JOURNAL OF SYNCHROTRON RADIATION

Volume 28 (2021)

Supporting information for article:

Polymer thin films as universal substrates for extreme ultraviolet absorption spectroscopy of molecular transition metal complexes

Yusef Shari'ati and Josh Vura-Weis

Table of Contents

S1. Materials & Methods

Materials. Polystyrene (M_w = 192,000), Fe^{III}TPPCl and $Co(acac)_3$ were obtained from Sigma-Aldrich, hemin and $Mn(acac)_3$ from Thermo-Fisher Scientific, and polyvinyl chloride (M_w = 275,000) from Scientific Polymer Products, Inc. $CoCl_2$•6 H_2O was obtained from Acros organics. Cubane (Chakrabarty *et al.*, 2007) and $Fe(bpy)_3Cl_2$ (Jaeger & van Dijk, 1936) were synthesized according to literature procedures, while samples of (^{tBu}N4)$NiCl_2$ were graciously provided by the Mirica group (Khusnutdinova *et al.*, 2013). SiN membrane windows (100 nm, frame 7.5 mm × 7.5 mm, window 3.0 mm × 3.0 mm) were obtained from Silson Ltd. Empty silicon frames (in which the central SiN membrane has broken) were used as sample mounts, as shown in Figure S1F.

General Method for Preparation of Polymer Films by Slip-Coating. Prior to film deposition, 75 mm × 25 mm glass slides (obtained from VWR) are cleaned with isopropanol and dried with a heat gun. Polymer solutions are prepared by sonication of the resin in solvent for at least 30 minutes so that no solids remain, then filtered over silica. A polymer film is deposited by first dispensing ~100 µL of solution on the slide. A second slide is laid upon the first, offset horizontally by 1 cm, taking care to introduce no air bubbles. The top slide is then removed in a single swift (ca. 5 cm/s) and steady sliding motion. The two slides, now evenly coated in polymer solution, are left to dry in ambient conditions for 60 s. Thereafter, the slides are further dried with a heat gun for 10 s to ensure complete solvent evaporation. Films are removed from the glass substrate by water flotation, or directly with adhesive tape. The thickness of deposited films is adjusted by changing polymer solution concentration accordingly (Stafford *et al.*, 2006). A photographic depiction of these processes is shown in Figure S1.

Preparation of PVC Films. A solution consisting of 1.5 wt% PVC in 93.5% THF, 5% cyclohexanone was slip-coated between glass slides. PVC films are delaminated by water flotation or directly with adhesive tape.

Preparation of PS Films. Neat polystyrene films were formed from 1.5 wt% polystyrene in dichloromethane (DCM) or 1,2-dichloroethane (DCE) by slip-coating, as above. All PS films were made freestanding by water flotation.

Water Flotation. All films prepared may be removed from the glass substrate by gradually lowering the slide into water at an oblique angle. The film floats on the surface of the water. The film is retrieved and mounted onto an empty silicon frame by bringing the latter up from underneath. The sample is gently dried with a heat gun, which also anneals any wrinkles in the freestanding film.

Spincasting on PVC. A section of PVC-coated glass (prepared via slip-coating as above) is spun at 1400 rpm and a single drop (~0.05 mL) of analyte solution is made to fall upon the center of rotation. Film formation is often improved with the immediate application of a heat gun. The resultant two-layer film is delaminated with adhesive tape.

Film Mounting. Freestanding thin films are mounted on empty 7.5 mm × 7.5 mm silicon frames, as shown in Figure S1F. The polymer films adhere naturally to the smooth frame surface, though double-sided adhesive tape can also be used.

Specific Film Preparation Conditions

[$Co^{III}_4O_4$] Cubane in PS: 118 mg of cubane solution (29 mM in DCM) was combined with 63 mg 3 wt% PS in DCE. The resultant dark green solution was slipcoated.

[$Co^{III}_4O_4$] Cubane on PVC: 44 mg (5.16×10^{-5} mol) cubane was dissolved in a mixed alcohol solution consisting of 1.20 g MeOH, 0.60 g iPrOH, and 0.30 g BuOH. This ~20 mM solution was spincoated onto PVC-coated glass with the immediate application of a heat gun. The resultant two-layered film was delaminated with adhesive tape.

(^{tBu}N4)$Ni^{II}Cl_2$: 6.0 mg (1.24×10^{-5} mol, 482.12 g/mol) was dissolved in a solution of 68 mg MeOH, 40 mg iPrOH, and 14 mg BuOH. The green solution (~80 mM) was filtered and then slipcoated onto a PVC-coated glass slide, with immediate heat gun application after removing the top slide. The film was delaminated with adhesive tape.

Fe^{III}TPPCl: A 3.6 mM solution (2.1 mg dissolved in 1.05 g DCE), without polymer, was slipcoated. The resultant golden-brown film was delaminated by water flotation and picked up onto a mounted 100 nm PVC film.

Hemin: 1.3 mg was dissolved in 80 mg MeOH, 65 mg iPrOH, 19 mg BuOH, and 22 mg triethylamine. The dark brown solution was spincoated onto a PVC-coated glass slide and the bilayer was delaminated with tape.

$Mn^{III}(acac)_3$: 100 mg of 27 mM compound was mixed with 110 mg of 3.0 wt% PS in DCE and the resulting dark brown solution was slipcoated.

$Co^{III}(acac)_3$: 70 mg of a 70 mM $Co(acac)_3$ DCE solution was added to 30 mg of 3.0 wt% PS in DCE. This deep green solution was slipcoated.

$Co^{II}Cl_2$: A blue 5.4 mM acetonitrile solution of $CoCl_2$•6 H_2O was spincast upon a mounted PVC membrane with immediate heat gun application to remove solvent. The PVC was then delaminated with adhesive tape.

$Fe^{II}(bpy)_3Cl_2$: 3.6 mg was dissolved in a solution of 70 mg MeOH, 45 mg iPrOH, and 40 mg BuOH. This deep red solution (~30 mM) was filtered, then spuncast with heating onto a PVC-coated glass slide. The film was removed with adhesive tape.

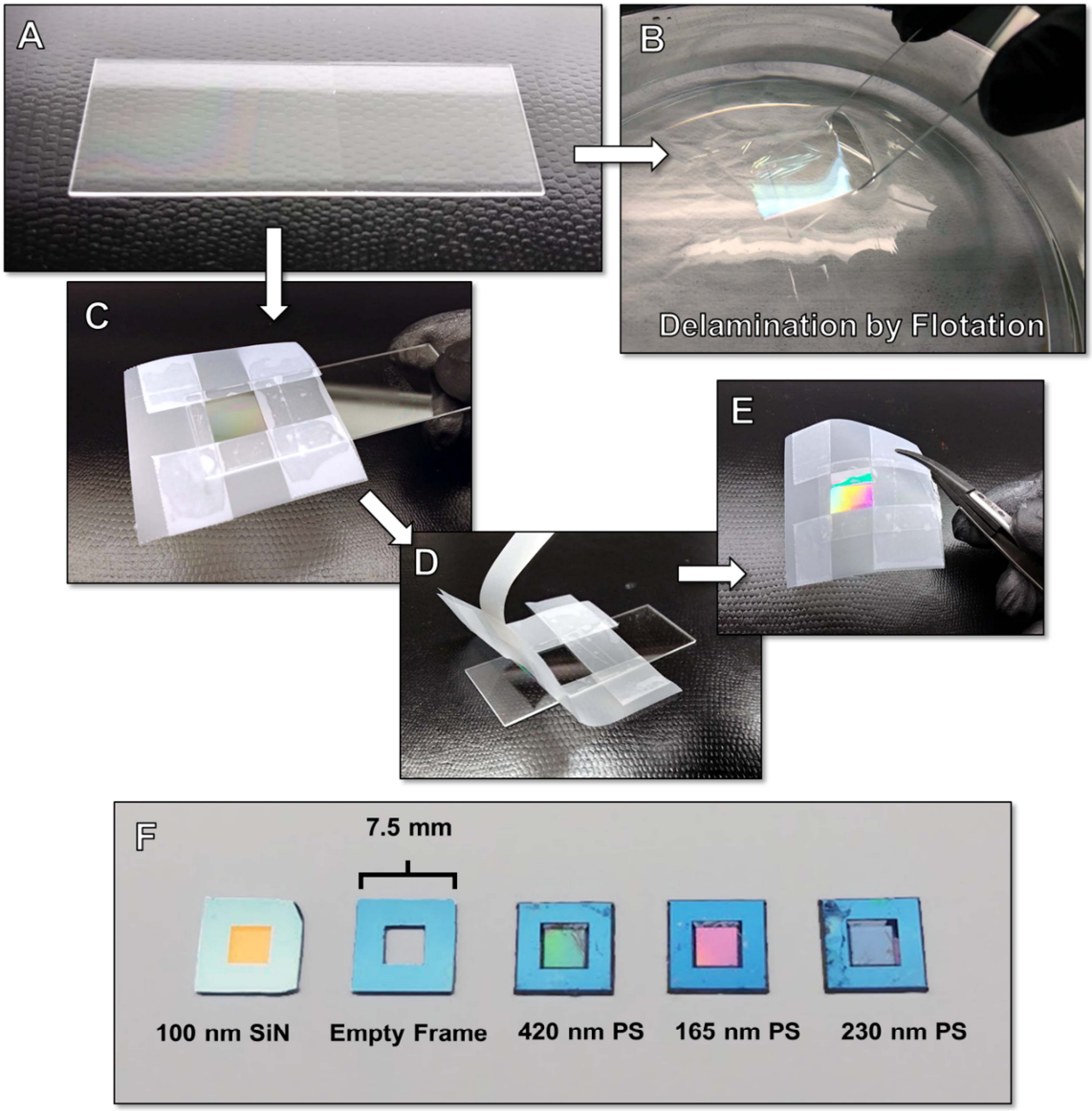

Figure S1 Photographic examples of the film preparation process; (A) A polystyrene film atop a glass substrate, prepared by slip-coating. A faint iridescence is visible due to the slight refractive index difference between PS and glass. (B) A PS film delaminating from its glass substrate via the action of water. (C) Adhesive tape is applied to the film. (D) Peeling up the adhesive tape delaminates the thin film along with it. (E) The free-standing film supported in its adhesive tape frame. (F) A selection of silicon frames; three mounted PS films are shown at right.

S2. UV-Vis Sample Characterization

Thin Film Interference. The effects of interference in thin films result in a wavelength-dependent reflection of incident light which is observable in the UV-visible spectrum. The ratio of transmitted light intensity I to the incident light intensity I_0 at a given wavelength λ, derived from the absorbance A, is given by equation (1). The parameter r is the Fresnel reflection coefficient, n is the index of refraction of the thin film, and d is the film thickness (Huibers & Shah, 1997).

$$\frac{I}{I_0} = 10^{-A} = \frac{(1-r)^2}{1 + r^2 - 2r\,cos\left(\frac{4\pi nd}{\lambda}\right)} \tag{1}$$

The Fresnel reflection coefficient at normal incidence is given by equation (2), where n_0 is the index of refraction of the medium surrounding the thin film, i.e. air (n_{air} = 1).

$$r = \left(\frac{n - n_0}{n - n_0}\right)^2 \tag{2}$$

The index of refraction for PVC (n_{PVC}) is nearly a constant 1.53 over the range of the UV-visible spectrometer (190-820 nm). However, the dispersion in PS is significant enough that n_{PS} must be modelled empirically with Cauchy's equation, shown in equation (3) with literature values for PS (Jones *et al.*, 2013).

$$n_{PS} = 1.5718 + \frac{8412\ nm^2}{\lambda^2} + \frac{2.35 \times 10^8\ nm^4}{\lambda^4} \tag{3}$$

Example Film Analysis. Displayed in Figure S2is the UV-visible spectrum of a thin film composed of cubane codeposited with PS. The experimental ("sample") spectrum is regarded as a sum of two component spectra: the periodic undulatory spectrum from interference and the absorbance spectrum due to electronic transitions in cubane. PS itself absorbs negligibly in the range displayed. The cubane portion of the total spectrum was obtained from the film prior to delamination (where the interference effect is not observed due to the similar refractive indices of PS and the underlying glass slide). The magnitude of the cross-section σ_{UV} of cubane in PS is assumed to be the same as that measured in dichloromethane solution. The refractive index of the sample is assumed to be negligibly changed from that of pure PS. Given the above, the least-squares fit indicates a sample thickness of 505 nm with a cubane concentration of 0.65 mol/L.

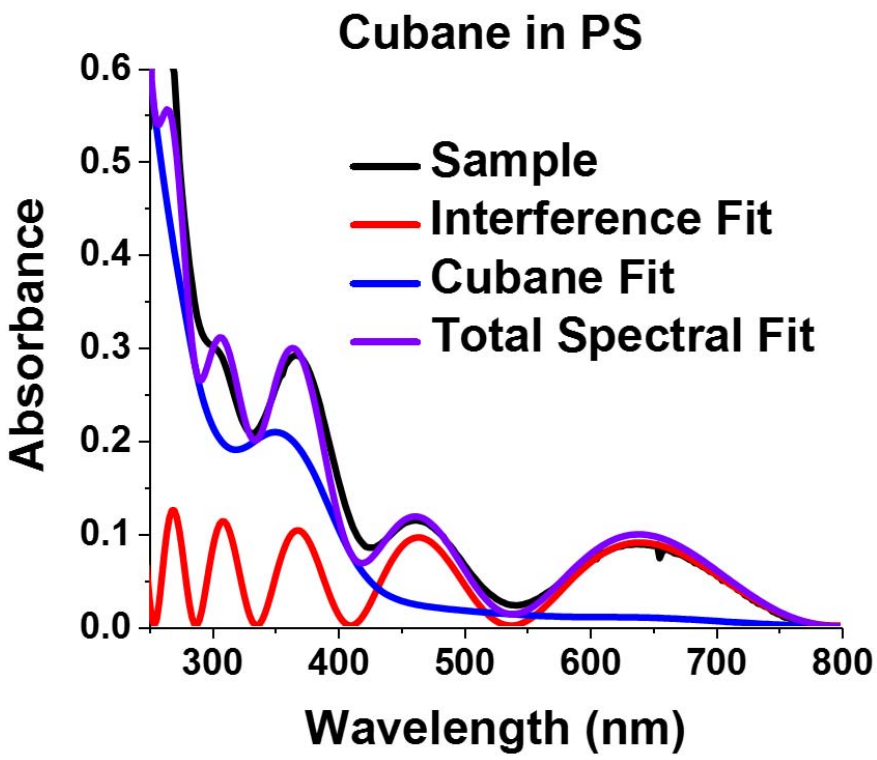

Figure S2 UV-visible spectra of cubane embedded in PS and its spectral components.

S3. M-edge XANES

XUV Probe Generation. High-harmonic generation (HHG) in a noble gas (Ar or Ne) produces the XUV probe, shown in Figure S3A. The periodic spikes in the continuum arising every 3.1 eV correspond to the odd harmonics of the 800 nm driving laser. A silicon mirror and 200 nm aluminum filter remove the residual IR, leaving the XUV light to be passed on through to the sample and then dispersed onto a CCD by a diffraction grating. A Zr filter can be exchanged with the Al filter to obtain intensity after the 72.6 eV aluminum absorption edge. The system is kept under high vacuum (10^{-6} torr) to mitigate XUV attenuation. Energy calibration parameters and spectrometer resolution (typically 0.35 eV FWHM) are computed daily from measurements of Fe_2O_3 (Vura-Weis *et al.*, 2013), NiO (Chiuzăian *et al.*, 2005; Wang *et al.*, 2013), and ionized xenon samples (Andersen *et al.*, 2001).

Pump-probe experiments utilized the output of a noncollinear optical parametric amplifier (TOPAS White) tuned to 525 nm. Power for the pump was 0.62 mJ and 1.65 mJ, for $Fe(bpy)_3Cl_2$ and $Fe(bpy)_3(PF_6)_2$ samples respectively. The pump beam spot size at the sample was 220 µm FWHM and the XUV beam size was 75 µm FWHM as measured by knife-edge scan. The low thermal conductivity of polymer films necessitated that a stream of low-pressure nitrogen gas be passed across samples to avoid pump-induced heating and damage.

M-Edge XANES Spectra. XUV absorbance spectra are generated using the base-10 logarithm of the ratio between transmitted counts through the sample and a reference, chosen to be of the same material and similar thickness as the sample substrate. The non-resonant absorbance background due to photoionization of valence electrons is approximated as a power law and removed by subtraction; the power law parameters are obtained from a fit to the pre-edge region. All reported M-edge XANES spectra are baselined in this way, as shown in Figure S3B.

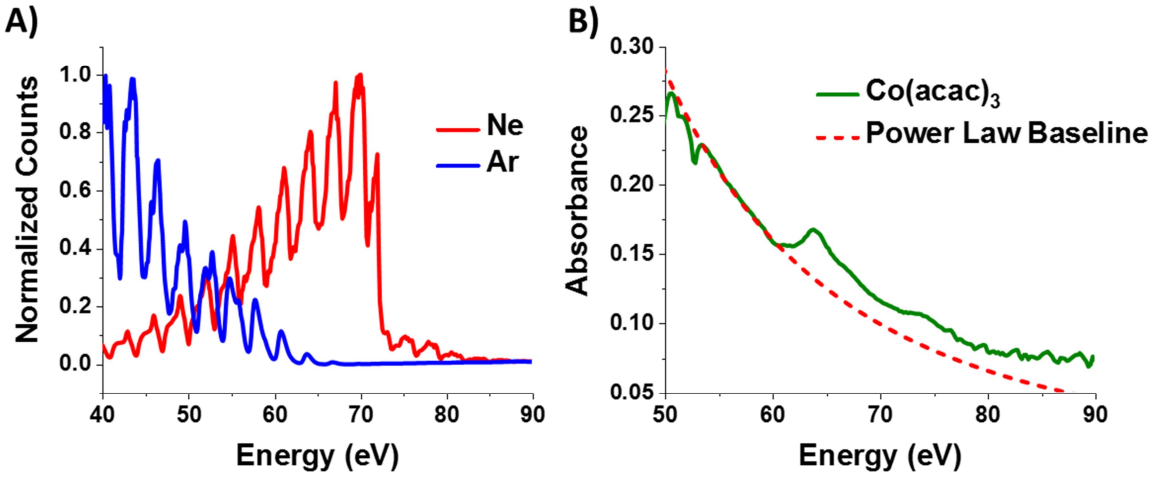

Figure S3 (A) The typical XUV continuum generated in argon and neon gases. (B) Raw XUV absorption spectrum of $Co(acac)_3$ acquired under neon HHG, shown also with power law fit to non-resonant photoionization background. The deviations from the power law below 55 eV are artifacts due to low photon flux.

Cross-Section Determination. The XUV resonant absorption cross-section σ_{XUV} was determined by comparison of the XUV and UV-visible spectrum for each sample. The known UV-visible cross-section allows calculation of σ_{XUV} via the following

$$\sigma_{XUV} = \sigma_{UV} \frac{A_{XUV}}{A_{UV}} \tag{4}$$

Where, in a particular sample, A_{XUV} is the XUV resonant absorbance and A_{UV} is the absorbance at a prominent wavelength chosen in the analyte's UV-visible spectrum. The cross-section σ_{UV} at that wavelength is independently calculated from analyzing separately deposited neat analyte films of known thickness according to equation (5), where ε is the molar extinction coefficient (L mol^{-1} cm^{-1}), MW is the molecular weight, h is the film thickness in nm, and ρ is the film density.

$$\varepsilon = 10^7 \left(\frac{nm}{cm}\right) \times \frac{A_{UV} \times MW}{1000 \times h \times \rho} \tag{5}$$

Power Law Fit Parameters. The non-resonant XUV absorbance of polymer and SiN films is well approximated by the power law shown in equation (6), where A is absorbance, α is an attenuation coefficient, d is the film thickness, E is energy, and E_0 is the reference energy (taken here to be 60 eV). Table S1 reports these parameters obtained from a least-squares fit to the experimental data for the three substrates described.

$$A = \alpha d \left(\frac{E}{E_0}\right)^{-k} \tag{6}$$

Table S1 Power law fit parameters for polymer substrates.

	α (nm^{-1})	***k***
SiN	5.69×10^{-3}	1.65
PS	3.61×10^{-3}	2.53(6)
PVC	2.76×10^{-3}	1.79(8)

S4. References

Andersen, P., Andersen, T., Folkmann, F., Ivanov V, K., Kjeldsen, H. & West, J. B. (2001). *J. Phys. B At. Mol. Opt. Phys.* **34**, 2009–2019.

Chakrabarty, R., Bora, S. J. & Das, B. K. (2007). *Inorg. Chem.* **46**, 9450–9462.

Chiuzăian, S. G., Ghiringhelli, G., Dallera, C., Grioni, M., Amann, P., Wang, X., Braicovich, L. & Patthey, L. (2005). *Phys. Rev. Lett.* **95**, 197402.

Huibers, P. D. T. & Shah, D. O. (1997). *Langmuir*. **13**, 5995–5998.

Jaeger, F. M. & van Dijk, J. A. (1936). *Zeitschrift Fur Anorg. Und Allg. Chemie*. **227**, 273–327.

Jones, S. H., King, D. & Ward, A. D. (2013). **15**, 20735–20741.

Khusnutdinova, J. R., Luo, J., Rath, N. P. & Mirica, L. M. (2013). *Inorg. Chem.* **52**, 3920–3932.

Stafford, C. M., Roskov, K. E., Epps, T. H. & Fasolka, M. J. (2006). *Rev. Sci. Instrum.* **77**, 023908.

Vura-Weis, J., Jiang, C. M., Liu, C., Gao, H., Lucas, J. M., De Groot, F. M. F., Yang, P., Alivisatos, A. P. & Leone, S. R. (2013). *J. Phys. Chem. Lett.* **4**, 3667–3671.

Wang, H., Young, A. T., Guo, J., Cramer, S. P., Friedrich, S., Braun, A. & Gu, W. (2013). *J. Synchrotron Radiat.* **20**, 614–619.