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## Multifunctional Organic Semiconductors Based on Polyhalogenated Thiele Hydrocarbons

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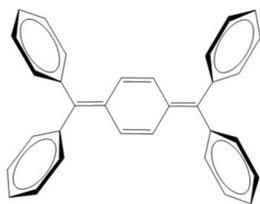
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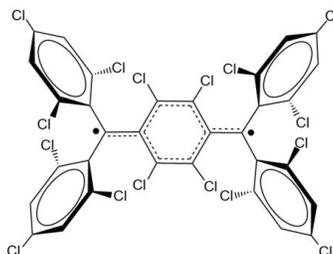
Efficient organic light-emitting diodes (OLEDs) with emission in the first biological transparency window (650 -900 nm)<sup>1</sup> are a useful tool for bioimaging and biosensing applications.<sup>2,3</sup> In this context, inert polyhalogenated triphenylmethyl radicals (PTMs) are emerging as one of the most promising materials for electroluminescence applications in the near infrared (NIR) region.<sup>4,5</sup> In fact, thanks to their doublet spin configuration due to the presence of an odd electron, it is possible to overcome the problems associated to the spin statistics which affect closed-shell fluorescent species (singlet emitters) when used in electroluminescent devices, making them one of the best alternatives to phosphorescent organometallic compounds. Radical-based OLEDs can reach values of internal quantum efficiency of 100% in a spectral range between 700-800 nm and with an emission life-time of few ns.<sup>6</sup> Although an impressive external quantum efficiency (EQE) of 27% in the NIR was reported, two major unresolved problems affect these devices: a severe roll-off and a device lifetime of few minutes.<sup>4,5</sup> A strong electron-trap behavior exerted by the singly occupied molecular orbital (SOMO) of the radical was suggested as one of the possible causes. An alternative to free radical, potentially capable to overcome these problems, is represented by fluorescent diradicaloids. In fact, singlet diradicaloids with a small or moderate diradical character exhibit very different physical properties compared with closed-shell molecules. They show a small HOMO-LUMO gap and amphoteric redox behavior which make them suitable for absorption toward the NIR and as active materials in ambipolar organic field-effect transistors (OFETs).<sup>7,8</sup> Although recently there has been an increased effort to design stable species, the synthesis of inert and fluorescent diradicaloids is still elusive. The first ever synthesized diradicaloid was the Thiele hydrocarbon (TH) (**Figure 1**), and in contrast with most diradicaloids with a stronger diradical character, the TH is a fluorescent species.<sup>9</sup> However, the TH is incompatible with device manufacturing because of its intrinsic instability, being a light and oxygen-sensitive species.

In this work we report polychlorination as a structural modification able to stabilize the TH, preserving at the same time its emissive properties. The TTM-like Thiele hydrocarbon (TTH) (**Figure 1**), *i.e.* a species with non-chlorinated *meta* positions of phenyl moieties, can represent an efficient platform for the development of fluorescent and ambipolar semiconductors with tunable transport and emitting properties suited for high-performing electroluminescent devices. The molecule exhibited an intense solvatochromic emission that was interpreted with the use of throughout computational tools indicating the key role of its diradical character in determining the unconventional fluorescence properties. Furthermore, this study enabled to open new insights into the nature of the emitting state of singlet diradicaloids and their future possible applications.

**Thiele Hydrocarbon (TH)**



**TTM-like Thiele Hydrocarbon (TTH)**



**Fig. 1.** Chemical structure of Thiele Hydrocarbon and TTM-like Thiele hydrocarbon

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