Hückel theory applied to molecular motors

December 11, 2019

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.[4] The unidirectional rotation of a motor was first reported in 1999 using UV-radiation and thermal relaxation.[5] 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 λ = 395 nm.

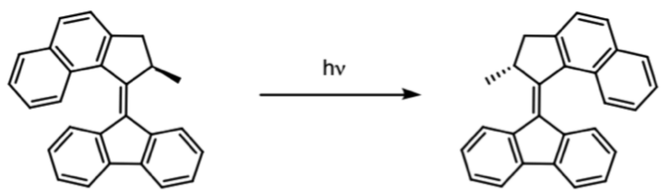

Figure 1: Molecular motor **1** isomerizes using a wavelength of λ = 395 nm.

However, UV-light can damage biological matter. Therefore, it is crucial that the excitation wavelength needed for isomerization is 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, termed motor **2** as shown in Figure 2, can red-shift the excitation wavelength of the molecular motor.[6]

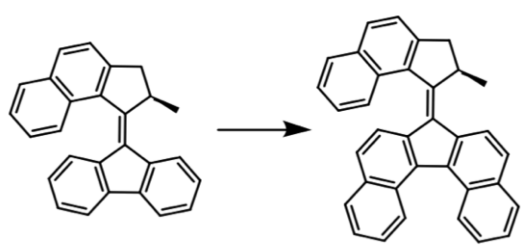

Figure 2: Substitution of the aromatic core of molecular motor **1** by a naphthalene causes a red-shift of the excitation wavelength to 491 nm.

Using Hückel theory calculations, this red-shifting can be predicted by comparing the HOMO-LUMO gaps of both motors. In this example, the tool HuLis is used.[3, 2] 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) compared to 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 β<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.

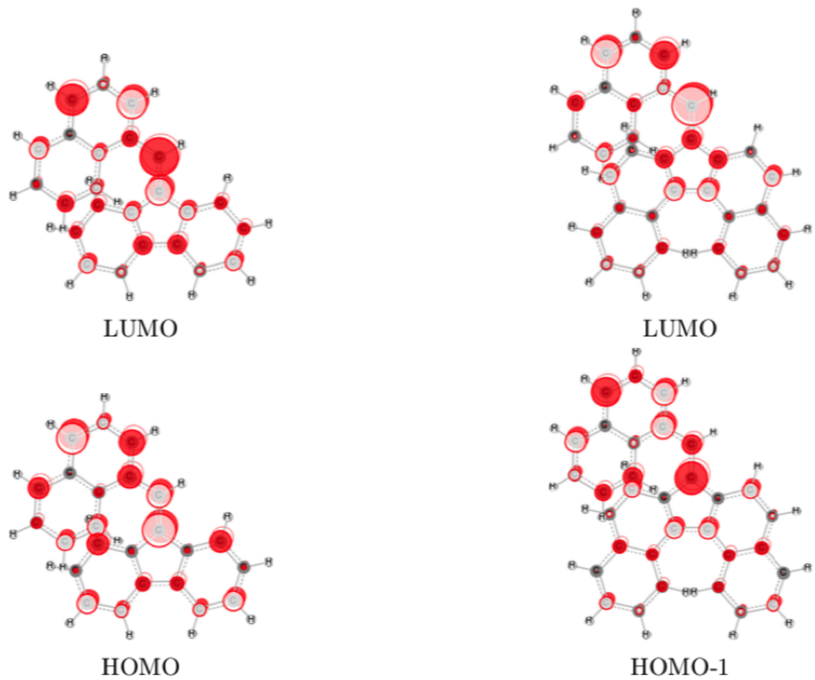

Figure 3: Molecular orbitals of motor **1** (left) and motor **2** (right) generated with HuLiS.

References

[1] Nobel prize chemistry, 2016.

[2] D.; Goudard N.; Humbel S. Carissan, Y.; Hagebaum-Reignier. Hulis code: Lewis embedded in hckel theory.

[3] Yannick Carissan, Denis Hagebaum-Reignier, Nicolas Goudard, and Stphane Humbel. Hückel-lewis projection method: A "weights watcher" for mesomeric structures. *The Journal of Physical Chemistry A*, 112(50):13256–13262, 2008. PMID: 19053557.

[4] B. L. Feringa and W. R. Browne. Molecular switches. *Angew. Chem. Int. Ed.*, 51:22812281, 2012.

[5] 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.

[6] 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.