Two-photon transitions in quadrupolar and branched chromophores: experiment and theory

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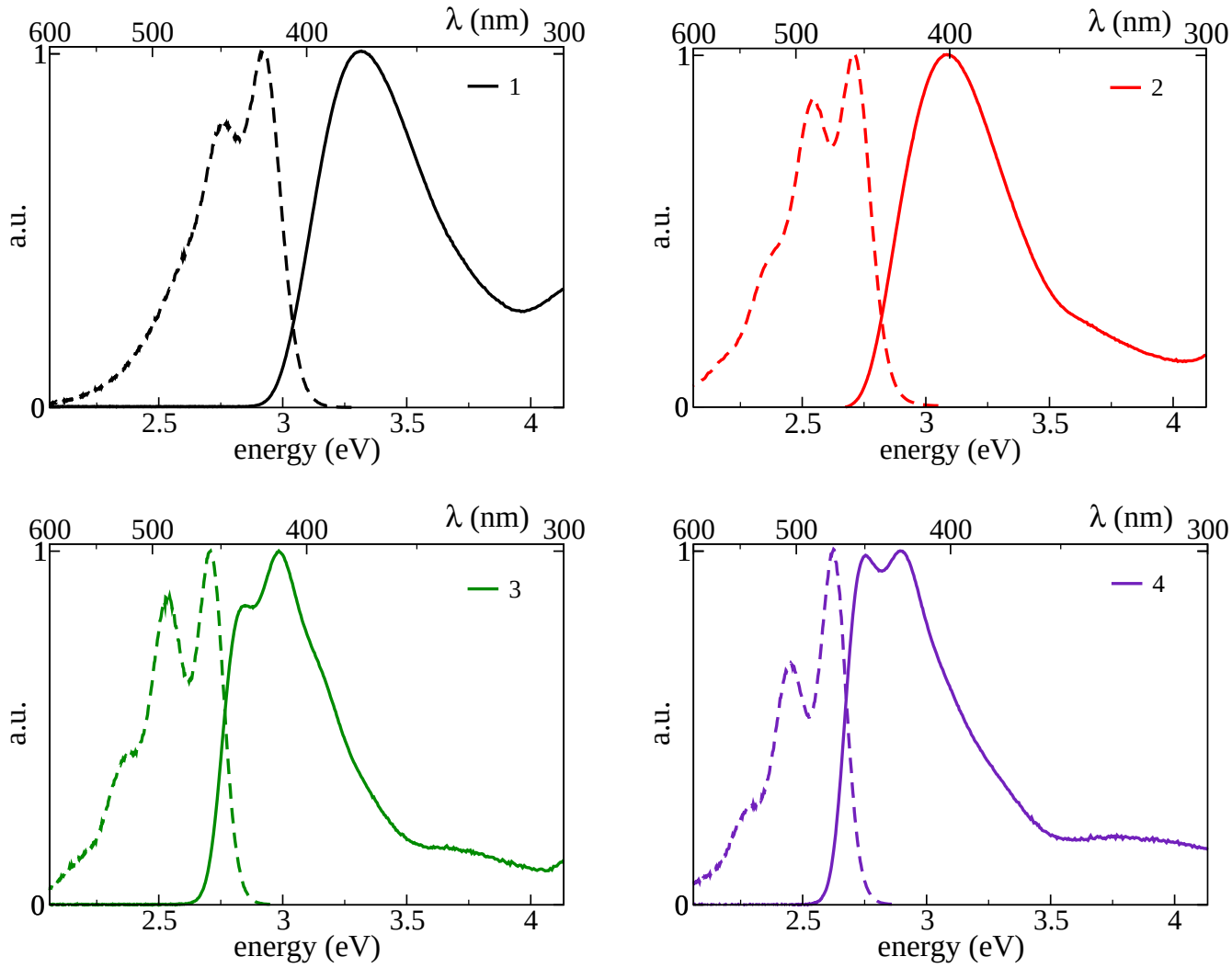


Figure S1. Normalized absorption (lines) and fluorescence (dotted lines) experimental spectra of chromophores **1**-**4** in toluene.

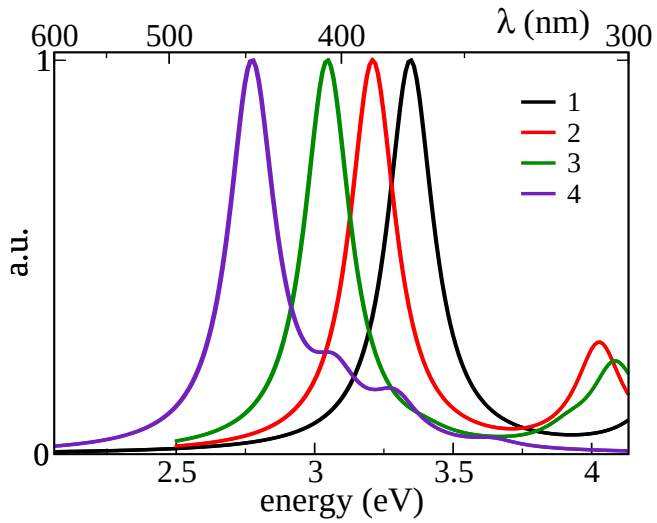


Figure S2. Normalized calculated absorption spectra of chromophores **1**-**4** using an empirical line width of 0.1eV.

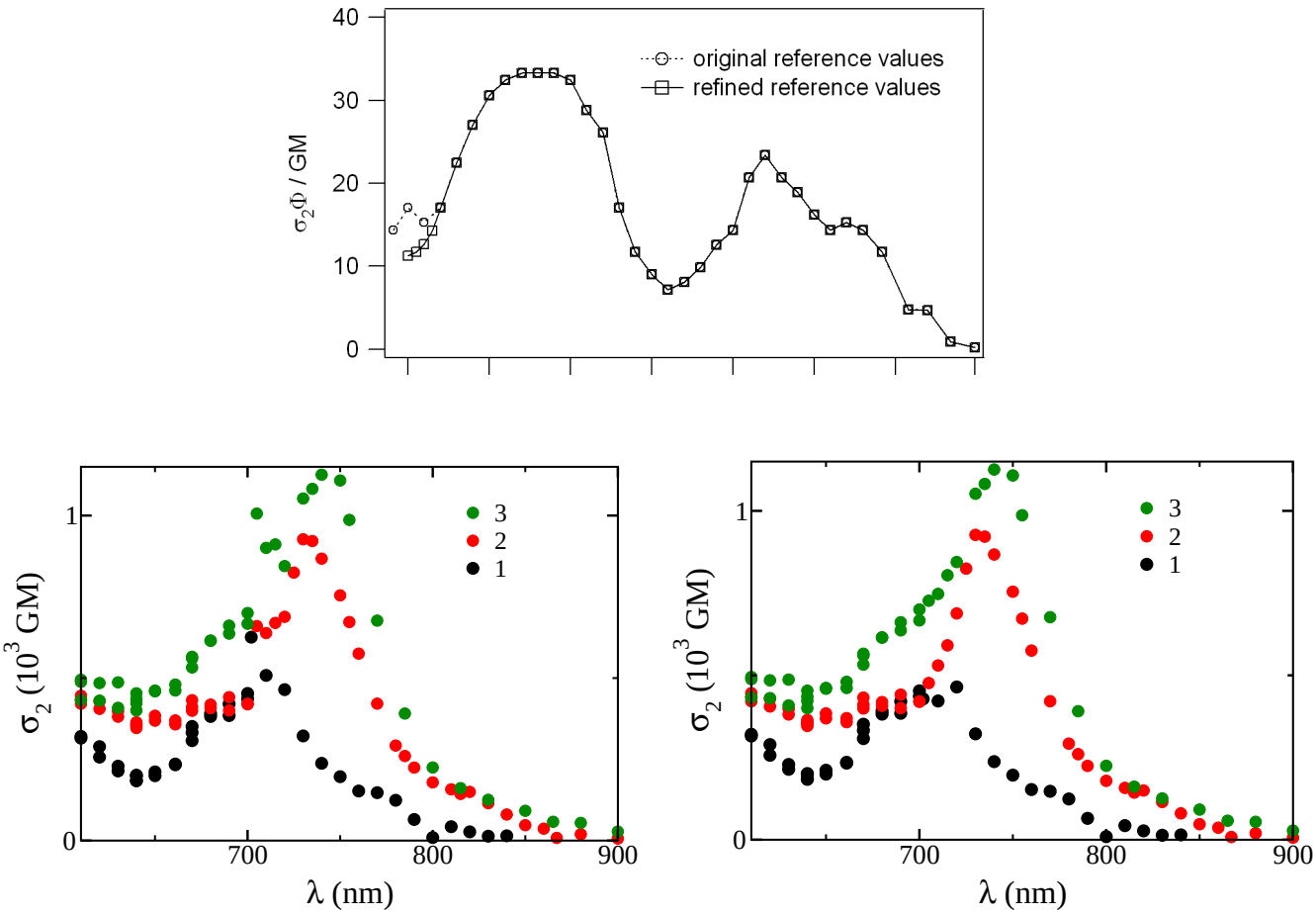


Figure S3. Top panel: original and refined reference values for the action cross sections of two-photon excited fluorescence (fluorescein, 0.01M aqueous NaOH). The original values were taken from Ref 1; the refined values were used for the determination of TPEF cross sections in this work. Middle and bottom panels: Experimental two-photon absorption cross-section of quadrupolar compounds **1-3** in toluene, calibrated relative to Bis-MSB (560-700nm) or fluorescein (700-920nm): Middle panel contains data obtained using original TEFP action cross section from Xu & Webb[1], Bottom panel contains data obtained using the refined values.

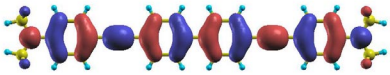
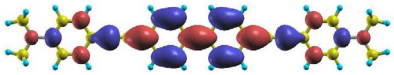
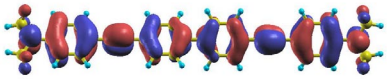
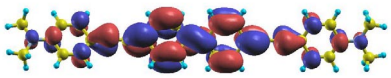
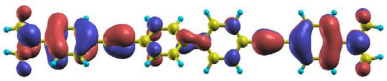
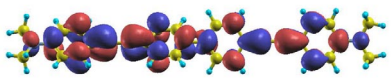
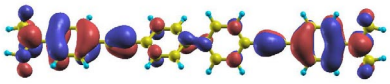
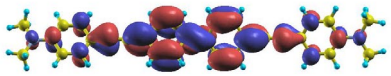
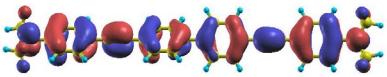
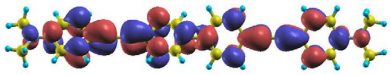
Em.	***Hole***	***Electron***
|1> **w=1.0** **2.74 eV**		
OPA	***Hole***	***electron***
|1> **w=.99** **3.34 eV**		
|4> **w=.89** **4.32 eV**		
TPA	***Hole***	***Electron***
|2> **w=.98** **3.63 eV**		
|3> **w=.97** **4.19 eV**		

Figure S4. Natural transition orbitals[2] of chromophore **1**: emission (top panel) absorption (all others). Right panels quote in sequence excited state number, associated eigenvalues and transition energies.

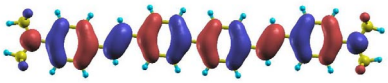
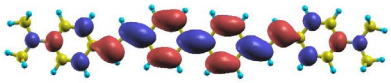
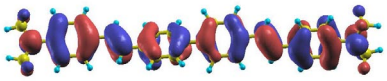
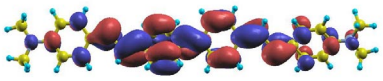
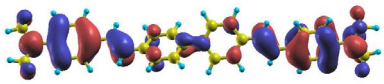
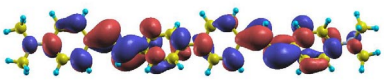
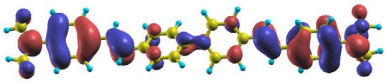
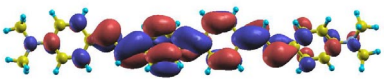
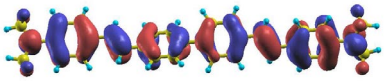
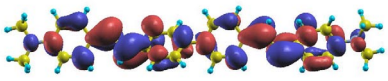
Em.	***Hole***	***electron***
|1> **w=1.0** **2.55 eV**		
OPA	***Hole***	***electron***
|1> **w=.99** **3.22 eV**		
|4> **w=.95** **4.03 eV**		
TPA	***Hole***	***electron***
|2> **w=.95** **3.50 eV**		
|3> **w=.95** **3.9 eV**		

Figure S5. Natural transition orbitals[2] of chromophore **2**: emission (top panel) absorption (all others). Right panels quote in sequence excited state number, associated eigenvalues and transition energies.

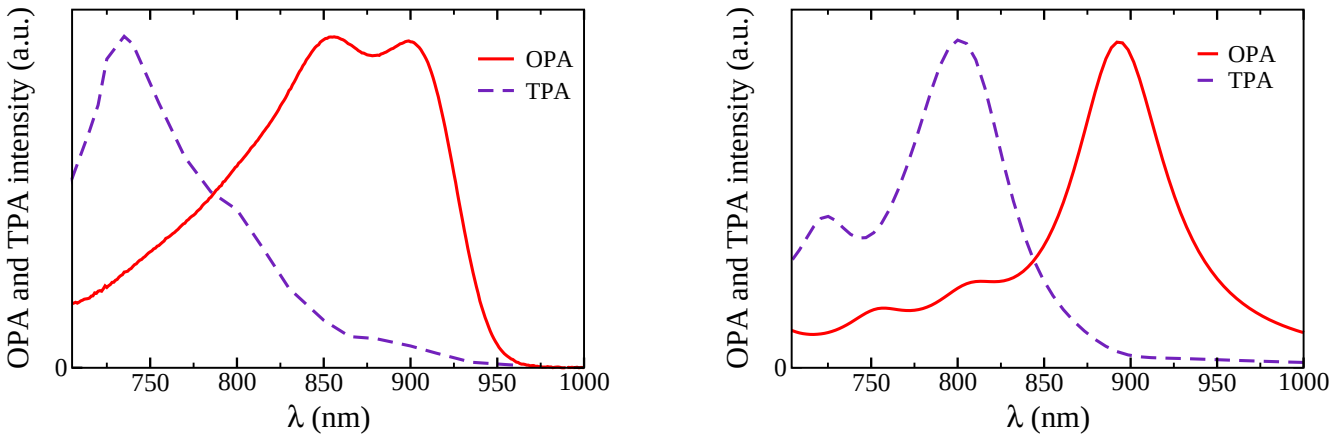


Figure S6. Experimental (left) and calculated (right) rescaled one photon absorption (OPA; continuous lines) and .two-photon (TPA; dashed lines) of chromophore 4.

References

(1) C. Xu, W. W. Webb, J. Opt. Soc. Am. B **1996**, 13, 481-491

(2) R. L. Martin, J. Chem. Phys. **2003**, 118, 4775-4777