Supporting Information

Functionalized 2D Nanomaterials with Switchable Binding to Investigate Graphene-Bacteria Interactions

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1. Experimental

Materials. Polyglycerol (PG) ($M_n = 11,000 \text{ g mol}^{-1}$, 13.5 mmol OH-groups g⁻¹) was prepared according to a published procedure. Methanesulfonyl chloride (MsCl) (\geq 99.7%), triphenylphoshine (PPh₃) (99%), sulfur trioxide pyridine complex (Py[•]SO₃⁻) (98%), phosphate buffer solution 1.0M, pH 7.4 (25°C) fluorescein isothiocyanate isomer I (FITC) $(\geq 90\%)$, N,N-dimethylformamide (DMF) ($\geq 99.8\%$), 1-methyl-2-pyrrolidinone (NMP) (99.5%). *N*-hydroxysuccinimid (NHS) (98%), N-(3-dimethylaminopropyl)-N'ethylcarbodiimide hydrochloride (EDC) and pyridine (99.8%) were purchased from Sigma Aldrich. Thermally-reduced graphene oxide (TRGO) was supplied by Prof. Dr. Rolf Mülhaupt from University of Freiburg. 2,4,6-trichloro-1,3,5-triazine (TCT) (99%) and sodium azide (NaN₃) (99%) were purchased from Acros Organics. Sodium hydroxide (NaOH) (99%) was purchased from Fisher chemical. Biotech cellulose ester dialysis bag MWCO 1000 g mol⁻¹ and MWCO 100,000 g mol⁻¹ was purchased from Spectrum labs. LIVE/DEAD® BacLightTM bacterial viability kit, for microscopy and quantitative assays was purchased from ThermoFisher Scientific. Escherichia coli (E. coli) strain (K12) OD₆₀₀~1.0 (1x10⁸ CFU mL⁻¹) was supplied by Prof. Dr. Anna Gorbushina from Department of Materials and Environment, Bundesanstalt für Materialforschung und -prüfung. All chemical compounds were used without further purification.

Methods. Nuclear magnetic resonance (NMR) data was obtained with a Bruker ECX 400 MHz, Jeol Eclipse 500 MHz, or Bruker AVANCE III 700 MHz NMR spectrometers. Fourier transform infrared (FTIR) spectroscopy was recorded on a Nicolet Avatar 320 FT-IR spectrometer. Elemental analysis was carried out on a VARIO EL III instrument (Elementar, Hanau, Germany) using sulfanilic acid as the standard. Centrifugation was carried out in a Rotina 380R Hettich GmbH Co. KG (Tuttlingen, Germany). The thermogravimetric analysis (TGA) was recorded on STA PT 1600 Linseis (Robbinsville, USA) and evaluated with Linseis Data Acquisition software. The measurements were

performed in aluminum oxide crucibles in a temperature range from 25 °C to 800 °C with a heating rate of 10 °C/min in the air environment.

2. Results and discussion

TRGO-PG, TRGO-PGS, TRGO-PGA, ZGNM_{50%}, and ZGNM_{90%} were synthesized by the top-down method to investigate the electrostatic interactions between graphene sheets and the *E. coli*. All compounds were characterized by IR, elemental analysis, TGA, XPS, NEXAFS spectroscopy, AFM, and zeta potential.

3. Elemental analysis and calculations of the number of functional groups

	C (%)	Н (%)	N (%)	S (%)
PG	47.85	8.16	0.17	0.00
PG-Mesyl	46.56	7.99	0.01	0.00
PG-N ₃	46.89	7.07	2.69	0.00
PGA	48.06	8.03	0.86	0.00
TRGO	87.75	1.74	0.06	0.00
TRGO-Trz	78.91	2.56	6.50	0.00
TRGO-PG	72.00	3.40	3.20	0.00
TRGO-PGS	43.30	3.76	3.00	10.17
TRGO-PGA	66.96	3.11	5.89	0.00
ZGNM _{50%}	50.80	3.10	6.50	5.50
ZGNM _{90%}	50.18	5.27	8.52	2.14

Table S1. Elemental analysis of polymer and graphene derivatives.

Calculation of the functional groups of graphene derivatives

a) TRGO-Trz building block

Calculation of the number of triazine groups per carbon atoms of graphene sheets by the nitrogen content (6.5%) of the TRGO-Trz

100 / X = 6.5 / 56; X = 861 (the molecular weight of the TRGO-Trz building block)

Molecular weight of triazine group is 163, therefore the number of carbon atoms to which one triazine is conjugated can be calculated as below:

861 - 163 = 698 / 12 = 58 number of carbon atoms per one triazine group.

b) PG (11 kD) with 100% sulfate groups

In the case of 100% sulfation, the molecular weight of sulfur atoms in the PG was $145 \times 32 = 4640$ Da.

(11,000 - 145 + 14935) / 100 = 4640 / X; X = 17.99% (sulfur content of this compound)

c) TRGO-Trz-PGS

The polymer/TRGO ratio was 0.5 (34% polymer contents). Therefore, each branch of polyglycerol was conjugated to (11,000 / 861) 12.77 building block of TRGO-Trz on average. The total molecular weight of building block TRGO-PGS (fully sulfated) was:

 $11,000 + (12.77 \times 861 - 35.5) + 14935 - 145 = 36331$ Da.

36,331 / 100 = 4640 / X; X = 12.77% for fully sulfated TRGO-PGS.

145 / X = 12.77 / 10.17; X = 115 number of sulfate groups on the PG of TRGO-PGS.

4. FTIR spectra of graphene derivatives



Figure S1. IR spectra of PG, PG-mesylate, PG-azide, and PGA_{4%}.



Figure S2. IR spectra of TRGO-PG, TRGO-PGS, TRGO-PGA, ZGNM_{50%}, and ZGNM_{90%}.

IR spectra in Figure S1 show the successful conversion of PG to PGA. In these spectra, absorbance bands at 1326.78 and 2088.53 cm⁻¹ corresponded to the SO₂ and azide stretching vibrations and proved the successful conversion of OH groups to mesyl groups and then azide groups, respectively. The reduction of azide groups to amine groups by triphenylphosphine were proven by the disappearing of the azide absorbance band.

Figure S2 shows the IR spectra of all TRGO derivatives. The signal of PG was weakened significantly after conjugation onto the surface of TRGO. Nevertheless, absorbance bands were detected at 1046.19 cm⁻¹, which corresponded to the C-O bond, 1539.88 and 1422.24 cm⁻¹, assigned to the triazine segment and C=C bonds, respectively. After sulfation of the TRGO-PG, the absorbance bands mentioned before remained. Additionally, a new intense absorbance band at 1215.89 cm⁻¹ assigned to the SO₂ groups was observed. This result proves the successful conversion of OH to sulfate groups. A similar situation occurred in the case of TRGO-PGA where the new absorbance band appeared at 1065.47 cm⁻¹. This band corresponds to the primary amine stretching. In the IR spectra of ZGNM, both absorbance bands for the sulfate and amine groups appeared. In the IR spectra of ZGNM_{50%}, the absorbance band at 1205.29 cm⁻¹. Vice versa, the amine stretching band at 1084.76 cm⁻¹ was much intense than the sulfate stretching band at 1216.86 cm⁻¹ in the case of ZGNM_{90%}.

5. Zeta potential of graphene derivatives

	Zeta potential (mV) at pH 7.4
TRGO-PG	-1
TRGO-PGS	-28
TRGO-PGA	+27
E. coli ⁷	-16

Table S2. Zeta potential of different graphene derivatives.

6. XPS and NEXAFS spectra of graphene derivatives



Figure S3. Overall XPS spectra of TRGO-PG, TRGO-PGA, TRGO-PGS, ZGNM_{50%}, ZGNM_{90%}. Ratios of elements is shown in Table S4.

XPS spectra showed a change in surface concentrations during the different reaction steps. The Nitrogen surface concentration for TRGO-PGA increased in comparison to TRGO-PG $(2.9\% \rightarrow 5.9\%)$ due to its additional amine groups. The Sulfur surface concentration increased from 0% to 2.3% upon sulfation process because of a successful production of TRGO-PGS. Formation of ZGNM_{50%} and ZGNM_{90%} was also proven by XPS. After conjugation of polyglycerolamine to TRGO-PGS, the nitrogen surface concentration increased from 3.2% to 6.6% in the case of ZGNM_{50%}. This result confirmed conjugation of polyglycerolamine to TRGO-PGS and successful synthesis of ZGNM.



Figure S4. C1s spectra of TRGO-PG, TRGO-PGS, ZGNM_{50%}, ZGNM_{90%}. After conjugation of PGA to TRGO-PGS, the peaks corresponding to the C-N and C-O bonds intensely increased as shown with arrows. Highly resolved C1s XPS spectra of TRGO-PG, TRGO-PGS, ZGNM_{50%}, ZGNM_{90%} are shown in Figure 2. Assignments of peaks are shown in Table S3.

The C1s spectra of TRGO-PG and TRGO-PGS are very similar confirming that these samples are characterized by similar carbon surface concentrations and PG backbones. This result reveal that the PG backbones at the functionalized sheets did not change upon sulfation.

C1s spectra showed peaks at 284.6 corresponding to graphene and 286.7, 287.1 eV, which are assigned to the carbon of polyglycerol, respectively.



Figure S5. Highly resolved N1s of (a) TRGO-PGA, (b) TRGO-PGS, and S2p XPS spectra of (c) TRGO-PGS, and (d) ZGNM_{50%}. Fitting parameters are shown in Table S3.

Table S3. Fitting parameters of XPS spectra of TRGO, TRGO-PG, TRGO-PGA, TRGO-PGS,ZGNM50%.

Sample	Spectrum	Binding	L-G	FWHM	Interpretation	Relat.	Abs.
		energy	Mixing			Area	Area
TRGO	C 1s	284.6	0.66	0.77	C-C sp ²	0.89	38852
		286.1	0. 69	0.86	С-О-С, С-О-Н	0.05	2247

		286.7	0. 69	0.86	O-C-O	0.02	923
		291.3	0. 69	0.86	π - π * shake ups	0.01	382
TRGO-PG	C1s	284.6	0.74	0.87	C-C sp ²	0.64	31661
		285.5	0.74	1.13	C-N-H	0.01	383
		286.7	0.74	1.13	С-О-С, С-О-Н	0.13	6599
		287.1	0.74	1.13	O-C-O	0.19	9756
		288.7	0.74	1.13	СОО, СООН	0.01	340
TRGO-PGA	C1s	284.6	0.54	0.93	C-C sp ²	0.43	16244
		285.8	0.54	1.10	C-N-H	0.10	3876
		286.5	0.54	1.10	С-О-С, С-О-Н	0.17	6597
		287.1	0.54	1.10	O-C-O	0.26	9875
		288.9	0.54	1.10	СОО, СООН	0.01	507
	N1s	398.9	0.23	1.16	C-N-C, C-N-H	0.09	434
		400.3	0.23	1.94	N-C=O	0.87	4297
		402.6	0.23	1.40	C-N=O	0.04	233
TRGO-PGS	C1s	284.6	0.73	0.83	C-C sp ²	0.62	32940
		285.5	0.73	1.04	C-N-H	0.01	169
		286.6	0.73	1.04	С-О-С, С-О-Н	0.19	10227
		287.2	0.73	1.04	O-C-O	0.15	7837
		288.4	0.73	1.04	СОО, СООН	0.01	772
		289.8	0.73	1.04	π - π * shake ups	0.01	252
	N1s	399.1	0	1.60	C-N-C, C-N-H	0.31	906
		400.6	0	1.60	N-C=O	0.56	1678
		402.3	0	1.60	C-N=O	0.13	394
	S 2p	169.3	0.22	1.14	-O-SO3	1	3539

ZGNM _{50%}	C1s	284.6	0.18	0.85	C-C sp ²	0.26	6795
		285.7	0.18	1.11	C-N-H	0.17	4503
		286.6	0.18	1.11	С-О-С, С-О-Н	0.19	5009
		287.1	0.18	1.11	С=0, 0-С-0	0.31	8207
		288.8	0.18	1.11	COO, COOH	0.04	924
	N1s	399.3	0.19	1.55	C-N-C, C-N-H	0.05	226
		400.7	0.19	1.55	N-C=O	0.60	2597
		402.4	0.19	1.55	C-N=O	0.35	1528
	S 2p	169.2	0.20	1.18	-O-SO ₃	1	1799
ZGNM _{90%}	C1s	284.6	0.18	1.03	C-C sp ²	0.14	2982
		285.7	0.18	1.23	C-N-H	0.24	5110
		286.8	0.18	1.03	С-О-С, С-О-Н	0.24	5195
		287.2	0.18	1.23	С=0, О-С-О	0.26	5488
		288.7	0.18	1.34	СОО, СООН	0.11	2290
	N1s	399.3	0.12	1.50	C-N-C, C-N-H	0.04	170
		400.6	0.12	1.50	N-C=O	0.88	3671
		402.4	0.12	1.50	C-N=O	0.08	334
	S 2p	169.1	0.24	1.23	-O-SO3	1	287

However, after conjugation of polyglycerolamine to TRGO-PGS, the intensity of carbon peaks at 286.6 and 287.1 eV increased. Also an increase in the peak at 285.7 eV assigned to the C-N bonds could be observed. This result proved that polglyceroamine conjugated to TRGO-PGS (Table S3).

Highly resolved N1s and S2p spectra proved successful functionalization of the graphene sheets. Splitting and shifting of the N1s peak after conjugation of polyglycerolamine to the

surface of TRGO-PGS proved the successful synthesis of ZGNM. S2p peak at 169.3 eV in the XPS spectra corresponding to the sulfate groups^[1] proved successful sulfation of TRGO-PG.

Sample	C _{PG} /C _{TRGO}	O/C ratio	N/C ratio	S/C ratio	N/S ratio
TRGO-PG	0.51	0.24	0.04	-	-
TRGO-PGA	1.01	0.23	0.08	-	-
TRGO-PGS	0.54	0.38	0.05	0.035	0.84
ZGNM _{50%}	1.94	0.35	0.10	0.033	2.30
ZGNM _{90%}	3.69	0.35	0.12	0.006	19

Table S4. Atomic ratios of the elements in the XPS spectra.



Figure S6. Full (a) C K-edge NEXAFS of TRGO, TRGO-PG, TRGO-PGA, (b) N K-edge NEXAFS of TRGO-PG, TRGO-PGA; expanded low energy section of (c) C K-edge

NEXAFS of TRGO, TRGO-PG, TRGO-PGA, (d) N K-edge NEXAFS of TRGO-PG, TRGO-PGA.

At the low-energy side the C K-edge spectra (Figures S6a,c) showed that the TRGOrelated π^* resonance intensity at photon energy of 285.4 eV (a) (corresponding to C1s $\rightarrow \pi^*$ transition^[2]) decreased with increasing polymer coverage. In Figure S6a π^* and σ^* refer to antibonding molecular orbitals of π and σ symmetry, respectively. A major change upon the modification in the C K-edge NEXAFS was the occurrence of the resonance (b) at 289.3 eV that was assigned to C–H* resonances related to PG.^[3] The presence of this signal proved the successful synthesis of TRGO-PG and TRGO-PGA. Another relevant feature is the doublestructured resonance around 292 eV that corresponds to C1s $\rightarrow \sigma^*$ transitions in graphene (TRGO).^[2a] It occurred from excitonic (resonance at 291.8 eV) and band-like contributions (broader signal at around 292.8 eV). In N K-edge NEXAFS (Figures S6b,d), the N1s $\rightarrow \sigma^*$ resonance of amines above 401 eV is present for TRGO-PGA and verifies successful conjugation of PGA with TRGO.^[2b]



Figure S7. Full (a) C K-edge NEXAFS of TRGO-PGS, ZGNM_{50%} and ZGNM_{90%}, (b) N K-edge NEXAFS of ZGNM_{50%} and ZGNM_{90%}, expanded low energy section of (c) C Kedge NEXAFS of TRGO-PGS, ZGNM_{50%}, and (d) N Kedge NEXAFS of ZGNM_{50%} and ZGNM_{90%}.

The C K-edge NEXAFS spectra (Figures S7a, S7c) of modifications of TRGO by polyglycerol amine and polyglycerol sulfate still showed the presence of an intense peak at 285.4 eV that corresponded to C1s $\rightarrow \pi^*$ transition.^[2]

Table S5. Resonances in the C and N K-edge NEXAFS measured with TRGO, TRGO-PG, TRGO-PGA, TRGO-PGS, ZGNM_{50%}.

Sample		Photon energy	Assignment				
	C K-edge NEXAFS						
TRGO	a	285.4 ^[2a]	$C1s \rightarrow \pi^*$				

TRGO-PG	a	285.4 ^[2a]	$C1s \rightarrow \pi^*$
	b	289.3 ^[1]	C-H*
TRGO-PGA	a	285.4 ^[2a]	$C1s \rightarrow \pi^*$
	b	289.3 ^[1]	С-Н*
TRGO-PGS	i	285.4 ^[2a]	$C1s \rightarrow \pi^*$
	j	287.2	
ZGNM _{50%}	i	285.4 ^[2a]	$C1s \rightarrow \pi^*$
	k	288.1	
	1	289.5	
ZGNM _{90%}	i	285.4 ^[2a]	$C1s \rightarrow \pi^*$
	k	288.1	
	1	289.5	
	1	N K-edge N	EXAFS
TRGO-PG	d	400.1	
	e	400.9	
	f	401.2	
	g	401.6 ^[2b, 4]	N1s $\rightarrow \pi^*$ (amine)
	h	401.8	
TRGO -PGA	c	399.1	
	d	400.1	
	e	400.9	
	f	401.2	
	g	401.6 ^[2b, 4]	N1s $\rightarrow \pi^*$ (amine)
	h	401.8	

ZGNM _{50%}	m	398.9	
	n	401.5 ^[2b, 4]	N1s $\rightarrow \pi^*$ (amine)
ZGNM _{90%}	m	398.9	
	n	401.5 ^[2b, 4]	N1s $\rightarrow \pi^*$ (amine)

The N K-edge spectra (Fig. S7b,d) consisted of intense resonances (n) which is related to the nitrogen atoms that are connected with carbon atoms in $ZGNM_{50\%}$ and $ZGNM_{90\%}$. Therefore, NEXAFS carried a self-sufficient evidence of the introduction of PGA to TRGO-PGS.

7. AFM height profile of graphene derivatives



Figure S8. Morphology of TRGO-PGS sheets imaged in MillliQ water. (a) Low resolution image, where the individual (upper region) sheets and sheet aggregation (lower right) are clearly seen. In (b) and (c) consecutively zoomed regions are shown where sheet topography can be appreciated in more detail. In (d) and (e), cross-section profiles for two sheets shown in (b). It can easily be seen that sheets imaged in liquid can present folded but crumbled conformations with wrinkles and twisted areas. This can notably increase their lateral height.



Figure S9. (a) and (d) show high resolution AFM height images of individual TRGO-PGA. In (b) and (e), a 3D reconstruction of the sheet morphology is provided where the high degree of bending and corrugation is evident. In (c) and (f), cross-section profiles of the sheets showing clear undulations across the sheets' surface.



Figure S10. Histogram for the mean sheet size measured with the AFM software Nanoscope Analysis 1.4. Since most of the imaged graphene sheets above in S14 and S15 showed a folded or wrinkled features, the real size of gthe sheets should therefore be slightly larger than the values shown in the histogram.

8. Live and dead assay



Figure S11. CLSM images of Syto 9 and PI stained *E. coli* at (a) pH 7.4, (b) pH 5.0, (c) pH 8.5, (d) incubated with TRGO-PG, (e) incubated with TRGO-PGS, and (f) incubated with TRGO-PGA. Live cells are stained green; dead cells are stained red.



Figure S12. CLSM images of Syto 9 and PI stained *E. coli* (a) incubated with ZGNM_{50%} at pH 7.4, (b) incubated with ZGNM_{50%} at pH 5.0, (c) incubated with ZGNM_{90%} at pH 8.5, and (d) incubated with ZGNM_{90%} at pH 7.4. Live cells are stained green; dead cells are stained red.

9. AFM force spectra of graphene derivatives incubated with E. coli



Figure S13. Representative force-separation curves of the interaction between AFM tips decorated with TRGO-PGA and cleaved mica surface in Milli-Q water. An strong adhesion force was obtained, since both surfaces were oppositely charged in solution. During retraction of the tip (red line) in (a), it is easy to observe the characteristic plateaus in the force, which resembles those usually found for the desorption of single polymer chains. Contrary to single linear chains, functionalized TRGO sheets are prone to bend, twist, wrinkle, or collapse in such a way that the force-response pattern during desorption can provide complex escenarios as shown in Figure b.



Figure S14. Representative force-separation curves for the non-specific adhesion (a) and repulsive behavior (b). In (a) a TRGO-PG sheet was probed against *E. coli* while in (b) a TRGO-PGS was used.



Figure S15. AFM image, in air, of biofilm monolayer of *E. coli* formed on a poly-L-lysine coated mica surface. Images show that a dense coverage by *E. coli* on the substrate is achieved. This *E. coli* covered platform is used in force spectroscopy experiments performed in buffer to test binding interactions between *E. coli* and functionalized TRGO and ZGNM. It can also be observed that although a dense biofilm is formed, the surface is not fully packed, and some regions from the substrate are still present between the bacteria. In b) 3D reconstruction of surface topography.

Table S6. Values obtained from force spectroscopy measurements for the interaction of differently functionalized TRGO sheets at different pH values and the sample surface. Because bacteria attached on the substrate not always presented a fully packed film, some nonspecific binding interactions were also obtained.

Material	рН	Binding %	Non-specific B.	Repulsive/no
			%	adhesion %
TRGO-PGA	7.4	82	10.5	7.5
TRGO-PGS	7.4	18.1	9.2	72.7
TRGO-PG	7.4	33.3	4.2	62.5
ZGNM _{50%}	7.4	36	64	-
ZGNM _{50%}	5.0	71.4	4.5	24.1
ZGNM _{90%}	7.4	73.7	18.2	8.18
ZGNM _{90%}	8.5	16.6	46.7	40.7

Figure S16 shows TGA of TRGO-PG-NH₂ and TRGO-NH₂. The polyglycerol content of TRGO-PG-NH₂ is more than 90% according to weight loss percent in TGA themogram of this compound. Also TRGO-NH₂ shows less than 15% weight loss up to 500 °C assigned to the triazine and ethylenediamine segments conjugated to graphene.

Figure S17 a and b show IR spectra of TRGO-PG-NH₂ and TRGO-NH₂, respectively. Strong absorbance bands at 3500 cm⁻¹, 2985 cm⁻¹ and 1150 cm⁻¹ are assigned to the hydroxyl, C-H and C-O stretching vibrations of polyglycerol branches conjugated to the surface of TRGO. A small absorbance band at 1550 cm⁻¹ is due to the C=C bonds of graphene sheets. In the IR spectra of TRGO-NH₂, a broad absorbance band at 1400-1650 cm⁻¹ is related to the C=C and C=N bonds of graphene and triazine functional groups, respectively. Absorbance band at 1300 cm⁻¹ is assigned to C-N stretching vibrations.



Figure S16. Thermogravimetric analysis (TGA) of graphene sheets with very high polyglycerolamine coverage (TRGO-PG-NH₂) and without polymer coverage (TRGO-NH₂).



Figure S17. IR spectra of a) TRGO-PG-NH $_2$ and b) TRGO-NH $_2$.

10. References

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