Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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

Hanne Jacob[a], *Sandra Ulrich*[b], *Ulrich Jung*[c], *Sonja Kuhn*[c], *Talina Rusch*[c], *Christian Schütt*[b], *Finn Petersen*[a], *Thomas Strunskus*[d], *Olaf Magnussen*[c], *Rainer Herges**[b] *and Felix Tuczek**[a]

[a]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Max-Eyth-Str.2, 24118 Kiel, Germany

[b]Institut für Organische Chemie, Christian-Albrechts-Universität Kiel, Otto-Hahn-Platz 4 24098 Kiel, Germany

[c]Institut für Experimentelle und Angewandte Physik der Christian-Albrechts-Universität Kiel, Leibnizstraße 11-19, 24118 Kiel, Germany

[d]Technische Fakultät der Christian-Albrechts-Universität Kiel, Kaiserstraße 2, 24143 Kiel, Germany

Corresponding authors:

RH: Email: rherges@ac.uni-kiel.de

FT: E-Mail: ftuczek@ac.uni-kiel.de, fax: +49 431 880-1523

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

XYZ file

90

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

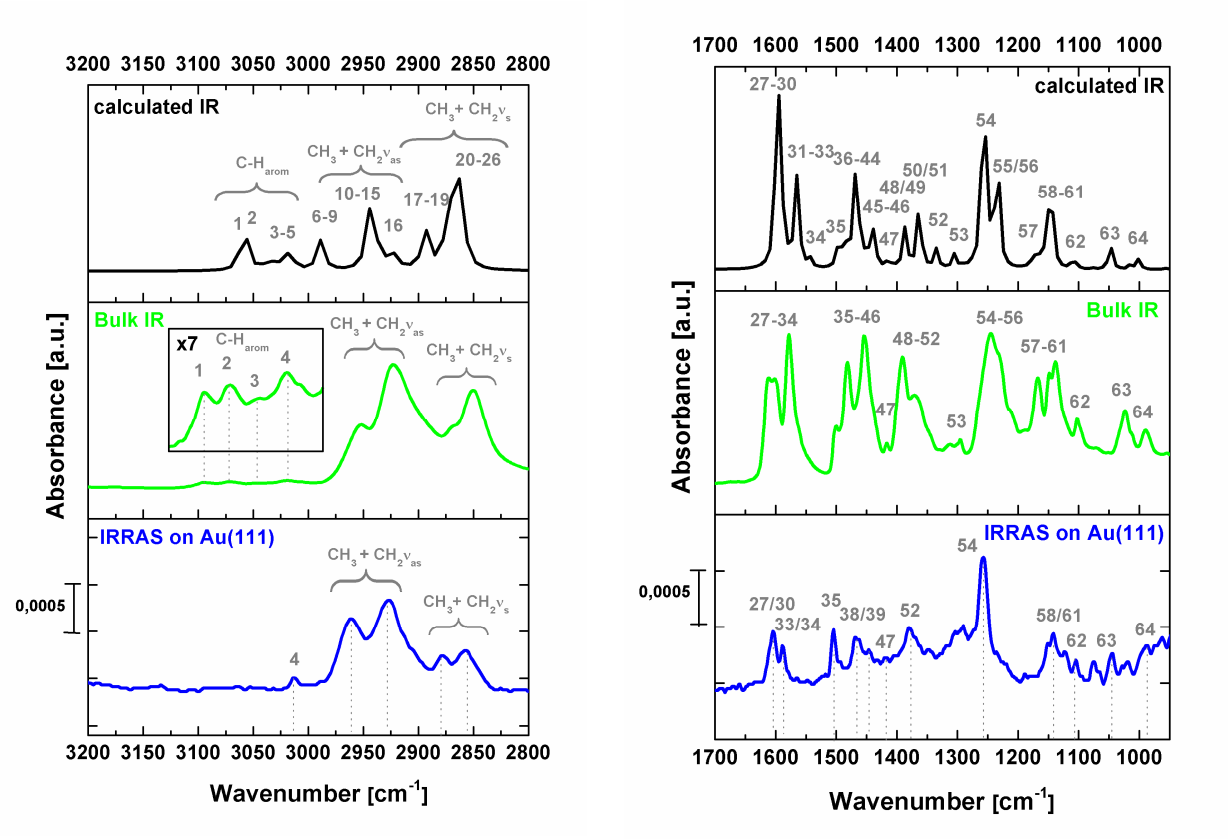

Figure S1. IR data of methoxy-azo-TATA. Left: CH-stretching vibration region, right: fingerprint region. The spectra in the top panels show the calculated, the spectra in the middle the bulk and the blue spectra at the bottom the IRRAS data of the surface-adsorbed monolayer. Band numbers correspond to 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: ⊥, 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			||	C-H stretching Ph_{TATA}
	262	3233.5	3060.8	15.5			||	C-H stretching Ph_{TATA}
	261	3229.8	3057.4	19.8			||	C-H stretching Ph_{TATA}
	260	3229.7	3057.2	8.7			||	C-H stretching Ph_{TATA}
	259	3228.9	3056.5	12.1			⊥	C-H stretching Ph_{top}
1	258	3228.1	3055.7	10.2	$C\text{-}H_{arom}$	-	/	C-H stretching Ph_{top}
2	257	3227.8	3055.5	13.0	$C\text{-}H_{arom}$	-	||	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			⊥	C-H stretching Ph_{bot}
3	250	3186.0	3016.7	13.8	$C\text{-}H_{arom}$	3014	/	C-H stretching Ph_{TATA}
4	249	3185.7	3016.5	16.5	$C\text{-}H_{arom}$		/	C-H stretching Ph_{TATA}
5	248	3185.4	3016.2	17.1	$C\text{-}H_{arom}$	-	/	C-H stretching Ph_{TATA}

6	247	3156.9	2989.7	16.7	CH_2 ν_{as}	-	∥	C-H stretching $Alkyl_{TATA}$
7	246	3156.4	2989.3	25.8	CH_3 ν_{as}	CH_3 ν_{as}	⊥	C-H stretching CH_3-methoxy
8	245	3155.9	2988.8	15.2	CH_2 ν_{as}	CH_2 ν_{as}	/	C-H stretching $Alkyl_{TATA}$
9	244	3154.4	2987.4	15.1	CH_2 ν_{as}	-	∥	C-H stretching $Alkyl_{TATA}$
10	243	3108.8	2945.2	29.6	CH_3 ν_{as}	CH_3 ν_{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 ν_{as}	CH_2 ν_{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 ν_{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 ν_s	CH_2 ν_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 ν_s	-	∥	C-H stretching CH_3-$Alkyl_{TATA}$
21	229	3030.3	2872.4	53.3	CH_3 ν_s	-	∥	C-H stretching CH_3-$Alkyl_{TATA}$
22	228	3030.1	2872.2	68.5	CH_3 ν_s	-	∥	C-H stretching CH_3-$Alkyl_{TATA}$
23	227	3021.6	2864.3	97.0	CH_3 ν_s	CH_3 ν_s	/	C-H stretching CH_3-methoxy
24	226	3019.4	2862.3	45.5	CH_2 ν_s	CH_2 ν_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			⊥	Alkine 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}

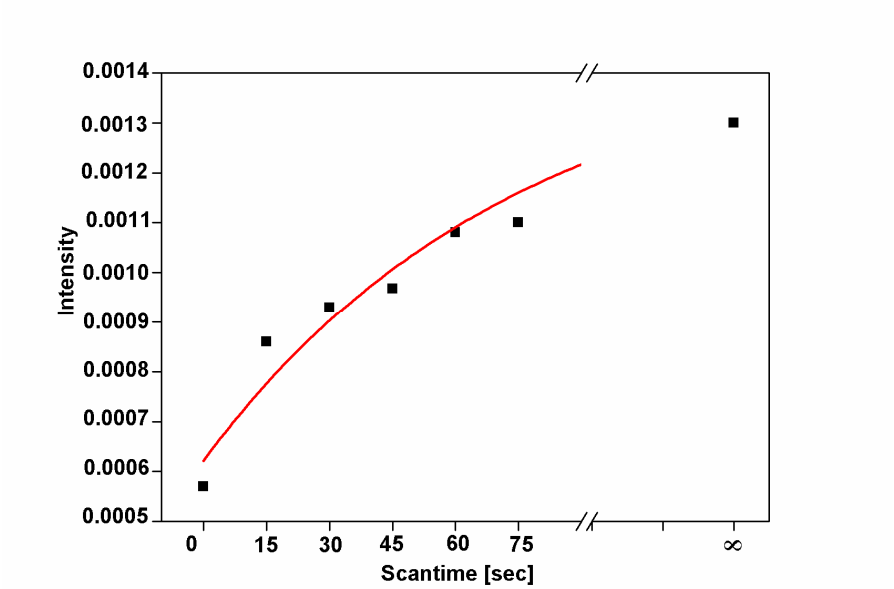

Figure S2. Intensity of the C(phenyl)-O stretch as a function of time and exponential function resulting from the fit of Figure 11 (main paper).