EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800101

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800101

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10.1002/ejoc.201800101

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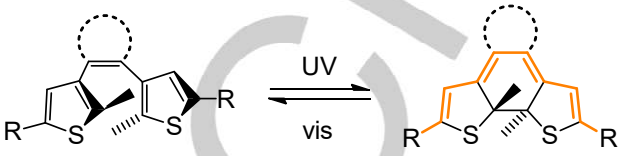
FULL PAPER

Photo-switchable π-extended dithienylethenes with an attached molecular recognition site

Iris Bittner,[a] and Ulrich Lüning*[a]

Abstract: Photo-switchable dithienylethenes have been extended in positions 5 and 5' with π-systems resulting in absorptions of light with longer wavelengths when electrocyclization and -reversion are carried out. The extended π-systems also improve conductivities potentially. *cis*-Orientation of the thienyl rings was accomplished by integrating the central double bond into maleic imides. The nitrogen atoms of the imides were substituted by a Hamilton receptor allowing supramolecular binding of complementary guests such as barbiturates. Both, a stiff and a flexible connection between photo-switch and receptor was realized. The resulting photo-switches showed reversible switching over several cycles and were able to bind diethyl barbiturate with binding constants of >10^4 M^{-1}.



Scheme 1. Electrocyclic ring-closure and –reversion for 2,2'-dimethylated dithienylethenes. Due to the conjugation in the cyclized form (right, indicated in orange), light of longer wavelength (vis) can be used for the back reaction than needed for the electrocyclization (UV). To guarantee a *cis*-orientation of the central double bond in the hexatriene (left), this double bond is part of a cyclic system.

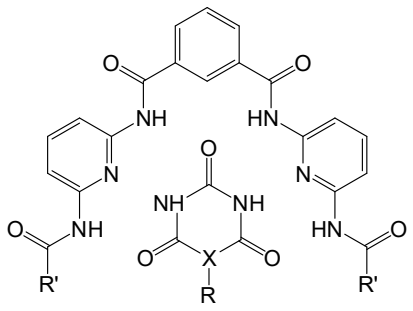
Introduction

The trend to miniaturize machinery more and more has reached nanometer dimensions.[1] Distinct manipulation of nanodevices is possible if one type of molecule can be addressed selectively in the presence of others. A control is possible by the application of suitable external forces. These can be of physical (e. g. electromagnetic fields) and chemical (pH, redox potential, a. s. o.) nature. Light is especially attractive because it interacts residue-free and a photon contains enough energy for a chemical transformation.[2]

Consequently, numerous photo-switches have been developed. Their switching reactions exploit different types of mechanisms, for instance *trans/cis* isomerizations (azobenzenes) or electro-cyclizations/-reversions (spiropyrans, diarylethenes).[3,4,5] Among the latter, 2,2'-dimethyl substituted dithienylethenes have been used prevailingly for the following reasons. (i) The electrocyclization of the hexatriene systeme in a diarylethene destroys the aromatic system in the aryl units. Rearomatization of the arene rings is a strong driving force for the back reaction. Thiophenes possess a smaller aromatic stabilization than benzene rings.[6] Therefore, thiophenes are preferred over benzenes. (ii) After cyclization, the central cyclohexadiene ring may gain stability by dehydrogenation (oxidation) to a benzene ring. Such a loss of hydrogen is not possible in the dimethylated systems.

In simple diarylethenes, the central double bond may isomerize from *cis* to *trans* and vice versa. Integration of this double bond into a cycle guarantees the *cis*-orientation of the outer double bonds. But this *cis*-orientation, and especially when the thienyl rings are carrying two methyl substituents at position 2 and 2', leads to a twist in the molecule. The central triene cannot be planar, and a conjugation through the entire molecule is not possible. In contrast after electrocyclization, the remaining four double bonds are conjugated (scheme 1). Substituents R in 5- and 5'-position may extend the π-system. The HOMO-LUMO gap will shrink upon electrocyclization leading (i) to a red shift in the absorption spectrum but (ii) also to an increased conductivity in assemblies of dithienylethenes.[2,7,8]

Therefore, we wanted to equip these photo-switches with a binding unit in order to be able to connect them to surfaces, nanoparticles or dendrimers, preferentially by connecting the switch via the central ring to the recognition site. Self-assembly exploits reversible (supramolecular) connections. In this work, a system which operates by multiple hydrogen bonds has been chosen: the Hamilton receptor/isocyanuric acid or barbituric acid pair.[9] The V-shaped isophthalic acid derivative of the Hamilton receptor possesses six hydrogen bond donors and acceptors prearranged for the binding of a barbiturate or isocyanuric acid derivative as a guest.



Scheme 2. A bis(acylaminopyridineamide) of isophthalic acid (Hamilton receptor) possesses six hydrogen bond donors and acceptors in a V-

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arrangement. Complementary guests are isocyanuric acids (X-R = NR') and barbituric acids (X-R = CR'_2), see scheme 10.

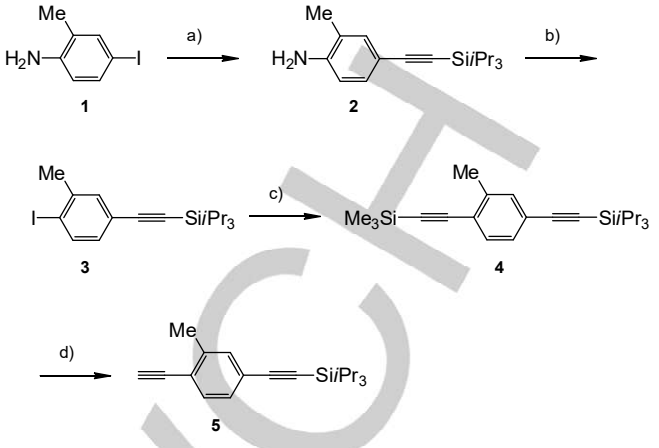
Results and Discussion

The envisioned photo-switches combine several building blocks: a diarylethene as the switching entity, extended π-systems, a central ring to ensure the *cis*-orientation of the aryl rings, and a supramolecular recognition unit. The synthetic strategy outlined in detail below realizes the following concept: as the core, a dithienyl substituted maleic anhydride or a respective maleimide had to be synthesized. Then, the supramolecular recognition unit, a Hamilton receptor, substituted with functional groups complementary to the anhydride or imide functionality had to be connected with the dithienyl moiety. Finally, the π-systems had to be added.

Extended π-systems

A conjugated π-system needs sp^2 or sp hybridized carbon atoms. Therefore, arenes, alkenes and alkynes can be combined. However, when aromatic units are connected directly, steric repulsion leads to a twist in the biphenyl subunits which somewhat diminishes the conjugation. Therefore, aryl-alkynyl connections were chosen in this work. In order to allow a further elongation of the π-system, the outermost alkynes in the final switches were silyl-protected.

Extended π-systems are flat and are able to stack on top of one another. This often leads to solubility problems. Adequate substitution, however, can improve the solubility. In the case of extended azo compounds,[10] we discovered that already the introduction of one methyl group raises the solubility. A single methyl group shapes the π-system less symmetric which in turn leads to an entropic penalty when the compound has to get oriented in the crystallization process. A symmetric dimethylation was less effective with regard to an increase in solubility.[10] Therefore, the synthesis of the π-building block for the switches started from commercially available mono-methyl 4-iodoaniline **1**. In a first Sonogashira coupling, the iodide in **1** was exchanged by a triisopropylsilyl protected ethynyl group. In 91 % yield, aniline **2** was obtained which was then converted to iodide **3** via diazotation and N_2^+/iodine exchange (Sandmeyer analogous reaction) in 76 % yield. This introduction of iodine allowed a second Sonogashira reaction, this time with trimethylsilyl protected ethyne. The unsymmetrically di-protected diethynylarene **4** was obtained in 90 % yield. In the final step, the trimethylsilyl protecting group was removed selectively due to the lower stability of a $SiMe_3$ protecting group in comparison to a $Si\mathit{i}Pr_3$ group. Mono-protected diethynylarene **5** was obtained quantitatively.



Scheme 3. Synthesis of the extended π-system. a) Tris(methylethyl)silylethyne, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, room temp., 91 %. b) (i) $NaNO_2$/HCl, acetone, 0 – 5 °C; (ii) KI, 50 °C, 76 %. c) Trimethylsilylethyne, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3, room temp., 90 %. d) K_2CO_3, MeOH, room temp., quant.

Hamilton receptors

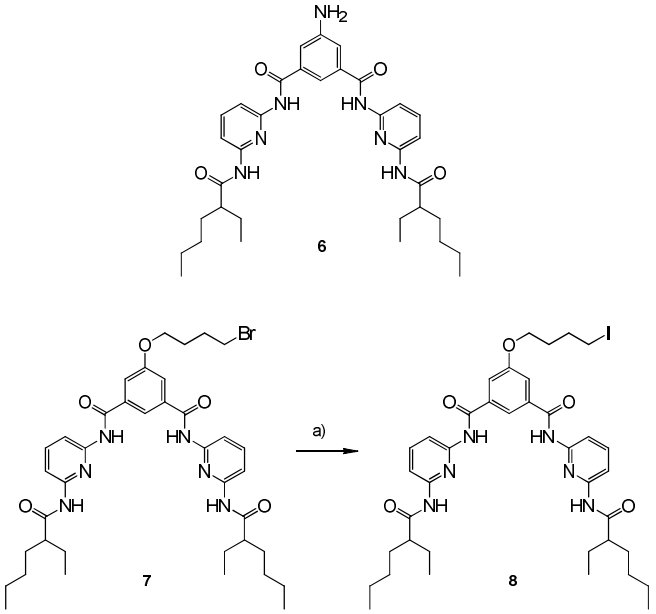
The central cyclopentane ring in a dithienyl switch often carries fluorine atoms to avoid side reactions, especially in the allylic positions. Alternatively, maleic acid derivatives can be used.[11] In particular, maleic imides allow a connection of the photoswitch to the desired recognition units.[12, 13] A respective connection can be established by reacting an anhydride with a primary amine or by alkylation of a preformed imide. Therefore, imide **17** and the respective anhydride **19** are interesting building blocks.

Depending on the connecting moiety, a stiff or a flexible connection can be established between the photoswitch and the recognition unit. Condensation of the anhydride **19** with an amine or alkylation of the imide **17** with an electrophile may introduce a recognition site, a Hamilton receptor in this work.

Hamilton receptors possess six hydrogen bond donors and acceptors. In addition, the receptors contain the amide carbonyl groups as additional hydrogen bond acceptors sites. This hydrogen bond donor and acceptor density combined with the flat structure of the Hamilton receptor is critical for a good solubility in non-polar solvents which in turn are necessary for a high binding constant between the Hamilton receptors and a respective guest. Therefore, a variant of the Hamilton receptor was chosen in which the outer amides were formed from 2-ethylhexanoic acid.[14] This substitution not only enhances solubility due to the branched nature of the residues. Each substituent contains a chiral center. The resulting Hamilton receptors therefore exist as a mixture of diastereoisomers increasing solubility even more.

As the reaction partner for maleic anhydride **19**, the literature known amino-substituted Hamilton receptor **6** was chosen for the condensation to the respective imide (vide infra). In contrast to the anhydride **19**, the nitrogen atom is already present in the five-membered imide ring of **17**. The acidity of the NH group in the imide allows alkylation of this position with a respective electrophile. A bromobutoxy substituted Hamilton receptor **7** has already been described in the literature.[14] In order to enhance its

electrophilicity, the bromide was substituted by iodide in a Finkelstein exchange yielding iodide **8** in 83 % yield.

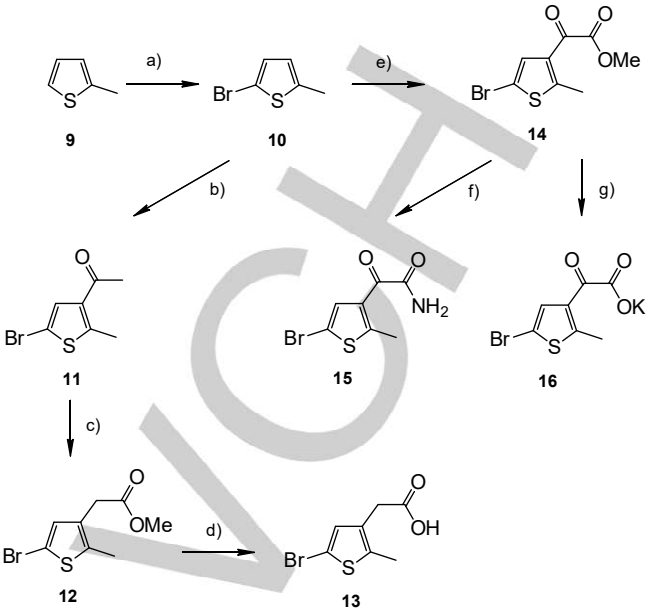


Scheme 4. Hamilton receptors **6** and **8**. a) KI, acetone, room temp., 83 %.

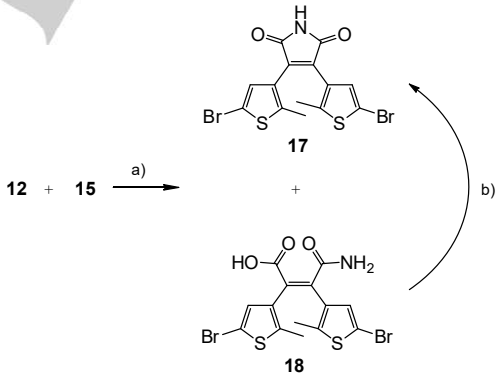
Dithienylethenes

The maleic acid derived dithienylethenes had to be 5,5'-disubstituted in order to allow the final extension of the π-system. Therefore, bromine substituents were chosen to allow cross coupling reactions such as a Sonogashira reaction with alkyne **5**.[15]

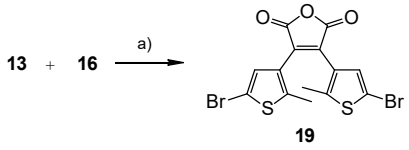
First, 2-methylthiophene (**9**) was brominated in 5-position to give 2-bromo-5-methylthiophene (**10**). Then, substituents were introduced in 3-position to allow the synthesis of the maleic acid derivatives **17** and **18**. The double bonds of the maleic acid derivatives were synthesized by condensation reactions. Thus, one thiophene had to carry a CH-acidic methylene group, the other one a carbonyl unit next to the heteroaromatic ring. Schemes 5 to 6 illustrate the reaction sequences.



Scheme 5. Substituted thiophenes. a) NBS, DMF, dark, room temp., 85 %. b) Ac_2O, $SnCl_4$, toluene, room temp., 89 %. c) $Tl(NO_3)_3$, $HClO_4$, MeOH, room temp., 83 %. d) NaOH, EtOH, room temp., 83 %. e) MeOOC-COCl, $AlCl_3$, CH_2Cl_2, 0 °C -> room temp., 68%. f) NH_4OH, THF, 0 °C -> room temp., 80 %. g) KOH, EtOH, room temp., 80 %.



Scheme 6. a) KO*t*Bu, room temp., 8 % **17** and 31 % **18**. b) Ac_2O, NaOAc, 80 °C, 98 %.



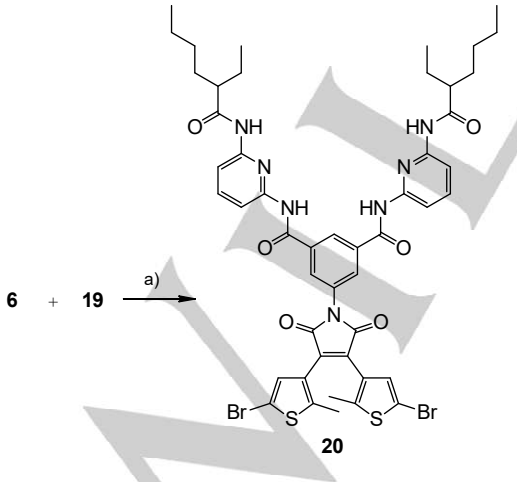
Scheme 7. a) Ac_2O, 110 °C, 32 %.

The CH-acidic building block **12** was obtained by an oxidative rearrangement of the acetyl substituted thiophene **11**. Its synthesis from 2-bromo-5-methylthiophene (**10**) could be performed with 89 % yield (51 % [16]). Reaction of the

acetylthiophene **10** with thallium(III) nitrate resulted in an oxidative rearrangement and thienylacetate **12** was obtained in 83 % yield. Please note that **12** cannot be stored without decomposition which asks for quick usage of this building block.
The reaction partners of **12** for the synthesis of the maleic anhydride **19** and imide **17** were also synthesized from bromomethylthiophene **10**. Reaction with methyl oxalylchloride gave methyl thienyloxoacetate **14** in 68 % yield. Aminolysis of ester **14** produced oxoamide **15** in 80 % yield.
The CH-acidic thienyl derivative **12** was then reacted with oxoamide **15** in the presence of *tert*-butanolate thus establishing the double bond of the maleic acid subunit. During this reaction, some ester and amide groups reacted to give the desired imide **17** but the product could only be isolated in 8 % yield. Most condensation product was not cyclized and 31 % of a maleic acid half amide **18** could by isolated as well. During the work-up, apparently, the methyl ester had been hydrolyzed to give the half-amide half-ester **18**. Using acetic anhydride to promote dehydration, **18** could be cyclized to the desired imide **17** in excellent yield (98 %).
The related maleic anhydride **19** was synthesized from acid **13** and potassium salt **16**. These building blocks were obtained from the esters **12** and **14**, respectively, by alkaline hydrolysis. Condensation of the CH acidic component **13** with carbonyl compound **16** and subsequent cyclization to the anhydride **19** were performed by heating in acetic anhydride.

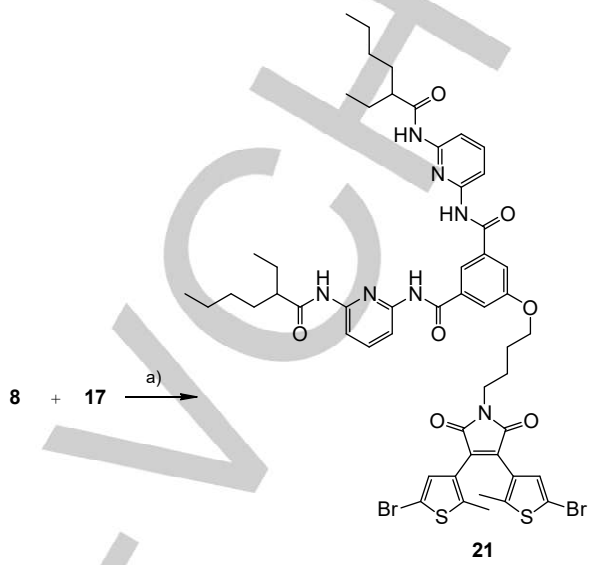
Hamilton substituted dithienylethenes

With imide **17** and anhydride **19** in hand, it was now possible to connect respective Hamilton receptors (**8** and **6**) with the dithienylethene photo-switch. When anhydride **19** was heated with Hamilton aniline **6**, the respective imide **20** was formed in 88 % yield. In this Hamilton receptor containing photo-switch, the two sub-units are directly connected. A stiff system is obtained.



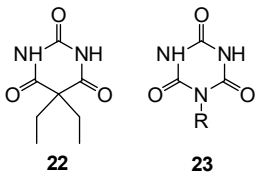
Scheme 8. a) Et_3N, 110 °C, 86 %.

In contrast to stiff **20**, the alkylation of imide **17** with Hamilton iodide **8** led to a product **21** (46 % yield) in which the Hamilton sub-unit and the dithienylethene are connected by a butoxy chain allowing conformational freedom between the two sub-units.



Scheme 9. a) KO*t*Bu, room temp., 65 °C, 46 %.

At this stage of the synthesis, the switching and binding properties of the stiff and the flexible Hamilton containing switches **20** and **21** were investigated. The Hamilton receptor binds via six hydrogen bonds (vide supra) either barbiturates such as diethyl barbital **22** or isocyanuric acid derivatives **23** as guests. In related hydrogen bond arrays, isocyanurates bind more tightly than barbitals.[17]



Scheme 10. Potential guests for Hamilton receptors: diethyl barbiturate (**22**) or isocyanuric acids **23**.

In the binding tests with **20** and **21**, diethyl barbiturate (**22**) was used because any decrease in binding would have a more distinct influence with the less binding guest. The titrations were performed in $CDCl_3$ and were analyzed by ^1H NMR. For both combinations (**20**·**22** and **21**·**22**), very strong binding was found (see supporting information, Fig SI-1 and SI-2). The magnitude of the resulting K_{ass} values was at the limit of NMR titrations. With certainty, it can be stated that the values exceed 10^4 M^{-1}, the regressions gave values of ca. 20000 M^{-1}. In comparison with the literature values[14] (also 10^4 M^{-1} and larger), no negative influence by the attached dithienylethene on the binding properties could be detected.

The photo-switching behaviour of **20** and **21** was tested at 25°C in dichloromethane. The solutions were irradiated alternatingly with light of wavelengths of 311 and 520 nm. Figures 1 and 2 show the UV spectra and the extinctions at 508 nm (**21**) and 525 nm (**20**), respectively, for several cycles of irradiations. The existence of isosbestic points in Figures 1a and 2a as well as the almost non-changing extinctions in Figures 1b and 2b were promising that the elongated final target photo-switches would behave as desired.

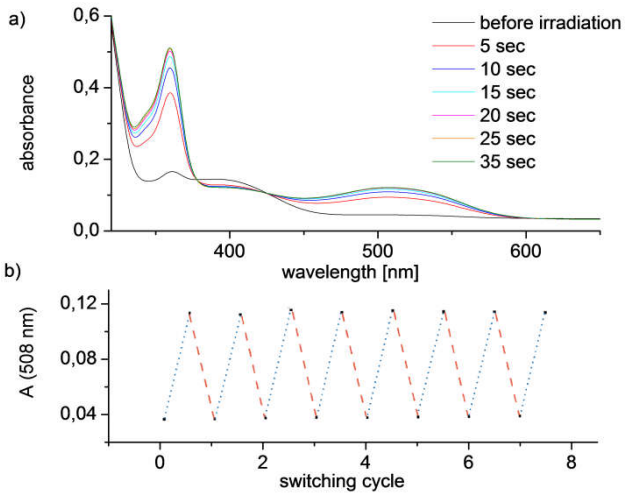


Figure 1. a) Overlay of UV spectra of flexible photo-switch **21** obtained while irradiating with 311 nm light until the photostationary state was reached. b) Alternating irradiation of **21** with 311 nm light (20 sec, dotted, blue) and 520 nm light (5 min, dashed, red). Detection at 508.0 nm.

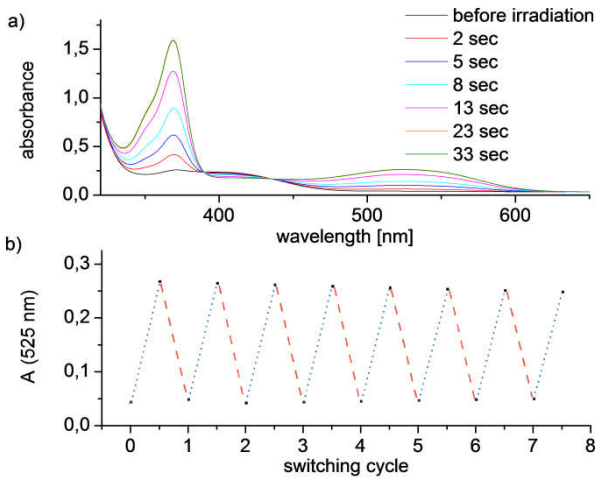
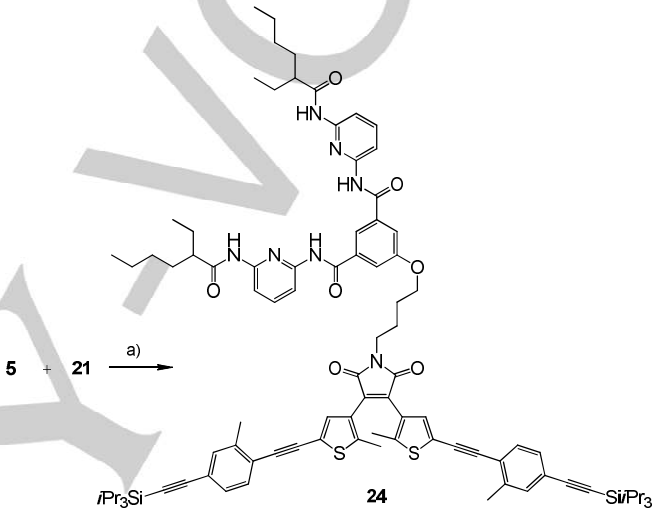


Figure 2. a) Overlay of UV spectra of stiff photo-switch **20** obtained while irradiating with 311 nm light until the photostationary state was reached. b) Alternating irradiation of **20** with 311 nm light (40 sec, dotted, blue) and 520 nm light (5 min, dashed, red). Detection at 524.5 nm.

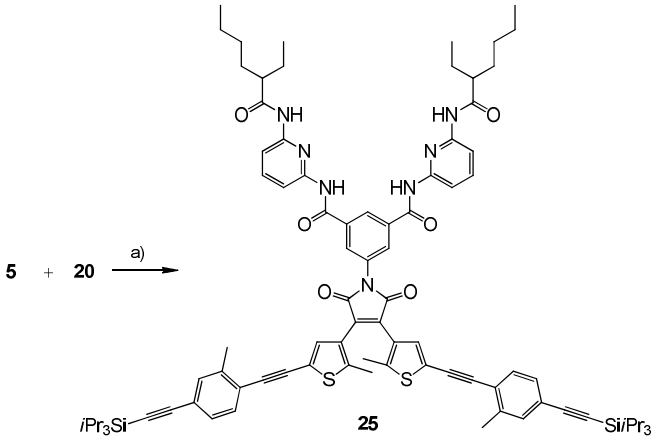
Hamilton receptor substituted dithienylethenes with elongated π-systems

The final task was to extend the photo-switches **20** and **21** with π-systems in the 5- and 5'-positions of the thienyl rings. Two equivalents of dialkynylarene **5** were reacted with flexible switch **21** under Sonogashira conditions. After 3 days at 50 °C, the desired tetraalkyne **24** could be isolated in 40 % yield. It must be noted that starting material **21**, the mono-coupled intermediate and the desired product **24** are quite similar concerning their chromatographic behaviour.



Scheme 11. a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, NEt_3, 50 °C, 40 %.

Analogously, the stiff switch **20** was reacted with two equivalents of the alkyne **5**. The reaction was slow, ca. 50 % of the starting material **20** was recovered. But 9 % of the desired photo-switch **25** were isolated, too.



Scheme 12. a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, NEt_3, 50 °C, 9 %.

The photo-switching of both π-extended dithienylmaleic acid derivatives **24** and **25** was investigated next using conditions comparable to those applied to the precursors **21** and **20**. Again, light with a wavelength of 311 nm was used to close the photo-switch. Figures 3a and 4a show the decrease of the starting materials upon irradiation and the simultaneous increase of the cyclized products. The existence of isosbestic points again argue for clean isomerization reactions. Due to the extended π-systems, the red field shift of the absorption of the cyclized product was pronounced. Therefore, 590 nm light was used for the ring-opening back reaction. In Figures 3b and 4b, several cycles of ring-closing and ring-opening have been followed. Very little fatigue could be observed. A close inspection of the extinctions show that the first cycle started from a larger extinction than the following ones indicating that the samples of open starting materials **24** and **25** already contained some cyclized product. Presumably, the energy of the ambient light was sufficient to cyclize the π-extended systems **24** and **25**. In Figure 3b, the extinctions of cyclized **24** in cycles 7 to 9 differ from those of cycles 1 through 6. Due to a defect in the spectrometer, the investigation has to be paused, some solvent evaporated and when the cuvette was refilled with solvent not the identical concentration was reached.

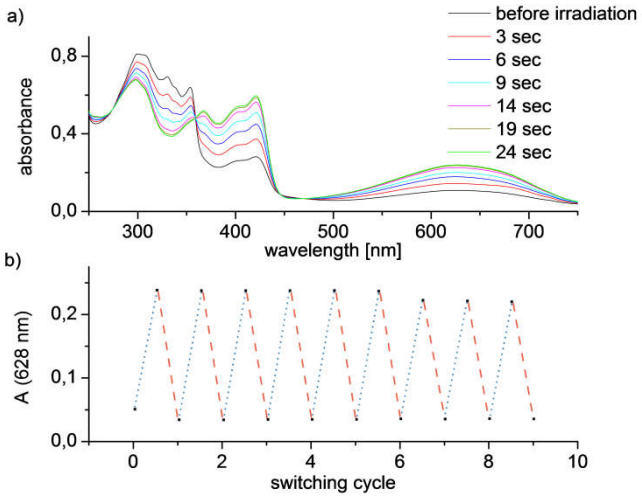


Figure 3. a) Overlay of UV spectra of flexible photo-switch **24** obtained while irradiating with 311 nm light until the photostationary state was reached. b) Alternating irradiation of **24** with 311 nm light (40 sec, dotted, blue) and 590 nm light (15 min, dashed, red). Detection at 628 nm.

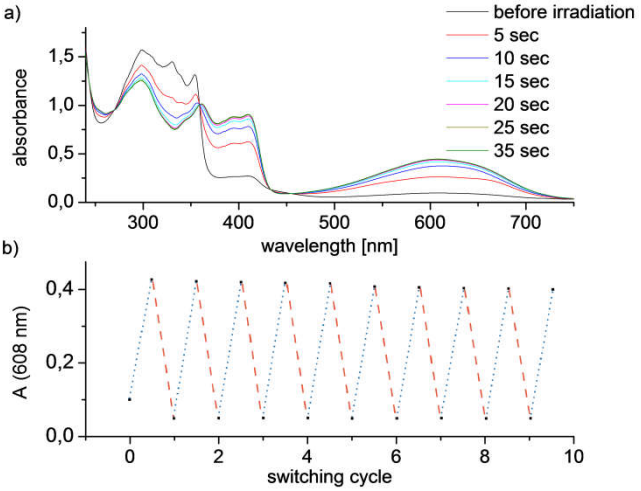


Figure 4. a) Overlay of UV spectra of stiff photo-switch **25** obtained while irradiating with 311 nm light until the photostationary state was reached. b) Alternating irradiation of **25** with 311 nm light (30 sec, dotted, blue) and 590 nm light (15 min, dashed, red). Detection at 608 nm.

Table 1 compares the dithienyl switches investigated in this work. The elongation of the system by additional π-systems not only had an influence on the absorption maxima (see also Figures 3 and 4) but on the extinction coefficients, too. Furthermore, the switching of the dithienylethenes **24** and **25** is more complete especially towards the closed form.

Table 1. Comparison of the photo-switching dithienylethenes. Wavelengths of red-most maximum and extinction coefficient, and open/closed ratios determined by NMR.

photo-switch	λ_{max} [nm] (ε [10^4 $M^{-1}cm^{-1}$])	open/closed after synthesis (or long wave irradiation)	open/closed at PSS[a] when UV irradiated
17	546.5 (1.06)	99:1	27:73
19	547.5 (1.13)	97:3	23:77
20	524.5 (1.37)	95:5	36:64
21	508.0 (1.25)	97:3	40:60
22	607.5 (3.30)	88:12 (94:6)	6:94
23	627.5 (3.12)	63:37 (91:9)	7:93

[a] Photostationary state.

Finally, the supramolecular complex formation with barbiturates had to be checked for **24** and **25**. Because hardly any differences could be found for the binding of diethyl barbiturate to several Hamilton receptors including the dithienylethenes **19** and **20** (see above), attention was paid to the binding behaviour of the cyclized form. A $CDCl_3$ solution of photo-switch **25** was placed in a NMR tube and a NMR spectrum was recorded. Figure 5 shows the methyl part of the ^1H NMR. As discussed above, ambient light is able to cyclize **25** in part. This becomes obvious in the NMR spectrum as well [red spectrum (a)]. Then, the sample was irradiated with 311 nm light. NMR measurements and irradiations were performed until the photostationary state was reached [green (b) and blue (c) spectra]. Diethyl barbiturate (**22**) was added in portions and a titration isotherm was recorded (see supporting information, Figure SI-3). Also for the cyclized form of **25**, a value $>10^4$ M^{-1} (single measurement: 18000 M^{-1}) for the binding of barbiturate **22** to the Hamilton receptor in **25** was obtained. This measurement shows that the binding of a barbiturate guest is strong regardless whether the photo-switch exist in its open or its closed form.

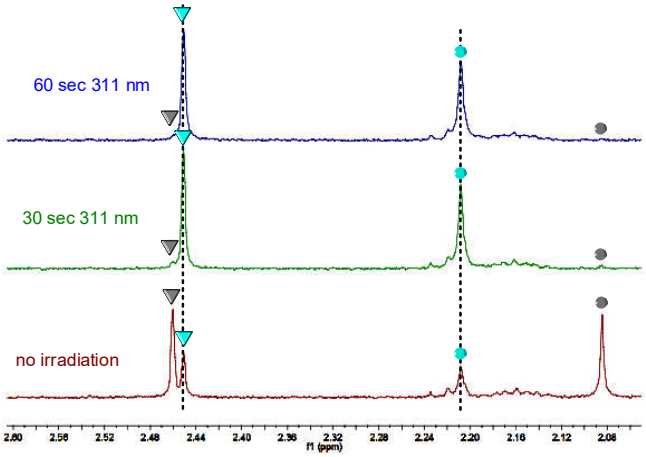


Figure 5. Excerpt of ^1H NMR spectra of **25** in $CDCl_3$ a) without, b) after 30 sec, and c) after 60 sec of irradiation with 311 nm light. Grey: open triene; light blue: cyclized photo-switch.

Conclusions

Dithienyl substituted maleimides were furnished with a supramolecular binding unit (Hamilton receptor) and two dialkynylarene substituents which extend the π-system. Two systems (**24** and **25**) were synthesized which differ in the type of connection between Hamilton receptor and diarylethene unit: flexible (butoxy) or stiff (direct) connection. All Hamilton substituted systems were able to bind diethyl barbiturate (**22**) effectively (K_{ass} $>10^4$ M^{-1}), also in the photo-cyclized form. All maleic acid based dithienyl photo-switches showed reversible switching behaviour, the systems were photostable for several cycles.

In future investigations, the developed photo-switches will be attached to barbiturate or isocyanuric acid covered surfaces. Photo-switching of the π-extended systems will reduce the HOMO-LUMO gap which shall facilitate electron transport between the units and thus will enhance conductivity across the surfaces.

Experimental Section

The following substances have been purchased: 4-iodo-2-methylaniline (**1**, Sigma-Aldrich), methyl oxalyl chloride (Sigma-Aldrich), bis(triphenylphosphine)-palladium(II) dichloride (ABCR), tris(methylethyl)silylethyne (VWR), trimethylsilylethyne (ABCR). Dry solvents were obtained using suitable desiccants. Other solvents were distilled before use. Column chromatography was carried out with silica gel (Macherey-Nagel, particle size 0.04–0.063 mm; Isolera One, Biotage). Melting points were measured with a Büchi 530 instrument. NMR spectra were recorded with a Bruker AC 200, DRX 500 or Avance 600 instrument at 300 K. All chemical shifts are referenced to tetramethylsilane or the residual proton or carbon signals of the solvent. Assignments are supported by COSY, HSQC, and HMBC. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. The following abbreviations have been used for the signal assigments: Ar = arene, Py: pyridine, thio: thiophen. HRMS-EI mass spectra were recorded with JEOL AccuTOF GCV 4G. MALDI-TOF mass spectra were recorded with a Bruker-Daltronics Biflex III with Cl-CCA (4-chloro-α-cyanocinnamic acid) as matrix. IR spectra were recorded with a Perkin-Elmer Spectrum 100 spectrometer equipped with a Golden Gate Diamond ATR unit A-531-G. Elemental analyses were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector. UV-vis spectroscopy was carried out with a Lambda 14 spectrometer (Perkin-Elmer) equipped with a Büchi thermostat. 311 nm was generated with a mercury lamp. Light of longer wavelength was produced with LEDs (508 nm, 520 nm, 590 nm) from Sahlmann Photochemical Solutions. The samples were placed 2 cm from the light sources.

2-Methyl-4-(tris[methylethyl]silylethynyl)-aniline (2)
Under nitrogen, tris[methylethyl]silylethyne (5.30 mL, 23.6 mmol) was added dropwise to a mixture of 4-iodo-2-methylaniline (**1**, 5.26 g, 22.6 mmol), bis(triphenylphosphine)palladium(II) dichloride (125 mg, 178 µmol) and copper(I) iodide (76.0 mg, 399 µmol) in dry triethylamine (80 mL). After 20 h of stirring at room temp., the mixture was filtered, the residue was washed with ethyl acetate and the filtrate was washed with sat. aqueous ammonium chloride solution (100 mL) and brine (150 mL). The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, dichloromethane, R_f = 0.60) yielding 5.93 g (20.6 mmol, 91 %) of a yellow solid, m. p. 49 °C. ^1H-NMR (500 MHz, $CDCl_3$): δ = 7.19 (br. s, 1 H, *H*-3), 7.17 (dd, ^3J = 8.1 Hz, ^4J = 1.9 Hz, 1 H, *H*-5), 6.58 (d, ^3J = 8.1 Hz, 1 H, *H*-6), 3.84 (br. s, 2 H, NH_2), 2.13 (s, 3 H, CH_3), 1.05-1.20 (m, 21 H, $CH(CH_3)_2$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 144.8 (s, *C*-1), 134.2 (d, *C*-3), 131.1 (d, *C*-5), 121.9 (s, *C*-2), 114.4 (d, *C*-6), 113.2 (s, *C*-4), 108.1 (s, *C*≡C-Si*i*Pr$_3$), 87.2 (s, C≡*C*-Si*i*Pr$_3$), 18.7 (d, $CH(CH_3)_2$), 17.1 (q, CH_3), 11.4 (q, $CH(CH_3)_2$) ppm. ESI-MS ($CHCl_3$/MeOH): *m/z* (%) = 289 (26) $[M+H]^+$, 288 (100) $[M]^{\bullet+}$. IR (ATR): $\tilde{\nu}$ =

3459, 3378 (N-H valenz), 2941, 2863 (aliph. C-H valenz), 2141 (C≡C valenz), 1503 (arom. C=C valenz), 1465 (aliph. C-H deform.) cm^{-1}. Elemental analysis**:** $C_{18}H_{29}NSi$ (287.52) calcd. C 75.19 H 10.17 N 4.87, $C_{18}H_{29}NSi \cdot 0.25\ C_6H_{12}$ (308.56)* calcd. C 75.91 H 10.45 N 4.54, found C 75.91 H 10.48 N 4.89. The analytical sample was treated with a mixture of cyclohexane and dichloromethane.

1-Iodo-2-methyl-4-(tris[methylethyl]silylethynyl)benzene (3)

Under nitrogen at 0 °C, hydrochloric acid (37 %, 15 mL) was slowly added to a solution of 2-methyl-4-(tris[methylethyl]silylethynyl)aniline (**2**, 3.51 g, 12.2 mmol) in acetone (100 mL). During 30 min, sodium natrium nitrite (1.08 g, 15.7 mmol) in demin. water (15 mL) was added in such a way that the temp. stayed between 0 and 5 °C. After additional 1.5 h of stirrong at 0 °C, potassium iodide (6.27 g, 37.8 mmol) was slowly added. The mixture was stirred for 30 min at room temp. and then for 15 min at 50 °C. After cooling to room temp., sat. Aqueous sodium thiosulfate solution (25 mL) and dichloromethane (25 mL) wwere added. The layers were separated and the aqueous layer was extracted with dichloromethane (2 x 20 mL) and the combined organic layer was dried with magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, cyclohexane, R_f = 0.73) yielding 3.69 g (9.28 mmol, 76 %) of a clolorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, ^3J = 8.1 Hz, 1 H, *H*-6), 7.33 (d, ^4J = 2.0 Hz, 1 H, *H*-3), 6.95 (dd, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 1H, *H*-5), 2.39 (s, 3 H, CH_3), 1.14-1.10 (m, 21 H, CH(CH_3)$_2$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 141.4 (s, *C*-2), 138.8 (d, *C*-6), 132.9 (d, *C*-3), 130.6 (d, *C*-5), 123.6 (s, *C*-4), 106.1 (s, *C*≡C-Si*i*Pr$_3$), 101.1 (s, *C*-1), 91.7 (s, C≡*C*-Si*i*Pr$_3$), 27.9 (q, *C*H$_3$), 18.7 (d, *C*H(CH$_3$)$_2$), 11.3 (q, CH(*C*H$_3$)$_2$) ppm. ESI-MS ($CHCl_3$/MeOH): *m/z* (%) = 437 (100) $[M+K]^+$. IR (ATR): $\tilde{\nu}$ = 2942, 2864 (aliph. C-H valenz), 2150 (C≡C valenz), 1468 (aliph. C-H deform.), 1072 (C-I valenz) cm^{-1}. Elemental analysis: $C_{18}H_{27}ISi$ (398.40) calcd. C 54.27 H 6.83, $C_{18}H_{27}ISi \cdot 0.08\ C_6H_{12}$ (405.13), calcd. C 54.88 H 6.85, found C 54.88 H 6.91.

2-Methyl-4-(tris[methylethyl]silylethynyl)-1-(trimethylsilylethynyl)benzene (4)

Under nitrogen, trimethylsilylethyne (400 µL, 280 mg, 2.89 mmol) was added to a suspension of 1-iodo-2-methyl-4-(tris[methylethyl]silylethynyl)benzene (**3**, 1.00 g, 2.51 mmol), bis(triphenylphosphine)-palladium(II) dichloride (17 mg, 24 µmol) and copper(I) iodide (9.0 mg, 47 µmol) in dry triethylamine (15 mL). After stirring for 20 h at room temp., the mixture was filtered and the residue was washed with cyclohexane. The filtrate was washed with demin. water (3 x 15 mL), dried with sodium sulfate and the solvent was evaporated in vacuo. Colmun chromatography (silica gel, cyclohexane, R_f = 0.67) yielded 837 mg (2.27 mmol, 90 %) of a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ* = 7.34 (d, ^3J = 8.0 Hz, 1 H, *H*-6), 7.30 (br.s, 1 H, *H*-3), 7.22 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, *H*-5), 2.39 (s, 3 H, CH_3), 1.13-1.11 (m, 21 H, CH(CH_3)$_2$), 0.26 (s, 9 H, Si(CH_3)$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): *δ* = 140.7 (s, *C*-2), 133.0 (d, *C*-3), 132.1 (d, *C*-6), 129.3 (d, *C*-5), 123.6 (s, *C*-4), 123.2 (s, *C*-1), 107.1 (s, *C*≡C-Si*i*Pr$_3$), 103.8 (s, *C*≡C-SiMe$_3$), 100.3 (s, C≡*C*-SiMe$_3$), 92.4 (s, C≡*C*-Si*i*Pr$_3$), 20.6 (q, *C*H$_3$), 18.9 (q, CH(*C*H$_3$)$_2$), 11.5 (d, *C*H(CH$_3$)$_2$), 0.2 (q, Si(*C*H$_3$)$_3$) ppm. MS (EI, 70 eV): *m/z* = 368 (20) $[M]^{\bullet+}$, 325 (100) $[M-C_3H_7]^+$. IR (ATR): $\tilde{\nu}$ = 2960, 2943, 2865, 2893 (aliph. C-H valenz), 2151 (C≡C valenz), 1603 (C=C valenz), 1463 (aliph. C-H deform.), 289 (1,2,4-trisubst. arom.) cm^{-1}. HRMS (EI): $^{12}C_{23}{}^{1}H_{36}{}^{28}Si_2$ calcd. 368.2356, found 368.2352 (Δ: 0.86 ppm). Elemental analysis: $C_{23}H_{36}Si_2$ (368.70) calcd. C 74.92 H 9.84, $C_{23}H_{36}Si_2 \cdot 0.125\ H_2O$ (370.95) ,calcd. C 74.47 H 9.85,. found C 74.49 H 10.07.

4-Ethynyl-3-methyl-1-(tris[methylethyl]silylethynyl)benzene (5)

Under nitrogen, potassium carbonate (236 mg, 1.71 mmol) was added to a solution of 2-methyl-4-(tris[methylethyl]silylethynyl)-1-(trimethylsilylethynyl)benzene (**4**, 225 mg, 610 µmol) in a mixture of dry methanol (20 mL) and dry dichloromethane (3 mL). The mixture was stirred for 17 h at room temp. After addition of demin. water (50 mL) and ethyl acetate (30 mL), the layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with demin. water (30 mL), dried with sodium sulfate, and the solvent was removed in vacuo yielding 180 mg (610 µmol, 100 %) of a yellow oil which was used without further purification to avoid decomposition. ^{1}H-NMR (200 MHz, $CDCl_3$): *δ* = 7.38 (d, ^3J = 8.0 Hz, 1 H, *H*-6), 7.32 (br. s, 1 H, *H*-3), 7.24 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1 H, *H*-5), 3.34 (s, 1 H, C≡C-*H*), 2.42 (s, 3 H, CH_3), 1.15-1.10 (m, 21 H, CH(CH_3)$_2$) ppm. Due to the quick decomposition of 11, no ^{13}C-NMR was recorded. MS (EI, 70 eV): *m/z* = 296 (24) $[M]^{\bullet+}$, 253 (100) $[M-C_3H_7]^+$. IR (ATR): $\tilde{\nu}$ = 3298 (C-H valenz, alkyne), 2952, 2942, 2891, 2865 (aliph. C-H valenz), 2149 (C≡C valenz), 1602, 1491 (C=C valenz, arom.), 1462 (aliph. C-H deform.), 829 (1,2,4-trisubst. arom.) cm^{-1}. HRMS (EI): $^{12}C_{20}{}^{1}H_{28}{}^{28}Si$ calcd. 296.1960, found 296.1957 (Δ: 1.00 ppm).

5-(4-Bromobutoxy)-1,3-benzenedicarboxylic acid dichloride

Under nitrogen, 5-(4-bromobutoxy)-1,3-benzene dicarboxylic acid[14] (113 mg, 356 µmol) and triphenylphosphine (3.0 mg, 0.01 mmol) were heated to reflux in thionylchloride (15 mL) for 1 h. After cooling to room temp., excess thionylchloride was removed with a flow of nitrogen at 60 °C. The crude product (126 mg) was used without further purification.

5-(4-Bromobutoxy)-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (7)

Under nitrogen, a solution of 5-(4-bromobutoxy)-1,3-benzenedicarboxylic acid dichloride (crude, 126 mg) in dry tetrahydrofuran (10 mL) was added dropwise during 1 h to a cold solution (0 °C) of *N*-(6-aminopyrid-2-yl)-2-ethylhexanoylamide[14] (170 mg, 722 µmol) in dry tetrahydrofuran (20 mL) and dry triethylamine (1.2 mL). After 1 h of stirring at 0 °C, the reaction was stopped by addition of demin. water (15 mL). The mixture was extracted with ethyl acetate (15 mL), dried with sodium sulfate and the solvent was evaporated in vacuo. Column chromatography (silica gel, cyclohexane/ethyl acetate (3:1), R_f = 0.16) yielded 173 mg of a colorless solid which contained some unknown impurities. M. p.: 98 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): *δ* = 8.40 (br. s, 2 H, ArCON*H*), 8.02 (d, ^3J = 8.2 Hz, 4 H, Py-*H*-3,5), 7.98 (br. s, 1 H, Ar-*H*-2), 7.80 (br. s, 2 H, N*H*COCH), 7.76 (t, ^3J = ~8 Hz, 2 H, Py-*H*-4), 7.61 (d, ^4J = 1.4 Hz, 2 H, Ar-*H*-4,6), 4.10 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 3.50 (t, ^3J = 6.5 Hz, 2 H, CH_2Br), 2.18 (m_c, 2 H, COC*H*), 2.12-2.04 (m, 2 H, CH_2CH$_2$Br), 2.02-1.96 (m, 2 H, OCH$_2$CH_2), 1.79-1.68 (m, 4 H, CHCH_aH$_b$CH$_2$, CHCH_aH$_b$CH$_3$), 1.64-1.55 (m, 2 H, CHCH$_a$*H*$_b$CH$_3$), 1.57-1.49 (m, 2 H, CHCH$_a$*H*$_b$CH$_2$), 1.37-1.28 (m, 8 H, CH_2CH_2CH$_2$CH$_3$), 0.97 (t, ^3J = 7.4 Hz, 6 H, CHCH$_2$CH_3), 0.88 (t, ^3J = 7.0 Hz, 6 H, CH$_2$CH$_2$CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): *δ* = 174.8 (s, *C*OCH), 164.1 (s, Ar-NHCO), 159.7 (s, Ar-*C*-5), 149.7 (s, Py-*C*-2), 149.2 (s, Py-*C*-6), 141.0 (d, Py-*C*-4), 136.2 (s, Ar-*C*-1,3), 117.4 (d, Ar-*C*-2), 117.0 (d, Ar-*C*-4,6), 110.2 (d, Py-*C*-3), 109.6 (d, Py-*C*-5), 67.7 (t, O*C*H$_2$), 50.8 (d, CO*C*H), 33.1 (t, *C*H$_2$Br), 32.4 (t, CH*C*H$_2$CH$_2$), 29.8 (t, *C*H$_2$CH$_2$CH$_3$), 29.3 (t, *C*H$_2$CH$_2$Br), 27.7 (t, OCH$_2$*C*H$_2$), 26.1 (t, CH*C*H$_2$CH$_3$), 22.8 (t, CH$_2$*C*H$_2$CH$_3$), 13.9 (q, CH$_2$CH$_2$*C*H$_3$), 12.1 (q, CH*C*H$_2$CH$_3$) ppm. MS (EI, 70 eV): *m/z* = 750 (<1), 752 (<1) $[M]^{\bullet+}$, 651 (36), 653 (38) $[M-C_7H_{15}]^+$, 615 (9) $[M-C_4H_8Br]^+$. IR (ATR): $\tilde{\nu}$ = 3292 (N-H valenz, amide), 2960, 2932, 2871 (aliph. C-H valenz), 1668 (C=O valenz, amide), 1582, 1506 (C=C valenz, arom.), 1118 (C-O valenz, ether), 798 (2,6-disubst. arom.) cm^{-1}.

5-(4-Iodobutoxy)-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (8)

Potassium iodide (189 mg, 1.14 mmol) was added to a solution of 5-(4-bromobutoxy)-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (**7**, 387 mg, 515 µmol)) in dry acetone (6 mL). After stirring under nitrogen for 23 h, a solid had formed which was filtered off and washed with little acetone. The solvent of the filtrate was evaporated and the residue was purified by column chromatography (silca gel, cyclohexane/ethyl acetate (5:1), *R*f = 0.18) yielding 343 mg (429 µmol, 83 %) of a colorless solid, m. p. 95 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 2 H, ArCON*H*), 8.02 (d, ^3J = 8.1 Hz, 2 H, Py-*H*-5), 8.00 (d, ^3J = 8.0 Hz, 2 H, Py-*H*-3), 7.98 (br. s, 1 H, Ar-*H*-4), 7.95 (s, 2 H, N*H*COCH), 7.74 (br. t, ^3J = ~8 Hz, 2 H, Py-*H*-4), 7.59 (d, ^4J = 1.4 Hz, 2 H, Py-*H*-6), 4.05 (t, ^3J = 6.0 Hz, 2 H, OCH_2), 3.26 (t, ^3J = 6.8 Hz, 2 H, CH_2I), 2.20 (m_c, 2 H, COC*H*), 2.06-1.97 (m, 2 H, $OCH_2CH_2CH_2$), 1.96-1.86 (m, 2 H, $OCH_2CH_2CH_2$), 1.77-1.67 (m, 4 H, $CHCH_aH_bCH_2$, $CHCH_aH_bCH_3$), 1.64-1.54 (m, 2 H, $CHCH_aH_bCH_3$), 1.57-1.48 (m, 2 H, $CHCH_aH_bCH_2$), 1.39-1.25 (m, 8 H, $CHCH_2CH_2CH_2CH_3$), 0.97 (t, ^3J = 7.4 Hz, 6 H, $CHCH_2CH_3$), 0.87 (t, ^3J = 7.0 Hz, 6 H, $CH_2CH_2CH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.2 (s, NH*C*OCH), 164.4 (s, Ar-*C*ONH), 159.9 (s, Ar-*C*-5), 150.0 (s, Py-*C*-2), 149.4 (s, Py-*C*-6), 141.1 (d, Py-*C*-4), 136.3 (s, Ar-*C*-1,3), 117.7 (d, Ar-*C*-2), 117.2 (d, Ar-*C*-4,6), 110.5 (d, Py-*C*-3), 109.8 (d, Py-*C*-5), 67.7 (t, OCH_2), 50.9 (t, *C*H$_2$I), 32.7 (t, $COCHCH_2CH_3$), 30.2 (t, OCH_2CH_2), 30.1 (t, $OCH_2CH_2CH_2$), 26.3 (t, $CHCH_2CH_3$), 23.0 (t, $CHCH_2CH_2CH_2CH_3$), 14.2 (q, $CHCH_2CH_2CH_2CH_3$), 12.3 (q, $CHCH_2CH_3$) ppm. MS (EI, 70 eV): *m/z* = 798 (<1%) $[M]^{+\bullet}$, 670 (4) $[M\text{-HI}]^+$, 699 (11) $[M\text{-}C_7H_{15}]^+$, 615 (8) $[M\text{-}C_4H_8I]^+$, 571 (54) $[M\text{-}C_{15}H_{31}O]^+$, 128 (100) $[HI]^+$. IR (ATR): $\tilde{\nu}$ = 3421 (N-H valenz, amide), 2959, 2931, 2874, 2860 (aliph. C-H valenz), 1671 (C=O valenz, amide), 1584, 1504 (C=C valenz, arom.), 1118 (C-O valenz, ether), 799 (2,6-disubst. arom.) cm^{-1}. Elemental analysis: $C_{38}H_{51}IN_6O_5$ (798.75) calcd. C 57.14 H 6.44 N 10.52, found C 56.96 H 6.52 N 10.21.

Methyl 2-(5-bromo-2-methylthiophen-3-yl)-acetate (12)

Against a flow of nitrogen, first perchloric acid (5.00 mL, 83.1 mmol) and then 3-acetyl-5-bromo-2-methylthiophen[16] (**11**, 2.21 g, 10.1 mmol) were added to a suspension of thallium(III) nitrate trihydrate (4.60 g, 10.4 mmol) in dry methanol (40 mL). After stirring at room temp. for 22 h, the precipitate was filtered off and washed with cold methanol. The filtrate was concentrated in vacuo, diluted with demin. water (70 mL) and extracted with chloroform (3 x 40 mL) extrahiert. The combined organic layer was dried with magnesium sulfate and the solvent was removed in vacuo. Column chromatography (silica gel, cyclohexane/dichloromethane (1:1), R_f = 0.30) yielded 2.10 g (8.43 mmol, 83 %) of a colorless oil. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.85 (s, 1 H, *H*-4), 3.70 (s, 3 H, OCH_3), 3.48 (s, 2 H, CH_2), 2.32 (s, 3 H, thio-CH_3) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 171.3 (s, *C*=O), 137.4 (s, *C*-3), 131.9 (d, *C*-4), 130.1 (s, *C*-2), 107.7 (s, *C*-5), 52.4 (q, OCH_3), 33.8 (t, *C*H$_2$), 13.3 (q, thio-*C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 248 (6), 250 (7) $[M]^{+\bullet}$, 234 (50), 236 (51) $[M\text{-}CH_2]^+$, 189 (98), 191 (100) $[M\text{-}C_2H_3O_2]^+$. HRMS (EI): $^{12}C_8{}^1H_9{}^{79}Br^{16}O_2{}^{32}S$: calcd. 247.9507, found 247.9506 (Δ: 0.22 ppm). $^{12}C_8{}^1H_9{}^{81}Br^{16}O_2{}^{32}S$: calcd. 249.9486, found 249.9494 (Δ: 2.92 ppm). IR (ATR): $\tilde{\nu}$ = 3085 (arom. C-H valenz), 2951, 2923, 2847 (aliph. C-H valenz), 1735 (C=O valenz, ester), 1434 (aliph. C-H deform.), 1193, 1168 (C-O valenz, ester) cm^{-1}. Elemental analysis: $C_8H_9BrO_2S$ (249.12) calcd. C 38.57 H 3.64 S 12.87, $C_8H_9BrO_2S \cdot 0.25\ H_2O$ (253.63) calcd. C 37.88 H 3.78 S 12.64, found C 37.93 H 3.57 S 12.42.

2-(5-Bromo-2-methylthiophen-3-yl)-acetic acid (13)

Under nitrogen, sodium hydroxide (518 mg, 12.7 mmol) was added to methyl 2-(5-bromo-2-methylthiophen-3-yl)-acetate (**12**, 2.10 g, 8.43 mmol) in ethanol (25 mL). After stirring at room temp. for 5 h, the solvent was distilled off in vacuo and volume was reduced demin. water (50 mL) was added. After extraction with ethyl acetate (2 x 20 mL), the aqueous layer was acidified to pH 1 with hydrochloric acid (37 %), the precipitate was filtered off and washed with demin. water yielding 1.65 g (7.02 mmol, 83 %) of an orange solid, m. p. 107 °C. ^{1}H-NMR (500 MHz, dmso-d_6): δ = 12.37 (s, 1 H, COO*H*), 6.97 (s, 1 H, *H*-4), 3.48 (s, 2 H, CH_2), 2.27 (s, 3 H, CH_3) ppm. ^{13}C-NMR (125 MHz, dmso-d_6): δ = 171.7 (s, *C*OOH), 136.7 (s, *C*-3)*, 132.6 (d, *C*-4), 131.8 (s, *C*-2)*, 105.7 (s, *C*-5), 33.1 (t, *C*H$_2$), 12.7 (q, *C*H$_3$) ppm. *assignment uncertain. MS (EI, 70 eV): *m/z* = 234 (57), 236 (58) $[M]^{+\bullet}$, 189 (96), 191 (100) $[M\text{-}CHO_2]^+$, 175 (20), 177 (22) $[M\text{-}C_2H_3O_2]^+$, 155 (4) $[M\text{-Br}]^+$. HRMS (EI): $^{12}C_7{}^1H_7{}^{79}Br^{16}O_2{}^{32}S$ calcd. 233.93501, found 233.93498 (Δ: 0.15 ppm). $^{12}C_7{}^1H_7{}^{81}Br^{16}O_2{}^{32}S$ calcd. 235.9330, found 235.9329 (Δ: 0.36 ppm). IR (ATR): $\tilde{\nu}$ = 2890, 2733, 2625 (O-H valenz, carboxylic acid), 1698 (C=O valenz, carboxylic acid), 930 (O-H deform.) cm^{-1}. Elemental analysis**:** $C_7H_7BrO_2S$ (235.10) calcd. C 35.76 H 3.00 S 13.64, found C 35.77 H 2.97 S 13.53.

Methyl 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetate (14)

At 0 °C and under nitrogen, methyl oxalyl chloride (2.95 mL (32.1 mmol) was slowly added to a suspension of aluminium trichloride (4.02 g, 30.1 mmol) in dry dichloromethane (100 mL). During 1.5 h, 5-bromo-2-methylthiophen[18] (**10,** 5.19 g, 28.9 mmol) was added dropwise and the mixture was stirred for additional 1.5 h keeping the temp. at 0 °C. In portions, the mixture was poured onto an ice-cold solution consisting of sat. aq. sodium hydrogencarbonate (100 mL) and water (100 mL). After extraction with dichloromethane (4 x 50 mL), the combined organic layer was washed with demin. water (150 mL) and dried with magnesium sulfate. Column chromatography (silica gel, cyclohexane/ethyl acetate (5:1), R_f = 0.43) yielded 5.13 g (19.6 mmol, 68 %) of a yellow solid, m. p. 39 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.50 (s, 1 H, *H*-4), 3.94 (s, 3 H, OCH_3), 2.71 (s, 3 H, thio-CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 179.1 (s, *C*O-COOMe), 163.6 (s, *C*OOMe), 155.9 (s, *C*-2), 132.2 (s, *C*-3), 131.9 (d, *C*-4), 108.5 (s, *C*-5), 53.2 (q, O*C*H$_3$), 16.4 (q, thio-*C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 262 (12), 264 (12) $[M]^{+\bullet}$, 203 (97), 205 (100) $[M\text{-}C_2H_3O_2]^+$. IR (ATR): $\tilde{\nu}$ = 3021 (arom. C-H valenz), 2960, 2921 (aliph. C-H valenz), 1726 (C=O valenz, ester), 1674 (C=O valenz, ketone), 1438 (aliph. C-H deform.), 1195, 1177 (C=O valenz, ester) cm^{-1}. Elemental analysis**:** $C_8H_7BrO_3S$ (263.11) calcd. C 36.52 H 2.68 S 12.19, found C 36.76 H 2.62 S 12.45.

2-(5-Bromo-2-methylthiophen-3-yl)-2-oxoacetamide (15)

Under nitrogen at 0 °C, a solution of methyl 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetate (**14,** 1.15 g, 4.38 mmol) in tetrahydrofuran (8 mL) was added dropwise to aqueous ammonia (28 %, 3.8 mL). After stirring for 30 min at 0 °C and 20 h at room temp., the precipitate was filtered off and washed with demin. water yielding 931 mg (3.52 mmol, 80 %) of a sand colored solid, m. p. 189 °C. ^{1}H-NMR (500 MHz, dmso-d_6): δ = 8.21 (s, 1 H, N*H*), 7.90 (s, 1 H, *H*-4), 2.64 (s, 3 H, CH_3) ppm. ^{13}C-NMR (125 MHz, dmso-d_6): δ = 184.2 (s, *C*O), 166.2 (s, *C*ON), 153.5 (s, *C*-2), 132.7 (s, *C*-3), 132.1 (d, *C*-4), 107.2 (s, *C*-5), 15.3 (q, *C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 247 (15), 249 (15) $[M]^{+\bullet}$, 203 (97), 205 (100) $[M\text{-}CH_2NO]^+$. IR (ATR): $\tilde{\nu}$ = 3407 (N-H valenz, amide), 3167, 3131 (N-H valenz, in H-bridge), 1723 (C=O valenz, ketone), 1652 (C=O valenz, amide), 1599, 1505 (C=C valenz, arom.) cm^{-1}. Elemental analysis**:** $C_7H_6BrNO_2S$ (248.10) calcd. C 33.89 H 2.44 N 5.65 S 12.92, found C 33.98 H 2.31 N 5.32 S 12.66.

Potassium 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetate (16)

Under nitrogen, methyl-2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetate (**14,** 1.94 g, 6.95 mmol) was dissolved in ethanol (21 mL) and potassium hydroxide (450 mg, 8.02 mmol) was added. After stirring at room temp. under nitrogen for 24 h, the reaction mixture was reduced in vacuo to 5 mL and 1.60 g (5.57 mmol, 80 %) of a solid was filtered off and used without further purification.

3,4-Bis(5-bromo-2-methylthiophen-3-yl)-1*H*-pyrrol-2,5-dione (17)

Method A: At 0 °C, a 1 M solution of potassium *tert*-butanolate in tetrahydrofuran (6.3 mL) was added dropwise to a solution of 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetamide (**15**, 870 mg (3.29 mmol) dry tetrahydrofuran (20 mL). After dropwise addition of methyl 2-(5-bromo-2-methylthiophen-3-yl)-acetate (**12**, 1.30 g, 4.90 mmol), the mixture was stirred for 21 h. 1 M hydrochloric acid (20 mL) was added, the layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with demin. water (20 mL) and brine (20 mL). After drying with sodium sulfate and evaporation of the solvent in vacuo, dichloromethane (5 mL) was added. Unsoluble side product was filtered off. The solvent of the filtrate was evaporated and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate (2:1), R_f = 0.35) yielding 125 mg (280 µmol, 8 %) of a yellow solid.

Method B: Under nitrogen, *Z*-3-aminocarbonyl-2,3-bis(5-bromo-2-methylthiophen-3-yl)-propenic acid (**18**, 416 mg, 894 µmol) and sodium acetate (1.21 g, 14.7 mmol) in acetic anhydride (30 mL) were heated to 80 °C for 1 h. After cooling to room temp., the mixture was poured onto ice water (100 mL) which then was extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with demin. water (3 x 15 mL), dried with sodium sulfate, and the solvent was removed in vacuo. Column chromatography (silica gel, cyclohexane/ethyl acetate (2:1), R_f = 0.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.39 (s, 1 H, N*H*), 7.02 (s, 2 H, *H*-4), 1.95 (s, 6 H, CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 169.5 (s, *C*O), 143.6 (s, *C*-2), 133.5 (s, *C*-3), 130.9 (d, *C*-4), 127.0 (s, pyrrol-*C*-3,4), 109.7 (s, *C*-5), 15.1 (q, *C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 445 (24), 447 (48), 449 (27) [M]$^{\bullet+}$, 366 (39), 368 (42) [M-Br]$^+$, 287 (100) [M-2Br]$^+$. HRMS (EI): $^{12}C_{14}{}^1H_9{}^{79}Br_2{}^{14}N^{16}O_2{}^{32}S_2$ calcd. 444.8442, found 444.8452 (Δ: 2.45 ppm). $^{12}C_{14}{}^1H_9{}^{79}Br_1{}^{81}Br_1{}^{14}N^{16}O_2{}^{32}S_2$ calcd. 446.8421, found 446.8433 (Δ: 2.60 ppm). $^{12}C_{14}{}^1H_9{}^{81}Br_2{}^{14}N^{16}O_2{}^{32}S_2$ calcd. 448.8401 found 448.8412 (Δ: 2.49 ppm). IR (ATR): $\tilde{\nu}$ = 3104 (arom. C-H valenz), 2953, 2923, 2857 (aliph. C-H valenz), 1768 C=O valenz, imide), 1631 (C=C valenz, alkene, 1390 (aliph. C-H symm. deform.) cm^{-1}.

(*Z*)-3-(Aminocarbonyl)-2,3-bis(5-bromo-2-methylthiophen-3-yl)-propenic acid (18)

Solid **18** which was gained as the side product during the synthesis (method A) of 3,4-bis(5-bromo-2-methylthiophen-3-yl)-1*H*-pyrrol-2,5-dione (**17**) was washed with little dichloromethane and dried in vacuo giving 468 mg (1.01 mmol, 31 %) of a white solid, m. p. 214 °C. ^{1}H-NMR (500 MHz, dmso-d_6): δ = 11.89 (s, 1 H COO*H*), 6.90 (s, 1 H, N*H*), 6.59 (s, 1 H, thio2-*H*-4), 6.01 (s, 1 H, thio1-*H*-4), 4.57 (s, 1 H, N*H*), 2.31 (s, 3 H, thio1-CH_3), 2.04 (s, 3 H, thio2-CH_3) ppm. ^{13}C-NMR (125 MHz, dmso-d_6): δ = 178.2 (s, *C*ONH$_2$), 175.0 (s, *C*OOH), 139.7 (s, thio2-*C*-2), 139.6 (s, thio1-*C*-2), 134.4 (s, thio2-*C*-3), 131.4 (s, thio1-*C*-3), 130.5 (d, thio1-*C*-4), 130.4 (d, thio2-*C*-4), 106.0 (thio2-*C*-5), 105.7 (thio1-*C*-5), 81.4 (s, thio1-C=*C*-thio2), 54.7 (s, thio1-*C*=C-thio2), 13.6 (q, thio2-*C*H$_3$), 12.8 (q, thio1-*C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 463 (5), 465 (14), 467 (8) [M]$^{\bullet+}$. IR (ATR): $\tilde{\nu}$ = 3175 (O-H valenz, in H-bridge), 3074 (arom. C-H valenz), 2908 (O-H valenz, carboxylic acid), 1714 (C=O valenz, carboxylic acid) cm^{-1}. Elemental analysis: $C_{14}H_{11}Br_2NO_3S_2$ (465.18) calcd. C 36.15 H 2.38 S 13.79 N 3.01, found C 36.01 H 2.29 S 13.57 N 3.15.

3,4-Bis(5-bromo-2-methylthiophen-3-yl)furan-2,5-dione (19)

Under exclusion of light, 2-(5-bromo-2-methylthiophen-3-yl)acetic acid (**13**, 1.11 g, 4.73 mmol)) and potassium 2-(5-bromo-2-methylthiophen-3-yl)-2-oxoacetate (**16**, 1.36 g, 4.73 mmol)) were mixed with acetioc anhydride (23 mL) and stirred for 4 h at 110 °C under nitrogen. After cooling to room temp., the mixture was poured onto ice-water (200 mL) and extracted with diethyl ether (3 x 20 mL Diethylether). The combined organic layer was dried with sodium sulfate, and the solvent was evaporated in vacuo entfernt. Column chromatography [silica gel, gradient cyclohexane → cyclohexane/dichloromethane (1:3)] and precipitation of the crude proiduct from dichloromethane gave 679 mg (1.52 mmol, 32 %) of a yellow solid, m. p. 208 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.05 (s, 2 H, *H*-4), 2.01 (s, 6 H, CH_3) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 164.3 (s, *C*O), 145.2 (s, Furan-*C*-3,4), 134.2 (s, *C*-2), 130.6 (d, *C*-4), 126.0 (s, *C*-3), 110.5 (s, *C*-5), 15.3 (q, *C*H$_3$) ppm. MS (EI, 70 eV): *m/z* = 446 (48), 447 (8), 448 (100), 449 (16), 450 (55), 451(9), 452 (5) [M]$^{\bullet+}$, 367 (20), 369 (22) [M-Br]$^+$, 288 (41) [M-2Br]$^+$. HRMS (EI): $^{12}C_{14}{}^1H_8{}^{79}Br_2{}^{16}O_3{}^{32}S_2$ calcd. 445.8282, found 445.8273 (Δ: 1.85 ppm). $^{12}C_{14}{}^1H_8{}^{79}Br_1{}^{81}Br_1{}^{16}O_3{}^{32}S_2$ calcd. 447.8261, found 447.8252 (Δ: 1.96 ppm), $^{12}C_{14}{}^1H_8{}^{81}Br_2{}^{16}O_3{}^{32}S_2$ calcd. 449.8241, found 449.8231 (Δ: 2.05 ppm). IR (ATR): $\tilde{\nu}$ = 3103 (arom. C-H valenz), 1843, 1767 (C=O valenz, carboxylic acid anhydride), 1631 (C=C valenz, alkene), 1246, 1179 (C-O valenz) cm^{-1}. Elemental analysis**:** $C_{14}H_8Br_2O_3S_2$ (448.15) calcd. C 37.52 H 1.80 S 14.31, found C 37.59 H 1.72 S 14.42.

5-{4-[(3,4-Bis{5-bromo-2-methylthiophen-3-yl})-2,5-dioxo-1*H*-pyrrol-1-yl]-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (20)

Under nitrogen, try triethylamine (0.2 mL) was dropped into a solution of 3,4-bis(5-bromo-2-methylthiophen-3-yl)furan-2,5-dione (**19**, 233 mg, 520 µmol)) and 5-amino-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide[19] (**6**, 401 mg, 651 µmol)) in dry toluene (20 mL). After heating to 110 °C for 24 h, the mixture cooled to room temp. and the solvent was evaporated in vacuo entfernt. Column chromatography (silica gel, dichloromethane, R_f = 0.74) yielded 467 mg (447 µmol, 86 %) of a yellow solid, m. p. 148°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.38 (s, 2 H, Py-N*H*COCH), 8.36 (s, 1 H, Ar-*H*-2), 8.24 (s, 2 H, Ar-*H*-4,6), 8.03 (d, ^3J = 8.1 Hz, 2 H, Py-*H*-3), 8.01 (s, 2 H, Ar-CON*H*), 7.94 (d, ^3J = 8.0 Hz, Py-*H*-5), 7.73 (br. t, ^3J = ~8 Hz, 2 H, Py-*H*-4), 7.09 (s, 2 H, thio-*H*-4), 2.22 (m$_c$, 2 H, COC*H*), 1.98 (s, 6 H, thio-CH_3), 1.77-1.67 (m, 4 H, CHCH_aH$_b$CH$_2$, CHCH_aH$_b$CH$_3$), 1.62-1.56 (m, 2 H, CHCH$_a$*H*$_b$CH$_3$), 1.56-1.48 (m, 2 H, CHCH$_a$*H*$_b$CH$_2$), 1.37-1.28 (m, 8 H, C*H*$_2$C*H*$_2$CH$_3$), 0.97 (t, ^3J = 7.3 Hz, 6 H, CHCH$_2$C*H*$_3$), 0.87 (t, ^3J = 6.8 Hz, 6 H, CH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.3 (s, Py-NH*C*OCH), 168.5 (s, pyrrol-*C*-2,5), 163.6 (s, Ar*C*ONH), 150.1 (s, Py-*C*-2), 149.2 (s, Py-*C*-6), 144.2 (s, thio-*C*-2), 141.1 (d, Py-*C*-4), 136.0 (s, Ar-*C*-5), 133.2 (s, Ar-*C*-1,3), 132.7 (s, thio-*C*-3), 131.0 (d, thio-*C*-4), 127.5 (d, Ar-*C*-4,6), 126.7 (s, pyrrol-*C*-3,4), 124.8 (d, Ar-*C*-2), 110.7 (d, Py-*C*-3), 110.0 (s, thio-*C*-5), 109.9 (d, Py-*C*-5), 50.9 (d, CO*C*H), 32.7 (t, CH*C*H$_2$CH$_2$), 30.0 (t, *C*H$_2$CH$_2$CH$_3$), 26.3 (t, CH*C*H$_2$CH$_3$), 23.0 (t, CH$_2$*C*H$_2$CH$_3$), 15.3 (q, thio-*C*H$_3$), 14.2 (q, CH$_2$CH$_2$*C*H$_3$), 12.3 (q, CHCH$_2$*C*H$_3$) ppm. MS (MALDI-TOF, Cl-CCA): *m/z* = 1044, 146, 148 [M+H]$^+$, 1066 [M+Na]$^+$. IR (ATR): $\tilde{\nu}$ = 2927, 2860 (aliph. C-H valenz), 1765, 1704 (C=O valenz, imide), 1678, 1513 (C=O valenz, amide), 1441 (aliph. C-H deform.), 798 (2,6-disubst. pyridine) cm^{-1}. Elemental analysis**:** $C_{48}H_{51}Br_2N_7O_6S_2$ (1045.90) calcd. C 55.12 H 4.91 N 9.37 S 6.13, $C_{48}H_{51}Br_2N_7O_6S_2 \cdot H_2O$ (1063.92) calcd. C 54.19 H 5.02 N 9.22 S 6.03, found C 54.12 H 4.85 N 9.20 S 6.13.

5-{4-[(3,4-Bis{5-bromo-2-methylthiophen-3-yl})-2,5-dioxo-1*H*-pyrrol-1-yl]-butoxy}-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (21).

Excluding light, 5-(4-iodobutoxy)-*N*,*N*'-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (**8**, 100 mg, 125 µmol), potassium *tert*-butanolate (14.0 mg, 125 µmol) and 3,4-bis(5-bromo-2-methylthiophen-3-yl)-1*H*-pyrrol-2,5-dione (**17**, 50.0 mg, 112 µmol) in dry DMF (6 mL) were stirred for 19 h at 65 °C. After cooling to room temp., the mixture was poured onto demin. water (50 mL) and the aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with demin. water (2 x 30 mL) and brine (10 mL). After drying with sodium

sulfate, evaporation of the solvent in vacuo and column chromatography (silica, cyclohexane/ethyl acetate (3:1), *R*f = 0.21), 57 mg (51 µmol, 46 %) of an orange colored solid remained, m. p. 110 °C. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.39 (s, 2 H, ArCONH), 8.04 (d, ^3J = 7.8 Hz, 2 H, Py-*H*-3), 8.02 (d, ^3J = 8.4 Hz, 2 H, Py-*H*-5), 7.98 (br. s, 1 H, Ar-*H*-2), 7.78 (br. t, ^3J = ~8 Hz, 2 H, Py-*H*-4), 7.92 (br. s, 2 H, CONHCH), 7.62 (d, ^4J = 1.2 Hz, 2 H, Ar-*H*-4,6), 7.05 (s, 2 H, thio-*H*-4), 4.13 (t, ^3J = 5.4 Hz, 2 H, OCH_2), 3.73 (t, ^3J = 6.3 Hz, 2 H, $OCH_2CH_2CH_2CH_2$), 2.17 (m_c, 2 H, COCH), 1.93 (s, 6 H, thio-CH_3), 1.92-1.87 (m, 4 H, $OCH_2CH_2CH_2$), 1.77-1.70 (m, 2 H, $CHCH_aH_bCH_3$), 1.72-1.67 (m, 2 H, $CHCH_aH_bCH_2$), 1.63-1.56 (m, 2 H, $CHCH_aH_bCH_3$), 1.56-1.50 (m, 2 H, $CHCH_aH_bCH_2$), 1.36-1.30 (m, 8 H, $CH_2CH_2CH_2CH_3$), 0.97 (t, ^3J = 7.4 Hz, 6 H, $CHCH_2CH_3$), 0.89 (t, ^3J = 6.9 Hz, 6 H, $CH_2CH_2CH_3$) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 175.0 (s, NHCOCH), 170.4 (s, pyrrol-*C*O), 164.3 (s, ArCONH), 160.0 (s, Ar-*C*-5), 149.9 (s, Py-*C*-2), 149.4 (s, Py-*C*-6), 143.4 (s, thio-*C*-2), 141.2 (d, Py-*C*-4), 136.4 (s, Ar-*C*-1,3), 132.4 (s, thio-*C*-3), 131.0 (d, thio-*C*-4), 127.3 (s, pyrrol-*C*-3,4), 117.7 (d, Ar-*C*-2), 117.2 (d, Ar-*C*-4,6), 110.4 (d, Py-*C*-5), 109.8 (d, Py-*C*-3), 109.6 (s, thio-*C*-5), 68.2 (t, OCH_2), 51.1 (d, COCH), 38.4 (t, $OCH_2CH_2CH_2CH_2$), 32.7 (t, $CHCH_2CH_2$), 30.0 (t, $CH_2CH_2CH_3$), 26.7 (t, $OCH_2CH_2CH_2$), 26.3 (t, $CHCH_2CH_3$), 25.5 (t, OCH_2CH_2), 23.0 (t, $CH_2CH_2CH_3$), 15.2 (q, thio-CH_3), 14.2 (q, $CH_2CH_2CH_3$), 12.3 (q, $CHCH_2CH_3$) ppm. MS (EI, 70 eV): *m/z* = 1115 (4), 1117 (10), 1119 (5) $[M]^{\cdot+}$, 1036 (5), 1038 (8) $[M\text{-}Br]^+$. HRMS (EI): $^{12}C_{52}{}^1H_{59}{}^{79}Br_2{}^{14}N_7{}^{16}O_7{}^{32}S_2$ calcd. 1115.2284, found 1115.2268 (Δ: 1.43 ppm). $^{12}C_{52}{}^1H_{59}{}^{79}Br_1{}^{81}Br_1{}^{14}N_7{}^{16}O_7{}^{32}S_2$ calcd. 1117.2264, found 1117.2258 (Δ: 0.47 ppm). $^{12}C_{52}{}^1H_{59}{}^{81}Br_2{}^{14}N_7{}^{16}O_7{}^{32}S_2$ calcd. 1119.2243, found 1119.2254 (Δ: 1.00 ppm). IR (ATR): $\tilde{\nu}$ = 3413, 3312 (N-H valenz, amide), 2959, 2929, 2857 (aliph. C-H valenz), 1698 (C=O valenz, imide), 1677 (C=O valenz, amide), 1583, 1503 (C=C valenz, arom.), 1241 (C-O valenz, ether), 800 (2,6-disubst. pyridine) cm^{-1}. Elemental analysis**:** $C_{52}H_{59}Br_2N_7O_7S_2$ (1118.01)

5-{4-[(3,4-Bis{2-methyl-5-[(2-methyl-4-{tris[methylethyl]silylethynyl}phenyl)ethynyl]thiophen-3-yl})-2,5-dioxo-1*H*-pyrrol-1-yl]-butoxy}-*N,N'*-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (24)

5-{4-[(3,4-Bis{5-bromo-2-methylthiophen-3-yl})-2,5-dioxo-1*H*-pyrrol-1-yl]-butoxy}-*N,N'*-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (**21**, 59 mg, 53 µmol), bis(triphenylphosphine)palladium dichloride (4.0 mg, 5.7 µmol), copper(I) iodide (2.0 mg, 11 µmol), and triphenylphosphine (5.0 mg, 19 µmol) were suspended in dry tetrahydrofuran (3 mL). Under nitrogen, first dry triethylamine (300 µL) and then 4-methyl-1-(tris[methylethyl]silylethynyl)-4-ethynylbenzene (**5**, 50.0 mg, 169 µmol), dissolved in dry tetrahydrofuran (1.5 mL), were added dropwise. After stirring for 3 d at 50 °C, the mixture was cooled to room temp. and the solvent was evaporated in vacuo. Column chromatography [silica gel, cyclohexane/ethyl acetate (3:1), *R*f = 0.24] yielded 32 mg (21 µmol, 40 %) of a green solid, m. p. 138-139 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.42 (br. s, 2 H, Ar^{1}CONH), 8.02 (d, ^3J = 8.0 Hz, 2 H, Py-*H*-3), 8.01 (d, ^3J = 8.0 Hz, 2 H, Py-*H*-5), 7.98 (br. s, 1 H, Ar^1-*H*-2), 7.79 (br. s, 2 H, NHCOCH), 7.75 (t, ^3J = 8.0 Hz, 2 H, Py-*H*-4), 7.62 (d, ^4J = 1.4 Hz, 2 H, Ar^1-*H*-4,6), 7.37 (d, ^3J = 8.0 Hz, 2 H, Ar^2-*H*-6), 7.33 (br. s, 2 H, Ar^2-*H*-3), 7.28 (s, 2 H, thio-*H*-4), 7.26 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 2 H, Ar^2-*H*-5), 4.12 (t, ^3J = 5.5 Hz, 2 H, OCH_2), 3.75 (t, ^3J = 6.0 Hz, 2, H, $OCH_2CH_2CH_2CH_2$), 2.43 (s, 6 H, Ar$_2$-CH_3), 2.17 (m_c, 2 H, COCH), 1.99 (s, 6 H, thio-CH_3), 1.94-1.87 (m, 4 H, $OCH_2CH_2CH_2$), 1.75-1.65 (m, 4 H, $CHCH_aH_bCH_2$, $CHCH_aH_bCH_3$), 1.61-1.54 (2 H, $CHCH_aH_bCH_3$), 1.54-1.49 (m, 2 H, $CHCH_aH_bCH_2$), 1.36-1.28 (m, 8 H, $CH_2CH_2CH_2CH_3$), 1.15-1.11 (m, 42 H, $CH(CH_3)_2$), 0.96 (t, ^3J = 7.4 Hz, 6 H, $CHCH_2CH_3$), 0.87 (t, ^3J = 7.0 Hz, $CH_2CH_2CH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.0 (s, NHCOCH), 170.6 (s, pyrrol-*C*-2,5), 164.3 (s, Ar^{1}CONH), 160.0 (s, Ar^1-*C*-5), 149.9 (s, Py-*C*-2), 149.4 (s, Py-*C*-6), 143.7 (s, thio-*C*-2), 141.2 (d, Py-*C*-4), 140.1 (s, Ar^2-*C*-2), 136.4 (s, Ar^1-*C*-1,3), 133.24* (d, thio-*C*-4), 133.15* (d, Ar^2-*C*-3), 132.9 (s, thio-*C*-3), 131.6 (d, Ar^2-*C*-6), 129.5 (d, Ar^2-*C*-5), 127.1 (s, pyrrol-*C*-3,4), 123.8 (s, Ar^2-*C*-4), 122.6 (s, Ar^2-*C*-1), 121.3 (s, thio-*C*-5), 117.7 (d, Ar^1-*C*-2), 117.2 (d, Ar^1-*C*-4,6), 110.4 (d, Py*C*-5), 109.8 (d, Py-*C*-3), 107.0 (s, Ar^2-*C*≡C-Si*i*Pr$_3$), 92.79* (s, Ar^2-C≡*C*-Si*i*Pr$_3$), 92.75* (s, thio-C≡*C*-Ar^2), 87.4 (s, thio-*C*≡C-Ar^2), 68.2 (t, Ar^{1}OCH_2), 51.0 (d, NHCOCH), 38.4 (t, $OCH_2CH_2CH_2CH_2$), 32.7 (t, $CHCH_2CH_2$), 30.0 (t, $CH_2CH_2CH_3$), 26.7 (t, OCH_2CH_2), 26.3 (t, $CHCH_2CH_3$), 25.5 (t, $OCH_2CH_2CH_2$), 23.0 (t, $CH_2CH_2CH_3$), 20.7 (q, Ar^2-CH_3), 18.9 (q, Si(CH(CH_3)$_2$)), 15.3 (q, thio-CH_3), 14.2 (q, $CH_2CH_2CH_3$), 12.3 (q, $CHCH_2CH_3$), 11.5 (d, Si($CH(CH_3)_2$)) ppm. For a better discrimination between the signal, the ppm values have been listed with an additional decimal digit. MS (MALDI-TOF, CI-CCA): *m/z* = 1548 $[M]^{\cdot+}$. IR (ATR): $\tilde{\nu}$ = 2957, 2941, 2892, 2864 (aliph. C-H valenz), 2179, 2145 (C≡C valenz), 1769, 1703 (C=O valenz, imide), 1584, 1498 (C=C valenz, arom.), 1444 (C-H def.), 800 (2,6-disubst. pyridine) cm^{-1}. Elemental analysis: $C_{92}H_{113}N_7O_7S_2Si_2$ (1549.23) calcd. C 71.32 H 7.35 N 6.33 S 4.14; $C_{92}H_{113}N_7O_7S_2Si_2 \cdot 2\ H_2O$ (1585.27) calcd. C 69.70 H 7.44 N 6.18 S 4.05; found C 69.89 H 7.35 N 6.22 S 3.86.

5-{4-[(3,4-Bis{2-methyl-5-[2-methyl-4-(tris[methylethyl]silylethynyl)phenyl]ethynyl}thiophen-3-yl)]-2,5-dioxo-1*H*-pyrrol-1-yl}-*N,N'*-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (25)

Sequentially and under nitrogen, dry triethylamine (300 µL) and 4-methyl-1-(tris[methylethyl]silylethynyl)-4-ethynylbenzene (**5**, 60.0 mg (203 µmol), dissolved in dry tetrahydrofuran (1.7 mL), were dropped into a suspension of 5-{4-[(3,4-bis{5-bromo-2-methylthiophen-3-yl})-2,5-dioxo-1*H*-pyrrol-1-yl]-*N,N'*-bis[6-(2-ethylhexanoylamino)pyrid-2-yl]-1,3-benzenedicarboxamide (**20,** 98 mg, 94 µmol)), bis(triphenylphosphine)-palladium(II) dichloride (4.0 mg, 5.7 µmol), copper(I) iodide (2.0 mg, 11 µmol) and triphenylphosphine (5.0 mg, 19 µmol) in dry tetrahydrofuran (3 mL). After stirring at 50 °C for 3 d, the mixture was cooled to room temp. and the solvent was removed. in vacuo. Column chromatography (silica gel, cyclohexane/ethyl acetate (5:1), R_f = 0.09) gave 13 mg (8.8 µmol, 9 %) of a yellow solid, m. p. 188 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.51 (br. s, 2 H, Py-NHCOCH), 8.30 (s, 2 H, Ar1-*H*-4,6), 8.19 (s, 1 H, Ar1-*H*-2), 8.09 (br. s, 2 H, Ar1-CONH), 8.02 (d, ^3J = 8.0 Hz, 2 H, Py-*H*-3), 7.97-7.92 (m, 2 H, Py-*H*-5), 7.71 (br. t, ^3J = ~8 Hz, 2 H, Py-*H*-4), 7.37 (d, ^3J = 7.5 Hz, 2 H, Ar2-*H*-6), 7.32 (m_c, 4 H, thio-*H*-4, Ar2-*H*-3), 7.26 (d, ^3J = 7.5 Hz, 2 H, Ar2-*H*-5), 2.43 (s, 6 H, Ar2-CH_3), 2.27-2.16 (m, 2 H, COCH), 2.04 (s, 6 H, thio-CH_3), 1.79-1.54 (m, 4 H, $CHCH_aH_bCH_2$, $CHCH_aH_bCH_3$), 1.63-1.57 (m, 2 H, $CHCH_aH_bCH_3$), 1.54-1.47 (m, 2 H, $CHCH_aH_bCH_2$), 1.36-1.28 (m, 8 H, $CH_2CH_2CH_2CH_3$), 1.14-1.12 (m, 42 H, $CH(CH_3)_2$), 0.96 (t, ^3J = 7.3 Hz, 6 H, $CHCH_2CH_3$), 0.88-0.84 (m, 6 H, $CH_2CH_2CH_3$) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.3 (s, Py-NHCOCH), 168.7 (s, pyrrol-*C*-2,5), 163.7 (s, Ar1CONH), 150.1 (s, Py-*C*-2), 149.3 (s, Py-*C*-6), 144.5 (s, thio-*C*-2), 141.2 (d, Py-*C*-4), 141.1 (s, Ar2-*C*-2), 136.0 (s, Ar1-*C*-5), 133.4 (s, Ar1-*C*-1,3), 133.2 (d, thio-*C*-4, Ar2-*C*-3), 129.7 (s, thio-*C*-3), 129.5 (d, Ar2-*C*-5), 128.3 (d, Ar1-*C*-2), 127.5 (d, Ar1-*C*-4,6), 126.5 (s, pyrrol-*C*-3,4), 124.3 (s, Ar2-*C*-4), 123.9 (d, Ar2-*C*-6), 122.5 (s, Ar2-*C*-1), 121.7 (s, thio-*C*-5), 110.6 (d, Py-*C*-3), 109.9 (d, Py-*C*-5), 107.0 (s, Ar2-*C*≡C-Si*i*Pr$_3$), 106.7 (s, thio-*C*≡C-Ar2), 93.1 (s, thio-C≡*C*-Ar2), 92.9 (s, Ar2-C≡*C*-Si*i*Pr$_3$), 50.8 (d, COCH), 32.7 (t, $CHCH_2CH_2$), 30.0 (t, $CH_2CH_2CH_3$), 26.3 (t, $CHCH_2CH_3$), 23.0 (t, $CH_2CH_2CH_3$), 18.9 (d, Si($CH(CH_3)_2$), 15.4 (q, thio-CH_3), 14.2 (q, $CH_2CH_2CH_3$), 12.3 (q, $CHCH_2CH_3$) 11.5 (d, Si($CH(CH_3)_2$) ppm. MS (MALDI-TOF, CI-CCA): *m/z* = 1499 $[M+Na]^+$, 1476 $[M]^{\cdot+}$, 1433 $[M\text{-}C_3H_7]^+$. IR (ATR): $\tilde{\nu}$ = 2958, 2939, 2927, 2863 (aliph. C-H valenz), 2177, 2148 (C≡C valenz), 1773, 1699 (C=O valenz, imide), 1583, 1500 (C=C valenz, arom.), 1443 (C-H deform.), 800 (2,6-disubst. pyridine) cm^{-1}. Elemental analysis*: $C_{88}H_{105}N_7O_6S_2Si_2$ (1477.12) calcd. C 71.55 H 7.16 N 6.64 S 4.34, $C_{88}H_{105}N_7O_6S_2Si_2 \cdot 1.5\ CH_2Cl_2$ (1604.52) calcd. C 66.66 H 6.78 N 6.06 S 3.97, found C 66.70 H 6.67 N 6.16 S 3.86. *After the spectroscopic investigations, **25** was recycled by dissolvation in

dichloromethane which was not removed completely prior to the elemental analysis.

Acknowledgements

We thank Prof. Dr. Burkhard König for insisting on trying imides and Dagmar Preugschat for exploring synthetic pathways.

Keywords: electrocyclic reaction • elongated π-systems • Hamilton receptor • hydrogen bonds • photo-switch

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FULL PAPER

Entry for the Table of Contents

FULL PAPER

A photo-switchable diarylethene was connected to a Hamilton receptor to allow supramolecular binding to respectively modified surfaces or dendrimers. The switches are substituted with extended π-systems to allow long wavelength absorptions and improved conductivities. The connection between the photo-switch and the binding site is either stiff (direct connection) or flexible (butyloxy).

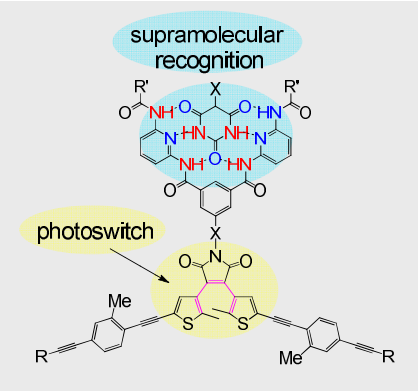

Photo-switch

*Iris Bittner and Ulrich Lüning**

Page No. – Page No.

Photo-switchable π-extended dithienylethenes with an attached molecular recognition site

[1] Nobel prize award 2016: a) J.-P. Sauvage *Angew. Chem.* **2017**, *129*, 11228–11242; *Angew. Chem. Int. Ed.* **2017**, *56*, 11080-11093; b) J. F. Stoddart, *Angew. Chem.* **2017**, *129*, 11244-11277; *Angew. Chem. Int. Ed.* **2017**, *56*, 11094–11125 c) B. L. Feringa, *Angew. Chem.* **2017**, *129*, 11206-11226; *Angew. Chem. Int. Ed.* **2017**, *56*, 11060–11078.
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