Near-IR absorbing 1,1,4,4-tetracyanobutadiene-functionalized Phenothiazine Sulfones

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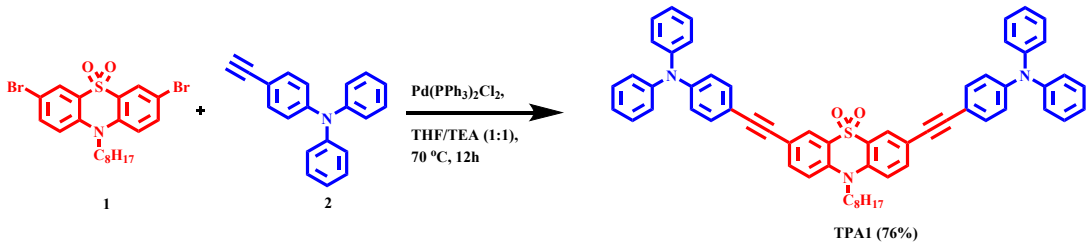


Scheme S1. Synthetic route of symmetrical phenothiazine sulfone based chromophores **TPA1**.

Solvatochromism.

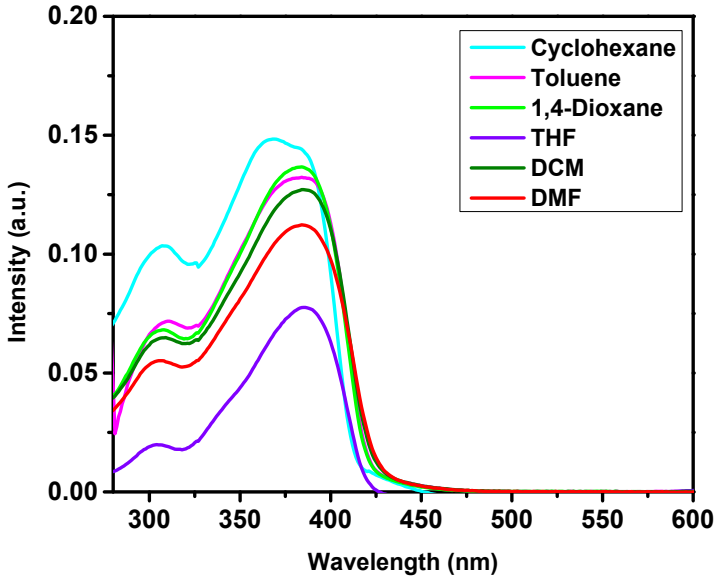


Fig. S1 Electronic absorption spectra of **TPA1**(excitation wavelength or λex=370 nm) in solvents of different polarities.

Aggregation Induced Emission.

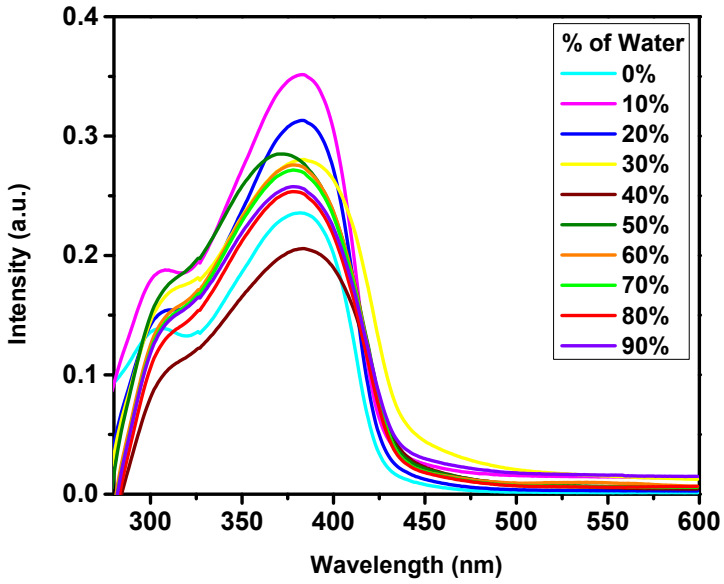


Fig. S2 Electronic absorption spectra of **TPA1** in DMF-water mixtures (0% to 90% water), Luminogen concentration: 10 μM; intensity calculated at λ_{max}.

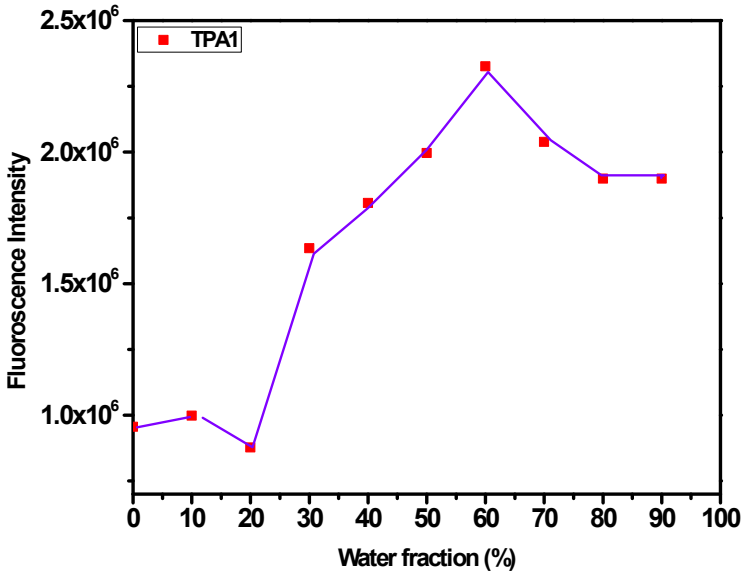


Fig. S3 Plot of fluorescence intensity *vs*. % of water fraction (f_w) for **TPA1**. Luminogen concentration: 10 μM; intensity calculated at $\lambda_{max.}$

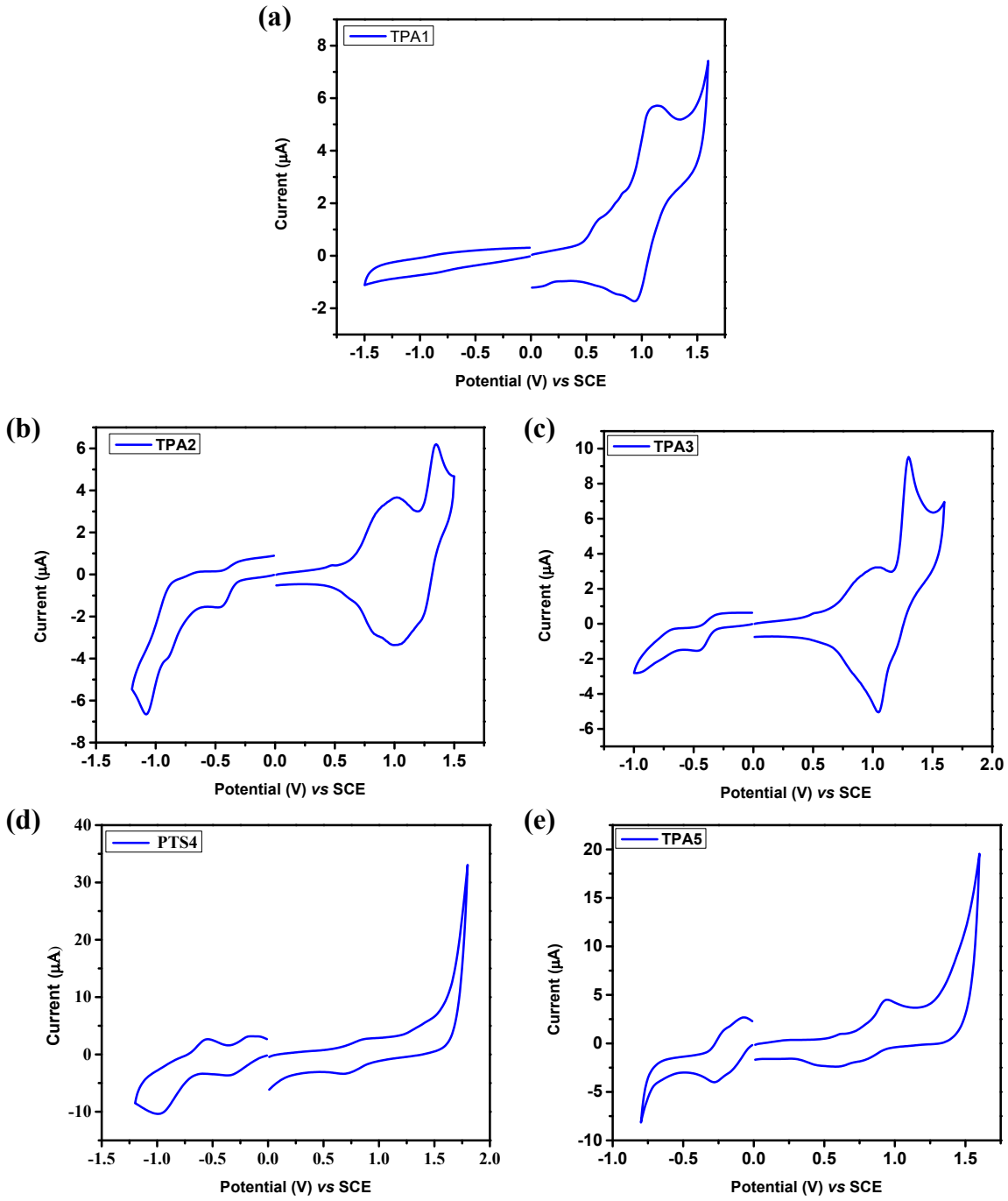


Fig. S4 Differential pulse voltammetry of **TPA1**–**TPA5** recorded in CH_2Cl_2 (0.1 M Bu_4NPF_6) at a glassy carbon working electrode and a voltage scan rate of 0.1 V s^{-1}.

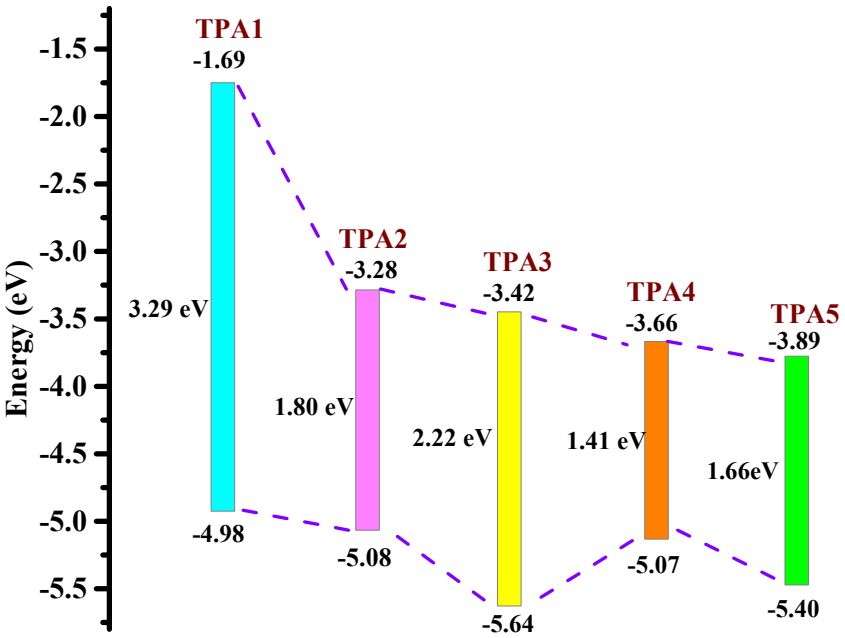


Fig. S5 Energy level diagram of the frontier orbitals of **TPA1**–**TPA5** estimated by DFT calculations.

Copies of NMR and Mass spectra of the new compounds

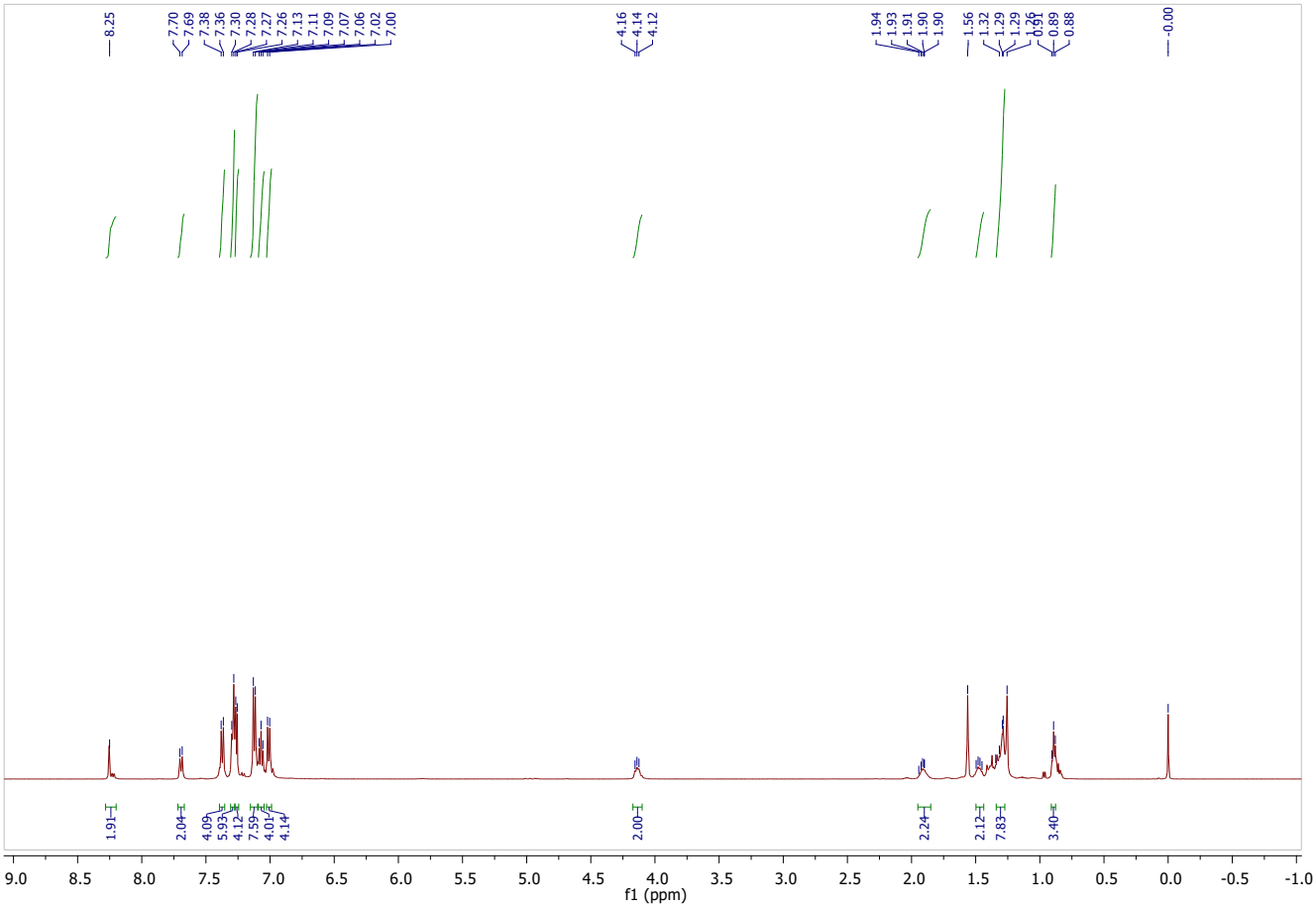


Fig. S6 ^{1}H-NMR of TPA1

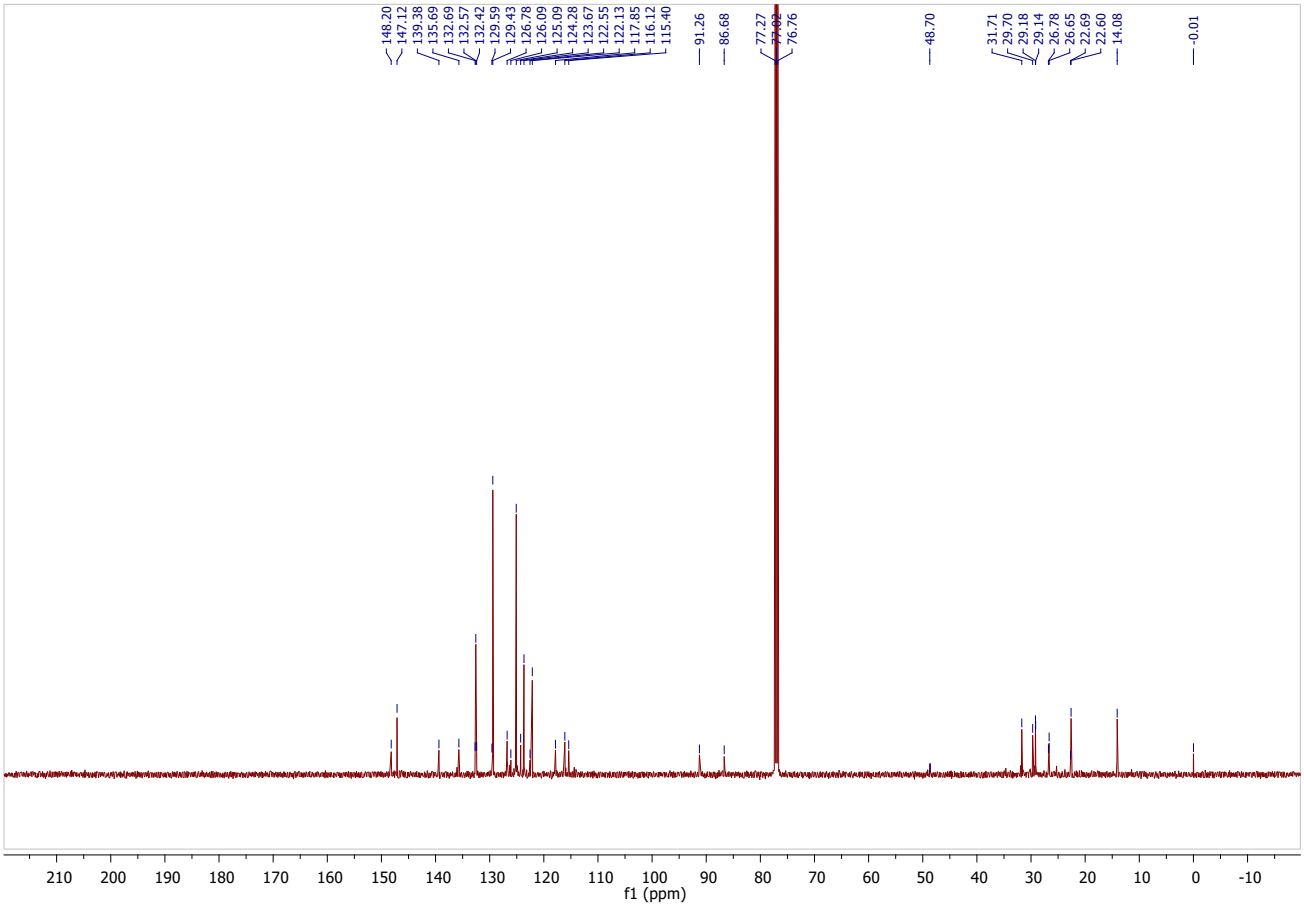


Fig. S7 ^{13}C-NMR of TPA1

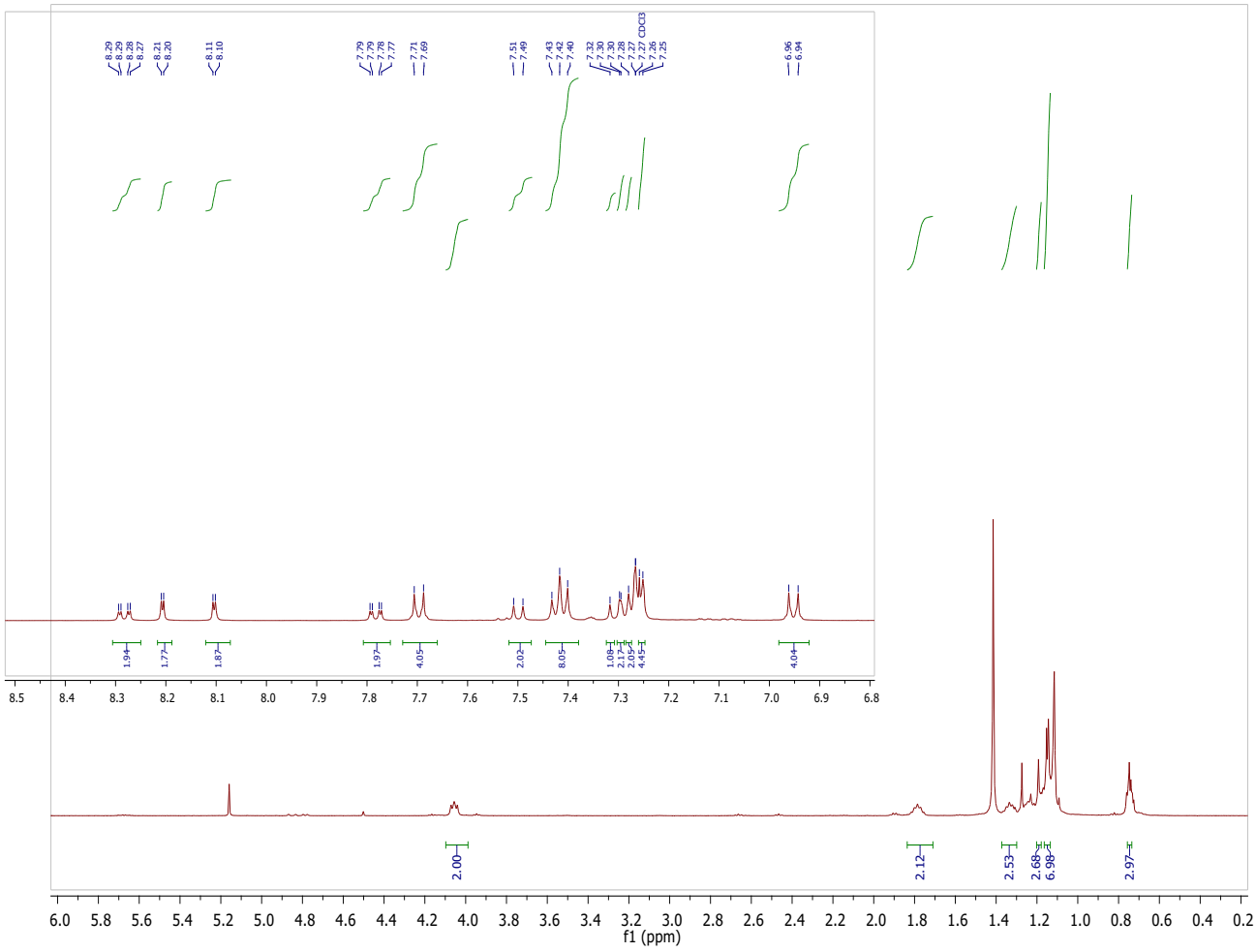


Fig. S8 ^{1}H-NMR of TPA2

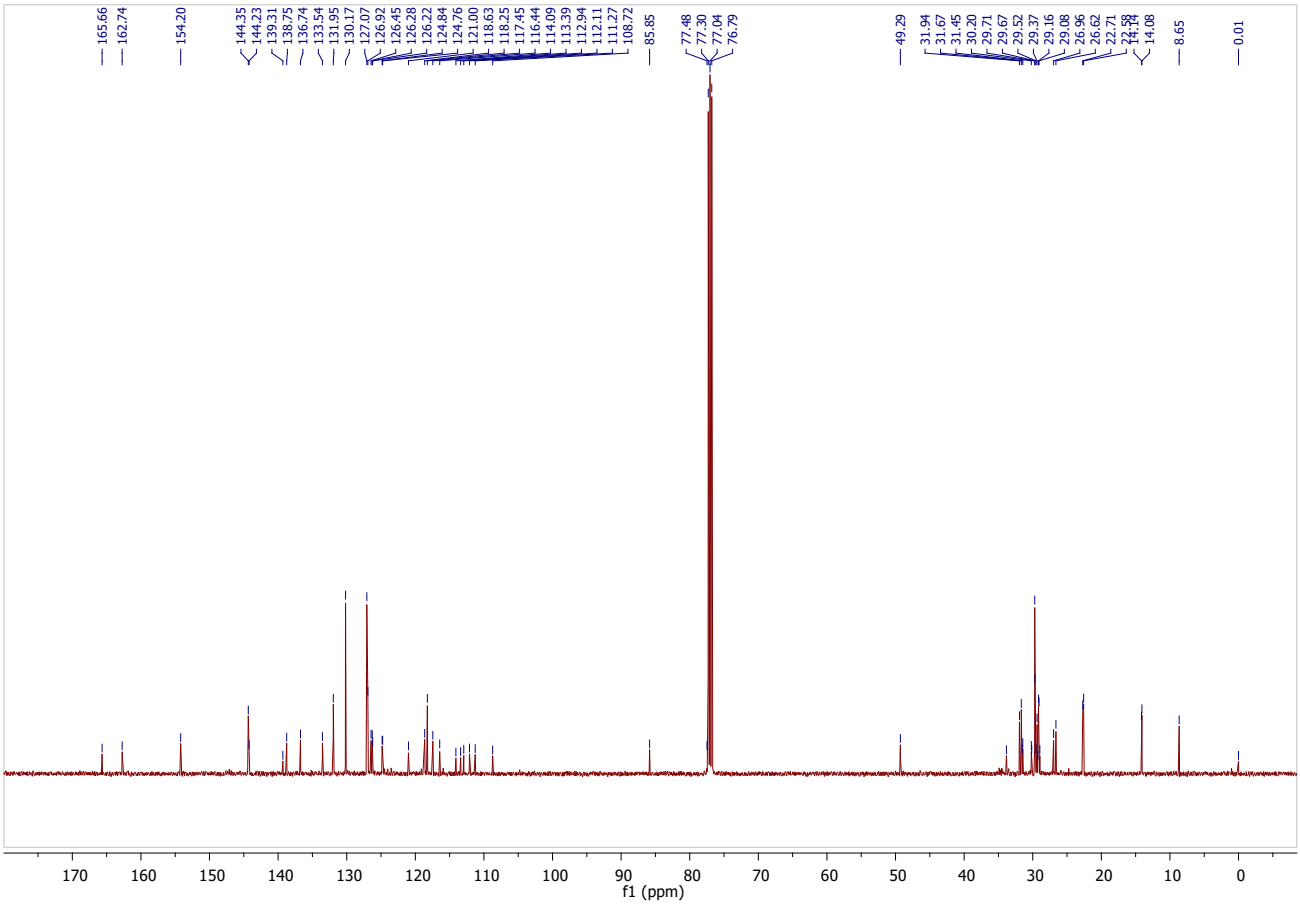


Fig. S9 ^{13}C-NMR of TPA2

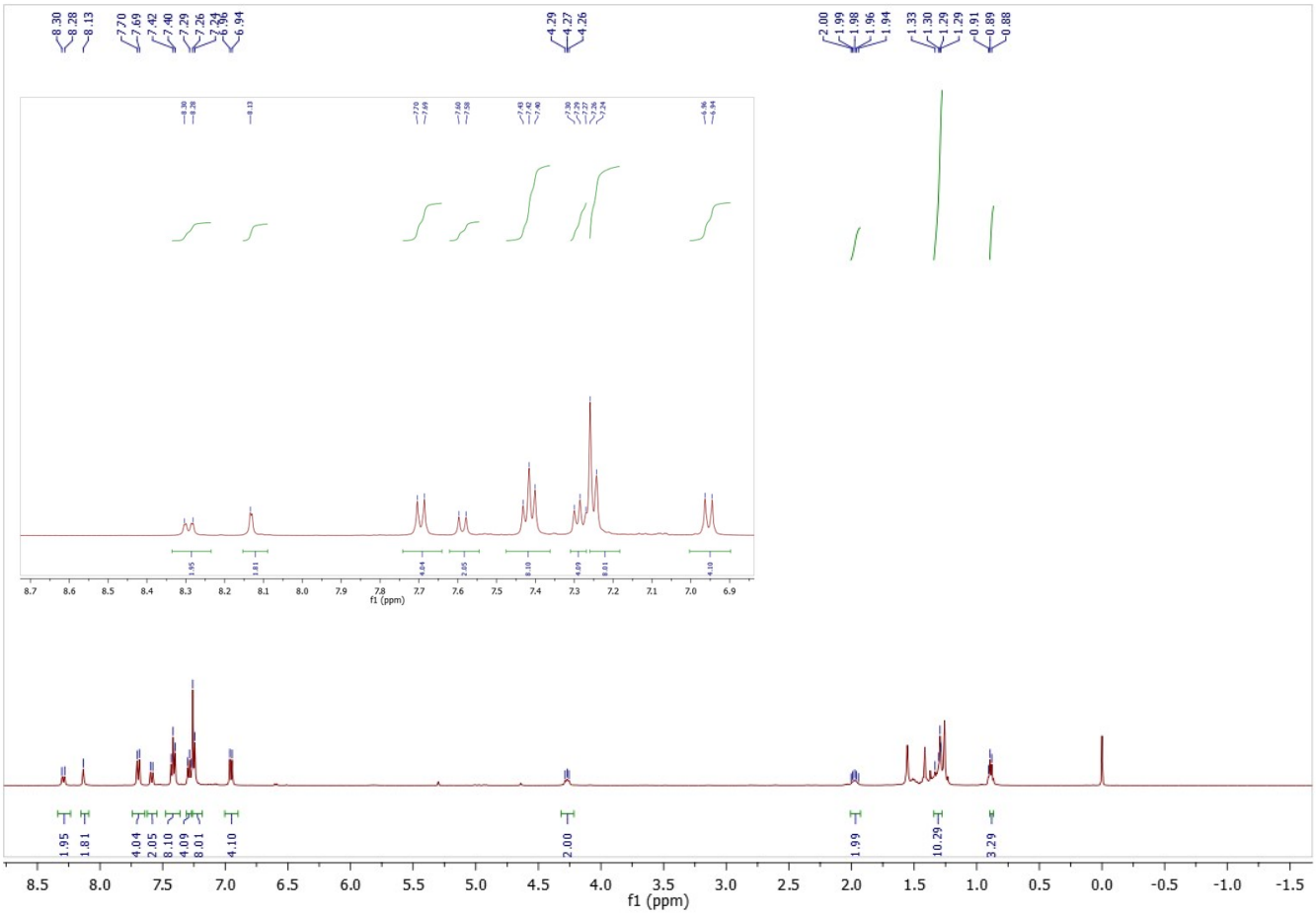


Fig. S10 ^{1}H-NMR of TPA3

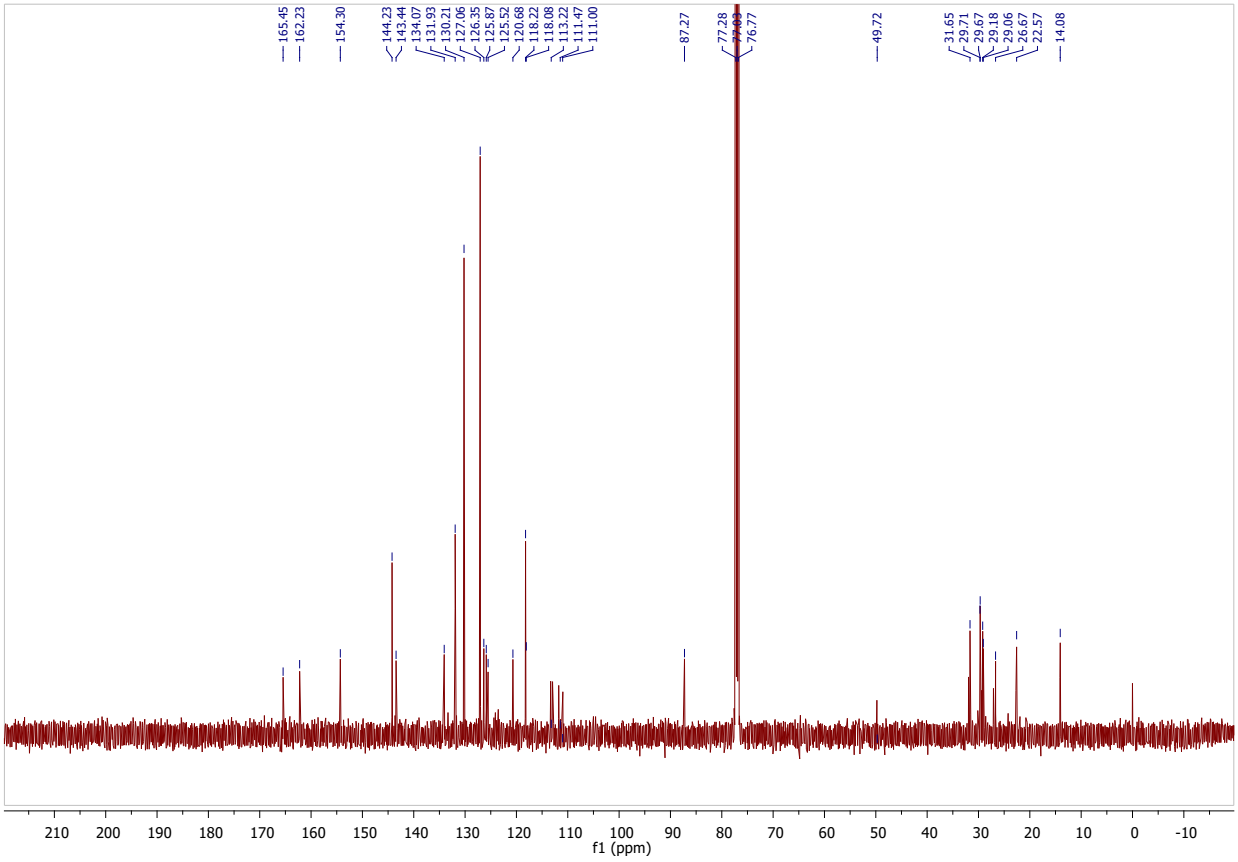


Fig. S11 ^{13}C-NMR of TPA3

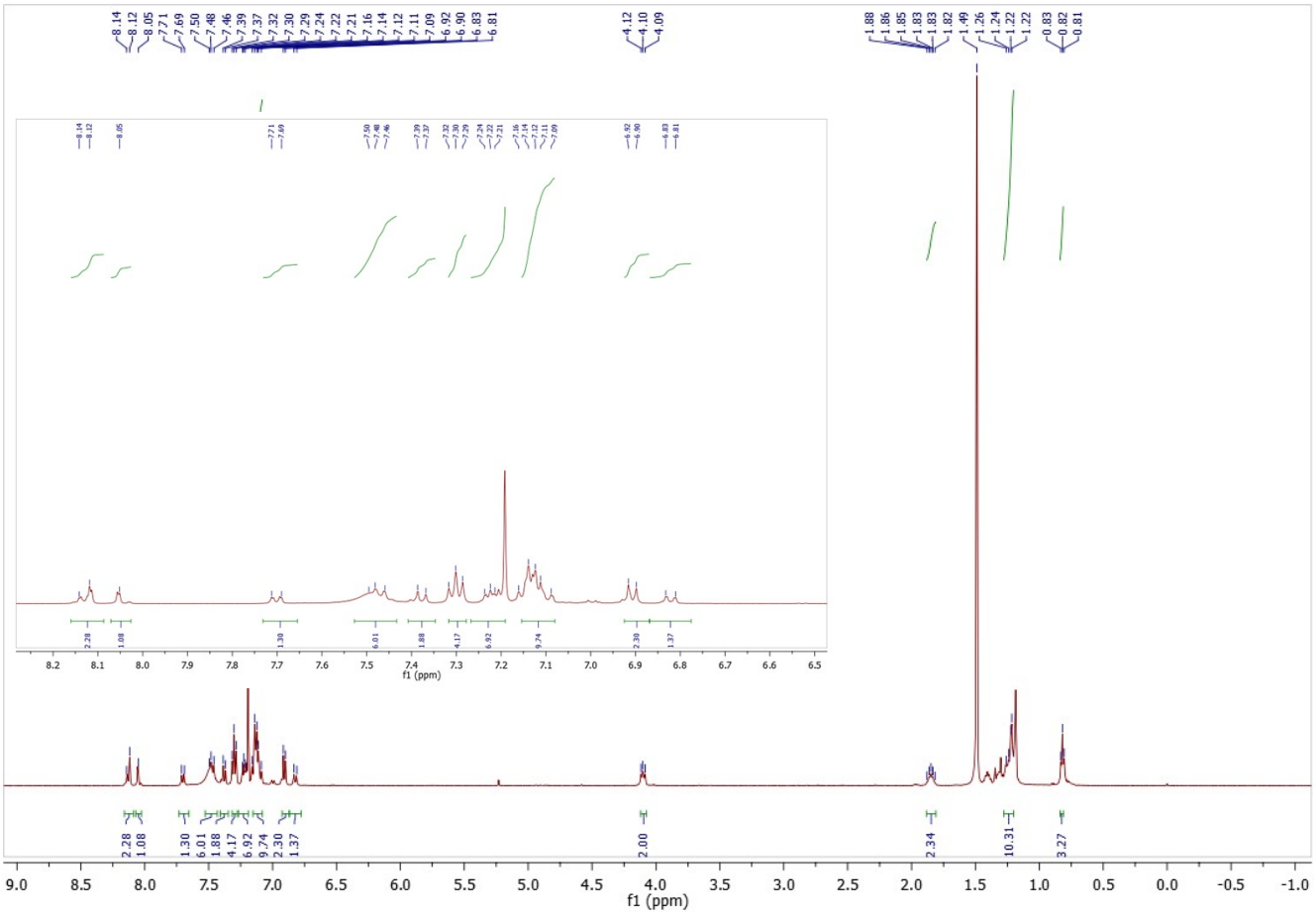


Fig. S12 ^{1}H-NMR of TPA4

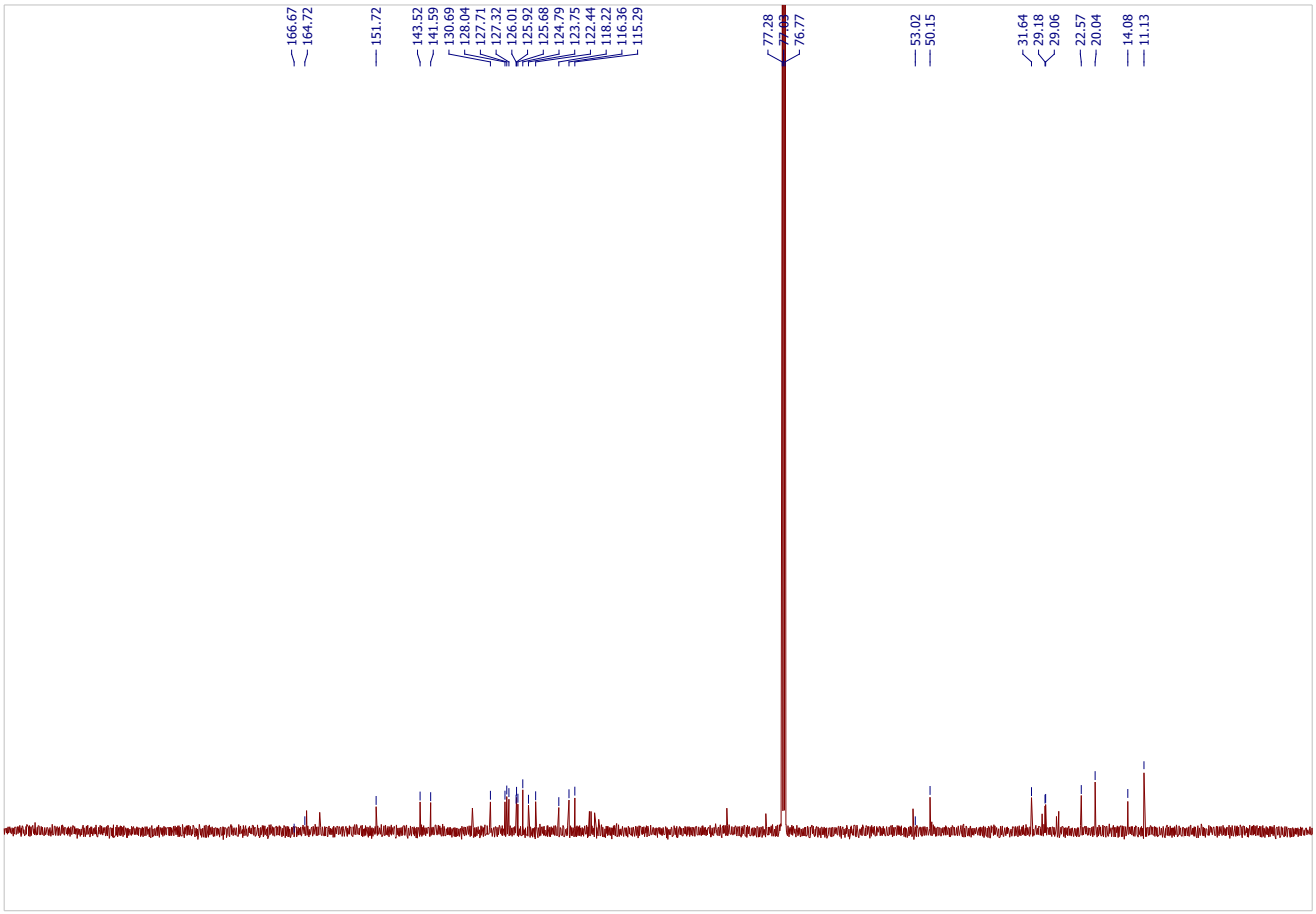


Fig. S13 ^{13}C-NMR of TPA4

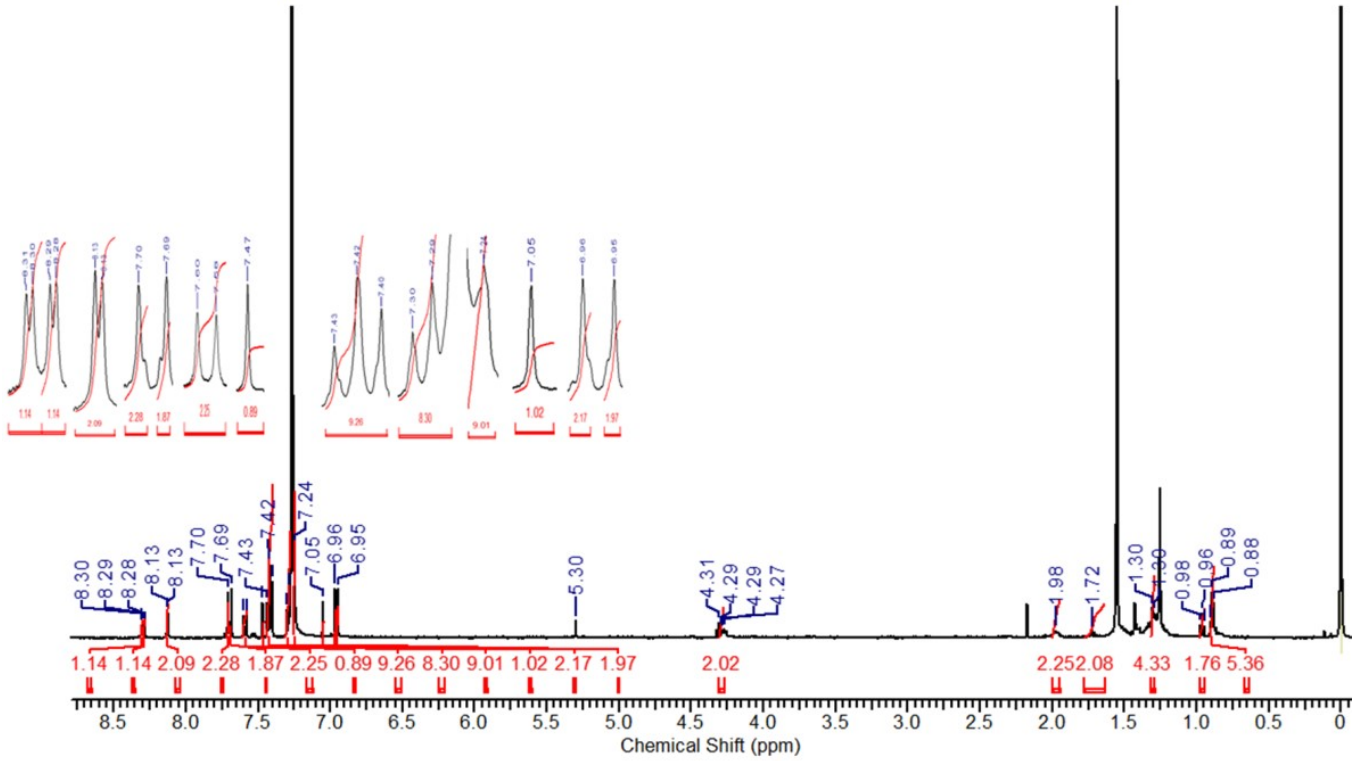


Fig. S14 ^{1}H-NMR of TPA5

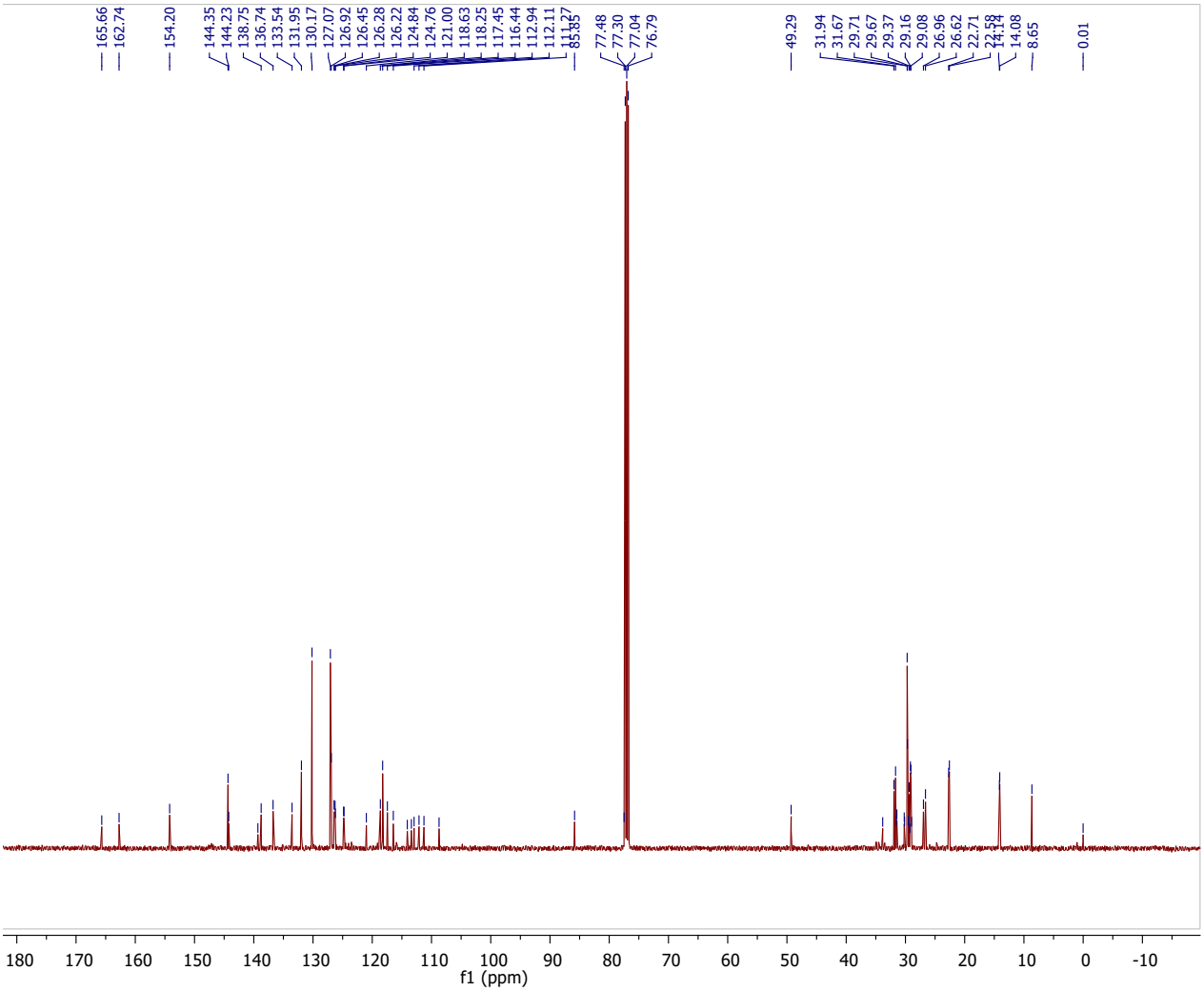


Fig. S15 ^{13}C-NMR of TPA5

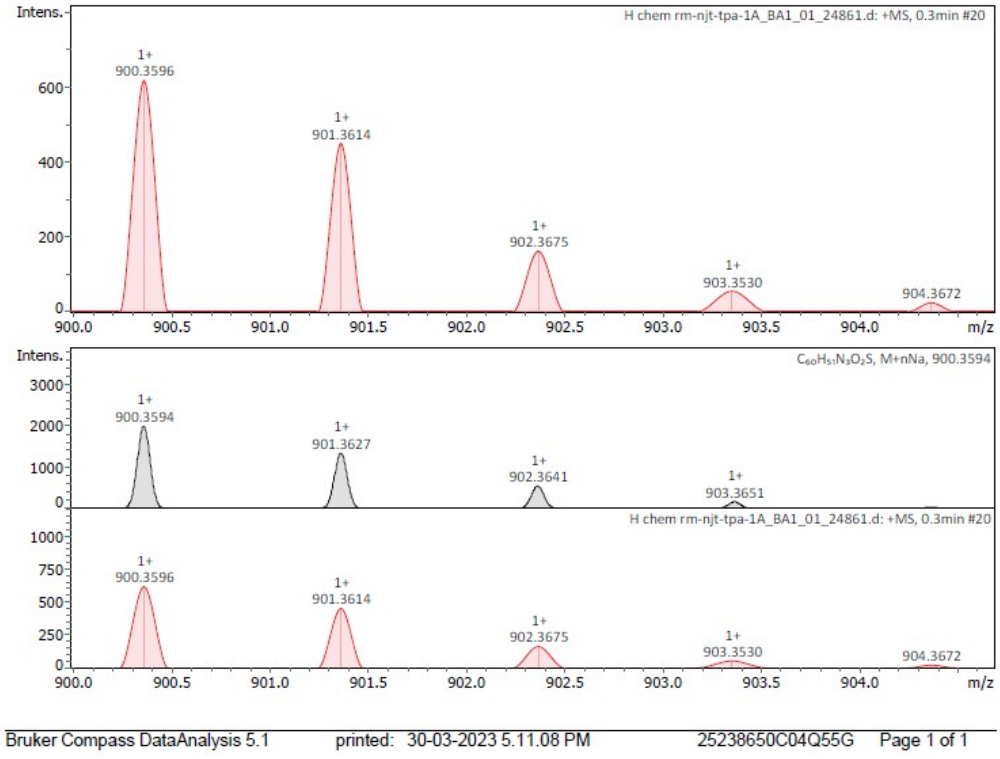


Fig. S16 HRMS of TPA1

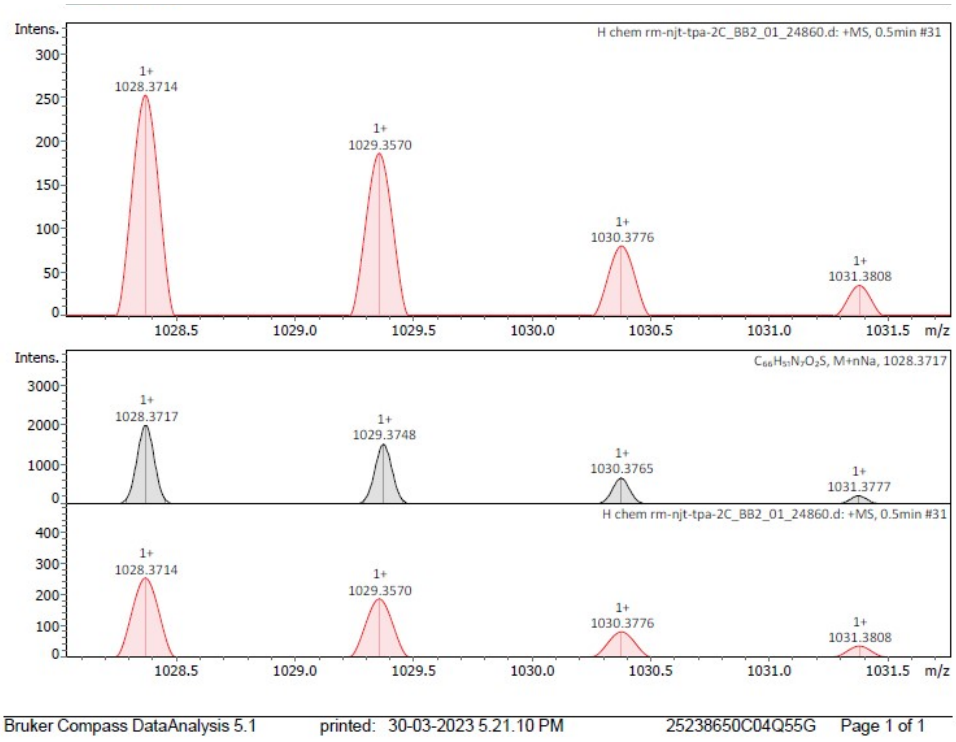


Fig. S17 HRMS of TPA2

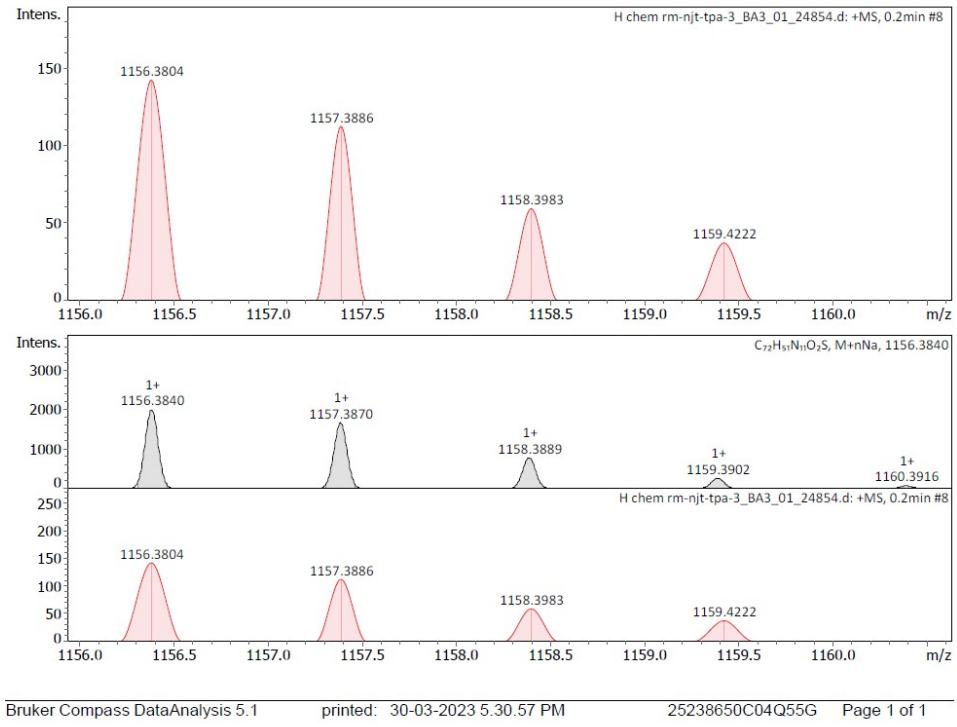


Fig. S18 HRMS of TPA3

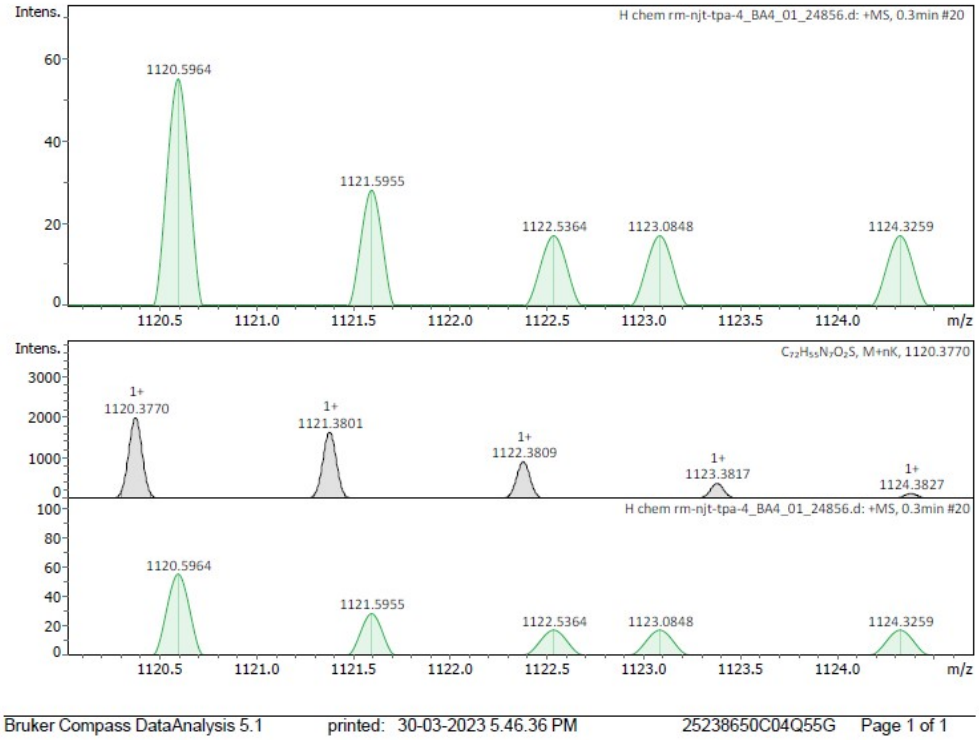


Fig. S19 Mass of TPA4

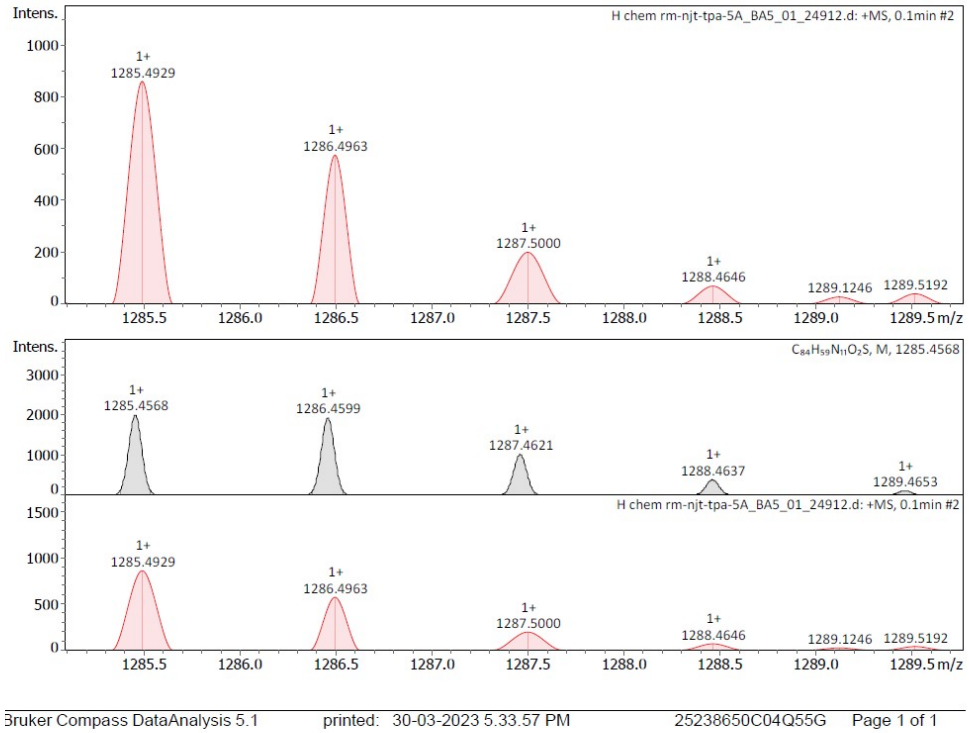


Fig. S20 Mass of TPA5

Operator ID:	SIC IIT Indore
Company name:	Thermo Finnigan
Method filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\CHNS system12-11-202
Method name:	NCHS
Analysed:	12-11-22 12:31
Printed:	11-12-2022 14:25
Elemental Analyser method:	
Sampler method:	
Sample ID:	RM-MI-TPA-1
Analysis type:	UnkNown
Chromatogram filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\DfchA020.DAT
Calibration method:	Least Squares to Linear fit
Sample weight:	1.926
Protein factor:	6.25

Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)	Area
Nitrogen	4.651	0.850	162453	51.40
Carbon	80.258	1.183	8350391	1.000
Hydrogen	5.372	3.433	1817787	4.593
Sulphur	3.244	6.733	143529	58.17

Fig. S21 Elemental analysis of TPA1

Operator ID:	SIC IIT Indore
Company name:	Thermo Finnigan
Method filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\CHNS system12-11-202
Method name:	NCHS
Analysed:	12-11-22 12:49
Printed:	11-12-2022 14:26
Elemental Analyser method:	
Sampler method:	
Sample ID:	RM-MI-TPA-2
Analysis type:	UnkNown
Chromatogram filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\DfchA021.DAT
Calibration method:	Least Squares to Linear fit
Sample weight:	1.807
Protein factor:	6.25

Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)	Area
Nitrogen	9.080	0.842	324993	21.86
Carbon	78.071	1.158	7105678	1.000
Hydrogen	5.761	3.375	1828924	3.885
Sulphur	3.052	6.717	134997	52.63

Fig. S22 Elemental analysis of TPA2

Operator ID:	SIC IIT Indore
Company name:	Thermo Finnigan
Method filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\CHNS system12-11-202
Method name:	NCHS
Analysed:	12-11-22 13:06
Printed:	11-12-2022 14:27
Elemental Analyser method:	
Sampler method:	
Sample ID:	RM-MI-TPA-3
Analysis type:	UnkNown
Chromatogram filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\DfchA022.DAT
Calibration method:	Least Squares to Linear fit
Sample weight:	1.112
Protein factor:	6.25

Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)	Area
Nitrogen	6.539	0.833	215109	17.01
Carbon	75.664	1.208	3660886	1.000
Hydrogen	4.221	3.250	824559	4.439
Sulphur	2.833	6.742	49913	73.34

Fig. S23 Elemental analysis of TPA3

Operator ID:	SIC IIT Indore
Company name:	Thermo Finnigan
Method filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\CHNS system12-11-202
Method name:	NCHS
Analysed:	12-11-22 13:18
Printed:	11-12-2022 14:27
Elemental Analyser method:	
Sampler method:	
Sample ID:	RM-MI-TPA-4
Analysis type:	UnkNown
Chromatogram filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\DfchA023.DAT
Calibration method:	Least Squares to Linear fit
Sample weight:	2.055
Protein factor:	6.25

Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)	Area
Nitrogen	9.394	0.825	1057398	7.915
Carbon	79.573	1.142	8369432	1.000
Hydrogen	5.210	3.225	1159020	7.221
Sulphur	2.874	6.733	43984	190.2

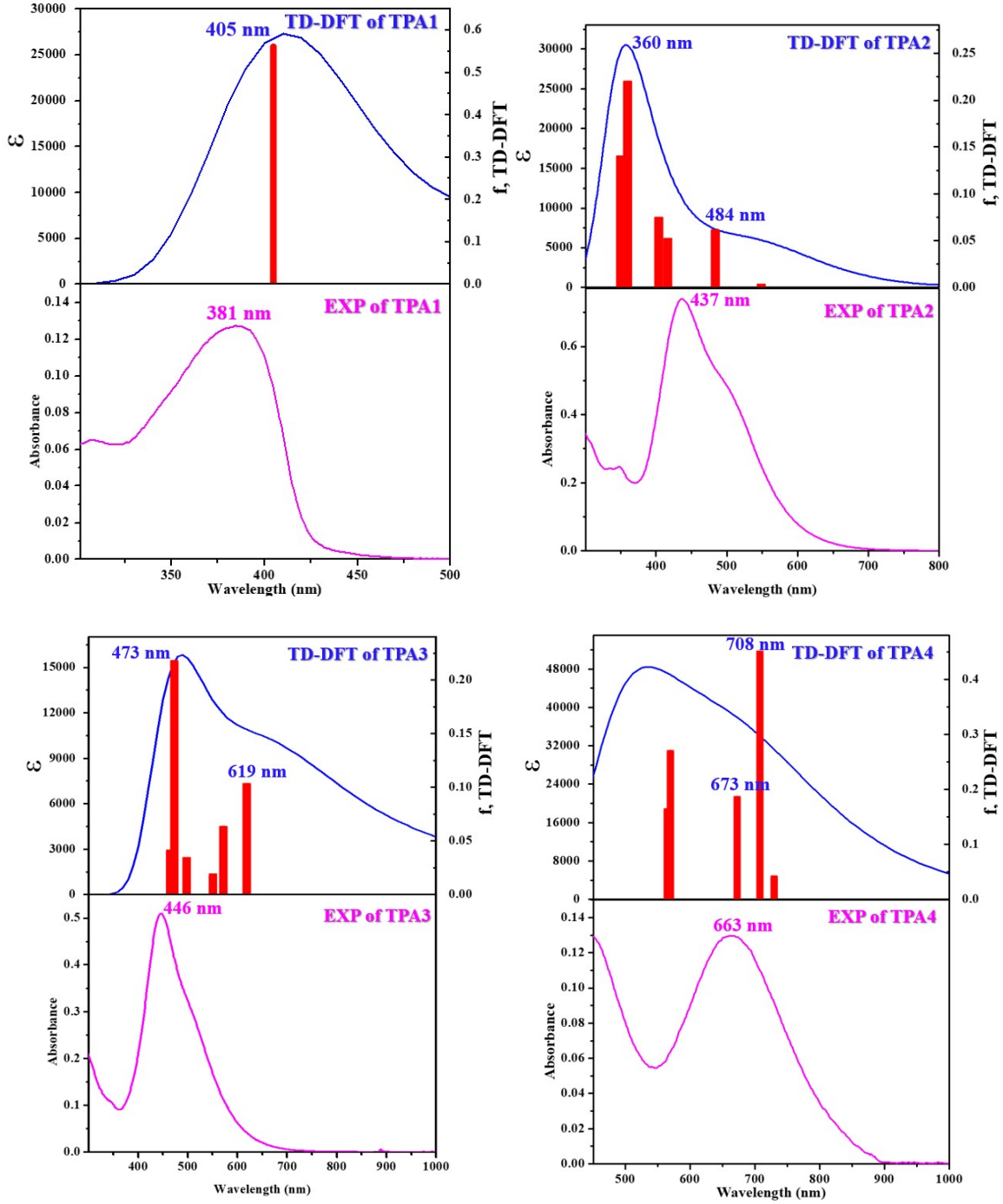
Fig. S24 Elemental analysis of TPA4

Operator ID:	SIC IIT Indore
Company name:	Thermo Finnigan
Method filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\CHNS system12-11-202
Method name:	NCHS
Analysed:	12-11-22 13:30
Printed:	11-12-2022 14:28
Elemental Analyser method:	
Sampler method:	
Sample ID:	RM-MI-TPA-5
Analysis type:	UnkNown
Chromatogram filename:	E:\Eager for FLASH\System defined methods\21. CHNS 9-11-2022\DfchA024.DAT
Calibration method:	Least Squares to Linear fit
Sample weight:	1.895
Protein factor:	6.25

Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)	Area
Nitrogen	10.849	0.833	608151	12.41
Carbon	77.990	1.175	7549396	1.000
Hydrogen	4.799	3.325	1597777	4.724
Sulphur	2.493	6.692	69257	109.0

Fig. S25 Elemental analysis of TPA5

TDDFT Calculations



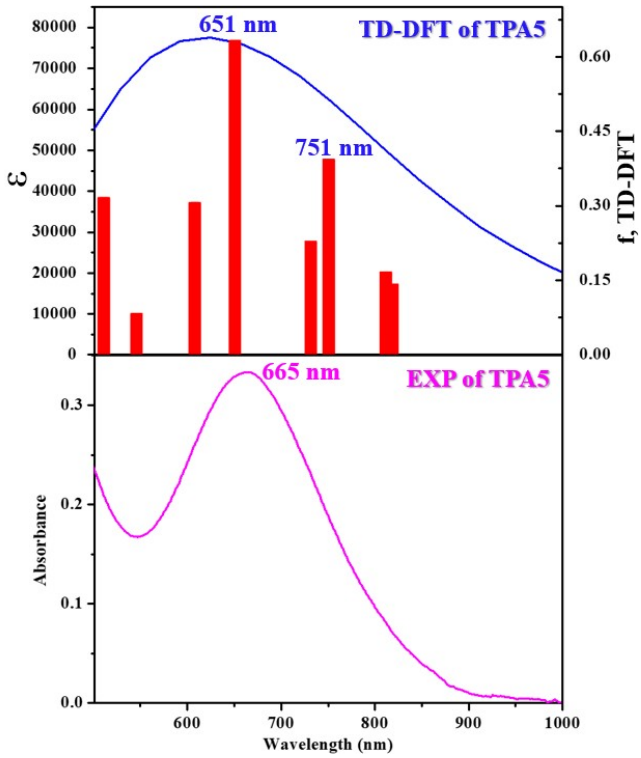


Fig. S26 Experimental (bottom) and TDDFT-predicted (top) UV-Vis absorption spectra of **TPA1**–**TPA5** in DCM.

TD-DFT Calculation data

Calculation method: B3LYP/6-31G(d,p) and CAM-B3LYP/6-31G(d,p) level in dichloromethane solvent.

TD-DFT of TPA1 in DCM solvent.

Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 0.7345 eV 1688.10 nm f=0.0900 <S**2>=0.000

205 -> 213 -0.16228

212 -> 213 0.89374

212 <- 213 -0.59222

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2832.47026288

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 0.9053 eV 1369.47 nm f=0.0003 <S**2>=0.000

211 -> 213 0.70299

Excited State 3: Singlet-A 1.2730 eV 973.97 nm f=0.0276 <S**2>=0.000

207 -> 213 0.14094

208 -> 213 0.22684

209 -> 213 0.33602

210 -> 213 0.54622

Excited State 4: Singlet-A 1.4241 eV 870.62 nm f=0.0036 <S**2>=0.000

207 -> 213 -0.23578

208 -> 213 -0.37720

209 -> 213 -0.32816

210 -> 213 0.43054

Excited State 5: Singlet-A 1.5782 eV 785.63 nm f=0.0205 <S**2>=0.000

202 -> 213 -0.22569

203 -> 213 -0.19328

205 -> 213 0.62440

212 -> 213 0.15530

212 <- 213 -0.11232

Excited State 6: Singlet-A 1.7230 eV 719.56 nm f=0.0617 <S**2>=0.000

206 -> 213 -0.11738

207 -> 213 -0.29436

208 -> 213 -0.33444

209 -> 213 0.51474

Excited State 7: Singlet-A 1.7528 eV 707.34 nm f=0.0635 <S**2>=0.000

210 -> 214 0.15729

211 -> 214 0.67298

Excited State 8: Singlet-A 1.8047 eV 687.02 nm f=0.0048 <S**2>=0.000

202 -> 213 -0.33299

203 -> 213 0.61437

Excited State 9: Singlet-A 1.8735 eV 661.77 nm f=0.1953 <S**2>=0.000

202 -> 213 0.20427

204 -> 213 0.10052

205 -> 213 0.15529

206 -> 213 0.46498

207 -> 213 0.26697

208 -> 213 -0.34720

Excited State 10: Singlet-A 2.0189 eV 614.13 nm f=0.1118 <S**2>=0.000

199 -> 213 0.10578

202 -> 213 0.49689

203 -> 213 0.25375

205 -> 213 0.20683

207 -> 213 -0.22715

208 -> 213 0.12646

212 -> 213 0.28566

212 <- 213 -0.21831

Excited State 11: Singlet-A 2.0764 eV 597.10 nm f=0.0124 <S**2>=0.000

200 -> 213 -0.12256

202 -> 213 0.11116

204 -> 213 -0.11500

206 -> 213 -0.43890

207 -> 213 0.44951

208 -> 213 -0.22090

Excited State 12: Singlet-A 2.1831 eV 567.92 nm f=0.0000 <S**2>=0.000

212 -> 214 0.70698

Excited State 13: Singlet-A 2.2399 eV 553.53 nm f=0.0147 <S**2>=0.000

199 -> 213 0.36906

200 -> 213 0.55795

204 -> 213 0.12345

206 -> 213 -0.12005

Excited State 14: Singlet-A 2.3867 eV 519.49 nm f=0.0011 <S**2>=0.000

199 -> 213 -0.18133

204 -> 213 0.65573

206 -> 213 -0.13711

Excited State 15: Singlet-A 2.4265 eV 510.97 nm f=0.0072 <S**2>=0.000

208 -> 214 0.24741

209 -> 214 -0.37832

210 -> 214 0.51097

Excited State 16: Singlet-A 2.6039 eV 476.14 nm f=0.0096 <S**2>=0.000

195 -> 213 -0.35834

196 -> 213 0.40193

212 -> 215 0.16936

212 -> 216 0.40082

Excited State 17: Singlet-A 2.6382 eV 469.97 nm f=0.0000 <S**2>=0.000

201 -> 213 0.70415

Excited State 18: Singlet-A 2.6562 eV 466.78 nm f=0.0009 <S**2>=0.000

198 -> 213 0.19688

199 -> 213 0.50089

200 -> 213 -0.37479

204 -> 213 0.15186

212 -> 216 0.10887

Excited State 19: Singlet-A 2.6823 eV 462.24 nm f=0.0040 <S**2>=0.000

195 -> 213 0.28918

196 -> 213 -0.31888

212 -> 215 0.22122

212 -> 216 0.48818

Excited State 20: Singlet-A 2.7658 eV 448.28 nm f=0.1104 <S**2>=0.000

206 -> 214 -0.18869

207 -> 214 0.33659

208 -> 214 -0.35324

209 -> 214 0.20470

210 -> 214 0.37385

211 -> 214 -0.16039

Excited State 21: Singlet-A 2.8726 eV 431.61 nm f=0.0007 <S**2>=0.000

197 -> 213 0.10593

198 -> 213 0.63889

199 -> 213 -0.23690

Excited State 22: Singlet-A 2.9292 eV 423.27 nm f=0.0256 <S**2>=0.000

212 -> 215 0.63325

212 -> 216 -0.27768

Excited State 23: Singlet-A 2.9725 eV 417.10 nm f=0.0121 <S**2>=0.000

190 -> 213 0.15595

192 -> 213 -0.14763

193 -> 213 -0.12627

194 -> 213 0.20772

195 -> 213 0.32928

196 -> 213 0.37430

197 -> 213 0.31808

198 -> 213 -0.16161

Excited State 24: Singlet-A 3.0053 eV 412.55 nm f=0.0030 <S**2>=0.000

193 -> 213 0.10368

195 -> 213 -0.19236

196 -> 213 -0.23184

197 -> 213 0.61574

Excited State 25: Singlet-A 3.0588 eV 405.34 nm f=0.5600 <S**2>=0.000

204 -> 214 -0.22922

206 -> 214 0.21212

207 -> 214 -0.24763

209 -> 214 0.25791

210 -> 214 0.15794

211 -> 215 0.43891

211 -> 216 -0.10111

TD-DFT of TPA2 in DCM solvent.

Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.1803 eV 568.66 nm f=0.0950 <S**2>=0.000

243 -> 245 0.70543

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3280.50257660

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.2555 eV 549.70 nm f=0.0021 <S**2>=0.000

244 -> 245 0.70236

Excited State 3: Singlet-A 2.5442 eV 487.33 nm f=0.0601 <S**2>=0.000

243 -> 246 0.70319

Excited State 4: Singlet-A 2.6073 eV 475.53 nm f=0.0259 <S**2>=0.000

242 -> 245 0.66579

244 -> 246 -0.18115

Excited State 5: Singlet-A 2.6266 eV 472.02 nm f=0.0012 <S**2>=0.000

242 -> 245 0.18187

244 -> 246 0.67666

Excited State 6: Singlet-A 2.9682 eV 417.71 nm f=0.0508 <S**2>=0.000

242 -> 246 0.67969

Excited State 7: Singlet-A 2.9937 eV 414.16 nm f=0.0056 <S**2>=0.000

233 -> 245 -0.10411

236 -> 245 0.12216

239 -> 245 0.16659

240 -> 245 0.66217

Excited State 8: Singlet-A 3.0503 eV 406.46 nm f=0.0555 <S**2>=0.000

235 -> 245 -0.17250

236 -> 245 0.20753

237 -> 245 -0.12134

238 -> 245 0.17802

239 -> 245 0.46164

240 -> 245 -0.15050

241 -> 245 -0.33297

Excited State 9: Singlet-A 3.0620 eV 404.91 nm f=0.0734 <S**2>=0.000

233 -> 245 0.10345

235 -> 245 -0.17107

236 -> 245 -0.25619

237 -> 245 -0.12454

238 -> 245 0.39923

239 -> 245 -0.30156

240 -> 245 0.17554

241 -> 245 -0.28299

Excited State 10: Singlet-A 3.1277 eV 396.41 nm f=0.0186 <S**2>=0.000

236 -> 245 0.57954

238 -> 245 0.14862

239 -> 245 -0.34596

Excited State 11: Singlet-A 3.2193 eV 385.13 nm f=0.0068 <S**2>=0.000

233 -> 245 0.11947

235 -> 245 -0.14466

237 -> 245 -0.12569

238 -> 245 0.35437

239 -> 245 0.15122

241 -> 245 0.54119

Excited State 12: Singlet-A 3.2558 eV 380.80 nm f=0.0190 <S**2>=0.000

233 -> 245 0.64373

236 -> 245 0.13547

236 -> 246 0.10134

238 -> 245 -0.13326

Excited State 13: Singlet-A 3.3020 eV 375.48 nm f=0.0002 <S**2>=0.000

237 -> 245 0.65353

238 -> 245 0.25328

Excited State 14: Singlet-A 3.3702 eV 367.89 nm f=0.0315 <S**2>=0.000

232 -> 245 -0.14016

233 -> 245 -0.10986

236 -> 246 0.22995

239 -> 246 0.25839

240 -> 246 0.56653

Excited State 15: Singlet-A 3.3894 eV 365.80 nm f=0.0235 <S**2>=0.000

231 -> 245 -0.16691

235 -> 245 0.48114

235 -> 246 -0.12399

237 -> 245 -0.13155

238 -> 245 0.22672

238 -> 246 0.17901

239 -> 246 0.12120

240 -> 246 -0.16746

241 -> 246 -0.19366

Excited State 16: Singlet-A 3.4059 eV 364.03 nm f=0.0217 <S**2>=0.000

232 -> 245 0.31064

232 -> 246 0.10335

235 -> 245 0.17178

236 -> 246 -0.34705

239 -> 246 -0.27529

240 -> 246 0.36576

Excited State 17: Singlet-A 3.4329 eV 361.16 nm f=0.2187 <S**2>=0.000

232 -> 245 -0.16012

234 -> 245 -0.13813

235 -> 245 0.32356

235 -> 246 0.19440

237 -> 246 0.13846

238 -> 246 -0.32782

241 -> 246 0.36022

Excited State 18: Singlet-A 3.4424 eV 360.17 nm f=0.0085 <S**2>=0.000

234 -> 245 0.69081

Excited State 19: Singlet-A 3.4878 eV 355.47 nm f=0.0366 <S**2>=0.000

232 -> 245 0.37252

236 -> 246 -0.14397

238 -> 246 -0.24522

239 -> 246 0.49815

Excited State 20: Singlet-A 3.5416 eV 350.08 nm f=0.1388 <S**2>=0.000

232 -> 245 0.41271

233 -> 246 -0.16745

236 -> 246 0.49267

239 -> 246 -0.18300

Excited State 21: Singlet-A 3.5899 eV 345.37 nm f=0.0234 <S**2>=0.000

233 -> 246 0.10911

235 -> 246 -0.14266

237 -> 246 -0.11923

238 -> 246 0.33000

239 -> 246 0.13922

241 -> 246 0.54580

Excited State 22: Singlet-A 3.6347 eV 341.11 nm f=0.0906 <S**2>=0.000

231 -> 245 0.12269

233 -> 246 -0.14761

242 -> 247 -0.17387

244 -> 247 0.63015

244 -> 248 -0.11831

Excited State 23: Singlet-A 3.6467 eV 339.99 nm f=0.0692 <S**2>=0.000

232 -> 245 0.14345

233 -> 246 0.62714

236 -> 246 0.12228

238 -> 246 -0.16217

244 -> 247 0.13349

Excited State 24: Singlet-A 3.6732 eV 337.54 nm f=0.0228 <S**2>=0.000

231 -> 245 0.43774

235 -> 245 0.12507

237 -> 246 0.40726

238 -> 246 0.28817

Excited State 25: Singlet-A 3.6777 eV 337.12 nm f=0.0341 <S**2>=0.000

231 -> 245 -0.42998

235 -> 245 -0.11782

237 -> 246 0.51821

TD-DFT of TPA3 in DCM solvent.

Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 0.8218 eV 1508.67 nm f=0.0010 <S**2>=0.000

276 -> 277 -0.25452

276 -> 278 0.66207

276 <- 277 0.12790

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3727.70824589

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.0307 eV 1202.94 nm f=0.0310 <S**2>=0.000

273 -> 277 0.35117

276 -> 277 0.77031

276 -> 278 0.21301

276 <- 277 -0.51622

Excited State 3: Singlet-A 1.2011 eV 1032.23 nm f=0.0000 <S**2>=0.000

276 -> 279 0.70132

Excited State 4: Singlet-A 1.3936 eV 889.65 nm f=0.0382 <S**2>=0.000

273 -> 277 0.60477

276 -> 277 -0.51303

276 <- 277 0.38041

Excited State 5: Singlet-A 1.5072 eV 822.61 nm f=0.0001 <S**2>=0.000

275 -> 277 0.70631

Excited State 6: Singlet-A 1.6458 eV 753.34 nm f=0.0612 <S**2>=0.000

274 -> 279 0.39329

275 -> 278 -0.13757

275 -> 279 0.56250

Excited State 7: Singlet-A 1.7081 eV 725.86 nm f=0.0071 <S**2>=0.000

276 -> 280 0.69759

Excited State 8: Singlet-A 1.7674 eV 701.51 nm f=0.0530 <S**2>=0.000

274 -> 277 0.24968

274 -> 278 -0.10368

274 -> 279 0.52504

275 -> 278 0.14824

275 -> 279 -0.35155

Excited State 9: Singlet-A 1.7751 eV 698.45 nm f=0.0064 <S**2>=0.000

274 -> 277 0.66058

274 -> 279 -0.20485

275 -> 279 0.12246

Excited State 10: Singlet-A 1.8284 eV 678.08 nm f=0.0025 <S**2>=0.000

275 -> 278 0.67449

275 -> 279 0.20259

Excited State 11: Singlet-A 2.0020 eV 619.29 nm f=0.1008 <S**2>=0.000

273 -> 278 0.69413

Excited State 12: Singlet-A 2.0913 eV 592.84 nm f=0.0003 <S**2>=0.000

274 -> 278 0.69251

274 -> 279 0.13829

Excited State 13: Singlet-A 2.1669 eV 572.17 nm f=0.0406 <S**2>=0.000

264 -> 277 -0.10602

266 -> 277 -0.19280

269 -> 277 0.57620

270 -> 277 -0.29836

Excited State 14: Singlet-A 2.2499 eV 551.07 nm f=0.0164 <S**2>=0.000

262 -> 277 -0.14960

264 -> 277 0.16383

265 -> 277 -0.18467

266 -> 277 0.55816

269 -> 277 0.29039

Excited State 15: Singlet-A 2.2671 eV 546.89 nm f=0.0009 <S**2>=0.000

273 -> 279 0.70250

Excited State 16: Singlet-A 2.3278 eV 532.61 nm f=0.0000 <S**2>=0.000

276 -> 281 0.70644

Excited State 17: Singlet-A 2.3670 eV 523.80 nm f=0.0046 <S**2>=0.000

266 -> 277 -0.12250

269 -> 277 0.14917

270 -> 277 0.34301

272 -> 277 0.58300

Excited State 18: Singlet-A 2.4146 eV 513.48 nm f=0.0058 <S**2>=0.000

266 -> 277 -0.13463

269 -> 277 0.20885

270 -> 277 0.50654

271 -> 277 -0.15173

272 -> 277 -0.39076

Excited State 19: Singlet-A 2.4808 eV 499.77 nm f=0.0013 <S**2>=0.000

270 -> 277 0.11744

271 -> 277 0.68079

Excited State 20: Singlet-A 2.4848 eV 498.97 nm f=0.0318 <S**2>=0.000

262 -> 277 0.23559

263 -> 277 0.11813

264 -> 277 -0.25985

265 -> 277 0.48001

266 -> 277 0.30887

271 -> 277 0.10745

Excited State 21: Singlet-A 2.5051 eV 494.93 nm f=0.0066 <S**2>=0.000

272 -> 278 -0.16253

272 -> 279 0.65551

275 -> 281 -0.14659

Excited State 22: Singlet-A 2.6027 eV 476.36 nm f=0.0549 <S**2>=0.000

262 -> 277 -0.27955

263 -> 277 -0.15387

264 -> 277 0.37695

265 -> 277 0.44734

270 -> 278 0.15784

Excited State 23: Singlet-A 2.6164 eV 473.87 nm f=0.2155 <S**2>=0.000

265 -> 277 -0.13519

269 -> 278 0.15578

270 -> 278 0.56311

270 -> 279 -0.17228

272 -> 278 0.23913

275 -> 281 -0.10674

Excited State 24: Singlet-A 2.6294 eV 471.54 nm f=0.0000 <S**2>=0.000

268 -> 277 0.70073

Excited State 25: Singlet-A 2.6660 eV 465.06 nm f=0.0387 <S**2>=0.000

263 -> 279 0.12039

268 -> 279 0.20050

270 -> 278 0.11461

271 -> 279 -0.28774

274 -> 281 0.31519

275 -> 281 0.46213

TD-DFT of TPA4 in DCM solvent.

Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 0.9994 eV 1240.55 nm f=0.0019 <S**2>=0.000

262 -> 265 0.55177

263 -> 265 -0.41174

264 -> 265 0.17715

262 <- 265 -0.13210

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3510.85180030

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.0242 eV 1210.59 nm f=0.0107 <S**2>=0.000

260 -> 265 0.10587

262 -> 265 0.46521

263 -> 265 0.46569

264 -> 265 -0.24567

262 <- 265 -0.10367

Excited State 3: Singlet-A 1.4279 eV 868.32 nm f=0.0010 <S**2>=0.000

263 -> 265 0.30272

264 -> 265 0.63347

Excited State 4: Singlet-A 1.4949 eV 829.39 nm f=0.0038 <S**2>=0.000

260 -> 267 0.21247

262 -> 267 0.18364

263 -> 267 0.57139

264 -> 267 -0.27966

Excited State 5: Singlet-A 1.6141 eV 768.15 nm f=0.0030 <S**2>=0.000

262 -> 266 0.69046

263 -> 266 -0.10522

Excited State 6: Singlet-A 1.6977 eV 730.31 nm f=0.0371 <S**2>=0.000

263 -> 266 0.25204

264 -> 266 0.64906

Excited State 7: Singlet-A 1.7263 eV 718.22 nm f=0.0015 <S**2>=0.000

262 -> 267 0.67682

263 -> 267 -0.16686

Excited State 8: Singlet-A 1.7498 eV 708.55 nm f=0.4461 <S**2>=0.000

260 -> 265 -0.29067

263 -> 266 0.57142

263 -> 268 0.12656

264 -> 266 -0.22305

Excited State 9: Singlet-A 1.8406 eV 673.59 nm f=0.1817 <S**2>=0.000

260 -> 265 0.57931

261 -> 265 0.19496

263 -> 265 -0.12791

263 -> 266 0.23730

263 -> 268 0.11824

264 -> 266 -0.10789

Excited State 10: Singlet-A 1.9325 eV 641.57 nm f=0.0038 <S**2>=0.000

260 -> 265 -0.18822

261 -> 265 0.66329

Excited State 11: Singlet-A 2.1578 eV 574.58 nm f=0.0068 <S**2>=0.000

263 -> 267 0.29799

264 -> 267 0.63523

Excited State 12: Singlet-A 2.1744 eV 570.20 nm f=0.2652 <S**2>=0.000

260 -> 266 -0.15113

261 -> 266 0.44324

263 -> 266 -0.13443

263 -> 268 0.44094

264 -> 268 -0.19940

Excited State 13: Singlet-A 2.1942 eV 565.04 nm f=0.1594 <S**2>=0.000

260 -> 266 0.13735

261 -> 266 0.52019

263 -> 268 -0.40066

264 -> 268 0.15975

Excited State 14: Singlet-A 2.3042 eV 538.07 nm f=0.0019 <S**2>=0.000

258 -> 265 0.13543

259 -> 265 0.67763

Excited State 15: Singlet-A 2.3263 eV 532.97 nm f=0.0182 <S**2>=0.000

262 -> 268 0.68047

264 -> 268 -0.16947

Excited State 16: Singlet-A 2.3694 eV 523.28 nm f=0.2184 <S**2>=0.000

260 -> 266 -0.14174

261 -> 268 0.10767

262 -> 268 0.16606

263 -> 268 0.22722

264 -> 268 0.61514

Excited State 17: Singlet-A 2.3938 eV 517.94 nm f=0.0187 <S**2>=0.000

255 -> 265 0.64177

255 -> 267 -0.13997

260 -> 267 -0.14434

Excited State 18: Singlet-A 2.5062 eV 494.72 nm f=0.1038 <S**2>=0.000

255 -> 265 0.18179

255 -> 267 0.11417

260 -> 266 -0.26703

260 -> 267 0.54801

261 -> 267 0.11077

263 -> 267 -0.18066

Excited State 19: Singlet-A 2.5170 eV 492.59 nm f=0.4016 <S**2>=0.000

253 -> 265 -0.13058

260 -> 266 0.53842

260 -> 267 0.25772

260 -> 268 0.12892

263 -> 266 -0.11943

263 -> 268 0.21238

Excited State 20: Singlet-A 2.5543 eV 485.40 nm f=0.0035 <S**2>=0.000

258 -> 265 0.66023

259 -> 265 -0.14423

Excited State 21: Singlet-A 2.5782 eV 480.90 nm f=0.0298 <S**2>=0.000

258 -> 265 0.10569

258 -> 266 0.17356

259 -> 266 0.65559

261 -> 266 -0.12409

Excited State 22: Singlet-A 2.6743 eV 463.61 nm f=0.0050 <S**2>=0.000

261 -> 267 0.68684

Excited State 23: Singlet-A 2.7113 eV 457.28 nm f=0.0707 <S**2>=0.000

261 -> 269 -0.14303

263 -> 269 0.28016

264 -> 269 0.58350

264 -> 270 -0.15490

Excited State 24: Singlet-A 2.7198 eV 455.86 nm f=0.0077 <S**2>=0.000

249 -> 265 -0.20911

253 -> 265 0.58566

255 -> 267 -0.18105

260 -> 267 0.13499

Excited State 25: Singlet-A 2.8003 eV 442.75 nm f=0.0029 <S**2>=0.000

249 -> 265 -0.10962

251 -> 265 -0.13061

257 -> 266 -0.10551

258 -> 266 0.56911

259 -> 266 -0.19693

260 -> 268 -0.21527

261 -> 268 -0.13223

TD-DFT of TPA5 in DCM solvent.

Calculation method: CAM-B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 0.3584 eV 3459.25 nm f=0.0304 <S**2>=0.000

313 -> 317 0.13362

316 -> 317 -1.14036

316 -> 319 -0.11581

313 <- 317 -0.14734

316 <- 317 0.89839

316 <- 319 0.10612

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -4187.61902154

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 1.1195 eV 1107.54 nm f=0.0680 <S**2>=0.000

308 -> 318 0.17986

309 -> 318 0.43948

309 -> 320 0.14557

312 -> 318 0.26198

315 -> 318 0.42902

315 <- 318 -0.17247

Excited State 3: Singlet-A 1.4495 eV 855.38 nm f=0.0007 <S**2>=0.000

305 -> 317 0.19957

307 -> 317 0.65528

Excited State 4: Singlet-A 1.5132 eV 819.33 nm f=0.1384 <S**2>=0.000

308 -> 318 0.16031

309 -> 318 0.21185

312 -> 318 -0.25677

314 -> 318 0.50451

315 -> 318 -0.25009

Excited State 5: Singlet-A 1.5254 eV 812.82 nm f=0.1627 <S**2>=0.000

301 -> 317 0.10444

310 -> 317 -0.28162

313 -> 317 0.58611

316 -> 319 0.18282

Excited State 6: Singlet-A 1.6504 eV 751.25 nm f=0.3896 <S**2>=0.000

308 -> 318 -0.13887

309 -> 318 -0.22767

312 -> 318 -0.24661

314 -> 318 0.25761

314 -> 320 0.12009

315 -> 318 0.54615

315 <- 318 -0.18516

Excited State 7: Singlet-A 1.6926 eV 732.49 nm f=0.2244 <S**2>=0.000

300 -> 317 -0.13059

301 -> 317 0.27816

302 -> 317 -0.14726

305 -> 317 0.39715

310 -> 317 0.29885

316 -> 319 0.28496

Excited State 8: Singlet-A 1.7060 eV 726.77 nm f=0.0000 <S**2>=0.000

315 -> 317 0.70672

Excited State 9: Singlet-A 1.7383 eV 713.25 nm f=0.0082 <S**2>=0.000

304 -> 317 0.69664

Excited State 10: Singlet-A 1.7770 eV 697.71 nm f=0.0060 <S**2>=0.000

303 -> 318 -0.14059

306 -> 318 -0.31513

308 -> 318 0.50066

308 -> 320 0.13850

309 -> 318 -0.27315

Excited State 11: Singlet-A 1.9023 eV 651.74 nm f=0.6286 <S**2>=0.000

301 -> 317 -0.20241

302 -> 317 0.10074

305 -> 317 -0.20819

313 -> 317 -0.14197

316 -> 319 0.58748

Excited State 12: Singlet-A 1.9145 eV 647.60 nm f=0.0053 <S**2>=0.000

316 -> 318 0.70352

Excited State 13: Singlet-A 2.0367 eV 608.75 nm f=0.3021 <S**2>=0.000

305 -> 317 -0.25668

307 -> 317 0.15042

310 -> 317 0.53673

313 -> 317 0.29395

316 -> 319 -0.10675

Excited State 14: Singlet-A 2.0519 eV 604.25 nm f=0.0162 <S**2>=0.000

306 -> 318 0.59590

306 -> 320 0.15078

308 -> 318 0.25593

309 -> 318 -0.16609

Excited State 15: Singlet-A 2.2700 eV 546.18 nm f=0.7908 <S**2>=0.000

314 -> 318 0.10123

314 -> 320 -0.12547

315 -> 319 -0.10032

315 -> 320 0.67043

Excited State 16: Singlet-A 2.4240 eV 511.48 nm f=0.3125 <S**2>=0.000

303 -> 318 0.19167

303 -> 320 0.10753

308 -> 318 -0.13627

309 -> 318 -0.19125

312 -> 318 0.47588

314 -> 318 0.35872

315 -> 320 -0.11572

Excited State 17: Singlet-A 2.4250 eV 511.28 nm f=0.0014 <S**2>=0.000

314 -> 317 0.70402

Excited State 18: Singlet-A 2.5941 eV 477.94 nm f=0.0070 <S**2>=0.000

299 -> 317 0.31201

301 -> 317 -0.21320

302 -> 317 0.20146

305 -> 317 0.19167

311 -> 317 0.41921

312 -> 317 0.18470

313 -> 317 0.14736

313 -> 319 -0.12349

Excited State 19: Singlet-A 2.6429 eV 469.12 nm f=0.0407 <S**2>=0.000

299 -> 317 0.55754

300 -> 317 -0.15137

301 -> 317 0.18591

305 -> 317 -0.25035

311 -> 317 -0.12308

313 -> 317 -0.10631

Excited State 20: Singlet-A 2.7379 eV 452.84 nm f=0.0169 <S**2>=0.000

299 -> 317 -0.14077

300 -> 317 -0.14644

301 -> 317 0.27781

305 -> 317 -0.24083

311 -> 317 0.39070

312 -> 317 0.31652

313 -> 319 0.14359

Excited State 21: Singlet-A 2.8236 eV 439.09 nm f=0.0141 <S**2>=0.000

316 -> 320 0.67788

316 -> 322 0.16531

Excited State 22: Singlet-A 2.8420 eV 436.26 nm f=0.0040 <S**2>=0.000

311 -> 317 -0.35445

312 -> 317 0.59458

Excited State 23: Singlet-A 2.8576 eV 433.87 nm f=0.2222 <S**2>=0.000

301 -> 317 -0.10145

313 -> 319 0.53557

314 -> 320 0.15298

316 -> 322 -0.31557

Excited State 24: Singlet-A 2.8662 eV 432.57 nm f=0.2755 <S**2>=0.000

313 -> 319 0.27080

314 -> 320 0.18042

316 -> 320 -0.16192

316 -> 322 0.56723

Excited State 25: Singlet-A 2.8740 eV 431.39 nm f=0.0304 <S**2>=0.000

313 -> 319 -0.24375

314 -> 320 0.53163

315 -> 321 -0.17806

316 -> 322 -0.10333