Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Can betaine pyridinium derivatives be used to control the photoejection of cation?

## Supporting Information

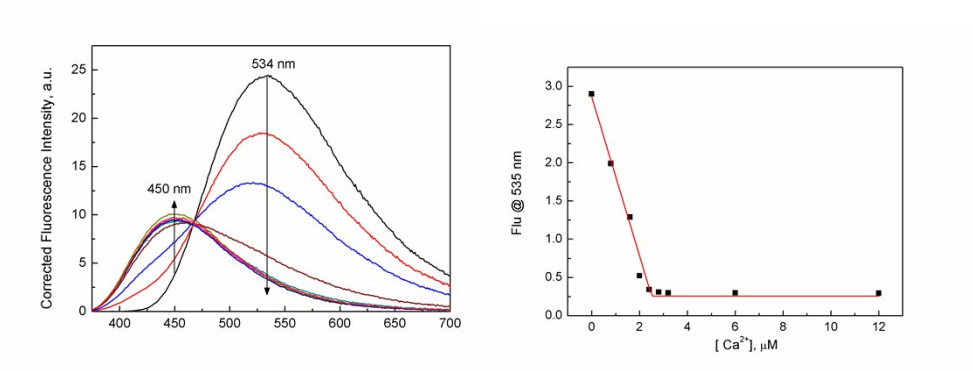


**Figure S1.** Fluorescence spectra of **PyB-Aza**, recorded 30 min after the addition of different concentrations of $Ca(ClO_4)_2$ in MeCN, [**PyB-Aza**] = 2.5 µM, [$Ca^{2+}$] = 0, 0.8, 1,6, 2.0, 2.4, 2.8, 3.2, 6.0, 12.0 µM, $\lambda_{ex}$ = 359 nm.

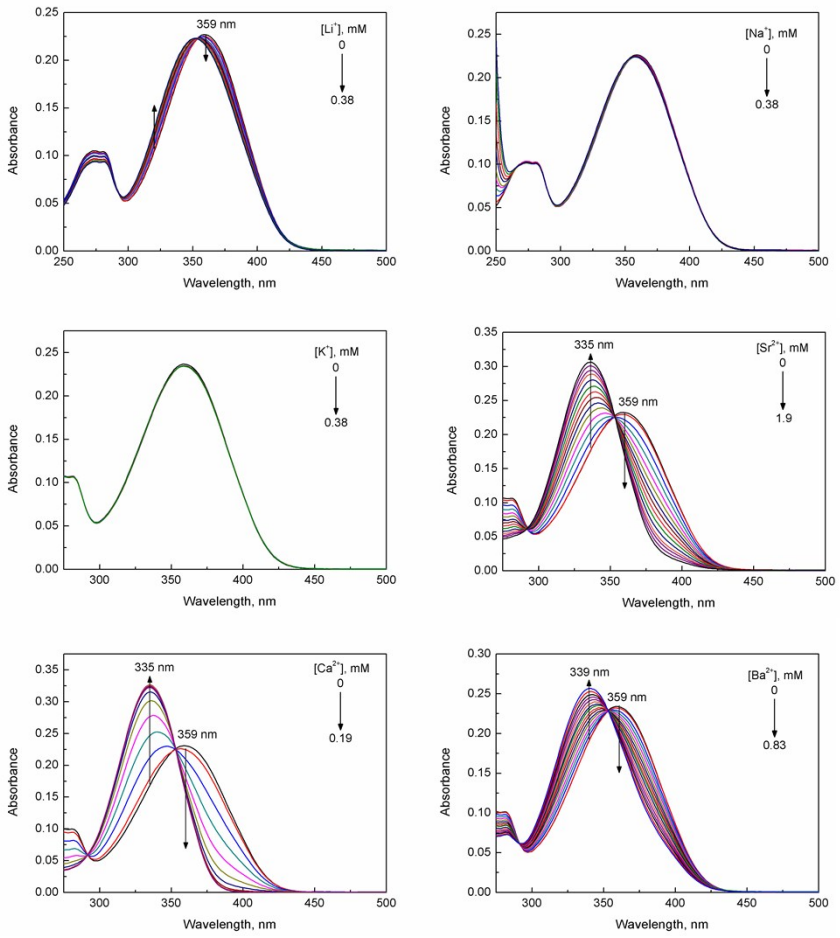


**Figure S2.** Absorption spectra of PyB-Aza in the presence of increasing concentrations of different metallic cation (perchlorate salt) in MeCN.

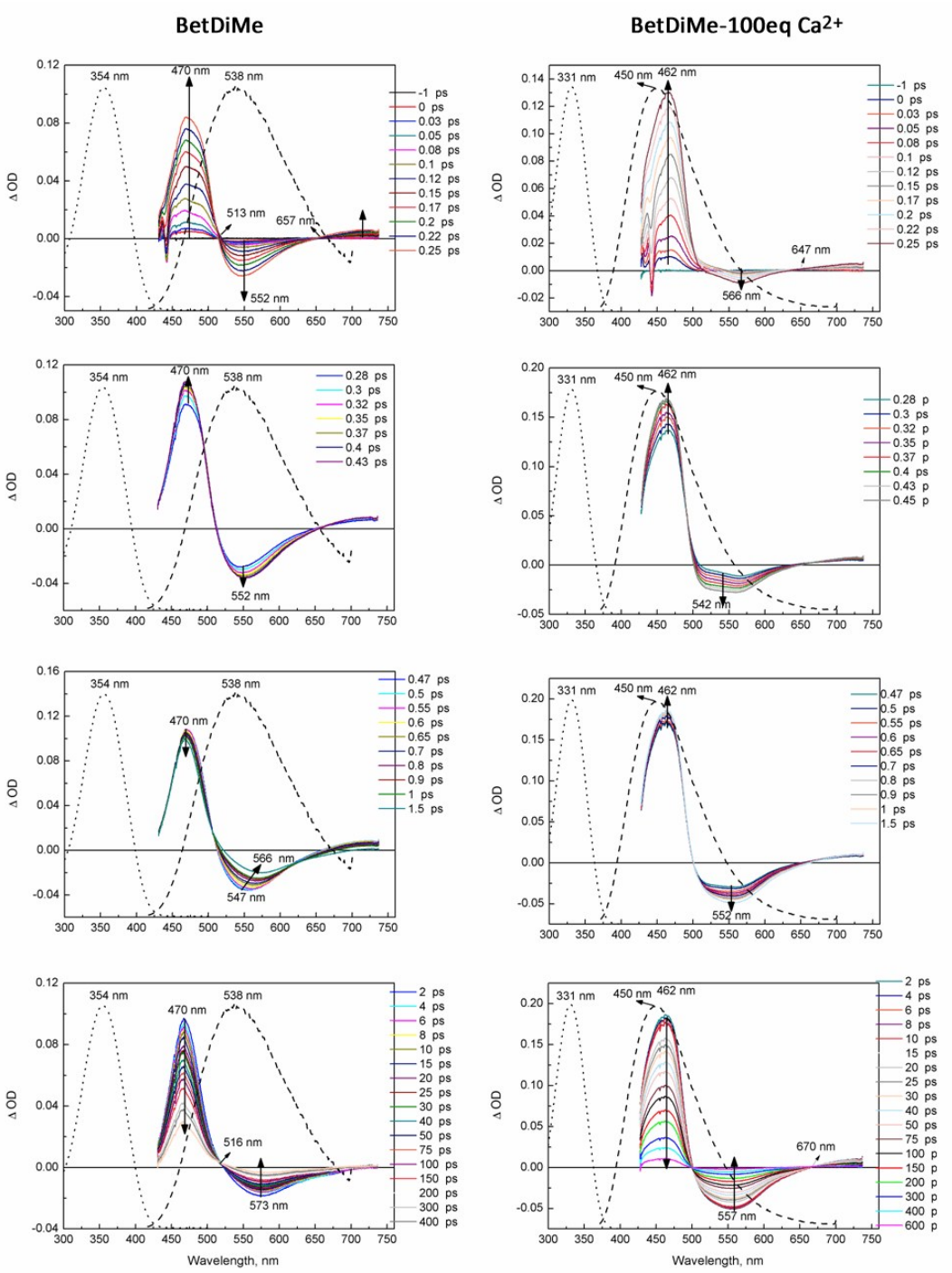


**Figure S3** (right) Femtosecond transient absorption spectra of 50 µM of PyB-DiMe in ACN following laser excitation at 320 nm, for distinct temporal windows (left) similar data with additional 100 eq of Ca2+ salt in the solution; Stationary absorption and emission spectra (dashed line) are indicated.

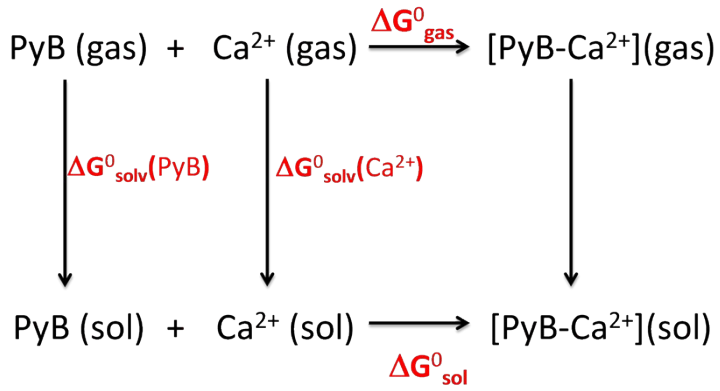


**Figure S4** Computational strategy to assess log K from DFT calculation

| No. | Solvents | ET(30) [kcal.mol$^{-1}$] | ε | *n* | α | β | π | $\lambda_{max}^{A}$ [nm] | $\nu^{A}$ [cm$^{-1}$] | $\lambda_{max}^{F}$ [nm] | $\nu^{F}$ [cm$^{-1}$] | $\Phi_F$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Toluene | 33.9 | 2.38 | 1.494 | 0 | 0.11 | 0.54 | 386 | 25907 | 534 | 18727 | 0.23 |
| 2 | THF | 37.4 | 7.58 | 1.405 | 0 | 0.55 | 0.58 | 380 | 26316 | 533 | 18762 | 0.19 |
| 3 | DCM | 40.7 | 8.93 | 1.421 | 0.13 | 0.1 | 0.82 | 367 | 27248 | 532 | 18797 | 0.20 |
| 4 | PhCN | 41.5 | 26.00 | 1.528 | 0 | 0.37 | 0.90 | 369 | 27100 | 529 | 18904 | 0.28 |
| 5 | Acetone | 42.2 | 20.56 | 1.356 | 0.08 | 0.43 | 0.71 | 365 | 27397 | 533 | 18762 | 0.15 |
| 6 | DMF | 43.2 | 36.71 | 1.428 | 0 | 0.69 | 0.88 | 365 | 27397 | 528 | 18939 | 0.18 |
| 7 | MeCN | 45.6 | 35.94 | 1.341 | 0.19 | 0.4 | 0.75 | 360 | 27778 | 533 | 18762 | 0.12 |
| 8 | BuOH | 50.2 | 17.8 | 1.399 | 0.84 | 0.84 | 0.47 | 357 | 28011 | 511 | 19569 | 0.27 |
| 9 | EtOH | 51.9 | 24.55 | 1.359 | 0.86 | 0.75 | 0.54 | 353 | 28329 | 512 | 19531 | 0.21 |
| 10 | MeOH | 55.4 | 32.66 | 1.326 | 0.98 | 0.66 | 0.6 | 347 | 28818 | 509 | 19646 | 0.17 |
| 11 | $H_2O$ | 63.1 | 78.36 | 1.333 | 1.17 | 0.47 | 1.09 | 341 | 29325 | 512 | 19531 | 0.04 |

**Table S1.** Photophysical data of **PyB-Aza** in different solvents, solvent properties (Dimroth-Reichardt $E_T(30)$ parameter, dielectric constant ε, refractive index *n*, Kamlet-Taft α, β and $\pi^*$ parameters) are given; fluorescence quantum yields were determined using Comarine 153 in EtOH ($\Phi = 0.53$) as a reference.[1]

| | Solvent NO. | Kamlet-Taft correlation coefficients | | | | |
|---|---|---|---|---|---|---|
| | | $\nu_0$ | *a* | *b* | *p* | $R^2$ |
| Absorption | 1-11 | 25130 ± 600 | 1690 ± 300 | 830 ± 620 | 1980 ± 660 | 0.86 |
| Fluorescence | 1-11 | 18675 ± 200 | 690 ± 90 | 390 ± 170 | -65 ± 180 | 0.93 |

**Table S2.** Corresponding Kamlet-Taft correlation coefficients obtained from the multiple linear regressions of solvatochromic data of **PyB-Aza**.

(1) Grabolle, M.; Spieles, M.; Lesnyak, V.; Gaponik, N.; Eychmuller, A.; Resch-Genger, U. *Anal Chem* **2009**, *81*, 6285.