DOI: 10.1002/ejoc.201000721

Novel Dithienylethenes with Extended π-Systems: Synthesis by Aldol Condensation and Photochromic Properties

Kai Altenhöner,[a] Jan-Hendrik Lamm,[a] and Jochen Mattay*[a]

Keywords: Photochromism / Photoswitches / Alkenes / Aldol reactions / Dithienylethene

A facile and stereoselective route to symmetric π-extended dithienylethene derivatives is described. The key step of this route is an aldol condensation of 1,2-bis(5-formyl-2-methylthiophen-3-yl)cyclopentene with a large variety of acyl compounds. All synthesized photoswitches can be reversibly converted into the closed form by irradiation with visible light. The photochromic properties of nine new dithienylethenes are discussed.

Introduction

Dithienylethenes display extremely favourable photochromic properties. Because of their high fatigue resistance and thermal stability this class of photoswitches is the target of increased interest for applications in fields of optical data storage and photoswitchable devices.[1–4] A large percentage of known dithienylethenes can only be switched by UV light. In an earlier publication we showed how to achieve a successive shift of the absorption bands of different dithienylethenes to the visible region of the electromagnetic spectrum by elongation of the conjugated π-system by using Wittig-type reactions. In most cases these dithienylethenes were obtained as mixtures of up to three isomers (*E-E, E-Z, Z-Z*).[5]

Results and Discussion

Herein we report a facile and stereoselective synthetic route to π-extended photochromic dithienylethenes. This route only leads to one isomer and gives a new access to dithienylethene chalcone derivatives with absorption bands in the visible range of the electromagnetic spectrum.

Aldol condensation reactions have been well studied for more than a century. This procedure can be used as a powerful tool for a selective synthesis of new dithienylethenes with extended conjugated π-systems. Starting from the well known 1,2-bis(5-formyl-2-methylthiophen-3-yl)cyclopentene **1**[6] and a large variety of acyl compounds **2**–**10** we performed several aldol condensation reactions in methanol simply by adding an excess of KOH (Figure 1). The reaction progress was monitored by TLC. In two cases (using **5** and **7**) the reaction proceeded at room temperature whereas heating to reflux was necessary for all other reactions. After completion of the reaction water was added to precipitate the chalcones **11**–**19**. Mostly the compounds were obtained in high purity. In some cases (**13**, **17**, **18**) further purification had to be performed by column chromatography on silica gel. All shown compounds **11**–**19** could be isolated in good or moderate yield (see Table 1). The synthesized chalcones **11**–**19** were characterized by ^{1}H and ^{13}C NMR and UV spectroscopy as well as by mass spectrometrical methods.

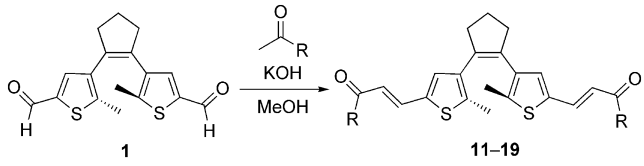

Figure 1. Aldol condensation reaction of **1** with different acyl compounds **2**–**10** leading to dithienylethenes **11**–**19**.

Due to the reaction pathway of an aldol condensation all the isolated compounds **11**–**19** were obtained as pure *E-E* isomers (shown in Figure 1). No other isomers were observed in the NMR spectra. All measured coupling constants were between 15 and 16 Hz which is typical for *trans* orientated double bond protons.[7] As shown in an earlier publication the values for *cis* orientated double bond protons in comparable systems were in a range of 11–12 Hz.[5] The *E-E* configuration is stable even after irradiation with 350 nm light for several minutes. ^{1}H NMR spectra show a mixture of the open and the closed isomers of the obtained chalcones **11**–**19** in *E-E* configuration but no *E-Z* or *Z-Z* isomer.

For a study of the photochromic behaviour and spectroscopic properties of the new dithienylethenes with altering the moiety R (see Figure 1) different types of functional groups were attached to the core unit **1** (aliphatic **11**, aro-

[a] Organische Chemie I, Universität Bielefeld,
Postfach 100131, 33501, Bielefeld, Germany
Fax: +49-(0)521-1066417
E-mail: oc1jm@uni-bielefeld.de

Table 1. Applied acyl components **2**–**10**, reaction times and yields.

R =	Reaction time [h]	Chalcone	Yield [%]
2	8[a]	**11**	73
3	6[a]	**12**	55
4	6[a]	**13**	27
5	20[a]	**14**	65
6	72[b]	**15**	75
7	7[a]	**16**	75
8	48[b]	**17**	30
9	9[a]	**18**	24
10	8[a]	**19**	60

[a] The reaction mixture was heated at reflux temperature. [b] The reaction mixture was stirred at room temperature.

matic with different functional groups **12**–**16**, phenylethenylic **17** and heteroaromatic moieties **18**–**19**) and UV/Vis spectra were recorded.

All chalcones **11**–**19** can be reversibly switched between their open and closed form and irrespective of the attached functionality all compounds could be transferred to the corresponding closed form by irradiation with 400 (or less) nm light. The back reaction could be induced by irradiation with 590 nm light (see Figure 2). The colour of the measured solutions changed form slightly yellow to green or blue.

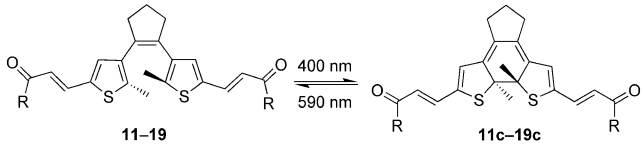

Figure 2. Photochromic reaction of dithienylethene chalcone derivatives **11**–**19** upon irradiation.

In comparison the absorption maxima of the open isomers of dithienylethenes **12**–**19** deviate only in a small region of the electromagnetic spectrum. All compounds possessing aromatic moieties **12**–**19** showed absorption maxima between 370 and 390 nm (see Table 2). Solely the aliphatic derivative **11** differed from these values (354 nm). UV/Vis spectra of selected chalcone derivatives are presented in Figure 3.

Table 2. Absorption maxima of the synthesized chalcones **11**–**19** in ethanol (open and closed form).

Chalcone	λ_{max} (open) [nm] (ε [10^3 $Lcm^{-1}mol^{-1}$])	λ_{max} (closed) [nm] (ε [10^3 $Lcm^{-1}mol^{-1}$])[a]
11	354 (29.2)	612 (17.5)
12	379 (10.2)	644 (7.0)
13	388 (36.9)	650 (9.5)
14	370 (33.3)	634 (13.8)
15	381 (38.1)	644 (24.1)
16	375 (34.3)	638 (20.0)
17	390 (34.1)	652 (19.1)
18	372 (19.4)	635 (4.8)
19	383 (12.5)	644 (5.5)

[a] At photostationary state.

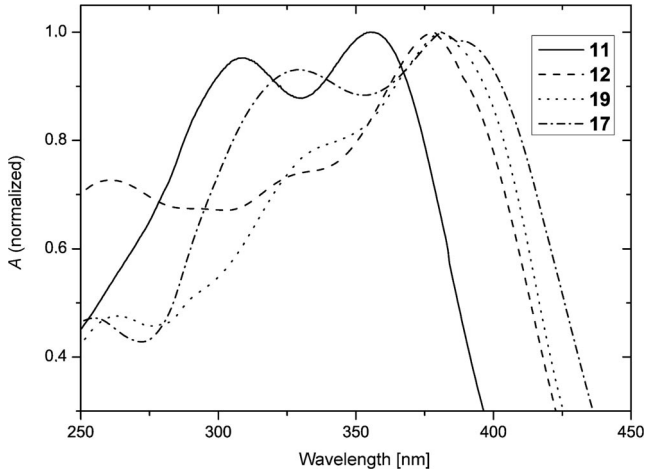

Figure 3. Comparison between UV/Vis absorption bands of chalcones **11**, **12**, **17** and **19** in ethanol.

Attachment of extended π-conjugated moieties R (Figure 1) to the chalcone core unit did not affect the absorption maximum significantly. The same trend could be observed for the corresponding closed form isomers of the dithienylethenes **11c**–**19c**. Absorption maxima of the here presented chalcones were only slightly depending on the length of the conjugated system of the attached moiety. Especially this becomes obvious by comparing chalcones **12** and **17**. The extension of the conjugated system in R only leads to a small change in the absorption maximum of 12 nm in the open form and 8 nm in the closed form. However, elongation of the conjugated π-system of the chalcone core unit by two additional double bonds leads to a bathochromic shift in the absorption maxima of 20 nm in the open form and 37 nm in the closed form as shown in former publications using comparable switches.[5] The most significant change in the absorption properties is caused by the exchange of the aliphatic substituent (R = *tert*-butyl **11**) by a phenyl moiety (e.g., **12**) which leads to a bathochromic

shift of 24/32 nm (open/closed form). Additional substituents on the benzene ring only slightly affect the absorption properties.

As an example for the switching process Figure 4 shows a complete open-close cycle of compound **11**. After irradiation at 400 nm the solution quickly turned blue. In the absorption spectrum the UV bands are diminished whereas a new band arises in the visible region at 610 nm. During successive irradiation an isosbestic point at 387 nm was observed. The conversion back to the open form could be performed with 590 nm light without any changes to the starting spectrum.

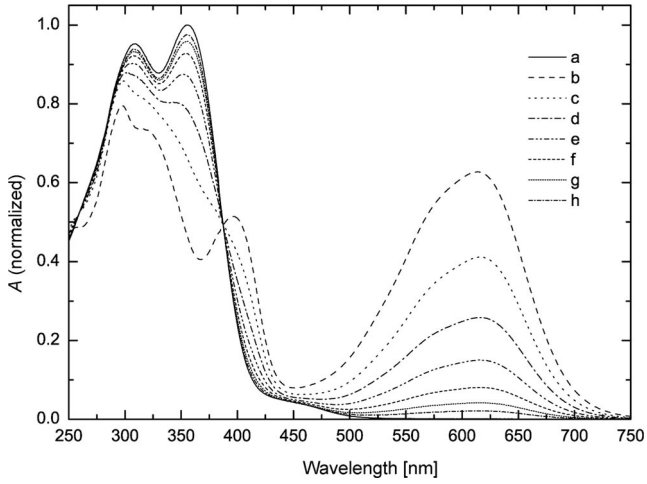

Figure 4. UV/Vis absorption spectrum of **11** in ethanol; a: before irradiation, b: after 30 s at 400 nm and c–h: after continuous irradiation time with 590 nm light after 6, 12, 18, 24, 30 and 36 min.

Conclusions

Several new dithienylethenes with an extended π-system were synthesized by a facile and stereoselective aldol condensation. These compounds can be switched reversibly between the open and closed forms by using visible light.

Experimental Section

General: Aldehyde **1** was prepared according to a literature procedure.[6] Furan **9** and thiophene **10** were prepared as described below. All other carbonyl compounds **2**–**8**, solvents and reactants were purchased from commercial sources and used without further purification.

3-Acetyl-2,5-dimethylfuran (9): Acetyl chloride (1.1 mL, 15.41 mmol) was added to a suspension of $AlCl_3$ (2.350 g, 17.62 mmol) in CH_2Cl_2 (70 mL) at 0 °C followed by dropwise addition of Dimethylfuran (1.50 mL, 14.12 mmol). After 2.5 h stirring at 0 °C the reaction was quenched with water (50 mL). The organic phase was separated and the aqueous solution was extracted twice with CH_2Cl_2 (40 mL). The combined organic phases were washed with satd. $NaHCO_3$ solution (40 mL) and dried with $MgSO_4$. All volatile components were removed in vacuo. The brown oily residue was filtered through silica gel eluting with cyclohexane/ethyl acetate (4:1). After evaporation of the solvents **9** was obtained as a brown oil; yield 1.190 g (8.58 mmol, 61%) (compound **9** was identified by ^{1}H NMR spectroscopy, by comparison with data from the literature[8]) ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.26 (s, 3 H), 2.37 (s, 3 H), 2.55 (s, 3 H), 6.20 (s, 1 H, 4-H) ppm.

2-Acetyl-5-methylthiophene (10): Acetyl chloride (0.81 mL, 11.36 mmol) was added to a suspension of $AlCl_3$ (1.680 g, 12.60 mmol) in CH_2Cl_2 (70 mL) at 0 °C followed by dropwise addition of 2-methylthiophene (1.00 mL, 10.33 mmol). After 1.5 h stirring at 0 °C the reaction was quenched with water (30 mL). The organic phase was separated and the aqueous layer was extracted twice with CH_2Cl_2 (40 mL). The combined organic phases were washed with satd. $NaHCO_3$ solution (40 mL) and dried with $MgSO_4$. After evaporation of all volatile components in vacuo **10** was obtained as a yellow crystalline solid; yield 1.420 g (10.13 mmol, 98%) (compound **10** was identified by ^{1}H NMR spectroscopy, by comparison with data from the literature[9]). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.48 (s, 3 H, SCCH_3), 2.50 (s, 3 H, COCH_3), 6.77 (d, $^3J_{H,H}$ = 3.8 Hz, 1 H, 3-H) 7.48 (d, $^3J_{H,H}$ = 3.8 Hz, 1 H, 4-H) ppm.

General Procedure for the Aldol Condensation Reactions Leading to Chalcones 11–19: (see Figure 5) An excess of KOH and of the respective acetyl compound **2**–**10** (applied amounts are listed below) were dissolved in methanol (20–30 mL). Aldehyde **1** (200 mg, 0.63 mmol) was added to this solution and the mixture was stirred at room temperature for 1 h. If after this time TLC controls showed no new photochromic compound the reaction mixture was heated to reflux. Reaction progress was monitored by TLC (reaction times were given in Table 1 and below). After completion of the reaction the mixture was cooled to room temperature and was diluted with water. The resulting precipitate was collected by filtration and dried in vacuo. In some cases the resulting solid needed to be purified by column chromatography [silica gel, cyclohexane/ethyl acetate (80:20)].

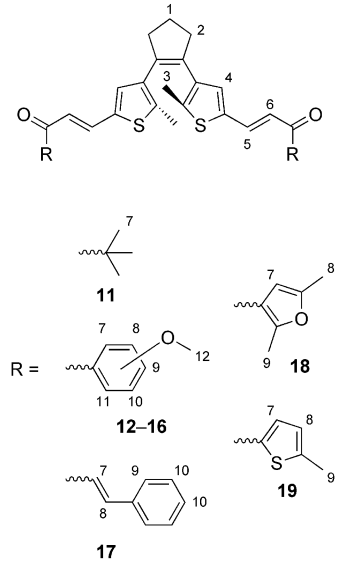

Figure 5. Proton labelling for ^{1}H NMR signal assignment.

Chalcone 11: KOH (380 mg, 6.77 mmol); pinacolone (**2**) (0.20 mL, 1.68 mmol); reflux for 8 h; yield 230 mg (0.48 mmol, 73%); R_f = 0.70 (cyclohexane/ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.21 (s, 18 H, 7-H), 1.99 (s, 6 H, 3-H), 2.08 (m, 2 H, 1-

H), 2.79 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 6.73 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H), 6.96 (s, 2 H, 4-H), 7.65 (d, $^3J_{H,H}$ = 15.7 Hz, 2 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.9, 22.9, 26.1, 38.3, 43.0, 118.6, 133.2, 134.6, 135.5, 136.5, 136.9, 138.5, 204.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 480.19 (41) $[M]^+$, 465.16 (28) $[M - CH_3]^+$, 423.12 (75) $[M - t\text{Bu}]^+$. HRMS: found for $C_{29}H_{36}O_2S_2$ [*m*/*z*]: 480.21460, calcd. [*m*/*z*]: 480.21567, deviation: 1.07 mmu, 2.23 ppm.

Chalcone 12: KOH (624 mg, 11.12 mmol); acetophenone (**3**) (0.16 mL, 1.39 mmol); reflux for 6 h; yield 180 mg (0.35 mmol, 55%); R_f = 0.59 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): δ = 2.04 (s, 6 H, 3-H), 2.13 (m, 2 H, 1-H), 2.88 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 7.29 (s, 2 H, 4-H), 7.34 (d, $^3J_{H,H}$ = 15.2 Hz, 2 H, 5-H), 7.51 (m, 4 H, 8-H, 11-H), 7.58 (m, 2 H, 10-H), 7.85 (d, $^3J_{H,H}$ = 15.2 Hz, 2 H, 6-H), 8.05 [d, ^3J(H,H) = 7.3 Hz, 4 H, 7-H, 12-H] ppm. ^{13}C NMR (125 MHz, [D$_8$]THF, 25 °C): δ = 15.0, 27.8, 39.2, 120.4, 129.1, 129.4, 133.3, 134.5, 135.7, 137.3, 137.9, 138.2, 139.4, 139.4, 188.6 ppm. EI, 70 eV): *m*/*z* (%) = 520.39 (61) $[M]^+$, 505.35 (100) $[M - CH_3]^+$. HRMS: found for $C_{33}H_{28}O_2S_2$ [*m*/*z*]: 520.15307, calcd. [*m*/*z*]: 520.15160, deviation: 1.47 mmu, 2.83 ppm.

Chalcone 13: KOH (380 mg, 6.77 mmol); *p*-iodoacetophenone (**4**) (39 mg, 1.60 mmol); reflux for 6 h. Column: silica gel [cyclohehane/ethyl acetate (80:20)]; yield 133 mg (0.17 mmol, 27%); R_f = 0.88 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.99 (s, 6 H, 3-H), 2.06 (m, 2 H, 1-H), 2.78 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 7.01 (s, 2 H, 4-H), 7.06 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H), 7.66 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, 8-H, 10-H), 7.77 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 6-H), 7.81 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, 7-H, 11-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 15.3, 38.3, 100.4, 129.7, 129.8, 134.7, 136.3, 137.1, 137.5, 137.7, 137.8, 138.8, 137.9, 139.8, 188.8 ppm. EI, 70 eV): *m*/*z* (%) = 771.90 (51) $[M]^+$, 756.88 (71) $[M - CH_3]^+$. HRMS: found for $C_{33}H_{26}I_2O_2S_2$ [*m*/*z*]: 771.94740, calcd. [*m*/*z*]: 771.94636, deviation: [mmu]: 1.04 [ppm]: 1.35.

Chalcone 14: KOH (380 mg, 6.77 mmol); *o*-methoxyacetophenone (**5**) (0.22 mL, 1.60 mmol); reflux for 20 h; yield 234 mg (0.40 mmol, 63%); R_f = 0.52 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$ 25 °C): δ = 1.96 (s, 6 H, 3-H), 2.04 (m, 2 H, 1-H), 2.76 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 3.87 (s, 6 H, 12-H), 6.94–7.01 (m, 8 H), 7.41–7.45 (m, 2 H), 7.56–7.59 (m; 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.9, 22.8, 38.3, 55.7, 111.6, 120.7, 124.9, 129.2, 130.2, 132.7, 133.2, 134.6, 135.9, 136.7, 136.9, 139.1, 158.0, 192.2 ppm. EI, 70 eV): *m*/*z* (%) = 580.13 (25) $[M]^+$, 565.11 (41) $[M - CH_3]^+$. HRMS: found for $C_{35}H_{32}O_4S_2$ [*m*/*z*]: 580.17450, calcd. [*m*/*z*]: 580.17420, deviation: [mmu]: 0.30, [ppm]: 0.52.

Chalcone 15: KOH (380 mg, 6.77 mmol); *m*-methoxyacetophenone (**6**) (0.22 mL, 1.60 mmol); stirring at room temperature for 72 h; yield 273 mg (0.47 mmol, 75%); R_f = 0.60 (cyclohexane/ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.99 (s, 6 H, 3-H), 2.07 (m, 2 H, 1-H), 2.79 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 3.86 (s, 6 H, 12-H), 7.03 (s, 2 H, 4-H), 7.10 (d, 2 H, 10-H), 7.12 (d, $^3J_{H,H}$ = 15.7 Hz, 2 H, 5-H), 7.38 (t, 2 H, 11-H), 7.49 (s, 2 H, 7-H), 7.54 (d, 2 H, 12-H), 7.78 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 15.0, 38.4, 55.5, 112.7, 119.2, 119.8, 120.9, 129.5, 133.8, 134.7, 136.6, 137.1, 137.4, 139.5, 139.7, 151.6, 160.0, 189.6 ppm. EI, 70 eV): *m*/*z* (%) = 580.13 (54) $[M]^+$, 565.11 (100) $[M - CH_3]^+$. HRMS: found for $C_{35}H_{32}O_4S_2$ [*m*/*z*]: 580.17570, calcd. [*m*/*z*]: 580.17420; deviation [mmu]: 1.50, [ppm]: 2.58.

Chalcone 16: KOH (380 mg, 6.77 mmol); *p*-methoxyacetophenone (**7**) (240 mg, 1.60 mmol); reflux for 7 h; yield 274 mg (0.47 mmol, 75%); R_f = 0.31 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.98 (s, 6 H, 3-H), 2.07 (m, 2 H, 1-H), 2.78 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 3.85 (s, 6 H, 12-H), 6.93 (d, 4 H, 8-H, 10-H), 7.00 (s, 2 H, 4-H), 7.15 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H), 7.77 (d, $^3J_{H,H}$ = 15.4 Hz, 2 H, 6-H), 7.98 (d, 4 H, 7-H, 11-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.9, 22.9, 38.4, 55.5, 113.8, 119.6, 130.7, 131.2, 133.4, 134.7, 136.6, 136.7, 137.0, 139.1, 163.3, 188.1 ppm. EI, 70 eV): *m*/*z* (%) = 580.15 (17) $[M]^+$, 565.13 (45) $[M - CH_3]^+$, 135.02 (100) $[C_8H_7O_2]^+$. HRMS: found for $C_{35}H_{32}O_4S_2$ [*m*/*z*]: 580.17300, calcd. [*m*/*z*]: 580.17420, deviation [mmu]: 1.20, [ppm]: 2.07.

Chalcone 17: KOH (340 mg, 6.06 mmol); benzalacetone (**8**) (240 mg, 1.64 mmol); stirring at room temperatur for 48 h; Column: silica gel [cyclohehane/ethyl acetate (80:20)]; yield 107 mg (0.18 mmol, 30%); R_f = 0.35 (cyclohexane/ethyl acetate); ^{1}H NMR (600 MHz, $CDCl_3$ 25 °C): δ = 1.99 (s, 6 H, 3-H), 2.06 (m, 2 H, 1-H), 2.78 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 6.69 (d, $^3J_{H,H}$ = 15.8 Hz, 2 H, 8-H), 6.97 (d, ^3JH,H = 15.8 Hz, 2 H, 5-H), 6.99 (s, 2 H, 4-H), 7.37 (m, 6 H, 10-H, 11-H), 7.57 (m, 4 H, 9-H), 7.67 (d, $^3J_{H,H}$ = 15.8 Hz, 2 H, 7-H), 7.70 (d, ^3JH,H = 15.8 Hz, 2 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 15.0, 22.9, 38.4, 123.2, 125.7, 128.4, 129.0, 130.4, 133.6, 134.7, 134.9, 136.0, 136.5, 137.1, 139.6, 142.9, 188.3 ppm. EI, 70 eV): *m*/*z* (%) = 572.17 (70) $[M]^+$, 557.14 (100) $[M - CH_3]^+$. HRMS: found for $C_{37}H_{32}O_2S_2$: [*m*/*z*]: 572.18610, calcd. 572.18437, deviation [mmu]: 1.73, [ppm]: 3.02.

Chalcone 18: KOH (400 mg, 7.11 mmol); 3-acetyl-2,5-dimethylfuran (**9**) (360 mg, 2.60 mmol); reflux for 9 h; Column: silica gel [cyclohehane/ethyl acetate (80:20)]; yield 86 mg (0.15 mmol, 24%); R_f = 0.55 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.95 (s, 6 H, 3-H), 2.24 (m; 8 H, 1-H, 8-H), 2.56 (s, 6 H, 9-H), 2.76 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 6.25 (s, 2 H, 7-H), 6.76 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H), 6.92 (s, 2 H, 4-H), 7.62 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.2, 14.4, 14.9, 22.9, 38.3, 105.6, 122.0, 122.5, 133.3, 134.7, 135.4, 136.5, 137.0, 138.9, 150.0, 157.6, 185.4 ppm. EI, 70 eV): *m*/*z* (%) = 556.14 (50) $[M]^+$, 541.11 (57) $[M - CH_3]^+$. HRMS: found for $C_{33}H_{32}O_4S_2$ [*m*/*z*]: 556.17530, calcd. [*m*/*z*]: 556.17420, deviation [mmu]: 1.10, [ppm]: 1.98.

Chalcone 19: KOH (380 mg, 6.77 mmol); 2-acetyl-5-methylthiophene (**10**) (270 mg, 1.93 mmol); reflux for 8 h; yield 212 mg (0.38 mmol, 60%); R_f = 0.43 (cyclohexane/ethyl acetate); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.97 (s, 6 H, 3-H), 2.06 (m, 2 H, 1-H), 2.53 (s, 6 H, 9-H), 2.78 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2-H), 6.80 (d, $^3J_{H,H}$ = 3.2 Hz, 2 H, 8-H), 6.97 (d, $^3J_{H,H}$ = 15.1 Hz, 2 H, 5-H), 7.00 (s, 2 H, 4-H), 7.60 (d, $^3J_{H,H}$ = 3.8 Hz, 2 H, 7-H), 7.76 (d, $^3J_{H,H}$ = 15.7 Hz, 2 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.9, 16.1, 22.9, 38.3, 119.3, 126.9, 132.1, 133.5, 134.7, 135.9, 136.4, 137.0, 139.2, 143.5, 149.8, 181.2 ppm. EI, 70 eV): *m*/*z* (%) = 560.08 (43) $[M]^+$, 545.05 (72) $[M - CH_3]^+$, 125.00 (100) $[C_6H_5OS]^+$. HRMS: found for $C_{31}H_{28}O_2S_4$ [*m*/*z*]: 560.09710, calcd. [*m*/*z*]: 560.09721, deviation [mmu]: 0.11, [ppm]: 0.20.

Acknowledgments

This work was supported by the Biophotonics Initiative of the German Ministry of Research and Education (BMBF) (grants 13N9234).

[1] M. Irie, *Chem. Rev.* **2000**, *100*, 1658–1716.
[2] J. Areephong, W. R. Browne, N. Katsonis, B. L. Feringa, *Chem. Commun.* **2006**, 3930–3932.
[3] H. Tian, S. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97.
[4] M. M. Krayushkin, V. A. Barachevsky, M. Irie, *Heteroatom Chemistry* **2007**, *18*, 557–567.

[5] O. Tosic, K. Altenhöner, J. Mattay, *Photochem. Photobiol. Sci.* **2010**, *9*, 128–130.
[6] L. N. Lucas, J. van Esch, R. M. Kellogg, B. L. Feringa, *Chem. Commun.* **1998**, 2313–2314.
[7] Manfred Hesse, Herbert Meier, Bernd Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, Thieme, Stuttgart, Germany, **2002**, 6th ed., p. 110.
[8] T. Yanami, A. Ballatore, M. Miyashita, M. Kato, A. Yoshikoshi, *J. Chem. Soc. Perkin Trans. 1* **1978**, *10*, 1144–1146.
[9] J. Drage, K. P. C. Vollhardt, *Organometallics* **1985**, *4*, 389–393.
Received: May 19, 2010
Published Online: August 25, 2010

