Electronic Supplemental Information (ESI)

Title

Enhancement of photocatalytic activity of rhenium (I) complexes by encapsulation in light-harvesting soft nanotubes

Authors

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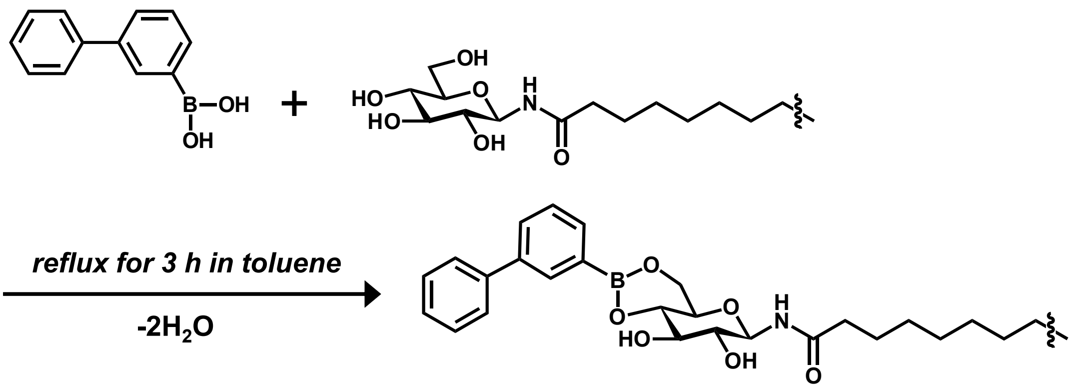


Scheme S1 Synthetic scheme of dye amphiphilic monomers.

Synthesis of **1**. The glycolipid, *N*-(9-*cis*-octadecenoyl)-*β*-D-glucopyranosylamine, was synthesized as reported previously.* 3-biphenylboronic acid was purchased from Tokyo Chemical Co. and was used in the following reaction without purification. Quantitative dehydration reaction between the glycolipid (1.0 g, 2.3 mmol) and 1-biphenylboronic acid (0.45 g, 2.3 mmol) in toluene was performed under the reflux condition equipped with a Dean-Stark apparatus. After 3 h, the solvent was completely removed by evaporation. The obtained residue was washed with anhydrous THF for several times and was stored in vacuum desiccators. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.39 (d, *J* = 9.1 Hz, 1H: NH), 8.11 (s, 1H: Biphenyl), 7.78 (d, *J* = 7.4 Hz, 1H: Biphenyl), 7.69–7.66 (m, 3H: Biphenyl), 7.48–7.45 (m, 1H: Biphenyl), 7.47 (t, *J* = 7.6 Hz, 1H: Biphenyl), 7.43 (t, *J* = 7.6 Hz, 1H: Biphenyl), 7.36 (t, *J* = 7.4 Hz, 1H: Biphenyl), 5.47 (d, *J* = 5.3 Hz, 1H: Glucose-3OH), 5.33 (m, 2H: -CH=CH-), 5.13 (d, *J* = 5.6 Hz, 1H: Glucose-2OH), 4.96 (t, *J* = 9.1 Hz, 1H: Glucose-1), 4.19 (m, 1H: Glucose-6), 3.95 (m, 1H, Glucose-4), 3.74–3.73 (m, 2H: Glucose-5, 6), 3.53 (m, 1H: Glucose-3), 3.27 (m, 1H: Glucose-2), 2.18 (t, *J* = 7.3 Hz, 2H: -COCH2-), 2.13 (m, 4H: -CH2-), 1.49 (m, 4H: -CH2-), 1.24 (m, 18H: -CH2-), 0.86 (t, *J* = 6.5 Hz, 3H: -CH3). ESI-MS (m/z): 604.4 $[M-H^+]^-$. Anal. calcd for C32H52BNO6: C 71.40, H 8.65, N 2.31. Found: C 71.10, H 8.70, N 2.40.

Synthesis of **2**. The glycolipid, *N*-(stearoyl)-*β*-D-glucopyranosylamine, was synthesized as reported previously.** Synthetic and purification procedures of **2** were similar to those of **1** as described above. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.24 (d, *J* = 8.9 Hz, 1H: NH), 8.11 (s, 1H: Biphenyl), 7.78 (d, *J* = 7.4 Hz, 1H: Biphenyl), 7.69–7.66 (m, 3H: Biphenyl), 7.48–7.45 (m, 1H: Biphenyl), 7.47 (t, *J* = 7.6 Hz, 1H: Biphenyl), 7.43 (t, *J* = 7.6 Hz, 1H: Biphenyl), 7.36 (t, *J* = 7.4 Hz, 1H: Biphenyl), 5.46 (d, *J* = 4.9 Hz, 1H: Glucose-3OH), 5.12 (d, *J* = 5.3 Hz, 1H: Glucose-2OH), 4.96 (t, *J* = 8.9 Hz, 1H: Glucose-1), 4.19 (dd, *J* = 4.9 and 10 Hz, 1H: Glucose-6), 3.89 (td, *J* = 3.1 and 9.1 Hz, 1H, Glucose-4), 3.68-3.65 (m, 2H: Glucose-5, 6), 3.50 (ddd, *J*

= 4.9, 7.3 and 9.1 Hz, 1H: Glucose-3), 3.26 (ddd, *J* = 5.3, 7.3 and 9.1 Hz, 1H: Glucose-2), 2.04–2.11 (m, 2H: -COCH2-), 1.47 (t, *J* = 6.3 Hz, 2H: -CH2-), 1.23 (m, 28H: -CH2-), 0.85 (t, *J* = 6.8 Hz, 3H: -CH3). ESI-MS (m/z): 606.4 $[M–H^+]^-$. Anal. calcd for C36H54BNO6: C 71.16, H 8.96, N 2.31. Found: C 71.19, H 8.95, N 2.39.

* S. Kamiya, H. Minamikawa, J. H. Jun, B. Yang, M. Masuda, T. Shimizu, *Langmuir*, 2005, **21**, 743.

** K. Ishikawa, N. Kameta, M. Aoyagi, M. Asakawa, T. Shimizu, *Adv. Funct. Mater.*, 2013, **23**, 1677.

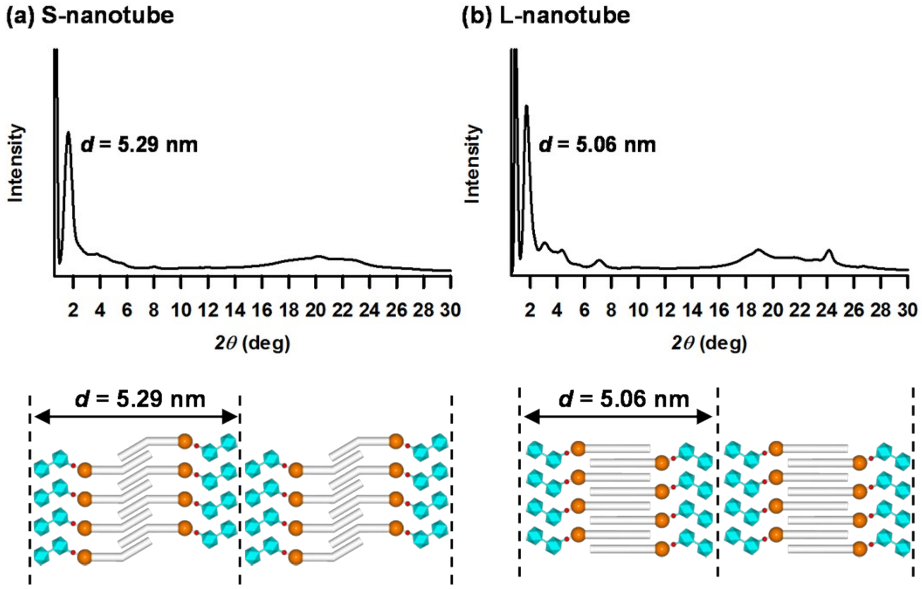


Fig. S1 Powder X-ray diffraction spectra of the S-nanotube and L-nanotube. Schematic images of the molecular packing within the bilayer membranes with the stacking periodicity (*d* spacing).

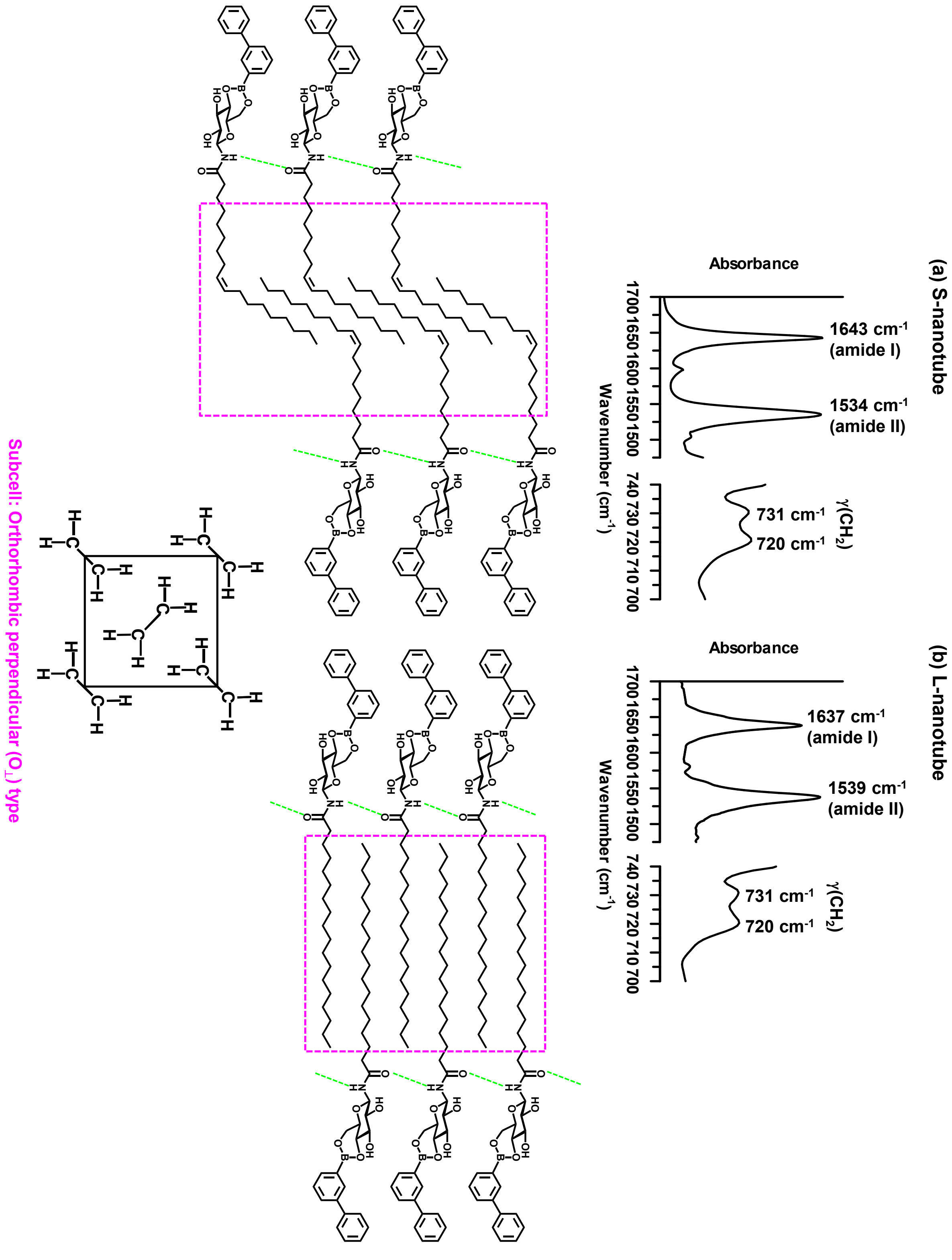


Fig. S2 Infrared spectra for the amide-I, amide-II, CH_2 rocking bands of the S-nanotube and L-nanotube. The intermolecular hydrogen bonding is shown as green dotted lines in the molecular packing images. The two peaks of the CH_2 rocking bands indicates that the lateral chain packing (subcell structure) of the hydrocarbon chains has an orthorhombic perpendicular (O$_\perp$) structure.

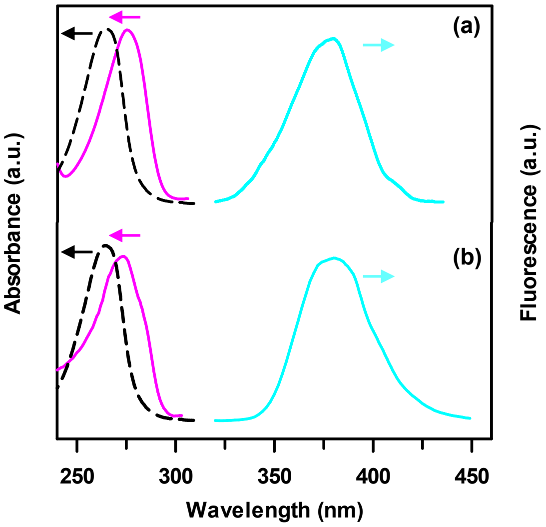


Fig. S3 (a) Absorption spectra of the monomer **1** in CH_3CN at 75 °C (black dotted line) and the S-nanotube in CH_3CN at 25 °C (pink solid line). Fluorescence spectrum of the S-nanotube in CH_3CN at 25 °C (blue solid line). Excitation wavelength at 275 nm. (b) Absorption spectra of the monomer **2** in CH_3CN at 75 °C (black dotted line) and the L-nanotube in CH_3CN at 25 °C (pink solid line). Fluorescence spectrum of the L-nanotube in CH_3CN at 25 °C (blue solid line). Excitation wavelength at 275 nm.

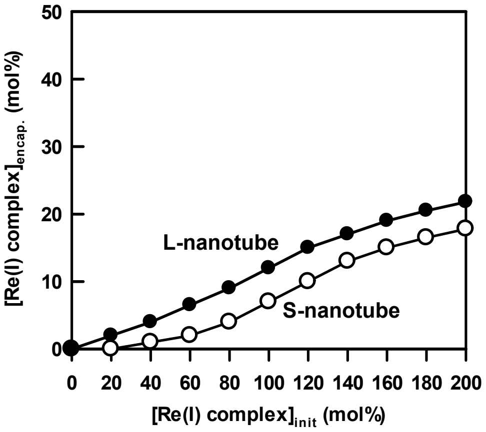


Fig. S4 Relationship between the initial concentration and encapsulated concentration of the Re(I) complex. The unit of the concentration (mol%) was used against the concentration of the biphenyl groups within bilayer membranes of the nanotubes.

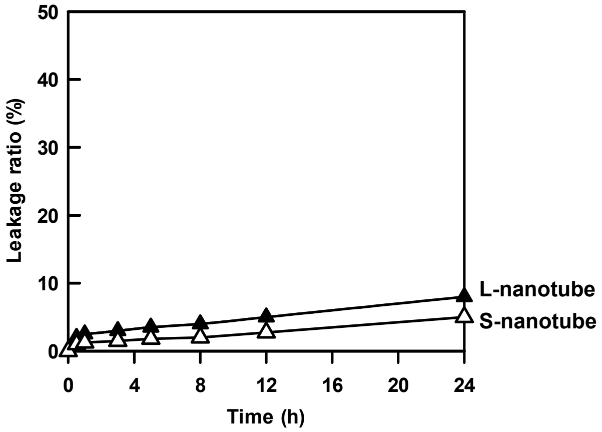


Fig. S5 Leakage profiles of the encapsulated Re(I) complex from the nanotubes to the CH_3CN bulk solution.

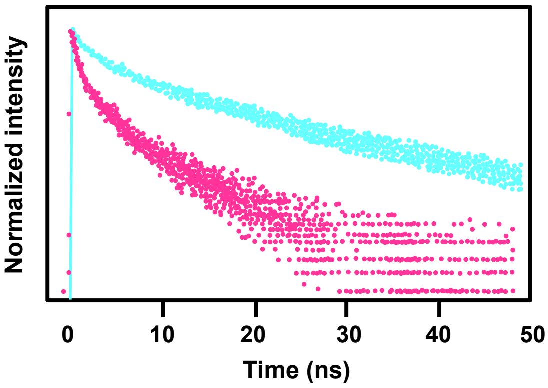


Fig. S6 Fluorescence decay profiles of the S-nanotube (blue plots) and the S-nanotube encapsulating the Re(I) complex (10 mol%; red plots) monitored at 380 nm. Excitation wavelength at 280 nm.

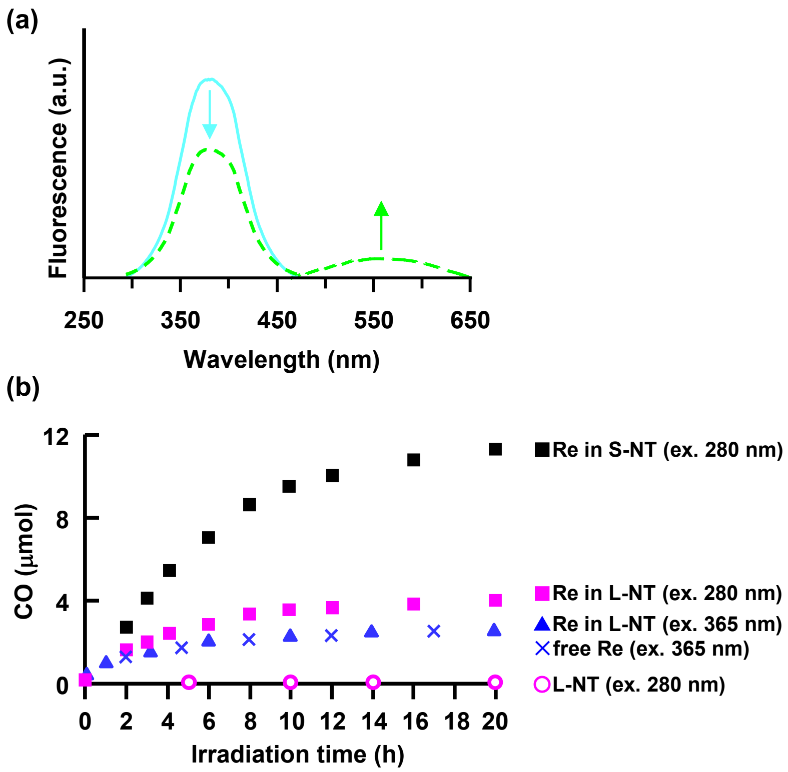


Fig. S7 (a) Fluorescence spectra of only the L-nanotube in CH_3CN excited at 275 nm (blue spectrum) and the L-nanotube encapsulating the Re(I) complex (10 mol% Re(I) complex / biphenyl in the L-nanotube) in CH_3CN excited at 275 nm (green spectrum). (b) CO evolution via photocatalytic CO_2 reduction with UV irradiation at 280 nm or 365 nm. ■ the encapsulated Re(I) complex in the S-nanotube; ■▲ the encapsulated Re(I) complex in the L-nanotube; × free Re(I) complex in the bulk solution; ○ the L-nanotube without the Re(I) complex

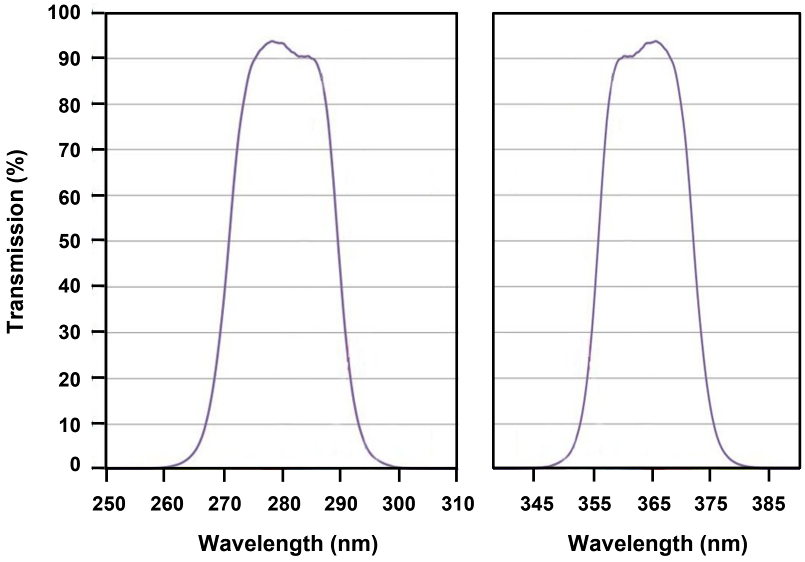


Fig. S8 Transmittance spectra of the bandpass filters (280 and 365 nm, half-width of 10 nm).

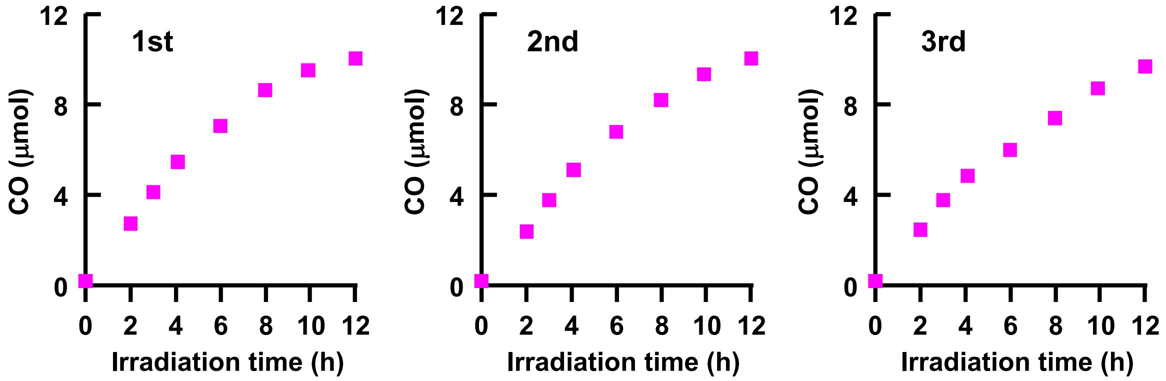


Fig. S9 1st (left), 2nd (middle), and 3rd (right) cycles of CO evolution via photocatalytic CO_2 reduction with UV irradiation at 280 nm for the encapsulated Re(I) complex in the S-nanotube. The substrate CO_2 was freshly purged after each cycle for 12 h.

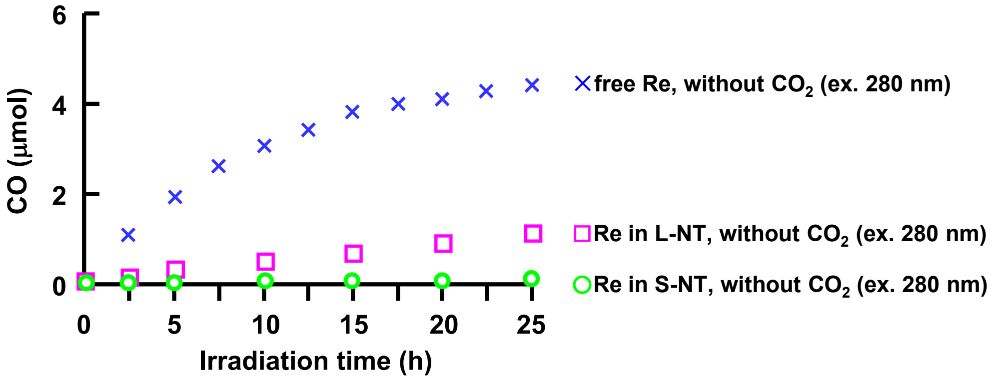
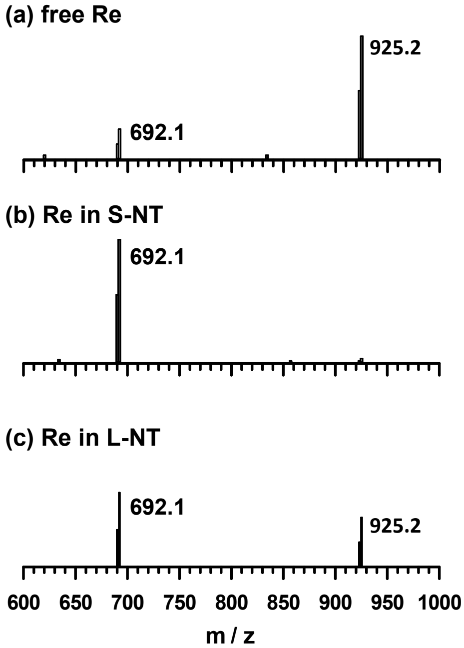


Fig. S10 CO evolution by the dissociation from the Re(I) complex through the UV irradiation at 280 nm without CO_2 in the atmosphere. × free Re(I) complex in the bulk solution; □ the encapsulated Re(I) complex in the L-nanotube; ○ the encapsulated Re(I) complex in the S-nanotube.



692.1: [Re(bipyridine)(CO)$_3$(PPh$_3$)]$^+$
925.2: [Re(bipyridine)(CO)$_2$(PPh$_3$)$_2$]$^+$

Fig. S11 Positive-mode electrospray ionization mass spectra of (a) the free Re(I) complex, (b) the encapsulated Re(I) complex in the S-nanotube and (c) the encapsulated Re(I) complex in the L-nanotube after UV irradiation at 280 nm for 25 h.