JOC The Journal of Organic Chemistry

Brief Communication

pubs.acs.org/joc

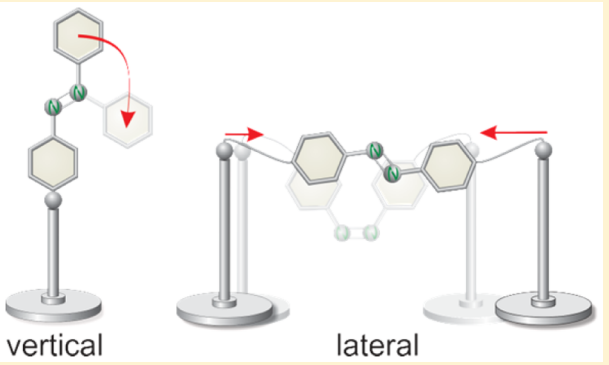
Laterally Mounted Azobenzenes on Platforms

Melanie Hammerich and Rainer Herges*

Otto Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, Kiel D-24119, Germany

Supporting Information

ABSTRACT: Triazatriangulenium ions have previously been used as platforms to prepare self-assembled monolayers of functional molecules such as azobenzenes with vertical orientation and that are free-standing on gold surfaces. We have now prepared azobenzenes that are spanned between two posts which are attached on two platforms. Absorbed on a gold surface, the azobenzene should be laterally oriented at a distance of more than 4 Å above and thus electronically decoupled from the surface, and the system should perform a muscle-type movement upon isomerization.



Photoactive molecules such as photochromic compounds or fluorescent dyes with their chromophores directly absorbed to a metal surface usually become photochemically inactive because their excited states are quenched by the metal.[1] A number of strategies have been used to attach functional molecules such as azobenzenes to metal surfaces using spacer groups which prevent direct contact and thus reduce electronic coupling to the surface.[2,3] Probably the most widely used method toward this end are alkanethiol spacer groups.[4−6] The sulfur attaches to the gold and in a densely packed monolayer the alkane chains prevent the chromophore on top from coupling with the surface underneath. Usually, self-assembled monolayers are formed by just dipping the gold surface into a dilute solution of the absorbate.[7] However, the free volumes in the densely packed monolayers often are not sufficient for a sterically demanding reaction (e.g., *cis*−*trans* isomerization of azobenzene),[8] and highly ordered monolayers are difficult to prepare because of the large degree of conformational freedom of the alkane chains.[9] A very successful strategy to enforce a defined (lateral) distance between the functional units and a vertical distance to the surface is the platform approach. Particularly suitable as molecular platforms are triazatriangulenium (TATA) ions.[10,11] The large π system has a high affinity to atomically flat gold surfaces. Even though the interaction with the Au(111) surface is almost exclusively dispersive, the binding energies of TATA platforms are similar to the affinity of thiols which attach via covalent bonds.[11] Dilute solutions of TATA form almost perfectly ordered monolayers on Au(111).[12,13] The size of the platform and thus the distance of the platforms to their next neighbors on the surface can be controlled by the size of the substituents at the nitrogen atoms.[14] The central carbon atom which formally bears the positive charge reacts with a number of carbanions that thus are covalently attached perpendicular to the plane of the platform. Ethynyl and phenyl groups are suitable spacers on top of which functional groups such as azobenzenes are attached.[15] The rigid, upright, and free-standing azobenzenes exhibit the same efficiency (extinction and quantum yield) in photochemical *cis*−*trans* isomerizations as the free azobenzenes in solution.[16] Whereas several strategies for a vertical attachment of functional molecules on surfaces have been developed,[17] very few approaches for a lateral orientation above the surface (without direct contact) have been published.[18−20] Our platform approach which has been successful for vertical mounting is particularly suitable for lateral mounting as well. We have designed and synthesized a compound which is able to span an azobenzene between two platforms and hold it above the surface. According to DFT calculations, the platforms slide over the surface with almost no barrier.[21] Upon alternating irradiation with UV and visible light, the azobenzene reversibly isomerizes (*cis trans* isomerization), and consequently, the distance between the platforms should contract and expand in a muscle-type movement.

According to PM3 model calculations, the structure shown in Figure 1 is a good candidate for the realization of the anticipated function. The *trans* isomer **1** ***trans*** exhibits a distance of 18.9 Å between the two centers of the TATA platforms. By switching the azobenzene to the *cis* isomer **1** ***cis*** the distance of the two platforms is reduced to 15.6 Å. To avoid strain, particularly in the cis form, the azobenzene unit is attached to the posts (phenylethynyl units) via flexible $-OCH_2-$ linkers.

For the sake of simplicity, the calculations have been performed without substitution at the angular nitrogen atoms. However, alkyl chains such as *n*-propyl and *n*-octyl are needed for the synthesis. For obvious reasons, the platforms should be

Received: September 28, 2015
Published: November 9, 2015

DOI: 10.1021/acs.joc.5b02262
J. Org. Chem. 2015, 80, 11233−11236

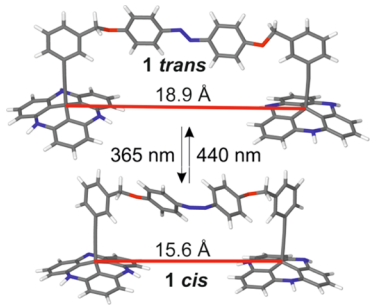
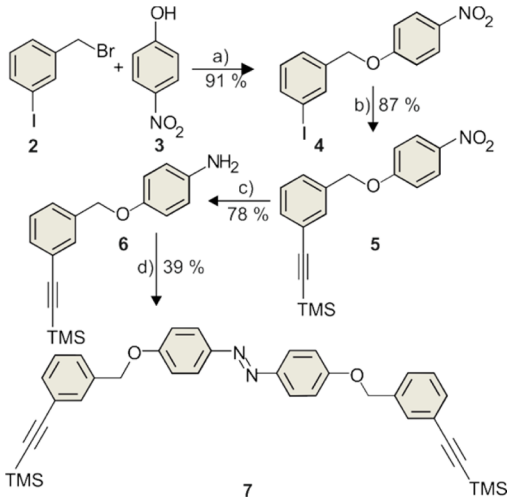


Figure 1. PM3-calculated geometries (fully optimized with the constraint that all angular nitrogen atoms are held in a plane) (top: *trans*, bottom: *cis*) of the "molecular muscle". By switching between the azobenzene isomers **1** ***trans*/*cis*** the distance between the platforms changes by about 3.3 Å (18.9 Å *trans* to 15.6 Å *cis*).

small enough not to hinder the contraction movement upon *trans* to *cis* isomerization. According to previous studies, the intermolecular spacing of the *n*-propyl-substituted platform in self-assembled monolayers is 11.0 ± 0.5 Å, and *n*-octyl TATA exhibits a spacing of 13.0 ± 0.5 Å.[10,14] Therefore, both platforms are sufficiently small to allow the muscle-type contraction on a gold surface.

The preparation of azobenzene **7** was achieved in a four-step synthesis (Scheme 1). *p*-Nitrophenol (**3**) reacts with benzyl

Scheme 1. Synthesis of the Azobenzene Unit[a]



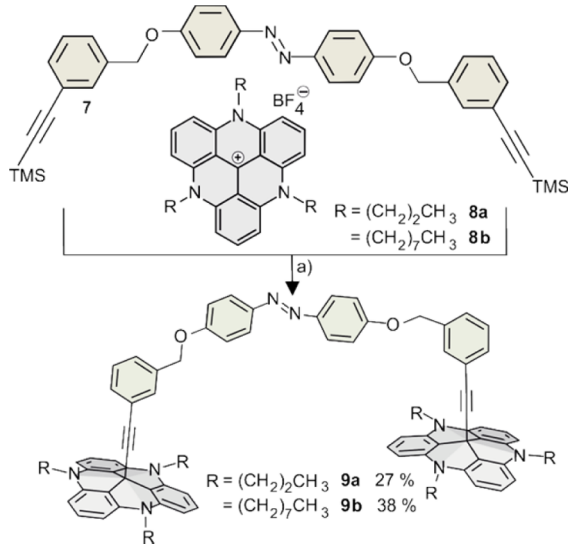
[a]Reagents and conditions: (a) K_2CO_3, acetone, 15 h, reflux; (b) TMSA, NEt_3, Cu(I)I, $Pd(PPh_3)Cl_2$ 40 °C 4 h, then rt 15 h ; (c) $SnCl_2$, EtOH, AcOH, 4 h, 80 °C; (d) Cu(I)Cl, pyridine, O_2, 18 h, rt.

bromide **2** forming ether **4** (91%). Sonogashira coupling with trimethylsilylacetylene gives compound **5** (87%). The standard reductive azobenzene coupling with zinc and barium hydroxide in ethanol was not successful.[22] Therefore, the nitro group was reduced with tin(II) chloride in ethanol yielding the corresponding amine **6** (78%). The oxidative azobenzene coupling was accomplished in pyridine with copper(I)chloride and air leading to the azobenzene linker **7** (39%).

The triazatriangulenium (TATA) platforms (**8a**/**b**) were synthesized according to a procedure from Laursen and Krebs in a three-step synthesis.[23]

Functionalization of the two TATA platforms (Scheme 2) was achieved by deprotection of the terminal silyl-protected

Scheme 2. Synthesis of the Molecular Muscle[a]



[a]Reagents and conditions: (a) KOH, THF, 16 h.

alkyne groups of the azobenzene unit with potassium hydroxide and in situ reaction with the cationic center of the platform to form the molecular muscles **9a**/**b** (**9a**, 27%; **9b**, 38%), which are indefinitely stable in toluene in the dark and as pure solids but instable in halogenated and acidic solvents.

The photophysical properties and particularly the switching behavior of compounds **9a**/**b** were determined in solution. UV/vis spectra and the photostationary states were measured upon irradiation at 365 and 440 nm (Figure 2).

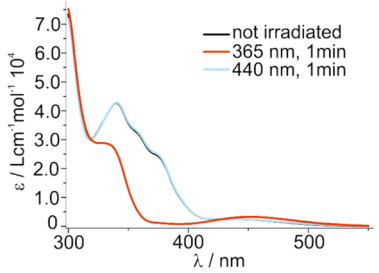


Figure 2. UV−vis spectrum of **9b** (29.1 μmol/L in toluene): black curve, pure *trans* isomer; red curve, photostationary equilibrium at 365 nm (~95% *cis*); blue curve, photostationary equilibrium at 440 nm.

Both substances show a strong ππ* band that decreases and shifts to shorter wavelengths upon irradiation with 365 nm, whereas the intensity of the nπ* band increases. This is in agreement with the UV spectra of typical azobenzenes.[24] After irradiation at 440 nm the solution exhibits the spectrum of the pure *trans* isomer.

Photostationary states were determined after irradiation in deuterated toluene with light of the wavelengths of 365 nm (*cis*) and 470 nm (*trans*) for 10 min. The *cis*/*trans* ratios were measured by ^{1}H NMR. Half-lives of the thermal back-isomerizations were determined by ^{1}H NMR measurements (Table 1).

In summary, we present the synthesis of a muscle-type molecule. An azobenzene unit is attached to molecular platforms at both *para* positions. According to previous studies, the platforms should absorb to Au(111) surfaces and therefore

DOI: 10.1021/acs.joc.5b02262
J. Org. Chem. 2015, 80, 11233−11236

Table 1. Photostationary States (PSS) of Azobenzenes in Toluene upon Irradiation with 365 nm (*Cis*) and 470 nm (*Trans*) Determined with ^{1}H NMR Spectroscopy (Toluene, 2 mmol/L)

	PSS at 365 nm (% *cis*)	PSS at 470 nm (% *trans*)	$t_{1/2}$ (h) (300 K)
9a	95	72	23.8
9b	95	76	21.4

should span the azobenzene at a distance of 4 Å above the surface. Photophysical experiments in solution exhibit a high switching efficiency and low fatigue of the photochromic system.

EXPERIMENTAL SECTION

General Experimental Methods. Acetone was dried and distilled from phosphorous pentoxide. Triethylamine was dried and distilled from calcium hydride, and tetrahydrofuran was dried and distilled from sodium/benzophenone. All compounds were characterized using ^{1}H and ^{13}C NMR spectroscopy. The signals were assigned using 2D spectroscopy. For ^{1}H and ^{13}C NMR assignment we performed HSQC and HMBC.

1-[(3-Iodophenyl)methoxy]-4-nitrobenzene (4). Potassium carbonate (3.77 g, 27.3 mmol) was added to a solution of 4-nitrophenol (**3**, 0.8 g, 5.75 mmol) in 25 mL of acetone under nitrogen atmosphere and stirred for 1 h at room temperature. 3-Iodobenzyl bromide (**2**, 1.76 g, 5.46 mmol) was added to the suspension and heated to 60 °C for 15 h. The solid was removed and the solvent evaporated. The solid was dissolved in ethyl acetate and washed with water and brine. The solution was dried over magnesium sulfate and evaporated. The crude product was recrystallized from cyclohexane to obtain colorless crystals (1.86 g, 5.24 mmol, 91%). Mp: 99 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 8.21 (d, ^3J = 9.3 Hz, 2 H), 7.79 (s, 1 H), 7.70 (d, ^3J = 7.8 Hz, 1 H), 7.38 (d, ^3J = 7.8 Hz, 1 H), 7.14 (t, ^3J = 7.8 Hz, 1 H), 7.02 (d, ^3J = 9.3 Hz, 1 H), 5.09 (s, 2 H) ppm. ^{13}C NMR (125.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 163.3, 141.9, 137.8, 137.5, 136.3, 130.5, 126.5, 126.0, 114.8, 94.6, 69.6 ppm. MS (EI, 70 eV): *m*/*z* 354 (11), 216 (100), 125 (11) IR: $\tilde{\nu}$ = 3120 (m), 3066 (m), 1609 (m), 1592 (s), 1565 (m), 1502 (s), 1328 (m), 1258 (m), 1173 (s), 1090 (s), 1063 (w), 844 (s), 769 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{10}INO_3$ (355.13): C, 43.97; H, 2.84; N, 3.94. Found: C, 44.12; H, 2.92; N, 4.11. UV (CH_2Cl_2): λ_{max} (log ε) 238 (4.14), 307 (4.15) nm.

1-[[3-(Trimethylsilylethynyl)phenyl]methoxy]-4-nitrobenzene (5). Under a nitrogen atmosphere, a suspension of 1-[(3-iodphenyl)methoxy]-4-nitrobenzene (**4**, 1.85 g, 5.21 mmol), bis-(triphenylphosphine)palladium(II) chloride (73.0 mg, 10 $^{-4}$ mol), copper iodide (9.9 mg, 0.520 μmol), and TMSA (0.9 mL, 6 mmol) in 20 mL of triethylamine was heated to 40 °C for 4 h and was stirred for another 15 h at room temperature. The solution was diluted with 40 mL of dichloromethane, washed with water, extracted with dichloromethane, and washed with brine. The solution was dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography (ethyl acetate/cyclohexane 1:4) to obtain a brown-orange solid (1.43 g, 4.39 mmol, 87%). Mp: 58 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 8.20 (d, ^{3}J = 9.3 Hz, 2 H), 7.53 (s, 1 H), 7.45 (d, ^3J = 6.9 Hz, 1 H), 7.33−7.37 (m, 2 H), 7.01 (d, ^3J = 9.3 Hz, 1 H), 5.12 (s, 2 H), 0.26 (s, 9 H) ppm. ^{13}C NMR (125.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 163.5, 141.8, 135.7, 132.0, 130.8, 128.7, 127.4, 126.0, 123.8, 114.9, 104.4, 95.0, 70.1, 0.1 ppm. MS (EI, 70 eV): *m*/*z* 325 (5), 231 (13), 187 (100). IR: $\tilde{\nu}$ 3085 (w), 2955 (m), 2154 (m), 1607 (m), 1510 (s), 1337 (s), 1242 (m), 1175 (m), 1111 (m), 996 (m), 836 (s), 796 (s), 751 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_3Si$ (325.43): C, 66.43; H, 5.88; N, 4.30. Found: C, 66.41; H, 6.08; N, 4.28. UV (CH_2Cl_2): λ_{max} (log ε) 249 (4.30), 260 (4.27), 308 (4.14) nm.

4-(3-Trimethylsilylethynylbenzyloxy)phenylamine (6).[25] Tin(II) chloride dihydrate (6.43 g, 28.3 mmol) was added to a solution of 1-[(3-(trimethylsilylethynyl)phenyl)methoxy]-4-nitrobenzene (**5**, 0.930 g, 2.83 mmol) in 5 mL of acetic acid and 35 mL of ethanol and heated to 80 °C for 4 h. The solution was poured onto iced water, and potassium hydroxide (30.8 g, 0.549 mol) was added. The two phases were separated and extracted with dichloromethane. The solution was dried over magnesium sulfate and evaporated to obtain an orange-brown oil. The crude product was purified by column chromatography (dichloromethane) to obtain a brown solid that was dissolved in diethyl ether and precipitated with pentane to obtain a colorless solid (0.66 g, 2.23 mmol, 78%). Mp: 58 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 7.53 (s, 1 H), 7.40 (d, ^3J = 7.6 Hz, 1 H), 7.36 (d, ^3J = 7.6 Hz, 1 H), 7.29 (t, ^3J = 7.6 Hz, 1 H), 6.79 (d, ^3J = 9.3 Hz, 2 H), 6.64 (d, ^3J = 9.3 Hz, 2 H), 4.94 (s, 2 H,), 3.24 (s, br, 2 H), 0.26 (s, 9 H) ppm. ^{13}C NMR (125.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 151.9, 140.2, 137.8, 131.3, 130.8, 128.4, 127.5, 123.4, 116.4, 116.1, 104.9, 94.4, 70.3, −0.0 ppm. MS (EI, 70 eV): *m*/*z* 295 (24), 187 (21), 172 (12), 108 (100) IR: $\tilde{\nu}$ 3360 (w), 3040 (w), 2958 (w), 2152 (w), 1605 (m), 1508 (s), 1429 (w), 1376 (w), 1248 (m), 1227 (s), 1121 (m), 916 (m), 839 (s), 758 (s), 690 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{21}NOSi$ (295.45): C, 73.17; H, 7.16; N, 4.74. Found: C, 73.34; H, 7.10; N, 4.90. UV (CH_2Cl_2): λ_{max} (log ε) 248 (4.47), 259 (4.34), 305 (3.41) nm.

1,2-Bis[4-[(3-trimethylsilylbenzyloxy)phenyl]]diazene (7). Copper(I) chloride (156 mg, 1.58 mmol) was suspended in pyridine, stirred for 15 min at room temperature, and filtrated. 4-(3-Trimethylsilylethynylbenzyloxy)phenylamine (**6**, 0.584 g, 1.98 mmol) was dissolved in pyridine, and the Cu(I)/pyridine solution was added. Air was sparged through the solution for 18 h. The residue was dissolved in 50 mL of 1 M hydrochloric acid and extracted with dichloromethane, washed with water, and dried over magnesium sulfate. The solution was evaporated, and the residue was purified by column chromatography (dichloromethane) to obtain an orange solid (0.227 g, 3.87 × 10 $^{-4}$ mol, 39%). Mp: 164 °C. ^{1}H NMR (500.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 7.87 (d, ^3J = 9.0 Hz, 2 H, H-10), 7.57 (s, 1 H, H-6), 7.44 (d, ^3J = 7.6 Hz, 1 H, H-2), 7.40 (d, ^3J = 7.6 Hz, 1 H, H 4), 7.33 (t, ^3J = 7.6 Hz, 1 H, H-3), 7.09 (d, ^3J = 9.3 Hz, 2 H, H-9), 5.10 (s, 2 H, H-7), 0.26 (s, 9 H, H-14) ppm. ^{13}C NMR (125.1 MHz, $CDCl_3$, 300 K, $CHCl_3$): δ 160.6, 147.3, 136.8, 131.7, 130.9, 128.6, 127.5, 124.4, 123.6, 115.1, 104.7, 94.7, 69.7, −0.0 ppm. MS (EI, 70 eV): *m*/*z* 586 (14), 187 (100), 172 (23), 108 (14). IR: $\tilde{\nu}$ 2958 (m), 2898 (m), 2145 (m), 1602 (m), 1581 (m), 1496 (m), 1455 (m), 1241 (s), 1146 (s), 1104 (m), 1052 (m), 922 (m), 837 (m), 785 (m), 754 (m), 687 (m), 645 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{38}N_2O_2Si_2$ (586.87): C, 73.68; H, 6.53; N, 4.77. Found: C, 73.73; H, 6.49; N, 4.82. UV (toluene): λ_{max} (log ε) 358 (4.48) nm.

1,2-Bis[4-[[3-(4,8,12-tris-*n*-propyl-4,8,12-triazatriangulaniumbenzyloxy)-12c-ethynyl]phenyl]]diazene (9a). A suspension of 1,2-bis[4-[(3-trimethylsilylbenzyloxy)pheny]]diazene (**7**) (150 mg, 2.56 μmol), *n*-propyl-TATA (**8a**) (508 mg, 1.02 mmol), and potassium hydroxide (362 mg, 6.95 mmol) in 50 mL of THF was refluxed for 17 h under nitrogen atmosphere. The solution was poured onto water, extracted with diethyl ether, and dried over magnesium sulfate. The solution was evaporated and purified by column chromatography (bas. Alox, ethyl acetate) to obtain an orange solid (87 mg, 16.9 × 10^{-5} mol, 27%). Mp: 163 °C. ^{1}H NMR (600.1 MHz, C_6D_6, 300 K, benzene): δ 8.03 (d, ^3J = 8.9 Hz, Ar-*H*, 4 H), 7.18 (t, ^3J = 8.2 Hz, Ar-*H*, 6 H), 6.95 (s, Ar-*H*, 6 H), 6.92 (d, ^3J = 7.8 Hz, Ar-*H*, 2 H), 6.87 (d, ^3J = 7.8 Hz, Ar-*H*, 6.65−6.69 (m, Ar-*H*, 6 H), 6.53 (d, ^3J = 8.2 Hz, Ar-*H*, 12 H), 4.24 (s, OCH_2, 4 H), 3.68 (t, ^3J = 7.9 Hz, NCH_2, 12 H); 1.73 (sext., ^3J = 7.7 Hz, CH_2, 12 H), 0.79 (t, ^3J = 7.4 Hz, CH_3,.18 H) ppm. ^{13}C NMR (150.9 MHz, C_6D_6, 300 K, benzene): δ 160.9, 147.7, 141.0, 136.4, 131.2, 130.9, 128.5, 126.3, 124.7, 124.3, 115.2, 110.9, 105.5, 94.7, 83.9, 69.4, 48.1, 30.1, 28.8, 19.2, 11.0 ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 1257. MS (ESI): *m*/*z* = 1257, 408, 365, 280. IR: $\tilde{\nu}$ 3025 (m), 2957 (m), 2921 (m), 2851 (m), 2341 (m), 1735 (w), 1614 (s), 1578 (s), 1483 (s), 1455 (s), 1396 (s), 1230 (s), 1145 (s), 1029 (m), 917 (m), 750 (s), 695 (m) cm^{-1}. Anal. Calcd for $C_{86}H_{80}N_8O_2$ (1257.61): C, 82.13; H, 6.41; N, 8.91. Found: C, 81.86; H, 6.48; N, 8.77. UV (toluene): λ_{max} (log ε) 290 (4.85), 340 (4.59) nm.

DOI: 10.1021/acs.joc.5b02262
J. Org. Chem. 2015, 80, 11233−11236

1,2-Bis[4-[[3-(4,8,12-tris-*n*-octyl-4,8,12-triazatriangulenium-benzyloxy)-12c-ethynyl]phenyl]]diazene (9b). A suspension of 1,2-bis[4-[(3-trimethylsilylbenzyloxy)pheny]]diazene (**7**) (50 mg, 8.52 × 10^{-5} mol), *n*-octyl-TATA (**8b**) (132 mg, 1.87 × 10^{-4} mol), and potassium hydroxide (129 mg, 2.30 mmol) in 50 mL of THF was refluxed for 17 h under nitrogen atmosphere. The solution was poured onto water, extracted with diethyl ether, and dried over magnesium sulfate. The residue was filtrated over Florisil (diethyl ether). The crude product was recrystallized from acetone to obtain an orange solid (54.9 mg, 3.27 × 10^{-5} mol, 38%). Mp: 126 °C. ^{1}H NMR (600.1 MHz, C_6D_6, 300 K, benzene): δ8.04 (d, ^3J = 8.9 Hz, Ar-*H*, 4 H), 7.25 (t, ^3J = 8.2 Hz, Ar-*H*, 6 H), 6.99 (s, Ar-*H*, 2 H), 6.97 (d, ^3J = 7.8 Hz, Ar-*H*, 2 H), 6.91 (d, ^3J = 7.6 Hz, Ar-*H*, 2 H), 6.70−6.73 (m, Ar-*H*, 6 H), 6.64 (d, ^3J = 8.2 Hz, Ar-*H*, 12 H), 4.28 (s, NCH_2, 4 H), 3.80 (t, ^3J = 7.8 Hz, CH_2, 12 H), 1.80 (quint, ^3J = 7.4 Hz, CH_2, 12 H), 1.25 (quint, ^3J = 6.5 Hz, CH_2, 12 H), 1.17−1.21 (m, CH_2, 36 H), 0.90 (t, ^3J = 7.20 Hz, CH_3, 18 H) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$, 300 K, TMS): δ 161.1, 147.8, 141.2, 136.6, 131.6, 131.2, 128.7, 128.4, 126.5, 124.8, 124.4, 115.3, 111.1, 105.7, 94.8, 84.2, 69.2, 46.7, 32.2, 30.2, 29.7, 29.0, 27.2, 26.2, 23.1, 14.4 ppm. MS (MALDI-TOF, Cl-CCA): *m*/*z* 1678 $[M]^+$. IR: $\tilde{\nu}$ 2922 (m), 2853 (m), 1615 (s), 1579 (s), 1483 (s), 1457 (s), 1396 (s), 1236 (s), 1168 (m), 1145 (m), 1010 (w), 912 (w), 772 (m), 750 (s), 690 (m) cm^{-1}. Anal. Calcd for $C_{116}H_{140}N_8O_2$ (1678.41): C, 83.01; H, 8.41; N, 6.68. Found: C, 82.91; H, 8.37; N, 6.52. UV (toluene): λ_{max} (log ε) 340 (4.58) nm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02262.

^{1}H NMR, ^{13}C NMR, and UV/vis spectra for compounds **4**−**7** and **9a**,**b** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rherges@oc.uni-kiel.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the Deutsche Forschungsgesellschaft (DFG) via the collaborative research center SFB 677, "Function by Switching".

■ REFERENCES

(1) Tegeder, P. *J. Phys.: Condens. Matter* **2012**, *24*, 394001.
(2) Pace, G.; Ferri, V.; Grave, C.; Elbing, M.; von Hänisch, C.; Zharnikov, M.; Mayor, M.; Rampi, M. A.; Samorì, P. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 9937−9942.
(3) Bléger, D.; Ciesielski, A.; Samoì, P.; Hecht, S. *Chem. - Eur. J.* **2010**, *16*, 14256−14260.
(4) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1170.
(5) Evans, S. D.; Johnson, S. R.; Ringsdorf, H.; Williams, L. M.; Wolf, H. *Langmuir* **1998**, *14*, 6436−6440.
(6) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421−432.
(7) Tamada, K.; Akiyama, H.; Wei, T. X. *Langmuir* **2002**, *18*, 5239−5246.
(8) Valley, D. T.; Onstott, M.; Malyk, S.; Benderskii, A. V. *Langmuir* **2013**, *29*, 11623−11631.
(9) Jung, U.; Filinova, O.; Kuhn, S.; Zargarani, D.; Bornholdt, C.; Herges, R.; Magnussen, O. *Langmuir* **2010**, *26*, 13913−13923.
(10) Baisch, B.; Raffa, D.; Jung, U.; Magnussen, O. M.; Nicolas, C.; Lacour, J.; Kubitschke, J.; Herges, R. *J. Am. Chem. Soc.* **2009**, *131*, 442−443.
(11) Otte, F. L.; Lemke, S.; Schütt, C.; Krekiehn, N. R.; Jung, U.; Magnussen, O. M.; Herges, R. *J. Am. Chem. Soc.* **2014**, *136*, 11248−11251.
(12) Jung, U.; Kuhn, S.; Cornelissen, U.; Tuczek, F.; Strunskus, T.; Zaporojtchenko, V.; Kubitschke, J.; Herges, R.; Magnussen, O. *Langmuir* **2011**, *27*, 5899−5908 PMID: 21506548.
(13) Ulrich, S.; Jung, U.; Strunskus, T.; Schütt, C.; Bloedorn, A.; Lemke, S.; Ludwig, E.; Kipp, L.; Faupel, F.; Magnussen, O.; Herges, R. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17053−17062.
(14) Lemke, S.; Ulrich, S.; Claußen, F.; Bloedorn, A.; Jung, U.; Herges, R.; Magnussen, O. M. *Surf. Sci.* **2015**, *632*, 71−76.
(15) Kubitschke, J.; Näther, C.; Herges, R. *Eur. J. Org. Chem.* **2010**, *2010*, 5041−5055.
(16) Jung, U.; Schütt, C.; Filinova, O.; Kubitschke, J.; Herges, R.; Magnussen, O. *J. Phys. Chem. C* **2012**, *116*, 25943−25948.
(17) Klajn, R. *Pure Appl. Chem.* **2010**, *82*, 2247−2279.
(18) Alemani, M.; Peters, M. V.; Hecht, S.; Rieder, K.-H.; Moresco, F.; Grill, L. *J. Am. Chem. Soc.* **2006**, *128*, 14446−14447.
(19) Zheng, X.; Mulcahy, M. E.; Horinek, D.; Galeotti, F.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **2004**, *126*, 4540−4542.
(20) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; et al. *J. Am. Chem. Soc.* **2005**, *127*, 9745−9759.
(21) Hauptmann, N.; Scheil, K.; Gopakumar, T. G.; Otte, F. L.; Schütt, C.; Herges, R.; Berndt, R. *J. Am. Chem. Soc.* **2013**, *135*, 8814−8817.
(22) Shine, H. J.; Chamness, J. T. *J. Org. Chem.* **1963**, *28*, 1232−1236.
(23) Laursen, B. W.; Krebs, F. C. *Chem. - Eur. J.* **2001**, *7*, 1773−1783.
(24) Rau, H. In *Photochemistry and Photophysics*; Rebeck, J. F., Ed.; CRC Press: Boca Raton, 1990; Vol. 2.
(25) Schmittel, M.; Saha, M. L.; Fan, J. *Org. Lett.* **2011**, *13*, 3916−3919.

DOI: 10.1021/acs.joc.5b02262
J. Org. Chem. 2015, 80, 11233−11236