Light-gated specific oxidase-like activity of self-assembled Pt(II) nanozyme for environmental remediation

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Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded on Bruker Ultrashield AV400 (400 MHz) and Bruker AV500 (500 MHz) high-resolution multinuclear FT-NMR spectrometers and chemical shifts were expressed in ppm using a residual protic solvent as the internal standard. All the NMR data were processed in MestreNova Lite software. The ESI-HRMS of ligands were recorded on a Xevo G2-XS Q-TOF instrument. Whereas, the mass of metal complexes was recorded on an Agilent 6540 UHD Accurate-Mass Q-TOF spectrometer. The UV-Vis absorption spectra, photoluminescence (PL) spectra, and kinetic analyses were acquired at room temperature using a Molecular Devices SpectraMax® M5e microplate reader. The absolute luminescence quantum yield was acquired by Quanta-ϕ Horiba Instrument linked with a Fluorolog spectrophotometer. The luminescence lifetimes were collected on a time-correlated single photon counting (TCSPC) lifetime fluorometer from DeltaPro™ (HORIBA Scientific). DLS measurement was performed on a Malvern Zetasizer Nano instrument. Field emission scanning electron microscope (FESEM) images were acquired using the Ultra55 FE-SEM Karl Zeiss EDS instrument with 5.0 kV emission voltage.
Scheme S1. Synthetic scheme of BiP, C6-BiP, and C8-BiP ligands.

**BiP:** $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (ppm) = 13.00 (bs, 2H), 8.35 (d, $J$ = 8.3 Hz, 2H), 8.15 (t, $J$ = 8.5 Hz, 1H), 7.76 (t, $J$ = 4.4 Hz, 4H), 7.33-7.30 (m, 4H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (ppm) = 150.9, 148.2, 139.6, 123.6, 121.8. **HRMS (ESI)** $[C_{19}H_{13}N_5 + H]^+$: calcd m/z 312.1244, found m/z 312.1245.

**C6-BiP:** $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$(ppm) = 8.31 (d, $J$ = 7.9 Hz, 2H), 8.02 (t, $J$ = 7.9 Hz, 1H), 7.88-7.84 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.29 (m, 4H), 4.68 (t, $J$ = 7.5 Hz, 4H), 1.75-1.68 (m, 4H), 1.08-1.00 (m, 12H), 0.61 (t, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$(ppm) = 150.2, 150.0, 142.8, 138.1, 136.3, 125.5, 123.5, 122.7, 120.3, 110.3, 44.9, 31.1, 30.0, 26.3, 22.3, 13.7. **HRMS (ESI)** $[C_{21}H_{17}N_5 + H]^+$: calcd m/z 480.3122, found m/z 480.3127.
Scheme S2. Synthetic scheme of Pt-1, Pt-6 and Pt-8.

Pt-6- $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.45 (t, $J = 8.1$ Hz, 1H), 8.18 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.07 (t, $J = 7.5$ Hz, 2H), 4.31 (t, $J = 6.5$ Hz, 4H), 1.74-1.67 (m, 4H), 1.41-1.26 (m, 12H), 0.90 (t, $J = 6.9$ Hz, 6H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 151.8, 146.9, 138.0, 133.5, 126.4, 126.0, 123.9, 115.36, 112.5, 40.4, 30.8, 29.6, 25.3, 21.9, 13.8. Calculated mass with isotopic distribution as shown in inset Fig. S9.

Pt-1- $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 8.49 (t, $J = 8.1$ Hz, 1H), 8.31 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 2H), 6.94 (d, $J = 8.1$ Hz, 2H), 3.81 (s, 6H). $^{13}$C NMR (100 MHz, DMSO-d$_6$): $\delta$(ppm) = 53.1, 147.6, 142.9, 138.2, 133.9, 126.8, 126.0, 125.2, 115.5, 112.6, 32.7. HRMS (ESI) [C$_{21}$H$_{17}$ClN$_5$Pt]$^+$: calcd m/z 569.0815, found m/z 569.0809

Pt-8- $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.95 (bs, 1H), 8.42 (bs, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.26m (t, $J = 7.1$ Hz, 2H), 7.12 (t, $J = 7.1$ Hz, 2H), 6.89 (d, $J = 8.1$ Hz, 2H), 4.5 (bs, 4H) ,1.84 (bs, 6H), 1.44-1.26 (m,18H), 0.87 (s, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.2, 147.3, 139.0, 133.9, 126.8, 125.9, 124.8, 117.1, 111.1, 44.5, 31.8, 30.4, 29.33, 29.1, 22.6,14.1 Calculated mass with isotopic distribution as shown in inset Fig. S9.
Fig. S1. $^1$H NMR spectrum of BiP in DMSO-$d_6$.

Fig. S2. $^{13}$C NMR spectrum of BiP in DMSO-$d_6$. 
Fig. S3. ESI-HRMS of C6-BiP

Fig. S4. $^1$H NMR spectrum of C6-BiP in CDCl$_3$. 
Fig. S5. $^{13}$C NMR spectrum of C6-BiP in CDCl$_3$.

Fig. S6. ESI-HRMS of C6-BiP.
Fig. S7. $^1$H NMR spectrum of Pt-6 in DMSO-$d_6$.

Fig. S8. $^{13}$C NMR spectrum of Pt-6 in DMSO-$d_6$. 
**Fig. S9.** ESI-MS of Pt-6. Inset: isotopic mass distribution pattern of Pt-6. Colour code: maroon corresponds to experimentally obtained and blue corresponds to theoretically simulated.

**Fig. S10a.** $^1$H NMR spectrum of Pt-1 in DMSO-d$_6$. 
**Fig. S10b.** $^{13}$C NMR spectrum of Pt-1 in DMSO-$d_6$.

**Fig. S10c.** ESI-MS of Pt-1. Inset: isotopic mass distribution pattern of Pt-1.
Fig. S11a. $^1$H NMR spectrum of Pt-8 in CDCl$_3$.

Fig. S11b. $^{13}$C NMR spectrum of Pt-8 in CDCl$_3$. 
**Fig. S11c.** ESI-MS of Pt-8. down: isotopic mass distribution pattern of Pt-8.

**Fig. S12.** Normalized PL intensity of Pt-6 at 650 nm with the increase in water fraction (0-0.99; v/v).
**Fig. S13.** Absolute luminescence quantum yield of NanoPtA

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<th>Start Wavelength</th>
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<th>End Wavelength</th>
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<td>4.53E+13</td>
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Quantum Yield: 12.67
Abs Error: 0.643
Relative Error: 0.05073

**Fig. S14.** (a) Bar plot of normalized PL intensity of Pt-1, Pt-6, and Pt-8 (10 µM) complexes at 650 nm in 99% water-methanol mixture. Luminescence lifetime of (b) Pt-1 and (c) Pt-8 in 99% water-methanol solution, whereas IRF is the instrument response function.
Fig. S15. Photoluminescence lifetime of Pt-6 at (a) 40%, (b) 60%, and (c) 80% water fractions, whereas IRF is the instrument response function.

Fig. S16. FESEM images of NanoPtA assembly formed in 99% water-methanol mixture.
Fig. S17. (a) Particle size distribution of NanoPtA in different water fractions at 40%, 60%, and 80% water-methanol mixture and (b) at 99% water-methanol mixture.

Fig. S18. UV absorption spectra of TMB (0.5 mM) in the presence of NanoPtA (10 µM) with the variation of visible light (at 470 nm) exposure time (0-16 min.) in acetate buffer (100 mM, pH 4.0).
Fig. S19. Absorbance (at 652 nm) of TMB (0.5 mM) oxidized product upon visible light (470 nm) irradiation for 10 min in the presence of Pt-1, Pt-6, and Pt-8 in acetate buffer (100 mM, pH 4.0).

Fig. S20. (a) Extent of TMB oxidation with different concentrations NanoPtA (0-50 µM). (b) Absorbance plot of oxidized TMB with increasing concentration of NanoPtA (0-500 µM). Condition: medium: acetate buffer (100 mM, pH 4.0) and irradiation of sunlight for 10 min.
Fig. S21. (a,b) UV absorption spectra of ABTS (0.5 mM) and OPD (0.5 mM) in the presence of NanoPtA (10 µM) upon irradiation with visible light 470 nm for 10 min. in acetate buffer (100 mM, pH 4.0).

Scheme S3. Reactions involved in the terephthalic acid assay.
Fig. S22. Effect of 2,4-DP concentrations on the catalytic activity of NanoPtA (10 µM) at 510 nm.

![Graph showing absorbance at 510 nm vs. [2,4-DP] (µM).]

Fig. S23. Michaelis Menten plot of oxidized dopamine absorbance (at 475 nm) catalyzed by NanoPtA (10 µM) in HEPES buffer (10 mM, pH 7.4). Light source = visible light 470 nm.

![Diagram showing the Michaelis Menten plot and the chemical structure of dopamine and its oxidized form.]
Fig. S24. (a) Plot of oxidized adrenaline absorbance at 475 nm versus adrenaline concentration catalyzed by NanoPtA (10 µM). (b) Plot of oxidized dopamine absorbance at 485 nm versus dopamine concentration catalyzed by NanoPtA (10 µM). The red line showed the linear fit of the data.

Fig. S25. Comparison of % trypan blue degradation under exposure to different irradiation sources in the presence of NanoPtA (10 µM and 20 µM). Light sources = Visible light at 470 nm, White light = 40W LED bulb, and Sunlight.
**Fig. S26.** (a) Absorbance at 590 nm for TrB dye degradation with time at various concentrations of H$_2$O$_2$ (0, 0.5, 1.5, 10 mM) in the absence of visible light. (b) absorbance at 590 nm for TrB dye degradation with time at various concentrations of H$_2$O$_2$ (0, 0.5, 1.5, 10 mM) with NanoPtA (10 µM) in the absence of visible light. (c) TrB dye degradation with time at various H$_2$O$_2$ concentrations (0, 0.5, 1.5, 10 mM) in the presence of visible light. (d) TrB dye degradation with NanoPtA (10 µM) at various H$_2$O$_2$ concentrations (0, 0.5, 1.5, 10 mM) in the absence and presence of visible light.
Fig. S27. a) Degradation of H\textsubscript{2}O\textsubscript{2} (25 µM) in the presence of NanoPtA (10µM) over time b) Degradation of TrB dye (20 µM) in the presence of NanoPtA alone and H\textsubscript{2}O\textsubscript{2} and NanoPtA mixture after degassing the vials with N\textsubscript{2}.

Fig. S28. Effect of temperature on % of trypan blue degradation.
Table S1. Comparison of the kinetic parameters between NanoPtA and reported oxidase, and oxidase-mimicking nanzymes.

<table>
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<tr>
<th>Catalysts and Substrate</th>
<th>$K_m$ (mM)</th>
<th>$V_{max}$ ($10^{-8}$ Ms$^{-1}$)</th>
<th>Reference</th>
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<tr>
<td>Dex-FeMnzyme (TMB)</td>
<td>0.33</td>
<td>13.29</td>
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<tr>
<td>CeO$_2$ NPs (TMB)</td>
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<tr>
<td>Fe-N/C (TMB)</td>
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<tr>
<td>Fe-Co-LDH (TMB)</td>
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<td>5.4</td>
<td>4</td>
</tr>
<tr>
<td>Fe single atom nanzyme (TMB)</td>
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<td>5</td>
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<td>Pd cage (TMB)</td>
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<td><strong>NanoPtA</strong> (TMB)</td>
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<td><strong>10.5</strong></td>
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</tr>
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References