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| Note | |

Supporting Information for

# Controlled Photoinduced Electron Transfer via Triplet in Polymer Matrix Using Electrostatic Interactions

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## 1. Experimental Section

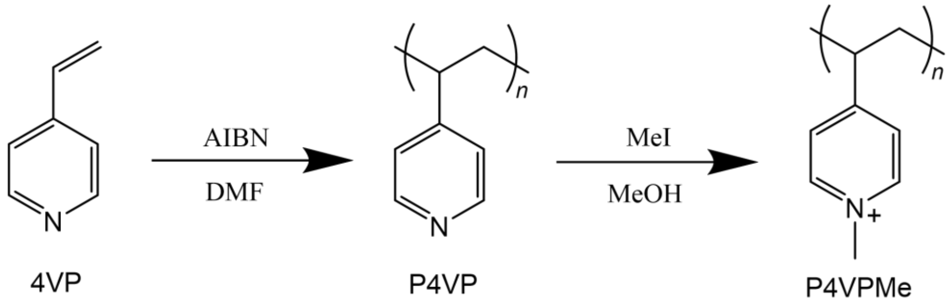
### Materials

5,10,15,20-Tetrakis-(4-sulfonatophenyl) porphyrin (TPPS) was purchased from TCI Co., Ltd., Tokyo, Japan. Methyl viologen hydrate, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid tetrasodium salt (EDTA), 4-vinyl pyridine and 2,2' azobis(2 methylpropionitrile) were purchased from Nacalai Tesque, Kyoto, Japan. All the reagents and solvents, except 4-vinyl pyridine, were used as received without further purification. 4-vinyl pyridine was distilled to remove the polymerization inhibitor (hydroquinone) within it before polymerization. Zinc *meso*-5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin (ZnTPPS) was prepared according to the method reported by Flamigni et al [1]. Poly 4-vinyl pyridine was synthesized by polymerization of 4-vinyl pyridine in DMF using 2,2' azobis(2 methylpropionitrile) as thermal initiator. P4VPMe was synthesized by methylating poly 4-vinyl pyridine in methanol using iodomethane.

### Methods

$^1$H NMR spectra were acquired with a JEOL JNM-ECA 500 MHz NMR spectrometer (Tokyo, Japan). The chemical shifts were referenced to the solvent value ($\delta = 4.79$ ppm for $D_2O$). UV-visible spectra were recorded using a SHIMADZU UV-2500PC spectrophotometer (Kyoto, Japan) at a temperature of 25 °C. A quartz cuvette with an optical path length of 1 cm was used for these measurements. Excitation and fluorescence spectra were obtained with a HITACHI F-2500 fluorescence spectrophotometer (Tokyo, Japan) at 25 °C, employing 1-cm quartz cuvettes. Irradiation experiments were conducted in a sealed 1-cm quartz cuvette using an USHIO SP-11 UV irradiation unit with a HOYA ND10 filter. Emission lifetimes were measured with a home-built setup based on time-correlated single-photon counting. The details were described in a previous report [2]. The pulsed light source was a Ti:sapphire oscillator, and the second harmonics at 420 nm was used for photoexcitation of the sample. The instrumental response function was evaluated as 48 ps. Transient absorption spectra in the nanosecond and microsecond time regions were measured using a home-built setup [3]. The excitation light source was a Nd:YAG laser and the second harmonics at 532 nm was used for photoexcitation of the sample. The time resolution of the measurement was ca. 50 ns. In the transient absorption measurements, the sample solution was filled into a 1 cm cuvette and treated with nitrogen bubbling in 10 minutes unless specifically mentioned.

## 2. Synthesis of P4VP and P4VPMe



**Scheme S1.** Synthesis of P4VPMe.

Poly(4-vinylpyridine) (P4VP) was synthesized by polymerizing 4-vinylpyridine in DMF using 2,2'-azobis(2-methylpropionitrile) as a thermal initiator (Scheme S1). Initially, 1.0 g (10.0 mmol) of distilled 4-vinylpyridine was dissolved in 10 mL of DMF. Varying amounts (0.1 mmol and 0.2 mmol) of AIBN were subsequently added, and the mixture was refluxed at 60°C for 24 hours. Following this, the solution was poured into 100 mL of diethyl ether, and the resulting particulate (P4VP) was collected after being washed three times with diethyl ether. GPC measurements (Fig. S1) revealed molecular weights of 3,700 and 6,400, respectively.

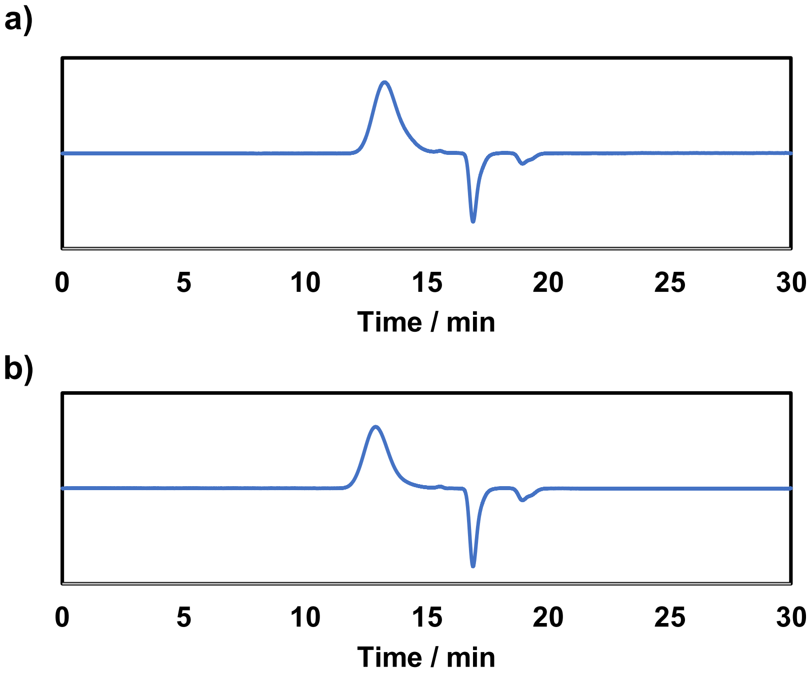


**Fig. S1.** GPC profiles of P4VP with molecular weights of 3,700 and 6,400.

P4VPMe was synthesized by methylating poly(4-vinylpyridine) in methanol using iodomethane

(Scheme S1). Initially, 0.1 g (1.0 mmol) of P4VP was dissolved in 5.0 mL of methanol. Then, 0.6 mL (10.0 mmol) of iodomethane was added, and the mixture was stirred at room temperature for 40 hours. Subsequently, the resulting particulate (P4VPMe) was collected by centrifugation and washed three times with methanol. Confirmation of full methylation was achieved via $^1$H NMR analysis (Fig. S2). The molecular weights of P4VPMe were calculated to be 4,300 and 7,400.

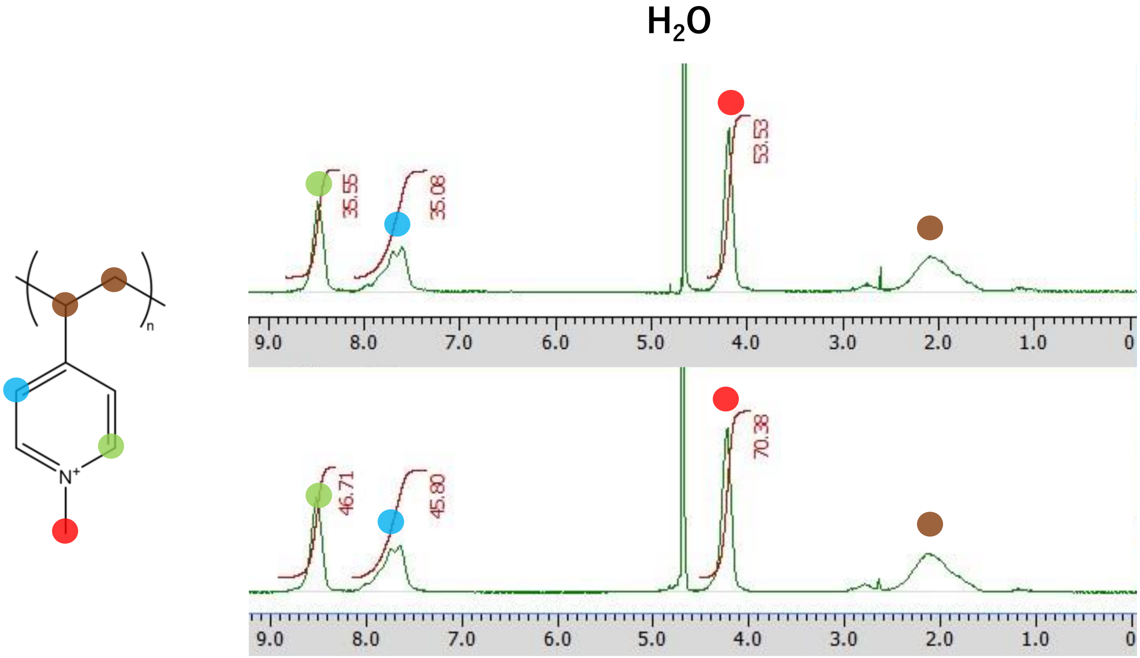


**Fig. S2.** $^1$H NMR spectra of P4VPMe with molecular weights of 4,300 and 7,400 (in $D_2O$).

## 3. Absorption and excitation spectra of mixing solutions of porphyrins and P4VPMe

Absorption and excitation spectra were acquired for mixed solutions of ZnTPPS or TPPS (0.6 µM) and P4VPMe (Mn = 4,300 and 7,400) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) (Figs. S3, S4 and S5). Similar spectral changes were observed when using P4VPMe with molecular weights of 4,300 and 7,400, indicating no discernible dependency on molecular weight.

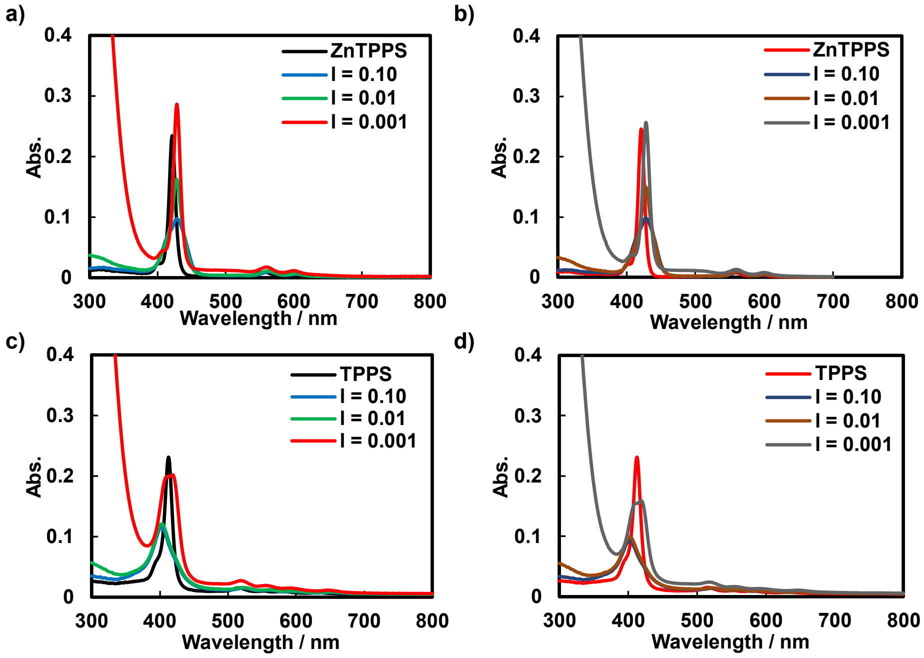


**Fig. S3.** Absorption spectra of 0.6 µM ZnTPPS upon the addition of P4VPMe with Mn = a) 4,300 and b) 7,400 at various charge ratios. Absorption spectra of 0.6 µM TPPS upon the addition of P4VPMe with Mn = c) 4,300 and d) 7,400 at various charge ratios.

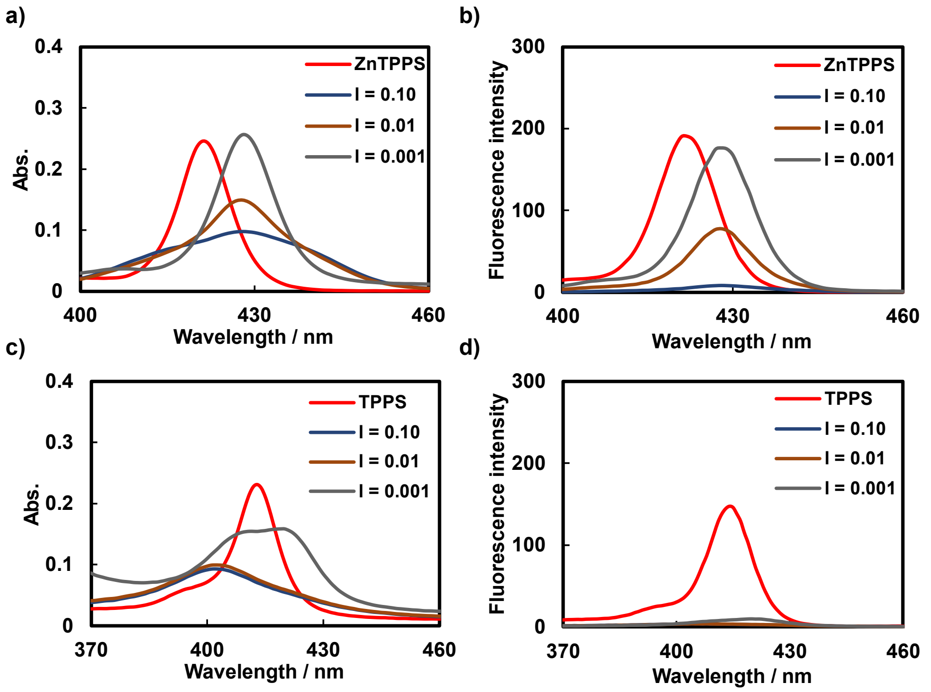


**Fig. S4.** Absorption spectra of 0.6 μM a) ZnTPPS and b) TPPS upon the addition of P4VPMe (Mn = 7,400) at various charge ratios. Excitation spectra of 0.6 μM c) ZnTPPS ($\lambda_{em}$ = 605 nm) and d) TPPS ($\lambda_{em}$ = 640 nm) upon the addition of P4VPMe (Mn = 7,400) at various charge ratios.

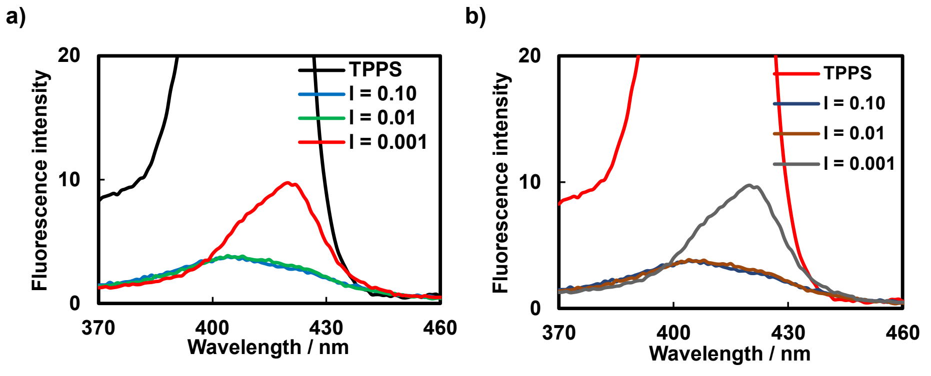


**Fig. S5.** Enlarged excitation spectra of 0.6 μM TPPS ($\lambda_{em}$ = 640 nm) upon the addition of P4VPMe Mn = a) 4,300 and b) 7,400 at various charge ratios.

## 4. Absorption and fluorescence spectra of ZnTPPS or TPPS upon the addition of $MV^{2+}$ in the presence of P4VPMe

Absorption and fluorescence spectra of ZnTPPS (0.6 μM) upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were observed (Fig. S6).

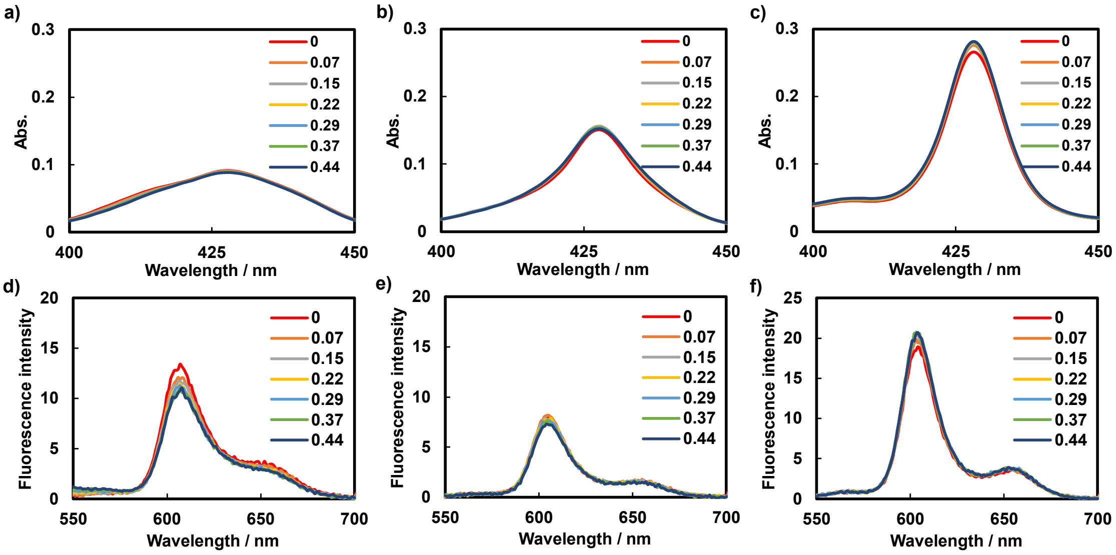


**Fig. S6.** Absorption spectra of 0.6 μM ZnTPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 4,300) at various charge ratios: a) I = 0.10, b) I = 0.01, and c) I = 0.001. Fluorescence spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 4,300) at various charge ratios: d) I = 0.10, e) I = 0.01, and f) I = 0.001. Concentrations of added $MV^{2+}$ are indicated in the figures.

Absorption and fluorescence spectra of ZnTPPS (0.6 μM) upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were observed (Fig. S7).

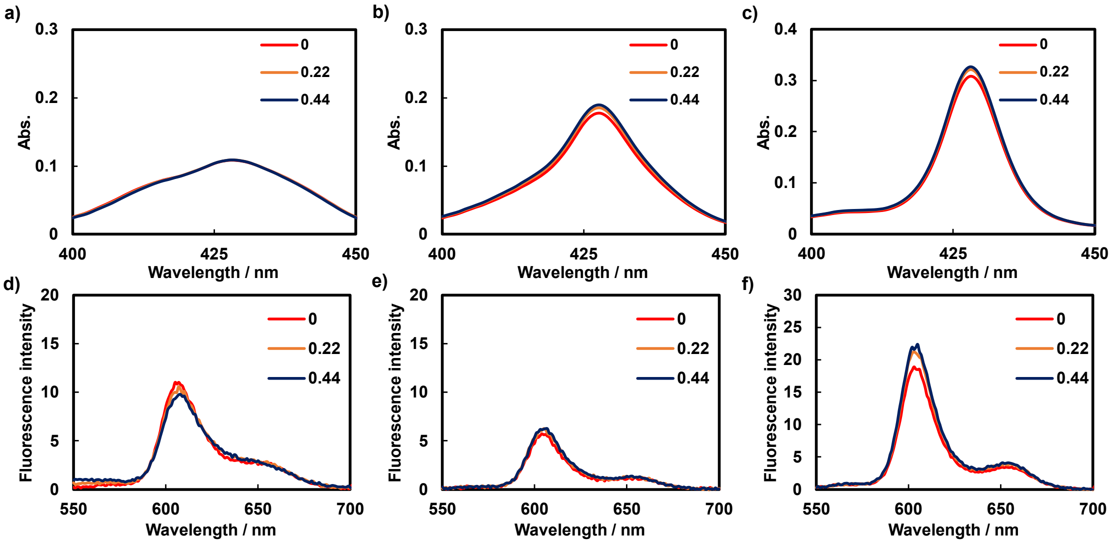


**Fig. S7.** Absorption spectra of 0.6 μM ZnTPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at various charge ratios: a) I = 0.10, b) I = 0.01, and c) I = 0.001. Fluorescence spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at various charge ratios: d) I = 0.10, e) I = 0.01, and f) I = 0.001. Concentrations of added $MV^{2+}$ are indicated in the figures.

Absorption and fluorescence spectra of TPPS (0.6 μM) upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were observed (Fig. S8).

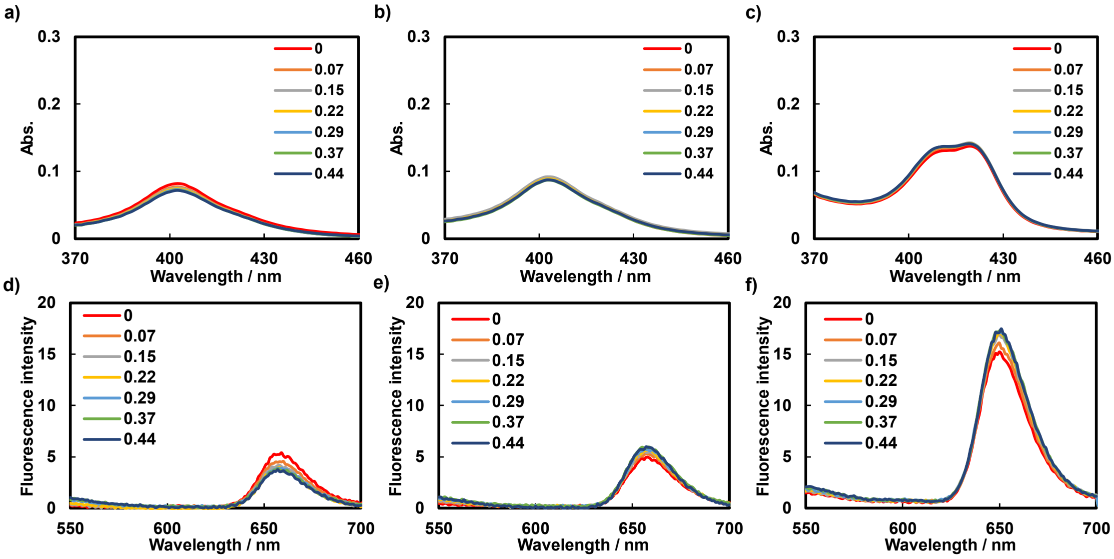


**Fig. S8.** Absorption spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of

P4VPMe (Mn = 4,300) at various charge ratios: a) I = 0.10, b) I = 0.01, and c) I = 0.001. Fluorescence spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 4,300) at various charge ratios: d) I = 0.10, e) I = 0.01, and f) I = 0.001. Concentrations of added $MV^{2+}$ are indicated in the figures.

Absorption and fluorescence spectra of TPPS (0.6 μM) upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were observed (Fig. S9).

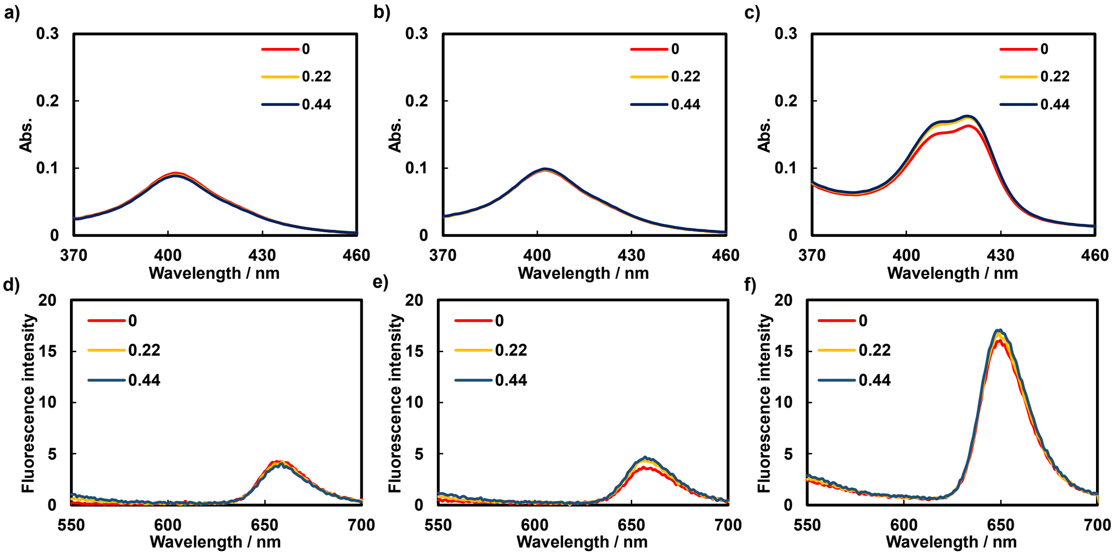


**Fig. S9.** Absorption spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at various charge ratios: a) I = 0.10, b) I = 0.01, and c) I = 0.001. Fluorescence spectra of 0.6 μM TPPS upon incremental addition of $MV^{2+}$ in the presence of P4VPMe (Mn = 7,400) at various charge ratios: d) I = 0.10, e) I = 0.01, and f) I = 0.001. Concentrations of added $MV^{2+}$ are indicated in the figures.

Based on the fluorescence intensities depicted in Fig. S4-S7 and Fig. 5, Stern-Volmer plots were generated to illustrate the quenching of ZnTPPS or TPPS by $MV^{2+}$ (Fig. S10). Notably, the quenching behavior of ZnTPPS or TPPS in the presence of P4VPMe with various molecular weights remained relatively consistent, suggesting an absence of molecular weight dependency.

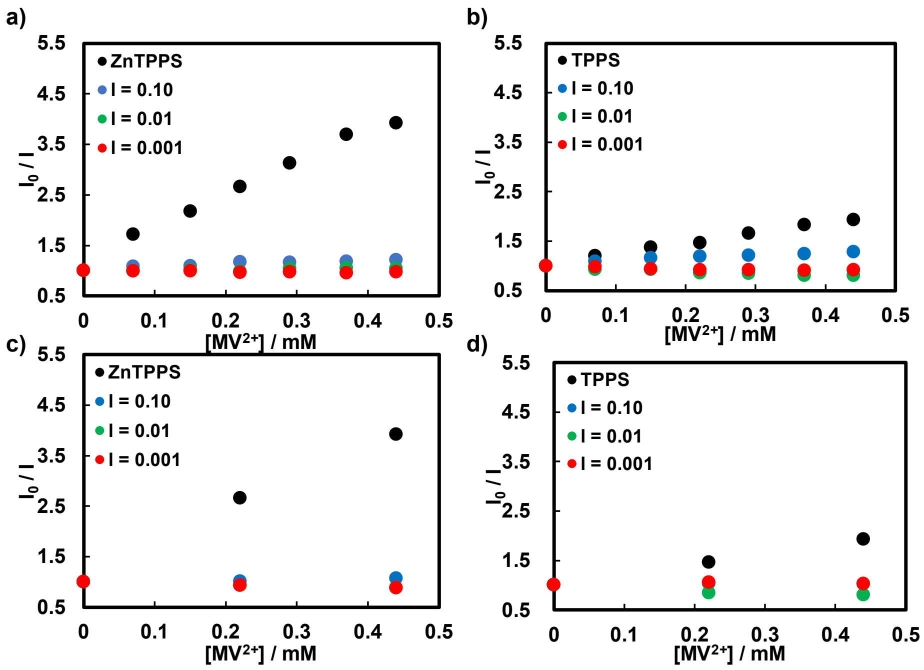


**Fig. S10.** Stern-Volmer plots for the quenching of a) ZnTPPS and b) TPPS in the absence and presence of P4VPMe (Mn = 4,300). Stern-Volmer plots for the quenching of c) ZnTPPS and d) TPPS in the absence and presence of P4VPMe (Mn = 7,400).

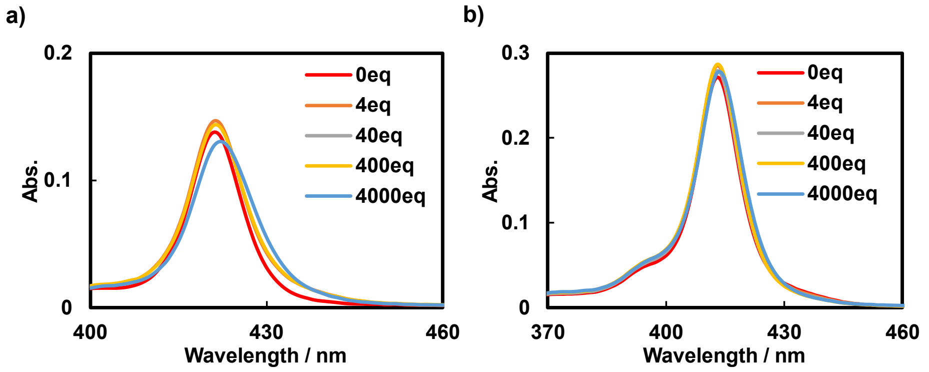


**Fig. S11.** Absorption spectra of a) ZnTPPS and b) TPPS upon the addition of DMP. The amounts of added DMP are indicated in the figures.

Absorption spectra were obtained for mixed solutions of ZnTPPS or TPPS (0.6 μM) and 1,4-dimethylpyridinium (DMP) at different mixing ratios in 0.01 M phosphate buffer (pH 8.0) (Fig. S11). Notably, no systematic spectral changes were observed, indicating that the interaction between DMP and ZnTPPS or TPPS is weak and lacks influence on their aggregate states, a contrast to the impact P4VPMe exerts.

## 5. Excited singlet-state lifetime measurement of ZnTPPS and TPPS in the absence and presence of P4VPMe.

Excited singlet-state lifetime measurements of ZnTPPS (0.6 μM) in the absence and presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were carried out (Fig. S12).

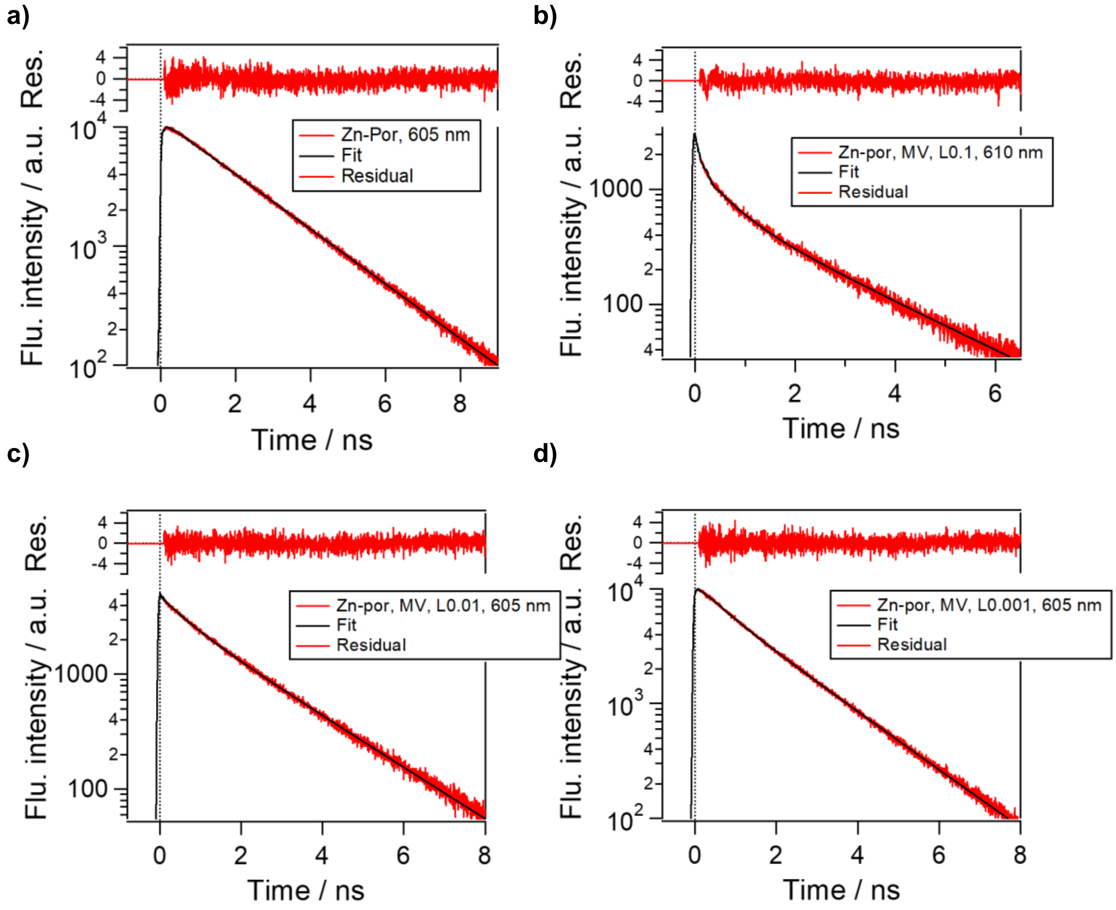


**Fig. S12.** Fluorescence decay profiles of ZnTPPS in the a) absence of P4VPMe and presence of P4VPMe (Mn = 4,300) at various charge ratios: b) I = 0.10, c) I = 0.01 and d) I = 0.001.

Excited singlet-state lifetime measurements of TPPS (0.6 μM) in the absence and presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were carried out (Fig. S13).

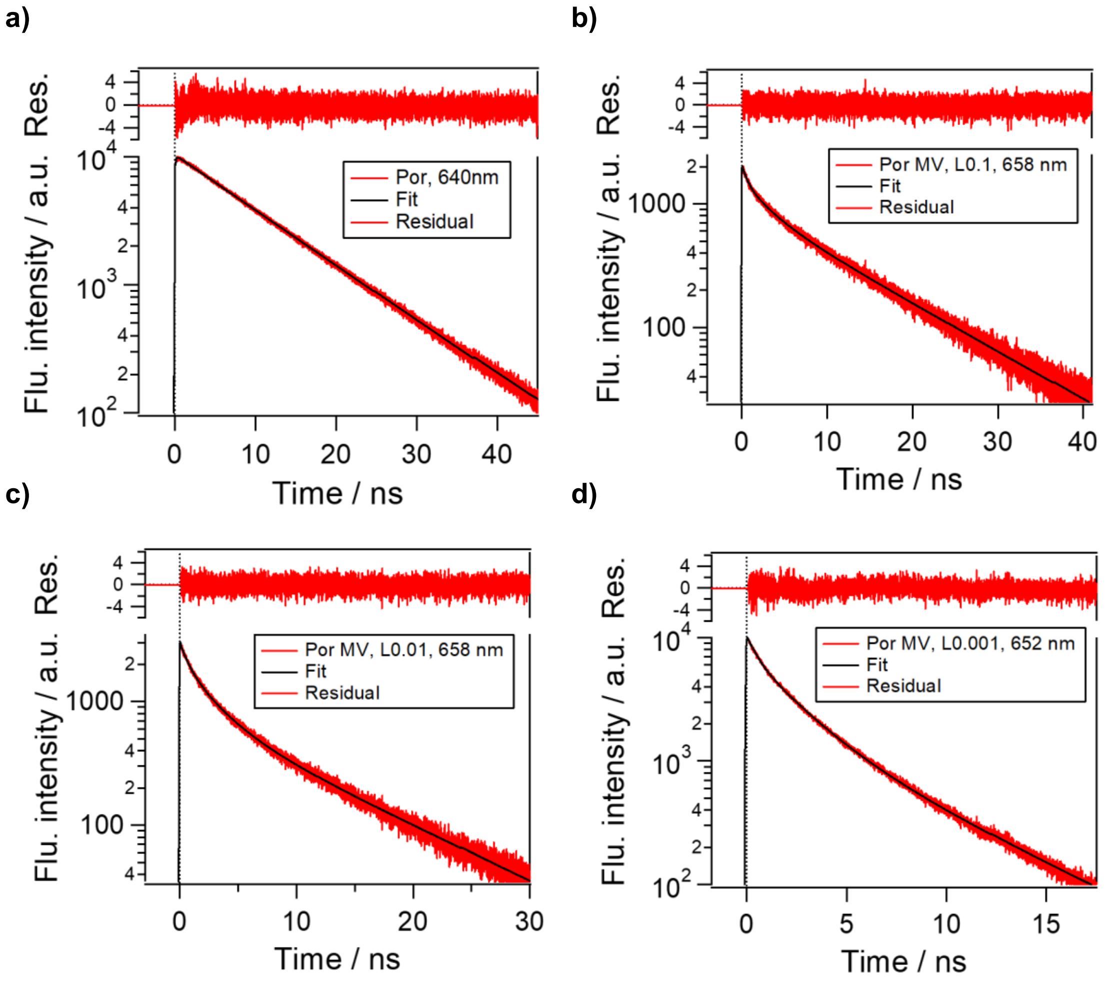


**Fig. S13.** Fluorescence decay profiles of TPPS (0.6 μM) in the a) absence of P4VPMe and presence of P4VPMe (Mn = 4,300) at various charge ratios: b) I = 0.10, c) I = 0.01 and d) I = 0.001.

Excited singlet-state lifetime measurements of ZnTPPS (0.6 μM) in the presence of $MV^{2+}$ (0.1 mM) and in the absence and presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were carried out (Fig. S14).

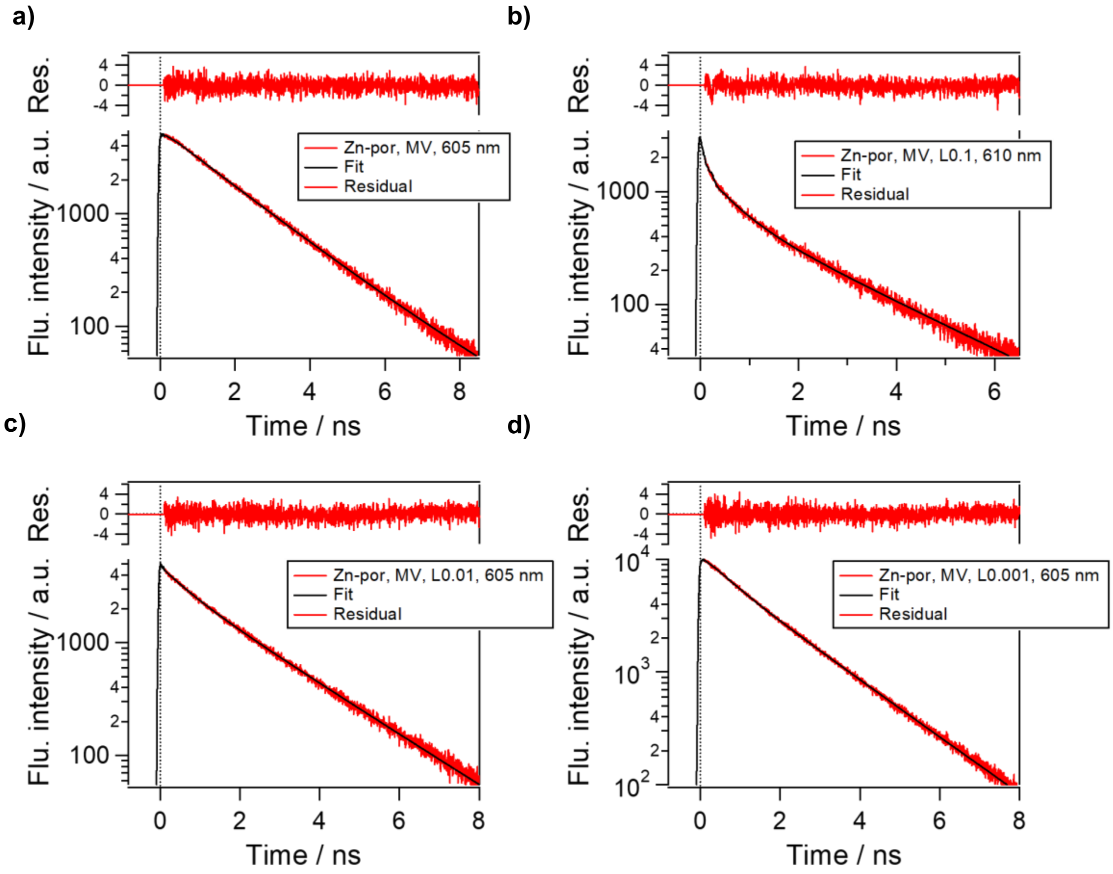


**Fig. S14.** Fluorescence decay profiles of ZnTPPS (0.6 μM) in the presence of $MV^{2+}$ (0.1 mM) and in the a) absence of P4VPMe and presence of P4VPMe (Mn = 4,300) at various charge ratios: b) I = 0.10, c) I = 0.01 and d) I = 0.001.

Excited singlet-state lifetime measurements of TPPS (0.6 μM) in the presence of $MV^{2+}$ (0.1 mM) and in the absence and presence of P4VPMe (Mn = 4,300) at varying charge ratios (0.10, 0.01 and 0.001) in 0.01 M phosphate buffer (pH 8.0) were carried out (Fig. S15).

Decay in Figs. S12 and S13 are fitted and the lifetimes are summarized in Table S1.

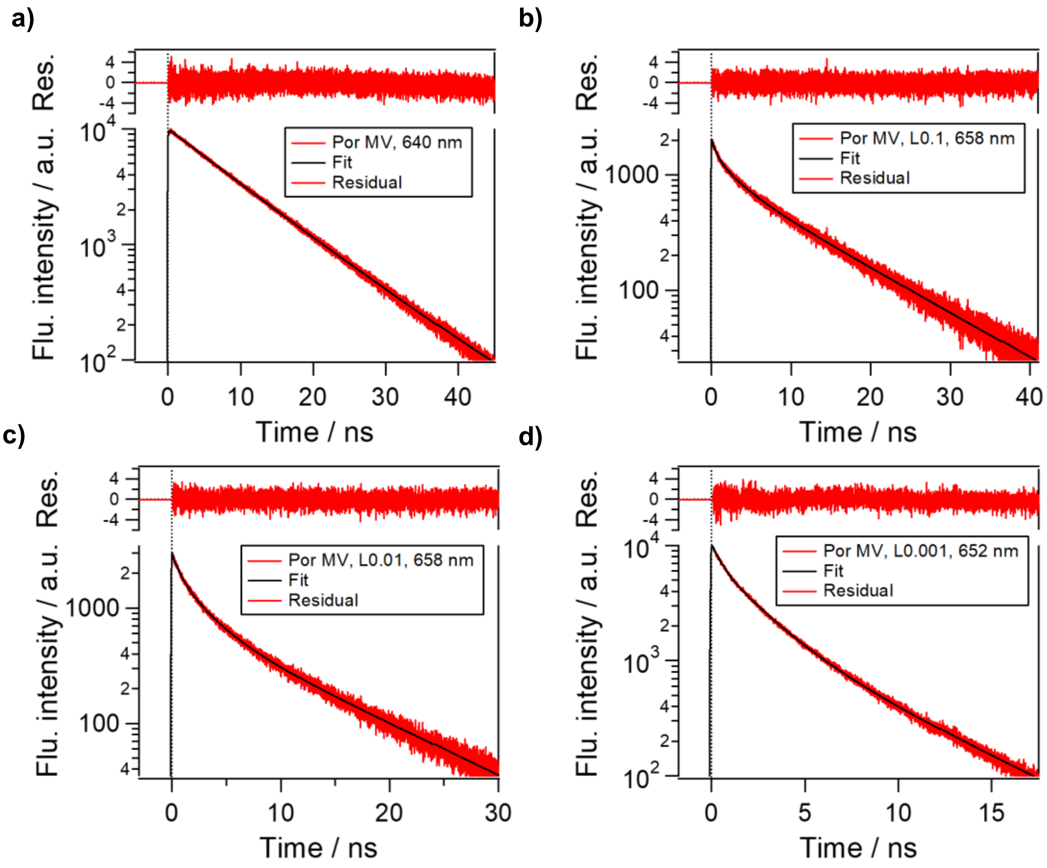


**Fig. S15.** Fluorescence decay profiles of TPPS (0.6 μM) in the presence of $MV^{2+}$ (0.1 mM) and in the a) absence of P4VPMe and presence of P4VPMe (Mn = 4,300) at various charge ratios: b) I = 0.10, c) I = 0.01 and d) I = 0.001.

**Table S1.** Excited singlet-state lifetimes,$\tau_i$ (i = 1–4), of ZnTPPS and TPPS in the presence of $MV^{2+}$ (0.1 mM) and in the absence and presence of P4VPMe. $A_i$ (i = 1–4) are corresponding pre-exponential factors in % and $\tau_{avg}$ is averaged lifetime.

| Sample | $\tau_1$ / ns | $\tau_2$ / ns | $\tau_3$ / ns | $\tau_4$ / ns | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\tau_{avg}$ / ns |
|---|---|---|---|---|---|---|---|---|---|
| ZnTPPS | 1.61 | 2.78 | | | 91 | 9 | | | 1.72 |
| I = 0.10 | 0.055 | 0.569 | 2.06 | | 73 | 14 | 13 | | 0.387 |
| I = 0.01 | 0.666 | 1.92 | | | 41 | 59 | | | 1.41 |
| I = 0.001 | 0.642 | 1.71 | | | 24 | 76 | | | 1.45 |
| TPPS | 8.23 | 11.2 | | | 68 | 32 | | | 9.18 |
| I = 0.10 | 0.650 | 2.87 | 11.0 | | 41 | 24 | 35 | | 4.81 |
| I = 0.01 | 0.726 | 2.53 | 9.49 | | 45 | 36 | 19 | | 3.04 |
| I = 0.001 | 0.390 | 2.03 | 5.50 | | 35 | 46 | 19 | | 2.12 |

## 6. $MV^{+•}$ generation experiments

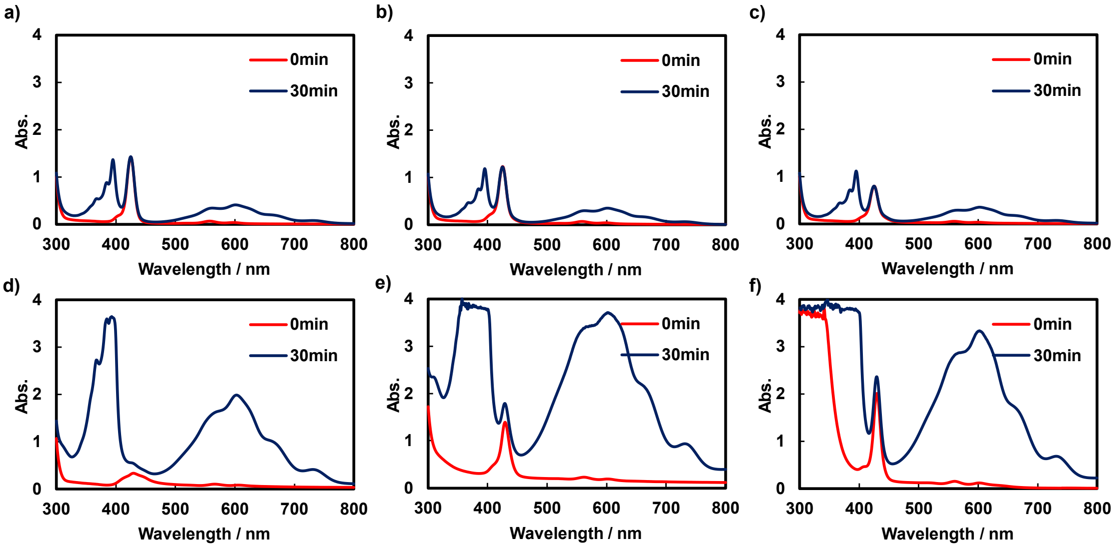


**Fig. S16.** Absorption spectra of mixing solutions of 6.0 µM ZnTPPS, 1.0 mM $MV^{2+}$, 0.1 mM EDTA-4Na before and after 30 min irradiation in the a) absence of P4VPMe and b)-f) presence of P4VPMe (Mn = 4,300) at various charge ratios: b) I = 4.00, c) I = 2.00, d) I = 0.10, e) I = 0.01 and f) I = 0.001.

Mixed solutions 3-mL containing ZnTPPS (6.0 µM), P4VPMe (Mn = 4,300, I = 4.00, 2.00, 0.10, 0.01, 0.001), $MV^{2+}$ (1.0 mM) and EDTA-4Na (10.0 mM) were degassed by 15 min $N_2$ bubbling in 3-mL cuvettes. After that the solutions were irradiated by UV light at ca.20 cm distant from the light source for 30 min. Absorption spectra of these solution before and after irradiation were recorded (Fig. S16).

Mixed solutions 3-mL containing ZnTPPS (6.0 µM), P4VPMe (Mn = 7,400, I = 4.00, 2.00, 0.10, 0.01, 0.001), $MV^{2+}$ (1.0 mM) and EDTA-4Na (10.0 mM) were degassed by 15 min $N_2$ bubbling in 3-mL cuvettes. After that the solutions were irradiated by UV light at ca.20 cm distant from the light source for 30 min. Absorption spectra of these solution before and after irradiation were recorded (Fig. S17).

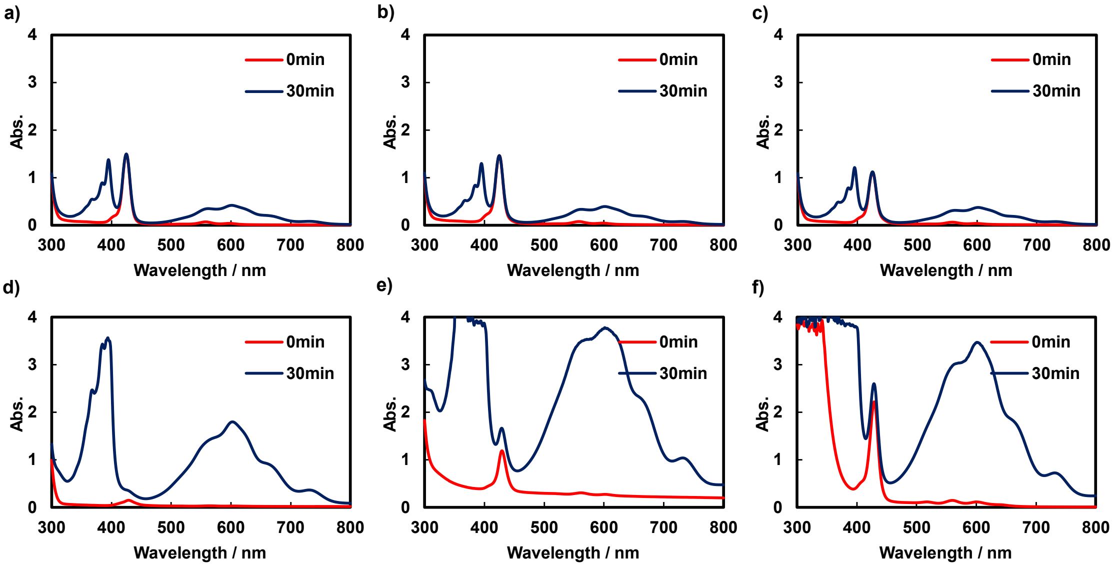


**Fig. S17.** Absorption spectra of mixing solutions of 6.0 μM ZnTPPS, 1.0 mM MV$^{2+}$, 0.1 mM EDTA-4Na before and after 30 min irradiation in the a) absence of P4VPMe and b)-f) presence of P4VPMe (Mn = 7,400) at various charge ratios: b) I = 4.00, c) I = 2.00, d) I = 0.10, e) I = 0.01 and f) I = 0.001.

Mixed solutions 3-mL containing TPPS (6.0 μM), P4VPMe (Mn = 4,300, I = 4.00, 2.00, 0.10, 0.01, 0.001), MV$^{2+}$ (1.0 mM) and EDTA-4Na (10.0 mM) were degassed by 15 min N$_2$ bubbling in 3-mL cuvettes. After that the solutions were irradiated by UV light at ca.20 cm distant from the light source for 30 min. Absorption spectra of these solution before and after irradiation were recorded (Fig. S18).

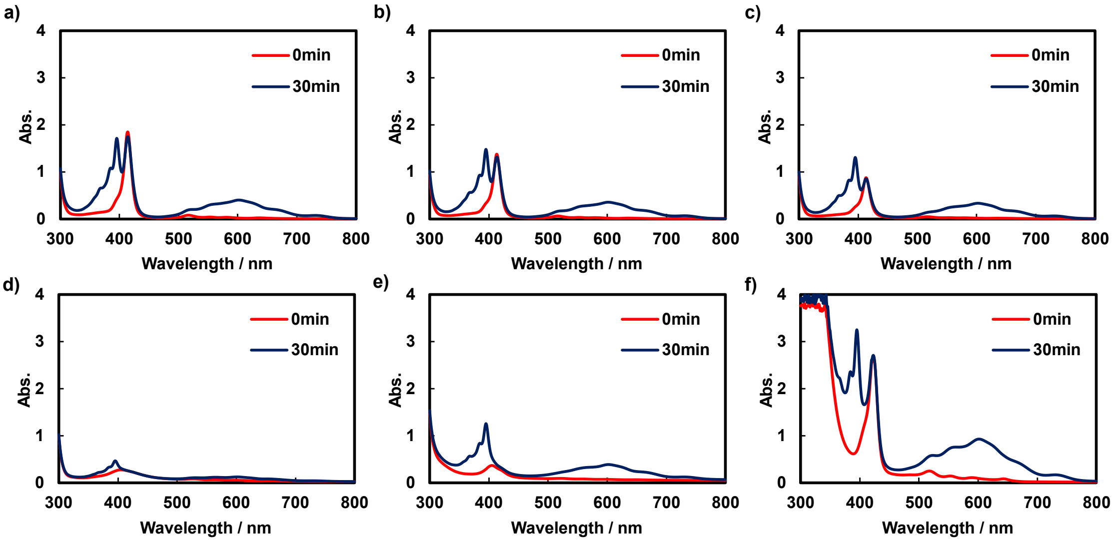


**Fig. S18.** Absorption spectra of mixing solutions of 6.0 μM TPPS, 1.0 mM MV$^{2+}$, 0.1 mM EDTA-4Na before and after 30 min irradiation in the a) absence of P4VPMe and b)-f) presence of P4VPMe

(Mn = 4,300) at various charge ratios: b) I = 4.00, c) I = 2.00, d) I = 0.10, e) I = 0.01 and f) I = 0.001.

Mixed solutions 3-mL containing TPPS (6.0 μM), P4VPMe (Mn = 7,400, I = 4.00, 2.00, 0.10, 0.01, 0.001), $MV^{2+}$ (1.0 mM) and EDTA-4Na (10.0 mM) were degassed by 15 min $N_2$ bubbling in 3-mL cuvettes. After that the solutions were irradiated by UV light at ca.20 cm distant from the light source for 30 min. Absorption spectra of these solution before and after irradiation were recorded (Fig. S19).

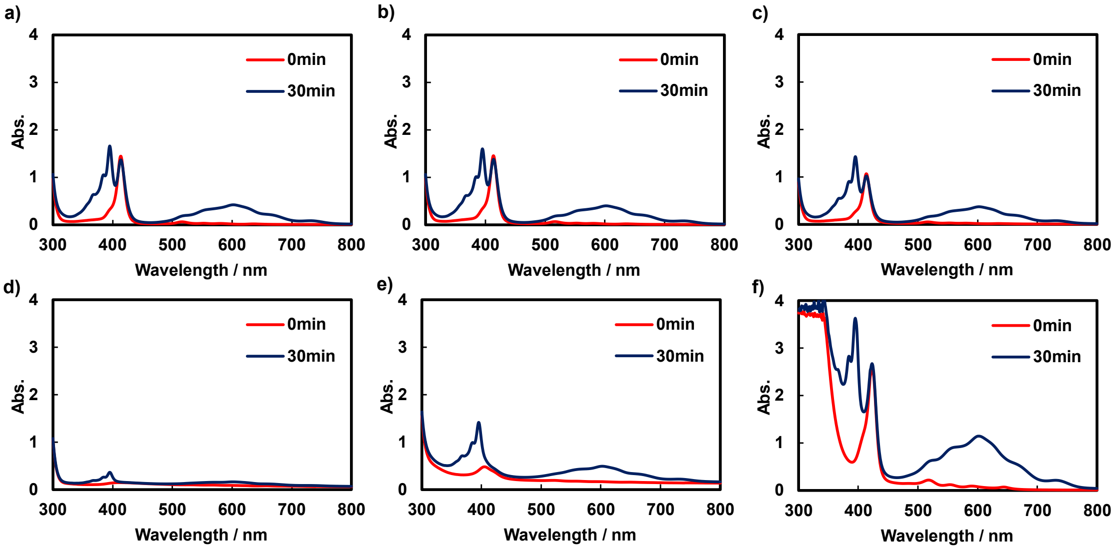


**Fig. S19.** Absorption spectra of mixing solutions of 6.0 μM TPPS, 1.0 mM $MV^{2+}$, 0.1 mM EDTA-4Na before and after 30 min irradiation in the a) absence of P4VPMe and b)-f) presence of P4VPMe (Mn = 7,400) at various charge ratios: b) I = 4.00, c) I = 2.00, d) I = 0.10, e) I = 0.01 and f) I = 0.001.

Mixed 3-mL solutions containing TPPS (6.0 μM), DMP (24.0 mM), $MV^{2+}$ (1.0 mM) and EDTA-4Na (10.0 mM) were degassed by 15 min $N_2$ bubbling in 3mL cuvettes. After that the solutions were irradiated by UV light ca.20 cm distant from the light source for 30 min. Absorption spectra of these solution before and after irradiation were recorded (Fig. S20).

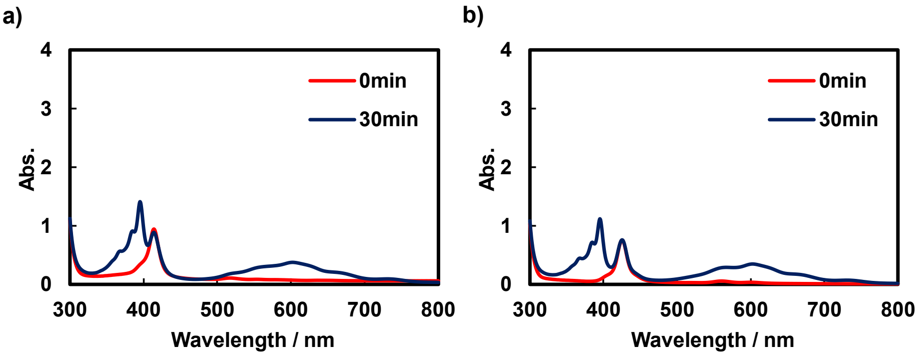


**Fig. S20.** Absorption spectra of a) mixing solutions of 6.0 µM ZnTPPS, 1.0 mM $MV^{2+}$, 0.1 mM EDTA-4Na and DMP, and b) mixing solutions of 6.0 µM TPPS, 1.0 mM $MV^{2+}$, 0.1 mM EDTA-4Na and DMP before and after 30 min irradiation.

Absorbance changes at 605 nm in Fig. S16-20were used to calculate the generated concentrations of $MV^{+•}$, and the results were summarized in Fig. S21.

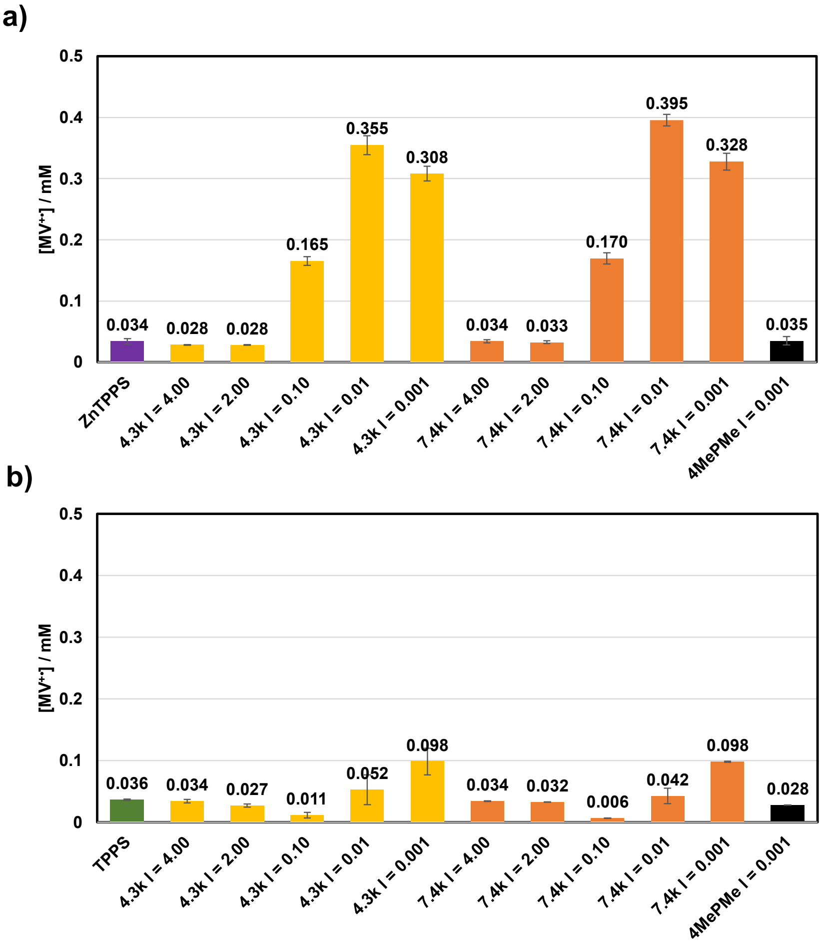


**Fig. S21.** Concentration of generated $MV^{+•}$ after 30 min irradiation in a) ZnTPPS systems and b)

TPPS systems.

## 7. Transient absorption spectra measurement for mixing solution of ZnTPPS, $MV^{2+}$, and PAA or P4VPMe

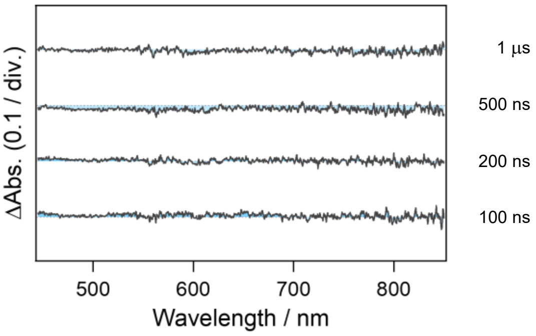


**Fig. S22.** Transient absorption spectra of mixing solution of ZnTPPS, $MV^{2+}$, and PAA in the nanosecond and microsecond time regions.

Transient absorption spectra were obtained for a mixing solution of ZnTPPS (0.12 mM), $MV^{2+}$ (0.02 M), and polyacrylic acid (PAA, 48.0 mM, I = 0.01) (Fig. S22). However, no transient absorption was detected, indicating that PAA lacks the capacity to impede the formation of charge-transfer complexes between ZnTPPS and $MV^{2+}$, a phenomenon effectively demonstrated by P4VPMe.

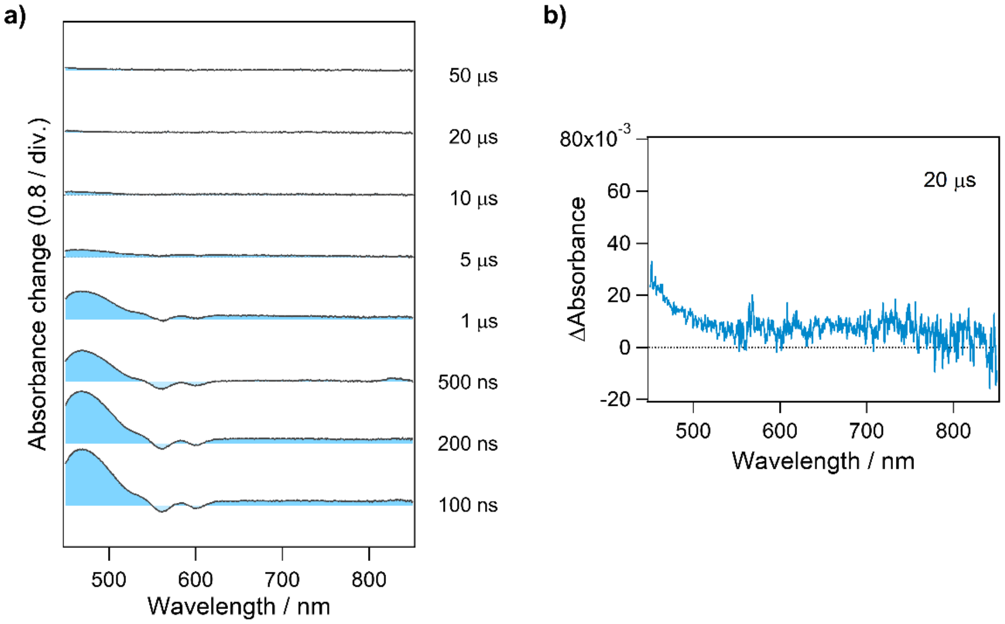


Fig. S23a) Transient absorption spectra of mixing solution of ZnTPP, $MV^{2+}$, and P4VPMe in the nanosecond and microsecond time regions. b) Enlarged spectrum recorded at 20 μs. The sample solution was air-saturated.

Transient absorption spectra were obtained for a mixing solution of ZnTPPS (0.12 mM), $MV^{2+}$ (0.02 M), and P4VPMe (I = 0.01) under air-saturated condition (Fig. S23).

We evaluated the quantum yield of electron transfer from ZnTPPS in the $T_1$ state to $MV^{2+}$ in the presence of P4VPMe in following two manners. In the first method, the quantum yield was estimated from difference in the lifetime of ZnTPPS in the $T_1$ state, that is, quenching experiments. Figure Sxxx1 shows time profiles of transient absorbance of ZnTPPS monitored at 470 nm in the presence and absence of $MV^{2+}$ and the decay curves can be fitted with an exponential function with time constants of 2.2 and 87 μs, respectively. These values correspond to the lifetime of the $T_1$ state, $\tau_{\mathrm{with\ MV^{2+}}}$ and $\tau_{\mathrm{w/o\ MV^{2+}}}$, which can be described by eqs. (1) and (2).

$$\tau_{\mathrm{with\ MV^{2+}}} = \frac{1}{k_{\mathrm{r}}+k_{\mathrm{nr}}+k_{\mathrm{ET}}} \qquad (1)$$

$$\tau_{\mathrm{w/o\ MV^{2+}}} = \frac{1}{k_{\mathrm{r}}+k_{\mathrm{nr}}} \qquad (2)$$

where $k_{\mathrm{r}}$, $k_{\mathrm{nr}}$ and $k_{\mathrm{ET}}$ are respectively rate constants of the radiative process, nonradiative process and electron transfer to $MV^{2+}$. Thus, the quantum yield of electron transfer, $\Phi_{\mathrm{ET}}$ can be defined by the eq. (3).

$$\Phi_{\mathrm{ET}} = \frac{k_{\mathrm{ET}}}{k_{\mathrm{r}}+k_{\mathrm{nr}}+k_{\mathrm{ET}}} \quad (3)$$

From the above equations, the rate constant and quantum yield of electron transfer were calculated to be $4.4\times10^{5}$ $s^{-1}$ and 0.97. Although $\Phi_{\mathrm{ET}}$ of almost 1 indicates that the electron transfer reaction proceeds in a quantitative manner, transient absorption spectra at a few tens of microseconds show the absorption band due to $MV^{+}$ with a rather small amplitude. To verify the above value, we next examined $\Phi_{\mathrm{ET}}$ in a different manner.

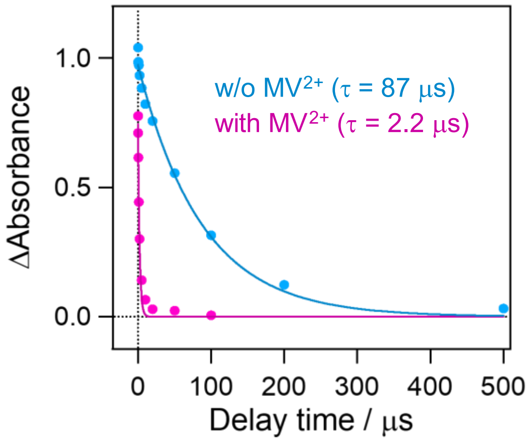


**Fig. S24.** Time profiles of transient absorbance of ZnTPPS in the presence and absence of $MV^{2+}$. The monitoring wavelength was set to 470 nm.

In the second evaluation, we rely on the amount of the reactant (ZnTPPS in the $T_1$ state) and product ($MV^+$) in the electron transfer. The molar absorption coefficient of $MV^+$ has been reported as 13700 $M^{-1}cm^{-1}$ at 606 nm [4]. The absorption coefficient of zinc tetraphenylporphyrin (ZnTPP) in the $T_1$ state (68000 $M^{-1}cm^{-1}$ at 470 nm) [5] was adopted as that of ZnTPPS. As shown in Fig. S25, the concentration of the $T_1$ state of ZnTPPS is estimated to be $1.1\times10^{-5}$ M from ΔAbsorbance of 0.77 at 470 nm in the spectrum at 100 ns. The concentration of $MV^+$ can be quantified to be $3.0\times10^{-6}$ M from ΔAbsorbance of 0.041 at 606 nm the transient spectrum at 10 µs. The concentration ratio of the product to the reactant is 0.27.

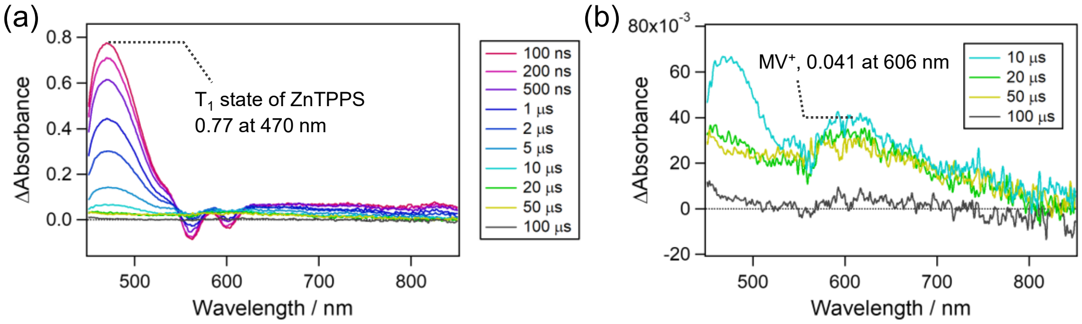


**Fig S25.** a) Transient absorption spectra of ZnTPPS in the presence of $MV^{2+}$. b) Enlarged view of the panel a for clarity of the spectra in the microsecond time region.

The disagreement of $\Phi_{ET}$ between the first and second evaluations is probably due to the faster charge recombination than the charge separation. Although the electron transfer takes place with the quantum yield of 0.97, the resultant charge-separated state undergoes the recombination process whose rate constant is affected by a distance between ZnTPPS and $MV^+$ in the polymer matrix. Reflecting the heterogeneity in the sample system, the recombination rapidly takes place in the charge-separated state with the shorter distance while it can survive with a longer lifetime in the case that the distance is sufficiently long. That is why the production yield of the charge-separated state is lower than the quantum yield of electron transfer. In the present study, we adopted the value of 0.27 as the quantum yield of electron transfer because only the charge-separated state free from the recombination contributes to the subsequent catalytic process.

## References

[1] L. Flamigni, A. Talarico, B. Ventura, R. Rein, N. Solladié, A versatile bis-porphyrin tweezer host for the assembly of noncovalent photoactive architectures: A photophysical characterization of the tweezers and their association with porphyrins and other guests, Chemistry-a European Journal 12 (2006) 701-712.

[2] Y. Nagasawa, T. Itoh, M. Yasuda, Y. Ishibashi, S. Ito, H. Miyasaka, Ultrafast Charge Transfer Process of 9,9′-Bianthryl in Imidazolium Ionic Liquids, Journal of Physical Chemistry B 112 (2008) 15758-15765.

[3] H. Sotome, D. Kitagawa, T. Nakahama, S. Ito, S. Kobatake, M. Irie, H. Miyasaka, Cyclization reaction dynamics of an inverse type diarylethene derivative as revealed by time-resolved absorption and fluorescence spectroscopies, Physical Chemistry Chemical Physics 21 (2019) 8623-8632.

[4] T. Ohgushi, Z. Li, F. Li, T. Komatsu, S. Takeoka, E. Tsuchida, Photoexcitation and electron transfer reactions of zinc lipidporphyrins in DMSO, Journal of Porphyrins Phthalocyanines, 3 (1999) 53-59.

[5] T. Watanabe and K. Honda, Measurement of the extinction coefficient of the methyl viologen cation radical and the efficiency of its formation by semiconductor photocatalysis, Journal of Physical Chemistry, 86 (1982) 2617-2619.