Novel germanium-based σ-π conjugated oligourethanes containing dibenzofuran moieties in the backbone: Thermal, optical, electronic properties and theoretical simulations

Jessop, I.A.
Mariman, A.
Sobarzo, P.A.
Hauyon, R.A.
Saldías, C.
Schott, E.
Zarate, X.
Rodríguez-González, F.E.
Medina, J.
González-Henríquez, C.M.
Tundidor-Camba, A.
Terraza, C.A.

Abstract
In the search of new photoactive materials for light-emitting applications, two new germanium-based oligourethanes (PUGe-27 and PUGe-28) were synthesized from 4,4-(diphenylgermarylene)bis(phenyl chloroformate) (1) and dibenzo[b,d]furan-2,7-diamine (2) or 4,4′-(dibenzo[b,d]furan-2,8-diyl)dianiline (3) through pyridine-catalysed polycondensation. The structural characterization of the oligourethanes was performed by elemental analysis (EA), IR and NMR techniques. All oligomers were soluble in common organic solvents including THF, which was used to prepare brittle films by casting method. Molecular weights were established in the range of 4.5–5.0 kDa by SEC measures. The samples exhibited a $TDT_{10\%}$ in the range of 307–351 °C, while T_g showed values near to 220 °C. Thermal behavior differences were consistent with the molecular flexibility's degree provided by the monomeric diamine. Suitable absorption and emission behavior were displayed for both germanium-based oligourethanes with moderate Stokes shifts. PUGe-28 showed a strong fluorescence in the blue region of the visible light (364 nm). Both PUGes had wide-band gap (3.76 eV) with interesting high-lying LUMO levels (ac. 2.04 eV). To better understand the experimental results, DFT and TD-DFT calculations were carried out. The results obtained could be used as a guide for future research on Ge-based PUs as photoactive materials.

Author keywords
Dibenzofuran
Light-emitting material
Optoelectronic devices
Tetraphenylgermanium
Urethane oligomers