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Thiol-free self-assembled oligoethylene glycols enable robust air-stable molecular electronics

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Self-assembled monolayers (SAMs) are widely used to engineer the surface properties of metals. The relatively simple and versatile chemistry of metal-thiolate bonds makes thiolate SAMs the preferred option in a range of applications, yet fragility and a tendency to oxidize in air limit their long-term use. Here, we report the formation of thiol-free self-assembled mono- and bilayers of glycol ethers, which bind to the surface of coinage metals through the spontaneous chemisorption of glycol ether-functionalized fullerenes. As-prepared assemblies are bilayers presenting fullerene cages at both the substrate and ambient interface. Subsequent exposure to functionalized glycol ethers displaces the topmost layer of glycol ether-functionalized fullerenes, and the resulting assemblies expose functional groups to the ambient interface. These layers exhibit the key properties of thiolate SAMs, yet they are stable to ambient conditions for several weeks, as shown by the performance of tunnelling junctions formed from SAMs of alkyl-functionalized glycol ethers. Glycol ether-functionalized spiropyran incorporated into mixed monolayers lead to reversible, light-driven conductance switching. Self-assemblies of glycol ethers are drop-in replacements for thiolate SAMs that retain all of their useful properties while avoiding the drawbacks of metal-thiolate bonds.

Self-assembled monolayers (SAMs) of thiols are ordered molecular assemblies formed by the spontaneous, covalent attachment of organic thiols onto surfaces, usually zerovalent coinage metals. Due to their relative simplicity and reproducibility and the versatility of organic and organometallic compounds, they have found applications across many scientific and engineering disciplines, for example, non-fouling surfaces¹, lubrication², corrosion resistance³, protein binding⁴, DNA assemblies⁵, cellular signalling and interactions⁶, photovoltaics⁷ and transistors⁸. In the field of molecular electronics, which is concerned with the flow of electrons across individual molecules spanning one or more electrodes, SAMs of thiols play a central role in the shift from fundamental studies of single molecules to static, functional devices by precisely defining the smallest dimensions of molecular junctions via self-assembly^{9–15}. However, their fragility and the spontaneous oxidation of metal–thiolate bonds in air^{16–18} remains a significant impediment to applications outside of the laboratory and their development within.

There are other SAMs that capture many of the useful properties of thiols, for example, carboxylic acids on metal oxides^{19,20}, alcohols²¹, amines²² and isonitriles^{23–25} on Pt and Au, alkynes on Au and Ag^{26,27}, aromatic compounds and amines on graphene^{28,29} and carbenes on Au^{30,31}. Although these SAMs have their own advantages and useful contexts, they are all either less stable than SAMs of thiols or introduce other tradeoffs and, therefore, lack the powerful simplicity of the spontaneous self-assembly of thiols on zerovalent coinage metals. Although encapsulation can physically protect SAMs to make them compatible with conventional semiconductor fabrication techniques³², explicit demonstrations of reproducible, air-stable electronic properties remain exceedingly rare^{33,34}. Moreover, encapsulation adds a layer of complexity and cost that is prohibitive for studies of structure–function relationships, which are already constrained by the significant overhead of organic synthesis.

We propose a robust, air-stable alternative to thiols: SAMs of molecules bearing glycol ether moieties that are attached non-covalently to a fullerene functionalized with triethylene glycol (PTEG-1) that binds to zerovalent coinage metals via the chemisorption of fullerenes to metal surfaces^{35–38}. These glycol ether SAMs (GESAMs) obviate thiols, eliminating sensitivity to oxidation, while retaining all of the useful features of SAMs of thiols. The self-assembly of GESAMs is driven by dipole–dipole interactions between the glycol ether (GE) chains, which lead to the formation of well-defined monolayers supported by a SAM of PTEG-1¹. We prepared myriad GESAMs by in-place exchange, a powerful technique used to make mixed monolayers that is almost exclusive to SAMs of thiols. Tunnelling junctions comprising GESAMs perform identically to their thiolate counterparts, yielding the same tunnelling decay coefficients and injection currents; however, unlike other SAMs, the tunnelling charge transport properties are stable under ambient conditions for weeks, without any special handling or encapsulation. We demonstrate the versatility of GESAMs beyond length dependence through the light-driven conductance switching of GE-functionalized spiropyran moieties. Given the sensitivity of tunnelling junctions to ordering and mechanical stability³⁹, the outstanding performance of GESAMs in tunnelling junctions suggests that they can be used as robust, air-stable replacements for SAMs of thiols in any context.

Mono- and bilayer characterization

The fabrication of GESAMs begins with the formation of a self-assembled bilayer (SAB) of PTEG-1, which we form by immersing freshly prepared, ultrasoft, template-stripped (TS) Au or Pt substrates (Au^{TS} or Pt^{TS}) into a toluene solution of PTEG-1 for 24 h. We hypothesized that the free PTEG-1 molecules in the solution first form a densely packed SAM on the surface of the metal through the strong interactions created by partial ground-state

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Fig. 1 | Characterization of the SAMs and SABs of PTEG-1. **a**, Schematic of the transition from a SAM of PTEG-1 into a SAB. **b–d**, Atomic force microscopy (AFM) height maps showing the growth stages of SABs of PTEG-1 on Au^{TS}: the monolayer (**b**), the incomplete bilayer (**c**) and the complete bilayer (**d**). **e**, Plots of $\log|J|$ versus potential for Au^{TS}/PTEG-1//EGaIn (monolayer) and Au^{TS}/PTEG-1//PTEG-1//EGaIn (bilayer) junctions. **f**, Plots of I versus potential for Au^{TS}/PTEG-1//Au^{AFM} (monolayer) and Au^{TS}/PTEG-1//PTEG-1//Au^{AFM} (bilayer) junctions. Error bars represent 95% confidence intervals. **g, h**, Scanning tunnelling microscopy (STM) images of a self-assembled monolayer of PTEG-1 on Au(111)/mica showing the presence of C₆₀ cages under a tip bias of 0.3 V (**g**) and –0.3 V (**h**) and with a set-point of 150 pA. The inset in **h** is a fast Fourier transform of the STM image giving information on the arrangement of PTEG-1 in the monolayer.

charge-transfer between the fullerene cage and the metal (that is, chemisorption)^{36,37,40}. The binding energy of fullerene–metal interactions is estimated to be 43 kcal mol^{–1} (ref. ⁴¹), which is similar to estimates for thiol–gold binding energies of 21 to 37 kcal mol^{–1} (ref. ⁴²). Figure 1a presents a schematic of how the packing of PTEG-1 into a SAM can create an assembly of GE chains, leading to a high free-energy solvent/GE interface that is then passivated by the assembly of a second layer of PTEG-1 via intermolecular dipole–dipole interactions between GE chains. The resulting bilayer is thermodynamically favoured because it minimizes interfacial free energy by creating fullerene/metal, GE/GE and fullerene/solvent interfaces. We determined the thicknesses of each of the three components of the bilayer—the bottom fullerene, the GE chains and the top fullerene—by X-ray reflectivity. In contrast to Al substrates⁴³, the polycrystalline nature of Au^{TS} and the large difference in electron density between Au and the SAB affected the complexity of the model used

to fit the reflectivity data (Supplementary Section 8); nevertheless, we were able to identify three distinct phases, the thicknesses of which are summarized in Table 1. The values for the top and bottom fulleroid layers are in good agreement with the diameter of C₆₀. The value for the centre layer, which comprises GE chains, is only 2 Å greater than the *trans*-extended lengths of a single GE chain (1.4 nm), in agreement with the arrangement shown in Fig. 2. This depiction is not meant to be atomically precise (for example, it ignores the stereocentre on PTEG-1, which is a racemate), but the data strongly suggest that GE chains are interdigitated.

To study the self-assembly process, we followed the evolution of the morphology of the SABs by atomic force microscopy (AFM) under intensive rinsing with toluene, which partially removes the top layer of PTEG-1 molecules from the SAB (Fig. 1d and Supplementary Fig. 15c), creating a partially covered bilayer (Fig. 1c and Supplementary Fig. 15b). The difference in height between the

Table 1 | Summary of the structural parameters extracted from the fitting of the X-ray reflectivity curves shown in Supplementary Fig. 32

	X-ray reflectivity parameters			
	Au	Fulleroid bottom	GE centre	Fulleroid top
ρ (e Å ⁻³)	4.46	2	0.1	2.5
t (nm)	–	0.9	1.6	0.8
σ (nm)	0.7	0.3	0.2	0.3

ρ , t and σ are the scattering length density, thickness and roughness of the layers, respectively.

top of the intact SAB and the portion of the SAM that is exposed by rinsing is equal to the diameter of C₆₀ (~1.0 nm), further confirming that the GE chains from the two PTEG-1 layers are interdigitated; otherwise the difference in height would include their *trans*-extended lengths. Further rinsing eventually results in a homogeneous monolayer of PTEG-1 (Fig. 1b and Supplementary Fig. 15a). This observation is in good agreement with the phase shifts measured by AFM, showing a distinct difference in the interaction between the AFM tip and the surface of bare Au^{TS} (8.8°; Supplementary Fig. 16c,f), the SAMs (4.2°; Supplementary Fig. 16a,d) and SABs (55.8°; Supplementary Fig. 16b,e) of PTEG-1. We confirmed the transition from SABs (25.1 Å to 27.0 Å) to SAMs (11.9 Å to 13.4 Å) of PTEG-1 by measuring their respective thicknesses using angle-resolved X-ray photoelectron spectroscopy (XPS) and ellipsometry, which are summarized in Supplementary Tables 7, 8 and 10.

Although individual GE chains are too mobile to be visible, we were able to visualize the C₆₀ cages in the SAMs of PTEG-1 by scanning tunnelling microscopy (STM; Fig. 1g,h and Supplementary Figs. 13a,b and 14a,b). Moreover, the diameter of the C₆₀ cages (~1.0 nm at full-width at half-maximum (FWHM)) determined by STM (Supplementary Fig. 13c) agrees perfectly with literature values for monolayers of pure C₆₀ (ref. 44), which suggests that PTEG-1 binds to metallic surfaces via similar interactions as C₆₀. A fast Fourier transform (FFT) of the STM image (inset, Fig. 1h) of the PTEG-1 SAM shows preferred directions for the arrangement of the PTEG-1 molecules. The spots with a periodicity of ~1 nm in a ring-like feature indicate that the arrangement of the nearest and the next-nearest neighbour PTEG-1 molecules occurs in almost all possible directions. The PTEG-1 molecules do not exhibit the same long-range order as films of pure C₆₀ grown from the gas phase and annealed⁴⁵, but they form densely packed, glassy structures, as shown by AFM and STM images. (See Supplementary Section 9 for a detailed discussion about the packing density.) The utility of SAMs derives from their homogeneity over macroscopic areas, for example enabling them to form robust tunnelling junctions that bear tunable electrical properties, as confirmed by FFT and the experiments described in the following sections.

Tunnelling charge transport measurements

We characterized the charge transport properties of SAMs and SABs of PTEG-1 by contacting them with sharp tips of eutectic GaIn (EGaIn)⁴⁵ and Au-coated AFM tips (Au^{AFM}) to form junctions with the structure Au^{TS}/SAM(or SAB)//EGaIn(or Au^{AFM}), where ‘/’ denotes interfaces defined by chemisorption and ‘//’ by physisorption. These high-throughput techniques allow for the elucidation of tunnelling charge transport properties without the need to fabricate devices. SAMs of PTEG-1 exhibit a significantly higher conductance than SABs in both EGaIn and conductive-probe AFM (CP-AFM) junctions, suggesting a dependence on thickness commensurate with tunnelling charge transport (Fig. 1e,f). Interestingly, the junctions comprising SABs exhibit asymmetric

J–*V* curves, but junctions comprising SAMs exhibit symmetric *J*–*V* curves. This difference is most prevalent at ±1 V in Fig. 1e, where the SABs and SAMs give almost the same value of log $|J|$ at +1 V, but the SABs give a significantly lower value at –1 V. Although the magnitude of the rectification ratio ($R = |J(+)|/|J(-)| \approx 10$) is not remarkable, the direction (that is, $|J(+)| > |J(-)|$) is the same as for Ag^{TS}/S(CH₂)_nC₆₀/EGaIn (or Au^{AFM}) junctions⁴⁶. In those junctions, the direction of rectification is ascribed to unoccupied molecular orbitals localized on the fullerene cage moving close to the Fermi level at positive bias and away at negative bias. Thus, the asymmetry in the *J*–*V* curves of SABs of PTEG-1 suggests that the symmetry of the junction is broken by the interaction of the bottom C₆₀ cage with the Au^{TS}, leaving the electronic structure of the top C₆₀ intact. This asymmetry is preserved in SABs of PTEG-1 formed on rough Au substrates, showing tolerance to defects in the substrate and the potential for practical uses (see Supplementary Information for a detailed discussion).

To evaluate the baseline potential of PTEG-1 bilayers for molecular electronics, we fabricated a series of GESAMs by exposing SABs of PTEG-1 to GE-functionalized alkanes (alkylGEs; see Supplementary Information for synthesis and characterization), exchanging the top layer of PTEG-1 with alkanes of various lengths by self-assembly (mass-action/in-place exchange, as depicted in Fig. 2). After forming SABs of PTEG-1 on Au^{TS} or Pt^{TS} substrates, we sequentially immersed them in toluene solutions of the alkylGEs for 24 h. Both angle-resolved XPS and ellipsometry show a clear dependence on the length of the alkylGE: ethylGE 13.3–14.1 Å, butylGE 16.1–18.6 Å, hexylGE 19.6–22.3 Å and octylGE 21.5–23.8 Å (Supplementary Tables 8 and 10). These thicknesses are unique and vary systematically with the identity of the alkylGE, indicating that they incorporate into the PTEG-1 SABs rather than leaving the SABs intact or forming SAMs comprising only PTEG-1. Moreover, the XPS spectra in Supplementary Fig. 30 show that the C–C (284.5 eV), C=C/C–N (285.9 eV) and C–O (288.7 eV) peaks of the C1s region and the O–C (532.0 eV) peaks of the O1s region are in good agreement with the spectra of SAMs of PTEG-1, indicating that PTEG-1 is still present after exchange, while the attenuation of the C–O photoelectrons increases with increasing lengths of the alkylGEs (Supplementary Table 6; from 9.6% for ethylGE to 2.7% for octylGE). These data prove that incubating SABs of PTEG-1 in toluene solutions containing alkylGEs results in incorporation of the alkylGEs without complete replacement of PTEG-1. The data also suggest that the GE portion sits below the alkyl portion, as further confirmed by water contact angle measurements (Supplementary Table 1).

We measured the length dependence of the GESAMs of alkylGEs exchanged onto PTEG-1 by forming Au^{TS} (or Pt^{TS})/PTEG-1//alkylGEs//EGaIn (or Au^{AFM}) junctions, observing a decrease in conductance with increasing lengths of the alkyl portion of the alkylGEs in the GESAMs. Figure 3 and Supplementary Fig. 21 show this exponential dependence of *J* (from EGaIn) and *I* (from CP-AFM), expressed as both the number of carbons in the alkyl portion of the alkylGEs and the thicknesses of the GESAMs (in ångströms), from which we extract the tunnelling decay coefficient β and injection current J_0 (or I_0) at ±0.5 V and ±1 V in EGaIn junctions and ±1 V and ±1.5 V for CP-AFM junctions. We found $\beta = 1.12 \text{ CH}_2^{-1}$ (0.80 Å⁻¹) and $J_0 = 1 \times 10^{1.84} \text{ A cm}^{-2}$ ($1 \times 10^{1.27} \text{ A cm}^{-2}$) for EGaIn junctions and $\beta = 1.13 \text{ CH}_2^{-1}$ (0.81 Å⁻¹) for CP-AFM junctions. (The conductance of the GESAMs of octylGE on PTEG-1 was below the detection limit of the CP-AFM instrument.) The consensus values of β and J_0 at $V = \pm 0.5 \text{ V}$ for tunnelling junctions comprising SAMs of alkanethiolates are approximately $\beta = 1.10 \text{ CH}_2^{-1}$ (0.70 Å⁻¹) and $J_0 = 1 \times 10^{2.38} \text{ A cm}^{-2}$ (Supplementary Fig. 22)¹³. Values close to these are a strong indication that the dominant mechanism of charge transport is non-resonant tunnelling through *trans*-extended alkyl chains and that the tunnelling barrier is defined only by the alkyl portion of the alkylGE.

Fig. 2 | Schematic of the exchange process in which SABs of PTEG-1 are converted to GESAMs of alkylGEs. We postulate that the chemisorption of the fullerene cage to Au^{TS} effectively renders it part of the electrode (indicated as E_F) and that the injection current (I_0) is defined by the interdigitated glycol ether phase. The thicknesses are taken from the X-ray reflectivity data in Table 1.

Fig. 3 | Characterization of the charge transport properties of SABs of alkylGEs on PTEG-1. **a**, Plots of $\log|J|$ versus potential of $\text{Au}^{\text{TS}}/\text{PTEG-1}/\text{alkylGEs}/\text{EGaln}$ junctions. **b**, Plots of $\log|J|$ determined at -1 V , -0.5 V , 0.5 V and 1 V in EGaln junctions versus the number of non-hydrogen atoms in alkylGEs and the number of carbon atoms in the alkyl chains. **c**, Plots of $\log|J|$ determined at -1 V , -0.5 V , 0.5 V and 1 V in EGaln junctions versus the thickness of the bilayers. **d**, Plots of I versus potential of $\text{Au}^{\text{TS}}/\text{PTEG-1}/\text{alkylGEs}/\text{Au}^{\text{AFM}}$ junctions. **e**, Plots of $\log|J|$ determined at -1.5 V , -1 V , 1 V and 1.5 V in CP-AFM junctions versus the number of non-hydrogen atoms in alkylGEs and the number of carbon atoms in the alkyl chains. **f**, Plots of $\log|J|$ determined at -1.5 V , -1 V , 1 V and 1.5 V in CP-AFM junctions versus the thickness of the bilayers. Error bars represent 95% confidence intervals. All dashed lines are linear fits to the data points excluding the PTEG-1 monolayers.

Fig. 4 | Characterization of SABs of SP-GE on PTEG-1 during switching. **a**, Plots of $\log[J]$ versus potential of $\text{Au}^{\text{TS}}/\text{PTEG-1}/\text{SP-GE}/\text{EGaIn}$ junctions as they switched after exposure to room light and UV light over two cycles. **b**, Evolution of $\log[J]$ at ± 1 V of $\text{Au}^{\text{TS}}/\text{PTEG-1}/\text{SP-GE}/\text{EGaIn}$ junctions after they switched after exposure to room light and UV over two cycles. Error bars represent 95% confidence intervals. Solid lines are guides for the eye. **c**, XPS spectra of the N1s regions for the SAB of PTEG-1 exchanged with SP-GE on Au^{TS} before UV exposure. **d**, XPS spectra of the N1s regions for the SAB of PTEG-1 exchanged with SP-GE on Au^{TS} after UV exposure. Coloured solid lines in the XPS spectra are fits to the background and peaks using a linear model and a Lorentzian–Gaussian model, respectively.

Although there is evidence that glycol ethers constitute unusually efficient tunnelling media^{47,48}, the results above suggest that the entirety of the C_{60} cage plus the (presumably) interdigitated GE chains present an equivalent tunnelling/injection barrier to S–Au in junctions comprising SAMs of alkanethiolates (as depicted schematically in Fig. 2). Variable-temperature measurements further confirm that the dominant mechanism is non-resonant tunnelling (Supplementary Fig. 20).

Reversible in-place exchange

To demonstrate the utility of the self-assembly process, we incorporated spiropyran (SP) photoswitches into GESAM-based tunnelling junctions. These switches have been shown to give increases in J of up to 1×10^3 when photo-isomerized to the merocyanine (MC) form in SAMs of thiols⁹. They are extraordinarily sensitive to the self-assembly process; in pure SAMs, switching is irreversible, but in mixed monolayers with alkanethiolates, formed by in-place exchange, they optimize their packing, imparting reversibility⁴⁹. We fabricated GESAMs of GE-functionalized spiropyran (SP-GE; see Supplementary Information) on PTEG-1 by immersing GESAMs of ethylGE in a toluene solution of SP-GE for 24 h and measured J – V curves in EGaIn junctions while cycling between the SP and MC forms via exposure to 365 nm light for 1 h (SP→MC) and visible light for 1 h (MC→SP). As can be seen in Fig. 4a,b, we observed reversible switching, with the SP form being more conductive

than the MC form, from an initial ratio of 230 to 43 at the final cycle (which is very similar to the results in ref. 49). Figure 4c,d and Supplementary Table 9 present XPS spectra of the GESAMs before and after exposure to UV light. The two main peaks in the N1s core-level region originate from the indoline nitrogen of the SP form (399.3 eV) and the NO_2 group (403.2 eV), which is present in both forms. After exposure to UV light, a new peak appears corresponding to N^+ in the MC form (402.2 eV), while the NO_2 peak is unaffected. Commensurate with this change is a shift in the ratios of the CIs of $\text{C}=\text{C}/\text{C}-\text{N}$ (from 4.8 to 11.3%), the OIs of O–N (from 31.8 to 35.8%) and the NIs of N–O (from 52.1 to 54.2%) peaks after exposure to UV light. These ratios reflect the fact that the photoelectrons from the NO_2 groups are less attenuated in the MC form because the relative position within the GESAM changes when the switches isomerize (which is facilitated by the optimized packing in mixed monolayers⁵⁰). The ratios between N–C and N^+-C show that the current switching results from 19.4% of the SP-GE photoisomerizing to the MC form. The XPS data are therefore consistent with the photoisomerization of SP to MC and not some other photochemical process specific to GESAMs of GE-functionalized molecules on PTEG-1. The data in Fig. 4 are unambiguous evidence that in-place exchange occurs by self-assembly and that the resulting packing of the SP switches is sufficiently similar to that of mixed monolayers of thiols on Au^{TS} formed by in-place exchange that the switches exhibit identical behaviour in EGaIn junctions.

Fig. 5 | The stability of tunnelling junctions comprising SABs of alkylGEs on PTEG-1 over 35 days. **a**, Values of β determined at -0.5 and 0.5 V in Au^{TS} /PTEG-1//alkylGEs//EGaIn junctions as a function of number of days. Error bars show the standard error of the linear fit to the tunnelling exponential length decay and 95% confidence level. **b**, Yields of working Au^{TS} /PTEG-1//alkylGEs//EGaIn and Au^{TS} /S(CH₂)_nCH₃//EGaIn junctions ($n = 7, 9, 11, 13, 15$) as a function of number of days. **c**, Plots of $\log[J]$ determined at -0.5 and 0.5 V in Au^{TS} /PTEG-1//alkylGEs//EGaIn junctions as a function of number of days. Error bars represent 95% confidence intervals. **d**, Plots of $\log[J]$ versus potential of Au^{TS} /PTEG-1//alkylGEs//EGaIn junctions measured at days 1 and 28. All samples were kept under ambient conditions. Error bars represent 95% confidence intervals. Solid lines are guides for the eye.

Stability

The tunnelling junctions of the SAMs of PTEG-1 are more mechanically robust than their thiolate counterparts (Supplementary Fig. 19), meaning they are more resistant to electrostatic pressure³⁹. This robustness translates into an improved yield of non-shorting tunnelling junctions compared to the SAMs of alkanethiols. We formed 60 EGaIn junctions comprising SABs of PTEG-1 and GESAMs of alkylGEs in parallel with SAMs of alkanethiols (SC_n, $n = 8, 10, 12, 14, 16$); the junctions of the GESAMs of alkylGEs did not short throughout a ± 1 V sweep and remained stable over 1,500 continuous bias sweeps (Supplementary Fig. 28), while the yield of the alkanethiols was 80%. Moreover, the GESAMs are chemically stable and do not oxidize or degrade in ambient conditions. After measuring the yields of working junctions and values of β and J_0 for the GESAMs and thiolate SAMs, we stored all of the substrates in ambient conditions, on the bench top, and tracked their electrical properties over a period of 35 days. The results are summarized in Fig. 5. The yield of junctions comprising SAMs of alkanethiols on Au^{TS} , Ag^{TS} and Pt^{TS} dropped to 0% (that is, 100% of junctions shorted) after only 1 day due to the spontaneous oxidation of surface-bound thiolates in air (Fig. 5b and Supplementary Fig. 25). The junctions comprising SABs of PTEG-1 and GESAMs of alkylGEs, by contrast, did not show any decrease in yield until 10 days, at which point the GESAMs of alkylGEs dropped to ~90% yield. More than 60% of the junctions comprising GESAMs of alkylGEs remained non-shorting even after a full 35 days in air, while the SABs of

PTEG-1 remained completely non-shorting. The evolution of β and $\log[J]$ shows that the length dependence of the alkylGEs persisted for 28 days and was eventually lost on day 35 (Fig. 5a,c). The I - V characteristics for the junctions of GESAMs of alkylGEs were also stable (notwithstanding minor difference in the low-bias region) until day 28 (Fig. 5d); however, the conductance of the junctions of ethylGE, hexylGE and octylGE drifted (Supplementary Fig. 26), which led to loss of the length dependence. Given the persistence of the relatively high yields of non-shorting junctions, we ascribe the decay in values of β to changes in the structure of the alkylGE top layer, possibly driven by the deliquescent nature of glycol ethers. The underlying PTEG-1 layer remained intact, preventing shorts.

Outlook

The ubiquity and myriad uses of SAMs are due largely to their robust self-assembly. Whether they are utilized to modify surface chemistry, as nano-objects, for nanofabrication and so on, the precision, reproducibility, self-correcting/healing, tolerance variations in the conditions under which they are grown and simplicity are central to their usefulness. They are critical for molecular electronics, where the subnanometre precision required to place molecules between static electrodes can be as simple as immersing a substrate in a solution. However, junctions comprising SAMs of thiolates do not survive for a single day in ambient conditions. We have shown that GESAMs retain the important properties of SAMs of thiolates: they are sufficiently ordered to show exponential length dependence,

they are sufficiently densely packed to modify water contact angles, they undergo in-place exchange, they are robust enough to survive thousands of J - V sweeps and they form by simply immersing a substrate in a solution containing PTEG-1. However, unlike any other kind of surface molecular self-assemblies, they combine all of those properties with stability in ambient conditions for at least a month. Such unprecedented stability facilitates rapid prototyping, long-term studies of tunnelling junctions and opens up the possibility of in-place exchange in operando, for self-repair and functionality that reflects past exposure to specific chemical compounds. Although more research is needed to understand the nature of the glycol ether phase and why it is such an efficient tunnelling medium, GESAMs can be formed from any molecule bearing a glycol ether tail, creating the opportunity to extract useful functionality from robust, static devices that, in part, fabricate themselves.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41563-019-0587-x>.

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Methods

Preparation of PTEG-1 monolayer and bilayer. SAMs and SABs of PTEG-1 were prepared by incubating freshly cleaved $1 \times 1 \text{ cm}^2$ Au^{TS} and Pt^{TS} surfaces for 24 h in 1.2 ml of 0.5 mM solution of PTEG-1 in toluene at room temperature. To form a monolayer, the substrates were rinsed gently with toluene ($3 \times 1 \text{ ml}$) and residual solvent on the surface was removed by gently blowing N₂. To form a bilayer, the substrates were taken out of the solution and rinsed gently with toluene (1 ml), then the residual solvent was gently blown away by N₂. To form a partial bilayer, the substrates were rinsed gently with toluene (2 ml) and residual solvent on the surface was removed by gently blowing N₂.

Preparation of PTEG-1/alkylGE bilayer. SABs of PTEG-1/alkylGE were prepared through exchange of PTEG-1 from its pristine bilayers with alkylGE through two steps. First, bilayers of PTEG-1 were formed by incubating freshly cleaved $1 \times 1 \text{ cm}^2$ Au^{TS} and Pt^{TS} surfaces for 24 h in 1.2 ml of 0.5 mM solution of PTEG-1 in toluene at room temperature. The substrates were then incubated for 24 h in 5 ml of 5 mM solution of alkylGEs in toluene at room temperature. After incubation, they were taken out of the solution, rinsed gently with toluene (1 ml), and the residual solvent was gently blown away by N₂.

SABs of PTEG-1/SP-GE were prepared through exchange of ethylGE from PTEG-1/ethylGE bilayers with SP-GE through two steps. First, bilayers of PTEG-1/ethylGE were formed by incubating freshly prepared pristine PTEG-1 bilayers in 5 ml of 5 mM toluene solution of ethylGE for 24 h at room temperature. The samples were then incubated for 24 h in 5 ml of 5 mM toluene solution of SP-GE at room temperature. After incubation, they were taken out of the solution, rinsed gently with toluene (1 ml) and the residual solvent was gently blown away by N₂. The bilayer was exposed to 365 nm UV light (Spectroline E-series UV lamp, model ENF-260C/FE, 6 W power output) in an inert atmosphere for 1 h to switch from the SP form to the MC form.

AFM. Peak force tapping AFM, CP-AFM and peak force quantitative nanomechanical mapping (PFQNM) AFM measurements were performed on a Bruker AFM multimode MMAFM-2 equipped with a PeakForce TUNA application module (Bruker). Pristine SAMs and SABs of PTEG-1 and bilayers exchanged with alkylGEs were characterized by AFM. Peak force tapping AFM was performed with a ScanAsyst-Air probe (resonant frequency 70 kHz, spring constant 0.4 N m^{-1} , Bruker) to characterize the surface morphology of the samples at a scan rate of 0.7 Hz and 800 samples per line. The data were analysed with Nanoscope Analysis 1.5 (provided by Bruker). In CP-AFM measurements, samples fabricated on Au^{TS} substrates were contacted with a Au-coated silicon nitride tip with a nominal radius of 30 nm (NPG-10, Bruker, tip A: resonant frequency 65 kHz, spring constant 0.35 N m^{-1}) in TUNA mode with a load force of 1.4 nN, and samples fabricated on Pt^{TS} substrates were contacted with a PtIr-coated silicon nitride tip with a nominal radius of 25 nm (SCM-PIT V2, Bruker, resonant frequency 75 kHz, spring constant 3 N m^{-1}) with other parameters identical to the Au arrangement. The AFM tip was grounded and the sample was biased from -1.5 V to $+1.5 \text{ V}$ and from $+1.5 \text{ V}$ to -1.5 V to record the I - V curves (512 data points per trace were taken): a maximum of 20 trace/retrace cycles per junction were performed. After every junction, the tip was withdrawn and moved to a different spot, and engaged again for a total of 50 junctions over three analysed samples. Between different samples a new tip was used. The data were analysed with the same software used for EGaIn using the current I instead of the current density J . Measurements of Young's modulus were performed in PFQNM mode. The samples were contacted with a silicon nitride tip with a nominal radius of 2 nm (ScanAsyst-Air, Bruker, resonant frequency 70 kHz, spring constant 0.4 N m^{-1}). The deflection sensitivity, spring constant of the cantilever and tip radius were calibrated both before and after measurements. Samples were first scanned at $5 \mu\text{m}$ at a rate of 1 Hz to select a region where dust particles or other contaminants were not present. Deformation and adhesion of the sample were measured under a load force ranging from 50 pN to 1.5 nN over an area of $250 \text{ nm} \times 500 \text{ nm}$ (a total of 256×512 data points were collected for each sample) and later used to calculate Young's modulus using the DMT model in Nanoscope Analysis (Bruker).

EGaIn measurement. Electrical measurements with EGaIn, as well as sample preparation and handling, were performed under ambient conditions. In the measurements, the sample was grounded and the EGaIn was biased. At least three samples were examined for monolayers/bilayers. The potential windows include the following: (1) $0 \text{ V} \rightarrow 1 \text{ V} \rightarrow -1 \text{ V} \rightarrow 0 \text{ V}$, steps of 0.05 V; (2) $0 \text{ V} \rightarrow 1 \text{ V} \rightarrow -1 \text{ V} \rightarrow 0 \text{ V}$, steps of 0.1 V. A total of five trace/retrace cycles were recorded for each junction, and shorts occurring during the measurement (short upon contact with a bias of 1 V or during the cycle) were counted as failure of the junction.

Water contact angle. Equilibrium contact angles were obtained by applying 1 μl water droplets on SAM-modified substrates using the sessile drop method. The contact angles were measured on two samples, at three different locations per sample, and the results were averaged with standard deviation as the error bars.

STM. All STM images were acquired at the solid-air interface under ambient conditions with a Molecular Imaging Keysight N9700C scanner, using mechanically cut Pt/Ir (90:10) wires (Goodfellow, 0.25 mm diameter) as tips. All

STM images were analysed and processed using WSxM 5.0³¹. All bias values are given with respect to a grounded tip.

XPS. To measure the thickness of the SAM, XPS measurements were performed using a VG Microtech spectrometer with a hemispherical electron analyser (Clam 100) and an Al K α (1,486.6 eV) X-ray source. The Au_{4f7/2} and Au_{4d5/2} peaks were acquired with the sample rotated under 0, 10, 20, 30, 40 and 50° with respect to the electron analyser. A Gaussian fit with background was made to the peaks to obtain their intensities. To correct for slow fluctuations in the X-ray source intensity, we acquired the spectra for each peak at 0° again after the sample was measured at an angle of rotation. These measurements were used to obtain a correction factor γ_f . The corrected peak intensities I^* are given by $I^* = \gamma_f I$ and can be used to determine the thickness of the layer. The values are provided in the Supplementary Information. The measured electrons in the peaks are the electrons that make it from the gold through the layer without scattering. The intensity of the peaks for different lengths of path through the overlayer is given by

$$I(\theta) = I_0 \exp\left(\frac{-L}{\lambda}\right) = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right) \quad (1)$$

where L is the length of the path through the layer, d is the thickness of the layer, λ is the inelastic mean free path and θ is the angle of rotation of the sample with respect to the analyser. λ depends on the kinetic energy of the observed electrons and the material through which the electrons move. We determined the value of λ for electrons originating from the Au_{4f7/2} and Au_{4d5/2} levels, from measurements on a SAM of decanethiols on gold, whose thickness has been well studied $17 \pm 1 \text{ \AA}$ (ref. ³²). This was found to be $36 \text{ \AA}$ for Au_{4d5/2}. With the values of λ we can make a fit to the corrected intensities to find the thickness of all samples (PTEG-1 bilayer $25.1 \pm 0.7 \text{ \AA}$, PTEG-1 monolayer $13.4 \pm 0.4 \text{ \AA}$, PTEG-1/ethylGE bilayer $13.3 \pm 0.4 \text{ \AA}$, PTEG-1/butylGE bilayer $18.6 \pm 0.5 \text{ \AA}$, PTEG-1/hexylGE bilayer $22.3 \pm 0.6 \text{ \AA}$, PTEG-1/octylGE bilayer $23.8 \pm 0.7 \text{ \AA}$). This treatment assumes the inelastic mean free path in all investigated samples to be equal to that in the decanethiol SAM.

Ellipsometry. Ellipsometry measurements were carried out in air, on a V-Vase Rotating Analyser equipped with a HS-190 monochromator ellipsometer from J.A. Woollam Co. at an incident angle of 65°, 70° and 75° with respect to the surface normal. A two-layer model consisting of a bottom Au layer, for which optical constants were calculated from freshly prepared template-stripped Au surfaces, and a Cauchy layer was used for the fit of the measurements on the SAMs. Chosen values of $An = 1.45$, $Bn = Cn = 0$ (three coefficients in the real part of the complex refractive index in the Cauchy model) and $k = 0.01$ (the coefficient in the imaginary part of the complex refractive index in the Cauchy model) at all wavelengths were used to fit the thickness. For every SAM, we measured six different spots in total (either two spots per sample for three samples or three spots per sample for two samples) and reported the thicknesses as an average with standard deviation as error bars.

Fabrication of soft devices for variable-temperature measurements. To elucidate the transport mechanism of PTEG-1-based devices, we measured the dependence of the electric behaviour on temperature. To do this, we fabricated encapsulated and addressable devices that were able to operate in a pressure- and temperature-controlled set-up. We thermally deposited Au in vacuum through a stencil mask of ten parallel electrodes onto 3 in. Si/SiO₂ wafer. The resulting 100 nm-thick electrodes were $50 \mu\text{m}$ wide, $10,000 \mu\text{m}$ long and had round pads ($d = 1,500 \mu\text{m}$) at their ends to facilitate addressing of the electrodes with probes. The Si/SiO₂ wafer with metal lines was functionalized with 1H,1H,2H,2H-perfluorooctyl trichlorosilane by gas deposition to minimize its interaction with the optical adhesive. The electrodes were then template-stripped onto clean $2 \times 1.5 \text{ cm}^2$ glass substrates to reduce the number of defects in the layer. We immersed each substrate in a solution of PTEG-1 for 4 h, then rinsed them with toluene to form monolayer of PTEG-1. To exchange with ethylGE, the samples were immediately immersed into a solution of ethylGE for another 4 h. The devices were then dried under nitrogen. We positioned PDMS microchannels ($20 \mu\text{m}$ wide, $50 \mu\text{m}$ deep, $10,000 \mu\text{m}$ long, with round inlet/outlet ($d = 1,000 \mu\text{m}$)) onto a piece of silicon wafer functionalized with 1H,1H,2H,2H-perfluorooctyl trichlorosilane by gas deposition. We filled the microchannels (one per experiment to avoid crosstalk) by gently injecting EGaIn through the inlet with the help of a metallic precision syringe and applying reduced pressure to the outlet of the channel. We then carefully peeled off the microchannels and positioned them perpendicular to the electrodes to form a crossbar structure of Au^{TS}/PTEG-1/ethylGE//EGaIn. The structures bonded with the substrates without any further steps.

Variable-temperature measurements. The variable-temperature measurements were performed on a custom-built cryogenic probe station in vacuum (pressures varied between 6×10^{-7} and 3×10^{-6} mbar). The devices were slowly cooled and their J - V characteristics were measured from 298 to 245 K. We biased the Ga₂O₃//EGaIn top electrodes and grounded the Au^{TS} bottom electrode. Using the area defined by the stencil mask and PDMS channels, we measured J as a function of V at intervals of 10 K, allowing the devices to stabilize before performing each scan. We fabricated 25 devices for each type of system (PTEG-1 monolayer, PTEG-1/ethylGE bilayer) and measured one of each at a time. The yield of the working

junctions of PTEG-1 monolayer on Au was 68% and for the PTEG-1/ethylGE bilayer on Au was 96%. Every scan of a junction was recorded individually and the aggregate dataset was treated identically to the room-temperature data, as described above. We biased from -0.5 V to $+0.5$ V in steps of 0.025 V with a delay of 0.1 s.

Data availability

The raw data used to prepare the STM, AFM, ellipsometry, water contact angle, EGAIn and XPS data in Figs. 1–5 and in the Supplementary Information are hosted at the University of Groningen according to the research data management plans described at <https://www.rug.nl/research/zernike/rdmp>. All raw and processed data are available for download from <https://hdl.handle.net/10411/13711>.

Code availability

All of the raw data acquired using EGAIn and CP-AFM were processed using Scientific Python. The source code is publicly available at <https://github.com/rchiechi/GaussFit> and is retained internally in accordance with the aforementioned data retention policies.

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Author contributions

X.Q. and R.C.C. conceived the idea. X.Q. designed the experiments, synthesized the alkylGEs, prepared all samples and junctions, performed the characterizations using EGAIn, AFM, XPS, ellipsometry and water contact angle, and analysed the data. V.I. synthesized SP-GE. L.Q. and J.C.H. synthesized PTEG-1. M.E. and M.S. performed STM measurements and analysed the data. S.R. synthesized the alkylC₆₆s. J.D. and G.P. performed grazing-incidence wide-angle X-ray scattering and X-ray reflectivity measurements and analysed the data. X.Q. wrote the paper with R.C.C. All of the authors edited the manuscript before submission.

Competing interests

The authors declare no competing interests.

Additional information

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