

SUPPORTING INFORMATION

Magnetic dimeric metal-porphyrin rings mechanically-bonded around carbon nanotubes: the role of nanotube defects modulating magnetic properties

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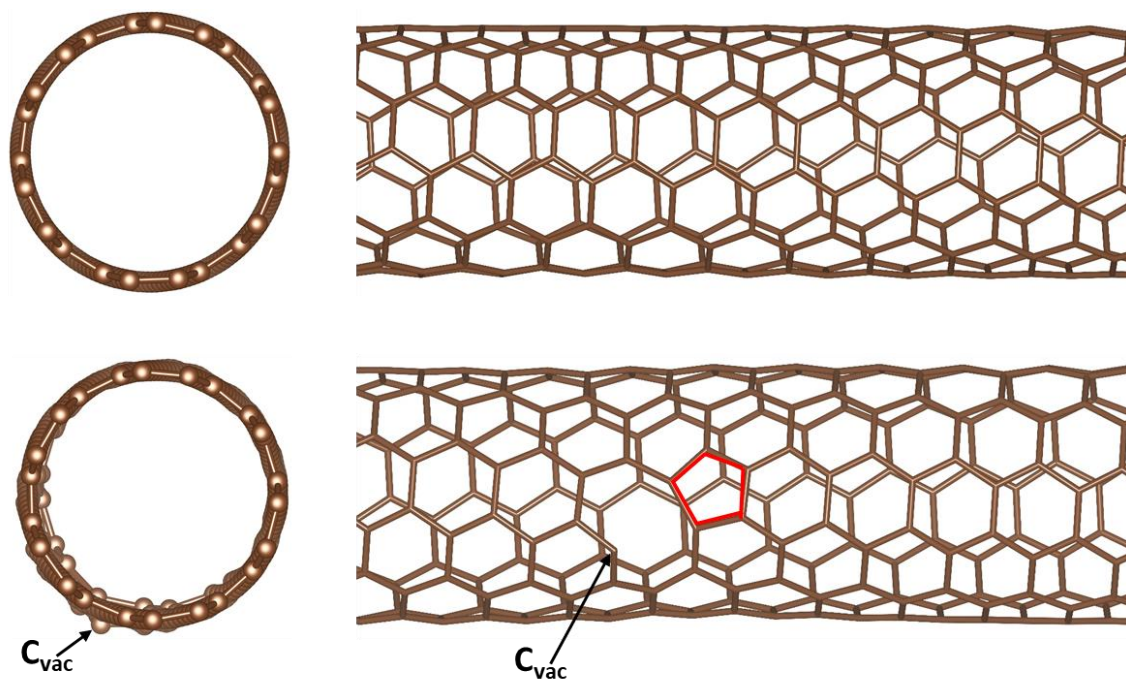


Figure S1. Optimized geometries of the pristine nanotube (top) and the defective nanotube (bottom). The removal of a carbon atom from the nanotube results in a noticeable distortion near the vacancy, leading to the formation of a new carbon-carbon bond and the creation of a pentagonal ring (highlighted in red). Additionally, there is an out-of-plane shift of the dangling carbon atom opposite the pentagon (labeled as C_{vac}).

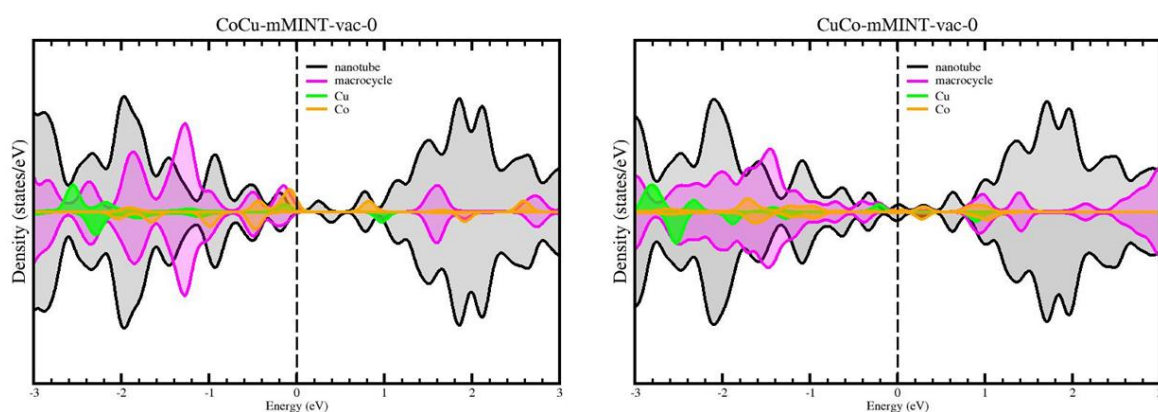


Figure S2. Projected Density of States for the mixed mMINTs with a defective nanotube, with Cu near the vacancy (left) or Co near the vacancy (right).

Table S1. Selected structural parameters calculated for various structures. For comparison, experimental Metal–N distances derived from EXAFS (Ref. 26) have been included in the table. To assess the effect of dimer and mMINTs formation on the porphyrin ring structure, the isolated CoP and CuP structures have been optimized and included in the table. The calculated distances show excellent agreement with the experimental data. We found nearly identical M-N distances and NMN angles for isolated porphyrins, dimers and mMINTs with pristine nanotubes for both metal, indicating that the dimer and mMINT formation does not affect the metal's coordination sphere. However, the formation of the mMINTs with defective nanotubes causes a distortion of the porphyrin planar structure. This effect is minor for the Cu derivative, but it is significant for the Co one. In the case of Co-mMINT-vac-0 there is an out-of-plane shift of the Co atom near the vacancy, which increases the Co-N distances and decreases the NCoN angle. These findings are consistent with experimental EXAFS results (Ref.26), which reported differences in the width of the spectral features for Co-dimer and Co-mMINTs, potentially due to mechanical strain from accommodating the adsorbed molecules and/or the fact that the two Co porphyrins are not entirely equivalent.

	Structure	M-N distance (Å)	N-M-N (°)
Experimental From Ref. 26	Cu-monomer	1.99	-
	Cu-dimer	2.00	-
	Cu-mMINT	1.99	-
	Co-monomer	-	-
	Co-dimer	1.95	-
	Co-mMINT	1.91	-
Calculated	CuP	2.02	180
	Cu-dimer-0	2.01	179
	Cu-mMINT-0	2.01	178
	Cu-mMINT-vac-0	2.01	179 Cu1
		2.03	174 Cu2
	CoP	1.98	180
	Co-dimer-0	1.97	180
	Co-mMINT-0	1.97	178
Co-mMINT-vac-0	1.97	180 Co1	
	2.00	160 Co2	

Table S2. Interaction energy (eV) for all the studied structures calculated as $E_{\text{int}} = E_{\text{mMINT}} - (E_{\text{nanotube}} + E_{\text{dimer}})$. The energies of the nanotube (E_{nanotube}) and the porphyrin dimeric rings (E_{dimer}) are obtained from a single point calculation of the carbon nanotube or the macrocycle with the optimized geometry of the whole mMINT system and using the same supercell as the whole system. Interaction energies are almost identical for Co and Cu derivatives in the absence of defects on the nanotube, but become 1.3 eV larger for Co-mMINT when one carbon vacancy is created on the nanotube. For mixed mMINTs interaction energies are similar to those of the homonuclear Cu-mMINT if Cu is close to the vacancy and similar to those of homonuclear Co dimers if Co is close to the vacancy.

Structure		E_{int} (eV)
mMINTs with pristine NT	Co-mMINT-0	-3.53
	Co-mMINT-2	-3.53
	Cu-mMINT-0	-3.51
	Cu-mMINT-2	-3.51
mMINTs with defective NT	Co-mMINT-vac-0	-4.88
	Co-mMINT-vac-2	-4.88
	Cu-mMINT-vac-0	-3.43
	Cu-mMINT-vac-2	-3.43
Mixed mMINTs with defective NT	CoCu-mMINT-vac-0	-3.42
	CoCu-mMINT-vac-2	-3.42
	CuCo-mMINT-vac-0	-4.90
	CuCo-mMINT-vac-2	-4.91