Electronic Supplementary Information for:

Visible light-absorbing Rhenium(I) tricarbonyl complexes as triplet photosensitizers in photooxidation and triplet-triplet annihilation upconversion

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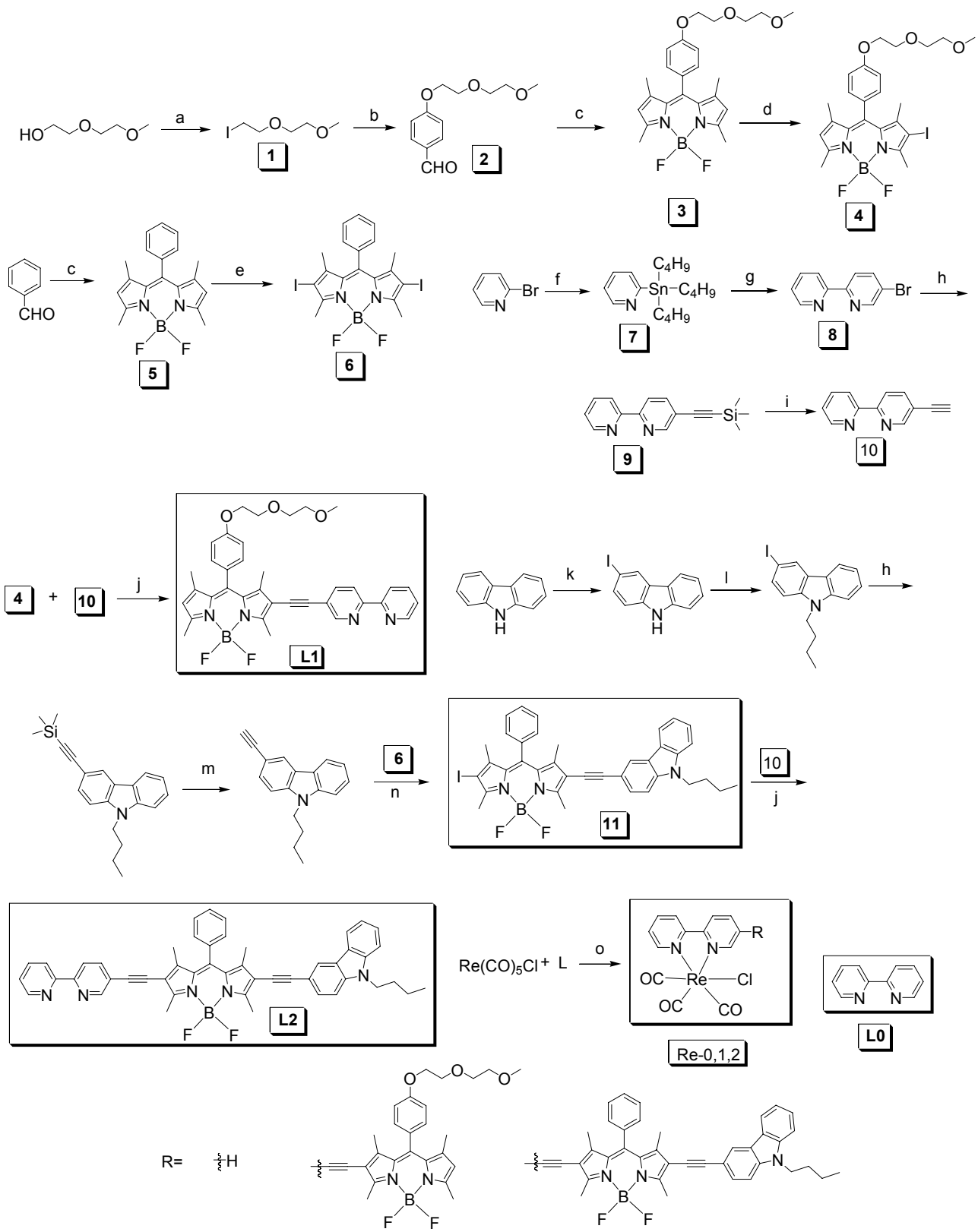


Scheme S1. Synthesis of **Re-0**, **Re-1** and **Re-2**. (a) *p*-toluenesulfonyl chloride, NaOH, H_2O, THF, 0°C, 3 h; NaI, acetone, room temperature, 24 h; (b) 4-hydroxybenzaldehyde, K_2CO_3, MeCN, 60°C, 12 h; (c) i) 2,4-dimethylpyrrole, TFA, DDQ, DCM, room temperature, 12 h; ii) Et_3N, $BF_3{\cdot}OEt_2$, room temperature, 12 h; (d) NIS(1eq), DCM, 10-15°C, 1 h; (e) NIS(4eq), DCM, room temperature, 1 h; (f) tributyltin chloride, *n*-BuLi, DEE; (g) 2,5-dibromopyridine, $Pd(PPh_3)_4$, Xylene; (h) Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI,THF/NEt_3; (i) TBAF, THF, Ar, room temperature; (j) $Pd(PPh_3)_4$, THF/NEt_3; (k) KIO_3, KI (l) NaH, n-C_4H_9Br; (m) K_2CO_3, CH_3OH/DCM, 3h; (n) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, THF/NEt_3; (o) toluene, 1 h.

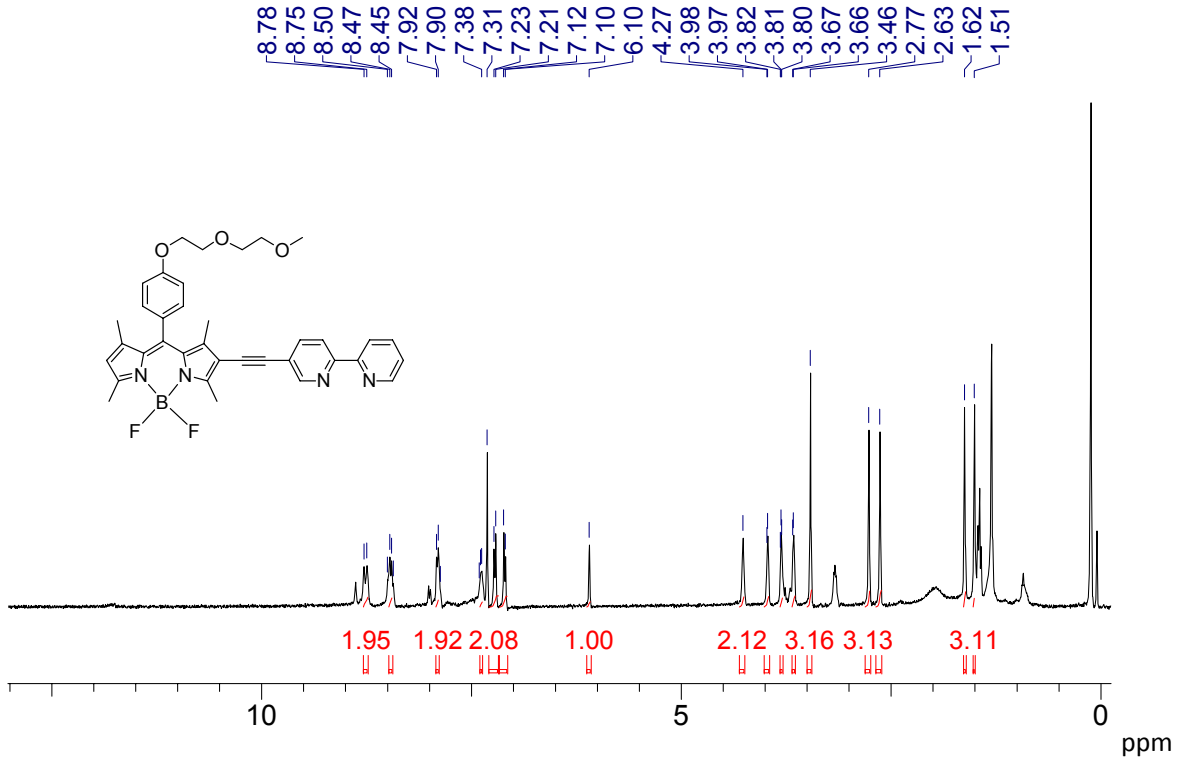


Fig. S1 ^{1}H NMR of **L-1** in $CDCl_3$ (400 MHz), 25°C.

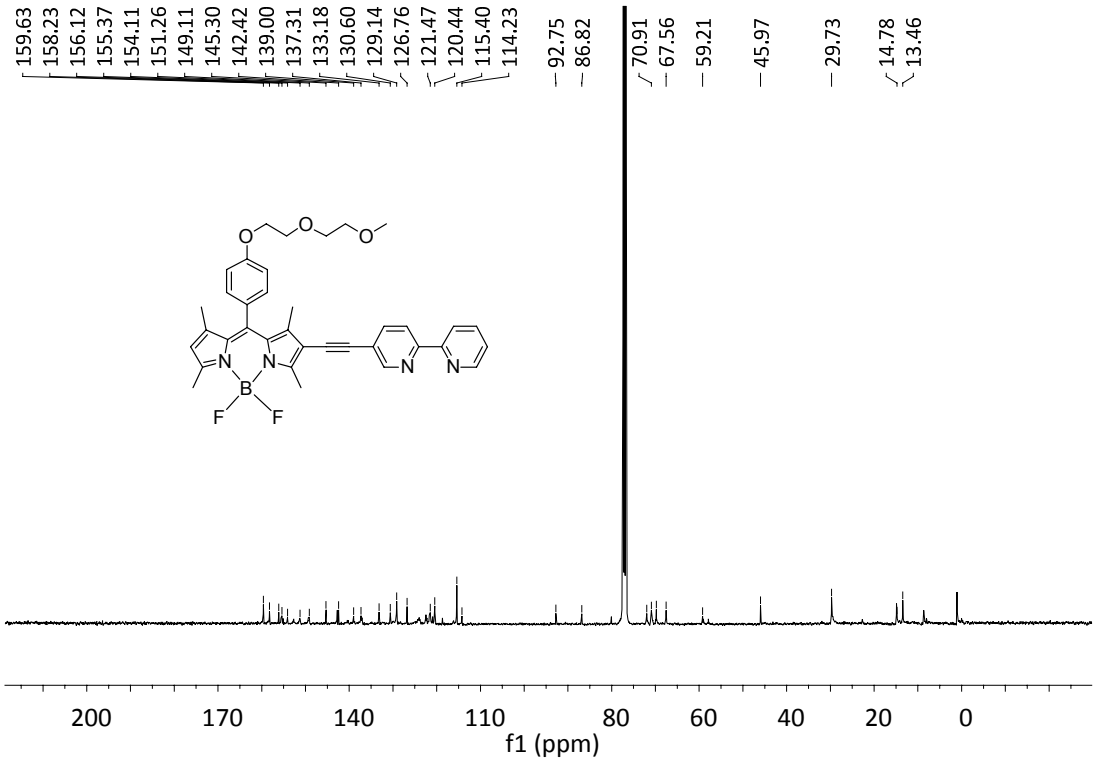


Fig. S2 ^{13}C NMR of **L-1** in $CDCl_3$(100 MHz), 25°C.

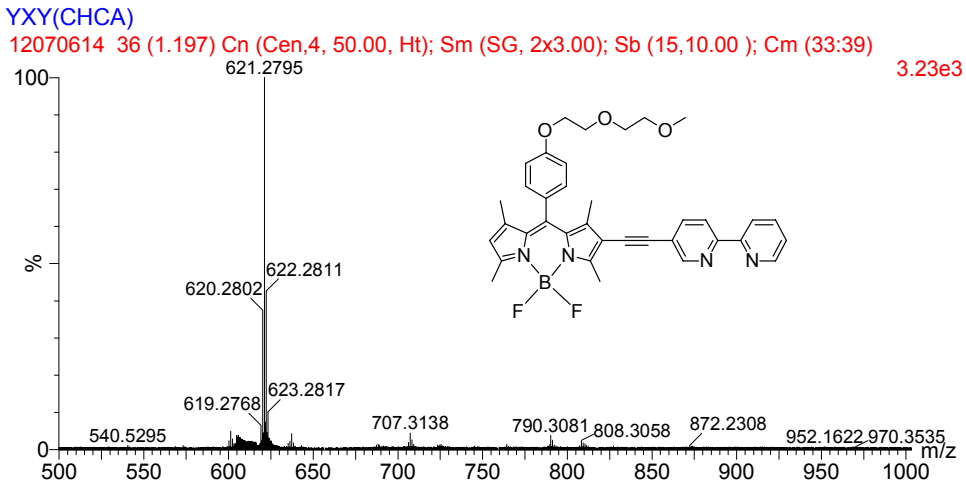


Fig. S3 MALDI-HRMS of **L-1**, 25 °C.

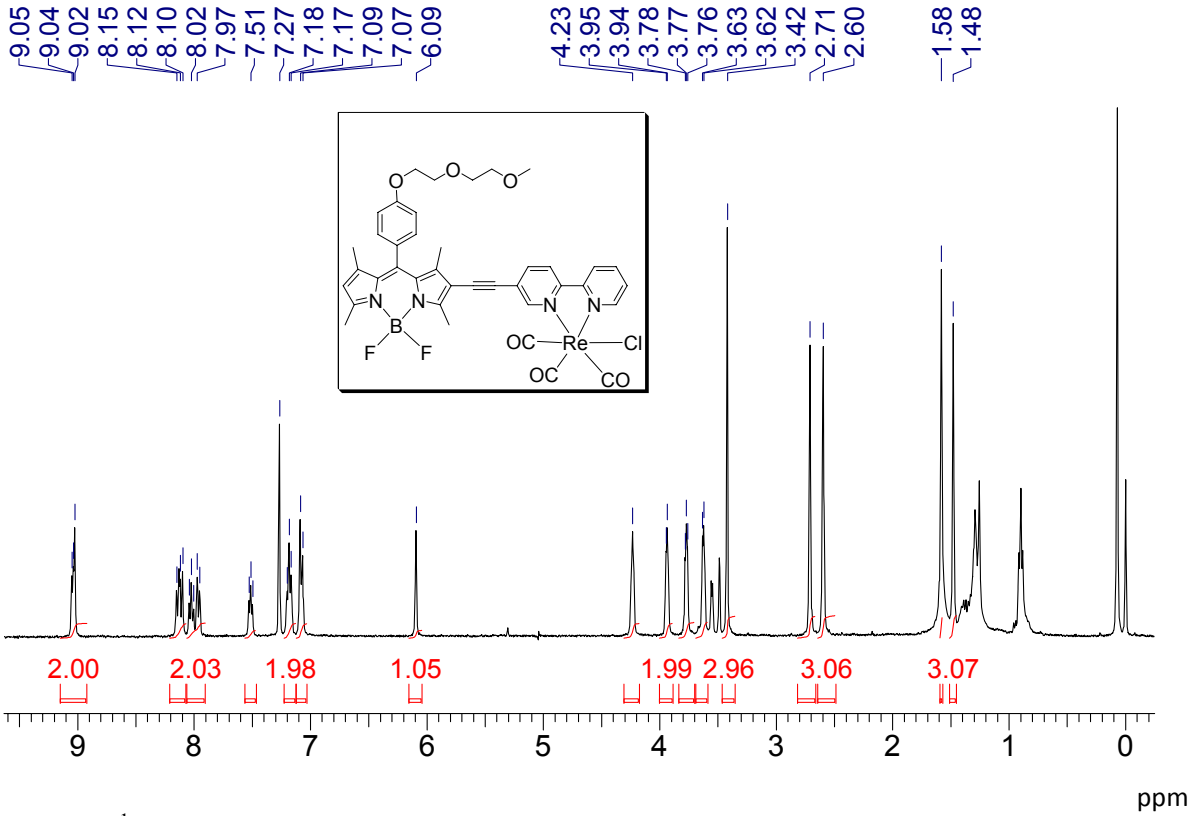


Fig. S4 ^{1}H NMR of **Re-1** in $CDCl_3$ (400 MHz), 25°C.

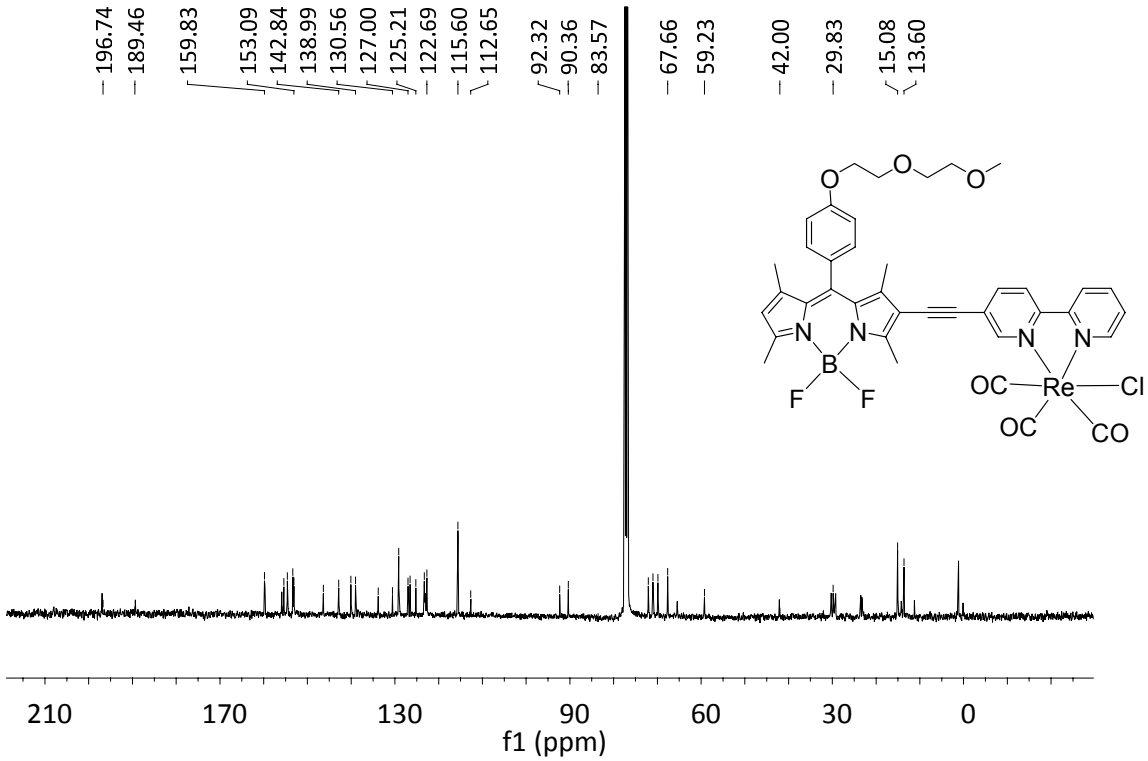


Fig. S5 ^{13}C NMR of **Re-1** in $CDCl_3$(100 MHz), 25°C.

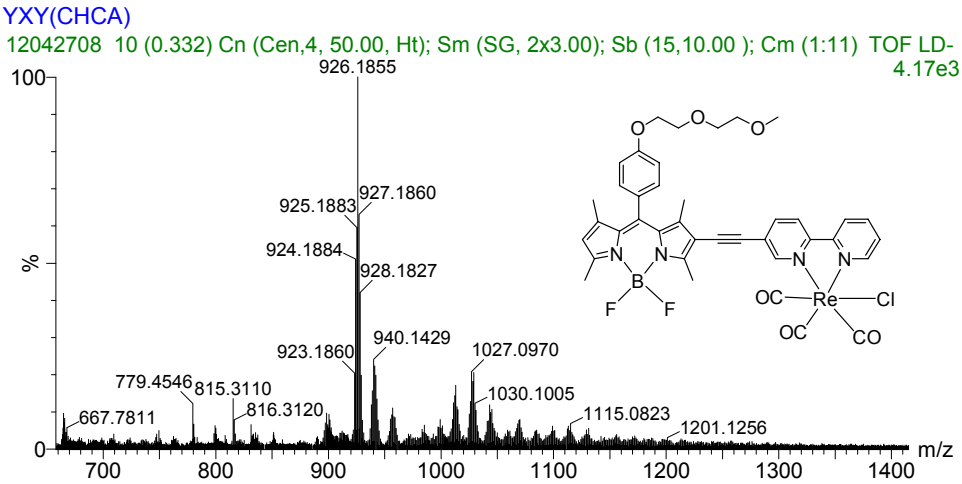


Fig. S6 MALDI-HRMS of **Re-1**, 25 °C.

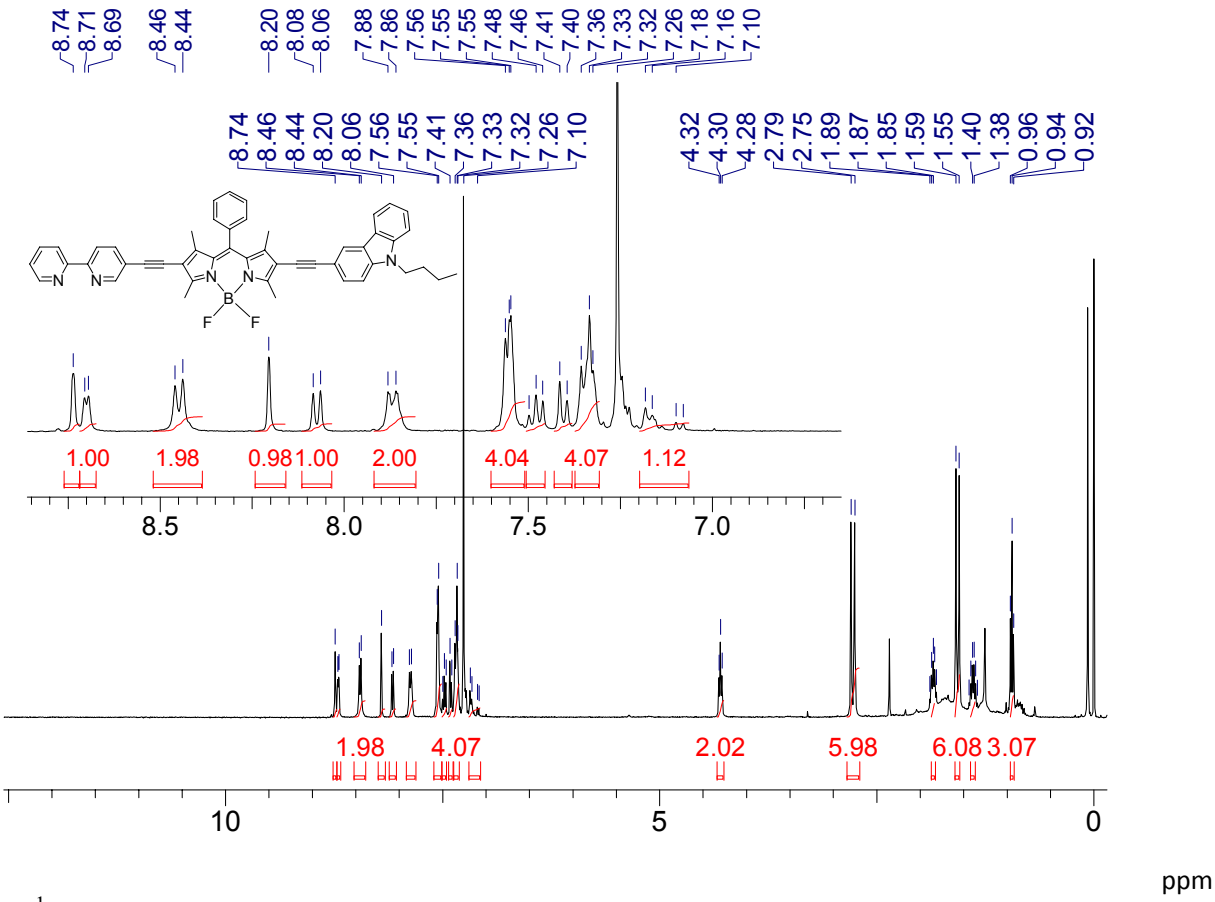


Fig. S7 ^{1}H NMR of **L-2** in $CDCl_3$ (400 MHz), 25°C.

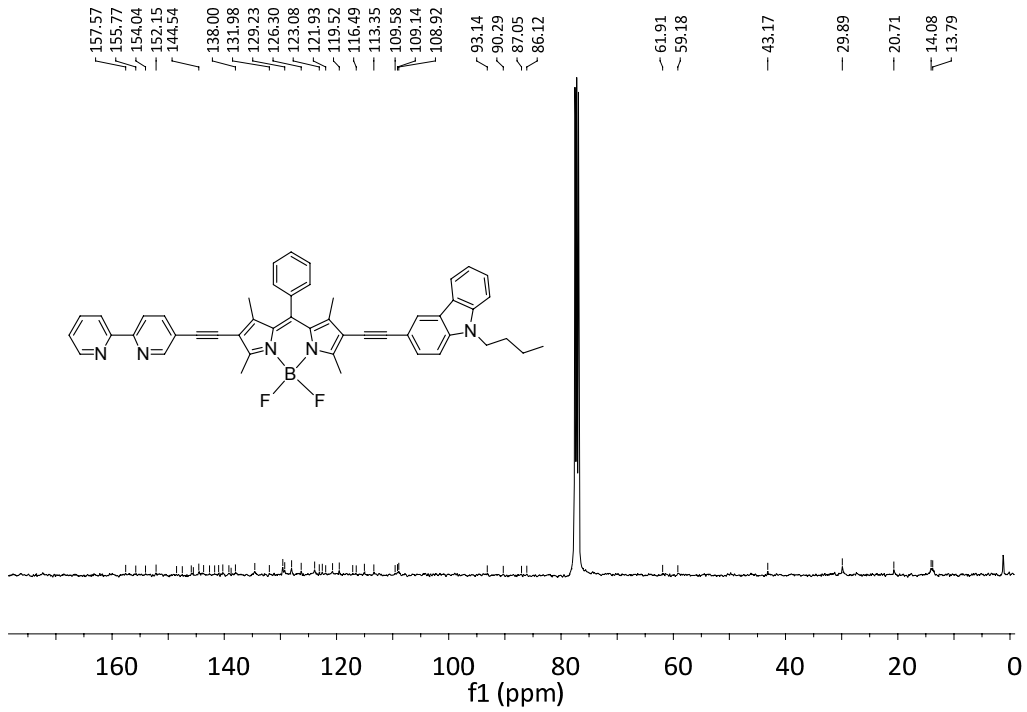


Fig. S8 ^{13}C NMR of **L-2** in $CDCl_3$(100 MHz), 25°C.

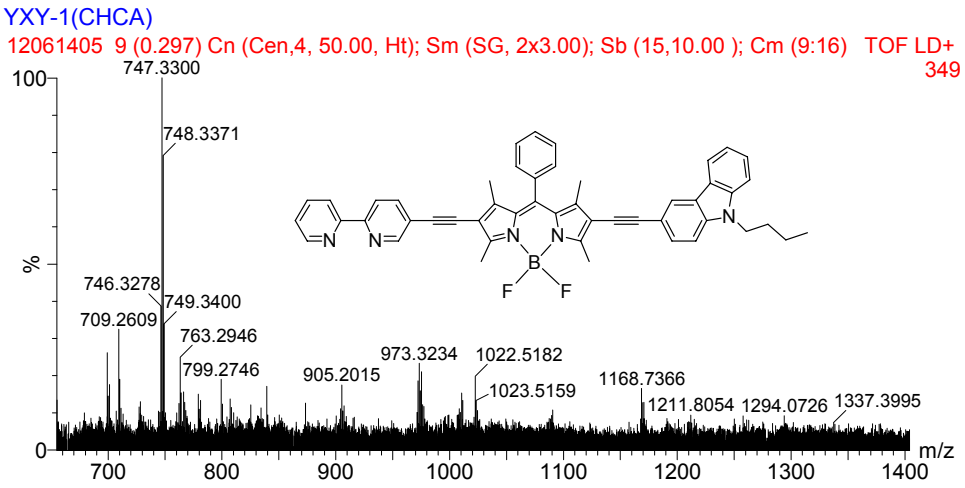


Fig. S9 MALDI-HRMS of **L-2**, 25 °C.

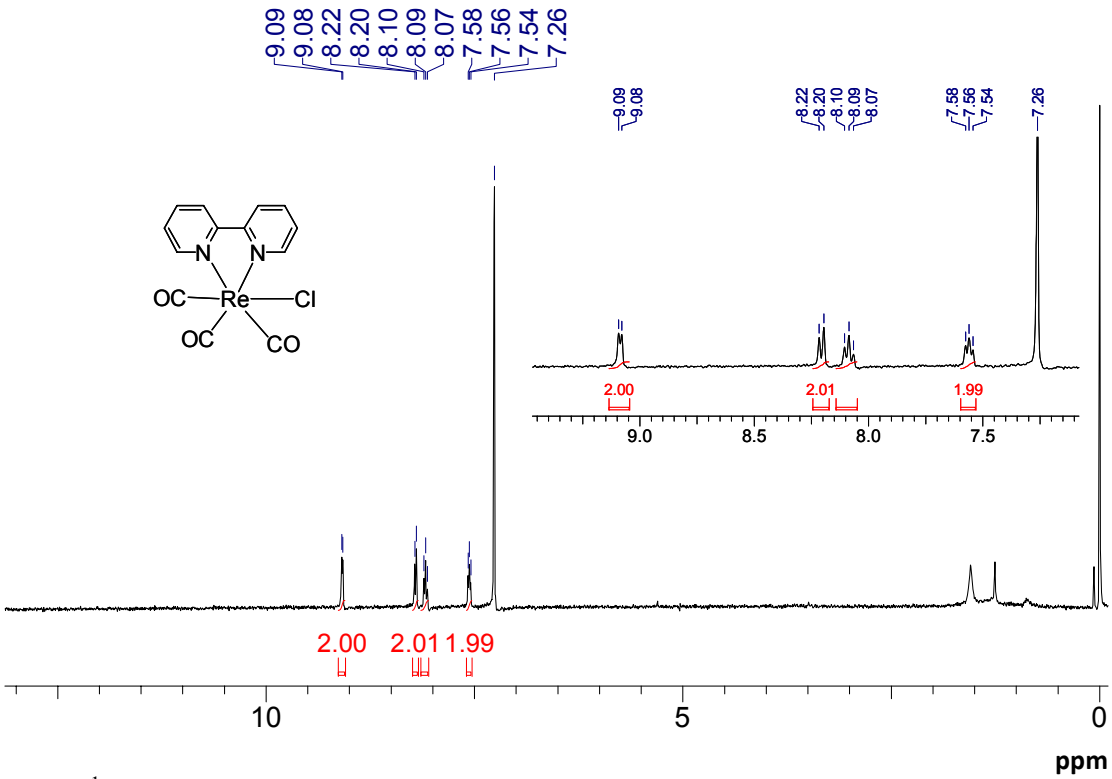


Fig. S10 ^{1}H NMR of **Re-0** in $CDCl_3$ (400 MHz), 25°C.

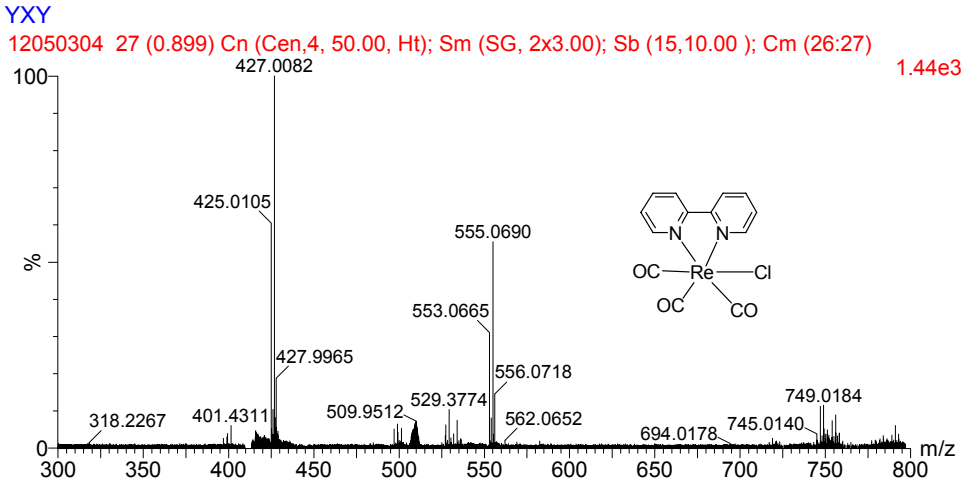


Fig. S11 MALDI-HRMS of **Re-0**, 25 °C.

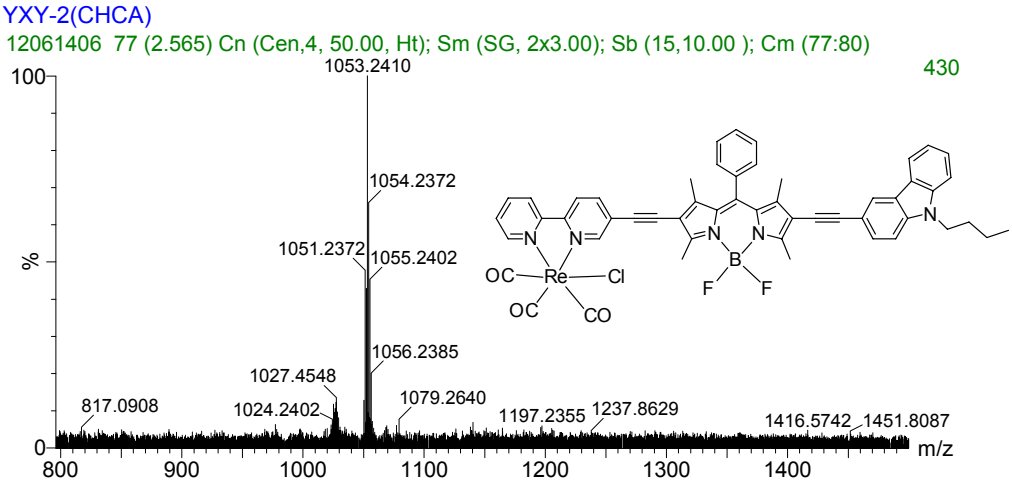


Fig. S12 MALDI-HRMS of **Re-2**, 25 °C.

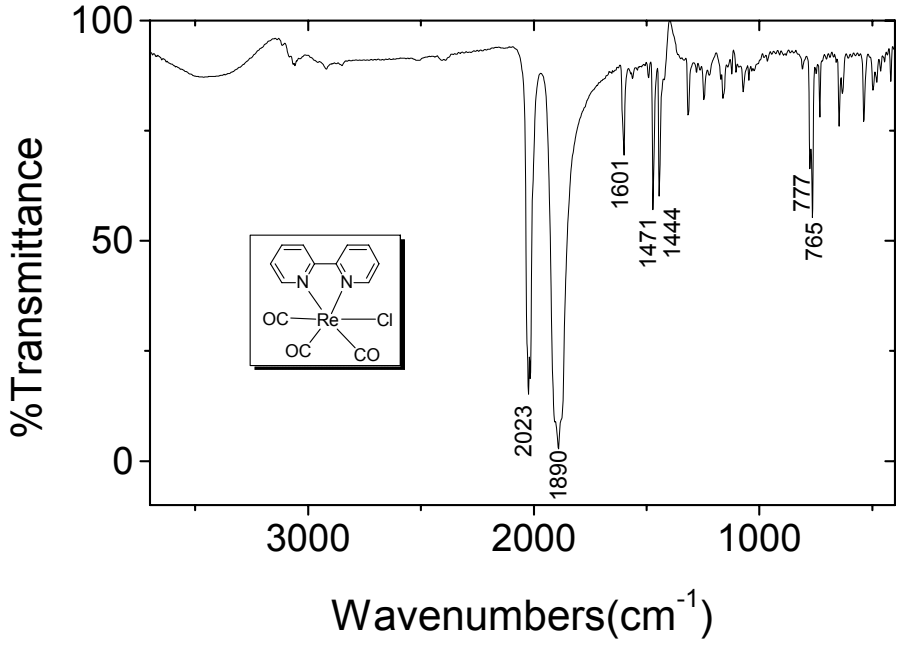


Fig. S13 Infrared spectroscopy (IR) of **Re-0**.

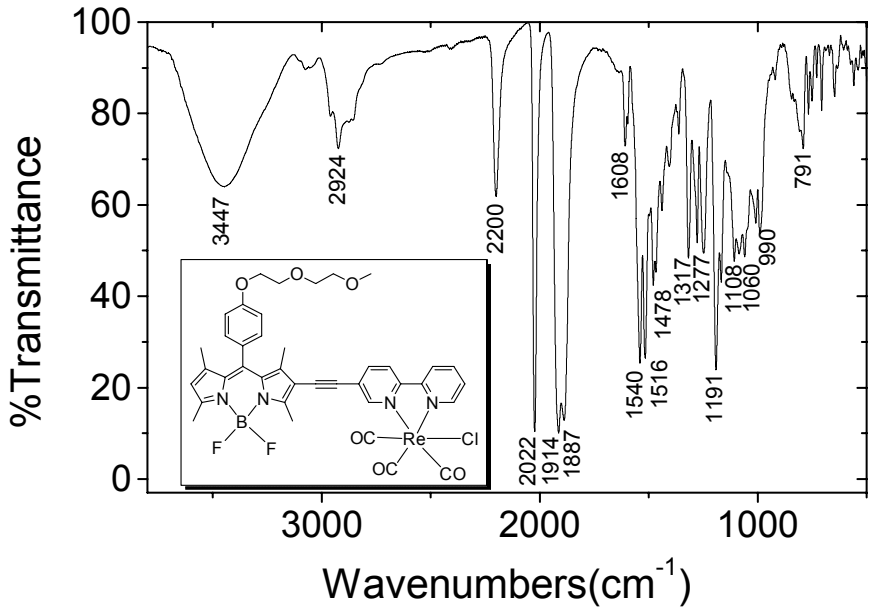


Fig. S14 Infrared spectroscopy (IR) of **Re-1.**

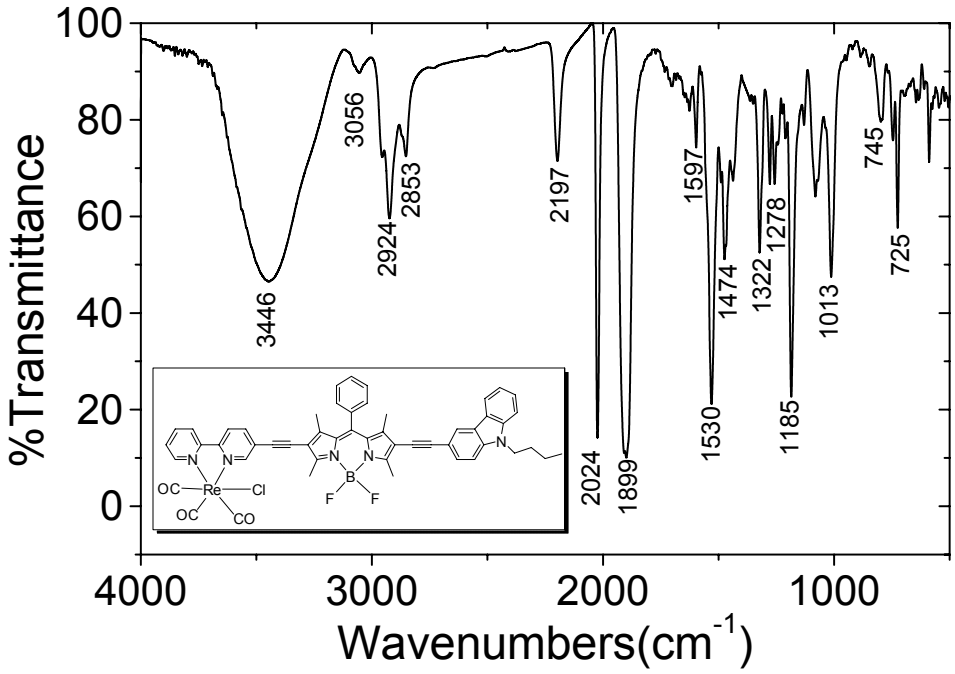


Fig. S15 Infrared spectroscopy (IR) of **Re-2.**

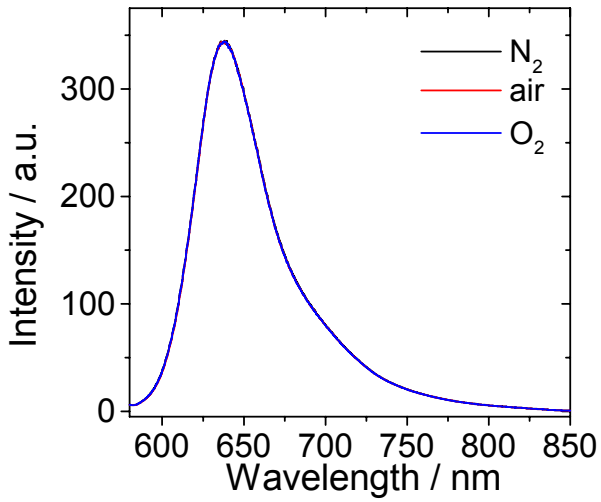


Fig. S16 The emission spectra of the **L-2** (λ_{ex} = 579 nm) under different atmosphere. c = 1.0 × 10^{-5} mol/dm^3 in toluene, 25 °C.

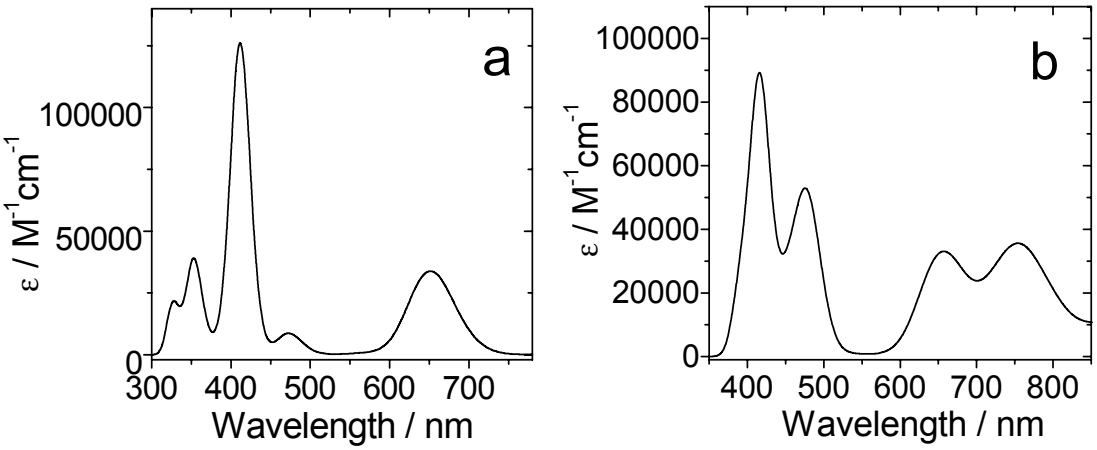


Fig. S17 The calculated transient absorption spectra were presented as (a) **Re-1** and (b) **Re-2**. Toluene was used as solvent in the calculations. Note the bleaching bands cannot be predicted with the TDDFT calculation. Calculated by DFT at the B3LYP/6-31G level using Gaussian 09W.

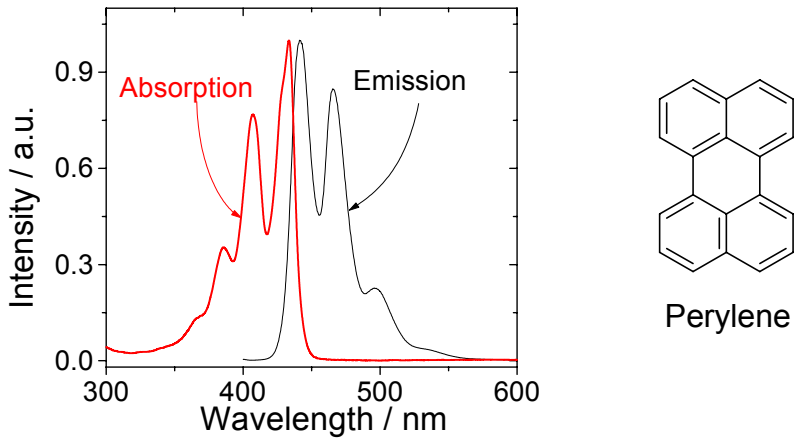


Fig. S18 Absorption and fluorescence spectra of perylene, λ_{ex} = 390 nm, c = 1.0 ×10^{-5} M. 20 °C.

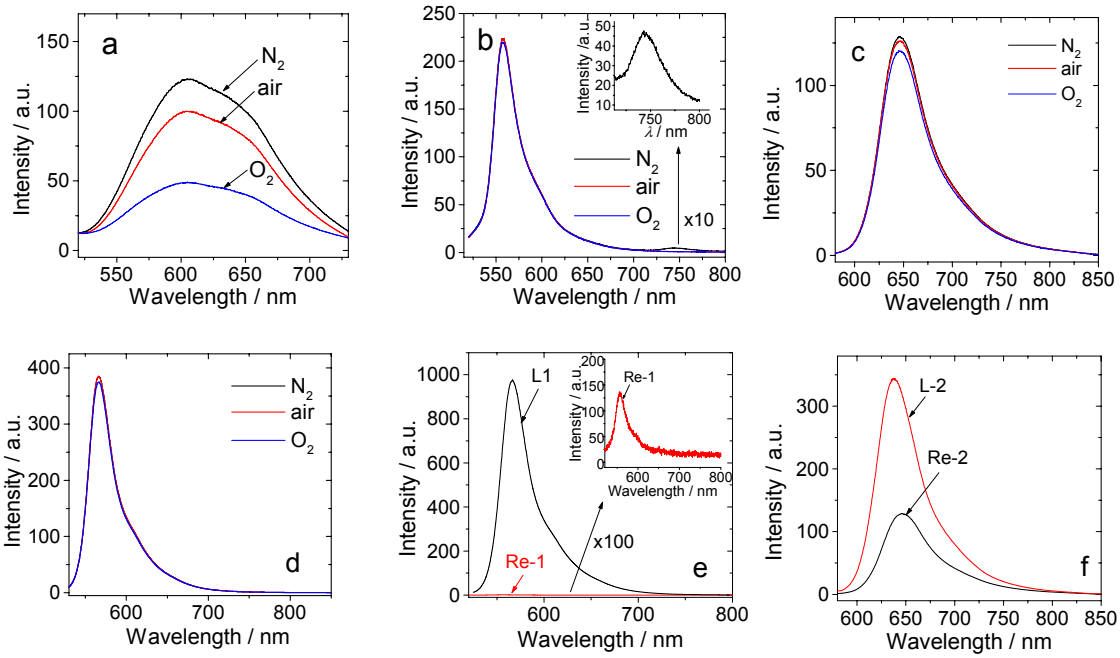


Fig. S19 The emission spectra of the Re(I) complexes under different atmosphere. (a) **Re-0** (λ_{ex} = 400 nm), (b) **Re-1** (λ_{ex} = 510 nm), (c) **Re-2** (λ_{ex} = 570 nm), (d) **L-1** (λ_{ex} = 525 nm), (e) **L-1** and **Re-1** (λ_{ex} = 525 nm), (f) **L-2** and **Re-2** (λ_{ex} = 578 nm), $c = 1.0\times10^{-5}$ mol/dm^3 in toluene, 25 °C.

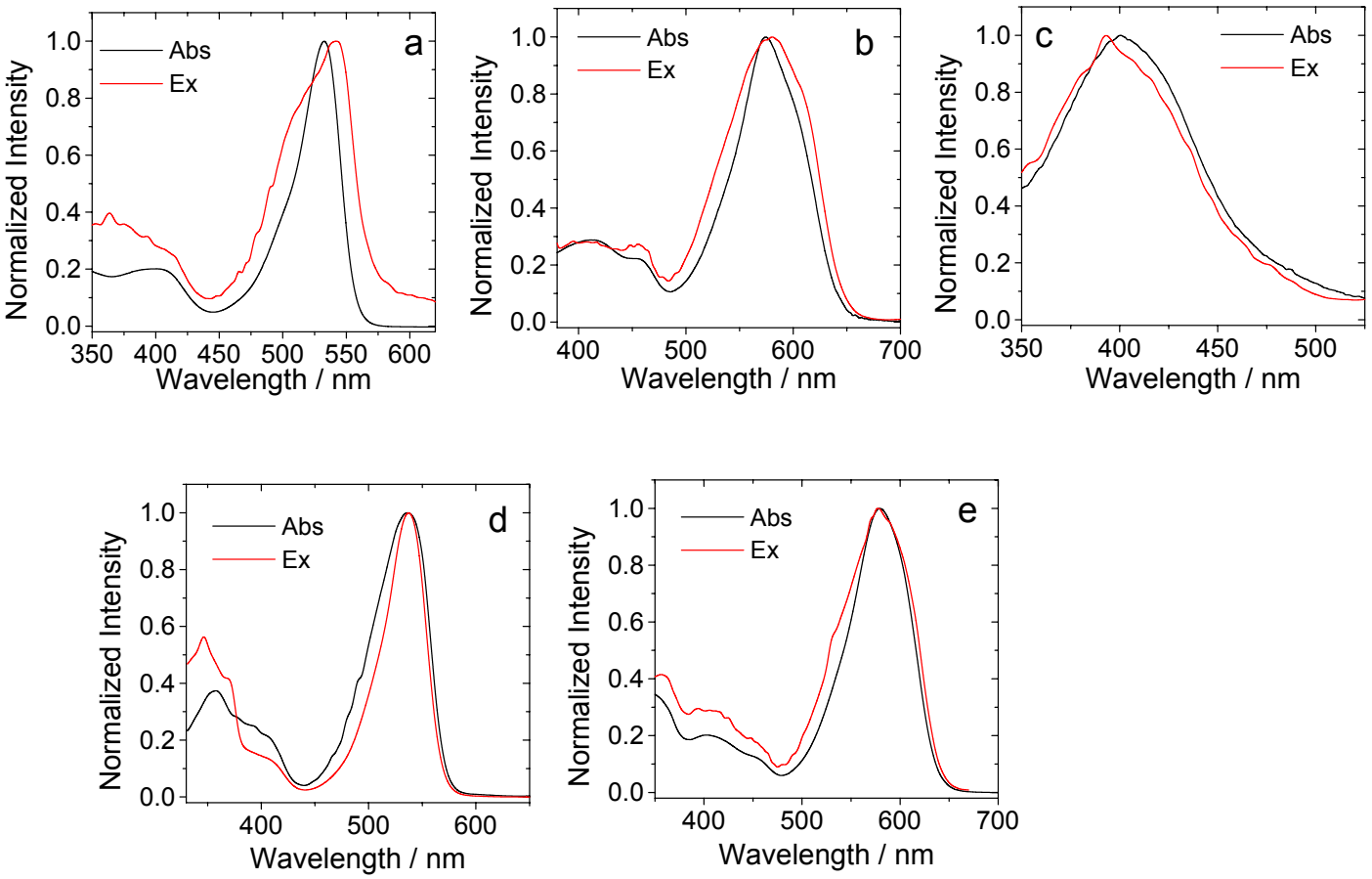


Fig. S20 Comparison of the normalized UV/Vis absorption and the excitation spectra: a) **Re-1**, λ_{em} = 640 nm, b) **Re-2**, λ_{em} = 750 nm, c) **Re-0**, λ_{em} = 670 nm, d) **L-1**, λ_{em} = 650 nm and e) **L-2**, λ_{em} = 720 nm (1.0×10^{-5} M in toluene, 20°C).

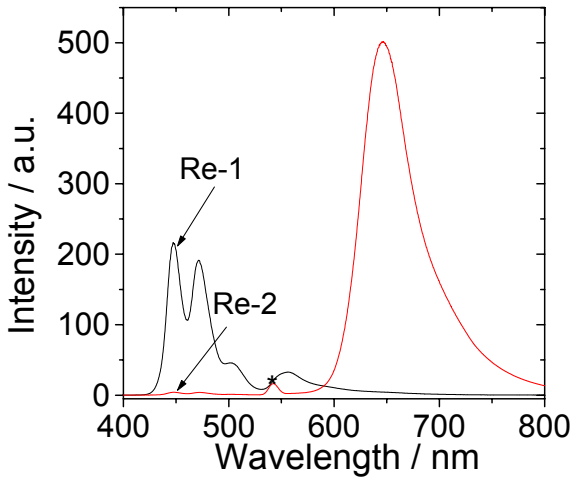


Fig. S21 Upconversion with a Shimadzu RF5301 spectrofluorometer, *c* [**Re-1**] = 1.0 × 10^{-5} M; *c* [**Re-2**] = 1.0 × 10^{-5} M; *c* [perylene] = 3.0 × 10^{-5} M; Power: 5 mW/cm^2. λ_{ex} = 544 nm. 25 °C.

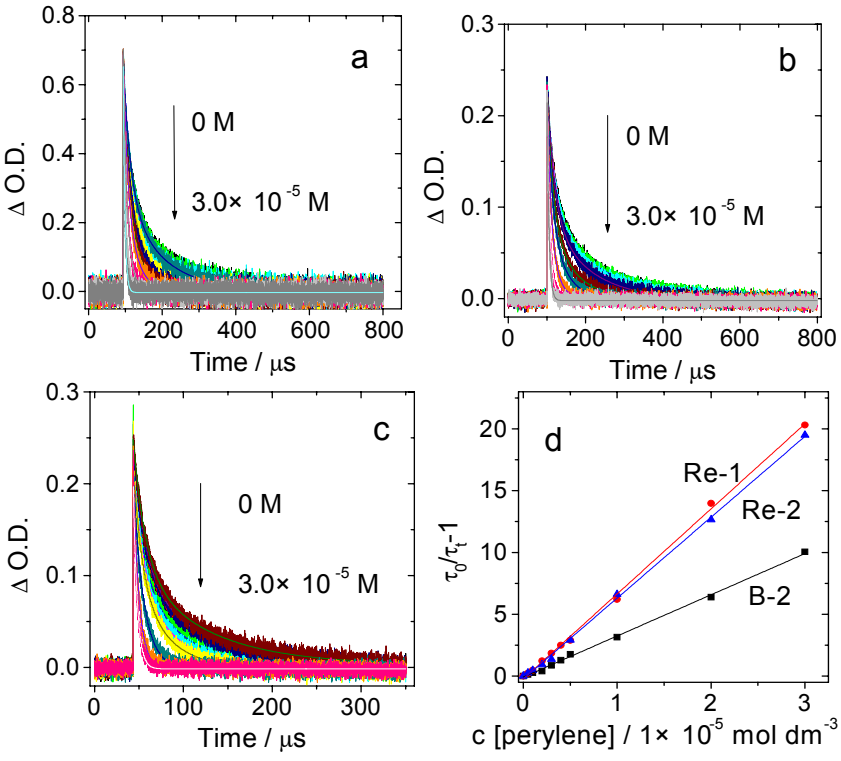


Fig. S22 Quenching of the lifetime of the triplet photosensitizers with increasing the concentration of perylene. Decay curves of (a) **Re-1**, (b) **Re-2**, (c) B-2, (d) Stern–Volmer plots for the lifetime quenching. *c* [photosensitizers] = 1.0×10^{-5} mol/L, in deaerated toluene. 25 °C.

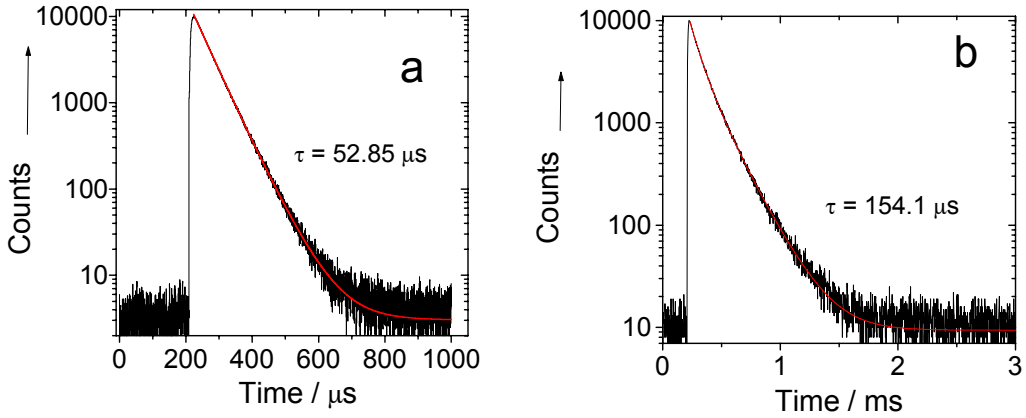


Fig. S23 Delayed fluorescence lifetime decay curves observed in the TTA upconversion with (a) **Re-2** and (c) **B-2** as triplet photosensitizer and perylene as the triplet acceptor. Excited at 532 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 445 nm. Under this circumstance the **Re-2** or B-2 is selectively excited. In deaerated toluene. *c* [Sensitizers] = 1.0×10^{-5} M; *c* [perylene] = 3.0×10^{-5} M; 25 °C.

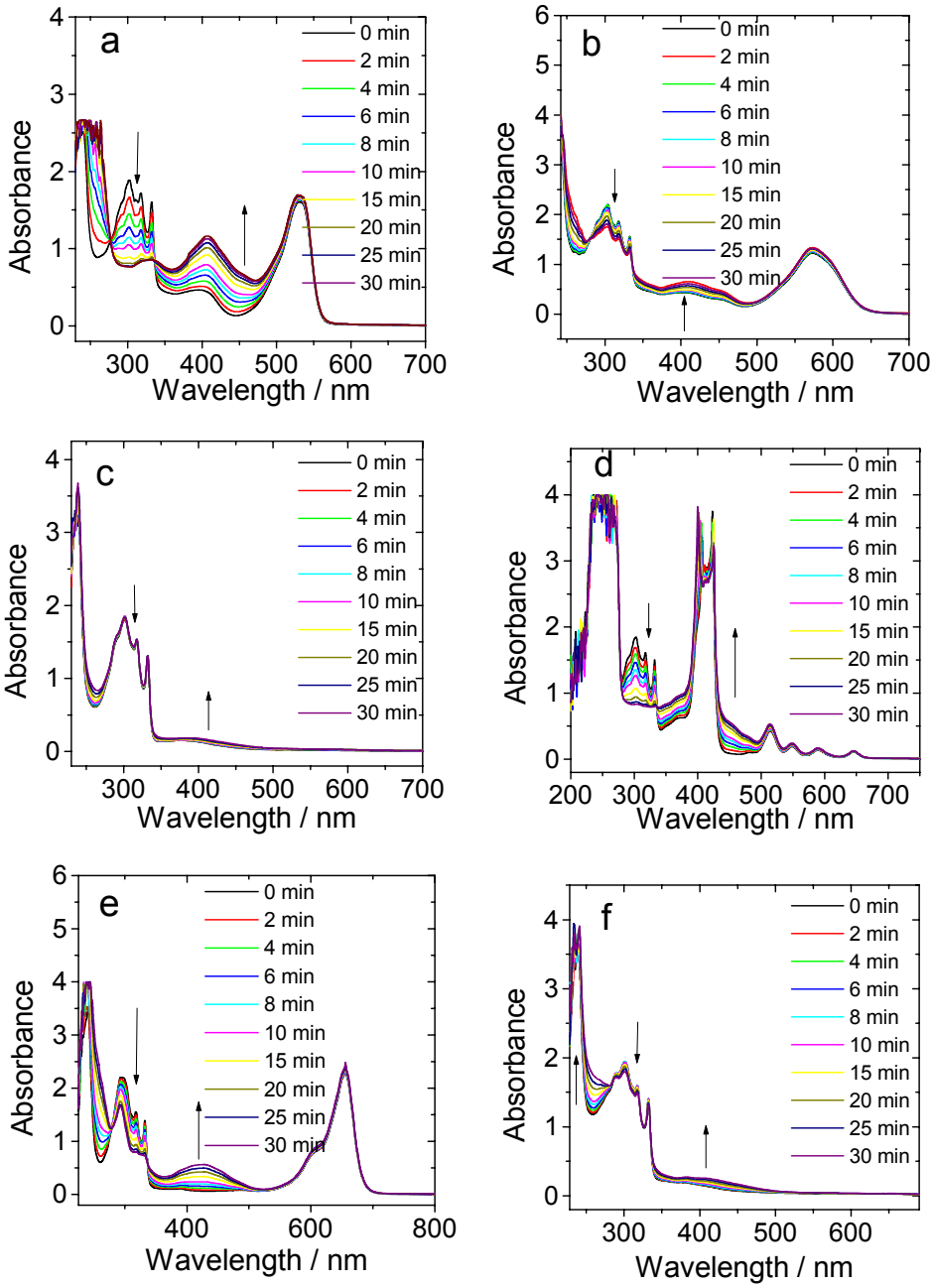


Fig. S24 Photosensitizing of $^1O_2$ with the complexes as photosensitizers. Irradiation time-dependent decrease of absorbance at 301 nm of DHN (2.0×10^{-4} M) with different $^1O_2$ sensitizers. (a) **Re-1**, (b) **Re-2**, (c) **Re-0**, (d) TPP, (e) MB, (f) $[Ir(ppy)_2(dpy)]^+$. *c* [sensitizers] = 2.0×10^{-5} M. *c* [DHN] = 2.0×10^{-4} M. In CH_2Cl_2/MeOH (9:1, v/v). 15 mW/cm^2. 25 °C.

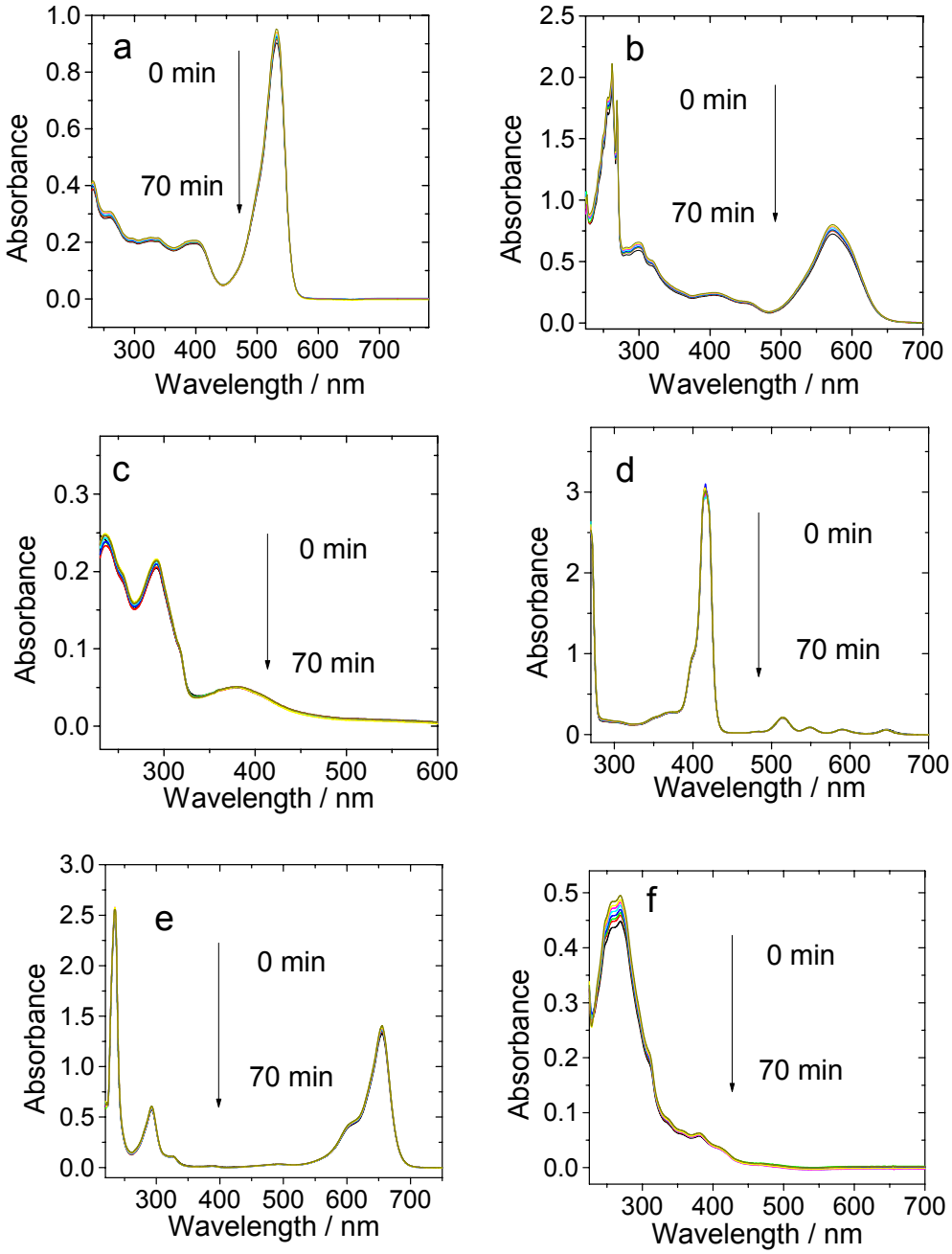


Fig. S25 Absorption spectral changes for the photooxidation of DHN with different triplet photosensitizers (a) **Re-1**, (b) **Re-2**, (c) **Re-0**, (d) TPP, (e) MB, (f) $[Ir(ppy)_2(dpy)]^+$. (1×10^{-5} mol/dm^3) under broad light (λ > 385 nm at 20 mW/cm^2). In CH_2Cl_2/MeOH (9 : 1 v/v), 35 W Xenon lamp, light power density: 20 mW/cm^2. 25 °C.

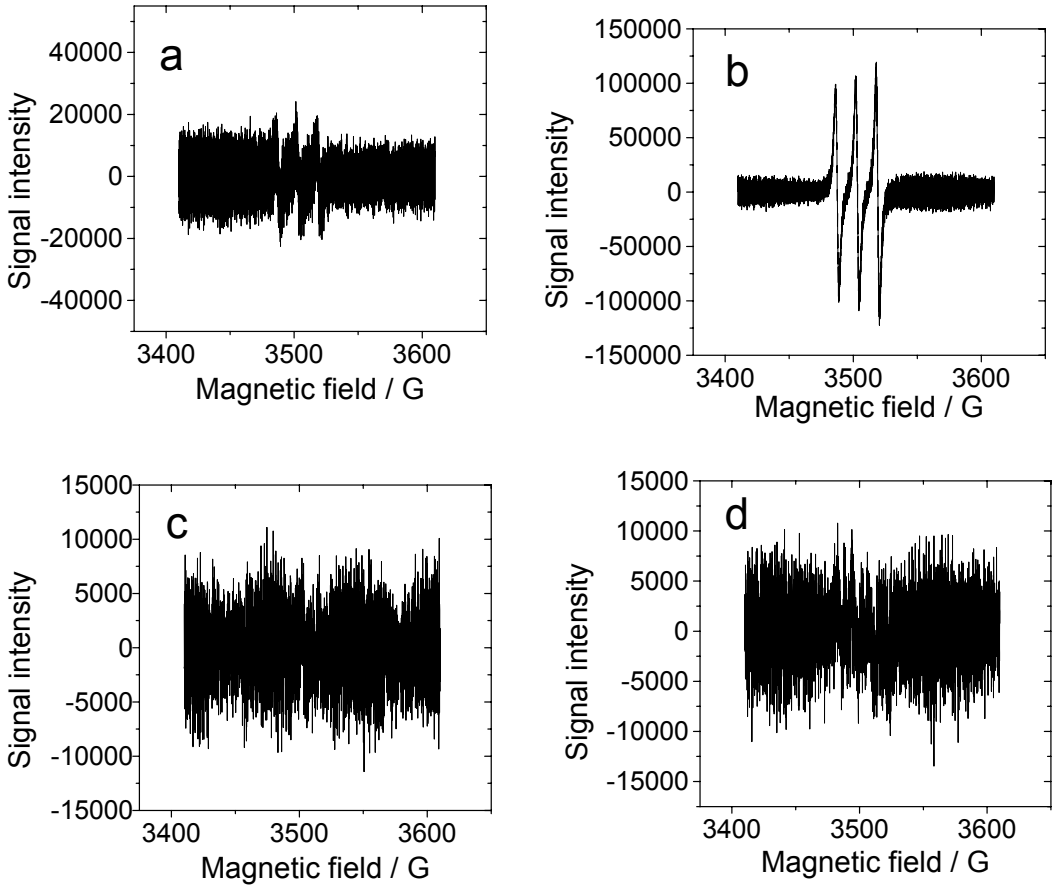
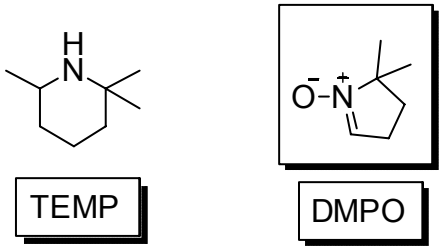


Fig. S26 (a) ESR spectrum of a solution of **Re-1** (1.0×10^{-4} M) and TEMP (0.12 M) in air-saturated CH_3CN. (b) ESR spectrum of a solution of **Re-1** (1.0×10^{-4} M) and TEMP (0.12 M) in air-saturated CH_3CN upon irradiation for 20s by 532 nm laser (141 mW/cm^2). (c) ESR spectrum of a solution of **Re-1** (1.0×10^{-4} M) DMPO (2.0×10^{-2} M) in air-saturated CH_3CN. (d) ESR spectrum of a solution of **Re-1** (1.0×10^{-4} M), DMPO (2.0×10^{-2} M), in air-saturated CH_3CN upon irradiation 20s for 532 nm laser 141 mW/cm^2. 22 °C

These results show that the singlet oxygen ($^1O_2$) was produced by **Re-1**, not $O_2^{\bullet-}$.

TEMP is scavenger for $^1O_2$, and DMPO is scavenger for $O_2^{\bullet-}$.



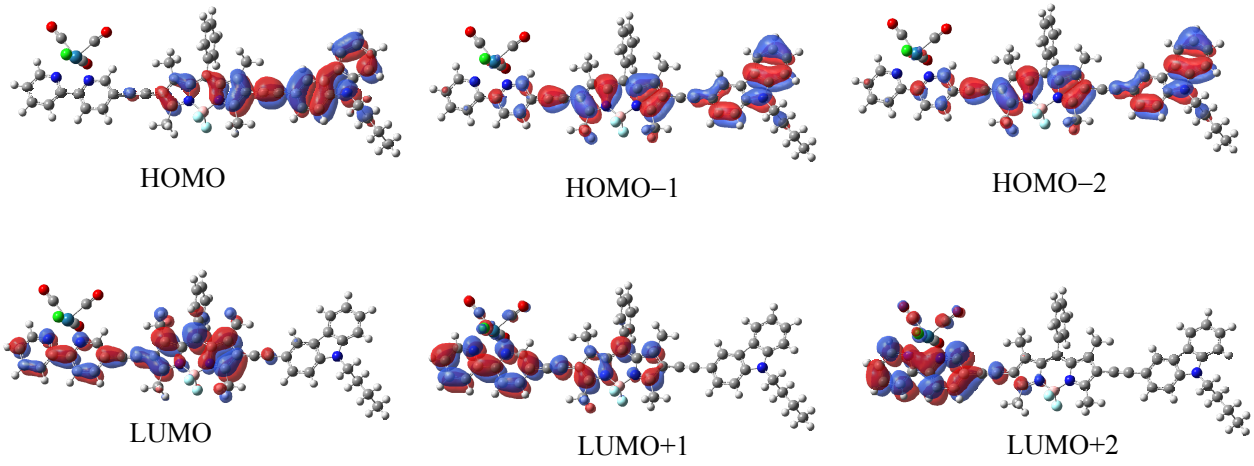


Fig. S27 Frontier molecular orbitals of **Re-2**. Calculated by DFT at the B3LYP/6-31G/LanL2DZ level using Gaussian 09W.

Table S1. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Re-2,** Calculated by TDDFT//B3LYP/6-31G/LanL2DZ, based on the DFT//B3LYP/6-31G/LanL2DZ Optimized Ground State Geometries.

	Electronic transition	TDDFT//B3LYP/6-31G				
		Energy (eV) [a]	*f* [b]	Composition [c]	CI [d]	character
Singlet	$S_0 \rightarrow S_1$	1.92 eV 646 nm	0.7348	H→L	0.6944	LLCT
	$S_0 \rightarrow S_2$	2.31 eV 537 nm	0.0236	H →L+1	0.6936	MLCT
	$S_0 \rightarrow S_3$	2.46 eV 505 nm	0.0493	H-2→L	0.4592	LLCT
	$S_0 \rightarrow S_4$	2.51 eV 493 nm	0.7512	H−1→L	0.5928	LLCT
Triplet	$T_1 \rightarrow S_0$	1.42 eV 870 nm	0.0000 [e]	H→L	0.5661	LLCT
				H−1→L	0.2784	LLCT
	$T_2 \rightarrow S_0$	1.88 eV 658 nm	0.0000	H−1→L	0.3713	LLCT
				H→L	0.3140	LLCT
	$T_3 \rightarrow S_0$	2.10 eV 535 nm	0.0000	H→L+1	0.4562	MLCT

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the *f* values are zero.