

Supporting Information

Monitoring the reversible photoisomerization of an azobenzene- functionalized molecular triazatriangulene platform on Au(111) by IRRAS

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Table S1. Cartesian coordinates of the optimized structure for methoxy-azo-TATA (propyl side chains) *trans*.

XYZ file

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Energy = -2008.147853891 Basis = RB3LYP 6-31++G(d,p), Charge 0, Singlet

C	3.9673356	1.9951678	-1.1887097
N	3.7169768	1.3405710	-2.4086399
C	3.7131519	-0.0668466	-2.4518879
C	3.4349548	-0.7880758	-1.2661601
C	3.0133737	-0.0367514	-0.0061244
C	3.7006529	1.3249226	0.0282536
C	3.9542420	1.9493814	1.2730930
N	3.6801526	1.2418173	2.4595123
C	3.6745915	-0.1646937	2.4406177
C	3.4197272	-0.8422233	1.2252023
C	3.9953742	-0.7846636	-3.6402232
C	3.9617283	-2.1833473	-3.6308746
C	3.6765189	-2.9030012	-2.4655329
C	3.4198689	-2.2026837	-1.2623749
N	3.1501584	-2.8869616	-0.0631139
C	3.4133347	-2.2563100	1.1683781
C	4.4832745	3.3137774	-1.1557025
C	4.7376452	3.9215787	0.0783031
C	4.4926374	3.2598209	1.2864429
C	3.9199662	-0.9168163	3.6151050
C	3.9244731	-2.3140732	3.5478931
C	3.6873274	-2.9920968	2.3470260
H	4.2684892	-0.2632361	-4.5677117
H	4.1851983	-2.7312646	-4.5611776

H	3.6783410	-4.0006821	-2.4917989
H	4.7089262	3.8559465	-2.0834539
H	5.1620113	4.9388512	0.1001290
H	4.7501611	3.7580256	2.2308774
H	4.1398821	-2.8960283	4.4591902
H	3.7457855	-4.0888963	2.3306655
C	1.5395275	0.1368587	-0.0092328
C	0.3142937	0.2581117	-0.0072291
C	-1.1061037	0.3759060	-0.0027081
C	-1.9273026	-0.7891121	-0.0282530
C	-1.7388457	1.6470235	0.0292178
C	-3.3153636	-0.6888109	-0.0212981
C	-3.9392960	0.5843966	0.0117210
C	-3.1313382	1.7446929	0.0362505
N	-5.3314493	0.7955394	0.0225559
N	-6.0377652	-0.2632053	0.0014276
C	-7.4272127	-0.0607840	0.0123860
C	-8.2286471	-1.2221207	-0.0122266
C	-9.6267420	-1.1424768	-0.0046416
C	-10.2486621	0.1253174	0.0286955
C	-9.4498687	1.2991877	0.0540267
C	-8.0638815	1.2095175	0.0460325
H	-1.4396372	-1.7774700	-0.0536940
H	-1.1153166	2.5545635	0.0484612
H	-3.9588734	-1.5813929	-0.0405844
H	-3.6382875	2.7225928	0.0615738
H	-7.7172762	-2.1976837	-0.0380395
H	-10.2215949	-2.0673638	-0.0246384
H	-9.9651727	2.2727876	0.0800961
H	-7.4282772	2.1078192	0.0652199

H	4.1296223	-0.4197847	4.5715869
C	3.4552273	1.9397525	3.7253146
H	4.2326132	1.6585721	4.4745531
H	3.5867375	3.0228196	3.5446912
C	2.6509254	-4.2605835	-0.1200996
H	3.3775654	-4.9245717	-0.6456328
H	2.5860855	-4.6416637	0.9157392
C	3.5206291	2.1376046	-3.6195277
H	4.4212792	2.7610896	-3.8322007
H	3.4253339	1.4415171	-4.4734828
O	-11.5906685	0.3266612	0.0390498
C	-12.4535041	-0.7960901	0.0151910
H	-12.3122175	-1.4050793	-0.9088674
H	-12.3043017	-1.4495288	0.9070105
H	-13.4856422	-0.3915861	0.0295559
C	1.2569513	-4.3769422	-0.7602882
H	1.2813339	-3.9625341	-1.7919614
H	0.5544843	-3.7329256	-0.1832331
C	2.2571087	3.0138521	-3.5753674
H	2.3026013	3.6955753	-2.6974438
H	1.3792593	2.3502264	-3.4077246
C	2.0742162	3.8279616	-4.8592742
H	1.1515239	4.4460408	-4.8136401
H	2.9306810	4.5189419	-5.0313937

Table S2. Raman band positions and assignments for methoxy-azo-TATA (propyl side chains) *trans*. The frequencies are given in wavenumbers (cm^{-1}) obtained from bulk Raman, calculated and SERS spectra. Mode numbers derive from the Gaussian frequency calculation (RB3LYP 6-31++G(d,p)).

Peak #	Mode No.	Calc. freq. uncorrected	Calc. freq. corrected	Calc. Intensity	Bulk freq.	SERS freq.	Assignment
	223	2301.8	2197.1	16040.9	2202	2198	Alkine stretching
30	219	1647.5	1590.6	4248.4	1598	1598	C=C stretching Ph _{top}
35	212	1547.1	1497.5	8318.3	1495	1493	N=N stretching. C-H bending Ph
43	204	1509.1	1462.2	9126.1	-	1485	C-H bending CH ₃ Methoxy
44	201	1505.9	1459.3	9093.8	1453	1452	C-H bending CH ₃ Methoxy
47	188	1456.8	1413.7	3849.1	1418	1417	C=C ring deformation Ph _{top}
	187	1442.3	1400.4	3711.0	1403	1403	C=C ring deformation Ph _{bot}
52	177	1371.9	1335.1	160.8	1363	-	C=C ring deformation, Ph _{top}
	173	1341.3	1306.7	620.6	1311	1312	C=C ring deformation, Ph _{bot}
	166	1322.9	1289.7	477.8	1302	1304	C-H bending Ph _{top}
	164	1305.2	1273.2	110.5	1287	-	C=C ring deformation Ph _{TATA}
	160	1281.2	1251.0	1797.6	1253	1253	C-Alkine stretching
55	154	1262.6	1233.7	17.0	1234	-	C-H twisting. Alkyl _{TATA}
56	153	1219.0	1193.3	4146.1	1188	1190	C-H bending Ph _{top} , Ph _{bot}
61	140	1163.4	1141.8	12937.3	1140	1140	C-H bending Ph _{top} , Ph _{bot}
	137	1125.2	1106.4	242.4	1103	1108	C-H bending Ph _{top} , Ph _{bot}
64	123	1011.4	1000.8	270.3	991	998	C _{tertTATA} -Alkine stretching

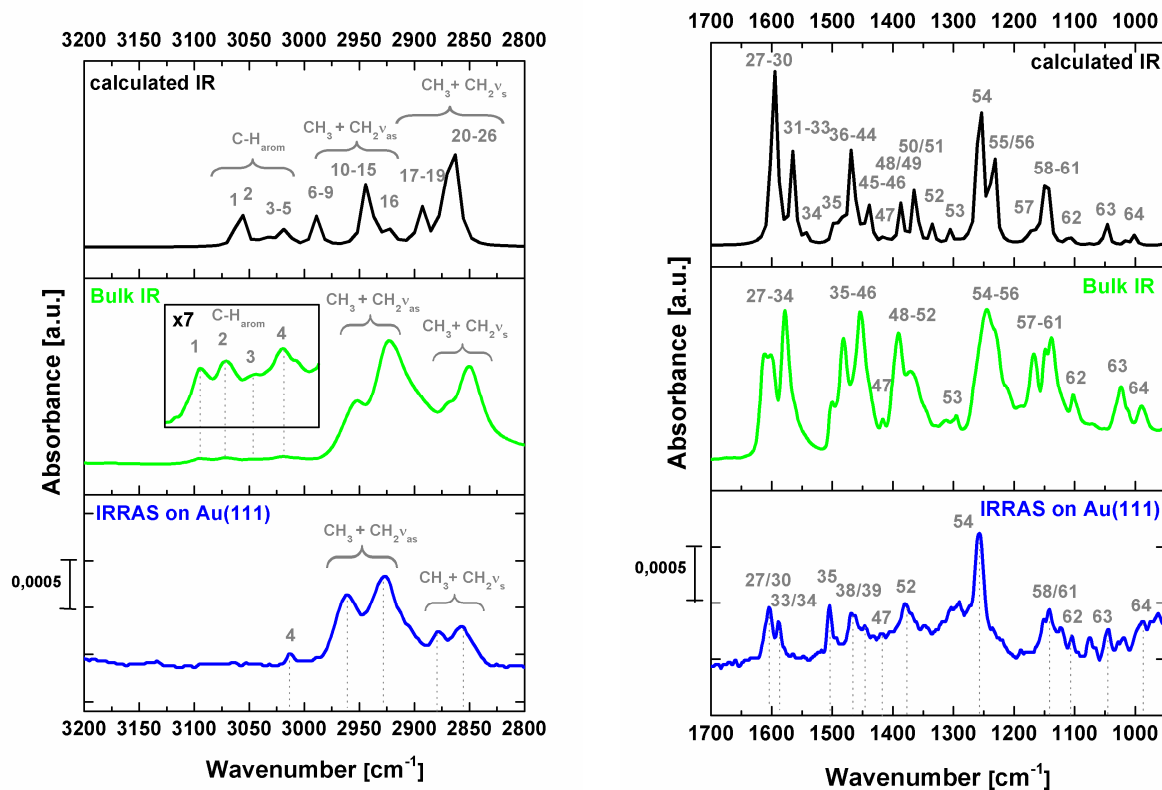


Figure S1. IR data of methoxy-azo-TATA. Left: CH-stretching vibration region, right: fingerprint region. The spectra in the top panels show the calculated, the spectra in the middle the bulk and the blue spectra at the bottom the IRRAS data of the surface-adsorbed monolayer. Band numbers correspond to Table S3.

Table S3. Infrared vibrational band assignments for methoxy-azo-TATA (propyl side chains) *trans*. The vibrational frequencies are given in wavenumbers (cm^{-1}) obtained from ATR, calculated and IRRAS. Mode numbers derive from the Gaussian frequency calculation (RB3LYP 6-31++G(d,p)). The orientation of the transition dipole moment (TDM) is given with respect to the surface plane (perpendicular: \perp , parallel: \parallel and neither totally parallel nor totally perpendicular: $/$). *For broad features the experimental frequency regime is indicated instead of exact wavenumbers

Peak #	Mode No.	Calc. freq. uncorrected	Calc. freq. corrected	Calc. Intensity	Bulk freq./ regime*	IRRAS freq.	TDM	Assignment
	264	3234.2	3061.4	8.0			/	C-H stretching Ph _{TATA}
	263	3233.8	3061.0	10.8			\parallel	C-H stretching Ph _{TATA}
	262	3233.5	3060.8	15.5			\parallel	C-H stretching Ph _{TATA}
	261	3229.8	3057.4	19.8			\parallel	C-H stretching Ph _{TATA}
	260	3229.7	3057.2	8.7			\parallel	C-H stretching Ph _{TATA}
	259	3228.9	3056.5	12.1			\perp	C-H stretching Ph _{top}
1	258	3228.1	3055.7	10.2	C-H _{arom}	-	/	C-H stretching Ph _{top}
2	257	3227.8	3055.5	13.0	C-H _{arom}	-	\parallel	C-H stretching Ph _{TATA}
	256	3227.1	3054.8	2.2			/	C-H stretching Ph _{bot}
	255	3213.0	3041.8	7.8			/	C-H stretching Ph _{bot}
	254	3205.0	3034.3	3.0			/	C-H stretching Ph _{top}
	253	3202.6	3032.1	8.5			/	C-H stretching Ph _{top}
	252	3200.2	3029.9	6.6			/	C-H stretching Ph _{bot}
	251	3197.7	3027.6	8.6			\perp	C-H stretching Ph _{bot}
3	250	3186.0	3016.7	13.8	C-H _{arom}	3014	/	C-H stretching Ph _{TATA}
4	249	3185.7	3016.5	16.5	C-H _{arom}		/	C-H stretching Ph _{TATA}
5	248	3185.4	3016.2	17.1	C-H _{arom}	-	/	C-H stretching Ph _{TATA}

6	247	3156.9	2989.7	16.7	CH ₂ v _{as}	-		C-H stretching Alkyl _{TATA}
7	246	3156.4	2989.3	25.8	CH ₃ v _{as}	CH ₃ v _{as}	⊥	C-H stretching CH ₃ -methoxy
8	245	3155.9	2988.8	15.2	CH ₂ v _{as}	CH ₂ v _{as}	/	C-H stretching Alkyl _{TATA}
9	244	3154.4	2987.4	15.1	CH ₂ v _{as}	-		C-H stretching Alkyl _{TATA}
10	243	3108.8	2945.2	29.6	CH ₃ v _{as}	CH ₃ v _{as}	/	C-H stretching CH ₃ -Alkyl _{TATA}
11	242	3108.4	2944.8	29.2			/	C-H stretching CH ₃ -Alkyl _{TATA}
12	241	3108.2	2944.6	29.4			/	C-H stretching CH ₃ -Alkyl _{TATA}
13	240	3104.4	2941.1	32.5	CH ₂ v _{as}	CH ₂ v _{as}	/	C-H stretching Alkyl _{TATA}
14	239	3104.3	2941.0	36.1			/	C-H stretching Alkyl _{TATA}
15	238	3104.1	2940.9	36.8			/	C-H stretching Alkyl _{TATA}
16	237	3087.4	2925.4	34.5	CH ₃ v _{as}	-		C-H stretching CH ₃ -methoxy
	236	3082.1	2920.4	5.0			/	C-H stretching Alkyl _{TATA}
	235	3081.6	2919.9	5.3			/	C-H stretching Alkyl _{TATA}
	234	3081.5	2919.9	6.0			/	C-H stretching Alkyl _{TATA}
17	233	3054.5	2894.8	30.7	CH ₂ v _s	CH ₂ v _s	/	C-H stretching Alkyl _{TATA}
18	232	3053.5	2893.9	30.8			/	C-H stretching Alkyl _{TATA}
19	231	3051.2	2891.8	36.0			/	C-H stretching Alkyl _{TATA}
20	230	3030.6	2872.7	39.2	CH ₃ v _s	-		C-H stretching CH ₃ -Alkyl _{TATA}
21	229	3030.3	2872.4	53.3	CH ₃ v _s	-		C-H stretching CH ₃ -Alkyl _{TATA}
22	228	3030.1	2872.2	68.5	CH ₃ v _s	-		C-H stretching CH ₃ -Alkyl _{TATA}
23	227	3021.6	2864.3	97.0	CH ₃ v _s	CH ₃ v _s	/	C-H stretching CH ₃ -methoxy
24	226	3019.4	2862.3	45.5	CH ₂ v _s	CH ₂ v _s	/	C-H stretching Alkyl _{TATA}
25	225	3017.9	2860.9	46.8			/	C-H stretching Alkyl _{TATA}
26	224	3016.9	2860.0	44.8			/	C-H stretching Alkyl _{TATA}
	223	2301.8	2197.1	28.9			⊥	Alkyne stretching

27	222	1655.5	1598.0	190.7	~1600	1606	⊥	C=C stretching Ph _{top}
28	221	1654.4	1596.9	266.0		-	∥	C=C stretching Ph _{TATA}
29	220	1654.3	1596.9	262.3		-	∥	C=C stretching Ph _{TATA}
30	219	1647.5	1590.6	203.2		1606	⊥	C=C stretching Ph _{top}
	218	1638.2	1581.9	17.7			⊥	C=C stretching Ph _{top}
31	217	1621.1	1566.0	139.0	~1590	-	∥	C=C stretching Ph _{TATA}
32	216	1620.7	1565.7	140.1	~1585	-	∥	C=C stretching Ph _{TATA}
33	215	1616.9	1562.2	69.9	~1580	1589	⊥	C=C stretching Ph _{top}
	214	1611.3	1557.0	0.1			/	C=C stretching Ph _{TATA}
34	213	1596.7	1543.4	28.6	~1580	1589	⊥	C=C stretching Ph _{bot}
35	212	1547.1	1497.5	59.4	~1500	1504	⊥	N=N stretching. C-H bending Ph.
36	211	1535.9	1487.1	64.0	~1485	-	⊥	C-H bending Ph _{top,bot}
37	210	1534.7	1485.9	46.9	~1475	-	⊥	C-H bending Ph _{top, Ph_{bot}}
38	209	1520.2	1472.5	24.8	~1470	1468	/	C-H bending Alkyl _{TATA}
39	208	1519.6	1472.0	26.8			/	C-H bending Alkyl _{TATA}
40	207	1517.6	1470.2	46.0	~1460	-	∥	C-H bending Alkyl _{TATA}
41	206	1516.0	1468.6	130.0		-	/	C-H bending Alkyl _{TATA}
42	205	1515.3	1468.0	106.7		-	∥	C-H bending Alkyl _{TATA}
43	204	1509.1	1462.2	41.5		-	⊥	C-H bending CH ₃ Methoxy
	203	1507.3	1460.6	2.8			∥	C-H bending Alkyl _{TATA}
	202	1507.3	1460.6	3.6			/	C-H bending Alkyl _{TATA}
44	201	1505.9	1459.3	23.2	~1460	-	⊥	C-H bending CH ₃ Methoxy
	200	1505.9	1459.2	4.8			/	C-H bending Alkyl _{TATA}
	199	1505.0	1458.4	8.3			/	C-H bending Alkyl _{TATA}
	198	1504.8	1458.3	12.2			/	C-H bending Alkyl _{TATA}

	197	1503.2	1456.8	11.0			/	C-H bending Alkyl _{TATA}
	196	1500.0	1453.8	0.4			/	C-H bending Alkyl _{TATA}
	195	1499.9	1453.7	0.7			/	C-H bending Alkyl _{TATA}
	194	1499.1	1452.9	0.3			/	C-H bending Alkyl _{TATA}
	193	1496.9	1451.0	8.5				C-H bending CH ₃ Methoxy
45	192	1486.4	1441.2	79.4	~1450	-		C=C ring deformation, Ph _{TATA}
46	191	1486.1	1440.9	76.8		-		C=C ring deformation, Ph _{TATA}
	190	1482.3	1437.4	1.5				C=C ring deformation, Ph _{TATA}
	189	1478.1	1433.6	19.3			⊥	C-H bending. CH ₃ -Methoxy
47	188	1456.8	1413.7	30.2	~1420	1420	⊥	C=C ring deformation, Ph _{top}
	187	1442.3	1400.4	5.2				C=C ring deformation, Ph _{bot}
48	186	1428.1	1387.1	67.9	~1390	-		C-H bending Alkyl _{TATA}
49	185	1427.7	1386.8	68.1		-		C-H bending Alkyl _{TATA}
	184	1421.3	1380.8	0.7				C-H bending Alkyl _{TATA}
	183	1418.2	1378.0	5.8				CH ₃ bending Alkyl _{TATA}
	182	1417.2	1377.1	2.7				CH ₃ bending Alkyl _{TATA}
	181	1416.4	1376.3	1.1				CH ₃ bending Alkyl _{TATA}
50	180	1402.4	1363.3	115.5	~1375	-		C-H bending Alkyl _{TATA}
51	179	1401.4	1362.4	119.8		-		C-H bending Alkyl _{TATA}
	178	1379.5	1342.1	0.3				C-H bending Alkyl _{TATA}
52	177	1371.9	1335.1	65.0	~1370	1380	⊥	C=C ring deformation, Ph _{top}
	176	1361.3	1325.2	1.1				C=C ring deformation,

								Ph _{TATA}
	175	1361.0	1325.0	1.3				C=C ring deformation, Ph _{TATA}
	174	1345.0	1310.2	0.3				C=C ring deformation, Ph _{TATA}
	173	1341.3	1306.7	4.9			/	C=C ring deformation, Ph _{bot}
53	172	1340.4	1305.8	22.2	~1295	-		C-H bending Alkyl _{TATA}
	171	1339.5	1305.0	4.5				C-H bending Alkyl _{TATA}
	170	1338.7	1304.3	16.6				C-H bending Alkyl _{TATA}
	169	1334.4	1300.3	1.3				C-H bending Alkyl _{TATA}
	168	1332.6	1298.7	0.5				C-H bending Alkyl _{TATA}
	167	1327.0	1293.5	0.3			/	C-H bending Alkyl _{TATA}
	166	1322.9	1289.7	6.5			⊥	C-H bending, Ph _{top}
	165	1317.8	1284.9	0.3				C-H bending, Ph _{bot}
	164	1305.2	1273.2	10.9			⊥	C=C ring deformation, Ph _{TATA}
54	163	1287.9	1257.2	645.3	~1245	1257	⊥	C-O stretching. C=C Ph _{top} . C-H bending CH ₃ Methoxy
	162	1286.7	1256.1	25.4				C-H twisting, Alkyl _{TATA}
	161	1285.8	1255.2	29.6				C-H twisting, Alkyl _{TATA}
	160	1281.2	1251.0	86.1			⊥	C-Alkine stretching
	159	1274.4	1244.7	17.7				C-H bending Ph _{TATA}
	158	1273.9	1244.2	12.9				C-H bending Ph _{TATA}
	157	1269.7	1240.3	2.9			/	C-H twisting, Alkyl _{TATA}
	156	1267.4	1238.2	11.0			⊥	C-N stretching, C-H bending Ph _{top} , Ph _{bot}
	155	1263.0	1234.1	209.2				C-H twisting, Alkyl _{TATA}

55	154	1262.6	1233.8	200.6	~1240	-		C-H twisting, Alkyl _{TATA}	
56	153	1219.0	1193.3	1.2		-	⊥	C-H bending Ph _{top} , Ph _{bot}	
	152	1215.8	1190.4	0.6			/	C-H bending Ph _{TATA}	
	151	1215.4	1190.0	1.0			/	C-H bending Ph _{TATA}	
	150	1211.3	1186.2	1.0			/	C-H bending Ph _{TATA}	
	149	1204.6	1180.0	13.5			/	C-H rocking, CH ₃ Methoxy	
57	148	1192.6	1168.8	23.4	~1165	-		C-H bending Ph _{TATA}	
	147	1192.2	1168.5	9.7					C-H bending Ph _{TATA}
	146	1192.1	1168.4	32.6					C-H bending Ph _{TATA}
58	145	1174.0	1151.6	175.2	~1160	1144	⊥	C-H bending, Ph _{top} , Ph _{bot}	
	144	1169.5	1147.4	0.8					C-H rocking CH ₃ Methoxy
	143	1167.3	1145.4	10.8					C-H rocking Alkyl _{TATA}
59	142	1166.4	1144.6	70.9	~1150	-		C-H rocking Alkyl _{TATA}	
60	141	1166.0	1144.2	65.8		-		C-H rocking Alkyl _{TATA}	
61	140	1163.4	1141.8	57.1	~1140	1144	/	C-H bending Ph _{top} , Ph _{bot}	
	139	1133.4	1114.0	0.2				/	ring deformation, Ph _{TATA}
62	138	1129.8	1110.7	18.5	~1100	1105	/	C-H bending Ph _{top} , Ph _{bot}	
	137	1125.2	1106.4	4.1				/	C-H bending Ph _{top} , Ph _{bot}
	136	1123.8	1105.1	6.1					ring deformation, Ph _{TATA}
	135	1123.3	1104.6	6.8				ring deformation, Ph _{TATA}	
	134	1121.6	1103.0	0.2				C-H rocking Alkyl _{TATA}	
	133	1118.8	1100.5	0.0				C-H rocking Alkyl _{TATA}	
	132	1118.5	1100.1	0.1				ring deformation, Ph _{TATA}	
	131	1094.0	1077.4	4.3			⊥	N-C stretching Alkyl _{TATA}	
63	130	1061.8	1047.6	86.8	~1130	1045	/	O-CH ₃ stretching Methoxy, ring	

								deformation Ph _{top}
	129	1043.2	1030.4	1.3			/	C-H bending, Ph _{TATA} , Alkyl _{TATA}
	128	1040.5	1027.9	0.1				C-C stretching Alkyl _{TATA}
	127	1039.2	1026.7	0.1				C-C stretching Alkyl _{TATA}
	126	1036.2	1023.8	0.0				C-C stretching Alkyl _{TATA}
	125	1026.3	1014.7	15.4			⊥	ring deformation, Ph _{bot}
	124	1017.4	1006.4	1.8			/	ring deformation, Ph _{top}
64	123	1011.4	1000.8	33.9	~998	998	⊥	C _{tertTATA} -Alkine stretching
	122	993.2	984.1	0.2				C-H twisting Ph _{bot}
	121	984.0	975.5	0.1				C-H twisting Ph _{top}
	120	979.8	971.6	0.4				C-H twisting Ph _{bot}
	119	965.5	958.3	0.8			/	C-H twisting Ph _{TATA}
	118	964.5	957.4	0.8				C-H twisting Ph _{TATA}
	117	962.8	955.8	0.6			⊥	C-H twisting Ph _{TATA}
	116	916.8	913.2	0.2			/	C-H twisting Ph _{TATA}
	115	960.9	954.1	0.2			/	C-H twisting Ph _{TATA}
	114	955.5	949.0	1.3				C-H twisting Ph _{top}

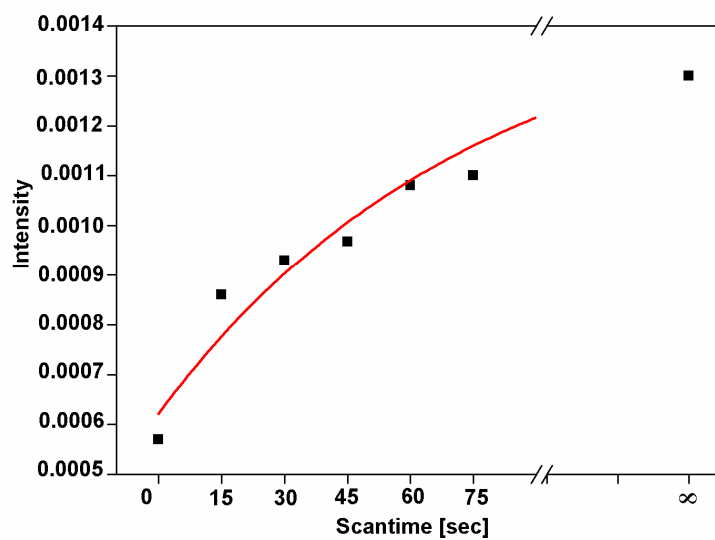


Figure S2. Intensity of the C(phenyl)-O stretch as a function of time and exponential function resulting from the fit of Figure 11 (main paper).