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FULL PAPER

Switchable mesomeric betaines derived from pyridinium-phenolates and bis(thienyl)ethane.

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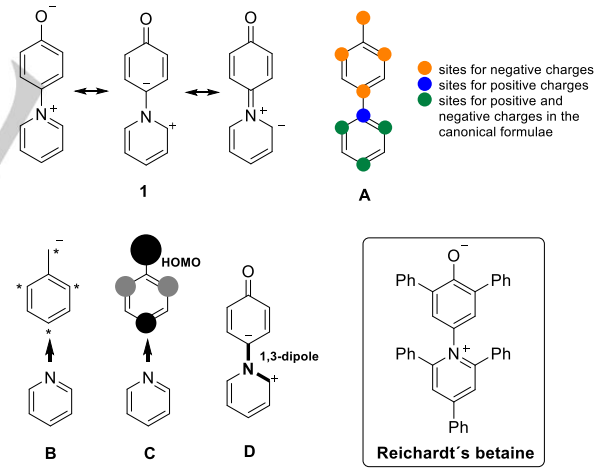
Abstract: Syntheses of push-pull substituted non-symmetric bis(thienyl)ethenes (BTEs) possessing a central perfluorocyclopentene core are described. The substituent effects of anisole, phenole, and phenolate as well as pyridine, pyridinium, and *N*-methylpyridinium substituents, joined *via* their 3- or 4-positions to the central BTE core, respectively, cover the range from very strongly electron-donating [σ(4-phenolate) = -1.00] to extremely strongly electron-withdrawing [σ(pyridinium-4-yl) = +2.57] in the title mesomeric betaines. The different isomers possessing 4-yl/4-yl, 4-yl/3-yl and 3-yl/3-yl substituents represent different combinations of conjugated and cross-conjugated partial structures and cause different spectroscopic properties. In addition, through-space conjugation between the 2- and 2´-position of the thiophenes can be observed which circumvents the charge-separation of through-bond cross-conjugation. The BTE possessing the push-pull chromophore consisting of 3-anisole and 4-pyridinium substituents (**24**) displays the best extinction coefficients within the series of compounds described here (ε = 33.8 / 15.7 L/mol•cm), while the mesomeric betaine possessing an *N*-methylpyridinium-4-yl and a 4-phenolate substituent (**29**) displays considerable bathochromic shifts to λ_{max} = 724 nm in its closed form.

Introduction

Mesomeric betaines are conjugated molecules which can exclusively be represented by dipolar canonical formulae in which the positive and negative charges are delocalized within a common π-electron system.[1] They play major roles as masked 1,3-dipoles in heterocyclic chemistry (sydnones,[2] münchnones[3]), as natural products,[4] biologically active molecules (*e.g.* Molsidomine[5]), *crypto*-N-heterocyclic carbenes[6] and as catalysts.[7] The chemical and physical properties of mesomeric betaines are dependent on their type of conjugation which can be identified in different ways. Thus, frontier orbital profiles, resonance forms, dipole increments, and isoconjugated equivalents[1] of alternant and nonalternant hydrocarbon anions and dianions, respectively, are characteristic of the different types of conjugation.[8] Recent connectivity matrices lead to five distinct classes of mesomeric betaines as a basis for a deeper understanding of structure - properties relationships.[9] Among those five distinct classes, conjugated, cross-conjugated, and pseudo-cross-conjugated mesomeric betaines are the most important.[10] Here, pyridinium-phenolate **1** is given as an example of conjugated mesomeric betaines, and these are the characteristics (Scheme 1): i) common atoms for either charges in the resonance forms exist (**A**), ii) cation and anion are joined through a starred position of the isoconjugate equivalent (**B**), iii) the starred positions are active sites of the highest occupied molecular orbital (HOMO, **C**), and iv) 1,3-dipoles can be dissected from the resonance forms (**D**). A prominent derivative of **1** is Reichardt´s betaine which has been used to define the $E_T(30)$ and E_T^N values of solvent polarities.[11]



Scheme 1. *Characteristics of conjugated mesomeric betaines.*

By contrast, betaine **2** is cross-conjugated and these are the characteristics (Scheme 2): i) positive and negative charges are strictly delocalized in separated parts of the common π-electron system according to the rules of resonance (**E**), ii) cation and anion are connected via an unstarred position of the isoconjugate equivalent (**F**), iii) the unstarred positions are nodal positions of the HOMO (**G**),[12] and iv) 1,4-dipoles can be dissected from the resonance forms (**H**). The alkaloid Punicine from *Punica granatum* is a derivative of **2** from nature and can exist as cross-conjugated mesomeric betaine as shown, or as its tautomer.[13]

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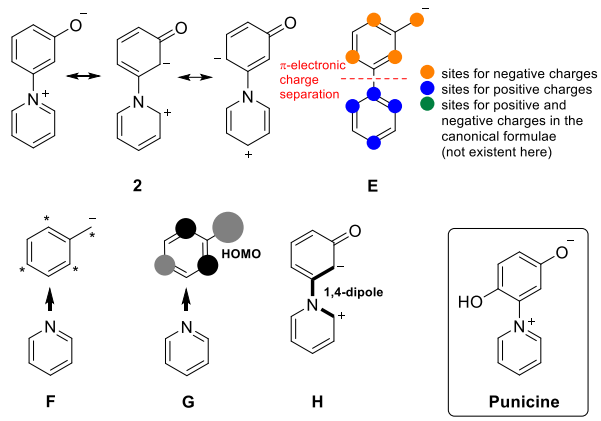
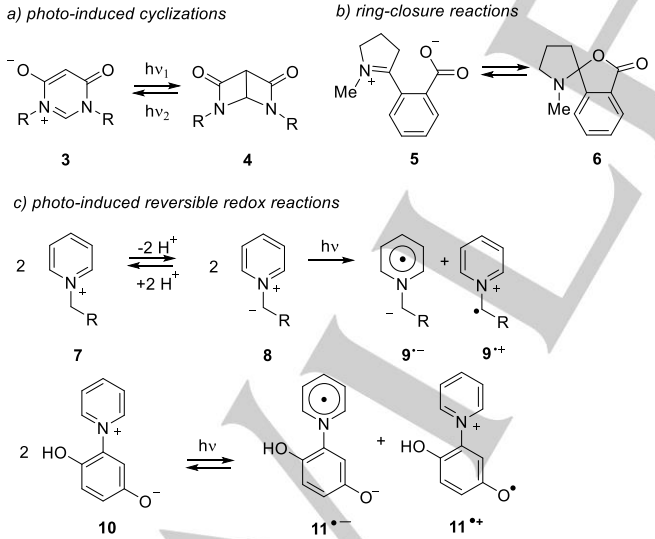


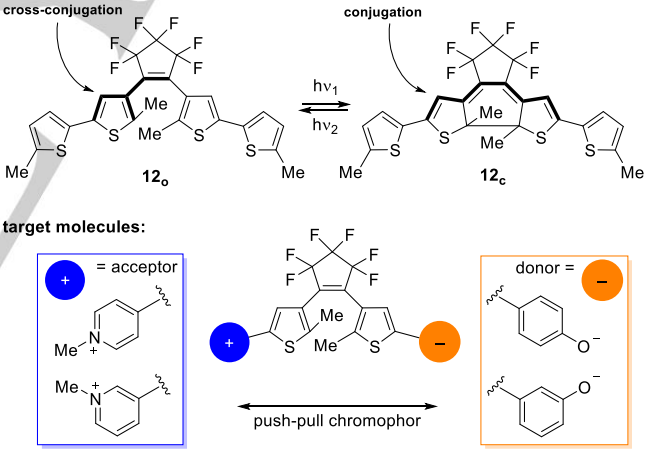
Scheme 2. *Characteristics of cross-conjugated mesomeric betaines.*

Molecular switches can take advantage of the different types of conjugation of mesomeric betaines. Thus, the 1,4-dipole **3** causes intramolecular cycloadditions on irradiation to yield a bis-lactam **4**[14] (Scheme 3). Under charge neutralization, the alkaloid Shihunine **5** can be switched into spiro compound **6**.[4] Conjugated pyridinium-ylides **8**, formed from pyridinium salts **7** by deprotonation, undergo reversible disproportionations to form radical anions **9**$^{\bullet-}$ and radical cations **9**$^{\bullet+}$.[15] Similarly, the aforementioned alkaloid Punicine **10**, especially its viologen derivative,[16] is switchable in terms of photo-induced reversible redox reactions to form **11**$^{\bullet-}$ and **11**$^{\bullet+}$ by disproportionation. The switching process is accompanied by color changes from yellow to deep blue.



Scheme 3. *Switchable mesomeric betaines.*

As part of an ongoing project we aimed at mesomeric betaines of the pyridinium-phenolate type such as Reichardt´s betaine (*c.f.* Scheme 1) and Punicine (*c.f.* Scheme 2) possessing bis(thienyl)ethene (BTE) moieties as switchable spacer between cationic and anionic partial structures (Scheme 4). To the best of our knowledge, only two mesomeric betaines derived from bis(thienyl)ethenes have been published so far,[17,18] although the BTE core is of great ongoing interest. BTE **12**$_o$ is a typical example with a broad variety of applications,[19] among those optical nanopattering[20] and ultra-compact nanophotonic optical modulators[21] as well as electrochemical switches.[22] Therefore, its properties has been examined experimentally[23] and theoretically.[24] In general, BTEs reversibly undergo photochemical 6π-electrocyclizations of their ring-opened form (**12**$_o$) *via* their 1,3,5-hexatriene partial structure to give ring-closed forms such as **12**$_c$. BTEs with a 4-hydroxyphenyl group at the 5-position of a thiophene ring and a 4-pyridyl moiety at the other have been studied in terms of photochemical pK_a-modulation,[25] as red fluorescent molecular switches,[26] for polarization optical recording,[27] and for metal complexations (Re, Ru, W) to modulate the spectroscopic properties.[28] These applications took advantage of the fact that the π-conjugated chain length can be controlled by the reversible hybridization from sp^2 to sp^3 of the C2-position of the thiophenes[29] and reversible changes from through-bond cross-conjugated systems to through-bond conjugated push-pull-chromophors. Phenolates and pyridinium substituents and their precursors cover the entire range from strongly electron-donating to strongly electron-withdrawing; Hammett σ-constants are shown in Table 1. In view of the ongoing interest in controlling molecular properties of BTEs we report here on variations of the connectivity *via* the α- and γ-positions of the pyridinium ring and the *para*- and *meta*-positions of the phenolate to realize different types of conjugation in the target molecules.



Scheme 4. *Cross-conjugation ↔ conjugation interconversions on switching bis(thienyl)ethenes.*

Table 1. *Hammett σ values of substituents*[34]

	substituent				
position	OMe	OH	O$^-$	pyridine	pyridinium
meta / 3-yl	+0.12	+0.12	-0.71	+0.55	+2.10
para / 4-yl	-0.27	-0.37	-1.00	-0.94	+2.57

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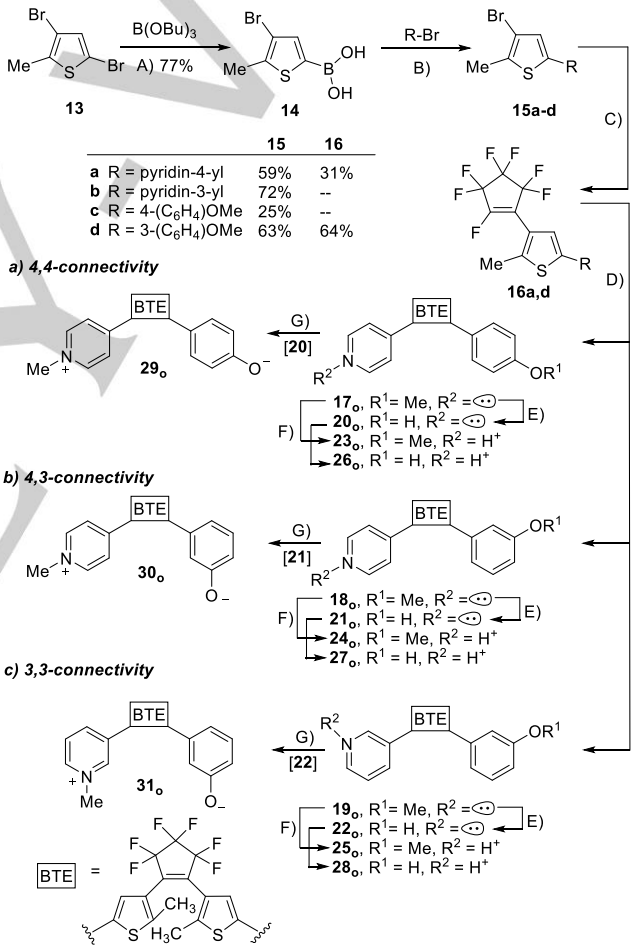
Results and Discussion

The target betaines were prepared starting from dibromomethylthiophene **13** which gave the boronic acid **14** in good yields according to modified literature procedures.[30] Best yields were achieved when the lowest amount of 1 M NaOH was used for the work-up procedure. 4-Bromopyridine, 3-bromopyridine, 4-bromoanisole, and 3-bromoanisole were then used to prepare the building blocks **15a-d** by Suzuki-Miyaura reactions.[31] We found that the order in which the chemicals were added had a considerable impact on the outcome of the reaction. Yields decreased considerably (to 23 - 45%) when the halide was added after the boronic acid and before the addition of the catalyst and the base. *Vice versa*, best yields were achieved (62 - 78%) when the reagents were added in the order (1.) boronic acid, (2.) solvent, (3.) base (as aq. solution), (4.) catalyst, (5.) halide. The subsequent synthesis to yield the non-symmetric BTEs were carried out in analogy to modified literature procedures.[32] The best compromise between yield and monosubstitution of perfluorocyclopentene to give **16a,d** was found when 1,5 eq. were used and added at once. The non-symmetric BTEs were then prepared starting from **16a,d** and **15b-d** and best yields were obtained when the reaction partners were cooled to -80°C prior to reaction. We prepared the 4,4-, 4,3- and 3,3-isomers **17$_o$**, **18$_o$** and **19$_o$** which readily undergo 6π-electrocyclizations on irradiation to yield their ring-closed forms **17$_c$**, **18$_c$**, and **19$_c$**, respectively. On irradiation of the open forms at 300 nm in $CDCl_3$ over a period of 120 min. at 0,5 mW applying a Xenarc lamb, 82% of the 4,4-isomer, 60% of the 4,3-isomer, and 56% of the 3,3-isomer were converted into their corresponding closed forms (*c.f.* Table 3), as determined by ^{1}H NMR spectroscopy. *O*-Demethylation was performed applying BBr_3 followed by hydrolysis which yielded the phenols **20$_o$**, **21$_o$**, and **22$_o$**, respectively. The phenol´s proton can be detected at δ = 9.7 ppm (DMSO-[D6]) in the ^{1}H NMR spectra. A series of methylation conditions [iodomethane, methyl triflate, Meerwein´s reagent (Me_3OBF_4)] was tested to prepare the *N*-methylpyridinium moieties. Best results were achieved when dimethylsulfate in the presence of catalytic amounts of nitrobenzene were used, and the successful reaction was unambiguously proved by shifts of the pyridine´s protons by approximately Δδ = 0.25 ppm (α-H) and Δδ = 0.85 ppm (β-H) to lower field. The target molecules **29$_o$**, **30$_o$**, and **31$_o$** were obtained as hygroscopic oils which are exclusively soluble in polar protic solvents such as aqueous alcohols and water. Under these conditions, they are in equilibrium with their phenols [**29$_o$**+H^+ OH^-], [**30$_o$**+H^+ OH^-], and [**31$_o$**+H^+ OH^-], as evidenced by NMR and UV/Vis spectroscopic examinations. In agreement with observations concerning the aforementioned pK_a-modulators[29] and also phenol-group substituted diarylethenes which are stabilized under acidic conditions,[33] the betaines are destabilized in the absence of water and decompose within some hours. Therefore, conversion rates of the betaines could not be determined. Of all target betaines, **29$_o$** has been prepared before following another protocol.[25] To gain information about the predominant tautomer of **20$_o$** – **22$_o$**, *i.e.* [pyridine-BTE-phenol] *vs.* [pyridinium$^+$-BTE-phenolate$^-$], we treated these phenols with gaseous HCl to form the corresponding pyridinium salts **26$_o$** – **28$_o$** as chlorides, whereupon all pyridine ^{1}H resonance frequencies shifted to lower field. The shift has the same magnitude as of the corresponding *O*-methylated species **23$_o$** – **25$_o$**, which cannot form tautomers, under identical conditions. The α-protons of the pyridine ring typically appear at approximately 8.60 ppm (**17$_o$**, **18$_o$**) and 8.82 ppm (singlet) (**19$_o$**) in the ^{1}H NMR spectra taken in DMSO-[D6], whereas the corresponding signals shift by approximately 0.18 ppm (**17$_o$**), 0.24 ppm (**18$_o$**), and 0.50 ppm (**19$_o$**) to lower field on formation of the corresponding pyridinium salts. In addition, bathochromic shifts of the UV absorption maxima up to 30 nm were observable on protonation to the pyridinium salts. The protonation was fully reversible in all cases. Thus, the predominant tautomer in solution is pyridine-BTE-phenol, as shown in Scheme 5, rather than the zwitterionic pyridinium-BTE-phenolate.



A) *n*-BuLi, -80°C, $B(OBu)_3$, Et_2O, 6 h. B) Na_2CO_3 (aq.) $Pd(PPh_3)_4$, THF, reflux, 24 h. C) [**16a,d**], *n*-BuLi, -80°C, octafluorocyclopentene, THF, 24 h. D) *n*-BuLi, -80°C [**16a+15c** -> **17$_o$** (50%], [**16a+15d** -> **18$_o$** (38%)],[**16b+15b** -> **19$_o$** (62%)]. E) BBr_3, CH_2Cl_2, rt, then H_2O. F) HCl_g, $CHCl_3$. G) Me_2SO_4, acetone, $PhNO_2$ (cat.), reflux, 6 h [**20** -> **29$_o$**+H^+, **21** -> **30$_o$**+H^+, **22** -> **31$_o$**+H^+], 1M NaOH to give **29$_o$** - **31$_o$**.

Scheme 5. *Synthesis of the target molecules* **29$_o$** – **31$_o$**.

In view of the theory of mesomeric betaines[1],[9] and its application to BTEs, the target betaines can be represented by several

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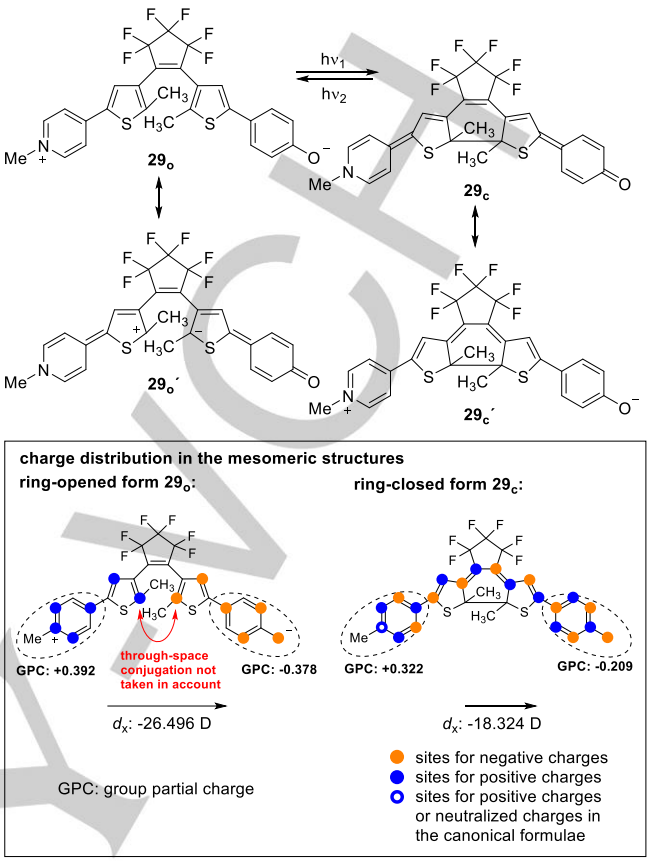
dipolar canonical forms, four of which are shown (**29o** / **29o´** / **29c** / **29c´**) (Scheme 6). According to the rules of resonance, through-bond cross-conjugation of the open form **29o** causes a π-electronic charge separation between the two wings of the molecule as indicated by strictly separated sites of positive and negative charges in the canonical formulae. In contrast to literature-known mesomeric betaines, however, additional aspects have be taken into account, as **29o** is not planar according to a DFT calculation (N31G6**/PBE0-d3) (Figure 1). As a consequence, the through-bond cross-conjugation is circumvented by through-space conjugation. Thus, whereas the pyridinium and phenolate rings are almost coplanar with their adjacent thiophene rings *in vacuo* (C1-C5-C6-C7= -3.337°; C1´-C5´-C6´-C7´= -3.326°), the thiophene-pyridinium and the thiophene-phenolate moieties are twisted by -45.6° and +46.5° from the plane of the double bond of the cyclopentene (C2-C3-C1´´-C2´´ & C2´-C3´-C2´´-C1´´). Due to steric reasons the 1,3,5-hexatriene partial structure is twisted as well. Thus, dihedral angles C2-C3-C1´´-C2´´ = 11.580° and C2´-C3´-C2´´-C1´´= 15.191° were calculated. As a consequence, the distance between the 2-positions of the thiophenes in the most stable conformation of **29o** was calculated to be 328.1 pm which is smaller than the sum of the van-der-Waals radii (340 pm). The 3-positions have a distance of 309.0 pm. This close proximity enables a spatial electron communication between the cationic and anionic parts of the betaine by through-space conjugation. π-Electronic short-circuits have only been documented for through-bond conjugated bridges in mesomeric betaines so far, which largely influence their physical and chemical properties,[1] but to the best of our knowledge through-space conjugations in mesomeric betaines have not yet been observed. Much interest has recently been directed to through-space conjugation in face-to-face aromatics[35] including cyclophanes,[36] hexaarylbenzenes,[37] helical foldamers[38] and others, due to their capacities to transport charges and energies *via* a spatial channel.[39] Interplane distances of π-stacked aromatic systems of 280 pm in cyclophanes[40] up to 349.4 pm[35] in π-stacked aromatics have been measured. In contrast to the aforementioned systems, the through-space conjugation in mesomeric betaine **29o** is enabled by the proximity of the 2-positions of the thiophenes and not by π-stacking between the pyridinium and the phenolate which required the formation of another conformer. Calculated partial charges of the pyridinium and phenolate segments (DFT, N31G6**/PBE0-d3) were determined to be +0.390 and -0.378, respectively, indicating a high degree of charge-separation in the ground state. On ring-closure these values decrease. However, their magnitude prove the considerable contribution of dipolar resonance forms such as **29c´** at the expense of the neutral conjugated form **29c**. Additionally, we re-orientated the y-axis with a different ZMAT, so that the y-axis is parallel to the line connecting the nitrogen and the oxygen atom. Along this axis the dipole moment was calculated to be -26.496 D for the open form **31o** and -18.324 D for the closed form **29c**. The change of the type of conjugation on irradiation is thus well reflected in these values. As summarized in Table 2, the bond lengths C1"-C3, C5-C6 and C5´-C6´ are shortened after the ring-closure due to increased π-contributions.



Scheme 6. *Characteristics of the 4,4-connectivity before (**29o**) and after the photochemical ring-closure (**29c**).*

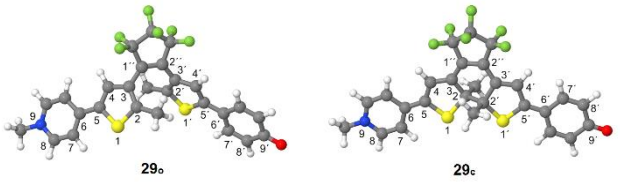


Figure 1. *Most stable conformation of **29o** and **29c**.*

Due to the through-space conjugation the frontier orbital profile of **29o** is not typical of cross-conjugated mesomeric betaines[12] to which it formally belongs (Figure 2).[1][4][9][10] Thus, the highest occupied molecular orbital (HOMO) of **29o** is essentially located in the phenolate ring and in the adjacent thiophene ring in accordance with the sites of negative charges in the resonance forms. In analogy, the lowest unoccupied molecular orbital (LUMO) of **29o** is essentially located in the pyridinium ring and in the adjacent C3 and C4 positions of the adjacent thiophene ring. However, the through-space conjugation causes active positions of the HOMO in the thiophen-2-yl pyridinium moiety, and, *vice versa*, of the LUMO in the thiophen-2-yl phenolate ring which sets the betaines clearly apart from typical examples.[12]

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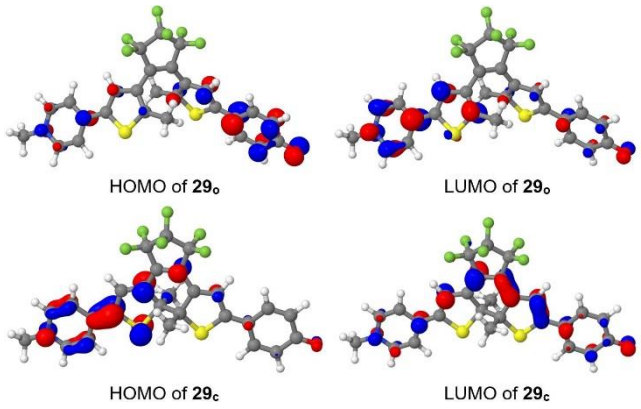
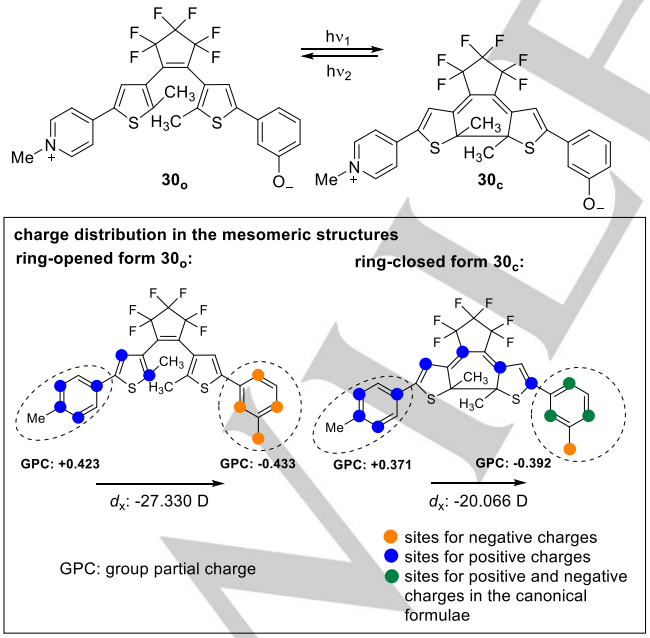


Figure 2. *Frontier orbital profiles of* **29o** *and* **29c**.

Marked differences exist between the 4,4-isomer **29** and the 4,3-isomer **30** (Scheme 7). According to the rules of resonance, the negative charge of **30o** is restricted to the phenolate ring which translates into increased group partial charges and a larger calculated permanent dipole moment in comparison to its isomer **29o**. Obviously, the connectivity of the phenolate influences the group partial charge of the pyridinium, which itself remained unchanged in comparison to **29**. In contrast to the 4,4-isomer, a conjugated mesomeric betaine **30c** is formed after the ring-closure reaction. This can easily be recognized by common atoms for either charges in the canonical formulae[1][4] and the group partial charges. As expected, the values of the latter are between those of cross-conjugated mesomeric betaines (c.f. **31c**) and conjugated systems (c.f. **29c**).



Scheme 7. *Characteristics of the 4,3-isomers* **30o** *and* **30c**.

The HOMO and LUMO of **30o** are essentially located in the phenolate and the pyridinium rings, respectively, with small contributions in the opposite wings of the molecule (Figure 3). The HOMO of **30c** is in well accord with a substituent in cross-conjugation, whereas the LUMO is diagnostic for a delocalized positive charge over the entire π-system. These characteristics sets the 4,3-isomer **30o** clearly apart from the 4,4-isomer **29o**.

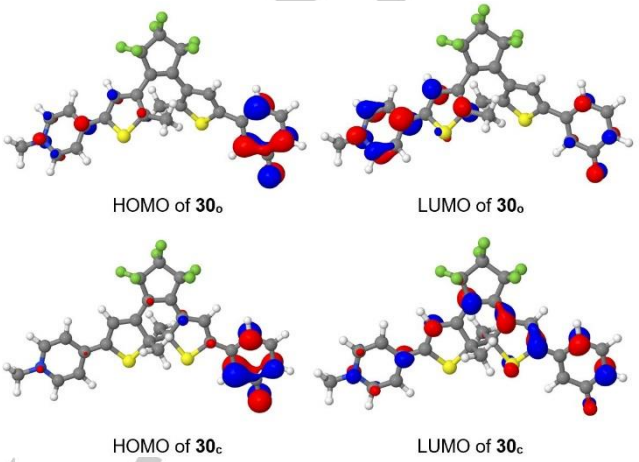
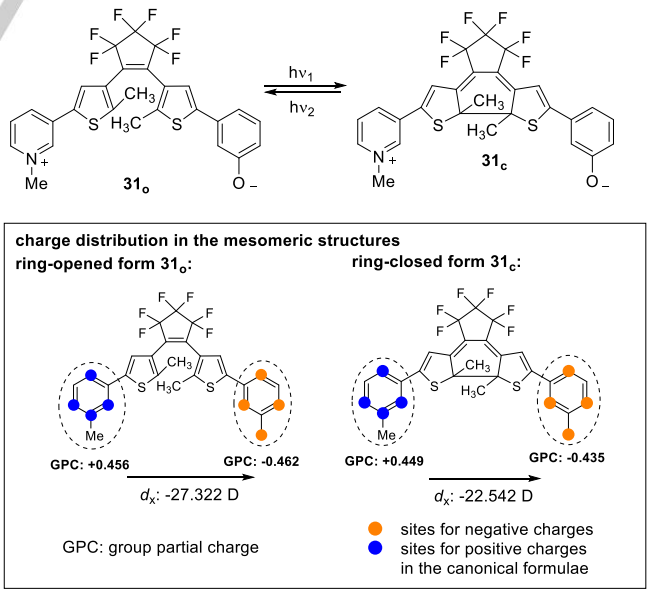


Figure 3. *Frontier orbital profiles of* **30o** *and* **30c**.

In contrast to the 4,4- and 4,3-isomers, the 3,3-isomer **31o** remains a formal cross-conjugated mesomeric betaine after the photochemical transformation to **31c**. As a consequence, the calculated permanent dipole moment of **31c** is the highest of the entire series (Scheme 8), and group partial charges indicate an effective π-electronic charge separation with respect to the frontier orbitals by cross-conjugation[1][4][12] before and after the ring-closure.



Scheme 8. *Characteristics of the 3,3-isomers* **31o** *and* **31c**.

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As expected, calculations predict that the 5,6- and 5´-6´ bond lengths are shortened to a much lesser extent due to much weaker π-interactions in comparison to the 4,4-connectivity. Table 2 summarizes selected calculated bond lengths of all isomers. As observed for the other isomers, the HOMO and LUMO of the open-form betaine **31o** are not strictly localized in separated parts of the π-electron system. In the ring-closed form **31c** the HOMO is almost exclusively located in the phenolate ring, whereas the LUMO is distributed over the entire molecule (Figure 4).

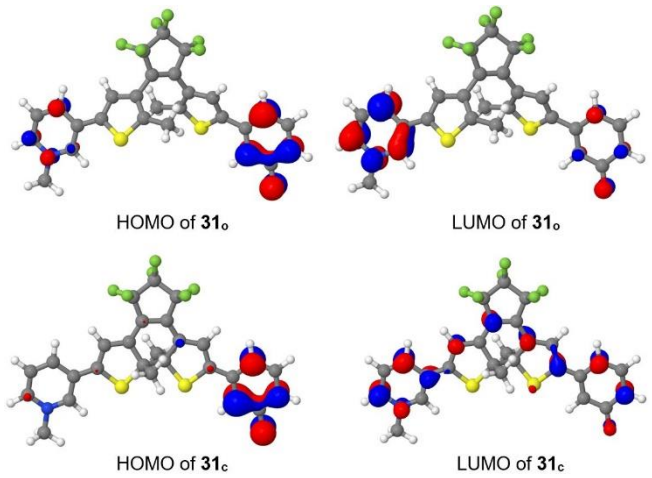

Figure 4. *Frontier orbital profiles of* **31o** *and* **31c**.

Table 2. *Selected calculated bond lengths before and after the ring-closure reaction*

Connectivity	Compound	Bond 1"-3	Bond 5-6	Bond 5´-6´
4,4	Ring-opened form **29o**	145.9 pm	141.6 pm	142.5 pm
	Ring-closed form **29c**	141.1 pm	138.8 pm	138.4 pm
	Difference	4.8 pm	2.8 pm	4.1 pm
4,3	Ring-opened form **30o**	146.2 pm	142.3 pm	146.3 pm
	Ring-closed form **30c**	140.1 pm	139.5 pm	143.4 pm
	Difference	6.1 pm	2,8 pm	2,9 pm
3,3	Ring-opened form **31o**	146.2 pm	145.1 pm	146.4 pm
	Ring-closed form **31c**	138.8 pm	143.6 pm	143.6 pm
	Difference	7.4 pm	1.5 pm	2.8 pm

The aforementioned discussed characteristics translate into spectroscopic properties. The ^{1}H NMR resonance frequencies of the thiophene´s unsubstituted positions are diagnostic of the type of conjugation. Thus, the pyridinium-4-yl substitution pattern which is in conjugation with the thiophene ring as realized in **29o** and **30o**, causes resonance frequencies at δ = 8.23 ppm - 8.24 ppm of the thiophene´s proton (4-*H*). Cross-conjugation between pyridinium and the thiophene, realized by the pyridinium-3-yl substitution pattern of **31o**, causes signals at considerably higher field, *i.e.* δ = 7.93 ppm in accordance with the distribution of the positive charge in the canonical formulae. The thiophene ring attached to the phenolate moiety (4´-*H*) behaves analogously. Thus, a phenolate in conjugation as in **29o** causes a resonance frequency at δ = 7.23 ppm of the thiophene´s proton, whereas cross-conjugation gives signals at approximately δ = 7.35 ppm (**30o**, **31o**) in accordance with the restricted delocalization of the negative charge. In general, the thiophen´s resonance frequencies of all compounds of the series described here display considerable up-field shifts on ring-closure (*c.f.* Table S1, Supporting Information). The following conclusions can be drawn from results of UV/Vis measurements of the mesomeric betaine precursors **17** – **28** (Table 3 and Supporting Information) which are soluble in chloroform: Exchange of the methoxy group towards the OH group has the largest influence on the absorption maxima of the 4,4-isomer (**17c→20c**; $\Delta\lambda_{max}$ = 14 nm; Δε = -0.2 L/mol•cm), but no effect on the corresponding ring-opened forms (**17o→20o**; $\Delta\lambda_{max}$ = 0 nm; Δε = -10.4 L/mol•cm). A small effect is observed on the absorption maximum of the cross-conjugated 3,3-isomer accompanied by a considerable effect on the extinction coefficient (**19c→22c**, $\Delta\lambda_{max}$ = 3 nm; Δε = -8.3 L/mol•cm). *N*-Protonation of the ring-closed forms results in considerable bathochromic shifts, the magnitude of which is dependent on the connectivity, as it is 72 - 61 nm for the 4,4- (**17c→23c**, **20c→26c**), 59 – 51 nm for the 4,3- (**18c→24c**, **21c→27c**), and 25 – 23 nm for the cross-conjugated 3,3-isomers (**22c → 28c**, **19c → 25c**), respectively. The BTE **27o** has the highest conversion rate of the series of compounds. Thus, after 2 h of irradiation with a Xenarc lamb at λ = 300 nm in $CDCl_3$ 85% were converted into the closed form **27c**, as determined by ^{1}H NMR spectroscopy.

Table 3. *UV/Vis spectroscopic properties of the target betaine precursors as well as of reference BTE* **12**.

	BTE	λ_{max}	ε/10^3	BTE	λ_{max}	ε/10^3	conversion
4,4	**17o**	300	31.1	**17c**	604	8.9	0.82
	20o	300	20.7	**20c**	618	8.7	0.69
	23o	293	18.8	**23c**	676	12.6	0.77
	26o	291	10.4	**26c**	679	6.2	0.66
4,3	**18o**	300	37.0	**18c**	604	13.7	0.60
	21o	300	9.8	**21c**	613	2.7	0.56
	24o	285	33.8	**24c**	663	15.7	0.58
	27o	353	8.3	**27c**	664	3.2	0.85
3,3	**19o**	300	21.2	**19c**	590	12.8	0.56
	22o	300	14.3	**22c**	593	4.5	0.75
	25o	305	17.1	**25c**	615	10.6	0.56
	28o	305	8.4	**28c**	616	2.6	0.71
Ref	**12o**	325	29.7	**12c**	613	17.5	0.70

All spectra were measured in chloroform with a concentration of 0.05 mg/mL. λ_{max} is given in [nm], ε/10^3 in [L / mol·cm]. Conversion refers to formation of the closed form starting from the opened form in $CDCl_3$ after irradiation time of 120 min. under the measurement conditions described, determined by ^{1}H NMR spectroscopy.

As the target betaines are hygroscopic and have a rather limited solubility in chloroform, UV/Vis measurements were performed in methanol (Table 4). As mentioned before, the mesomeric betaines predominantly exist in their protonated form under these conditions. To obtain the UV-Vis spectra of the betaines, the protonated open-form compounds (**29o**+H$^+$), (**30o**+H$^+$), and

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($\mathbf{31_o}$+H$^+$) were dissolved in methanol, switched to the closed form and then treated with aq. 1M NaOH aq. solution. As evidenced by ^{19}F NMR spectroscopy, no substitution of the fluorine atoms takes place under these conditions. On betaine formation, the 3,3-connectivity results in a hypsochromic shift [($\mathbf{31_c}$+H$^+$)→$\mathbf{31_c}$, $\Delta\lambda_{max}$ = 24 nm), whereas the other isomers display bathochromic shifts on betaine formation [($\mathbf{29_c}$+H$^+$) →$\mathbf{29_c}$, $\Delta\lambda_{max}$ = 61 nm, ($\mathbf{30_c}$+H$^+$) → $\mathbf{30_c}$, $\Delta\lambda_{max}$ = 33 nm]. Betaine synthesis starting from the 4-pyridyl-BTE-4-anisol precursor **17c** thus results in a bathochromic shift of more than approximately 120 nm to λ_{max} = 724 nm. The target betaines, however, proved to be too sensitive to determine accurate conversion rates to calculate extinction coefficients. Concerning the photostability, we chose BTE **24** for a comparison with the reference BTE **12**, because it has the highest extinction coefficient of the entire series which we prepared. We subjected **12** and **24** dissolved in $CDCl_3$ to irradiation with a Jasco FP-8500 spectrofluorometer (Xenarc lamp with 10 nm bandwidth and an intensity of 0.5 mW) to monitor the behaviour by means of ^{1}H and ^{13}C NMR spectroscopy. After 24 h the NMR spectra did not show any decomposition products.

Table 4. *UV/Vis spectroscopic properties of the target betaines.*

	Compd.	λ_{max} [nm]	Compd.	λ_{max} [nm]
4,4	$\mathbf{(29+H^+)_o}$	294	$\mathbf{(29+H^+)_c}$	663
	$\mathbf{29_o}$	316	$\mathbf{29_c}$	724
4,3	$\mathbf{(30+H^+)_o}$	342	$\mathbf{(30+H^+)_c}$	641
	$\mathbf{30_o}$	300	$\mathbf{30_c}$	608
3,3	$\mathbf{(31+H^+)_o}$	307	$\mathbf{(31+H^+)_c}$	602
	$\mathbf{31_o}$	300	$\mathbf{31_c}$	626

All spectra were measured in methanol with a concentration of 0.05 mg/mL.

Conclusions

Series of push-pull substituted non-symmetric bis(thienyl)ethenes (BTEs) possessing a central perfluorocyclopentene core under variation of the connectivity and the type of conjugation have been prepared, among those the target mesomeric betaines of the pyridinium-phenolate type. The non-planarity of the BTEs enable through-space conjugations by a close proximity of the 2/2´-positions of the thiophene rings which short-circuit the through-bond cross-conjugation of the ring-opened form. Depending on the 4,4-, 4,3-, and 3,3-connectivities of anisole, phenole, and phenolate in combination with pyridine, pyridinium, and *N*-methylpyridinium substituents, photochemical conversions change the type of conjugation which is well reflected in calculated permanent dipole moments, group partial charges, frontier orbital profiles as well as spectroscopic properties. Among the switchable molecules prepared in this project, robust BTEs possessing push-pull chromophores have been identified, among those the cationic 4-pyridinium-BTE-3-methoxyphenyl derivative **24** which displays the highest extinction coefficient of the series of BTEs described here (ε = 33.8 / 15.7 L/mol•cm) in its ring-opened and ring-closed form, respectively. Concerning the absorption maxima, the mesomeric betaine possessing *N*-methylpyridinium-4-yl and 4-phenolate substituents $\mathbf{29_c}$ displays considerable bathochromic shifts to λ_{max} = 724 nm in comparison to the reference BTE 4,4''-(perfluorocyclopent-1-ene-1,2-diyl)bis(5,5'-dimethyl-2,2'-bithiophene) **12** from the literature.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2). The mass spectra (EIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS. The HR-MS spectra were obtained with a Bruker Impact II and Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer. UV measurements were performed using a Jasco FP-8500 spectrofluorometer. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F254, company MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230 400 mesh) of the company MERCK KGAA.

Calculations:

Calculations. All density-functional theory (DFT)-calculations were carried out by using the multithreaded Firefly 8.2.0 QC package,[42] which is partially based on the GAMESS (US)[43] source code, running on Windows 10 Pro (Version 10.0.17763.914) (x86_64) on an 16 core AMD 2950X processor workstation. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented N31G6** basis set and with the PBE0 density functional including D3 dispersion correction. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Orbital plots were obtained using Jmol 14.27.2.[44] Compositions of molecular orbitals were calculated using the AOMix program.[45],[46] Partial charges were obtained with NBO 5.9 from the results of the DFT calculations.[47]

4,4''-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5,5'-dimethyl-2,2'-bithiophene ($\mathbf{12_o}$). The reaction is carried under light protection. A solution of 2.71 g (9.9 mmol) of 4-bromo-5,5'-dimethyl-2,2'-bithiophene in dry THF is cooled to -80°C. This mixture is treated with 5.80 mL (10.4 mmol) of *n*-BuLi (1.8 M in hexane). After 30 min 0.66 mL (4.9 mmol) of octafluorocyclopentene are added and the reaction is stirred for 3 hours at -80°C. After the mixture reached room temperature, the reaction is quenched with water and extracted with diethyl ether. The organic phases were collected and dried over $MgSO_4$. The solvent was removed *in vacuo*. Column chromatography was used to purify the crude product using hexanes as eluent to afford the pure product, stored light protected in a fridge. Yield 1.49 g (54%), a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 2H, 3-H), 6.84 – 6.83 (m, 2H, 3'-H), 6.66 – 6.65 (m, 2H, 4'-H), 2.40 (s, 3H, 6-H), 1.85 (s, 3H, 6'-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[20a]

3,5-Dibromo-2-methylthiophene (13). To a solution of 10.00 g (101.9 mmol) of 2-methylthiophene in glacial acetic acid 36.3 g (203.7 mmol) of NBS are added in portions. The reaction is stirred at room temperature for 48 h. The reaction mixture is extracted with DCM and the organic phase is washed with 1 M aqueous NaOH (2 L). After the organic phase is dried over $MgSO_4$ the solvent is removed *in vacuo* to afford the product. Yield 25.92 g (99%), a yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.86 (s, 1H,

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4-H), 2.33 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[19g]

(4-Bromo-5-methylthiophen-2-yl)boronic acid (14). A solution of 17 g (66.4 mmol) of dibromothiophene **13** in dry diethyl ether is cooled to -80°C followed by the addition of 24.9 mL (69.7 mmol) of a 2.8 M *n*-BuLi in cyclohexane solution. After 10 min of stirring at this low temperature 19.7 mL (73.06) mmol of $B(OBu)_3$ is added. The reaction is allowed to warm to room temperature. 1 M aqueous HCl is added to the reaction followed by the extraction with diethyl ether. The organic phase is collected and treated with 1 M NaOH aqueous solution. The aqueous layer is collected. Under virgorous stirring 37% of HCl is slowly added to the solution until a precipitate is formed. The solid is filtered and dried *in vacuo*. Yield 11.35 g (77.4%), orange powder. ^{1}H-NMR (400 MHz, DMSO d_6): δ = 8.35 (s, 2H, 6-H), 7.49 (s, 1H, 3-H), 2.36 (s, 3H, 7-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[30]

General procedure of the Suzuki-Miyaura Coupling to prepare 15a-d (Procedure 1): The reaction is carried out under nitrogen atmosphere. The boronic acid (**13**) is dissolved in dry tetrahydrofuran. To this solution was added a solution of Na_2CO_3 in water followed by 1 eq. of the halide and 5 mol-% of $Pd(PPh_3)_4$. The reaction outcome is monitored by TLC. After the conversion water is added to the solution, the solution is filtered through celite and extracted with diethylether. The organic phase is then washed with water and dried over $MgSO_4$. The solvent is removed *in vacuo* followed by column chromatography to afford the desired product.

4-(4-Bromo-5-methylthiophen-2-yl)pyridine (15a). According to Procedure 1, a solution of 4.50 g (20.4 mmol) of **13**, 8.64 g (81.5 mmol) of soda, 3.22 g (20.4 mmol) of 4-bromopyridine hydrochloride and 1.18 g of $Pd(PPh_3)_4$ (1.02 mmol) is reacted. Ethyl acetate is used as eluent. Yield 3.06 g (59.2%), a yellowish brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.59 – 8.57 (m, 2H, 3'-H), 7.38 – 7.36 (m, 2H, 2'-H), 7.31 (s, 1H, 3-H), 2.44 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[31b]

3-(4-Bromo-5-methylthiophen-2-yl)pyridine (15b). According to Procedure 1, a solution of 3.50 g (15.9 mmol) of **13**, 6.72 g (63.4 mmol) of soda, 2.50 g (15.9 mmol) of 3-bromopyridine and 0.92 g of $Pd(PPh_3)_4$ (0.8 mmol) is reacted. Petroleum ether and ethyl acetate is used as eluent (5:1). Yield 2.88 g (71.5%), brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.78 (m, 1H, 2'-H), 8.52 – 8.50 (m, 1H, 4'-H), 7.77 – 7.74 (m, 1H, 6'-H), 7.30 – 7.27 (m, 1H, 5'-H), 7.15 (s, 1H, 3-H), 2.43 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[31d]

3-Bromo-5-(4-methoxyphenyl)-2-methylthiophene (15c). According to Procedure 1, a solution of 3.50 g (15.9 mmol) of **13**, 6.72 g (63.4 mmol) of soda, 2.96 g (15.9 mmol) of 4-bromoanisole and 0.92 g of $Pd(PPh_3)_4$ (0.8 mmol) is reacted. Petroleum ether is used as eluent. Yield 1.12 g (25.0%), a bright yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.44 – 7.42 (m, 2H, 2'-H), 6.98 (s, 1H, 4-H), 6.91 – 6.89 (m, 2H, 3'-H), 3.82 (s, 3H, 5'-H), 2.40 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[31a]

3-Bromo-5-(3-methoxyphenyl)-2-methylthiophene (15d). According to Procedure 1, a solution of 12.00 g (54.3 mmol) of **13**, 23.03 g (217.3 mmol) of soda, 10.16 g (54.3 mmol) of 3-bromoanisole and 3.14 g of $Pd(PPh_3)_4$ (2.7 mmol) is reacted. Petroleum ether is used as eluent. Yield 9.76 g (63.4%), brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, $J_{H,H}$ = 7.9 Hz, 1H, 5'-H), 7.10 – 7.08 (m, 1H, 4'-H), 7.09 (s, 1H, 4-H), 7.03 – 7.02 (m, 1H, 6'-H), 6.84 – 6.81 (m, 1H, 2'-H) 3.83 (s, 3H, 7'-H), 2.41 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[31c]

General procedure for the synthesis of a BTE-precursors 16a,d (Procedure 2):
The reaction is carried out under nitrogen atmosphere. 1 eq. halide is dissolved in dry THF and the mixture is cooled to -80°C. To this solution 1.1 eq of 2.8 M *n*-BuLi in cyclohexane solution are added. After 30 – 60 min octafluorocyclopentene (1.5 eq.) is added in one portion. After 2 h the reaction is allowed to warm up to room temperature and is stirred overnight. Water is added to the solution. Diethyl ether is used for extraction, the organic phase is washed with water. The combined organic layers are dried over $MgSO_4$ and the solvent is removed *in vacuo* followed by column chromatography to afford the target molecule.

4-(5-Methyl-4-(perfluorocyclopent-1-en-1-yl)thiophen-2-yl)pyridine (16a). According to Procedure 2, a solution of 3.00 g (11.8 mmol) of **15a**, 4.2 mL (11.8 mmol) *n*-BuLi and 2.2 mL (16.5 mmol) of octafluorocyclopentene are reacted. Ethyl acetate is used as eluent. Yield 1.357 g (31.3%), black oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.63 – 8.61 (m, 2H, 3'-H), 7.45 – 7.43 (m, 2H, 2'-H), 7.44 (s, 1H, 3-H), 2.52 (s, 3H, 6-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[32b]

5-(3-Methoxyphenyl)-2-methyl-3-(perfluorocyclopent-1-en-1-yl)thiophene (16d). According to Procedure 2, a solution of 4.6460 g (16.2 mmol) of **15d**, 5.8 mL (16.2 mmol) of *n*-BuLi and 3.0 mL (22.7 mmol) of octafluorocyclopentene are reacted. Petroleum ether is used as eluent. Yield 4.10 g (63.7%), yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 (t, $J_{H,H}$ = 7.9 Hz, 1H, 5'-H), 7.23 (s, 1H, 4-H), 7.14 – 7.11 (m, 1H, 4'-H), 7.07 – 7.05 (m, 1H, 6'-H), 6.87 – 6.84 (m, 1H, 2'-H) 3.83 (s, 3H, 7'-H), 2.46 (s, 3H, 6-H) ppm.. Spectroscopic data are in agreement with those reported in the literature.[32b]

General Procedure for the Synthesis of the non-symmetric BTEs 17_o-19_o (Procedure 3):
The reaction is carried out under nitrogen atmosphere. 1 eq. of the halide is dissolved in dry THF and the mixture is cooled to -80°C. To this solution 1.1 eq of 2.8 M *n*-BuLi in cyclohexane solution is added. After 30 – 60 min a solution of the cyclopentene unit dissolved in dry THF at -80°C is added. After 2 h the reaction is allowed to warm up to room temperature and is stirred overnight. Water is added to the solution. Diethyl ether is used for extraction, the organic phase is washed with water. The combined organic layers are dried over $MgSO_4$ and the solvent is removed *in vacuo* followed by column chromatography to afford the BTE.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(4-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridine (17_o). According to Procedure 3, a solution of 1.28 g (4.5 mmol) of **15c**, 1.6 mL (4.5 mmol) of *n*-BuLi and 1.67 g (4.5 mmol) of **16a** were reacted. Petroleum ether and ethyl acetate is used as eluent (1:1). Yield 1.395 g (50.4%), a beige powder. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.61 – 8.59 (m, 2H, 3'''-H), 7.48 (s, 1H, 4'-H), 7.47 – 7.45 (m, 2H, 2''-H), 7.42 – 7.40 (m, 2H, 2'''-H), 7.14 (s, 1H, 3-H), 6.92 – 6.90 (m, 2H, 3''-H), 3.83 (s, 3H, 6''-H), 2.01 (s, 3H, 6-H), 1.95 (s, 3H, 6'-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[32b]

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridine (18_o). According to Procedure 3, a solution of 1.00 g (3.9 mmol) of **16d**, 1.4 mL (3.9 mmol) of *n*-BuLi and 1.56 g (3.9 mmol) of **15a** are reacted. Petroleum ether and ethyl acetate is used as eluent (1:1). Yield 0.824 g (38.0%), beige powder. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.61 – 8.60 (m, 2H, 3'''-H), 7.48 (s, 1H, 4'-H), 7.41 – 7.40 (m, 2H, 2'''-H), 7.29 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.25 (s, 1H, 3-H), 7.13 – 7.11 (m, 2H, 4''-H), 7.05 – 7.04 (m, 1H, 6''-H), 6.86 – 6.83 (m, 1H, 2''-H), 3.83 (s, 3H, 7''-H), 2.00 (s, 3H, 6-H), 1.97 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.1 (o, 3''-C), 150.4 (+, 3'''-C), 143.8 (o, 2'-C), 142.4 (o, 2-C), 141.3 (o, 5-C), 139.0 (o, 5'-C), 136.9 (o, 7-C), 135.5 (o, 7'-C), 134.5 (o, 1'-C), 130.1 (+, 5''-C), 126.4 (o, 3'-C), 125.6 (o, 4-C), 125.0 (+, 4'-C), 122.6 (+, 3-C), 119.6 (+, 2'''-C), 118.2 (+, 6''-C), 116.2 (o, 8-C, 8''-C), 113.4 (+, 4''-C), 111.5 (+, 2''-C), 111.1 (o, 9-C), 55.4 (+, 7''-C), 14.7 (+, 6-C), 14.6 (+, 6'-C) ppm. IR (ATR):

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$\tilde{\nu}$ = 2953, 2922, 2840, 1735, 1592, 1436, 1334, 1268, 1190, 1110, 1047, 984, 892, 811, 776, 686, 535, 477 cm^{-1}. HRMS (ESI): calc.: 552.0885 [M+H$^+$], found: 552.0879 [M+H$^+$]. mp.: 51.1 °C.

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1'-yl)-5'-methylthiophen-2'-yl)pyridine (19$_o$). According to Procedure 3, a solution of 1.20 g (4.7 mmol) of **16d**, 1.7 mL (4.7 mmol) of *n*-BuLi and 1.87 g (4.7 mmol) of **15b** are reacted. Petroleum ether and ethyl acetate is used as eluent (1:1). Yield 1.612 g (62.2%), a beige powder.^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.83 – 8.81 (m, 1H, 2'''-H), 8.56 – 8.52 (m, 1H, 4'''-H), 7.82 – 7.79 (m, 1H, 6'''-H), 7.33 (s, 1H, 4'-H), 7.29 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.26 (s, 1H, 3-H), 7.16 – 7.15 (m, 1H, 5'''-H), 7.13 – 7.11 (m, 1H, 6''-H), 7.05 – 7.05 (m, 1H, 2''-H), 6.86 – 6.83 (m, 1H, 4''-H), 3.84 (s, 3H, 7''-H), 2.00 (s, 3H, 6-H), 1.98 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.1 (o, 3''-C), 148.9 (+, 4'''-C), 146.7 (+, 2'''-C), 142.6 (o, 2'-C), 142.3 (o, 2-C), 141.3 (o, 5-C), 138.4 (o, 5'-C), 136.7 (o, 7-C), 135.8 (o, 7'-C), 134.5 (o, 1'-C), 132.7 (+, 6'''-C), 130.1 (+, 5''-C), 126.2 (o, 3'-C), 125.7 (o, 4-C), 124.2 (+, 5'''-C), 123.7 (+, 4'-C), 122.6 (+, 3-C), 118.2 (+, 6''-C), 116.2 (o, 8-C, 8''-C), 113.4 (+, 4''-C), 111.5 (+, 2''-C), 111.1 (o, 9-C), 55.4 (+, 7''-C), 14.6 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 2969, 2928, 2882, 1463, 1373, 1306, 1125, 949, 816, 641 cm^{-1}. HRMS (ESI): calc.: 574.0704 [M+Na$^+$], found: 574.0707 [M+Na$^+$]. mp.: 85.4 °C.

General Procedure for the Protonation of the Pyridine of the BTEs to form 23$_o$-25$_o$ (Procedure 4):
The BTE is dissolved in chloroform and treated with gaseous HCl. The solvent is removed *in vacuo* to obtain the fully protonated BTE.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(4-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium(23$_o$). According to Procedure 4 100 mg (0.2 mmol) of BTE **17$_o$** are treated with gaseous HCl. Yield 102 mg (96%), beige powder. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.79 – 8.72 (m, 2H, 3'''-H), 7.87 – 7.83 (m, 2H, 2'''-H), 7.73 (s, 1H, 4'-H), 7.45 – 7.42 (m, 2H, 2''-H), 7.10 (s, 1H, 3-H), 6.91 – 6.89 (m, 2H, 3''-H), 3.82 (s, 3H, 5''-H) 2.07 (s, 3H, 6-H), 1.94 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 159.8 (o, 3''-C), 148.6 (o, 2'-C), 147.3 (o, 1'''-C), 143.0 (o, 2-C), 142.9 (+, 3'''-C), 140.4 (o, 5-C), 138.2 (o, 7-C), 135.8 (o, 5'-C), 134.3 (o, 7'-C), 129.2 (o, 1''-C), 127.0 (+, 2''-C), 125.8 (o, 3'-C), 125.2 (o, 4-C), 121.7 (+, 2'''-C), 120.9 (+, 3-C), 116.0 (o, 8-C, 8''-C), 114.5 (+, 3''-C), 111.5 (o, 9-C), 14.9 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3275, 2248, 2122, 1655, 1023, 821, 759, 618 cm^{-1}. HRMS (ESI): calc.: 574.0699 [M+Na$^+$], found: 574.0704 [M+Na$^+$]. mp.: 99.1 °C.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium(24$_o$). According to Procedure 4 100 mg (0.2 mmol) of BTE **18$_o$** are treated with gaseous HCl. Yield 106 mg (99%), beige powder. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.90 – 8.83 (m, 2H, 3'''-H), 8.02 – 7.97 (m, 2H, 2'''-H), 7.84 (s, 1H, 4'-H), 7.28 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.22 (s, 1H, 3-H), 7.10 – 7.08 (m, 1H, 4''-H), 7.03 – 7.01 (m, 1H, 6''-H), 6.86 – 6.83 (m, 1H, 2''-H), 3.83 (s, 3H, 7''-H), 2.00 (s, 3H, 6-H), 1.97 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.2 (o, 3''-C), 149.7 (o, 2'-C), 142.9 (o, 2-C), 141.7 (+, 3'''-C),141.5 (o, 5-C), 139.0 (o, 5'-C), 138.3 (o, 7-C), 135.2 (o, 7'-C), 134.3 (o, 1'-C), 130.2 (+, 5''-C), 126.4 (o, 3'-C), 125.6 (o, 4-C), 125.1 (+, 4'-C), 122.6 (+, 3-C), 121.7 (+, 2'''-C) 118.2 (+, 6''-C), 116.0 (o, 8-C, 8''-C), 113.5 (+, 4''-C), 111.6 (+, 2''-C), 111.0 (o, 9-C), 55.4 (+, 7''-C), 14.8 (+, 6-C), 14.2 (+, 2'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3055, 2923, 2838, 2569, 2077, 1629, 1498, 1629, 1498, 1336, 1269, 1193, 1110, 1047, 984, 893, 812, 732, 687, 559 cm^{-1}. HRMS (ESI): calc.: 552.0885 [M], found: 552.0879 [M]. mp.: 67.3 °C.

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-methoxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium(25$_o$). According to Procedure 4 100 mg (0.2 mmol) of BTE **19$_o$** are treated with gaseous HCl. Yield 100 mg (94%), beige powder. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.03 – 8.83 (m, 1H, 2'''-H), 8.67 – 8.50 (m, 1H, 4'''-H), 7.58 – 7.50 (m, 1H, 6'''-H), 7.43 – 7.37 (m, 1H, 5'''-H), 7.34 (s, 1H, 4'-H), 7.29 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.25 (s, 1H, 3-H), 7.13 – 7.11 (m, 1H, 6''-H), 7.05 – 7.03 (m, 1H, 2''-H), 6.85 – 6.83 (m, 1H, 4''-H), 3.83 (s, 3H, 7''-H), 2.00 (s, 3H, 6-H), 1.97 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.1 (o, 3''-C), 147.8 (+, 4'''-C), 145.7 (+, 2'''-C), 142.7 (o, 2'-C), 142.2 (o, 2-C), 141.3 (o, 5-C), 137.9 (o, 5'-C), 136.6 (o, 7-C), 135.6 (o, 7'-C), 134.5 (o, 1'-C), 133.3 (+, 6'''-C), 130.0 (+, 5''-C),127.0 (+, 5'''-C), 126.2 (o, 3'-C), 125.5 (o, 4-C), 124.0 (+, 4'-C), 122.5 (+, 3-C), 118.1 (+, 6''-C), 116.1 (o, 8-C, 8''-C), 113.3 (+, 4''-C), 111.4 (+, 2''-C), 110.9 (o, 9-C), 55.3 (+, 7''-C), 14.5 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3151, 2918, 2252, 1600, 1273, 1118, 903, 727, 649 cm^{-1}. HRMS (ESI): calc.: 538.0729 [M], found: 538.0729 [M]. mp.: 102.0 °C.

General Procedure for the Demethylation of the Anisole BTEs to give 20$_o$ -22$_o$ (Procedure 5):
To a solution of the anisole BTE in dry DCM 1.2 eq. of BBr_3 is added at room temperature. The reaction is controlled *via* TLC. If necessary more BBr_3 is added till full completion. Water is added to the solution. Diethyl ether is used for extraction, the organic phase is washed with water. The combined organic layers are dried over $MgSO_4$ and the solvent is removed *in vacuo* followed by column chromatography to afford the deprotected BTE.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenol (20$_o$). According to Procedure 5 576 mg (1.0 mmol) of BTE **17$_o$** is treated with 607 mg (2.4 mmol) of BBr_3. Yield 454 mg (81%), light yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* = 8.63 – 8.57 (m, 2H, 3'''-H), 7.50 (s, 1H, 4'-H), 7.48 – 7.45 (m, 2H, 2''-H), 7.40 – 7.38 (m, 2H, 2'''-H), 7.10 (s, 1H, 3-H), 6.87 – 6.85 (m, 2H, 3''-H), 2.03 (s, 3H, 5-H), 1.97 (s, 3H, 2'-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[32b]

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenol (21$_o$). According to Procedure 5 800 mg (1.5 mmol) of BTE **18$_o$** is treated with 843 mg (3.4 mmol) of BBr_3. Yield 584 mg (75%), a light yellow solid ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.66 – 8.59 (m, 2H, 3'''-H), 7.48 (s, 1H, 4'-H), 7.46 – 7.44 (m, 2H, 2'''-H), 7.23 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.23 (s, 1H, 3-H), 7.09 – 7.07 (m, 1H, 5'''-H), 7.04 – 7.03 (m, 1H, 2''-H), 6.81 – 6.79 (m, 1H, 4''-H), 2.00 (s, 3H, 6-H), 1.95 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 156.7 (o, 3''-C), 150.2 (+, 3'''-C), 144.0 (o, 2'-C), 142.3 (o, 2-C), 141.3 (o, 5-C), 140.8 (o, 1'''-C), 138.8 (o, 5'-C), 136.9 (o, 7-C), 135.5 (o, 7'-C), 134.7 (o, 1''-C), 130.4 (+, 5''-C), 126.5 (o, 3'-C), 125.6 (o, 4-C), 125.2 (+, 4'-C), 122.4 (+, 3-C), 119.9 (+, 2'''-C), 117.8 (+, 6''-C), 116.2 (o, 8-C, 8''-C), 115.2 (+, 4''-C), 112.7 (+, 2''-C), 111.1 (o, 9-C), 14.8 (+, 6-C), 14.6 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 2910, 2787, 2671, 2573, 1734, 1600, 1467, 1333, 1270, 1186, 1107, 1051, 984, 895, 850, 814, 779, 736, 689, 562, 530, 475 cm^{-1}. HRMS (ESI): calc.: 538.0729 [M+Na$^+$], found: 538.0728 [M+Na$^+$]. mp.: 123.9 °C.

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-(pyridin-3-yl)thiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)phenol (22'o). According to Procedure 5 950 mg (1.7 mmol) of BTE **19$_o$** is treated with 999 mg (4.0 mmol) of BBr_3. Yield 870 mg (94%), light yellow solid · ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 9.69 (s, 1H, 7''-H), 8.83 – 8.81 (m, 1H, 2'''-H), 8.49 – 8.47 (m, 1H, 4'''-H), 8.02 – 7.99 (m, 1H, 6'''-H), 7.61 (s, 1H, 4'-H), 7.43 – 7.41 (m, 1H, 5'''-H), 7.35 (s, 1H, 3-H), 7.18 (t, $J_{H,H}$ = 7.7 Hz, 1H, 5''-H), 7.01 – 6.99 (m, 1H, 6''-H), 6.96 – 6.95 (m, 1H, 2''-H), 6.73 – 6.71 (m, 1H, 4''-H), 1.96 (s, 3H, 6-H), 1.94 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.5 (o, 3''-C), 147.8 (+, 4'''-C), 145.2 (+, 2'''-C), 142.8 (o, 2'-C), 142.4 (o, 2-C), 140.9 (o, 5-C), 137.9 (o, 5'-C), 137.0 (o, 7-C), 136.4 (o, 7'-C), 134.9 (+, 1C, 6'''-C), 134.1 (o, 1''-C), 130.8 (+, 5''-C), 129.8 (o, 1C, 3'-C),125.7 (o, 1'''-C), 125.2 (+, 5'''-C), 125.1 (o, 4-C), 124.5 (+, 4'-C), 122.7 (+, 3-C), 116.6 (+, 6''-C), 116.2 (o, 8-C, 8'-C), 115.8 (+, 4''-C), 112.4 (+, 2''-C), 111.2 (o, 9-C), 14.5 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 2972, 2935, 2737, 2674, 2489, 1589, 1441, 1332, 1269, 1185, 1113, 1049,

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985, 896, 848, 797, 679, 465 cm^{-1}. HRMS (ESI): calc.: 560.0548 [M+Na$^+$], found: 560.0554 [M+Na$^+$]. mp.: 130.1 °C.

Protonation to give 26_o – 28_o.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(4-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium (26_o). According to Procedure 4 100 mg (0.2 mmol) of BTE **20_o** are treated with gaseous HCl. Yield 99 mg (93%), yellow solid. (600 MHz, DMSO-d_6): δ = 8.83 – 8.77 (m, 2H, 3'''-H), 8.21 – 8.20 (m, 2H, 2'''-H), 8.19 (s, 1H, 4'-H), 7.39 – 7.38 (m, 2H, 2''-H), 7.23 (s, 1H, 3-H), 6.79 – 6.77 (m, 2H, 3''-H), 2.05 (s, 3H, 6-H), 1.91 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.3 (o, 3''-C), 149.7 (o, 2'-C), 147.4 (o, 1'''-C), 143.5 (+, 3'''-C), 143.1 (o, 2-C), 140.3 (o, 5-C), 138.1 (o, 7-C), 136.5 (o, 5'-C), 135.5 (o, 7'-C), 130.8 (o, 1''-C), 127.3 (+, 2''-C), 124.9 (o, 3'-C), 124.0 (o, 4-C), 122.1 (+, 2'''-C), 120.7 (+, 3-C), 116.4 (+, 3''-C), 116.3 (o, 8-C, 8''-C), 111.5 (o, 9-C), 14.9 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3275, 2248, 2122, 1655, 1023, 821, 759, 618 cm^{-1}. HRMS (ESI): calc.: 538.0729 [M$^+$], found: 538.0733 [M$^+$]. mp.: 130.4 °C.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium (27_o). According to Procedure 4 100 mg (0.2 mmol) of BTE **21_o** are treated with gaseous HCl. Yield 104 mg (97%), yellow solid. ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.85 – 8.78 (m, 2H, 3'''-H), 8.27 – 8.25 (m, 2H, 2'''-H), 8.25 (s, 1H, 4'-H), 7.36 (s, 1H, 3-H), 7.18 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.01 – 6.99 (m, 1H, 4''-H), 6.95 – 6.94 (m, 1H, 6''-H), 6.73 – 6.71 (m, 1H, 2''-H), 2.06 (s, 3H, 6-H), 1.95 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.4 (o, 3''-C), 149.1 (o, 2'-C), 142.8 (o, 2-C), 142.6 (+, 3'''-C),141.7 (o, 5-C), 138.0 (o, 7-C), 135.5 (o, 7'-C), 136.3 (o, 5'-C), 134.1 (o, 1'-C), 131.2 (+, 4'-C), 130.9 (+, 5''-C), 126.9 (o, 3'-C), 124.9 (o, 4-C), 122.3 (+, 3-C), 122.3 (+, 2'''-C) 116.6 (+, 6''-C), 116.0 (o, 8-C, 8''-C), 115.9 (+, 4''-C), 112.4 (+, 2''-C), 110.9 (o, 9-C), 14.9 (+, 6-C), 14.6 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3199, 3065, 2921, 2843, 1628, 1439, 1335, 1269, 1189, 1109, 1052, 984, 893, 781, 638, 540, 466 cm^{-1}. HRMS (ESI): calc.: 574.0699 [M+Na$^+$-H$^+$], found: 574.0704 [M+Na$^+$-H$^+$]. Mp: 139.3 °C

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)pyridin-1-ium (28_o). According to Procedure 4 100 mg (0.2 mmol) of BTE **22_o** are treated with gaseous HCl. Yield 106 mg (99%), yellow solid. ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 9.72 – 9.68 (m, 1H, 2'''-H), 9.48 – 9.44 (m, 1H, 4'''-H), 8.33 – 8.30 (m, 1H, 6'''-H), 7.84 – 7.82 (m, 1H, 5'''-H), 7.48 (s, 1H, 4'-H), 7.24 (t, $J_{H,H}$ = 7.7 Hz, 1H, 5''-H), 7.23 (s, 1H, 3-H), 7.10 – 7.08 (m, 1H, 6''-H), 7.03 – 7.02 (m, 1H, 2''-H), 6.81 – 6.78 (m, 1H, 4''-H), 2.08 (s, 3H, 6-H), 2.00 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, $CDCl_3$): δ = 156.2 (o, 3''-C), 144.8 (+, 4'''-C), 142.5 (+, 2'''-C), 142.4 (o, 2'-C), 141.4 (o, 2-C), 139.4 (o, 5-C), 139.0 (+, 6'''-C), 137.7 (o, 7-C), 135.8 (o, 7'-C), 134.5 (o, 5'-C), 133.8 (o, 1'-C), 132.7 (+, 5'''-C), 130.4 (+, 5''-C), 129.7 (o, 3'-C), 126.8 (o, 4-C), 125.3 (+, 4'-C), 122.4 (+, 3-C), 118.1 (+, 6''-C), 116.4 (o, 8-C, 8''-C), 115.2 (+, 4''-C), 112.7 (+, 2''-C), 111.0 (o, 9-C), 14.9 (+, 6-C), 14.7 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3198, 2755, 2263, 1559, 1440, 1269, 1188, 1108, 984, 790, 670, 540, 461 cm^{-1}. HRMS (APCI): calc.: 538.0722 [M], found: 538.0722 [M]. mp.: 145.2 °C.

General Procedure for the *N*-Methylation of the BTEs to give the Target Betaines 29_o + H$^+$ – 31_o + H$^+$ (Procedure 6):
The phenol BTE is dissolved in acetone. To this reaction 1.5 eq. of dimethylsulfate (DMS) and a few drops of nitrobenzene are added and then the solution is heated at reflux temperature for 6 h. After cooling down to room temperature the reaction is treated with diethyl ether and extracted with bidest. water. The aqueous phase is collected and the water is removed *in vacuo* to afford the methylpyridinium salt. The equivalents of $MeSO_4^-$ ions in the spectra are 3 instead of 1. Possible are coordinations of two more ions ore traces of the excess of DMS. Because of the appearance of an oil there is no crystallization performable.

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(4-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)-1-methylpyridin-1-ium (29_o + H$^+$). According to Procedure 6 300 mg (0.6 mmol) of BTE **20_o** are treated with 0.1 mL (1.0 mmol) of DMS. Yield 284 mg (77%), red oil. ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.82 – 8.80 (m, 2H, 3'''-H), 8.29 – 8.28 (m, 2H, 2'''-H), 8.24 (s, 1H, 4'-H), 7.40 – 7.38 (m, 2H, 2''-H), 7.23 (s, 1H, 3-H), 6.78 – 6.76 (m, 2H, 3''-H), 4.21 (s, 3H, 5'''-H), 2.06 (s, 3H, 6-H), 1.91 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.2 (o, 3''-C), 149.6 (o, 2'-C), 146.9 (o, 1'''-C), 146.1 (+, 3'''-C), 143.1 (o, 2-C), 140.3 (o, 5-C), 137.4 (o, 7-C), 135.7 (o, 5'-C), 135.2 (o, 7'-C), 131.6 (o, 1''-C), 127.3 (+, 2''-C), 124.9 (o, 3'-C), 124.0 (o, 4-C), 122.5 (+, 2'''-C), 120.7 (+, 3-C), 116.6 (+, 3''-C), 116.3 (o, 8-C, 8''-C), 111.5 (o, 9-C), 47.6 (+, 5'''-C), 15.0 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 2960, 1638, 1445, 1197, 1055, 996, 764 cm^{-1}. HRMS (ESI): calc.: 552.0885 [M], found: 552.0880 [M+H$^+$].

4-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)-1-methylpyridin-1-ium (30_o + H$^+$). According to Procedure 6 300 mg (0.6 mmol) of BTE **21_o** are treated with 0.1 mL (1.0 mmol) of DMS. Yield 319 mg (86%), a green oil. ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.81 – 8.80 (m, 2H, 3'''-H), 8.28 – 8.26 (m, 2H, 2'''-H), 8.23 (s, 1H, 4'-H), 7.34 (s, 1H, 3-H), 7.17 (t, $J_{H,H}$ = 8.3 Hz, 1H, 5''-H), 7.00 – 6.98 (m, 1H, 5'''-H), 6.93 – 6.92 (m, 1H, 2''-H), 6.71 – 6.69 (m, 1H, 4''-H), 4.22 (s, 3H, 5'''-H), 2.04 (s, 3H, 6-H), 1.93 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.4 (o, 3''-C), 149.5 (o, 2'-C), 146.9 (o, 1'''-C), 146.1 (+, 3'''-C), 142.6 (o, 2-C), 141.7 (o, 5-C), 138.1 (o, 7-C), 135.8 (o, 5'-C), 135.6 (o, 7'-C), 134.0 (o, 1'''-C), 131.5 (+, 4'-C), 130.9 (+, 5''-C), 126.5 (o, 3'-C), 127.0 (o, 4-C), 122.6 (+, 3-C), 122.5 (+, 2'''-C), 116.6 (+, 6''-C), 116.2 (o, 8-C, 8''-C), 115.9 (+, 4''-C), 112.4 (+, 2''-C), 111.3 (o, 9-C), 47.6 (+, 5'''-C), 14.9 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3262, 3065, 2956, 1637, 1137, 1032, 877, 572 cm^{-1}. HRMS (ESI): calc.: 552.0885 [M], found: 552.0885 [M].

3-(4-(3,3,4,4,5,5-Hexafluoro-2-(5-(3-hydroxyphenyl)-2-methylthiophen-3-yl)cyclopent-1-en-1-yl)-5-methylthiophen-2-yl)-1-methylpyridin-1-ium (31_o + H$^+$). According to Procedure 6 300 mg (0.6 mmol) of BTE **22_o** are treated with 0.1 mL (1.0 mmol) of DMS. Yield 257 mg (70%), green oil. ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 9.39 – 9.38 (m, 1H, 2'''-H), 8.83 – 8.82 (m, 1H, 4'''-H), 8.71 – 8.69 (m, 1H, 6'''-H), 8.08 – 8.05 (m, 1H, 5'''-H), 7.93 (s, 1H, 4'-H), 7.36 (s, 1H, 3-H), 7.18 (t, $J_{H,H}$ = 7.7 Hz, 1H, 5''-H), 7.02 – 6.99 (m, 1H, 6''-H), 6.95 – 6.94 (m, 1H, 2''-H), 6.72 – 6.70 (m, 1H, 4''-H), 4.33 (s, 2H, 7'''-H), 1.99 (s, 3H, 6-H), 1.93 (s, 3H, 6'-H) ppm. ^{13}C-NMR (150 MHz, DMSO-d_6): δ = 158.3 (o, 3''-C), 144.2 (+, 4'''-C), 142.6 (+, 2'''-C), 142.5 (o, 2'-C), 141.7 (o, 2-C), 140.7 (o, 5-C), 140.4 (+, 6'''-C), 137.7 (o, 7-C), 135.8 (o, 7'-C), 134.5 (o, 5'-C), 134.0 (o, 1'-C), 132.8 (+, 5'''-C), 130.9 (+, 5''-C), 128.4 (o, 3'-C), 126.1 (o, 4-C), 125.1 (+, 4'-C), 122.6 (+, 3-C), 116.6 (+, 6''-C), 116.4 (o, 8-C, 8''-C), 115.9 (+, 4''-C), 112.4 (+, 2''-C), 111.1 (o, 9-C), 48.6 (+, 7'''-C), 14.7 (+, 6-C), 14.5 (+, 6'-C) ppm. IR (ATR): $\tilde{\nu}$ = 3206, 3100, 2922, 1630, 1185, 1046, 882, 576 cm^{-1}. HRMS (ESI): calc.: 552.0885 [M], found: 552.0895 [M].

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Keywords: BTE • through-space conjugation • mesoionic compounds • cross-conjugation • charge-separation

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