Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Reduction reactions at metal/non-aqueous interfaces can be sensed with the turn-on fluorophore resazurin

Zachary Gatland,[1] Daniel Madrid,[1] Mark Siegel,[1] Lydia Kisley[1,2]

[1]Department of Physics and [2]Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7079

* lydia.kisley@case.edu, ORCID: 0000-0002-8286-5264

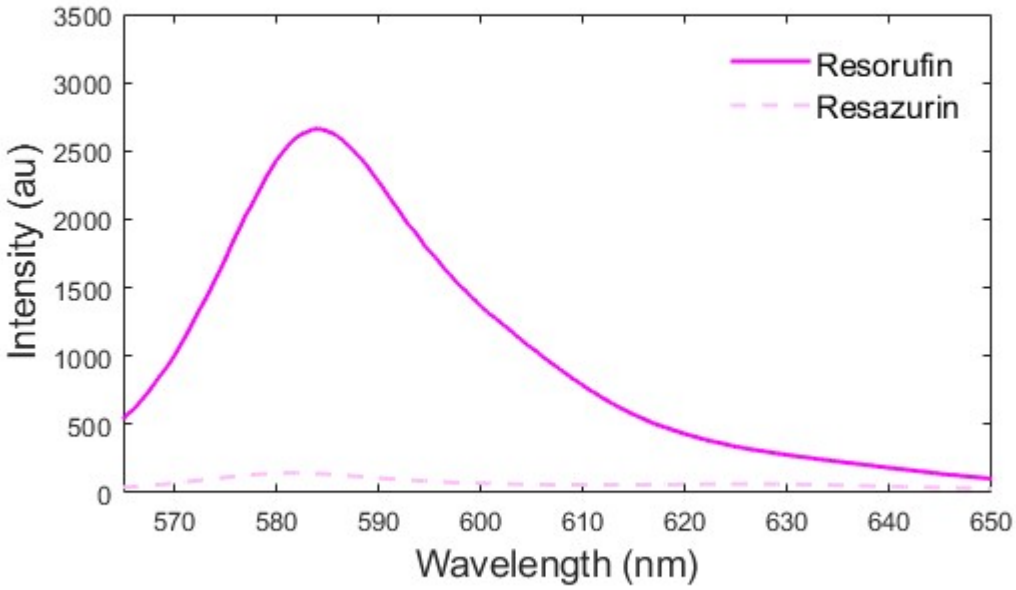

Figure S1: The fluorescence emission spectra for resorufin and resazurin in H_2O.

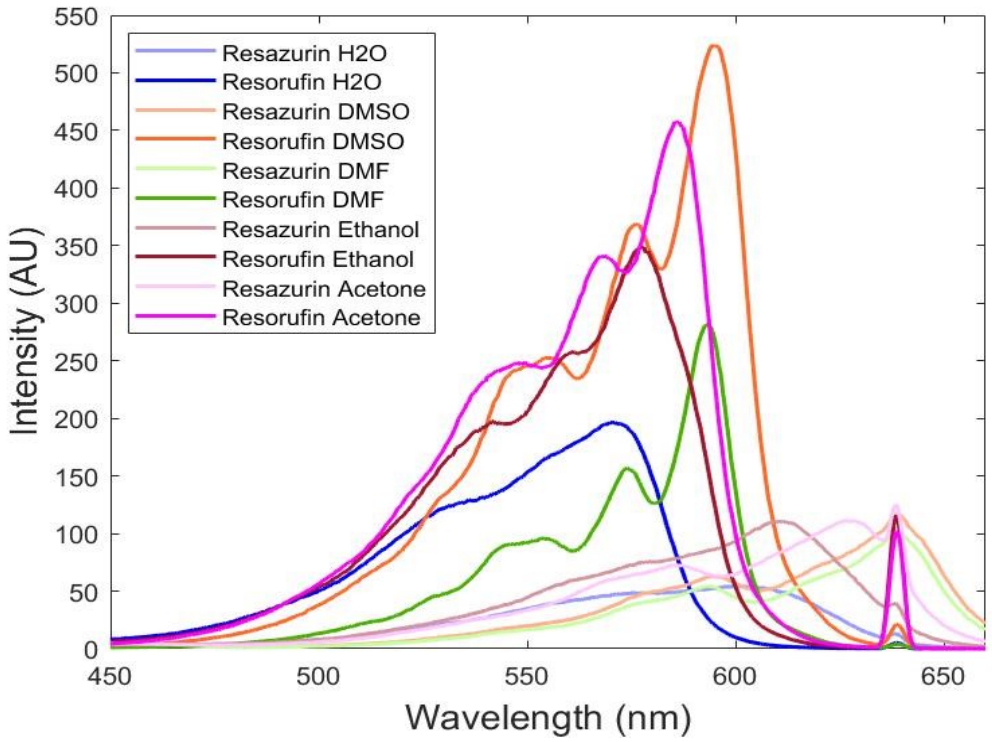

Figure S2: The fluorescence excitation spectra for resorufin and resazurin in H_2O, ethanol, DMSO, DMF, and acetone.

Experimental	Ethanol	DMF	Acetone	Acetone 1hr
1% H_2O	0.90 ± 0.07	0.95 ± 0.02	0.8 ± 0.2	0.7 ± 0.2
3% H_2O	0.96 ± 0.02	0.95 ± 0.01	1.7 ± 0.8	5 ± 4
5% H_2O	1.09 ± 0.04	0.94 ± 0.01	10.0 ± 0.3	6.2 ± 0.5
7% H_2O	1.35 ± 0.02	0.95 ± 0.02	11 ± 3	5 ± 1
10% H_2O	1.47 ± 0.01	0.95 ± 0.01	11 ± 1	3.7 ± 0.3

Table S1: The relative change in integrated fluorescence emission intensity of organic solvent solutions with various concentrations of water after exposure to iron for six hours (and after one hour in acetone-based solution).

Control	Ethanol	DMF	Acetone	Acetone 1hr
1% H_2O	0.96	0.98	1.03	1.02
3% H_2O	0.96	0.98	1.08	1.11
5% H_2O	0.96	1.01	1.00	1.11
7% H_2O	1.00	1.04	1.10	0.90
10% H_2O	0.96	0.95	1.20	0.98

Table S2: The relative change in integrated fluorescence emission intensity of organic solvent solutions with various concentrations of water after 6 hours with no exposure to iron (and after one hour with no exposure to iron in acetone-based solutions).

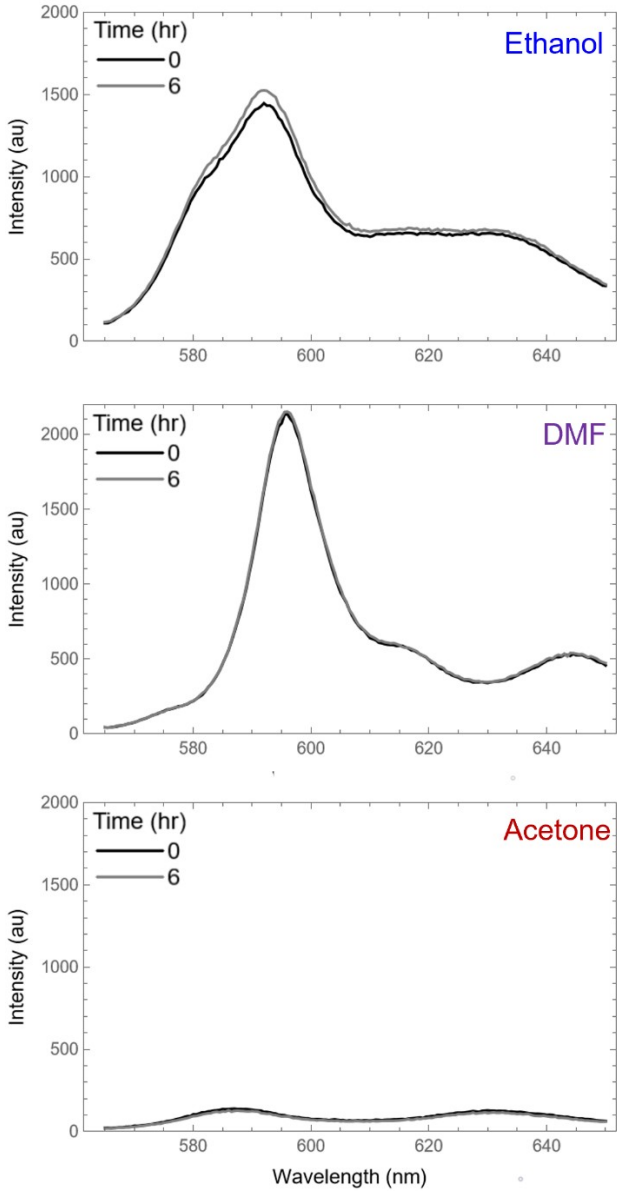

Figure S3. Representative spectra of resazurin fluorescence in organic solvent solutions before and after 6 hours with no exposure to iron. The solutions were prepared in the following manner. Stock solutions of 50 mM LiCl (98.5%; Fisher Chemical) and 100 µM resazurin for each solvent (ethanol, DMF, acetone) were used to make 10 mL sample solutions of 2 mM LiCl, 5 µM resazurin. Samples measuring 240 µL of each solution were collected and measured in spectrofluorometer shortly after mixing sample solutions together. Solutions were stored where they would be protected from light, then 240 µL of each solution was measured again six hours later.

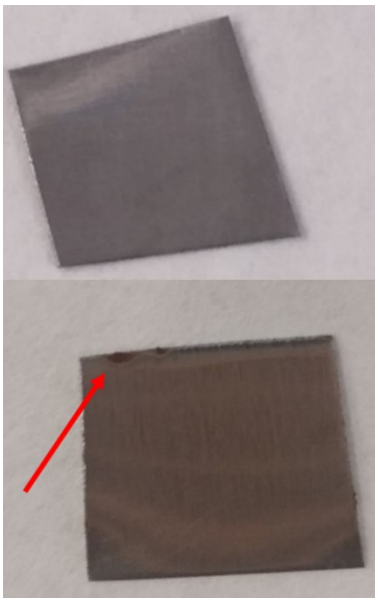

Figure S4: a109 low-carbon steel before (top) and after (bottom) five days of exposure to DMF-based corrosive solution containing 10%v H_2O. Though effects of corrosion are visible, no significant change in fluorescence emission intensity was detected in the solution. The squares are 400 mg mass before corrosion and roughly 2 x 2 cm in size.

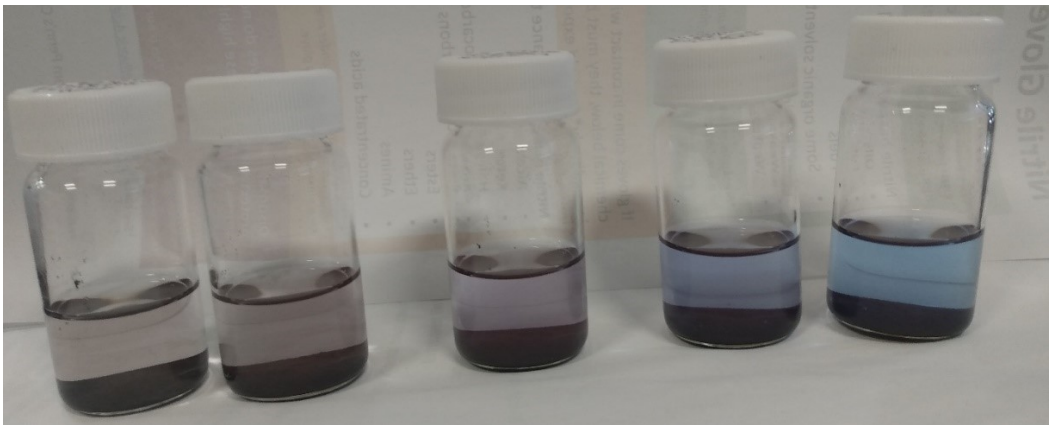

Figure S5: Acetone-based solutions containing resazurin 30 minutes after the addition of iron. From left to right, 1%, 3%, 5%, 7%, and 10% H_2O by volume. A shift in solution color from blue to pink occurs as resazurin is reduced to resorufin. A shift in solution color from pink to clear occurs as resorufin is further reduced to dihydroresorufin.

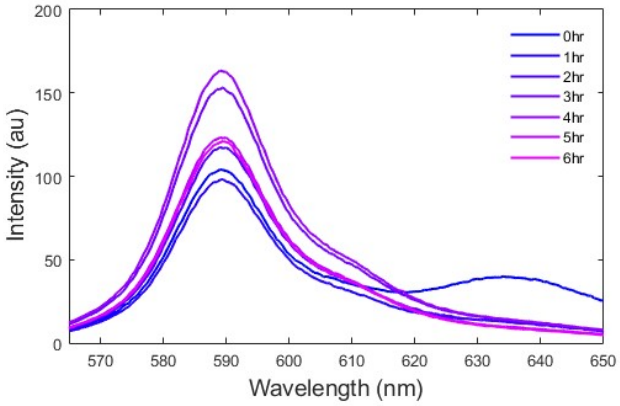

Figure S6: Fluorescence emission spectra for acetone-based solution containing resazurin and 1% v/v H_2O after exposure to iron. The distinctive, but low intensity single peak attributed to resorufin can be seen after 0 hr indicates a reduction of resazurin to resorufin, followed by the further reduction of resorufin to dihydroresorufin. The reduction from resorufin to dihydroresorufin is reversible, resulting in a small concentration of resorufin remaining in the solution.

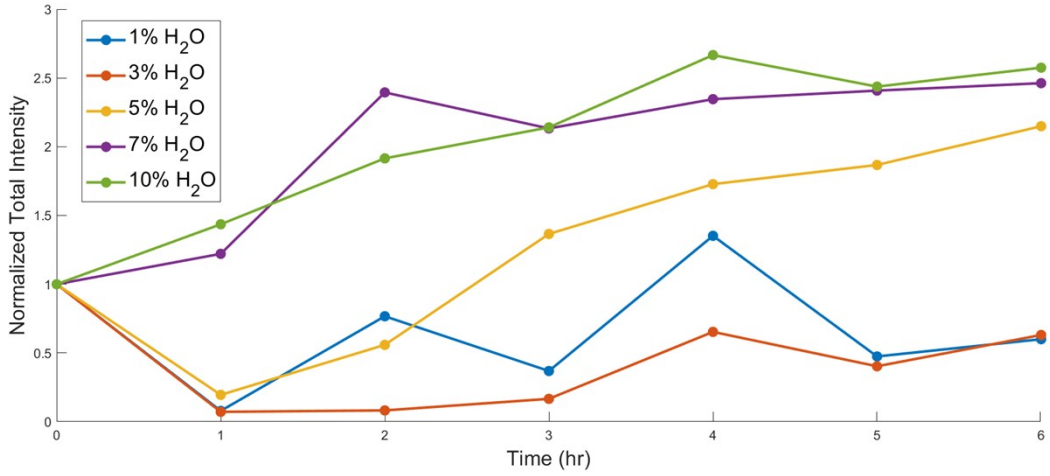

Figure S7: Normalized integrated fluorescence intensity over time for DMSO-based solutions containing 50 µM resazurin and 1%, 3%, 5%, 7%, and 10% H_2O by volume after being introduced to iron. Because of supply chain issues and the fast degradation rate of DMSO upon exposure to air we have been unable to collect replicate data.

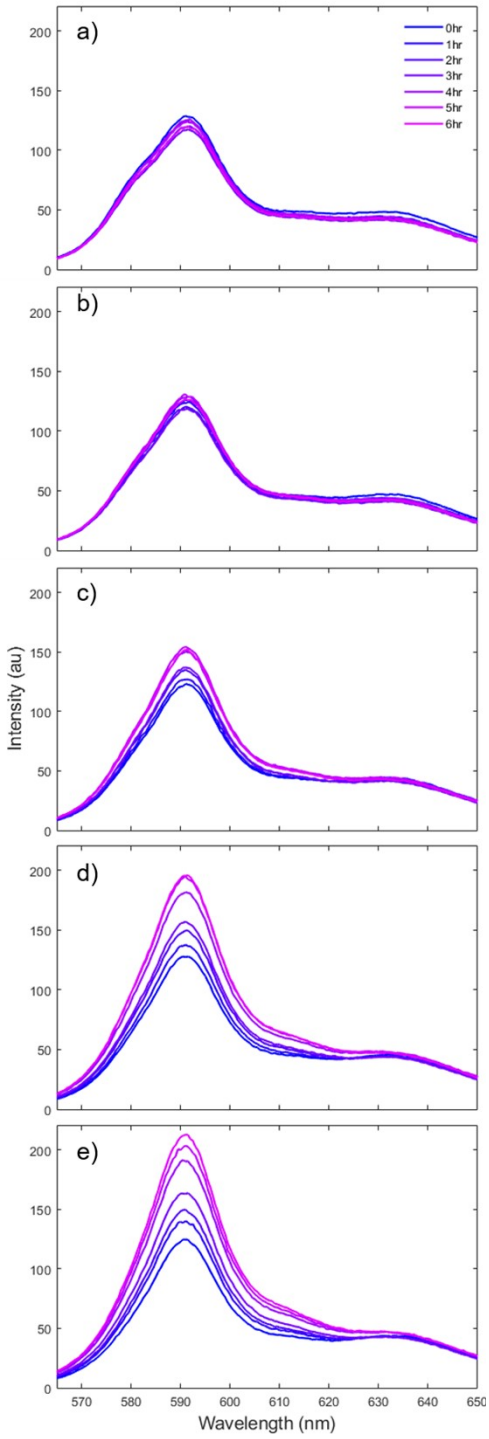

Figure S8: Fluorescence emission spectra for ethanol-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume after being introduced to iron.

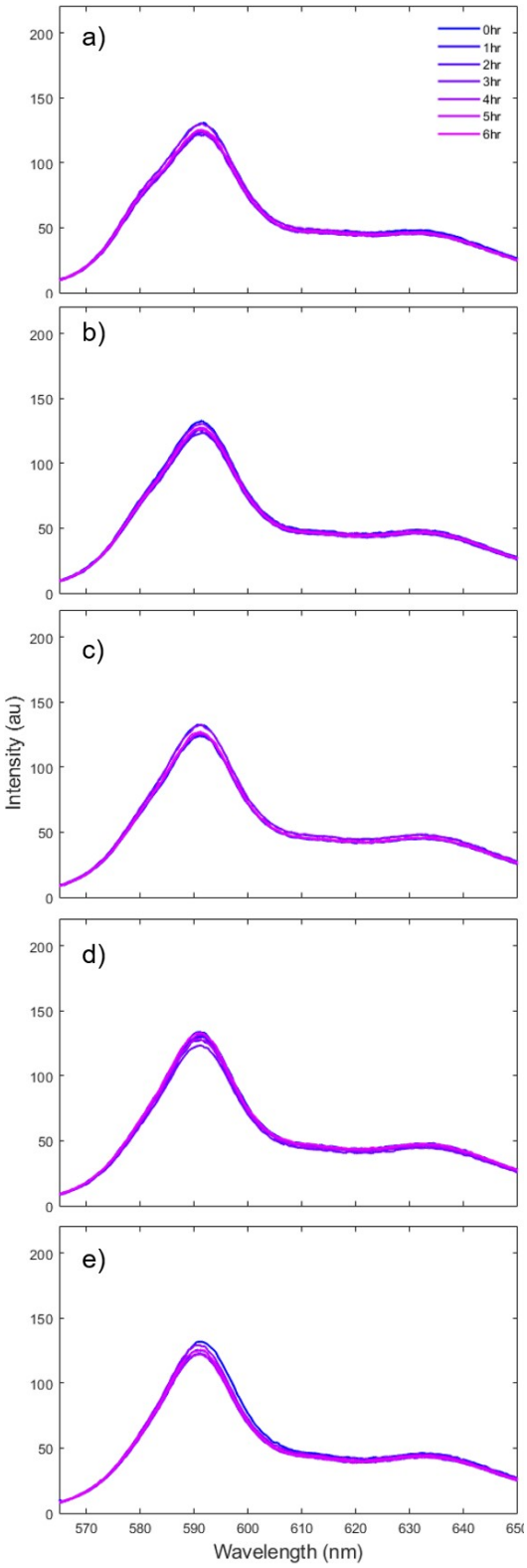

Figure S9: Fluorescence emission spectra for ethanol-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume.

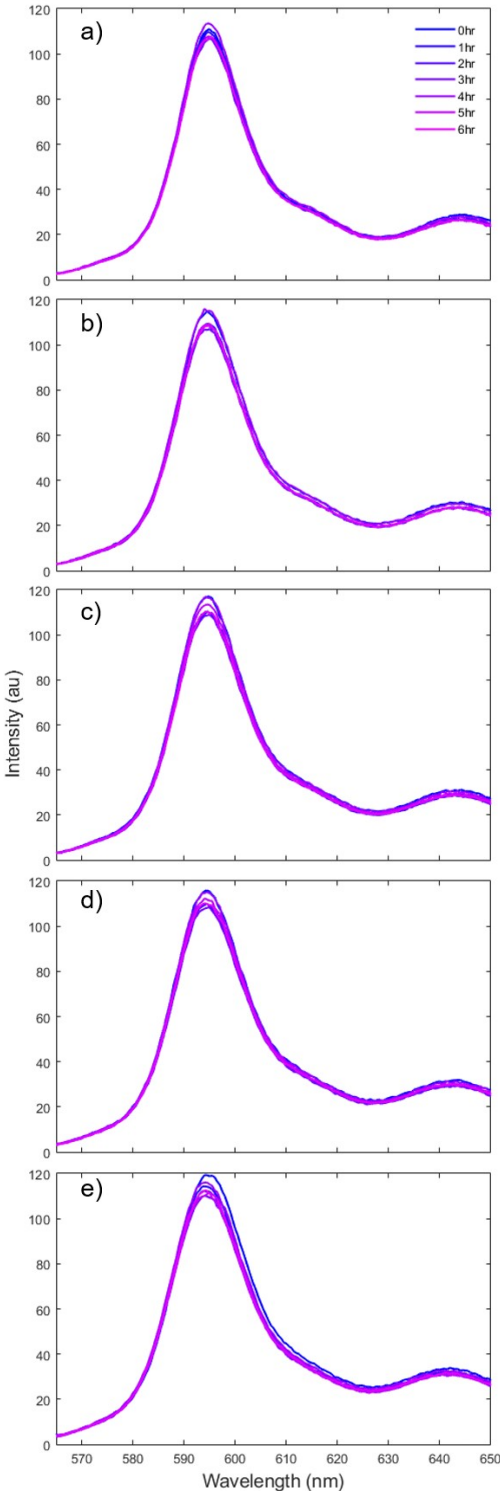

Figure S10: Fluorescence emission spectra for DMF-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume after being introduced to iron.

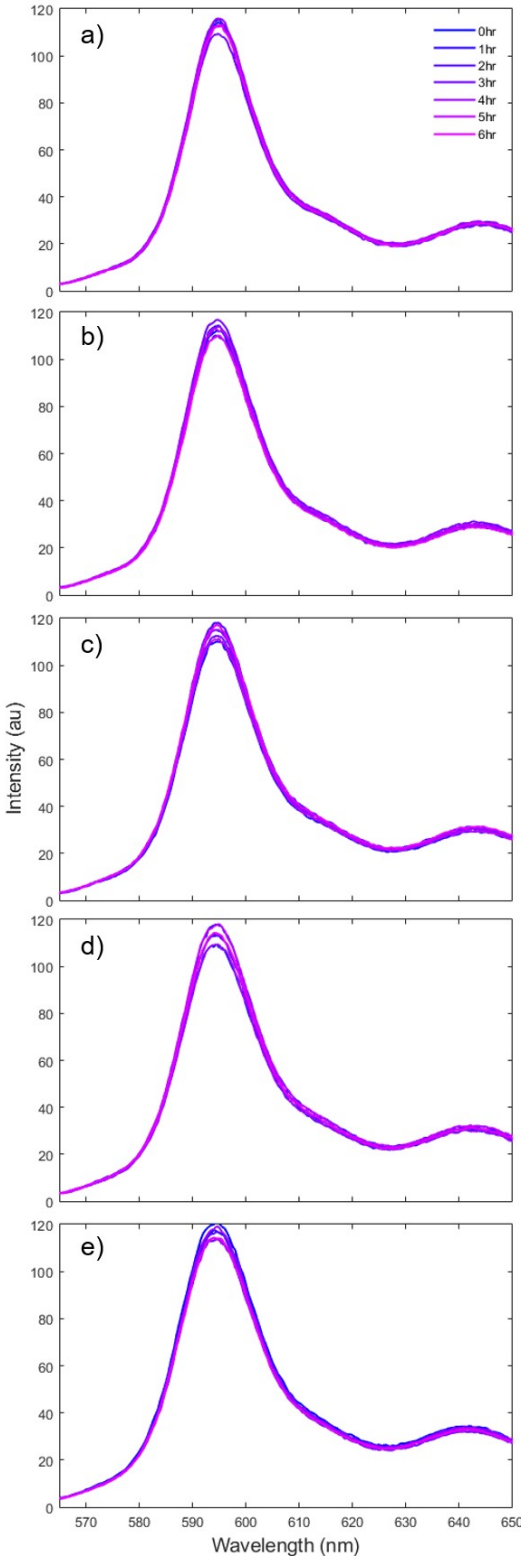

Figure S11: Fluorescence emission spectra for DMF-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume.

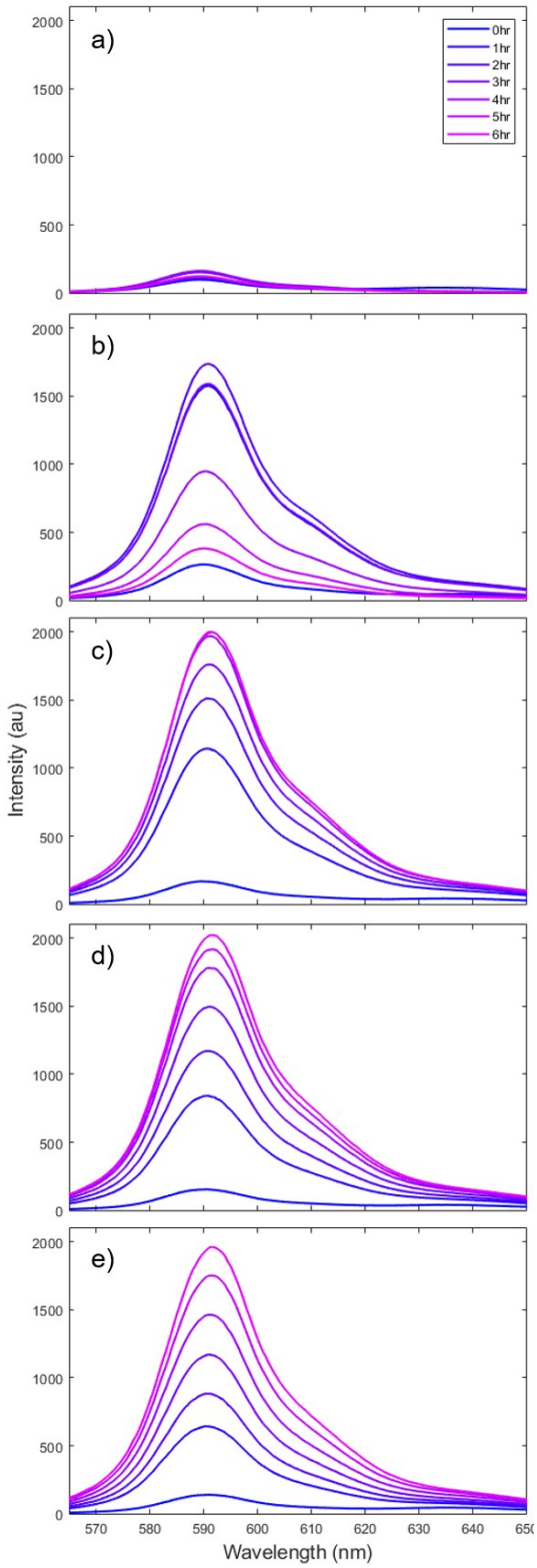

Figure S12: Fluorescence emission spectra for acetone-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume after being introduced to iron.

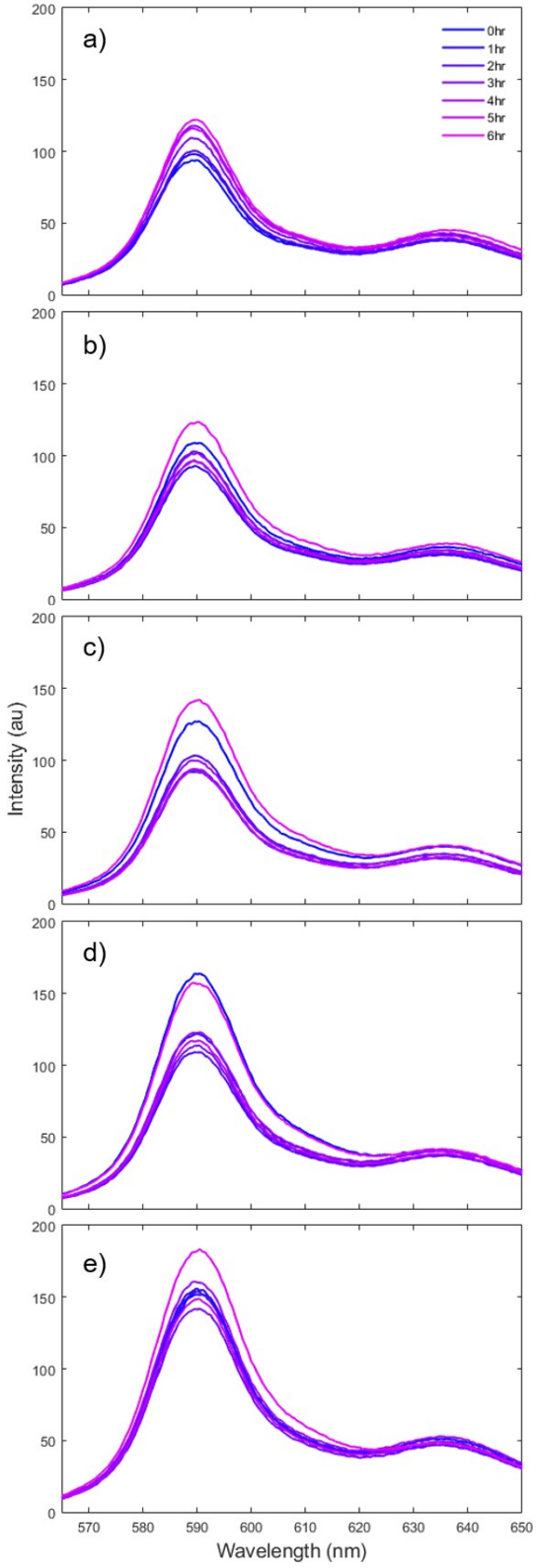

Figure S13: Fluorescence emission spectra for acetone-based solutions containing resazurin and a) 1%, b) 3%, c) 5%, d) 7%, and e) 10% H_2O by volume.

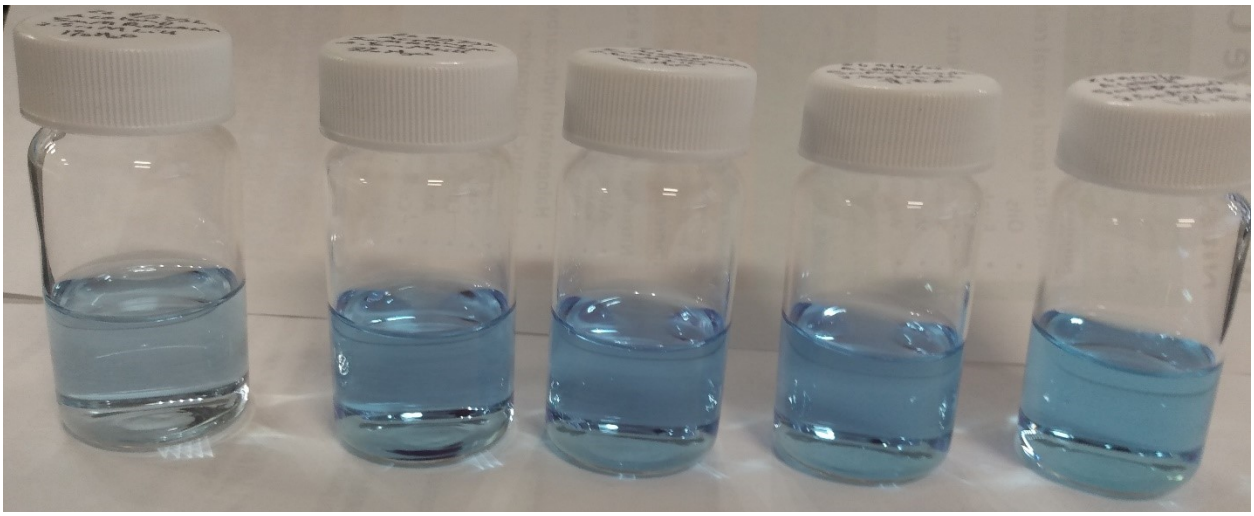

Figure S14: Acetone-based solutions containing resazurin before the addition of iron. From left to right, 1%, 3%, 5%, 7%, and 10% H_2O by volume.

Reaction	Half potential (E° vs. Ag/AgCl)
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$	+0.402 V
Resazurin + $2e^-$ ⟶ resorufin	−0.47 V [ref 1]
Resorufin + $2e^-$ ⟶ dihydroresorufin	−0.56 V [ref 1]

Table S3. Half reaction potentials for relevant reactions.

[1] J. Lu, Y. Fan, M. D. Howard, J. C. Vaughan and B. Zhang, *Journal of the American Chemical Society*, 2017, **139**, 2964–2971.