Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information for

Single-chirality single-wall carbon nanotubes for electrochemical biosensing

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Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology (NIST), nor does it imply the materials are necessarily the best available for the purpose.

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A. Methods for fabrication of electrochemical sensors

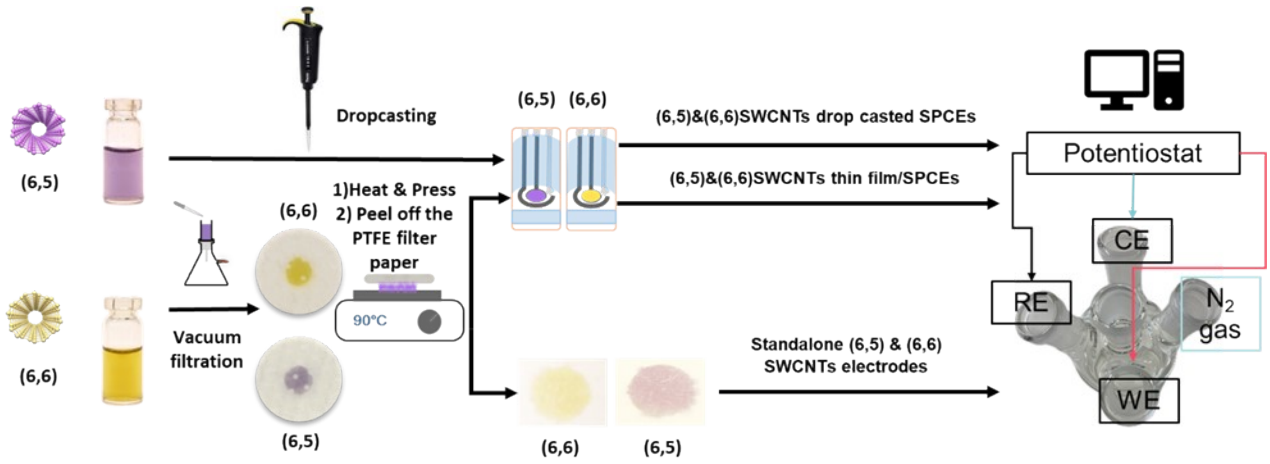

Figure S1. The steps to prepare the electrochemical sensors for use as the working electrode (WE) using screen-printed carbon electrodes (SPCEs) and glass (standalone) as substrates

B. SEM images of SWCNT drop casted SPCEs

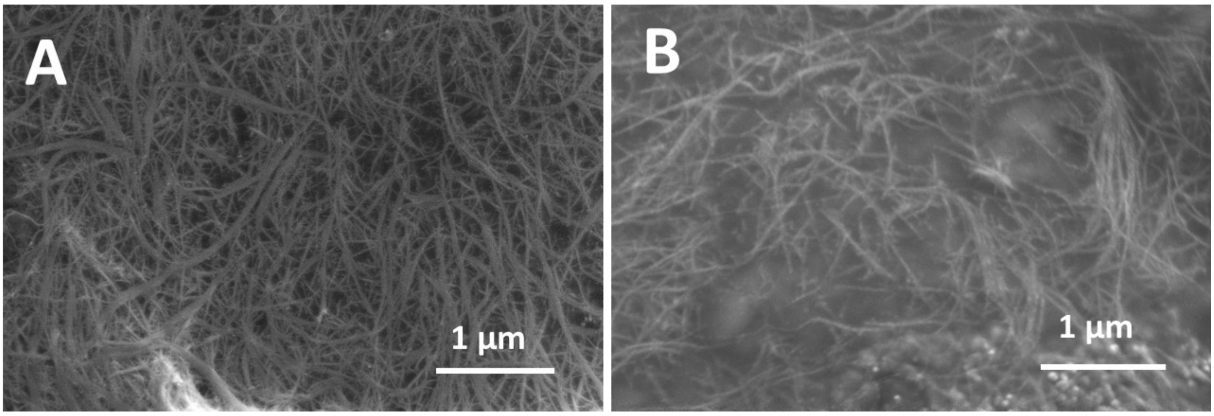

Figure S2. A. (6,5) SWCNTs drop casted SPCE and B. (6,6) SWCNTs drop casted SPCE.

C. XPS spectra

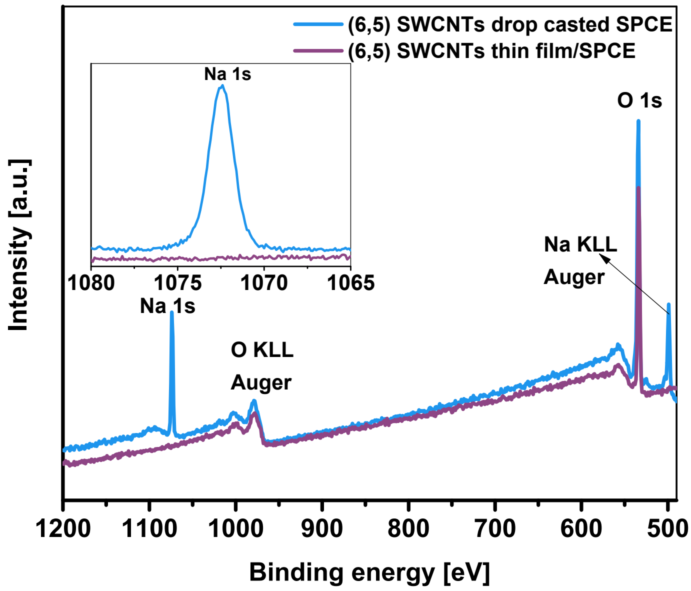

Figure S3. XPS spectra of (6,5) SWCNTs drop casted SPCE and thin film/SPCE

D. Four-point probe measurements

Table S1. Sheet resistance, resistivity, and conductivity for standalone single-chirality SWCNTs electrodes (n=3). The standard deviation was calculated using three data points.

Sensor	Mean Sheet Resistance (Ω/sq)	Mean Resistivity (Ω·m)	Mean Conductivity (S/m)
standalone (6,5) SWCNTs electrode	1387311 ± 295401	0.28 ± 0.06	3.73 ± 0.91
standalone (6,6) SWCNTs electrode	4868 ± 1586	0.0010 ± 0.0003	1092 ± 300

The sheet resistance (R_s) was calculated from the equation, $R_s = \frac{\rho}{t}$ (1) where ρ is the resistivity and t is the sample thickness. The conductivity (σ_s) was calculated from the equation, $\sigma_s = \frac{1}{R_s \times t}$ (2).

E. Density determination of (6,5) and (6,6) SWCNTs

The method used to determine the extinction coefficient of (6,6) and (6,5) SWCNTs follows the protocol established previously by Khriprin et al.[1] The SWCNTs were dispersed in water using a single-stranded DNA oligomer $(GT)_{20}$. Next, the SWCNTs were separated into fractions based on their length by size exclusion chromatography (SEC). This process also removes unbound DNA. The mass ratio of DNA: SWCNT carbon concentration in their length-fractionated samples was found to be constant by X-ray photon spectroscopy (XPS). Therefore, after unbound DNA was removed, the measured DNA concentration can be used to calculate the SWCNT carbon concentration. To quantify DNA on purified DNA-wrapped (6,5) and (6,6), the DNA-SWCNTs are run through SEC using 1% sodium deoxycholate (DOC) as the mobile phase to separate the DNA from (DOC-coated) SWCNTs. The DNA peak in the recorded SEC chromatogram is then used for DNA quantification according to a predetermined calibration.

1. Beer-Lambert law

$$A = \varepsilon l[SWCNTs]$$

$$A = Absorbance\ or\ Optical\ density\ (OD)$$

$$\varepsilon = Molar\ extinction\ coefficient\left(M^{-1}cm^{-1}\right)$$

$$[SWCNTs] = SWCNT carbon\ concentration\ (M)$$

$$l = Path\ length\ (cm)$$

Using the measured DNA concentration and the known DNA mass ratio (n), we have [SWCNTs] = n [DNA]. Thus, the ε can be determined by:

$$\varepsilon = \frac{l \cdot n\,[DNA]}{A}$$

Table S2. Extinction Coefficient for (6,5) and (6,6) SWCNTs determined by this work.

(n,m)	[SWCNT]/1 OD at M_{11} or S_{11}	Extinction Coefficient at M_{11} or S_{11}
(6,5)	3.7 $\pm$ 1 μg/mL	3200 $M^{-1}cm^{-1}$/C atom
(6,6)	13 $\pm$ 1 μg/mL	920 $M^{-1}cm^{-1}$/C atom

2. Working area

- Diameter of the working electrode (cm) = 0.4

  Thus, WE Area (cm^2) = 0.126
- Inner diameter of filtration film (cm) =1.8, Outer diameter of filtration film (cm) = 2.5

  Thus, $PTFE\ Membrane\ filter\ working\ area\ (cm^2) = \pi \times (1.8)^2 = 2.545$

3. Density of (6,5) SWCNTs ($\mu g/cm^2$)

$$= \frac{[(6,5)\ SWCNTs]\left(\frac{\mu g}{mL}\right)}{1OD\ \ at\ S_{11}} \times 1\ OD \times Volume\ of\ the\ solution\ (mL) \div [WE\ area\ or\ f$$

]

1) **OD of (6,5) SWCNTs = 0.319 (absorbance at 989 nm taken from Figure 1)**

- Dilution factor for UV-Vis = 100 times

  Thus, 1 OD = 31.9

2) **Standalone electrode**

- Volume of the solution (mL) = 0.04 mL

  Thus, the density on the standalone electrode = 1.86 $\mu g/cm^2$

3) **SWCNT drop casted SPCE and SWCNT thin film/SPCEs**

- Volume of the solution (mL) = 0.002 mL

Thus, the density of the SWCNTs drop casted SPCEs or SWCNTs thin film/SPCEs = 1.88 μg/cm²

4. Density of (6,6) SWCNTs (μg/cm²)

$$\frac{[(6,6)\ SWCNT]\left(\frac{\mu g}{mL}\right)}{1OD\ \ at\ M_{11}} \times 1\ OD \times Volume\ of\ the\ solution\ (mL) \div [WE\ area\ or\ filter\ area\ (cm^2)] =$$

1) **OD of (6,6) SWCNTs = 0.2654 (absorbance at 456nm taken from Figure 1)**

- Dilution factor for UV-Vis = 10 times

  Thus, 1 OD = 2.654

2) **Standalone electrode**

- The volume of the solution used (mL) = 0.136 mL

  Thus, the density of the standalone electrode = 1.84 μg/cm²

3) **SWCNTs drop casted SPCE and SWCNTs thin film/SPCEs**

- The volume of the solution used (mL) = 0.00675 mL

  Thus, the density of SWCNTs drop casted SPCEs or SWCNTs thin film/SPCEs= 1.85 μg/cm²

F. Film thickness comparison using AFM

Table S3. 2 μg/cm² thickness comparison of standalone (6,5) SWCNTs and (6,6) SWCNTs electrodes (n=3). The standard deviation was calculated using three data points.

Sensor	Thickness (nm)
Standalone (6,5) SWCNTs electrode	44.4 ± 4.7

Standalone (6,6) SWCNTs electrode	41.5 ± 13.6

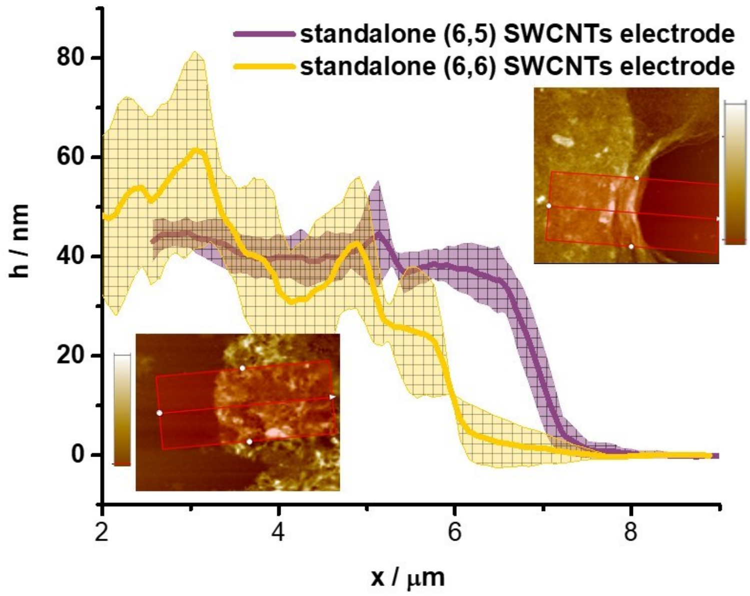

Figure S4. 2 µg/cm² thickness comparison of (6,5) SWCNTs in purple and (6,6) SWCNTs in yellow (n=3),

The legend shows a height range from 0 to 50 nm for (6,5) SWCNTs film (right) and from 0 to 80 nm for (6,6) SWCNTs film (left) in the AFM images.

G. Concentration study of (6,5) and (6,6) SWCNTs thin film/SPCEs

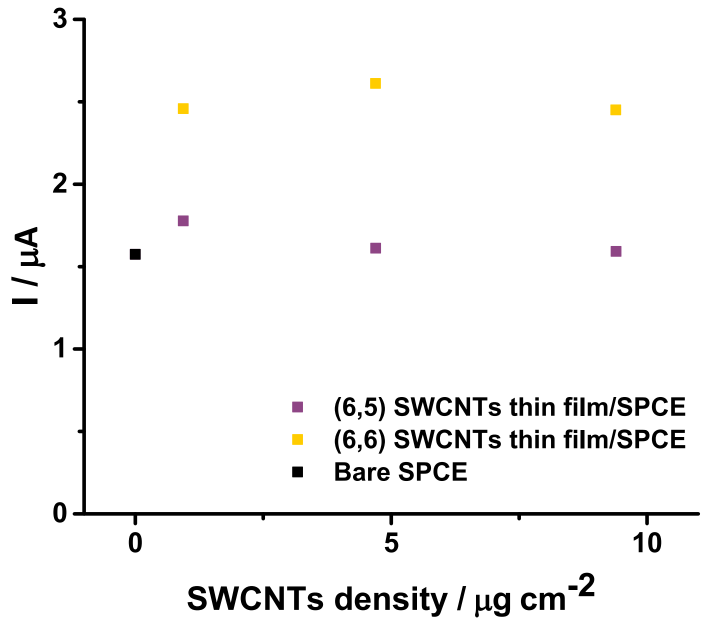

Figure S5. Peak anodic current ($i_{p,a}$) by different densities of SWCNTs thin film/SPCEs

towards DA 50 μM at a scan rate of 400 mV/s.

Based on this concentration study of SWCNTs, modifying the SPCEs does not require a higher density over 2 μg/cm^2. Considering that the standalone electrodes give a stable current with a SWCNT density of 2 μg/cm^2, nearly 2 μg/cm^2 is used for SPCE modification.

H. SWCNTs drop casted SPCEs

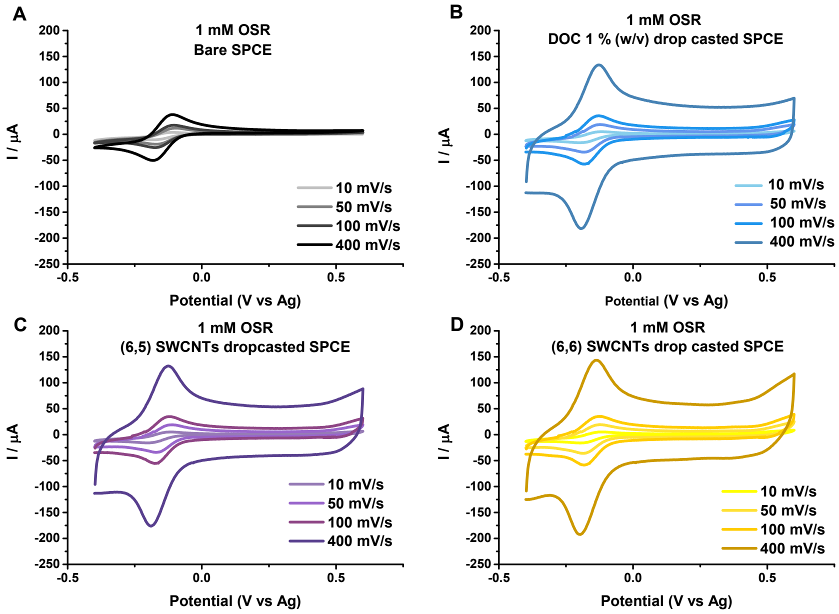

Figure S6. Comparison between bare and SWCNTs drop casted SPCEs towards OSR concentration of 1 mM.

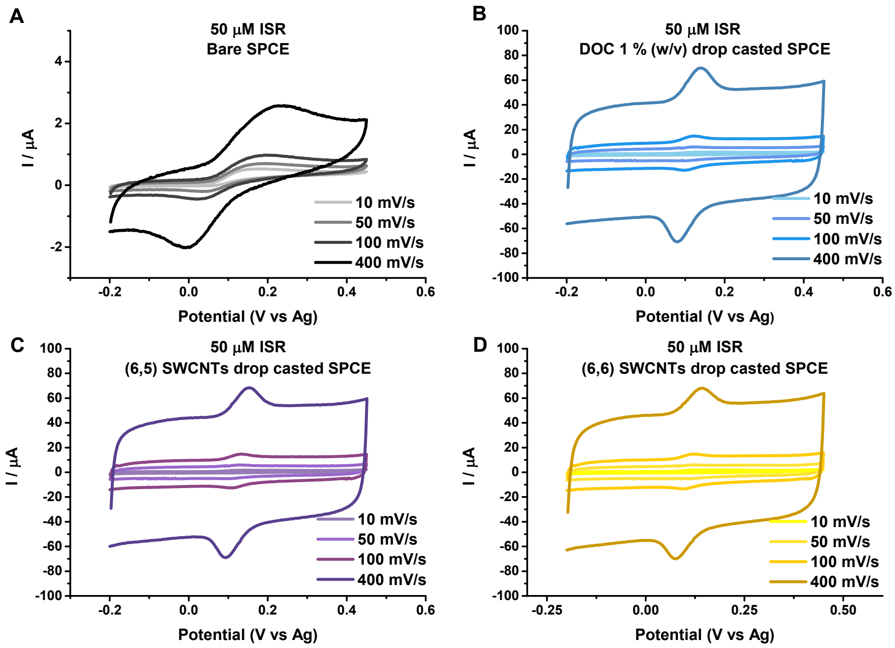

Figure S7. Comparison between bare and SWCNTs drop casted SPCEs towards ISR concentration of 50 μM.

I. SWCNTs thin film/SPCEs

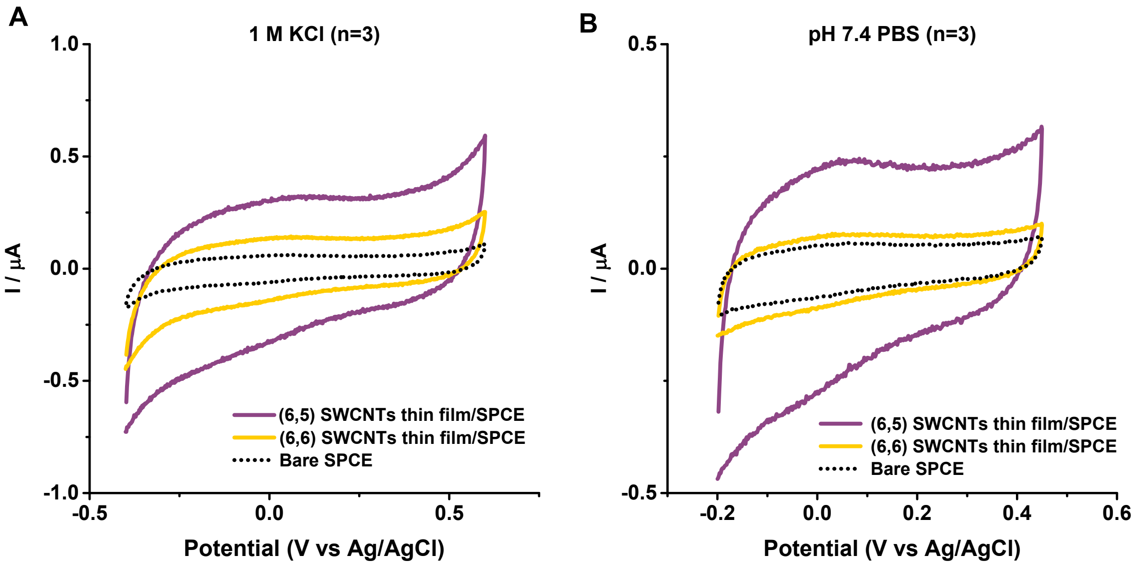

Figure S8. Cyclic voltammograms with a scan rate of 100 mV/s in (A) 1 M KCl and (B) pH 7.4 PBS.

J. Electron transfer kinetics of (6,6) and (6,5) SWCNTs thin film/SPCEs

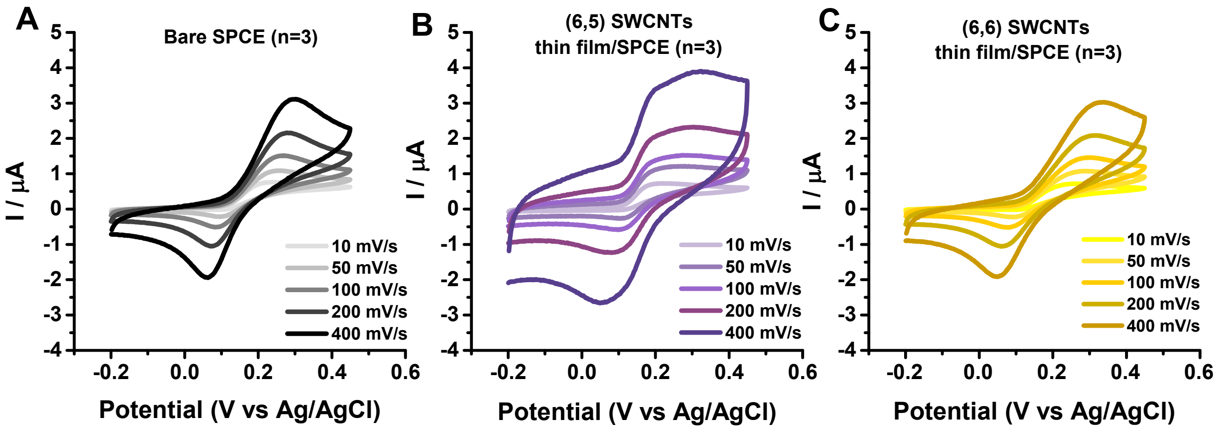

Figure S9. Cyclic voltammograms of Bare SPCEs, (6,6) and (6,5) SWCNTs thin film/SPCEs in DA 50 µM with varying scan rates.

Slopes of Log v vs. Log ($i_{p,a}$) in Table 2 were calculated from Figure S9.

K. Calibration plots of (6,6) and (6,5) SWCNTs thin film/SPCEs

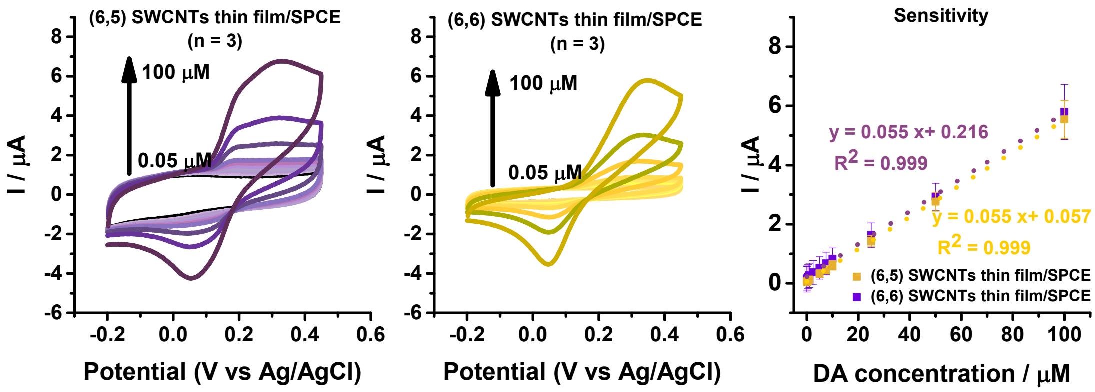

Figure S10. Concentration series of DA (0.05 μM – 100 μM) with a scan rate of 400 mV/s.

Reference

1C. Y. Khripin, X. Tu, J. Howarter, J. Fagan and M. Zheng, *Anal. Chem.*, 2012, **84**, 8733–8739.