FP7-Fission-2012-323-282

Radiolytic and hydrolytic stability of the highly selective nitrogen donor ligands $CyMe_4BTBP$ and $CyMe_4BTPhen$

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SACSESS international workshop, Warsaw
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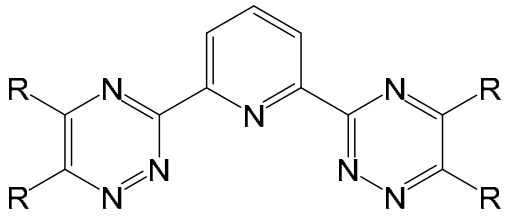
[3] Institute of Inorganic Chemistry, Rež, Czech Republic

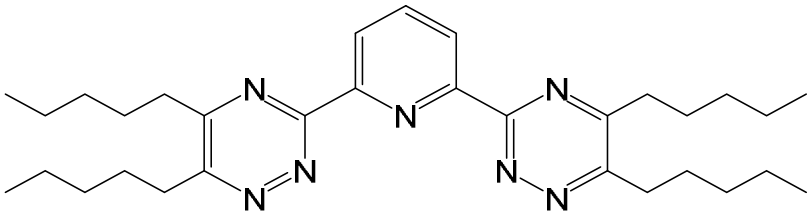
Evolution of nitrogen donor ligands

For separation of Actinides(III) from Lanthanides(III)



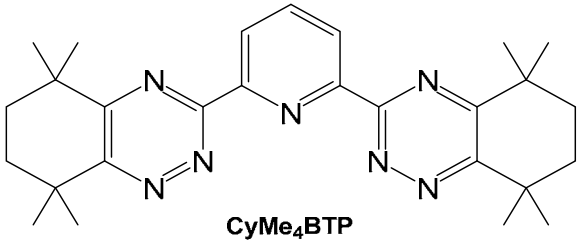
BTP-general structure

- ☺ High selectivity
- ☺ Tridentate arrangement of soft donor nitrogen atoms
- ☺ No synergist necessary – nitrate as counterion sufficient



C5-BTP

- ☺ High selectivity
- ☺ Large alkyl substituents
  ⇨ solubility of the protonated form in the aqueous phase is minimized
- ☹ weak radiolytic stability
- ☹ weak hydrolytic stability



$CyMe_4BTP$

BATPs – annulated alkyl substituents

- ☺ Branching of alkyl groups protects against radiolysis
- ☺ Much higher radiolytic stability
- ☹ Clearly increased D-values with addition of the $CyMe_4$ – group to ~5000
  ⇨ back extraction (stripping) not possible

Mincher, B.J. et al. Solvent Extr. Ion Exch. **2010**, *28* (4), 415-436.
Ekberg, C. et al. Radiochim. Acta **2008**, *96* (4-5), 225-233.
Case, F.H. J. Heterocycl. Chem. **1971**, *8* (6), 1043-1046.

Evolution of nitrogen donor ligands

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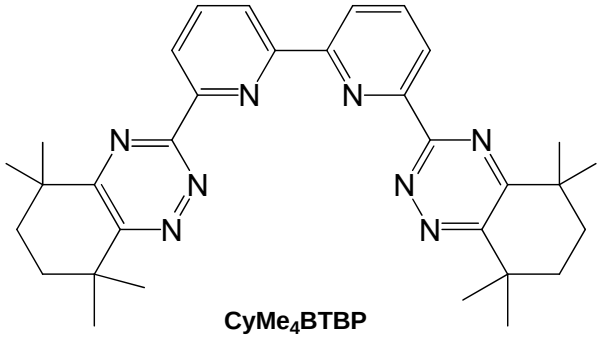
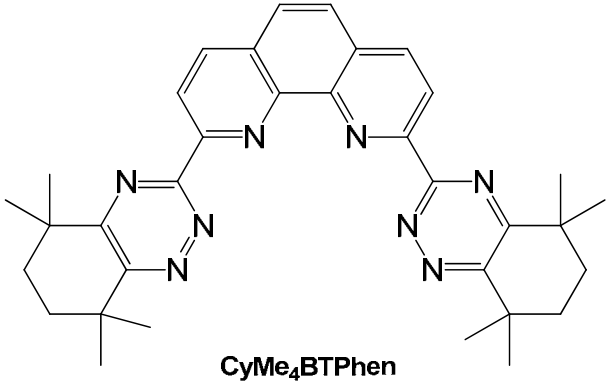


CyMe$_4$BTBP

- ☺ High selectivity
- ☺ Higher hydrolytic stability
- ☺ Successful processes were developed
- ⇨ Current reference molecule @ SACSESS
- ☹ Slow kinetics



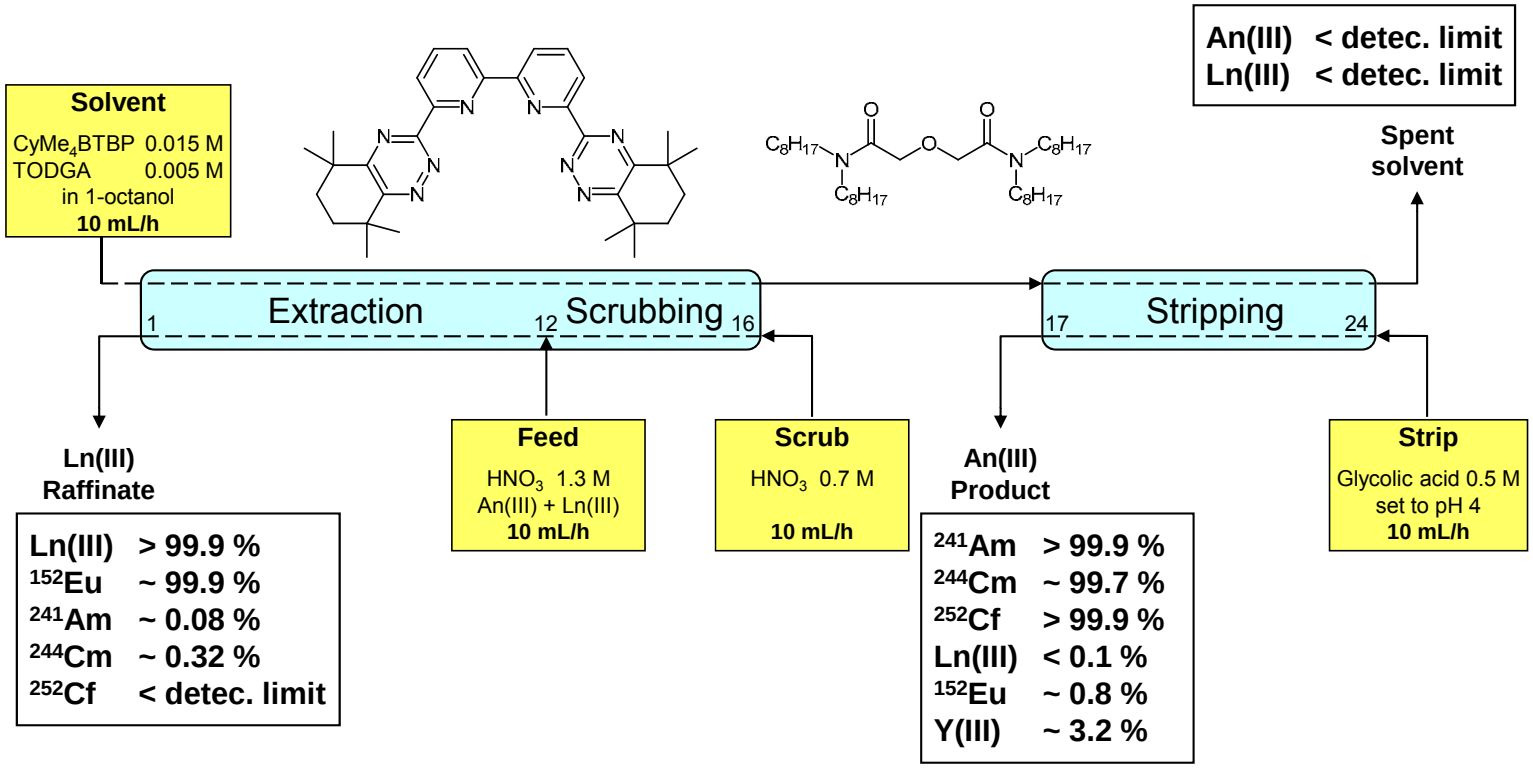
CyMe$_4$BTPhen

- ☺ High selectivity
- ☺ Fast kinetics
- ☺ Promising alternative investigated @ SACSESS

Mincher, B.J. et al. Solvent Extr. Ion Exch. **2010**, *28* (4), 415-436.
Ekberg, C. et al. Radiochim. Acta **2008**, *96* (4-5), 225-233.
Geist, A. et al. Solvent Extr. Ion Exch. **2006**, *24* (4), 463-483.
Lewis, F.W. et al. J. Am. Chem. Soc. **2011**, *133* (33), 13093-13102.

SANEX process

- Successful use of $CyMe_4BTBP$ in a spiked lab-scale demonstration
  - High recovery of An(III)
  - Good separation from Ln



- Successful performed hot test
- Radiolytic and hydrolytic stability required

Modolo, G. et al. Radiochim. Acta **2013**, *101* (3), 155-162.
Magnusson, D. Solvent Extr. Ion Exch. **2009**, *27* (1), 26-35.

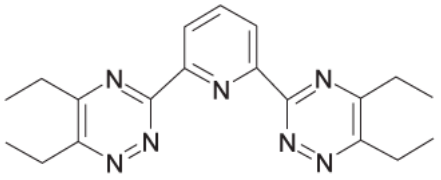
Radiolysis of alcohols

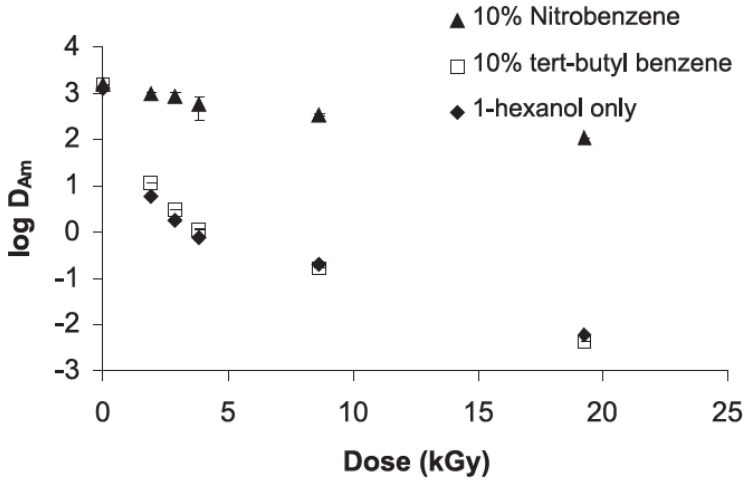
a short review on literature data

- Commonly high excess of solvent
- Mainly radiolysis of solvent
- Indirect radiolysis of ligand molecules likely
- Radiolysis of alcohols is well described

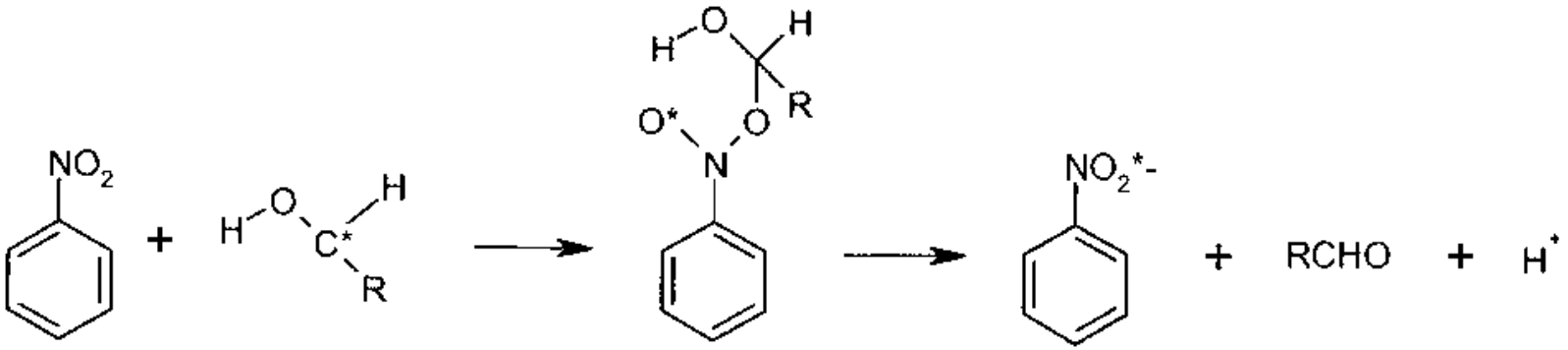
$$RCH_2OH + \gamma \rightarrow [RCH_2OH]^*$$
$$[RCH_2OH]^* \rightarrow e^-_{solv} + [RCH_2OH]^+$$
$$[RCH_2OH]^+ + \gamma \rightarrow RC^{\bullet}HOH + H^+$$

- Indirect radiolysis of α-hydroxy octyl radical
- Protection against radiolysis is described





1.8 mmol/L tE-BTP
0.99 mol/L $NaClO_4$, 0.01 mol/L $HClO_4$, ^{241}Am tracer



Nilsson, M. et al. Radiochim. Acta **2006**, *94* (2), 103-106.
Mincher, B.J. et al. Appl. Radiat. Isot. **1994**, *45* (8), 879-887.

Radiolysis of $CyMe_4BTBP$

selected previous work

Radiolysis of $CyMe_4BTBP$ was studied by Magnusson et al.:

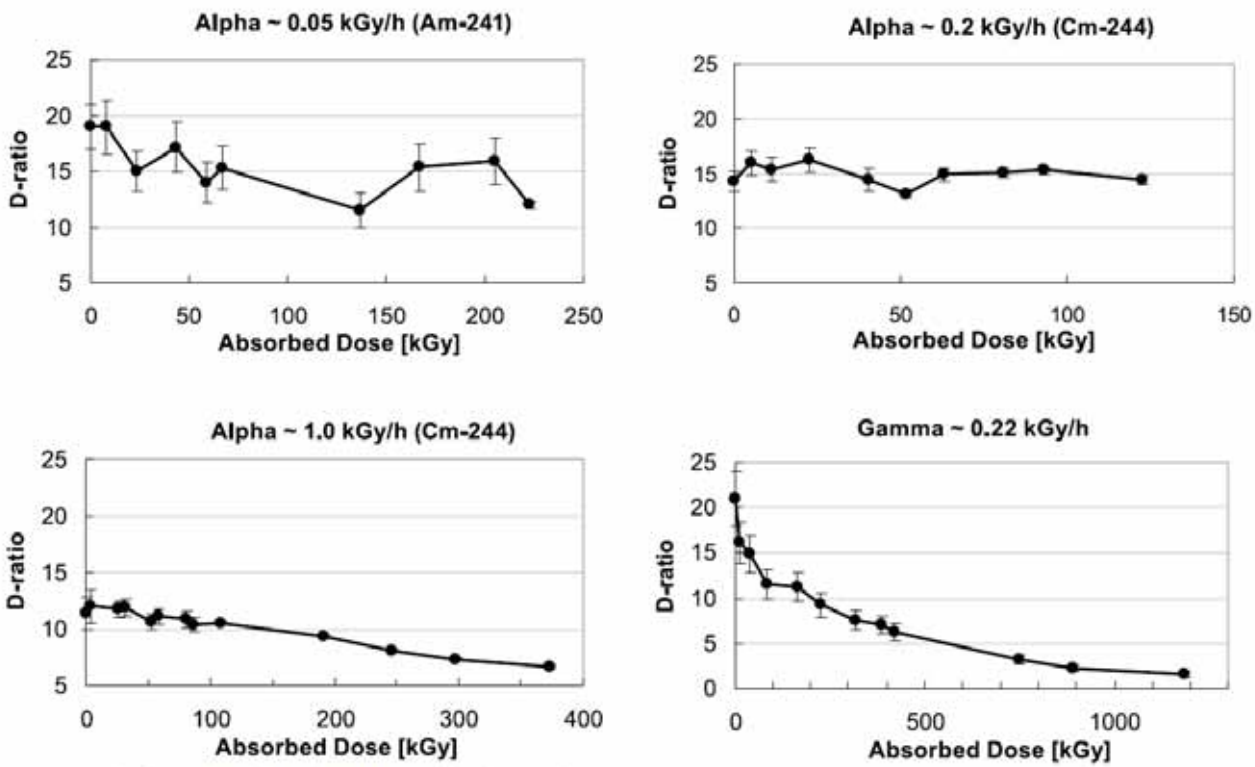


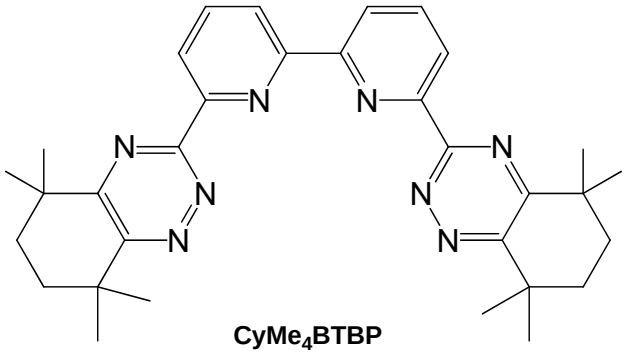
Fig. 4. Results from the alpha and gamma radiolysis experiments.

0.25 mol/L DMDOHEMA in 1-octanol, equilibrated in 1 mol/L HNO3: 15 mmol/L $CyMe_4BTBP$
1 mol/L HNO_3

- Radiolysis of $CyMe_4BTBP$ was observed mainly by γ radiolysis
- Smaller effect of α radiolysis

Magnusson, D. et al. Radiochim. Acta **2009**, *97* (9), 497-502.

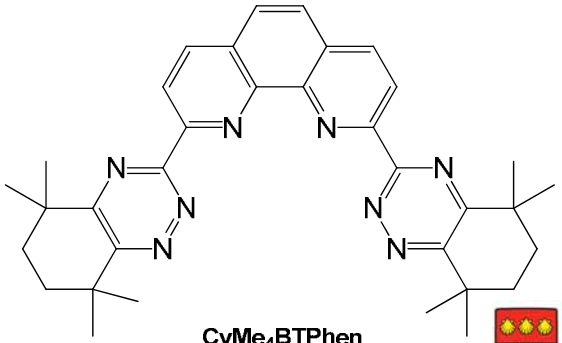
Investigated molecules in this work



CyMe$_4$BTBP

cis-/ trans- conformation possible

trans-conformation favored, barrier to overcome: ~12 kcal/ 50kJ mol^{-1}



CyMe$_4$BTPhen

New molecule investigated in ACSEPT

cis-locked molecule
"preorganized for metal binding"

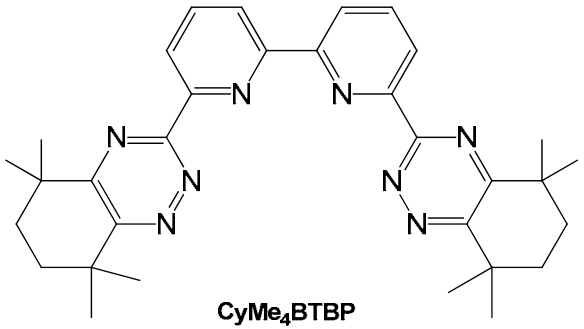
Higher D-values than CyMe$_4$BTBP

- Direct comparison is not available up to now
- CyMe$_4$BTBP as reference molecule of European research
- Safety aspects studied in SACSESS
  - Hydrolytic stability
  - Radiolytic stability

Lewis, F.W. et al. J. Am. Chem. Soc. **2011**, *133* (33), 13093-13102.
Lewis, F.W.; Harwood, L.M.; Hudson, M.J.; et. al.; Inorg. Chem. **2013**, *52*, 4993-5005

Radiolysis experiments

@ CHALMERS University, Gothenburg, Sweden

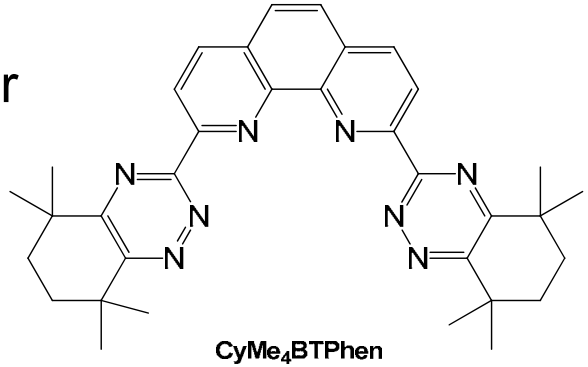


CyMe$_4$BTBP

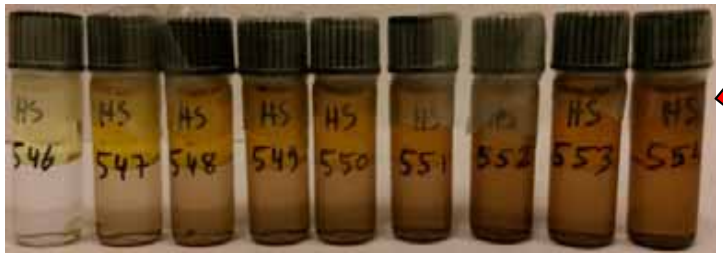
Comparative experiments under „process typical“conditions

10 mmol/L ligand in 1-octanol

different [HNO_3] up to 4 mol/L



CyMe$_4$BTPhen

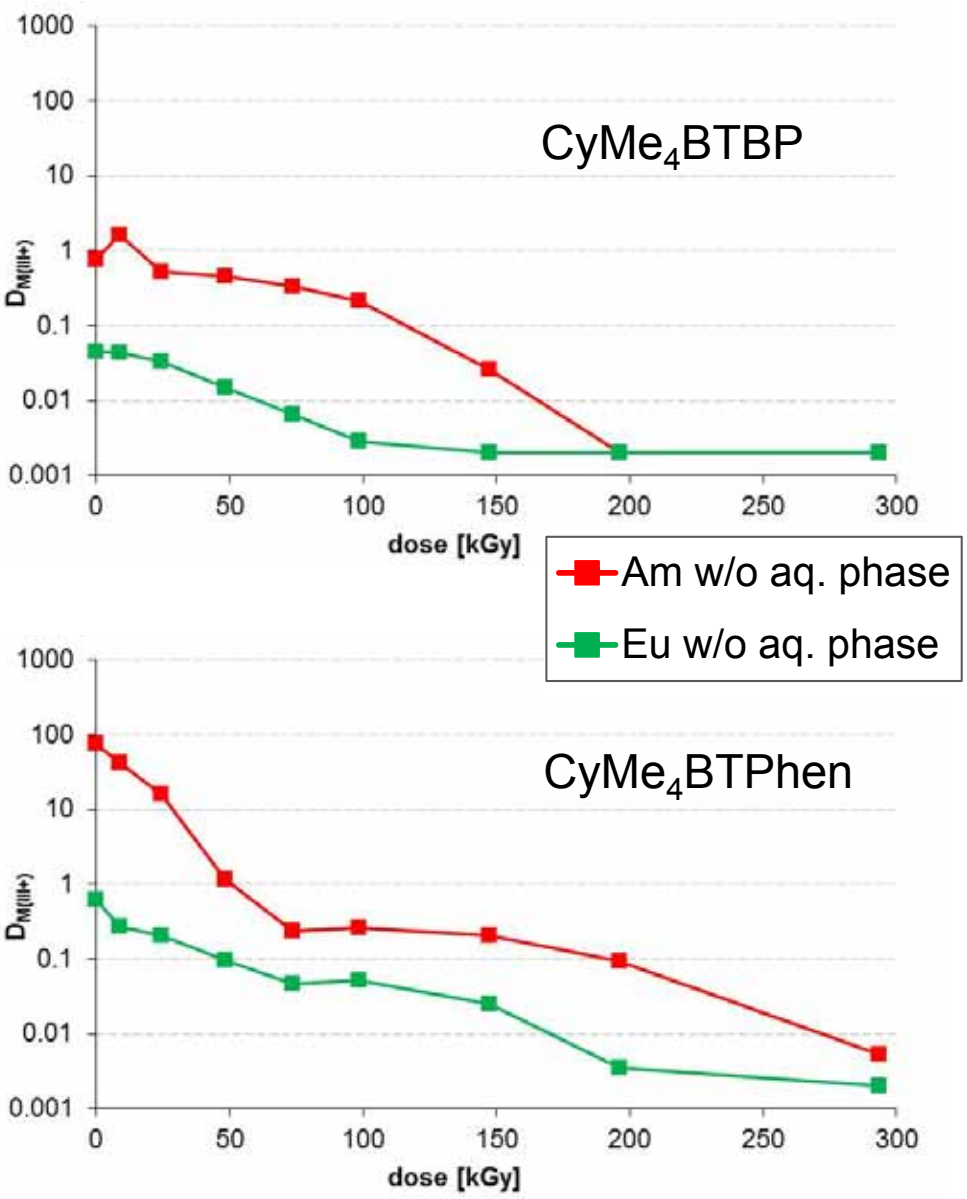


absorbed doses: 0 to 300 kGy
dose rate: ~ 9.5 kGy/h

After irradiation:

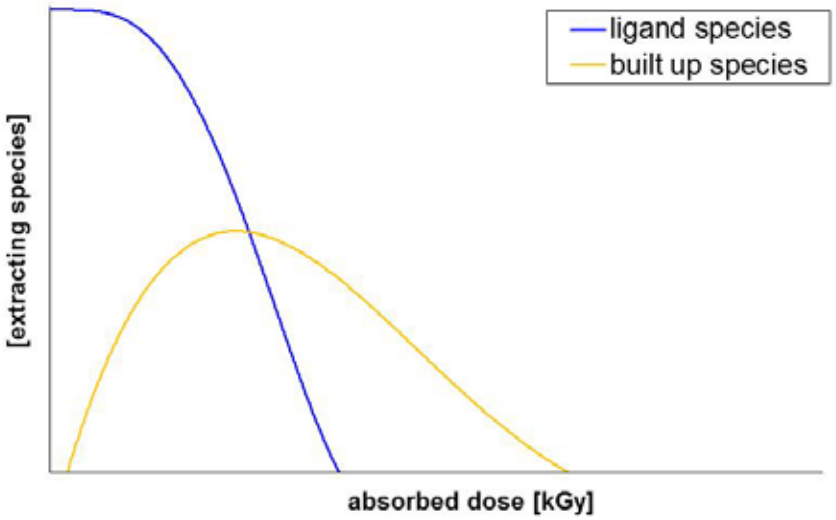
- phase separation
- analytics
  - Solvent extraction
  - HPLC - MS

Liquid-liquid extraction



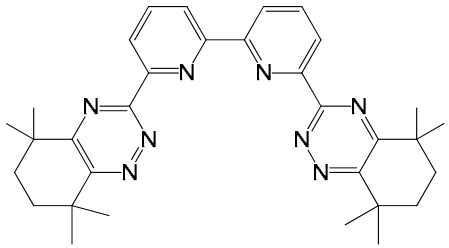
Org.: irrad.10 mmol/L ligand in 1-octanol
Aq.: fresh 1.0 mol/L HNO_3 + $^{241}Am/^{152}Eu$ tracer

- Decreasing D-values with increasing absorbed dose
- $CyMe_4BTPhen$ shows some kind of 'two-step' decreasing
- Hypothesis: ligand species decreases, second species is built up and destroyed afterwards

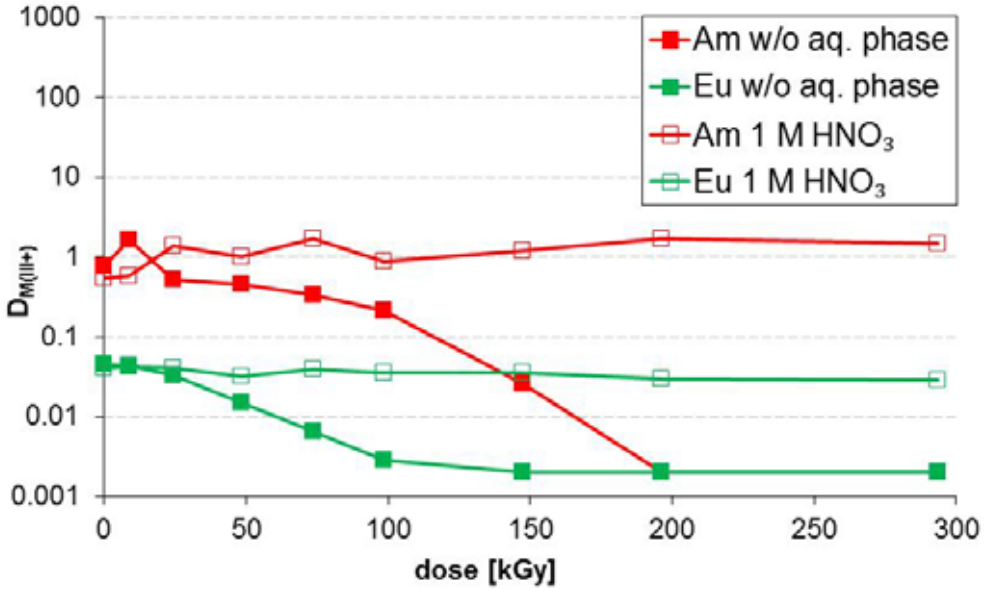


Liquid-liquid extraction ($CyMe_4BTBP$)

comparison to HPLC-DAD results



- Decreasing D-values with increasing dose
- HPLC-DAD shows reduction of molecule concentration
- Nitric acid while irradiation stabilizes D-values
- 50% reduction of ligand concentration detected by HPLC-DAD
  ⇨ due to 1:2 complex, D-value should decrease ~ one order of magnitude



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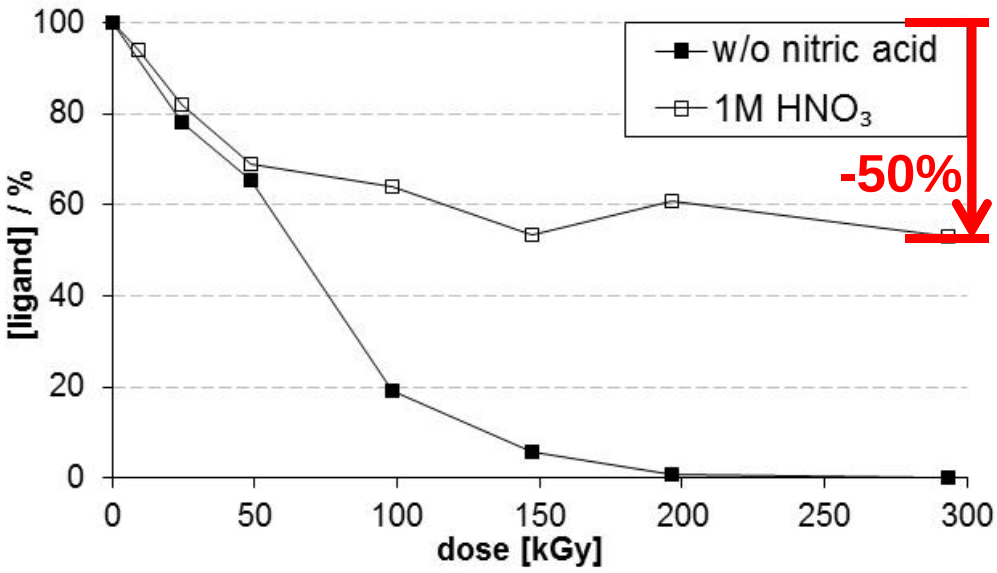

Liquid-liquid extraction ($CyMe_4BTPhen$)

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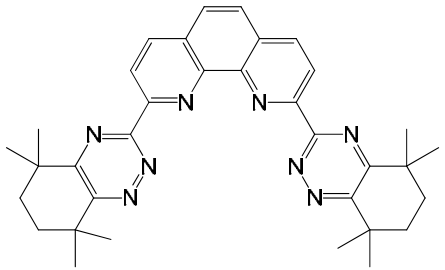
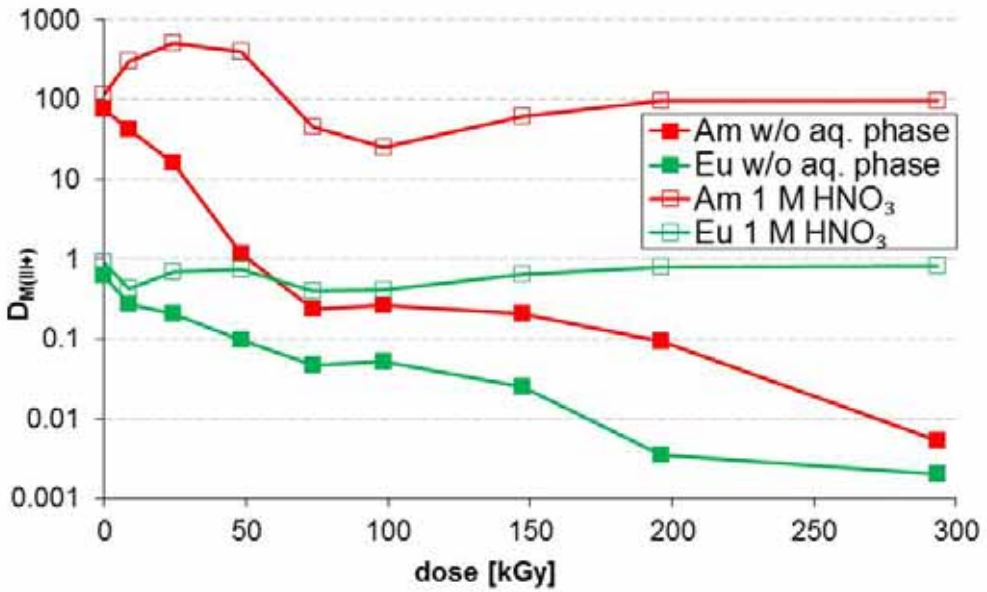


- Decreasing D-values with increasing dose
- HPLC-DAD shows reduction of molecule concentration
- Nitric acid while irradiation stabilizes D-values
- 90% reduction of ligand concentration detected by HPLC-DAD
  ⇨ due to 1:2 complex, D-value should decrease ~ two orders of magnitude

New built species during radiolysis, able to extract An/Ln
⇨ mass spectroscopy



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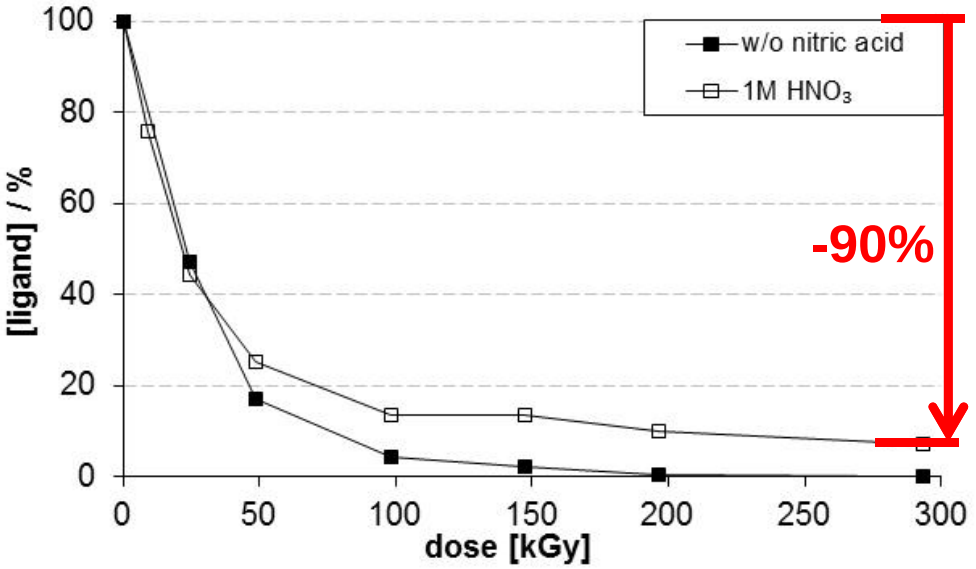


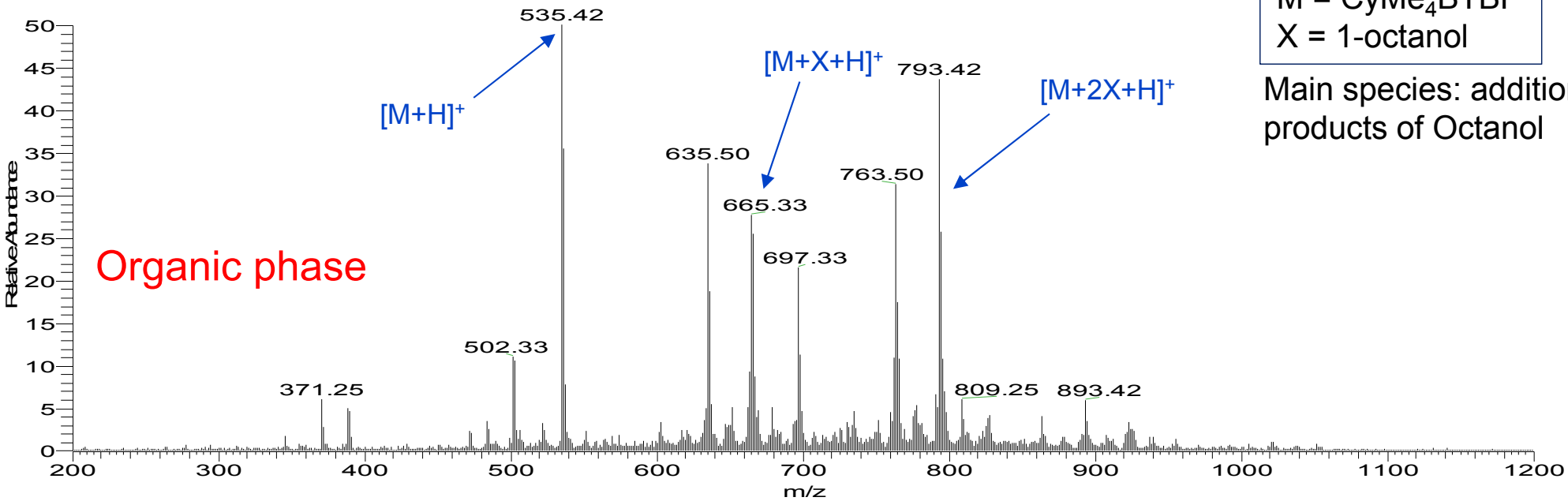
Mass spectroscopic analysis

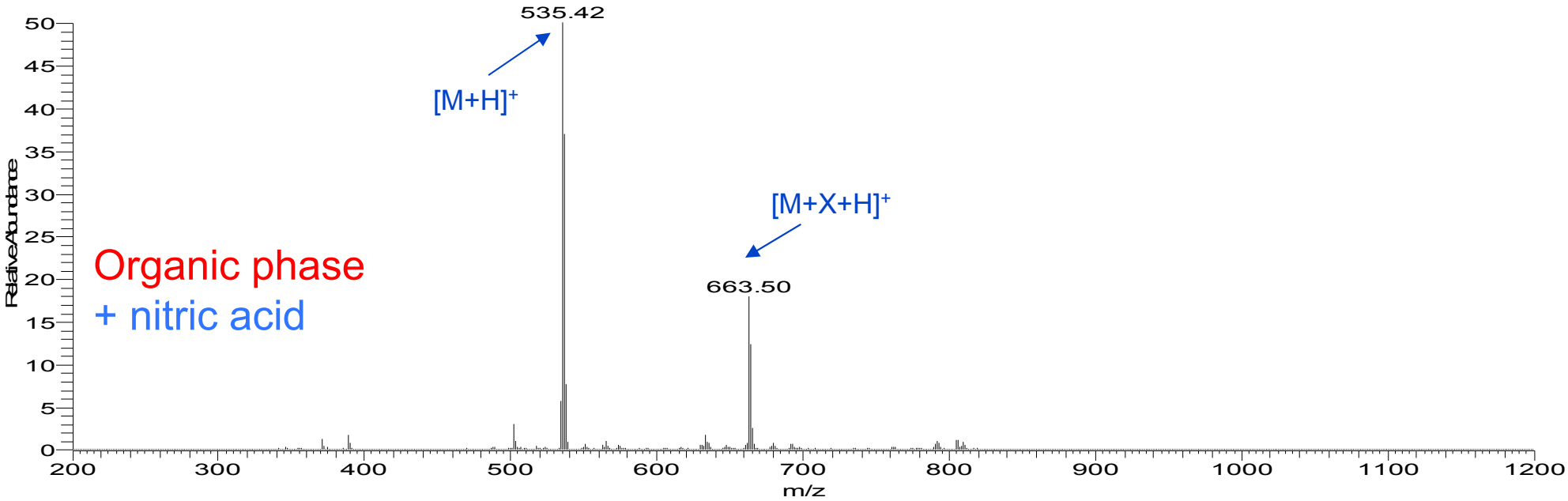
JÜLICH FORSCHUNGSZENTRUM

$CyMe_4BTBP$ in 1-octanol irradiated to 100 kGy

M = $CyMe_4BTBP$
X = 1-octanol

Main species: addition products of Octanol





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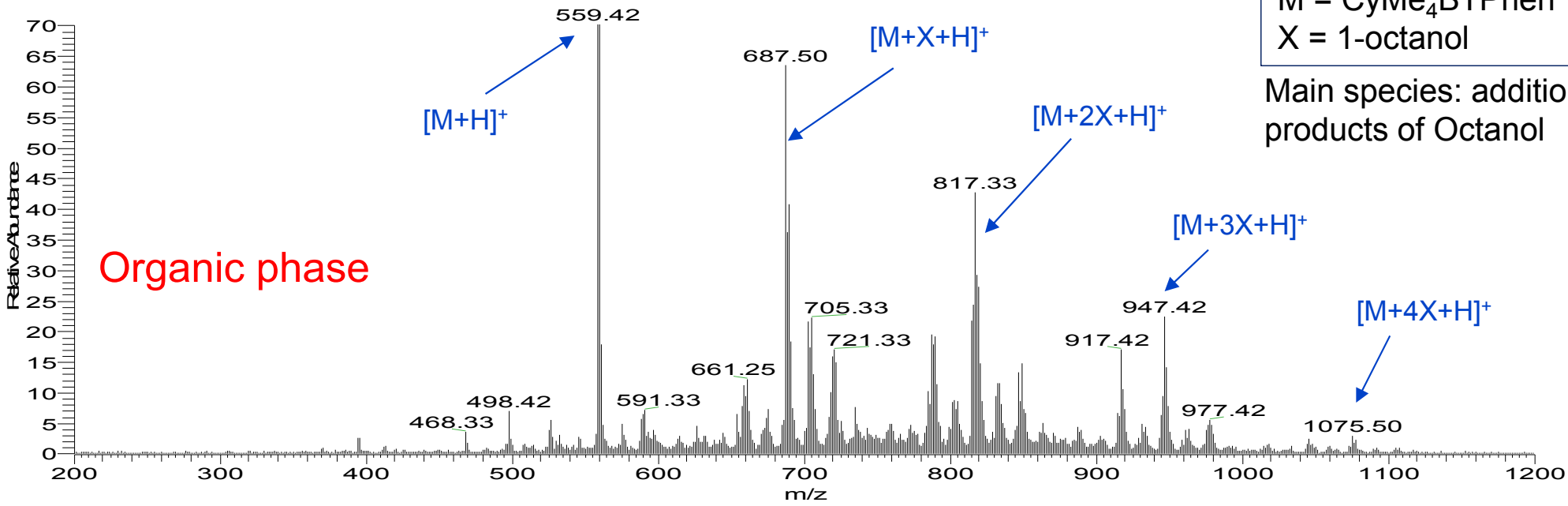

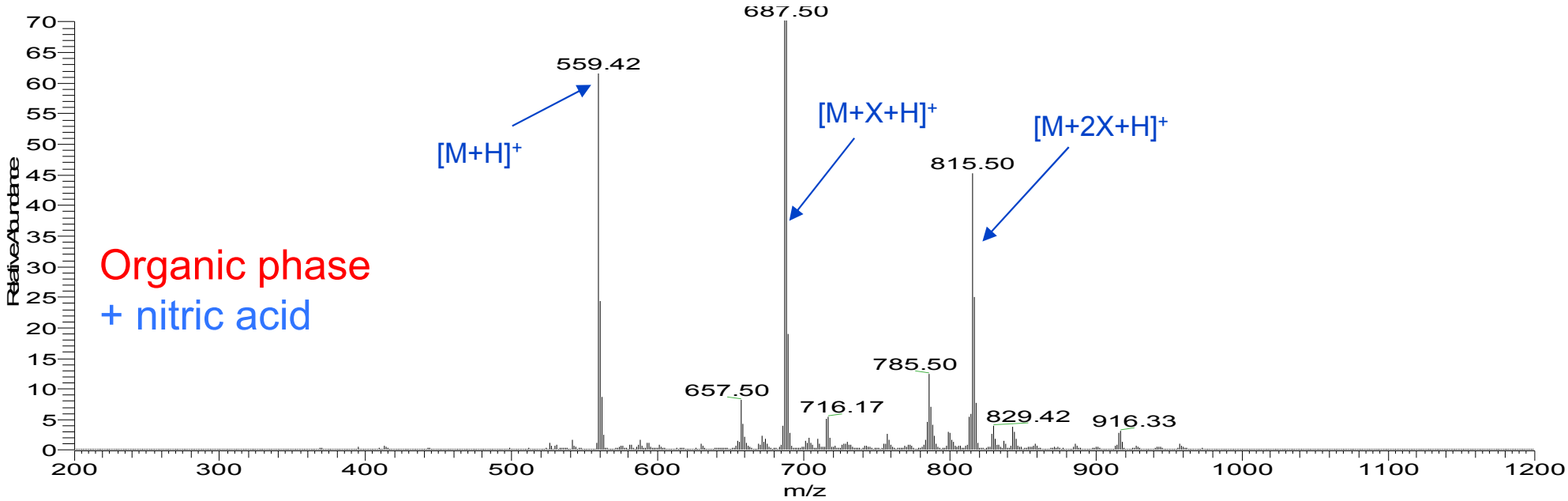

Conclusion and Outlook

- Radiolytic and hydrolytic degradation is of main interest for process development
- Radiolysis of $CyMe_4BTBP$ as well as $CyMe_4BTPhen$ leads to clearly lower D-values
  ⇨ no extraction at higher doses
- Mainly radiolysis of bulk material (1-octanol) leads to 1-octanol-adducts (M+X, M+2X, …)
- Nitric acid during irradiation is able to protect ligand against degradation
  ⇨ less degradation products besides M+X/ M+2X
- Both ligands are stable against hydrolysis, MS spectra without significant changes, D-values stable ⇨ no build up of addition products

- Identification of degradation products (MS does not provide structures)
- Main radiolysis-products should be synthesized and tested in liquid-liquid extraction experiments (octanol-adducts)
- G-values of ligand degradation shall be determined

Acknowledgements

PD Dr. Giuseppe Modolo
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Jenny Halleröd

IIC, Prague:
Dr. Bohumir Grüner
Jaroslav Švehla

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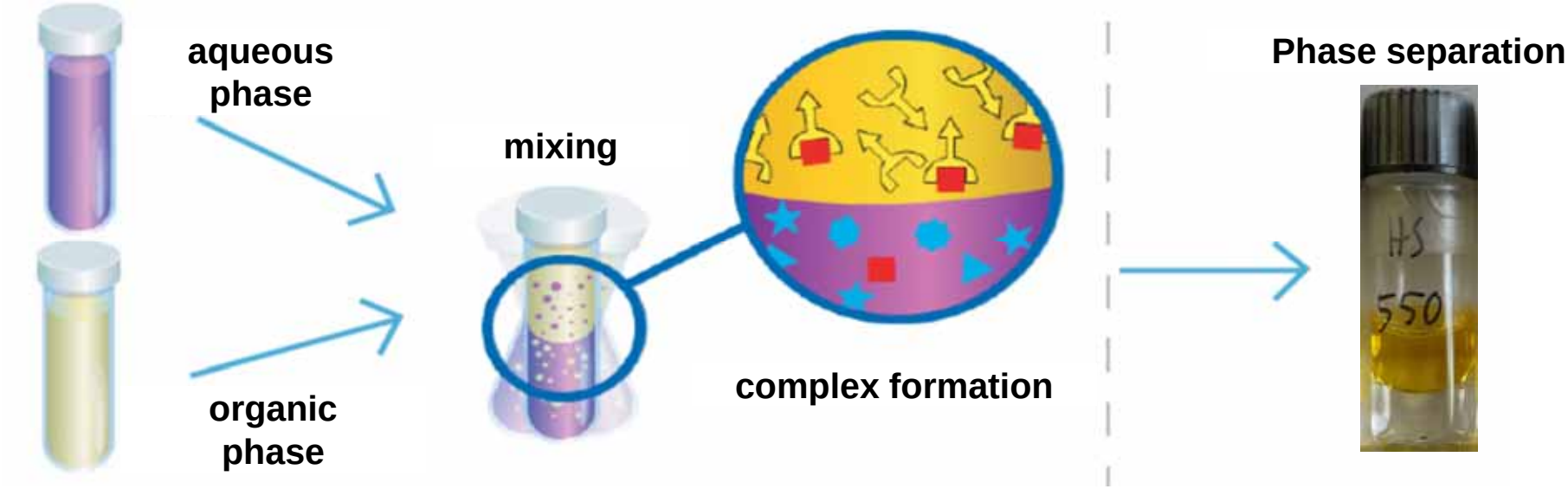
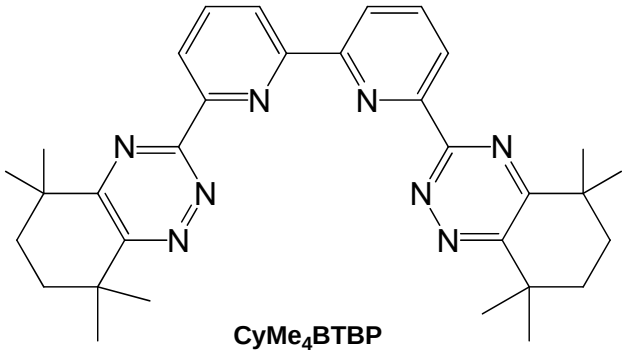
Thank you for your kind attention!

liquid-liquid extraction

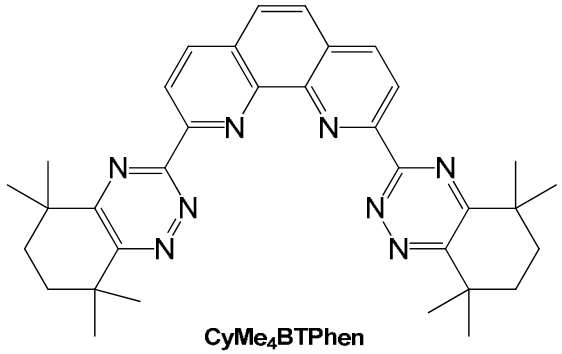


$$M_{aq} \underset{k_{back}}{\overset{k_{for}}{\rightleftarrows}} M_{org} \qquad D_M = \frac{[M]_{org}}{[M]_{aq}} \qquad SF_{M1/M2} = \frac{D_{M1}}{D_{M2}}$$

Comparison of $CyMe_4BTBP$ / $CyMe_4BTPhen$



$CyMe_4BTBP$

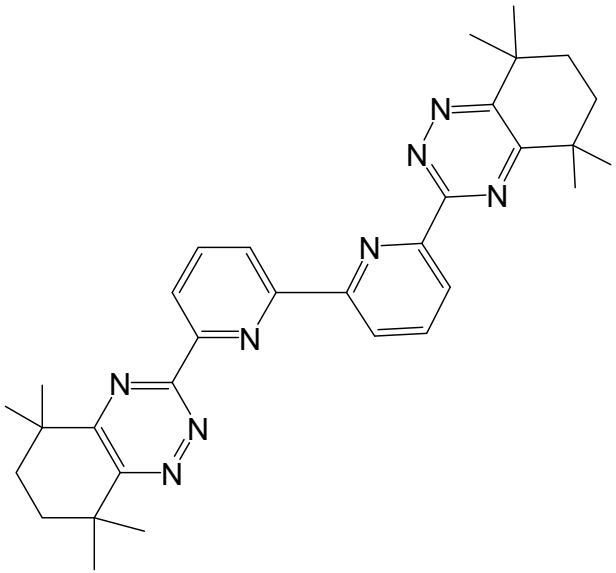


$CyMe_4BTPhen$

cis-/ trans- conformation possible

trans-conformation favored, barrier to overcome: ~12 kcal/ 50kJ mol^{-1}[2]

only *cis*-conformation possible
steric hindrance
“preorganized for metal binding”



- Favored *trans*-conformation as reason for “worse” D-values

[5] Lewis, F.W.; Harwood, L.M.; Hudson, M.J.; et. al.; Inorg. Chem. **2013**, *52*, 4993-5005.

Dosimetry

- Ferrous-Cupric Dosimeter (modified Fricke Dosimeter)
  range: 0.5 kGy – 50 kGy
  uncertainty < 2%

- 0.001 mol/L $FeSO_4$
  0.010 mol/L $CuSO_4$
  0.005 mol/L H_2SO_4

  Fe^{2+} ~~> Fe^{3+}

- spectrophotometric measurement of ferric ion concentration (303 nm)

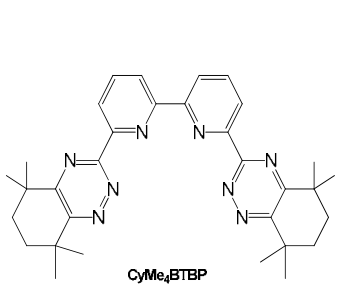
- G-value (µmol J^{-1}):
  “Efficiency of conversion of radiation energy to chemical products“
  “the moles of material formed or changed by an energy absorption of 1 joule”

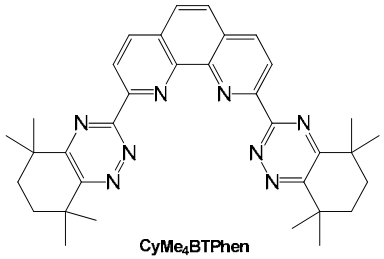
- extinction → concentration → dose → doserate

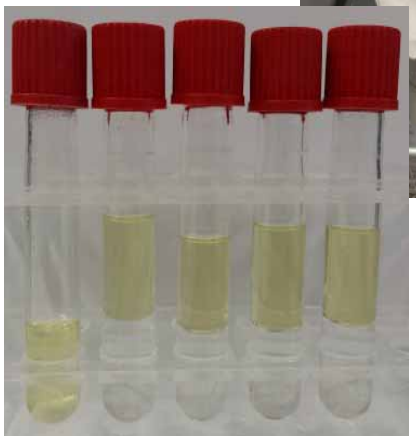
Hydrolysis experiments

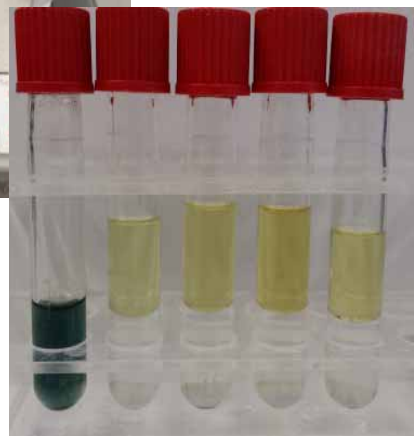
Mixing of equal amounts of
- organic phase — 10 mmolar solutions in 1-octanol
- selected aqueous phase — different [HNO_3] up to 4 mol/L

Vigorous mixing at room temperature
Liquid-liquid extraction experiments as described above







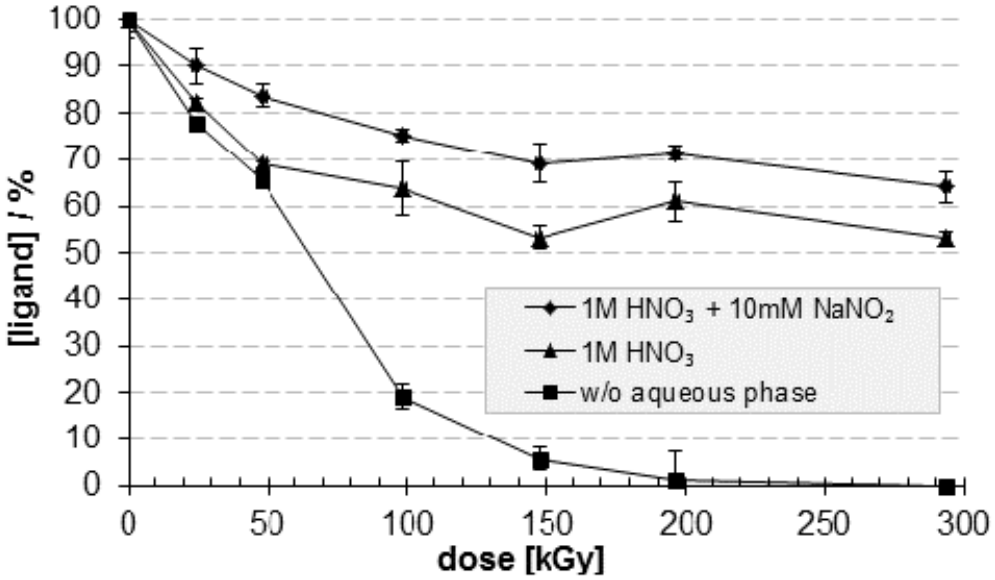


Both ligands are stable against hydrolysis
D-values don't change at all
MS spectra without significant changes

HPLC – concentration measurements

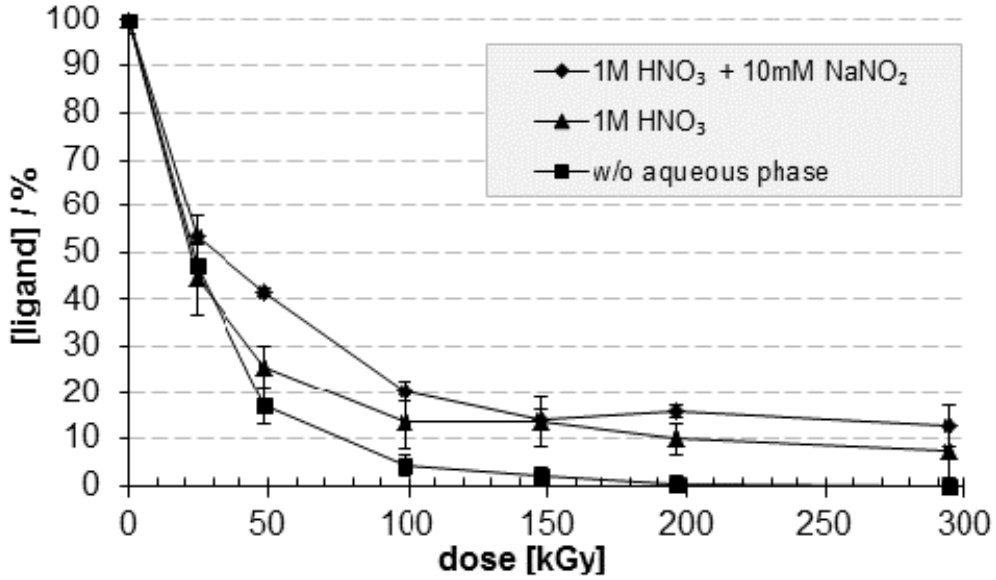
@ IIC, Prague

$CyMe_4BTBP$



Merck Purospher Star C8, 250x 2 mm I.D. UV
Detection at 237 nm
Samples diluted in CH_3CN

$CyMe_4BTPhen$



Gemini C8, 150x 3 mm I.D.
UV Detection at 259 nm
Samples diluted in CH_3CN