

Supporting Information

Poly[di(2-thiophenyl)carborane]s: Conducting Polymers with High Electrochemical and Thermal Resistance

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Experimental

General. All commercially available solvents and starting materials were used without further purification. All reactions were monitored by TLC using 0.25 mm silica gel plates with or without UV indicator (60F-254). Silica gel Sorbent Technologies 32-63 μm was used for flash column chromatography. A solution of 1 g PdCl_2 in 80 mL water and 20 mL 36% HCl solution was used to detect carborane-containing molecules upon heating the TLC plates. ^1H - and ^{13}C -NMR were obtained on a DPX-250 or an ARX-300 Bruker spectrometer; chemical shifts (δ) are given in ppm relative to CDCl_3 (7.26 ppm, ^1H). MALDI-TOF mass spectra were obtained on an Applied Biosystems QSTAR XL.

Synthesis of thiophene 1o: Synthesis of 2, 2'-ethylenethiophene was finished in 71 % yield according to literature.¹

A mixture of decaborane(14) (0.36 g, 3.0 mmol) and Et_2S (1.80 mL, 7.5 mmol) in 15 mL of dry toluene was heated at 40 °C for 2 h under Ar, then the temperature was raised to 60 °C for 3 h. A solution of 2,2'-ethylenethiophene (synthesized in 71% yield as described in the literature¹) (0.38 g, 2.0 mmol) in 10 mL toluene was added to the reaction mixture via syringe, and the final mixture was heated to 80 °C for 2 days, under Ar, until complete disappearance of 2,2'-ethylenethiophene by TLC analysis. The mixture was cooled to room temperature and excess decaborane was destroyed by adding methanol. The solvent was removed under reduced pressure and ethanol was added for co-distillation with Et_2S . The residue was purified by silica gel chromatography using 10% dichloromethane in hexane, giving the target compound 0.21 g in 33 % yield as white power. Crystals of **1o** were grown by slow evaporation of dichloromethane solution. ^1H -NMR (250 MHz, CDCl_3) δ 7.20-7.25 (4H, m), 6.82-6.85 (2H, m), 1.5-3.5 (10H, br). ^{13}C -NMR (63 MHz, CDCl_3) δ 134.9, 133.2, 129.9, 127.5, 81.4. MALDI-TOF $[\text{M}+\text{H}]^+$: 309.41, calcd. for $\text{C}_{10}\text{H}_{16}\text{B}_{10}\text{S}_2$: 309.49.

Synthesis of thiophenes 1m and 1p: A solution of *m*-carborane (1.44 g, 10 mmol) in 30 mL of dry 1,2-dimethoxyethane was added dropwise a 1.60 M solution of *n*-BuLi in *n*-hexane (13.7 mL, 22 mmol) at 0 °C under Ar. This mixture was stirred for 30 min, then dry CuI (4.2 g, 22 mmol) was added in one portion, and the final mixture was stirred at room temperature for 2 h. Pyridine (6 mL), and 2-iodothiophene (4.6 g, 21 mmol) were added in

¹ M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.*, 2002, 4, 3199.

one portion, and the resulting mixture was refluxed for 2 days. After cooling to room temperature, insoluble materials were removed by filtration through celite and the filtrate was washed with 2 N HCl solution, water and brine, dried over MgSO₄, and concentrated under vacuum. The residue was purified by silica gel column chromatography using hexane for elution to give 1.10 g (36 %) of **1m** (third fraction) as a colorless solid. Crystals of **1m** were grown by slow evaporation of a dichloromethane solution. ¹H-NMR (250 MHz, CDCl₃) δ 7.14-7.16 (2H, m), 7.03-7.05-6.85 (2H, m), 6.84-6.88 (2H, m), 1.5-3.5 (10H, br). ¹³C-NMR (63 MHz, CDCl₃) δ 138.6, 127.4, 126.9, 126.2, 72.8. MALDI-TOF [M+H]⁺: 309.56, calcd. for C₁₀H₁₆B₁₀S₂: 309.49.

Thiophene **1p** was prepared from *p*-carborane using a similar methodology as described above for **1m** and isolated in 39% yield. Crystals of **1p** were grown by slow evaporation of a dichloromethane solution. ¹H-NMR (250 MHz, CD₂Cl₂) δ 7.09-7.11 (2H, m), 6.77-6.79 (4H, m), 1.5-3.5 (10H, br). ¹³C-NMR (63 MHz, CD₂Cl₂) δ 127.1, 127.0, 127.4, 125.4, 76.1. MALDI-TOF [M+H]⁺: 309.39, calcd. for C₁₀H₁₆B₁₀S₂: 308.49.

Electrochemical Characterizations.

Tetra-*n*-butylammonium hexafluorophosphate Bu₄NPF₆ was purchased from Fluka (puriss, electrochemical grade). Anhydrous methylene chloride CH₂Cl₂ (less than 50 ppm water from Merck) was used as received. The electrolytic medium was dried *in situ* over activated, neutral alumina from Aldrich. Alumina was previously activated at 450 C under vacuum for several hours.

Linear potential sweep cyclic voltammetry experiments were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System GPES software (version 4.5 for Windows). The working electrode was a 1 mm-diameter platinum disk (area: 0.8 mm²) and the counter electrode was a glassy carbon rod. Potentials were relative to the system 10⁻² M Ag⁺ | Ag in acetonitrile and the ferrocene/ferrocenium couple in CH₂Cl₂ + 0.2 M Bu₄NPF₆ was observed at $E^{\circ\prime} = 0.19$ V vs this reference. Solution resistance was compensated by positive feedback. All electrochemical measurements were carried out at room temperature (20 ± 2 °C) and under a constant flow of argon.

UV-visible spectroelectrochemistry.

UV-visible absorption spectra were recorded on a Shimadzu Multispec-1501 spectrophotometer (190-1100 nm scan range) interfaced with a microcomputer for data acquisition and quartz SUPRASIL[®] cells from Hellma (1 cm pathlength) were used. The polymer films were grown on an indium tin oxide (ITO) coated glass slide electrode.

***In situ* conductivity measurements**

The polymer films were electrogenerated on array of platinum interdigitated microelectrodes (IMEs). The device used in this study was purchased from BAS Inc. and consisted of two buses of 65 10 μm wide platinum lines separated by 5 μm intervals (model 2048). The length is 2 mm.

The conductivities of the polymers σ were determined using a procedure similar to that described by Simone and Swager² (eq 1).

² D. L. Simone, T. M. Swager, *J. Am. Chem. Soc.*, 2000, **122**, 9300.

$$\sigma = \frac{I_d}{V_d} \times \frac{d}{NTL} \quad (1)$$

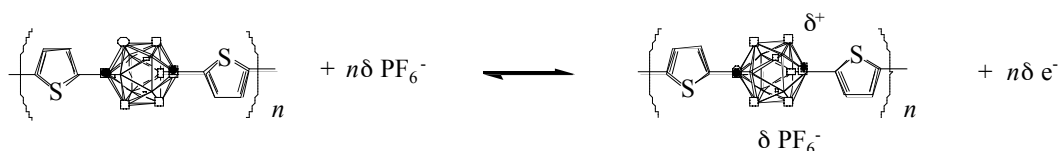
where I_d is the measured drain current, V_d the applied offset potential (0.05 V), d the interdigit spacing (5×10^{-4} cm), N the number of interdigit gaps ($(2 \times 65) - 1 = 129$), T the film thickness (cm) and L the length of the electrode (0.2 cm).

T is given by eq 2

$$T = \frac{m_{pol}}{\rho A} \quad (2)$$

where m_{pol} is the electrodeposited polymer mass, ρ is the density of the polymer film (g cm^{-3}) and A the area of the electrode (cm^2).

m_{pol} can be estimated by considering the reversible p -doping electrochemical reaction of the polymer (for example for poly(**1p**)):



So, the corresponding anodic charge Q_a under the polymer voltammetric response is equal to:

$$Q_a = n\delta F \quad (3)$$

where n is the number of electropolymerized monomer units, δ is the doping level of the polymer and F is Faraday's constant (96500 C mol^{-1}).

It can thus be deduced that

$$m_{pol} = n \left[M_{mono} - 2 + \delta M_{PF_6^-} \right] = \frac{Q_a}{\delta F} \left[M_{mono} - 2 + \delta M_{PF_6^-} \right] \quad (4)$$

where M_{mono} is the molar mass of the monomer (g mol^{-1}) and $M_{\text{PF}_6^-}$ is the molar mass of PF_6^- used as the electrolyte anion.

From eq. 2 and 4, T is given by

$$T = \frac{Q_a}{\delta F \rho A} \left[M_{\text{mono}} - 2 + \delta M_{\text{PF}_6^-} \right] \quad (5)$$

For poly(**1o**)

$Q_a = 4.15 \times 10^{-4} \text{ C}$ (Figure S2C), $\delta = 0.5$, $\rho = 1.305 \text{ g cm}^{-3}$ obtained from the X-ray crystal structure of **1o**, $A = 6 \times 10^{-2} \text{ cm}^2$, $M_{\text{mono}} = 308.47 \text{ g mol}^{-1}$ and $M_{\text{PF}_6^-} = 145 \text{ g mol}^{-1}$.

$T = 4.1 \times 10^{-5} \text{ cm}$ and $\sigma = 9.31 \times I_d$. The maximum conductivity $\sigma_{\text{max}} = 9.31 \times I_{d_{\text{max}}} = 1.05 \times 10^{-3} \text{ S cm}^{-1}$ considering the $I_{d_{\text{max}}}$ value determined from Figure S2C.

For poly(**1m**)

$Q_a = 2.48 \times 10^{-4} \text{ C}$ (Figure S2B), $\delta = 0.07$, $\rho = 1.311 \text{ g cm}^{-3}$ obtained from the X-ray crystal structure of **1m**, $A = 6 \times 10^{-2} \text{ cm}^2$, $M_{\text{mono}} = 308.47 \text{ g mol}^{-1}$ and $M_{\text{PF}_6^-} = 145 \text{ g mol}^{-1}$.

$T = 1.5 \times 10^{-4} \text{ cm}$ and $\sigma = 2.62 \times I_d$. The maximum conductivity $\sigma_{\text{max}} = 2.62 \times I_{d_{\text{max}}} = 6.3 \times 10^{-4} \text{ S cm}^{-1}$ considering the $I_{d_{\text{max}}}$ value determined from Figure S2B.

For poly(**1p**)

$Q_a = 1.40 \times 10^{-4} \text{ C}$ (Figure S2A), $\delta = 0.06$, $\rho = 1.309 \text{ g cm}^{-3}$ obtained from the X-ray crystal structure of **1p**, $A = 6 \times 10^{-2} \text{ cm}^2$, $M_{\text{mono}} = 308.47 \text{ g mol}^{-1}$ and $M_{\text{PF}_6^-} = 145 \text{ g mol}^{-1}$.

$T = 9.7 \times 10^{-5} \text{ cm}$ and $\sigma = 3.99 \times I_d$. The maximum conductivity $\sigma_{\text{max}} = 3.99 \times I_{d_{\text{max}}} = 6.4 \times 10^{-4} \text{ S cm}^{-1}$ considering the $I_{d_{\text{max}}}$ value determined from Figure S2A.

In order to correct the conductivity to a known standard, a poly(3-methylthiophene) film (PMeTh) was electrodeposited on the 5 μm interdigitated microelectrodes and studied under the same conditions as the carborane-substituted polymers.³

For poly(MeTh)

$Q_a = 6 \times 10^{-4} \text{ C}$, $\delta = 0.25$, $\rho = 1.46 \text{ g cm}^{-3}$, $A = 6 \times 10^{-2} \text{ cm}^2$, $M_{\text{mono}} = 96 \text{ g mol}^{-1}$ and $M_{\text{PF}_6^-} = 145 \text{ g mol}^{-1}$.

$T = 3.7 \times 10^{-5} \text{ cm}$ and $\sigma = 10.48 \times I_d$. $I_{d_{\text{max}}} = 3.05 \times 10^{-4} \text{ A}$ and consequently $\sigma_{\text{max}} = 3.2 \times 10^{-3} \text{ S cm}^{-1}$.

So, the relation used to correct the poly(**1o**), poly(**1m**) and poly(**1p**) conductivities follows as:

$$\frac{\sigma_{\text{1o,1m,1p}}}{\sigma_{\text{PMeTh}}} \times 60 = \sigma_{\text{1o,1m,1p}}^{\text{corr}} \quad (6)$$

The value of 60 S cm^{-1} was obtained for poly(3-methylthiophene) by Zotti and co-workers.⁴

Thus, the corrected maximum conductivity values for poly(**1o**), poly(**1m**) and poly(**1p**) are:

$$\sigma_{\text{1o,max}}^{\text{corr}} = 19.7 \text{ S cm}^{-1}$$

$$\sigma_{\text{1m,max}}^{\text{corr}} = 11.8 \text{ S cm}^{-1}$$

$$\sigma_{\text{1p,max}}^{\text{corr}} = 12 \text{ S cm}^{-1}$$

³ R. P. Kingsborough, T. M. Swager, *Adv. Mater.*, 1998, **10**, 1100.

⁴ G. Zotti, G. Schiavon, *Synth. Met.*, 1990, **39**, 183. G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.*, 1989, **32**, 209.

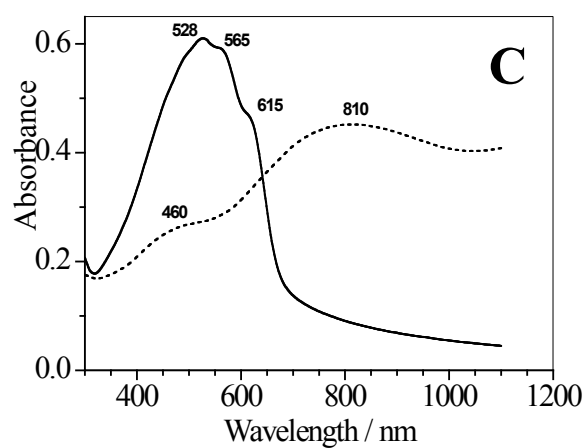
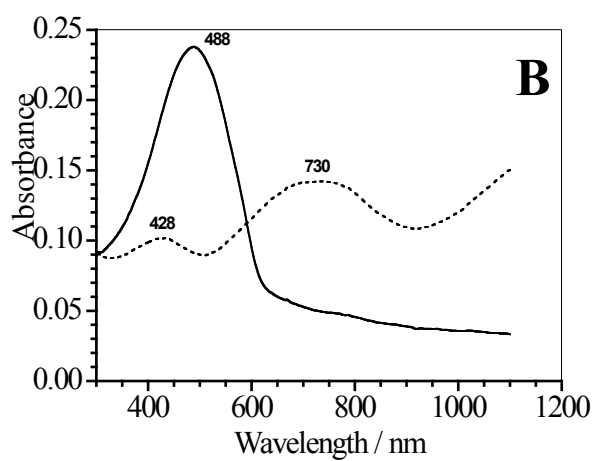
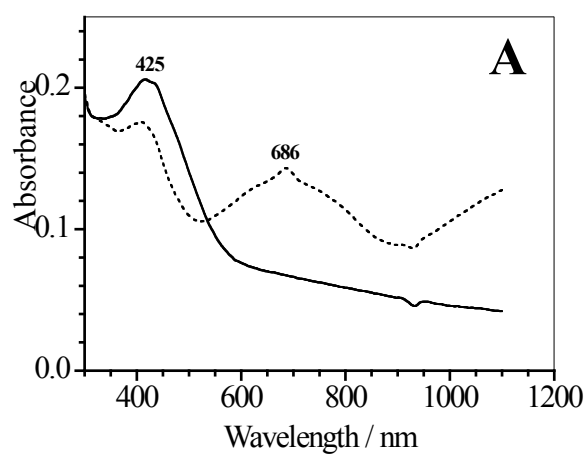


Figure S1

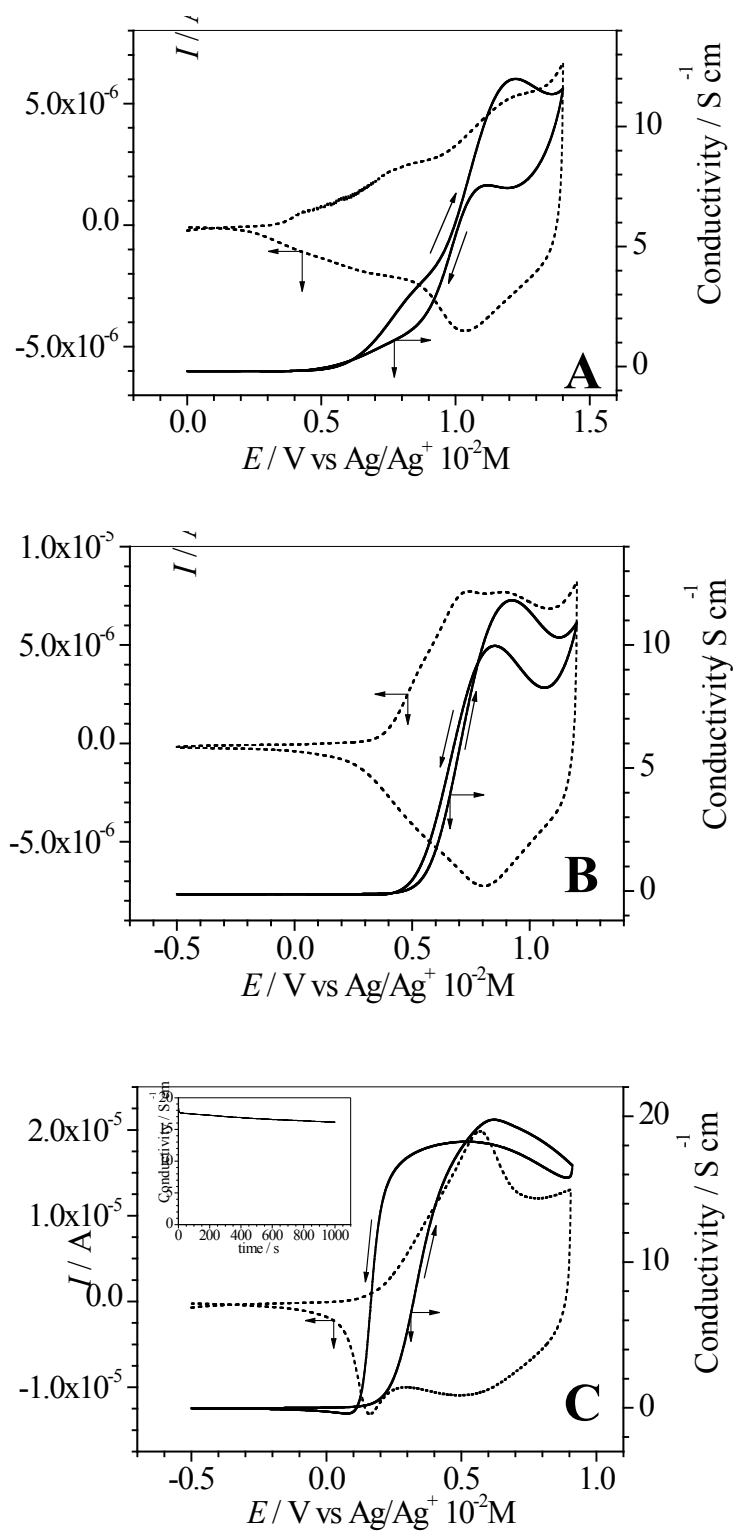


Figure S2