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Supplementary Information

Photoelectrochemical Alcohol Oxidation by Mixed-Linker Metal-Organic Frameworks

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1.) ICP Analysis of RuB-RuTB-UiO-67-TiO2/FTO films used in catalysis

The films that were used in catalysis, along with the solutions in which the catalysis occurred were analyzed via ICP to determine the extent of leeching. As shown from Table 3 below, the leaching ratio was determined to be 0.04 ± 0.03, indicating minimal leaching.

Table 1. Thin film mixed-linker MOF digestion data

	[Ru] ppb	Ru mass in 1:10 dilution ug	Ru mass in original sample, 4 mL ug	mol Ru
Thin Film 1	147.28	1.47	5.89	5.83E-08
Thin Film 2	152.20	1.52	6.09	6.03E-08
Thin Film 3	138.03	1.38	5.52	5.47E-08

Table 2. MOF catalysis solution data

Thin Film #	Catalysis Solution	[Ru] ppb	Ru mass in 1:10 dilution ug	Ru mass in original sample, 1:4 dilution*40 mL sample ug	mol Ru
1	before	0.1	0.001	0.119	1.18E-09
1	after	0.3	0.003	0.436	4.32E-09
2	before	0.1	0.001	0.173	1.71E-09
2	after	0.1	0.001	0.192	1.90E-09
3	before	0.1	0.001	0.116	1.15E-09
3	after	0.3	0.003	0.518	5.12E-09

Table 3. Leaching ratio data

	mol Ru in thin films	mol Ru in catalysis solutions (after - before catalysis)	
Thin Film 1	5.83E-08	3.14E-09	
Thin Film 2	6.03E-08	1.93E-10	
Thin Film 3	5.47E-08	3.97E-09	
			Leaching Ratio
Average	5.78E-08	2.43E-09	**0.04**
Std. Dev.	2.85E-09	1.99E-09	**0.03**

2.) ^{1}H-NMR determination of RuB:RuTB ratio in RuB-RuTB-UiO-67-TiO_2/FTO TAS samples

To determine the relative RuB:RuTB ratios in the films used for transient absorption spectroscopy, the individual dye peaks were first analyzed in 1.0 M NaOD/D_2O (Figures S1 & S2). One peak from each spectrum was chosen as a reference for the individual compounds (RuB, 7.15 ppm; RuTB, 7.04 ppm). With these reference peaks established, a small amount (~5 mg) of the residual MOF powder formed during the film synthesis was dissolved in 1.0 M NaOD/D_2O and filtered through packed glass wool and the ^{1}H-NMR spectrum was obtained (Figure S3). The RuTB reference peak (6.99 ppm) was set to a value of 1 and the integrated RuB reference peak (7.15 ppm) had a value of 1.54, meaning that for every 2 RuTB ligands present, there are 3 RuB ligands in the MOF.

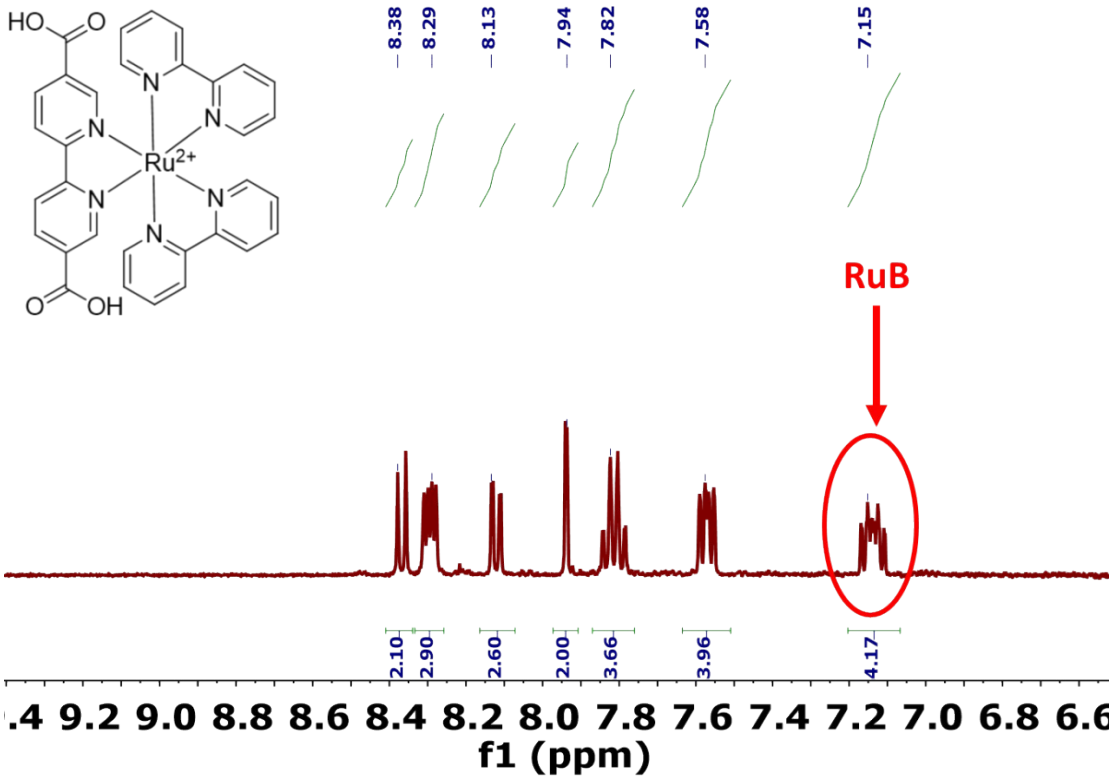

Figure S1. RuB ^{1}H-NMR in 1.0 M NaOD/D_2O.

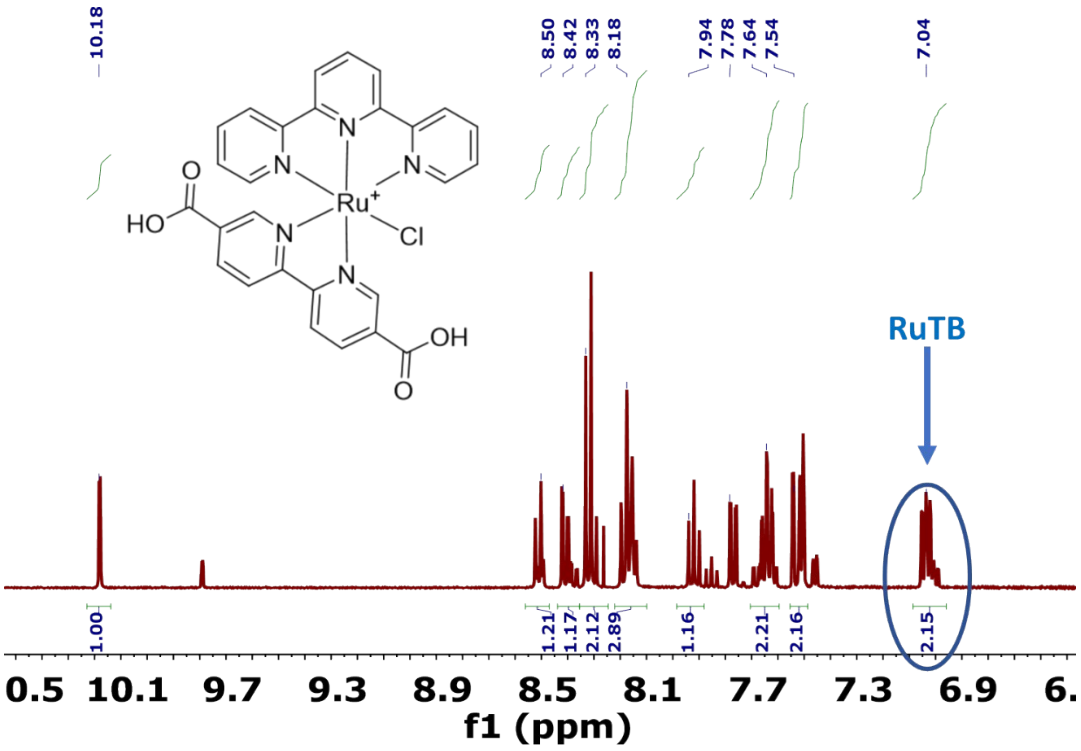

Figure S2. RuTB ^{1}H-NMR in 1.0 M NaOD/D_2O.

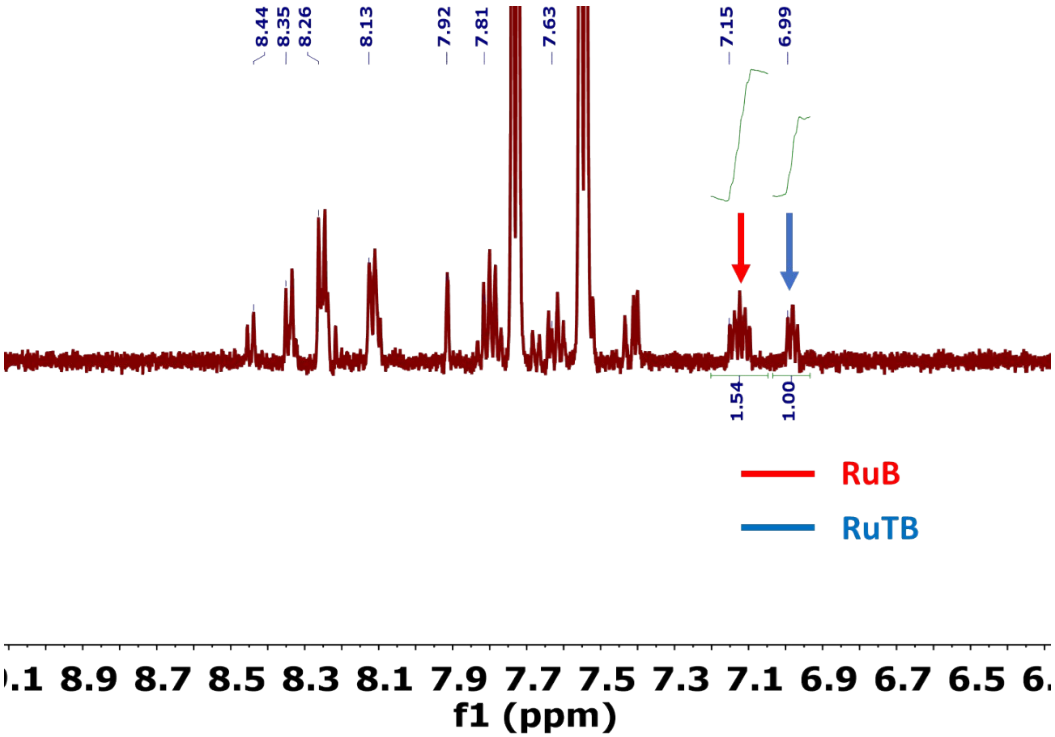

Figure S3. Digested RuB-RuTB-UiO-67 ^{1}H-NMR in 1.0 M NaOD/D_2O.

3.) Benzyl alcohol oxidation GC data

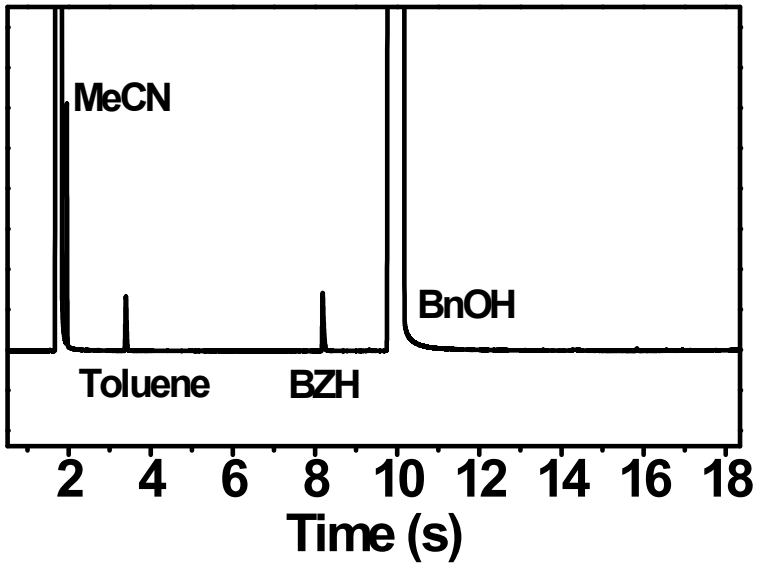

Figure S4. Example gas chromatogram from the photoelectrochemical oxidation of BnOH to BZH.

4.) Transient absorbance spectra

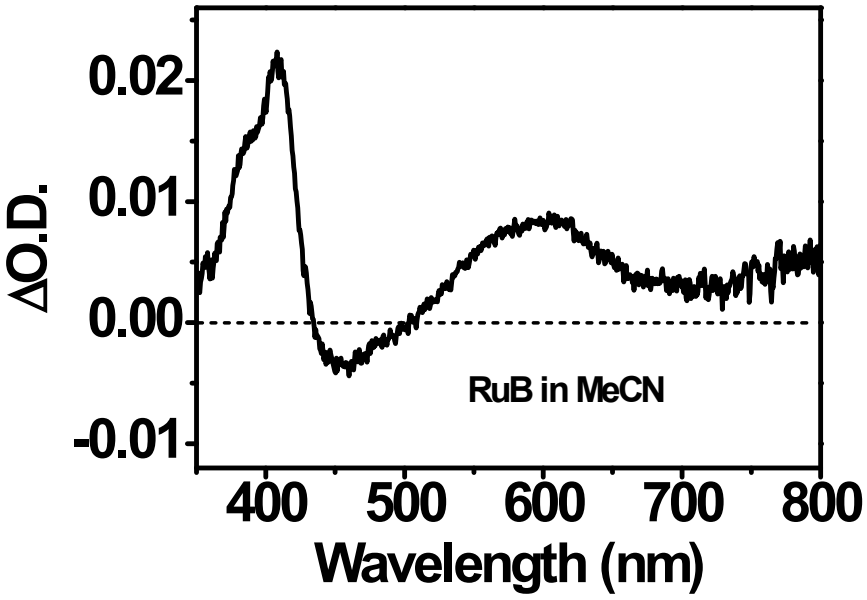

Figure S5. Transient absorbance spectrum of RuB in MeCN.

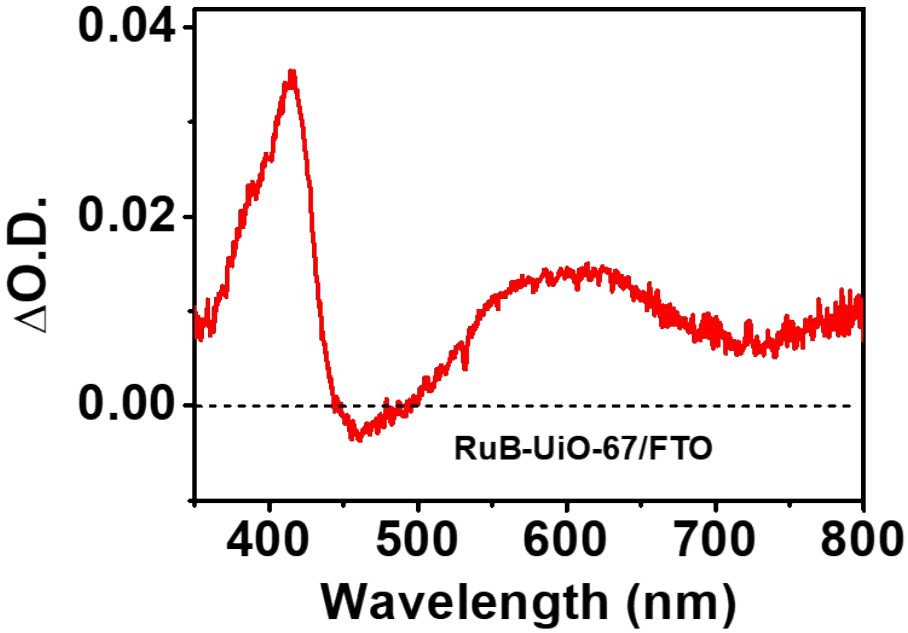

Figure S6. Transient absorption spectrum of RuB-UiO-67/FTO.

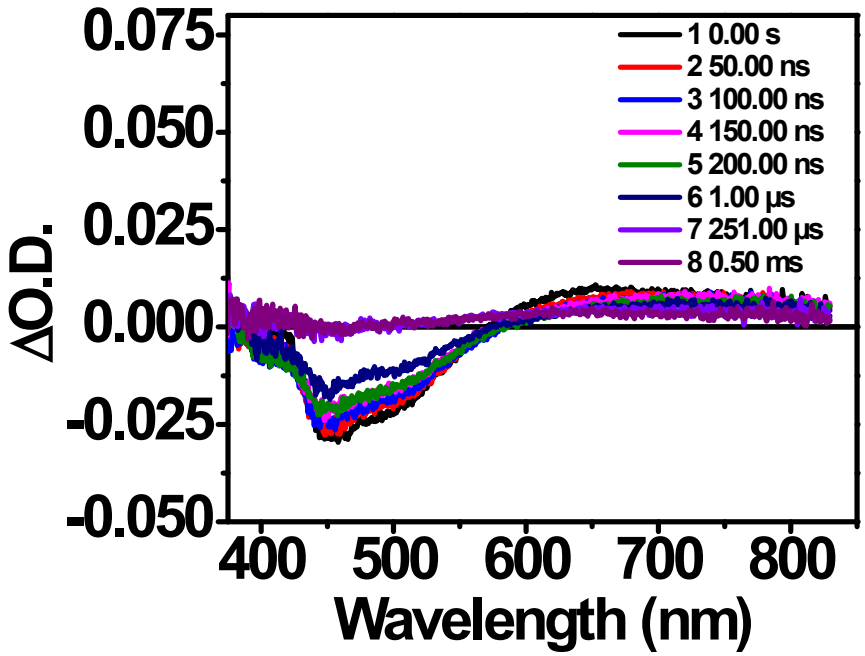

Figure S7. Transient spectral mapping of RuB-UiO-67-TiO_2/FTO from 0 – 1 µs, 0.251 ms, and 0.5 ms.

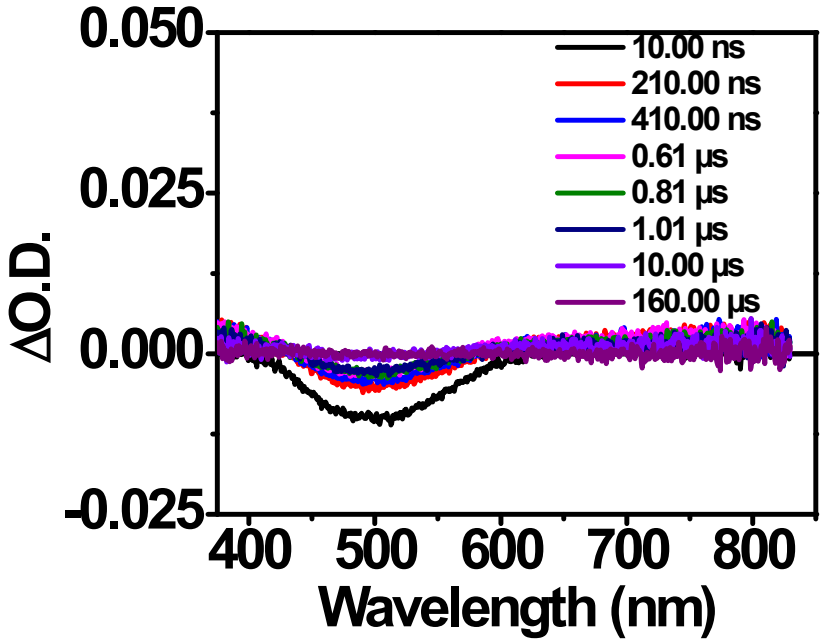

Figure S8. Transient spectral mapping of RuTB-UiO-67-TiO_2/FTO from 0 – 1 µs, 10 µs, and 160 µs.

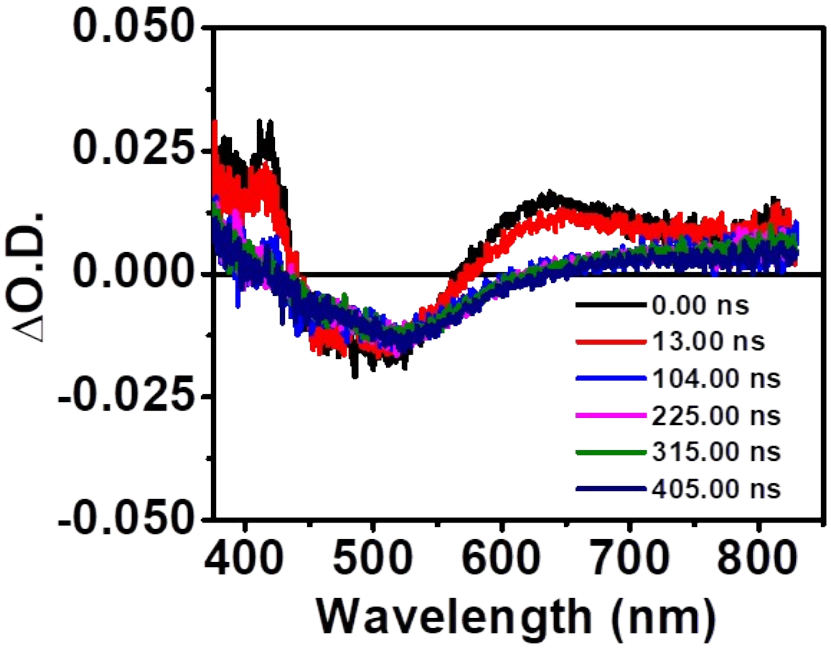

Figure S9a. Transient spectral mapping of RuB-RuTB-UiO-67-TiO_2/FTO from 0 – 405 ns.

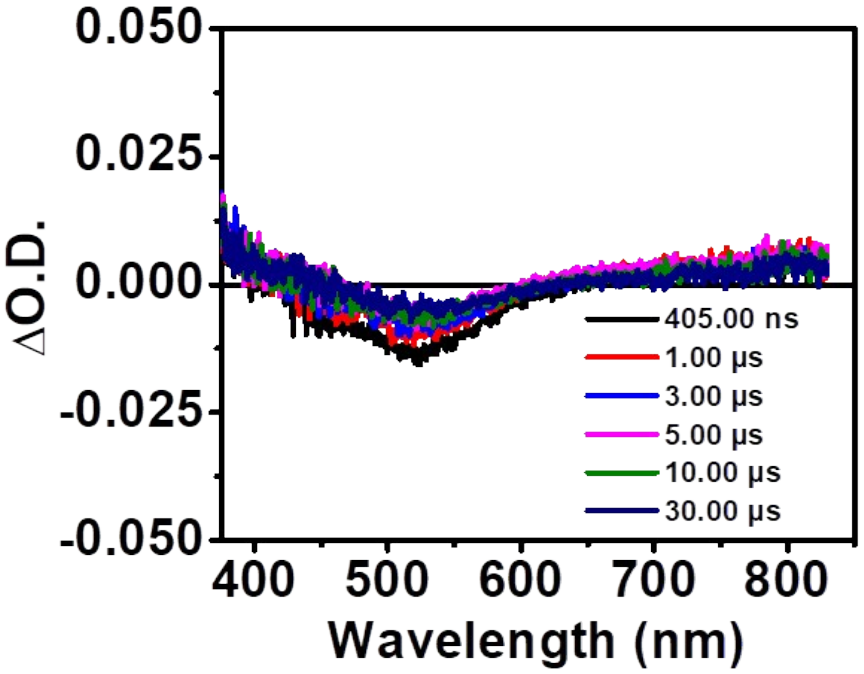

Figure S9b. Transient spectral mapping of RuB-RuTB-UiO-67-TiO_2/FTO from 405ns – 30 µs.

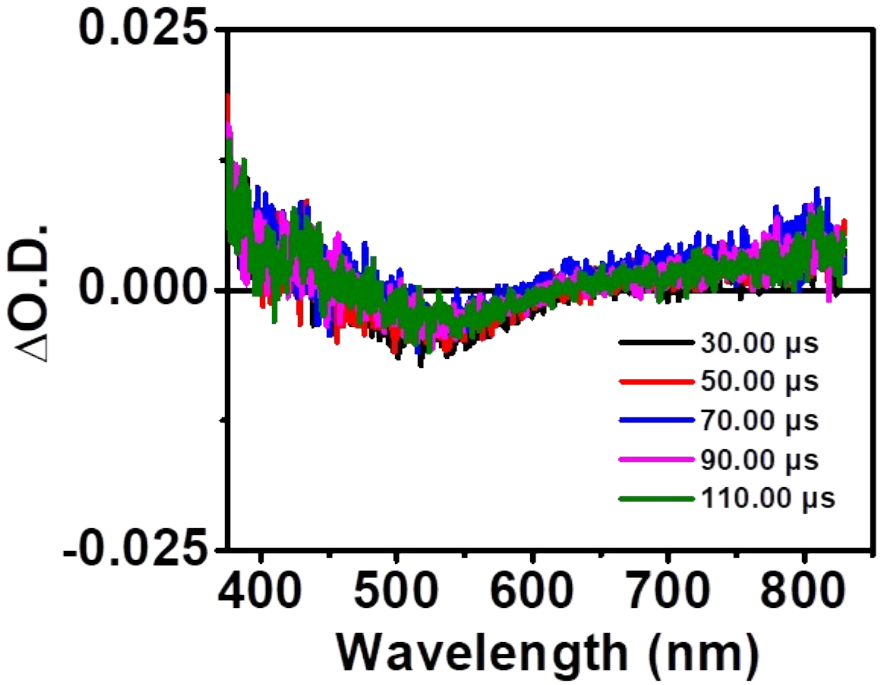

Figure S9c. Transient spectral mapping of RuB-RuTB-UiO-67-TiO_2/FTO from 30 – 110 µs.

5.) Ground-state bleach kinetic traces at 500 nm

The kinetics of RuB-UiO-67-TiO_2/FTO, RuTB-UiO-67-TiO_2/FTO, and RuB-RuTB-UiO-67-TiO_2/FTO were all probed at 500 nm (bleach location of the films), shown below. Because there are multiple kinetic processes occurring within the bleach lifetime, a Kohlrausch-Williams-Watts fitting model was used:

$$I(t) = y_0 + Ae^{-\left(\frac{t}{t_0}\right)^{\beta}} \#(1)$$

where y_0 is the intensity when y = 0, A is the initial signal intensity at t = 0, t_0 is the observed lifetime, and β (0 < β < 1) is the stretching parameter. The area under the curve is referred to as the average lifetime or mean relaxation time, τ_{avg}, which can be determined via the following relation:

$$\tau_{avg} = \frac{\tau_0}{\beta}\Gamma\left(\frac{1}{\beta}\right) \#(2)$$

where $\Gamma(\beta^{-1})$ is the gamma function of β^{-1}.

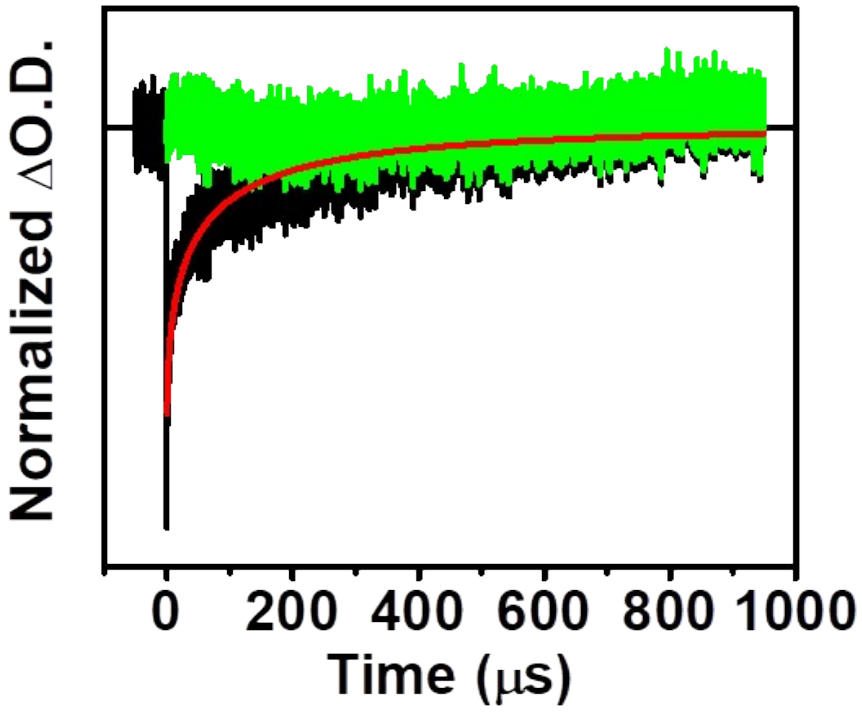

Figure S10. RuB-UiO-67-TiO_2/FTO ground-state bleach kinetic data

RuB-UiO-67-TiO_2/FTO was fit and provided an average lifetime (τ_{avg}) of 105 ± 1 μs, with a stretching exponent (β) value of 0.44 ± 0.003.

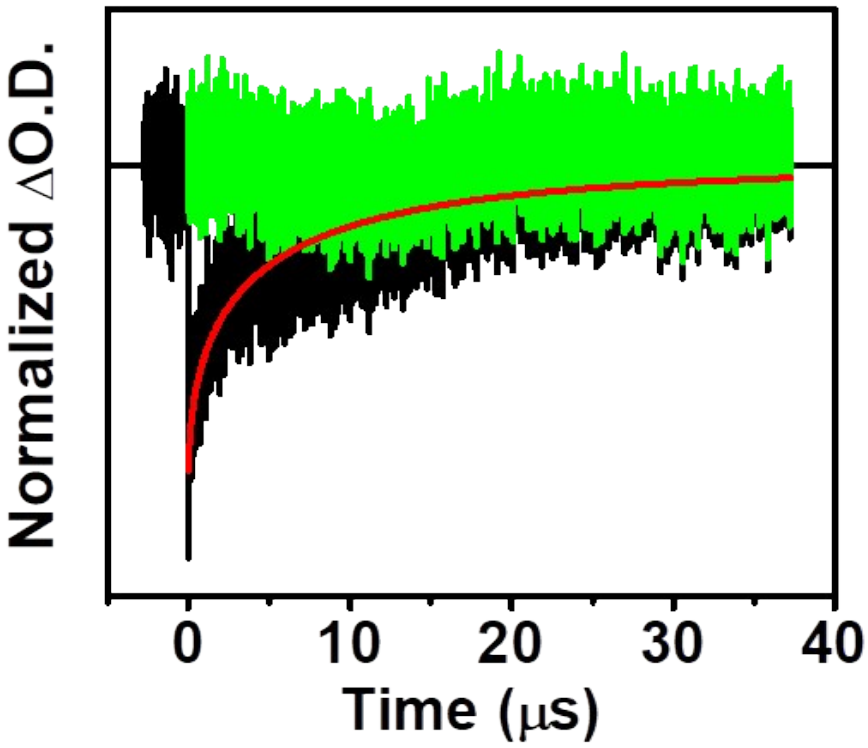

Figure S11. RuTB-UiO-67-TiO_2/FTO ground-state bleach kinetic data

RuTB-UiO-67-TiO_2/FTO provided an average lifetime (τ_{avg}) of 7.16 ± 0.08 μs, with a stretching exponent (β) value of 0.520 ± 0.004.

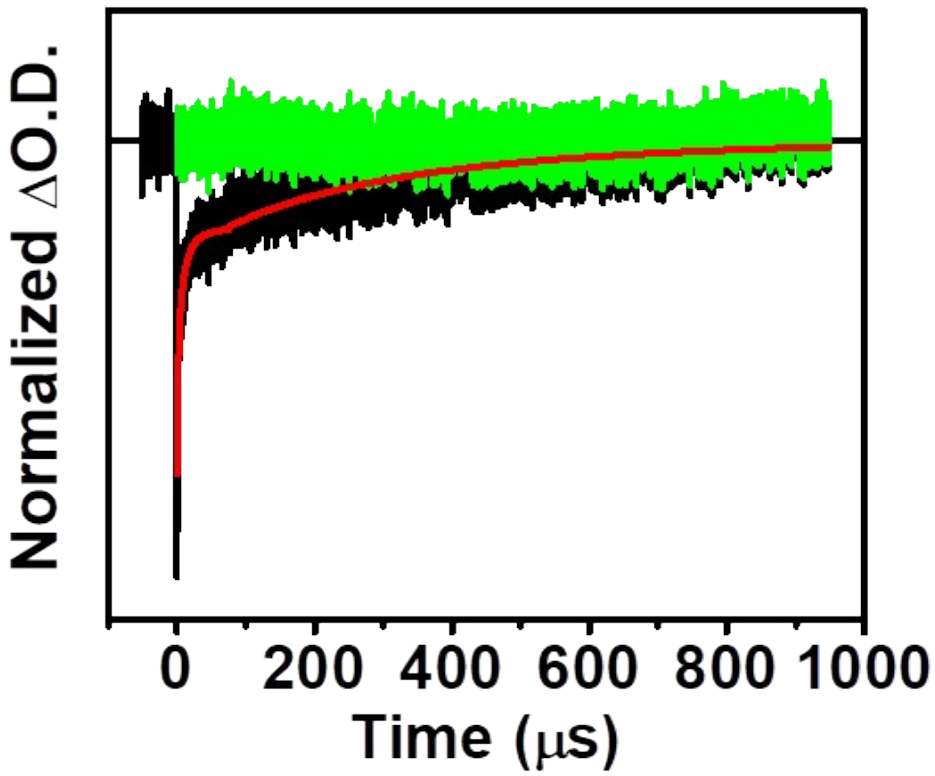

Figure S12. RuB-RuTB-UiO-67-TiO_2/FTO ground-state bleach kinetic data

To obtain the best fit for the RuB-RuTB-UiO-67-TiO_2/FTO kinetic trace at 500 nm, two stretched exponentials had to be used. We deemed this necessary because previous attempts using discrete exponential (mono-, bi- and tri-exponential) fits, as well as singular stretched exponential fits resulted in lifetime values outside of the probed time window. The first 50 μs provided an average lifetime (τ_{avg}) of 5.8 ± 0.3 μs with a stretching exponent (β) value of 0.53 ± 0.03. The remaining decay provided an average lifetime (τ_{avg}) of 283 ± 2 μs, with a stretching exponent (β) value of 0.85 ± 0.09.

7.) RuB-UiO-67-TiO_2/FTO and RuTB-UiO-67-TiO_2/FTO ES absorption and emission kinetics

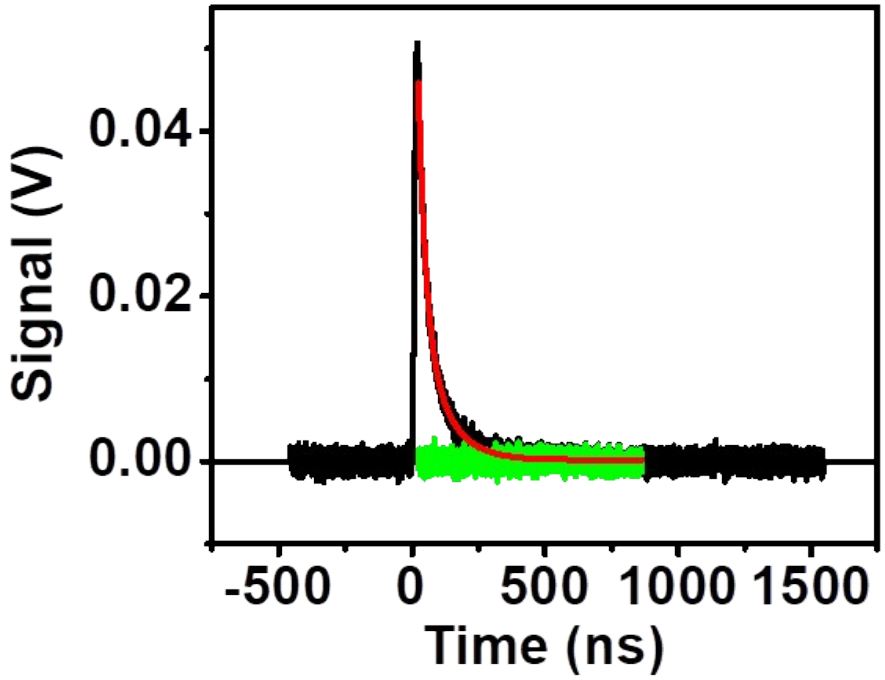

Figure S13. Emission decay of RuB-UiO-67-TiO_2/FTO at 680 nm.

The emission decay of RuB-UiO-67-TiO_2/FTO was fit to a biexponential decay, with a τ_1 of 26.2 ± 0.6 ns, a τ_2 of 92 ± 2 ns and an R^2 of 0.99.

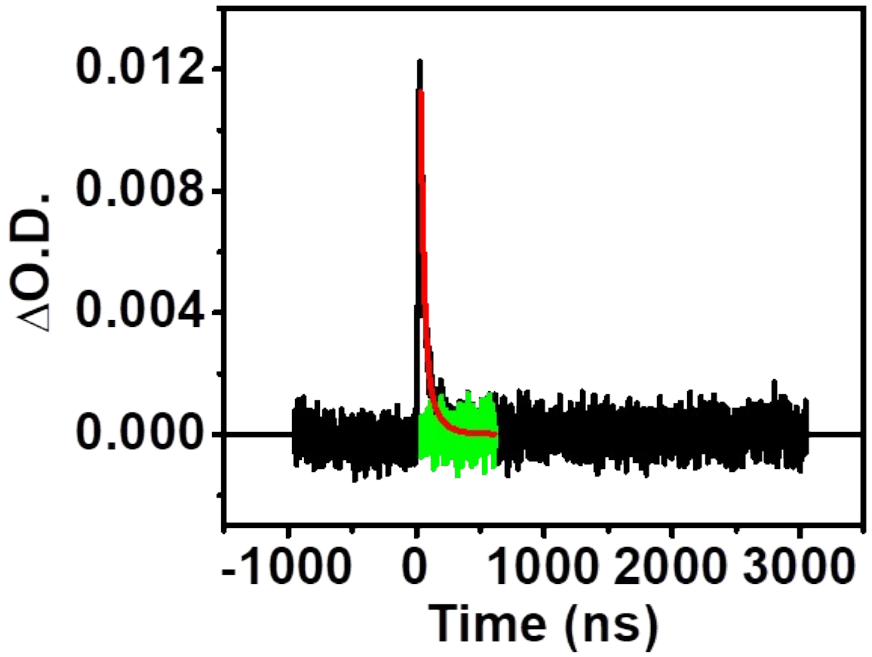

Figure S14. Excited state absorption decay of RuB-UiO-67-TiO_2/FTO at 600 nm.

The excited state absorption decay of RuB-UiO-67-TiO_2/FTO was fit to a biexponential decay, with a τ_1 of 25 ± 1 ns, a τ_2 of 92 ± 10 ns and an R^2 of 0.95.

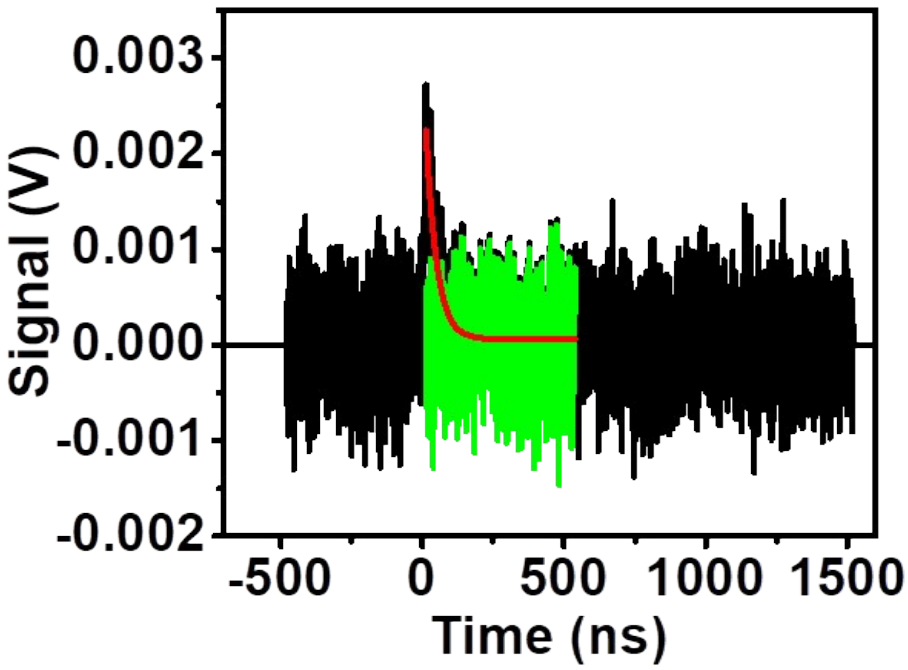

Figure S15. Emission decay of RuTB-UiO-67-TiO_2/FTO at 675 nm.

The weak emission decay of RuTB-UiO-67-TiO_2/FTO was fit to a monoexponential decay, with a τ of 37 ± 2 ns and an R^2 of 0.48. An excited state decay curve was unable to be obtained with RuTB-UiO-67-TiO_2/FTO.