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Origin of Unusual Dependencies of LUMO Levels on Conjugation Length in Quinoidal Fused Oligosiloles NANA MISAWA, Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, MIKIYA FUJII, Department of Chemical System Engineering, School of Engineering, The University of Tokyo, RYO SHINTANI, TOMOHIRO TSUDA, KYOKO NOZAKI, Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, KOICHI YAMASHITA, Department of Chemical System Engineering, School of Engineering, The University of Tokyo — Quinoidal fused oligosiloles, a new family of silicon-bridged π-conjugated compounds, have been synthesized and their physical properties showed a unique trend in their LUMO levels, which become higher with longer π-conjugation.[1] Although this trend was reproduced by the DFT calculations, its origin remained to be discussed. In this work we performed quantum chemical calculations and discovered that the unusual LUMO trend is attributable to the π-frameworks. We elucidated its origin by orbital correlation diagrams based on classical Hückel calculations, essentially. However, LUMO trends cannot fully be explained only by Hückel calculations because of the lack of the consideration of geometries. In the case of quinoidal fused oligosiloles, judging from DFT calculation results, the presence of silole fused structure play an important role in fixing the bond angles of the linear polyenes as an interior angle of siloles, leading to the unusual LUMO behavior. The qualitative but essential understanding of these LUMO trend would provide new insight into molecular design of π-conjugated compounds for tuning their LUMO levels.

[1]Nozaki el.al, *JACS.* **2016**, *138*, 3635

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