Data Article

Experimental and computational data on two-photon absorption and spectral deconvolution of the upper excited states of dye IR780

Luis Guillermo Mendoza-Luna a,b,1,∗, Cesar A. Guarin a,b,1,∗, Emmanuel Haro-Poniatowski a, José Luis Hernández-Pozos a

a Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco No. 186 Col. Vicentina, C.P. 09340 México D.F., México
b Cátedras CONACYT - Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco No. 186 Col. Vicentina, C.P. 09340 México D.F., México

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A B S T R A C T
Evaluating candidates for novel materials with high non-linear absorption properties for applications as biomarkers is a very important field of research. In this context, experimental and computational information on the two-photon absorption (TPA) properties of the dye IR780 is shown. The two-photon absorption data from 850 to 1000 nm for IR780 and other two well-known dyes, taken as reference, are presented. The experimental data were collected via an implementation of the two-photon induced fluorescence technique, while the quantum chemical data were produced by implementing DFT (Density-functional theory) methods. The data presented here supplement the paper “Two-photon absorption spectrum and characterization of the upper electronic states of dye IR780” by Guarin et al. (2021).

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∗ Corresponding authors at: Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Av. San Rafael Atlixco No. 186 Col. Vicentina, C.P. 09340 México D.F., México
E-mail addresses: luisgml@xanum.uam.mx (L.G. Mendoza-Luna), cesar.guarin@conacyt.mx (C.A. Guarin).
Social media: (L.G. Mendoza-Luna), (C.A. Guarin)
1 LGML and CAG share first authorship.

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### Specifications Table

| Subject                  | Physical Sciences. |
|--------------------------|--------------------|
| Specific subject area    | Two-photon absorption, ultrafast spectroscopy, dyes as biomarkers. |
| Type of data             | Tables and figures. |
| How data were acquired   | A two-photon induced fluorescence (TPIF) scheme was implemented: an excitation beam was produced by an optical parametric amplifier (model TOPAS by Light Conversion) pumped by a regenerative amplifier (Legend Elite-DUO, Coherent Inc.) operating at 1 kHz. The amplifier produced 80 fs pulses, centered at 800 nm (spectral width of 20 nm) with an energy of 4.5 mJ per pulse. The TOPAS was tuned from 850 to 1000 nm and the power delivered to the sample was controlled with a λ/2 plate. The fluorescence of the samples was detected with an f = 30 cm Czerny-Turner monochromator fitted with a PMT (R12896, Hamamatsu Photonics) coupled to an oscilloscope (Tektronix TBS 1102B-EDU), where the signal was averaged over 64 samples. |
| Data format              | Raw. Analyzed. |
| Parameters for data collection | The dyes used in this experiment were IR780, Rhodamines B and 6G in a methanol (HPLC-grade) solution with concentrations of 2.25 × 10⁻⁵ M, 7.65 × 10⁻⁶ M and 8.06 × 10⁻⁶ M, respectively. The excitation beam was focused with a microscope objective (NA=0.1, 4x). The energy of the excitation beam was varied between 0.002 and 0.35 μJ. UV–vis and luminescence spectra for IR780 in methanol were recorded in Perkin-Elmer spectrometers. |
| Description of data collection | The logarithm of the intensity of the fluorescence was plotted vs. the logarithm of the peak intensity of the excitation light. The deconvolutions and the fit of the Gaussian peaks were made with the Levenberg-Marquardt method implemented in Origin 2020b. The raw data and the fits have been supplied as Excel files (.xlsx). Computational data were obtained from optimization and vertical transitions routines implemented in quantum-chemical programs Gaussian 09 and GAMESS-US, respectively. |
| Data source location     | Femtosecond spectroscopy laboratory at the Physics Department of Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, Mexico. |
| Data accessibility       | Relevant data reported in this article and available at [1]. Repository identification number: Mendeley Data. Data identification number: https://doi.org/10.17632/2b3x7pgmfx.3 (https://data.mendeley.com/datasets/2b3x7pgmfx/3) |
| Related research article | Authors: Cesar A. Guarin, Luis Guillermo Mendoza-Luna, Emmanuel Haro-Poniatowski, José Luis Hernández-Pozos. Title: “Two photon absorption spectrum and characterization of the upper electronic states of the dye IR780". Journal: Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 249 (2021) 119291. https://doi.org/10.1016/j.saa.2020.119291 |

### Value of the Data

- These data show a measurement of the two-photon absorption band of the dye IR780.
- The data and associated calculations are useful for researchers interested in the nonlinear properties of cyanines as well as users looking into the potential of these substances as biomarkers excitable via IR radiation.
- The fits of the UV bands in the 1PA (one-photon absorption) spectrum can serve as reference for the fitting of the absorption spectra of other cyanines.
1. Data Description

The data presented here are experimental results to better understand the two-photon absorption processes involved in cyanine IR780 (2-[2-[2-Chloro-3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)ethylidene]1-cyclohexen-1-yl]thienyl]-3,3-dimethyl-1-propylindolium iodide).

Fig. 1 shows the quadratic dependence of the logarithm of the integrated fluorescence vs. the logarithm of the peak intensity of the pump beam for IR780, rhodamine B and rhodamine 6G; this is done for several wavelengths ranging from 850 to 1000 nm. Figs. 2-6 show each of them successive 5-Gaussian peak, 6-Gaussian peak, 7-Gaussian peak, 8-Gaussian peak and 9-Gaussian peak fits of the 1PA spectrum of IR780 in the spectral range 18350–35980 cm⁻¹, respectively. Fig. 7 shows the optimized structure of the molecule IR780 after applying three functionals.

![Graphs showing quadratic dependence](image)

**Fig. 1.** Set of graphs of the Log of the integrated fluorescence in methanol vs. the Log of the irradiation peak power for Rhodamine 6G, Rhodamine B and IR780 for several excitation wavelengths.
Fig. 1. Continued

c) 868 nm:

\[ \text{Log of Int. Fluorescence (a.u.)} \]
\[ \text{Log of Peak Intensity (I/(W/cm}^2)) \]

- Triangles: Rhodamine 6G experiment
- Red line: slope = 2.04, R^2 = 0.97

- Triangles: Rhodamine B experiment
- Red line: slope = 2.05, R^2 = 0.98

- Triangles: IR780 experiment
- Red line: slope = 2.00, R^2 = 0.97


d) 870 nm:

\[ \text{Log of Int. Fluorescence (a.u.)} \]
\[ \text{Log of Peak Intensity (I/(W/cm}^2)) \]

- Triangles: Rhodamine 6G experiment
- Red line: slope = 1.95, R^2 = 0.96

- Triangles: Rhodamine B experiment
- Red line: slope = 2.09, R^2 = 0.95

- Triangles: IR780 experiment
- Red line: slope = 1.99, R^2 = 0.97
Fig. 1. Continued
Fig. 1. Continued
Fig. 1. Continued
k) 915 nm:

![Graph showing data for 915 nm with various experiments and their slopes.]

l) 920 nm:

![Graph showing data for 920 nm with various experiments and their slopes.]

Fig. 1. Continued
m) 925 nm:

Fig. 1. Continued

n) 930 nm:

Fig. 1. Continued
Fig. 1. Continued

o) 985 nm:

- Rhodamine 6G experiment: slope=2.07, R^2=0.98
- Rhodamine B experiment: slope=2.02, R^2=0.95
- IR780 experiment: slope=2.08, R^2=0.96

p) 1000 nm:

- Rhodamine 6G experiment: slope=1.98, R^2=0.97
- Rhodamine B experiment: slope=2.05, R^2=0.97
- IR780 experiment: slope=2.08, R^2=0.90
Fig. 2. Curve fitting (5 Gaussian peaks) of the spectral bands of the upper states $S_n$ of IR780.

Fig. 3. Curve fitting (6 Gaussian peaks) of the spectral bands of the upper states $S_n$ of IR780.
Fig. 4. Curve fitting (7 Gaussian peaks) of the spectral bands of the upper states $S_n$ of IR780.

Fig. 5. Curve fitting (8 Gaussian peaks) of the spectral bands of the upper states $S_n$ of IR780.
Fig. 6. Curve fitting (9 Gaussian peaks) of the spectral bands of the upper states $S_n$ of IR780.

Fig. 7. Optimized structures of molecule IR780 as per functionals PBE (left), PBE0 (center) and CAM-B3LYP (right).

Tables 1–5 feature the results of the Gaussian-peak fitting procedures. Table 6 reports on the area under the curve (AUC) pertaining to the Gaussian fitting procedure. Table 7 shows the calculated oscillator strengths of the excited states $S_n$ of IR780 in methanol. Table 8 contains results furnished from the data and the energy gap law formalism. Tables 9–11 show the results of vertical transition calculations with different functionals and, finally, Table 12 reports the TPA cross-sections of IR780 estimated via quantum chemical calculations and three functionals.

Supporting files in [1] contain the raw data that substantiate Figs. 1-6.

Table 1
5-Gaussian peak fit of the spectral bands of states $S_n$ of IR780. $y_0$ is $95 \pm 24$ M$^{-1}$cm$^{-1}$. Reduced Chi-Sqr: 17627.6; R-Square: 0.9964; Adjusted R-Square: 0.9962.

| Peak | $x_c$ (cm$^{-1}$) | $w$ (cm$^{-1}$) | $A$ (M$^{-1}$cm$^{-1}$) |
|------|------------------|----------------|------------------------|
| 1    | 22500 ± 11       | 331 ± 15       | 1997 ± 79              |
| 2    | 23348 ± 32       | 1085 ± 22      | 3560 ± 58              |
| 3    | 26069 ± 10       | 374 ± 17       | 2675 ± 143             |
| 4    | 27173 ± 34       | 1150 ± 24      | 5109 ± 57              |
| 5    | 34615 ± 27       | 2580 ± 29      | 6928 ± 36              |
Table 2
6-Gaussian peak fit of the spectral bands of states $S_n$ of IR780. $y_0$ is $46 \pm 23$ M$^{-1}$cm$^{-1}$. Reduced Chi-Sqr: 10613.6; R-Square: 0.9979; Adjusted R-Square: 0.9977.

| Peak | $x_c$ (cm$^{-1}$) | $w$ (cm$^{-1}$) | $A$ (M$^{-1}$cm$^{-1}$) |
|------|------------------|----------------|------------------------|
| 1    | 21170 ± 67       | 461 ± 61       | 558 ± 40               |
| 2    | 22556 ± 19       | 483 ± 18       | 4325 ± 135             |
| 3    | 23821 ± 35       | 608 ± 36       | 3132 ± 80              |
| 4    | 26059 ± 10       | 343 ± 16       | 2159 ± 100             |
| 5    | 27035 ± 24       | 1269 ± 17      | 5269 ± 46              |
| 6    | 34596 ± 20       | 2549 ± 22      | 6996 ± 31              |

Table 3
7-Gaussian peak fit of the spectral bands of states $S_n$ of IR780. $y_0$ is $49 \pm 18$ M$^{-1}$cm$^{-1}$. Reduced Chi-Sqr: 8705.7; R-Square: 0.9983; Adjusted R-square: 0.9981.

| Peak | $x_c$ (cm$^{-1}$) | $w$ (cm$^{-1}$) | $A$ (M$^{-1}$cm$^{-1}$) |
|------|------------------|----------------|------------------------|
| 1    | 21155 ± 36       | 422 ± 0        | 567 ± 35               |
| 2    | 22545 ± 17       | 483 ± 12       | 4252 ± 129             |
| 3    | 23819 ± 29       | 633 ± 34       | 3166 ± 59              |
| 4    | 26048 ± 9        | 346 ± 15       | 2204 ± 103             |
| 5    | 27026 ± 24       | 1227 ± 19      | 5248 ± 45              |
| 6    | 34597 ± 106      | 2729 ± 80      | 6222 ± 34              |
| 7    | 34597 ± 260      | 1338 ± 98      | 850 ± 0                |

Table 4
8-Gaussian peak fit of the spectral bands of states $S_n$ of IR780. $y_0$ is $19 \pm 14$ M$^{-1}$cm$^{-1}$. Reduced Chi-Sqr: 3303.7; R-Square: 0.9994; Adjusted R-Square: 0.9993.

| Peak | $x_c$ (cm$^{-1}$) | $w$ (cm$^{-1}$) | $A$ (M$^{-1}$cm$^{-1}$) |
|------|------------------|----------------|------------------------|
| 1    | 21268 ± 48       | 564 ± 43       | 607 ± 22               |
| 2    | 22511 ± 8        | 437 ± 12       | 3572 ± 218             |
| 3    | 23732 ± 23       | 803 ± 56       | 3312 ± 82              |
| 4    | 26092 ± 9        | 452 ± 14       | 3960 ± 266             |
| 5    | 27309 ± 18       | 555 ± 25       | 2304 ± 194             |
| 6    | 27441 ± 126      | 1467 ± 82      | 2929 ± 186             |
| 7    | 34918 ± 44       | 27801 ± 74     | 6070 ± 35              |
| 8    | 33816 ± 76       | 1432 ± 86      | 1200 ± 0               |

Table 5
9-Gaussian peak fit of the spectral bands of states $S_n$ of IR780. $y_0$ is $19 \pm 0$ M$^{-1}$cm$^{-1}$. Reduced Chi-Sqr: 2690; R-Square: 0.9995; Adjusted R-Square: 0.9995.

| Peak | $x_c$ (cm$^{-1}$) | $w$ (cm$^{-1}$) | $A$ (M$^{-1}$cm$^{-1}$) |
|------|------------------|----------------|------------------------|
| 1    | 21282 ± 29       | 686 ± 0        | 609 ± 18               |
| 2    | 22544 ± 3        | 460 ± 3        | 3737 ± 34              |
| 3    | 23881 ± 0        | 816 ± 10       | 3390 ± 16              |
| 4    | 26091 ± 10       | 508 ± 7        | 5331 ± 100             |
| 5    | 27388 ± 19       | 655 ± 17       | 5071 ± 54              |
| 6    | 28765 ± 0        | 564 ± 44       | 1520 ± 121             |
| 7    | 29972 ± 111      | 686 ± 0        | 676 ± 65               |
| 8    | 32303 ± 0        | 285 ± 81       | 163 ± 36               |
| 9    | 34544 ± 10       | 2382 ± 18      | 7084 ± 13              |
Table 6
AUC from the fits of Section 2.2.

| Excited State | 5-peaks | 6-peaks | 7-peaks | 8-peaks | 9-peaks |
|---------------|---------|---------|---------|---------|---------|
| $S_2$         | -       | 9.43    | 9.70    | 9.66    | 11.73   |
| $S_3$         | 2.44    | 55.99   | 55.08   | 45.36   | 45.49   |
| $S_4$         | 10.89   | 53.50   | 56.74   | 63.72   | 71.25   |
| $S_5$         | 3.28    | 24.54   | 25.63   | 74.36   | 74.36   |
| $S_6$         | 16.24   | 175.18  | 169.59  | 114.16  | 74.79   |

Table 7
Oscillator strengths of the upper excited states $S_n$ of IR780 in methanol as a function of the number of Gaussian peaks used in the fitting.

| Excited state | 5-peaks | 6-peaks | 7-peaks | 8-peaks | 9-peaks |
|---------------|---------|---------|---------|---------|---------|
| $S_2$         | -       | 0.004   | 0.004   | 0.004   | 0.005   |
| $S_3$         | 0.011   | 0.024   | 0.024   | 0.020   | 0.020   |
| $S_4$         | 0.047   | 0.023   | 0.025   | 0.028   | 0.031   |
| $S_5$         | 0.014   | 0.011   | 0.011   | 0.032   | 0.032   |
| $S_6$         | 0.070   | 0.076   | 0.073   | 0.049   | 0.032   |

Table 8
$\gamma$, C and A calculated within the framework of the energy gap law. i.a.s., r.c.s. and c.o.b stand for indolyl-aromatic stretching, resonant-conjugated stretching and C-H aliphatic unsaturated trans out-of-plane bending, respectively.

| Vibrational Modes | $\hbar\omega$ (cm$^{-1}$) | $\gamma$ | C (cm$^{-1}$) | $A \times 10^{12}$ (s$^{-1}$) |
|-------------------|---------------------------|----------|--------------|------------------|
| i.a.s.            | 1562                      | 1.04     | 655          | 62.30            |
| i.a.s.            | 1556                      | 1.03     | 649          | 61.14            |
| r.c.s.            | 1512                      | 0.98     | 605          | 53.09            |
| r.c.s.            | 1507                      | 0.97     | 600          | 52.22            |
| r.c.s.            | 1482                      | 0.94     | 575          | 47.99            |
| i.a.s.            | 1449                      | 0.89     | 543          | 42.76            |
| i.a.s.            | 1427                      | 0.86     | 522          | 39.48            |
| r.c.s.            | 1412                      | 0.84     | 507          | 37.33            |
| i.a.s.            | 1395                      | 0.82     | 491          | 35.00            |
| r.c.s.            | 1380                      | 0.80     | 477          | 33.02            |
| r.c.s.            | 1363                      | 0.78     | 461          | 30.86            |
| r.c.s.            | 1290                      | 0.69     | 395          | 22.65            |
| c.o.b             | 1255                      | 0.64     | 365          | 19.29            |
| c.o.b             | 1227                      | 0.60     | 341          | 16.86            |
| c.o.b             | 1168                      | 0.53     | 293          | 12.44            |
| c.o.b             | 1148                      | 0.50     | 277          | 11.15            |
| c.o.b             | 1118                      | 0.46     | 254          | 9.39             |
| c.o.b             | 1097                      | 0.43     | 239          | 8.28             |
| c.o.b             | 1079                      | 0.41     | 226          | 7.41             |
| c.o.b             | 1050                      | 0.37     | 206          | 6.14             |
| c.o.b             | 1031                      | 0.35     | 193          | 5.40             |
| c.o.b             | 992                       | 0.30     | 168          | 4.09             |
| c.o.b             | 976                       | 0.27     | 158          | 3.63             |
| c.o.b             | 893                       | 0.17     | 112          | 1.82             |
| c.o.b             | 788                       | 0.03     | 65           | 0.62             |
| c.o.b             | 741                       | -0.03    | 49           | 0.35             |
| c.o.b             | 707                       | -0.08    | 39           | 0.22             |
### Table 9
Results of the vertical transition calculation of the IR780 with functional PBE.

| Transition | Energy [eV] | Lambda [nm] | O.S. |
|------------|------------|--------------|------|
| **PBE-Gas-phase** | | | |
| $S_1$ | 2.083 | 595 | 2.026 |
| $S_2$ | 2.502 | 496 | 0.001 |
| $S_3$ | 2.823 | 439 | 0.021 |
| $S_4$ | 2.827 | 439 | 0.003 |
| $S_5$ | 3.007 | 412 | 0.096 |
| $S_6$ | 3.313 | 374 | 0.060 |
| **PBE-Methanol** | | | |
| $S_1$ | 1.951 | 636 | 2.248 |
| $S_2$ | 2.541 | 488 | 0.001 |
| $S_3$ | 2.951 | 420 | 0.014 |
| $S_4$ | 2.962 | 419 | 0.008 |
| $S_5$ | 3.048 | 407 | 0.032 |
| $S_6$ | 3.305 | 375 | 0.096 |

### Table 10
Results of the vertical transition calculation of the IR780 with functional PBE0.

| Transition | Energy [eV] | Lambda [nm] | O.S. |
|------------|------------|--------------|------|
| **PBE0- Gas-phase** | | | |
| $S_1$ | 2.214 | 560 | 2.248 |
| $S_2$ | 3.091 | 401 | 0.003 |
| $S_3$ | 3.595 | 345 | 0.025 |
| $S_4$ | 3.638 | 341 | 0.008 |
| $S_5$ | 3.680 | 337 | 0.001 |
| $S_6$ | 3.893 | 319 | 0.112 |
| **PBE0-Methanol** | | | |
| $S_1$ | 2.058 | 603 | 2.411 |
| $S_2$ | 3.124 | 397 | 0.004 |
| $S_3$ | 3.685 | 337 | 0.009 |
| $S_4$ | 3.783 | 328 | 0.029 |
| $S_5$ | 3.803 | 326 | 0.010 |
| $S_6$ | 3.825 | 324 | 0.124 |

### Table 11
Results of the vertical transition calculation of the IR780 with functional CAM-B3LYP.

| Transition | Energy [eV] | Lambda [nm] | O.S. |
|------------|------------|--------------|------|
| **CAM-B3LYP- Gas-phase** | | | |
| $S_1$ | 2.226 | 557 | 2.292 |
| $S_2$ | 3.614 | 343 | 0.014 |
| $S_3$ | 4.265 | 291 | 0.001 |
| $S_4$ | 4.316 | 287 | 0.116 |
| $S_5$ | 4.496 | 276 | 0.010 |
| $S_6$ | 4.522 | 274 | 0.011 |
| **CAM-B3LYP-Methanol** | | | |
| $S_1$ | 2.051 | 605 | 2.422 |
| $S_2$ | 3.594 | 345 | 0.022 |
| $S_3$ | 4.248 | 292 | 0.143 |
| $S_4$ | 4.334 | 286 | 0.003 |
| $S_5$ | 4.628 | 268 | 0.021 |
| $S_6$ | 4.654 | 266 | 0.010 |
Table 12
Results of the TPA cross-sections of IR780 in the gas-phase and in methanol.

| Excited State | TPA cross-sections (GM) |
|---------------|-------------------------|
|               | PBE0 | Methanol | PBE | Methanol | CAM-B3LYP | Methanol |
| S₁            | 1    | 4        | 11  | 0.24     | 17       | 17       |
| S₂            | 2311 | 2267     | 4236| 996      | 14654    | 7268     |
| S₃            | 754  | 1658     | 198 | 99       | 28131    | 25405182 |
| S₄            | 1406 | 25790    | 56  | 71       | 178559488| 82380    |
| S₅            | 270  | 5648     | 1388| 385      | 754507725| 3167077 |
| S₆            | 490587| 253451   | 195344| 45648   | 6266    | 50341    |

Scheme 1. Molecular structure of the IR780.

2. Experimental Design, Materials and Methods

In the experiment, dyes IR780, rhodamine B and rhodamine 6G were irradiated with a beam produced in an optical parametric amplifier (OPA) within a wavelength range of 850–1000 nm and the two-photon induced fluorescence was recorded to measure the two-photon absorption cross-section of IR780. The molecular structure of the cyanine IR780 is shown in Scheme 1.

The dyes and the methanol (HPLC-grade) used for the solutions employed in the measurements were purchased from Sigma-Aldrich. The concentrations utilized for the experiments were 2.25 × 10⁻⁵ M for IR780, 7.65 × 10⁻⁶ M for rhodamine B and 8.06 × 10⁻⁵ M for rhodamine 6G. The solutions were used immediately after preparation and, while the experiment was carried out, the temperature of the laboratory was kept at 20 ± 0.6 °C and the relative humidity at 45 ± 5%.

The laser system consists of a Ti:Sapphire mode-locked laser (Vitara-T, Coherent) seeding a regenerative amplifier (Legend-Elite DUO, Coherent) which, in turn, pumps an optical parametric amplifier (TOPAS OPA, Light Conversion). The output of the Legend (4.5 mJ per pulse, 1 kHz repetition rate, 80 fs, and pulse centered at 800 nm) is fed to the TOPAS where, in this case, radiation from 850 to 1000 nm is obtained. The power of the output beam from the OPA is controlled via OD filters and the polarization of the light at the sample is always vertical.

The excitation beam was expanded by a telescope and then steered to a microscope objective (Rossbach Kyowa) with NA = 0.1, 4x which focuses the light into the sample container, a sealed quartz cuvette with a 10 mm-optical path. The focal point was placed approximately 1 mm from the side wall of the cuvette. The pulse energy was varied between 0.002 and 0.35 μJ, producing peak intensities of about 5.0 × 10¹⁰ to about 7.9 × 10¹² W cm⁻² and controlled so the peak power never exceeded 8 × 10¹² W cm⁻². The fluorescence from the dyes was collected at right angles with respect to the propagation vector of the excitation beam by an f = 50 mm, 1 in. diameter biconvex lens and focused to the entrance slit of an f = 300 mm Czerny-Turner monochromator coupled to a photomultiplier tube (PMT) (R12896, Hamamatsu Photonics). The output signal of the PMT was monitored with an oscilloscope (Tektronix 1102B-EDU). The peak power of the OPA was also independently monitored with a high-speed Si photodetector (DET110, 17.5 MHz...
bandwidth, 350–1100 nm, Thorlabs) also connected to the Tektronix oscilloscope and set to average over 64 samples.

Steady-state (linear) absorption and fluorescence spectra of the dyes were recorded for calibration purposes and were carried out in a Lambda-40 VU/vis and LS50B Luminescence spectrophotometers, both apparatus from Perkin-Elmer.

2.1. Quadratic dependence of the fluorescence for all the excitation wavelengths

In this section, a linear relationship between the Logarithm of the Integrated Fluorescence and the Logarithm of the peak intensity with slope 2 for each of the three compounds of interest (Rhodamine 6G, Rhodamine B and IR780) is shown. See Fig. 1. The raw data of the plots in Fig. 1 can be found in [1].

2.2. Deconvolution of the spectral bands of the states $S_n$

The spectral bands were fitted using Gaussian functions described by the following equation

$$y = y_0 + A \exp \left[ -0.5 \left( \frac{x - x_c}{w} \right)^2 \right], \quad (1)$$

where $y_0$ is the offset, $x_c$ is the centroid, $w$ is the width and $A$ is the amplitude of each peak. Tables 1–5 and Figs. 2–6 show the parameters of the fit for the upper states and the gaussian functions in the spectral range 18350 - 35980 cm$^{-1}$, respectively.

A 10-peak fit of the spectral bands of the states $S_n$ can be found in [2].

2.3. Experimental oscillator strength derived from the fitting of the upper excited states $S_n$

The following equation was used to calculate the oscillator strength (O.S.) $[3,4]$:

$$F_{exp} = \frac{4ln10\varepsilon_0 mc^2}{N_e e^2} \int \varepsilon(\nu) \text{d}\nu, \quad (2)$$

where $\varepsilon_0$ is the vacuum permittivity (in C$^2$/Nm$^2$), $m$ is the electron mass (in kg), $c$ is the speed of light (in m/s), $N_a$ is Avogadro’s number $(6.02214076 \times 10^{23}$ mol$^{-1}$), $e$ is the electron charge (in C) and the integral of $\varepsilon(\nu)$ is the area under the curve (AUC) of the peak-fitting by gaussian functions $[5,6]$. The AUC is to be multiplied by a factor of 10 $[3]$. Tables 6 and 7 show the calculated AUC and O.S.’s of the excited states $S_2$, $S_3$, $S_4$, $S_5$ and $S_6$ of IR780 in methanol, respectively.

2.4. Non-radiative decay properties of IR780 within the framework of the energy gap law

In this section, parameters $\gamma$ (Potential Energy Surfaces shift), the matrix element of the vibrational coupling between electronic states (C) and the preexponential factor (A) from the energy gap law $[2]$ are calculated (taking into account several vibrational modes ($\hbar\omega$ in Eq. (3)) of the cyanines).

From the slope (-6.0 $\times$ 10$^{-4}$) and $\Delta E = 6786$ cm$^{-1}$ in [2], $\gamma$ and $A$ can be calculated via Eqs. (3) and (4), respectively:

$$\gamma = -1 - 2.3\hbar\omega \left( \text{slope} + \frac{1}{4.6\Delta E} \right) \quad (3)$$

$$A = \frac{\sqrt{2\pi}C^2}{\hbar\sqrt{\hbar\omega\Delta E}} \quad (4)$$

Table 8 shows these results for $\gamma$, $C$ and $A$. 
2.5. Computational results on the TPA cross-section of IR780

Quantum-mechanical calculations were carried out to gain further insight into the TPA properties of IR780. The molecular geometry of IR780 was optimized using Gaussian 09 [7]. The optimized structures (Fig. 7) were then used as input for TPA calculations (for six singlet excited states) carried out with GAMESS-US (The General Atomic and Molecular Electronic Structure System) [8]. TPA calculations were made in both the gas-phase and in a solvent (methanol) at the PBE0/6-31Gd, PBE/6-31Gd and CAM-B3LYP/6-31Gd levels of theory (CAM-B3LYP is the Coulomb Attenuating Method-Becke, 3-parameter, Lee-Yang-Parr; and PBE is the Perdew–Burke–Ernzerhof exchange-correlation functional).

The findings are summarized in Tables 9–11. Two photon absorption cross-sections were calculated by using Eqs. (2) and (10) in [9].

CRediT Author Statement

Cesar A. Guarin: Conceptualization, original draft preparation, methodology, investigation, software, data curation, validation, formal analysis; Luis Guillermo Mendoza-Luna: Original draft preparation, software, data curation, validation, methodology, investigation, formal analysis; Emmanuel Haro-Poniatowski: Supervision, funding acquisition, writing, investigation, writing - review and editing; José Luis Hernández-Pozos: Resources, funding acquisition, writing, investigation, writing - review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

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