Electronic Supplementary Material (ESI) for Materials Advances.

Concentration-Dependent Emission from Low Molecular Weight Benzoyl Pyrazinium Salts

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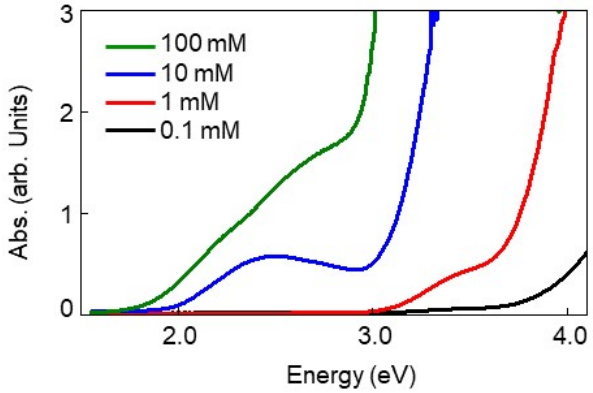


Figure S1. Absorption spectra for H-BF4 demonstrating absorption edge shifting to higher energies with decreasing concentration.

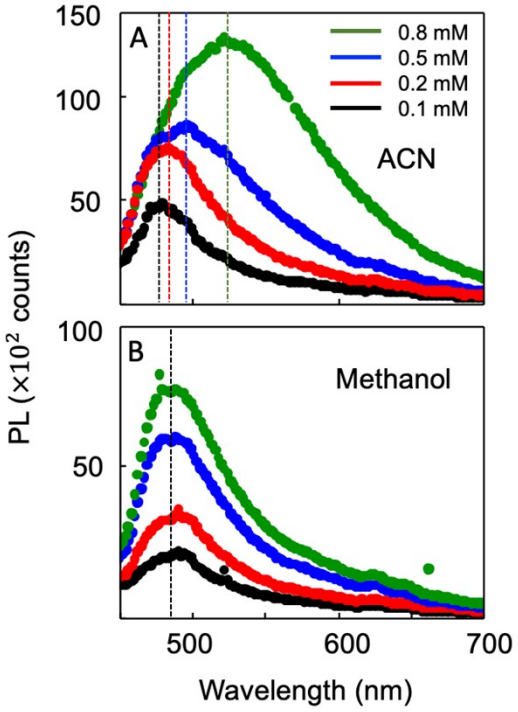


Figure S2. PL emission over a range of concentrations of H-BF_4 in (A) ACN and (B) methanol. When dissolved in ACN, emission shifts to longer wavelengths with increasing concentration, a consequence of increasing aggregation. When dissolved in methanol the emission over the same concentration range the emission wavelength remains constant. This would indicate methanol disrupts the formation of aggregates. The spectra intensities have been adjusted to clearly highlight the spectral positions.

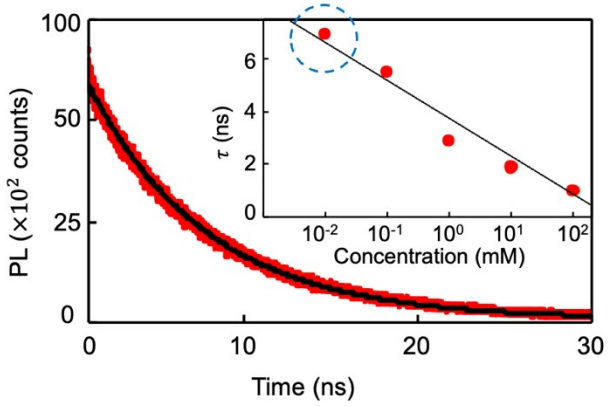


Figure S3. Time-resolved PL data of H-BF_4 at 0.01 mM concentration. The PL intensity I_{PL} is fitted with a single exponential $I_{PL} = Ae^{-t/\tau}$ and τ = 6.9 ns. The inset plots the average recombination lifetime as a function of concentration, and the newly added result at 0.01 mM solution is circled. It fits well into the established trend. Single exponential decay would suggest minimal presence of aggregates at this concentration.

Concentration	PLQY
100 mM	11%
10 mM	26%
1 mM	32%
0.1 mM	60%

Table S1. Photoluminescence quantum yield (PLQY) of H-BF_4 is measured using an integrating sphere with excitation at 400 nm and the results at different concentrations listed in the table. PLQY decreases with increasing concentration, which is expected since increased aggregation would result in higher non-radiative recombination rates, reducing radiative recombination and decreasing QY.

$H\text{-}BF_4$

Sample	1 mM	10 mM	100 mM
Y Max (counts)	10634	1595	842
X at Ymax (nm)	550 nm	658	743
Area	1510430	127073	16666
FWHM (nm)	148	140	126
TRPL (ns)	3.61	2.68	1.73

$F\text{-}BF_4$

Sample	1 mM	10 mM	100 mM
Y Max (counts)	47660	1301	1166
X at Ymax (nm)	479	610	618
Area	3383497	32318	37894
FWHM (nm)	71	71	95
TRPL (ns)	5.49	2.3	1.35

$OMe\text{-}BF_4$

Sample	1 mM	10 mM	100 mM
Y Max (counts)	17568	9314	955
X at Ymax (nm)	477	480	523
Area	1168847	557494	20378
FWHM (nm)	68	65	98
TRPL (ns)	5.19	3.05	1.47

Table S2. Summary of spectroscopic trends for all three samples at different concentrations.

General Considerations. Reagents and solvents were purchased and used without purification. Yields refer to homogenous material that is purified by silica-gel chromatography and spectroscopically pure (>95%) by ^{1}H NMR and ^{13}C NMR. Reactions were monitored by thin-layer chromatography using 0.25 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on a Varian-INOVA 400 MHz or 500 MHz spectrometer, calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$ – ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm; $(CD_3)_2CO$ – ^{1}H NMR: 2.05 ppm and 2.86 ppm H_2O (or HOD), ^{13}C NMR: 206.7 ppm and 29.9 ppm). The following abbreviations were used to explain multiplicities (s–singlet, d–doublet, t–triplet, q–quartet, m–multiplet). The samples were analyzed by mass spectrometry using a Q-Exactive Hybrid Quadrupole-Orbitrap mass spectrometer couple to Vanquish Flex UHPLC system (Thermo Scientific) and processed using Biopharma Finder software.

General procedure to synthesize phenylglyoxal hydrate

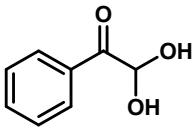
Selenium (IV) dioxide (0.231g, 2.1mmol, 1.1eq) is added to the reaction vessel along with a stir bar, water (0.108mL, 6.0mmol, 3.3eq), and 4mL of dioxane. The reaction vessel is evacuated and backfilled with nitrogen gas. It is then heated to 60^{o}C until all the selenium (IV) dioxide has dissolved.
Acetophenone (0.233mL, 2.0mmol, 1.0eq) is added through septa via syringe. The temperature is then increased to 101^{o}C, and refluxed, for 24 hours. After 24 hours, the reaction is removed from the hot plate and the conversion is checked via TLC. Once the reaction flask has cooled to room temperature, the solution is vacuum filtered through a pad of celite to remove selenium. The filtrate is transferred to a clean reaction flask and concentrated in vacuo. 10mL of water is added to the solution. The reaction is heated to 101^{o}C under reflux, overnight. The reaction flask is removed from the hot plate and filtered while hot via Buchner funnel to remove any excess selenium. The filtrate is allowed to cool to room temperature and the precipitated solid is filtered via Buchner funnel and allowed to dry for an hour before being collected pure (yielded 80% or greater).

General procedure to synthesize of benzoyl pyrazine

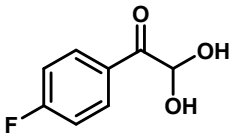
The following dry reagents are added to the reaction flask along with a stir bar: phenylglyoxal hydrate (61mg, 0.4mmol, 2.0eq), pyrazine (16mg, 0.2mol, 1.0eq), selectfluor (141mg, 0.4mmol, 2.0eq), and silver nitrate (0.006g, 0.04mmol, 0.2eq). A mixture (1ml) of 1:1 H2O/DCE is added to the reaction flask followed by trifluoroacetic acid (0.03mL, 0.4mmol, 2.0eq). The reaction flask is then heated to 50^{o}C for 24 hours. The flask is removed from the hot plate, cooled to room temperature, and quenched with 1mL of 4M NaOH. The reaction is extracted 3 times with 5mL of dichloromethane and the combined organic extract is dried over magnesium sulfate and concentrated in vacuo. The crude material is purified via column chromatography with silica gel and 20:80 ethyl acetate/hexane mixture producing the final benzoyl pyrazine product (yielded 70% or greater).

Alkylation and ion-exchange of benzoyl pyrazine

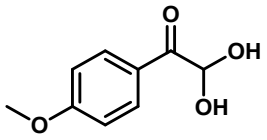
Benzoyl pyrazine (0.164g, 0.89mmol, 1.0eq) and methyl iodide (0.188g, 1.33mmol, 1.5eq) are added to a reaction vessel along with a stir bar and 0.89mL of acetonitrile. The reaction vessel is heated to 60°C for 24 hours. The reaction solution is removed from hot plate and concentrated via rotary evaporator, resulting in a dark red solid. The reaction conversion is checked via NMR, and resubjected if necessary. Approximately 2mL of ethyl acetate is added to the reaction flask causing orange solid to precipitate out immediately. The solid is filtered from the solution via Buchner funnel yielding the Iodo salt. The Iodo salt is then redissolved in acetonitrile and 15mol% of silver tetrafluoroborate is added. AgI precipitates out and is filtered away resulting in the desired product. NMR shows 100% conversion.



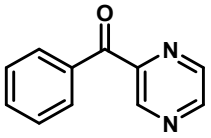
2,2-dihydroxy-1-phenylethan-1-one:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 8.17 (d, J= Hz, 2H), 7.67-7.70 (t, J= Hz, 1H), 7.55 -7.58 (t, J= Hz, 2H), 5.95-5.99 (t, J+ Hz, 1H), 5.70-5.72 (d, J= Hz, 2H). **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 195.73, 133.67,133.63, 129.50, 128.53, 88.05. White Solid.



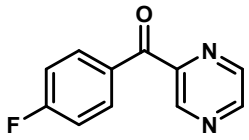
1-(4-fluorophenyl)-2,2-dihydroxyethan-1-one:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 8.26-8.28 (t, J= 5.67Hz, 2H), 7.33-7.30 (t, J=8.80 Hz, 1H), 5.98 -5.94 (t, J= 7.82Hz, 2H), 5.82-5.80 (d, J= 7.98Hz, 1H). **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 194.45, 164.86, 164.86, 132.61,132.53,115.62,115.44,88.39. White Solid.



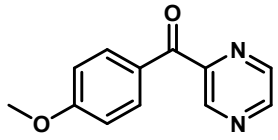
2,2-dihydroxy-1-(4-methoxyphenyl)ethan-1-one:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 8.14-8.16 (d, J= 8.98Hz, 2H,) 7.06-7.08 (d, J= 8.97 Hz, 2H), 5.90 (s, 1H), 5.74 (bs, 2H), 3.94 (s, 3H). **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 194.30, 164.11, 131.93, 126.25, 113.79, 88.72, 55.13. White Solid.



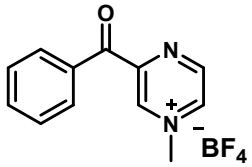
phenyl(pyrazin-2-yl)methanone:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 9.25 (s, 1H), 8.78 (d, J= 2.31Hz, 1H), 8.68 (s, 1H), 8.07 (d, J= 7.31 Hz, 2H), 7.64-7.65 (t, J = 7.41Hz, 1H), 7.49-7.53 (t, J= 7.70Hz, 2H), **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 192.24, 149.91, 146.79, 146.09, 142.91, 135.48, 133.55, 130.86, 128.37. Yellow Solid.



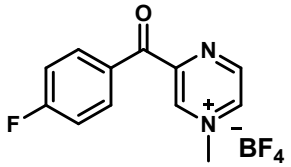
(4-fluorophenyl)(pyrazin-2-yl)methanone:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 9.17 (s,1H), 8.87 (d, J= 2.28, 1H), 8.75 (s, 1H), 8.22-8.24 (m, 2H), 7.30-7.33 (t, J=8.69Hz, 2H). **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 190.20,164.65 (d, J=253Hz), 149.83, 147.24, 145.63. Yellow Solid.



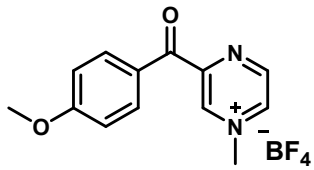
(4-methoxyphenyl)(pyrazin-2-yl)methanone:
H^1 NMR (500MHz, $(CD_3)_2(CO)$: 1H: 9.12 (s,1H), 8.85 (d, J=2.47Hz, 1H), 8.76 (m, 1H), 8.15(d, J= 8.96Hz, 2H), 7.10 (d, J=8.95Hz,2H), 3.94 (s, 3H) **^{13}C NMR** (500MHz, $(CD_3)_2(CO)$: 190.19, 164.09, 150.81, 146.76, 145.44, 142.95, 133.28,128.47, 113.59, 55.15. Yellow Solid.



3-benzoyl-1-methylpyrazin-1-ium tetrafluoroborate:
H^1 NMR (500MHz, CD_3CN): 1H: 9.45(s,1H), 9.32 (s, 1H), 8.99 (s, 1H), 8.07 (d, J= 7.74, 2H), 7.77 (t, J = 7.36, 1H), 7.60 (t, J=7.64, 2H), 4.48 (s, 3H) **^{13}C NMR** (500MHz, CD_3CN): 188.80, 155.02, 149.17, 139.24- 139.39 (m), 138.86-139.01 (m), 134.69, 134.02, 131.02, 128.74, 49.68. **HR-MS** (ESI) m/z: calcd for $C_{12}H_{11}N_{2O}$ [M+H]: 199.0871; found 199.0795. MP: 109 °C, Red solid.



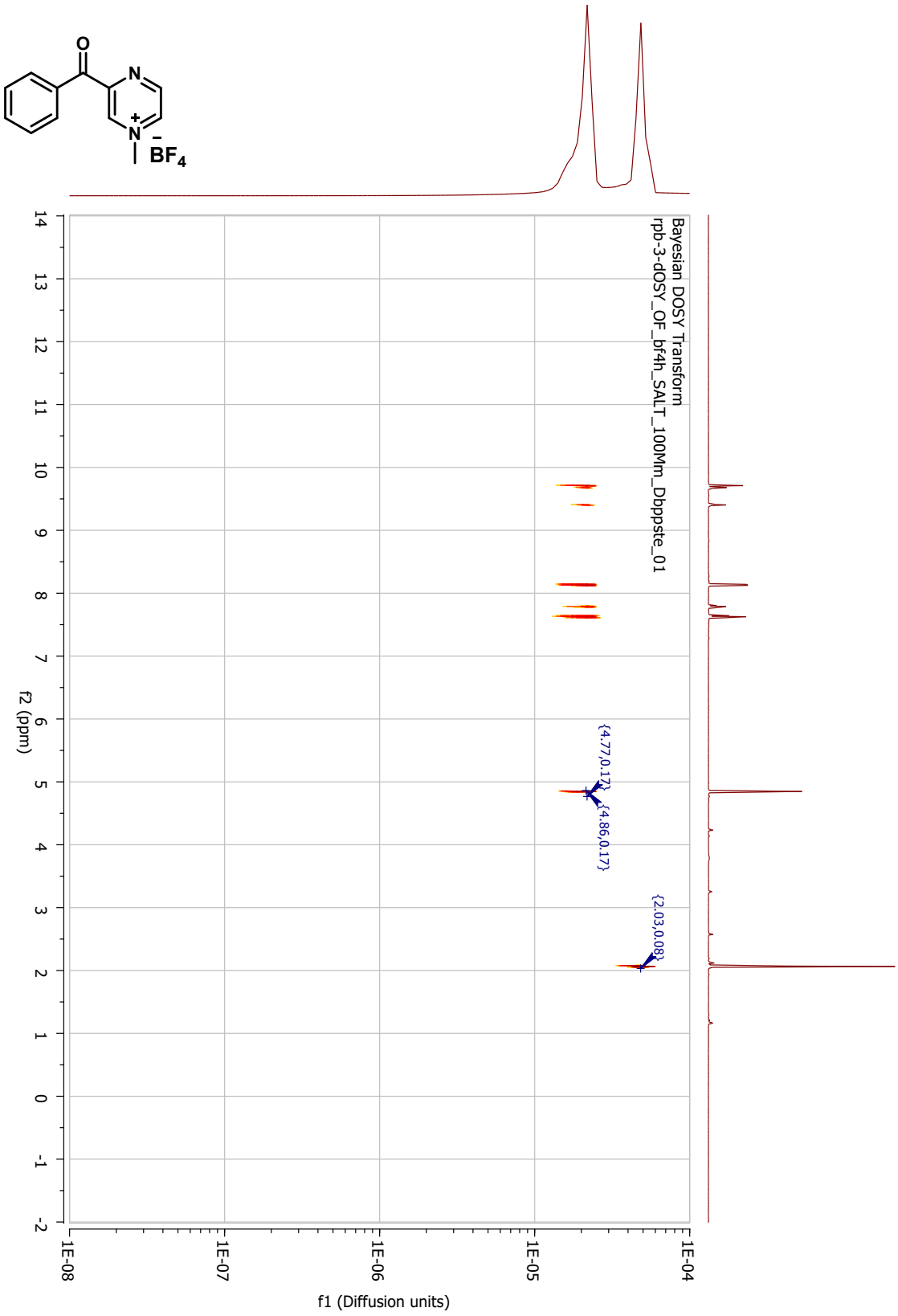
3-(4-fluorobenzoyl)-1-methylpyrazin-1-ium tetrafluoroborate:
H[1] NMR (500MHz, CD3CN): 1H: 9.76 (s, 1H), 9.61 (s,1H), 9.40 (d, J= 3.40Hz), 8.13-8.16 (m, 2H), 7.45-7.49 (t, J= 8.86 Hz), 4.51 (s, 3H) **[13]C NMR** (500MHz, CD3CN): 188.06, 166.14 (d, J= 254.54Hz), 154.31, 149.13, 140.12(m), 134.57 (d, J= 9.85Hz), 131.13 (d, J= 2.76 Hz),116 (d, J= 22.18Hz), 44.94. **HR-MS** (ESI) m/z: calcd for $C_{12}H_{10}FN_2O^+$ [M+H]: 217.0772; found 217.0696. MP: 129 °C, Red solid.



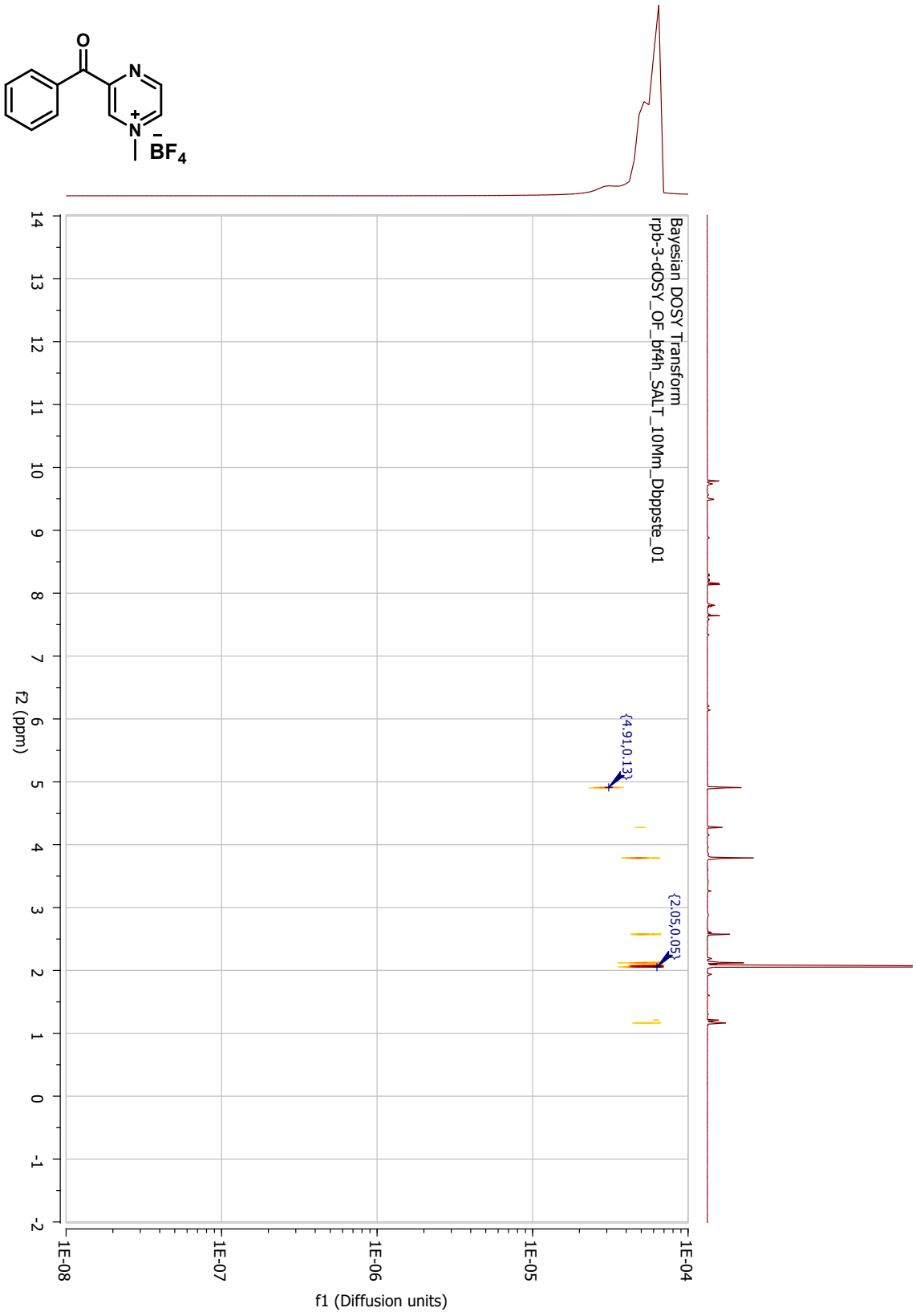
3-(4-methoxybenzoyl)-1-methylpyrazin-1-ium tetrafluoroborate:
H[1] NMR (500MHz, CD3CN): 1H: 9.40 (s, 1H), 9.17 (s, 1H), 8.84 (d, J= 3.25Hz, 1H), 8.04 (d, J=11.91Hz, 2H), 7.04 (d, J=11.91Hz, 2H), 4.46 (s, 3H), 3.87 (s,3H). **[13]C NMR** (500MHz, CD3CN): 187.53, 166.04, 157.00, 150.17,140.06-140.25 (m), 139.67-139.85 (m), 134.83,127.60, 115.24, 56.71, 50.50. **HR-MS** (ESI) m/z: calcd for $C_{13}H_{13}N_2O_2^+$ [M+H]: 229.0972; found 229.0893. MP: 190 °C, Red solid.

Procedure for diffusion-ordered NMR spectroscopy.
BPL samples were analyzed via DOSY-NMR in deuterated acetone using spectroscopic concentrations with a magnetic gradient of 63g/cm^2 using a double stimulated echo pulse sequence. Self-diffusion coefficients (SDCs) were extracted using MNOVA's BAYSIAN transform of 15 H^1-NMR spectra to form a pseudo 2D spectra where the cross-peaks correlate to SDC.

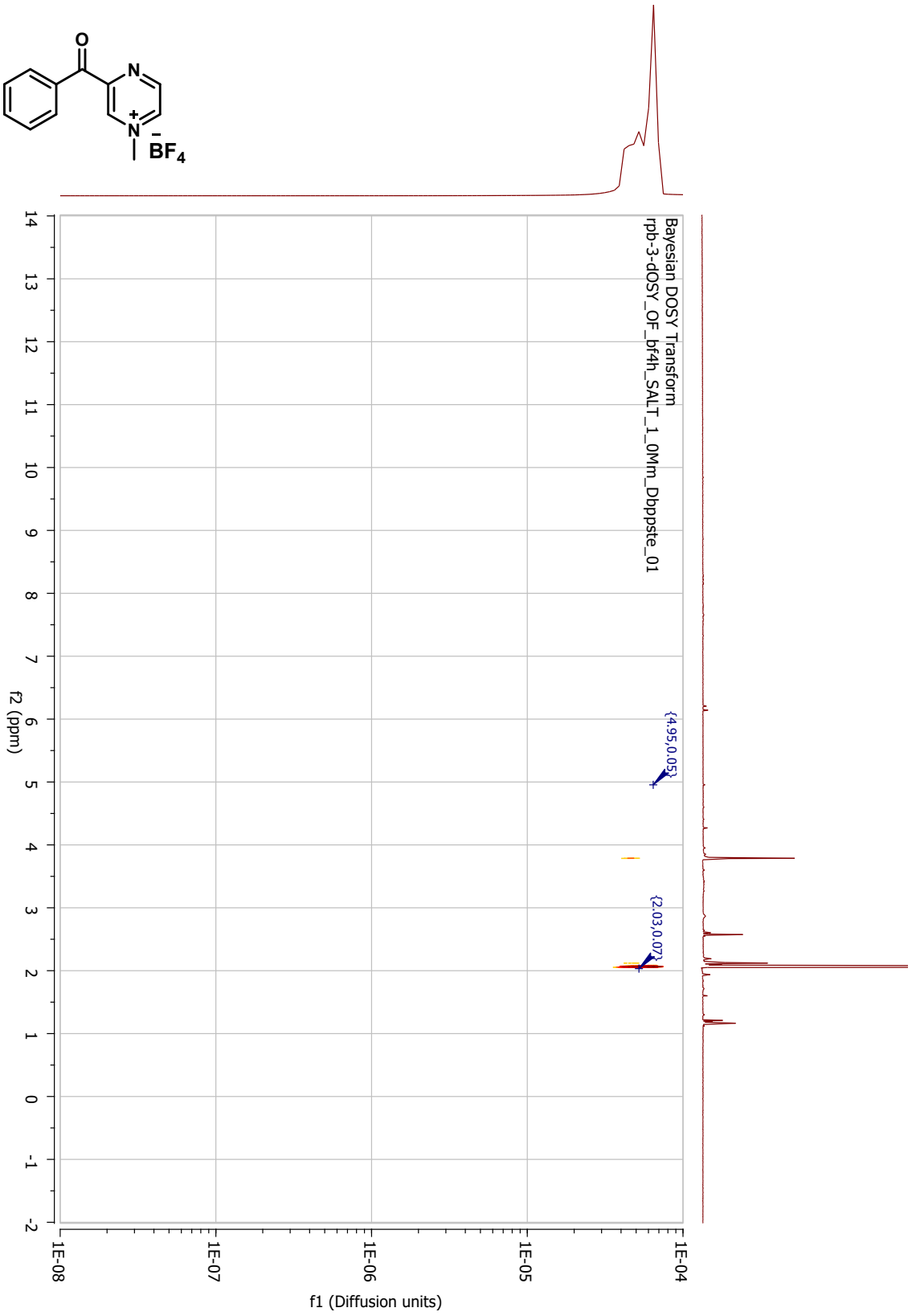
100Mmol Concentration



10 Mmol Concentration



1.0 Mmol Concentraion



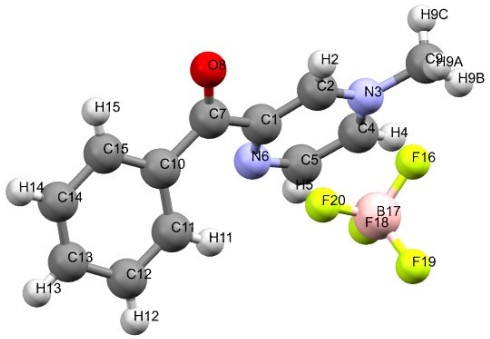


Figure S4. Crystal structure of **3-benzoyl-1-methylpyrazin-1-ium tetrafluoroborate**.

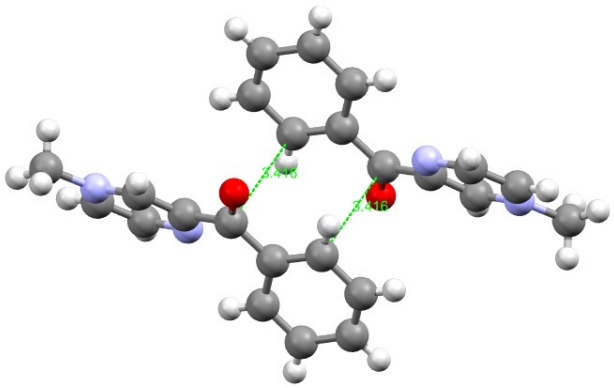


Figure S5. Packing of **3-benzoyl-1-methylpyrazin-1-ium tetrafluoroborate** crystals with the bond length (3.416 Å) shown for the closest atoms.