Synthesis and Optical Properties of POSS-introduced Non-benzene Aromatic Compounds

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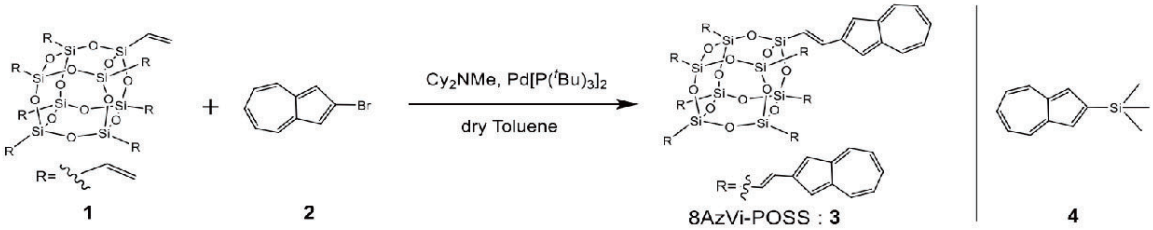
Abstract: Caged silsesquioxane (POSS) has been attracting attention as a promising building block for organic-inorganic hybrid materials. Recently, it has been reported that the incorporation of an organic chromophore into the side chain of POSS leads to a bathochromic shift of the photoluminescence (PL) peak with maintaining the absorption peak[1]. This phenomenon was attributed to the electron-withdrawing effect of POSS on the energy levels of the chromophore. In this study, we focused on azulene, a non-benzene aromatic compound known for its polarized structure, to elucidate the effect of its integration into POSS based on the absorption and PL spectra.



Scheme 1 Synthesis route of 8AzVi-POSS (3) and chemical structure of model compound (4).

According to Scheme 1, 8AzVi-POSS (3) was synthesized from Vi-POSS (1) with bromo□2-azulene (2) via the Mizoroki-Heck reaction. A model compound (4) was also synthesized for comparative studies. 4 in dichloromethane exhibited fluorescence (FL) at 425 nm (Fig. 1). DFT calculations indicated that the MOs contributing to the FL of 4 are distributed from the azulene to Si atom (Fig. 2). The wavelength range and the spectral shape of FL for 3 are similar to those of 4 (Fig. 1), suggesting that the FL of 3 primarily originate from the vinyl-2-azulene moiety. Since the electronic state of azulene can be controlled by substituent addition, an introduction of electron-donating groups to the azulene moiety of 3 is expected to manipulate the correlation between the polarized structure of organic chromophore and its integration into POSS.

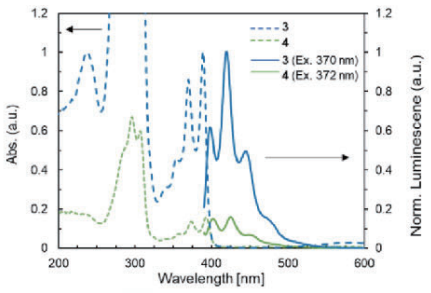


Fig. 1 UV-vis absorption and photo-luminescence spectra of 3 and 4 in dichloromethane.

Keywords: POSS, Azulene, Optical Property, Mizoroki-Heck reaction

References

[1] N. R. Vautravers, P. Andre, D. Cole-Hamilton, J. Mater. Chem., 19, 4545-4550 (2009).

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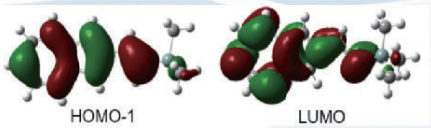

Fig. 2 Spatial distribution of HOMO-1 and LUMO of 4.