

Review

A Review on The Development of Lutetium Selective Ion Sensors

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Abstract- Given the importance of developing cost and time saving tools, techniques and procedures for analyzing of lanthanide ions in various media, development and use of ion selective sensors for these ions is important. In this light, studying the various ion selective electrodes developed for a specific target species can create insight about the factors creating selectivity in these devices. Therefore, a review is made on the ion selective sensors prepared for lutetium over the past years. The authors have tried to provide detailed information on the composition and function of each sensor to provide better understanding for further research on the construction, as well as, the mechanism of action of these devices.

Keywords- Lutetium; Ionophore; Ion selective electrode; Potentiometric sensor

1. INTRODUCTION

As a rare-earth element lutetium has applications in various devices including color TVs, various fluorescent and energy-saving light sources, glass formulations, and optical fibers [1]. Lu(III) texaphyrin is used in photodynamic therapy and photoangioplasty as a photosensitizer

[2]. Lutetium is also used in catalyst formulations and glass polish, which increase the chances of the appearance of relatively high concentrations of the element in soil and water, and subsequently in human and animal bodies, which can bioaccumulate and damage the liver [1]. In the case of waterborne animals, Lu has been found to induce cell membrane damage, negatively affecting reproductive and nervous system functions [3].

The increased industrial applications and the subsequent emissions of Lu compounds have increased the need for the trace analysis of Lu(III) compounds in different media. The most common techniques used for the low-level analysis of Lu(III) compounds include ICP-MS [4,5], ICP-AES [6], spectrophotometry [7,8], and X-ray fluorescence spectrometry [9], which are time and energy intensive approaches, requiring multiple samples handling steps. Various recent studies, on the other hand, have focused on the synthesis of selective ion carriers for various use in ion-selective sensors [10]. and various ionophores have been designed and successfully used in selective electrodes for lanthanide ions like Yb^{3+} , Gd^{3+} , La^{3+} , Eu^{3+} , Dy^{3+} , Tb^{3+} , Pr^{3+} , Sm^{3+} , and some other metal ions [11–34]. Since the first report on a Lu^{3+} sensor, using an asymmetric S–N Schiff's base, was published in 2006 [35], there has been a range of reports on the application of selective sensors for analyzing this rare earth element and the present review tends to provide an overview on design and application of different ionophore for use in the electrochemical analysis of this species.

2. LUTETIUM SELECTIVE ION SENSORS

The first report on the development of a lutetium sensor, as mentioned before, can be traced back to the work of Ganjali et al who used *N*-(thien-2-ylmethylene)pyridine-2,6-diamine (Figure 1) in a liquid membrane sensor further composed of poly(vinyl chloride) (PVC), *o*-nitrophenyloctyl ether (NPOE) and sodium tetraphenyl borate and found the sensor to show proper selective response Lu^{3+} ions [35]. The electrode had a calibration plot with a slope of 20.5 ± 0.4 mV/ decade of concentration in a Lu^{3+} ion from 1.0×10^{-6} and 1.0×10^{-2} M and its detection limit was 8.0×10^{-7} M in the case of the optimal membrane concentration of 32% PVC, 58% of NPOE, 4% of sodium tetraphenyl borate and 6% of the ligand.

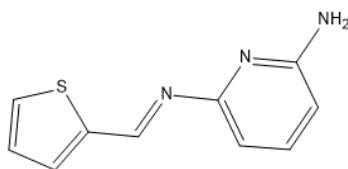


Figure 1. *N*-(thien-2-ylmethylene)pyridine-2,6-diamine

The optimal membrane revealed good selectivity for lutetium ion in the presence of interfering ions like Na^+ : 3.2×10^{-4} , K^+ : 6.3×10^{-4} , Ca^{2+} : 1.6×10^{-4} ; Mg^{2+} : 2.5×10^{-3} ; Pb^{2+} : 7.9×10^{-4} ;

Cu^{2+} 2.5×10^{-3} , La^{3+} 7.9×10^{-4} , Pr^{3+} 1.0×10^{-3} ; Nd^{3+} 2.0×10^{-2} ; Sm^{3+} 2.5×10^{-4} ; Gd^{3+} : 6.3×10^{-3} , Dy^{3+} : 8.0×10^{-3} , Ho^{3+} ; 4.5×10^{-3} , Er^{3+} ; 7.9×10^{-4} , Tm^{3+} ; 6.2×10^{-4} , Yb^{3+} ; 5.3×10^{-3} .

Almost at the same time M.R. Ganjali et al., used a very similar ion carrier namely N-(2-furylmethylene) pyridine-2,6-diamine to construct a selective microelectrode for Lu^{3+} ions [36]. The optimal membrane composition further contained 32% wt. of PVC, 60% wt. of NPOE, and 4% wt. of potassium tetrakis (p-chlorophenyl) borate (KTPCIPB). The developed sensor had an almost identical Nernstian behavior (of 20.5 ± 0.2 mV/decade of concentration), in comparison with the former electrode, yet its response was rather narrower but extended in a far lower concentration range of 1.0×10^{-11} to 1.0×10^{-6} M and a very low limit of detection (LOD) of 3.0×10^{-11} M was achieved, which was attributed to the small dimensions of the developed electrode.

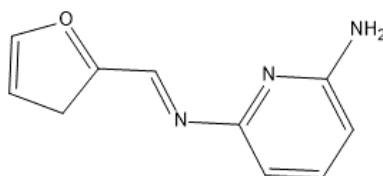


Figure 2. N-(2-furylmethylene) pyridine-2,6-diamine

The developed microelectrode had good selectivity against lanthanides like Dy^{3+} , Gd^{3+} , Sm^{3+} , Tm^{3+} , Yb^{3+} , Ce^{3+} , as well as ions of main and transition metal groups like Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cu^{2+} , Pb^{2+} .

In a later work a symmetrical ion carrier (N,N'-bis(2-pyridinecarboxamide)-1,3-benzene (Figure 3)) was used for constructing a sensor for Lu^{3+} ions with a linear response between 1.0×10^{-6} M and 1.0×10^{-1} M and a LOD of 6.3×10^{-7} M of the optimal concentration of the membrane was reported to be 30% wt. of PVC, 63% wt. of benzyl acetate (BA), 5% wt. of the ion carrier, and 2% wt. of sodium tetraphenyl borate (NaTPB).

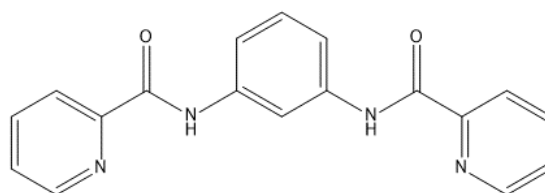


Figure 3. N,N'-bis(2-pyridinecarboxamide)-1,3-benzene

The choice of the ion carrier for the preparation of the sensor was regarding the complexation constants of the ligand with a range of ligands [37] which was maximal for Lu^{3+} ion in a range of ions including Na^+ , K^+ , Co^{2+} , Ca^{2+} , Mg^{2+} , Pb^{2+} , Pr^{3+} , Eu^{3+} , Sm^{3+} , Gd^{3+} , Nd^{3+} , Ho^{3+} , Tm^{3+} , Yb^{3+} , and La^{3+} , which was later reflected by the selectivity of the membrane

sensors for Lu^{3+} . The highest interference coefficients were recorded for Er^{3+} (7.5×10^{-4}), Tm^{3+} (5.8×10^{-4}) and Eu^{3+} (3.0×10^{-4}) respectively.

Another lutetium ion sensor was developed a short time later using N,N'-bis(2-pyridinecarboxamide)-1,2-ethane. The sensor had a linear response behavior in the concentration window of 1.0×10^{-6} M- 1.0×10^{-1} M (LOD: 6.0×10^{-7} M). The optimal sensor had a composition of PVC (30% wt.), NPOE (63% wt.), sodium tetraphenylborate (2% wt.) and 5% wt. of the ion carrier [38].

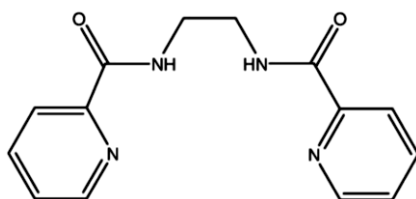


Figure 4. N,N'-bis(2-pyridinecarboxamide)-1,2-ethane

The matched potential method selectivity coefficients of different ions were calculated and reported as Ho^{3+} (2.5×10^{-2}); Ce^{3+} (1.5×10^{-2}); Pb^{2+} (1.0×10^{-4}); Mg^{2+} (3.0×10^{-4}); Na^{+} (2.5×10^{-4}); Cu^{2+} (3.0×10^{-3}); K^{+} (9.0×10^{-4}); Pr^{3+} (3.2×10^{-4}); Sm^{3+} (5.0×10^{-3}); Eu^{3+} (2.0×10^{-4}); Gd^{3+} (1.7×10^{-4}); Tm^{3+} (4.2×10^{-3}); Yb^{3+} (1.7×10^{-4}); Li^{+} (2.0×10^{-3}); NH_4^{+} (8.0×10^{-3}); Mn^{2+} (2.5×10^{-3}); Ca^{2+} (8.0×10^{-4}); Tb^{3+} (2.5×10^{-4}); Ho^{3+} (7.0×10^{-4}); Er^{3+} (2.0×10^{-4}); Dy^{3+} (8.0×10^{-3}); La^{3+} (7.0×10^{-4}). The evaluations revealed the considerable selectivity of the sensor with the maximum interference from Ho^{3+} (2.5×10^{-2}); Ce^{3+} (1.5×10^{-2}) [38].

The next Lu^{3+} sensor was reported using N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-[(Z)-1-(2-thienyl)methylidene]amino)benzyl)phenyl] amine (Figure 5). The electrode response in the range of 1.0×10^{-6} to 1.0×10^{-2} M was 19.8 ± 0.5 mV/decade of concentration and the electrode had a low limit of detection (7.2×10^{-7} M).

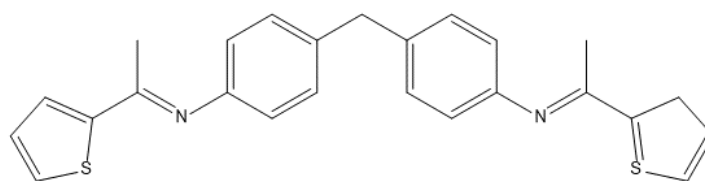


Figure 5. N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-[(Z)-1-(2-thienyl)methylidene]amino)benzyl)phenyl] amine

The best response was observed when 30% PVC, 3% the ion carrier, 2% NaTPB and 65% of acetophenone were used. Among the interfering ions used to evaluate the matched potential selectivity coefficients (K_{MPM}) (La^{3+} (7.4×10^{-4}); Pr^{3+} (7.8×10^{-4}); Nd^{3+} (6.5×10^{-3}); Eu^{3+} (2.1×10^{-3}); Gd^{3+} (4.7×10^{-3}); Dy^{3+} (6.2×10^{-3}); Tb^{3+} (8.4×10^{-4}); Tm^{3+} (7.2×10^{-3}); Er^{3+} (7.4×10^{-3}); Sm^{3+} (8.5×10^{-4}); Yb^{3+} (5.8×10^{-3}); Ho^{3+} (2.3×10^{-2}); Na^{+} (8.7×10^{-4}); K^{+} (2.1×10^{-3}); Cr^{3+} ($8.6 \times$

10^{-4}); Fe^{3+} (1.0×10^{-3}) the highest interference was from Ho^{3+} , yet the sensor had acceptable selectivity even in the case of this ion [39].

Abedi et al used 2,2'-dithiobis(4-methylthiazole) (Figure 6) in a Lu^{3+} ion sensor and reported a calibration plot slope of 19.6 ± 0.4 mV/decade of concentration from 1.0×10^{-6} to 1.0×10^{-2} M (LODt: 6.8×10^{-7} M) [40].

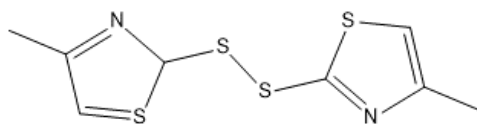


Figure 6. 2,2'-dithiobis(4-methylthiazole)

The optimal membrane sensor composition was reported to be 2% wt. of NaTPB, 66% wt. of acetophenone, 30 % wt. of PVC, and 2% wt. of 2,2'-dithiobis(4-methylthiazole). The interference of Nd^{3+} , Tm^{3+} , Er^{3+} , La^{3+} , Ho^{3+} , Yb^{3+} , Gd^{3+} , Cr^{3+} , Fe^{3+} , Cd^{2+} , Co^{2+} , Ca^{2+} , Na^+ were evaluated and the highest interference was reported to be in the case of Ho^{3+} , Gd^{3+} , Yb^{3+} with respective K_{MPM} values of 4.6×10^{-3} , 4.2×10^{-3} , 3.8×10^{-3} [40].

Norouzi et al [41] reported using a known selectrophore namely N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-[[[(Z)-1-(2-thienyl)methylidene] amino]benzyl)phenyl] amine (Figure 5) to construct a carbon paste sensor for Lu^{3+} ions. The carbon pastes composed of multi-walled carbon nanotubes modified with amine groups (MWCNT-NH₂), nanosilica (NS), graphite, and an ionic liquid at respective amounts of 5%, 1%, 49%, 20%, and 25% wt. of the selectophore, and the resulting sensor produced a Nernstian response of 19.8 ± 0.2 mV decade of concentration from 1.0×10^{-6} - 1.0×10^{-2} M (LOD: 9.5×10^{-7} M). The carbon paste electrode showed good selectivity in the presence of Na^+ , K^+ , Cu^{2+} , Pb^{2+} , Co^{2+} , Zn^{2+} , Gd^{3+} , Yb^{3+} , Nd^{3+} , Tb^{3+} , Ho^{3+} , La^{3+} , Sm^{3+} , Dy^{3+} , Pr^{3+} , Eu^{3+} , Ce^{3+} , Tm^{3+} , Er^{3+} , and the maximum interference was caused by Ho^{3+} with an MPM selectivity coefficient of 9.6×10^{-3} [41].

Another lutetium ion sensor was constructed using 3% wt. of (2-oxo-1,2-diphenylethylidene)-N-phenylhydrazinecarbothioamide, 65% wt. of dibutyl phthalate, 2 of sodium tetraphenyl borate and 30% of PVC to obtain a membrane sensor with a Nernstian slope of 19.8 ± 0.3 mV/decade of concentration from 1.0×10^{-6} and 1.0×10^{-2} M and a LOD of 6.8×10^{-7} M. The experiments were based on the complexation constants of the ionophore and a range of ions (i.e. The selectivity behavior was evaluated against Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , La^{3+} , Yb^{3+} , Ce^{3+} , Lu^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Fe^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+}) which proved the ligand to have a strong tendency to interact with lutetium. The highest interferences were caused by Eu^{3+} , Sm^{3+} , Dy^{3+} , and Gd^{3+} , which also had high complex formation constants [42].

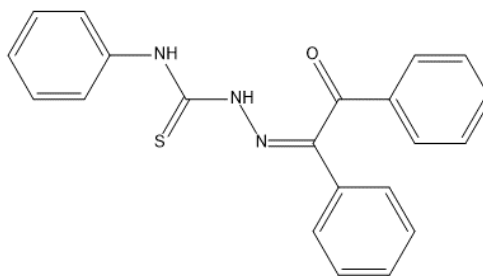


Figure 7. (2-oxo-1,2-diphenylethylidene)- *N*-phenylhydrazinecarbothioamide

M. R. Pourjavid et al used a derivative of thiazole (AAT) for constructing the Lu^{3+} PVC-based liquid membrane electrode, with a Nernstian response in the range of 1.0×10^{-6} to 1.0×10^{-1} M with a LOD of 5.7×10^{-7} M. The polymeric membrane with optimal response was composed of 30% PVC, 63% wt. of benzyl acetate, 5% wt. of the ionophore, and 2% wt. of NaTPB [43].

The only report on a lutetium ion sensing membrane based on a closed ring ion carrier with hard oxygen donor atoms is the work of S. Karimian et al who developed a membrane [44]. They used 4'-carboxybenzo-18-crown-6 (Figure 8) in a composition of 30% wt. of PVC, 63% wt. of dibutyl phthalate, 2% wt of the ion carrier and 5% wt. of oleic acid and reported as Nernstian response of 19.8 ± 0.4 mV per decade of concentration from 1.0×10^{-6} to 1.0×10^{-2} M and a LOD of 6.5×10^{-7} M. Even the most interfering species, namely Eu^{3+} and Na^{+} had a rather low selectivity coefficient of 1.0×10^{-3} [44].

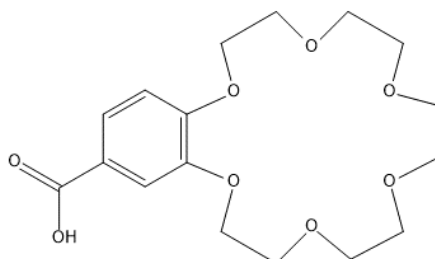


Figure 8. 4'-carboxybenzo-18-crown-6

S. Pasyar et al. [45] described developing a Lu^{3+} ion membrane sensor using an ionophore that was rather different from the ones used for the same purpose before, in that although it was an open ring molecule, almost all of the donor atoms were hard oxygen atoms, as in the case of S. Karimian [44]. The optimal electrode was composed of 30% wt. of PVC, 8% wt. of the ion carrier, 60% wt. of nitrobenzene and 2% wt. NaTPB. The sensor produced a slope of 20.5 ± 0.3 mV/decade of concentration from 1.0×10^{-7} to 1.0×10^{-2} M and an LOD of 7.5×10^{-8} M. None of the interfering ions evaluated (i.e. Na^{+} , K^{+} , Ca^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Hg^{2+} , Pb^{2+} , Dy^{3+} , Yb^{3+} , Tb^{3+} , Tm^{3+} , Pr^{3+} , La^{3+} , Ho^{3+} , Sm^{3+} , Gd^{3+} , Er^{3+} , Eu^{3+} , Cr^{3+} , Fe^{3+}) produced selectivity coefficients larger than 8.2×10^{-4} (Cr^{3+} and Zn^{2+}) [45].

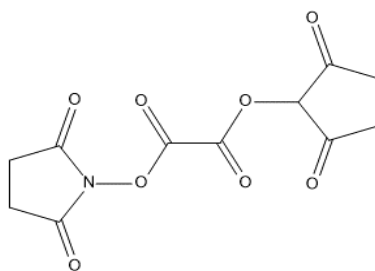


Figure 9. Di(N-succinimidyl)oxalate

1,2-bis(2-hydroxynaphthamido)-4,5-dimethylbenzene (Figure 10) was also used in constructing a membrane sensor for lutetium(III). 5% wt. of the ionophore was used together with 63% wt. of nitrobenzene, 2% of NaTPB and 30% of PVC powder in the optimal membrane which had a linear response with a Nernstian slope of 19.6 ± 0.2 mV/decade of concentration from 1.0×10^{-6} to 1.0×10^{-2} M (LOD: 8.0×10^{-7} M). The highest selectivity coefficients were from 1.0×10^{-2} to 4.0×10^{-2} and were reported for Pr^{3+} , Ho^{3+} , Mg^{2+} , Dy^{3+} , Pb^{2+} , Cd^{2+} , Ca^{2+} , Gd^{3+} , Co^{2+} , Sm^{3+} , and Eu^{3+} , yet even these values could not be considered very high, indicating the selectivity of the membrane sensor towards lutetium [46].

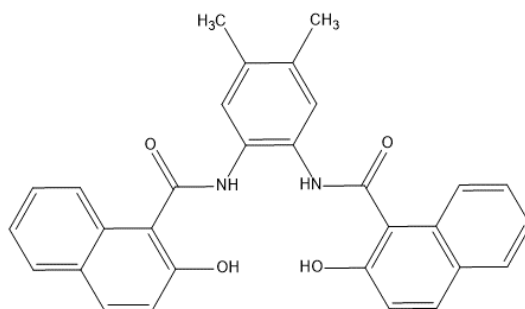


Figure 10. 1,2-bis(2-hydroxynaphthamido)-4,5-dimethylbenzene

Another Lutetium sensor was reported using 2-((2-(pyridine-2-yl)hydrazono)methyl)phenol as an ionophore. The sensor had a Nernstian calibration plot (19.7 ± 0.5 mV per decade of concentration) from 1.0×10^{-7} to 1.0×10^{-2} M and a LOD of 7.6×10^{-8} M when the electrode had a composition of 30% wt. of PVC, 66% wt. of benzyl acetate, 2% of the ionophore and 2% wt. of NaTPB. The small selectivity coefficients of the electrode for interfering species (Nd^{3+} (4.3×10^{-4}), Pr^{3+} (8.8×10^{-4}), Er^{3+} (2.5×10^{-3}), Dy^{3+} (5.4×10^{-3}), Eu^{3+} (1.0×10^{-3}), Yb^{3+} (2.7×10^{-3}), Sm^{3+} (7.3×10^{-4}), Cr^{3+} (1.0×10^{-3}), Fe^{3+} (8.7×10^{-4}), Ni^{2+} (4.2×10^{-3}), Cd^{2+} (2.8×10^{-3}), Zn^{2+} (3.3×10^{-3}), Ca^{2+} (6.5×10^{-4}), Na^+ (6.7×10^{-4}) were indicative of its selectivity for the target ion. [47].

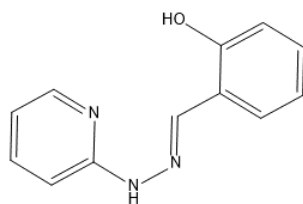


Figure 11. 2-((2-(pyridine-2-yl)hydrazono)methyl)phenol

In 2014 a lutetium ion sensor was reported A. Tamaddon et al. They incorporated 3-[(pyridine-2-ylmethylene)- amino]-2-thioxo-4-one into a paste of unmodified multiwalled carbon nanotubes and compared the results obtained using functionalized MWCNTs (Figure 13). The pastes are further composed of graphite powder and paraffin oil. Both pastes were used to construct carbon paste electrodes (CPEs) for the selective analysis of lutetium ions. The compositions of the optimal CPE were reported to be 20% wt. of paraffin oil, 56% wt. of graphite powder, 18% wt. of the ion carrier, and 6% wt. of functionalized MWCNTs, which led to a linear calibration plot with Nernstian a slope of 21.1 mV/decade of concentration from 1.0×10^{-6} – 1.0×10^{-1} M [48].

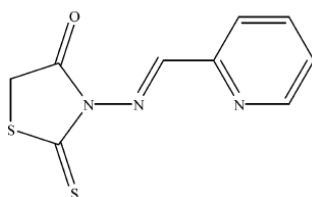


Figure 12. 3-[(pyridine-2-ylmethylene)- amino]-2-thioxo-4-one (PAT) ionophore

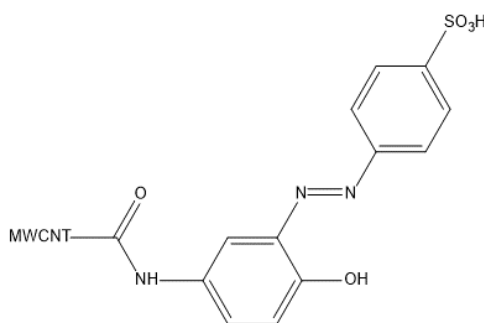


Figure 13. f-MWCNTs

The electrodes had good selectivity against a range of common interfering ions (Yb^{3+} , Na^+ , Pr^{3+} , K^+ , Nd^{3+} , Ca^{2+} , Dy^{3+} , Mg^{2+} , Ir^{3+} , Cu^{2+} , Fe^{3+} , Zn^{2+} , Cr^{3+} , Co^{2+} , Pb^{2+} , Ni^{2+}) and the selectivity coefficients were 1.0×10^{-2} (in the case of Cr^{3+}) or smaller.

In another work, a formerly used ion carrier, namely 2,2'-dithiobis(4-methylthiazole) (Figure 6) was used in a paste further composed of MWCNT, graphite powder, nanosilica and

paraffin oil to construct a CPE for Lu^{3+} ions. The optimal composition of the paste was reported to be 3% wt. of the ion carrier, 25% wt. of paraffin oil, 3% wt. of MWCNT, 0.5% wt. of nanosilica, and 68.5% wt. of graphite powder. The response was found to be linear in the range of 5.0×10^{-8} - 1.0×10^{-2} M and the slope of the linear section of the calibration plot was reported to be 19.9 ± 0.3 mV decade of concentration [49]. Among the tested interfering ions (i.e. Pr^{3+} , La^{3+} , Tm^{3+} , Nd^{3+} , Eu^{3+} , Ho^{3+} , Gd^{3+} , Sm^{3+} , Er^{3+} , Tb^{3+} , Dy^{3+} , Yb^{3+} , Mg^{2+} , Pb^{2+} , Na^+ , K^+ , Co^{2+} , Cd^{2+} , Ca^{2+} , Fe^{3+} , Cr^{3+} , Ni^{2+}) the highest matched potential selectivity coefficient was 9.0×10^{-3} (for Fe^{3+}) reflecting the considerably selective behavior of the electrode [49].

The last work on the development of a lutetium ion sensor is the work of N. Ardakanifard et al. [50] who used 2,2'-[propane-1,3-diylbis(thio)]dianiline as an ionophore, together with PVC powder, nitrobenzene and NaTPB to obtain a selective membrane for use in a sensor for Lu^{3+} . Under optimal conditions the sensor with the best composition 66% wt. of nitrobenzene, 30% t. of PVC, 1% wt. of NaTPB and 3%wt. of the ion carrier had a Nernstian behavior (19.8 ± 0.4 mV decade of concentration) from 1.0×10^{-6} to 1.0×10^{-2} M with a LOD of 8.2×10^{-7} M. The electrode had selectivity coefficients below 9.5×10^{-4} for various interfering ions including Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} , Er^{3+} , Dy^{3+} , La^{3+} , Tm^{3+} , Nd^{3+} , Ho^{3+} , Gd^{3+} , Sm^{3+} , Yb^{3+} , Pr^{3+} , Eu^{3+} and Tb^{3+} [50].

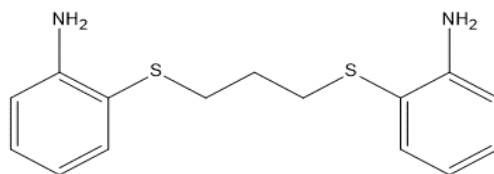


Figure 14. 2,2'-[propane-1,3-diylbis(thio)]dianiline

3. CONCLUSION

Among the various sensor designed and constructed for lutetium ions, the majority were based on acyclic ligands with soft or medium donor atoms. These include *N*-(thien-2-ylmethylene)pyridine-2,6-diamine (3 N and 1 S donor atoms) (Figure 1); *N*-(2-furylmethylene)pyridine-2,6-diamine (3 N and 1 O donor atom) (Figure 2); *N,N'*-bis(2-pyridinecarboxamide)-1,3-benzene (4 N and 2 O donor atoms) (Figure 3); *N,N'*-bis(2-pyridinecarboxamide)-1,2-ethane (4 N and 2 O donor atoms) (Figure 4); *N*-[(*Z*)-1-(2-thienyl)methylidene] -*N*-[4-(4-[(*Z*)-1-(2-thienyl) methylidene]amino)benzyl)phenyl] amine (2 N and 2 S donor atoms) (Figure 5); 2,2'-dithiobis(4-methylthiazole) (2 N and 4 S donor atoms) (Figure 6); (2-oxo-1,2-diphenylethylidene)- *N*-phenylhydrazinecarbothioamide (3 N and 1 S and 1 O donor atoms) (Figure 7); 1,2-bis(2-hydroxynaphthamido)-4,5-dimethylbenzene (2 N and 4 O donor atoms) (Figure 10); 2-((2-(pyridine-2-yl)hydrazono)methyl)phenol (3 N and 1 O donor atoms) (Figure

11); 3-[(pyridine-2-ylmethylene)- amino]-2-thioxo-4-one (PAT) ionophore (3 N, 2 S and 1 O donor atoms) (Figure 12); 2,2'-[propane-1,3-diylbis(thio)]dianiline

(2 N and 2 S donor atoms) (Figure 14). These support the claims that lanthanide ions show better interactions with medium or soft donor atoms and acyclic ligands can form wrap-around complexes with specific lanthanide ions inducing selectivity. Yet there are examples of a cyclic ligand with hard donor atoms (i.e. 4'-carboxybenzo-18-crown-6 (Figure 8) (6 O donor atoms)) as well as an acyclic ligand with hard donor atoms (i.e. Di(N-succinimidyl)oxalate (Figure 9) (8 O donor atoms)) which indicate that size of the ring and possibly the optimal size of the wrap-around complex can also induce selectivity in some ion carriers.

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