrium, $C_{\rm i}$ and $C_{\rm e}$ symbolize the initial metal-ion concentration and the concentration at equilibrium, respectively, *V* is the volume of the solution, and *M* is the weight of the adsorbent (g). To determine the saturated adsorption amount $Q_{\rm m}$ (mg/g), Langmuir adsorption was employed [Equation (2)].^[39]

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{C_{\rm e}}{Q_{\rm m}} + \frac{1}{K\alpha Q_{\rm m}}$$
(2)

The straight line obtained for a plot of C_e/Q_e against C_e confirms the viability of a Langmuir adsorption phenomenon. Explicitly, Q_m was calculated through the reciprocal of the slope of the straight line generated by the Langmuir linear fitting of the adsorption isotherm curve (Figure 10). The high model-fit parameters (R^2) in both cases (Table 2) support the fact that the adsorption phenomenon follows the Langmuir criterion, which



Figure 10. Langmuir adsorption isotherm for the adsorption of (A) Cu²⁺ and (B) Pb²⁺ ions.



proposes that adsorption occurs at specific homogeneous sites within the adsorbent and is suited to monolayer adsorption processes.^[40]

Table 2. The relevant parameters of the Langmuir fit.

Adsorbed metal ion	R ²	Q _m [mmol/g]	K _a [L/mmol]
Cu ²⁺	0.9875	0.3817	1.67
Pb ²⁺	0.9925	0.4210	2.16

Conclusions

Acylthiourea-tethered heterocyclic rings have been attached to silatrane through a C_3 linker and probed as receptors for heavyand transition-metal ions. The tuning of the electronic properties by variation of the substituents in these derivatives resulted in differential sensitivity and selectivity towards the tested metal ions. In addition, a protocol for the fabrication of magnetic silica nanospheres functionalized by the pyridine-based bis(AcTu-OS) is presented. In addition to supplying a straightforward methodology for the synthesis of magnetic core–shellstructured organosilica nanocarriers, this study underlines their strong adsorption activity for copper and lead ions. This new type of silatrane-based advanced material can be applied in the detection and removal of heavy-metal ions.

Experimental Section

General Materials and Methods: Furan-2-carboxylic acid (Avra), thiophene-2-carboxylic acid (Aldrich), picolinic acid (Aldrich), pyrazine-2-carboxylic acid (Merck), 2,6-pyridinedicarboxylic acid (Spectrochem), 3-aminopropyltrimethoxysilane (APTMS, Aldrich), tetraethyl orthosilicate (TEOS, Aldrich) and triethanolamine (Merck) were used directly as received. Thionyl chloride (SDFCL) was distilled before use. 3-Aminopropylsilatrane (APS) was prepared by following a previously reported method.^[41] Potassium thiocyanate was vacuum-dried for 2 h before use. The organic solvents were dried according to standard procedures.^[42]

The melting points were measured with a Mel Temp II device with the compounds in sealed capillaries. The ¹H and ¹³C NMR spectra were recorded with a JEOL (AL 400 MHz) spectrometer with CDCl₃ as an internal reference, and the chemical shifts are reported relative to tetramethylsilane. The electronic spectra were recorded with a JASCO V-530 UV/Vis spectrophotometer. The infrared spectra of neat samples were recorded with a Thermo Scientific NICOLET IS50 spectrophotometer. Elemental analyses were obtained with a Perkin-Elmer Model 2400 CHNS elemental analyzer. The mass spectral measurements (ESI source with capillary voltage, 3000 V) were performed with a WATERS Q-TOF micro mass spectrometer. The morphology of the H-NPs was scrutinized by TEM at 80 kV (Hitachi H-7500). XRD was performed with a PANalytical X'pert PRO diffractometer with Cu-K_a radiation. For the FE-SEM analysis, a Hitachi SU8010 ultrahigh-resolution scanning electron microscope was used. The EDX was performed with an adjacent EDAX Inc. system. The TG analyses were performed with an SDT g600 V20.9 Build 20 TGA instrument. The samples were loaded in alumina pans, and the temperature was ramped at 10 °C/min from 25-1000 °C in dry air at 60 mL/min.

General Procedure for the Synthesis of Acyl Chlorides 2a–2e: Acid chlorides were prepared by the literature method.^[43] In a typical experiment, the carboxylic acid (1.00 g) and *N*,*N*-dimethylforma-



mide (three drops) were placed in a round-bottomed flask maintained at 0 °C. To this mixture, thionyl chloride in excess (10 equiv.) was added slowly (Table T1, Supporting Information). The mixture was then heated at 80 °C for 6 h, after which the evolution of HCI gas declined. Dry toluene was then added to the mixture for the azeotropic removal of excess thionyl chloride with a Dean–Stark extraction trap. Petroleum ether was added to wash the residue, and the final product was obtained after vacuum-filtration. No further attempts were made to purify the acid chlorides, and the products were used as obtained in the subsequent reactions.

General Procedure for the Synthesis of Acylthiourea-Linked Organosilatranes 4a-4e: To a suspension of acid chloride (1.00 equiv.) in freshly dried acetonitrile (20 mL), KNCS (1.50 equiv.) was added. The mixture was heated under reflux for 2 h. A gradual change from colourless/brown to dark orange along with the formation of a precipitate signified the successful formation of the corresponding organic acyl isothiocyanate (3a-3e). The byproduct KCI was removed by vacuum-filtration, and the filtrate containing acyl isothiocyanate was not further worked upon for isolation. To the filtrate, APS (0.80 equiv.) was added, and the resultant mixture was heated under reflux for 24 h. After cooling to room temperature, the mixture was poured into water, and chloroform (25 mL) was added. The organic layer was gradually washed with brine and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure to furnish the corresponding AcTu-OS derivatives in high yields.

N-[3-(Silatranyl)propylcarbamothioyl]furan-2-carboxamide (4a): The reactants used were **2a** (0.38 mL, 3.83 mmol), KNCS (0.56 g, 5.77 mmol) and APS (0.72 g, 3.10 mmol), m.p. 143–145 °C. C₁₅H₂₃N₃O₅SSi (385.51): calcd. C 46.7, H 6.0, N 10.9, S 8.3; found C 46.4, H 6.2, N 10.7, S 8.4. IR (neat): $\tilde{v} = 3403 [v(N-H)]$, 3178 [v(N-H)], 1642 [v(C=O)], 1260 [v(C=S)], 1096 [v(Si-O)], 581 $[v(N \rightarrow Si)]$ cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 0.49$ (m, 2 H, SiCH₂), 1.80 (m, 2 H, CCH₂C), 2.81 (t, *J* = 5.7 Hz, 6 H, NCH₂), 3.68 (m, 2 H, CH₂NH), 3.77 (t, *J* = 5.7 Hz, 6 H, OCH₂), 6.59 (t, *J* = 4.5 Hz, 1 H, H³), 7.30 (d, *J* = 4.6 Hz, 1 H, H²), 7.56 (d, *J* = 4.6 Hz, 1 H, H⁴), 9.03 (s, 1 H, NH), 10.46 (s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 13.34$ (SiCH₂), 2.395 (CCH₂C), 49.19 (CH₂NH), 51.11 (NCH₂), 57.69 (OCH₂), 113.17 (C³), 118.14 (C²), 145.39 (C⁴), 146.03 (C¹), 156.44 (C=O), 178.62 (C= S) ppm. MS: *m/z* (%) = 385 (100) [M]⁺.

N-[3-(Silatranyl)propylcarbamothioyl]thiophene-2-carboxamide (4b): The reactants used were 2b (0.37 mL, 3.41 mmol), KNCS (0.50 g, 5.15 mmol) and APS (0.63 g, 2.71 mmol), m.p. 139– 141 °C. $C_{15}H_{23}N_3O_4S_2Si$ (401.57): calcd. C 44.9, H 5.8, N 10.4, S 15.9; found C 44.7, H 5.7, N 10.7, S 15.7. IR (neat): \tilde{v} = 3223 [v(N–H)], 3121 [v(N–H)], 1644 [v(C=O)], 1261 [v(C=S)], 1077 [v(Si–O)], 592 [v(N→Si)] cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.51 (m, 2 H, SiCH₂), 1.74 (m, 2 H, CCH₂C), 2.81 (t, *J* = 5.7 Hz, 6 H, NCH₂), 3.46 (m, 2 H, CH₂NH), 3.77 (t, *J* = 5.7 Hz, 6 H, OCH₂), 7.48 (t, *J* = 4.5 Hz, 1 H, H³), 7.59 (m, *J* = 5.0 Hz, 1 H, H²), 7.80 (d, *J* = 3.6 Hz, 1 H, H⁴), 9.38 (s, 1 H, NH), 10.40 (s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 13.92 (SiCH₂), 23.74 (CCH₂C), 48.13 (CH₂NH), 50.14 (NCH₂), 56.78 (OCH₂), 128.12 (C³), 131.77 (C²), 133.75 (C⁴), 136.97 (C¹), 161.91 (C= O), 179.27 (C=S) ppm. MS: *m/z* (%) = 424 (100) [M + Na]⁺.

N-[3-(Silatranyl)propylcarbamothioyl]pyridine-2-carboxamide (4c): The reactants used were **2c** (0.50 g, 2.81 mmol), KNCS (0.41 g, 4.22 mmol) and APS (0.52 g, 2.24 mmol), m.p. 127–129 °C. C₁₆H₂₄N₄O₄SSi (396.54): calcd. C 48.5, H 6.1, N 14.1, S 8.1; found C 48.4, H 5.8, N 14.5, S 8.3. IR (Neat): $\tilde{v} = 3375 [v(N-H)]$, 1649 [v(C=O)], 1273 [v(C=S)], 1082 [v(Si-O)], 582 [$v(N\rightarrow Si)$] cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 0.43$ (m, 2 H, SiCH₂), 1.67 (m, 2 H, CCH₂C), 2.76 (t, *J* = 5.8 Hz, 6 H, NCH₂), 3.37 (m, 2 H, CH₂NH), 3.70 (t, *J* = 5.7 Hz, 6





H, OCH₂), 8.20 (m, 1 H, H⁴), 8.42 (m, 1 H, H³), 8.49 (d, J = 4.7 Hz, 1 H, H²), 8.58 (d, J = 5.0 Hz, 1 H, H⁵), 10.17 (s, 1 H, NH), 10.29 (s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 13.46$ (SiCH₂), 24.60 (CCH₂C), 50.75 (CH₂NH), 52.58 (NCH₂), 57.45 (OCH₂), 127.19 (C²), 129.90 (C⁴), 137.05 (C³), 147.66 (C⁵), 151.54 (C¹), 162.61 (C=O), 179.92 (C=S) ppm. MS: m/z (%) = 420 (100) [M + Na + H]⁺.

N-[3-(Silatranyl)propylcarbamothioyl]pyrazine-2-carboxamide (4d): The reactants used were 2d (0.50 g, 2.79 mmol), KNCS (0.41 g, 4.22 mmol) and APS (0.52 g, 2.23 mmol), m.p. 135–137 °C. C₁₅H₂₃N₅O₄SSi (397.52): calcd. C 45.3, H 5.8, N 17.6, S 8.1; found C 45.5, H 5.5, N 17.2, S 8.2. IR (Neat): $\tilde{v} = 3223$ [v(N–H)], 3183 [v(N– H)], 1654 [v(C=O)], 1251 [v(C=S)], 1087 [v(Si–O)], 586 [v(N \rightarrow Si)] cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 0.30$ (m, 2 H, SiCH₂), 1.67 (m, 2 H, CCH₂C), 2.83 (t, *J* = 5.7 Hz, 6 H, NCH₂), 3.54 (m, 2 H, CH₂NH), 3.70 (t, *J* = 5.7 Hz, 6 H, OCH₂), 7.80 (d, *J* = 4.6 Hz, 1 H, H⁴), 8.15 (s, 1 H, H³), 8.30 (d, *J* = 4.7 Hz, 1 H, H²), 10.81 (s, 1 H, NH), 11.10 (s, 1 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 13.61$ (SiCH₂), 29.54 (CCH₂C), 50.78 (CH₂NH), 52.76 (NCH₂), 57.49 (OCH₂), 145.35 (C²), 146.25 (C⁴), 149.34 (C¹), 151.60 (C³), 163.56 (C=O), 179.48 (C= S) ppm. MS: *m/z* (%) = 398 (100) [M + H]⁺.

*N*²,*N*⁶-Bis[3-(silatranyl)propylcarbamothioyl]pyridine-2,6-dicarboxamide (4e): The reactants used were 2e (0.50 g, 2.08 mmol), KNCS (0.60 g, 6.19 mmol) and APS (0.77 g, 3.32 mmol), m.p. 140– 142 °C. $C_{27}H_{43}N_7O_8S_2Si_2$ (713.97): calcd. C 45.4, H 6.1, N 13.7, S 9.0; found C 45.1, H 6.3, N 13.4, S 9.2. IR (Neat): $\tilde{v} = 3256$ [v(N–H)], 3170 [v(N–H)], 1646 [v(C=O)], 1240 [v(C=S)], 1096 [v(Si–O)], 587 [v(N→Si)] cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): $\delta = 0.52$ (m, 4 H, SiCH₂), 1.76 (m, 4 H, CCH₂C), 2.81 (t, *J* = 5.7 Hz, 12 H, NCH₂), 3.49 (m, *J* = 7.3 Hz, 4 H, CH₂NH), 3.76 (t, *J* = 5.7 Hz, 12 H, OCH₂), 8.12 (t, *J* = 9.1 Hz, 1 H, H³), 8.30 (d, *J* = 7.9 Hz, 2 H, H^{2.4}), 10.53 (s, 2 H, NH), 10.71 (s, 2 H, NH) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): $\delta = 13.26$ (SiCH₂), 25.15 (CCH₂C), 49.24 (CH₂NH), 51.13 (NCH₂), 5.7.71 (OCH₂), 124.54 (C³), 138.64 (C^{2.4}), 149.33 (C^{1.5}), 163.50 (C=O), 180.83 (C=S) ppm. MS: *m/z* (%) = 791 (100) [M + 2K]⁺.

Fe₃O₄ Nanoparticles: The Fe₃O₄ magnetic nanoparticles were synthesized by following the coprecipitation method without the aid of any external stabilizer.^[44] In general, a mixture of FeCl₃•6H₂O (1.0 g, 3.70 mmol) and FeCl₂•4H₂O (0.367 g, 1.85 mmol) was dissolved in deionized water (30 mL) in a 100 mL round-bottomed flask under an inert atmosphere (Figure 11). The solution was stirred vigorously (ca. 10 min), and aqueous NH₃ solution (25 %, 15 mL) was added. Immediately, a black precipitate formed; the mixture was stirred for 1 h, and the precipitate was magnetically separated from the reaction vessel. Repeated washing (three times) with distilled water and ethanol led to the desired product.



Figure 11. Schematic representation of the functionalization of the magnetite silica surface with **4e**.

Silicified Magnetic (Fe₃O₄@SiO₂) Nanoparticles: The bare Fe₃O₄ nanoparticles are highly prone to oxidation and aggregation, which results in the deterioration of their magnetic character. Therefore, these particles were embedded into inert silica shells to provide superior magnetic benefits to the composite formed. The synthesis of Fe₃O₄@SiO₂ nanoparticles was established by following the modified Stöber method.^[45] Firstly, the Fe₃O₄ nanoparticles (0.5 g) were dispersed in ethanol (30 mL) by vigorous stirring for 15 min, and then aqueous NH₃ solution (25 %, 10 mL) was added to the mixture. Afterwards, TEOS (1.0 mL) was added, and the mixture was heated under reflux for 4 h. The precipitated Fe₃O₄@SiO₂ nanoparticles were separated magnetically, washed with ethanol and dried. The merit of this protocol is that the silica nanoparticles are prepared only in the presence of Fe₃O₄ nanoparticles so that the magnetic nanoparticles can be incorporated inside the silica shells during the synthesis process itself and the extra step of grafting can be eliminated.^[46]

Fe₃O₄@SiO₂-Silatrane Hybrid Nanoparticles (H-NPs): For the organic coverage of the Fe₃O₄@SiO₂ surface, the prepared Fe₃O₄@SiO₂ nanoparticles (200 mg) and 4e (300 mg) were suspended in anhydrous toluene (20 mL). The mixture was heated under reflux for 24 h. The resultant nanoparticles were isolated magnetically and washed with dichloromethane to remove excess or physically adsorbed silatrane. The final product was obtained after 4 h of drying. The justification behind the selection of 4e as the grafting precursor is that it is composed of two silatrane units in the periphery to hook the organic units onto two surfaces simultaneously (Figure 11) along with the best chelating system, as discussed previously. The steric hindrance between the binding source and the silica surfaces is relieved by the flexible intervening propyl chains present on both sides. This kind of functional tailoring results in the effective fastening of the chelating site by making it an integral part of the material. Such a protocol for the synthesis of organic-inorganic hybrid materials by the hydrolysis and condensation reactions of bridged organosilanes (RO)₃Si-R'-Si(OR)₃ has already been performed, and promising results such as better hydrothermal stabilities, large surface areas and ordered pore systems encouraged us to undertake the present work.[47]

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Keywords: Organic–inorganic hybrid composites · Nanoparticles · Core–shell structures · Sensors · Organosilatranes

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Organosilatranes

G. Singh,* S. Rani 1–13

Organosilatranes with Acylthiourea Derivatives – Metal-Ion Binding, Substituent-Dependent Sensitivity, and Prospects for the Fabrication of Magnetic Hybrids



Acylthiourea-tethered organosilatranes are synthesized by the coupling of carboxylic acids with (aminopropyl)silatrane through acyl isothiocyanates. These derivatives are probed for metal-ion sensing. One of the silatranes is further immobilized onto the surface of magnetic silica nanospheres, and the hybrid is characterized and tested for the adsorption of copper and lead ions.

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