Hybrid Nanomaterials based on BODIPY-Functionalized Octasilsesquioxanes

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Fully condensed polyhedral oligosilsesquioxanes (POSS) are nanometer-sized materials.[1] Their rigid inorganic core ensures a considerable chemical and thermal stability. Moreover, these nanoparticles are well dispersed at the molecular level and can be readily functionalized with different organic molecules, for instead monomers. In this way novel hybrid materials can be obtained with improved homogeneity and transparency. Owing to these properties, currently POSS nanoparticles are widely applied in photonics and electronic devices.

Another possibility never exploited before, is to use these POSS nanoparticles as random materials. Dye molecules grafted to POSS can be adequately dispersed, leading to a homogeneous material. The weak scattering of the POSS cores should provide an extra feedback elongating the light path in the gain media. Such phenomenon is known as incoherent random laser and results in an improvement of the lasing performance. The chosen dye was BoronDiPyrromethene (BODIPY) which nowadays is probably the benchmark in efficiency and photostability in tunable dye lasers.[2]

Therefore, in the present work we show the characterization of the corresponding BODIPY model to be attached to the POSS core, together with mono- and octasubstituted-POSS derivatives (Figure 1). The incorporation of the linking chain at central position of the BODIPY chromophore does not alter its photophysical properties. As result, such spacer is adequate to covalently bound the BODIPY to the POSS core. The photophysical properties of the monosubstituted-POSS are close to those of the free BODIPY indicating that the greafting process has been successful. Even more, the lasing properties of the BODIPY are enhanced by the presence of POSS due to the above commented extra feedback provided by the light scattering of the POSS nanoparticles. However, the octasusbtituted-POSS has no lasing emission and very low fluorescence intensity. The reason of such behavior is the interaction between neighbors BODIPY molecules. The proximity of the BODIPY fluorophores around the POSS core and the flexibility of the linking chain facilitates that the molecules adopt different conformations. Indeed, the absorption spectrum is not the sum of eight BODIPY chromophores and the absorption intensity increase in the shoulder region at higher energies. Such feature indicates the presence of H-type aggregates as is also supported by the theoretical simulated ground state geometry (Figure 1). This kind of association is characterized by an inactive absorption of the light and the fluorescence quenching of the emission coming from the monomer, with the consequent deleterious effect in the lasing emission.

In short, the unique photophysical properties of BODIPY are kept in spite of being linked to POSS. The light scateering of the POSS core ameliorates the lasing efficiency of the BODIPY dye. However, this hold true for the monosusbtituted derivative, since in the octasubstituted one the interaction between the dye molecules (aggregation) drastically decrease both the fluorescence and lasing ability. This work is

the platform for future POSS based systems, where a POSS core is functionalized both with a fluorophore and a bio-recognition element, with potential applications as bioimaging agents.

References

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Figures

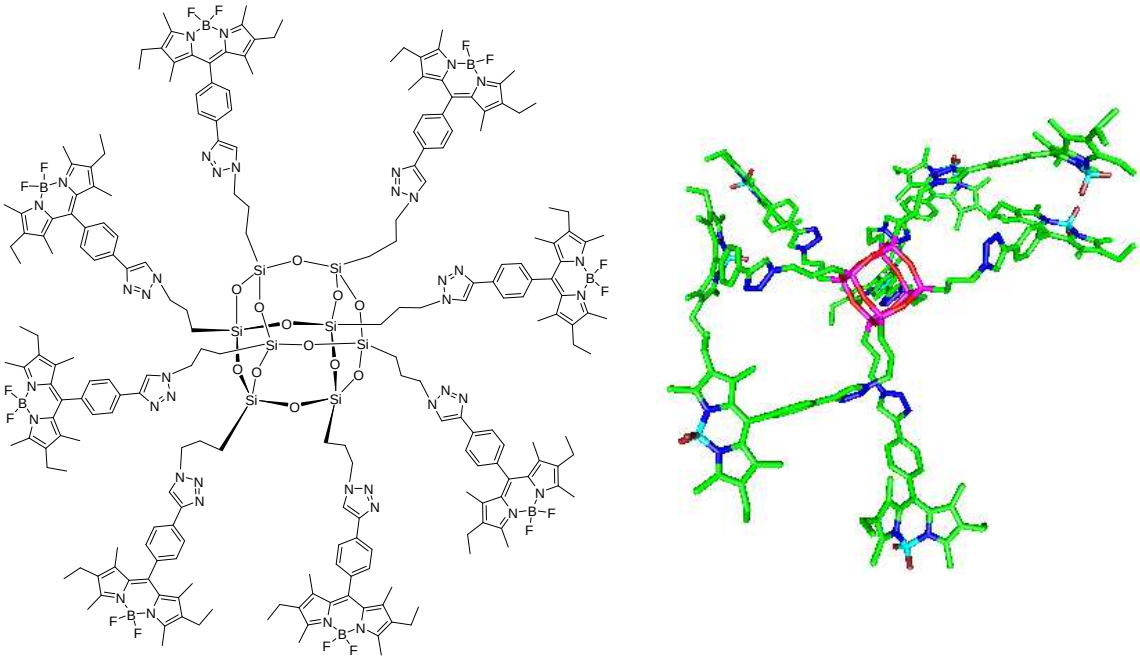

***Figure 1**. Molecular structure of the POSS core bearing eight BODIPYs. The corresponding ground state optimized geometry is also depicted.*