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Identification of porphyrin-single walled carbon nanotube's supramolecular structure via scanning probe microscopy: towards SWNT absolute handedness chirality determination

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KEYWORDS

Porphyrin, Single walled carbon nanotubes (SWNT), Scanning tunneling microscopy (STM), Supramolecular structure, Atomic force microscopy (AFM), Handedness Chirality.

SHORT SUMMARY

The future of nanomolecular electronics can be significantly developed by enhancing the optoelectronic properties of its building blocks and/or components. Nanocarbons (i.e. single-walled carbon nanotube (SWNT), highly oriented pyrolytic graphite (HOPG), fullerene, and graphene) as well as large π-organic molecules (i.e. porphyrins) are substantial building blocks for electronics. Therefore, anchoring SWNT with porphyrin via covalent or non-covalent functionalization will result in an efficient nanocomposite; thus, it is anticipated that the properties of the resulting nanocomposite will be tuned. However, the supramolecular structure of SWNT/porphyrin conjugates has not yet well-identified. Here in, we have succeeded to identify the supramolecular structure of different porphyrin derivatives on SWNT surface using scanning probe microscopy i.e. scanning tunneling microscopy (STM). Consequently, that ultimately leads to successful assignment, for the first time, of SWNT absolute handedness chirality.

EXTENDED ABSTRACT

Introduction

One of the most important approaches for fabricating electronic devices is the supramolecular chemistry techniques and/or self-assembly of many candidates i.e. organic molecules, carbon nanotubes, proteins and others. Self-assembly is defined as the ability of molecules, atoms to be arranged spontaneously producing regular pattern with no outside interference. One of the interesting aspects in molecular electronic devices is that the molecular behaviour and/or properties can be changed considerably based on the surroundings [1].

Nanocomposites of SWNT and porphyrin are noteworthy because they combine the outstanding features of two distinct materials. The composite behaviour will be enhanced by combining SWNT's unique characteristics and the porphyrin on its surface. To do so, the supramolecular structure of SWNT/porphyrin conjugates should be well-identified but unfortunately, to date it isn't.

In this study, we have succeeded to identify the supramolecular structure of different porphyrin derivatives on SWNT surface using scanning probe microscopy i.e. scanning tunneling microscopy (STM). Therefore, we could also use this finding to assign, for the first time, the SWNT absolute handedness chirality.

STM measuments of SWNT/porphyrin conjugates

From 2018 to date, we [2-4] are doing an outstanding efforts in identifying the supramolecular structures of different porphyrin candidates on SWNT surface by using mainly scanning tunneling (STM) imaging technique. Our findings are promising compared to the little previous trials due to the very high and clear resolution images obtained. Different porphyrin molecules were used i.e. 5,15-bis(3,5-

bis(isopentyloxyphenyl))-10,20-bis(trimethylsilylethynyl)porphinato with different metal centers i.e. Zn, Ni, and Co [2], 5,15-bisdodecylporphyrin (BDP) [3] and its Ni(II) complex (Ni-BDP) [4], as displayed in Fig. 1.

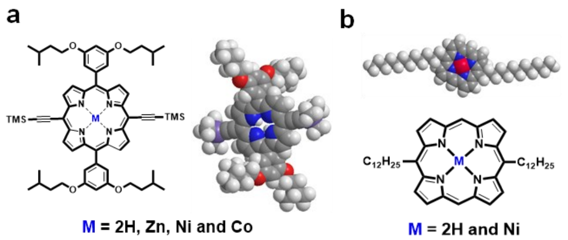

Figure 1. Chemical structures of (a) 5,15-bis(3,5-bis(isopentyloxyphenyl))-10,20-bis(trimethylsilylethynyl)porphinato with its Zn(II), Ni(II), and Co(II) complexes. (b) 5,15-bisdodecylporphyrin (BDP) and its Ni(II) complex (Ni-BDP). Adapted from [5].

We [2] have successfully identified the supramolecular structure of Zn(II), Ni(II), and Co(II) porphyrin complexes that anchoring non-covalently to the SWNT surface (Fig. 2a-c). The figure shows the STM images of different metalloporphyrins that apparently adsorbed on SWNT surface presenting an obvious debundling effect with different arrays. Consequently, by changing the porphyrin central metal, different supramolecular structures can be observed on the SWNT surface.

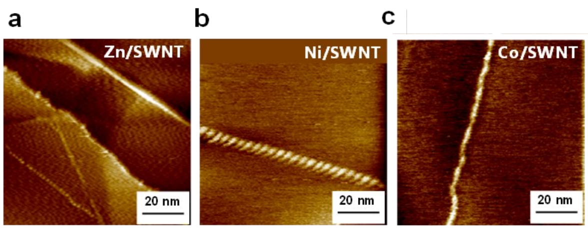

Figure 2. STM images for the supramolecular structures (on HOPG surface) of (a) ZnPor/SWNT, (b) NiPor/SWNT, and (c) CoPor/SWNT complexes. STM imaging parameters: $V_{sample} = 0.100$ V and $I_t = 0.010$ nA, Adapted from [5].

By knowing how the porphyrin molecules could align on the SWNT surface, we [3] could investigate, for the first time, the first assignment of the SWNT absolute handedness chirality via STM measuments of the supramolecular structure of porphyrin derivatives (BDP, Fig. 1b).

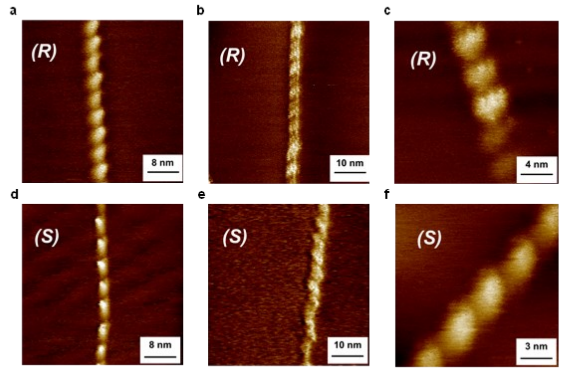

Figure 3. (a-f) STM images of (R)-type (aligned to right) and (S)-type (aligned to left) of BDP/chiral-SWNT composites on HOPG surface under ambient conditions. STM parameters: $V_{sample} = 0.100$ V and $I_t = 0.010$ nA. Adapted from [5].

We could observe two opposite chiral supramolecular structures of porphyrin molecule on SWNT surface under ambient conditions (Fig. 3a-f) identifying the two SWNT enantiomers handedness chirality, where the supramolecular structures of porphyrin molecules are so sensitive to the SWNT chirality as an adsorbent.

The previous findings will pave the way towards designing and fabricating novel supramolecular architectures for porphyrin/SWNT-based devices with potential applications i.e. catalysts, sensors, optoelectronic, photonic and spintronic devices as an approach for the future development of molecular electronics field.

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