

Supplementary information for

A supramolecular pyrenyl glycoside-coated 2D MoS₂ composite electrode for selective cell capture

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Content list

- S1. Additional figures S1-S5
- S2. Experimental section
- S3. Original spectral copies of new compounds

S1. Additional figures S1-S5

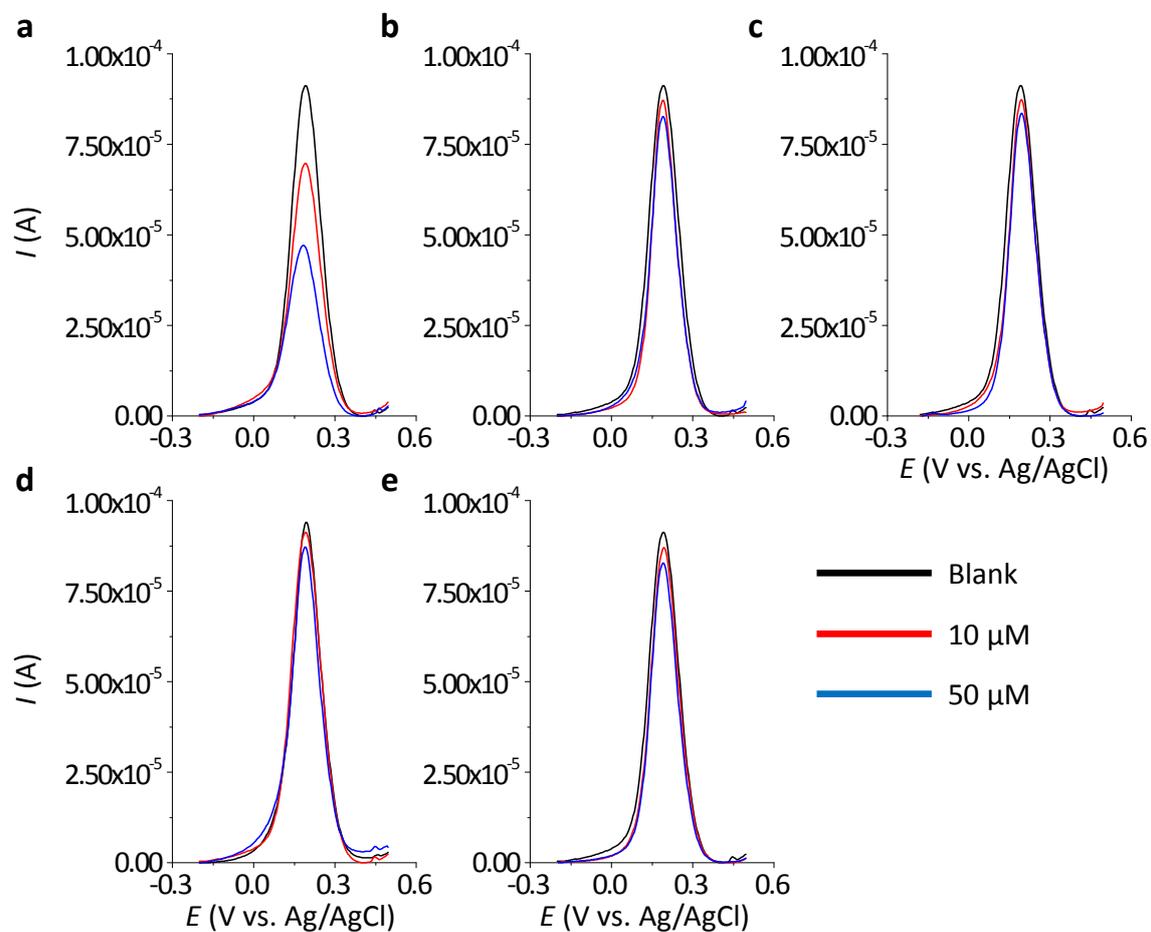


Figure S1. Differential pulse voltammetry of 2D composite material coated electrode (blank) in the presence of (a) peanut agglutinin, (b) concanavalin A, (c) bovine serum albumin, (d) pepsin and (e) wheat germ agglutinin.

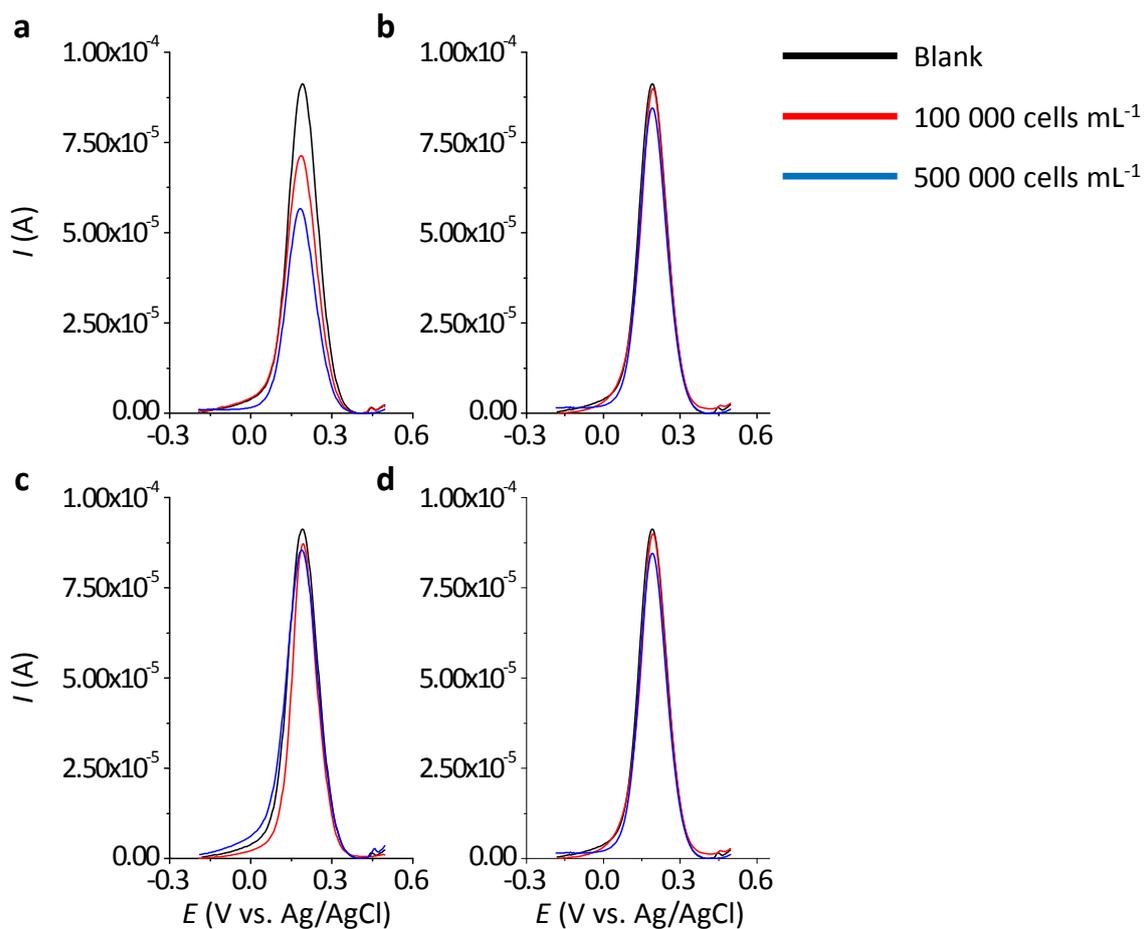


Figure S2. Differential pulse voltammetry of 2D composite material coated electrode (blank) in the presence of (a) Hep-G2, (b) sh-ASGPr, (c) HeLa and (d) A549.

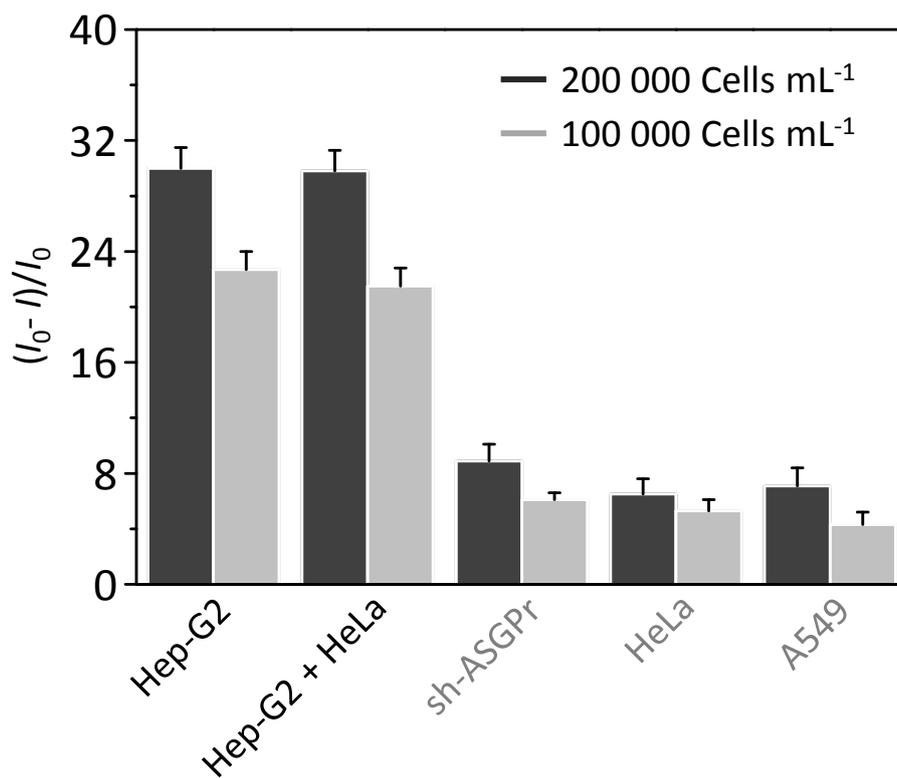


Figure S3. Current intensity change of electrosensor in the presence of different cells, where I and I_0 are the current intensity of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the presence and absence of an analyte, respectively (Hep-G2 = human hepatoma cell line; sh-ASGPr = Hep-G2 with reduced ASGPr expression; HeLa = human cervical cancer cells; A549 = human lung cancer cells). *Note that “Hep-G2 + HeLa” means a mixed cell culture with 200 000 or 100 000 cells mL⁻¹ each.*

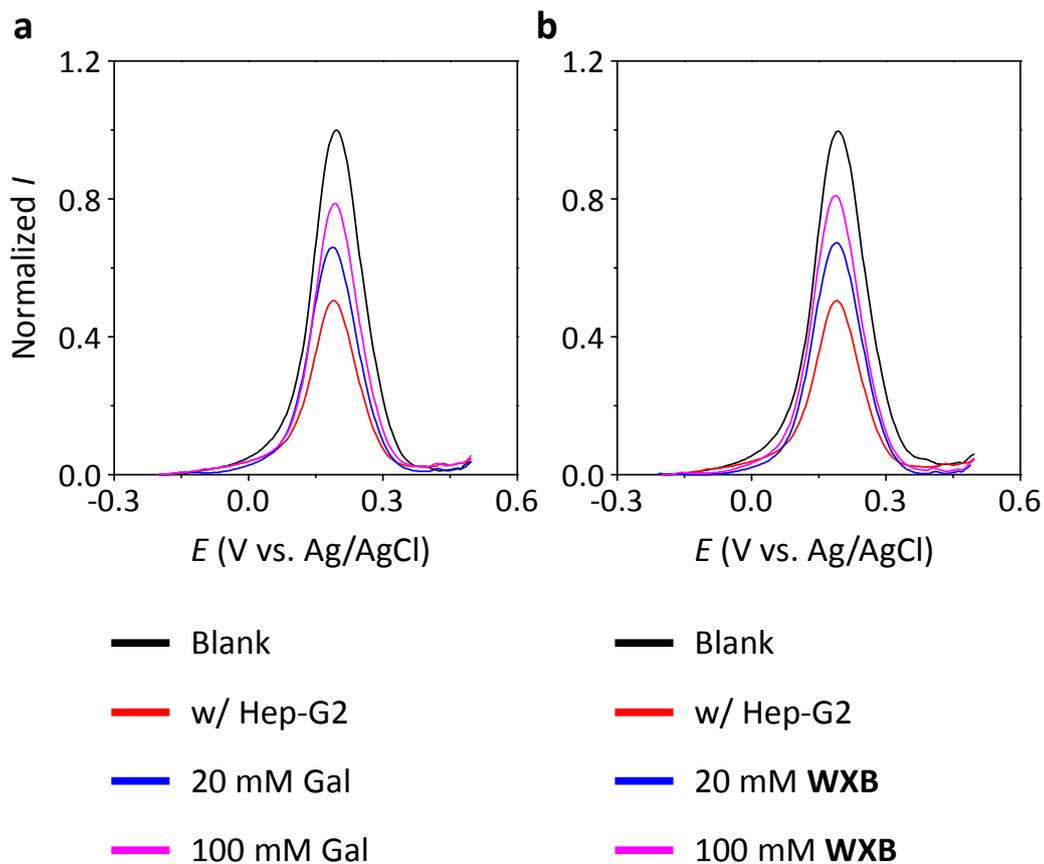


Figure S4. Differential pulse voltammetry of 2D composite material coated electrode (blank) in the presence of Hep-G2 (500 000 cells mL⁻¹) with or without a preincubation (for 30 min) with (a) 20 and 100 mM free D-galactose and (b) 20 and 100 mM **WXB**.

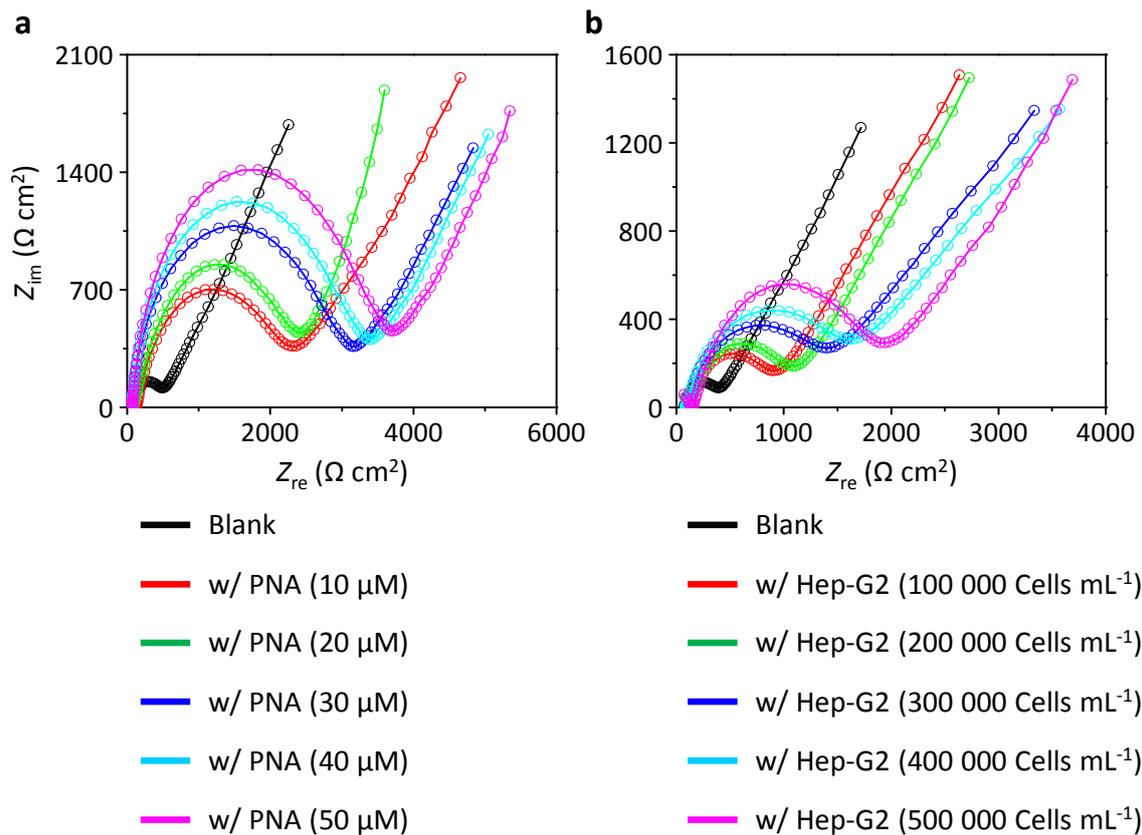


Figure S5. Nyquist plots of 2D composite electrode (blank) in the presence of increasing PNA (peanut agglutinin) and Hep-G2 (human hepatoma) cells obtained with a CHI660E apparatus in the presence of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (5 mM) redox couple in 0.1 M KCl solution with a frequency range of 10 mHz to 100 KHz (perturbation signal: 5 mV). All data collected were fitted with the software ZSimpWin.

S2. Experimental section

General remarks. All purchased chemicals and reagents are of high commercially available grade. Solvents were purified by standard procedures. Ultrapure water was obtained from a Milli-Q integral Pure/Ultrapure Water Production unit. Reactions were monitored by TLC (thin-layer chromatography) using E-Merck aluminum precoated plates of Silica Gel with detection by UV or by spraying with 6 M H₂SO₄ and charring at 300 °C. Pyrene-1-butyrac acid, concanavalin A (Con A), peanut agglutinin (PNA), wheat germ agglutinin (WGA), bovine serum albumin (BSA), and pepsin (Pep) were purchased from Sigma-Aldrich or Shanghai Shrek biotechnology Co., Ltd. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer using tetramethylsilane as the internal standard (chemical shifts in parts per million). HPLC was carried out on an Agilent 1100 HPLC system. High resolution mass spectra (HRMS) were recorded using a Waters LCT Premier XE spectrometer instrument. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. Dynamic light scattering (DLS) was carried out on a Horiba LB-550 Dynamic Light Scattering Nano-Analyzer. Transmission electron microscope was carried out on a JEOL 1400 equipped with a Gatan Orius charged-coupled device camera and Tridiem energy filter operating at 200 kV.

Synthesis of azido pyrene (c). To a solution of pyrene-1-butyrac acid **b** (250 mg, 0.87 mmol) and azido PEG **a** (267 mg, 0.87 mmol) in CH₂Cl₂ (5 mL) were added EDC·HCl (1.2 equiv.) and DMAP (0.5 equiv.). This mixture was stirred at 40 °C (reflux) for 6 h and then diluted with CH₂Cl₂ and washed with brine. The combined organic layer was dried over MgSO₄, filtered and then concentrated in vacuum to give a crude product, which was purified by column chromatography (CH₂Cl₂/MeOH = 30:1, v/v) to afford **c** (355 mg, 71%) as a yellow syrup. *R_f* 0.35 (CH₂Cl₂/MeOH = 10:1, v/v). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.39 (d, *J* = 9.3 Hz, 1H), 8.30–8.25 (m, 2H), 8.25–8.20 (m, 2H), 8.13 (d, *J* = 1.4 Hz, 2H), 8.05 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 4.17–4.13 (m, 2H), 3.62–3.58 (m, 2H), 3.55 (dd, *J* = 5.6, 4.3 Hz, 2H), 3.53–3.45 (m, 8H), 3.45–3.39 (m, 8H), 3.36–3.32 (m, 2H), 3.18 (d, *J* = 5.2 Hz, 2H), 2.09–1.98 (m, 2H), 1.29 (s, 1H), 1.24 (s, 1H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.7, 136.1, 130.8, 130.4, 129.3, 128.1, 127.5, 127.4, 127.2, 126.5(2), 126.1, 124.9, 124.8, 124.2, 124.1, 123.4, 69.7(2), 69.7, 69.6, 69.2, 68.3, 63.1, 54.9, 49.9, 48.6, 33.1, 31.8, 31.1, 29.8, 26.8. HR-ESI-MS (*m/z*): calcd. for [C₃₂H₃₉N₃O₇ + Na]⁺ 600.2686, found 600.2682. HPLC: *t_R* 4.45 min over 12 min of eluent (Methanol/MeCN = 8:2, v/v), purity 99.7%.

Synthesis of azido pyrenyl glycoside (WXB). To a solution of azide **c** (250 mg, 0.43 mmol) and alkyne **d** (113.4 mg, 0.52 mmol) in a solvent mixture of CH₂Cl₂ (10 mL), TBA (1 mL) and H₂O (1 mL) were added CuSO₄·5H₂O (216.4 mg) and Na ascorbate (343.4 mg). This mixture was stirred overnight at room temperature. Then, the resulting mixture was concentrated in vacuum to remove TBA, and then diluted with CH₂Cl₂ and washed with brine. The combined organic layer was dried over MgSO₄, filtered and concentrated in vacuum to give a crude product, which was then purified by column chromatography (CH₂Cl₂/MeOH = 10:1, v/v) to afford **WXB** (138 mg, 42%) as a yellow syrup. ¹H NMR (400 MHz, CDCl₃) δ 8.27–8.24 (d, *J* = 9.2 Hz, 1H), 8.14–8.11 (m, 2H), 8.08–8.05 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.98–7.93 (m, 4H), 7.82–7.80 (d, *J* = 7.8 Hz, 1H), 4.46 (s, 2H), 4.22–4.20 (t, *J* = 4.8 Hz, 2H), 3.76–3.70 (dd, *J* = 10.5, 3.6 Hz, 6H), 3.64–3.56 (m, 3H), 3.55–3.48 (m, 20H), 3.36–3.31 (m, 3H),

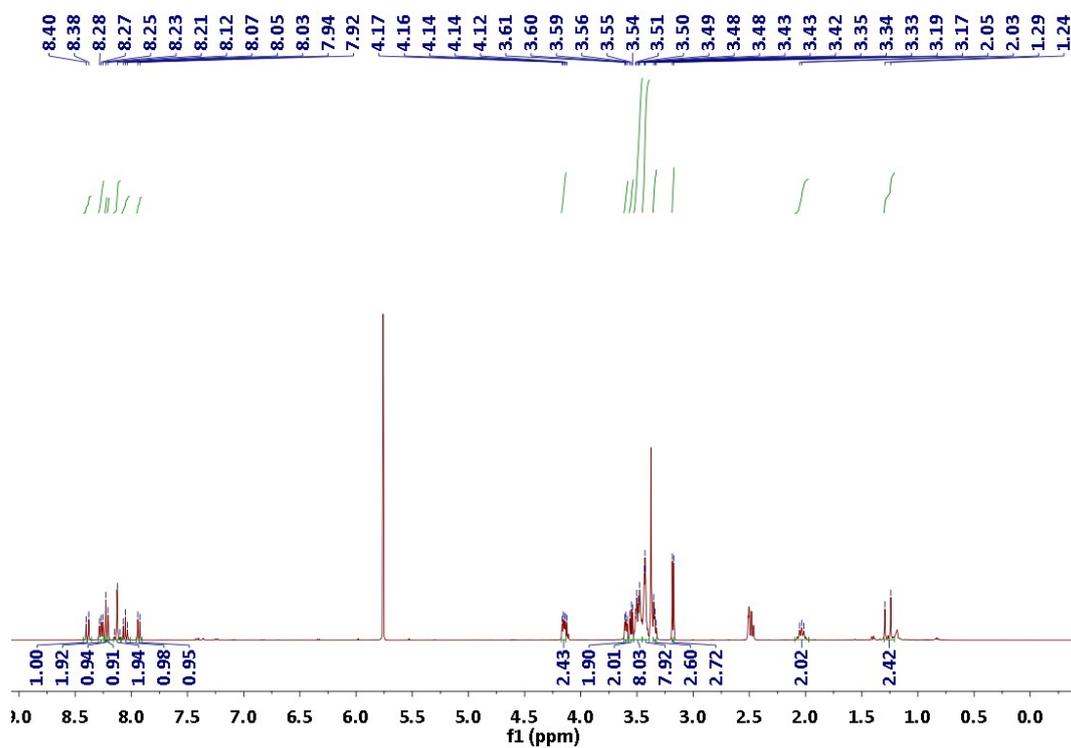
2.47–2.44 (t, $J = 6.0$ Hz, 2H), 2.19–2.11 (m, 4H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 172.7, 143.6, 136.0, 130.8, 130.3, 129.3, 128.1, 127.4, 127.3, 127.2, 126.4(2), 126.0, 124.8, 124.7, 124.4, 124.2, 124.1, 123.3, 102.6, 75.2, 73.4, 70.4(3), 69.7, 69.7, 69.6, 69.5, 69.4, 68.6, 68.2, 68.1, 63.1, 61.3, 60.4, 54.7, 49.2, 33.1, 31.8, 26.7. HR-ESI-MS (m/z): calcd for $\text{C}_{41}\text{H}_{54}\text{N}_3\text{O}_{13}$ 796.3657, found 796.3655. HPLC: t_{R} 4.24 min over 12 min of eluent (Methanol/MeCN = 8:2, v/v), purity 97.4%.

Raman spectroscopy. Raman spectra were performed on a Renishaw InVia Reflex Raman system (Renishaw plc, Wotton-under-Edge, UK) that employs a grating spectrometer with a Peltier-cooled charge-coupled device (CCD) detector coupled to a confocal microscope, and were then processed with Renishaw WiRE 3.2 software. The Raman scattering was excited by an argon ion laser ($\lambda = 514.5$ nm).

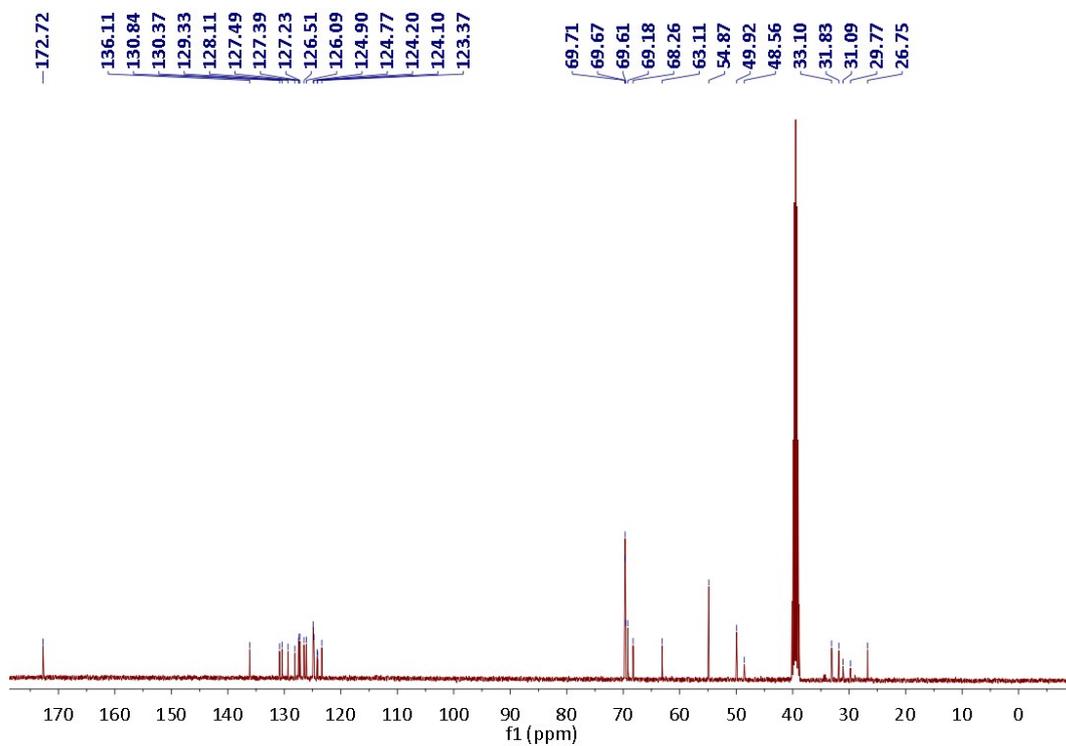
Surface-immobilization of 2D composite. Screen-printed electrodes (SPEs) with a graphite working electrode were used. A drop (4 μL) of 2D MoS_2 ($\mu\text{g mL}^{-1}$) solution (dissolved in Tris-HCl, 0.01 M, pH 7.4, with 1/1000 [w/w] TX-100) was spotted onto the working electrode area of SPE and incubated for 30 min. Then, a drop (4 μL) of **WXB** solution (1 mM) (dissolved in a mixed solvent containing 80% deionized water and 20% methanol) was dripped onto the 2D molybdenum disulfide (MoS_2) coated working electrode area and incubated for 30 min. After rinsing with Tris-HCl (0.01 M, pH 7.4) three times, the electrode was dried at room temperature, and then immersed in degassed Tris-HCl buffer for electrochemical measurement.

Differential pulse voltammetry (DPV). Electrochemical experiments were carried out with a personal computer controlled CHI 1211B electrochemical station (Chenhua Co. Ltd, Shanghai, China). DPVs were performed with an amplitude of 0.1 V, a pulse width of 0.2 s, a standing time of 2 s, and a scanning range from -0.5 V to -0.2 V in the presence of the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ (5 mM) redox couple in 0.1 M KCl solution. For protein and cell detection, a drop (4 μL) of different proteins and cells was spotted onto the working electrode area functionalized with the 2D composite and incubated for 30 min. Then, the working electrode area was rinsed by Tris-HCl (0.01 M, pH 7.4) three times, dried at room temperature, and then immersed in degassed Tris-HCl (0.01 M, pH 7.4) for electrochemical measurements.

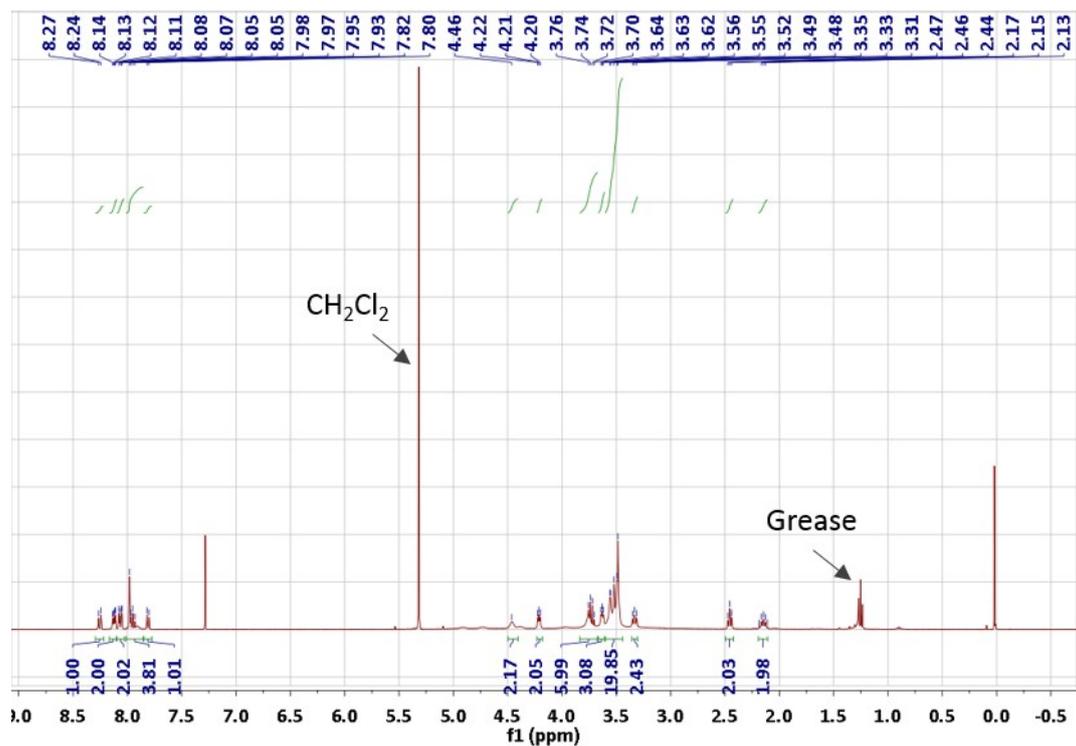
S3. Original spectral copies of new compounds



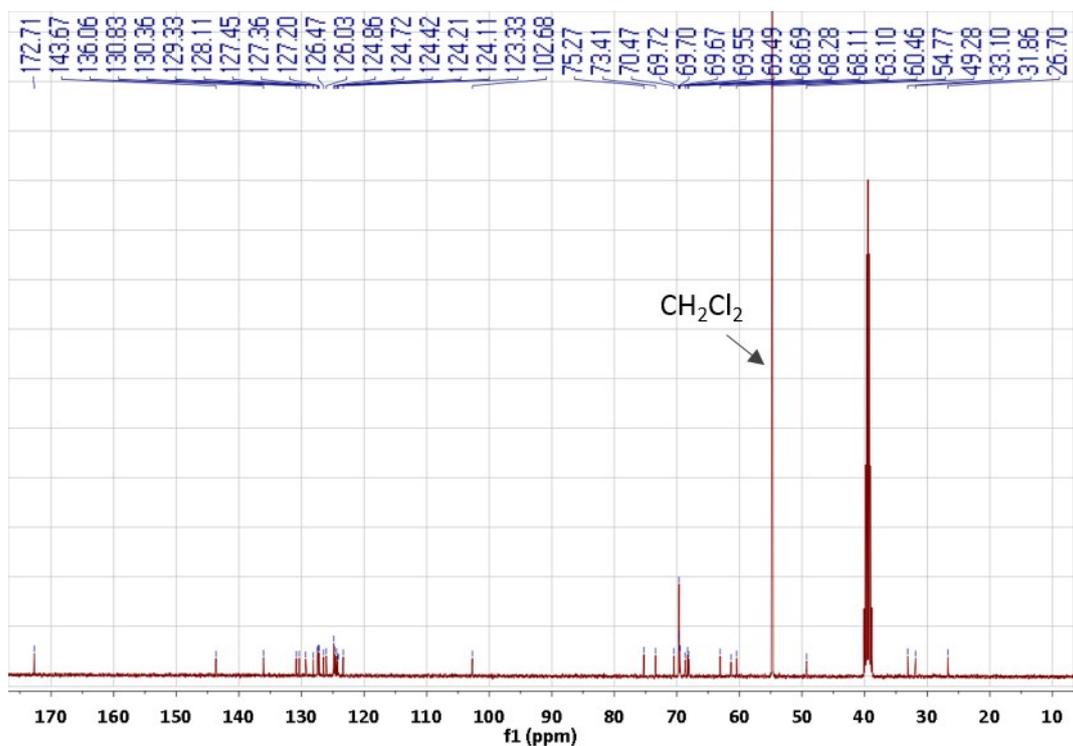
^1H NMR of (c)



^{13}C NMR of (c)



^1H NMR of (WXB)



^{13}C NMR of (WXB)