

Impact of charge switching stimuli on supramolecular perylene monoimide assemblies

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We have designed and synthesized a novel water-soluble perylene monoimide amphiphile with a hydroxyl group, which exhibits reversible structural, optical, and electrochemical properties in response to pH. The increase in electron donating ability of the deprotonated hydroxyl anion compared to the protonated analog results in a substantial increase in the energy levels of the dye and a significant reduction in the bandgap. The addition of a second negative charge to the PMI core after deprotonation hinders the formation of extended supramolecular structures, while crystalline nanoribbons can be observed when the hydroxyl group is protonated. This chromophore was also shown to participate in the photocatalytic reduction of protons or carbon dioxide under acidic and basic conditions, respectively, demonstrating the ability to control the photosensitizing properties of supramolecular assemblies.

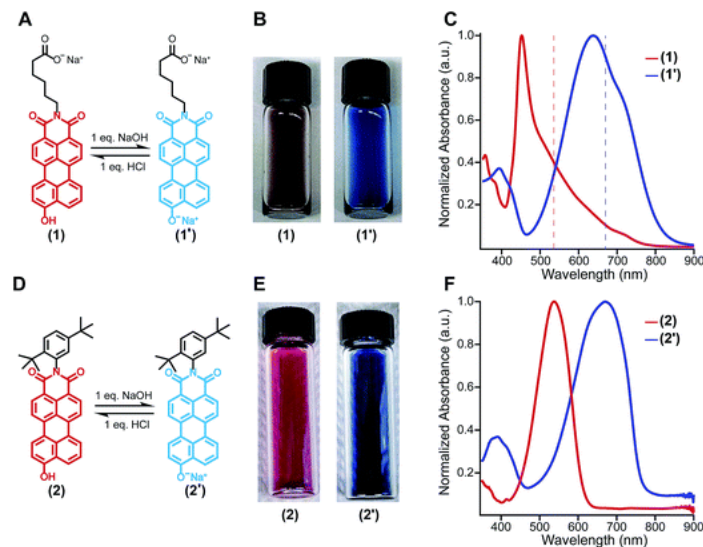


Fig. 1 (A) Chemical structures showing the reversible ionization of **1**. (B) Photographs of aqueous solutions of protonated (**1**, left) and deprotonated (**1'**, right) (C) UV-vis absorbance spectra of **1** (8.7 mM) in water. (D) Chemical structures showing the reversible change in ionization state of **2**. (E) Photographs of aqueous solutions of **2** in 9:1 DCM/MeOH while protonated (**2**, left) and deprotonated (**2'**, right) (F) UV-vis absorbance spectra of **2** in 9:1 DCM/MeOH (0.87 mM).