(Photo)electrocatalysis of molecular oxygen reduction by S-doped graphene decorated with a star-shaped oligothiophene

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Figure S1. $^1$H and $^{13}$C NMR spectra of compound 2 obtained in CDCl$_3$. 
Figure S2. $^1$H NMR spectrum of compound 3 obtained in CDCl$_3$. 

![Figure S2. $^1$H NMR spectrum of compound 3 obtained in CDCl$_3$.](image)
Figure S3. $^1$H NMR spectrum of compound 4 obtained in CDCl$_3$. 
Figure S4. $^1$H NMR spectrum of star-shaped compound 5 obtained in CDCl$_3$. 

[Image of the NMR spectrum]
Figure S5. $^{13}$C NMR spectrum of compound 5 obtained in CDCl$_3$. 
Figure S6. $^1$H and $^{13}$C NMR spectra of star-shaped oligothiophene 1 obtained in CDCl$_3$. 
Figure S7. MALDI-TOF mass spectrum of oligothiophene I.
Figure S8. ATR-IR spectra of (a) GO (grey) and SG (black), and (b) 1 (orange) and 1/SG (red).
Figure S9. TGA graphs of (a) GO (grey), (b) SG (black) and (c) 1/SG (red). Dotted lines represent the first derivative of mass/temperature.
**Figure S10.** (a) UV-Vis and (b) fluorescence emission ($\lambda_{\text{exc}}$ 441 nm) spectra of 1 (orange) and 1/SG (red) recorded in benzonitrile. (c, d) UV-Vis and fluorescence emission ($\lambda_{\text{exc}}$ 441 nm) spectra of reference 1/GO (blue). The insets of (b, d) represent the magnified fluorescence emission intensity of the ensembles.
Figure S11. CV of 1 (magenta), 1/SG (red) and 1/GO (blue) in N$_2$-saturated 0.1 M TBAPF$_6$ in benzonitrile.
Figure S12. CV curves for GO, SG, 1, 1/GO, 1/SG and commercial Pt/C in N₂ (black) and O₂ (red) saturated aqueous 0.1M KOH electrolyte.
Figure S13. LSV curves for GO, SG, 1, 1/GO, 1/SG and commercial Pt/C in N₂ (black) and O₂ (red) saturated aqueous 0.1M KOH electrolyte.
Table S1. Onset ($E_{on}$) and peak ($E_p$) reduction potentials of the electrocatalytic O$_2$ reduction derived from the CV and LSV curves recorded in O$_2$ saturated aqueous 0.1M KOH electrolyte and at a scan rate of 50 mV/s. All potentials are versus the Hg/HgO electrode, at 25°C.

| Material | ORR $E_{on}$ (CV) | ORR $E_p$ (CV) | ORR $E_{on}$ (LSV) | ORR $E_p$ (LSV) |
|----------|------------------|----------------|--------------------|-----------------|
| 1        | -194mV           | -391mV         | -172mV             | -386mV          |
| GO       | -181mV           | -390mV         | -172mV             | -398mV          |
| SG       | -133mV           | -377mV         | -132mV             | -383mV          |
| 1/GO     | -179mV           | -345mV         | -184mV             | -336mV          |
| 1/SG     | -129mV           | -320mV         | -120mV             | -327mV          |
| Pt/C (5% Pt) | -76mV     | -315mV         | -78mV              | -323mV          |
**Figure S14.** ORR polarization curves at 1600 rpm for SG (left panel) and 1/SG (right panel) recorded in O$_2$ saturated aqueous 0.1M KOH electrolyte vs Hg/HgO.
Figure S15. Capacitance curves for SG (up left panel), 1/SG (up right panel) and GO (bottom panel) recorded in N$_2$ saturated aqueous 0.1M KOH electrolyte at different scan rates (0.1, 0.2, 0.5 and 1.0 V/s) vs Hg/HgO. The capacitance was calculated to be $0.8 \times 10^{-4}$ F for GO, $1.4 \times 10^{-4}$ F for SG and $9.5 \times 10^{-4}$ F for $1/SG$ ensembles, by integrating the average graph-area derived by the voltammographs in different scan rates.
Figure S16. Tauc plots of 1/SG (red) and 1 (orange) for calculating the band-gap.