Supporting Information

Covalent Decoration onto the Outer Walls of Double Wall Carbon Nanotubes with Perylenediimides: Synthesis, Characterization and Photoinduced Electron Transfer

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Experimental section

Materials and instruments

Ultra Purity DWCNTs (catalog number: XNM-UP-11050, purity > 98%) were purchased from XinNano Materials, Inc. (www.xinnanomaterials.com). All manipulations were carried out under dry argon atmosphere by using standard Schlenck-type techniques. Sample sonication was carried out by using an Elasonic P 300 H sonicator bath (37 kHz). All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. Column chromatography: SiO$_2$ (40-63 µm) TLC plates coated with SiO$_2$ 60F254 were visualized by UV light. NMR spectra were measured with a Bruker AC 300 and with a Bruker TopSpin AV-400 spectrometer. UV-vis and IR spectra were recorded with a Helios Gamma and a Nicolet Impact 400D spectrophotometers, respectively and also IR spectra were obtained on a Fourier Transform IR spectrometer (Avatar 370), in KBr pellets. Fluorescence spectra were recorded with a Perkin Elmer LS 55 and on a Cary Eclipse fluorescence spectrophotometer. Fluorescence quantum efficiencies in solution were measured using N,N'-di(1'-hexylheptyl)perylene-3,4:9,10-tetracarboxidiimide internal reference. Mass spectra were obtained from a Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) and from a VOYAGER DETM STR mass spectrometer (MALDI-TOF) using dithranol as matrix. Raman spectra were performed on Renishaw inVia Raman microscope at room temperature with two different exciting laser sources ($\lambda = 532$ and 785 cm$^{-1}$). Measurements were taken with 10 s of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 100× objective. Raman spectra were collected on numerous spots on the sample and recorded with a Peltier cooled CCD camera. The intensity ratio I$_D$/I$_G$ was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software. The thermogravimetric analysis was performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo.
collected under inert atmosphere of nitrogen, with a rate of 10°C min⁻¹, and the weight changes were recorded as a function of temperature. TEM observations were carried out using TOPCON002B (Topcon CO.) at an acceleration voltage of 120 kV. AFM images were acquired in tapping mode using a Multimode V8.10 (Veeco Instruments Inc., Santa Barbara, USA) with a NanoScope V controller (Digital Instruments, Santa Barbara, USA). The cantilevers (RTESP from Bruke Probes) were silicon cantilevers with a resonance frequency of 300 kHz and a nominal force constant of 40 Nm⁻¹. The images were processed using WSxM (freely downloadable scanning probe microscopy software from www.nanotec.es) operating at room temperature in ambient air conditions. The functionalized samples (0.5 mg mL⁻¹) were prepared by sonication (frequency: 37 kHz; power 380 W) in distilled water with sodium dodecylbenzene sulfonate (NaDDBS, 25 mg mL⁻¹) for 90 min. Surface preparation: Mica surfaces were prepared just before the chemical deposition and were cleaved with adhesive tape. Exfoliation Procedure: 1 mg of corresponding DWCNT-PDI was dispersed with NaDDBS (25 mg mL⁻¹) in distilled water. The suspension was sonicated with an ultrasonication bath (Elma, 37 kHz and 380 W) during 90 min. Thereafter, the suspension was centrifuged at 12600 rpm for 15 min, and deposited 20 µL by drop casting on mica substrate for 10 min. The sample washed with water, dried with argon and analyzed by AFM. Incubation of DWCNT-PDIs suspensions on the surface for 10 min gives nanotubes with different diameter sizes according to theoretical studies. Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and an MgKα (hv = 1253.6 eV, 1 eV = 1.6302 x 10⁻¹⁹ J, X-ray source, powered at 100 W. The background pressure in the analysis chamber was kept below 7 x 10⁻⁹ mbar during data acquisition. The area under analysis was around 7.4 mm² and the pass energy of the analyser was set at 50 eV, for which the resolution as measured by the full width at half maximum (FWHM) of the Au4f 7/2 core level was 0.86 eV. High resolution spectra were recorded in increments of 0.1 eV with dwell times of 50 ms. Charge effects on the samples were corrected by fixing the binding energy of the major component of C 1s core-level at 284.8 eV. High-resolution
spectra envelopes were obtained by curve fitting synthetic peak components using the software “XPS peak” after subtracting an S-shaped background. Symmetric Gaussian-Lorentzian product functions (90G/10L) were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors. Osteryoung Square Wave Voltammetry (OSWV) was performed in ODCB/Acetonitrile 4:1 solution. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (0.1 M as supporting electrolyte) was purchased from Aldrich-Sigma and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment, which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\Omega = 2$ mm) and a platinum wire counter electrode. A scan rate of 0.1 V.s$^{-1}$ was used. An Ag/AgNO$_3$ electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc$^+$) before and after each experiment. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator, which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.
Synthesis

\[ N-(4\text{-aminophenyl})-N'-(1\text{-hexylheptyl})\text{-perylene-3,4,9,10-tetracarboxydiimide (PDI 2) was prepared following the experimental procedure described elsewhere.}^1 \]

\[ N,N'\text{-di(1-hexylheptyl)-1-(4-(N-Boc)aminophenoxy)perylene-3,4,9,10-tetracarboxydiimide (4):} \]

A mixture of \( N\text{-Boc-4-hydroxyaniline (306 mg, 1.46 mmol), } \] 
\( K_2CO_3 \) (400 mg, 2.90 mmol) and 18-Crown-6 (1.55 g, 5.87 mmol) was stirred in dry toluene (100 mL) under argon for 20 min. Then, \( N,N'\text{-di(1'-hexylheptyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide}^2 \) (302 mg, 0.36 mmol) was added and the reaction mixture was stirred for 5 h at 80ºC under argon atmosphere. After cooling to room temperature, the solvent was distilled off and the residue was purified by column chromatography (SiO\(_2\), dichloromethane), yielding 208 mg (60%) of 4 as a red solid. \(^1\)H NMR (300 MHz, CDCl\(_2\)CDCl\(_2\), 333 K, \( \delta \)): \( \delta = 9.57 \) (d, 1H, \( J=8.4 \) Hz, 1\( x\)-H-PDI), 8.74 -8.64 (m, 5H, 5\( x\)-H-PDI), 8.28 (s, 1H, 1\( x\)-H-PDI), 7.53 (d, 2H, \( J=8.9 \) Hz, 2\( x\)-H-Ph), 7.18 (d, 2H, \( J=8.9 \) Hz, 2\( x\)-H-Ph), 6.60 (s, 1H, 1\( x\)-NH-Boc), 5.23-5.11 (m, 2H, 2\( x\)-CH-alkyl chain), 2.29-2.15 (m, 4H, 2\( x\)-N-CH(CH\(_2\)\(_4\)-CH\(_3\))\(_2\)), 1.94-1.83 (m, 4H, 2\( x\)-N-CH(CH\(_2\)(CH\(_2\)\(_4\)-CH\(_3\))\(_2\)), 1.57 (s, 9H, 1\( x\)-Boc), 1.35-1.27 (m, 32H, 16\( x\)-CH\(_2\)-alkyl chain), 0.87 (t, 12H, \( J=6.9 \) Hz, 4\( x\)-CH\(_3\)) ppm.; \(^{13}\)C NMR (75 MHz, CDCl\(_2\)CDCl\(_2\)): \( \delta = 156.3, 152.5, 149.8, 135.9, 134.3, 134.2, 133.5, 129.1, 128.5, 128.3, 126.9, 125.6, 123.5, 122.9, 122.2, 120.7, 120.3, 80.7, 54.6, 32.3, 32.2, 31.6, 31.5, 29.0, 28.9, 26.8, 22.4, 13.9 ppm.; IR (KBr) \( \nu \): 2954, 2925, 2855, 1697 (C=O imide), 1655 (C=O imide), 1592, 1506, 1407, 1333, 1259, 1198, 1157, 810 cm\(^{-1}\); UV/Vis (chloroform), \( \lambda_{\max} \) (log \( \varepsilon \)): 391 (3.73), 506 (4.55), 542 nm (4.71); HR-MS (MALDI-TOF): m/z: calcd for C\(_{61}\)H\(_{75}\)N\(_3\)O\(_7\): 961.5610 \([M]\); found: m/z: 961.5649 \([M]\). 

\[ N,N'\text{-di(1-hexylheptyl)-1-(4-aminophenoxy)perylene-3,4,9,10-tetracarboxydiimide (PDI 1):} \] 

PDI derivative 4 (150 mg, 0.16 mmol) was dissolved in dichloromethane (2 mL) under argon. Then, trifluoroacetic acid (2 mL) was added and the reaction mixture was stirred for 4 h at 0ºC. When the reaction reached room temperature, the solvent was
distilled off and the residue was purified by column chromatography (SiO2, dichloromethane), yielding 70 mg (52%) of **PDI 1** as a dark red solid. \(^1\)H NMR (300 MHz, CDCl\(_2\)CDCl\(_2\), 333 K, \(\delta\)): \(\delta = 9.63\) (d, 1H, \(J=8.4\) Hz, 1xH-PDI), 8.73 -8.61 (m, 5H, 5xH-PDI), 8.26 (s, 1H, 1xH-PDI), 7.07 (d, 2H, \(J=8.6\) Hz, 2xH-Ph), 6.82 (d, 2H, \(J=8.6\) Hz, 2xH-Ph), 5.23-5.11 (m, 2H, 2xCH-alkyl chain), 2.67 (br. s, 2H, 1xNH\(_2\)), 2.30 -2.16 (m, 4H, 2xN-CH(CH\(_2\)H-CH\(_2\)H-CH\(_3\))\(_2\)), 1.92-1.88 (m, 4H, 2xN-CH(CH\(_3\)H-CH\(_2\)H-CH\(_3\))\(_2\)), 1.35 -1.25 (m, 32H, 16xC\(_2\)H\(_2\)-alkyl chain), 0.87 (m, 12H, 4xC\(_3\)H\(_2\)-alkyl chain), ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_2\)CDCl\(_2\)): \(\delta = 157.3, 146.2, 144.2, 134.4, 134.0, 133.8, 129.1, 128.4, 128.3, 126.9, 125.2, 123.4, 122.2, 122.0, 121.3, 116.6, 54.7, 54.5, 32.3, 32.2, 31.6, 31.5, 29.0, 28.9, 26.8, 22.4, 13.9 ppm; IR (KBr) \(\nu\): 2953, 2924, 2855, 1696 (C=O imide), 1655 (C=O imide), 1592, 1505, 1459, 1423, 1407, 1332, 1301, 1257, 1196, 810, 749 cm\(^{-1}\); UV/Vis (chloroform), \(\lambda_{\text{max}}\) (log \(\varepsilon\)): 388 (3.73), 512 (4.60), 547 nm (4.73); HR-MS (MALDI-TOF): m/z: calcd for C\(_{56}\)H\(_{67}\)N\(_3\)O\(_5\): 861.5086 [\(M^+\)]\(^-\); found: m/z: 861.5533 [\(M^+\)]\(^-\).

**N-(3-azidopropyl)-N'-(2-ethylpropyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 3):**

A mixture of \(N-(3\text{-Azidopropyl})-3,4,9,10\text{-perylenetetracarboxy}-3,4\text{-anhydride}-9,10\text{-imide}\)\(^{32}\) (1.60 g, 3.38 mmol) and 2-ethylhexylamine (1.20 g, 9.30 mmol) were suspended in a solution of imidazole (49 g) and DMF (60 ml). The mixture was heated overnight at 120 °C before being cooled to room temperature. The addition of ethanol (200 ml) followed by the addition of aqueous citric acid (10%, 200 ml) generated a solid, which was removed by filtration. The residue was purified by column chromatography (SiO\(_2\), chloroform: acetone 50:1), yielding 372 mg (24%) of **PDI 3** as a brown-red solid. \(^1\)H NMR (300 MHz, CDCl\(_2\)CDCl\(_2\), 333 K, \(\delta\)): \(\delta = 8.60\) (d, 2H, \(J=7.6\) Hz, 2xH-PDI), 8.57 (d, 2H, \(J=7.6\) Hz, 2xH-PDI), 8.48 (d, 2H, \(J=8.0\) Hz, 2xH-PDI), 8.47 (d, 2H, \(J=8.0\) Hz, 2xH-PDI), 4.32 (t, 2H, \(J=6.9\) Hz, 1xN-CH\(_2\)-CH\(_2\)-CH\(_2\)-N\(_3\)), 4.14 (m, 2H, 2xN-CH\(_2\)-R), 3.51 (t, 2H, \(J=6.7\) Hz, 1xN-CH\(_2\)-CH\(_2\)-CH\(_2\)-N\(_3\)), 2.12 (q, 2H, \(J=6.8\) Hz, 1xN-CH\(_2\)-CH\(_2\)-CH\(_2\)-N\(_3\)), 2.00 (m, 1H, 1xCH-alkyl chain), 1.40-1.30 (m, 8H, 4xCH\(_2\)-alkyl chain), 1.01-0.91 (m, 6H, 2xCH\(_3\)) ppm; \(^{13}\)C NMR (75 MHz, CDCl\(_2\)CDCl\(_2\)): \(\delta = 163.8, 163.5, 135.0, 134.5, 131.7,
131.6, 129.6, 129.5, 126.6, 126.5, 123.7, 123.5, 123.3, 120.7, 50.0, 44.5, 38.5, 38.3, 31.3, 29.1, 28.0, 24.6, 23.4, 14.4, 11.1 ppm; IR (KBr) ν: 2957, 2859, 2096 (N\textsubscript{3}), 1695 (C=O imide), 1654 (C=O imide), 1593, 1578, 1440, 1345, 1248, 1170, 1126, 1096, 853, 809, 794, 744 cm\textsuperscript{-1}; UV/Vis (chloroform), λ\textsubscript{max} (log ε): 459 (4.25), 490 (4.64), 526 nm (4.71); HR-MS (MALDI-TOF): m/z: calcd for C\textsubscript{35}H\textsubscript{31}N\textsubscript{5}O\textsubscript{4}: 585.2376 [M]\textsuperscript{-}; found: m/z: 585.2745 [M]\textsuperscript{-}.

Synthesis of PDIs control 1-3:

N,N’-di(1-hexylheptyl)-1-[4’-(benzoylamino)phenoxy]perylene-3,4,9,10-tetracarboxydiimide (PDI 1C): To a solution of PDI 1 (15 mg, 0.018 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was added benzoyl chloride (1.16 mg, 0.008 mmol) dissolved in CH\textsubscript{2}Cl\textsubscript{2} (30 mL). After stirring 48 h at room temperature, water (30 mL) and concentrated HCl (20 mL at 37 %) were added. The mixture was filtered and the solid product washed with water and then with acetone affording 5 mg (65%) of PDI 1C as a red-orange colored solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 298 K, δ): δ = 9.58 (d, 1H, J=8.4 Hz, 1xH-PDI), 8.72 -8.60 (m, 5H, 5xH-PDI), 8.30 (s, 1H, 1xH-PDI), 7.92-7.89 (m, 3H, 3xH-Ph), 7.78 (d, 2H, J=8.6 Hz, 2xH-Ph), 7.56-7.50 (m, 3H, 3xH-Ph), 7.24 (d, 1H, J=8.6 Hz, 1xH-Ph), 5.20-5.16 (m, 2H, 2xCH-alkyl chain), 2.21 (br. s, 1H, 1xNH), 1.87-1.80 (m, 4H, 2xN-CH(CH\textsubscript{2})\textsubscript{4}-CH\textsubscript{3}), 1.60-1.56 (m, 4H, 2xN-CH(CH\textsubscript{2})(CH\textsubscript{2})\textsubscript{4}-CH\textsubscript{3})), 1.35-1.25 (m, 32H, 16xC-alkyl chain), 0.82 (m, 12H, 4xC\textsubscript{3}-alkyl chain), ppm; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ = 165.7, 142.3, 135.4, 134.7, 134.4, 132.1, 129.3, 128.9, 128.6, 127.0, 125.9, 124.9, 123.7, 122.3, 120.6, 54.7, 53.4, 32.3, 31.7, 30.9, 29.7, 29.2, 29.1, 26.9, 22.5, 14.0 ppm; IR (KBr) ν: 2926, 2857, 1697 (C=O imide), 1656 (C=O imide), 1594, 1510, 1440, 1337, 1249, 1198, 810 cm\textsuperscript{-1}; UV/Vis (benzonitrile), λ\textsubscript{max} (log ε): 510 nm (5.70), 526 nm (5.83); HR-MS (m/z) (MALDI-TOF): calculated for C\textsubscript{63}H\textsubscript{71}N\textsubscript{5}O\textsubscript{6}: 965.5348 [M]\textsuperscript{+}; found: 965.5572 [M]\textsuperscript{+}.
**N-[4’-(benzoylamino)aminophenyl]-N’-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 2C):** To a solution of PDI 2 (15 mg, 0.023 mmol) in CH₂Cl₂ (30 mL) was added benzoyl chloride (1.6 mg, 0.011 mmol) dissolved in CH₂Cl₂ (30 mL). After 20 h stirring at room temperature, water (30 mL) and concentrated HCl (20 mL at 37%) were added. The mixture was filtered and the solid product washed with water and then with acetone yielding 6 mg (71%) of PDI 2C as a red-orange colored solid. ¹H NMR (400 MHz, CDCl₃, 298 K, δ): δ = 8.88-8.81 (m, 8H, 8xH-PDI), 8.31 (br. s., 1H, 1xNH), 7.88-7.86 (m, 4H, 4xH-Ph), 7.68 (t, 1H, J=7.7 Hz, 1xH-Ph), 7.59 (t, 2H, J=7.9 Hz, 2xH-Ph), 7.42 (d, 2H, J=8.7 Hz, 2xH-Ph), 5.25-5.21 (m, 1H, 1xCH-alkyl chain), 2.25-2.20 (m, 4H, 2xCH₂-alkyl chain), 1.93-1.87 (m, 4H, 2xCH₂-alkyl chain), 1.33-1.23 (m, 10H, 5xCH₂-alkyl chain), 0.84 (m, 6H, 2xCH₃-alkyl chain), ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 162.3, 161.8, 161.4, 160.9, 137.8, 136.2, 134.9, 133.3, 129.9, 129.5, 129.3, 127.2, 126.6, 126.3, 124.4, 123.9, 122.4, 122.2, 118.4, 115.5, 112.7, 109.9, 56.1, 53.5, 52.9, 52.7, 32.3, 31.6, 29.1, 26.8, 22.5, 13.9 ppm; IR (KBr) ν: 2960, 2923, 2857, 1703 (C=O imide), 1656 (C=O imide), 1598, 1520, 1407, 1352, 1257, 1176, 1103, 813 cm⁻¹; UV/Vis (benzonitrile), λ_max (log ε): 463 nm (4.84), 494 nm (5.23), 532 nm (5.43); HR-MS (m/z) (MALDI-TOF): calculated for C₅₀H₄₅N₃O₅: 767.3365 [M⁺]; found: 767.3288 [M⁺].

**N-[3’-(4’’-phenyl-1’’-,2’’,3’’-triazol-1’’-yl)propyl]-N’-(2-ethylhexyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 3C):** To a solution of PDI 3 (15 mg, 0.026 mmol) and phenylacetylene (2.62 mg, 0.026 mmol) in a mixture of CH₂Cl₂ (2 mL) and water (2 mL), was added CuSO₄.5H₂O (0.64 mg, 0.0026 mmol) and sodium ascorbate (0.77 mg, 0.0039 mmol). The oxygen was removed by several cycle of vacuum/argon. Finally, the solution was stirred at room temperature for 24 h. The organic layer was then diluted with CH₂Cl₂, washed with water, dried on MgSO₄, filtered and evaporated to dryness. Purification of the residue by column chromatography (SiO₂, eluent: chloroform:acetone 8:2) gave pure PDI 3C (9 mg, 60%) as a red-orange colored solid. ¹H NMR (300 MHz, CDCl₂/CDCl₂, 333 K, δ): δ = 8.72-8.59 (m, 8H, 8xH-PDI), 7.93 (s, 1H, 1xH-triazole), 7.73 (d, 2H, J=7.8
Hz, 2xH-Ph), 7.36 (t, 2H, J=7.8 Hz, 2xH-Ph), 7.29-7.26 (m, 1H, 2xH-Ph), 4.59 (t, 2H, J=6.8 Hz, 1xN-CH₂-CH₂-CH₂-triazole), 4.40 (t, 2H, J=6.8 Hz, 1xN-CH₂-CH₂-CH₂-triazole), 4.24-4.12 (m, 2H, 2xN-CH₂-R), , 2.60-2.51 (m, 2H, 1xN-CH₂-CH₂-CH₂-triazole), 2.08-1.97 (m, 1H, 1xCH-alkyl chain), 1.47-1.36 (m, 8H, 4xCH₂-alkyl chain), 1.02-0.91 (m, 6H, 2xCH₃) ppm; ¹³C NMR (75 MHz, CDCl₂CDCl₂): δ = 163.5, 163.3, 135.1, 134.8, 134.3, 132.0, 131.5, 131.4, 131.3, 128.6, 125.6, 123.3, 123.2, 122.9, 122.7, 30.7, 29.5, 28.6, 24.1, 22.9, 13.9, 10.6; IR (KBr) ν: 2962, 2929, 2857, 1696 (C=O imide), 1652 (C=O imide), 1589, 1437, 1344, 1248, 1173, 854, 807, 741 cm⁻¹; UV/Vis (benzonitrile), λₘₐₓ (log ε): 462 nm (5.01), 494 nm (5.41), 532 nm (5.61); ); HR-MS (m/z) (MALDI-TOF): calculated for C₄₃H₃₇N₅O₄: 687.2851 [M⁺]; found: 687.2912 [M⁺].

**General procedure for the modification of DWCNT with aryl diazonium salts**

To a dispersion of **pristine** DWCNT (40 mg) in NMP (70 mL) was added 2 equiv of the phenyl derivative and 2.4 equiv of isoamyl nitrite. The reaction mixture was stirred for 48 h at 70ºC, and then filtered through a polytetrafluoroethylene (PTFE) membrane with an average pore size of 0.2 µm. The black precipitate was washed with NMP and dichloromethane (CH₂Cl₂) and then dried in the oven under reduce pressure obtaining the corresponding DWCNT-phenyl derivative.

**Functionalization of DWCNT with 4-aminobenzoic acid**

According to the general procedure, to a dispersion of DWCNT (40 mg) in NMP (70 mL) was added 4-aminobenzoic acid (915 mg, 6.66 mmol) and isoamyl nitrite (937 mg, 8 mmol) yielding 48 mg of the desired material.

**Functionalization of DWCNT with 4-[(2-trimethylsilyl)ethynyl]aniline**

According to the general procedure, to a dispersion of DWCNT (40mg) in NMP (70mL) was added 4-[(2-trimethylsilyl)ethynyl]aniline (1.2 gr, 6.66 mmol) and isoamyl nitrite (937 mg, 8 mmol) affording 56 mg of the functionalized material.
**N,N'-di(1-hexylheptyl)-1-(4-(N-Boc)-aminophenoxy)perylene-3,4,9,10-tetracarboxydiimide (4)**

**Fig S1** $^1$H-NMR-(CDCl$_3$CDCl$_2$-d$_2$) of PDI-4

**Fig S2** $^{13}$C-NMR-(CDCl$_3$CDCl$_2$-d$_2$) of PDI-4
Fig S3 HR-MS of PDI-4

Fig S4 FT-IR spectrum (KBr) of PDI-4
$N,N'$-di(1-hexylheptyl)-1-(4-aminophenoxy)perylene-3,4,9,10-tetracarboxydiimide (PDI 1):

Fig S5 $^1$H-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI-1

Fig S6 $^{13}$C-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI-1
Fig S7 HR-MS of PDI-1

Fig S8 FT-IR spectrum (KBr) of PDI-1
N-(3-azidopropyl)-N’-(2-ethylpropyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 3)

Fig S9 $^1$H-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI-3

Fig S10 $^{13}$C-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI-3
Fig S11 HR-MS of PDI-3

Fig S12 IR spectrum (KBr) of PDI-3
$N,N'$-di(1-hexylheptyl)-1-[4'-(benzoylamino)phenoxy]perylene-3,4,9,10-tetracarboxydiimide (PDI 1C):

Fig S13 $^1$H-NMR (CDCl$_3$) of PDI-1C

Fig S14 $^{13}$C-NMR (CDCl$_3$) of PDI-1C
Fig S15 HR-MS of PDI 1C

Fig S16 FT-IR spectrum (KBr) of PDI 1C
N-4′-(benzoylamino)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 2C)

Fig S17 $^1$H-NMR-(CDCl$_3$) of PDI 2C

Fig S18 $^{13}$C-NMR-(CDCl$_3$) of PDI 2C
Fig S19 HR-MS of PDI 2C

Fig S20 FT-IR spectrum (KBr) of PDI 2C
**N-[3''-(4''-phenyl-1''',2''',3''-triazol-1''-yl)propyl]-N'-(2-ethylhexyl)perylene-3,4,9,10-tetracarboxydiimide (PDI 3C):**

Fig S21 $^1$H-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI 3C

Fig S22 $^{13}$C-NMR-(CDCl$_2$CDCl$_2$-d$_2$) of PDI 3C
Fig S23 HR-MS of PDI 3C

Fig S24 FT-IR spectrum (KBr) of PDI 3C
**Fig S25.** TGA curves recorded at 10 ºC / min under N₂ of *pristine* and functionalized DWCNTs: (A) containing **PDI 1**; (B) containing **PDI 2** and (C) containing **PDI 3**.
**Fig S26.** Raman spectra of **PDI**s **1-3** samples at 785 nm excitation. The examination of the spectrums show the typical fingerprint of perylenes bands at around 1300, 1370 and 1600 cm\(^{-1}\) as most intense peaks.
Fig S27. Raman spectra (G’ band region) for *pristine* DWCNT sample, DWCNT-PDI 1, DWCNT-PDI 2 and DWCNT-PDI 3 (785 nm laser excitation). In all functionalized DWCNTs, this band is slightly depress compared with pristine material due to reduced structural symmetry of the nanotube.
Fig S28 IR spectra (KBr) of DWCNT-PDIs 1-3
Table S1. Binding energy (eV) of the core-level atoms of DWCNT samples and its precursors.

The peak percentages are indicated in brackets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE (eV) C1s (%)</th>
<th>BE (eV) O1s (%)</th>
<th>BE (eV) N1s (%)</th>
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<tr>
<td></td>
<td>C sp²</td>
<td>C sp³</td>
<td>C-O</td>
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<tr>
<td><strong>pristine DWCNT</strong></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>284.8 (69)</td>
<td>-</td>
<td>286.2 (16)</td>
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<tr>
<td><strong>DWCNT-COOH</strong></td>
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</tr>
<tr>
<td></td>
<td>284.8 (65)</td>
<td>-</td>
<td>286.3 (22)</td>
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<tr>
<td><strong>DWCNT-TMS</strong></td>
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<td></td>
<td>284.8 (68)</td>
<td>-</td>
<td>286.3 (20)</td>
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<td><strong>PDI 1</strong></td>
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<td>284.8 (52)</td>
<td>285.3 (34)</td>
<td>286.3 (18)</td>
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<tr>
<td><strong>PDI 2</strong></td>
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<td></td>
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<tr>
<td></td>
<td>284.8 (52)</td>
<td>285.3 (34)</td>
<td>286.3 (18)</td>
</tr>
<tr>
<td><strong>PDI 3</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>284.8 (55)</td>
<td>285.3 (31)</td>
<td>-</td>
</tr>
<tr>
<td><strong>DWCNT-PDI 1</strong></td>
<td></td>
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<tr>
<td></td>
<td>284.8 (60)</td>
<td>285.4 (6)</td>
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<td><strong>DWCNT-PDI 2</strong></td>
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<td></td>
<td>284.8 (82)</td>
<td>285.3 (4)</td>
<td>286.2 (6)</td>
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<td><strong>DWCNT-PDI 3</strong></td>
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<td>284.8 (78)</td>
<td>285.3 (3)</td>
<td>286.3 (13)</td>
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</table>

*The area of C-N component is included together with that of C-O bonds.

*DWCNT-TMS shows the Si 2p emission at a BE = 101.5 eV
Fig S29. Survey, C1s and O1s core-level spectra of pristine DWCNT

Fig S30. Survey, C1s and O1s core-level spectra of DWCNT-COOH
**Fig S31.** Survey, C1s, O1s and N1s core-level spectra of **DWCNT-PDI 1** and its precursor **PDI 1**
Fig S32. Survey, C1s, O1s and N1s core-level spectra of DWCNT-PDI 2 and its precursor PDI-2
Fig S33. Survey, C1s and O1s core-level spectra of DWCNT-TMS
Fig S34. Survey, C1s, O1s and N1s core-level spectra of DWCNT-PDI 3 and its precursor PDI -3
Fig S35. AFM images and height profile along the region indicated for pristine DWCNT together with its height distribution histogram showing the diameter distribution of the sample.
**Fig S36.** Osteryoung Square Wave Voltammetry (scan rate = 0.1 V.s⁻¹) of **DWCNT-PDIs 1-3** (black line) and control compounds **PDI 1C-3C** (red line) in o-DCB/acetonitrile 4:1 solution containing 0.1 M NBu₄PF₆ at room temperature.
Fig S37. UV-vis absorption spectra of DWCNT PDI 1-3 and its control PDI 1C-3C recorded in PhCN (left column) and in NMP (right column).
**Fig. S38.** Emission spectra of both HIPCO SWCNT and DWCNT dispersed in aqueous 2% sodium cholate hydrate, exciting at 659nm.
Fig. S39. (a) Femtosecond transient spectra of PDI 1C in Ar- saturated NMP at the excitation wavelength of 400 nm at the indicated time intervals. Figure b shows the time profiles of the 530 and 693 nm bands.

Fig. S40. Femtosecond transient spectra of DWCNT-PDI 1 in Ar- saturated NMP at the excitation wavelength of 400 nm at the indicated time intervals. Figure b shows the time profile of the 1200 nm peak.
**Fig. S41.** Mechanistic details of electron pooling in DWCNT-PDI- hybrid catalyzed photochemical reaction. See text for abbreviations.
**Fig. S42.** Absorption spectra of a mixture of **DWCNT** and **PDI-3C** in NMP, just prepared (black line) and after 5h (red line).

**References:**
