

Difluorenyl carbo-Benzenes: Synthesis, Electronic Structure, and Two-Photon Absorption Properties of Hydrocarbon Quadrupolar Chromophores.

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Abstract

The synthesis, crystal and electronic structures, and one- and two-photon absorption properties of two quadrupolar fluorenyl-substituted tetraphenyl carbo-benzenes are described. These all-hydrocarbon chromophores, differing in the nature of the linkers between the fluorenyl substituents and the carbo-benzene core (C-C bonds for 3 a, C=C-C expanders for 3 b), exhibit quasi-superimposable one-photon absorption (1PA) spectra but different two-photon absorption (2PA) cross-sections σ_{2PA} . Z-scan measurements (under NIR femtosecond excitation) indeed showed that the C \equiv C expansion results in an approximately twofold increase in the σ_{2PA} value, from 336 to 656 GM (1 GM = 10^{-50} cm⁴ s molecule⁻¹ photon⁻¹) at $\lambda = 800$ nm. The first excited states of Au and Ag symmetry accounting for 1PA and 2PA, respectively, were calculated at the TDDFT level of theory and used for sum-over-state estimations of $\sigma_{2PA}(\lambda_i)$, in which $\lambda_i = 2 hc/E_i$, h is Planck's constant, c is the speed of light, and E_i is the energy of the 2PA-allowed transition. The calculated σ_{2PA} values of 227 GM at 687 nm for 3 a and 349 GM at 708 nm for 3 b are in agreement with the Z-scan results.