Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information

Photoinduced triplet-state electron transfer of platinum porphyrin: A one-step direct method for sensing iodide to an unprecedented detection limit

Dilshad Masih, Shawkat M. Aly[†], Erkki Alarousu and Omar F. Mohammed*

Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

*Corresponding author, Email: omar.abdelsaboor@kaust.edu.sa

Estimation of Detection Limit for Iodide with Pt(II)TMPyP in Aqueous Phase

$$
\begin{aligned}
\text{Detection Limit} &= 3\sigma/\text{slope} \\
&= 3 \times 0.025/67.54 \\
&= \mathbf{1\ pmol}
\end{aligned}
$$

Multiple number of PL spectra (5–7) were recorded for the aqueous phase Pt(II)TMPyP alone. Sample Standard Deviation was calculated for the peak intensity value using ‘Statistics on Columns’ option in origin software and verified with online calculator. Sample Standard Deviation (0.025) is close to Population Standard Deviation (0.022). Standard deviation for the blank fluorophore, Pt(II)TMPyP porphyrin solution, without the addition of iodide was 0.025.

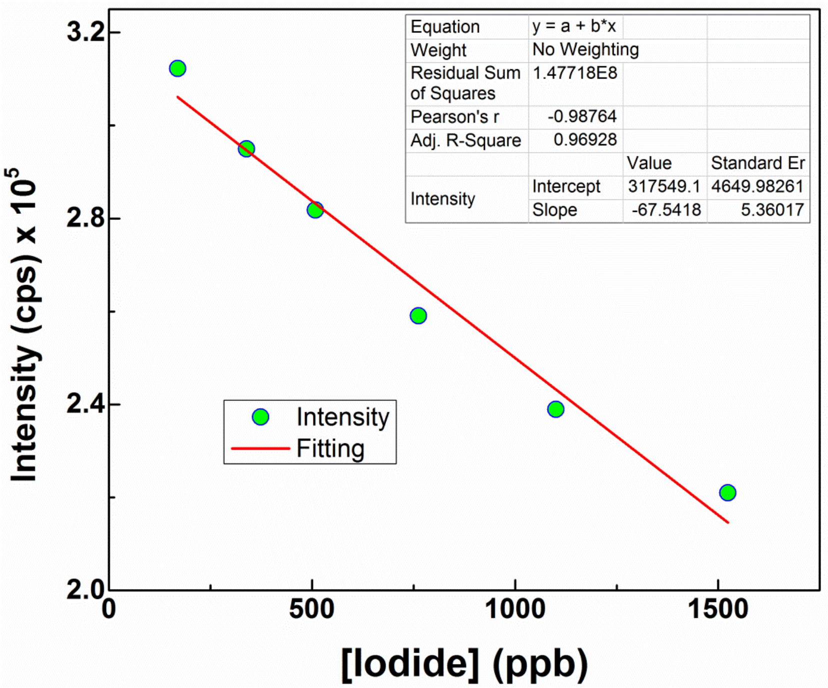

Fig. S1 Relation of photoluminescence intensity against the iodide added into Pt(II)TMPyP and linear fit for estimation of detection limit.

Steady-State UV-Vis Absorption and PL Spectra for Pt(II)TMPyP, and with Halides

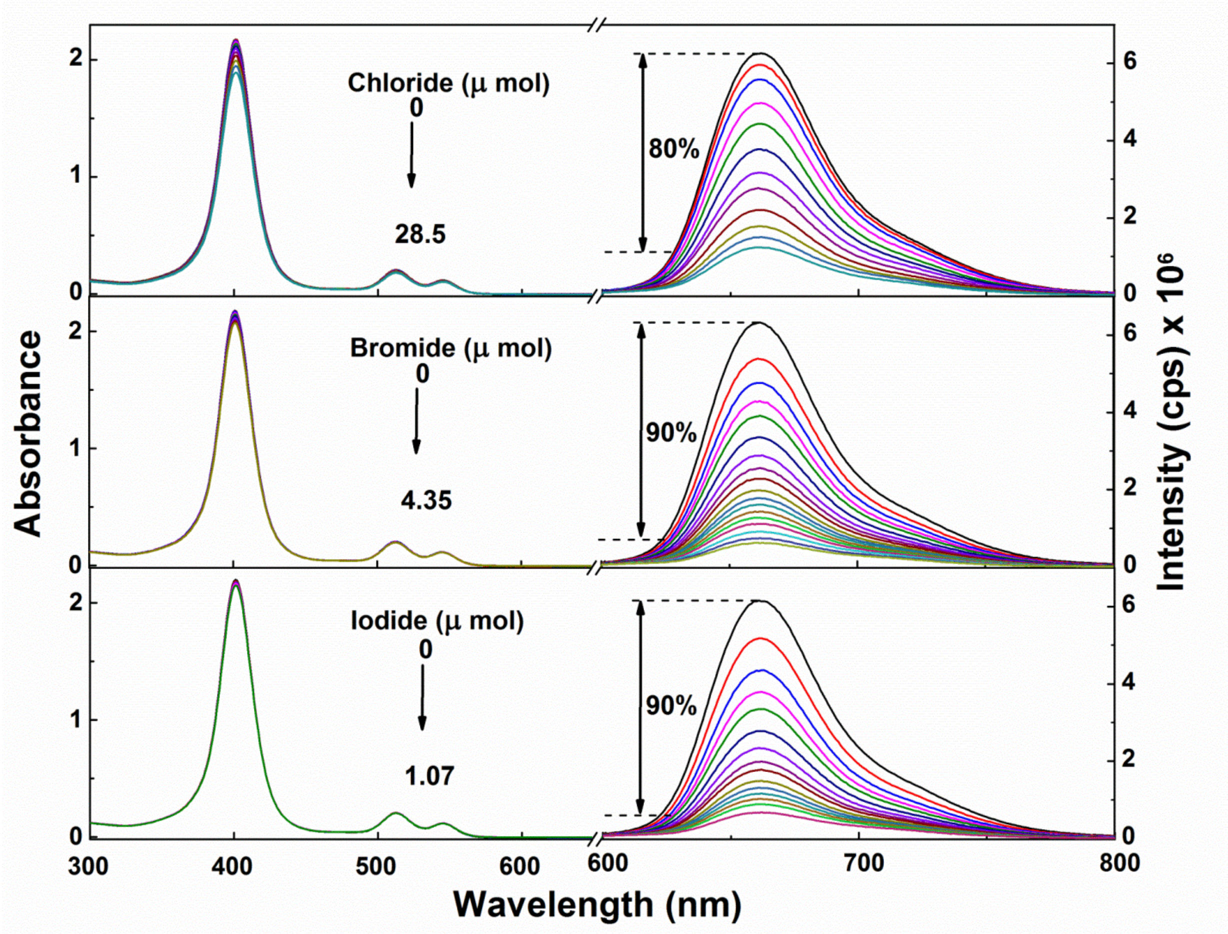

Fig. S2 UV-Vis absorption (left), and photoluminescence (right, λ_{ex} = 512 nm) spectra for Pt(II)TMPyP and after successive additions of various halides i. e. chloride, bromide, and iodide in aqueous phase.

Stern-Volmer Plots Corresponding to Steady-State PL Spectra for Pt(II)TMPyP-Halide Systems

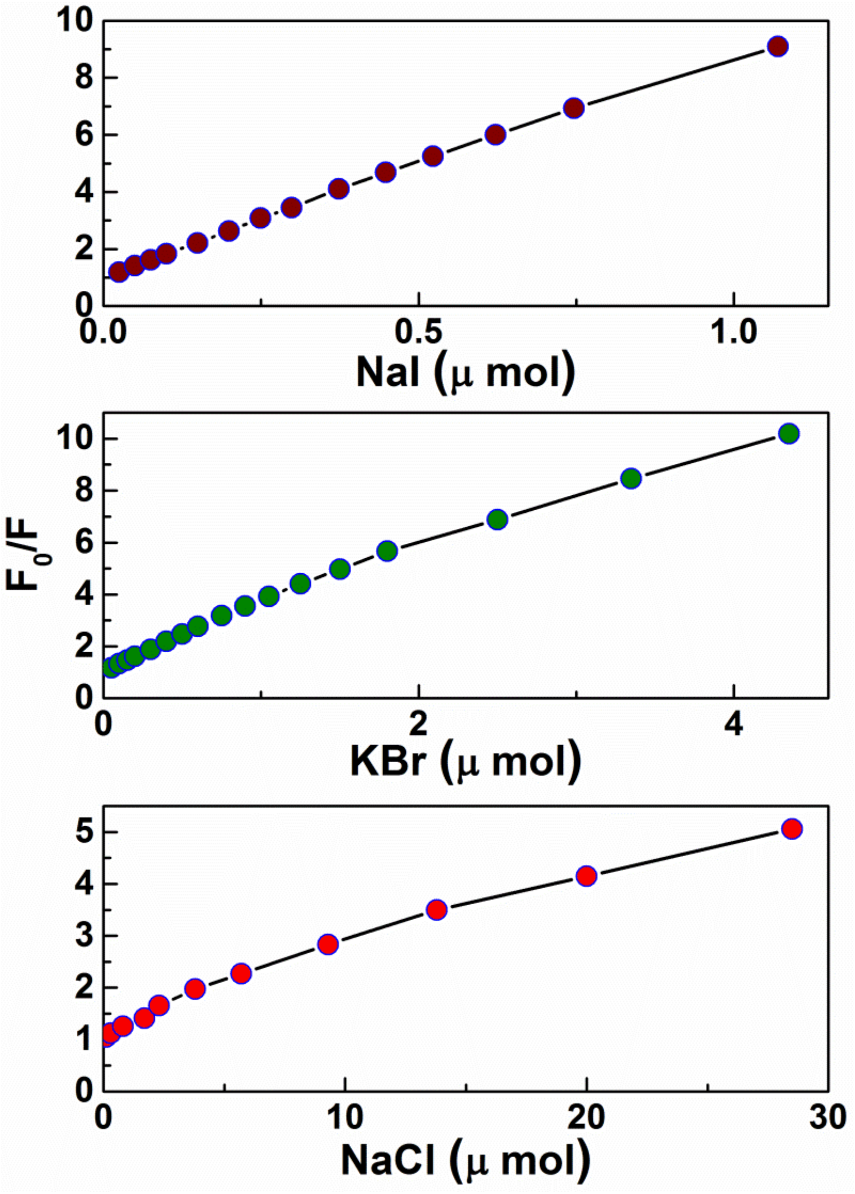

Fig. S3 Stern-Volmer plots for Pt(II)TMPyP, and with the maximum amounts of halides added into it for similar quenching (corresponding to PL spectra in Fig. S2).

Time Correlated Single Photo Counting of Pt(II)TMPyP, and with Iodide

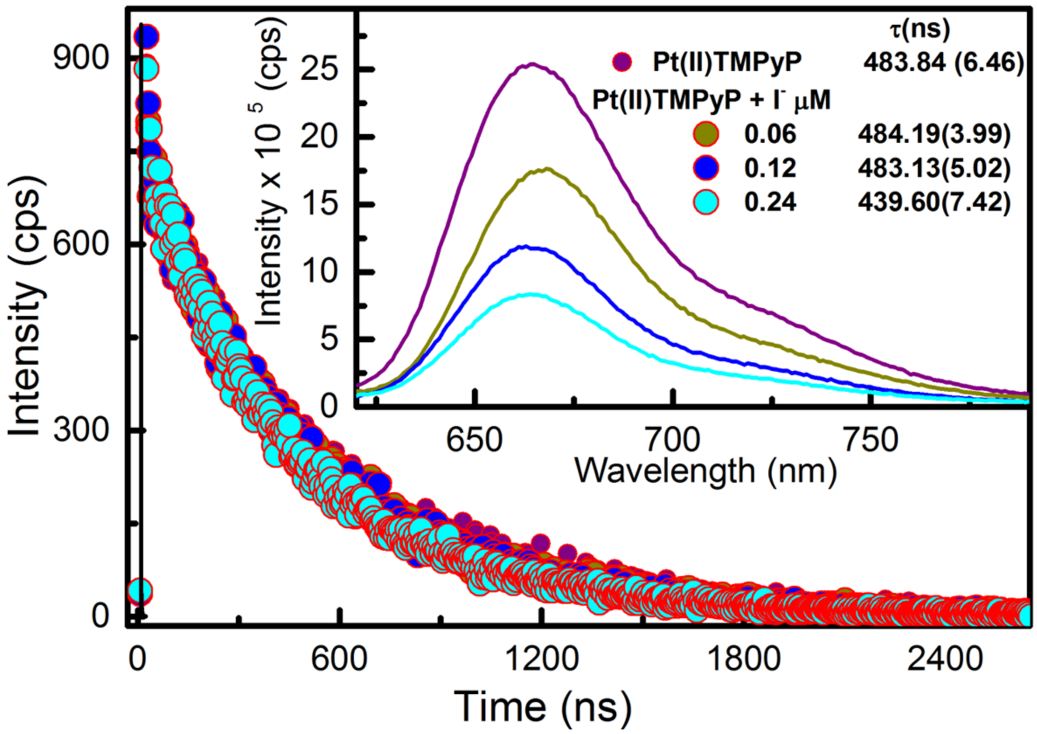

Fig. S4 Time correlated single photon counting for Pt(II)TMPyP porphyrin, and with successive additions of iodide in aqueous phase. Corresponding lifetimes extracted from kinetic traces monitored at λ_{em} = 660 nm are given on graph and standard errors included in parenthesis.

UV-Vis Absorption and PL Spectra for Pt(II)TMPyP, and with Iodide in Methanol

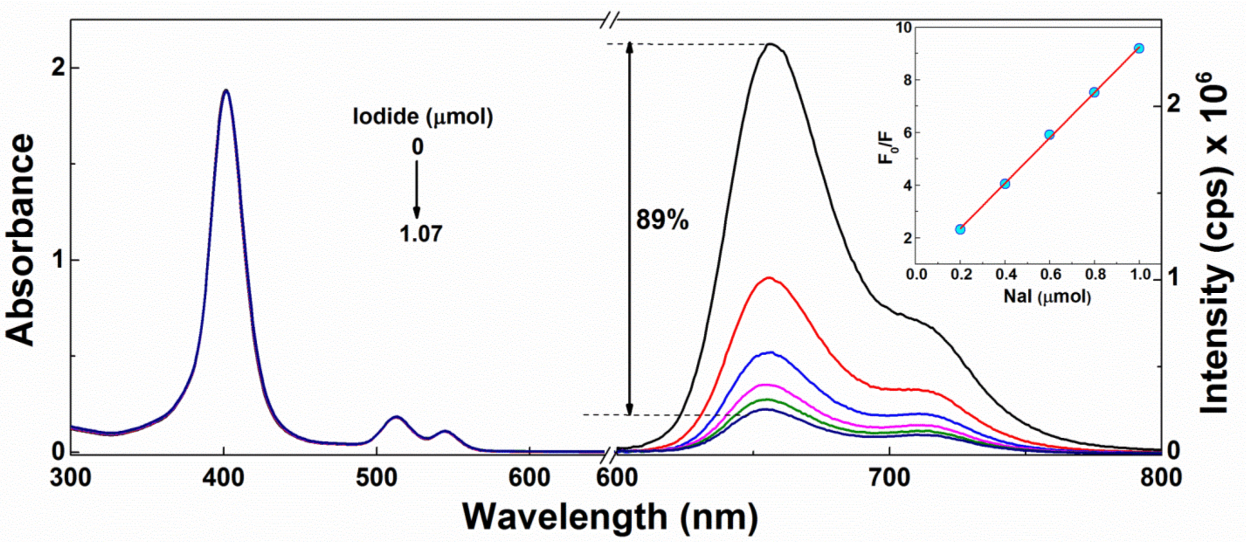

Fig. S5 UV-Vis absorption (left), and photoluminescence (right, λ_{ex} = 512 nm) spectra for Pt(II)TMPyP, and after successive additions of iodide in organic phase, methanol.

UV-Vis Absorption and PL Spectra for Zn(II)TMPyP, and with Iodide

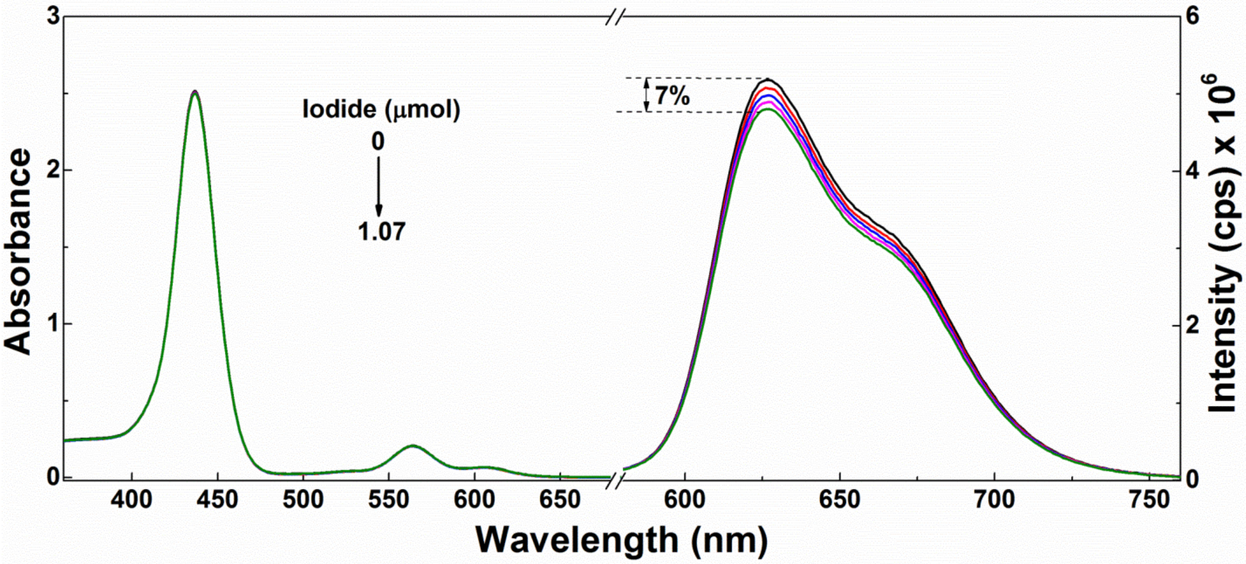

Fig. S6 UV-Vis absorption (left), and photoluminescence (right, λ_{ex} = 563 nm) spectra for Zn(II)TMPyP and after successive additions of iodide in aqueous phase.

Transient Absorption Studies on Zn(II)TMPyP, and with Iodide

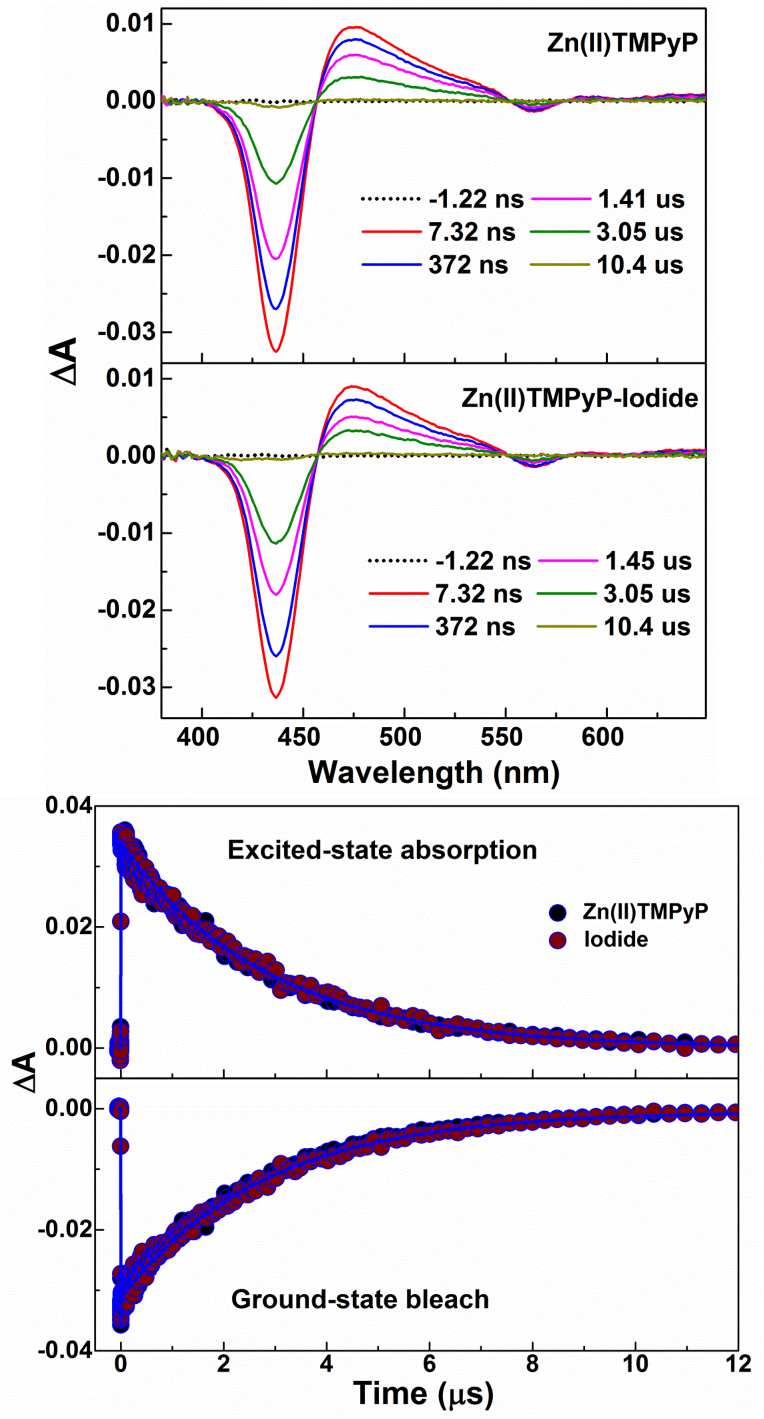

Fig. S7 Transient absorption spectra (top), and kinetics (bottom) for Zn(II)TMPyP porphyrin, and upon its interaction with iodide in aqueous phase (λ_{ex} = 350 nm; $\lambda_{monitoring}$ 350–900 nm), excitation energy density = 0.36 mJ/cm^2. Monitoring wavelengths are 470 nm for excited-state absorption and 440 nm for ground-state bleach.

Helios – Femtosecond Transient Absorption of Pt(II)TMPyP, and with Iodide

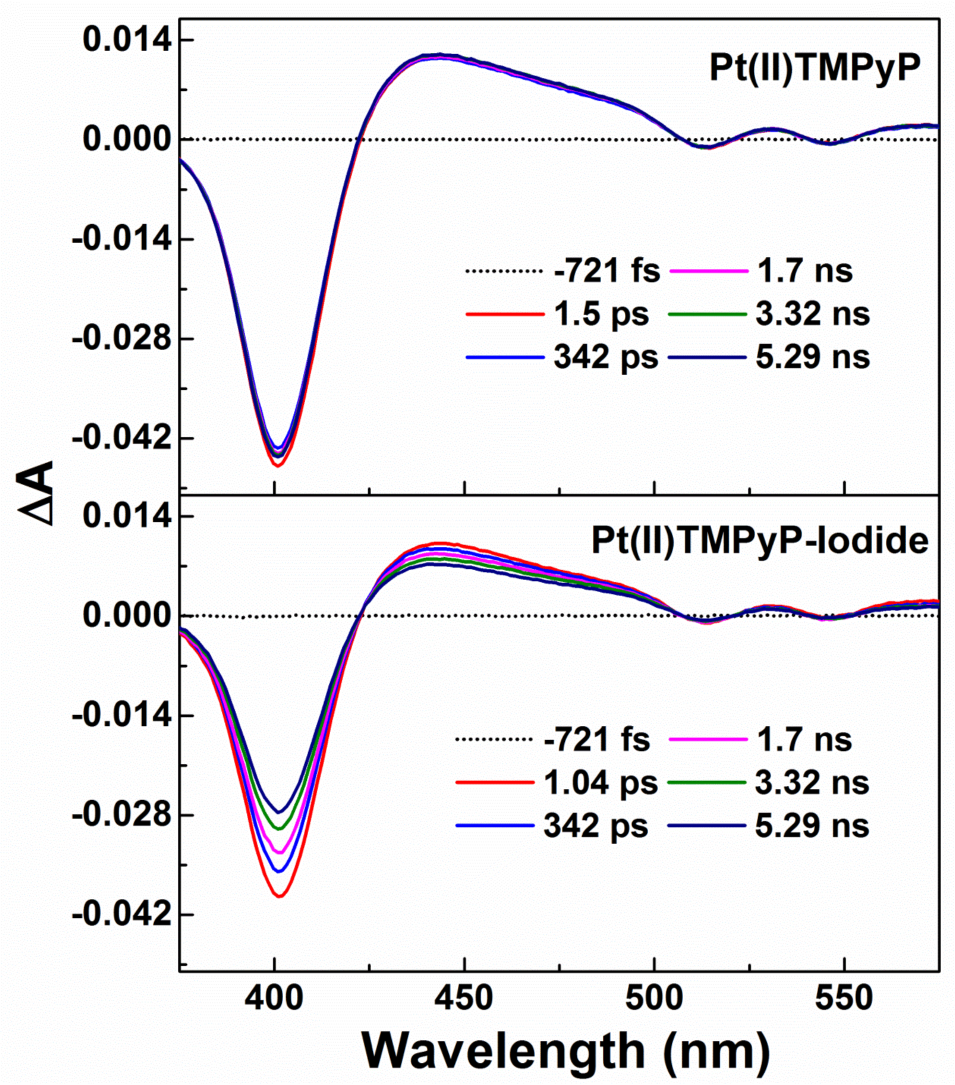

Fig. S8 Femtosecond transient absorption spectra of Pt(II)TMPyP porphyrin, and with addition of iodide in aqueous phase (λ_{ex} = 350 nm; $\lambda_{monitoring}$ 350–700 nm), excitation energy density = 1.44 mJ/cm^2.

Kinetics of Femtosecond TA Spectra of Pt(II)TMPyP, and with Iodide

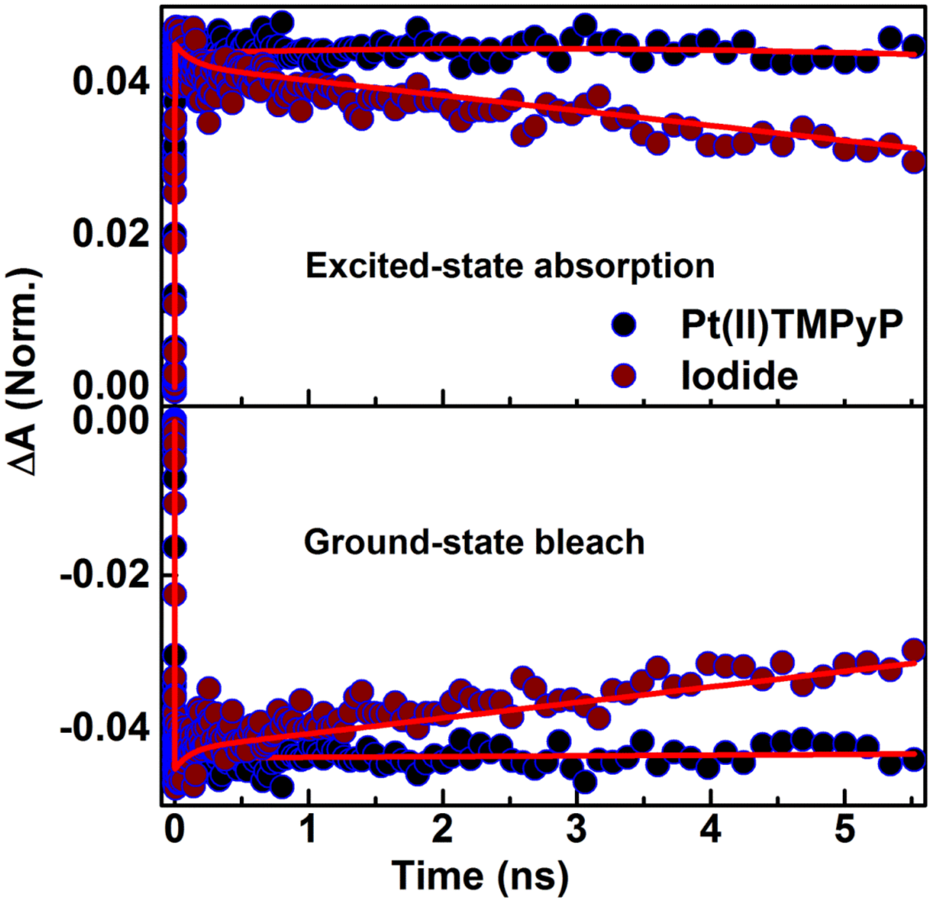

Fig. S9 Kinetics of femtosecond transient absorption spectra of Pt(II)TMPyP porphyrin, and with addition of iodide in aqueous phase. Monitoring wavelengths are 443 nm for excited-state absorption and 401 nm for ground-state bleach.

Steady-State UV-Vis Absorption and PL Spectra for Pt(II)TMPyP, and with Fluoride

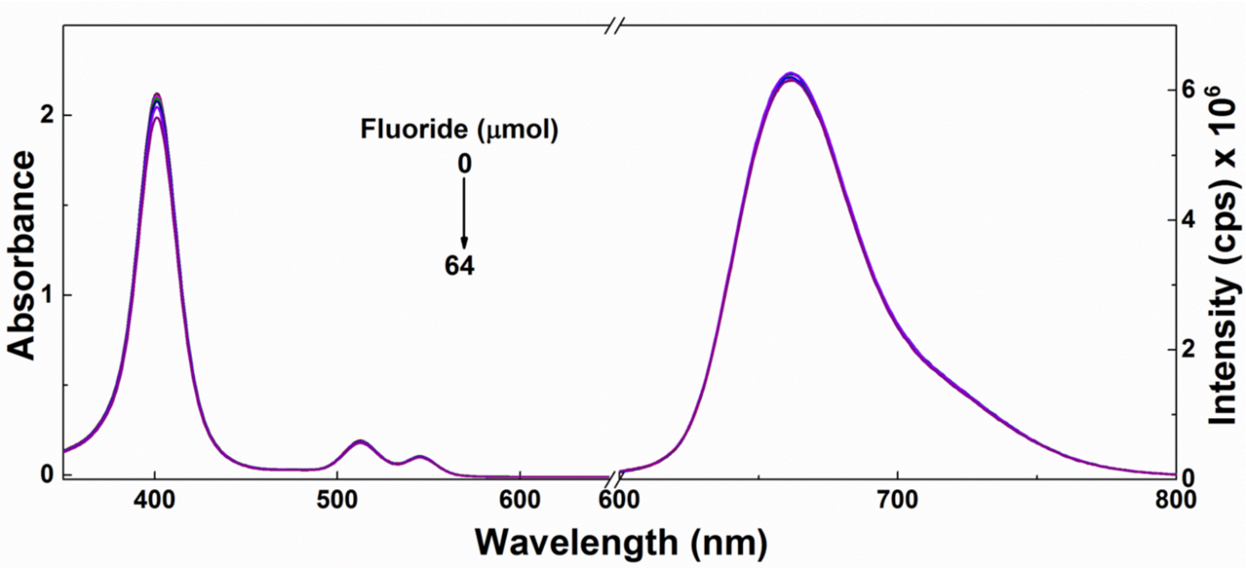

Fig. S10 UV-Vis absorption (left), and photoluminescence (right, λ_{ex} = 512 nm) spectra for Pt(II)TMPyP, and after successive additions of fluoride in aqueous phase.

Detailed Description of Ultra-sensitive Halide Detection with Pt(II)TMPyP Porphyrin

In the presence of halide ions, the quenching of the photoluminescence of Pt(II)TMPyP can be directly monitored upon irradiation with visible light. Pt(II) porphyrin phosphorescence was quenched to different magnitudes through the use of different halides (Fig. 1). The efficiency of quenching was experimentally demonstrated to increase in the order chloride < bromide < iodide. In the Pt(II)TMPyP porphyrin, the central cavity is filled with Pt(II) metal and that makes it interesting candidate as a senor for the detection of halides. A previous study with metal-free porphyrin dissolved in organic solvent reported a poor sensitivity towards detection of halide (Ref. 19; *Makrogeterotsikly*, 2008, 50). It is interesting to note that Pt(II) porphyrin demonstrated similar sensitivity towards iodide detection in methanol (Fig. S5), and in aqueous phase (Fig. S2). A specific metal filling the central cavity of porphyrin has important role, and when Pt(II) was exchanged with Zn(II) sensing function for similarly dilute aqueous solutions of halides was almost lost (Fig. S6). It would mean that the Pt metal center is the key component of the sensing down to such an extremely detection limit.

The photoluminescence quenching upon the addition of halides indicates the presence of a photoinduced electron transfer event between the halide donor and the Pt(II)TMPyP acceptor. Non-linear Stern-Volmer plots for all of the detected halide ions indicate a static reaction for the quenching process (Fig. S3). Furthermore, the bimolecular quenching rate constant, $k_q \approx 7.8 \times 10^{12}$ $M^{-1}s^{-1}$ far exceeds the diffusion-controlled limit ($\sim 3 \times 10^{10}$ $M^{-1}s^{-1}$) establishing the fact that the quenching is due to static interaction, and confirmed by recording phosphorescence lifetimes (Fig. S4).

The transient absorption spectra of Pt(II)TMPyP-halides demonstrate shortening in the order; Pt(II)TMPyP alone > chloride > bromide > iodide (Fig. 2). And this was confirmed from the kinetic traces for the ground-state bleach recovery time values extracted from the transient absorption spectra (Fig. 3). This overall fast deactivation of the triplet signal implies the presence of an extra process involved in deactivation of the excited state when halides are present compared to the case of free Pt(II) porphyrin. Moreover, for the control experiment with Zn(II)TMPyP-iodide system, no appreciable changes were observed in transient absorption spectra and corresponding kinetics making a confirmation that the interaction occurs only with the Pt(II) at the macrocycle center of the porphyrin (Fig. S7).