

Alexandra I. Costa^{1,2*}, Patrícia D. Barata^{1,2}, Carina B. Fialho¹, José V. Prata^{1,2}

¹Laboratório de Química Orgânica, Área Departamental de Engenharia Química, ISEL, IPL,

R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal

²Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal.

*acosta@deq.isel.ipl.pt

OUTLINE

- Calix[4]arenes, an interesting bow-shaped macrocycles, have been explored due to their valuable properties, e.g. molecular recognition, proving outstanding complex ability towards neutral and ionic guests of several origins. [1-5]
- In this communication we report the synthesis and the chemosensing ability on the solid state of a new bicyclic calix[4]arene-based polymers integrating phenylene-ethynylene-carbazole units as fluorescent segments (**Calix-OCP-PPE-CBZs**), in the detection of several nitroanilines (NAs) in vapor phase.

RESULTS AND DISCUSSION

SYNTHESIS

- Calix-OCP-PPE-CBZs (3-6)** were prepared by a Sonogashira-type cross-coupling reaction. After purification brownish yellow compounds were obtained in 58-78% (Scheme 1).

- The polymers were characterized by FTIR, GPC and were achieved in good isolated yields (58-78%), having M_n ranging from 3200-16000 g mol^{-1} (Figure 1).

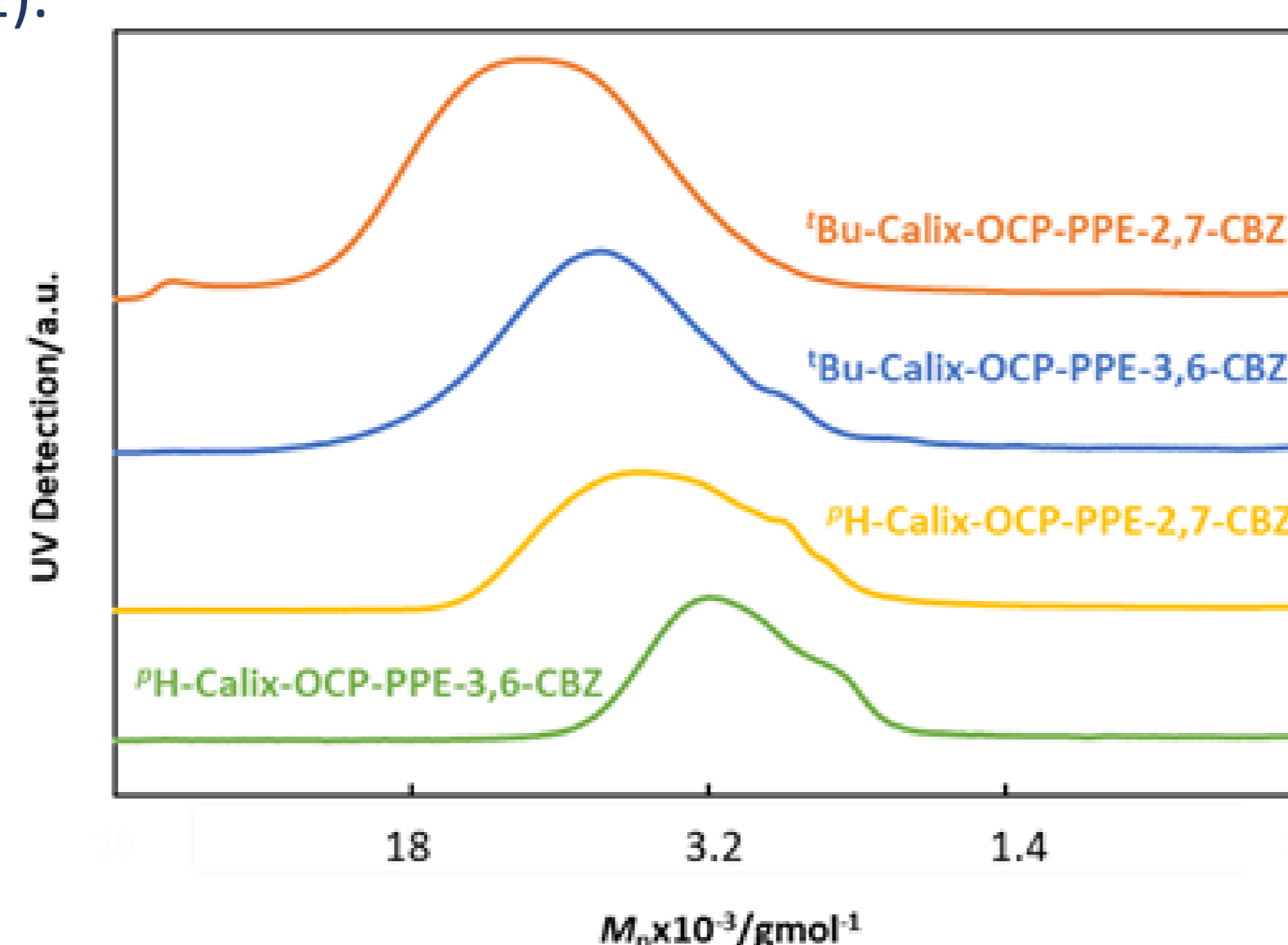
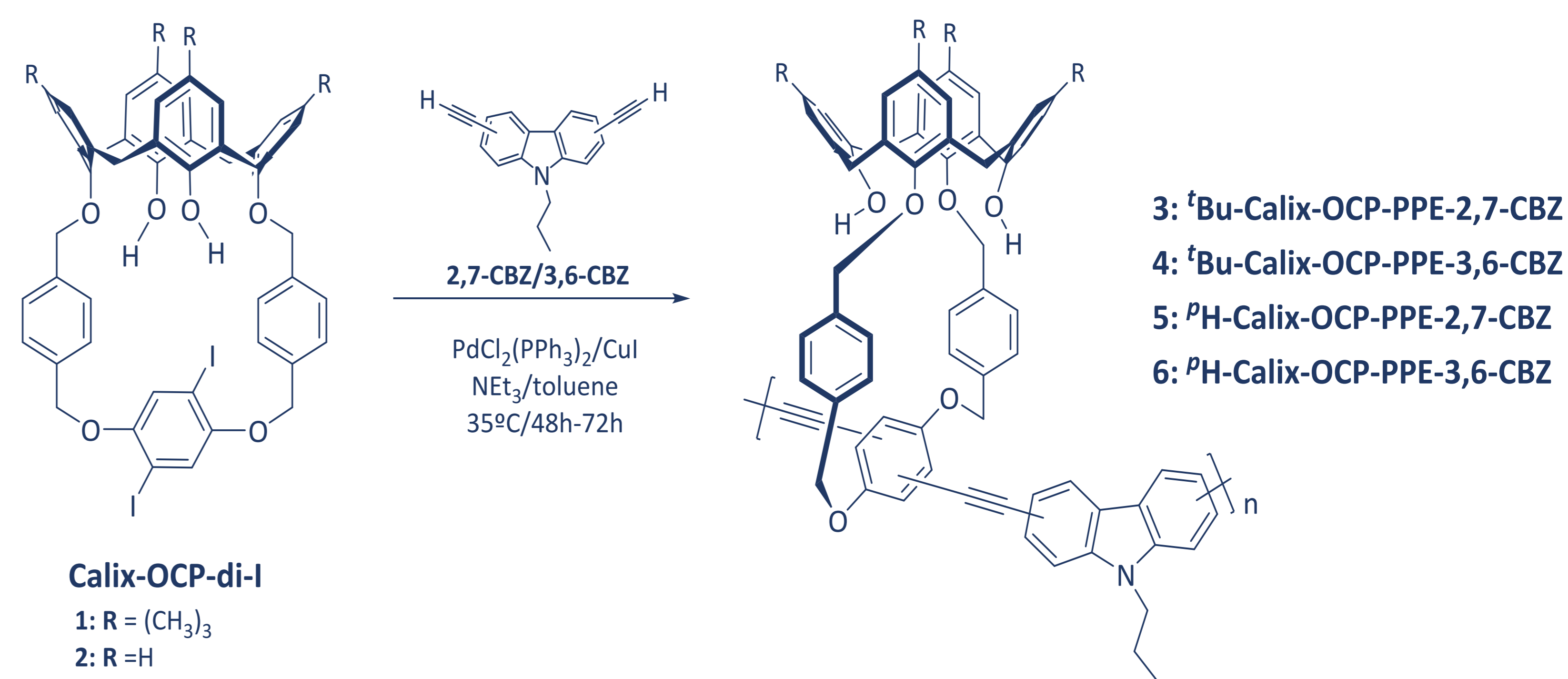


Figure 1 - GPC traces of isolated **Calix-OCP-PPE-CBZs** against monodisperse polystyrene standards.



Scheme 1 - Cross-coupling polymerization of **Calix-OCP-di-I** (1 and 2) and ethynyl carbazole derivatives (**2,7-CBZ** and **3,6-CBZ**).

SOLID-STATE QUENCHING STUDIES

- The films showed good photochemical stability as demonstrated by the fact that the intensity and the profile of the emission barely changed under the same conditions of the quenching experiments.
- The fluorescence response of the ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**) in the solid state upon exposure to *o*-NA (11.3 ppm @ 25°C), *m*-NA (126 ppb @ 25°C) and *p*-NA (4.2 ppb @ 25°C) vapors were evaluated through steady-state fluorescence quenching experiments with the materials as neat films. Quenching efficiency determined for thin films of ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**) using *o*-NA as analyte is shown in Figure 2.

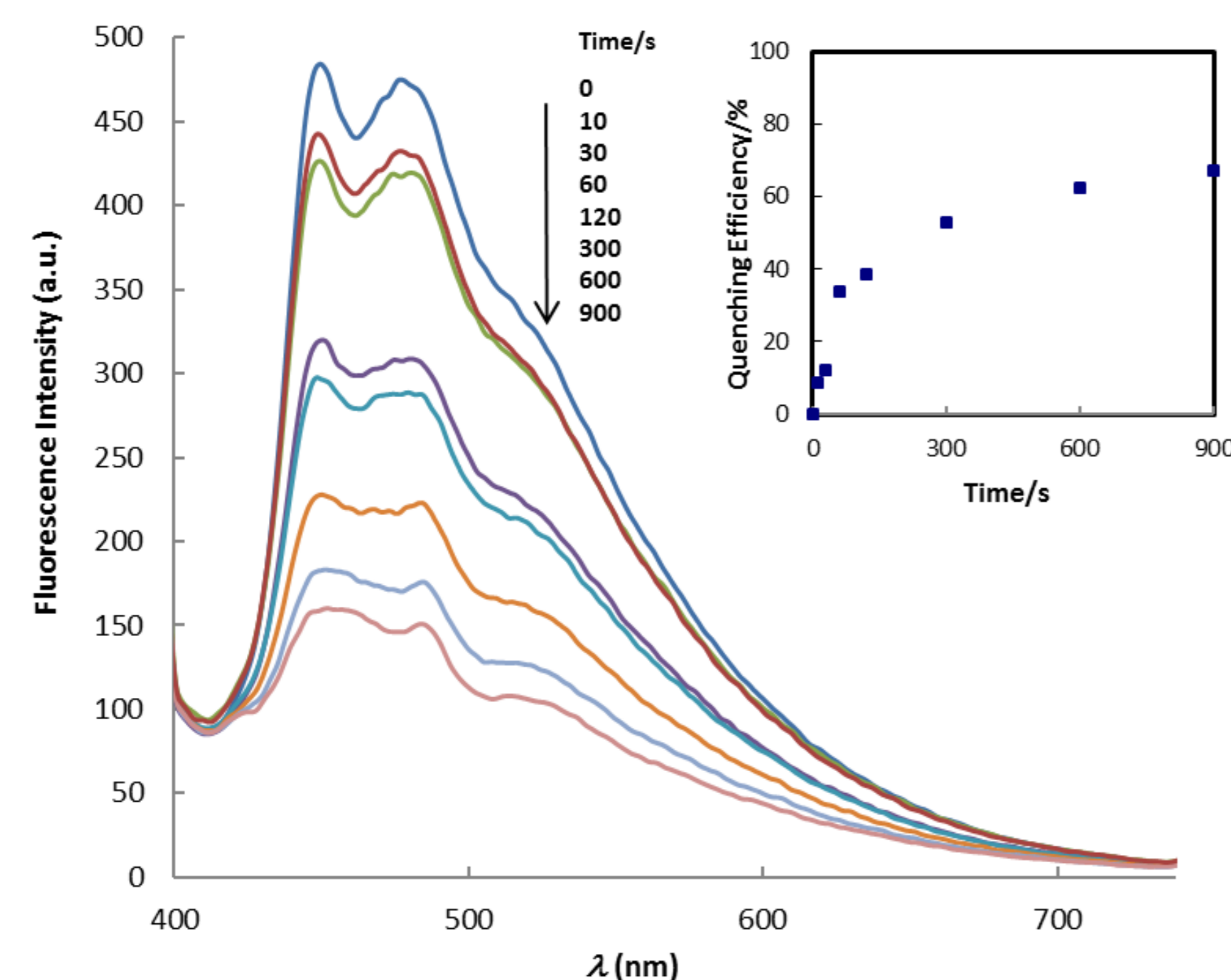


Figure 2. Time-dependent emission intensities of ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**) thin film after being exposed to saturated *o*-NA vapors (0, 10, 30, 60, 120, 300, 600 and 900 s, from top to bottom); $\lambda_{\text{exc}}=380$ nm. Corresponding inset refer quenching efficiency.

- The ^tBu-Calix-OCP-3,6-CBZ (**4**) polymer and debutylated polymers (**5** and **6**) did not afford good films for sensory applications.
- It was found that ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**) showed a remarkable sensitivity and moderate response for *o*-NA vapors as compared with other isomeric NAs. After 60 s of exposure to equilibrium vapor of *o*-NA more than 30% fluorescence quenching was observed against 14% and 2% for *m*-NA and *p*-NA, respectively (Figure 3).

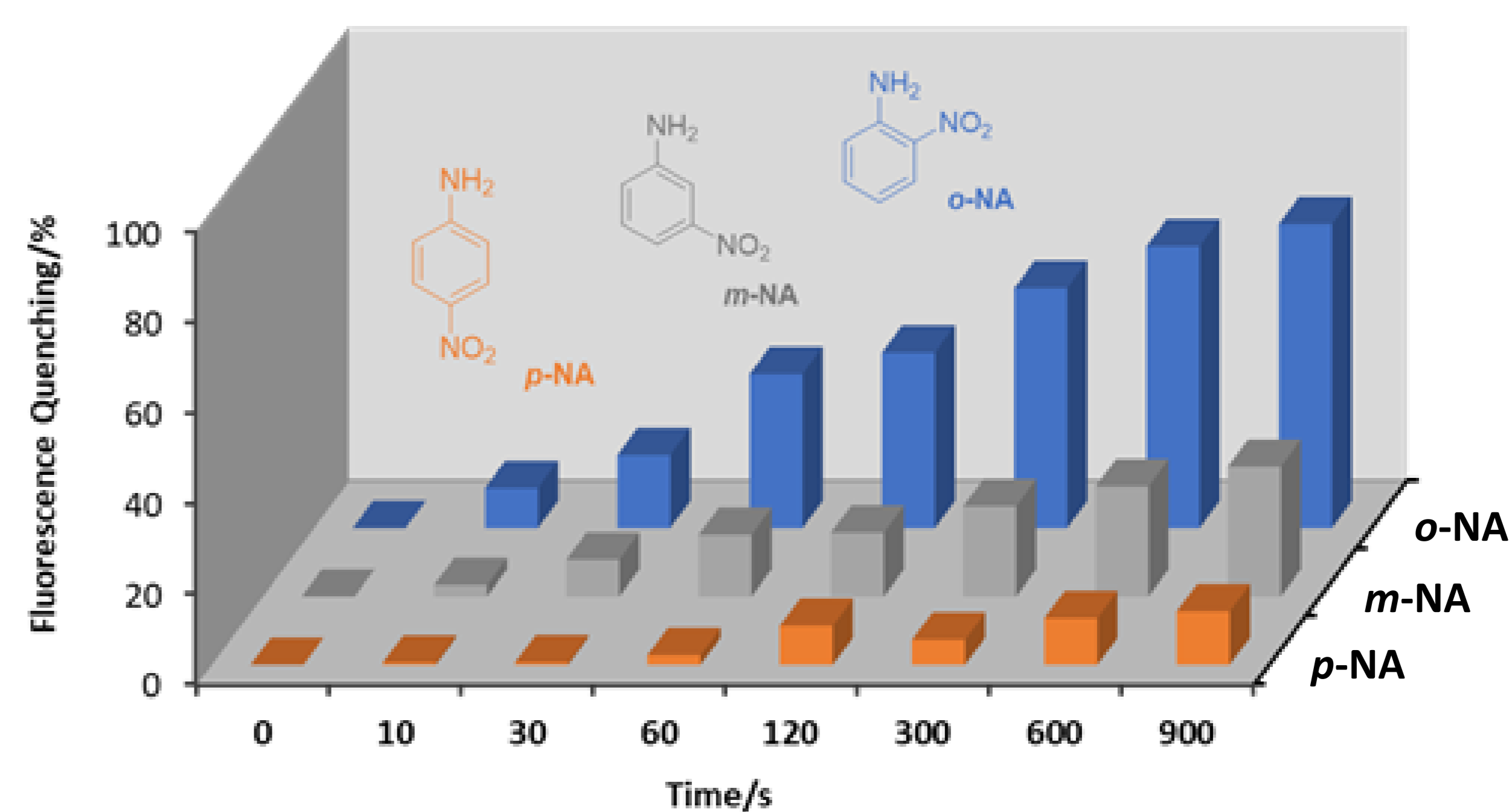


Figure 3. Time-dependent fluorescence quenching efficiencies of ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**), after being exposed to NAs vapors at rt (excitation at 380 nm).

CONCLUSIONS

- Results have shown that even using non-optimized film thicknesses, ^tBu-Calix-OCP-PPE-2,7-CBZ (**3**) displays high sensitivity and selectivity toward *o*-NA vapors. The extinction efficiencies achieved correlate well with the analytes vapor pressures (*o*-NA > *m*-NA > *p*-NA).
- Extension of this work in order to explain extinction mechanism is in progress.

ACKNOWLEDGMENTS

We thank IPL (Project IPL/2016/NoSeMeTox/ISEL) and FCT/MCTES (UID/QUI/00616/2013) for financial support. **October 2018**

REFERENCES

- C. M. Teixeira, A. I. Costa, J. V. Prata, *Tetrahedron Lett.*, 54 (2013) 6602-6606.
- P. D. Barata, A. I. Costa, J. V. Prata, *React. Funct. Polym.*, 72 (2012) 627-634.
- P. D. Barata, J. V. Prata, *Supramol. Chem.*, 25 (2013) 782-797.
- A. I. Costa, J. V. Prata, *Sensors and Actuators B*, 161 (2012) 251-260.
- A. I. Costa, H. D. Pinto, L.F.V. Ferreira, J.V. Prata, *Sensors and Actuators B*, 161 (2012) 702-713.