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Perylene bisimide metal complexes as new MWCNTs dispersants: Role of the metal ion in stability and temperature sensing

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HIGHLIGHTS

- Metal complexes of a perylene bisimide are proposed as MWCNTs dispersants.
- Ionic charges endow perylene derivative enhanced MWCNTs dispersibility.
- Electrical resistances strongly rely on the MWCNTs dispersion efficiency.
- Temperature sensors comparable to thermistors are prepared.
- Resistance variations are found to be unaffected by dispersant nature.

GRAPHICAL ABSTRACT
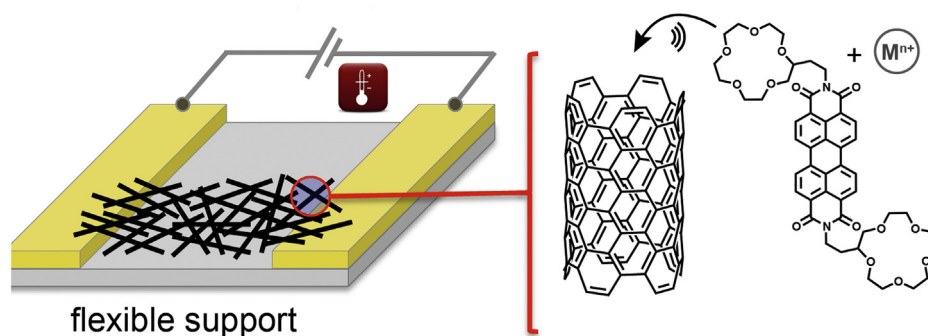
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ABSTRACT

We report on new dispersants based on metal complexes of an extended polycylic aromatic perylene bisimides (PeryC_M), suitable for the exfoliation of MWCNTs. The formal 1:1 metal complexes provided well-disentangled and undamaged MWCNTs and with a content at least 35 wt.% higher than that given by the bare ligand. The ionic charges at the periphery of PeryC_M endowed the π – conjugated perylene core with electrostatic repulsions, thus enhancing MWCNTs dispersibility. MWCNT-based mixtures displayed electrical resistance depending on the MWCNTs content and a typical semiconducting (activated) electrical transport with decreased resistance when heated within the physiological temperature range, i.e. from 20 to 40 °C. While perypheral charges are meaningful for MWCNTs deboundling and stabilization, they do not play any significant role in determining resistance sensitivity to temperature variations within the physiological regime. A negative temperature coefficient of about 10^{-2} K^{-1} and comparable to that of common thermistors was found for the investigated sensors.

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1. Introduction

Carbon nanotubes (CNTs) are nanostructured one-dimensional graphitic materials that possess several outstanding properties [1–4] that are adversely affected by the strong van der Waals interactions between single tubes, which favour the formation solid bundles. Non-covalent functionalization has been demonstrated

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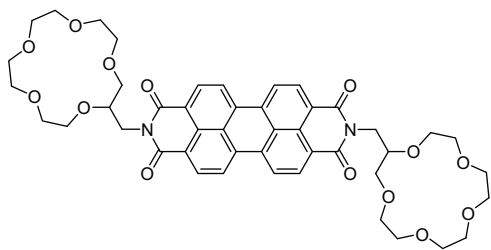 E-mail address: andrea.pucci@unipi.it (A. Pucci).

Fig. 1. Chemical structure of *N,N'*-bis(2-aminomethyl-15-crown-5)-3,4,9,10-perylenetetracarboxylic acid diimide (PeryC).

2. Experimental section

2.1. Materials

Perylene-3,4:9,10-tetracarboxylic acid bisanhydride, 2-aminomethyl-15-crown-5, imidazole, $Ca(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $[Pb(ClO_4)_2 \cdot 3H_2O]$ and $[Fe(ClO_4)_3 \cdot H_2O]$, were supplied by Aldrich and used without further purification. Acetonitrile (CH_3CN) was HPLC-grade (purity >99.8%) from Sigma. Vapour grown multi-walled carbon nanotubes (MWCNTs, Baytubes C150 P), from Bayer Material Science, were used as received. They consist of 3–15 graphitic layers with diameters range from 13 to 16 nm and lengths between 1 and 10 μm. The density is 1.4–1.6 g/cm³ [20].

2.2. Synthesis of N,N'-bis(2-aminomethyl-15-crown-5)-3,4,9,10-perylenetetracarboxylic acid diimide (PeryC)

Perylene-3,4:9,10-tetracarboxylic acid bisanhydride (0.3400 g, 1.14 mmol), 2-aminomethyl-15-crown-5 (0.39 mL, 1.68 mmol), and imidazole (5 g) were heated at 140 °C for 10 h under stirring. 2N HCl (200 mL) was added and the mixture was stirred for 1 h at room temperature. The resulting dark-red solid was filtered off and washed with several portions of distilled water until the pH of the washings was neutral and dried under vacuum. The crude product was purified by column chromatography on silica gel using chloroform/ethyl acetate 10:1 by volume as the eluent: 0.4584 g (0.53 mmol, yield: 60.3%) of a deep-red solid was recovered.

IR (KBr): 3093 (υCH arom), 2952, 2948, 2857 (υCH aliph), 1695, 1653, 1594 (υCO imide), 1504, 1440, 1398, 1342 (υCC ring) cm-1. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): 8.5 (m, 8H, $-CH_2$- arom), 4.3 (m, 4H, N-CH2), 3.6–3.8 (m, 36H, O-CH_2-CH_2-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): 162 (CO), 137, 131, 129, 122 (CC arom) ppm. UV–vis absorption ($CHCl_3$): $\lambda_{max} = 524$ nm, $\varepsilon = 29100$ L cm^{-1} mol^{-1}). Emission ($CHCl_3$, $\lambda_{exc} = 300$ nm): $\lambda_{emmax} = 541$ nm. Elemental analysis: calcd ($C_{48}H_{54}N_2O_{14}$): 65.3% C, 6.2% H, 3.2% N; found: 65.5% C, 5.9% H, 3.8% N.

2.3. Preparation of stock solution of PeryC and metal binding experiments

Stock solutions of PeryC ($2.59 \cdot 10^{-5}$ M) were prepared by dissolving a proper amount of the perylene derivative in CH_3CN. Stock solutions of the metal ions (0.2 M) were obtained by dissolving a proper amount of the relevant chlorate salt in CH_3CN; the concentration was checked by EDTA titration of an opportune dilution of the stock in water solvents (CH_3CN negligible) following known procedures [21]. The total molar concentration of the PeryC dye is indicated as C_L, whereas the total molar concentration of the metal ion is indicated as C_M. In the metal binding experiments, opportune dilutions of the stock were titrated with metal ions solutions directly into the spectrophotometer cell (1 cm path length), which contained a known volume of the PeryC solution. The additions were made using a Hamilton syringe connected to a micrometric screw that enabled volumes as small as 0.166 μL to be added. The metal complex (PeryC_M) formation data were analysed by means of the HypSpec14 software (Protonic Software UK) [22]. HypSpec2014 enables the determination of equilibrium constants from spectrophotometric data obtained during UV–vis titrations by an interactive fitting on all selected wavelengths for all selected spectra (total concentration of metal and ligand at each step provided as input). Complex models can be defined, factor analysis (principal component analysis) helping in individuating the number of active species. The PeryC_M complexes to add to the MWCNTs

as an effective tool in nanotubes deboundling since it preserves their structural graphitic integrity as well as their unique electronic properties. Recently, perylene bisimides (PBIs) have been successfully utilized as surfactants for the CNTs dispersion in aqueous and organic media [5–12]. PBIs allowed their effective dispersion in solution due to their polycyclic planar structure that is a renowned binding unit to the sp^2 carbon lattice of CNTs. PBIs are widely used as fluorophores, dyes and n-type semiconductors with excellent photostability and optical features depending on the particle size and supramolecular packing. For these appealing properties, PBIs have been largely investigated for the preparation of luminescent solar concentrators, lasers, photovoltaic cells and organic light-emitting diodes (OLEDs) [13–16]. These features flanked by the effective interactions with CNTs make CNT/PBI nanostructured systems intriguing solutions for the development of innovative smart electronic devices and sensors. For example, the effective π-associations between an ionic surfactant based on extended polycyclic aromatic perylene bisimides and exfoliated MWCNTs, were found to be worthwhile for the preparation of sensitive and reproducible sensors to measure body temperature [17].

This study examines the synthesis of a new perylene derivative, the *N,N'*-bis(2-aminomethyl-15-crown-5)-3,4,9,10-perylenetetracarboxylic acid diimide (PeryC, Fig. 1) and its ability to coordinate metal ions and to stabilise MWCNTs in organic media. Notably, MWCNTs exfoliation and dispersion stabilization could be amplified by adding peripheral charges to the perylene nucleus thanks to the electrostatic repulsion imparted by the metal ions. Moreover, such amplification could be modulated by the valence of the metal ion employed. Even if the interaction between dyes and CNTs has been already investigated [18], no such demonstration has ever been offered. First of all, we analysed the affinity of the crown ether ligand towards different metal ions in acetonitrile, by titrating PeryC with the chlorate salts of different cations ($Ca(ClO_4)_2$, $Pb(ClO_4)_2$, $Ni(ClO_4)_2$, $Co(ClO_4)_2$ and $Fe(ClO_4)_3$). The different ability to form the relevant metal complex (PeryC_M) was enlightened, as analogously reported in literature for perylene bisimide derivatives possessing crown ether receptors at the 1,7 bay-positions [19]. The cations that quantitatively bind PeryC (Ca^{2+}, Pb^{2+} and Fe^{3+}) were used for the subsequent evaluations in CNTs mixtures, whereas weakly binding ions (Co^{2+} and Ni^{2+}) were disregarded.

The MWCNT/PeryC and MWCNT/PeryC_M dispersions were obtained by ultrasonication and the exfoliated CNTs were investigated to assess their structural integrity. Nanocomposite solid dispersions were obtained by drop casting and resistance variations as a function of temperature variations were investigated to explore the role of the metal ion in temperature sensing.