Supporting Information

An OFF-OFF-ON Fluorescence Sensor for Metal Ions in Stepwise Complex Formation of 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (TPPZ) with Metal Ions

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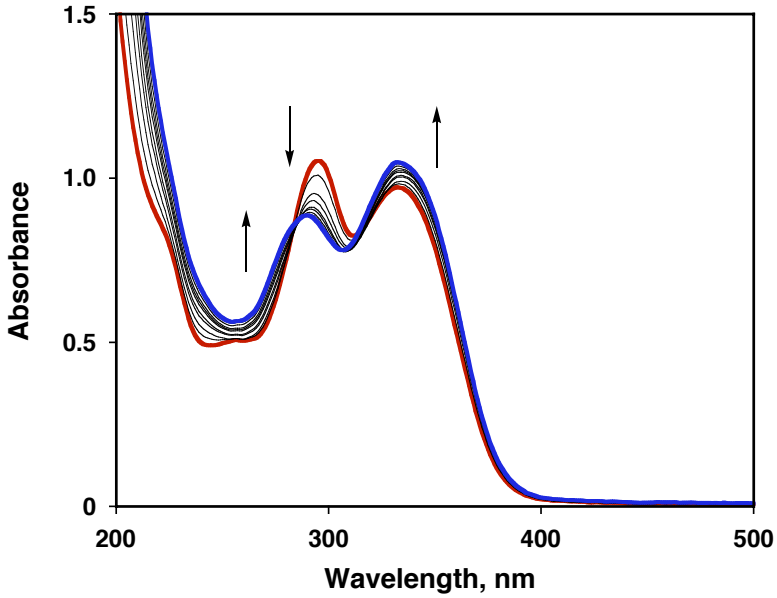


Figure S1. UV-vis absorption spectra of TPPZ (3.0×10^{-5} M) in the presence of Sc^{3+} [8.0×10^{-4} M (red line) – 1.6×10^{-2} M (blue line)] in MeCN at 298 K.

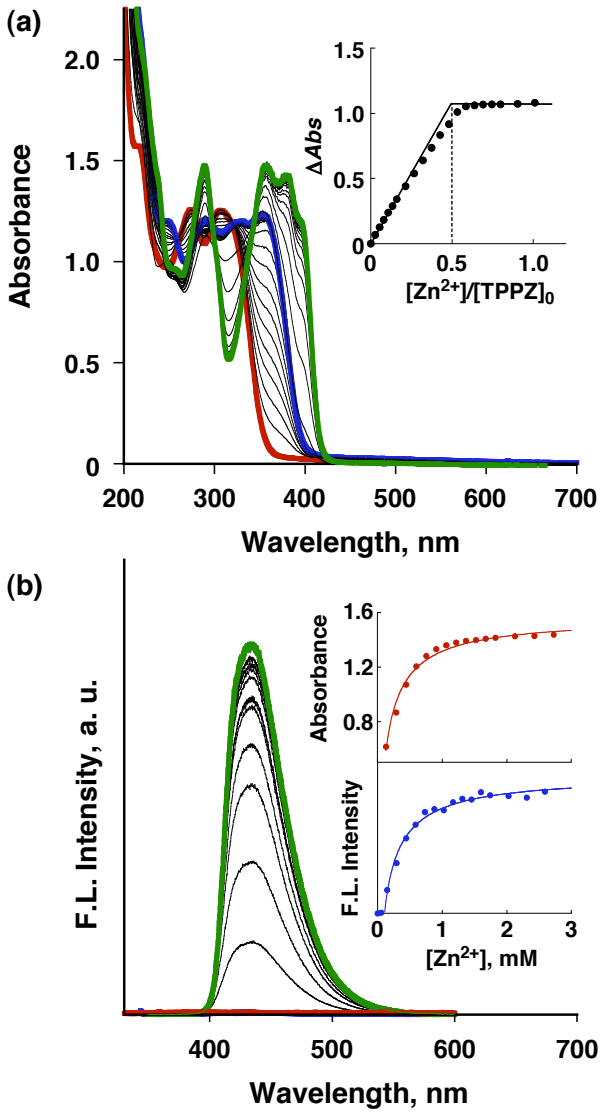


Figure S2. (a) UV-vis absorption and (b) fluorescence spectra of TPPZ (5.7×10^{-5} M) in the presence of Zn^{2+} [0 M (red line) – 3.0×10^{-5} M (blue line) – 3.1×10^{-3} M (green line)] in MeCN at 298 K. The excitation wavelength was λ = 343 nm. Insets: (a) Plot of ΔAbs vs $[Zn^{2+}]/[TPPZ]_0$ at λ = 355 nm; (b) plots of absorbance at λ = 381 nm (●) and fluorescence intensity at λ = 432 nm (●) vs $[Zn^{2+}]$.

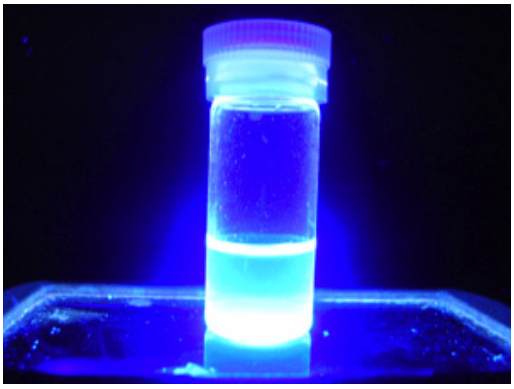
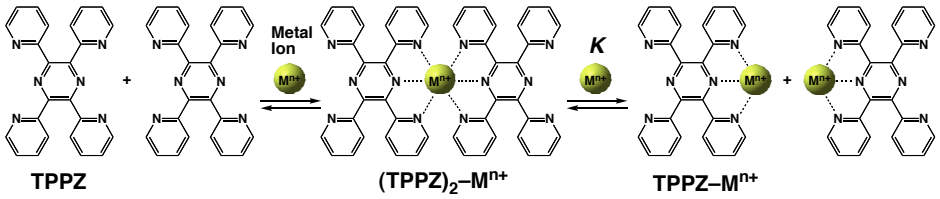


Figure S3. Photograph of a H_2O solutions of TPPZ (2.0×10^{-4} M) in the presence of Zn^{2+} (5.0×10^{-2} M) under UV-light irradiation.



The formation constant (K) of TPPZ–M^{n+} is expressed by eq 1 at concentrations of metal ions (M^{n+}) above the 1:2 ratio of metal ion concentration to the initial concentration of TPPZ ($[M^{n+}]/[TPPZ]_0 > 0.5$).

$$K = \frac{[\text{TPPZ–M}^{n+}]^2}{([\text{TPPZ}]_0/2 - [\text{TPPZ–M}^{n+}]/2) \times ([\text{M}^{n+}] - [\text{TPPZ}]_0/2 - [\text{TPPZ–M}^{n+}]/2)} \quad (1)$$

Eq 2 is derived from eq 1.

$$(4 - K)[\text{TPPZ–M}^{n+}]^2 + 2K[\text{M}^{n+}][\text{TPPZ–M}^{n+}] - K[\text{TPPZ}]_0(2[\text{M}^{n+}] - [\text{TPPZ}]_0) = 0 \quad (2)$$

The concentration of TPPZ–M^{n+} ([TPPZ–M^{n+}]) is therefore expressed by eq 3.

$$[\text{TPPZ–Mn}^{+}] = \frac{-K[\text{M}^{n+}] + \sqrt{K^2[\text{M}^{n+}]^2 + (4 - K)K[\text{TPPZ}]_0(2[\text{M}^{n+}] - [\text{TPPZ}]_0)}}{4 - K} \quad (3)$$

Then, absorbance and fluorescence intensity changes due to the TPPZ–M^{n+} complex formation is expressed by eq 4, where A_0 and A_∞ are absorbance due to $(TPPZ)_2$–M^{n+} and TPPZ–M^{n+}, respectively.

$$\underset{(\text{or } I)}{(A - A_0)} = \underset{(\text{or } I_\infty)}{(A_\infty - A_0)} \times \frac{-K[\text{M}^{n+}] + \sqrt{K^2[\text{M}^{n+}]^2 + (4 - K)K[\text{TPPZ}]_0(2[\text{M}^{n+}] - [\text{TPPZ}]_0)}}{4 - K} \quad (4)$$