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Colorimetric sensing of non-ionic and cationic surfactants using a versatile anionic poly(3,4-propylenedioxythiophene) derivative

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A novel anionic water-soluble poly(3,4-propylenedioxythiophene) derivative (WSPProDOT) has been prepared through FeCl₃ oxidative polymerization with a subsequent post-polymerization defunctionalization process, and applied as a colorimetric sensor to determine and discriminate non-ionic and cationic surfactants in aqueous solutions. The de-aggregation, conformation change of WSPProDOT and its colorimetric and fluorescent responses toward non-ionic and cationic surfactants have been studied by absorption and emission spectroscopy. The solution color of WSPProDOT changes from purple to blue upon addition of a non-ionic surfactant and from purple to black for a cationic surfactant. Therefore, non-ionic and cationic surfactants can be discriminated and detected using this versatile sensing platform.

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Introduction

Conjugated polyelectrolytes (CPEs) are polymers with π -conjugated backbones and ionic side groups.¹ Strong absorption and emission due to rapid exciton transport along the conjugated backbones and good water solubility inherited from the hydrophilic nature of ionic side groups make CPEs unique candidates for chemo- and bio-sensors in aqueous media.²

Among various sensing modes, colorimetric sensing is of peculiar interest as it utilizes the shift of the absorption wavelength due to an analyte-induced conformation change or aggregation/deaggregation of CPEs exhibited by a color change that is visible to the naked eye, thereby, providing a simple, direct and instrument-free signal output.^{1,2}

Water-soluble polythiophenes (WSPTs) are of peculiar importance for colorimetric sensing as their chain conformation and/or aggregation behaviour are sensitive to external stimuli such as the introduction of chemical and biochemical targets.¹ A famous star sensor platform, water-soluble poly(3-alkoxy-4-methyl thiophene) (P3RO4MeT), has been chosen as a model CPE for sensor applications because its conformation is outstandingly sensitive to various analytes as a result of the presence of sterically demanding side chains (*i.e.* the 4-methyl group on the thiophene ring).³

Until now, a variety of biomacromolecules (DNA and proteins) and small molecules (inorganic anions, heavy metal ions, small biomolecules and surfactants) have been detected using WSPTs as fluorometric and/or colorimetric sensors.^{1,2,4}

Among various analytes, surfactants are one of the major components of environmental pollutants due to their anthropogenic origins and extensive applications in domestic detergents, industrial and agricultural fields.⁵ Thus, it is important to be able to detect easily the concentration of surfactants in water. Martinez-Manez *et al.* reported a colorimetric detection method for ionic surfactants using simple silica supports functionalised with suitable binding groups and a dye.⁶ The sensing mechanism was based on the adsorption of surfactants on the charged surfaces and subsequently further extraction of the corresponding dye. While polydiacetylenes (PDAs) with functional groups were synthesized by Yoon *et al.* and used for colorimetric sensing of ionic surfactants based on unique color changes induced by penetration processes of surfactants into PDAs.⁷ And a series of cationic or anionic polythiophenes have been synthesized and applied as colorimetric and/or fluorescent sensors to detect surfactants with oppositely charged head-groups based on the change of polymer chain conformation and aggregation behaviour induced by interaction with surfactants.^{5,8} However, to the best of our knowledge, only few colorimetric sensors thus far have been utilized to detect nonionic surfactants in colorimetric mode perhaps due to the absence of strong ionic electrostatic interactions between sensor molecules and nonionic surfactants.^{5a} Moreover there is no report on one sensor for both non-ionic and cationic surfactants which have different hydrophilic headgroups.

To this end, we report a novel anionic water-soluble poly(3,4-propylenedioxythiophene) derivative (WSPProDOT) based on 3,4-propylenedioxythiophene (ProDOT) with a diethyl malonate pendant group (ProDOTDEM) and its application as a colorimetric sensor to determine nonionic surfactants in aqueous solutions. At the same time, the cationic surfactant can also be distinguished using this versatile sensor platform based on an

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anionic polythiophene derivative as indicated by the experimental results in this study or reported by others.^{5a} The main novelty of the present work is the versatility of the sensor platform reported here as it can be utilized in sensing non-ionic and cationic surfactants simultaneously.

Results and discussion

The synthetic route is depicted in Scheme 1. Synthesis of the monomer ProDOTDEM initiated from the transesterification of 3,4-dimethoxythiophene (DMOT) with 2,2-bis(bromomethyl) propane-1,3-diol, yielding ProDOT(CH₂Br)₂ followed by the procedures reported by Reeves *et al.*⁹ Subsequently in a straightforward reaction step, the double nucleophilic substitution between ProDOT(CH₂Br)₂ and diethyl malonate (DEM) formed the monomer ProDOTDEM in a 53% yield.

The polymer PProDOTDEM was prepared by oxidative coupling of ProDOTDEM with excess anhydrous ferric chloride (FeCl₃) in a chloroform/ethyl acetate mixture at room temperature, with subsequent reduction by hydrazine. It is important that an adequate amount of ethyl acetate was added to ensure the excellent solubility of FeCl₃ in the solvent, affording an initially homogeneous reaction mixture, facilitating the rapid polymerization.¹⁰ As recommended by Sugimoto¹¹ and Aleman¹² when the oxidant is ferric chloride, the oxidant : monomer molar ratio is 4 : 1 to keep the oxidizing strength of the polymerization sufficiently high to maximize the yield and molecular weight. It is worth noting that, by following the suggestion of Liu *et al.*,¹³ in the post-treatment washing the polymer with methanol to remove the oligomers is very important. To this end, PProDOTDEM was obtained as a purple-red solid (*M*_w = 5.74 kDa, *M*_n = 4.35 kDa, and PDI = 1.32). Subsequently PProDOTDEM was suspended in a 1 M solution of NaOH in methanol. The polymer suspension is stirred and refluxed for 24 h, then filtered and washed with a CH₃OH/H₂O mixture (99.5/0.5 v/v) several times to yield a fine purple-blue powder of partially hydrolyzed PProDOT-Salt (WSPProDOT).

The post-polymerization functionalisation process was monitored by attenuated total reflectance infrared (ATR-IR)

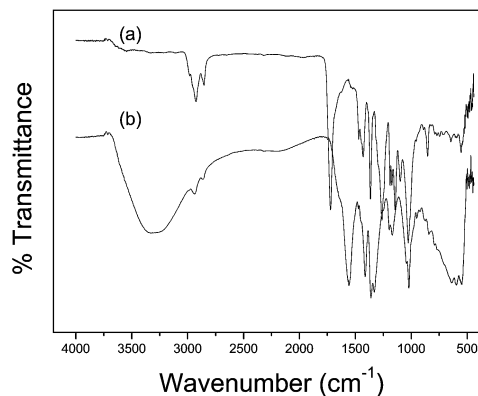


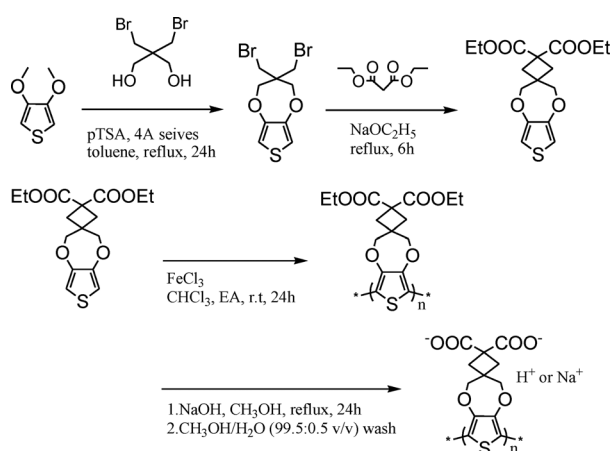
Fig. 1 ATR-IR spectra of (a) PProDOTDEM and (b) partially hydrolyzed PProDOT-Salt.

spectroscopy and the results are shown in Fig. 1. The band at 1722 cm⁻¹ in Fig. 1a is the characteristic of the C=O vibration of the ester derivative PProDOTDEM,¹⁴ and the band at 1262 cm⁻¹ and 1027 cm⁻¹ correspond to C-O-C vibration. By conversion to WSPProDOT, the C=O band is shifted to a lower frequency. In Fig. 1b, the bands at 1558 cm⁻¹ and 1412 cm⁻¹ correspond to the -COO⁻ group.¹⁴ In addition, the bottom of the band at 1558 cm⁻¹ is broadened and the broad strong -OH vibration band at 3660–2500 cm⁻¹ emerges, indicating that the salt is partially hydrolyzed to its acid form. It is worth noting that WSPProDOT has a good solubility in water (>8 mg mL⁻¹).

Fig. 2a illustrates absorption spectra of WSPProDOT aqueous solution (0.3 mM in the monomer unit) upon addition of different amounts of Triton X-100 (polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether) from 0.0001 mM to 0.1 mM. WSPProDOT shows an absorption maximum at 530 nm. Upon the addition of increasing amounts of Triton X-100, the absorption was shifted to 550 nm and a broad shoulder peak at 596 nm emerges. The most salient feature of Fig. 2a is that the absorbance of the shoulder peak at 596 nm increases gradually with the concentration of Triton X-100. Simultaneously, a solution color change from purple to blue was observed by the naked eye, signifying that WSPProDOT could be applied as a probe for colorimetric sensing of the non-ionic surfactant. Fig. 2b displays a linear relationship between *A*₅₉₆/*A*₄₀₀ and the concentration of Triton X-100 (*R* = 0.988 from 0.001 mM to 0.1 mM), indicating that this sensor platform is applicable to the colorimetric detection of Triton X-100, and the detection limit is evaluated to be 10⁻⁶ M.

It is well known that conformational changes and interchain interactions play decisive roles in controlling the emissive properties of conjugated polymers.^{5a} Thus, to elucidate the mechanism behind the color change observed for WSPProDOT in the presence of non-ionic surfactant, the emission spectra were further examined as shown in Fig. 2c.

It can be seen that Triton X-100 shows negligible emission and WSPProDOT exhibits a weak emission band around 585 nm upon excitation at 530 nm. Upon addition of increasing amounts of Triton X-100, the emission maximum was red-shifted to about 600 nm gradually. It has been well noted that



Scheme 1 Synthesis of the monomer ProDOTDEM and the polymer.

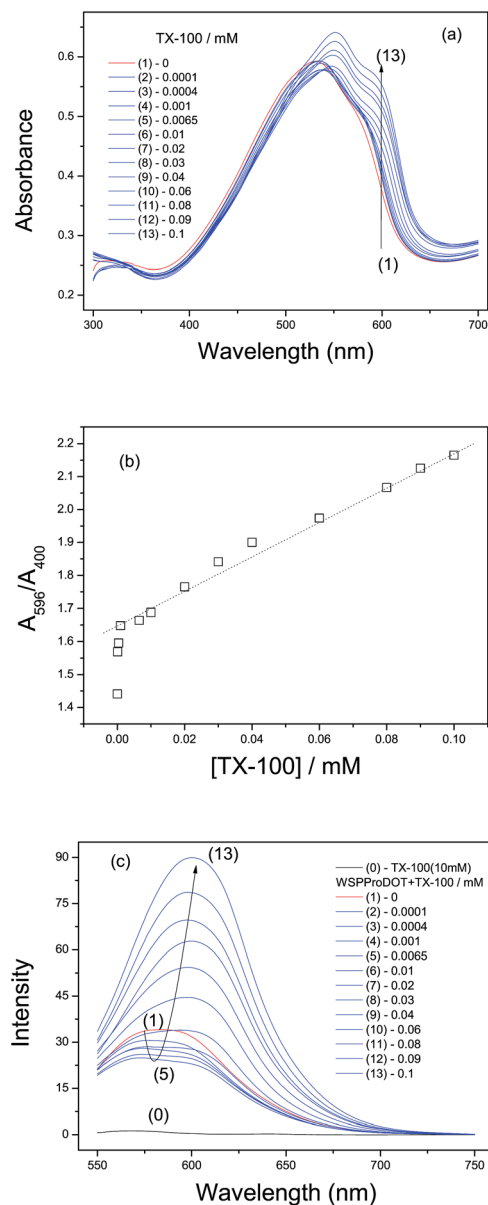


Fig. 2 (a) Variation in the absorption spectra of WSPProDOT (0.3 mM) with increasing concentrations of Triton X-100 as indicated; (b) the relationship between A_{596}/A_{400} and the concentration of Triton X-100 from 0.0001 to 0.1 mM; (c) emission spectra of Triton X-100, WSPProDOT (0.3 mM), and WSPProDOT (0.3 mM)/Triton X-100 complex upon excitation at 530 nm.

Triton X-100 interacts with amphiphilic polymers, forming polymer-surfactant aggregates through hydrophobic association.¹⁵ The emission intensity of WSPProDOT is first reduced with the concentration of Triton X-100 from 0.0001 mM to 0.0065 mM, indicating that the first association of the surfactant with more than one polymer chains induces slight enhancement of aggregation of WSPProDOT. And then the emission intensity increased from 0.0065 mM to 0.1 mM. It is well noted that the interaction of surfactants with conjugated polymers can enhance emission intensities of conjugated polymers in water as aggregates of conjugated polymers are

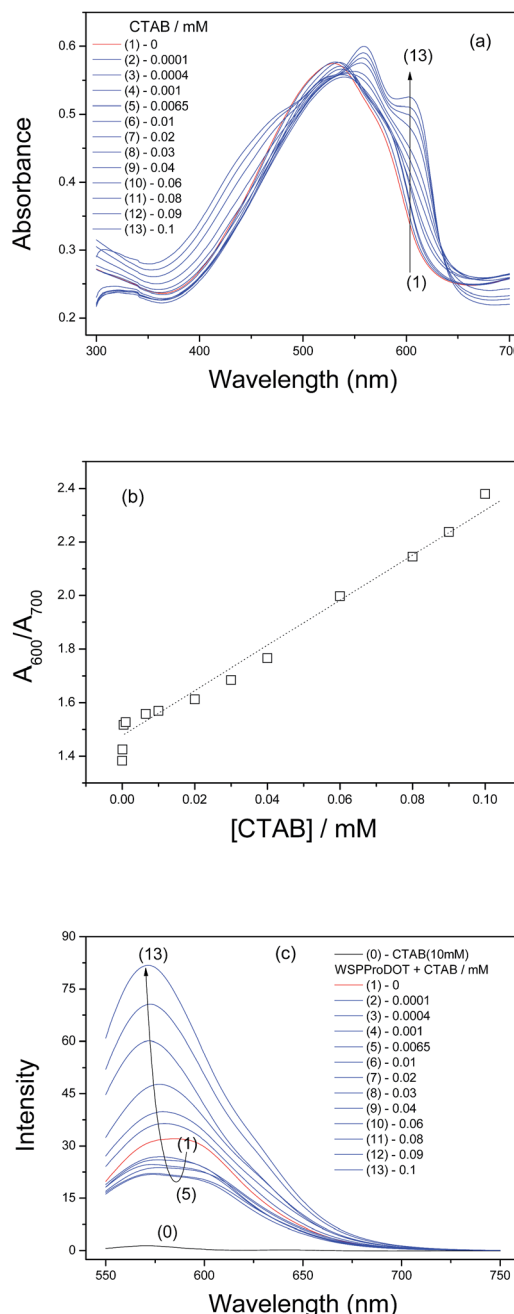


Fig. 3 (a) Variation in the absorption spectra of WSPProDOT (0.3 mM) with increasing concentrations of CTAB as indicated; (b) the relationship between A_{600}/A_{700} and the concentration of CTAB from 0.0001 to 0.1 mM; (c) emission spectra of CTAB, WSPProDOT (0.3 mM), and WSPProDOT (0.3 mM)/CTAB complex upon excitation at 530 nm.

broken up and the effect of self-quenching is diminished.^{14a} Similar to the rigid phenyl group introduced to the 3-position of the thiophene ring reported by Wang *et al.*¹⁶ in copolythiophene-derived colorimetric and fluorometric sensors for lipopolysaccharide, the relatively rigid cyclobutane moiety in the side chain of WSPProDOT can be used as a blocking unit to force the polythiophene backbone to adopt a twisted conformation. Upon interaction with TX-100, the de-aggregation of

WSPProDOT reduces the steric hindrance from the rigid cyclobutane group and the polymer backbone becomes more coplanar. Such a de-aggregation and conformation change result in red-shifts in both the absorption and fluorescence wavelengths of WSPProDOT which has also been observed in other polythiophenes.¹⁶ Therefore, the color change of WSPProDOT upon addition of Triton X-100 from 0.001 mM to 0.1 mM could be attributable to the de-aggregation and conformation change of polymer chains induced by the hydrophobic interaction of the non-ionic surfactant and the polymer.

In the case of the addition of CTAB (cetyltrimethylammonium bromide) to WSPProDOT, the similar absorption changes were observed except that the absorption at the shorter wavelength 400–480 nm was enhanced with the increased concentration of CTAB as indicated in Fig. 3a.

Upon the addition of increasing amounts of CTAB, the absorption of PProDPOT was shifted from 530 nm to 550 nm and a broad shoulder peak at 600 nm emerges. The solution color simultaneously changes from purple to black induced by the enhancement absorption at 400–480 nm and 550–650 nm in the full visible region. Fig. 3b displays a linear relationship between A_{600}/A_{700} and the concentration of CTAB ($R = 0.985$ from 0.001 mM to 0.1 mM), indicating that this sensor platform is applicable to the colorimetric detection of CTAB, and the detection limit is evaluated to be 10^{-6} M.

It has been well known that in addition to the hydrophobic interaction, the strong electrostatic interaction between the cationic headgroup of CTAB and oppositely charged polyelectrolytes induces the formation of polymer-surfactant aggregates and the shrinkage of the polymer chain attributed to the reduction of intra-chain electrostatic repulsion.¹⁷ Upon the binding of CTAB to anionic sidechains of WSPProDOT, the polymer chains shrink, and therefore, the conjugation length reduces, corresponding to the enhanced shorter wavelength absorption at 400–480 nm. And this is corroborated by the blue-shift of the emission maximum from 585 nm to 570 nm indicated in Fig. 3c. This blue shift is attributed to a decrease in the conjugation length, arising from the de-aggregation of the WSPProDOT aggregates and the formation of random-coiled conformation.^{5a} The emission intensity of WSPProDOT first reduced with the concentration of CTAB from 0.0001 mM to 0.0065 mM which is similar to Triton X-100 and subsequently

increased from 0.0065 mM to 0.1 mM induced by de-aggregation of polymer chains. Thus the color change of WSPProDOT upon addition of CTAB from 0.001 mM to 0.1 mM could be attributable to the de-aggregation and the formation of the random-coiled conformation of polymer chains induced by the electrostatic and hydrophobic interactions of the cationic surfactant and the polymer.

To address the specificity of WSPProDOT toward non-ionic and cationic surfactants, absorption spectra and the colorimetric response of the WSPProDOT probe upon addition of anionic surfactants, SDS and SDBS, non-ionic surfactants, Triton X-100, OP-10 (polyoxyethylene octylphenol ether), and Tween 80 (polyoxyethylene (20) sorbitan monooleate), cationic surfactants, CTAB, CTAC (cetyltrimethylammonium chloride), and CPyC (cetylpyridinium chloride), and simple ions including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , CO_3^{2-} , SO_4^{2-} and PO_4^{3-} were examined. It should be noted that the concentration of Ca^{2+} and Mg^{2+} was set as 0.02 mM because larger amounts of these two ions induce the precipitation of the polymer. It is demonstrated in Fig. 4 that the color of WSPProDOT changes from purple to blue only for the non-ionic surfactant and to black only for the cationic surfactant, whereas upon the introduction of the anionic surfactant and simple ions, the solution color remains purple. It is clear from these results that the probe exhibits satisfied selectivity toward non-ionic and cationic surfactants.

Stimulated by the favourable features of the sensing platform, the performance of WSPProDOT of colorimetric sensing of non-ionic and cationic surfactants was examined in the

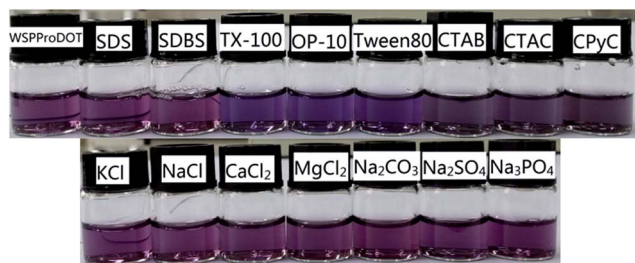


Fig. 4 Changes in the color of WSPProDOT in water induced by addition of various analytes. [WSPProDOT] = 0.3 mM, [surfactant] = [simple ions] = 0.1 mM, and $[Ca^{2+}] = [Mg^{2+}] = 0.02$ mM.

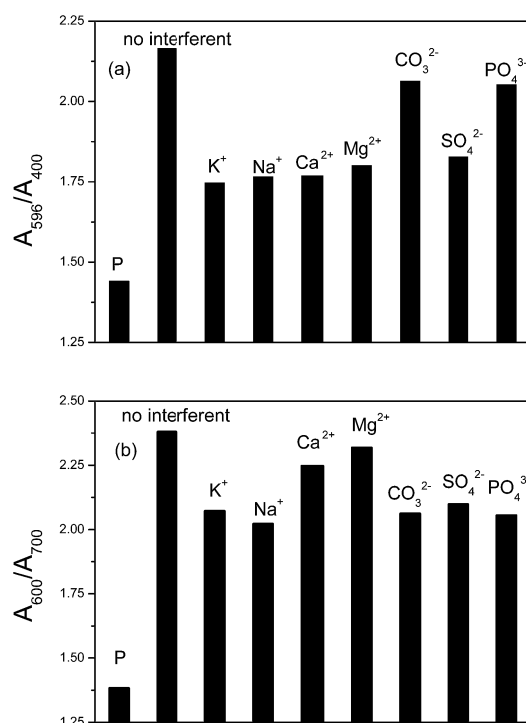


Fig. 5 (a) A_{596}/A_{400} of WSPProDOT (P)/Triton X-100 complex and (b) A_{600}/A_{700} of WSPProDOT (P)/CTAB complex in the presence of different ions. [WSPProDOT] = 0.3 mM, [surfactant] = [simple ions] = 0.1 mM, and $[Ca^{2+}] = [Mg^{2+}] = 0.02$ mM.

presence of anions and cations usually existing in aqueous solution. As shown in Fig. 5 the spectral characteristics of WSPProDOT toward Triton X-100 (Fig. 5a) and CTAB (Fig. 5b) were scarcely influenced upon addition of various simple ions, indicating that no remarkable interference to the surfactant detection was found in the presence of these chemical species. These results verify the feasibility of the present colorimetric sensing platform.

Conclusions

In conclusion, we have developed a versatile colorimetric sensor for both non-ionic and cationic surfactants in water, which is based on a novel anionic poly(3,4-propylenedioxythiophene) derivative WSPProDOT. Absorption spectra can be utilized to detect the aggregation and conformation changes of WSPProDOT induced by the addition of non-ionic and cationic surfactants, realizing the colorimetric sensing of these two species. The color of WSPProDOT aqueous solution changes from purple to blue for the non-ionic surfactant and from purple to black for the cationic surfactant, and the detection limit can be as low as 10^{-6} M. The most salient feature of this versatile sensing platform is that it shows good selectivity toward both non-ionic and cationic surfactants simultaneously in aqueous solutions which could be beneficial to convenient environmental monitoring.

Experimental

Materials

All starting materials were purchased from Sinopharm Chemical Reagent Co. Ltd, except 3,4-di(methoxy)thiophene (DMOT), which was purchased from Aladdin Industrial Inc and used as received unless otherwise noted. 3,3-Bis(bromomethyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (ProDOT(CH₂Br)₂) was synthesized followed by the procedures reported by Reeves *et al.*⁹

ATR-IR spectra were recorded on a Nicolet iS10 infrared spectrometer (Thermo Fisher Scientific). NMR spectra were collected on a 400 MHz Bruker Avance 400 spectrometer in deuteriochloroform (CDCl₃). Mass spectra were obtained on an Electrostatic Field Orbital Trap Mass Spectrometer (Thermo, Orbitrap XL ETD). Gel permeation chromatography (GPC) was performed on an Agilent LC1200 liquid chromatography system using HPLC graded THF as the eluent. Monodispersed polystyrenes were used to generate the calibration curve. UV-vis spectroscopy and fluorescence spectroscopy studies were carried out using a Jasco V-670 UV-vis-NIR spectrometer and a Jasco FP-8300 fluorometer.

Synthesis of ProDOTDEM

64 mmol sodium ethoxide in ethanol and 32 mmol diethyl malonate were mixed and the mixture was refluxed under N₂ for 0.5 h. A solution of 16 mmol ProDOT(CH₂Br)₂ was added dropwise to the mixture, and then the mixture was refluxed under N₂ for 6 h. After returning to room temperature H₂O was

added. The collected water phase was extracted with diethyl ether. The organic phase was dried with MgSO₄, filtered and evaporated to dryness. The crude product was submitted to column chromatography (silica gel, petroleum ether/ethyl acetate = 10 : 1) to give 2.9 g (53%) ProDOTDEM as a white solid. ¹H-NMR (CDCl₃, TMS, 400 MHz): 6.5 (s, 2H), 4.25 (q, 4H), 3.97 (s, 4H), 2.52 (s, 4H), 1.27 (t, 6H). HRMS *m/z* = 340.10526 [M + H]⁺, calc. for C₁₆H₂₀O₆S = 340.10.

Synthesis of PProDOTDEM and partially hydrolyzed PProDOT-salt

13.6 mmol ferric chloride and 3.4 mmol ProDOTDEM were dissolved in a chloroform/ethyl acetate mixture and stirred under ambient atmosphere for 24 h at room temperature. The mixture was concentrated to 20 mL and 50 mL methanol was added. The doped polymer was collected by suction filtration and washed *via* Soxhlet extraction for 48 h with methanol, then suspended in 100 mL chloroform and 2 mL hydrazine was added. The solution was stirred for 5 minutes. Then the mixture was concentrated and precipitated in methanol again. The polymer was washed with methanol, collected, and dried *in vacuo*. The polymer yield was 0.8 g (70%). GPC (THF vs. PS standard): *M_w* ca. 5.74 kDa, *M_n* ca. 4.35 kDa, PDI = 1.32. ATR-IR: 1722 cm⁻¹(s), 1262 cm⁻¹(s), and 1027 cm⁻¹(s).

Subsequently PProDOTDEM was suspended in a 1 M solution of NaOH in methanol. The polymer suspension is stirred and refluxed for 24 h, then filtered and washed with a CH₃OH/H₂O mixture (99.5/0.5 v/v) several times to yield a fine purple-blue powder of partially hydrolyzed PProDOT-Salt (WSPProDOT). ATR-IR: 3660–2500 cm⁻¹(s), 1558 cm⁻¹(s), and 1412 cm⁻¹(s).

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