

Supporting information

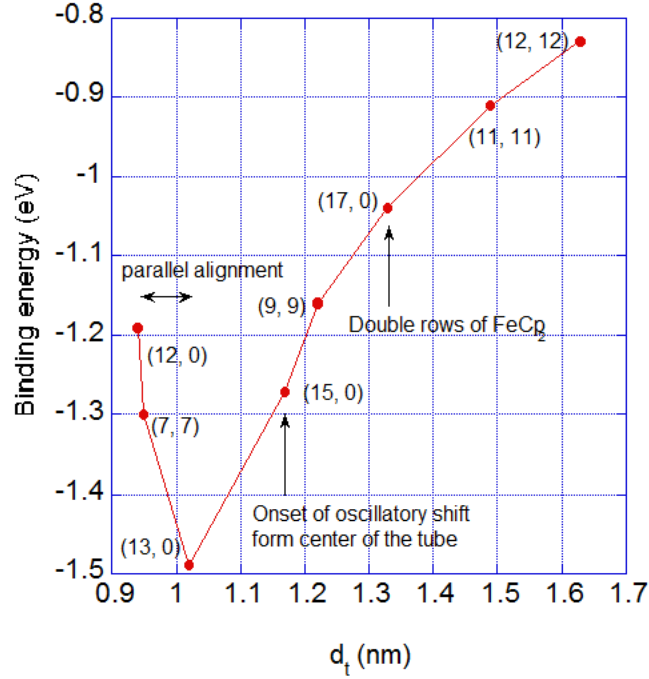
## **Diameter Selective Electron Transfer from Encapsulating Ferrocenes to Single-Walled Carbon Nanotubes**

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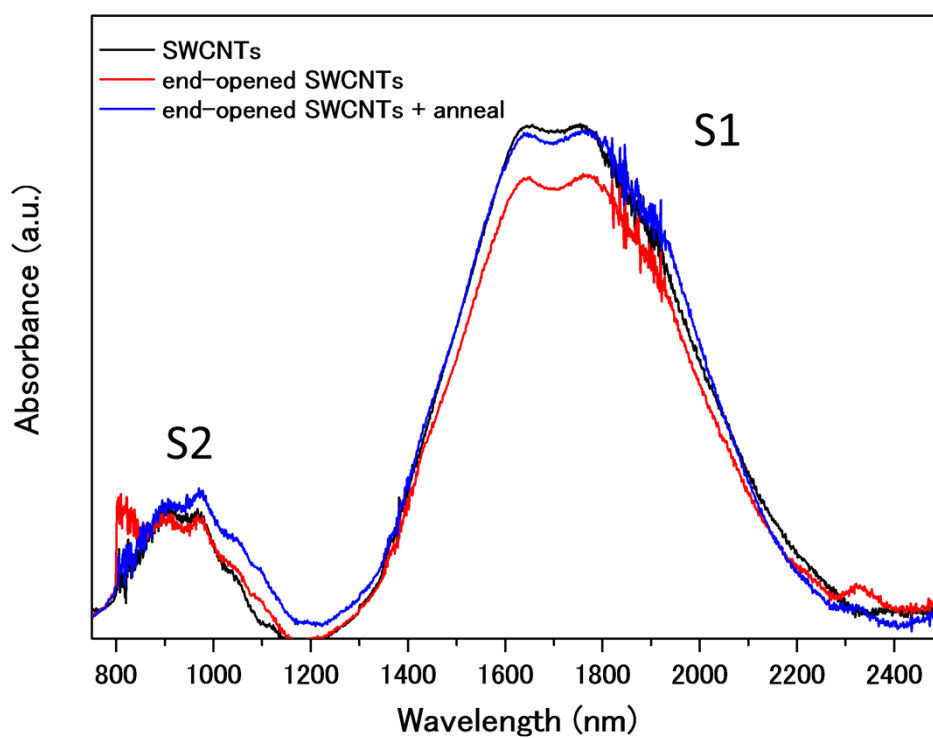
## 1. Previously reported calculated binding energies of FeCp<sub>2</sub>@SWCNTs<sup>1</sup>



**Figure S1.** Calculated binding energies as a function of tube diameter. The binding energy was calculated as  $E_B = E_{\text{FeCp}_2@\text{SWCNTs}} - E_{\text{SWCNTs}} - E_{\text{FeCp}_2}$ , where  $E_{\text{FeCp}_2@\text{SWCNTs}}$ ,  $E_{\text{SWCNTs}}$ , and  $E_{\text{FeCp}_2}$  were the energies for FeCp<sub>2</sub>@SWCNTs, the SWCNTs, and FeCp<sub>2</sub>, respectively. The details are described in reference 1.

## 2. End-opening effect on the electronic state of SWCNTs

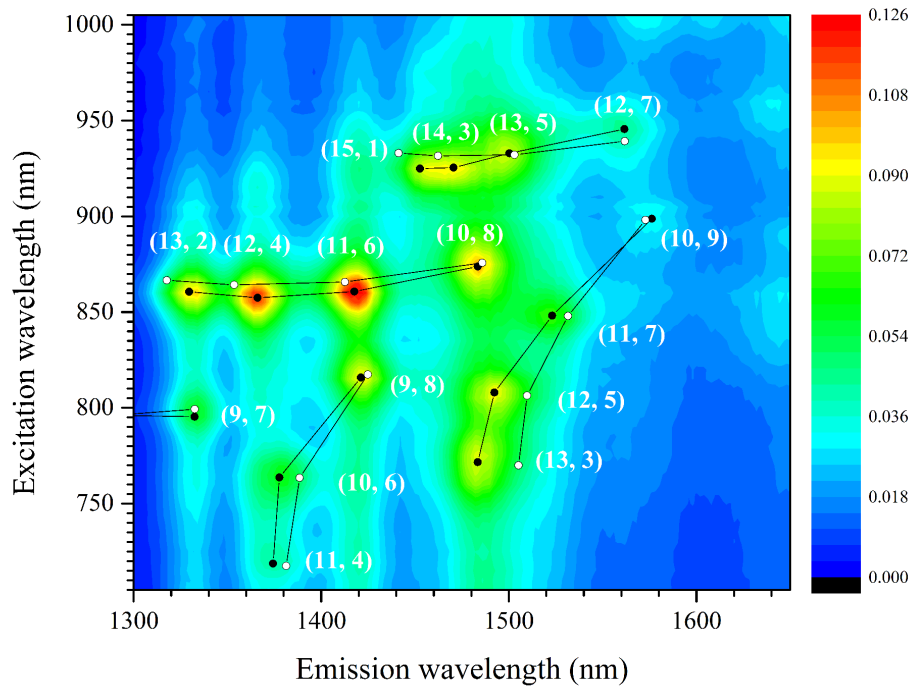
The SWCNTs used here were annealed to remove impurities under vacuum after the end-opening processes, which may have weakened the doping effects in the original SWCNTs. To check the doping level of the original SWCNTs used here (before encapsulation), we measured the absorption spectra of the original SWCNTs before and after vacuum annealing process. A Shimadzu UV3150 was used for the optical absorption measurements. As clearly seen in Fig. S2, the intensity of the S1 absorption decreases after the tube opening process, and returns to the almost original position by the vacuum annealing process. This means that our SWCNTs were not p-doped very much.



**Figure S2.** Optical absorption spectra of end-opened SWCNTs thin films before and after vacuum annealing processes. The signal intensities were normalized by the heights of the S2 transition peaks.

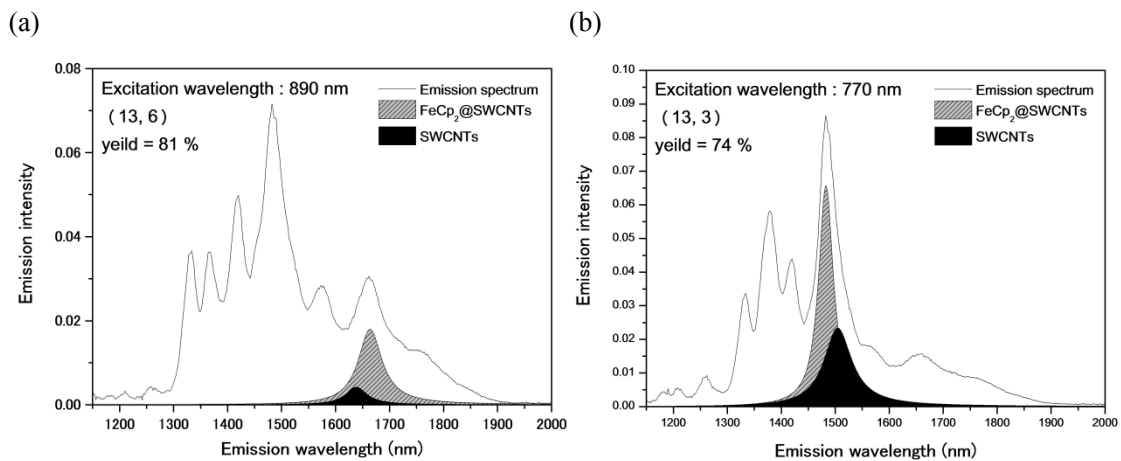
### 3. Expanded view of PL contour map of FeCp<sub>2</sub>@SWCNTs in SDBS-D<sub>2</sub>O

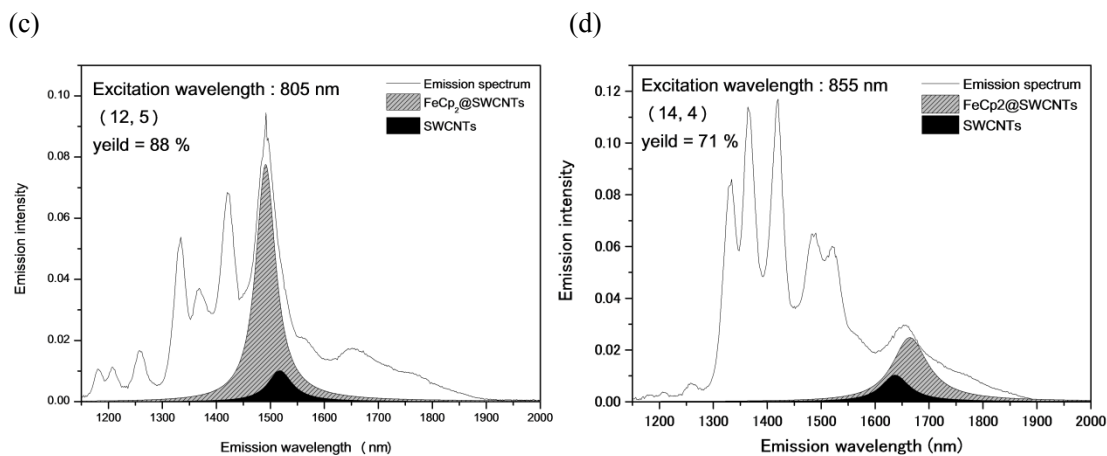
Figure S3 shows an expanded view of Fig. 2(b). Clearly, the PL peak shifted upon the encapsulation of FeCp<sub>2</sub> for SWCNTs with  $d_t > 0.92$  nm.



**Figure S3.** Expanded view of PL contour map of FeCp<sub>2</sub>@SWCNTs in SDBS-D<sub>2</sub>O (Fig. 2(b)). The black and white circles denote the PL peak positions of each (*n*, *m*) FeCp<sub>2</sub>@SWCNTs and the SWCNT control sample.

The filling yield of FeCp<sub>2</sub> in SWCNTs was estimated as ~80 % from the relative intensity of the PL peaks of the filled and the empty (12, 5), (13, 3), (13, 6) and (14, 4) SWCNTs (Figs. S3 and S4). We selected these SWCNTs for the analysis because the PL peak positions of the filled SWCNTs are substantially shifted from the empty ones (Fig. S3).

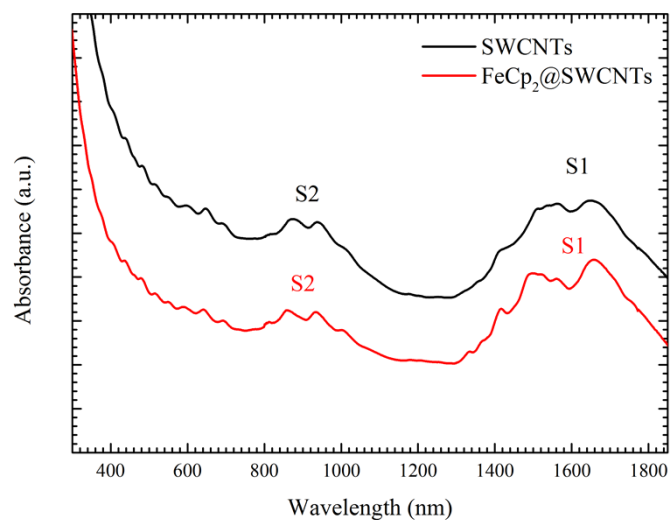




**Figure S4.** Peak fitting analyses of the observed PL peaks of the filled and the empty (12, 5), (13, 3), (13, 6) and (14, 4) SWCNTs.

#### 4. Optical absorption spectra of FeCp<sub>2</sub>@SWCNTs micelle solution

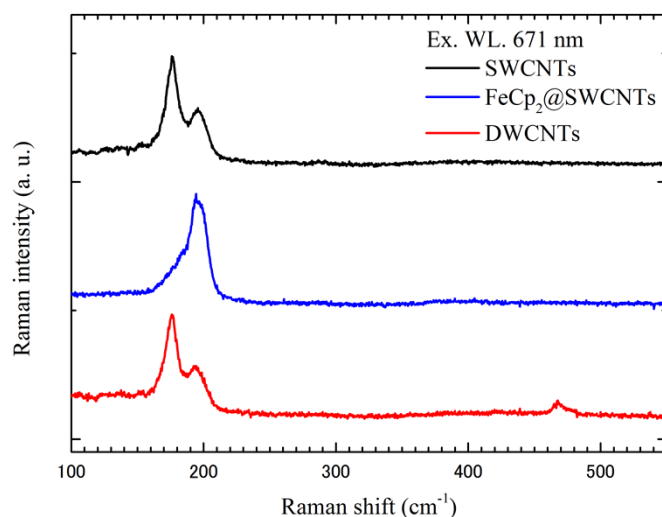
Figure S5 shows the optical absorption spectra of FeCp<sub>2</sub>@SWCNTs and the SWCNTs control sample in SDBS-D<sub>2</sub>O. The spectral shape of the FeCp<sub>2</sub>@SWCNTs trace was very similar to that of the SWCNTs.



**Figure S5.** Optical absorption spectrum of FeCp<sub>2</sub>@SWCNTs in SDBS-D<sub>2</sub>O, together with a spectrum of the SWCNT control sample.

## 5. Resonance Raman measurements

Figure S6 shows the resonance Raman spectra of the control SWCNTs sample, the FeCp<sub>2</sub>@SWCNTs, and the FeCp<sub>2</sub>@SWCNT-derived double-walled carbon nanotubes (DWCNTs). DWCNTs were synthesized by annealing the FeCp<sub>2</sub>@SWCNTs at 1150°C for 1 h. Resonance Raman spectroscopy was conducted with a Horiba JY T64000 system. The excitation wavelength was 671 nm. In this region, the radial breathing mode (RBM) of SWCNTs was observed. The RBM peak at ~470 cm<sup>-1</sup> was clearly seen in the Raman spectrum of DWCNTs (red line), which could be assigned to the produced inner shell of the DWCNTs. The observation of the RBM peak of the inner shell was evidence for FeCp<sub>2</sub> encapsulation. For the Raman measurements, we used thin films of the SWCNTs (so-called “back papers”).



**Figure S6.** Resonance Raman spectra of SWCNTs (black), FeCp<sub>2</sub>@SWCNTs (blue), and FeCp<sub>2</sub>@SWCNTs-derived DWCNTs (red).

## Supporting Information References

1. Plank, W.; Pfeiffer, R.; Schaman, C.; Kuzmany, H.; Calvaresi, M.; Zerbetto, F.; Meyer, J. *ACS Nano*, **2010**, *4*, 4515–4522.