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-ethylen-carbazole units as fluorescent segments (Calix-OCP-PPE-CBZs), in the detection of several nitroanilines (NAs) in vapor phase.

RESULTS AND DISCUSSION

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_r, ranging from 3200-16000 g/mol (Figure 1).

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 1Bu-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 1Bu-Calix-OCP-PPE-2,7-CBZ (3) using o-NA as analyte is shown in Figure 2.

The 1Bu-Calix-OCP-3,6-CBZ (4) polymer and debutyalted polymers (5 and 6) did not afford good films for sensory applications.

It was found that 1Bu-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).

CONCLUSIONS

Results have shown that even using non-optimized film thicknesses, 1Bu-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.

REFERENCES