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Perylene bisimide/MWCNTs Water Dispersions for Miniaturized Temperature Sensors

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Abstract

We report on a new ionic surfactant based on the extended polycyclic aromatic perylene bisimides (PBI), namely *N,N'*-bis(2-(1-piperazino)ethyl)-3,4,9,10-perylenetetracarboxylic acid diimide dichloride (PZPERY), suitable for the exfoliation of multi-walled carbon nanotubes (MWCNTs). The ultrasonication (400 W for 5 min) of MWCNT/PZPERY water mixtures followed by centrifugation (4000 rpm for 30 min) provided disentangled and undamaged MWCNTs, which interact with the PZPERY molecules through π - π stacking interactions. The deposition of MWCNT/PZPERY dispersions on plastic film supporting gold electrodes allowed the fabrication of temperature sensors showing reproducible electrical resistances and typical semiconducting (activated) electrical transport with decreased resistivity when heated from 20 to 40 °C. The resistivity-temperature profile was very reproducible and with a negative temperature coefficient of about -0.02 K^{-1} , a value comparable to that found in common thermistors. Our results suggest that MWCNT/PZPERY based films have utility for the formation of sensitive, stable and reproducible sensors to measure body temperature.

1. Introduction

Carbon nanotubes (CNTs) are a third allotropic form of carbon, which have become a dominant class of nanostructured carbon-based materials with unique mechanical, electrical and thermal properties that depend critically on their structural perfection and high aspect ratio (typically >102).¹⁻⁴ Single-walled CNTs (SWCNTs) consist of single graphene sheets (monolayer of sp^2 bonded carbon atoms) wrapped into cylindrical tubes with a diameter ranging from 0.7 to 2 nm and lengths up to micrometers. Multi-walled CNTs (MWCNTs) consist of concentric assemblies of SWCNTs and are therefore characterized by larger average diameters. The exceptional properties shown by SWCNTs and MWCNTs have led to an expanding number of applications including the production of strong and lightweight materials, the fabrication of electronic nano-devices and electrochemical sensors.^{2,3,5} However, the strong van der Waals interactions between individual nanotubes hinder the uniform dispersion at the nanoscale level and make their large-scale utilization problematic. Ultrasonication⁶ as well as covalent⁷⁻¹⁰ and non-covalent functionalization methods¹¹⁻¹⁴ have proven to be highly effective for the exfoliation and dispersion of CNTs in several media and polymer matrices. More specifically, non-covalent functionalization by surfactants has attracted considerable attention as it is highly scalable, reversible, and preserves the structural integrity of the graphitic network, which is a fundamental requisite to preserve the electronic properties of CNTs.

Recently, the extended polycyclic aromatic perylene bisimides (PBI) have enabled the dispersion of graphitic materials, such as CNTs, by means of the non-covalent functionalization through strong π - π stacking interactions.¹⁵⁻¹⁸ PBI was found to constitute an exceptionally well-suited anchor unit to the sp^2 carbon network of CNTs and allowed their effective dispersion in solution.^{17,19,20} In this process, the energy dissipated with sonication disassemble CNT bundles that are immediately surrounded by PBI molecules that bind *via* strong π - π interactions and prevent rebundling. PBIs are widely used as pigments and dyes, with colors ranging from red to black depending on the particle size and crystal packing of the dye molecules.²¹⁻²⁴ In addition to optical features such as

strong absorption in the visible region, high quantum yields and excellent photostability, PBIs also display low reduction potentials,²⁵ which enables their use as electron-acceptors and n-type semiconductors in photoinduced charge-transfer reactions. For these appealing properties, perylene derivatives have been extensively studied for the fabrication of field-effect transistors,²⁶ luminescent solar concentrators,²⁷ dye lasers,²⁸ photovoltaic cells²⁹ and organic light-emitting diodes (OLEDs).³⁰ Researchers tried to identify structure-property relationships of perylene/CNT mixtures in order to provide innovative materials for nanostructured electronic devices and sensors.**This sentence probably needs more justification with references. How about an alternative: “These properties and the strong associations with CNTs make integrated perylene/CNT materials systems attractive candidates for the generation of nanostructured electronic devices and sensors.” In this work, we report the preparation and characterization of MWCNTs water dispersions by using the N,N'-bis(2-(1-piperazino)ethyl)-3,4,9,10-perylenetetracarboxylic acid diimide dichloride (PZPER) as ionic surfactant (Figure 1).

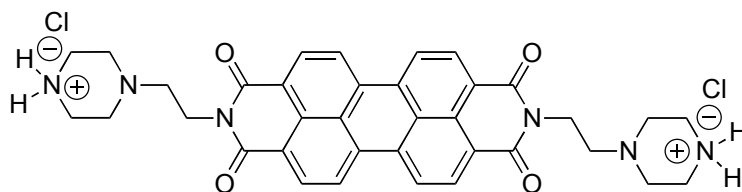


Figure 1. Chemical structure of the N,N'-bis(2-(1-piperazino)ethyl)-3,4,9,10-perylenetetracarboxylic acid diimide dichloride (PZPERY)

The ability of PZPER molecules to generate π - π stacking interactions has been previously utilized by our group for the preparation of chromogenic plastic materials as temperature indicators.³¹ The effective π -associations between PZPERY and MWCNTs suggested to us that these nanocomposites should function as temperature sensors, since both semiconducting and metallic CNTs are characterized by a temperature sensitive resistivities. Previous investigations have demonstrated the possibility of fabricating wearable temperature sensors based on MWCNT/polymer composites for use in monitoring of body temperature in the range 20–40 °C, and in particular the bed temperature of chronic wounds.^{6,32} However, these systems displayed a

resistance sensitivity of only -0.004 K^{-1} , a value which is comparable to that found in metals.^{6,32,33} Such low sensitivity was ascribed to the polymeric dispersants, such as poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (SEBS)⁶ or poly(vinylbenzyl chloride) derivative with triethylamine,³² and the insulating nature of these components limit the thermal and electronic conductivities of the nanocomposite. In the present paper, we explore the possibility that the highly conjugated core of the PZPERY surfactant will be able to produce higher performance (resolution) temperature sensors.

The MWCNT/PZPERY dispersions were obtained by ultrasonication of their mixtures in water for five minutes followed by centrifugation, and the quantity of dispersed CNTs was quantified by gravimetric analyses. Raman spectroscopy and transmission electron microscopy (TEM) were employed to assess the structural integrity of MWCNTs. The electrical resistance of films, obtained by drop casting aliquots of MWCNT/PZPERY dispersions, was investigated over the range 20–40 °C to explore their potential for the development of sensitive, stable, and reproducible temperature sensors.

2. Experimental part

Materials

Perylene-3,4,9,10-tetracarboxydianhydride (PTCDA), imidazole, 1-(2-aminoethyl)piperazine were supplied by Aldrich and used without further purification. Multi-walled carbon nanotubes (MWCNTs, Baytubes C150 P), a generous gift from Bayer Material Science, were used as received. These nanotubes are vapor grown and typically consist of 3–15 graphitic layers wrapped around a hollow 4 nm core. Typical diameters range from 13 to 16 nm, and the lengths are between 1 and 10 μm .

Synthesis of N,N'-Bis(2-(1-piperazinyl)ethyl)-3,4,9,10-perylenetetracarboxylic acid diimide dichloride (PZPER)

PTCDA (1 g, 2.55 mmol) was dissolved in 20 mL of 1-(2-aminoethyl)piperazine at 160 °C and

stirred for 22 h under nitrogen. After cooling to room temperature, the solution was treated with 100 mL of 2 N HCl. The dark violet solution was stirred for 12 h. The hydrochloride salt reaction products precipitated in acetone, where separated by filtration, and then washed thoroughly with distilled water until the pH of the washings were neutral. The dried product 1.3 g (1.92 mmol, yield: 75.6%) was a deep-red solid.

FT-IR (KBr): 2926 (ν CH aliph), 1695, 1656, 1593 (ν CO imide), 1508, 1441, 1401, 1362 (ν CC ring) cm^{-1} .

^1H NMR δ : 8.8-8.9 (d, 4H arom, $J = 15$ Hz), 4.7-4.9 (m, 4H, $\text{N}_{\text{imm}}\text{-CH}_2$), 4.4-4.5 (m, 4H, $\text{N}_{\text{pip}}\text{-CH}_2$) 4.0 (m, 16H, CH_2) ppm.

^{13}C NMR δ : 31.2, 37.8, 45.5, 52.8, 117.5, 120.4, 122.5, 125.4, 129.3, 132.5, 162.5 ppm.

elemental analysis calcd. ($\text{C}_{36}\text{H}_{38}\text{Cl}_2\text{N}_6\text{O}_4$): 62.9% C, 5.3% H, 12.2% N; found: 63.5% C, 5.7% H, 12.4% N.

Preparation of the MWCNT/PZPERY dispersion

Stock solutions (1 mg/mL) of PZPERY were prepared in ultra-pure water (purified by a Millipore S.A. 670120 water purification system) and kept in the dark at 4 °C until use within two days. The concentration (either mmol/mL or mg/mL) of PZPERY is indicated as C_{pery} . Aliquots of this solution (10 mL) were poured in vials containing 1 mg of MWCNTs. Uniform dispersions were then obtained by ultrasonication (UP 400 S, Hielscher) the MWCNTs/PZPERY mixtures for five minutes at full power (about 400 W) and a frequency of 24 kHz. Cooling with a stirred water/ice bath limited the increase in temperature and the loss of water during sonication to negligible levels (less than 0.4% by weight). The ultrasonic device was fixed so that its sonotrode could be reproducibly dipped into the dispersions, which were in prepared in vials of the same volume and shape**if important, perhaps give the vial's volume (mL) and dimensions (diameter and height)**. This procedure and the accurate weighing limits the variability of the process, evaluated as the fraction of dispersed nanotubes, to within 2%. The resulting dispersions were centrifuged at 4000 rpm for 30 min and then filtered to remove the residual MWCNT agglomerates. The final

MWCNT/PZPERY weight ratio in the solution was measured by thermogravimetric analyses (TGA) of the dried materials. Three different MWCNT/PZPERY dispersions, I, II, and III, were prepared according to the same procedure. The electrical resistances of films obtained after casting two 10 μ L aliquots of each MWCNT/PZPERY dispersion onto gold electrodes supported on a plastic film (Figure S1) was measured at different temperatures.

Apparatuses

^1H - and ^{13}C NMR spectra were recorded by a Varian Gemini 300 MHz instrument using 5-10% CF_3COOD (Aldrich, 99.5 atom % D) solutions. NMR spectra were recorded at 20 $^\circ\text{C}$, and the chemical shifts were assigned in ppm using the solvent signal as a reference. FT-IR spectra were recorded in KBr dispersions with the help of a PerkinElmer Spectrum One spectrometer. The UV-vis spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer having temperature control to within ± 0.1 $^\circ\text{C}$. Two different sets of experiments were performed for inspection of high dye concentration ranges: for the diluted dye a 1.0 cm path was used (until Abs < 1.0), whereas for concentrated solutions a 1.0 mm thick cell was used. In order to process and display data, the first data set was normalized to a 1.0 mm path to be merged together with the second set. Fluorescence spectra were recorded using a Perkin Elmer LS55 spectrofluorometer with temperature control (± 0.1 $^\circ\text{C}$, quartz cell of 1 cm path length). Increasing amounts of either the PZPERY solution or the PZPERY/MWCNT mixture were made using a Hamilton syringe connected to a micrometric screw enabling to dispense volumes down to 0.166 μL . All measurements were performed at 25.0 $^\circ\text{C}$.

Thermogravimetric scans were carried out by a Mettler Toledo Starc System (TGA/SDTA851e). Samples were heated from 100 to 850 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ under a nitrogen flow. Samples were annealed at 100 $^\circ\text{C}$ for 10 min before measurement to remove water. The morphologies of the MWCNT/PZPERY films were examined with a Philips CM12 transmission electron microscope (TEM). Raman spectra of solid dispersion obtained by drop casting the supernatant of each sample (after centrifugation) onto glass substrates were measured with a Horiba LabRAM HR Raman

Spectrometer at an excitation wavelength of 532 nm. Sensors were fabricated by casting MWCNT/PZPERY dispersions in water onto supports (Cad Line, Pisa, Italy) consisting of a polyimide film (Kapton[®], thickness 50 μm) and suitable electrodes. Kapton[®] was chosen due to its flexibility, chemical inertness, and low permeability to water and vapors, which helps the protection of the sensing film. Copper tracks were prepared by photolithography and then electroplated with nickel and gold for electrode fabricate (dimensions: length 7 mm, width 1 mm, distance 2 mm; thickness of copper 35 μm , nickel 3.0 μm , gold 1.2 μm). Sensor calibration in the range 20–40 $^{\circ}\text{C}$ was performed by placing the sensors in a temperature controlled hot stage and measuring the electrical resistance with a digital multimeter (KEITHLEY Mod. 2700).

3. Results and discussion

A PZPERY/MWCNT dispersion was prepared in a 10:1 PZPERY:MWCNT weight ratio: 1.0 mg of CNT was added to 10.0 mL of aqueous solution of PZPERY 1.0 mg/mL ($C_{\text{pery}} = 1.46 \text{ mmol/mL}$). This mixture was sonicated (400 W for 5 min) and then centrifugated (4000 rpm for 30 min). The fluorescence of its precipitate, which had been removed and resuspended, was negligible, meaning that all of the PZPERY remained in solution.

A thermogravimetric analysis permitted the quantification of the amount of MWCNTs included in the MWCNT/PZPERY dispersion (Figure 2).

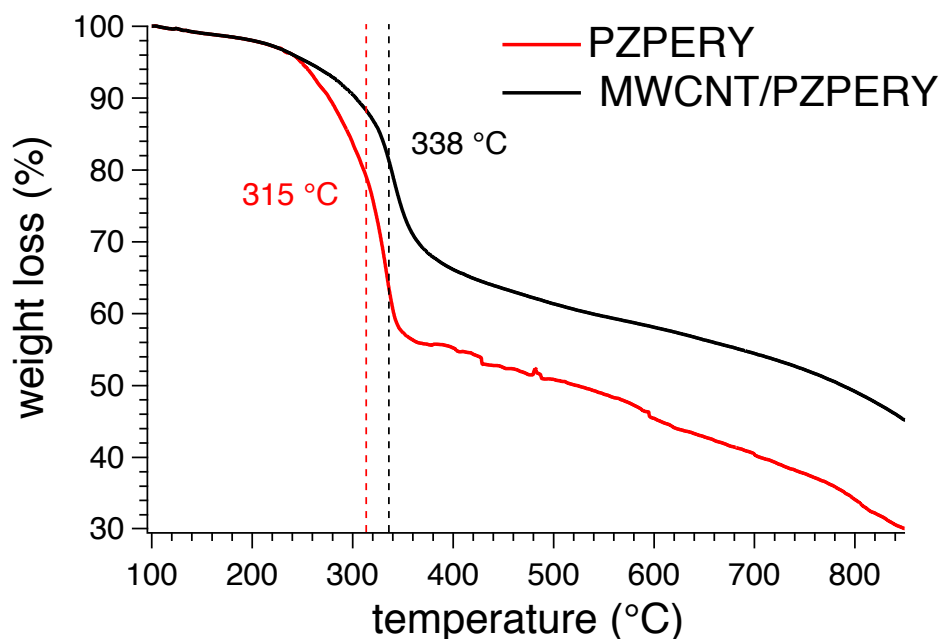


Figure 2. TGA analyses of PZPERY (red curve) and MWCNT/PZPERY dispersion (black curve)

The thermal degradation of PZPERY was observed to occur at a temperature of about 20 °C higher in the presence of MWCNTs (i.e. 338 instead of 315 °C), suggesting extra stability *via* the existence of effective interactions between the dye and the graphitic material. A weight percentage of 16.5 % was determined for MWCNTs from the difference in weight between the residuals of the same amount of MWCNT/PZPERY and PZPERY at 850 °C, i.e. after the complete degradation of the organic matrix. This allowed us to conclude that the dispersion contained 1.0 mg/mL and MWCNT 0.0165 mg/mL (PZPERY:MWCNT \approx 61) (Figure S2).

Spectroscopy

UV-vis and fluorescence spectroscopies were used to study the stabilizing effect of PZPERY in aqueous suspensions of MWCNTs. Spectra were recorded for different concentrations of the MWCNT/PZPERY dispersion. In these mixtures the $C_{\text{pery}}/C_{\text{MWCNT}}$ ratio remains constant (high dye excess, see above), so that the appearance of a dye aggregation is indicative of dye condensation on the surface of MWCNTs, a process that can lead to MWCNTs aggregation/precipitation *via* PZPERY bridges.

As shown in the supporting information (Figure 3S) the UV-vis spectra recorded with increasing concentrations of the perylene dye did not display new bands or shoulders appear, suggesting that it persists as a stable monomeric form over the explored range. Figure 3a shows a plot of the recorded absorbance vs. C_{pery} (squares): the linear trend further confirms that no aggregation of the dye alone occurs under the explored conditions. To further investigate possible auto-aggregation effects, the Franck–Condon progression can also be used ($\text{Abs}_{0-0}/\text{Abs}_{0-1}$), where Abs_{0-0} is the absorption at $\lambda = 500$ nm and Abs_{0-1} is the absorption at $\lambda = 550$ nm. A decrease in the $\text{Abs}_{0-0}/\text{Abs}_{0-1}$ value is considered indicative of an aggregation process.¹¹ Figure 3b (squares) shows a constant (within the experimental error) $\text{Abs}_{0-0}/\text{Abs}_{0-1}$ ratio over our concentration range and confirms the absence of auto-aggregation of PZPERY under the explored conditions.

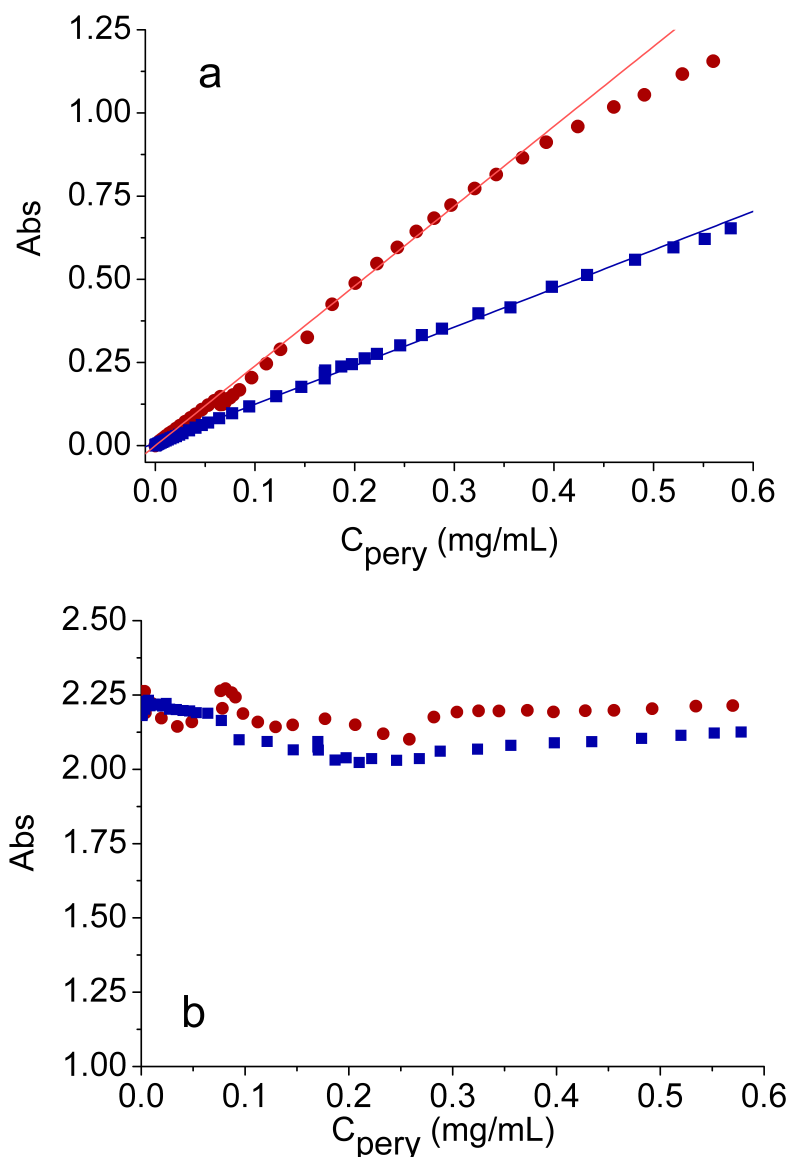


Figure 3. (a) Plot of absorbance vs. concentration for PZPERY alone in water (squares, $\lambda = 548$ nm) and of the MWCNT/PZPERY dispersion (circles, $\lambda = 538$ nm, $C_{CNT} \approx C_{pery}/61$); (b) evolution of the Franck-Condon correlation ($Abs_{0.0}/Abs_{0.1}$) at different concentrations of the dye (squares) and the dye/MWCNT dispersion (circles).

Figures 3a and 3b (circles) show the relevant absorbance values corrected from scattering effects using a procedure based on double logarithmic plots.^{34,35} Linearity up to a concentration of 0.4 mg/mL and a constant $Abs_{0.0}/Abs_{0.1}$ ratio are observed and both indicate that the MWCNT dispersion is efficiently stabilised by PZPERY. The fluorescence emission data suggested similar conclusions. As shown in the supporting information (Figure S4) the emission characteristics of PZPERY were not significantly affected by the presence of MWCNTs. This confirmed that the

interaction of the excess PZPERY with MWCNTs does not result in an aggregation of the dye on the MWCNT surface but had a stabilizing effect on the dispersion.

Raman spectroscopy is a versatile technique used for the structural characterization of CNTs, as well as for studying their interaction with the exfoliating agents. Figure 4 shows the Raman spectrum of the MWCNT/PZPERY dispersion compared to a previously investigated MWCNT composite with a thermoplastic elastomer, i.e. the poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (SEBS), which had been reported to be very effective in CNT exfoliation and dispersion.^{6,33} The most prominent features in a Raman spectrum of MWCNTs are the G and D bands (Figure 4). The G-band at 1560 cm^{-1} is an intrinsic feature of CNTs related to the planar vibration of carbon atoms in most sp_2 graphitic materials. Conversely, the disorder-induced D-band at 1320 cm^{-1} is attributed to the scattering from defects breaking the basic symmetry of the graphene sheet. MWCNTs typically show the highest ratio (I_D/I_G) between the intensities of these peaks among all carbon nanotubes, since a large number of structural defects are present within the multiple graphite layers.

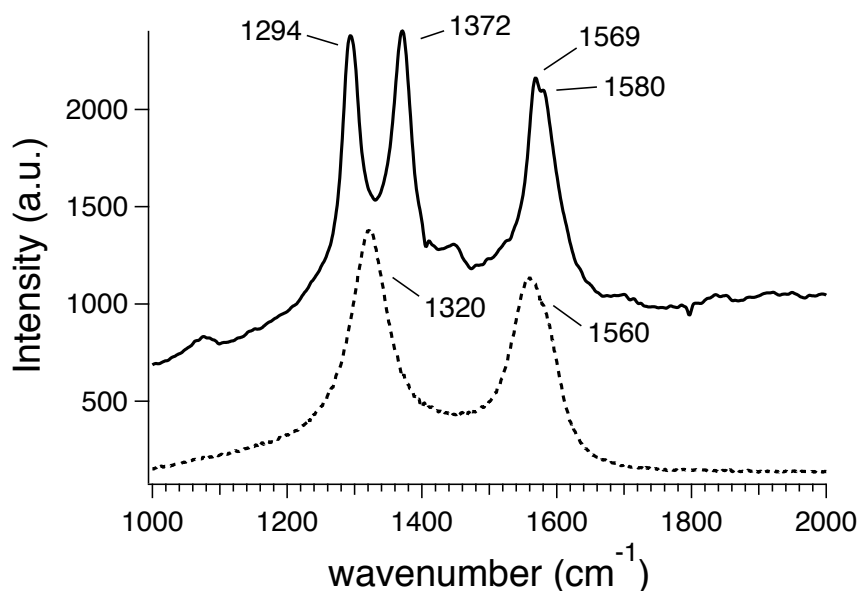


Figure 4. Raman spectra of MWCNT/PZPERY (solid line) and MWCNT/poly(styrene-*b*-(ethylene-co-butylene)-*b*-styrene) (SEBS) (dashed line)⁶ films ($\lambda_{\text{exc.}} = 532\text{ nm}$). The wavenumbers (cm^{-1}) of the peaks are reported as insets

In the spectrum of MWCNT/PZPERY films, the two lines of PZPERY at 1294 and 1372 cm^{-1} are well resolved and superimposed on an underlying fluorescent background.³⁶ The D band of MWCNTs is obscured by the large PZPERY scattering, and its low intensity may be also the result of a shielding effect from the dye coating and the CNTs defects.³⁷ It is worth noticing that the G band in the MWCNT/PZPERY dispersion is split in two unresolved peaks, which are blue-shifted of about 15-20 cm^{-1} with respect to the SEBS based nanocomposite. This feature may be a consequence of the effective π -interactions between MWCNTs and the PZPERY molecules, which favor the exfoliation of CNTs by keeping them apart (i.e., isolated double bonds resonate at higher frequencies than in the G band of interacting CNTs).³⁸

Morphology

In order to evaluate if our procedure allowed the effective exfoliation of MWNTs, the MWCNT/PZPERY mixtures were analyzed by transmission electron microscopy (TEM). The TEM images (Figure 5) clearly show single (unbundled) nanotubes as the dominant species, thus confirming the good interactions of PZPERY with MWCNTs in water. Moreover, the average length of MWCNTs is comparable to their nominal length (1–10 μm), thus suggesting that the CNTs are not severely damaged by the exfoliation process.

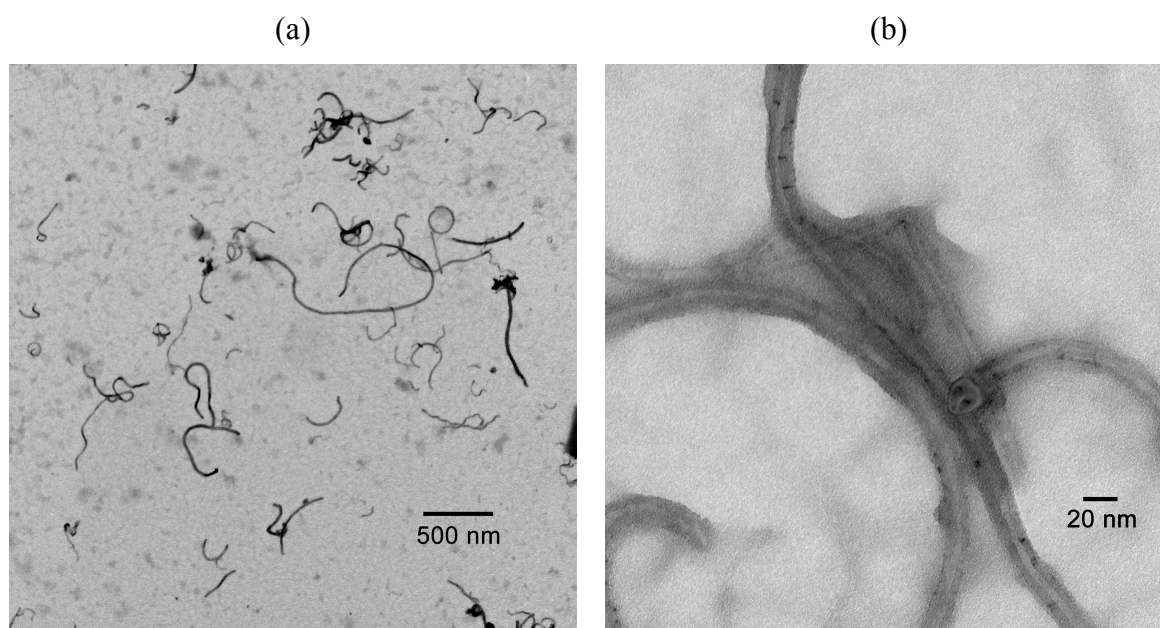


Figure 5. TEM images of the MWCNT/PZPERY dispersion at low (a) and high (b) magnification

Resistance sensitivity to temperature

Aliquots (10 μL) of three replicate MWCNT/PZPERY dispersions (namely, I, II and III) were drop cast onto the previously described electrodes on plastic support to fabricate six temperature sensors (two duplicates for each dispersion). Their electrical resistivities were measured after the complete evaporation of water and ranged between 24 and 54 $\text{k}\Omega$ (Table 1). CNTs show a temperature dependent resistivity, which makes them suitable for the fabrication of small-size temperature sensors. Table 1 reports the electrical resistances of the sensors at different temperatures. A typical semiconducting behavior, with decreasing resistance values with increasing temperatures from 23.7 to 40.0 $^{\circ}\text{C}$, was obtained. Figure 6 plots the resistance versus temperature variation for the MWCNT/PZPERY IIIa sensor, showing the classic Arrhenius behavior $R=R_0 \cdot e^{-B/T}$, with B as an experimental parameter and T as the absolute temperature.³⁹

Table 1. Electrical resistances of the MWCNT/PZPERY based sensors at different temperatures

T ($^{\circ}\text{C}$)	R($\text{k}\Omega$)					
	<i>Ia</i>	<i>Ib</i>	<i>IIa</i>	<i>IIb</i>	<i>IIIa</i>	<i>IIIb</i>
23.7	46	27	24	54	46	43
27.0	37	25	22	46	42	38
29.0	32	24	21	40	38	34
30.2	30	23	20	38	37	34
31.5	29	22	19	35	35	33
34.0	27	20	18	33	33	31
35.6	26	19	18	32	32	30
40.0	24	18	16	29	30	28

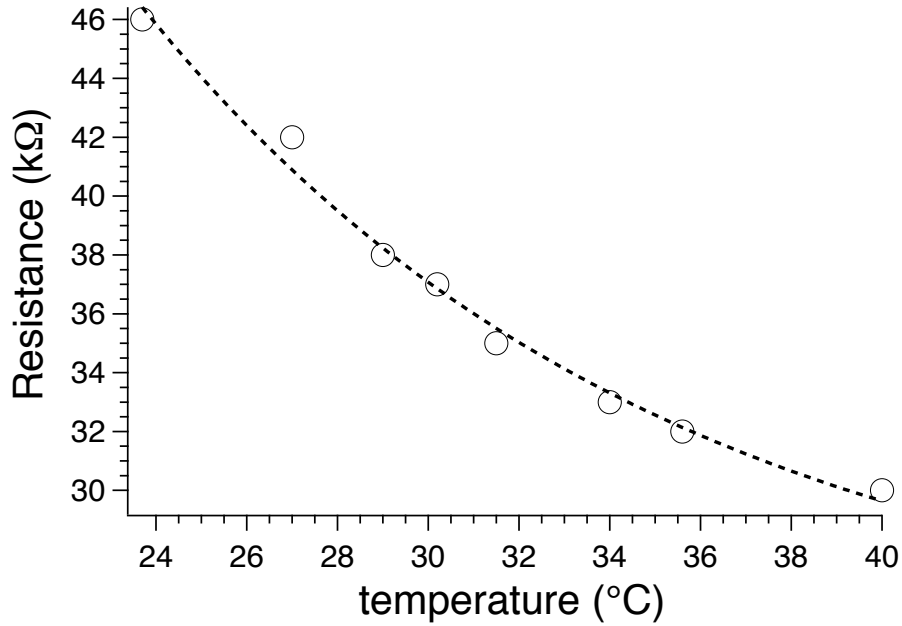


Figure 6. Electrical resistance of the MWCNT/PZPERY IIIa sensor as a function of temperature, and exponential fit to the data ($y_0+A \cdot e^{-B/T}$; with $y_0 = 24.28 \pm 2.54$, $A = 174.2 \pm 57.7$, $1/B = 0.087 \pm 0.018$; $R^2 = 0.98$).

Resistivity variations of more than 35% were recorded over the 23.7 to 40.0 °C temperature interval for all the sensors. The behavior of sensors from the dispersion III, displayed an almost equivalent response to temperature (Table 1) and were further investigated in successive calibration cycles.

The resistance responses of the MWCNT/PZPERY III sensors were determined over four successive heating cycles (Table 2). Reproducible resistance variations were observed, with maximum amplitudes of 30 kΩ within the temperature interval of 20 °C. These features support the use of the MWCNT/PZPERY system as a resistive sensor for temperature variations within the physiological regime.

Table 2. Resistance variations for all the MWCNT/PZPERY depositions as a function of the temperature

1 st cycle			2 nd cycle			3 rd cycle			4 th cycle		
T (°C)	R(kΩ)		T (°C)	R(kΩ)		T (°C)	R(kΩ)		T (°C)	R(kΩ)	
	IIIa	IIIb		IIIa	IIIb		IIIa	IIIb		IIIa	IIIb
23.7	46	43	21.5	70	70	21.8	77	68	21.4	81	72
27.0	42	38	28.0	56	56	32.0	63	54	25.0	74	62
29.0	38	34	31.0	51	51	37.0	52	45	27.2	69	58
30.2	37	34	33.5	47	47	38.5	50	44	29.9	65	56
31.5	35	33	34.0	46	46	40.0	48	43	31.3	61	54
34.0	33	31	35.0	45	44				33.4	58	50
35.6	32	30	36.5	43	43				37.0	54	48
40.0	30	28	38.5	42	42				38.5	53	46
			39.5	41	41				41.5	51	44
			40.4	40	40						

It is worth noting that, plotting the natural logarithm of the resistance variation (R/R_0 , with R_0 the resistance at the lowest temperature) against the inverse of the temperature in K, that a linear Arrhenius type behavior is evident in all the heating cycles (Figure 7). Moreover, the linear correlation ($R^2 \approx 0.99$) appears almost identical for all the experiments, thus confirming that the MWCNT/PZPERY system is a highly reproducible temperature sensor.

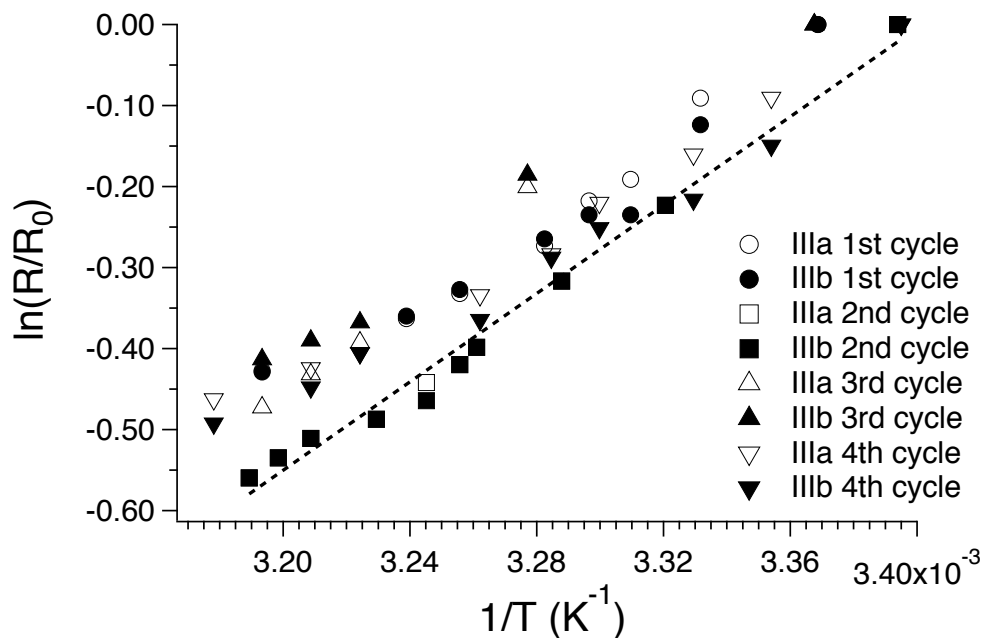


Figure 7. Arrhenius plot of the natural logarithm of the resistance variation as a function of the reciprocal of the absolute temperature according to the Arrhenius equation for successive heating cycles of MWCNT/PZPERY III dispersions, and linear fit ($R^2 = 0.99$) of IIIb 2nd cycle

The temperature coefficient of the MWCNT/PZPERY sensor was calculated according to the equation 1 and the values reported in Table 3:

$$R(T) = R(T_0) \cdot [1 + \alpha \cdot (T - T_0)] \quad (\text{eq.1})$$

where α is the temperature coefficient expressed in K^{-1} .

Table 3. Temperature coefficient (α) of MWCNT/PZPERY III dispersions after successive heating cycles

α (K^{-1})							
1 st cycle		2 nd cycle		3 rd cycle		4 th cycle	
<i>IIIa</i>	<i>IIIb</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IIIa</i>	<i>IIIb</i>
-0.021	-0.021	-0.023	-0.023	-0.023	-0.021	-0.019	-0.020

The MWCNT/PZPERY sensor displayed sensitivity corresponding to a negative temperature coefficient of -0.02 K^{-1} , an absolute value that is comparable to the highest values found in common thermistors (0.044 K^{-1}) and an order of magnitude higher than those of metals ($0.0037\text{--}0.006 \text{ K}^{-1}$; 0.00385 K^{-1} for a Pt(100) sensor). Notably, α maintains a constant value for every measurement cycle, thus confirming the relevant properties of the prepared temperature sensor.

4. Conclusions

We have demonstrated that PZPERY, a water soluble PBI dye, is an effective surfactant for MWCNTs exfoliation. Spectroscopy studies (i.e., UV-vis, fluorescence and Raman) together with microscopic investigations (TEM) revealed that PZPERY molecules are able to generate non-covalent functionalization of the MWCNT graphitic materials through π - π stacking interactions, and that the exfoliation process does not do significant damage to the one-dimensional CNT structure. PZPERY/MWCNT based sensors showed reproducible resistance values, thereby confirming the reliability and validity of the exfoliation procedure. Notably, the resistance of the PZPERY/MWCNT films varied considerably with the increase of temperature (about $30 \text{ k}\Omega$ over the temperature interval of $20 \text{ }^\circ\text{C}$) showing the semiconducting behavior between 20 and $40 \text{ }^\circ\text{C}$. Measurements repeated over four successive heating cycles revealed highly reproducible resistance

variations with negative temperature coefficient of about -0.02 K^{-1} an absolute value comparable to the values found in common thermistors. All these features support the use of the MWCNT/PZPERY system as a highly sensitive resistive sensor for temperature variations within the physiological regime.

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Supplementary information of the manuscript entitled “*Perylene bisimide/MWCNTs Water Dispersions for Miniaturized Temperature Sensors*” by Tarita Biver, Francesco Criscitiello, Fabio Di Francesco, Matteo Minichino, Andrea Pucci, Timothy Swager

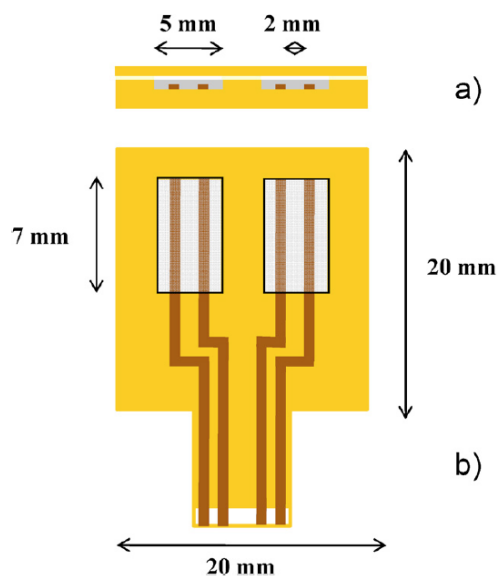


Figure S1. Schematic diagram of the sensor: (a) section and (b) top view

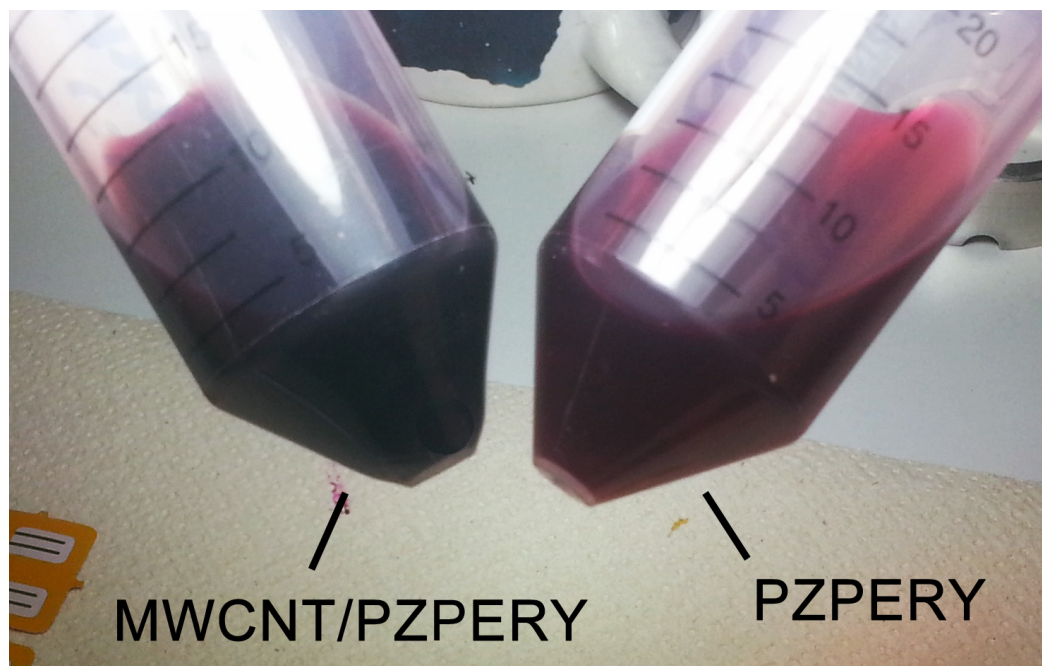


Figure S2. Picture of and MWCNT/PZPERY water dispersion (left, PZPERY concentration = 1 mg/mL; MWCNT concentration = 0.0165 mg/mL) and PZPERY water solution (right, PZPERY concentration = 1 mg/mL)

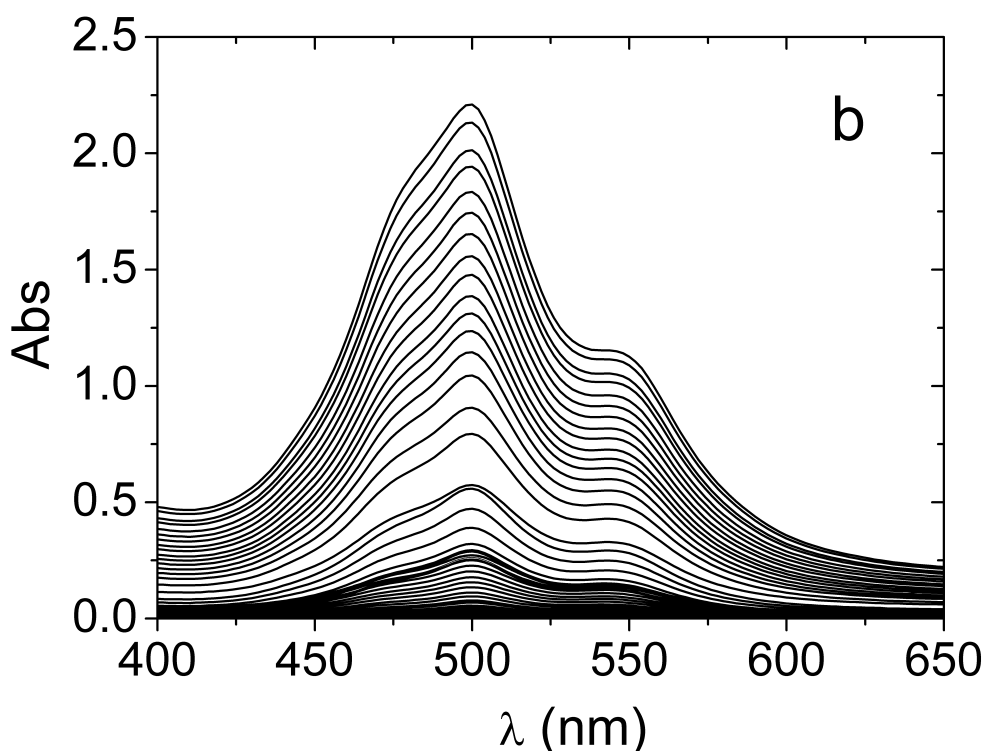
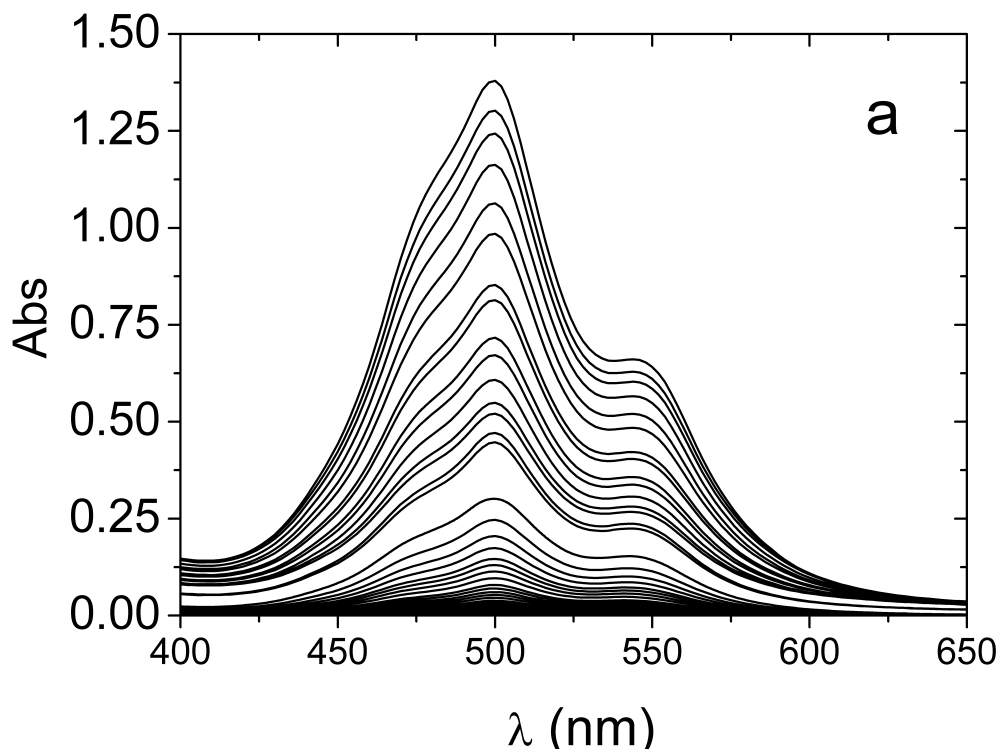


Figure S3. (a) UV-vis spectra in water of increasing concentrations of PZPERY (C_{pery} from 0 to 0.6 mg/mL) and (b) of increasing concentrations of the PZPERY/MWCNT dispersion (C_{pery} from 0 to 0.6 mg/mL, $C_{\text{MWCNT}} \approx C_{\text{pery}}/61$).

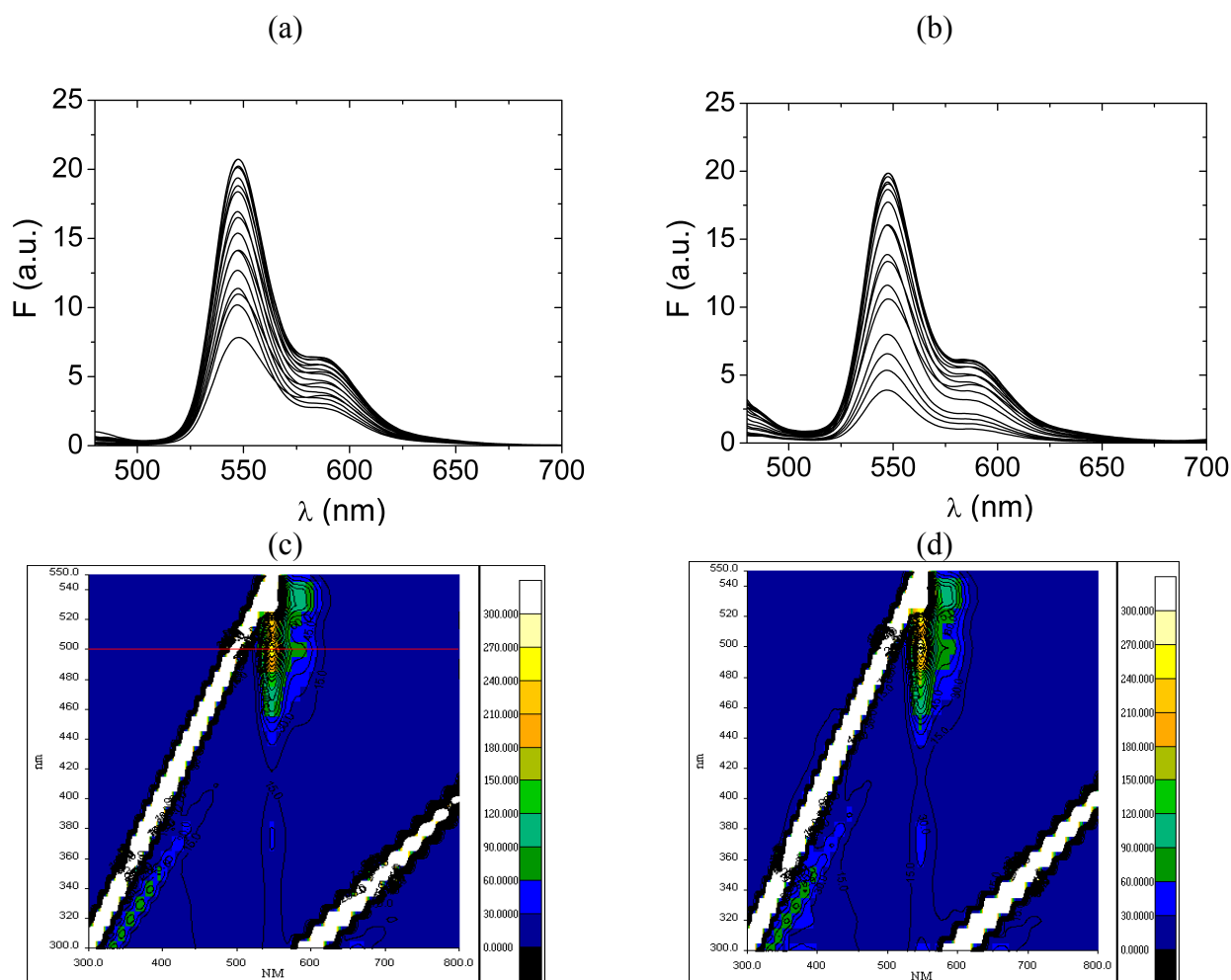


Figure S4. (a) Fluorescence spectra in water of increasing concentrations of PZPERY alone (C_{pery} from 1.6×10^{-4} to 0.09 mg/mL, $\lambda_{\text{ex}} = 460$ nm) and (b) of increasing concentrations of the PZPERY/MWCNT dispersion (C_{pery} from 1.6×10^{-4} to 0.09 mg/mL, $C_{\text{MWCNT}} \approx C_{\text{pery}}/61$, $\lambda_{\text{ex}} = 460$ nm). (c) 3D spectra of the fluorescent features of perylene dye alone ($C_{\text{pery}} = 1.0$ mg/mL) and (d) of increasing concentrations of the PZPERY/CNT dispersion ($C_{\text{pery}} = 1.0$ mg/mL); x-axis is the emission wavelength, y-axis is the excitation wavelength, intense diagonal signal are due to non-chemical scattering effects.