Supporting Information

An Aqueous, Organic Dye Derivatized SnO_2/TiO_2 Core/Shell Photoanode

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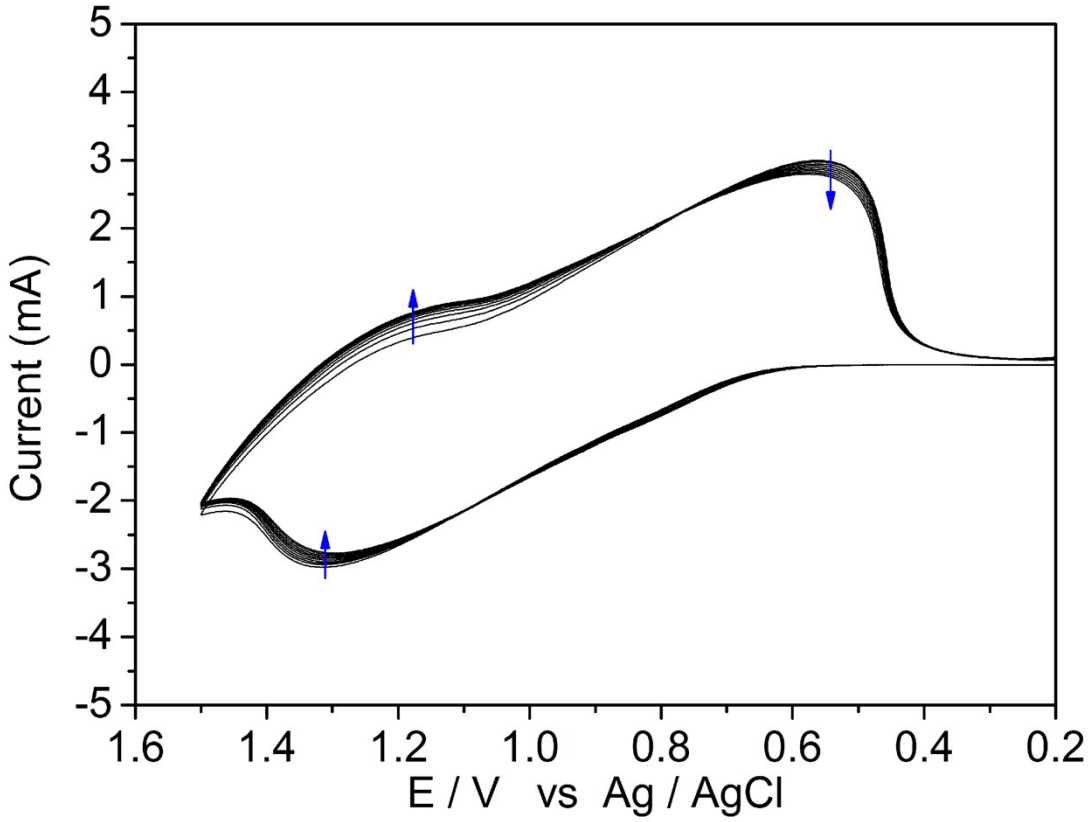

Figure S1. CV trace of FTO|TiO_2|-[**P-A-π-D**] film in 0.1 M tetrabutylammonium perchlorate (TBAP) containing acetonitrile solvent at 20 mV/s scan rate with 50 cycles of CVs.

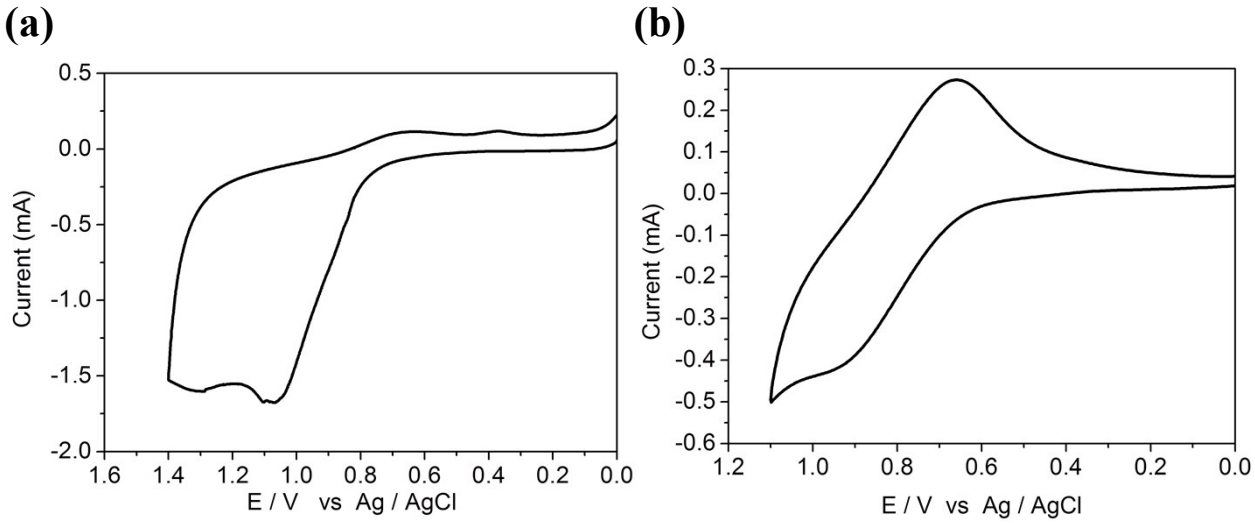

Figure S2. CV traces of FTO|TiO_2|-[**P-A-π-D**] film (a) from 0.0 to 1.1 V and (b) from 0.0 to 1.4 V in pH 7 phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 at 20 mV/s scan rate.

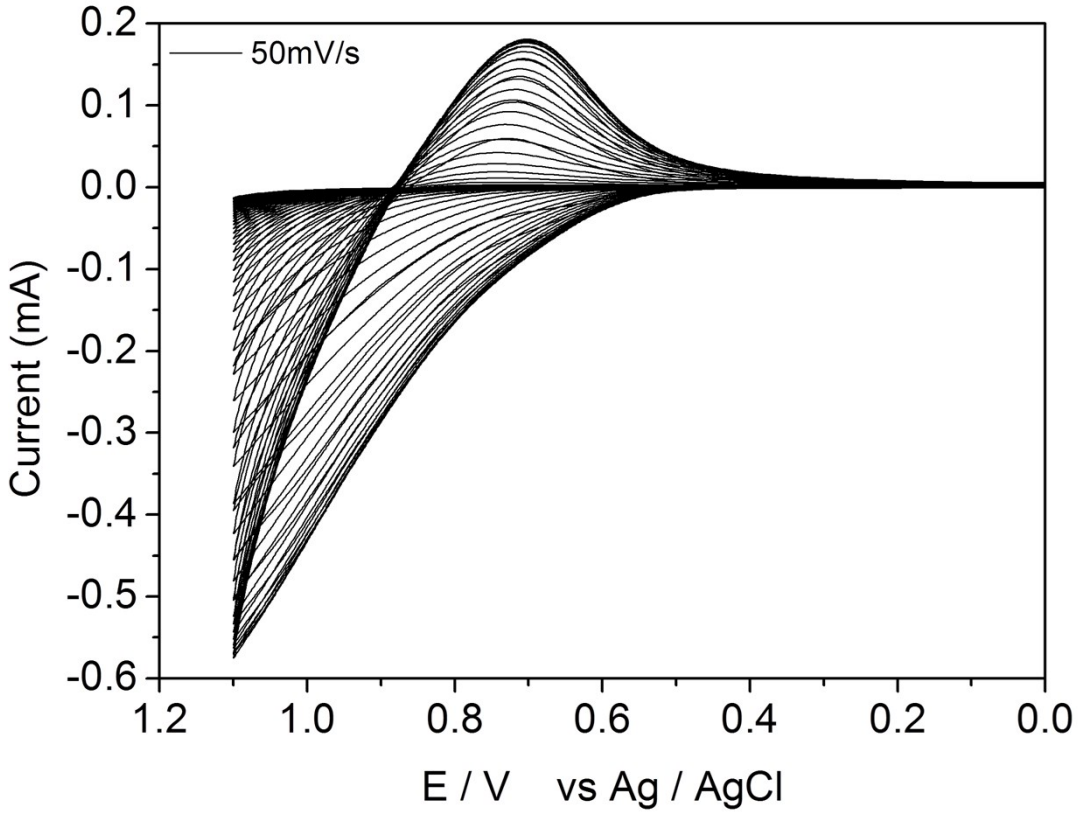

Figure S3. 50 Cycles of CVs for FTO|TiO_2|-[**P-A-π-D**] film in pH 7 phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 at 50 mV/s scan rate.

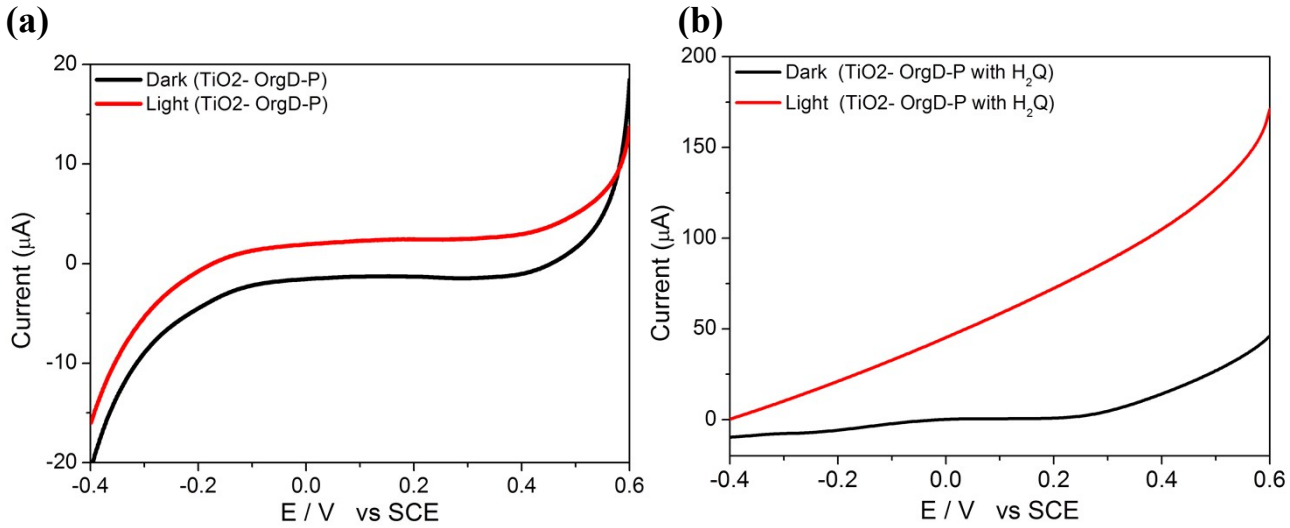

Figure S4. Linear scan voltammetric (LSV) trace of FTO|TiO_2|-[**P-A-π-D**] electrode in pH 7 phosphate buffer solution vs. SCE containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 under dark and light (100 $mWcm^{-2}$, 400 nm cut-off filter) (a) w/o and (b) w/ 20 mM of hydroquinone (H_2Q), scan rate = 20 mV/s.

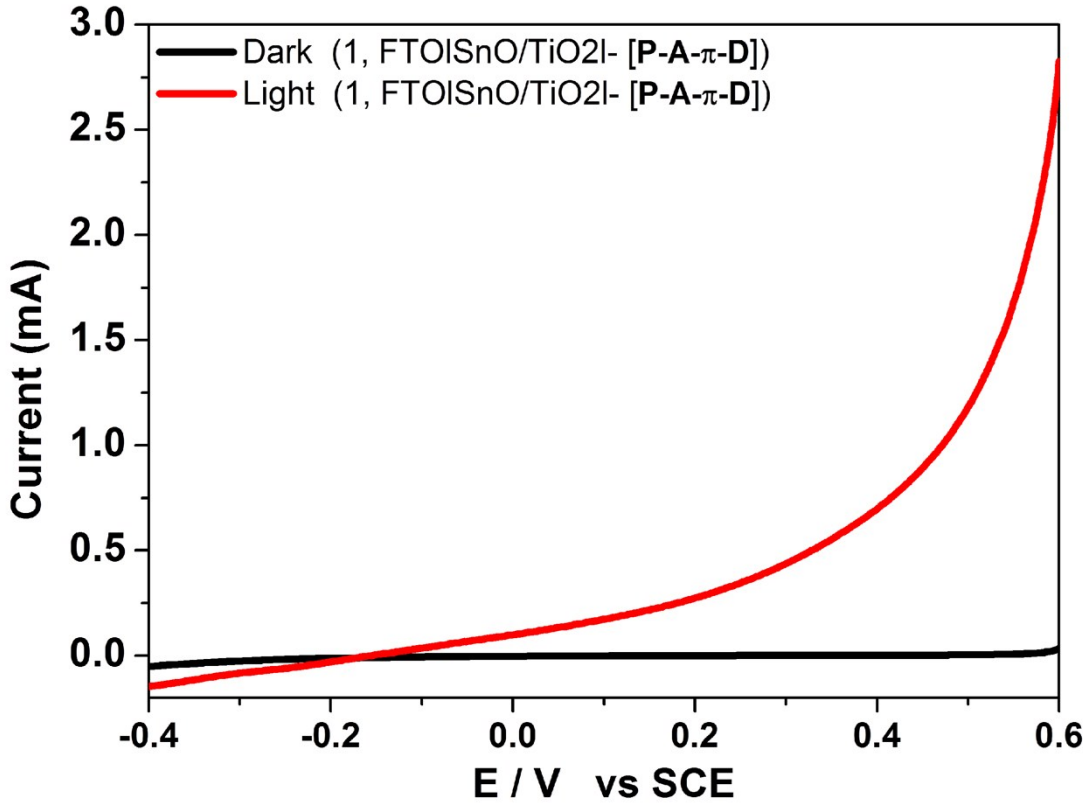

Figure S5. LSV trace of FTO|SnO_2/TiO_2|-[**P-A-π-D**] electrode vs. SCE in pH 7 phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 under dark and light (100 $mWcm^{-2}$, 400 nm cut-off filter) in the present of 20 mM of hydroquinone (H_2Q), scan rate = 20 mV/s.

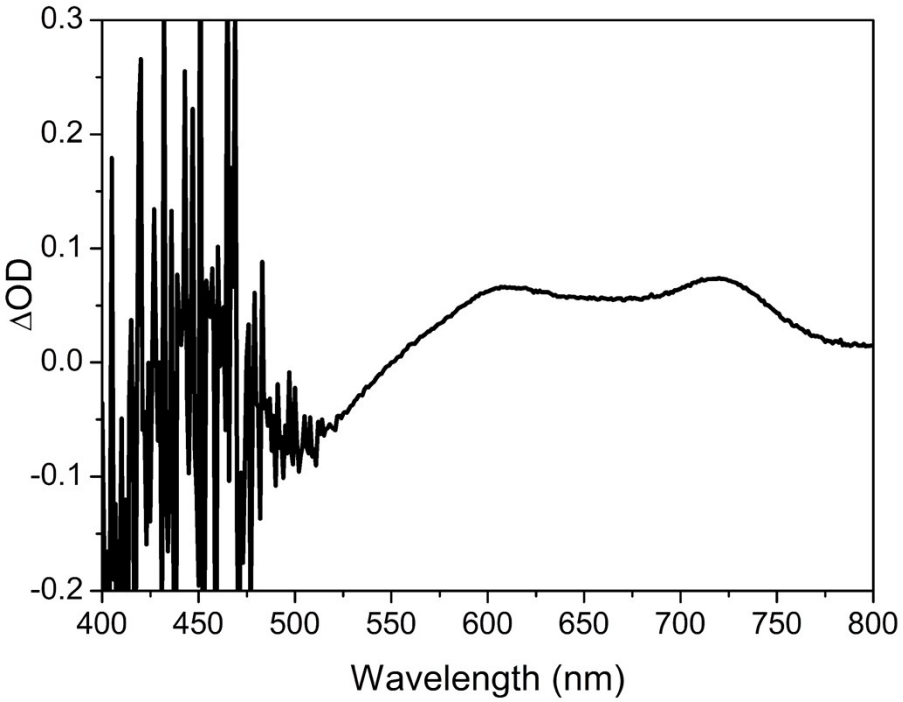

Figure S6. UV-Visible absorption changes of FTO|SnO_2/TiO_2|-[**P-A-π-D**] film in pH 7 phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 under light illumination (white light, 100 $mWcm^{-2}$, 400 nm cut-off filter).

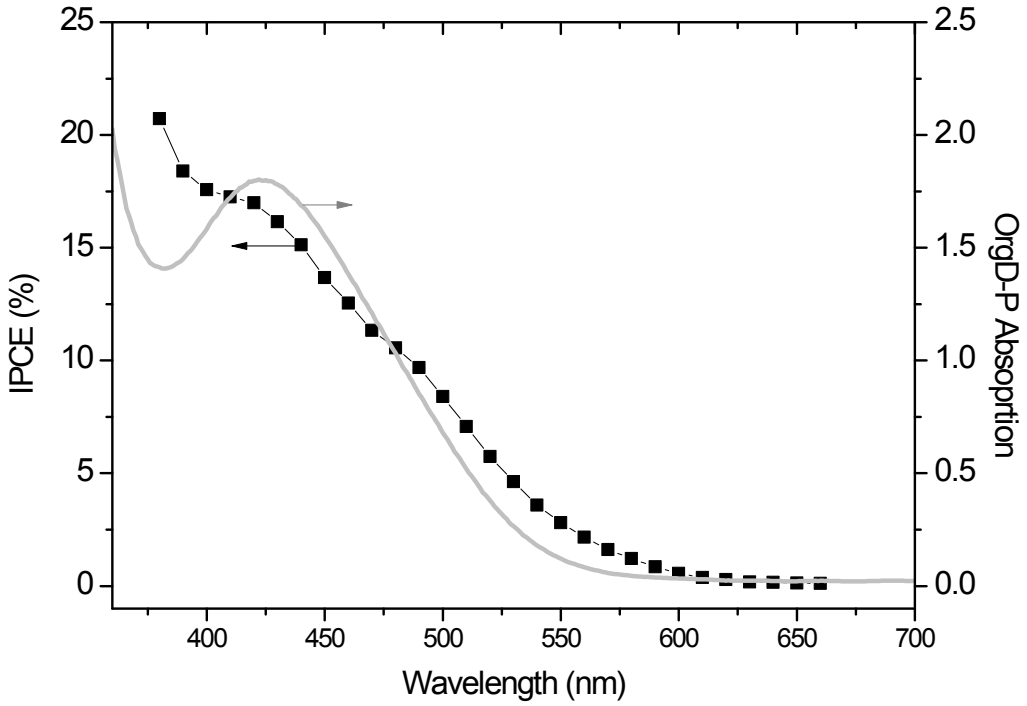

Figure S7. Incident photon to current efficiency (IPCE) data for FTO|SnO_2/TiO_2(3nm)|-[**P-A-π-D**] electrodes in pH 7, 0.1M phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 with 20 mM H_2Q with an applied bias of 0.2 V versus SCE.

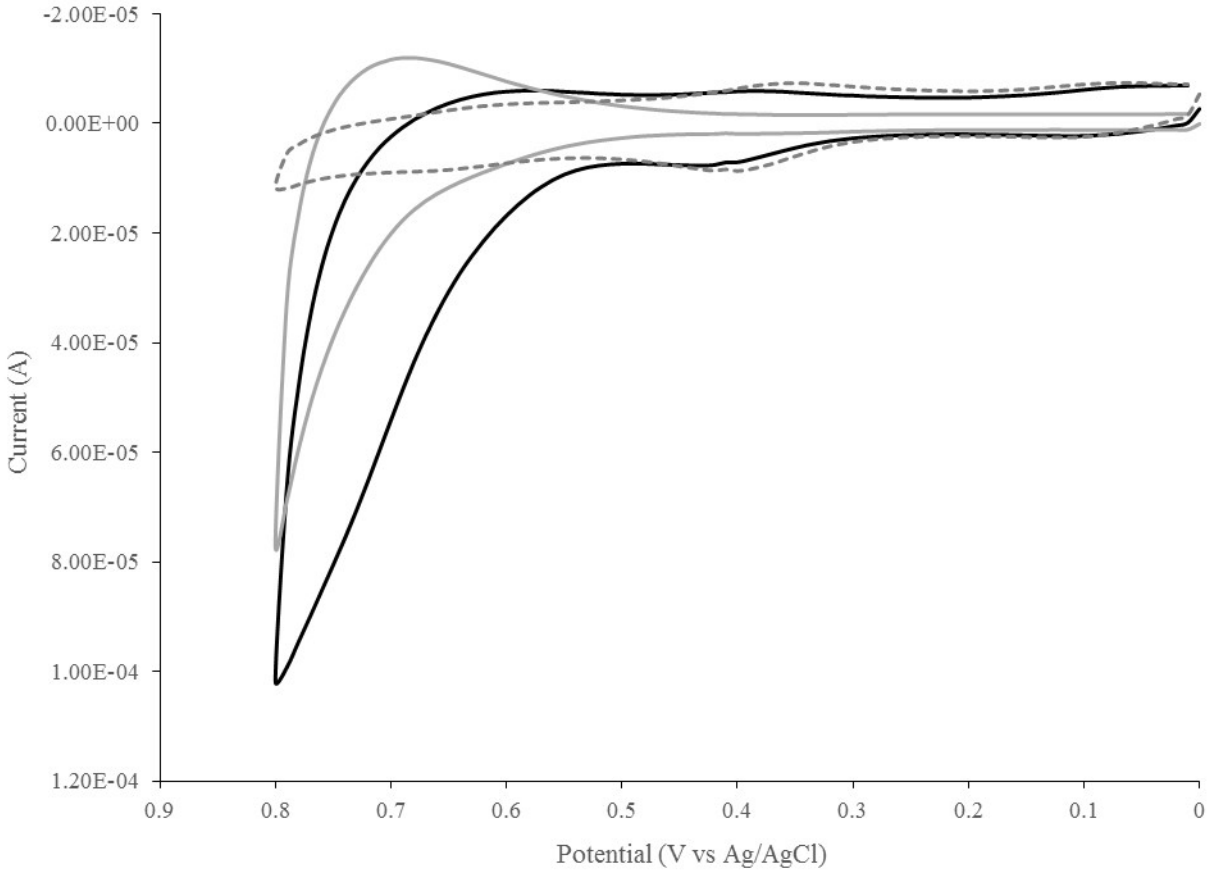

Figure S8. CV trace vs. AgCl/Ag for -[Ru(bda)(pyP$_2$)] (dotted gray), -[**P-A-π-D]** (gray), and 1:5 -[**P-A-π-D**+Ru(bda)(pyP$_2$)] (black) on 1 cm^2 FTO electrodes in pH 7, 0.1M phosphate, 0.5M $NaClO_4$, v = 50 mV/s.

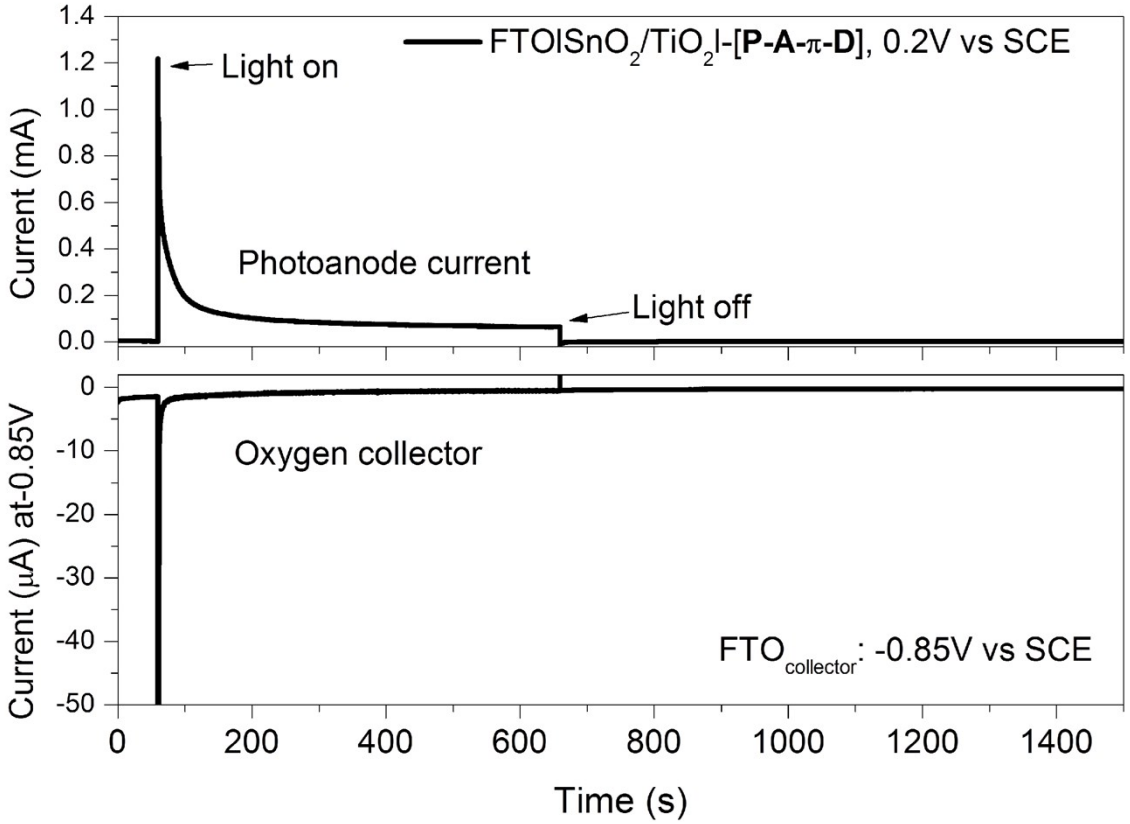

Figure S9. Upper: current–time trace (60–600 s) at light illuminated (100 mWcm^{-2}, 400 nm cut-off filter) FTO|SnO_2/TiO_2|-[**P-A-π-D**] in 0.1 M phosphate buffer at pH 7 with an applied bias of 0.2 V versus SCE. Lower: current trace measured at an FTO electrode ca.1 mm from FTO|SnO_2/TiO_2|-[**P-A-π-D**] electrode at an applied bias of -0.85 V versus SCE concurrently with the photoelectrochemical trace.

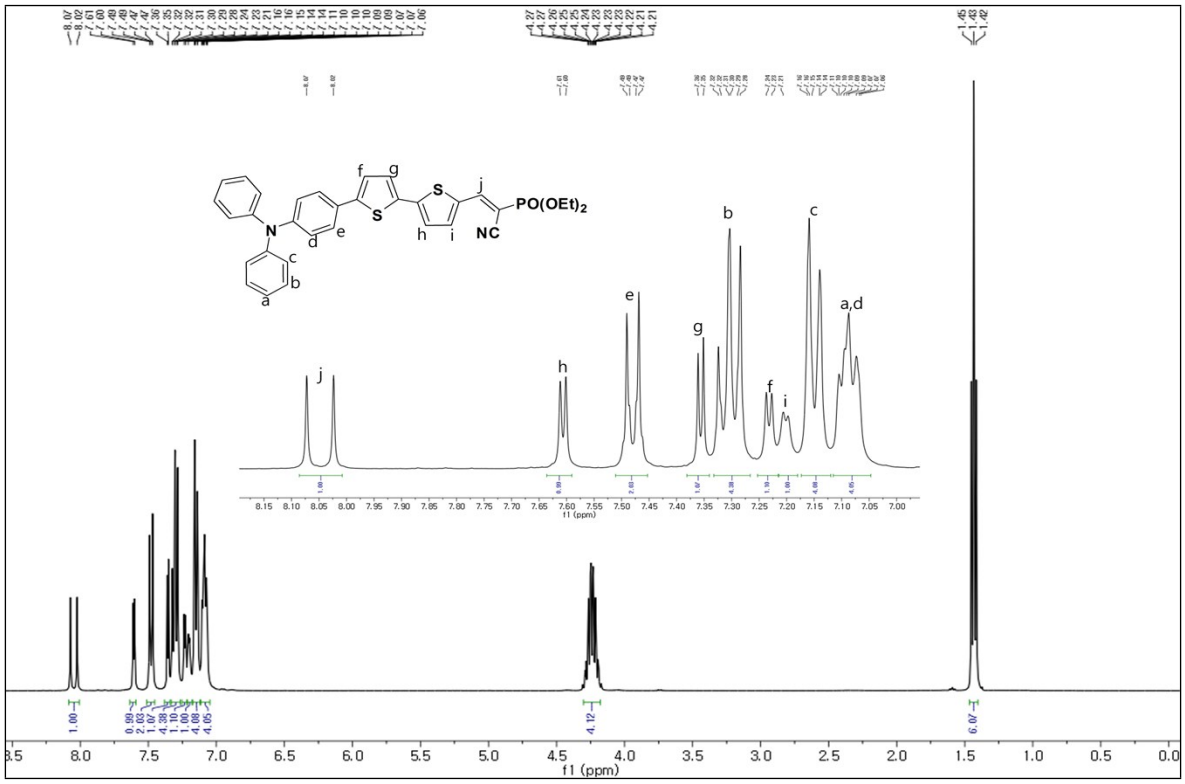

Figure S10-1. ^{1}H-NMR spectrum of OrgD-POEt in $CDCl_3$ solvent.

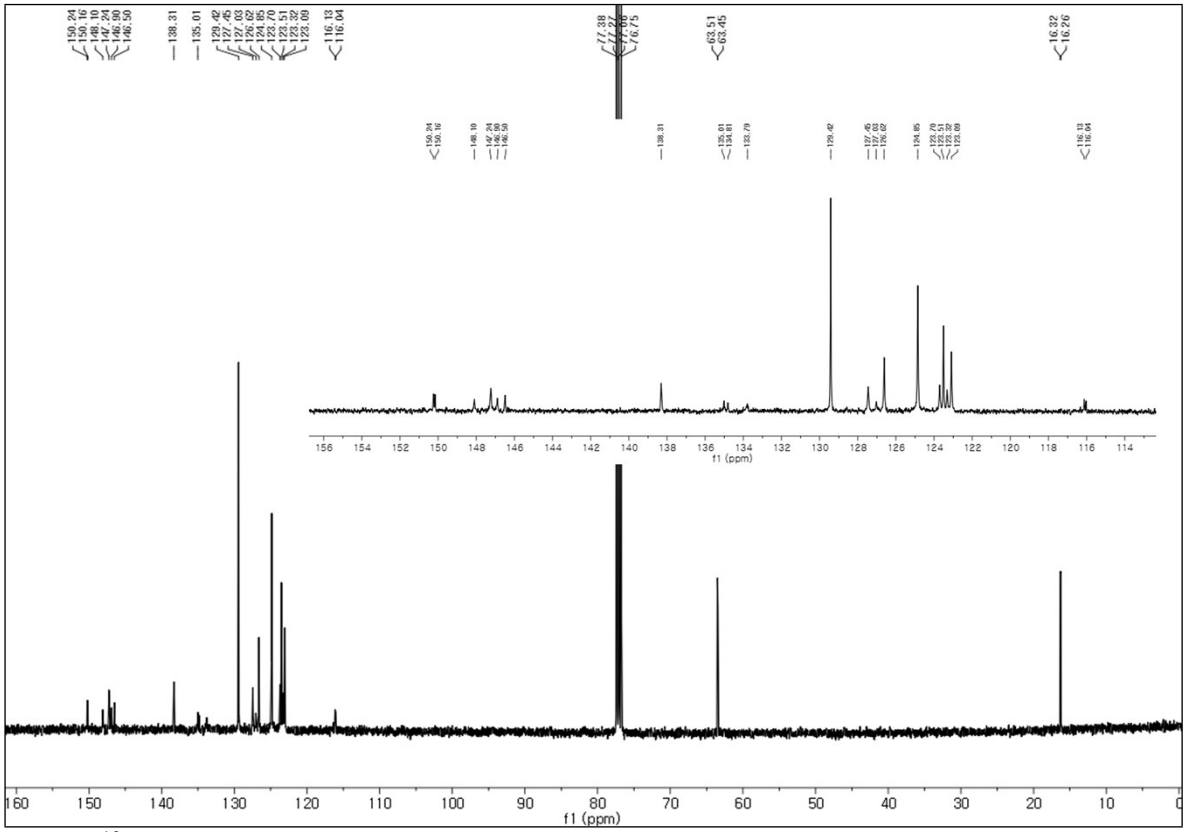

Figure S10-2. ^{13}C-NMR spectrum of OrgD-POEt in $CDCl_3$ solvent.

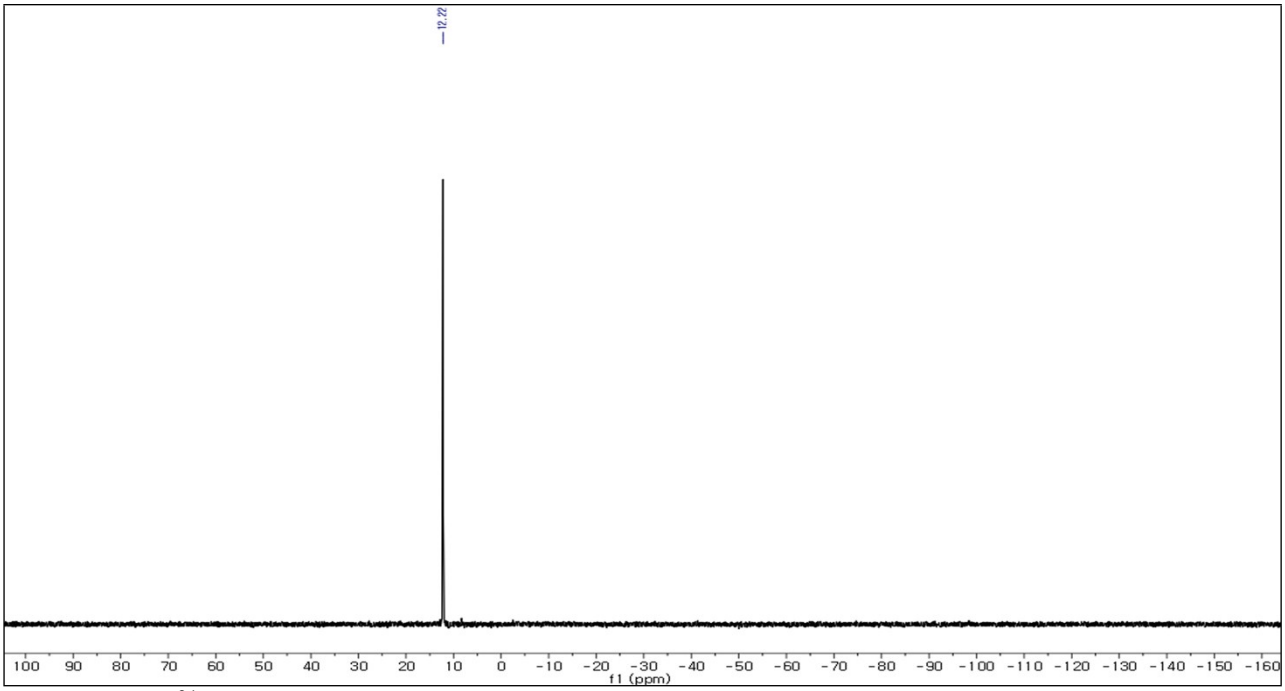

Figure S10-3. ^{31}P-NMR spectrum of OrgD-POEt in $CDCl_3$ solvent.

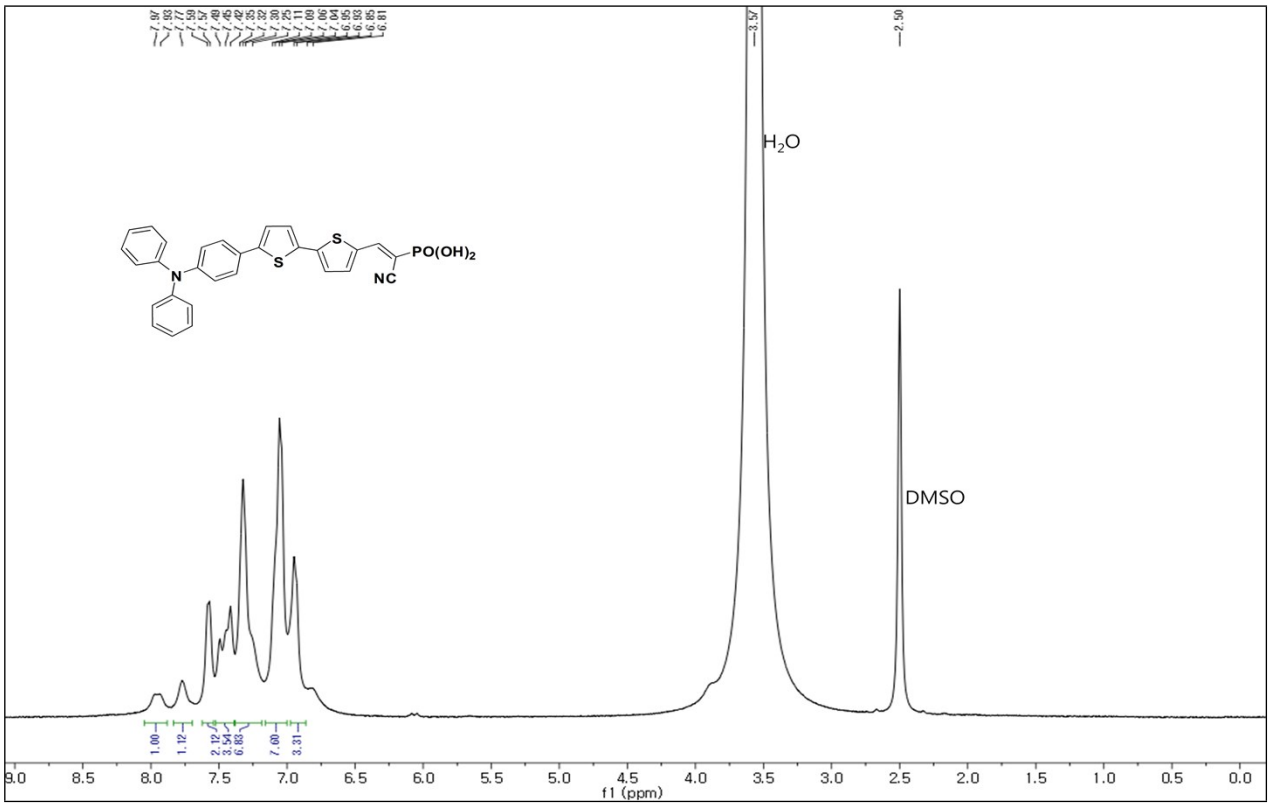

Figure S11-1. [1]H-NMR spectrum of **P-A-π-D** in DMSO solvent.

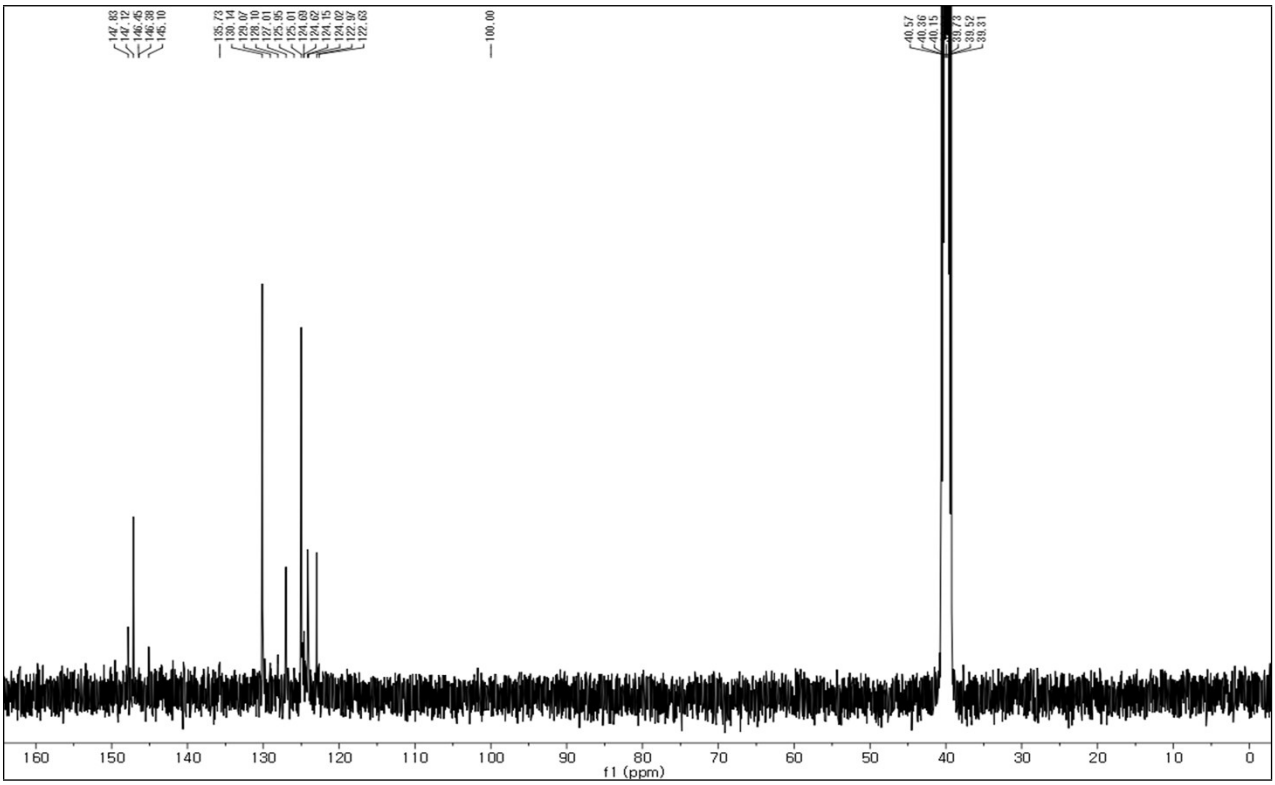

Figure S11-2. [13]C-NMR spectrum of **P-A-π-D** in DMSO solvent.

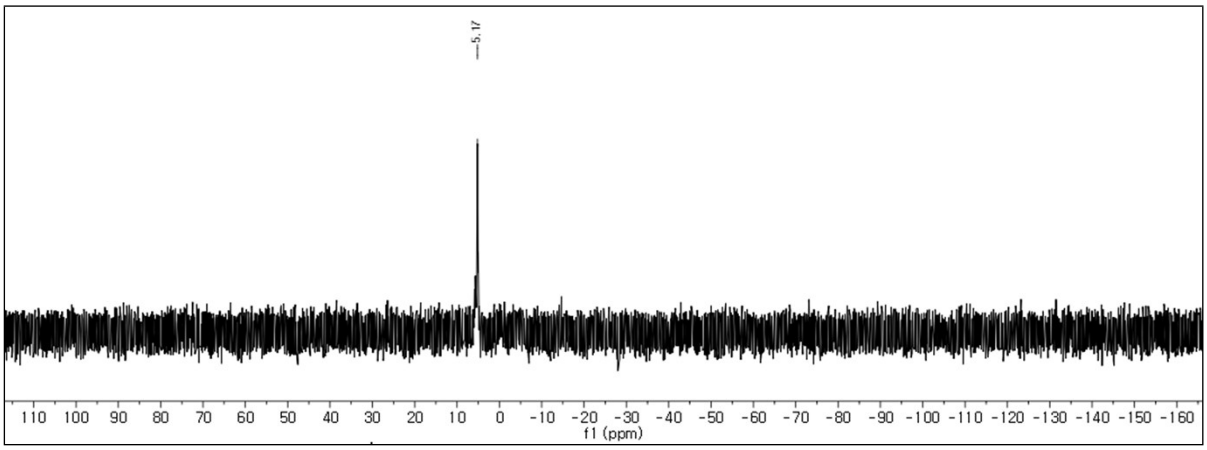

Figure S11-3. ^{31}P-NMR spectrum of **P-A-π-D** in DMSO solvent.

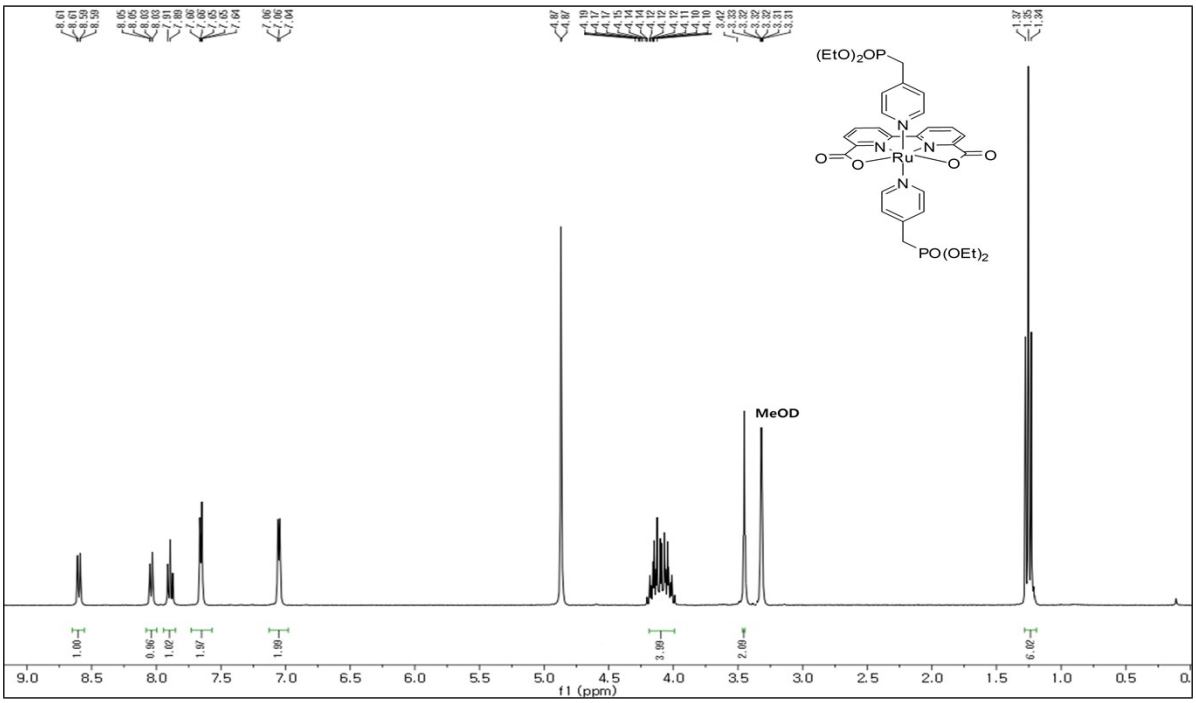

Figure S12-1. ^{1}H-NMR spectrum of Ru(bda)(pyPO_3Et_2)$_2$ in MeOD solvent.

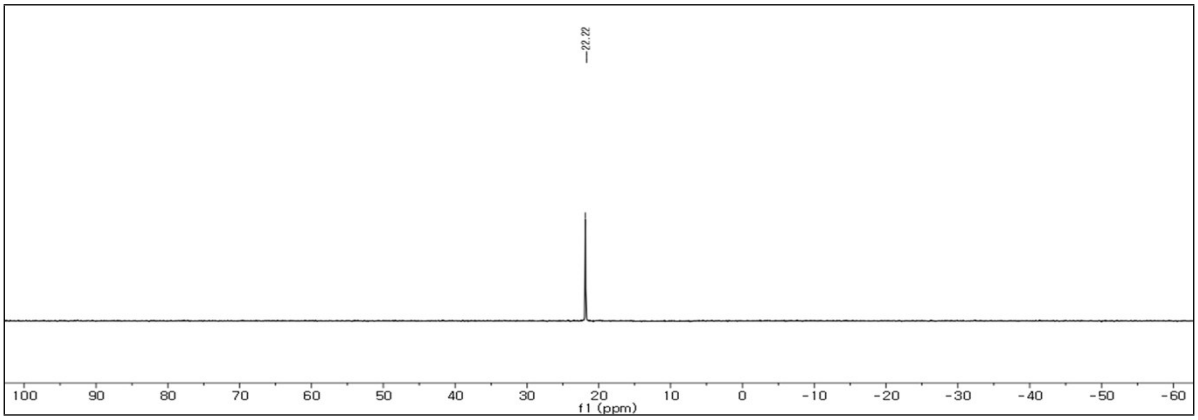

Figure S12-2. ^{1}P-NMR spectrum of Ru(bda)(pyPO_3Et_2)$_2$ in MeOD solvent.

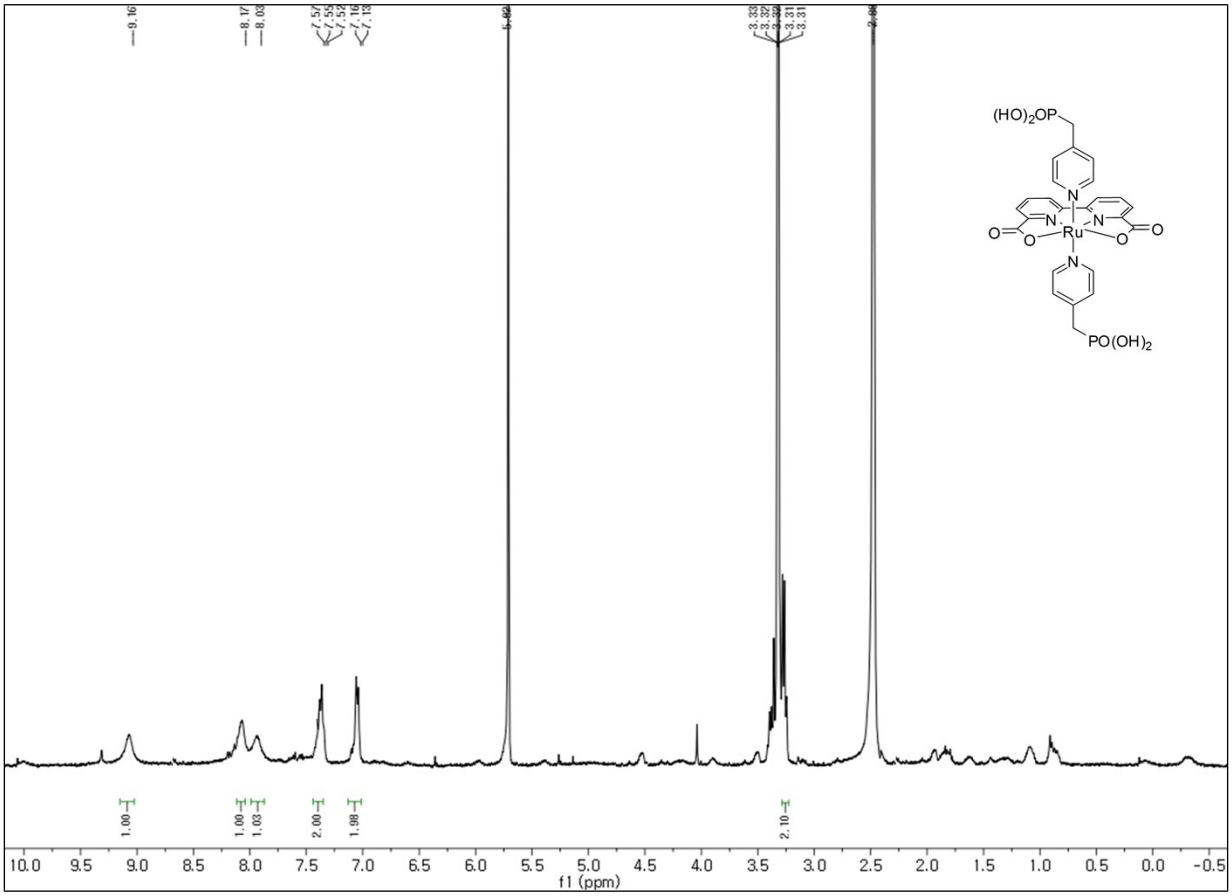

Figure S13-1. ^{1}H-NMR spectrum of Ru(bda)(pyP)$_2$ in DMSO solvent.

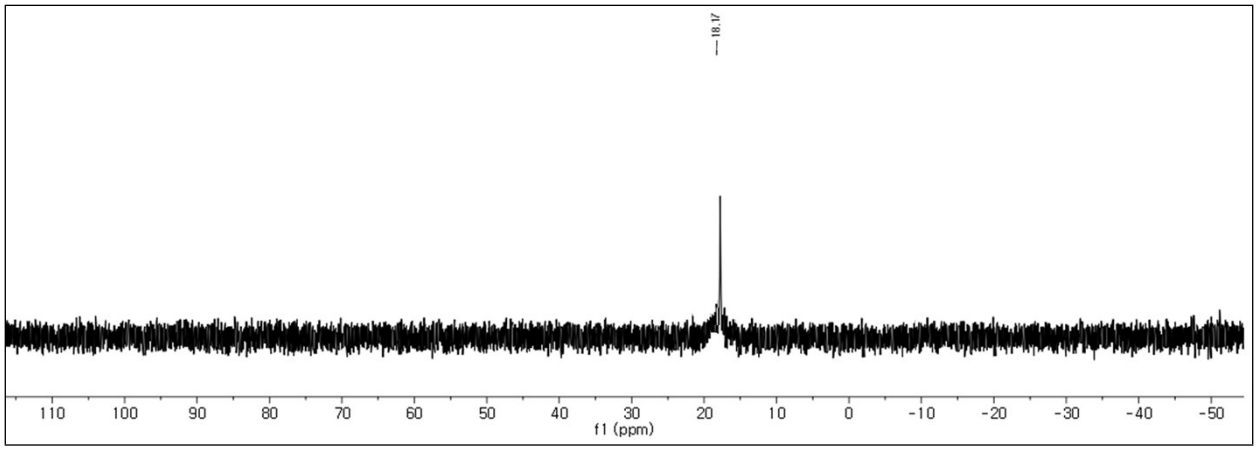

Figure S13-2. ^{1}P-NMR spectrum of Ru(bda)(pyP)$_2$ in DMSO solvent.

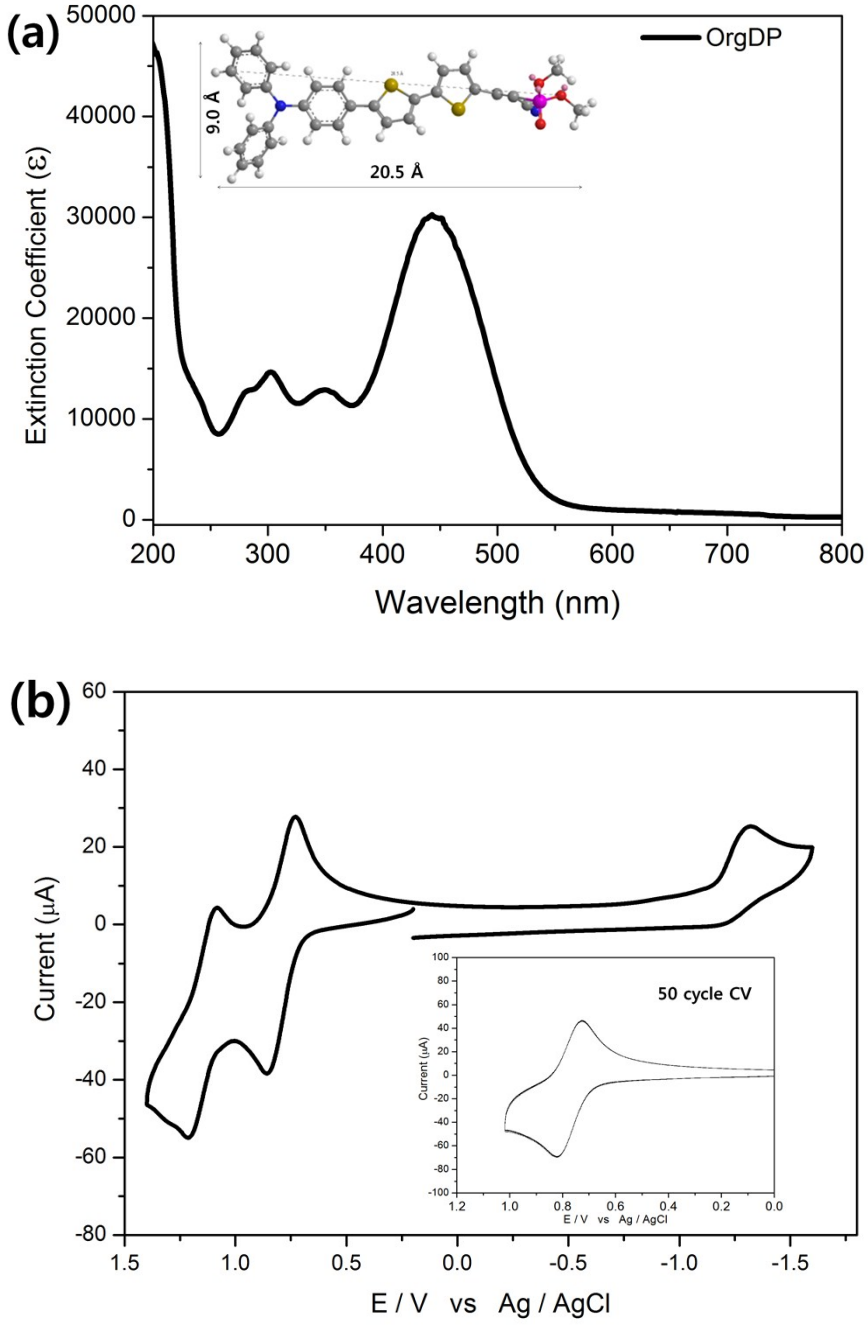

Figure S14. (a) UV-vis absorbance of **P-A-π-D** in CH_2Cl_2 solvent. (b) CV trace of **P-A-π-D** in 0.1 M tetrabutylammonium perchlorate (TBAP) containing CH_2Cl_2 solvent at 20 mV/s scan rate with 50 cycles of CVs.

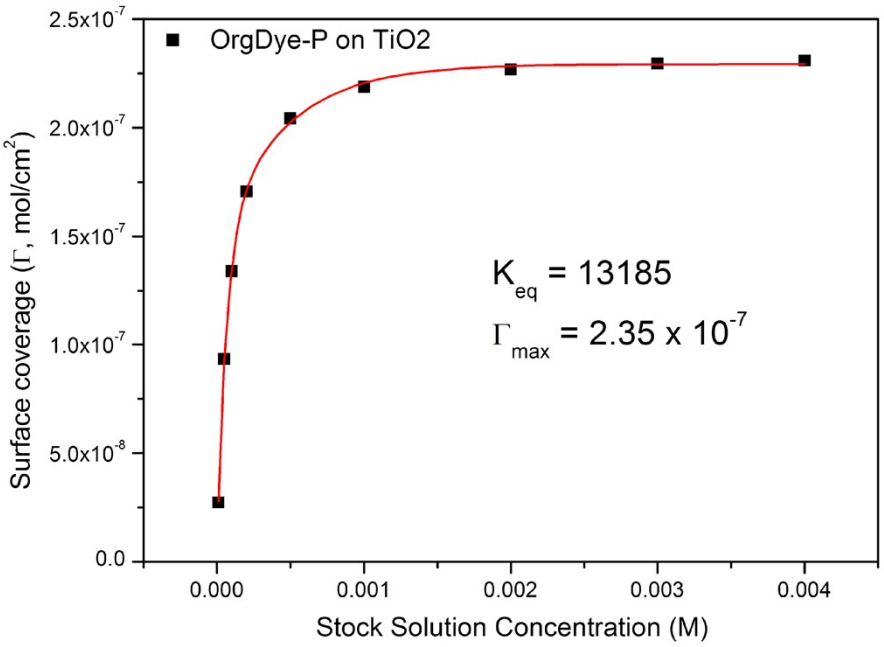

Figure S15. Adsorption isotherms of **P-A-π-D** on TiO_2 loaded from 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 3.0, and 4.0 mM solutions in CH_2Cl_2. The red lines are the best fits to the Langmuir isotherm equation.

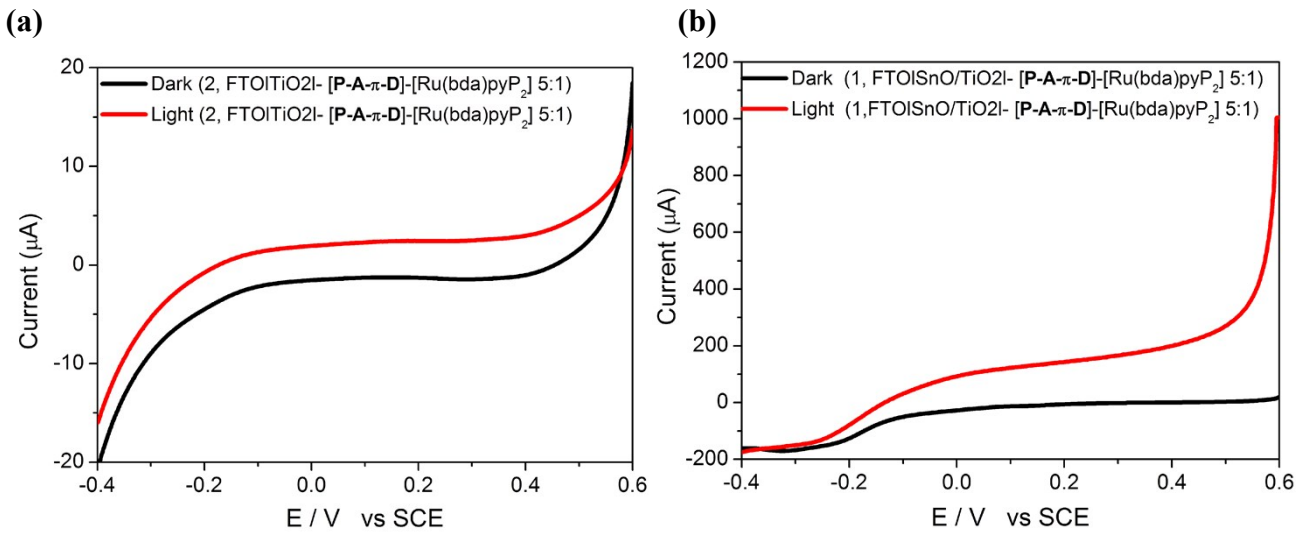

Figure S16. LSV trace of (a) FTO|TiO_2|-[**P-A-π-D**]-[Ru(bda)$(pyP)_2$] and (b) FTO|SnO_2/TiO_2|-[**P-A-π-D**]-[Ru(bda)$(pyP)_2$] (loading ratio, **P-A-π-D** : Ru(bda)$(pyP)_2$ = 5 : 1) electrode in pH 7 phosphate buffer solution containing 0.1 M $H_2PO_4^-$/ HPO_4^{2-}, 0.5 M KNO_3 under dark and light (100 $mWcm^{-2}$, 400 nm cut-off filter), scan rate = 20 mV/s.