

## **Supporting Information**

### **Materials and methods**

All reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO) and used as received without further purification. The structures of the samples were confirmed by Matrix Assisted Laser Desorption-Ionization Time-of-flight Mass Spectrometer (Waters Micromass) with 2, 5-dihydroxybenzoic acid (DHB) as a matrix. Transmission Electron Microscope (Philips EM400T) was used to determine the morphology, size, geometry and shape of the samples with a carbon-coated copper grid.

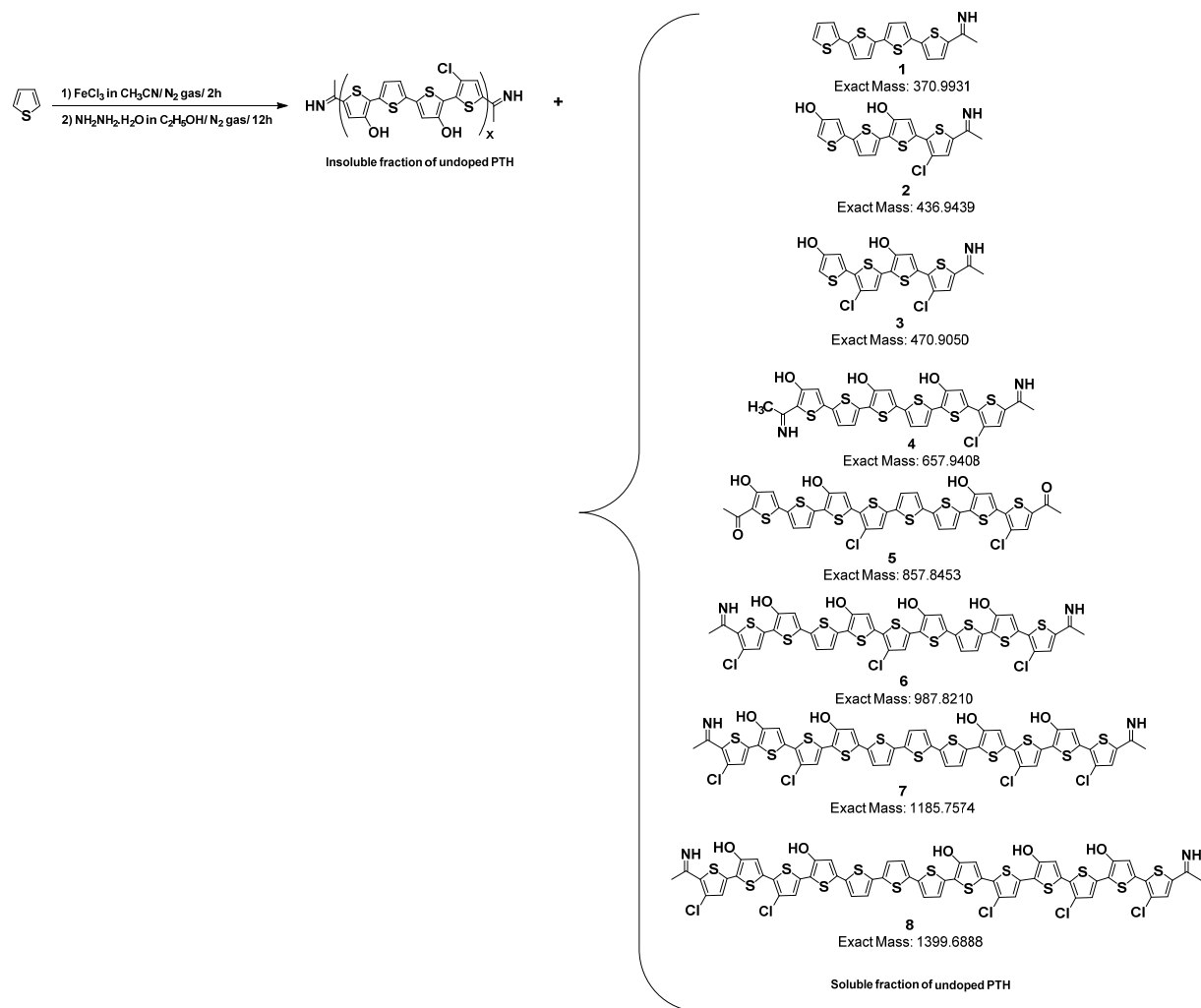
### **Synthesis of doped polythiophene**

A typical polymerization procedure is as follows: Thiophene monomer (1ml, 12.5mmol) was added in a 500ml round- bottle flask and dissolved in anhydrous acetonitrile (60ml) equipped with a magnetic stirring bar and N<sub>2</sub> inlet. Anhydrous FeCl<sub>3</sub> (1M) was dissolved in anhydrous acetonitrile (10ml) and added to the mixture that produced an immediate darkening of the solution. The reaction was kept stirring for 2h and then the black precipitate was suction filtered and washed by copious amount of acetonitrile and dried in the vacuum oven at 80°C for 12h, yielding 250mg doped polythiophene with the room temperature conductivity ~3S/cm (pressed pellet).<sup>[1]</sup>

### **Synthesis of undoped polythiophene**

As-produced doped polythiophene (100mg) was suspended in 100ml ethanol and excess amount of hydrazine hydrate (2ml, 40mmol) was then added and kept stirring for 12h. The mixture's colour was converted to red, undoped natural form. The red precipitate

was suction filtered and washed by copious amount of ethanol and dried in the vacuum oven at 80°C for 12h, yielding 90mg undoped polythiophene.



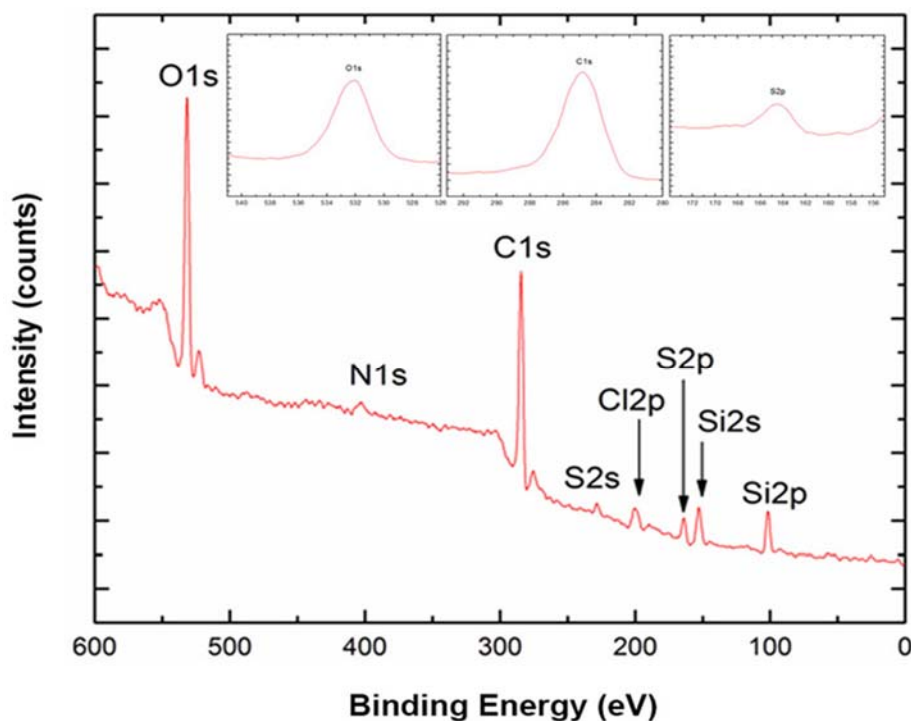
**Scheme 1.** Proposed chemical structures of the soluble fraction of undoped polythiophene.

## Characterization

### X-ray photoelectron spectroscopy (XPS) and sample preparation

X-ray photoelectron spectroscopy (XPS) performed with a Kratos XSAM800 surface analysis system. XPS is a true surface technique, allowing detection of all elements of the

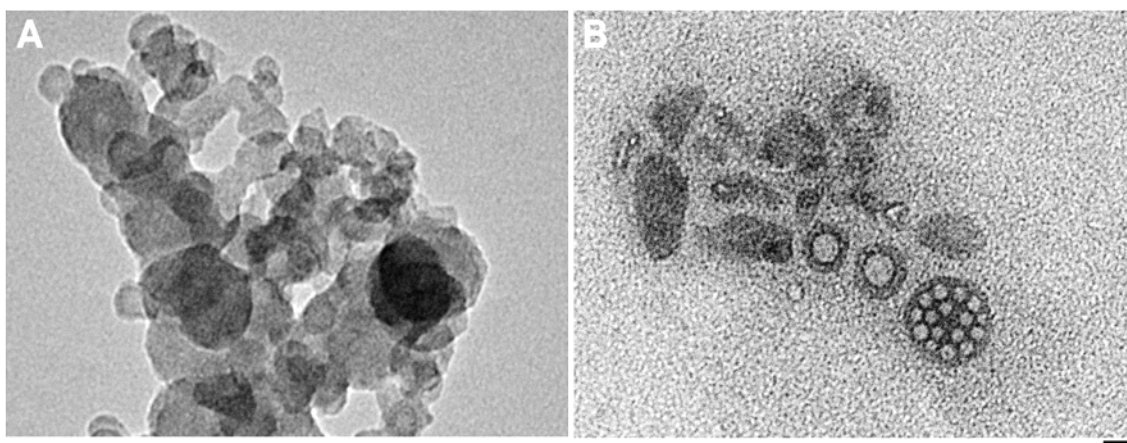
period table (except H) located within the first 50Å of the analyzed surface to a sensitivity of  $\sim 0.01$  atom % (parts per hundred thousand, volumetrically). XPS provides an area-averaged analysis over roughly a 2mm x 2mm area on the surface. Powdered undoped polythiophene was spread uniformly over a round piece of double-side carbon tape and then pressed into the tape with a clean glass slide. The excess was then removed with a solvent soaked cotton swab. The sample was then mounted into the AES/XPS system with no additional pretreatment or special handling.



**Figure S1.** X-ray photoelectron spectroscopy of undoped polythiophene obtained by hydrazine hydrate reduction of doped polythiophene powder.

## Transmission Electron Microscopy (TEM) from solutions in DMSO and THF

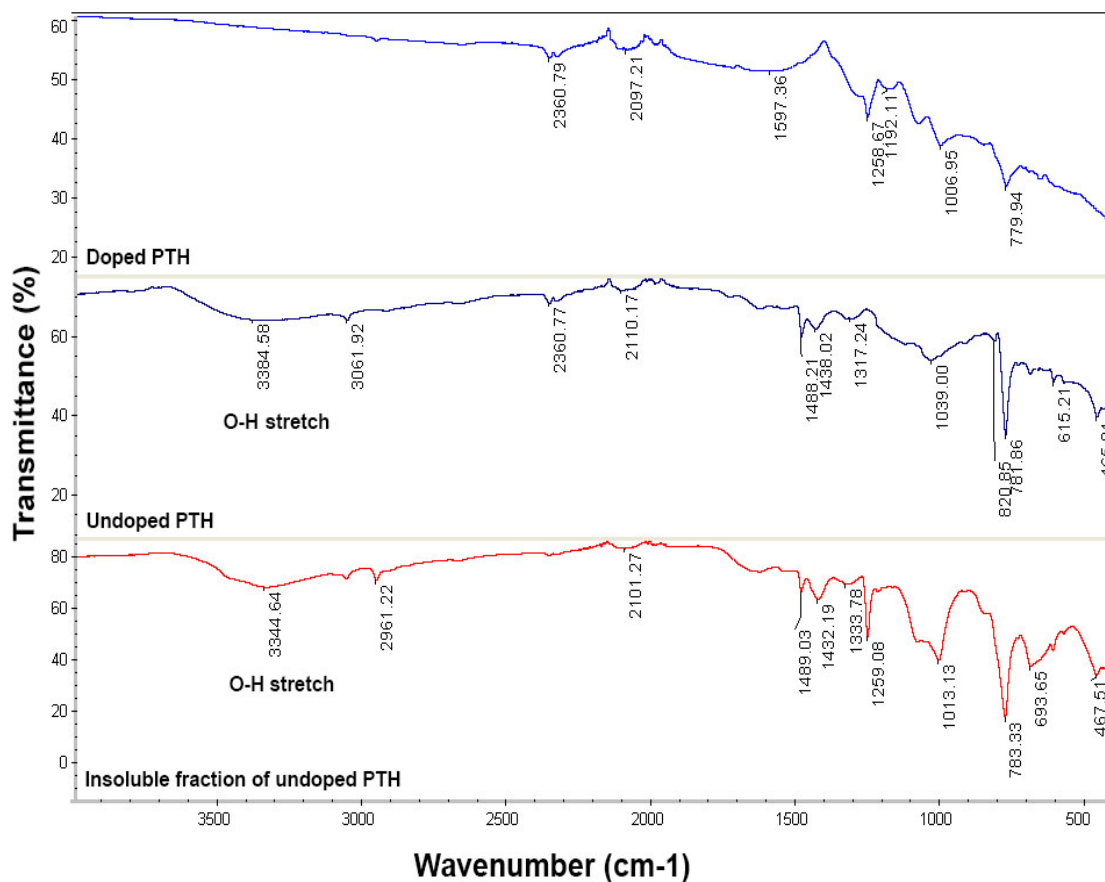
One  $\mu\text{L}$  of the filtered soluble fraction of undoped polythiophene in DMSO/or THF was placed onto a carbon-coated copper grid of mesh size 400. The excess of the sample was removed from the edge of the grid by a filter paper. The grid was kept in a vacuum oven for 5 minutes before immediate examination.



**Figure S2.** TEM images of (a) the soluble filtered fraction of undoped polythiophene in DMSO, and (b) the soluble filtered fraction of undoped polythiophene in THF. The scale bar: 20nm.

## Fourier transform infrared (FTIR) spectroscopy

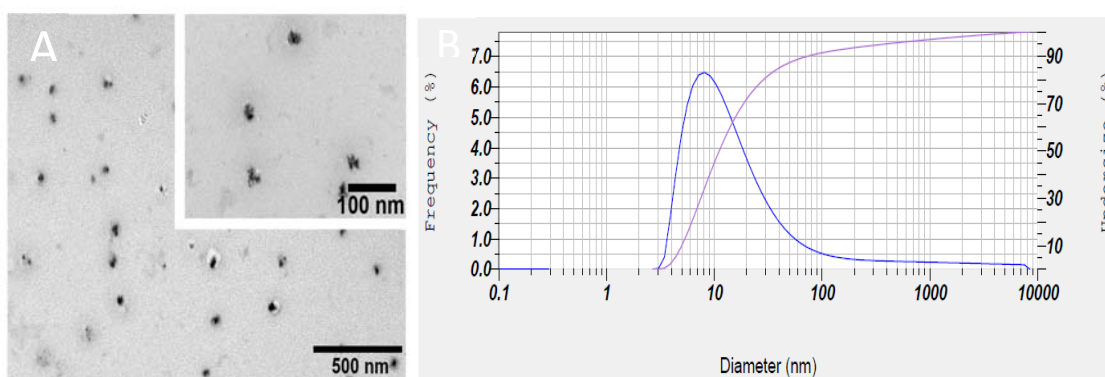
Fourier transform infrared (FTIR) spectroscopy measurement was carried out using a ThermoScientific Nicolet 4700 FTIR with a smart orbit Attenuated Total Reflectance (ATR) accessory. The vibrational spectra of vacuum dried and doped polythiophene, undoped polythiophene, and 80% insoluble fraction of undoped polythiophene in DMSO samples were determined from an average of 200 scans with 4  $\text{cm}^{-1}$  resolution.<sup>[3,4]</sup>



**Figure S3.** FT-IR spectra of doped polythiophene, undoped polythiophene, and insoluble fraction of undoped polythiophene.

## Dynamic Light Scattering (DLS)

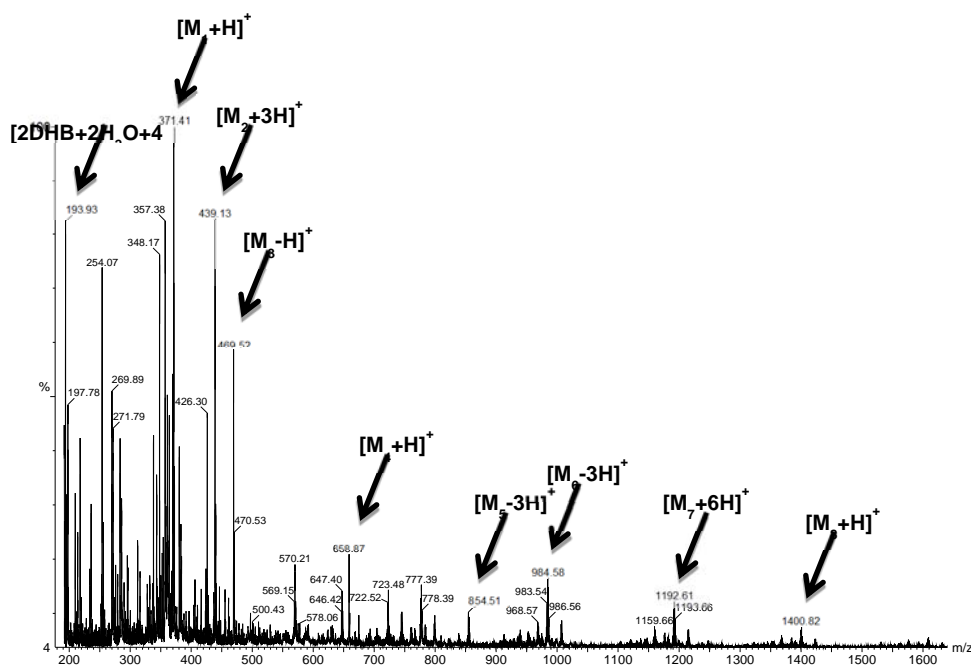
Fifty milligrams of undoped polythiophene was added to 2ml of D.I. water under bath sonication. Hundred microliter of the non-ionic surfactant Tween 80 was added and the dispersion was further sonicated for 30min. The solution was filtered through a 0.45micron filter. Particle size was measured on a Horiba SZ-100 instrument.



**Figure S4.** TEM images of (a) undoped polythiophene dispersion in water; dispersion made by bath sonicating undoped polythiophene powder in water containing 2wt% Tween-80 and filtered through a 0.45 micron filter, and (b) corresponding DLS profile showing average diameter ~14nm.

## Matrix assisted laser desorption ionization mass spectrometry (MALDI) and sample preparation.

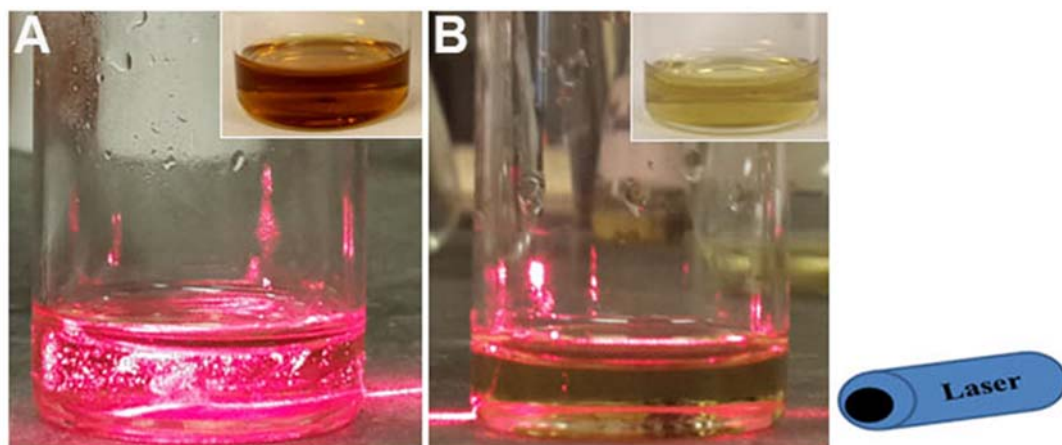
Matrix-assisted laser desorption ionization mass spectra were recorded on a WATERS Micromass MALDI-TOF mass spectrometer equipped with a 337nm N<sub>2</sub> laser. The undoped polythiophene in DMSO was analysed in reflectron mode. The matrix solution was prepared by dissolving 20mg of 2,5-dihydroxy benzoic acid in 1ml of DMSO (20mg/ml). The soluble filtered fraction of undoped polythiophene in DMSO and the matrix solution were mixed in the 1:2 volume ratio and 1  $\mu$ L of the resulting solution was spot and evaporated on the MALDI target plate.<sup>[5]</sup>



**Figure S5.** MALDI-TOF mass spectrum of the soluble fraction of undoped polythiophene dissolved in DMSO.

### Light scattering by a “laser pointer”

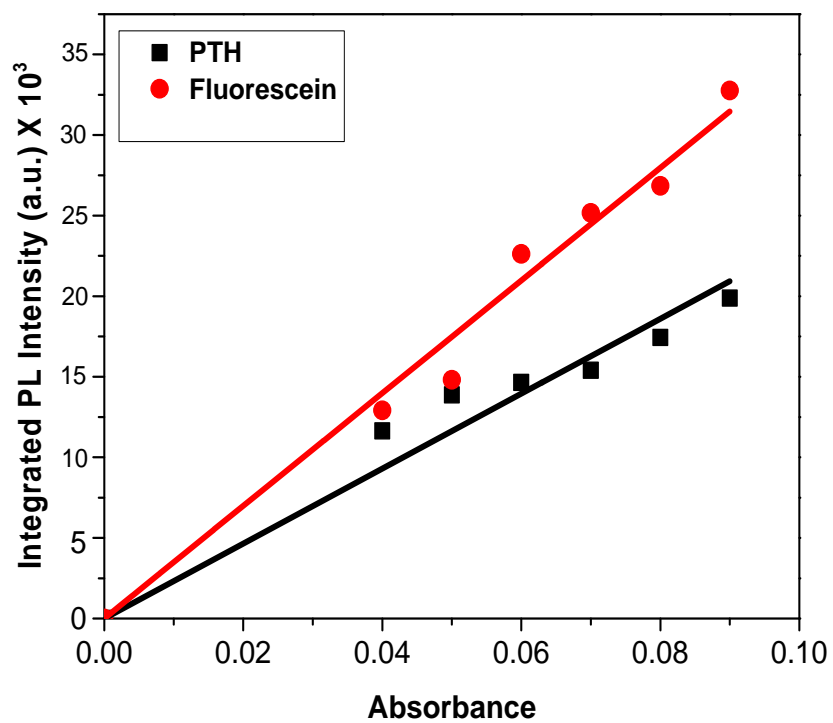
Hundred milligrams of undoped polythiophene was added to 5ml of DMSO in a 20ml vial glass. A laser beam was passed through the soluble fraction of undoped polythiophene before and after filtration (0.45 $\mu$ m pore size filter).



**Figure S6.** Light scattering of (a) the unfiltered soluble fraction of polythiophene, and (b) the filtered soluble fraction of polythiophene in DMSO.



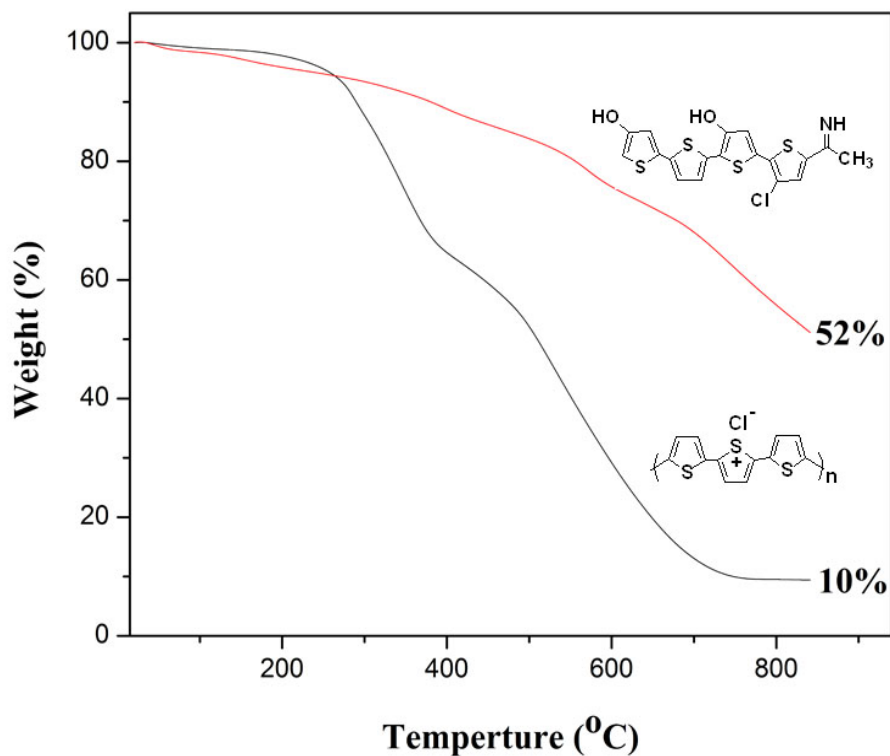
## Quantum Yield<sup>[6]</sup>



**Figure S7.** Integrated fluorescence intensity versus absorbance of polythiophene and fluorescein.

## Thermal Degradation Studies

Thermogravimetric analysis (TGA) of samples was done using a TGA Q 50 under nitrogen. Ten milligrams of samples were weighed and heated from room temperature to 800°C at a constant heating rate of 20°C/min.



**Figure S8.** TGA curve of (a) doped polythiophene, and (b) undoped polythiophene samples.

**Table 1.** Optical properties of undoped polythiophene dispersion in different solvents

Condition	$\lambda_{Ex.max}$ [nm]	$\lambda_{Em.max}$ [nm]	FWHM [nm]
MeOH	353	458	99.4
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	404	497	81.2
CHCl <sub>3</sub>	423	518	60.6
DMF	427	533	86.1
NMP	439	555	80.2

### Cytotoxicity assay

PC3-wild type cell were seeded in 96-well plates (Costar, Corning, NY, USA) at a density of 5000 cells in 200µl of medium per well and maintained at 37°C (5% CO<sub>2</sub>). Each treatment condition was assessed in quadruplicate. After 24h at 37°C, the medium was aspirated and 200µl new medium containing different concentrations of polythiophene/DMSO and polythiophene/DMF, respectively was added. Plates were incubated at 37°C for the indicated time, and then the total number of cells was determined using a crystal violet assay. Briefly, the medium was aspirated and 1% glutaraldehyde (100µl per well, Sigma, St. Louis, MO, USA) in PBS was added for a 15min incubation at room temperature (RT). After removal of glutaraldehyde, 0.5% crystal violet (100µl per well, Sigma) solution was added for a further 15min incubation at RT. Plates were then

washed three times in water and left to dry at RT. To the dried plates 100µl of Sorenson's solution (9g trisodium citrate in 305ml of distilled water, 195ml 0.1N HCl, 500ml 90% ethanol) was added to elute/dissolve the crystal violet. After 30min, 50µl of the resulting solution in each test well was transferred into a 96-well plate and read at 540nm using an ELX800 microplate reader (Bio-Tek Instruments, Winooski, VT, USA).<sup>[7, 8]</sup>

### **Fluorescence imaging**

Polythiophene/DMSO and polythiophene/DMF with fluorescence emission peaks in the blue ranges were used. Imaging was performed using a multispectral CRi Maestro fluorescent imaging system (Waltham, MA) with blue filter. For *in vitro* fluorescent imaging experiments 10µL of polythiophene were added to a plate and observed. For *in vivo* fluorescent imaging experiments polythiophene/DMSO (20µl) and polythiophene/DMF were injected subcutaneously into nude mice at one or more locations. A nude mouse was anesthetized using a ketamine, xylazine, acepromazine mixture. Fluorescent images were acquired 10min, 30min, 60min and 24h after administration of polythiophene. For clearance studies, fluorescent images were acquired in once per week in the following 4 weeks.<sup>[7, 9-12]</sup>

## References (supporting information)

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