# *Fluorescence labeling of polymers for automatic identification in mixed plastic waste streams. Thermal and photochemical stability.*

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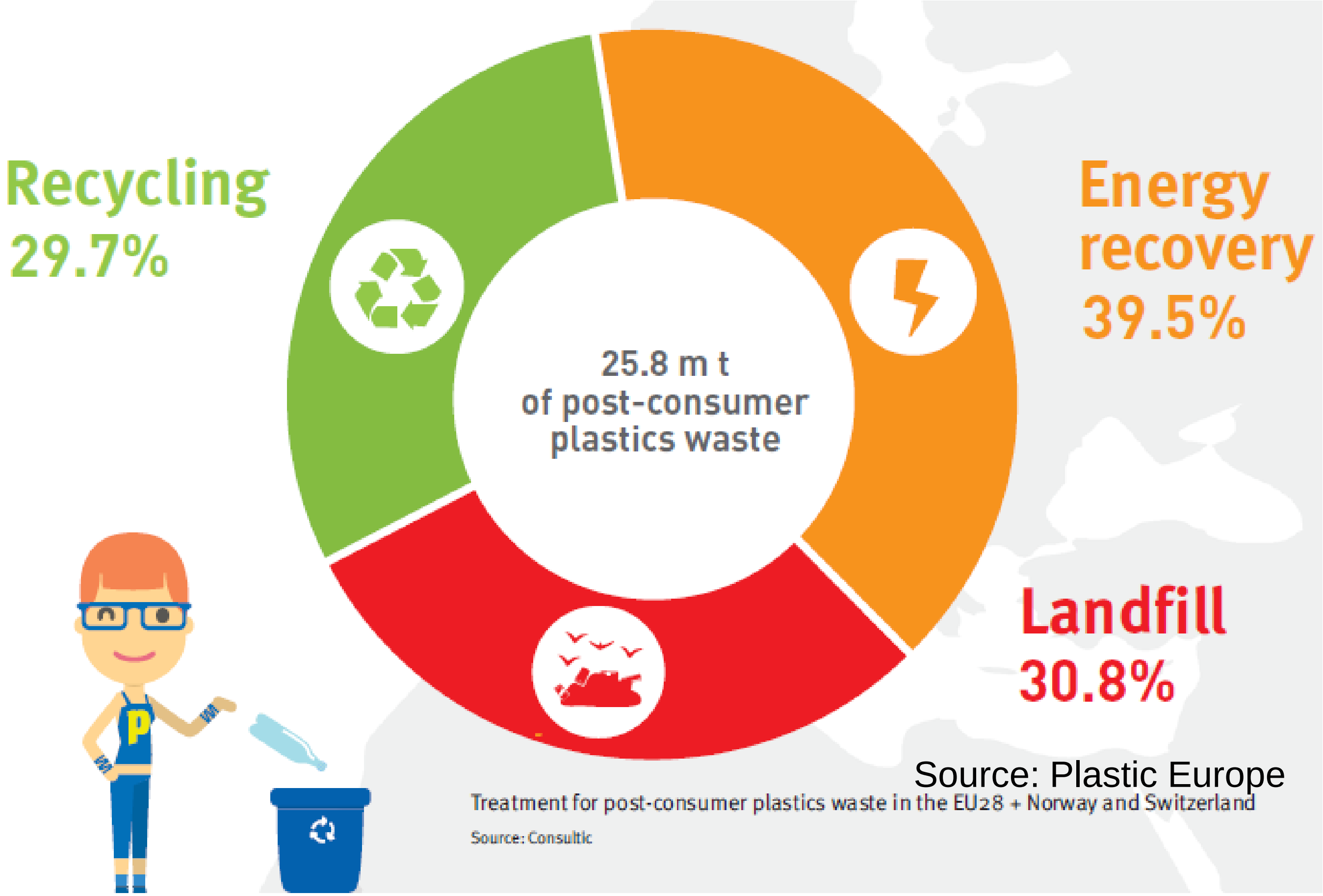
# Introduction



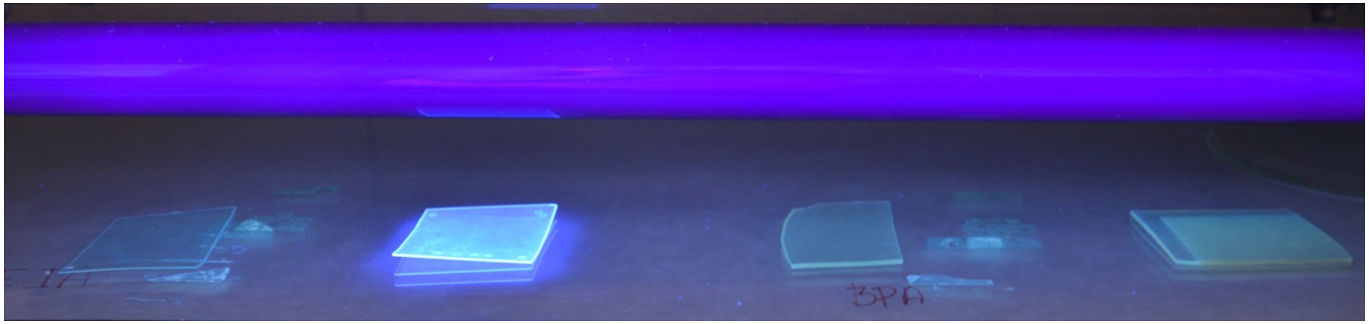

Source: Plastic Europe

Mechanical (secondary) recycling is the best alternative for most plastics. The new EU targets are very ambitious and represent a big scientific and technological challenge.

# Introduction

Nowadays manual and automated separation processes are used for the sorting. Automated processes are cheap but their actual separation capacity is still far away from 100 %.

In recent years, different methods based on the use of fluorescent markers have been proposed for the identification and automated sorting of different plastics waste.



# Introduction

2
HDPE

HDPE is growing in the recycling market because it is easy to be recovered and reprocessed and there are applications for the recycled plastic, for instance in the packaging of cleaning products (not in food packaging).

Recovered HDPE

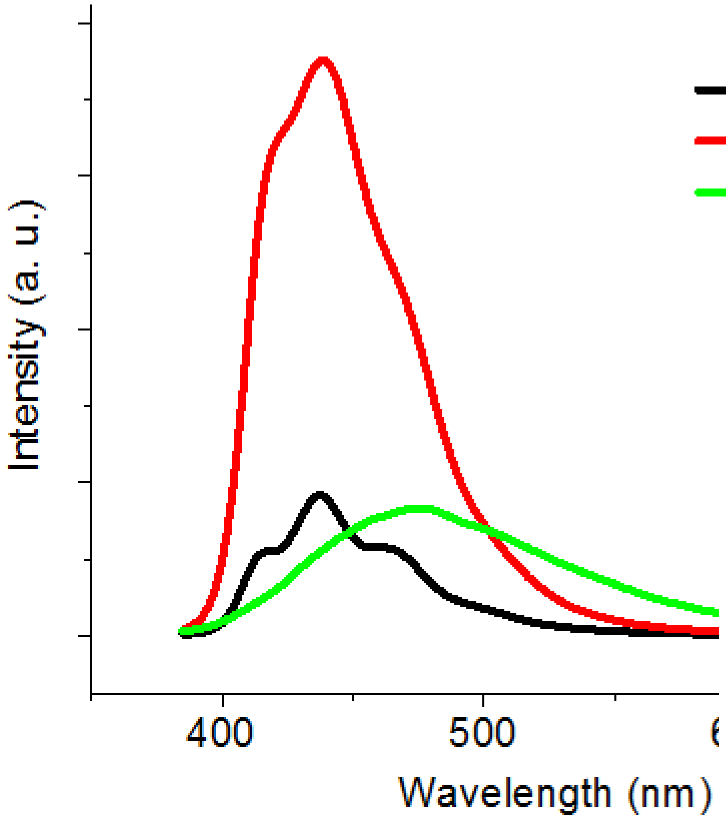

# The tracer

We have studied the use of fluorescent tracers to aid in removing certain HDPE products.

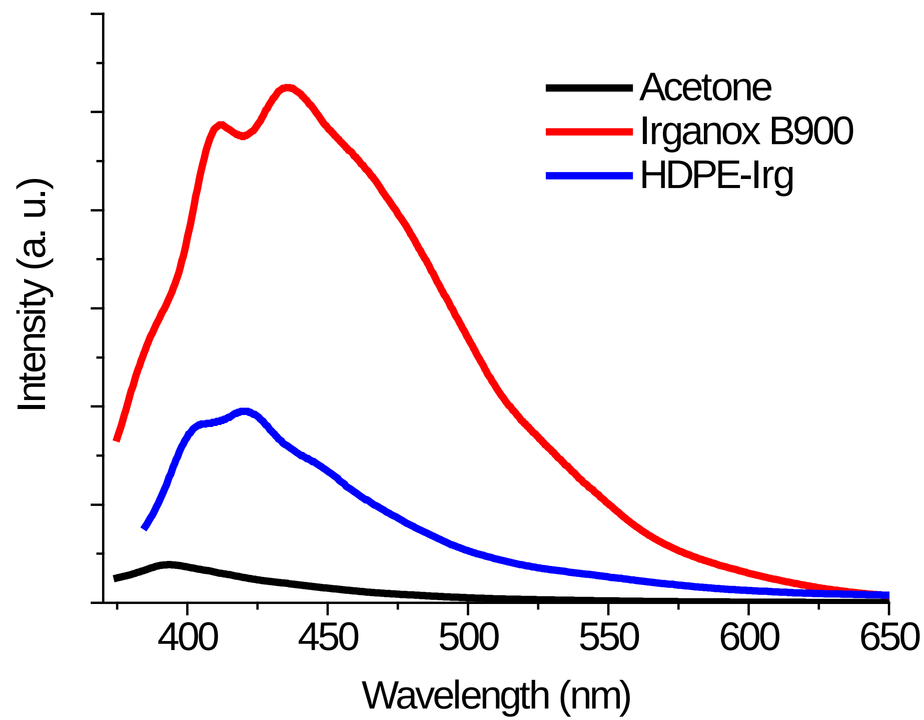
Among the required conditions for the tracer, the following can be highlighted:

1. *The fluorescent emission must be clearly distinguishable.*
2. *The emission intensity should be high enough to keep the concentration of tracer to a ppm level.*
3. *The fluorescent tracer must be easily incorporated into the plastic.*
4. *The migration of the tracer to the environment must be minimal.*
5. *The fluorescent labeling must be resistant against thermal, photochemical and hydrothermal degradation.*

# Tracers



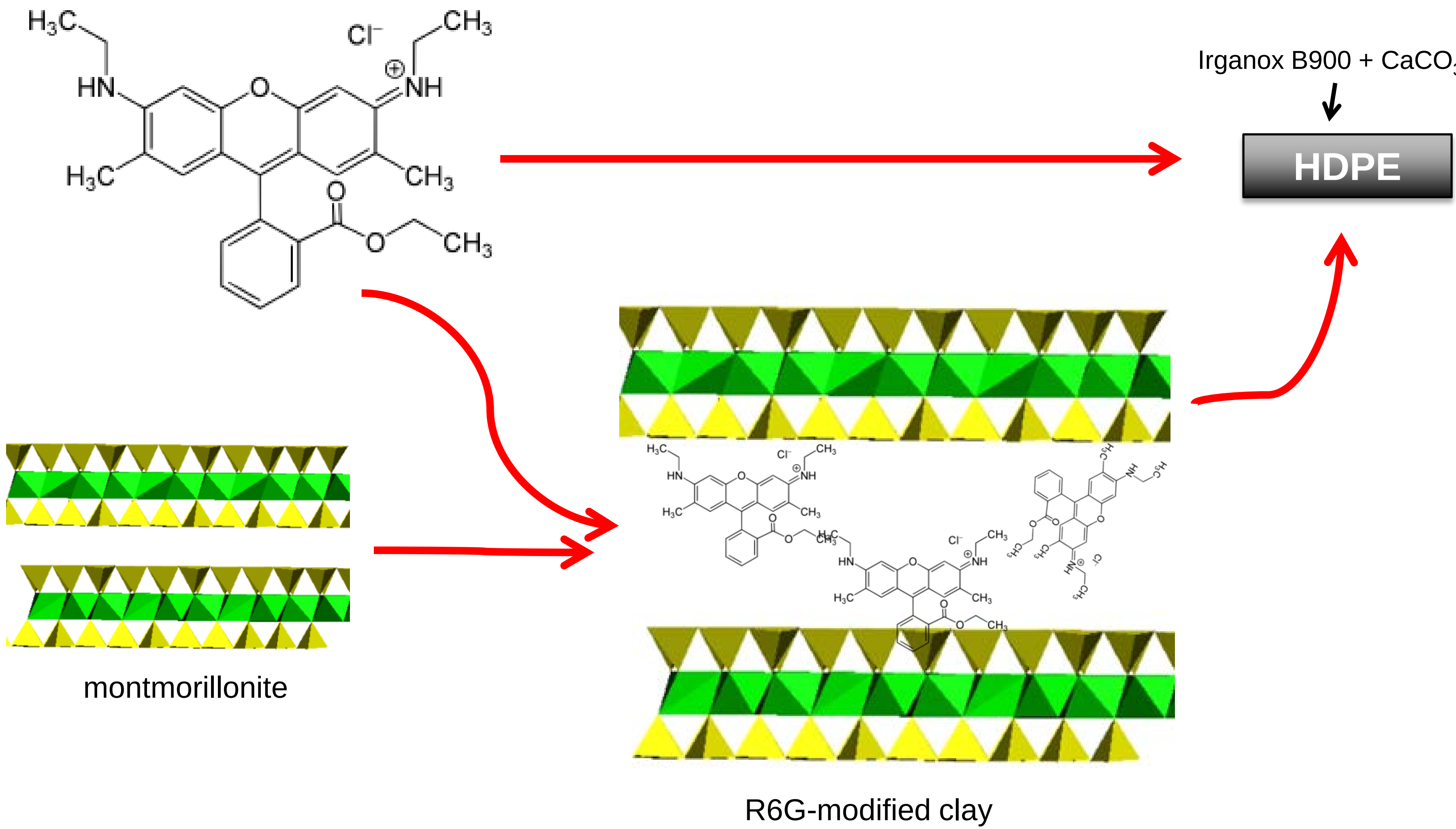

Fluorescence of commercial products



# Tracers

Two markers were evaluated. Rhodamine 6G is a commercial cationic fluorescent dye, which was introduced into HDPE in two ways, either directly or immobilized in a layered silicate

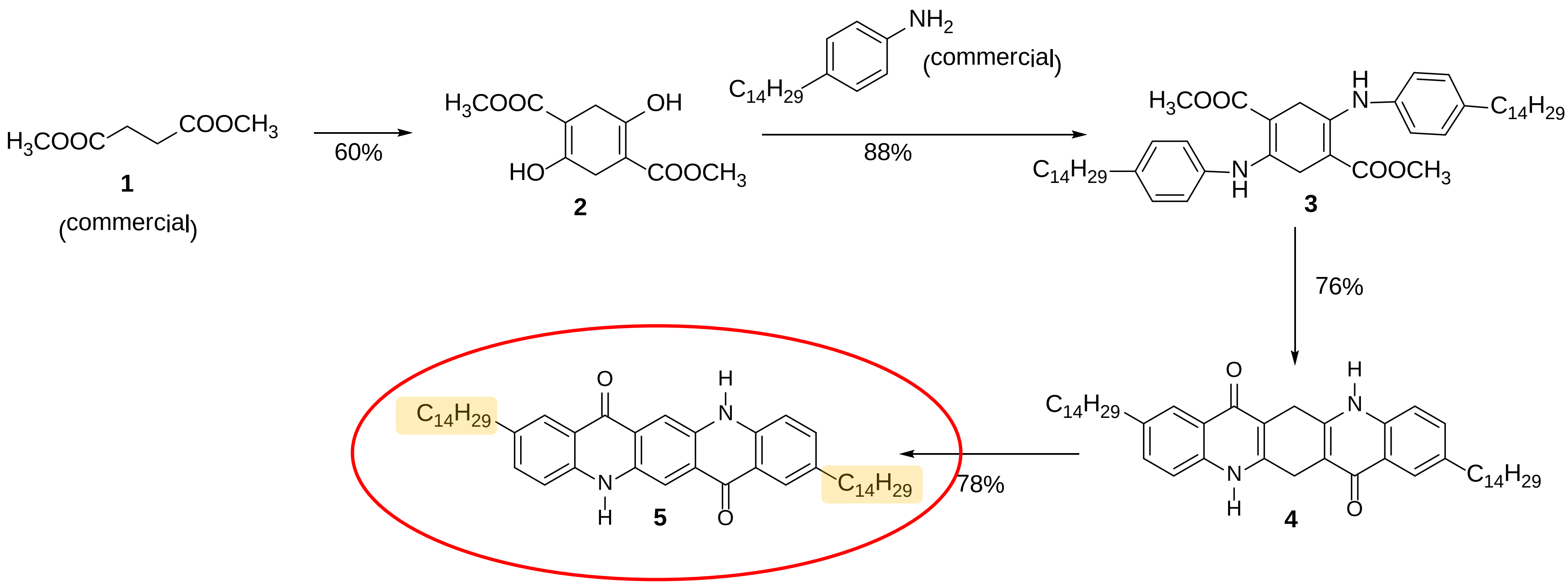
Rhodamine-6G (R6G)



# Tracers



The second marker (V-Quin) was a quinacridone synthesized in the laboratory with C14 substituents for improving the stability in HDPE.



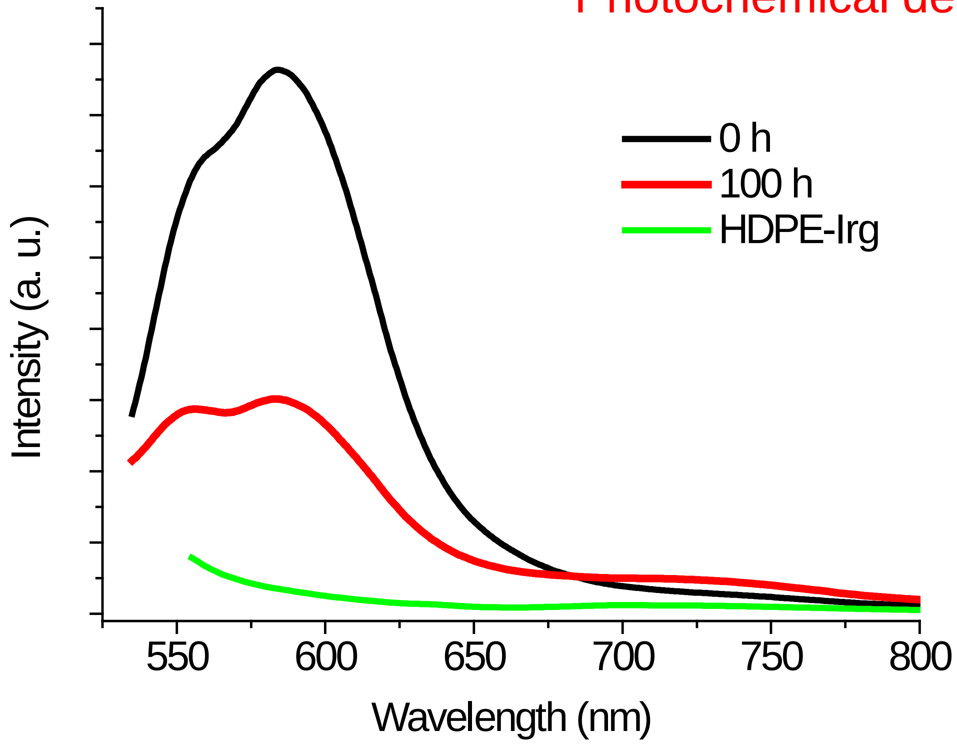

Synthesis of quinacridone with C14 substituents (V-Quin)

# Results



## Fluorescence and stability of labeled plastics

HDPE labeled with R6G-Clay.
Photochemical degradation

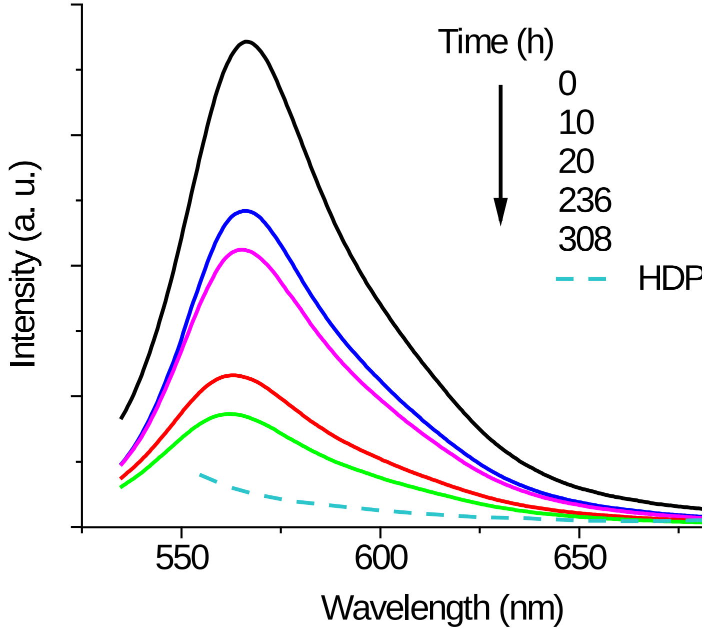



Fluorescence emission spectra ($\lambda_{ex}$ = 510 nm) corresponding to HDPE labeled with R6G-modified clay, measured before (black) and after (red) 100 h of photochemical degradation.

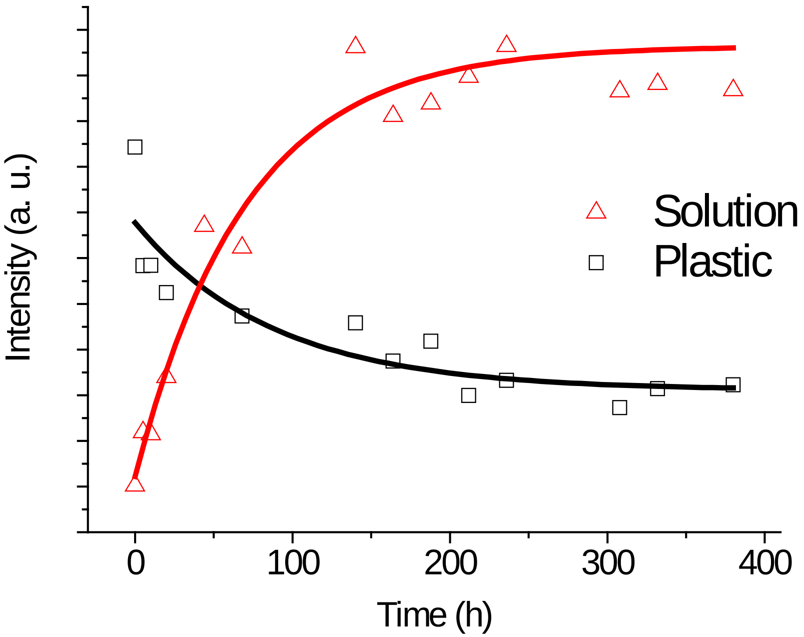
# Results

## Fluorescence and stability of labeled plastics

### HDPE labeled with R6G without clay. Hydrothermal degradation




Evolution of the fluorescence emission of HDPE-R6G ($\lambda_{ex}$ = 510 nm) during the hydrothermal degradation at 80 ºC.

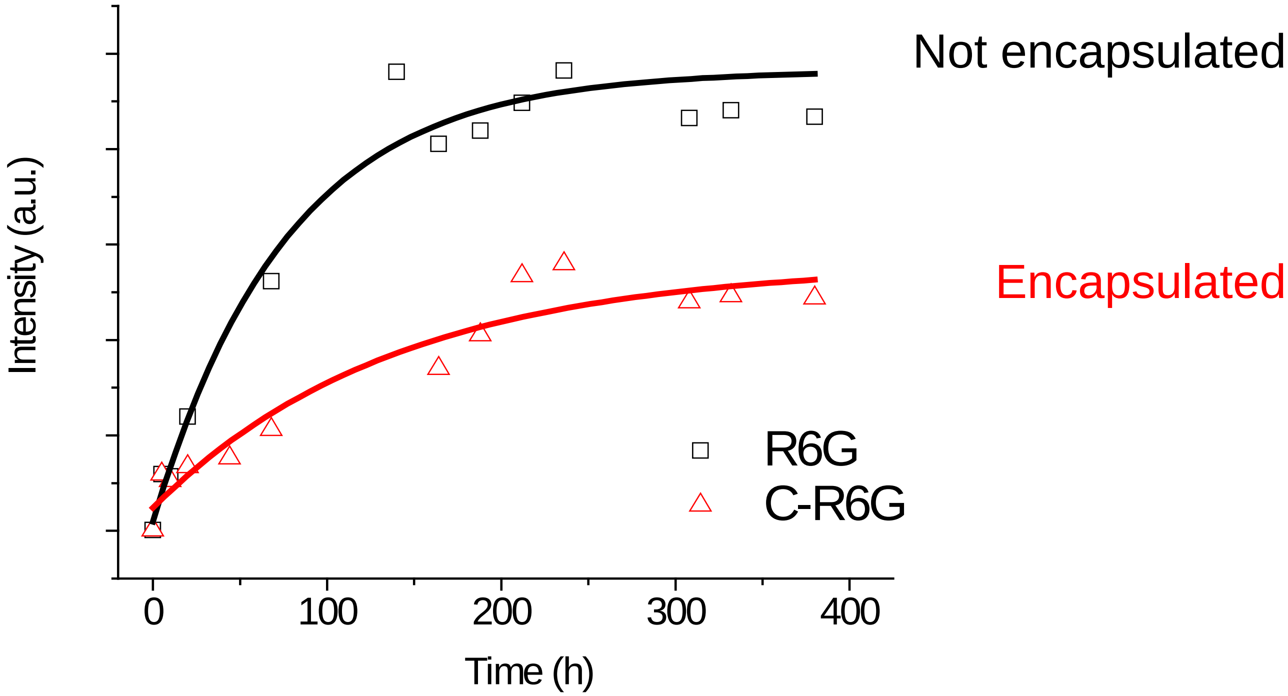



Time evolution of the emission intensity ($\lambda_{ex}$ = 510 nm) of HDPE marked with R6G and its immersion medium during the hydrothermal degradation.

# Results



## Migration of R6G

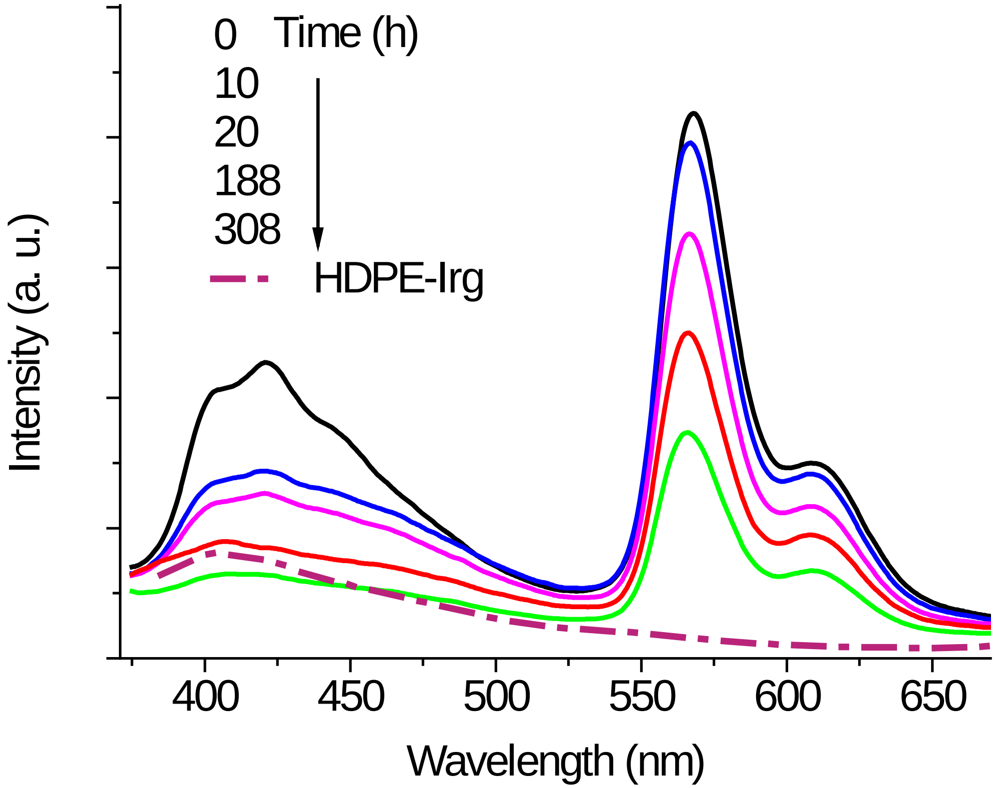



Time evolution of the emission intensity of the immersion media ($\lambda_{ex}$ = 510 nm) during the hydrothermal degradation of HDPE marked with R6G and R6G-modified clay.

# Results

## Fluorescence and stability of labeled plastics

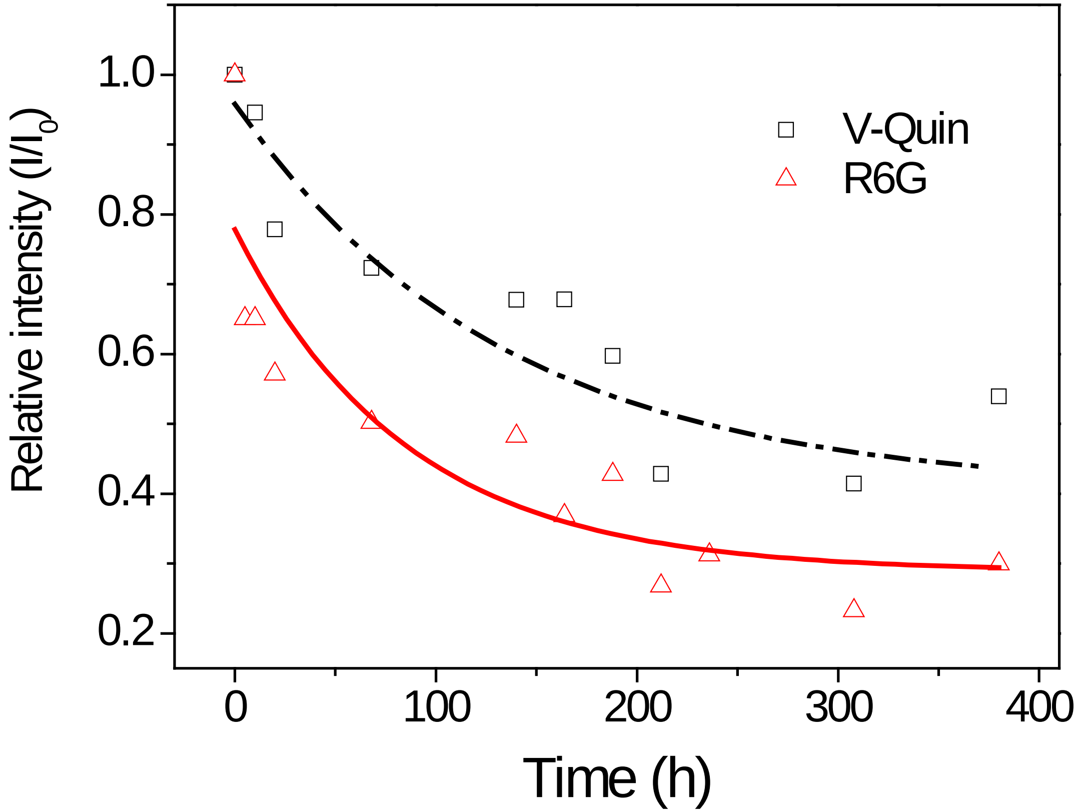
HDPE labeled with V-Quin.
Hydrothermal degradation




Evolution of the fluorescence emission of HDPE marked with V-Quin ($\lambda_{ex}$ = 350 nm) during the hydrothermal degradation at 80 ºC.

# Results

## Stability with R6G and V-Quin




Retention of the fluorescence emission of HDPE marked with R6G and V-Quin during the hydrothermal degradation.

# Conclusions



1. *The fluorescent tracers rhodamine-6G and V-Quin allow the correct identification of the marked HDPE in mixed plastics streams.*
2. *The good stability of the fluorescent emission indicates that the marked plastics will be properly detected even after a long lifetime.*
3. *The intercalation of rhodamine-6G between clay nanosheets reduces the leaching of the tracer during the hydrothermal degradation.*
4. *V-Quin shows better stability and better anchoring to polyethylene than rhodamine-6G.*
5. *The fluorescent labeling of some products can be very useful for improving the recycling of HDPE.*

# Thanks for your attention

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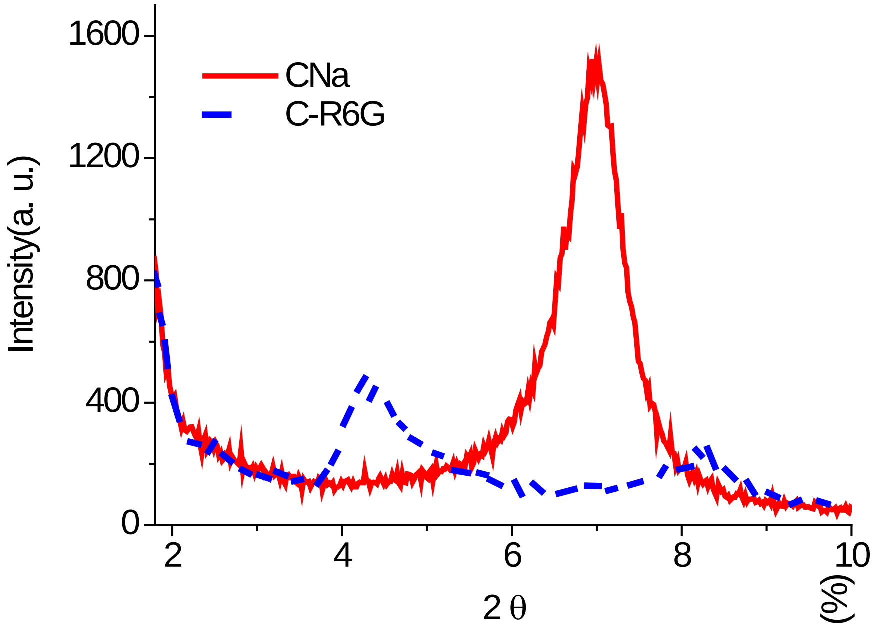
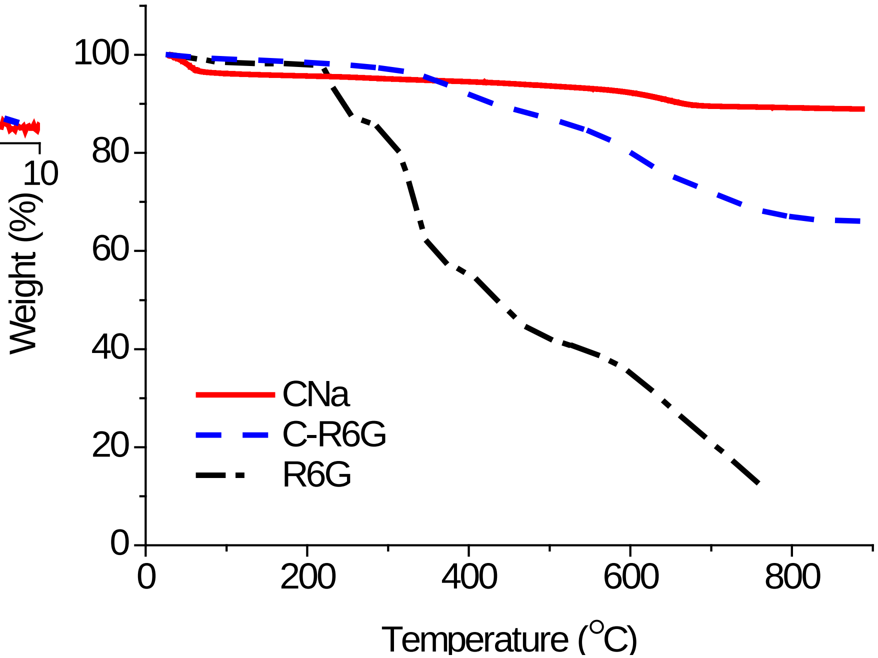
# Tracers



Characterization of the modified montmorillonite.




XRD traces corresponding to unmodified clay (CNa) and CNa modified with R6G




Thermogravimetric traces corresponding to unmodified clay (CNa), R6G and CNa modified with R6G



$$AlP + 3\ H_2O \rightarrow Al\ (OH)_3 + PH_3$$