Pyridyl CO_2 Fixation Enabled by a Secondary Hydrogen Bonding Coordination Sphere

Jacqueline N. Gayton,[a,] Qing Li,[a] Lakeeta Sanders,[b] Roberta R. Rodrigues,[a] Glake Hill,[b] and Jared H. Delcamp[a,]*

[a] Department of Chemistry and Biochemistry, University of Mississippi, University, MS, 38677

[b] Department of Chemistry, Jackson State University, Jackson, MS, 39217

* email: delcamp@olemiss.edu

Table of Contents

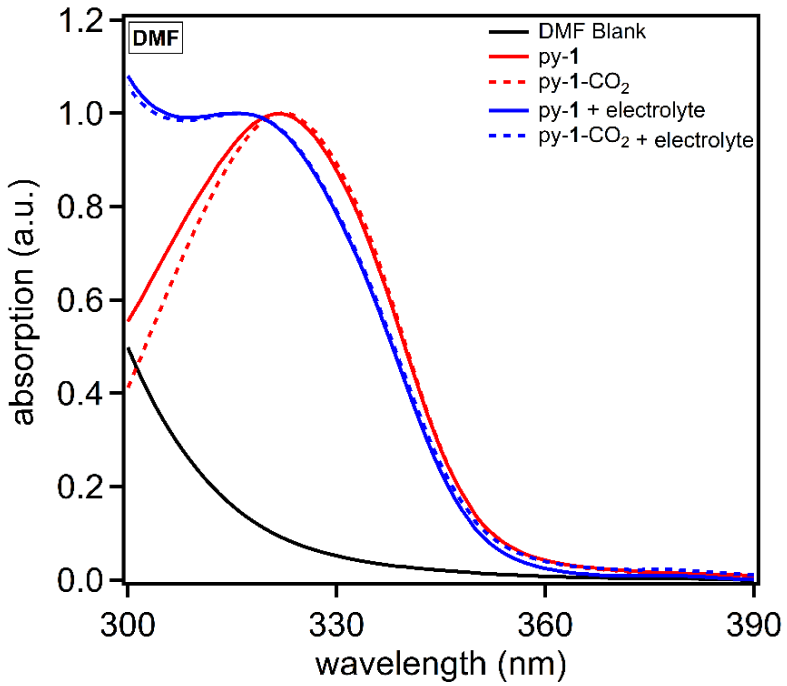

Figure S1. Absorption spectrum of py-**1** in DMF with and without electrolyte with the absorption curve peaks normalized.

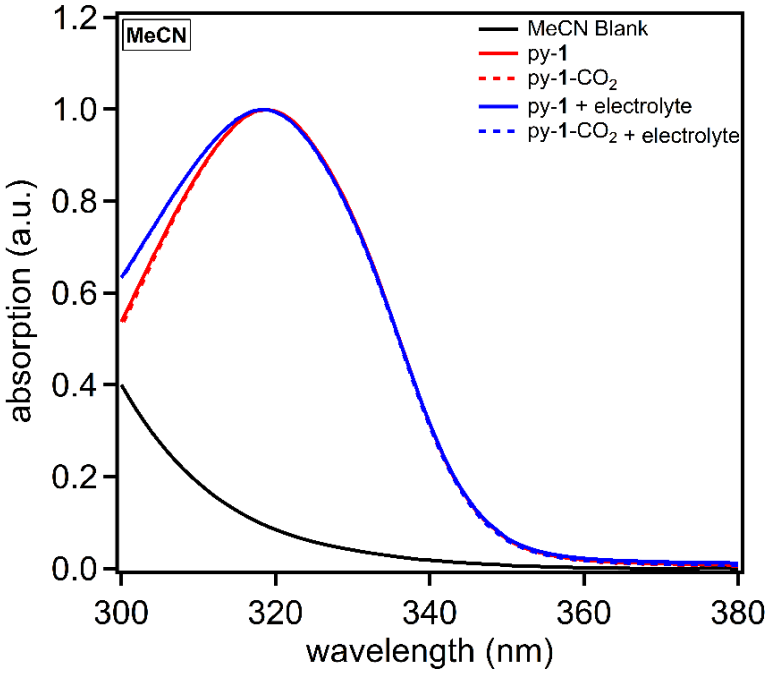

Figure S2. Absorption spectrum of py-**1** in MeCN with and without electrolyte with the absorption curve peaks normalized.

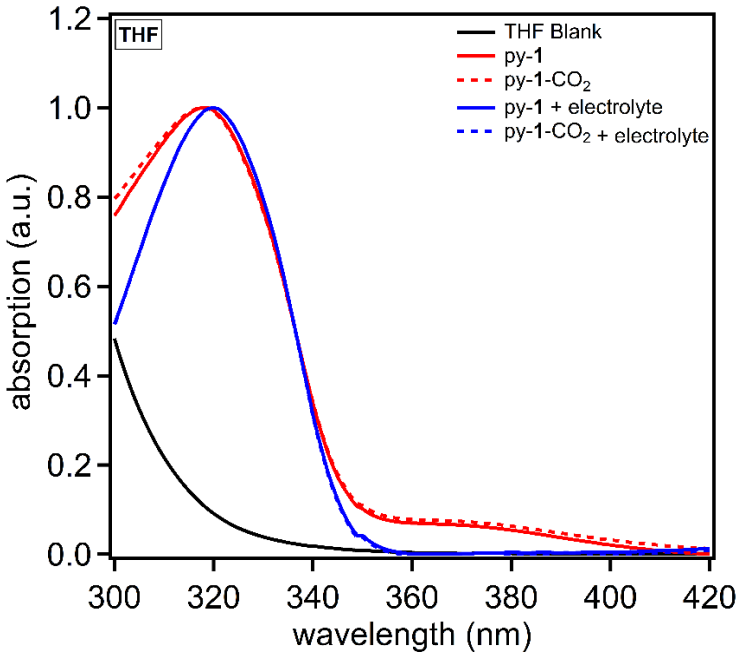

Figure S3. Absorption spectrum of py-**1** in THF with and without electrolyte with the absorption curve peaks normalized.

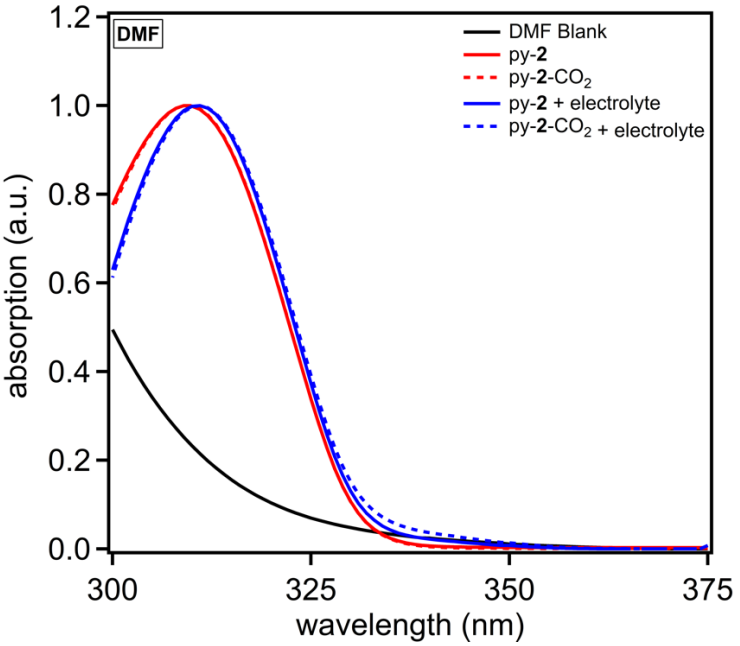

Figure S4. Absorption spectrum of py-**2** in DMF with and without electrolyte with the absorption curve peaks normalized.

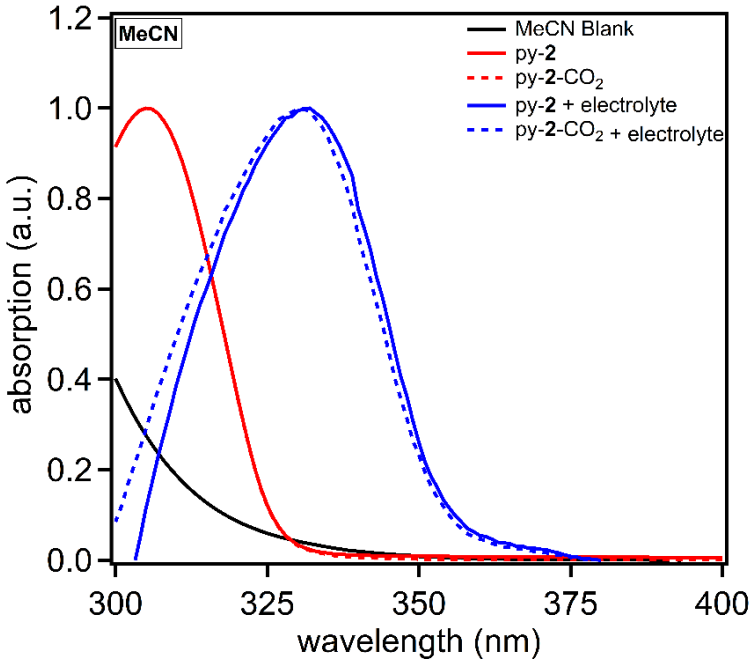

Figure S5. Absorption spectrum of py-**2** in MeCN with and without electrolyte with the absorption curve peaks normalized.

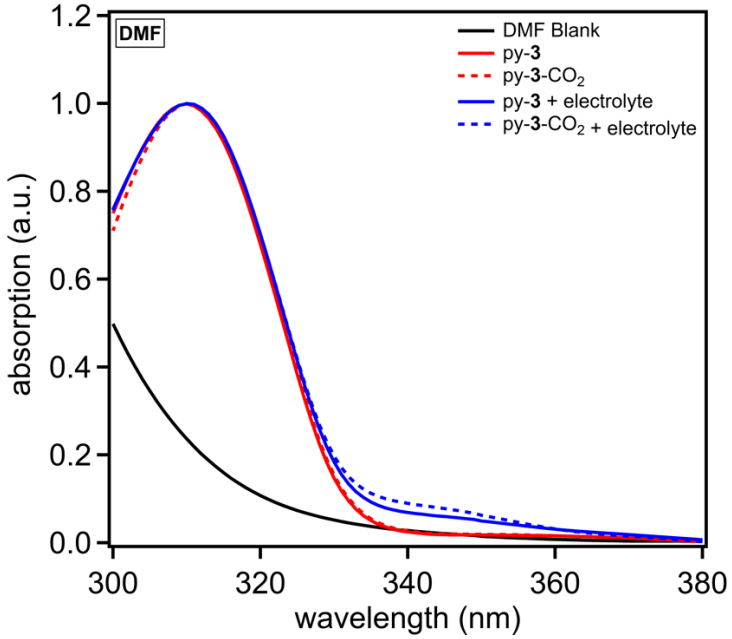

Figure S6. Absorption spectrum of py-**3** in DMF with and without electrolyte with the absorption curve peaks normalized.

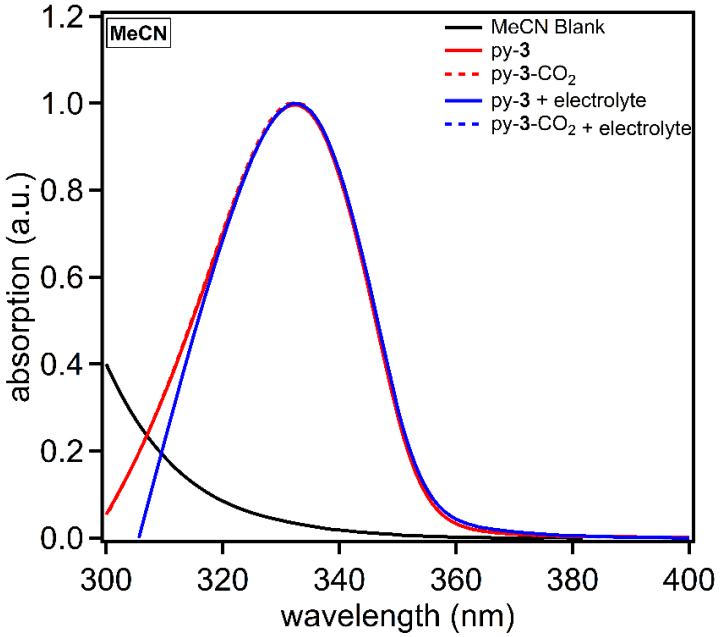

Figure S7. Absorption spectrum of py-**3** in MeCN with and without electrolyte with the absorption curve peaks normalized.

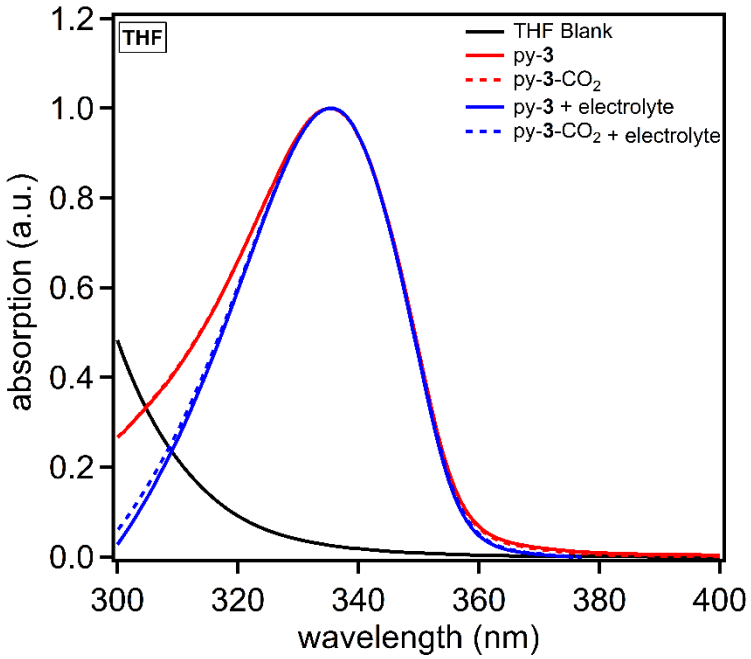

Figure S8. Absorption spectrum of py-**3** in THF with and without electrolyte with the absorption curve peaks normalized.

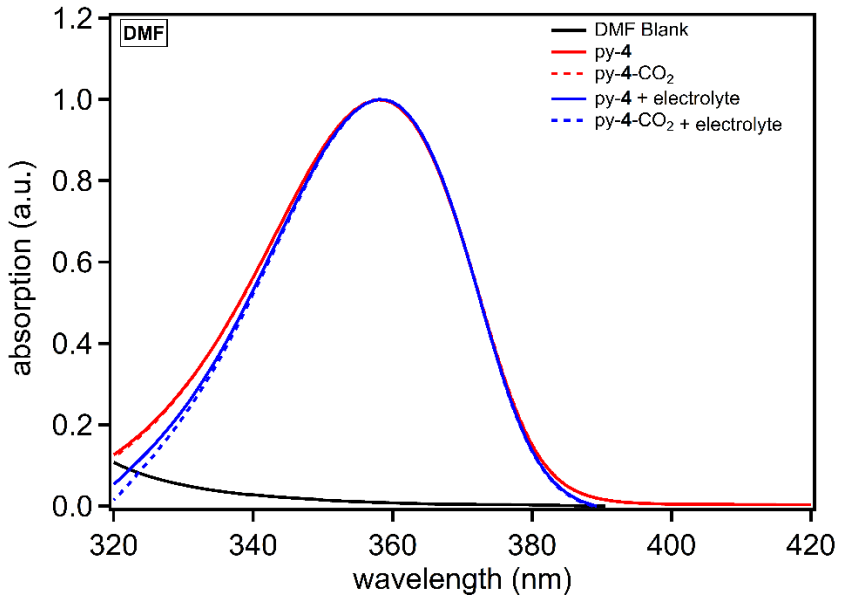

Figure S9. Absorption spectrum of py-**4** in DMF with and without electrolyte with the absorption curve peaks normalized.

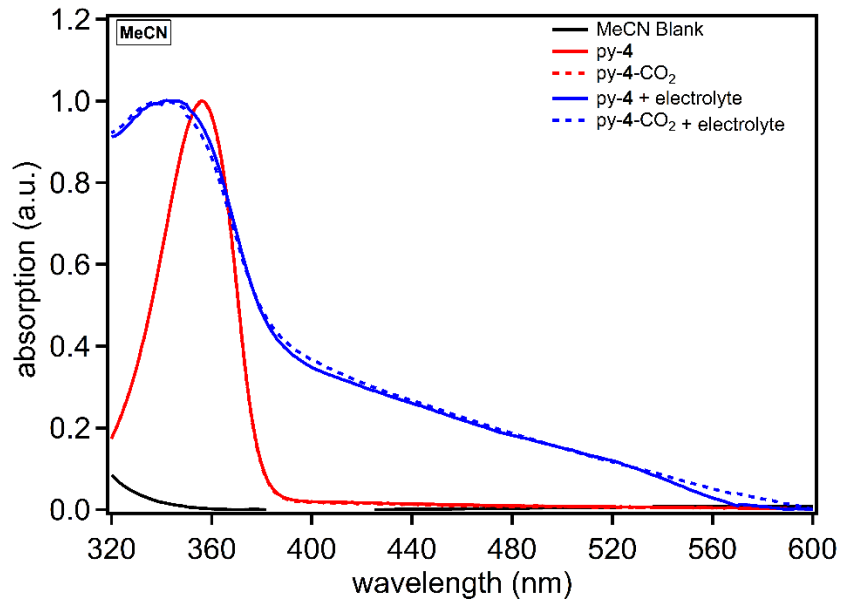

Figure S10. Absorption spectrum of py-**4** in MeCN with and without electrolyte with the absorption curve peaks normalized.

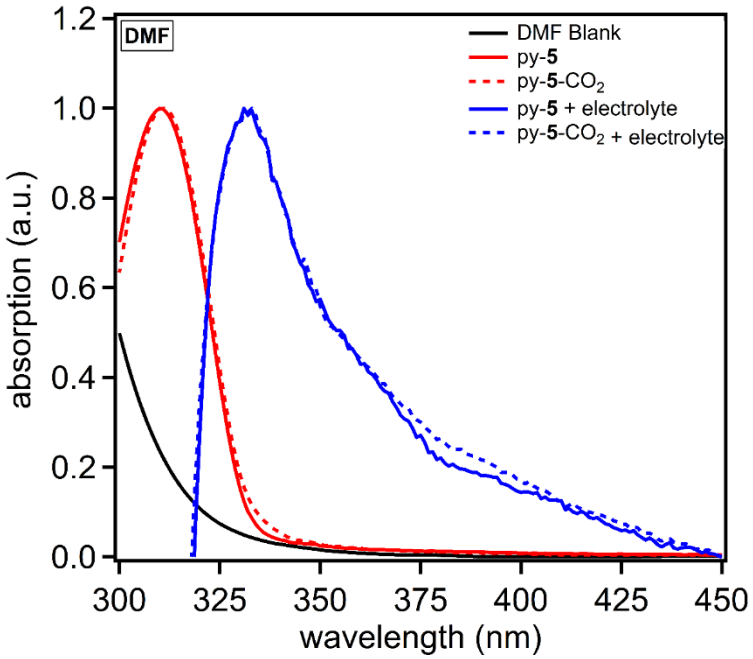

Figure S11. Absorption spectrum of py-**5** in DMF with and without electrolyte with the absorption curve peaks normalized.

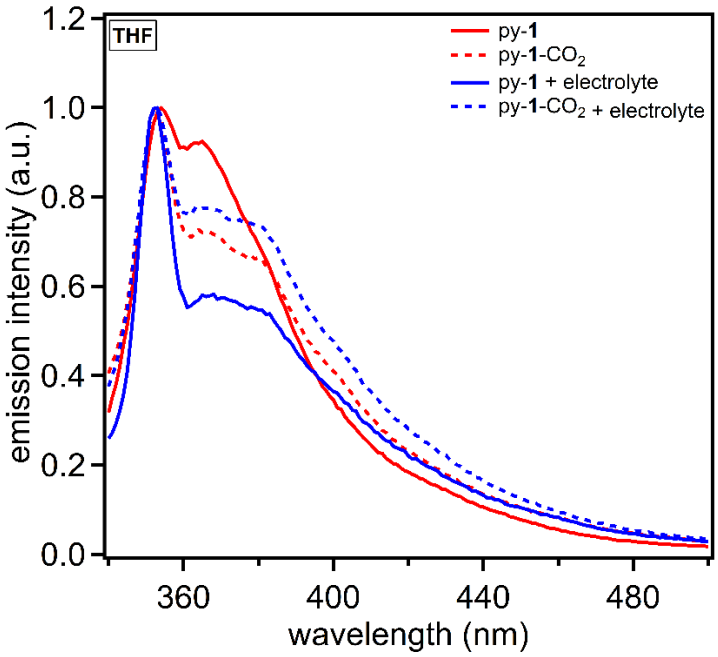

Figure S12. Emission spectrum of py-**1** in THF with and without electrolyte with the emission peak intensity normalized.

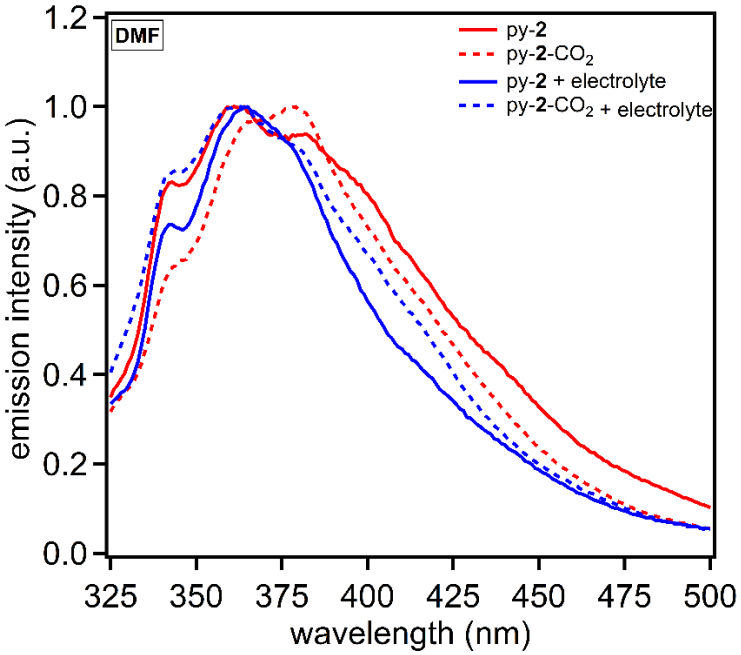

Figure S13. Emission spectrum of py-**2** in DMF with and without electrolyte with the emission peak intensity normalized.

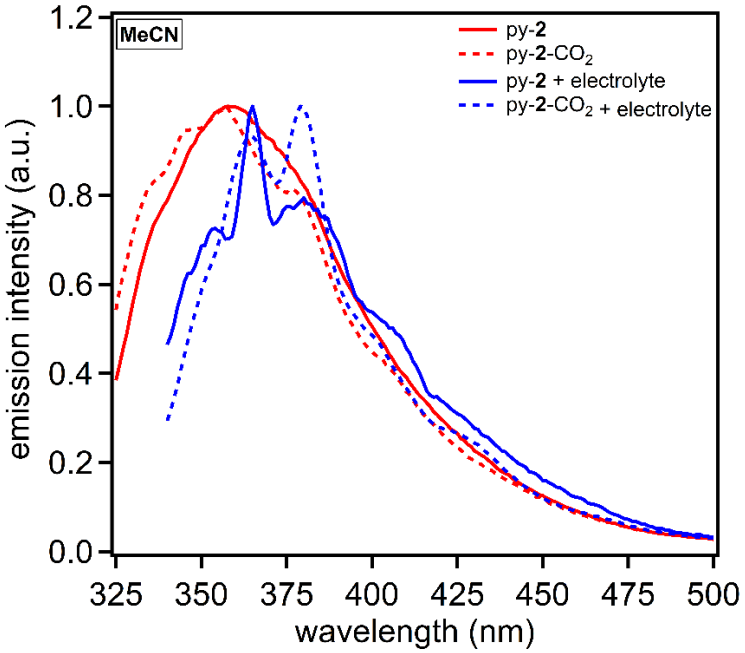

Figure S14. Emission spectrum of py-**2** in MeCN with and without electrolyte with the emission peak intensity normalized.

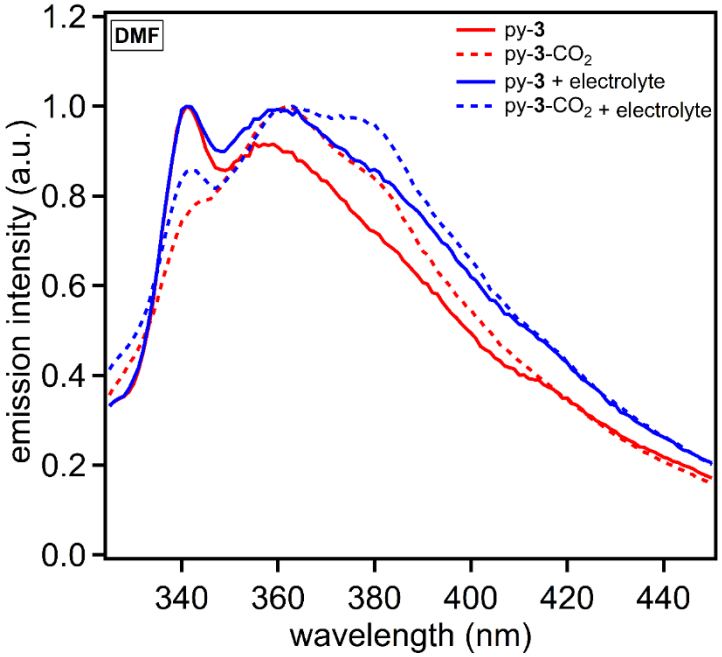

Figure S15. Emission spectrum of py-**3** in DMF with and without electrolyte with the emission peak intensity normalized.

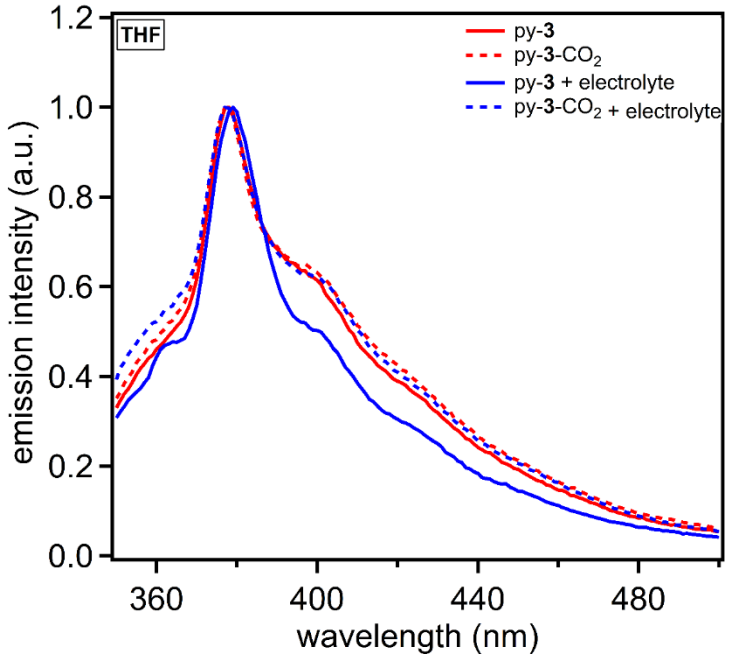

Figure S16. Emission spectrum of py-**3** in THF with and without electrolyte with the emission peak intensity normalized.

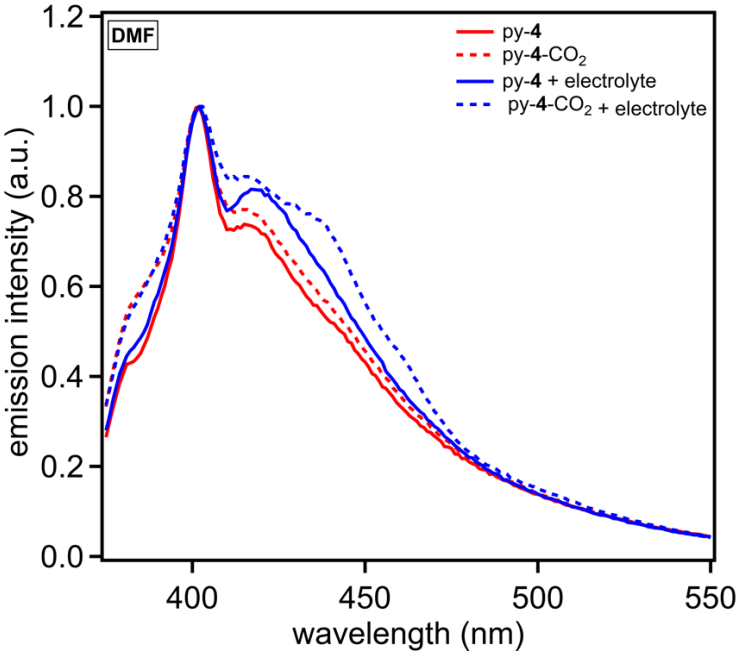

Figure S17. Emission spectrum of py-**4** in DMF with and without electrolyte with the emission peak intensity normalized.

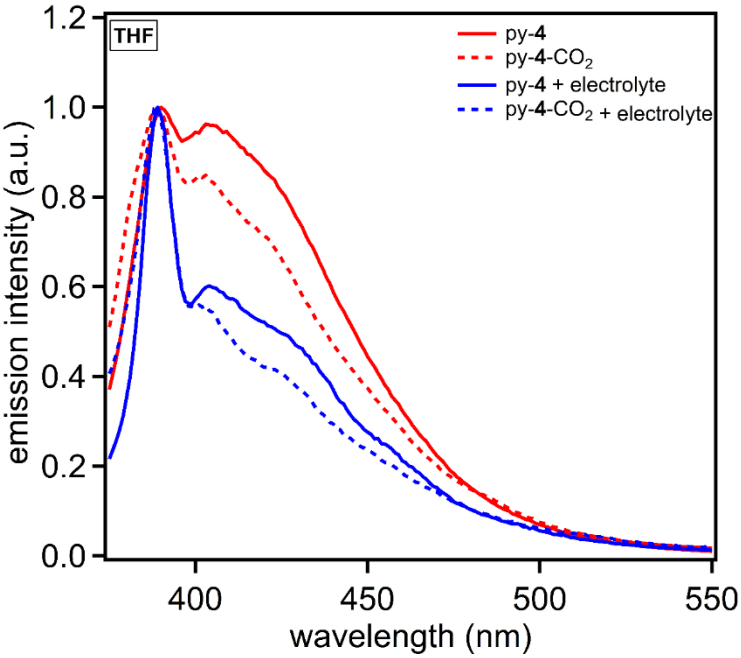

Figure S18. Emission spectrum of py-**4** in THF with and without electrolyte with the emission peak intensity normalized.

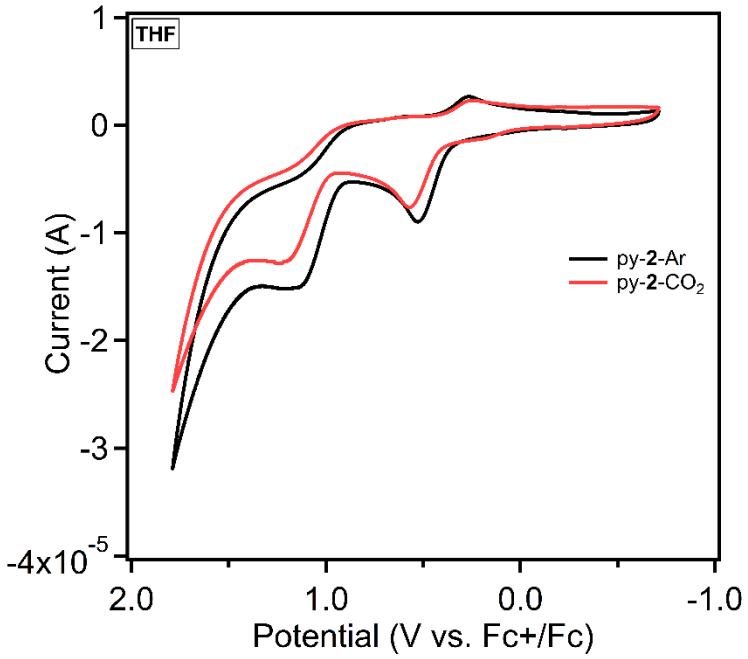

Figure S19. Cyclic voltammetry of py-**2** in THF with electrolyte under argon and CO_2.

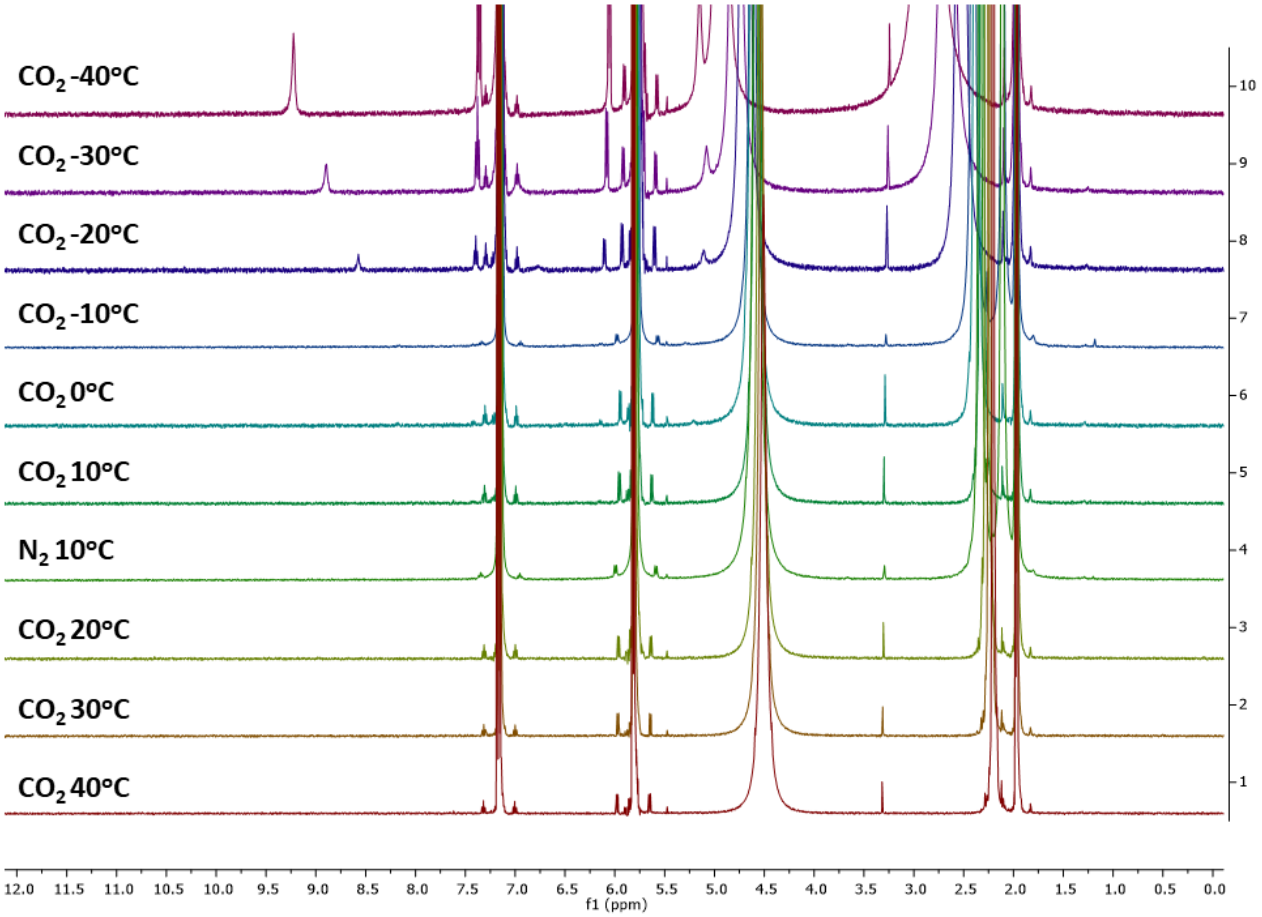

Figure S20. ^{1}H NMR data showing CO_2 binding with py-**2** in CD_3CN-d_3.

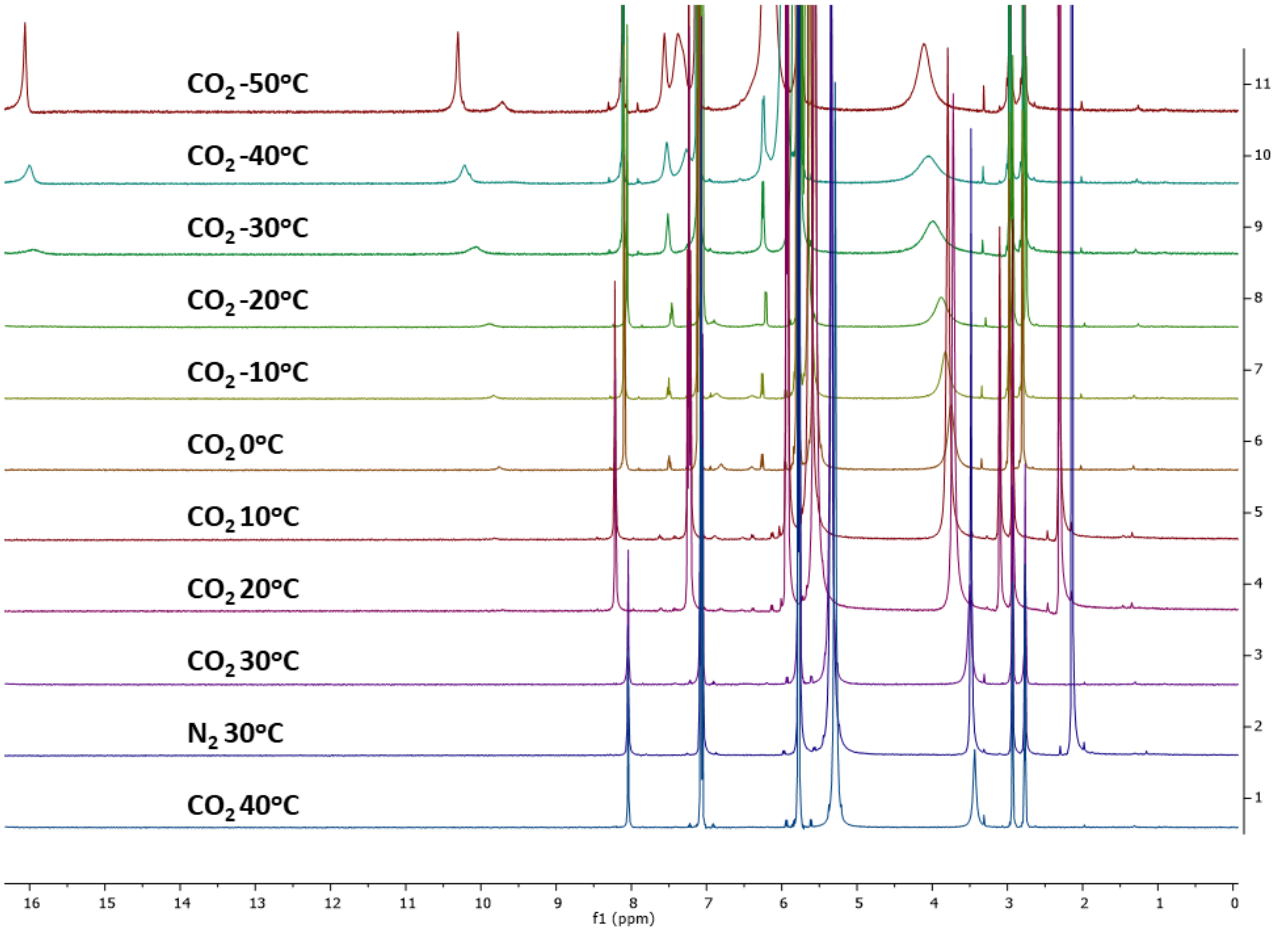

Figure S21. ^{1}H NMR data showing CO_2 binding with py-**2** in DMF-d_7.

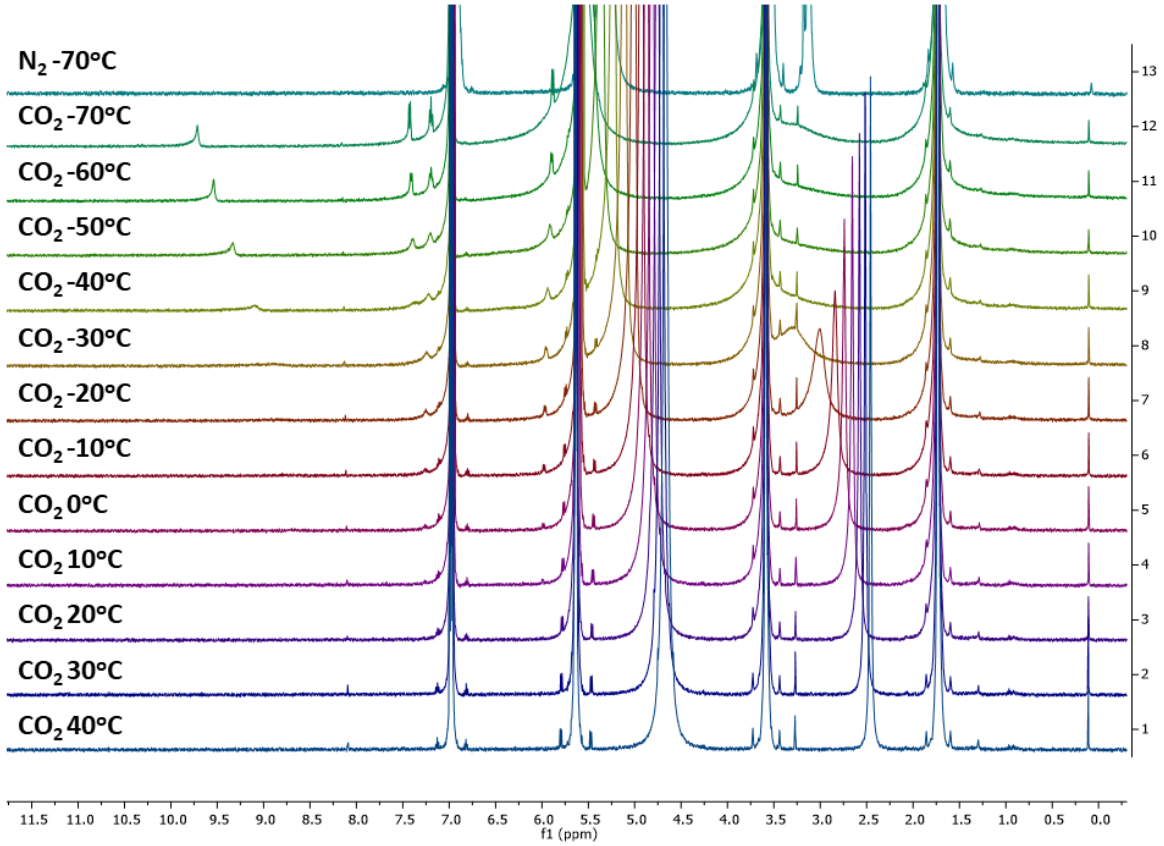

Figure S22. ^{1}H NMR data showing CO_2 binding with py-**2** in THF-d_8.

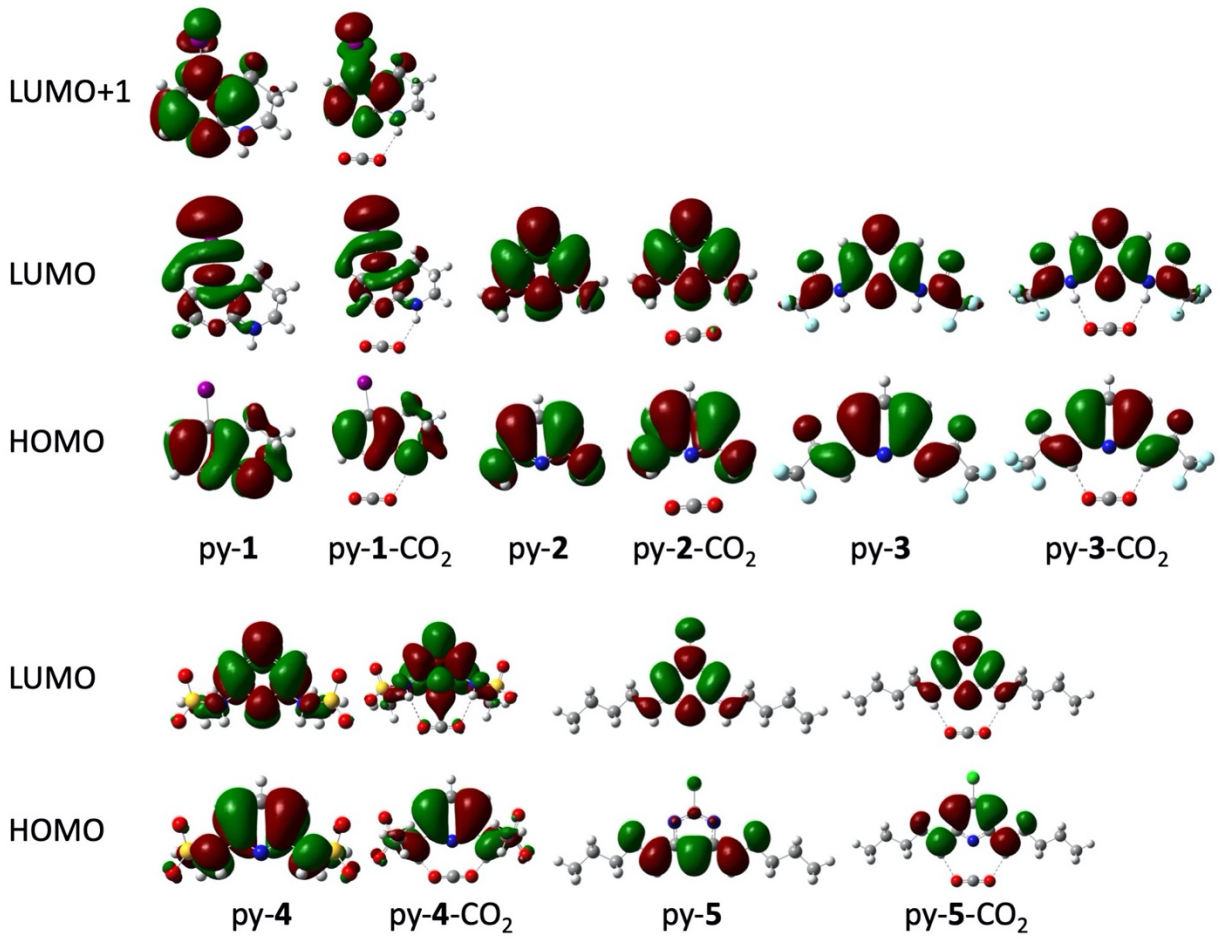

Figure S23. HOMO, LUMO, and select LUMO+1 orbitals (based on significant contributions to the S_0 -> S_1 vertical transition) for py-**1** through py-**5** with and without CO_2 bound.

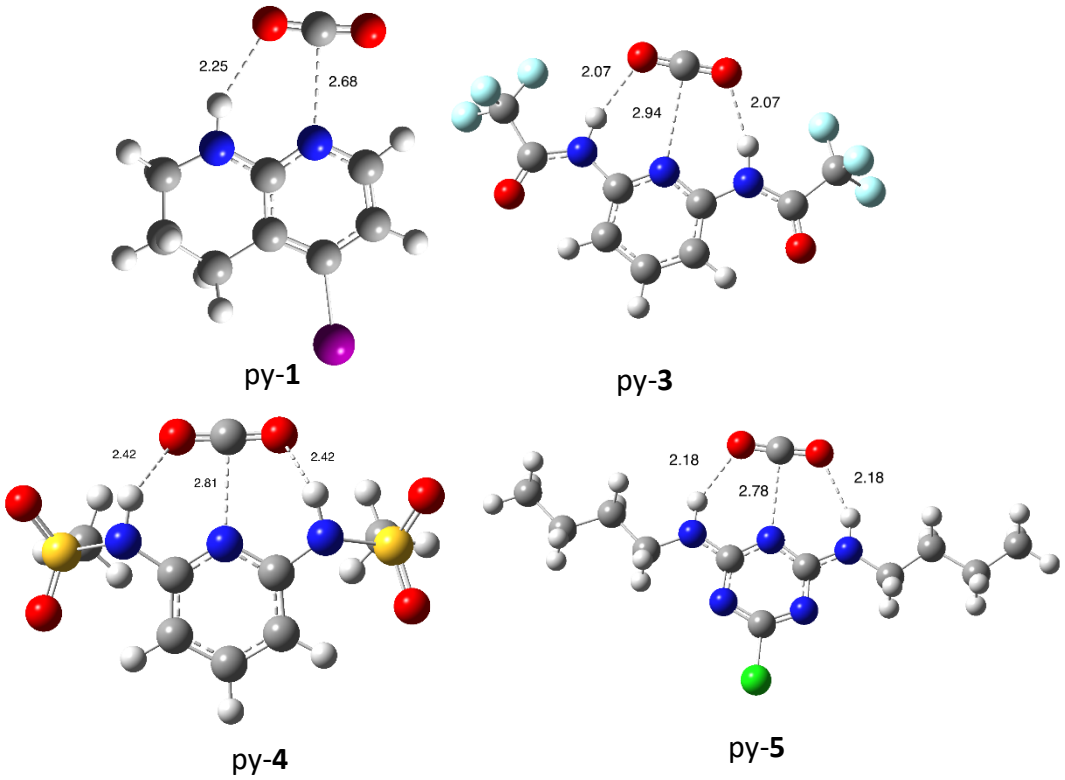

Figure S24. Optimized geometries at the M06-2X/6-311G(*d*) level for computational models of py-**1**, py-**3**, py-**4**, and py-**5** with CO_2 bound. Bond lengths are given in angstroms.

py-**1** XYZ Coordinates (the first column is atomic number)

6	-0.939230	2.691730	0.054911
6	-2.075400	0.715036	0.016553
6	-0.882735	-0.055593	0.026924
6	0.292780	0.673494	0.030265
6	0.296815	2.065988	0.049012
1	-0.998327	3.776307	0.070739
6	-0.949590	-1.565970	0.017102
1	1.215242	2.635714	0.053648
6	-2.339098	-2.084683	0.387894
6	-3.412578	-1.304933	-0.359620
1	-0.207107	-1.968960	0.709533
1	-2.414569	-3.149439	0.158841
1	-4.408537	-1.653698	-0.082884
7	-3.298664	0.092014	0.009165
1	-4.064386	0.716251	-0.195644
7	-2.101702	2.048152	0.031515
1	-0.665676	-1.930095	-0.977174
1	-2.508541	-1.960721	1.460650
1	-3.293789	-1.450365	-1.443298
53	2.173632	-0.317105	-0.025989

py-**1** with CO_2 XYZ Coordinates (the first column is atomic number)

6	-1.200105	-1.794758	-0.148725
6	-1.359324	0.487875	-0.063840
6	0.052738	0.652062	-0.041302
6	0.787880	-0.518341	-0.052833
6	0.182675	-1.773208	-0.111366
1	-1.735728	-2.738677	-0.196910
6	0.652027	2.038722	0.003679
1	0.759748	-2.686874	-0.123378
6	-0.354536	3.111198	-0.411958
6	-1.683070	2.893613	0.299441
1	1.527033	2.079167	-0.648317
1	0.039244	4.103329	-0.183134
1	-2.418933	3.634162	-0.016882
7	-2.182941	1.578735	-0.047905
1	-3.159739	1.365328	0.092485
7	-1.960638	-0.703539	-0.119240
1	1.018369	2.239794	1.017171
1	-0.526752	3.060758	-1.490353
1	-1.547212	2.999055	1.385288
53	2.910563	-0.455326	0.053017
6	-4.590729	-1.205431	0.073189
8	-4.396644	-2.334967	-0.055673
8	-4.870376	-0.090098	0.211476

py-**2** XYZ Coordinates (the first column is atomic number)

6	1.145641	-0.288874	-0.009523
6	1.203029	1.111520	-0.010884
6	0.000004	1.798745	-0.000009
6	-1.203029	1.111520	0.010888
6	-1.145649	-0.288864	0.009624
1	2.155051	1.627033	-0.034890
1	-0.000000	2.883633	-0.000049
1	-2.155045	1.627049	0.034813
7	-0.000001	-0.970949	0.000045
7	-2.296602	-1.050638	0.071813
1	-3.132018	-0.634099	-0.306915
1	-2.156543	-2.014128	-0.191806
7	2.296596	-1.050633	-0.071887
1	3.132053	-0.634095	0.306751
1	2.156582	-2.014132	0.191726

py-**2** with CO_2 XYZ Coordinates (the first column is atomic number)

6	-0.760924	-1.147586	0.056603
6	-2.161947	-1.200229	0.058385
6	-2.849361	0.000180	0.000285
6	-2.161827	1.200406	-0.058109
6	-0.760726	1.147504	-0.056772
1	-2.677173	-2.150975	0.115067
1	-3.934243	0.000215	0.000449
1	-2.676820	2.151279	-0.114820
7	-0.075172	-0.000043	-0.000188
7	-0.014396	2.299621	-0.166254
1	-0.467138	3.155547	0.109583
1	0.947012	2.217483	0.126556
7	-0.014637	-2.299752	0.165540
1	-0.467781	-3.155765	-0.109349
1	0.946577	-2.217938	-0.127956
6	2.754116	-0.000018	0.000178
8	2.793818	1.099231	0.352724
8	2.794059	-1.099252	-0.352303

py-**3** XYZ Coordinates (the first column is atomic number)

6	-1.140208	0.716485	0.003289
6	-1.209789	2.108774	0.003384
6	-0.000006	2.788754	-0.000184
6	1.209771	2.108770	-0.003611
6	1.140185	0.716479	-0.003242
1	-2.159916	2.618412	0.006365
1	-0.000005	3.872502	-0.000293
1	2.159900	2.618405	-0.006670
7	2.268176	-0.122048	-0.006306
1	2.042260	-1.107374	-0.008840
7	-2.268201	-0.122036	0.006502
1	-2.042292	-1.107363	0.009248
7	-0.000011	0.034854	0.000089
6	3.572718	0.253609	-0.008868
8	4.015425	1.371205	-0.011982
6	-3.572743	0.253625	0.009257
8	-4.015448	1.371221	0.012503
6	4.560880	-0.933519	0.001486
6	-4.560873	-0.933522	-0.001503
9	3.935012	-2.120941	-0.053291
9	5.286747	-0.906670	1.112717
9	5.377498	-0.852697	-1.040137
9	-3.935061	-2.120868	0.055519
9	-5.284814	-0.907844	-1.114061
9	-5.379283	-0.851658	1.038585

py-**3** with CO_2 XYZ Coordinates (the first column is atomic number)

6	1.143036	1.058172	0.009361
6	1.207897	2.448844	-0.066238
6	-0.000050	3.128446	-0.104126
6	-1.208008	2.448892	-0.066185
6	-1.143167	1.058209	0.009348
1	2.157411	2.958210	-0.091648
1	-0.000023	4.210601	-0.162927
1	-2.157526	2.958261	-0.091525
7	-2.282697	0.238814	0.056188
1	-2.086557	-0.752614	0.114039
7	2.282539	0.238728	0.056130
1	2.086416	-0.752737	0.113793
7	-0.000084	0.373009	0.044784
6	-3.580953	0.639289	0.037319
8	-4.007742	1.762154	-0.010352
6	3.580782	0.639226	0.037332
8	4.007589	1.762096	-0.010255
6	-4.584116	-0.535449	0.048047

6	4.584082	-0.535385	0.048086
9	-4.001938	-1.700132	0.368959
9	-5.126603	-0.671709	-1.159607
9	-5.551474	-0.301099	0.921407
9	4.001873	-1.700374	0.367825
9	5.550745	-0.301426	0.922319
9	5.127505	-0.670761	-1.159252
6	0.000229	-2.567792	-0.131302
8	1.154725	-2.584245	-0.131720
8	-1.154246	-2.585103	-0.130944

py-**4** XYZ Coordinates

C	1.14145200	0.23349600	0.46783800
C	1.20878500	1.57118800	0.07526500
C	0.00003300	2.22287800	-0.12307900
C	-1.20873200	1.57115100	0.07517000
C	-1.14143100	0.23348500	0.46778500
H	2.15820400	2.08005400	-0.01095400
H	0.00000300	3.26853000	-0.40897400
H	-2.15813400	2.08002300	-0.01120100
N	-2.28124500	-0.54199700	0.72633200
H	-2.08561600	-1.49088000	1.02207300
N	2.28128600	-0.54196800	0.72642400
H	2.08561400	-1.49086200	1.02209800
N	0.00002500	-0.42724900	0.64009300
S	-3.77482900	-0.34922200	0.00800800
S	3.77480100	-0.34925100	0.00799100
O	-4.55400600	-1.46260000	0.48976600
O	-4.19543100	1.01914700	0.19170700
O	4.55393900	-1.46270500	0.48964500
O	4.19551800	1.01910500	0.19173900
C	-3.45814700	-0.57541100	-1.73369200
H	-4.40314400	-0.40986300	-2.24856300
H	-2.72012600	0.15880600	-2.05418300
H	-3.10560900	-1.59168600	-1.89485200
C	3.45804400	-0.57532500	-1.73371100
H	2.72016700	0.15904100	-2.05418700
H	4.40308300	-0.40990200	-2.24854700
H	3.10534900	-1.59153200	-1.89494300

py-**4** with CO_2 XYZ Coordinates

C	1.14511019	-0.74004451	-0.46972549
C	1.20831445	-2.00373307	0.11823927
C	-0.00016441	-2.61609680	0.41662416
C	-1.20859932	-2.00360334	0.11830239
C	-1.14526693	-0.73991674	-0.46961637
H	2.15834331	-2.49277987	0.27829837
H	-0.00020583	-3.60622359	0.85793348
H	-2.15867838	-2.49254992	0.27838250
N	-2.28964922	-0.03056092	-0.86070614
H	-2.09679505	0.87055471	-1.28185599
N	2.28957620	-0.03080704	-0.86076540
H	2.09690243	0.87034626	-1.28194370
N	-0.00005548	-0.10696566	-0.72995301
S	-3.75979705	-0.06543296	-0.06264326
S	3.75960841	-0.06562779	-0.06246731
O	-4.56396103	0.91857794	-0.74266083
O	-4.17303964	-1.44371068	0.05661835
O	4.56386852	0.91843704	-0.74229523
O	4.17297412	-1.44385609	0.05696096
C	-3.38879041	0.52485228	1.57959478
H	-4.31654399	0.47291499	2.14720730
H	-2.63881899	-0.12902546	2.02337487
H	-3.03367547	1.54985883	1.50569768
C	3.38829509	0.52465997	1.57970223
H	2.63814302	-0.12913368	2.02330146
H	4.31590728	0.47260408	2.14753583
H	3.03334556	1.54971805	1.50571099
C	0.00061357	2.57883356	0.11541197
O	-1.15420666	2.60004159	0.12654311
O	1.15547976	2.59917456	0.12319621

py-**5** XYZ Coordinates

C	-0.00004000	1.72373800	0.00022100
N	-1.18593000	1.16090700	-0.00788500
C	-1.12178000	-0.19004900	-0.01826500
C	1.12173900	-0.19005300	-0.01306300
N	1.18584100	1.16097800	-0.00157600
N	0.00002900	-0.91463500	-0.02221600
Cl	-0.00016600	3.47183700	0.01463300
N	2.29055800	-0.85098700	-0.01490200
H	2.23142600	-1.85712500	-0.02855200
N	-2.29047700	-0.85126200	-0.02392800
H	-2.23092400	-1.85725800	-0.04478900
C	3.58828300	-0.19609900	-0.01118600
C	4.69669900	-1.23806200	0.00517600

H	3.66178000	0.45828800	0.86230900
H	3.67607300	0.44573800	-0.89302800
C	6.08495500	-0.60397000	0.01010000
H	4.58228400	-1.87560700	0.88995700
H	4.59578900	-1.88983400	-0.87099400
C	7.19757300	-1.64786400	0.02750600
H	6.19297400	0.03702900	-0.87090500
H	6.17972700	0.05203600	0.88152800
H	8.18404800	-1.18122100	0.03081000
H	7.12635200	-2.28211600	0.91472300
H	7.13962300	-2.29759300	-0.84943600
C	-3.58836300	-0.19677800	-0.03490900
C	-4.69656800	-1.23816500	0.00920900
H	-3.67889900	0.42400400	-0.93170200
H	-3.65937500	0.47801500	0.82282500
C	-6.08490900	-0.60427600	0.00066200
H	-4.59762000	-1.91163500	-0.85074000
H	-4.58002400	-1.85342200	0.90923900
C	-7.19735000	-1.64745100	0.04726100
H	-6.17786700	0.07384700	0.85519100
H	-6.19487900	0.01395100	-0.89623400
H	-8.18387500	-1.18094000	0.04114900
H	-7.14153200	-2.31932000	-0.81298700
H	-7.12383200	-2.25889900	0.95015100

py-**5** with CO_2 XYZ Coordinates

C	-0.00036300	2.21925200	-0.01397800
N	-1.18593000	1.65684200	-0.01256300
C	-1.12681900	0.30582200	-0.00646200
C	1.12656900	0.30613800	-0.00467800
N	1.18536100	1.65717000	-0.01063000
N	-0.00003900	-0.41924900	-0.00335700
Cl	-0.00060000	3.96684400	-0.02159200
N	2.29633800	-0.34809700	0.00068800
H	2.25234000	-1.35599100	-0.00096000
N	-2.29649800	-0.34864300	-0.00202100
H	-2.25254000	-1.35653100	-0.00623900
C	3.58791700	0.32043600	-0.00623900
C	4.70514700	-0.71154200	0.03022600
H	3.65376100	0.99137600	0.85509700
H	3.67064300	0.94731800	-0.89925600
C	6.08755200	-0.06491500	0.02403600
H	4.59508900	-1.33375600	0.92621900
H	4.61009300	-1.38109900	-0.83293900
C	7.20946000	-1.09823900	0.06312600
H	6.19111200	0.55966400	-0.86928200
H	6.17565300	0.60900200	0.88248300

H	8.19180900	-0.62291200	0.05852800
H	7.14241000	-1.71571700	0.96239500
H	7.15829100	-1.76557700	-0.80089800
C	-3.58816200	0.31967700	-0.01307000
C	-4.70528000	-0.71211300	0.03146700
H	-3.67185600	0.94046000	-0.91033500
H	-3.65322900	0.99644100	0.84366200
C	-6.08773500	-0.06563400	0.02174100
H	-4.61098500	-1.38775900	-0.82705700
H	-4.59436400	-1.32797400	0.93170300
C	-7.20954800	-1.09871700	0.06901000
H	-6.17519300	0.61432200	0.87547700
H	-6.19203500	0.55262700	-0.87587700
H	-8.19192700	-0.62348300	0.06201100
H	-7.15914000	-1.77204900	-0.79039800
H	-7.14163700	-1.70992500	0.97248700
C	0.00111300	-3.20020900	-0.05249800
O	1.15563600	-3.23722300	-0.05142500
O	-1.15336500	-3.23786200	-0.05490800