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# Dynamic Switching of Ferrocene and Plasmonic Interactions in Au/ Self-Assembled Monolayer/Single Ag Nanocube Molecular Junctions

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Marcus-Landauer model. We determine the highest occupied molecular orbital of the Fc<sup>+</sup> and Fc<sup>0</sup> states at 0.54 and 0.42 eV below the Fermi energy, respectively, with a weak reorganization energy <0.1 eV upon switching. Under plasmonic excitation, the hysteresis and NDC behaviors are no longer observed, and the I-V characteristics of the Au-ferrocenyl-alkylthiol/AgNC junctions become similar to Au-ferrocenyl-alkylthiol SAMs. A virtual molecular orbital due to the plasmon-induced coupling (fast electron transfer) between the two redox states of the Fc is determined at 0.46 eV. This dynamic behavior opens perspectives in artificial synaptic devices for neuromorphic computing with the additional function to turn on/off this synaptic behavior on-demand by light.

# INTRODUCTION

Molecular plasmonic devices belong to a field of research at the interface between physics, nanotechnology, materials science, and molecular engineering. Plasmonic nanostructures are used to improve the light-harvesting efficiency in systems such as solar cells, 1-3 or to improve the efficiency of light harvesting by nanorectennas.<sup>4-7</sup> In data storage and communication technologies, plasmonic waveguides and circuits offer the potential of miniaturized components operating at optical frequencies.<sup>1</sup> In the field of molecular electronics, by incorporating molecules with specific chemical functions into plasmonic nanostructures, we can create devices that respond selectively to different stimuli with foreseen applications for sensors, photonics, and optoelectronics.<sup>8</sup> Plasmon-molecule interactions are subtle, resulting in a large variety of behaviors. Experimental and theoretical results are reviewed in refs 8-10. Many studies have reported the plasmon-assisted increase of the electrical conductance in various molecular junctions (MJs). Among other results, plasmonic enhancement of the current<sup>11</sup> was reported for various molecules and device architectures: in 2D arrays of nanoparticles linked by alkylthiols,<sup>12</sup> oligo-(phenylenevinylene)dithiols<sup>13</sup> and dithiol-Zn-porphyrins;<sup>14</sup> in

"suspended-wire" molecular junctions connecting self-assembled monolayers of alkylthiols;<sup>15,16</sup> down to single-molecule junctions with diaminofluorene.<sup>17</sup> Most of the time, this conductance enhancement is explained by plasmon-assisted tunneling,<sup>18</sup> but bolometric photoconductance can also come into play.<sup>12</sup> Conversely, the conductance of the molecular junctions is able to control quantum charge transfer plasmons.<sup>19,20</sup> The interaction of plasmons with molecular switches can also increase the switching speed (e.g., a  $\approx$ 50% faster switching for diarylethenes due to the plasmonic electric field enhancement),<sup>21</sup> as well as plasmon-induced trans-cis isomerization of azobenzene derivatives at visible light with a faster isomerization kinetics than under the usual UV light illumination (by at least a factor  $\approx 10$ ).<sup>22</sup> However, if the

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molecular spacer between the photochromic moiety and the nanoparticle (e.g., typically an alkyl chain or a  $\pi$ -conjugated oligomer) is too short (<4 carbon atoms in alkyl chains), the photoisomerization is quenched by the surface plasmon resonance.<sup>23,24</sup> Under plasmonic excitation, a redox organic nanowire (PEDOT, poly(3,4-ethylenedioxythiophene)) can be switched from its high to low conductance states with an on/off ratio of  $\approx 10^3$  due to plasmon-induced hot-electron injection from the nanoparticle into the PEDOT nanowire that turns the PEDOT into its insulating reduced state.<sup>25</sup> In the case of a strong plasmon-molecule coupling and the creation of hybrid light-matter states,<sup>26,27</sup> chemical and photochemical reactions are strongly modified, slowing down the rate, or even completely suppressing the photochemical reactions.<sup>28,29</sup>

Ferrocene (Fc) is an archetype of redox molecules with potential applications in molecular electronic nanodevices (see recent reviews in refs 30 and 31). The Fc molecule is an organometallic molecule featuring a single iron atom sandwiched between two cyclopentadienyl rings. The reversible Fe(II)/Fe(III) redox couple provides a very reliable and welldefined electrochemical property, and the Fc molecule is stable under ambient conditions. The functionalization of the cyclopentadienyl rings makes it easy to tune the electrochemical properties of Fc and to allow its insertion in more complex molecular architectures. Focusing on molecular electronics, ferrocene molecules and derivatives have been used in rectifying molecular diodes,<sup>32,33</sup> with a high rectification current ratio (ratio between the forward and reverse currents) up to  $6.3 \times 10^5$ for a specific  $Fc-C \equiv C-Fc$  moiety.<sup>34</sup> The Fc-based molecular diodes were operated at microwave frequencies ( $\approx 20$  GHz) with an extrapolated bandwidth of  $\approx 600$  GHz,<sup>35</sup> making them prone to high-frequency molecular electronics. As a single molecule junction, high conductances, near the conductance quantum  $G_0$  (7.75 × 10<sup>-5</sup> S), were reported ( $\approx 0.7-0.8 G_0$ ) due to low-lying (i.e., very close to the Fermi energy of electrodes, i.e.,  $\approx$ 30 meV) molecular orbitals of the Fc molecules coupled with the metal electrodes.<sup>36,37</sup> A Fc-based light switchable single-molecule device was also recently demonstrated.<sup>38</sup> Upon a photooxidation reaction, a direct metal-metal contact between the oxidized Fe(III) and the gold tip apex is formed (STM break junction in solution), leading to an enhanced conductance with respect to the Au tip/cyclopentadienyl contact (by a factor  $\approx 15$ ).<sup>38</sup> Memory and switching devices were also investigated owing to the bistable redox states of Fc derivatives. Almost all the studied Fc-based molecular junctions used an Au substrate as the bottom electrode and thiol chemistry to graft the molecules on the substrate. From the perspective of integrating Fc-based devices with the mainstream semiconductor technologies, Fc derivatives were also chemically attached to silicon substrates<sup>39–41</sup> for memory and light-stimulated switching applications.<sup>42–44</sup> Memories based on self-assembled monolayers (SAM) of Fc derivatives were reported with the advantage of operating at a low voltage (<1 V) and a high density of charge storage ( $\approx 40 \, \mu C/cm^2$ ) owing to a high surface coverage of Fc molecules ( $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$ ) for densely packed SAMs.<sup>45–47</sup> More recently, Fc molecules were combined with 2D materials for exploring new concepts and nanoscale devices. Using a graphene monolayer as the top electrode, it was possible to decouple the redox electrochemistry and the charge transport in the molecular junction on either side of the graphene layer, resulting in a switching on/off ratio of  $\approx$ 120, the neutral state having a higher conductance than the oxidized state.<sup>48</sup> Ferrocene derivatives were also used to

functionalize 2D transition metal dichalcogenide (e.g.,  $MoS_2$ ) layers and tune the electron transport properties of these 2D materials and devices (e.g.,  $MoS_2$  transistors) depending on the Fc redox state.<sup>49–51</sup> Finally, Fc-based self-assembled diodes, embedded in plasmonic nanostructures, were proposed as a suitable platform for rectenna applications,<sup>52,53</sup> which forms the backdrop to the work reported in the following.

Here, we studied the redox switching of ferrocene moieties embedded in a double tunnel barrier plasmonic cavity, and we compared the electron transport properties of this molecular device in the dark and under light irradiation at the plasmonic resonance wavelengths. In earlier works, hysteresis and negative differential conductance (NDC) in the current-voltage characteristics have been observed in experiments at the nanoscale (STM or C-AFM) on Fc-based MJs. Some authors have attributed the NDC behavior to resonant charge tunneling through a molecular orbital, like in semiconductor resonant tunnel diodes,<sup>54,55</sup> while other works correlated the hysteresis and NDC with the Fc redox switching.<sup>56–59</sup> However, the Fc redox switching interactions with light in a single nanoparticle plasmonic cavity have not been reported to date. The plasmonic MJ was fabricated on ultra-flat gold surfaces covered with a selfassembled monolayer (SAM) of ferrocenyl-alkylthiol. Silver nanocubes (AgNCs), which are capped by an ultrathin layer of poly(vinylpyrrolidone) (PVP), were deposited at a low concentration on the SAM surface so as to obtain single isolated AgNCs. The metallic tip of a conductive-AFM (C-AFM) is used to electrically contact a single Au-ferrocenyl-alkylthiol/AgNC to study its electron transport properties. In the dark, we observed a dual behavior in the current–voltage (I-V) characteristics. Two remarkable features were observed: a large hysteresis loop at positive voltages and a hysteretic NDC at negative voltages. We explained this dual behavior within the framework of a generalized electron transport theory combining the Marcus and Landauer approaches.  $^{60-69}$  With the help of control experiments on the same SAMs (without the AgNC) and SAMs without the ferrocene moieties, these behaviors are explained by the redox switching of ferrocene between its neutral  $(Fc^{0})$  and oxidized  $(Fc^{+})$  states and by the double tunnel barrier structure of the device (alkyl chains and PVP layer). This double barrier configuration induces a weak coupling of the Fc with the electrodes, which increases the lifetime of the Fc<sup>0</sup> state, making it observable. Under plasmonic excitation, the hysteresis and NDC behaviors are suppressed, and the current-voltage curves of the Au-ferrocenyl-alkylthiol/AgNC junctions are quite similar to those recorded on the same Au-ferrocenyl-alkylthiol SAMs directly contacted by the C-AFM tip near the AgNCs. We hypothesize that the plasmonic-enhanced electrical field in the cavity induces a coupling (fast electron transfer) between the two redox states of the Fc, leading to a virtual molecular orbital in the Au-ferrocenyl-alkylthiol/AgNC. This dynamic behavior (hysteresis loop and NDC) opens perspectives in artificial synaptic devices for neuromorphic computing,<sup>70</sup> with the additional function to turn on/off this synaptic behavior ondemand by light in our plasmonic Au-ferrocenyl-alkylthiol/ single AgNC molecular junctions.

## EXPERIMENTAL METHODS

**Molecule Synthesis and SAM Junction Fabrication.** The molecules were commercially available or were synthesized as reported in earlier studies.<sup>71,72</sup> The SAMs were made in two steps as reported elsewhere.<sup>71,72</sup> We prepared ultra-flat template-stripped gold surfaces (<sup>TS</sup>Au), with rms roughness of



**Figure 1.** (a) Scheme (not on scale) of the <sup>TS</sup>Au-S- $C_{8/11}$ -Fc SAM connected by AgNC/C-AFM tip (left) or directly by the C-AFM tip (right), and of the alkyl-Fc molecule. PVP around the AgNC is symbolized in light green. (b) Topographic images of three individual AgNC (nominal size of 60 nm) deposited on the <sup>TS</sup>Au-S- $C_{8/11}$ -Fc SAM. (c) Height profiles (not deconvoluted from the tip shape). The black arrows indicate the nominal size. Two AgNCs have a height and diameter of ca. 60 nm.

 $\sim$ 0.3–04 nm, according to methods already reported.<sup>73–76</sup> The binary SAMs of octane-1-thiol and 11-azidoundecane-1-thiol were prepared on these <sup>TS</sup>Au substrates in solution (1 mM of the two molecules at a 1:1 ratio in ethanol for ca. 1 day). The octane-1-thiol is used as a diluent to favor: (i) a good organization of the alkyl chains in the SAMs and (ii) an efficient grafting of Fc in the second step.<sup>71,72</sup> The second step consists of attaching the ferrocene moieties by click chemistry on the N<sub>3</sub> terminal groups of the 11-azidoundecane-1-thiol available at the SAM surface (see details in refs 71 and 72). The detailed structural characterizations of these SAMs were reported elsewhere (cyclic voltammetry, IR spectroscopy, XPS, ellipsometry, contact angles measurements, refer to "SAM3" and "SAM4" in refs 71 and 72 for the binary SAMs of octane-1-thiol and 11-azidoundecane-1thiol and with the ferrocene moieties after the click reaction, respectively). The thicknesses of the SAMs (spectroscopic ellipsometry measurements see details in the Supporting Information) are  $1.7 \pm 0.2$  nm (without the Fc) and  $2.8 \pm 0.2$ nm with the Fc in reasonable agreement with the expected length of the molecules (1.7 nm for  $SC_{11}N_3$ , 2.6 nm when the ferrocene moiety is added, geometry optimized MM2) and previously reported values for the same SAMs.<sup>71,72</sup> The topographic AFM images (Figure S1) of the SAMs (with and without Fc) reveal flat and homogeneous SAMs, free of gross defects (neither pinhole nor aggregate). The measured rms roughness value for the surface of the  $^{TS}Au-S-C_{8/11}$  SAM is 0.39 nm, and 0.66 nm for the  $^{TS}Au-S-C_{8/11}$ -Fc SAM (see the Supporting Information). Additional XPS measurements were conducted in this work to better characterize the grafting of the molecules on the Au substrate and to determine the charge

states of the ferrocene moieties. They clearly show (see the Supporting Information) the characteristic feature of the S–Au bond, and from the Fe 2p region, we estimated a ratio  $[Fe(III)]/[Fe(II)] \approx 6$ .

Silver Nanocube Synthesis and Deposition on SAMs. Silver nanocubes were synthesized using polyol synthesis. First, 25 mL of ethylene glycol was added to a round-bottom flask and preheated to 160 °C with stirring at 300 rpm. After reaching 160 °C, 300  $\mu$ L of 3 mM sodium hydrosulfide was added. Two minutes later, 2.5 mL of 3 mM hydrochloric acid and 6.25 mL of 20 mg/mL polyvinylpyrrolidone (PVP) were added. Another 2 min later, 2 mL of 282 mM silver trifluoroacetate was introduced. The reaction was quenched in an ice-water bath after 1.5 h for 50 nm nanocubes and 2 h for 60 nm nanocubes. The size of the nanocubes was determined using UV-vis spectrometry. The nanocubes were collected by centrifugation and washed with acetone and deionized water. They were redispersed in water. For further processing, 10  $\mu$ L of the nanocube stock solution was mixed with 100  $\mu$ L of 100 mM sodium borohydride in deionized water for 3-5 min to remove residual PVP. Then,  $2-5 \ \mu L$  of this mixture was drop-cast on Au/SAMs substrates and pressed with a glass coverslip for 2 min. The samples were rinsed with DI water, dried with N<sub>2</sub> gas, resulting in sparse single nanocube deposition.

**Conductive-AFM Measurements.** For the C-AFM measurements, we used a Dimension Icon microscope (Bruker) installed in an air-conditioned laboratory ( $T_{amb} = 22.5$  °C, relative humidity of 35–40%). We used a conductive PtIr metal-plated tip (model RMN-12PT400B from Bruker). The voltage was applied to the <sup>TS</sup>Au substrate, and the C-AFM tip was



**Figure 2.** (a) I-V data set (90 traces) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions. The dark lines are the mean  $\overline{I}-V$  for the forward (red) and backward (blue) traces. (b) I-V data set (156 traces) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/C-AFM tip junction. The back line is the mean  $\overline{I}-V$  from all the traces. The current density scales are calculated with the estimated areas of the AgNC and C-AFM tip, respectively (see the Supporting Information).

grounded. To contact an individual AgNC, we followed a procedure already reported to electrically characterize NCs (of about the same size but of a different chemical nature).<sup>78</sup> In brief, a topographic image in tapping mode (with the PtIr tip) is used to target an isolated AgNC, then we switched from the tapping to contact mode with the tip almost at a stationary point above a given AgNC, the *x*- and *y*-scans turned off (see details of the method in ref 78). We used a loading force of ca. 11-15 nm to ensure a good mechanical contact on the AgNC through the ultrathin PVP layer. Twenty I-V traces were acquired, repeated on 5 different AgNC to build the raw data set (100 I-V traces). For the I-V measurements directly on the SAMs, we defined a square grid of  $10 \times 10$  points (pitch of 50 to 100 nm and at each point, a back and forth I-V curve was acquired (given 200 traces in the raw data set). A smaller loading force is used in that case (3-5 nN). All the *I*-*V*s were acquired at a voltage sweep rate of  $\approx$ 0.5 V/s (otherwise specified). Then, the raw set of *I*-*V* data was inspected and some I-V curves were discarded from the analysis (see details in the Supporting Information). The final number of I-V traces retained for analysis is indicated in the figure captions.

**Light Illumination.** We used LEDs (from ThorLabs, LED MBB1F1 broadband 470–850 nm and LED M470F4 at 470 nm with a fwhm of 20 nm) coupled with a multimode optical fiber (BF20HSMA01, ThorLabs). The output of the optical fiber is placed close to the C-AFM tip (a few cm), and the light has an angle of incidence of  $\approx$ 45°. In this geometrical configuration, the incident light intensity is  $\approx$ 28 W/m<sup>2</sup> for both the broadband LED (almost constant in the 500–800 nm range) and for the M470F4 LED measured at 470 nm (measured with a ThorLabs power meter PM204, the silicon S120VC photodetector being at the position of the sample).

# RESULTS

The MJ is a binary SAM of octane-1-thiols and 11azidoundecane-1-thiols chemisorbed on template-stripped Au (<sup>TS</sup>Au), functionalized in a second step with ferrocene moieties by click chemistry as reported in ref 72 (see Experimental Methods), referred to as <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc. AgNCs (60 nm side length, capped with a 1–3 nm thick layer of PVP)<sup>79</sup> were synthesized (see Experimental Methods), deposited from the solution on the SAMs, and individually connected by a conductive-AFM tip (Figure 1a, see Experimental Methods). The PVP layer provides a coating barrier, preventing the easy oxidation of AgNC. The octane-1-thiol is used as a spacer to control the density of Fc moieties in the SAM<sup>72</sup> and to minimize the  $\pi-\pi$  interactions between neighboring Fc, which disturb the energetics of the Fc in the molecular junctions.<sup>80</sup> Figure 1b,c show a topographic AFM image of a few individual AgNCs deposited on the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc SAM and the corresponding height profile, clearly indicating the presence of individual AgNCs. Ellipsometry and topographic AFM measurements show that homogeneous and compact SAMs are formed on the <sup>TS</sup>Au substrates (see Experimental Methods and the Supporting Information).

Figure 2a shows the back-and-forth current-voltage (I-V)characteristics recorded on 5 <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions (see details in Experimental Methods). The red traces are the forward traces  $(-1 \text{ V} \rightarrow 1 \text{ V})$ , and the backward traces  $(1 \text{ V} \rightarrow -1 \text{ V})$  are in blue. At positive voltages, we observed a large hysteresis between the back-and-forth I-Vtraces and an NDC peak for the negative voltages (only for backward traces, i.e., a hysteretic NDC). The mean on/off ratio (i.e., the current ratio of the mean backward trace over the mean forward one) is high with a maximum value of  $\approx$ 700 (at 0.7 V, see Figure S6 in the Supporting Information). The mean ratio between the peak current (at  $\approx -0.1$  V) and the valley current  $(at \approx -0.4 \text{ V})$  is  $\approx 3$  (Figure 2a). The NDC peak is observed only after having applied positive voltages on the junctions (i.e., no NDC for a back and forth voltage scan limited between -1 and 0 V, Figure S7 in the Supporting Information). As a control experiment, the same SAMs were measured without AgNC by gently contacting the C-AFM tip directly on the SAM near an AgNC (details in Experimental Methods). Figure 2b shows the I-V traces acquired in the same conditions as for the <sup>TS</sup>Au-S- $C_{8/11}$ -Fc/AgNC/C-AFM tip junction (back and forth from -1to 1 V, at the same voltage scan rate  $\approx 0.5$  V/s). The large hysteresis and the NDC feature are no longer observed in that case. To check the role of the ferrocene moiety, we also measured the I-Vs of <sup>TS</sup>Au-S-C<sub>8/11</sub> SAMs directly contacted by the C-AFM tip and with the AgNCs (Figure 4). Again, no large hysteresis nor NDC peak is observed.

The I-V data sets were analyzed by a single energy level (SEL) model.<sup>81,82</sup> This model assumes that the electron transport through the molecular junction is mediated by the molecular orbital, HOMO or LUMO depending on the molecule that is the closest to the Fermi energy of the electrodes. An analytical equation (see the Supporting



**Figure 3.** Histograms of energy level  $\varepsilon_0$  of the molecular orbitals involved in the electron transport. The lines are the fit with Gaussian distributions with the values (mean  $\pm$  standard deviation) given in the panels: (a) <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions, from *I*–*V* data sets shown in Figure 2a (fit only on the backward 1  $\rightarrow$  0 V traces, see the Supporting Information), (b) <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/C-AFM tip junctions, from *I*–*V* data sets (full voltage range) shown in Figure 2b.



**Figure 4.** (a) I-V data set (120 traces) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>/AgNC/C-AFM tip junction. The dark lines are the mean  $\overline{I}-V$  for the forward (red) and backward (blue) traces. (b) I-V data set (49 traces) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>/C-AFM tip junction. The back line is the mean  $\overline{I}-V$  for mall the traces. The current density scales are calculated with the estimated areas of the AgNC and C-AFM tip, respectively (see the Supporting Information). (c,d) Histograms of energy level  $\varepsilon_0$  of the molecular orbitals involved in the electron transport. The lines are the fit with Gaussian distributions with the values (mean  $\pm$  standard deviation) given in the panels: (c) <sup>TS</sup>Au-S-C<sub>8/11</sub>/AgNC/C-AFM tip junctions, from I-V data sets shown in Figure 4a, (d) <sup>TS</sup>Au-S-C<sub>8/11</sub>/C-AFM tip junctions, from I-V data sets shown in Figure 4b.

Information, eq S4) was fit to all the I-V traces of the data set to obtain histograms of the energy level  $\varepsilon_0$  (with respect to the Fermi energy); see details on the fit protocol in the Supporting Information. Figure 3 shows the energy level  $\varepsilon_0$  histograms for the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions and <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/C-AFM tip junctions obtained from the I-V data sets given in Figure 2. Note that for the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions, only the backward traces from 1 to 0 V were used (see details in the Supporting Information, the forward traces cannot be used to the fit due to the large plateau at the sensitivity limit of the experimental setup, the backward curves from 0 to -1 V, which show the NDC effect, cannot be fit with

this model and another model was used in that case, vide infra in the Discussion section). Under this limit, the ET through the  $^{\rm TS}{\rm Au}\text{-}{\rm S}\text{-}{\rm C}_{8/11}\text{-}{\rm Fc}/{\rm Ag}{\rm NC}/{\rm C}\text{-}{\rm AFM}$  tip junction is characterized by a lower energy of the MO  $\varepsilon_0$  (0.42  $\pm$  0.05 eV) than the same SAM directly contacted by the C-AFM tip ( $\varepsilon_0$  = 0.54  $\pm$  0.07 eV). Thus, the top contact with the AgNCs clearly modifies the ET of the  $^{\rm TS}{\rm Au}\text{-}{\rm S}\text{-}{\rm C}_{8/11}\text{-}{\rm Fc}$  SAM.

To further analyze the role of the AgNCs, we have also conducted the same experiments with <sup>TS</sup>Au-S-C<sub>8/11</sub> SAMs without the click chemistry step. Figure 4 shows the I-V data sets and the energy level  $\varepsilon_0$  histograms for the <sup>TS</sup>Au-S-C<sub>8/11</sub>/



**Figure 5.** (a) Typical I-V curves in the dark of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions (other NCs than in Figure 2). Only a few traces were recorded to check the hysteresis and NDC. The dark lines are the mean  $\overline{I}-V$  for the forward (red) and backward (blue) traces. (b) I-V data set (45 traces) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junction under light illumination (470–850 nm wavelength). The back line is the mean  $\overline{I}-V$  from all the traces. (c) Histograms of energy level  $\varepsilon_0$  of the molecular orbitals involved in the electron transport under illumination (SEL model applied on data shown in Figure 5b). The lines are the fit with Gaussian distributions with the values (mean  $\pm$  standard deviation) given in the panel.

AgNC/C-AFM tip and <sup>TS</sup>Au-S-C<sub>8/11</sub>/C-AFM tip junctions (see details for SEL model fits in the Supporting Information). In both cases, almost the same *I*–*Vs* and the same energetics of the molecular junctions were obtained, with  $\varepsilon_0 = 0.71 \pm 0.09$  eV and  $\varepsilon_0 = 0.76 \pm 0.08$  eV with and without the AgNCs, respectively. We only note a small hysteresis with the AgNCs at positive voltages (Figure 4a), which likely induces the larger distribution in the histograms with a tail at high  $\varepsilon_0$  values (Figure 4c).

Under light illumination (see Experimental Methods) of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions, the I-V hysteresis and NDC behavior are suppressed (Figure 5). The I-Vdata set measured under light is similar to the one measured for the same SAMs without the NC, and the SEL analysis gives an energy distribution of the molecular orbital at  $\varepsilon_0 = 0.46 \pm 0.05$ eV (Figure 5c). We have used a broadband light source (wavelengths 450–870 nm, see Experimental Methods) because the plasmonic resonances for these structures are not accurately known. The exact value of the plasmonic resonance wavelengths may vary from single device to device, since the SAM thickness may slightly vary from place to place, as well as the PVP thickness<sup>79</sup> around the AgNC ( $1.5 \pm 0.9$  nm). Nevertheless, the plasmonic excitations are expected to be in the range 600-800 nm<sup>79,83</sup> (see the Supporting Information for simulations). When the same <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions were illuminated with a small bandwidth light source (470 nm, fwhm 20 nm, see Experimental Methods), i.e., outside the plasmon excitation range, both the hysteresis and NDC behaviors are unaffected (Figure S10 in the Supporting Information). We conclude that the excitation of plasmon modes is required to observe the suppression of the hysteresis and NDC.

We also note that the same broadband light illumination on the same SAMs (without the AgNCs) has no effect on the I-Vbehavior (Figure S11). Under our conditions (wavelength and light intensity, see Experimental Methods), there are no detectable photocurrents in the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/C-AFM tip junctions: no HOMO–LUMO gap photoexcitation (the Fc HOMO–LUMO gap is too large  $\approx 2.8$  eV), nor measurable internal photoemission at the molecule/electrode interfaces. Thus, we assume that photocurrents through the SAM play no role and that the observed suppression of the hysteresis and NDC behaviors is related to the plasmonic structure. With an incident light intensity of  $\approx 28$  W/m<sup>2</sup> (see Experimental Methods), the free space ac electric field is  $1.5 \times 10^{-7}$  V/nm (or a light-induced voltage of ca. 0.4  $\mu$ V through the ca. 2.8 nm thick -S-C<sub>8/11</sub>-Fc SAM) and no plasmon-assisted tunneling is expected under the C-AFM tip even with a typical plasmon amplification factor of the electric field of  $10^2-10^4$  in the Au surface/SAM/C-AFM tip MJs.<sup>7,16,84,85</sup>

## DISCUSSION

We first briefly discuss the results for the <sup>TS</sup>Au-S-C<sub>8/11</sub> SAMs. The molecular orbital at ≈0.71-0.76 eV (Figure 4) is in agreement with several results for SAMs of alkylthiols on Au.<sup>86–88</sup> Whether this molecular orbital is the HOMO or the LUMO of the alkylthiol chains,<sup>87,89,90</sup> it is at an energy (with respect to the electrode Fermi energy) larger than the molecular orbital of the ferrocene (see below) and the electron transport through the alkylthiol spacers is off-resonant tunneling, which cannot explain the hysteresis and NDC behavior. The small hysteresis with the AgNCs at positive voltages (Figure 4a) and the tail at high  $\varepsilon_0$  values (Figure 4c) is likely due to charging/ impurity in the PVP tunnel barrier. For the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc SAMs directly connected with the C-AFM tip, the molecular orbital at  $\varepsilon_0 = 0.54 \pm 0.07$  eV (Figure 3b) is consistent with the energy position of the Fc HOMO as determined previously for the same SAMs by CV measurements.<sup>72</sup> It is also in agreement with several other reports for alkyl-Fc SAMs.<sup>32,80,91</sup> Further DFT simulations should confirm the energetics and electron transport properties of these MJs. A majority of the ferrocene are in their oxidized state Fc<sup>+</sup> in these SAMs (see XPS measurements in the Supporting Information, we estimated a ratio  $[Fc^+]/[Fc^0] \approx 6)$  exposed to ambient conditions,<sup>35,80</sup> thus we ascribe the level at 0.54 eV to the HOMO of the oxidized state Fc<sup>+</sup>.

The hysteresis and NDC effects are due to the double tunnel barrier structure of the device (alkyl chains and PVP layer on each side of the Fc layer). Several works have already reported I-V hysteresis loops<sup>56,92–94</sup> and NDC<sup>54,55,57–59,95–97</sup> in MJs with redox molecules.<sup>30</sup> In the case of Fc-based MJs, these earlier experiments have attributed the NDC behavior to resonant charge tunneling through a molecular orbital, by analogy with semiconductor resonant tunnel diodes.<sup>54,55</sup> Other works ascribed the hysteresis and NDC with Fc redox switching.<sup>56,58,59</sup> More generally, these redox-mediated electron transport behaviors can be understood in the framework of combined Marcus and Landauer theories that have been developed by



**Figure 6.** (a) Mean  $\overline{I}$ –V of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC/C-AFM tip junctions (from Figure 2a) and the electron transport scenarios associated with the different parts of the  $\overline{I}$ –V. (b) Schematic energy scheme of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC junction at zero bias with the energy levels of the molecular orbitals as discussed in the text. The molecular orbitals of the alkylthiol C<sub>11</sub> and PVP layers are omitted for clarity. Both have a large band gap (ca. 8–9 and 5–6 eV for the alkylthiol and PVP, respectively) and the electron transport through these spacer layers is dominated by off-resonant tunneling. (c) Electron transport scenario I. From –1 V to V<sub>th</sub>, there is no molecular orbital between the Fermi energy of the electrodes (or energy window). Note that in panels b and c, the Fc<sup>+</sup> energy level is stable below the Fermi energy since the molecule is weakly coupled to the electrodes (weak electron transport scenario II. Above V<sub>th</sub>, the Fc<sup>+</sup> energy level enters the energy window defined by the applied voltage and starts switching to Fc<sup>0</sup> adding a resonant electron transport channel. (e) Electron transport scenario III. A majority of ferrocene moieties are in the Fc<sup>0</sup> state. The electron transport occurs through the HOMO of Fc<sup>0</sup>, which is closer to the electrode Fermi energy than the one of Fc<sup>+</sup>. (f) Electron transport scenario IV. At low negative bias (–0.4 to 0 V), the dynamic switching between Fc<sup>0</sup> and Fc<sup>+</sup> gives rise to the NDR peak (see text) until all the ferrocenes turn to the Fc<sup>+</sup> at larger negative voltages (V < -0.4 V) and the system returns to scheme I.

several groups, i.e., Kuznetsov and co-workers, $^{60-63}$  Migliore and Nitzan, $^{64-66}$  and Sowa et al. $^{67-69}$ 

The hysteresis and NDC behaviors shown in Figure 2a are explained considering four electron transport schemes (Figure

Scheme I (Figure 6a,c). Starting the measurement at -1 V, and assuming that the Fc is initially in its oxidized state, Fc<sup>+</sup>, with a HOMO at  $\approx$ 0.54 eV (Figure 6b) below the electrode Fermi energy (vide supra) the electron transport occurs coherently off resonance up to a threshold  $V_{th} \approx 0.7$  V.



**Figure 7.** (a) Fit of the Fc redox switching (part II of the I-V in Figure 5a) and (b) fit of the NDC peak (part IV of the I-V in Figure 5a) with analytical equations based on Marcus–Landauer electron transport theory as developed in ref 64.

Scheme II (Figure 6a,d). Above this  $\approx 0.7$  V threshold, the HOMO approaches the energy window defined by the difference of the Fermi energies of the two electrodes and the electron transport takes place by sequential hopping processes (curved black arrows) and the Fc<sup>+</sup> moieties switch to a neutral state Fc<sup>0</sup> (symbolized by the upward white arrow in Figure 6d), thus a second conduction channel is gradually opened (light red arrows) whereby the electron transport is coherently resonant. This situation has been theoretically described with a two conduction channels model where a "fast" channel (here Fc<sup>0</sup> with the closest HOMO with respect to the Fermi energy) mainly imposes the measured current, and a "slow" channel (here Fc<sup>+</sup> with a deeper HOMO) determines the charge state of the molecule.<sup>66</sup>

Scheme III (Figure 6a,e). The Fc<sup>0</sup> state has a HOMO energy closer to the electrode Fermi levels, ≈0.42 eV (as determined above, Figures 3a and 6b), a larger current is measured through the molecular junction during the backward scan from 1 to 0 V. The smaller energy of the  $Fc^0$  HOMO (with respect to the Fermi energy) is opposite to the classical Gerischer model (oxidized state above the neutral one),<sup>98,99</sup> but this model holds for a semiconductor or metal/redox molecule interface directly in contact with an electrolyte. This is not likely relevant here for a solid-state device with two insulating barriers between the redox molecule and the electrodes. Our energetic picture is in agreement with combined electrochemistry and UPS/XPS experiments on a similar Fc SAM that show the same trend as proposed here.<sup>100</sup> We also note that a similar behavior was observed (UPS experiments and DFT calculations) for a submonolayer of  $C_{60}^{}$  molecules deposited on a thin insulating MoO<sub>3</sub> layer on Au.<sup>101</sup> The cationic C<sub>60</sub> molecules have a higher ionization energy than the neighboring neutral ones due to onsite and intersite Coulomb interactions.

Scheme IV (Figure 6a,f). At very low negative bias, the Fc<sup>0</sup> and Fc<sup>+</sup> HOMOs are close to the Fermi energy and the two conductance channels are competing. Electron detrapping from the Fc<sup>0</sup> state switches the molecules to the Fc<sup>+</sup> state while an electron trapping from the Au electrode switches back to the Fc<sup>0</sup> state until all the ferrocenes turn to the Fc<sup>+</sup> at larger negative voltages (V < -0.4 V) and the system returns to scheme I.

Within the theoretical framework of a generalized Marcus– Landaueur electron transport theory, both I-V hysteresis loops and NDC peaks, qualitatively similar to the ones described in Figure 2, have been simulated (e.g., see Figures 5 and 9 in ref 66). However, these simulations required sophisticated computations.<sup>66</sup> Nevertheless, the Fc<sup>+</sup>/Fc<sup>0</sup> switching (part II of the *I*–*V* curve in Figure 6a) can be fit by the analytical expressions given by eqs (12, 33, 34) developed in ref 64. The fit is shown in Figure 7a with an energy for the redox  $Fc^+/Fc^0$  transition at 0.46 eV and a reorganization energy  $\lambda \approx 0.02$  eV (see details in the Supporting Information). The weak reorganization energy suggests that only the inner-sphere reorganization is involved ( $\approx 0.03$  eV according to ref 97) in this switching process.

For the 0 to -1 V scan, at very low bias (up to the NDC peak at  $\approx -0.1$  V), the electron transport still occurs through the Fc<sup>0</sup> HOMO since we note a similar level of current as the 1 to 0 V branch (light red arrows in Figure 6f). Between  $\approx -0.1$  V and  $\approx$ -0.4 V (the valley of the NDC), we assume a competition between electron detrapping from the Fc<sup>0</sup> to the AgNC (switching back to the Fc<sup>+</sup> state) and electron trapping from the Au substrate (favoring Fc<sup>0</sup> state), scheme IV, symbolized by the double white arrow in Figure 6f and the total current is fixed by the weighted contributions of two conductions channel depending on the concentrations of the two Fc charge states, which evolves with the applied voltage. This is consistent with two-level fluctuations noise measurements on alkyl-ferrocene molecular junctions whereby the rate of Fc oxidation and the rate of Fc<sup>+</sup> reduction are almost equal at a low voltage  $|V| \approx 0.25$ V.<sup>102</sup> Increasing the voltage (abs value), the concentration of Fc<sup>0</sup> gradually decreases while the one of Fc<sup>+</sup> increases. This dynamic switching between the Fc<sup>0</sup> and Fc<sup>+</sup> states gives rise to the observed NDC peak.

We were able to fit the NDC peak (Figure 7b) considering such a two-channel system and the eq 28 in ref 64 (see details in the Supporting Information). The energies for the two channels are  $\varepsilon_1 \approx 0.2$  eV and  $\varepsilon_2 \approx 0.04$  eV, respectively, with a reorganization energy  $\lambda \approx 0.1$  eV. These values are not exactly the same as deduced above from the  $Fc^+/Fc^0$  switch (Figure 7a), but the mechanisms and model are more complex for the NDC effect (see Supporting Information). Moreover, given the restricted voltage range used for the fit (from V = -0.25 to 0 V), these values can be considered as a rough estimate. However, we note that the "fast" second conduction channel is almost resonant with the Fermi energy of the electrodes, and that these values are roughly consistent with the ones (energy 0.17 eV,  $\lambda \approx$ 0.3 eV) derived from real-time redox switching detection measurements, for which a competition between the oxidation and reduction takes place as for the NDC.<sup>102</sup> Below  $\approx -0.4$  V, the ferrocene molecules have completely switched back to the Fc<sup>+</sup> state, and the current returns to an almost similar curve as for the -1 to 0 V scan. These effects are observed because the lifetime of the Fc<sup>0</sup> state is long enough (with respect to the voltage sweep time) due to the presence of the double tunnel barrier. The observation of these hysteretic NDC and large hysteresis loops is made possible because the MJs are in the weak electrode coupling regime, enabling long-lived redox states. When the C-AFM is directly contacting the Fc moiety, this  $Fc^{0}$ lifetime is too short, and we do not observe the hysteresis and NDC effects. An intermediate case was observed for samples of a second batch of <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC samples (fabricated with the same protocol). For these samples, the level of current is higher than for the samples shown in Figure 2a, but the hysteresis at V > 0 has a weaker amplitude and the NDC effect at V < 0 is reduced (Figure S9 in the Supporting Information, the backward mean  $\overline{I} - \overline{V}$  just show a bump because only a small fraction ( $\approx 10\%$ ) of the *I*-*V* traces display a marked NDC effect). Due to the large dispersion of the PVP layer capping the AgNC (transmission electron microscope measurements:  $1.5 \pm$ 0.9 nm),<sup>79</sup> the currents through the PVP layer span over large values (from  $10^{-9}$  A to above  $5x10^{-7}$  A at  $\pm 1$  V, Figure S8 in the Supporting Information). We assume that the higher level of current for batch #2 samples ( $\approx 10^{-8} - 10^{-7}$  A at  $\pm 1$  V) comes from AgNCs with a thinner PVP layer (varying between 1 and 3 nm, see ref 79) than for batch #1 samples  $(I \approx 10^{-10} - 10^{-8} \text{ A at})$  $\pm$  1 V). In that case, the Fc moiety is less isolated from the Ag electrode and the  $Fc^+/Fc^0$  switching is less observable. The determination of the switching kinetics would require detailed voltage pulse experiments. Here we can only estimate that the switching occurs in less than  $\approx 600$  ms (i.e., the voltage window of  $\approx 0.3$  V for zones II and IV in the *I*–*V*, Figure 6a, divided by the voltage sweep rate of 0.5 V/s). This upper limit is not in disagreement with the switching time constant of  $\approx 100$  ms determined from CV measurements.<sup>72</sup> The asymmetric behavior (hysteresis at V > 0 vs. NDC at V < 0), as well as the slightly different values for the redox and reorganization energies, are likely due to the asymmetry of the tunnel barriers (electron injection through PVP at V > 0 and undecanethiol at V < 0), the exact density of charges in the ferrocene layer (when in the Fc<sup>+</sup> state), resulting in different potential landscape across these barriers, all these parameters determining how the HOMOs of Fc<sup>0</sup> and Fc<sup>+</sup> states align with the electrode Fermi energy windows imposed by the applied voltage.

Under plasmon excitation, it was theoretically predicted that the interaction of a surface plasmon polariton and a two-level molecular system can reduce the conductance through the molecular junctions.<sup>103,104</sup> Such a current decrease is not clearly observed (Figure 5). We propose that the plasmon-enhanced field in the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/AgNC cavity (a factor ca. 70–140, see the Supporting Information) increases the Fc<sup>+</sup>/Fc<sup>0</sup> redox switching rates (as observed for molecular photochromic switches  $\tilde{\textbf{)}}^{21}$  and that the switching is no longer observable since the state lifetimes are faster than the typical time-scale of the I-V measurements as it is the case for the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/ C-AFM tip junctions. The I-V data set of the <sup>TS</sup>Au-S-C<sub>8/11</sub>-Fc/ AgNC/C-AFM tip under light (Figure 5b) was analyzed with the SEL model, leading to a molecular orbital energy distribution (Figure 5c)  $\varepsilon_{0,light} = 0.46 \pm 0.05$  eV. We note that this energy level lies between the  $Fc^+$  (at 0. 54 eV) and the  $Fc^0$ (at 0.42 eV) states determined in the dark (Figure 6b) suggesting that this level might be a virtual molecular orbital due to the plasmon-induced coupling (fast electron transfer) between the two redox states of the Fc. Finally, in all our experiments with light, a thermal effect can be excluded considering the low light intensity ( $\approx 28 \text{ W/m}^2$ ) compared to

previous experiments reporting bolometric plasmon enhanced photocurrent ( $\approx 10^7 \text{ W/m}^2$ ).<sup>12</sup> Further theoretical works will be appealing to comfort the proposed plasmon-assisted mechanism for the suppression of the hysteresis and NDC behaviors.

## CONCLUSIONS

We have observed the dynamic switching of the ferrocene moiety  $(Fc^0/Fc^+$  states) in a double-barrier molecular junction when the ferrocene is connected to the Au electrode and the Ag nanocube through two insulating ultrathin layers (a selfassembled monolayer of alkylthiols and a PVP layer, respectively). This switching manifests in the current-voltage curves as a large hysteresis behavior at positive voltages and as a negative differential conductance behavior at negative voltages. We have suggested a phenomenological model to explain these behaviors. Further experiments are now required to confirm this model, e.g., dependence on the alkyl chain length, PVP thickness (thinner the barrier, faster the lifetime), effect of temperature (lower the temperature, slower the lifetime, if the switching is thermally activated), and voltage pulse experiments to determine the switching rates. This dual behavior opens perspectives to use these Au-ferrocenyl-alkylthiol/AgNC molecular junctions as artificial synaptic devices for neuromorphic computing.<sup>70</sup> When light at plasmonic resonance is shone on the devices, the current hysteresis loop and the NDC behaviors are suppressed, likely due to plasmon-induced fast electron transfer between the two redox states (lifetime reduction of the states).

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.4c07890.

Ellipsometry, topographic AFM images, protocol for conductive-AFM measurements, C-AFM contact area, number of molecules contacted, details on the fits of the I-V curves with the analytical SEL model, fits of the Fc switching and NDC behaviors, additional plots and control experiments, additional data under light illumination, XPS measurements, and plasmonic simulations (PDF)

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## **Author Contributions**

M.B.Y. did all the electrical measurements. P.P., O.M., and B.S. synthesized the silver nanocubes and developed the deposition protocol on SAMs. H.B. and D.G. synthesized the molecules and the SAMs. H.A.-Y. and J.L.R. prepared the <sup>TS</sup>Au substrates. H.A.-Y., J.L.R., and D.D. did the plasmonic simulations. M.B.Y. and D.V. analyzed the data. The manuscript was written by D.V. with the contributions and comments of all the authors. All authors have given approval of the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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