Supplementary Material (ESI) for New Journal of Chemistry

Electronic supplementary material for

From dinuclear to tetranuclear zinc complexes through carboxylate donors: structural and luminescence studies

Matilde Fondo,*[a] Ana M. García-Deibe,[a] Noelia Ocampo,[a] Jesús Sanmartín,[b] Manuel R. Bermejo,[b] Elisabete Oliveira,[c] Carlos Lodeiro*[c]

[a] *Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, E-27002 Lugo, Spain. E-mail: qimatf69@usc.es*

[b] *Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*

[c] *REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal. E-mail: lodeiro@dq.fct.unl.pt*

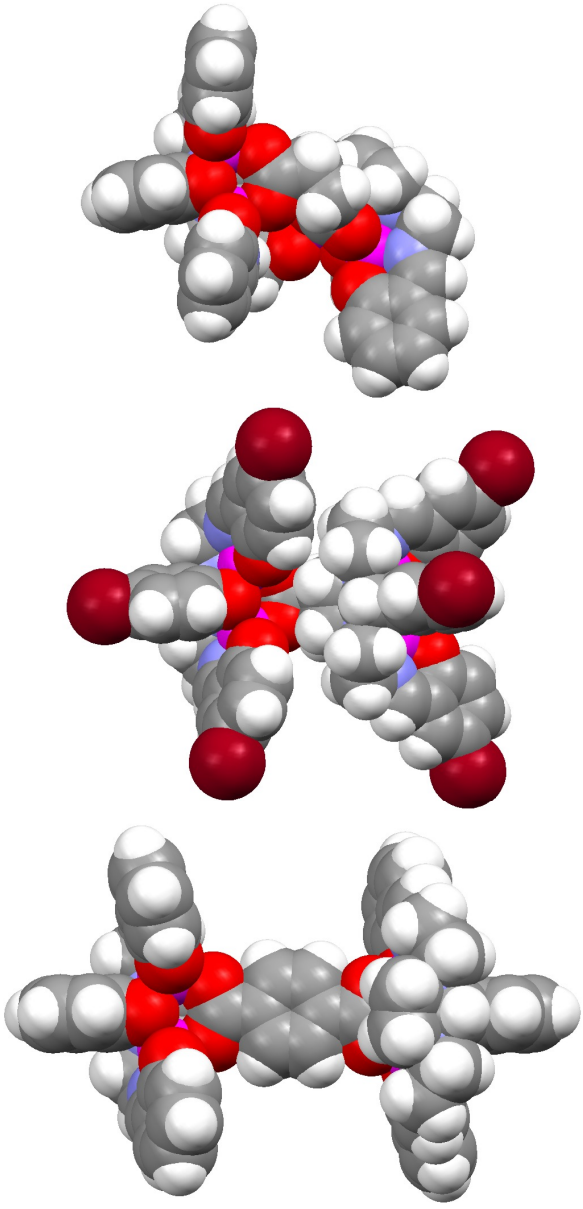

Figure S1 Space-filling diagrams for the molecular structures of the three tetranuclear complexes **2** (top), **3** (middle) and **4** (bottom) comparing their intramolecular arrangements, which clearly depend on the flexibility of their spacers. Flexible ethylene bridges of succinate ligands allow to keep both $[ZnL^{x}]^{+}$ subunits almost perpendicular in two different ways, whereas rigid terephthalate anion separates and turns 180º both dinuclear nodes, as occurred in the corresponding carbonate complex.[11a]

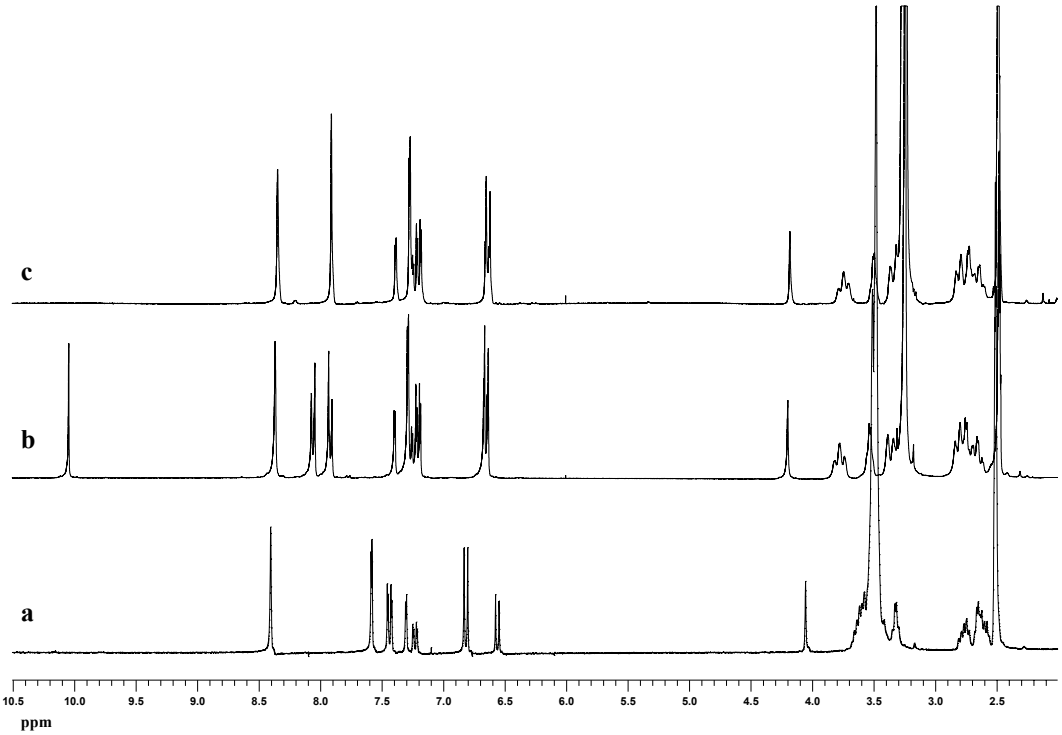

Figure S2 ^{1}H NMR spectra for: a) H_3L^2; b) $[(Zn_2L^2)_2(p\text{-}OOC\text{-}C_6H_4\text{-}CHO)]\cdot 2H_2O$ and c) $[Zn_2L^2(p\text{-}OOC\text{-}C_6H_4\text{-}COO)]\cdot 2H_2O$ in DMSO-d_6

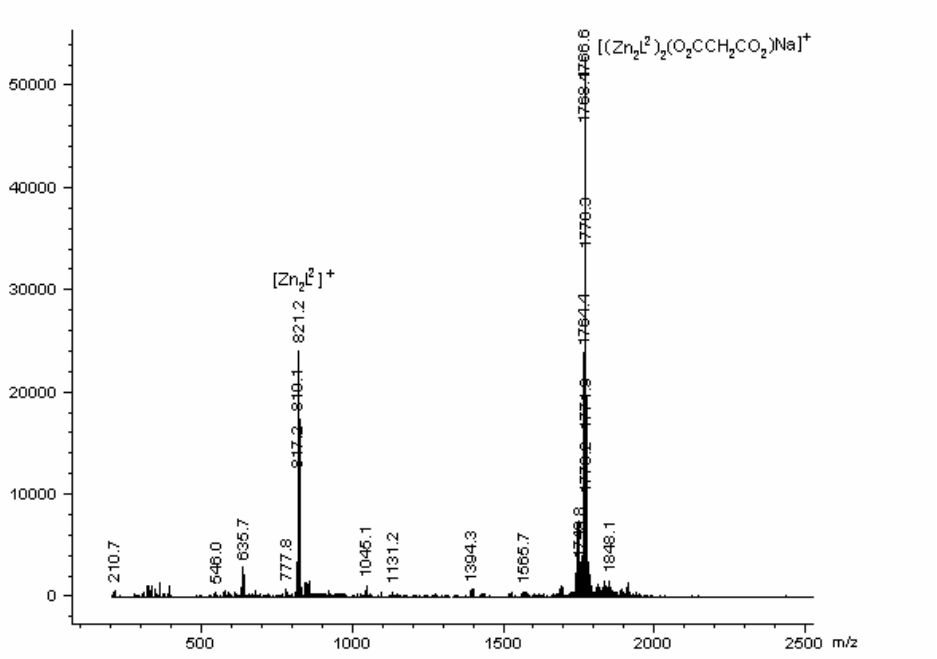

Figure S3 ES mass spectrum for $[(Zn_2L^2)_2(OOC\text{-}CH_2\text{-}COO)]\cdot 6H_2O$ in MeOH as solvent

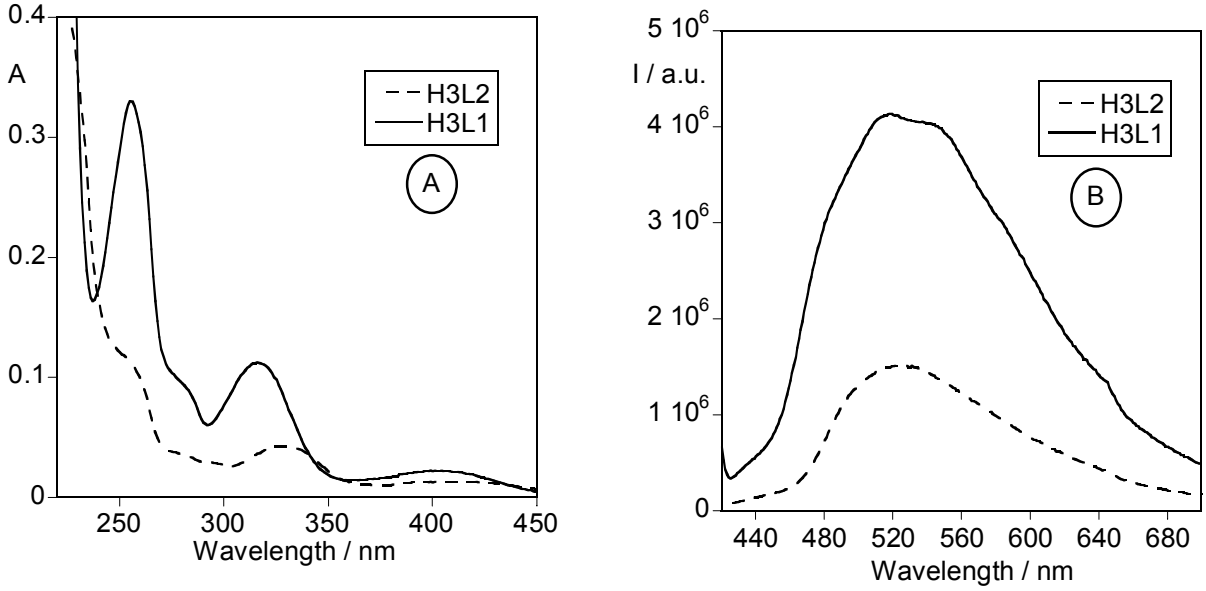

Figure S4 A) Absorption spectrum of ligands H_3L^1 and H_3L^2 in absolute ethanol at 298 K ($[H_3L^1] = [H_3L^2] = 10^{-5}$ M); B) Solid state emission of ligands H_3L^1 and H_3L^2. λexc = 400 nm

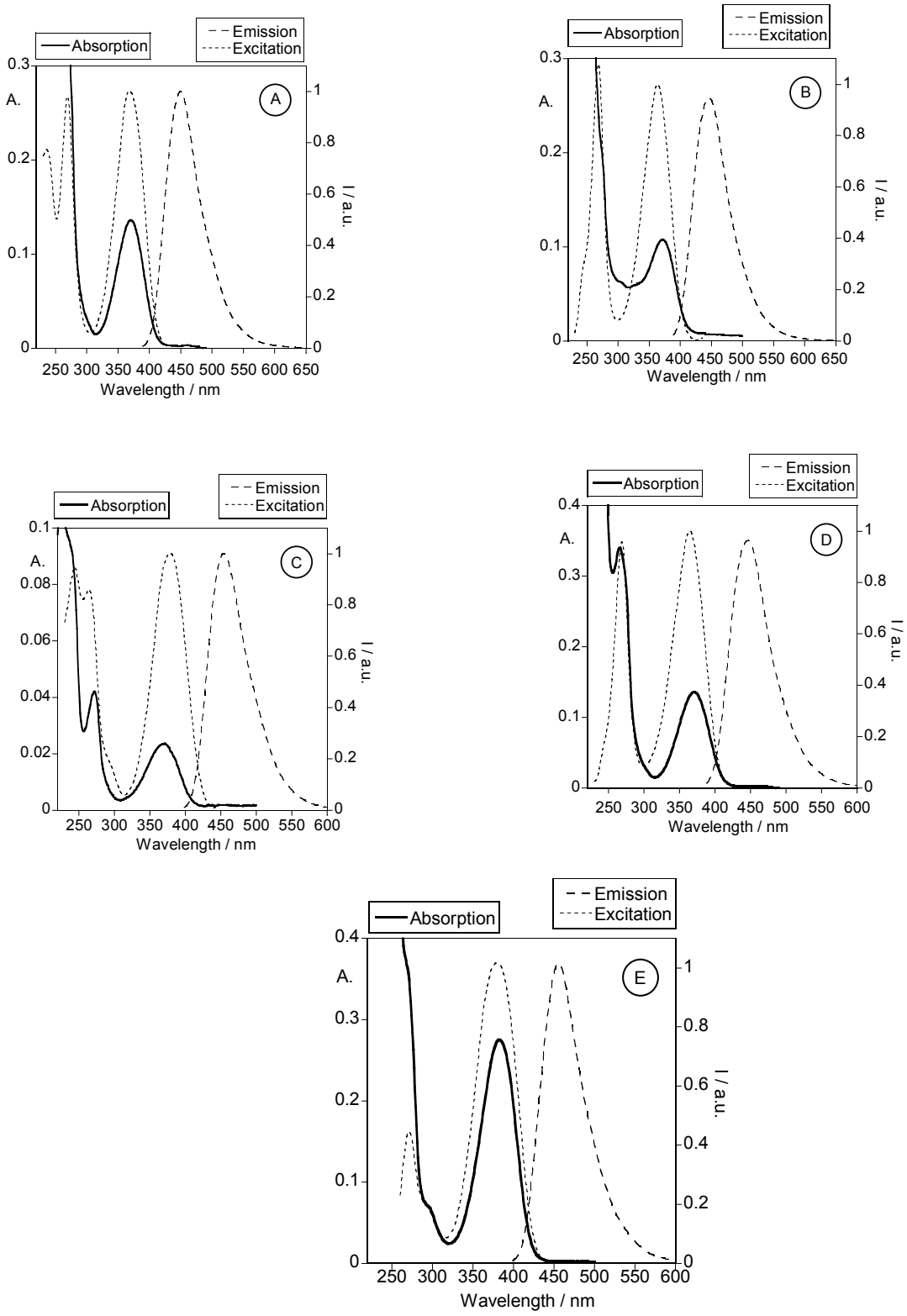

Figure S5 Absorption, emission and excitation spectra of Zn(II) complexes with H_3L^1: A) $[Zn_2L^1(OOC\text{-}C_6H_4\text{-}CHO)]\cdot 4H_2O$ in absolute ethanol (3) ([3] = 10^{-5} M, λexc = 370 nm, 298 K); B) $[Zn_2L^1(o\text{-}OOC\text{-}C_6H_4\text{-}COOH)]\cdot 6H_2O$ in absolute ethanol/DMSO 90/10 v/v (5) ([5] = 10^{-5} M, λexc = 370 nm, 298 K); C) $[(Zn_2L^1)_2(OOC\text{-}CH_2\text{-}COO)]\cdot 10H_2O$ in absolute ethanol (7) ([7] = 10^{-6} M, λexc = 380 nm, 298 K); D) $[(Zn_2L^1)_2(p\text{-}OOC\text{-}C_6H_4\text{-}COO)]\cdot 11H_2O$ in absolute ethanol/DMSO 90/10 v/v (9) ([9] = 10^{-5} M, λexc = 370 nm, 298 K); E) $[(Zn_2L^1)_2(O_2C\text{-}CH_2CH_2\text{-}CO_2)]\cdot 4.25H_2O$ in DMSO (11) ([11] = 10^{-5} M, λexc = 370 nm, 298 K)

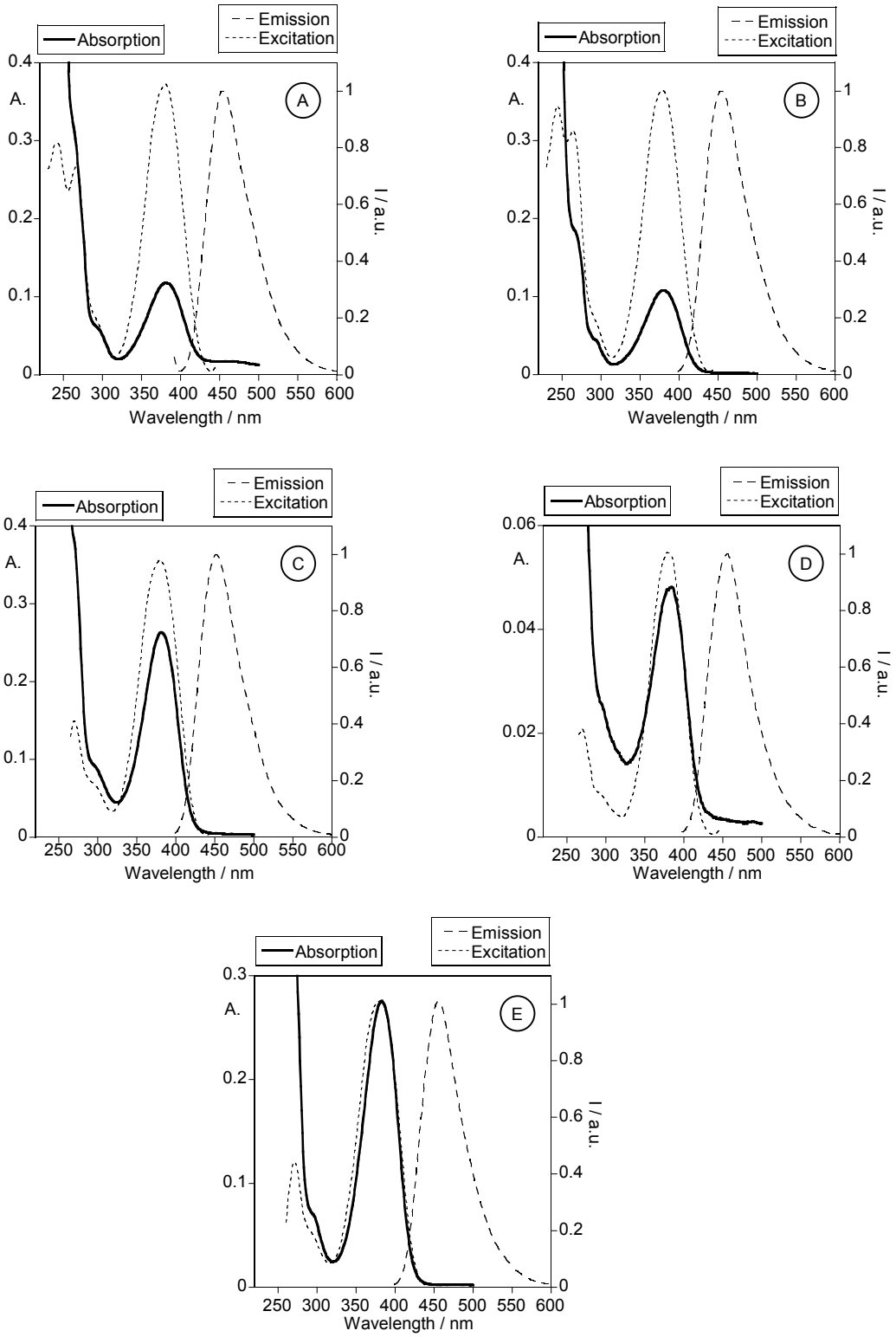

Figure S6 Absorption, emission and excitation spectra of Zn(II) complexes with H_3L^2: A) $[Zn_2L^2(OOC\text{-}C_6H_4\text{-}CHO)]\cdot 2H_2O$ (4) in absolute ethanol ([4] = 10^{-5} M, λexc = 382 nm, 298 K); B) $[Zn_2L^2(o\text{-}OOC\text{-}C_6H_4\text{-}COOH)]\cdot 3H_2O$ in absolute ethanol (6) ([6] = 10^{-5} M, λexc = 380 nm, 298 K); C) $[(Zn_2L^2)_2(OOC\text{-}CH_2\text{-}COO)]\cdot 10H_2O$ in DMSO (8) ([8] = 10^{-5} M, λexc = 381 nm, 298 K); D) $[(Zn_2L^2)_2(p\text{-}OOC\text{-}C_6H_4\text{-}COO)]\cdot 2H_2O$ in DMSO (10) ([10] = 3.55 x 10^{-5} M, λexc = 372 nm, 298 K); E) $[(Zn_2L^2)_2(O_2C\text{-}CH_2CH_2\text{-}CO_2)]\cdot 5H_2O$ in DMSO (12) ([12] = 1.05 x 10^{-5} M, λexc = 372 nm, 298 K).