Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effective π-electron number and Symmetry Perturbation Effect on the Two-photon Absorption of Oligofluorenes

Luis M. G. Abegão[a,b*], Leandro H. Z. Cocca[a], Jean-Christophe Mulatier[d], Delphine Pitrat[d], Chantal Andraud[d], Lino Misoguti[a], Cleber R. Mendonça[a], Marcelo G. Vivas[c] and Leonardo De Boni[a,*]

[a] Photonics Group, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

[b] Grupo de Fotônica, Instituto de Física, Universidade Federal de Goiás, 74690-900, Goiânia, GO, Brazil

[c] Laboratório de Espectroscopia Ótica e Fotônica, Universidade Federal de Alfenas, 37715-400 Pocos de Caldas, MG, Brazil

[d] Laboratoire de Chimie, Univ Lyon, Ens de Lyon, CNRS UMR 5182, , F69342 Lyon, France

* Author to whom correspondence should be addressed: luis.abegao@ufg.br, deboni@ifsc.usp.br

SUPPORTING INFORMATION

1 – Experimental

1.1 – Dipole moments determination

Aiming to determine the electronic transition dipole moment (μ_{01}), the following equation was used:[1]

$$\mu_{01} = \sqrt{\frac{3\,x\,10^3 \ln(10)\, hc\, n}{8\pi^3} \frac{1}{N_A L^2 \omega_{01}} \int \varepsilon(\omega) d\omega} \quad (1),$$

in which L $= \frac{3n^2}{2n^2+1}$ is the Onsager local field factor, h is the Planck constant, n is the refractive index of the solvent which was used (toluene), N_A is the Avogadro number, ω_{01} is the transition frequencies (in rad/s), and ε is the molar absorptivity.

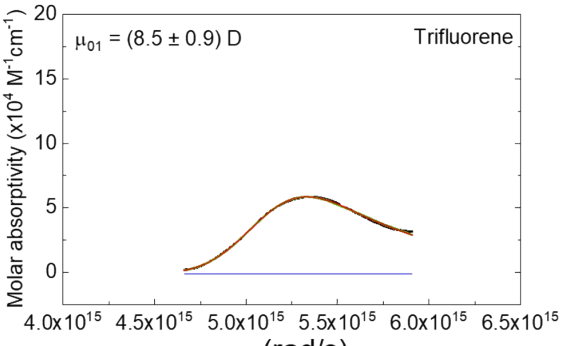
The difference between the first excited state permanent electric dipole moment and the ground state permanent electric dipole moment ($\Delta\mu_{01} = \mu_{11} - \mu_{00}$) of the studied oligofluorenes was achieved by solvatochromic measurements. The oligomers were dissolved in five different solvents (toluene, chloroform, tetrahydrofuran, dichloromethane, and acetonitrile) at low concentrations, as mentioned in the manuscript, to record the difference between the maxima absorption and emission spectra, i.e., the Stokes shift ($\Delta\nu$) for all investigated compounds. To estimate the value of $\Delta\mu_{01}$ the Lippert-Mataga equation [2] was used:

$$\left|\Delta\vec{\mu}_{01}\right|^2 = \frac{3}{4\pi} hc \frac{\partial\upsilon}{\partial F} vol \quad (2),$$

in which c is the light speed, h is the Planck constant, vol is the volume of the molecular cavity presents while surrounded by the solvent, and $\Delta F = 2\left(\frac{(\varepsilon-1)}{2\varepsilon+1} - \frac{(n-1)}{2n^2+1}\right)$ is the Onsager polarity function. It is important to highlight that the vol was determined by quantum chemical calculations (QCC).

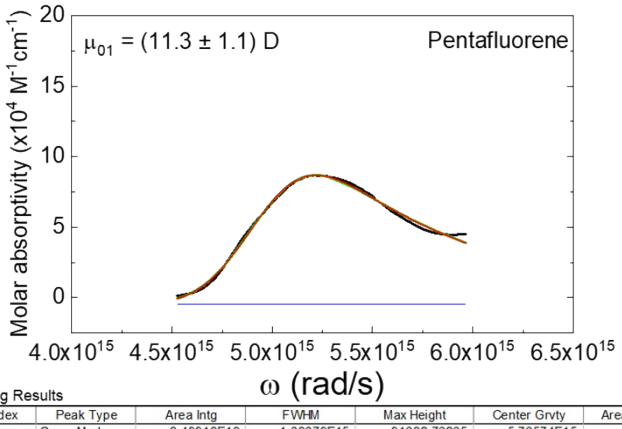
1.2 Absorption bands decomposition

Figure S1 presents the gaussian decompositions performed at the lower energy absorption band of every studied compound, aiming to evaluate the integral in Eq. 1 from the manuscript.



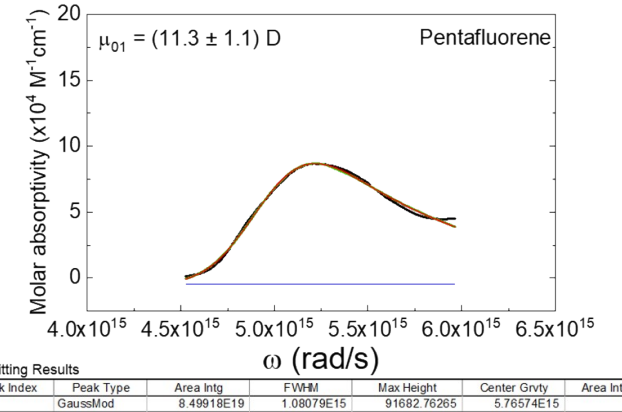
Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	GaussMod	4.7709E19	9.5912E14	59721.11467	5.71861E15	100



Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	GaussMod	8.49918E19	1.08079E15	91682.76265	5.76574E15	100



Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	GaussMod	8.49918E19	1.08079E15	91682.76265	5.76574E15	100

Figure S1: Gaussian decompositions (green lines), performed in the molar absorptivity spectra (black

lines) for each sample. The red lines show the fit between the decompositions and molar absorptivity spectra.

1.3 Solvatochromic measurements

The solvatochromic measurements were performed for five different solvents. The figure below (figure 2 – left column) presents the normalized absorbance and fluorescence spectra. The determination of $\Delta\nu/F$ is achieved through the linear fitting shown below (figure 2 – right column).

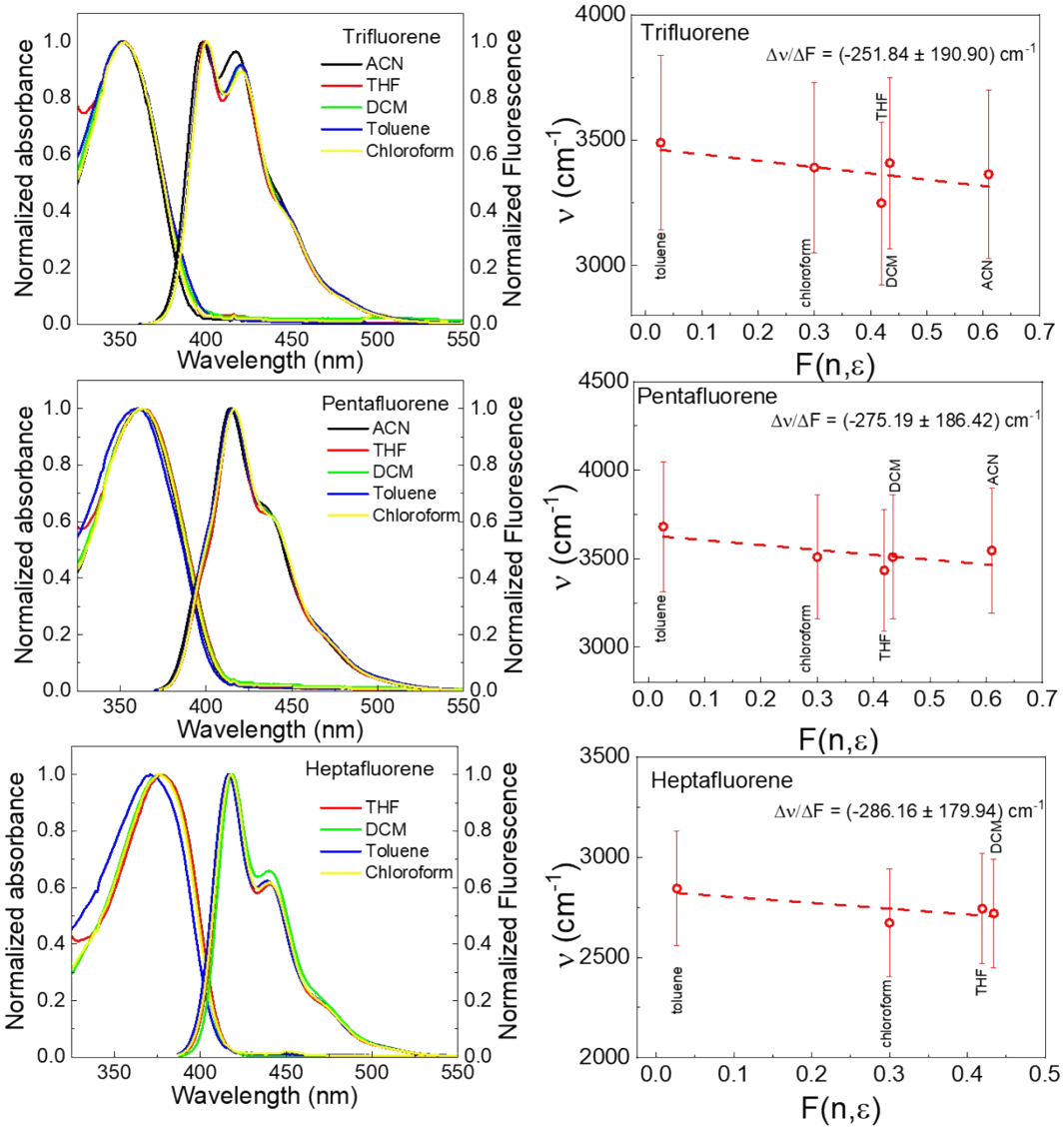


Figure S2: S Solvatochromic measurements (solid lines) and the linear fitting used to evaluate $\Delta\nu/F$ (dashed line).

1.4 Z-scan measurements

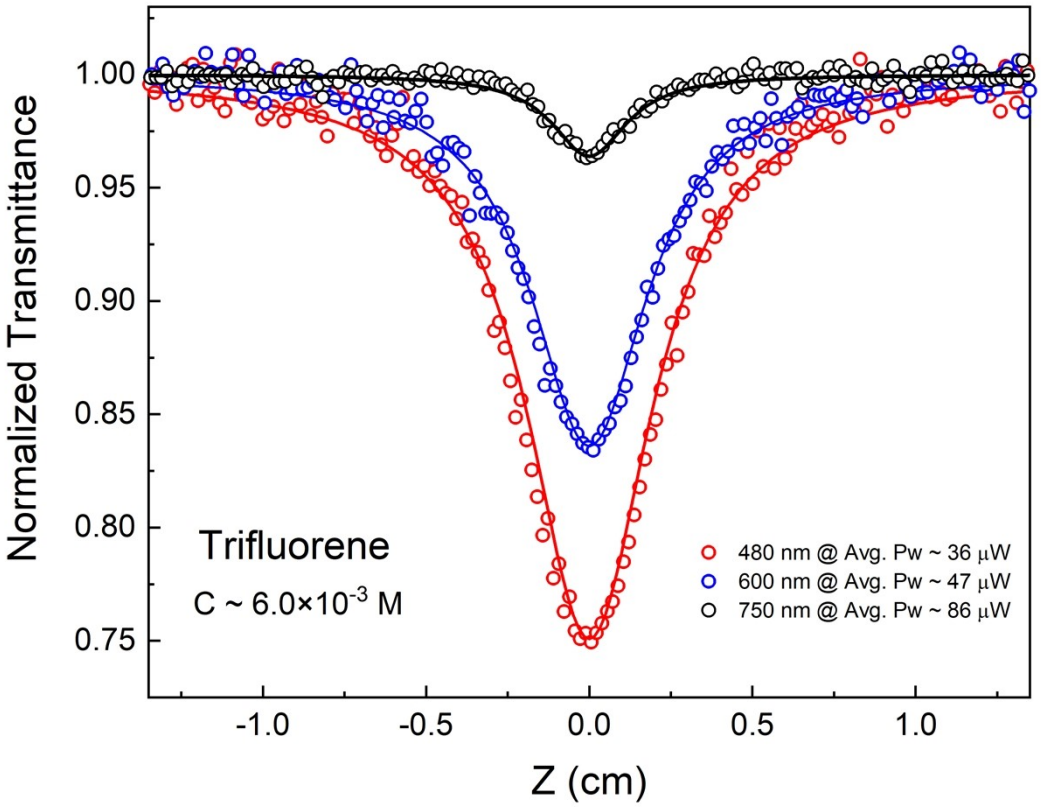
The open-aperture Z-Scan is a well-established technique that consists of translating a sample around the focal region of a focused laser beam along the *z*-axis

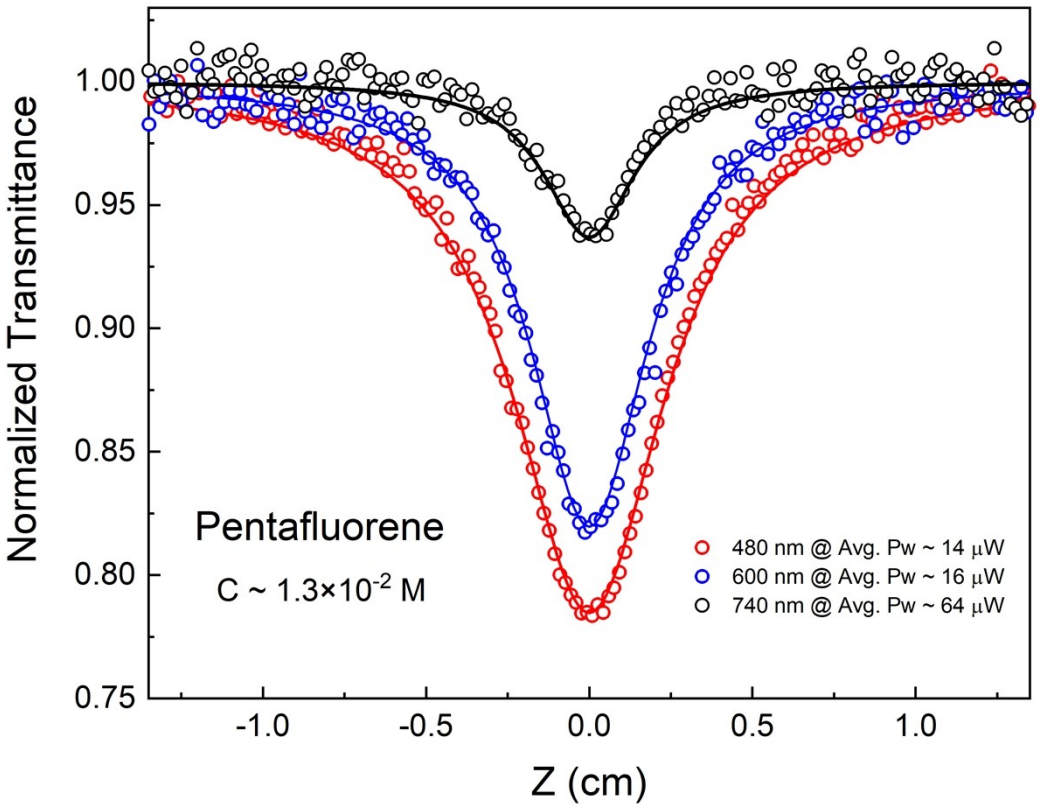
and then acquire the total beam transmission as a function of *z*-position at the far-field. This transmission can be normalized by the signal without nonlinear effect, the Normalized Transmittance (NT). Here, to measure the 2PA and determine the $\sigma_{2PA}(\lambda)$ it is possible to fit the experimental NT with a theoretical NT given by:

$$T(z) = \frac{1}{\sqrt{q}q_0(z,0)} \int_{-\infty}^{\infty} ln\left[1 + q_0(z,0)e^{-\tau^2}\right] d\tau \quad (3),$$

$$q_0 = \beta I_0 L \left(1 + \left(\frac{z^2}{z_0^2}\right)\right)^{-1} \quad (4),$$

in which I_0 is the laser peak irradiance at the focal point, z is the sample position, L is the cuvette path length (2 mm), and β is the nonlinear absorption coefficient. Finally, the $\sigma_{2PA}(\lambda)$ can be determined from $\sigma_{2PA}(\lambda) = \frac{\hbar\omega\beta(\lambda)}{N}$, given in GM (1 GM = 10^{-50} cm^4 s $photon^{-1}$).[1]


Normalized Transmittance
1.00
0.95
0.90
0.85
0.80
0.75
Trifluorene
C ~ 6.0×10-3 M
480 nm @ Avg. Pw ~ 36 μW
600 nm @ Avg. Pw ~ 47 μW
750 nm @ Avg. Pw ~ 86 μW
-1.0
-0.5
0.0
0.5
1.0
Z (cm)


Normalized Transmittance
1.00
0.95
0.90
0.85
0.80
0.75
Pentafluorene
C ~ 1.3×10-2 M
480 nm @ Avg. Pw ~ 14 μW
600 nm @ Avg. Pw ~ 16 μW
740 nm @ Avg. Pw ~ 64 μW
-1.0
-0.5
0.0
0.5
1.0
Z (cm)

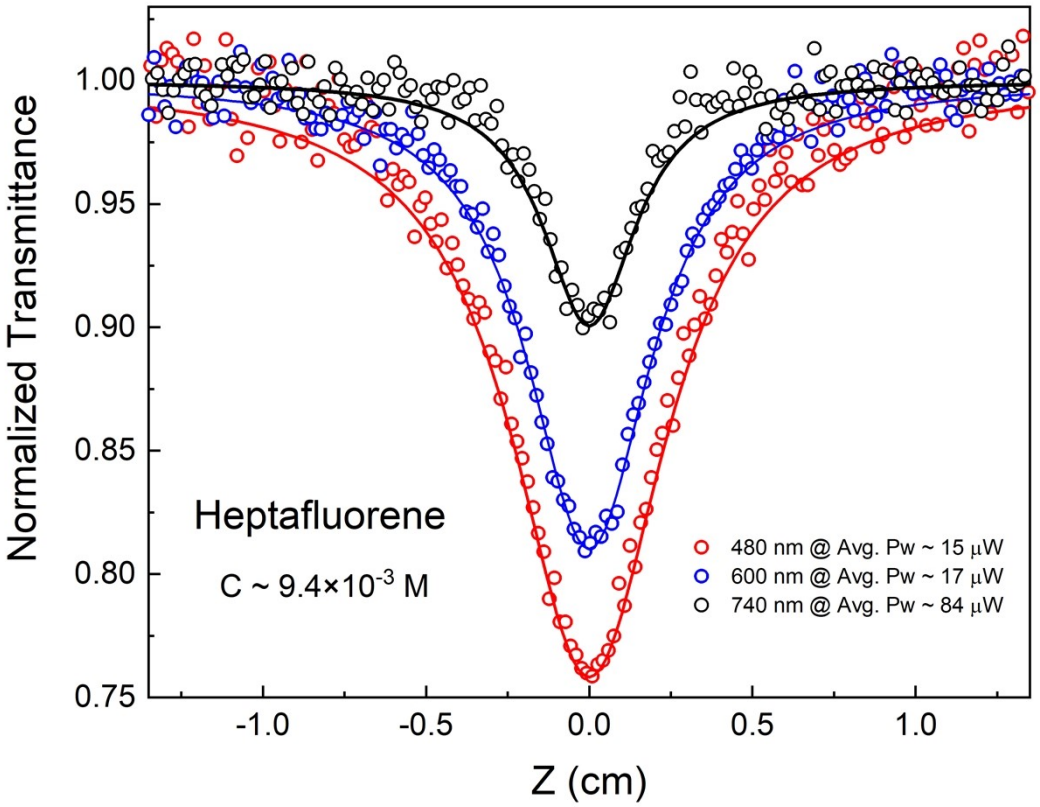


Figure S3: Z-scan curves from the investigated samples at three distinguish spectral regions: enhanced resonance region (red color), highest-energy 2PA peak (blue color), and lowest-energy 2PA peak (black color). The experimental data are plotted with symbols, while its corresponding theoretical fitting is plotted with lines, using Eq. 3 from the manuscript.

2 Quantum Chemical Calculations Section

a) **Optimized geometries used to calculate the cubic radius of each compound**

Trifluorene in toluene				Pentafluorene in toluene			
CAM-B3LYP/6-311++G(2d,p)				CAM-B3LYP/6-311++G(2d,p)			
H	-0.10841	-1.26604	1.45724	H	16.07187	-0.88194	3.17339
C	-0.11512	-0.99875	0.39714	C	16.36263	-0.89329	2.11949
H	-0.19148	-1.93298	-0.16550	H	16.53186	-1.93880	1.84825
C	-1.23878	-0.04866	0.06573	C	15.31917	-0.24718	1.24310
C	-0.72343	1.14795	-0.43957	C	15.86755	0.84731	0.57002
C	0.73752	1.04863	-0.47436	C	17.27675	0.97458	0.95374
C	1.10980	-0.20799	0.01059	C	17.58109	-0.04221	1.86413
C	2.43903	-0.56565	0.09013	C	18.85375	-0.15237	2.38930
C	3.42823	0.33262	-0.31594	C	19.82489	0.76123	1.99945
C	4.86134	-0.03460	-0.23617	C	19.52227	1.77171	1.09466
C	5.81482	0.90133	0.16976	C	18.24611	1.88633	0.56489
C	7.14462	0.54316	0.24020	C	15.08107	1.59885	-0.28814
C	8.33418	1.37110	0.65711	C	13.75326	1.24839	-0.46334
H	8.46506	2.24740	0.01657	C	13.19106	0.15657	0.20296
H	8.23434	1.73907	1.68181	C	11.76731	-0.19903	-0.00064
C	9.47812	0.39827	0.51892	C	10.79176	0.79551	-0.09743
C	9.00566	-0.84215	0.07912	C	9.47091	0.44792	-0.28625
C	9.88011	-1.89928	-0.12068	C	9.09393	-0.89422	-0.38333
C	11.23102	-1.70438	0.12315	C	10.05123	-1.89178	-0.29001
C	11.70071	-0.47158	0.56006	C	11.37567	-1.53650	-0.09956
C	10.82473	0.58778	0.76039	C	7.64345	-0.95834	-0.57689
C	7.55246	-0.75112	-0.09176	C	7.13929	0.34483	-0.59759
C	6.61779	-1.69009	-0.49743	C	5.79012	0.57427	-0.76550
C	5.28418	-1.32487	-0.56574	C	4.91328	-0.50222	-0.91585
C	3.04100	1.58511	-0.79906	C	3.46087	-0.27357	-1.09744
C	1.70809	1.94986	-0.88177	C	2.52550	-1.09959	-0.47054
C	-1.58132	2.17398	-0.80237	C	1.17733	-0.87218	-0.64911
C	-2.94591	1.99294	-0.65526	C	0.73239	0.17952	-1.45467
C	-3.47551	0.80206	-0.15194	C	1.64914	1.00647	-2.08399
C	-4.93966	0.62995	-0.00505	C	3.00133	0.77364	-1.90006
C	-5.54834	-0.58589	-0.32271	C	-0.73237	0.17952	-1.45465
C	-6.91234	-0.73091	-0.18046	C	-1.17730	-0.87219	-0.64909
C	-7.69695	0.32869	0.28133	C	-2.52546	-1.09961	-0.47050
C	-7.10651	1.54056	0.60180	C	-3.46085	-0.27358	-1.09736
C	-5.73700	1.68068	0.45565	C	-4.91326	-0.50223	-0.91575
C	-9.09522	-0.10970	0.32712	C	-5.79012	0.57425	-0.76543
C	-9.15781	-1.43585	-0.11189	C	-7.13928	0.34481	-0.59752
C	-10.36895	-2.09732	-0.16803	C	-7.64344	-0.95836	-0.57678
C	-11.52199	-1.42563	0.21807	C	-6.78529	-2.03623	-0.72518
C	-11.45968	-0.10769	0.65444	C	-5.43156	-1.79947	-0.89246
C	-10.24617	0.56051	0.71225	C	-9.09392	-0.89423	-0.38324
C	-7.77896	-1.93074	-0.46969	C	-9.47091	0.44791	-0.28618
H	-7.71515	-2.23506	-1.51787	C	-10.79176	0.79549	-0.09739
H	-7.48876	-2.79721	0.13063	C	-11.76732	-0.19905	-0.00062
C	-2.59902	-0.22362	0.20840	C	-13.19107	0.15656	0.20295
H	2.72224	-1.53308	0.48783	C	-13.99614	-0.59228	1.06368
H	5.50191	1.90038	0.44952	C	-15.31922	-0.24724	1.24299

H	9.52002	-2.86250	-0.46144
H	11.92759	-2.51959	-0.02805
H	12.75894	-0.33651	0.74572
H	11.19774	1.54657	1.10139
H	6.91771	-2.69570	-0.76663
H	4.55379	-2.04915	-0.90354
H	3.80109	2.27803	-1.13707
H	1.43704	2.92486	-1.26842
H	-1.19940	3.10507	-1.20341
H	-3.62063	2.78391	-0.95734
H	-4.94775	-1.40437	-0.70189
H	-7.69876	2.36994	0.96913
H	-5.26888	2.61901	0.72492
H	-10.42467	-3.12511	-0.50752
H	-12.47804	-1.93255	0.17893
H	-12.36812	0.40116	0.95185
H	-10.20427	1.58792	1.05327
H	-2.99167	-1.14561	0.62097

C	-15.86755	0.84734	0.57002
C	-15.08102	1.59895	-0.28804
C	-13.75322	1.24846	-0.46325
C	-17.27676	0.97462	0.95372
C	-17.58115	-0.04226	1.86400
C	-18.85382	-0.15243	2.38913
C	-19.82492	0.76124	1.99936
C	-19.52225	1.77181	1.09469
C	-18.24607	1.88645	0.56496
C	-16.36272	-0.89340	2.11929
H	-16.53198	-1.93889	1.84793
H	-16.07198	-0.88218	3.17320
C	-11.37567	-1.53651	-0.09953
C	-10.05123	-1.89180	-0.28994
C	-8.25888	1.33749	-0.40735
H	-8.11242	1.94889	0.48709
H	-8.34132	2.02591	-1.25260
C	-3.00133	0.77365	-1.89996
C	-1.64914	1.00648	-2.08393
C	0.00002	-1.61672	-0.07055
H	0.00002	-2.67000	-0.36344
H	0.00003	-1.59103	1.02244
C	5.43158	-1.79946	-0.89261
C	6.78531	-2.03621	-0.72532
C	8.25888	1.33751	-0.40740
H	8.11242	1.94889	0.48704
H	8.34132	2.02594	-1.25264
C	13.99609	-0.59221	1.06378
H	19.09656	-0.93793	3.09544
H	20.82667	0.68614	2.40361
H	20.29119	2.47554	0.80134
H	18.01639	2.67607	-0.14020
H	15.49238	2.44547	-0.82451
H	13.14104	1.81970	-1.14961
H	11.07510	1.83706	-0.00142
H	9.77785	-2.93686	-0.37195
H	12.12957	-2.31187	-0.04821
H	5.40230	1.58612	-0.75941
H	2.86430	-1.90320	0.17266
H	1.32229	1.82091	-2.71915
H	3.72067	1.40383	-2.40759
H	-2.86424	-1.90322	0.17271
H	-5.40231	1.58611	-0.75935
H	-7.16017	-3.05260	-0.72012
H	-4.76082	-2.63796	-1.03114
H	-11.07509	1.83704	-0.00139
H	-13.57080	-1.42925	1.60486
H	-15.49229	2.44564	-0.82432
H	-13.14097	1.81983	-1.14944
H	-19.09667	-0.93806	3.09518
H	-20.82671	0.68615	2.40349
H	-20.29113	2.47570	0.80143
H	-18.01631	2.67626	-0.14004
H	-12.12957	-2.31189	-0.04820
H	-9.77784	-2.93688	-0.37187

H	-3.72068	1.40385	-2.40746
H	-1.32232	1.82094	-2.71908
H	4.76084	-2.63795	-1.03130
H	7.16020	-3.05258	-0.72029
H	13.57070	-1.42911	1.60503

Table S1: Optimized geometries obtained using the CAM-B3LYP/6-311++(2d,p) level of theory in toluene medium for compounds tri and pentafluorene.

Heptafluorene in toluene			
CAM-B3LYP/6-311++G(2d,p)			
H	-25.03275	0.57177	-1.70704
C	-24.91244	0.83675	-0.65317
H	-25.04538	-0.08317	-0.07745
C	-23.57425	1.47805	-0.38430
C	-23.75253	2.76159	0.13764
C	-25.19019	3.03266	0.23257
C	-25.88369	1.90962	-0.22916
C	-27.26469	1.89954	-0.24762
C	-27.95263	3.02064	0.19917
C	-27.26332	4.13660	0.65827
C	-25.87701	4.15136	0.67864
C	-22.65142	3.53512	0.46781
C	-21.38278	3.01600	0.27375
C	-21.18905	1.73405	-0.24694
C	-19.82151	1.19976	-0.44518
C	-18.82097	1.43560	0.50003
C	-17.55375	0.92969	0.30169
C	-17.25576	0.18130	-0.84023
C	-18.23815	-0.05923	-1.78748
C	-19.50900	0.44996	-1.58188
C	-15.84926	-0.22301	-0.77889
C	-15.29507	0.27252	0.40443
C	-13.97259	0.03600	0.71458
C	-13.17332	-0.70421	-0.15918
C	-11.75078	-0.96881	0.15880
C	-10.77548	-0.91468	-0.83925
C	-9.45599	-1.16413	-0.52628
C	-9.08054	-1.47392	0.78367
C	-10.03754	-1.53157	1.78419
C	-11.36043	-1.27858	1.46405
C	-7.63158	-1.68517	0.81597
C	-7.12630	-1.50255	-0.47407
C	-5.77790	-1.64013	-0.72717
C	-4.90302	-1.96513	0.31172
C	-3.45131	-2.11705	0.05828
C	-2.51430	-1.64247	0.97867
C	-1.16674	-1.79319	0.72922
C	-0.72346	-2.41860	-0.43926
C	-1.64176	-2.89395	-1.36187
C	-2.99351	-2.73937	-1.10588
C	0.74131	-2.43406	-0.43292
C	1.18750	-1.81797	0.73942
C	2.53576	-1.69557	1.00047
C	3.47035	-2.18928	0.08778

C	4.92269	-2.06678	0.35325
C	5.81149	-1.75220	-0.67696
C	7.16015	-1.64083	-0.41250
C	7.65175	-1.84070	0.88027
C	6.78178	-2.15451	1.91218
C	5.42878	-2.26416	1.64051
C	9.10447	-1.65525	0.86074
C	9.49574	-1.34278	-0.44392
C	10.82169	-1.11302	-0.74443
C	11.78791	-1.19069	0.26091
C	13.21704	-0.94615	-0.04332
C	14.02186	-0.23037	0.84563
C	15.35039	-0.01207	0.54841
C	15.90530	-0.50120	-0.63724
C	15.11885	-1.21344	-1.52857
C	13.78538	-1.42872	-1.22491
C	17.31854	-0.11882	-0.68318
C	17.62210	0.60236	0.47468
C	18.89495	1.08779	0.68746
C	19.89514	0.86079	-0.26029
C	21.26808	1.37533	-0.04755
C	21.99883	1.91526	-1.10787
C	23.27518	2.39094	-0.89244
C	23.84983	2.33813	0.37981
C	23.13718	1.80389	1.44116
C	21.85590	1.32897	1.21910
C	25.19713	2.91165	0.30903
C	25.43735	3.31607	-1.00780
C	26.64316	3.89481	-1.35230
C	27.61166	4.06848	-0.37168
C	27.37270	3.66658	0.93701
C	26.16374	3.08530	1.28760
C	24.23630	3.01924	-1.87014
H	24.48231	2.34147	-2.69199
H	23.82386	3.92655	-2.31965
C	19.57697	0.13860	-1.41320
C	18.30111	-0.35229	-1.63204
C	16.39493	0.73234	1.34194
H	16.11722	1.77804	1.49907
H	16.54619	0.29186	2.33102
C	11.38182	-1.50411	1.56051
C	10.05232	-1.73685	1.86826
C	8.29142	-1.30288	-1.35127
H	8.37256	-2.02467	-2.16837
H	8.15968	-0.31871	-1.80878
C	3.00976	-2.80212	-1.08026
C	1.65729	-2.92889	-1.34757
C	0.01151	-1.35672	1.56351
H	0.02224	-0.27428	1.71681
H	0.00236	-1.81779	2.55471
C	-5.42283	-2.14546	1.59605
C	-6.77557	-2.00876	1.85650
C	-8.24394	-1.15086	-1.42405
H	-8.33100	-1.87612	-2.23744
H	-8.09151	-0.17193	-1.88636

C	-13.74072	-1.19254	-1.33882
C	-15.06834	-0.95980	-1.65498
C	-16.33307	1.04430	1.18026
H	-16.03661	2.08565	1.33175
H	-16.50337	0.61521	2.17126
C	-22.30807	0.96661	-0.57637
H	-27.80856	1.03254	-0.60432
H	-29.03542	3.02592	0.19003
H	-27.81516	5.00221	1.00299
H	-25.34538	5.02443	1.03749
H	-22.77149	4.53565	0.86539
H	-20.51951	3.62519	0.51006
H	-19.05186	1.99714	1.39765
H	-18.02238	-0.63016	-2.68252
H	-20.27382	0.28213	-2.32961
H	-13.54287	0.44022	1.62357
H	-11.05787	-0.65457	-1.85264
H	-9.76511	-1.77820	2.80329
H	-12.11435	-1.34421	2.23833
H	-5.38903	-1.47546	-1.72510
H	-2.85105	-1.13744	1.87630
H	-1.31661	-3.38849	-2.26920
H	-3.71386	-3.12983	-1.81359
H	2.87554	-1.19787	1.90108
H	5.43341	-1.57464	-1.67685
H	7.14678	-2.32123	2.91844
H	4.74863	-2.53096	2.43951
H	11.11637	-0.84989	-1.75350
H	13.59213	0.16968	1.75644
H	15.53464	-1.60727	-2.44814
H	13.17323	-2.00395	-1.90797
H	19.11898	1.66453	1.57711
H	21.55023	1.97841	-2.09229
H	23.57098	1.74730	2.43223
H	21.30383	0.89096	2.04102
H	26.83614	4.21074	-2.37094
H	28.56140	4.52087	-0.62835
H	28.13863	3.80929	1.68909
H	25.98330	2.77404	2.30946
H	20.35288	-0.06077	-2.14151
H	18.08562	-0.91688	-2.53117
H	12.12815	-1.58859	2.34026
H	9.76759	-1.98643	2.88327
H	3.72801	-3.20730	-1.78183
H	1.32960	-3.41732	-2.25731
H	-4.75423	-2.42054	2.40193
H	-7.15138	-2.16281	2.86080
H	-13.13287	-1.78607	-2.00997
H	-15.48394	-1.35862	-2.57248
H	-22.17613	-0.03766	-0.96146

Table S2: Optimized geometries obtained using the CAM-B3LYP/6-311++(2d,p) level of theory in toluene medium for heptafluorene.

1. M. G. Vivas, L. De Boni and C. R. Mendonca, in *Molecular and Laser Spectroscopy*, ed. V. P. Gupta, Elsevier2018, vol. 1.
2. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer2006.