Valdés, Aristides C.; Pina-Luis, Georgina; Rivero, Ignacio A.
Parallel Synthesis of Polystyrene Anchored Imine Sulfide Materials: Sorption and Metal Sensing Studies
Journal of the Mexican Chemical Society, vol. 51, núm. 2, 2007, pp. 87-95
Sociedad Química de México
Distrito Federal, México

Available in: http://www.redalyc.org/articulo.oa?id=47551208
Parallel Synthesis of Polystyrene Anchored Imine Sulfide Materials: Sorption and Metal Sensing Studies

Aristides C. Valdés, Georgina Pina-Luis, Ignacio A. Rivera*

Centro de Graduados e Investigación. Instituto Tecnológico de Tijuana. Apartado Postal 1166. 22000. Tijuana, Baja California México. E-mail: irivero@tec.tijuana.mx

Recibido el 15 de enero de 2007; aceptado el 10 de abril de 2007

Abstract: In the present work we report the synthesis of a combinatorial library of 30 phenyl-ethyl based N-derivatives [nitro, amines and imines] bound to PS-thiophenol resin. The five step reaction sequence was characterized by 1H NMR, MS and fluorescence spectroscopy of resin beads. The imines were screened for those that exhibited a large sorption capacity for Cu(II) and Pb(II) ions and those exhibiting a large fluorescence change upon the metal binding.

Keywords: Combinatorial library, solid phase, sensors, fluorescence.

Introduction

Recent progress in combinatorial chemistry has indeed provided an easy access to produce compounds which are screened, or tested, against biological targets as part of the drug discovery process. However, it is still a tough task to rationally design active recognition motifs having a proper receptor arrangement for metal ion binding and in the pursuit for new sensing candidates. In the field of combinatorial chemistry, solid phase organic synthesis (SPOS) is a rapidly growing research area [1-3]. The attractiveness of this technique lies in the possibility of conducting multistep reactions and to drive reactions to completion, which may increase the rate of investigations of new receptors and sorbent materials [1].

It is known that the selective interaction of transition and heavy metal cations may be achieved by chelating receptors. Ligands containing oxygen/sulfur and nitrogen donors have been of research interest because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate amine precursors and ring substituents [4]. The organic compounds known as imines, anils or Schiff’s bases have the azomethine group (>C=N-) in their structure and are of great interest in chemistry and medicine [5]. For example, bidentate ligands containing imine groups have been used as modulators of electronic and structural properties of transition metal centers [6]. Additionally, imines have been attracting much attention because of their wide variety of applications in the field of electronics, opto-electronics and photonics [7]. Schiff bases are one of the most versatile and thorough ligands for recovery and complexation of metal ions; however, only a few Schiff bases have been immobilized to solid supports and used for metal ion removal and/or sensing studies [8, 9]. Our research group has been exploring the feasibility of using combinatorial chemistry to incorporate binding motifs into solid supports in order to prepare sorbent and/or sensing materials for metal ions [10-12]. Our objective is now the formation of Schiff base type chelating ligands with S- and N-donor groups attached to a polystyrene resin and the introduction of specific functionalities at the periphery of the coordinating imine moiety that may rise to develop sorbent/sensing tailored materials for metal ions. As a proof of the principle, Cu(II) and Pb(II), were selected as metal ions of environmental concern.

We describe for the first time the synthesis of a combinatorial library of thio-ether imine derivatives bound to PS-thiophenol resin as potential attached receptors for Cu(II) and Pb(II) ions. The materials display a suitable combination of donor atoms for metal complexation/sorption and π-conjugated systems for optical transduction. Starting from o-, m- and p-hydroxybenzaldehydes, a library of ten nitrolefins (a-j) were condensed to the PS-thiophenol resin (Scheme 1), which was subsequently reduced to the amine group to get a new library. Screening of the library members for their metal binding response was performed using fluorescence spectral changes and atomic absorption spectroscopy was used to evaluate their sorption capacity. The role of the substituents in the sensing properties is outlined.

Results and Discussion

The first phase of our study centered on the generation of a combinatorial library created according to the synthetic route outlined in Scheme 1, in which the solid support was a PS-thiophenol resin while ten benzaldehyde derivatives and three different substituents (Table 1) were used to impart diversity/selectivity. For the ultimate application as sensors, an imine group was used to allow for metal interaction.
Seven hydroxybenzaldehydes were treated with methyl iodide or benzyl chloride in DMF in presence of K₂CO₃ to give the methyl and benzyl ethers 1a-g, (Scheme 1, Table 1). Then, all benzaldehydes were condensed with nitromethane in the presence of ammonium acetate to give the nitro-olefins (2a-j) in excellent yields. Michael addition of PS-thiophenol resin with a catalytic amount of N-isopropylcyclohexylamine to each nitro-olefin was performed to obtain the supported compounds 3a-j. This coupling reaction was simultaneously acting as a protective one and eventually, it was possible to remove the resin and recover the corresponding nitro-olefin. After exploring two methods for the nitro reduction, we found that the use of lithium aluminum hydride as the reducing agent (rt, THF) produced the desired amines 4a-j. For compounds 1i, 2i and 3i R₃ = -NO₂, so that during the reduction step this group also suffered the redox process to give 4i. The supported amines 4a-j were finally treated with benzaldehyde to give the imines 5a-j. Both amine groups in 4i reacted to form the imine (5i).

Spectral characteristics of the fluorescents materials

As a complementary tool to the analytical techniques used in the characterization of the different products in Scheme 1 (see Experimental Section), we have used an efficient and fast technique to monitor the synthesis progress and the chemical
changes on the solid phase. This approach is based in fluorescence measurements made directly on the solid phase [13]. In Figure 1, we can observe that immobilisation of 2i (–R3 = –NO2) onto the PS-resin to render 3i resulted in a red-shift of both the excitation and emission bands with a drastic decrease in the fluorescence intensity (Figure 1a). The nitrogen in nitro compounds is trigonally planar with electrons delocalized between the nitrogen and the two oxygen atoms in a 120° angle configuration. Although nitro groups are well known fluorescence quenchers due to both their electron inductively and mesomerically withdrawing properties [14, 15], the high fluorescence quantum yield of 2i may be the result of an intramolecular charge delocalization between the aromatic ring (the donor) and the electron accepting groups, the nitro bonded to the ring and that in the branch, thus extending the conjugation length of the chromophore (Figure 2). The nitro group is forced to be in-plane with the benzene moiety and the enhancement of the rigidity of the molecule favored the radiational deactivation of the lowest singlet excited state. In 3i the nitro-branch group may be twisted out of the conjugation chain, thus rendering the attached derivative noticeably less fluorescent than 2i (Figure 1b). Fluorescence is restored upon reduction of the nitro groups to the corresponding amino-group (electron donor), 4i. The high fluorescence quantum yield of 4i may be the result of the amine groups, in particular to that bonded to the ring, with the lone pair electrons occupying a π-orbital. This is antisymmetric to the plane of the ring and can conjugate with the π-orbitals of the latter so that only π*–π transitions are expected (Figure 2).

The fluorescence properties of the bound nitro-olefins (3a-3j) also depended on the nature of the remaining substituent as well as on their relative positions in the benzene ring. In fact, taking 3h as reference (–R1 = –R2 = –R3 = –H), electron withdrawing substituents (e.g., –NO2 and -F in 3i and 3j, respectively) caused a remarkable fluorescence quenching, while a marginal fluorescence increase was observed when the nitro-olefin bear a –OCH3 electron donor group in R3 position (3f) and an important fluorescence increase when the group –OCH3 was in R1 and R2 positions, simultaneously (3g, Figure 3). The presence of –OCH3 groups, either the position, resulted in a fluorescence quenching effect (3a-e). The directive effect of substituents in the benzene ring follows the sequence: benzyl³ methoxy>hydrogen. Based on this, one would expect the fluorescence intensity to follow the same trend. The low intensity of benzyl substituent could be explained by a preferred conformation where the two benzene rings are parallel to each other (Figure 4), suggesting a transfer of energy from one ring to another [16, 17].

On the other hand, there seems to be a correlation between the electron donating/acceptor properties of the substituents and the spectral characteristics of the derivatives. Taking 3h as reference (see Table 2), the large spectral red-shifting observed for 3i and 3j may be due to the influence of electron withdrawal groups in position R1 and R3 of the ring system while the large spectral blue-shifting observed for the 3g derivative could be explained by the presence of two donat-
ing groups in positions R2 and R3 (see Table 1). In Table 2, the influence of the nitro-reduction and the imine-reaction with introduction of the R4 substituent on the fluorescence intensities of the different library members is shown. We can observe that the general trend is followed: nitro-compounds are less fluorescent than the corresponding amine- or imine- compounds. In Table 2 the spectral characteristics of these materials are summarized.

### Binding properties towards Pb(II) and Cu(II) ions

In order to evaluate the binding properties of 3(a-j), 4(a-j) and 5(a-j) towards Pb(II) and Cu(II) ions, the array of materials was screened for its metal ion binding capacity by batch method, treating the above mentioned materials with the metal ions at room temperature and mild reaction conditions. The influence of pH on the sorption of Cu(II) and Pb(II) was studied by varying the pH of the mixture from 2 to 8, using buffer solutions. Typical sorption profiles for Cu(II) and Pb(II) by the 5g library member are shown in Figure 5. Maximum Cu(II) and Pb(II) uptake happened at pH 7.5-8. Similar trends were observed for the rest of the 5a-j library members. A pH 6 was selected in further experiments as a compromise between a relatively high retention and prevention of metal ion hydrolysis at elevated pHs. At pH 6, Cu(II) and Pb(II) sorption percentages by the 5a-j library members are gathered in Table 3. Focusing on these data, it appears that at pH 6, ca. 50% sorption of Pb(II) ions was achieved when using the 5g library member while lower values were observed with the remaining materials. In the case of Cu(II) ions sorption values around 50% were obtained with 5g and 5j being the uptake of Cu(II) ions higher than that of Pb(II) with most of the remaining 5a-i materials, thus indicating the higher affinity of Cu(II) ions by the chelating motif on the solid phases.

These results also suggest the important role of the aromatic ring substituents: the presence of -OCH3 groups in meta- and para- positions seemed to favor the interaction between the metal ions and the binding positions (S and N atoms, Scheme 1) while the presence of bulky groups (e.g. -OCH2Φ) seemed to restrict the accessibility of the metal ions to the -S- and -N- binding sites.

### Sensing properties towards Pb(II) and Cu(II) ions

Cu(II) and Pb(II) binding to 5a-j materials was studied as a function of their fluorescence quenching/enhancement efficiency. These materials were contacted for 12h with the corresponding metal solution at pH 6, after which the solids were removed, packed into a conventional flow cell and the fluorescence spectra recorded. Fluorescence intensity and spectral characteristics of raw 5a-j imines after their interaction with

### Table 2. Spectral characteristics of 3a-j, 4a-j and 5a-j libraries

<table>
<thead>
<tr>
<th>Compounds</th>
<th>3 (-NO2)</th>
<th>4 (-NH2)</th>
<th>5 (-N=C-Ph)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λem</td>
<td>I_f</td>
<td>λem</td>
</tr>
<tr>
<td>a</td>
<td>530</td>
<td>266</td>
<td>540</td>
</tr>
<tr>
<td>b</td>
<td>530</td>
<td>144</td>
<td>540</td>
</tr>
<tr>
<td>c</td>
<td>530</td>
<td>246</td>
<td>520</td>
</tr>
<tr>
<td>d</td>
<td>530</td>
<td>175</td>
<td>555</td>
</tr>
<tr>
<td>e</td>
<td>530</td>
<td>218</td>
<td>555</td>
</tr>
<tr>
<td>f</td>
<td>561</td>
<td>390</td>
<td>555</td>
</tr>
<tr>
<td>g</td>
<td>460</td>
<td>615</td>
<td>535</td>
</tr>
<tr>
<td>h</td>
<td>555</td>
<td>330</td>
<td>544</td>
</tr>
<tr>
<td>i</td>
<td>650</td>
<td>61</td>
<td>555</td>
</tr>
<tr>
<td>j</td>
<td>650</td>
<td>54</td>
<td>535</td>
</tr>
</tbody>
</table>

Fig. 4. Quenching by energy transfer between aromatic rings in 3a-e library members.

Fig. 5. pH influence on the Cu(II) and Pb(II) uptake using 5g as sorbent.
Cu(II) and Pb(II) are illustrated in Figure 6 and Table 4. As expected, the fluorescence of all materials was quenched by both metal ions, indicating a typical behavior of paramagnetic and heavy metals, respectively. The quenching of the fluorescence by paramagnetic metal ions, such as Cu(II) having unpaired d-electrons (d^9), is a well-known phenomenon. Quenching by Cu(II) ions may be explained by electron transfer and/or energy transfer to low-lying metal centred excited states might well account for explaining the efficient quenching of the singlet excited state of luminophors in materials. On the other hand, fluorescence quenching by closed-shell heavy metal ions, such as Pb(II), have been explained by non-fluorescent complex formation followed by rapid intersystem crossing. However, the quenching rates are, in these cases, much lower compared to those of paramagnetic metal ions, which evidences the efficient quenching of imines by Cu(II) compared to lower quenching by Pb(II) ions (see Figure 6).

Table 3. Pb(II) and Cu(II) sorption by 5a-j library. pH 6.

<table>
<thead>
<tr>
<th>Library member</th>
<th>% Sorption Pb(II)</th>
<th>Standard Deviation (σ)*</th>
<th>% Sorption Cu(II)</th>
<th>Standard Deviation (σ)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>32.0</td>
<td>0.14</td>
<td>39.0</td>
<td>0.05</td>
</tr>
<tr>
<td>b</td>
<td>30.4</td>
<td>0.10</td>
<td>38.2</td>
<td>0.03</td>
</tr>
<tr>
<td>c</td>
<td>30.8</td>
<td>0.08</td>
<td>40.1</td>
<td>0.05</td>
</tr>
<tr>
<td>d</td>
<td>36.2</td>
<td>0.10</td>
<td>44.3</td>
<td>0.06</td>
</tr>
<tr>
<td>e</td>
<td>30.4</td>
<td>0.11</td>
<td>36.8</td>
<td>0.05</td>
</tr>
<tr>
<td>f</td>
<td>16.0</td>
<td>0.03</td>
<td>26.0</td>
<td>0.06</td>
</tr>
<tr>
<td>g</td>
<td><strong>50.4</strong></td>
<td><strong>0.21</strong></td>
<td><strong>50.1</strong></td>
<td><strong>0.10</strong></td>
</tr>
<tr>
<td>h</td>
<td>28.8</td>
<td>0.05</td>
<td>35.2</td>
<td>0.05</td>
</tr>
<tr>
<td>i</td>
<td>32.0</td>
<td>0.13</td>
<td>40.5</td>
<td>0.06</td>
</tr>
<tr>
<td>j</td>
<td>29.3</td>
<td>0.09</td>
<td><strong>53.5</strong></td>
<td><strong>0.10</strong></td>
</tr>
</tbody>
</table>

Table 4. Spectral characteristics of 5a-j library after reaction with Cu(II) and Pb(II). pH=6, 12 h, ultrasonic.

<table>
<thead>
<tr>
<th>Material</th>
<th>λ_em</th>
<th>If</th>
<th>λ_em</th>
<th>If</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>535</td>
<td>22</td>
<td>530</td>
<td>42</td>
</tr>
<tr>
<td>b</td>
<td>535</td>
<td>30</td>
<td>535</td>
<td>54</td>
</tr>
<tr>
<td>c</td>
<td>535</td>
<td>24</td>
<td>525</td>
<td>84</td>
</tr>
<tr>
<td>d</td>
<td>555</td>
<td>0</td>
<td>555</td>
<td>0</td>
</tr>
<tr>
<td>e</td>
<td>555</td>
<td>0</td>
<td>560</td>
<td>0</td>
</tr>
<tr>
<td>f</td>
<td>560</td>
<td>0</td>
<td>560</td>
<td>0</td>
</tr>
<tr>
<td>g</td>
<td>560</td>
<td>0</td>
<td>560</td>
<td>0</td>
</tr>
<tr>
<td>h</td>
<td>560</td>
<td>16</td>
<td>534</td>
<td>33</td>
</tr>
<tr>
<td>i</td>
<td>515</td>
<td>40</td>
<td>520</td>
<td>75</td>
</tr>
</tbody>
</table>

Fig. 6. Fluorescence intensity of raw 5a-j imines after their interaction with Pb(II) and Cu(II) ions.

Conclusions

Concluding, phenyl ethyl amines receptors bound to PS-thiophenol resins were synthesized. The fluorescence spectra of intermediates and products provided evidence for the progress of the ongoing structural changes, demonstrating the efficacy of the direct fluorescence measures on solid phase. The study of analytical potential of these materials reveals that resins of imine type (5i, 5j) present the best properties. The presence of –OCH_3 groups in meta- and para- positions seem to favor the interaction between the metal ions and the binding positions (S and N atoms) while the presence of bulky groups (e.g. –OCH_3Φ) or competing binding groups (e.g.–NH_2) seem to restrict the accessibility of the metal ions to the –S– and –N– binding sites. Although our work solely describes measurements of copper and lead, application for immobilization and analysis of other metal ions can be envisaged. The results presented in this paper will undoubtedly form the foundations for future approaches capable of monitoring transition metal ions in real-time and real-space.
Experimental

Materials

The PS-thiophenol (1.54 mmol/g) resins were purchased from Argonaut. All other reagents, if not specified, were purchased from Aldrich. All other chemicals, buffers and solvents were of analytical reagent grade and were used without further purification. All aqueous solutions were prepared using deionized water. Standard solutions of Cu(II) and Pb(II) at different concentrations were prepared in the buffer solution.

Instrumentation

All fluorescence intensity measurements were made with a Shimadzu RF-5301 PC spectrometer which has a xenon discharge excitation source (pulse width at peak half-height < 10 μs). The 3 nm slit width for both excitation and emission intensities were used. Instrumental parameters and processing data are controlled by the Fluorescence Data manager software. A Hellma Model 176.52 flow cell (25 μL) was used. Beads were washed free of any starting materials and solvents and were packed into the flow-through cell. Measures of fluorescence intensity were obtained directly from the resin beads. pH measurements were obtained directly from the resin beads.

General procedure for protection of phenol groups

To a solution of 2, 3 or 4-hydroxybenzaldehyde (5.0 g, 40 mmol), K₂CO₃ (6.8 g, 49.3 mmol) in dry DMF (20 mL), benzyl bromide (5.26 mL, 44 mmol) were added. The mixture was stirred for 3 h at RT after which the reaction mixture was quenched with water (50 mL). The organic phase was extracted with CH₂Cl₂ (3 × 20 mL) and dried over anhydrous sodium sulfate. The clear solution was concentrated under low pressure to give the solids 1a-j.

4-Benzoxyl-benzaldehyde (1a): (Yield, 74.2%). Mp 71-74 °C. IR (KBr): 3024 (C-H), 2929 (C-H), 2833 (C-H), 1682 (C=O), 1595 (C=C), 1268,1024 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.78 (s, 1H, CHO), 7.40-7.33 (m, 8H, Ar-H), 7.05 (d, J = 8.8 Hz, 2H, Ar-H), 7.05 (d, J = 8.8 Hz, 2H, Ar-H), 5.12 (s, 2H, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 190.8, 190.3, 154.6, 148.3, 135.9, 129.6, 128.3, 128.2, 127.8, 127.6, 127.2, 127.2, 125.0, 120.9, 113.0, 70.6. EIMS m/z [M⁺] 242 (11), 91 (100).

3-Benzoxyl-benzaldehyde (1b): (Yield, 78.1%). Mp 57-60 °C. IR (KBr): 3101, 3036 (C=C-H), 2926, 2858 (C-H), 1680 (C=O), 1592 (C=C), 1266, 1024 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.78 (s, 1H, CHO), 7.46-6.91 (m, 8H, Ar-H), 5.12 (s, 2H, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 192.0, 159.3, 137.8, 136.3, 128.7, 128.5, 128.2, 127.5, 123.7, 122.2, 113.2, 70.2. EIMS m/z [M⁺] 212 (9), 91 (100).

2-Benzoxyl-benzaldehyde (1c): (Yield, 75.2%). Mp 61-64 °C. IR (KBr): 3070, 3025 (C-H), 2926, 2760 (C-H), 1690 (C=O), 1598 (C=C), 1240, 1015 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.85 (s, 1H, CHO), 7.40-7.35 (m, 5H, Ar-H), 7.05 (d, J = 8.8 Hz, 2H, H₂, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 190.8, 163.1, 136.0, 131.9, 130.7, 128.7, 128.3, 127.5, 115.1, 70.2. EIMS m/z [M⁺] 212 (7), 91 (100).

2-Benzoxyl-4-methoxy-benzaldehyde (1d): (Yield, 73.9%). Mp 59-62 °C. IR (KBr): 3101, 3036 (C=C-H), 2926, 2858 (C-H), 1680 (C=O), 1587 (C=C), 1266, 1015 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.78 (s, 1H, CHO), 7.46-6.91 (m, 8H, Ar-H), 5.12 (s, 2H, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 189.6, 161.0, 136.0, 135.9, 128.7, 128.3, 128.2, 127.7, 127.6, 127.2, 125.0, 120.9, 113.0, 70.3. EIMS m/z [M⁺] 212 (9), 91 (100).

3-Benzoxyl-4-methoxy-benzaldehyde (1e): (Yield, 76.0%). Mp 61-64 °C. IR (KBr): 3070, 3025 (C=C-H), 2833 (C=O), 2730 (C=O), 1682 (C=O), 1587 (C=C), 1266, 1015 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.78 (s, 1H, CHO), 7.46-6.91 (m, 8H, Ar-H), 5.12 (s, 2H, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 190.3, 154.6, 148.3, 135.9, 129.6, 128.3, 128.7, 126.6, 111.1, 110.5, 70.6, 56.0. EIMS m/z [M⁺] 242 (11), 91 (100).

4-Benzoxyl-3-methoxy-benzaldehyde (1f): (Yield, 72.0%). Mp 62-65 °C. IR (KBr): 3063 (C=C-H ), 3030 (C=C-H ), 2936 (C=H), 2865 (OC-H), 2740 (OC-H), 1680 (C=O), 1586 (C=C), 1268, 1025 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.78 (s, 1H, CHO), 7.40-7.33 (m, 8H, Ar-H), 5.12 (s, 2H, O-CH₂). ¹³C NMR (50 MHz, CDCl₃): δ 190.8, 153.5, 149.9, 130.2, 128.6, 128.3, 128.1, 127.2, 126.5, 112.3, 109.3, 70.7, 55.9. EIMS m/z [M⁺] 242 (14), 91 (100).

General procedure for derivatives of (E)-1-(2-nitrovinyl)benzene

To a solution of benzaldehyde (2.5 g, 23.6 mmol) in acetic acid (15 mL), ammonium acetate (1.9 g, 24.6 mmol) and water. A Hellma Model 176.52 flow cell (25 μL) was used. Beads were washed free of any starting materials and solvents and were packed into the flow-through cell. Measures of fluorescence intensity were obtained directly from the resin beads. pH measurements were obtained directly from the resin beads.

General procedure for protection of phenol groups

To a solution of 2, 3 or 4-hydroxybenzaldehyde (5.0 g, 40 mmol), K₂CO₃ (6.8 g, 49.3 mmol) in dry DMF (20 mL), benzyl bromide (5.26 mL, 44 mmol) were added. The mixture was stirred for 3 h at RT after which the reaction mixture was quenched with water (50 mL). The organic phase was extracted with CH₂Cl₂ (3 × 20 mL) and dried over anhydrous sodium sulfate. The clear solution was concentrated under low pressure to give the solids 1a-j. The crude products were chromatographed through silica-gel with ethyl acetate and ethyl ether (1:1) to get pure solids.

4-Benzoxyl-benzaldehyde (1a): (Yield, 74.2%). Mp 71-74 °C. IR (KBr): 3024 (C-H), 2828, 2743 (C-H), 1687 (C=O), 1600 (C=C), 1259, 1018 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 9.85 (s, 1H, CHO), 7.81(d, J = 8.8 Hz, 2H, Ar-H₂, Ar-H₃).
Parallel Synthesis of Polystyrene Anchored Imine Sulfide Materials

**3.4-dimethoxy-β-nitro styrene (2g):** (Yield, 69.3%). Mp 140-144 °C. IR (KBrs): 3126, 3044, 3003 (C=H); 2948, 2839 (C-H); 1626, 1595 (C=C); 1514, 1340 (C-NO2); 1269, 1017 (C-NO2) cm⁻¹. ³¹P NMR (200 MHz, CDCl3): δ 7.98 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.50 (s, 2H, Ar-H); 7.40 (dd, J = 8.8, 2.2 Hz, 1H, H); 7.02 (d, J = 8.4 Hz, 1H, H); 6.93 (s, 4H, OCH3). ¹³C NMR (50 MHz, CDCl3): δ 152.3, 149.6, 139.3, 135.1, 124.6, 122.8, 111.4, 110.3, 56.1, 56.0. EIMS m/z [M⁺] 209 (100).

**β-nitrostyrene (2h):** (Yield, 74.0%). Mp 55-58 °C. IR (KBrs): 3106, 3035 (C=H); 2964, 1627, 1602 (C=C); 1514, 1340 (C-NO2) cm⁻¹. ¹¹B NMR (200 MHz, CDCl3): δ 8.28 (d, J = 8.8 Hz, 2H, H); 8.18 (s, 2H, CH=CH-NO2); 8.03 (d, J = 8.8 Hz, 2H, H). ¹³C NMR (50 MHz, CDCl3): δ 148.9, 140.7, 136.6, 136.6, 130.5. EIMS m/z [M⁺] 194 (100).

**3-benzyloxy-4-methoxy-β-nitrostyrene (2d):** (Yield, 76.1%). Mp 128-132 °C. IR (KBrs): 3106, 3021 (C=H); 2936, 2886 (C-H); 1624, 1595 (C=C); 1510, 1333 (C-NO2); 1265, 1003 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl3): δ 7.90 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.43 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.44-7.31 (m, 5H, Ar-H); 7.19 (dd, J = 8.4, 1.6 Hz, 1H, H); 7.03 (d, J = 1.6 Hz, 1H, H); 6.92 (d, J = 8.4 Hz, 1H, H); 5.07 (s, 2H, OCH3); 3.07 (s, 3H, OCH3). ¹³C NMR (50 MHz, CDCl3): δ 153.8, 148.6, 139.3, 136.3, 135.1, 132.8, 128.6, 128.3, 127.3, 124.9, 122.7, 113.2, 111.8, 72.1, 56.1. EIMS m/z [M⁺] 285 (6), 91 (100).

**4-benzyloxy-3-methoxy-β-nitrostyrene (2e):** (Yield, 71.6%). Mp 122-125 °C. IR (KBrs): 3106, 3039, 3000 (C=C); 2934, 2872 (C-H); 1631, 1595 (C=C); 1510, 1333 (C-NO2); 1262, 1028 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl3): δ 6.794 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.51 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.45-7.35 (m, 5H, Ar-H); 7.00 (dd, J = 8.2, 2.2 Hz, 1H, H); 6.91 (d, J = 8.6 Hz, 1H, H); 5.21 (s, 2H, OCH3); 3.92 (s, 3H, OCH3). ¹³C NMR (50 MHz, CDCl3): δ 151.9, 150.0, 139.3, 136.1, 135.2, 128.7, 128.2, 127.2, 124.4, 123.1, 113.4, 110.8, 70.9, 56.1. EIMS m/z [M⁺] 285 (8), 91 (100).

**4-methoxy-β-nitrostyrene (2f):** (Yield, 37.9%). Mp 85-88 °C. IR (KBrs): 3112 (C=C); 2941, 2901, 2839 (C-H); 1622, 1602 (C=C); 1514, 1327 (C-NO2); 1252, 1031 (C-O-C) cm⁻¹. ¹H NMR (200 MHz, CDCl3): δ 7.97 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.51 (d, J = 13.6 Hz, 1H, CH=CH-NO2); 7.45 (d, J = 9.0 Hz, 2H, H); 6.95 (d, J = 9.0 Hz, 2H, Ar-H). ¹³C NMR (50 MHz, CDCl3): δ 163.0, 139.1, 135.0, 131.2, 122.6, 114.9, 55.5. EIMS m/z [M⁺] 179 (53), 132 (100).
General procedure for coupling of nitroolefins to solid phase (3a-j)

The PS-thiophenol resin (200 mg, 0.274 mmol) was swollen in CH₂Cl₂ (15 mL) and the nitro-olefins (0.548 mmol) and 4 drops of isopropylcyclohexylamine were added. The mixture was stirred at RT for 30 min. The resins were filtered and washed with CH₂Cl₂ (5 mL), H₂O (5 mL), MeOH (5 mL) and CH₂Cl₂ (5 mL). The solids were dried under reduced pressure. The MS data were obtained to follow the general method to liberate the products (nitroolefins).

**PS-(1-(4-(benzoxyl)phenyl)-2-nitroethyl)-sulfane (3a):**
(Yield, 95%). IR (KBr): 3417 (N-H), 3051, 3021 (C=C-H); 2920, 2870 (C-H); 1670 (N-C=O), 1607, (C=C); 1558, 1373 (NO₂); 1247, 1020 (C-O-C) cm⁻¹. Fl 266 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 255 (9), 110 (100).

**PS-(1-(3-benzoxyphenyl)-2-nitroethyl)-sulfane (3b):**
(Yield, 96%). IR (KBr): 3417 (N-H), 3051, 3023 (C=C-H); 2920, 2870 (C-H); 1671 (N-C=O), 1598, (C=C); 1551, 1365 (NO₂); 1265, 1021 (C-O-C) cm⁻¹. Fl 140 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 255 (9), 110 (100).

**PS-(1-(2-benzoxyphenyl)-2-nitroethyl)-sulfane (3c):**
(Yield, 95%). IR (KBr): 3408 (N-H), 3051, 3023 (C=C-H); 2910, 2845 (C-H); 1659 (N-C=O), 1593, (C=C); 1547, 1369 (NO₂); 1229, 1014 (C-O-C) cm⁻¹. Fl 246 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 255 (4), 118 (26), 91 (100).

**PS-(1-(3-benzoxy)-4-metoxophenyl)-2-nitroethyl)-sulfane (3d):**
(Yield, 96%). IR (KBr): 3408 (N-H), 3056, 3032 (C=C-H); 2920, 2850 (C-H); 1668 (N-C=O), 1603, (C=C); 1555, 1365 (NO₂); 1257, 1019 (C-O-C) cm⁻¹. Fl 175 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 285 (6), 91 (100).

**PS-(1-(4-benzoxy)-3-metoxophenyl)-2-nitroethyl)-sulfane (3e):**
(Yield, 96%). IR (KBr): 3412 (N-H), 3055, 3009 (C=C-H); 2917, 2844 (C-H); 1674 (N-C=O), 1600, (C=C); 1555, 1371 (NO₂); 1261, 1018 (C-O-C) cm⁻¹. Fl 178 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 285 (8), 91 (100).

**PS-(1-(3,4-dimetoxophenyl)-2-nitroethyl)-sulfane (3f):**
(Yield, 92%). IR (KBr): 3420 (N-H), 3057, 3013 (C=C-H); 2922, 2845 (C-H); 1678 (N-C=O), 1595, (C=C); 1559, 1355 (NO₂); 1260, 1018 (C-O-C) cm⁻¹. Fl 615 au, Eₚₑₜ = 460 nm, (Eₚₑₜ=395 nm). EIMS m/z [M⁺] 209 (100).

**PS-(1-(2-fluorophenyl)-2-nitroethyl)-sulfane (3g):**
(Yield, 96%). IR (KBr): 3418 (N-H), 3057, 3022 (C=C-H); 2925, 2845 (C-H); 1674 (N-C=O), 1602, (C=C); 1555, 1366 (NO₂); cm⁻¹. Fl 54 au, Eₚₑₜ = 625 nm, (Eₚₑₜ=550 nm). EIMS m/z [M⁺] 167 (11), 91 (100).

**PS-(1-(4-(metoxophenyl)-2-nitroethyl)-sulfane (3h):**
(Yield, 90%). IR (KBr): 3419 (N-H), 3047, 3024 (C=C-H); 2921, 2901 (C-H); 1683 (N-C=O), 1610, (C=C); 1560, 1370 (NO₂); 1254, 1028 (C-O-C) cm⁻¹. Fl 390 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 179 (53), 132 (100).

**PS-(1-(phenyl)-2-nitroethyl)-sulfane (3i):**
(Yield, 94%). IR (KBr): 3411 (N-H), 3047, 3021 (C=C-H); 2909, 2848 (C-H); 1671 (N-C=O), 1602, (C=C); 1552, 1359 (NO₂); 1269, 1017 (C-O-C) cm⁻¹. Fl 330 au, Eₚₑₜ = 530 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 149 (46), 77 (100).

**PS-(1-(4-(nitrophenyl))-2-nitroethyl)-sulfane (3j):**
(Yield, 95 %). IR (KBr): 3409 (N-H), 3112, 3022 (C=C-H); 2916, 2845 (C-H); 1678 (N-C=O), 1599, (C=C); 1559, 1339 (NO₂); cm⁻¹. Fl 61 au, Eₚₑₜ = 650 nm, (Eₚₑₜ=465 nm). EIMS m/z [M⁺] 194 (M⁺), 100 (100).

General Methods for reduction of nitro group

**Method A (LiAlH₄)**

The supported nitrolefins 5a-j (200 mg, 0.274 mmol) were swollen during 15 minutes in dried THF (15 mL) and cooled to 3 °C. A solution of LiAlH₄ (1 mL, 1 mol/L) in diethyl ether was then added. The mixture was filtered and another 1 mL of LiAlH₄ was added and kept for 24 h at RT. The resins were filtered and washed with THF (3 × 25 mL), THF:HCl (10%) in proportion 9:1 (3 × 25 mL), THF:TEA 9:1 (3 × 25 mL) and disopropylamine (3 × 10 mL). Finally, the solids were dried under reduced pressure.

**Method B (Zn/HCl)**

The supported nitrolefins 5a-j (200 mg, 0.274 mmol) were swollen during 15 min in CH₂Cl₂ (15 mL) and AcOH (2 mL) and powder Zn (141 mg, 2.15 mmol) were added. Then, concentrated HCl (2 mL) was added dropwise and the solution was stirred overnight at RT. The resin was filtered and washed with THF (3 × 25 mL), MeOH (3 × 25 mL) and CH₂Cl₂ (3 × 25 mL). The solids were dried under reduced pressure. The resulting reduction materials were used for the next step.

Synthesis of Imines:

The supported amines 6a-j (200 mg, 0.24 mmol) were swollen during 15 min in THF:DMSO 4:1 (15 mL) and benzaldehyde (127 mg, 1.2 mmol) and sodium sulfate anhydrous (1.0 g, 7 mmol) was added. The solution was stirred overnight at RT. The resins were filtered and washed with CH₂Cl₂ (3 × 25 mL), H₂O (3 × 25 mL), MeOH (3 × 25 mL) and CH₂Cl₂ (3 × 25 mL). The solids were dried under reduced pressure.

7a: (Yield 92%). IR (KBr): 3419 (N-H), 3056, 3021 (C=C-H); 2920, 2870 (C-H); 1681 (C=N), 1654 (N-C=O), 1600, (C=C); 1247 (C-O-C) cm⁻¹. Fl 580 au, Eₚₑₜ = 540 nm, (Eₚₑₜ=465 nm).
Parallel Synthesis of Polystyrene Anchored Imine Sulfide Materials

7b: (Yield 90%). IR (KBr): 3417 (N-H), 3054, 3023 (C=C-H); 2922, 2866 (C-H); 1681 (C=N), 1658 (N=C=O), 1598, (C=C); 1265 (C-O-C) cm⁻¹. FI 480 au, $E_{\text{em}}$=540 nm, ($E_{\text{ex}}$=465 nm).

7c: (Yield 89%). IR (KBr): 3418 (N-H), 3051, 3023 (C=C-H); 2920, 2845 (C-H); 1685 (C=N), 1659 (N=C=O), 1593, (C=C); 1229 (C-O-C) cm⁻¹. FI 445 au, $E_{\text{em}}$=525 nm, ($E_{\text{ex}}$=465 nm).

7d: (Yield 90%). IR (KBr): 3418 (N-H), 3056, 3022 (C=C-H); 2921, 2850 (C-H); 1682 (C=N), 1655 (N=C=O), 1603, (C=C); 1257 (C-O-C) cm⁻¹. FI 161 au, $E_{\text{em}}$=560 nm, ($E_{\text{ex}}$=465 nm).

7e: (Yield 90%). IR (KBr): 3417 (N-H), 3055, 3019 (C=C-H); 2920, 2845 (C-H); 1250 (C-O-C) cm⁻¹. FI 246 au, $E_{\text{em}}$=560 nm, ($E_{\text{ex}}$=465 nm).

7f: (Yield 92%). IR (KBr): 3419 (N-H), 3054, 3020 (C=C-H); 2921, 2846 (C-H); 1683 (C=N), 1653 (N=C=O), 1610, (C=C); 1250 (C-O-C) cm⁻¹. FI 246 au, $E_{\text{em}}$=560 nm, ($E_{\text{ex}}$=465 nm).

7g: (Yield 94%). IR (KBr): 3420 (N-H), 3057, 3017 (C=C-H); 2920, 2845 (C-H); 1681 (C=N), 1658 (N=C=O), 1598, (C=C); 1250 (C-O-C) cm⁻¹. FI 440 au, $E_{\text{em}}$=515 nm, ($E_{\text{ex}}$=465 nm).

7h: (Yield 88%). IR (KBr): 3417 (N-H), 3057, 3023 (C=C-H); 2920, 2848 (C-H); 1681 (C=N), 1656 (N=C=O), 1599, (C=C) cm⁻¹. FI 245 au, $E_{\text{em}}$=545 nm, ($E_{\text{ex}}$=465 nm).

7i: (Yield 90%). IR (KBr): 3420 (N-H), 3122, 3022 (C=C-H); 2916 (C-H); 1680 (C=N), 1658 (N=C=O), 1599, (C=C) cm⁻¹. FI 20 au, $E_{\text{em}}$=560 nm, ($E_{\text{ex}}$=465 nm).

7j: (Yield 89%). IR (KBr): 3418 (N-H), 3057, 3022 (C=C-H); 2922, 2845 (C-H); 1680 (C=N), 1654 (N=C=O), 1600 (C=C) cm⁻¹. FI 580 au, $E_{\text{em}}$=376 nm, ($E_{\text{ex}}$=465 nm).

General Method for liberate the products from the resin:

The supported sulfanes 3a-j (200 mg), were swollen during 15 min in THF:H₂O 4:1 (5 mL) and then a solution of potassium periodate (280 mg, 1.23 mmol) in water (1 mL) was added. The mixtures were refluxed for 18 h. The residues were filtered and washed with THF (3 × 25 mL), H₂O (3 × 25 mL), MeOH (3 × 25 mL) and CH₂Cl₂ (3 × 25 mL). Dry toluene and sodium carbonate (1.5 g, 14 mmol) was added the solids and the mixtures were refluxed over night. The mixtures were filtered and washed with CH₂Cl₂ (3 × 5 mL). The aliquots were combined and the excess of solvent was eliminated under reduced pressure to get the products. The crude were redissolved in methanol (1 mL) and analyzed by EIMS.

General Method for evaluate sorption percentage:

50 mg of the corresponding material were incubated with the different metal stock solutions (10 mL, 25 mg L⁻¹) at different pHs. The reaction mixture was subjected to ultrasonic shaking for 12 h after which the concentration of copper and lead in the supernatant was determined by atomic absorption spectroscopy.

Acknowledgments

The authors gratefully acknowledge support from Consejo Nacional de Ciencia y Tecnología, México, (CONACYT, Grant No. SEP-204-CO1-47835), Dirección General de Educación Superior Tecnológica, México (DGEST, 2007), A. C. Valdes thanks COSNET and Instituto de Materiales y Reactivos de la Universidad de la Habana, Cuba, for their support and Dra Marta Elena Díaz García for technical assistance.

References

16. Chem3D ULTRA Chem3D 9.0 CambridgeSoft, 100 CambridgePark Drive, Cambridge, MA 02140 USA.
17. Gaussian 03, Gaussian, Inc. 340 Quinnipiac St Bldg 40 Wallingford, CT 06492 USA.