Unique AIE Behavior of a Macrocyclic 1, 4-Bis(4-pyridylethynyl)benzene

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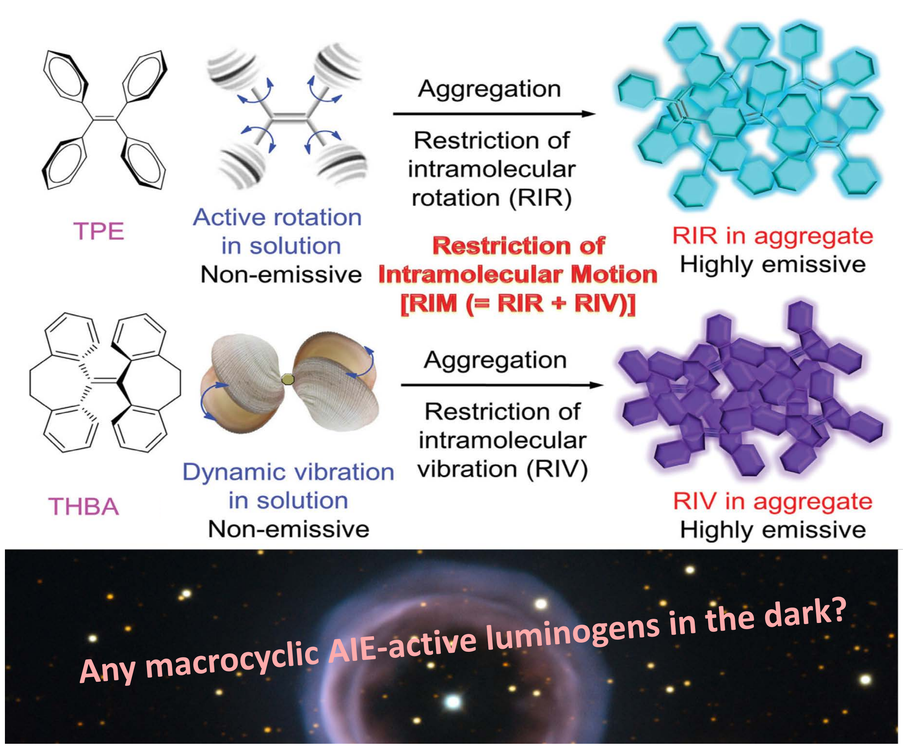
1. INTRODUCTION



AIE (aggregation-induced emission) has become a highly interdisciplinary research field and is making a significant impact on the development of chemical, materials, and biological sciences. Design and discovery of new AIE-active fluorogens are a key issue in this flourishing field. An AIE-active fluorogen usually takes a propeller- or shell-like configuration (Fig. 1). Can be there any macrocyclic AIE-active fluorogens? How about their fluorescent behaviors? The unique AIE behavior of a macrocyclic molecule constructed by 1,4-bis(4-pyridylethynyl)benzene is demonstrated.

Fig. 1. Illustration of the molecular configuration and working mechanism of two main types of AIE-active luminogens. TPE=tetraphenylethene, THBA=10,10′,11,11′-tetrahydro-5,5′-bidibenzo[a, d][7]annulenylidene.

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2. Macrocyclic Luminogen: Molecular design, preparation and emission behaviors

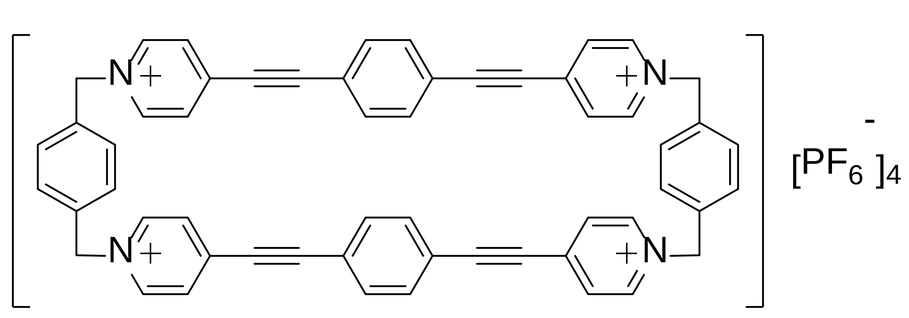

Fig. 2. Chemical structure of the target macrocyclic luminogen (Box). Efficient synthetic route led to target product and the overall yield was ~ 60%, quite high for macrocyclic organic compounds.

Water clusters help the RIR process and turn on the emission in DMSO/H_2O mixtures; $[PF_6]^-$ anions strut big space for intramolecular rotations thus quenched emission.

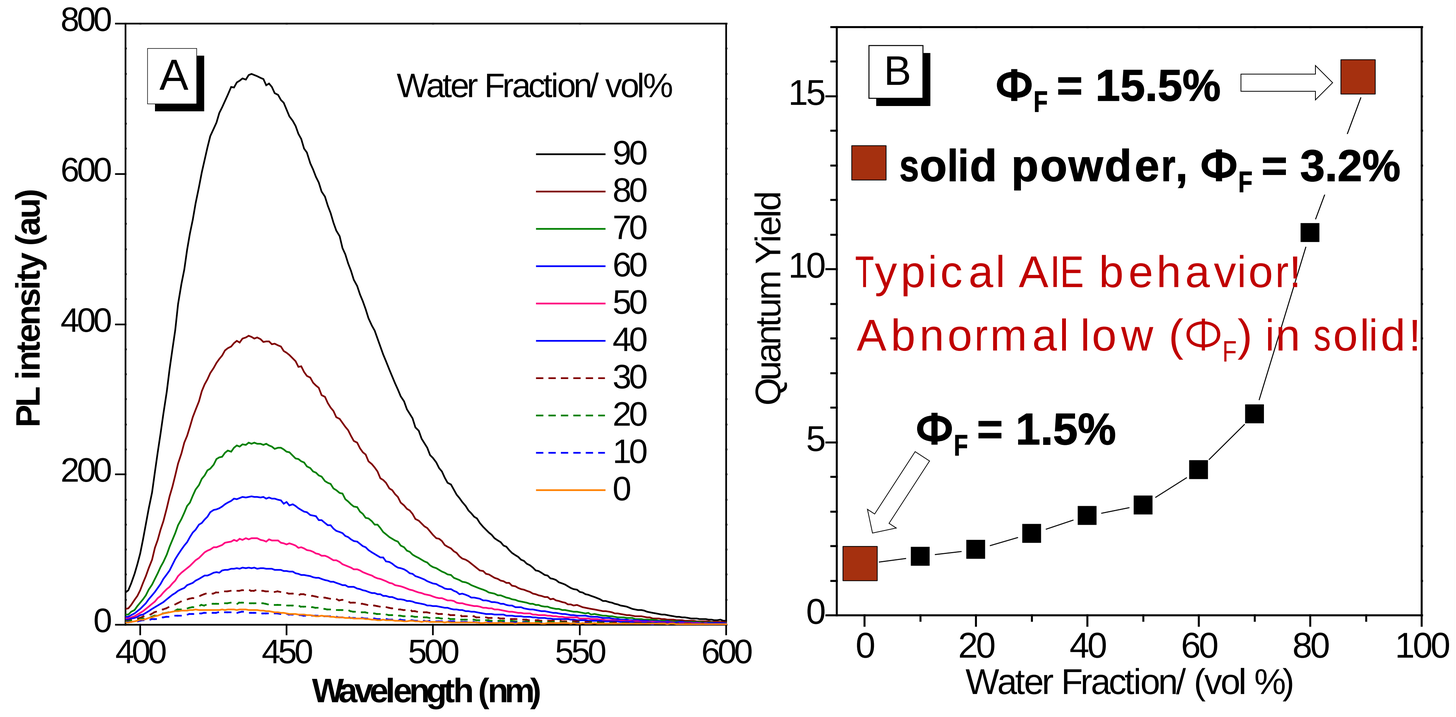

Fig. 3. (A) Photoluminescence (PL, λ_{ex} = 375 nm) spectra of Box in DMSO/H_2O mixtures with different H_2O fractions (f_W). (B) Changes in PL quantum yield (Φ_F) in DMSO/H_2O mixtures. [Box] = 10 μM.

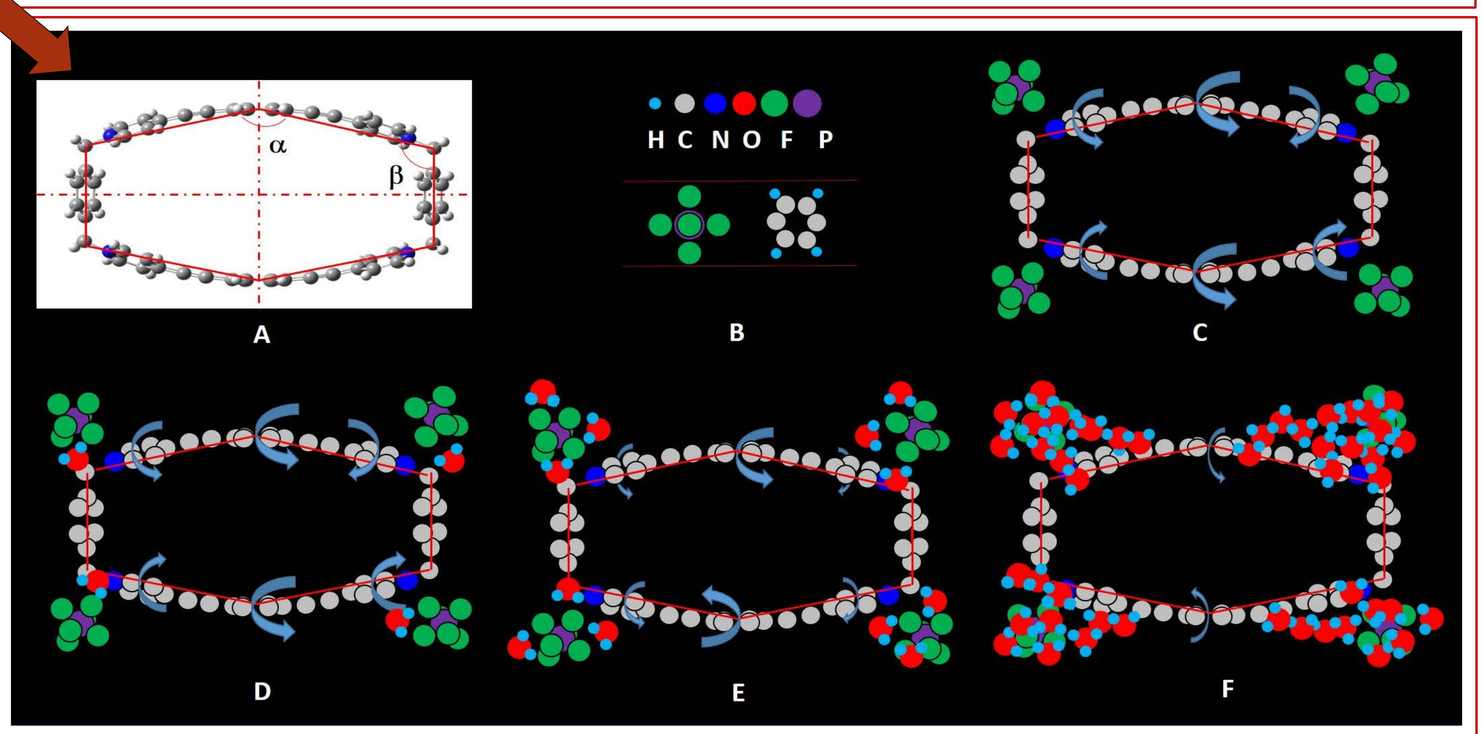

Fig. 4 (A) Optimized geometric structure of Box, α = 156°, β = 102°. (B) Illustration of the relative size of H, C, N, O, F, P atoms and the dimension of $[PF_6]^-$ and phenyl groups. (C) to (F) are cartoons showing a Box molecule in different situations: (C) in dilute DMSO solution; (D), (E) and (F) in DMSO/water mixtures with low, moderate and high f_W. At high f_W, water clusters formed by H-bonding and localized around the $[PF_6]^-$ and pyridinium ions due to the hydrophilic interaction. (F) In solid, the geometry is similar to (C), but no solvent molecules.