Hybrid materials combine not only the advantages of both organic (solubility, processability, flexibility) and inorganic (robustness, transparency, mechanical strength), but also present the exciting possibility of emergent properties and multifunctionality due to synergistic interactions between the constituents. We have recently revisited a class of hybrid materials known as ureasils, which are formed from polyether-based chains grafted to a siliceous backbone through urea cross-linkages using sol-gel chemistry. While the ureasils themselves are intrinsically photoluminescent, we have demonstrated that the introduction of complementary lumophores such as conjugated polymers, organic dyes and quantum dots, through either physical immobilisation or covalent grafting, results in a significant enhancement in the optical properties (e.g. quantum yield, colour tenability, refractive index). Selected highlights from our recent work will be presented, with specific focus placed on the targeted design of this unique class of materials for application as luminescent solar concentrators to enhance the light-harvesting capability of solar cells.