Supporting Information
for

Two-photon absorbing and triplet excited state quenching of near-IR region aza-BODIPY photosensitizers via triphenylamine moiety despite heavy bromine atoms

Ahmet Karatay[a,*], Halil Yılmaz[b], Elif Akhuseyin Yildiz[a], Gökhan Sevinç[c], Mustafa Hayvali[b,*], Bahadır Boyacıoğlu[e], Huseyin Unver[f], Ayhan Elmali[a]

[a]Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Beşevler, Ankara, Türkiye
[b]Department of Chemistry, Faculty of Science, Ankara University, Beşevler, 06100 Ankara, Türkiye
[c]Department of Chemistry, Faculty of Science and Literature, Bilecik Şeyh Edebali University, 11230, Bilecik, Türkiye.
[e]Vocational School of Health Services, Ankara University, 06290 Kecioren-Ankara, Türkiye

[f]Department of Physics, Faculty of Science, Ankara University, 06100 Besevler-Ankara, Türkiye

*Corresponding Author(s): akaratay@eng.ankara.edu.tr (Ahmet Karatay), hayvali@science.ankara.edu.tr (Mustafa Hayvalı)

Table of Contents

1. Materials and Equipment

All solvents were purchased from common commercial sources. The melting points of the synthesized compounds were determined in open capillaries using Barnstead Electrothermal IA9100. Fluorimetric measurements were applied on a Perkin Elmer LS55 Spectrometer and electronic excitation spectra were recorded on a Shimadzu UV1800 spectrophotometer. Mass spectral analyses were performed on an Agilent 6224 LC/MS spectrometer. ^{1}H-NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by chloroform (δ = 7.26 ppm). ^{13}C NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer. The ^{13}C NMR chemical shifts (δ) are reported in ppm with the internal $CDCl_3$ δ 77.0 ppm as standard. A Perkin–Elmer 100 spectrometer (equipped with an ATR unit) was used for FT-IR spectra of the compounds in the range of 650–4000 cm^{-1}.

2. Determination of Fluorescence Quantum Yields (Φ_F)

The luminescence quantum yields of the aza-BODIPYs were measured by the comparative method using the analogue compound (3,5-Diphenyl-1H-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)amine, Φ_F=0.34 in $CHCl_3$) [1]. The formula used is as follows [2] (Eq. 1):

$$\Phi_F = \Phi_F(Std)\frac{F.A_{Std}.n^2}{F_{Std}.A.\,n_{Std}^2}$$

(1)

$\Phi_F(Std)$ denotes the fluorescence quantum yield of the reference compound, while F and F_{Std} show the areas under the emission curves of the samples and the reference, respectively. A and A_{Std} are the absorbance values of the samples and the reference compound at their excitation wavelengths. n and n_{Std} denote the refractive indices of the solvents. The concentrations of the aza-BODIPY solutions were fixed at 5 x 10^{-6} M in chloroform. Among the synthesized compounds, only compound **4** gave very low fluorescence peak (Φ_F: 0.003). Compounds 3 and 5 have no emissions. The emission spectrum of the compound **4** is given in figure S1 and the photophysical parameters are given in table 1.

Table 1 Photophysical parameters of compounds 3, 4, and 5

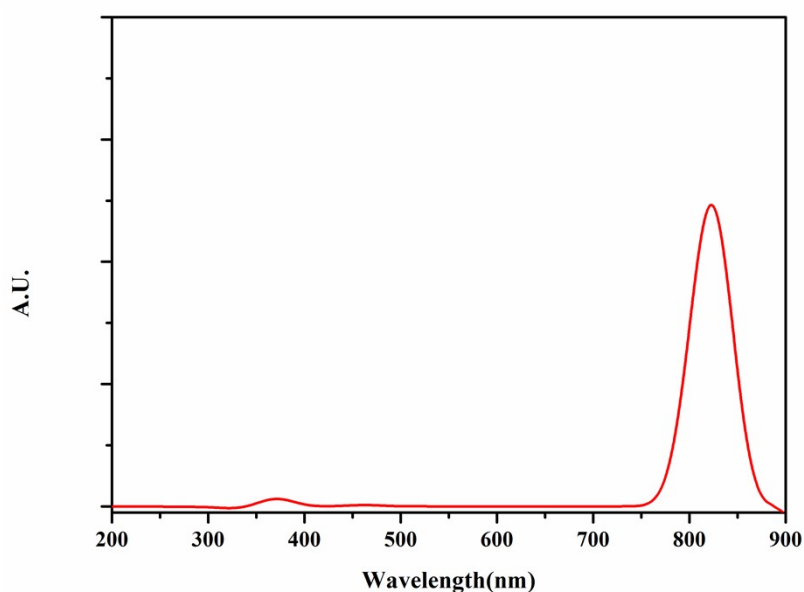| Compound	$\lambda_{abs(nm)}$	$\lambda_{em(nm)}$	ε [M^{-1} cm^{-1}]	FWHM (nm)	Stokes Shifts (cm^{-1})	Φ_F
3	331/653	-	38600/26800	75/139	-	-
4	304/335 647/749	823	48000/44000 48600/57000	-	176/74	0.003
5	314/674	-	52400/57800	163	-	-

Figure S1. Emission spectra of the compound **4**

3. Determination of Singlet Oxygen Quantum Yields (Φ_Δ)

To investigate the singlet oxygen generation properties of the compounds, experiments were carried out in dichloromethane (DCM) with 1,3-diphenylisobenzofuran (known as DPBF) as a chemical single oxygen trap [3].

The absorbance of DPBF was set at around 1.0 at 414 nm, and the absorbance of the sensitizers in DCM solution was set between 0.2 and 0.3. Both the aza-BODIPYs and the single oxygen trap (DPBF) were excited by a single wavelength (630 nm) of light using a Perkin Elmer L5S55 fluorometer for 2 seconds at every turn. Methylene blue (MB in DCM, M = 0.57) was used as a standard compound for the determination of the singlet oxygen quantum yields (Φ_Δ) by

plotting the ΔOD of 1,3-diphenylisobenzofuran against the irradiation time. The following equation was used [3].

$$\Phi_{\Delta sam} = \Phi_{\Delta std}\left(\frac{m_{sam}}{m_{std}}\right)\left(\frac{F_{std}}{F_{sam}}\right)$$

$$(2)$$

In equation 2, std and sam denote the MB and aza-BODIPY compounds, respectively. The absorption correction factor (F) was calculated by $1-10^{-OD}$. The OD refers to the optical density, showing the absorbance value. The varying absorption of the DPBF at 414 nm gave the m value as the slope of the graph depending on the irradiation time. Right after the photosensitizers were exposed to monochromatic light at their absorption maxima, the UV/Vis spectra were taken for each measurement. The change in the maximum absorbance values of DPBF at 414 nm was monitored by plotting them against the irradiation time.

Singlet oxygen quantum efficiencies were measured with 1,3-Diphenylisobenzofuran (DPBF) as a chemical singlet oxygen trap. Absorption spectra of 1,3-diphenylisobenzofuran (DPBF) as a chemical singlet oxygen probe upon irradiation in the presence of compound **5** were given in Figure S2.a and the change in the absorbance of DPBF under illumination in the presence of methylene blue (MB) as standard and compound 5 in CH_2Cl_2 was given in Figure S2.b.
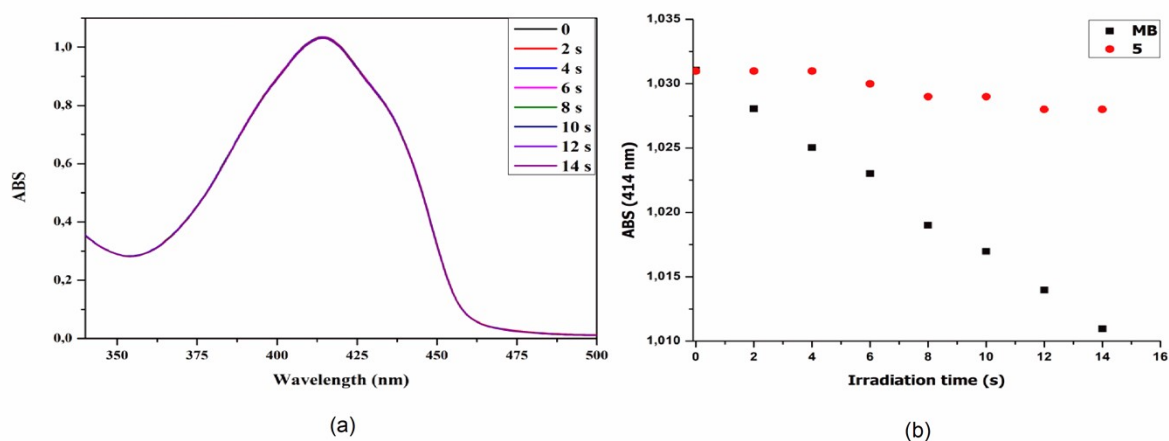

Figure S2. a) Absorption spectra of DPBF upon irradiation in the presence of the compound **5** for 14 s (recorded at 2 s interval), b) The change in the absorbance of DPBF under illumination (λ_{exc} = 630 nm) at 414 nm in the presence of methylene blue (MB) as standard and the compound 5 in CH_2Cl_2.

As can be seen from the related graphs, the absorbance band of the DPBF was nearly untouched in the presence of brominated compound **5** while a drastic decrease with the methylene blue. In contrast to general heavy atoms substituted aza-BODIPYs, no singlet oxygen generation was

observed. The molecular structures are closely linked to heavy atoms such as bromine and iodine to provide functionality in singlet oxygen production. This result may reveal that all systems containing heavy atoms cannot be beneficial for singlet oxygen production. The resistance of compound **5** to produce singlet oxygen that could be related to the triplet formation was investigated by using ultrafast pump-probe spectroscopy experiments and theoretical calculations.

"The triplet state of the aza-BODIPYs with triphenylamine moieties at the -1,-7 positions of the core could be quenched by the efficient intramolecular charge transfer between the planar core structure and triphenyl amine groups. In such a case, no intersystem crossing can be expected to be observed. Indeed, it is supportive that compound 5 does not produce singlet oxygen in the presence of two bromine atoms. From the point of view of theoretical calculation, since the value of CT percentage (66%) of compound 5 is significantly larger than the LE percentage (39%), It can be concluded that there is a stronger charge transfer from triphenylamine groups to indacene core in compound 5. Similarly, based on the pump-probe spectroscopy measurements, there is regardless effect of bromine atoms bounded to -2,-6 positions of the aza-BODIPY core to the generation of triplet excited state. The transition to the triplet state is not allowed due to dominating of triphenylamine groups leading to the intramolecular charge transfer process. One can say that the ct level and the triplet level are in competition with each other and prefer ct in the presence of triphenylamine groups following excitation of the molecule."

In our previous work, we synthesized -2, -6 dibromide substituted aza-BODIPYs **AA1** and **CC1** (scheme 2) with high singlet oxygen quantum yields (71% and 74% against methylene blue, respectively)[4]. In addition to the previous compound, we have designed novel compounds **4** and **5** to investigate the relationship between charge transfer and singlet oxygen generation efficiency for aza-BODIPYs. Although we expected high singlet oxygen quantum yields due to the heavy atoms effect of bromine at the -2,6 position of compound **5**, we have not observed
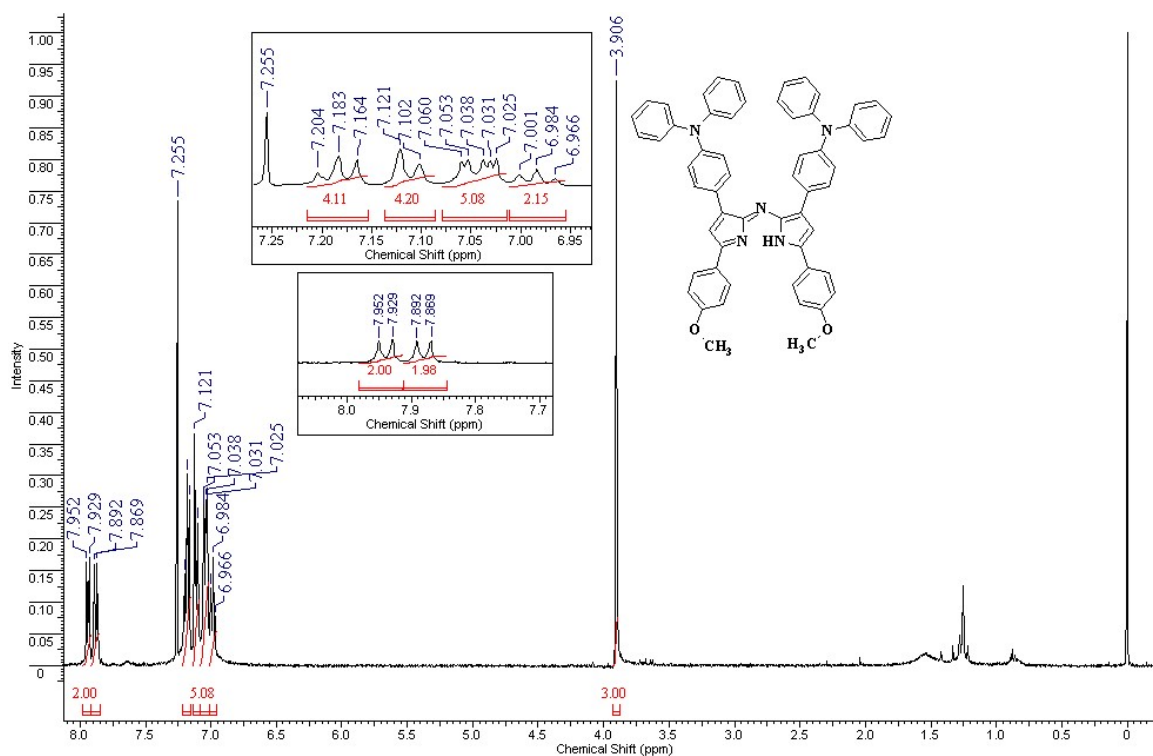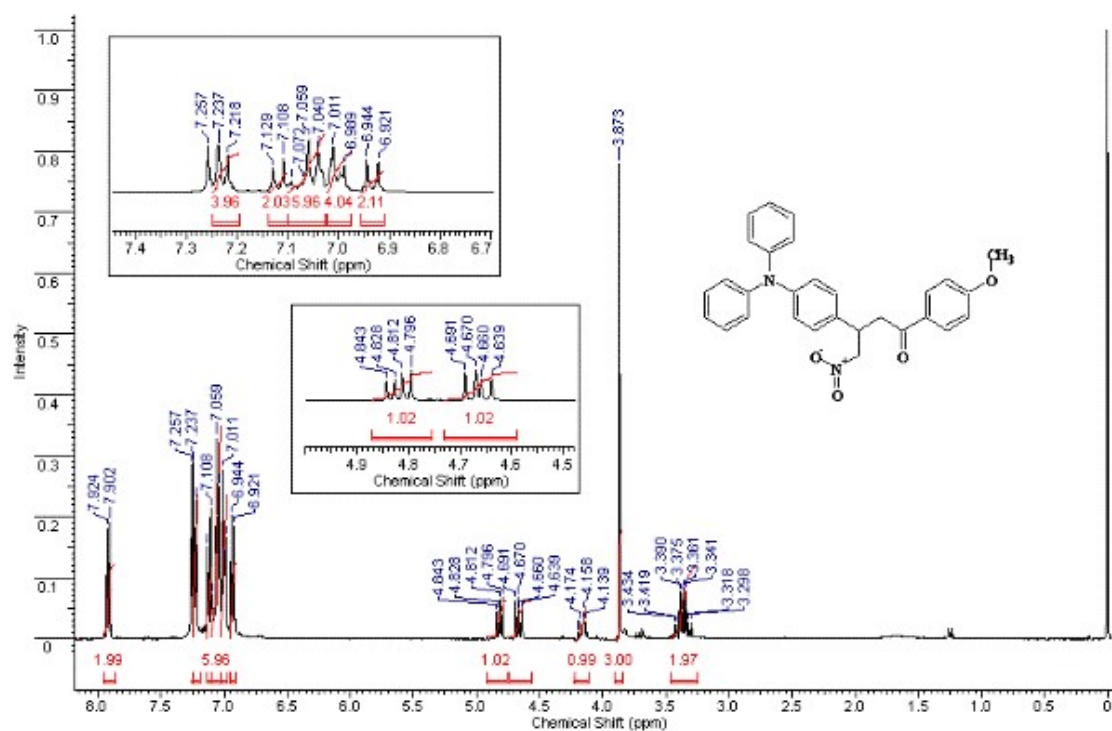
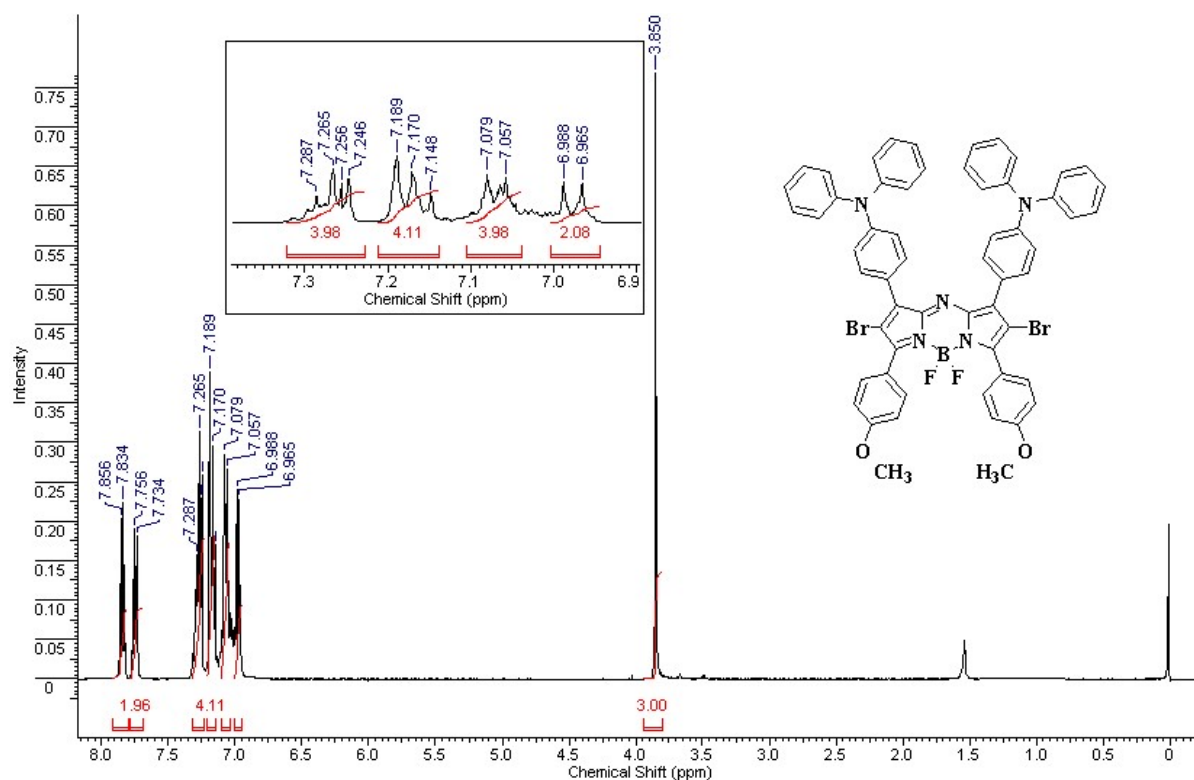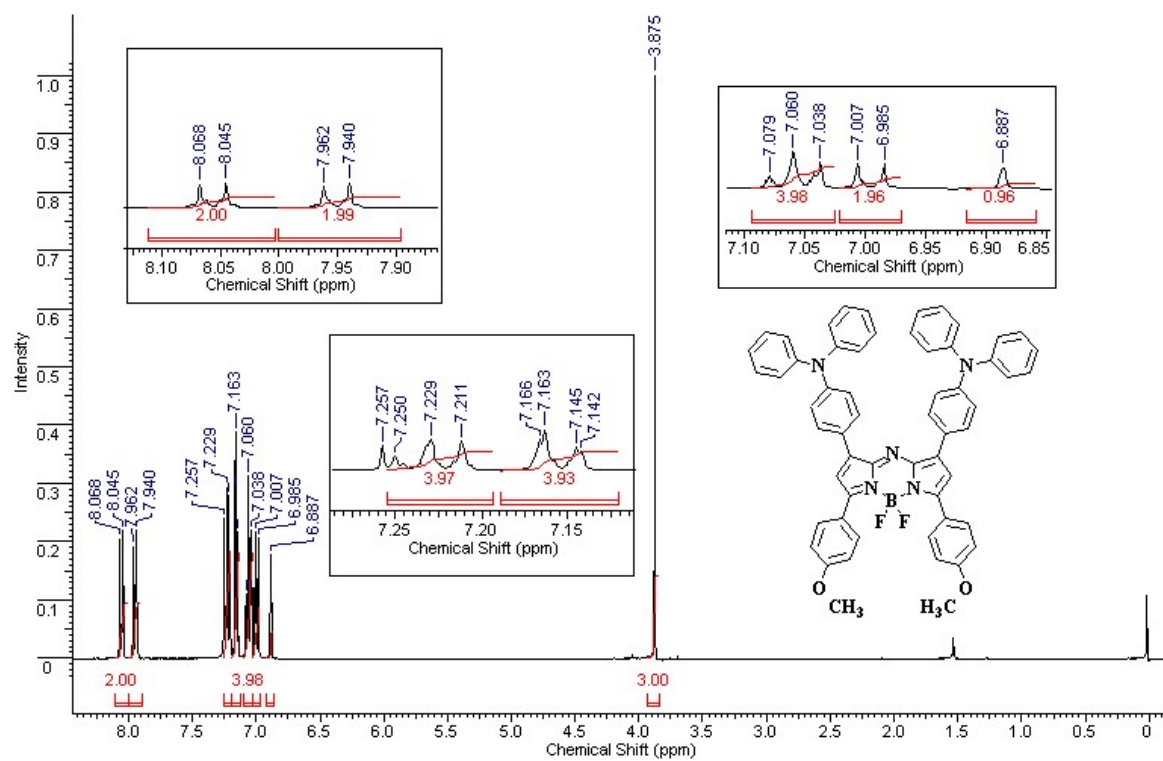## 4. Femtosecond Transient Absorption Spectroscopy Studies

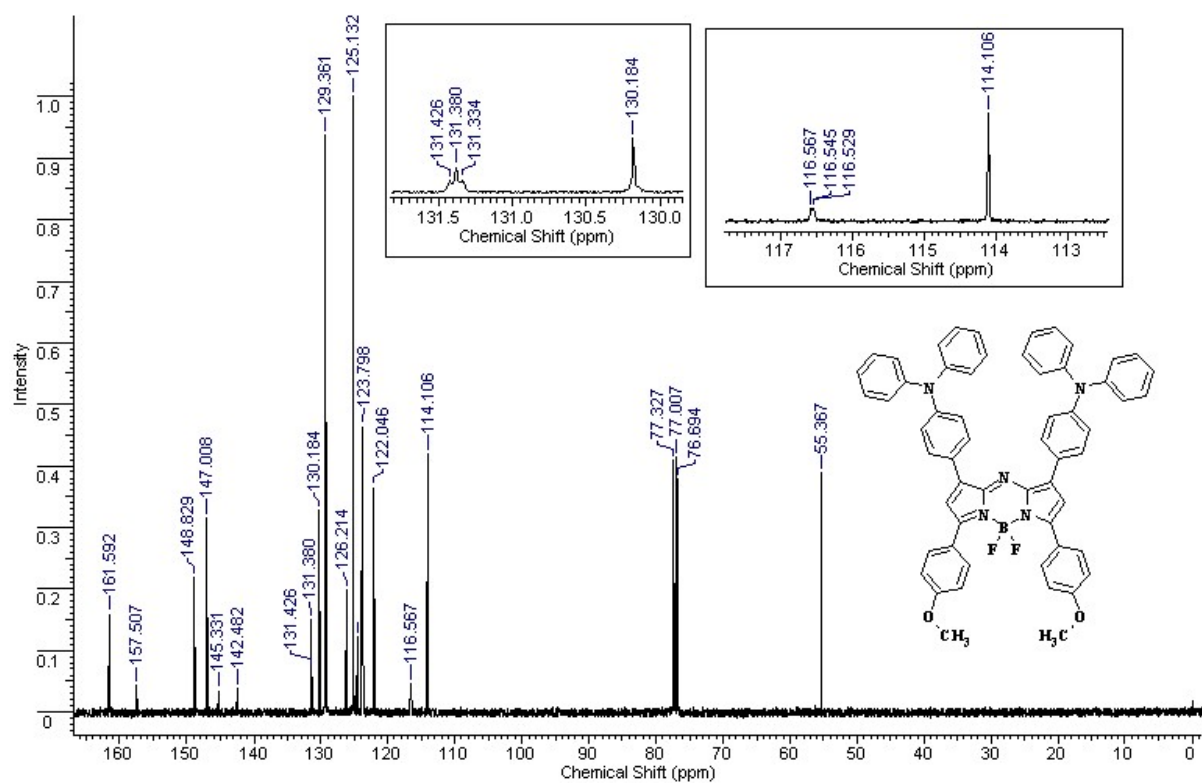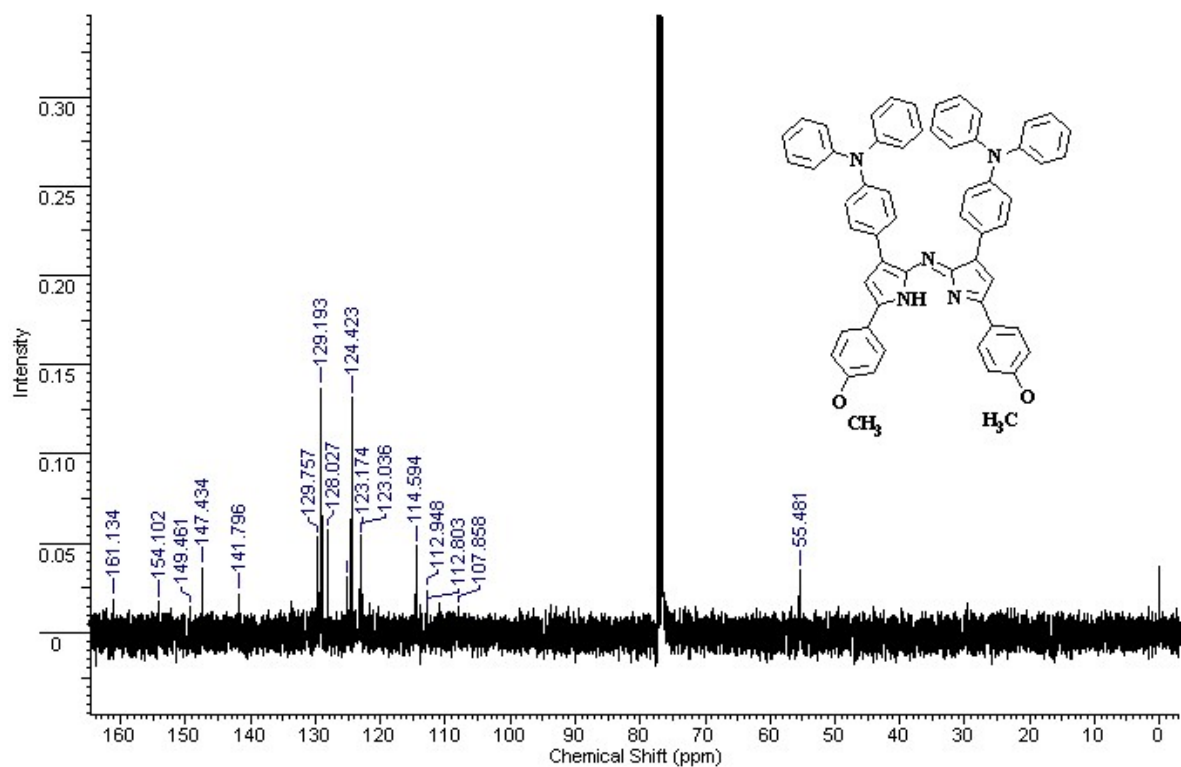The transient absorption data was fitted using an exponential equation which is given below.

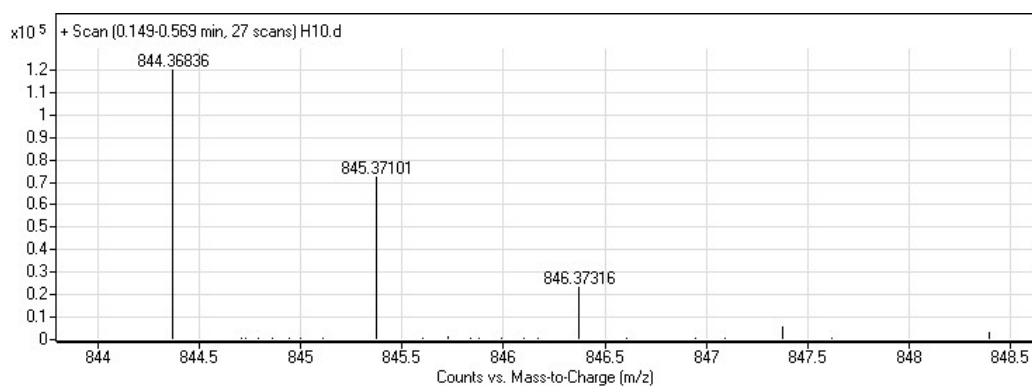$$S(t) = e^{-\left(\frac{t-t_0}{t_p}\right)^2} * \sum_i A_i e^{-\frac{t-t_0}{t_i}}, \ t_p = \frac{IRF}{2\cdot ln2}$$
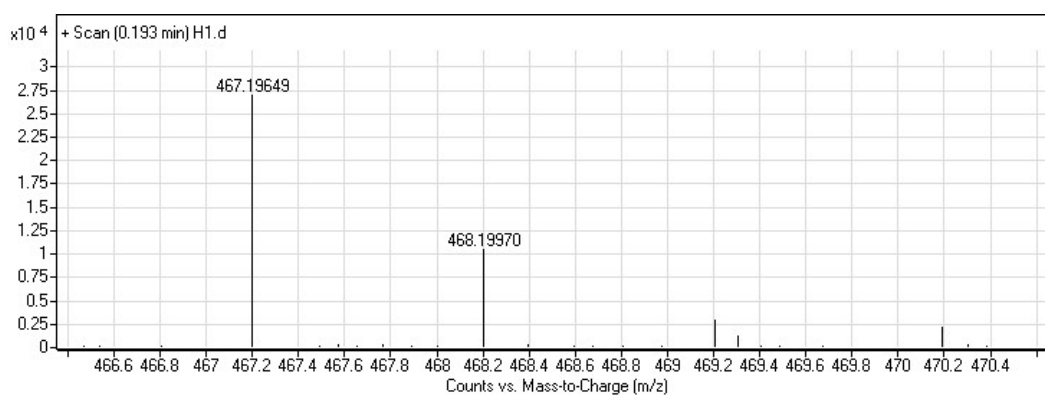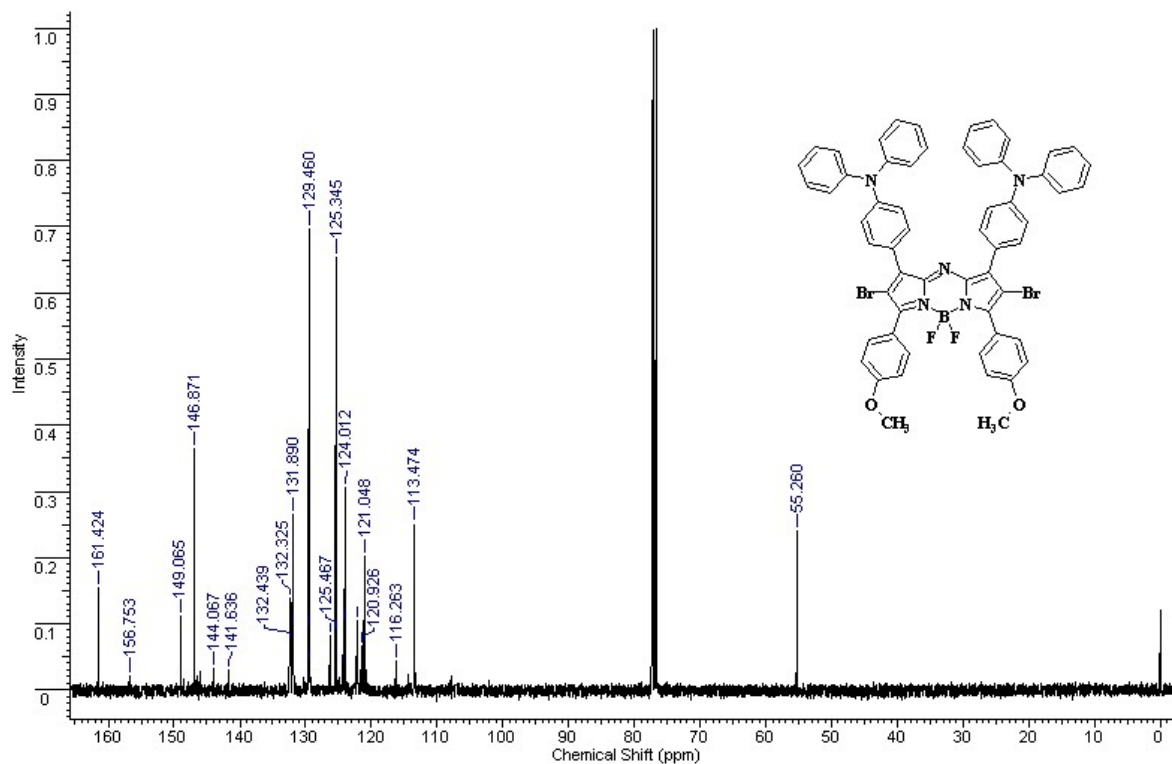
Where *IRF* is the width of instrument response function (full width half maximum), t_0 is time zero, A_i and t_i are amplitudes and decay times respectively, * is convolution.
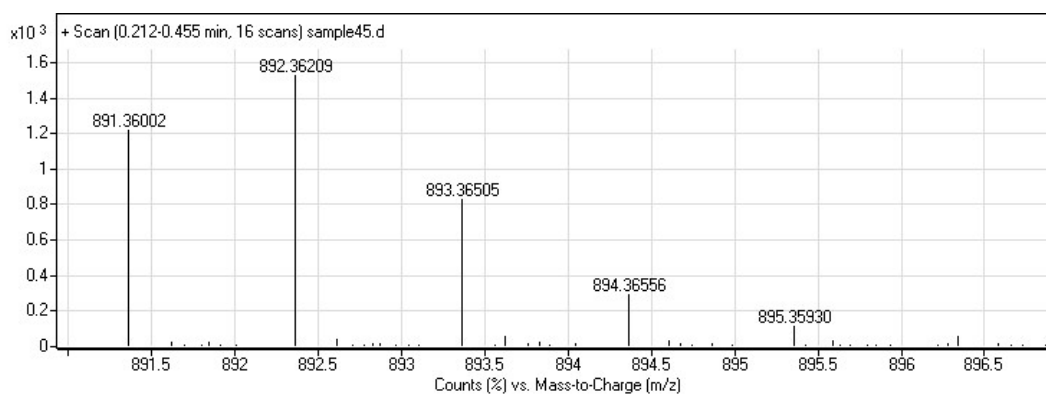
5. Characterization

Figure S3. ^{1}HNMR for compound **2** in DMSO at 400 MHz

Figure S4. ^{1}HNMR for compound **3** in CDCl$_3$ at 400 MHz

Figure S5. ^{1}HNMR for compound **4** in CDCl$_3$ at 400 MHz

Figure S6. ^{1}HNMR for compound **5** in CDCl$_3$ at 400 MHz

Figure S7. ^{13}CNMR for compound **3** in CDCl$_3$ at 100 MHz

Figure S8. ^{13}CNMR for compound **4** in CDCl$_3$ at 100 MHz

Figure S9. ^{13}CNMR for compound **5** in CDCl$_3$ at 100 MHz

Figure S10. HRMS-TOF-ESI for compound **2**

Figure S11. HRMS-TOF-ESI for compound **3**
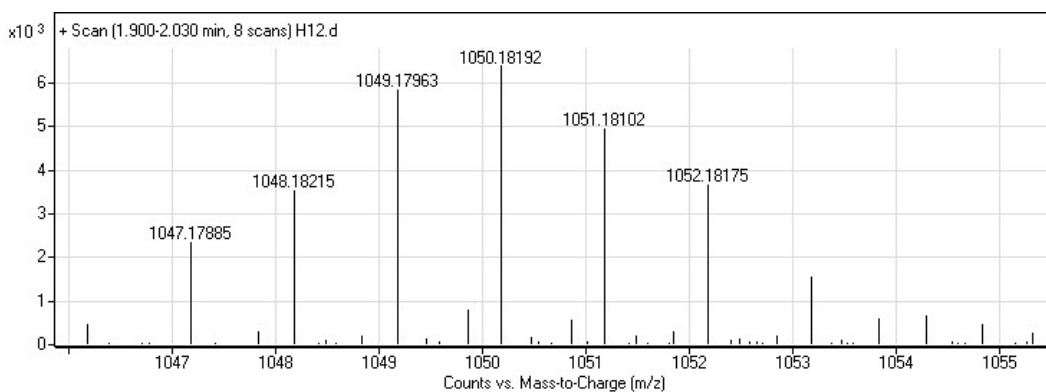
10

Figure S12. HRMS-TOF-ESI for compound **4**
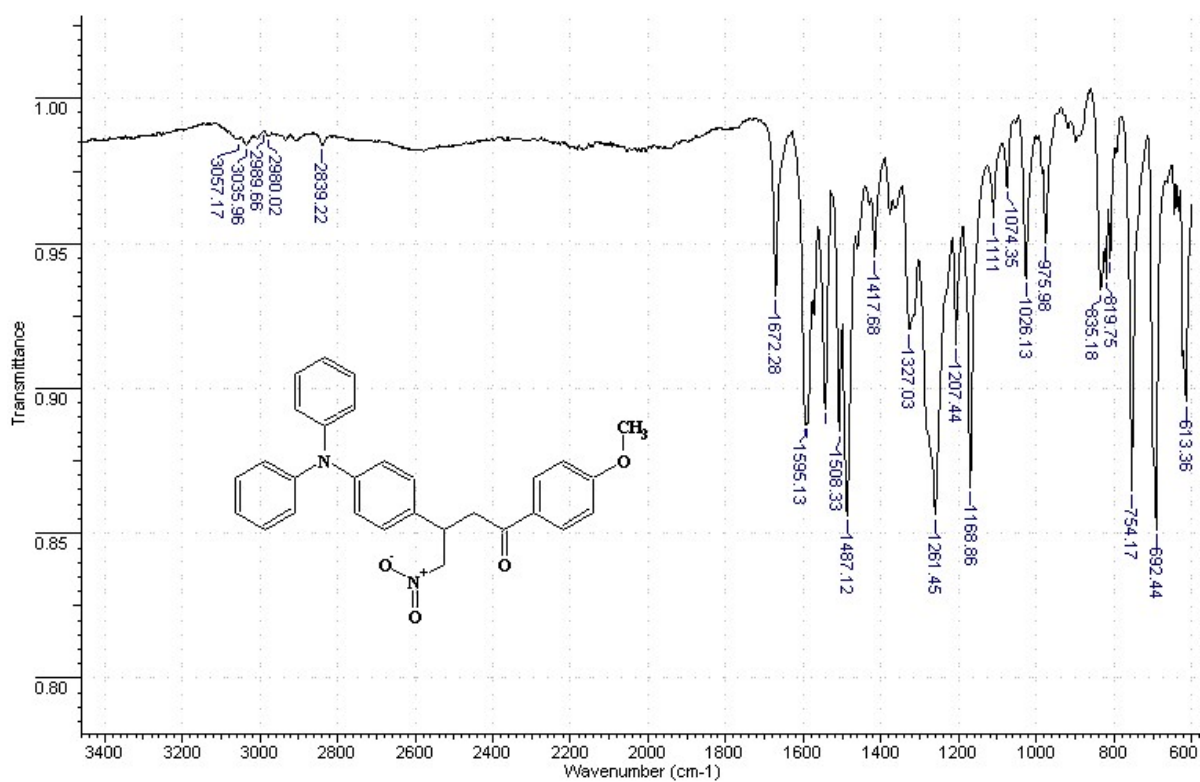

Figure S13. HRMS-TOF-ESI for compound **5**

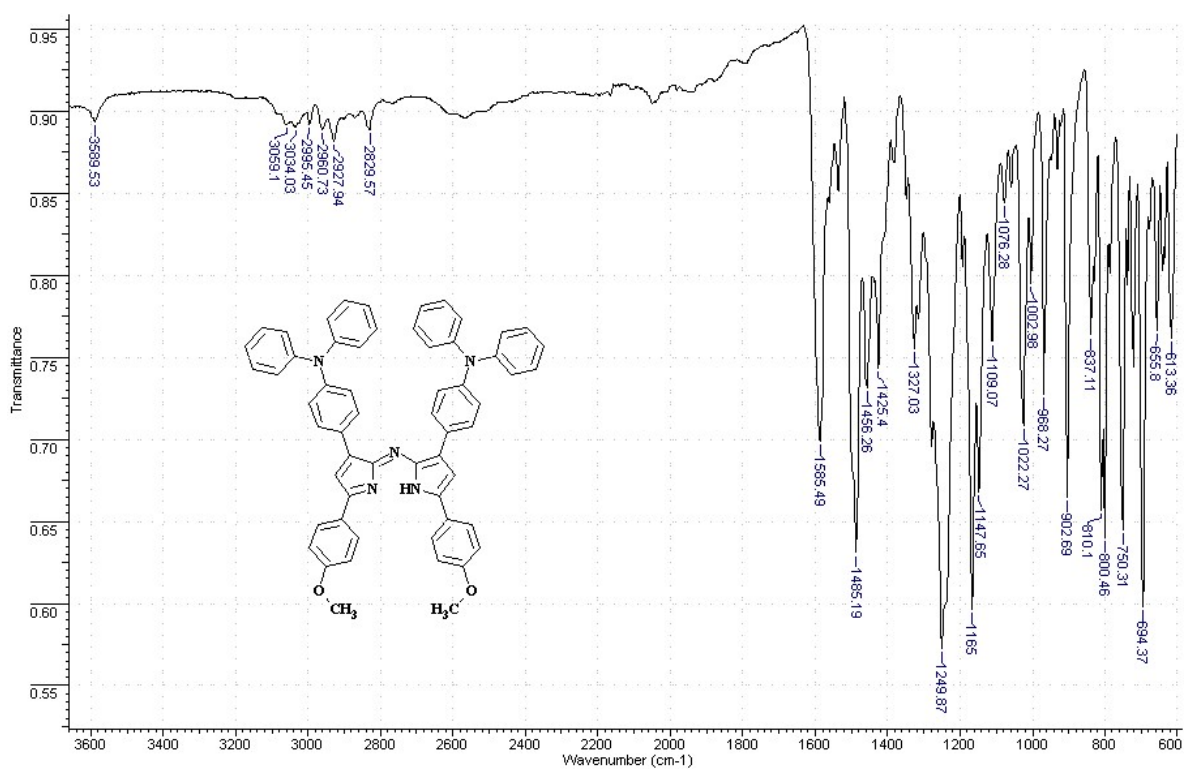Figure S14. IR for compound **2**
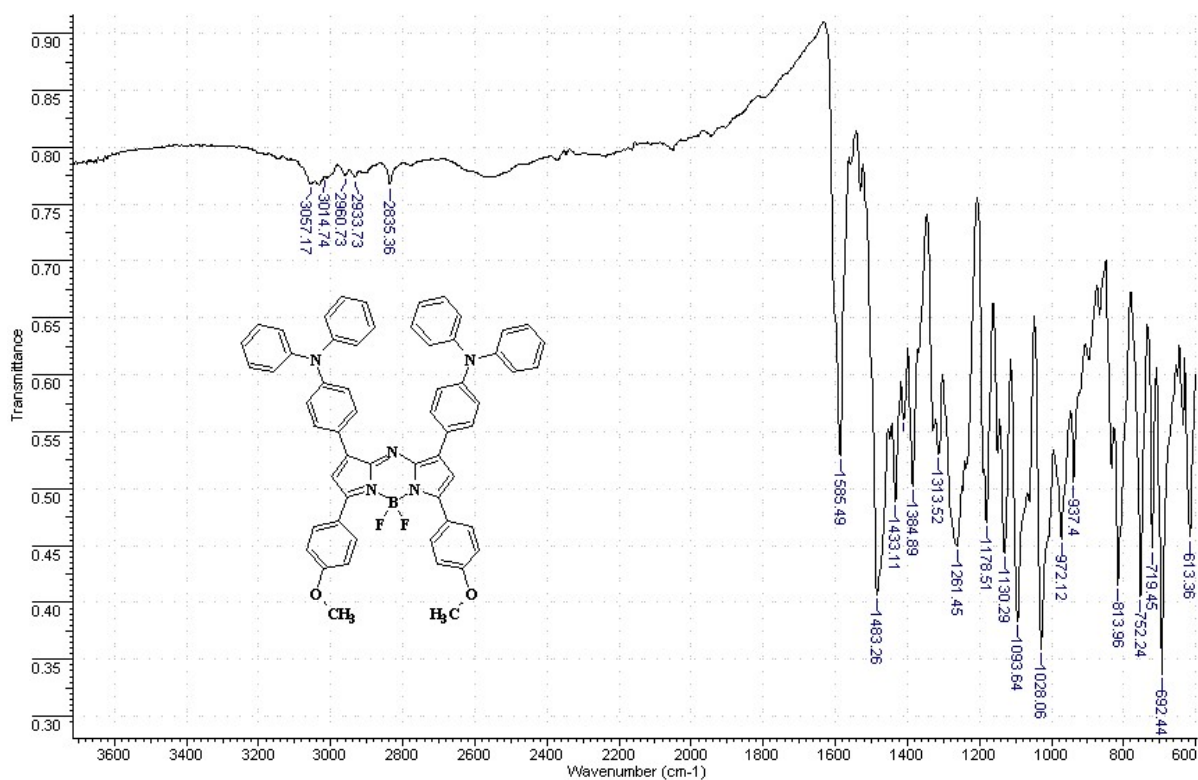
Figure S15. IR for compound **3**

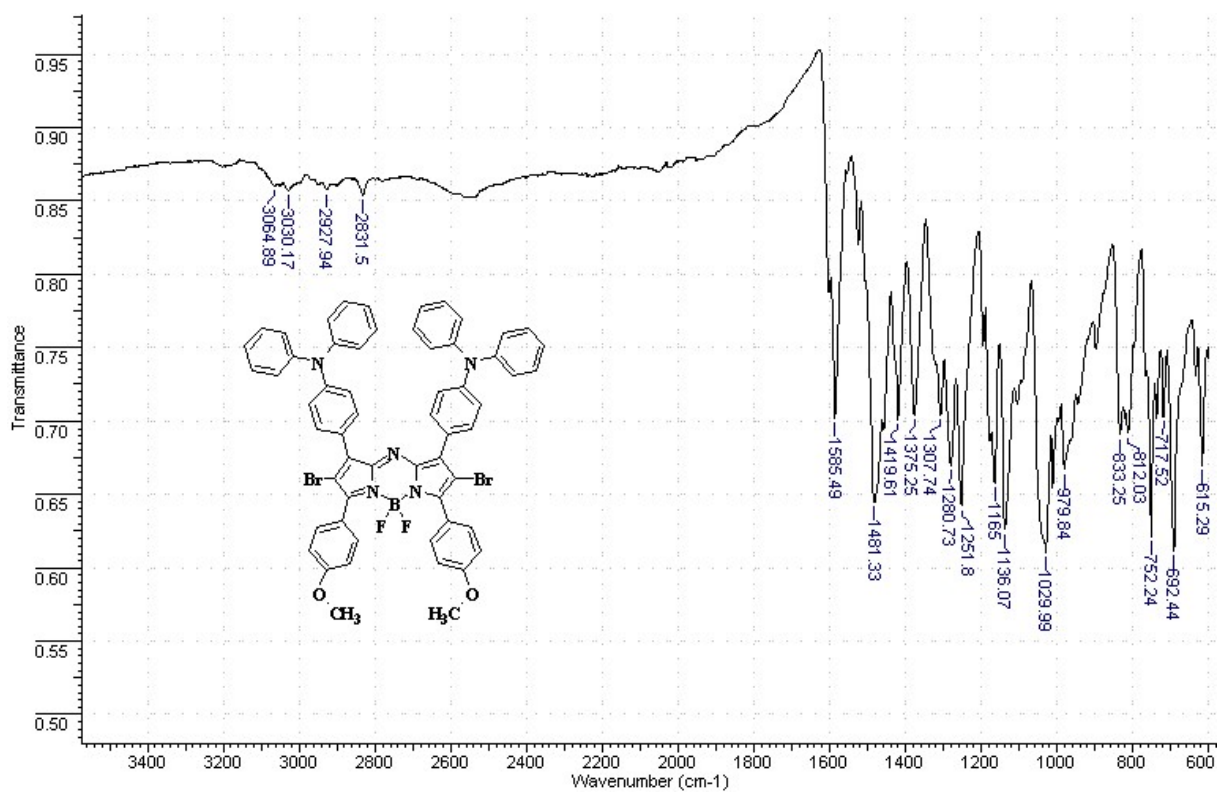Figure S16. IR for compound **4**

Figure S17. IR for compound **5**

References

[1] Gorman A, Killoran J, O'Shea C, Kenna T, Gallagher WM, O'Shea DF. In vitro demonstration of the heavy-atom effect for photodynamic therapy. J Am Chem Soc. 2004;126(34):10619-31.

[2] Fery-Forgues S, Lavabre D. Are fluorescence quantum yields so tricky to measure? A demonstration using familiar stationery products. Journal of Chemical Education. 1999;76(9):1260-4.

[3] Ma J, Yuan X, Kucukoz B, Li S, Zhang C, Majumdar P, et al. Resonance energy transfer-enhanced rhodamine-styryl Bodipy dyad triplet photosensitizers. J Mater Chem C. 2014;2(20):3900-13.

[4] Yilmaz H, Sevinc G, Hayvali M. 3, 3,5 and 2,6 Expanded Aza-BODIPYs Via Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Reactions: Synthesis and Photophysical Properties. J Fluoresc. 2021;31(1):151-64.