Supporting Information

D Europium-Based Optical Sensor for the Detection of Carbon Dioxide and Its Application for a Fermentation Reaction

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Single crystal X-ray data for investigated compound was collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source as well as a low-temperature Oxford Cryostream 800 liquid nitrogen cooling system at 100(2) K. Data collection strategy was calculated within CrysAlisPro (1.171.40.12b; Rigaku Oxford Diffraction, 2018) to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structure was solved using ShelXT[1], all non-hydrogen atoms were refined anisotropically using ShelXL[2] and space group was unambiguously verified by PLATON[3]. All hydrogen atoms were attached via the riding model at calculated positions. The large (2.56 $eÅ^{-3}$) residual electron density located close to the europium atom (0.94 Å) is attributed to imperfect absorption corrections frequently encountered in heavy-metal atom structures. Olex2[4] was used for the preparation of the publication materials.

Table S1: Crystal structure data for the K [$Eu(hfa)_4$] complex.

Empirical Formula	$C_{20}H_4EuF_{24}KO_8$
Formula Weight	1019.29
Temperature (K)	100
Crystal System	Triclinic
Space group	*P-1*
a (Å)	11.8320(3)
b (Å)	12.1224(2)
c (Å)	13.3146(3)
α (°)	73.434(2)
β (°)	65.661(2
γ (°)	64.528(2)
Volume ($Å^3$)	1557.31(7)
Z	2
Density calculated (g/mL)	2.174
Absorption coefficient (mm^{-1})	2.335
2θmax (°)	25.679
Reflections Collected	21379
Independent Reflections	5917 [R(int) = 0.0382]
Absorption Correction	Semi-empirical from equivalents
Goodness-of-Fit on F^2	1.066
Final R Indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0914
R Indices (all data)	R1 = 0.0400, wR2 = 0.0931
Largest Diff. Peak and Hole	2.535 and -1.002 $e.Å^{-3}$

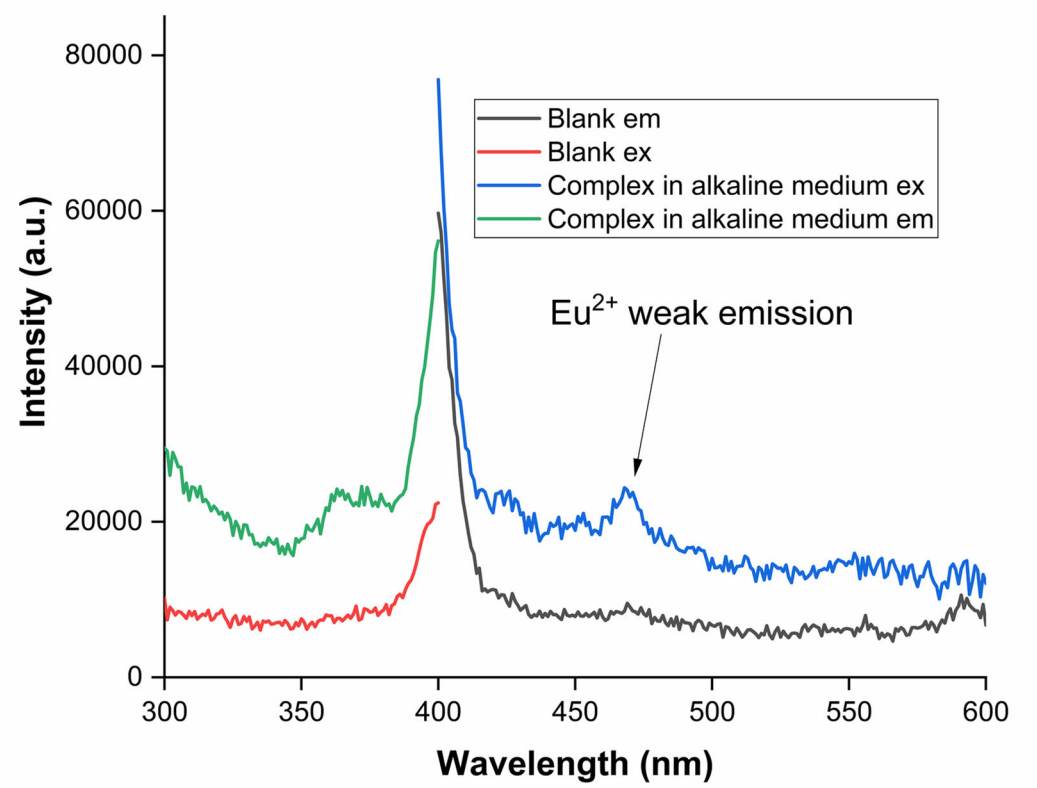


Figure S1: PL spectra of K[Eu(hfa)4] in alkaline medium (pH 8). Blank sample consist of methanol and PSS base. Sensor sample consists of methanol, PSS base and $K[Eu(hfa)_4]$. Graph shows the weak Eu^{2+} peak at 468nm.

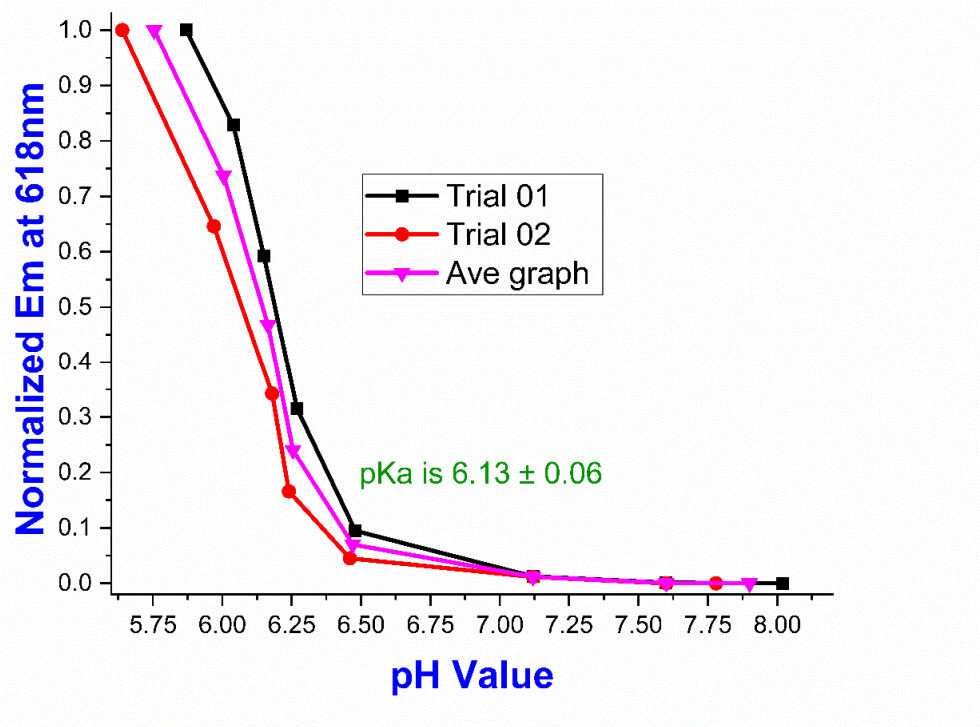


Figure S2: pKa determination of the complex K[Eu(hfa)4]in under constant μ =0.01 M of NH_4OH in Ethylene glycol/H_2O. pKa was determined by taking 0.5 Normalized data point.

Table S2: pKa calculations. pKa was determined by taking 0.5 Normalized data point.

trial 01 (pKa)	6.07008664
trial 02 (pKa)	6.1856817
AVE pKa	6.12788417
SD	0.05779753

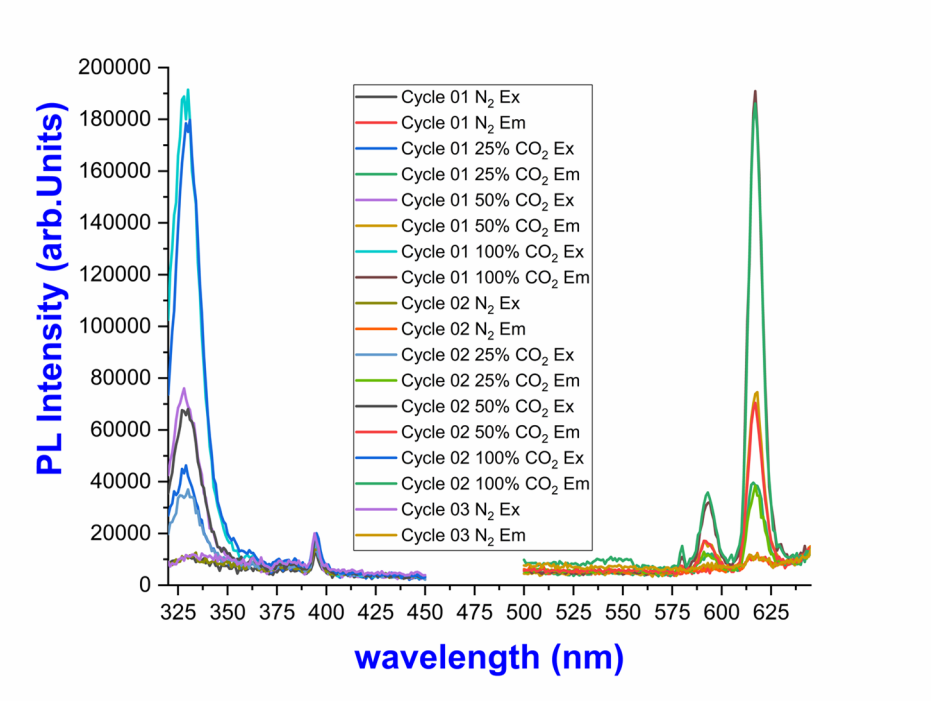


Figure S3a: Effect of Solvents towards CO_2 sensing in 100% MeOH

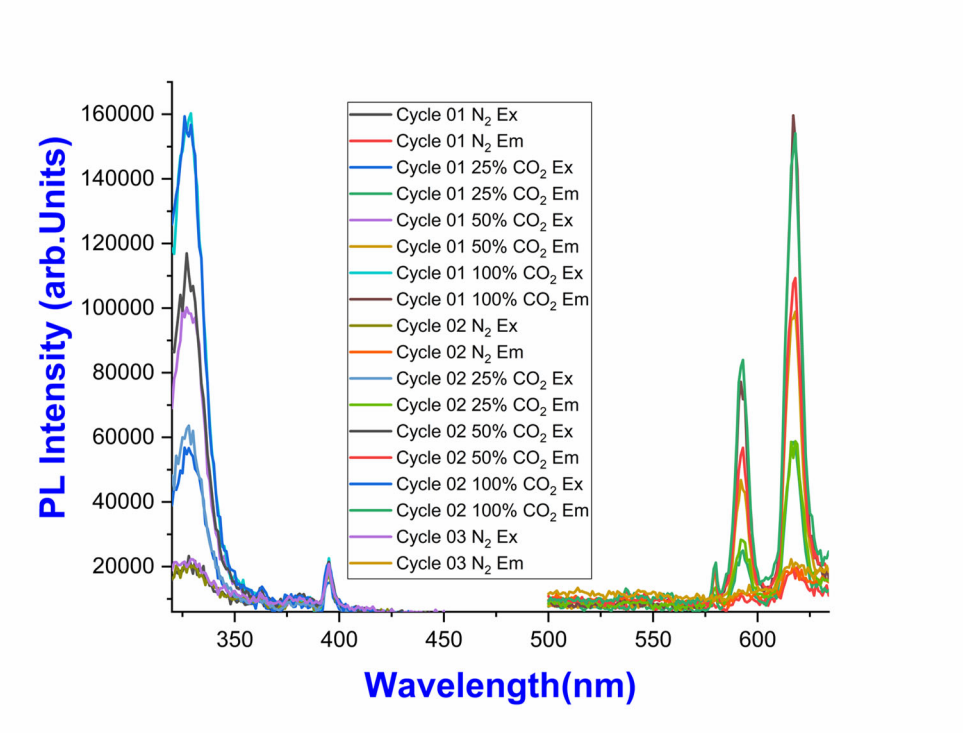


Figure S3b: Effect of Solvents towards CO_2 sensing 50:50 MeOH: H_2O

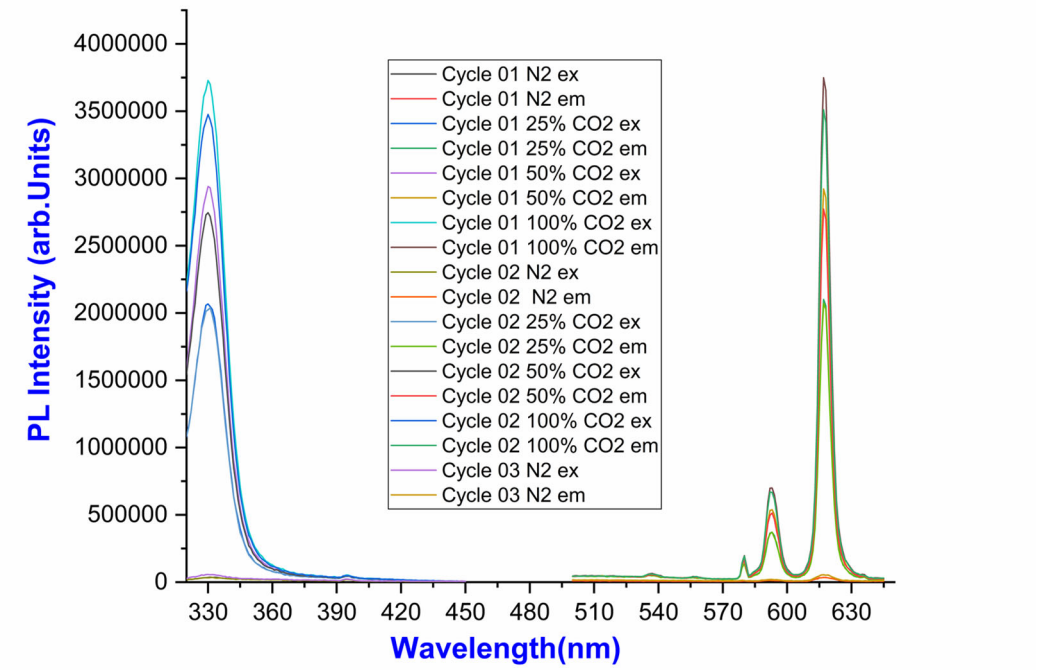


Figure S3c: Effect of Solvents towards CO_2 sensing 100% ethylene Glycol.

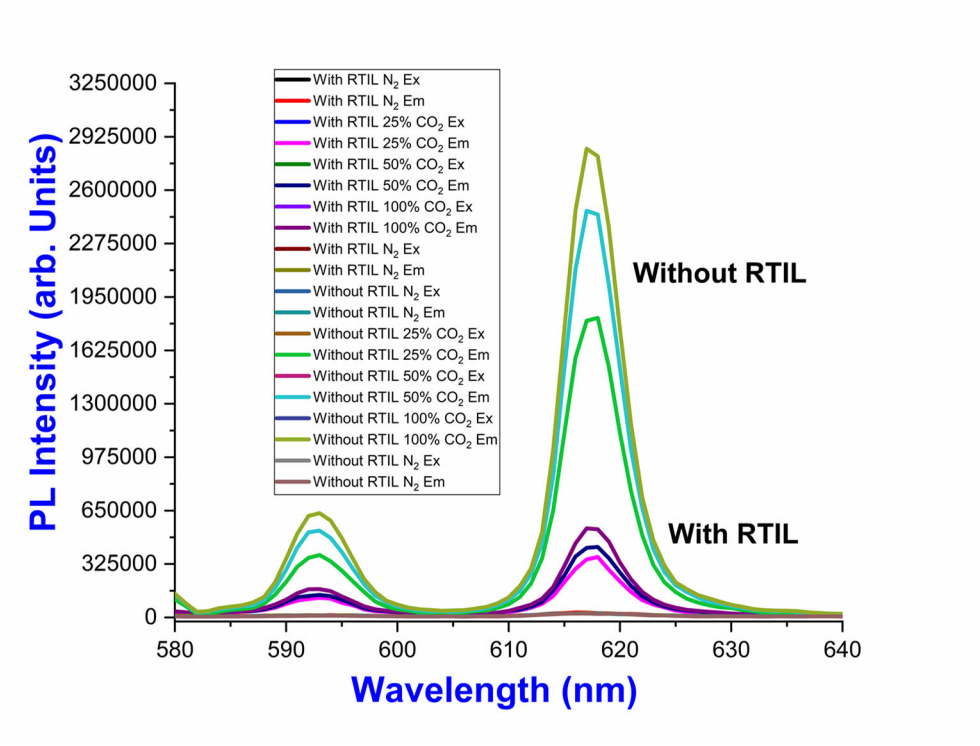


Figure S4: Effect of RTIL [1-butyl-3-methylimidazolium tetrafluoroborate (1B3MIMBF4)] in solution phase study for CO_2 sensitivity.

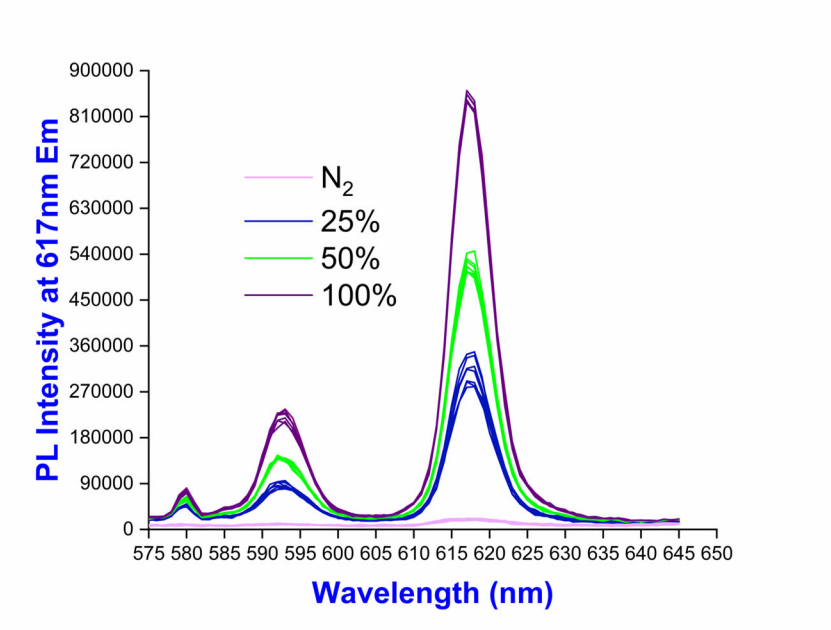


Figure S5: Fluorescence intensity of K[Eu(hfa)4] in ethylene glycol medium- Seven consecutive cycles. One Cycle sequence as follows: N_2, 25% CO_2, 50%CO_2 and 100%CO_2.

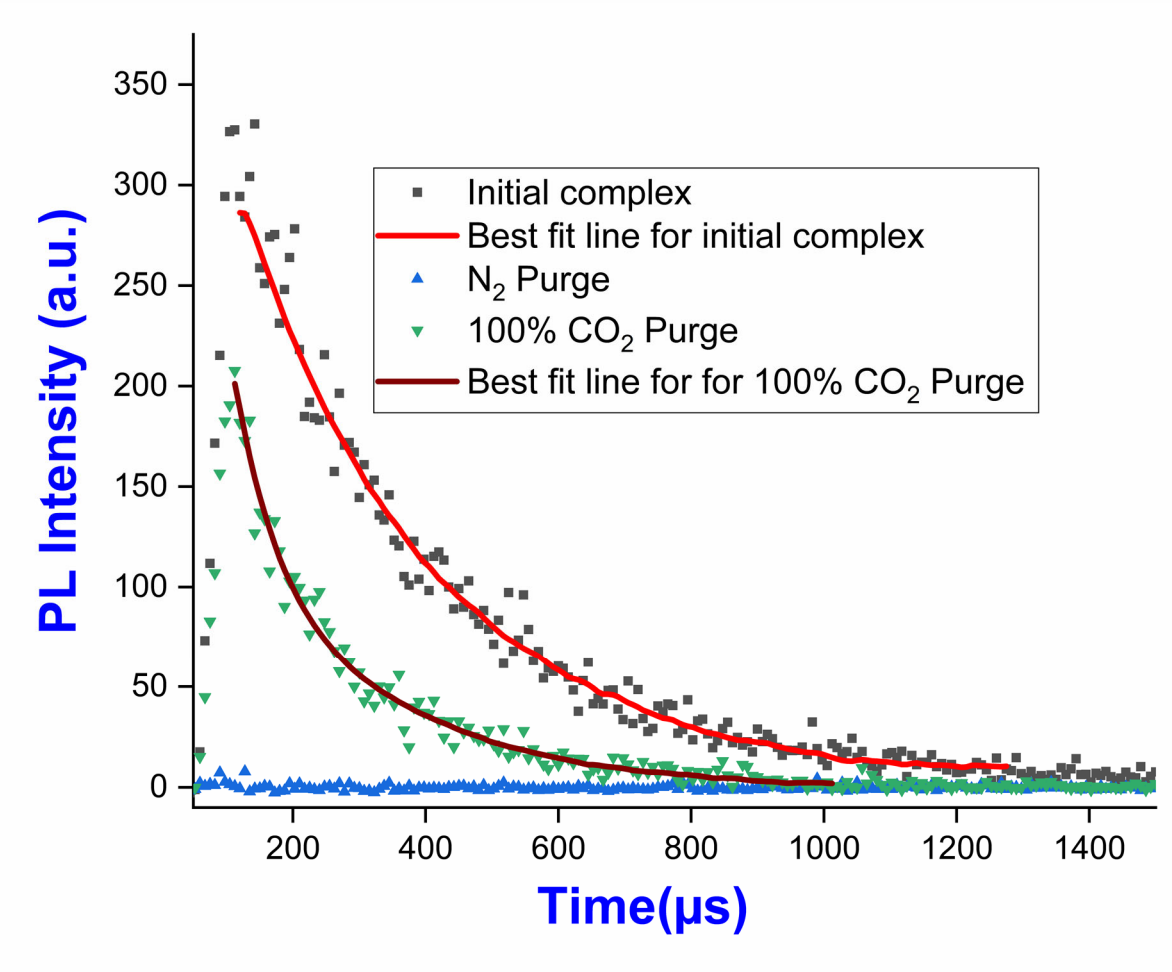


Figure S6: Emission lifetime data of K[Eu(hfa)4] for initial complex, after base/ N_2 purge and 100% CO_2 purge.

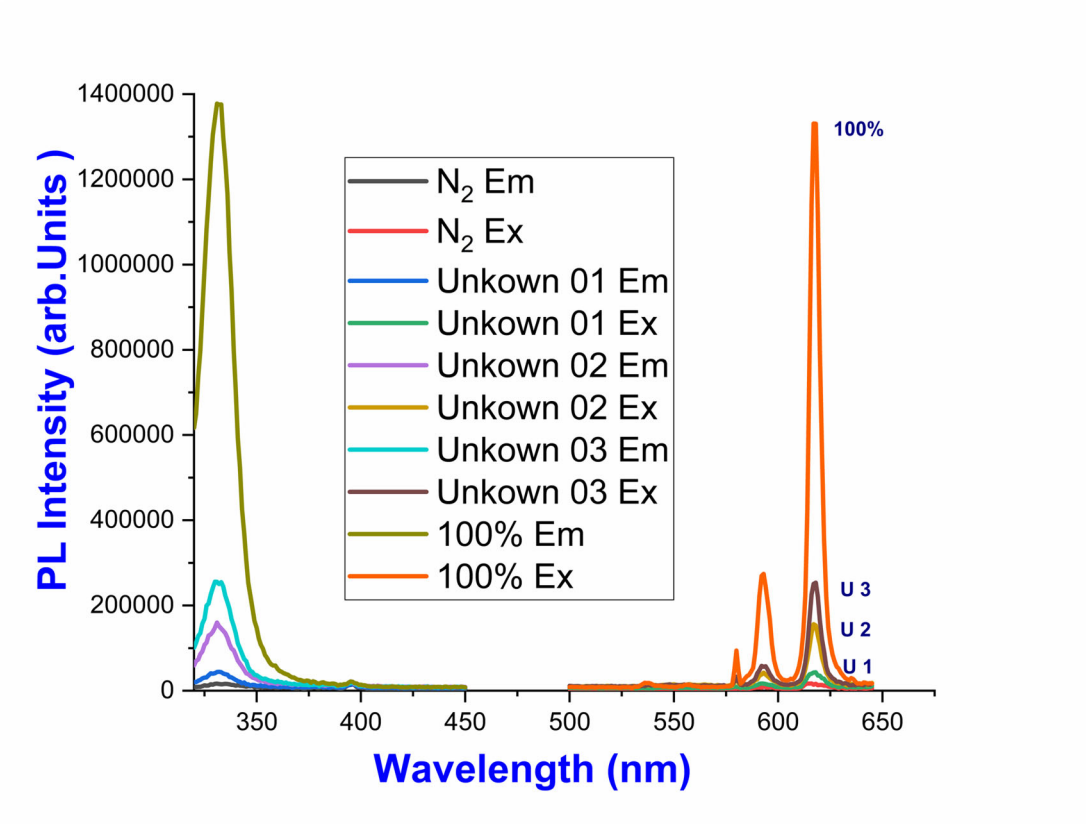


Figure S7: Fluorescence intensity of the sensor at unknown concentrations of gases.

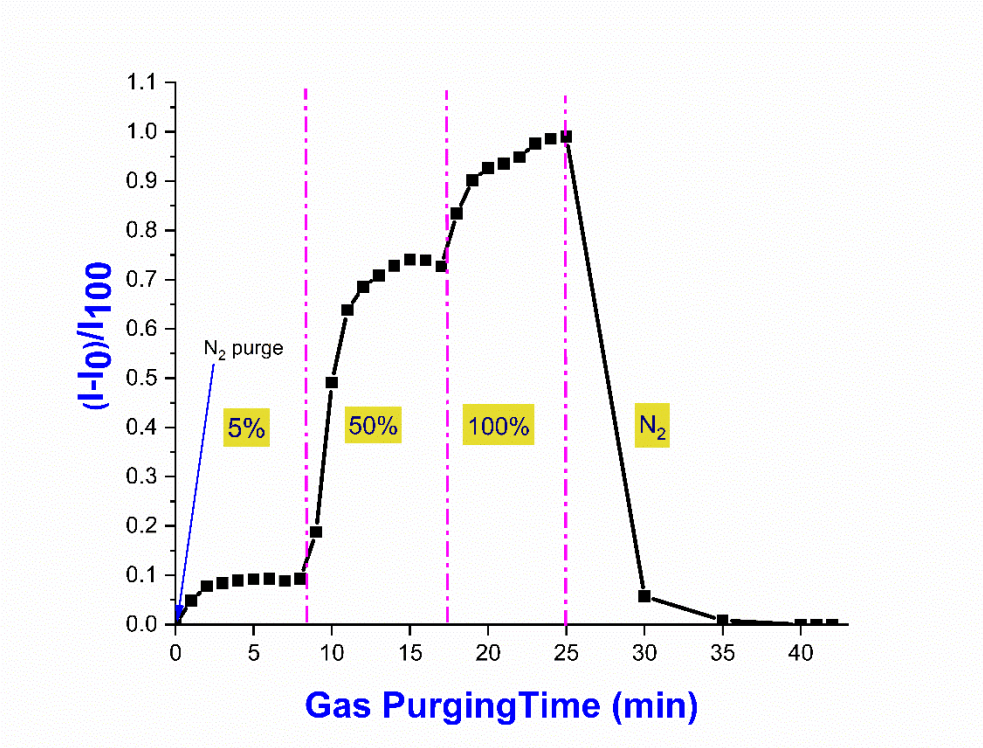


Figure S8: Response time of sensor switching between different concentrations of CO_2 gas.

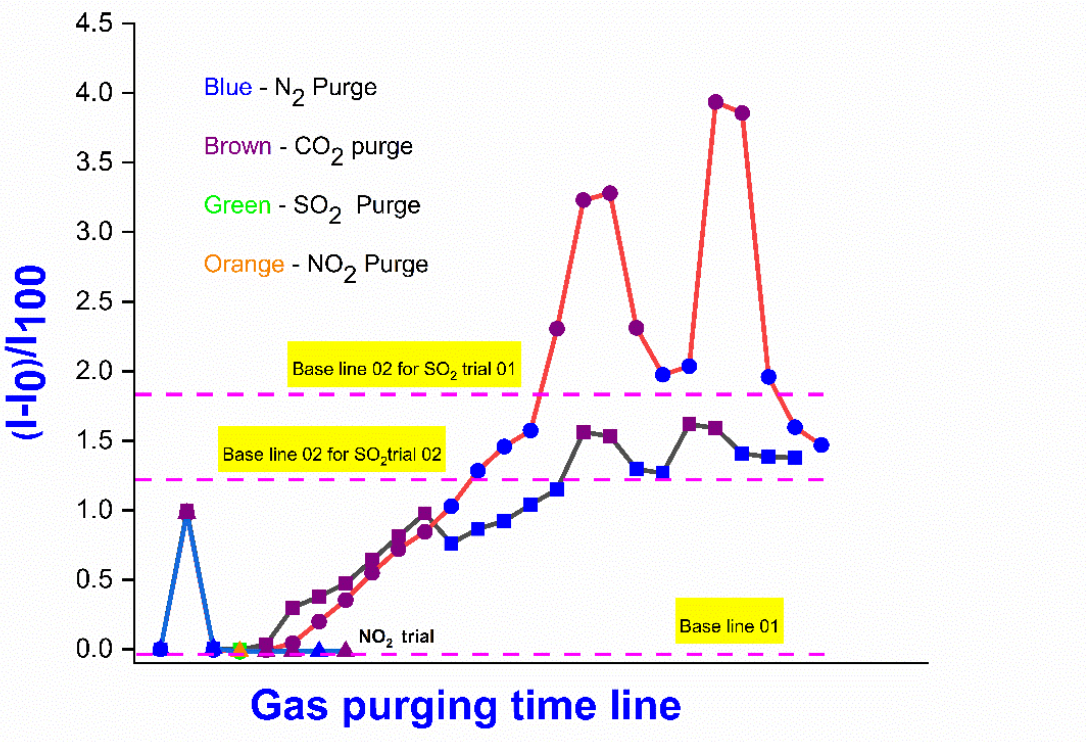


Figure S9: Fluorescence intensity of the sensor on purging with SO_2 and NO_2 gas to understand the interference.

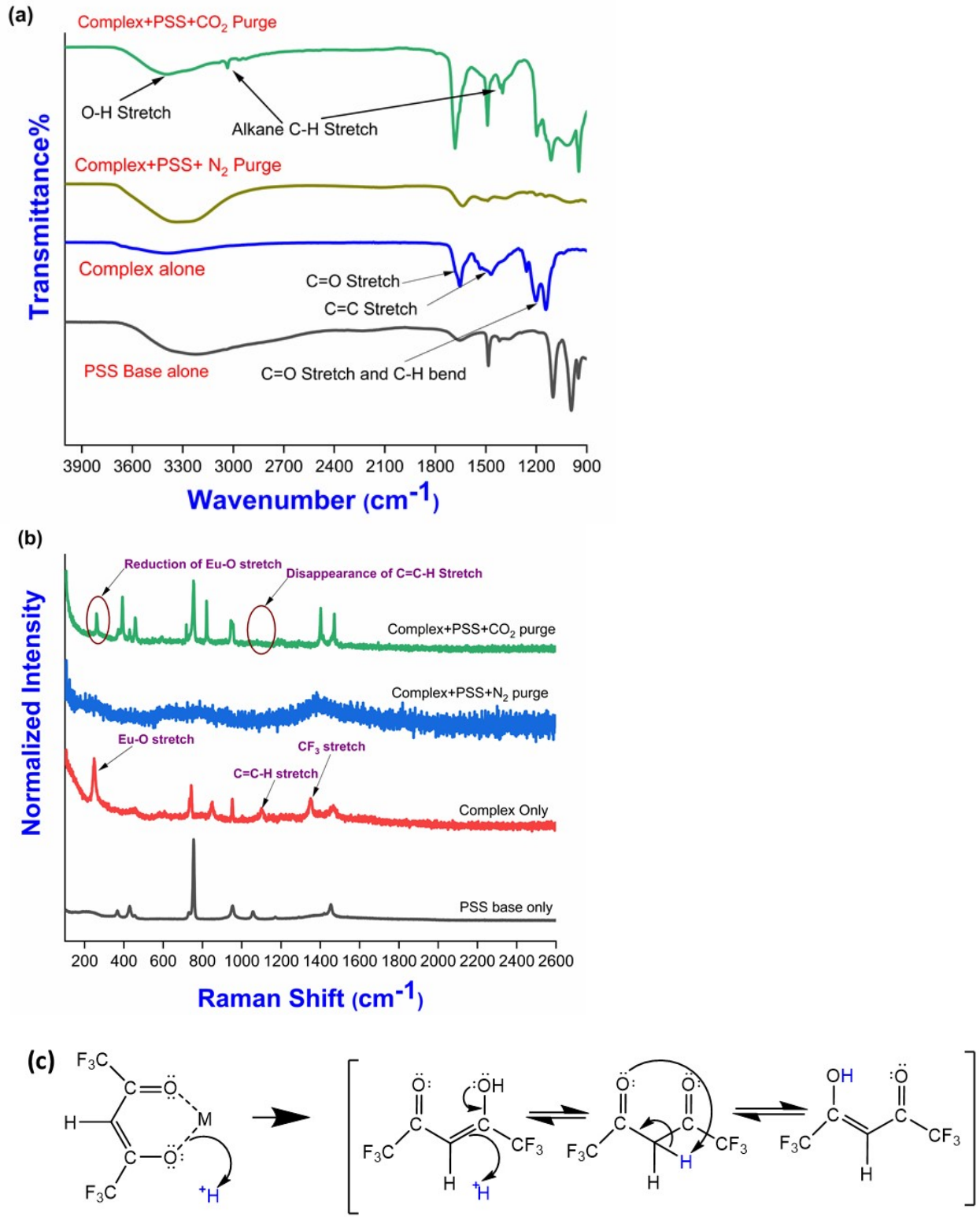


Figure S10: K[Eu(hfa)$_4$] sensor was subjected 100% CO_2 purging and prepared solid sample for testing. (a) FTIR (b) Raman Spectroscopy was taken from the same solid samples (c) Schematic of enol formation of hfa ligands. FTIR and Raman spectroscopy of PSS (base) were included to identify the matrix influence on spectra.

Table S3a: Fluorescence intensities of three consecutive cycles of CO_2 purge (1%, 5%,10%, 25%, 50%,100%)

	[CO_2%]	I_0	I	I/I_0
	0	19491.2	19491.2	1
	1	19491.2	35410.9	1.816764
	5	19491.2	142505.1	7.311256
	10	19491.2	257637.5	13.21815
	25	19491.2	653727.4	33.53963
	50	19491.2	1031532	52.92297
Cy 1	100	19491.2	1489809	76.43495
Cy2	0	17518.89	17518.89	1
	1	17518.89	45313.57	2.586554
	5	17518.89	150879.4	8.612384
	10	17518.89	257224.5	14.68269
	25	17518.89	646551.5	36.90595
	50	17518.89	1051304	60.00969
	100	17518.89	1496022	85.39477
	0	19379.7	19379.7	1
	1	19379.7	42660.98	2.201323
	5	19379.7	146686.9	7.5691
	10	19379.7	280531.9	14.47555
	25	19379.7	676368.6	34.90088
	50	19379.7	1056604	54.52117
Cy 3	100	19379.7	1531647	79.03355
Cy 4	0	23105.01	23105.01	1

Table S3b: CO_2% calculations for three consecutive cycles.

CO_2 %	Ave Intensity	Standard Deviation.
0-1%	2.2	0.31
0-5%	7.83	0.56
0-10%	14.13	0.65
0-25%	35.12	1.38
0-50%	55.82	3.03
0-100%	80.39	3.65

Table S4: Emission lifetime data for initial complex, N2 Purge and 100% CO_2 purge.

	Lifetime data
Initial complex	303.3 ± 0.2209 (100%) Chi2:0.9056 Durbin Watson: 1.663 Z=0.001563
After base/N_2 purge	0
After 100% CO_2 purge	Lifetime 1: 260.6 ± 0.3026 (46.64%) Lifetime 2: 56.1 ± 0.3282 (53.36%) Chi2:0.9432 Durbin Watson: 2.035 Z=0.04991

Table S5: LOD calculations using Residual standard deviation method.

CO_2 %	Ave	Residual=Y res	Y-Yres	$(Y-Yres)^2$	Ave $(I-I_0)/I_{100}$= Y
	$(I-I_0)/I_{100}$ = Y				
0	0	-0.002	0.002	0.000004	0
1	0.014821651	0.015	-0.00018	3.18E-08	0.014821651
5	0.084943849	0.083	0.001944	3.78E-06	0.084943849
10	0.163527684	0.168	-0.00447	2.00E-05	0.163527684
25	0.425043126	0.423	0.002043	4.17E-06	0.425043126

Residual SD	0.003265
Slop	0.017
LOD	0.57

Table S6a: $I\text{-}I_0/I_{100}$ Vs $[CO_2\%]$ calculations

	$[CO_2\%]$	I_0	I	I-Io	$I\text{-}I_0/I$	$(I\text{-}I_0)/I_{100}$
	0	19491.2	19491.2	0	0	0
	1	19491.2	35410.9	15919.71	0.449571	0.010685737
	5	19491.2	142505.1	123013.9	0.863225	0.082570269
	10	19491.2	257637.5	238146.4	0.924346	0.159850257
	25	19491.2	653727.4	634236.2	0.970185	0.42571648
	50	19491.2	1031532	1012041	0.981105	0.679309015
Cy 1	100	19491.2	1489809	1470317	0.986917	0.986916648
Cy2	0	17518.89	17518.89	0	0	0
	1	17518.89	45313.57	27794.68	0.613385	0.018579055
	5	17518.89	150879.4	133360.5	0.883888	0.089143437
	10	17518.89	257224.5	239705.6	0.931893	0.160228643
	25	17518.89	646551.5	629032.6	0.972904	0.420470157
	50	17518.89	1051304	1033785	0.983336	0.691022328
	100	17518.89	1496022	1478503	0.98829	0.988289601
	0	19379.7	19379.7	0	0	0
	1	19379.7	42660.98	23281.28	0.545728	0.01520016
	5	19379.7	146686.9	127307.2	0.867884	0.08311784
	10	19379.7	280531.9	261152.2	0.930918	0.170504153
	25	19379.7	676368.6	656988.9	0.971347	0.428942741
	50	19379.7	1056604	1037224	0.981659	0.677195397
Cy 3	100	19379.7	1531647	1512267	0.987347	0.987346907
Cy 4	0	23105.01	23105.01	0	0	0

Table S6b: $I\text{-}I_0/I_{100}$ Vs $[CO_2\%]$ average and standard deviation calculations

CO_2 %	Ave $(I\text{-}I_0)/I_{100}$	SD
0	0	0
1	0.014821651	0.003234
5	0.084943849	0.002978
10	0.163527684	0.004936
25	0.425043126	0.003492
50	0.682508914	0.006081
100	0.987517719	0.000573

Table S7: CO_2 Probe Validation with Carbon dioxide Cylinders.

CO_2% in Cylinder	Reading on the Probe	Pictures of the CO_2 reading
1%	1%	
25%	26.16%	
50%	52.31%	
100%	100%	

Table S8: Fermentation trial 1 data Pictures from the CO_2 Probe on sugar in respective time intervals.

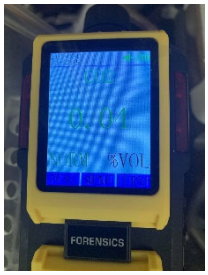
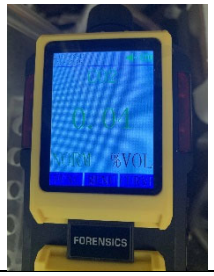
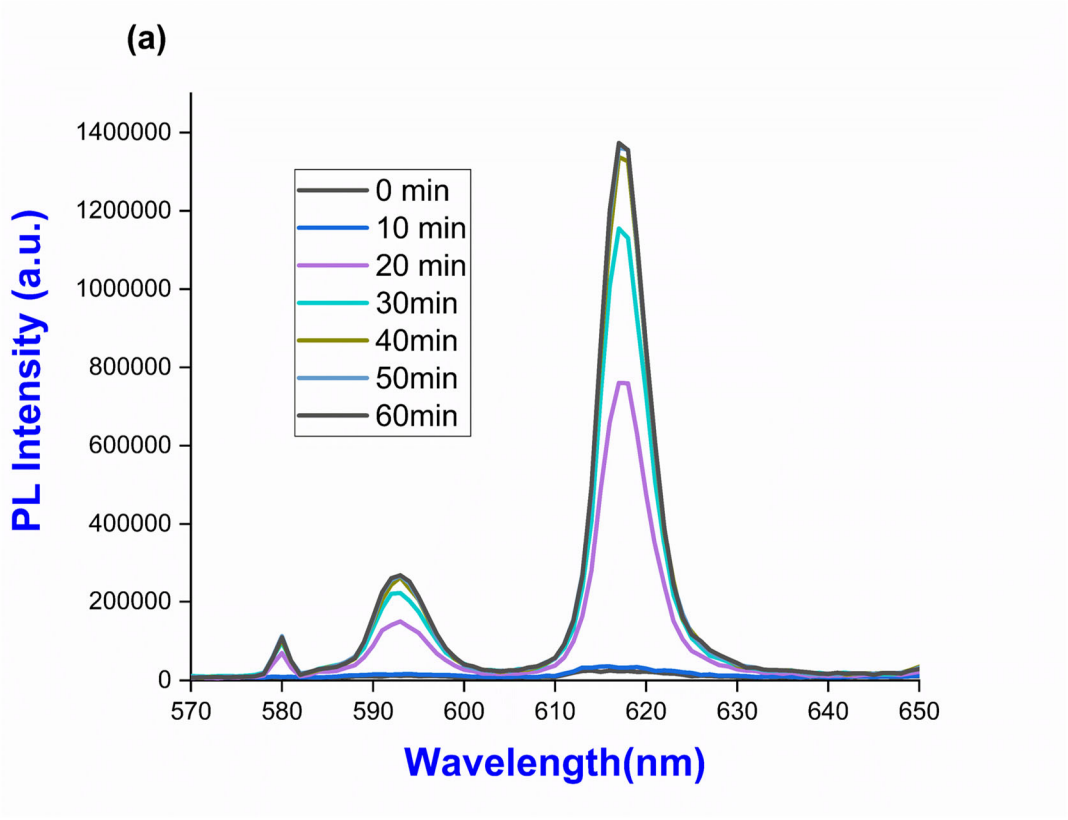
Time (Min)	Pictures	Time (Min)	Pictures
0 min		10 min	
20 min		30 min	
40 min		50 min	
60 min			

Table S9: Fermentation trial 2 data Pictures from the CO_2 Probe on sugar in respective time intervals.

Time (Min)	Pictures	Time (Min)	Pictures
0 min		10 min	
20 min		30 min	
40 min		50 min	
60 min			



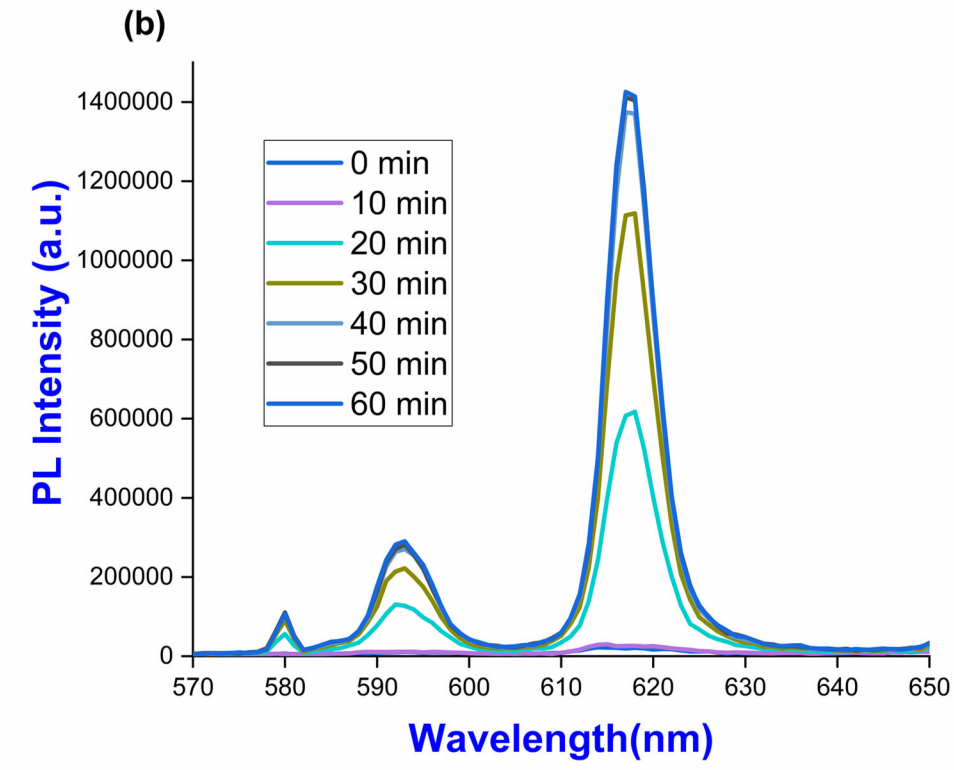


Figure S11: Fermentation experiments conducted with 0.93M sugar concentration and 2.5g of yeast for one hour. The readings were taken after every 10 min. (a) trial 01 (b) trial 02

Reference

1. Sheldrick, G.M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. A Found. Adv.* **2015**, *71*, 3–8.
2. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2014**, *71*, 3–8.
3. Spek, A.L. Structure validation in chemical crystallography. *Acta Crystallogr. Sect. D Biol. Crystallogr.* **2009**, *65*, 148–155, https://doi.org/10.1107/s090744490804362x.
4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J; Howard, J.A.K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.