Supporting Information

A Covalent Organic Cage Compound Acting as a Supramolecular Shadow Mask for the Regioselective Functionalization of C_{60}

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Content

1 General Information

Synthesis and Reagents:

Cages **1**,[S1] **S1**[S2] and TBTQ **S2**[S1] were synthesized as previously reported. C_{60} and C_{70} were purchased from SOLENNE BV, Netherlands. All chemicals and reagents were purchased from commercial suppliers MERCK, SIGMA-ALDRICH, TCI and were used without further purification. Solvents were purchased from FISHER SCIENTIFIC.

Technical equipment:

NMR spectroscopy: BRUKER AVANCE 400 and BRUKER AVANCE DMX 600. Chemical shifts are indicated in ppm in relation to the particular internal standard (^{1}H-NMR: 7.26 ppm for $CDCl_3$; ^{13}C-NMR: 77.16 ppm for $CDCl_3$). Processing of the raw data was performed with the program Topspin 3.0.[S3]

Mass spectroscopy (MALDI): BRUKER autoflex II. Matrices: DCTB (*trans*-2-(3-(4-*t*-Butylphenyl)-2-methyl-2-propenylidene)malononitrile or TCNQ (Tetracyanoquinodimethane).

UV/Vis absorption spectroscopy: JASCO V-670. Samples were measured as $CHCl_3$ solutions (FISHER SCIENTIFIC) in quartz glass cuvettes (HELLMA) with path lengths of 1 mm, 1 cm or 10 cm.

Single-Crystal X-ray Diffraction: BRUKER D8 Quest diffractometer with Photon 100 CMOS APS detector and Montel multilayer optics with Ni-filtered K_α-radiation (λ = 1.54060 Å).

HPLC: JASCO PU-2080 PLUS pump system, LG 2080-02 ternary gradient unit, DG-2080-53 three-line degasser, and MD-2015 PLUS multiwavelength detector. Column: Nucleosil® (MACHERY-NAGEL). Chromatograms were obtained with toluene/ethyl acetate 2:1 as eluent (HPLC grade from FISHER SCIENTIFIC) and a flow rate of 1.0 mL min^{-1}. C_{60} derivatives were detected via UV/Vis absorption at 310 nm.

Flash Chromatography: INTERCHIM PuriFlash XS 420. Silica gel columns: INTERCHIM PuriFlash PF-15SIHP-F0025, 15 μm, 22 bar. Silica gel conditioning: five column volumes 100 % triethylamine to remove traces of acid, ten column volumes 100 % toluene. Compound separation with toluene and toluene/ethyl acetate 95/5 as eluents.

2 Molecular Modeling

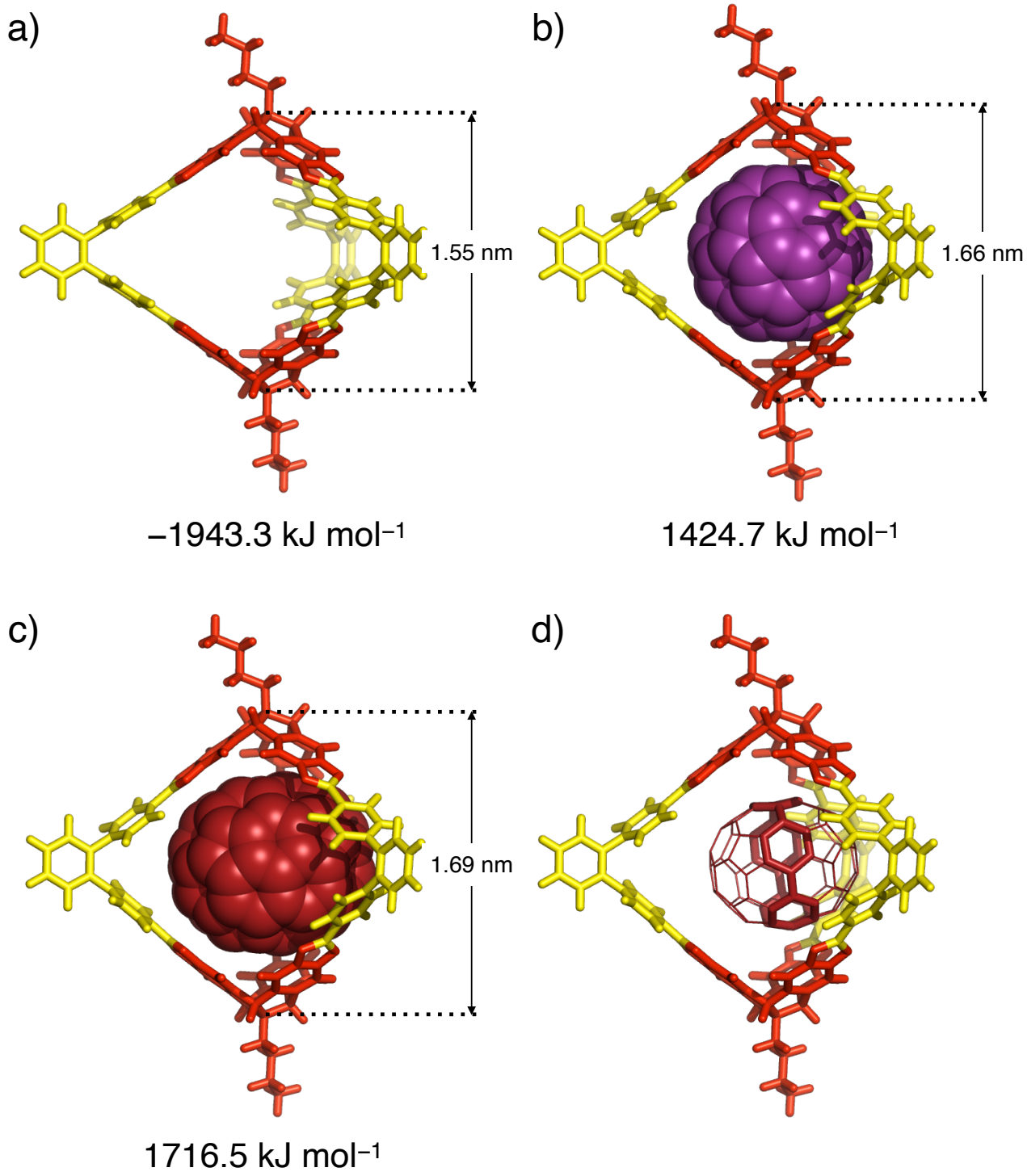


Fig. S1. Geometry-optimized molecular structures and heats of formation obtained by semiempirical PM6 modelling with Spartan'18[S4] for a) **1**, b) C_{60}⊂**1**, c) C_{70}⊂**1** and d) positions of the benzenoid hexagons in C_{70}⊂**1**.

Table S1. Atomic coordinates for PM6 geometry-optimized model for **1.**

number	element	x	y	z
1	H	-4.671	-0.534	4.987
2	C	-5.039	0.060	4.156
3	C	-6.002	1.672	1.931
4	C	-4.729	1.409	4.025
5	C	-5.845	-0.467	3.145
6	C	-6.314	0.317	2.062
7	C	-5.200	2.197	2.937
8	H	-6.354	2.281	1.103
9	C	-7.187	-0.486	1.132
10	H	-8.191	-0.013	1.035
11	C	-7.283	-1.919	1.785
12	C	-6.606	-2.919	0.770
13	H	-7.301	-3.740	0.480
14	C	-8.711	-2.316	2.156
15	H	-8.699	-3.305	2.658
16	H	-9.105	-1.605	2.911
17	C	-5.266	-2.897	2.783
18	C	-3.524	-4.829	1.892
19	C	-5.409	-3.475	1.498
20	C	-4.245	-3.270	3.661
21	C	-3.380	-4.248	3.185
22	C	-4.539	-4.458	1.019
23	H	-4.125	-2.830	4.646
24	H	-4.638	-4.904	0.034
25	C	-6.577	-0.715	-0.228
26	C	-5.486	-1.576	-2.600
27	C	-6.366	0.258	-1.208
28	C	-6.251	-2.079	-0.431
29	C	-5.696	-2.544	-1.625
30	C	-5.813	-0.205	-2.396
31	H	-6.608	1.306	-1.060
32	H	-5.439	-3.586	-1.789
33	C	-6.349	-1.886	3.061
34	H	-6.903	-2.156	3.988
35	O	-5.512	0.527	-3.526
36	O	-4.967	-1.755	-3.866
37	O	-2.540	-5.775	1.687
38	O	-2.301	-4.808	3.839
39	O	-3.967	2.184	4.877
40	O	-4.751	3.496	3.064

41	C	-0.720	2.449	-8.473
42	C	0.827	0.195	-7.841
43	C	-0.945	1.229	-9.130
44	C	0.281	2.540	-7.502
45	C	1.050	1.415	-7.197
46	C	-0.174	0.101	-8.811
47	H	0.460	3.485	-6.987
48	H	-0.359	-0.844	-9.319
49	H	-1.327	3.318	-8.719
50	C	-1.990	1.137	-10.179
51	C	-3.921	0.978	-12.205
52	C	-1.645	1.420	-11.510
53	C	-3.311	0.772	-9.864
54	C	-4.272	0.695	-10.884
55	C	-2.607	1.341	-12.518
56	H	-0.621	1.703	-11.751
57	H	-5.295	0.412	-10.638
58	H	-2.334	1.563	-13.549
59	H	-4.672	0.917	-12.992
60	C	-3.715	0.466	-8.471
61	C	-4.520	-0.117	-5.870
62	C	-3.637	-0.852	-7.994
63	C	-4.189	1.492	-7.639
64	C	-4.593	1.198	-6.334
65	C	-4.041	-1.143	-6.688
66	H	-3.260	-1.642	-8.641
67	H	-4.240	2.513	-8.013
68	H	-4.962	1.992	-5.682
69	H	-3.981	-2.166	-6.311
70	H	1.429	-0.679	-7.587
71	B	2.167	1.522	-6.143
72	B	-4.985	-0.443	-4.439
73	C	-2.758	7.074	4.747
74	C	-2.579	4.604	6.065
75	C	-2.054	6.967	5.956
76	C	-3.375	5.945	4.201
77	C	-3.285	4.720	4.866
78	C	-1.961	5.731	6.614
79	H	-3.924	6.022	3.260
80	H	-1.406	5.653	7.548
81	H	-2.820	8.034	4.238
82	C	-1.422	8.169	6.551

83	C	-0.280	10.456	7.706
84	C	-2.162	8.955	7.448
85	C	-0.101	8.534	6.232
86	C	0.463	9.680	6.814
87	C	-1.594	10.093	8.023
88	H	-3.185	8.670	7.693
89	H	1.486	9.960	6.566
90	H	-2.173	10.698	8.718
91	H	0.163	11.343	8.154
92	C	0.714	7.730	5.290
93	C	2.285	6.253	3.529
94	C	1.507	6.678	5.775
95	C	0.704	8.035	3.920
96	C	1.492	7.292	3.037
97	C	2.295	5.937	4.890
98	H	1.505	6.442	6.837
99	H	0.081	8.847	3.550
100	H	1.487	7.524	1.971
101	H	2.913	5.118	5.260
102	H	-2.509	3.639	6.571
103	B	-3.984	3.483	4.274
104	B	3.171	5.449	2.559
105	C	1.176	-7.425	4.662
106	C	-0.156	-7.576	2.197
107	C	1.594	-8.344	3.687
108	C	0.089	-6.585	4.404
109	C	-0.571	-6.670	3.176
110	C	0.930	-8.417	2.453
111	H	-0.240	-5.868	5.157
112	H	1.265	-9.126	1.698
113	H	1.699	-7.368	5.614
114	C	2.730	-9.254	3.970
115	C	4.838	-11.017	4.527
116	C	2.474	-10.499	4.565
117	C	4.052	-8.892	3.653
118	C	5.102	-9.780	3.935
119	C	3.523	-11.376	4.842
120	H	1.449	-10.777	4.809
121	H	6.125	-9.499	3.689
122	H	3.318	-12.341	5.304
123	H	5.657	-11.701	4.744
124	C	4.364	-7.587	3.024

125	C	5.000	-5.146	1.844
126	C	4.391	-7.473	1.626
127	C	4.649	-6.473	3.830
128	C	4.967	-5.249	3.236
129	C	4.709	-6.247	1.034
130	H	4.161	-8.338	1.006
131	H	4.619	-6.566	4.914
132	H	5.189	-4.380	3.858
133	H	4.730	-6.152	-0.053
134	H	-0.675	-7.627	1.239
135	B	-1.782	-5.759	2.901
136	B	5.372	-3.802	1.192
137	C	6.610	0.354	-0.049
138	C	5.836	-2.268	-0.342
139	C	6.376	-0.363	1.126
140	C	6.460	-0.227	-1.334
141	C	6.068	-1.556	-1.512
142	C	5.986	-1.685	0.949
143	H	6.484	0.074	2.114
144	H	5.947	-2.008	-2.491
145	C	7.069	1.787	-0.138
146	H	8.017	1.930	0.429
147	C	6.802	0.752	-2.428
148	H	7.610	0.344	-3.079
149	C	7.270	2.060	-1.679
150	C	6.230	3.186	-2.067
151	H	6.728	4.070	-2.524
152	C	6.032	2.785	0.310
153	C	4.166	4.767	0.698
154	C	5.562	3.571	-0.772
155	C	5.580	2.969	1.619
156	C	4.638	3.977	1.786
157	C	4.615	4.584	-0.604
158	H	5.931	2.370	2.453
159	H	4.246	5.188	-1.427
160	C	5.618	1.172	-3.260
161	C	3.551	2.363	-4.628
162	C	4.912	0.362	-4.153
163	C	5.298	2.538	-3.059
164	C	4.254	3.169	-3.740
165	C	3.873	0.990	-4.830
166	H	5.147	-0.686	-4.310

167	H	3.998	4.213	-3.590
168	O	4.035	4.379	2.960
169	O	3.249	5.694	1.150
170	O	5.704	-2.618	1.926
171	O	5.453	-3.589	-0.223
172	O	2.490	2.724	-5.434
173	O	3.026	0.438	-5.769
174	C	-9.666	-2.365	0.956
175	H	-9.288	-3.077	0.196
176	H	-9.694	-1.381	0.449
177	C	-11.084	-2.769	1.386
178	H	-11.060	-3.756	1.888
179	H	-11.467	-2.055	2.141
180	C	-12.038	-2.820	0.196
181	H	-11.710	-3.547	-0.556
182	H	-12.117	-1.847	-0.303
183	H	-13.048	-3.109	0.510
184	C	8.696	2.478	-2.034
185	H	8.939	3.428	-1.516
186	H	8.752	2.709	-3.118
187	C	9.752	1.421	-1.683
188	H	9.527	0.469	-2.203
189	H	9.709	1.182	-0.602
190	C	11.163	1.896	-2.054
191	H	11.394	2.844	-1.529
192	H	11.211	2.131	-3.136
193	C	12.218	0.847	-1.710
194	H	13.223	1.193	-1.977
195	H	12.043	-0.094	-2.244
196	H	12.226	0.618	-0.638

Table S2. Atomic coordinates for PM6 geometry-optimized model for C_{60}⊂**1.**

number	element	x	y	z
1	C	3.334	-3.738	6.610
2	C	3.504	-2.169	6.634
3	C	4.005	-4.235	5.267
4	C	1.787	-4.015	6.457
5	C	2.881	-4.840	4.464
6	C	1.636	-4.707	5.127
7	C	2.100	-1.621	6.616
8	C	1.137	-2.656	6.509

9	C	3.003	-5.461	3.218
10	C	1.814	-5.922	2.665
11	C	0.561	-5.780	3.327
12	C	0.443	-5.181	4.575
13	H	-0.517	-5.080	5.073
14	C	-0.235	-2.397	6.466
15	H	-0.980	-3.182	6.380
16	C	-0.590	-1.054	6.525
17	C	0.377	-0.015	6.642
18	C	1.742	-0.273	6.695
19	H	2.472	0.526	6.780
20	O	-1.859	-0.515	6.461
21	O	-0.249	1.215	6.661
22	C	4.582	-2.995	4.632
23	C	4.292	-1.836	5.393
24	C	5.312	-2.945	3.441
25	H	5.540	-3.828	2.852
26	C	5.717	-1.676	3.045
27	C	5.417	-0.509	3.805
28	C	4.708	-0.561	5.000
29	H	4.487	0.334	5.573
30	O	6.412	-1.331	1.903
31	H	1.405	-4.664	7.279
32	H	4.803	-4.987	5.455
33	H	4.048	-1.831	7.545
34	O	5.907	0.611	3.165
35	O	1.636	-6.533	1.440
36	C	3.950	-4.428	7.826
37	H	3.844	-5.527	7.717
38	H	5.043	-4.237	7.841
39	H	3.953	-5.569	2.704
40	O	-0.451	-6.293	2.540
41	C	3.337	-3.987	9.161
42	H	2.246	-4.179	9.163
43	H	3.442	-2.891	9.286
44	C	3.994	-4.711	10.344
45	H	5.084	-4.515	10.349
46	H	3.884	-5.807	10.225
47	C	3.387	-4.275	11.676
48	H	3.861	-4.796	12.516
49	H	2.313	-4.490	11.722
50	H	3.512	-3.200	11.846

51	C	-3.360	3.611	-6.651
52	C	-4.439	2.793	-5.835
53	C	-2.212	2.588	-7.011
54	C	-2.732	4.645	-5.638
55	C	-0.984	3.112	-6.310
56	C	-1.273	4.273	-5.550
57	C	-4.448	3.412	-4.460
58	C	-3.482	4.442	-4.346
59	C	0.300	2.566	-6.379
60	C	1.271	3.235	-5.643
61	C	0.983	4.408	-4.889
62	C	-0.293	4.956	-4.827
63	H	-0.504	5.847	-4.244
64	C	-3.287	5.154	-3.160
65	H	-2.545	5.941	-3.059
66	C	-4.100	4.776	-2.098
67	C	-5.079	3.748	-2.216
68	C	-5.279	3.046	-3.399
69	H	-6.023	2.259	-3.478
70	O	-4.092	5.274	-0.811
71	O	-5.727	3.570	-1.010
72	C	-2.688	1.256	-6.488
73	C	-3.942	1.370	-5.838
74	C	-2.019	0.036	-6.611
75	H	-1.056	-0.060	-7.103
76	C	-2.662	-1.056	-6.040
77	C	-3.926	-0.943	-5.393
78	C	-4.598	0.269	-5.281
79	H	-5.558	0.346	-4.782
80	O	-2.213	-2.359	-5.976
81	H	-2.850	5.693	-5.997
82	H	-2.043	2.536	-8.111
83	H	-5.448	2.857	-6.300
84	O	-4.319	-2.172	-4.905
85	O	2.601	2.893	-5.496
86	C	-3.979	4.274	-7.880
87	H	-4.448	3.498	-8.519
88	H	-4.811	4.936	-7.560
89	H	0.531	1.675	-6.954
90	O	2.123	4.851	-4.248
91	C	-2.976	5.083	-8.713
92	H	-2.144	4.432	-9.047

93	H	-2.504	5.867	-8.089
94	C	-3.652	5.726	-9.932
95	H	-4.481	6.383	-9.602
96	H	-4.120	4.944	-10.562
97	C	-2.659	6.532	-10.765
98	H	-3.148	6.988	-11.633
99	H	-1.843	5.905	-11.142
100	H	-2.205	7.342	-10.183
101	C	8.685	4.118	-2.973
102	C	11.442	4.345	-2.488
103	C	9.269	3.421	-1.902
104	C	9.491	4.931	-3.791
105	C	10.860	5.044	-3.551
106	C	10.651	3.539	-1.670
107	H	9.037	5.471	-4.622
108	H	11.475	5.675	-4.190
109	H	11.102	2.997	-0.838
110	H	12.511	4.431	-2.299
111	C	7.243	4.024	-3.302
112	C	4.579	3.926	-4.112
113	C	6.723	2.844	-3.856
114	C	6.414	5.143	-3.123
115	C	5.076	5.091	-3.524
116	C	5.388	2.798	-4.268
117	H	7.363	1.970	-3.970
118	H	6.816	6.050	-2.675
119	H	4.428	5.958	-3.384
120	H	4.984	1.887	-4.714
121	C	8.486	2.567	-0.978
122	C	7.179	0.972	0.896
123	C	8.659	1.174	-1.000
124	C	7.626	3.155	-0.037
125	C	6.976	2.354	0.908
126	C	8.000	0.374	-0.063
127	H	9.312	0.720	-1.744
128	H	7.474	4.233	-0.040
129	H	6.320	2.809	1.652
130	H	8.131	-0.709	-0.077
131	B	3.122	3.890	-4.609
132	B	6.505	0.097	1.969
133	C	-6.562	5.361	5.417
134	C	-7.438	6.047	7.995

135	C	-5.936	4.802	6.543
136	C	-7.631	6.258	5.593
137	C	-8.067	6.600	6.873
138	C	-6.380	5.154	7.830
139	H	-8.116	6.690	4.718
140	H	-8.894	7.296	6.999
141	H	-5.892	4.720	8.702
142	H	-7.776	6.314	8.995
143	C	-6.135	5.062	4.030
144	C	-5.444	4.672	1.359
145	C	-4.944	5.609	3.528
146	C	-6.961	4.288	3.197
147	C	-6.611	4.090	1.859
148	C	-4.601	5.418	2.186
149	H	-4.294	6.186	4.183
150	H	-7.874	3.849	3.596
151	H	-7.249	3.488	1.209
152	H	-3.684	5.855	1.788
153	C	-4.823	3.828	6.442
154	C	-2.765	1.950	6.457
155	C	-3.520	4.218	6.793
156	C	-5.083	2.501	6.063
157	C	-4.051	1.559	6.078
158	C	-2.488	3.276	6.796
159	H	-3.319	5.252	7.068
160	H	-6.089	2.209	5.768
161	H	-4.252	0.523	5.800
162	H	-1.474	3.575	7.068
163	B	-5.092	4.505	-0.131
164	B	-1.640	0.900	6.521
165	C	-3.115	-8.742	-4.141
166	C	-3.144	-11.542	-3.926
167	C	-2.475	-9.369	-3.060
168	C	-3.772	-9.526	-5.107
169	C	-3.787	-10.916	-5.001
170	C	-2.493	-10.772	-2.963
171	H	-4.268	-9.038	-5.945
172	H	-4.298	-11.515	-5.753
173	H	-1.995	-11.257	-2.122
174	H	-3.154	-12.627	-3.842
175	C	-3.118	-7.272	-4.330
176	C	-3.185	-4.543	-4.887

177	C	-4.308	-6.548	-4.148
178	C	-1.953	-6.616	-4.757
179	C	-1.989	-5.248	-5.043
180	C	-4.339	-5.179	-4.424
181	H	-5.204	-7.058	-3.798
182	H	-1.026	-7.176	-4.873
183	H	-1.090	-4.737	-5.390
184	H	-5.261	-4.613	-4.283
185	C	-1.785	-8.614	-1.987
186	C	-0.491	-7.374	0.146
187	C	-2.533	-7.924	-1.020
188	C	-0.383	-8.648	-1.901
189	C	0.265	-8.022	-0.833
190	C	-1.883	-7.308	0.053
191	H	-3.618	-7.879	-1.105
192	H	0.194	-9.167	-2.664
193	H	1.353	-8.045	-0.763
194	H	-2.463	-6.785	0.816
195	B	-3.238	-3.046	-5.248
196	B	0.221	-6.739	1.356
197	C	-1.575	2.561	-1.892
198	C	-1.312	3.218	-0.604
199	C	-2.024	2.842	0.523
200	C	-3.043	1.787	0.430
201	C	-3.290	1.167	-0.784
202	C	-2.535	1.566	-1.979
203	C	0.132	3.472	-0.512
204	C	-1.334	2.696	1.811
205	C	-2.982	0.988	1.661
206	C	-3.494	-0.286	-0.841
207	C	-2.272	0.361	-2.773
208	C	-0.295	2.409	-2.594
209	C	-3.437	-1.039	0.320
210	C	-3.173	-0.383	1.607
211	C	-2.748	-2.336	0.319
212	C	-2.320	-1.275	2.403
213	C	0.783	3.335	0.703
214	C	-2.058	-2.482	1.607
215	C	0.028	2.935	1.898
216	C	-1.064	0.218	-3.436
217	C	-0.047	1.272	-3.344
218	C	0.761	2.972	-1.742

219	C	-0.375	-1.079	-3.437
220	C	2.005	2.366	-1.689
221	C	-1.324	-0.745	3.206
222	C	0.881	2.043	2.694
223	C	1.069	-0.826	-3.346
224	C	3.384	0.922	-0.401
225	C	2.162	1.891	1.990
226	C	0.322	0.962	3.356
227	C	1.011	-0.335	3.355
228	C	3.121	0.266	-1.689
229	C	2.929	-1.105	-1.742
230	C	2.989	-1.903	-0.511
231	C	1.873	-1.667	-2.595
232	C	-2.155	-2.807	-0.841
233	C	2.219	-0.478	2.693
234	C	-0.934	-2.161	-2.775
235	C	-0.081	-3.053	-1.979
236	C	2.811	0.668	1.989
237	C	-0.006	-1.389	3.263
238	C	0.242	-2.527	2.513
239	C	3.442	0.169	0.760
240	C	3.237	-1.284	0.703
241	C	1.281	-2.813	-1.892
242	C	1.971	-2.959	-0.604
243	C	-0.836	-3.452	-0.784
244	C	-0.814	-3.089	1.660
245	C	-0.185	-3.590	0.431
246	C	1.259	-3.334	0.523
247	C	1.522	-2.678	1.810
248	C	2.482	-1.684	1.898
249	C	2.695	2.220	-0.401
250	C	2.101	2.690	0.759
251	C	-1.926	1.550	2.514
252	C	-1.122	0.709	3.265
253	C	1.272	0.628	-3.288
254	C	2.268	1.159	-2.485
255	C	-2.215	-2.009	-2.072
256	C	-2.864	-0.785	-2.071

Table S3. Atomic coordinates for PM6 geometry-optimized model for C_{70}⊂**1.**

number	element	x	y	z
1	C	3.348	-3.795	6.792
2	C	3.516	-2.225	6.789
3	C	4.062	-4.321	5.484
4	C	1.806	-4.073	6.597
5	C	2.962	-4.941	4.657
6	C	1.694	-4.771	5.266
7	C	2.112	-1.678	6.746
8	C	1.153	-2.715	6.631
9	C	3.122	-5.595	3.433
10	C	1.946	-6.033	2.834
11	C	0.668	-5.831	3.430
12	C	0.513	-5.214	4.666
13	H	-0.465	-5.075	5.117
14	C	-0.219	-2.459	6.574
15	H	-0.962	-3.245	6.483
16	C	-0.577	-1.117	6.627
17	C	0.386	-0.075	6.750
18	C	1.751	-0.330	6.818
19	H	2.478	0.470	6.909
20	O	-1.847	-0.580	6.547
21	O	-0.243	1.153	6.758
22	C	4.651	-3.093	4.835
23	C	4.322	-1.915	5.552
24	C	5.415	-3.065	3.665
25	H	5.678	-3.962	3.113
26	C	5.800	-1.801	3.235
27	C	5.446	-0.616	3.942
28	C	4.715	-0.645	5.123
29	H	4.457	0.263	5.659
30	O	6.503	-1.477	2.092
31	H	1.403	-4.722	7.409
32	H	4.855	-5.067	5.712
33	H	4.051	-1.869	7.699
34	O	5.900	0.495	3.260
35	O	1.803	-6.650	1.607
36	C	3.924	-4.458	8.042
37	H	3.821	-5.559	7.954
38	H	5.016	-4.267	8.089
39	H	4.090	-5.740	2.964
40	O	-0.324	-6.295	2.591

41	C	3.268	-3.987	9.347
42	H	2.178	-4.180	9.318
43	H	3.370	-2.889	9.453
44	C	3.887	-4.686	10.566
45	H	4.977	-4.490	10.602
46	H	3.780	-5.784	10.468
47	C	3.238	-4.221	11.868
48	H	3.685	-4.724	12.734
49	H	2.163	-4.435	11.884
50	H	3.359	-3.142	12.018
51	C	-3.573	3.827	-6.648
52	C	-4.627	2.978	-5.829
53	C	-2.435	2.824	-7.078
54	C	-2.921	4.829	-5.617
55	C	-1.190	3.323	-6.388
56	C	-1.465	4.437	-5.555
57	C	-4.633	3.583	-4.448
58	C	-3.667	4.612	-4.325
59	C	0.092	2.784	-6.514
60	C	1.075	3.398	-5.746
61	C	0.797	4.510	-4.901
62	C	-0.475	5.063	-4.794
63	H	-0.676	5.911	-4.148
64	C	-3.475	5.316	-3.133
65	H	-2.734	6.101	-3.026
66	C	-4.290	4.929	-2.076
67	C	-5.271	3.904	-2.204
68	C	-5.469	3.211	-3.392
69	H	-6.214	2.426	-3.478
70	O	-4.272	5.406	-0.780
71	O	-5.911	3.708	-0.997
72	C	-2.883	1.475	-6.574
73	C	-4.104	1.563	-5.860
74	C	-2.208	0.265	-6.752
75	H	-1.275	0.186	-7.301
76	C	-2.802	-0.842	-6.156
77	C	-4.022	-0.751	-5.427
78	C	-4.707	0.449	-5.272
79	H	-5.638	0.508	-4.715
80	O	-2.327	-2.137	-6.124
81	H	-3.025	5.886	-5.953
82	H	-2.297	2.807	-8.183

83	H	-5.642	3.026	-6.283
84	O	-4.355	-1.985	-4.905
85	O	2.403	3.039	-5.634
86	C	-4.232	4.532	-7.833
87	H	-4.715	3.777	-8.487
88	H	-5.058	5.175	-7.464
89	H	0.314	1.934	-7.152
90	O	1.939	4.886	-4.223
91	C	-3.259	5.378	-8.664
92	H	-2.433	4.746	-9.047
93	H	-2.773	6.141	-8.024
94	C	-3.975	6.064	-9.836
95	H	-4.798	6.701	-9.456
96	H	-4.456	5.303	-10.482
97	C	-3.012	6.908	-10.666
98	H	-3.530	7.394	-11.501
99	H	-2.204	6.302	-11.092
100	H	-2.545	7.699	-10.066
101	C	8.490	3.943	-3.005
102	C	11.264	4.125	-2.598
103	C	9.091	3.234	-1.953
104	C	9.287	4.744	-3.845
105	C	10.663	4.836	-3.644
106	C	10.483	3.331	-1.760
107	H	8.818	5.293	-4.661
108	H	11.270	5.458	-4.300
109	H	10.948	2.780	-0.942
110	H	12.339	4.193	-2.439
111	C	7.040	3.886	-3.310
112	C	4.379	3.906	-4.136
113	C	6.507	2.774	-3.981
114	C	6.222	4.987	-3.012
115	C	4.886	4.995	-3.424
116	C	5.174	2.788	-4.401
117	H	7.137	1.909	-4.184
118	H	6.633	5.837	-2.471
119	H	4.248	5.850	-3.197
120	H	4.761	1.933	-4.939
121	C	8.335	2.390	-0.998
122	C	7.139	0.816	0.968
123	C	8.530	0.998	-0.997
124	C	7.501	2.983	-0.037

125	C	6.907	2.193	0.952
126	C	7.927	0.210	-0.013
127	H	9.158	0.539	-1.758
128	H	7.327	4.058	-0.059
129	H	6.273	2.654	1.712
130	H	8.078	-0.871	-0.009
131	B	2.927	3.942	-4.653
132	B	6.524	-0.044	2.088
133	C	-6.586	5.297	5.505
134	C	-7.422	5.937	8.109
135	C	-5.936	4.725	6.610
136	C	-7.658	6.185	5.716
137	C	-8.074	6.503	7.007
138	C	-6.362	5.055	7.910
139	H	-8.161	6.629	4.856
140	H	-8.903	7.192	7.159
141	H	-5.856	4.609	8.767
142	H	-7.744	6.185	9.119
143	C	-6.189	5.032	4.102
144	C	-5.576	4.738	1.399
145	C	-5.001	5.577	3.590
146	C	-7.048	4.304	3.262
147	C	-6.738	4.153	1.908
148	C	-4.698	5.435	2.233
149	H	-4.324	6.117	4.250
150	H	-7.958	3.864	3.667
151	H	-7.402	3.588	1.253
152	H	-3.783	5.871	1.828
153	C	-4.818	3.759	6.487
154	C	-2.756	1.885	6.514
155	C	-3.517	4.153	6.840
156	C	-5.072	2.433	6.103
157	C	-4.039	1.492	6.124
158	C	-2.483	3.213	6.849
159	H	-3.319	5.188	7.114
160	H	-6.076	2.138	5.802
161	H	-4.236	0.456	5.845
162	H	-1.471	3.514	7.125
163	B	-5.261	4.620	-0.104
164	B	-1.630	0.836	6.598
165	C	-2.910	-8.520	-4.200
166	C	-2.872	-11.326	-4.077

167	C	-2.247	-9.165	-3.144
168	C	-3.555	-9.290	-5.186
169	C	-3.538	-10.682	-5.127
170	C	-2.232	-10.572	-3.095
171	H	-4.069	-8.786	-6.005
172	H	-4.040	-11.267	-5.895
173	H	-1.718	-11.073	-2.274
174	H	-2.856	-12.413	-4.028
175	C	-2.960	-7.047	-4.360
176	C	-3.153	-4.325	-4.930
177	C	-4.156	-6.358	-4.099
178	C	-1.846	-6.356	-4.863
179	C	-1.946	-4.993	-5.155
180	C	-4.251	-4.993	-4.382
181	H	-5.010	-6.892	-3.687
182	H	-0.911	-6.888	-5.036
183	H	-1.088	-4.456	-5.564
184	H	-5.179	-4.455	-4.184
185	C	-1.565	-8.445	-2.042
186	C	-0.301	-7.331	0.179
187	C	-2.311	-7.714	-1.105
188	C	-0.174	-8.574	-1.886
189	C	0.459	-8.012	-0.775
190	C	-1.678	-7.163	0.012
191	H	-3.384	-7.589	-1.245
192	H	0.406	-9.118	-2.629
193	H	1.538	-8.112	-0.650
194	H	-2.258	-6.610	0.753
195	B	-3.276	-2.837	-5.310
196	B	0.385	-6.766	1.438
197	C	0.238	-1.012	-3.950
198	C	0.524	-2.381	-3.516
199	C	1.783	-2.710	-3.034
200	C	2.829	-1.681	-2.969
201	C	2.550	-0.388	-3.388
202	C	1.217	-0.049	-3.889
203	C	-0.679	-2.871	-2.839
204	C	1.904	-3.558	-1.843
205	C	3.598	-1.893	-1.736
206	C	3.013	0.761	-2.607
207	C	0.879	1.308	-3.427
208	C	-1.142	-0.679	-3.554

209	C	3.733	0.563	-1.452
210	C	4.035	-0.798	-1.003
211	C	3.459	1.396	-0.266
212	C	3.924	-0.794	0.457
213	C	-0.566	-3.665	-1.723
214	C	3.576	0.569	0.896
215	C	0.759	-4.020	-1.209
216	C	0.473	3.255	-1.465
217	C	-0.621	2.760	-2.246
218	C	-1.703	-1.811	-2.880
219	C	-0.063	3.734	-0.178
220	C	-2.645	0.770	-2.374
221	C	3.387	-1.880	1.107
222	C	0.663	-4.002	0.251
223	C	-1.515	3.539	-0.179
224	C	-3.756	0.103	-0.411
225	C	-0.720	-3.655	0.626
226	C	1.712	-3.524	1.001
227	C	1.447	-2.674	2.176
228	C	-3.539	1.547	-0.306
229	C	-3.220	2.125	0.914
230	C	-3.099	1.277	2.106
231	C	-2.173	3.154	0.980
232	C	2.075	2.019	2.082
233	C	-2.221	-2.205	1.811
234	C	0.656	3.536	0.977
235	C	-0.030	3.131	2.206
236	C	-2.971	-1.999	0.608
237	C	2.467	-1.673	2.240
238	C	-0.052	-1.227	3.359
239	C	-3.643	-0.691	0.706
240	C	-3.308	-0.091	2.000
241	C	-1.405	2.943	2.213
242	C	-1.977	1.782	2.908
243	C	0.849	2.178	2.886
244	C	0.968	-0.224	3.424
245	C	0.313	1.092	3.535
246	C	-1.137	0.887	3.553
247	C	-1.362	-0.555	3.428
248	C	-2.413	-1.029	2.680
249	C	-3.205	-0.361	-1.697
250	C	-1.470	-3.450	-0.577

251	C	3.025	-3.052	-1.040
252	C	2.927	-3.041	0.343
253	C	-1.857	2.921	-1.461
254	C	-2.836	1.957	-1.523
255	C	1.958	2.847	0.919
256	C	1.973	1.804	-2.649
257	C	2.542	2.476	-0.319
258	C	1.769	2.688	-1.559
259	C	-0.461	1.680	-3.150
260	C	-1.512	0.647	-3.216
261	C	-2.652	-1.658	-1.837
262	C	-2.531	-2.511	-0.638
263	C	-1.003	-2.930	1.811
264	C	0.124	-2.421	2.617
265	C	2.204	-0.376	2.749
266	C	2.780	0.790	2.049

3 NMR Spectroscopy

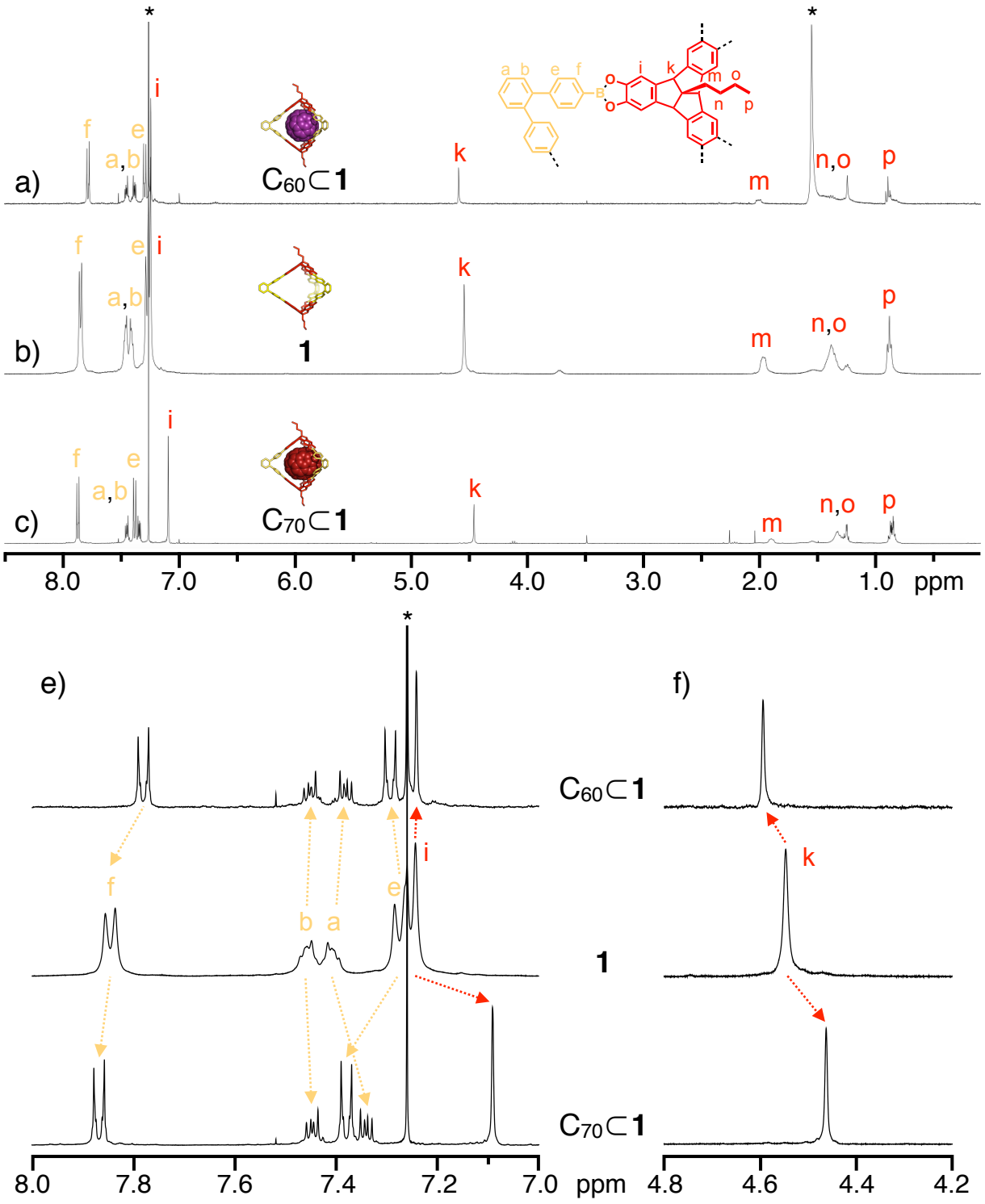


Fig. S2. ^{1}H-NMR spectra (400 MHz, $CDCl_3$, rt) of a) C_{60}⊂**1**, b) **1** and c) C_{60}⊂**1**; zoom-in for e) aromatic (7–8 ppm) and f) TBTQ bridgehead region (4.2–4.8 ppm) indicate changes in chemical shift upon complexation. * Indicates residual solvent $CHCl_3$ and H_2O.

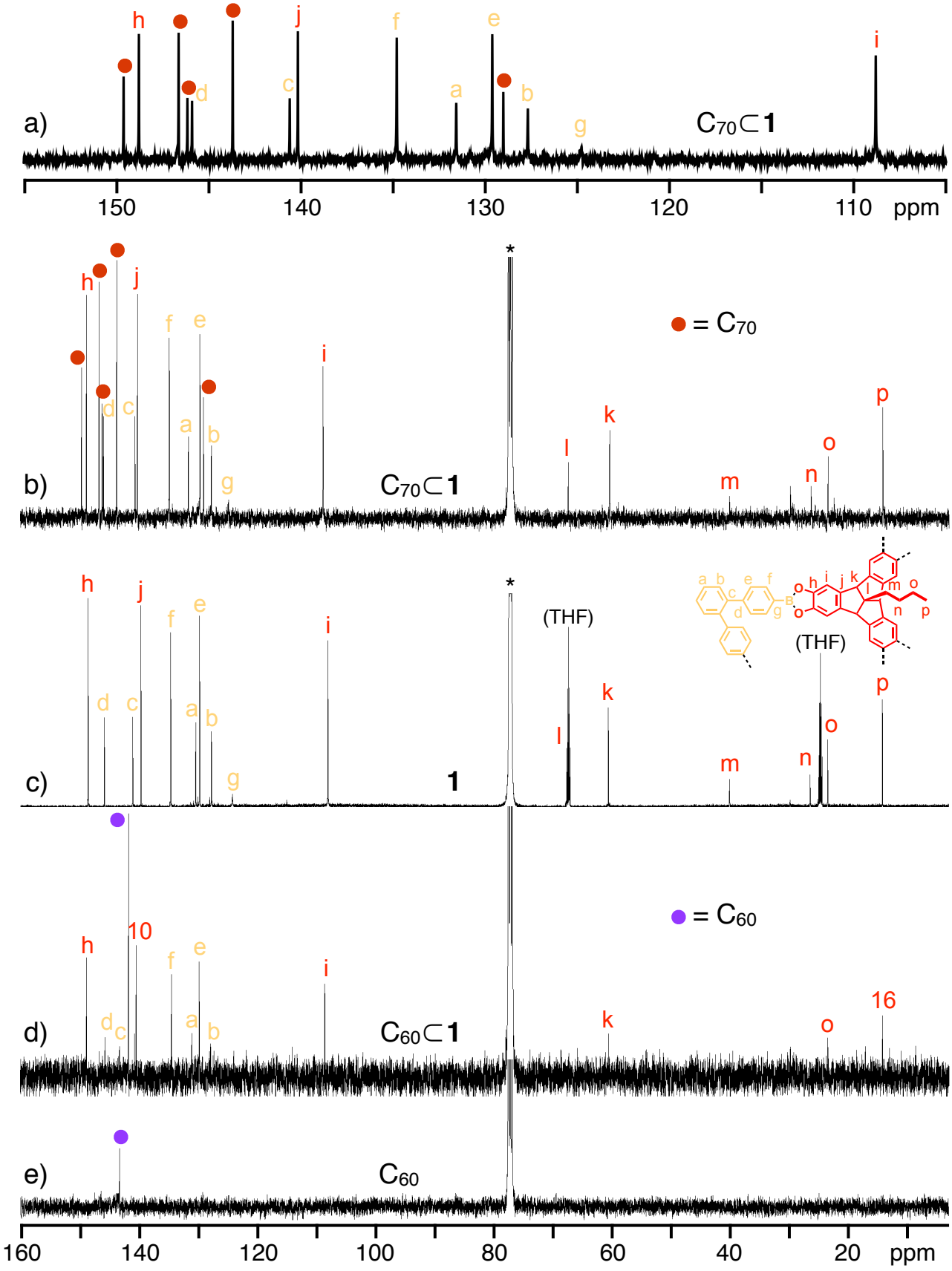


Fig. S3. ^{13}C-NMR spectra (100 MHz, $CDCl_3$, rt) for a) aromatic region (100–160 ppm) of C_{70}⊂**1**, b) C_{70}⊂**1**, c) **1** (150 MHz), d) C_{60}⊂**1** and e) C_{60}. * Indicates $CDCl_3$ signals.

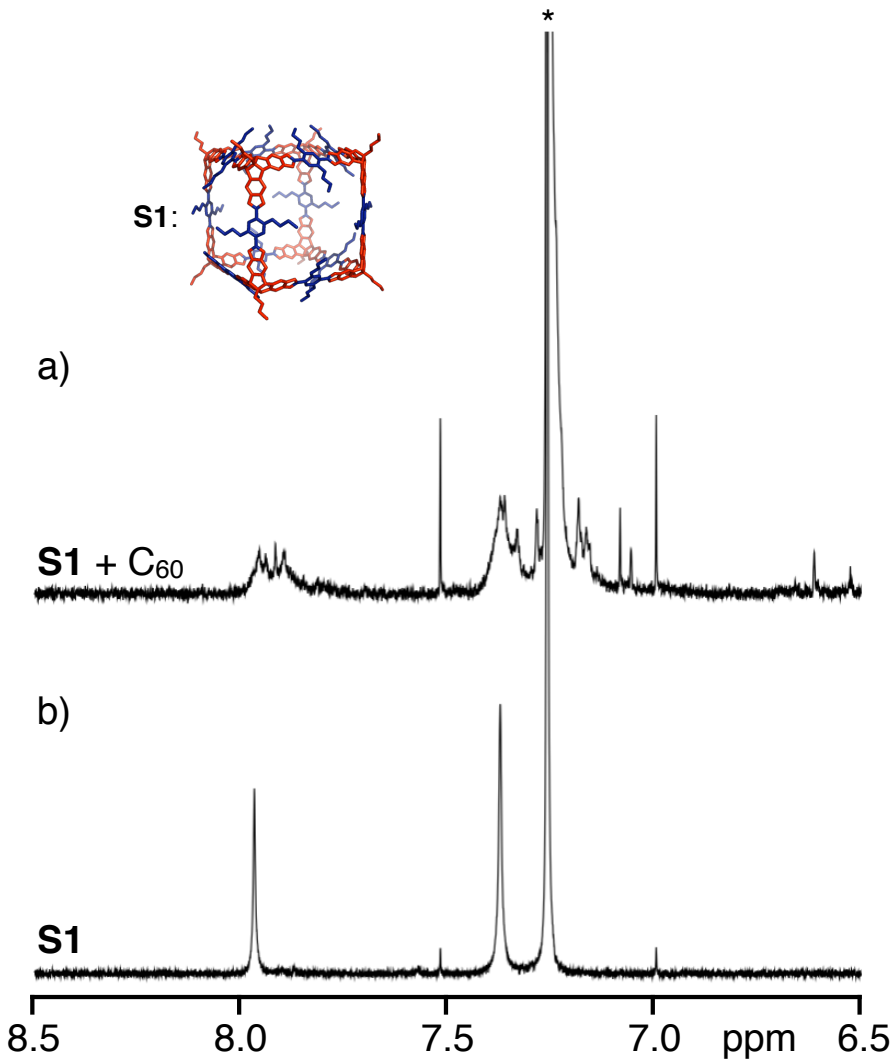


Fig. S4. ^{1}H-NMR spectra (400 MHz, $CDCl_3$, rt) for a mixture of cubic cage **S1** and C_{60} indicating no complex formation.

4 UV/Vis Absorption Spectroscopy

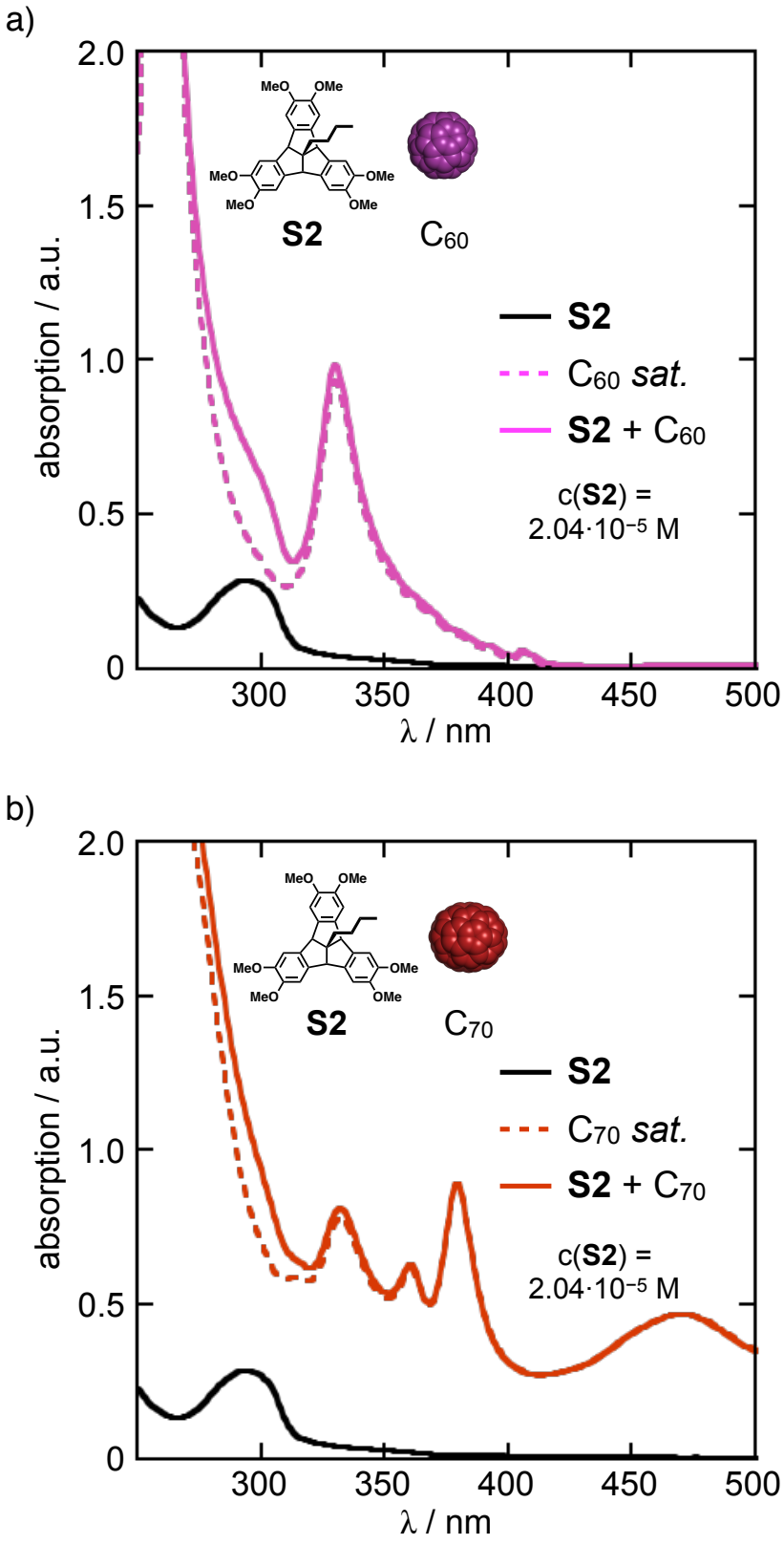


Fig. S5. UV/Vis absorption spectra ($CHCl_3$, rt) for hexamethoxy TBTQ **S2** (black, c(**S2**) = $2.04 \cdot 10^{-5}$ M) in saturated solutions of a) C_{60} (magenta, dotted line without **S2**) and b) C_{70} (brown, dotted line without **S2**).

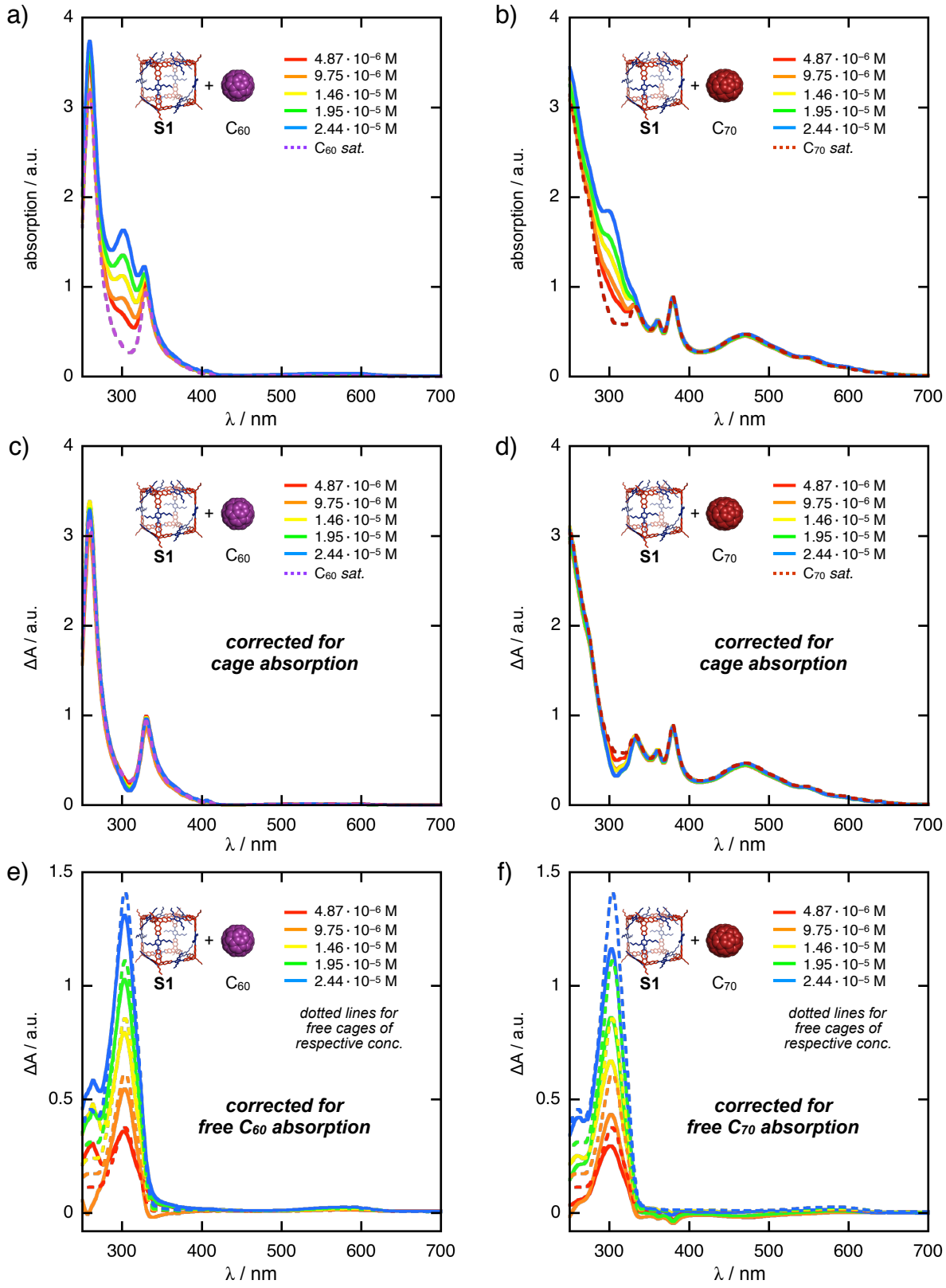


Fig. S6. UV/Vis absorption spectra ($CDCl_3$, rt) for mixtures of cubic cage **S1** with fullerenes: a) **S1** + C_{60}, b) **S1** + C_{70}, c) **S1** + C_{60} (cage absorption subtracted), d) **S1** + C_{70} (cage absorption subtracted), e) **S1** + C_{60} (saturated C_{60} absorption subtracted) and f) **S1** + C_{70} (saturated C_{70} absorption subtracted).

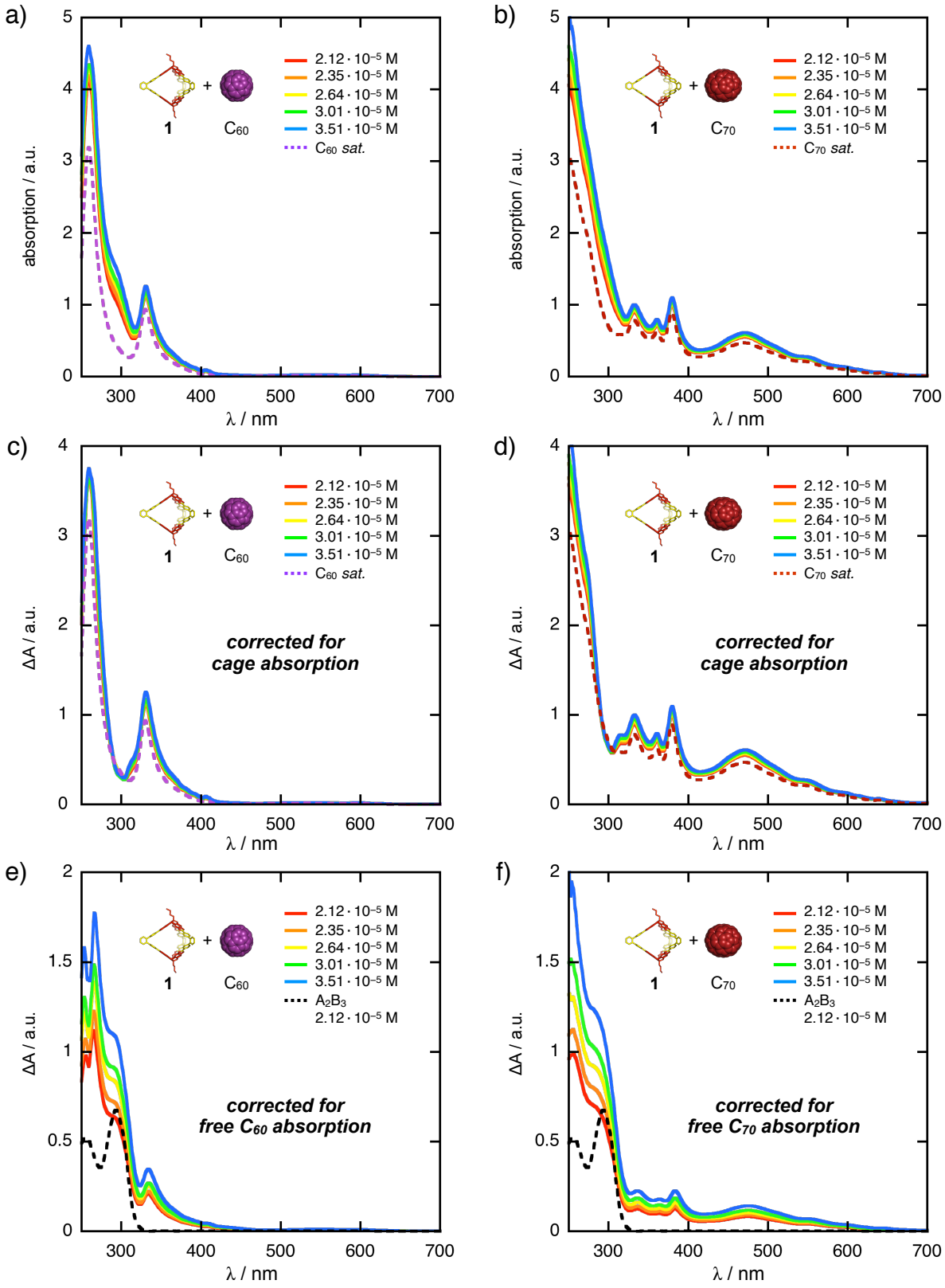


Fig. S7. UV/Vis absorption spectra ($CDCl_3$, rt) for mixtures of **1** with fullerenes: a) **1** + C_{60}, b) **1** + C_{70}, c) **1** + C_{60} (cage absorption subtracted), d) **1** + C_{70} (cage absorption subtracted), e) **1** + C_{60} (saturated C_{60} absorption subtracted) and f) **1** + C_{70} (saturated C_{70} absorption subtracted).

Determination of binding constants by quantitative UV/Vis titration experiments:

Quantitative UV/Vis absorption measurements were performed in $CHCl_3$ (HPLC grade from FISHER SCIENTIFIC) in 10 cm cuvettes. Fullerene solutions of constant concentration ($c(C_{60}) = c(C_{70}) = 1.00 \cdot 10^{-6}$ mol·L^{-1}) were titrated with varying amounts of a stock solution of cage **1** ($c(\mathbf{1}) = 6.00 \cdot 10^{-6}$ mol·L^{-1}) ranging from $1.15 \cdot 10^{-7}$ mol·L^{-1} to $3.00 \cdot 10^{-6}$ mol·L^{-1} (see Figures S8 and S9 for UV/Vis absorption spectra for titration experiments with C_{60} and C_{70}, respectively). All samples were measured after equilibration for 24 hours at room temperature. Data sets were fitted to equation 1 according to a 1:1 binding model with the software package OriginPro 2015.[S5]

$$\Delta A = \left(\frac{\mathbf{d}\cdot\Delta\varepsilon}{\mathbf{2}}\right)\left([\mathbf{C_{60}}]^{\mathbf{0}} + [1]^{\mathbf{0}} + \frac{\mathbf{1}}{K_{\mathbf{a}}} - \sqrt{\left([\mathbf{C_{60}}]^{\mathbf{0}} + [1]^{\mathbf{0}} + \frac{\mathbf{1}}{K_{\mathbf{a}}}\right)^{\mathbf{2}} - \mathbf{4}[\mathbf{C_{60}}]^{\mathbf{0}}[1]^{\mathbf{0}}}\right) \quad \text{equation 1}$$

$$\Delta A = A_{\mathbf{obs}} - (A_{\mathbf{C_{60}}} + A_1) \quad \text{equation 2}$$

$$\Delta\boldsymbol{\varepsilon} = \varepsilon_{\mathbf{C_{60}}\subset 1} - (\varepsilon_{\mathbf{C_{60}}} + \varepsilon_1) \quad \text{equation 3}$$

$$d = \text{length of cuvette}$$
$$[C_{60}]^0 = \text{total concentration of } C_{60}$$
$$[\mathbf{1}]^0 = \text{total concentration of cage } \mathbf{1}$$

ΔA was calculated from titration spectra ($\mathbf{A_{obs}}$) and reference measurements for C_{60} and **1** ($\mathbf{A}_{C60}$ and $\mathbf{A_1}$) according to equation 2.

$\boldsymbol{K}_{\mathbf{a}}$ and $\boldsymbol{\Delta\varepsilon}$ were obtained via global fit to equation 1 for λ = 309–408 (C_{60}) and 335–424 (C_{70}) nm. Remaining $\boldsymbol{\Delta\varepsilon}$ (λ = 250–308 and 409–700 nm for C_{60}; λ = 250–308 and 409–700 nm for C_{70}) were obtained after fitting to equation 1 with constant $\boldsymbol{K}_a$ obtained from the global fit.

$\boldsymbol{\varepsilon}_{C60\subset\mathbf{1}}$ were calculated according to equation 3 and plotted in Figure 2c,d.

$$\boldsymbol{K}_{\mathbf{a}}(C_{60}\subset\mathbf{1}) = 6.3\pm0.4\times10^5\ M^{-1}$$
$$\boldsymbol{K}_{\mathbf{a}}(C_{70}\subset\mathbf{1}) = 5.3\pm0.4\times10^5\ M^{-1}$$

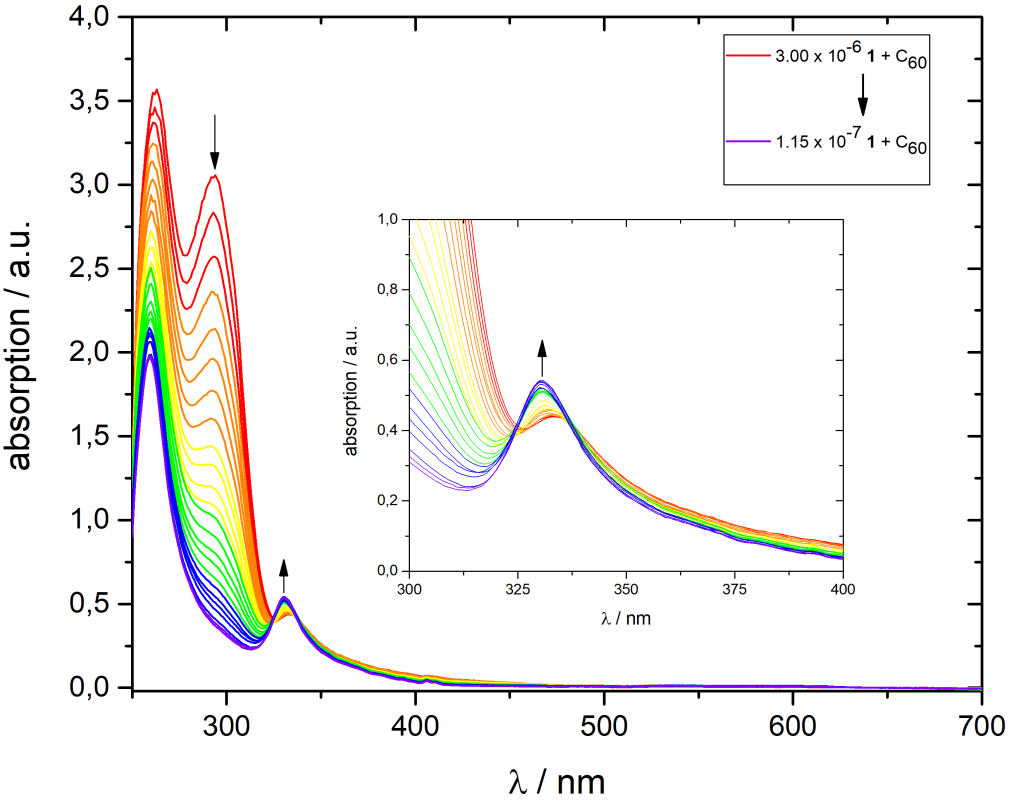


Fig. S8. UV/Vis absorption spectra ($CHCl_3$, 298 K) for titration of C_{60} ($1.00 \cdot 10^{-6}$ mol·L^{-1}) with cage **1** ($1.15 \cdot 10^{-7}$–$3.00 \cdot 10^{-6}$ mol·L^{-1}).

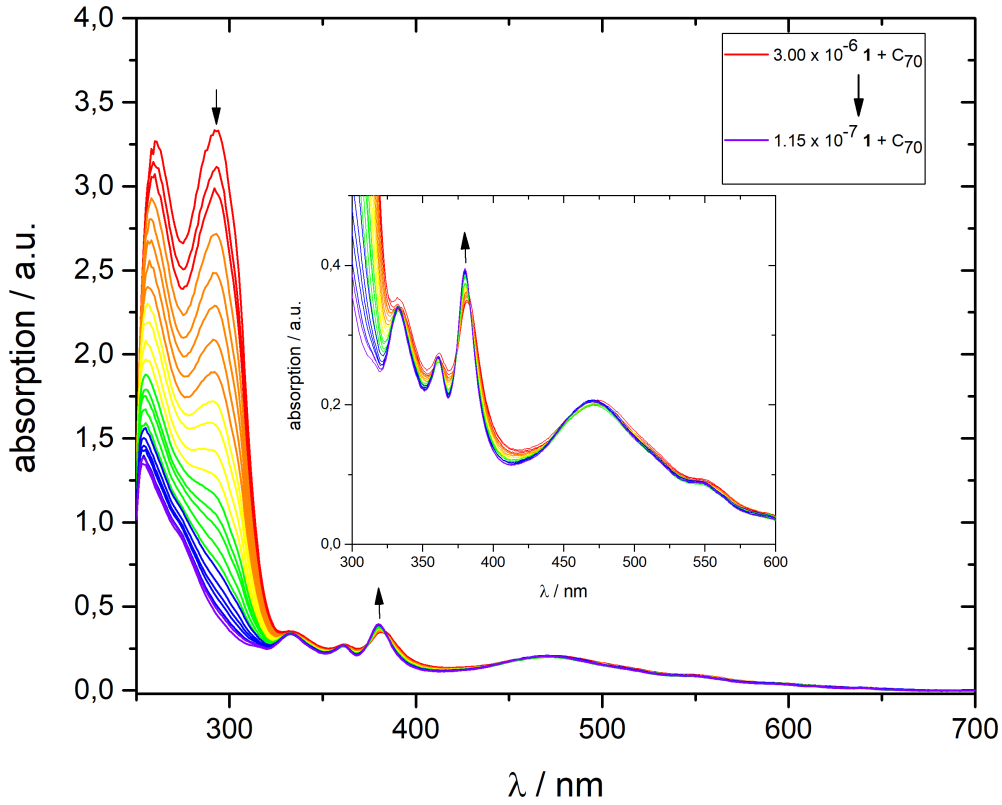


Fig. S9. UV/Vis absorption spectra ($CHCl_3$, 298 K) for titration of C_{70} ($1.00 \cdot 10^{-6}$ mol·L^{-1}) with cage **1** ($1.15 \cdot 10^{-7}$–$3.00 \cdot 10^{-6}$ mol·L^{-1}).

5 Mass Spectrometry

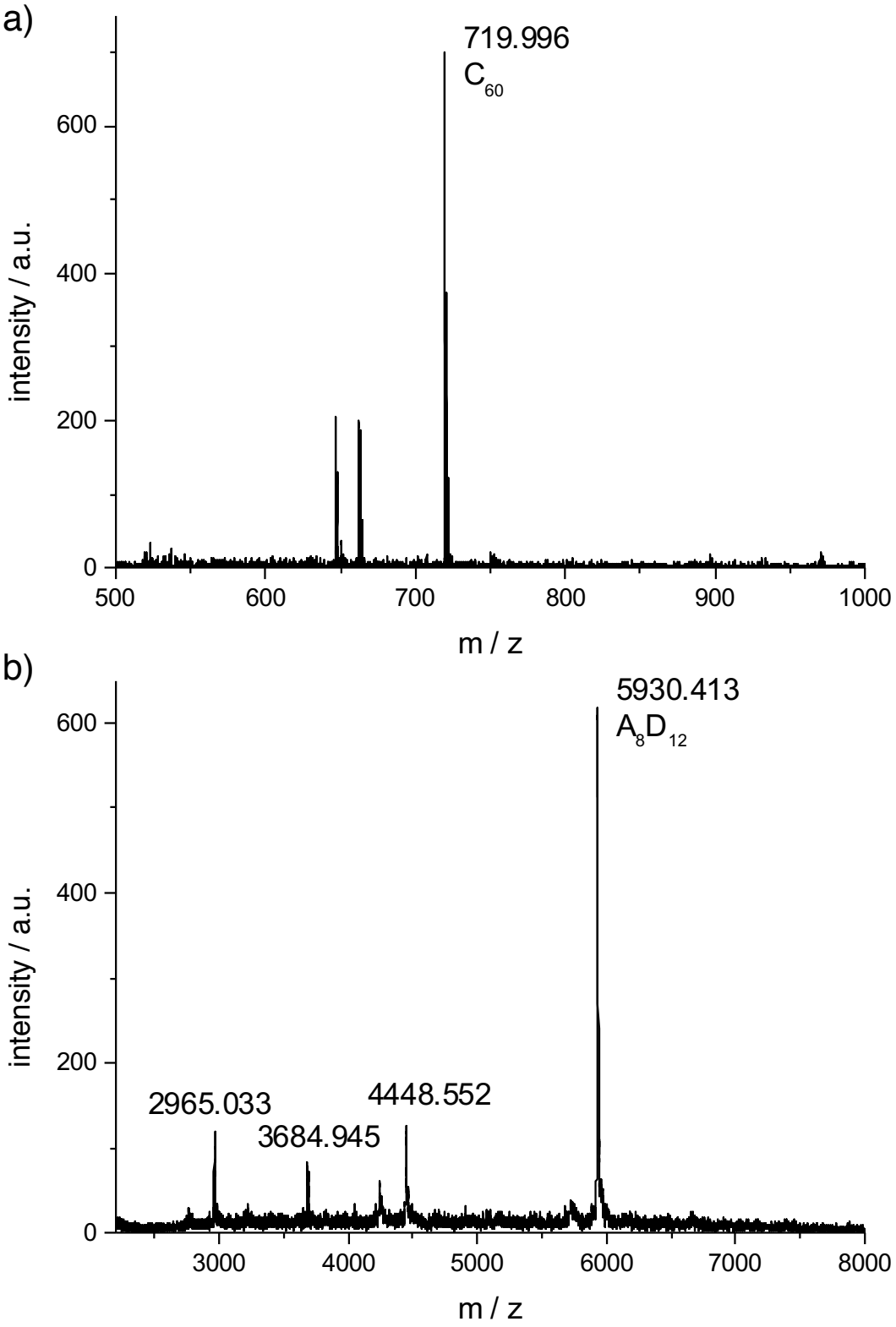


Fig. S10. MALDI-TOF mass spectrum ($CHCl_3$, matrix DCTB) from a $CHCl_3$ solution of mixtures of cubic cage **S1** and C_{60} indicating no complex formation.

6 Crystallographic Data

Single crystals suitable for X-ray diffraction were obtained after initial attempts to perform Bingel-type reactions on C_{60}⊂**1**: C_{60} (4.00 mg, 5.55 µmol, 1 eq) was added to a solution of **1** (10.3 mg, 6.43 µmol, 1.1 eq) in dry $CHCl_3$ (8 mL). After stirring over night at room temperature, the solution was sonicated for one hour at room temperature and the insoluble residues were removed by filtration through a syringe filter. Na_2CO_3 (15.5 mg), dry DMSO (1 mL) and diethyl bromomalonate (9 µL) were added and the mixture was stirred at 0 °C for two hours. After aqueous work up, the organic layer was dried over Na_2SO_4 and single crystals were grown after slow evaporation of the solvent overnight.

Single crystals were mounted on a 100 μm MiTeGen MicroLoop using perfluorinated polyalkylether. Single crystal X-ray diffraction data were collected at 100 K on a Bruker D8 Quest Kappa diffractometer with a Photon100 CMOS detector and multi-layered mirror monochromated $Cu_{K\alpha}$ radiation. The images were processed with the Bruker software packages and equivalent reflections were merged. The data were corrected for absorption effects using the multi-scan method. Corrections for Lorentz and polarization effects were applied. The structures were solved by direct methods, refined with the SHELXTL software package,[S6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to geometrically idealized positions and were included in structure factor calculations.

Crystal data and refinement details for C_{60}⊂1:

Supplementary crystallographic data for C_{60}⊂**1** can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif, CCDC 1913637.

C_{60}⊂**1** cocrystallized with one molecule of diethyl bromomalonate, which remained from the synthesis attempts under Bingel conditions.

All atoms for cage **1** could be anisotropically refined with reasonable atomic displacement parameters. Due to very low internal rotational barriers, refinement for the encapsulated C_{60} appeared to be much more difficult. We therefore used an idealized molecular geometry for C_{60} (based on DFT calculations) for an AFIX restraint and refined this molecule with 50% occupancy (C_2 axis through the center of the cage pores). ISOR restraints were applied to all C_{60} atoms. We note that this simple refinement model still does not fully describe the C_{60} rotation but we refrained from introducing further disorder for the guest as refinement was not further improved.

Twofold disorder was obtained for both $COOCH_2CH_3$ substituents of the diethyl bromomalonate molecule (59.1/40.9 and 68.6/31.4 % occupancy, respectively) and DELU and SIMU restraints were applied to atoms of both side arms.

In order to remove the electron density from highly disordered solvent molecules that could not be modeled satisfactorily, the data set was treated with the PLATON SQUEEZE[S7] function. Hence, two pores (2544 Å^3, 880 electrons) per unit cell were obtained occupying 31% of the unit cell volume.

Table S4. Crystal data and structure refinement for $C_{60}\subset$**1**

Empirical formula	$C_{60}\subset C_{106}H_{72}B_6O_4 \cdot (C_7H_{11}BrO_4)_2$
Formula weight	2801.23 g mol^{-1}
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal System, space group	Monoclinic, *C*2/*c* (No. 15)
Unit cell dimensions	a = 23.3258(10) Å, α = 90° b = 22.5169(10) Å, β = 91.177(2)° c = 31.3889(12) Å, γ = 90°
Volume	16482.7(12) Å^3
Z, calculated density	4, 1.129 g cm^{-3}
Absorption coefficient	1.121 mm^{-1}
F(000)	5736
Crystal size	0.500 · 0.110 · 0.090 mm^3
θ range for data collection	2.728–72.361°
Index ranges	$-28 \le h \le 28$, $-27 \le k \le 27$, $-38 \le l \le 35$
Reflections collected / unique	168505 / 16220 [R_{int} = 0.0337]
Completeness to θ = 67.679°	99.9 %
Absorption correction	multi-scan
Max. and min. transmission	0.7536 and 0.4906
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16220 / 490 / 1100
Goodness-of-fit on F^2	2.266
Final R indices [$I > 2(\sigma(I)$]	R_1 = 0.1218, wR_2 = 0.4333
R indices (all data)	R_1 = 0.1264, wR_2 = 0.4437
Largest diff. peak and hole	1.799 and −2.476 e Å^{-3}

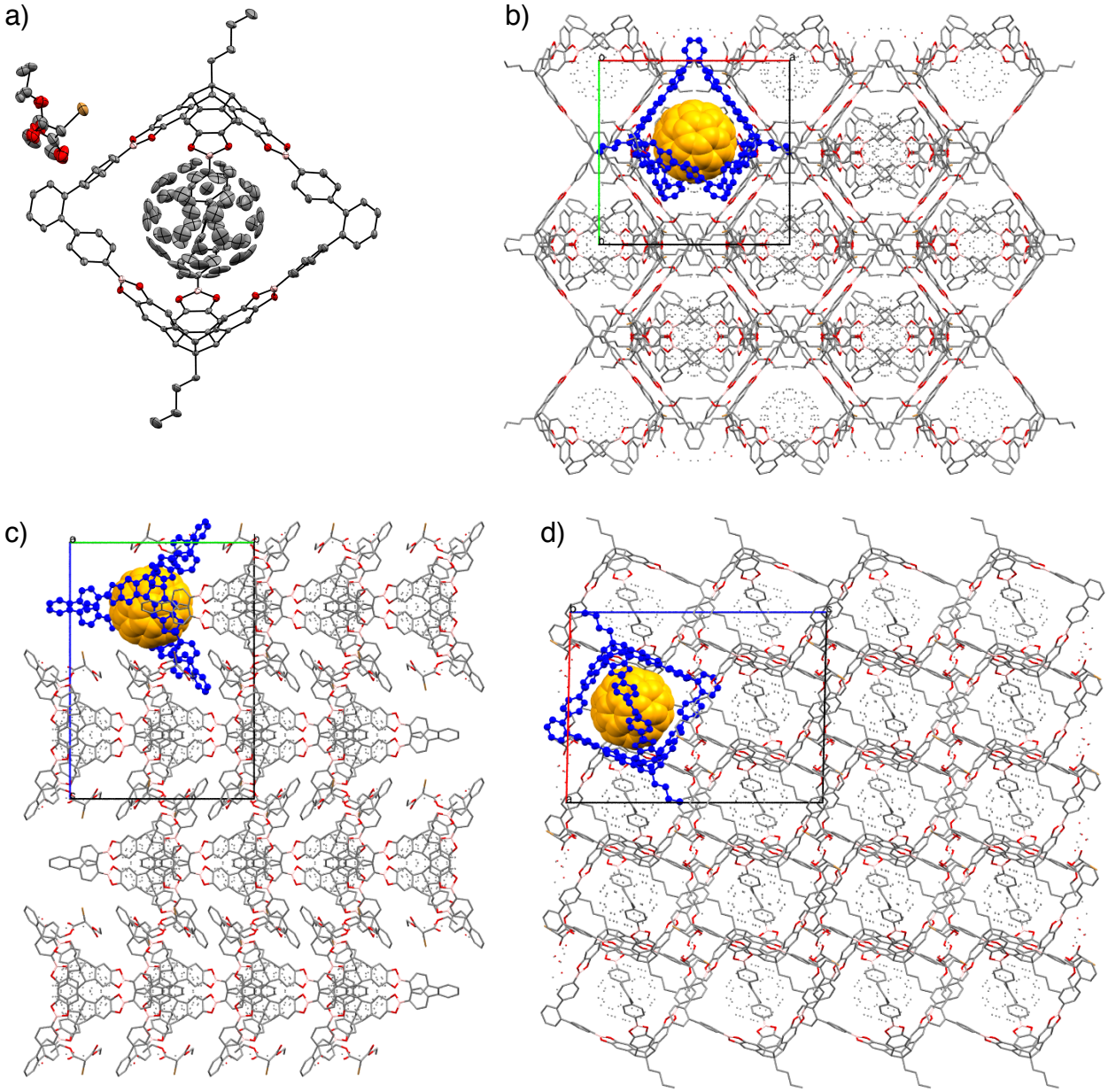
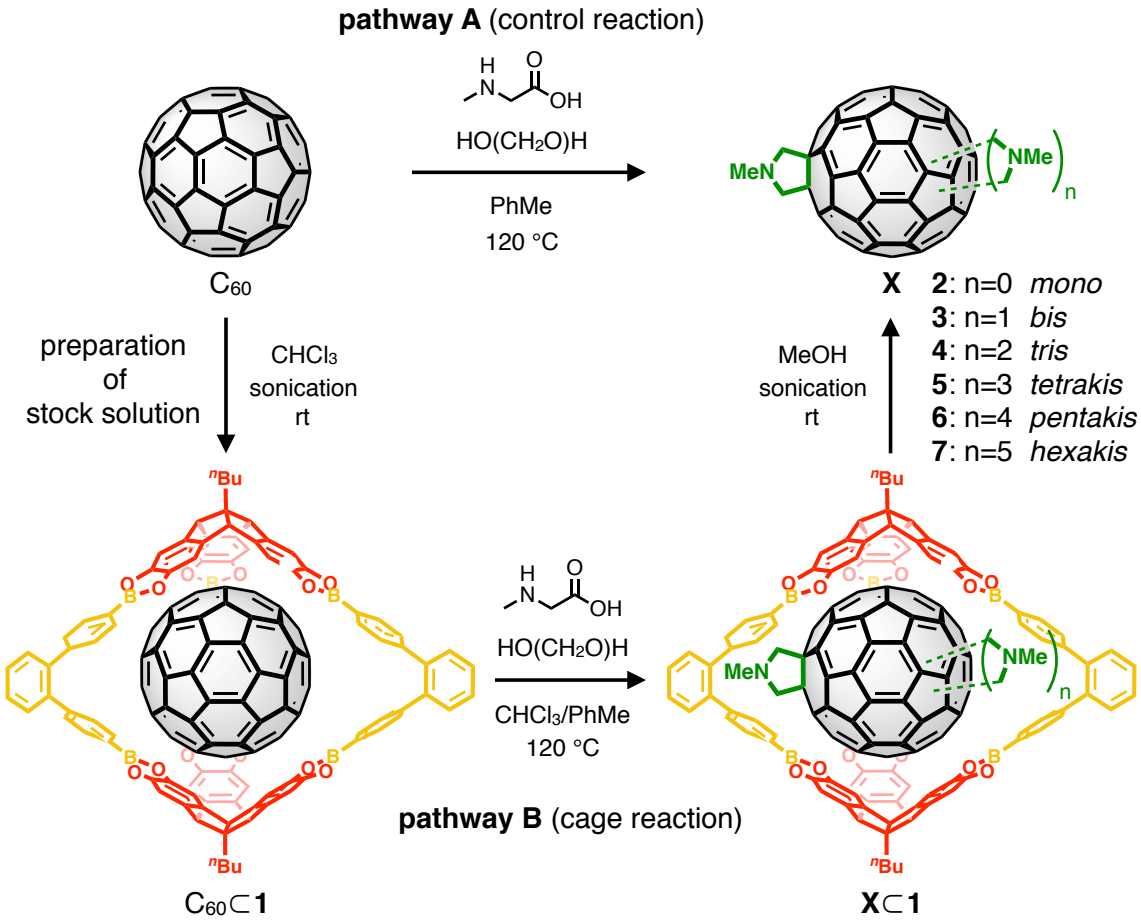


Fig. S11. SC-XRD of C_{60}⊂**1**: a) ORTEP representation of single complex C_{60}⊂**1** (thermal ellipsoids set to 50% probability, C grey, O red, B light red, Br yellow, hydrogen atoms omitted for clarity); crystal packing with views along the crystallographic (b) c, (c) a and (d) b axis (single cage **1** and C_{60} are highlighted in blue and orange, respectively).

7 Synthesis of *N*-Methylfulleropyrrolidines

Synthesis of *N*-methylfulleropyrrolidines $C_{60}(CH_2NCH_3CH_2)_n$ (**2** (mono, n=1), **3** (bis, n=2), **4** (tris, n=3), **5** (tetrakis, n=4), **6** (pentakis, n=5), **7** (hexakis, n=6) was performed according to a previously reported procedure.[S8]



Scheme 1. Synthesis of *N*-methylfulleropyrrolidines from C_{60} as control reaction (pathway **A**) and in cage-templated reactions from C_{60}⊂**1** (pathway **B**).

Preparation of stock solution for C_{60}⊂1:

C_{60} (4.00 mg, 5.55 µmol, 1 eq.) was added to a solution of **1** (10.7 mg, 6.68 µmol, 1.2 eq.) in dry $CHCl_3$ (8 mL). The suspension was stirred overnight at room temperature. Subsequently, the solution was sonicated for four hours at room temperature. After filtration of insoluble residues, another 0.2 equivalents of **1** were added and the solution was diluted with dry toluene (8 mL).

General procedure for the synthesis of *N*-methylfulleropyrrolidines:[S8]

C_{60} was dissolved in toluene (pathway **A**) or used as stock solution of C_{60}⊂**1** (pathway **B**). *N*-methylglycine and paraformaldehyde were added and the reaction mixture was heated to reflux. Progress of the reaction was followed by MALDI-TOF MS. For pathway **B**, reactions were quenched with MeOH. Regioisomeric mixtures of bis- and trisadducts were analyzed via analytical HPLC by comparison of the order of eluation and UV/Vis absorption spectra to published data for *N*-methylfulleropyrrolidine bis- and trisadducts.[S9,S10] Relative yields were estimated by integration of the eluation peaks detected via UV/Vis absorption at λ = 310 nm with the OriginPro 2015[S5] software.

Table S5. Different batches for the synthesis of *N*-methylfulleropyrrolidines.

	C_{60}			*N*-methylglycine			PFA[1]	toluene	time
	M / mg	N / μmol	eq.	M / mg	N / μmol	eq.	M / mg	V / ml	T / h
A0	1000	1380	1	250	2780	2	310	700	8
A1	4.05	5.55	1	1.66	18.6	3.3	2.03	8	42
A2	4.49	6.23	1	2.99	33.6	5.4	3.34	8	20
B1	$C_{60}\subset$**1** (16 mL stock solution)			1.66	18.3	3.3	2.03	—	42
B2	$C_{60}\subset$**1** (16 mL stock solution)			2.57	28.8	5.2	3.27	—	20
B3	$C_{60}\subset$**1** (16 mL stock solution)			4.38	49.2	8.9	5.45	—	20

[1]PFA = paraformaldehyde

Table S6. Relative yields[1] for *N*-methylfulleropyrrolidines.

	C_{60}	monoadduct **2**	bisadducts **3**	trisadducts **4**
A0	4.71 %	28.0 %	65.5 %	1.78 %
B1	42.2 %	34.3 %	22.1 %	1.48 %
B2	38.6 %	34.1 %	24.4 %	2.92 %
B3	6.60 %	12.0%	17.4 %	63.8 %

[1]Estimated based on integration of HPLC eluation peaks detected by UV/Vis absorption at λ = 310 nm.

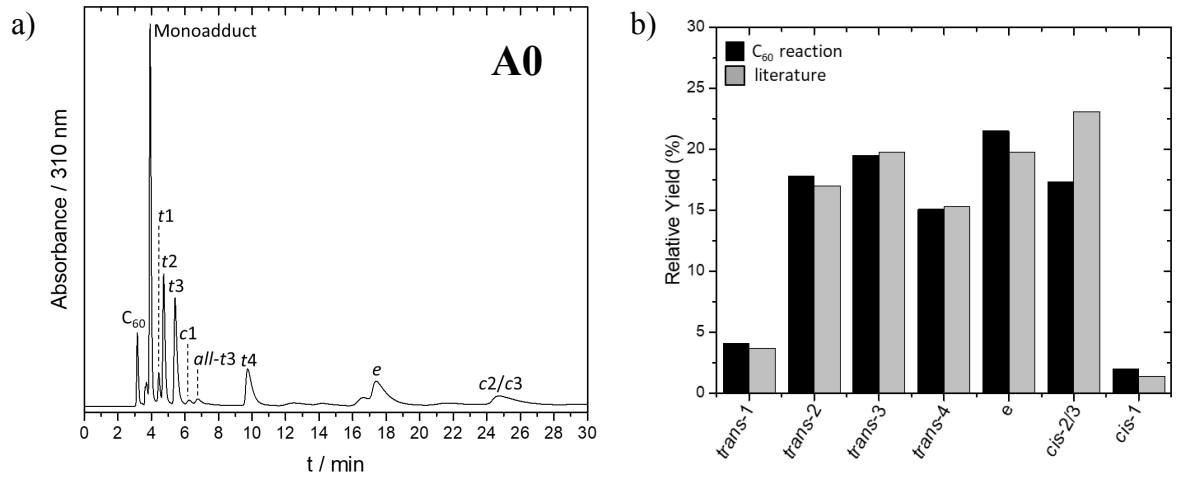


Fig. S12. a) HPLC chromatogram for control reaction **A0** (C_{60}, 2 eq. *N*-methylglycine, 8h) and relative yield for regioisomeric bisadducts **3** (literature values[S10] in grey for comparison).

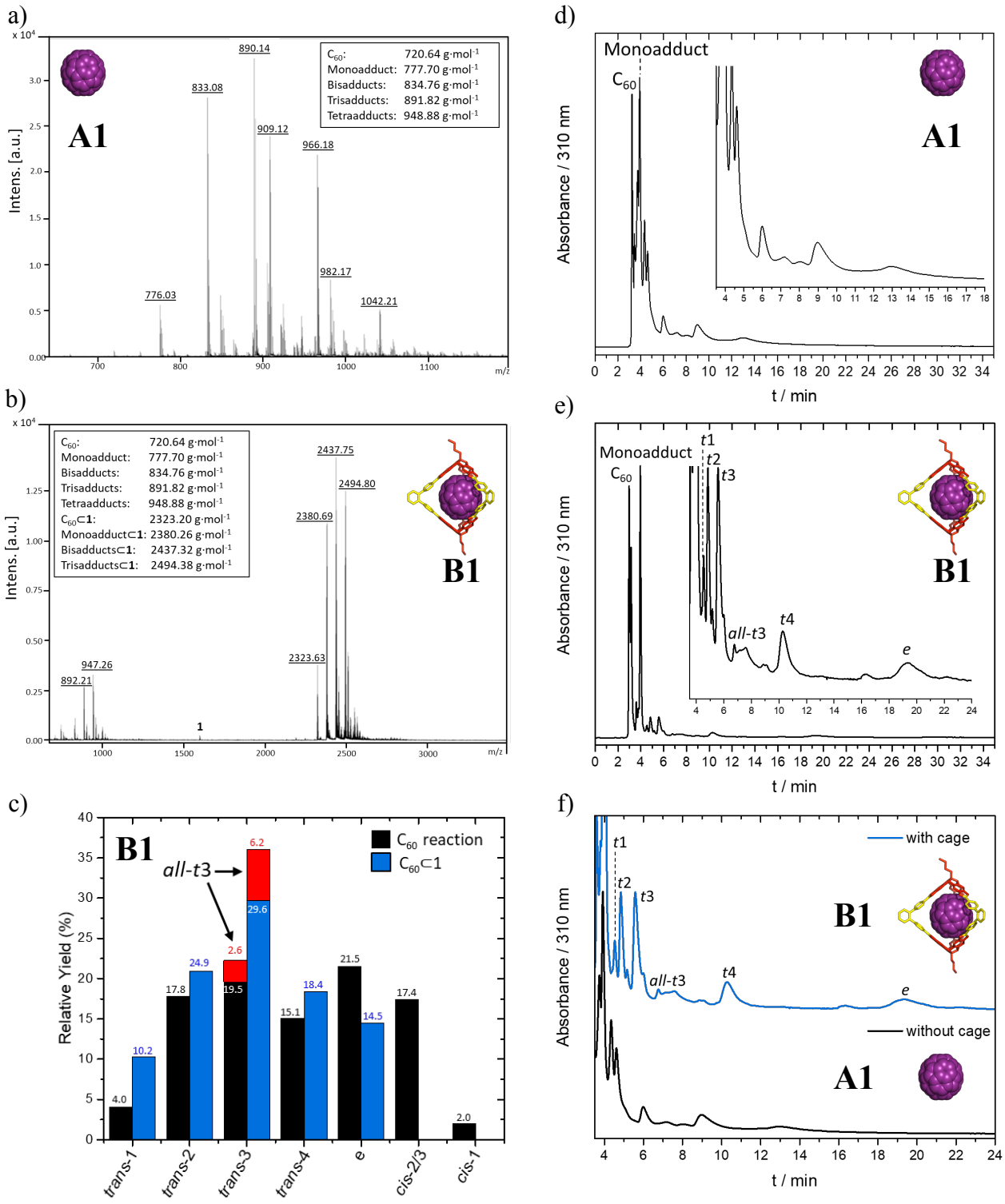


Fig. S13. MALDI-TOF MS (DCTB, $CHCl_3$) for a) control reaction **A1** (C_{60}, 3 eq. *N*-methylglucine, 42h) and b) cage reaction **B1** (C_{60}⊂**1**, 3 eq. *N*-methylglycine, 42h); c) relative yields for regioisomeric bisadducts **3** and trisadduct **4**-*t*3,*t*3,*t*3 (red) for **A0** (black) and **B1** (blue); HPLC chromatograms (UV/Vis detection at λ = 310 nm) for d) **A1**, e) **B1** and f) comparison of bisadduct region for **A1** and **B1**.

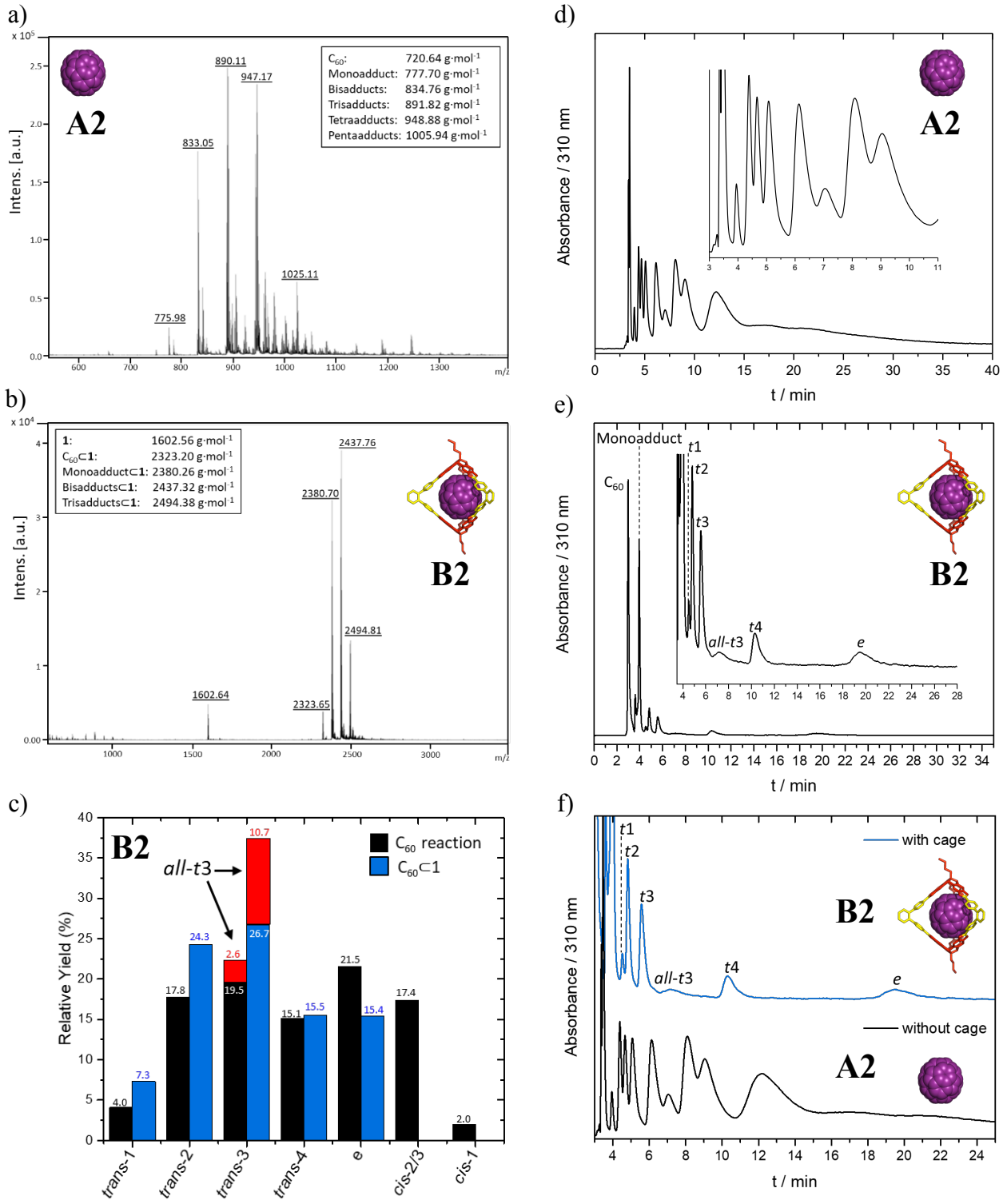


Fig. S14. MALDI-TOF MS (DCTB, $CHCl_3$) for a) control reaction **A2** (C_{60}, 5 eq. *N*-methylglucine, 20h) and b) cage reaction **B2** (C_{60}⊂**1**, 5 eq. *N*-methylglycine, 20h); c) relative yields for regioisomeric bisadducts **3** and trisadduct **4**-*t*3,*t*3,*t*3 (red) for **A0** (black) and **B2** (blue); HPLC chromatograms (UV/Vis detection at λ = 310 nm) for d) **A2**, e) **B2** and f) comparison of bisadduct region for **A2** and **B2**.

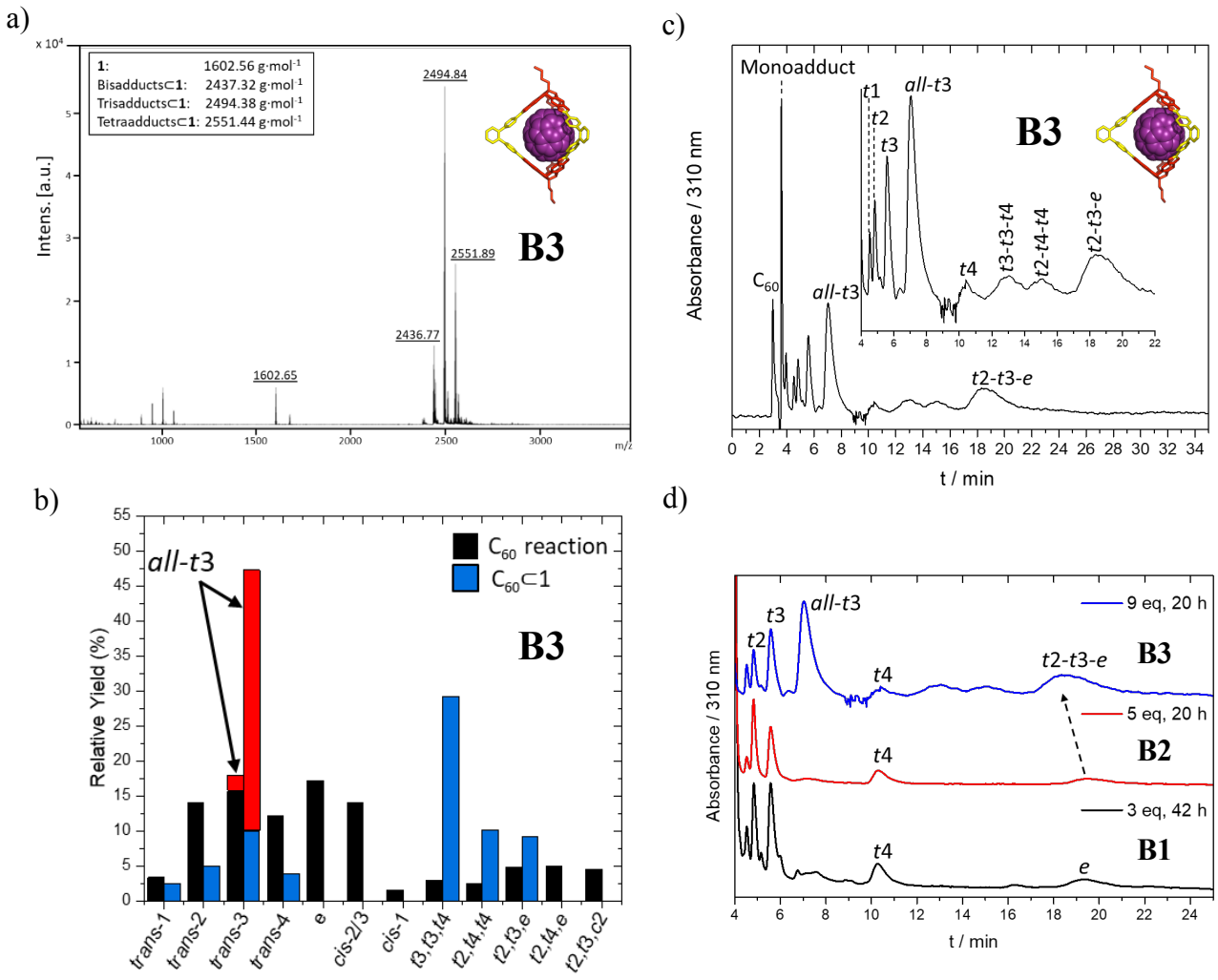


Fig. S15. a) MALDI-TOF MS (DCTB, $CHCl_3$) for cage reaction **B3** (C_{60}⊂**1**, 9 eq. *N*-methylglycine, 20h); b) relative yields for regioisomeric bisadducts **3** and trisadduct **4**-*t*3,*t*3,*t*3 (red) for **A0** (black) and **B3** (blue); HPLC chromatograms (UV/Vis detection at λ = 310 nm) for c) **B3** and d) comparison of bisadduct region for **B1** (black, 3 eq., 48h), **B2** (red, 5 eq., 20h) and **B3** (blue, 9 eq., 20h).

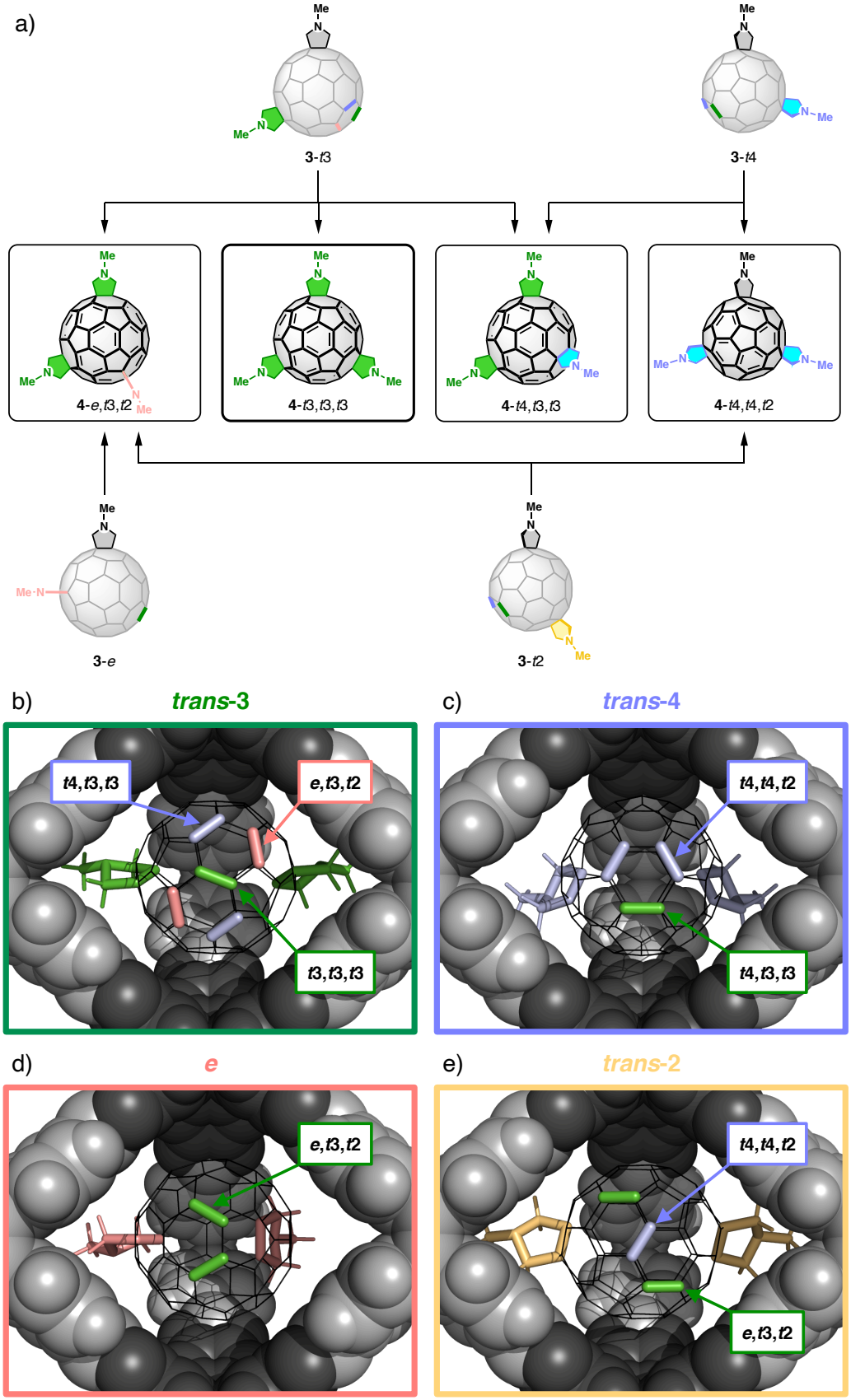


Fig. S16. a) Synthesis of specific regioisomeric trisadducts **4** from *trans*- and *e*-bisadducts **3** and illustration of accessible double bonds in cage-templated syntheses of trisadducts **4** from bisadduct complexes b) **3**-*t*3⊂**1**, c) **3**-*t*4⊂**1**, d) **3**-*e*⊂**1** and e) **3**-*t*2⊂**1**.

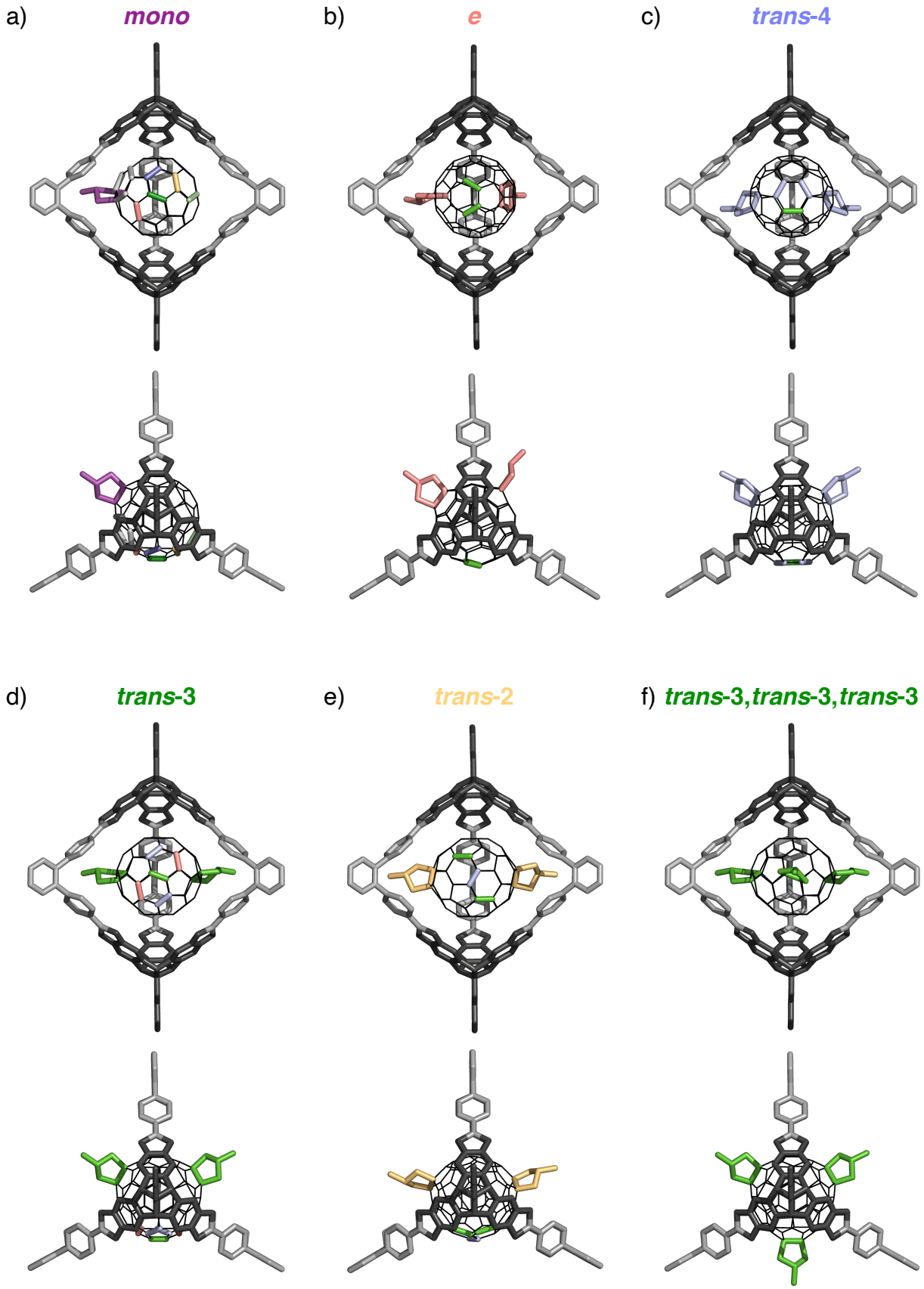


Fig. S17. Front and top views for structural models of a) **2**⊂**1** (mono), b) **3**-*e*⊂**1**, c) **3**-*t*4⊂**1**, d) **3**-*t*3⊂**1**, e) **3**-*t*2⊂**1** and f) **4**-*t*3,*t*3,*t*3⊂**1**.

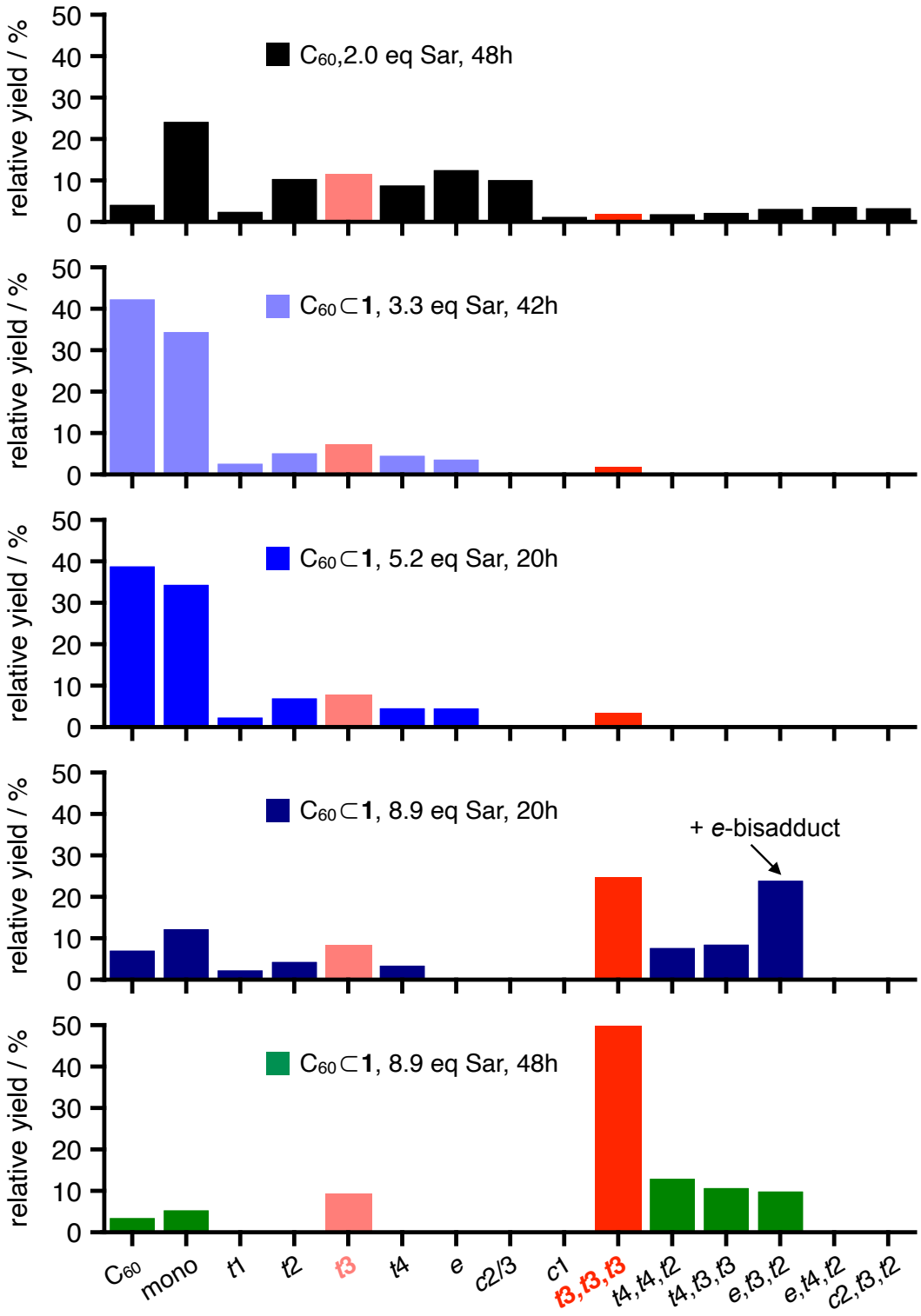
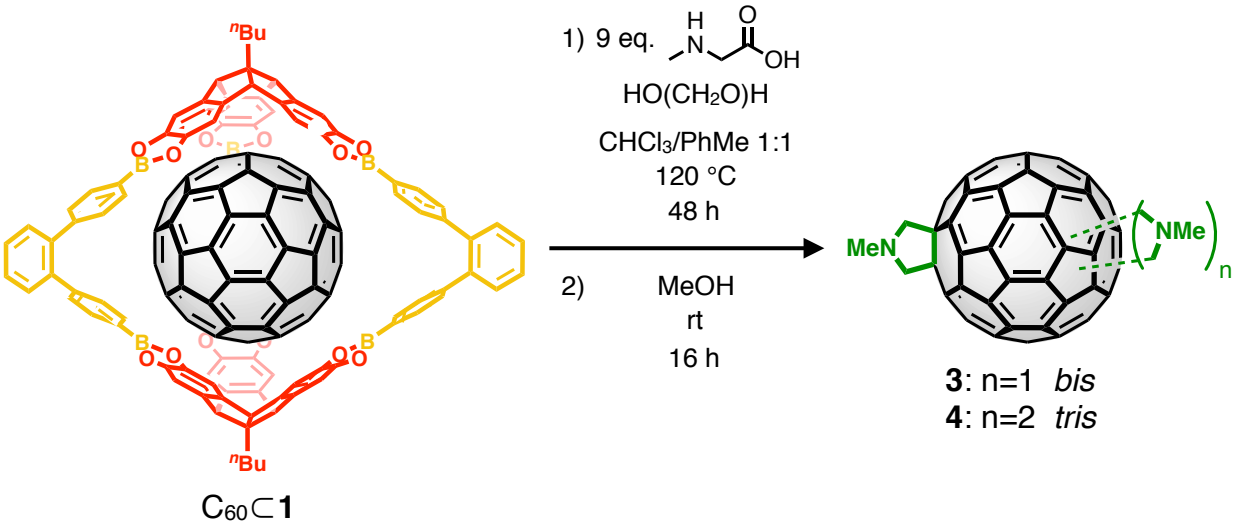


Fig. S18. Relative yields for C_{60}, monoadduct **2**, bisadducts **3** and trisadducts **4** control experiment with C_{60} (2.0 eq Sar, 8h, black, top) and cage-templated reactions with C_{60}⊂**1** (blue, middle) and cage reaction on preparative scale (9 eq Sar, 48h, green, bottom); yields for **3**-*t*3 and **4**-*t*3,*t*3,*t*3 are indicated in light red and red, respectively.

Synthesis of *N*-methylfulleropyrrolidine bis- and trisadducts on preparative scale:



Scheme S2. Synthesis of *N*-methylfulleropyrrolidines.

C_{60} (44.6 mg, 61.9 µmol, 1 eq.) was added to a solution of **1** (121 mg, 75.6 µmol, 1.2 equiv) in dry $CHCl_3$ (150 mL) an stirred overnight at room temperature. Subsequently, the suspension was sonicated for four hours at room temperature. After filtration of insoluble residues, another 0.2 equivalents of **1** were added and the solution was diluted with dry toluene (150 mL). To the stock solution of C_{60}⊂**1**, paraformaldehyde (50.5 mg) and sarcosine (16.1 mg, 181 µmol, 2.9 eq) were added and the reaction mixture was heated to reflux for eight hours. After the addition of more sarcosine (17.1 mg, 190 µmol, 3.1 eq), the reaction mixture was refluxed again for 20 hours. Finally, one last portion of sarcosine (16.0 mg, 179 µmol, 2.9 eq.) was added and the reaction mixture was refluxed for 20 hours. After removal of the solvent under reduced pressure, the residue was suspended in MeOH (100 mL), sonicated for 30 minutes and subsequently stirred overnight at room temperature. After removal of MeOH via evaporation, the crude product was dried in high vacuum and purified by automated flash chromatography with PhMe and PhMe/EtOAc 95:5 as eluents. Five fractions were isolated and analyzed and identified by mass spectrometry and comparison of UV/Vis absorption spectra to literature data.[S9, S10]

Bisadduct **3**-*t*3: 1.2 mg (1.44 µmol, 2.3%); **^{1}H NMR** (400 Mz, $CDCl_3$): δ 4.38 (d, J = 9.3 Hz, 2H), 4.31 (d, J = 9.3 Hz, 2H), 4.14 (d, J = 9.1 Hz, 2H), 4.05 (d, J = 9.4 Hz, 2H), 2.91 (s, 6H), **MS** (MALDI-TOF, DCTB in $CHCl_3$): m/z = 833.13 $[M]^+$; **UV/Vis** (CH_2Cl_2, rt): λ_{max} = 412 (sh), 462, 487 (sh), 639 nm.

Trisadduct **4**-*t*3,*t*3,*t*3: 3.4 mg (3.81 µmol, 6.1 %); **^{1}H NMR** (400 Mz, $CDCl_3$): δ 3.96 (s, 12H), 2.78 (s, 9H), **MS** (MALDI-TOF, DCTB in $CHCl_3$): m/z = 891.13 $[M]^+$; **UV/Vis** (CH_2Cl_2, rt): λ_{max} = 440, 494, 538 nm.

Trisadduct **4**-*t*4,*t*4,*t*2: 0.5 mg, (0.56 µmol, 0.9 %). This fraction was not obtained as a pure compound after one run of automated flash chromatography. Due to the very small amount, further purifications were not feasible and the addition pattern was assigned based on comparison of the order of eluation with previous literature reports.[S8]

Trisadduct **4**-*t*4,*t*4,*t*3: 1.4 mg (1.57 µmol, 5.5%); **MS** (MALDI-TOF, DCTB in $CHCl_3$): m/z = 890.12 $[M]^+$; **UV/Vis** (CH_2Cl_2, rt): λ_{max} = 478, 530, 573 nm.

Trisadduct **4**-*e*,*t*3,*t*2: 3.5 mg (3.92 µmol, 6.3%); **MS** (MALDI-TOF, DCTB in $CHCl_3$): m/z = 890.11 $[M]^+$; **UV/Vis** (CH_2Cl_2, rt): λ_{max} = 466, 544, 650 nm.

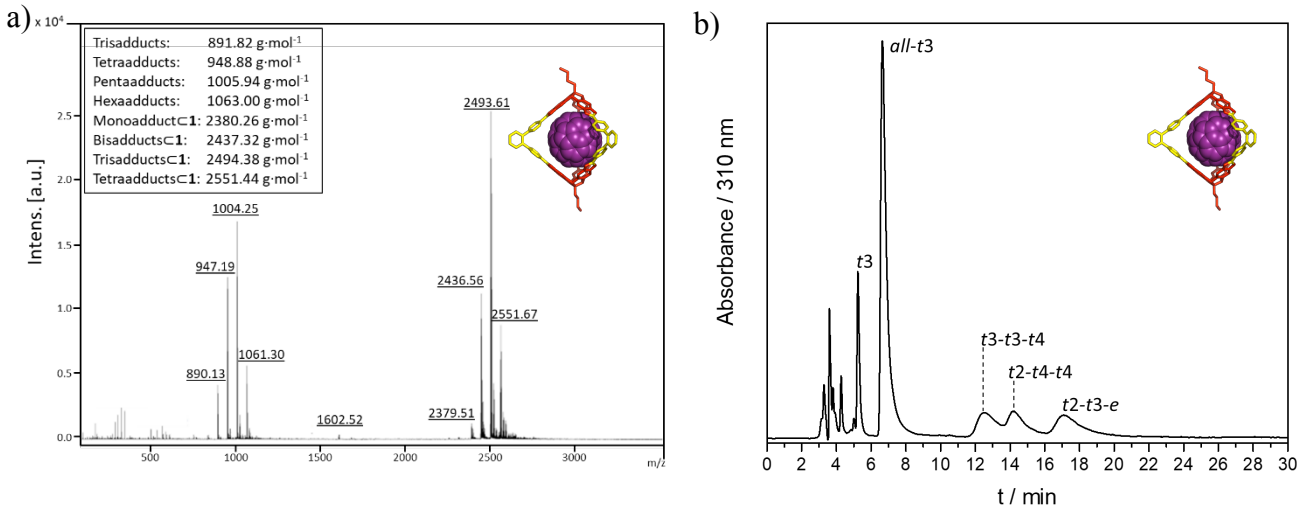


Fig. S19. Monitoring of reaction progress for reaction of C_{60}⊂**1** with 9 equivalents of *N*-methylglycine on a preparative scale: a) MALDI-TOF MS (DCTB, $CHCl_3$) and b) HPLC chromatogram for crude reaction product after 48 hours.

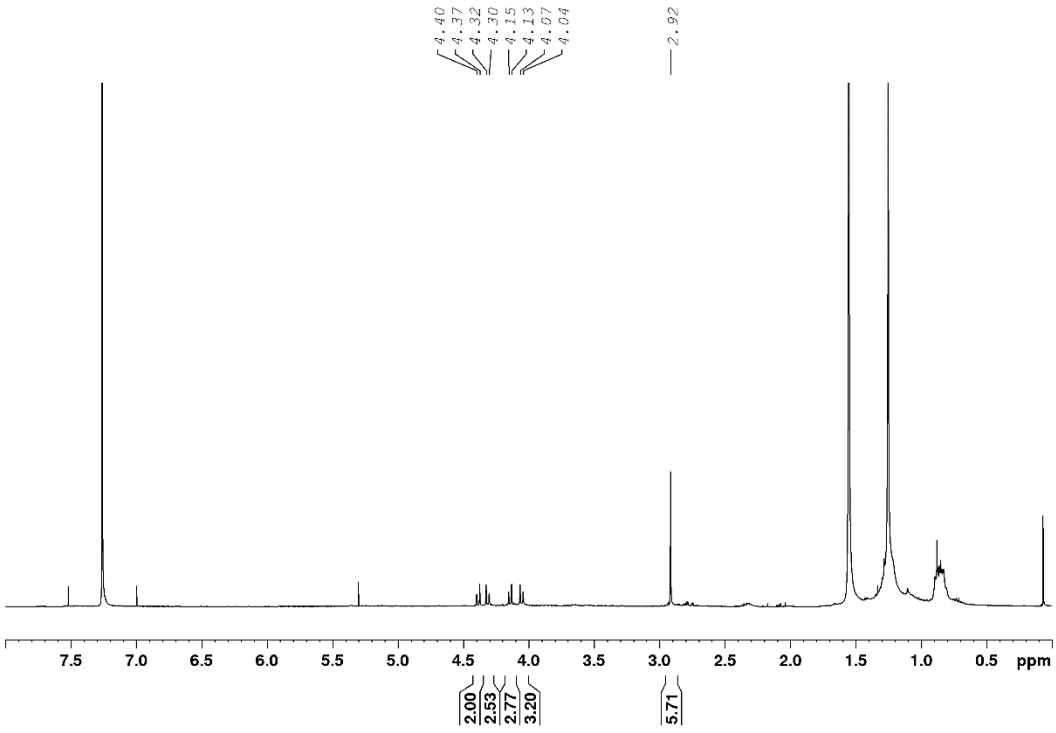


Fig. S20. ^{1}H-NMR spectra (400 MHz, $CDCl_3$, rt) for bisadduct **3**-*t*3 after isolation by automated flash chromatography.

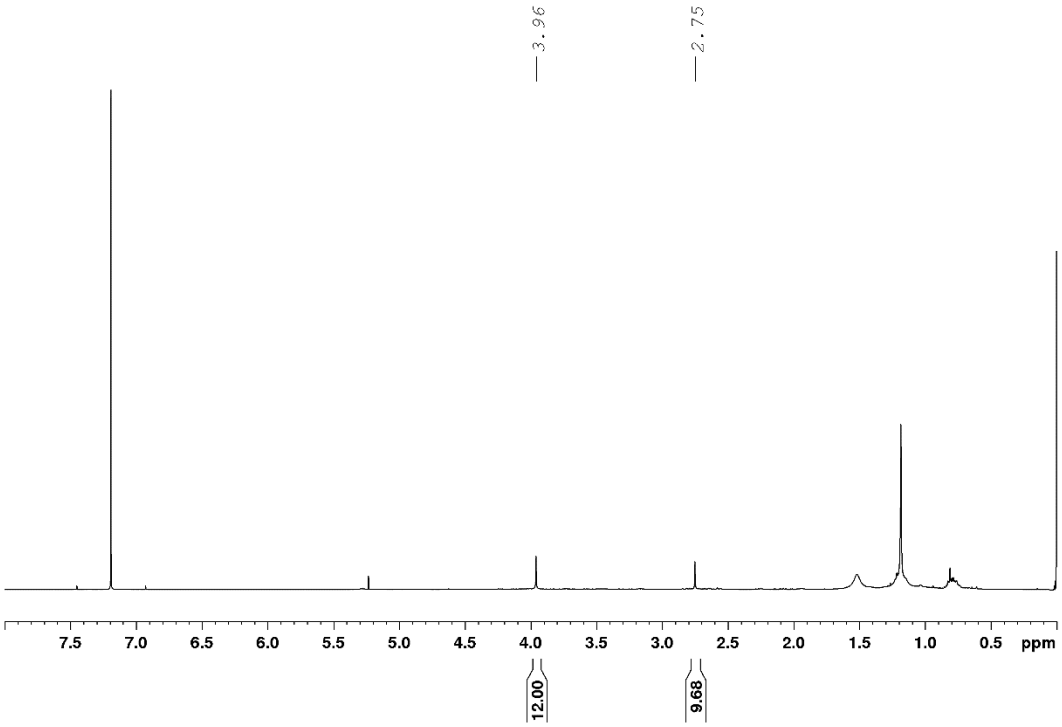


Fig. S21. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, rt) of trisadduct **4**-*t*3,*t*3,*t*3 after isolation by automated flash chromatography.

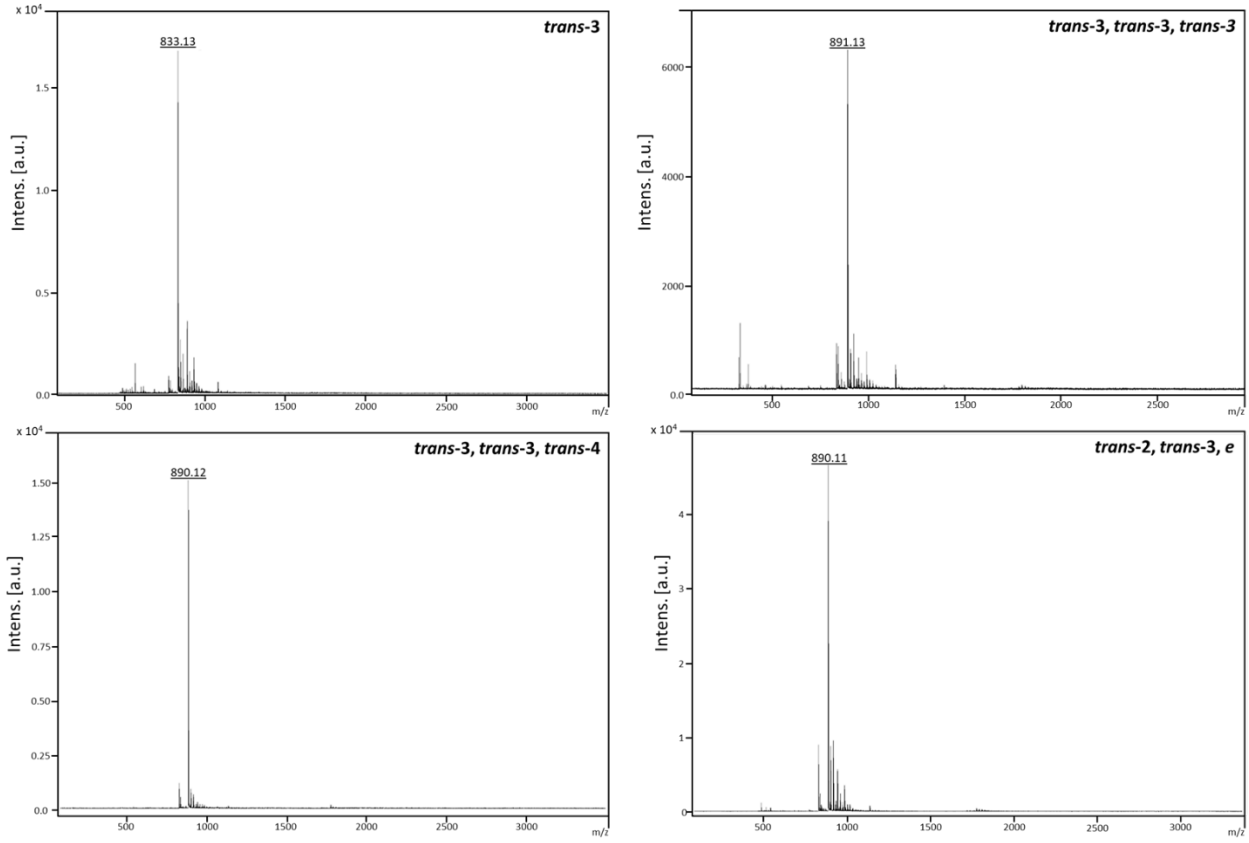


Fig. S22. Mass spectra (MALDI-TOF, DCTB, $CHCl_3$) for bis- and trisadducts after isolation by automated flash chromatography.

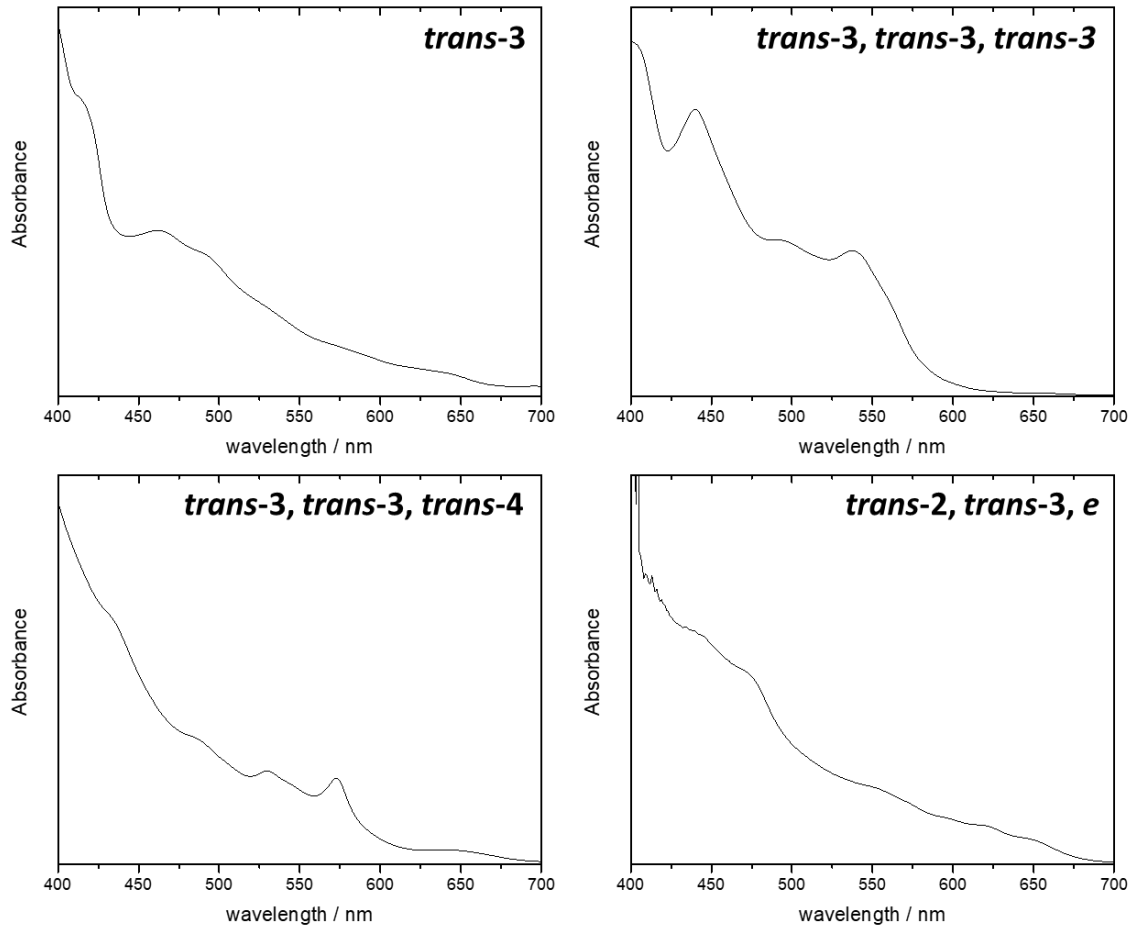


Fig. S23. UV/Vis absorption spectra (CH_2Cl_2, rt) for bis- and trisadducts after isolation by automated flash chromatography. Spectra are in accordance with literature data.[S8–S10]

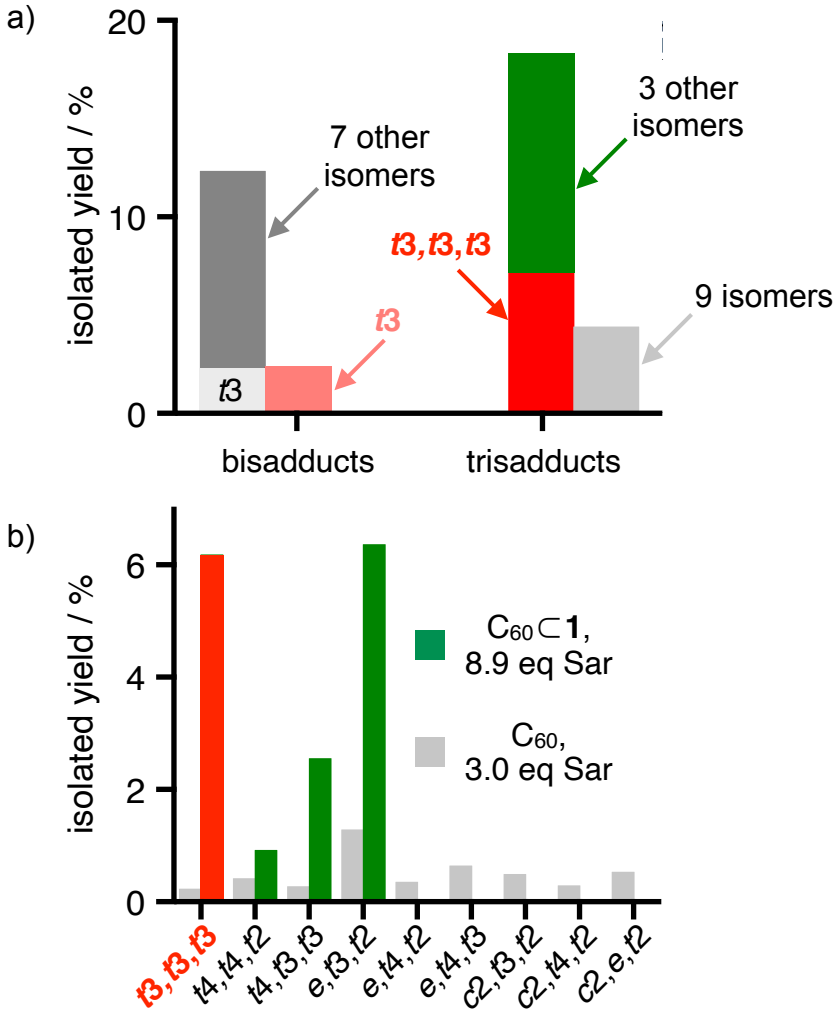


Fig. S24. a) Combined isolated yields for bis- and trisadducts for control reactions starting from C_{60} (grey)[S8] and cage-templated reaction starting from C_{60}⊂**1** (green) and b) isolated yields for pure regioisomeric trisadducts (yields for **3**-*t*3 and **4**-*t*3,*t*3,*t*3 are indicated in light red and red, respectively).

8 References

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