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Quantitative Exploration of Electron Transfer in a Single Noncovalent Supramolecular Assembly

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Supporting Information

ABSTRACT: Electron transfer through a noncovalent interaction bears essential relevance to the functions of bottom-up supramolecular assembly. However, rather little knowledge regarding such phenomena at the single-molecule level is currently available. Herein we report the direct quantification of electron-transfer processes for a single noncovalently linked porphyrin–fullerene dyad. Facilitated electron transfer via a charge-transfer interaction in-between was successfully measured by utilizing a fullerene molecular tip. The rectification property of the supramolecular assembly was determined and quantitatively assessed. The present study opens up a way to explore quantitatively the rich electronic properties of supramolecules at the single-molecule level.

Supramolecular donor–acceptor dyads constitute a versatile class of molecular assemblies with a variety of attractive electronic properties for molecular electronics, solar energy conversion, and catalytic and sensing applications.[1] Porphyrin–fullerene dyads are among the most extensively studied systems because of their rich photo- and redox chemistry. Electronic interactions and electron transfer between the porphyrin and fullerene in solution have been well explored and documented through ensemble measurements.[2] Recently, there have been significant advances in the measurement of electron transport through single molecules.[3] Break-junction and similar methodologies based on scanning tunneling microscopy (STM) have been successfully applied to electron-transport measurements.[4] These studies have deepened the understanding of electronic functions of molecules, including porphyrins[5] and fullerenes,[6] at the single-molecule level, which is vital for rational construction of molecular entities and nanostructures with sophisticated functionality. For example, the single-molecule conductance of a covalently bound porphyrin–fullerene dyad was measured under light illumination, allowing the observation of a long-lived charge-separated state.[7] However, knowledge concerning electron transfer between the single molecules within an assembly of single molecules interacting noncovalently, including supramolecular donor–acceptor dyads, remains severely limited. To date, measurements of electron transfer between single molecules via hydrogen bonding[8,9] and aromatic π–π coupling[10] have been reported. Understanding charge transfer within a single supramolecular assembly is critical for building functional electronic devices, especially by a self-assembly or bottom-up process, where spontaneous formation of the supramolecular assembly plays a central role in device construction as well as conferring useful electronic functionalities.[11]

Herein we demonstrate the successful quantification of electron transfer in a single noncovalent porphyrin–fullerene dyad using a fullerene-functionalized STM tip (a C_{60} tip) prepared by chemical modification of the Au tip with a fullerene derivative, *N*-methyl-2-(2-propyldithiophenyl)-fulleropyrrolidine. The sample dyad desirably demonstrates current rectification, which was quantitatively assessed herein at the single-molecule level. A novel method for electrical connection of a sample molecule to a Au substrate for molecular conductance measurements, namely, ligation-mediated coupling, is also introduced. Linking groups (e.g., thiols) that couple the sample with the electrodes are mandatory for conventional conductance measurements and are currently the subject of extensive research in the field of molecular electronics.[12] In contrast to the conventional approach, the ligation-mediated coupling protocol facilitates the detection of electron transfer without the use of a linking group and thus without chemical modification of the sample porphyrin.

Initially, electron transfer between the fullerene and porphyrin was measured using the C_{60} tip and 5,10,15,20-tetraphenylporphyrinatocobalt (CoTPP) directly adsorbed on a Au(111) surface (Figure 1a). The C_{60} tip was brought into

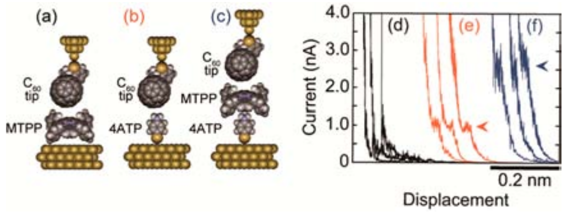

Figure 1. (a–c) Schematic illustration of molecular junctions created using a C_{60} tip. Sample surfaces: (a) MTPP directly adsorbed on Au; (b) 4ATP chemisorbed on Au; (c) MTPP axially ligated with 4ATP chemisorbed on Au. MTPP stands for a metallotetraphenylporphyrin, and M is either Co or Zn. (d–f) Representative *I*–*z* traces for the molecular junctions presented in (a–c), respectively. Each plot has been horizontally shifted for clarity. Arrowheads indicate plateaus. Bias voltage = −0.5 V (sample negative); initial set-point current = 7.5 nA.

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close proximity to, but not into contact with, the CoTPP-modified surface. This procedure was achieved by applying a large set-point current (7.5 nA) in the STM feedback control. The C_{60} tip was then pulled up with the feedback disabled, and current−distance ($I-z$) traces were recorded. These conditions prevented direct contact between the tip and substrate, unlike in break-junction techniques,[4] but it has been shown that molecular junctions can be formed at set-point currents of several nanoamperes.[13] Nonetheless, in the present measurements, the $I-z$ traces exhibited no plateaus (constant-current regions), indicating that no molecular junctions were formed. In addition, the $I-z$ curves were significantly noisy compared with those measured using the C_{60} tip and an unmodified Au substrate (Figure S1 in the Supporting Information), which may be indicative of supramolecular fullerene−porphyrin association. The absence of plateaus may be ascribed to insufficient electronic coupling between CoTPP and the Au(111) surface. Terminal linking groups in the sample molecule are generally required for electronic coupling with the electrodes in single-molecule conductance measurements. However, CoTPP bears no linking group, and thus, the requisite electronic coupling with the Au substrate could not be established.

Rather than introducing linking groups into the sample porphyrin, an alternative protocol for electrical connection of the molecule with the electrode was developed for the single-molecule conductance measurements: ligation-mediated coupling. The Au(111) surface was initially modified with 4-aminothiophenol (4ATP) via S−Au chemisorption. The 4ATP-modified substrate was washed and then immersed in a solution of CoTPP. This resulted in immobilization of CoTPP on the Au surface by 4ATP through axial ligation,[14,15] with consequent formation of the molecular assembly depicted in Figure 1c. Adsorption of CoTPP on the Au surface was confirmed via transmission UV/vis spectroscopy (Figure S2).

We first investigated the electron transfer between the C_{60} tip and 4ATP without CoTPP ligation. The current measurements depicted in Figure 1b gave rise to $I-z$ curves characterized by plateaus (Figure 1e). These plateaus indicate the formation of a molecular junction consisting of fullerene on the tip and ATP on the substrate via noncovalent interaction and successive electron transfer. For statistical analysis, a current histogram was constructed from the I values for the data points in the $I-z$ curves (Figure 2a). In this procedure, $I-z$ curves that showed plateaus longer than 0.02 nm were selected, and at least 1500 selected curves were included in constructing the histogram. A single pronounced peak on an exponentially decaying background was evident, and the position of the peak corresponded to the statistical current value at which the plateaus were observed in the $I-z$ curves (Figure 1e). On the basis of the peak current of 0.99 nA determined by fitting the histogram, the conductance of the fullerene−ATP molecular junction was 2.0 nS (or $2.6 \times 10^{-5} G_0$, where G_0 is the fundamental conductance quantum). The formation of the molecular junction is ascribed to a charge-transfer interaction between the two constituent molecules. Small association constants[16] and very weak intermolecular charge-transfer interactions[17] were previously reported for fullerene−aniline noncovalent assemblies. However, the close proximity between the C_{60} moiety and 4ATP achieved herein under STM mechanical control facilitated the weak charge-transfer interaction. Although an amine group is a suitable linking group for single-molecule conductance measurements,[12] control experiments excluded the possibility of direct contact between 4ATP and the Au tip under the fullerene adlayer (Figure S3).

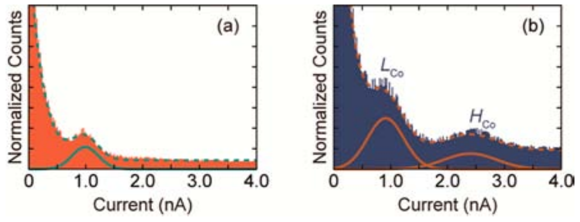

Figure 2. Current histograms constructed from the $I-z$ traces measured using a C_{60} tip and (a) 4ATP chemisorbed on Au or (b) CoTPP axially ligated with 4ATP chemisorbed on Au. Bin size = 10 pA. Total fitting curves (dashed lines) and Gaussian fitting components (solid lines) are also shown.

We next turned to quantifying the electron transfer for the single-molecular assembly comprising the fullerene and porphyrin. $I-z$ measurements were performed using the C_{60} tip and a sample surface on which CoTPP was adsorbed via axial ligation to chemisorbed 4ATP (Figure 1c). Steplike plateaus were apparent in the $I-z$ curves (Figure 1f), and the current histogram complied from the $I-z$ curves clearly exhibited two peaks (Figure 2b). Thus, two Gaussian functions along with an exponential decay having a constant offset were used to fit the histogram. These functions fit the data very well, and the current (conductance) values for the peaks at higher and lower current in Figure 2b (labeled "H_{Co}" and "L_{Co}", respectively) were 2.4 nA (4.8 nS, $6.2 \times 10^{-5} G_0$) and 0.91 nA (1.8 nS, $2.4 \times 10^{-5} G_0$), respectively. The L_{Co} peak agrees with the peak in Figure 2a and is therefore attributed to electron transfer through a molecular junction containing the fullerene and 4ATP devoid of CoTPP ligation. In the $I-z$ curves, the plateau at the L_{Co} peak current always appeared without the plateau at the H_{Co} peak current. This observation supports the assignment of the L_{Co} peak (Figure S4). In contrast, the H_{Co} peak appeared only when CoTPP was adsorbed on 4ATP by axial ligation and should thus be associated with CoTPP. No plateau was observed in the $I-z$ traces of control experiments carried out for the same sample composition (CoTPP on chemisorbed 4ATP) using unmodified Au tips. Taken together, these results indicate that electron transfer between the C_{60} tip and CoTPP gave rise to the H_{Co} peak. Thus, the conductance of the molecular junction consisting of the fullerene and porphyrin was successfully determined by the use of the C_{60} tip and ligation-mediated coupling of the porphyrin. It has been suggested that the molecular plane of cobalt porphyrin ligated by 4ATP on Au(111) is tilted with respect to the substrate surface.[15] In the present measurements, the fullerene and the tilted porphyrin were mechanically forced into a face-to-face arrangement, which is favorable for the charge-transfer interaction, as has been demonstrated for elegantly designed fullerene−porphyrin dyads.[18] Since the porphyrin possesses conformational freedom induced by ligation via 4ATP,[15] the CoTPP plane gradually becomes untilted as the molecular junction stretches out during the pulling-up movement of the tip in the $I-z$ measurements, resulting in the junction structure shown in Figure 1c. The conductance of the molecular junction was *larger* with CoTPP ligation than without such ligation (Figure 2; also see Figure 4), despite the fact that the junction length was *increased* by ligation. This is notable because single-molecule conductance generally *decreases exponentially* with *increasing* molecular length.[3,4] The favorable charge-transfer interaction between the fullerene and porphyrin compared with the weak interaction between the fullerene and 4ATP is the most probable cause of this anomalous behavior.

The detection of electron transfer for a single porphyrin−fullerene dyad was further substantiated by using 5,10,15,20-tetraphenylporphyrinatozinc (ZnTPP) axially ligated to 4ATP adsorbed on the Au substrate instead of CoTPP, which also gave rise to plateaus in the $I-z$ curves (Figure S5); the current histogram constructed from these data is presented in Figure 3.

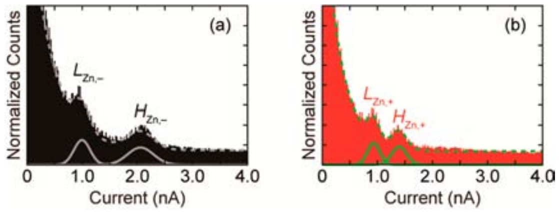

Figure 3. Current histogram constructed from the $I-z$ traces measured using a C_{60} tip and ZnTPP axially ligated with 4ATP chemisorbed on Au. Bias voltages: (a) −0.5 V (sample negative); (b) +0.5 V (sample positive). Initial set-point current = 7.5 nA; bin size = 10 pA. Total fitting curves (dashed lines) and Gaussian fitting components (solid lines) are also shown.

Under a sample-negative bias voltage as used in Figure 2, two clear peaks were observed (Figure 3a). By the fitting procedure used for analysis of the histogram in Figure 2b, the current (conductance) values for the peaks at higher and lower current (labeled "$H_{Zn,-}$" and "$L_{Zn,-}$", respectively) were found to be 2.1 nA (4.1 nS, $5.3 \times 10^{-5} G_0$) and 1.0 nA (2.0 nS, $2.6 \times 10^{-5} G_0$), respectively. The $L_{Zn,-}$ conductance value agrees well with that from Figure 2a and is ascribed to the molecular junction consisting of fullerene and 4ATP without ZnTPP. The $H_{Zn,-}$ peak is assigned to charge transfer between the fullerene and ZnTPP adsorbed on 4ATP, analogous to the CoTPP congener. Comparison of Figure 2b and Figure 3a reveals that the conductance of the molecular junction of the fullerene−CoTPP ligated to 4ATP is higher than that of the ZnTPP counterpart (Figure 4). The higher conductance suggests that the C_{60} moiety of the molecular tip experiences a stronger electronic interaction with CoTPP than with ZnTPP. The favorable interaction in the Co porphyrin−fullerene conjugate compared to the Zn porphyrin−fullerene congener has indeed been confirmed in prior electrochemical studies.[19] In the case of the Co porphyrin, significant interactions between the d orbital of the central Co atom and the p_z orbital of the fullerene carbon atom, in addition to the charge-transfer interactions commonly observed between the metalloporphyrin and the fullerene, enhance the total porphyrin−fullerene interaction.[20]

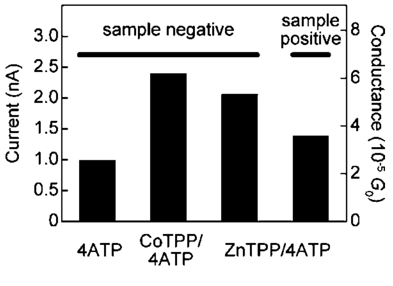

Figure 4. Bar graph of current and conductance values at the peak position in the histograms. Each bar is labeled with the molecular species present on the Au substrate. Slashes represent the axial ligation. The L_{Co}, $L_{Zn,-}$, and $L_{Zn,+}$ peaks are the same as the peak observed for 4ATP and thus have been omitted.

We previously demonstrated the rectification property of a porphyrin−fullerene pair;[21] this characteristic renders the molecular assembly particularly attractive in molecular electronics. Here the rectification was assessed quantitatively. The experimental system was the same as used for the measurements in Figure 3a, but an opposite (sample-positive) bias voltage was applied. Plateaus were observed in these measurements (Figure S5), and two peaks were evident in the current histogram constructed from these $I-z$ curves (Figure 3b). Fitting analogous to that in Figures 2b and 3a gave current (conductance) values of 1.4 nA (2.8 nS, $3.6 \times 10^{-5} G_0$) and 0.93 nA (1.9 nS, $1.9 \times 10^{-5} G_0$) for the peaks at higher and lower current ("$H_{Zn,+}$" and "$L_{Zn,+}$", respectively). The $H_{Zn,+}$ and $L_{Zn,+}$ peaks were again assigned to the molecular junctions containing fullerene and 4ATP with and without ZnTPP ligation, respectively. The $L_{Zn,+}$ peak position is consistent with that in Figure 2a. The value of the current at the $H_{Zn,+}$ peak is considerably lower than that at the $H_{Zn,-}$ peak (Figure 4). Both peaks arise from electron transfer between the fullerene and ZnTPP on 4ATP. Under the sample-positive bias voltage, electrons are transferred from the electron-deficient fullerene to the electron-rich porphyrin. This direction is unfavorable for the molecular diode by the acceptor−donor configuration,[21] leading to the decreased conductance. The asymmetric current flow in Figure 3 was quantitatively estimated by an asymmetry ratio (R), defined as $R = |I(-V)|/|I(V)|$ at a given voltage V. The $I-z$ measurements were conducted at bias voltages ranging from −0.3 to −0.8 and +0.3 to +0.8 V to investigate the R values. The peak currents in the resulting current histograms (Figure S6) depended linearly on the bias voltage over the investigated range (Figure S7a,b), indicating that the tunneling is in the off-resonant regime. Nevertheless, $R = 1.5-1.6$ over the voltage range (Figure S7c), demonstrating the rectifying behavior. Previously, ab initio calculations were performed for fullerene and organic donor complexes. The calculated $I-V$ curves exhibited rectification due to polarity-dependent modification of the electron densities of these molecular assemblies. It was also found that the rectification occurred over a broad voltage range, even at small bias voltages.[22] Those results are consistent with the rectifying properties observed here (Figure S7c). In contrast, rectification was not observed ($R = 1.0$) when the sample surface was modified with non-ZnTPP-ligated 4ATP (Figure S8). Previously, we observed such rectification by scanning tunneling spectroscopy (STS).[21] The present R value agrees with R value of 1.6 over the same bias voltage range obtained by STS. It should be noted that in STS there existed tunneling gap of an unknown width between the porphyrin and fullerene. In contrast, this ambiguity has been eliminated in the present measurements because the measured conductance values arise from the porphyrin−fullerene assembly at the most favorable configuration.[9]

In summary, a molecular tip was used to quantify electron transfer in a single fullerene−porphyrin assembly linked by noncovalent interactions. The novel ligation-mediated coupling technique was developed to connect a porphyrin to a metal substrate without introducing a linking group. The combination of the molecular tip and ligation-mediated coupling enabled quantitative characterization of the conductance and rectification properties of the single fullerene−porphyrin assembly. The present study opens up a way to explore quantitatively the rich electronic properties of supramolecules at the single-molecule level. The present technique can be extended to the detection of photoinduced electron transfer between a porphyrin and fullerene, thereby furnishing useful information at the single-molecule level for the development of organic photovoltaics. Moreover, ligation with a ligand molecule affects the electronic properties of a porphyrin, similar to introducing linking groups into the sample molecule, and therefore, further systematic and theoretical investigations of this effect are required.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

I−*z* curves measured using a C_{60} tip and an unmodified Au substrate, transmission UV/vis spectroscopy of porphyrins axially ligated with 4ATP chemisorbed on Au, control experiments using a Au tip and a 4ATP-modified Au substrate, additional *I*−*z* curves measured using the C_{60} tip and CoTPP axially ligated with 4ATP chemisorbed on Au, *I*−*z* curves measured using the C_{60} tip and ZnTPP axially ligated with 4ATP chemisorbed on Au, current histograms obtained with the C_{60} tip and ZnTPP axially ligated with 4ATP at different bias voltages, current histograms obtained with the C_{60} tip and 4ATP under negative and positive bias voltages, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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