Stability of radical-functionalized gold surfaces by self-assembly and on-surface chemistry

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1) SAM2 Survey.

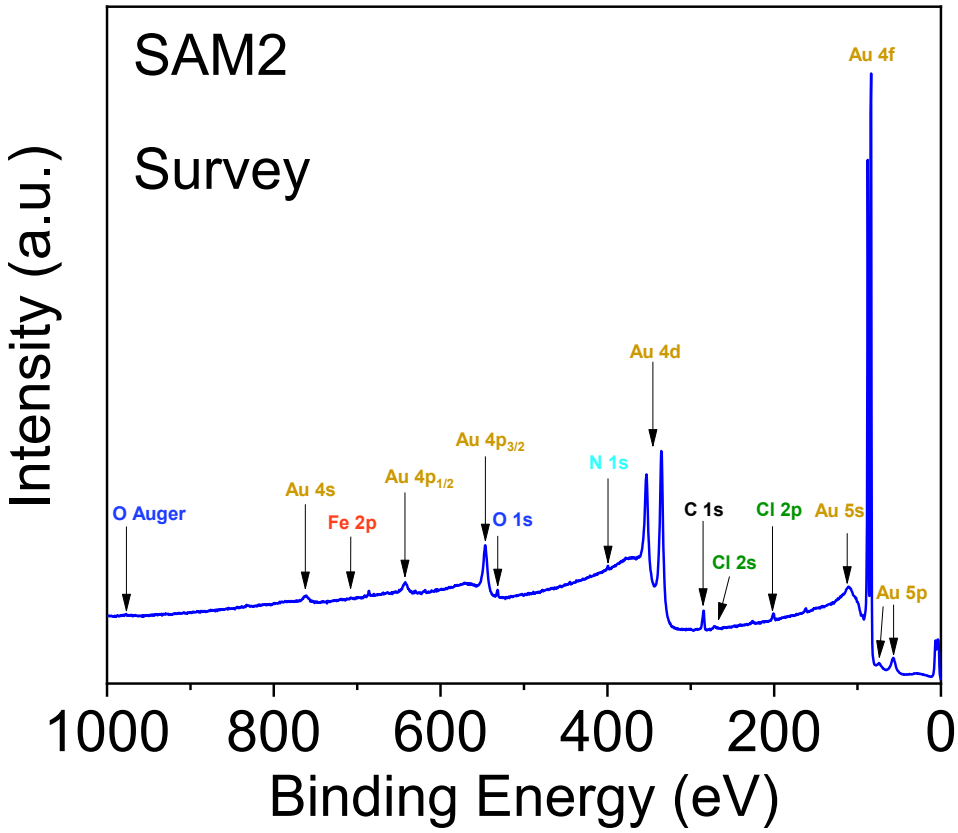

Figure S1. SAM2 XPS survey spectrum (photon energy: 1486.6 eV).

Stoichiometric and experimental elemental ratios for SAM2.

	C	**N**	**Cl**	**Fe**
Sensitivity factor*	0.25	0.42	0.73	3
Number of atoms	50	3	13	1
Theoretical values (%)	75	4	19	2
SAM2F (%)	84.3	5.2	10.0	0.5

Table S1. Stoichiometric and experimental elemental ratios for SAM2.

*C. D. Wagner, *J. Electron Spectrosc. Relat. Phenom.* **1983**, *32*, 99-102.

Table S2. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.2	0.08	1.00	19.9	22
C-H	284.6	0.08	1.00	36.5	46
S_1	285.3	0.08	1.00	11.9	
C-N	285.7	0.08	1.00	6.6	6
C-Cl	286.3	0.08	1.30	21.8	26
S_2	288.1	0.08	1.30	3.3	

C-C + C-H + S_1 = 68.3 %

C-Cl + S_2 = 25.1 %

2) SAM1 Survey.

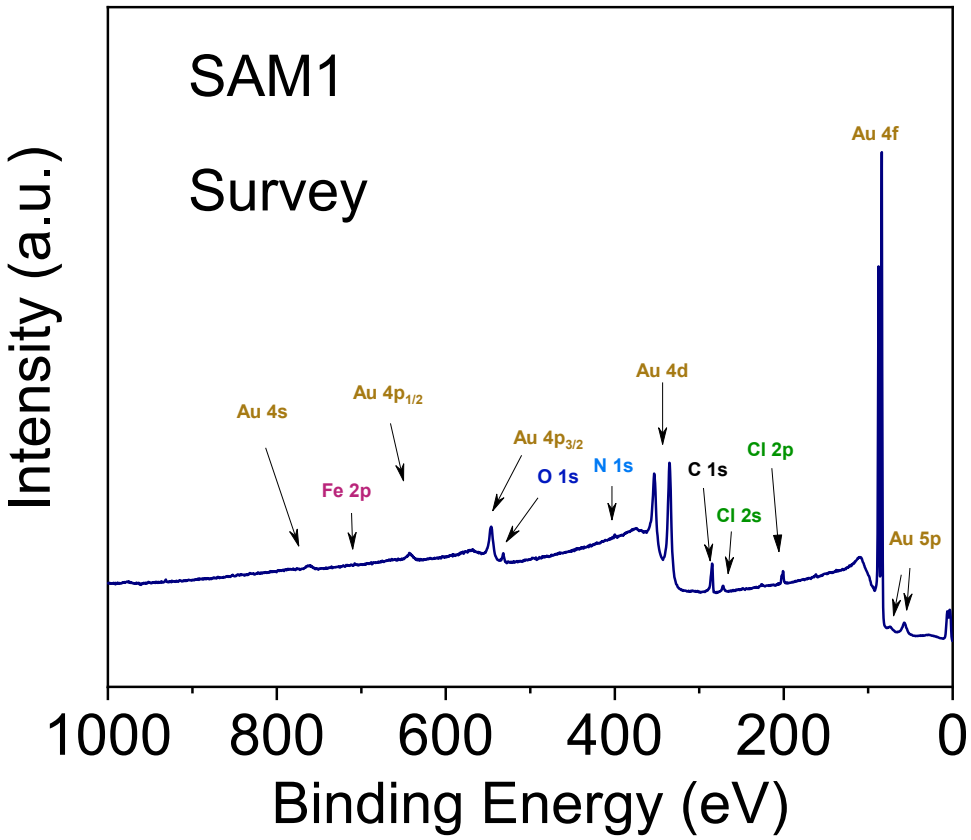

Figure S2. SAM1 XPS survey spectrum of (photon energy: 1486.6 eV).

	C	N	Cl	Fe
Sensitivity factor*	0.25	0.42	0.73	3
Number of atoms	50	3	13	1
Theoretical values (%)	75	4	19	2
SAM1 (%)	79	6	14	1

Table S3. Stoichiometric and experimental elemental ratios for SAM1.

*C. D. Wagner, *J. Electron Spectrosc. Relat. Phenom.* **1983**, *32*, 99-102.

Table S4. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM1 C 1s spectra.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.3	0.08	0.88	23.0	20
C-H	284.9	0.08	0.88	33.4	48
S_1	285.5	0.08	0.88	10.0	
C-N	285.7	0.08	0.89	6.1	6
C-Cl	286.5	0.08	1.10	23.4	26
S_2	288.5	0.08	1.50	4.1	

C-C + C-H + S_1 = 66.4 %

C-Cl + S_2 = 27.5 %

3) C 1s core level spectra at 460 and 640 eV.

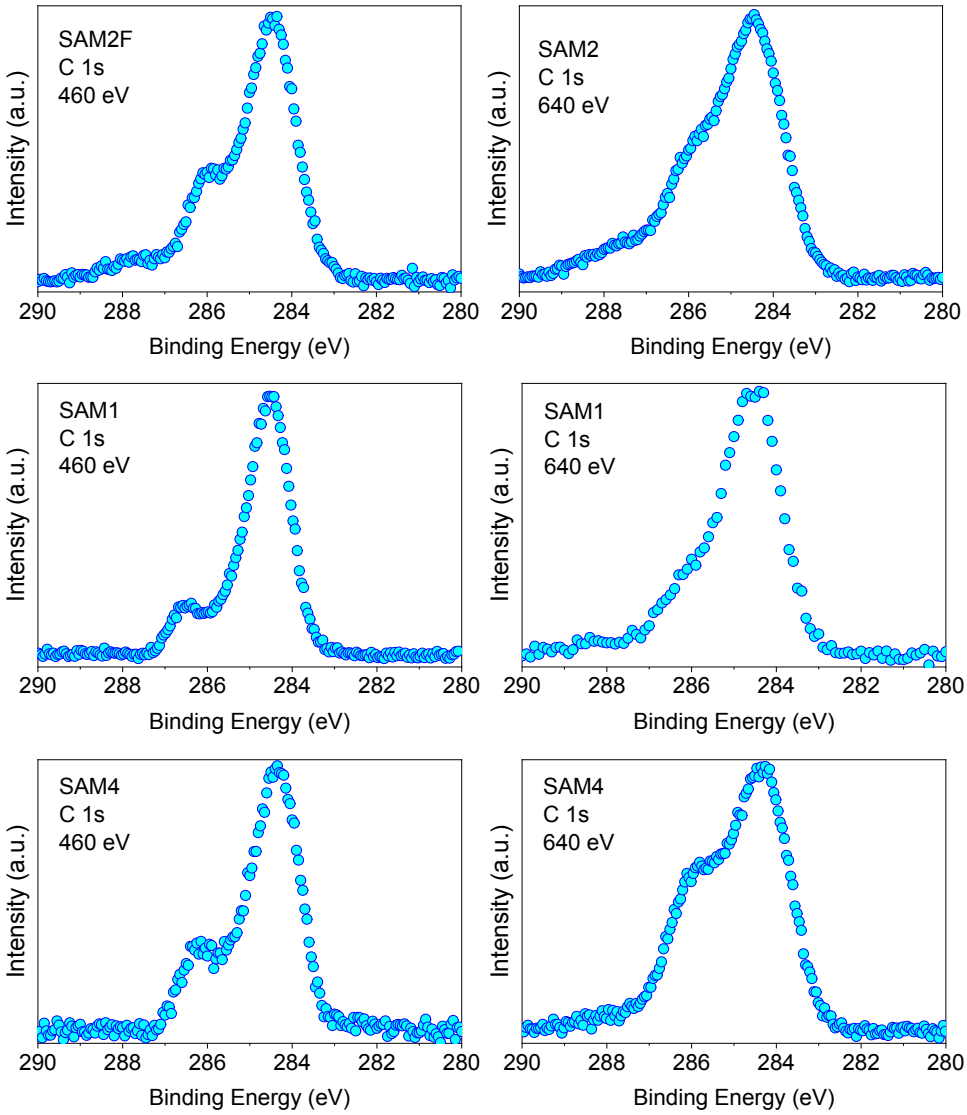

Figure S3. C 1s core level spectra at 460 and 640 eV, as indicated. Upper panel: SAM2. Middle panel: SAM1. Lower panel: SAM4. Intensities are normalized to the peak maximum to allow comparison.

4) Fit results for SAM2 and SAM4 at 460 eV.

Table S5. SAM2 C 1s at 460 eV. Fit results for the energy positions and relative intensities.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.1	0.08	1.05	19.0	22
C-H	284.5	0.08	1.05	41.5	46
S_1	285.1	0.08	1.05	9.0	
C-N	285.5	0.08	1.05	6.5	6
C-Cl	286.1	0.08	1.05	19.0	26
S_2	287.8	0.08	1.35	5.0	

C-C + C-H + S_1 = 69.50 %

C-Cl + S2 = 24.00 %

Table S6. SAM4 C 1s at 460 eV. Fit results for the energy positions and relative intensities.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.1	0.08	1.05	19.3	22
C-H	284.4	0.08	1.05	42.6	46
S_1	285.1	0.08	1.05	9.1	
C-N	285.5	0.08	1.05	6.6	6
C-Cl	286.3	0.08	1.05	18.3	26
S_2	288.1	0.08	1.35	4.1	

C-C + C-H + S_1 = 71 %

C-Cl + S2 = 22.4 %

5) Fit results for SAM2 and SAM4 at 640 eV.

Table S7. SAM2 C 1s at 640 eV. Fit results for the energy positions and relative intensities.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.1	0.08	1.30	17.9	22
C-H	284.5	0.08	1.30	37.7	46
S_1	285.1	0.08	1.30	8.3	
C-N	285.5	0.08	1.30	6.0	6
C-Cl	286.0	0.08	1.30	21.0	26
S_2	287.7	0.08	1.70	9.1	

C-C + C-H + S_1 = 63.9 %

C-Cl + S2 = 30.1 %

Table S8. SAM4 C 1s at 640 eV. Fit results for the energy positions and relative intensities.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.0	0.08	1.30	17.6	22
C-H	284.4	0.08	1.30	37.3	46
S_1	285.0	0.08	1.30	8.4	
C-N	285.5	0.08	1.30	6.1	6
C-Cl	286.0	0.08	1.30	26.8	26
S_2	287.7	0.08	1.70	3.8	

C-C + C-H + S_1 = 63.3 %

C-Cl + S2 = 30.6 %

6) Electrochemical measurements

Cyclic voltammetry experiments were performed with an AUTOLAB 204 potentiostat equipped with NOVA 2.3 software. A Pt mesh was used as the counter electrode, Ag/AgCl 3M KCl was used as reference electrode. For the electrochemical characterization of the SAMs, the modified Au was used as the working electrode (area exposed of 1 cm^2). A 0.2M solution of $TBAPF_6$ in dry CH_2Cl_2 was used as the electrolytic medium, under argon atmosphere.

The redox peaks corresponding to PTM radical ↔ PTM anion and ferrocene ↔ ferrocenium redox process are clearly observed.

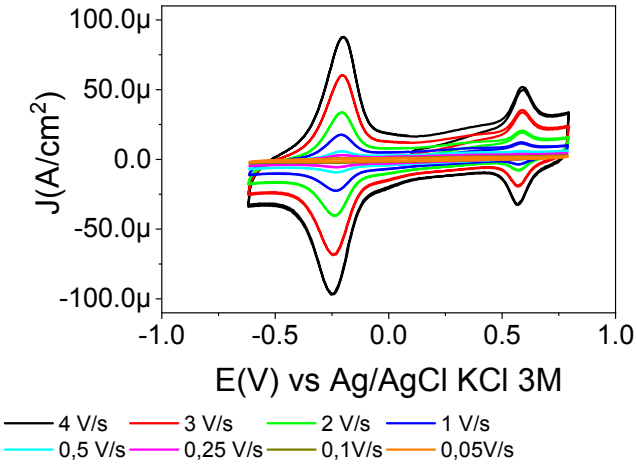

Figure S4. Cyclic voltammetry behavior of SAM4 using as electrolytic medium solution 0.2M $TBAPF_6$/ CH_2Cl_2, under argon atmosphere.

7) Stability under air exposure.

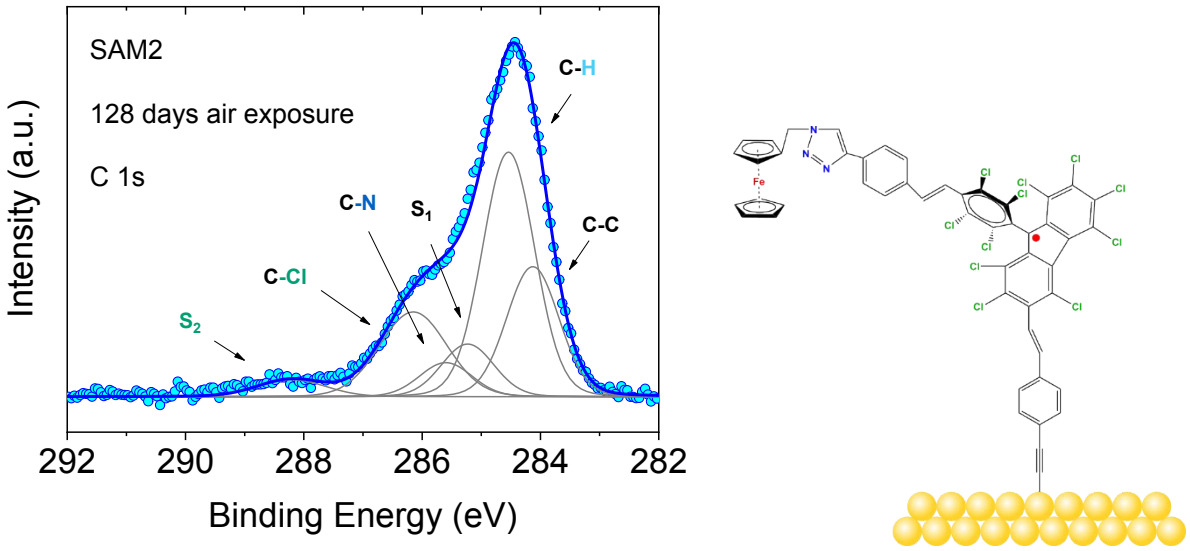

Figure S5. C1s core level spectrum together with its fit analysis after 128 days air exposure. The fit hypothesis was based on the switch to the PPF radical (chemical structure on the right, photon energy: 1486.6 eV).

Table S9. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra after 128 days air exposure, light-induced ring closure hypothesis.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.1	0.08	1.0	22.0	26
C-H	284.5	0.08	1.0	41.3	46
S_1	285.2	0.08	1.0	8.9	
C-N	285.6	0.08	1.0	5.8	6
C-Cl	286.2	0.08	1.3	18.3	22
S_2	288.2	0.08	1.3	3.7	

C-C + C-H + S_1 = 72.2 %

C-Cl + S_2 = 22.0 %

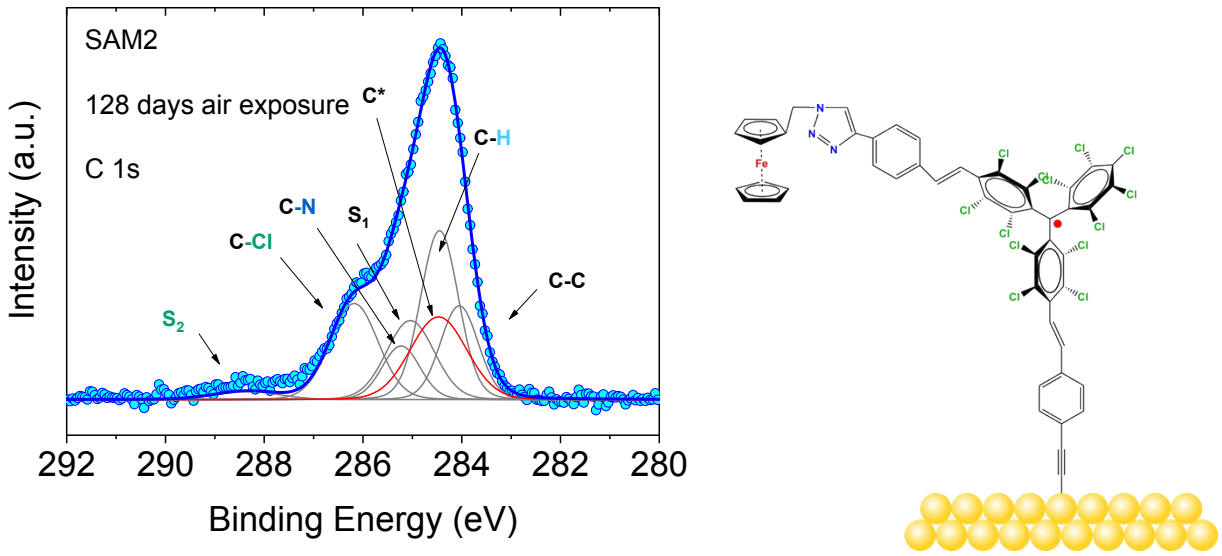

Figure S6. C1s core level spectrum together with its fit analysis after 128 days air exposure. The fit hypothesis was based on considering carbon contaminant adsorption, C*, on intact molecules (chemical structure on the right, see main text) (photon energy: 1486.6 eV).

Table S10. Fit results for the energy positions and relative intensities of the photoemission lines in the SAM2 C 1s spectra after 128 days air exposure, contaminant adsorption, C*; on intact molecules.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.2	0.08	1.0	16.6	22
C-H	284.5	0.08	1.0	30.1	46
S_1	285.3	0.08	1.0	9.9	
C-N	285.6	0.08	1.0	5.2	6
C-Cl	286.2	0.08	1.3	18.1	26
S_2	288.2	0.08	1.3	3.6	
C*	284.5	0.08	1.3	16.5	

8) Stability under beam exposure.

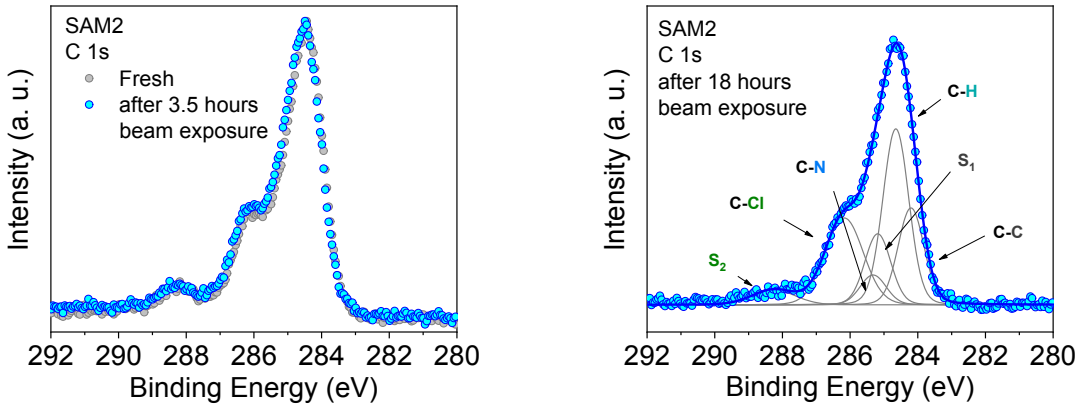

Figure S7. SAM2 C 1s spectra (left) after 3.5 hours beam exposure compared to the fresh film spectrum. No changes are detected. (right) After 18 hours beam exposure, together with its best fit (photon energy: 1486.6 eV).

Table S11. Fit results for the energy positions and relative intensities of the photoemission lines for the fresh film.

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.1	0.08	0.86	20.3	22
C-H	284.5	0.08	0.86	36.9	46
S_1	285.2	0.08	0.86	10.5	
C-N	285.3	0.08	0.87	6.1	6
C-Cl	286.2	0.08	1.07	19.8	26
S_2	288.2	0.08	1.40	6.4	

Table S12. Fit results for the energy positions and relative intensities of the photoemission lines after 18 hours X-ray (photon energy: 1486.6 eV).

	Energy (eV)	Lorentzian Width (eV)	Gaussian Width (eV)	Intensity (%)	Theoretical values (%)
C-C	284.2	0.08	0.86	20.5	22
C-H	284.7	0.08	0.86	36.0	46
S_1	285.3	0.08	0.86	11.1	
C-N	285.4	0.08	0.87	6.3	6
C-Cl	286.2	0.08	1.18	22.4	26
S_2	288.1	0.08	1.51	3.7	