1st International Conference on Recent Developments in Science, Humanities & Management-2018
Amar Singh College Cluster University, Gogji Bagh, Srinagar (J&K) (ICRDSHM-18)
17th-18th April 2018 www.conferenceworld.in ISBN : 978-93-87793-09-5

Fluorescent Polymer Films as Advanced Vapochromic Materials For Sensing Applications

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ABSTRACT

The harmful effects of Volatile Organic Compounds (VOCs) demand simple sensitive, selective and cost effective sensors for their detection. Considering this fact, the sensing ability of the fluorescent molecules for the detection of VOCs is demonstrated in this work. In particular, we investigated the vapochromic behaviour of special fluorescent molecules known as fluorescent molecular rotors (FMRs), sensitive to both viscosity and polarity of the environment. The higher sensitivity of FMRs in determining the microviscosity changes inspired us to explore their application as sensors for VOCs. The sensor system was prepared by the dispersion of a very small amount (0.05-0.1 wt. %) of 4-(diphenylamino)phthalonitrile (DPAP) within poly(methyl methacrylate) (PMMA) and polycarbonate (PC) films. DPAP/PMMA films show a good and reversible vapochromism when exposed to the VOCs with high polarity index and favourable interaction with the polymer matrix such as tetrahydrofuran (THF), chloroform ($CHCl_3$) and acetonitrile. Analogously, DPAP/PC films exposed to polar and highly polymer-interacting solvents, that is, toluene, THF, and $CHCl_3$ show a gradual decrease and red-shift of the emission. Contrary to DPAP/PMMA films, an unexpected increase and further red-shift of fluorescence is observed at longer exposure times after the initial decrease as a consequence of an irreversible, solvent-induced crystallization process of PC. The vapochromism of DPAP-doped polymer films is rationalized on the basis of alterations of the rotor intramolecular motion and polarity effects stemming from the environment, which, in concert, influence the deactivation pathways of the DPAP intramolecular charge transfer state. The present results support the use of DPAP-enriched plastic films as a new chromogenic material suitable for the detection of VOCs.

The vapochromic properties of a solvatochromic dye 3-[2-(4-nitrophenyl) ethenyl]-1-(2-ethylhexyl)-2-methylindole (NPEMI-E) characterized by intramolecular charge transfer (ICT) character, dispersed in polycarbonate (PC) films is also reported. NPEMI-E solvatochromism is investigated by means of experimental and computational methods. NPEMI-E/PC films show remarkable and reversible vapochromism when exposed to VOCs with high polarity index and favourable interaction with PC matrix such as $CHCl_3$. Only minor variations of the emission wavelength are actually recorded for all other classes of VOCs investigated. Overall, the present results support the use of NPEMI-E/PC films for the cost-effective detection of $CHCl_3$ vapours.