Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Enzyme-Coupled Artificial Photosynthesis System Prepared from Antenna Protein-Mimetic Tyrosyl Bolaamphiphile Self-Assembly

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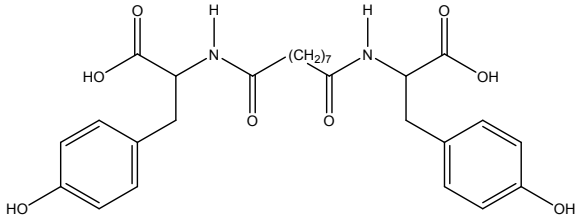
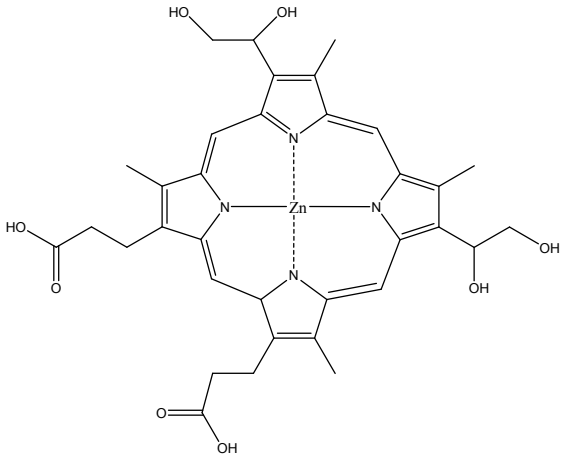
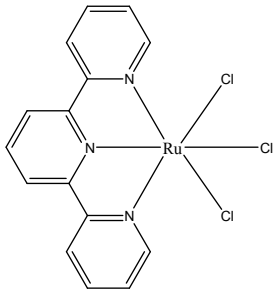
S1. Structures of the photochemical compounds



(a)



(b)



(c)

Figure S1. Chemical structures of the compounds used in developing the photosynthesis system. (a) Tyrosyl bolaamphiphile molecule (Tyr-C7), (b) Zn(II) deuteroporphyrin IX 2,4 bis ethylene glycol (ZnDPEG), (c) Ruthenium bis-terpyridine ($Ru(trpy)Cl_3$).

S2. Microscopy image of the prepared light-harvesting system

Individual nanospherical assembly functions as a light-harvesting system through association with photosensitizing components while keeping its spherical shape.

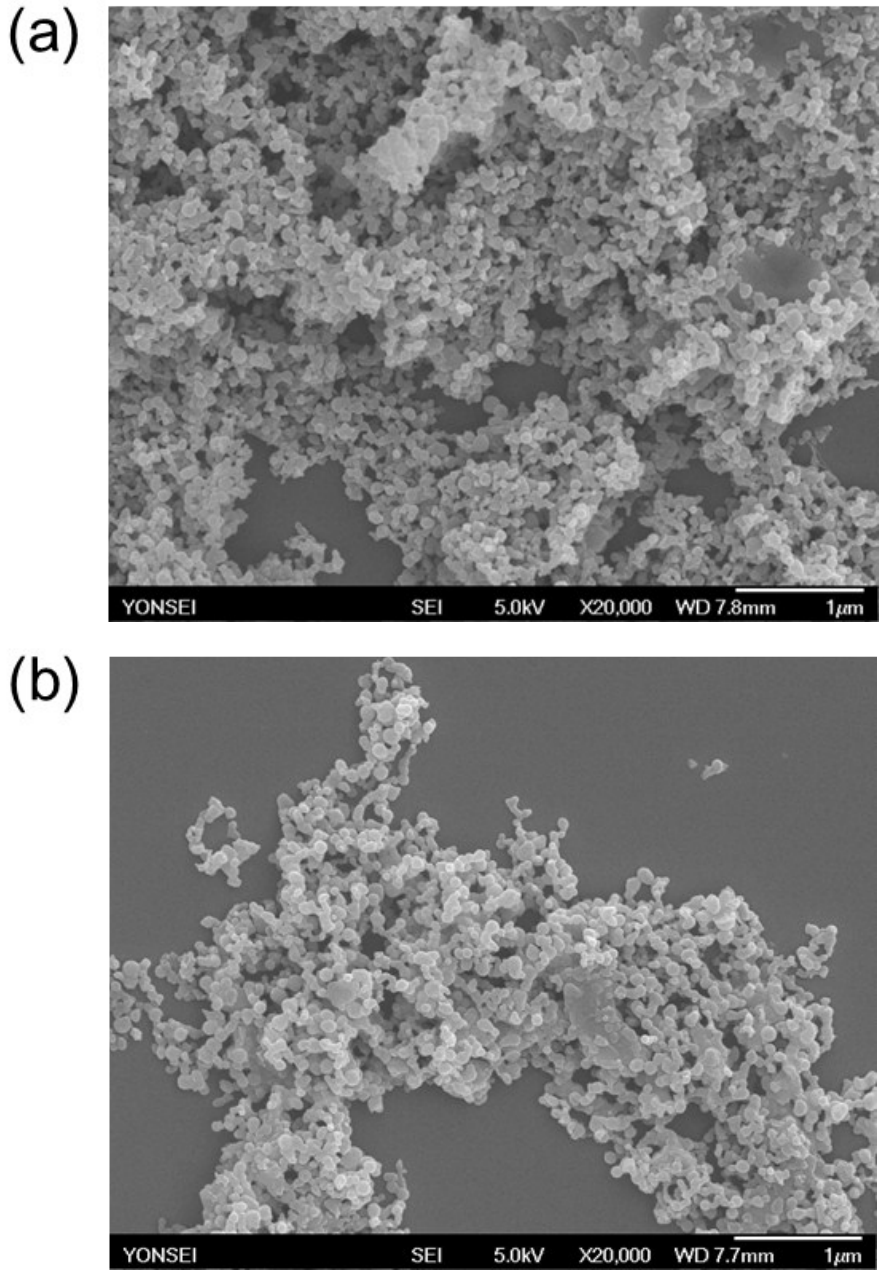


Figure S2. Scanning electron microscopy (SEM) images of (a) intact Tyr-C7 self-assemblies and (b) the light-harvesting systems associated with photochemical compounds.

S3. FT-IR spectra of intact and ZnDPEG-bound Tyr-C7 self-assemblies

Characteristic carboxyl groups of Tyr-C7 self-assemblies disappeared after binding of ZnDPEG.

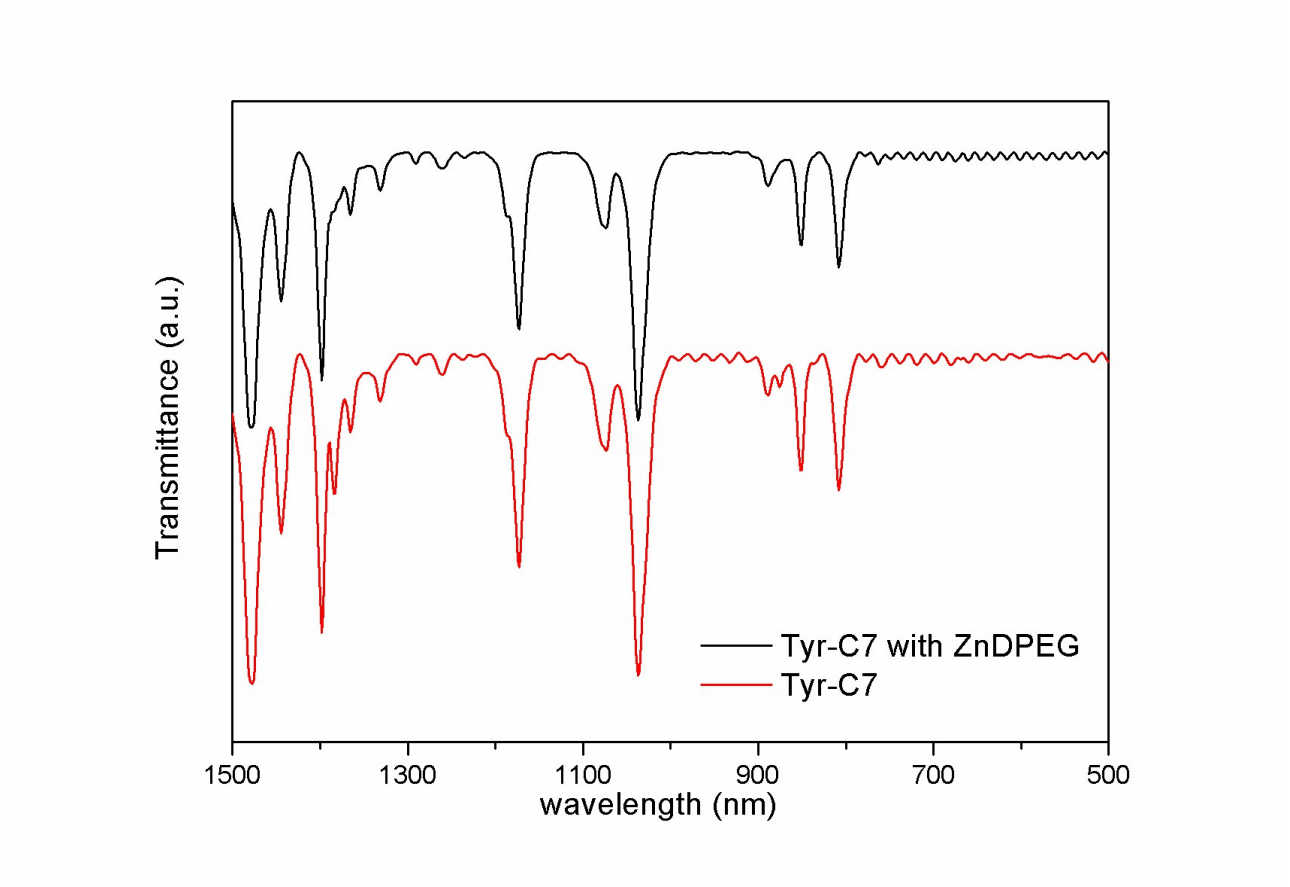


Figure S3. FT-IR spectra of intact and ZnDPEG-bound Tyr-C7 self-assemblies

S4. UV-vis spectra of photosystems

The photosystems containing ZnDPEG and other photochemical compounds promoted electron transfer from TEOA leading to NAD+ reduction to NADH. Characteristic peak of NADH appeared at 340 nm with concentration of each component.

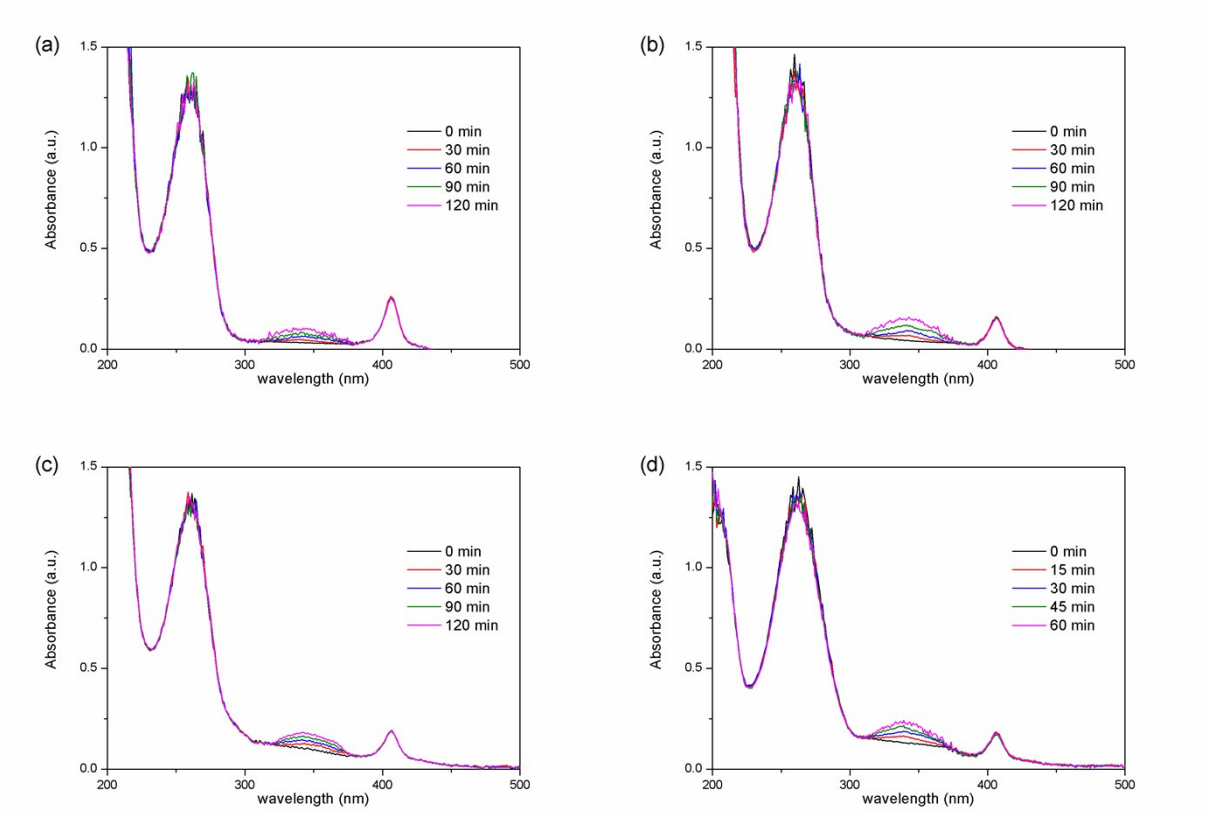


Figure S4. UV-vis spectra of NADH whose absorbance peak appeared at 340 nm from photosystems composed of (a) ZnDEPG only, (b) ZnDPEG + Tye-C7 self-assembly, (c) ZnDPEG + $Ru(trpy)Cl_3$ and (d) ZnDPEG + Tyr-C7 self-assembly + $Ru(trpy)Cl_3$. UV-vis spectra were taken with time.

S5. Production of NADH with increasing concentration of ZnDPEG

NADH concentrations were plotted against the ZnDPEG and Tyr-C7 concentrations, respectively.

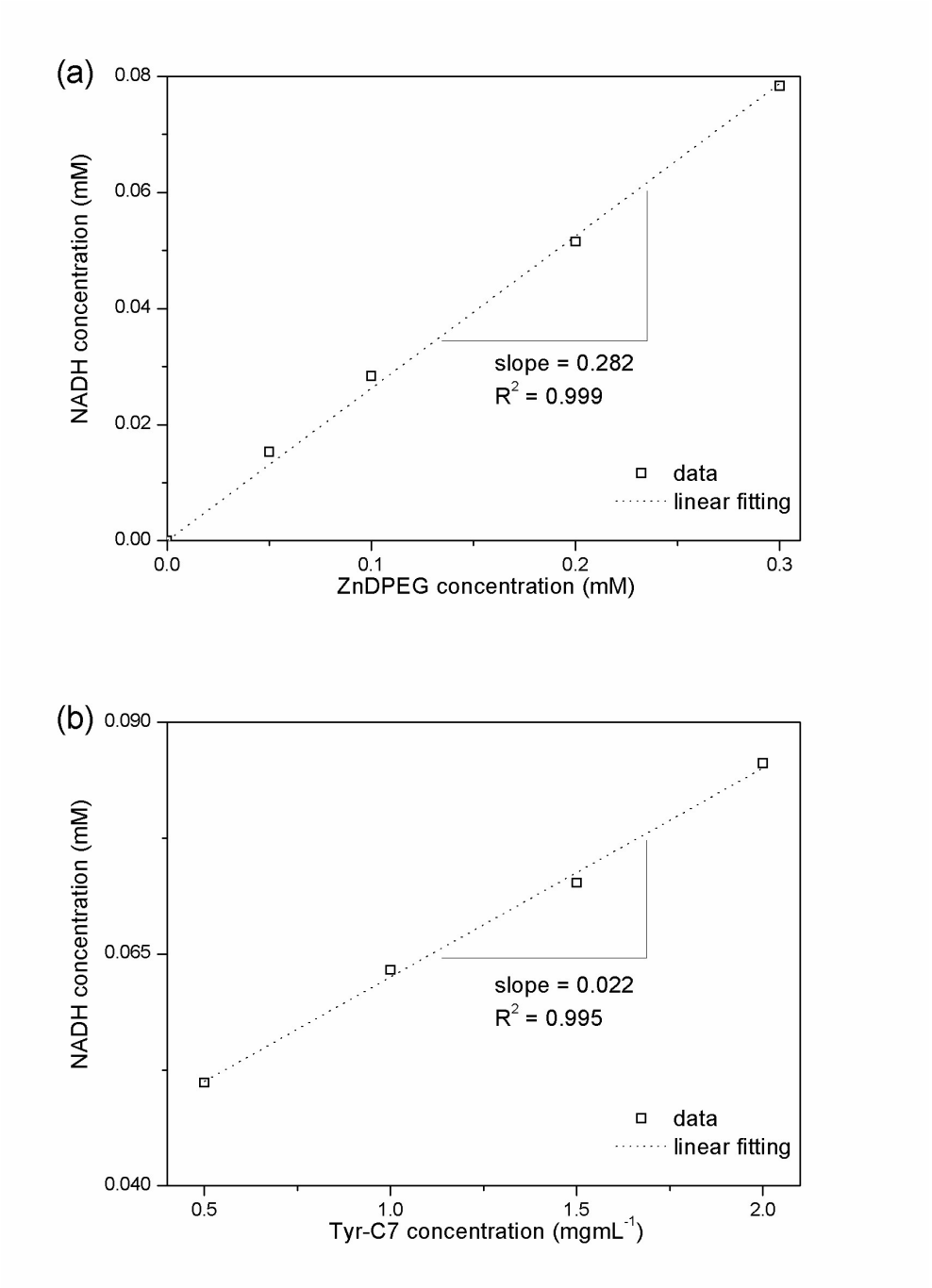


Figure S5. Linear dependency of NADH concentration to (a) ZnDPEG (at t = 15 min) and (b) Tyr-C7 concentration (at t = 60min).

S6. pH variation after irradiation of light

With the progress of the NAD+ conversion into NADH, pH of the light-harvesting system decreased because NAD+ reduction is carried out according to the following process:

$$NAD^+ + 2e^- + 2H^+ \rightarrow NADH + H^+$$

Above chemical reaction tells that single proton is generated during the NAD+ reduction process, such that solution pH decays. pH variation of each sample is summarized below.

Table S1. pH values of sample systems before and after the light-harvesting reaction

	Sample	Z	ZR	ZT	ZTR
pH	Before reaction	7.0	6.9	6.9	6.9
	After reaction	6.9	6.7	6.6	6.4
	Δ pH	0.1	0.2	0.3	0.5

S7. Effect of the Tyr-C7 concentration on the photosynthesis

The photosynthesis efficiency increased with rise of Tyr-C7 concentration under 2 mg/ml. However, over this concentration, little light-harvesting efficiency increment was observed.

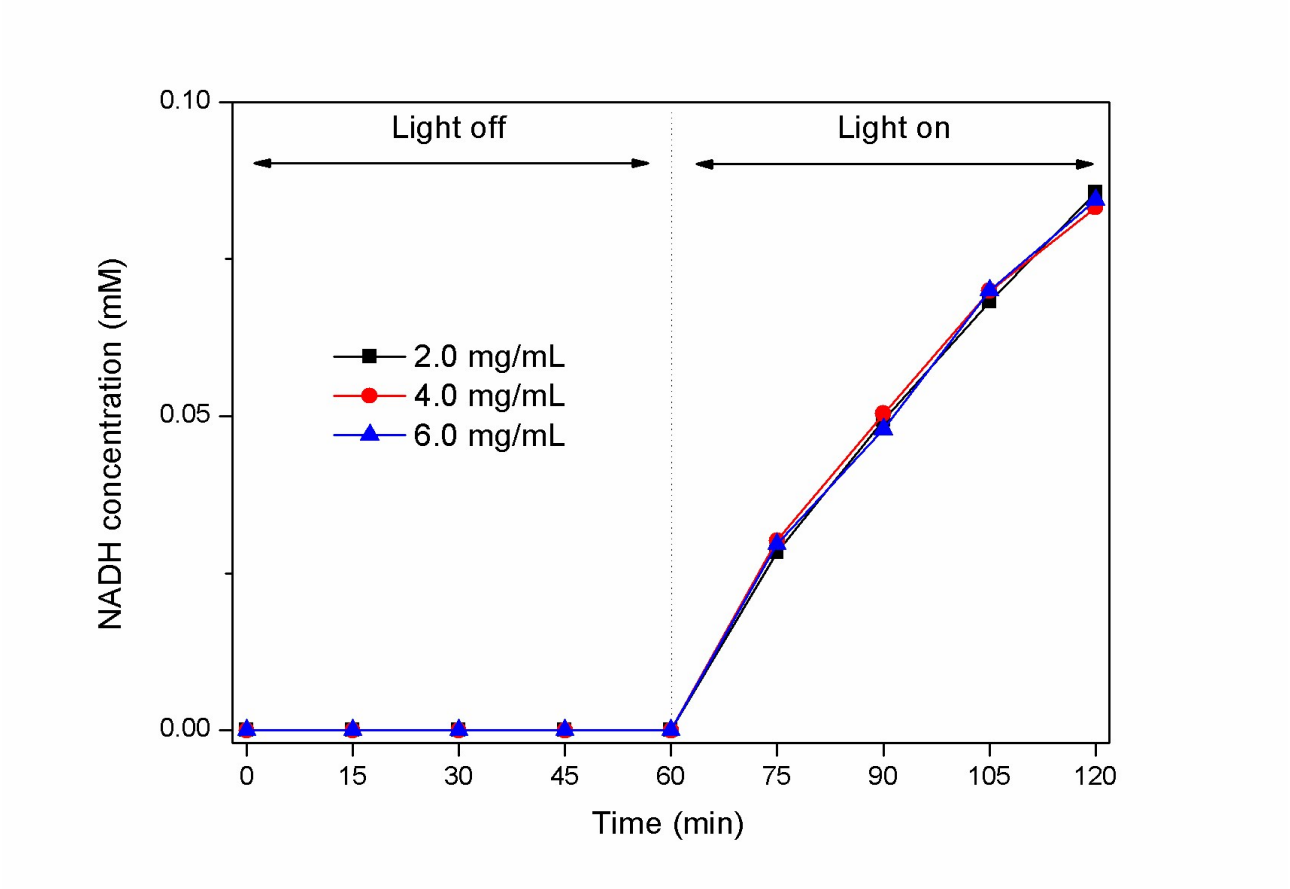


Figure S6. NADH concentration profile with increasing Tyr-C7 concentration over 2 mg/ml. Little change was observed over 2 mg/ml concentration of Tyr-C7.

S8. Cyclovoltametry of the photochemical compounds

Cyclovoltametry (CV) curves of the photochemical compounds were scanned in order to determine the reduction potential.

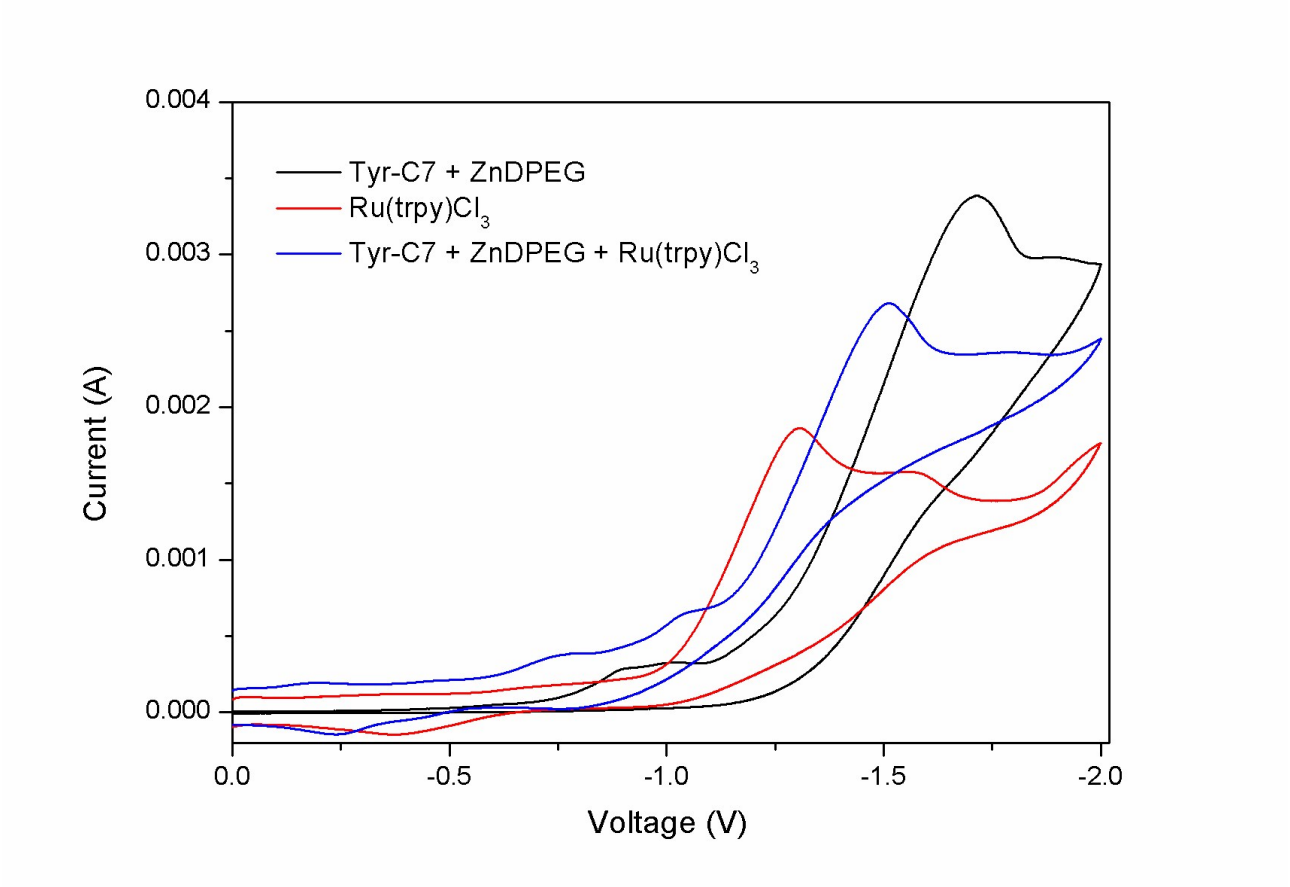


Figure S7. CV curves of the photochemical compounds used in creating the photosynthesis system.