Mechanically interlocked carbon nanotubes as a stable electrocatalytic platform for oxygen reduction

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Supporting information

1. Synthesis and characterization of 2,6-bis(oct-7-en-1-yloxy)anthracene-9,10-dione (C8-AQ-C8):

![Synthesis reaction scheme of mac-AQ.](image)

Supporting Information Figure S1: Synthesis reaction scheme of mac-AQ.

Anthraflavic Acid (0.5 g, 2.08 mmol, 1 eq) was dispersed with sonication in dry dimethylformamide (DMF) (21 mL, 0.1 M). Then, dry carbonate potassium (K₂CO₃) (0.86 g, 6.24 mmol, 3 eq), 8-Bromo-1-octene (0.7 mL, 4.16 mmol, 2 eq) and catalytic amount of sodium iodide (NaI) were added and the mixture was refluxed overnight under N₂ atmosphere. The next day, the crude of the reaction was allowed to rt and was poured into ice-cold 1 M HCl and the precipitate was filtered. The solid was redissolved in dichloromethane (DCM) and washed with water twice times. The organic phase was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. Finally, the crude was purified by flash chromatography (DCM) to obtain the product in 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 2.6 Hz, 2H), 7.21 (dd, J = 8.7, 2.7 Hz, 2H), 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H), 5.07 – 4.90 (m, 4H), 4.14 (t, J = 6.5 Hz, 4H), 2.07 (q, J = 6.9 Hz, 4H), 5-1
1.90 – 1.78 (m, 4H), 1.55 – 1.32 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 182.5, 164.2, 139.1, 136.0, 129.8, 127.1, 121.1, 114.5, 110.7, 68.9, 33.8, 29.1, 28.9, 26.0. MALDI calculated for C$_{30}$H$_{36}$NaO$_4$ [M+Na]+$^+$: 483.2506; found 483.2522.

Figure S 2: $^1$H-NMR spectrum of $\text{C}_8\text{A}_4\text{C}_8$ (CDCl$_3$, 298 K).
**Figure S3:** $^{13}$C-NMR spectrum of $\text{Cs-AQ-Cs}$ (CDCl$_3$, 298 K).

**Figure S4:** MALDI spectra of $\text{Cs-AQ-Cs}$. 
2. **Synthesis and characterization of MINT**

The (6,5)-enriched SWCNTs purchased from Sigma Aldrich were purified previously. 100 mg of SWCNTs were suspended in 70 mL of 35 % HCl, and sonicated for 10 min. The mixture was poured in 200 mL of MQ water and filtered through a polycarbonate membrane of 0.2 µm pore size. The solid was washed with water to neutral pH and then dried in an oven at 350 °C for 30 min. Pristine plasma-purified SWCNTs were used without previous purification.

The pristine (10 mg) were suspended in 10 mL of tetrachloroethane through sonication (10 min) and mixed with 0.01 mmol of linear bisalkene U-shaped mac-AQ, and Grubbs’ second-generation catalyst at room temperature for 72 h under N₂ atmosphere. After this time, the suspension was filtered through a PTFE membrane of 0.2 µm pore size and the solid washed profusely with DCM. The solid was re-suspended in 10 mL of DCM through sonication for 10 min and filtered through a PTFE membrane of 0.2 µm pore size again. This washing procedure was repeated three times. The sample obtained was denoted as AQ-MINT. The synthesis of the supramolecular complex was denoted as AQ@SW-CNT and was performed by the direct mixing of the adequate amounts of 6,5-SW-CNT and the corresponding macrocycle without catalyst to achieve the same functionalization loading of organic material over the nanotube compared to their respective MINT sample. Two samples with different loading of the macrocycle have been synthesized.

![Figure S5: TGA plots (ramp of 10 °C min⁻¹ under air from 100 to 900 °C) of SW-CNT (black), AQ-MINT (green), AQ@SW-CNT (red), AQ-MINT with low loading (green dashed line) and AQ@SW-CNT with low loading (red dashed line).](image_url)
3. **Determination of hydrogen hydroxide (H$_2$O$_2$) production**

The detection of H$_2$O$_2$ was done accordingly to recent literature reports$^{1,2}$. Mixtures in a 1:1 ratio of 4 mM $p$-nitrophenyl boronic acid ($p$NBA, Sigma Aldrich, >95%) in DMSO (VWR) and a 150 mM Na$_2$CO$_3$/NaHCO$_3$ (Fluka, >99.5%; Sigma Aldrich, 99.7-100.3%) buffer solution pH 9 were mixed with the sample. After 36 min incubation at room temperature under dark condition, the absorbance at 411 nm was recorded using a Thermo Fischer Multiskan Go Microplate Spectrophotometer. The amount of H$_2$O$_2$ was determined using a calibration curve made from H$_2$O$_2$ standard solution (Merck, 30%) (Figure S7). The measured absorbance was subtracted with the absorbance of blank sample (incubation of deionized water with chromophore). The subtracted value, Δabsorbance, was used for the quantification.

**Figure S7**: a) Absorption spectra of standard H$_2$O$_2$ solution at various concentrations and b) calibration curves of the H$_2$O$_2$ quantification including the formula.
4. **Spectroscopical characterization of MINT**

![UV-Vis spectra](image1)

*Figure S8: UV-Vis spectra (D$_2$O / SDS (1 wt. %) at room temperature) of SW-CNT (black), AQ-MINT (green) and AQ@SW-CNT (red).*

![Raman spectroscopy](image2)

*Figure S9: Raman spectroscopy. Average (N = 25). Raman spectra of SWNT (black), AQ-MINT (green) and AQ@SWCNT (red).*
Figure S 10: PLE map of a) (6,5)-SWNT, b) AQ-MINT and c) AQ@SWCNT.
5. **Homogeneous CV investigations**

As mentioned in the article, an octyloxy-AQ derivative was chosen to compare it to the AQ-MINT electrochemical experiments. In the following Figure S11 the CV of 2.5 mM AQ is compared with the CV of 1mM octyloxy-AQ in 0.1 M TBAPF₆ in MeCN solution.

The CV curves shown in Figure S11 show, that the alkoxy substituents shift the first reduction wave cathodically by 130 mV whereas the second reduction wave is nearly unaffected.

6. **CV study of SW-CNT**

Complementary to Figure 2a and 4a in the main text, the following Figure S 12 shows a the CV curve of SW-CNT sample in 0.1M Na₂SO₄ under N₂ and O₂:

As can be seen from Figure S 12, also pristine SWCNT show a reductive step upon O₂ addition, which is already a hint for oxygen reduction.
7. **Cycle stability – non-aqueous conditions**

In the following Figure S13, the cycle stability of AQ-MINT in the organic conditions of 0.1M TBAPF₆ in MeCN is shown.

![CV curve of AQ-MINT in MeCN containing 0.1 M TBAPF₆ upon 50 sweeping cycles.](image)

*Figure S13: CV curve of AQ-MINT in MeCN containing 0.1 M TBAPF₆ upon 50 sweeping cycles.*

In general, a similar behaviour like in aqueous solution (see Figure 3) was observed. The lower \( j_P \) can be explained by the fact that, in organic solvents in this potential range only a 1-electron reduction process is taking place.

8. **Kinetic investigations**

Regarding the cycle stability test, AQ-MINT was reasonably stable, while AQ@SWCNT suffered from severe loss of \( j_P \) over 50 cycles. Nevertheless, kinetic studies of both AQ-MINT and AQ@SWCNT were performed by CV with varied scan rate (Figure 3a and b). Due to the fact that especially the AQ@SWCNT sample with the 15% loading (and also the AQ-MINT sample with 13%) suffered from significant loss of \( j_P \) during the kinetic studies, from continuous delamination over the experiment time, no further kinetic data could be extracted thereof. The investigation of samples with lower loadings proved sufficient stability, therefore the mentioned kinetic studies and analysis could be determined.

In the following Figure S14 all the CV’s of AQ-MINT (4% m/m) as well as AQ@SWCNT (6% m/m) on GC electrodes in 0.1M Na₂SO₄ in H₂O are shown.
The curves shown in Figure S14 were analysed concerning peak currents $j_p$’s and the resulting plots as are shown as insets. In both cases, a linear correlation of the $j_p$ with the scan rate ($v$) was observed. Also, the integrated peak charges were calculated where in case of both AQ-MINT batches quite stable values of, in case of both AQ@SWCNT due to degradation over the cycles only decreasing values were observed.

9. Further investigations on $O_2$ reduction with AQ-MINT and SWCNT

In order to prove, that the AQ-MINT is stable on the electrode over the time of the electrolysis, in the following Figure S15, CV curves before and after were compared:

From the CV in Figure S15 it can be stated, that the AQ-MINT is very stable under the conditions of electrolysis and shows just a slight decrease in $j_p$ of 6.3%.

All details on the kinetic parameters like the total moles of $H_2O_2$ produced, the rate and the Faradaic efficiency (FE) of oxygen reduction electrolysis at different conditions are displayed in the following Table S1:
Table S1: Electrocatalytic activities of SW-CNT, AQ-MINT and AQ@SWCNT in 0.1M Na₂SO₄ and 0.1 M NaOH for 8-h electrolysis at -330mV vs. SHE at room temperature. 0.1 mg of the compound was drop-casted in each case.

### SWCNT

| Time / h | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M Na₂SO₄ | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M NaOH |
|----------|-------------------|---------------------------------------------|----------|-----------------|-------------------|---------------------------------------------|----------|--------------|
| Initial  | 0.94              | n. d.                                       | n. d.    | 0.16            | n. d.              | n. d.                                       | n. d.    |              |
| 1        | 0.85              | n. d.                                       | n. d.    | 0.29            | 1.28              | 14.7                                        |          |              |
| 2        | 0.80              | n. d.                                       | n. d.    | 0.60            | 3.19              | 43.0                                        |          |              |
| 4        | 1.09              | 1.46                                        | 17.4     | 1.09            | 2.42              | 36.0                                        |          |              |
| 6        | 1.35              | 1.33                                        | 19.9     | 1.97            | 4.39              | 78.6                                        |          |              |
| 8        | 1.41              | 0.26                                        | 4.7      | 2.37            | 2.02              | 43.7                                        |          |              |

### AQ-MINT

| Time / h | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M Na₂SO₄ | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M NaOH |
|----------|-------------------|---------------------------------------------|----------|-----------------|-------------------|---------------------------------------------|----------|--------------|
| Initial  | 0.20              | n. d.                                       | n. d.    | 0.46            | n. d.              | n. d.                                       | n. d.    |              |
| 1        | 0.29              | 0.86                                        | 2.5      | 1.69            | 12.31             | 50.7                                        |          |              |
| 2        | 0.48              | 1.91                                        | 5.4      | 2.85            | 11.66             | 51.6                                        |          |              |
| 4        | 1.24              | 3.81                                        | 11.2     | 4.34            | 7.44              | 34.8                                        |          |              |
| 6        | 1.50              | 1.32                                        | 3.8      | 6.02            | 8.38              | 41.5                                        |          |              |
| 8        | 2.14              | 3.19                                        | 9.6      | 7.46            | 7.20              | 36.7                                        |          |              |

### AQ@SWCNT

| Time / h | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M Na₂SO₄ | n(H₂O₂)[a] / µmol | H₂O₂ production rate[b] / µmol H₂O₂ mg⁻¹ h⁻¹ | FE[b] / % | In 0.1M NaOH |
|----------|-------------------|---------------------------------------------|----------|-----------------|-------------------|---------------------------------------------|----------|--------------|
| Initial  | 0.39              | n. d.                                       | n. d.    | 1.54            | n. d.              | n. d.                                       | n. d.    |              |
| 1        | 0.48              | 0.86                                        | 4.4      | 2.06            | 5.18              | 14.6                                        |          |              |
| 2        | 0.67              | 1.89                                        | 10.8     | 2.47            | 4.13              | 17.2                                        |          |              |
| 4        | 0.98              | 1.57                                        | 8.1      | 3.36            | 4.48              | 27.4                                        |          |              |
| 6        | 1.38              | 1.97                                        | 10.1     | 4.41            | 5.25              | 47.5                                        |          |              |
| 8        | 1.80              | 2.15                                        | 11.7     | 5.95            | 7.68              | 84.6                                        |          |              |

[a] Cumulative, absolute amount of H₂O₂ detected by spectrophotometer.

[b] Calculated per time interval
10. **RDE Experiments**

Samples of SW-CNT, AQ-MINT and AQ@SWCNT were drop-casted onto RDE electrodes with the same loading and tested under O\textsubscript{2} saturation in 0.1M NaOH solution. The rotation speed was varied between 100 and 3600 rpm. In order to show ORR, linear sweep voltammograms (LSV) of an intermediate and representative speed of 1200 rpm was chosen to compare the three samples in Figure 4c.

Comparing the current densities of the three samples revealed that AQ-MINT shows the highest catalytic current. Nevertheless, performing Koutecki-Levich-Analysis\textsuperscript{5} using eq. 1 showed that assuming the geometric electrode surface area is significantly underestimating the real electrode surface area with the CNT structure.

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{0.62 n F A D^{2/3} v^{-1/6} c_0} \cdot \frac{1}{\omega^{1/2}}
\]

Although the lack of the exact electrode area hinders further analysis of the slope in Koutecki-Levich-Plot, still the values of \(i_K\) correlate with the rate constant \(k\), as shown in eq. 2:

\[
i_K = n F A k_f(E)c_0
\]

As those values of \(i_K\) refer to the exchange current without any convection effects, it can still be regarded as value for comparing the three systems as they arrange on the electrode surface.

**Figure S16:** a) Koutecki-Levich plots of AQ-MINT in 0.1M NaOH at potentials between -0.1 and -0.6V. b) \(i_K\) values of AQ-MINT, AQ@SW-CNT and SW-CNT determined from the intercept of the Koutecki-Levich plots depending on the potential applied.

As can be seen from Figure S16a, the Koutecki-Levich plots for AQ-MINT show a reasonable linear trend for those potentials applied. Plotting the \(i_K\) values of AQ-MINT, AQ@SWCNT and SWCNT from the Koutecki-Levich plots show that at more positive potentials AQ@SWCNT and SWCNT
differ but come to quite close values at more negative potentials. In all potentials regarded, AQ-MINT shows the highest $i_K$ which can be regarded as a hint for a higher electrocatalytic activity.

As a result, we propose that the different CNT samples with and without AQ modification arrange in a different way on the GC surface, which also affects the real, electroactive surface area. Unfortunately, because of insufficient resolution of the SEM facilities available, we were not able to proof this assumption.

References:

(1) Su, G.; Wei, Y.; Guo, M. Direct Colorimetric Detection of Hydrogen Peroxide Using 4-Nitrophenyl Boronic Acid or Its Pinacol Ester. *Am. J. Anal. Chem.* **2011**, *2*, 879–884. https://doi.org/10.4236/ajac.2011.28101.

(2) Apaydin, D. H.; Seelajaroen, H.; Pingsakul, O.; Thamyongkit, P.; Sariciftci, N. S.; Kunze-Liebhäuser, J.; Portenkirchner, E. Photoelectrocatalytic Synthesis of Hydrogen Peroxide by Molecular Copper-Porphyrin Supported on Titanium Dioxide Nanotubes. *ChemCatChem* **2018**, *10* (8), 1793–1797. https://doi.org/10.1002/cctc.201702055.

(3) Canevet, D.; Gallego, M.; Isla, H.; Juan, A. De; Emilio, M. P. Macro cyclic Hosts for Fullerenes : Extreme Changes in Binding Abilities with Small Structural Variations. *J. Am. Chem. Soc.* **2011**, *133* (9), 3184–3190. https://doi.org/10.1021/ja111072j.

(4) Blanco, M.; Nieto-Ortega, B.; De Juan, A.; Vera-Hidalgo, M.; Lópezmoreno, A.; Casado, S.; González, L. R.; Sawada, H.; González-Calbet, J. M.; Pérez, E. M. Positive and Negative Regulation of Carbon Nanotube Catalysts through Encapsulation within Macro cyclics. *Nat. Commun.* **2018**, *9* (2671), 1–7. https://doi.org/10.1038/s41467-018-05183-8.

(5) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd Ed.; John Wiley & Sons, Inc.: New York, 2001.