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Halochromic switch from the 1st to 2nd Near Infrared window of Diazapentalene-Dithienosilole copolymers

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Up to now, halochromism has mostly been demonstrated on chromophores absorbing in the UV-visible range. However, research in the field of Infra-Red (IR) technologies is in strong development, driven by technological needs in military and civilian applications, such as imaging, optical communications, energy or sensing.[1] Also, since 50 % of the solar energy falls into the IR spectral region, photovoltaic materials are under development to increase solar cells efficiency.[2] IR-materials are also synthesized for biosensing and bioimaging because IR light penetrates into tissues, the so-called "biological window".[3] To design organic IR materials, the basic principle is to reduce the bandgap. Specifically, synthesis of electron donor-acceptor (D-A) alternating conjugated copolymers has demonstrated high potential to decrease the bandgap under 1.5 eV, leading to IR-absorbing or emitting materials.[4] For the moment, most of these organic materials showed a maximum absorption peaks falling in the first NIR optical window covering 750–1000 nm. Actually, the second NIR optical window covering 1000–1350 nm is more promising for biological applications due to its higher photothermal conversion and deeper tissue penetration.[5]

In this presentation, we will report the synthesis of a low bandgap copolymer based on the 2,5-diazapentalene (DAP) unit, derived from the diketopyrrolopyrrole (DPP) chromophore. We combine the strong acceptor DAP unit with the dithienosilole (DTS), a photostable electron donor [6] that allows the introduction of solubilizing alkyl chains onto the silicon atom. As the result of the polymerization, an IR-material was synthesized with a maximum absorption at 850 nm in chloroform solution. Upon protonation of the DAP unit with Brønsted acids or its complexation with Lewis acids, the maximum of absorption is further shifted up to 1100 nm (edge at 1500 nm) in the second NIR optical window. To the best of our knowledge, this halochromic behavior is the highest reported up to now. Using a combination of spectrometry, cyclic voltammetry and DFT calculations, we identified the Brønsted and Lewis adducts that are formed. We can demonstrate that this optical shift is correlated with a decrease of the copolymers bandgap associated to the decrease in the LUMO energy and enhancement of the pi-electron delocalization along the conjugated backbone, as revealed by the lowering of the bond length alternation.[7]

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