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Electronic Supplementary Information

Distinguishing Photodegradation Pathways of Organic Semiconductors on Different Electrode Contacts using FTIR Spectroscopy with Multivariate Analysis

Sarah M. Tyler[a] and Jeanne E. Pemberton*[a]

[a]Department of Chemistry and Biochemistry
University of Arizona
1306 East University Boulevard
Tucson, AZ 85721
United States

*Corresponding author: pembertn@arizona.edu

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I. FBTF spectral data: Synthesis of 4,7-bis(9,9-dimethyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (FBTF) – Method 1

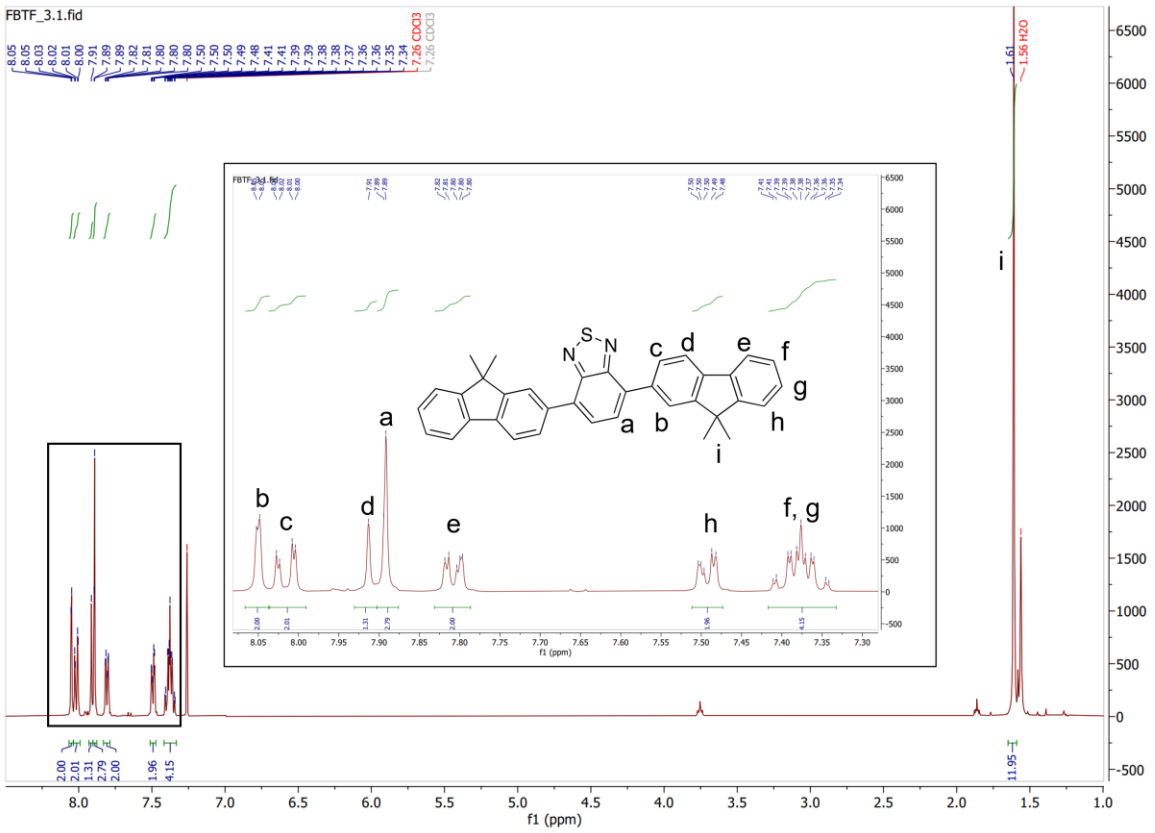

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of FBTF synthesized with the method in Scheme S1. δ 8.05 (d, *J* = 1.6 Hz, 2H), 8.02 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.91 (s, 2H), 7.89 (d, *J* = 1.1 Hz, 2H), 7.83 – 7.79 (m, 2H), 7.51 – 7.47 (m, 2H), 7.42 – 7.33 (m, 4H), 1.61 (s, 12H).

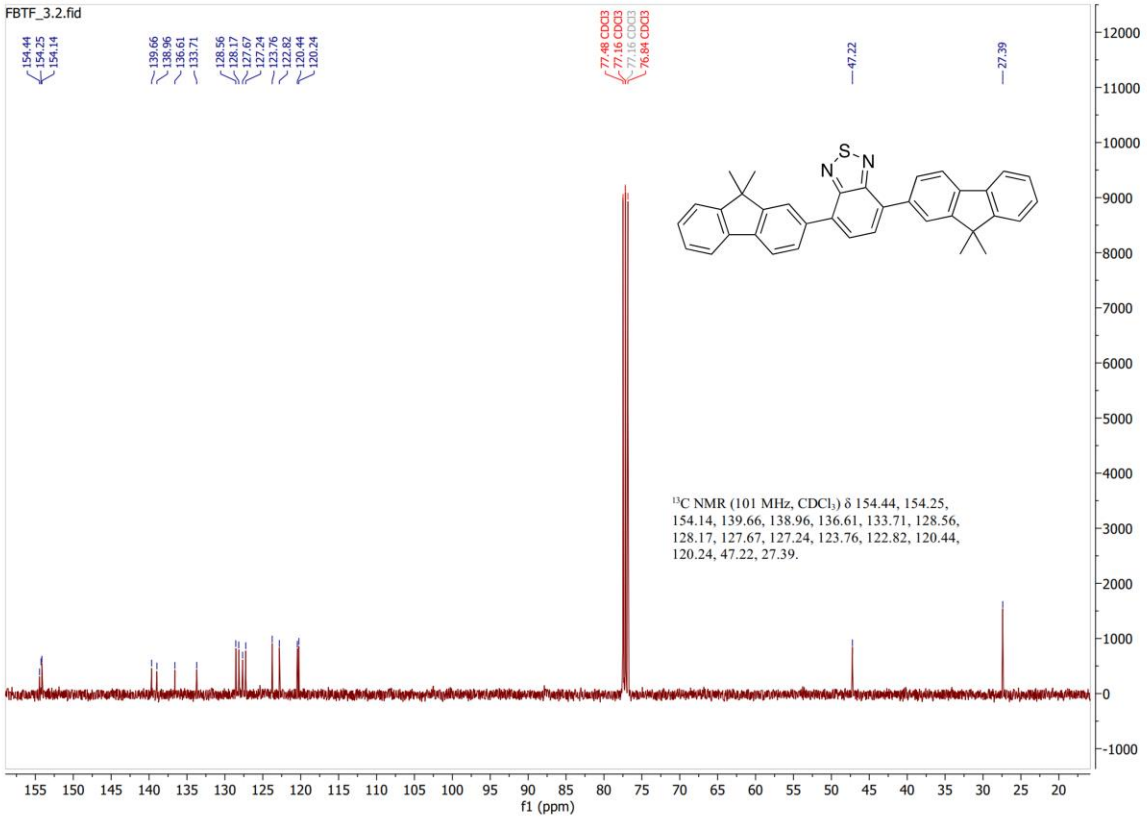

Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) of FBTF synthesized with the method in Scheme 1. δ 154.44, 154.25, 154.14, 139.66, 138.96, 136.61, 133.71, 128.56, 128.17, 127.67, 127.24, 123.76, 122.82, 120.44, 120.24, 47.22, 27.39.

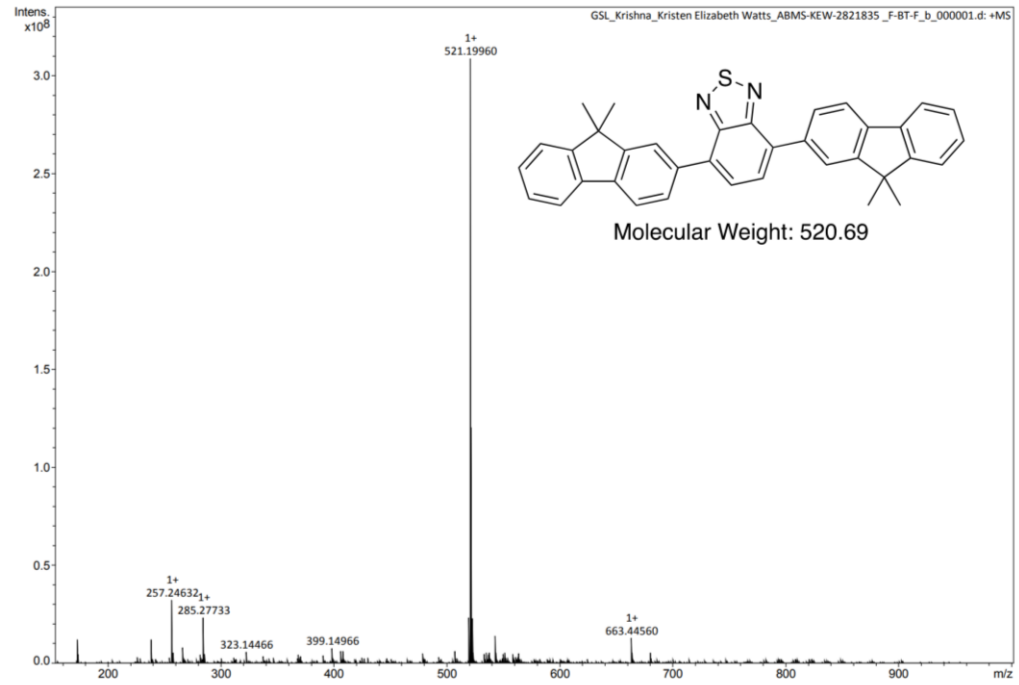

Figure S3. FT-ICR mass spectrum of FBTF synthesized with the method in Scheme 1.

II. FBTF spectral data: Synthesis of 4,7-bis(9,9-dimethyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole (FBTF) – Method 2

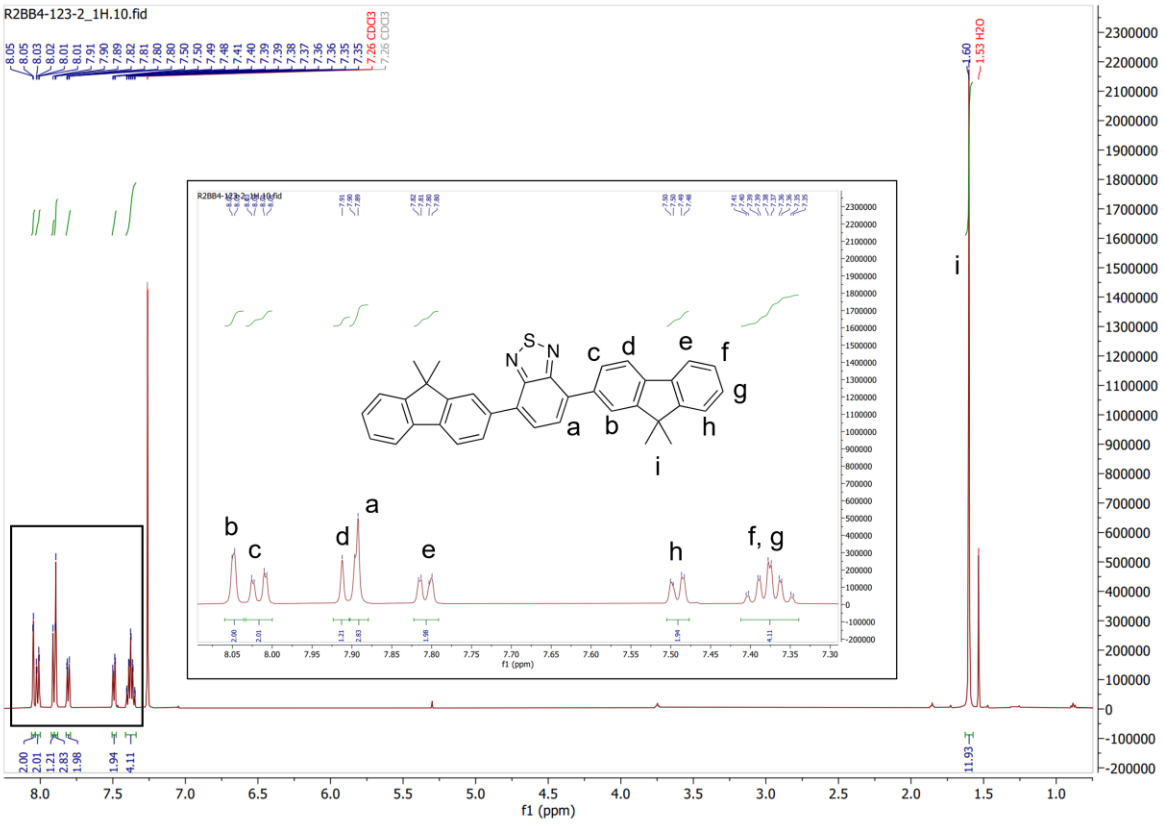

Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) of FBTF synthesized with the method in Scheme 2. δ 8.05 (d, *J* = 1.6 Hz, 2H), 8.02 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.91 (s, 2H), 7.89 (d, *J* = 2.1 Hz, 2H), 7.81 (dd, *J* = 6.8, 1.8 Hz, 2H), 7.49 (dd, *J* = 6.9, 1.7 Hz, 2H), 7.38 (pd, *J* = 7.4, 1.5 Hz, 4H), 1.60 (s, 12H).

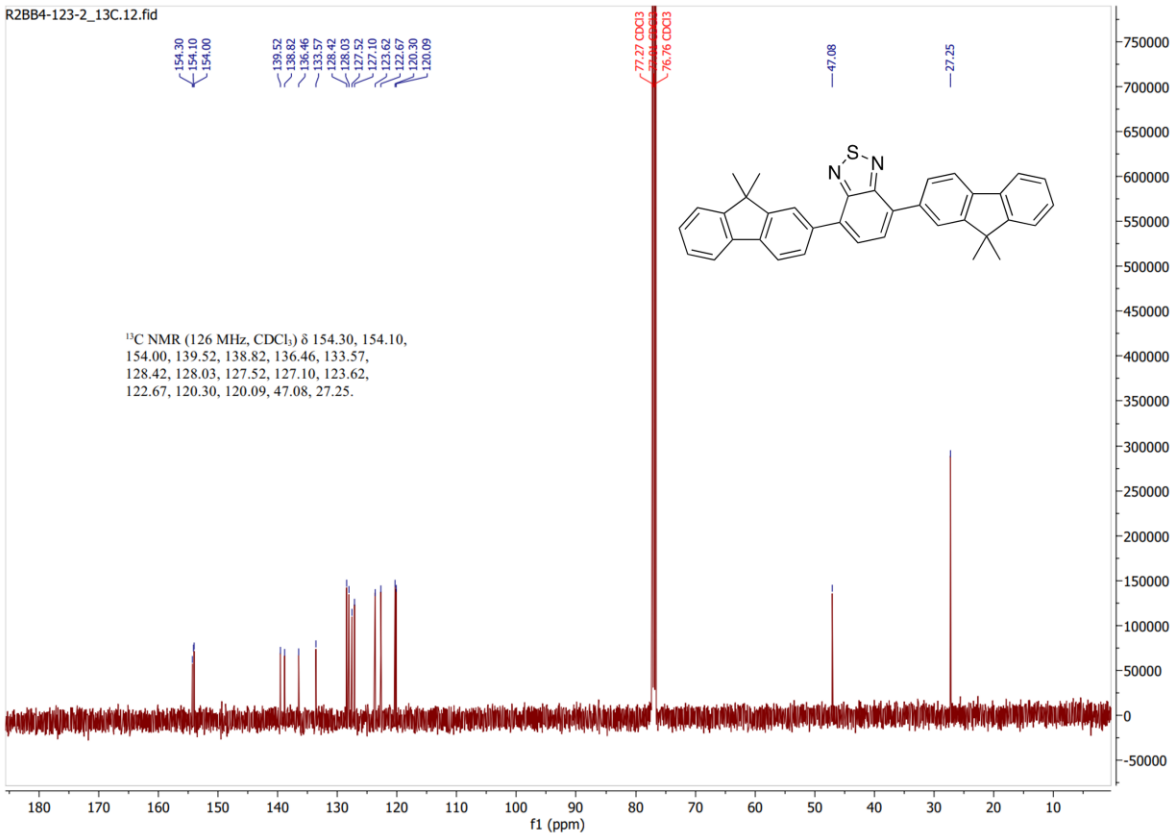

Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$) of FBTF synthesized with the method in Scheme 2. δ 154.30, 154.10, 154.00, 139.52, 138.82, 136.46, 133.57, 128.42, 128.03, 127.52, 127.10, 123.62, 122.67, 120.30, 120.09, 47.08, 27.25.

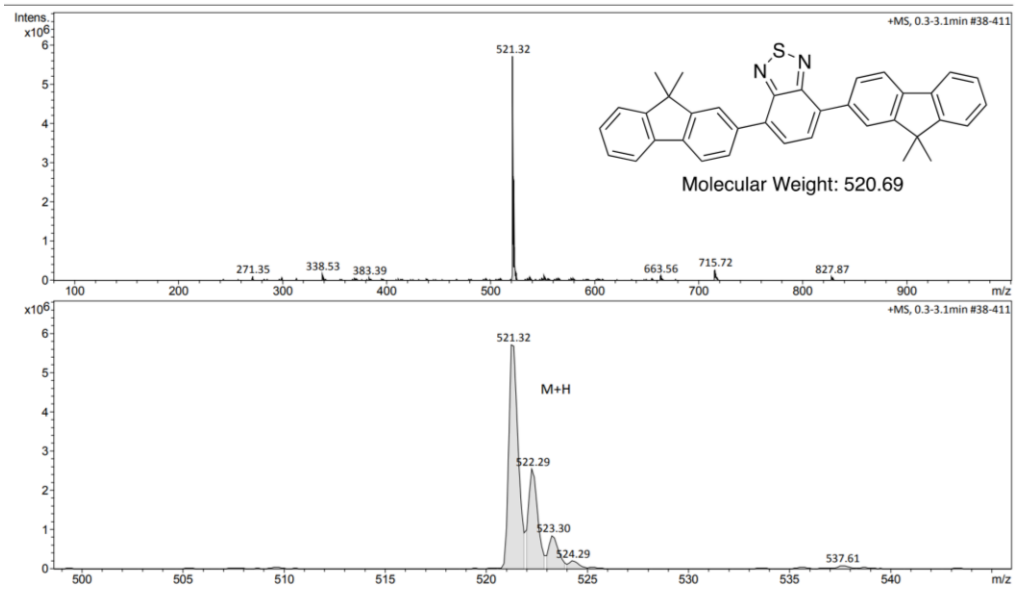

Figure S6. APCI mass spectrum of FBTF synthesized with the method in Scheme 2.

III. FBTF FTIR spectral characterization

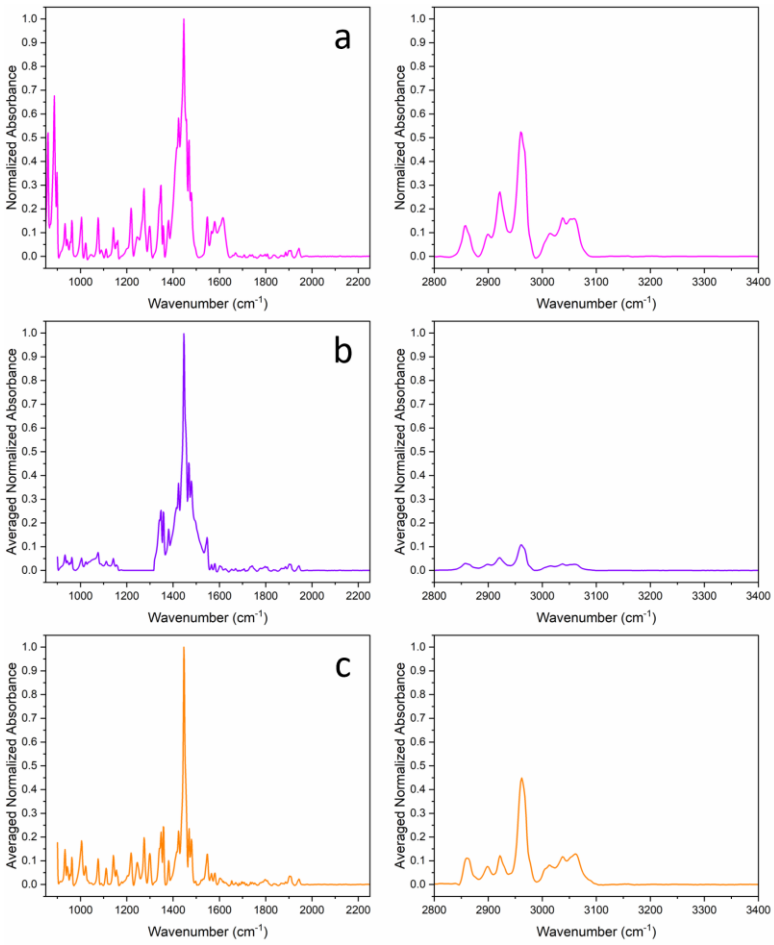

Figure S7. a) Transmission spectrum of FBTF synthesized with the method in Scheme S1 in KBr. IRRA spectra of pristine FBTF thin films drop cast onto b) Ag and c) ITO. Spectra collected with 2000 scans at 4 cm^{-1} resolution. Intensities plotted as normalized values with respect to the most intense spectral feature, the ν(C=C) band at 1446 cm^{-1}.

Table S1: FTIR bands and assignments for FBTF based on F8BT, polyfluorene, polyfluorenone, and thiadiazole derivatives.

FBTF Wavenumber (cm^{-1})	Assignment	Polymeric System, Wavenumber (cm^{-1})
1348	ν(C-C)	F8BT: 1343[1]
1381	δ(CH)	F8BT: 1377[1] Polyfluorene: 1377[2]
1446	$\nu(C=C)_{ring}$	F8BT, 1460[1] Polyfluorene: 1460[2]
1549	ν(C=C)	F8BT: 1545[1]
1565, 1580	ν(C=N)	Thiadiazole derivatives: 1550-1600[3]
1616	ν(C=C)	F8BT: 1605[1]
2857, 2921, 2960	$\nu(CH_3)$	Polyfluorene: 2855, 2926, 2953[2]
3037, 3053, 3058	$\nu(CH)_{ring}$	Polyfluorone: 3013, 3061[4]

IV. Additional IRRA spectra for FBTF on Ag and ITO

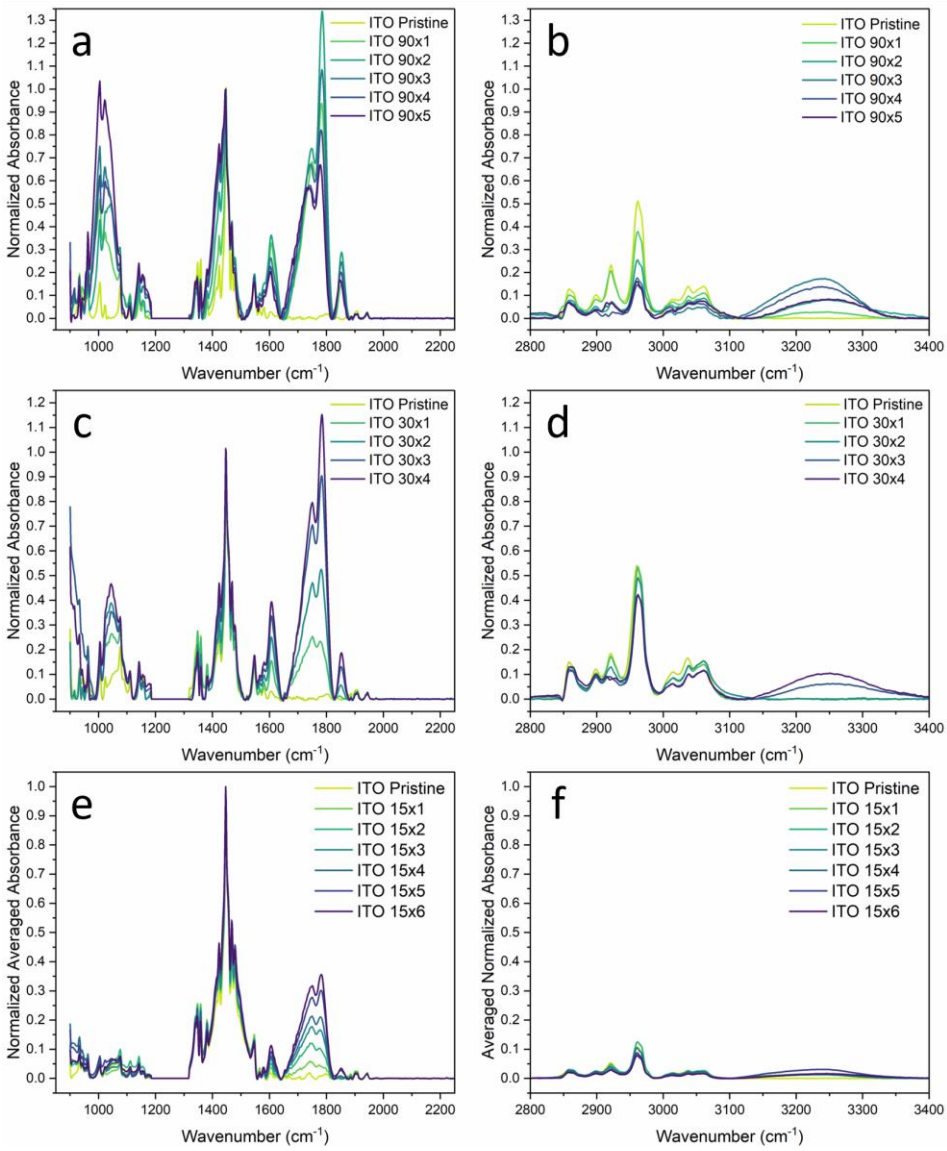

Figure S8. IRRA spectra of pristine and degraded FBTF films on ITO after a series of sequential radiant exposures of a), b) 90 min, c), d) 30 min, and e), f) 15 min. Intensities plotted as absorbance values normalized to the most intense band in each pristine spectrum.

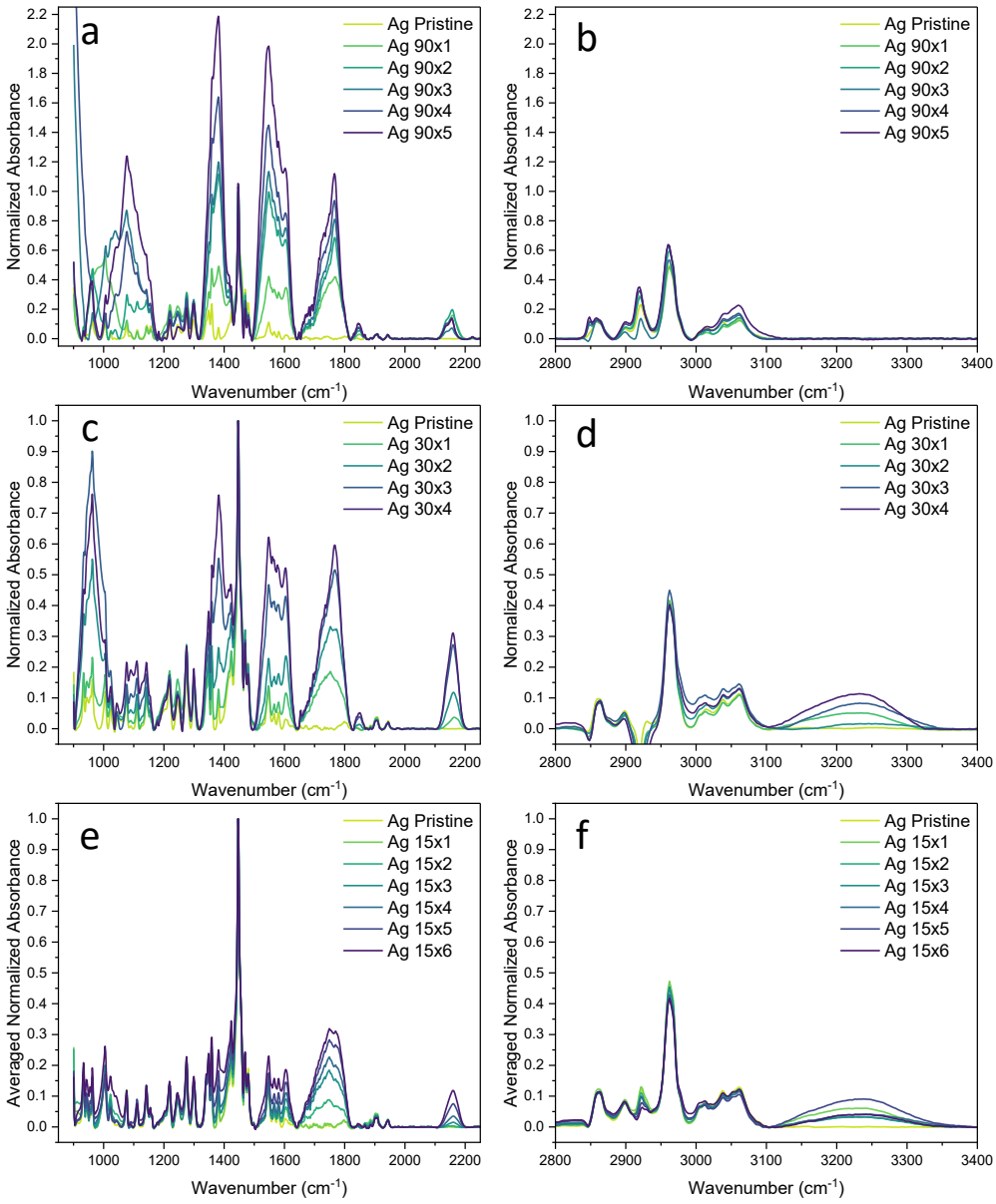

Figure S9. IRRA spectra of pristine and degraded FBTF films on Ag after a series of sequential radiant exposures of a), b) 90 min, c), d) 30 min, and e), f) 15 min. Intensities plotted as absorbance values normalized to the most intense band in each pristine spectrum.

V. Multivariate analysis for IRRA spectral region 1300-1500 cm^{-1}

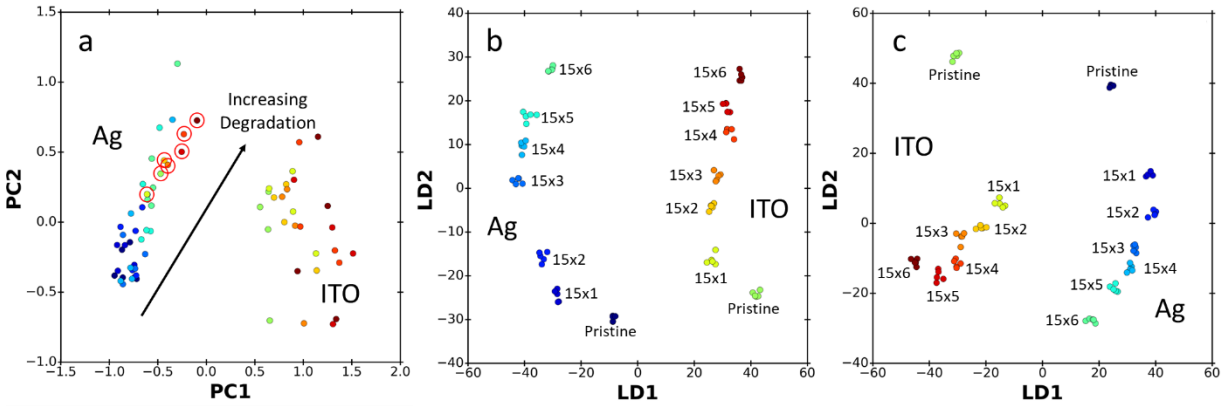

Figure S10. Results from a) PCA, b) LDA, and c) PCA-LDA on FBTF IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

VI. Principal component analysis of IRRA spectral data

Table S2: Calculated principal components and their % variances for FBTF IRRA spectral data.

PC	1300-1900 cm^{-1} % Variance	1300-1500 cm^{-1} % Variance
1	51.1%	79.1
2	36.3%	16.7
3	8.7%	2.2
4	2.1%	0.87
5	0.81%	0.70
6	0.43%	0.14
7	0.16%	0.067

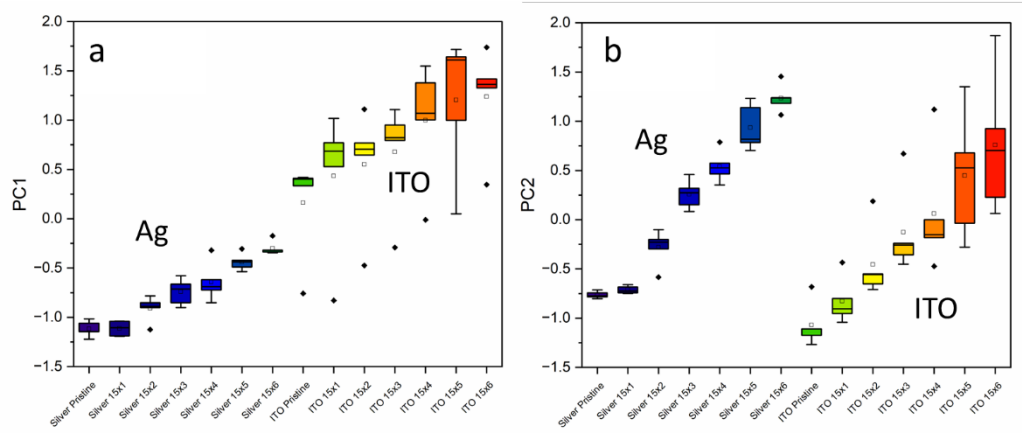

Figure S11: Box plot analysis on the first two PCs for IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures. Box plots for a) PC1 and b) PC2 values for spectra labeled by substrate type and exposure.

Table S3. ANOVA of PC1 and PC2 scores calculated from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	PC1 Scores					PC2 Scores				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	47.56947	3.65919	18.92054	<0.0001	13	33.78994	2.59923	19.14295	<0.0001
Error	56	10.83028	0.1934			56	7.60367	0.13578		
Total	69	58.39974				69	41.39361			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S4. Post hoc Tukey's test results for mean PC1 and PC2 values for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

PC1								PC2									
Sample	**Mean**	**Groups**						**Sample**	**Mean**	**Groups**							
ITO 15x6	1.23862	A						**Silver 15x6**	1.2347	A							
ITO 15x5	1.20361	A						**Silver 15x5**	0.93533	A	B						
ITO 15x4	0.99734	A	B					**ITO 15x6**	0.75762	A	B	C					
ITO 15x3	0.6765	A	B					**Silver 15x4**	0.54122	A	B	C	D				
ITO 15x2	0.55108	A	B	C				**ITO 15x5**	0.44843	A	B	C	D	E			
ITO 15x1	0.43436	A	B	C	D			**Silver 15x3**	0.25746		B	C	D	E	F		
ITO Pristine	0.16178		B	C	D	E		**ITO 15x4**	0.06212			C	D	E	F	G	
Silver 15x6	-0.30171			C	D	E	F	**ITO 15x3**	-0.12678				D	E	F	G	H
Silver 15x5	-0.43836				D	E	F	**Silver 15x2**	-0.28204					E	F	G	H	I
Silver 15x4	-0.64096					E	F	**ITO 15x2**	-0.45661						F	G	H	I
Silver 15x3	-0.74151					E	F	**Silver 15x1**	-0.71167							G	H	I
Silver 15x2	-0.9098						F	**Silver Pristine**	-0.7638								H	I
Silver 15x1	-1.1134						F	**ITO 15x1**	-0.82713								H	I
Silver Pristine	-1.11755						F	**ITO Pristine**	-1.06884									I

Means that do not share a letter are significantly different.

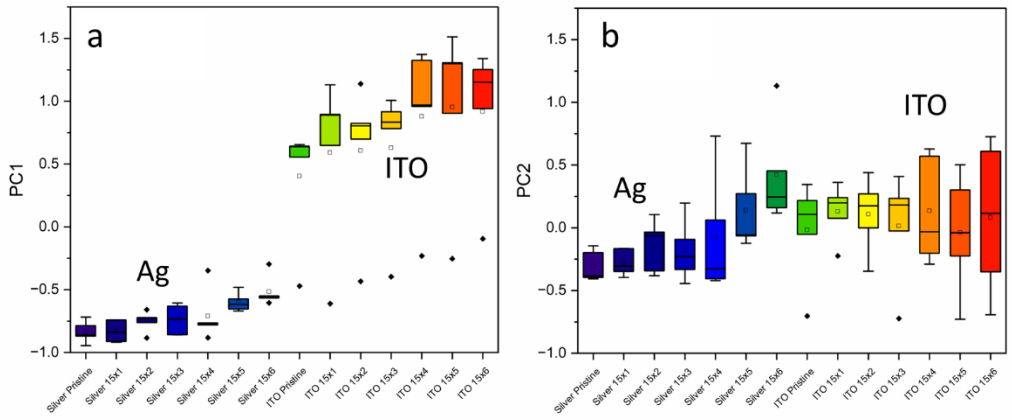

Figure S12: Box plot analysis on the first two PCs for IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures. Box plots for a) PC1 and b) PC2 values of spectra labeled by substrate type and exposure.

Table S5. ANOVA of PC1 scores calculated from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	PC1					PC2				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	37.12349	2.85565	14.31793	<0.0001	13	2.39956	0.18458	1.32453	0.22692
Error	56	11.16897	0.19945			56	7.80394	0.13936		
Total	69	48.29246				69	10.20349			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S6. Post hoc Tukey's test results for mean PC1 and PC2 values for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

PC1					PC2		
Sample	**Mean**	**Groups**			**Sample**	**Mean**	**Groups**
ITO 15x5	0.95379	A			**Silver 15x6**	0.42159	A
ITO 15x6	0.9178	A			**Silver 15x5**	0.13975	A
ITO 15x4	0.87902	A			**ITO 15x4**	0.13464	A
ITO 15x3	0.62847	A			**ITO 15x1**	0.13055	A
ITO 15x2	0.6064	A			**ITO 15x2**	0.10787	A
ITO 15x1	0.59063	A			**ITO 15x6**	0.08144	A
ITO Pristine	0.40366	A	B		**ITO 15x3**	0.01492	A
Silver 15x6	-0.5156		B	C	**ITO Pristine**	-0.01709	A
Silver 15x5	-0.59892			C	**ITO 15x5**	-0.03759	A
Silver 15x4	-0.71058			C	**Silver 15x4**	-0.0719	A
Silver 15x3	-0.73737			C	**Silver 15x2**	-0.14329	A
Silver 15x2	-0.75108			C	**Silver 15x3**	-0.17993	A
Silver 15x1	-0.83041			C	**Silver 15x1**	-0.2757	A
Silver Pristine	-0.83581			C	**Silver Pristine**	-0.30527	A

Means that do not share a letter are significantly different.

VII. Linear discriminant analysis of IRRA spectral data

Table S7: Calculated linear discriminants, % variances, and mean accuracy calculated via k-fold cross validation for FBTF IRRA Spectral Data. Data classed by substrate type and degradation extent.

LD	1300-1900 cm^{-1} % Variance	1300-1900 cm^{-1} Mean Accuracy	LD	1300-1500 cm^{-1} % Variance	1300-1500 cm^{-1} Mean Accuracy
1	50.9	83.1% (5 splits, 5 repeats)	1	67.2	76.0% (5 splits, 5 repeats)
2	35.1		2	21.6	
3	5.4		3	3.9	
4	2.9		4	3.3	
5	2.5		5	1.4	
6	1.3		6	1.1	

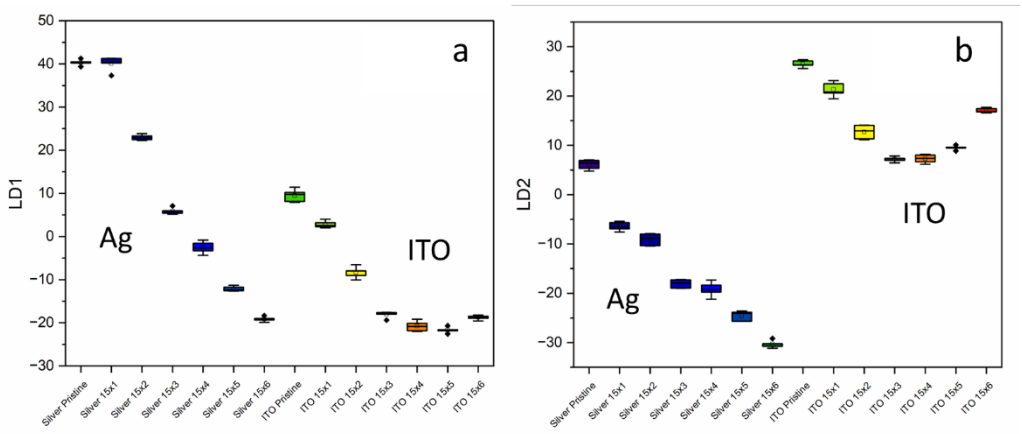

Figure S13: Box plot analysis on the first two LDs for IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures. Box plots for a) LD1 and b) LD2 values for spectra labeled by substrate type and exposure.

Table S8. ANOVA of LD1 and LD2 scores calculated from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	LD1					LD2				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	30306.52175	2331.2709	2331.2709	<0.0001	13	20916.94176	1608.99552	1608.99552	<0.0001
Error	56	56	1			56	56	1		
Total	69	30362.52175				69	20972.94176			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S9. Post hoc Tukey's test results for mean LD1 and LD2 values for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

LD1													LD2												
Sample	**Mean**	**Groups**											**Sample**	**Mean**	**Groups**										
Silver Pristine	40.32131	A											**ITO Pristine**	26.51384	A										
Silver 15x1	40.0664	A											**ITO 15x1**	21.30336		B									
Silver 15x2	22.95148		B										**ITO 15x6**	17.078			C								
ITO Pristine	9.48042			C									**ITO 15x2**	12.70772				D							
Silver 15x3	5.82834				D								**ITO 15x5**	9.49317					E						
ITO 15x1	2.81612					E							**ITO 15x4**	7.27601						F					
Silver 15x4	-2.53669						F						**ITO 15x3**	7.18155						F					
ITO 15x2	-8.3206							G					**Silver Pristine**	6.10408						F					
Silver 15x5	-12.11359								H				**Silver 15x1**	-6.42757							G				
ITO 15x3	-18.06308									I			**Silver 15x2**	-9.08658								H			
ITO 15x6	-18.77238									I	J		**Silver 15x3**	-18.06732									I		
Silver 15x6	-19.15876									I	J		**Silver 15x4**	-19.1788									I		
ITO 15x4	-20.79747										J	K	**Silver 15x5**	-24.5736										J	
ITO 15x5	-21.7015											K	**Silver 15x6**	-30.32386											K

Means that do not share a letter are significantly different.

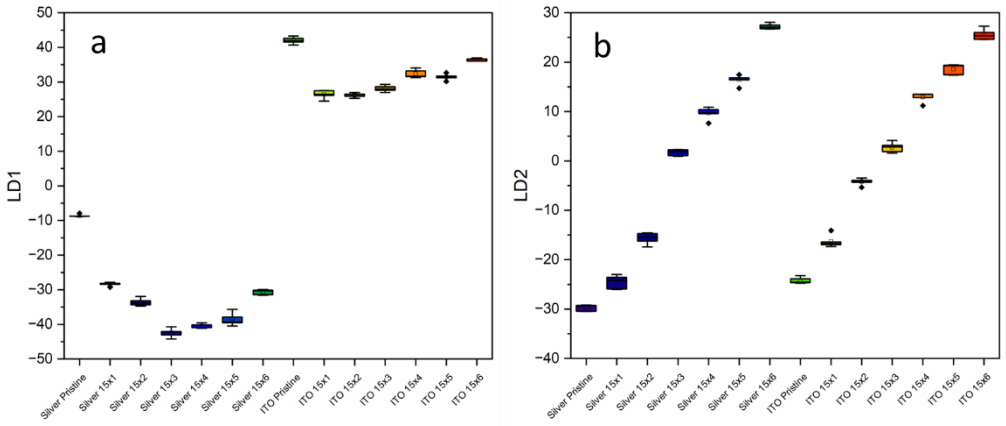

Figure S14: Box plot analysis on the first two LDs for IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures**.** Box plots for a) LD1 and b) LD2 values for spectra labeled by substrate type and exposure.

Table S10. ANOVA of LD1 and LD2 scores from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	LD1					LD2				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	75904.4534	5838.80411	5838.80411	<0.0001	13	24407.91092	1877.53161	1877.53161	<0.0001
Error	56	56	1			56	56	1		
Total	69	75960.4534				69	24463.91092			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S11. Post hoc Tukey's test results for mean LD1 and LD2 values for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

LD1												LD2										
Sample	**Mean**	**Groups**										**Sample**	**Mean**	**Groups**								
ITO Pristine	41.98936	A										**Silver 15x6**	27.22769	A								
ITO 15x6	36.45477		B									**ITO 15x6**	25.56006	A								
ITO 15x4	32.36957			C								**ITO 15x5**	18.58031		B							
ITO 15x5	31.42006			C								**Silver 15x5**	16.43145		B							
ITO 15x3	28.0858				D							**ITO 15x4**	12.89016			C						
ITO 15x1	26.41866				D							**Silver 15x4**	9.63178				D					
ITO 15x2	26.1226				D							**ITO 15x3**	2.71473					E				
Silver Pristine	-8.60122					E						**Silver 15x3**	1.67396					E				
Silver 15x1	-28.42129						F					**ITO 15x2**	-4.2319						F			
Silver 15x6	-30.67891							G				**Silver 15x2**	-15.67831							G		
Silver 15x2	-33.61948								H			**ITO 15x1**	-16.30647							G		
Silver 15x5	-38.56671									I		**ITO Pristine**	-24.22515								H	
Silver 15x4	-40.5398									I	J	**Silver 15x1**	-24.52673								H	
Silver 15x3	-42.43341										J	**Silver Pristine**	-29.74157									I

Means that do not share a letter are significantly different.

VIII. Combined principal component-linear discriminant analysis of IRRA spectral data

Table S12: Calculated linear discriminants after PCA treatment, % variances, and mean accuracy calculated via k-fold cross validation for FBTF IRRA spectral data. Data was classed by substrate type and degradation extent.

LD	1300-1900 cm^{-1} % Variance	1300-1900 cm^{-1} Mean Accuracy	LD	1300-1500 cm^{-1} % Variance	1300-1500 cm^{-1} Mean Accuracy
1	51.5	69.4% (5 splits, 5 repeats)	1	64.1	67.1% (5 splits, 5 repeats)
2	32.8		2	28.4	
3	8.5		3	3.7	
4	3.1		4	2.0	
5	1.7		5	0.83	
6	0.99		6	0.31	

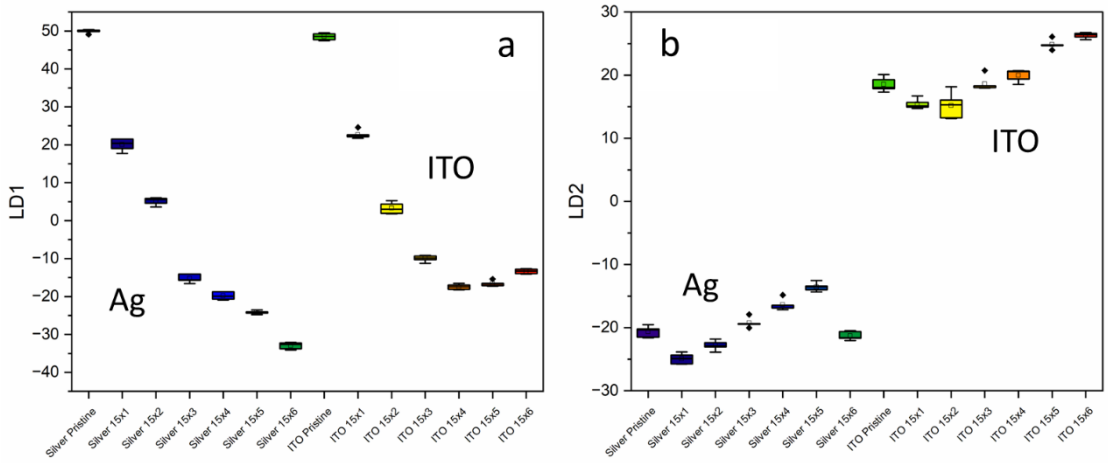

Figure S15: Box plot analysis on the first two LDs after PCA treatment for IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures. Box plots for a) LD1 and b) LD2 values for spectra labeled by substrate type and exposure.

Table S13. ANOVA of LD1 and LD2 scores calculated after PCA treatment from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	LD1					LD2				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	44749.02949	3442.23304	3442.23304	<0.0001	13	28540.28418	2195.40648	2195.40648	<0.0001
Error	56	56	1			56	56	1		
Total	69	44805.02949				69	28596.28418			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S14. Post hoc Tukey's test results for mean LD1 and LD2 values after PCA treatment for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1900 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

LD1													LD2									
Sample	**Mean**	**Groups**											**Sample**	**Mean**	**Groups**							
Silver Pristine	49.93391	A											**ITO 15x6**	26.2856	A							
ITO Pristine	48.49173	A											**ITO 15x5**	24.84676	A							
ITO 15x1	22.66808		B										**ITO 15x4**	19.96638		B						
Silver 15x1	20.03374			C									**ITO 15x3**	18.60932		B						
Silver 15x2	5.13335				D								**ITO Pristine**	18.52116		B						
ITO 15x2	3.27389				D								**ITO 15x1**	15.4393			C					
ITO 15x3	-9.98027					E							**ITO 15x2**	15.17789			C					
ITO 15x6	-13.36021						F						**Silver 15x5**	-13.57369				D				
Silver 15x3	-15.21215						F	G					**Silver 15x4**	-16.36964					E			
ITO 15x5	-16.59953							G	H				**Silver 15x3**	-19.24581						F		
ITO 15x4	-17.4336								H				**Silver Pristine**	-20.6476						F	G	
Silver 15x4	-19.80145									I			**Silver 15x6**	-21.28576						F	G	
Silver 15x5	-24.17487										J		**Silver 15x2**	-22.80785							G	H
Silver 15x6	-32.97261											K	**Silver 15x1**	-24.91605								H

Means that do not share a letter are significantly different.

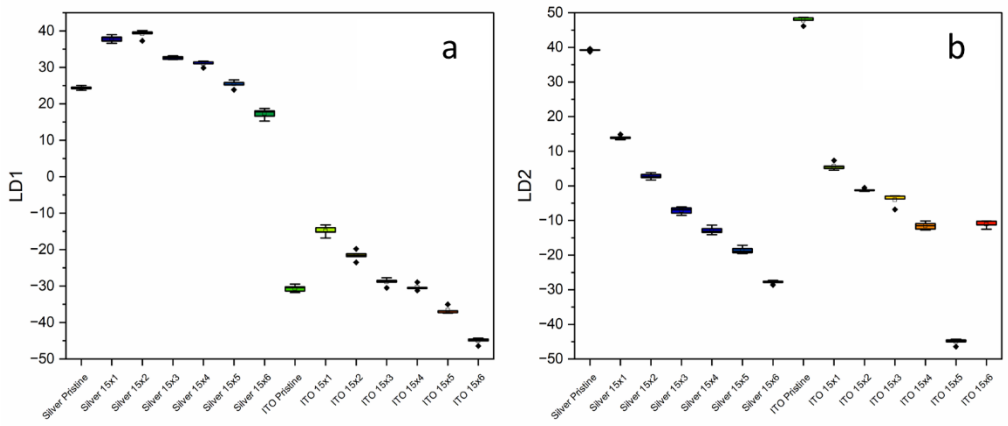

Figure S16: Box plot analysis on the first two LDs after PCA treatment for IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures. Box plots for a) LD1 and b) LD2 values for spectra labeled by substrate type and exposure.

Table S15. ANOVA of LD1 and LD2 scores calculated after PCA treatment from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

	LD1					LD2				
	DF	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**	**DF**	**Sum of Squares**	**Mean Square**	**F Value**	**Prob>F**
Model	13	66440.98849	5110.84527	5110.84527	<0.0001	13	38124.95754	2932.68904	3368.73339	<0.0001
Error	56	56	1			56	48.75143	0.87056		
Total	69	66496.98849				69	38173.70898			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Table S16. Post hoc Tukey's test results for mean LD1 and LD2 values after PCA treatment for each substrate and degradation grouping calculated from the IRRA spectral data between 1300-1500 cm^{-1} for FBTF on Ag and ITO under sequential 15 min radiant exposures.

LD1											LD2												
Sample	**Mean**	**Groups**									**Sample**	**Mean**	**Groups**											
Silver 15x2	39.21655	A									**ITO Pristine**	47.80425	A										
Silver 15x1	37.88632	A									**Silver Pristine**	39.19274		B									
Silver 15x3	32.63891		B								**Silver 15x1**	13.97533			C								
Silver 15x4	31.02216		B								**ITO 15x1**	5.62796				D							
Silver 15x5	25.46461			C							**Silver 15x2**	2.74752					E						
Silver Pristine	24.36609			C							**ITO 15x2**	-1.22146						F					
Silver 15x6	17.31115				D						**ITO 15x3**	-4.04377							G				
ITO 15x1	-14.87408					E					**Silver 15x3**	-7.14299								H			
ITO 15x2	-21.57812						F				**ITO 15x6**	-11.08399									I		
ITO 15x3	-28.83077							G			**ITO 15x4**	-11.54035									I		
ITO 15x4	-30.30695							G			**Silver 15x4**	-12.87271									I		
ITO Pristine	-30.64877							G			**Silver 15x5**	-18.60559										J		
ITO 15x5	-36.66806								H		**Silver 15x6**	-27.77536											K	
ITO 15x6	-44.99904									I	**ITO 15x5**	-44.99904												L

Means that do not share a letter are significantly different.

IX. References

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