First example of an electropolymerizable heptazine bearing oligothiophene arms; a new way to produce a well-defined heptazine containing polymer.

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1) Synthesis

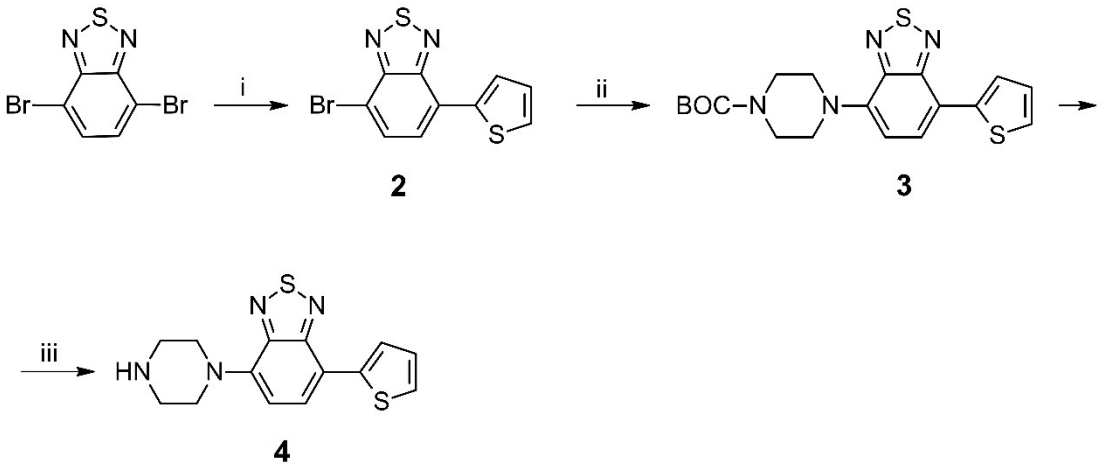
Characterization techniques

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury (500 and 125 MHz) spectrometer and referenced with respect to TMS and solvents. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Mass spectra were measured by ESI method on an AMD 604 mass spectrometer.

Reagents

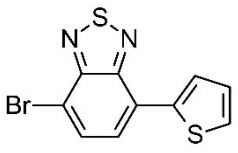
4,7-dibromobenzo[c][1,2,5]thiadiazole, 2-(tributylstannyl)thiophene, *tert*-butyl piperazne-1-carboxylate, bis(triphenylphosphine)palladium(II) dichloride, $PdCl_2(PPh_3)_2$, palladium acetate, $Pd(OAc)_2$, tri-*tert*-butyl phosphine, *t*-Bu_3P, sodium *tert*-butoxide, Na(*t*-BuO), potassium carbonate, K_2CO_3, anhydrous toluene, anhydrous THF, anhydrous DMF were purchased from Aldrich.

All glassware was oven dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.



2 **3** **4**

Scheme S1. Synthetic routes to the studied derivatives of benzothiadiazole: i) 2-(tributylstannyl)thiophene, $PdCl_2(PPh_3)_2$, THF, 85°C, ii) *tert*-butyl piperazne-1-carboxylate, sodium *tert*-butoxide, Na(*t*-BuO), $Pd(OAc)_2$, *t*-Bu_3P, toluene, 110°C, iii) TFA, CH_2Cl_2, K_2CO_3.



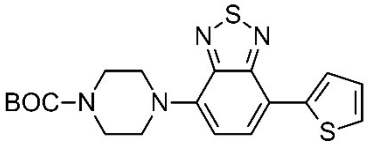
2

4-Bromo-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 2

4,7-dibromobenzo[c][1,2,5]thiadiazole, 2.94 g (10 mmol), 2-(tributylstannyl)thiophene, 3.5 ml (11 mmol), $PdCl_2(PPh_3)_2$, 70.2 mg (0.1 mmol) were dissolved in 25 ml of anhydrous THF under

Ar. The mixture was heated overnight at 85°C. After cooling to RT 20 ml of saturated solution of NH_4Cl was added and the product was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$. The crude product was purified by chromatography on silica gel eluting with hexanes/CH_2Cl_2 (1:1) to give 2.09 g (7.04 mmol) of yellow powder with the yield of 70%.

^{1}H NMR (500 MHz, CHD_3) δ, 8.08 (dd, *J* = 3.5, 1.0 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 5.5, 1.0 Hz, 1H), 7.21-7.19 (m, 1H).

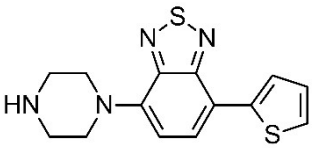


3

4-(N-BOC-piperazine)-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 3

4-Bromo-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 594 mg (2 mmol), *tert*-butyl piperazine-1-carboxylate 391 mg (2.1 mmol), sodium *tert*-butoxide, 250 mg (2.6 mmol), Palladium acetate, 22.5 mg (0.1 mmol), tri-*tert*-butylphosphine, 60.7 mg (0.3 mmol) were dissolved in 15 ml of anhydrous toluene under Ar. The mixture was heated overnight at 110°C. After cooling to RT 10 ml of distilled water was added and the product was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$. The crude product was purified by chromatography on silica gel eluting with hexanes/ethyl acetate (3:1) to give 0.57 g (1.4 mmol) of yellow powder with the yield of 71%.

^{1}H NMR (500 MHz, CHD_3) δ, 7.95 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.75 (d, *J* = 9.5 Hz, 1H), 7.36 (dd, *J* = 6.5, 1.5 Hz, 1H), 7.18-7.16 (m, 1H), 6.84 (d, *J* = 9.5 Hz, 1H), 3.74 (t, *J* = 6.0 Hz, 1H), 3.53 (t, *J* = 6.0 Hz, 1H), 1.51 (s, 9H).

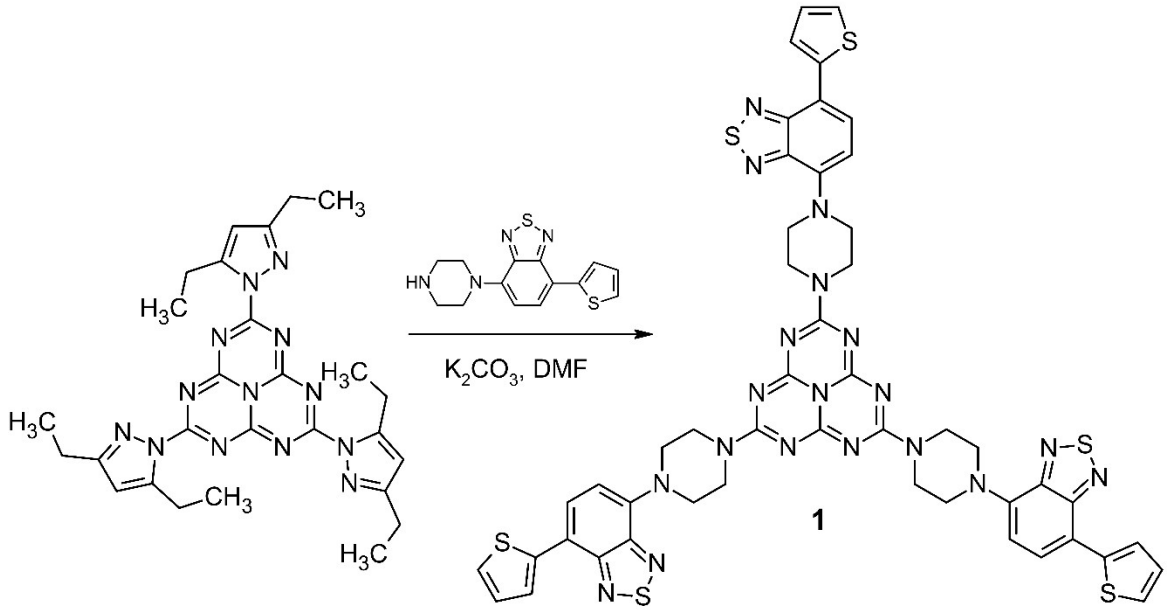


4

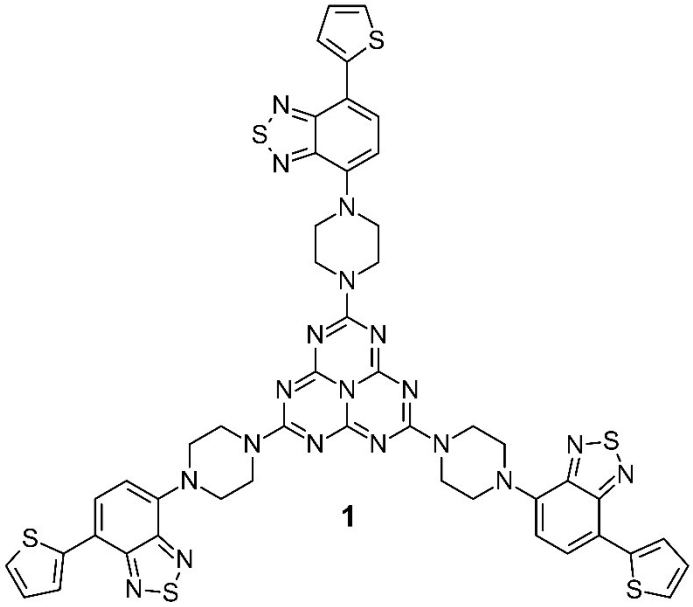
4-piperazine-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 4

4-(N-BOC-piperazine)-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 0.19 g (0.47 mmol) was dissolved in 10 ml of CH_2Cl_2 and cooled to 0°C. 3 ml of TFA was mixed with 3 ml of CH_2Cl_2 and added to the solution of **3**. Thus obtained mixture was stirred for 0.5 h at 0°C and then at RT. The solvent was evaporated. 10 ml of 1 M solution of K_2CO_3 was added to the residue, the product was extracted with CH_2Cl_2 and dried with Na_2SO_4. The solvent was evaporated to give 0.11 g (0.36 mmol) of yellow powder with the yield of 77%.

^{1}H NMR (500 MHz, CHD_3) δ, 7.94 (dd, J = 4.5, 1.5 Hz, 1H), 7.75 (d, J = 10 Hz, 1H), 7.35 (dd, J = 6.5, 1.5 Hz, 1H), 7.17-7.15 (m, 1H), 6.78 (d, J = 10 Hz, 1H), 3.57 (t, J = 6.25 Hz, 4H), 3.21 (t, J = 6.25 Hz, 4H).



Scheme S2. Synthetic procedure for the preparation of 2,5,8-tri(4-piperazine-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole)-heptazine.



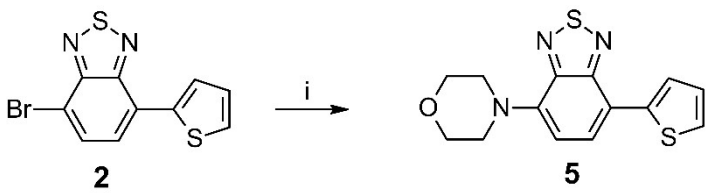
1

Compound 1

Compound **4**, 0.406 g(1.34 mmol), TDPH, 0.22 g (0.407 mmol, prepared after ref.[1]), K_2CO_3, 0.222 g (1.61 mmol) were mixed in 6 ml of anhydrous DMF. The mixture was stirred at RT for 1 h and then heated at 100°C overnight. After cooling to room temperature distilled water was added, the crude product was extracted with CH_2Cl_2 and dried with $MgSO_4$. The crude product was purified by chromatography on silica gel eluting with methanol/CH_2Cl_2 (1:1) to give 0.38 g (0.35 mmol) of red-orange powder with the yield of 87%.

^{1}H NMR (500 MHz, CHD_3) δ, 7.94 (dd, J = 4.5, 1.5 Hz, 3H), 7.48 (d, J = 9.5 Hz, 3H), 7.35 (dd, J = 6.5, 1.5 Hz, 3H), 7.17-7.15 (m, 3H), 6.78 (d, J = 9.5 Hz, 3H), 3.55 (t, J = 6.0 Hz, 12H), 3.18 (t, J = 6.0 Hz, 12H).

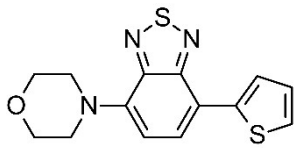
^{13}C NMR (125 MHz, CHD_3) δ, 153.91, 149.95, 143.73, 140.10, 127.86, 127.41, 125.85, 125.14, 120.04, 111.94, 51.49, 46.23.



2 **5**

Scheme S3 a. Synthetic routes to the benzothiadiazole derivative: i) morpholine, sodium *tert*-butoxide, Na(*t*-BuO), $Pd(OAc)_2$, *t*-Bu_3P, toluene.

Scheme S3 b. Synthetic routes to the benzothiadiazole derivative: i) morpholine, sodium *tert*-butoxide, Na(*t*-BuO), $Pd(OAc)_2$, *t*-Bu_3P, toluene.



5

4-(morpholine)-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 5

4-Bromo-7-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole, 260 mg (0.875 mmol), morpholine, 114 mg (1.31 mmol), sodium *tert*-butoxide, 125 mg (1.3 mmol), Palladium acetate, 9.9 mg (0.044 mmol), tri-*tert*-butylphosphine, 26.7 mg (0.132 mmol) were dissolved in 7 ml of anhydrous toluene under Ar. The mixture was heated overnight at 110°C. After cooling to RT 10 ml of distilled water was added and the product was extracted with ethyl acetate. The organic phase was dried over $MgSO_4$. The crude product was purified by chromatography on silica gel eluting with hexanes/ethyl acetate (2:1) to give 0.13 g (0.43 mmol) of red powder with the yield of 49%.

^{1}H NMR (400 MHz, CHD_3) δ, 7.95 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.17 (m 1H), 4.03 (d, *J* = 5.7 Hz, 4H), 3.60 (d, *J* = 5.7 Hz, 4H).

^{13}C NMR (125 MHz, CHD_3) δ, 153.89, 149.72, 142.66, 139.88, 127.94, 127.87, 127.20, 127.16, 125.37, 112.27, 66.93, 50.69.

2. NMR spectra

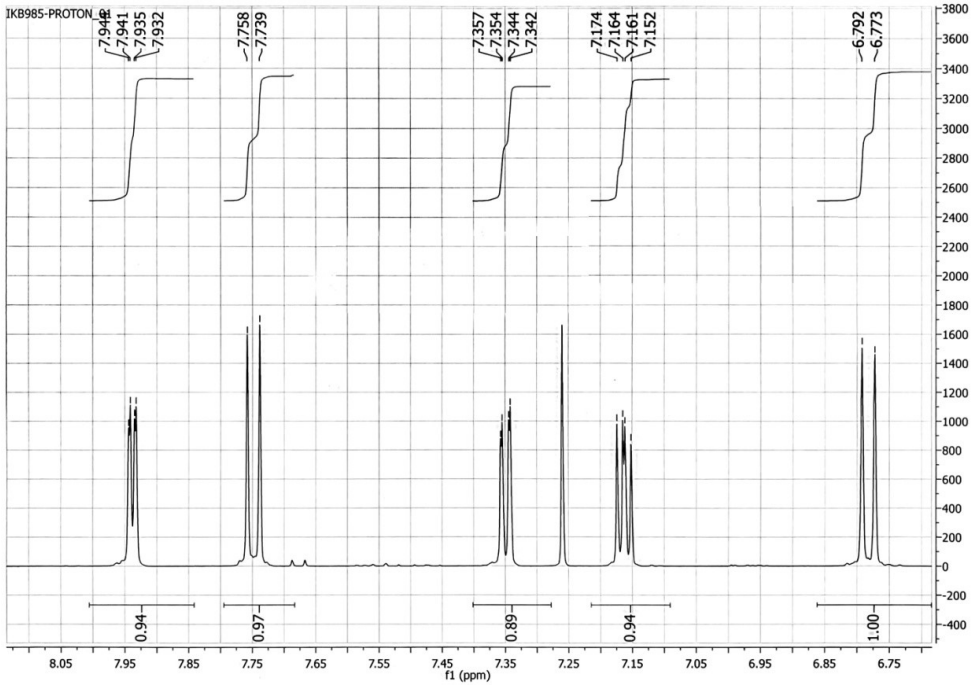


Figure S1a. ^{1}H NMR spectrum of the compound **1** in $CDCl_3$ (8 – 6.5 ppm range).

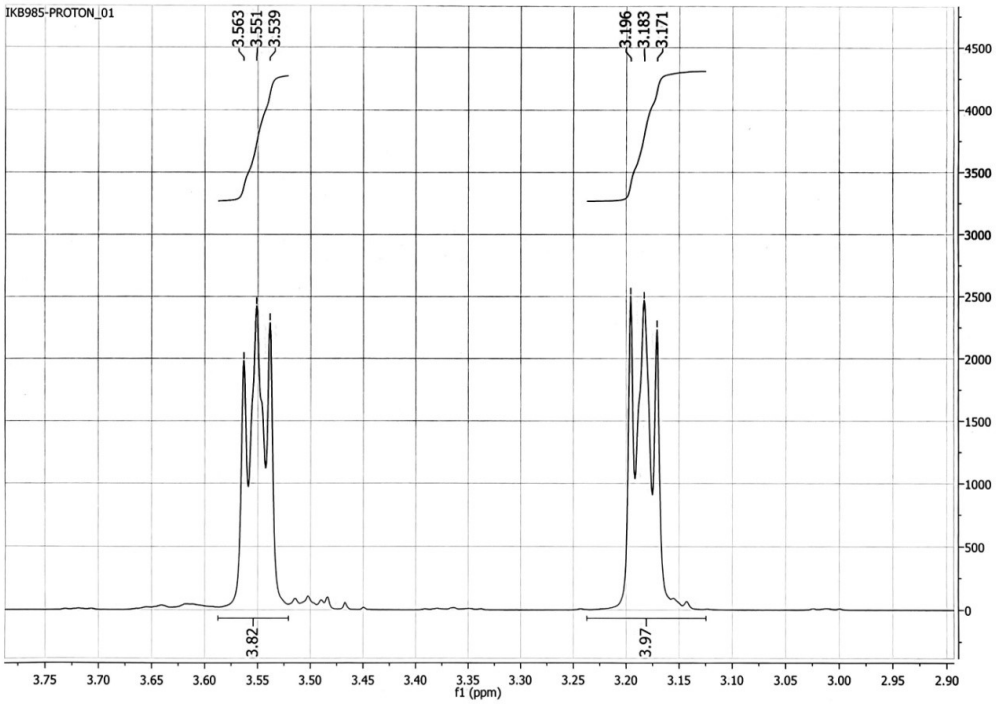


Figure S1b. ^{1}H NMR spectrum of the compound **1** in $CDCl_3$ (4 – 2.9 ppm range)

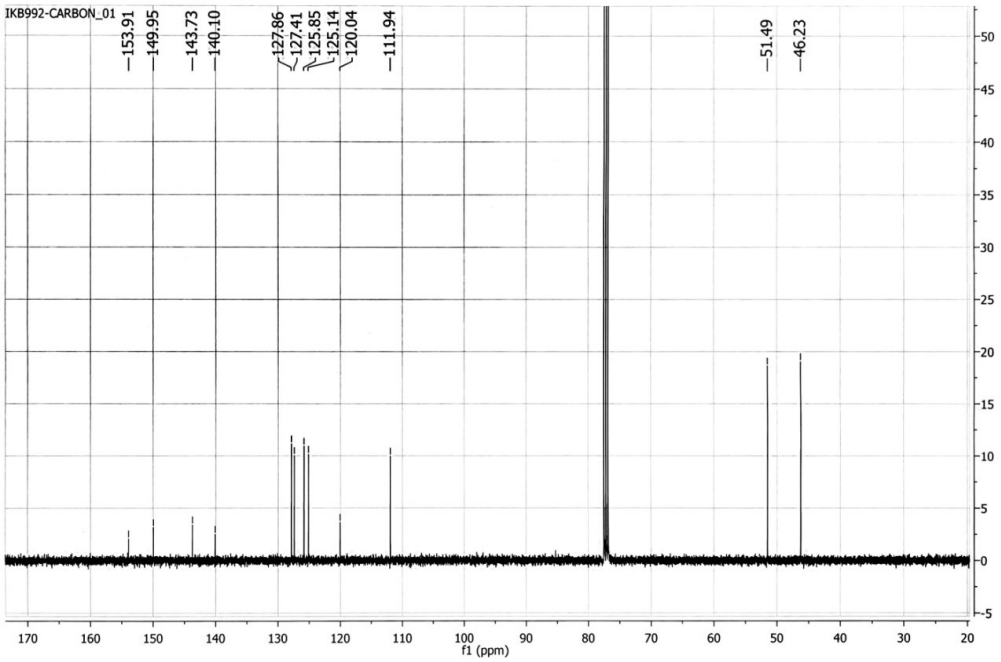


Figure S2. Full range ^{13}C NMR spectrum of the compound **1** in $CDCl_3$.

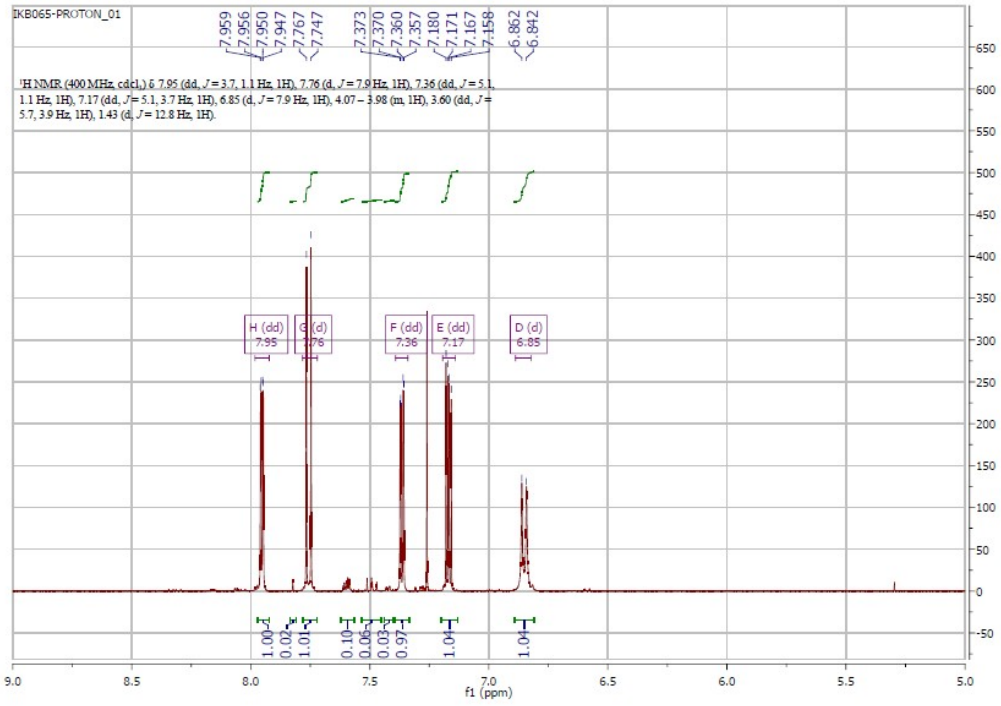


Figure S3a. ^{1}H NMR spectrum of the compound **5** in $CDCl_3$ (8 – 6.5 ppm range).

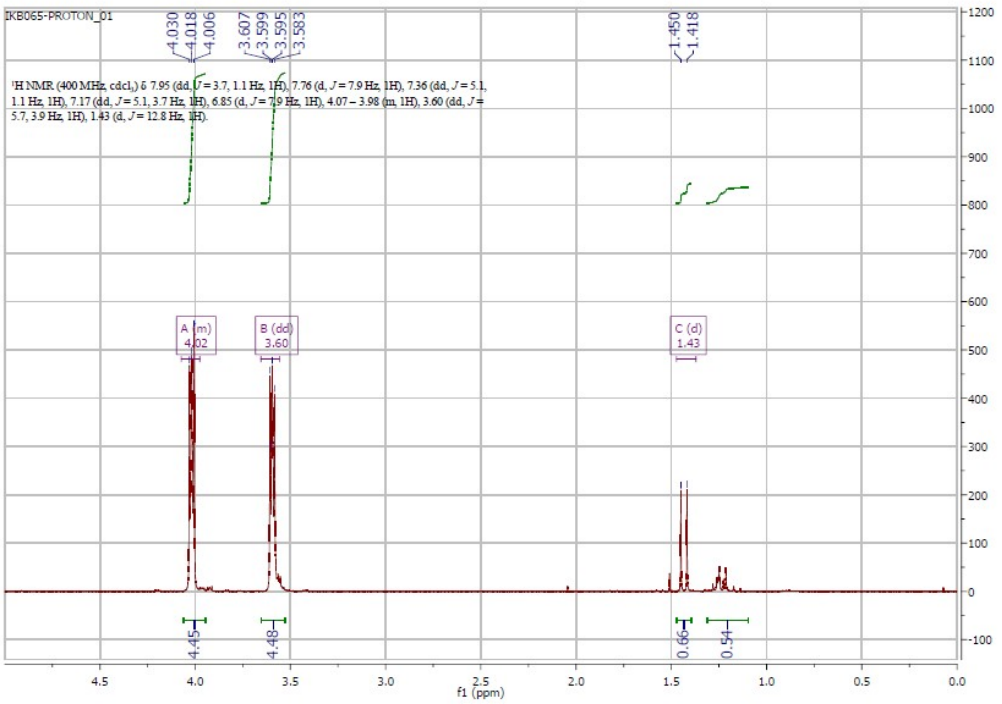


Figure S3b. Full range ^{1}H NMR spectrum of the compound **5** in $CDCl_3$ (4.5 – 0 ppm range) Note: This compound was prepared solely for comparing the spectroscopy and electrochemistry with **1**, the trace impurity at 1.55 being likely a tiny amount of adventitious water).

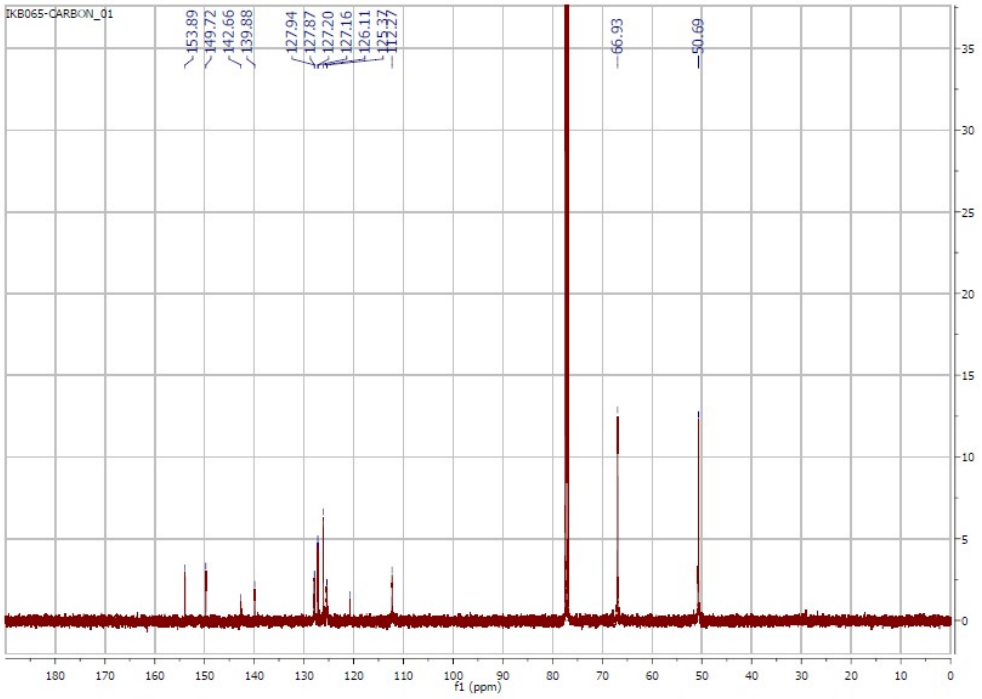
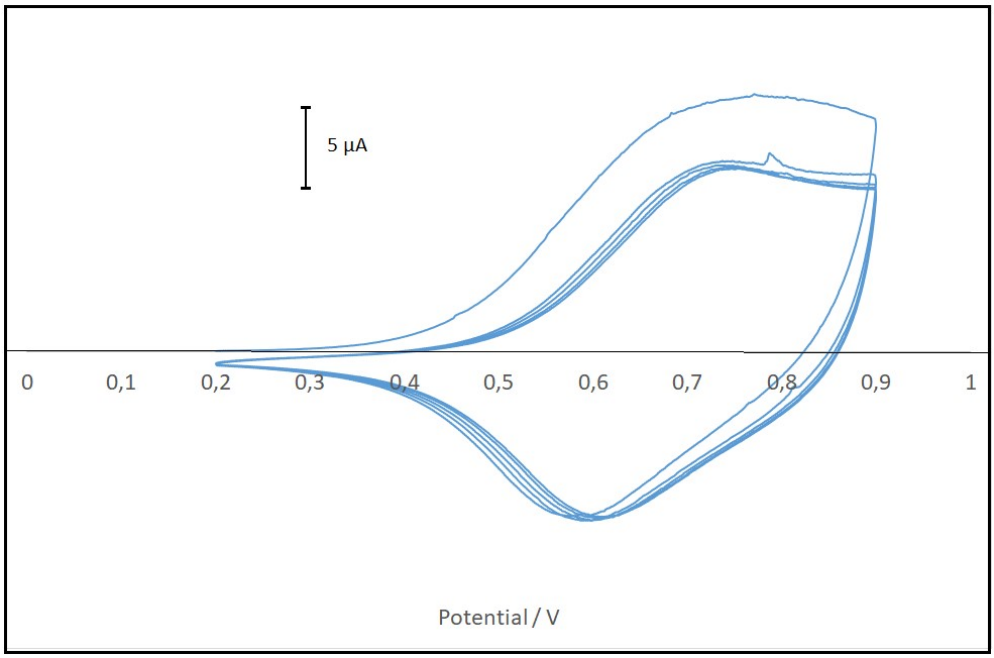


Figure S4. ^{13}C NMR spectrum of the compound **5** in $CDCl_3$.



3. Electrochemical studies

Fig. S5: CV response of Poly(**1**) in a clean electrolyte (DCM/TBAFP).

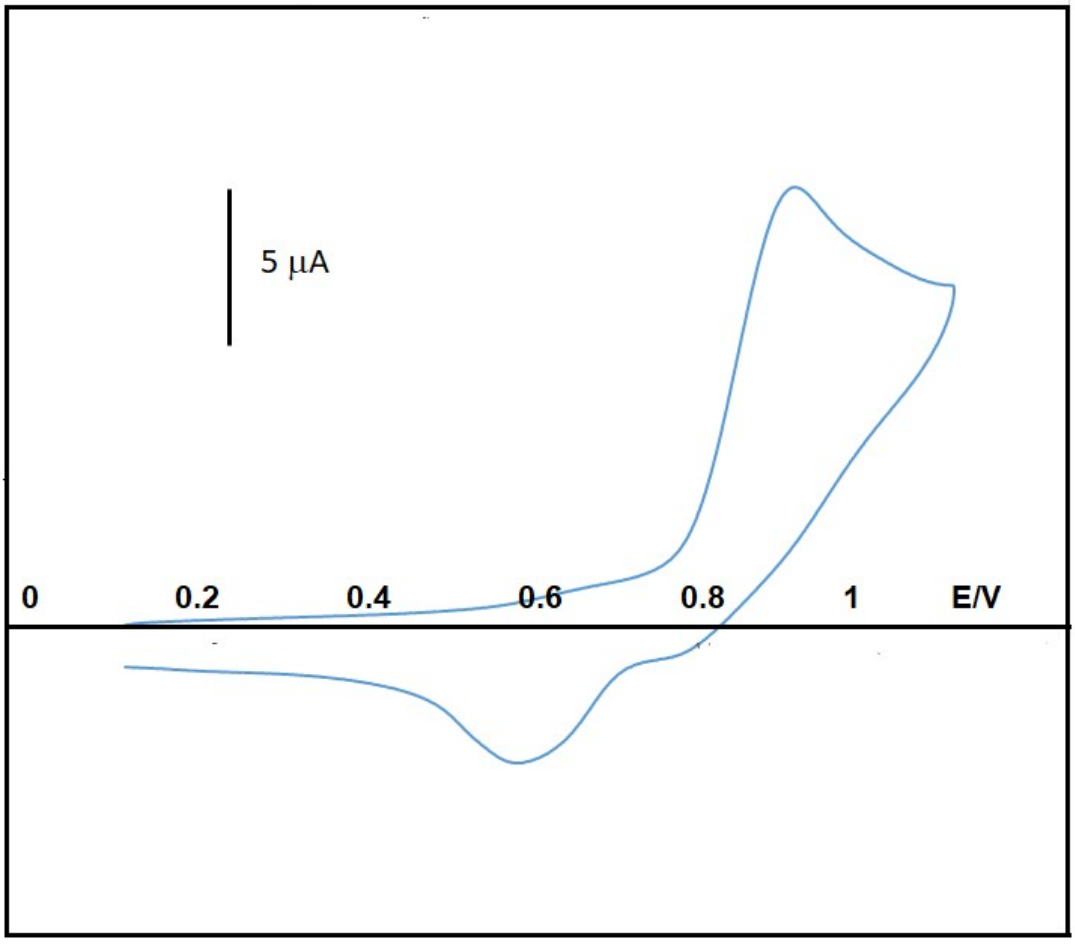


Fig. S6: Electrochemistry of compound **5** (the “branch” of the star molecule **1**) in oxidation.

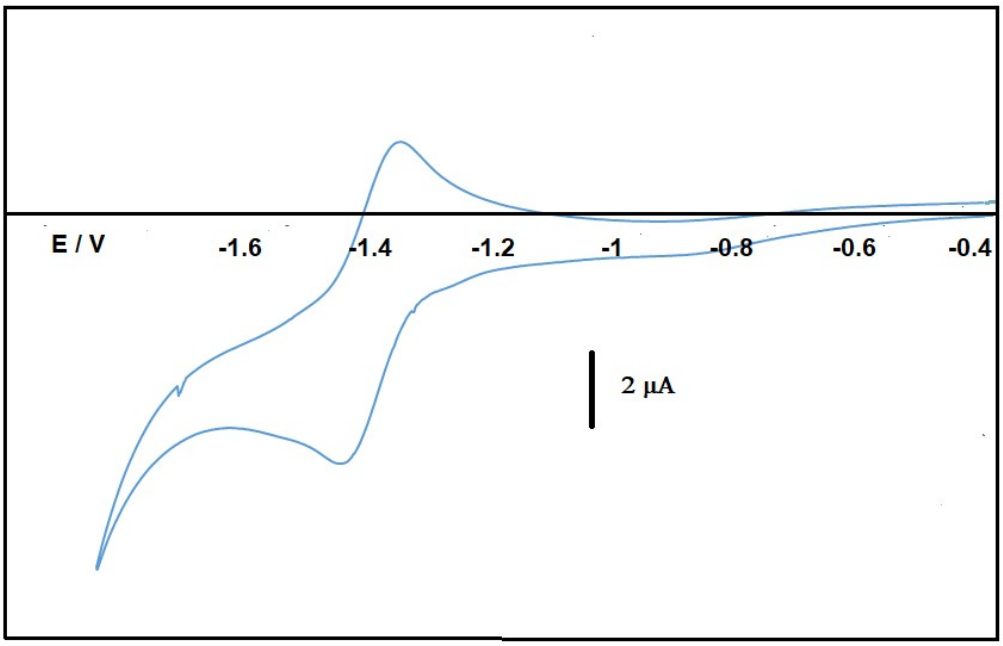


Fig. S7: Electrochemistry of compound **5** (the “branch” of the star molecule **1**) in reduction.

4. Optical studies

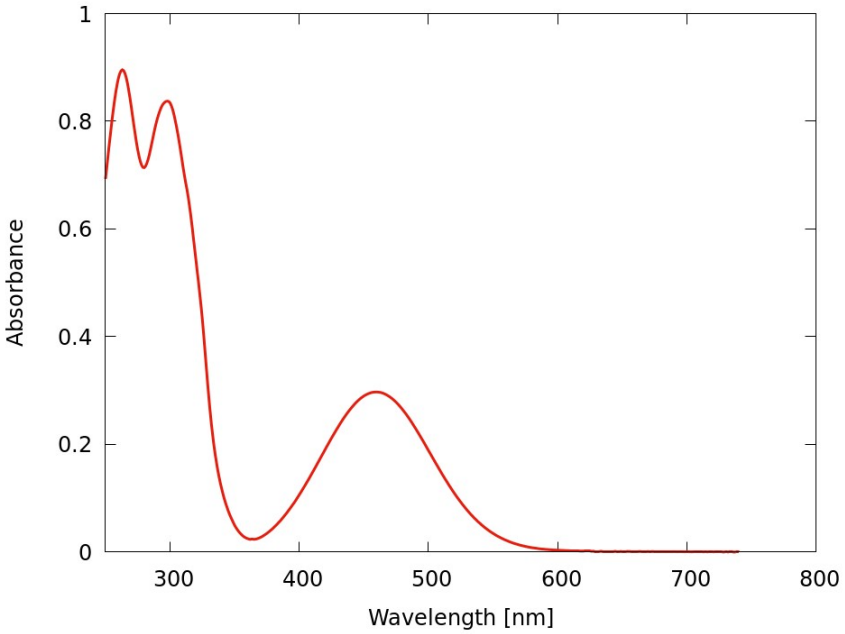


Figure S8: UV-Vis spectrum of monomer **1** in CH_2Cl_2.

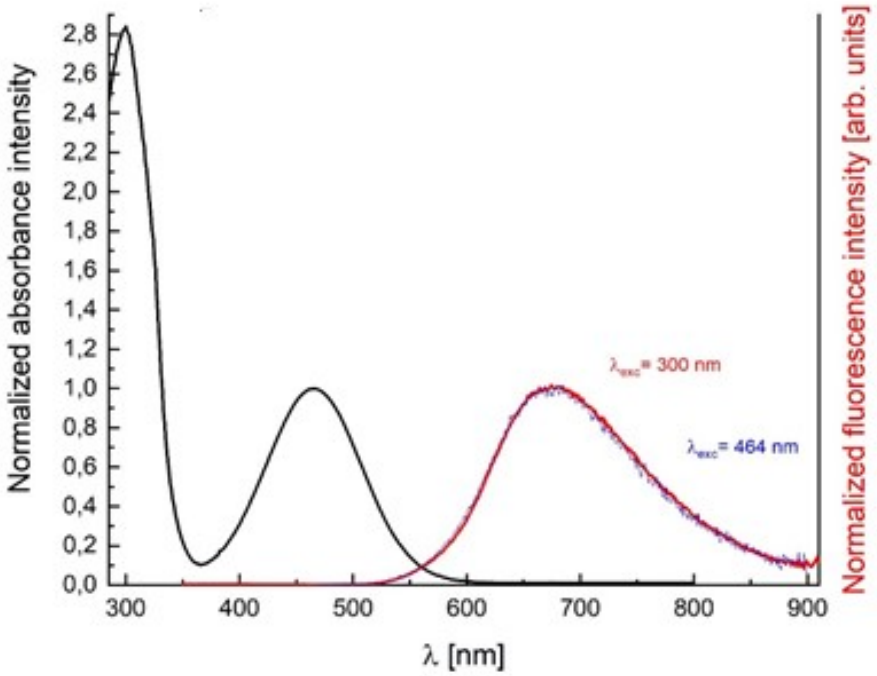


Figure S9: UV-Vis and fluorescence spectra of monomer **1** in toluene.

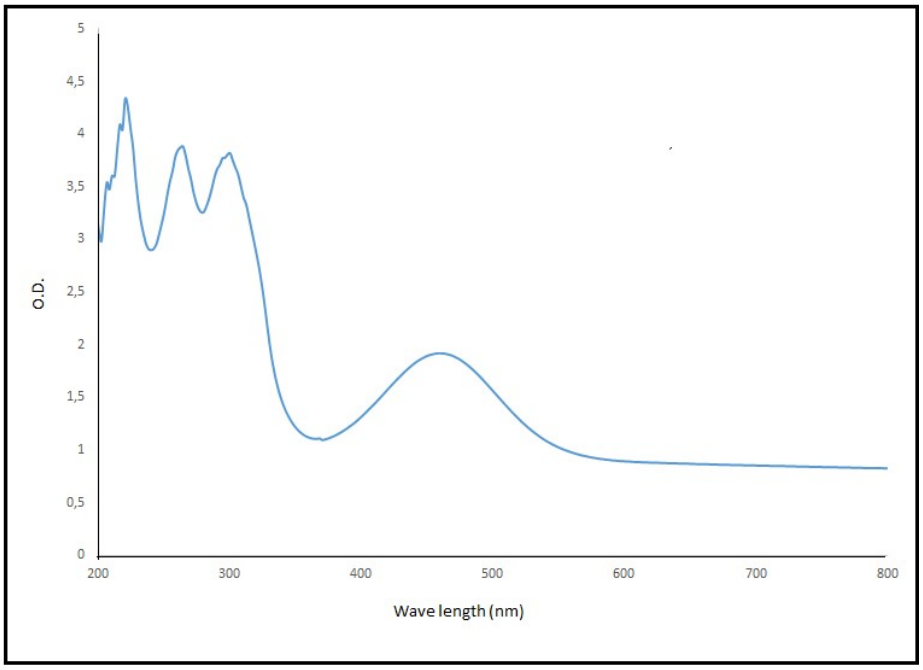


Fig. S10. Absorption spectrum of compound **5** in toluene

5-Porosity checking of an electropolymerized film

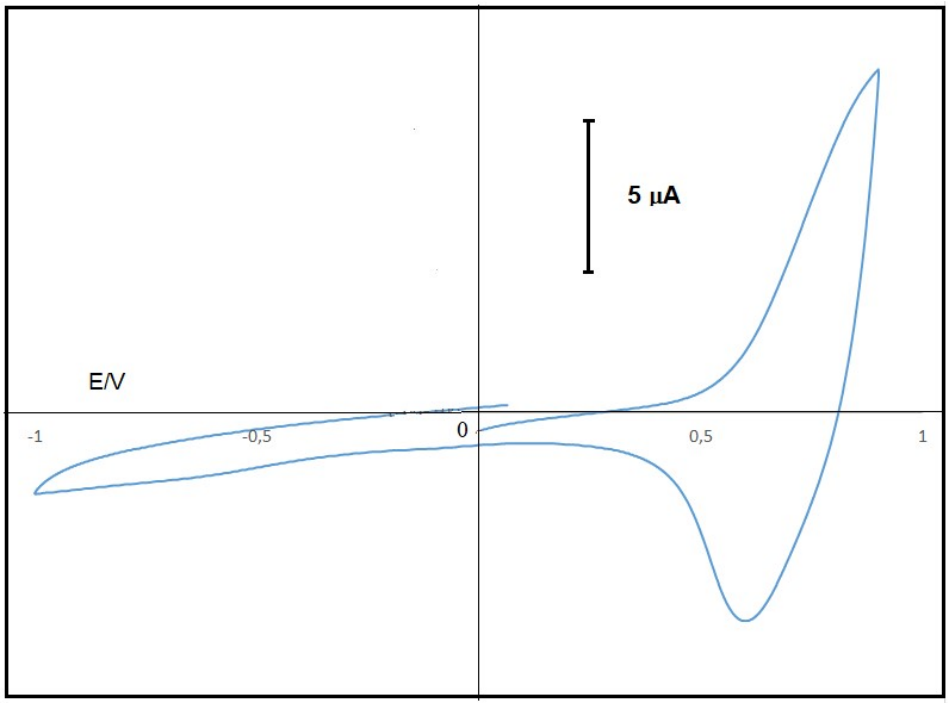


Fig. S11: Electrochemical response on an extended range (down to -1 V) of a poly(1) film, prepared on a 1 mm diameter Pt electrode by 7 sweeps at 100 mVs^{-1} between 0 and +1.2 V from a solution of 1g/l of compound **1**.

Fig. S12: Electrochemical response on an extended range (down to -1 V) of the same poly(1) film than on Fig. S11, in the presence of anthraquinone in solution (about 5 10^{-3} M).

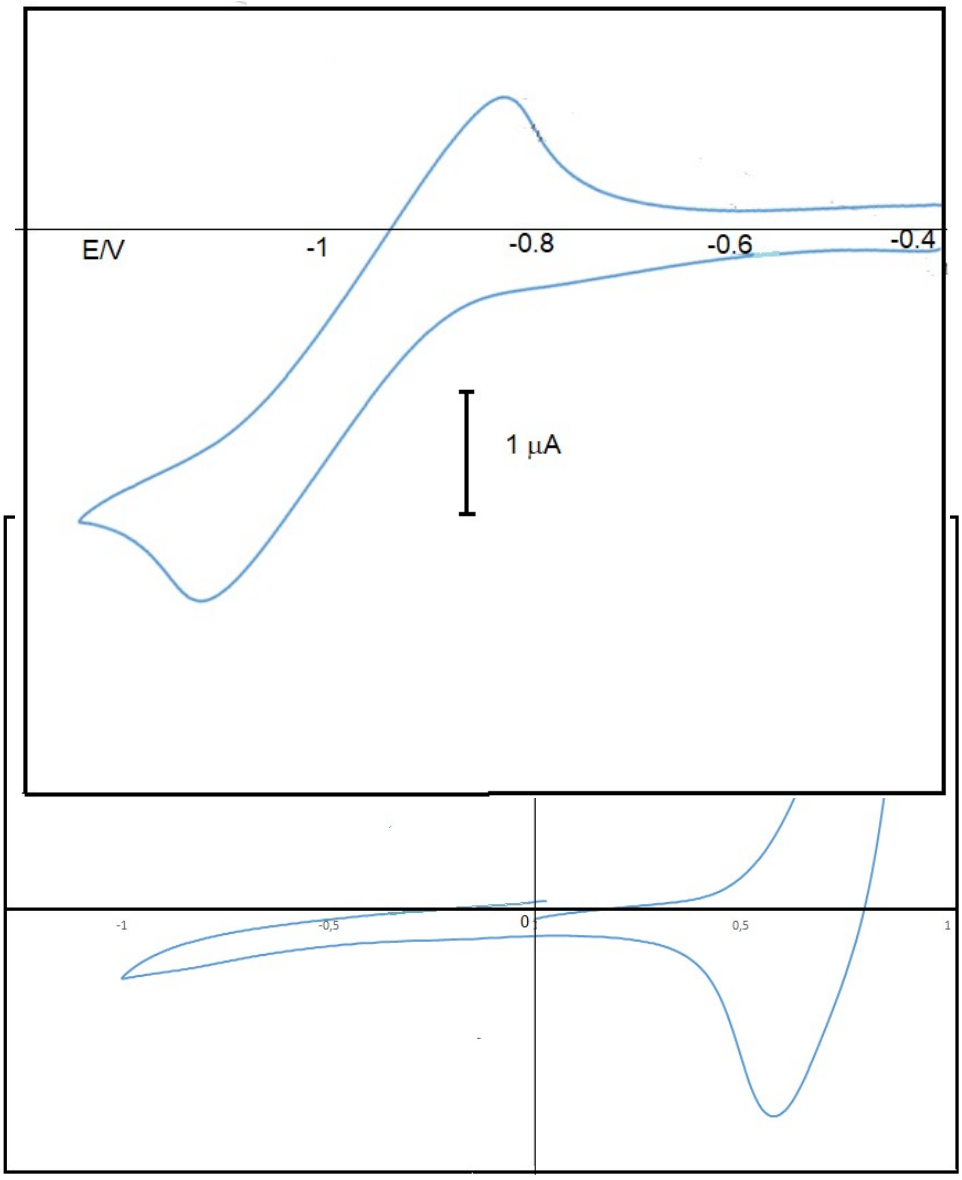


Fig S13: CV of the same anthraquinone solution than Fig. S12, (about 5 10^{-3} M), on the same Pt electrode (1mm diameter) but clean (uncovered with polymer)

1. L. Galmiche, C. Allain, T. Le, R. Guillot and P. Audebert, *Chemical Science*, 2019, **10**, 5513-5518.