Conducting polymers: synthesis and kinetic study by pulsed radiolysis

Cecilia Coletta

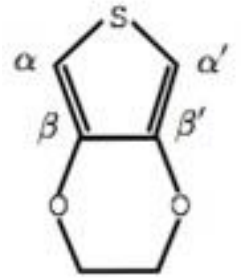
Supervisors:

Samy Remita and Jean-Louis Marignier

Université Paris Sud, Laboratoire Chimie Physique
Rue Michel Magat, 91400 Orsay, France

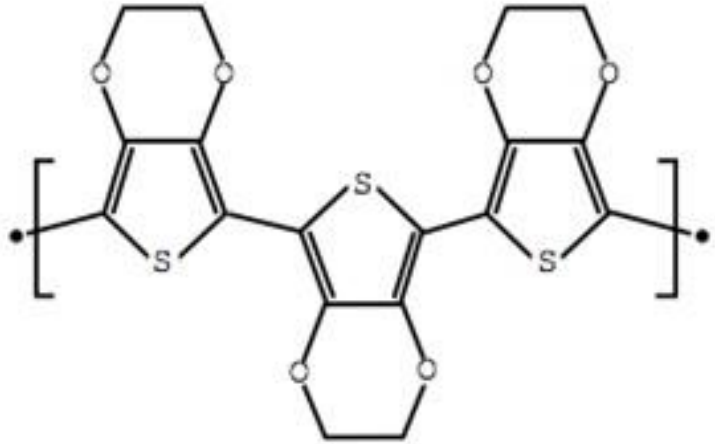
Conductive polymers: PEDOT

from EDOT…



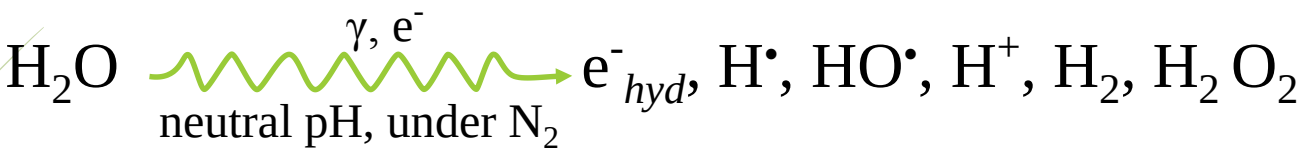
- Thiophene derived
- Soluble in water and organic solvents
- Protected in β et β’ position
- Low potential redox

to PEDOT



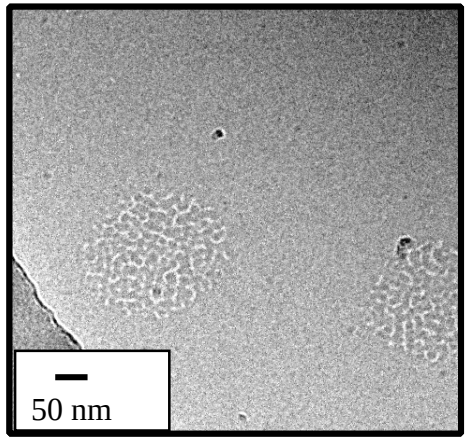
- High stability
- High conductivity
- Transparent

Water radiolysis

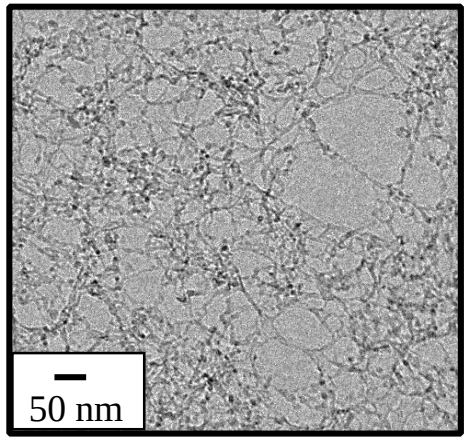


Water radiolysis

$$H_2O \xrightarrow[\text{neutral pH, under } N_2]{\gamma,\ e^-} e^-_{hyd},\ H^{\bullet},\ HO^{\bullet},\ H^+,\ H_2,\ H_2O_2$$



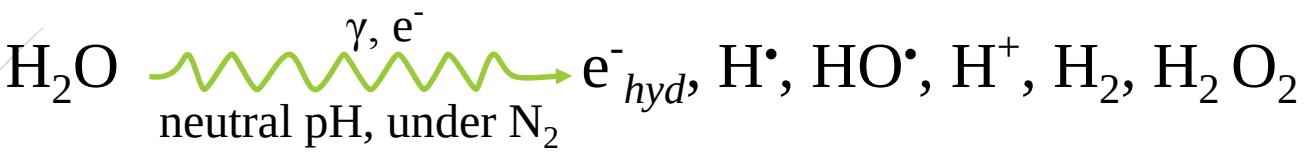
PEDOT by $HO^{\cdot}$



PEDOT by $N_3^{\cdot}$

Lattach, Y. *et al. ChemPhysChem.* 82 (2013): 44-53

Water radiolysis



Advantages of radiolysis synthesis:

- Synthesis in water solution at ambient temperature
- Pulse radiolysis : kinetic study
- Selection of oxidizing radical:
  - Under N_2O:

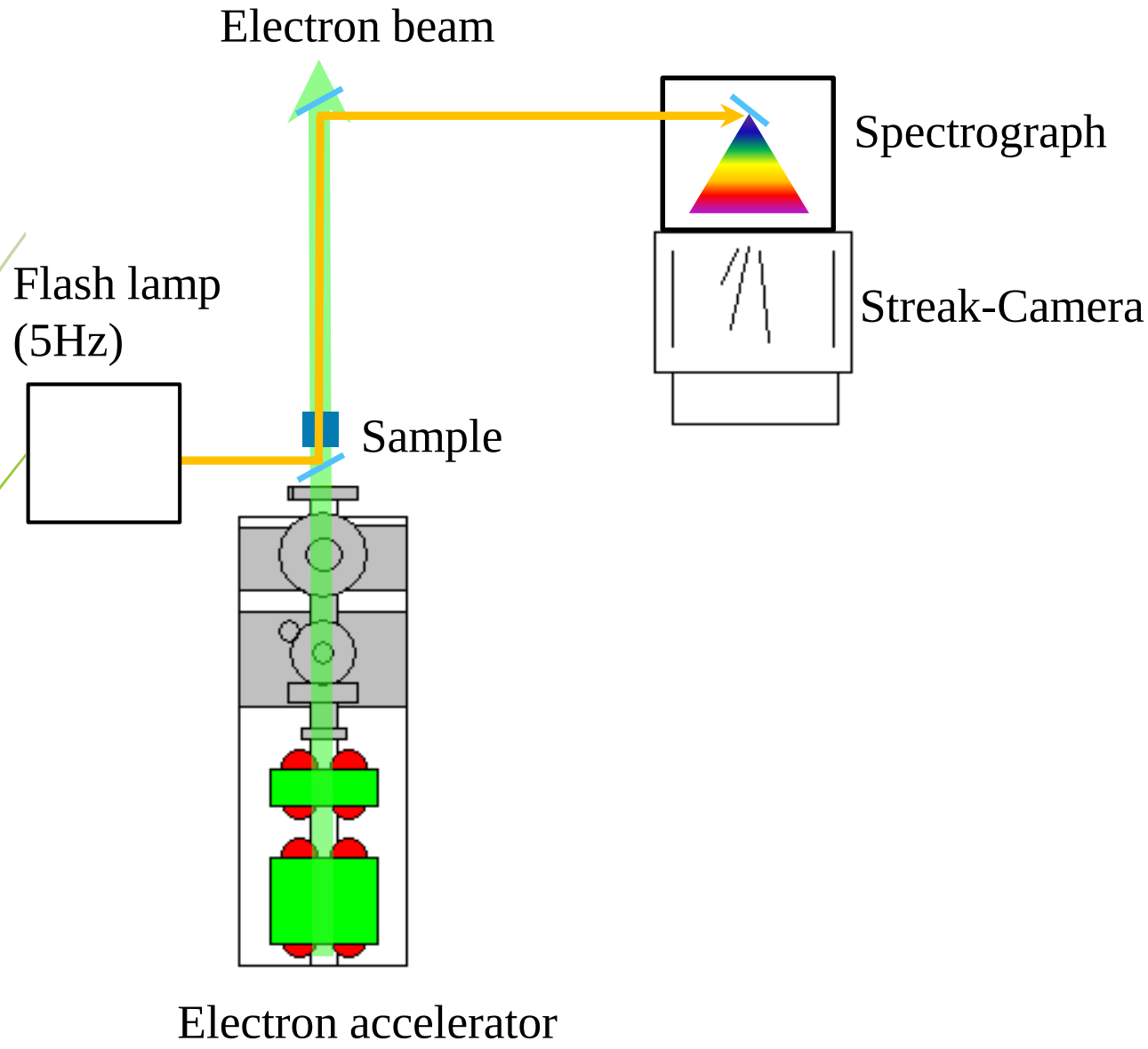
$$N_2O + e^-_{hyd} \rightarrow HO^\bullet + HO^- + N_2$$

  - Under N_2O but in presence of Na_2CO_3

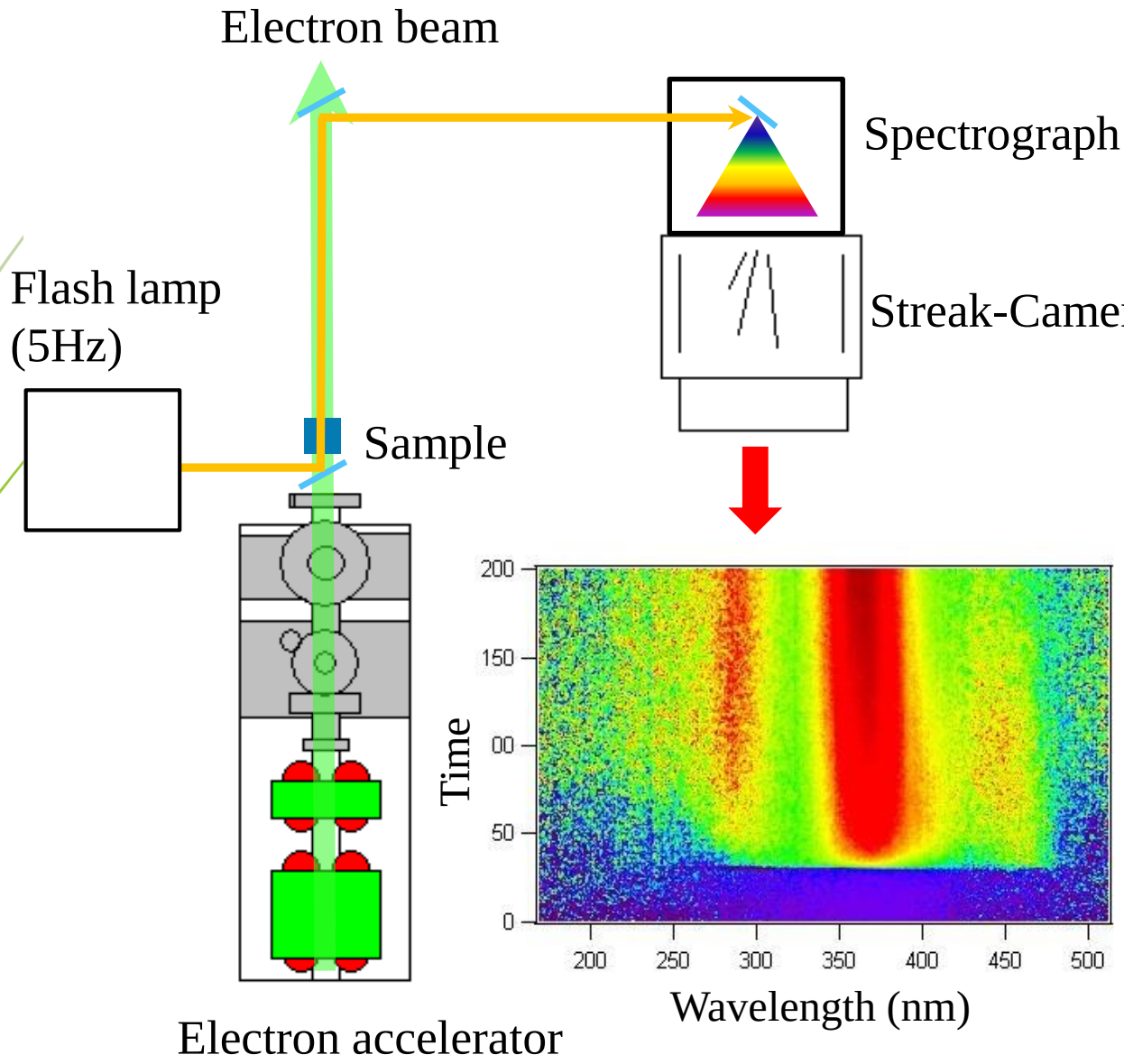
$$HO^\bullet + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet -}$$

(or other salts as NaN_3 which gives $N_3^\bullet$ or NaBr which gives $Br^\bullet$)

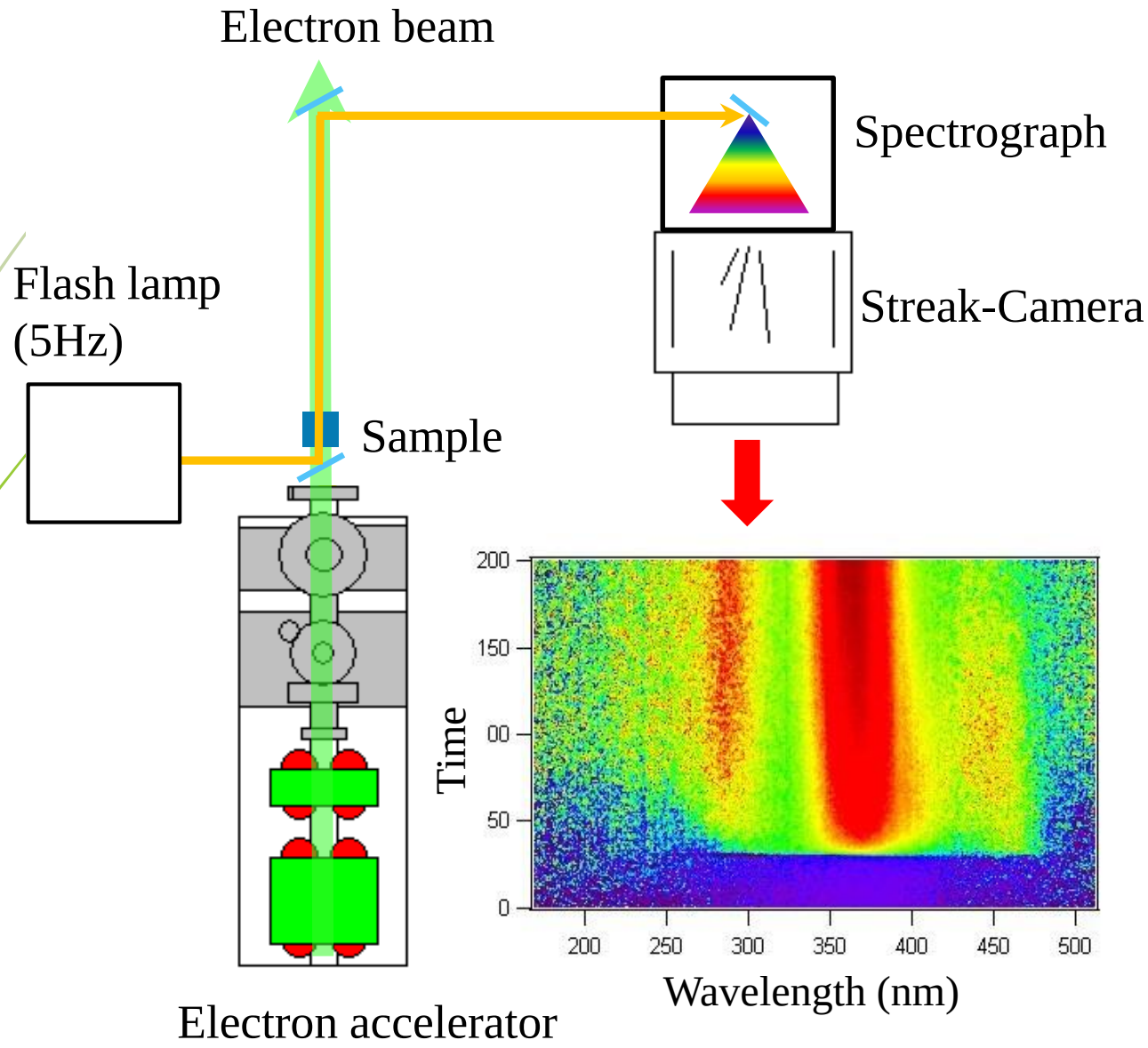
Pulse radiolysis on ELYSE electron accelerator

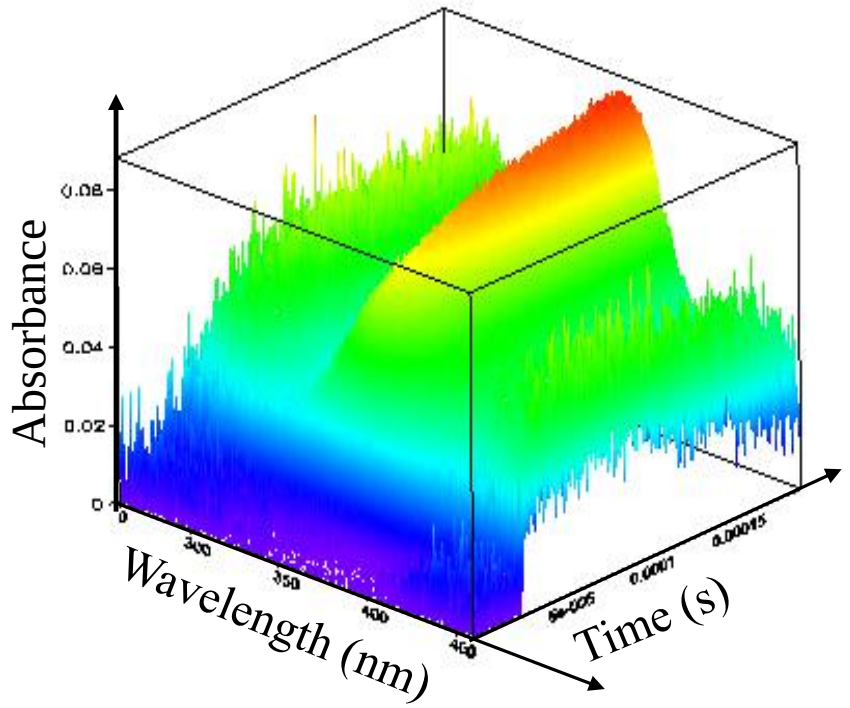


Pulse radiolysis on ELYSE electron accelerator



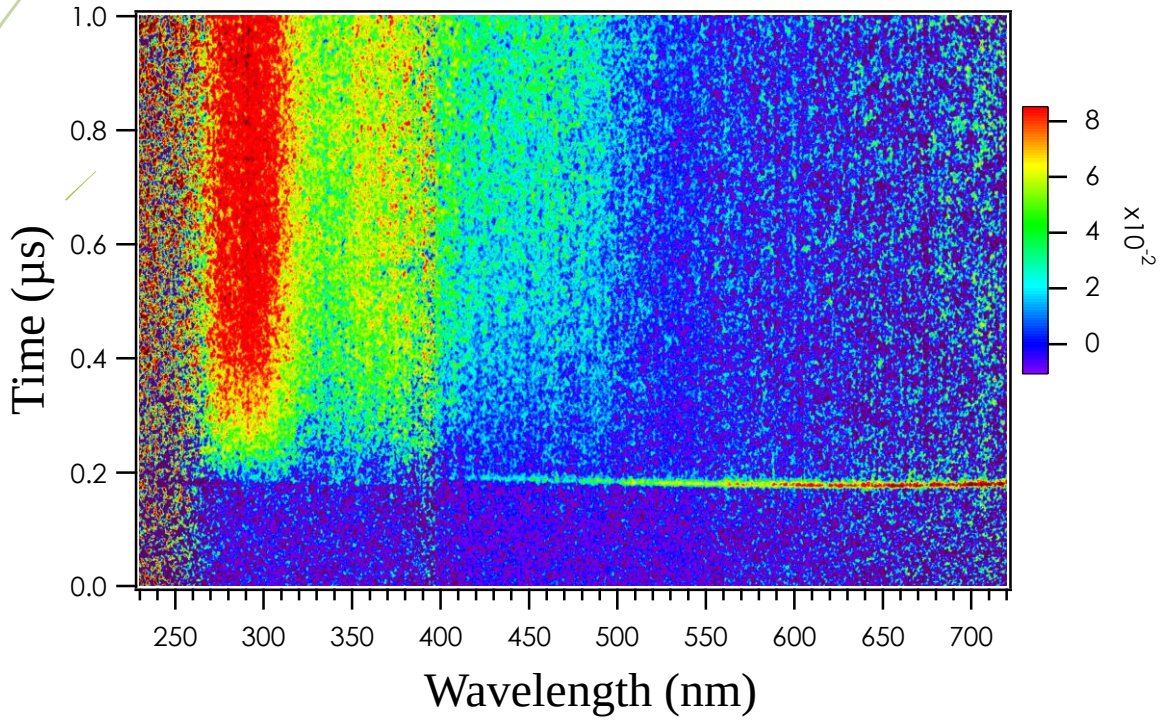
Pulse radiolysis on ELYSE electron accelerator





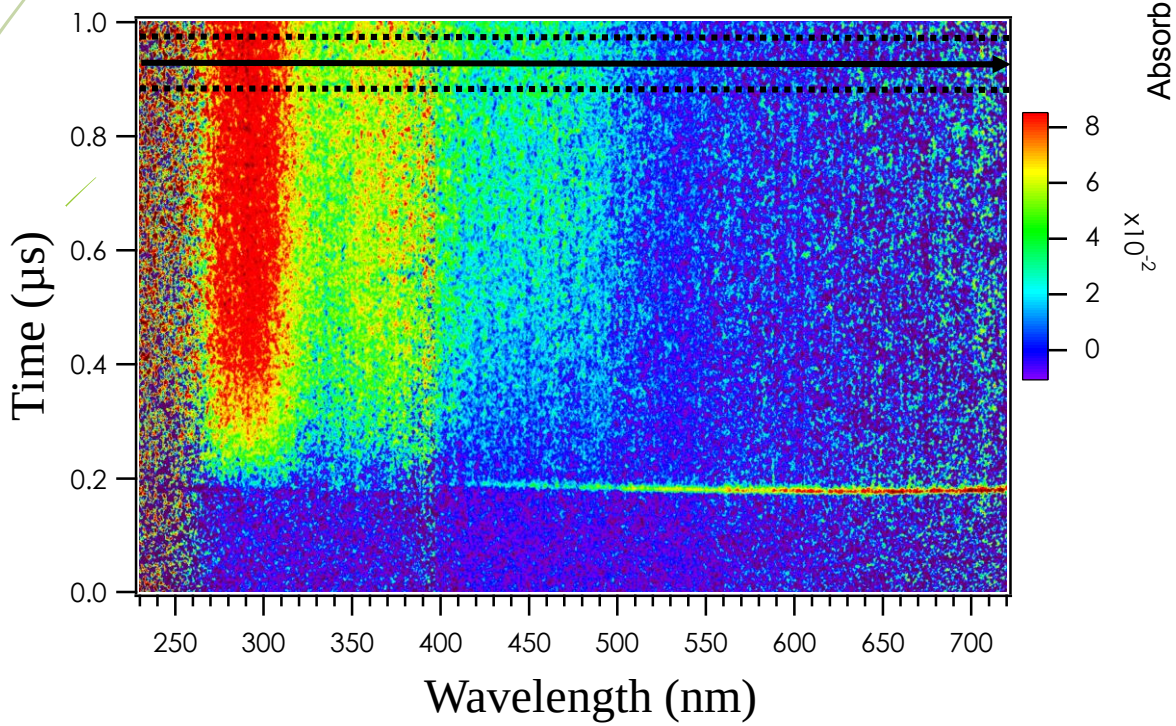
Data analysis

1 mM EDOT saturated with N_2O
$HO^{\bullet}$ oxydation

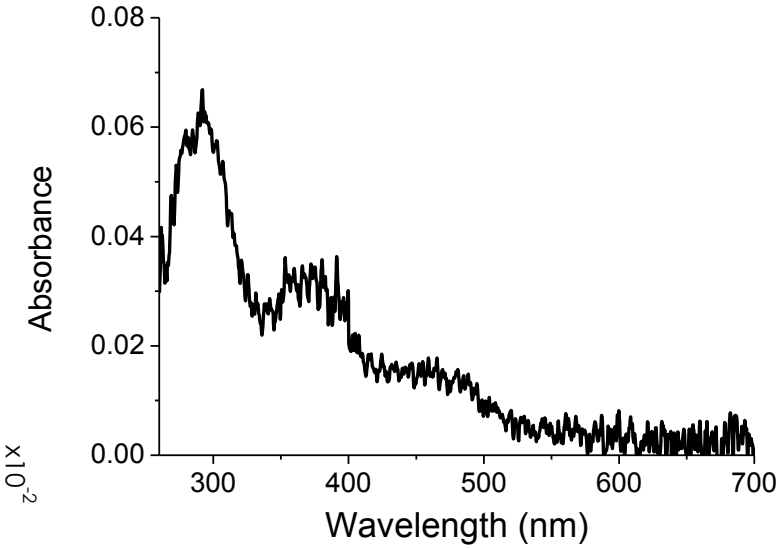


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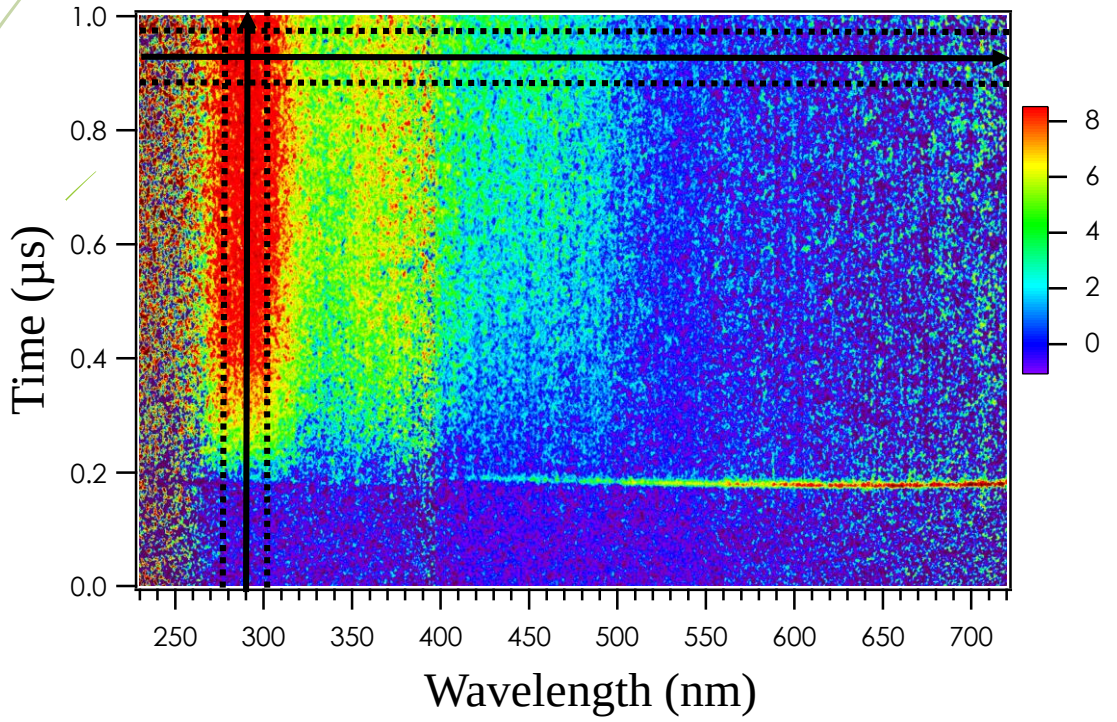


Absorption spectrum at 800 ns

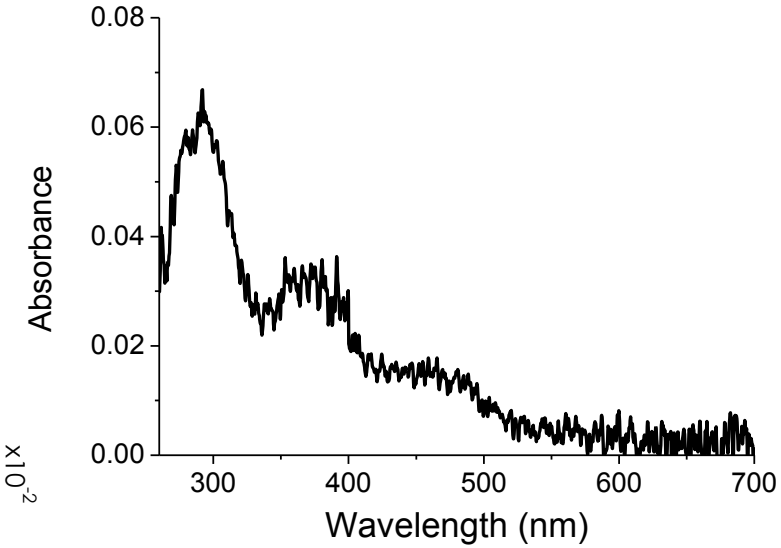


Data analysis

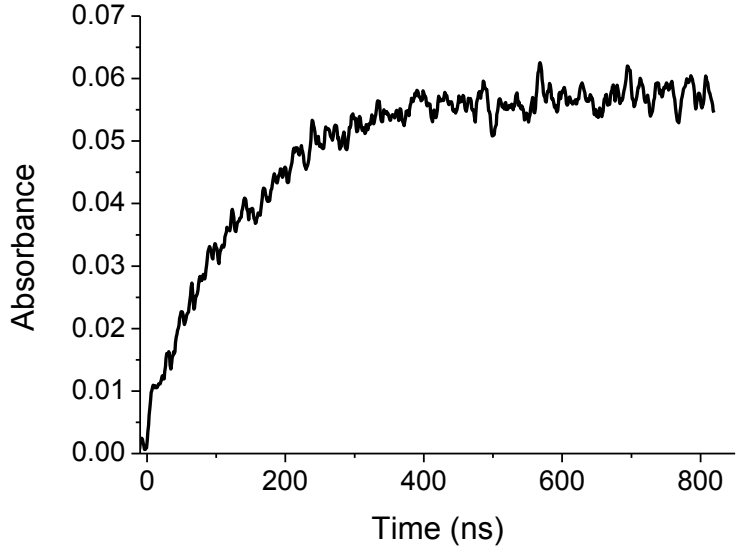
1 mM EDOT saturated with N_2O
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Absorption spectrum at 800 ns

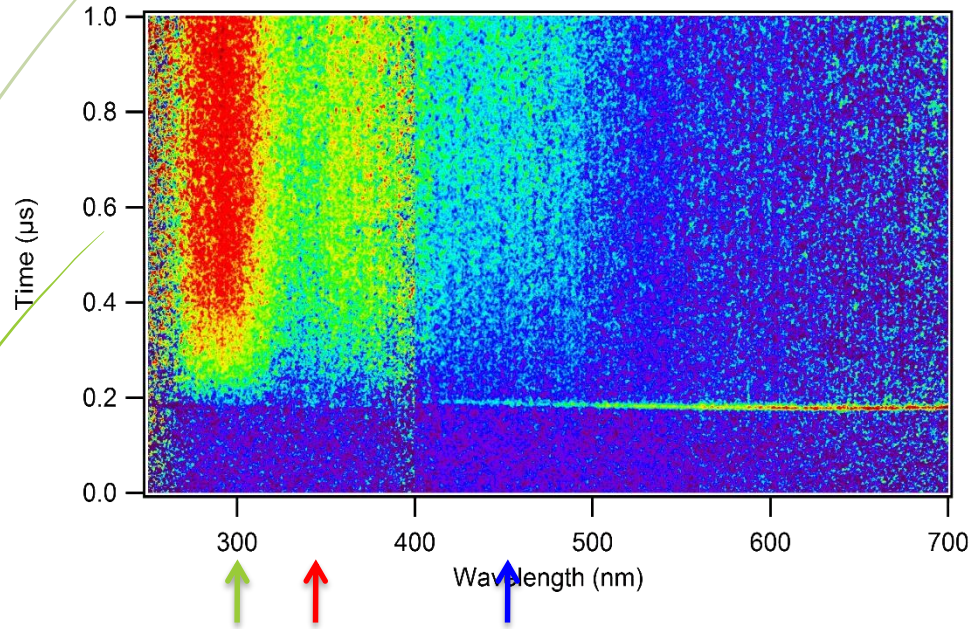


Kinetic profile on 1 µs at 290 nm



Hydroxyl radical action (ns-scale)

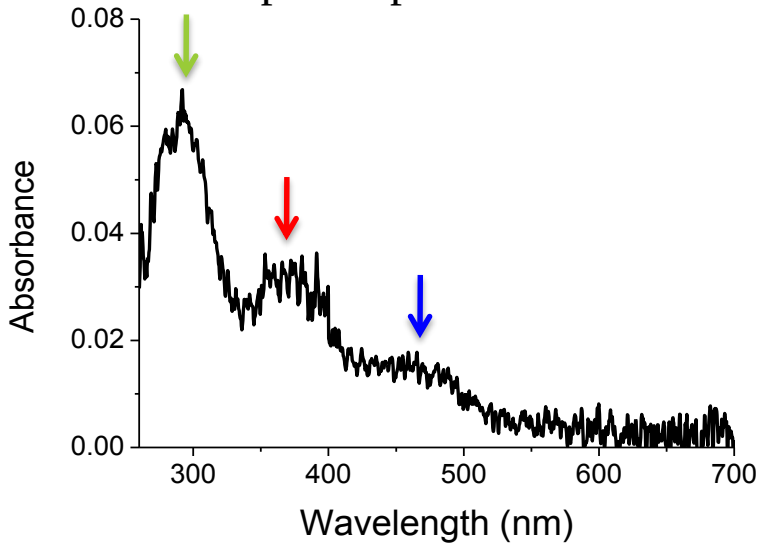
1 mM EDOT saturated with N_2O
$HO^{\bullet}$ oxydation



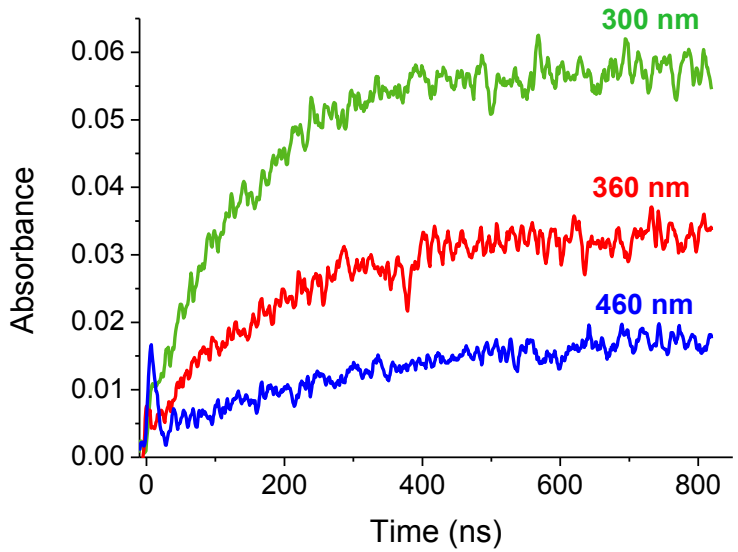
- Dose: 37 $J{\cdot}kg^{-1}$/electron pulse
- $[OH^{\bullet}] = 1.26\ 10^{-5}$ $mol.L^{-1}$
- pH = 8

Coletta *et al.* J. Phys. Chem. B. 2015;119(16):5282-98

Absorption spectrum at 800 ns

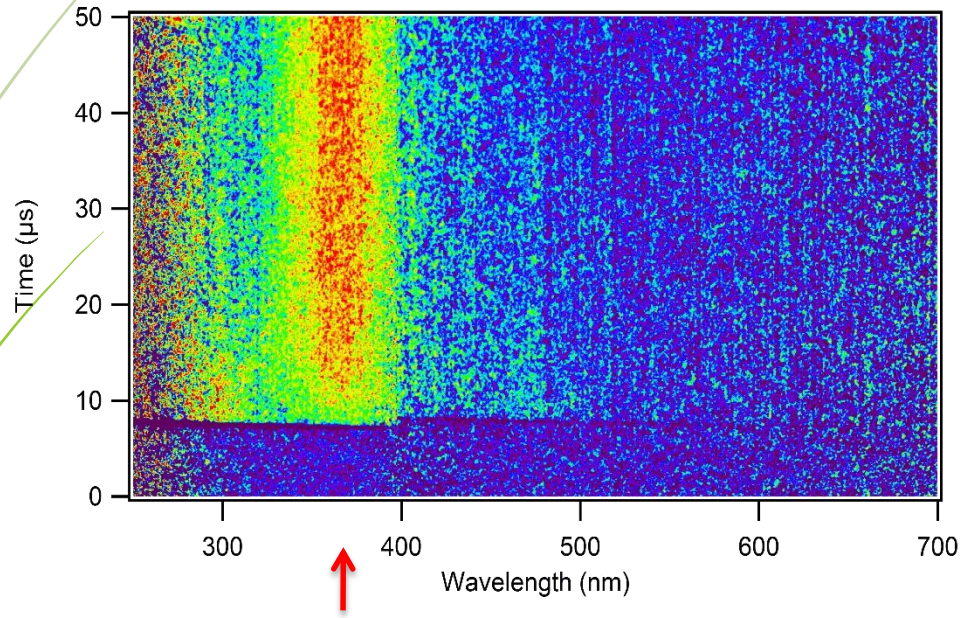


Kinetic profile on 1 µs



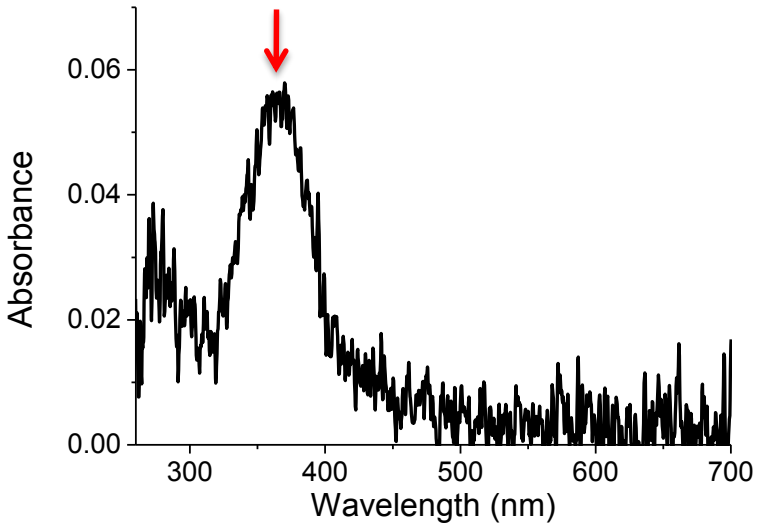
Hydroxyl radical action (µs-scale)

1 mM EDOT saturated with N_2O
$HO^{\bullet}$ oxydation

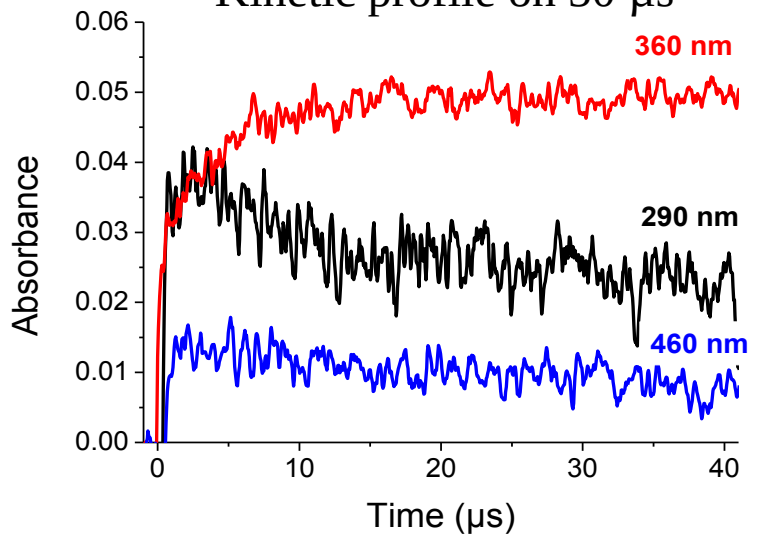


- Dose: 37 $J \cdot kg^{-1}$/electron pulse
- $[OH^{\bullet}] = 1.26\ 10^{-5}$ $mol.L^{-1}$
- pH = 8

Absorption spectrum at 45 µs

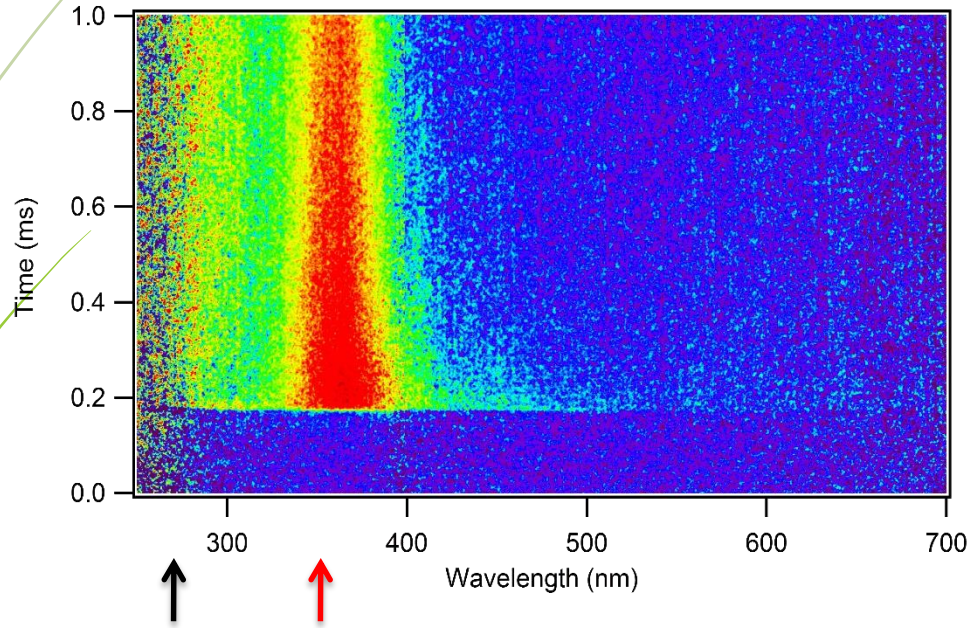


Kinetic profile on 50 µs



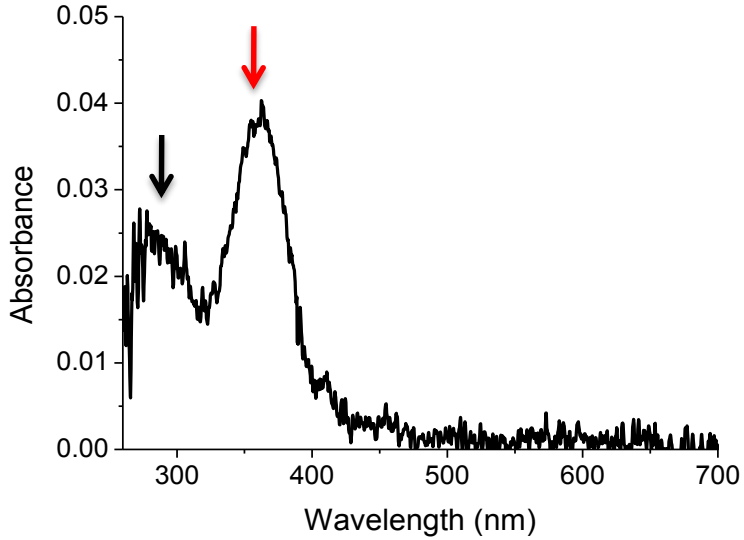
Hydroxyl radical action (ms-scale)

1 mM EDOT saturated with N_2O
$HO^{\bullet}$ oxydation

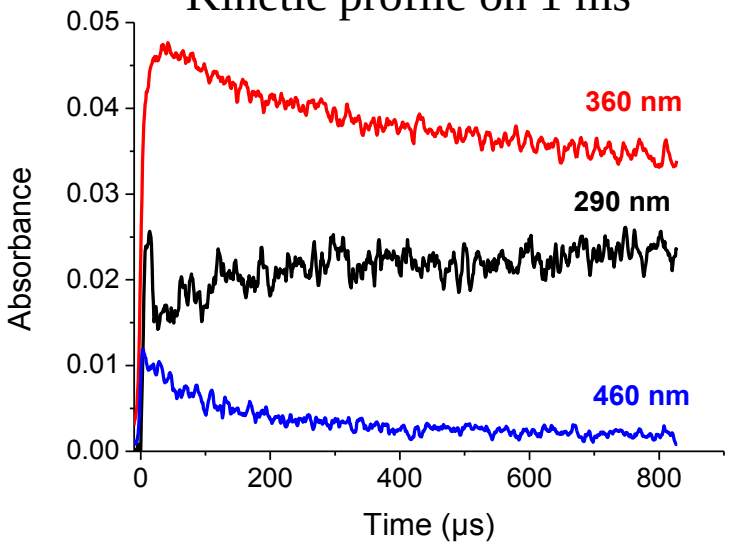


- Dose: 37 $J \cdot kg^{-1}$/electron pulse
- $[OH^{\bullet}] = 1.26\ 10^{-5}\ mol.L^{-1}$
- pH = 8

Absorption spectrum at 800 µs

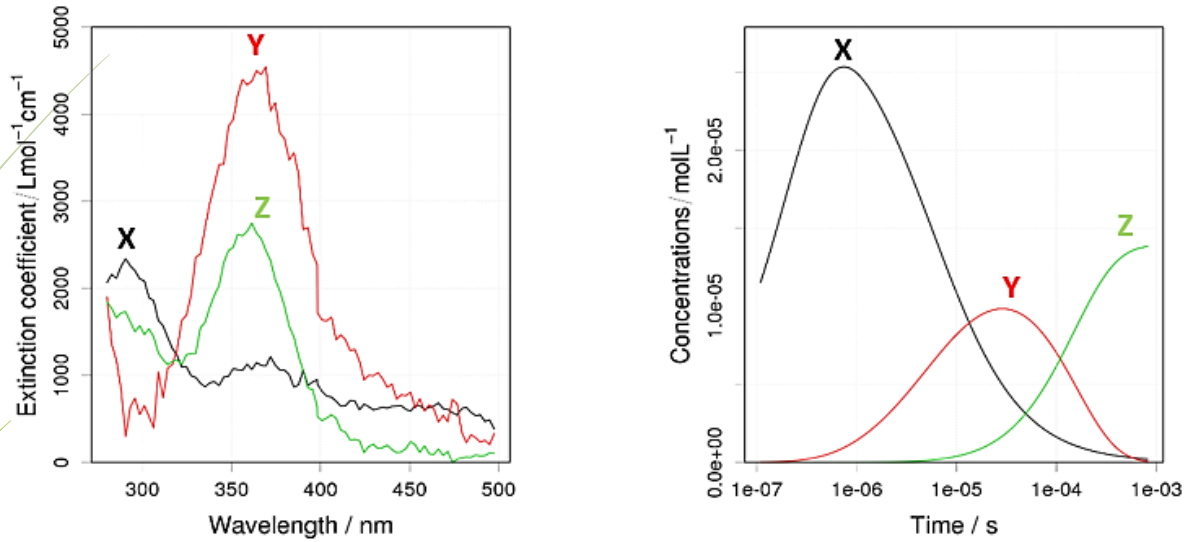


Kinetic profile on 1 ms



Theoretical deconvolution by SVD method

First mechanism

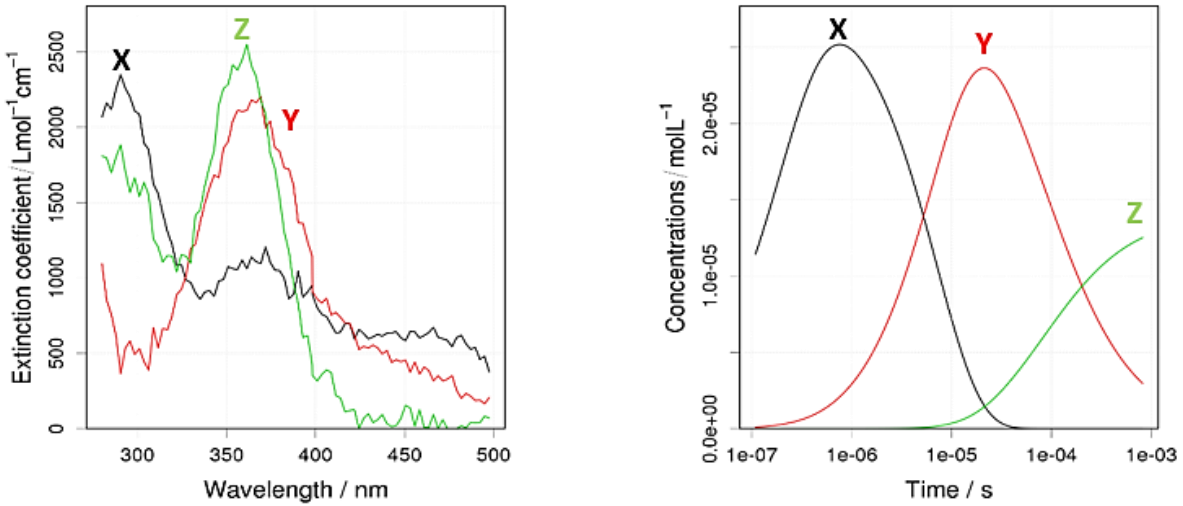


$EDOT + HO^{\cdot} \rightarrow X$

$X + X \rightarrow Y$

$Y \rightarrow Z$

Second mechanism



$EDOT + HO^{\cdot} \rightarrow X$

$X \rightarrow Y$

$Y + Y \rightarrow Z$

Collaboration with P. Pernot

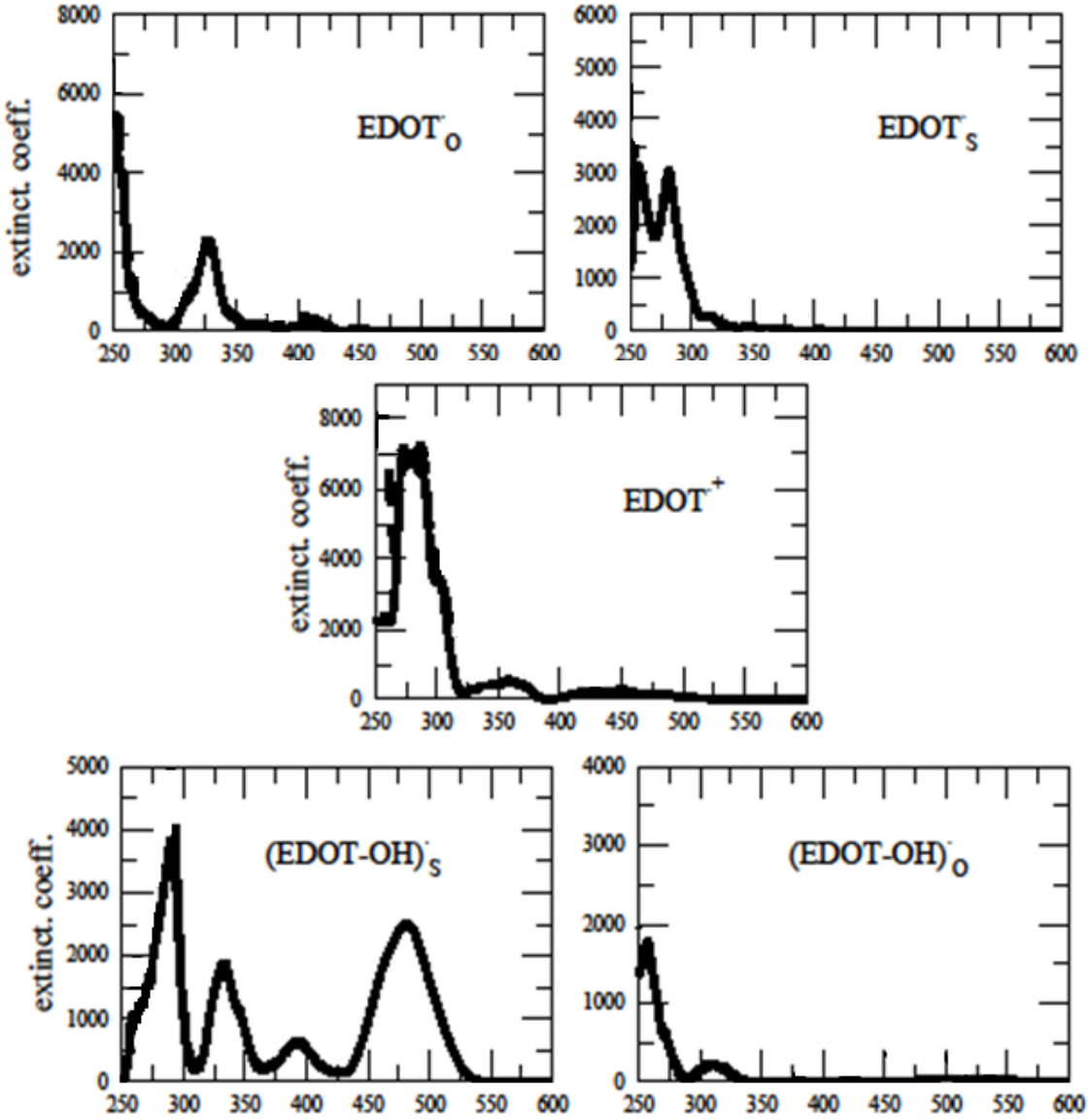
Species identification using simulated absorption spectrum

First reaction:

$EDOT + HO^{\cdot} \rightarrow X$

Absorption bands of X:

300 , 360 and 460 nm



Collaboration with P. Archirel
(Monte Carlo / TD-DFT)

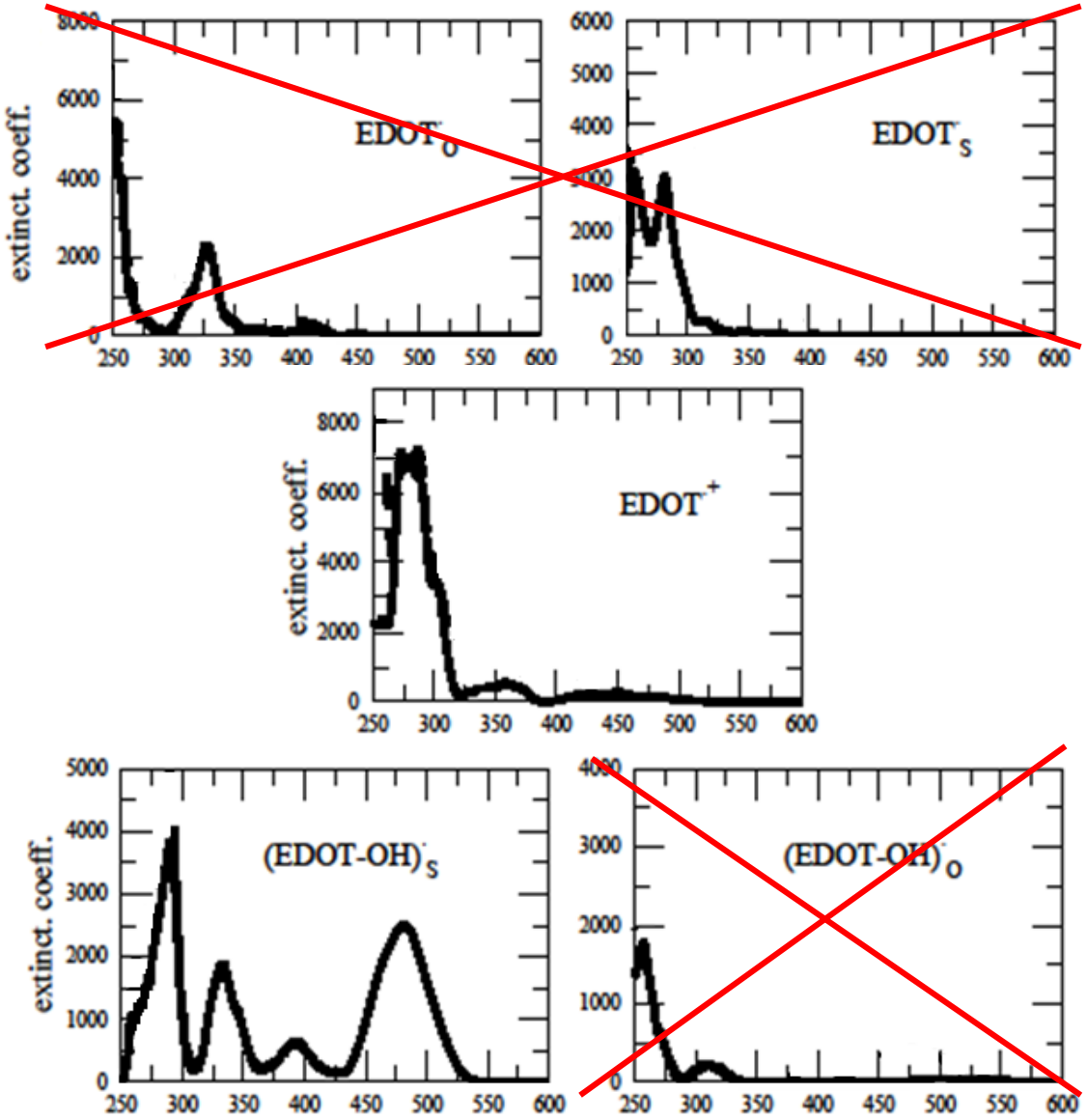
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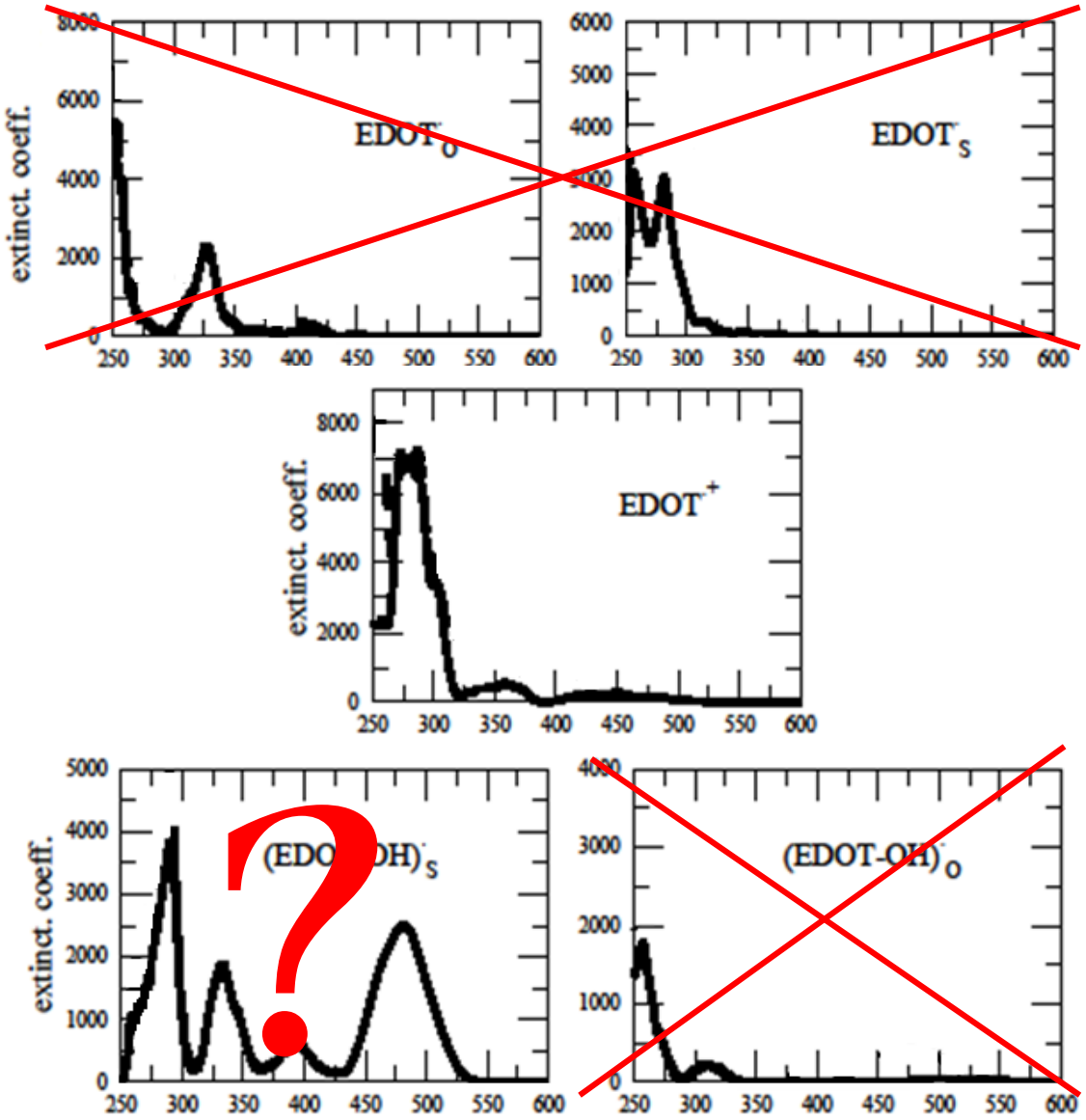
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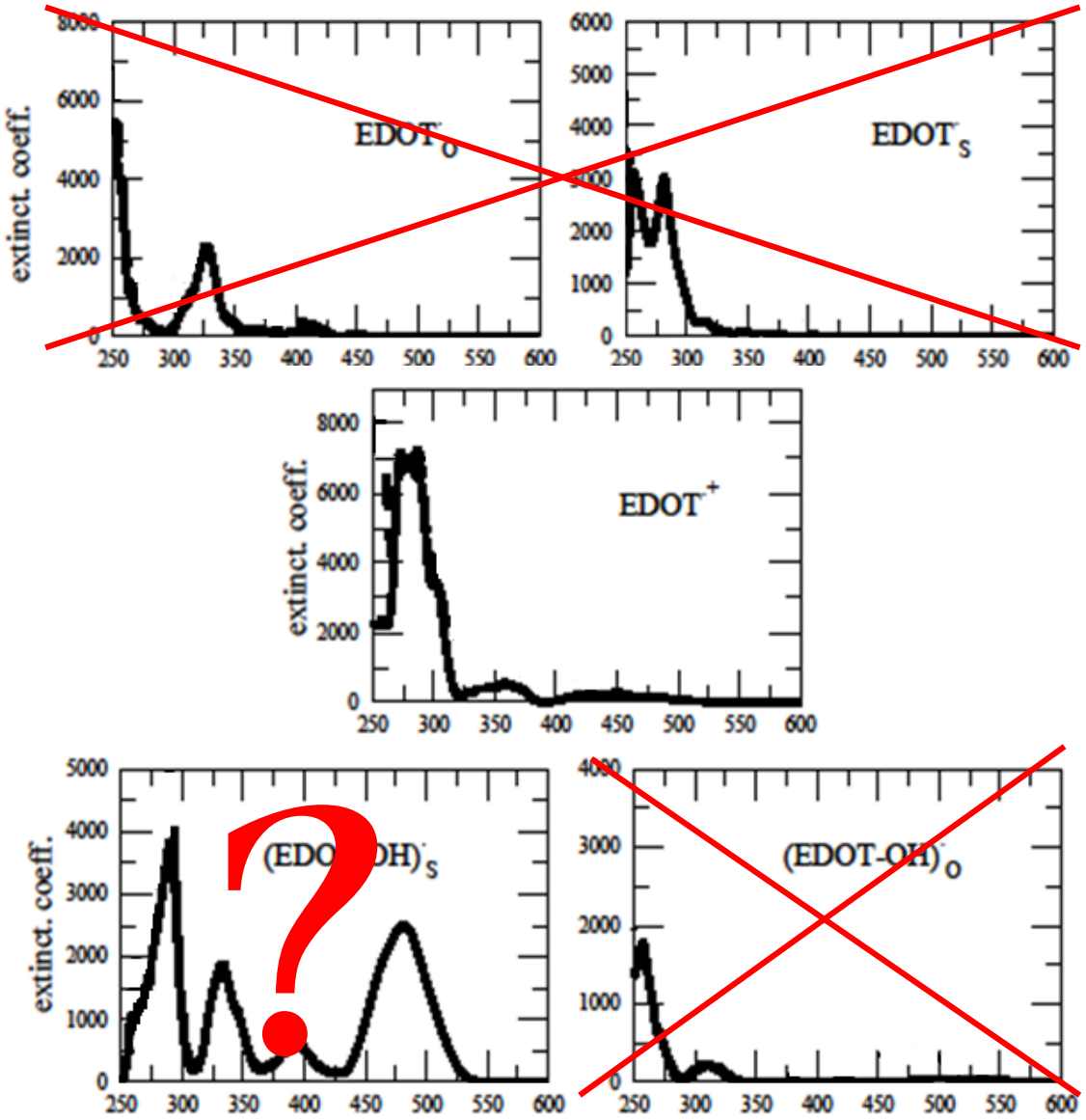
First reaction:

EDOT + $HO^{\cdot}$ → X

Absorption bands of X:

300 , 360 and 460 nm

→ X = $EDOT^{\bullet+}$

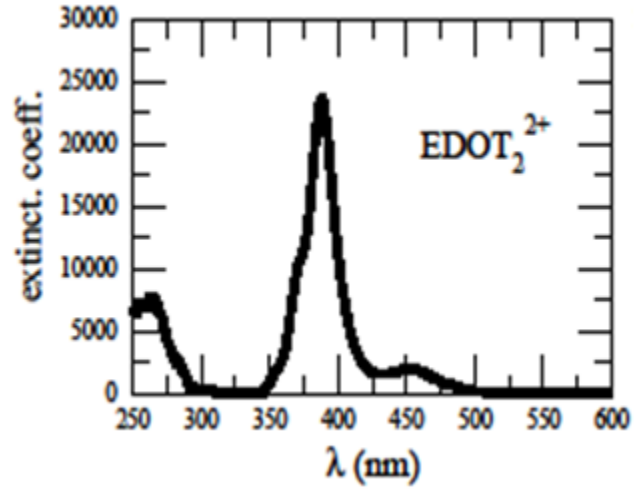


Collaboration with P. Archirel
(Monte Carlo / TD-DFT)

Species identification

Second reaction:

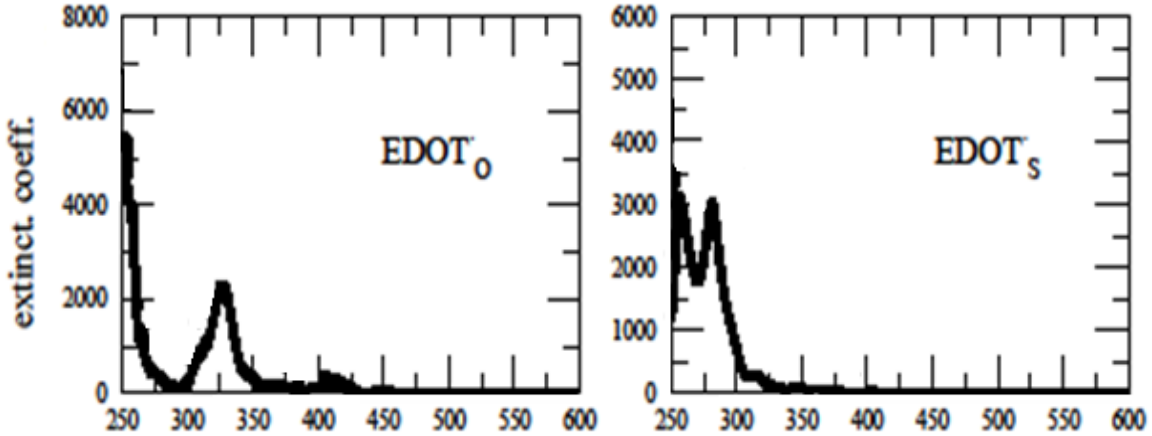
- $X + X \rightarrow Y$ (first mechanism)



- $X \rightarrow Y$ (second mechanism)

Absorption band of Y:

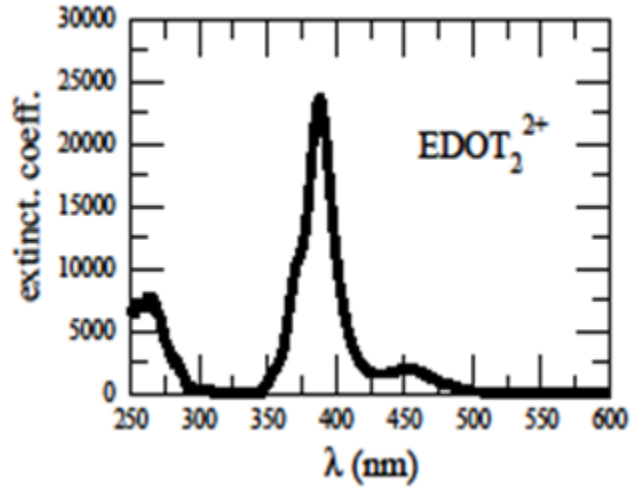
360 nm



Species identification

Second reaction:

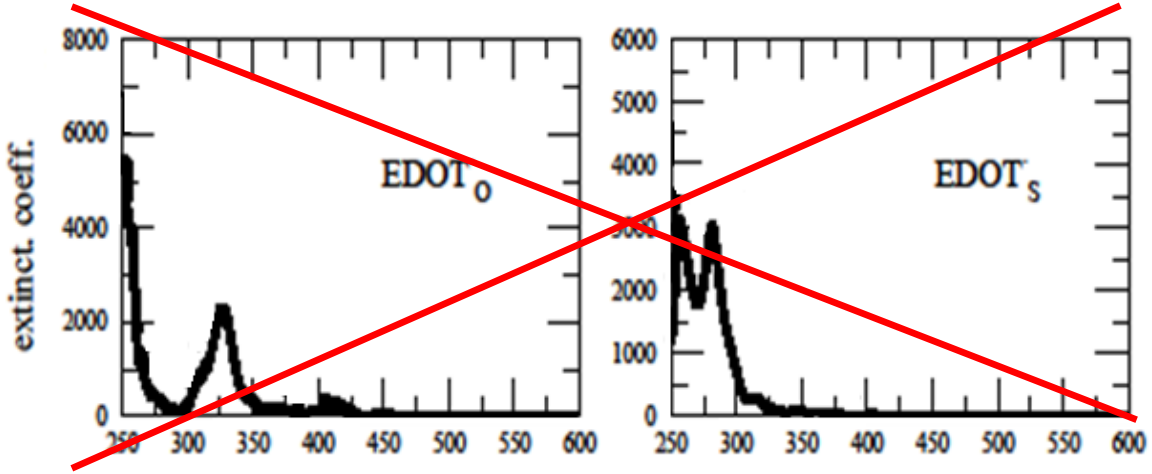
- X + X→ Y (first mechanism)



- X → Y (second mechanism)

Absorption band of Y:

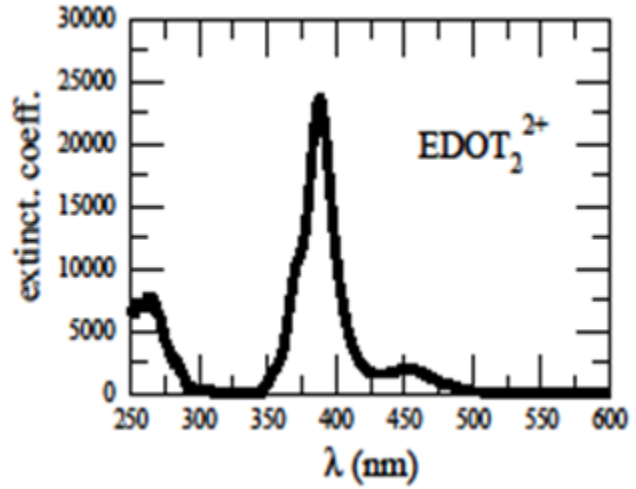
360 nm



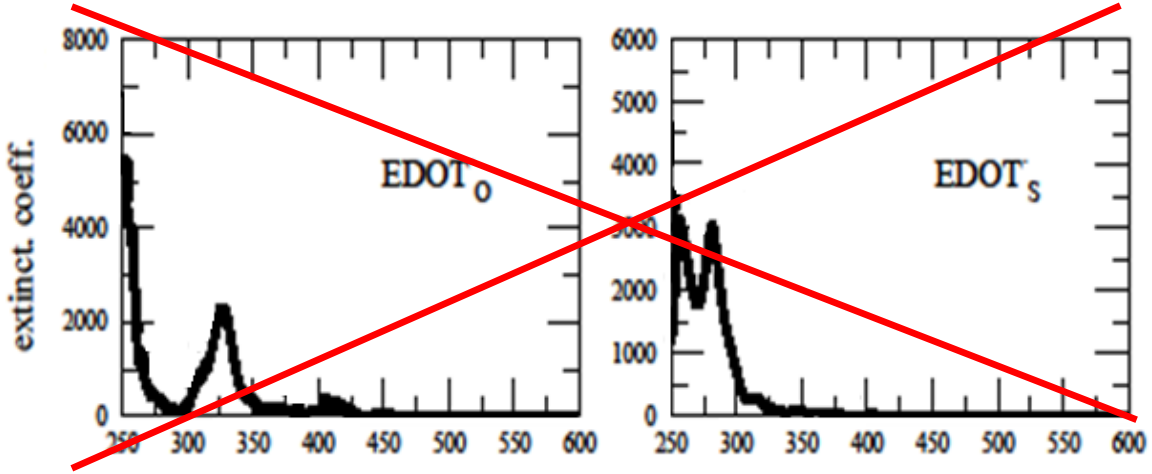
Species identification

Second reaction:

- X + X→ Y (first mechanism)



- X → Y (second mechanism)



Absorption band of Y:

360 nm

→ Y = EDOT$_2^{2+}$

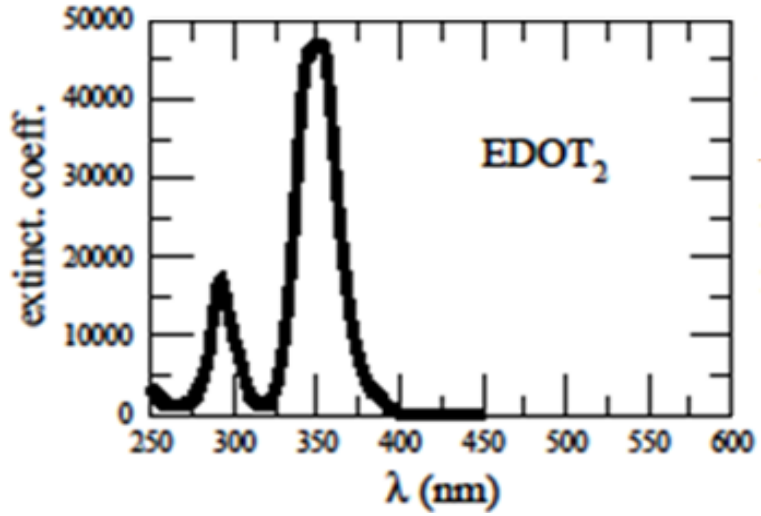
Species identification and mechanism

Third reaction of first mechanism:

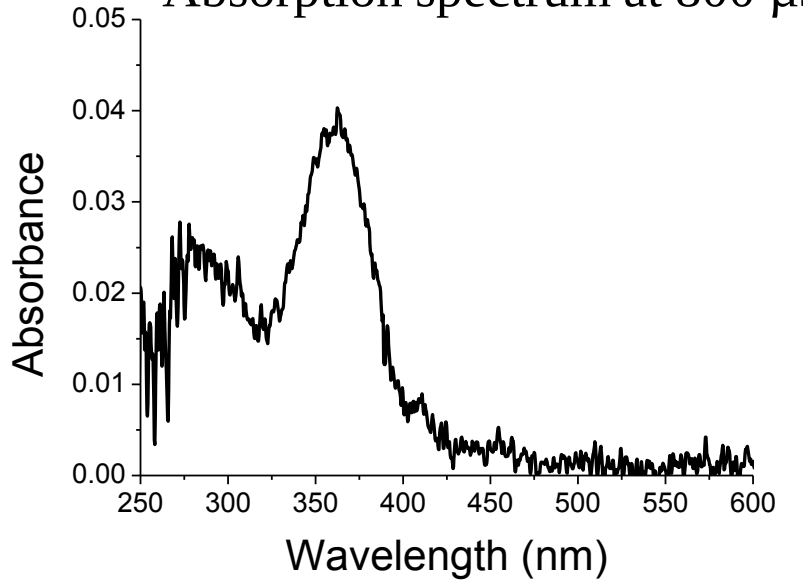
- $Y \rightarrow Z$

Absorption bands of Z:

290 and 360 nm



Absorption spectrum at 800 µs



Species identification and mechanism

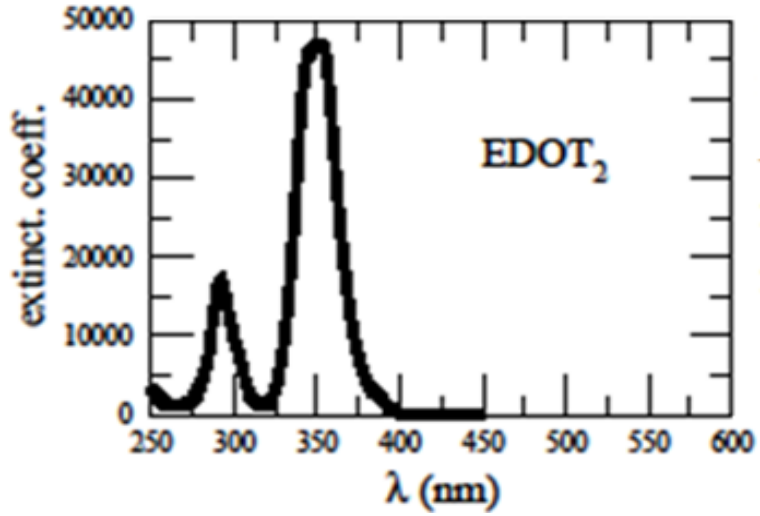
Third reaction of first mechanism:

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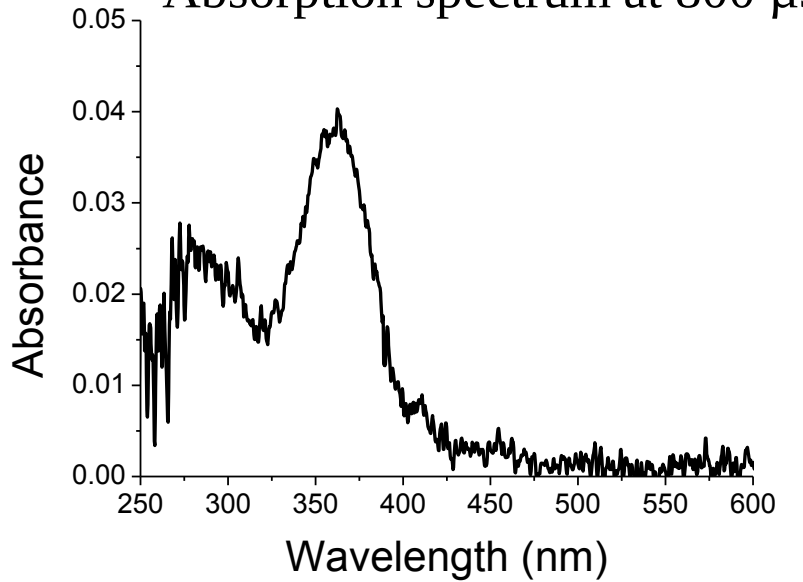
Absorption bands of Z:

290 and 360 nm

→ Z = $EDOT_2$



Absorption spectrum at 800 µs



Characterization of polymers

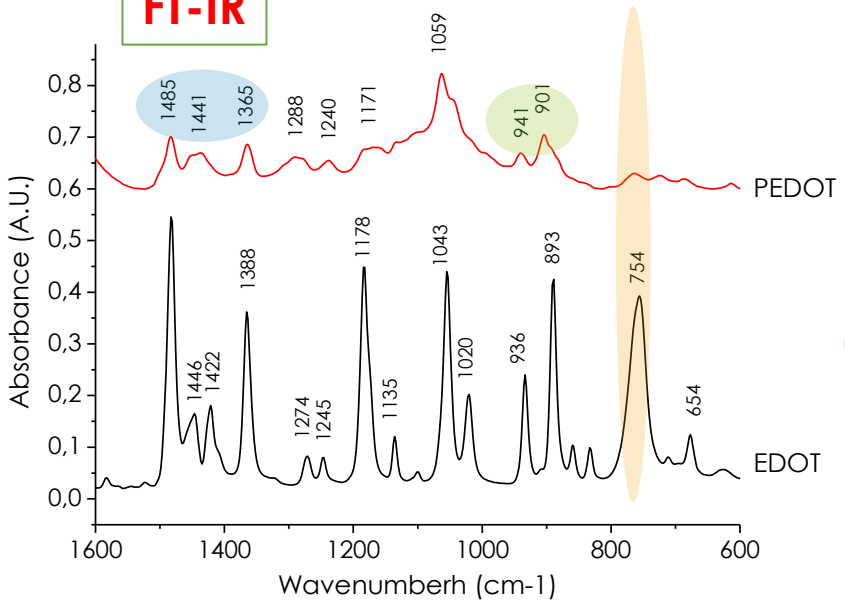
Electron accelerator

e^-



- Water solution of 10 mM EDOT
- under N_2O atmosphere
- Dose = 180 kGy (dose rate= 40 Gy/pulse)
- Frequency: 10 Hz
- 4500 pls

FT-IR



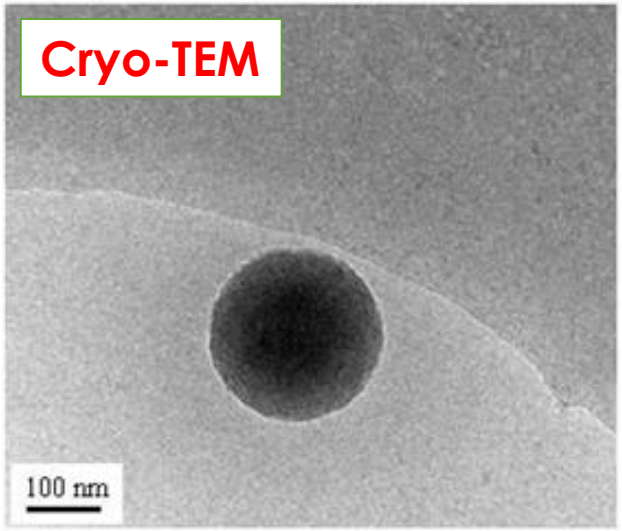
C-S

C=C
C-C

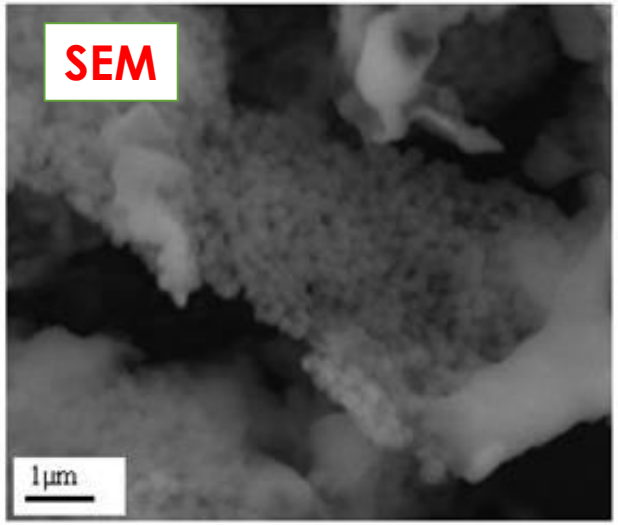
Lyophylization



Cryo-TEM



SEM



Conclusion and perspectives

- Kinetic studies:

i. Rate constant ;

ii. Identification of a step-by-step mechanism ;

iii. Identification of chemical species

- Synthesis by electrons

- PEDOT Polymerization by other radicals ($N_3^{\cdot}$, $CO_3^{\cdot -}$, $SO_4^{\cdot -}$)
- Other conducting polymers in water (polypyrrole)
- Hydrophobic polymers in organic solvants(poly-DPB)
- Conducting polymers in micellar environment (SDS)



Acknowledgments

Directors: S. Remita et J-L. Marignier

Collaborators: P. Archirel, P. Pernot, J-M Guigner, A. Dazzi,

ELYSE group: J-P. Larbre, P. Jeunesse, A. Gayral and N. Decovemaker

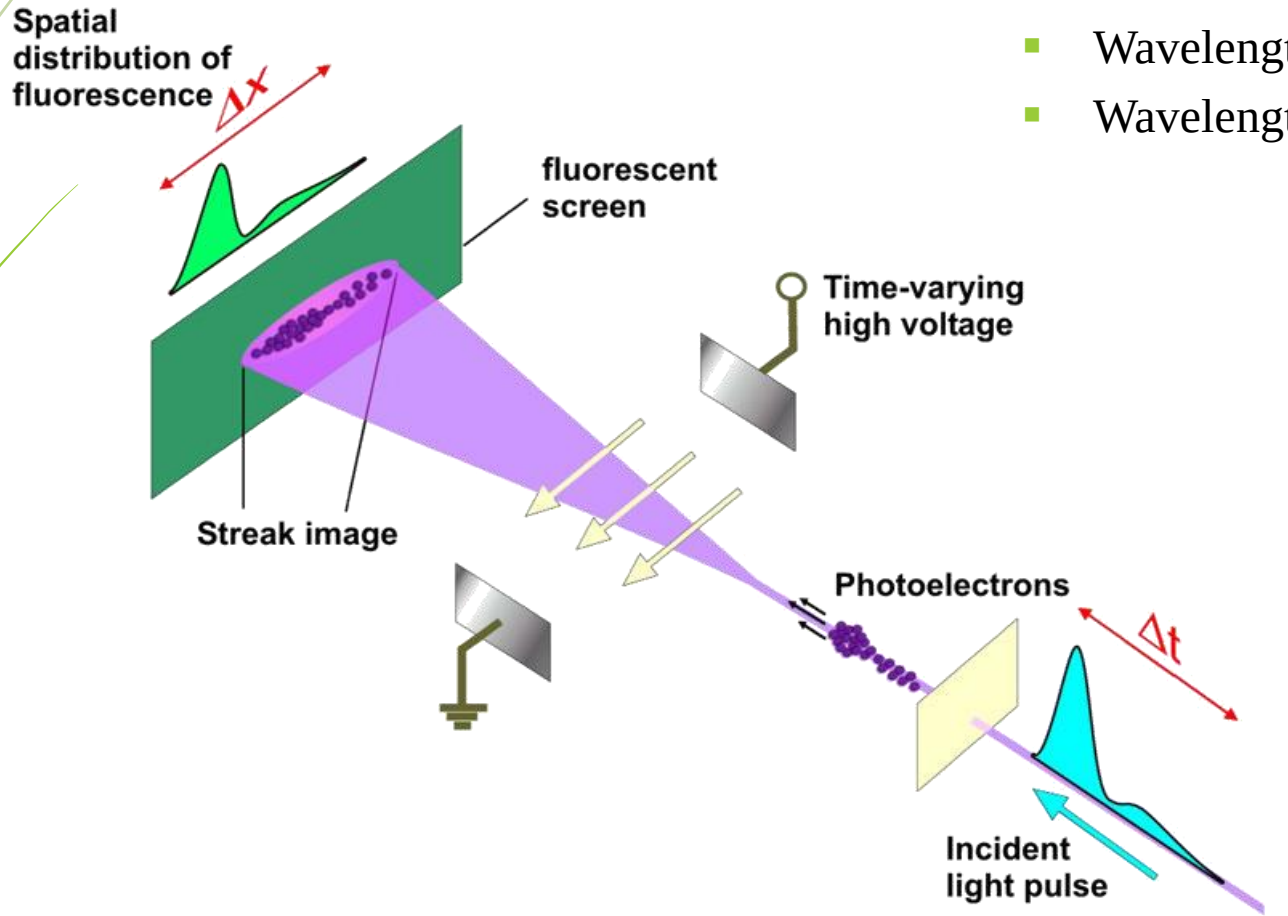
All the members of TEMiC Group

Collegues: Z.Cui

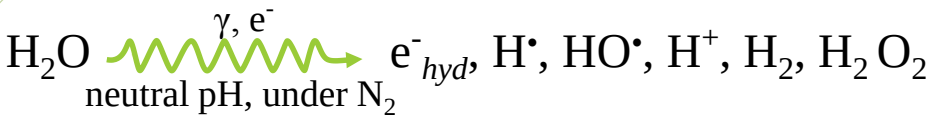
Thank you

Streak Camera

- Time range ***500 ps à 1 ms***
- Time resolution ***3,7 ps***
- Wavelength range ***250 nm à 850 nm***
- Wavelength resolution ***1 nm***



Water Radiolysis



Dose measurement:

$A_{660nm,\ 3ns} \rightarrow [e^-_{hyd}] = 1.4\ 10^{-5}$ M

$G(e^-)_{3ns} = 3.45\ 10^{-7}$ mol J^{-1}

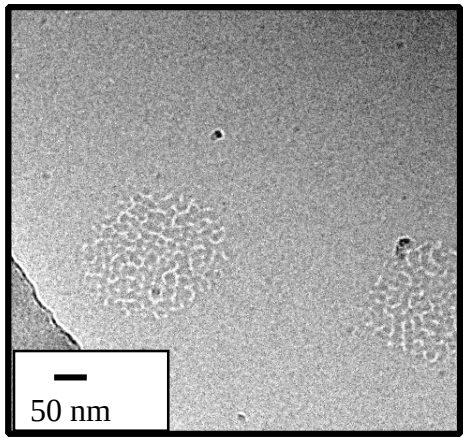
$\varepsilon_{660\ nm} = 1.8\ 104$ L mol^{-1} cm^{-1}

C=DG

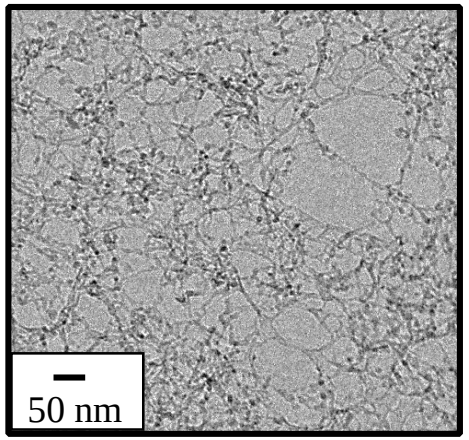
$G(HO^\bullet)_{100ns} = G(HO^\bullet) + G(e^-_{hyd}) = 5.45\ 10^{-7}$ mol J^{-1}

$[HO^\bullet] = 2,2\ 10^{-5}$ $molL^{-1}$ << [EDOT]

Gamma induced synthesis of conducting polymers

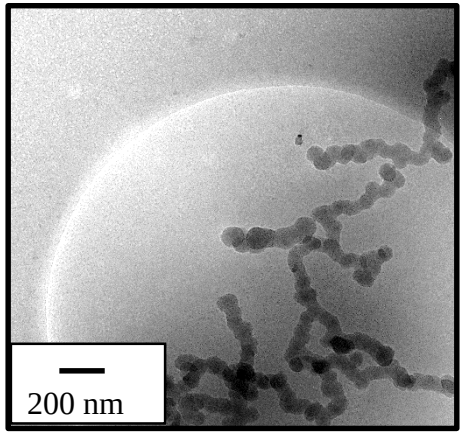


PEDOT by $HO^{\cdot}$

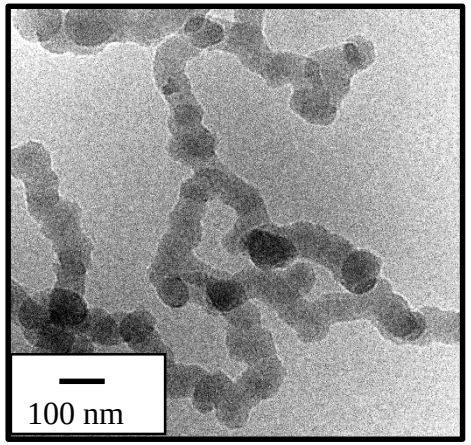


PEDOT by $N_3^{\cdot}$

Lattach, Y. *et al. ChemPhysChem.* 82 (2013): 44-53



PPy by $HO^{\cdot}$



Cui, Z., *et al. Langmuir*, *30*(2014): 14086-14094.