Influence of the Aromatic Moiety on Gas Phase Reactions of Heptamethine Cyanine Dyes Using Femtosecond-Laser-Pulse Induced Photodissociation

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Materials and Methods

- Stability and fragmentation pathways of heptamethine cyanine dyes with indole moieties: benzo[e]indole (ICG) and indole (IR 746) (figure 1).
- Dye molecules contain two butane-1-sulfonate chains and coordinate up to two monovalent cations.
- Different alkali metal ion adducts formed by dissolving the corresponding alkali metal salt together with the analyte in a mixture of MeOH/H_2O (1:1) with 0.2 % formic acid. Employed salts: NaCl, CsI, RbBr and KCl.

Experimental

- Mass spectrometer: APEX III Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonik, Bremen), 7.05 T, Apollo^{TM} ESI-source.
- Photodissociation (PD): femtosecond laser system (150 fs pulse duration), approx. 790 nm, Ti:sa laser as seed laser (Ti-Light, Quantronix, USA) pumped by a cw-Nd:YAG laser system (Opus 5W, Laser Quantum Inc., USA). A home-built shutter for the control of irradiation time.

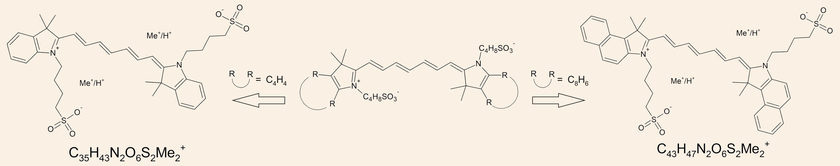


Fig. 1: Structures of the molecular anion (MA) of IR 746 (left) and indocyanine green (right) with metal cations (Me^+) or protons (H^+). Basic structure (center) is used in the following.

Conclusions

- Aromatic moieties (indole and benzo[e]indole) do not lead to major differences in the fragmentation products.
- Applied energy does not exceed the threshold for decomposition of aromatic core structure.
- Different intensity distribution of fragment peaks for ICG and IR 746.
→ The metal cations are coordinated by aromatic moieties as well.
- Loss of butane-1-sulfonate chain, presumably as the cyclic sulfonic ester 1,4-butanesultone.
→ Major fragmentation pathway.
- Green group: when two metal cations compete, higher fragment intensity for coordination of larger cation.
→ Better coordination of alkali metal ions with larger radius.

Results

IR 746

- Less intense fragmentation and intensity loss of the molecule peak for IR 746 than ICG.
→ Weaker absorption at 790 nm (In MeOH λ_{max}(IR 746)≈746 nm vs. λ_{max}(ICG)≈810 nm).
- Loss of methyl radical exclusively observed for the adducts with Na+K and Na+Cs.

- Selected PD-spectra of alkali metal ion adducts of both dyes with two mixed metal ions were compared (figure 2&5).
- Similar fragmentation pattern for different metal adducts in most cases. In figure 2, 3, 4 and 5 the analogue fragments are marked with the same colour. The assumed structures are shown in scheme 1.
- HIgh intensity for loss of butane-1-sulfonate chain in all spectra. Occurance of cyclic sulfonic ester 1,4-butanesultone with a metal cation only for some Cs adducts at very low intensities (not marked).
- Red/brown group of peaks (figure 2&5): abundance of fragments $C_{14}H_{18}NSO_3Me_2^+$ (IR 746) low, whereas the intensities of $C_{18}H_{20}NSO_3Me_2^+$ (ICG) nearly equal to intensities of $C_{39}H_{39}N_2SO_3Me_2^+$ → coordination of two cations depends on size of aromatic moiety.
  - Green group of fragments: intensities of peaks with the same molecular formula (linked with dashed lines in figure 3 and 4) are higher for adducts with larger metal cations.
  - In the PD spectra of IR 746 (figure 3), only the fragment $C_{20}H_{23}NSO_3Me^+$ occurred with both alkali metals. Other fragments appeared at low intensities and always contained the larger metal cation.

ICG

- Loss of two methyl radicals with very low intensities, presumably from the methyl groups at the five-membered heterocycles.

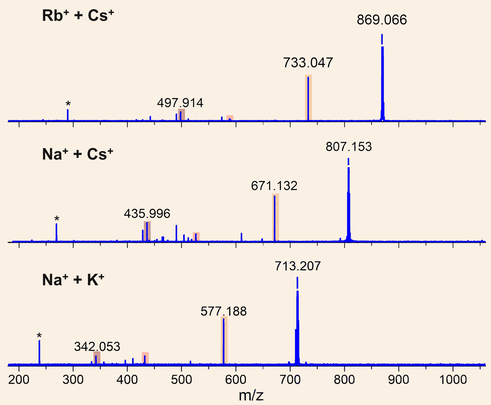


Fig. 2: PD spectra of IR 746 adducts with different combinations of alkali metal ions. The signals marked with an asterisk are the triple frequencies of the isolated adducts.

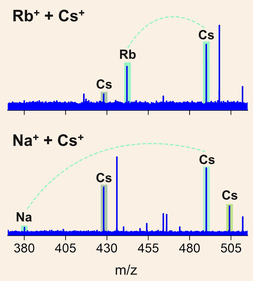
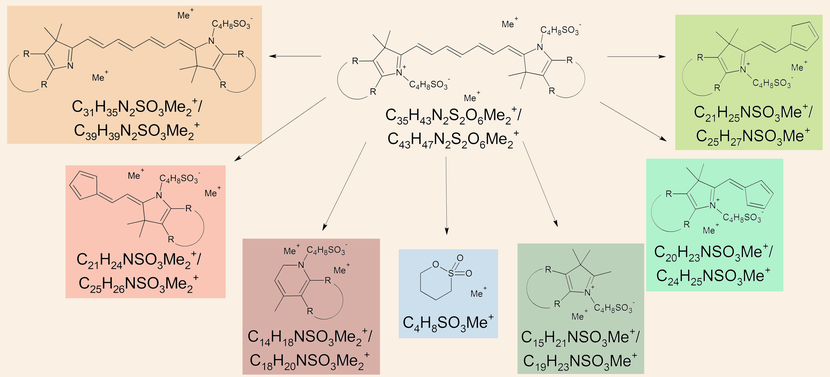


Fig. 3: Excerpt of figure 2 with marked fragments containing one metal cation.



Scheme 1: Possible photofragmentation reactions. Fragments containing two metal ions are marked in red and brown colours (left) and those with one metal ion in green colours (right). The metal ion adduct of the butane-1-sulfonate chain is marked with blue colour (center).

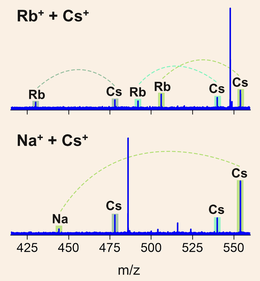


Fig. 4: Excerpt of figure 5 with marked fragments containing one metal cation.

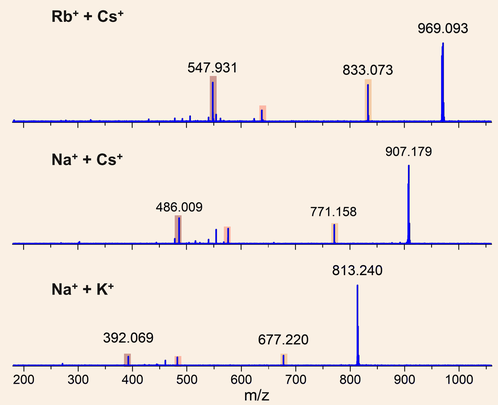


Fig. 5: PD spectra of ICG adducts with different combinations of alkali metal ions.