



FUNCTIONAL GROUP GATING OF DIBENZO-18-CROWN-6: TOWARDS THE DEVELOPMENT OF LEAD (II) ION SENSING ELECTRODES

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ABSTRACT

The relevance of lead (II) sensors emanates from the environmental abundance of this toxic heavy metal, due to a variety of natural and manmade processes. However, given the adverse physiological effects of lead(II) in humans, significant research efforts have been dedicated towards the development of techniques allowing lead analysis and sequestration. However, affordability, sensitivity and selectivity remains challenging. As such, dibenzo-18-crown-6 (DB18C6) and three strategic derivatives (-COCH₃, -NO₂ and -Br) were synthesized and probed via Density Functional Theoretical (DFT) modelling, absorption spectroscopy (UV-Vis spectroscopy), Differential Pulse Anodic Stripping (DPASV), Cyclic (CV) and Square Wave (SWV) voltammetries, as possible materials for preparing plasticiser free lead(II) ion selective electrodes, capable of quantifying lead(II) ions at concentrations below 10 mg L⁻¹ with minimal interference from other metal ions except Hg²⁺ and Al³⁺.

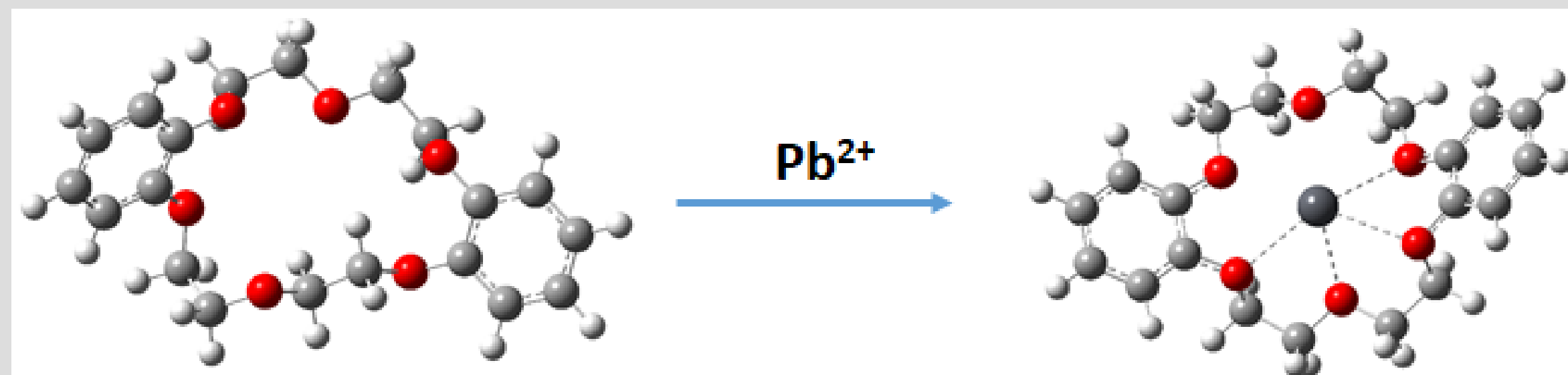
Keywords: Ion selective electrodes; Dibenzo-18-crown-6; Density Functional Theory; lead(II) ions.

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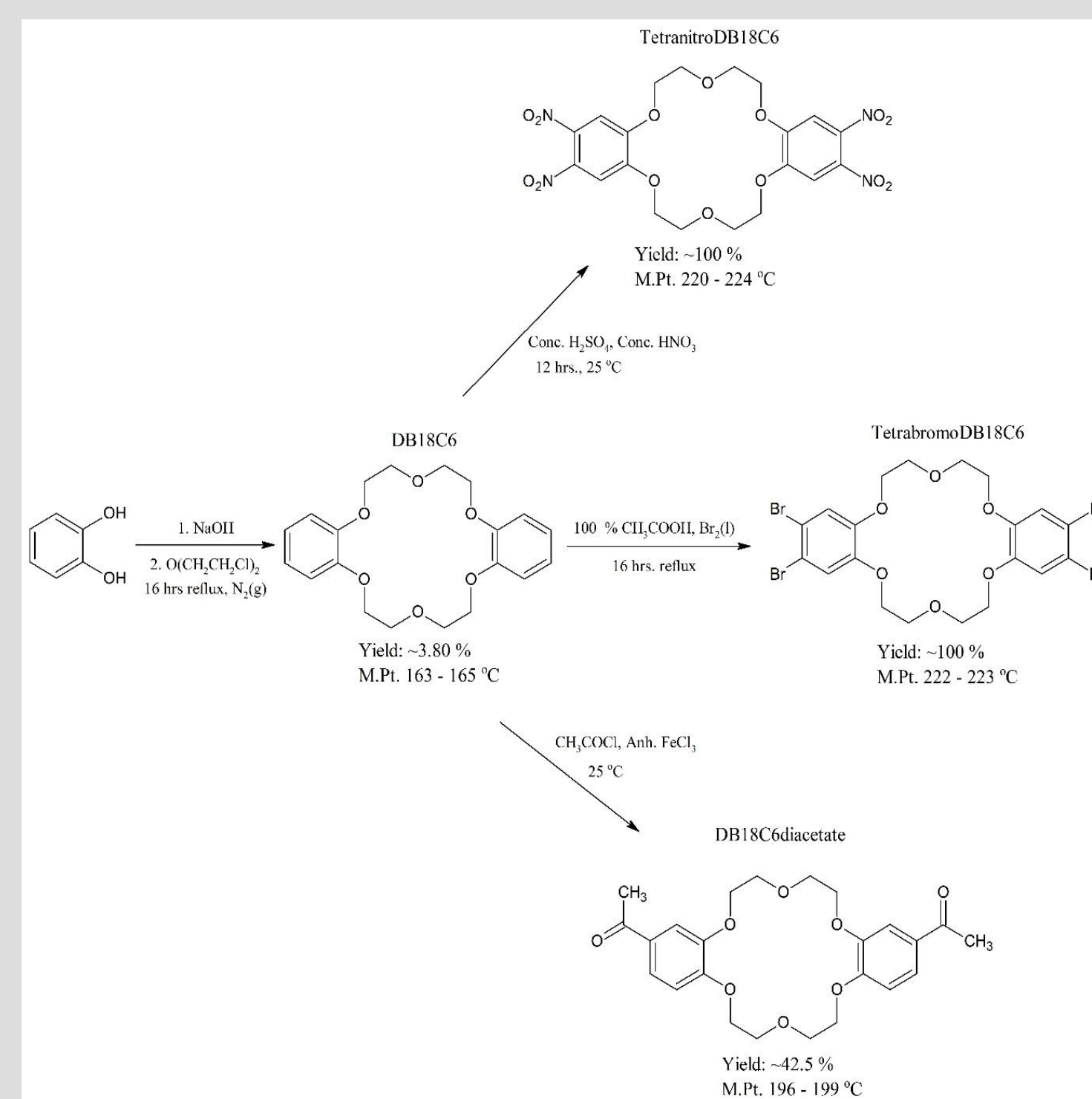
INTRODUCTION

The toxicity of Pb²⁺ highlights the need for highly sensitive methodologies, offering cheap and convenient detection. Hence, compleximetric techniques, applying various ligand systems, have been investigated by numerous researchers for their ability to allow accurate and rapid quantification of this heavy metal. Among these ligand systems are cryptands, calixarenes and crown ethers, due to their ability to size bind metal ions. However, though reports on these systems indicate some level of success, selectivity and sensitivity remains a work in progress, hence, modification of the type of coordinating atoms and even the three dimensional structure of these host systems have been investigated for improved selectivity and sensitivity. However, though various studies have been carried out on these systems, for crown ethers such as DB18C6, adjustment of their electronic structures by side arm modification remains unrealized.



Scheme 1. Binding of Pb²⁺ by DB18C6

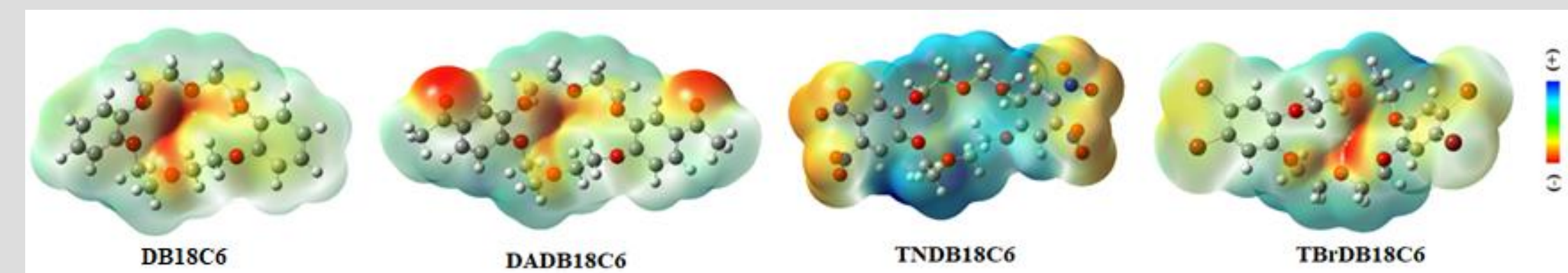
SYNTHESIS



Scheme 2. Synthetic scheme for DB18C6 derivatives

RESULTS & DISCUSSION

The interactions of Dibenzo-18-crown-6 derivatives and Pb²⁺ were probed via DFT, UV-Vis spectroscopy and various electrochemical Methods (CV, SWV, and DPASV). All derivatives spontaneously coordinate with Pb²⁺ in their free/ monomeric form; the most exergonic binding as well as the most favourable linear range (LR), limit of detection (LOD) and limit of quantification (LOQ) are exhibited by the brominated derivative which forms a 2:1 metal: ligand complexes with Pb²⁺, compared to the 1:1 complexes formed with other derivatives; a process driven by entropic effects due to solvent rearrangement and substituent effects.



Scheme 3: Electrostatic potential maps as calculated for DB18C6 derivatives

Additionally, these systems were found to passivate, *via* electropolymerization, a platinum working electrode surface, except for the nitrated derivative which forms a chemisorbed electroactive coating, hence, all compounds allow the preparation of modified electrodes, capable of quantifying Pb²⁺ at concentrations below 10 mg L⁻¹ with minimal errors in the presence of other mono-, di- and tri-valent metal ions, except Al³⁺ and Hg²⁺ which offer significant coordination competition.

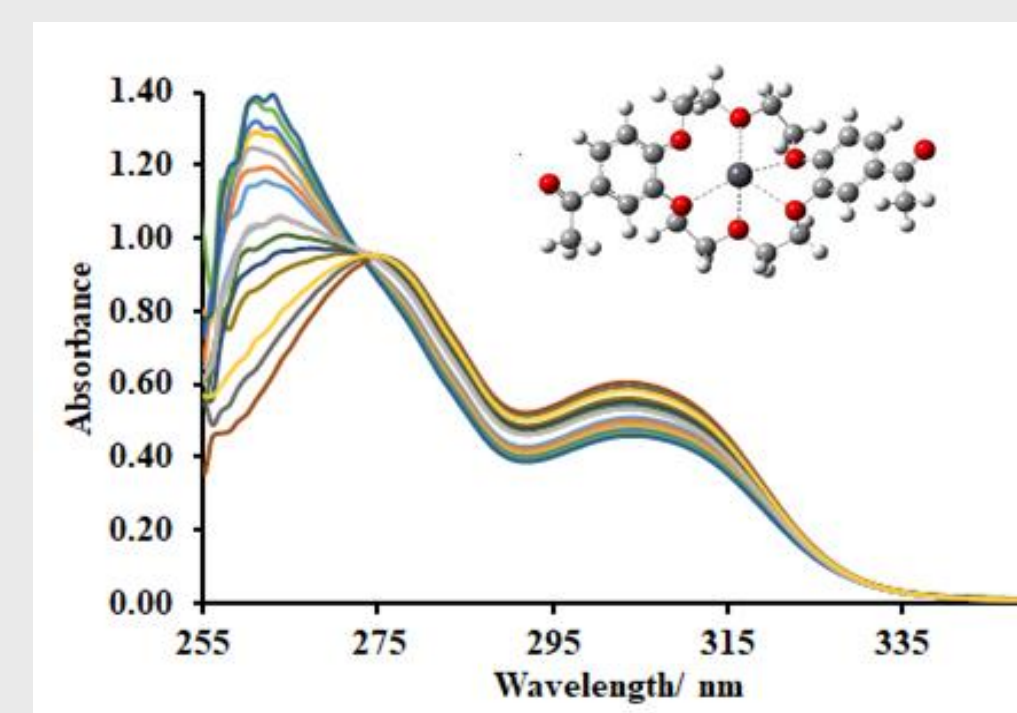


Figure 1: UV-Vis Spectrum of DADB18C6 in the presence of Pb²⁺

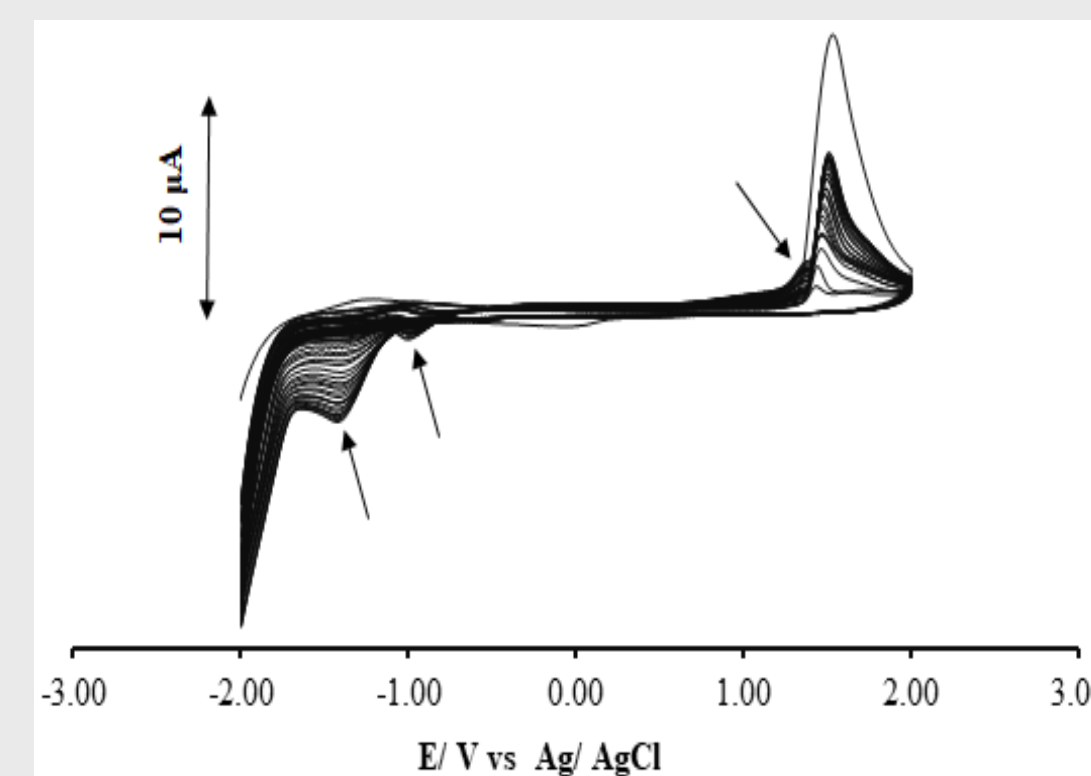


Figure 2: Electropolymer of DB18C6 (30 consecutive cyclic voltammograms).

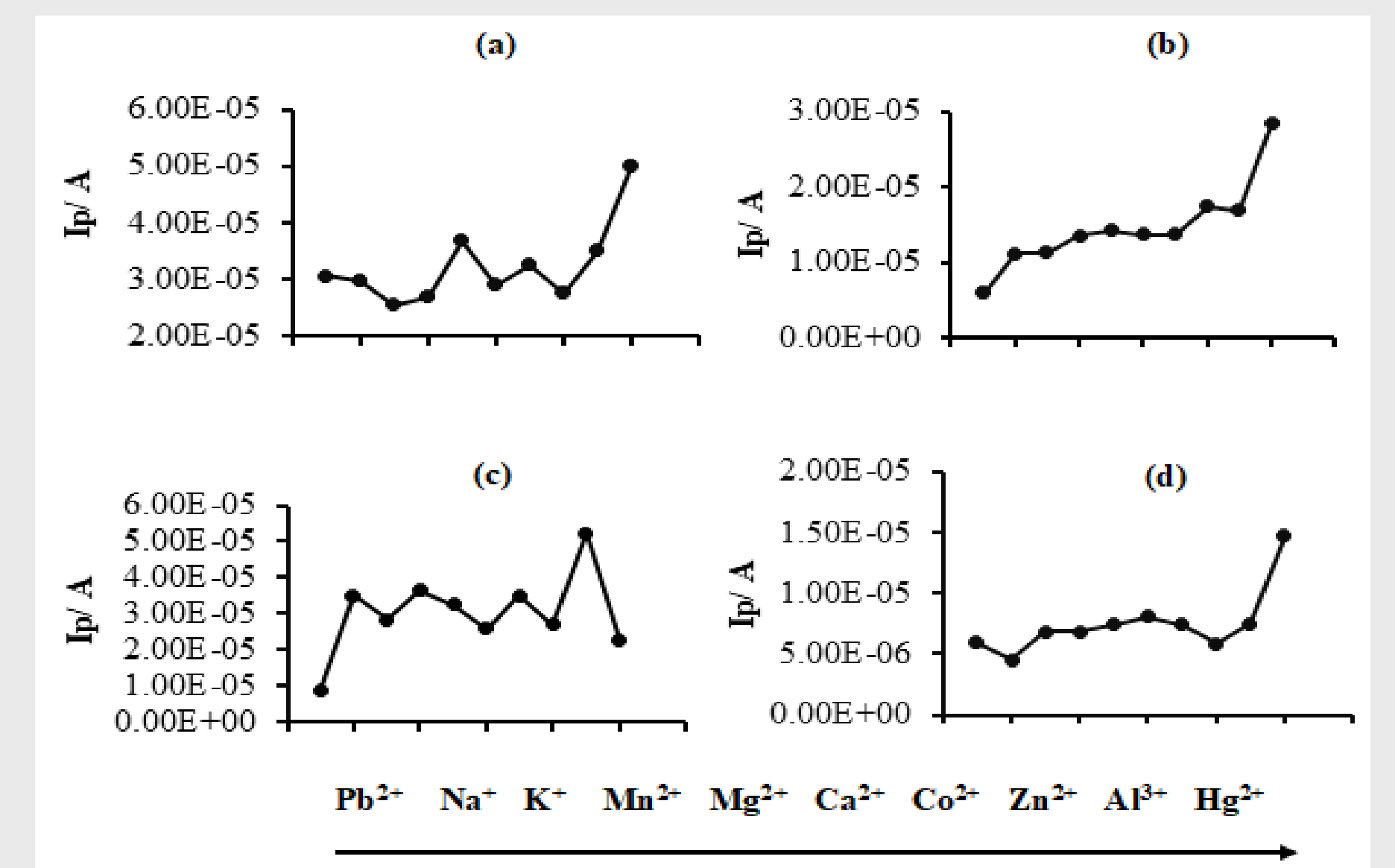
Table 1: Pb²⁺ complexation thermodynamic parameters for DB18C6 derivatives at 298 K

Compound	ΔG_{298}° / (kJ mol ⁻¹)	ΔH_{298}° / R (K ⁻¹)	ΔS_{298}° /R
DB18C6	-20.32	18462.5 ± 610.8	70.1 ± 2.1
TBrDB18C6	-29.49	25777.4 ± 2922.2	98.8 ± 9.8
TNDB18C6	-16.02	3648.6 ± 313.5	18.6 ± 1.1
DADB18C6	-21.89	21487.5 ± 3198.0	80.8 ± 10.7

Table 2: Linear range, LOD and LOQ of for DB18C6 Functionalized Electrodes

Compound	LR/ mg L ⁻¹	LOD/ mg L ⁻¹	LOQ/ mg L ⁻¹
DB18C6	8.49 – 56.60	3.06	9.27
TBrDB18C6	2.85 – 59.14	4.56	13.38
TNDB18C6	2.85 – 54.05	11.11	33.65
DADB18C6	5.68 – 59.14	5.27	15.97

Figure 3: Effects of presence of other metal ions [Conc. 10 ppm] on the current response obtained for lead [Conc. 50 ppm] when the electrode surface is modified with (a) DB18C6, (b) DADB18C6, (c) TNDB18C6 and (d) TBrDB18C6.



CONCLUSIONS

- Dibenzo-18-crown-6 and its acetylated, brominated and nitrated derivatives are able to spontaneously coordinate Pb²⁺ in their free monomeric form; a process controlled by entropic effects.
- Their ability to passivate a platinum electrode surface allows the preparation of modified electrodes, capable of quantifying lead(II) ion at concentrations below 10 mg L⁻¹
- There was minimal errors in the presence of other metal ions, except for Al³⁺ and Hg²⁺ which results in coordination competition to Pb²⁺ ions.

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