

## Supporting Information

# Two-Photon Laser Printing of 3D Multicolor Emissive Polymer Microstructures

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### Outline:

1. General Information
2.  $^1\text{H}$  and  $^{13}\text{C}$  Spectra
3. UV/Vis and Fluorescent Spectra
4. Two-photon Absorption
- 5. Formulations with the Maximum Emitter Concentration**
6. Dose Test Images
7. SEM Images of Resolution Test
8. SEM Image of Z-Stack Multimaterial Print
9. References

## 1. General Information

**Materials:** All chemicals and solvents were purchased from commercial suppliers and used without further purification. Solvents were dried according to standard procedures. Deuterated solvents were bought from Euriso Top or Sigma–Aldrich and used as received.

**Methods:** The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded with a Bruker 300, 400, 500, or 600 MHz spectrometer and are referenced to the residual signal of  $\text{CDCl}_3$  ( $^1\text{H}$ : 7.26 ppm and  $^{13}\text{C}$ : 77.16 ppm).<sup>[1]</sup> Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used to describe the multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, and m = multiplet. The mass spectra were recorded by the department of the organic Chemistry of the University of Heidelberg under the direction of Dr. J. Gross. MALDI spectra were measured on a Bruker ApexQe hybrid 9.4 T FT-ICR or a AutoFlex Speed TOF. EI- spectra were recorded on an AccuTOF GCx from Bruker. The absorption spectra were recorded on a Jasco V-770 UV/Vis spectrometer and were baseline and solvent corrected. The fluorescence spectra were recorded on a Jasco FP-8500 spectrophotometer and emission quantum yields ( $\Phi$ ) were also measured on a JASCO spectrofluorometer FP-8500 equipped with an ILF-835j100 mm integrating sphere.

## 2. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

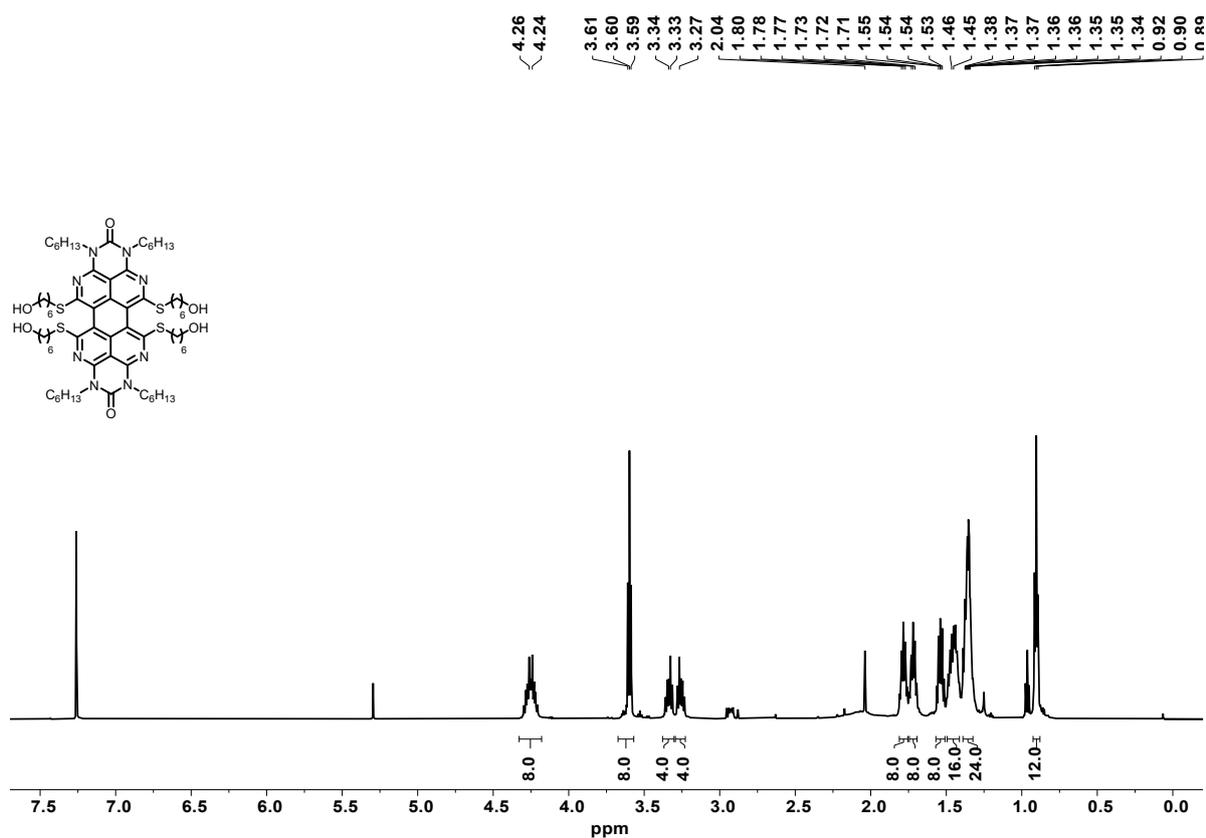


Figure 1:  $^1\text{H}$  NMR spectrum of **2** (600 MHz,  $\text{CDCl}_3$ , rt).

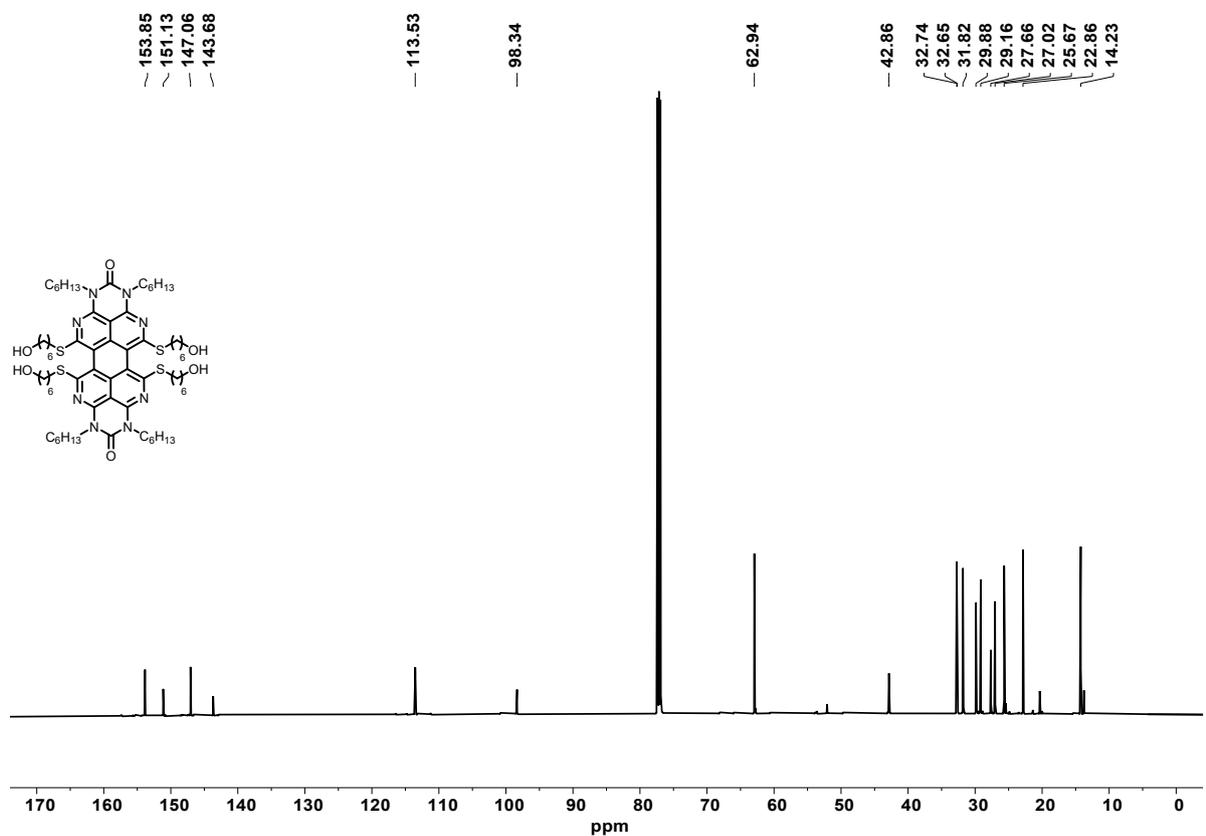


Figure 2:  $^{13}\text{C}$  NMR spectrum of **2** (151 MHz,  $\text{CDCl}_3$ , rt).

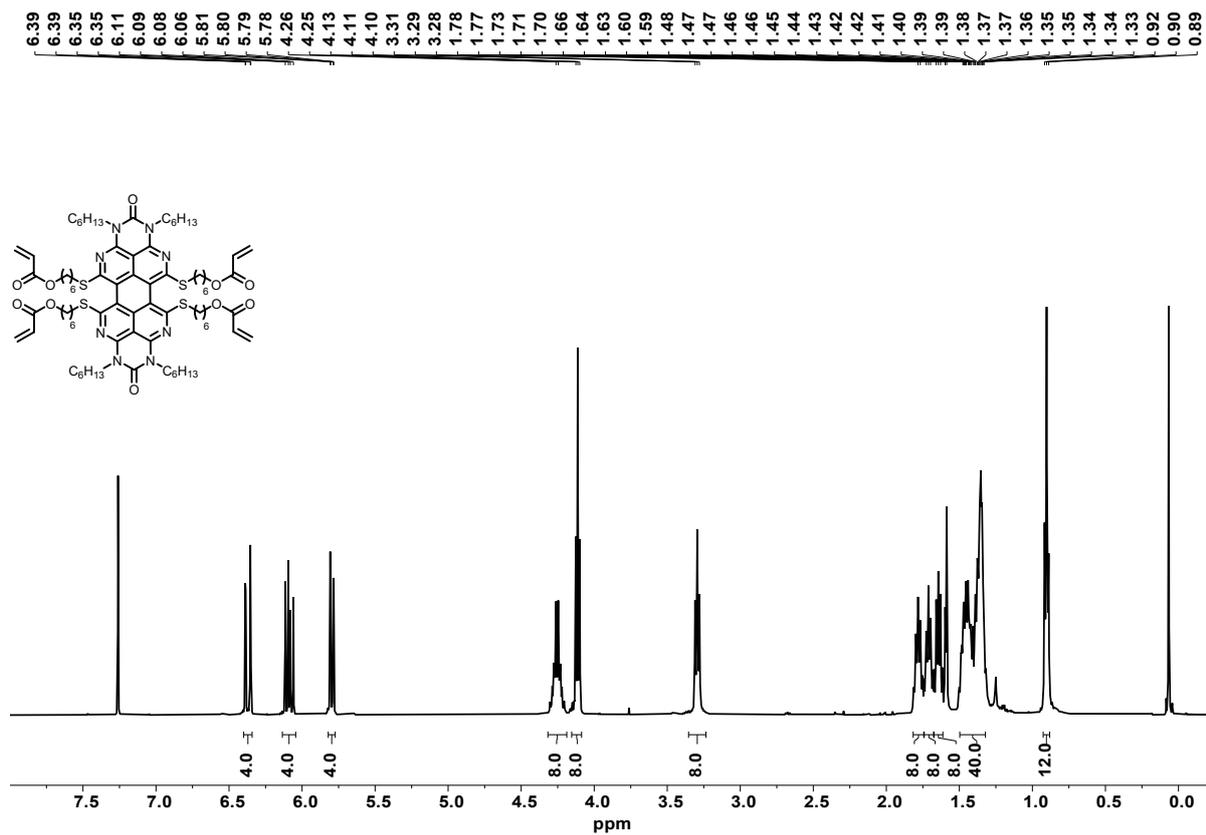


Figure 3: <sup>1</sup>H NMR spectrum of OAPPDO-A4 (500 MHz, CDCl<sub>3</sub>, rt).

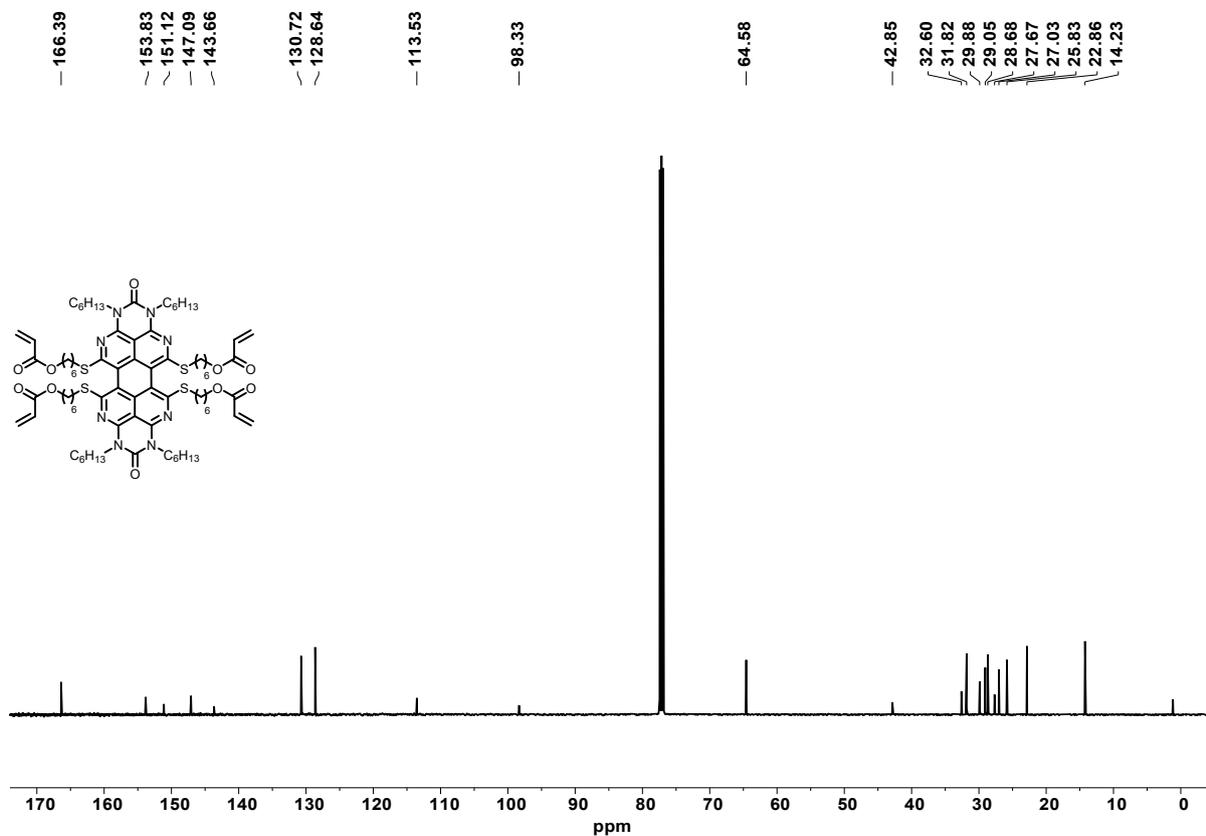


Figure 4: <sup>13</sup>C NMR spectrum of OAPPDO-A4 (126 MHz, CDCl<sub>3</sub>, rt).

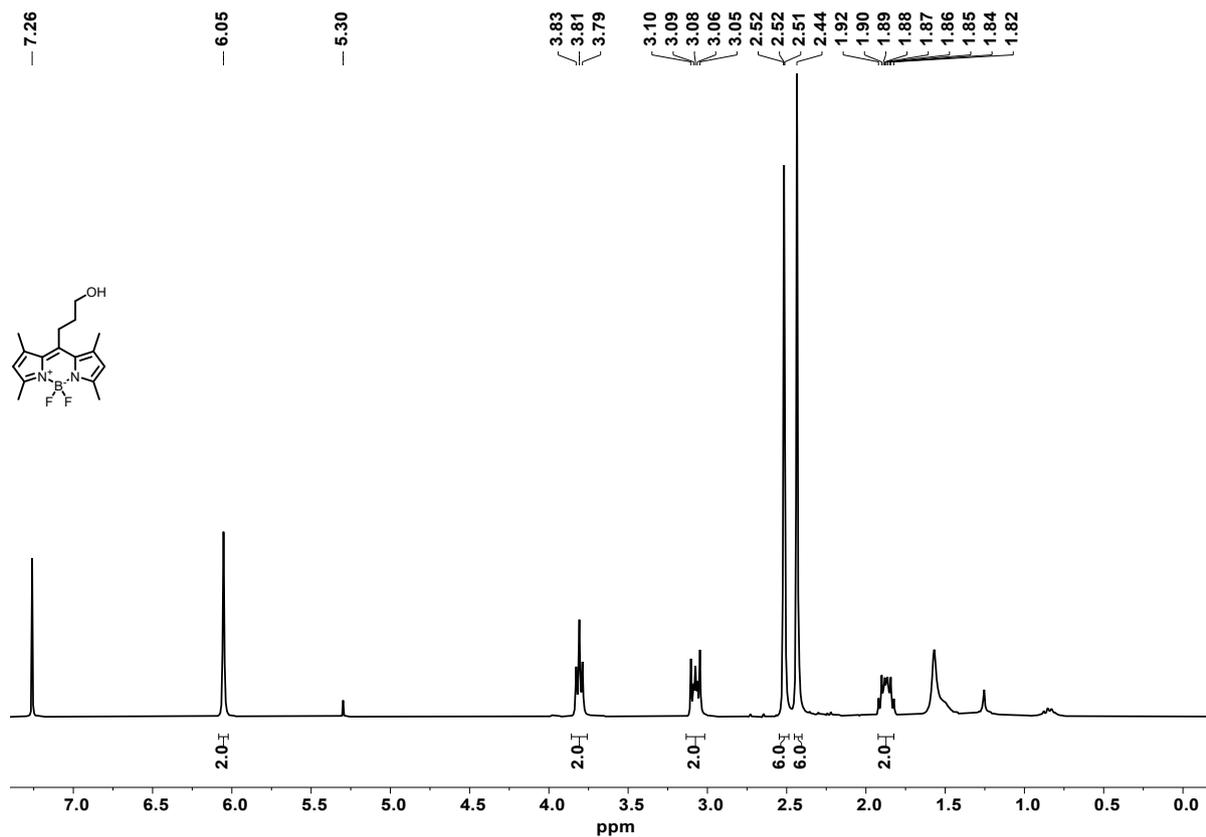


Figure 5: <sup>1</sup>H NMR spectrum of **3** (300 MHz, CDCl<sub>3</sub>, rt).

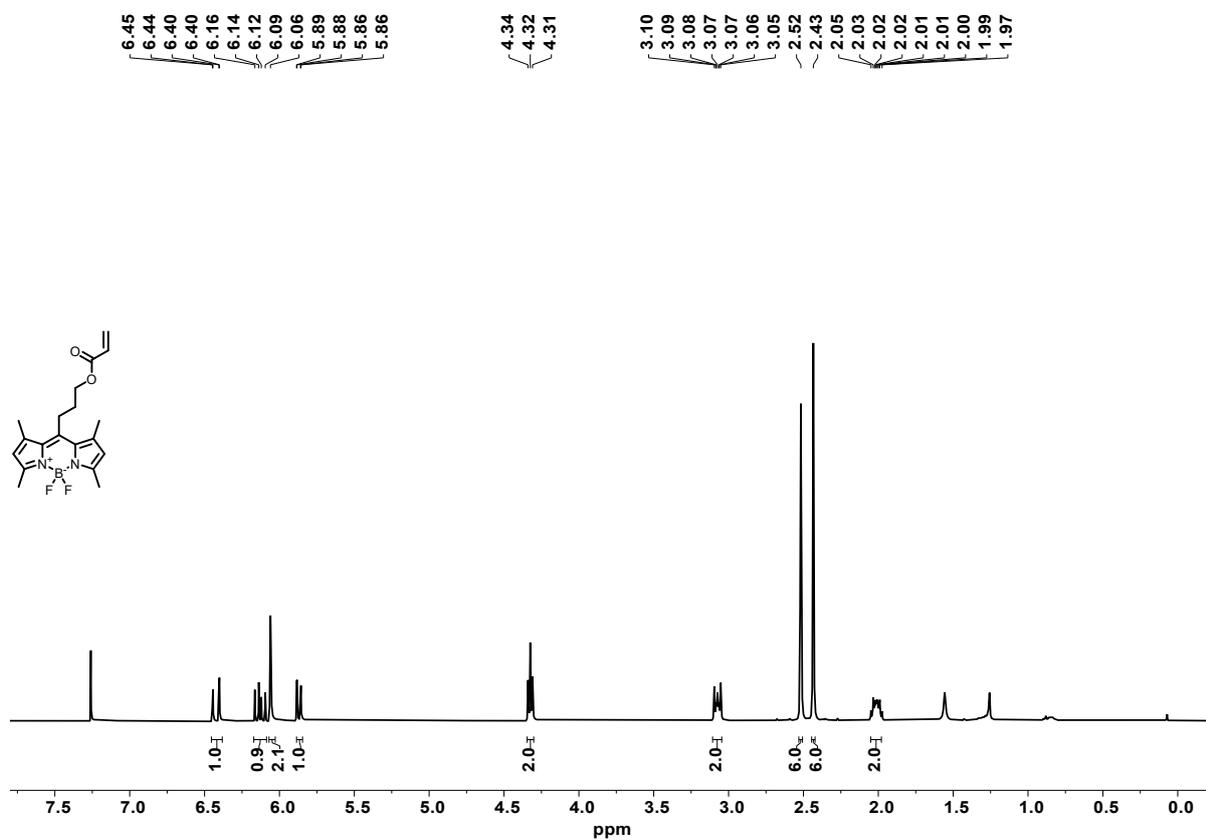
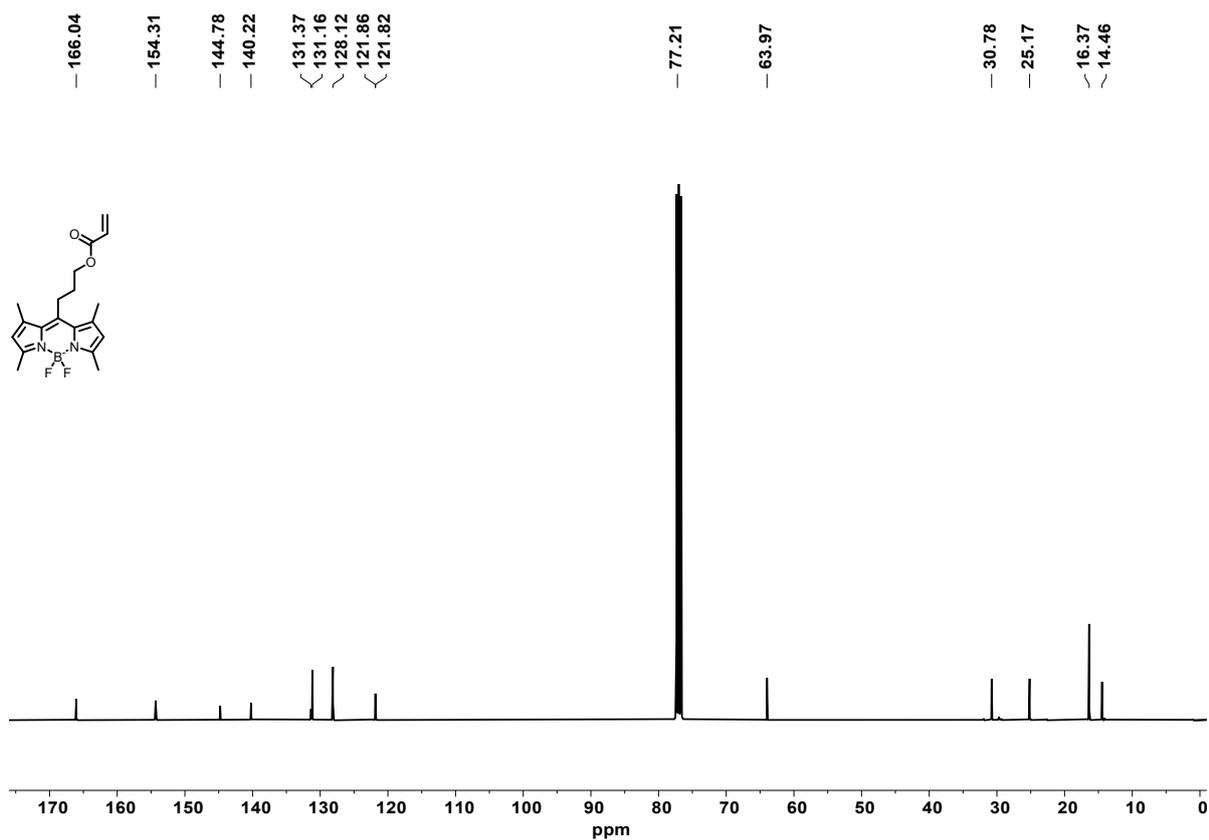
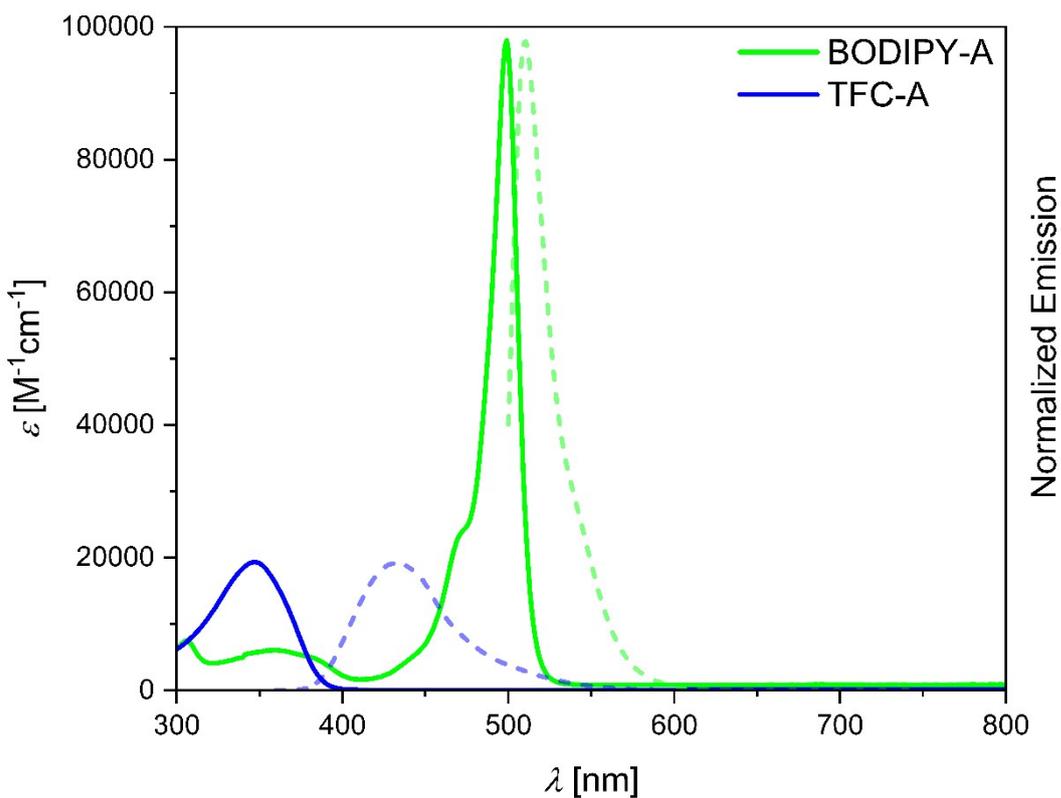


Figure 6: <sup>1</sup>H NMR spectrum of **BODIPY-A** (400 MHz, CDCl<sub>3</sub>, rt).

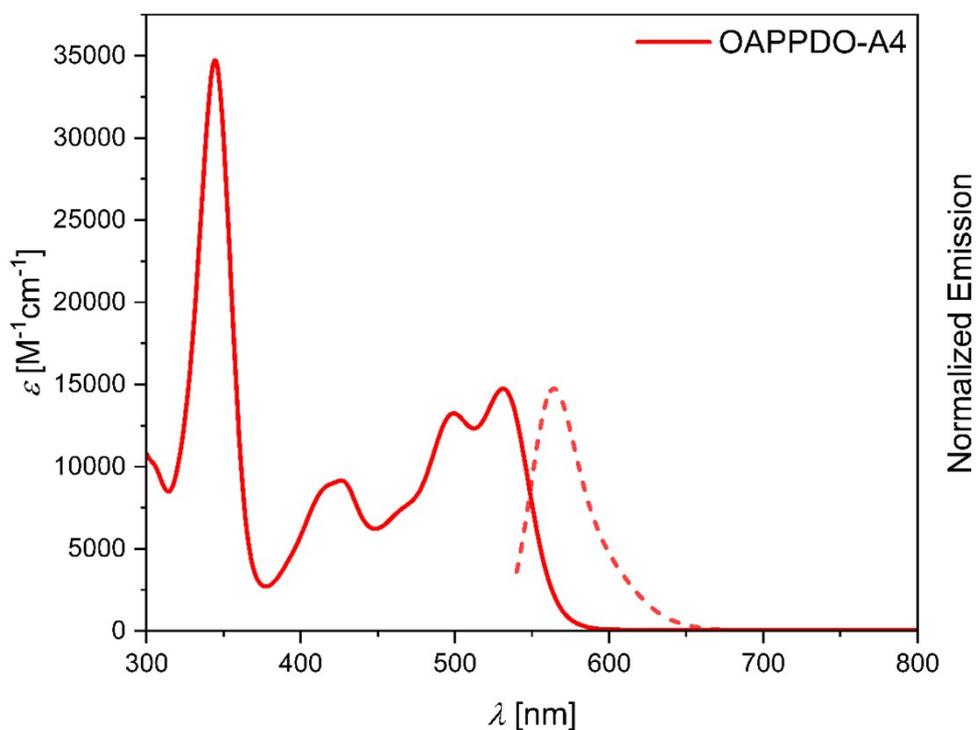


**Figure 7:** <sup>13</sup>C NMR spectrum of **BODIPY-A** (101 MHz, CDCl<sub>3</sub>, rt).

### 3. UV/Vis and Fluorescent Spectra



**Figure 8:** UV/Vis (solid line) and fluorescens spectra (dashed line) of **BODIPY-A** and **TFC-A** measured in DMSO at ambient temperature. Excitation wavelength for the emission spectra for the respective compound **BODIPY-A** (499 nm) and **TFC-A** (347 nm). ( $c \approx 10^{-5}$  M).



**Figure 9:** UV/Vis (solid line) and fluorescens spectra (dashed line) of **OAPPDO-A4** measured in o-xylene at ambient temperature. Excitation wavelength for the emission spectra is 531 nm. ( $c \approx 10^{-5}$  M).

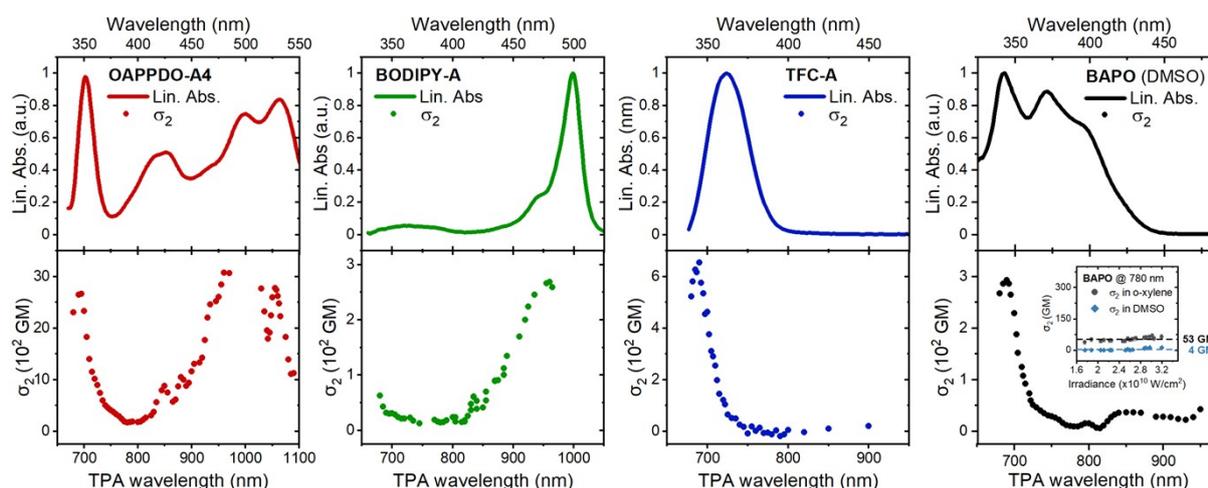
**Table 1:** Photophysical properties of **OAPPDO-A4**, **BODIPY-A**, and **TFC-A**, measured at ambient temperature ( $c \approx 10^{-5}$  M) in DMSO or o-xylene as stated in **Figures 8** and **9**. Fluorescence quantum yields were measured with an Ulbricht sphere (extinction  $E < 0.1$ ).

Dye	$\lambda_{\text{abs,max}}$ [nm]	$\epsilon_{\lambda,\text{max}}$ [M <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_{\text{em,max}}$ [nm]	$\Phi$ [%]	0-0 transition [nm]	Stokes shift [cm <sup>-1</sup> ]
<b>OAPPDO-A4</b>	531	14749	564	77	548	1102
<b>BODIPY-A</b>	499	97927	511	91	505	470
<b>TFC-A</b>	347	19359	432	4	386	5670

#### 4. Two-photon Absorption Measurements

In Figure 10, we present the two-photon absorption measurements of the applied dyes under and the used photoinitiator, among themselves with the linear absorption spectrum at half-wavelength. The wavelength of primary interest is the printing wavelength at  $\lambda = 780 \text{ nm}$ .

The four compounds showcased in the graph - **OAPPDO-A4** (in *o*-xylene), **BODIPY-A** (in DMSO), **TFC-A** (in DMSO), and **BAPO** (in DMSO) - are represented in the colors red, green, blue, and black respectively. At the chosen printing wavelength, all these compounds are observed to be distant from their maximum two-photon absorption, thereby exhibiting a relatively low two-photon absorption cross section ( $\sigma_2$ ). This characteristic is advantageous for the dyes as it prevents unnecessary absorption of photons and thus is not hindering the photoinitiation process.

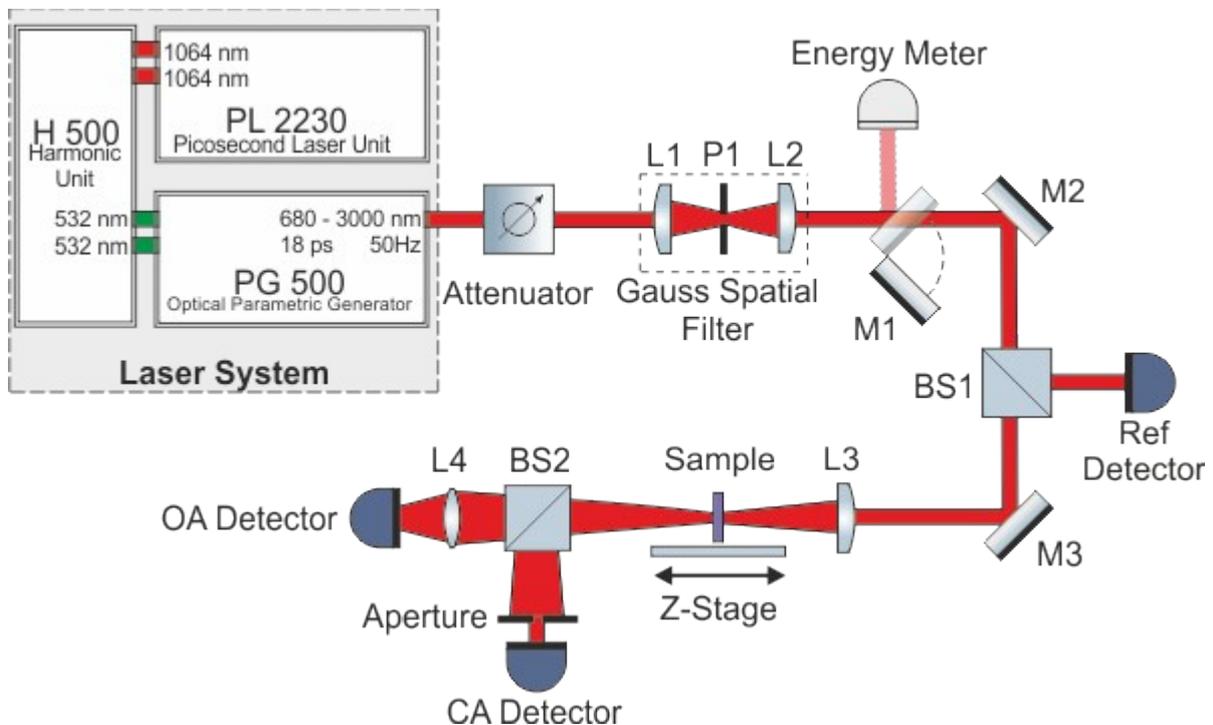


**Figure 10:** Linear absorption (top solid lines) and two-photon absorption cross section ( $\sigma_2$ ) of **OAPPDO-A4** in *o*-xylene (red), **BODIPY-A** in DMSO (green), **TFC-A** in DMSO (blue), and **BAPO** in DMSO (black). Each  $\sigma_2$  represents a z-scan measurement at the given excitation wavelength.

The  $\sigma_2$  values are derived using the well-established z-scan technique.

## Z-Scan Technique and Analysis

The z-scan technique is a method used to measure the nonlinear optical properties of a material. It involves moving a sample along the z-axis of a focused laser beam and measuring the transmittance through the sample. The change in transmittance on intensity modulation provides information about the nonlinear absorption and refraction of the material. A picosecond Nd:YAG laser (Ekspla PL2230) with 50 Hz repetition rate was employed and tuned over a wide near-infrared (NIR) region using a combination of a harmonic generator and a parametric generator. This enabled the recording of Z-scan traces over a wide spectral range with a narrow pulse width ( $\lambda_p = 3.7$  nm). The laser pulses had a Gaussian temporal profile with a full width at half maximum (FWHM) of 18 ps with a gaussian spatial profile.



**Figure 11:** Schematic depiction of the experimental Z-scan setup. L: Lens; P: Pinhole; M: Mirror; BS: Beamsplitter, OA: Open Aperture Detector, CA: Closed Aperture Detector.

The z-scan curves obtained are analyzed and fitted with the theoretical models to extract the two-photon absorption cross-section values ( $\sigma_2$ ).

## Analysis

In open-aperture z-scan traces, the absence of beam gives direct sensitivity to nonlinear absorption. For a temporally Gaussian pulse the normalized transmitted energy can be fitted to the traces for a given sample position  $z$  by:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{\infty} \ln [1 + q_0(z, 0) e^{-t^2}] dt, \quad (4)$$

where  $q_0(z,t) = \beta I_0 L_{\text{eff}} / (1 + x^2)$ , and  $x = z/z_0$  with  $z_0$  being the Rayleigh length,  $\beta$  being the two-photon absorption (2PA) coefficient,  $I_0$  the maximum irradiance and  $L_{\text{eff}}$  the effective sample length.<sup>[2]</sup>

The 2PA cross section  $\sigma_2$  was calculated by:

$$\sigma_2 = \frac{h\nu\beta}{N_A d},$$

with  $N_A$  the Avogadro's constant,  $h\nu$  is the photon energy and  $d$  the concentration.

The 2PA cross section is reported in Göppert–Mayer (GM) units (  $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s molecule}^{-1} \text{ photon}^{-1}$  ).

## Sample Preparation

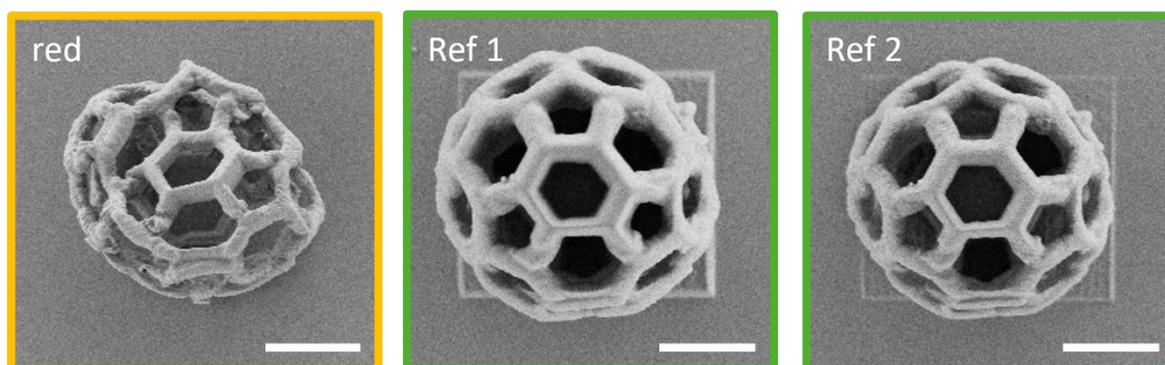
Z-scan measurements were performed in solutions with concentrations of 0.69 mM (in o-xylene) for **OAPPDO-A4**, 4.1 mM (in DMSO) for **BODIPY-A** and 10.6 mM (in DMSO) for **TFC-A** in 2 mm path length Infrasil cuvettes (Starna 1/ST/C//2).

## 5. Formulations with the Maximum Emitter Concentration

**Table 2:** Maximal concentration of the fluorophores to obtain a homogeneous formulation with 80 wt% of a baseformulation containing crosslinker and photoinitiator.

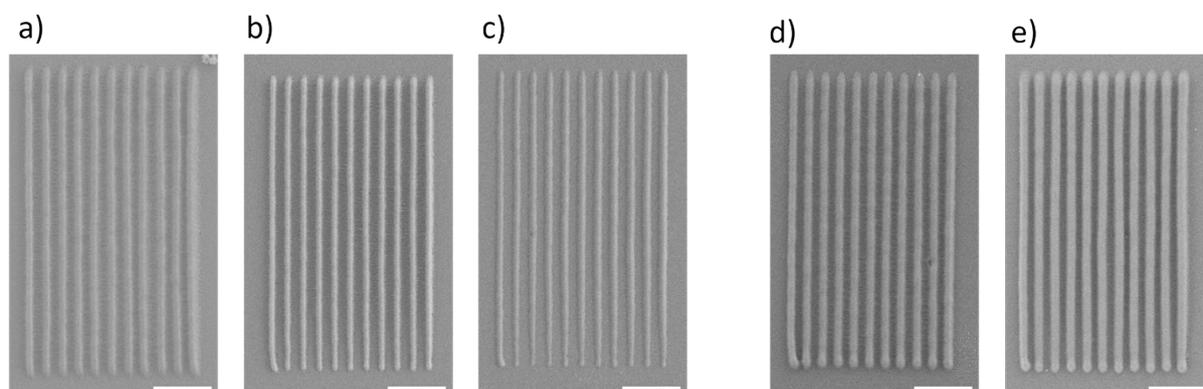
	<b>Crosslinker</b>	<b>Photoinitiator</b>	<b>Emitter</b>	<b>Solvent</b>
	[wt%; mol%]	[wt%; mol%]	[wt%; mol%]	[wt%; mol%]
<b>A</b>	PETA 76.8; 63.1	BAPO 2.1; 1.3	<b>OAPPDO-A4</b> 6.1; 1.0	o-xylene 15.0; 34.6
<b>B</b>	PETA 78.1; 56.0	BAPO 2.1; 1.1	<b>BODIPY-A</b> 5.3; 3.2	DMSO 14.5; 39.8
<b>C</b>	PETA 78.8; 57.9	BAPO 2.1; 1.1	<b>TFC-A</b> 3.6; 2.8	DMSO 13.6; 38.2

## 6. Dose Test Images



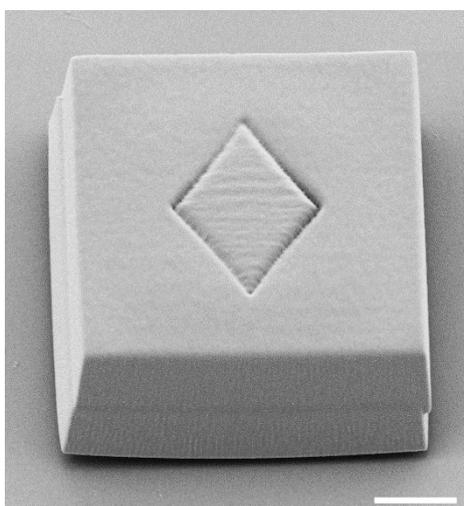
**Figure 12:** SEM images of the printability test for the RGB and two reference formulations using buckyball microstructures. An example for a Buckyball in the yellow region containing **OAPPDO-A4** and the two buckyballs fabricated from the reference formulations in their respective printing window are shown (Scalebars = 5  $\mu\text{m}$ ).

## 7. Resolution and Minimal Feature Size Analysis



**Figure 13:** Resolution tests with the working formulations. a) **TFC-A** containing formulation, b) **BODIPY-A** containing formulation, c) **Ref2** formulation d) **OAPPDO-A4** containing formulation e) **Ref1** formulation (All scalebars = 2  $\mu\text{m}$ ).

## 8. SEM Image of Z-Stack Multimaterial Print



**Figure 14:** Tilted SEM image of the 2PLP fabricated multi-material z-stack (Scalebar = 5  $\mu\text{m}$ ).

## 9. References

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176.
- [2] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, E. W. van Stryland, *IEEE J. Quantum Electron.* **1990**, 26, 760.