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Supplementary information

The Energy Level Alignment of the Ferrocene-EGaIn Interface Studied with Photoelectron Spectroscopy

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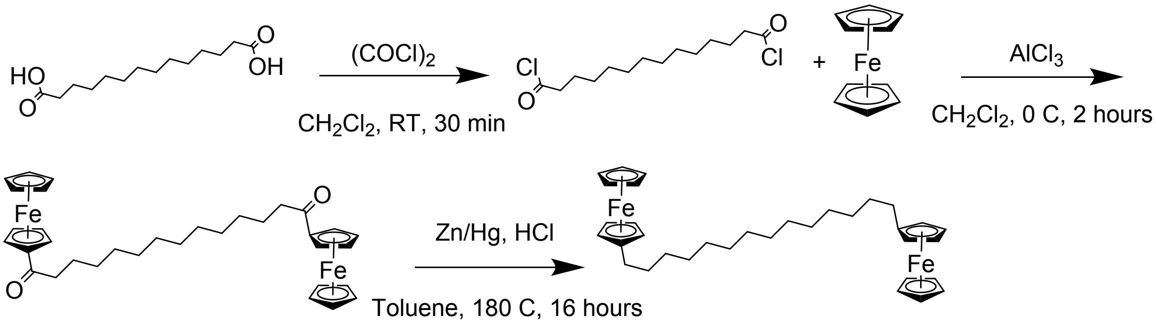
S1. Materials and Synthesis

Chemicals and solvents were purchased from Sigma-Aldrich (polydimethyl siloxane (PDMS, Sylgard 184), ferrocene, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOTS), aluminium trichloride, 1,14-tetradecanedioic acid, oxalyl chloride, 37% HCl, EGaIn, mercuric chloride and zinc granules), Fisher Scientific (dichloromethane (DCM)) and VWR Chemicals (ethyl acetate, toluene and hexane) and used without further purification. All reactions were performed under a nitrogen atmosphere unless stated otherwise. An ELGA PureLab Option-Q water purifier was used to obtain deionised water and the DCM was distilled over $CaCl_2$. ^1H and $_{13}C$ NMR spectra were recorded on Bruker Avance 300 MHz (AV300), Bruker Avance 400 MHz (AV400) and Bruker Avance 500 MHz (AV500) spectrometers using deuterated chloroform-D (Cambridge Isotope Laboratories) as solvent. Mass spectra and high-resolution mass spectra (HR-ESI) were recorded on a Bruker micrOTOF-QII mass spectrometer.



Scheme S1: Synthesis of 1, 14-diferrocenyl tetradecane (Fc-$(CH_2)_{14}$-Fc). Previously reported procedures[1] were modified for the synthesis procedures described herein.

Synthesis of 1, 12-diferrocenoyl dodecane

The 1,14-tetradecanedioic acid (1.00 g, 3.87 mmol) was converted into 1,14-tetradecanoyl chloride by reaction with (2.60 mL, 31.00 mmol) oxalyl chloride with 3-5 drops of dimethylformamide at room temperature under an inert atmosphere. The volatile components were removed under vacuum. The 1,14-tetradecanoyl chloride was utilised in the next step without further purification.

Friedel-crafts acylation of ferrocene with 1,14-tetradecanoylchloride

Ferrocene (1.43g, 7.74 mmol) was dissolved in 30 mL dry DCM at 0° C under an inert atmosphere followed by addition of anhydrous $AlCl_3$ (1.25 g, 9.20 mmol). During this addition the colour of the reaction mixture changed from orange to deep purple. Next, the 1,14-tetradecanoyl chloride synthesised in the previous step was dissolved in dry DCM and added dropwise the reaction mixture under constant stirring. The stirring was continued for 2 h at 0° C under an inert atmosphere. The reaction mixture was quenched by addition of DI water after which stirring was continued for an additional 10 min. The orange organic layer was collected, and the blue aqueous layer was discarded. The organic layer was washed with 20 mL DI water, neutralised with aqueous 0.1 M $NaHCO_3$, dried over $MgSO_4$ and concentrated in vacuo. The crude dried product (an orange powder) was purified by column chromatography. First, hexane was used as the eluent to remove unreacted ferrocene. Then, a 9:1 mixture of hexane: ethyl acetate was used as the eluent after which the next orange coloured fraction was collected and concentrated to yield the product as an orange powder. The yield was 41 % (0.94 g). ^1H NMR: (300 MHz, $CDCl_3$): δ 7.26, 4.81 – 4.75 (m), 4.50 – 4.44 (m), 4.19, 2.72 – 2.66 (m), 1.71 (q, J = 7.4 Hz), 1.32 (d, J = 21.2 Hz). ^{13}C NMR: (126 MHz, CDCl3) δ 204.90, 79.48, 77.41, 77.16, 76.91, 72.31, 72.28, 69.95, 69.93, 69.56, 69.54, 39.96, 32.05, 31.57, 30.33, 29.82, 29.75, 29.71, 29.65, 29.48, 24.80, 22.82. HR MS: Experimental m/z: 595.15, theoretical m/z: 594.19

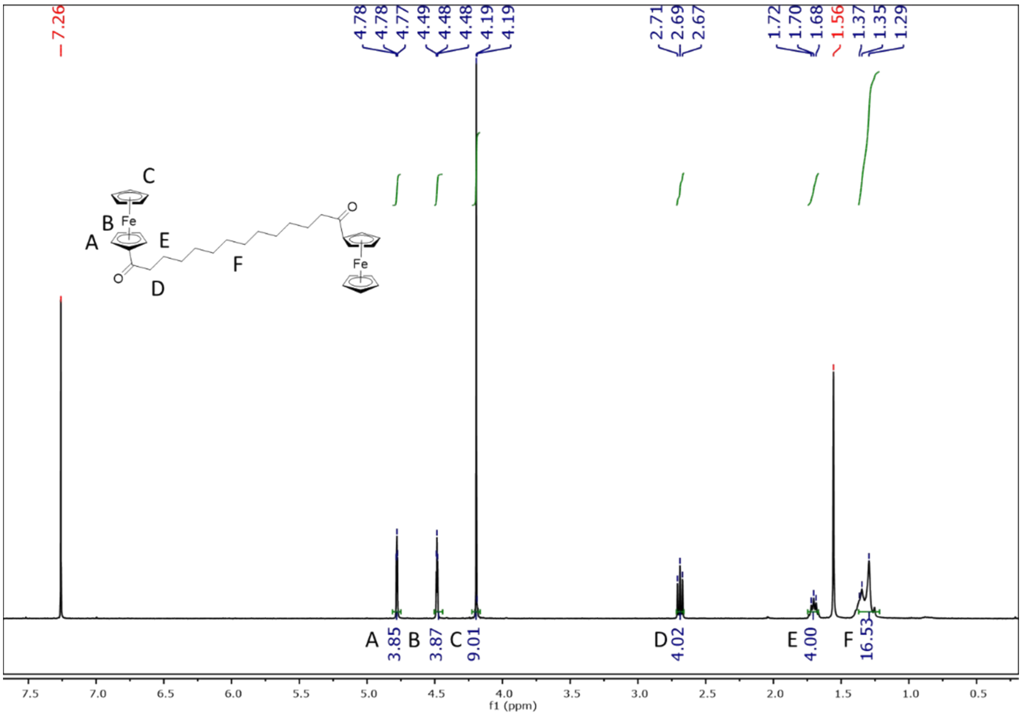


Figure S1: ^{1}H NMR of 1,14-diferrocenoyltetradecane, the red peaks correspond to the $CDCl_3$ solvent.

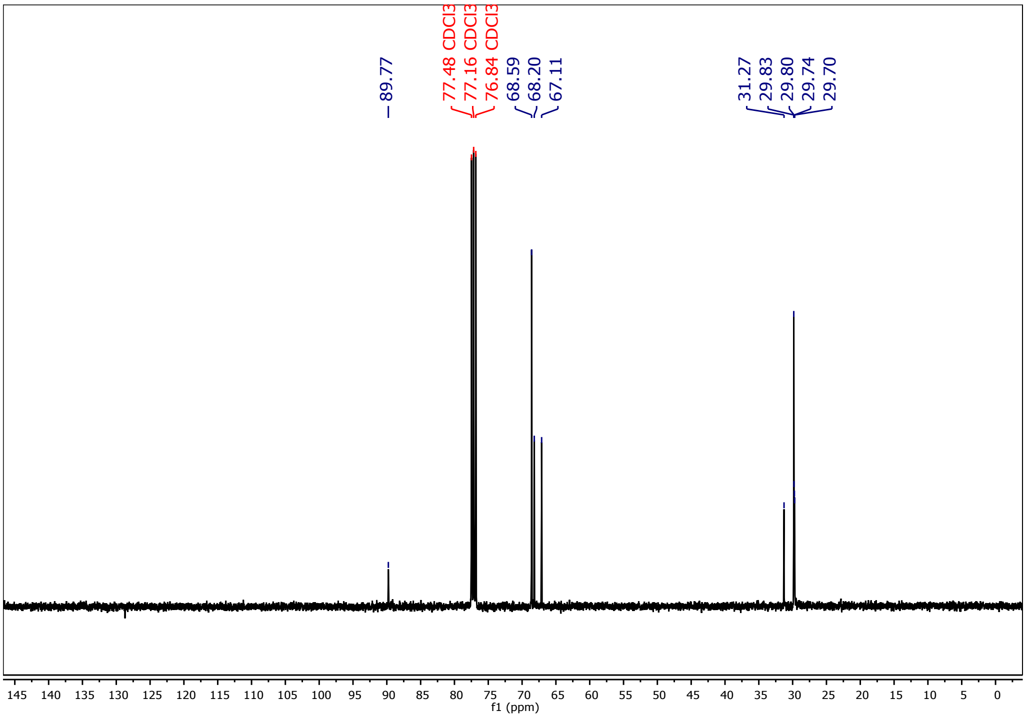


Figure S2: ^{13}C NMR of 1,14-diferrocenoyltetradecane, the red peaks correspond to the $CDCl_3$ solvent.

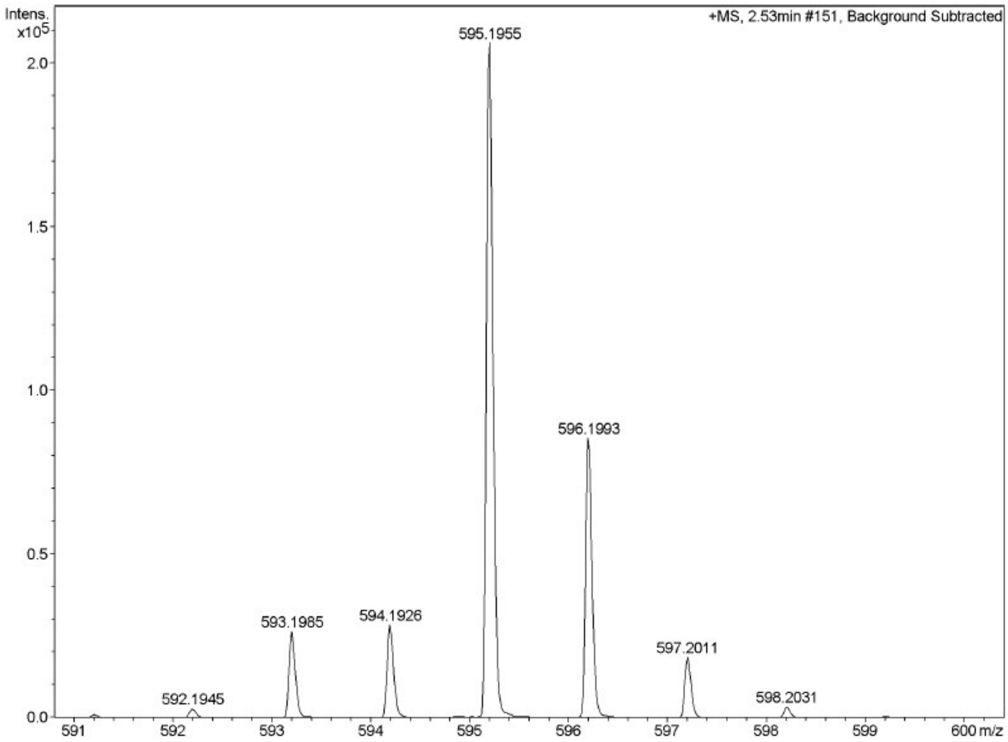


Figure S3: HR-MS of 1,14-diferrocenoyltetradecane.

Synthesis of 1,14-diferrocenyltetradecane by reduction of 1,12-diferrocenoyldodecane

An amalgam of zinc-mercury was freshly prepared by addition of (~0.50 g, ~7.50 mmol) Zn granules to (~0.03 g, ~0.13 mmol) $HgCl_2$ in (5.00 mL) in toluene followed by addition of DI (5 mL) water and (2.50 mL, 12.00 M) aq. HCl. (0.15 g, 0.25 mmol). Next, 0.05 g (0.09 mmol) 1,12-diferrocenoyl dodecane (1) was added to this two-phase system followed by refluxing with constant stirring for 16 h at 120° C. After cooling the reaction mixture down to room temperature, the organic layer was washed three times with DI water (10 mL), dried over $MgSO_4$ and concentrated in vacuo. We used column chromatography to isolate the product with hexane as the eluent. Only one fraction was observed, and it was orange coloured. This fraction contained the product which was isolated as an orange powder after removal of the solvent in vacuo. The yield was 75 % (0.11 g). ^1H NMR: (300 MHz, $CDCl_3$) δ=4.07 (s, 10H; Cp-H), 4.03 (m, 4H; 2,5-H), 4.01 (m, 4H; 3,4-H), 2.29 (m, 4H; 6-H), 1.47 (m, 4H; 7-H), 1.27 (m, 4H; 8-H), 1.25 ppm (m, 16H; 9,10,11,12-H). ^{13}C NMR (127 MHz, $CDCl_3$): δ=89.6 (C1), 68,4 (Cp), 68.1 (C2, C5), 66.9 (C3, C4), 31.1 (C7), 29.67, 29.64, 29.57, 29.55 ppm (C6, C8, C9, C10, C11, C12), HR-MS: Experimental m/z: 566.2306, theoretical m/z: 566.43.

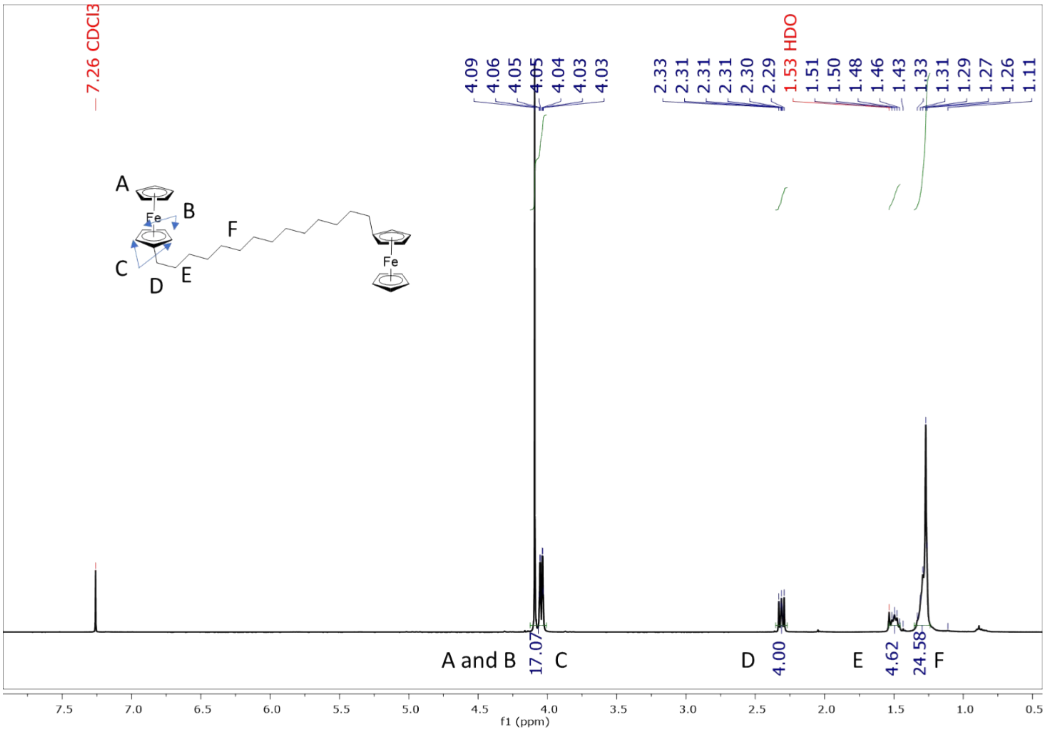


Figure S4: ^{1}H NMR of 1,14-diferrocenyltetradecane (Fc-$(CH_2)_{14}$-Fc), the red peaks correspond to the $CDCl_3$ solvent.

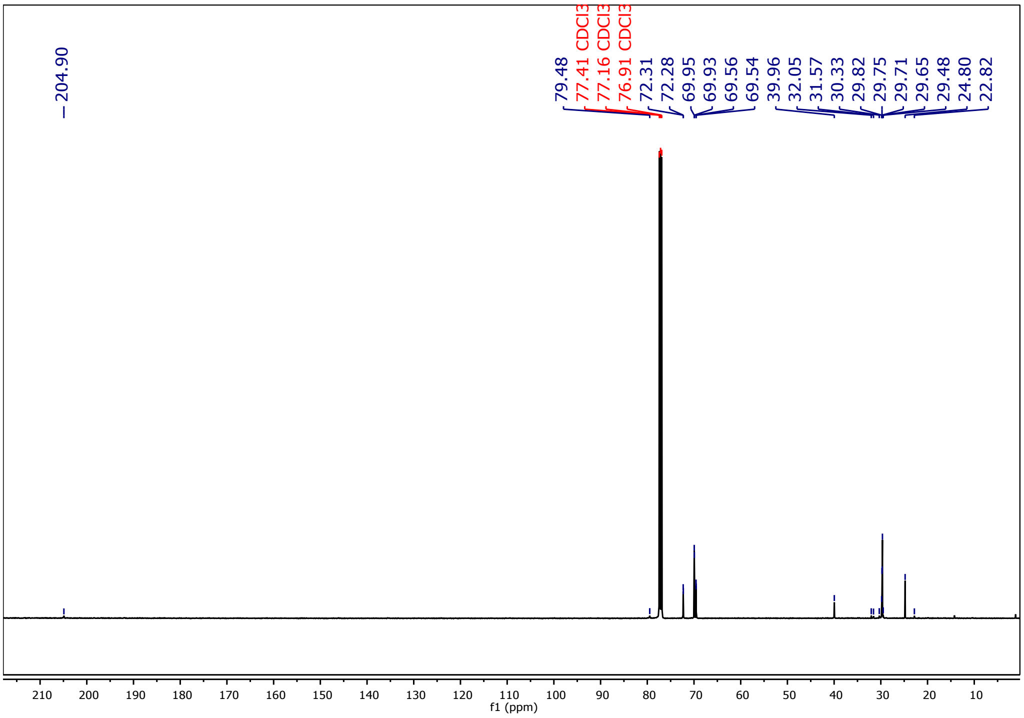


Figure S5: ^{13}C NMR of 1,14-diferrocenyltetradecane (Fc-$(CH_2)_{14}$-Fc), the red peaks correspond to the $CDCl_3$ solvent.

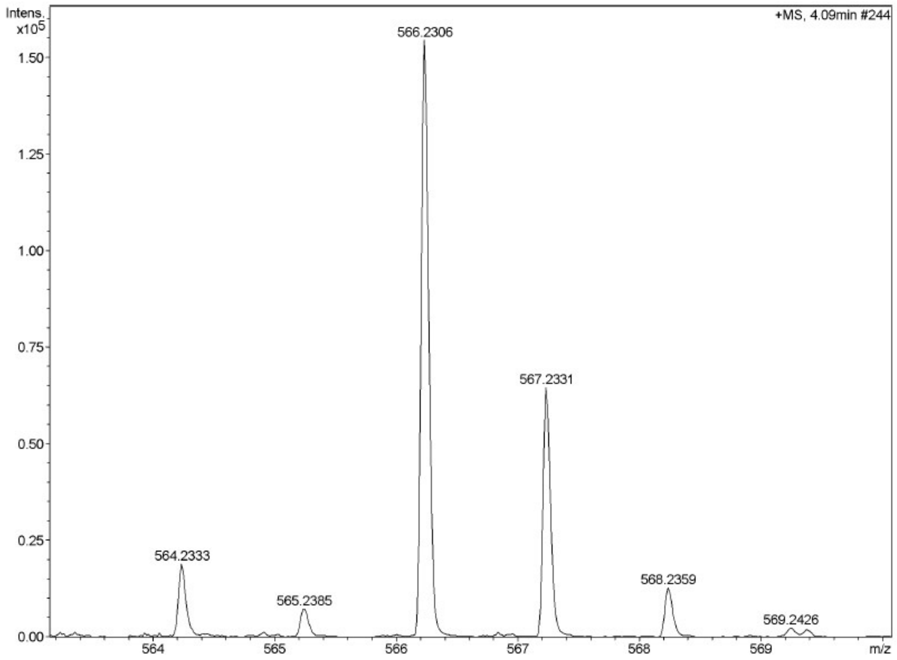


Figure S6: HR-MS of 1,14-diferrocenyltetradecane (Fc-$(CH_2)_{14}$-Fc).

S2: Preparation of EGaIn thin films

Figure S8 shows the photographs of the workflow for the preparation of the EGaIn thin films. Previously reported procedures[2–4] were modified to suit our requirements. We prepared flat PDMS stamps on a Si wafer. To reduce adhesion between the PDMS and the Si wafer, the Si wafer was passivated with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FOTS) under reduced pressure of 20-50 mbar for 30 min in a desiccator. Next, we placed the wafer in a wafer carrier tray (Micro-Tec) and poured the PDMS (1:15 ratio of curing agent to elastomer base) which was followed by curing at 80° C for 20 min to yield a slap of flat PDMS with a thickness of 0.3 – 0.5 cm.[2] From this slab of PDMS, we cut the pieces of PDMS we used in our experiments which were larger than the Si substrates. The Si substrates used for preparation of the EGaIn thin film were cleaned by sonication in a freshly prepared piranha solution for 15 min to enhance the adhesion of the EGaIn to followed by drying an oven at 80° C for 3 h after rinsing with de-ionised water. A drop of EGaIn (50 – 100 μL) was placed on the Si substrate Fig. S8A) with a syringe and the roller was used to spread out the EGaIn over the substrate (Fig. S8B). The roller was immersed in EGaIn prior to use to improve adhesion of the EGaIn with the roller. We found that the EGaIn film was uneven and excess of EGaIn was still present several areas as indicated in Fig. S8C. To remove such "puddles" of EGaIn, we used a flat piece of PDMS and pressed it gently to the thin film (Fig. S8D) of EGaIn. Removal of the slab of PDMS resulted in the removal of the excess EGaIn as it sticks to the PDMS (Fig. S8E). The resulting EGaIn films were stable and flat enough to conduct our experiments.

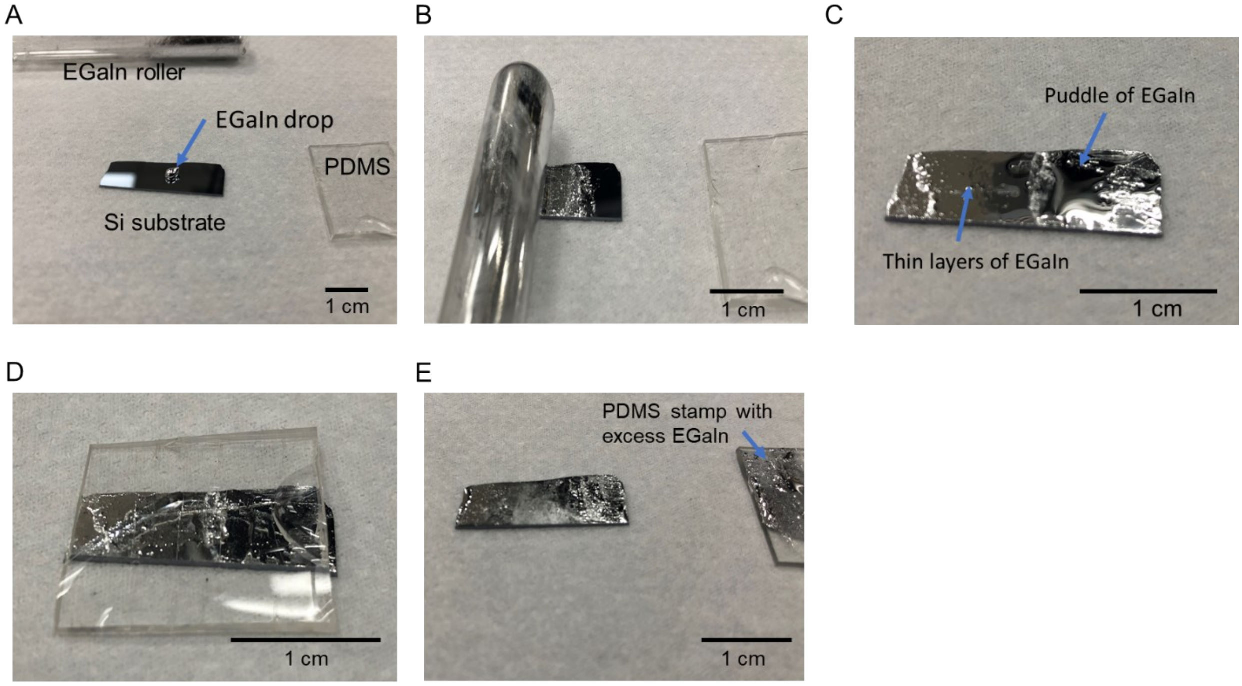


Figure S7: (A) A photograph of the Si substrate with a droplet of EGaIn, a flat slab of PDMS and a glass roller. (B) The EGaIn droplet is spread out evenly over the substrate with the roller. (C) The resulting film contains areas with excess EGaIn; one such "puddle" of EGaIn is indicated by the arrow. (D) The flat PDMS slab is pressed against the EGaIn film followed by removal of the PDMS along with the excess EGaIn that sticks the PDMS slab (E).

S3: X-Ray Photoelectron Spectroscopy

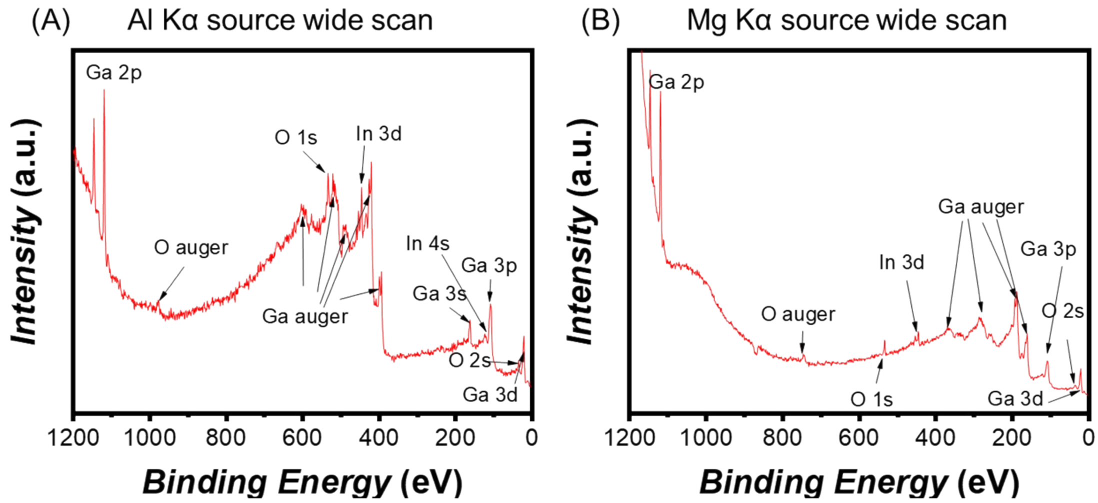


Figure S8: Wide scan of EGaIn thin film after cleaning with sputtering for 10 min with 2 keV Ar plasma with (A) Al Kα source and (B) Mg Kα source.

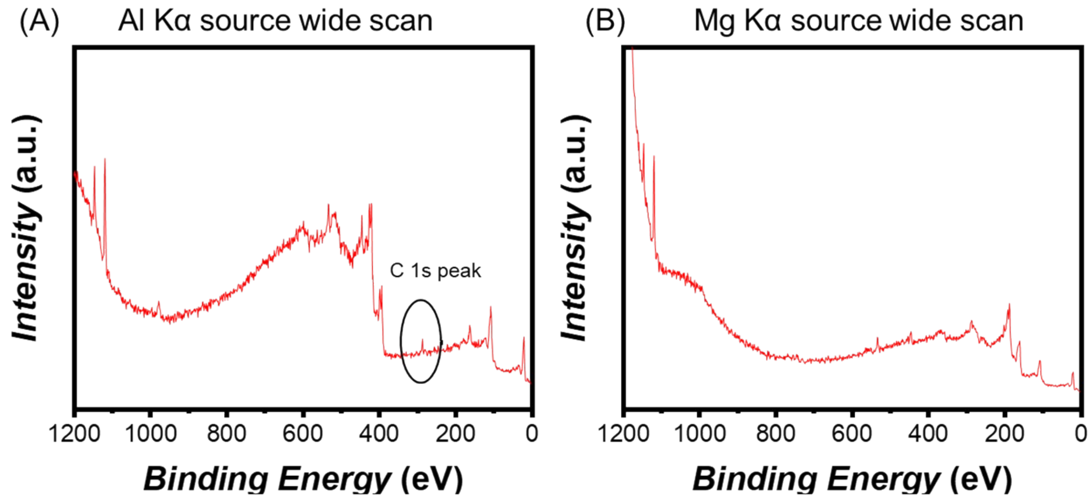


Figure S9: Wide scan of EGaIn thin film after deposition of 0.5 nm of the Fc-$(CH_2)_{14}$-Fc with 2 keV Ar plasma with (A) Al Kα source and (B) Mg Kα source.

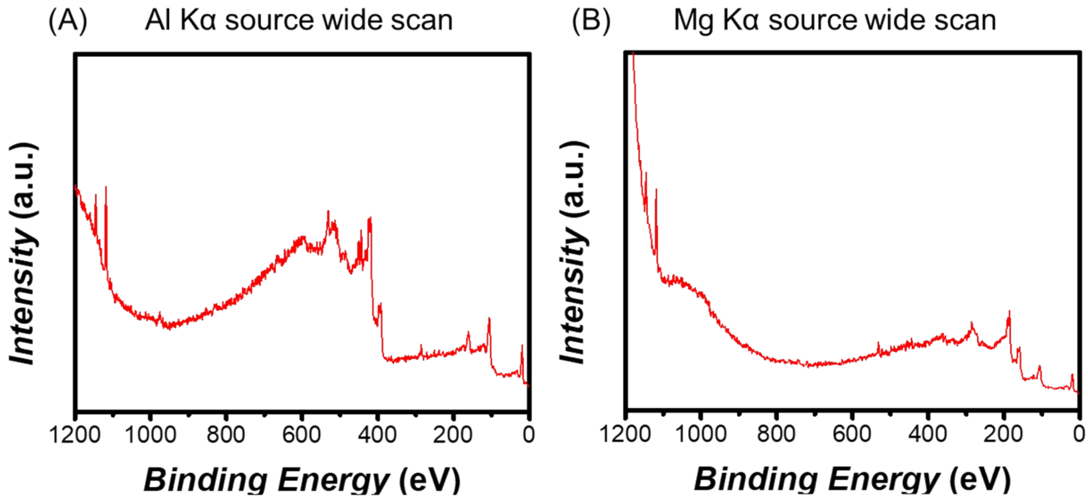


Figure S10: Wide scan of EGaIn thin film after deposition of 1.0 nm of the Fc-$(CH_2)_{14}$-Fc with 2 keV Ar plasma with (A) Al Kα source and (B) Mg Kα source.

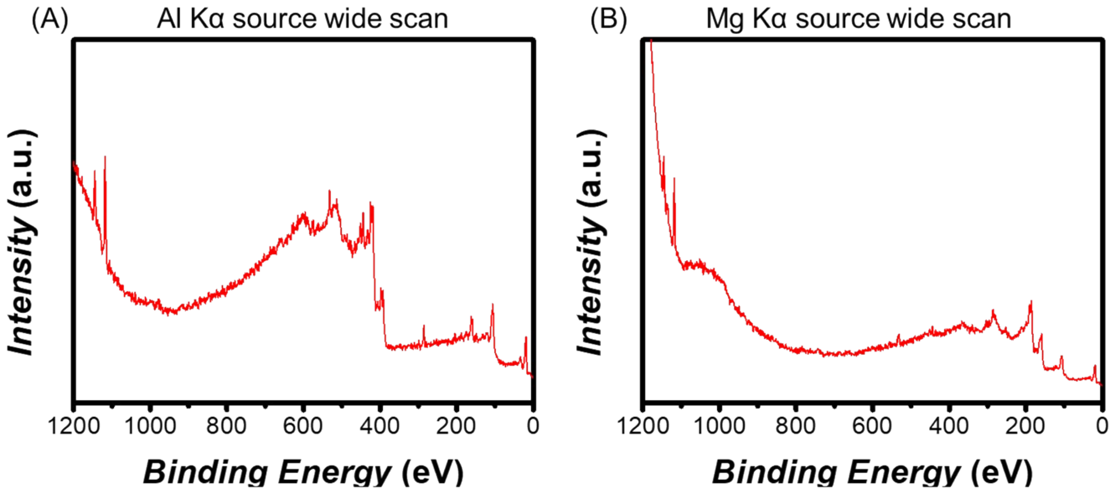


Figure S11: Wide scan of EGaIn thin film after cleaning after deposition of 2.0 nm of the Fc-$(CH_2)_{14}$-Fc with 2 keV Ar plasma with (A) Al Kα source and (B) Mg Kα source.

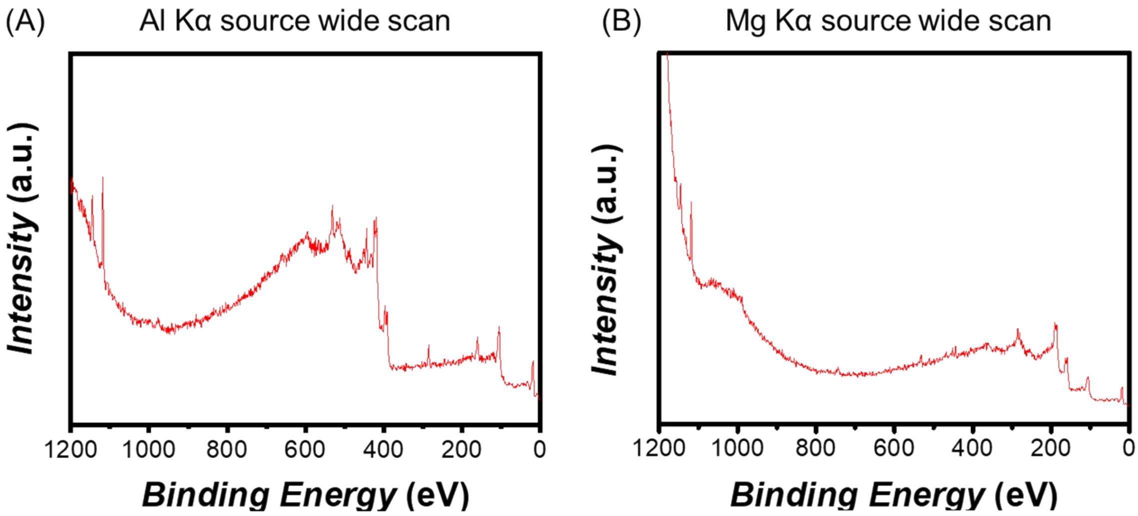


Figure S12: Wide scan of EGaIn thin film after cleaning after deposition of 5.0 nm of the Fc-$(CH_2)_{14}$-Fc with 2 keV Ar plasma with (A) Al Kα source and (B) Mg Kα source.

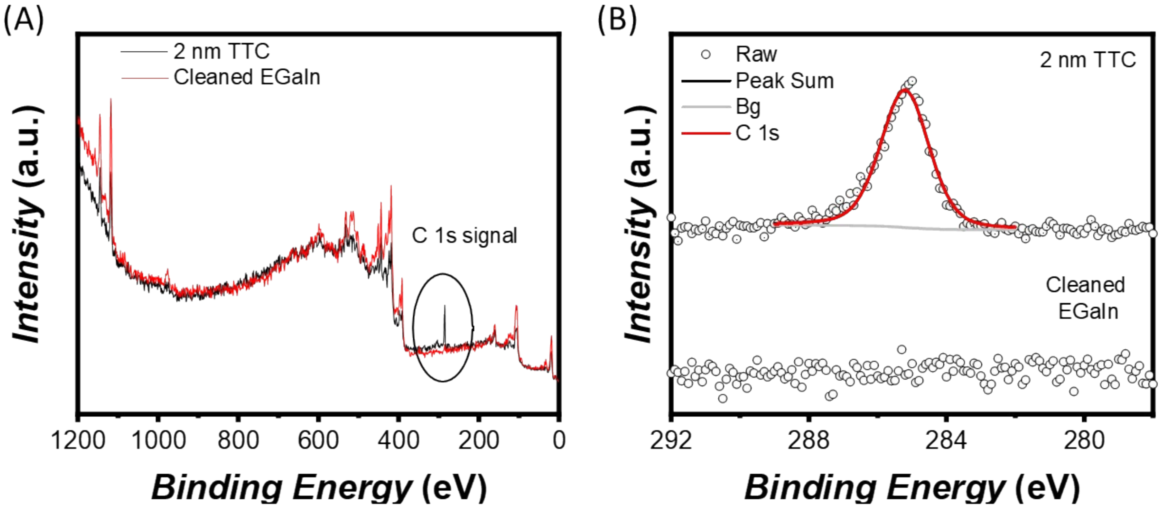


Figure S13: Wide scan of EGaIn thin film after cleaning after deposition of 5.0 nm of the Fc-$(CH_2)_{14}$-Fc with 2 keV Ar plasma with (A) Al Kα source and XPS of the (B) C 1*s*.

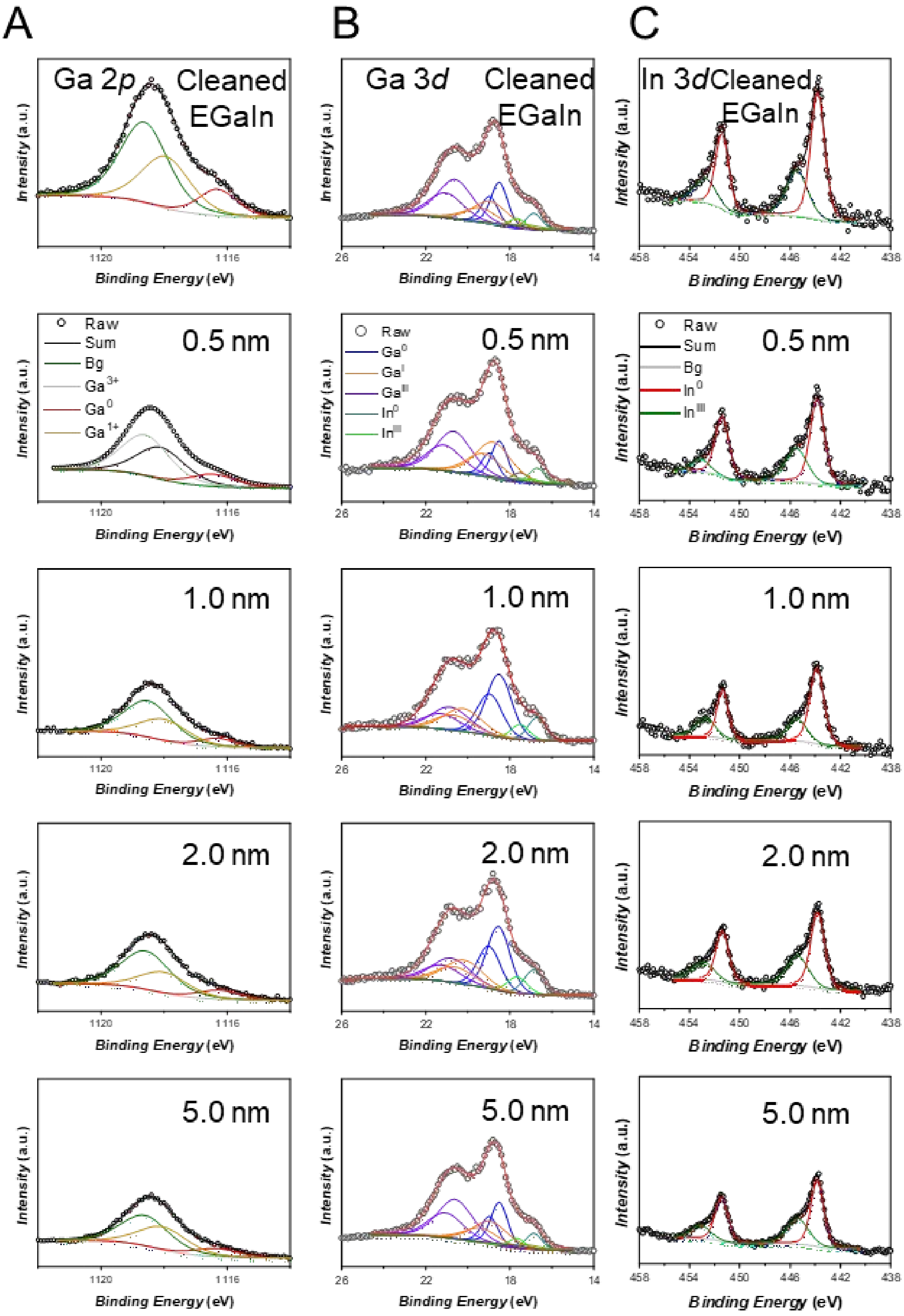


Figure S14: XPS of (A) Ga 2*p*, (B) Ga 3*d*, and (C) In 3*d* for the cleaned EGaIn thin films, 0.5 nm, 1.0 nm, 2.0 nm and 5.0 nm thicknesses of the Fc-$(CH_2)_{14}$-Fc.

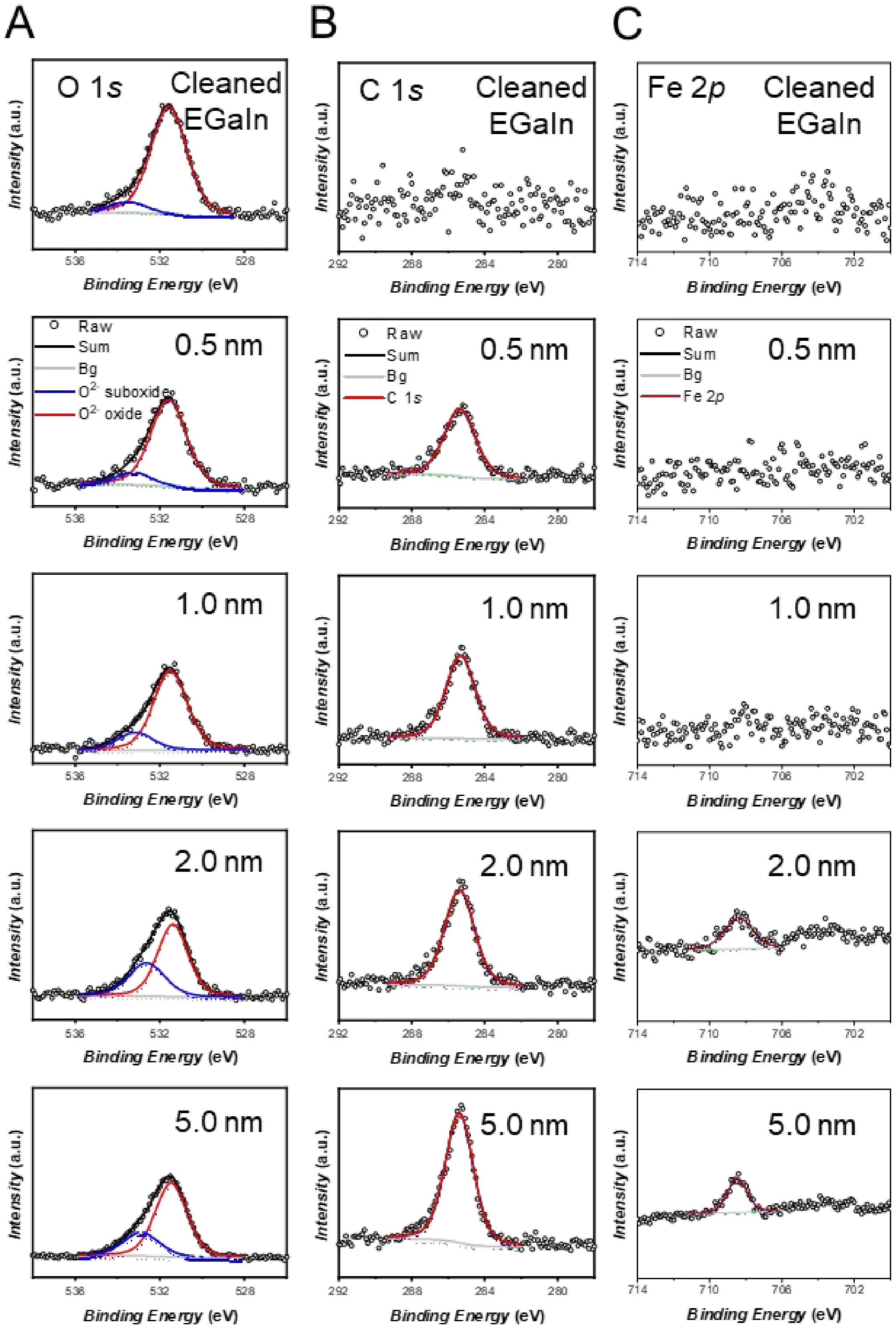


Figure S15: XPS of (A) O 1*s*, (B) C 1*s* and (C) Fe 2*p* for the cleaned EGaIn thin films, 0.5 nm, 1.0 nm, 2.0 nm and 5.0 nm thicknesses of the Fc-$(CH_2)_{14}$-Fc.

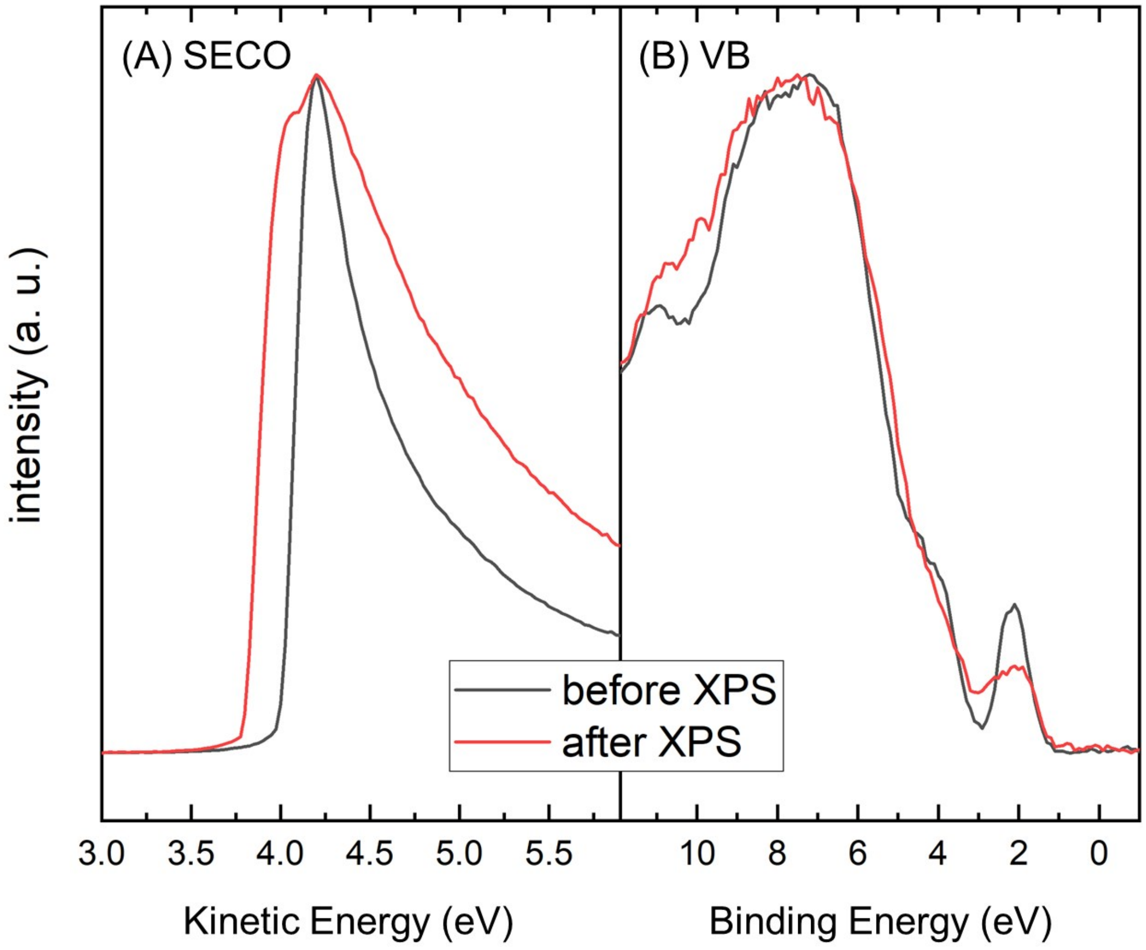


Figure S16: Assessment of the beam damage to the (A) SECO and (B) VB spectra of the EGaIn thin films with 2.0 nm Fc-$(CH_2)_{14}$-Fc deposited on. The beam damage study was done with a He (II) excitation in contrast to the He (I) source used in the other measurements. Based on these experiments, we collected the UPS spectra immediately after the deposition of the Fe-$(CH_2)_{14}$-Fc to minimise the adverse impact of beam damage on our experiments.

S4: Ultraviolet Photoelectron Spectroscopy

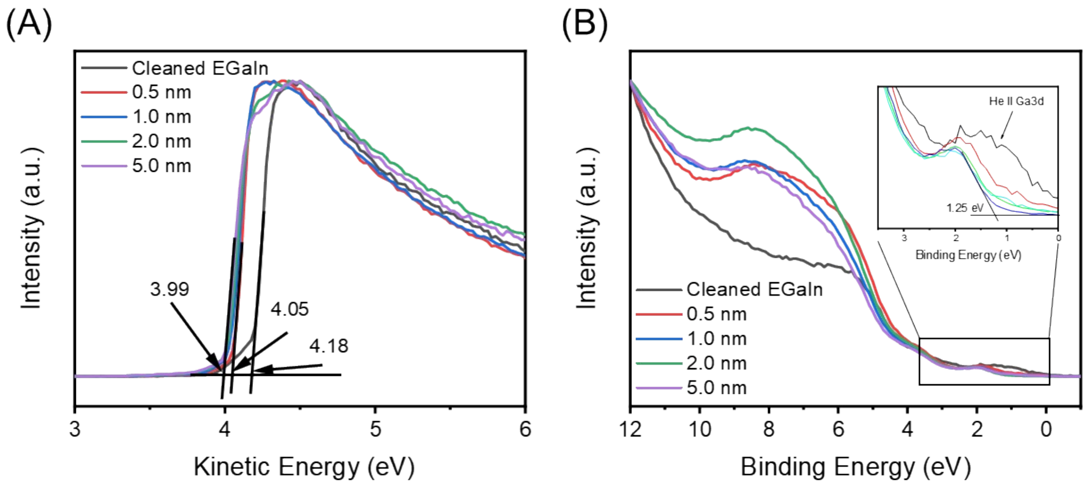


Figure S17: (A) The SECO and (B) VB spectra for cleaned EGaIn thin films (black) and after deposition of 0.5, 1.0, 2.0 and 5.0 nm Fc-$(CH_2)_{14}$-Fc measured with He (I) excitation. The cut-off positions and HOMO onset or VB onset are marked with black, respectively. The Φ values in Panel A are denoted alongside. The inset in (B) indicates the He (II) satellite from the Ga 3*d* core level.

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