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Photoinduced Processes of the Supramolecularly Functionalized Semi-Conductive SWCNTs with Porphyrins via Ion Pair Interactions

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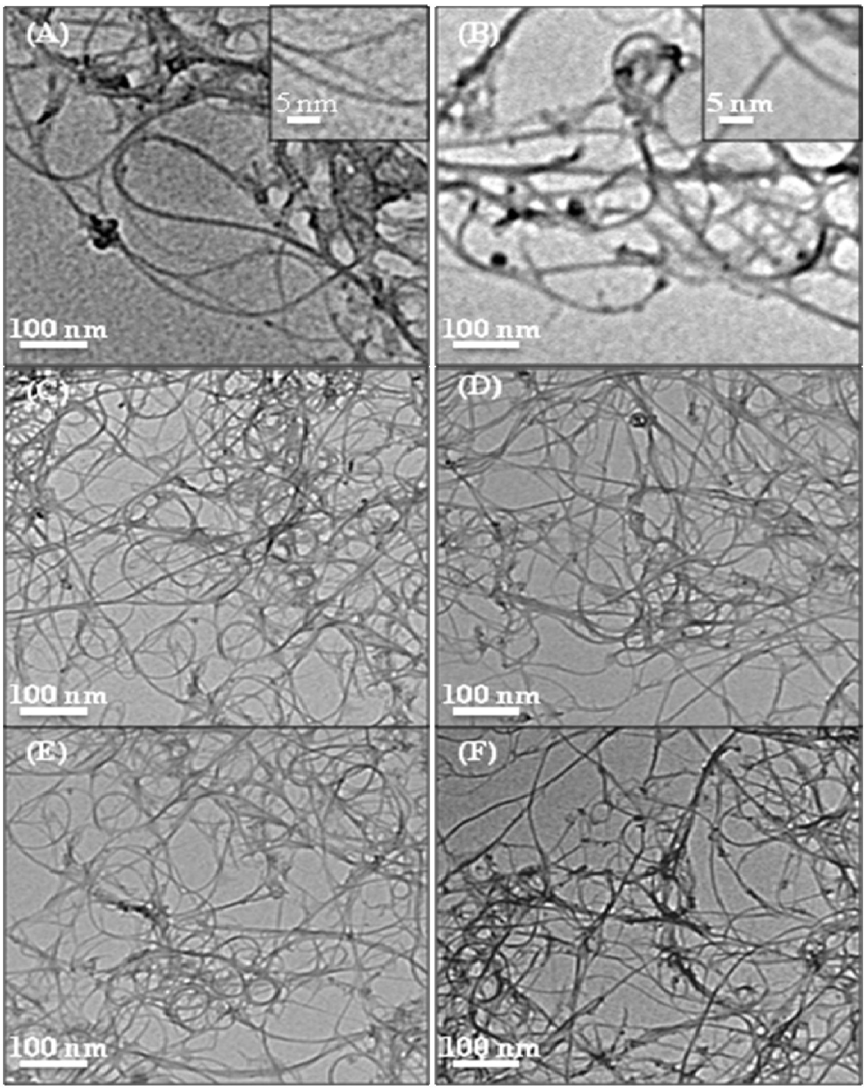


Fig. S1. TEM images for dried samples prepared from homogenous DMF solution. (A) SWCNT(6,5)/PyrCOO^{-}, (B) SWCNT(7,6)/PyrCOO^{-}, (C) SWCNT(6,5)/PyrCOO^{-}/(TMPyP^{+})H_2, (D) SWCNT(7,6)/PyrCOO^{-}/(TMPyP^{+})H_2, (E) SWCNT(6,5)/PyrCOO^{-}/(TMPyP^{+})Zn, and (F) SWCNT(7,6)/ PyrCOO^{-}/(TMPyP^{+})Zn.

Estimation of Molecular Stoichiometry of the Nanohybrids

Estimation of ratio of Pyr-R to SWCNT

1) MW of Pyr-R ≈ 400

   mol of 4 mg of Pyr-R ≈ 0.004/400 ≈ 1×10^{-5} mol:

2) MW of SWCNT(ϕ1nm x 800 nm) ≈ 1×10^{6} SWCNT

   mol of 2 mg of SWCNT ≈ 0.002/1×10^{6} ≈ 2×10^{-9} mol.

3) Pyr-R/SWCNT ≈ $1 \times 10^{-5}/2 \times 10^{-9}$ = 5000 mols per one mol of 800 nm SWCNT.

4) length of Pyr-R ≈ 0.5 nm, length of SWCNT≈ 800 nm,

   5000 x 0.5 = 2500 nm/800nm = ca. 3 (Pyr-R every 3 molecules on 1 nm of SWCNT).

Estimation of ratio of MP to SWCNT

5) Porphyrins; Abs. = 1 (1 cm cell, from Fig. 2), molar extinction coefficient = 10^{5} M^{-1} cm^{-1}.
   Concentration = $1/10^{5}$ =1 x 10^{-5} mol/L;

6) In 15 mL, $1 \times 10^{-5} \times 1.5 \times 10^{-3}$ mol = 15×10^{-9} mol

7) 15 molecules on SWCNT; one MP every 75 nm of SWCNT.

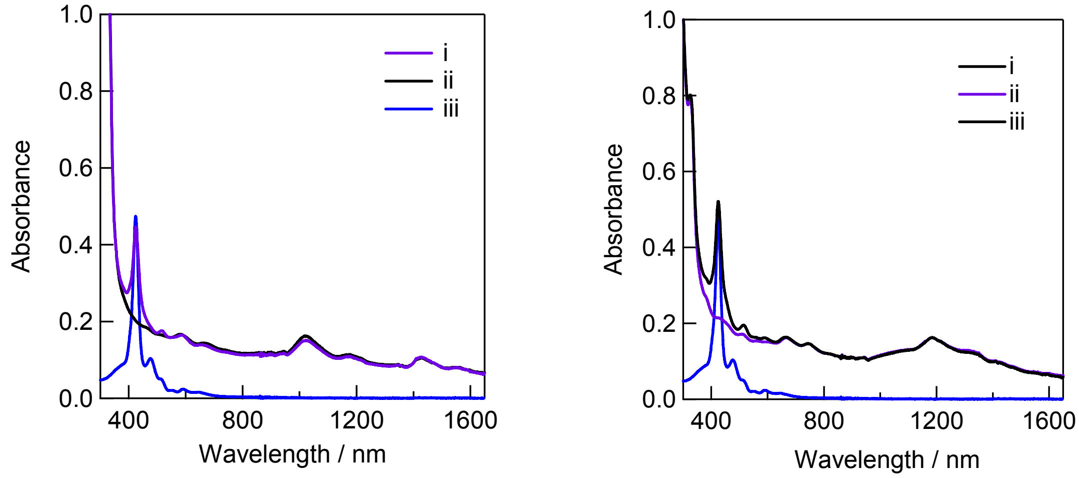


Fig. S2-1. Absorption spectra in DMF: (**Left**) (i) SWCNT(6,5)/PyrCOO$^{\square}$/(TMPyP^{+})H_2, (ii) SWCNT(6,5)/PyrCOO$^{\square}$, and (iii) (TMPyP^{+})H_2, and (**Right**) (i) SWCNT(7,6)/PyrCOO$^{\square}$/(TMPyP^{+})H_2, (ii) SWCNT(7,6)/PyrCOO$^{\square}$, and (iii) (TMPyP^{+})H_2.

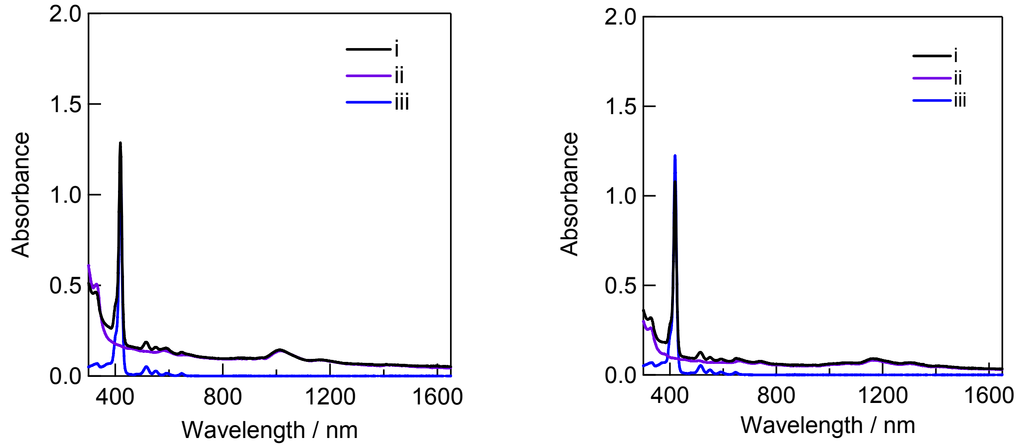


Fig. S2-2. Absorption spectra in DMF: **(Left)** (i) SWCNT(6,5)/PyrNH_3^{+}/(TPPS^{-})H_2, (ii) SWCNT(6,5)/PyrNH_3^{+}, and (iii) (TPPS^{-})H_2. **(Right)** SWCNT(7,6)/PyrNH_3^{+}/(TPPS^{-})H_2, (ii) SWCNT(7,6)/PyrNH_3^{+}, and (iii) PyrNH_3^{+}.

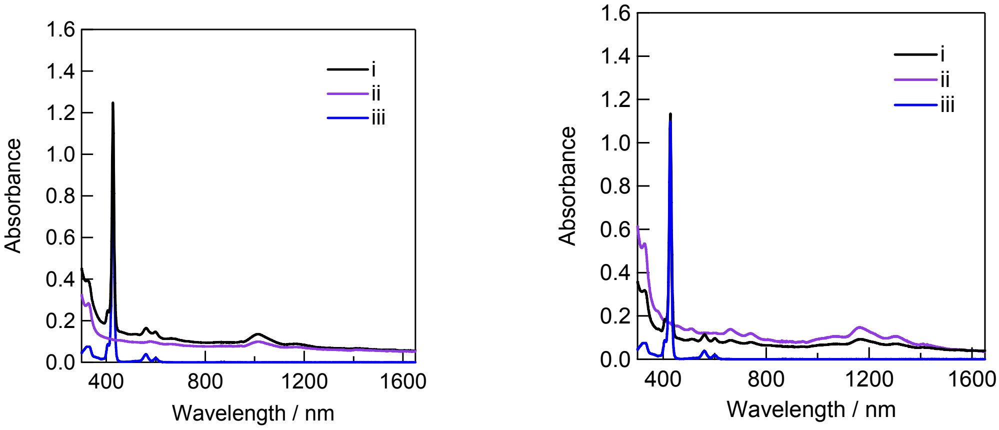


Fig. S2-3. Absorption spectra in DMF: **(Left)** (i) SWCNT(6,5)/$PyrNH_3^+$/($TPPS^-$)Zn, (ii) SWCNT(6,5)/$PyrNH_3^+$, and (iii) ($TPPS^-$)Zn. **(Right)** SWCNT(7,6)/$PyrNH_3^+$/($TPPS^-$)Zn, (ii) SWCNT(7,6)/$PyrNH_3^+$, and (iii) $PyrNH_3^+$.

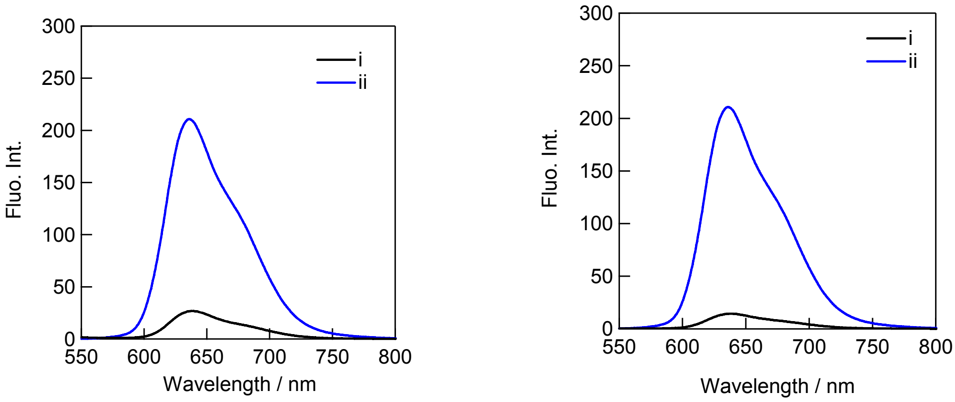


Fig. S3-1. Steady-state fluorescence spectra in DMF(λ_{ex} = 425 nm). **Left** (i) SWCNT(6,5)/ $PyrCOO^{-}$/($TMPyP^+$)Zn and (ii) ($TMPyP^+$)Zn. **Right** (i) SWCNT(7,6)/$PyrCOO^{-}$/($TMPyP^+$)Zn and (ii) ($TMPyP^+$)Zn.

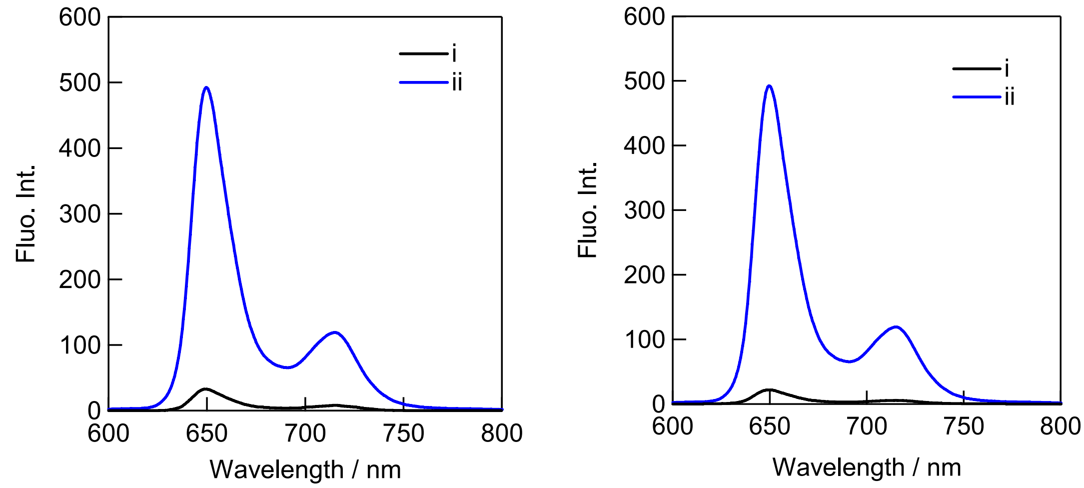


Fig. S3-2. Steady-state fluorescence spectra in DMF (λ_{ex} = 428 nm). **(Left)** SWCNT(6,5)/$PyrNH_3^+$/$(TPPS^-)H_2$ and (ii) $(TPPS^-)H_2$. $(TMPyP^+)Zn$ (i) SWCNT(7,6)/$PyrNH_3^+$/ $(TPPS^-)H_2$ and (ii) $(TPPS^-)H_2$.

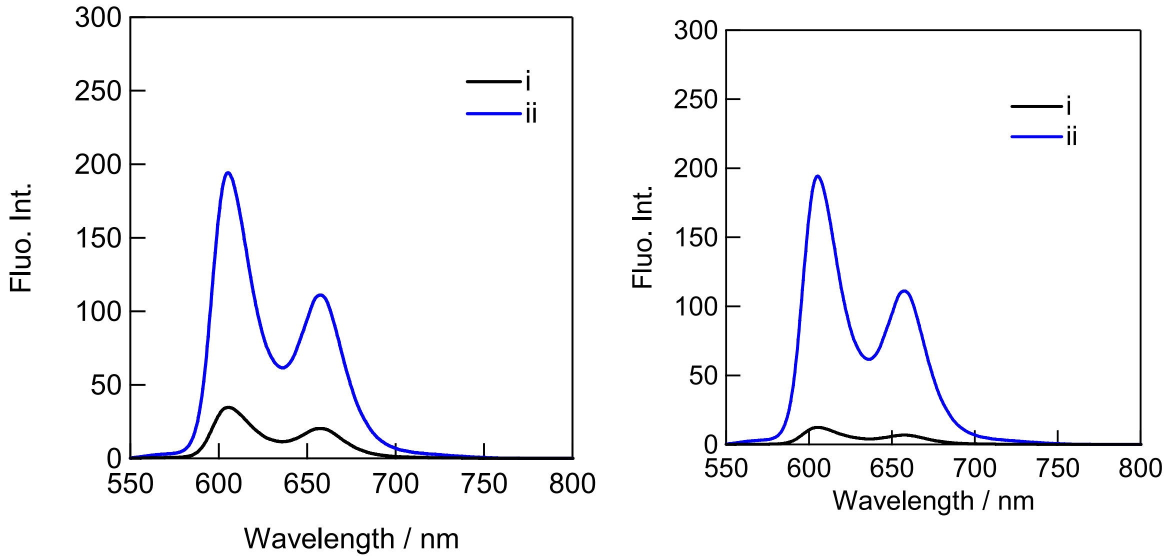
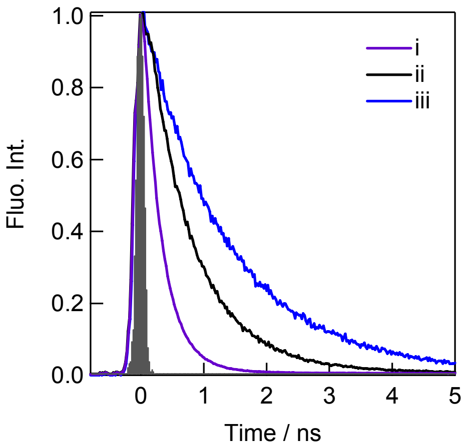


Fig. S3-3. Steady-state fluorescence spectra in DMF (λ_{ex} = 428 nm). **(Left)** SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)Zn and (ii) (TPPS$^-$)Zn. (TMPyP$^+$)Zn (i) SWCNT(7,6)/PyrNH$_3^+$/(TPPS$^-$)Zn and (ii) (TPPS$^-$)Zn.



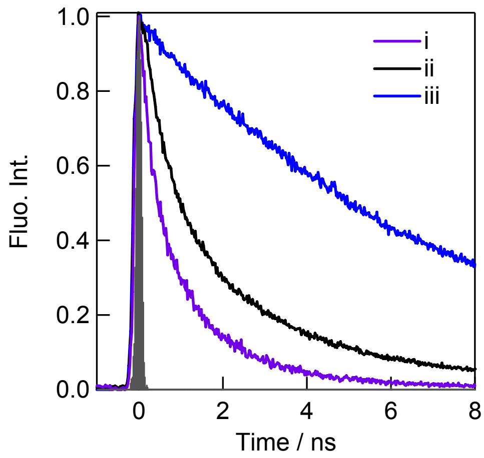


Fig. S4-1 Fluorescence decays in DMF. λ_{ex} = 408 nm. (Left) (i) SWCNT(7,6)/PyrNH$_3^+$/(TPPS$^-$)Zn, (ii) SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)Zn and (iii) (TPPS$^-$)Zn. (Right) (i) SWCNT(7,6)/PyrNH$_3^+$/(TPPS$^-$)H$_2$, (ii) SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)H$_2$, and (iii) (TPPS$^-$)H$_2$.

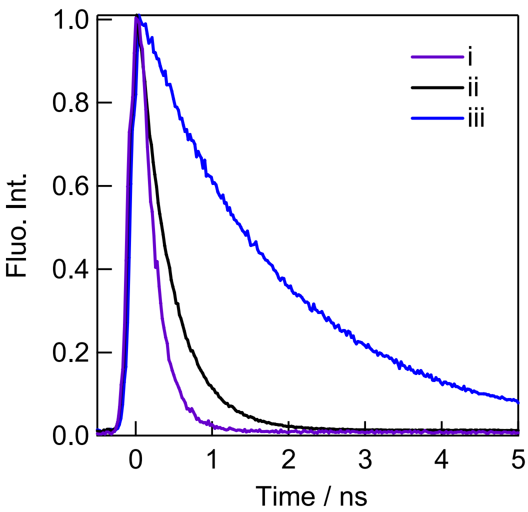


Fig. S4-2. Fluorescence decays of (i) SWCNT(7,6)/PyrCOO□/(TMPyP$^+$)Zn (ii) SWCNT(6,5) /PyrCOO□/(TMPyP$^+$) Zn and (iii) (TMPyP$^+$)Zn in DMF. λ_{ex} = 408 nm.

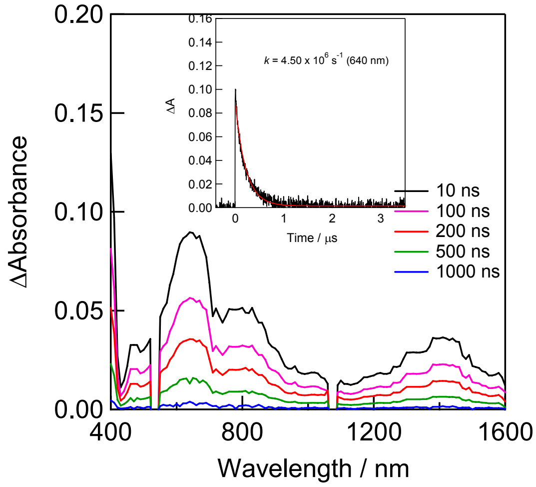


Fig. S5-1. Nanosecond transient absorption spectra of SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)Zn observed by 532 nm (ca. 3 mJ/ pulse) laser irradiation in DMF. Inset: Absorption-time profile.

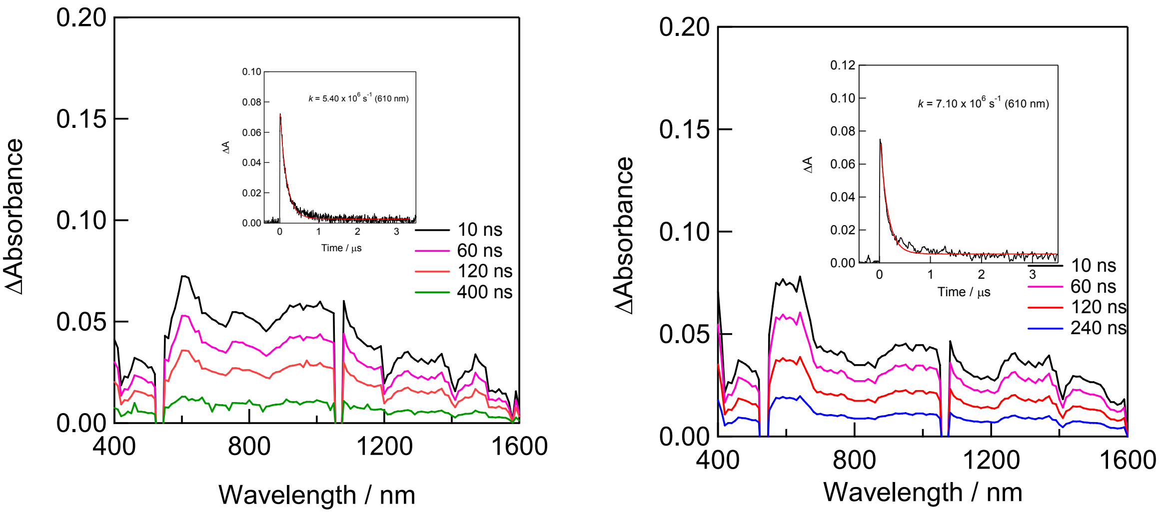


Fig. S5-2. Nanosecond transient absorption spectra of SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)H$_2$, SWCNT(7,6)/PyrNH$_3^+$/(TPPS$^-$)H$_2$ observed by 532 nm (ca. 3 mJ/ pulse) laser irradiation in DMF. Inset: Absorption-time profile.

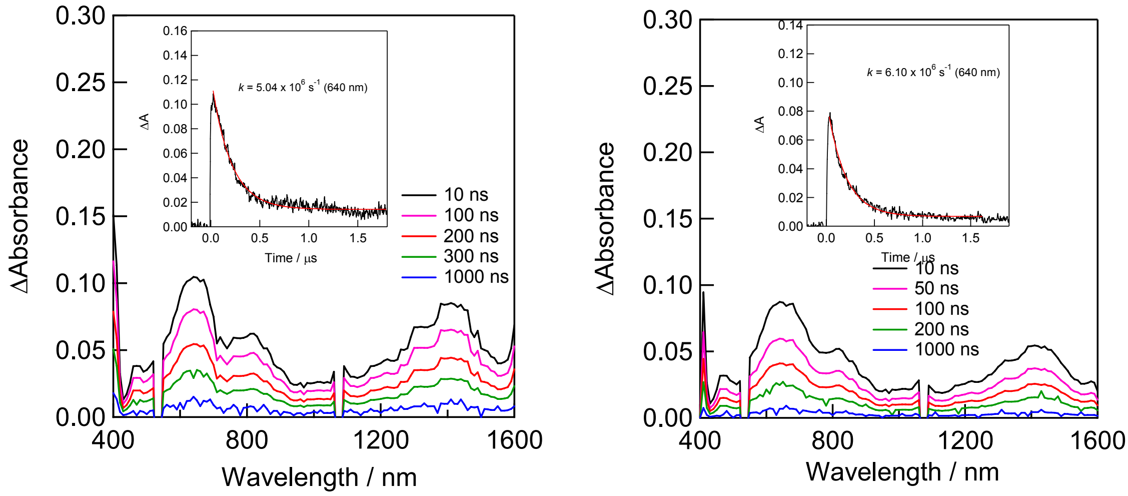


Fig. S5-3. Nanosecond transient absorption spectra of SWCNT(6,5)/PyrCOO^{-}/(TMPyP^{+})Zn and SWCNT(7,6) /PyrCOO^{-}/(TMPyP^{+})Zn observed by 532 nm (ca. 3 mJ/ pulse) laser irradiation in DMF. Inset: Absorption-time profile.

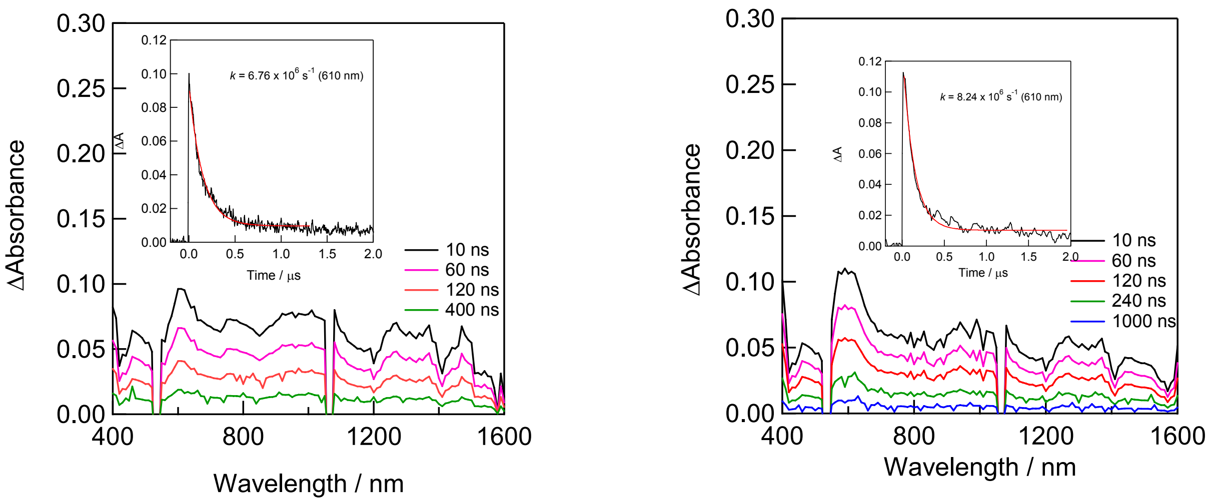


Fig. S5-4. Nanosecond transient absorption spectra of SWCNT(6,5)/PyrCOO^{-}/(TMPyP^{+})H_2 and SWCNT(7,6)/PyrCOO^{-}/(TMPyP^{+})H_2 observed by 532 nm (ca. 3 mJ/ pulse) laser irradiation in DMF. Inset: Absorption-time profile.

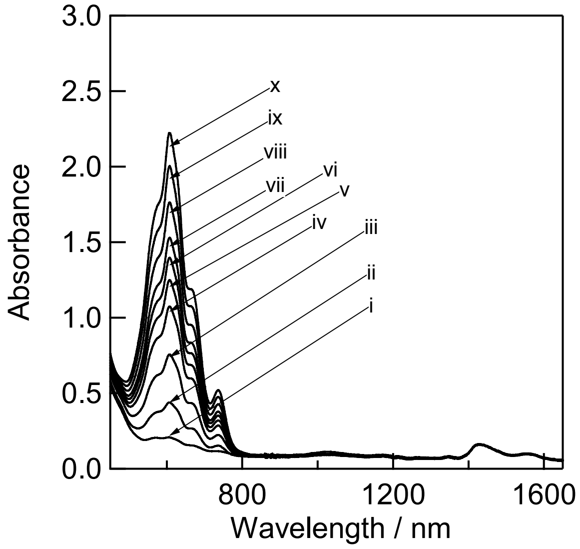


Fig. S6-1. Steady-state absorption spectra of SWCNT(6,5)/PyrCOO□/(TMPyP^{+})Zn in Ar-saturated DMF solution measured after 5 laser-shots with laser light (6-ns pulse width) at 532-nm in the presence of HV^{2+} (0.5 mM) and BNAH (i) 0, (ii) 0.5, (iii) 1.0, (iv) 1.5, (v) 2.0 (vi) 2.5 (vii) 3.0 (viii) 3.5 and (ix) 4.0 mM.

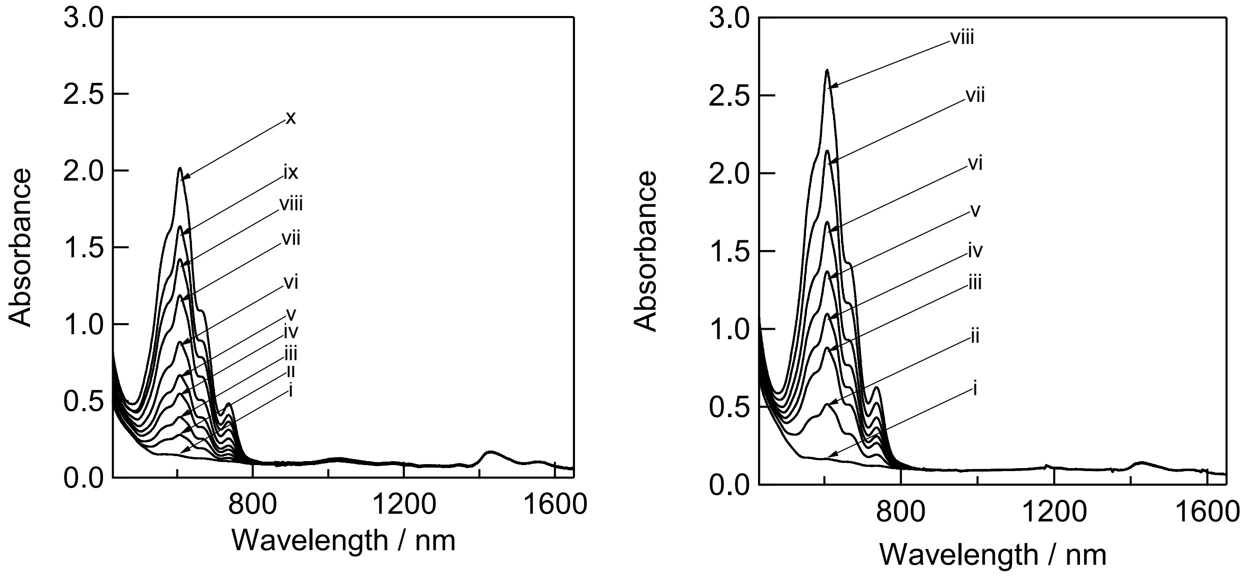


Fig. S6-2. Steady-state absorption spectra of (Left) SWCNT(6,5)/PyrCOO□/(TMPyP^{+})H_2 and (Right) SWCNT(7,6)/PyrCOO□/(TMPyP^{+})H_2 in Ar-saturated DMF solution measured after 5 laser-shots with laser light (6-ns pulse width) at 532-nm in the presence of HV^{2+} (0.5 mM) and BNAH (i) 0, (ii) 0.5, (iii) 1.0, (iv) 1.5, (v) 2.0 (vi) 2.5 (vii) 3.0 (viii) 3.5 and (ix) 4.0 mM.

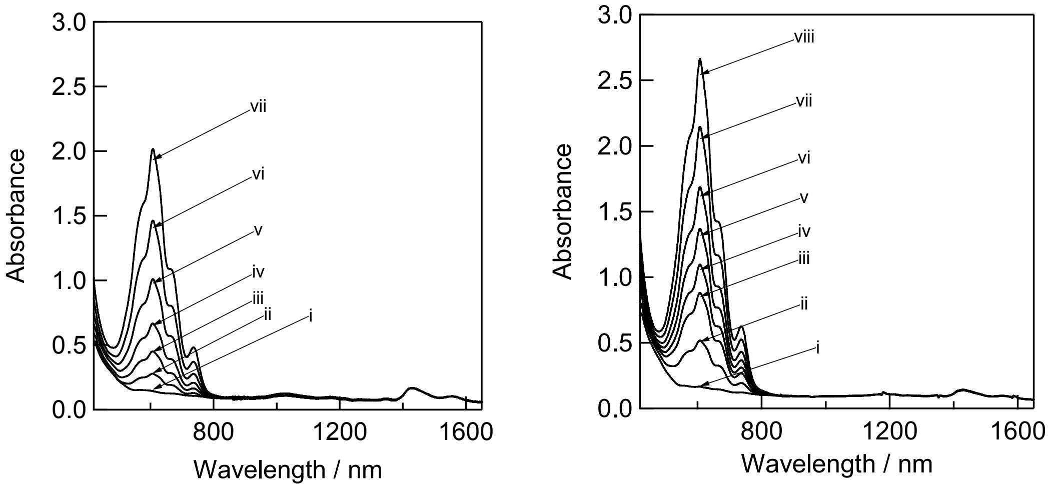


Fig. S6-3. Steady-state absorption spectra of (Left) SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)H$_2$ and (Right) SWCNT(7,6)/PyrNH$_3^+$/(TPPS$^-$)H$_2$ in Ar-saturated DMF solution measured after 5 laser-shots with laser light (6-ns pulse width) at 532-nm in the presence of HV^{2+} (0.5 mM) and BNAH (i) 0, (ii) 0.5, (iii) 1.0, (iv) 1.5, (v) 2.0 (vi) 2.5 (vii) 3.0 (viii) 3.5 and (ix) 4.0 mM.

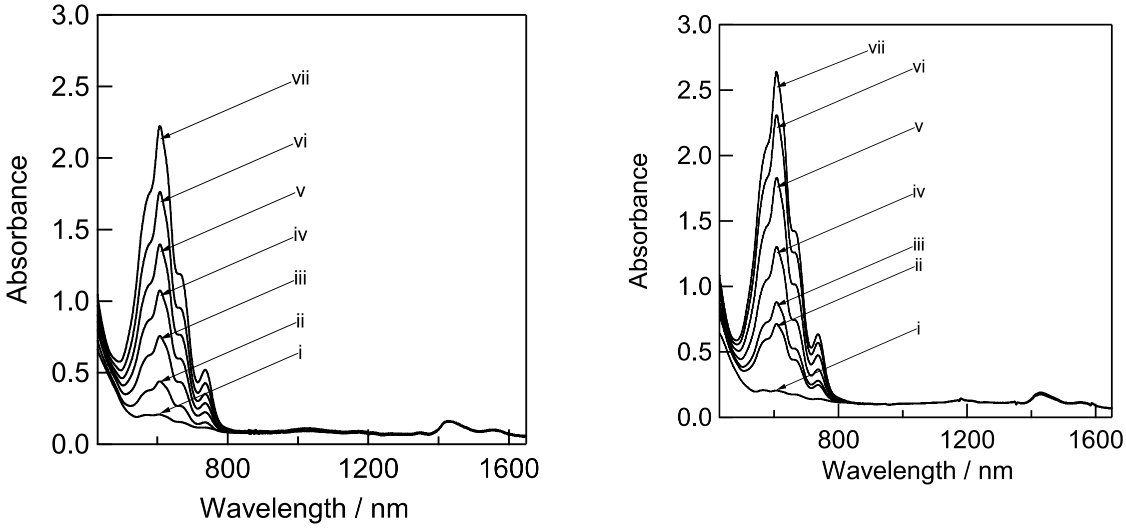


Fig. S6-4. Steady-state absorption spectra of (Left) SWCNT(6,5)/PyrNH$_3^+$/(TPPS$^-$)Zn and (Right) SWCNT(7,6) /PyrNH$_3^+$/(TPPS$^-$)Zn in Ar-saturated DMF solution measured after 5 laser-shots with laser light (6-ns pulse width) at 532-nm in the presence of HV^{2+} (0.5 mM) and BNAH (i) 0, (ii) 0.5, (iii) 1.0, (iv) 1.5, (v) 2.0 (vi) 2.5 (vii) 3.0 (viii) 3.5 and (ix) 4.0 mM.