A selective fluorescent probe for Gadolinium^{III} in water based on a Pd^{II} - preorganized chromone-receptor

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Electronic Supplementary Information

Additional crystal description

In the asymmetric unit of [Pd(H$_{-2}$**L2**)](H$_2$O)$_6$ one [Pd(H$_{-2}$**L2**)] complex and six crystallization water molecules are present.

Similarly to the complexes of the analogous ligand (H$_{-2}$**L1**)$^{-2}$, N1, N2, O1 and O4 are quite coplanar (being the maximum deviation due to N2, 0.023(6) Å), with the Pd(II) cation lying on the mean plane defined by these four atoms.

The aromatic rings form an angle of 19.2(1) and 15.2(1)°, respectively, with the mean plane defined by the four coordinating atoms (see Table S1), while the angle between them is 20.3(1)°. Finally, the two methyl groups point in opposite direction with respect to the coordinating plane (see Fig. 1, main text).

A search performed in the CSD[21main text] allowed us to retrieve 25 structures of metal complexes having the fragment reported in Scheme S2. None of these is a palladium complex and six have as ligand the related ligand **L1** (see main text for more details).[22main text]

Table S1. Selected bond distances (Å) and angles (°) for [Pd(H$_{-2}$**L2**)](H$_2$O)$_6$.

Distances	(Å)	Angles	(°)
Pd1-O1	2.006(4)	O1-Pd1-O4	87.4(2)
Pd1-O4	2.014(4)	O1-Pd1-N1	91.6(2)
Pd1-N1	2.038(5)	O1-Pd1-N2	179.0(2)
Pd1-N2	2.033(5)	O4-Pd1-N1	177.6(2)
O1···O4	2.777(6)	O4-Pd1-N2	93.6(2)
O1···O3	2.661(6)	N1-Pd1-N2	87.4(2)
O3···O6	6.018(6)		
O4···O6	2.703(5)	N1-C1-C13-N2	-53.8(7)
		A / B^1	19.2(1)
		A / C	15.2(1)
		B / C	20.3(1)

A = mean plane defined by: O1, O4, N1, N2; B = mean plane defined by the non-hydrogen atoms of the 3-hydroxy-4-chromone bearing the O1-O3 oxygen atoms; C = mean plane defined by the mean plane defined by non-hydrogen atoms of the 3-hydroxy-4-chromone bearing the O4-O6 oxygen atoms.
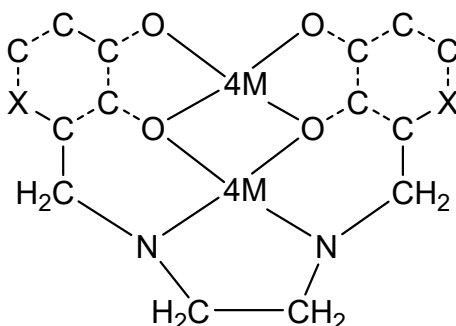
Scheme S1. Fragment searched in the CSD. X = any atom; 4M = any metal: dashed line = any bond type.
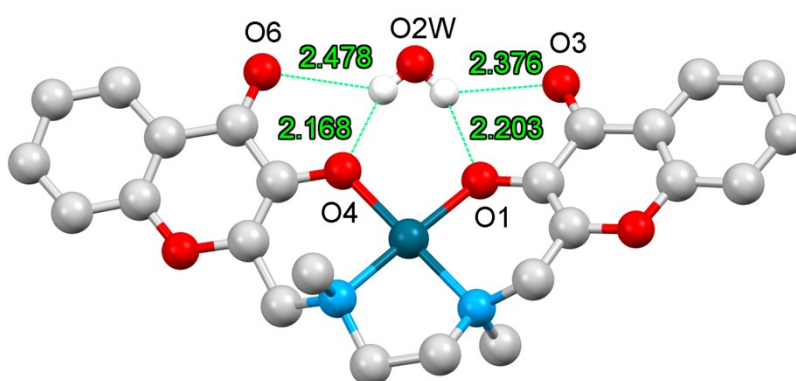
**Figure S1.** Ball and stick view of the water molecule (O2w) in the negative pocket of [Pd(H$_{-2}$**L2**)].

Concerning the crystal packing, due to the presence of a $\pi\cdots\pi$ interaction (distance between the centroid of one 3-hydroxy-4-chromone moiety and the mean plane containing the other ring= 2.288(7) Å; angle between the line connecting the centroids of the two rings and the mean plane defined by one ring = 16.0(2)°) involving one 3-hydroxy-4-chromone moiety and a symmetry related unit (-x+1, -y+1, -z+1), a dimer is formed (see Figure S2).

These dimers are connected *via* a net of hydrogen bonds that involves the six crystallization water molecules giving rise to a ribbon the propagates along the b axis direction. Such ribbons interact *via* weak hydrogen bonds.

**Table S2.** Selected hydrogen bond distances (Å) and angles (°) for [Pd(H$_{-2}$**L2**)](H$_2$O)$_6$.

X-H···Y	X···Y (Å)	H···Y (Å)	X-H···Y (°)
O1w-H1w1···O4w	2.867(9)	2.040(6)	168(6)
O1w-H1w2···O1[1]	2.854(8)	2.02(2)	170(2)
O2w-H2w1···O4	2.882(6)	2.17(5)	144(2)
O2w-H2w1···O6	3.104(6)	2.48(3)	132(2)
O2w-H2w2···O1	2.916(6)	2.20(4)	144(3)
O2w-H2w2···O3	2.985(6)	2.37(5)	131(3)
O3w-H3w2···O1w[2]	2.780(8)	1.97(6)	161(6)
O3w-H3w1···O5w[3]	2.992(7)	2.19(6)	160(5)
O4w-H4w2···O6w[4]	2.856(7)	2.07(5)	154(5)
O4w-H4w1···O5w[5]	2.839(9)	2.10(8)	146(7)
O5w-H5w2···O4w	3.081(8)	2.26(4)	164(3)
O5w-H5w1···O2w	2.771(8)	1.93(3)	171(2)
O6w-H6w2···O3w	2.828(9)	2.05(4)	154(4)
O6w-H6w1···O6[2]	2.941(7)	2.22(6)	144(3)

[1]= x,y+1,z; [2]= x-1/2,-y+3/2, z-1/2; [3]= x-1/2,-y+1/2, z-1/2; [4]= -x+1,-y+1,-z+1; [5]= -x+3/2, y+1/2,-z+3/2
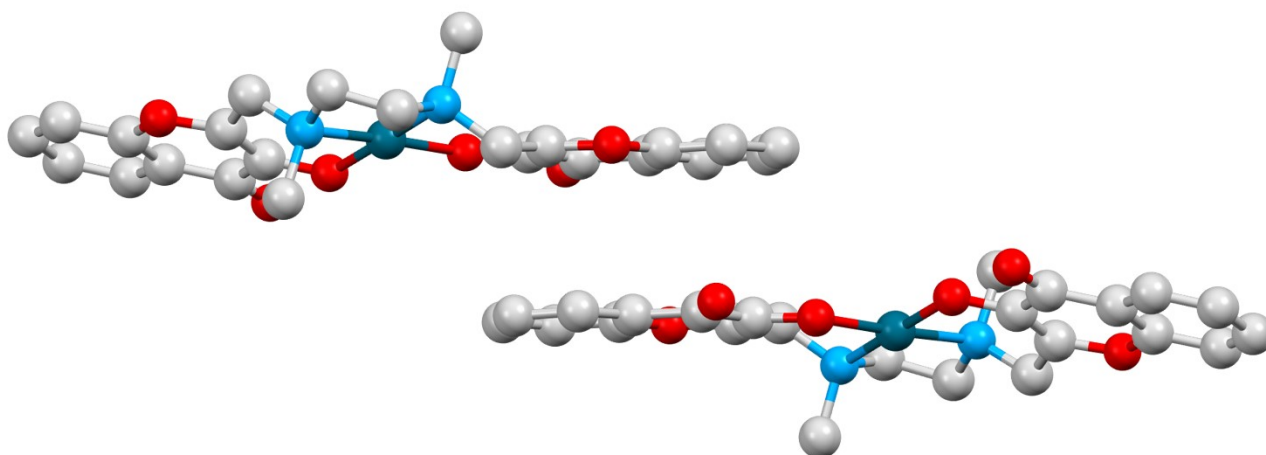
Figure S2. [Pd(H$_{-2}$**L2**)] dimer.

**Table S3**. Crystallographic data and refinement parameters for [Pd(H$_{-2}$**L2**)](H$_2$O)$_6$.

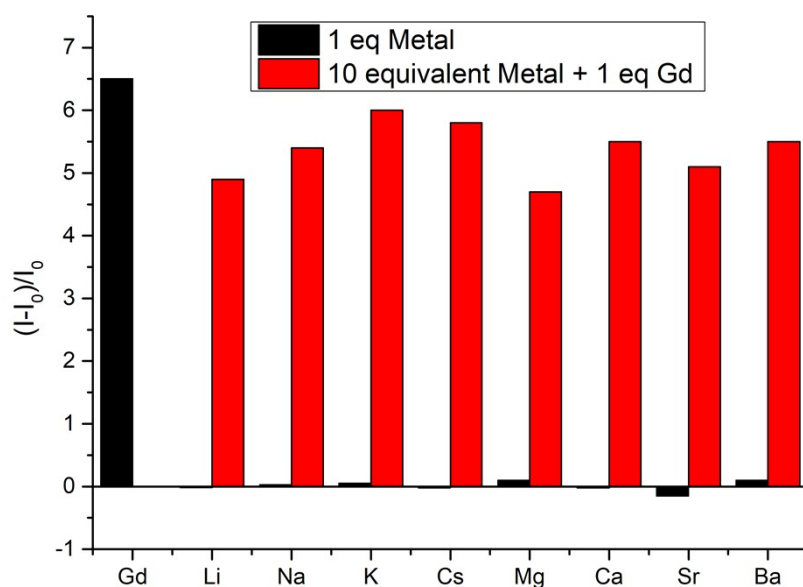|	[Pd(H$_{-2}$**L2**)](H$_2$O)$_6$
Formula	C$_{24}$H$_{34}$N$_2$O$_{12}$Pd
M	648.93
T (K)	100
λ (Å)	1.54184
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions (Å, °)	a = 13.8990(5)
	b = 9.2755(5); β = 100.880(5)
	c = 20.2093(5)
V (Å^3)	2558.6(3)
Z, ρ (mg/cm3)	4, 1.685
μ (mm^{-1})	6.468
F(000)	1336
Crystal size	0.22 X 0.28 X 0.32
2θ range (°)	8.52 − 144.96
Reflns collected / unique (R$_{int}$)	19062 / 5059 (0.1034)
Data / parameters	5059 /388
Final R indices [I > 2σ]	R1 = 0.0606, wR2 = 0.1317
R indices (all data)	R1 = 0.0926, wR2 = 0.1498
GoF	1.063
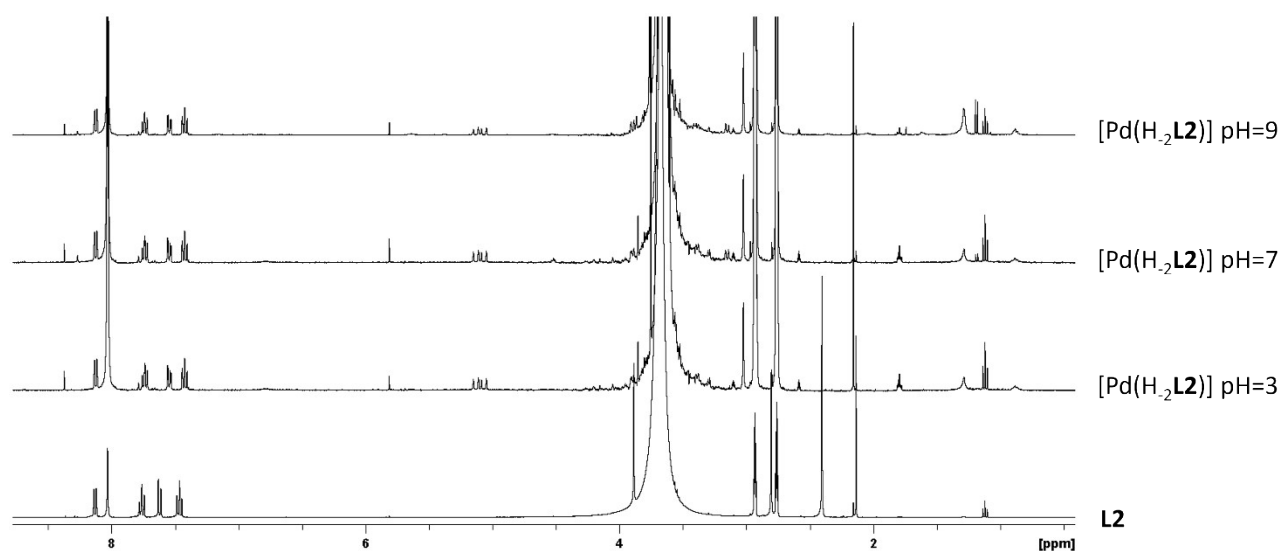
Figure S3. ¹H-NMR spectra of ligand **L2** and [Pd(H₋₂**L2**)] complex in DMF-*d7* prepared at pH=3, 7 and 9. The complex were obtained as crystals by adding one equiv. of K₂PdCl₄ to a hydroalcoholic solution of **L2** and setting the pH value at 3, 7 and 9. The three solid complexes were filtered, washed, dried and dissolved in DMF-*d7* to acquire the spectra.
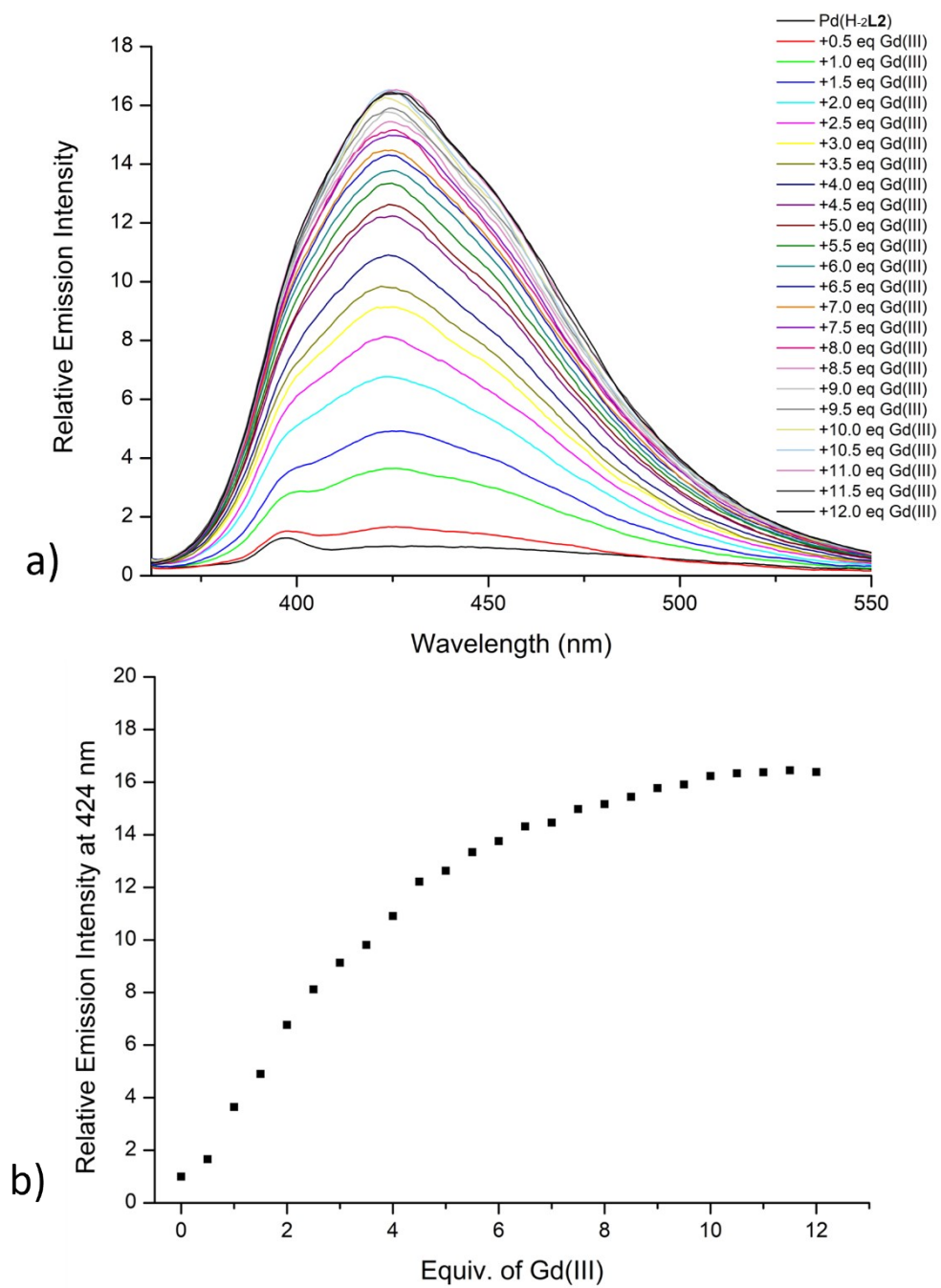
**Figure S4.** a) Fluorescence titration of [Pd(H$_{-2}$**L2**)] with Gd^{III} in aqueous solution at pH=7 (TRIS 10^{-3} mol dm^{-3}). b) Trend of the emission intensity at 424 nm as a function of equiv. of Gd^{III} added. Experimental conditions: [[Pd(H$_{-2}$**L2**)]]= 1·10^{-5} mol dm^{-3}, addition of 0→12 equiv. of Gd^{III} as an aqueous solution of Gd$_2$(SO$_4$)$_3$ (λ$_{ex}$=350 nm).
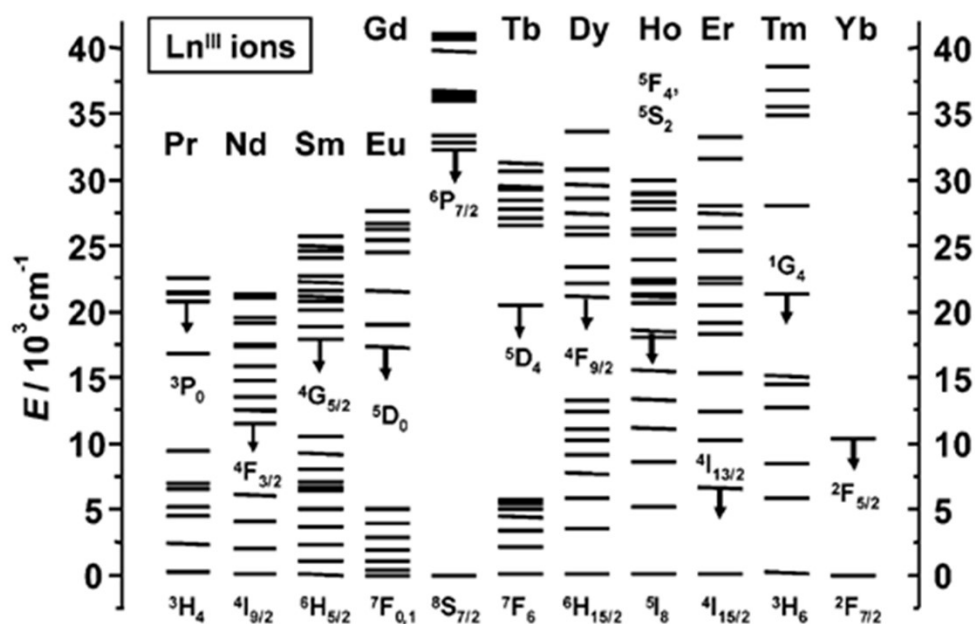
Figure S5. Partial energy diagrams of lanthanide trivalent ions. Reprinted with permission from Ref. [1]. Copyright © 2006, American Chemical Society.

Figure S6. Effect of the presence of alkali and earth-alkali metal ions on the fluorescence response to [Pd(H$_{-2}$**L2**)] sensor. Black bars: only metal ion; red bars: co-presence of Gd^{III} and 10 equiv. of metal ion.
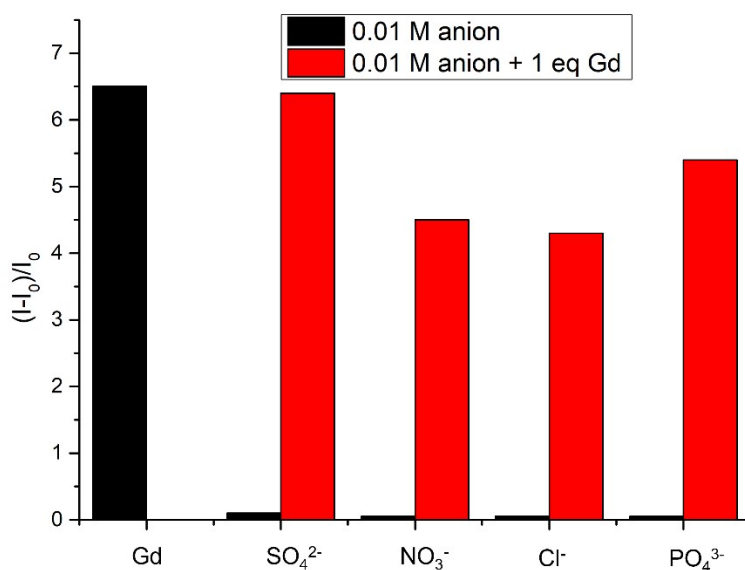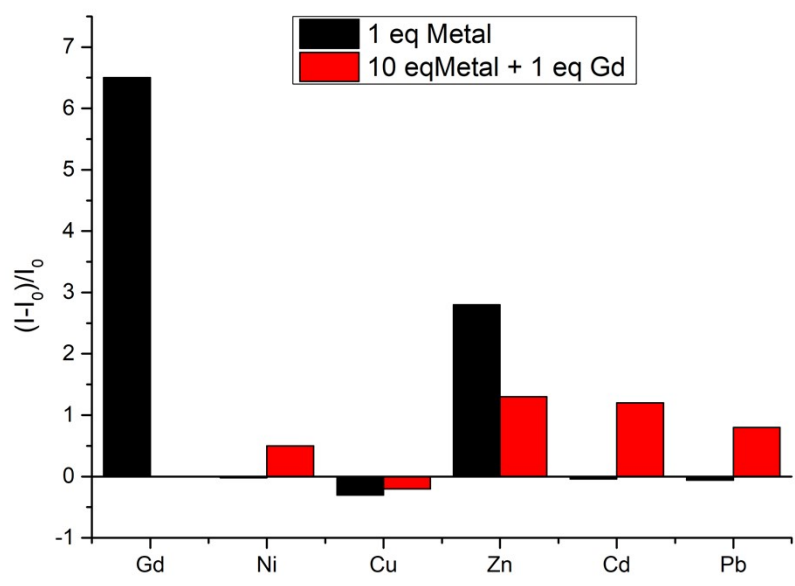
Figure S7. Effect of the presence of anions on the fluorescence response to [Pd(H$_{-2}$**L2**)] sensor. Black bars: only anion; red bars: co-presence of Gd^{III} and anion.
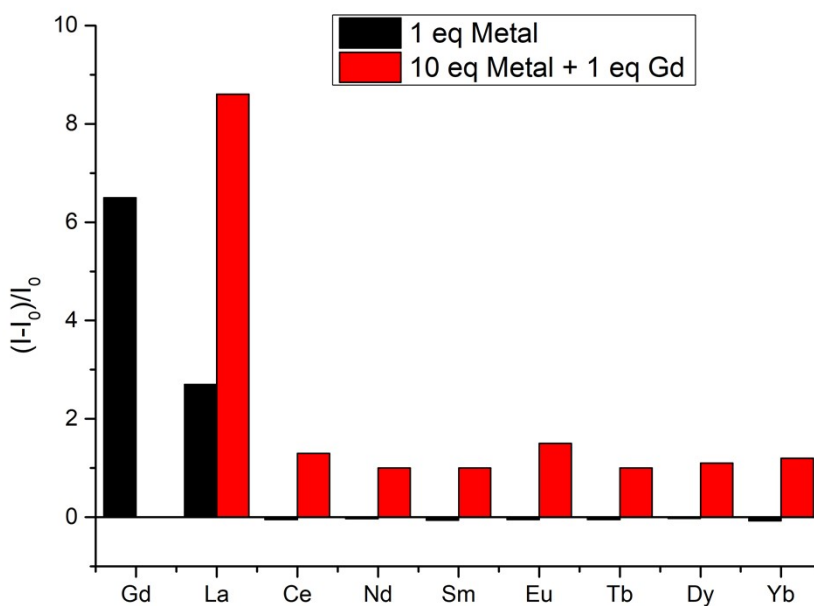
Figure S8. Effect of the presence of RE ions on the fluorescence response to [Pd(H$_{-2}$**L2**)] sensor. Black bars: only RE ion; red bars: co-presence of Gd^{III} and 10 equiv. of RE ion.

Figure S9. Effect of the presence of transition metal ions on the fluorescence response to [Pd(H$_{-2}$**L2**)] sensor. Black bars: only metal ion; red bars: co-presence of Gd^{III} and 10 equiv. of metal ion.

Determination of LOD, LOQ and LOL

LOD and LOQ were determined using the linear regression method, that consist in the calculating a calibration curve measuring the fluorescence response Y of a series of standard solution of the analyte of concentration X. This method assumes that the instrument response Y is linearly related to the standard concentration X for a limited range of concentration, and it can be expressed using the equation of the line Y=A+BX as mathematic model. The two parameters A and B, that are the intercept and the slope of the line, were calculated with the minimum square method together with their respective standard deviation S_A and S_B. In our case the response is the ratio between the emission intensity of each sample and the emission intensity of the blank at 423 nm by exciting at 350 nm (Figure S8).
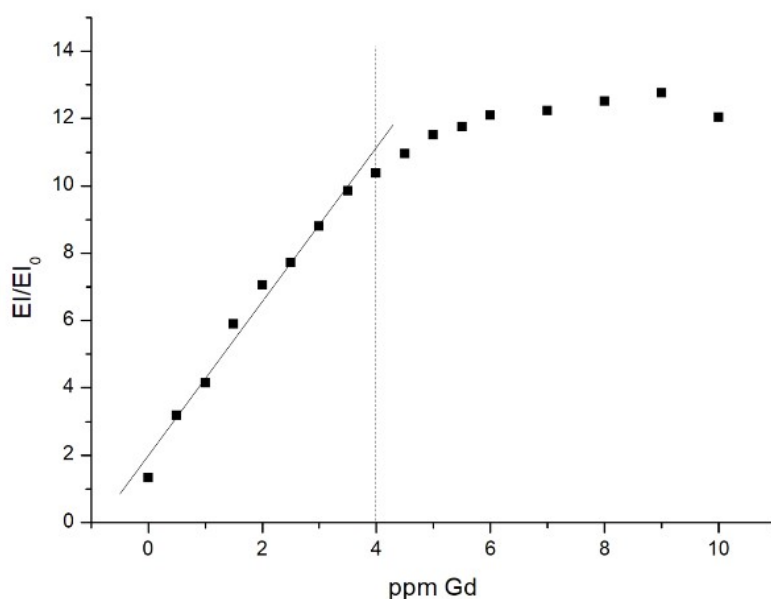
Figure S10. Trend of the normalized emission intensity at 423 nm (λ_{ex}=350 nm) of tap water samples polluted with Gd^{III} (0-10 ppm) treated as described in the main text. EI_0 is the Emission Intensity of a sample of crude tap water without adding gadolinium treated as described in the main text. Linear regression from 0 to 4 ppm: Y=A + B·X; A=1.998 (S_A = 0.278), B=2.244 (S_B = 0.117), R=0.9907.

The LOD and LOQ were calculated as:

LOD=$3S_A$ /B = 3·0.278/2.244=0.372≈0.4 ppm

LOQ=$10S_A$ /B = 10·0.278/2.244=1.23≈1.2 ppm

The linearity of the response with the concentration were observed in the concentration range 0-4 ppm of gadolinium (R=0.99), thus the LOL has been fixed at tis last concentration (ref 37 main text).