Long-lived excited states of platinum(II)-porphyrin for highly

efficient photocatalytic hydrogen evolution

Govardhana Babu Bodedla,^{a, b} Yu Dong,^c Geliang Tang,^c Jianzhang Zhao,^c Fuxiang Zhang,^d Xunjin Zhu, ^{b,*} and Wai-Yeung Wong ^{a,*}

^a Department of Applied Biology & Chemical Technology and Research Institute for Smart Energy, The Hong Kong Polytechnic University, Hong Kong, P. R. China, and

The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, P. R.

China. E-mail: wai-yeung.wong@polyu.edu.hk.

^b Department of Chemistry, Hong Kong Baptist University, Hong Kong, P. R. China. E-mail: xjzhu@hkbu.edu.hk.

^c School of Chemical Engineering and State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, P. R. China.

^d State Key Laboratory of Catalysis, *i*ChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China.

Experimental Section

Materials and Methods

All the chemicals used in this work were purchased from commercial sources and used as received. Solvents were dried by distilling over suitable dehydrating agents according to standard procedures. Purification of the compounds was performed by column chromatography with 100-200 mesh silica gel. ¹H NMR spectra were recorded in an NMR spectrometer operating at 400.00 MHz. The chemical shifts were calibrated from the residual peaks observed for the deuterated solvent chloroform (CDCl₃) at δ 7.26 ppm for ¹H and ¹³C NMR spectra.

High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer. The optical absorption and emission spectra of the porphyrins were measured for the freshly prepared air equilibrated solutions (10 μ M) at room temperature by using UV-Vis spectrophotometer and spectrofluorimeter, respectively. Cyclic voltammetry experiments were conducted on an electrochemical workstation (CHI660C Instruments, China) with standard three-electrode cell. A glassy carbon working electrode, a nonaqueous Ag/Ag⁺ reference electrode, and a platinum wire counter electrode were used for the measurements. It was measured at room temperature in THF solution (100 μ M). Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Ferrocene (100 μ M) was added as the internal reference. Agilent 7900 quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) was employed for the elemental analysis. 1000 mg/mL Pt single element standard (Inorganic ventures, VA, USA) and Milli-Q water (18.2 M Ω cm) were employed in preparation of the solutions for ICP-MS analysis. All solutions we prepared in 2% HNO₃ and diluted to concentration below 50 mg/L before analysis.

Preparation of photocatalytic systems

A multichannel photochemical reaction system fixed with LED white light (PCX50B, 148.5 mW/cm^2) was used as the light source. The PHE evolution experiments were performed in a quartz vial reactor (20 mL) sealed with a rubber septum, gas-closed system, at ambient temperature and pressure. Initially, 10 μ M of porphyrins in THF/H₂O (2:1; v/v) solution sonicated for 5 min and 0.4 M of TEA was added. The resulting solution was purged with argon gas for 15 min to ensure anaerobic conditions and then it was placed in a multichannel photochemical reaction system. After 1 h of irradiation, the released gas (400 μ L) was collected by syringe from the headspace of the reactor and was analyzed by gas chromatography (Shimadzu, GC-2014, Japan, with ultrapure Ar as a carrier gas) equipped with a TDX-01(5 Å

molecular sieve column) and a thermal conductivity detector (TCD). Eventually, the total content of PHE was calculated according to the standard curve.

Photoelectrochemical Measurement

The transient photocurrent response (I–t curves) studies were performed using an electrochemical workstation (CHI660C Instruments, China) with a Pt wire (counter electrode), a non-aqueous Ag/AgNO₃ (reference electrode) and fluorine-doped tin oxide (FTO) glass coated with porphyrins on the conductive surface (working electrode) upon irradiation of LED monochromatic point lamp (3 W, 420 nm). The light spot effective area on the working electrode was set as 28.26 mm². Typically, the working electrode was prepared by drop-casting a 100 μ M solution of porphyrins on the conductive surface of the FTO glass. A 5 mL volume of 0.5 M Na₂SO₄ aqueous solution acted as the electrolyte. The open-circuit voltages were set as the initial bias voltages in the transient photocurrent response tests.

Nanosecond transient absorption spectra

The nanosecond transient absorption spectra were measured with an LP980 laser flash photolysis spectrometer (Edinburgh Instruments, U.K.). The samples were excited with a nanosecond pulsed laser (OPOLette 355II) with tunable wavelength in the range of 210–2400 nm (OPOTEK, USA). The transient signals were digitized with a Tektronix TDS 3012B oscilloscope, and the typical laser energy is ca. 5 mJ per pulse. The triplet-state lifetimes were obtained with the L900 software. All samples were deaerated with nitrogen (N₂) for about 15 min before measurement. Triplet state quantum yield was determined with the ground state bleaching method, with TPP as standard ($\Phi_T = 0.85$ in THF), according to eq 1. In the equation, "sam" and "std" represent the sample and standard, respectively. Φ is the triplet-state quantum yield, ε is the molar absorption coefficient of the ground state determined by UV–vis absorption

spectra, ΔA is the optical density of the ground-state bleaching band determined by nanosecond transient absorption spectra.

$$\Phi_{\rm sam} = \Phi_{\rm std} \left(\frac{\varepsilon_{\rm std}}{\varepsilon_{\rm sam}} \right) \left(\frac{\Delta A_{\rm sam}}{\Delta A_{\rm std}} \right)$$
(eq. 1)

Singlet oxygen quantum yield (Φ_{Δ})

The singlet oxygen quantum yield (Φ_{Δ}) was measured with 1,3-diphenylisobenzofuran (DPBF) as the ¹O₂ scavenger, [Ru(bpy)₃]Cl₂ as standard ($\Phi_{\Delta} = 0.57$ in ACN) as standard, according to equation 2.

$$\Phi_{\rm sam} = \Phi_{\rm std} \left(\frac{1 - 10^{-A_{\rm std}}}{1 - 10^{-A_{\rm sam}}} \right) \left(\frac{m_{\rm sam}}{m_{\rm std}} \right) \left(\frac{\eta_{\rm sam}}{\eta_{\rm std}} \right)^2 \tag{eq.2}$$

In the above equation, 'sam' and 'std' represent the sample and the standard. Φ , A, m and η represent the singlet oxygen quantum yield, the absorbance at excitation wavelength, the slope of the plot of the absorbance of DPBF changes over photo-irradiation time, and the refractive index of the solvent used for measurement, respectively. Optically matched solutions were used (the solutions of the sample and the standard give same absorbance at the excitation wavelength).

Density functional theory calculations

Density Functional Theory (DFT) calculations were used for geometry optimization and the frontier molecular orbitals (in a vacuum) of the complexes. All the calculations were performed with the Gaussian 09W program. The geometry optimization of the ground state was performed at the B3LYP/6-31G(d) level for C, H, N and O atoms and at B3LYP/GENECP level for Pt atoms. No imaginary frequency was observed for the computations.

Synthesis

Platinum(II)-tetraphenylporphyrin (PtTPP) was prepared for comparison.¹

PtD(*p*-NI)PP:

A mixture of PtCl₂ (61 mg, 0.23 mmol) and benzonitrile (15 mL) was bubbled with N₂ for 20 min and heated at 100 °C for 1 h under a N₂ atmosphere. To this mixture, free-base porphyrin D(*p*-NI)PPH2 (50 mg, 0.05 mmol) was added and the mixture was refluxed until the free-base porphyrin disappeared (ca. 2.5 h). After completion of the reaction, benzonitrile was removed under reduced pressure. The resulting crude black solid containing product was purified by column chromatography with silica gel using CHCl₃/hexane (1:1, v/v) as eluant. Orange color solid; yield: 58 mg, 92.0%. ¹H NMR (CDCl₃, 400.00 MHz) δ 0.88-1.02 (m, 12 H), 1.37-1.48 (m, 16 H), 2.01-2.08 (m, 2 H), 4.17-4.28 (m, 4 H), 7.89-7.92 (m, 6 H), 8.06 (d, *J* = 7.6 Hz, 2 H), 8.36 (d, *J* = 7.6 Hz, 4 H), 8.68-8.82 (m, 6 H), 9.04 (d, *J* = 4.8 Hz, 4 H), 9.25 (d, *J* = 4.8 Hz, 4 H), 10.15 (s, 2 H) ppm. ¹³C NMR (CDCl₃, 100.00 MHz) δ 10.83, 14.25, 23.23, 24.23, 28.87, 30.92, 38.09, 44.32, 119.08, 120.43, 120.56, 122.05, 123.10, 126.80, 127.10, 127.86, 128.26, 128.32, 128.90, 130.14, 131.00, 131.37, 132.58, 134.68, 134.89, 138.20, 142.18, 142.60, 146.45, 164.57, 164.73. MALDI–TOF; m/z calculated for C₇₂H₆₂N₆O₄Pt: 1270.4497 found 1270.4440.



Scheme S1. Synthetic route for the preparation of the Pt(II)-porphyrins.

PtT(p-NI)PP:

A mixture of PtCl₂ (30 mg, 0.12 mmol) and benzonitrile (15 mL) was bubbled with N₂ for 20 min and heated at 100 °C for 1 h under a N₂ atmosphere. To this mixture, free-base porphyrin T(*p*-NI)PPH2 (50 mg, 0.03 mmol) was added and the mixture was refluxed until the free-base porphyrin disappeared (ca. 4.0 h). After completion of the reaction, benzonitrile was removed under reduced pressure. The resulting crude black solid containing product was purified by column chromatography with silica gel using CHCl₃/hexane (1:1, v/v) as eluant. Orange color solid; yield: 57 mg, 94.0%. ¹H NMR (CDCl₃, 400.00 MHz) δ 0.91-1.01 (m, 24 H), 1.33-1.49 (m, 32 H), 2.00-2.07 (m, 4 H), 4.16-4.27 (m, 8 H), 7.87-7.91 (m, 4 H), 7.95 (d, *J* = 8.0 Hz, 8 H), 8.08 (d, *J* = 7.6 Hz, 4 H), 8.41 (d, *J* = 8.0 Hz, 8 H), 8.69 (dd, *J* = 8.4, 1.2 Hz, 4 H), 8.75 (dd, *J* = 7.2, 1.2 Hz, 4 H), 8.82 (d, *J* = 7.6 Hz, 4 H), 9.01 (s, 8 H). ¹³C NMR (CDCl₃, 100.00 MHz) δ 10.79, 14.21, 23.18, 24.19, 28.82, 30.88, 38.06, 44.32, 119.46, 119.60, 120.93, 122.12, 123.13, 126.89, 127.14, 128.02, 128.28, 128.41, 128.92, 130.14, 131.01, 131.41, 132.50, 134.71, 134.95, 138.37, 141.97, 142.39, 142.43, 146.34, 164.54, 164.70. MALDI–TOF; m/z calculated for C₁₂₄H₁₁₂N₈O₈Pt: 2036.8274 found 2036.8246.

DFT calculations

Compound	States	Electronic transition	Energy ^{<i>a</i>} [eV / nm]	f^b	Composition ^c	CI ^d
PtT(p-NI)PP	Singlet	$S_0 \rightarrow S_1$	2.47 / 503	7/503 0.0216 H→L		0.4856
		$S_0 \rightarrow S_2$	3.24 / 383	1.8271	H−1→L	0.3404
		$S_0 \rightarrow S_3$	3.35 / 370	0.0063	$H-3\rightarrow L+2$	0.5691
	Triplet	$S_0 \rightarrow T_1$	1.85 / 672	0.0000	H→L	0.5289
		$S_0 \rightarrow T_2$	2.16 / 574	0.0000	H−1→L	0.5502
		$S_0 \rightarrow T_3$	2.25 / 552	0.0000	H−5→L+4	0.3474
PtD(p-NI)PP	Singlet	$S_0 \rightarrow S_1$	2.52 / 491	0.0032	$H\rightarrow L+2$	0.4777
		$S_0 \rightarrow S_2$	2.81 / 441	0.1344	H→L	0.5306
		$S_0 \rightarrow S_3$	3.30 / 376	2.3714	H−1→L+2	0.4220
		$S_0 \rightarrow S_4$	3.57 / 347	0.0440	H–4→L+1	0.4476
	Triplet	$S_0 \rightarrow T_1$	1.88 / 659	0.0000	$H \rightarrow L+3$	0.4776
		$S_0 \rightarrow T_2$	2.24 / 553	0.0000	H–4→L+1	0.4396

Table S1. Calculated electronic transition properties of the low-lying electronic excited states

 of porphyrin compounds based on B3LYP/GENECP/LANL2DZ level.

^{*a*} Only the selected low-lying excited states are presented. ^{*b*} Oscillator strengths. ^{*c*} Only the main configurations are presented. ^{*d*} The CI coefficients are in absolute values.



Fig. S1 Jablonski energy diagram of PtT(*p*-NI)PP based on the computation at B3LYP/GENECP/LANL2DZ level. Ethylhexyl chains were modified to methyl groups for simplicity.



Fig. S2 Jablonski energy diagram of PtD(*p*-NI)PP based on the computation at B3LYP/GENECP/LANL2DZ level. Ethylhexyl chains were modified to methyl groups for simplicity.



Fig. S3 Theoretically calculated energy level alignments of PtT(*p*-NI)PP and PtD(*p*-NI)PP.



Fig. S4 Cyclic voltammograms of Pt(II)-porphyrins recorded in THF solution (100 μ M) at room temperature under an argon atmosphere.



Fig. S5 Photoluminescence lifetime spectra of PtD(p-NI)PP and PtT(p-NI)PP recorded in THF/H₂O (2:1; v/v) solution at room temperature under an argon atmosphere.



Fig. S6 Photocurrent response spectra of PtD(*p*-NI)PP and PtT(*p*-NI)PP.



Fig. S7 Photocatalytic systems (a) PtT(*p*-NI)PP and (b) PtD(*p*-NI)PP before and after

irradiation.



Fig. S8. ICP-MS spectrum of photocatalytic system of PtD(*p*-NI)PP.



Fig. S9. ICP-MS spectrum of photocatalytic system of PtT(*p*-NI)PP.



Fig. S10. ICP-MS spectrum of Pt single element standard.



NI)PP.

	Sample				194 Pt [No Gas]			195 Pt [No Gas]				196 Pt [No Gas]					
Rjct	Data File	Acq. Date-Time	Туре	Level	Sample Name	CPS	Conc.	CPS RSD	Conc. RSD	CPS	Conc.	CPS RSD	Conc. RSD	CPS	Conc.	CPS RSD	Conc. RSD
####	001SMPL.d	5/4/2022 12:39 PM	Sample		acid	43.37666667		70.501165		10.01		100		43.37666667		35.250582	
####	002SMPL.d	5/4/2022 12:43 PM	Sample		acid	20.02		100		26.69333333		43.30127		16.68333333		69.282032	
****	003SMPL.d	5/4/2022 12:47 PM	Sample		acid	46.71333333		61.858957		23.35666667		89.214257		36.70333333		83.319558	
####	004SMPL.d	5/4/2022 12:51 PM	Sample		acid	23.35666667		65.465367		20.02		86.60254		20.02		132.28757	
****	005SMPL.d	5/4/2022 12:56 PM	Sample		acid	23.35666667		24.743583		26.69333333		57.282196		23.35666667		107.85478	
####	006CALS.d	5/4/2022 1:00 PM	CalStd	1	0	70.07	0	24.743583	N/A	56.72333333	0	44.410791	N/A	63.39666667	0	32.868411	N/A
####	007CALS.d	5/4/2022 1:04 PM	CalStd	2	1	55186.46	1.00489	0.9111628	0.91232116	56720.74333	1.02251	1.934551	1.93648759	43629.78	1.00877	1.8391208	1.841797
####	008CALS.d	5/4/2022 1:08 PM	CalStd	3	5	269194.66	4.9067	0.0979506	0.09797613	274470.9167	4.95183	1.8128101	1.81318479	207042.6233	4.79258	0.4404148	0.44054968
####	009CALS.d	5/4/2022 1:12 PM	CalStd	4	10	552053.44	10.0638	0.38038	0.3804283	552454.41	9.96806	0.6278186	0.62788305	417325.3933	9.66165	0.8250261	0.82515143
####	010CALS.d	5/4/2022 1:17 PM	CalStd	5	30	1645201.09	29.9941	1.9032182	1.90329928	1663553.263	30.0179	1.5766463	1.57670004	1302038.14	30.1471	1.4448148	1.44488518
####	011SMPL.d	5/4/2022 1:21 PM	Sample		acid	323.6666667	0.00462	10.861163	13.8621557	343.6866667	0.00518	8.8979463	10.6567814	260.2666667	0.00456	17.626936	23.3032144
####	012SMPL.d	5/4/2022 1:25 PM	Sample		acid	110.11	0.00073	27.272727	75	123.4566667	0.0012	4.6812184	8.66025404	113.4466667	0.00116	18.367641	41.63332
####	013SMPL.d	5/4/2022 1:29 PM	Sample		Pt-D 100x	523.8733333	0.00827	12.433159	14.352914	513.8633333	0.00825	21.011716	23.6189147	447.1233333	0.00889	8.475793	9.87610496
####	014SMPL.d	5/4/2022 1:34 PM	Sample		Pt-T 100x	2122.31	0.03742	9.8048157	10.1395833	2265.823333	0.03986	5.0836346	5.21416772	1671.793333	0.03724	7.3584674	7.6485092
****	015SMPL.d	5/4/2022 1:38 PM	Sample		acid	93.42666667	0.00043	43.30127	173.205081	106.7733333	0.0009	28.641098	61.1010093	83.41666667	0.00046	24.979992	104.0833
####	016SMPL.d	5/4/2022 1:42 PM	Sample		acid	96.76333333	0.00049	36.329841	131.695672	60.06	6E-05	66.666667	1200	100.1	0.00085	43.588989	118.879062
####	017SMPL.d	5/4/2022 1:46 PM	Sample		acid	50.05	<0.000	69.282032	N/A	73.40666667	0.0003	43.834776	192.873015	46.71333333	<0.000	65.465367	N/A
####	018SMPL.d	5/4/2022 1:51 PM	Sample		acid	66.73333333	<0.000	34.641016	N/A	56.72333333	<0.000	56.727357	N/A	50.05	<0.000	69.282032	N/A



Fig. S11 η H₂ of photocatalytic systems of PtD(*p*-NI)PP and PtT(*p*-NI)PP (a) PS (10 μ M) + TEOA (0.4 M) + THF/H₂O (2:1 v/v), and (b) PS (10 μ M) + AA (0.4 M) + THF/H₂O (2:1 v/v)) under irradiation for 5 h.



Fig. S12 η H₂ of photocatalytic systems of PtTPP, PtD(*p*-NI)PP and PtT(*p*-NI)PP (a) PS (10 μ M) + TEA (0.4 M) + THF/H₂O (2:1 v/v) under irradiation for 5 h.



Fig. S13 Phosphorescence quenching of (a) PtT(p-NI)PP and (b) PtD(p-NI)PP in THF/H₂O (2:1, v/v) solution with TEA as the quencher.

GB-181-1





Fig. S14 ¹H NMR spectrum of PtD(*p*-NI)PP.



Fig. S15 ¹³C NMR spectrum of PtD(*p*-NI)PP.

GB-145 Pt





Fig. S16 ¹H NMR spectrum of PtT(*p*-NI)PP.



Fig. S17 ¹³C NMR spectrum of PtT(*p*-NI)PP.





Bruker Daltonics





Fig. S19 MALDI-TOF spectrum of PtT(p-NI)PP.

Reference

1. L. M. Mink, M. L. Neitzel, L. M. Bellomy, R. E. Falvo, R. K. Boggess, B. T. Trainum and P. Yeaman, *Polyhedron*, 1997, **16**, 2809-2817.