

Photophysical Challenges and Antenna Effect Between Click Reaction-based Bodipy Derivatives Manufactured From Knorr Pyrrole

ahmed nuri kursunlu (✉ ankursunlu@gmail.com)

Selçuk Üniversitesi Fen Fakültesi: Selçuk Üniversitesi Fen Fakültesi <https://orcid.org/0000-0002-5490-668X>

Akif Kagan Yilmaz

Selçuk University Faculty of Science: Selçuk Üniversitesi Fen Fakültesi

Elif Bastug

Selçuk Üniversitesi Fen Fakültesi: Selçuk Üniversitesi Fen Fakültesi

Ersin Guler

Selçuk Üniversitesi Fen Fakültesi: Selçuk Üniversitesi Fen Fakültesi

Short Report

Keywords: Bodipy, fluorescent, click, Knorr pyrrole, spectroscopy

Posted Date: September 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-890447/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

In this paper, a series of click reaction-based Bodipy derivatives have been synthesized as part of a preliminary study. Following the characterization of the four challenger molecules, the photophysical properties (absorption, emission, excitation, molar absorption coefficient, quantum yield, etc.) were examined in various organic solvents. The results showed that the energy transfer from the Bodipy cores to other moieties was calculated between 71% and 93% depending on different π -electron configurations and chromophore groups.

Introduction

Bodipy dyes including high electron affinity have been often preferred in photophysical applications and organic electronics due to their tunable emission and extraordinary fluorescence properties. The importance of Bodipy compounds to be used as sources of fluorescence properties has increased in the last decade [1–3]. So, Bodipy can be shown to have a high photo-stability degree and a sharp fluorescence profile depending on the properties of the linked organic groups [3–6]. The synthesis, reaction and applications of Bodipy compounds have been emphasized as fluorescence chemosensors in many review articles on dipyrin complexes and Bodipy [6–9]. For this reason, researchers have synthesized a lot of Bodipy derivatives with several reaction techniques like click chemistry to obtain a shift in emission and absorption wavelengths [10–12]. Bodipy fluorophores, which can be used in the detection of metal ions by making use of changes in fluorescence wavelength and intensity, just as in porphyrins and phthalocyanines, are increasingly significant for bio-imaging applications and cytotoxicity [13–16]. Moreover, Bodipy fluorophores undertake to the tasks of photodynamic therapy studies, which the principle that the photo-stimulant creates cytotoxic singlet oxygen around it after absorbing light in the near-infrared region [17–20]. Increasing interest in light-harvesting based molecules also makes the tendencies towards the preparing of these compounds meaningful [21–24]. Otherwise, the fluorescent materials including multi-Bodipy can act as an energy transfer cassette that can significantly transfer energy through the bond and space and exhibit self-laser behavior [25]. As a photo-active material, Bodipy's have also a great potential for bio-imaging applications due to superior fluorescence abilities [26–28].

Herein, we report an UV-visible and fluorometric study supported by a series of various photophysical parameters on four target compounds. We investigated the fluorescent molecules including mono or poly Bodipy groups. The conjugation and amounts of Bodipy core were compared with the spectroscopic data for intramolecular energy transfers and j-j dimer effect.

Methods And Materials

2.1. Instruments, methods and materials

The Bodipy derivative including azide terminal, A-Bodipy, was prepared with a classical condensation reaction from Knorr pyrrole [22]. Four target challenger compounds were synthesized by using click reaction under an inert atmosphere and named C1, C2, C3 and C4, respectively (Scheme 1). The reagents were supplied from Sigma-Aldrich, Merck, Acros and used as received. The compounds were characterized (data in SI) with NMR (Varian 400), FTIR (Bruker Fourier Transform Infrared, ATR), elemental analysis (Leco CHNS 932) and melting points (Gallenkamp) methods. The absorption and emission&excitation measurements were carried out by a PerkinElmer LS 55 fluorimeter and a Perkin Elmer UV-Vis spectrophotometer, respectively.

The absorption properties of target compounds were investigated by Uv-vis measurements (Fig.1). The starting azide-based Bodipy, A-Bodipy, presents to three main transitions in absorption curve at 498, 265 and 225 nm that the hill at 498 nm assigns to classic S_0 - S_1 transition of Bodipy's. Unlike the fluorescence measurements, the wavelength of this band did almost not change by click reactions used for target challenger molecules. However, the amounts of absorbance changed that the Bodipy's band expanded, and other hillocks shifted to red or blue. Especially, the broad band assigned the anthraquinone unit in compound **C1** raised around 340 nm that it was attributed to multi π - π^* transitions. The bands of target compounds in lower wavelengths can be explained by π - π^* and n - π^* transitions depending on intramolecular conjugation and multi chromophore groups. The shifting reason for the band of 1,8- hydroxyanthraquinone as the starting material around 325 nm can be also explained as an energy transfer between Bodipy and anthraquinone units [26].

To examine the fluorescence properties of challenger molecules, the emission spectra were also recorded in acetone medium. As depicted in Fig. 2, the emission maximum of the starting molecule (A-Bodipy) used in the preparation of target molecules appeared at 501 nm and almost a 300 intensity (a.u.). Following the click reaction conversions, (mono, dual or triple) the fluorescence intensity of all compounds broadened with some shifts in the wavelength. An obvious shifting was observed in the fluorescence curve of **C1** that the maximum emission band appeared around 535 nm. The emission wavelength of **C2** and **C4** did almost changed while the fluorescence intensity of the compounds increased. Otherwise, the emission band of **C3** both increased and hypsochromically shifted to red that the band was observed at 514 nm. The increased fluorescence intensity can be explained with different π systems of compounds and the number of Bodipy units on the main skeleton. So, three Bodipy cores of **C3** lead to a higher fluorescence intensity when compared with other click reaction-based compounds. The anthraquinone group of **C1** provided a more effective π -electron delocalization that the emission wavelength shifted to the red region. Although the structure of the **C2** and **C4** compounds is very similar to each other, the quinoline fragment in compound **C2** presented a higher fluorescence intensity without any shifting in the wavelength. Otherwise, the emission increasing in compound **C3** can be explained with the J-dimer clustering effect, as known the S_0 - S_1 transition, which led to the increasing in the fluorescence intensity [25].

The excitation curves of target compounds were obtained at a fixed emission of 505 nm (see Fig. 3). As expected, the starting compound, A-Bodipy, has the smallest band. Although the excitation spectra of the challenger molecules are similar, **C1** has the largest band in the parallel of absorption measurements. The larger curve in C1 shows than in other compounds due to a higher degree of conjugation between the anthraquinone and Bodipy components. Otherwise, the compound **C2** including the quinoline fragment submitted a more different curve and the fluorescent character of the compound affects this situation. The hummock around 360 nm is the best proof of molecular exchange. The results also support by the broader spectral overlaps and the occurrence of internal energy transfer between the chromophores and Bodipy units in molecules.

The wavelengths of the absorption and emission spectra as well as the Stokes' shifts are reported by using several solvents in Table 1. The dipole moment and dielectric constant of solvents affected the spectral data of compounds that the absorption/emission maxima shifted hypsochromically/bathochromically to different wavelengths. Dimethylformamide changed to the spectroscopic properties of target molecules owing to its high polarity that the quantum yields decreased generally by the increasing polarity of solvents. Although it is a known fact that solvents affect spectral properties, donor atoms on the molecules and conjugation. The quantum yields were given in Table 1 that A-Bodipy indicated a good quantum yield, 0.45-0.61, range of several solvents. Depending on the increasing in polarity, the molar absorption coefficients decreased that the results are

not surprising. So, the high polarity causes to more molecular interactions like hydrogen bonding. Especially, dimethylformamide decreased to the molar absorption coefficients of all compounds. Following the click reactions, as expected, the quantum yields decreased due to the circulation of electrons on more atoms and distorting conjugation -CH₂ fragments. The decrease can be explained by an energy transfer from Bodipy cores to other moieties that antenna effect-light harvesting of Bodipy works in these molecules. The energy transfer from Bodipy cores to other moieties were calculated by the equation:

$$\Phi_{ENT} = 1 - \Phi_{Challenger} / \Phi_{A-Bodipy}$$

in which Φ_{ENT} is the percentage of energy transfer, $\Phi_{Challenger}$ and $\Phi_{A-Bodipy}$ are the fluorescence quantum yields of target challenger compounds in several solvents. The best energy transfer was observed in compound **C1** the this clearly shows to more extended conjugation characteristic of the reduced states of the anthraquinone unit. Similar energy transfer was recorded in compound **C2** due to structure served to high conjugation while compounds **C3** and **C4** gave a lower energy transfer mechanism. The fluorescent compounds are substituted with aromatic groups including multi Bodipy units. When the fluorescence quantum yields of the compounds is compared, **C3** has a better quantum yield while **C1** molecule has the lowest yield. The difference can be explained with the J-dimer stacking that its triangular-like structure enables to more molecular interactions. Otherwise, the quantum yield of **A-Bodipy** decreased with the reaction organic groups depending on the increasing atom numbers and the decreasing conjugation.

Table 1 Photophysical properties of the challenger molecules the starting material (**A-Bodipy**) **C1**, **C2**, **C3** and **C4** in different solvents

Challenger Compound	Solvent	λ_{abs} (nm)		ϵ_{max} ($M^{-1}cm^{-1}$)	λ_{emmax} (nm)	λ_{fix-ex} (nm)	Φ^* (10^{-2})	Φ_{ENT} (%)
		<i>Bodipy moiety</i>	<i>Other moieties</i>					
A-Bodipy	Acetone	499	268 222	98000	505	330	57.2	-
	Ethanol	497	271 225	95600	503	330	55.1	-
	THF	500	269 223	105600	503	330	58.2	-
	Chloroform	503	274 232	109300	514	330	61.3	-
	DMF	495	265 221	88400	500	330	45.8	-
C1	Acetone	501	338 235	270000	538	330	5.3	91
	Ethanol	499	337 234	265300	534	330	4.1	93
	THF	503	339 232	277400	535	330	5.1	91
	Chloroform	505	340 237	281900	543	330	6.2	89
	DMF	498	336 231	225700	533	330	3.3	93
C2	Acetone	501	273 240	115000	506	330	9.9	82
	Ethanol	497	270 241	111200	503	330	9.2	83
	THF	502	275 243	113400	505	330	9.1	84
	Chloroform	508	276 246	118200	511	330	10.2	83
	DMF	497	269	99400	502	330	5.6	88

			238					
C3	Acetone	502	269	170000	514	330	16.7	71
			232					
	Ethanol	499	267	150200	510	330	11.8	78
			230					
	THF	504	273	168900	512	330	16.4	72
			236					
	Chloroform	507	277	166900	519	330	15.1	75
			232					
	DMF	498	267	132600	510	330	9.2	80
			230					
C4	Acetone	501	280	109000	505	330	12.1	79
			240					
	Ethanol	499	280	108400	504	330	11.3	79
			241					
	THF	504	283	105600	505	330	9.1	84
			242					
	Chloroform	506	280	113800	508	330	13.2	78
			239					
	DMF	499	277	98700	502	330	7.9	82
			238					

* In comparison with fluorescein in basic ethanol was used as the reference ($\Phi = 0.92$)

Conclusion

In conclusion, we have improved to four fluorescent Bodipy derivatives using Huisgen cycloaddition. The binding groups to the main Bodipy skeleton presented different quantum yields and energy transfer amounts depending on their conjugation structure and chromophores. Compound C4 including anthraquinone fragment and dual Bodipy cores has the best energy transfer mechanism due to its more conjugated constructions. The conjugated system among the aromatic groups in the neutral state that the anthraquinone core may act as an electrochemical switch and allows it in both reduced states. On the other hand, compound C3 reached the highest quantum yield and fluorescence intensity because of the triple Bodipy characteristic. The prepared compounds having energy transfer principle can also be modified by Knoevenagel reactions for the novel Bodipy derivatives using Knorr pyrrole as the starting material that they could be open new research avenues in laser dyes, optoelectronic devices, liquid crystals, sensors, photovoltaic cells, etc.

Declarations

Acknowledgments

We thank the Selçuk University BAP (Project Number: 20201001), Konya, Turkey and for financial support of this work produced from Akif Kagan Yilmaz's Ms. Thesis.

Funding Not applicable

Conflict of interest Not applicable

Ethics approval/declarations Not applicable

Consent to participate Not applicable

Consent for publication Not applicable

Availability of data and material/ Data availability Not applicable

Code availability Not applicable

Authors' contributions

A.N.K. coordinated all study. AKY synthesized and characterized to all compounds. EB carried out the spectroscopic experiments. EG performed the writing of paper.

References

- [1] Kaur B, Kaur N, Kumar S. Colorimetric metal ion sensors—a comprehensive review of the years 2011–2016. *Coord Chem Rev* 2018;358:13–69.
- [2] Jiao Y., Zhang L., Zhou P., A rhodamine B-based fluorescent sensor toward highly selective mercury (II) ions detection, *Talanta*, 2016, 150, 14-19.
- [3] Baslak C., Kursunlu A. N., A naked-eye fluorescent sensor for copper (II) ions based on a naphthalene conjugate Bodipy dye. *Photochem. Photobiol. Sci.*, 2018, 17, 1091-1097.
- [4] Huang Y, Li C-F, Shi W-J, Tan H-Y, He Z-Z, Zheng L, et al. A near-infrared BODIPY- based fluorescent probe for ratiometric and discriminative detection of Hg²⁺ and Cu²⁺ ions in living cells. *Talanta* 2019;198:390–397.
- [5] Xue Z., Liu T., Liu H., Naked-eye chromogenic and fluorogenic chemosensor for mercury (II) ion based on substituted distyryl BODIPY complex. *Dyes Pigments* 2019, 165, 65-70.
- [6] Culzoni M. J., Peña A. M., Machuca A., Goicoechea H. C., Babiano R., Rhodamine and BODIPY chemodosimeters and chemosensors for the detection of Hg²⁺, based on fluorescence enhancement effects, *Anal. Methods*, 2013, 5, 30-49.
- [7] Çetindere S., Cosut B., Yesilot S., Durmus M., Kılıç A., Synthesis and properties of axially-BODIPY conjugated subphthalocyanine dyads, *Dyes Pigments*, 2014, 101, 234-239.

- [8] Kostereli Z., Ozdemir T., Buyukcakir O., Akkaya E.U. Letter Tetrasteryl-BODIPY-based dendritic light harvester and estimation of energy transfer efficiency, *Org Lett.* 2012, 14, 3636-3639
- [9] Bilgiç A., Cimen A. Two Novel BODIPY-Functional Magnetite Fluorescent Nano-Sensors for Detecting of Cr (VI) Ions in Aqueous Solutions, *J. Fluorescence*, 2020, 867-881.
- [10] Kursunlu A.N., Güler E., Facile assembly of Bodipy-based metal ion sensor using click chemistry, *Supramol. Chem.*, 2013, 25, 512-521.
- [11] Şenkuytu E., Eçik E.T., Çoşut B., Bodipy decorated triazine chemosensors for Ag⁺ ions with high selectivity and sensitivity. *J Luminescence*, 2018, 203, 639-645.
- [12] Jiao Y., Zhang L., Zhou P., A Rhodamine B-Based Fluorescent Sensor toward Highly Selective Mercury (II) Ions Detection *Talanta*, 150, 2016, 14–19.
- [13] Tümay S.O., Okutan E., Sengul I.F., Özcan E., Kandemir H., Doruk T., Çetin M., Çoşut B., Naked-eye fluorescent sensor for Cu (II) based on indole conjugate BODIPY dye. *Polyhedron* 2016, 117, 161–171
- [14] Gul A., Oguz M., Kursunlu A.N., Yilmaz M., A novel colorimetric/fluorometric dual-channel sensor based on phenolphthalein and Bodipy for Sn (II) and Al (III) ions in half-aqueous medium and its applications in bioimaging, *Dyes Pigments*, 2020, 176, 108221
- [15] Günsel A., Atmaca G.Y., Taslimi P., Bilgiçli A.T., Gülçin İ., Erdoğan A., Yarasir M. N., Synthesis, characterization, photo-physicochemical and biological properties of water-soluble tetra-substituted phthalocyanines: antidiabetic, anticancer and anticholinergic, *J. Photochem. Photobio. A: Chem.*, 2020, 396, 112511.
- [16] Giuntini F., Bryden F., Boyle R.W., Daly R., Scanlan E.M., Huisgen-based conjugation of water-soluble porphyrins to deprotected sugars: towards mild strategies for the labelling of glycans, *Org. Biomol. Chem.* 2014, 12, 1203-1206.
- [17] Qi X., Jun E.J., Kim L.X.S.-J., Hong J.S.J., Yoon Y.J., Yoon J., New BODIPY derivatives as OFF-ON fluorescent chemosensor and fluorescent chemodosimeter for Cu²⁺: cooperative selectivity enhancement toward Cu²⁺, *J. Org. Chem.* 71 (2006) 2881–2884.
- [18] Li Q., Guo Y., Shao S. A BODIPY based fluorescent chemosensor for Cu(II) ions and homocysteine/cysteine. *Sensors Actuat. B*, 2012, 171–172, 872-877.
- [19] Bilgiç A., Çimen A., A highly sensitive and selective ON-OFF fluorescent sensor based on functionalized magnetite nanoparticles for detection of Cr (VI) metal ions in the aqueous medium, *J. Mol. Liquids*, 2020, 312, 113398.
- [20] Zhang J., Zhao B., Lia C., Zhu X., Qiao R., A BODIPY-based “turn-on” fluorescent and colorimetric sensor for selective detection of Cu²⁺ in aqueous media and its application in cell imaging, *Sens. Actuators, B*, 2014, 196, 117-122.

- [21] Yildiz E.A., Sevinc G., Yaglioglu H.G., Hayvali M. Strategies towards enhancing the efficiency of BODIPY dyes in dye sensitized solar cells. *J. Photochem. Photobio. A: Chem.*, 2019, 375, 148-157.
- [22] Bastug E., Kursunlu A.N., Guler E., A fluorescent clever macrocycle: Deca-bodipy bearing a pillar[5]arene and its selective binding of asparagine in half-aqueous medium, *J. Luminescence*, 2020, 225, 117343.
- [23] Kursunlu A. N., Baslak C., A Bodipy-bearing pillar[5]arene for mimicking photosynthesis: Multi-fluorophoric light harvesting system, *Tetrahedron Lett.*, 2018, 59 1958-1962.
- [24] Culzoni M.J., Pena A.M., Machuca A., Goicoechea H.C., Babiano R., Rhodamine and BODIPY chemodosimeters and chemosensors for the detection of Hg^{2+} , based on fluorescence enhancement effects, *Anal. Methods*, 2013, 5, 30-49.
- [25] Kursunlu A.N., Synthesis and photophysical properties of modifiable single, dual, and triple-boron dipyrromethene (Bodipy) complexes, *Tetrahedron Lett.* 2015, 56, 1873-1877.
- [26] H. Yu, Y. Xiao, H. Guo, X. Qian, "Convenient and efficient FRET platform featuring a rigid biphenyl spacer between rhodamine and BODIPY: transformation of 'turn-on' sensors into ratiometric ones with dual emission, *Chemistry* 17 (2011) 3179–3191.

Figures

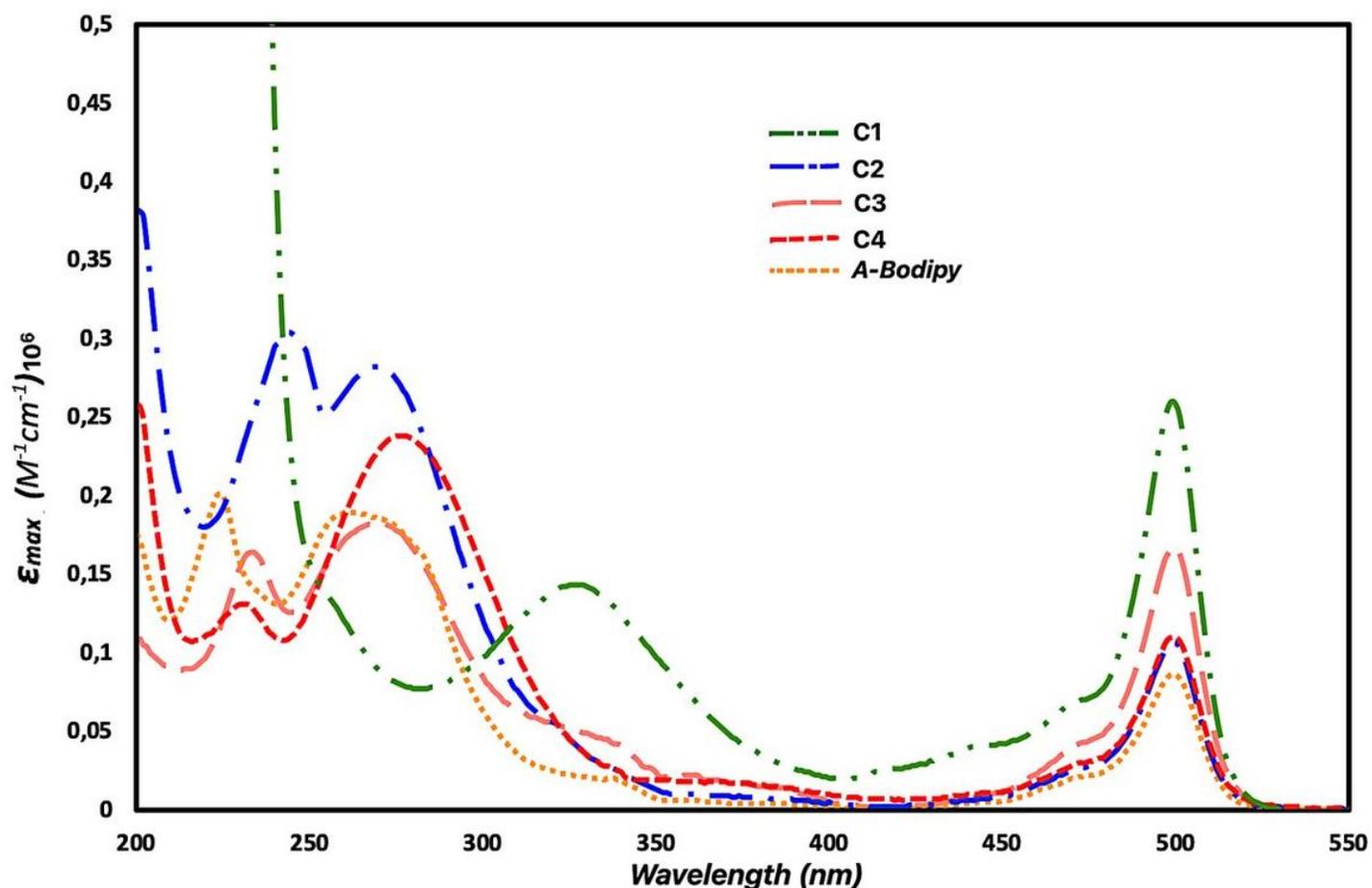


Figure 1

The absorption spectra of A-Bodipy, C1, C2, C3 and C4 in acetone (1×10^{-6} M).

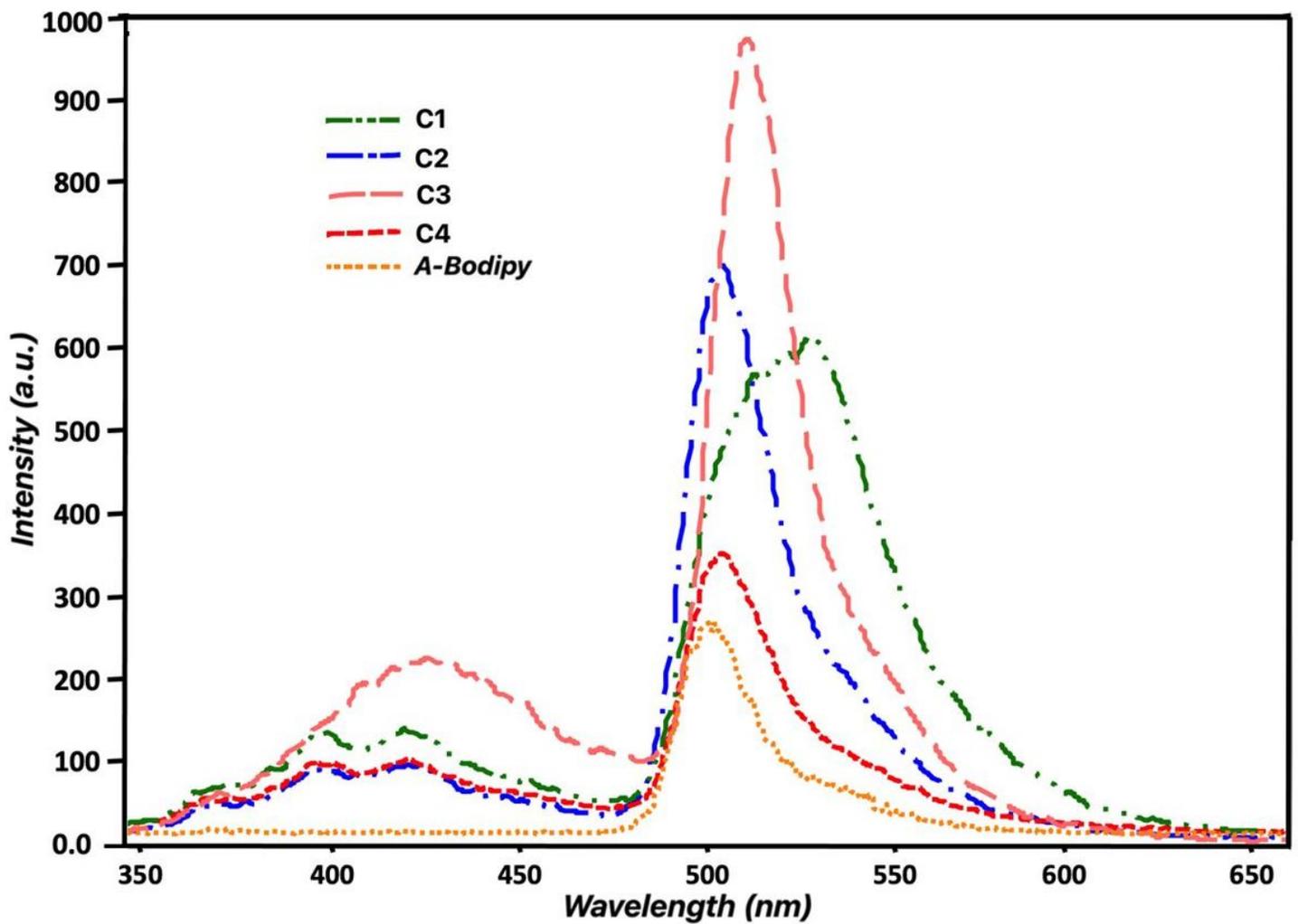


Figure 2

The fluorescence spectra of A-Bodipy, C1, C2, C3 and C4 in acetone (1×10^{-6} M), λ_{ex} : 330 nm, slit: 8.

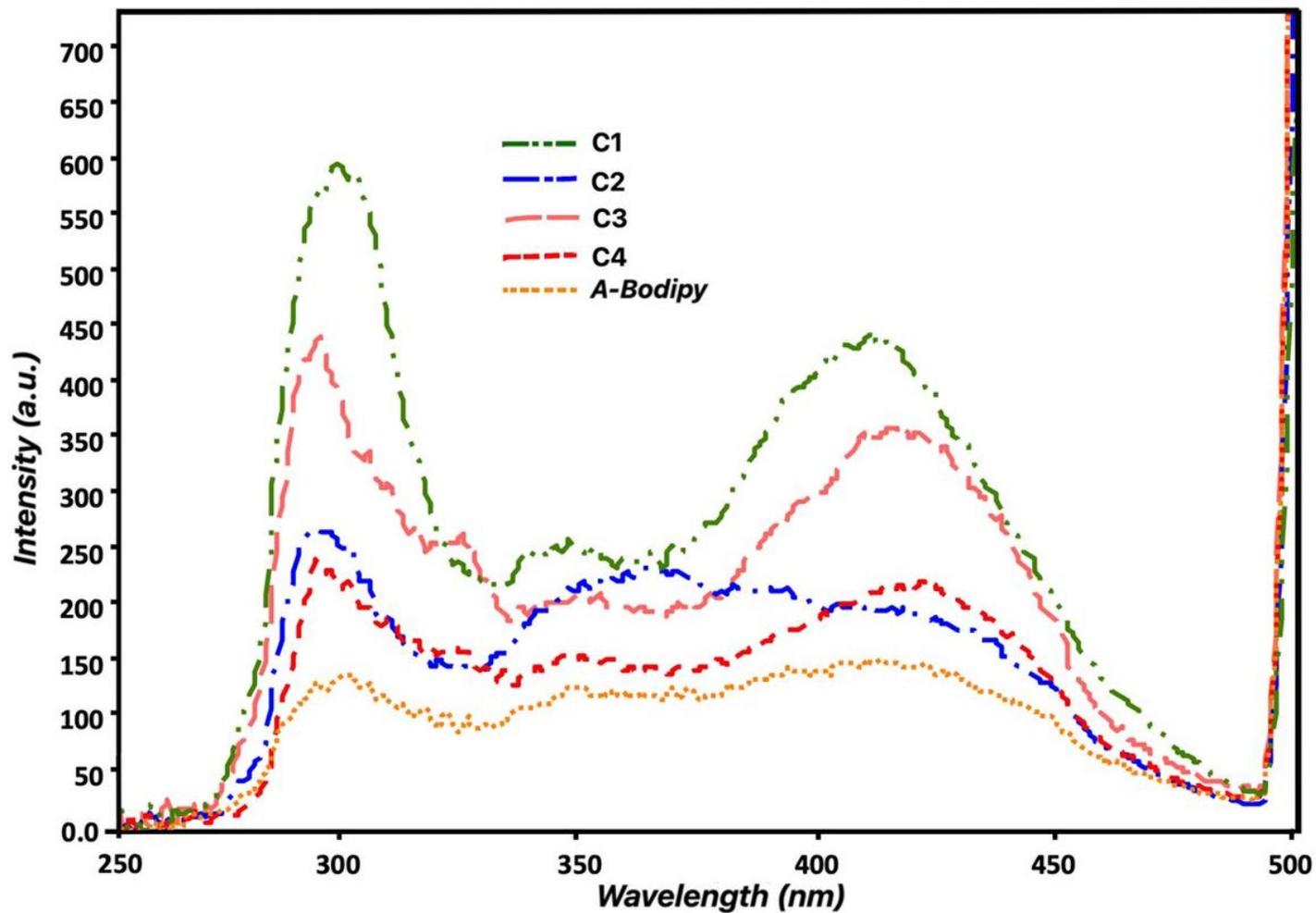


Figure 3

The excitation spectra of A-Bodipy, C1, C2, C3 and C4 in acetone (1×10^{-6} M), λ_{em} : 505 nm, slit:5.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [scheme1.jpg](#)