

How the control of aggregation state surprises us?

So far, regardless of the importance of various liquids and solutions, lots of materials with different functions should be utilized in the solid state. This is also the case for organic solids, a special kind of materials, possessing the structure of π system, with peculiar optical, electronic and magnetic properties. Actually, in addition to the modification of the π systems with different structures, their different packing states, would result in much different opto-electronic properties. However, as the π systems could inherently affect their possible packing states to regulate the material performance, the molecular design plays a key role in the research field of organic solids. Thus, once a new fundamental molecular design principle is proposed, it would evoke the rapid development of the related research fields, as demonstrated by the recent arising hot topic of AIEgens (their molecular structures are controlled as propeller shape) with the characteristic of aggregation induced emission (AIE) [1]. This standpoint, somehow, might be confirmed once again by a new story initiated this April [2].

To pursue the high efficiency and better performance in the applications of photovoltaics, bioimaging, light emitting diodes, and photocatalytic reactions etc., phosphorescent materials are favorite rather than their fluorescent competitors, especially those active at room temperature. However, the lack of good metal-free organic phosphors, caused by the ultrafast deactivation of the lowest triplet excited state (T1), nearly makes room temperature phosphorescence a solely happy game just played by organometallic chelates, no matter the former ones possess some advantages in a variety of imaging and displaying applications. Excitedly, significant progress on this issue was reported this April online by the group of Wei Huang and Runfeng Chen at Nanjing University of Posts and Telecommunications and the group of Xiaogang Liu at National University of Singapore. They intelligently designed three kinds of metal-free organic molecules containing O, N and P atoms (there are one pair of electrons on the N and P atoms, and two on the O atom, chart 1), which are capable of promoting spin-forbidden singlet-triplet intersystem cross through $n-\pi^*$ transition. Coupled with the formation of H aggregates of

the molecules induced by their planar structures, the T1 state could be stabilized, thus, possibly led to the formation of a new triplet excited state (T1*) at a lower energy level, realizing the phosphorescence with dramatically increased lifetime (up to 1.35 s versus general several ms). This design principle, involving the stabilization of the triplet excitons through the molecular H-aggregation, opens up a new avenue for the development of purely organic molecules with room temperature phosphorescence, being superior to the previous organic phosphorescent systems of crystals and host-guest materials containing heavy halogen or deuterated carbons. According to this relatively simple principle, much more metal-free organic phosphors should be yielded with ultralong lifetime. Furthermore, stimulated by this exciting finding, how about other aggregation forms, but not limited to the above mentioned Tang's AIE case and Huang's H aggregate? Perhaps, the aggregation state could be further controlled through the molecular design more intelligently, to achieve something new to surprise us. Surely, it is a challenge, but the mission and enjoyment of scientists exist here.

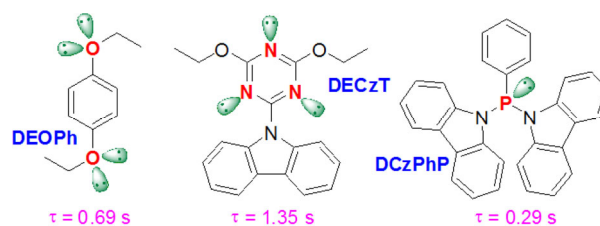


Chart 1 Structures of three organic molecules with ultralong room temperature phosphorescence.

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