The Delayed Box: Biphenyl-bisimide Cyclophane, a Supramolecular Nano–environment for Efficient Generation of Delayed Fluorescence

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The burgeoning field of host-guest chemistry recently created immense attention in supramolecular chemistry due to their strong binding affinity and selectivity. Moreover, cyclophane hosts recently started blossoming due to their unique molecular design and functional relevance in sensing and catalysis. However, triplet-induced functional properties are still unknown in this scientific realm and remain a holy grail. In this context, we propose a strategy for efficient delayed fluorescence emission in a dilute solution state using a non-covalent approach via supramolecular nano–environment formation. We aim to create supramolecular nanocavity for triplet exciton stabilization by reducing vibrational dissipation and lowering the singlet-triplet energy gap for efficient delayed fluorescence emission. We elegantly entrench the design to alleviate the scenario using a novel small biphenyl bisimide-derived cyclophane, an electron-deficient and efficient triplet-generating host. We intend to form an emissive charge-transfer (CT) state close to the triplet level of the biphenyl bisimide upon encapsulating carbazole-derived guest inside the nanocavity of cyclophane. The experimental results of host-guest studies manifest high association constants up to 10^4 M^{-1}, which help in strong inclusion complex formation, prerequisites for emissive CT state evolution, and triplet-state stabilization in a diluted solution. According to our hypothesis, we realize tunable delayed fluorescence emission from carbazole-encapsulated biphenyl bisimide cyclophane in methylcyclohexane carbon tetrachloride solution via non-covalent supramolecular strategy with significantly high quantum yield (QY) of up to 15.6 % for the first time in solution. Further crystal structure analysis and solid-state photophysical study validate our hypothesis and elucidate the delayed fluorescence emission mechanism.

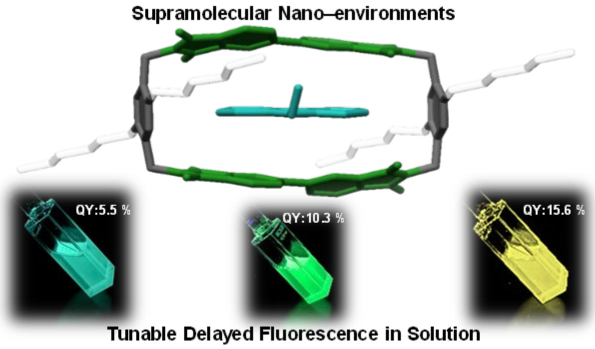

Figure 1: Single-crystal X-ray analysis of the host-guest complex and tunable delayed fluorescence of the host-guest complexes in MCH/CCl_4 (1:3) solvent mixture in an inert atmosphere under 365 nm UV light.

References:

[1] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **2012,** *492*, 234–238.
[2] P. Spenst, F. Würthner, *Angew. Chem. Int. Ed.* **2015**, *54*, 10165–10168.