Meso-Zn(II)porphyrins of tailored functional groups for intensifying the photoacoustic signal

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ABSTRACT

Development of efficient molecular photoacoustic contrast agents plays a significant role in next generation biomedical imaging techniques. This article demonstrates a design criterion for small molecules to exhibit a large photoacoustic effect by density functional theory (DFT) and its experimental validation. The method relies on controlling the effect of resonating structures on the vibrational energies of small molecules such that rapid thermalization pathways exist near higher-order unoccupied molecular orbitals. A series of Zn(II)porphyrin derivatives (Por-Cn-RAm, where n = 12 or 8 and m = 1–4) is designed as a model system by DFT and demonstrated a systematic variation in the absorption coefficients of C–H vibrational modes occurring in the high-frequency spectral region. A systematic decrease in absorption coefficients was observed, and therefore a similar variation in the photoacoustic signals is predicted. To validate the theoretical results, four Zn(II)porphyrin based molecules showing a systematic variation in absorption coefficients, viz.Por-C12-RA1, Por-C12-RA2, Por-C12-RA3, and Por-C8-RA4, are synthesized in good yields (40–70%) and their optoelectronic properties are systematically studied and the effect of resonating structures in these molecules in determining the vibrational energies is discussed. The theoretical predictions are validated by photoacoustic coefficient measurements and photoacoustic tomography. The photoacoustic coefficients and tomographic intensities decreased in the order Por-C12-RA1 > Por-C12-RA2 > Por-C12-RA3 > Por-C8-RA4, as predicted by DFT. A large photoacoustic coefficient is observed for Por-C12-RA1, which is superior to that of existing small molecules. Besides offering a superior molecule for photoacoustic tomography, the present criterion adopted here would enable the design of simpler molecules with superior photoacoustic and other nonlinear optical properties.

KEYWORDS: photoacoustic signal, Zn(II)porphyrin

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