

Synthesis and Properties of BODIPY Appended Tetraphenylethylene Scaffolds as Photosensitizer Arrays

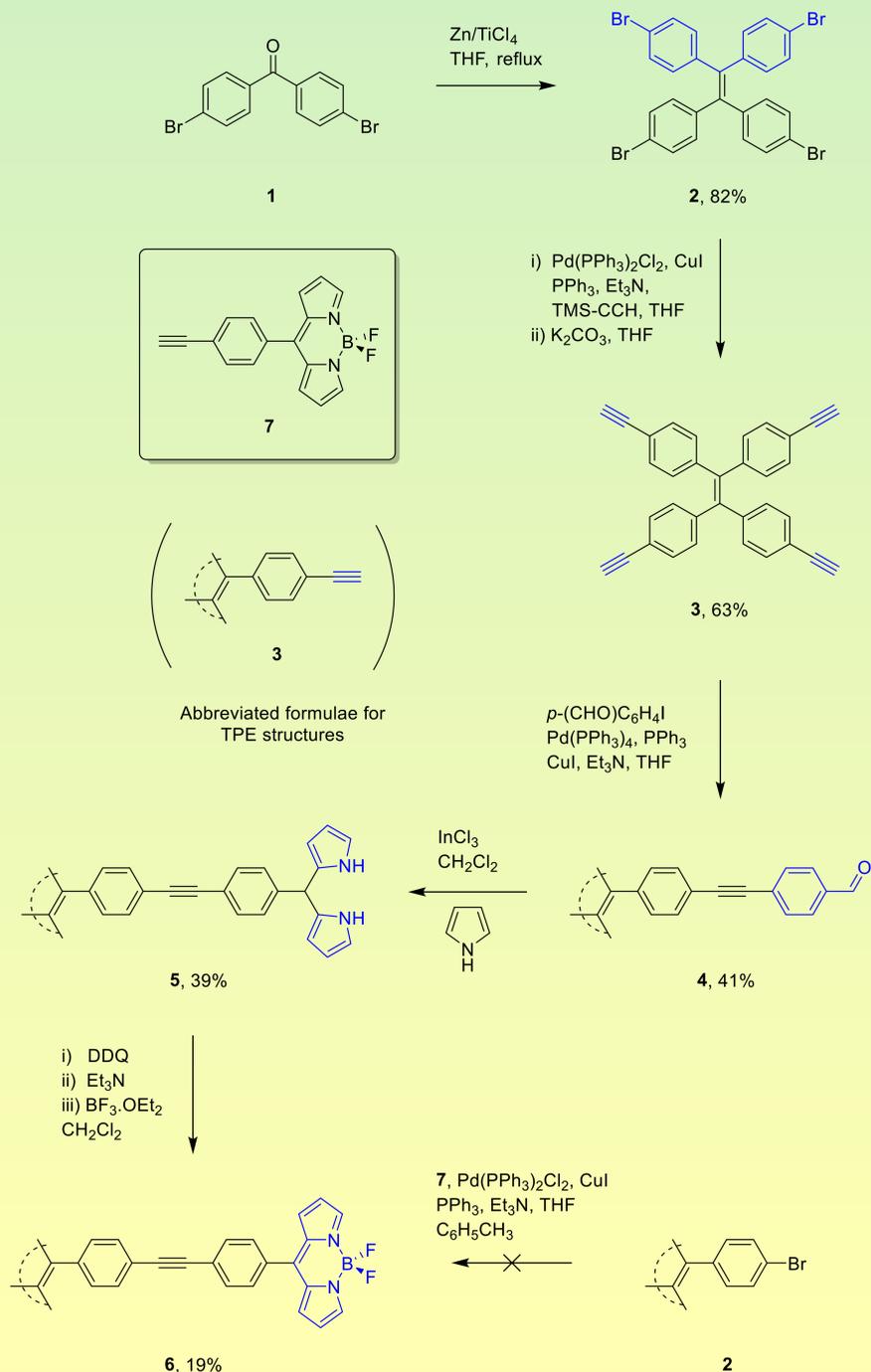
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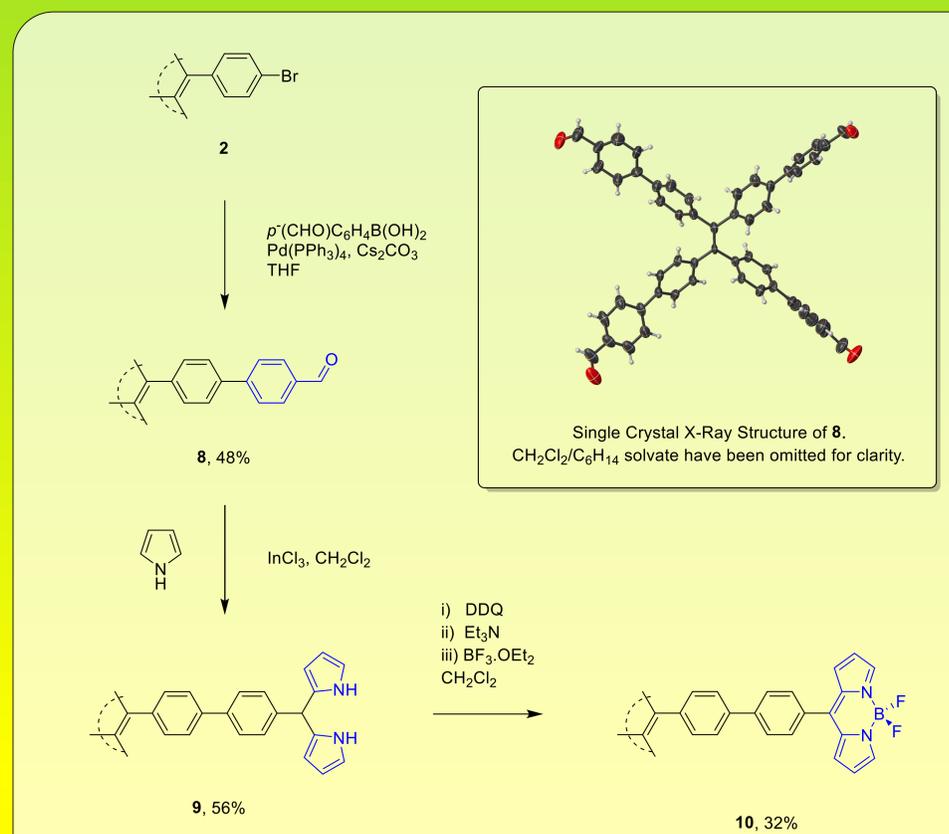
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Scheme 1: Synthesis of TPE-BODIPY conjugate **2**, containing an ethynyl spacer, from the readily available TPE-Br₄ (**4**), and the failed Sonogashira reaction of **4** to yield conjugate **2**.

Abstract: Since the first exhibition of the phenomenon that is aggregation induced emission (AIE) in 2001, [1] molecules that demonstrate this property have been under the spotlight for myriad application. [2] One such motif is 1,1,2,2-tetraphenylethylene (TPE): facile in its synthesis and modification, it is currently an invaluable scaffold in materials chemistry. [3] Recently, the Senge group has shown the utility of boron dipyrromethene (BODIPY) photosensitizers in photodynamic therapy. [4] The subsequent combination of these two motifs would provide multiple photometric responses and subsequently a greater understanding of the systems into which they are placed. Herein we present the synthesis of two novel TPE-BODIPY arrays in which the distance between the TPE and BODIPY cores is varied, through the utilization of differing palladium-catalyzed cross coupling reactions. We find that in organic solvents, both arrays exhibit the expected locally excited BODIPY photometric response, however in THF/H₂O systems we observe an aggregation induced dual emission response from only one of the arrays. Furthermore, we have found that both of these arrays possess the ability to produce singlet oxygen. We propose that these arrays present themselves for applications including; light harvesting arrays, delivery of photosensitizers for photodynamic therapy, intracellular imaging, and the construction of porous materials.



Scheme 2: Synthesis of TPE-BODIPY conjugate **1**, containing a direct TPE-BODIPY linkage. Inset: Single Crystal X-ray structure of tetra-aldehyde intermediate **9**.

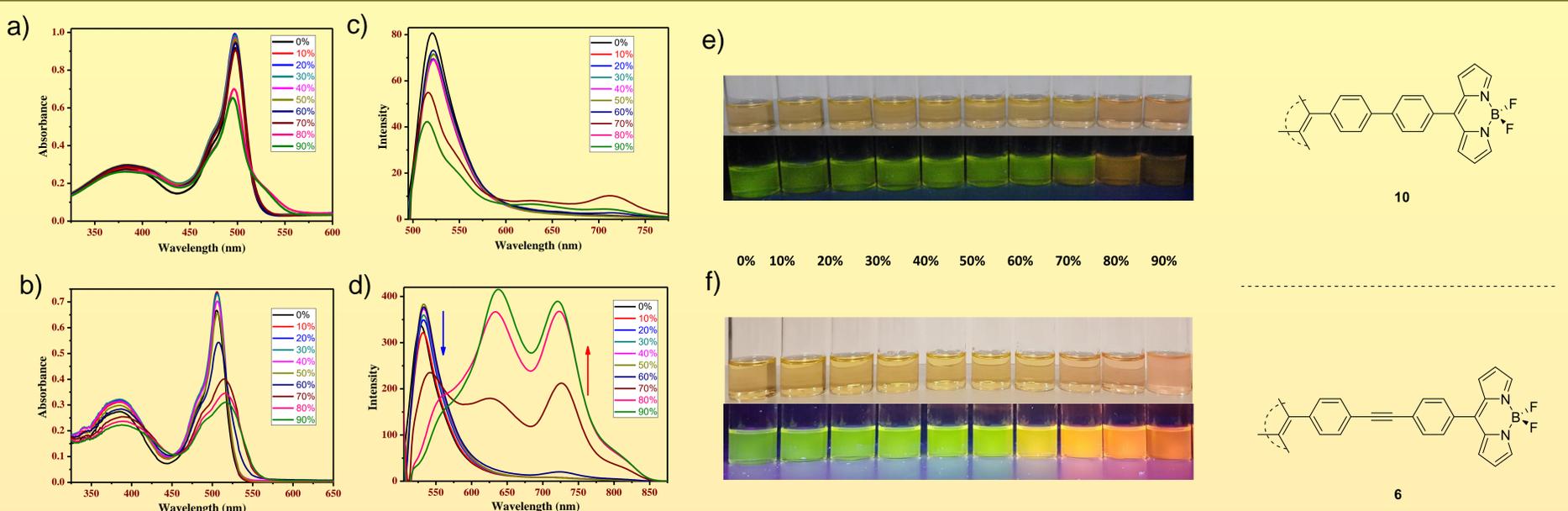


Figure 1: Top: Absorption (a) and Emission (c) spectra for **10** in varying solution of THF:H₂O (10⁻⁴ M) with pictorial representation (e) of these solutions under ambient lighting (top) and UV illumination (bottom, λ = 360 nm). Bottom: Absorption (b) and Emission (d) spectra for **6** in varying solution of THF:H₂O (10⁻⁴ M) with pictorial representation (f) of these solutions under ambient lighting (top) and UV illumination (bottom, λ = 360 nm).

Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement n°764837, Science Foundation Ireland (SFI, IVP 13/IA/1894), and Irish Research Council (GOIPG/2017/1395).



Conclusion: Herein, we have presented the synthesis of two novel tetra-BODIPY appended TPEs, along with the crystal structure of one of the intermediates (**8**, Scheme 2 inset). We find that the addition of an ethyne linkage, as observed in **2**, between the TPE core and the BODIPY fluorophore results in a better display of the AIE phenomenon than in **1**, where there is a direct C-C linkage between the TPE core and BODIPY fluorophore, in THF:H₂O systems. We are currently investigating the reasoning behind this more thoroughly along with attempting to append other pyrrolic fluorophores to the TPE scaffold.

Literature: [1] J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; [2] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.*, 2015, **115**, 11718; Z. Zhu, C. W. T. Leung, X. Zhao, Y. Wang, J. Qian, B. Z. Tang, S. He, *Sci. Rep.*, 2015, **5**, 15189; [3] K. Li, Z. Li, D. Liu, M. Chen, S.-C. Wang, Y.-T. Chan, P. Wang, *Inorg. Chem.*, 2020, **59**, 6640; [4] M. A. Filatov, S. Karuthedath, P. M. Polestshuk, H. Savoie, K. J. Flanagan, C. Sy, E. Sitte, M. Telitchko, F. Laquai, R. W. Boyle, M. O. Senge, *J. Am. Chem. Soc.*, 2017, **139**, 6282; S. Callaghan, M. A. Filatov, H. Savoie, R. W. Boyle, M. O. Senge, *Photochem. Photobiol. Sci.*, 2019, **18**, 495.