

DOCTORAL THESIS

Ultra-fast spectroscopy investigation on organic molecules two photon absorption

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Ultra-Fast Spectroscopy Investigation on Organic Molecules Two-Photon Absorption

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A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor : **Prof. CHEAH Kok Wai**

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Abstract

In this thesis, ultra-fast spectroscopy was utilized to investigate the structure-property of organic materials with high two-photon absorption (TPA) cross-section for potential applications. In summary, four significant areas have been worked on including detailed background reviews of TPA, theoretical expression and modification of two TPA cross-section measuring techniques, two experimental setups for the sensitive determination of TPA cross-section and TPA properties of two newly synthesized compound series with high TPA cross-section.

The structure-property of 1D D- π -D quadrupolar oligophenylenevinylenes (OPVs) **OPV(n)** showed they had high TPA cross-sections ($>1000\text{GM}$) and also high fluorescence quantum yield ($>80\%$). For example, **OPV(6)** in CHCl_3 had 1203GM at excitation of 750nm with 84% quantum efficiency. The relationship of TPA cross-sections and conjugation length was not linear and was closer to quadratic. However, enlarging conjugation length caused red-shifts both in the absorption and emission spectra. In addition, polarization analysis of **OPV(n)** showed that amplified spontaneous emission (ASE) appeared in the vertical emission. The amplification of vertical emission to horizontal emission was about 3.66 for vertical excitation and 1.19 for horizontal excitation at peak power of $0.475\text{GW}/\text{cm}^2$. However, the amplified signal was not too strong to form a lasing effect. The vertical ASE excitation was more efficient because **OPV(n)** was probably sensitive on gravitational force. Therefore, **OPV(n)** complexes can be applied as horizontal indicators.

The structure-property of multi-dipolar zig-zag oligoaryleneethynyls (OAEs) **DA(n)** and **D-Ar-A(n)** can easily be modified or enhanced by incorporating or extending with various central aryleneethynyl moieties within the dipolar units. The experimental results showed that OAEs exhibited a linear increase in TPA cross-section with increased number of covalently linked dipolar units without red-shifting the absorption and emission spectra. Hence, TPA cross-section can easily be enhanced at a specific wavelength by means of increasing the number of dipolar unit within a zig-zag molecule. Furthermore, the largest TPA cross-sections was obtained for **D-TF-A(4)** in DCM solvent to be 1522.3GM at 750nm which showed potential for practical applications.

Table of Contents

Declaration	i
Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Figures	viii
List of Tables	xiii
List of Abbreviations	xv
List of Symbols	xviii
1. Introduction	1
1.1. General introduction to TPA of organic materials	1
1.2. Motivation of my research	3
1.3. Scope, aim and contents of my study	4
1.4. References	6
2. Background Reviews	8
2.1. Introduction of nonlinear optics	8
2.2. Introduction to TPA	11
2.3. Mechanism of TPIF	13
2.4. Measurement Methods of TPA cross-section	15
2.5. Theoretical consideration of TPA	16
2.6. Quantum computational calculation of TPA cross-section	18
2.7. Applications of TPA	21
2.7.1. 3D optical data storage and microfabrication	22

2.7.2.	3D fluorescence microscopy	24
2.7.3.	Two-photon pumped lasing	26
2.7.4.	Optical power limiting	26
2.8.	References	27
3.	<i>Measurement Methods of Two-Photon Absorption Cross-section</i>	32
3.1.	Introduction	32
3.2.	Two-photon fluorescence induced (TPIF) methods	34
3.2.1.	Introduction	34
3.2.2.	Theory of TPIF methods	35
3.2.3.	Notes on TPIF methods	40
3.2.4.	Advantages of TPIF methods	42
3.2.5.	Recent literatures of TPA cross-section using TPIF methods	43
3.3.	Nonlinear transmission methods	45
3.3.1.	Introduction	45
3.3.2.	Open aperture Z-scan technique	46
3.3.2.1.	Original theoretic framework	46
3.3.2.2.	Limitations of original theoretical framework	52
3.3.2.3.	Modified theoretical framework	58
3.3.3.	Nonlinear transmission technique (NLT)	71
3.3.4.	Notes and advantages of nonlinear transmission methods	75
3.3.5.	Recent literatures of TPA cross-section using NLT methods	78
3.4.	Summary	81
3.5.	References	82
4.	<i>Experimental Methodology</i>	89
4.1.	Introduction to experimental setup	89

4.2. Linear optical characterization	91
4.2.1. UV-Vis absorption measurement	91
4.2.2. OPIF measurement and fluorescence quantum yields	92
4.2.3. OPIF emission lifetime	93
4.3. Nonlinear optical characterization	94
4.3.1. Experimental setup of TPIF technique	95
4.3.2. Experimental setup of open aperture Z-scan technique	105
4.4. References	108
5. <i>Experimental Calibration Using Rhodamine 6G</i>	109
5.1. Experimental calibration using known dyes	109
5.2. Calibration of TPIF technique	111
5.2.1. UV-Vis absorption of Rh6G	114
5.2.2. TPA excitation spectrum of Rh6G	115
5.2.3. OPIF and TPIF spectra of Rh6G	116
5.2.4. Concentration effect of Rh6G	117
5.2.5. Power dependence of TPIF for Rh6G	118
5.2.6. Excitation polarization analysis of Rh6G	119
5.2.7. Emission polarization analysis of Rh6G	121
5.2.8. OPIF and TPIF lifetimes of Rh6G	123
5.3. Calibration of Z-scan technique	124
5.3.1. Irradiance effect of Rh6G	125
5.3.2. Concentration effect of Rh6G	127
5.3.3. Discussion of results	130
5.4. Comparison between TPIF and Z-scan techniques	131
5.5. References	132

6. Two-Photon Absorption in One-Dimensional π-Conjugated	
<i>Oligophenylenevinylenes (OPVs)</i>	134
6.1. Introduction of 1D organic molecules	134
6.2. Introduction of 1D π -conjugated OPV(n) series	136
6.3. Linearly optical properties of OPV(n) series	138
6.4. TPIF spectra of OPV(n) series	140
6.5. TPA and TPE cross-sections of OPV(n) series	145
6.6. Power dependences of OPV(n) series	149
6.7. TPIF lifetimes of OPV(n) series	151
6.8. Photo-mechanism of TPIF	152
6.9. Polarization analysis of OPV(n) series	153
6.10. Conclusion	162
6.11. References	163
7. Two-Photon Absorption in Multi-Dipolar Zig-Zag	
<i>Oligoaryleneethynylenes (OAEs)</i>	165
7.1. Introduction of multi-dipolar zig-zag OAEs series	165
7.2. Linearly optical properties of zig-zag OAEs series	168
7.3. TPA properties of zig-zag OAEs series	172
7.4. Conclusion	177
7.5. References	178
8. Conclusion	179
List of Conference Presentations/Papers	181
List of Publications	183
Curriculum Vitae	189