



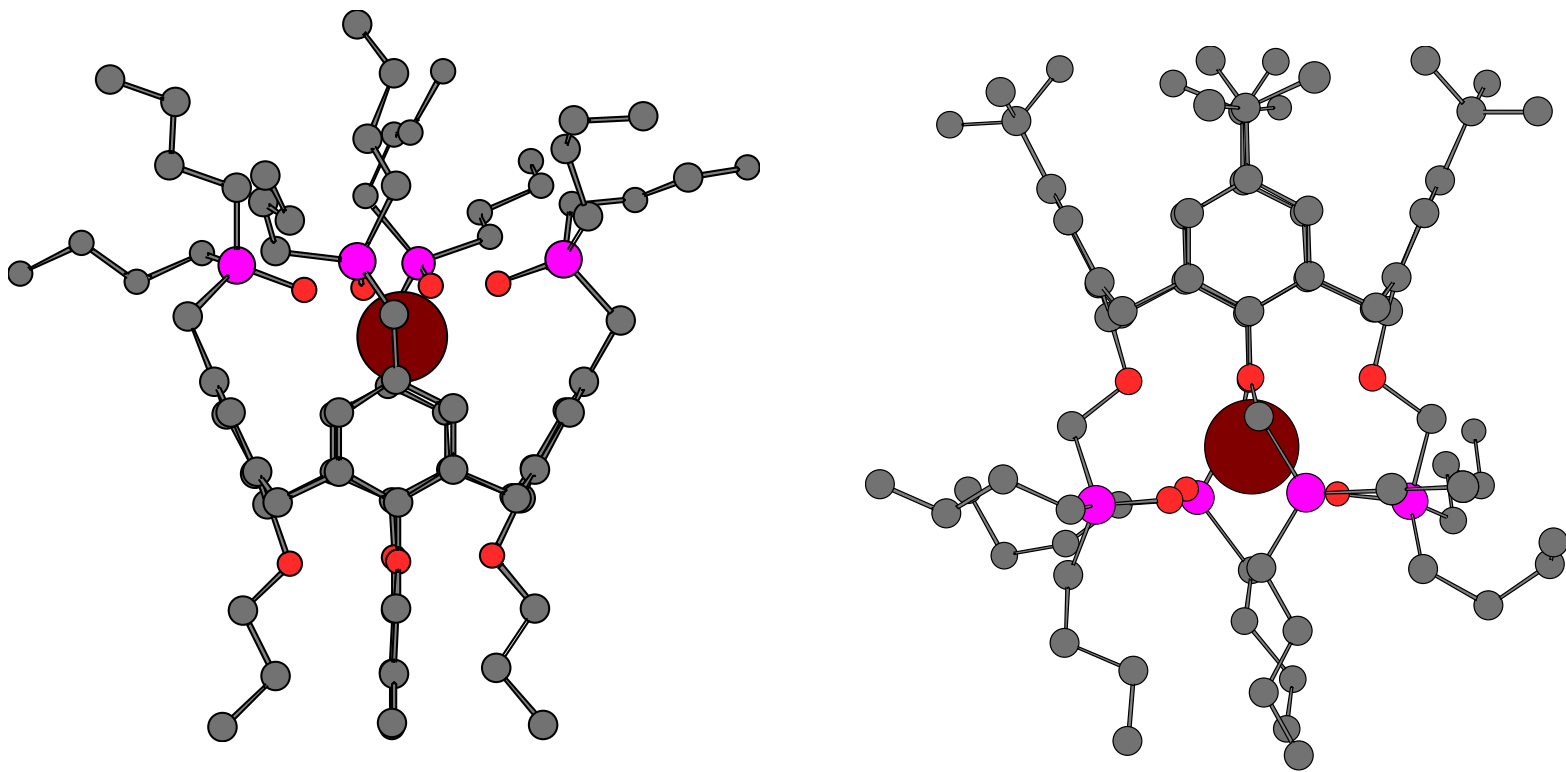
International Workshop
MOLECULAR RECOGNITION OF RADIONUCLIDES
Saint-Petersburg, 18-20 June 2009

P-, N-, and S-containing Calixarenes.
Synthesis, Structure, Properties

Vitaly KALCHENKO

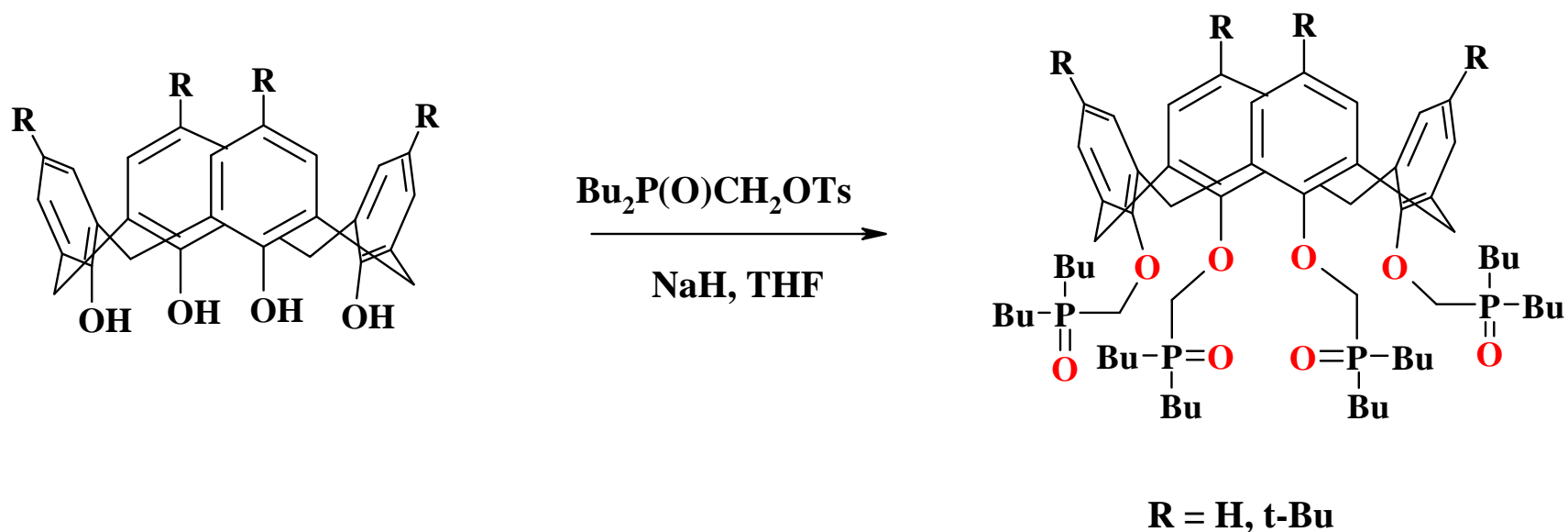
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**Complexes of calix[4]arene trialkylphosphine oxides
with metal cation**
MACROMODEL- 5.5, AMBER

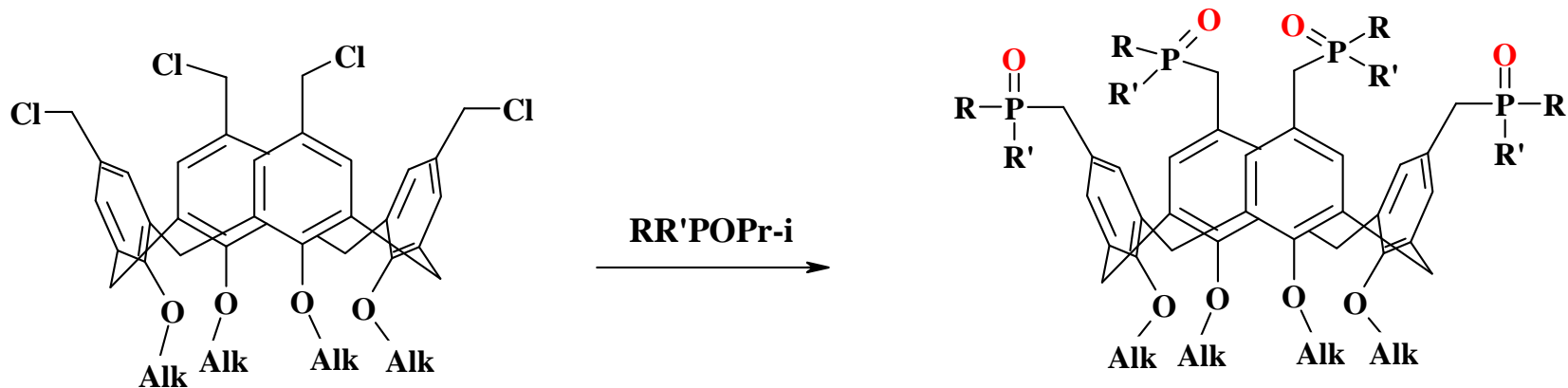


G. Wipff, A. Varnek

Phosphinomethyl-calix[4]arenes



Phosphinoylmethyl-calix[4]arenes



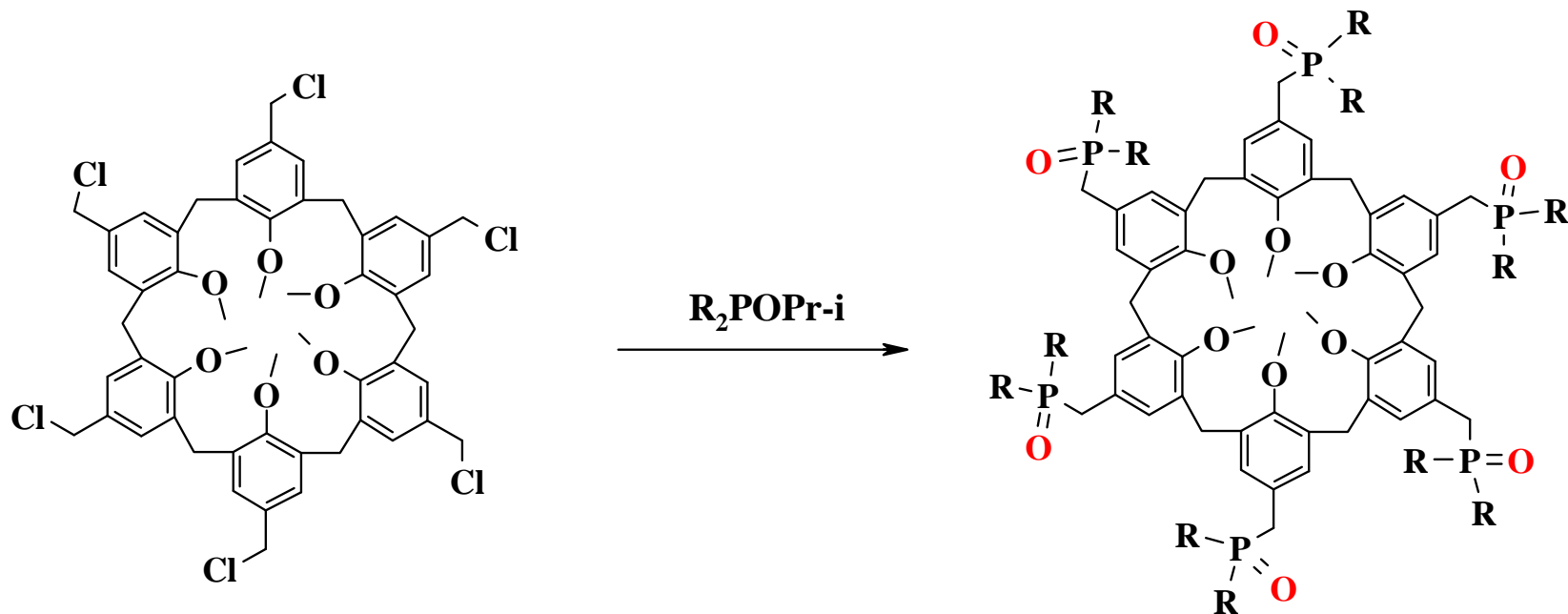
| | |
|-----------------------------------------|-----|
| Alk = Pr, R = Me, R' = Me | 85% |
| Alk = Pr, R = Et, R' = Et | 98% |
| Alk = Pr, R = Pr, R' = Pr | 96% |
| Alk = Pr, R = i-Pr, R' = i-Pr | 83% |
| Alk = Pr, R = Bu, R' = NEt ₂ | 68% |
| Alk = Hex, R = Et, R' = Et | 86% |
| Alk = Hex, R = Bu, R' = Bu | 86% |
| Alk = Hex, R = Ph, R' = Ph | 97% |

J. Incl. Phenom. and Macrocyclic Chem. 2004. 49. 47-56

Radiochim. Acta. 2007. 95. 97-102

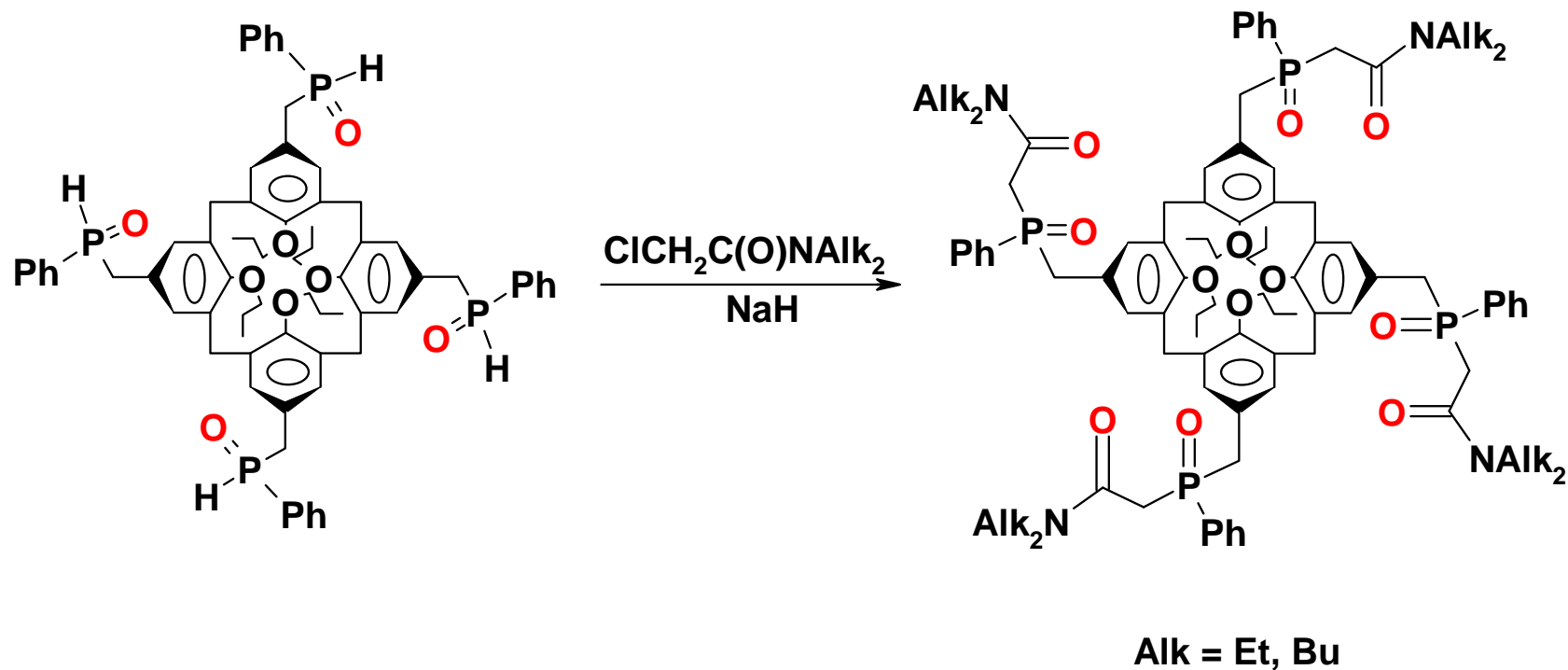
J. Incl. Phenom. and Macrocyclic Chem. 2008. 62. 51-58

Phosphinoylmethyl-Calix[6]arene



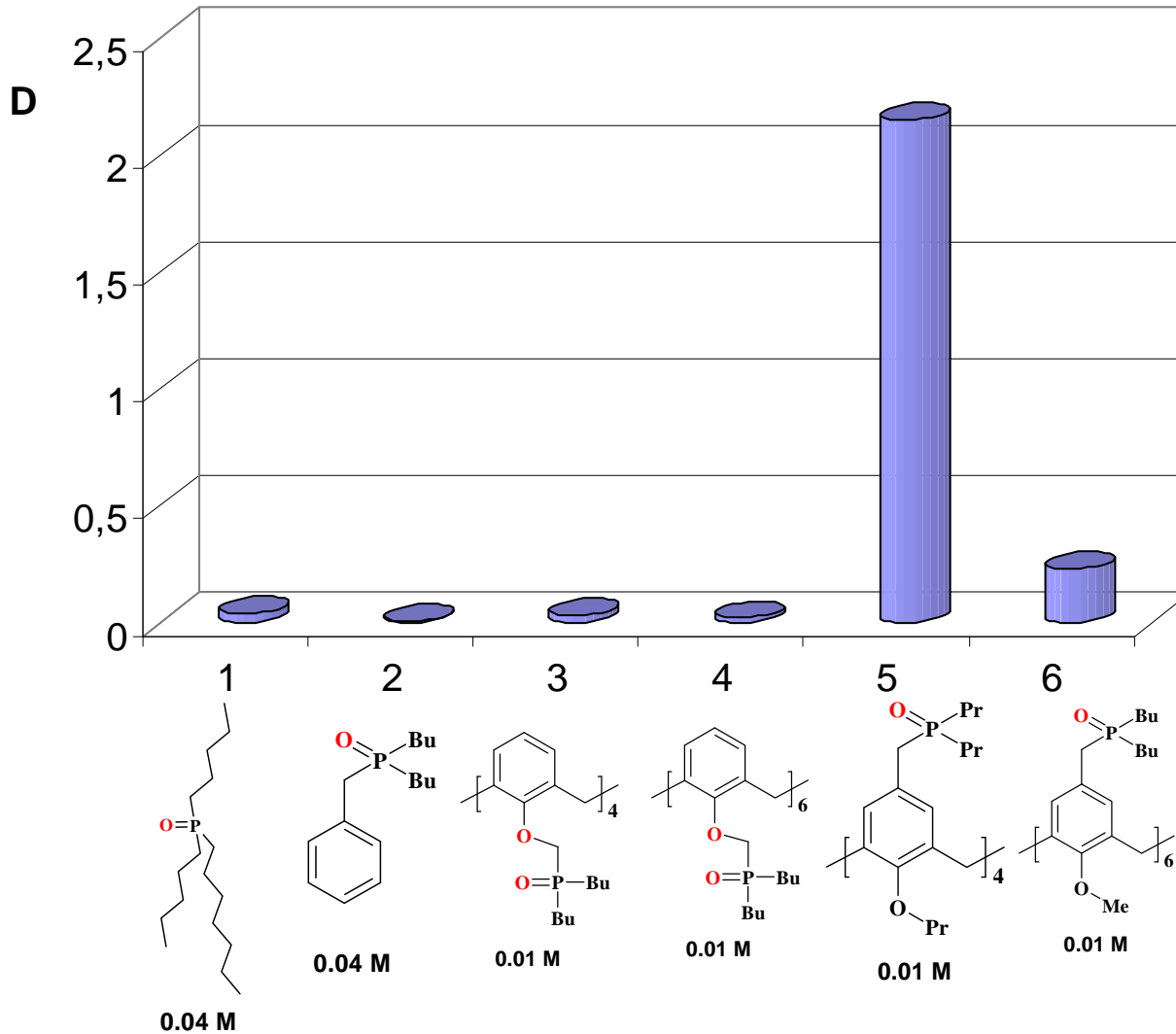
R = Et 92%
R = Bu 64%
R = Ph 93%

Calix[4]arene carbamoyl phosphine oxides



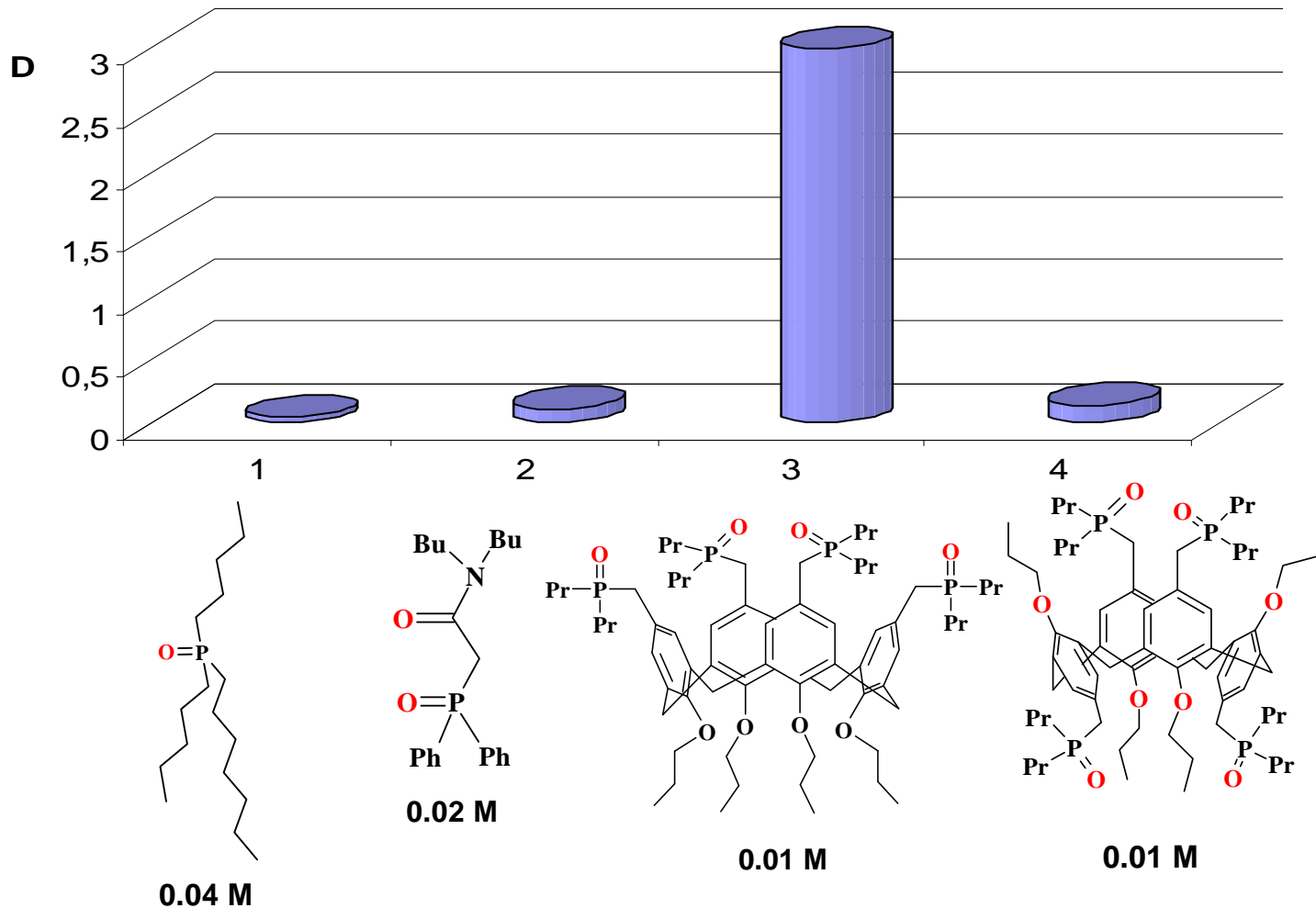
Am³⁺ extraction

Distribution *D* between nitrobenzotrifluoride and HNO₃ (0.1M)



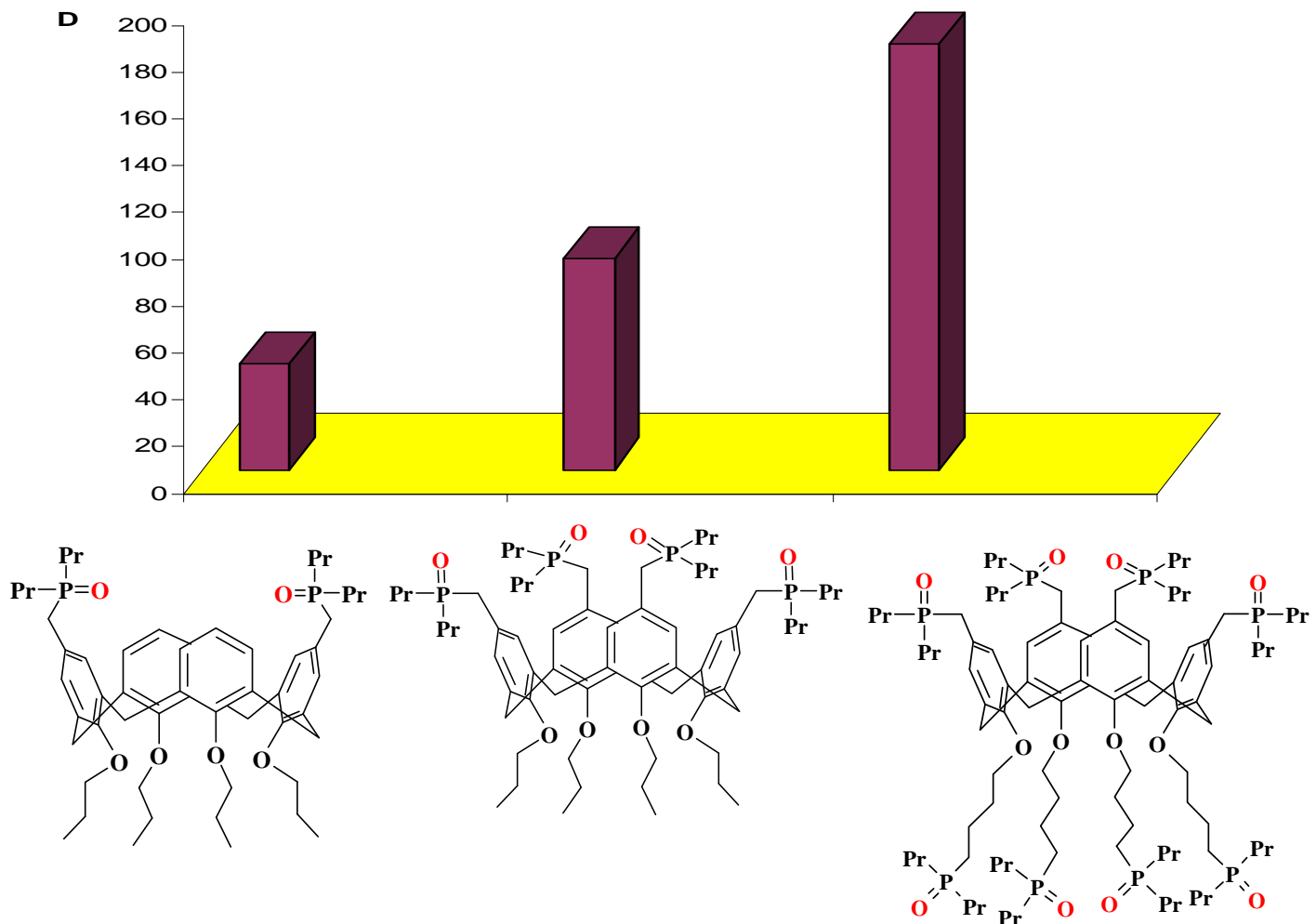
Am³⁺ extraction

Distribution *D* between nitrobenzotrifluoride and HNO₃ (0.1M)



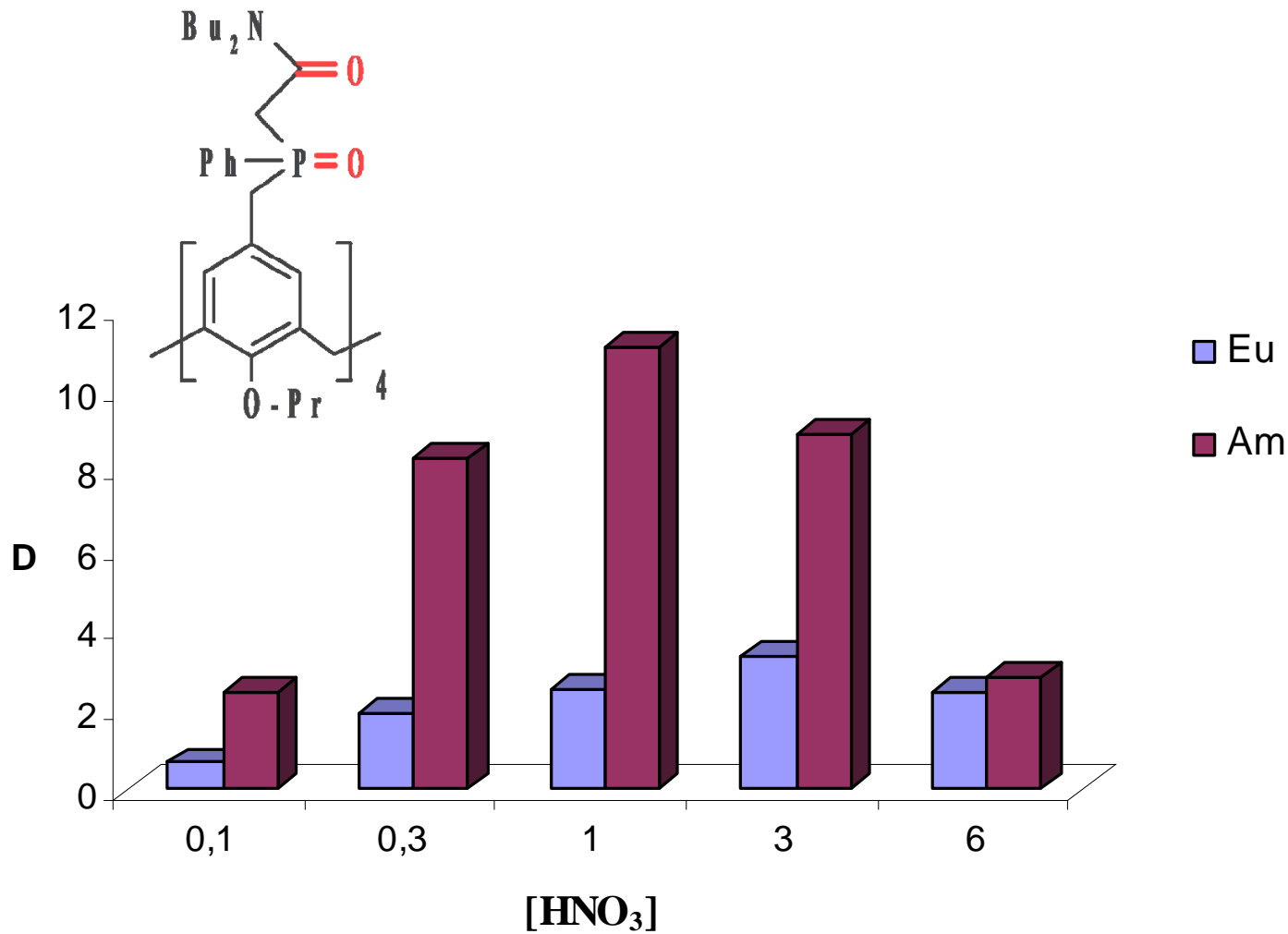
Tc extraction

Distribution D between nitrobenzotrifluoride and HNO_3 (0.3M)



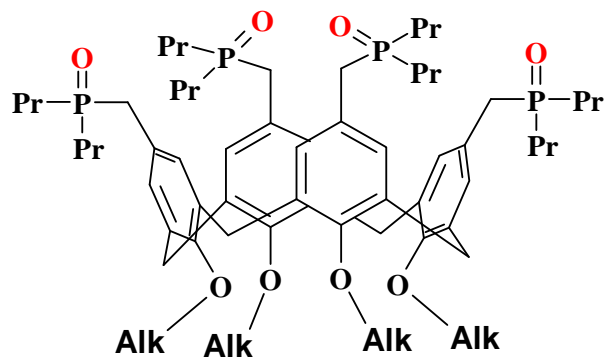
Am³⁺ / Eu³⁺ separation by Calixarene-CMPO

Distribution *D* between nitrobenzotrifluoride and HNO₃



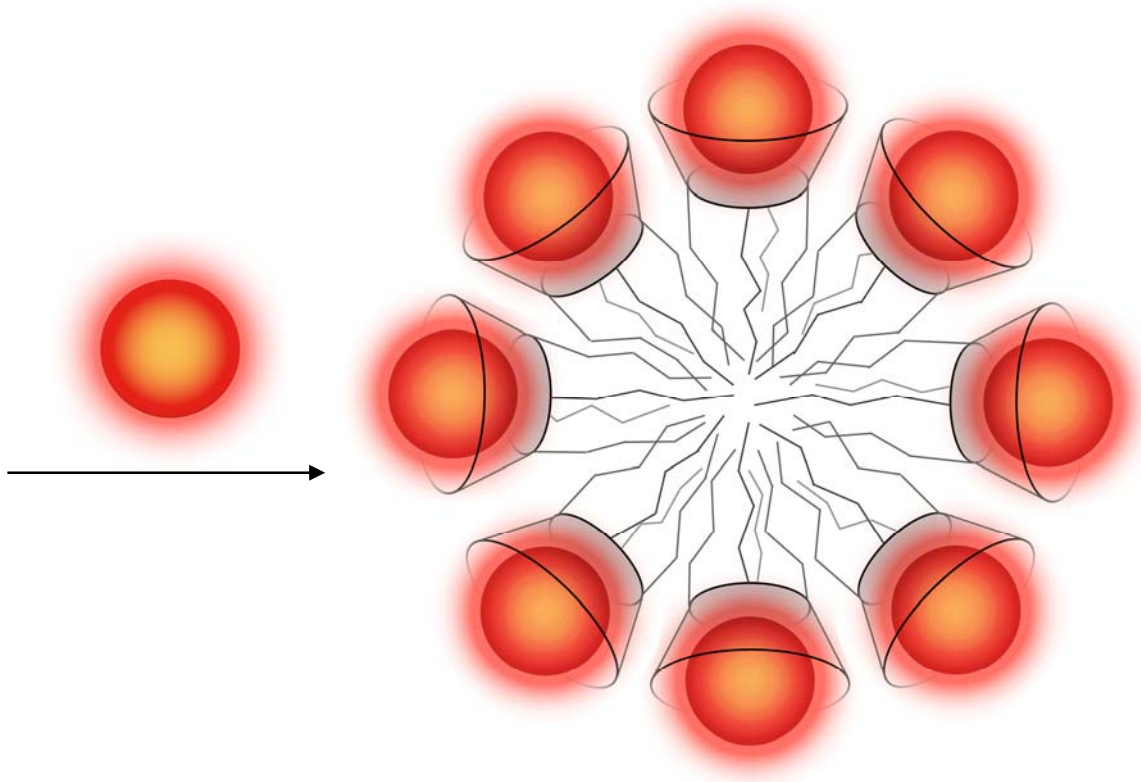
Calixarene Micellar Complex

Hydrophilic Rim



Hydrophobic Rim

Amphiphilic Calixarenes



Micelle-mediated purification of radioactive water of SHELTER (Chernobyl)

Membrane Ultrafiltration

| No | Calixarene-Uranium weight ratio | Uranium conc., mg/L (purification, %) | Activity, Bq/L (purification, %) | | |
|--------|---------------------------------|---------------------------------------|----------------------------------|----------------------------|----------------------------|
| | | | ^{238,239,240} Pu | ²⁴¹ Am | ²⁴⁴ Cm |
| 012/16 | - | 29 | $4.0 \cdot 10^3$ | $2.7 \cdot 10^4$ | $1.2 \cdot 10^3$ |
| | 5:1 | 15 (48.3) | - | - | - |
| 012/5 | - | 32 | $2.1 \cdot 10^3$ | $2.3 \cdot 10^4$ | $1.2 \cdot 10^3$ |
| | 10:1 | 2.5 (92.2) | $9.4 \cdot 10^1$ (95.5) | $2.0 \cdot 10^2$ (99.1) | $1.0 \cdot 10^1$ (99.2) |
| 012/7 | - | 65 | $8.8 \cdot 10^3$ | $1.3 \cdot 10^5$ | $6.6 \cdot 10^3$ |
| | 12.5:1 | 3.4 (94.8) | $2.0 \cdot 10^2$ (97.7) | $4.5 \cdot 10^2$ (99.7) | $2.8 \cdot 10^1$ (99.6) |



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Molecular modelling

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Extraction

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Phosphorylated calixarenes for selective extraction of actinides from radioactive wastes

Thank you !

