

DOI:10.1002/ejic.201500726

# Synthesis and Photophysical Investigation of Tetraazaporphyrin Substituted with Aggregation-Induced Emission (AIE) Active Moieties

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**Keywords:** Porphyrinoids / Aggregation / Absorption / Circular dichroism / Magnetic properties

The synthesis and characterization of free-base and Zn<sup>II</sup> tetraazaporphyrins with tetraphenylethylene (TPE) or diphenylphenanthrene (DPP) moieties that are known to be aggregation-induced emission (AIE) active is reported. The optical spectra contain the characteristic Q and B absorption bands of Gouterman's four-orbital model and a broad envelope of weaker charge-transfer bands in the 450–600 nm region. The observed fluorescence emission lies beyond

670 nm and originates exclusively from the decay of the S<sub>1</sub> state of the macrocycle, regardless of the excitation wavelength used. Theoretical calculations provide further evidence of strong electronic communication between the peripheral TPE or DPP moieties and the central ring. The Zn<sup>II</sup> complexes were found to have relatively high singlet-oxygen quantum yields.

## Introduction

In recent years, there has been considerable interest in the design of novel near-infrared (NIR) absorbing and emitting compounds owing to their potential applications in solar cells and in biomedical fields.<sup>[1]</sup> For example, in the former case, these dyes can be used to capture the 50% of the incident solar photon flux that lies beyond 700 nm in the NIR region. Dyes that absorb light in the optical window for tissue penetration between 700 and 900 nm can also be used for photodynamic therapy (PDT) and NIR bioimaging. Absorption at longer wavelengths is usually observed in chromophores with extended  $\pi$  conjugation, such as tetraazaporphyrins (TAPs) and phthalocyanines (Pcs) owing to a narrowing of the HOMO–LUMO gap. However, as the  $\pi$  system of a molecule expands, so does the tendency for the dye to aggregate in solution, thereby resulting in nonradiative deactivation of the excited state when face-to-face  $\pi$  stacking occurs. This phenomenon can result in short-lived charge-separated species and in fluorescence quenching, and this often limits the utility of NIR-region dyes for applications.<sup>[2]</sup>

To address this aggregation-caused quenching (ACQ) problem, planar and conjugated chromophores have been modified with propeller-shaped moieties, such as tetraphenylethylene (TPE), which exhibit aggregation-induced emission (AIE) behavior.<sup>[3]</sup> AIE luminogens usually have several phenyl rotors in their structures that can deactivate fluorescence intensity in solution through free rotation. In the solid state and in aggregates in solution, however, intramolecular motion is restricted, and emission intensity increases significantly. Zhao and co-workers have recently shown that structural modification of perylene-3,4,9,10-tetracarboxylic bisimide (PBI) with TPE moieties resulted in a compound with no emission in solution and strong red fluorescence upon aggregation.<sup>[4]</sup> A similar effect was reported by Atilgan et al.<sup>[5]</sup> and Tang et al.<sup>[6]</sup> for boron dipyrromethene (BODIPY) dyes substituted with TPE groups at the *meso*- and  $\beta$ -carbon positions.

In a similar manner to perylene and BODIPYs, TAPs are ACQ-type molecules that possess interesting properties such as structural versatility, chemical stability, and intense absorption/emission in the UV/Vis/NIR region.<sup>[7]</sup> The design of TAPs with enhanced emission behavior in aggregates would therefore represent a significant advance in the chemistry of porphyrinoids and further expand their potential utility for applications. With this in mind, the aim of the study was to investigate the fluorescence response of TAP macrocycles peripherally modified with the AIE luminogens such as TPE and diphenylphenanthrene (DPP), a TPE analogue that contains a phenanthrene unit. We recently reported that 2-butenedinitriles, which are suitable precursors for the synthesis of TAPs, exhibit AIE behavior

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