Supplementary Materials

Includes:

Structure of the ligands.

Fig. S1: UV-Visible spectra of TPS and TPSM(II) in ethanol water 98/2 v/v.

Fig. S2: UV-Visible spectra of TPT and TPTM(II) in ethanol water 98/2 v/v.

Fig. S3: Normalized fluorescence emission spectra of TPS in ethanol:water (98:2) (10^{-5} M) upon addition of Zn(II) (λ_{ex} = 340 nm).

Fig. S4: Normalized fluorescence emission spectra of TPT in ethanol (10^{-5} M) upon addition of Zn(II) (λ_{ex} = 359 nm).

Fig. S5: Normalized fluorescence emission spectra of TPS in ethanol:water (98:2) (10^{-5} M) upon addition of Cu(II) (λ_{ex} = 340 nm).

Fig. S6: Normalized fluorescence emission spectra of TPT in ethanol:water (98:2) (10^{-5} M) upon addition of Cu(II) (λ_{ex} = 359 nm).

Fig. S7: Normalized fluorescence emission spectra of TPT in ethanol:water (98:2) (10^{-5} M) upon addition of Cd(II) (λ_{ex} = 359 nm).

Fig. S8: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of fluoride in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S9: Evolution of the normalized intensity of $ZnTPT^{2+}$ with fluoride concentration.

Fig. S10: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of chloride in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S10: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of chloride in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S11: Evolution of the normalized intensity of $ZnTPT^{2+}$ with chloride concentration.

Fig. S12: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of bromide in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S13: Evolution of the normalized intensity of $ZnTPT^{2+}$ with bromide concentration.

Fig. S14: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of iodide in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S15: Evolution of the normalized intensity of $ZnTPT^{2+}$ with iodide concentration.

Fig. S16: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of cyanide in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S17: Evolution of the normalized intensity of $ZnTPT^{2+}$ with cyanide concentration.

Fig. S18: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of thiocyanate in water (10^{-3} M) (λ_{ex} = 359

Fig. S19: Evolution of the normalized intensity of $ZnTPT^{2+}$ with thiocyanate concentration.

Fig. S20: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of nitrite in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S21: Evolution of the normalized intensity of $ZnTPT^{2+}$ with nitrite concentration.

Fig. S22: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of nitrate in water (10^{-3} M) (λ_{ex} = 359 nm).

Fig. S23: Evolution of the normalized intensity of $ZnTPT^{2+}$ with nitrate concentration.

Figs. S24 and S25. Detection Limits.

Fig. S26. Comparison between the fluorescence changes produced by the different anions.

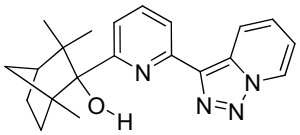
Special Details of the X-ray refinement

Fig. S27. Fraction of the crystal packing along the b-axis. Hydrogen atoms, CH_3CN molecules and ClO_4^- counter-anions are not shown

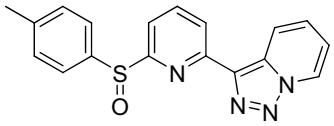
Fig. S28. ^{1}H-NMR comparison between TPT (up) and $TPTZnCl_2$ (down)

Structures

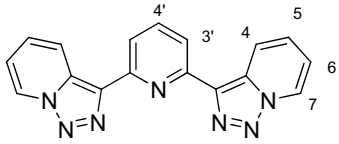
(2*R*)-2-(6-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridin-2-yl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol (2) (TPF)



3-(6-(*p*-tolylsulfinyl)pyridin-2-yl)-[1,2,3]triazolo[1,5-*a*]pyridine (4) (TPS)



2,6-di([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)pyridine (6) (TPT)



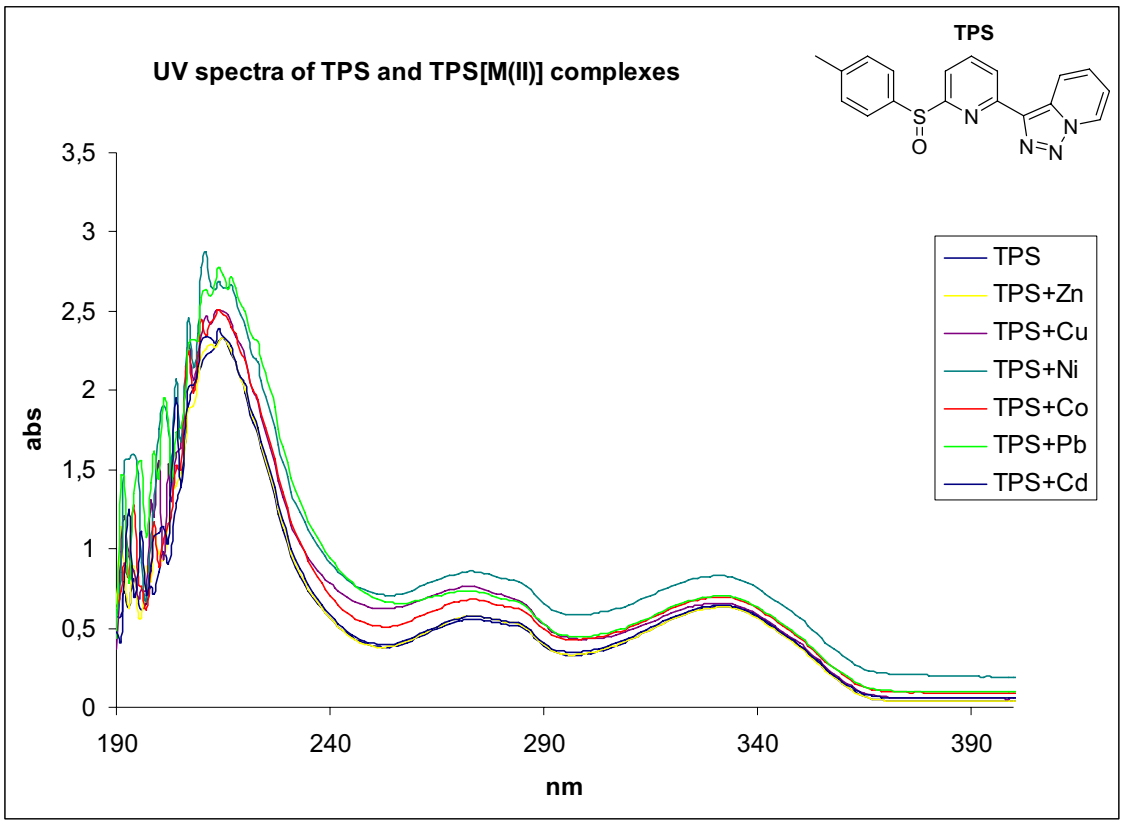


Fig. S1: UV-Visible spectra of TPS and TPSM(II) in ethanol:water 98/2 v/v.

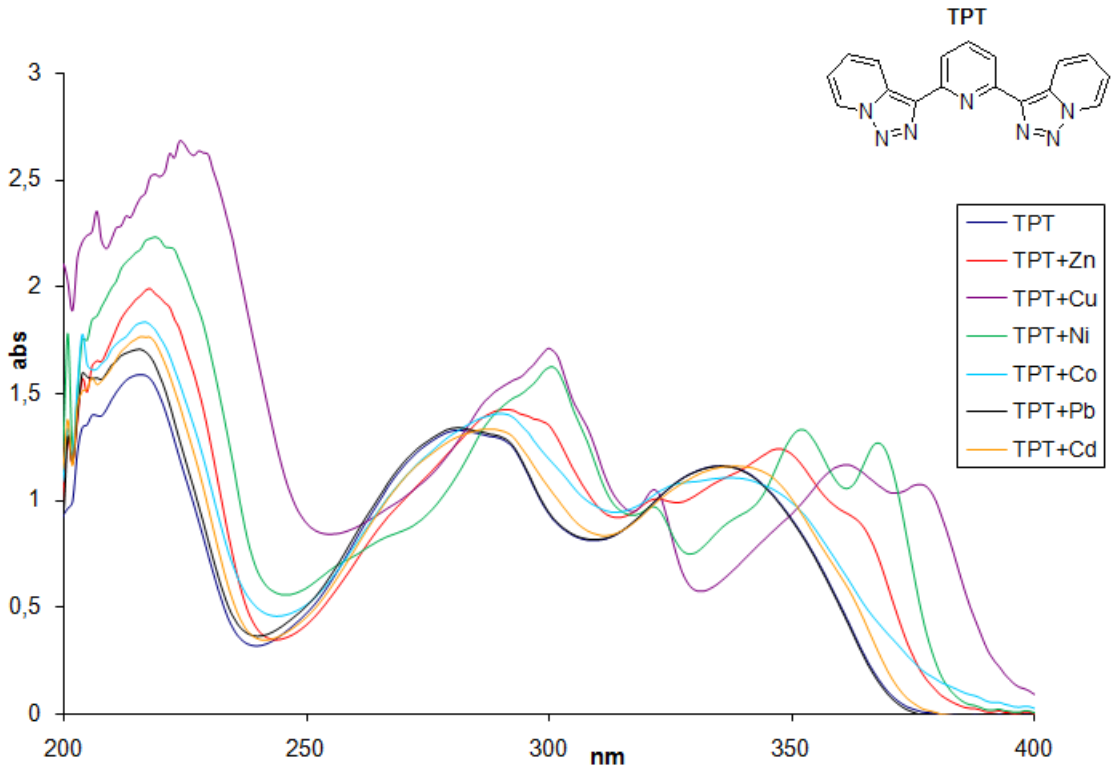


Fig. S2: UV-Visible spectra of TPT and TPTM(II) in ethanol:water 98/2 v/v.

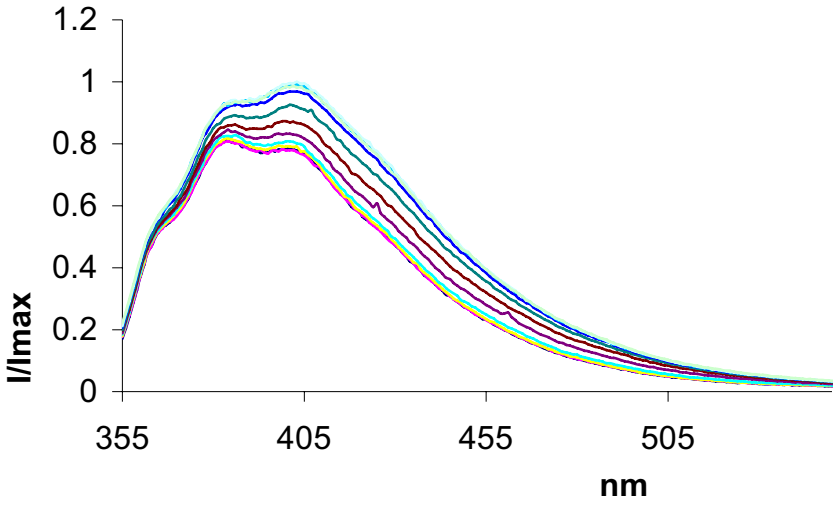


Fig. S3: Normalized fluorescence emission spectra of TPS in ethanol:water (98:2) (10^{-5} M) upon addition of Zn(II) (λ_{ex} = 340 nm).

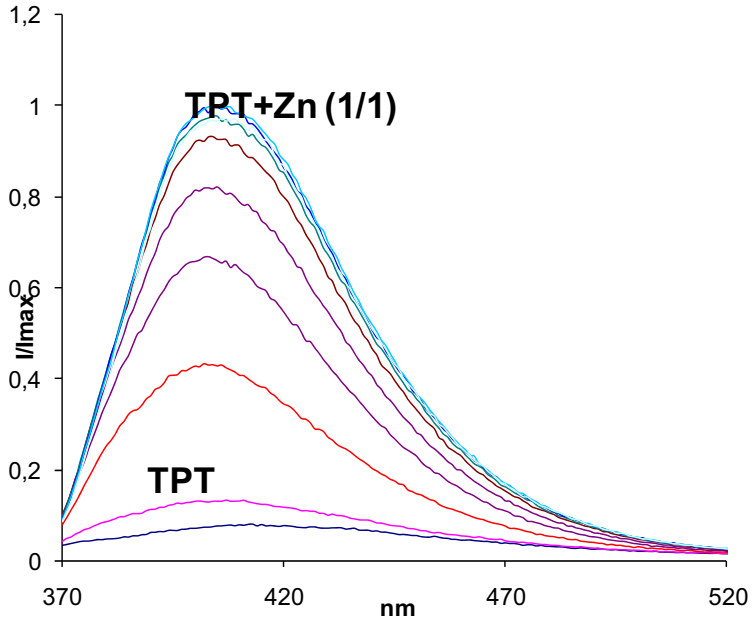


Fig. S4: Normalized fluorescence emission spectra of TPT in ethanol (10^{-5} M) upon addition of Zn(II) (λ_{ex} = 359 nm).

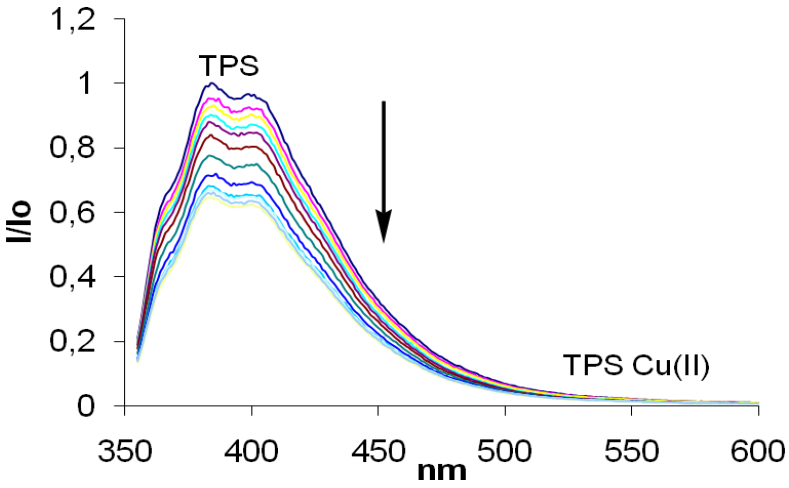


Fig. S5: Normalized fluorescence emission spectra of TPS in ethanol:water (98:2) (10^{-5} M) upon addition of Cu(II) (λ_{ex} = 340 nm).

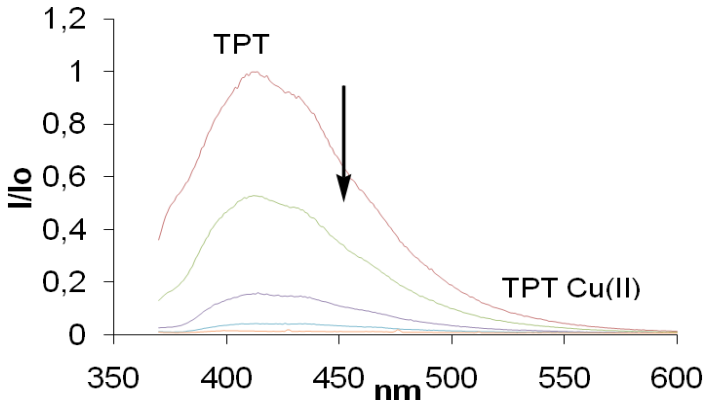


Fig. S6: Normalized fluorescence emission spectra of TPT in ethanol:water (98:2) (10^{-5} M) upon addition of Cu(II) (λ_{ex} = 359 nm).

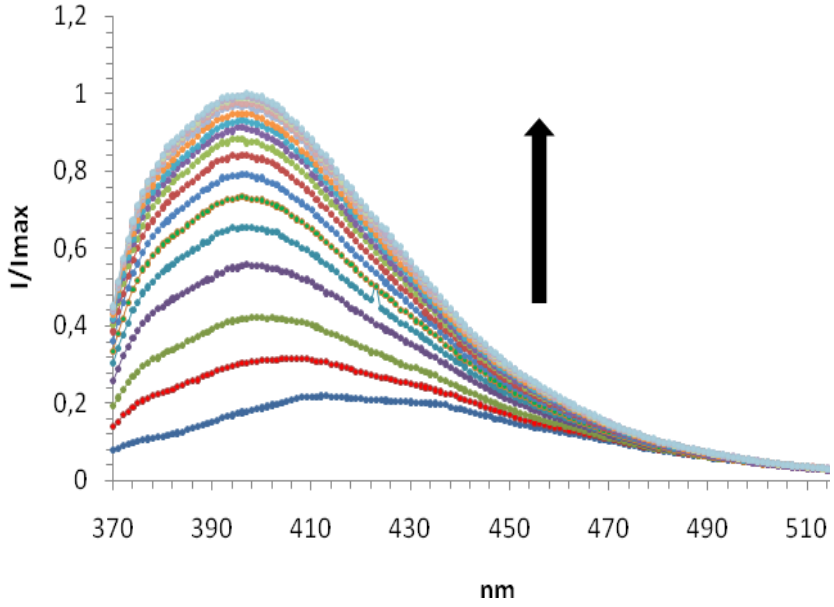


Fig. S7: Normalized fluorescence emission spectra of TPT in ethanol:water (98:2) (10^{-5} M) upon addition of Cd(II) (λ_{ex} = 359 nm).

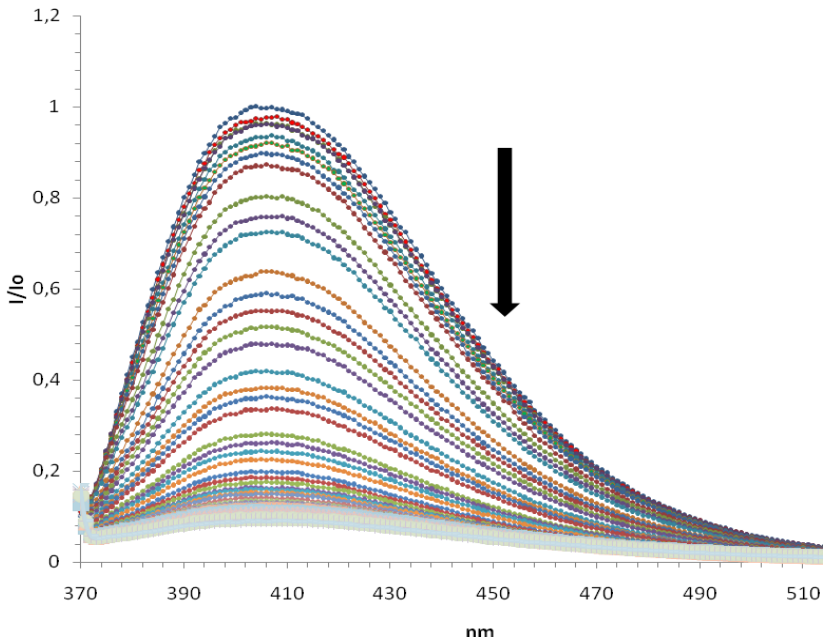


Fig. S8: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of fluoride in water (10^{-3} M) (λ_{ex} = 359 nm).

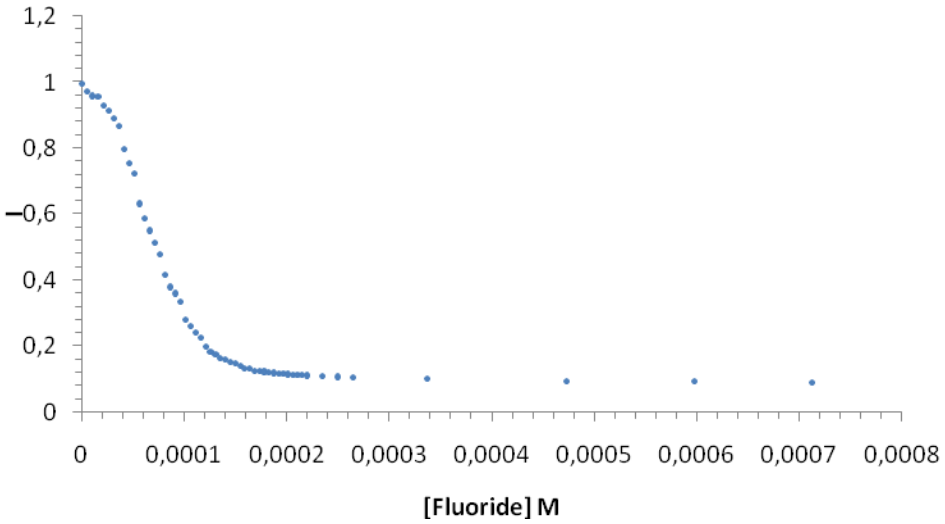


Fig. S9: Evolution of the normalized intensity of $ZnTPT^{2+}$ with fluoride concentration.

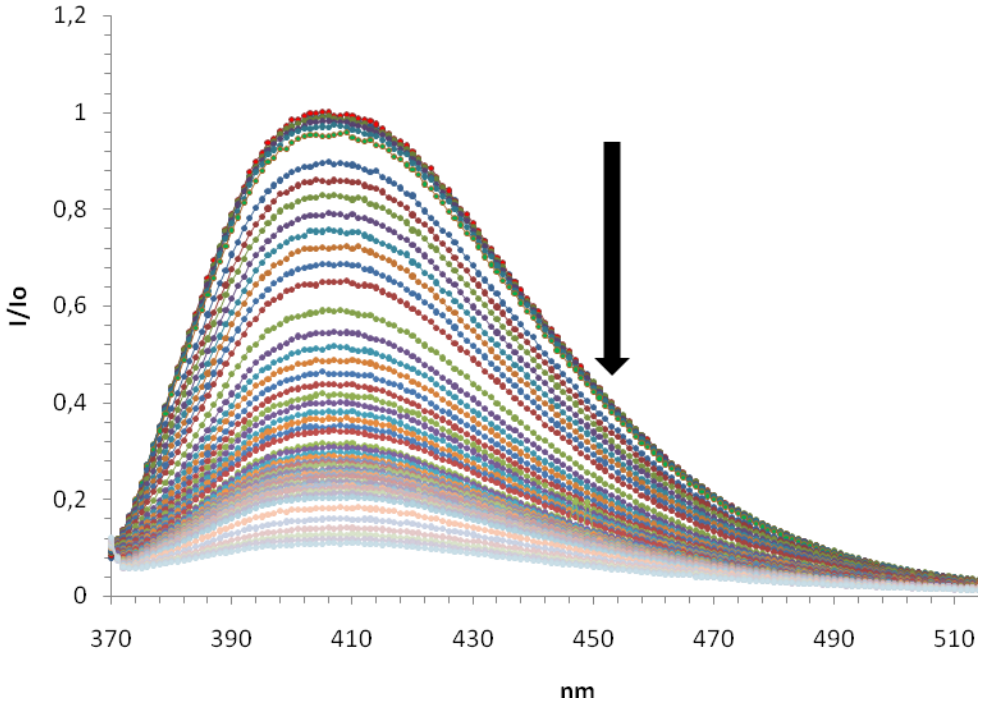


Fig. S10: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of chloride in water (10^{-3} M) (λ_{ex} = 359 nm).

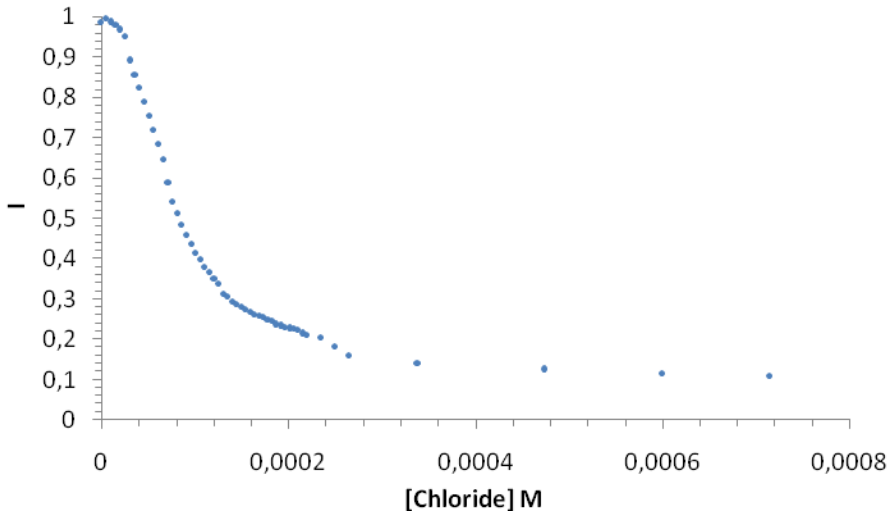


Fig. S11: Evolution of the normalized intensity of $ZnTPT^{2+}$ with chloride concentration.

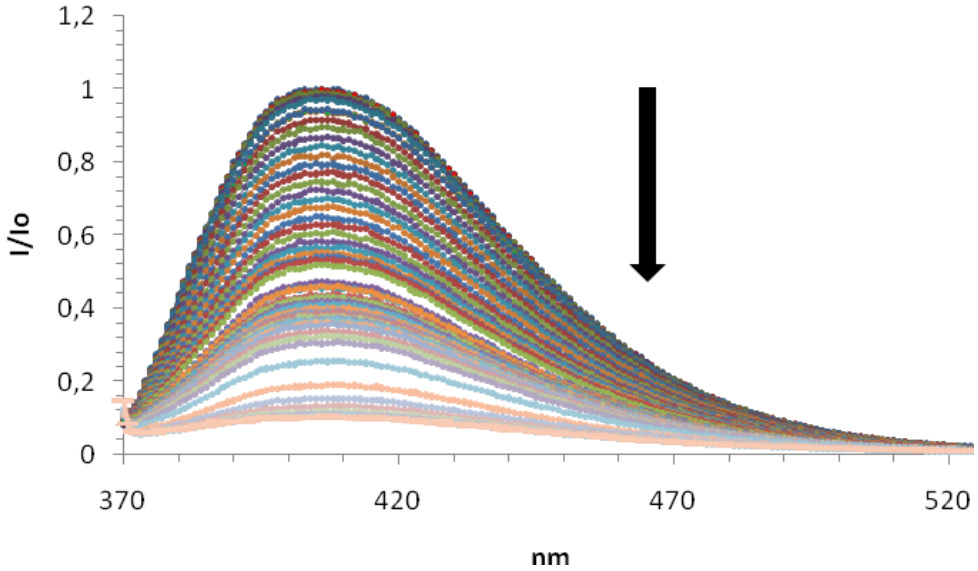


Fig. S12: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of bromide in water (10^{-3} M) (λ_{ex} = 359 nm).

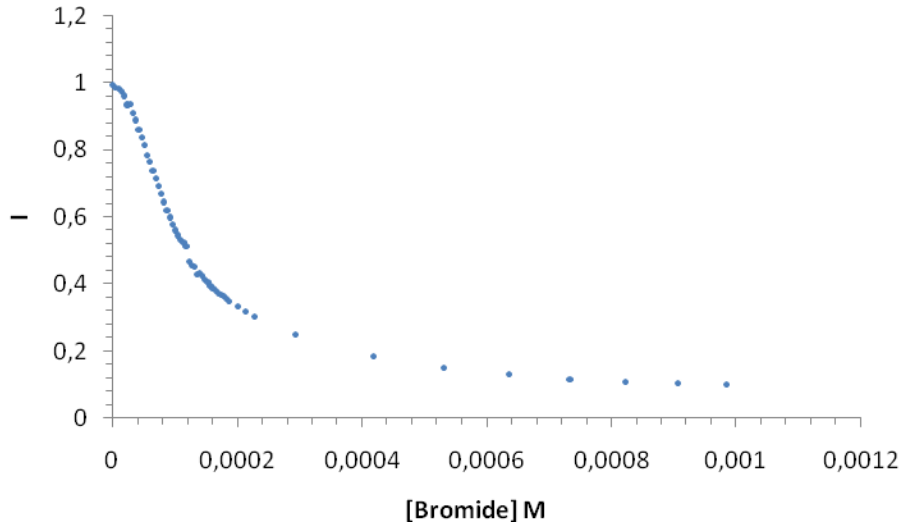


Fig. S13: Evolution of the normalized intensity of $ZnTPT^{2+}$ with bromide concentration.

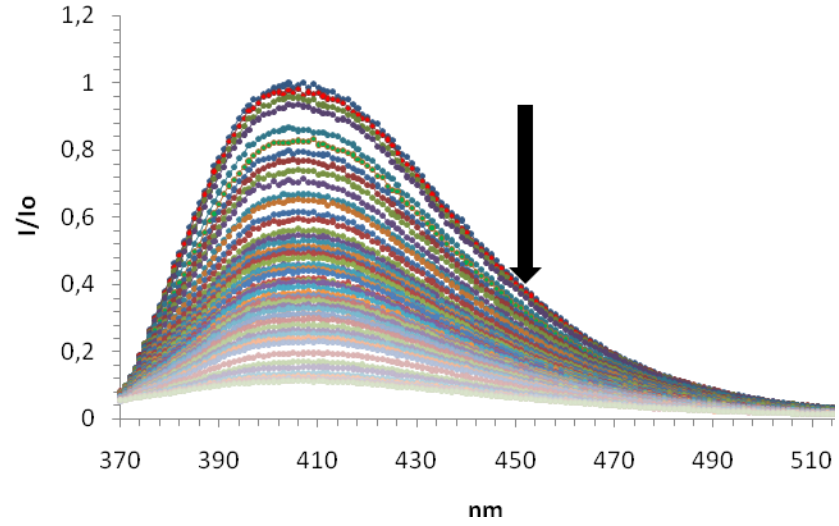


Fig. S14: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of iodide in water (10^{-3} M) (λ_{ex} = 359 nm).

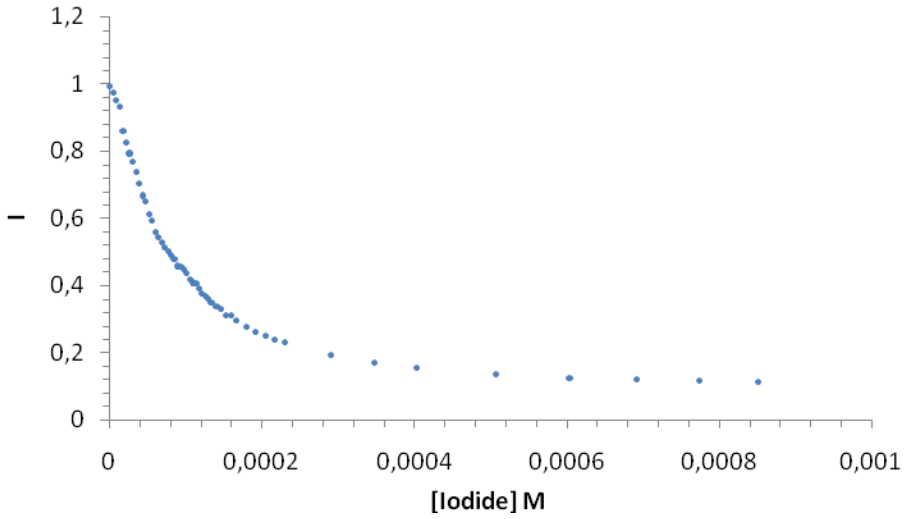


Fig. S15: Evolution of the normalized intensity of $ZnTPT^{2+}$ with iodide concentration.

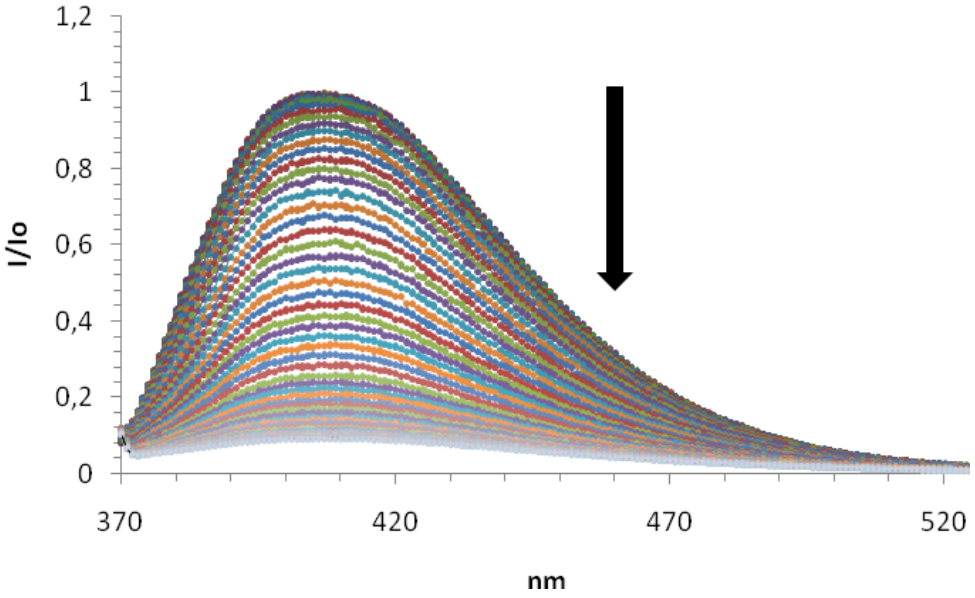


Fig. S16: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of cyanide in water (10^{-3} M) (λ_{ex} = 359 nm).

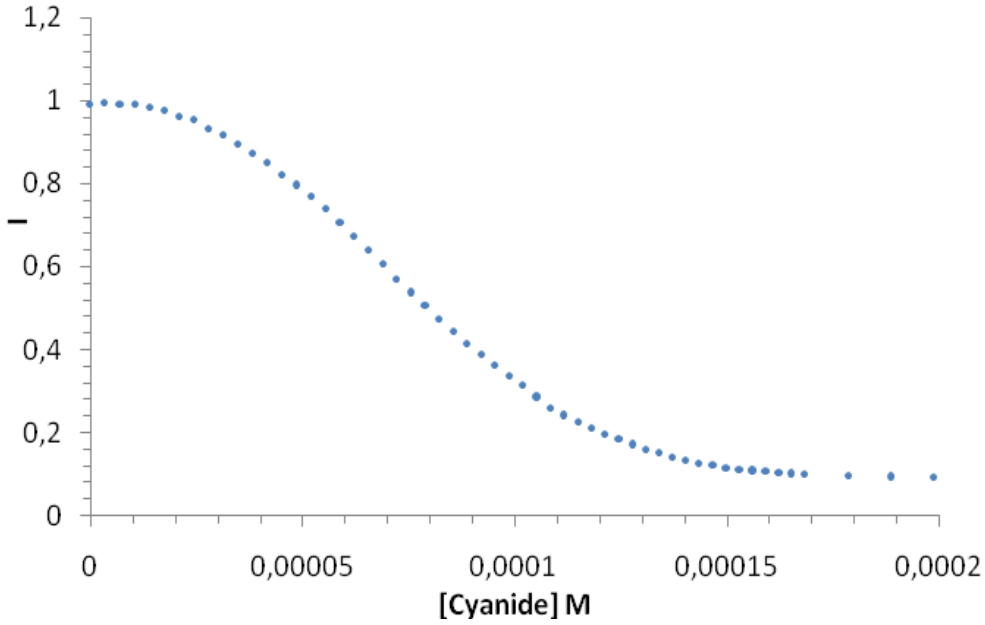


Fig. S17: Evolution of the normalized intensity of $ZnTPT^{2+}$ with cyanide concentration.

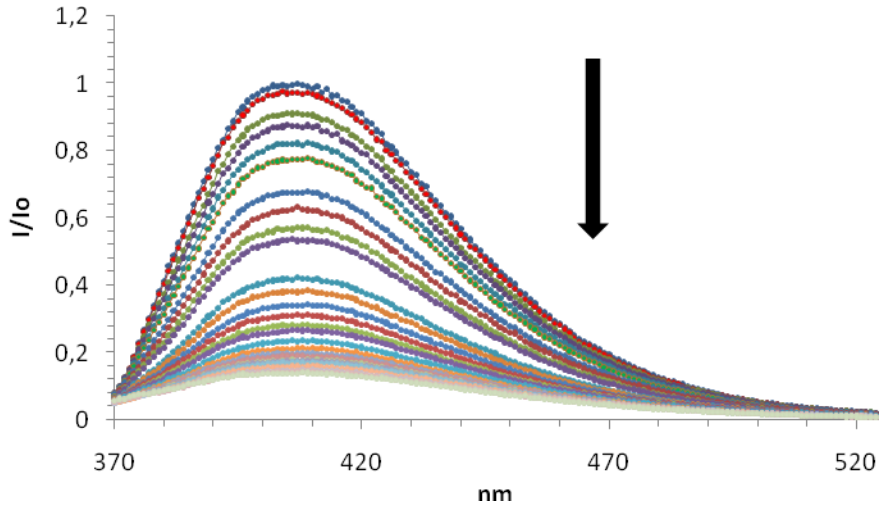


Fig. S18: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of thiocyanate in water (10^{-3} M) (λ_{ex} = 359 nm).

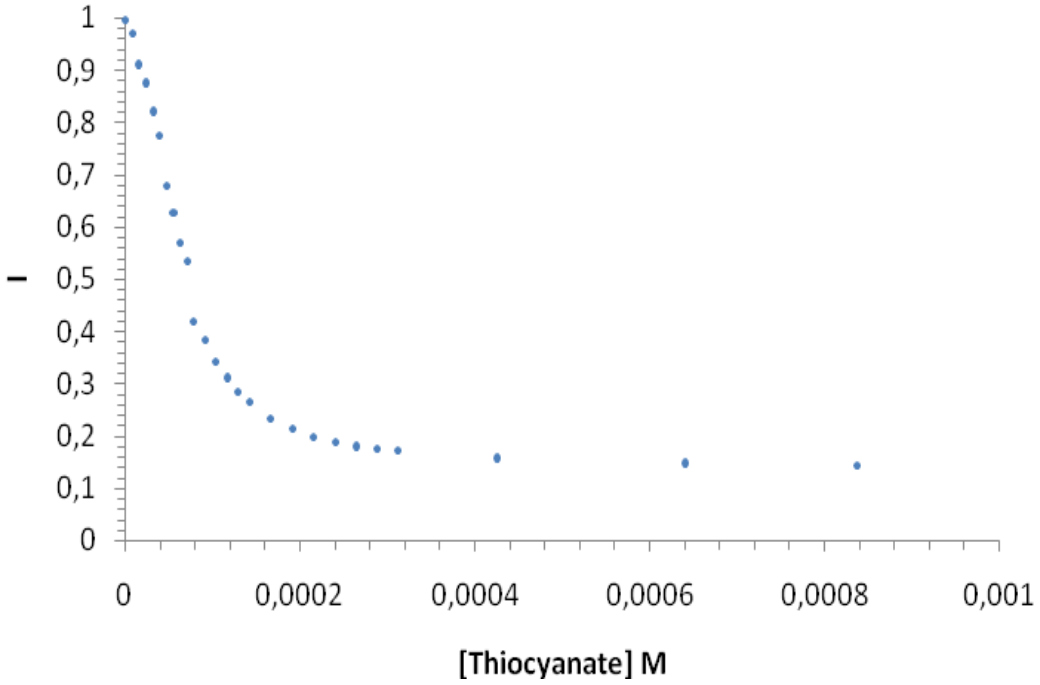


Fig. S19: Evolution of the normalized intensity of $ZnTPT^{2+}$ with thiocyanate concentration.

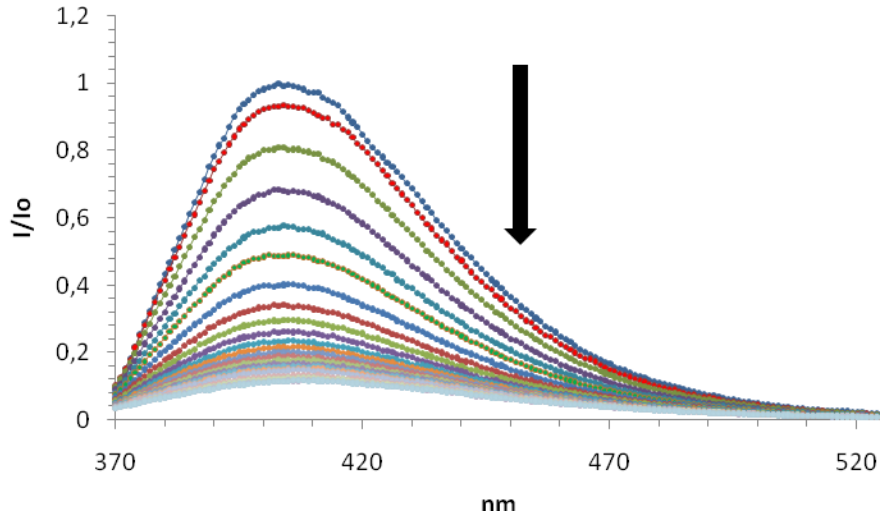


Fig. S20: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of nitrite in water (10^{-3} M) (λ_{ex} = 359 nm).

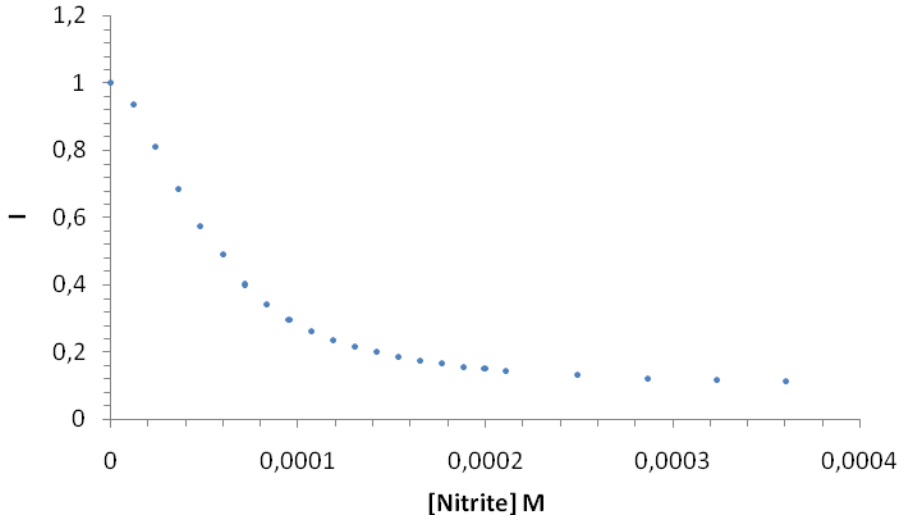


Fig. S21: Evolution of the normalized intensity of $ZnTPT^{2+}$ with nitrite concentration.

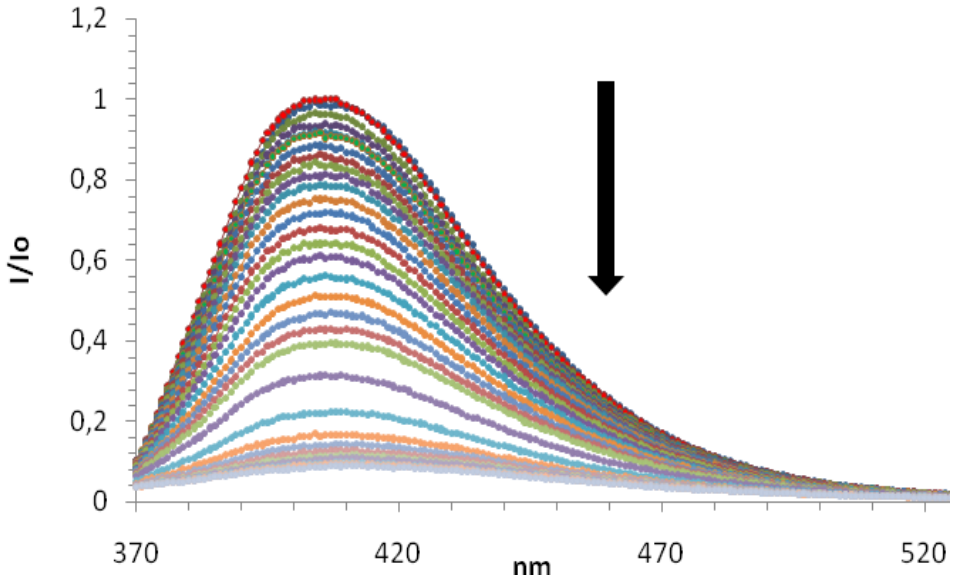


Fig. S22: Normalized fluorescence emission spectra of $ZnTPT^{2+}$ in ethanol:water (98:2, v/v) (10^{-5} M) upon addition of nitrate in water (10^{-3} M) (λ_{ex} = 359 nm).

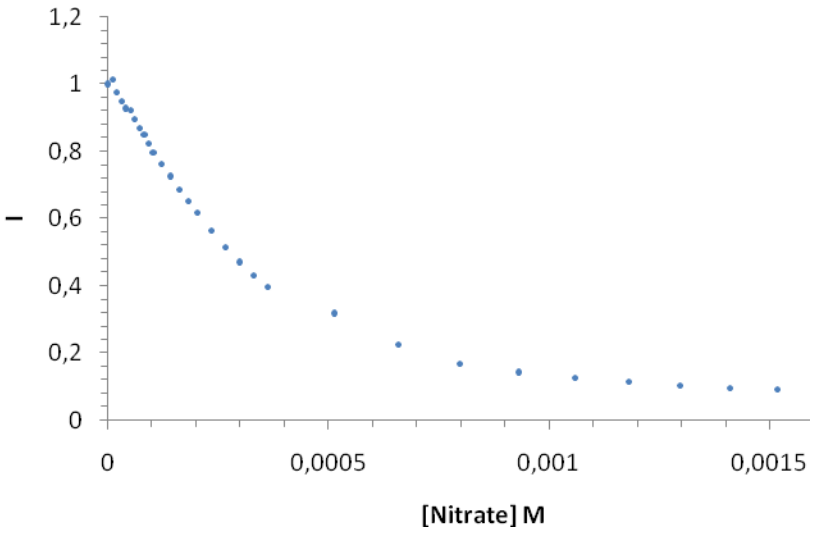


Fig. S23: Evolution of the normalized intensity of $ZnTPT^{2+}$ with nitrate concentration.

Detection Limits:

The detection limit depends on the instrumentation (*i.e.* the Signal-to-Noise Ratio gives a quantitative indication of the sensitivity; in this case this value is 133) and on the sensitivity of the ligand defined as the Δ(luminiscence)/Δ[substrate]. Using these two parameters, the limit of detection (LOD) can then be calculated as 3*SNR/sensitivity.

Cyanide:

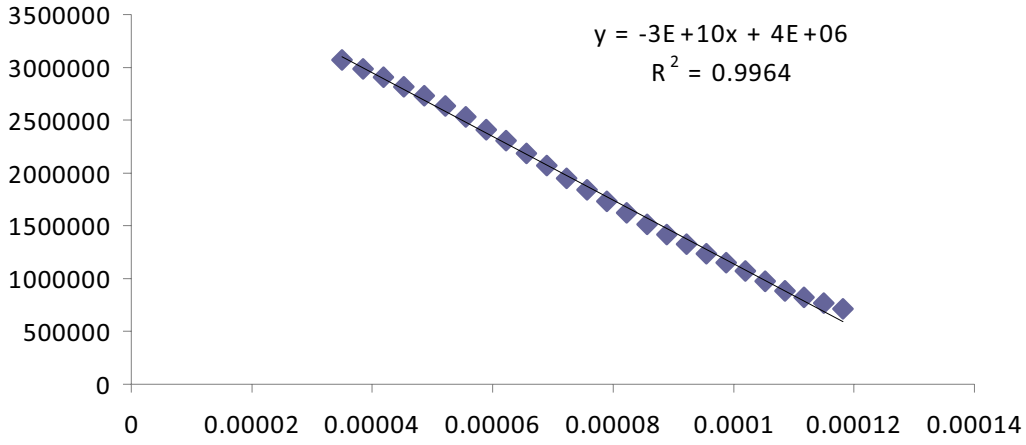


Fig. S24: : Evolution of the intensity of $ZnTPT^{2+}$ with cyanide concentration.

LOD (ppm) = [3×133/3E+10]×1000×M.W.$^{(KCN)}$ = 0.00087 ppm.

Nitrite

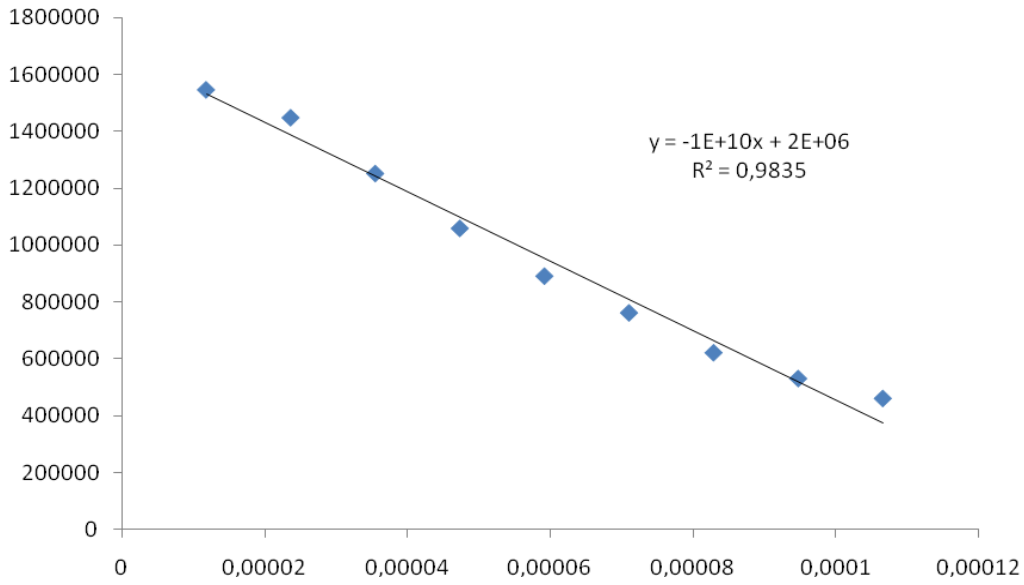


Fig. S25: : Evolution of the intensity of $ZnTPT^{2+}$ with nitrite concentration.

LOD (ppm) = [3×133/1E+10]×1000×M.W.$^{(NaNO2)}$ = 0.0032 ppm.

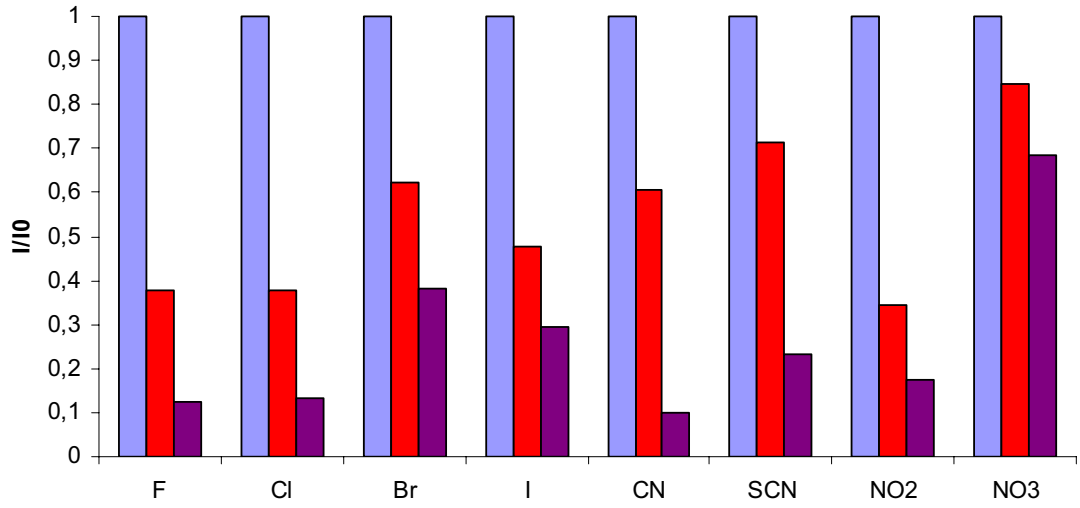


Fig. S26. Comparison between different anions $TPTZn^{2+}$ (blue), after the addition of 1 eq of anion (red), after the addition of 2 eq. of anion (purple).

X-ray stucture:

The structure was solved and refined in space group Pc (SHELXS-97 and SHELXL-97, G.M. Sheldrick, University of Göttingen, 1997). The structure was refined as an enantiomeric twin with components 0.405(12) and 0.595(12). Three perchlorate anions are disordered over two sites. Residual electron density was tentatively identified as a disordered molecule of CH_3CN. The disordered atoms were refined isotropically. Residual electron density was tentatively refined as a disordered CH3CN molecule. The structure possible higher (pseudo) symmetry (P2(1)/C space group) as suggested by ADDSYM has been closely examined. The true space group is Pc and the extra symmetry is pseudo symmetry but, in the presence of disorder, an unambiguous decision is difficult. Attempts of refinement in space group P2(1)/c afford

- Extinction coeficient 0.001196

- R1= 0.1299

- wR2=0.3201

- GooF = S = 1.109

- 11 Systematic absence violations

h	k	l	Fo^2	Sigma(Fo^2)
0	9	0	79.10	3.30
0	13	0	8.80	1.40
0	13	0	6.40	0.80
0	15	0	6.40	0.90
0	15	0	4.00	0.90
0	17	0	22.30	1.30
0	17	0	21.10	1.50
0	23	0	5.60	1.30
-3	0	1	1.40	0.20
1	0	1	1.80	0.30
2	0	1	2.10	0.50

Other special features of refinement are as follows. Both disordered perchlorate anions and solvent CH3CN molecule were refined with appropriate similarity restraints (command SAME). Disordered atom U value components were restrained to be equal (commands DELU, SIMU, ISOR). Local ring geometry of aromatic groups was also restrained (commands FLAT, SAME).

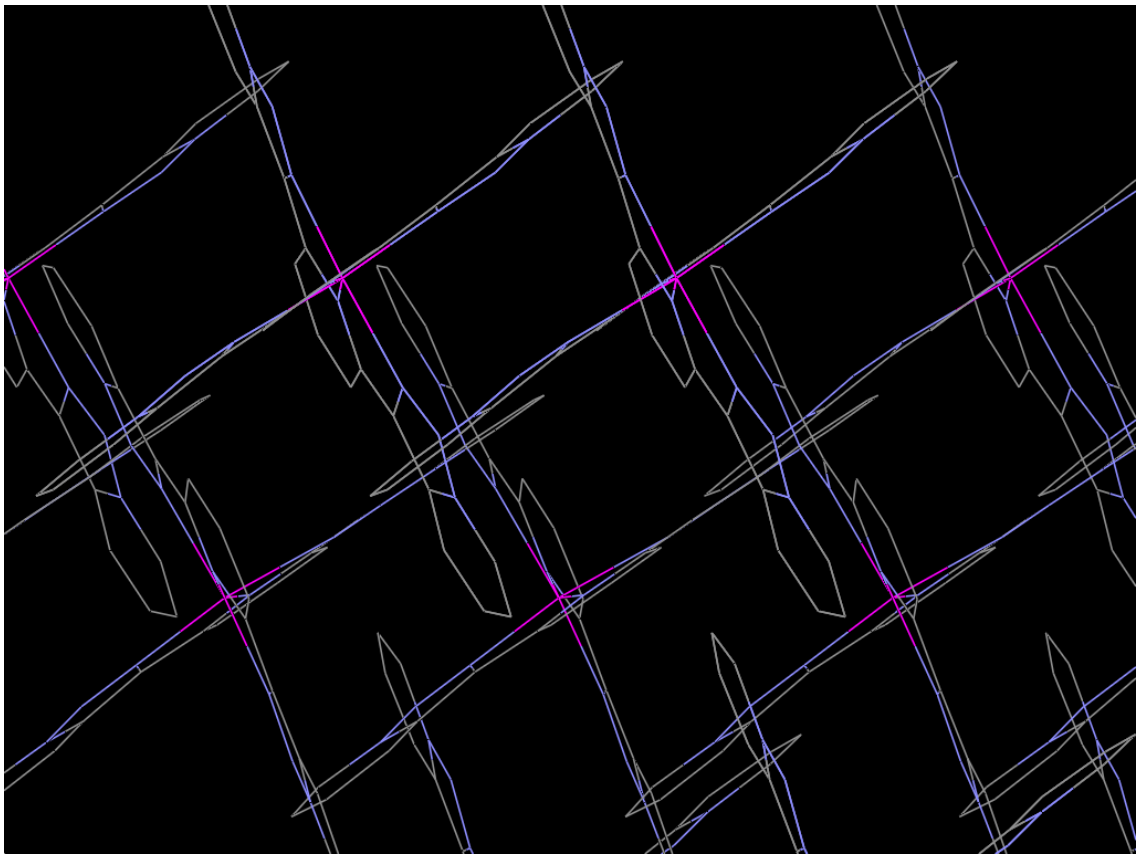


Fig. S27. Fraction of the crystal packing along the b-axis. Hydrogen atoms, CH_3CN molecules and ClO_4^- counter-anions are not shown.

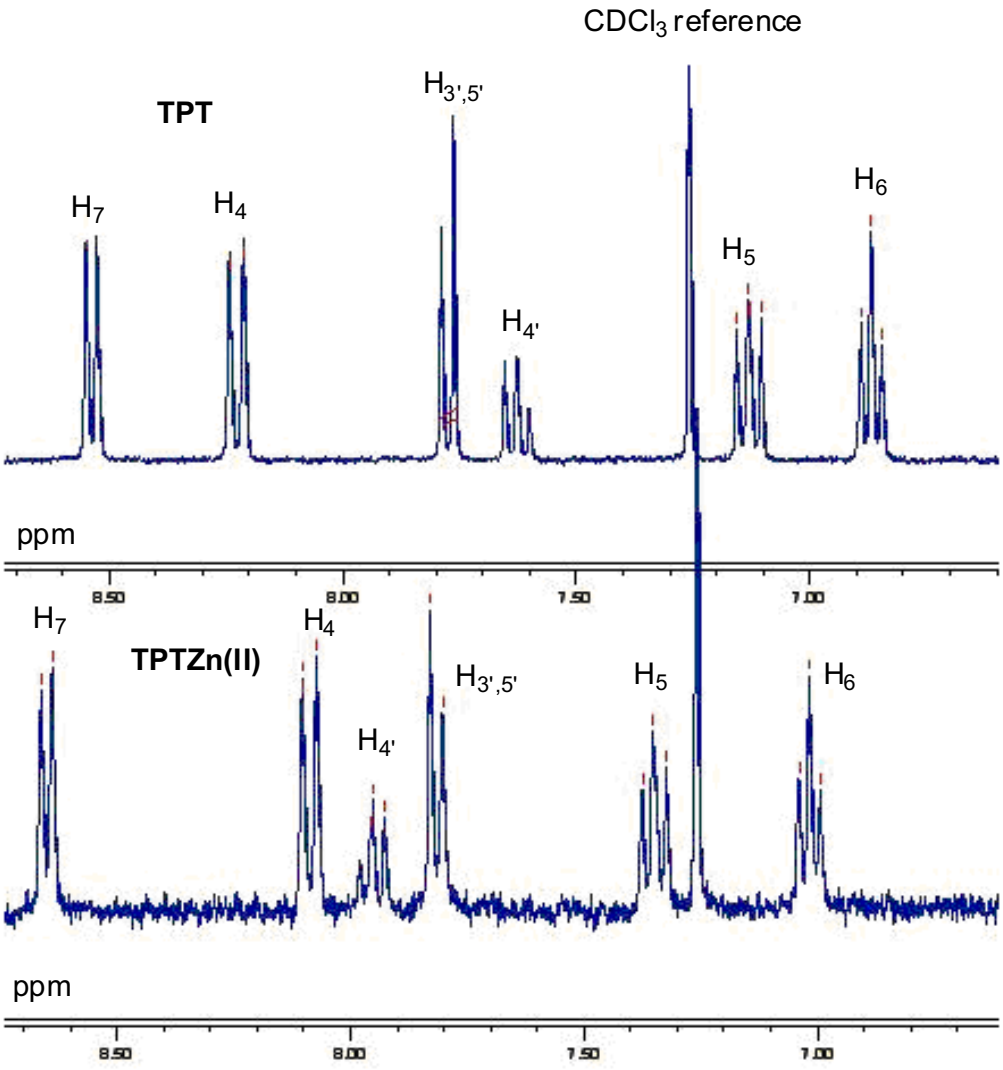


Fig. S28. ^{1}H-NMR comparison between TPT (up) and $TPTZnCl_2$ (down)