Supporting Information

Investigation of the Chemical Structure of Fluorinated Diazonium Salts on the Electrografting Behavior and Thin Film Properties

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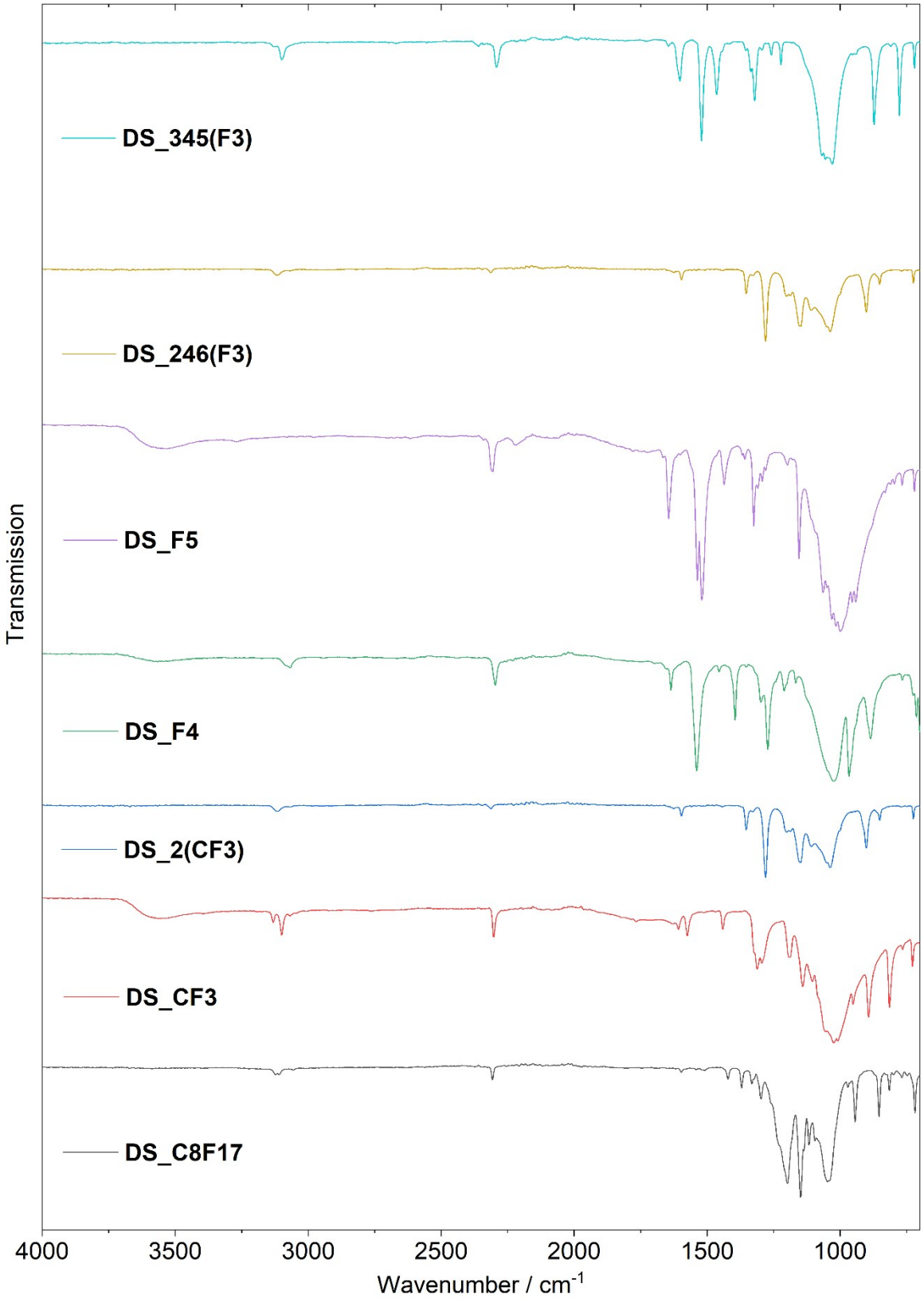


Figure S1 : IR-ATR spectra of **DS_246(F3)**, **DS_345(F3)**, **DS_F4**, **DS_F5**, **DS_C8F17**, **DS_CF3** and **DS_2(CF3)**.

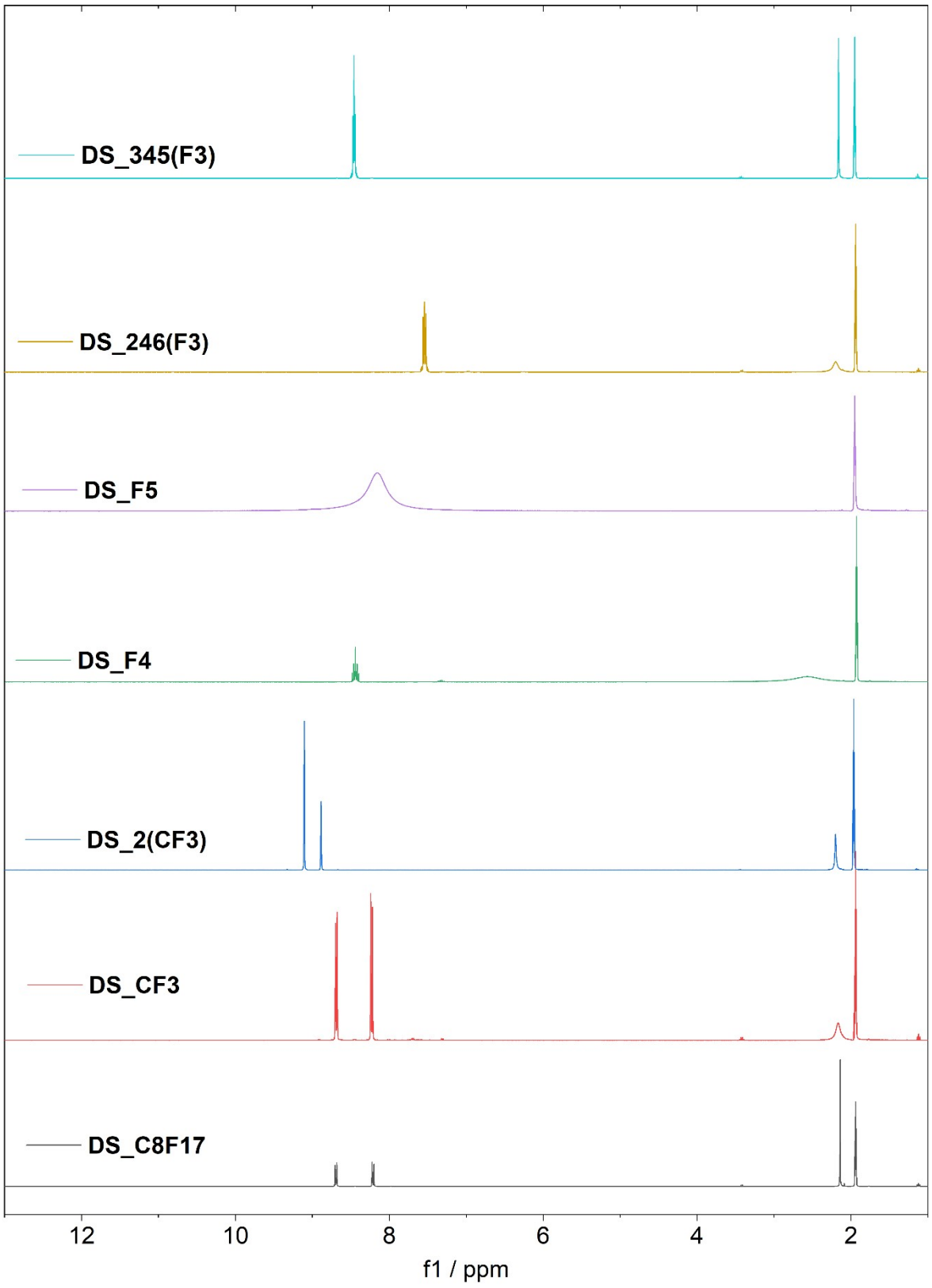


Figure S2 : ^{1}H NMR spectra of diazonium salts recorded in CD_3CN at room temperature.

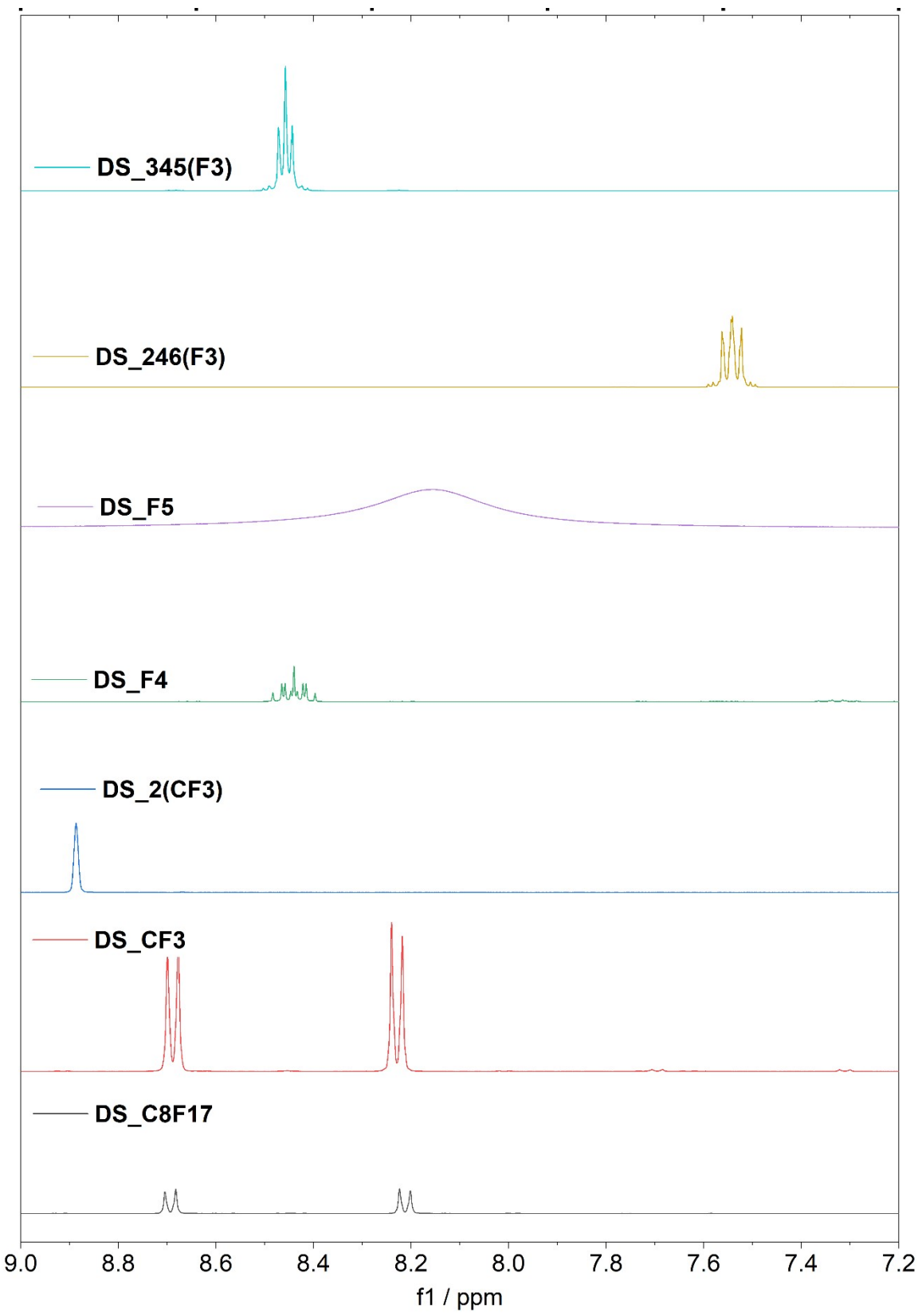


Figure S3 : ^{1}H NMR spectra zoom of diazonium salts recorded in CD3CN at room temperature.

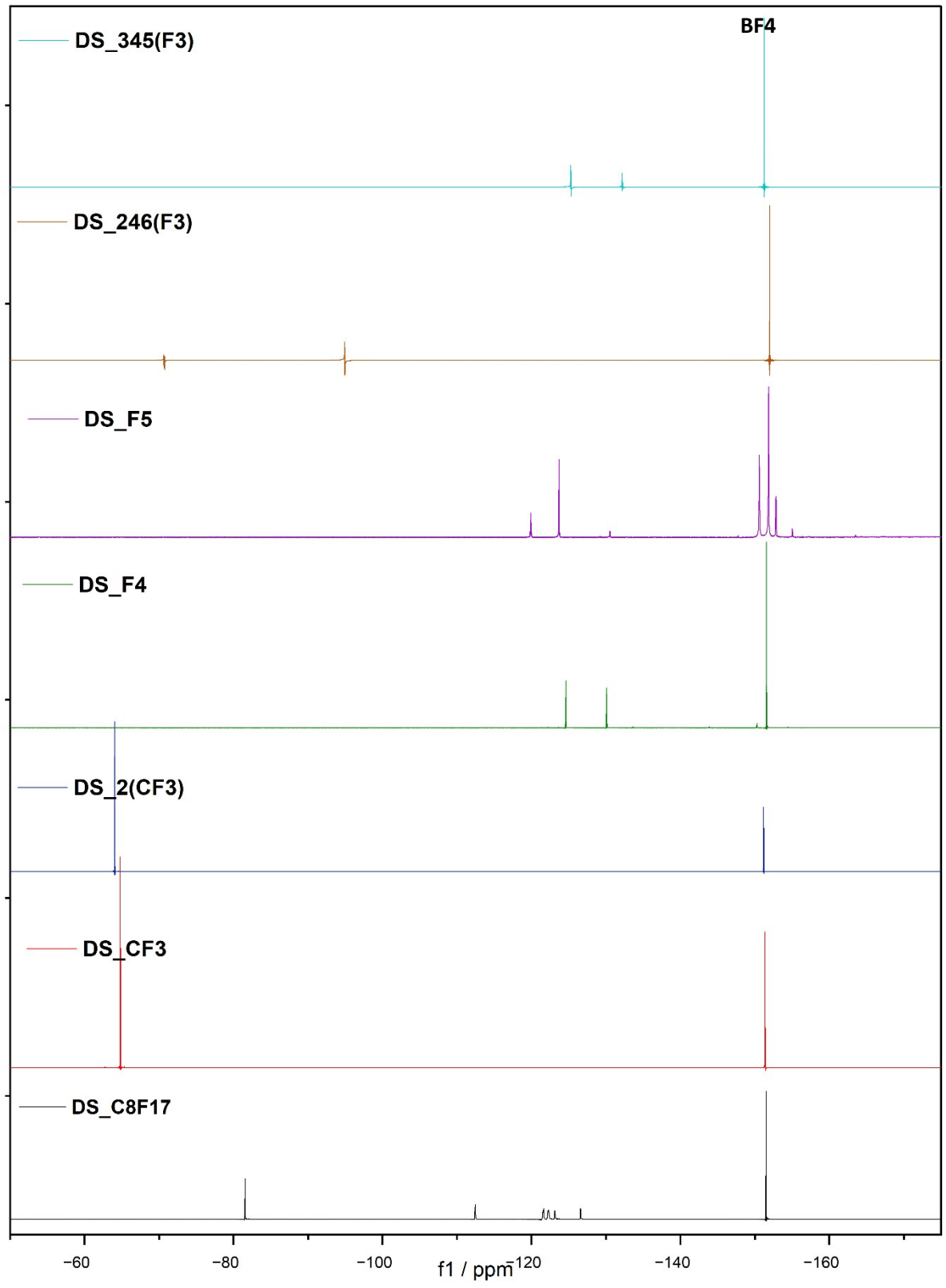


Figure S4 : ^{19}F NMR spectra of diazonium salts recorded in CD_3CN at room temperature.

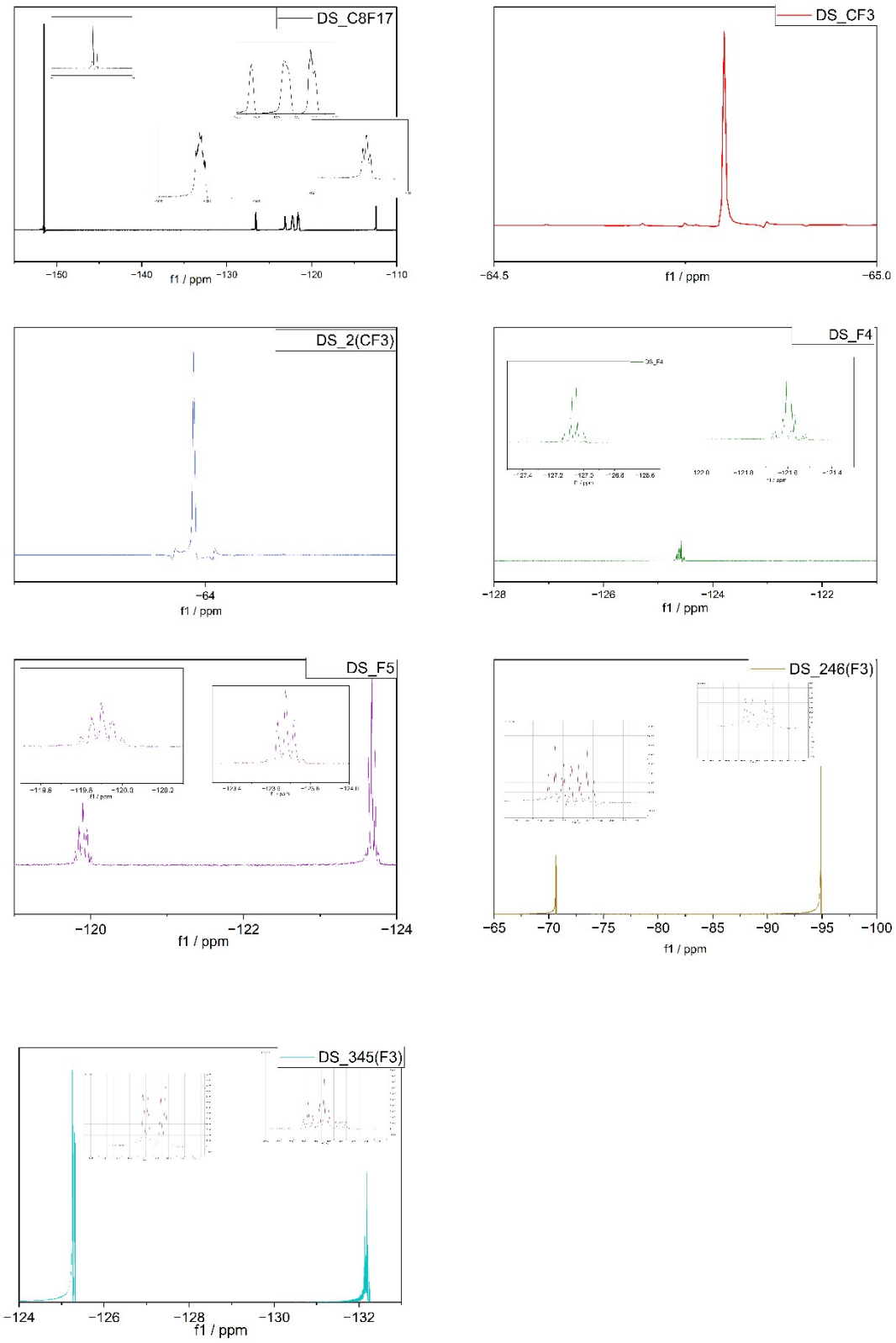


Figure S5 : ^{19}F NMR spectra zoom of diazonium salts recorded in CD_3CN at room temperature.

Synthesis reagents and NMR and infrared characterizations.

- 4-Heptadecafluorobenzene diazonium tetrafluoroborate (**DS_C8F17**): 4-(Heptadecafluorooctyl)aniline (1g, 1.96 mmol), $NOBF_4$ (274 mg, 2.35 mmol) and ACN (5 mL) yield to **DS_C8F17** (710 mg, 60% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 8.25 (2H, d, ^3J=8.60 Hz), 8.72 (2H, d, ^3J=8.60 Hz). ν_{max}/cm^{-1}: 3118, 2308 ($\nu_{N=N}$), 1371, 1198, 1148, 944, 854, 815, 649, 581, 529.

- 4-(Trifluoromethyl)benzene diazonium tetrafluoroborate (**DS_CF3**): 4-(Trifluoromethyl)aniline (1 g, 9.93 mmol), $NOBF_4$ (0.870 g, 11.92 mmol) and ACN (8 mL) yield to **DS_CF3** (1.52 g, 93% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 8.26 (2H, d, ^3J= 8.60 Hz), 8.70 (2H, d, ^3J=8.60 Hz). ν_{max}/cm^{-1}: 3100, 2303 ($\nu_{N=N}$), 1575, 1441, 1321, 1140, 1024, 893, 815, 728; 682, 519.

- 3,5-Bis(trifluoromethyl)benzene diazonium tetrafluoroborate (**DS_2(CF3)**): 3,5-Bis(trifluoromethyl)aniline (2.9 g, 12.66 mmol), $NOBF_4$ (1.77 g, 15.19 mmol) and ACN (10 mL) yield to **DS_2(CF3)** (2.41 g, 58% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 8.89 (1H, s), 9.12 (2H, s). ν_{max}/cm^{-1}: 3118, 2313 ($\nu_{N=N}$), 1596, 1445, 1353, 1280, 1149, 1037, 769, 725, 597.

- 2,3,4,5,6-Pentafluorobenzene diazonium tetrafluoroborate (**DS_F5**): 2,3,4,5,6-Pentafluoroaniline (2.0 g, 12.66 mmol); $NOBF_4$ (1.53 g, 13.11 mmol) and ACN (10 mL) yield to **DS_F5** (1.40 g, 46% yield). ν_{max}/cm^{-1}: 2306 ($\nu_{N=N}$); 1645, 1557, 1520, 1436, 1155, 999.

- 2,3,5,6-Tetrafluorobenzene diazonium tetrafluoroborate (**DS_F4**): 2,3,5,6-Tetrafluoroaniline (1.78 g, 10.79 mmol); $NOBF_4$ (1.51 g, 12.95 mmol) and ACN (8 mL) yield to **DS_F4** (1.94 g, 68% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 11.87 (1H, tt, $^3J_{H-F}$=10.00 Hz, $^4J_{H-F}$=7.50 Hz). ν_{max}/cm^{-1}: 3071, 2297 ($\nu_{N=N}$), 1636, 1539, 1395, 1272, 1210 1023, 966, 885, 713.

- 2,4,6-Trifluorobenzene diazonium tetrafluoroborate (**DS_246(F3)**): 2,4,6-Trifluoroaniline (1.65 g, 11.18 mmol); $NOBF_4$ (1.57 g, 13.42 mmol) and ACN (5 mL) yield to **DS_246(F3)** (2.3 g, 84% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 7.57 (2H, t, $^3J_{H-F}$=7.70 Hz). ν_{max}/cm^{-1}: 3065, 2308 ($\nu_{N=N}$), 1600, 1477, 1400, 1028, 1028, 868.

- 3,4,5-Trifluorobenzene diazonium tetrafluoroborate (**DS_345(F3)**): 3,4,5-Trifluoroaniline (0.625 g, 4.25 mmol); $NOBF_4$ (0.596 g, 5.10 mmol) and ACN (3 mL) yield to **DS_345(F3)** (0.810 g, 77% yield). δ ^{1}H NMR (400 MHz; CD_3CN): 8.48 (2H, dd, $^3J_{H-F}$= 5.90 Hz, $^4J_{H-F}$= 5.90 Hz). ν_{max}/cm^{-1}: 3093, 2306 ($\nu_{N=N}$), 1523, 1523, 1463, 1325, 1017, 866, 778.

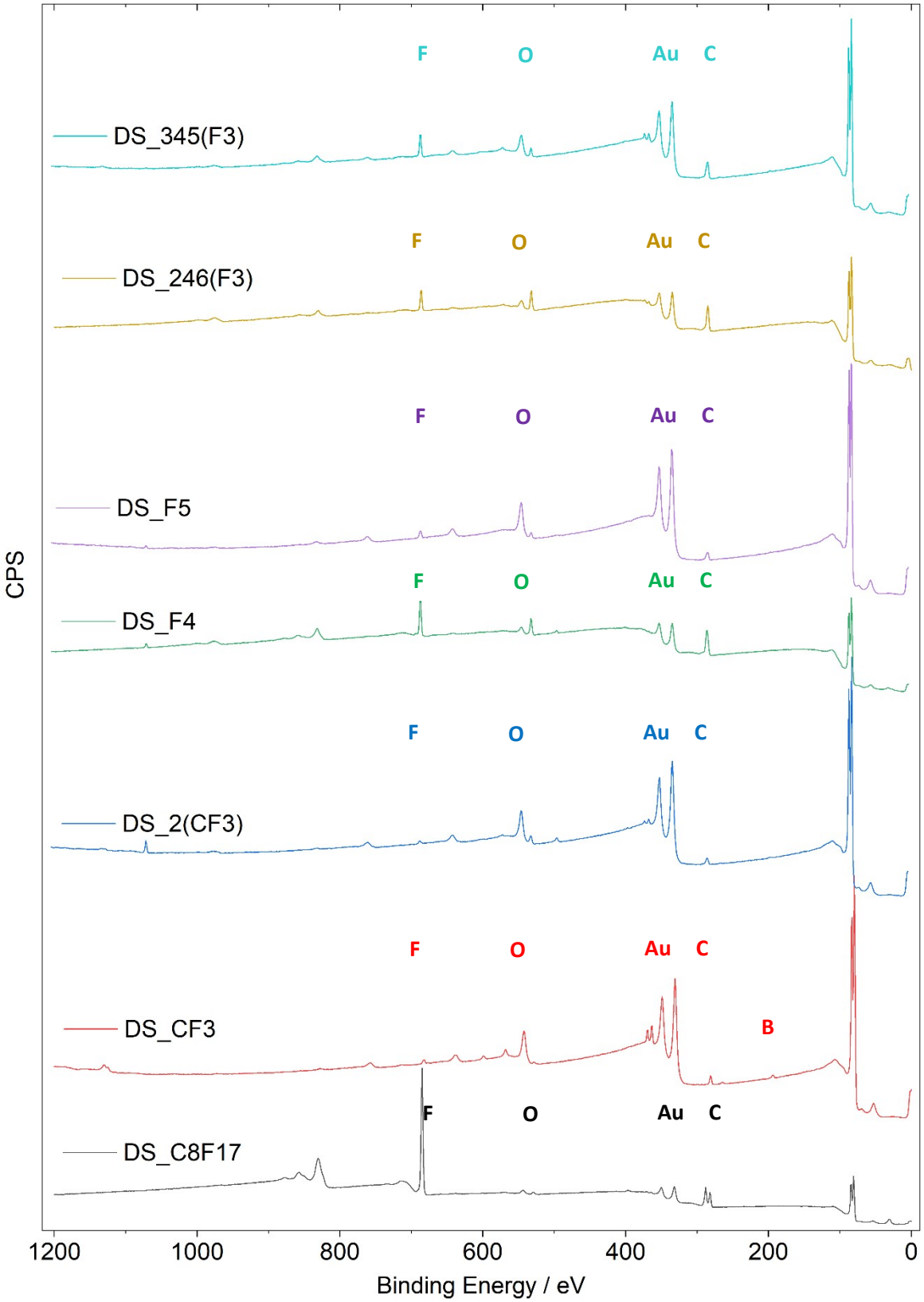


Figure S6 : XPS spectra of electrochemically grafted layers on a gold plate obtained after electrochemical grafting of diazonium salts.

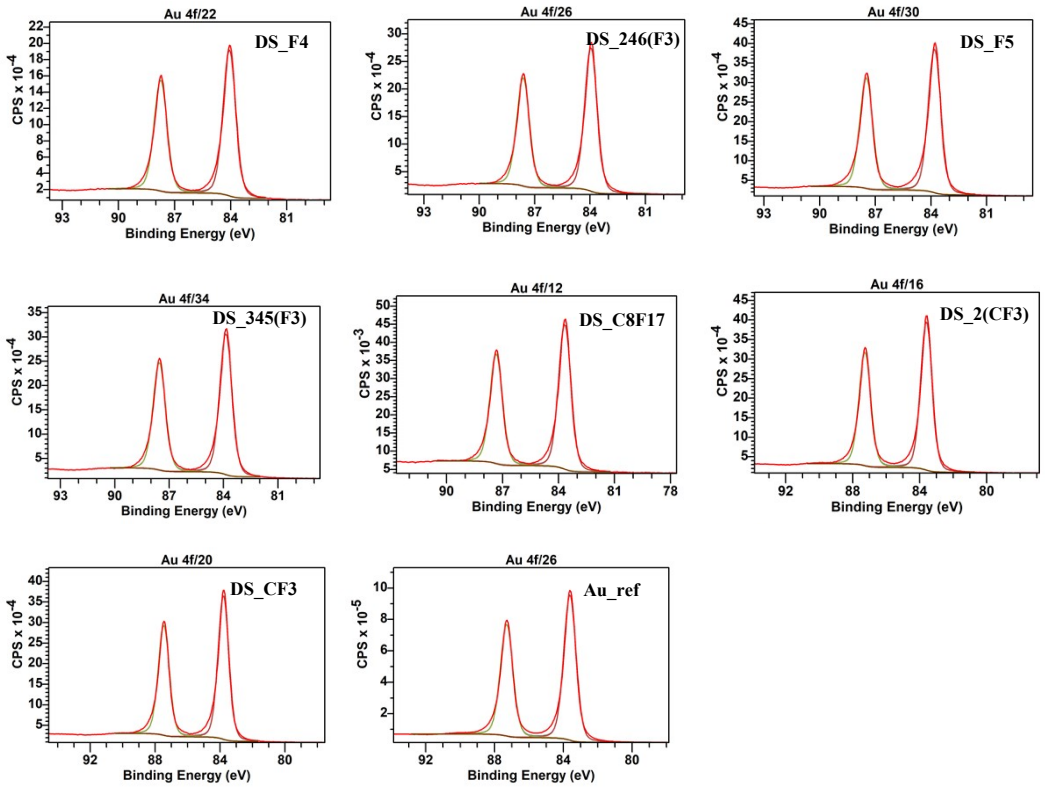


Figure S7 : XPS Au4f core level spectra of electrochemical grafted layers on gold plate obtained after electrochemical grafting of diazonium salts.

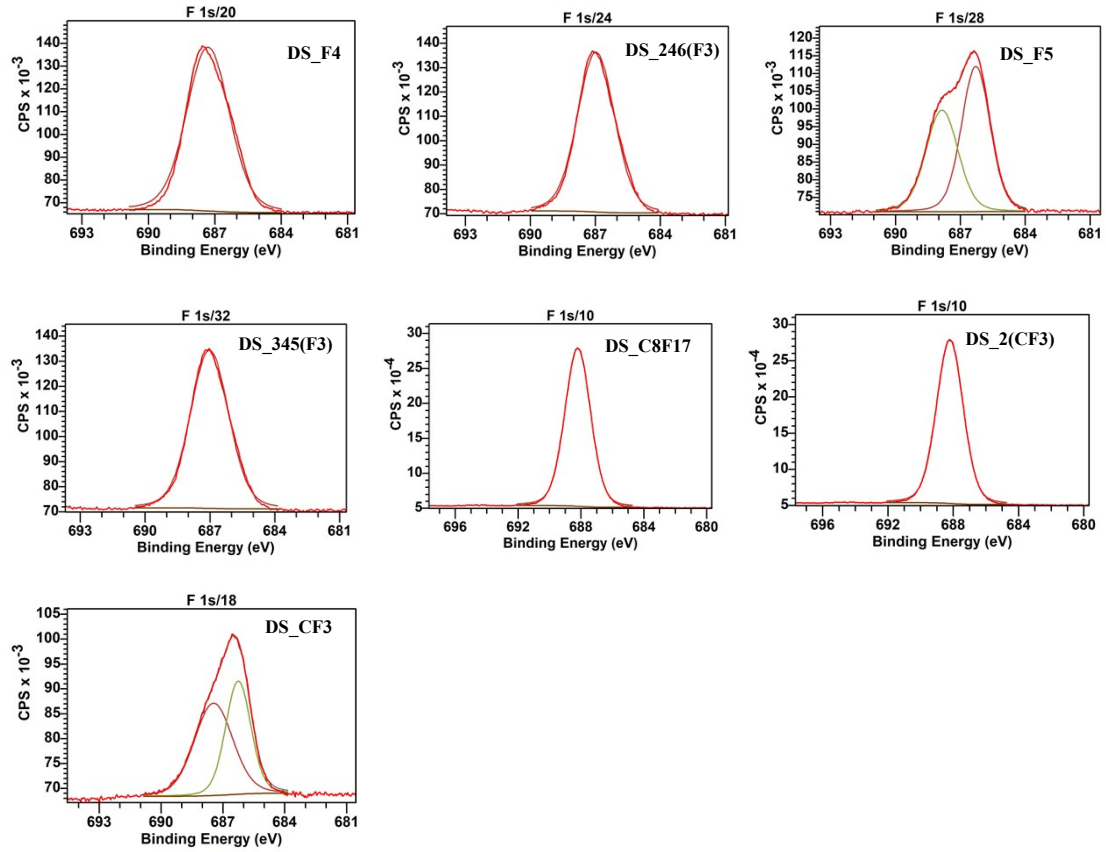


Figure S8 : XPS F1s core level spectra of electrochemical grafted layers on gold plate obtained after electrochemical grafting of diazonium salts.

Table S1 : Contact angle of Glassy carbon and gold surface before and after grafting the different diazonium salts.

Contact angle (°)	GC electrode	Gold electrode
Ref	57.7	33.1
DS_C8F17	112.2	102.2
DS_2(CF3)	105.0	108.0
DS_CF3	96.2	93.3
DS_F5	93.3	97.4
DS_345(F3)	99.6	88.6
DS_F4	86.6	90.1
DS_246(F3)	89.6	85.6

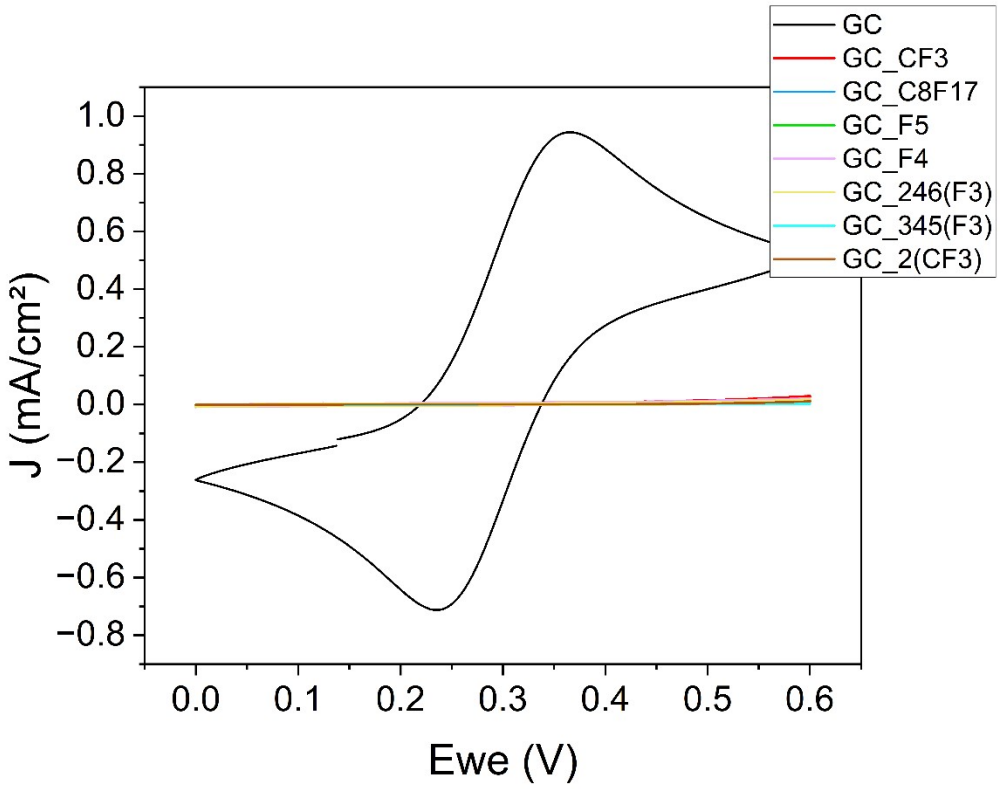


Figure S9 : Cyclic voltammograms at a scan rate of 50 mV/s for gold electrodes in a 5 mM $Fe(CN)_6^{3-/4-}$ solution before and after deposition of different diazonium salts : **DS_CF3** (red); **DS_C8F17** (blue); **DS_F5** (green); **DS_F4** (pink); **DS_246(F3)** (orange); **DS_345(F3)** (cyan); and **DS_2(CF3)** (brown).

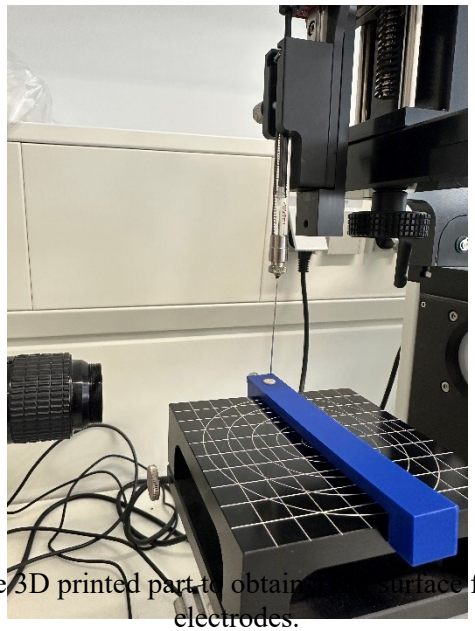


Figure S10 : Picture of the 3D printed part to obtain a flat surface for analysis of commercial electrodes.

Table S2: Contact angle of Glassy carbon and gold surface after grafting the DS_C8F17, DS_2(CF3) and DS_F4 with different solvents : water, squalene and ethanol.

	DS_C8F17		**DS_2(CF3)**		**DS_F4**	
	GC	*Au*	*GC*	*Au*	*GC*	*Au*
Water	115	109	105	98	85	87
Squalene	60	69	42	30	21	22
Ethanol	19	19	6	5	19	15

Table S3 : Surface energy, dispersive component and polar component at 25° for water, ethanol and squalene.

	Water	***Squalane***	***Ethanol***
Surface energy γ, mJ/m²), T=25°C	72.8	27.6	23.3
Dispersive component (γ^d)	21.8	27.6	18.8
Polar component (γ^p)	51	0	3.5

The measured contact angles (***Table S2***) and known surface energy values of the solvents (**Table S*3***) were used to construct a plot according to the model:

$$X = \sqrt{\frac{\gamma^{p}_{solvant}}{\gamma^{d}_{solvant}}} \quad \textit{Equation 1}$$

$$Y = \frac{\gamma_{solvant}\,(1 + cos\theta)}{2x\sqrt{\gamma^{d}_{solvant}}} \quad \textit{Equation 2}$$

γ the surface tension, γ^d the dispersive component and γ^p the polar component and θ the contact angle.

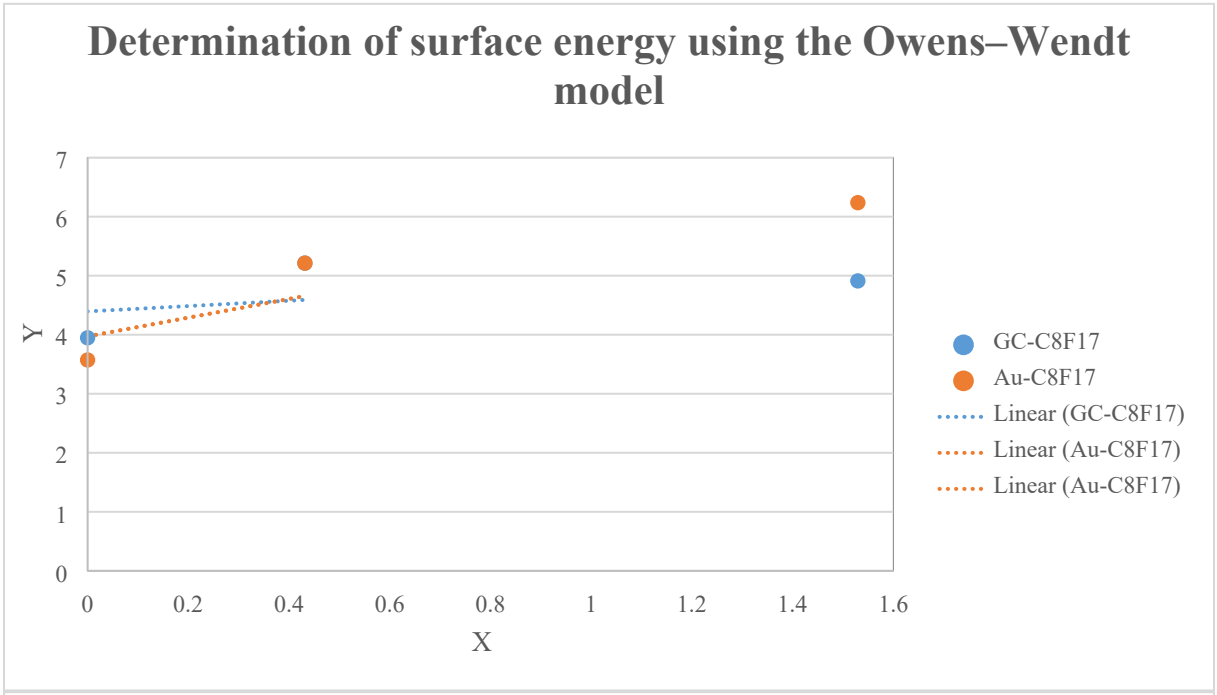
The linear equation was determined (***Figure S11***). The slope and y-intercept of the fitted line were then used to calculate the surface energy of the grafted surface using the following equations:

$$a^2 = \gamma_{surface}^{p} \quad \textit{Equation 3}$$

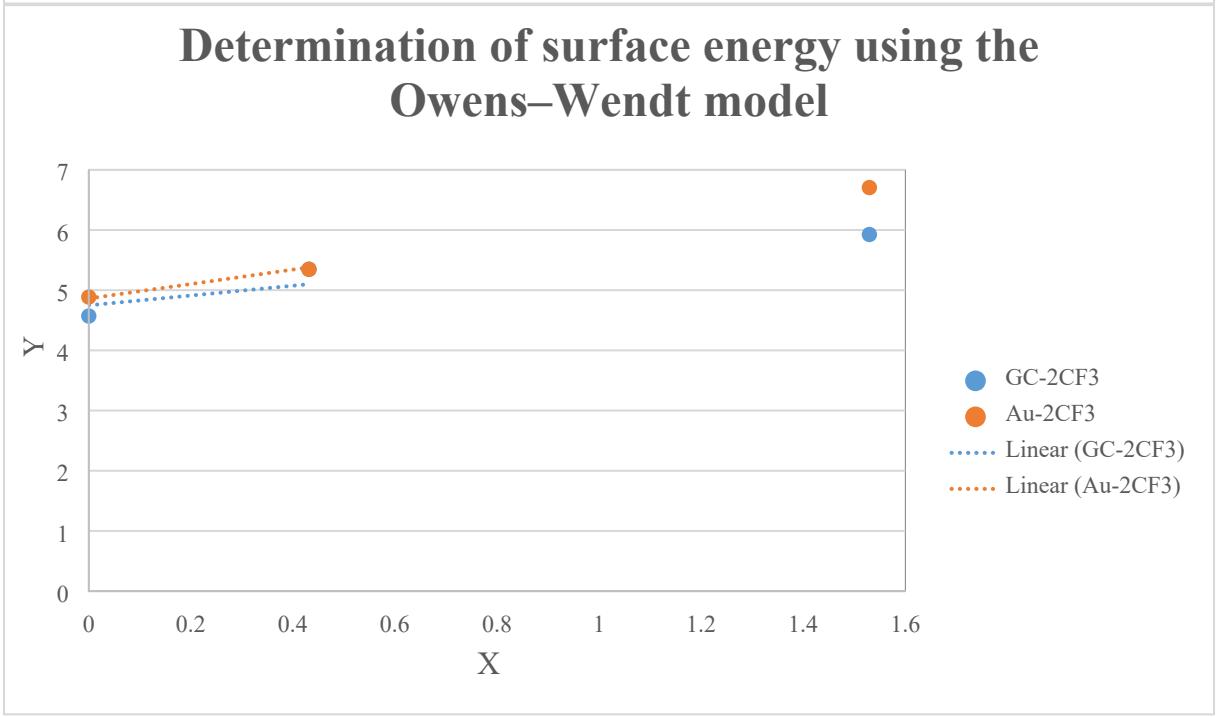
$$b^2 = \gamma_{surface}^{d} \quad \textit{Equation 4}$$

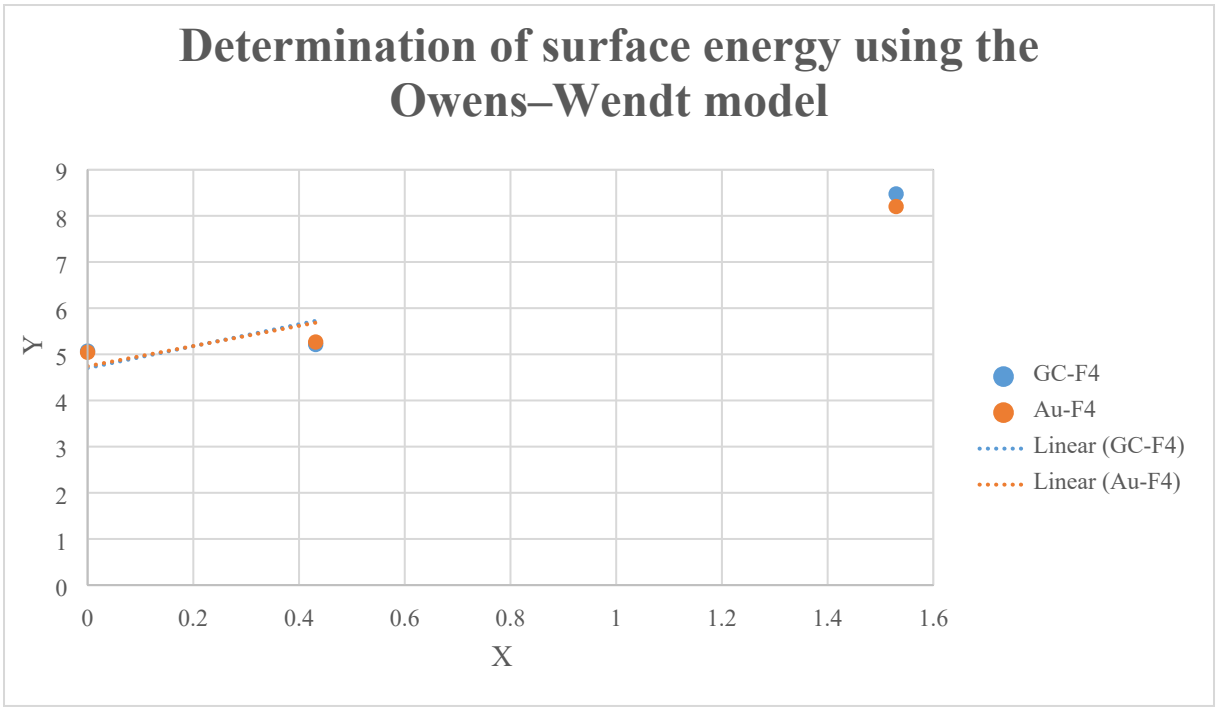
$$\Rightarrow \gamma_{surface} = \gamma_{surface}^{p} + \gamma_{surface}^{d} \quad \textit{Equation 5}$$

(A)



(B)





(C)

Figure S11 : Determination of surface energy using the Owens–Wendt model for **DS_C8F17** (A), **DS_2(CF3)** (B) and **DS_F4** (C) : X(eq.1) in function of Y(eq.2).