



## Research paper

## Synthesis and two-photon absorption spectrum of fluorenone-based molecules



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## ABSTRACT

The two-photon absorption (2PA) of five symmetrical fluorenone-based molecules is studied by femtosecond wavelength-tunable Z-scan, as well as quantum-chemical calculations. The molecules are transparent for wavelengths greater than 500 nm and two main one-photon absorption bands are observed in the blue region; one weak, centered at 450 nm, and a stronger one at approximately 360 nm. We observed a strong 2PA band located around 720 nm with maxima 2PA cross-sections between 100 and 230 GM. Quantum chemical calculations employing the response function formalism were performed at the Density Function Theory level to support the interpretation of the experimental nonlinear spectra.

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## 1. Introduction

Fluorene compounds are known for their large two-photon absorption (2PA) cross-sections [1]. As an alternative to fluorene compounds, fluorenone-based compounds, originated from the oxidation of the methylene bridge of the fluorine, have been advancing as an interesting option. Even though such family of molecules presents, in general, lower 2PA cross-sections than the fluorene-based ones [2,3], they may present other interesting features that can make them interesting candidates for applications in biological systems, for instance, as fluorescent molecular probes to indicate pH, nucleic acids and nitric oxide, as well as to investigate specific organelles.

Two-photon fluorescence microscopy [4] has been exploited as a valuable tool to study cell organelles, since it provides high resolution three-dimensional images. Besides, two-photon fluorescence microscopy is a non-invasive method, i.e., it allows great image quality of the studied cells while they are still functional. In this method, cells are stained by chromophores that present 2PA in the spectral range of 700–1000 nm. Therefore, the 2PA cross-section of the molecules used for this purpose should present high values within this range. As mentioned before, Fluorenone-based compounds have shown to present low cytotoxicity [5] and good 2PA cross-section in the near infra-red region [6], interesting features for two-photon microscopy.

Within this context, we present a study on the 2PA cross-section spectrum of five different symmetrical fluorenone derivatives. The 2PA spectra present a peak at approximately 720 nm, with values ranging from 100 to 230 GM, corresponding to the strong one-photon absorption band at 360 nm. The experimental results for the different molecules were compared to theoretical ones, obtained by quantum chemical calculations; the same trend was observed for the 2PA cross-section values within the family of molecules, although the measured ones are smaller than the theoretical.

## 2. Experimental

## 2.1. Chemical syntheses

The Fluorenone derivatives studied here were synthesized by coupling a fluorenone molecule with a halogen, specifically iodine with terminal alkynes. Subsequently, the replacement of iodine atoms of the fluorenone ring by terminal acetylenes is performed. The catalysis is carried out in the presence of the Pd(II) or Pd(0) complexes, copper iodide and a base, via the Sonogashira reaction [7]. The synthesis of the 2,7-di-iodine-9H-fluorenone was made from fluorenone and *N*-iodinesuccinimide, in the presence of sulfuric acid, according to procedures reported in the literature [8] and shown schematically in Fig. 1.

After the syntheses of the double substituted fluorenone-derivatives, the hydrogen in positions 2 and 7 were replaced by

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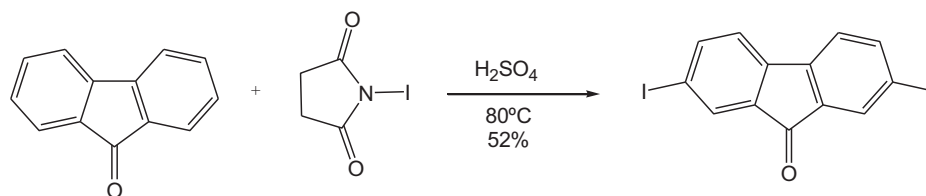


Fig. 1. Synthesis of 2,7-di-iodine-9H-fluoren-9-one.

groups with a triple bond connecting them to the main fluorenone structure. Five different groups (benzonitrile, benzomethoxy, benzene, thiophene and benzothiophene) were coupled to the fluorenone with a triple bond via the Sonogashira reaction. The five obtained molecules, with the substituents 2-benzothiophene (F-benzothiophene), 4-cyanophenyl (F-cyano), benzene (F-phenyl), 4-benzomethoxy (F-methoxy) and, 2-thiophene (F-thiophene) are shown in Fig. 2.

## 2.2. General methods

All commercially available reagents were used without any further purification and the reactions were monitored by TLC analysis with TLC plates containing GF<sub>254</sub> (E. Merck). Triethylamine and

dimethylformamide were dried under potassium hydroxide and calcium hydride, respectively, and distilled before use. Melting points were determined on a Büchi apparatus and are uncorrected. Column chromatography was performed on Silica Gel 60 (70–230 mesh, E. Merck). NMR spectra were recorded with a Varian Unity Plus 300 MHz or a Varian UNMRS 400 MHz spectrometer. Infrared spectra were obtained on a Bruker IFS66 FT-IR, using KBr pellets. Elemental analysis was performed with a Carlo Erba instrument model E-1110. 2,7-Diiodofluorenone was prepared according to earlier literature [8].

### 2.2.1. Synthesis of 2,7-disubstituted fluorenones via Sonogashira coupling reaction

In a 50 mL Schlenk flask, under argon atmosphere, it was dissolved 0.1 g (0.23 mmol, 1.0 eq) of 2,7-diiodo-9H-fluoren-9-one, 8 mg (0.011 mmol, 0.05 eq) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 4.4 mg (0.023 mmol, 0.1 eq) of CuI in a mixture of 2:1 v/v of dried and degassed triethylamine: DMF. Then it was added, dropwise, 0.5 mmol (2.5 eq) of the corresponding terminal alkyne. The mixture was allowed to react at room temperature for 24 h. At the end of the reaction, it was added concentrated HCl until the pH became acidic, and then the mixture was poured into a beaker containing iced water. The solid formed was filtered in vacuum and redissolved in ethyl acetate. To this organic phase, it was added anhydrous sodium sulfate which was vacuum filtered over celite in a sintered glass funnel. The solvent was evaporated and the residue chromatographed on silica gel.2.3.

### 2.2.2. Characterization

**2,7-Bis-phenylethynyl-fluoren-9-one:** yellow solid; m.p: 183–186 °C; Rf: 0,43 (chloroform:hexanes, 3:7, v/v); Yield: 41%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 7,35–7,37 (m, 6H, H<sub>arom</sub>); 7,48–7,56 (m, 6H, H<sub>arom</sub>); 7,64 (dd, 2H, J = 8,7 Hz, 1,2 Hz, H<sub>arom</sub>); 7,79 (s, 2H, H<sub>arom</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 77,0; 88,5; 91,4; 120,5; 122,7; 124,5; 127,3; 128,4; 128,6; 131,6; 134,4; 137,7; 143,1; 192,2. IR (KBr pellet) ν<sub>max</sub>/cm<sup>-1</sup>: 1717; 1492; 753; Calculated elemental analysis for C<sub>29</sub>H<sub>16</sub>O: C, 91,07%; H, 4,74%; found: C, 91,35%; H, 4,52%.

**2,7-Bis-(4-methoxy-phenylethynyl)-fluoren-9-one:** yellow solid; m.p.: 193–195 °C; Rf: 0.5 (hexanes:ethyl acetate, 9:1, v/v); Yield: 51%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 3.84 (s, 6H, OCH<sub>3</sub>); 6.89 (d, 4H, J = 8.4 Hz); 7.47 (dd, 2H, J = 8.4 Hz, 2.4 Hz); 7.50 (dd, 4H, J = 8.4 Hz, 2.4 Hz); 7.62 (d, 2H, J = 8.4 Hz); 7.78 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 30.3; 87.4; 91.5; 114.1; 114.8; 120.5; 124.8; 127.2; 133.2; 134.4; 137.5; 142.9; 159.9; 192.4; 194.7. IR (KBr pellet) ν<sub>max</sub>/cm<sup>-1</sup>: 1510; 1717; 2837; 2958. Calculated elemental analysis for C<sub>31</sub>H<sub>20</sub>O<sub>3</sub>: C, 84.14%; H, 5.48%; found: C, 83.79%; H, 5.01%.

**4,4'-(9-Oxo-9H-fluorene-2,7-diyl)-bis-(ethyne-2,1-diyl)-dibenzonitrile:** orange solid, m. p.: 269–272 °C; Rf: 0.6 (hexanes:ethyl acetate 9:1, v/v); Yield: 42%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 7.58 (d, 4H, J = 7.8 Hz, J = 1.8 Hz); 7.66 (dd, 4H, J = 8.1 Hz, 1.8 Hz); 7.69 (dd, 4H, J = 7.8 Hz, 1.5 Hz); 7.83 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ: 89.7; 92.5; 111.9; 118.3; 120.8; 123.6; 127.5; 127.6; 132.1; 134.5; 138.1; 143.7; 191.7. IR (KBr pellet) ν<sub>max</sub>/cm<sup>-1</sup>:

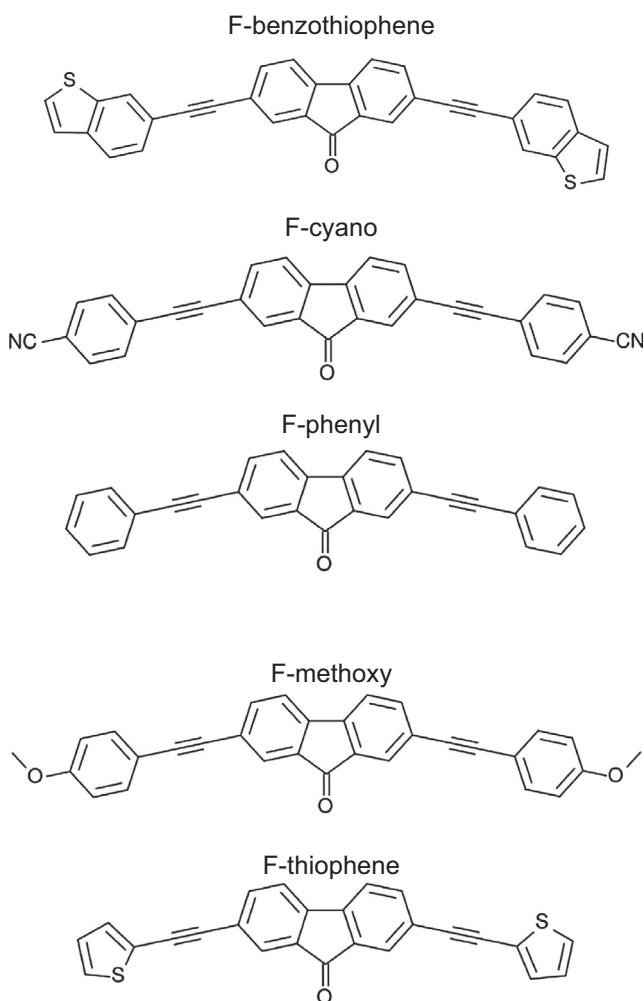


Fig. 2. Structures of F-benzothiophene (2,7-bis(benzo[b]thiophen-2-etyl)-9H-fluoren-9-one), F-cyano (4,4'-(9-oxo-9H-fluorenone-2,7-diyl)bis(ethyne-2,1-diyl)dibenzonitrile), F-phenyl (2,7-bis(fenylethynyl)-9H-fluoren-9-one), F-methoxy (2,7-bis((4-methoxyphenyl)ethynyl)-9H-fluoren-9-one) and F-thiophene (2,7-bis(thiophen-2-etyl)-9H-fluoren-9-one).

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