Hückel theory applied to molecular motors

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In 2016, the Chemistry Nobel Prize was awarded to Fraser Stoddart, Jean-Pierre Sauvage and Ben Feringa "for the design and synthesis of molecular machines.[1] A special type of these molecular machines is the molecular motor. A molecular motors has light-addressable switches and can isomerize under the influence of UV-light.[2] The unidirectional rotation of a motor was first reported in 1999 using UV-radiation and thermal relaxation.[3] This lead to the radical idea that these molecular motors can be used potentially as nanorobots used in drug delivery. An example is shown in Figure 1 of how molecular motor 1 isomerizes at $\lambda = 395$ nm.

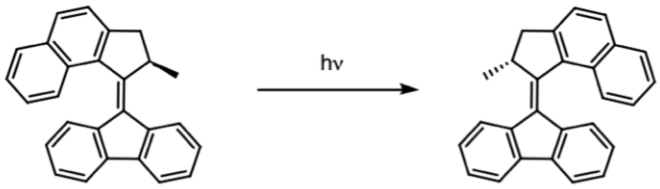

Figure 1: Molecular motor 1 isomerizes using a wavelength of $\lambda = 395$ nm.

However, UV-light can damage biological matter. Therefore, it is crucial that the excitation wavelength needed for isomerization could be reduced to lower wavelengths. A recent experimental study by Feringa et al. showed that extending the aromatic core by substituting the benzene-core by a naphthalene-core, see Figure 2, can red-shift the excitation wavelength of the molecular motor.[4]

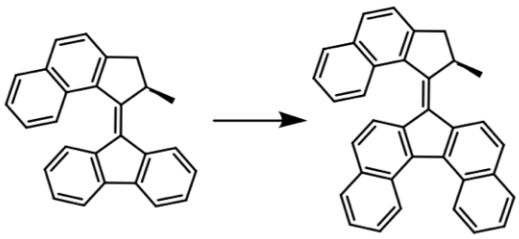

Figure 2: Substitution of the aromatic core of molecular motor 1 by a naphthalene causes a red-shift of the excition wavelength to 491 nm.

Using HuLiS, this red-shifting can be predicted by comparing the HOMO-LUMO gaps of both motors. The HOMO-LUMO gap of motor 1 is E_{LUMO} - E_{HOMO} = (α - 0.28β) - (α + 0.43β) = -0.71β. It is expected that the same gap should be calculated for motor 2. Feringa et al. found that the HOMO-1 to LUMO excitation has a significant larger oscillator strength (0.6241) than that of the HOMO to LUMO excitation (0.0105) for molecular motor 2. A higher oscillation strengths implies a large transition probability for excitation. Therefore, the excitation energy for motor 2 is calculated from the HOMO-1 LUMO gap and results in (α - 0.21β) - (α + 0.47β) = -0.68β. Since $\beta<0$, the red-shift is indeed predicted. Moreover, visualization of the HOMO, HOMO-

1 and LUMO of motors 1 and 2, shown in Figure 3, agree surprisingly well with TD-DFT (B3LYP 6-31(d,g)) calculations of Fergina et al.

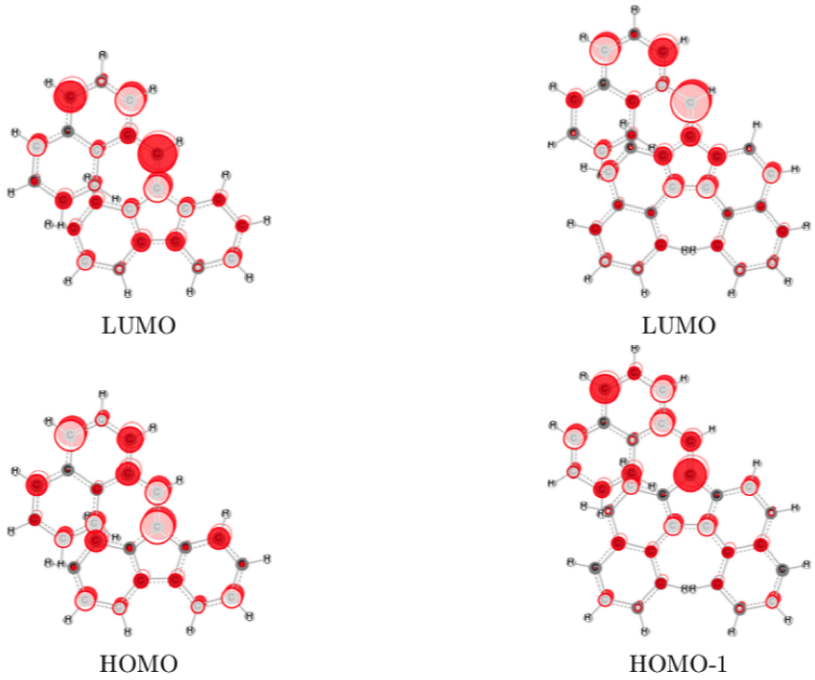

Figure 3: Molecular orbitals of motor 1 (left) and motor 2 (right) genereated with HuLiS.

References

[1] Nobel prize chemistry, 2016.

[2] B. L. Feringa and W. R. Browne. Molecular switches. *Angew. Chem. Int. Ed.*

[3] Nagatoshi Koumura, Robert W. J. Zijlstra, Richard A. van Delden, Nobuyuki Harada, and Ben L. Feringa. Light-driven monodirectional molecular rotor. *Nature*, 401(6749):152–155, 1999.

[4] Thomas van Leeuwen, Jasper Pol, Diederik Roke, Sander J. Wezenberg, and Ben L. Feringa. Visible-light excitation of a molecular motor with an extended aromatic core. *Organic Letters*, 19(6):1402–1405, 2017.