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Isabelle Billard

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1 **SYNTHESIS OF NEW CALIXARENE-PHOSPHINE OXIDES**
2 **AND THEIR EXTRACTION PROPERTIES IN IONIC LIQUIDS**

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7 **Abstract** *New calix[4]arenes functionalized by Alk₂P(O)CH₂ binding groups and N-*
8 *methylimidazolium groups at the opposite rims of the macrocyclic skeleton have been*
9 *synthesized and characterized. Their extraction properties towards of Eu³⁺ and Am³⁺ in ionic*
10 *liquid were investigated.*

11 **Keywords** Calixarenes; ionic liquids; phosphine oxides

12 **INTRODUCTION**

13 The use of nuclear power has led to the accumulation of great amounts of both high-
14 and medium-level activity radioactive wastes, which require efficient methods of separation
15 and safe disposal. The main method for the decontamination of radioactive wastes is
16 liquid-liquid extraction of hazardous radionuclides followed by burial or transmutation. A
17 modern approach in the design of efficient and selective extractants of radioanuclides is
18 based on the functionalization of calixarene platform by several P=O containing fragments,
19 capable of cooperatively binding metal cations.¹ Room temperature ionic liquids (RTIL)
20 are promising solutions for the extraction of the radionuclides from spent nuclear fuel.²

22 **RESULTS AND DISCUSSION**

23 We present in this article the synthesis of a series of new *cone*-shaped calix[4]arenes
24 possessing CH₂P(O)Alk₂ metallocomplexing groups at the macrocyclic wide and narrow
25 rim and N-methylimidazolium groups at the narrow rim. Extraction properties of the
26 calixarene synthesized and dissolved in ionic liquid were investigated.

27 Calix[4]arenes **3–10** functionalized by four or eight Alk₂P(O)CH₂ binding groups
28 have been synthesized by the Arbuzov reaction of tetrachloromethylcalix[4]arenes **1, 2** with
29 dialkylphosphinites.

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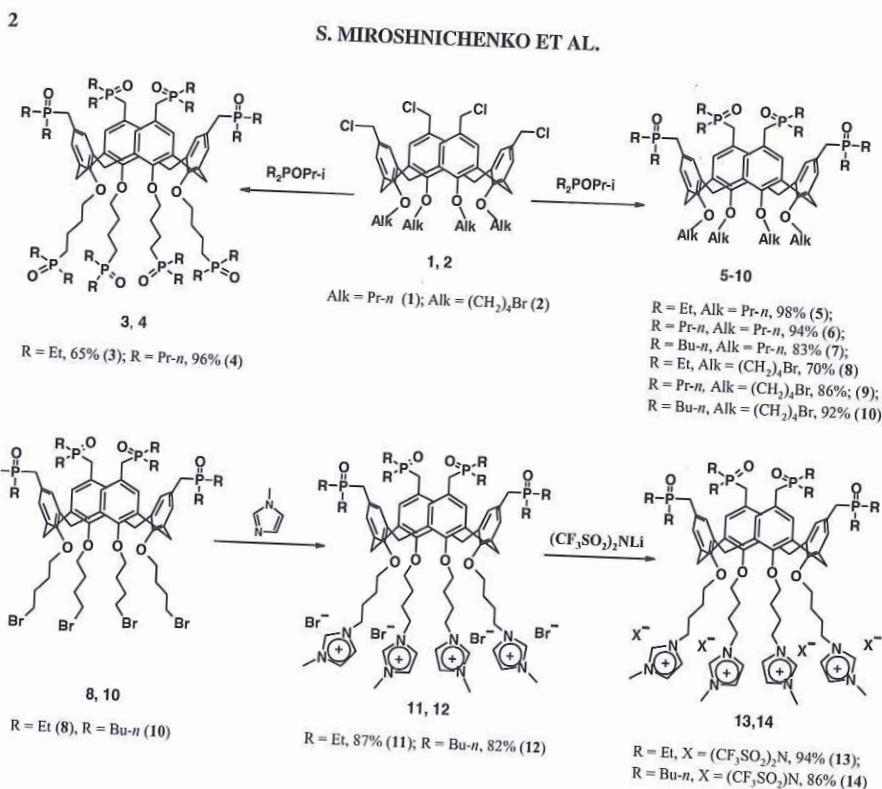


Figure 1 Synthesis of calixarene phosphine oxides.

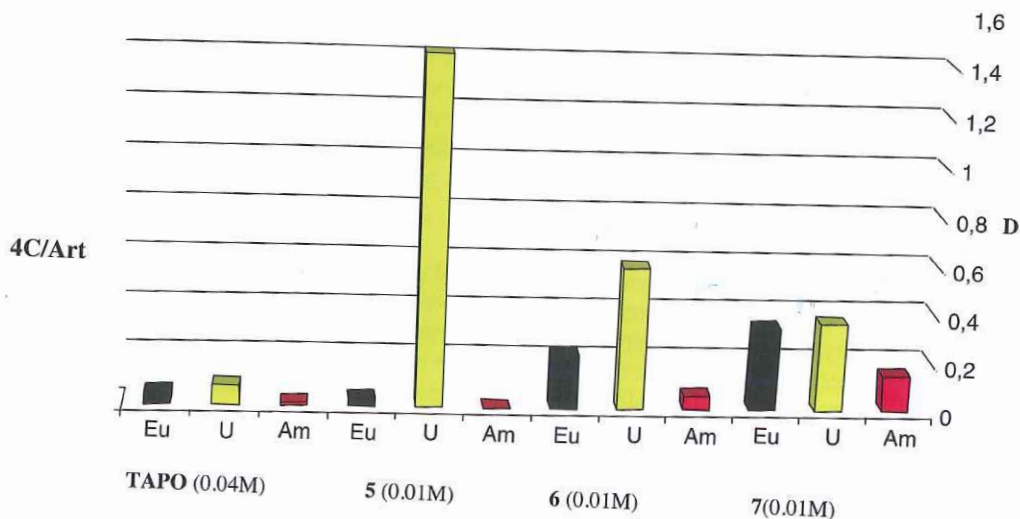


Figure 2 Extraction of Eu³⁺, UO₂²⁺, Am³⁺ by phosphine oxides from HNO₃ (0.3M) into *N*-butyl-*N*-methylimidazolium × Tf₂N. D—distribution ratio of the metal cations between the ionic liquid and HNO₃ phases; TAPO—trioctylphosphine oxide.

30 Tetra(*N*-methylimidazolium) derivatives **11**, **12** were prepared by the reaction of
31 bromobutoxycalixarenes **8**, **10** with *N*-methylimidazole. Metathetical reactions of bromides
32 **11**, **12** with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in DMF gave new quaternary salts **13**, **14** (Figure 1).

33 Extraction properties of some calixarene phosphine oxides towards of Eu^{3+} , UO_2^{2+} ,
34 and Am^{3+} were investigated in ionic liquid *N*-butyl-*N*-methylimidazolium \times Tf_2N (Figure
35 2). The calixarene tetraphosphine oxides **5–7** are more efficient extractants than industrial
36 trialkylphosphine oxides. Calixarene **5** demonstrates high selectivity in UO_2^{2+} extraction.

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