

## Dithia[3.3]paracyclophane Core: a Versatile Platform for Fine Triplet State Tuning and Through Space TADF Emission.

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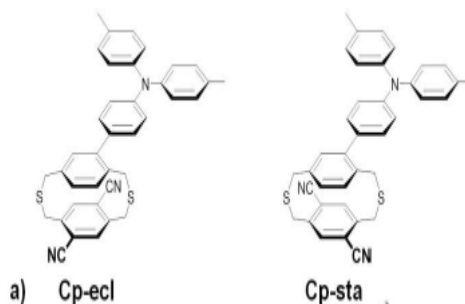
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Since the pioneering work of Tang and VanSlyke<sup>[1]</sup> and later on by Friend et al.<sup>[2]</sup>, fluorescent-based organic light-emitting diodes (OLEDs) have been intensively studied. After the second generation of OLEDs based on phosphorescent materials,<sup>[3]</sup> recently an alternative approach allowing 100% of IQE in OLEDs has been successfully developed based on metal-free, thermally activated delayed fluorescence (TADF) emitters, leading to the third generation of OLEDs.<sup>[4]</sup> The common strategy consists in maintaining a weak electronic communication between Donor and Acceptor groups by a central core, either through an intensely twisted conjugated linker<sup>[5]</sup>, or a single  $\sigma$ -bond<sup>[6]</sup>, or via through-space interactions.<sup>[7]</sup> In this context, novel TADF isomers using a dithia[3.3]-paracyclophane building block as a versatile 3D platform to promote through-space interactions is presented.<sup>[8]</sup> Such a 3D platform allows to bring together the D and A units into close proximity and to probe the effect of their orientation, contact site and distance on their TADF emission properties. This study provides evidence that dithia[3.3]paracyclophane core is a promising platform to control intramolecular through-space interactions and obtain an efficient TADF emission with short RISC lifetimes. In addition, this study demonstrates that this design can tune the energy levels of the triplet states and leads to an upconversion from 3CT to 3LE that promotes faster and more efficient RISC to the 1CT singlet state.



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