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Nanosensors for industrial applications

One-Step Fabrication of Multifunctional Core-Shell Nanofibres by Co-Electrospinning

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Overview

Introduction

- Optical sensors for O_2 and pH
- Incorporation of magnetic properties
- Three functionalities in one-step synthesis: our proposal

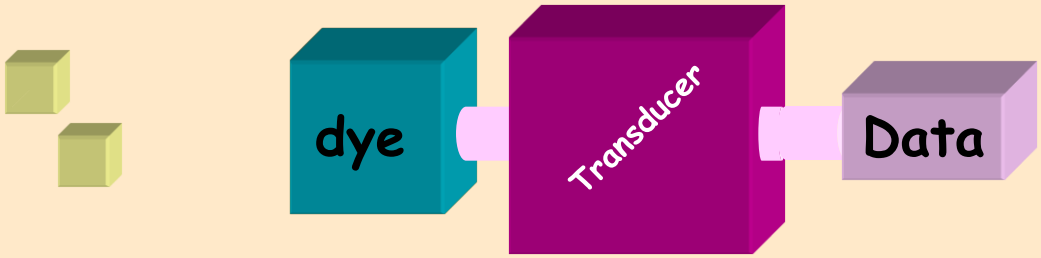
Experimental

- Shell: pH-sensitive polymer
- Core: magnetic and O_2-sensitive
- Synthesis of magnetic, pH and O_2-sensitive tissues
- Analytical properties

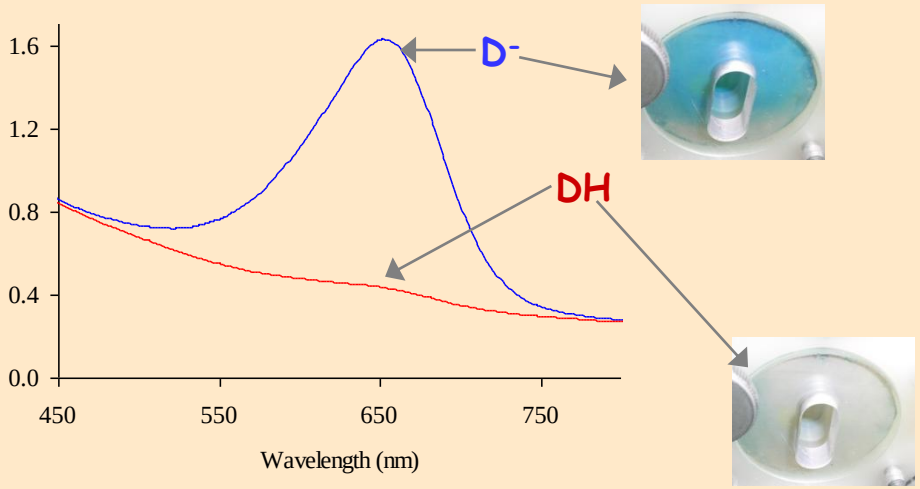
Conclusions

Acknowledges

Optical sensors for pH and O_2

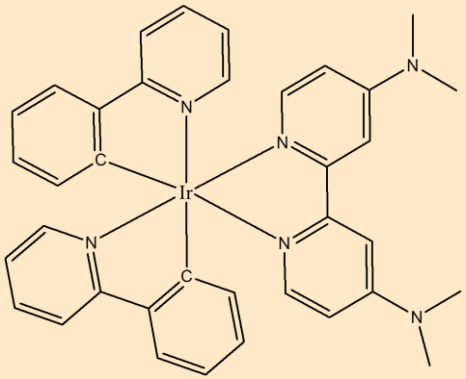


pH determination: change in absorption or emission of light

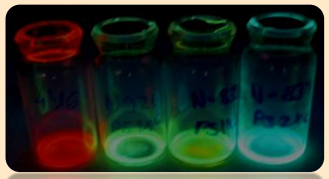


Optical sensors for pH and O_2

O_2 determination: luminescence quenching

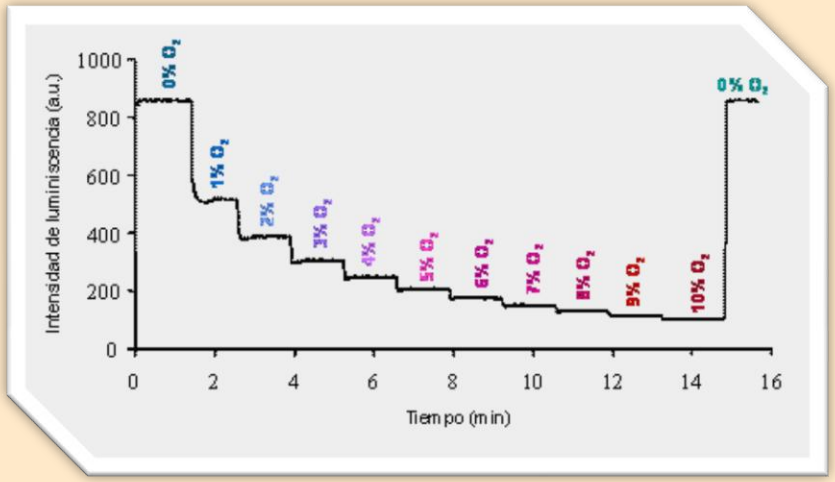


Presence of O_2



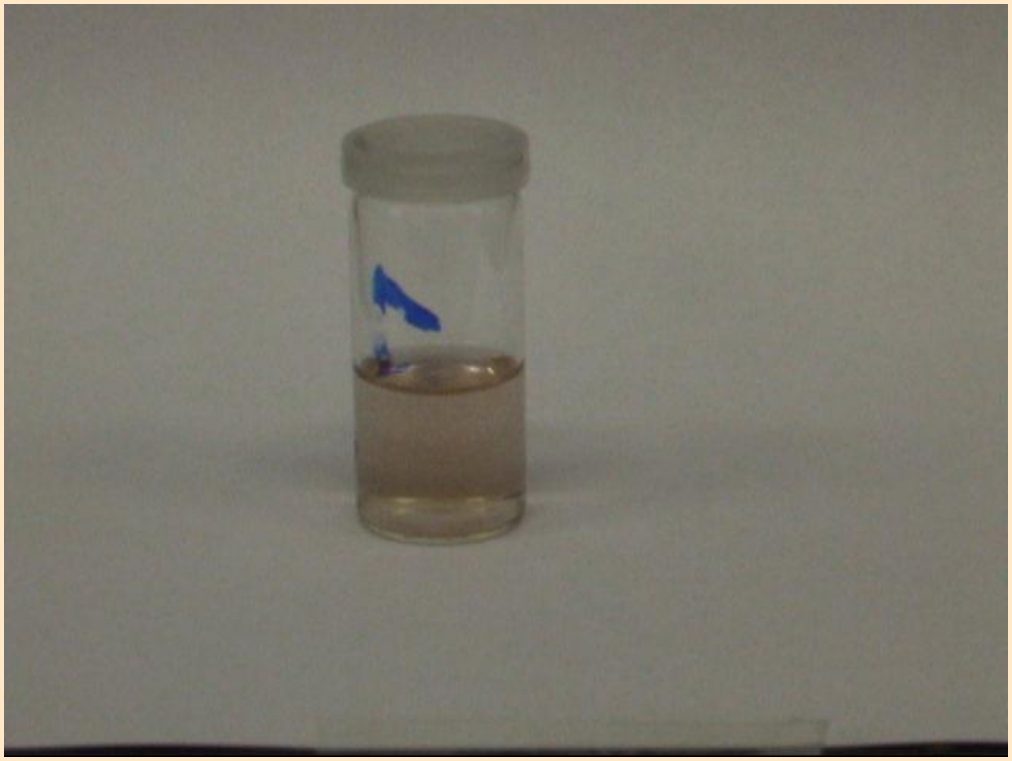
Absence of O_2

$I/I_0 \alpha [O_2]$

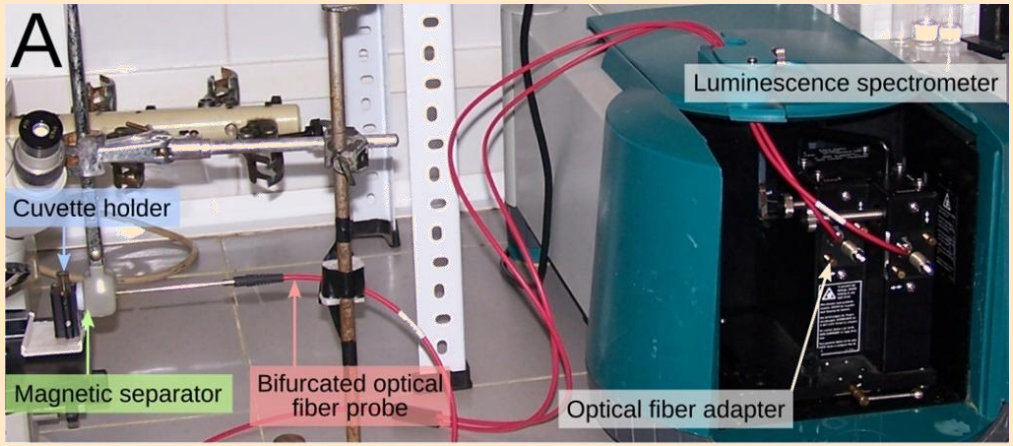


Incorporation of magnetic properties

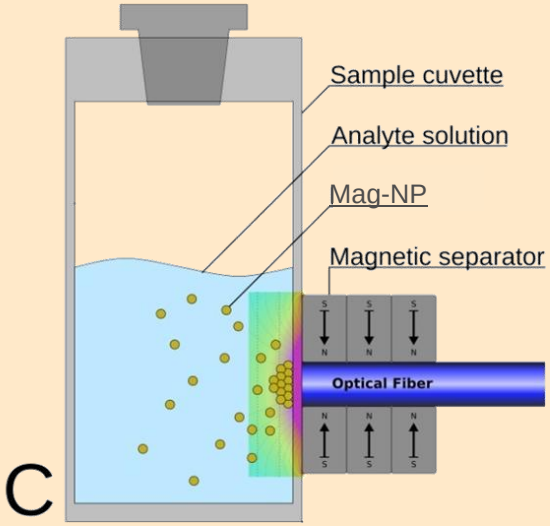
The incorporation of magnetic properties into the sensing material allows the *in situ* formation of sensor spots by magnet separation and optical readout from the outside or an easy way to fix the sensing material at the tip of an optical fiber.



Incorporation of magnetic properties



Front view of the magnetic separator



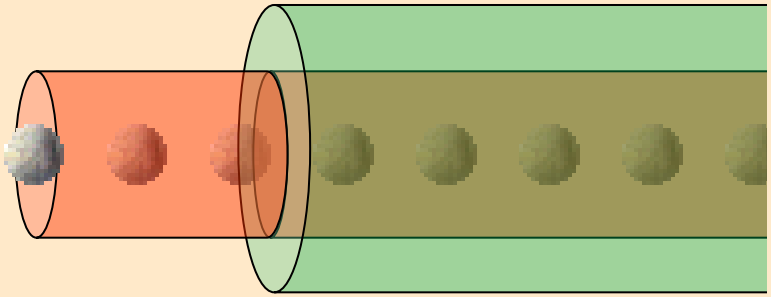
Our proposal

Sensitive to O_2 + Magnetic + Sensitive to pH

For the successful conjugation of these three functionalities, two different chemical environments on the same material are necessary: a hydrophilic environment for the pH indicator and a hydrophobic environment for the O_2 indicator. The magnetic susceptibility could be incorporated in either of these environments.

Core (hydrophobic):

Magnetic
Sensitive to O_2



Shell (hydrophilic):

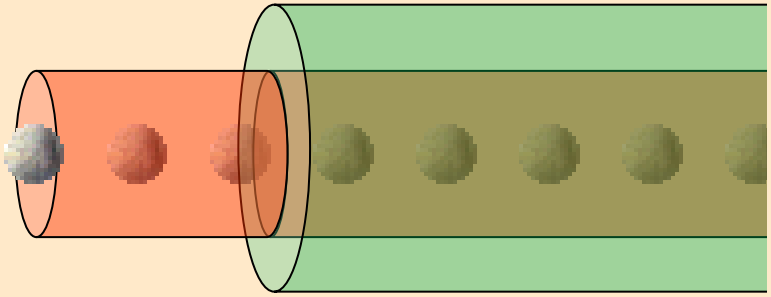
Sensitive to pH

Our proposal

Core (hydrophobic):

Magnetic

Sensitive to O_2



Shell (hydrophilic):

Sensitive to pH

Magnetic nanoparticles

O_2-sensitive dye

Polymer

pH-sensitive polymer

Co-electrospinning technique allows a strict control of the process and thus the design of well-organized multifunctional materials; thus by one-step fabrication different pairs of copolymers can be processed as coaxial micro- and nano-fibres .

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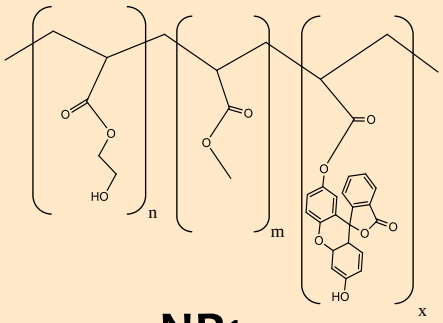
Shell: pH-sensitive polymer

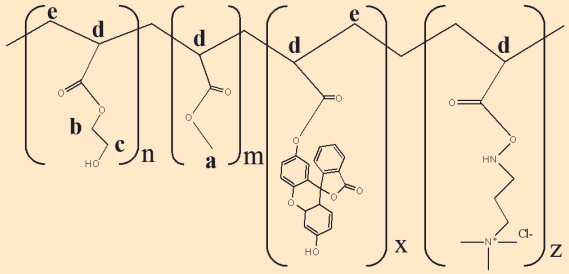
Lineal copolymer with a pH-sensitive fluorescent probe covalently attached. It should be water-insoluble and soluble in polar organic solvents.

These copolymers are based on the copolymerization of FOA, MMA and HEMA (poly FOA-co-MMA-co-HEMA) by reverse ATRP. In addition, MAPTAC or AAMPs can be added to change slightly the charge and therefore the pK_a.



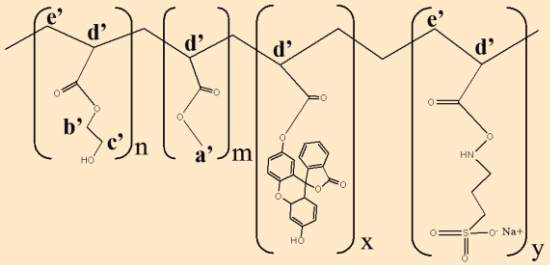
NP1

pK_a= 8.5



NP1(X)

pK_a= 7.5



NP1(-)A

pK_a= 9.6

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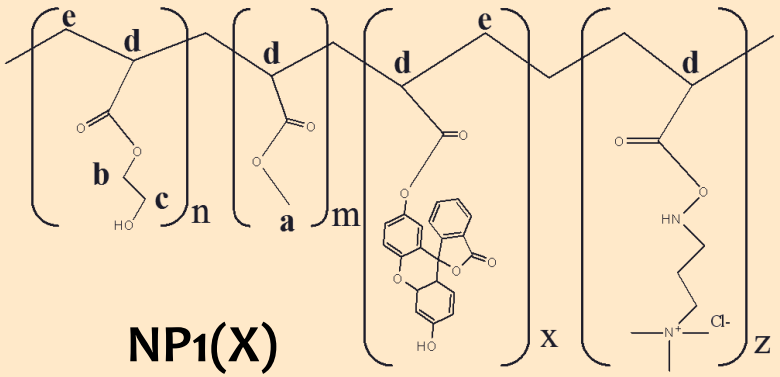
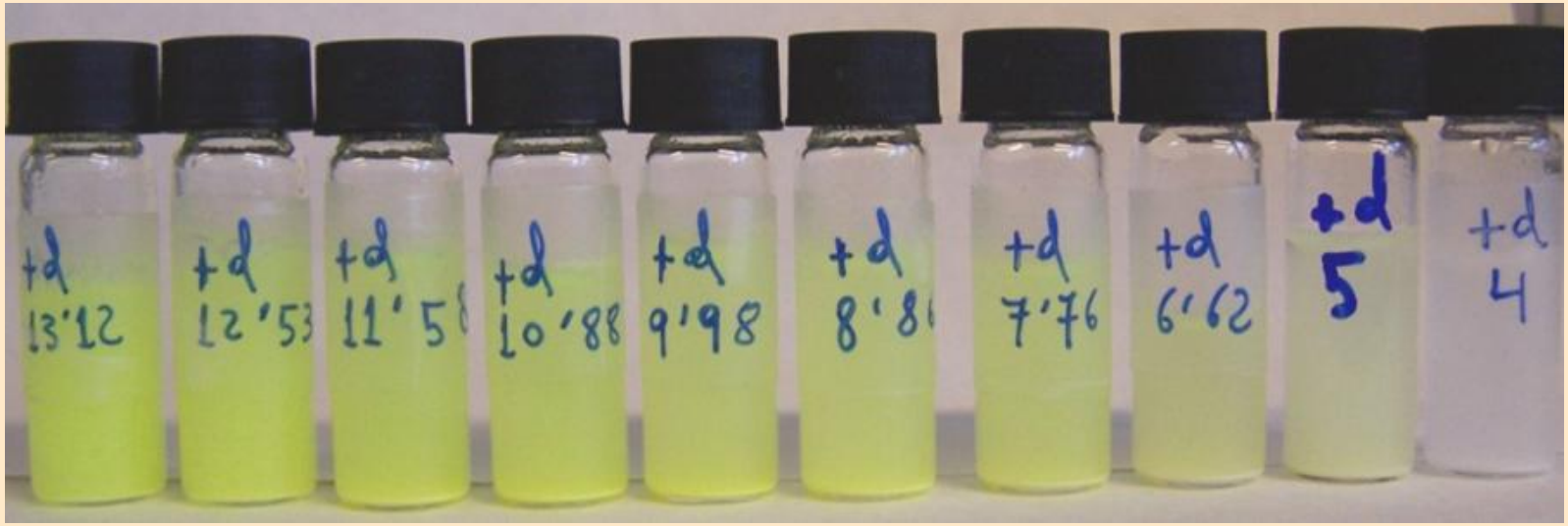
Shell: pH-sensitive polymer



NP1(X)

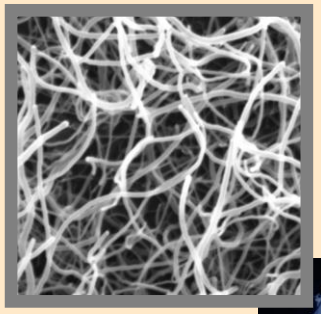
pK_a= 7.5
M_w=104517 Dalton
M_w/M_n: 1.4
Intrinsic Viscosity: 0.28 dL/g



J. Mater. Chem., 2011, 21, 6742

Shell: pH-sensitive polymer

pH-sensitive nanofibres mats



169±24 nm diameter

2.5 h to collect 20 cm diameter

Syringe

Polymer solution

30 wt% NP1(X)
1.75 wt% HCl
DMF
Conductivity: 678 S/cm

Spinning nozzle ($\Phi_{ext/int}$=1.5/1.1 mm)

Injector voltage: 16.4 kV

High voltage for injection

Distance: 29.5 cm

Fibers

Collector

High voltage for collection

Collector voltage: -9.7 kV

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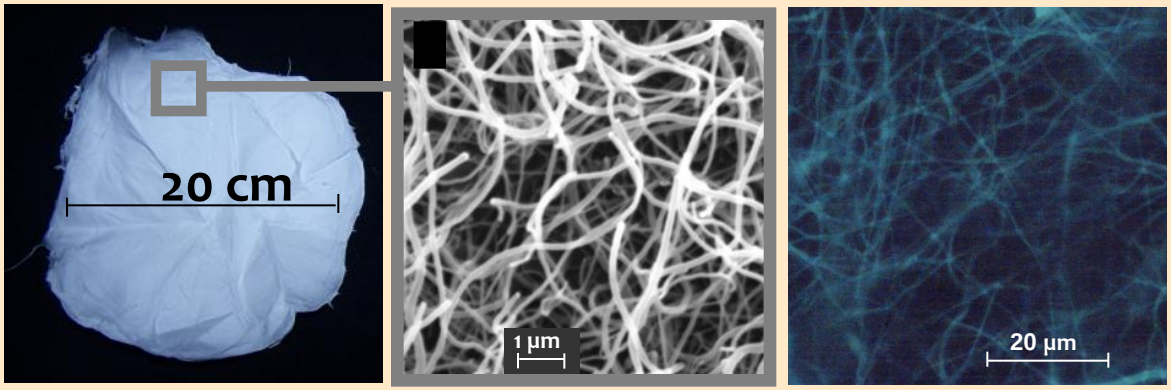
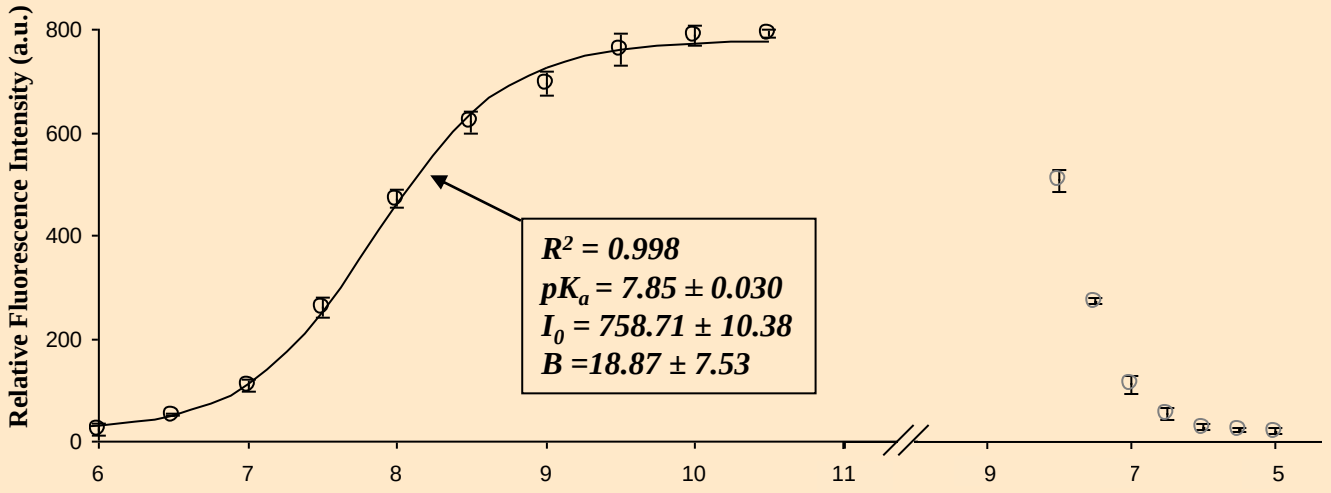
Shell: pH-sensitive polymer

pH-sensitive nanofibres mats





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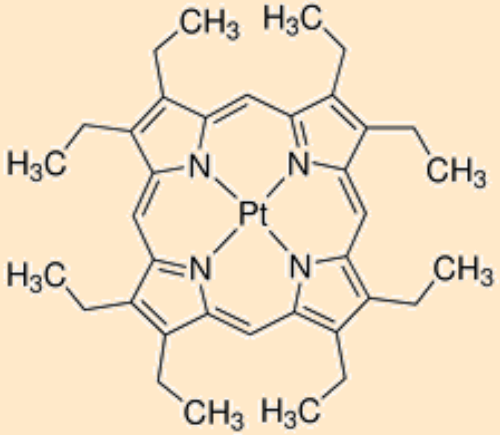
Core: Magnetic and O_2-sensitive

To incorporate oxygen-sensitive properties it is necessary to immobilize a O_2-sensitive complex.

These kind of complexes are hydrophobic.

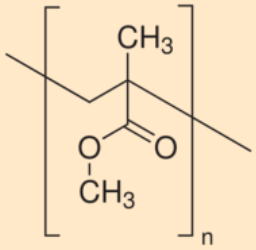


PtOEP

Solvent

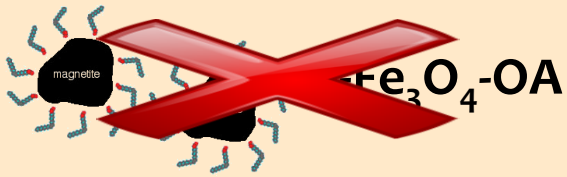
THF

Polymer



PMMA

Magnetic particles

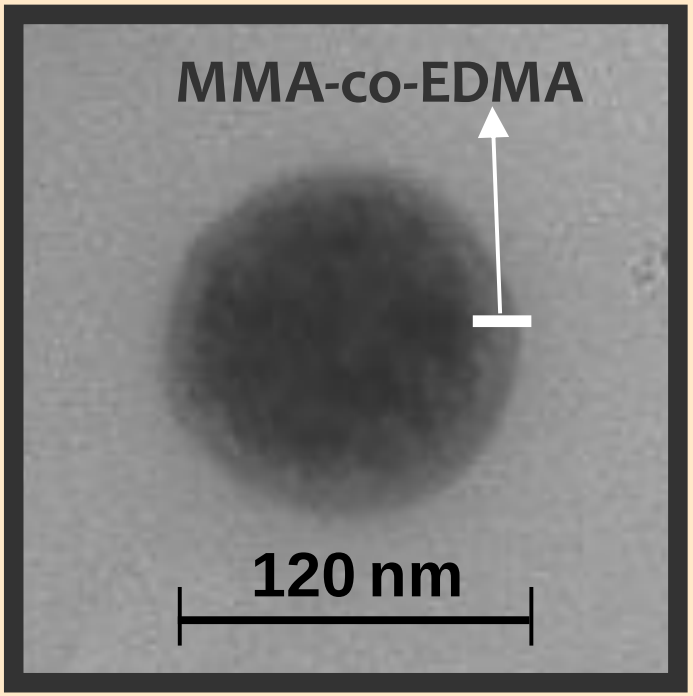


It decants in few minutes

Adv. Funct. Mater., 2011, 21, 3844

Core: Magnetic and O_2-sensitive

To increase the stability of γ-Fe_3O_4-OA in PMMA/THF, we used γ-Fe_3O_4-OA encapsulated into MMA-co-EDMA



nanomyp® magNP particles

MMA-co-EDMA matrix is chemically similar to PMMA and thus the chemical affinity between them is maximized.

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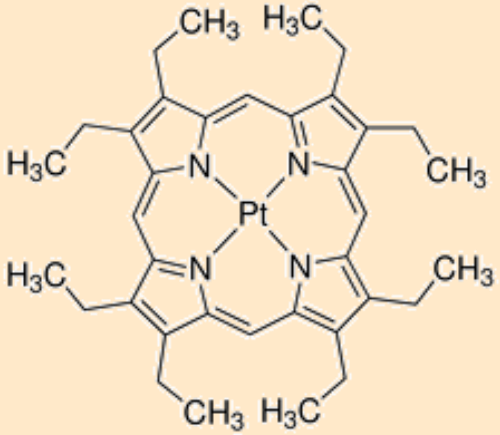
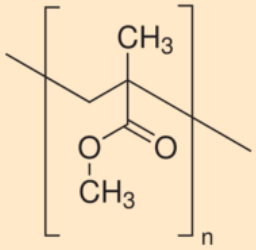


PtOEP

Solvent

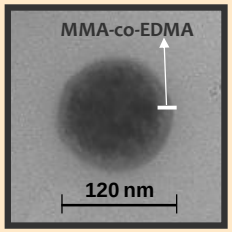
THF

Polymer



PMMA

Magnetic particles



They provide a highly stable inner suspension which allows a coaxial cone in steady state for a long time (more than 4 h).

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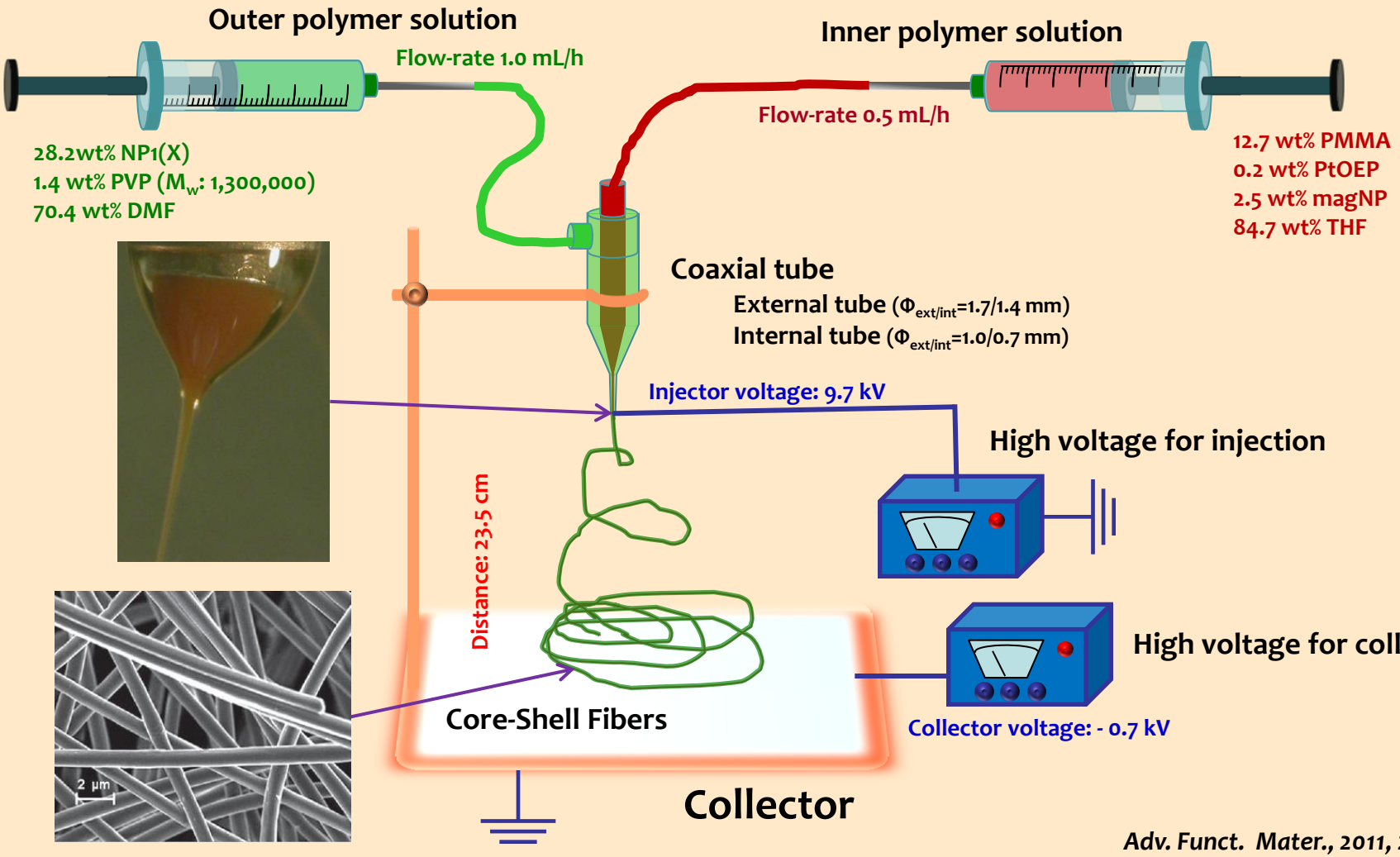
Synthesis of magnetic, pH and O_2-sensitive tissues



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Synthesis of magnetic, pH and O_2-sensitive tissues

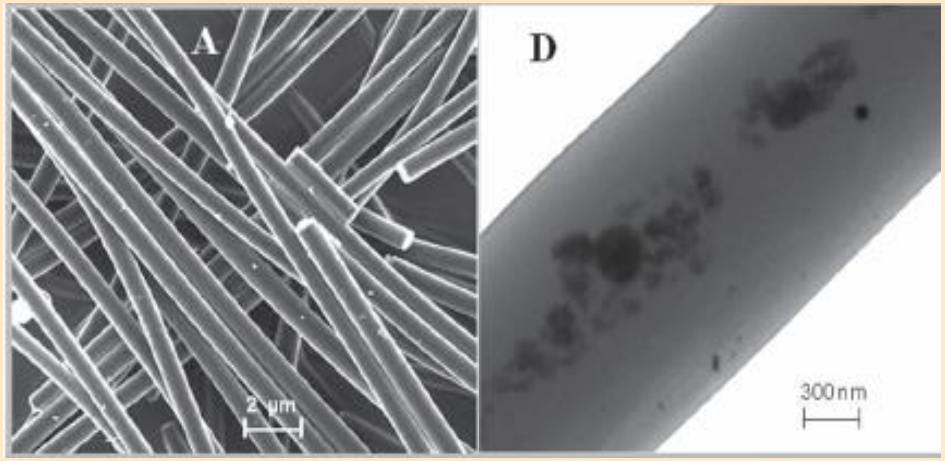
Effect of composition: amount of mag-NP

Outer polymer solution

28.2wt% NP1(X)
1.4 wt% PVP (M_w: 1,300,000)
70.4 wt% DMF

Inner polymer solution

13.3 wt% PMMA
0.0 wt% PtOEP
0.6 wt% magNP
84.7 wt% THF



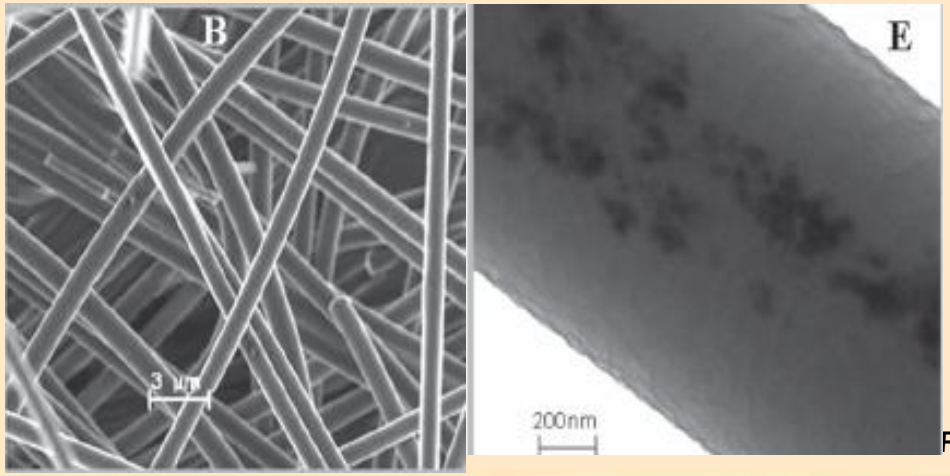
C1

Outer polymer solution

28.2wt% NP1(X)
1.4 wt% PVP (M_w: 1,300,000)
70.4 wt% DMF

Inner polymer solution

12.7 wt% PMMA
0.0 wt% PtOEP
2.5 wt% magNP
84.7 wt% THF



C2

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Synthesis of magnetic, pH and O_2-sensitive tissues

Effect of composition: incorporation of PtOEP

Outer polymer solution

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1.4 wt% PVP (M_w: 1,300,000)
70.4 wt% DMF

Inner polymer solution

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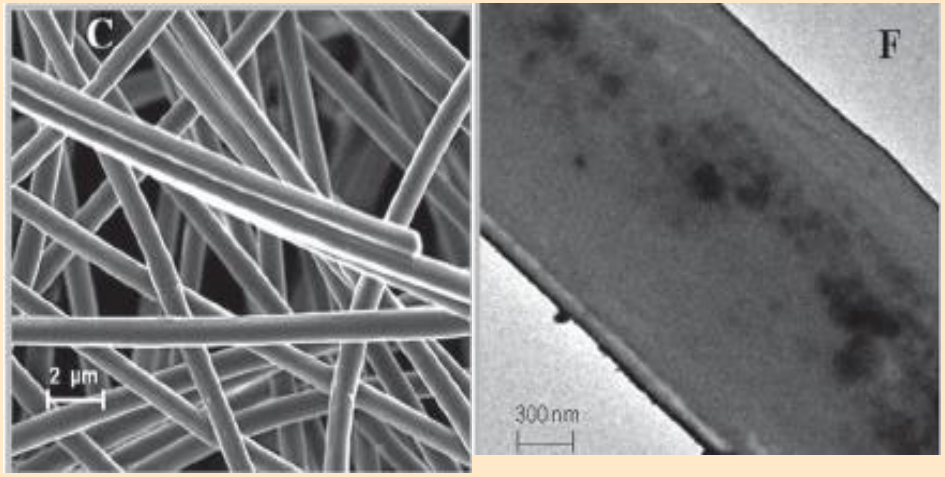
84.7 wt% THF



C2

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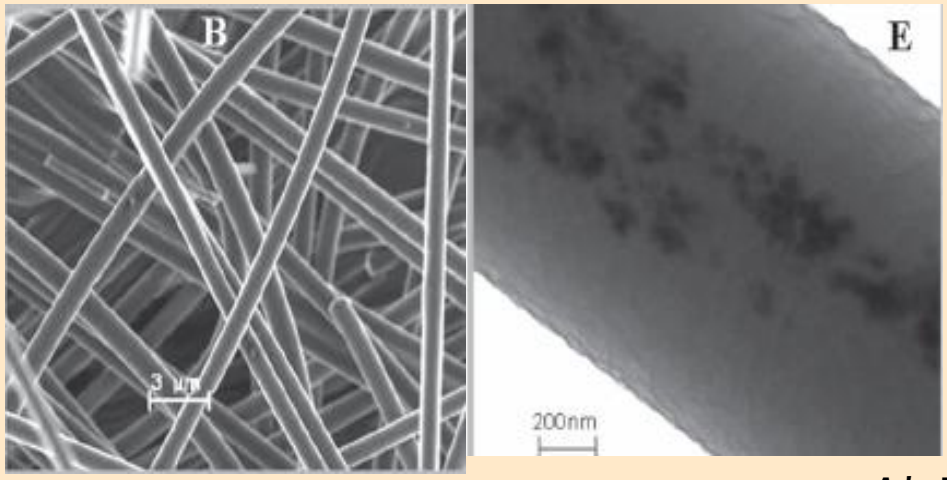

C2-O2

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Synthesis of magnetic, pH and O_2-sensitive tissues

Effect of composition: incorporation of PtOEP

Outer polymer solution

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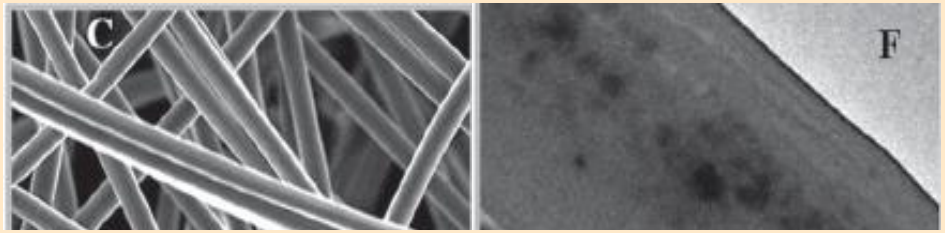
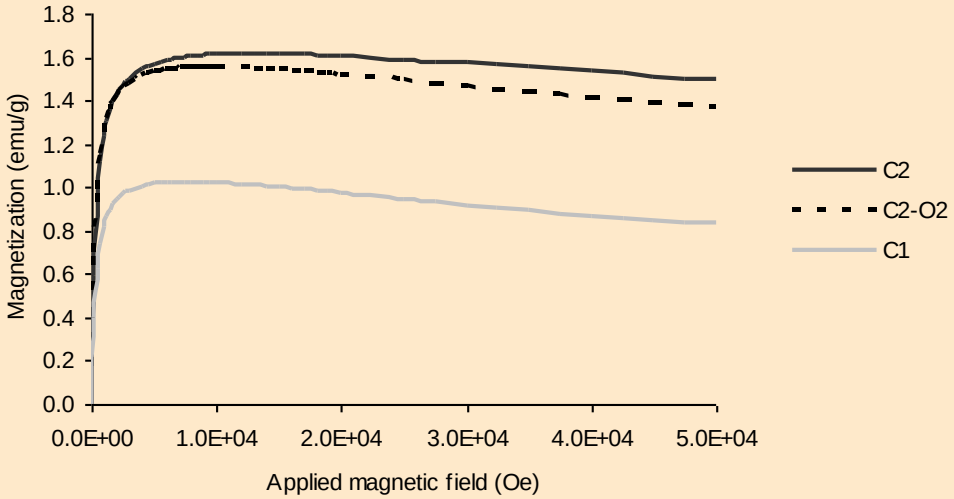
1.4 wt% PVP (M_w: 1,300,000)
70.4 wt% DMF

Inner polymer solution

12.7 wt% PMMA
0.0 wt% PtOEP
2.5 wt% magNP
84.7 wt% THF



C2



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C2-O2

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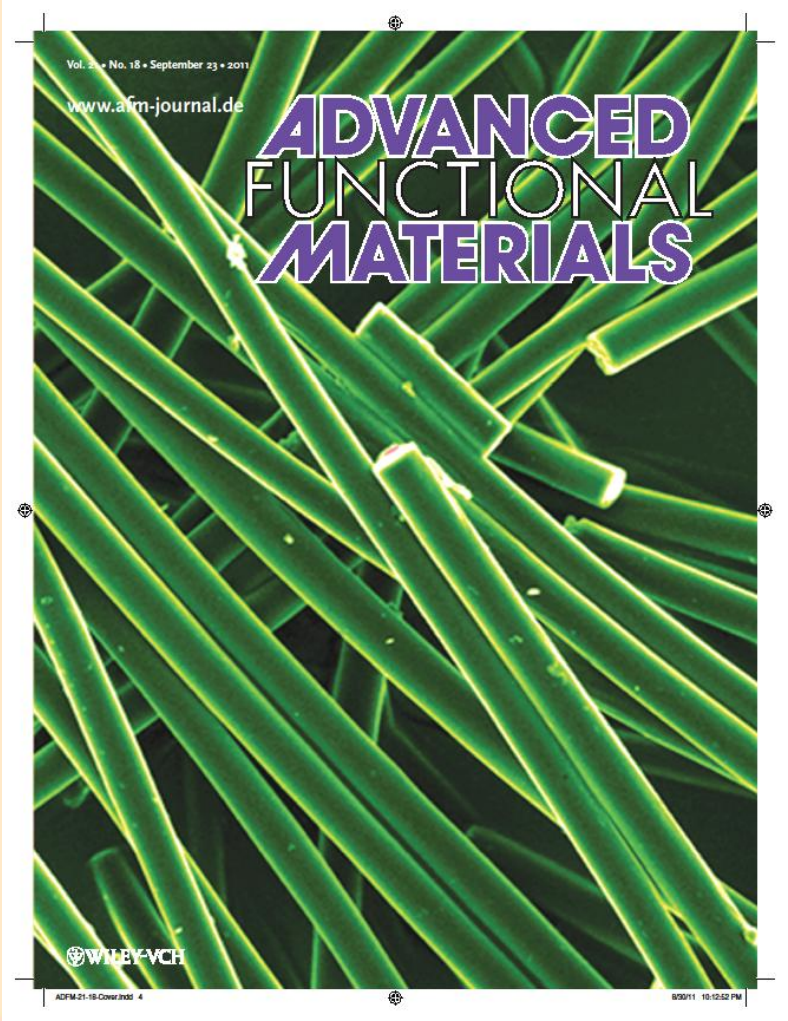
Synthesis of magnetic, pH and O_2-sensitive tissues

Distribution of NP1(X) and PtOEP



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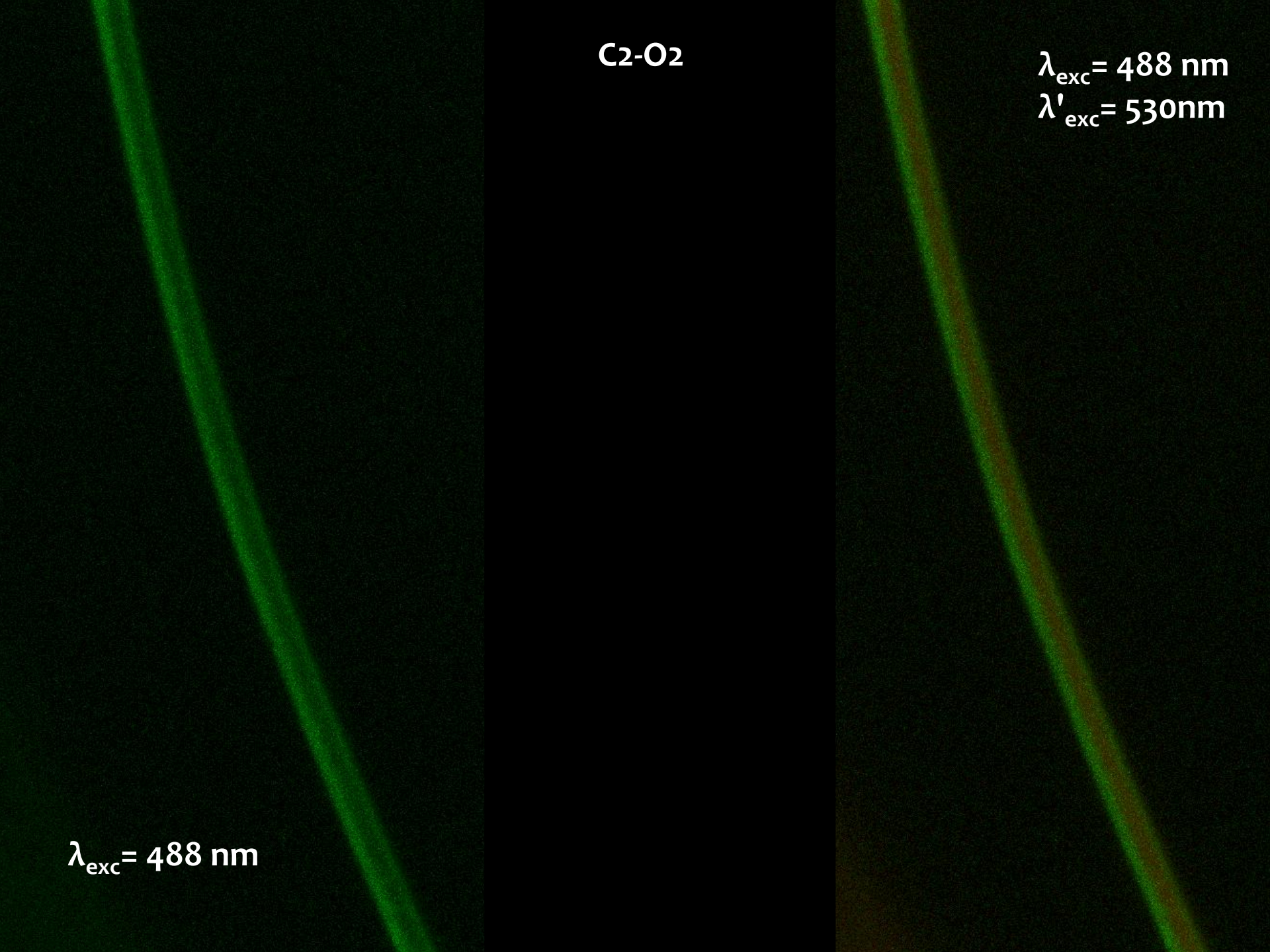
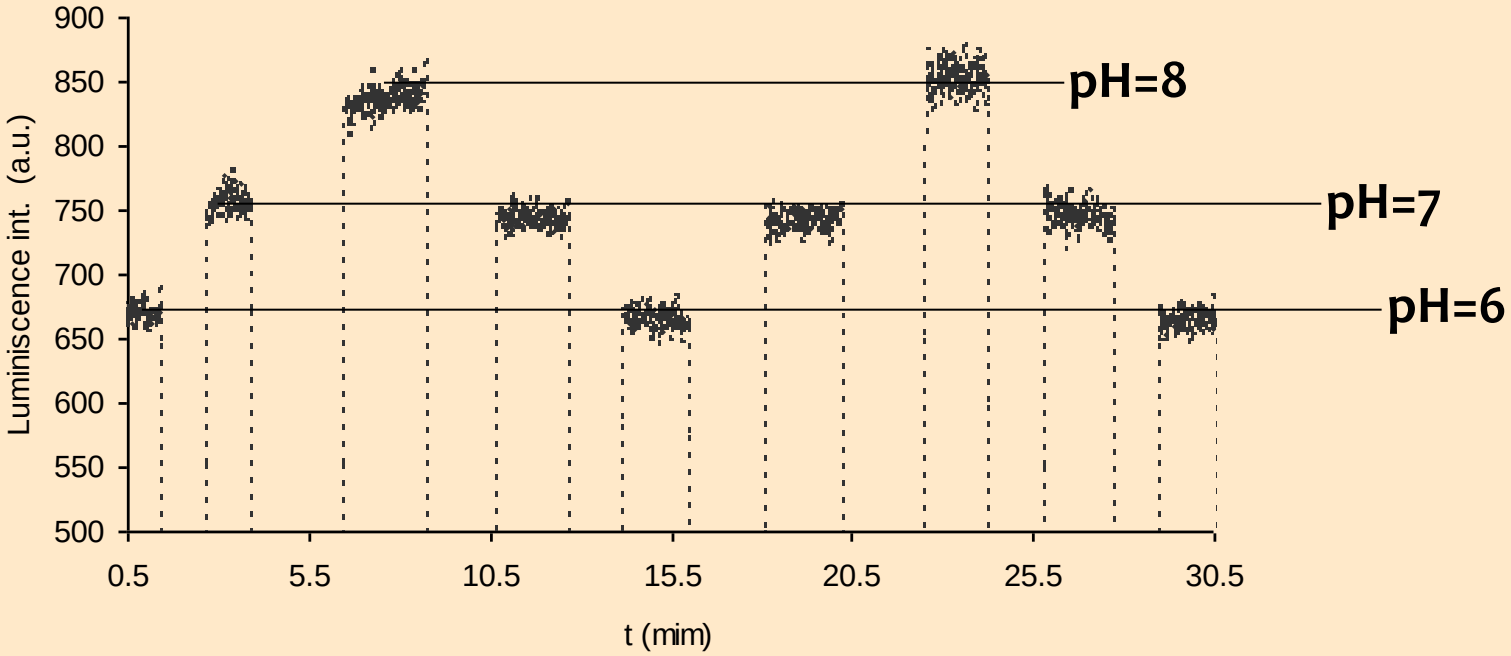

C2-O2
λ_{exc}= 488 nm
λ'_{exc}= 530nm
λ_{exc}= 488 nm

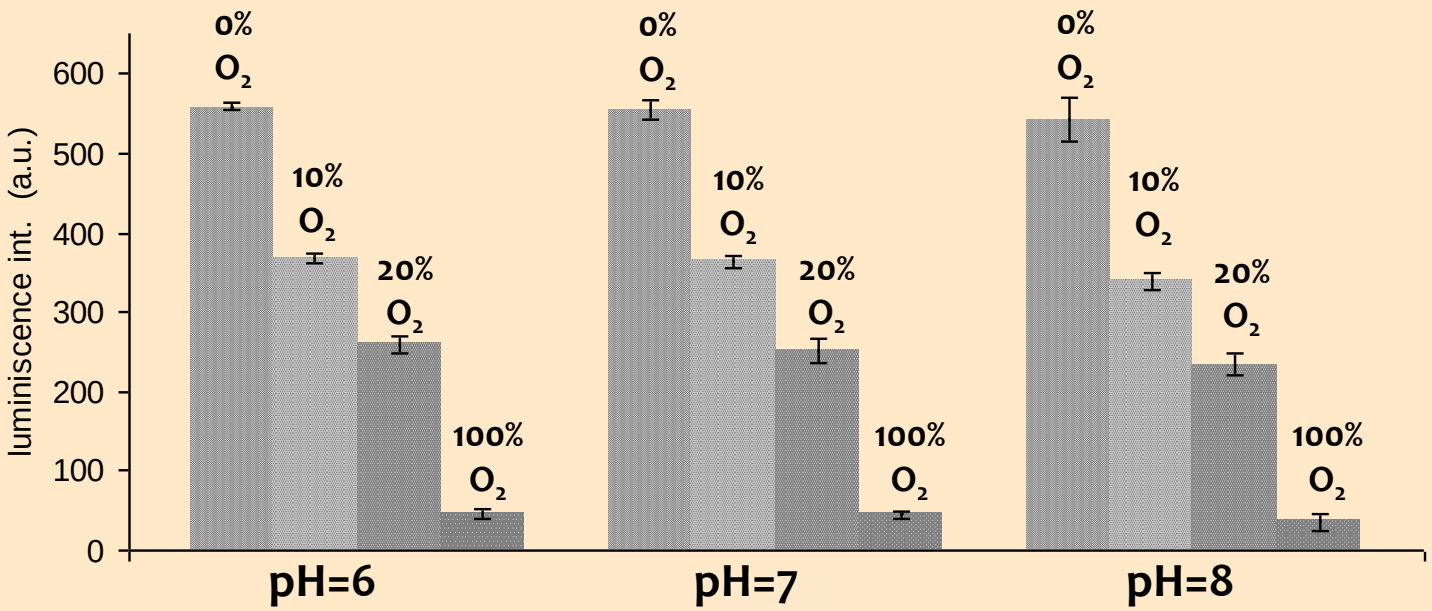
Analytical properties

pH calibration and reversibility



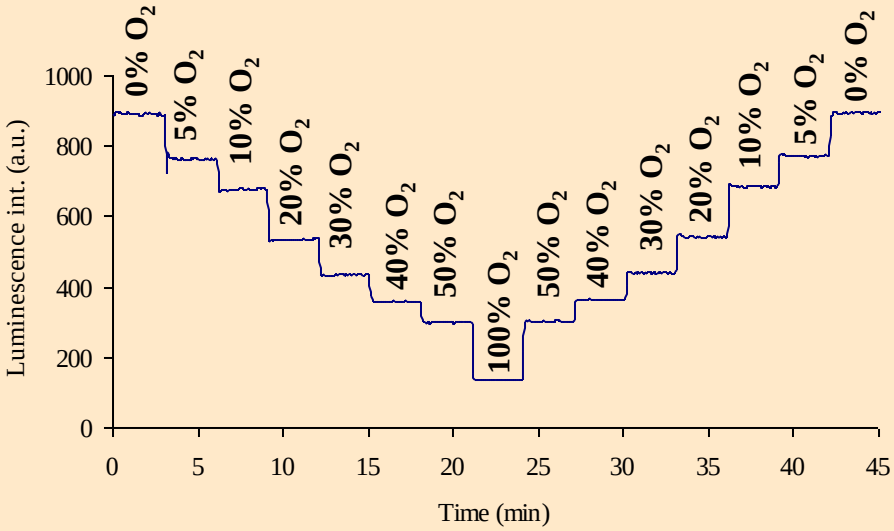
Analytical properties

Effect of pH on the determination of O_2

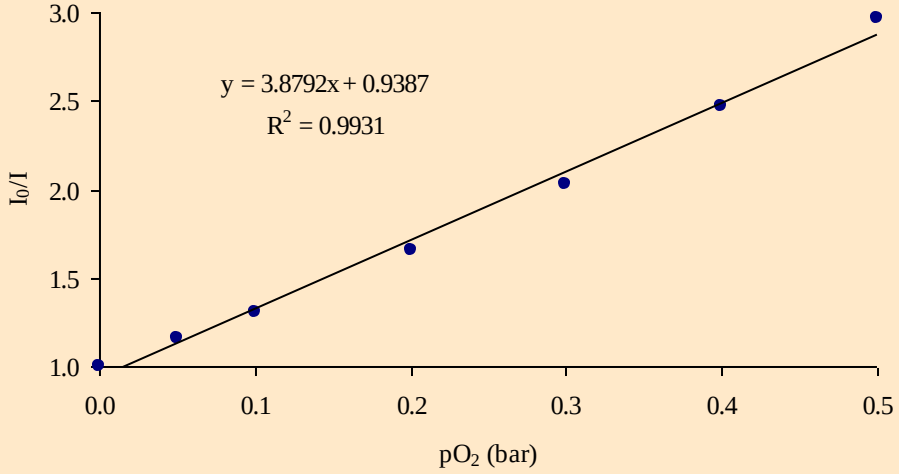


Analytical properties

Stern-Volmer plot in gas phase



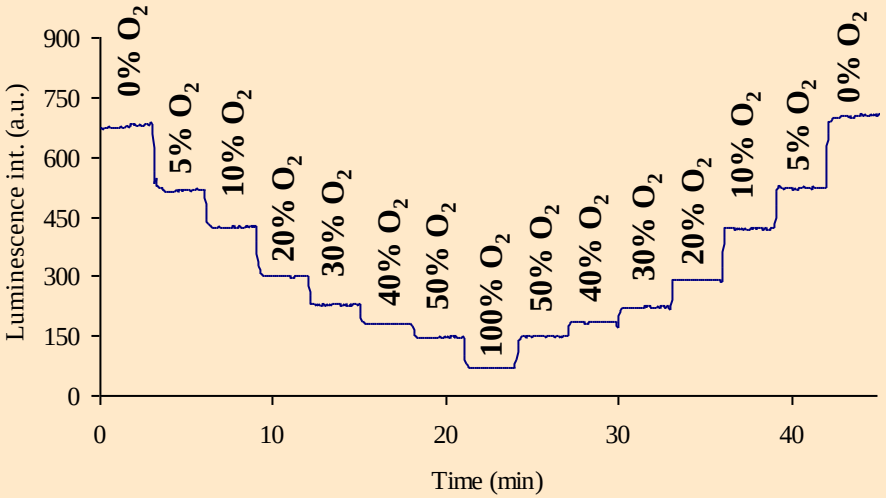
t_{90} (0-5%) = 15 s
t_{90} (5-0%) = 12 s



K_{sv}= 3.88 bar^{-1}

Analytical properties

Stern-Volmer plot in solution



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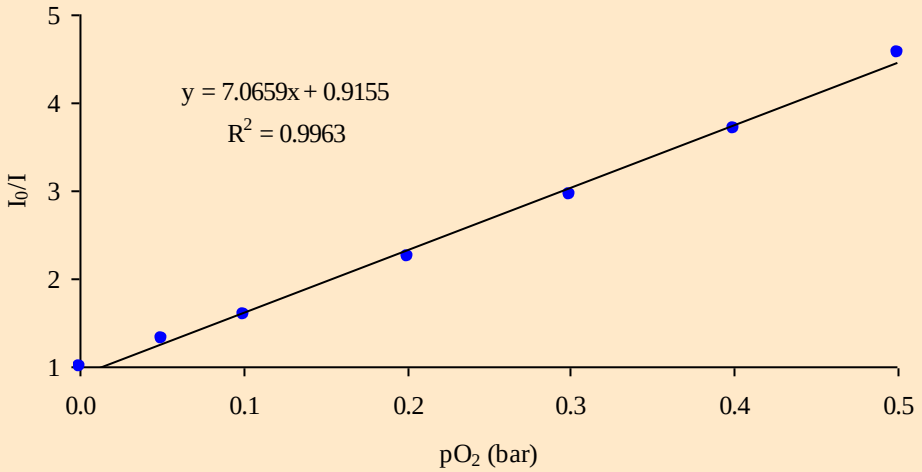

K_{sv}= 7.07 bar^{-1}

Conclusions

- Novel lineal, pH-sensitive, water insoluble copolymers have been synthesized.

- Co-electrospinning is a powerful tool to design multifunctional core-shell fibres with controlled distributions of axial anisotropies in composition with high production and cost effectiveness.

- The new, advanced multifunctional material are magnetic and have a well-organised structure which allows the optical monitoring of pH and O_2, in situ, at real time and simultaneously.

- The magnetic susceptibility of the core-shell fibres can be tuned by changing the percentage of mag-NP particle in the inner suspension.

Acknowledgment





Nanotechnology and Sensors research line of FQM-297

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Thank you for your attention!!!

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