Electronic Supplementary Material (ESI) for Faraday Discussions.


# Nanocollision mediated electrochemical sensing of host-guest chemistry at a nanoelectrode surface

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**S1. GNE fabrication, modification and characterization**

**S2. Bias dependence of NP impact measurements**

**S3. The statistical lifetime for S and L types of signals obtained from different molecular systems.**

**S4. CB7 mediated molecular recognition of two guest molecules**

## S1. GNE fabrication, modification and characterization

The detail of the GNE fabrication has been described elsewhere[1-4]. In brief, the GNE was prepared from a 0.2 mm diameter gold wire via an electrochemical etching method. The etched GNE has a typical apex radius of ~300 nm. After cleaning, the GNE was partially insulated with a high-density polyethylene (HDPE) coating to achieve the partial insulation. CB7 solution was prepared by dissolving CB7 powders into DI water to a final concentration of 0.5mM. The host-guest complex solution was prepared by mixing the host (CB7) and guest molecule at 1:2 stoichiometry in DI water, followed by a treatment of sonication for ~30 minutes. Ferrocene is less soluble than the other two guest molecules, so the sonication time is prolonged to more than one hour. The concentration of the complexed host-guest solution was 0.5mM[2]. For chemical modification, the insulated GNE was immersed in the molecule solution for at least 12-14 hours at room temperature. The successful modification of CB7 and CB7 based host-guest complexes on GNE is confirmed by means of cyclic voltammetry (CV) as shown in Figure 1A-C. The CV was carried out in 1M KCl solution with 100 mM ferrocyanide ion and the functionalized electrode shows a decrease in diffusion current. Figure S1D shows the UV absorption spectrum with a peak at ~530 nm. The SEM image of a few GNPs is shown in Figure S1E and the statistical histogram of the GNP diameter is ~41.95nm. Because of charging, the GNPs appear slightly bigger than 40 nm. Figure S1F shows a SEM image of a GNE performed after NP-impact experiment. A few GNPs are adsorbed on the surface.

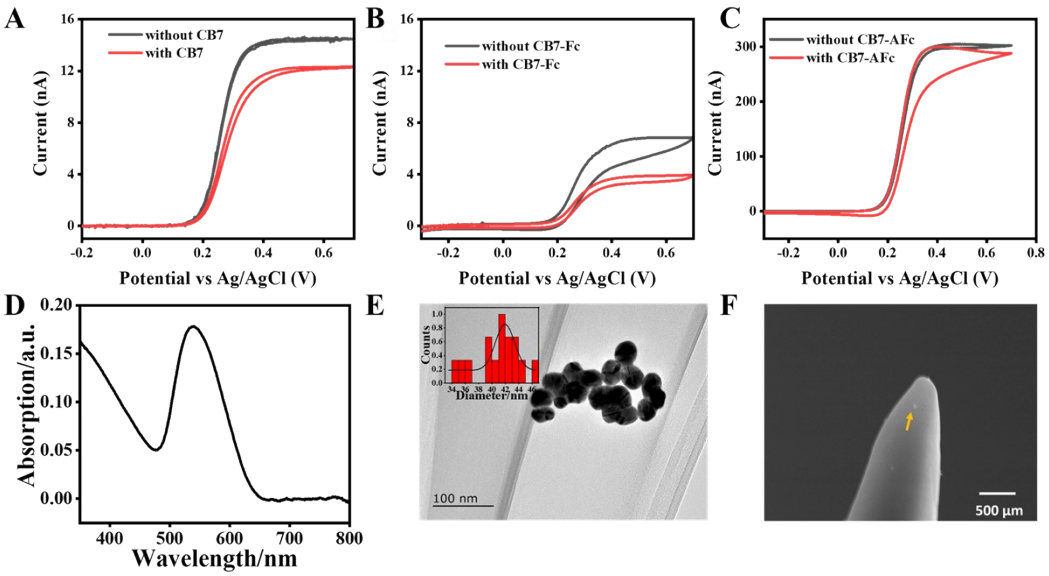


**Figure S1.** CV characterization of the GNE before and after functionalization of CB7 (A), CB7-FC (B) and CB7-AFC (C). (D) The UV absorption spectrum and (E) the SEM image of GNPs. The inset E shows the histogram of the GNP diameter is ~41.95nm. (F)SEM image of a GNE performed after NP-impact experiment showing GNPs adsorbed on the surface.

## S2. Bias dependence of NP impact measurements

To detect the collision event of individual GNPs at the GNE modified with CB7 and its host-guest complexes, we first carried out a series of measurements by monitoring the event counts of current spikes while systematically changing the voltage applied to GNE over a large range. In this way, we obtained the most favorable voltage for the collision event measurement of CB7 and its complexes. Figure S2A displays the event counts of current spikes at different voltage. The event counts are obtained by counting the occurrence of switching signals within 60s. When voltage is smaller than 500 mV, there are no events

observed. As voltage increases, the event counts keep increasing. At 900 mV, the current baseline becomes unstable, as shown in Figure S2B. In this work, we recorded the measurements at a bias voltage of 800 mV

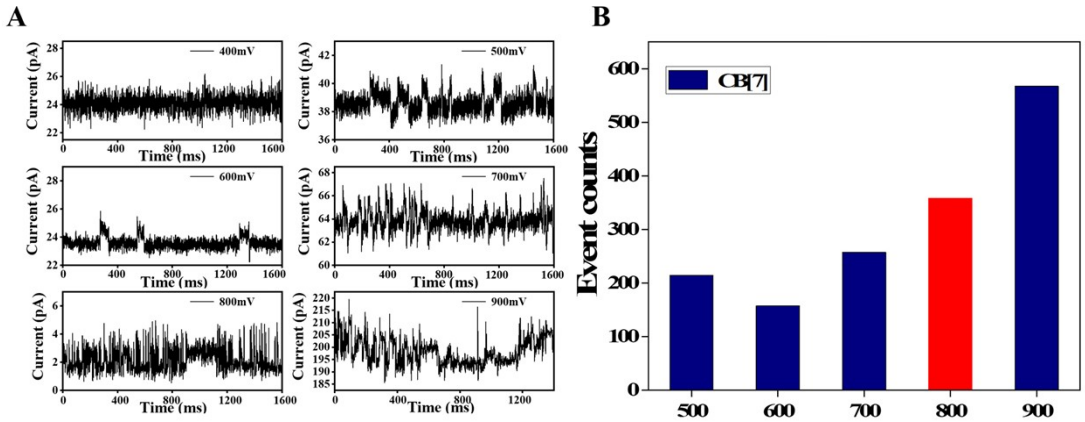


**Figure S2.** A. Typical current-time traces collected at different bias voltages. B. Histograms of event counts at different applied bias.

## S3. The statistical lifetime for S and L types of signals obtained from different molecular systems.

The histograms of the durations of the two types of collision signals for each molecular system are listed in Figure S3 and fitted with Gaussian. There is no much difference in the event lifetime for both types of signals between different chemistry.

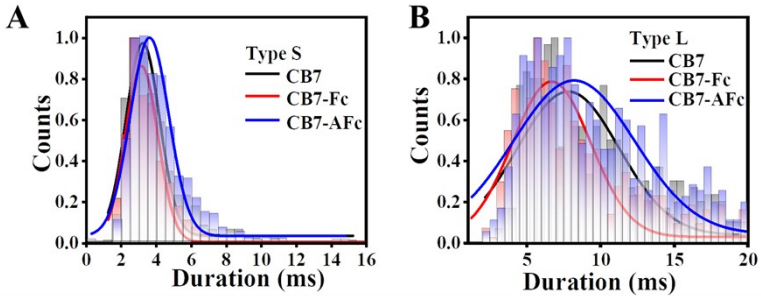


**Figure S3.** Statistical histograms of the lifetime of the type S (A) and type L (B) signals and corresponding Gaussian fittings (solid lines) for three different molecular systems. The histograms are constructed from 1000 events.

## S4. CB7 mediated molecular recognition of two guest molecules

Further experiments are conducted to explore the recognition of different guest molecules in CB[7] modified platform, and the corresponding results are shown in Figure S4. In the first 20 minutes, no guest molecules are present in the testing solution. At 20 min, 1 mM FC was added to the solution and at 40 min 1mM AFC was added. Figure S4 shows the statistical histograms of the amplitude of collected EC current signals recorded and analyzed in every 5 minutes in the above-mentioned testing solution.

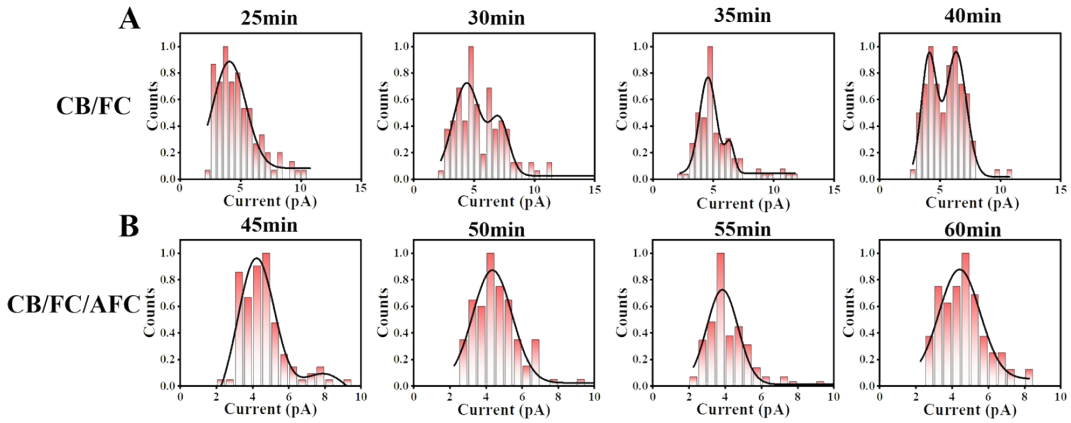


**Figure S4.** Statistical histograms of the peak current amplitude recorded and analyzed in every 5 minutes in a testing solution (5 mM phosphate buffer and 3 mM potassium ferrocyanide, pH = 7.4). 1 mM FC is added at 20 min to the solution and 1 mM AFC is added to the same solution at 40 min.

## Reference


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