Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Autonomous aqueous H_2O_2 production with a carboxylate-functionalized polythiophene

Cecilia Bruschi[*ab], Asaminew Yerango Shimolo[ac], Johanna Heimonen[ac], Qilun Zhang[d], Mats Fahlman[a], Mikhail Vagin[ab] and Renee Kroon[abc]*

[a]Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Bredgatan 33, 60221, Sweden. E-mails: cecilia.bruschi@liu.se, renee.kroon@liu.se

[b]Wallenberg Initiative Materials Science for Sustainability, Linköping University, Bredgatan 33, 60221, Sweden

[c]Wallenberg Wood Science Center, Linköping University, Bredgatan 33, 60221, Sweden

[d]Department of Materials Science and Engineering, Stanford University, 496 Lomita Mall, CA 94305 Stanford, USA

Table of contents

Materials and methods

Purchasing

All chemicals, 3,3'-dibromo-2,2'-bithiophene, triethylene glycol, copper iodide, 1,10-phenanthroline, n-butyl acrylate, sodium hydroxide, dichloromethane, deuterated chloroform, 2,5-bis(trimethylstanyl)thiophene, tri(*o-tolyl*)phosphine, tris(dibenzylideneacetone)dipalladium(0), methanol, potassium hydroxide, tetrahydrofuran (THF), N-bromo succinimide (NBS), sodium bicarbonate, magnesium sulfate ($MgSO_4$), petroleum ether, acetone, ethyl acetate and diethyl ether were purchased from commercial sources (Sigma-Aldrich, Fischer scientific) and used without further purification. The dioxygen gas used for the H_2O_2 production experiments was purchased from Linde (high purity oxygen, oxygen chemical 3.5= 99.5 %).

Analysis

NMR

Nuclear magnetic resonance spectra were recorded on a Bruker 500 spectrometer (^{1}H: 500 MHz and ^{13}C: 150 MHz). The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton signal of the deuterated solvent ($CDCl_3$: δ (^{1}H) = 7.26 ppm; δ (^{13}C) = 77.16 ppm).

Absorption spectra measurements in solution and in solid state

UV-Vis-NIR absorption spectra in aqueous solution and in solid state were recorded with a fiber optic spectrometer, equipped with AvaLight-HAL-S-Mini (Halogen lamp, 360-2500 nm range) as light sources and with AvaSpec-NIR (1000-2500 nm) and AvaSpec-2048L (200-1100 nm) as detectors. The absorption value at 653 nm for the HRP/TMB assay was recorded with a Synergy H1 Microplate reader (BioTek® Instruments, Inc.).

Electrochemistry

For electrochemical measurements a Biologic SP299 potentiostat was used. For the cyclic voltammetry, a glassy carbon disk was used as working electrode, a Pt-wire as counter and an Ag/AgCl electrode as reference. A KCl (1M) aqueous solution was used as electrolyte.

GPC analysis

GPC/SEC analysis of the P(2CAT-Me) prepolymer was performed on an Agilent 1280 Infinity system with 2 columns and precolumn (Polargel M 300x7,5 mm, 8 µm pore size, mixed pores) fitted with refractive index and viscometry detectors. The eluent was 1 w% LiBr in DMF at 70 °C, calibration curves were obtained from Agilent EasyVial PMMA standards, and all data analysis was performed in the Agilent GPC software.

FTIR analysis

The FTIR spectra were performed for solid powder samples using a PerkinElmer Spectron 3 in diamond ATR mode.

UPS spectroscopy

UPS experiments were carried out using spin-coated polymer films in a home-designed XPS/UPS spectrometer in a vacuum lower than 1×10^{-9} mbar. The excitation source was monochromatic He radiation with a photon energy of 21.22 eV. The work function was derived from the secondary electron cut-off measured under sample bias. The vertical IE was obtained from the leading edge of the frontier occupied density of states as per standard practice. Both WF and IE were obtained with an error margin of ±0.05 eV.

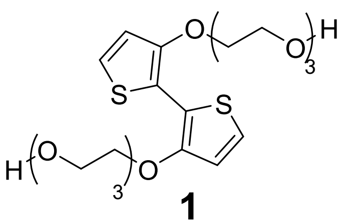
Dynamic Light Scattering (DLS)

Nanoparticle size was characterized using a Zetasizer Ultra (Malvern Instruments), using a non-invasive back scatter (NIBS). All samples were diluted to a known concentration of 0.3 mg mL^{-1} to 0.003 mg mL^{-1} to ensure an intercept > 0.7 and measurements were repeated at least 3 times for each sample. An average number of 20 runs were used per measurements.

Synthesis

Experimental details

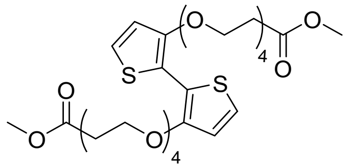
2,2'-(((((([2,2'-bithiophene]-3,3'-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-ol) (1)



1

To 100 ml 2-necked round bottom flask containing degassed triethyleneglycol (12.97 g, 86.4 mmol, 11.5 ml, 14 eq), potassium tert-butoxide (2.077 g, 18.51 mmol, 3 eq) was added slowly under nitrogen atmosphere. The light-yellow solution was stirred at 0 °C for 20 min until the base was dissolved. Then the flask warmed to RT and continued stirring for another 10 min. To this mixture copper iodide (0.117 g, 0.617 mmol, 0.1 eq) and 1,10-phenanthroline (0.220 g, 1.234 mmol, 0.2 eq) were added and the content was stirred for 1 h at 50 °C during which the light-yellow solution was converted first to light brown and upon heating, to dark brown. The 3,3'-dibromo-2,2'-bithiophene (2 g, 6.17 mmol, 1 eq) was added and the content was heated to 110 °C for 36 h. When the reaction was completed, the vessel was cooled to room temperature. The content was transferred to a separatory funnel containing DCM (20 ml). To this mixture, H_2O (50 ml) was added, and an emulsion formed which was broken by addition of brine solution. The aqueous phase was extracted with dichloromethane (2 x 20 ml). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered off and concentrated under reduced pressure. The crude product was adsorbed on silica and purified with column chromatography using ethyl acetate: methanol (10:1) as eluent. The desired compound was obtained as a light-yellow oil (1.36 g, 54.17%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, J = 5.6 Hz, 2H), 6.83 (d, J = 5.6 Hz, 2H), 4.25 – 4.17 (m, 4H), 3.87 (dd, J = 5.6, 4.2 Hz, 4H), 3.75 – 3.62 (m, 12H), 3.56 (dd, J = 5.3, 3.9 Hz, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 150.17 (C-3), 119.68 (C-5), 115.88 (C-4), 110.15 (C-2), 72.54, 71.67, 70.96, 70.47, 69.92, 61.81.

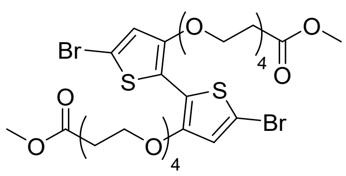
Dimethyl 3,3'-(((((([2,2'-bithiophene]-3,3'-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dipropionate (2)



2

A dry 50 ml 2-necked round bottom flask was charged with compound (**1**) (0.59 g, 1.29 mmol), and THF (4 ml) and degassed for 30 min under nitrogen atmosphere. NaOH (0.52 g, 1.29 mmol, 1 eq) was added and degassed for another 20 minutes. Then n-butyl acrylate (0.99 g, 7.7 mmol, 6.0 eq) was added slowly through septum. The vessel was covered with aluminum foil from light and continued stirring overnight. To this mixture methanol (40 ml) was added and heated to reflux for 24 h. The vessel was cooled to RT and the content was transferred to separatory funnel containing DCM (20 ml) and the phases were separated. Deionized H_2O (30 ml) was added, and the aqueous phase was extracted with DCM (2 x 20 ml). The combined organic phase was dried over anhydrous $MgSO_4$, filtered off and concentrated under reduced pressure. The crude product was purified with column chromatography using ethyl acetate: methanol (10:1) as eluent to yield the desired compound as light-yellow oil (0.37 g, 45.7%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (ddd, *J* = 5.9, 3.9, 1.8 Hz, 2H), 6.83 (td, *J* = 5.1, 1.8 Hz, 2H), 4.22 (dq, *J* = 6.8, 3.9 Hz, 4H), 3.88 (dh, *J* = 5.1, 2.2 Hz, 4H), 3.75 – 3.53 (m, 26H), 2.57 (tdd, *J* = 6.5, 5.0, 1.6 Hz, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 172.04 (C-i), 172.03 (C-3), 151.72 (C-5), 116.57 (C-4), 114.74 (C-2), 114.72, 71.38, 70.92, 70.91, 70.53, 70.52, 70.42, 70.06, 70.02, 66.58, 51.66, 51.65, 34.86.

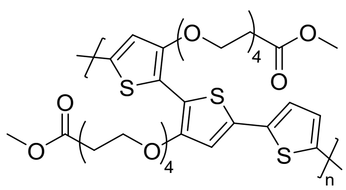
Dimethyl 3,3'-((((((((5,5'-dibromo-[2,2'-bithiophene]-3,3'-diyl)bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dipropionate (3)



3

A dry 50 ml 2-necked round bottom flask was charged with degassed THF (20 ml) and compound (**2**) (0.75 g, 1.18 mmol) and degassed for 30 minutes. N-bromosuccinimide (0.42 g, 2.37 mmol, 2.0 eq) was added and the vessel was cooled to -20 °C in ice-salt bath and stirred for 3 h under nitrogen atmosphere. After 3 h the reaction was observed to be completed, and the content was transferred to separatory funnel. Saturated aq. $NaHCO_3$ (30 ml) solution and deionized H_2O were added, and the phases were separated. The aqueous phase was extracted with diethyl ether (30 ml). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered off and concentrated under reduced pressure. The resulting oil was purified with column chromatography using ethyl acetate: methanol (10: 1) with a few drops of triethylamine to yield the desired compound as solid (0.76 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 2H), 4.21 – 4.15 (m, 4H), 3.88 – 3.82 (m, 4H), 3.77 – 3.58 (m, 26H), 2.59 (t, J = 6.5 Hz, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 172.04 (C-i), 150.19 (C-3), 119.65 (C-4), 115.85 (C-2), 110.05 (C-5), 71.70, 70.92, 70.71, 70.44, 69.88, 66.59, 51.67, 34.88.

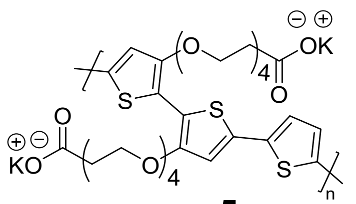
P(2CAT-Me) (4):



4

A dry 50 ml 2-necked round bottom flask was charged with monomer (**3**) (0.3 g, 0.426 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.0078 g, 0.0085 mmol, 2 mol-%), tri(*o-tolyl*)phosphine (0.0104 g, 0.034 mmol, 8 mol-%) and 2,5-bis(trimethylstanyl)thiophene (0.2 g, 0.49 mmol, 1.15 eq) and degassed for 30 minutes. To this mixture, dry and degassed THF (10 ml) was added under nitrogen atmosphere. The dark purple mixture was heated to 60 °C with vigorous stirring and reacted over the weekend. The content was then cooled to room temperature and precipitated in petroleum ether and subjected to centrifugation. The polymer in the centrifugation flask was transferred to the vessel. Due to catalyst removal, the obtained polymer was dissolved in THF (5 ml), a solution of sodium diethyldithiocarbamate (0.24 g) in deionized H_2O (0.5 ml) was added and the mixture was vigorously stirred at 50 °C for 1 h. The polymer solution was precipitated in petroleum ether and the precipitate was collected by centrifugation. The polymer pellet in centrifugation flask was transferred to Soxhlet thimble. The crude polymer was purified by subsequent extraction with petroleum ether, isopropanol, diethyl ether, ethyl acetate and chloroform, respectively. The chloroform solution containing the polymer was concentrated and precipitated in petroleum ether. The precipitate was collected through centrifugation. The high molecular weight polymer that did not extract by chloroform was transferred to a vial to yield 240 mg. The polymer fractions were dried in vacuum oven at 40 °C and yielded 80.5% product. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H), 7.01 – 6.a (m, 2H), 4.37 – 4.27 (m, 4H), 3.97 (q, *J* = 5.1 Hz, 4H), 3.83 – 3.56 (m, 26H), 2.57 (q, *J* = 6.0 Hz, 4H).

P(2CAT-K) (5):



5

A dried 2- necked round bottom flask was charged with polymer (**4**) (120 mg), dry and degassed DMSO (5 ml) and stirred at 60 °C under nitrogen atmosphere. KOH (5 eq) was dissolved in degassed DI water and added to the vessel containing P(2CAT-K). Then additional degassed DI water (4 ml) was added and stirred overnight. The reaction mixture was cooled to RT and precipitated in isopropanol. The polymer precipitate was collected by centrifugation. The polymer in centrifugation flask was rinsed with isopropanol (4 x 40 ml), diethyl ether (40 ml) and acetone (40 ml). The fluffy polymer in centrifugation flask was transferred to weighted vial and dried on vacuum line to yield 115 mg, 94 % polymer (P(2CAT-K)). ^{1}H NMR in D_2O did not result in any discernible peaks. Instead, the deprotection of the polymer was confirmed by FTIR (Fig. S9). A lower molecular weight batch of P(2CAT-K) analyzed with ^{1}H NMR in D_2O showed that the deprotection was successful.

NMR spectra

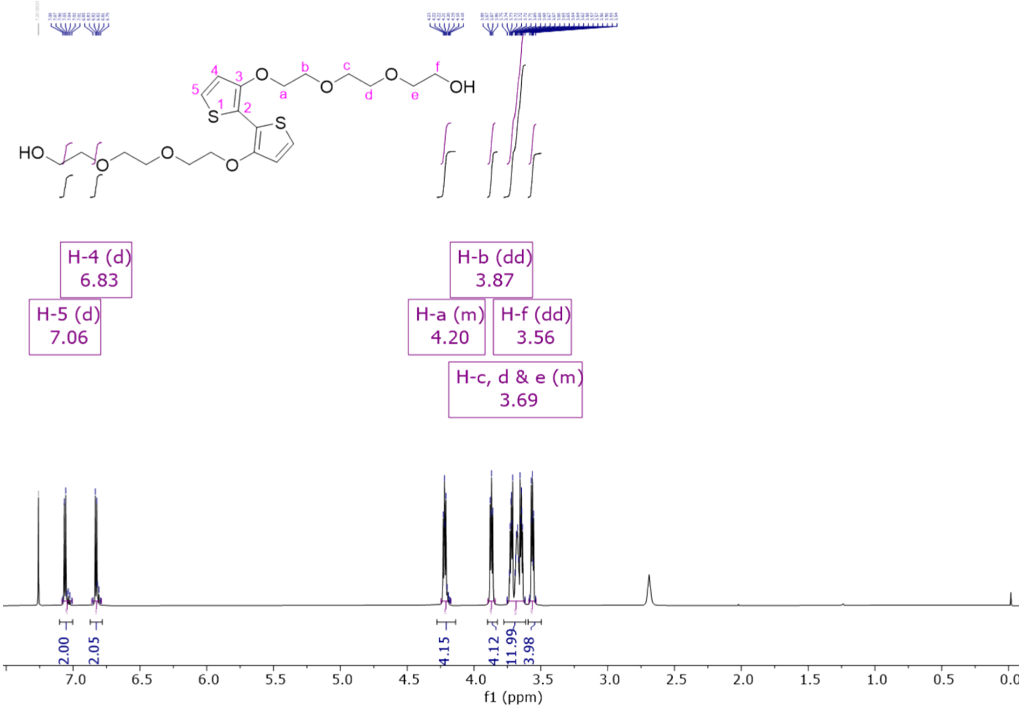


Fig. S1: ^{1}H NMR in $CDCl_3$ of compound **1**.

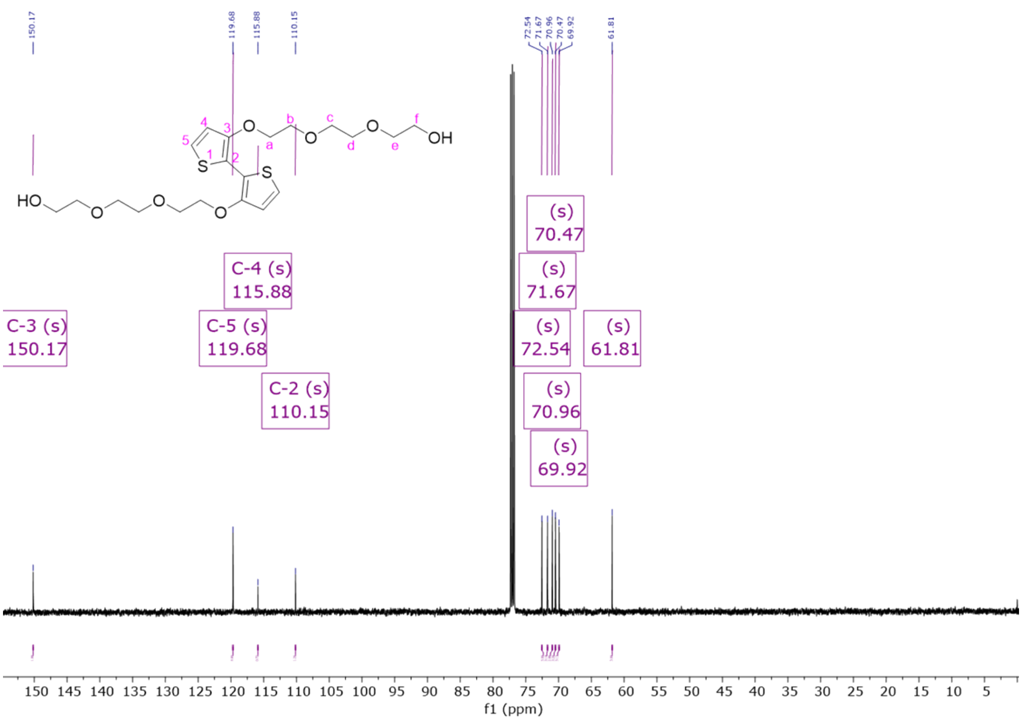


Fig. S2: ^{13}C NMR in $CDCl_3$ of compound **1**.

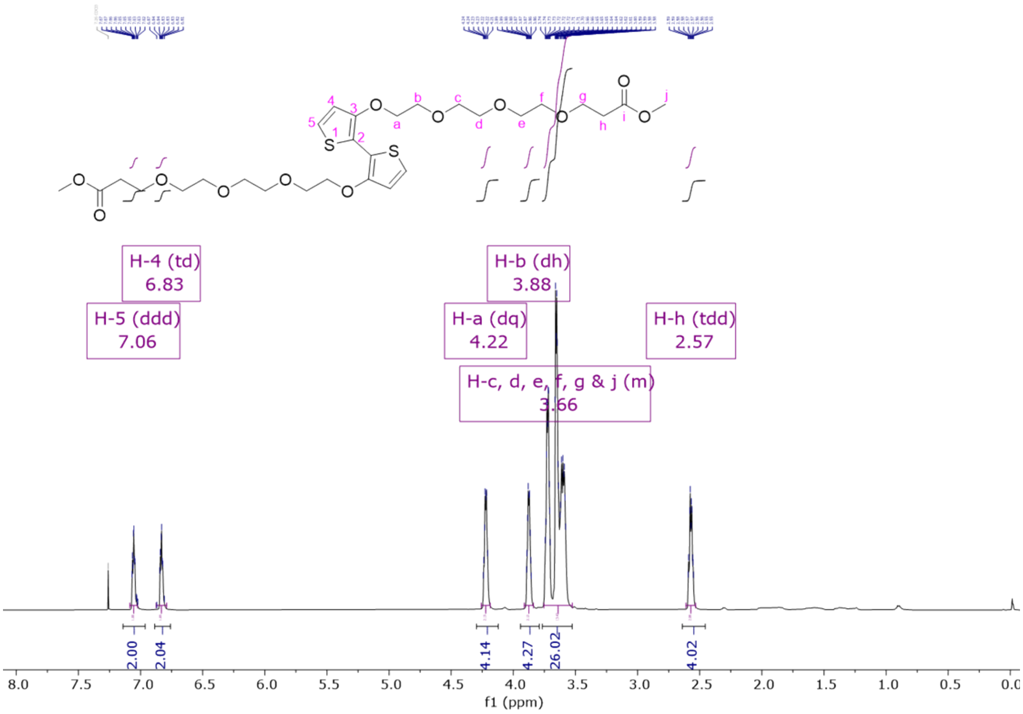


Fig. S3: ^{1}H NMR in $CDCl_3$ of compound **2**.

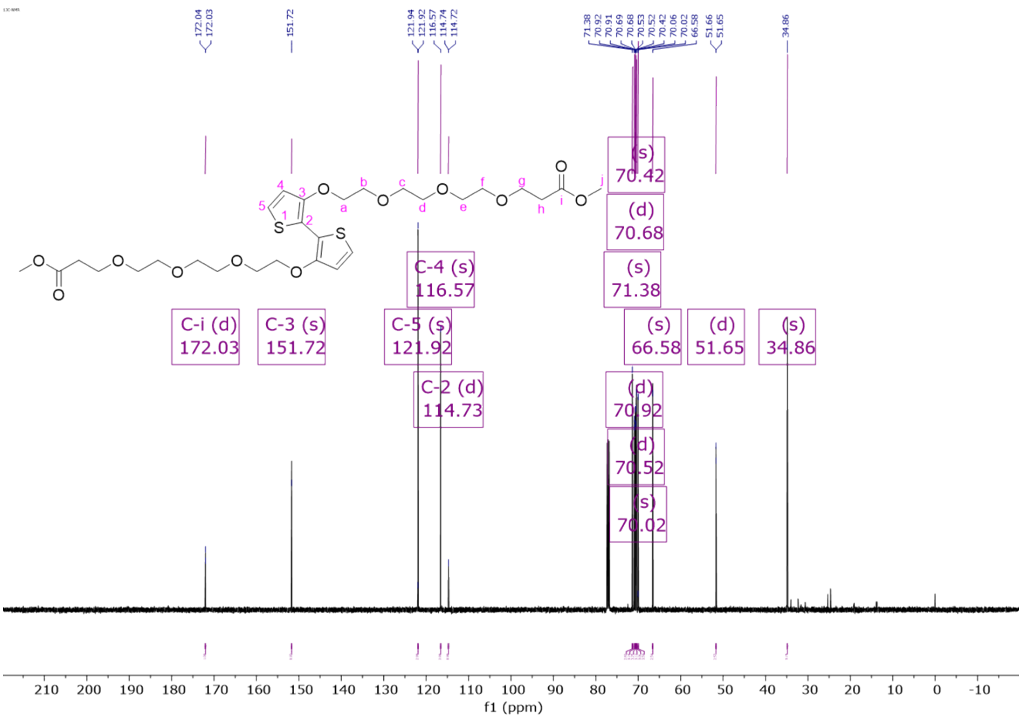


Fig. S4: ^{13}C NMR in $CDCl_3$ of compound **2**.

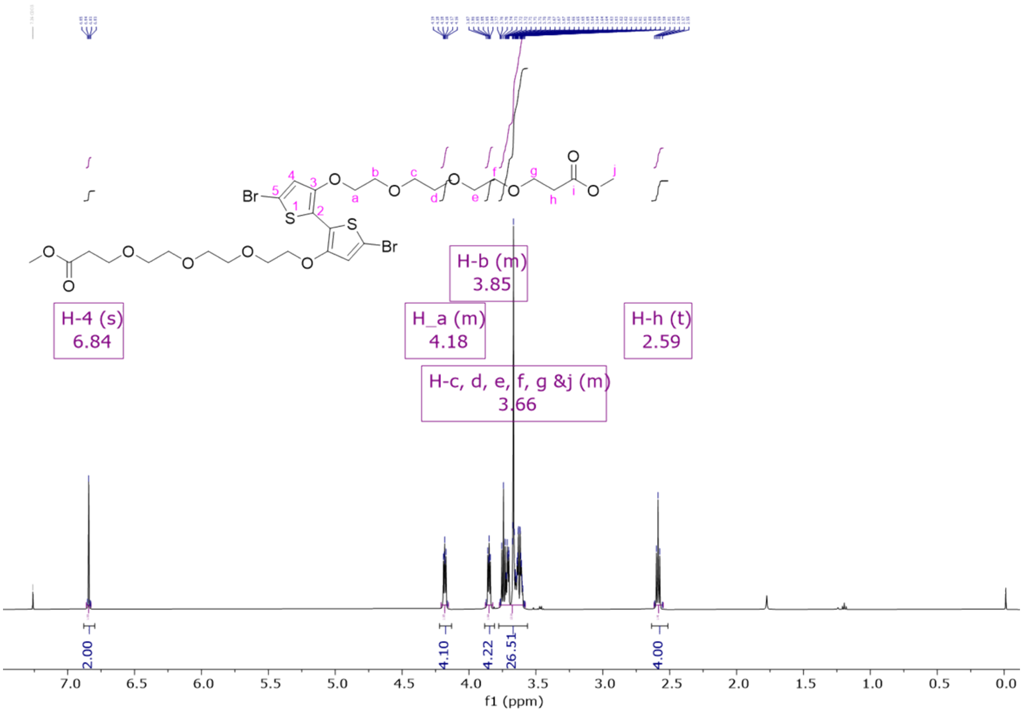


Fig. S5: ^{1}H NMR in $CDCl_3$ of compound **3**.

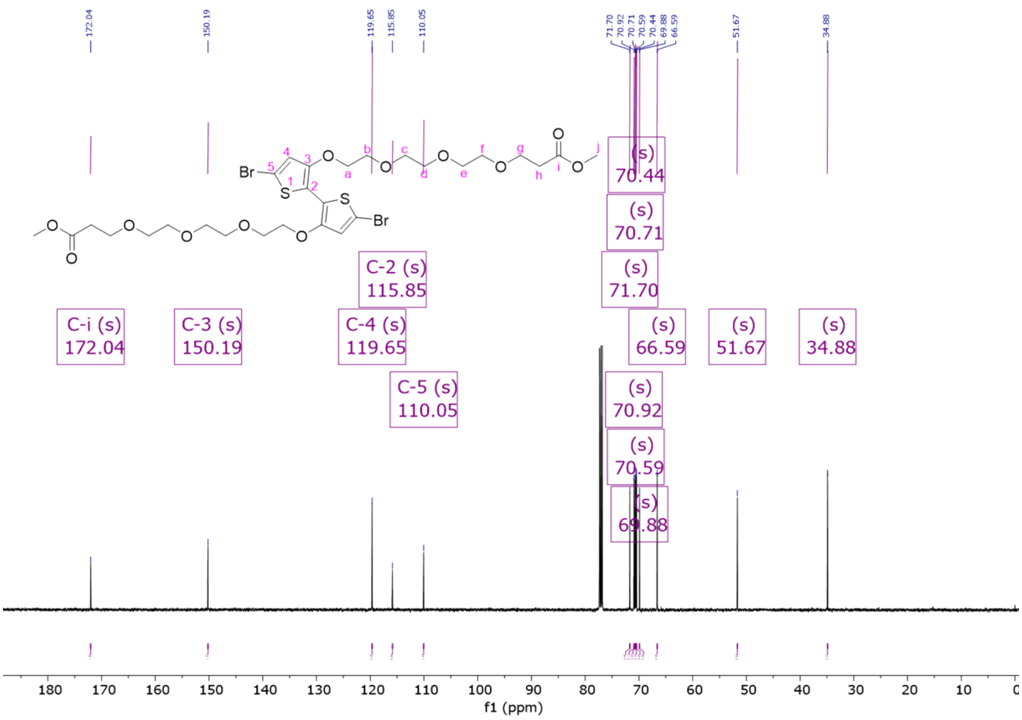


Fig. S6: ^{13}C NMR in $CDCl_3$ of compound **3**.

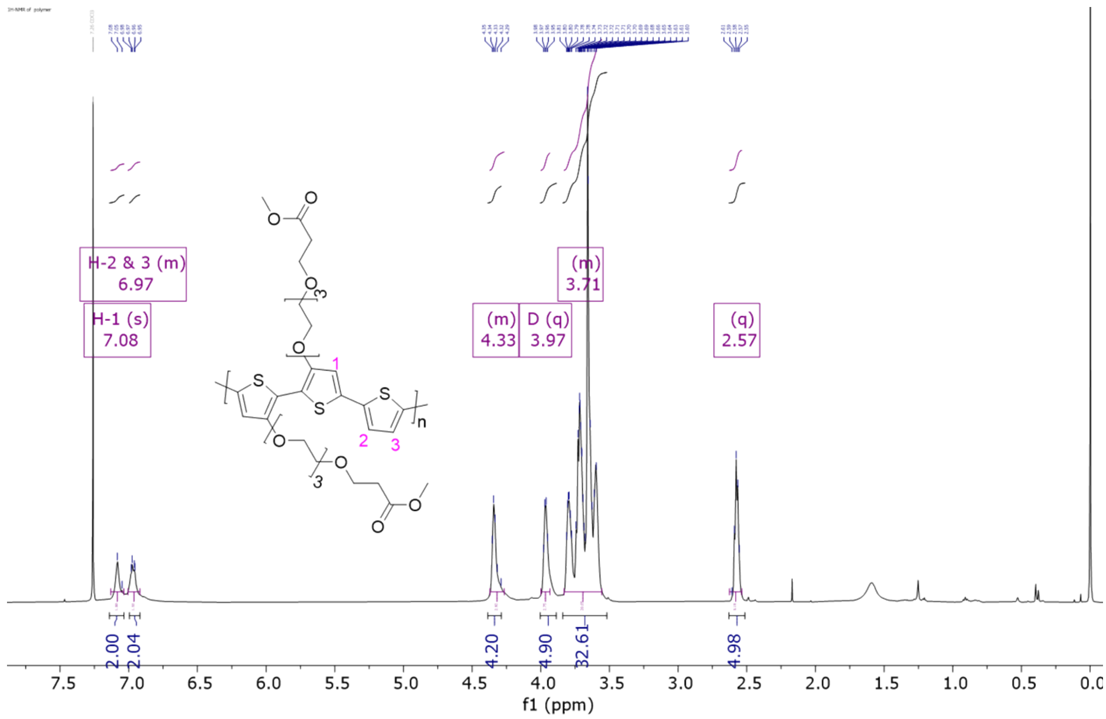


Fig. S7: ^{1}H NMR in $CDCl_3$ of P(2CAT-Me) (compound **4**).

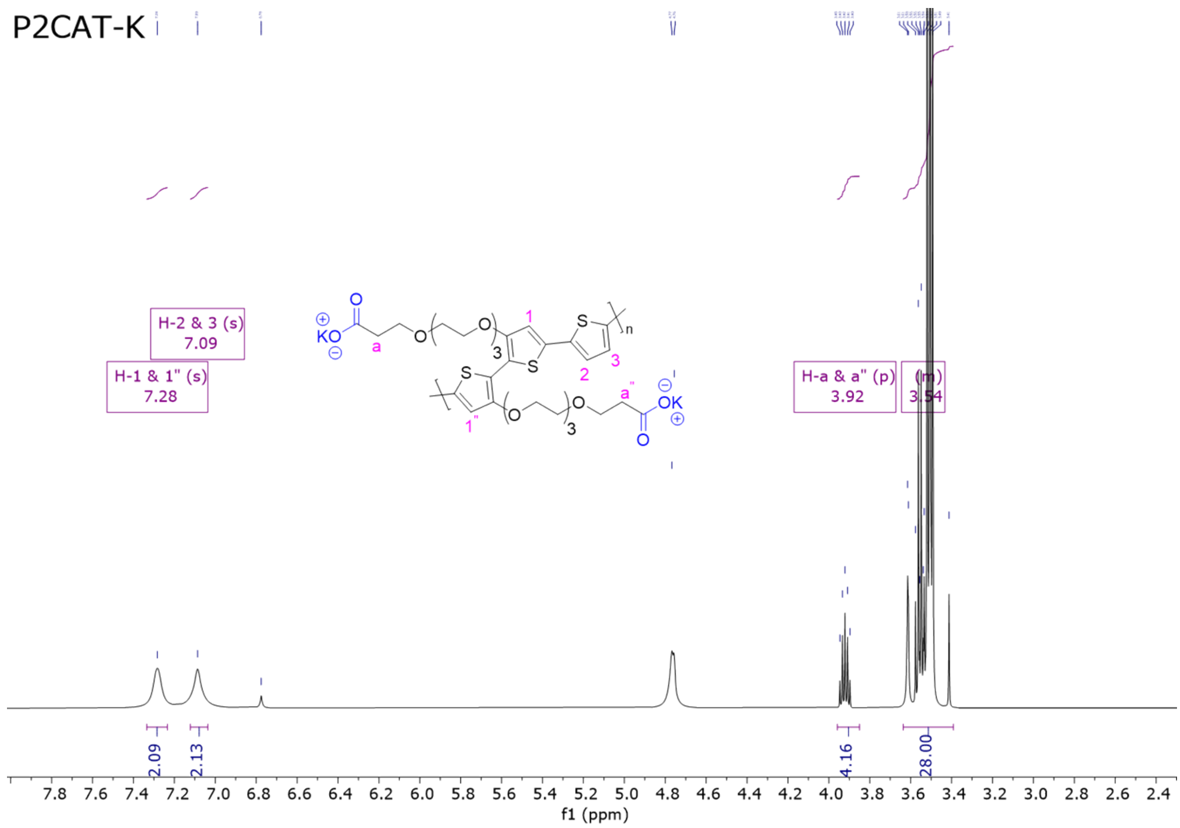


Fig. S8: ^{1}H NMR in D_2O of lower molecular weight (Mn = 25.7 Kd) P(2CAT-K) (compound **5**).

GPC analysis

Mn (g/mol)	PDI	K (10e-5) dl/g)	Alpha
26420	2.46	128.4	0.3908

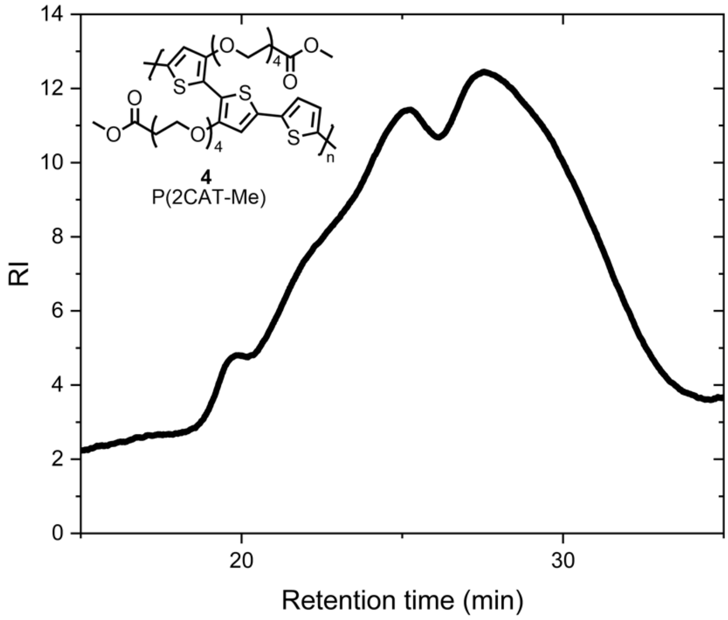


Fig. S9: Size exclusion chromatogram of P(2CAT-Me) (precursor) in dimethyl formamide.

FTIR analysis

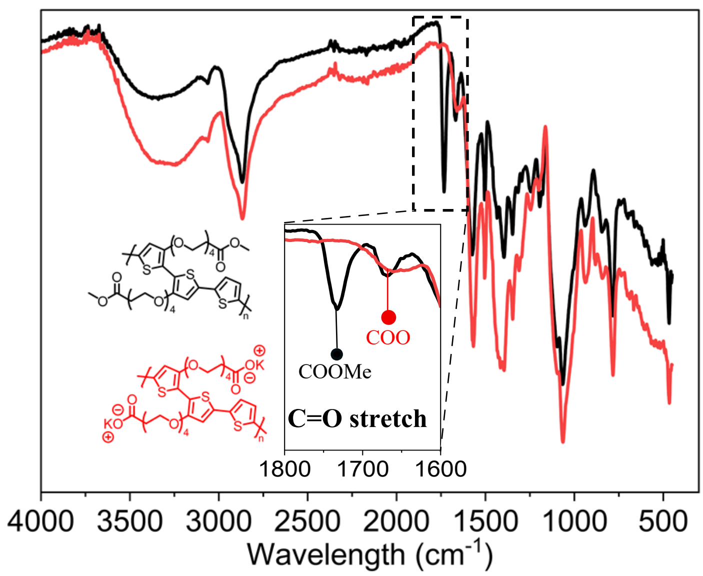


Fig. S10: FTIR of the precursor polymer P(2CAT-Me) (black) and P(2CAT-K) (red).

Dynamic Light Scattering (DLS)

DLS analysis was performed for P(2CAT-K) dispersions with three different concentrations (0.3, 0.03 and 0.003 mg mL^{-1}). The results obtained are reported in Table S10 and Figure S11.

Table S11: Nanoparticle size and PDI measured for dispersions of P(2CAT-K).

[P(2CAT-K)] (mg mL^{-1})	Size (nm)	PDI
0.3	214	0.7
0.03	139 ± 7	0.43 ± 0.06
0.003	133 ± 2	0.47 ± 0.05

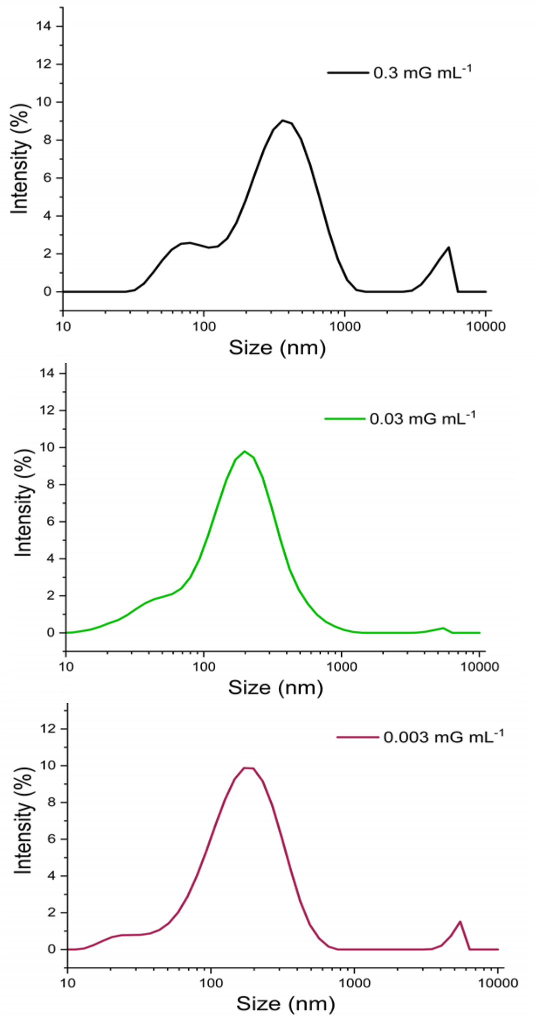


Fig.S12: Dynamic Light Scattering size distribution of P(2CAT-K) dispersions with three different concentrations (0.3, 0.03 and 0.003 mg mL^{-1}).

Electrochemistry

Cyclic voltammetry of P(2CAT-K) in solution

Attempts to perform a cyclic voltammetry (CV) of P(2CAT-K) in aqueous solution failed due to precipitation of the polymer in the highly concentrated electrolyte solution, which we believe is due to a salting-out effect. However, a gradual deposition of a P(2CAT-K) film from the suspension (0.3 mg/mL) in KCl (0.01 M) solution was observed on the glassy carbon (GC) working electrode. After allowing the polymer film to grow for 1h 30 min, the film-covered GC electrode was transferred to a citric acid solution (20 mg/mL) for a few minutes for the acid fixation of the polymer to prevent dissolution once the polymer would be fully reduced during the CV scan. After washing with distilled water, the GC was immersed in a clean KCl (0.1 M) solution and a CV was recorded, using Ag/AgCl as reference electrode and a Pt-wire as counter electrode (Fig. S13). The obtained voltammogram shows a peak from -0.3 V to 0.2 V, corresponding to the oxidative doping process, followed by a predominantly capacitive current, correlated to the conductive region. This result is similar to the CV obtained for the drop-cast film, except for the much lower current intensity recorded for the deposited film.

Cyclic voltammetry of P(2CAT-K) in solid state

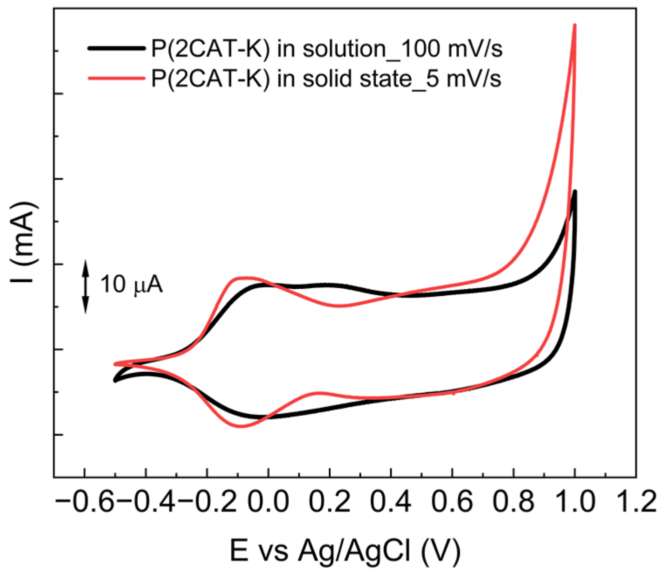


Fig. S13: CV of the film deposited from suspension of polymer electrolyte solution recorded in KCl (0.1 M) with a scan rate of 100 mV/s (black line) and CV of the drop-cast polymer film recorded in in KCl (0.1 M) with a scan rate of 5 mV/s (red line).

For the CV recorded for the P(2CAT-K) film, 10 µL of an aqueous dispersion of the polymer (1.6 mg/mL) were drop-cast on the working area of a glassy carbon electrode and the film was let dry in the oven at 60 °C for 20 min. Then it was dipped in a citric acid solution (20 mg/mL) for acid fixation and, after washing, it was allowed to dry in the oven at the same condition reported before. The CV of the final drop-cast film (Fig. S13) was recorded in KCl (0.1 M) solution using Ag/AgCl as reference electrode and a Pt-wire as counter electrode. Cyclic voltammetry of the drop-cast film at different scan rates were recorded (Figure S15). The linearity obtained reporting the measured current at 0.8 V versus the scan rate further suggests a surface-confined process.

Fig. S14: Picture of the drop-cast polymer film (1.6 mg/mL) on the working area of the GC working electrode.

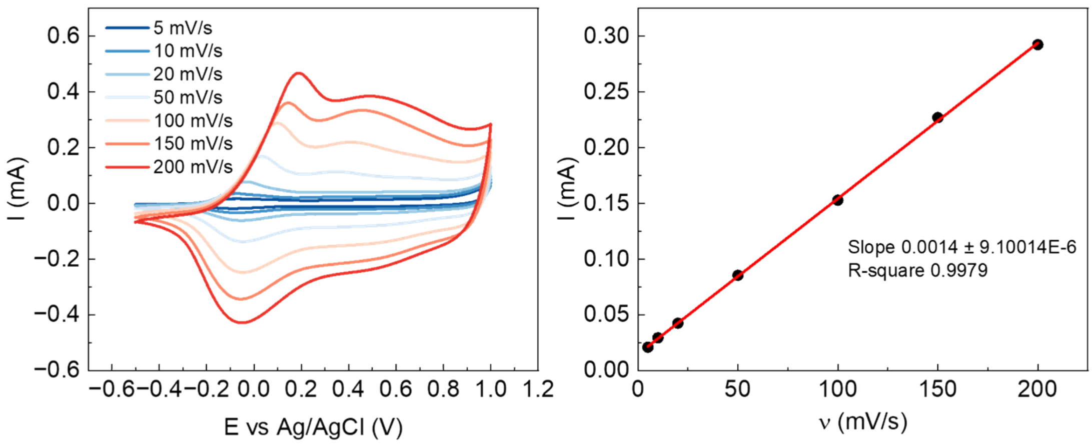


Fig. S15: On the left: cyclic voltammetry of the drop-cast film at different scan rates. On the right: Linear fitting of the recorded currents vs. the scan rate.

UV-Vis spectroscopy

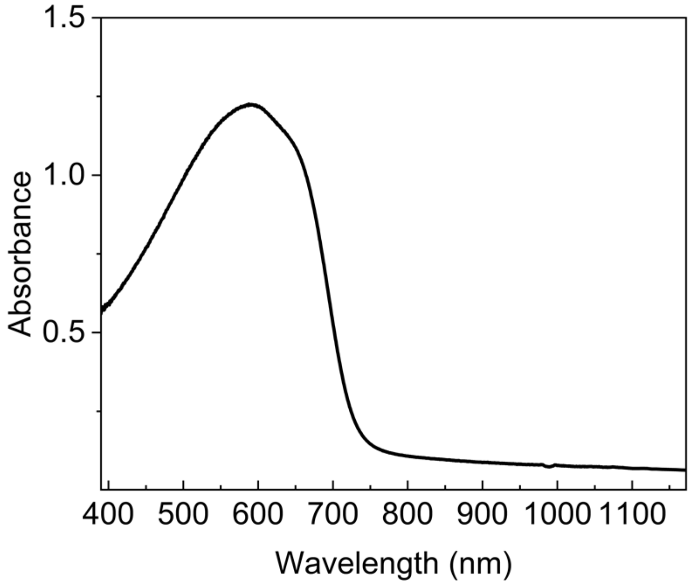


Fig. S16: Absorption spectra of a P(2CAT-K) film.

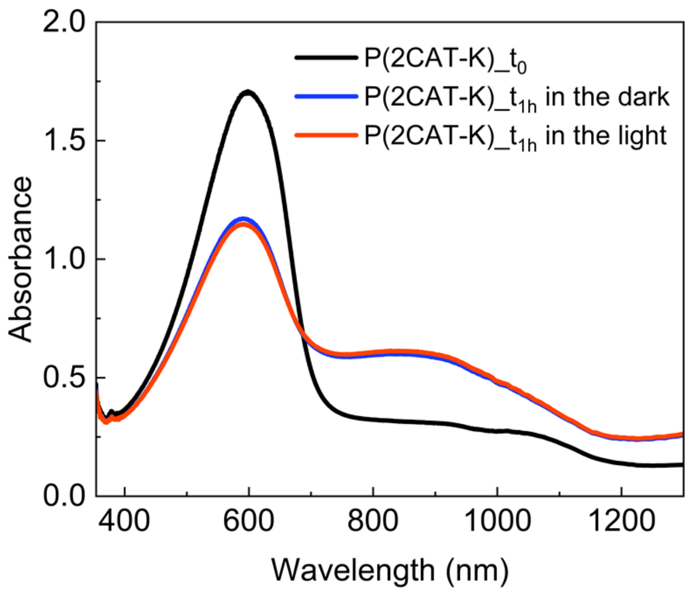


Fig. S17: Absorption spectra of a freshly prepared aqueous P(2CAT-K) nanodispersion (black line) and of the same nanodispersion kept for one hour in the dark (blue line) and in the light (red line). The obtained UV-Vis spectra are similar regardless of reaction condition (light or dark) and allow us to exclude a photocatalytic oxidation process.

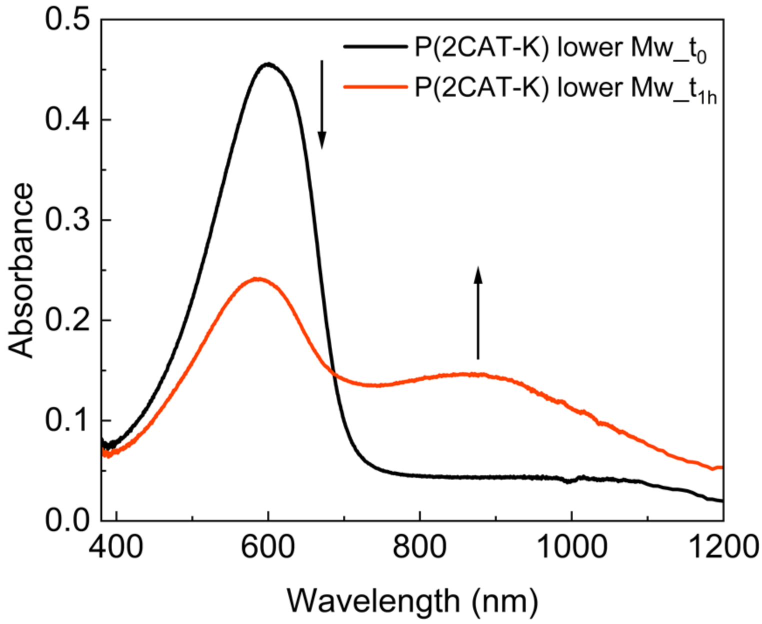


Fig. S18: Absorption spectra of a fresh lower molecular weight P(2CAT-K) (black line) and after one hour under air. In this case, the water was degassed with N_2 before dissolving P(2CAT-K).

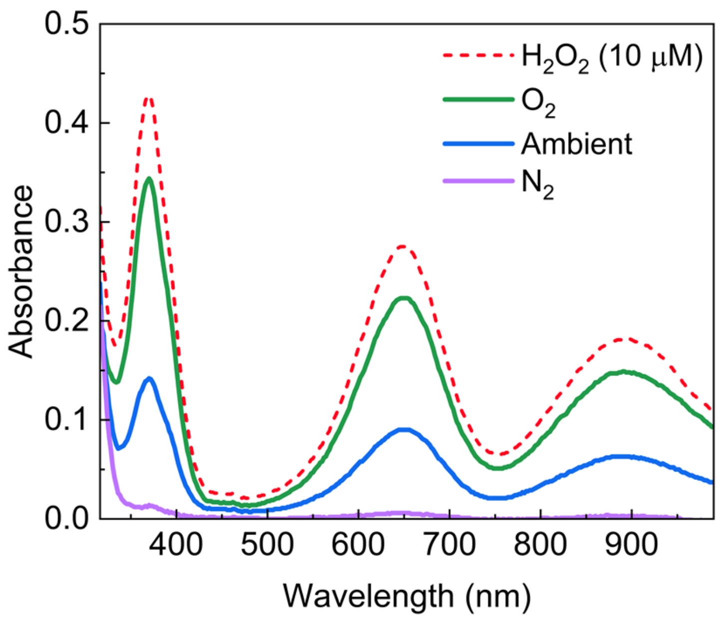


Fig. S19: Absorption spectra of the HRP/TMB assay solution after removal of P(2CAT-K), where ORR reactions were either sparged with O_2 (green line), N_2 (purple line) or left under ambient air (blue line). The graph also displays a reference spectrum that was obtained when mixing the HRP/TMB assay with a known amount of H_2O_2 (dashed red line). It is worth noting that in order to quantify the amount of

H_2O_2 produced in the aqueous solutions of the polymer, the value of [H_2O_2] obtained from these spectra need then be corrected for the dilution factor.

H_2O_2 production and quantification

Experimental procedure for H_2O_2 production and quantification

10 mL of water was deoxygenated by sparging with N_2 overnight. An aqueous polymer nanodispersion (0.5 mg/mL) was prepared under N_2 condition. 1 mL of polymer dispersion was added under N_2 in three different closed vial glass, previously filled with N_2, using a steel needle as outlet. The first dispersion was purged with O_2 (flow controlled by a rotameter: 75 mL/min), a second one was purged with $N_{2,}$ and a third one was left under ambient condition (the closure cap was loosened to allow air to slowly replace N_2). After one hour, 100 µL of a $CaCl_2$ aqueous solution (0.18 M) were added in each vial to precipitate the polymer. The solution was then filtered using a 0.22 µM PTFE filter. Lastly, H_2O_2 concentration was determined by monitoring the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) catalyzed by horseradish peroxidase (HRP) enzyme in phosphate-citric acid buffer (pH 6), following a previously published procedure.[1, 2] The TMB is rapidly oxidized by the H_2O_2 in the presence of HRP, producing a blue charge-transfer complex that shows a characteristic absorption peak at λ= 653 nm[3] from which we can calculate the concentration of H_2O_2 through interpolation with a calibration curve. Therefore, aliquots of 50 to 100 µL of the filtered solutions were mixed with 250 to 200 µL of a prepared HRP assay mixture, consisting of 992 µL of phosphate-citric acid buffer solution, 6 µL of a 0.04 M solution of TMB in DMSO and 2 µL of a HRP aqueous solution (ca. 311 U/mL). Then the absorbance of the solution with a final volume of 300 µL was measured at 653 nm. The absorbance value obtained was used to extract the concentration of H_2O_2 from a previously established calibration curve.

Calibration curve

As previously described, a calibration curve for the determination of H_2O_2 using an HRP/TMB assay is required. Each time a new experiment was performed, a new calibration curve was created. All the obtained calibration curves presented similar values. One example of the obtained calibration curve is displayed (Figure S20).

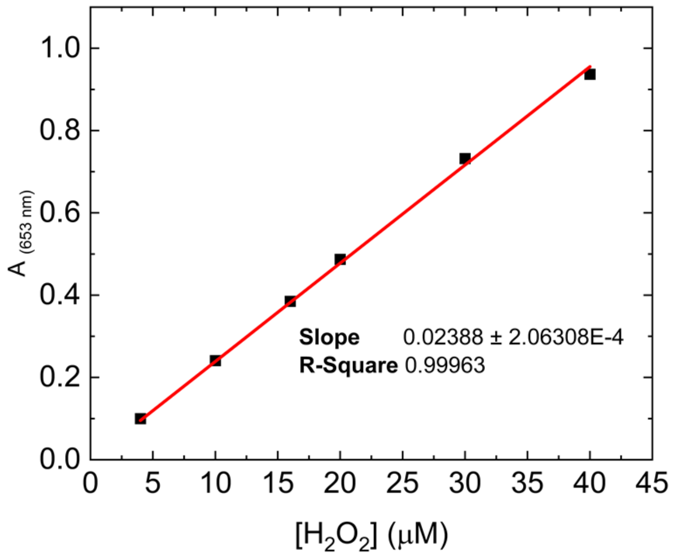


Fig. S20: Calibration curve measured for the HRP/TMB assay.

Table S21: Measured [H_2O_2] for different environmental conditions

Condition	[H_2O_2] (μM)	[repeating unit][a] (μM)	(2*[H_2O_2]/ [repeating unit]) (%)
N_2	0.95 ± 0.29[b]	655.31	0.29 ± 0.09
Ambient	23.54 ± 4.86	655.31	7.18 ± 1.49
O_2	58.86 ± 16.10	655.31	17.96 ± 4.91

[a] This value was calculated for a 0.5 mg/mL polymer aqueous nanodisperion used for the experiment (Mw repeating unit = 763 g/mol). [b] It should be noted that the absorption measured for the N_2 sparged solutions was very low, and therefore the value reported for the corresponding [H_2O_2] measurement is more subject to error.

ORR polymer-mediated experiments in presence of added H_2O_2

From a thermodynamical point of view, the oxygen reduction reaction (ORR) to H_2O_2 (E°′ vs. NHE=+0.28 V, at pH 7 and at 25 °C) is a much less favourable process compared to both H_2O_2 reduction to water (E°′ vs. NHE=+1.35 V, at pH 7 and at 25 °C) and ORR to water (E°′ vs. NHE=+0.817 V, at pH 7 and at 25 °C). Therefore, to evaluate if the polymer kinetically favours ORR to H_2O_2 or if it further reduces H_2O_2 to water, we performed ORR polymer-mediated experiments in the presence of added amount of H_2O_2. We prepared two different fresh aqueous dispersions of P(2CAT-K) (2 mg mL^{-1}). One was used as a reference, and a known amount of H_2O_2 was added to the second one. Both dispersions were purged for one hour with O_2. Then, the amount of H_2O_2 produced by the two dispersions was quantified following the same HRP/TMB assay procedure described before. The same experiment was performed three times and increasing amount of added H_2O_2 were used (100 µM, 200 µM and 400 µM), corresponding to almost 0.5, 1 and 2 times the amount of H_2O_2 produced by the reference. In all cases, a higher amount of H_2O_2 was observed than the one initially added at the beginning of the experiment (ΔC_1). While increasing the amount of added H_2O_2, the amount of hydrogen peroxide produced by the polymer mixed with H_2O_2 decreases compared to the one produced by the dispersion of the polymer alone (ΔC_2). These results prove that even if the polymer can further reduce H_2O_2 to water, it still produces H_2O_2 kinetically.

Table S22. Comparison of H_2O_2 production by ORR mediated by P(2CAT-K) (2 mg mL^{-1}) in presence and in absence of added amount of H_2O_2.

N°. Test	**Condition**	**H_2O_2 quantified**	**ΔC_1 (H_2O_2 observed - H_2O_2 added)**	**ΔC_2 (H_2O_2 produced by polymer alone - H_2O_2 produced by polymer mixed with additional H_2O_2)**
1°	Polymer	172 µM	/	/
1°	Polymer+ 100 µM H_2O_2	257 µM	157 µM	15 µM
2°	Polymer	212 µM	/	/
2°	Polymer+ 200 µM H_2O_2	321 µM	121 µM	91 µM
3°	Polymer	236 µM	/	/
3°	Polymer+ 100 µM H_2O_2	495 µM	95 µM	141 µM

Doping/dedoping cycle of P(2CAT-K)

The P(2CAT-K) aqueous nanodispersion mixed with Et_3N reducing agent (black line) was purged again with O_2, which resulted in a partial doping of the polymer (red line). The addition of more Et_3N allowed the regeneration of the neutral polymer (blue line), demonstrating the reversibility of the H_2O_2 production process.

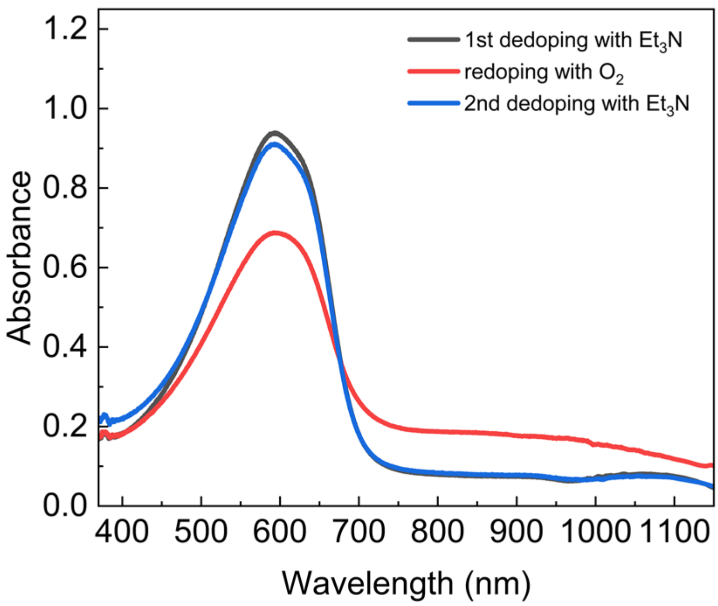


Fig. S23: Absorption spectra of the first dedoping with of Et_3N (black line), of the redoping with O_2 (red line) and second dedoping with further fresh Et_3N (blue line).

References

1. M. Jakešová, D. H. Apaydin, M. Sytnyk, K. Oppelt, W. Heiss, N. S. Sariciftci and E. D. Głowacki, *Advanced Functional Materials*, 2016, **26**, 5248-5254.
2. M. Gryszel, R. Rybakiewicz and E. D. Głowacki, *Advanced Sustainable Systems*, 2019, **3**, 1900027.
3. P. D. Josephy, T. Eling and R. P. Mason, *Journal of Biological Chemistry*, 1982, **257**, 3669-3675.