

**Effect of excited state self-quenching on singlet oxygen
photogeneration using nanosheet surface assembled zinc
phthalocyanine**

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Figure S1. UV-Vis absorption spectra of ZnPc^{4+} in PBS (black: 5.7×10^{-7} M, gray: 9.5×10^{-7} M, red: 1.3×10^{-6} M, blue: 1.9×10^{-6} M, orange: 2.9×10^{-6} M, green: 3.8×10^{-6} M), inset is Lambert-Beer plot of ZnPc^{4+} in PBS (open circle: 641 nm, closed circle: 683 nm).

Figure S2. Transient absorption decay profile of ZnPc/SAP , fitting and residual error (loading level of ZnPc^{4+} is 1.1% versus CEC).

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CEC) (red : under N₂, blue : under air (in the presence of ³O₂)).

Figure S9. Normalized transient absorption decay profile of ZnPc⁴⁺/Sap (49% vs. CEC) (red : under N₂, blue : under air (in the presence of ³O₂)).

Figure S10. Fluorescence spectra of ZnPc⁴⁺/SAP dispersion (loading level was varied from 0.086, 0.14, 0.29, 0.57, 1.4, 2.9, 5.7, 17, 29, 40, 51% versus CEC).

Synthesis of 3-(4-methylpyridin-2-yloxy)phthalonitrile

3-nitrophthalonitrile (0.82 g, 4.74 mmol) and 5-hydroxy-2-methylpyridine (1.02 g, 9.35 mmol) were dissolved in 10 mL of dry *N,N*-dimethylformamide at 50 °C under N₂. Potassium carbonate (2.11 g, 15.3 mmol) was added to the reaction solution in 5 portions every 5 min. The reaction mixture was heated for 48 h at 50 °C, then cooled to room temperature, and poured into 100 mL of ice-water. The crude product was extracted for the reaction liquid using 50 mL of CHCl₃ at 3 times. The crude product was redeposited using Diethyl ether. The precipitate was obtained as a pink powder. Yield, 0.47 g (42.2 % (based on 3-nitrophthalonitrile)).

Anal. Calc. for C₁₄H₉N₃O: C; 70.17, H; 4.12, N; 16.37. Found: C; 69.93, H; 4.21, N; 16.08 %. HR-MS (ESI-TOF): Found 236.0816 *m/z*. [M+nH]⁻ (calcd. for C₁₄H₉N₃O 236.0818). ¹H NMR (CDCl₃): δ= 8.37(s, 1H,Py-H), 7.59 (t,1H,*J* = 16.4 Hz, Ar-H), 7.50 (d,1H,*J* = 7.64 Hz, Ar-H), 7.36 (d,1H,*J* = 8.41 Hz, Py-H), 7.26 (d,1H,*J* = 8.41 Hz, Py-H), 7.06 (d,1H,*J* = 9.00 Hz, Ar-H), and 2.61 ppm (s,3H,CH₃).

Synthesis of 1,8,15,22-tetrakis-[(4-methyl-3-pyridyloxy)phthalocyaninato] zinc(II)

Phthalonitrile (0.41 g, 1.74mmol) and zinc acetate dihydrate (0.11 g, 0.05 mmol) was induced in *n*-pentanol (10 mL) in the presence of 0.3 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under N₂. The mixture was heated at 145 °C for 24 h and then cooled to room temperature, and poured into 100 mL of ice-water. The crude product was extracted for the reaction liquid using 50 mL of CHCl₃ at 3 times. The crude product was redeposited using Diethyl ether. The precipitate was obtained as a blue-green solid. Yield, 0.30 g (68.4 % (based on Phthalonitrile **3**)). Anal. Calc. for C₅₆H₃₆N₁₂O₄Zn + H₂O: C;65.66, H;3.74, N;16.41. Found: C;65.43, H;4.02, N;16.24%. UV-vis (CHCl₃): λ_{max}(ε/ mol⁻¹dm³ cm⁻¹)□ = 326 (3.9×10⁴), 624 (2.1×10⁴), and 693 nm (12.2×10⁴).

Synthesis of 1,8,15,22-tetrakis-[*N*-methyl-(4-methylpyridinium-3yloxy) phthalocyaninato] zinc(II) iodide

Zinc phthalocyanine (0.10 g, 0.10 mmol) and 5.0 mL of CH₃I were stirred at 50 °C under N₂. After 1 day, CH₃I was removed under reduced pressure. The crude product was washed with acetone and CHCl₃ to obtain the cationic compound as a green solid. Yield, 0.13 g (83.1 % (based on Zinc phthalocyanine)). Anal. Calcd. for

$C_{60}H_{48}I_4N_{12}O_4Zn + CHCl_3$: C; 43.26, H; 2.92, N; 9.93. Found: C; 43.42, H; 3.06, N; 9.71 %. UV-vis(DMSO): $\lambda_{max}(\epsilon/\text{mol}^{-1}\text{dm}^3\text{ cm}^{-1}) = 382 (1.8 \times 10^4)$, 620 (1.4×10^4), and 689 nm (8.5×10^4).

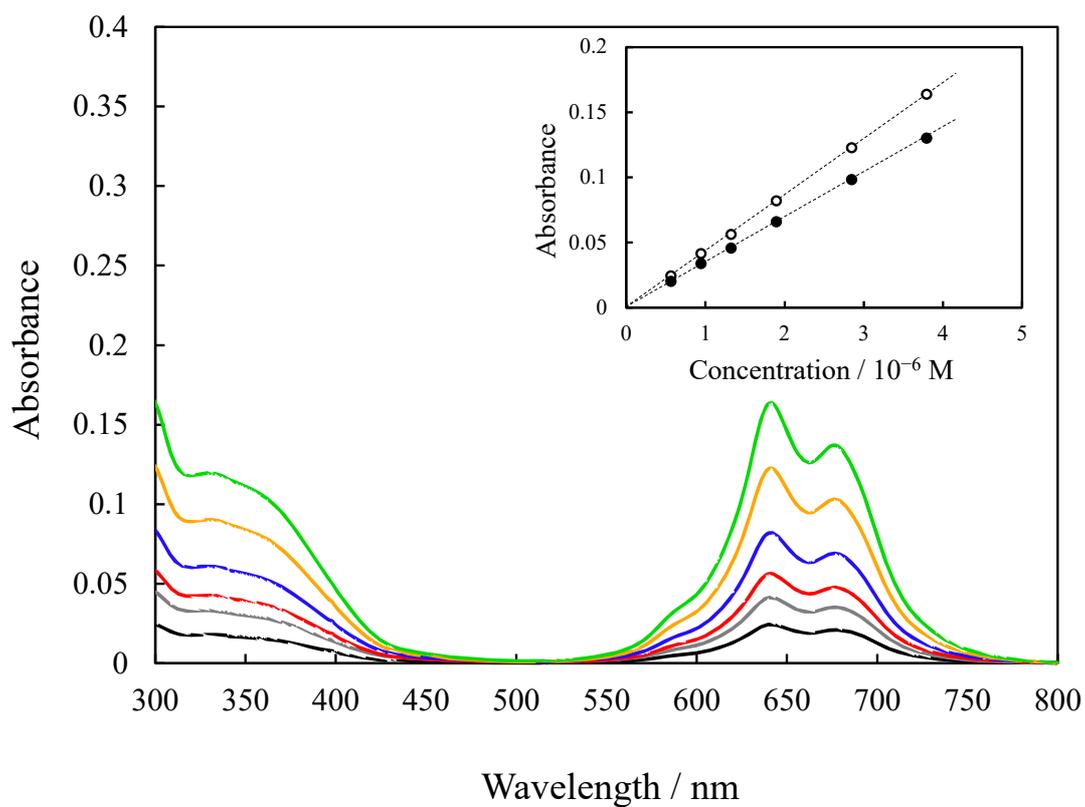


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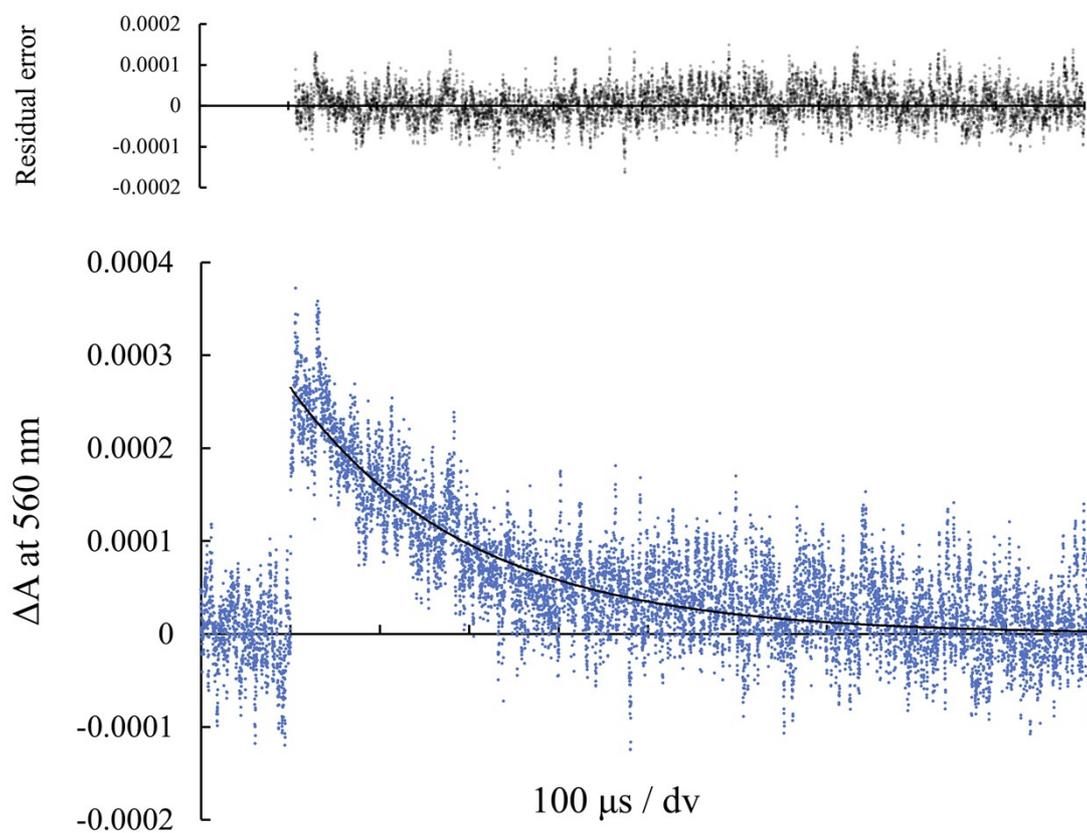


Figure S2. Transient absorption decay profile of $\text{ZnPc}^{4+}/\text{SAP}$, fitting and residual error (loading level of ZnPc^{4+} is 1.1% versus CEC).

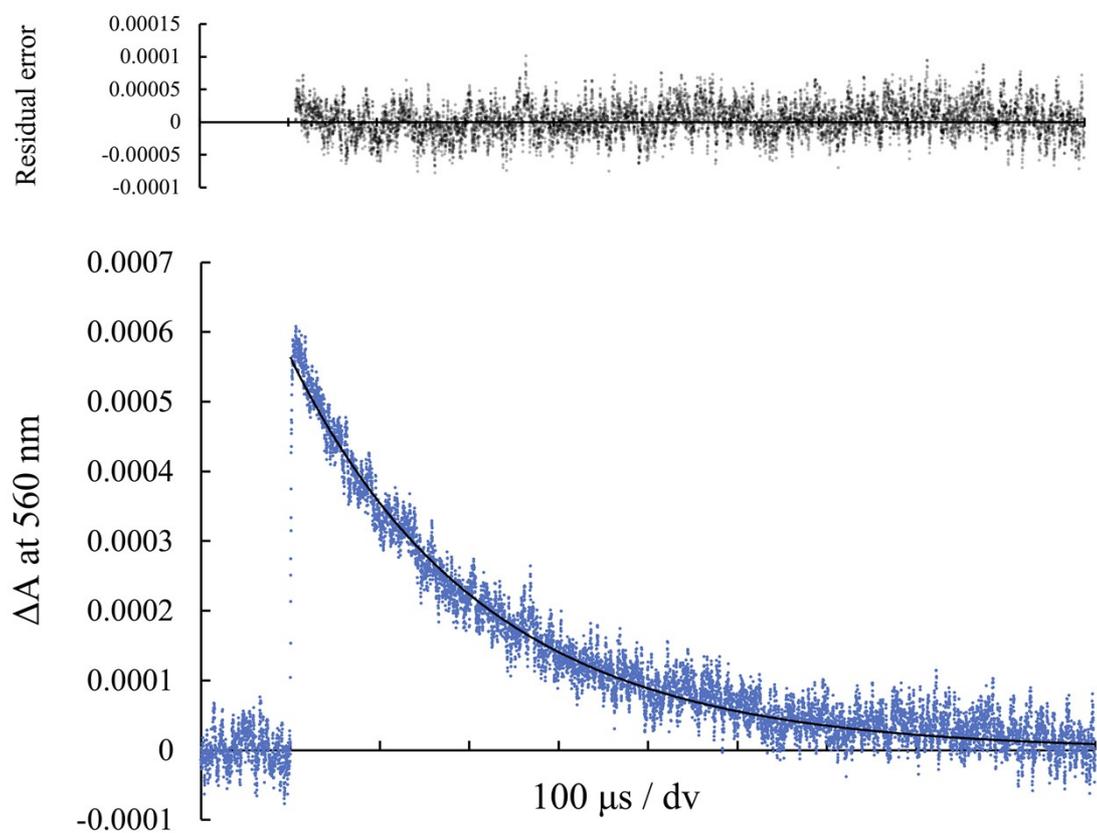


Figure S3. Transient absorption decay profile of ZnPc⁴⁺/SAP, fitting and residual error (loading level of ZnPc⁴⁺ is 5.3% versus CEC).

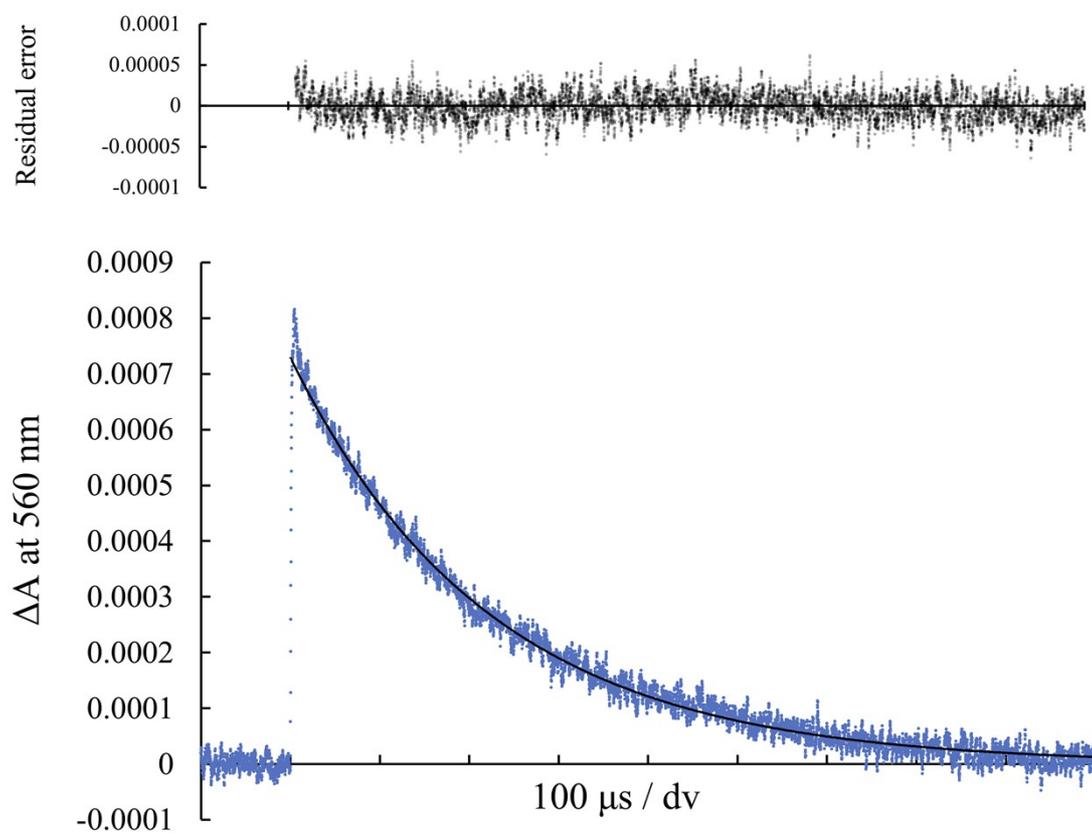


Figure S4. Transient absorption decay profile of ZnPc⁴⁺/SAP, fitting and residual error (loading level of ZnPc⁴⁺ is 12% versus CEC).

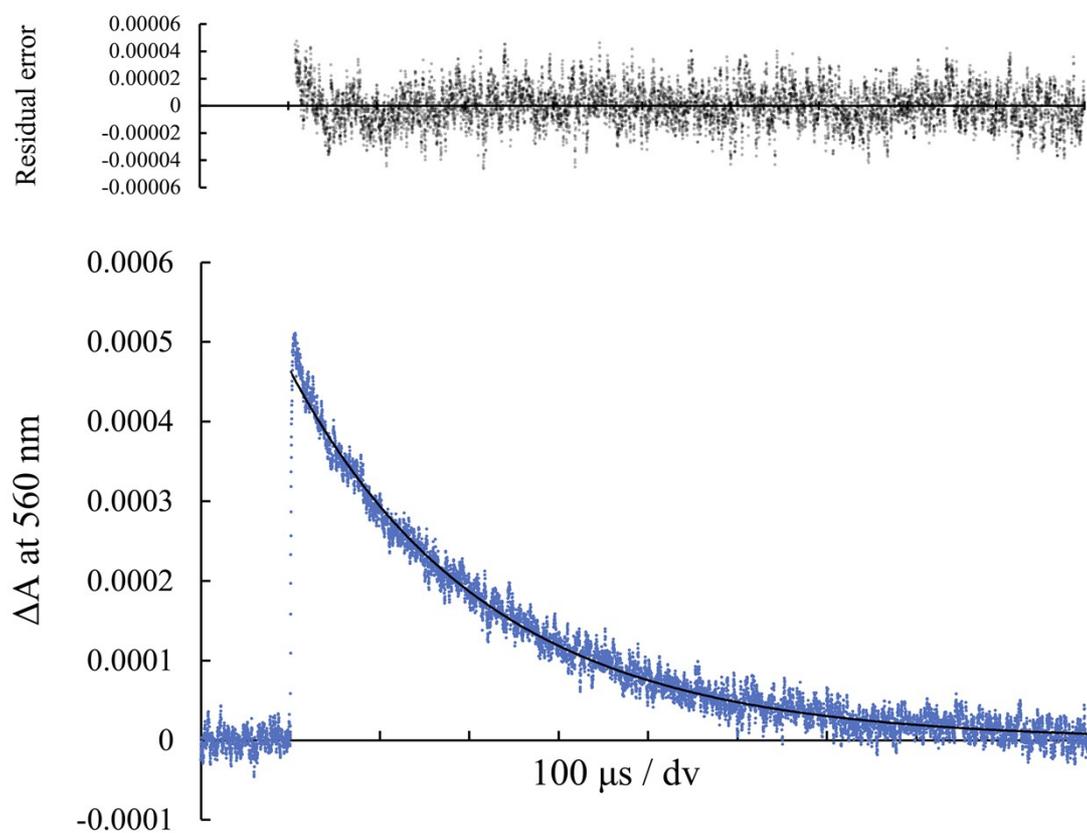


Figure S5. Transient absorption decay profile of ZnPc⁴⁺/SAP, fitting and residual error (loading level of ZnPc⁴⁺ is 20% versus CEC).

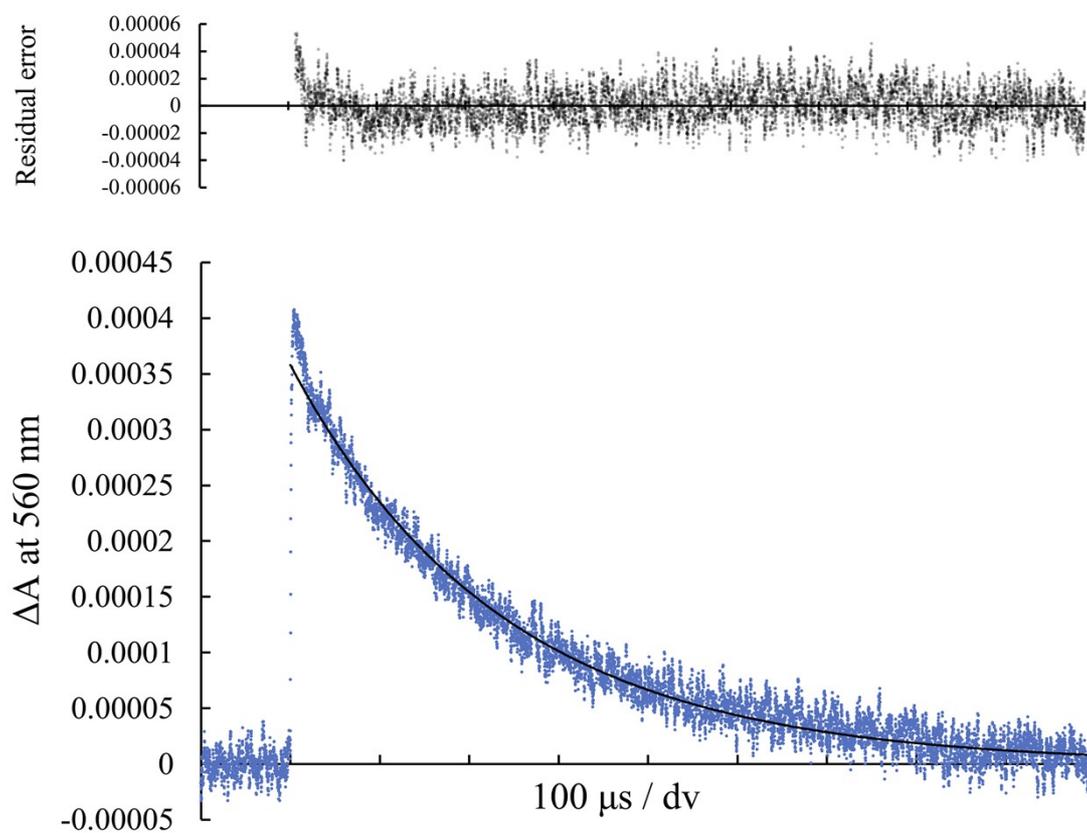


Figure S6. Transient absorption decay profile of $\text{ZnPc}^{4+}/\text{SAP}$, fitting and residual error (loading level of ZnPc^{4+} is 32% versus CEC).

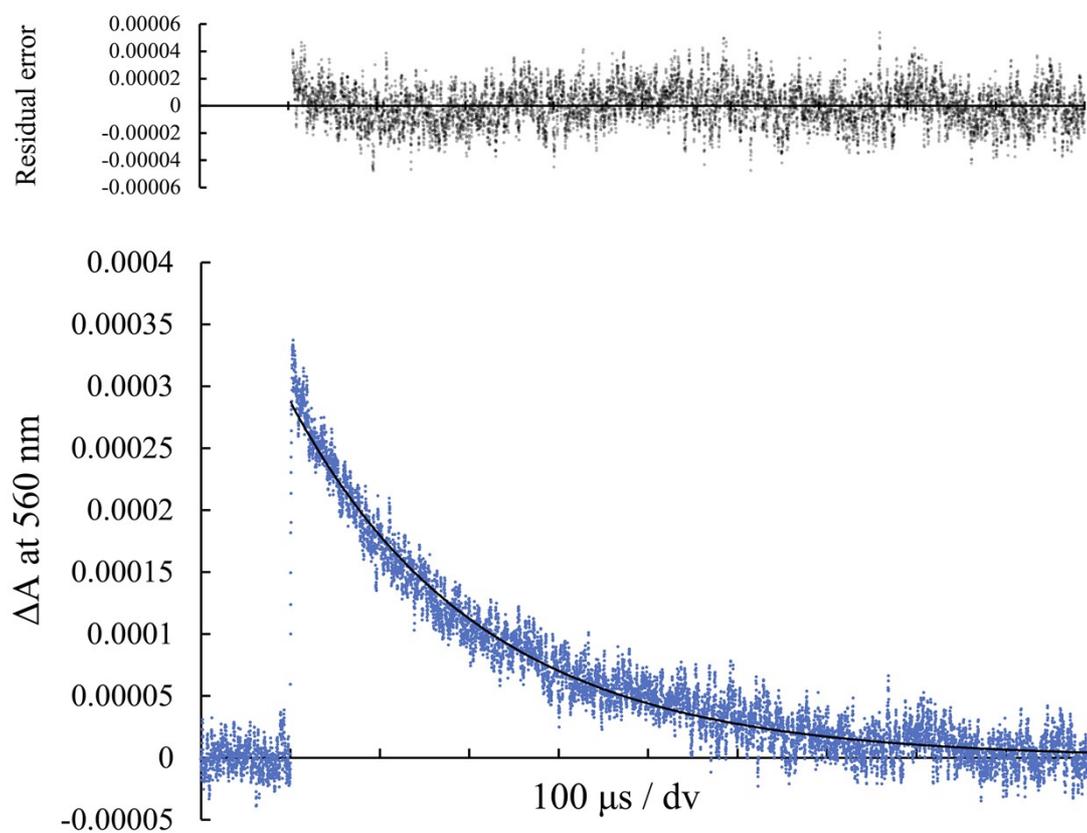


Figure S7. Transient absorption decay profile of ZnPc⁴⁺/SAP, fitting and residual error (loading level of ZnPc⁴⁺ is 49% versus CEC).

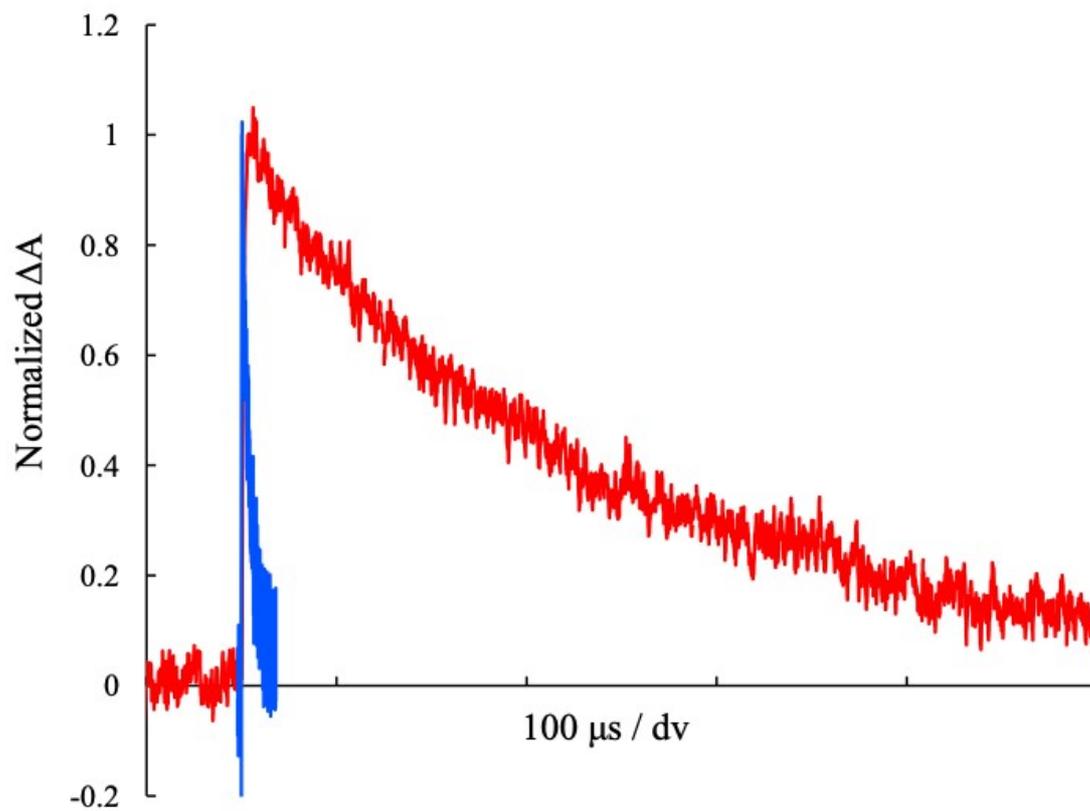


Figure S8. Normalized transient absorption decay profile of ZnPc⁴⁺/Sap (3.2% vs. CEC) (red : under N₂, blue : under air (in the presence of ³O₂)).

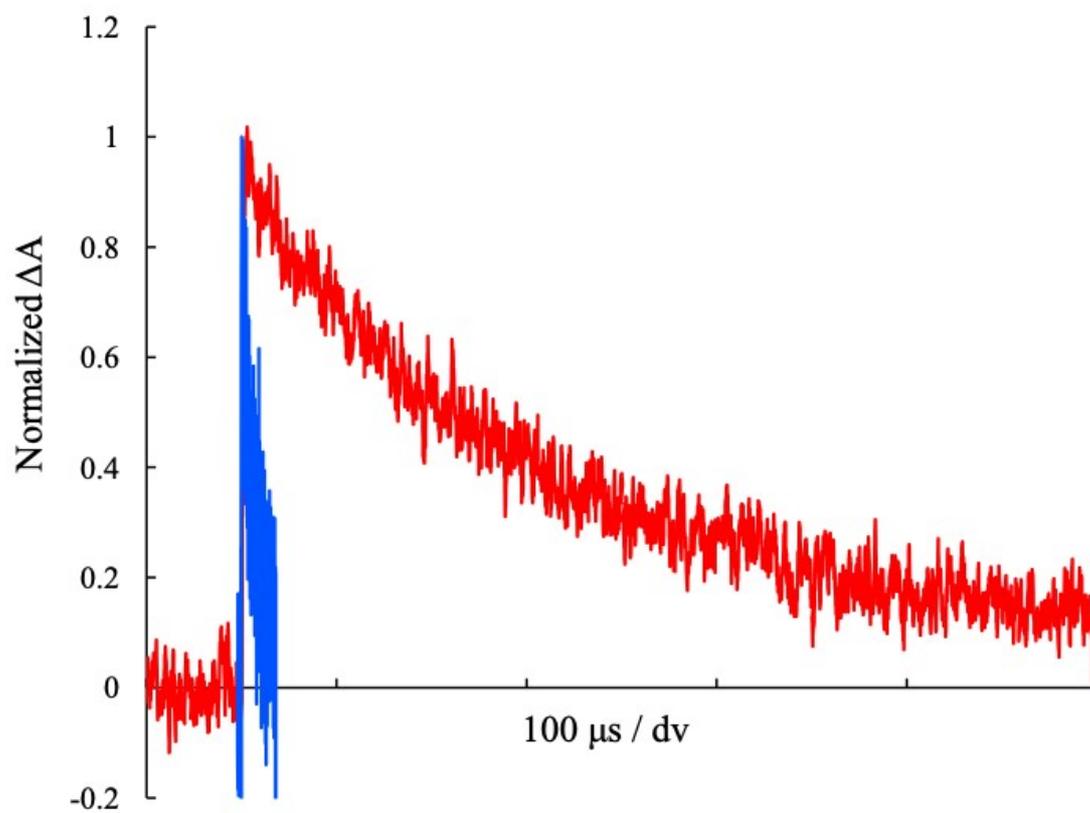


Figure S9. Normalized transient absorption decay profile of ZnPc⁴⁺/Sap (49% vs. CEC) (red : under N₂, blue : under air (in the presence of ³O₂)).

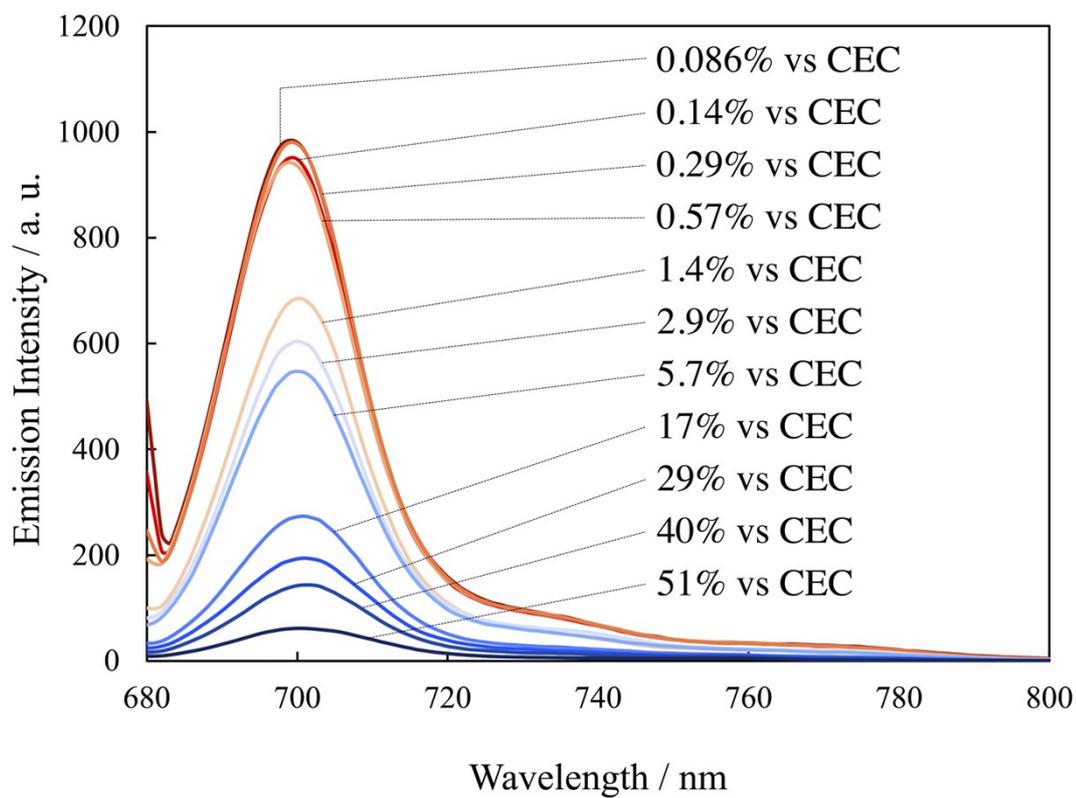


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