Electronic Supplementary Information

Strong ion pair charge transfer interaction of 1,8-naphthalimide-bipyridinium conjugates with basic anions – Towards the development of new type turn-on fluorescent anion sensors

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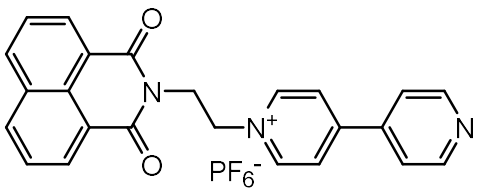
S1. Synthetic methods

Solvents, reagents and starting materials were obtained from commercial supplier and used without further purification. **NI** and **PiNi**[1,2] were prepared as previously described. The starting bromoetyl-naphthalimides **1**[3] and **2**[2] were prepared according to the literature. The NMR spectra were taken on a Bruker Avance DRX-500 or DRX-300 spectrometer with chemical shifts reported in ppm (the residual solvents were used as internal standards). The exact mass measurements were performed using a Q-TOF Premier mass spectrometer (Waters Corporation, 34 Maple St, Milford, MA, USA) using Electrospray ionization in positive mode.

For an overview of the synthesis of the napthalimide-viologen conjugates see Scheme 1 in the main article.

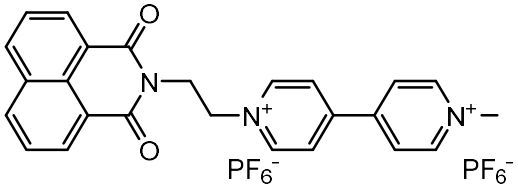
Synthesis of 4,4′-bipyridynium-1-[2-(1,8-naphthalimid-9-yl)ethyl] PF_6 (NIBP)



A solution of *N*-(2-bromoethyl)-1,8-naphthalimide (**1**, 0.75 g, 2.5 mmol) and 4,4'-bipyridine (1.56 g, 10 mmol) was refluxed in 30 ml acetonitrile for 48 hours. After cooling to room temperature, the product was filtered and washed with acetonitrile and with acetone 3 times. After drying, the bromide salt was

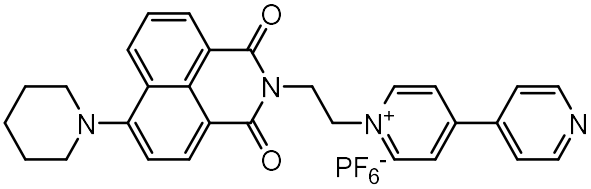
dissolved in 50 ml of hot water/methanol mixture (1:1 volume ratio) and NH_4PF_6 (1.63 g, 10 mmol) was added in 40 ml water. The white precipitate was filtered, washed with water thoroughly and dried to give 1.06 g white product as hexafluorophosphate salt. Yield: 82%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.36 (d, *J* = 6.5 Hz, 2H), 8.87 (d, *J* = 6.1 Hz, 2H), 8.62 (d, *J* = 6.4 Hz, 2H), 8.48 (d, *J* = 8.2 Hz, 2H), 8.41 (d, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 6.2 Hz, 2H), 7.86 (t, *J* = 7.8 Hz, 2H), 4.99 (br s, 2H), 4.66 (br s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.30, 152.95, 151.52, 146.64, 141.07, 135.14, 131.84, 131.36 (two overlapping signals), 128.07, 127.75, 125.47, 122.34, 60.00, 41.30 HRMS: calculated 380.1399 for $[M]^+$ $C_{24}H_{18}N_3O_2$ found: 380.1397.

Synthesis of 4,4′-bipyridynium-1-[2-(1,8-naphthalimid-9-yl)ethyl]-4’-methyl PF_6 (**NIV**)



To a solution of **3** (250 mg, 0.475 mmol) in 10 ml acetonitrile and 4 ml DMF was added methyl iodide (0.15 ml, 2.4 mmol). The mixture was stirred at reflux for 18 hours and cooled to room temperature, then 10 ml of acetone was added. The yellow diiodide salt was filtered and washed with acetone three times. The dried solid was dissolved in 15 ml water/methanol mixture (1:1 volume ratio) and NH_4PF_6 (619 mg, 3,8 mmol) was added in 15 ml water. The white precipitate was filtered, washed with water several times and dried to give 122 mg white product as di(hexafluorophosphate) salt. Yield 37%. ^{1}H NMR (300 MHz, CD_3CN) δ 9.02 (d, *J* = 6.3 Hz, 2H), 8.85 (d, *J* = 6.2 Hz, 2H), 8.49 (d, *J* = 7.3 Hz, 2H), 8.45 – 8.32 (m, 6H), 7.84 (t, *J* = 7.8 Hz, 2H), 5.02 (t, *J* = 5.4 Hz, 2H), 4.77 (t, *J* = 5.1 Hz, 2H), 4.41 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 164.44, 150.27, 149.39, 146.52, 146.37, 134.97, 131.77, 131.32, 128.13, 127.26, 126.98, 126.85, 122.01, 60.51, 48.63, 40.63. HRMS: calculated 540.1276 for $[M+PF_6^-]^+$ $C_{25}H_{21}N_3O_2PF_6$ found: 540.1278. Note that in the ESI-HRMS, fragmentation occured that produced *N*-methyl-4,4’-bipyridinium (**MB**) (calculated: 171.0917, found:171.0923 for $[M]^+$) and *N*-allyl-1,8-naphthalimide (calculated: 224.0712, found: 224.0712 for $[MH]^+$). See Section ’HRMS analysis’ for details.

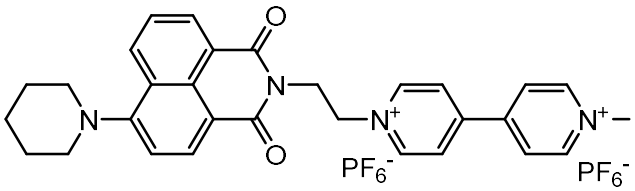
Synthesis of 4,4′-bipyridynium-1-[2-(4-piperidino-1,8-naphthalimid-9-yl)ethyl] PF_6 (**PiNI**)



A solution of *N*-(2-bromoethyl)-4-piperidinyl-1,8-naphthalimide (**2**, 434 mg, 1.12 mmol) and 4,4’-bipyridine (700 mg, 4.48 mmol) was refluxed in 25 ml acetonitrile for 48 hours. After cooling to room temperature, the product was filtered and washed with cold acetonitrile three times. After drying, 20 ml of water and 5 ml of methanol was added, and the mixture was filtered to remove impurities. To this solution was added NH_4PF_6 (730 mg, 4.48 mmol) in 5 ml water. The orange precipitate was filtered, washed with water thoroughly and dried to give 362 mg orange product as hexafluorophosphate salt. Yield: 53%. ^{1}H NMR (500 MHz, CD_3CN) δ 8.85 – 8.80 (m, 5H), 8.44 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.39 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 6.9 Hz, 2H), 7.75 (d, *J* = 6.3 Hz, 2H), 7.69 (t, *J* = 8.3, 7.4 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 4.90 (t, *J* = 5.5 Hz 2H), 4.68 (t, *J* = 5.5 Hz 2H), 3.22 (t, *J* = 5.3 Hz, 4H), 1.85 (p, *J* = 5.7 Hz, 4H), 1.70 (p, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.60, 164.91, 158.92,

155.46, 152.23, 146.67, 142.00, 133.80, 132.49, 132.07, 131.03, 127.04, 126.74, 126.67, 123.46, 122.80, 115.87, 115.69, 61.02, 55.30, 41.39, 26.97, 25.07. HRMS: calculated 463.2129 for $[M]^+$ $C_{29}H_{27}N_4O_2$ found: 463.2139.

Synthesis of 4,4′-bipyridynium-1-[2-(4-piperidino-1,8-naphthalimid-9-yl)ethyl]-4′-methyl PF_6 (PiNIV)



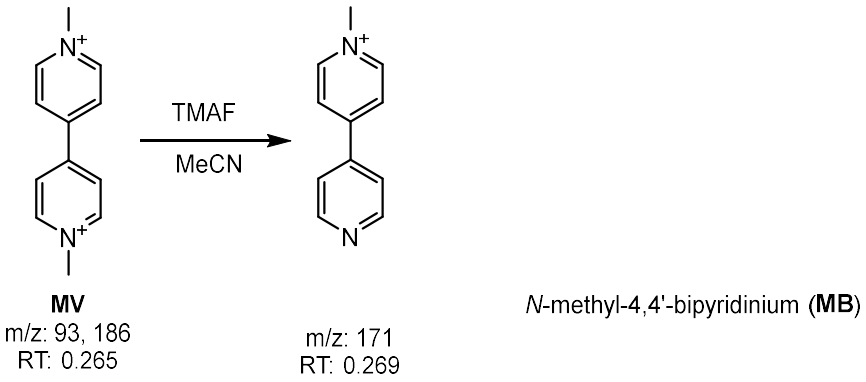
To a solution of **4** (100 mg, 0.164 mmol) in 5 ml acetonitrile was added methyl iodide (0.05 ml, 0.82 mmol). The mixture was stirred at reflux for 18 hours and cooled to room temperature, then evaporated to dryness. The crude product was dissolved in 5 ml methanol and 2 ml acetonitrile and poured to an aqueous solution of NH_4PF_6 (213 mg, 1.31 mmol in 20 ml water). The orange product was filtered and washed with plenty of water to give 93 mg orange solid as di(hexafluorophosphate) salt. Yield 74%. ^{1}H NMR (300 MHz, CD_3CN) δ 8.99 (d, *J* = 6.3 Hz, 2H), 8.84 (d, *J* = 6.3 Hz, 2H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 7.3 Hz, 1H), 8.37-8,31 (m, 5H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 4.99 (t, *J* = 5.4 Hz, 2H), 4.72 (t, *J* = 5.4 Hz, 2H), 4.40 (s, 3H), 3.24 (t, *J* = 5.2 Hz, 4H), 1.90 – 1.81 (m, 4H), 1.77 – 1.64 (m, 2H). ^{13}C NMR (75 MHz, CD_3CN) δ 165.62, 164.92, 158.91, 147.47, 147.34, 133.81, 132.49, 132.07, 131.02, 127.88, 127.82, 127.00, 126.63, 123.4343, 115.83, 115.66, 61.64, 55.26, 41.42, 30.90, 26.92, 25.02. HRMS: calculated 623.2005 for $[MPF_6]^+$ $C_{30}H_{30}N_4O_2$ found: 623.2014. Note that in the ESI-HRMS, fragmentation occured that produced *N*-methyl-4,4′-bipyridinium (calculated: 171.0917, found:171.0923 for $[M]^+$) and *N*-allyl-4-piperidin-1-yl-1,8-naphthalimide (calculated: 307.1441, found: 307.1447 for $[MH]^+$

S2. Degradation products

S2.1. LC-MS analysis

The RP-HPLC-UV/Vis-MS measurements were employed using a Shimadzu LCMS-2020 instrument applying a Gemini C18 column (100 x 2.00 mm I.D.) in which the stationary phase is 5 μm silica with a pore size of 110 Å. The chromatograms were detected by a UV-Vis diode array (220-800 nm) and an ESI-MS detector. The following linear gradient elution profile was applied, 0 min 0 % B; 1.0 min 100 % B; 3.5 min 100 % B; 4.5 min 0 % B; 5.0 min. 0 % B) with eluent A (2 % HCOOH, 5 % MeCN and 93 % water) and B (2 % HCOOH, 80 % MeCN and 18 % water).

According to the LC-MS measurements, the main degradation products arose from the dealkylation of the bipyridinium on both positively charged nitrogen. The demethylation could be easily followed due to the appearance of the corresponding *N*-alkyl-bipyridinium derivative. The *N*-dealkylation of the viologen close the naphthalimide moiety resulted in *N*-methyl-bypiridinium (**MB**) and multiple products containing the fluorophore. The overview of the reactions and chromatograms can be seen in Schemes S1-S3and Figs. S2-S4.



Scheme S1. Degradation of **MV**

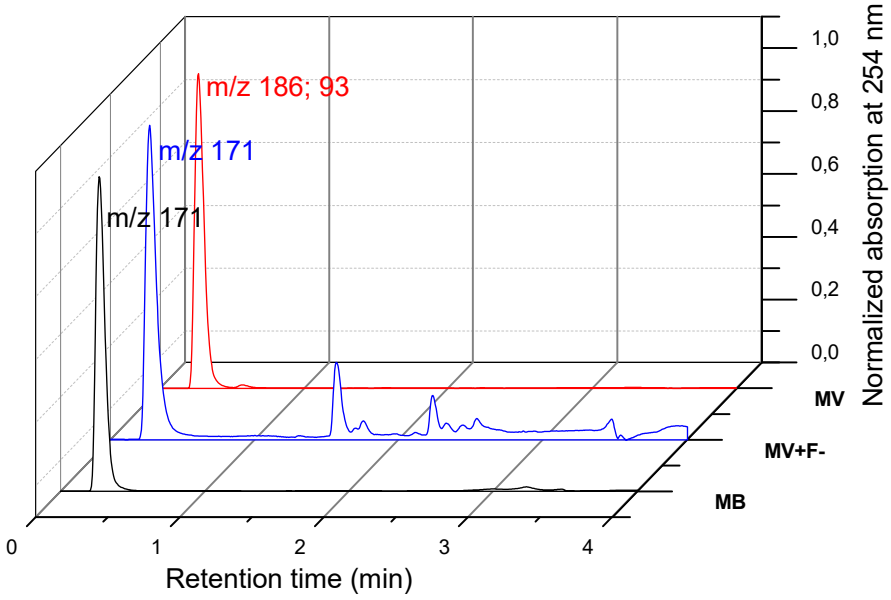
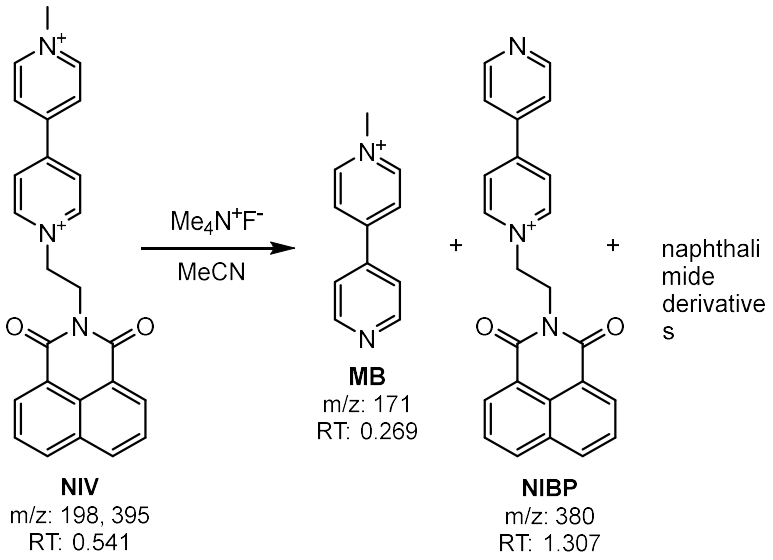


Figure S1. LC-MS traces of **MV**, **MV+fluoride** and **MB**



Scheme S2. Degradation of **NIV**

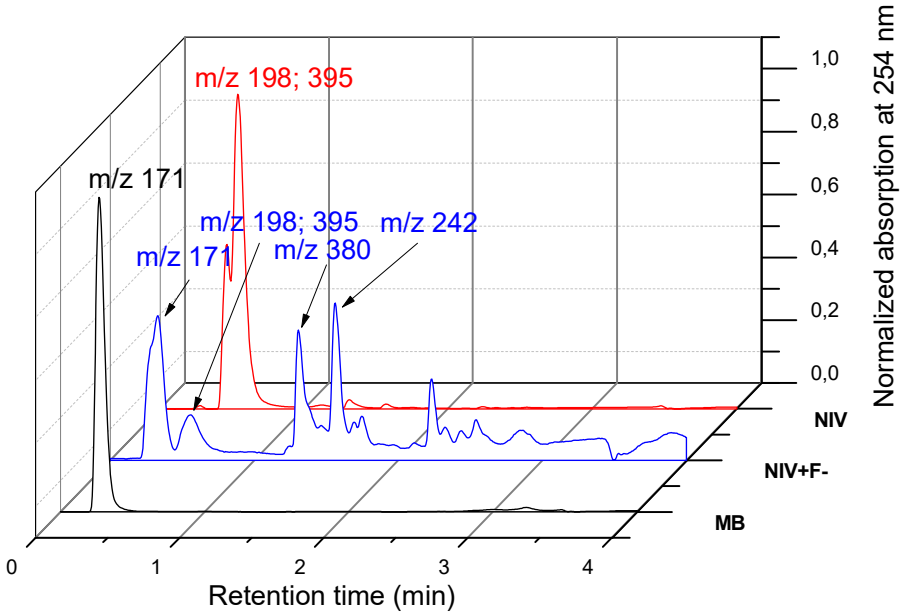
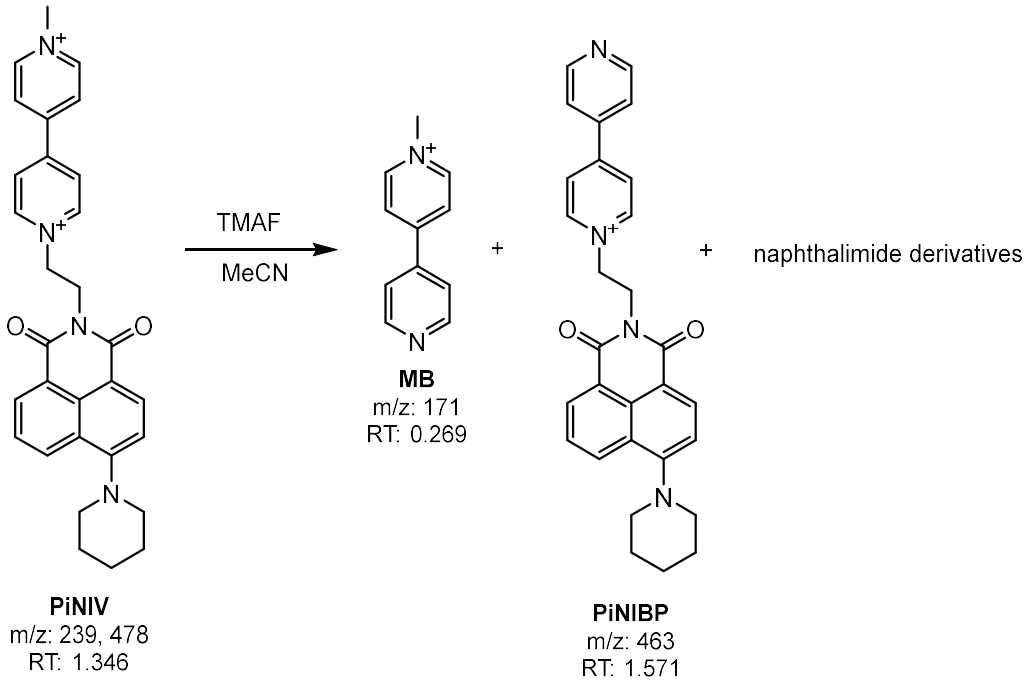


Figure S2. LC-MS traces of **NIV**, **NIV+fluoride** and **MB**



Scheme S3. Degradation of **PiNIV**

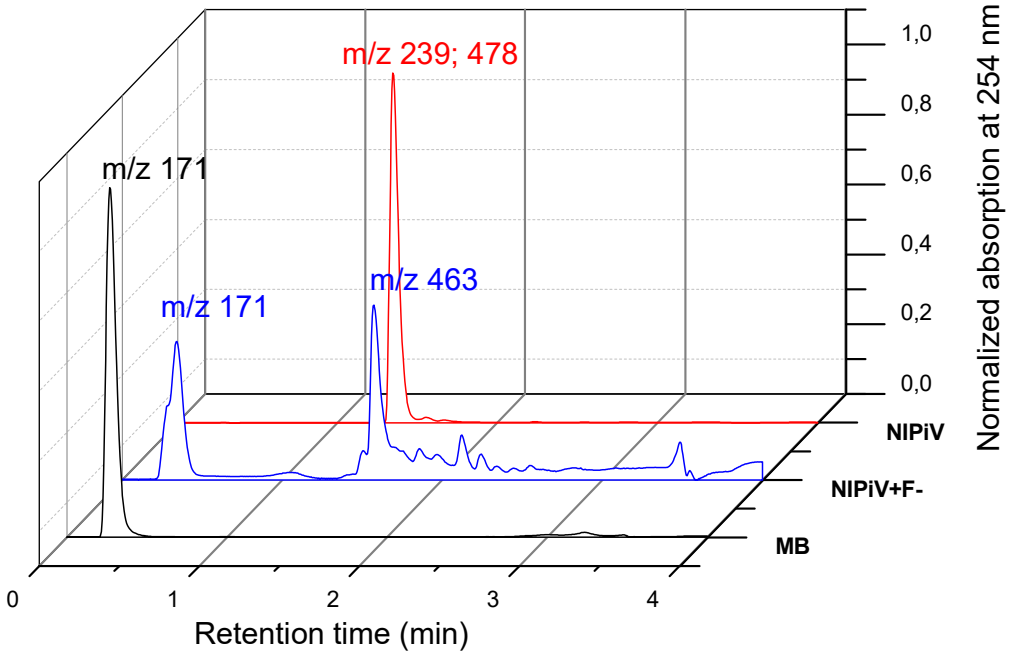
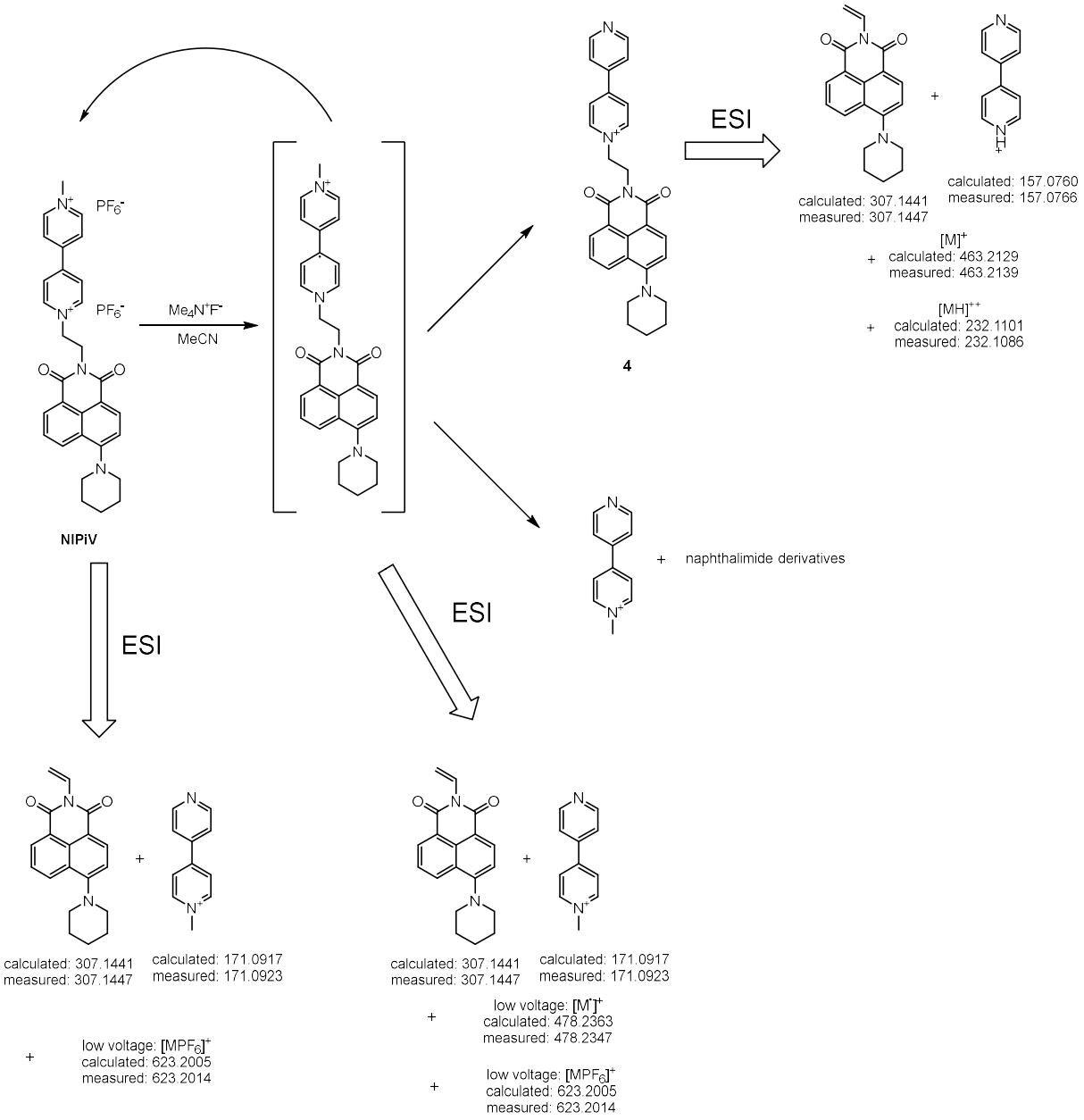


Figure S3. LC-MS traces of **PiNIV**, **PiNIV+fluoride** and **MB**

S. 2. 2. HRMS analysis

The exact mass measurements were performed using a Q-TOF Premier mass spectrometer (Waters Corporation, 34 Maple St, Milford, MA, USA) using electrospray ionization in positive mode.

The decomposition reactions were further studied using high resolution mass spectrometry with electrospray ionization (ESI). Interestingly, all the viologen derivatives showed degradation in the ESI-HRMS ion source, the identified derivatives were also dealkylated products and allyl-naphthalimides. Upon addition of TMAF, we could also observe the product of the demethylation reaction just as in the case of the LCMS analysis. Scheme S4 shows the reaction of **PiNIV** with TMAF.



Scheme S4. Potential reactions in the ESI-HRMS and degradation of **PiNIV** upon addition of TMAF

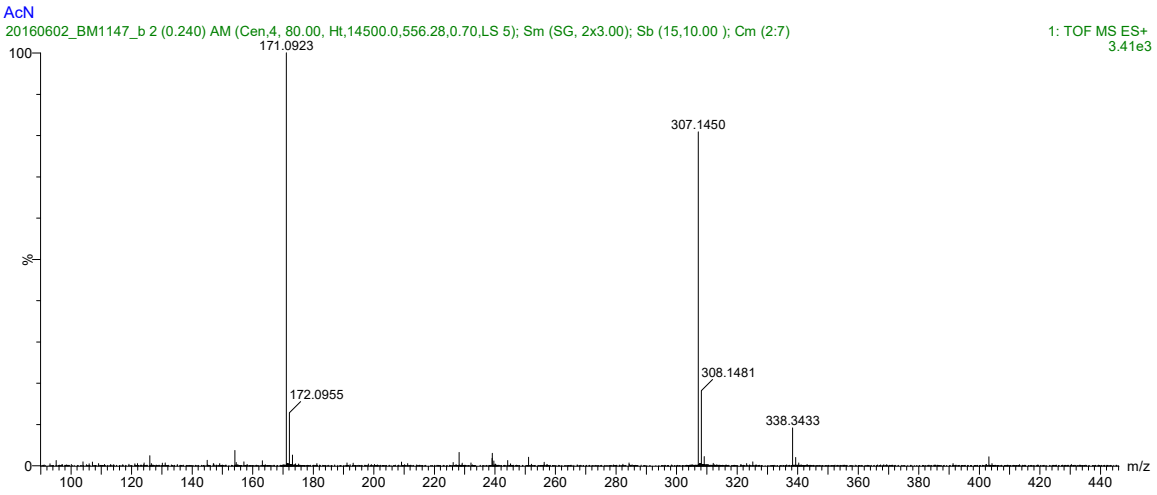


Figure S4. HRMS mass spectrum of **PiNIV**

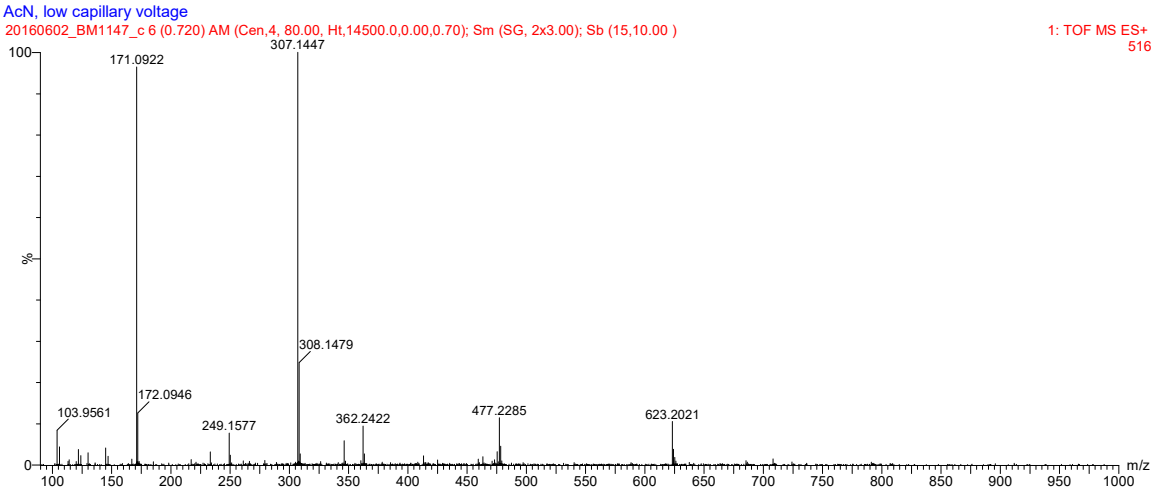


Figure S5. HRMS mass spectrum of **PiNIV** using low capillary voltage

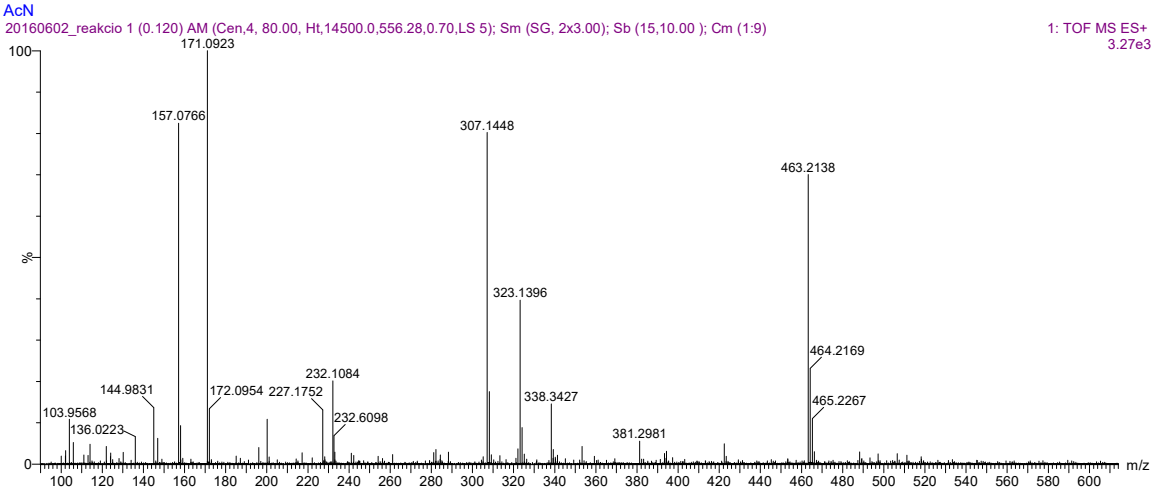
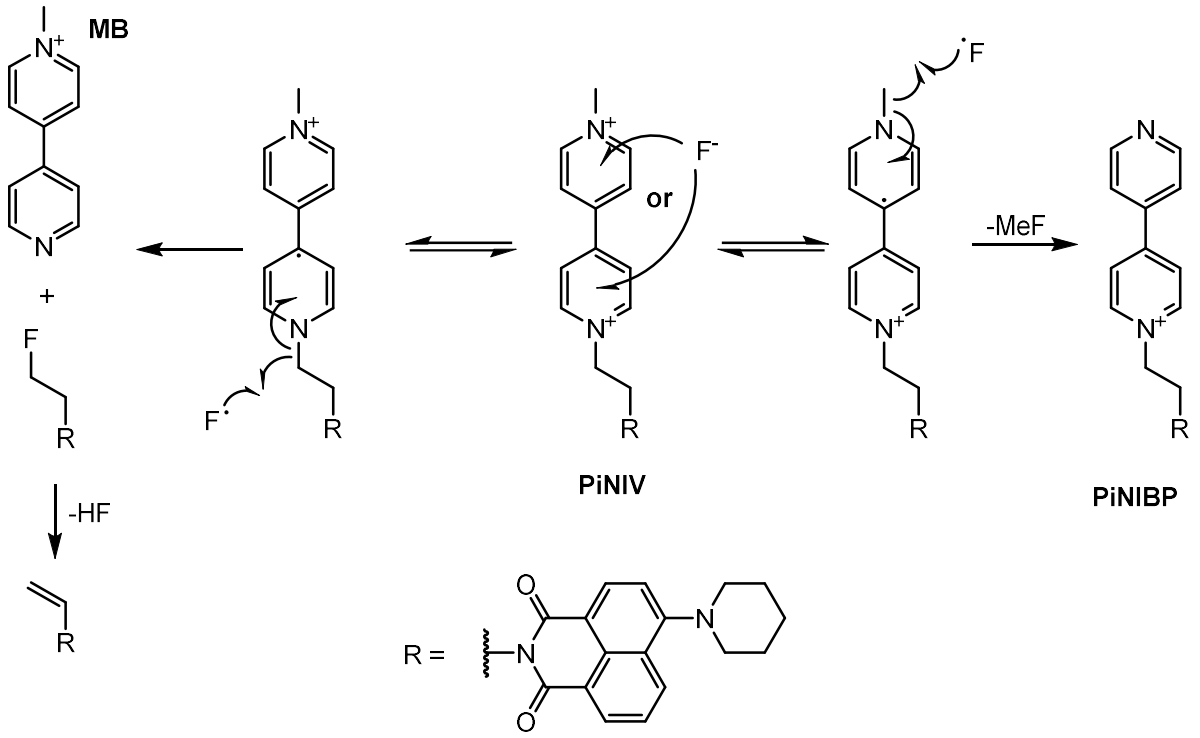


Figure S6. HRMS mass spectrum of **PiNIV** upon addition of fluoride

S 2. 4. Reaction mechanism



Scheme S5. Potential reaction mechanism and degradation pathway of **PiNIV** (as an example) by fluoride anion

It is known in the literature that in strongly basic solutions viologens pass through a dealkylation reaction.[4] Our results suggest a reaction mechanism in which there is radical intermediate formed via a complete electron transfer from the anion to the viologen.[5] The as-formed radical cations can either revert to the original dication V^{2+} or degrade by the strong oxidant radical fluorine or other species. The presence of the dealkylated products in the mixtures allows us to suggest a potential degradation pathway which involves the heterolytic breaking of the C-N bond. This results in the formation of a stable bipyridinium cation and the corresponding fluoride (Scheme S5).

S3. Cyclic voltammetry

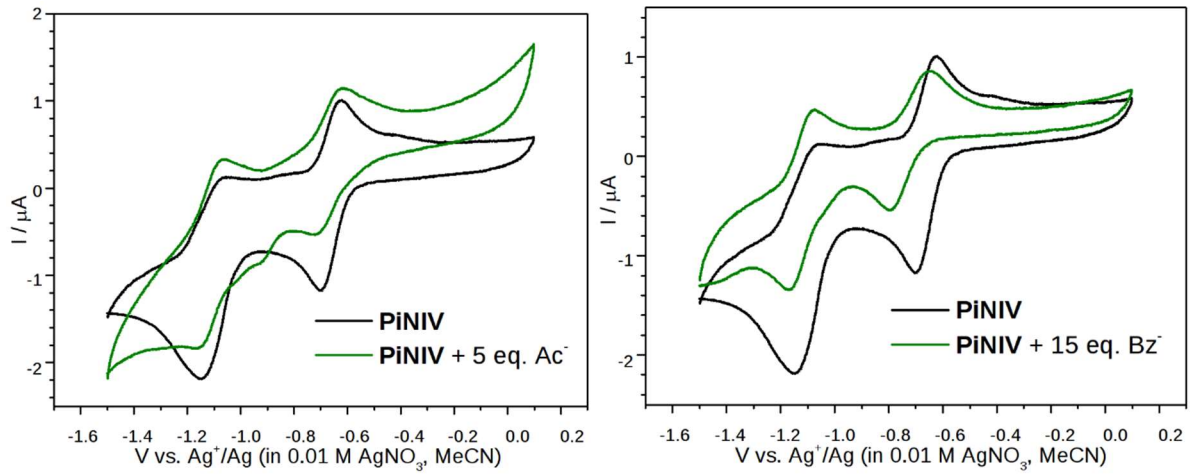


Figure S7. Cyclic voltammograms of **PiNIV** in 0.2 mM acetonitrile solutions in the absence and in the presence of 5 eq. Ac^- and 15 eq. BzO^- ions.

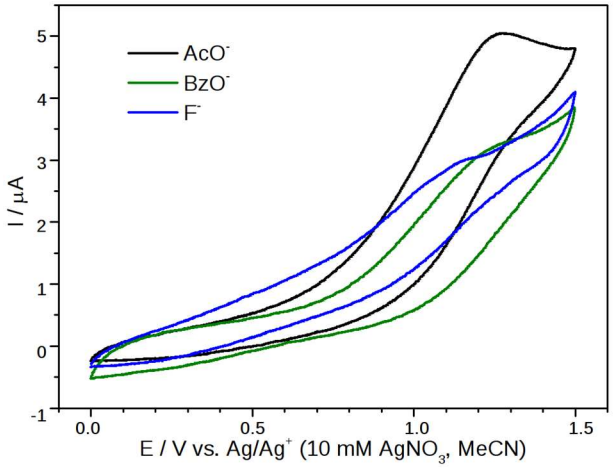


Figure S8. Cyclic voltammograms of TMA fluoride, TBA acetate and TBA benzoate in 0.2 mM acetonitrile solutions.

References

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(2) D. Wang, X. Zhang, C. He, C. Duan, *Org. Biomol. Chem.,* 2010, ***8***, 2923.

(3) S. U. Hossain, S. Sengupta, S. Bhattacharya, *Bioorganic Med. Chem.* 2005, ***13***, 5750-5758.

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