

## Supporting Information

### Photocatalytic Function of B<sub>12</sub> Complex with Cyclometalated Iridium(III) Complex as Photosensitizer under Visible Light Irradiation

Hui Tian,<sup>a</sup> Hisashi Shimakoshi,<sup>\*a</sup> Sinheui Kim,<sup>b</sup> Gyurim Park,<sup>b</sup> Youngmin You<sup>\*b</sup> and Yoshio Hisaeda<sup>\*a</sup>

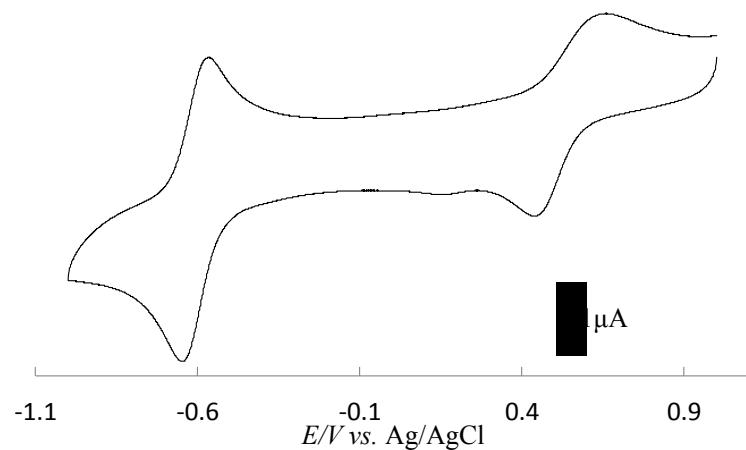
<sup>a</sup> Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Motooka, Fukuoka 819-0395, Japan.

E-mail: [shimakoshi@mail.cstm.kyushu-u.ac.jp](mailto:shimakoshi@mail.cstm.kyushu-u.ac.jp), [yhisatcm@mail.cstm.kyushu-u.ac.jp](mailto:yhisatcm@mail.cstm.kyushu-u.ac.jp)  
Fax: +81-92-802-2828; Tel: +81-92-802-2828

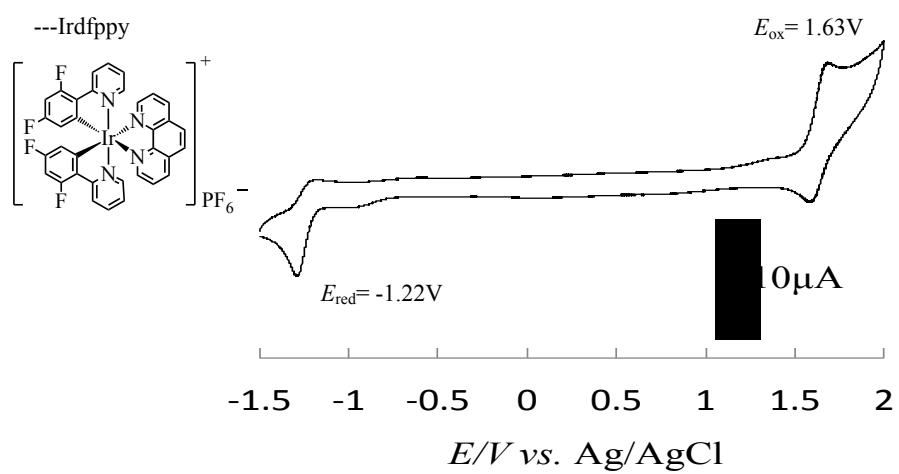
<sup>b</sup> Division of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Republic of Korea.

E-mail: [odds2@ewha.ac.kr](mailto:odds2@ewha.ac.kr)

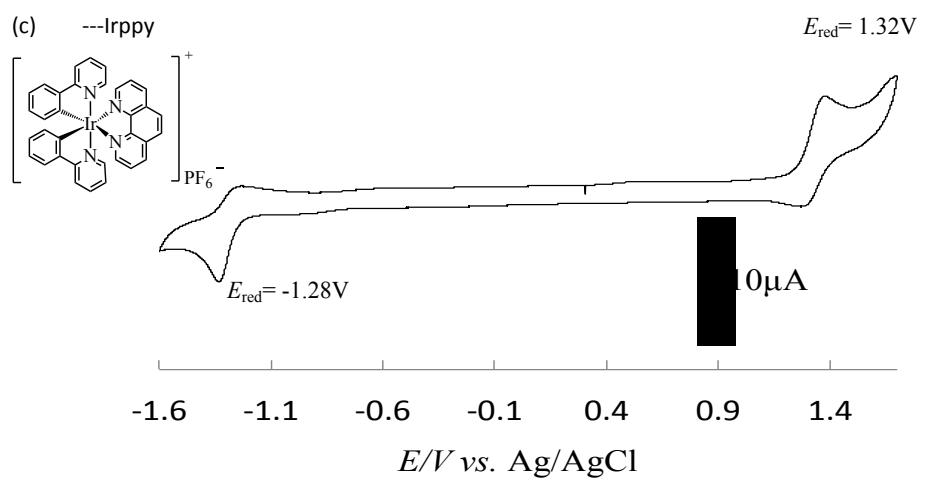
(a) ---B<sub>12</sub> complex

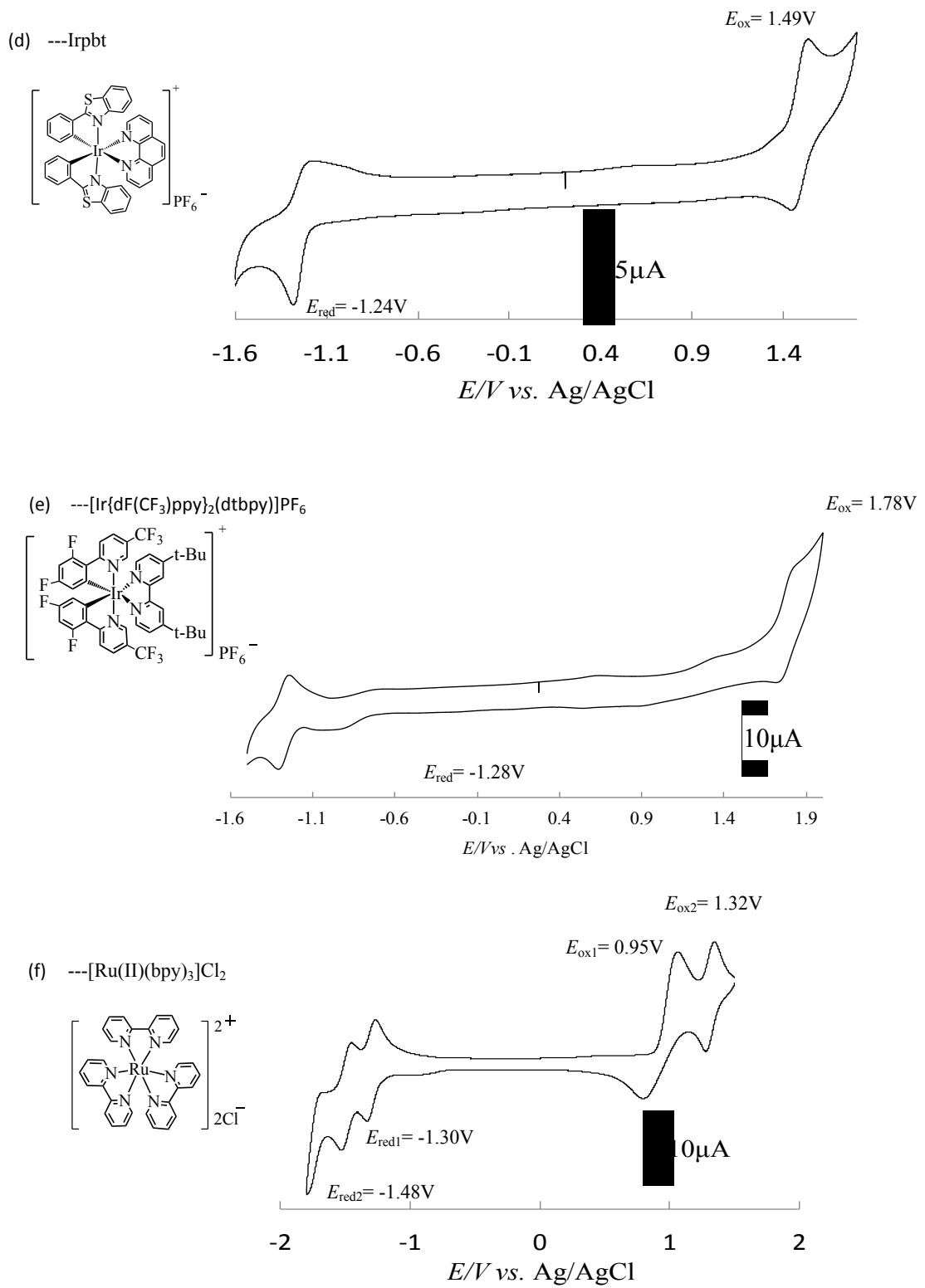


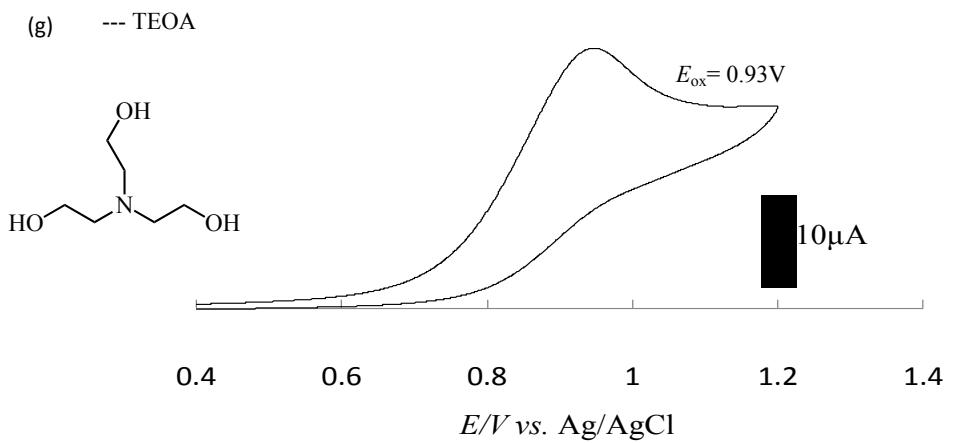
(b) ---Irdfppy



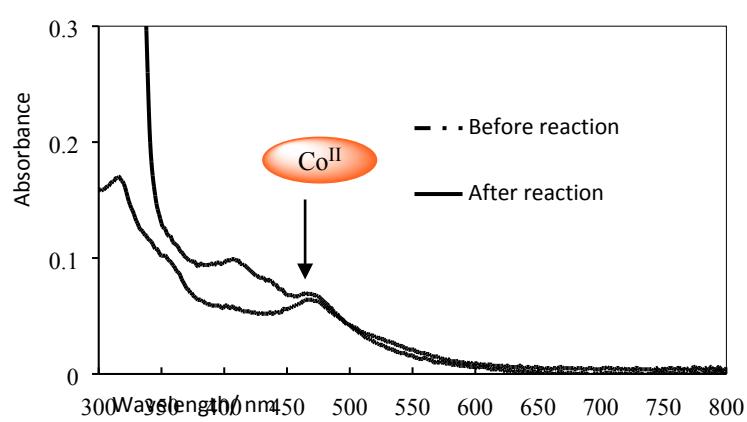
(c) ---Irppy



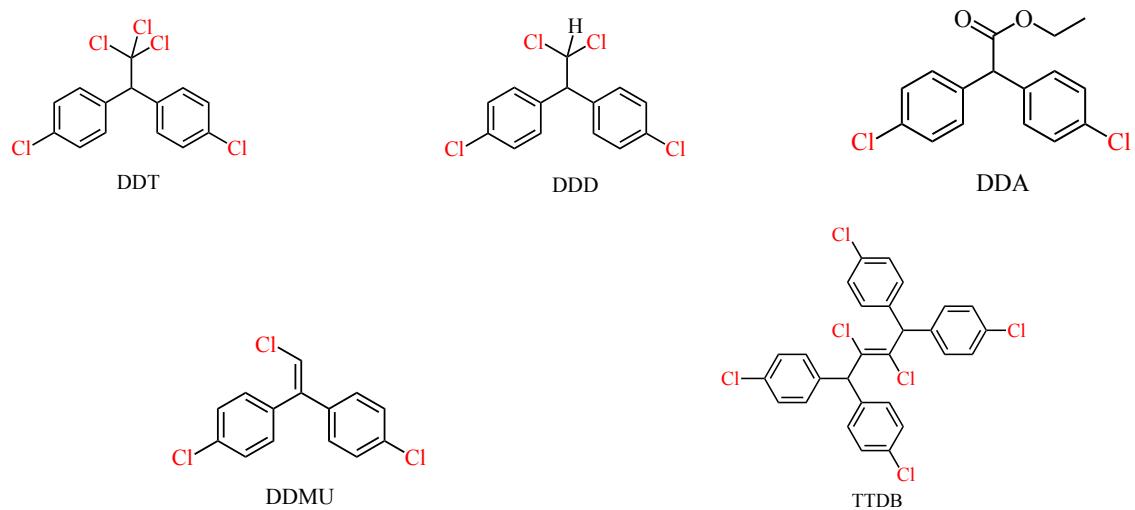




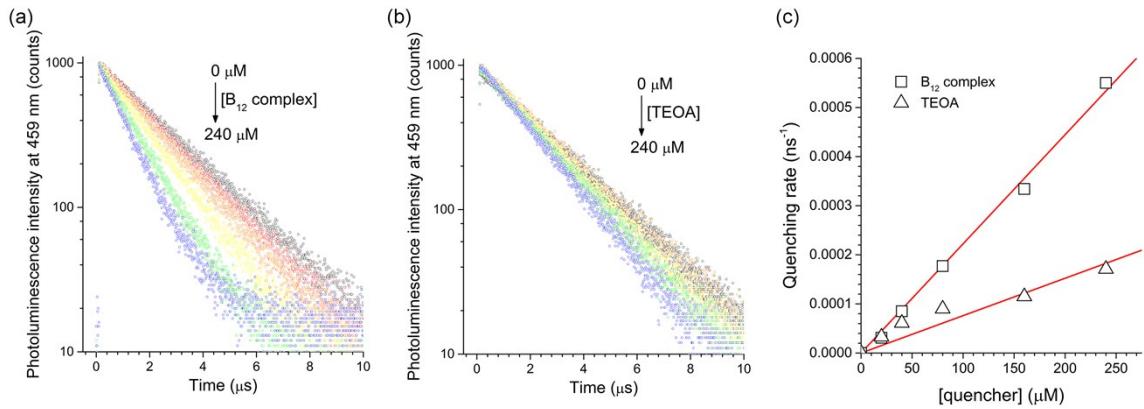
**Fig. S1** CVs of  $\text{B}_{12}$  complex (1mM) (a), Irdfppy (1mM) (b), Irppy (1mM) (c), Irpbt (1mM) (d), [Ir{dF(CF<sub>3</sub>)ppy}<sub>2</sub>(dtbppy)]PF<sub>6</sub> (1mM) (e), [Ru(II)(bpy)<sub>3</sub>]Cl<sub>2</sub> (1mM) (f) TEOA (1mM) (g), in CH<sub>3</sub>CN containing of 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> under N<sub>2</sub>.



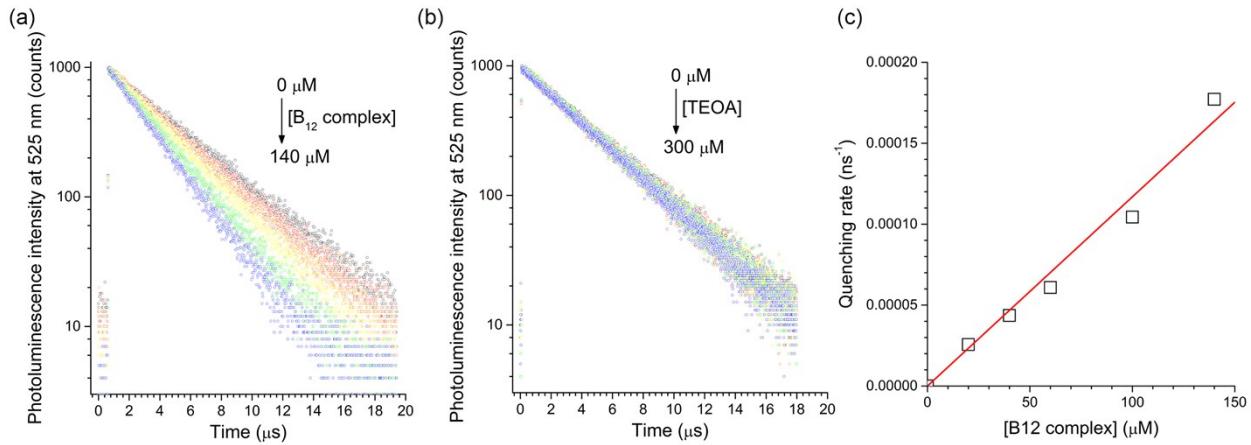
**Fig. S2** UV-vis spectral change of reaction solution ( $B_{12}$  complex as catalyst): before reaction (dotted line), after reaction (solid line).



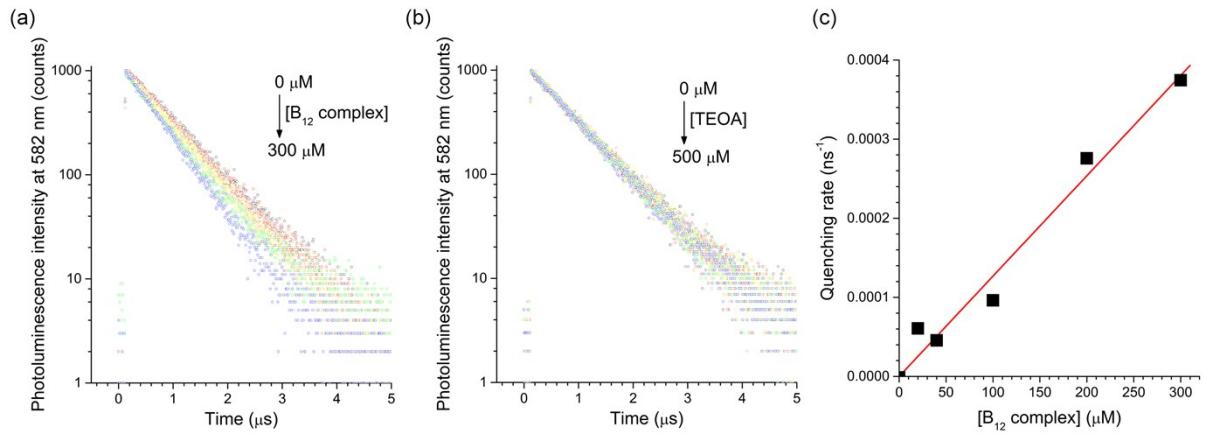
**Fig. S3** Structure of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD), ethyl 2,2-bis(4-chlorophenyl)acetate (DDA), 1-chloro-2,2-bis(4-chlorophenyl)ethylene (DDMU) and 1,1,4,4-tetrakis(4-chlorophenyl)-2,3-dichloro-2-butene (TTDB).



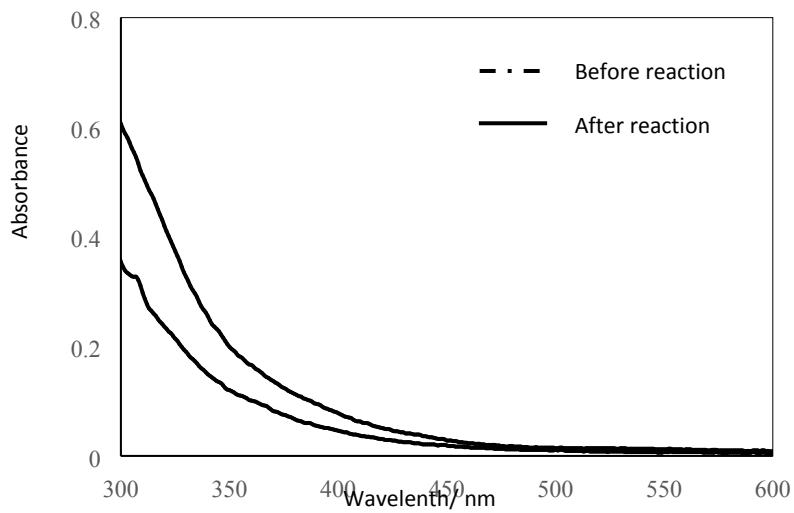
**Fig. S4** (a,b) Phosphorescence decay traces of  $100 \mu\text{M}$   $\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbpy})\text{PF}_6$  (Ar-saturated  $\text{CH}_3\text{CN}$ ) with increasing the concentration of  $\text{B}_{12}$  complex (a) or TEOA (b). (c) Pseudo first order fit of the quenching rate as a function of the added concentrations of  $\text{B}_{12}$  complex (squares) and TEOA (triangles).



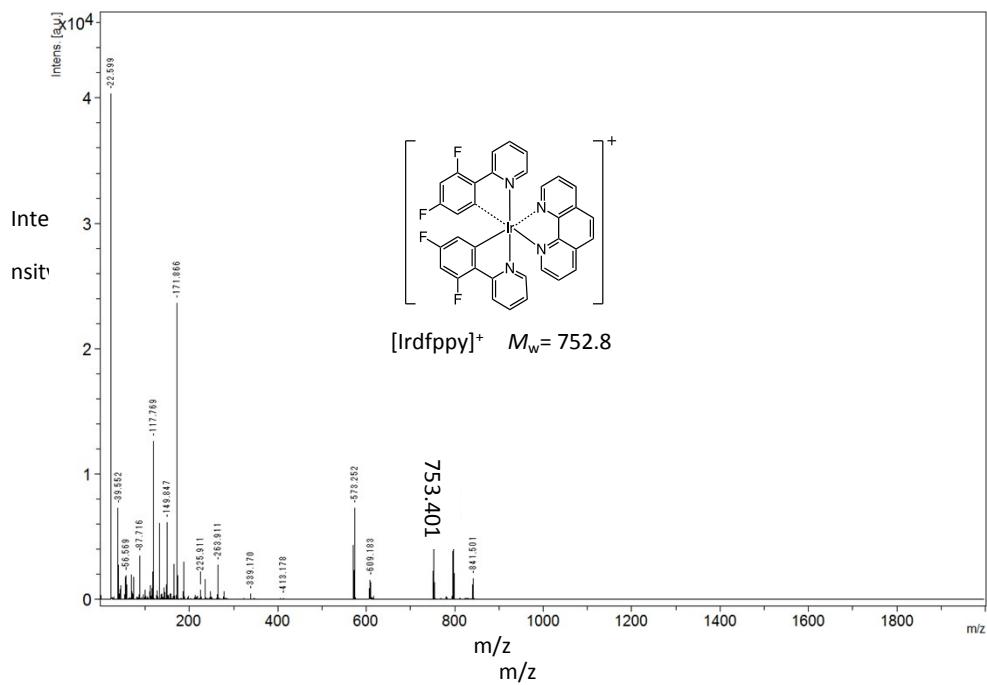
**Fig. S5** (a,b) Phosphorescence decay traces of  $100 \mu\text{M}$  Irpbt (Ar-saturated  $\text{CH}_3\text{CN}$ ) with increasing the concentration of  $\text{B}_{12}$  complex (a) or TEOA (b). (c) Pseudo first order fit of the quenching rate as a function of the added concentrations of  $\text{B}_{12}$  complex.



**Fig. S6** (a,b) Phosphorescence decay traces of 100  $\mu\text{M}$  Irppy (Ar-saturated  $\text{CH}_3\text{CN}$ ) with increasing the concentration of  $B_{12}$  complex (a) or TEOA (b). (c) Pseudo first order fit of the quenching rate as a function of the added concentrations of  $B_{12}$  complex.



**Fig. S7** UV-vis spectral change of reaction solution ( $\text{Co(III)(DO)(DOH)}\text{Br}_2$  as catalyst): before reaction (dotted line), after reaction (solid line).



**Fig. S8** MALDI-TOF mass spectrum of  $\text{Co(III)(DO)(DOH)}\text{Br}_2$  (not detected) and Irdfppy after catalytic reaction.