

Supplementary Information for “Electrochemical impedance determination of polychlorinated biphenyl using pyrenecyclodextrin-decorated single-walled carbon nanotube hybrid”

Experimental Section

Chemical Reagents. 3,3',4,4'-tetrachlorobiphenyl (PCB-77), 1,3,5-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene were purchased from 125 Market ST· New Haven, CT 06513· USA. β -cyclodextrin was obtained from Sinopharm Chemical Reagent Co., Ltd. SWCNTs were obtained from Chengdu Institute of Organic Chemistry of the Academy of Sciences. Dipterex (>95%), imidacloprid (>98.5%), acephate(>95%), omethoate(>99%), acetofenate(>99%), fenpropathrin(>98%), cypermethrin(>98%) were kindly donated by National center of Agricultural Standardization And Supervision of China, Anhui, China, and were used as received. All other chemicals were of analytical grade. Ultrapure fresh water obtained from a Millipore water purification system (MilliQ, specific resistivity >18 M Ω cm, S.A., Molsheim, France) and used in all runs. A phosphate-buffered saline solution (PBS, pH 7.4) was prepared by dissolving 1.6 g of KCl, 64 g of NaCl, 1.92 g of KH₂PO₄, and 11.52 g of K₂HPO₄ in 800 mL of ultrapure fresh water.

Apparatus. Electrochemical experiments were recorded using a CHI 660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China) with a standard three-electrode system. A bare glassy carbon electrode (GCE, diameter of 3 mm) or modified GCE served as a working electrode; a platinum wire was used as a counter-electrode with a saturated calomel electrode (SCE, ChenHua Instruments Co., Shanghai, China) completing the cell assembly. The electrolyte solutions were deoxygenated with nitrogen bubbling for 10 min before each voltammetric run, and all experiments were performed at a temperature of 25 \pm 1 $^{\circ}$ C and under nitrogen atmosphere.

The morphology of SWCNT/PyCD films on electrode surface was verified by field-emission scanning electron microscopy (FESEM, Quanta 200 FEG, FEI Company, USA). Transmission electron microscopy (TEM) was performed using a JEM-2010 microscope equipped with Oxford INCA EDS operated at 200 kV accelerating voltage (Quantitative method: Cliff Lorimer thin ratio section). FTIR was performed using a model MB-154 analyzer (Bomem, Inc.).

Preparation of the SWCNT, PyCD, SWCNT/PyCD, and SWCNT/CD Modified Electrode. The pyrenecyclodextrin derivative was synthesized as follows: A single tosylate group was introduced in cyclodextrin to obtain CDtos, subsequently, nucleophilic substitution of the tosylate group in CDtos using sodium azide furnished the corresponding monoazide intermediate CD-N₃, which was reduced to amine CD-NH₂ using standard Staudinger conditions. Finally, CD-NH₂ was coupled with the 1-pyrenebutyric acid through amidation reaction to give PyCD. The glassy carbon

electrodes were polished prior to each experiment, first using a 1.0 μm alumina-water slurry (Buehler, Illinois) on a polishing pad (Kermet, Kent, UK) followed by a 0.3 and 0.05 μm alumina-water slurry (Buehler) on a polishing cloth (Microcloth, Buehler). The electrode was then successively washed using ultrapure fresh water and anhydrous ethanol in an ultrasonic bath. Periodic inspection of the electrodes using optical microscopy was performed to ensure that the disk had not recessed into the glass surface. 1.0 mg of SWCNTs was firstly dispersed in 10 ml of acetone with the aid of ultrasonic agitation to form a “casting” suspension. SWCNT electrode was prepared by pipetted 5 μL of SWCNT aliquot onto the surface of a freshly polished glassy carbon electrode and dried at room temperature, followed by exhaustive washing using ethanol and ultrapure fresh water and then dried again at ambient conditions. The fabrication of the self assembly monolayer of PyCD over the SWCNT electrode was carried out by immersing the clean SWCNT GCE into 1.13 mM N,N-dimethyl formamide (DMF) solution of PyCD for 4 hrs at room temperature. The SWCNT electrode was then washed using ultrapure fresh water to remove the nonadsorbed PyCD molecules or SWCNT/PyCD layers. SWCNT/CD electrode was prepared in the same way when using the β -CD instead of PyCD. PyCD electrode was prepared by placing a freshly pretreated glassy carbon electrode into 1.13 mM pyrenecyclodextrin solution for 4 hrs at room temperature, and then rinsed twice with double-distilled water.

Electrochemical Measurements. Standard stock solutions of PCB-77 (25 mg L^{-1}) and other interference test samples (20 mg L^{-1}) were prepared in methanol. All solutions were stored in the dark at 4 $^{\circ}\text{C}$. Working solutions were prepared by dilution of standard stock solution with distilled water. The prepared SWCNT/PyCD and other modified electrodes were preconcentrated with PCB-77 solution of different concentrations at room temperature for 3 hrs and carefully washed using PBS. The electrochemical measurements including CV (cyclic voltammograms) and EIS (electrochemical impedance spectra) were performed in a degassed PBS solution with a high purity N_2 (Nanjing Special Gases Factory Co., Ltd.) containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl. Similar process (see above) was employed to interference studies, and the frequency range is from 0.1 Hz to 10000 kHz with a signal amplitude of 5 mV, and the scan rate is 100 mV s^{-1} . The results, such as the experimental condition, optimization, and calibration curve, were statistical analysis and presented as mean \pm SD (standard deviation).

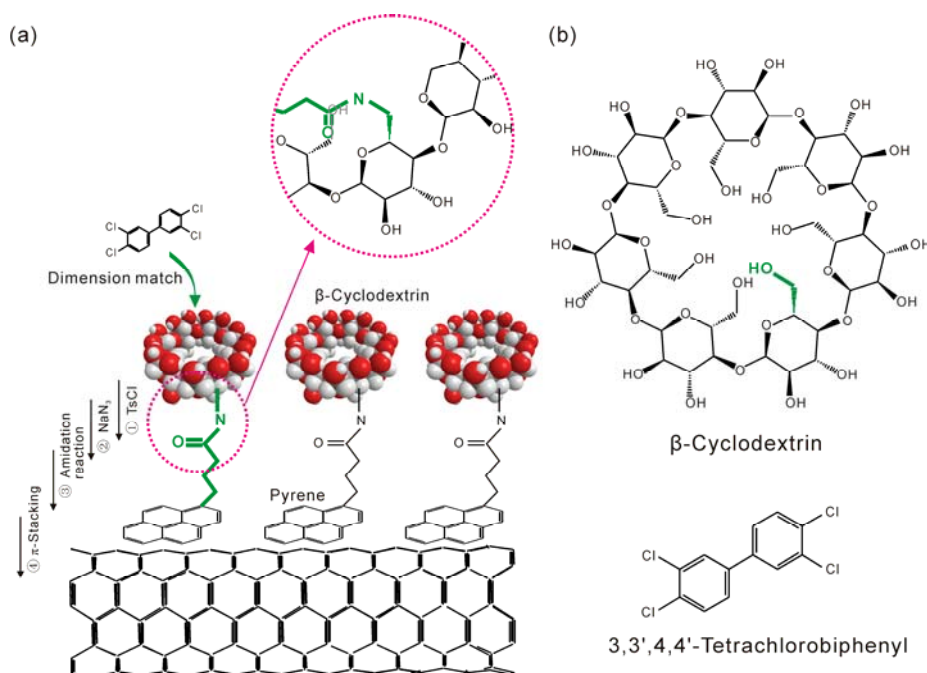


Fig.S1 (a) Schematic diagram outlining the irreversibly adsorbing of pyrenecyclodextrin onto the sidewall of a SWCNT via π - π stacking. It is expected that the capture of a guest molecule, such as PCB-77, by the cavities of the pyrenecyclodextrin hosts results in a change of electrochemical impedance originated from the electron-transfer resistance (R_{et}). (b) Chemical structures of β -cyclodextrin and PCB-77 molecules.

The strategy used here to create electrochemical impedance sensing interface with pyrenecyclodextrin self-assembled onto SWCNT is illustrated in Fig.S1a. β -cyclodextrin was adsorbed onto the sidewalls of single-walled carbon nanotubes via pyrenyl group. Due to highly aromatic in nature, pyrenyl group interacts strongly with the basal plane of graphite via π - π stacking, thus providing an irreversibly adsorbing for cyclodextrin on the nanotubes. For electrochemical measurements, this highly stability of the anchored molecules of cyclodextrin against desorption leads to not only the high reaction to the guest molecules, such as PCB-77, that exist in abundance in aqueous solutions, but also a high degree of efficiency and specificity in subsequent immobilization of various organic molecules onto nanotubes. The determination mechanism of guest molecules immobilized on nanotubes mainly involves a change of electrochemical impedance originated from the electron-transfer resistance (R_{et}). If guest molecules are captured by the cavities of the pyrenecyclodextrin hosts (Fig.S1a), the formation of guest-host complexes could create a further barrier for the electrochemical process, thereby hindering the access of the redox probe ($\text{Fe}(\text{CN})_6^{3-/4-}$) to the electrode surface, resulting in an further increase in the electron-transfer resistance. The magnitude of the increase in electron-transfer resistance is related to the number of guest molecules captured by the hosts. An increase in the electron-transfer resistance would be expected. The important advantage of such a system is that at electrode surfaces the presence of extended, delocalized π -electron

systems is very useful for charge transfer and charge transport.²⁰ Accordingly, the resistance of sensing material itself was eliminated and it could be beneficial for analysis of impedance spectrum, as well as equivalent circuit, as described in the following section.

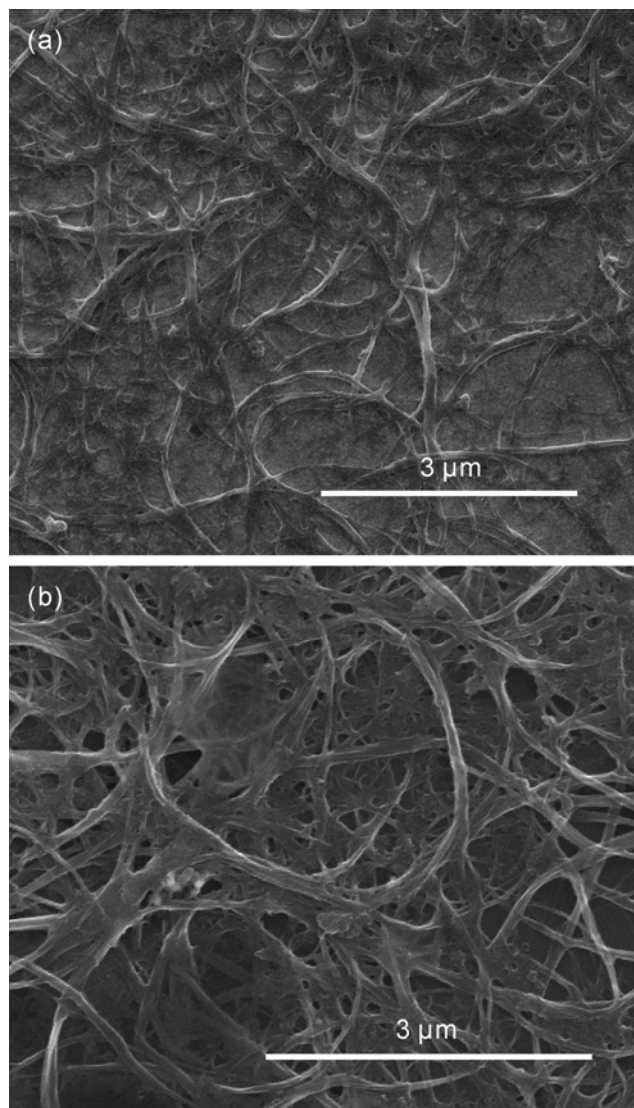


Fig.S2 SEM images of (a) pristine SWCNT and (b) SWCNT/PyCD film on glassy carbon electrode surface.

Fig.S2 displays representative SEM images of part of pristine SWCNT (Fig.S2a) and SWCNT/PyCD film (Figure 2b) on glassy carbon electrode surface. It is easily visible that the pyrenecyclodextrin layer is homogeneously deposited along the nanotube (Fig.S2b). Slight differences observed in the friction at the nanotube surface, which can be seen by some color differences on the coated tubes; tend to show that the pyrenecyclodextrin layer thickness is not completely uniform. Again, three dimensional porous interspaces are seen due to a number of randomly tangled carbon nanotubes, to ensure more CD cavity appeared outside.

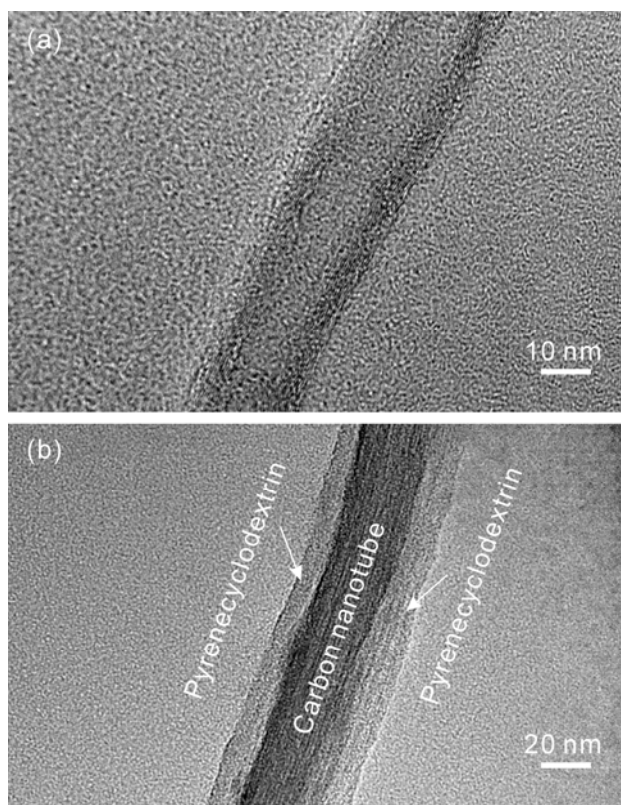


Fig.S3 TEM images of (a) pristine SWCNT and (b) SWCNT/PyCD.

Besides, HRTEM images (Fig.S3) of the SWCNTs and SWCNTs/PyCD show the presence of individual SWCNTs with specific rugged surface, which can also confirm that, the cyclodextrin functional groups have been contacted on the nanotube sidewalls.

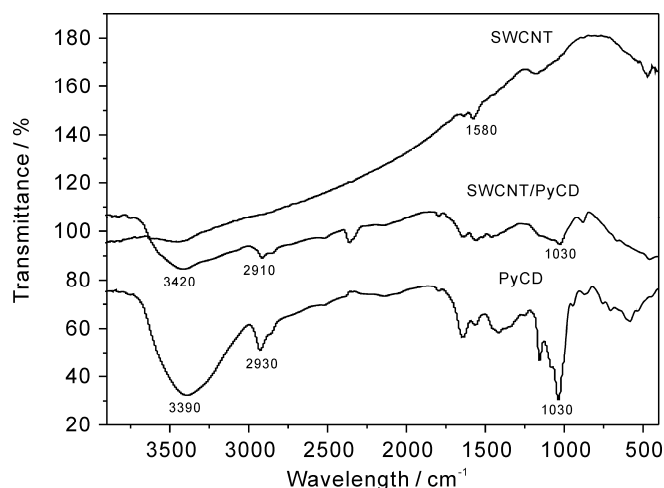


Fig.S4 FTIR spectrum of pristine SWCNT, PyCD, and SWCNT/PyCD.

The SWCNT/PyCD hybrid was further characterized by FTIR spectra. Fig.S4 displays the FTIR spectra of pristine SWCNT, PyCD, and SWCNT/PyCD hybrid. The characteristic FTIR peaks of PyCD are around 1030.5, 1079.3, and 1155.5 cm⁻¹, which are in agreement with the previous report.¹ It is found that the FT-IR spectrum of SWCNTs is essentially featureless except the C=C conjugation (1580 cm⁻¹), etc. Whereas the FT-IR spectrum of SWCNTs/PyCD exhibits typical PyCD absorption features of the coupled C-O/C-C stretching/O-H bending vibrations at 1030 cm⁻¹, CH₂ stretching vibrations at 2910 cm⁻¹, and O-H stretching vibrations at 3420 cm⁻¹. This clearly confirms that PyCD molecules are attached to the surface of SWCNTs. This analysis confirms the existence of pyrenecyclodextrin on the SWCNTs in a noncovalent way. Based on the SEM, TEM, and FTIR results, we concluded that the pyrene units in the pyrenecyclodextrin derivatives associate with the side wall of the SWCNTs by means of π - π stacking interactions facilitating the formation of the pyrenecyclodextrin-SWCNT hybrids.

1 Z. H. Wang, Y. M. Wang and G. Luo, *Analyst*, 2002, 127, 1353-1358.

Equivalent circuit analysis

The R_s(CPE-PR) equivalent circuit applied to fit the impedance spectroscopy using a constant phase element (CPE) instead of capacitance owing to the rough surface in the presence of the redox couple of Fe(CN)₆^{3-/4-} is shown in the inset of Fig.1a. The circuit of present system includes the following four elements: (i) the ohmic resistance of the electrolyte solution, R_s; (ii) the Warburg impedance, Z_w, resulting from the diffusion of ions from the bulk electrolyte to the electrode interface; (iii) the interfacial double layer capacitance (Cdl) between an electrode and a solution, relating to the surface condition of the electrode; since the surface of the SWCNT/PyCD electrode was very rough, it had a larger real surface area; therefore, we used a constant phase element (CPE) instead of the classical capacitance to fit the impedance data, because the electrolyte side of the interface dominated the impedance

of the interface; (iv) the electron-transfer resistance, R_{et} , which exists if a redox probe is present in the electrolyte solution. The parallel elements (CPE and $Z_w + R_{et}$) of the equivalent circuit were introduced since the total current through the working interface was the sum of respective contributions from the Faradaic process and the double layer charging. Ideally, Z_w and R_s represent the bulk properties of the electrolyte solution and diffusion features of the redox probe in solution and, thus, are not affected by modifications on the electrode surface. As can also be seen in Figure 4a, the changes in R_{et} were much larger than those in other impedance components. R_{et} was therefore considered as a suitable signal for sensing the interfacial properties of the prepared sensor during all these assembly procedures.

Cyclic voltammograms (See Fig.1b)

The electron-transfer behavior of a bare GCE, SWCNT/PyCD GCE, and SWCNT/PyCD after preconcentration of 10 μ M PCB-77 was further compared using cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-/4-}$, as presented in **Fig. 1b**. It is clear that a decrease in the amperometric response and an increase in the peak-to-peak separation between the cathodic and anodic waves of the redox probe after each assembly step, accounting for the electron-transfer kinetics of $\text{Fe}(\text{CN})_6^{3-/4-}$ is obstructed. After the glassy carbon electrode was modified by SWCNT/PyCD composite, the electron-transfer between the electrochemical probe and electrode surface was inhibited, owing to the attachment of SWCNT/PyCD hybrid to the glassy carbon electrode surface. When preconcentration of PCB-77, the electron-transfer between $\text{Fe}(\text{CN})_6^{3-/4-}$ and electrode surface was further inhibited.

Expectedly, a decrease in the amperometric response and an increase in the peak-to-peak separation between the cathodic and anodic waves of the redox probe after SWCNT and SWCNT/PyCD modification, demonstrating that PyCD further hinders the access of the redox probe ($\text{Fe}(\text{CN})_6^{3-/4-}$) to the electrode surface.

Table S1 Electron-transfer Resistance, R_{et} , in the Equivalent Circuit of Different

Ratio of PyCD to SWCNT after Preconcentration of 10 μM PCB-77 in the Solution of 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and 0.1 M KCl

Ratio (PyCD:SWCNT)	$R_{\text{et}}(\Omega)$	$\Delta R_{\text{et}}(\Omega)$
1:1	1800	1300
1:2	2100	3900
1:3	3000	1100
1:4	3500	600
1:6	6200	800
2:1	4500	1200

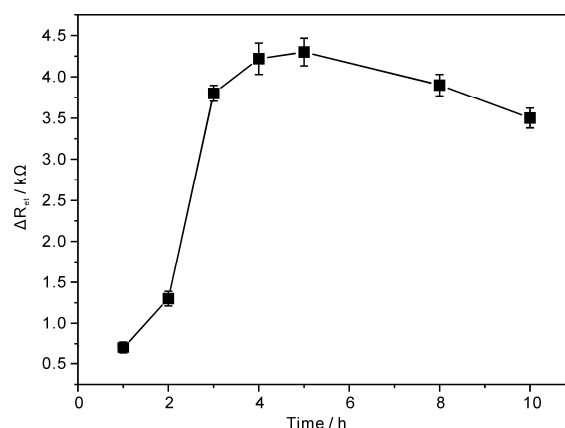


Fig.S5 The effect of preconcentration time on the response of electrochemical impedance spectra. Data were collected from Nyquist diagrams.

A preconcentration step is needed to guarantee the capture of PCB-77 molecules by the cavities of the PyCD hosts prior to EIS measurements. The performance of the hybrid electrode was investigated varying the preconcentration time from 1 to 10 hrs for the determination of 10 μM PCB-77 (Fig.S5). During the preconcentration, the test solution was stirred for effective accumulation in a required preconcentration time. The value of ΔR_{et} was found to increase very quickly within the first 3 hrs, and then slowly increase during the next 2 hrs. Upon increasing the preconcentration time further, instead, the ΔR_{et} decreases, which is likely to be due to the loss of film stability in a longer time. As a result the determination limit can be further improved by increasing preconcentration time without degradation in the film due to the favorable kinetics and low hydrodynamic impedance of the present system.

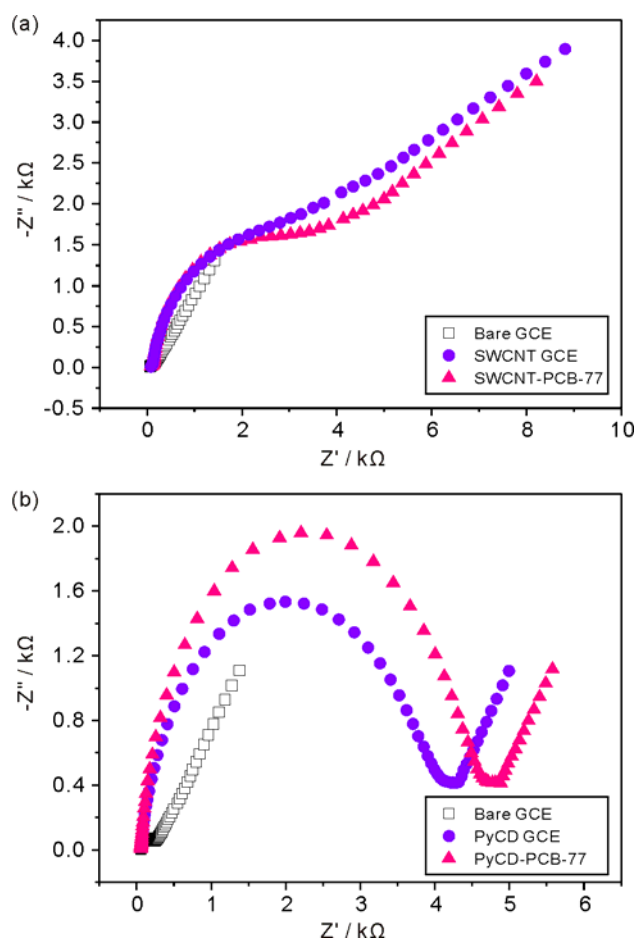


Fig.S6 Nyquist diagram of electrochemical impedance spectra of a single-SWCNT GCE (a) and single-PyCD (b) after preconcentration of $10 \mu\text{M}$ PCB-77 in the solution of $5 \text{ mM Fe(CN)}_6^{3-/4-}$ and 0.1 M KCl .

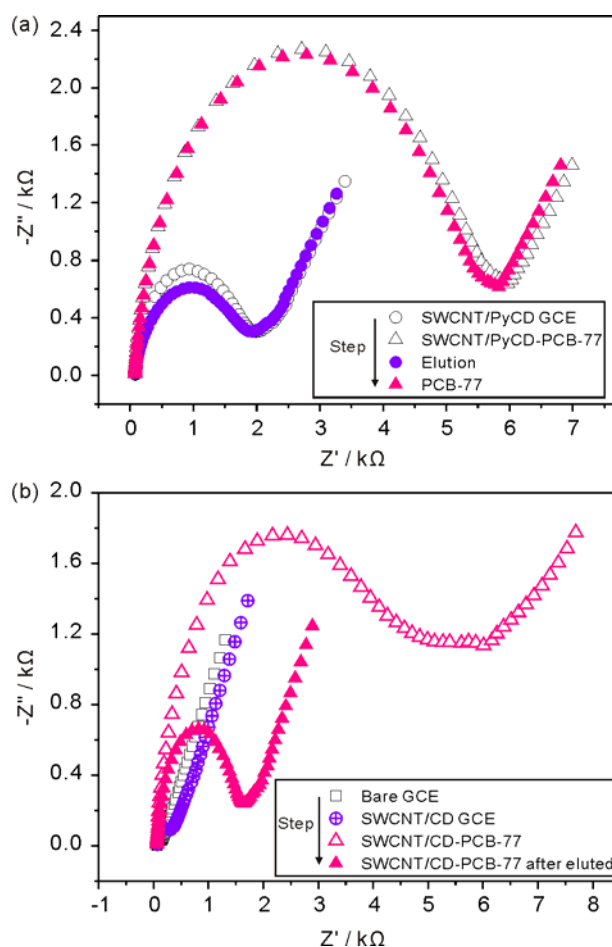


Fig.S7 Reproducibility of a SWCNT/PyCD system. Nyquist diagram of electrochemical impedance spectra of a SWCNT/PyCD GCE (a) and a SWCNT/CD GCE in the absence of pyrene ring (b) after exhaustive washing using ethanol saturated solution of sodium acetate, followed by preconcentration of $10 \mu\text{M}$ PCB-77 in the solution of $5 \text{ mM Fe}(\text{CN})_6^{3-/4-}$ and 0.1 M KCl .

In Fig.S7, repetitive preconcentration- measurement-regeneration cycles were then performed to characterize the reproducibility of the electrode performance. Transferring the electrode after tetrachlorobiphenyl determination to ethanol saturated solution of sodium acetate and then scanning in the same potential window achieved regeneration.

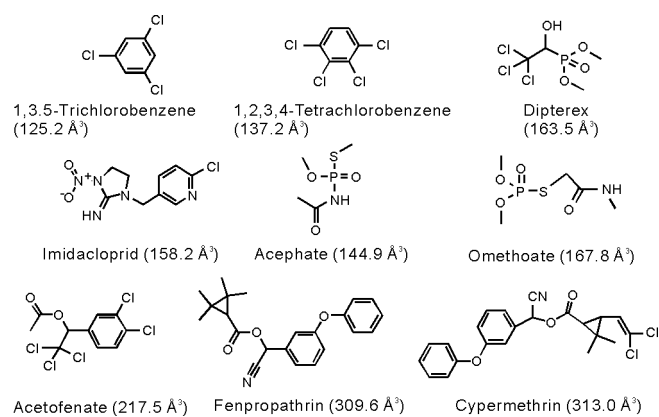


Fig.S8 Molecular structures of nine organic compounds and their volumes.