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SUPPORTING INFORMATION

Preparation and electrical properties of a copper-conductive polymer hybrid nanostructure

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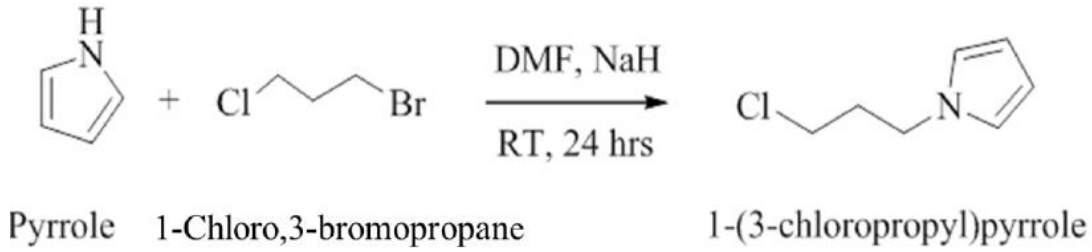
Contents

1. Monomer (NPPBH) synthesis and characterisation

Reagents of the highest available purity from Aldrich/Sigma/Fluka (Germany) were used without further purification. N-(3-pyrrol–1–yl–propyl)-4,4`-bipyridinium hexafluorophosphate (NPPBH) was synthesized in reasonable yields (details below) in a two-step process. The product was characterized by means of elemental analysis, ^{1}H NMR, FTIR and MS (ESI).

1.1 Synthesis of 1-(3-chloropropyl)pyrrole



Pyrrole 1-Chloro,3-bromopropane 1-(3-chloropropyl)pyrrole

In a 250 ml two-necked round bottom flask, pyrrole (6.9 mL, 100 mmol) was added to DMF (250 mL) under N_2 at room temperature while stirring. NaH (60% in oil) (4.0g, 100 mmol) was then added to the solution under N_2 and stirred for 30 min at room temperature. 1-Chloro-3-bromopropane (50 ml, 500 mmol) was then added and the mixture was allowed to stir overnight. The reaction mixture was filtered using a Buchner funnel through filter agent (CELITE 521) and then the solvent was removed in vacuum. The product was extracted with ethyl acetate (three times), dried over anhydrous magnesium sulphate, and the solvent removed in vacuum. The product was purified by silica column chromatography using hexane : ethyl acetate (95:5 v/v) as the eluting solvent to give 1-(3-chloropropyl)pyrrole as a yellow oil (Yield 5.0 g, 35 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ = 2.18 ppm (2H, m, *CH_2*), 3.51 ppm (2H, t, *Cl-CH_2*,), 4.12 ppm (2H, t, *N-CH_2*), 6.21 ppm (2H, d, *β CH-pyrrole*), 6.71 ppm (2H, d, *α CH-pyrrole*). FTIR: 3101 cm^{-1} (C-H, pyrrole), 2933, 2880 cm^{-1} (C-H aliphatic stretching), 1090 cm^{-1} (C-N), 1497, 1361 and 1282 cm^{-1} (CH bend and coupled pyrrole ring modes).

1.2 Synthesis of N-(3-pyrrol–1–yl–propyl)-4,4'-bipyridinium hexafluorophosphate (NPPBH) Adapted from Refs 1-2.

In a two-necked round bottom flask 4,4'-dipyridyl (0.60 g, 3.85 mmol) which was dissolved in dry ethanol (2.0 ml) under nitrogen and 1-(3-chloropropyl)pyrrole (0.5 g, 3.5 mmol) was added to the solution while stirring. The solution was refluxed overnight under nitrogen. After 24 hours, the reaction solution was allowed to cool to the room temperature. The ethanol was removed on a rotary evaporator. To the resulting residue chloroform was added and this was extracted with water (3 x 20 ml). The product was obtained from the aqueous solution by addition of a saturated solution of potassium hexaflorophosphate. The brownish yellow precipitate was dried (Yield 1.5 g, 95 %), Mp. 174.0 ^{o}C. Elemental analysis: $C_{17}H_{18}N_3$ PF_6^- theoretical: C, 49.88%, H, 4.40, %, N, 10.27%; found: C, 48.18%, H, 4.13%, N, 9.65%. ^{1}H NMR (300 MHz, D_2O, 25 °C) δ = 2.55 ppm (2H, m, *CH_2*), 4.09 ppm (2H, t, *CH_2*), 4.61 ppm (2H, t, *CH_2*), 6.04 ppm (2H, t, *β CH-pyrrole*), 6.68 ppm (2H, t, α *CH-pyrrole*), 7.82 ppm (H, m, *CH-pyridyl*), 8.23 ppm (H, m, *CH-pyridyl*), 8.71 ppm (H, m*, CH-pyridyl*). FTIR: 3129, 3051 cm^{-1} (C–H aromatic stretching), 2924, 2872 cm^{-1} (C–H aliphatic stretching), 1641 cm^{-1} (C=C aromatic ring stretching), 1458 cm^{-1} (C-H bend and coupled ring modes), and 1166 cm^{-1} ($H_2C–N^+$) and 812 cm^{-1} (PF_6^- stretching vibration). HRMS (ESI, m/z): calculated for $C_{17}H_{18}N_3^+$: 264.1495, found: 264.1508.

2. Fourier transform infrared spectroscopy (FTIR)

Transmission FTIR spectra in the range 600–2000 cm^{-1} were recorded with a Bio-Rad Excalibur FTS-40 spectrometer (Varian Inc., Palo Alto, CA) equipped with a liquid-nitrogen-cooled deuterated triglycine sulfate (DTGS) detector. 128 scans were co-added and averaged and the resolution was 4 cm^{-1}.

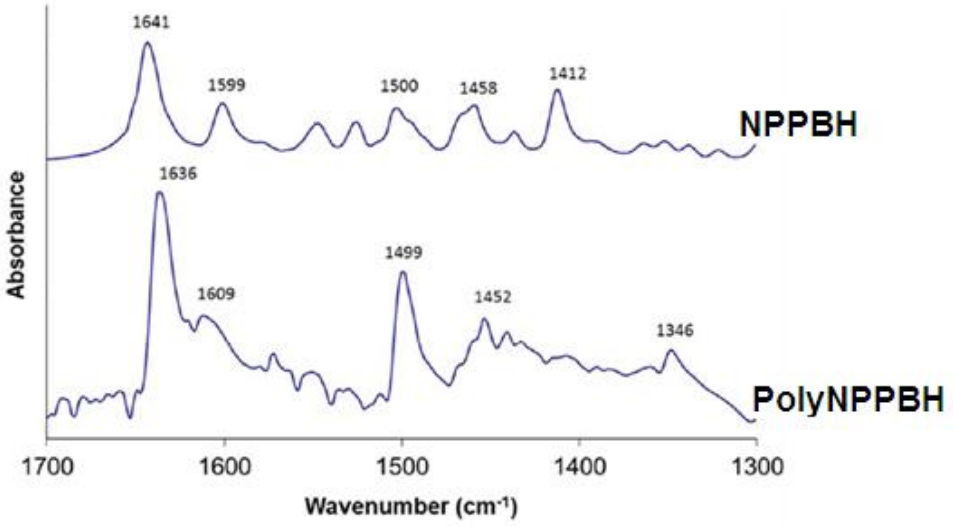


Figure S1. The main bands observed in the FTIR spectra of NPPBH(upper trace) and polyNPPBH (lower trace) in the 1700-1300 cm^{-1} region.

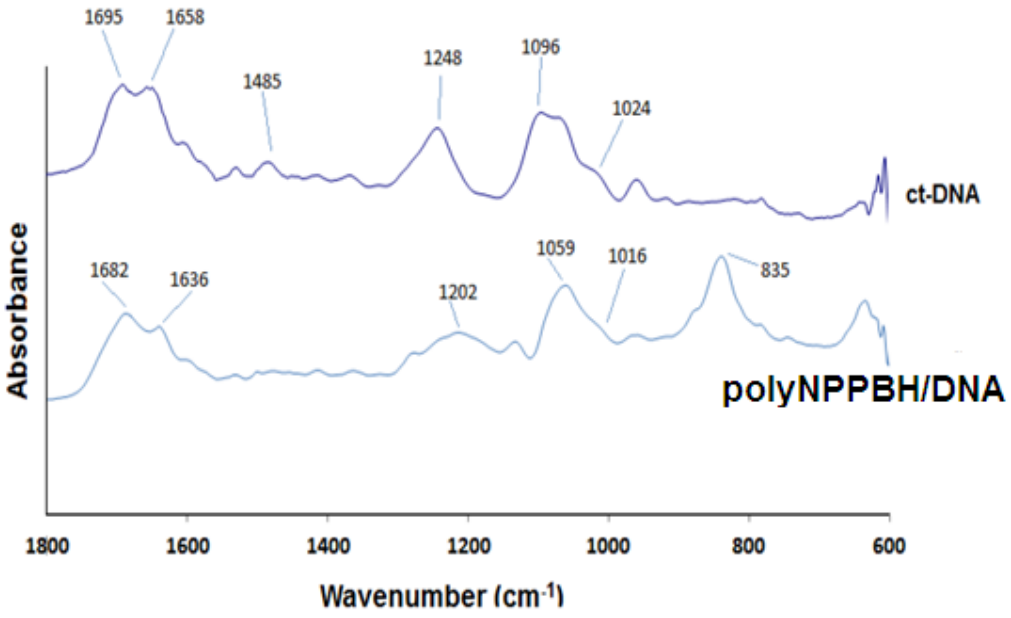


Figure S2. The main bands observed in the FTIR spectra of CT-DNA (upper trace) and polyNPPBH/DNA (lower trace) in the 1800-600 cm^{-1} region.

The P-O stretching modes of the phosphate groups of DNA are substantially shifted upon templating NPPBH on DNA – see table S1.

The spectrum of Cu/polyNPPBH/DNA is shown in the main text, but the important bands are tabulated below.

Table S1. The main bands observed in the FTIR spectra of CT-DNA, polyNPPBH and Cu/polyNPPBH/DNA in the 1800-800 cm^{-1} region. FTIR spectral references (3-5).

Wavenumber (cm^{-1})			**Assignment**
CT-DNA	PolyNPPBH	Cu/polyNPPBH/DNA	
1658	1636	1634	C-N stretch, Adenine (C=N stretch of the guanine)
1530	1525	1525	in-plane C=N vibration of cytosine and guanine
1248	1202	1193	PO_2^- asymmetric stretch, deoxyribose-phosphate
1096	1059	1055	PO_2^- symmetric stretch, deoxyribose-phosphate
952	948	948	C-O deoxyribose, C-C
-	835	837	PF_6^- P-F stretch

The calf thymus DNA (CT-DNA) spectrum shows the characteristic in-plane vibrations of bare DNA; 1118 cm^{-1} (PO_2^- symmetric stretch), 1232 cm^{-1} (PO_2^- asymmetric stretch), 1408 cm^{-1} (C-H, N-H deformation, C-N stretch thymine, adenine), 1490 cm^{-1} (C8-N coupled with a ring vibration of guanine), 1556 cm^{-1} (in plane vibrations of cytosine and guanine) and 1658 cm^{-1} (purine stretch, N7). In addition to, the broad band centered at about 3300 cm^{-1} in the DNA sample is due to O-H stretching vibrations from groove-bound water molecules as well as a contribution from N-H stretches in the DNA nucleobases, and is noted to be reduced in intensity in the polyNPPBH/DNA spectrum. This loss of intensity is proposed to be the result of displacement of water molecules that were bound to the DNA.[6,7]

3. UV-vis absorption spectroscopy (UV-vis)

UV–vis absorbance spectra were recorded on a Varian-Cary 100 Bio spectrophotometer at room temperature over a wavelength range of 250–600 nm.

Figure S3 shows the optical absorbance of the monomer NPPBH and of polyNPPBH.

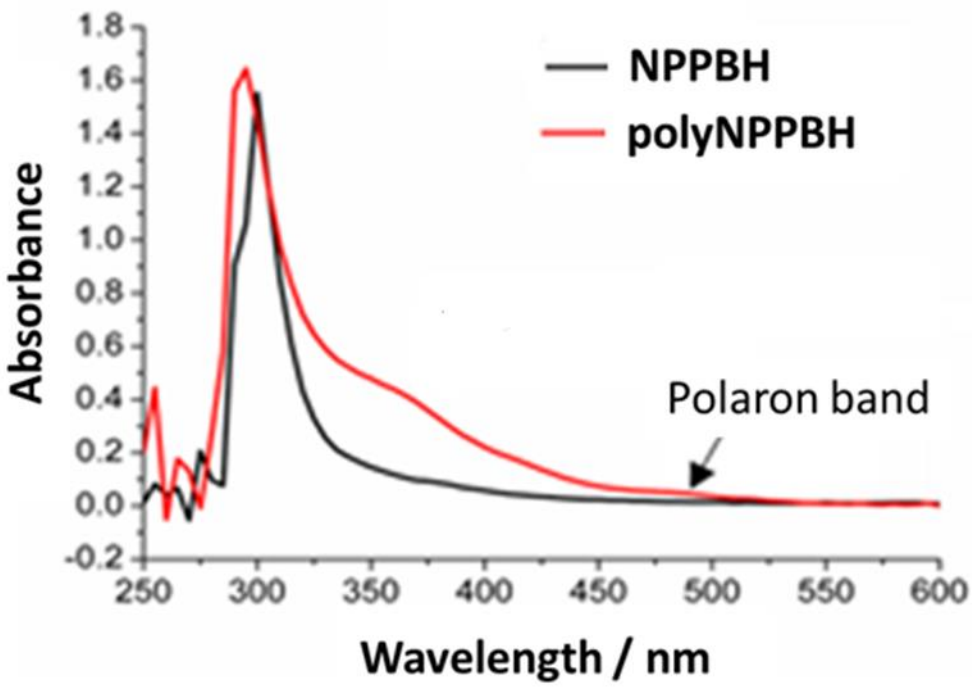


Figure S3. UV-vis absorption spectra of NPPBH and poly NPPBH prepared by chemical polymerization using $FeCl_3$ as oxidizing agent.

4. X-ray Photoelectron Spectroscopy (XPS)

A Kratos Axis Ultra 165 photoelectron spectrometer equipped with a monochromic Al K- X-ray excitation source (1486.7 eV) with an operating power of 150 W (15 kV, 10 mA) was used to collect photoemission spectra of Cu/polyNPPBH/DNA sample. The chamber pressure was 3.2 x 10^{9}Torr. The photoelectrons were filtered by the hemispherical analyzer and recorded by multichannel detectors.

Four components were observed in C_{1s} spectra of pure DNA by previous workers[8]. The two components at the lowest binding energy are assigned to C-H and C-C or C-N species from polyNPPBH and DNA. The 'hydrocarbon-like' component due to C-H at 284.6 eV was used to check the energy scale. The third peak at 288.2 eV for Cu/polyNPPBH/DNA is attributed to carbons in functional group of the type, C=N, mainly from pyrrole and bipyridyl moieties, because this feature is more intense than in pure DNA. The fourth, weak, peak at 289.1 eV for Cu/polyNPPBH/DNA is

assigned to C=N$^+$ carbons[6] in bipyridyl species and/or to carbon adjacent to N that is bonded to copper (C=N-Cu), due to the formation of a Cu-N coordinate bond.

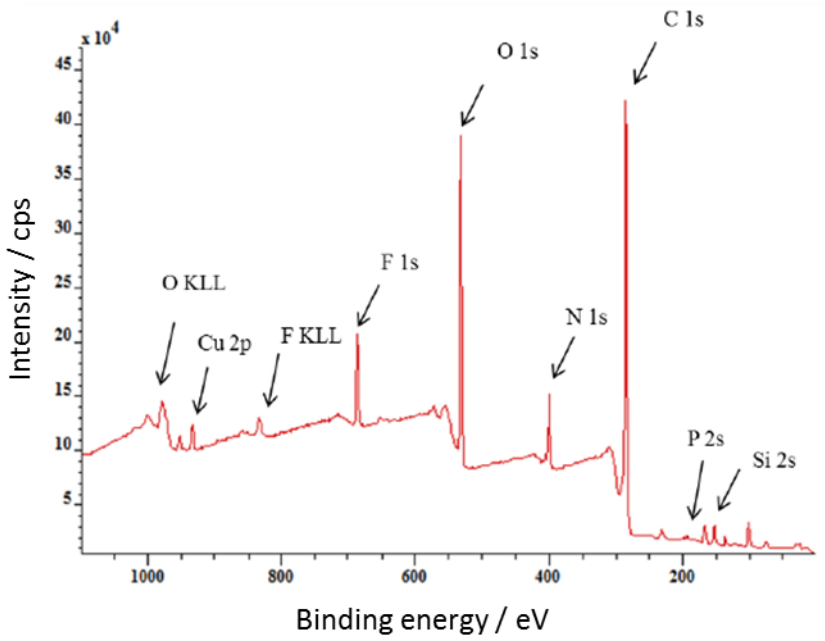


Figure S4. X-ray photoelectron survey spectrum of the Cu/polyNPPBH/DNA nanowires.

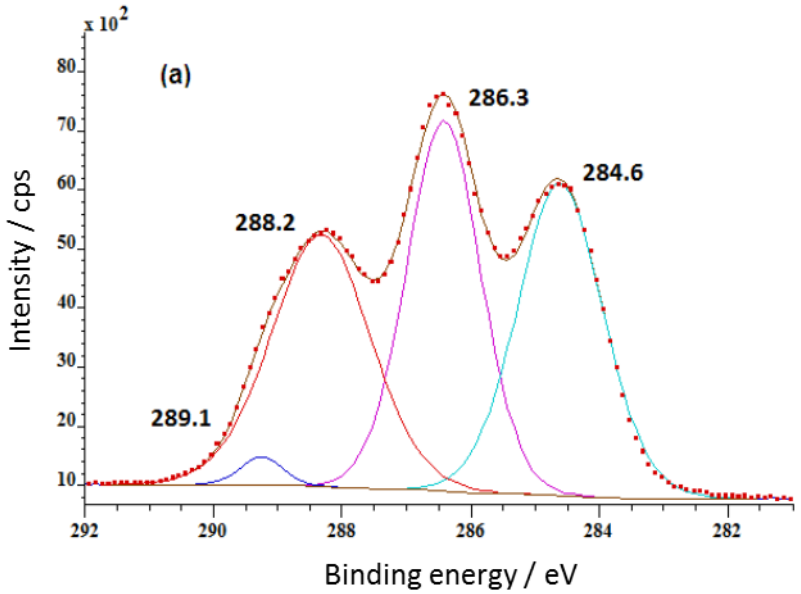


Figure S5. X-ray photoelectron spectra of the Cu/polyNPPBH/DNA nanowires. C1s spectrum. Spectral peaks were fitted with mixed singlet functions using the WinSpec program developed by LISE laboratory, Universitaires Notre-Dame de la Paix, Namur, Belgium.

5. Atomic force microscopy (AFM)

Atomic force microscopy (AFM) imaging was performed in air on a Dimension Nanoscope V (Veeco Inc., Metrology group) in tapping mode™ using NanoProbe tips (Veeco Inc.).

Figure S6 shows the AFM height distribution of ~100 CT-DNA molecules before treatment with polyNPPBH; the bare DNA thickness is 1-2 nm and the small number of features with 5 - 6 nm heights are due to bundles of DNA molecules. The mean height is 2.6 nm.

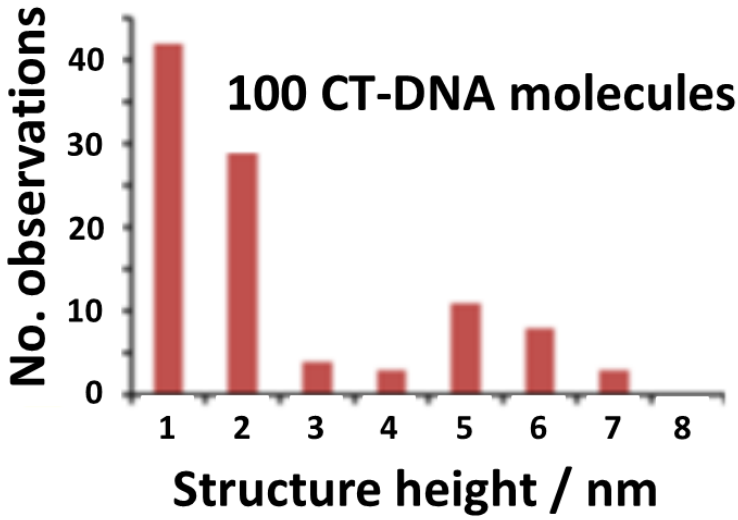


Figure S6. Diameters of free CT-DNA determined from AFM height measurements.

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