Supporting Information

Osmium(II) Complexes for Light-Driven Aerobic Oxidation of Amines to Imines

EXPERIMENTAL SECTION

General Experimental. All of the synthetic reactions for the complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques. The workup and purification procedures were performed using reagent-grade solvents in air. Unless otherwise noted, all chemical reagents were commercially available and used as received without further purification. ^{1}H NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer at room temperature. Microanalyses (C, H, N) were performed on a Perkin-Elmer 240C element analyzer. The UV-vis spectra were measured using a Varian Cary 50 UV–Vis spectrophotometer in the wavelength range (nm) 200–800 for solutions. The fluorescence emission spectra and emission decay time data were collected on a Horiba Jobin-Yvon Fluorolog-3-21-TCSPC spectrometer. Electrochemical properties of the complexes in solution were evaluated in a conventional air-tight three-electrode cell consisting of a glassy carbon disk (3 mm diameter disk) working electrode, an auxiliary platinum wire and an Ag/AgCl (saturated) reference electrode using a PARSTAT-2273 advanced electrochemical system. The crystal structure images were generated using the program Olex2.[1]

Theoretical Calculations. All calculations were performed using the Gaussian 09 program based on the density functional theory (DFT) method and time-dependent DFT (TD-DFT) calculations.[2] The geometry optimizations of the complexes were performed for the ground states and excited state using DFT with the hybrid Perdew, Burke, and Ernzerhof functional (PBE) in conjunction with the conductor-like polarizable continuum model (CPCM) in CH_3CN. The geometric and energy optimisations of the complexes were performed with the use of B3LYP/LANL2DZ. The numerical calculations in this paper were performed on the IBM Blade cluster system at the High Performance Computing Center (HPCC) of Nanjing University.

Synthetic procedure for Os(II) complexes:

The complexes were synthesized according to a method reported in literature.[3] All the compounds were isolated and separated using flash chromatography on silica gel with a mixture of EtOAc/hexane (1:1). The products were further purified by recrystallisation from a mixture of dichloromethane and diethyl ether at room temperature to afford the desired complexes.

$[Os(fptz)_2(PPhMe_2)_2]$ **(1).** Yield: 316 mg (53%). ^{1}H NMR (Acetone-d6, 300 MHz): δ 10.14 (2H, d, $J = 5.7$), 7.81-7.66 (4H, m), 7.25 (2H, ddd), 7.09 (2H, d, *J* = 7.4), 6.93 (4H, t), 6.40-6.31 (4H, m), 0.85 (s, 6H), 0.68 (s, 6H). Elemental analyses (%) calcd for $C_{32}H_{30}F_6N_8OsP_2$: C, 43.05; H, 3.39; N, 12.55. Found: C, 43.42; H, 3.17; N, 12.67. ESI-MS (CH_3OH): *m/z* found 895.08 $[M+H]^+$. Calcd: *m/z* 894.16.

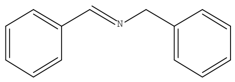
Synthesis of [Os(fptz)$_2$(CO)(PPh$_3$)] (2) and [Os(fptz)$_2$(CO)(Py)] (3). The mixture of $Os_3(CO)_{12}$ (300 mg, 0.33 mmol), fptzH (490 mg, 2.30 mmol) and diethylene glycol monomethyl ether (DGME, 20 mL) was heated at 190 °C under nitrogen for 24 hours; then cooled. Me_3NO (156 mg, 2.08 mmol) was quickly added and the reaction mixture was stirred to 110 °C for 1 h. Then $PPhMe_2$ (546 mg, 2.08 mmol) for **2** or pyridine (165 mg, 2.08 mmol) for **3** was added, and the solution was heated to 190 °C with stirring for 12 h. Afterwards, the mixture was cooled to room temperature, after which the solvent was evaporated to dryness under reduced pressure. The residue was redissolved with CH_2Cl_2; then the resulting solution was purified on silica gel (EA/hexane, 1:1), followed by recrystallization from a CH_2Cl_2 solution diffused with diethyl ether to afford the desired complexes **2** or **3** as light-yellow crystals.

[Os(fptz)$_2$(CO)(PPh$_3$)] **(2).** Yield: 316 mg (65%). ^1H NMR (MeOD, 300 MHz): δ 8.76 (d, *J* = 5.7 Hz, 1H), 8.31 (dd, 1H), 8.26 (d, *J* = 5.8 Hz, 1H), 8.18 (d, 1H), 7.96-7.89 (m, 1H), 7.84 (dt, 1H), 7.47-7.38 (m, 3H), 7.32 (dd, 12H), 7.22 (ddd, 1H), 7.00 (ddd, 1H). Elemental analyses (%) calcd for $C_{35}H_{23}F_6N_8OOsP$: C, 46.36; H, 2.56; N, 12.36. Found: C, 46.58; H, 2.18; N, 12.48. ESI-MS (CH_3OH): *m/z* found 931.11 $[M+Na]^+$. Calcd: *m/z* 908.13.

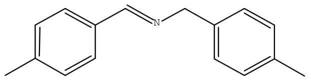
[Os(fptz)$_2$(CO)(Py)] **(3).** Yield: 232 mg (81%). ^1H NMR ($CDCl_3$, 300 MHz): δ 10.38 (d, *J* = 5.5 Hz, 2H), 8.11 (dd, 4H), 7.98 (td, 2H), 7.63-7.55 (m, 3H), 7.07 (dd, 2H). Elemental analyses (%) calcd for $C_{22}H_{13}F_6N_9OOs$: C, 36.52; H, 1.81; N, 17.42. Found: C, 36.71; H, 1.62; N, 17.54. ESI-MS (CH_3OH): *m/z* found 726.17 $[M+H]^+$. Calcd: *m/z* 725.08.

Singlet Oxygen Detection in Solution. The capacity of singlet oxygen generation of **1** was observed by detecting the decrease of flurescence intensity of 9,10-dimethylanthracene (DMA) using a fluorence spectrophotometer.[4] In a typical experiment, DMA (50 μL, 1.0 mM) in CH_3CN was added to a solution of **1** (1×10^{-5} M, 3 mL) into a 1-cm path length quartz cuvette of a spectrofluorometer. Immediately afterwards, the sample solution of the cuvette was irradiated from the side with a visibe light ($\lambda > 420$ nm, 180 mW cm^{-2}) at a fixed distance of 5 cm for 10 min. Every minute, the fluorescene spectra of the solution containing DMA (λ_{ex} = 360 nm) was recorded. This experiment was also carried out without irradiation for comparison.

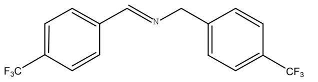
Procedure for the Photochemical Oxidative Coupling of Amines: To a dry 100 mL round-bottom flask were added catalyst (1 mg), benzylamine (2 mmol) or other amines, and acetonitrile (50 mL). The reaction mixture was stirred under air atmosphere at room temperature and irradiated for the required time at a distance of ca. 10 cm from a 300 W Xe lamp with a 420 nm-cutoff filter (180 mW cm^{-2}). After reaction, the reaction solvent was evaporated away under reduced pressure, and the resulting residue was analyzed by ^1H NMR to determine the conversion. Each experiments was repeated twice to confirm the results, and the average values were used.



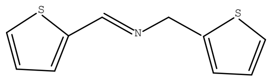
N-benzylidine-1-phenylmethanamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.82 (d, *J* = 3.5 Hz, 2H), 7.45 (d, *J* = 2.2 Hz, 3H), 7.37 (s, 4H), 7.29 (s, 1H), 4.86 (d, *J* = 0.9 Hz, 2H).



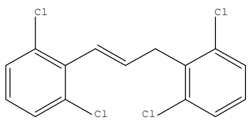
N-(4-Methylbenzylidine)-1-(p-tolyl)methanamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 6.3 Hz, 4H), 7.17 (s, 2H), 4.78 (s, 2H), 2.37 (d, *J* = 13.5 Hz, 6H).



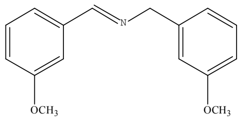
N-(4-trifluoromethylbenzylidene)-4-trifluoromethylbenzylamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.69(d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.90 (s, 2H).



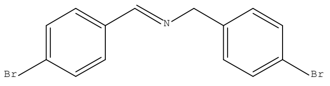
(thiophen-2-yl)-*N*-((thiophen-2-yl)methylene)methanamine
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 0.8 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.36 (d, *J* = 3.2 Hz, 1H), 7.24 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.08 (s, 1H), 6.99 (d, *J* = 4.6 Hz, 2H), 4.95 (s, 2H).



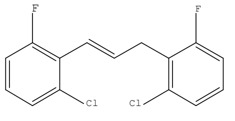
N-(2,6-Dichlorobenzylidine)-o,p-dichlorobenzylamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.38 (s, 1H), 7.34 (s, 1H), 7.22 – 7.18 (m, 2H), 7.09 (s, 2H), 5.23 (d, *J* = 1.6 Hz, 2H).



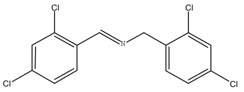
N-(4-methoxybenzylidine)-1-(4-methoxyphenyl)methanamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.40 (d, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 4.4 Hz, 2H), 7.27 (d, *J* = 3.2 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.91 (d, *J* = 2.3 Hz, 2H), 6.86 – 6.780 (m, 1H), 4.81 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H).



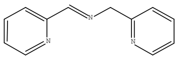
N-(4-bromobenzylidene)(4-bromophenyl)methanamine
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.63 (s, 2H), 7.57 (s, 2H), 7.46 (s, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 4.75 (s, 2H).



2-chloro-N-[(2-chloro-6-fluorophenyl)methylene]-6-fluoro-benzylamine
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.23 (d, *J* = 2.2 Hz, 3H), 7.07 – 7.03 (m, 1H), 7.02 (s, 2H), 5.08 (s, 2H).

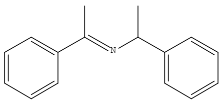


N-(2,4-Dichlorobenzylidine)-o,p-dichlorobenzylamine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.31 (s, 1H), 7.28 – 7.21 (m, 2H), 4.84 (s, 2H).



N-(2-pyridinylmethylene)-2-Pyridinemethanamine

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.24 – 8.18 (m, 1H), 7.92 (ddd, *J* = 12.1, 6.1, 4.5 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.71 – 7.65 (m, 2H), 6.98 (t, *J* = 8.2 Hz, 1H), 6.92 – 6.83 (m, 1H), 4.79(d, *J* = 5.8 Hz, 2H).



1-Phenyl-N-(1-phenylethyl)ethan-1-imine:
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.46 (ddd, *J* = 7.3, 4.0, 2.3 Hz, 2H), 7.38 – 7.26 (m, 4H), 7.26 – 7.14 (m, 1H), 4.16 (d, *J* = 6.6 Hz, 1H), 2.61 (s, 3H), 1.44 – 1.32 (m, 3H).

References

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, et al. Gaussian, Inc., Wallingford CT, 2009.

3 Liao, J. L.; Chi, Y.; Liu, S. H.; Lee, G. H.; Chou, P. T.; Huang, H. X.; Su, Y. D.; Chang, C H.; Lin, J. S.; Tseng, M. R. *Inorg. Chem.* **2014**, *53*, 9366–9374.

4 Lu, Y.; Xue, F.; Zhou, Z.; Shi, M.; Yan, Y.; Qin, L.; Yang, H.; Yang, S. *Chem. Eur. J.* **2014**, *20*, 16242–16247.

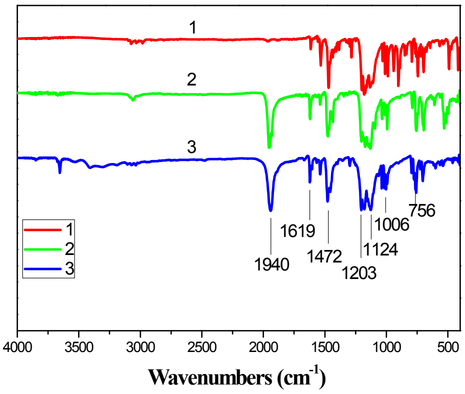


Figure S1. FTIR spectra of **1-3** at 298 K.

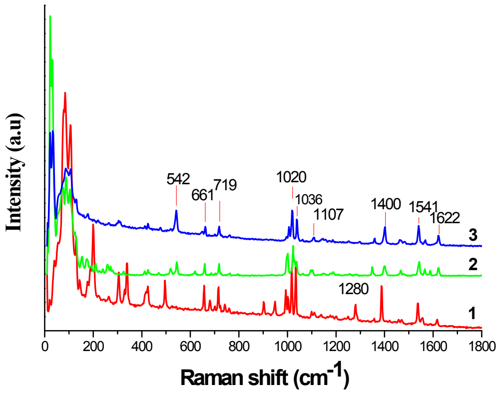


Figure S2. Raman spectra for complexes **1-3** at 298 K.

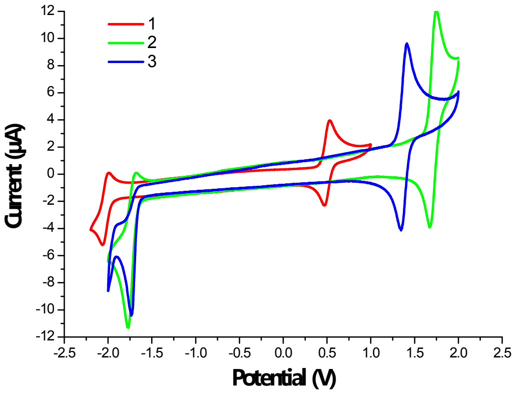


Figure S3. Cyclic voltammogram of **1-3** in a MeCN solution at 298 K.

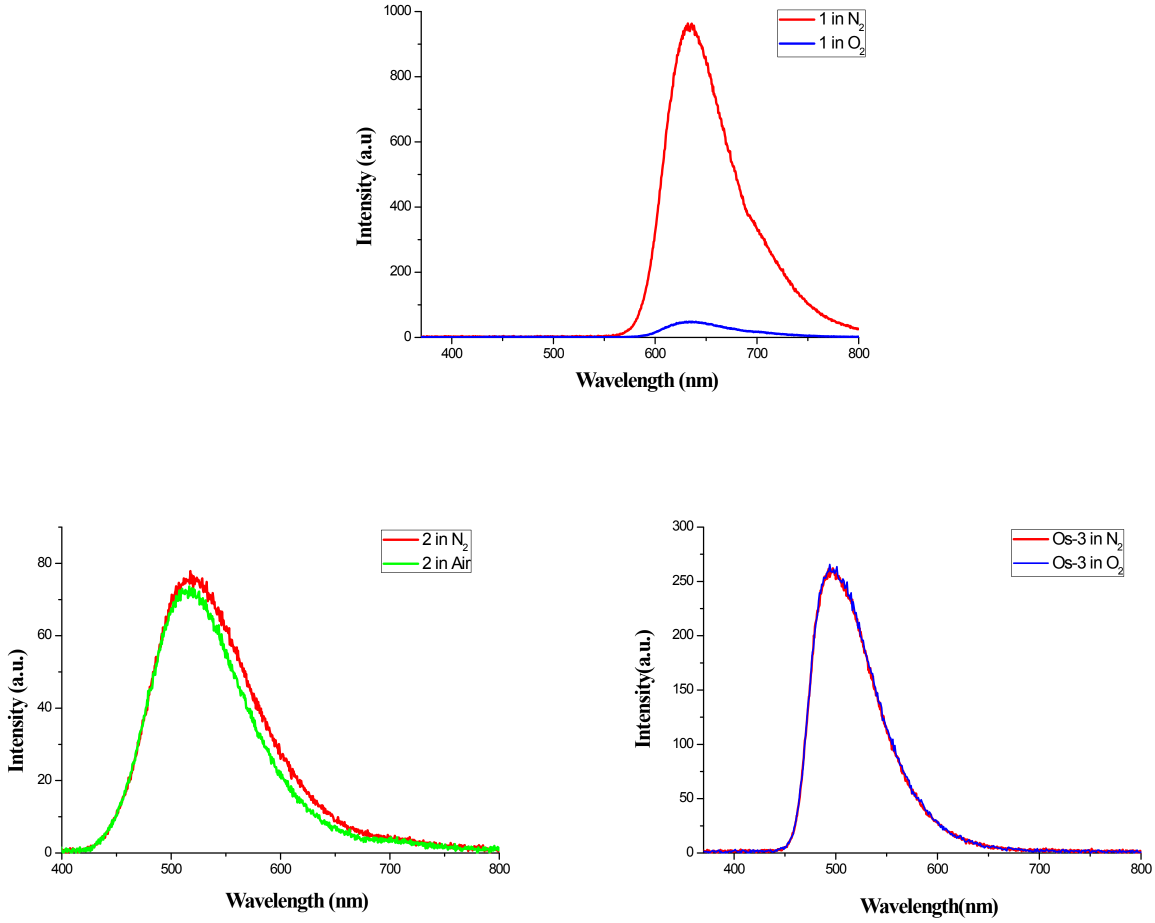


Figure S4. Photoluminescence emission spectra for complex **1-3** under a difference atmosphere of nitrogen and air.

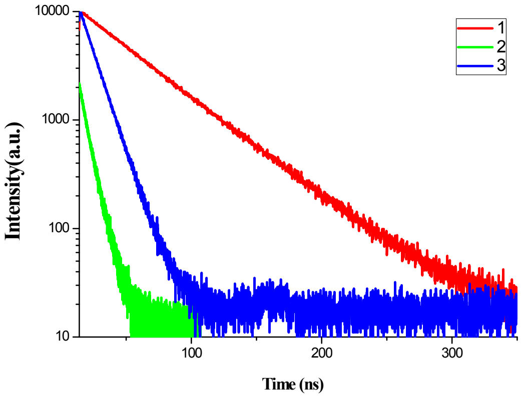


Figure S5. Emission decay kinetics for complexes **1-3** measured in nitrogen-saturated CH_2Cl_2.

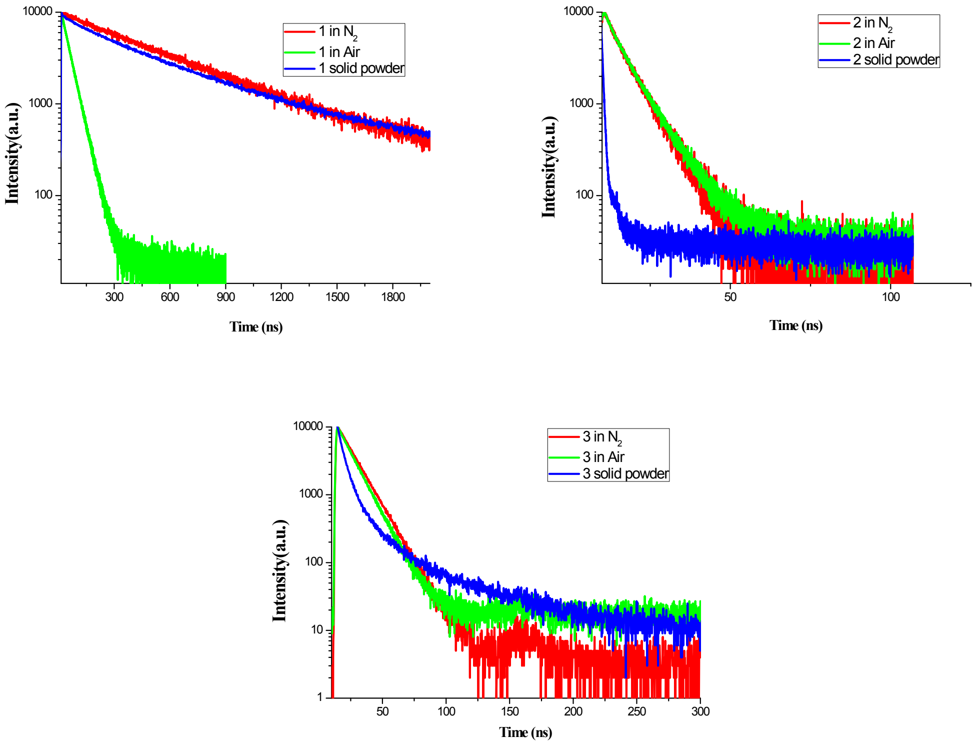


Figure S6. Emission decay kinetics for complexes **1-3** measured in different conditions.

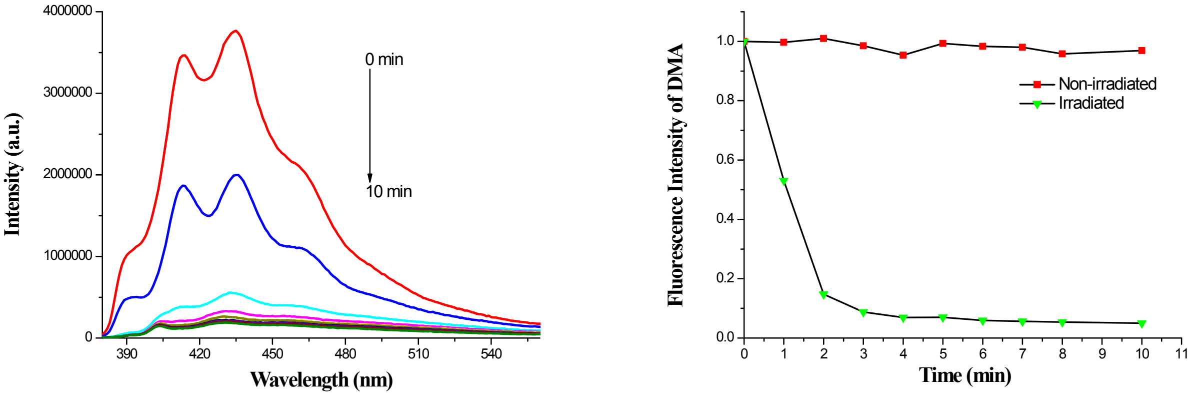


Figure S7. Changes in the fluorescence spectra of DMA solution in the presence of **1** and Changes in the fluorescence intensity of DMA solution at 435 nm with or without irradiated by visible light.

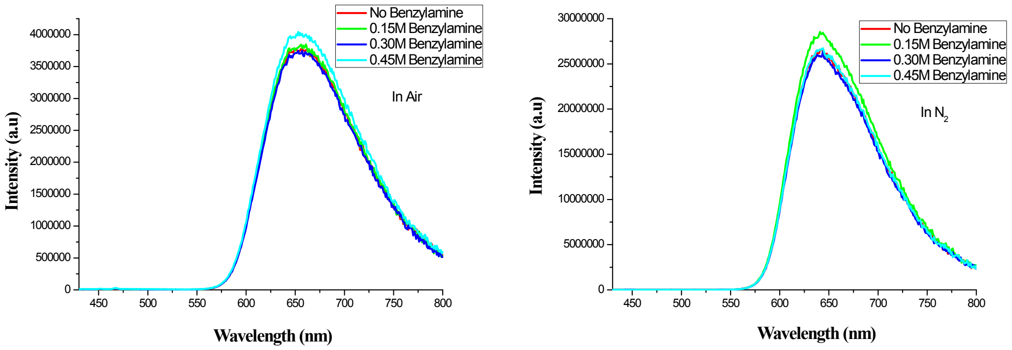


Figure S8. Photoluminescence emission spectra for complex **1** in the presence of benzylamine.

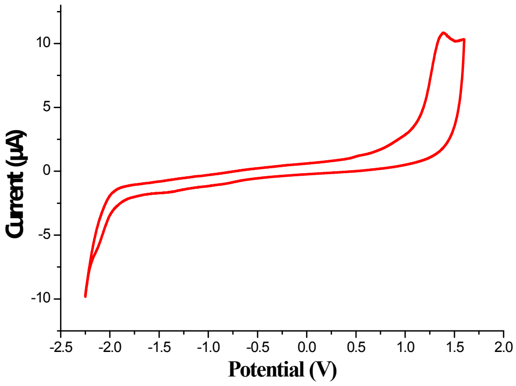


Figure S9. Cyclic voltammogram of benzylamine in MeCN solution at 298 K.

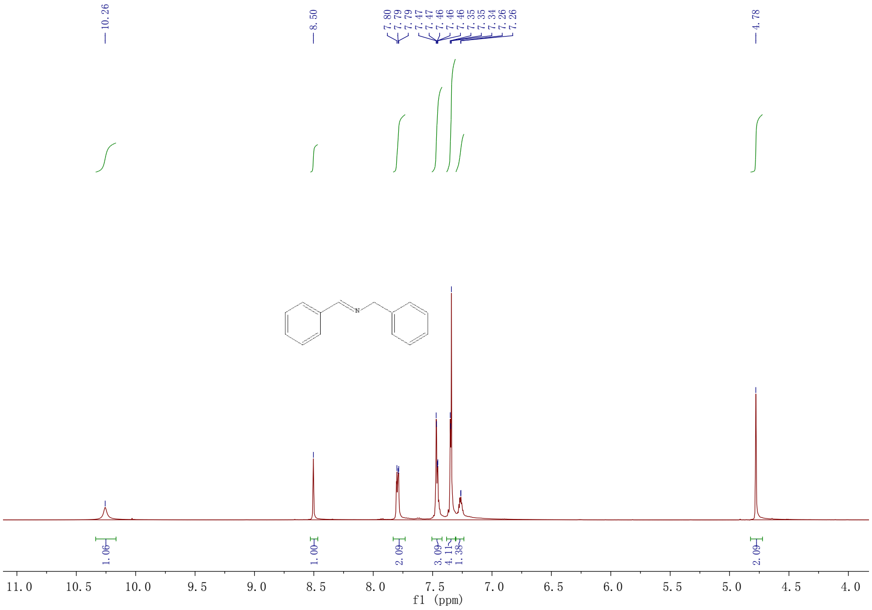
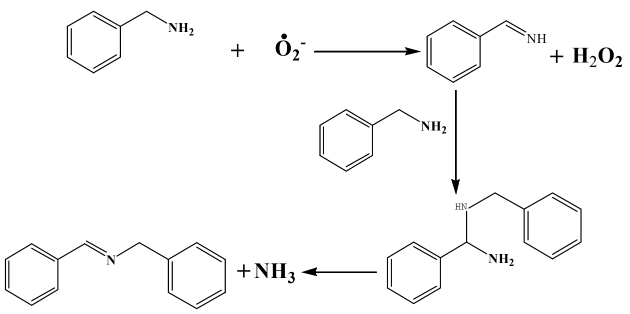


Figure S10. The detection of H_2O_2 by ^{1}H-NMR spectra after reaction using complex **1.**



Scheme S1 The main mechanism of the photoinduced oxidative coupling of benzylamine to imine.

	HOMO（eV）	LUMO（eV）
Complex **1**	-5.22	-2.04
Benzylamine	-6.78	-0.57
O_2	-0.87	-3.54

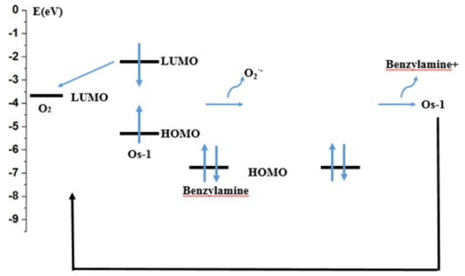
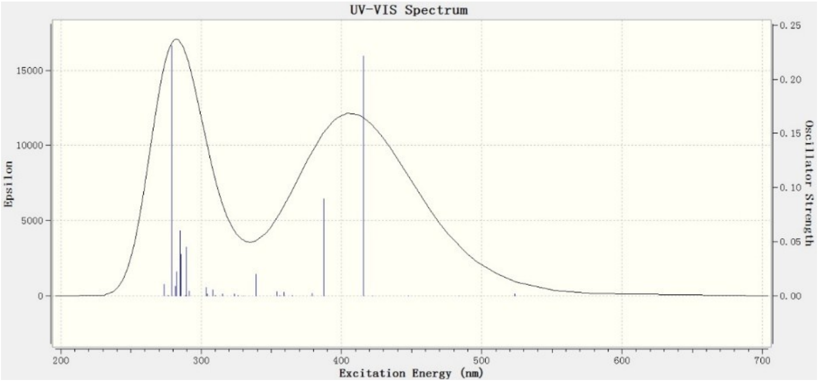
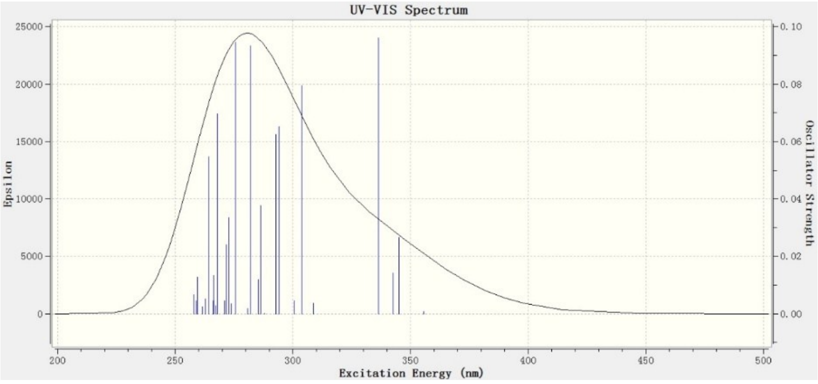


Figure S11 Calculated energy level diagram.





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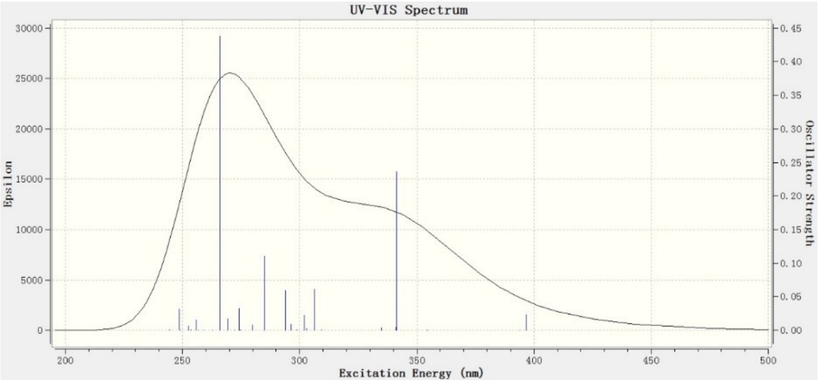

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Figure S12. The ultraviolet absorption spectrum of complexes **1-3** with FWHM of 0.5eV calculated at the PBE1PBE level of theory with 6-31G (d, p) and SDD (with f-type polarization functions) basis sets.

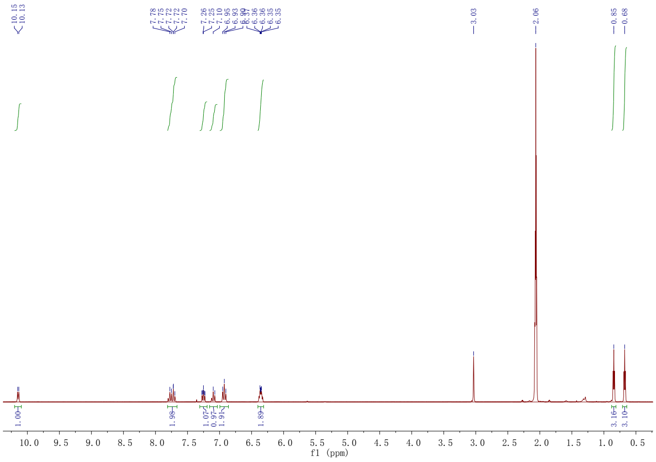


Figure S13. ^{1}H-NMR spectra of complex **1.**

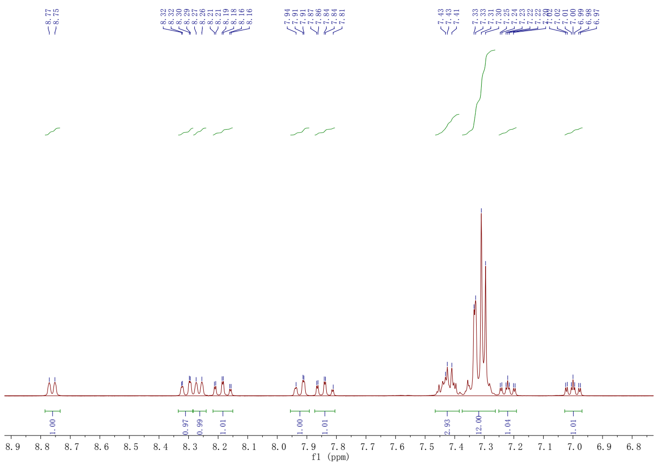


Figure S14. ^{1}H-NMR spectra of complex **2.**

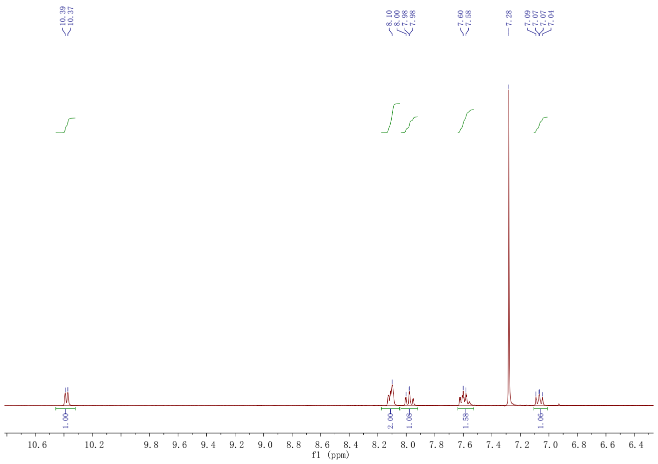


Figure S15. ^{1}H-NMR spectra of complex **3.**

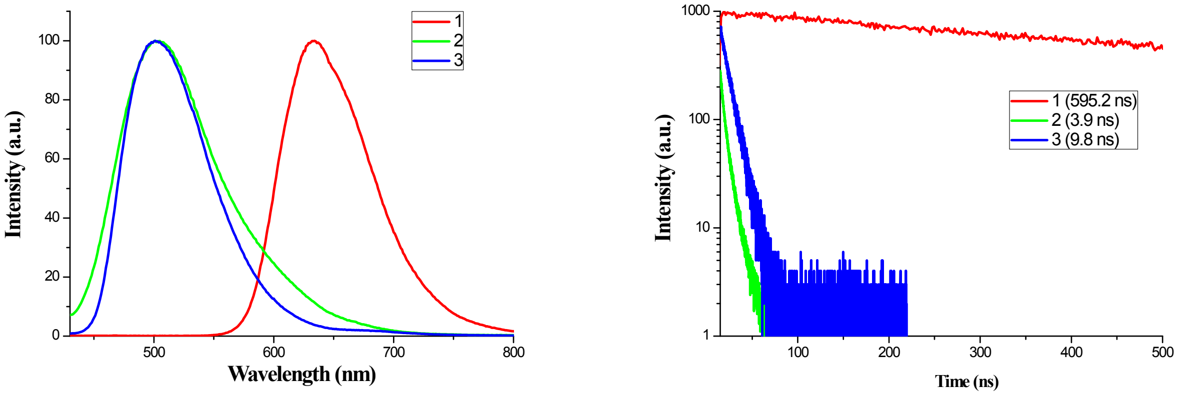
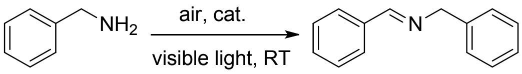


Figure S16 Photoluminescence emission spectra (Left) and Emission decay kinetics (Right) for complexes **1-3** measured in nitrogen-saturated CH_3CN (ca. 10^{-5} M).

Table S1. Crystal data and structure refinements for complexes **2** and **3**.

	2·CH_2Cl_2	**3**
Empirical formula	$OsC_{35}H_{23}F_6N_8OP·CH_2Cl_2$	$OsC_{22}H_{13}F_6N_9O$
Formula weight	991.71	723.61
Temperature (K)	171(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	0.22×0.21×0.18	0.19×0.17×0.13
a (Å)	10.8160(5)	11.3688(8)
b (Å)	13.4759(6)	11.6384(8)
c (Å)	14.5272(6)	13.3026(9)
α (°)	62.8130(10)	68.593(2)
β (°)	89.808(2)	69.189(2)
γ (°)	84.357(2)	84.135(2)
Volume (Å^3)	1872.29(14)	1531.02(18)
Z	2	2
Density (called), g/cm^3	1.759	1.570
Absorpt coefficient, mm-1	3.663	4.230
F(000)	968	692
Theta range for data collection (°)	3.16-25.25	3.17-25.48
Limiting indices	-12≤h≤12	-13≤h≤13
	-13≤k≤16	-13≤k≤14
	-17≤l≤17	-15≤l≤16
Indep reflns Data/restraints/params	6639[R(int)=0.0418]	5466[R(int)=0.0667]
GOF on F^2	6639/0/496	5466/1377/650
R1, wR2, [I >2σ(I)]	1.023	1.017
R index (all data)	0.0317 and 0.0628 0.0451	0.0400 and 0.0825
	and 0.0669	0.0639 and 0.0877

Table S2. Light-driven transformation of benzylamine to an imine using different photocatalysts. Standard reaction conditions: benzylamine (2 mmol), photocatalyst (0.06 mol %), solvent (50 mL), in air, 1 h and room temperature. [b] Conversion data were determined using ^{1}H NMR spectroscopy.



Entry	Photocatalyst	Cond.	Conv. [%][b]
1	**2**	CH_3CN (Xe arc lamp)	27
2	**3**	CH_3CN (Xe arc lamp)	49
3	**3**	CH_3CN (λ > 420 nm)	28

Table S3 Light-driven oxidation of various amines to the corresponding imines using **2** (0.11 mol %) under irradiation with an unfiltered Xe arc lamp.

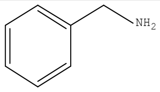
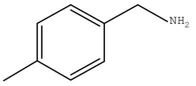
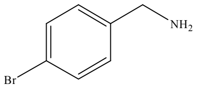
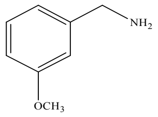
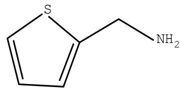
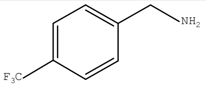
Entry	Substrate	Time(h)	Conv(%)
1		1	29
2		5	88
3		1	23
4		5	89
5		1	39
6		5	51
7		1	12
8		5	19
9		1	15
10		5	65
11		1	36
12		5	56

Table S4 Light-driven oxidation of various amines to the corresponding imines using **3** (0.14 mol %) under irradiation with an unfiltered Xe arc lamp.

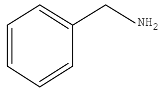
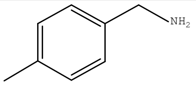
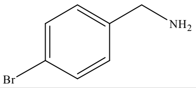
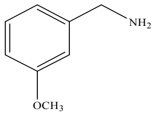
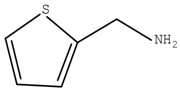
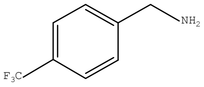
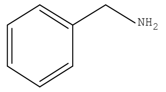
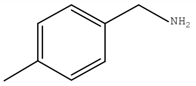
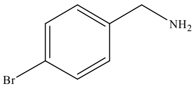
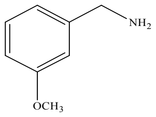
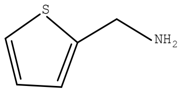
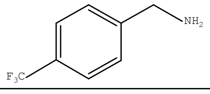
Entry	Substrate	Time(h)	Conv(%)
1		1	51
2		5	75
3		1	45
4		5	91
5		1	47
6		5	68
7		1	23
8		5	32
9		1	39
10		5	83
11		1	30
12		5	50

Table S5 Light-driven oxidation of various amines to the corresponding imines using **3** (0.14 mol %) (visible light, $\lambda > 420$ nm).

Entry	Substrate	Time(h)	Conv(%)
1		1	33
2		5	56
3		1	34
4		5	65
5		1	26
6		5	67
7		1	14
8		5	31
9		1	23
10		5	54
11		1	24
12		5	40