Supporting Information

Molecularly Tunable Fluorescent Quantum Defects

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Figure S1. Nanotube structure-dependent defect photoluminescence. The excitation-emission maps of (a), (6,5)-SWCNT; (b), (8,3)- and (8,4)-SWCNT; (c), (7,6)- and (8,4)-enriched SWCNTs; and (d), the mixed chirality of HiPco. Controlled sidewall alkylation induces new PL peaks (marked by *) in (e), (6,5)-SWCNT-CF₂(CF₂)₄CF₃; (f), (8,3)/(8,4)-SWCNT-CF₂(CF₂)₄CF₃; (g), (7,6)/(8,4)-SWCNT-CF₂(CF₂)₄CF₃; and (h), the mixed chirality of HiPco-SWCNT-CF₂(CF₂)₄CF₃. The nanotubes are stabilized in D₂O by 1 wt.% SDS.

Figure S2. Nanotube structure-dependent defect photoluminescence. Emission energy of defect photoluminescence is dependent on the nanotube diameter. All chirality-enriched carbon nanotubes used here are functionalized with -C₆F₁₃ groups.
Figure S3. Brightening of nanotube defect photoluminescence. (a) Exitation-emission map of pristine CoMoCAT (6,5)-SWCNT. (b) Excitation-emission map of CoMoCAT (6,5)-SWCNT-C₆F₁₃. (c) Emission spectra at 565 nm excitation. (d) UV-vis-NIR absorption spectra.
Figure S4. Correlated spectral characterization of functionalized SWCNTs at increasing molar reactant ratios of CF₃(CF₂)₄CF₂I (RX) to the mixed chirality of HiPco SWCNT carbon. (a) Raman scattering. The excitation line is 532 nm. (b) XPS (taken at 25 °C). The O1s peak is marked with an asterisk (*). (c) Photoluminescence. (d) The ratio of covalently attached function group to nanotube carbon, [R]/[C], as determined from XPS, increases linearly with the reactant ratio, [RX]/[C]. (e) Raman D/G ratio of SWCNT-CF₂(CF₂)₄CF₃ at increasing [RX]/[C].
Figure S5. High resolution XPS of C 1s at 175 °C for SWCNT-CF$_2$(CF$_2$)$_4$CF$_3$. (a) Non-functionalized control. (b), [C]:[RX]=1:50. (c), [C]:[RX]=1:500. (d), [C]:[RX]=1:2500. The nanotubes used here are a sample of mixed chirality HiPco SWCNTs.

Figure S6. High resolution XPS of F 1s at 175 °C for SWCNT-CF$_2$(CF$_2$)$_4$CF$_3$. (a) Non-functionalized control. (b), [C]:[RX]=1:50. (c) [C]:[RX]=1:500. (d), [C]:[RX]=1:2500. The nanotubes used here are a sample of mixed chirality HiPco SWCNTs.
Figure S7. Tunable defect photoluminescence from (6,5)-SWCNTs with (a) six-carbon alkyl chains, (b) monovalent and divalent alkyl groups, and (c) monovalent and divalent aryl groups. The emission spectra were taken at 565 nm and the peak intensity was normalized by the peak intensity of the defect PL. Note that the asterisked (*) sidebands may be due to trapped trions\textsuperscript{1}. 
Table S1. Alkyl/aryl halides used in this study and their defect photoluminescence.

| (6,5)-SWCNT-R | $E_{11}$ (nm) | $E_{11}'$ (nm) | $\Delta E$ (meV) | Source of Precursor | -X |
|---------------|--------------|--------------|---------------|------------------|---|
| Non-functionalized | 979 | - | - | - | - |
| $-{\text{CH}}_3$ | 980 | 1094 | 132 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_3$ | 984 | 1099 | 132 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | 981 | 1096 | 133 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ | 980 | 1097 | 135 | Sigma Aldrich | Br |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3$ | 980 | 1099 | 137 | Oakwood chemical | I |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ | 980 | 1102 | 140 | Sigma Aldrich | Br |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CF}_3$ | 981 | 1101 | 140 | Santa Cruz Biotech. | I |
| $-{\text{CH}}_2\text{CH}_2\text{CH}_2\text{CF}_3$ | 979 | 1104 | 143 | Aurum Pharmatech LLC. | I |
| $-{\text{CH}}_2\text{CF}_3$ | 981 | 1110 | 147 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1107 | 146 | Matrix Scientific | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1111 | 150 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1111 | 152 | Pfaltz and bauer | I |
| $-{\text{CH}}_2\text{(12C)}$ | 980 | 1121 | 159 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{(13C)}$ | 984 | 1127 | 160 | AstaTech, Inc. | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 979 | 1121 | 160 | Enamine LLC | I |
| $-{\text{CH}}_2\text{(12C)}$ | 979 | 1125 | 164 | Sigma Aldrich | I_2 |
| $-{\text{CH}}_2\text{(13C)}$ | 980 | 1125 | 163 | Cambridge Isotope | I_2 |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 979 | 1125 | 164 | Hit2lead | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1129 | 168 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1131 | 169 | TCI | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1133 | 171 | Spectra Group Limited Inc | I_2 |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 983 | 1137 | 170 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 983 | 1139 | 173 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 979 | 1138 | 177 | Sigma Aldrich | I |
| $-{\text{CH}}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 980 | 1145 | 182 | Combiphos catalysts, INC | I |
| $-{\text{CF}}_3$ | 979 | 1152 | 190 | Sigma Aldrich | I |
| $-{\text{CF}}_3$ | 986 | 1162 | 190 | Sigma Aldrich | I_2 |
| $-{\text{CF}}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 981 | 1155 | 190 | Sigma Aldrich | I |
| $-{\text{CF}}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 979 | 1155 | 193 | Sigma Aldrich | I |
| $-{\text{CF}}_2$ | 980 | 1158 | 194 | Sigma Aldrich | I |
| $-{\text{CF}}_2$ | 980 | 1164 | 200 | SynQuest Lab | I_2 |
Figure S8. PL energy shifts versus calculated inductive constant ($\sigma^*$). (a) -($CH_2)_nCF_3 (n = 0-5). (b), $C_6H_{13-n}F_n (n=0, 3, 5, 9, and 13). (c) The combined graph of (a) and (b).

Figure S9. Distribution of Mulliken charges in (6,5)-SWCNTs with a single monovalent defect (left) and the relative energy diagrams of (6,5)-SWCNTs with two monovalent defects (right). (a) CH$_3$. (b) CF$_3$. Note that the most thermodynamically stable structure of methyl functionalized (6,5)-SWCNT is 1,4-para position (m), where the Mulliken charges were highly negative.
Table S2. Orbital energies of simulated structures. Note that all conformations of (6,5)-SWCNT-(CF3)n (n=1, 2) produce larger shifts in emission energy (E11-E11') compared to their respective -CH3 defects.

| Model  | EHOMO-1 (eV) | EHOMO (eV) | E_LUMO (eV) | E_LUMO-1 (eV) | EHOMO* (eV) | E_LUMO* (eV) | E_LUMO-1* (eV) | E11-E11' (meV) |
|--------|--------------|------------|-------------|---------------|-------------|-------------|---------------|----------------|
| pristine | -4.603       | -4.593     | -3.001      | -3.000        | 1.592       | 1.603       | -             |
| k_CH3  | -4.599       | -4.488     | -3.196      | -2.956        | 1.292       | 1.643       | 351           |
| l_CH3  | -4.599       | -4.534     | -3.032      | -2.947        | 1.503       | 1.652       | 149           |
| m_CH3  | -4.614       | -4.520     | -3.103      | -2.941        | 1.417       | 1.672       | 256           |
| o_CH3  | -4.598       | -4.459     | -3.176      | -2.949        | 1.283       | 1.649       | 366           |
| k_CF3  | -4.634       | -4.542     | -3.308      | -2.993        | 1.234       | 1.641       | 407           |
| l_CF3  | -4.633       | -4.592     | -3.118      | -2.988        | 1.474       | 1.645       | 171           |
| m_CF3  | -4.644       | -4.573     | -3.207      | -2.979        | 1.366       | 1.664       | 298           |
| o_CF3  | -4.607       | -4.470     | -3.192      | -2.957        | 1.278       | 1.650       | 372           |

Figure S10. Bond lengths of (6,5)-SWCNT ›CH2. C-C bond length around the ›CH2 defect is slightly longer than that in the pristine SWCNT (1.42 Å). The circumferential C-C bond at the defect site is increased to 2.17 Å and thus is broken to adopt an opened three-membered ring.
Figure S11. Distribution of Mulliken charges in (6,5)-SWCNTs with single divalent defect (left) and the relative energy diagram of (6,5)-SWCNTs with two divalent defects (right). (a) ›CH₂. (b) ›CF₂.
Figure S12. Frontier orbitals of non-functionalized control and (6,5)-SWCNTs with a covalently attached single ›CH₂, -CH₃, ›CF₂, and -CF₃ group. The HOMOs and LUMOs were plotted at their iso-surface equal to 0.003.
**Time-Dependent DFT Calculations**

The electronically excited states can be described in terms of excitation amplitudes based on a set of ground state orbitals. For example, in the time-dependent density functional theory-based approach\(^2\)-\(^{10}\) the excited states are derived from density functional theory ground states. Here the random phase approximation expands the reference states to the many electron space consisting of all single particle-hole excitations. The end result of such a calculation is an excitation energy and a set of coefficients (excitation amplitudes) describing the contribution that each electron-hole pair makes to the excited state.

Here we focus on the absorption spectra of two aryl-based functionalizations of (6,5)-SWCNT. The functionalization patterns (Figure S13 left panel) are chosen to be generally relevant to the functionalization discussed in this work. For this task, we employed the asymptotically corrected wB97XD functional of Chai and Head-Gordon\(^{11}\) which has a 100% fraction of the HF exchange at long-range and about 22% at short-range and incorporates empirical dispersion corrections. The STO-3G basis set was used in the TD-DFT calculations. The lowest 44 excited-state transition energies and their respective oscillator strengths were computed. The absorption spectra were further simulated using a Gaussian line shape with empirical line-broadening parameters to mimic various broadening effects occurring under experimental conditions.

The incorporation of aryl groups leads to brightening of the lowest energy exciton a (Figure S13 right panel) that is optically dark for the pristine (6,5)-SWCNT. The red-shifts of the lowest state upon covalent functionalization, as well as brightening of this transition observed in simulated absorption spectrum could be associated with the experimentally observed E\(_{11}\) peaks in PL spectra. The E\(_{11}\) peak in the absorption spectra of the defect-tailored SWCNTs exhibits a blue shift and is broadened compared to the pristine SWCNT.

Except structure II, the rest of the structures show dominance of ground state HOMO→LUMO transitions contributing to the lowest energy exciton as assigned in Table S3. The energy and the oscillator strength of the lowest energy transition are sensitive to the atomic configuration of the defect. Both degree of brightening (Figure S13 right panel) and localization of HOMO/LUMO orbitals (Figure S14) are also strongly dependent on the functionalization pattern.
Figure S13. Configurations of aryl defect-tailored (6,5)-SWCNT (left panel) and corresponding absorption spectra (right panel). Configurations I and III in this picture correspond to configurations k and n in Figure S9b, correspondingly. Spectra calculated for pristine (6,5)-SWCNT (dotted blue line) and various aryl defect-tailored (6,5)-SWCNT (solid red line).
Table S3. Contributions of ground state orbitals to excitonic transitions assigned in Figure S13.

| Structure label | Excitation energy, eV | Peak label | Type of orbitals | Contribution of ground state orbitals to excitation |
|----------------|-----------------------|------------|------------------|--------------------------------------------------|
| I              | 1.838                 | a          | HOMO-2 → LUMO    | 0.25                                             |
|                |                       |            | HOMO-2 → LUMO+2  | 0.22                                             |
|                |                       |            | HOMO-1 → LUMO    | -0.18                                            |
|                |                       |            | HOMO-1 → LUMO+1  | -0.13                                            |
|                |                       |            | HOMO → LUMO      | 0.49                                             |
|                | 2.4619                | b          | HOMO-7 → LUMO+1  | 0.10                                             |
|                |                       |            | HOMO-6 → LUMO    | -0.22                                            |
|                |                       |            | HOMO-5 → LUMO+2  | -0.11                                            |
|                |                       |            | HOMO-3 → LUMO+2  | -0.16                                            |
|                |                       |            | HOMO-3 → LUMO+3  | 0.28                                             |
|                |                       |            | HOMO-2 → LUMO+3  | 0.17                                             |
|                |                       |            | HOMO-1 → LUMO+4  | -0.11                                            |
|                |                       |            | HOMO → LUMO+6    | -0.21                                            |
| III            | 1.3447                | a          | HOMO → LUMO      | 0.65                                             |
|                | 1.9326                | b          | HOMO-2 → LUMO    | 0.10                                             |
|                |                       |            | HOMO-2 → LUMO+1  | -0.15                                            |
|                |                       |            | HOMO-1 → LUMO    | -0.21                                            |
|                |                       |            | HOMO-1 → LUMO+1  | 0.45                                             |
|                |                       |            | HOMO-1 → LUMO+2  | 0.22                                             |
|                |                       |            | HOMO-1 → LUMO+3  | -0.13                                            |
|                |                       |            | HOMO → LUMO+1    | -0.16                                            |
|                |                       |            | HOMO → LUMO+2    | -0.20                                            |
|                | 2.3372                | c          | HOMO-11 → LUMO   | 0.11                                             |
|                |                       |            | HOMO-6 → LUMO    | 0.20                                             |
|                |                       |            | HOMO-6 → LUMO+1  | -0.11                                            |
|                |                       |            | HOMO-4 → LUMO    | 0.10                                             |
|                |                       |            | HOMO-4 → LUMO+4  | -0.14                                            |
|                |                       |            | HOMO-3 → LUMO+3  | -0.13                                            |
|                |                       |            | HOMO-3 → LUMO+4  | 0.22                                             |
|                |                       |            | HOMO-2 → LUMO+1  | 0.16                                             |
|                |                       |            | HOMO-2 → LUMO+2  | -0.17                                            |
|                |                       |            | HOMO-2 → LUMO+3  | -0.11                                            |
|                |                       |            | HOMO-1 → LUMO    | -0.17                                            |
|                |                       |            | HOMO-1 → LUMO+2  | -0.14                                            |
|                |                       |            | HOMO-1 → LUMO+3  | 0.12                                             |
|                |                       |            | HOMO → HOMO-2    | 0.15                                             |
| IV             | 1.1683                | a          | HOMO-1 → LUMO    | -0.22                                            |
| Energy | 1.8183 b | 2.3075 c | 1.6751 a | 2.016 b | 2.1912 c | 2.3743 d |
|--------|-----------|-----------|-----------|----------|-----------|----------|
| **HOMO→LUMO** | 0.63 | 0.14 | 0.11 | -0.41 | -0.14 | -0.11 |
| **HOMO→LUMO+1** | 0.12 | -0.13 | 0.11 | 0.13 | 0.17 | 0.10 |
| **HOMO-5 → LUMO** | 0.11 | -0.13 | | | | |
| **HOMO-5 → LUMO+5** | 0.13 | | | | | |
| **HOMO-1 → LUMO** | -0.24 | | | | | |
| **HOMO-1 → LUMO+1** | 0.48 | | | | | |
| **HOMO → LUMO** | -0.13 | | | | | |
| **HOMO → LUMO+1** | 0.33 | | | | | |
| **HOMO-5 → LUMO+5** | 0.11 | | | | | |
| **HOMO-4 → LUMO+2** | 0.13 | | | | | |
| **HOMO-4 → LUMO+4** | -0.17 | | | | | |
| **HOMO-3 → LUMO** | -0.10 | | | | | |
| **HOMO-2 → LUMO+2** | 0.44 | | | | | |
| **HOMO-2 → LUMO+4** | -0.18 | | | | | |
| **HOMO-1 → LUMO+5** | -0.12 | | | | | |
| **HOMO-6 → LUMO** | -0.12 | | | | | |
| **HOMO-6 → LUMO+6** | -0.13 | | | | | |
| **HOMO-5 → LUMO+1** | -0.11 | | | | | |
| **HOMO-4 → LUMO+2** | 0.13 | | | | | |
| **HOMO-3 → LUMO** | -0.13 | | | | | |
| **HOMO-1 → LUMO+2** | -0.11 | | | | | |
| **HOMO → LUMO+1** | 0.37 | | | | | |
| **HOMO → LUMO+2** | 0.12 | | | | | |
| **HOMO → LUMO+3** | 0.12 | | | | | |
| **HOMO → LUMO+5** | 0.36 | | | | | |
| **HOMO → LUMO+6** | -0.13 | | | | | |
| **HOMO-2 → LUMO+1** | -0.41 | | | | | |
| **HOMO-2 → LUMO+2** | 0.47 | | | | | |
| **HOMO-2 → LUMO+5** | 0.13 | | | | | |
| **HOMO-14 → LUMO** | -0.14 | | | | | |
| **HOMO-8 → LUMO** | 0.17 | | | | | |
| **HOMO-4 → LUMO** | 0.26 | | | | | |
| **HOMO-3 → LUMO+1** | 0.12 | | | | | |
| **HOMO-3 → LUMO+2** | 0.11 | | | | | |
| **HOMO-1 → LUMO+4** | -0.13 | | | | | |
| **HOMO-1 → LUMO+5** | 0.11 | | | | | |
| **HOMO → LUMO+2** | -0.26 | | | | | |
| **HOMO → LUMO+6** | 0.17 | | | | | |
| **HOMO → LUMO+7** | -0.20 | | | | | |
| **HOMO-6 → LUMO** | -0.11 | | | | | |
| **HOMO-5 → LUMO+1** | 0.10 | | | | | |
| Energy (eV) | Transition | E (eV) |
|------------|------------|--------|
| a 1.7748   | HOMO-2 → LUMO+18 | -0.12 |
|           | HOMO-1 → LUMO | 0.25  |
|           | HOMO-1 → LUMO+2 | 0.12  |
|           | HOMO → LUMO   | 0.46  |
|           | HOMO → LUMO+1 | -0.32 |
| b 2.1883   | HOMO-6 → LUMO | -0.11 |
|           | HOMO-5 → LUMO | 0.23  |
|           | HOMO-5 → LUMO+1 | -0.18 |
|           | HOMO-4 → LUMO+1 | 0.10  |
|           | HOMO-2 → LUMO | -0.17 |
|           | HOMO-2 → LUMO+1 | 0.16  |
|           | HOMO-2 → LUMO+2 | 0.24  |
|           | HOMO-1 → LUMO+2 | -0.13 |
|           | HOMO-1 → LUMO+5 | 0.15  |
|           | HOMO → LUMO+2 | -0.20 |
|           | HOMO → LUMO+4 | 0.13  |
|           | HOMO → LUMO+5 | 0.17  |
| c 2.3434   | HOMO-7 → LUMO | 0.17  |
|           | HOMO-5 → LUMO+1 | -0.11 |
|           | HOMO-4 → LUMO+1 | -0.17 |
|           | HOMO-4 → LUMO+4 | 0.12  |
|           | HOMO-4 → LUMO+5 | -0.13 |
|           | HOMO-3 → LUMO+3 | 0.35  |
|           | HOMO-1 → LUMO+4 | 0.15  |
|           | HOMO-1 → LUMO+5 | -0.12 |
|           | HOMO → LUMO+7 | -0.12 |
|           | HOMO → LUMO+8 | -0.15 |
| d 2.5177   | HOMO-8 → LUMO | 0.13  |
|           | HOMO-7 → LUMO+2 | 0.15  |
|           | HOMO-7 → LUMO+3 | -0.13 |
|           | HOMO-6 → LUMO+1 | 0.12  |
Figure S14. Functionalization pattern-dependent localization of frontier orbitals. Shown are two aryl functional groups in various atomic configurations in comparison with the non-functionalized structure.
Figure S15. pH-responsive defect photoluminescence. (a) monovalent and (b) divalent aminobenzene-functionalized (6,5)-SWCNTs.

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