

# Supporting Information

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# 1. Centripetal triazines 1-4

## 1.1. Synthesis and characterization of chromophores 1-4

### General Methods

THF was dried in Puresolv™ micro solvent purification system. All commercial chemicals and solvents were purchased from suppliers such as Sigma Aldrich and TCI at reagent grade and were used as obtained. All reactions were carried out in flame-dried flasks under argon. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 365 nm). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400/500 and 100/125 MHz, respectively, with Bruker AVANCE 400/500 instruments. Chemical shifts in <sup>1</sup>H, <sup>13</sup>C spectra are reported in ppm relative to the signal of Me<sub>4</sub>Si. The residual solvent signal in the <sup>1</sup>H and <sup>13</sup>C-NMR spectra was used as an internal reference (CDCl<sub>3</sub> 7.25 and 77.23 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet), and m (multiplet), apparent coupling constants of multiplets (<sup>3</sup>J or <sup>4</sup>J) are given in Hz. High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive- or negative-ion mode over a normal mass range (*m/z* 50 – 2000) with resolution 100,000 at *m/z* = 400. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The used matrix was 2,5-dihydroxybenzoic acid (DHB). Mass spectra were averaged over the whole MS record for all measured samples. Absorption and fluorescence spectra were measured on a Duetta™ HORIBA spectrophotometer in THF, toluene or acetone at 25 °C.

### Chromophore 1

4-(*N,N*-Diphenylamino)benzonitrile **6** (246 mg; 0.91 mmol) was dissolved under the inert atmosphere of argon in CHCl<sub>3</sub> (5 mL), the solution was cooled to 0 °C, trifluoromethanesulfonic acid (343 mg; 2.28 mmol) was added dropwise and the reaction mixture was stirred for 6 days at 25 °C. The mixture was extracted with dichloromethane (3 × 50 mL), the combined organic extracts were washed with aq. NaHCO<sub>3</sub> (50 mL), water (50 mL), brine (50 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography (SiO<sub>2</sub>; hexane/DCM 1:1). The title compound **1** (25 mg, 10 %) was

isolated as a yellow powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.08–7.13 (m, 12H), 7.16 (d,  $J$  = 7.5 Hz, 12H), 7.3 (t,  $J$  = 7.5 Hz, 12H), 8.52 (d,  $J$  = 9.0 Hz, 6H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 121.44, 124.18, 125.70, 129.53, 129.66, 130.16, 147.19, 151.70, 170.70 ppm. HR-MALDI-MS (DHB): calcd for  $\text{C}_{57}\text{H}_{42}\text{N}_6$  ( $\text{M}^+$ ) 810.34655, found 810.34761.

### Chromophore 2

2,4,6-Trimethyl-1,3,5-triazine **7** (11 mg; 0.09 mmol) and KOH (0.2 g; 3.57 mmol) were dissolved in methanol (1 mL) in the round bottom flask. A solution of 4-(*N,N*-diphenylamino)benzaldehyde **5** (95 mg; 0.35 mmol) in methanol (2 mL) and THF (1 mL) was added and the reaction mixture was refluxed for 4 h. The mixture was extracted with dichloromethane (3  $\times$  50 mL), the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography ( $\text{SiO}_2$ ; hexane/DCM 1:4). The title compound **2** (21 mg, 26 %) was isolated as an orange powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.00 (d,  $J$  = 15.5 Hz, 3H), 7.04 (d,  $J$  = 9 Hz, 6H, Ar), 7.09 (t,  $J$  = 7.5 Hz, 6H, Ar), 7.15 (d,  $J$  = 7.5 Hz, 12H), 7.30 (t,  $J$  = 7.5 Hz, 12H), 7.52 (d,  $J$  = 9 Hz, 6H), 8.18 (d,  $J$  = 15.5 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 122.13, 124.04, 124.12, 125.52, 129.01, 129.43, 129.65, 141.07, 147.24, 149.58, 171.46 ppm. HR-MALDI-MS (DHB): calcd for  $\text{C}_{63}\text{H}_{48}\text{N}_6$  ( $\text{M}^+$ ) 888.39350, found 888.39471.

### Chromophore 3

2,4,6-Tris(4-bromophenyl)-1,3,5-triazine **9** (100 mg; 0.183 mmol), 2-(4-(*N,N*-diphenylamino)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **10** (400 mg; 1.1 mmol) and  $\text{K}_2\text{CO}_3$  (759 mg; 5.5 mmol) were dissolved in THF (10 mL) and water (1 mL) under Ar inert atmosphere. The reaction mixture was bubbled with argon for 20 minutes, whereupon  $\text{PdCl}_2(\text{PPh}_3)_2$  (46 mg; 0.066 mmol) was added. The reaction mixture was refluxed for 24 h and cooled to room temperature. The mixture was extracted with dichloromethane (3  $\times$  50 mL), the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography ( $\text{SiO}_2$ ; hexane/DCM 1:1). The title compound **3** (120 mg, 63 %) was isolated as a yellow powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.05 (t, 6H,  $J$  = 7.5 Hz), 7.14–7.17 (m, 14H), 7.26–7.29 (m, 16H), 7.58 (d,  $J$  = 8.5 Hz, 6H), 7.77 (d,  $J$  = 8.5 Hz,

6H), 8.82 (d,  $J = 8.5$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 123.43, 123.73, 124.89, 126.87, 128.13, 129.57, 129.70, 134.06, 134.92, 144.75, 147.72, 148.13, 171.51$  ppm. HR-MALDI-MS (DHB): calcd for  $\text{C}_{75}\text{H}_{54}\text{N}_6$  ( $\text{M}^+$ ) 1038.44045, found 1038.44249.

#### Chromophore 4

2,4,6-Tris(4-bromophenyl)-1,3,5-triazine **9** (55 mg; 0.1 mmol), *N,N*-diphenyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline **11** (200 mg; 0.5 mmol) and  $\text{K}_2\text{CO}_3$  (370 mg; 2.68 mmol) was dissolved in THF (10 mL) and water (1 mL) under Ar inert atmosphere. The reaction mixture was bubbled with argon for 20 minutes and  $\text{PdCl}_2(\text{PPh}_3)_2$  (23 mg; 0.033 mmol) was added. The reaction mixture was refluxed for 24 h and cooled to room temperature. The mixture was extracted with dichloromethane ( $3 \times 50$  mL), the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography ( $\text{SiO}_2$ ; hexane/DCM 1:1). The title compound **4** (46 mg, 41 %) was isolated as a yellow powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.02\text{--}7.07$  (m, 12H), 7.10–7.12 (m, 12H), 7.19–7.28 (m, 18H, overlapped with residual  $\text{CHCl}_3$ ), 7.41 (d,  $J = 8.5$  Hz, 6H), 7.66 (d,  $J = 8.5$  Hz, 6H), 8.73 (d,  $J = 8.5$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 123.44, 123.48, 124.89, 126.48, 126.64, 127.88, 129.55, 130.36, 131.17, 135.27, 141.95, 147.64, 148.03, 171.29$  (one signal is missing) ppm. HR-MALDI-MS (DHB): calcd for  $\text{C}_{81}\text{H}_{60}\text{N}_6$  ( $\text{M}^+$ ) 1116.48740, found 1116.48955.

#### Precursor 6

4-(*N,N*-Diphenylamino)benzaldehyde **5** (300 mg; 1.01 mmol), hydroxylamine hydrochloride (92 mg; 1.32 mmol), acetic acid (226 mg; 3.75 mmol) and pyridine (130 mg; 1.65) were stirred at 150 °C for 2.5 h. The mixture was cooled to room temperature, extracted with dichloromethane ( $3 \times 50$  mL) and the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried ( $\text{Na}_2\text{SO}_4$ ). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography ( $\text{SiO}_2$ ; hexane/DCM 1:1). The title compound **6** (246 mg, 83 %) was isolated as a white powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.94\text{--}6.96$  (m, 2H, Ar), 7.13–7.17 (m, 6H, Ar), 7.31–7.34 (m, 4H, Ar), 7.4–7.41 (m, 2H, Ar) ppm.  $^{13}\text{C}$  NMR

(125 MHz, CDCl<sub>3</sub>):  $\delta$  = 102.44, 119.7, 119.8, 125.17, 126.2, 129.81, 133.22, 145.97, 151.6 ppm. The obtained characteristics agree with the reported data.<sup>1</sup>

### Precursor 9

4-Bromobenzonitrile **8** (1.5 g; 8.2 mmol) was slowly added to trifluoromethanesulfonic acid (4 mL; 15.7 mmol) placed in a round bottom flask at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at 25 °C for 48 h. Water (5 mL) was added and the mixture was neutralized with aq. NaOH. The mixture was extracted with dichloromethane (3 × 50 mL) and the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The organic solvents were evaporated in vacuo. The title compound **9** (1.252 g, 83%) was isolated as a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.7 (d, *J* = 8.5 Hz, 2H, Ar), 8.6 (d, *J* = 8.5 Hz, 2H, Ar) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 128.06, 130.7, 132.23, 134.98, 171.3 ppm. HR-MALDI-MS (DHB): calcd for C<sub>21</sub>H<sub>13</sub>Br<sub>3</sub>N<sub>3</sub> [(M+H)<sup>+</sup>] 543.86541, found 543.86622. The obtained characteristics agree with the reported data.<sup>2</sup>

### Precursor 11

4-Bromo-*N,N*-diphenylaniline **12** (470 mg; 1.45 mmol) and vinylboronic acid pinacol ester **13** (231 mg; 1.5 mmol) were dissolved in toluene (8 mL) and diisopropylamine (0.84 mL) under Ar inert atmosphere. The reaction mixture was bubbled with argon for 20 minutes, whereupon Pd[P(*t*Bu)<sub>3</sub>]<sub>2</sub> (38 mg; 0.074 mmol) was added. The reaction mixture was refluxed for 24 h, cooled to room temperature, extracted with dichloromethane (3 × 50 mL) and the combined organic extracts were washed with water (50 mL), brine (50 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The organic solvents were evaporated in vacuo and the crude product was purified by column chromatography (SiO<sub>2</sub>; hexane/DCM 1:1). The title compound **11** (200 mg, 34 %) was isolated as a yellow solid mixture of *E/Z* isomers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.38 (s, 12H, CH<sub>3</sub>), 6.09 (d, *J* = 18.4 Hz, 1H), 7.06–7.08 (m, 2H, Ar), 7.09–7.13 (m, 3H, Ar), 7.16–7.18 (m, 4H, Ar), 7.31–7.33 (m, 4H, Ar), 7.41–7.44 (m, 2H, Ar) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 25.01, 83.42, 122.78, 123.53, 125.07, 128.22, 129.45, 129.52, 131.48, 147.55, 148.75, 149.21 ppm. HR-MALDI-MS (DHB): calcd for C<sub>26</sub>H<sub>28</sub>BNO<sub>2</sub> (M<sup>+</sup>) 397.22076, found 397.22178

<sup>1</sup> S. B. Mane et al., *Tetrahedron* 2015, **71**, 7977.

<sup>2</sup> T. He et al., *J. Am. Chem. Soc.* 2020, **142**, 13491.

## 1.2. NMR spectra

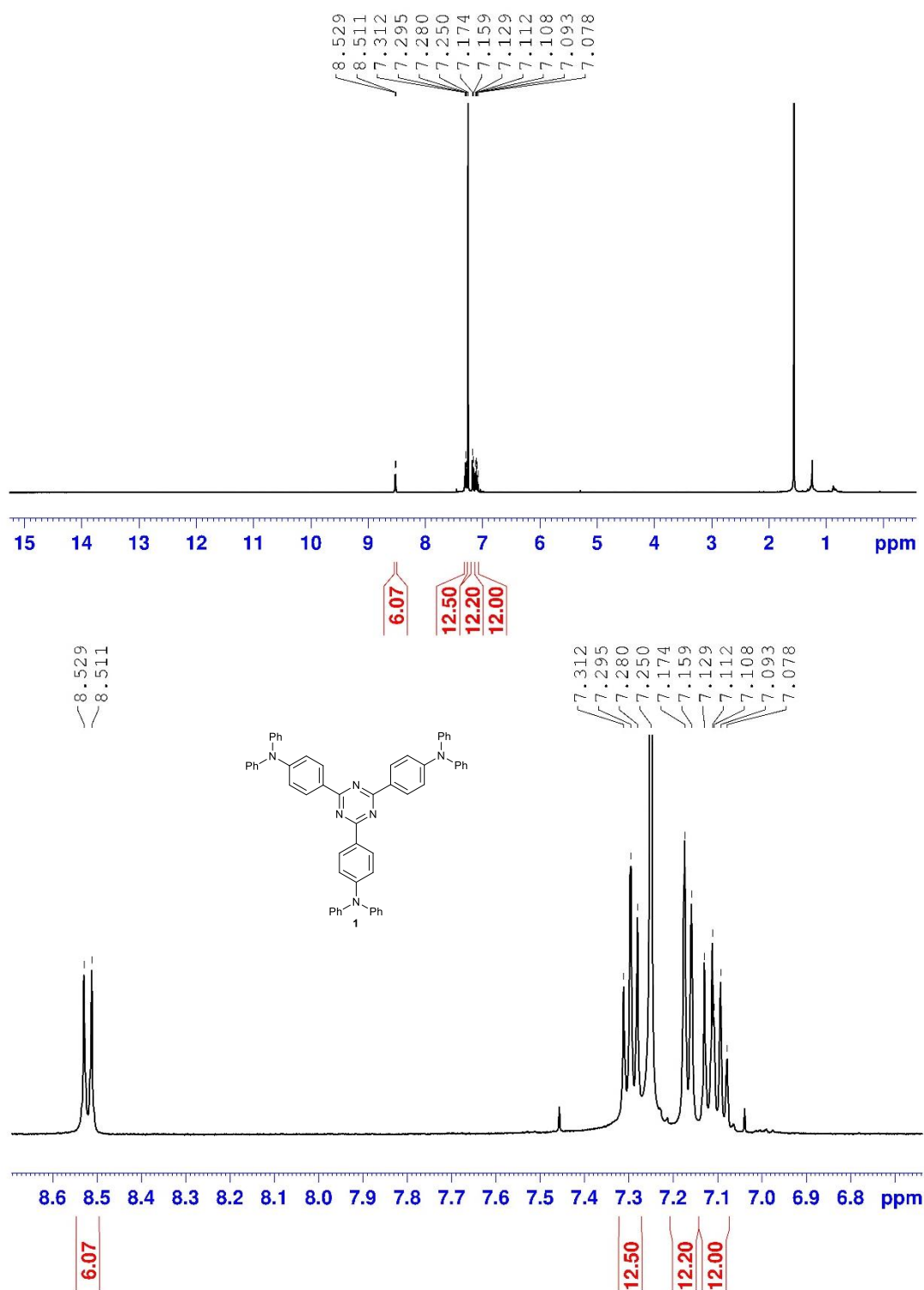


Figure S1. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) spectra of chromophore 1.

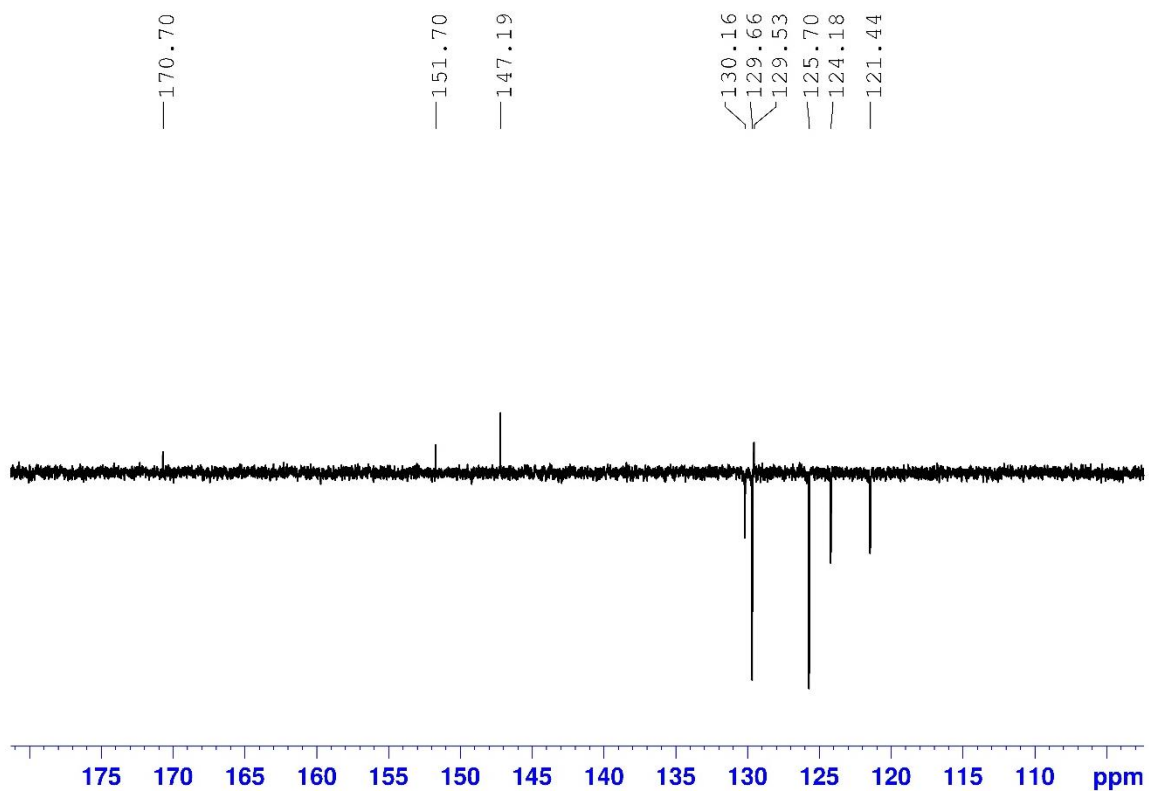
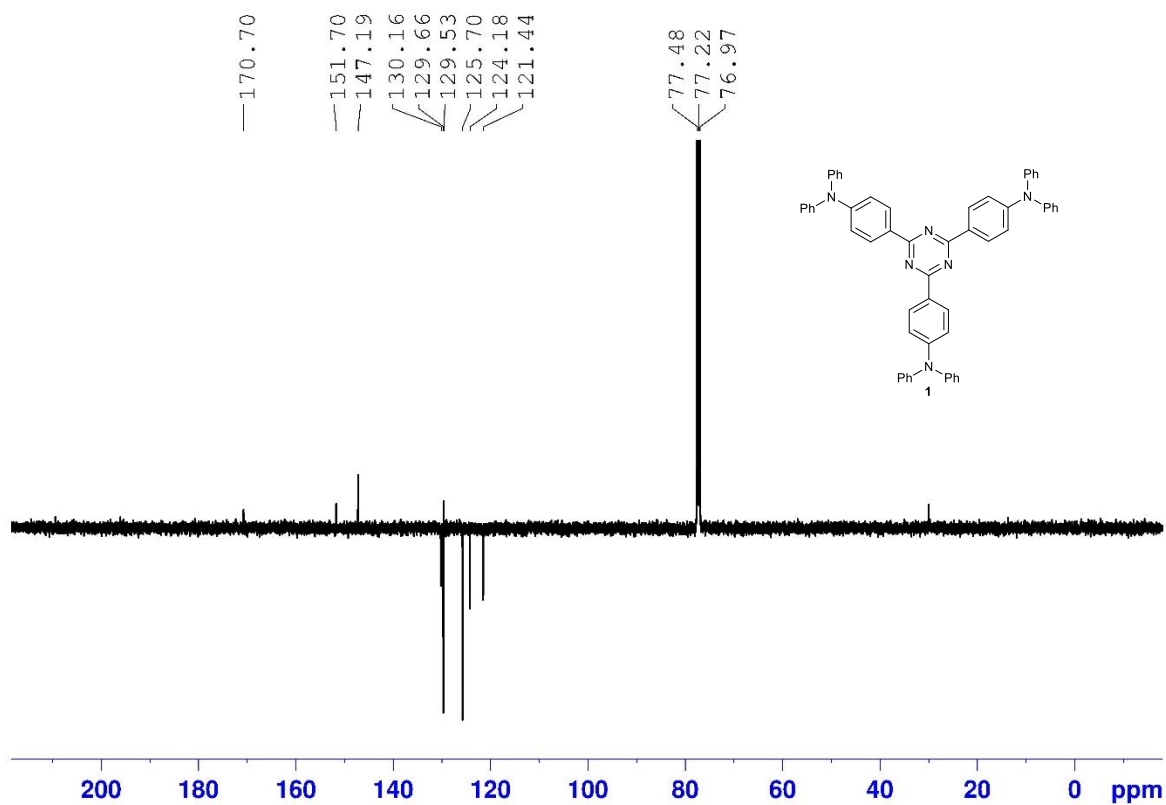
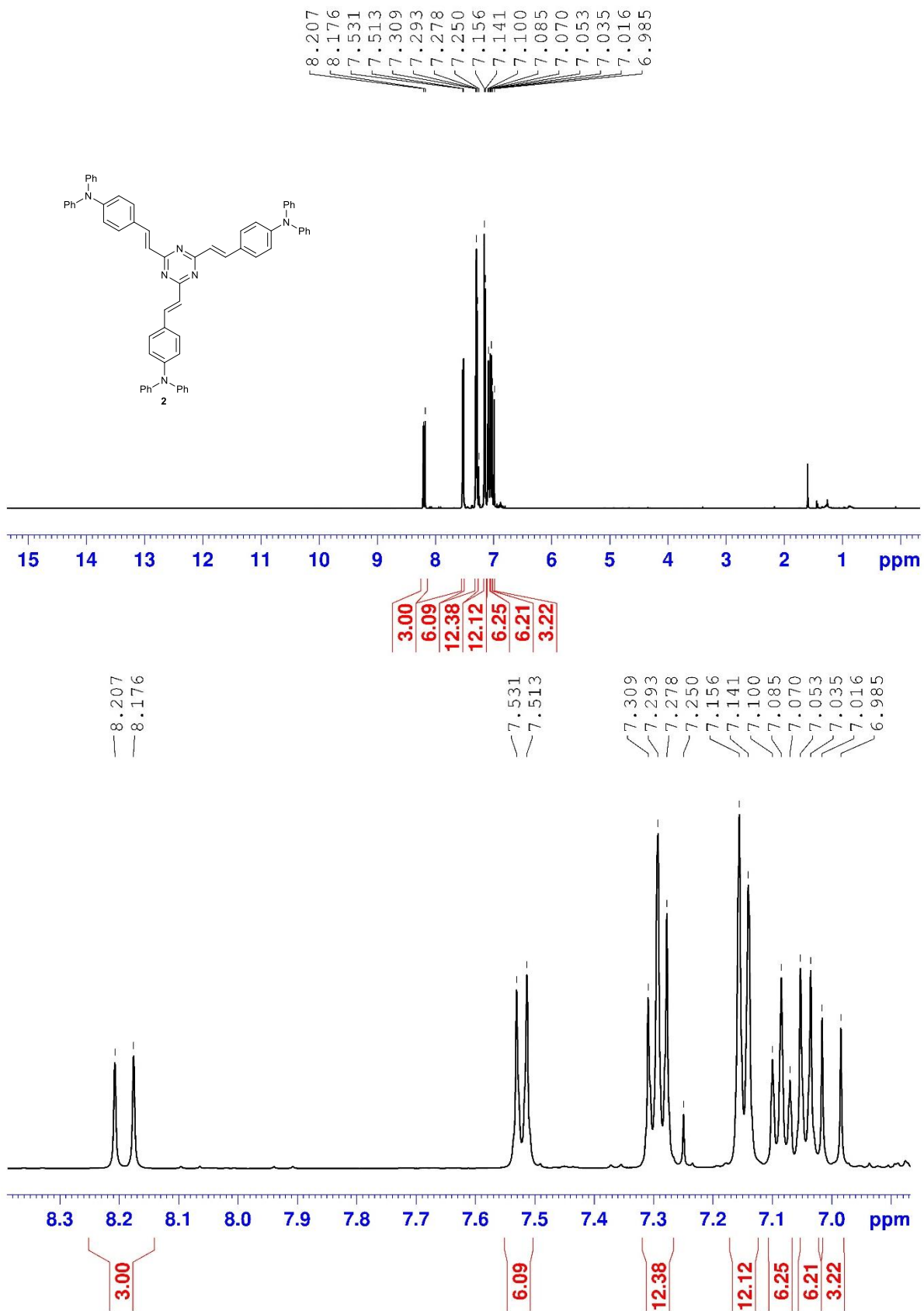
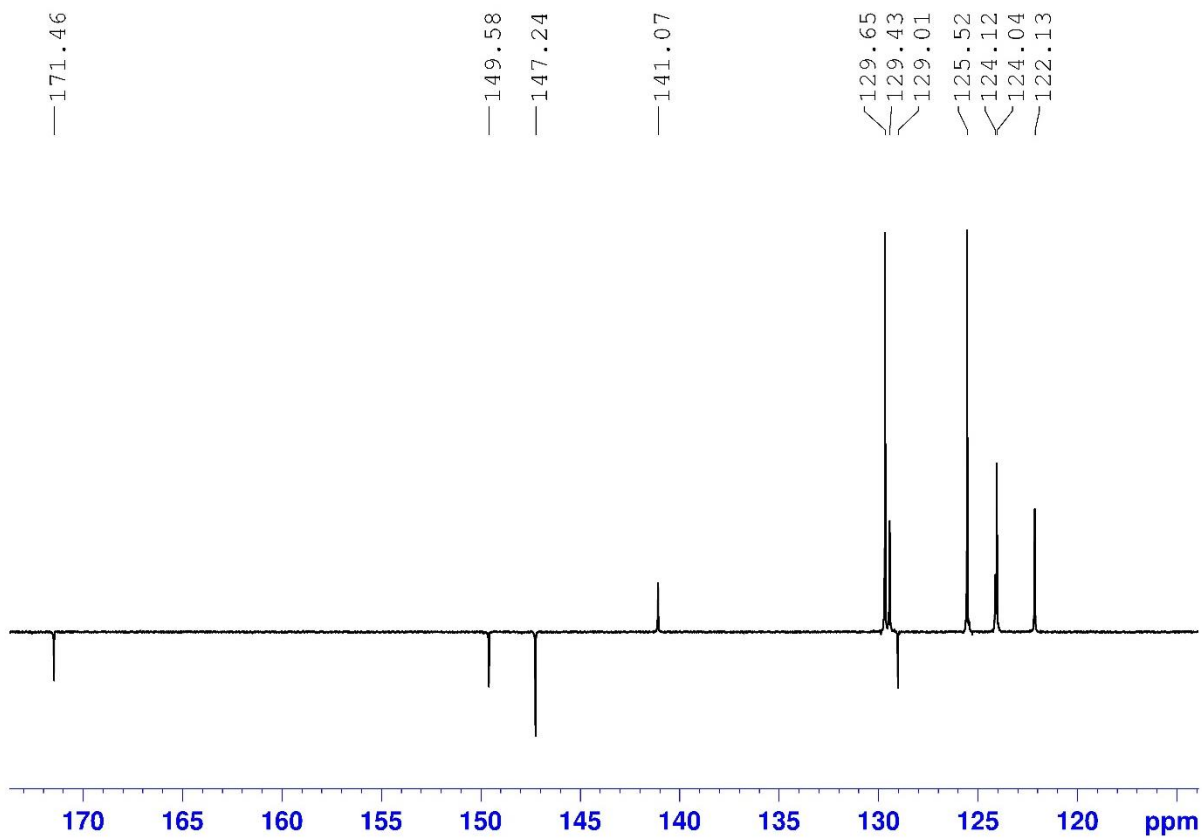
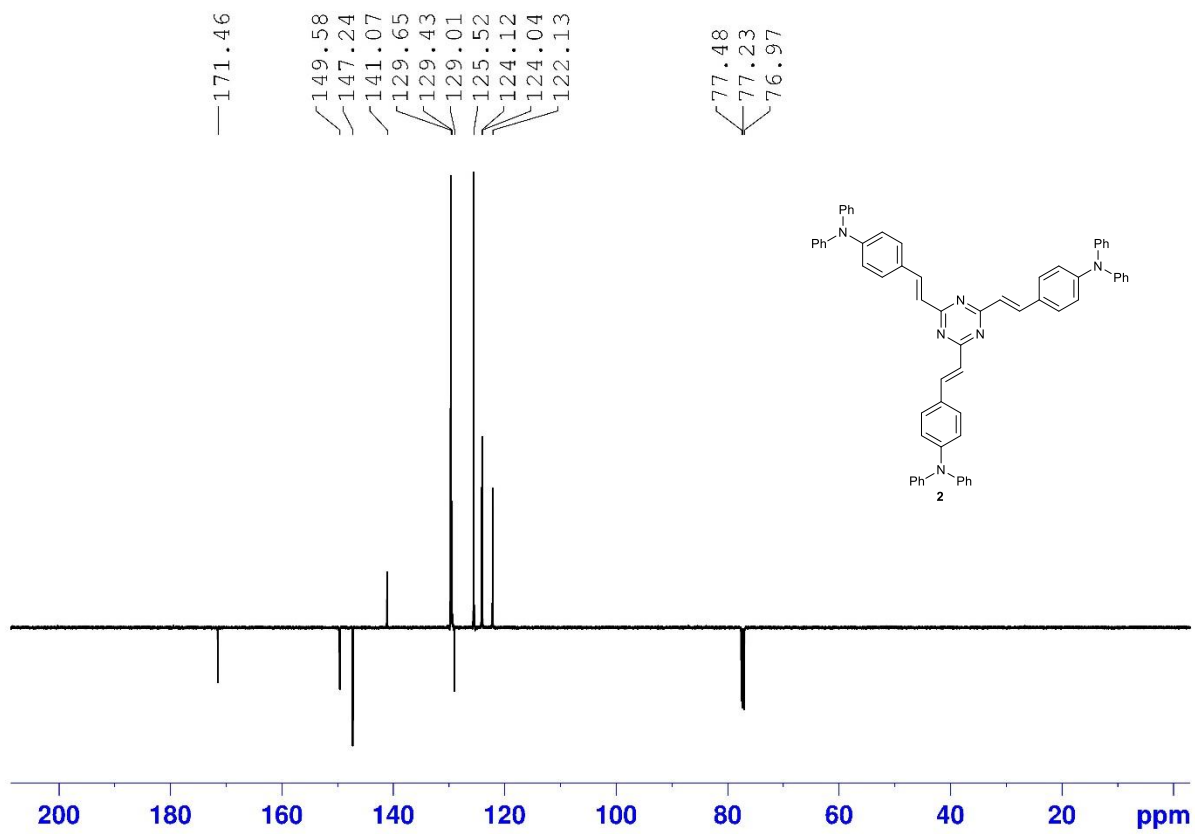


Figure S2.  $^{13}\text{C}$ -NMR APT (125 MHz,  $\text{CDCl}_3$ ) spectra of chromophore 1.



**Figure S3.** <sup>1</sup>H-NMR spectra of chromophore 2 (500 MHz, CDCl<sub>3</sub>).





**Figure S4.**  $^{13}\text{C}$ -NMR spectra of chromophore **2** (125 MHz,  $\text{CDCl}_3$ ).

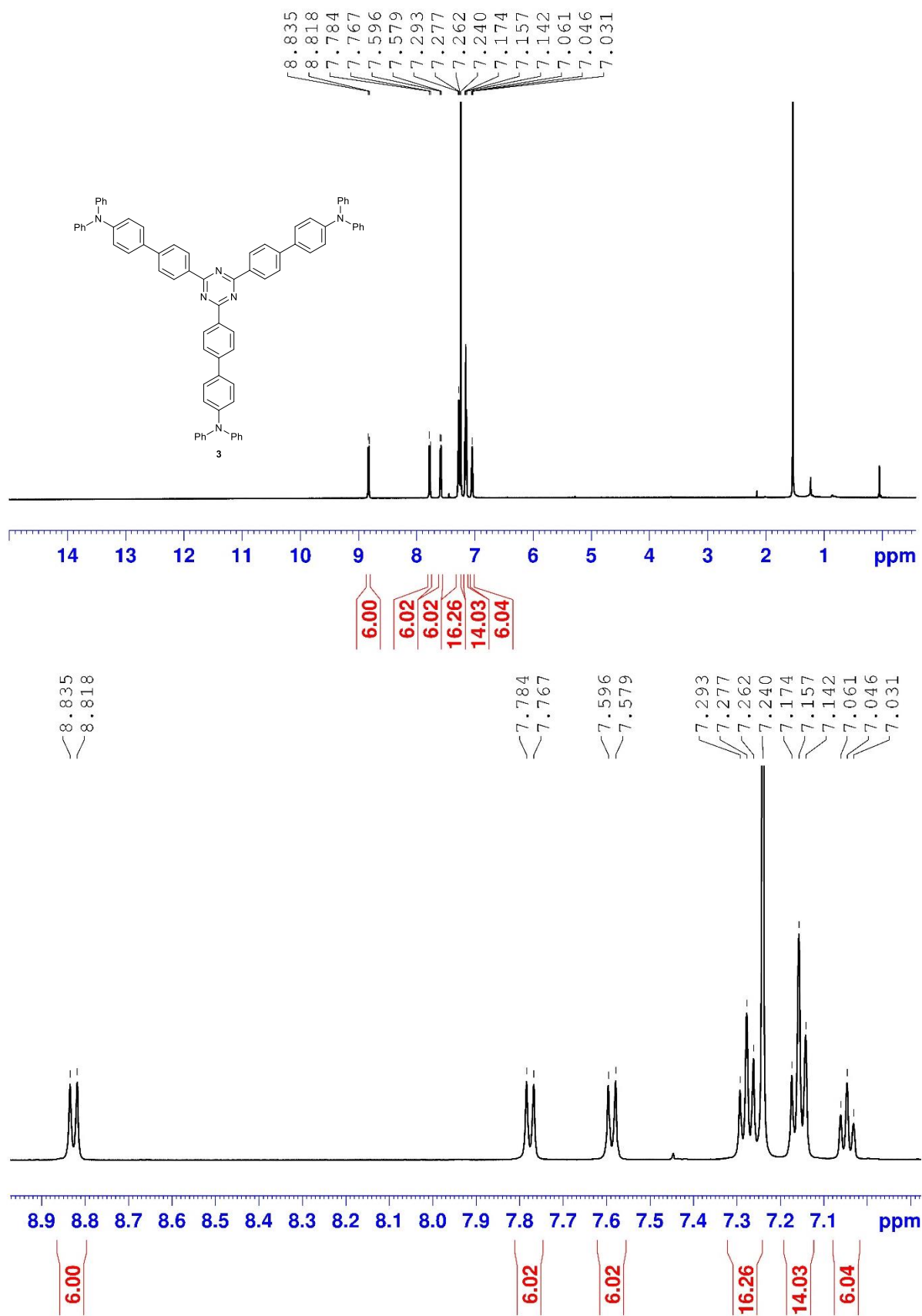


Figure S5. <sup>1</sup>H-NMR spectra of chromophore **3** (500 MHz, CDCl<sub>3</sub>).

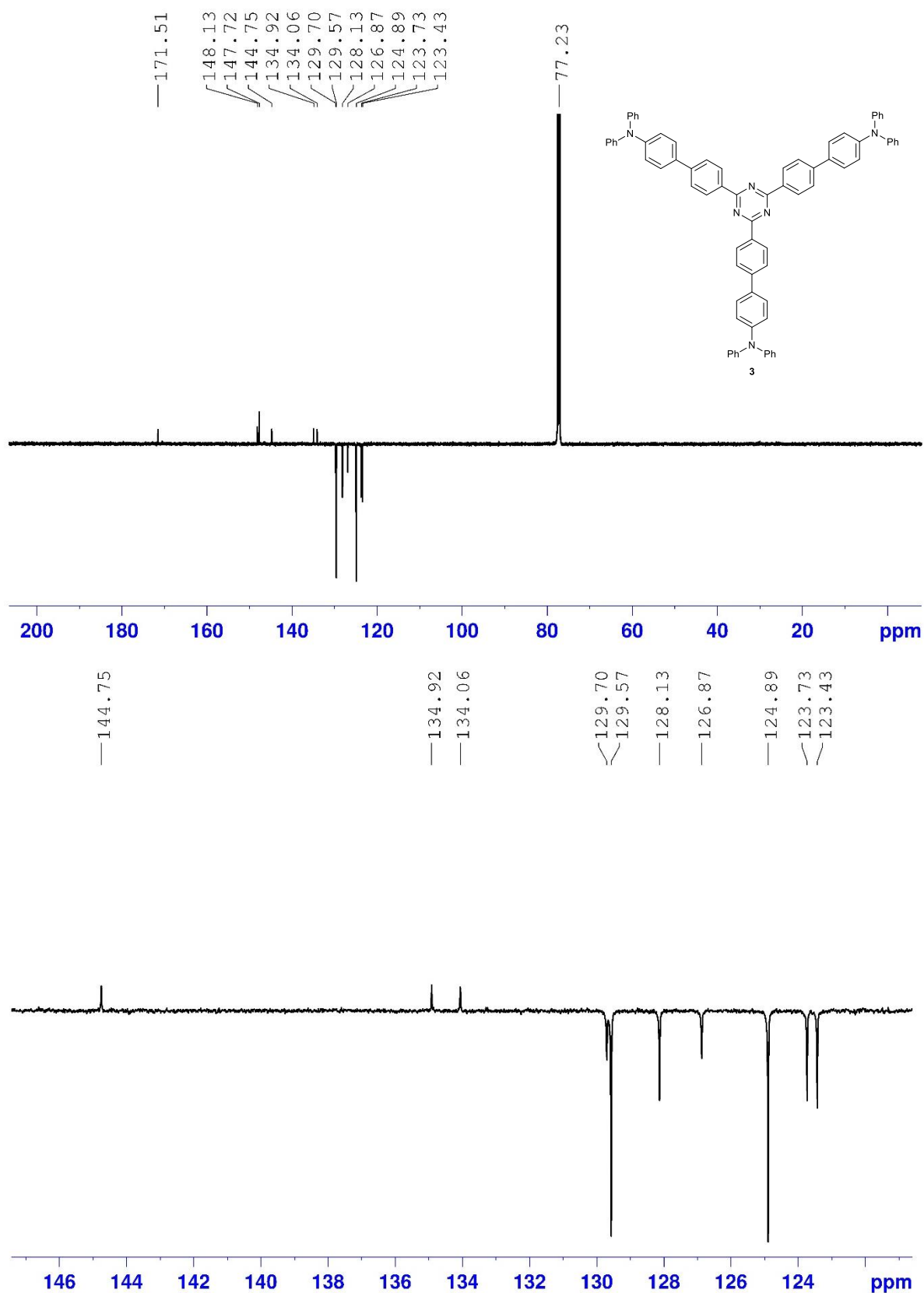
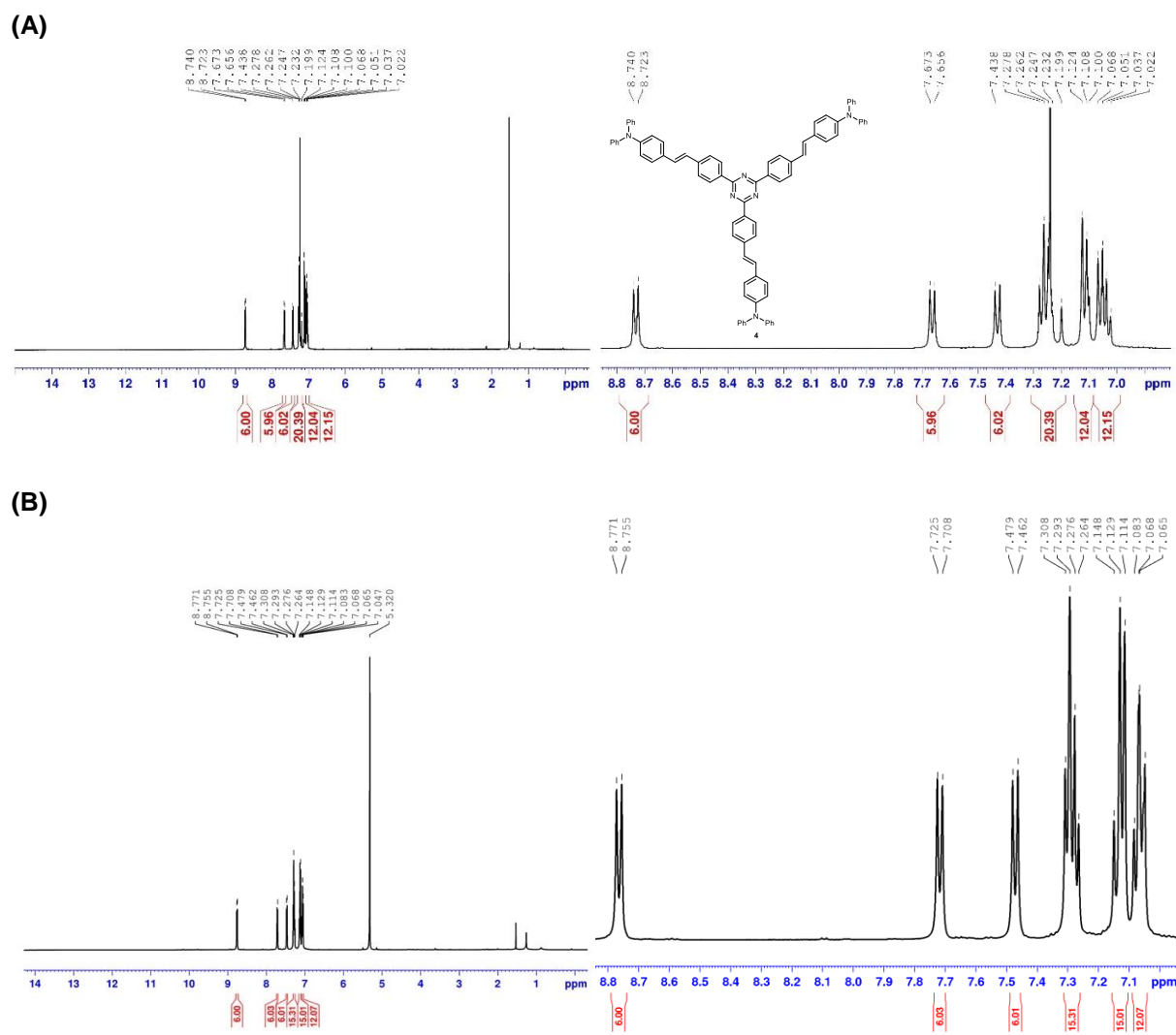


Figure S6. <sup>13</sup>C-NMR spectra of chromophore 3 (125 MHz, CDCl<sub>3</sub>).



**Figure S7.**  $^1\text{H-NMR}$  spectra of chromophore **4** (500 MHz) measured in  $\text{CDCl}_3$  (A) and  $\text{CD}_2\text{Cl}_2$  (B).

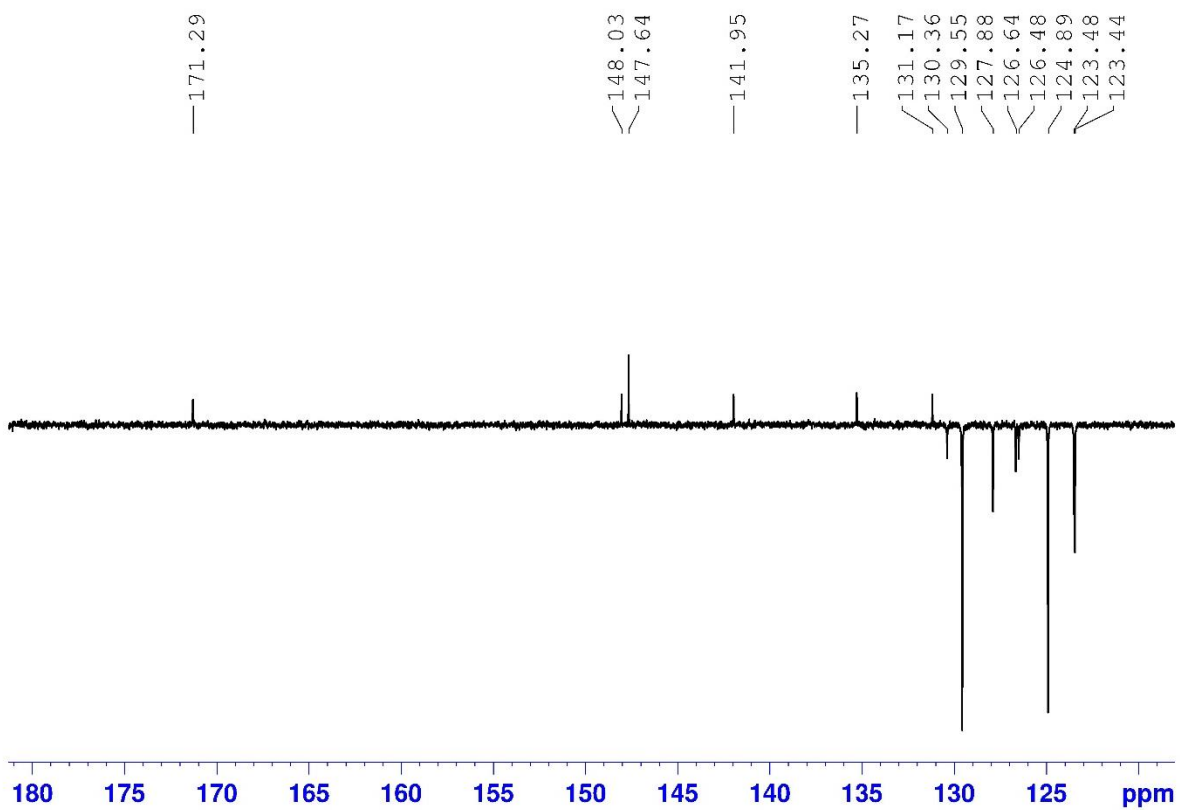
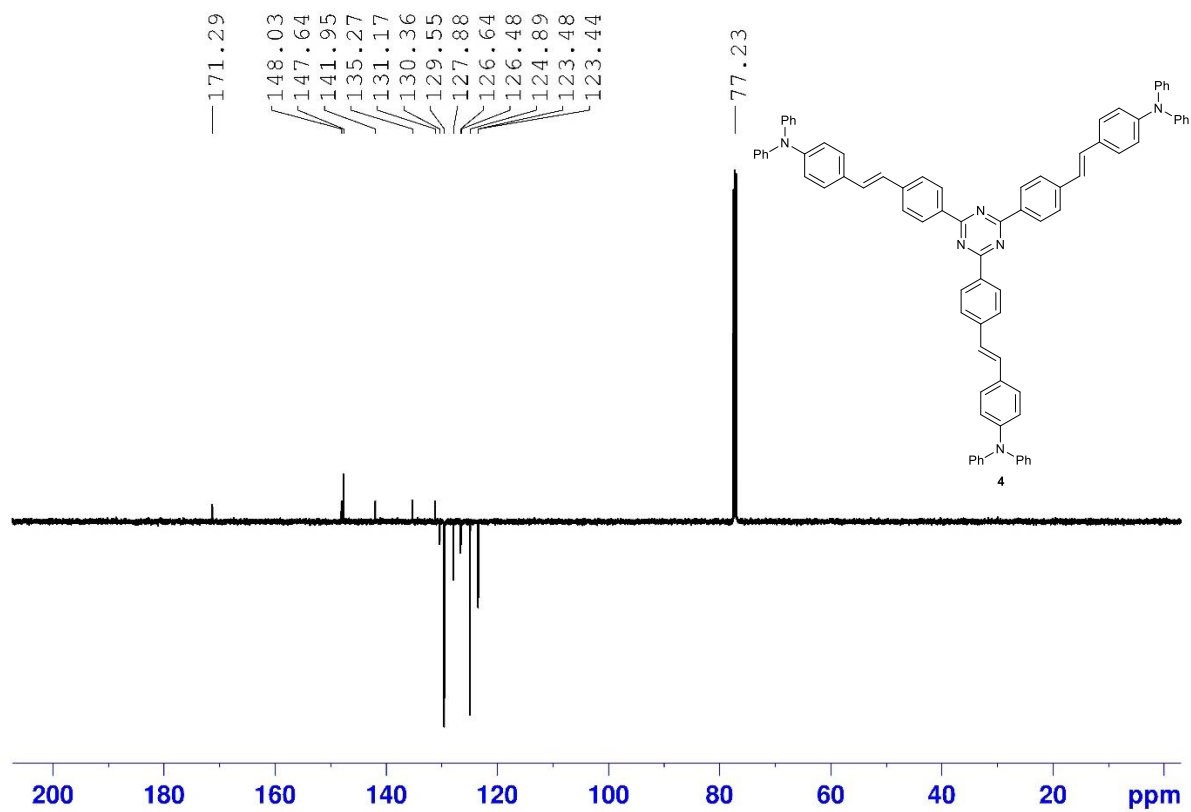


Figure S8. <sup>13</sup>C-NMR spectra of chromophore 4 (125 MHz, CDCl<sub>3</sub>).

### 1.3. HR-MALDI-MS

Theoretical HR-MALDI-MS spectra were calculated using Qual Browser, Thermo Xcalibur 4.0.27.10 software (Thermo Scientific).

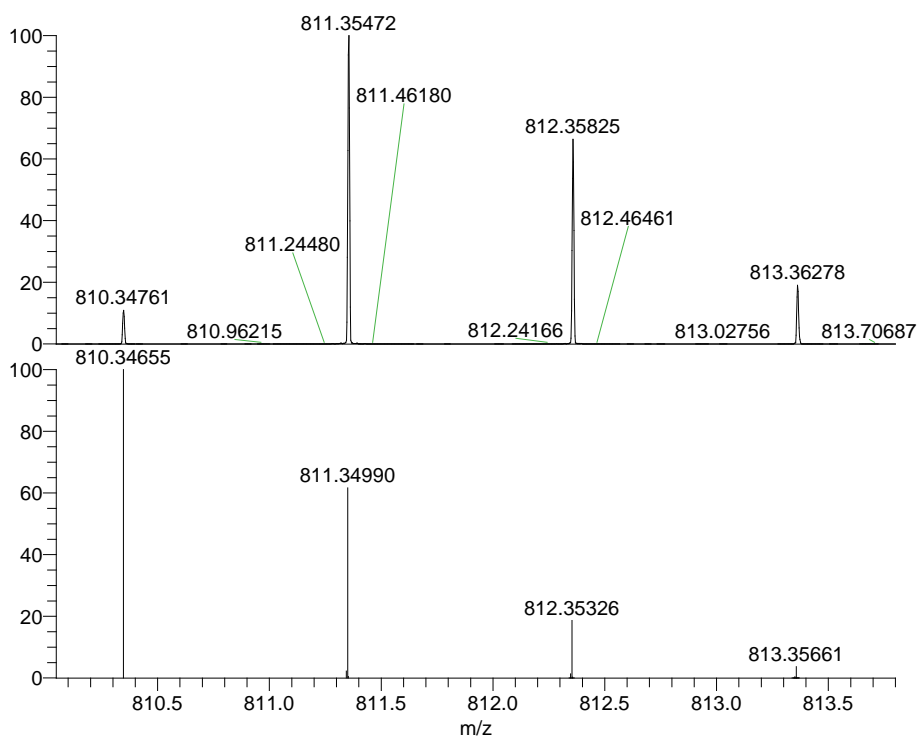


Figure S9. Experimental (top) and calculated (bottom) HR-MALDI-MS of **1**.

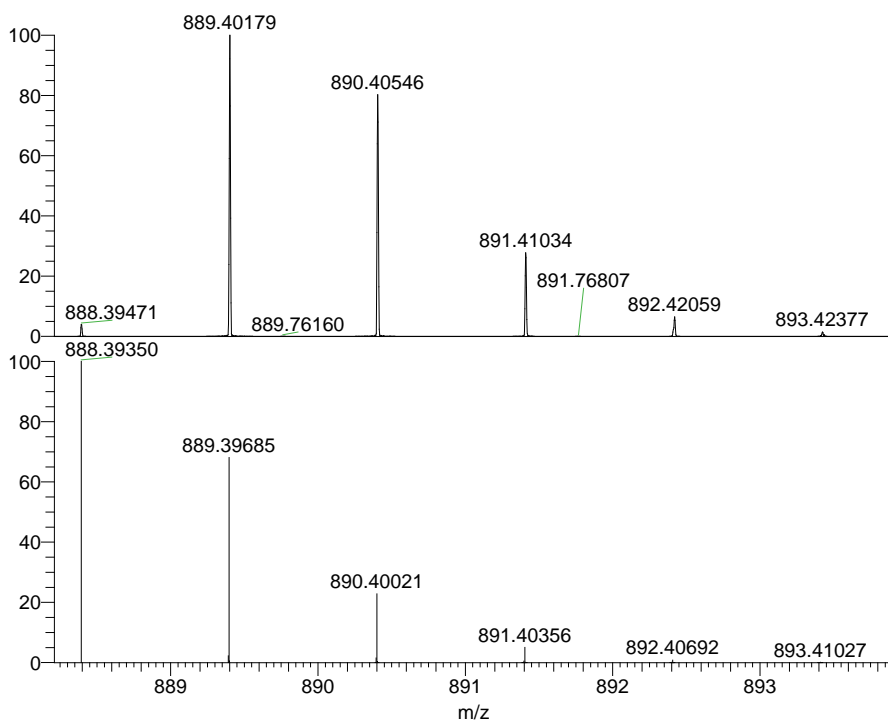
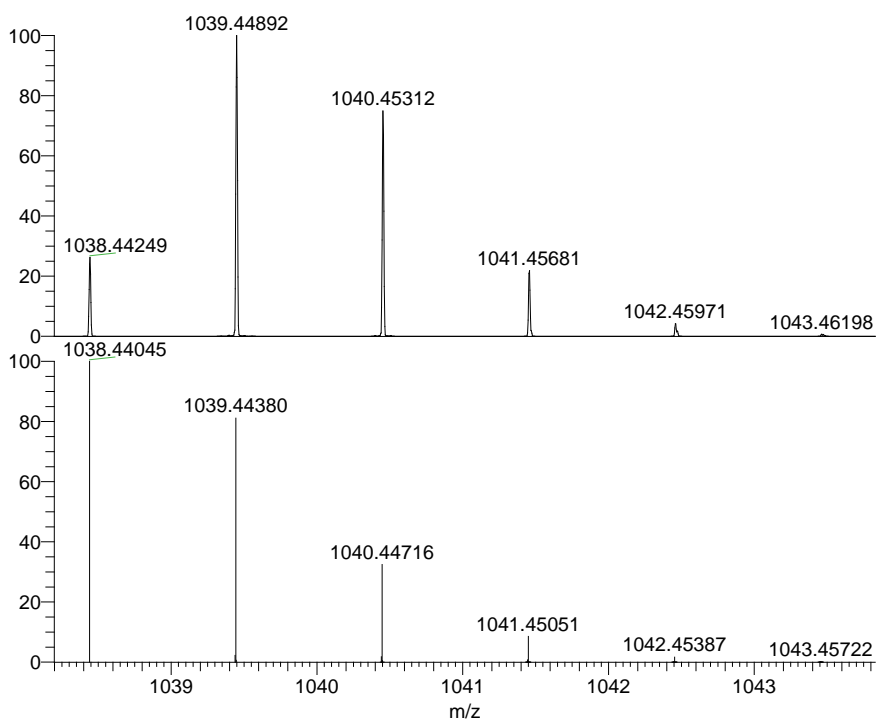
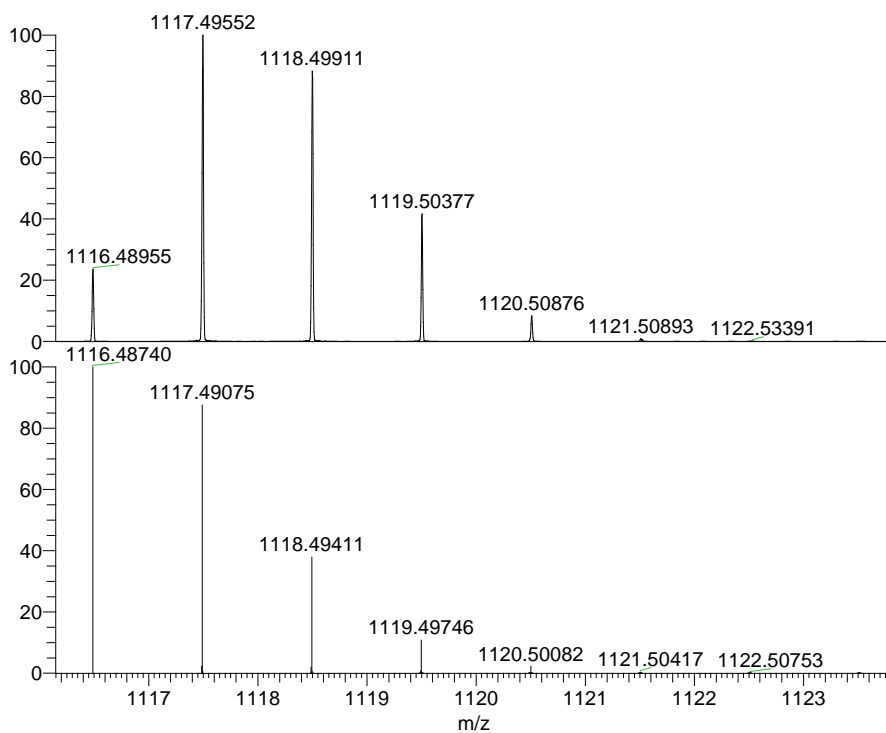


Figure S10. Experimental (top) and calculated (bottom) HR-MALDI-MS of **2**.



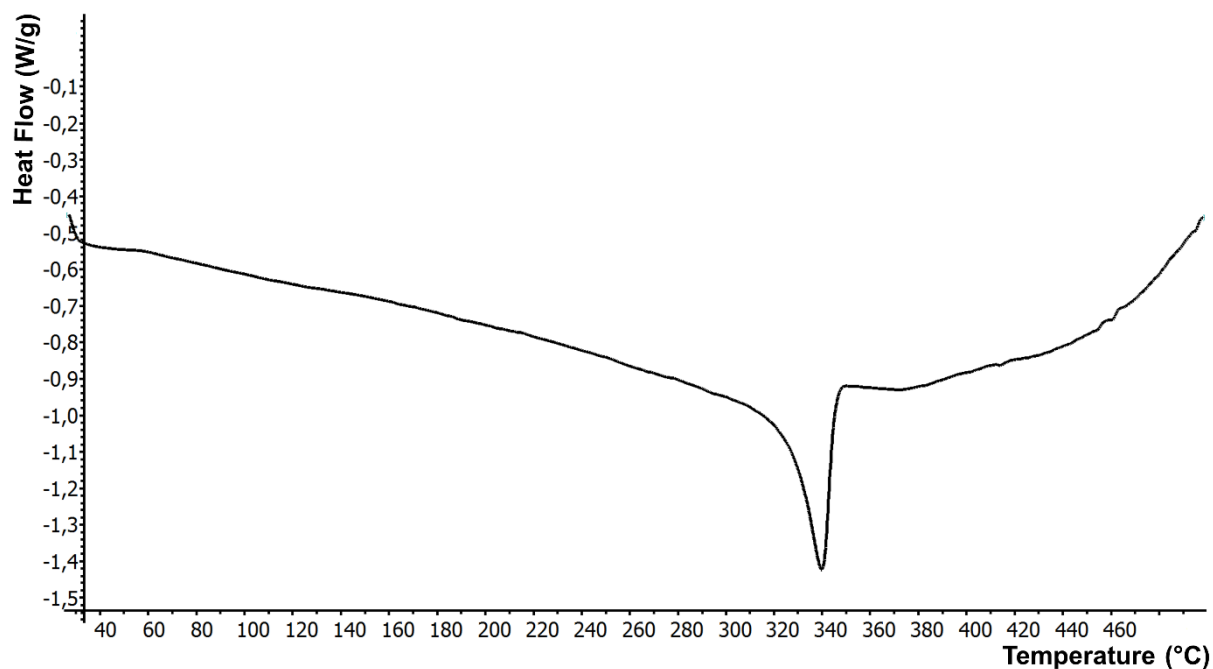
**Figure S11.** Experimental (top) and calculated (bottom) HR-MALDI-MS of **3**.



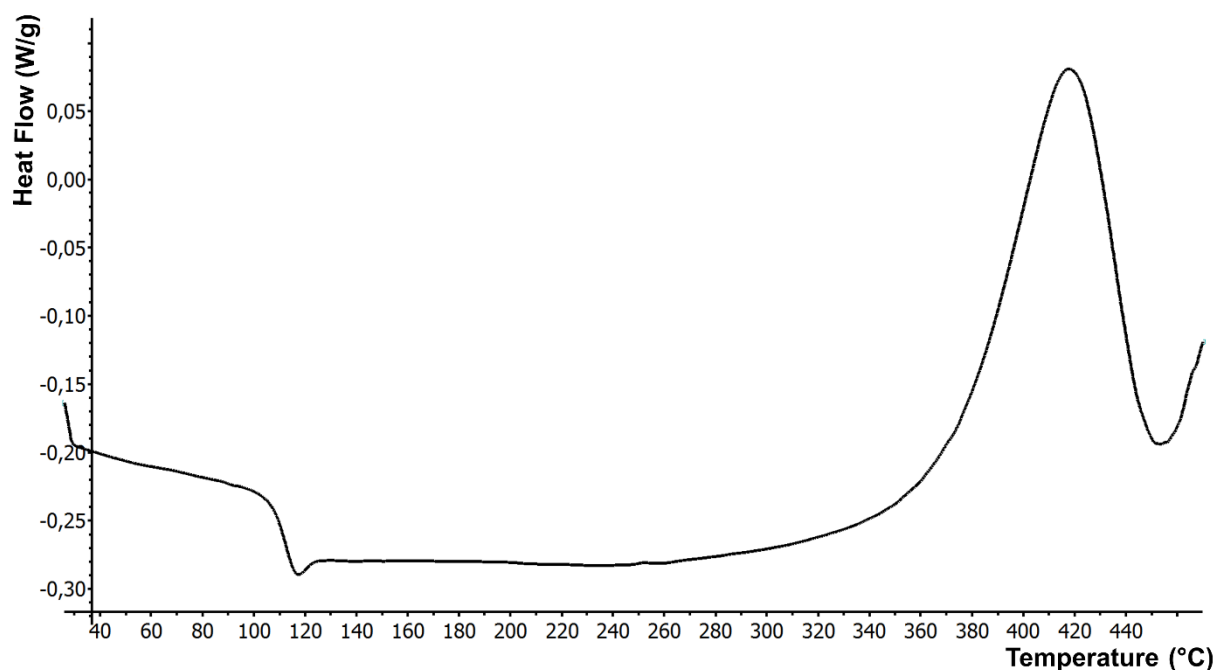
**Figure S12.** Experimental (top) and calculated (bottom) HR-MALDI-MS of **4**.

## 1.4. Thermal properties

Thermal properties of compounds **1–4** were investigated by DSC measurements with a Mettler-Toledo STARE System DSC 2/700 equipped with FRS 6 ceramic sensor and cooling system HUBER TC100-MT. Thermal behaviour of the target chromophores were measured in open aluminous crucibles under N<sub>2</sub> inert atmosphere. DSC curves were determined with a scan rate of 10 °C/min within the range 25–600 °C.

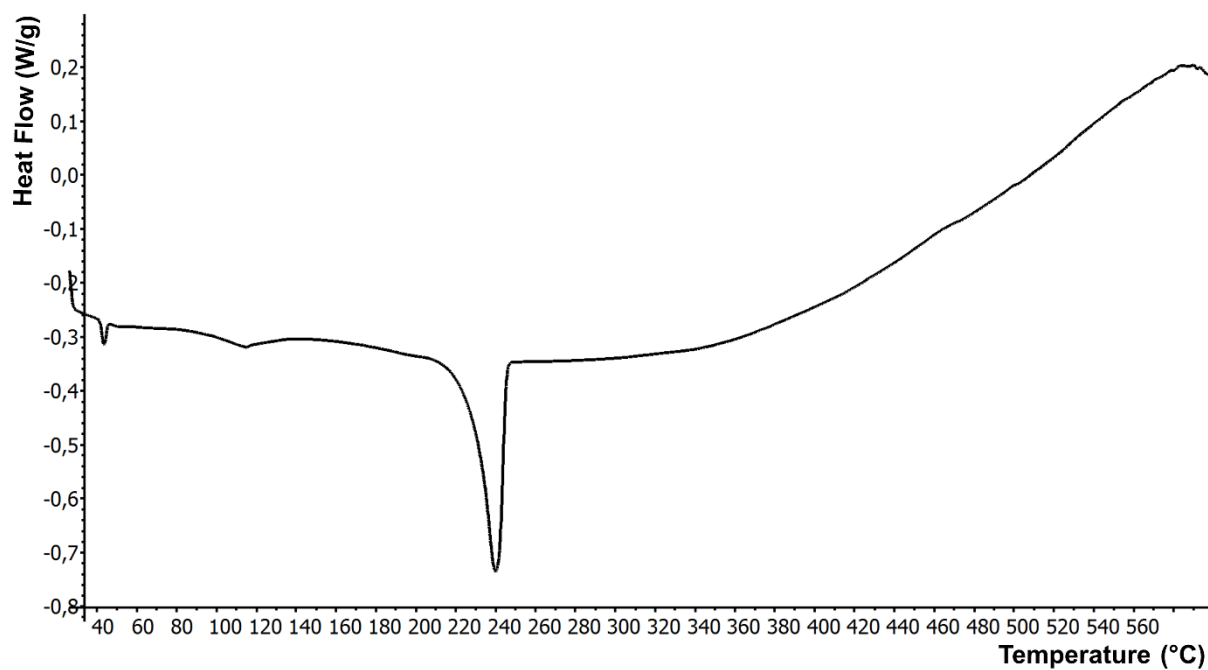


**Figure S13.** DSC thermogram of compound **1** determined with a heating rate of 10 °C/min under N<sub>2</sub>.

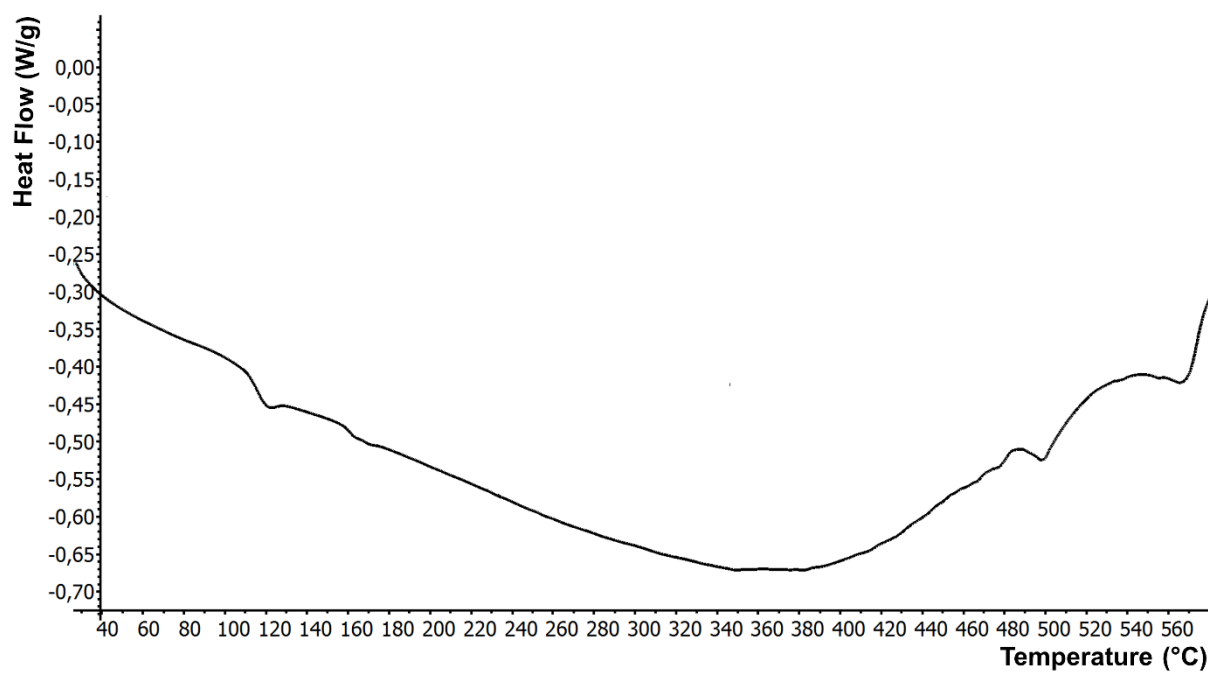


**Figure S14.** DSC thermogram of compound **2** determined with a heating rate of 10 °C/min under N<sub>2</sub>.





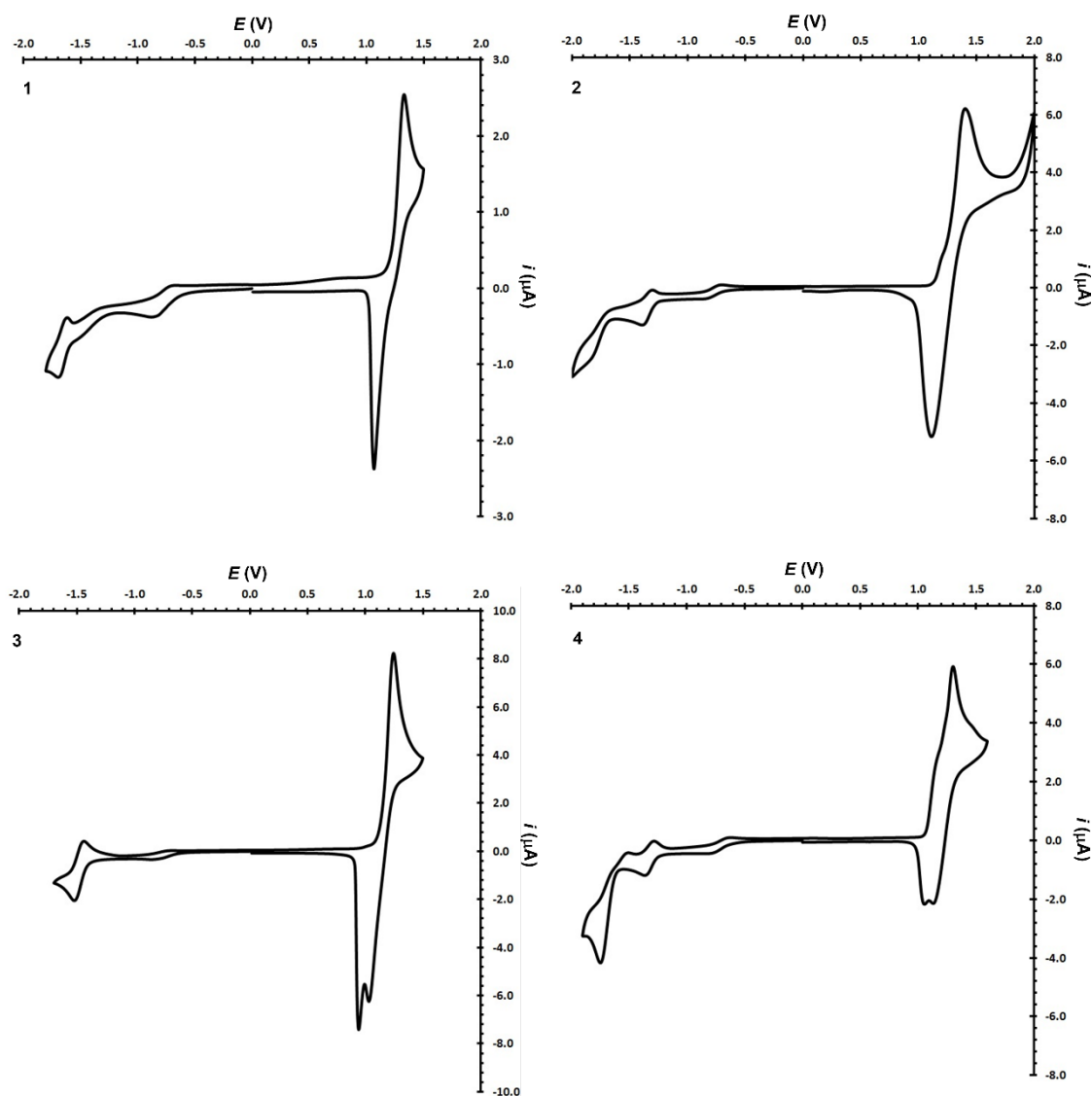
**Figure S15.** DSC thermogram of compound **3** determined with a heating rate of 10 °C/min under N<sub>2</sub>.



**Figure S16.** DSC thermogram of compound **4** determined with a heating rate of 10 °C/min under N<sub>2</sub>.

## 1.5. Electrochemistry

The electrochemical behaviour of target chromophores **1–4** were investigated in THF containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in a three-electrode cell by cyclic voltammetry (CV). The working electrode was glassy carbon disk (1 mm in diameter). As the reference and auxiliary electrodes were used leak-less Ag/AgCl electrode (SSCE) containing filling electrolyte (3.4 M KCl) and titanium rod with a thick coating of platinum, respectively. All peak potentials are given vs. SSCE. Voltammetric measurements were performed on an integrated potentiostat system ER466 (eDAQ Europe, Warsaw, Poland) operated with EChem Electrochemistry software. Although the measured solution was intensively bubbled with argon before the voltammetric analysis, a residual reversible peak of oxygen reduction was recorded at around  $-0.8$  V vs. SSCE for all samples.



**Figure S17.** Cyclic voltammograms of target chromophores **1–4** measured in THF containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at glassy carbon electrode;  $v = 100$  mVs<sup>-1</sup>.

## 1.6. One-photon absorption and emission

Absorption, transmittance and photoluminescence spectra were measured on a Duetta™ HORIBA spectrophotometer at room temperature. To record their emission spectra, chromophores **1–4** were generally excited at their longest-wavelength absorption maxima  $\lambda_{\max}^A$  (band of the lowest energy).

**Table S1.** Optical properties of chromophores **1–4** in toluene and acetone.

Toluene					
Comp.	$\lambda_{\max}^A$ (nm/eV)	$\varepsilon$ [mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> ]	$\lambda_{\max}^E$ (nm/eV)	$\Phi^F$ (%) <sup>h</sup>	Stokes shift (cm <sup>-1</sup> /eV)
<b>1</b>	394/3.15	68 900	444/2.79	80	2860/0.36
<b>2</b>	431/2.88	75 200	478/2.59	49	2280/0.28
<b>3</b>	390/3.18	68 800	457/2.71	91	3760/0.39
<b>4</b>	418/2.97	105 000	485/2.56	69	3304/0.41
Acetone					
Comp.	$\lambda_{\max}^A$ (nm/eV)	$\varepsilon$ [mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> ]	$\lambda_{\max}^E$ (nm/eV)	$\Phi^F$ (%) <sup>h</sup>	Stokes shift (cm <sup>-1</sup> /eV)
<b>1</b>	390/3.18	16 200	511/2.43	48	6072/0.75
<b>2</b>	425/2.92	99 200	572/2.17	6	6047/0.75
<b>3</b>	389/3.19	42 400	574/2.16	20	8286/1.03
<b>4</b>	415/2.99	75 000	602/2.06	3	7485/0.93

Fluorescence quantum yields ( $\pm 10\%$ ) were determined relative to that of 9,10-bis(phenylethynyl)anthracene in cyclohexane ( $\Phi_F = 1.00$ ).<sup>3</sup>

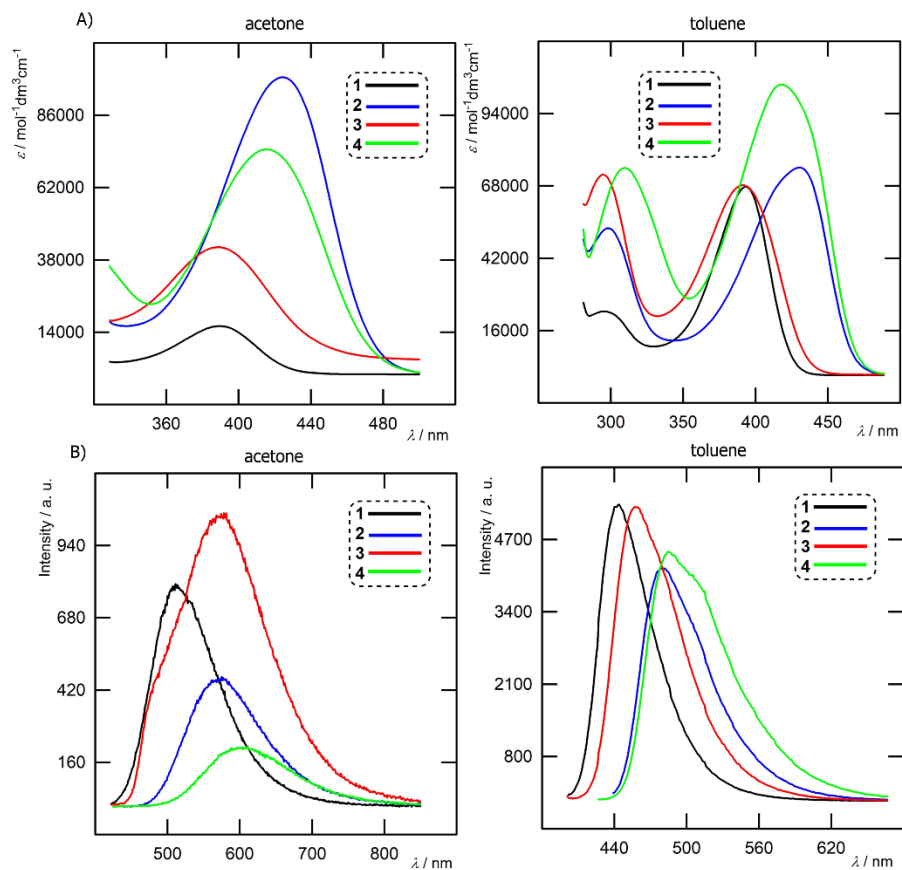
**Table S2.** Fitting parameters for the ns fluorescence decays of chromophores **1–4** in toluene, THF and acetone.

Sample	$\lambda_{\text{det}}$ (nm)	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\langle \tau \rangle$ (ns)
<b>1</b> /Toluene	443	-	-	1	2.19	2.19
<b>1</b> /THF	479	-	-	1	3.78	3.78
<b>1</b> /Acetone	518	0.11	0.16	0.89	4.54	4.08
Sample	$\lambda_{\text{det}}$ (nm)	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\langle \tau \rangle$ (ns)
<b>2</b> /Toluene	483	0.13	0.43	0.87	1.54	1.40
<b>2</b> /THF	524	0.23	0.98	0.76	2.86	2.42
<b>2</b> /Acetone	573	0.57	0.23	0.43	0.72	0.44
Sample	$\lambda_{\text{det}}$ (nm)	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\langle \tau \rangle$ (ns)
<b>3</b> /Toluene	462	0.05	0.79	1	1.66	1.66
<b>3</b> /THF	520			1	3.08	3.08
<b>3</b> /Acetone	586	0.11	0.21	0.89	2.09	1.89
Sample	$\lambda_{\text{det}}$ (nm)	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\langle \tau \rangle$ (ns)
<b>4</b> /Toluene	487	0.15	1.02	0.85	1.47	1.40
<b>4</b> /THF	556	0.06	0.68	0.94	2.22	2.13
<b>4</b> /Acetone	612	0.76	0.21	0.24	0.31	0.24

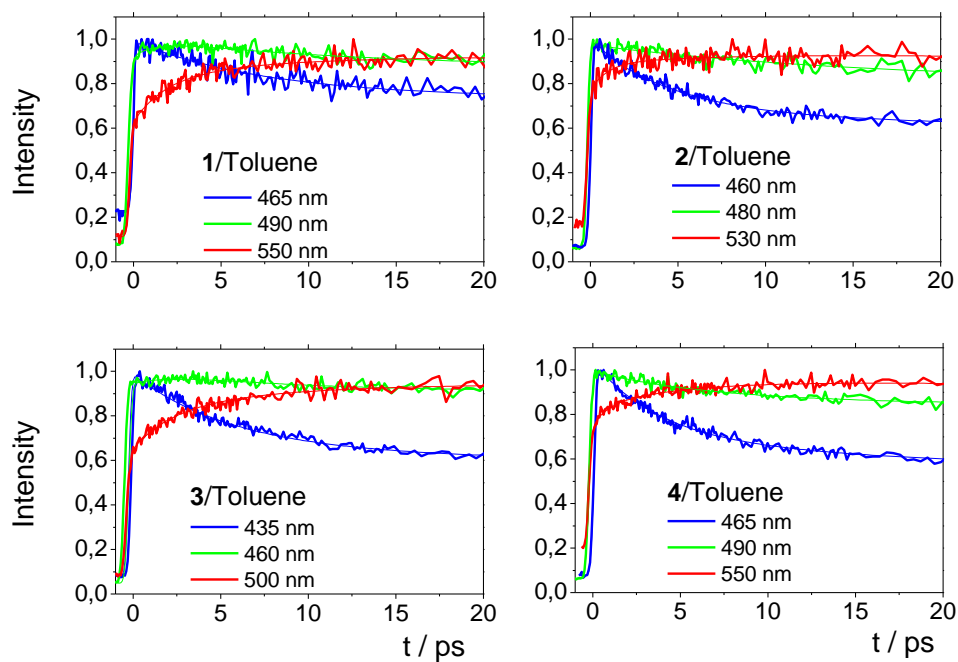
<sup>3</sup> D. F. Eaton, *Pure Appl. Chem.* 1988, **60**, 1107.

**Table S3.** Fitting parameters for the ps fluorescence dynamics of chromophores 1–4 in toluene and THF.

Sample	$\lambda_{\text{det}}$ (nm)	A <sub>1</sub>	$\tau_1$ (ps)	A <sub>2</sub>	$\tau_2$ (ps)	$\tau_3$ (ns)
<b>1/Toluene</b>	425	0.03	1.86	0.21	7.68	2.19
	445	-0.12		0.14		
	480	-0.21		-0.11		
<b>2/Toluene</b>	460	0.05	0.92	0.32	5.41	1.40
	480	-0.05		0.12		
	530	-0.13		-0.07		
<b>3/Toluene</b>	435	0.01	2.11	0.38	6.37	1.66
	460	-0.08		0.10		
	500	-0.14		-0.18		
<b>4/Toluene</b>	465	0.09	1.20	0.36	5.95	1.40
	490	-0.02		0.14		
	550	-0.12		-0.11		
<b>1/THF</b>	445	0.36	0.99	0.35	3.13	3.78
	480	-0.33		0.31		
	530	-0.38		-0.11		
<b>2/THF</b>	480	0.70	0.89	0.27	3.87	2.42
	530	-0.20		0.23		
	590	-0.33		-0.10		
<b>3/THF</b>	480	0.14	0.85	0.68	2.18	3.08
	530	-0.77		0.31		
	580	-0.32		-0.13		
<b>4/THF</b>	510	0.38	1.02	0.51	2.30	2.13
	560	-0.55		0.48		
	630	-0.35		-0.05		

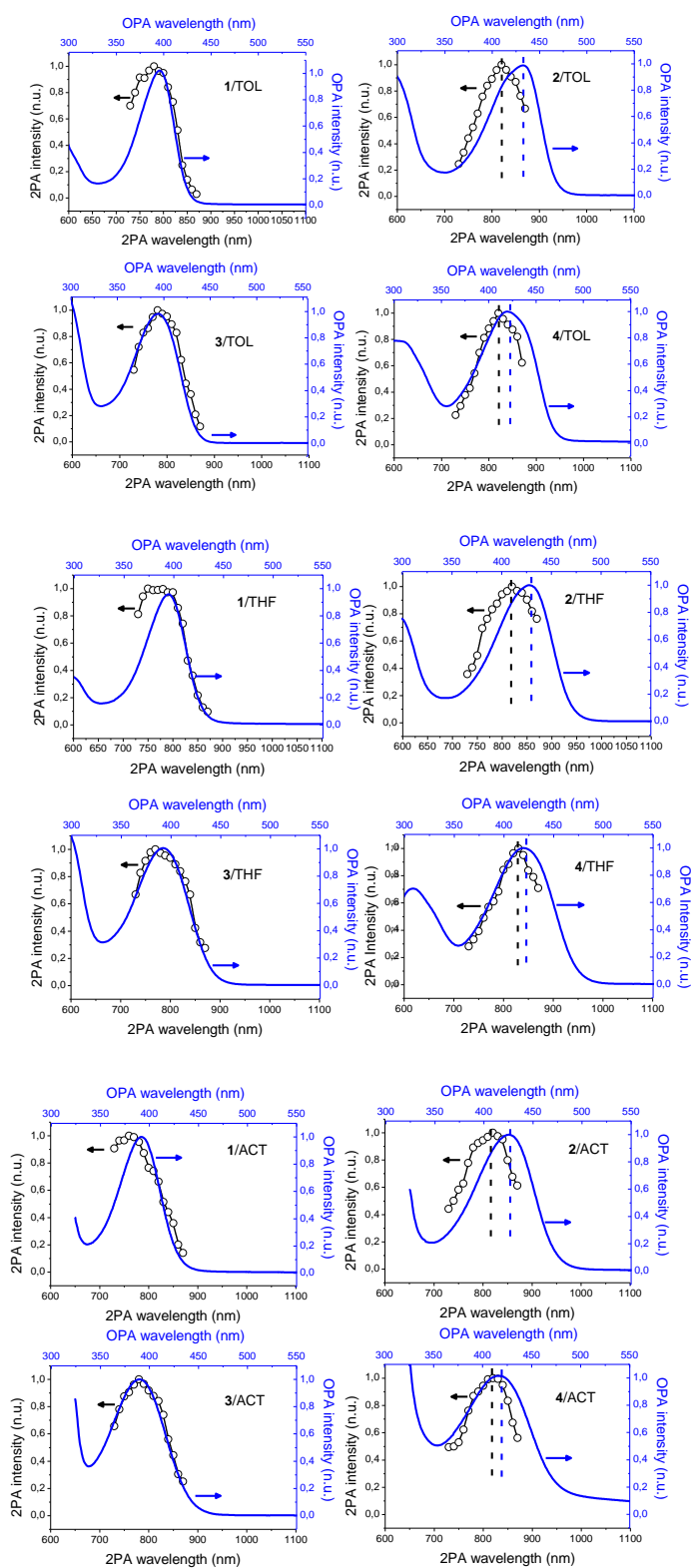


**Figure S18.** Absorption (A) and emission (B) spectra of triazines 1–4 in toluene and acetone at concentration  $c = 1 \times 10^{-5}$  M.



**Figure S19.** Fluorescence dynamics of chromophores 1–4 in the ps timescale in toluene at different emission wavelengths.

## 1.7. Two-photon absorption



**Figure S20.** Comparison of the 2PA and one-photon absorption spectra of compounds 1-4 in toluene, THF and acetone. Vertical lines are shown for a better comparison of the spectral shifts.

**Table S4.** Calculated cavity radius and permanent dipole moment difference between ground and excited state determined by the 2PA cross section  $\Delta\mu_{2PA}$  and the solvatochromism method  $\Delta\mu_S$ .

Molecule	Cavity radius (Å)	$\Delta\mu_{2PA}$ (D)	$\Delta\mu_S$ (D)
<b>1</b>	6.23	11.8	19.1
<b>2</b>	6.41	17.1	21.5
<b>3</b>	6.58	19.0	24.6
<b>4</b>	6.64	17.9	24.0

## 1.8. Quantum chemical calculations

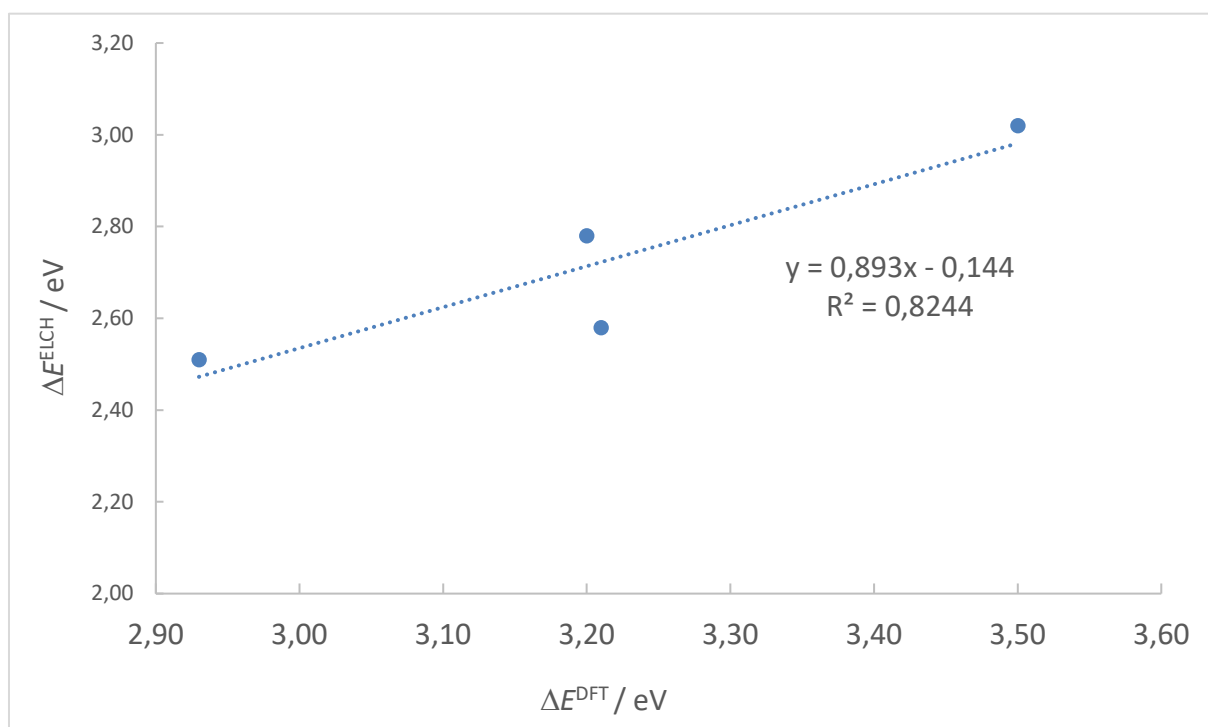


Figure S21. Correlation of DFT-calculated and electrochemical gaps  $\Delta E$ .

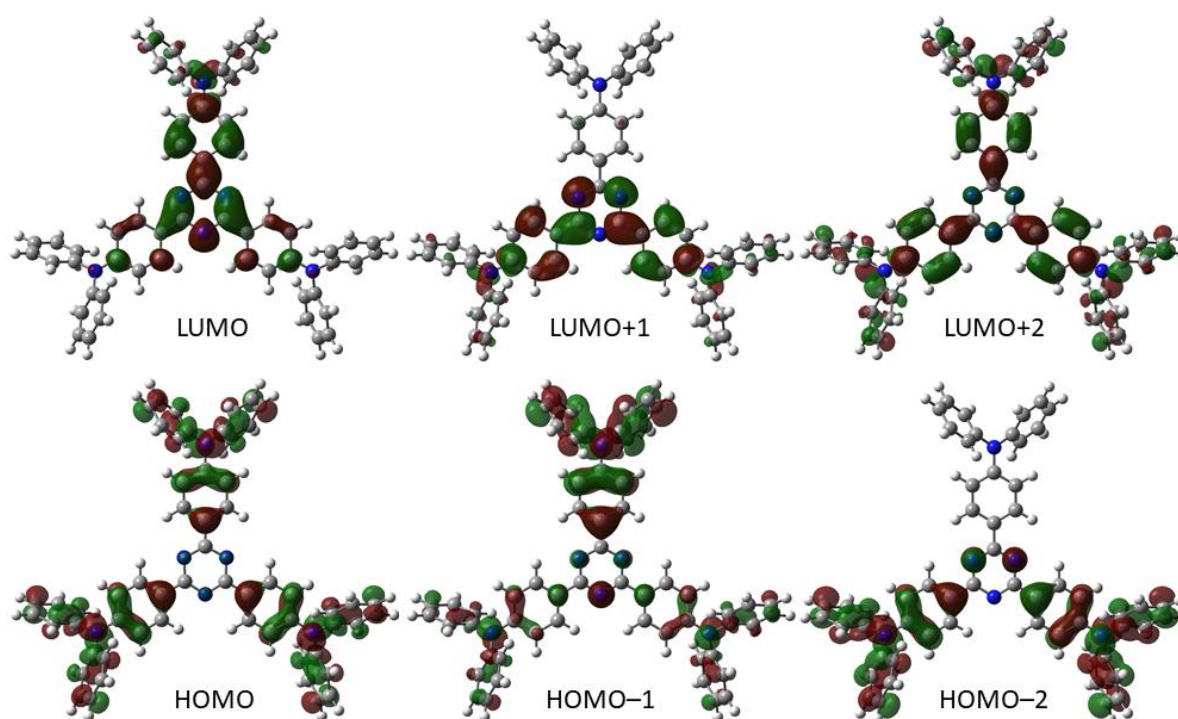
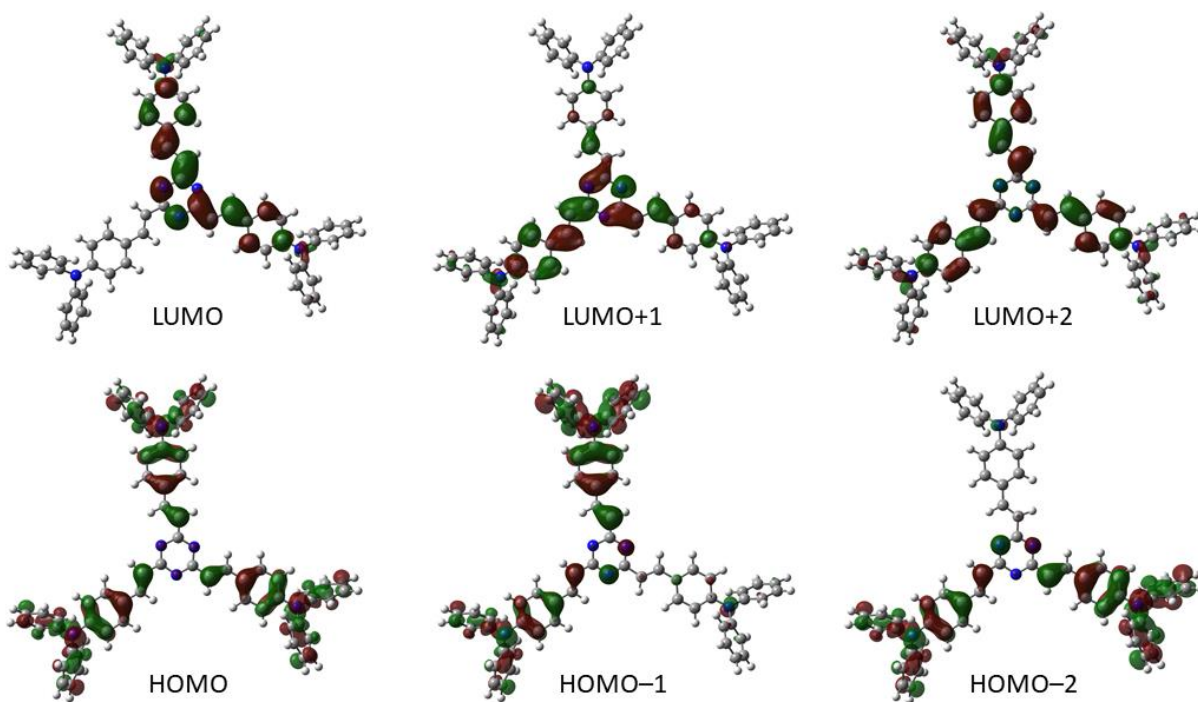
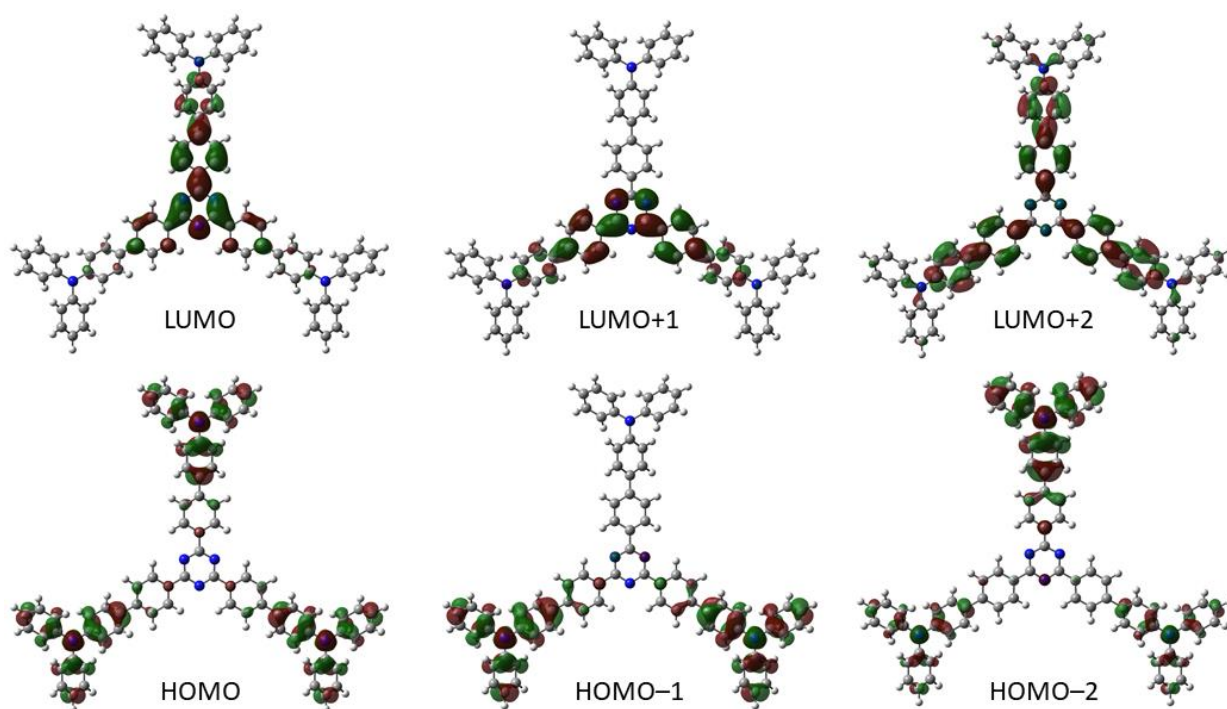


Figure S22. DFT-calculated HOMO and LUMO localizations in chromophore 1.





**Figure S23.** DFT-calculated HOMO and LUMO localizations in chromophore **2**.



**Figure S24.** DFT-calculated HOMO and LUMO localizations in chromophore **3**.

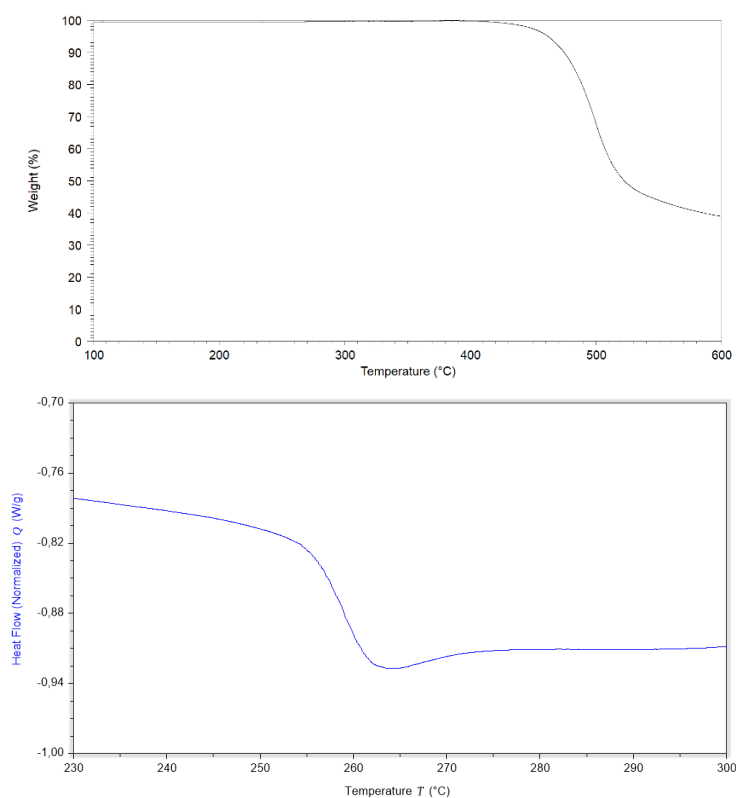
## 2. PI films

### 2.1 General synthesis of PI films

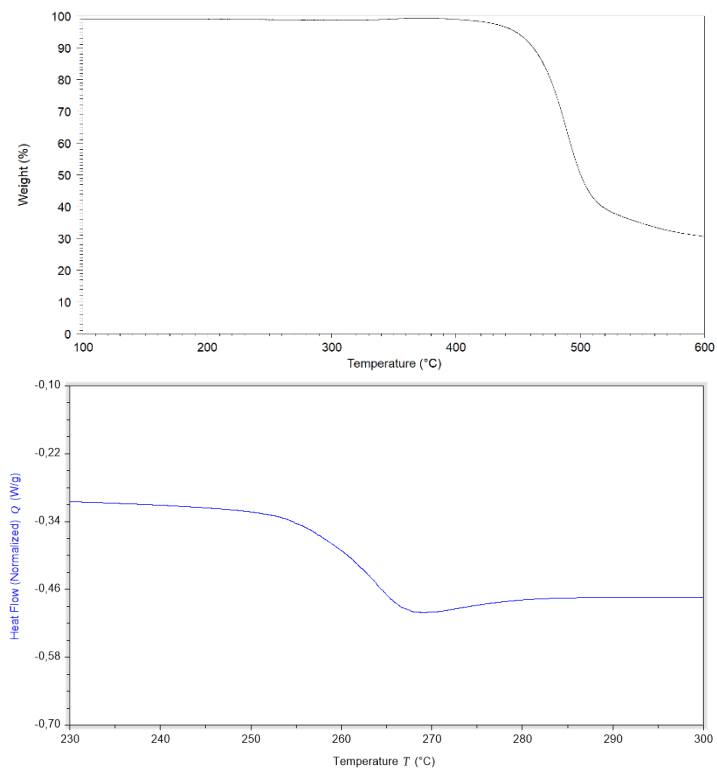
BAPP (821 mg; 2.0 mol) and CHDA (448 mg; 2.0 mol) were added to DMAC (5.08 g) and the mixture was stirred under N<sub>2</sub> at 25 °C, whereupon chromophore **1–4** (1.4-1.1 mmol; 1.2 mg) was added and the stirring continued for 24 h. The resulting polyamic acid (PAA) solution was casted into PAA films and these were imidized into polyimide in a high temperature furnace according to the following protocol: (1) heating to 150 °C at a rate of 2 °C/min and annealing at 150 °C for 1 h to remove any residual solvent, (2) heating at a rate of 2 °C/min and annealing at 250 °C for 1 h, (3) heating at a rate of 2 °C/min and annealing at 300 °C for 2 h to complete the imidization process. The imidization process was running under high vacuum. Undoped CHDA-BAPP polyimide was prepared analogously without adding **1–4**.

## 2.2 Thermal properties

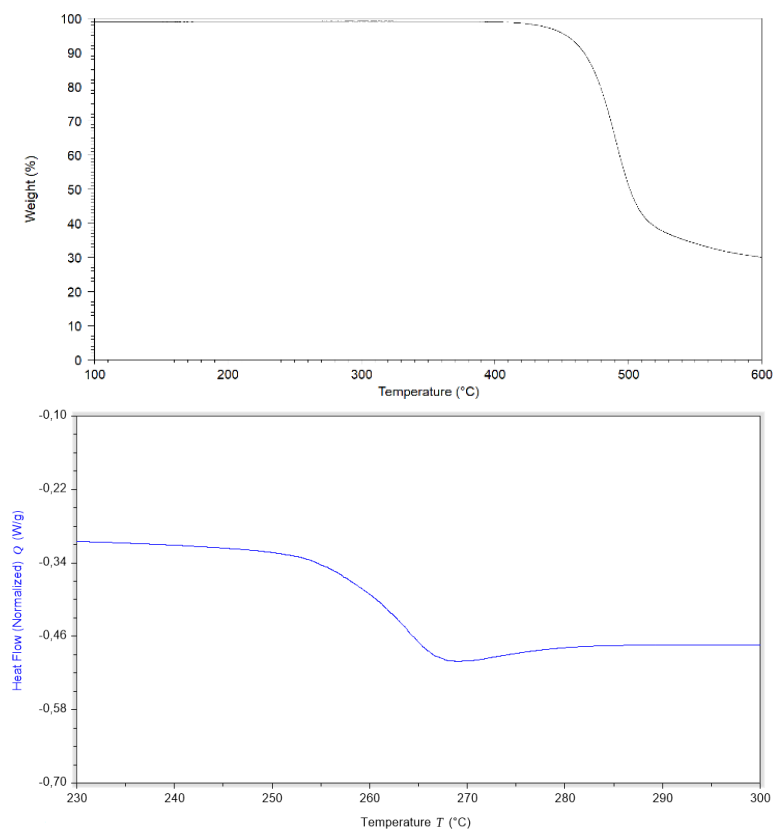
Thermal properties of polyimides were investigated by DSC and TGA. Glass transition temperature was measured using DCS 250 (TA Instruments, New Castle, DE, USA) under nitrogen gas flow with a heating rate of 20 °C/min with range 25–300 °C. TGA was carried out with a TGA Q500 (TA Instruments, New Castle, DE, USA) under nitrogen gas flow with a heating rate of 10 °C/min with the range 25–600 °C in open platinum sample pan.



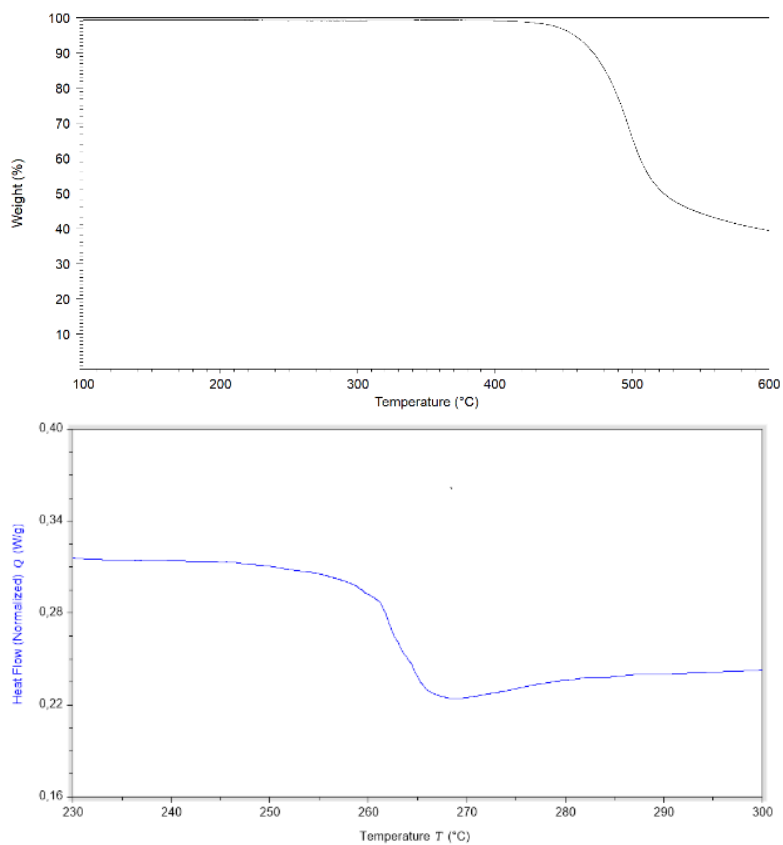
**Figure S25.** TGA (up) and DSC (down) curves of polyimide **CHDA-BAPP** determined with a heating rate of 10 °C/min under N<sub>2</sub>.



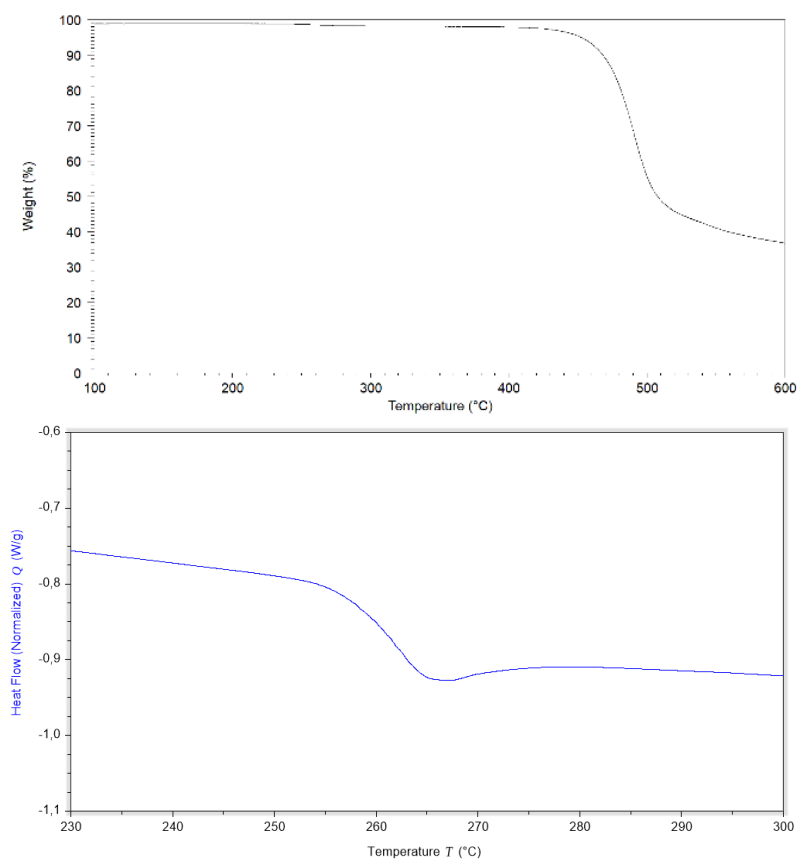
**Figure S26.** TGA (up) and DSC (down) curves of polyimide **CHDA-BAPP+1** determined with a heating rate of 10 °C/min under N<sub>2</sub>.



**Figure S27.** TGA (up) and DSC (down) curves of polyimide **CHDA-BAPP+2** determined with a heating rate of 10 °C/min under N<sub>2</sub>.



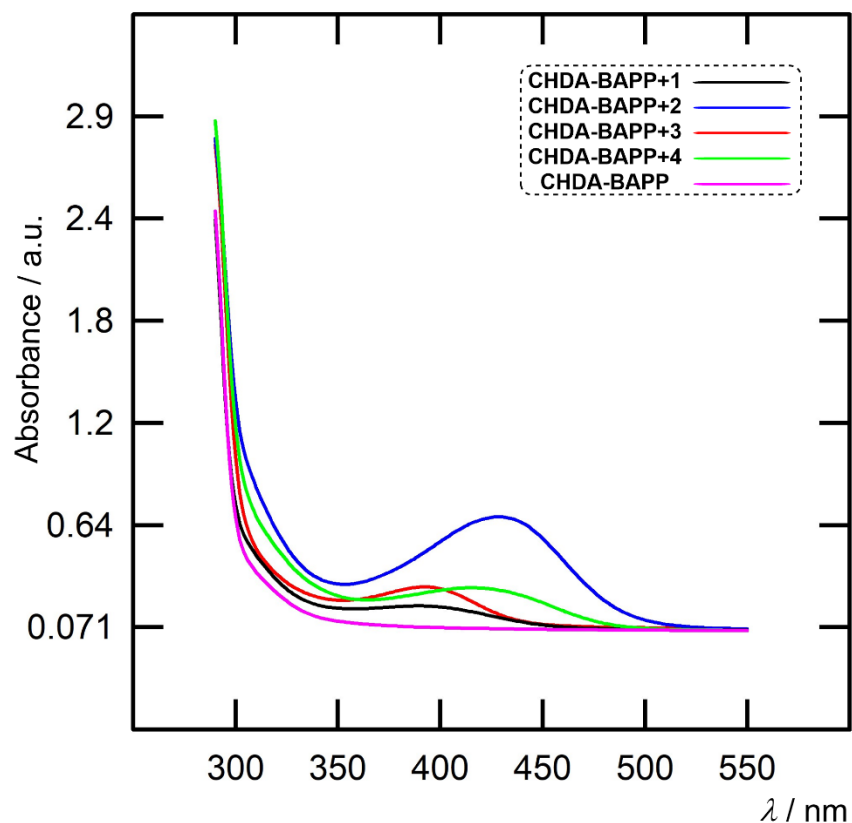
**Figure S28.** TGA (up) and DSC (down) curves of polyimide **CHDA-BAPP+3** determined with a heating rate of 10 °C/min under N<sub>2</sub>.



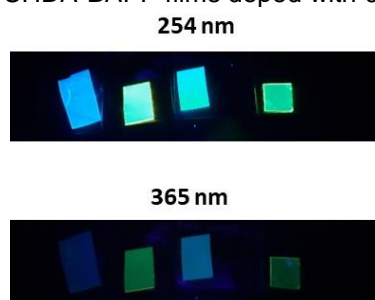
**Figure S29.** TGA (up) and DSC (down) curves of polyimide **CHDA-BAPP+4** determined with a heating rate of 10 °C/min under N<sub>2</sub>.

### 2.3 Optical properties of PI films

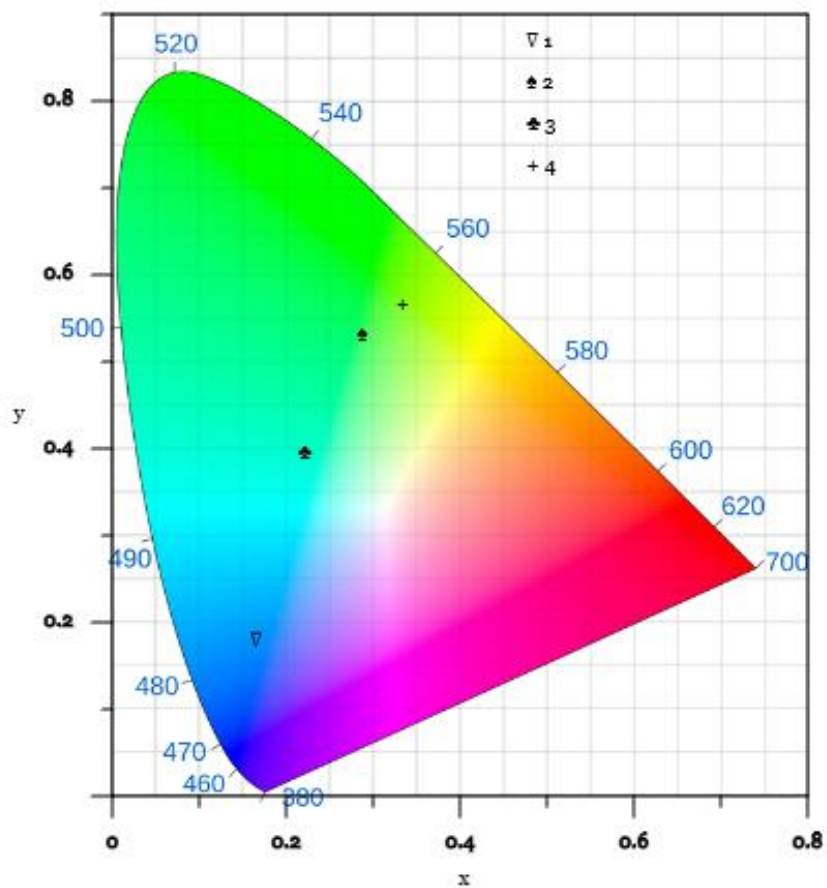
Absorption, transmittance and photoluminescence spectra of PI films were measured on a Duetta™ HORIBA spectrophotometer at room temperature. CHDA-BAPP+1–4 films were generally excited at their longest-wavelength absorption maxima  $\lambda_{\max}^A$  (band of the lowest energy).



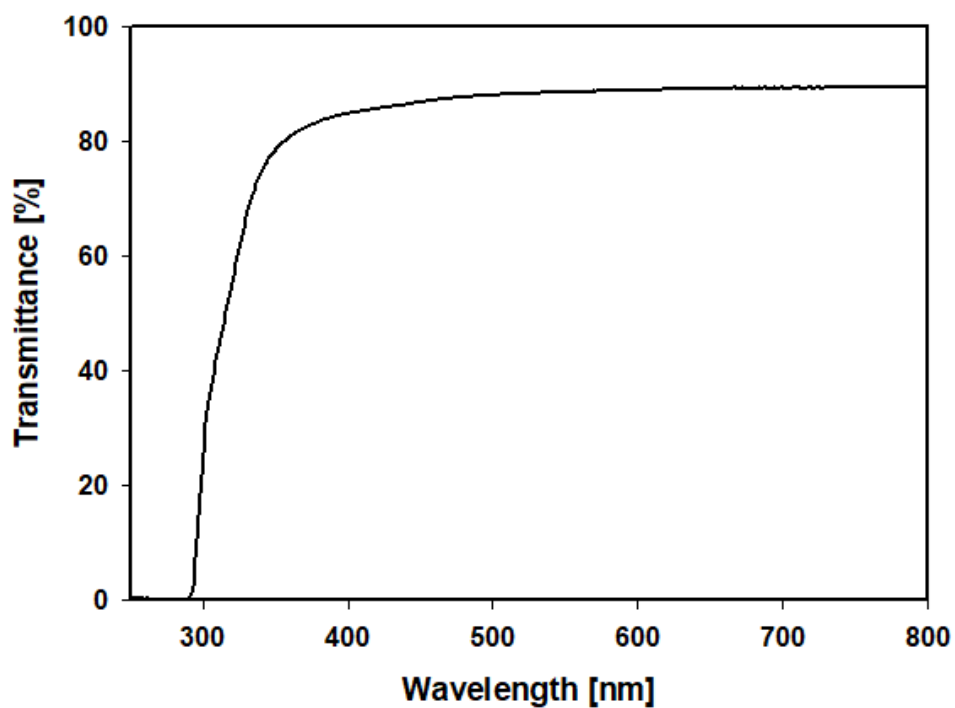
**Figure S30.** Absorption spectra of CHDA-BAPP films doped with 0.1% of 1–4.



**Figure S31.** Polyimide CHDA-BAPP films doped with 1–4 (from left to right) under UV irradiation of 254 and 356 nm.



**Figure S32.** CIE chromaticity diagram 1931 of emissive CHDA-BAPP films doped with 1–4.<sup>4</sup>



**Figure S33.** Transmittance of polyimide CHDA-BAPP.

<sup>4</sup> E. H. H. Hasabeldaim 2021, "CIE chromaticity diagram 1931" <https://sciapps.scisim.com/CIE1931.html>.

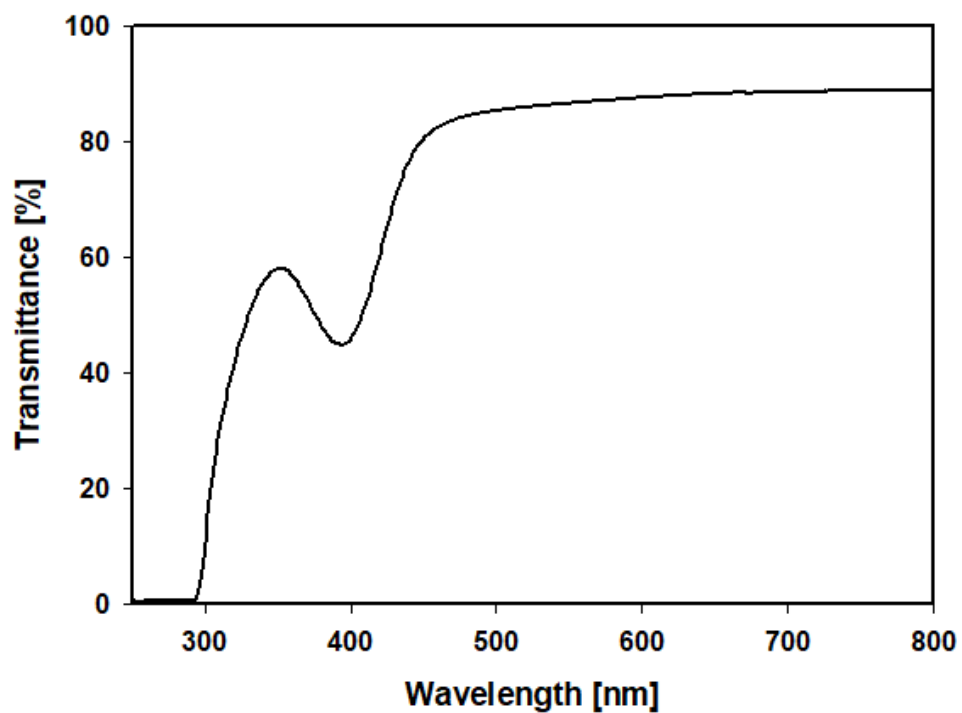


Figure S34. Transmittance of polyimide CHDA-BAPP+1.

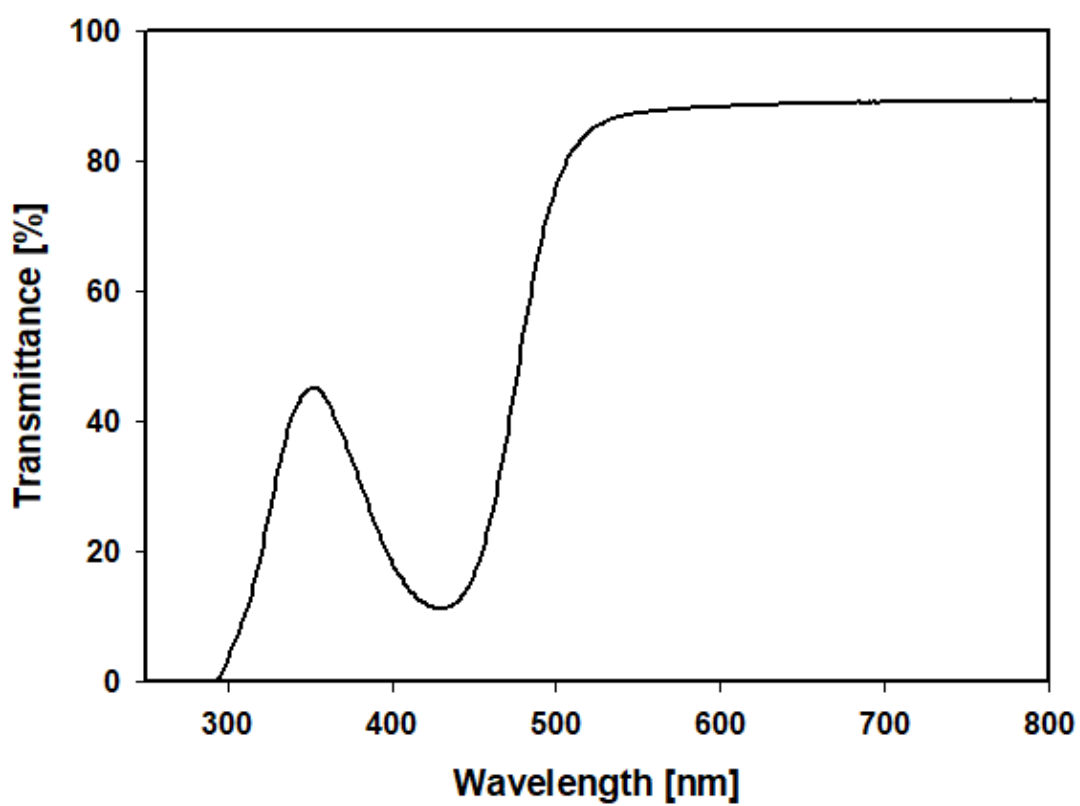


Figure S35. Transmittance of polyimide CHDA-BAPP+2.



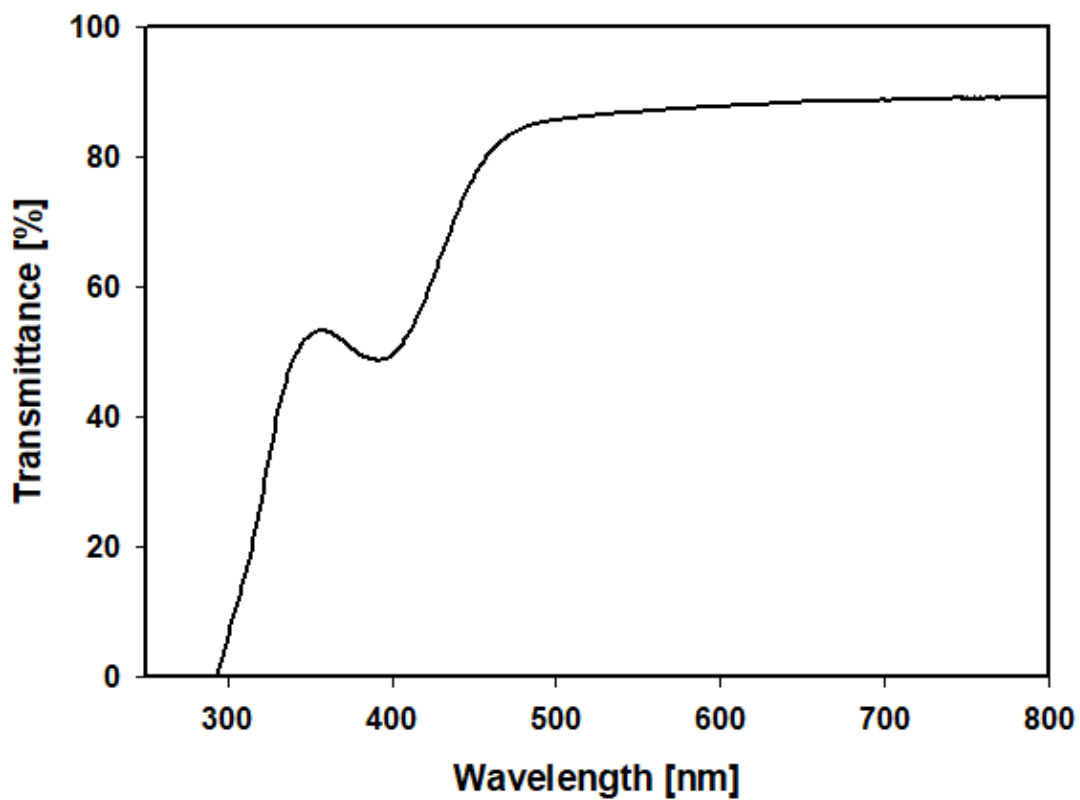


Figure S36. Transmittance of polyimide CHDA-BAPP+3.

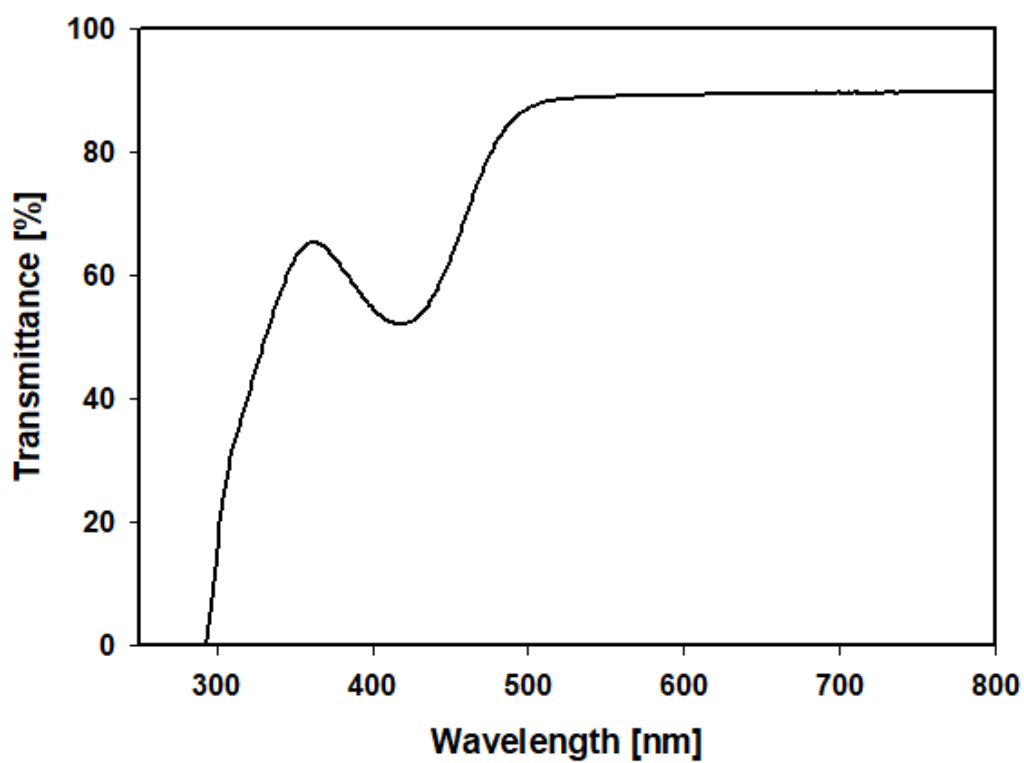
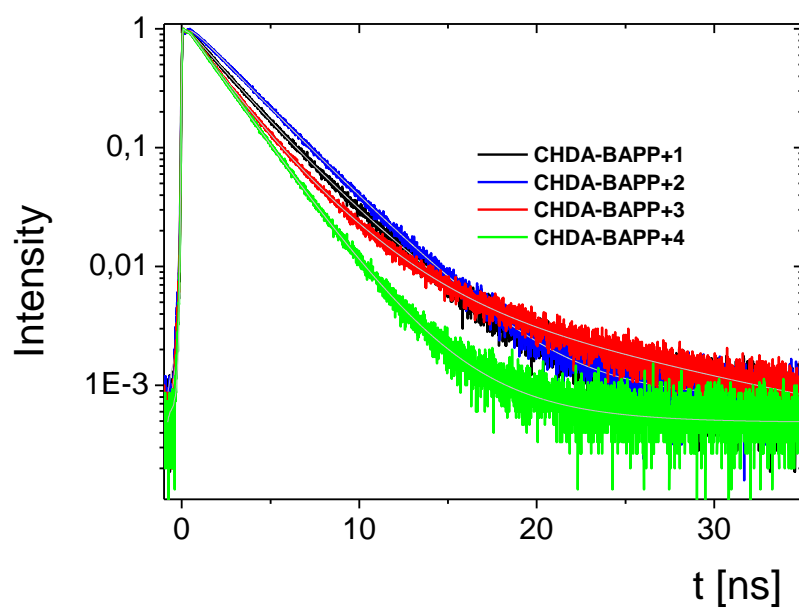


Figure S37. Transmittance of polyimide CHDA-BAPP+4.

**Table S5.** Fitting parameters for the ns fluorescence decays of chromophores 1–4 in PI films.

Sample	$\lambda_{\text{det}}$ (nm)	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	$\langle\tau\rangle$ (ns)
CHDA-BAPP+1	461	0.79	2.27	0.21	3.89	2.61
CHDA-BAPP+2	515	0.85	2.68	0.15	3.76	3.44
CHDA-BAPP+3	495	0.69	1.79	0.31	3.15	2.32
CHDA-BAPP+4	526	0.97	2.03	0.03	4.13	2.09



**Figure S38.** Fluorescence dynamics of chromophores 1–4 in PI films.