Polyaniline-Carbon Nanotube Composites: From Wrapping and Self-Alignment to Solubility and Enhancement Effects

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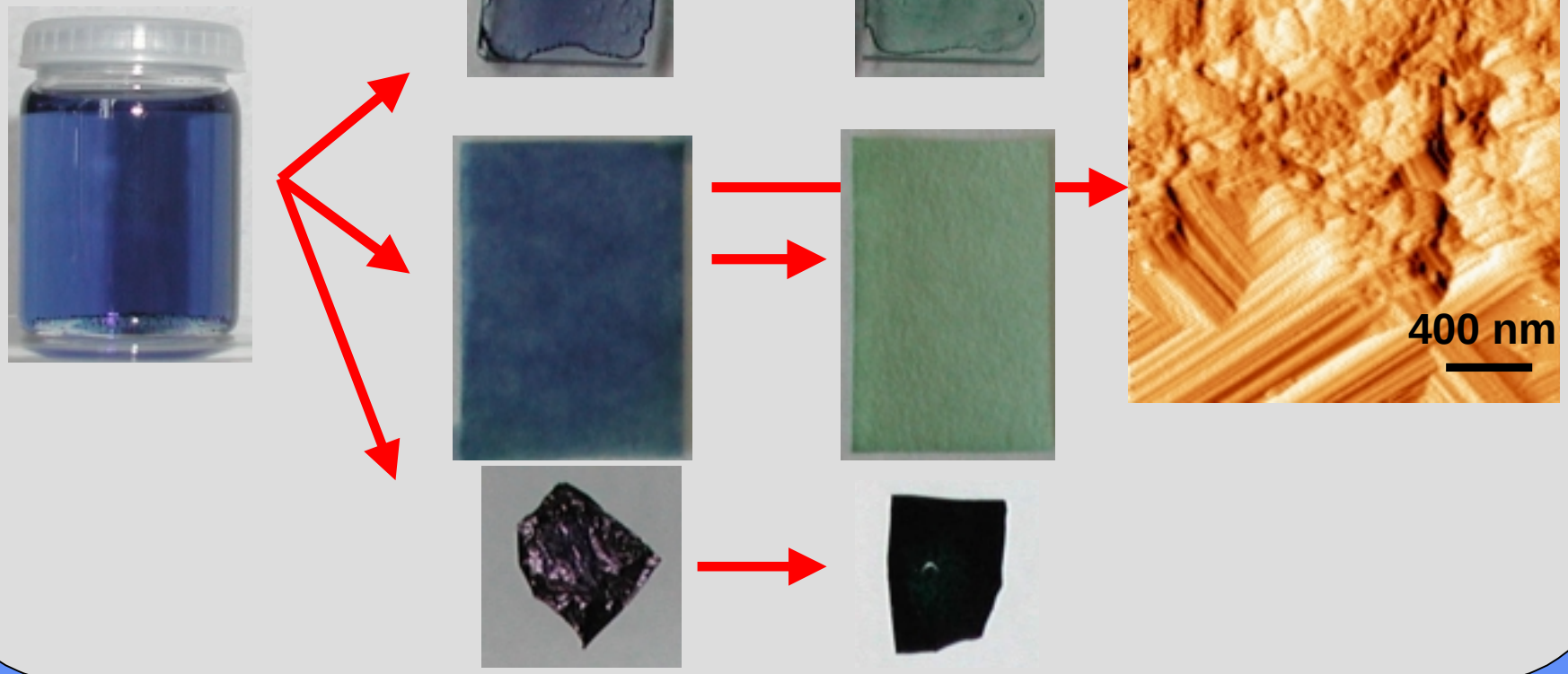


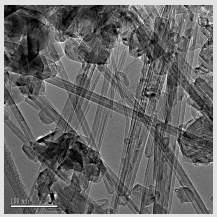
SOLUBLE

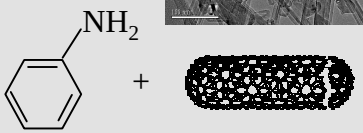
PROCESABLE, TRANSFORMABLE

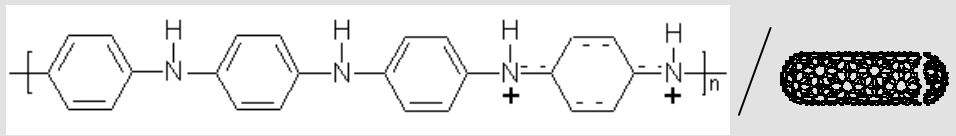
Aligned

Polyaniline / Multi-wall Carbon Nanotube Composite

IN-SITU POLYMERIZATION

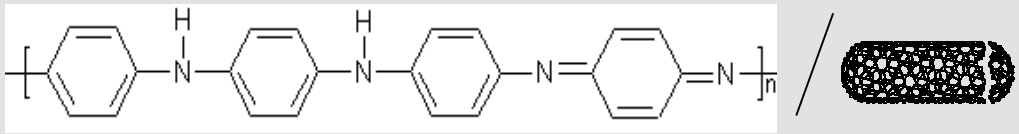






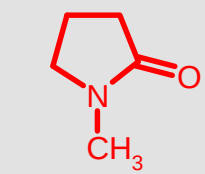
Emeraldine Salt/MWNT

NH_4OH

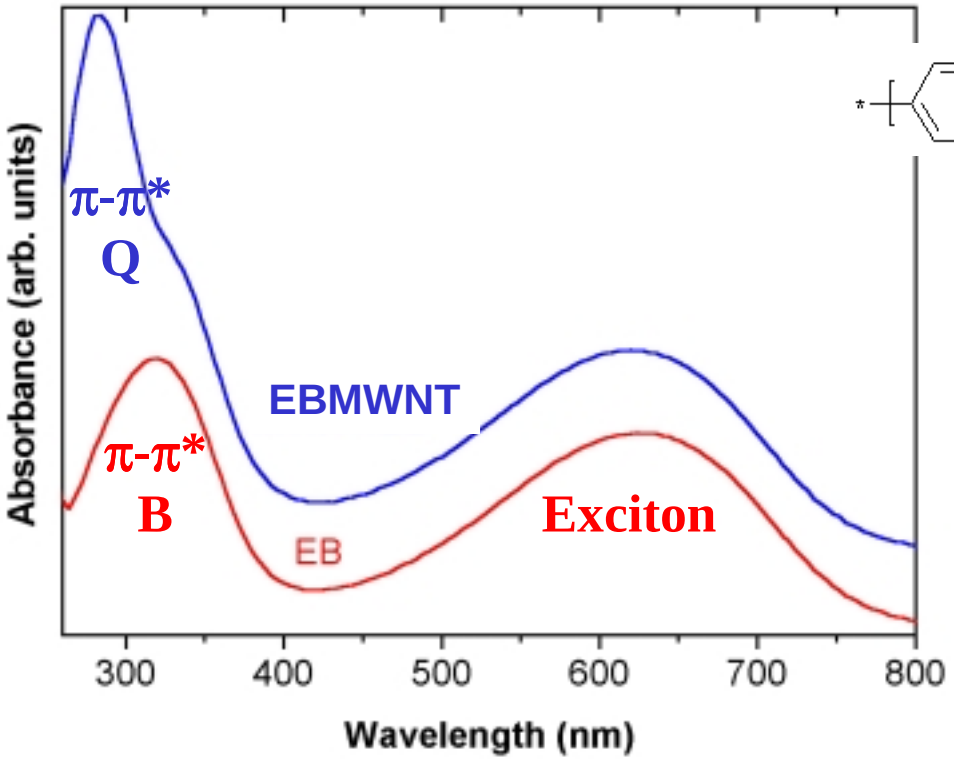


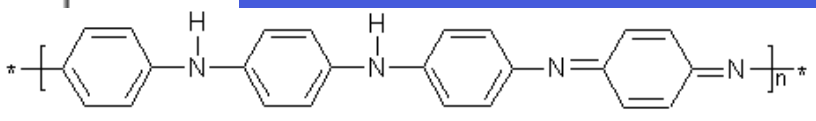
Emeraldine Base/MWNT

Soluble in NMP



UV-Vis
EB and EBMWNT in NMP

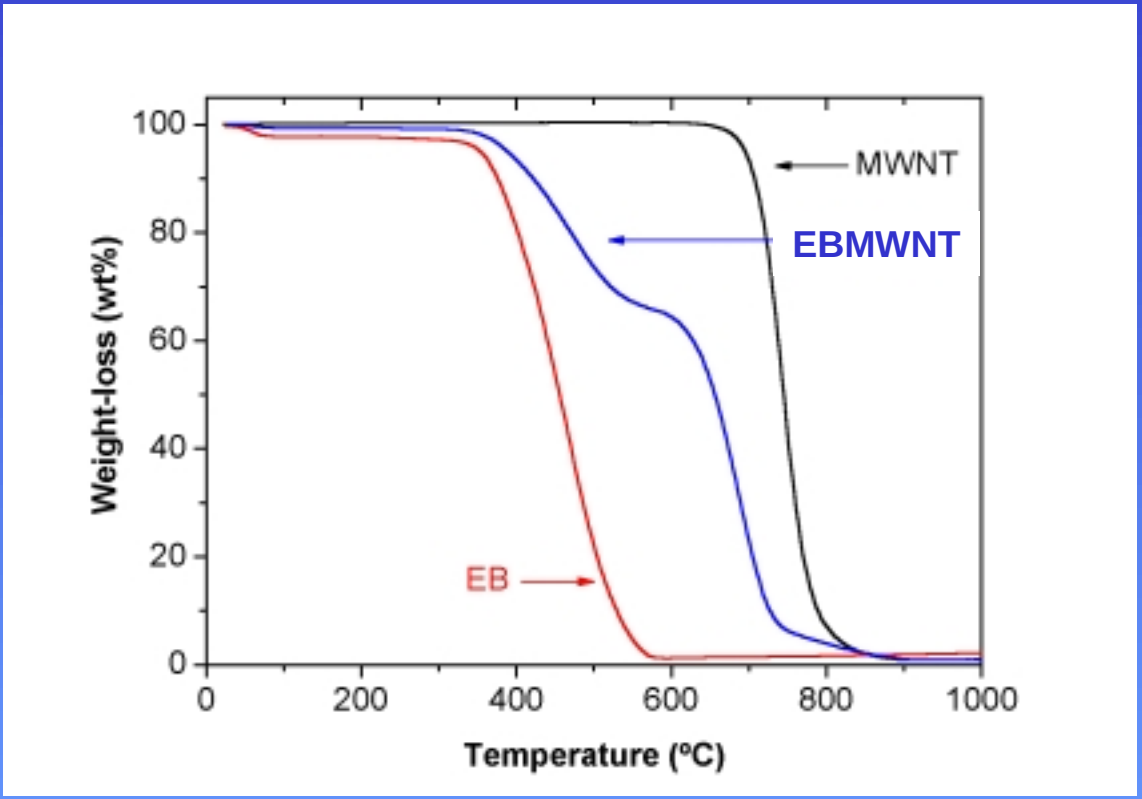




EB

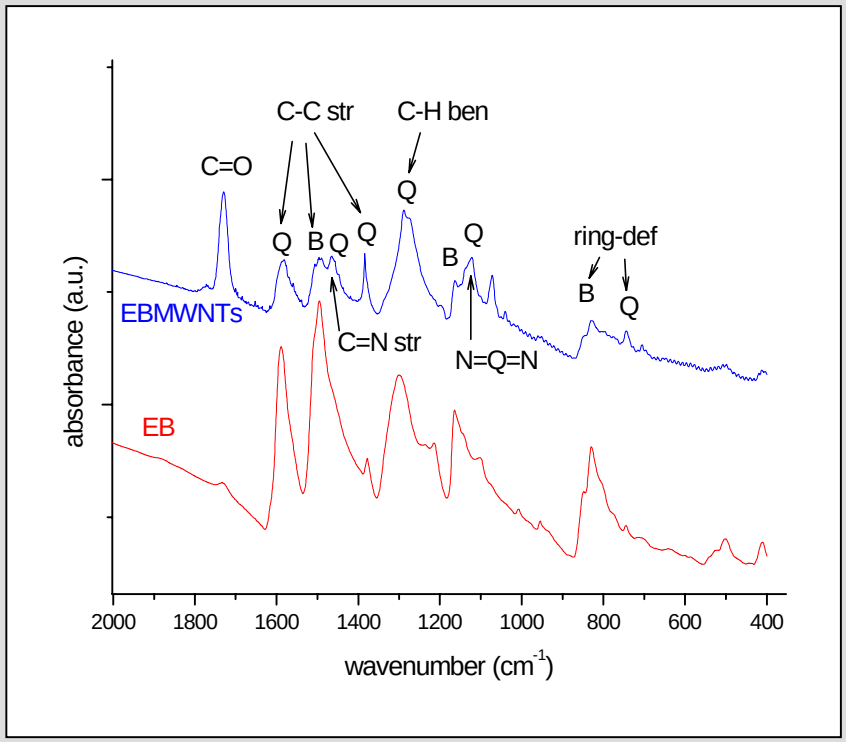
- "FREE EB"
- QUNIOID ENHANCED RESPONSE OF EB IN THE COMPOSITE;
- MWNT related

THERMOGRAVIMETRIC ANALISIS



- Two-phases (EB + new Q-rich EB)
- Thermal stability EBMWNT > EB

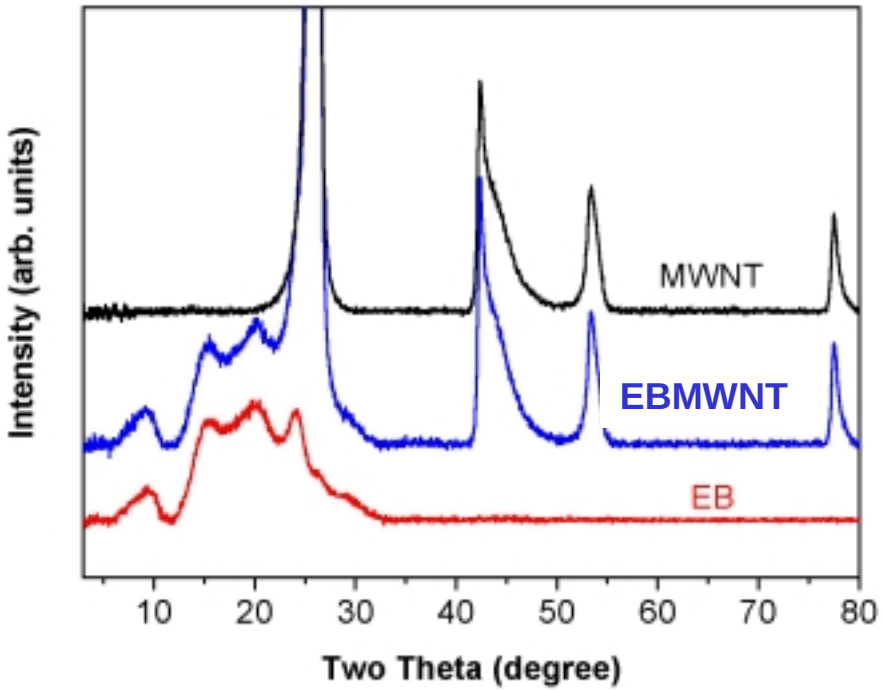
FTIR SPECTROSCOPY



ν (cm^{-1})	Assignment	Rel.Int. EB	Rel.Int. EB-MWNT
1585	C=C (Q)	< 1	1
1494	C-C (B)	~ 1	~ 1
1465	C=N (Q)	< 1	1
1380	C-C (Q)	<< 1	1
1165	B related	< 1	< 1
1122	N=Q=N	< 1	1

QUINOID RELATED PEAKS INCREASED COMPARED TO BENZENOID IN EBMWNT

X-RAY DIFFRACTION

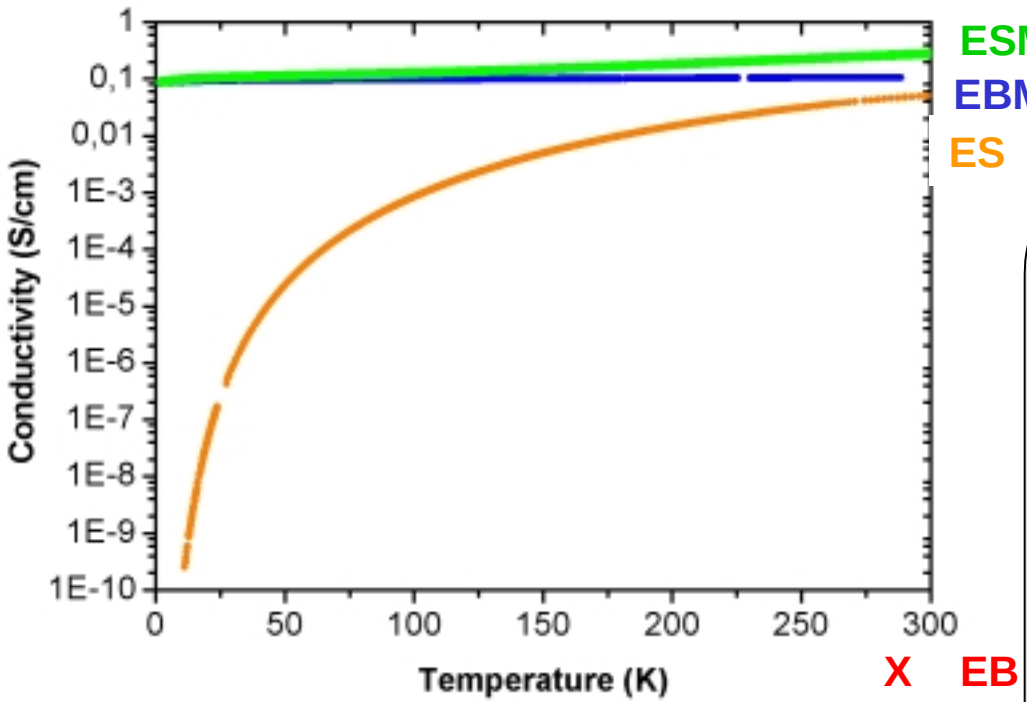


EB-I unit-cell:

- **c = 0.94 nm,**
- **b = 0.57 nm,**
- **a = 0.45 nm**

- **Only seen: “free EB-I” and MWNT**
- **MWNTs do not affect EB unit cell**
- **Quinoid-rich PANI phase???**

CONDUCTIVITY



At RT:

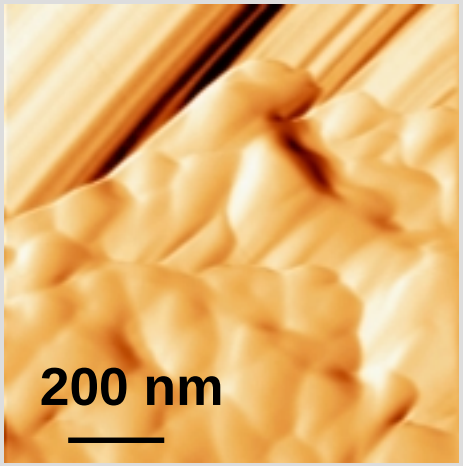
σ(EB) $\leq 10^{-10}$ S/cm

σ(EBMWNT) $\approx$ 0.1 S/cm $\approx$ σ(ESMWNT)

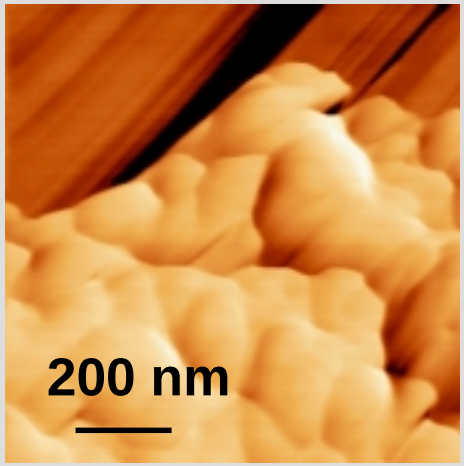
σ(EBMWNT) < 1-10 S/cm = σ(MWNT)

- **EBMWNT conductivity is 9 orders of magnitude higher than EB**
- **Conduction through a percolated 3D network of MWNTs**
- **Existence of additional tunnelling barriers between MWNTs**

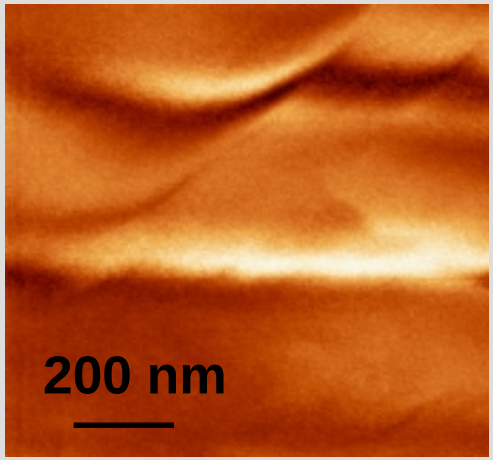
ATOMIC FORCE MICROSCOPY



Topography



Phase



Adhesion

- **"Free EB"**
- **Bundles of aligned polyaniline covered MWNTs**

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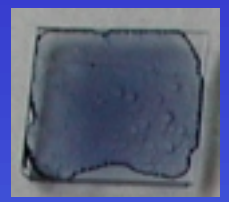
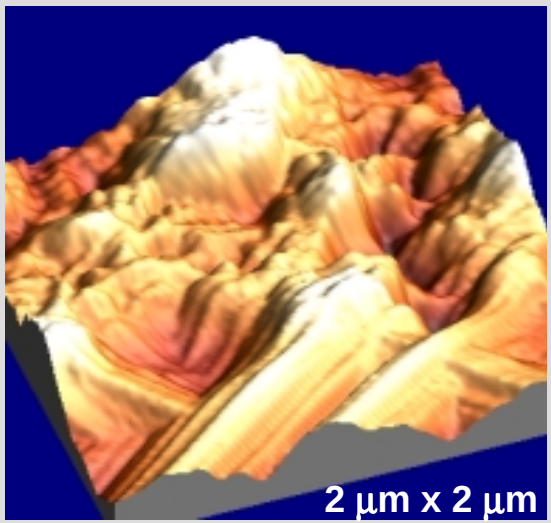
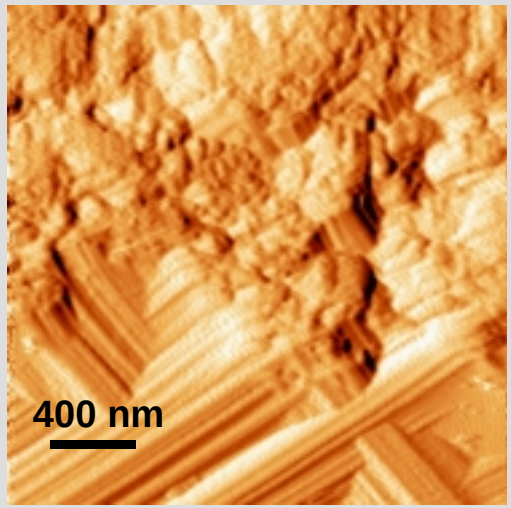




3D Topography



Topography

- **3D NETWORK OF ALIGNED PANI-COVERED MWNTs**

WHAT IS GOING ON?

- TWO PHASES: FREE EB AND MWNTs+EB
- QUINOID ENHANCED RESPONSE IN EB-MWNT

Key: ⇓ **In-situ polymerization**

- CHANGE OF THE EB CONFORMATION
- MORE PLANAR CONFORMATION ALONG MWNTs

Conformational Changes

- new, more planar, conformation of PANI wrapping around MWNTs

- Stabilization by

  - strong π- π interaction and simultaneously

  - self-organization of randomly oriented planar-PANI-covered MWNTs into aligned bundles

- Solubility and Processability
- Enhanced functionality (electrical and thermal properties) of PANI-MWNT composite

Summary

- Completely soluble EB/MWNT composite composed of a pure EB matrix and of EB-coated MWNTs
- MWNT coating EB layer has a more planar conformation favouring the interaction between EB and MWNTs
- EB-coated MWNTs form aligned bundles resulting in a 3D network throughout the EB matrix
- Processable, highly conducting, thermally stable and luminiscent EB/MWNT composite

R. Sainz, Adv. Mater, 17, 281 (2005)
R. Sainz, Nanotechnology, 16, 150 (2005)

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