Electronic Supplementary Material (ESI) for Chemical Communications

Immobilisation of Photoswitchable Diarylcyclohexenes Synthesised via Cobalt-Mediated Diels-Alder Reaction

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Supporting Information

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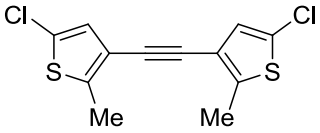
General experimental conditions

The following compounds were prepared according to literature methods: 1,2-bis(2-methyl-5-phenylthiophene-3-yl)ethyne,[1] 3-((2,5-dimethylthiophen-3-yl)ethynyl)-2-methyl-5-phenyl-thiophene,[1] and 4,4,5,5-tetramethyl-2-(2-methylenebut-3-en-1-yl)-1,3,2-dioxaborolane.[2] All other reagents were obtained from commercial sources and used without further purification. IR spectra were obtained using an IFS 200 Interferometer or an Alpha-P FT-IR-spectrometer both manufactured by Bruker Physics. ^{1}H NMR spectra were recorded either on an AV-300 (300 MHz) or DRX-500 (500 MHz) both manufactured by Bruker Physics. ^{13}C NMR spectra were recorded on either an AV-300 (75 MHz) or a DRX-500 (125 MHz) both manufactured by Bruker Physics. The NMR spectra were recorded in $CDCl_3$ or MeOD as solvent and chemical shifts are reported in ppm. High-resolution mass spectra (HRMS) were recorded as electron ionisation spectra (EI/HRMS, 70 eV) on a Finnigan MAT 95S Mass Spectrometer or as electron spray ionisation (ESI/HRMS) on a Micromass VG AutoSpec Mass Spectrometer. The detected ion masses (m/z) are given in u. Thin layer chromatography (TLC) was carried out on prefabricated plates (silica gel 60, F254 with fluorescence indicator) manufactured by Merck. Flash chromatography (FC) was carried out on silica gel 60 (40 – 64 µm, 230 – 400 mesh ASTM) purchased from Macherey-Nagel. Petroleum ether (PE) bp: 30-60 °C.

Preparation of compounds and spectroscopic data

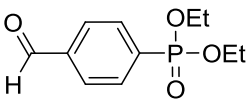
1,2-Bis(5-chloro-2-methylthiophen-3-yl)ethyne: A mixture of NEt_3 (10 mL) and THF (20 mL) was degassed for 10 min and 5-chloro-3-iodo-2-methylthiophene (2.97 g, 11.5 mmol), 5-chloro-3-ethynyl-2-methylthiophene (1.20 g, 7.7 mmol), bis-triphenyl-phosphinpalladium(II)-chlorid (110.0 mg, 2.0 Mol-%), triphenylphosphine (80.0 mg, 4.0 Mol-%) and CuI (60.0 mg, 4.0 Mol-%) were added under nitrogen and the solution was refluxed for 24 h at 60 °C. After cooling to room temperature 50 mL 1 M aqueous HCl were added. The organic phase was separated, washed with water (2 x 50 mL) and the organic phase was dried over $MgSO_4$. The solvent was evaporated and the precipitate was purified by silica gel chromatography (petrol ether). The product was obtained as a white solid in 64% yield (2.00 g, 6.9 mmol). M.p. 64-66 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (s, 2H), 2.37 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 127.9, 125.8, 115.1, 77.2, 14.5 ppm; HRMS (EI): m/z calculated for $C_{12}H_8Cl_2S_2$: m/z = 285.9445; found: 285.9443.



General Procedure for the synthesis of dithienylcyclohexenes

Anhydrous zinc iodide (2.0 eq.), zinc powder (2.0 eq.) and Co(dppe)Br_2 (1.0 eq.) were suspended in anhydrous dichloromethane (concentration of Co(dppe)Br_2: 0.2 M) under an argon atmosphere in a flame dried Schlenk tube fitted with a teflon screwcap. The internal alkyne (1.0 eq.) and 4,4,5,5-tetramethyl-2-(2-methylenebut-3-enyl)-1,3,2-dioxaborolane **2** (= boroprene, 3.0-5.0 eq.) were added and the mixture was stirred at room temperature until complete conversion of the starting materials was indicated by TLC. The reaction mixture was cooled to 0 °C, the aldehyde **4** (4.0–10.0 eq.) was added and the mixture was stirred at 0 °C. The progress of the reaction was monitored by TLC. Triethanolamine (1.2 eq. based on the dioxoborolane) was added at room temperature. After stirring for 1 h the reaction mixture was adsorbed on a small amount of silica gel and purified by column chromatography to afford the desired compound.

Diethyl(4-formylphenyl)phosphonate: A mixture of triethyl phosphite (1.35 g, 8.1 mmol), 4-bromobenzaldehyde (1.36 g, 7.4 mmol) and $NiBr_2$ (35.0 mg, 0.16 mmol) was heated for 4 h at 170 °C. The reaction mixture was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate 9:1 v/v), followed by vacuo short path distillation. The product was obtained as a colourless oil in 58% yield (1.03 g, 4.25 mmol). The analytical data are in agreement with the literature.[3]



(*E*)-1-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylencyclohex-3-en-1-yl)but-2-en-1-ol (5a): The product was obtained as a brownish solid after purification by column chromatography on silica gel (pentane/diethyl ether, 1:1 v/v) in 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49-7.43 (m, 4H), 7.35-7.30 (m, 4H), 7.24-7.20 (m, 2H), 7.00 (s, 1H), 6.90 (s, 1H), 5.84 (qd, *J* = 6.4, 12.9 Hz, 1H), 5.55 (ddd, *J* = 1.5, 8.3, 15.2 Hz, 1H), 5.12 (d, *J* = 7.6 Hz, 2H), 4.29 (t, *J* = 8.9 Hz, 1H), 3.33-3.14 (m, 2H), 2.69-2.53 (m, 2H), 2.04 (s, 3H), 2.01 (s, 3H), 1.85 (d, *J* = 2.0 Hz, 1H), 1.80 (dd, *J* = 1.5, 6.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.7, 139.8, 139.62, 139.56, 139.4, 134.53, 135.48, 134.15, 134.07, 132.3, 130.2, 129.8, 128.8, 127.0, 125.32, 125.26, 124.2, 124.1, 111.7, 72.9, 48.2, 37.3, 35.1, 17.9, 14.4, 14.3 ppm; IR (KBr): $\bar{\nu}$ = 689, 728, 754, 840, 902, 965, 1004, 1076, 1116, 1159, 1200, 1304, 1376, 1437, 1499, 1598, 1651, 1798, 1871, 1947, 2243, 2911, 3022, 3062, 3434 cm^{-1}; HRMS (EI): m/z calculated for $C_{33}H_{32}OS_2$: 508.1895; found: 508.1898.

Tert-butyl (2-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)-2-hydroxyehtyl)carbamate (5b): The product was obtained as a purple solid after purification by column chromatography on silica gel (pentane/diethyl ether, 1:1 v/v) in 25% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58-7.44 (m, 4H), 7.36-7.28 (m, 4H), 7.25-7.17 (m, 3H), 6.99 (s, 1H), 5.12 (d, *J* = 0.9 Hz, 1H), 5.11-5.02 (m, 2H), 3.99 (t, *J* = 7.1 Hz, 1H), 3.69-3.62 (m, 1H), 3.33-3.11 (m, 3H), 2.84-2.46 (m, 4H), 2.02 (s, 6H), 1.47 (m, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.7, 144.6, 139.8, 139.74, 139.70, 139.5, 134.69, 134.61, 134.5, 134.2, 130.4, 129.9, 128.92, 128.85, 127.1, 127.0, 125.45, 125.44, 124.8, 124.1, 111.8, 79.8, 71.0, 45.6, 44.7, 38.1, 35.2, 28.5, 14.54, 14.47 ppm; IR (film): 692, 756, 846, 898, 1033, 1094, 1166, 1251, 1367, 1397, 1442, 1503, 1599, 1701, 2857, 2971, 2972, 3065, 3426 cm^{-1}; HRMS (ESI): calculated for $C_{36}H_{39}NO_3S_2$ + Na^+: m/z = 620.2264; found m/z = 620.2261.

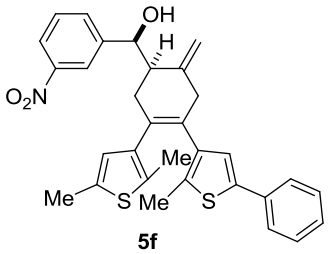
(3,4-Bis(2-methyl-5-phenylthiophen-3-yl)-6-methylencyclohex-3-enyl)(3-nitrophenyl)-methanol (5c): The product was obtained as a purple solid after purification by column chromatography on silica gel (pentane/diethyl ether, 1:1 v/v) in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34-8.32 (m, 1H), 8.19 (ddd, *J* = 1.0, 2.2, 8.2 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.58-7.48 (m, 4H), 7.43-7.29 (m, 5H), 7.24-7.19 (m, 2H), 7.04 (s, 1H), 6.83 (s, 1H), 5.25 (s, 2H), 4.99 (d, *J* = 9.8 Hz, 1H), 3.42-3.23 (m, 2H), 2.85-2.79 (m, 1H), 2.62-2.53 (m, 2H), 2.09 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.4, 144.4, 143.8, 139.9, 139.3, 139.2, 134.4, 134.2, 134.1, 133.3, 130.4, 129.5, 129.2, 128.8, 127.1, 125.3, 125.2, 123.8, 123.6, 123.2, ,122.3, 113.1, 73.3, 50.2, 37.1, 34.8, 14.5, 14.4 ppm; IR (KBr): $\bar{\nu}$ = 687, 729, 756, 809, 841, 901, 971, 1028, 1147, 1199, 1346, 1437, 1470, 1499, 1527, 1597, 1646, 1947, 2248, 2912, 3064, 3533 cm^{-1}; HRMS (EI): m/z calculated for $C_{36}H_{31}NO_3S_2$: m/z = 589.1745; found: 589.1756.

Diethyl (4-((3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl) (hydroxyl)methyl)phenyl)phosphonate (5d): The product was obtained as a pink-coloured oil after purification by column chromatography on silica gel (ethyl acetate) in 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ =7.83 (dd, *J* = 8.1, 13.1 Hz, 2H), 7.53 (dd, *J* = 3.9, 8.1 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.39 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 2H), 7.02 (s, 1H), 6.79 (s, 1H), 5.21 (s, 2H), 4.90 (d, *J* = 9.9 Hz, 1H), 4.17-4.01 (m, 4H), 3.43 (d, *J* = 19.8 Hz, 1H), 3.24 (d, *J* = 19.9 Hz, 1H), 2.85-2.81 (m, 1H), 2.56 (s, 1H), 2.54-2.50 (m, 1H), 2.09-2.05 (m, 1H), 2.07 (s, 3H), 1.98 (s, 3H), 1.29 (dt, *J* = 2.0, 7.1 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.8 (d, *J* = 3.1 Hz), 144.3, 139.8, 139.6, 139.4, 139.3, 134.4, 134.30, 134.26, 134.0, 132.1 (d, *J* = 10.2 Hz), 130.2, 129.4, 128.78, 128.77, 127.4 (d, *J* = 15.3 Hz), 127.02, 126.99, 125.3, 125.2, 123.9, 112.5, 73.7, 62.2 (d, *J* = 2.2 Hz), 62.1 (d, *J* = 2.0 Hz), 50.0, 37.2, 34.9, 16.31, 16.26, 14.5, 14.4 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 17.8 ppm; IR (film): $\bar{\nu}$ = 693, 757, 961, 1022, 1130, 1160, 1233, 1347, 1440, 1499, 1600, 2918, 2979, 3374 cm^{-1}; HRMS (ESI): m/z calculated for $C_{40}H_{41}O_4PS_2$+H$^+$: m/z = 681.2257; found: 681.2253.

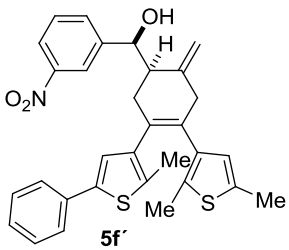
(*E*)-1-(3,4-bis(5-chloro-2-methylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)but-2-en-1-ol (5e): The product was obtained as a brownish solid after purification by column

chromatography on silica gel (pentane/diethyl ether, 1:1 v/v) in 32% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.52 (s, 1H), 6.42 (s, 1H), 5.81-5.72 (m, 1H), 5.50 (ddd, *J* = 1.7, 8.3, 15.2 Hz, 1H), 5.08-5.04 (m, 2H), 4.17 (t, *J* = 8.6 Hz, 1H), 3.15 (d, *J* = 19.8 Hz, 1H), 3.02 (d, *J* = 19.7 Hz, 1H), 2.55-2.47 (m, 2H), 2.29-2.26 (m, 1H), 1.95 (s, 3H), 1.92 (s, 3H), 1.77 (dd, *J* = 1.6, 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.3, 138.2, 137.9, 133.1, 133.0, 132.3, 130.5, 130.2, 129.8, 126.9, 126.7, 125.3, 125.2, 112.1, 73.0, 48.1, 37.3, 35.1, 18.0, 14.3, 14.2 ppm; IR (film): $\bar{\nu}$ = 680, 730, 829, 910, 970, 1090, 1120, 1210, 1340, 1380, 1420, 1499, 1601, 1670, 1800, 1854, 1950, 2240, 2920 cm^{-1}; HRMS (EI): m/z calculated for $C_{21}H_{22}OS_2Cl_2$: m/z = 424.0489; found 424.0487.

(3-(2,5-Dimethylthiophen-3-yl)-4-(2-methyl-5-phenylthiophen-3-yl)-6-methylene-cyclohex-3-en-1-yl)(3-nitrophenyl)methanol (5f) and (4-(2,5-dimethylthiophen-3-yl)-3-(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)(3-nitrophenyl)-methanol (5f´): The product was obtained as a brownish solid after purification by column chromatography on silica gel (pentane/diethyl ether, 7:3 v/v) in 30% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32-8.28 (m, 2H), 8.20-8.16 (m, 2H), 7.72 (t, *J* = 6.6 Hz, 2H), 7.57-7.52 (m, 2H), 7.51-7.47 (m, 2H), 7.42-7.39 (m, 2H), 7.37-7.30 (m, 4H), 7.26-7.19 (m, 2H), 6.98 (s, 1H), 6.78 (s, 1H), 6.44 (d, *J* = 0.9 Hz, 1H), 6.25 (d, *J* = 0.9 Hz, 1H), 5.22 (s, 2H), 5.21 (s, 2H), 4.95 (d, *J* = 9.7 Hz, 2H), 3.39 (t, *J* = 19.7 Hz, 2H), 3.20 (t, *J* = 19.5 Hz, 2H), 2.81-2.75 (m, 2H), 2.57-2.46 (m, 4H), 2.36 (s, 3H), 2.29 (s, 3H), 2.07 (s, 3H), 2.03 (dd, *J* = 2.1, 17.2 Hz, 2H), 2.00 (s, 3H), 1.99 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.6, 148.5, 144.5, 144.20, 144.18, 139.7, 139.6, 139.5, 138.0, 137.9, 135.6, 135.5, 134.6, 134.5, 134.4, 134.2, 133.5, 133.4, 132.2, 131.9, 130.9, 129.8, 129.7, 129.64, 129.62, 128.9, 128.6, 127.2, 125.9, 125.7, 125.4, 125.3, 124.1, 123.9, 123.3, 123.2, 122.5, 122.4, 113.12, 113.08, 73.4, 50.50, 50.47, 37.3, 37.2, 34.9, 15.3, 15.2, 14.6, 14.5, 14.4, 14.3; IR (film): $\bar{\nu}$ = 691, 758, 814, 901, 1047, 1088, 1145, 1205, 1314, 1349, 1440, 1500, 1530, 1598, 1651, 1698, 2857, 2917, 3069, 3543; HRMS (ESI): calculated for $C_{31}H_{29}NO_3S_2$ + Na^+: m/z = 550.1481; found m/z = 550.1482. Regioisomeric ratio: **5f**:**5f´** = 59:41.



5f



5f´

Immobilisation on silica gel

Diarylcyclohexene **5d** (100 mg, 0.15 mmol) was dissolved in dichloromethane (20 mL) and silica gel (100 mg, 0.04 – 0.063 mm) was added. The mixture was stirred over night at room temperature and then the silica gel was filtered off, washed with dichloromethane (4 x 5 mL) and ethanol (4 x 5 mL) until the rinsing solution showed no UV-absorption after irradiation with UV-light (312 nm). After drying the immobilisation rate of **8** was determined by elementary analysis to be $2.2 \cdot 10^{-5}$ $mmol_{dye}/mg_{silicagel}$.

Preparation of a photoswitchable paint

Poly-2-ethyloxazoline (100 mg, Aquazol 200: molecular weight = 200.000 g/mol) was dissolved in water (2.0 mL), the coated silica gel (100 mg) was suspended and after stirring a jellylike gel was obtained.

Preparation of a photoswitchable cellulose sheet

The diarylcyclohexene **5c** (100 mg, 0.15 mmol) was dissolved in dry tetrahydrofuran (20 mL) under nitrogen atmosphere. Then K_2CO_3 (56 mg, 0.4 mmol) and cyanuric chloride (27 mg, 0.15 mmol) were added and the mixture was stirred over night at room temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petrol ether/ethyl acetate 9:1 v/v). A red oil (90 mg) was obtained which contained traces of unidentified by-products. The roughly purified reactive dye was dissolved in dry dimethylformamide (20 mL) under nitrogen atmosphere. Then K_2CO_3 (38 mg, 0.28 mmol) and a cellulose tissue were added to the mixture and the solution was heated to 60 °C over night. The cellulose tissue was washed with dichloromethane, ethanol and acetone until no coloration of the rinsing solution was detected after irradiation with UV-light.

Table S1. Immobilisation of diarylcyclohexene **5c** on cellulose.

Cellulose sheet before immobilisation [mg]	**Cellulose-sheet after immobilisation [mg]**	**Immobilised dye [mg]**	**Immobilised dye [mmol]**	**Dye[mmol]/ cellulose [mg]**
176	198	22	$3.7 \cdot 10^{-2}$	$2.1 \cdot 10^{-4}$
170	208	38	$6.5 \cdot 10^{-2}$	$3.8 \cdot 10^{-4}$
195	230	35	$5.9 \cdot 10^{-2}$	$3.0 \cdot 10^{-4}$

Midpoint: $3.0 \cdot 10^{-4}$ $mmol_{dye}/mg_{cellulose}$.

Standard aberration: $0.8 \cdot 10^{-4}$ $mmol_{dye}/mg_{cellulose}$.

Immobilisation (%) = 5.2 (assumption: only the primary hydroxyl group is reactive).

NMR and UV-Spectra

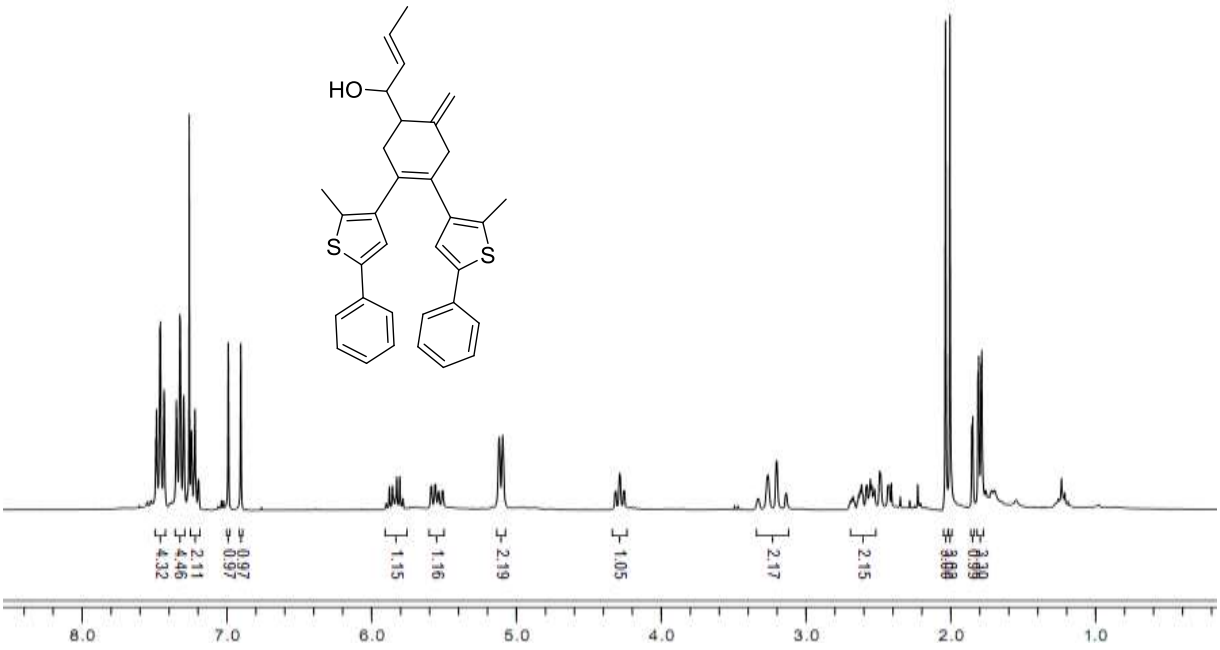


Fig.S1. ^{1}H NMR (300 MHz, $CDCl_3$) of (2*E*)-1-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-enyl)but-2-en-1-ol **(5a)**.

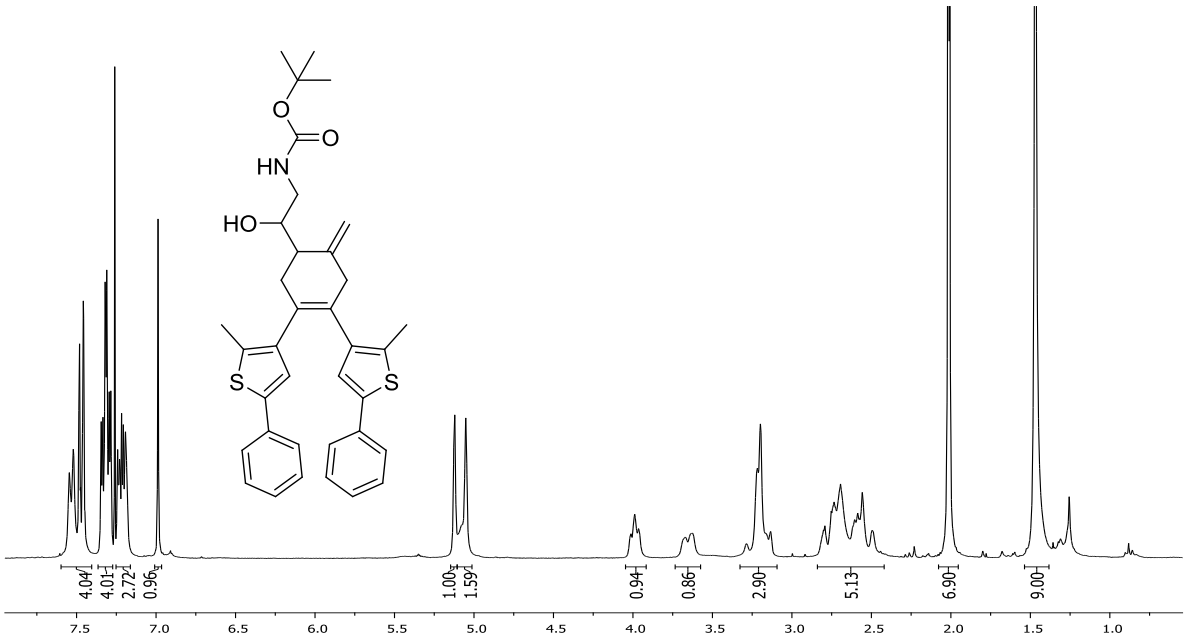


Fig.S2. ^{1}H NMR (300 MHz, $CDCl_3$) of tert.-butyl (2-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)-2-hydroxyehtyl)carbamate **(5b)**.

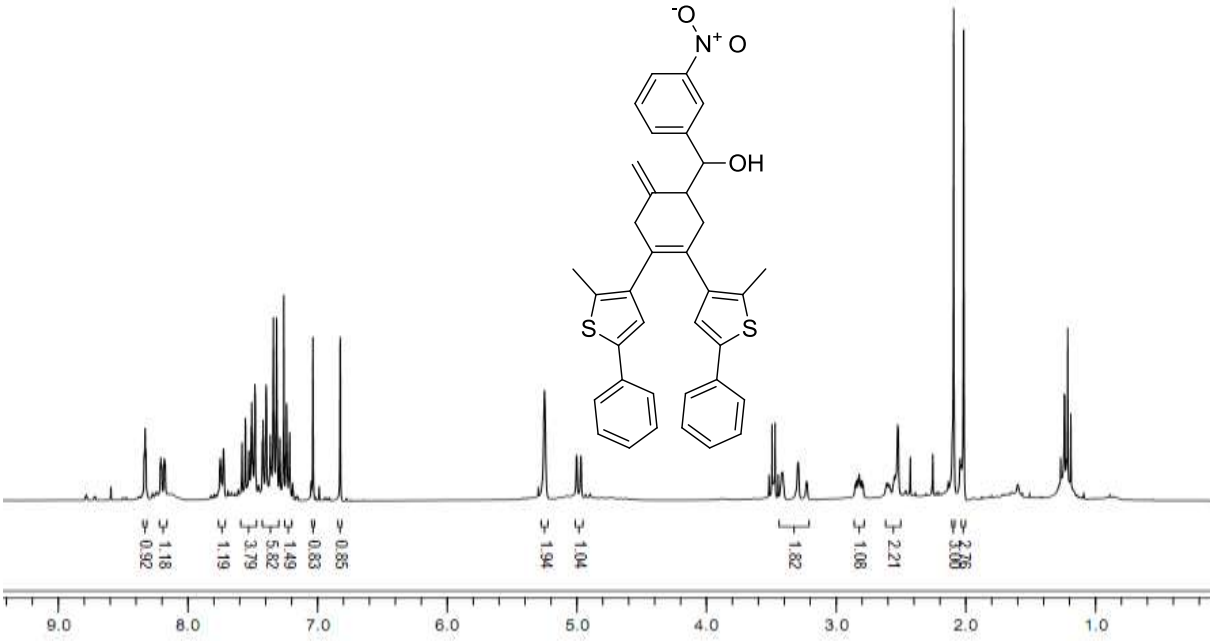


Fig.S3. ^{1}H NMR (300 MHz, $CDCl_3$) of (3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylene-cyclohex-3-enyl)(3-nitrophenyl)-methanol **(5c)**.

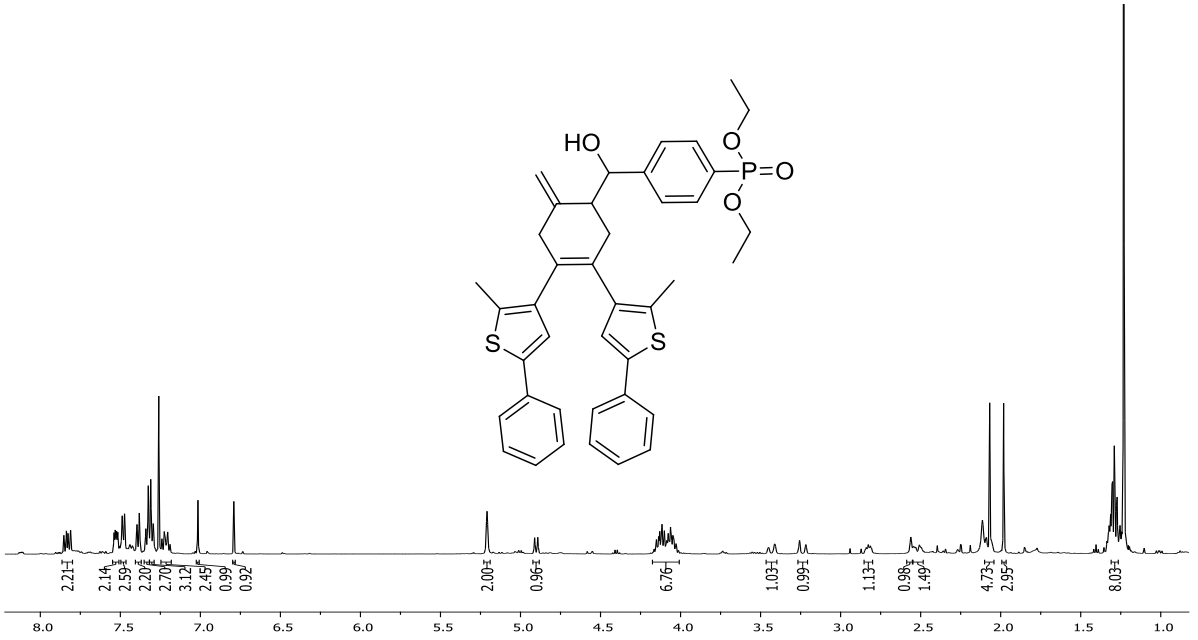


Fig.S4. ^{1}H NMR (500 MHz, $CDCl_3$) of diethyl-4-((3,4-bis(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-enyl)(hydroxyl)methyl)phenylphosphonate (**5d**).

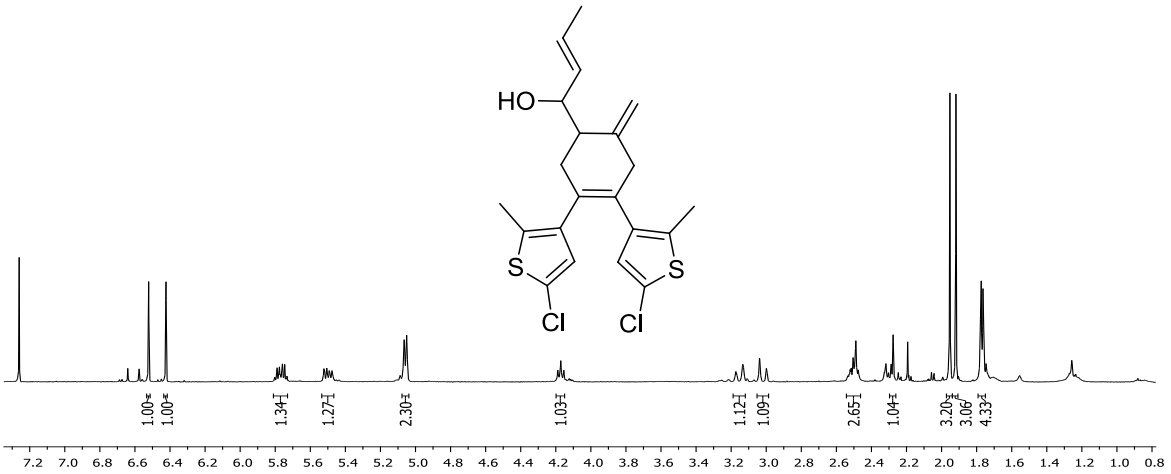


Fig.S5. ^{1}H NMR (500 MHz, $CDCl_3$) of (2*E*)-1-(3,4-bis(5-chloro-2-methylthiophen-3-yl)-6-methylenecyclohex-3-enyl)but-2-en-1-ol (**5e**).

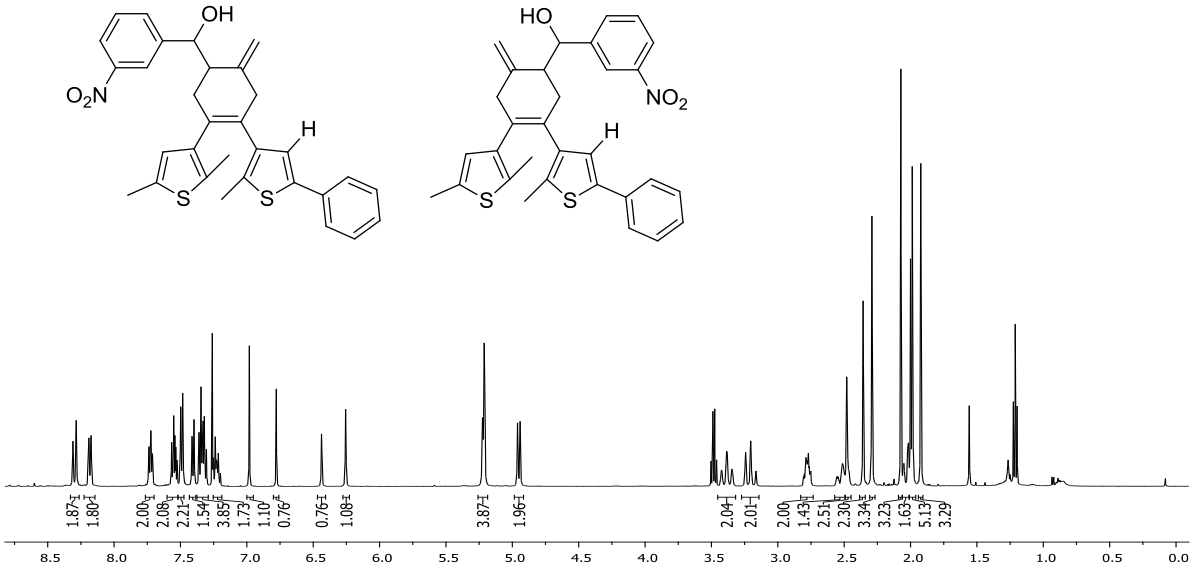


Fig.S6. ^{1}H NMR (500 MHz, $CDCl_3$) of (3-(2,5-dimethylthiophen-3-yl)-4-(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)(3-nitrophenyl)methanol **(5f)** and (4-(2,5-dimethylthiophen-3-yl)-3-(2-methyl-5-phenylthiophen-3-yl)-6-methylenecyclohex-3-en-1-yl)(3-nitrophenyl)methanol **(5f´)**. Regioisomeric ratio **5f**:**5f´** = 59:41.

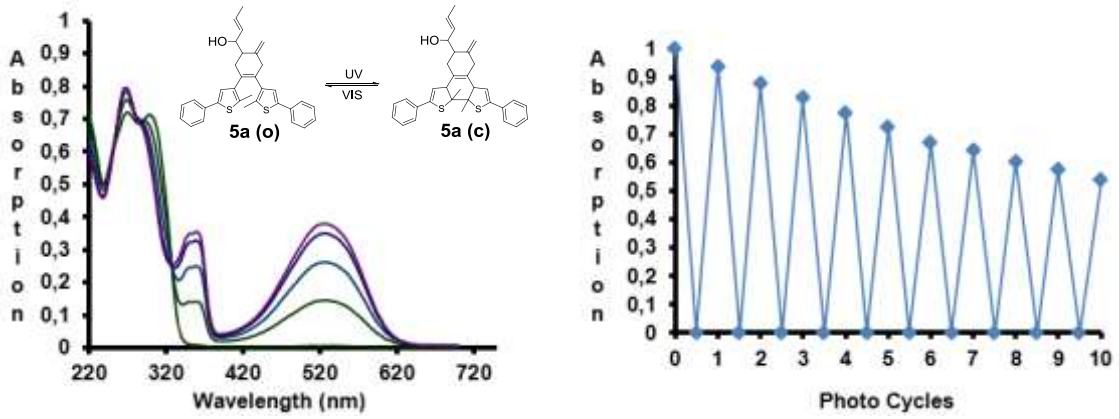


Fig.S7 UV-absorption spectrum of compound **5a** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in methanol). Left: Irradiation of diarylcyclohexene **5a** with UV-light (312 nm) in methanol. Irradiation times were 15, 30, 45 and 60 s. Right: Photocycles of diarylcyclohexene **5a** in methanol (detection wavelength: 520 nm).

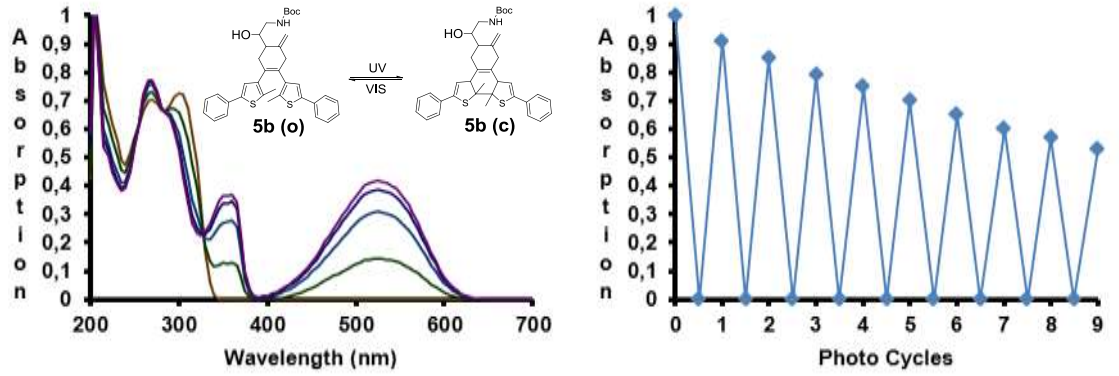


Fig.S8. UV-absorption spectrum of compound **5b** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in methanol). Left: Irradiation of diarylcyclohexene **5b** with UV-light (312 nm) in methanol. Irradiation times were 15, 30, 45 and 60 s. Right: Photocycles of diarylcyclohexene **5b** in methanol (detection wavelength: 520 nm).

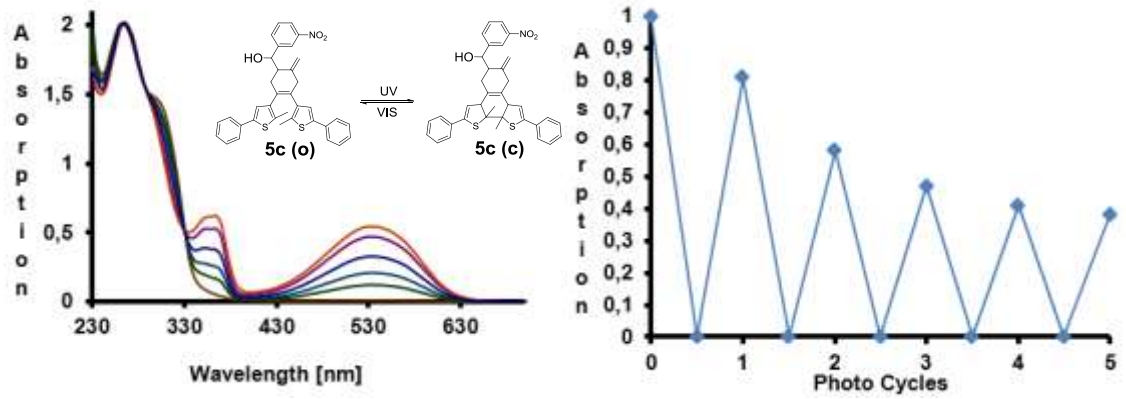


Fig.S9. UV-absorption spectrum of compound **5c** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in methanol). Left: Irradiation of diarylcyclohexene **5c** with UV-light (312 nm) in methanol. Irradiation times were 15, 25, 40 60 and 75 s. Right: Photocycles of diarylcyclohexene **5c** in methanol (detection wavelength: 530 nm).

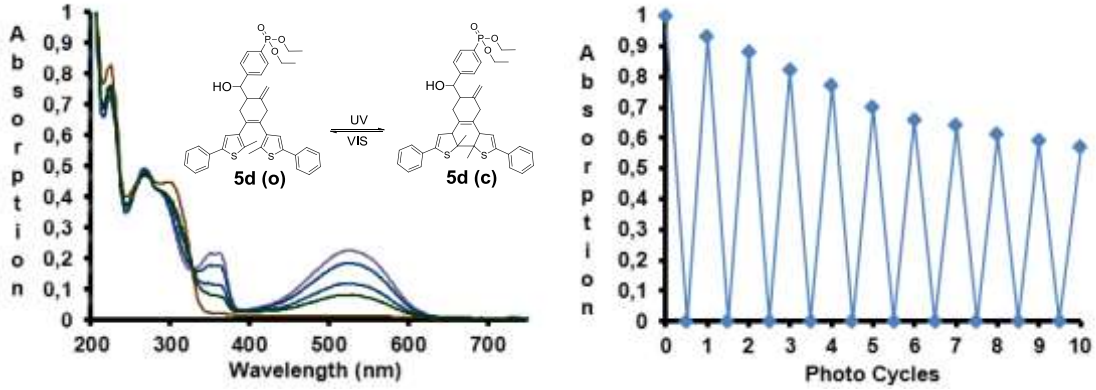


Fig.S10. UV-absorption spectrum of compound **5d** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in methanol). Left: Irradiation of diarylcyclohexene **5d** with UV-light (312 nm) in methanol. Irradiation times were 15, 25, 45 and 60 s. Right: Photocycles of diarylcyclohexene **5d** in methanol (detection wavelength: 530 nm).

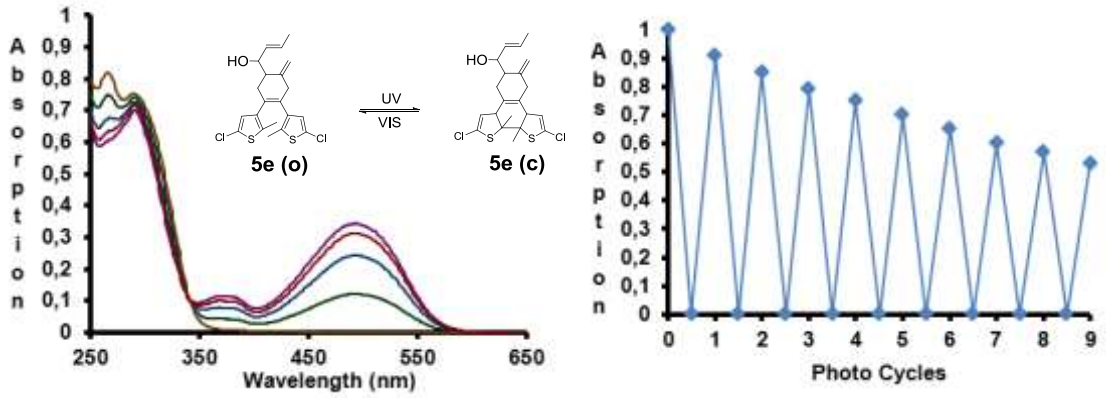


Fig.S11. UV-absorption spectrum of compound **5e** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in dichloromethane). Left: Irradiation of diarylcyclohexene **5e** with UV-light (312 nm) in dichloromethane. Irradiation times were 30, 45, 60 and 75 s. Right: Photocycles of diarylcyclohexene **5e** in dichloromethane (detection wavelength: 490 nm).

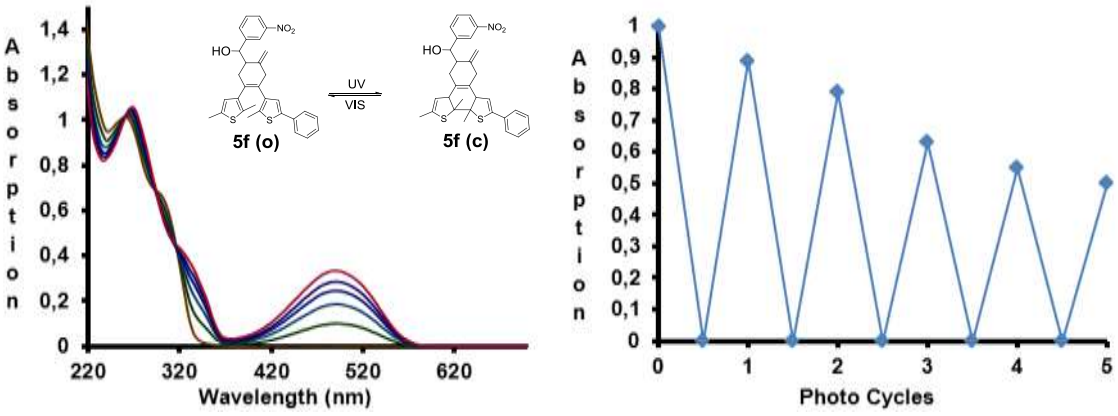


Fig.S12 UV-absorption spectrum of **5f/5f´** (c = $3.0 \cdot 10^{-5}$ mmol·L^{-1} in methanol). Left: Irradiation of diarylcyclohexene **5f/5f´** with UV-light (312 nm) in methanol. Irradiation times were 15, 30, 40, 50 and 60 s. Right: Photocycles of diarylcyclohexene **5f/5f´** (Regioisomeric ratio = 59:41) in methanol (detection wavelength: 490 nm).

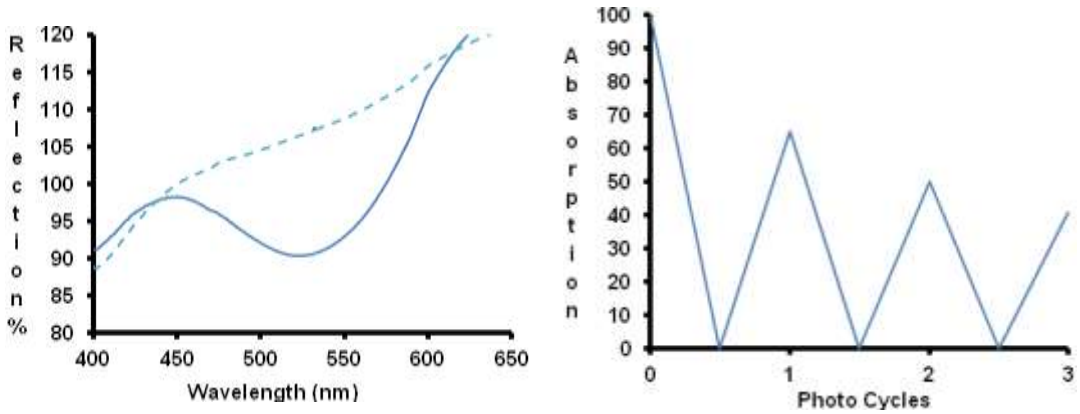


Fig.S13 Left: Solid state UV-spectra changes of SiO_2 with immobilized compound **5d** upon irradiation with UV-light of 312 nm and visible light. Dashed line: Spectrum before UV-irradiaton. Solid line: Spectrum after 30 s UV-irradiation. Right: Photocycles of diarylcyclohexene **5d** immobilized on SiO_2.

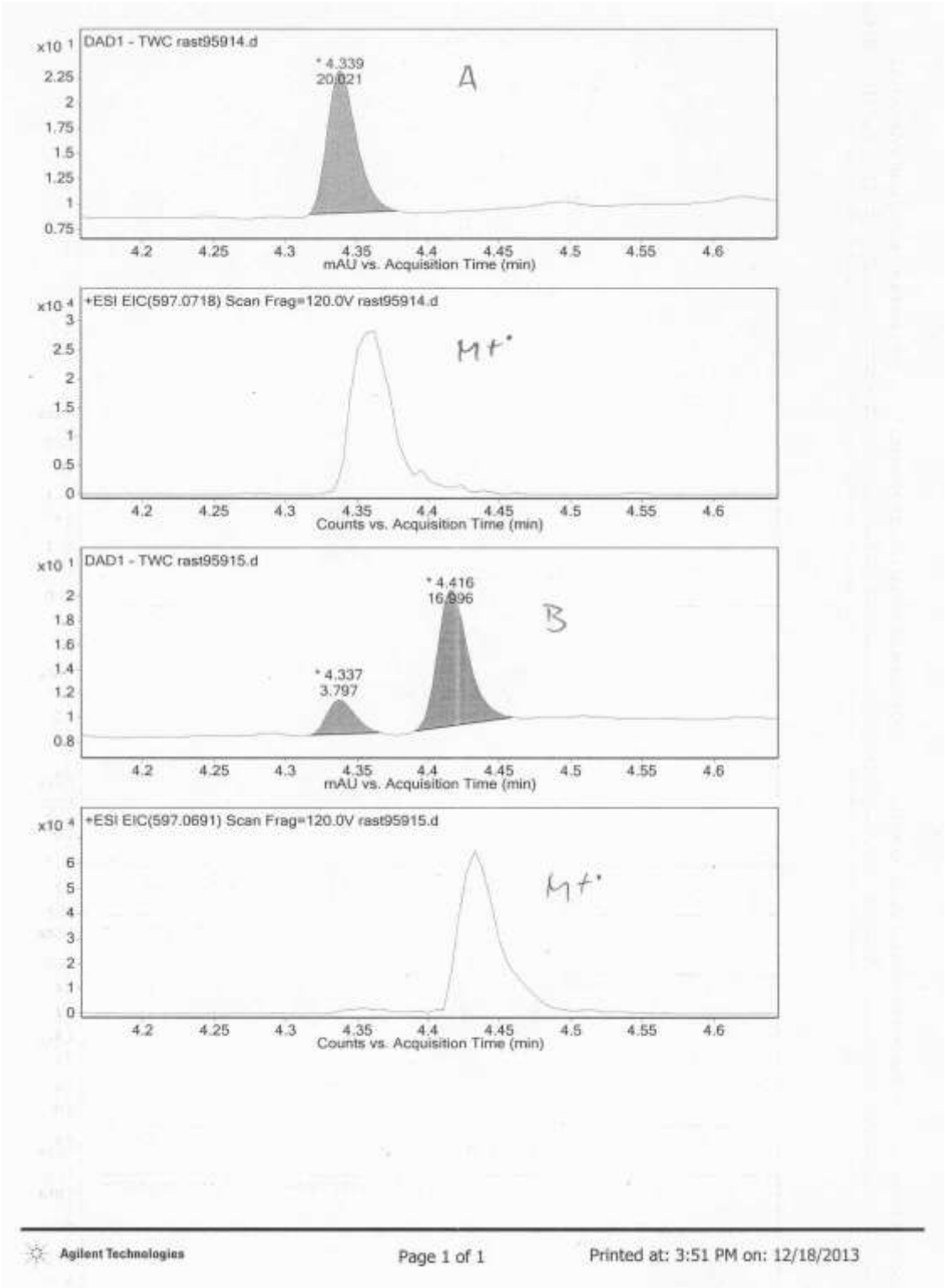


Fig. S14 HPLC trace / ESI spectra of **5b** (c = $3.0 \cdot 10^{-5}$ mol·L^{-1}) before (**A** – open form) and after (**B** – closed form) irradiation at 520 nm for 90 s.

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