**Extraction and complexation of lanthanide ions by**

**dihomooxacalix[4]arene and calix[4]arene tetraketone derivatives:**

**an experimental and molecular dynamics investigation**

**Supporting Information**

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|  |  |  |
| --- | --- | --- |
|  | In acetonitrile, with TfO− | In dichloromethane, with Pic− |
| La3+⊂**1d** |  |  |
|  | *8.9 + 1.0* | *7.1 + 3.9* |
| La3+⊂**2d** |  |  |
|  | *8.0 + 1.0* | *8.0 + 2.0* |
| Yb3+⊂**1d** |  |  |
|  | *4.0 + 3.6* | *5.9 + 4.1* |
| Yb3+⊂**2d** |  |  |
|  | *7.9 + 1.6* | *8.0 + 0.0* |

**Fig. S1**. M3+…calixarene and M3+…anions radial distribution functions (RDFs) as a function of the distance (in Å) in pure acetonitrile and dichloromethane (Ocalixarene, OPic, OTfO are the reference centers). Color codes: M3+…calixarene in red, M3+…ani−ons in blue. Integration numbers (up to 4 Å) of the RDFs are given in italics below the corresponding curves.

MD Simulations

Solute and solvent atom pairs *i* and *j* display Coulomb interactions via their charges *qi* and *qj*. Cross terms in van der Waals interactions were constructed using the Lorentz-Berthelot rules. The structures of the free **1d** and **2d** calixarenes and lanthanide complexes were optimized by QM calculations at the B3LYP/6-31G(d,p) level with large ECPs for La and Yb. Calixarene parameters come from ref [1] with RESP charges calculated on the full uncomplexed calixarene. Lanthanide cations were described with a +3 charge. Water was represented with the TIP3P model [2], acetonitrile with the model from ref [3] and a 5 points model for dichloromethane was used [4]. La3+ and Yb3+ are from ref [5], triflate (TfO−) anions are from Baaden et al. [6] and picrate (Pic−) anion from ref [7]. The solutions were simulated with 3D-periodic boundary conditions, using an atom-based cutoff of 12 Å for non-bonded interactions, and correcting for the long-range electrostatics by using the Ewald summation method. The characteristics of all simulated systems are given in Table S1. The MD simulations were performed at 300 K starting with random velocities. The temperature was monitored via a coupling to a thermal bath using the Berendsen algorithm [8] with a relaxation time of 0.2 ps. In the (NPT) simulations, the pressure was similarly coupled to a barostat with a relaxation time of 0.2 ps. A time step of 2 fs was used to integrate the equations of motion via the Verlet leapfrog algorithm. After 1000 steps of energy minimization, 0.25 ns of dynamics were performed with the ions in order to allow the solvent to relax around the solute. This was followed by a dynamics of 0.25 ns at constant volume and of 1 ns at a constant pressure of 1 atm. The evolution of the mixture was then followed for 50 ns of dynamics (NVT ensemble).

**Table S1.** Characteristics of the simulated systems (composition, box size, time)

|  |  |  |  |
| --- | --- | --- | --- |
| System | Number and type of solvent | Box size  (x,y,z) in Å | Time  (in ns) |
| M3+⊂ **1d**; 3 TfO− | 1500 MeCN | 51.9 x 51.9 x 51.9 | 50 |
| M3+⊂ **2d**; 3 TfO− | 1500 MeCN | 51.9 x 51.9 x 51.9 | 50 |
| M3+⊂ **1d**; 3 Pic− | 650 CH2Cl2 | 42.1 x 42.1 x 42.1 | 50 |
| M3+⊂ **2d**; 3 Pic− | 650 CH2Cl2 | 42.1 x 42.1 x 42.1 | 50 |
| M3+⊂ **1d**; 3 Pic− | 1000 CH2Cl2 + 4000 H2O | 39.1 x 39.1 x 154.1 | 10 |
| M3+⊂ **2d**; 3 Pic− | 1000 CH2Cl2 + 4000 H2O | 39.1 x 39.1 x 154.1 | 10 |

M3+ = La3+ or Yb3+

Free energy profile (PMF simulation)

The change of free energy *G*(*d*) was calculated for the interface crossing of the calixarene as a function of the z position (*d)* of M3+ (see Fig. 6 of main text). We proceed starting from the position of the complexes in the organic phase obtained after the MD simulation (=1), the z position of the cation is then increased by 100 Å ( =0) to move the complex into the aqueous phase, by *d* steps of 0.5 Å. At each step 200 ps of equilibration + 200 ps of sampling were performed. See, for example, ref [9, 10] for computational details and tests at liquid/liquid interfaces.

Changes in free energy were calculated using the thermodynamic integration (TI) method based on Equation (1) [11]:

(1)

Analysis of results

The trajectories were analyzed using our MDS software [12]. Snapshots were drawn with the VMD software [13]. Total potential energy *E*pot and interactions between selected neutral groups (IL ions, MCln ions, water) were calculated using Ewald summation. The radial density functions (RDFs) were calculated, unless otherwise specified, between selected atoms during the last 5 ns of dynamics.

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