Investigation of Three- and Two-Photon Absorption Processes in Novel $D_2 - A - A - D_2$ Type Diquinoxaline Derivatives

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In recent years, there has been a growing search for novel fluorescent organic compounds capable of absorbing two- and three-photons (2PA and 3PA). This is due to the potential use of these compounds as fluorescent probes for 2PA and 3PA to non-invasively visualize biological analytes, anatomical structures, and processes using appropriate contrast agents [1]. 2PA and 3PA fluorescence microscopy offer several advantages over their linear counterpart (1PA fluorescence microscopy), including [2]: (I) improved penetration depth when operating within the transparency windows of living organisms in the near-infrared region; (II) minimized scattering losses when using longer wavelengths; and (III) enhanced spatial resolution. In this context, the 3PA process is even more advantageous than 2PA, as it occurs at longer wavelengths. However, there are still challenges that need to be overcome for the use of organic compounds as imaging agents (probes) for 2PA and 3PA. The main challenges are [3]: (i) developing compounds with 1PA above 450 nm, which typically results in 2PA and 3PA above 900 nm and 1350 nm, respectively; (ii) creating compounds with good multiphoton absorption capacity, allowing for reduced excitation intensity; (iii) obtaining spectral information regarding the 2PA and 3PA cross-sections (σ_{2PA} and σ_{3PA}), indicating the optimal excitation point; and (iv) developing compounds with sufficiently high fluorescence quantum efficiency to produce high-contrast images. These are some of the challenges that have not yet been completely overcome in this area. To address some of these challenges, this study investigated three diquinoxalines (DQ) derivatives, which contain a promising structure for multiphoton absorption of the $D_2 - A - A - D_2$ type, where D represents an electron-donating group and A represents an electron-accepting group. The difference between the compounds lies in the electron-donating fraction, which in this case are: diphenylamine (DQ-DPA), tetrahydro-3H-dibenzo[b,f]azepine (DQ-DDA), and 5H-dibenzo[b,f]azepine (DQ-IMD). The multiphoton absorption measurements were performed using the non-referenced two- and three-photon excited fluorescence technique. To understand the electronic and structural properties of the compounds, several linear measurements were conducted, as well as DFT calculations. The results showed that the compounds DQ-DPA and DQ-IMD exhibited excellent emissive properties, with fluorescence quantum yield (ϕ_{fl}) of 28% and 14%, respectively. On the other hand, the compound DQ-DDA experienced fluorescence quenching, presenting a ϕ_{fl} of only 2%. Additionally, it was observed that the compounds exhibit a 2PA absorption band at approximately 700 nm with a σ_{2PA} of about 230 GM and a second 2PA band at approximately 830 nm with a σ_{2PA} of about 130 GM. Finally, the DQ derivatives exhibited a σ_{3PA} of approximately 0.02×10^{-78} $cm^6 s^2/photon^2$ at 1100 nm, with these values being 4 times higher than those found in molecules such as rhodamine 6G and BDPAS, and up to 2000 times higher than the σ_{3PA} of fluorescein. Therefore, this work presents a promising perspective for the application of DQ-derived compounds as fluorescent probes.

References

[1] Z Zheng, H Zhang, H Cao *et al.*, ACS Nano **16**, 6444 (2022); DOI: 10.1021/acsnano.2c00672

[2] J Liu, G Li and Y Wang, J. Phys. Chem. A **116**, 7445 (2012); DOI: 10.1021/jp301657g

[3] P A Shaw, E Forsyth, F Haseeb, S Yang, Mark Bradley and M Klausen, Front. Chem. **10**, 921354 (2022); DOI: 10.3389/fchem.2022.921354

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