Electronic Supplementary Information (ESI)

Near Infrared Photoluminescence Modulation by Defect Site Design Using Aryl Isomers in Locally Functionalized Single-walled Carbon Nanotubes

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Materials

The SWNTs (CoMoCAT (6,5) rich) were purchased from SouthWest Nanotechnologies. Acetonitrile, diethyl ether, and *m*-nitroaniline were purchased from Wako Pure Chemical Industries, Ltd. Sodium dodecyl benzene sulfonate (SDBS), 2-nitroaniline, *p*-toluidine, *m*-toluidine, *o*-toluidine, *m*-anisidine, *o*-anisidine, 3,5-dinitroaniline, *N*,*N*-diethyl-1,4-phenylenediamine, and 4-nitrobenzenediazonium tetrafluoroborate were obtained from the Tokyo Chemical Industry Co. Tetrafluoroboric acid (48 wt.% aqueous solution), nitrosonium tetrafluoroborate (NOBF₄), 4-bromobenzenediazonium tetrafluoroborate, and 4-methoxybenzenediazonium tetrafluoroborate were purchased from the Sigma-Aldrich Co. D₂O, 3-bromoaniline, and sodium nitrite (NaNO₂) were purchased from Cambridge Isotope Laboratories, Alfa Aesar, Nacalai tesque, Inc., respectively. All chemicals were used as received.

Instruments

The ¹H and ¹³C NMR spectra were recorded using a Bruker AV300m spectrometer (300 MHz). The high-resolution electrospray mass measurements (HR-ESI-MS) were carried out using a Bruker MicroTOF-QIII electrospray ionization time-of-flight (ESI-TOF) mass spectrometer equipped with a CryoSpray source unit. The UV/vis/NIR and PL together with the 2D PL mapping spectra were measured using a V-670 (JASCO) and a HOLIBA JOBIN YVON spectrofluorometer (FluorologR-3 with FluorEssence), respectively. The Raman spectra (excitation at 532 nm) were recorded by a RAMANtouch spectrometer (Nanophoton Corporation). Quartz cells with a 1-cm path length were used for the optical measurements. MilliQ water was prepared by an ultrapure water system equipped with an Elix-5 kit (Millipore Co.). For preparation of the SWNT solutions, a bath-type sonicator (AS ONE, US-1R), a tip-type sonicator (MISONIX, XL-2000) and an ultracentrifuge (Hitachi, himac CS 100 GXL) were used. A magnetic stirrer with a cooling function (Nissinrika, Co., SWC-L20) was used for the synthesis of the diazonium salts in acetonitrile. The density functional theory (DFT) calculation was performed using Gaussian 09W based on the B3LYP 6-31G++ level.

Synthesis

Synthesis of diazonium salts were carried out in water^[1] or acetonitrile^[2] based on consideration of their solubility and stability. Typical procedures are described as follows.

Synthesis in water (for 3,5-NO₂-Dz, pCH_3 -Dz, $pN(C_2H_5)_2$ -Dz, mNO_2 -Dz, mCH_3 -Dz, mBr-Dz, oNO_2 -Dz, and oBr-Dz): Each aniline derivative (0.485 mmol) was mixed with 0.27 mL aq. HBF₄ and 0.30 mL water in a 10-mL round flask. The solution was cooled in an ice bath, then an aqueous solution (0.20 mL) of NaNO₂ (0.971 mmol) was dropwise added. After a 120-min stirring, the resultant precipitate was collected by filtration and washed with cold water, then with diethyl ether. The obtained product was dried in vacuo to provide a colorless solid. Synthesis in acetonitrile (for mCl-Dz, oCH₃-Dz,and mOCH₃-Dz): To a 50-mL two-neck flask, each aniline derivative (2.42 mmol) and 12 mL of acetonitrile were added and cooled at -21 °C using a magnetic stirrer with a cooling function. NOBF₄ (2.69 mmol) was dissolved in 5 mL of acetonitrile and cooled in an ice bath, then dropwise injected to the aniline derivative solution. After a 1-h stirring, the temperature was raised to 0 °C and the solution was poured into 100 mL of diethyl ether to produce precipitates, which were collected by filtration, then washed with cold water and then with diethyl ether. After drying in vacuo, a colorless solid was obtained.

<u>3,5-NO₂-Dz</u>: Yield 49%. ¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 9.6 (s, 2H), 9.5 (s, 1H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₆H₃N₄O₄⁺: 195.0149, found: 195.0193; FT-IR: v/cm⁻¹ = 2319 (N=N).

<u>pCH₃-Dz</u>: Yield 8%. ¹H NMR (300 MHz, DMSO-d₆) δ /ppm = 8.6 (d, 2H), 7.8 (d, 2H), 2.3 (s, 3H); ¹⁹F NMR (300 MHz, DMSO-d₆) δ /ppm = -149; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₇H₇N₂⁺: 119.0604, found: 119.0607; FT-IR: v/cm⁻¹ = 2290 (N=N).

<u>*p*N(C₂H₅)₂-Dz</u>: Yield 47%. ¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 8.0 (d, 2H), 6.9 (d, 2H), 1.9 (q, 4H), 1.3 (t, 6H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = −151; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₁₀H₁₄N₃⁺: 176.1182, found: 176.1179; FT-IR: v/cm⁻¹ = 2155 (N≡N).

<u>mNO₂-Dz</u>: Yield 55%. ¹H NMR (300 MHz, DMSO-d₆) δ /ppm = 9.6 (s, 1H), 9.0 (m, 2H), 8.3 (t, 1H); ¹⁹F NMR (300 MHz, DMSO-d₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₆H₄N₃ O₂⁺: 150.0298, found: 150.0317; FT-IR: v/cm⁻¹ = 2306 (N=N).

<u>mCH₃-Dz</u>: Yield 13%. ¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 7.3 (t, 1H), 7.2 (d, 1H), 7.15 (s, 1H), 7.1 (d, 1H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [[M]⁺ = C₇H₇N₂⁺: 119.0604, found: 119.0603; FT-IR: v/cm⁻¹ = 2300 (N=N).

<u>mBr-Dz</u>: Yield 28%.¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 8.6 (d, 1H), 8.5 (d, 1H), 8.4 (t, 1H), 7.8 (s, 1H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [[M]⁺ = C₆H₄BrN₂⁺: 182.9552, found: 182.9547; FT-IR: v/cm⁻¹ = 2306 (N=N).

<u>oNO₂-Dz</u>: Yield 18%.¹H NMR (300 MHz, DMSO-d₆) δ /ppm = 9.1 (d, 1H), 8.8 (d, 1H), 8.5 (t, 1H), 8.4 (t, 1H); ¹⁹F NMR (300 MHz, DMSO-d₆) δ /ppm = -149; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₆H₄N₃ O₂⁺: 150.0298, found: 150.0307; FT-IR: v/cm⁻¹ = 2294 (N=N).

<u>oBr-Dz</u>: Yield 28%.¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 8.6 (d, 1H), 8.1 (d, 1H), 7.9 (m, 2H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [[M]⁺ = C₆H₄BrN₂⁺: 182.9552, found: 182.9555; FT-IR: v/cm⁻¹ = 2291 (N=N).

<u>mCl-Dz</u>: Yield 60%.¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 8.5 (s, 1H), 8.3 (m, 2H), 7.9 (t, 1H), 7.8 (s, 1H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -152; HR-ESI-MS *m/z* calcd. for cationic moiety [[M]⁺ = C₆H₄ClN₂⁺: 139.0058, found: 139.0060; FT-IR: v/cm⁻¹ = 2309 (N=N).

<u>oCH₃-Dz</u>: Yield 13%. ¹H NMR (300 MHz, DMSO-d₆) δ /ppm = 7.3-7.0 (m, 4H), 3.5 (s, 3H); ¹⁹F NMR (300 MHz, DMSO-d₆) δ /ppm = -149; HR-ESI-MS *m/z* calcd. for cationic moiety [M]⁺ = C₇H₇N₂⁺:

119.0604, found: 119.0590; FT-IR: $v/cm^{-1} = 2285$ (N=N).

<u>mOCH₃-Dz</u>: Yield 47%.¹H NMR (300 MHz, CD₃CN₆) δ /ppm = 8.1 (d, 1H), 7.9 (t, 1H), 7.8 (m, 2H), 3.9 (s, 3H); ¹⁹F NMR (300 MHz, CD₃CN₆) δ /ppm = -151; HR-ESI-MS *m/z* calcd. for cationic moiety [[M]⁺ = C₇H₇N₂O⁺: 135.0553, found: 135.0054; FT-IR: v/cm⁻¹ = 2304 (N=N).



Chart S1 Chemical structures of (a) synthesized and (b) purchased diazonium salts.



Fig. S1 PL peak wavelengths of E_{11}^* (black circle) and E_{11} (red square) as a function of the concentration of *m*Br-Dz for the synthesis of the lf-SWNTs-*m*Br.



Fig. S2 The ratios of I_G/I_D of lf-SWNTs-*m*Br calculated from the Raman spectra as a function of the concentrations of *m*Br-Dz for synthesis of the lf-SWNTs-*m*Br.



Fig. S3 Vis/NIR absorption spectra of lf-SWNTs-*m*Br (black solid line) and the pristine SWNTs (red dotted line) in D_2O containing 0.20 wt% SDBS. The concentration of *m*Br-Dz was 2.5 µg/mL for the synthesis of the lf-SWNTs-*m*Br.



Fig. S4 Excitation spectra of E_{11}^* PL of lf-SWNTs-*m*Br (black solid line) and lf-SWNTs-*p*Br (red dotted line).



Fig. S5 PL spectra of lf-SWNTs-*p*Br (black solid line) and the pristine SWNTs (red dotted line) in D₂O containing 0.20 wt% SDBS. The concentration of *p*Br-Dz was 2.5 μ g/mL for the synthesis of the lf-SWNTs-*p*Br. $\lambda_{ex} = 570$ nm.



Fig. S6 Plot of the ΔE in units of nm as a function of the σ values of the substituents in the aryl groups introduced on lf-SWNTs-*i*X. The data points are shown using black circles for the lf-SWNTs-*p*X and red squares for the lf-SWNTs-*m*X with legends representing the substituents. The black straight line was obtained by a linear approximation method using all the synthesized lf-SWNTs-*p*X (see Fig. S7).



Fig. S7 Plots of the ΔE in units of (a) meV and (b) nm as a function of the σ values of the substituents in the aryl groups introduced on If-SWNTs-*p*X, in which the straight line was obtained by a linear approximation method (R² = (a) 0.995 and (b) 0.997).



Fig. S8 Calculated dipole moments of the *m*Br and *p*Br whose magnitudes were 2.44 and 2.60 Debye, respectively. The DFT calculation based on the B3LYP 6-31G++ level was conducted and these simplified models have a methyl group as the sp³ carbon on the defect site of the lf-SWNTs.



Fig. S9 PL spectra of lf-SWNTs-oNO₂ (blue line) and lf-SWNTs-oCH₃ (green line) synthesized with $[oX-Dz] = 2.5 \ \mu$ g/mL in D₂O containing 0.20 wt% SDBS. $\lambda_{ex} = 570 \text{ nm}$.



Fig. S10 Vis/NIR absorption spectra of lf-SWNTs-oBr (solid line) and pristine SWNTs (dotted line) in D₂O containing 0.20 wt% SDBS. The concentration of oBr-Dz was 2.5 µg/mL for the synthesis of the lf-SWNTs-oBr.



Fig. S11 Excitation spectra of lf-SWNTs-*o*Br measured at 1143-nm and 1279-nm emission wavelengths (black and red lines, respectively).



Fig. S12 The ratios of I_G/I_D of lf-SWNTs-*o*Br calculated from the Raman spectra as a function of the concentration of *o*Br-Dz for the synthesis of the lf-SWNTs-*o*Br.



Fig. S13 XPS spectra of the Br 3d for the SWNTs reacted with *o*Br-Dz (black line) and the pristine SWNTs treated by mixing with *o*-bromoaniline followed by washing through a filtration process (blue line). The measured samples were the solid states of the SWNTs collected by filtration.

References for ESI

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[2] R. Polsky, J. C. Harper, D. R. Wheeler, D. C. Arango, S. M. Brozik, *Angew. Chem. Int. Ed.* 2008, 47, 2631-2634.