Electronic Supplementary Information for:

Towards large area surface functionalization with luminescent and magnetic lanthanoid complexes

Guillem Gabarró-Riera,[a,b] Jesús Jover,[b,c] Juan Rubio Zuazo,[d,e] Elena Bartolomé,[f] E. Carolina Sañudo[a,b]*

[a] Institut de Nanociència i Nanotecnologia, Universitat de Barcelona (IN2UB), 08028 Barcelona, Spain

[b] Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, C/Martí i Franqués 1-11, 08028, Barcelona, Spain

[c] Institut de Química Teòrica i Computacional, Universitat de Barcelona, (IQTC-UB), 08028, Barcelona, Spain

[d] BM25-SpLine beamline at the ESRF, 71 Avenue des Martyrs, 38043, Grenoble, France

[e] Instituto de Ciencia de Materiales de Madrid-CSIC, Sor Juana Inés de la Cruz, 3, Cantoblanco, 28049 Madrid, Spain
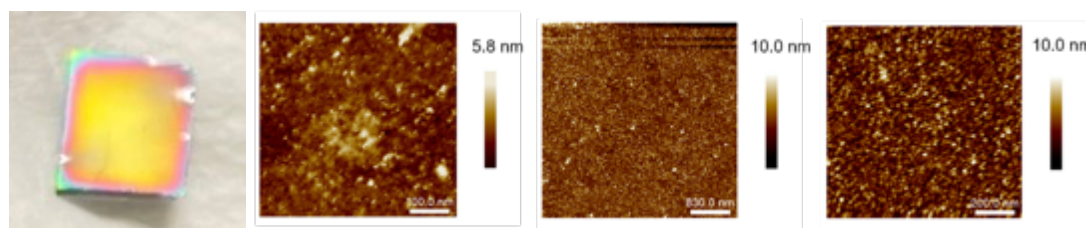
[f] Escola Universitària Salesiana de Sarrià (EUSS), Passeig Sant Joan Bosco, 74, 08017 Barcelona, Spain
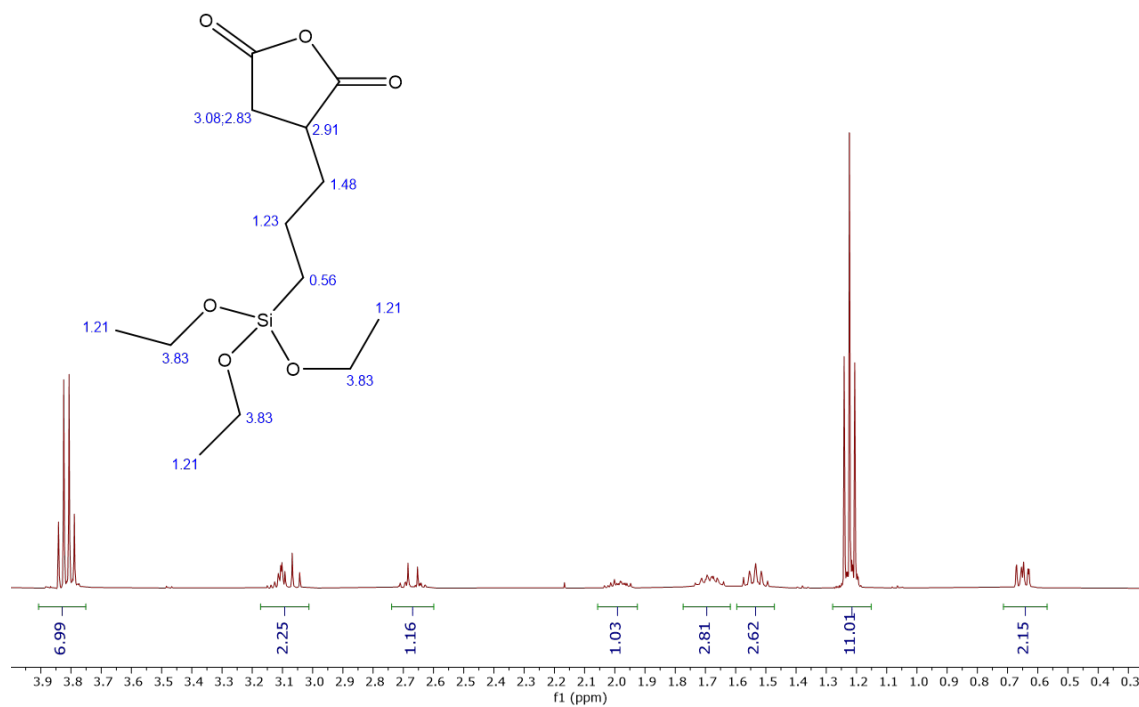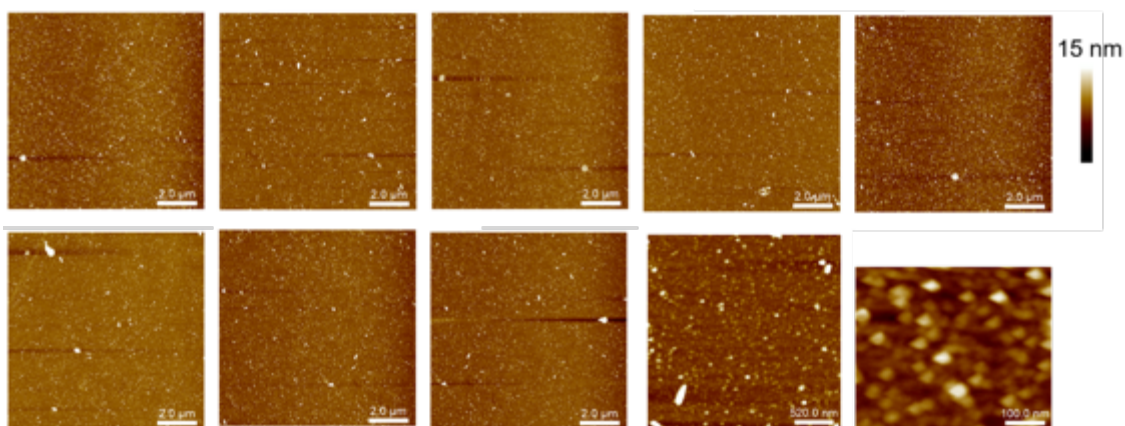
Figure S1. ¹H NMR spectrum for the silane [(3-triethoxysilyl)propyl]succinic anhydrid in deuterated CDCl₃.
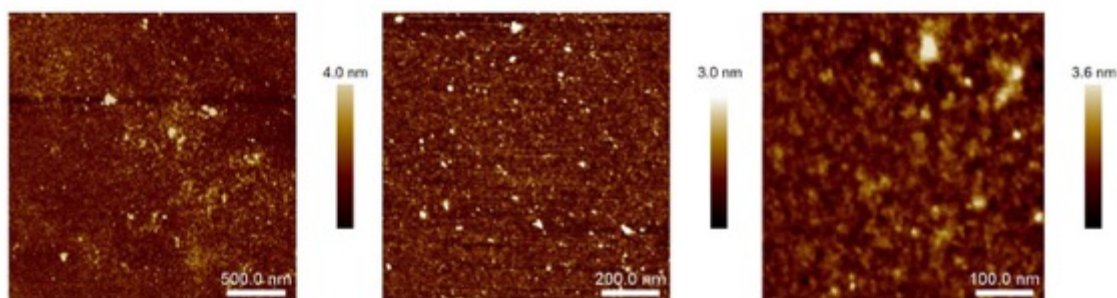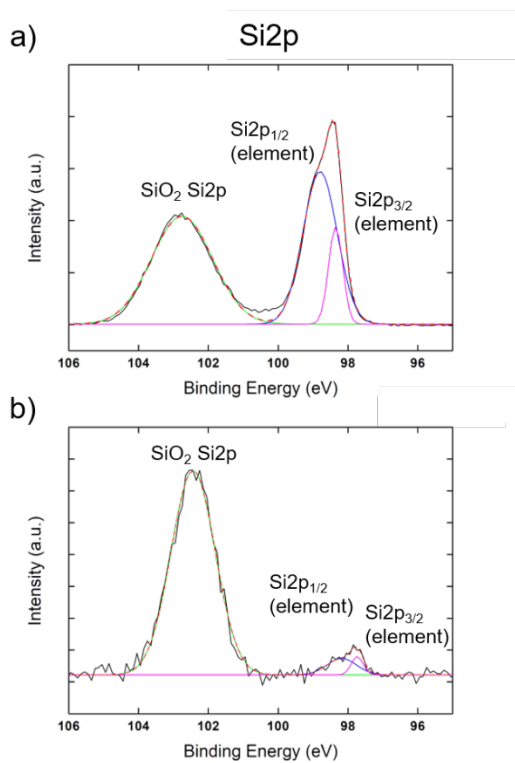

Figure S2. AFM images of Si-TSP.

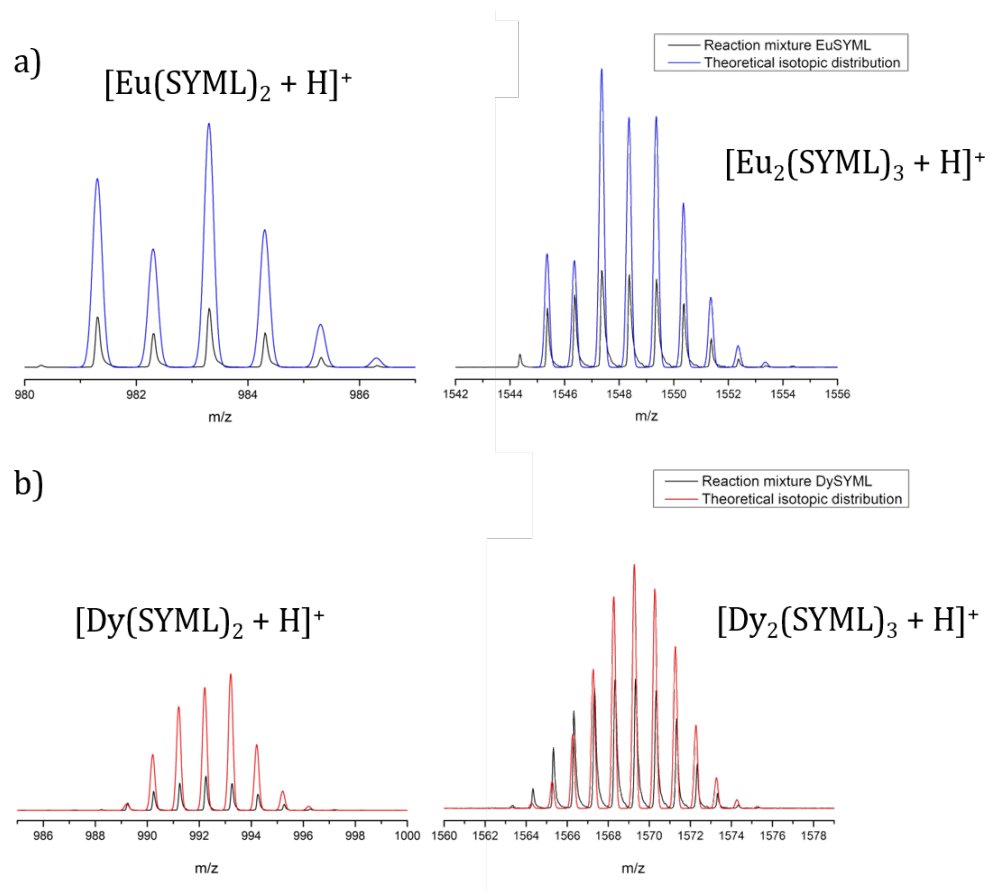**Figure S3** . Picture of **1Si-3**, where bulk-like layers of **1** can be observed with the naked eye and AFM images of **2Si-2** after 24 h deposition time.

Figure S4. Set of AFM images of **1Si-1** on different parts of the same 0.5 cm x 0.5 cm wafer, corroborating the homogeneity of the surface.

Figure S5. Comparison between Si2p XPS peaks of (a) **2Si-1** (1 nm thick layer) and (b) **2Si-2** (4 nm thick layer).

a)

$[Eu(SYML)_2 + H]^+$

$[Eu_2(SYML)_3 + H]^+$

— Reaction mixture EuSYML
— Theoretical isotopic distribution

b)

$[Dy(SYML)_2 + H]^+$

$[Dy_2(SYML)_3 + H]^+$

— Reaction mixture DySYML
— Theoretical isotopic distribution

Figure S6. MALDI-ToF peaks from the reaction mixture of **1** (a) and **2** (b).
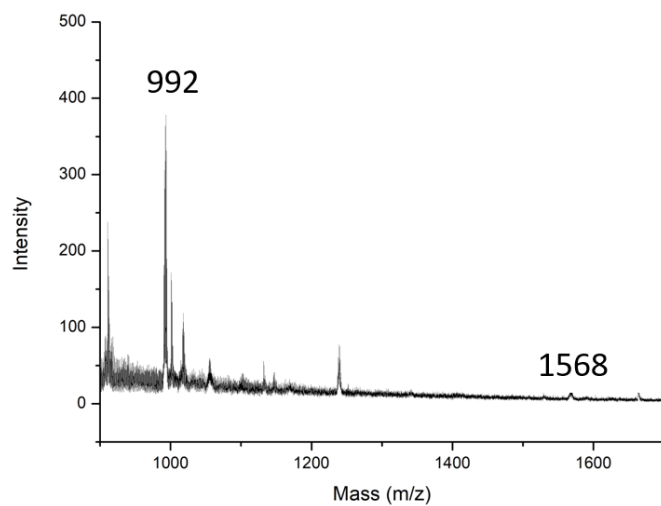
Figure S7. The MALDI-ToF spectra from **2Si-2** (4 nm thick layer).
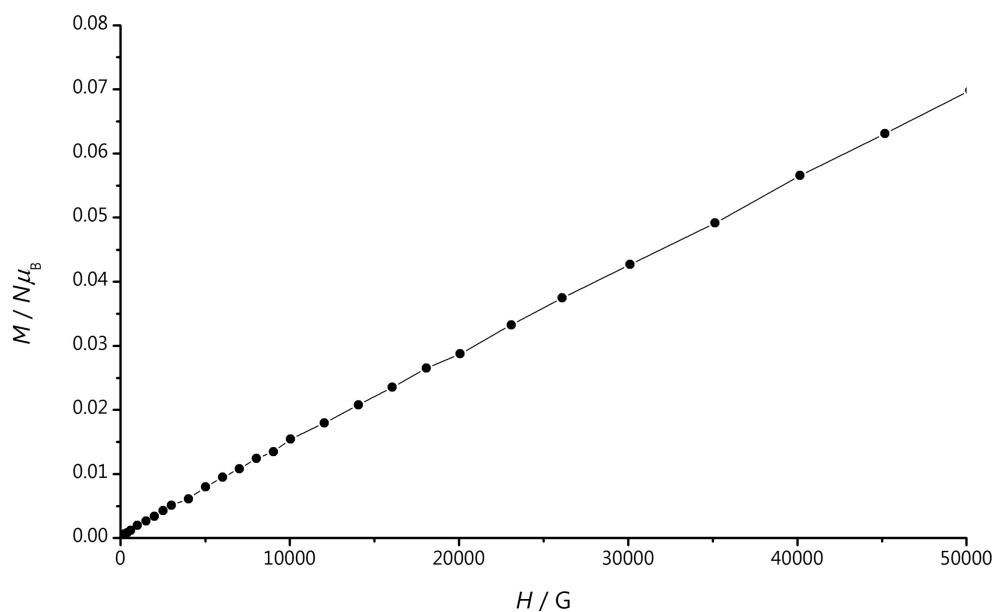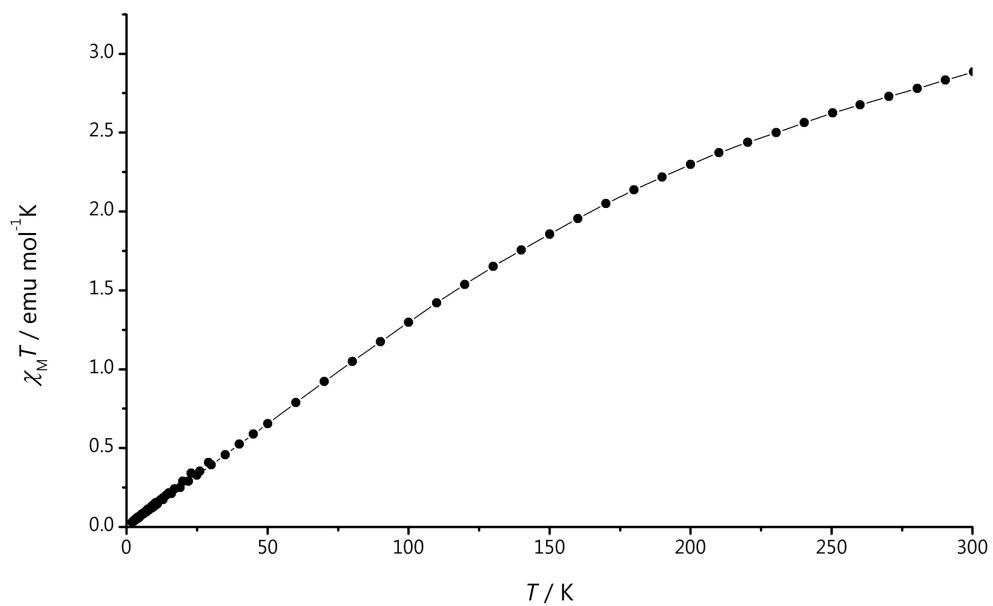
Figure S8. Magnetism for **1** [(Eu$_2$(SYML)$_3$(H$_2$O)]·H$_2$O. The χT value decreases as T decreases, to a value of nearly zero at 2 K, in agreement with weak antiferromagnetic interactions between the Eu(III) ions. The magnetization vs. field data at 2 K are in agreement with a diamagnetic ground state at 2 K with population of excited states due to the Zeeman effect as the field increases.

Computational details: *Ab initio* calculations

The *ab initio* magnetic study of complexes **1** and **2** was carried out using the dinuclear units extracted from the crystal structures. The electronic structure of the complexes, including spin-orbit effects, was computed with CASSCF as implemented in the openMolcas 18.09 package. [1] In these calculations one of the central Eu or Dy atoms was replaced by the diamagnetic analog La(III) in order to eliminate the magnetic interaction between lanthanoid centers and thus, to produce a clean spin-orbit pattern. In order to get the electronic structure for each lanthanoid, two independent calculations were performed for each complex. *Ab initio* CASSCF(7,6) calculations, including 7, 140, 113 and 123 states for septet, quintet, triplet and singlet multiplicities, respectively, were performed for complex **1**. In the case of complex **2**, these calculations imply a (7,9) active space for which 21, 128, and 98 states were considered to describe the sextet, quartet, and doublet multiplicities, respectively. The all-electron ANO-RCC basis set [2] was employed in these calculations, including the following contractions: Eu, Dy and La [8s7p4d3f2g1h], O and N [4s3p2d1f] and [3s2p1d] for atoms directly attached or far away from the metal centers, respectively, C [3s2p] and H [2s]. The spin−orbit coupling was introduced as implemented in the Restricted Active Space State Interaction (SO-RASSI) approach, and the magnetic properties were obtained with the SINGLE_ANISO code. [3]

The Magellan software [4,] has been employed to estimate the main anisotropy axis for the Dy atoms in compound **2**.

References

[1] I. Fdez. Galván, M. Vacher, A. Alavi, C. Angeli, F. Aquilante, J. Autschbach, J. J. Bao, S. I. Bokarev, N. A. Bogdanov, R. K. Carlson, L. F. Chibotaru, J. Creutzberg, N. Dattani, M. G. Delcey, S. S. Dong, A. Dreuw, L. Freitag, L. M. Frutos, L. Gagliardi, F. Gendron, A. Giussani, L. González, G. Grell, M. Guo, C. E. Hoyer, M. Johansson, S. Keller, S. Knecht, G. Kovačević, E. Källman, G. Li Manni, M. Lundberg, Y. Ma, S. Mai, J. P. Malhado, P. Å. Malmqvist, P. Marquetand, S. A. Mewes, J. Norell, M. Olivucci, M. Oppel, Q. M. Phung, K. Pierloot, F. Plasser, M. Reiher, A. M. Sand, I. Schapiro, P. Sharma, C. J. Stein, L. K. Sørensen, D. G. Truhlar, M. Ugandi, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, O. Weser, T. A. Wesołowski, P.-O. Widmark, S. Wouters, A. Zech, J. P. Zobel, R. Lindh, *J. Chem. Theor. Comput.* **2019**, *15*, 5925-5964.

[2] a) B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, *J. Phys. Chem. A* **2004**, *108*, 2851-2858; b) B. O. Roos, V. Veryazov, P.-O. Widmark, *Theo. Chem. Acc.* **2004**, *111*, 345-351; c) B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, *J. Phys. Chem. A* **2005**, *109*, 6575-6579; d) B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, *Chem. Phys. Lett.* **2005**, *409*, 295-299; e) L. Ungur, L. F. Chibotaru, *Phys. Chem. Chem. Phys.* **2011**, *13*, 20086-20090; f) L. F. Chibotaru, L. Ungur, *J. Chem. Phys.* **2012**, *137*, 064112.

[3] a) L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet, D. Luneau, *J. Am. Chem. Soc.* **2008**, *130*, 12445-12455; b) L. F. Chibotaru, L. Ungur, A. Soncini, *Angew. Chem. – Int. Ed.* **2008**, *47*, 4126-4129.

[4] N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny, A. Soncini, *Nat. Commun.* **2013**, *4*, 2551.