

## Control over Rectification in Supramolecular Tunneling Junctions\*\*

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We report herein the concept of using a supramolecular platform on which dendrimers can be immobilized to result in tunneling junctions formed from assemblies with well-defined structures. In this way, the rectification can be controlled by changing only the chemical structure of the termini of the dendrimers, while minimizing the changes of the whole supramolecular assemblies. This method makes it possible to perform physical organic studies of charge transport across self-assembled monolayer (SAM)-based junctions. These junctions were fabricated by using ultraflat template-stripped Au bottom electrodes (Au<sup>TS</sup>) and liquid-metal top electrodes of an eutectic Ga–In (EGaIn) alloy with a superficial layer of Ga<sub>2</sub>O<sub>3</sub>. Junctions with monolayers of dendrimers that possess terminal moieties with accessible highest occupied molecular orbital (HOMO) levels, such as ferrocene (Fc), immobilized on a supramolecular platform of a self assembled monolayer (SAM) of β-cyclodextrin (βCD), rectified currents with rectification ratios (*R*; at ±2.0 V) that have a log mean value ( $\mu_{\log}$ ) of approximately  $1.7 \times 10^2$  and a log standard deviation<sup>[1]</sup> ( $\sigma_{\log}$ ) of approximately 1.9 [Eq. (1); *J* = current density (A cm<sup>-2</sup>) and *V* = voltage (V)]. In contrast, the junctions with monolayers of dendrimers that possess terminal moieties without accessible HOMO levels, such as adamantyl (Ad), did not rectify currents (*R* = 0.70;  $\sigma_{\log}$  = 2.5), nor did the bare supramolecular platform (*R* = 1.0;

$\sigma_{\log}$  = 3.0). These experiments show that the rectification is dependent on the chemical structures of the molecules in these SAM-based junctions, and that the rectification does not originate from any of the other asymmetries in the junctions or the Ga<sub>2</sub>O<sub>3</sub> layer.<sup>[2]</sup>

$$R = |J|(-2.0 \text{ V})/|J|(2.0 \text{ V}) \quad (1)$$

A fundamental understanding of the mechanism of charge transport in tunneling junctions is important in molecular electronics, and, more broadly, in understanding charge transport through organic matter<sup>[3]</sup> in biochemistry,<sup>[3a]</sup> energy harvesting,<sup>[3b]</sup> information storage,<sup>[3c,d]</sup> and sensing.<sup>[3e]</sup> Studies of charge transport across SAM-based junctions, however, have been difficult because an “ideal” technique to contact SAMs is not available. Potential problems include formation of shorts,<sup>[4]</sup> filaments of metal,<sup>[5]</sup> or altering the molecular and supramolecular structure of the SAMs,<sup>[5a,b]</sup> impeding the formation of working devices in a high yield without defects caused by surface roughness of the electrodes, impurities, pin holes, step edges, or grains.<sup>[6]</sup> Indeed, “working” junctions or devices often are ill-defined terms. Lee and co-workers<sup>[4a,c]</sup> recognized these problems and analyzed large numbers of data statistically to determine yields in working devices, reproducibility, and the mechanism of charge transport in the devices. We believe that physical-organic studies with statistically large numbers of data without “selecting” data are required to account for defects in the junctions, discriminate artifactual data from real data,<sup>[7]</sup> and to determine that the mechanism of charge transport across these junctions, and that the electrical characteristics, such as tunneling, switching, or rectification, of the junctions, are dominated by the molecules inside the junctions.<sup>[2,8]</sup>

Molecular rectification<sup>[9]</sup> has been reported for molecules in a variety of molecular tunneling junctions.<sup>[10]</sup> Overall, the mechanism of charge transport, or if the rectification was caused by the SAMs inside the junctions, could not be unambiguously determined for four main reasons: Firstly, the poorly defined structures of the SAMs make it difficult to study the mechanism of charge transport as a function of molecular structure.<sup>[10b,11]</sup> Secondly, physical organic studies with statistically large numbers of data have not been performed. Thirdly, it has been difficult to acquire large numbers of data because of the instability, low yield, and low reproducibility of the molecular junctions.<sup>[4a]</sup> Finally, some experimental data can be misleading, as molecular junctions that have their top and bottom electrodes fabricated from different materials have the possibility of rectifying in the absence of any structural or asymmetric organic components.<sup>[12]</sup>

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Through the recent development of the  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  technique,<sup>[13]</sup> the difficulty in forming stable, reproducible, molecular tunneling junctions in high yields has been addressed, so that statistically large numbers of data can be accumulated. This technique allowed an investigation of charge transport on SAMs of Fc-functionalized alkanethiolates on template-stripped silver ( $\text{Ag}^{\text{TS}}$ ) with a  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  top electrode. The Fc-functionalized alkanethiolates were found to rectify currents with  $R = 1.0 \times 10^2$  ( $\sigma_{\log} = 3.0$ ) at  $\pm 1.0$  V.<sup>[2]</sup>

We have fabricated supramolecular tunneling junctions comprising SAMs of dendrimers with different termini. The dendrimers are multivalently adsorbed on a supramolecular platform, that is, the  $\beta\text{CD}$  SAM. We have synthesized and characterized these supramolecular systems<sup>[14]</sup> by using AFM,<sup>[14b,c,j]</sup> STM,<sup>[14i]</sup> cyclic voltammetry (CV),<sup>[14b,e-h]</sup> electrochemical impedance spectroscopy (EIS),<sup>[14b,g]</sup> differential pulse voltammetry (DPV),<sup>[14f-h]</sup> scanning electrochemical microscopy (SEM),<sup>[14k]</sup> surface plasmon resonance (SPR),<sup>[14c,f,h]</sup> and SPR and CV combined<sup>[14f,h]</sup> to determine the thickness, molecular orientation, and packing density of the supramolecular platform itself, and the coverage and conformation of the adsorbed dendrimers (including the number of interactions of the dendrimer with the  $\beta\text{CD}$  SAM; Table 1). In addition, Thompson<sup>[15]</sup> has modeled (with molecular dynamics) the adsorption of the Fc dendrimers on the supramolecular platform, and the reported findings support our conclusions. Thus, the supramolecular platform provides optimal control over kinetics and thermodynamics to result in well-defined supramolecular structures immobilized at the Au electrodes (Figure 1). As these supramolecular interactions ( $\beta\text{CD} + \text{guest}$ ) have been reported to be stable in a dry state over prolonged periods (i.e., more than six months),<sup>[16]</sup> we extend the use of the supramolecular platform to perform studies of charge transport across SAMs as a function of chemical composition of the SAM, and to prove that the electrical characteristics are molecular in origin.

Figure 1 shows the construction of the supramolecular tunneling junctions. A well-defined, hexagonally packed SAM of heptathioether-functionalized  $\beta\text{CD}$ <sup>[14a,b]</sup> is formed on  $\text{Au}^{\text{TS}}$  to create the supramolecular platform.  $\text{Au}^{\text{TS}}$  are used as the root-mean-square (RMS) roughness of these surfaces is five times less than that of evaporated surfaces,<sup>[17]</sup> thus ensuring the optimization of the working devices. The use of

dendrimers as guest molecules allows for multivalent host-guest interactions with the supramolecular platform to increase the stability of the supramolecular structures (single  $\beta\text{CD}$ -Fc interactions are too weak to obtain a fully covered  $\beta\text{CD}$  SAM with native Fc). Dendrimer guest molecules with three different terminal functionalities were adsorbed onto the platform: 1) ferrocene, 2) biferrocene (BFc), and 3) adamantyl (Ad). The Fc- and BFc-functionalized dendrimers<sup>[18]</sup> are important for providing molecular orbitals that are spatially asymmetrically located within the junction and energetically accessible (see below), and the Ad-functionalized dendrimers serve as a control. After dendrimer immobilization, or directly after the formation of the supramolecular platform (depending on the desired supramolecular junction), the top contact was applied using the  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  technique.<sup>[13]</sup>

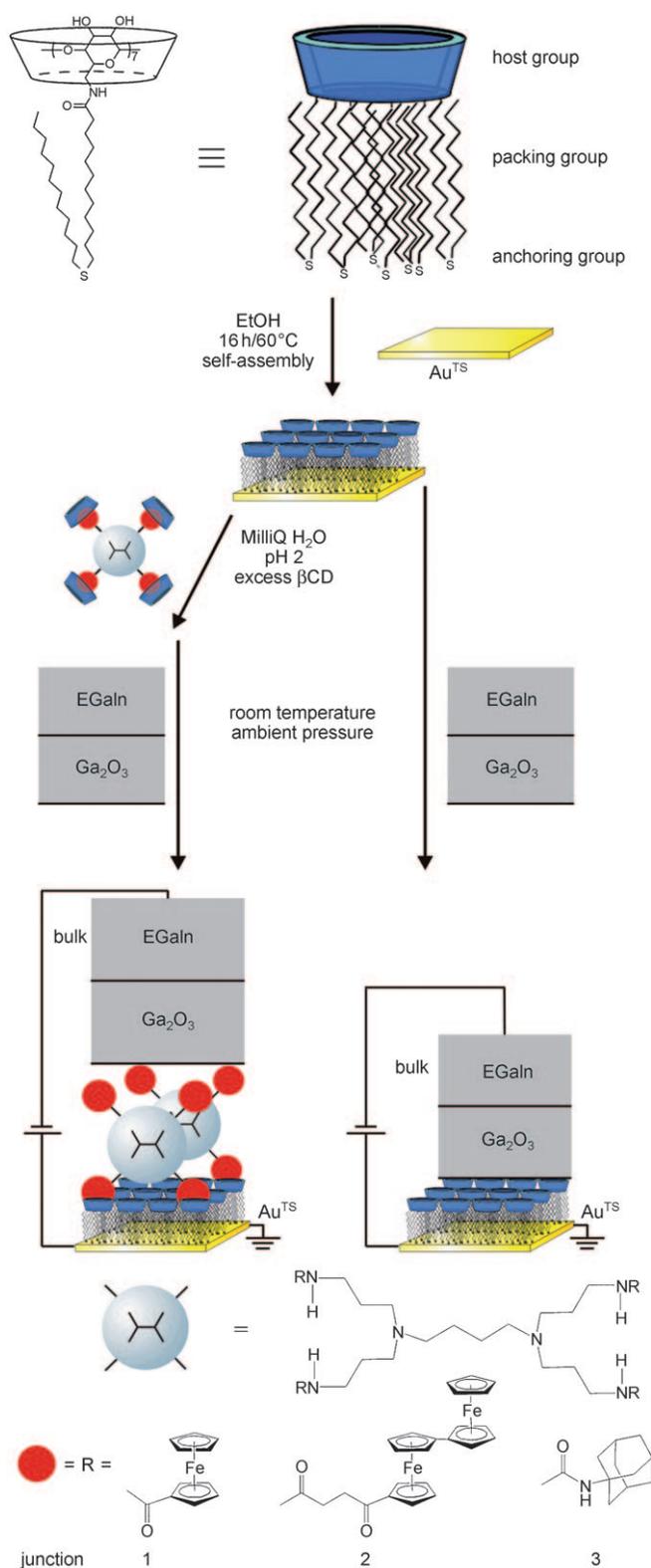
All the junctions are described using the nomenclature  $\text{Au}^{\text{TS}}-\beta\text{CDSAM}/\text{X}/(\text{Ga}_2\text{O}_3)\text{EGaIn}$  where “-” in  $\text{Au}^{\text{TS}}-\beta\text{CD}$  represents the noncovalent interface of the Au surface and the sulfur of the heptathioether functionalized  $\beta\text{CD}$ , “/” represents the supramolecular host-guest interaction between the  $\beta\text{CD}$  and the terminal functional group of the dendrimer, “X” represents the dendrimer, “ $(\text{Ga}_2\text{O}_3)$ ” represents the gallium oxides present on the surface of the EGaIn, and “//” represents the Van der Waals interactions at the interface between the terminal group of the molecular structure and the  $\text{Ga}_2\text{O}_3$  on the surface of the EGaIn.

We investigated four different types of tunneling junctions. Two supramolecular junctions contained Fc moieties: one junction consisted of a generation one ferrocene-functionalized poly(propylene) imine dendrimer ( $\text{G1-PPI}(\text{Fc})_4$ ) immobilized on a  $\beta\text{CD}$  monolayer,  $\text{Au}^{\text{TS}}-\beta\text{CDSAM}/\text{G1-PPI}(\text{Fc})_4/(\text{Ga}_2\text{O}_3)\text{EGaIn}$  (1), and the other consisted of a  $\text{G1-PPI}(\text{BFc})_4$  functionalized dendrimer immobilized on a  $\beta\text{CD}$  monolayer,  $\text{Au}^{\text{TS}}-\beta\text{CDSAM}/\text{G1-PPI}(\text{BFc})_4/(\text{Ga}_2\text{O}_3)\text{EGaIn}$  (2). Two other junctions did not contain ferrocene moieties: one junction consisted of a  $\text{G1-PPI}(\text{Ad})_4$ -functionalized dendrimer immobilized on a  $\beta\text{CD}$  monolayer,  $\text{Au}^{\text{TS}}-\beta\text{CDSAM}/\text{G1-PPI}(\text{Ad})_4/(\text{Ga}_2\text{O}_3)\text{EGaIn}$  (3), and the other was simply the bare  $\beta\text{CD}$  monolayer,  $\text{Au}^{\text{TS}}-\beta\text{CDSAM}/-(\text{Ga}_2\text{O}_3)\text{EGaIn}$  (4) (Figure 1). Junctions 3 and 4 served as control junctions to ensure that any possible characteristic trends seen in the  $J$ - $V$  measurements of junctions 1 and 2 were attributed to the Fc or BFc moieties and did not arise

**Table 1:** Statistical overview of all  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  junctions measured.

Molecular junction	No. of substrates <sup>[a]</sup>	No. of junctions created	No. of working junctions (%)	No. of shorts	No. of unstable junctions	Total scans <sup>[b]</sup>	$R$	Error (68%) <sup>[c]</sup>	No. of interactions with $\beta\text{CD}$ SAM <sup>[d]</sup>	Surface coverage [%] <sup>[e]</sup>
1 (Fc)	4	22	17 (77)	3	2	340	7.7	2.5–24	2	$\approx 89$
2 (BFc)	3	21	20 (95)	1	0	400	$1.7 \times 10^2$	89– $3.2 \times 10^2$	3	$\approx 100$
3 (Ad)	7	30	24 (80)	4	2	480	0.70	0.28– 1.8	2	$> 95$
4 (-)	7	30	25 (83)	4	1	500	1.0	0.33– 3.0	–	–

[a]  $1 \text{ cm} \times 1 \text{ cm}$   $\text{Au}^{\text{TS}}$  surface on glass. [b] Voltage sweep,  $0.0 \text{ V} \rightarrow +2.0 \text{ V} \rightarrow 0.0 \text{ V} \rightarrow -2.0 \text{ V} \rightarrow 0.0 \text{ V}$ . [c] One log standard deviation, i.e., 68% of the data is within one log standard deviation of the log mean. [d] Amount of dendrimer terminal moieties that form host-guest interactions with the  $\beta\text{CD}$  SAM, out of a possible total of four. [e] Surface coverage [%] of the dendrimer adsorbed on the  $\beta\text{CD}$  SAM.



**Figure 1.** Fabrication process of the molecular junctions. The eutectic gallium–indium (EGaIn) is represented with a Ga<sub>2</sub>O<sub>3</sub> layer on the surface.

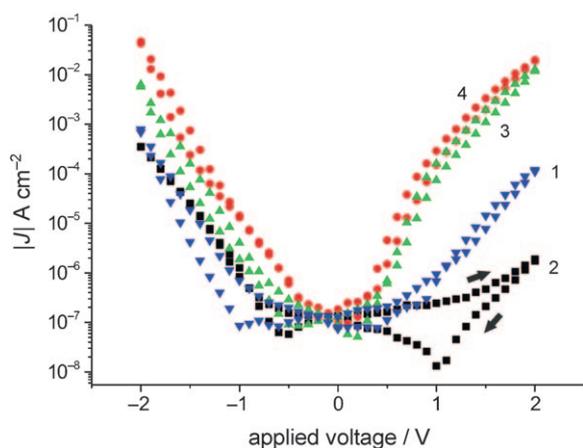
from the supramolecular platform or the additional structural asymmetry created within the supramolecular tunneling junction by adsorbing a dendrimer to the platform.

The (Ga<sub>2</sub>O<sub>3</sub>)EGaIn electrodes are large on the molecular scale (100 to 300 μm<sup>2</sup>),<sup>[13]</sup> therefore these so-called large-area tunneling junctions contain in the order of 10<sup>6</sup>–10<sup>7</sup> molecules within the junction. The junctions in this study, as do all large area junctions, contain defects that arise, for example, from surface roughness of the electrodes (step edges, grains), defects in the SAMs, impurities.<sup>[6–7]</sup> The amount and types of defects vary from junction to junction and from substrate to substrate, so it is essential to collect a statistically large amount of data from different Au<sup>TS</sup> substrates in order to draw significant conclusions.<sup>[4a]</sup> We collected large numbers of data (Table 1) and performed a statistical analysis similar to that reported by Whitesides and co-workers<sup>[2]</sup> (for experimental details and analysis see the Supporting Information).

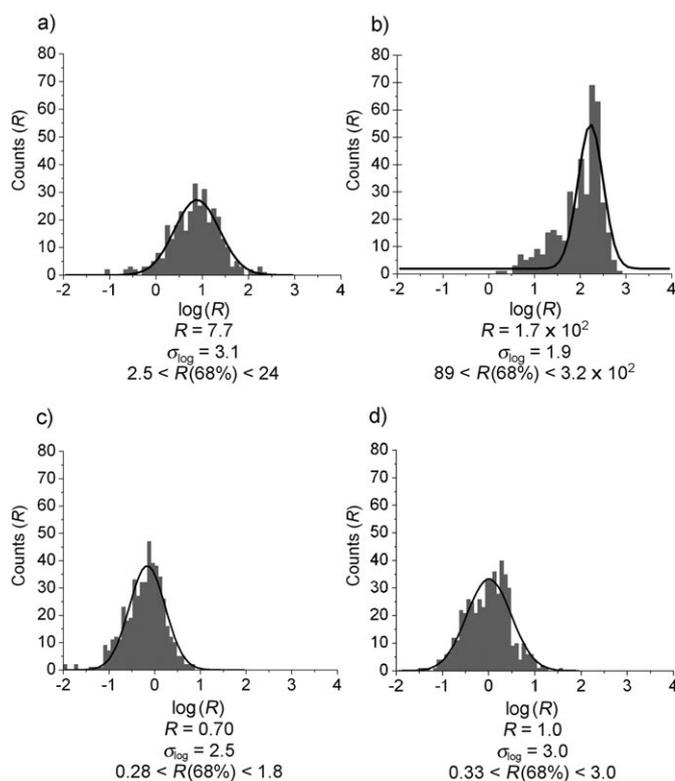
*J–V* measurements were performed by biasing the (Ga<sub>2</sub>O<sub>3</sub>)EGaIn top electrode and connecting the Au bottom electrode to ground. These (Ga<sub>2</sub>O<sub>3</sub>)EGaIn junctions were characterized as either a “working junction” (a junction that gave 20 reproducible scans at ±2.0 V with the current measured being within 3σ<sub>log</sub> of the μ<sub>log</sub> value), a short (a junction that produced an immediate ohmic response, or a junction that suddenly produced an ohmic response during scanning at ±2.0 V), or an “unstable junction” (during the 20 scans at ±2.0 V, the current measured varied greater than 3σ<sub>log</sub> from the μ<sub>log</sub> value; Table 1). When all the junction structures were considered, an average of 80–85 % junctions were formed (Table 1), which is in accordance with other molecular structures measured in (Ga<sub>2</sub>O<sub>3</sub>)EGaIn junctions.<sup>[2,13]</sup>

In Figure 2 the change of the *R* value of all four junctions is clearly seen when comparing when comparing the relative difference in current densities at the outermost voltage points, that is, -2.0 V and +2.0 V. The *R* value [Eq. (1)] was calculated for each individual scan for each junction, and statistically analyzed (Figure 3, see the Supporting Information).<sup>[2]</sup> Junctions 3 and 4 have small *R* values close to unity (Table 1). On the other hand, junctions 1 and 2 have significant *R* values of 7.7 (σ<sub>log</sub> = 3.1)<sup>[19]</sup> and 1.7 × 10<sup>2</sup> (σ<sub>log</sub> = 1.9), respectively. Junction 3 has an *R* value of 0.70 (σ<sub>log</sub> = 2.5) as these junctions, unlike the other junctions, have larger *J* values at positive bias than at a negative bias. It seems that neither the bare supramolecular platform nor the additional asymmetry created within the junction by adsorbing a dendrimer on the supramolecular platform caused rectification. Thus, the significant *R* values of junctions 1 and 2 indicate the Fc or BFc moieties are required for this supramolecular junction to act as a molecular rectifier.

The Fc and BFc-functionalized dendrimers are important for providing a low-lying HOMO level, that is, a HOMO level close to that of the Fermi levels of the electrodes. The HOMO level of the Fc and BFc dendrimers estimated from CV<sup>[14f,h]</sup> (see the Supporting Information) are approximately -5.1 eV and -5.0 eV, respectively, which fulfills the energy level requirement, as the Fermi levels of Au and (Ga<sub>2</sub>O<sub>3</sub>)EGaIn are approximately -5.1 eV and -4.3 eV, respectively. We believe that junctions 1 and 2 rectify current by the mechanism proposed by Baranger and co-workers,<sup>[20]</sup> and Williams and co-workers,<sup>[21]</sup> and more importantly, experimentally confirmed and discussed by Whitesides and co-workers<sup>[2,8,22]</sup> (see



**Figure 2.** Semilog plot of the averaged absolute current density versus voltage for junctions 1–4. The difference in the rectification ratio ( $R$ ) for each junction structure at  $\pm 2.0$  V is apparent. Scan direction is indicated by arrows. (Error bars are not shown for clarity; see the Supporting Information for full statistical analysis and error details.)



**Figure 3.** Histograms of  $\log(R)$  for molecular junctions 1 (a), 2 (b), 3 (c), and 4 (d). All histograms were fitted with a Gaussian curve to obtain the log mean ( $\mu_{\log}$ ) and log standard deviation ( $\sigma_{\log}$ ), thus allowing for the calculation of  $R(68\%)$ .

Figure S3 in the Supporting Information). These studies proposed that an asymmetrically positioned molecular orbital, (either HOMO or lowest unoccupied molecular orbital, LUMO) inside a tunneling junction can rectify current. As our Fc and BFc dendrimers in junctions 1 and 2 are placed spatially asymmetrically inside the junction, that is, close to

and coupled with the  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  top electrode and separated from the  $\text{Au}^{\text{TS}}$  bottom electrode by the  $\beta\text{CD}$  SAM, with HOMO levels that have energies close to that of the Fermi levels of the electrodes, they satisfy the criteria for a molecular rectifying junction (Figure S3 in the Supporting Information).

The large difference of two orders of magnitude in the  $R$  values measured for the Fc- and BFc-functionalized systems is most likely caused by the fact that  $\text{G1-PPI}(\text{Fc})_4$  forms a discontinuous monolayer on the  $\beta\text{CD}$  SAM, while  $\text{G1-PPI}(\text{BFc})_4$  forms a continuous monolayer (Table 1).<sup>[13e–h]</sup> Thus, contacting the sub-monolayer of  $\text{G1-PPI}(\text{Fc})_4$  on the  $\beta\text{CD}$  SAM results in junctions in which the  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  top electrodes form contacts with the  $\text{G1-PPI}(\text{Fc})_4$  dendrimers (ca. 90% per unit area) and with the  $\beta\text{CD}$  SAM (ca. 10% per unit area). The areas where  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  is in contact with the  $\beta\text{CD}$  SAM can be referred to as “thin-area defects”.<sup>[7]</sup> The tunneling current  $J$  decays exponentially with the distance between the two electrodes  $d$  ( $\text{\AA}$ ), as approximated by a simple form of the Simmons equation,  $J = J_0 e^{-\beta d}$  (where  $J_0$  is the current density flowing through the electrode–SAM interfaces in the hypothetical case of  $d = 0$   $\text{\AA}$ , and  $\beta$  ( $\text{\AA}^{-1}$ ) is the decay constant). Consequently, these thin-area defects dominate the measured tunneling current,<sup>[7]</sup> which, in turn, decreases the  $R$  value (see above). Unlike the  $\text{G1-PPI}(\text{Fc})_4$  dendrimer, the  $\text{G1-PPI}(\text{BFc})_4$  dendrimer is able to bind to the supramolecular platform with three out of its four BFc terminal moieties,<sup>[14h]</sup> as the BFc moieties (which are also larger than Fc moieties) are connected to the dendritic core by longer tethers than those used to connect the Fc moieties. This binding results in a densely packed monolayer on the platform, which, in turn, minimizes the formation of direct contact of the top electrode with the  $\beta\text{CD}$  SAM. Consequently, these junctions are dominated by the dendrimers within the molecular junctions and thus rectify more.

Interestingly, we do not understand the differences in the average  $J$  values (see the Supporting Information) or the hysteresis of the supramolecular junctions. However the concept of using a supramolecular platform in tunneling junctions allows us to systematically vary the type of functional dendrimer in the junction and investigate these unclear phenomena, rectification, and the mechanism of charge transport in more detail.

In summary, firstly, a method is presented to fabricate well-defined tunneling junctions. This method allows physical organic studies to be carried out by altering only the end-group functionality of dendrimers anchored on a supramolecular platform while keeping other possible structural changes to a minimum. Secondly, the stability of the junctions permits the accumulation of statistically large amounts of data, thus allowing a statistical analysis to account for defects in the junctions. Thirdly, our physical organic study shows that the rectification is induced by the Fc and BFc moieties, which are positioned asymmetrically inside the junction, and is of molecular origin and is not due to any other asymmetries in the junction. Finally, we control the rectification ratio by changing the end-group functionality of the dendrimer. We are currently further exploiting these supramolecular surface interactions in  $(\text{Ga}_2\text{O}_3)\text{EGaIn}$  tunneling junctions by varying

the dendrimer generation and core type, with a possible additional variation in functionality. This variation will allow for the rectification within the supramolecular junction to be further controlled and contribute to the fundamental understanding of charge transport in molecular tunneling junctions.

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- [1] 68% of the distribution of  $R$  lies within one log standard deviation ( $\sigma_{\log}$ ) of the log mean ( $\mu_{\log}$ ), for example if  $\mu_{\log} = 1.7 \times 10^2$  and  $\sigma_{\log} = 1.9$  than 68% of the distribution of  $R$  ( $R(68\%)$ ) lies within the range of 89 ( $1.7 \times 10^2/1.9$ ) and  $3.2 \times 10^2$  ( $1.7 \times 10^2 \times 1.9$ ).
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