

Electronic Supplementary Information

Dimetallic complexes of macrocycles with two rigid dibenzofuran units as receptors for detection of anionic substrates

Feng Li,^{a,f} Sílvia Carvalho,^a Rita Delgado,^{a,b,*} Michael G. B. Drew,^c and Vítor Félix^d

^a Instituto de Tecnologia Química e Biológica, UNL, Av. da República - EAN, 2780-157 Oeiras, Portugal, email: delgado@itqb.unl.pt ^b Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. ^c School of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD UK. ^d Departamento de Química, CICECO, and Secção Autónoma de Ciências da Saúde, Universidade de Aveiro, 3810-193 Aveiro, Portugal.

Dinuclear copper(II) complexes

The thermodynamic stability constants of the dinuclear complexes with both ligands are very high. In the experimental conditions mixture used, MeOH/DMSO (1:1 v/v), mononuclear complexes CuL^{2+} ($\text{L} = [28](\text{DBF})_2\text{N}_6$ and $[32](\text{DBF})_2\text{N}_6$) were not found, and the dinuclear complexes are formed in > 99%, which precludes a direct determination of the stability constants (corresponding to the equilibrium $2 \text{Cu}^{2+} + \text{L} \rightleftharpoons \text{Cu}_2\text{L}^{4+}$). To accomplish this task a competition with another ligand (L') is necessary, for which the knowledge of the stability constant values of its copper(II) complex in the same experimental conditions are required. The amount of supplementary work necessary for this determination is not justified as our aim is the study of the binding behaviour of the Cu_2L^{4+} species as receptors for anions. The spectra corresponding to the titration of $[28](\text{DBF})_2\text{N}_6$ with a copper(II) solution are shown in Fig. S1 together with the mole ratio plot, testifying the complete formation of the complex with 2:1 Cu:L stoichiometry.

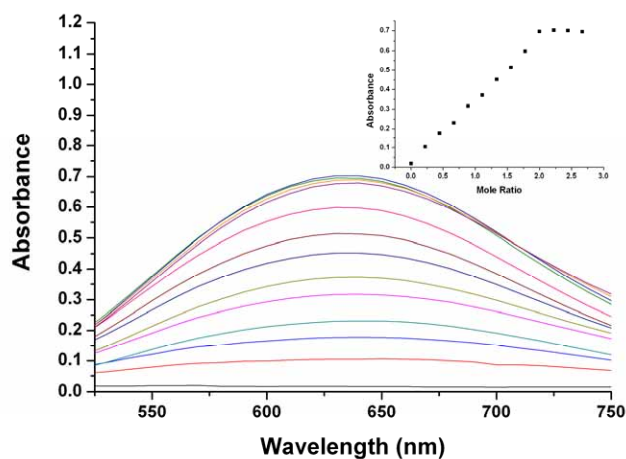


Fig. S1 Absorption spectra obtained by titration of $[28](DBF)_2N_6$ ($1.81 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) with copper(II) ($0.039 \text{ mol} \cdot \text{dm}^{-3}$) in solution with constant steps of 0.020 cm^3 from 0 to 0.200 cm^3 and of 0.050 cm^3 from 0.200 to 0.400 cm^3 . Inset: titration profile of the absorbance at 630 nm in function of the mole ratio. The data were taken in MeOH/DMSO (1:1 v/v) solution and 293.2 K.