**Supporting Information**

for

**Water-soluble host-guest complexes between fullerenes and a sugar-functionalized tribenzotriquinacene assembling to microspheres**

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**1H NMR, 13C NMR spectroscopy and mass spectrometry of all new compounds, the xyz coordinates (in Å) of TBTQ-(OG)6 ⊂ C60 complex**

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Table S3. Extracted data from the MALDI mass spectrum of **TBTQ-(OG)6**S12

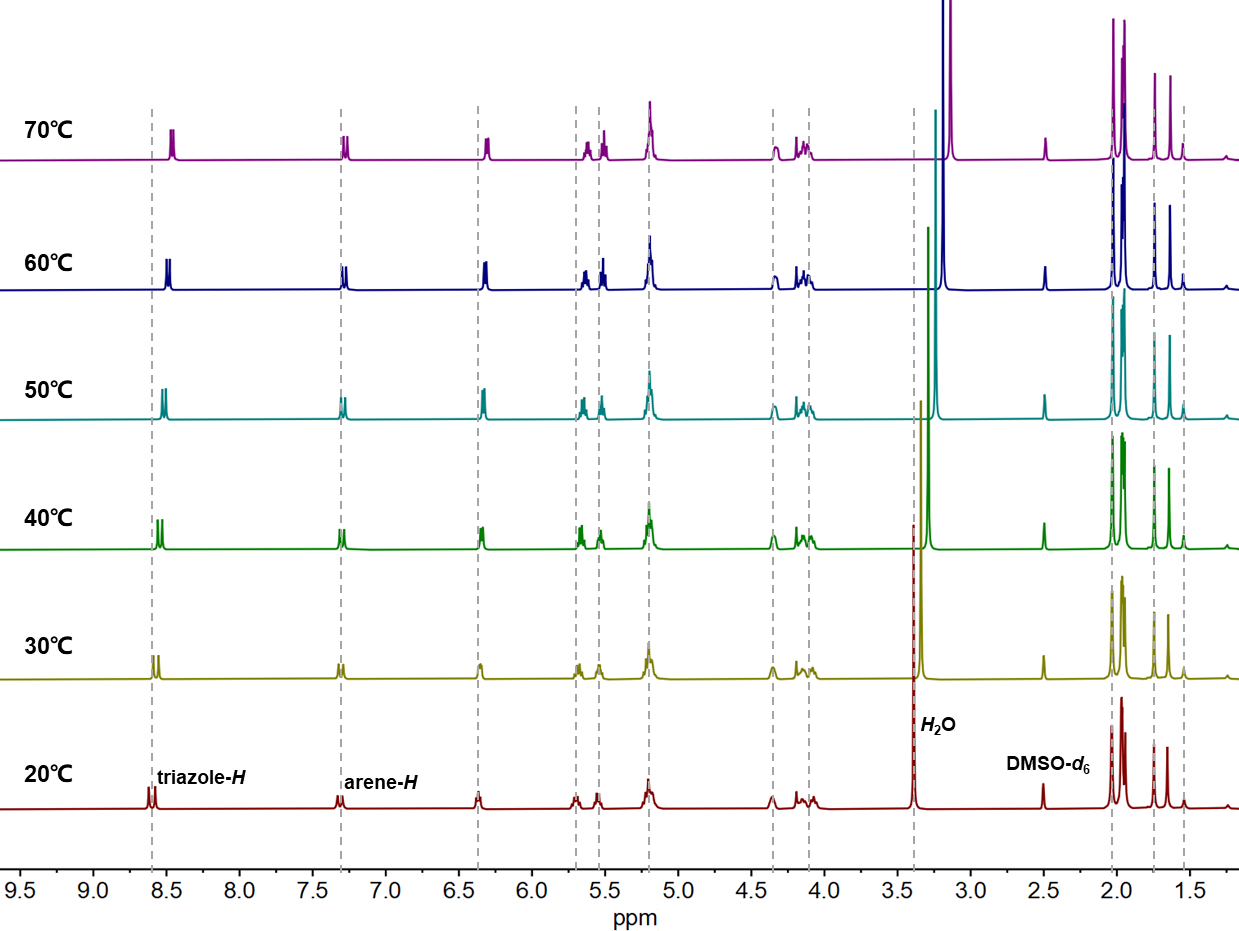
Figure S14. ESI-HRMS spectrum of **TBTQ-(OG)6**S13

Table S4. Abundance pattern of the [M – 2 H]2− ions from the

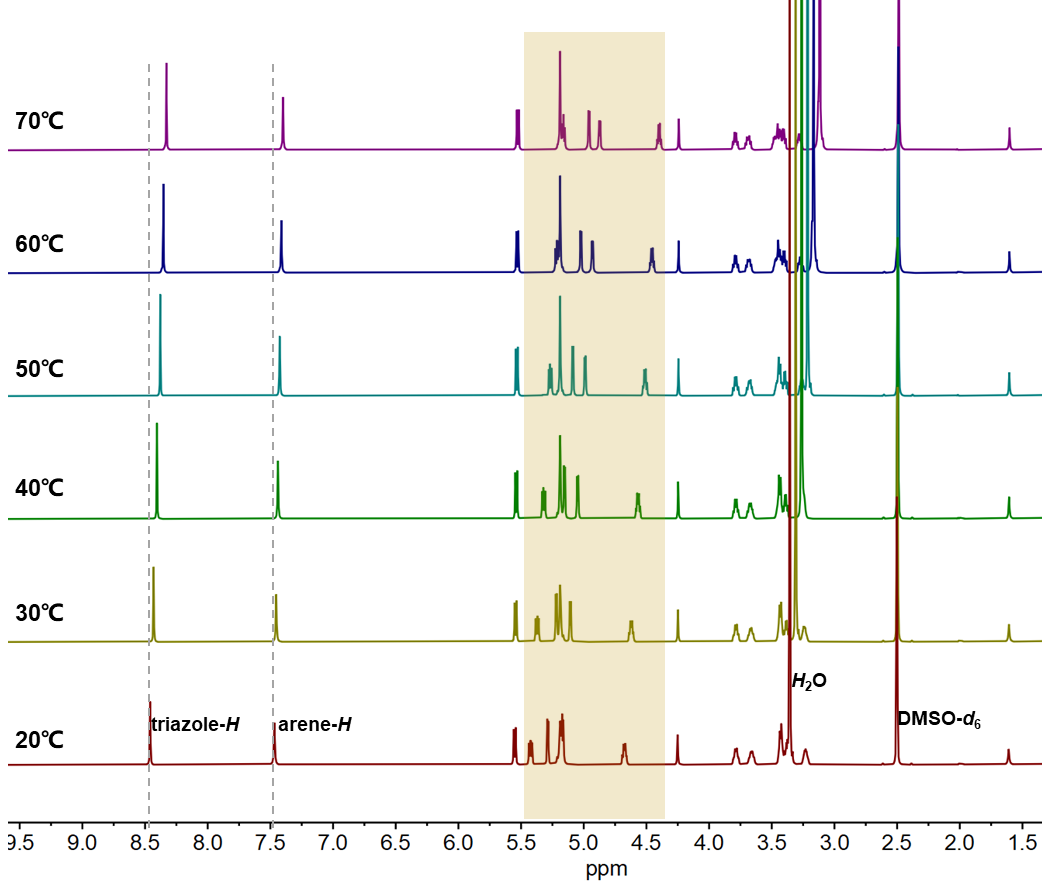
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Figure S15. Optical images of C60, **TBTQ-(OG)6** ⊂ C60, C70 and **TBTQ-(OG)6** ⊂ C70 dispersed in water at different timesS13

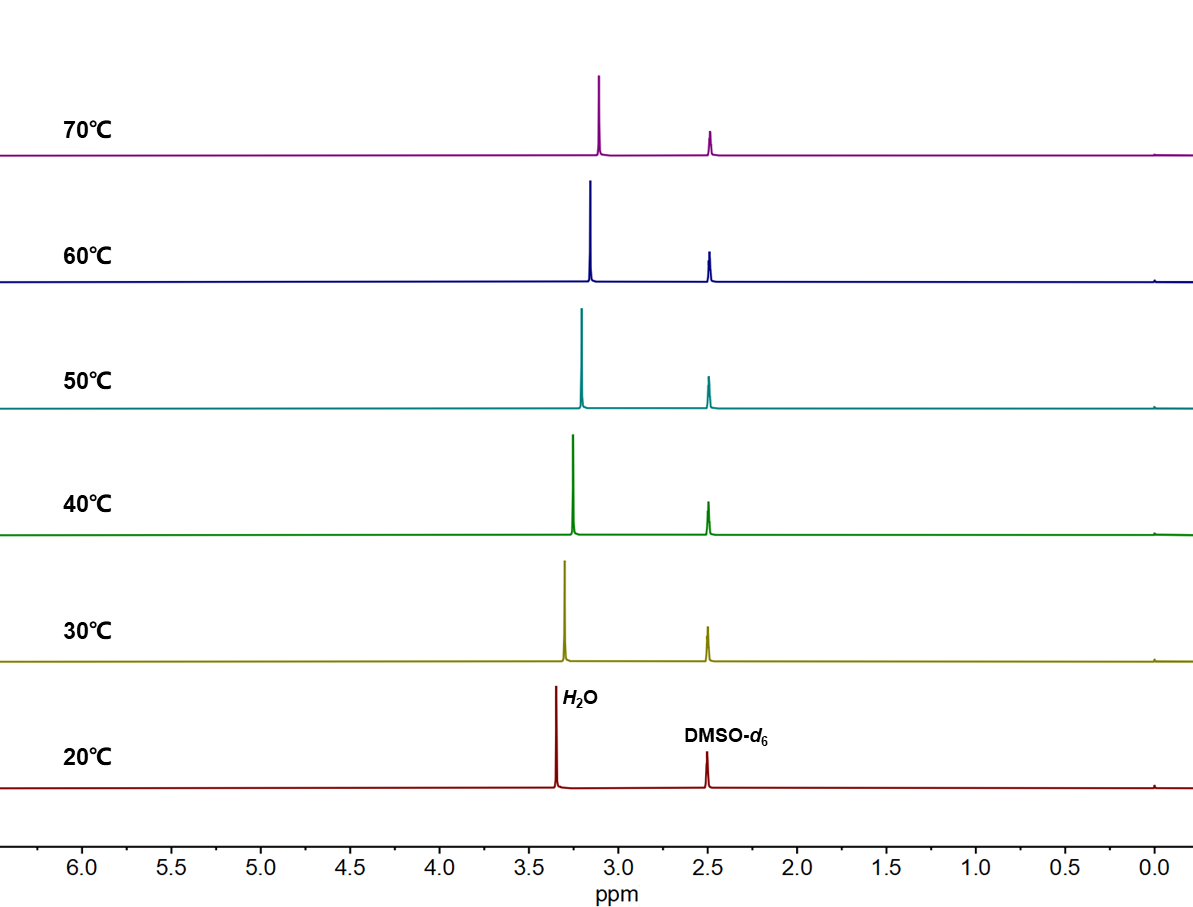
Table S5. Xyz coordinates of **TBTQ-(OG)6** ⊂ C60 complexS14



**Figure S1.** 1H NMR spectra of **TBTQ-(OAcG)6** at different temperatures (DMSO-*d*6, 400 MHz).

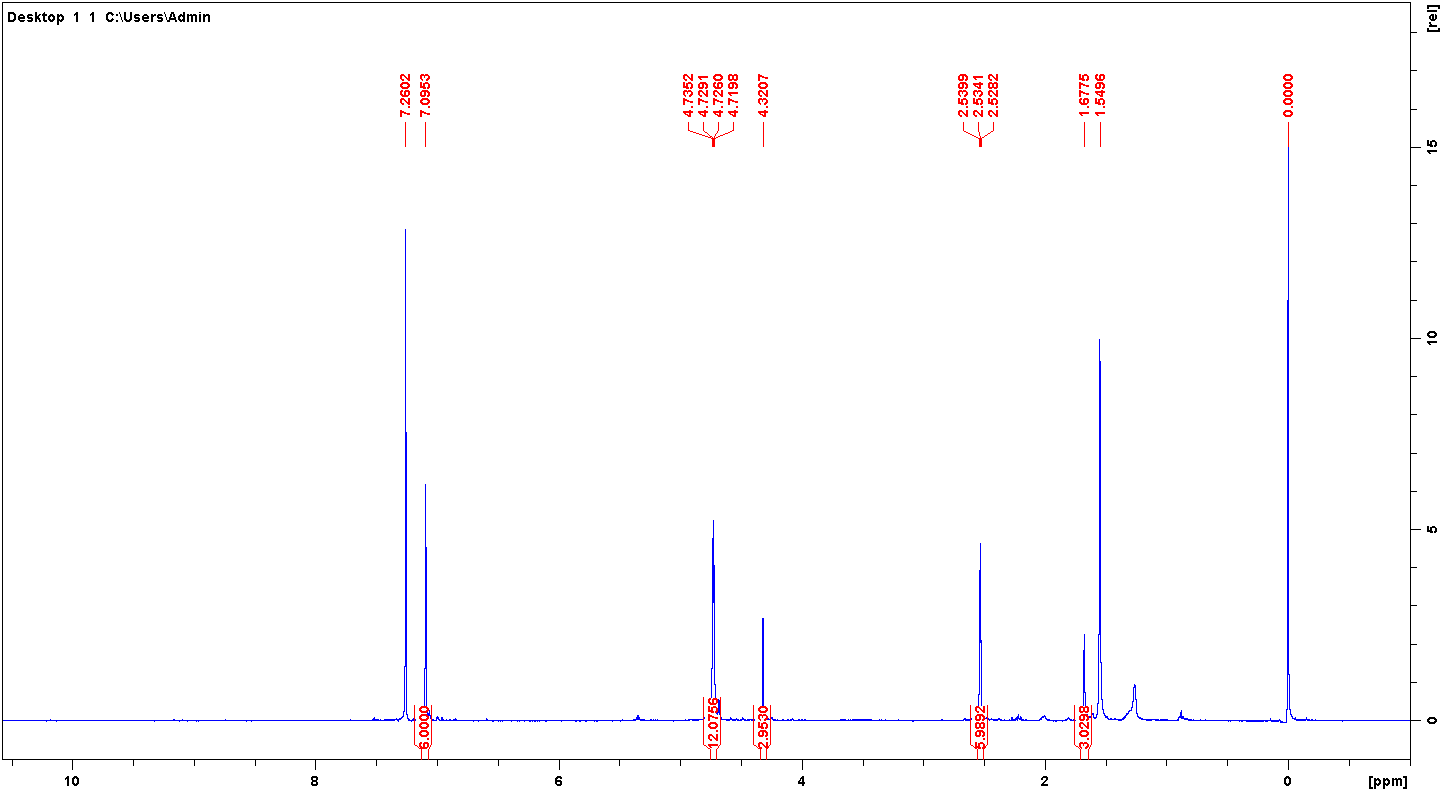


**Figure S2.** 1H NMR spectra of **TBTQ-(OG)6** at different temperatures (DMSO-*d*6, 400 MHz).

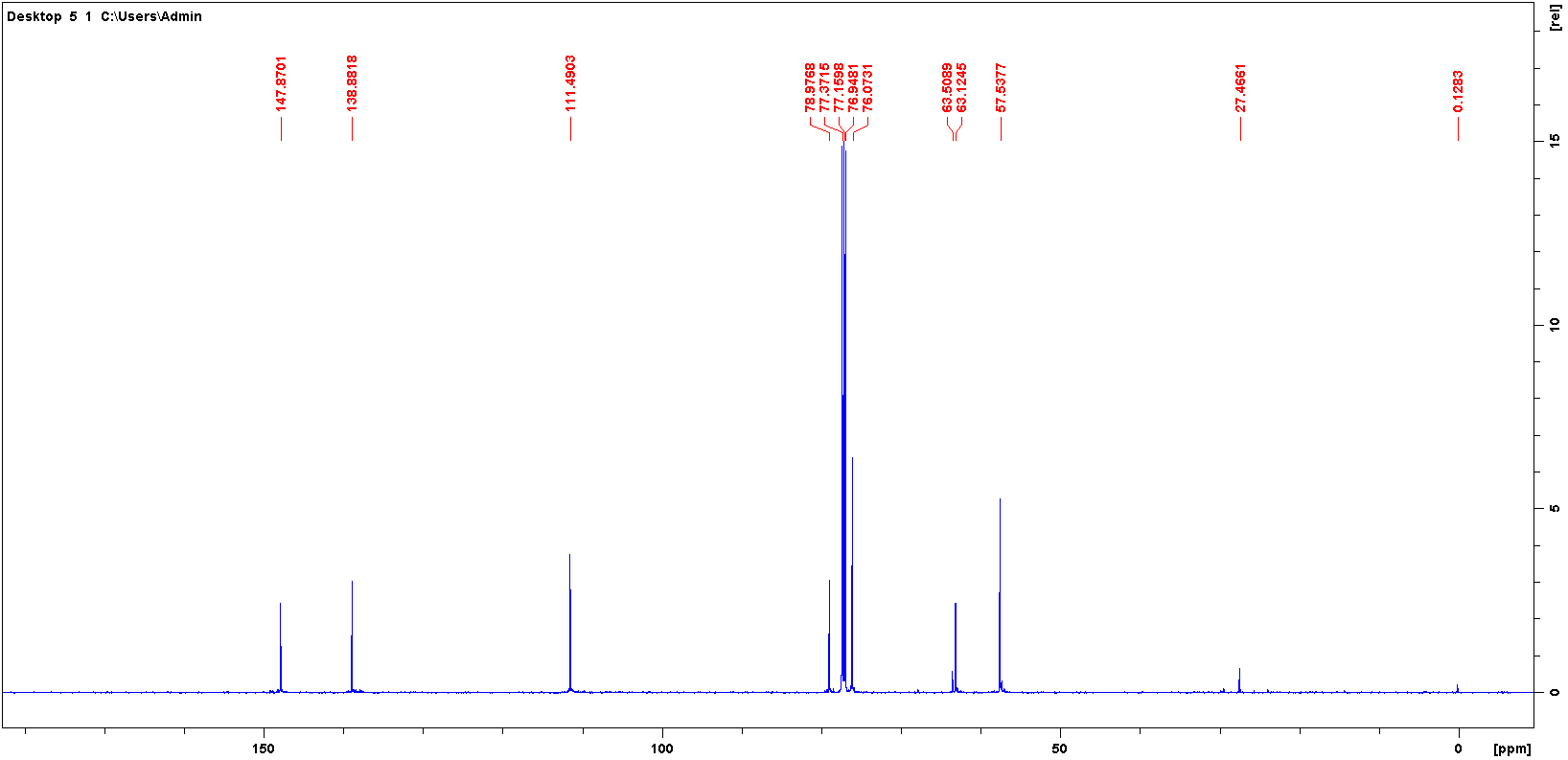
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**Figure S3.** Blank 1H NMR spectra of waterin DMSO-*d*6 (400 MHz) at different temperatures.

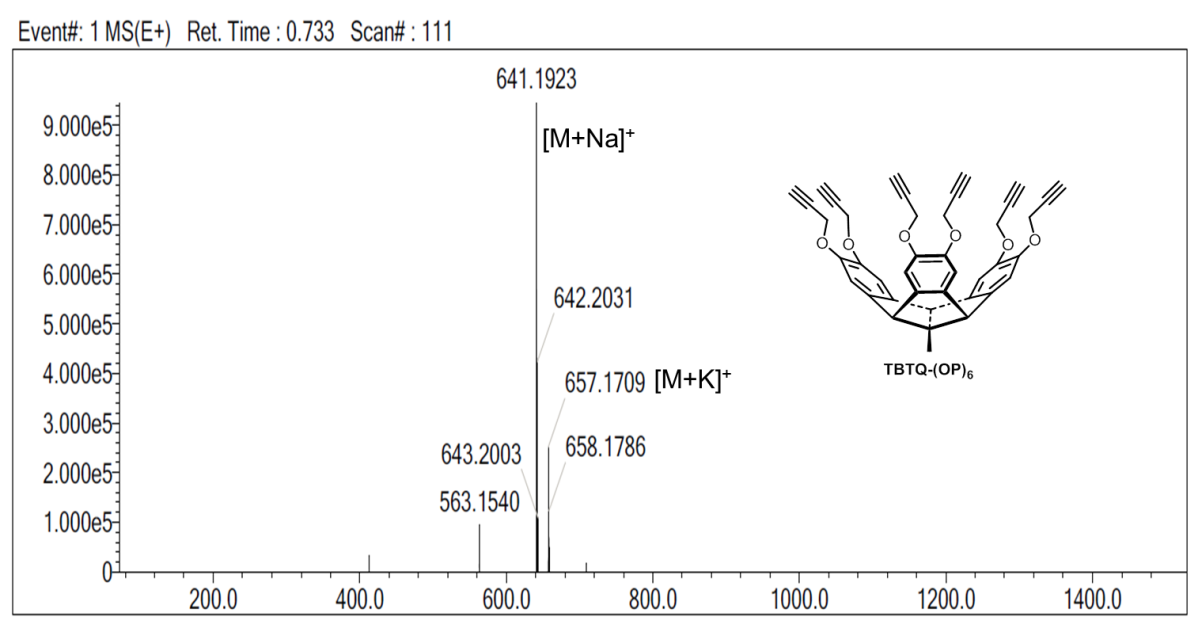
Note: The signal of the water protons shows the same chemical shift changes as does the corresponding signal in the spectra of Figures S1 and S2. This proves that these shifts are independent of the presence of **TBTQ-(OAcG)6** and **TBTQ-(OG)6**.

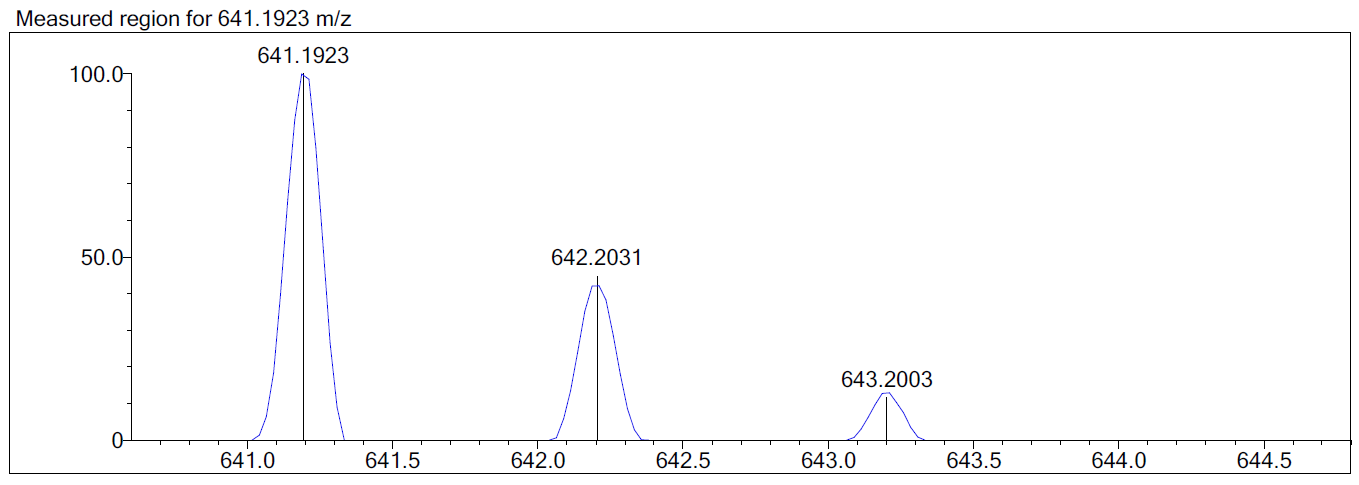
****

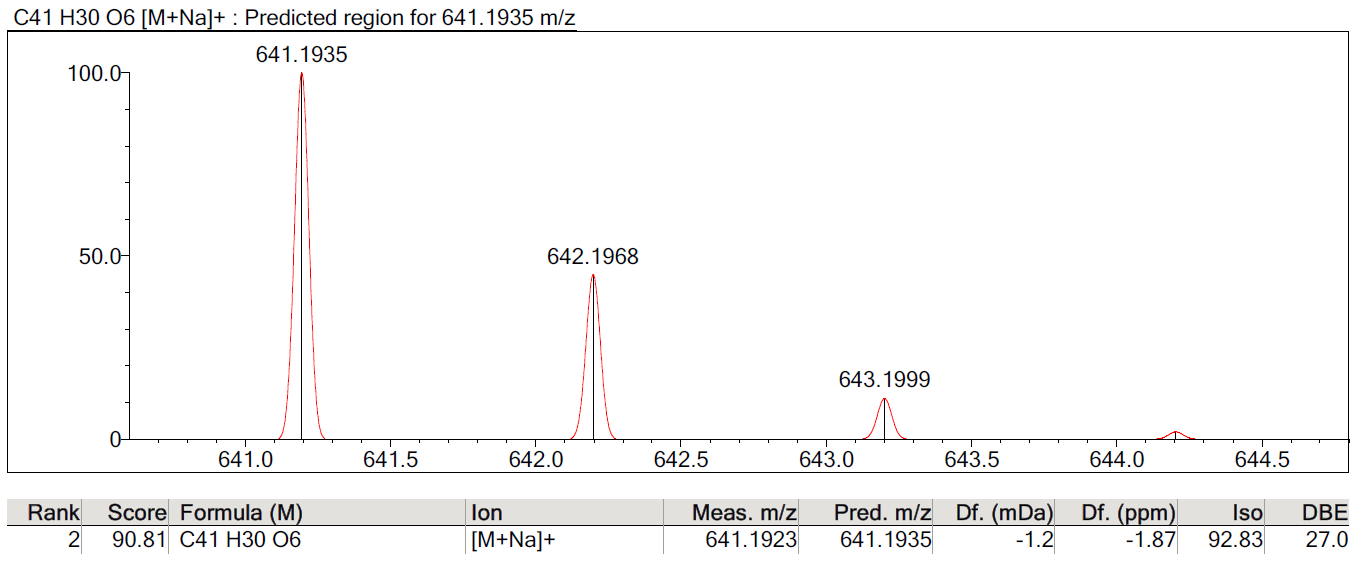
**Figure S4.** 1H NMR spectrum of **TBTQ-(OP)6** (400 MHz, CDCl3).

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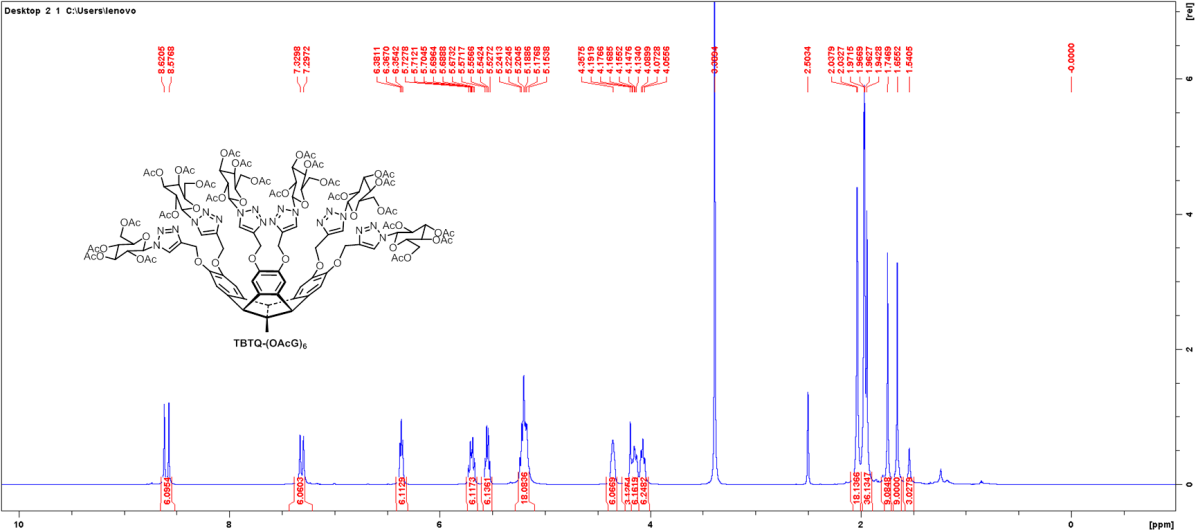
**Figure S5.** 13C NMR spectrum of **TBTQ-(OP)6** (100 Mz, CDCl3).

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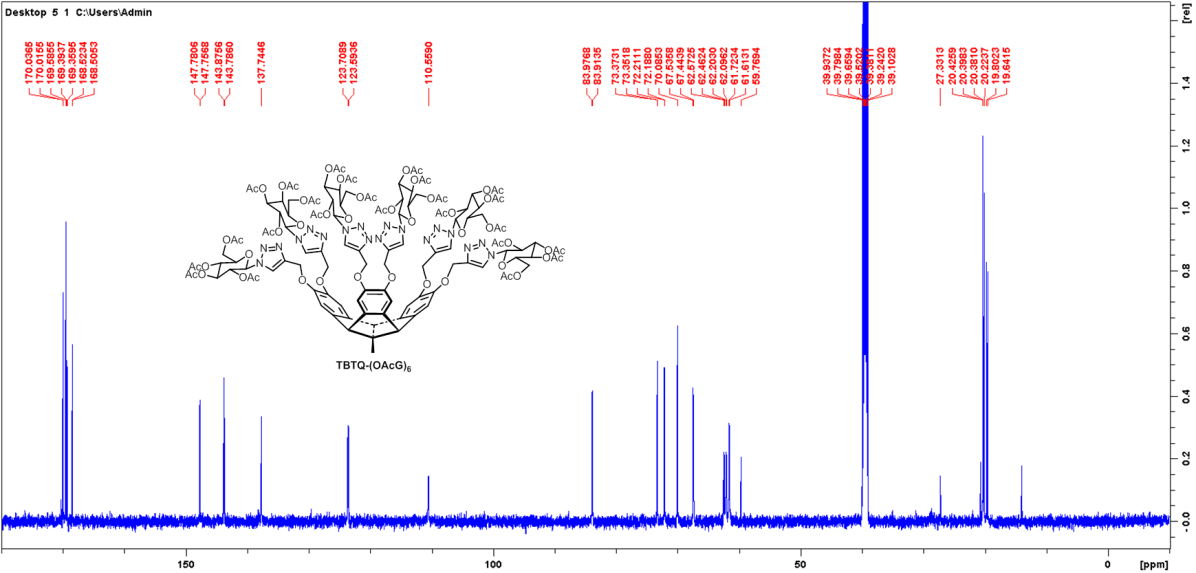
****

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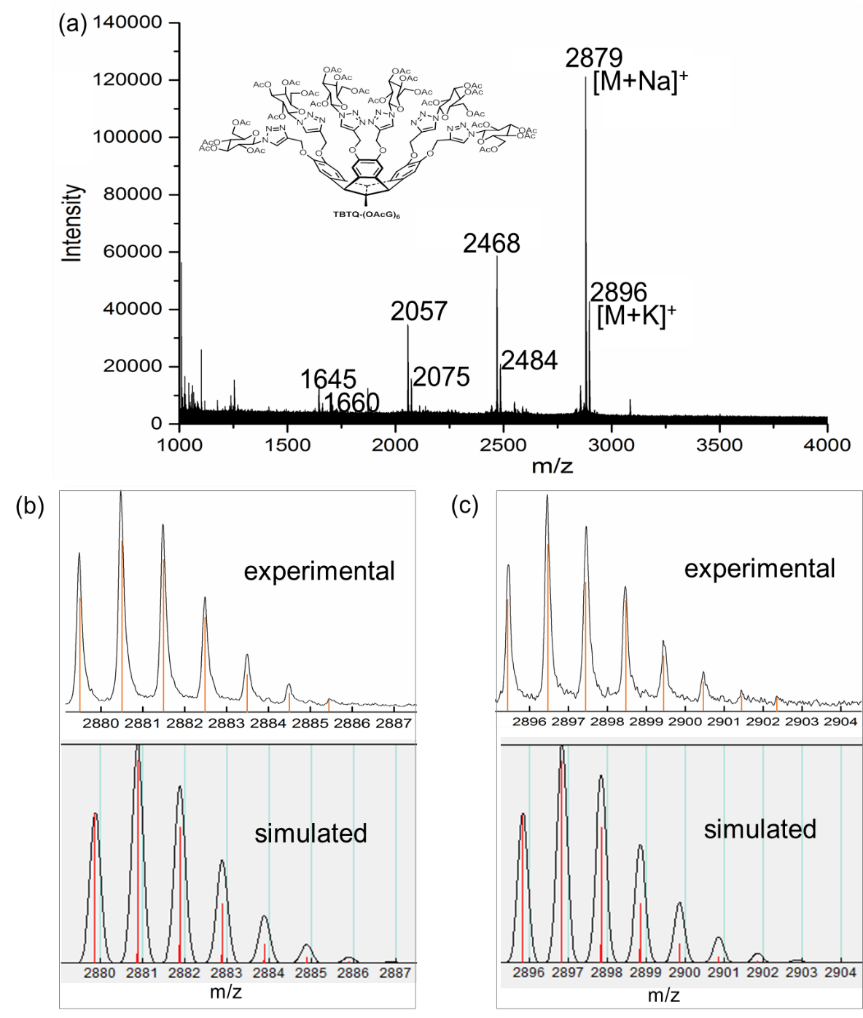
**Figure S6.** ESI-HRMS spectrum of **TBTQ-(OP)6**.

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**Figure S7.** 1H NMR spectrum of **TBTQ-(OAcG)6** (400 MHz, DMSO-*d*6).

****

**Figure S8.** 13C NMR spectrum of **TBTQ-(OAcG)6** (100 MHz, DMSO-*d*6).

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**Figure S9.** MALDI mass spectrum of **TBTQ-(OAcG)6**: (a) full spectrum, (b) isotopic distribution of the [M + Na]+ molecular adduct ions (top: experimental, bottom: simulated), (c) isotopic distribution of the [M + K]+ molecular adduct ions (top: experimental, bottom: simulated).

**Table S1.** Extracted data from MALDI mass spectrum of **TBTQ-(OAcG)6**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Na+ adduct ions** | ***m*/*z*** | **Intensity** | **K+ adduct ions** | ***m*/*z*** | **Intensity** |
| [M + Na]+ | **2879.479**  2880.471  2881.476 | 87414  121107  102767 | [M + K]+ | **2895.450**  2896.457 2897.452 | 29538  42732  36721 |
| [M + Na − Tcle]+• | **2468.404** 2469.406  2470.408 | 47195  58681  40665 | [M + K − Tcle]+• | **2484.372**  2485.377  2486.371 | 19272  20901  16783 |
| [M + Na − 2Tcle]+ | **2057.336**  2058.327  2059.339 | 34724  34118  21604 | [M + K – 2 Tcle]+ | **2073.310**  2074.316  2075.310 | 15908  15173  12577 |
| [M + Na – 3 Tcle]+• | **1645.248**  1646.269  1647.262  1648.265 | 9364  13563  10072  7480 | [M + K – 3 Tcle]+• | **1661.250**  1662.257  1663.245  1664.233 | 5869  7323  6040  769 |

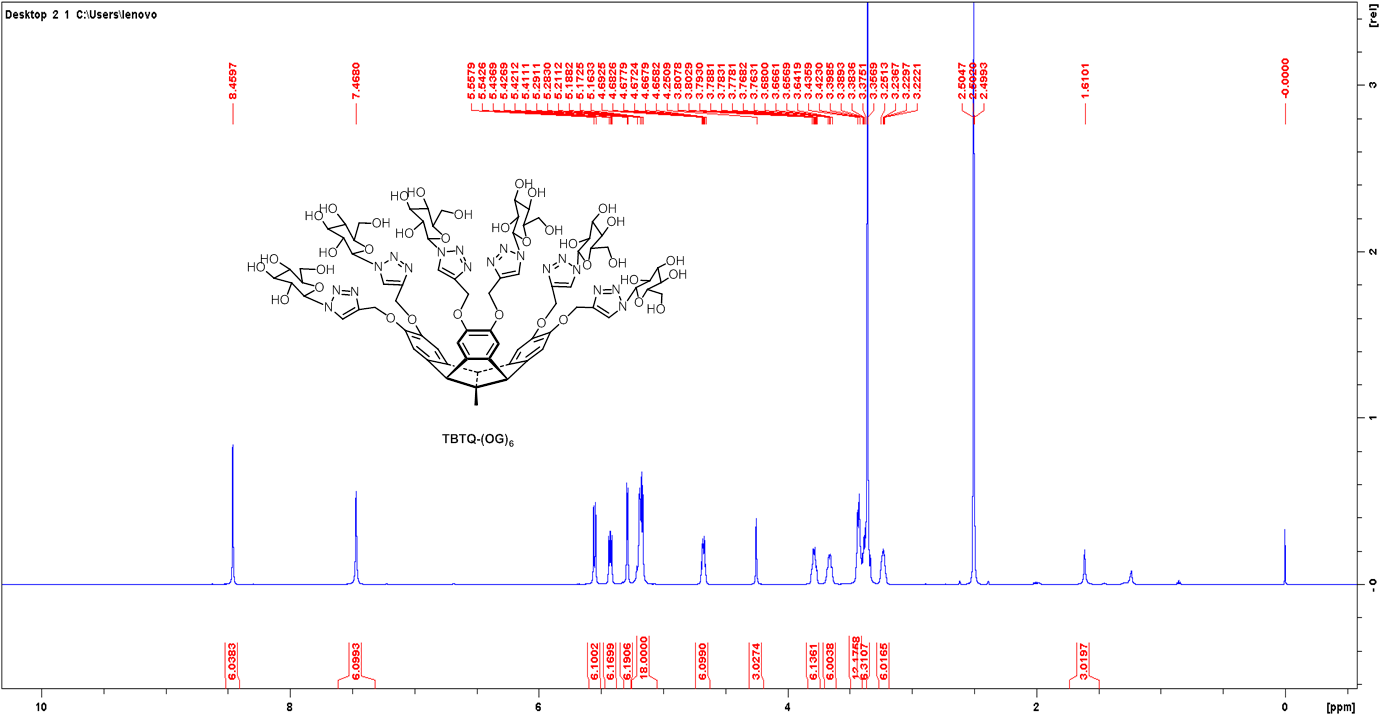
***Comment:*** In most cases, the mass difference is 411 u. This does not simply correspond to the loss of the tentacle-like residue, “Tcle”, but to subsequent addition of a H atom to the remaining phenoxy-type fragment ion, leading to a fragment ions [M + Na – n ⋅ Tcle + H]+ (n = 1−3). It is well possible that this reduction process happens in the matrix under laser irradiation. – The *m*/*z* values of the monoisotopic ions are given in boldface.



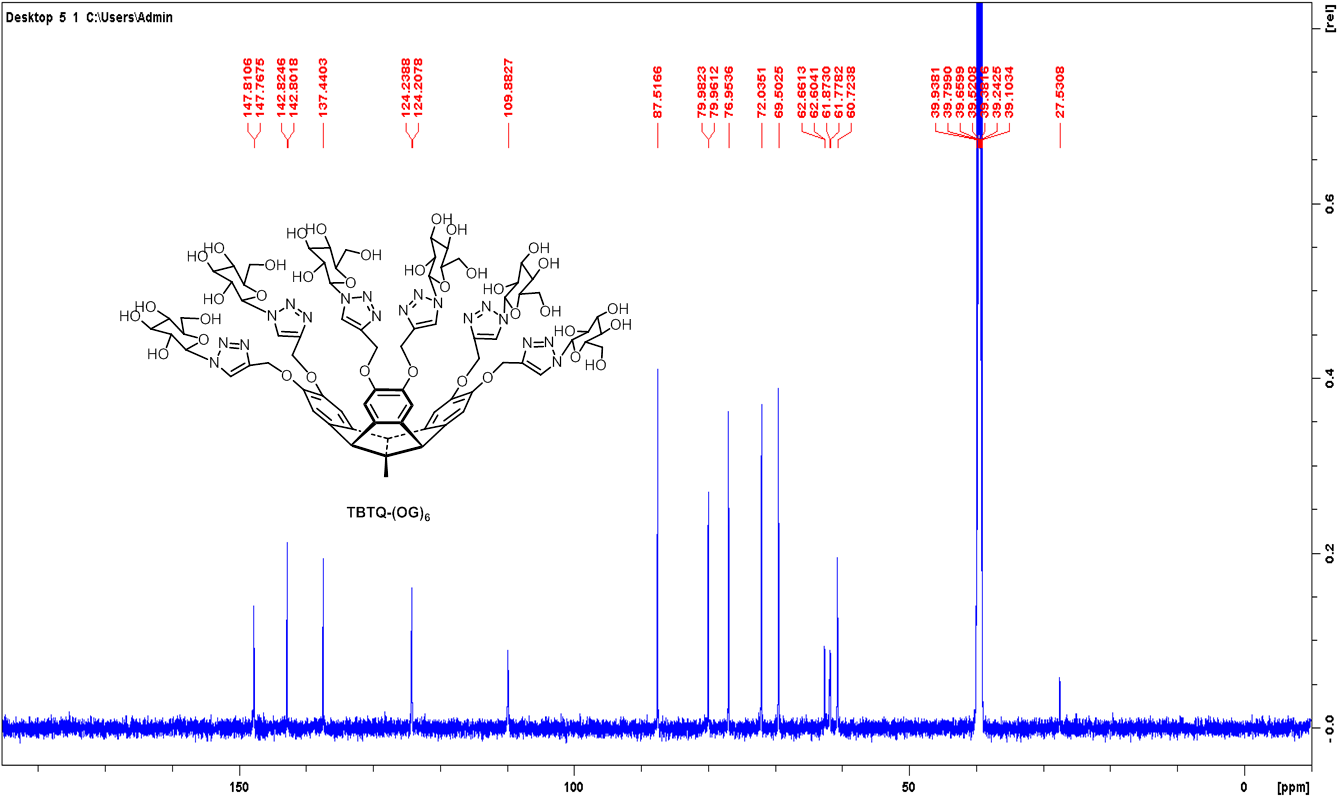
**Figure S10.** ESI-HRMS spectrum of **TBTQ-(OAcG)6**. The peak labeled “1505.9690” corresponds to the [M + 1] ions (mainly the 13C1-isotopolog).

**Table S2.** Abundance pattern of the [M + 6 H2O + 2 Na]2+ ions from the ESI mass spectrum of **TBTQ-(OAcG)6** (low resolution).

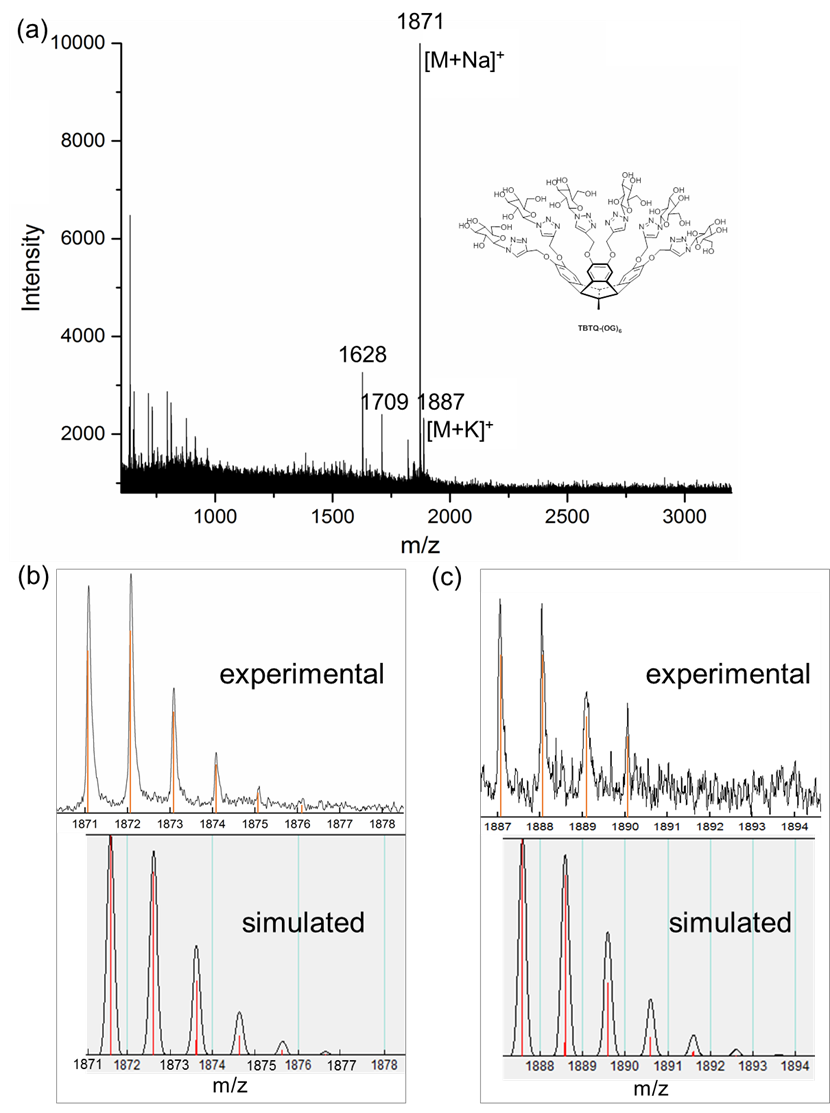
|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *m*/*z* | 1505.5 | 1506.0 | 1506.5 | 1507.0 | 1507.5 | 1508.0 | 1508.5 | 1509.0 |
| Calc’d (% B) | 68.5 | 100.0 | 81.8 | 48.4 | 22.9 | 9.2 | 3.2 | 1.0 |
| Exp’l (% B) | 58 | 100 | 94 | 64 | 23 | 4 | 1 | < 1 |

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**Figure S11.** 1H NMR spectrum of **TBTQ-(OG)6** (400 MHz, DMSO-*d*6).

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**Figure S12.** 13C NMR spectrum of **TBTQ-(OG)6** (100 MHz, DMSO-*d*6).

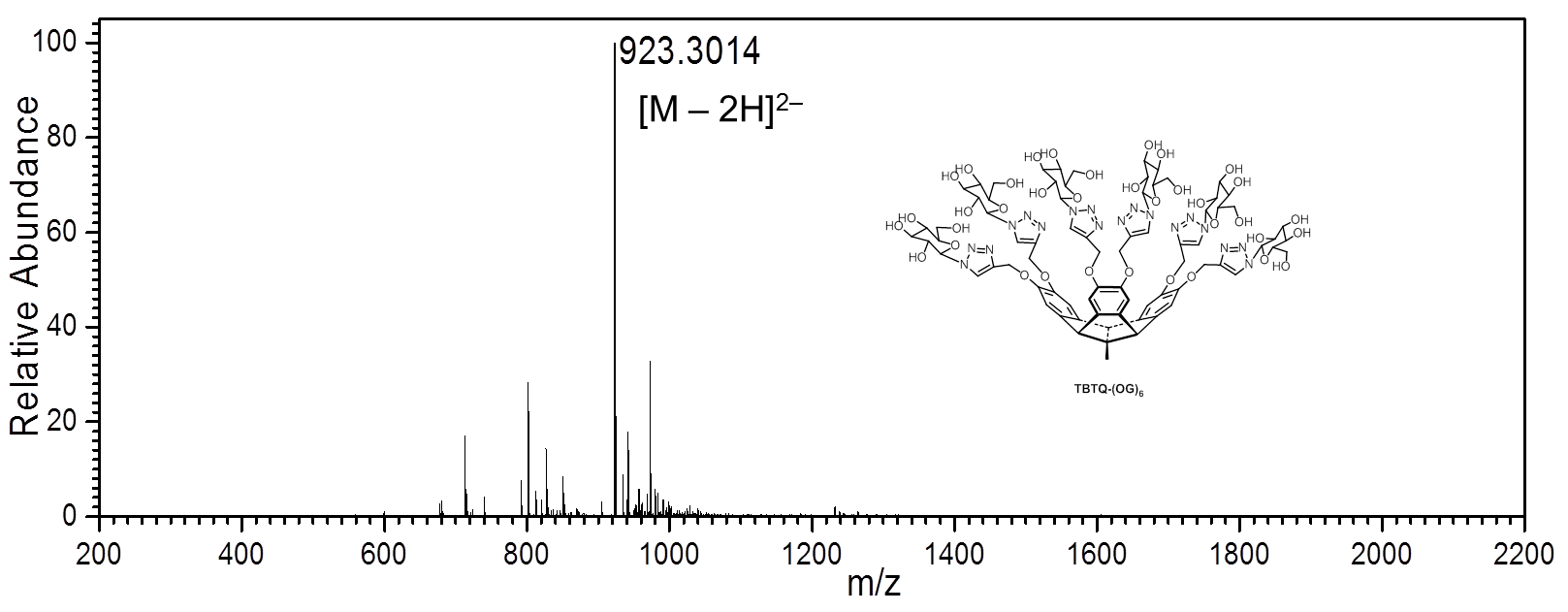


**Figure S13.** MALDI mass spectrum of **TBTQ-(OG)6**. (a) full spectrum, (b) isotopic distribution of [M + Na]+ molecular adduct ions (top: experimental, bottom: simulated), (c) isotopic distribution of [M + K]+ molecular adduct ions (top: experimental, bottom: simulated).

**Table S3.** Extracted data from MALDI mass spectrum of **TBTQ-(OG)6**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Na+ adduct ions** | ***m*/*z*** | **Intensity** | **K+ adduct ions** | ***m*/*z*** | **Intensity** |
| [M + Na]+ | **1871.085**  1872.082  1873.090 | 11032  11573  6428 | [M + K]+ | **1887.057**  1888.038  --- | 2330  2295  --- |
| [M + Na − C6H10O5]+ | **1709.086**  1710.098  --- | 2311  2404  --- | --- | --- | --- |
| [M + Na − Tcle]+• =  [M + Na − C9H14N3O5]+• | **1628.080**  1629.078  1630.056 | 3268  2775  1726 | --- | --- | --- |

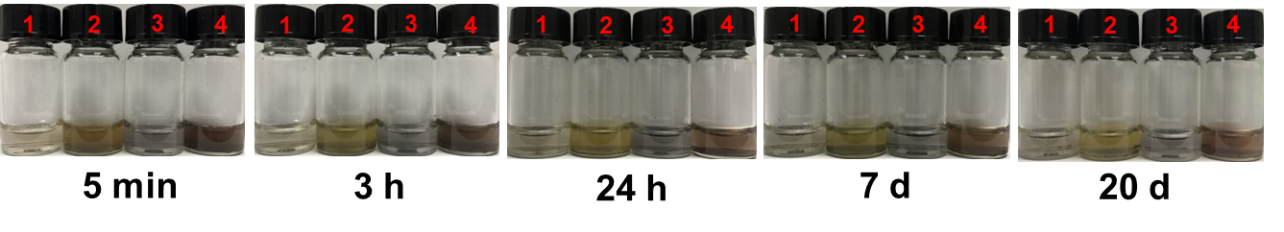
***Comment:*** Here, the observed mass differences are 162 u and 243 u. In the first case, this corresponds to the loss of glycosyl residue (as a radical); in the second case, this corresponds to the loss of the entire tentacle (as a radical) with subsequent transfer of a H atom, probably from the matrix to the remaining phenoxy-type fragment ion, leading to a fragment ions [M + Na – Tcle + H]+. It is assumed that this reduction process happens in the matrix under laser irradiation. – The *m*/*z* values of the monoisotopic ions are given in boldface.

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**Figure S14.** ESI-HRMS (negative mode) mass spectrum of **TBTQ-(OG)6**. The peak labeled “923.3014” corresponds to the monoisotopic ion.

**Table S4.** Abundance pattern of the [M – 2 H]2− ions from the ESI mass spectrum of **TBTQ-(OG)6** (low resolution).

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *m*/*z* | 923.3 | 923.8 | 924.3 | 924.8 | 925.3 | 925.8 | 926.3 |
| Calc’d (% B) | 100.0 | **92.3** | 49.5 | 19.5 | 6.2 | 1.7 | 0.4 |
| Exp’l (% B) | 100 | 98 | 55 | 21 | 8 | 1 | < 1 |

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**Figure S15.** Optical images of **1**: C60, **2**: **TBTQ-(OG)6** ⊂ C60, **3**: C70 and **4**: **TBTQ-(OG)6** ⊂ C70 dispersed in water at different times without centrifugation [C60: 2 mM; C70: 2 mM; **TBTQ-(OG)6**: 20 mM].

**Table S5.** The xyz coordinates (in Å) of **TBTQ-(OG)6** ⊂ C60 complex at the B3LYP/6-31G(d) level of theory.

The number of imaginary frequencies: 0

Total Energy (optimized structures)：–8970.94451731 a.u.

Optimized Coordinates: (1-227：**TBTQ-(OG)6**；228-287：C60)

1 C 0.531 -2.337 5.919

2 C 0.120 -0.943 6.542

3 C 1.860 -2.091 5.259

4 C -0.627 -2.719 5.041

5 C 1.238 0.084 6.120

6 C 2.277 -0.752 5.423

7 C -1.205 -0.500 5.806

8 C -1.624 -1.714 5.020

9 C 0.539 1.067 5.220

10 C 1.077 2.227 4.678

11 C 0.242 3.059 3.917

12 C -1.103 2.685 3.665

13 C -1.636 1.505 4.219

14 C -0.815 0.717 5.011

15 C -0.845 -3.947 4.431

16 C -2.119 -4.215 3.909

17 C -3.144 -3.239 3.967

18 C -2.875 -1.952 4.460

19 C 3.548 -0.344 5.038

20 C 4.422 -1.304 4.510

21 C 3.984 -2.631 4.267

22 C 2.688 -3.027 4.653

23 C -0.057 -1.018 8.046

24 O 0.614 4.308 3.448

25 O -2.037 3.407 2.954

26 O 5.754 -1.069 4.235

27 O 4.679 -3.649 3.645

28 O -4.384 -3.707 3.588

29 O -2.383 -5.522 3.513

30 C 6.265 1.203 3.672

31 C 6.932 1.256 2.441

32 N 6.561 2.491 1.900

33 N 5.687 3.129 2.760

34 N 5.500 2.381 3.800

35 C 6.907 2.789 -2.241

36 C 6.196 4.004 -1.611

37 C 5.951 3.856 -0.099

38 C 7.084 3.126 0.666

39 O 7.621 1.997 -0.050

40 C 8.093 2.318 -1.382

41 C 8.681 0.983 -1.859

42 O 7.744 -0.091 -1.706

43 O 5.966 5.194 0.406

44 O 4.936 4.056 -2.296

45 O 7.525 3.192 -3.472

46 C 6.359 0.159 4.716

47 C 6.524 -3.322 2.129

48 C 6.495 -4.209 1.041

49 N 7.082 -3.502 -0.014

50 N 7.426 -2.242 0.421

51 N 7.108 -2.123 1.673

52 C 6.195 -4.494 -4.006

53 C 7.368 -3.502 -3.868

54 C 7.508 -2.937 -2.441

55 C 7.372 -4.044 -1.365

56 O 6.215 -4.871 -1.603

57 C 6.228 -5.552 -2.886

58 C 4.955 -6.409 -2.851

59 O 5.183 -7.582 -2.071

60 O 8.847 -2.452 -2.355

61 O 7.003 -2.433 -4.754

62 O 6.347 -5.256 -5.207

63 C 6.128 -3.583 3.536

64 C 2.109 5.105 1.817

65 C 1.373 6.111 1.168

66 N 1.865 6.125 -0.141

67 N 2.863 5.189 -0.257

68 N 3.019 4.583 0.882

69 C -1.034 7.890 -2.548

70 C -0.438 6.589 -3.160

71 C 0.638 5.908 -2.290

72 C 1.430 6.881 -1.364

73 O 0.766 8.045 -0.939

74 C -0.671 8.090 -1.059

75 C -1.398 7.099 -0.149

76 O -1.586 7.639 1.156

77 O 1.596 5.412 -3.225

78 O -1.528 5.709 -3.421

79 O -2.461 7.889 -2.627

80 C 2.030 4.573 3.201

81 C -1.531 4.390 2.000

82 C -5.546 -2.847 3.739

83 C -5.863 -2.290 2.402

84 N -7.174 -2.189 1.895

85 N -7.129 -1.761 0.670

86 N -5.817 -1.562 0.310

87 C -4.986 -1.877 1.393

88 C -5.966 -0.421 -3.782

89 C -6.651 -1.701 -3.242

90 C -5.841 -2.334 -2.088

91 C -5.386 -1.249 -1.065

92 O -6.033 0.011 -1.334

93 C -5.689 0.583 -2.637

94 C -6.636 1.790 -2.674

95 O -6.451 2.592 -1.492

96 O -4.650 -2.861 -2.665

97 O -7.954 -1.379 -2.775

98 O -4.742 -0.718 -4.437

99 C -3.610 -5.452 1.433

100 N -3.741 -4.672 0.268

101 N -4.993 -4.619 -0.074

102 N -5.750 -5.315 0.838

103 C -4.896 -5.863 1.807

104 C -8.513 -6.904 -1.584

105 C -8.412 -5.364 -1.624

106 C -7.938 -4.719 -0.309

107 C -7.207 -5.637 0.703

108 O -7.280 -7.032 0.479

109 C -7.308 -7.545 -0.870

110 C -5.990 -7.339 -1.630

111 O -4.930 -8.021 -0.965

112 O -9.131 -4.305 0.358

113 O -7.429 -4.950 -2.587

114 O -8.431 -7.364 -2.944

115 C -2.314 -5.768 2.085

116 C -2.551 4.455 0.929

117 N -2.224 4.216 -0.427

118 N -3.267 4.444 -1.166

119 N -4.315 4.828 -0.370

120 C -3.895 4.838 0.970

121 C -7.171 7.523 -0.060

122 C -7.225 6.250 0.809

123 C -6.787 5.012 0.009

124 C -5.612 5.252 -0.976

125 O -5.449 6.560 -1.491

126 C -5.785 7.724 -0.706

127 C -4.708 8.090 0.320

128 O -3.675 8.886 -0.262

129 O -7.941 4.677 -0.762

130 O -6.299 6.325 1.905

131 O -7.438 8.579 0.873

132 H 0.659 -3.111 6.714

133 H 1.678 0.604 7.000

134 H -2.003 -0.224 6.535

135 H 2.121 2.489 4.848

136 H -2.672 1.243 4.017

137 H -0.076 -4.718 4.397

138 H -3.633 -1.173 4.445

139 H 3.855 0.695 5.145

140 H 2.370 -4.053 4.481

141 H -0.837 -1.738 8.325

142 H 0.869 -1.329 8.546

143 H -0.343 -0.047 8.468

144 H 7.569 0.536 1.946

145 H 6.187 1.962 -2.445

146 H 6.743 4.955 -1.825

147 H 4.959 3.373 0.091

148 H 7.918 3.830 0.923

149 H 8.877 3.107 -1.322

150 H 9.602 0.733 -1.302

151 H 8.871 1.015 -2.954

152 H 7.407 -0.124 -0.767

153 H 5.342 5.252 1.177

154 H 4.302 4.629 -1.792

155 H 6.828 3.527 -4.086

156 H 5.926 0.472 5.684

157 H 7.409 -0.176 4.858

158 H 6.104 -5.206 0.947

159 H 5.229 -3.937 -4.046

160 H 8.330 -3.943 -4.217

161 H 6.790 -2.097 -2.277

162 H 8.292 -4.681 -1.322

163 H 7.137 -6.191 -2.956

164 H 4.729 -6.803 -3.867

165 H 4.090 -5.849 -2.450

166 H 5.340 -7.326 -1.135

167 H 8.818 -1.577 -1.851

168 H 7.642 -1.688 -4.657

169 H 6.393 -4.638 -5.977

170 H 6.566 -2.846 4.239

171 H 6.415 -4.612 3.845

172 H 0.604 6.782 1.538

173 H -0.710 8.779 -3.140

174 H -0.026 6.780 -4.187

175 H 0.184 5.061 -1.715

176 H 2.355 7.266 -1.882

177 H -0.864 9.143 -0.729

178 H -0.816 6.178 0.023

179 H -2.390 6.845 -0.582

180 H -2.240 8.394 1.095

181 H 2.140 4.692 -2.815

182 H -1.720 5.101 -2.664

183 H -2.789 6.992 -2.973

184 H 2.661 3.667 3.328

185 H 2.297 5.334 3.960

186 H -1.437 5.351 2.552

187 H -0.536 4.087 1.609

188 H -6.319 -3.566 4.086

189 H -5.395 -2.065 4.506

190 H -3.907 -1.832 1.389

191 H -6.585 0.038 -4.589

192 H -6.817 -2.447 -4.056

193 H -6.446 -3.159 -1.616

194 H -4.277 -1.117 -1.097

195 H -4.615 0.879 -2.609

196 H -7.698 1.475 -2.710

197 H -6.402 2.476 -3.511

198 H -6.324 1.992 -0.709

199 H -4.324 -3.633 -2.131

200 H -7.892 -0.872 -1.919

201 H -4.252 -1.449 -3.967

202 H -5.225 -6.438 2.656

203 H -9.465 -7.225 -1.108

204 H -9.385 -4.903 -1.927

205 H -7.306 -3.827 -0.588

206 H -7.680 -5.541 1.724

207 H -7.472 -8.632 -0.660

208 H -5.739 -6.269 -1.764

209 H -6.041 -7.830 -2.625

210 H -4.787 -7.613 -0.083

211 H -8.996 -3.417 0.778

212 H -7.405 -5.606 -3.336

213 H -9.324 -7.402 -3.350

214 H -2.111 -6.862 2.067

215 H -1.463 -5.224 1.637

216 H -4.532 5.104 1.805

217 H -7.967 7.482 -0.841

218 H -8.253 6.106 1.223

219 H -6.551 4.172 0.708

220 H -5.761 4.655 -1.930

221 H -5.814 8.493 -1.520

222 H -4.258 7.199 0.795

223 H -5.123 8.749 1.113

224 H -3.375 8.501 -1.143

225 H -7.797 3.779 -1.194

226 H -6.461 7.167 2.402

227 H -7.577 9.430 0.406

228 C -0.204 -4.169 -1.105

229 C -1.277 -1.913 -3.689

230 C -1.087 -3.561 -1.982

231 C -1.984 -2.506 -1.498

232 C -1.021 -2.769 0.764

233 C -0.170 -3.761 0.306

234 C -2.038 -0.700 0.191

235 C -1.952 -2.123 -0.168

236 C -0.647 -3.193 -3.335

237 C -2.102 -1.488 -2.553

238 C -0.554 1.719 0.377

239 C -1.163 -0.471 1.347

240 C -0.437 0.706 1.432

241 C 1.707 1.680 1.109

242 C 2.911 -3.499 -3.006

243 C 0.298 2.441 -2.252

244 C -1.386 1.502 -0.708

245 C 1.398 -2.456 -4.510

246 C 3.441 1.777 -0.646

247 C 3.383 0.996 -3.392

248 C 2.529 1.987 -2.936

249 C -0.574 -0.969 -4.421

250 C 4.399 -1.072 -2.819

251 C 2.058 -4.217 -0.377

252 C 3.007 1.415 0.710

253 C 3.307 -3.650 -0.567

254 C 1.182 2.670 -1.100

255 C 2.796 -2.484 -4.061

256 C 2.559 2.386 -1.524

257 C 4.349 0.728 -1.129

258 C 1.570 0.001 -4.748

259 C 1.175 -4.449 -1.528

260 C 2.935 -0.804 1.794

261 C 1.588 -4.101 -2.804

262 C 4.506 -2.028 -1.823

263 C 4.317 0.348 -2.462

264 C 3.016 -2.226 1.432

265 C -0.950 1.875 -2.061

266 C -0.660 0.453 -4.064

267 C 4.472 -0.285 -0.071

268 C 0.771 2.321 0.177

269 C -0.532 -1.749 1.702

270 C 1.226 -3.793 0.758

271 C 3.643 0.138 1.065

272 C 0.653 -3.456 -3.734

273 C 0.961 0.679 1.884

274 C 4.544 -1.625 -0.413

275 C 1.131 2.017 -3.386

276 C -2.152 0.257 -0.804

277 C 1.555 -0.526 2.219

278 C 2.889 -0.027 -4.326

279 C 0.666 1.053 -4.266

280 C 3.520 -1.305 -3.972

281 C -1.445 0.854 -2.995

282 C 1.691 -2.828 1.637

283 C 3.741 -3.276 -1.919

284 C 0.788 -1.776 2.123

285 C 0.804 -1.249 -4.844

286 C 3.802 -2.627 0.364

287 C -2.187 -0.147 -2.217