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Fabrication of Multi-Pyridine Functionalized Carbon Nanotubes as Versatile Coordination Nano-Linkers

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Synthesis of multi-pyridine functionalized carbon nanotubes

A typical experiment on the surface functionalization of MWNTs was performed as follows: H_2N-C_6H_4-CH_2-Br was produced in a 50 mL flask from commercially available 4-(hydroxymethyl) aniline (0.5 g, 4.1 mmol) and tetrabutylammonium bromide (1.63 g) by heating at 150^{o}C for 24 h in 48% HBr (15 mL). After the mixture was cooled to 0^{o}C, a cooled aqueous $NaNO_2$ (0.31 g, 4.5 mmol) solution (3.0 mL) was slowly added to form the diazonium salt $^+N_2$-C_6H_4-CH_2-Br. The resulting yellow solution was stirred at 0°C for 30 min; a cooled MWNT (15 mg) dispersed solution in 15 mL N,N-dimethylformamide was then added. This reaction system was stirred at 0°C for another 4 h, followed by stirring at room temperature overnight. Finally, the benzyl bromide-functionalized product MWNT-BenBr was obtained by centrifugation and washed well with copious amounts of 48% HBr and dimethylformamide.

The pyridine-functionalized MWNTs-Py hybrid materials were formed by reacting the as-prepared MWNT-BenBr with pyridine-contained compounds of BPy, DPy, TPyP, $Fe(Pyterpy)_2$ and PVP in dimethylformamide or chloroform. The products were collected by centrifugation and well washed by the solvents.

Pd-Mediated Assembly of Layered Ultrathin Films

The multilayer of Pd/MWNT-TPyP was assembled on a quartz substrate surface using the layer-by-layer (LBL) method. The assembly process was shown in Scheme S1, which included the following main steps.[26] Firstly, the hydrophilic quartz substrate was immersed in a methanol solution

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of 0.2 mg/mL (*p*-chloromethylphenyl)trichlorosilane over night to form a layer of $O_3SiC_6H_4CH_2Cl$, which was then covalently attached to the PVP layer (Scheme S1, **A**) by refluxing the substrate in a 0.2 mg/mL PVP methanol solution. Secondly, the PVP-modified quartz substrate was dipped into a 0.1 mmol/L Na_2PdCl_4 aqueous solution to form the PVP-Pd layer (**B**). Thirdly, substrate **B** was immersed into a methanol solution of MWNT-TPyP (**C**). Finally, the above processes (**B** and **C**) were repeated. All of the assembly experiments were performed at room temperature.

Synthesis of Terpyridine-Functionalized Carbon Nanotubes and Their Metal-Complexes

Terpyridine-functionalized hybrids (Figure 2A) were prepared by stirring chloroform solution of MWNT-Py with excess 4-(2,2':6'2"-terpyridin-4'-yl)benzyl bromide at 60^{o}C overnight. The products of MWNT-TPy hybrids were collected by centrifugation and well washed by the solvents. The MWNT-TPy-metal (M = Fe^{2+}, Eu^{3+} and Tb^{3+}) complexes were prepared by stirring_methanol solutions of MWNT-TPy with excess $Fe(BF_4)_2$, $Eu(NO_3)_3$ or $Tb(NO_3)_3$ at room temperature overnight. The MWNT-MTPy complexes were collected by centrifugation and well washed by water.

Preparation of Zinc Porphyrin-Functionalized MWNT-Py Composites

Zinc porphyrin functionalized MWNT-Py composite was obtained via an axial coordination of the central Zn(II) ion of zinc tetra(pyridylporphyrin) chloride tetrakis(methochloride) (ZnTMPyP) with the pyridyl substituent of the MWNT-Py hybrids (Figure 2B), which was done by stirring a mixture of ZnTMPyP and MWNT-Py hybrids in a methanol solution for 24 h.[27] The solid powders were then collected by centrifugation, well washed by methanol and water to remove unreacted ZnTMPyP, and finally dried under vacuum at room temperature.

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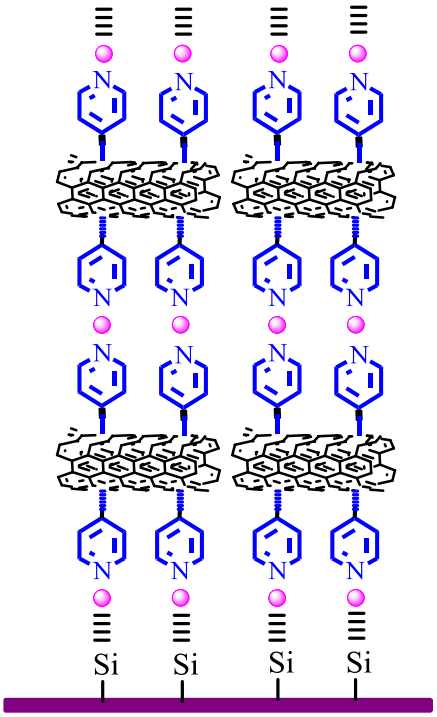

Scheme S1. Schematic representation of the Pd(II)/MWNT-TPyP LBL multilayers.

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Table S1. Binding Energy (eV) for the detected elements of the LBL multilayers

	C (1s)	N (1s)	O (1s)	Cl (2p)	Pd (3d)	Br (3d)
Qz/BPy	284.8	400.0	532.6	198.1		
Qz/BPy/Pd	284.8	400.1	532.2	198.2	337.4, 343.0	
Qz/BPy/Pd/ CNTs-TPyP	284.8	400.2	532.6	198.6	338.0, 343.2	69.2

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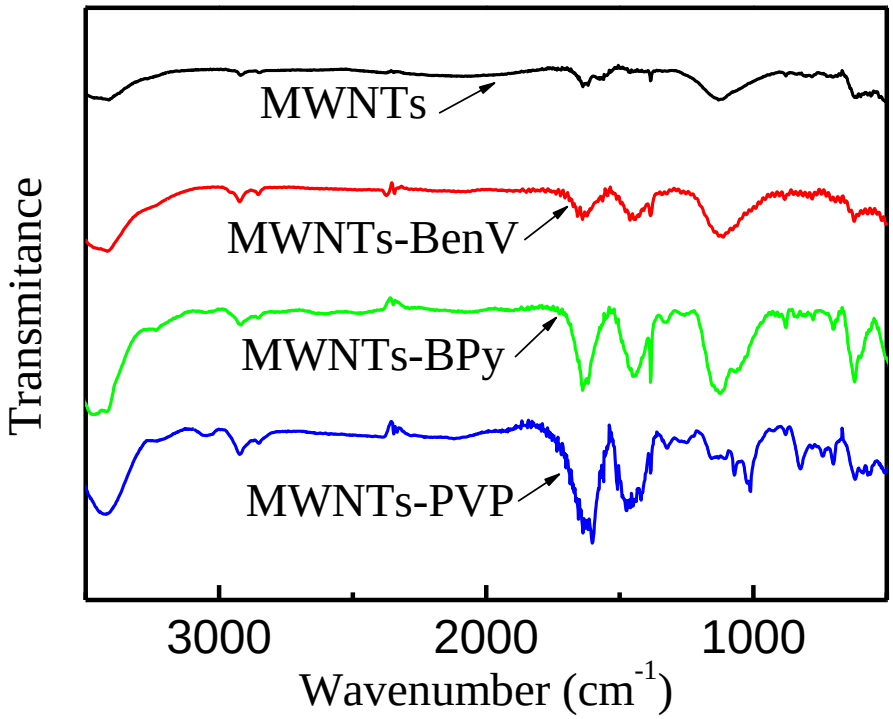

Figure S1. FTIR spectra of multi-pyridine functionalized MWNTs together with that of the commercial MWNTs.

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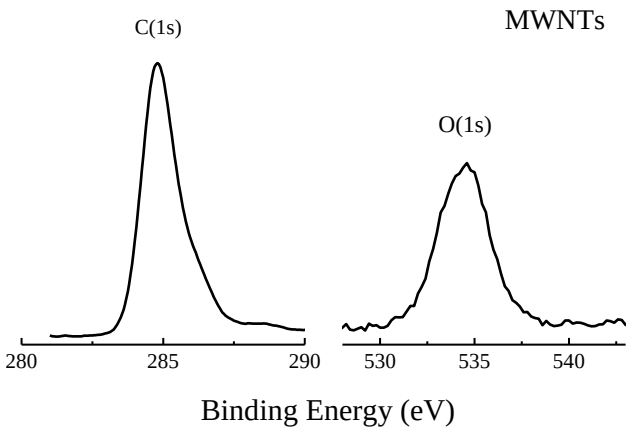

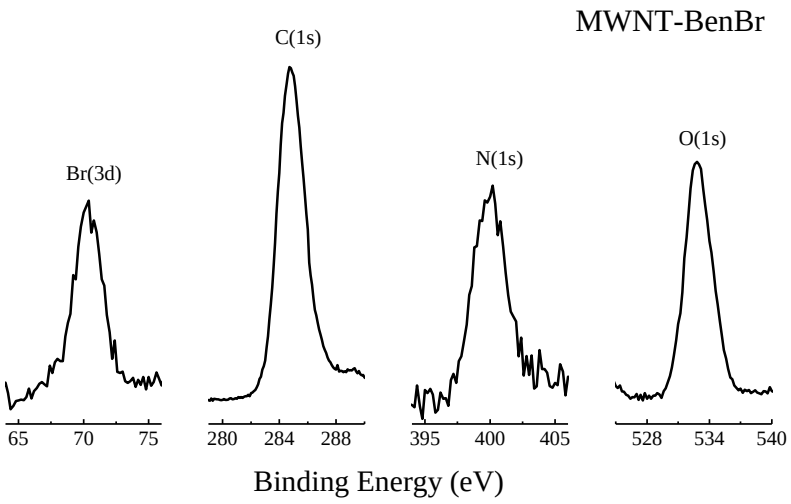

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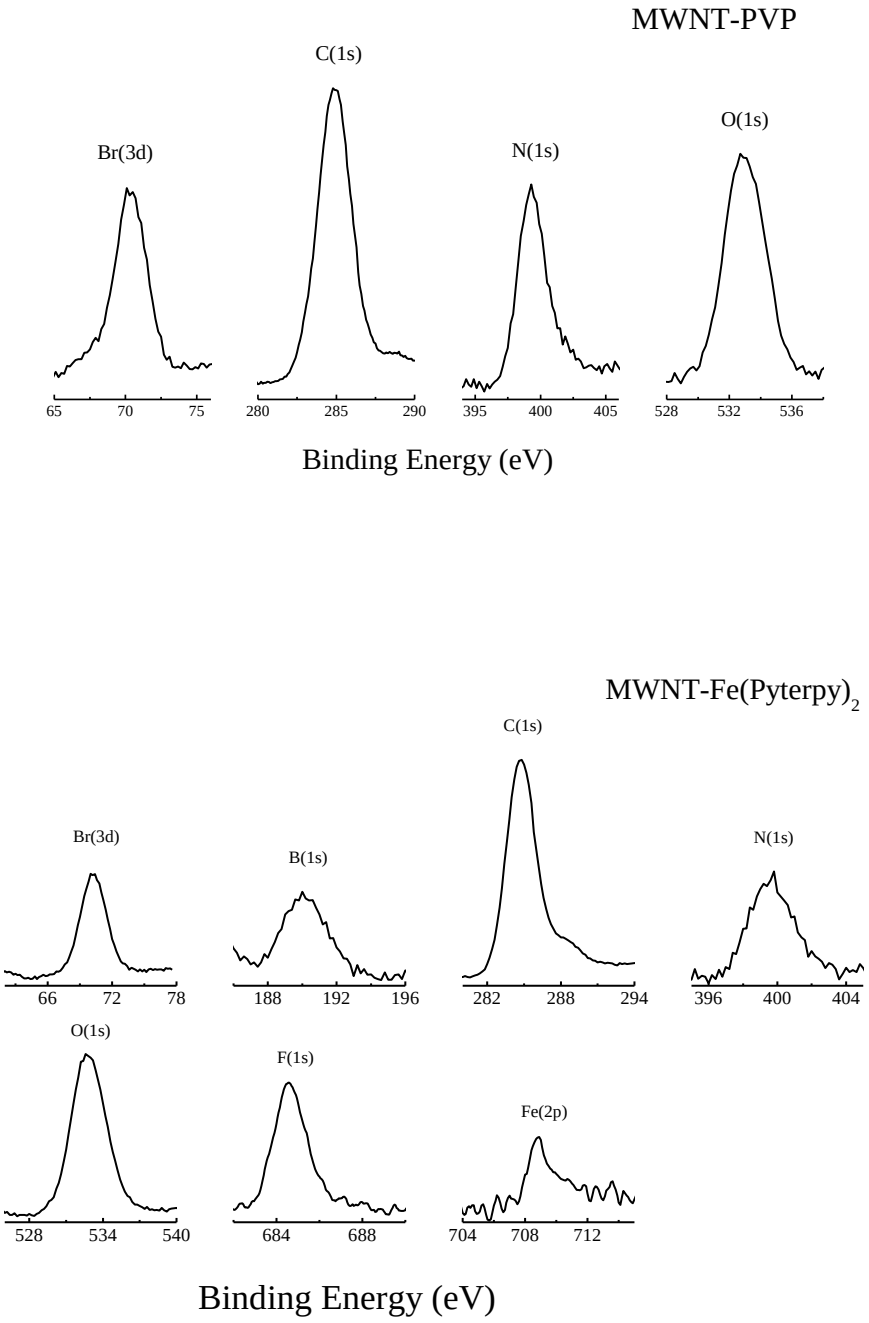

Figure S2. High resolution XPS spectra of commercial MWNTs as well as BenBr, PVP and $Fe(Pyterpy)_2$ functionalized MWNT hybrids.

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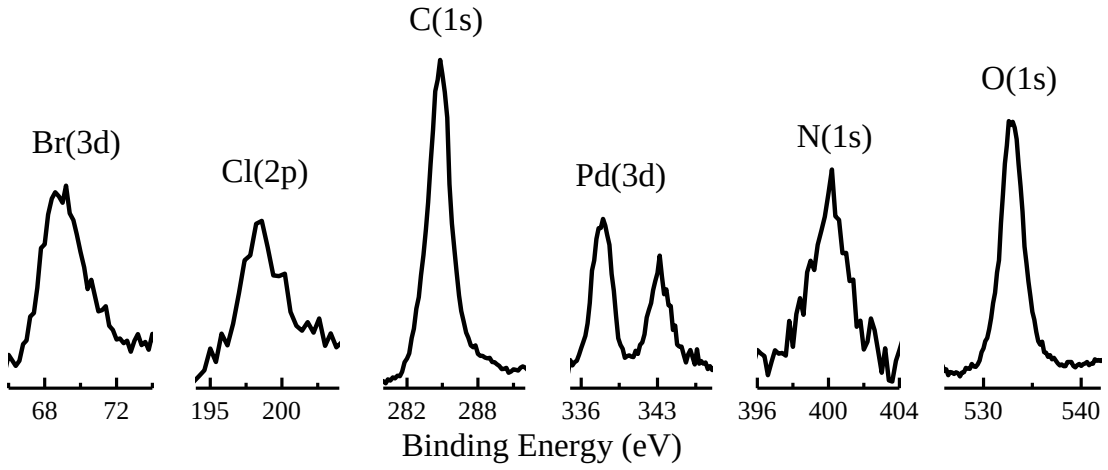

Figure S3. High resolution XPS spectra of Pd/MWNTs-TPyP LBL multilayers on quartz substrate surface.

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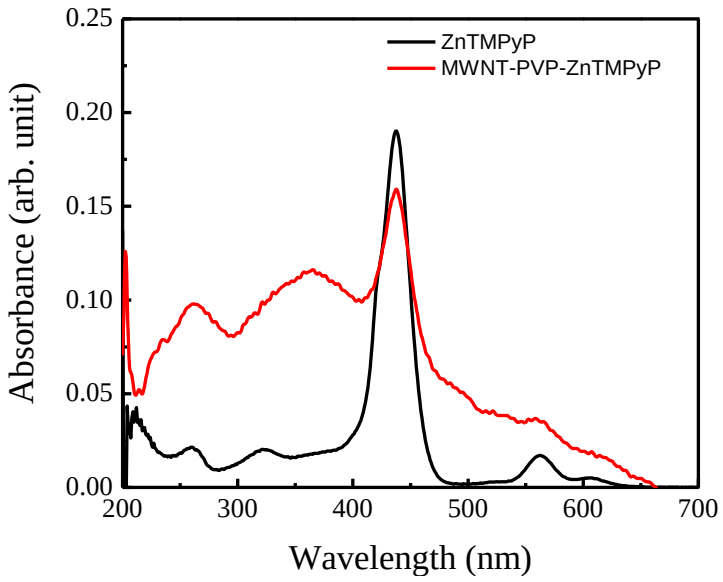

Figure S4. UV-vis absorption spectra of ZnTMPyP and its axial coordination nanocomposites with pyridine-functionalized nanotubes (MWNT-PVP-ZnTMPyP) in the methanol solutions.

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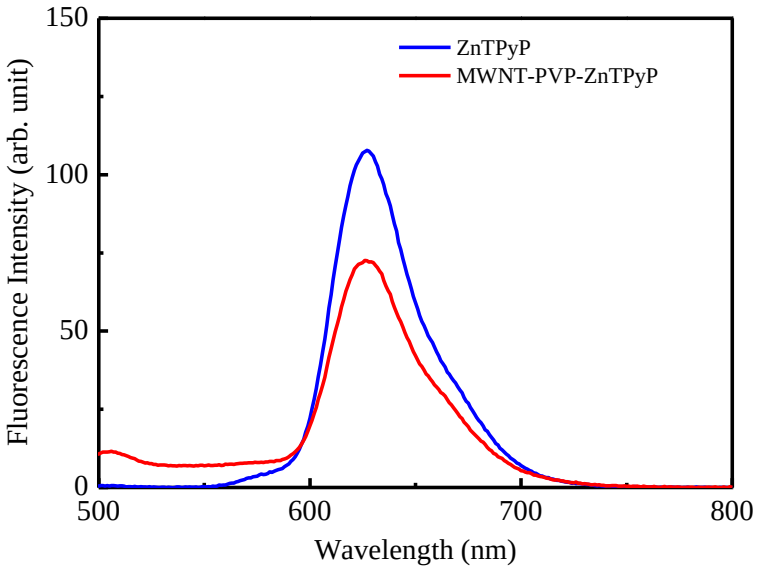

Figure S5. Fluorescence emission spectra of ZnTMPyP and its axial coordination nanocomposites with pyridine-functionalized nanotubes (MWNT-PVP-ZnTMPyP) in the methanol solutions.

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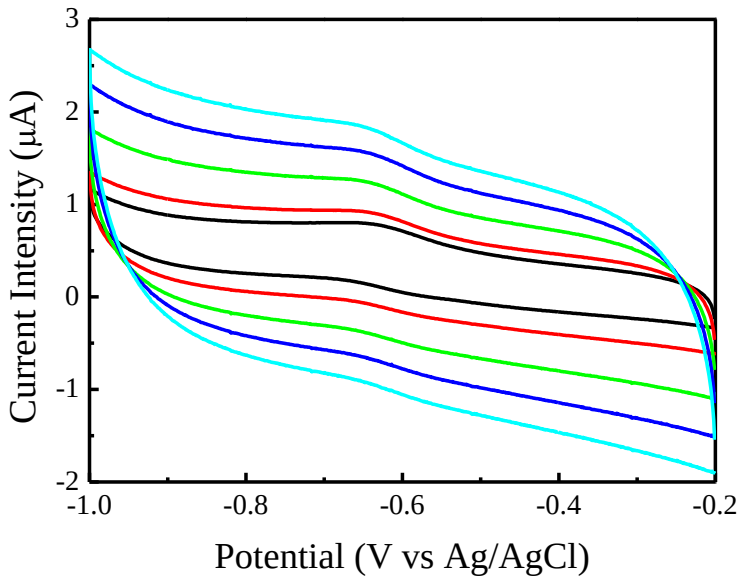

Figure S6. Cyclic voltammograms for the glass carbon electrode covered by the casting film of MWNTs-Fe(Pyterpy)$_2$ hybrids in the 0.05 M KCl electrolyte solution at the potential scan rates of 0.05, 0.1, 0.2, 0.3 and 0.4 V/s.