Prussian blue nanoparticles protected by the water-soluble π-conjugated polymer PEDOT-S: synthesis and multiple-color pH-sensing with a redox reaction†

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Prussian blue nanoparticles (PB NPs), stabilized for the first time by the π-conjugated polymer poly(4-(2,3-dihydrothieno-[3,4-*b*][1,4]dioxin-2yl-methoxy-1-butanesulfonic acid, potassium salt) (PEDOT-S), demonstrated a novel multiple-color pH-sensing function with a redox reaction based on the electronic interaction between the PB nano-core and the PEDOT-S shell.

The science of metal organic frameworks (MOFs) is attractive because of the versatile properties of MOFs, which depend on their crystal structure using different organic ligand and metal ions.[1] Among these MOFs, Prussian blue and its analogues (PBs), generally formulated as $A_{2x}M^{II}_{(1.5-x)}[M'^{III}(CN)_6]$ (x = 0–1; A = alkali metal ion; M, M′ = transition metal ions), are some of the most widely known MOFs with a face centered cubic (fcc) structure.[2] PBs are promising organic–inorganic hybrid materials that exhibit interesting characteristics, such as photo-induced magnetization,[3] electrochromism,[4] pressure tuning,[5] and biosensing.[6] As the next stage, preparation of PBs as "nano"-materials would enable their application in growing new nanodevices, and has been investigated using several techniques.[7] The simplest way is to crystallize PBs in a dilute solution containing an organic polymer to give polymer-stabilized PB nanoparticles (NPs). However, the problem to be urgently solved is that the range of polymers used up to now has been extremely limited, including for example, nonionic (poly(vinylpyrrolidone); PVP)[7c,d] and cationic (poly(diallyl-dimethylammonium chloride; PDDA) polymers.[7e] Expanding polymer variation is a vital challenge for wider applications of PB NPs.[8]

This communication reports the first synthesis of "π-conjugated" polymer-stabilized PB NPs. The π-conjugated polymer chosen here is poly(4-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-2yl-methoxy-1-butanesulfonic acid, potassium salt) (PEDOT-S; Fig. 1). PEDOT-S was recently used in an electro-luminescence device or a solar cell due to its high conductivity with high transparency and excellent stability in its doped state.[9] We demonstrate that an "anionic" pendant group of sulfonates in PEDOT-S presents effective surface protection from Fe cations to PB NPs, compared to the protection provided by previously used nonionic or cationic polymers. Further, PEDOT-S-surrounded PB NPs (PEDOT-S/PB NPs) provide a novel multiple-color pH-sensing function with a redox reaction based on the electronic interaction between the PB nano-core and the PEDOT-S shell.

PEDOT-S (M_n = 91700, M_w = 10400, M_w/M_n = 1.14) was synthesized in eight steps, using a monomer of potassium 4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methoxybutane-1-sulfonate (EDOT-S)[10] (for detailed experimental techniques and measurements, see the ESI†). PEDOT-S/PB NPs were obtained as follows: 10 mL of an aqueous mixture of 4.5 mM $FeCl_2·6H_2O$ and 7.5 mM PEDOT-S (the concentration is calculated per one monomer molecule) was added to 10 mL of 3.0 mM aqueous $K_3[Fe(CN)_6]$ with vigorous stirring for 24 h. The resulting blue solution was poured into ~20 mL of methanol. The precipitate was filtered using a membrane, washed with methanol three times, and dried overnight in air at room temperature to yield powdery PEDOT-S/PB NPs quantitatively.

The X-ray diffraction (XRD) pattern of the obtained compound exhibited an fcc crystal structure with the main peaks at 17.52° (200), 24.64° (220), 35.32° (400) and 39.60° (420) (Fig. S1†), suggesting the formation of PB crystals.[7e] PEDOT-S/PB NPs easily redissolved in water to give a transparent blue solution without any precipitates (Fig. S2a†).

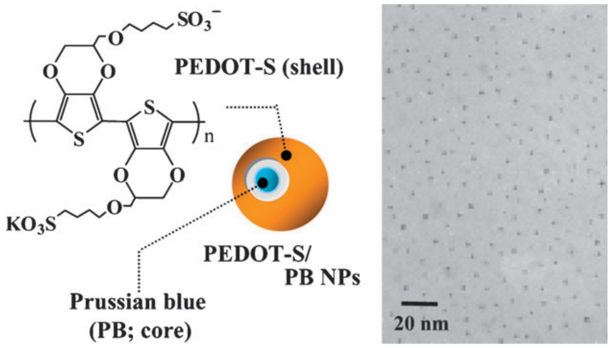

Fig. 1 (Left) Illustration and (right) TEM image of the prepared Prussian blue nanoparticles protected by the water-soluble π-conjugated polymer PEDOT-S (PEDOT-S/PB NPs).

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† Electronic supplementary information (ESI) available: Experimental details and additional results for XRD, UV-Vis, FT-IR, CV, and film formation for PEDOT-S/PB NPs, photographs of PEDOT-S as a function of pH, and the referenced experimental photograph for PVP-stabilized PB NPs. See DOI: 10.1039/b917552k

The UV-Vis-NIR spectrum showed absorption intensity maxima at λ_{max} = 714 nm and 350 nm, assigned to the intervalence transfer (IT) band between the Fe^{II} and Fe^{III} sites through CN ligands of PB[7e] and the π–π* transition of PEDOT-S,[11] respectively (Fig. 3b, left). It should be mentioned that the as-prepared PEDOT-S has a broad absorption peak at 800–1100 nm, characteristic of the oxidized state of p-doped polythiophene chains (Fig. S2b†)[12] that overlaps with the strong peak of the IT band of the PB nano-cores.

The transmission electron microscopy (TEM) image demonstrates spherical particles with an average diameter of d_{av} = 3.6 ± 0.3 nm (Fig. 1, right). In the FT-IR spectrum, ν(CN) at 2087 cm^{-1} was detected due to PB.[7e] The peaks at 2977 and 2904 cm^{-1} of $\nu(CH_2)$ and at 1203 cm^{-1} and 1170 cm^{-1} of ν_{as}(S=O) were attributed to PEDOT-S (Fig. 2).[11] The latter peak at 1170 cm^{-1} of ν_{as}(S=O) appears only in the product, by hybridization to PB. This negative shift of ν_{as}(S=O) is direct evidence that the sulfonate groups of PEDOT-S provide protection by partially coordinating to the Fe ions located on the surface of the PB nano-cores. In addition, the molar ratio of the monomer unit of PEDOT-S to iron in the reaction mixture was set as 1. This value is extremely small compared to the PB NPs stabilized by nonionic PVP and cationic PDDA, which require molar ratios of at least 20 to achieve the stable protection of PB NPs (Fig. S3†).[7c–e] This finding reveals that PEDOT-S with "anionic" sulfonate groups acts as an excellent surface stabilizer for PB NPs.

Fig. 3a shows photographs of the prepared PEDOT-S/PB NPs in water as a function of pH. When hydrazine is added to the aqueous solution of PEDOT-S/PB NPs, the color is dramatically altered from blue to red, and the pH of the solution is measured as 9.20. Here, hydrazine is used as both a reducing and an alkaline agent (see below). The subsequent addition of conc. HCl to the solution adjusted the pH value in steps from pH 9.20 to pH 1.70, accompanied by multiple color changes to red, yellow, green and blue (Fig. 3a from left to right). This behavior was never observed in the case of the PEDOT-S only (Fig. S4†).

The color variation of PEDOT-S/PB NPs is reflected in the UV-Vis-NIR spectra of the solutions shown in Fig. 3b (left).

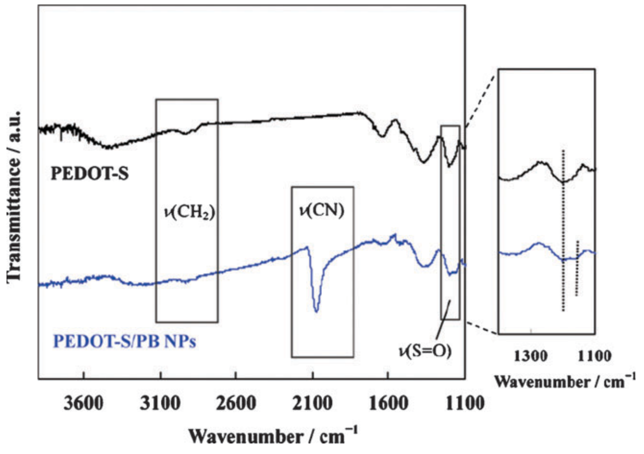

Fig. 2 FT-IR spectra of PEDOT-S and PEDOT-S/PB NPs.

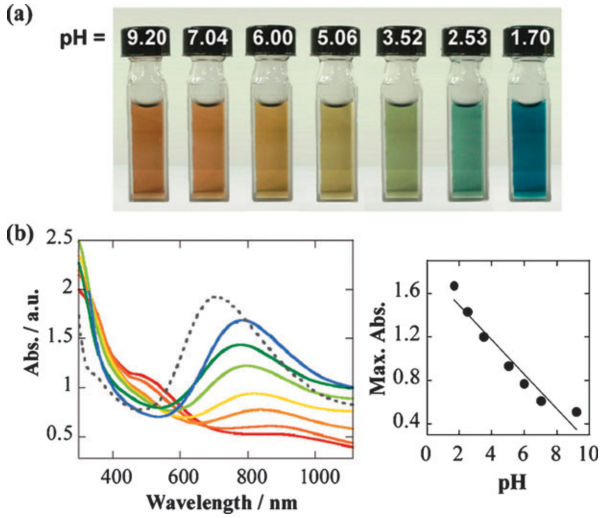

Fig. 3 (a) Photographs and (b, left) UV-Vis spectra of 1.0 mg PEDOT-S/PB NPs in 4 mL of deionized water at pH values of 9.2 (dark red), 7.04 (red), 6.00 (orange), 5.06 (yellow), 3.52 (yellow–green), 2.53 (green) and 1.70 (blue) adjusted by the addition of 4 μL of hydrazine followed by sequential additions of conc. HCl. The UV-Vis spectrum of the original solution is also illustrated as a reference (black dashed line). (b, right) Relationship between the pH value and the intensity of the absorption maximum (Max. Abs.) in Fig. 3b.

The addition of hydrazine results in the disappearance of the absorption maximum at 714 nm due to the Fe^{II}–CN–Fe^{III} units of the PB nano-core (Fig. 3b from the dotted line to the dark red one), indicating that the Fe^{III} sites are reduced by hydrazine to give Fe^{II}–CN–Fe^{II} units, which are transparent and colorless.[13] At the same time, the new absorption peak at 515 nm appears to be attributed to the neutral form of the polythiophene chains of PEDOT-S,[11] produced by reducing the first oxidized state (see above). This spectral change induced by hydrazine accounts for the color change from the original blue to dark red.

Then, the addition of conc. HCl leads to a gradual decrease in absorption due to the neutral polythiophene of PEDOT-S, with an increase in the broad absorption in the short NIR region (Fig. 3b from dark red line to blue one). This phenomenon is typical of acid doping of polythiophene chains of PEDOT-S to yield the oxidized states of PEDOT-S.[11] Simultaneously, the absorption at *ca.* 850 nm is gradually blue-shifted to recover a spectrum close to the original one (Fig. 3b, blue line), which suggests that the reduced Fe^{II}–CN–Fe^{II} sites of the PB nano-cores are successively oxidized by the surrounding acid-doped PEDOT-S to reproduce the oxidized Fe^{II}–CN–Fe^{III} units with a blue color. This mechanism is reasonable when considering the electronic interaction between a PB-nano-core and a PEDOT-S shell to be significant; λ_{max} of Fe^{II}–CN–Fe^{III} at pH 1.70 is much red-shifted from the original one due to the electrostatic field of the acid-doped PEDOT-S shell decreasing the Coulombic energy for the electron transfer from Fe^{II} to Fe^{III}.[7e] In addition, the redox potential $E_{1/2}$ between PEDOT-S and PB appears near at 0.1–0.5 (broad)[11] and 0.17 V[13] *vs.* Ag/AgCl, respectively. The cyclic voltammogram (CV) of PEDOT-S/PB NPs shows broad quasi-reversible redox peaks at $E_{1/2}$ = 0.30 V *vs.* Ag/AgCl (Fig. S5†), indicating that

PEDOT-S/PB NPs are an electronically interactive hybrid system. Note that the intensity of the absorption maximum is almost proportional to the pH value (Fig. 3b, right). It is also possible to synthesize PEDOT-S/PB NPs within a film by layer-by-layer deposition, which could enable other applications (Fig. S6†).

In conclusion, we have synthesized a novel hybrid nanomaterial of Prussian blue nanoparticles (PB NPs) stabilized by the π-conjugated polymer PEDOT-S. PEDOT-S/PB NPs thus prepared were effectively protected by the anionic sulfonate groups of PEDOT-S, and the resulting NPs were water-soluble. PEDOT-S/PB NPs present the unique property of multiple-color pH-sensing with a redox reaction induced by the interaction between the PB nano-core and the PEDOT-S shell. These findings may lead to variable control of the properties of nanometric MOFs because of the versatile electronic interactions on their surface modification.

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