Benzodithiophene and benzotrithiophene as Ï cores for two-and three-blade propeller-shaped ferrocenyl-based conjugated systems

Publisher:
Wiley-VCH Verlag

Published version:
DOI: 10.1002/ejoc.201701045

European Journal of Organic Chemistry

Benzodithiophene and Benzotrithiophene as π-Core for Two- and Three-Blade Propeller-Shaped Ferrocenyl-Based Conjugated Systems

--Manuscript Draft--

Manuscript Number:	ejoc.201701045
Article Type:	Full Paper
Corresponding Author:	Saverio Santi University of Padova Padova, ITALY
Corresponding Author E-Mail:	saverio.santi@unipd.it
Order of Authors (with Contributor Roles):	Saverio Santi
	Serena Rossi
	Annalisa Bisello
	Roberta Cardena
	Laura Orian
Keywords:	benzotrithiophene; benzodithiophene; triferrocenyl; diferrocenyl; TD-DFT calculations
Manuscript Classifications:	Annulation; Cross-coupling; Density functional calculations; Metallocenes
Suggested Reviewers:	Evert Jan Baerends Vrije Universiteit Amsterdam F.M.Bickelhaupt@vu.nl He is an expert of structure and chemical bonding in Kohn-Sham Density Functional Theory (DFT),
	Marcel Swart Universitat de Girona marcel.swart@icrea.cat He works in the field of theoretical transition-metal complexes and develops computational tools for these studies.
	Cornelius J. Elsevier University of Amsterdam C.J.Elsevier@uva.nl He is an expert of Molecular Chemistry with special attention for Inorganic, Organometallic chemistry and Catalysis.
	Thomas E. Bitterwolf University of Idaho bitterte@uidaho.edu He is an expert of organometallic chemistry, in particular in the design and rational synthesis of new organometallic compounds with complex functionality
	Yibiao Li University of Wuyi, Jiangmen, China leeyib268@126.com He is an expert of the synthesis of functionalized benzo[b]thiophene via thio-lation annulation of fluorinated derivatives.
	Roberto Sanz Universidad de Burgos rsd@ubu.es He is an expert of the synthesis of functionalized benzo[b]thiophene via thio-lation annulation of brominated derivatives.
Opposed Reviewers:	Kazuo Takimiya University of Hiroshima ktakimi@hiroshima-u.ac.jp

	Takimiya works in the same filed of BTT syntesis. However, as pointed out in the manuscript, other authors and us have stated that his tyioannulation reactions suffer of the harsh conditions and the yields found often do not correspond to those published.
Abstract:	The syntheses of linear and star-shaped bis and tris(ferrocenyl) derivatives of benzo[1,2-b:4,5-b']dithiophene and benzo[1,2-b:3,4-b':5,6-b'']trithiophene are described via one-pot CuI/TMEDA catalyzed manifold annulation of bromoethynilbenzenes with sodium sulfide. In addition, an approach to prepare in good yield and short reaction time the parent benzotrithiophene is achieved via threefold annulation of 1,3,5-trifluoro-2,4,6-tris(trimethylsilyl)ethynyl-benzene. The computed structural and electronic features of these ferrocenyl derivatives and their UV-vis spectra are discussed, providing insight on the presence of three rather than two ferrocenyl units.
Author Comments:	Dear Prof. König, please find the online submission of our paper entitled: "Benzodithiophene and Benzotrithiophene as π-Core for for Two- and Three-Blade Propeller-Shaped Ferrocenyl-based Conjugated Systems", by Serena Rossi, Annalisa Bisello, Roberta Cardena, Laura Orian and Saverio Santi. I should appreciate if you will consider the manuscript for publication in the European Journal of Organic Chemistry. There is presently a great interest towards the synthesis of (multi)thiophene fused-aromatic compounds, which are attracting current attention as promising electronic materials. In addition, (multi)ferrocenyl compounds with conjugated spacer groups and displaying multielectron redox chemistry are of particular concern owing to their unpaired electron density migration properties. However, for the further development of new materials based on benzo(b)thiophene, it is of primary importance to plan efficient synthetic methods. In fact, the utility and applicability of the benzothioannulation reaction, previously reported by Takimiya, frequently suffer from harsh reaction conditions (over 180 °C) and long reaction times that may prejudice the desired results, as verified by us and other groups. In this paper we report novel and shortened routes to synthesize new (multi)ferrocenyl derivatives of benzodithiophene (BDT) and benzotrithiophene (BTT), the bis(ferrocenyl)-BDT and tris(ferrocenyl)-BTT. The literature reports that thiophene spacers exhibit better communication compared to phenyl spacers in donor-acceptor systems, while ferrocene is a widely studied strong donor. Therefore, in this work we have combined ferrocenyl moieties with both BTT and BDT. Please note that examples of bimetallic BDT derivatives are quite rare and, at the best of our knowledge no BTT trimetallic complexes have been reported so far. The ferrocenyl compounds described in our manuscript were obtained via one-pot catalyzed manifold annulation of substituted ethynilbenzenes in good or quantitative yields and in noticeably short reaction times. In addition, an in-depth computational study on the structural and electronic features of these ferrocenyl derivatives and their UV-vis spectra provided insight on the strong effect of third ferrocenyl unit. Thank you very much for your kind attention. NB We were not able to use the Wiley SSR to check the key compounds since it seems not possible to introduce the ferrocenyl moiety.
Section/Category:	
Additional Information:	
Question	**Response**
Dedication	
Submitted solely to this journal?	Yes
Has there been a previous version?	No
Have you used the **Wiley SSR ^{13}C NMR data checking service** for this submission?	No
We recommend that all authors make use of the free **Wiley SSR ^{13}C NMR data checking service**, which can be accessed here: https://www.wsslabs.com. Wiley SSR checks the assignment of ^{13}C NMR	ok

spectra and provides a report that shows whether the assignment is likely to be correct. We advise that it is used for key representative compounds for your manuscript; however its use is not mandatory. Wiley SSR is based on the CSEARCH Robot Referee system. as follow-up to "Have you used the **Wiley SSR ^{13}C NMR data checking service** for this submission?"	

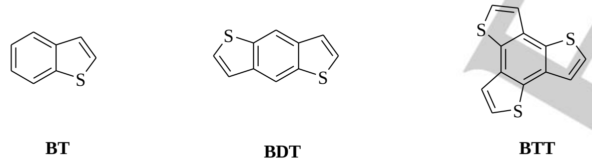
Benzodithiophene and Benzotrithiophene as π-Core for Two- and Three-Blade Propeller-Shaped Ferrocenyl-Based Conjugated Systems

Serena Rossi,[a] Annalisa Bisello,[a] Roberta Cardena,[a] Laura Orian and Saverio Santi*[a]

Abstract: The syntheses of linear and star-shaped bis and tris(ferrocenyl) derivatives of benzo[1,2-*b*:4,5-*b*']dithiophene and benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene are described via one-pot CuI/TMEDA catalyzed manifold annulation of bromoethynilbenzenes with sodium sulfide. In addition, an approach to prepare in good yield and short reaction time the parent benzotrithiophene is achieved via threefold annulation of 1,3,5-trifluoro-2,4,6-tris(trimethylsilyl)ethynyl-benzene**.** The computed structural and electronic features of these ferrocenyl derivatives and their UV-vis spectra are discussed, providing insight on the presence of three rather than two ferrocenyl units.

Introduction

Benzo[*b*]thiophene (**BT**, Scheme 1) and its related derivatives represent an important class of fused-thiophene compounds due to their wide range of biological properties[1,2] and also various applications in material science.[3]



Scheme 1. Fused-thiophene compounds: benzo[b]thiophene (**BT**), benzo[1,2-*b*:4,5-b']dithiophene (**BDT**) and benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (**BTT**).

In particular, (multi)thiophene fused-aromatic compounds are attracting current interest as promising electronic materials for organic conductors,[4] organic light-emitting diode[5] photovoltaic cells[6] and field-effect transistors.[7] For this reason thiophene-based-π-conjugated oligomers have been widely investigated as organic semiconductors.[8]

Recently, many efforts have been focused on benzo[1,2-*b*:4,5-*b*']dithiophene (**BDT**) and benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (**BTT**) (Scheme 1) as potential π-core for a new class of organic semiconductors since they contain two or three identical thiophene moieties with C_{2h} or C_{3h} symmetries that enable two-dimensional and three-dimensional molecular extensions.

BDT is a fused dithiophene which has been widely used as semiconductors[9] and building block in organic solar cells.[10] **BTT** is a fused trithiophene with a sulfur-rich, planar and extended π-system.[11] Among the possible isomeric members of the benzotrithiophene family, **BTT** has been studied thoroughly and used as a core for the construction of star-shaped oligomers and dendrimers.[12]

In addition, it was reported that the peculiar aromatic structure containing three thiophene units fused to a central benzene ring confers a completely planar and highly electron-rich system, thus making it a promising candidate for organic photovoltaic (OPV) devices.[13] Despite its particular molecular structure and potential use as a building block for organic electronic devices, the application of **BTT** remains limited. **BDT** and **BTT** derivatives have become major components or key precursors for the design and synthesis of novel material. Some patents[14] describe the methods to provide these cores at industrially applicable level and innovative materials having liquid crystalline and semiconductor properties.

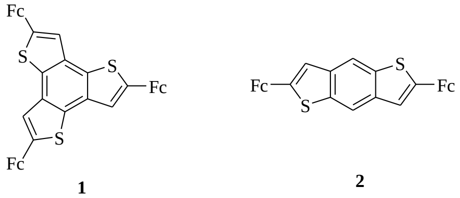
The preparation of multicomponent molecules with specific redox, optoelectronic and conductive properties is currently fundamental for modern technology.[15] In particular (multi)ferrocenyl compounds with conjugated spacer groups and displaying multielectron redox chemistry are of particular interest owing to their unpaired electron density migration properties.[16,17] Ferrocene is one of the most employed organometallic components. Its stability, redox properties, specific electron donor character and well-developed functionalization chemistry make it a primary candidate for testing the communication properties in conjugated systems. The literature reports that thiophene spacers exhibit better communication compared to phenyl spacers in donor-acceptor systems, while ferrocene is a widely studied strong donor.[16a,18] Therefore, in this work we have combined the ferrocenyl moiety with both **BTT** and **BDT**. Examples of bimetallic **BDT** derivatives are rather rare[19] and at the best of our knowledge no **BTT** trimetallic complexes have been reported so far.

On the basis of these premises, our aim was to synthetize end-capped ferrocenyl **BTT** and **BDT** conjugated systems, 2,5,8-triferrocenylbenzo[1,2-3,4-5,6]trithiophene (**1**) and 2,6-diferrocenylbenzo[1,2-4,5]-dithiophene (**2**) (Scheme 2). In fact, for the further development of new materials based on **BTT** and **BDT**, it is of primary importance to plan effective synthetic methods.

---

[a] Department of Chemical Sciences
University of Padova
Via Marzolo 1, 35131 Padova, Italy
E-mail:saverio.santi@unipd.it

Supporting information for this article is given via a link at the end of the document

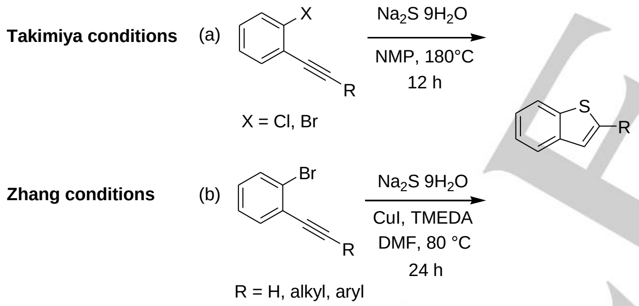


1 **2**

Scheme 2. 2,5,8-tris(ferrocenyl)benzo[1,2-*b*:3,4-*b*':5,6-*b*'']-trithiophene (**1**) and 2,6-bis(ferrocenyl)benzo[1,2-*b*:4,5-*b*']-dithiophene (**2**) complexes.

Results and Discussion

Takimiya and co-workers[20] proposed a new route to introduce sulfur functional groups to aromatic rings with $Na_2S\cdot 9H_2O$ in N-methyl-2-pyrrolidone (NMP) at 180 °C for 12 h (Scheme 3a). They reported that 1,3,5-trichloro-2,4,6-triiodiobenzene, accessible by iodination of 1,3,5-trichlorobenzene with periodic acid, can be utilized as starting compound material for the preparation of 1,3,5-trichloro-2,4,6-tris-(trimethylsilyl)ethynylbenzene (**5a**) with ethynyltrimethyl-silane in Sonagashira-coupling conditions (Scheme 4). Compound **5a** was the precursor of the cyclization reactions affording the fused-thiophene **BTT**. However, as recently reported by Zhang[21] and Sanz,[22] the utility and applicability of the above reactions suffer from the harsh reaction conditions and low yield.

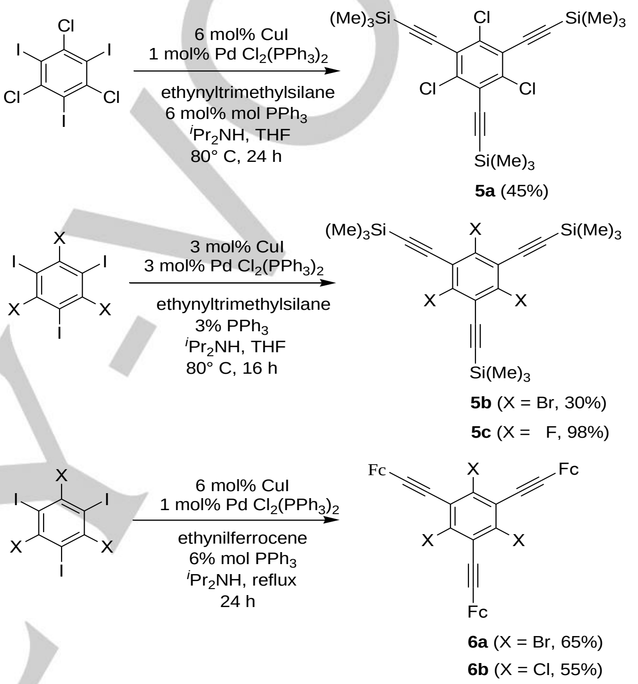


Scheme 3. Syntheses of benzo[*b*]thiophenes.

Actually, we tested the thioannulation reaction of **5a** under Takimiya's conditions but we obtained only traces of **BTT** (Table 1). Therefore, we changed strategy towards a more appropriate route for the preparation of **BTT**.

Alternative routes for the synthesis of **BTT** from 1,3,5-trichlorobenzene[12d] and from hydroxyarenes[23] were reported, but they required several steps and very long reaction time.

Recently, transition-metal-catalyzed carbon-sulfur bond forming reactions have been developed.[24] In this context, Zhang worked out a copper-catalyzed thiolation-annulation reaction of bromoalkynylbenzenes giving differently substituted benzo[*b*]thiophenes with sodium sulfate in presence of CuI and N,N,N',N'-tetramethylethylenediamine (TMEDA) in dimethylformamide (DMF) at 80 °C for 24 h (Scheme 3b).[21] Accordingly, we prepared 1,3,5-tribromo-2,4,6-tris(trimethylsilyl)-ethynylbenzene[25] (**5b**) starting from 1,3,5-tribromo-2,4,6-triiodiobenzene[26] (Scheme 4). Howsoever, this step proceeded in low yield (30%). Besides, the thioannulation of **5b** under Zhang's conditions was unsuccessful (Table 1, entry *d*).



Scheme 4. Synthesis of substituted tris(ethynilbenzenes).

Table 1. Optimization of the Thioannulation Reaction Conditions

product	substrate	catalyst	ligand	solvent	T (°C)	time (h)	yield (%)
BTT[a]	**5a**	-	-	NMP	180	24	<5
BTT[b]	**5a**	CuI	TMEDA	NMP	120	24	-
BTT[c]	**5b**	-	-	NMP	180	12	<5
BTT[d]	**5b**	CuI	TMEDA	DMF	80	24	10
BTT[e]	**5c**	CuI	TMEDA	DMF	110	2	78
1[f]	**6a**	CuI	TMEDA	DMF	110	2	98
1[g]	**6b**	CuI	TMEDA	DMF	110	24	<5
1[h]	**6b**	-	-	NMP	180	12	7
1[i]	**6b**	CuI	-	DMSO	60	8	<5
2[f]	**7**	CuI	TMEDA	DMF	110	2	55

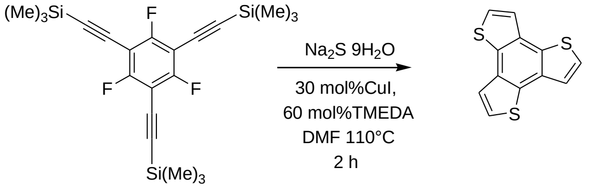
Reaction conditions: All the reactions were performed under argon atmosphere. [a]**5a** (0.5 mmol), $Na_2S\cdot 9H_2O$ (3 mmol) in NMP (12 mL). [b]**5a** (0.15 mmol), $Na_2S\cdot 9H_2O$ (1.35 mmol), CuI (30 mol%) and ligand (60 mol%). [c]**5b** (0.5 mmol), $Na_2S\cdot 9H_2O$ (4.5 mmol) in NMP (12 mL). [d]**5b** (0.2 mmol), $Na_2S\cdot 9H_2O$ (1.8 mmol), CuI (30 mol%), ligand (60 mol%) in DMF (15 mL). [e]**5c** (0.23 mmol), $Na_2S\cdot 9H_2O$ (2.07 mmol), CuI (30 mol%), ligand (60 mol%) in DMF (17 mL).

[f]See xperimental Section. [g]**6b** (0.12 mmol), $Na_2S\cdot9H_2O$ (1.08 mmol), CuI (30 mol%), ligand (60 mol%) in DMF (9 mL). [h]**6b** (0.09 mmol), $Na_2S\cdot9H_2O$ (0.81 mmol) in NMP (6 mL). [i]**6b** (0.08 mmol), $Na_2S\cdot9H_2O$ (0.72 mmol), CuI (30 mol%) in DMSO (6 mL).

Interestingly, it was reported the annulation reaction of trifluoro-trialkynylbenzenes with $CsOH\cdot H_2O$ or RNH_2 obtaining benzotrifuranes and benzotripyrrol[27] and of fluoro-phenylacetylene derivatives with KOH or Na_2S giving benzofuranes and benzothiophenes.[28]

Thus, we synthesized 1,3,5-trifluoro-2,4,6-tris(tri-methylsilyl)-ethynyl-benzene (**5c**)[29] starting from 1,3,5-trifluoro-2,4,6-triiodio-benzene[30] (Scheme 4).

At long last, the twofold thioannulation reaction of the fluorinated derivative **5c** was successful (Scheme 5) and **BTT** was obtained in good yield and after 2 h.

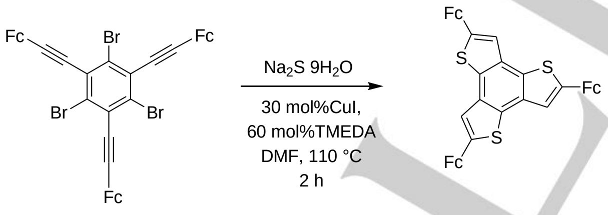


5c

BTT (78%)

Scheme 5. Synthesis of **BTT**.

The preparation of the 2,5,8-triferrocenylbenzo[1,2-*b*;3,4-*b*';5,6-*b*'']trithiophene (**1**) (Scheme 6) was achieved starting from 1,3,5-tribromo-2,4,6-tris(ethynilferrocene)-benzene (**6a**) obtained through Sonagashira-coupling of 1,3,5-tribromo-2,4,6-triiodio-benzene with ethynilferrocene (Scheme 4).



6a

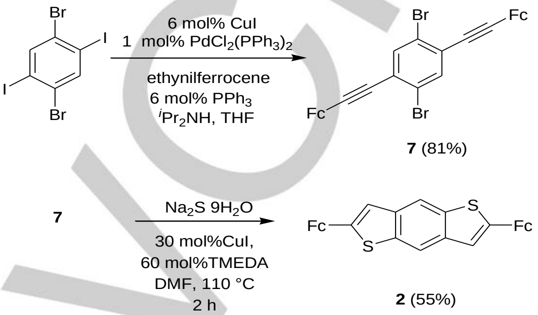
1 (98%)

Scheme 6. Synthesis of **1**.

The threefold thioannulation of **6a** proceeded in the presence of CuI and TMEDA at 110 °C for 2 h. After appropriate work-up, compound **1** was isolated without further purifications in almost quantitative yield as a red compound (Table 1).

Conversely, the reaction of 1,3,5-trichloro-2,4,6-tris(ethynilferrocene)-benzene[31] (**6b**) in the same reaction conditions, and also with DMSO/CuI or NMP, gave **1** in poor yield (Table 1).

The successful synthesis of **1** prompted us to apply it to for the preparation of 2,6-diferrocenylbenzo[1,2-4,5]dithiophene (**2**) (Scheme 7). The formation of 1,4-dibromo-2,5-bis(ethynyl-ferrocenyl)-benzene (**7**) was obtained through Sonagashira-coupling of 1,4-dibromo-2,5-diiodio-benzene[32] with ethynyl-ferrocene. Finally, the twofold thioannulation reaction of **7** with 30% mol of CuI, 40% mol of TMEDA and 6 eq. of $Na_2S\cdot9H_2O$ produced the desired compound **2**.



7 (81%)

7

2 (55%)

Scheme 7. Synthesis of **2**.

The UV–Vis electronic spectra of complexes **1** and **2** between 230 and 700 nm are reported in Figure 1. The spectra show similarities, but the bands of **2** are much less intense. Thus, the electronic structure and the spectral properties of both compounds were theoretically investigated.

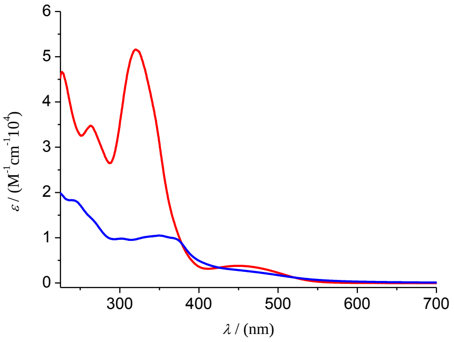
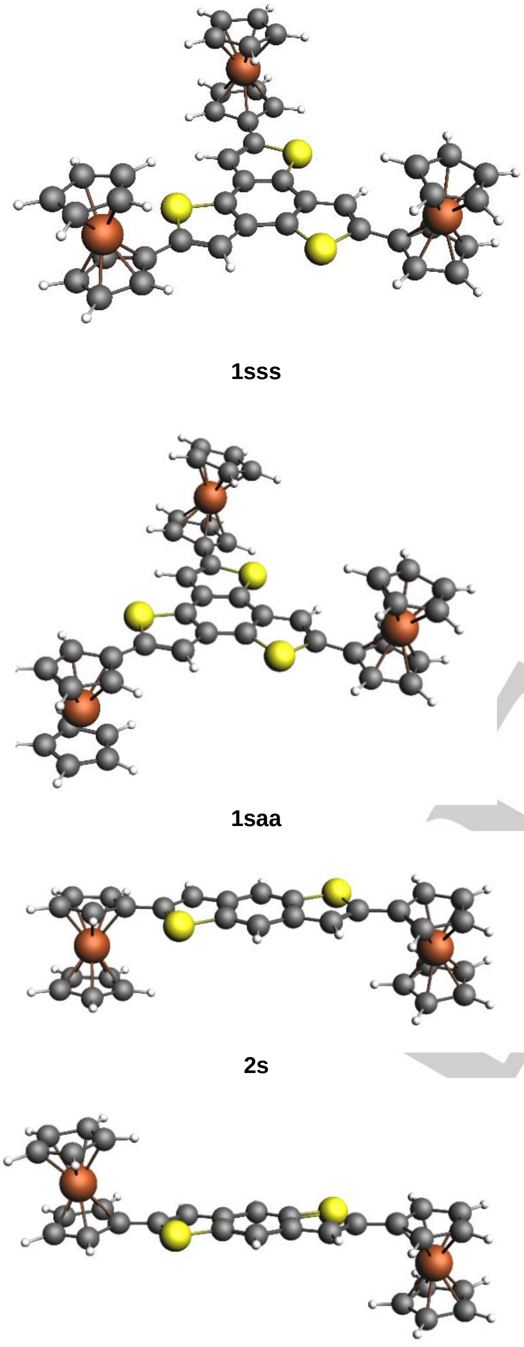


Figure 1. UV-vis spectra of 0.4 mM **1** (red line) and 0.2 mM **2** (blue line) in CH_2Cl_2. The absorbance was corrected for compound concentration and optical path.

The molecular structures of **1** and **2** have been calculated using state-of-the-art DFT methods (Figure 2). In **1,** the three ferrocenyl groups can be arranged in *syn/syn/syn* (**1sss**) or in *syn/anti/anti* (**1saa**) conformation; both converged geometries have eclipsed Cp rings. The metal-metal distance ranges between 10.7 and 11.2 Å in **1sss** and between 10.8 and 11.6 Å in **1saa**. The energy difference between **1sss** and **1saa** is negligible and the barrier associated to the rotation of a ferrocenyl pendant about the carbon-carbon bond connecting the pendant to the polycyclic core, is estimated about 5 kcal mol^{-1} (level of theory: OPBE/TZP sc; Figure S14).

In both conformers, the couples HOMO/HOMO−1 and LUMO/LUMO+1 are very close in energy and an identical HOMO-LUMO gap is computed (2.47 eV).



1sss

1saa

2s

2a

Figure 1 Fully optimized conformers of **1** and **2**; level of theory: OPBE/TZ2P.

These four molecular orbitals have metal d lobes on the iron nuclei as well as carbon/sulfur p lobes of the π linker.

Table 2 Computed excitation energies (level of theory: COSMO-SAOP/TZ2P all electron) and experimental visible absorptions of the **1sss**, **1saa**, **2s** and **2a**. The values in italics were obtained at COSMO-SAOP/TZP all electron level. Only contributions above 10% are shown.

	COSMO-TDDFT values	**Electronic transitions**	**Exp. values [assignment]**
1sss	2.8213 eV (0.15954) 440 nm	H→L (31%) H–1→L+1 (20%) H–1→L (18%) H→L+1 (13%)	450 nm [MLCT]
	2.8308 eV (0.17610) 438 nm	H–1→L (25%) H→L+1 (24%) H→L (23%)	
	3.0558 eV (0.5520) 405 nm	H→L+2 (44%) H–2→L (31%)	
	3.0679 eV (0.44558) 404 nm	H–1→L+2 (48%) H–2→L+1 (29%)	
	3.2093 eV (0.11808) *386 nm*	*H-6→L (51%)* *H-7→L+1 (13%)*	
	3.2134 eV (0.11067) *386 nm*	*H-7→L (43%)* *H-6→L+1 (21%)*	
	3.3232 eV (0.12264) *373 nm*	*H-9→L (57%)*	
	3.3267 eV (0.13192) *373 nm*	*H-9→L+1 (38%)* *H-10→L (28%)*	
	3.6422 eV (0.02501) *340 nm*	*H-2→L+4 (21%)* *H-2→L+3 (13%)*	
	3.6474 eV (0.03605) *340 nm*	*H-2→L+3 (30%)* *H-1→L+7 (13%)* *H-2→L+4 (11%)*	
	3.6504 eV (0.03314) *340 nm*	*H-2→L+5 (38%)* *H→L+7 (17%)*	
	3.6632 eV (0.08423) *339 nm*	*H→L+7 (20%)* *H-1→L+6 (15%)* *H-2→L+3 (11%)*	320 nm
1saa	2.8277 eV (0.16676) 439 nm	H–1→L (27%) H→L+1 (26%) H→L (16%) H–1→L+1 (11%)	450 nm [MLCT]
	2.8323 eV (0.17201) 438 nm	H–1→L+1 (46%) H→L (23%) H–2→L+2 (12 %)	
	3.0605 eV (0.47844) 405 nm	H→L+2 (47%) H–2→L (31%)	
	3.0697 eV (0.44286) *404 nm*	*H–1→L+2 (50 %)* *H–2→L+1 (29 %)*	
	3.2036 eV (011412) *387 nm*	*H-6→L (60%)* *H-7→L+1 (13%)*	
	3.2119 eV (0.10644) *386 nm*	*H-7→L (42%)* *H-6→L+1 (22%)*	
	3.3208 eV (0.10141) *373 nm*	*H-9→L (48%)* *H-10→L (20%)*	
	3.3237 eV (0.16653) *373 nm*	*H-9→L+1 (36%)* *H-10→L (21%)* *H-6→L+2 (18%)*	
	3.6437 eV (0.03554) *340 nm*	*H-2→L+5 (17%)* *H-2→L+4 (17%)*	
	3.6490 eV (0.03272) *340 nm*	*H-2→L+4 (25%)* *H-2→L+5 (11%)* *H-1→L+7 (10%)*	
	3.6528 eV (0.01630) *339 nm*	*H-2→L+5 (28%)* *H-2→L+3 (23%)* *H→L+7 (11%)*	320 nm
	3.6668 eV (0.10178) *338 nm*	*H-1→L+7 (31%)* *H→L+6 (19%)* *H-2→L+6 (15%)*	
2s	2.605 eV (0.77727) 476 nm	H→L (95%)	470 nm [MLCT]
	2.914 eV (0.26572) 425 nm	H–4→L (85%)	
	3.2815 eV (0.48424) 378 nm	H–7→L (90%)	340–350 nm
2a	2.608 eV (0.82516) 475 nm	H→L (90%)	470 nm [MLCT]
	2.915 (0.27125) 425 nm	H-4→L (85%)	

3.2838 (0.51365) 378 nm	H–7→L (90%)	
3.6676 (0.10677) 338 nm	H→L+5 (79%)	330–370 nm

The percentage contribution of Fe orbitals is almost 60% in the filled MOs and decreases to 20% in the empty ones in both conformers.

Also in **2**, different conformations are predicted, i.e. with *syn* (**2s**) or *anti* arrangement (**2a**) of the two ferrocenyl pendants. The energies of these two conformers are almost identical and a low barrier for their interconversion is computed (about 4 kcal mol^{-1} at OPBE/TZP sc; Figure S15). The ferrocenyl moieties show eclipsed Cp rings, which are tilted with respect to the thioindacenyl plane in opposite directions by approximately 10º; the Fe-Fe distance is 12.6 Å in **2s** and 12.9 Å in **2a**, respectively. In both conformers, the frontier molecular orbitals are delocalized. The percentage contribution of Fe d orbitals to the HOMOs is almost 60 % and decreases to slightly less than 20% in the LUMOs. The HOMO-LUMO gap of both conformers is 2.18 eV.

The excitation energies have been computed for **1sss**, **1saa**, **2s** and **2a** at COSMO-SAOP/TZ2P all electron level of theory in dichloromethane. The strongest absorptions falling in the visible range are reported in Table 2. The lowest values for **1sss** (**1saa**) are 440 and 438 nm (439 and 438 nm) and correspond to transitions mainly involving the frontier molecular orbitals HOMO–1/HOMO and LUMO/LUMO+1. These energies closely match to the experimental band centered at approximately 450 nm. Another couple of rather strong absorptions is found at 404 and 405 nm for both conformers. Based on the percentage contribution of Fe d orbitals to the filled and the empty MOs involved in these transitions, which remarkably decreases, to all these bands computed in the 500-400 nm range we can assign metal to ligand charge transfer (MLCT) character.

When going from **1** to **2**, the recorded spectrum become flatter and the lowest peaks are bathochromically shifted. This is well reproduced in the model. In fact, the lowest absorption of **2s** (**2a**) is at 476 nm (475 nm) and is an almost pure monoelectronic HOMO-LUMO transition, to which MLCT character is assigned. Also the close absorptions at 425 nm have a high contribution from the monoelectronic transition H–4→LUMO and the drastic decrease of iron d contribution when going from the filled to the empty molecular orbital allows to assign the MLCT character to these bands. In contrast, the excitation energies computed below 400 nm, i.e. at 378 nm, involve the HOMO–7 and LUMO MOs which are both delocalized with similar metal-linker composition (about 20-80%).

Summarizing, the bands in the visible region between 400 and 500 nm of both **1** and **2** are MLCT transitions, the number of which doubles in the former due to the presence of the third ferrocenyl pendant, thus justifying the more intense signals recorded in the experiment. Also in the higher energy part of the spectrum of the triferrocenyl conformers **1sss** and **1saa**, multiple absorptions are computed in the range 386-338 nm; in contrast, for the biferrocenyl conformers only two absorptions are computed at 378 and 338 nm. They all fall in the region where the largest intensity variation is recorded between the spectra of **1** and **2**. Unluckily, for these absorptions below 400 nm, the composite nature of the transition and the nature of the involved MOs which have Fe d and linker π system contributions, preclude a precise assignment. Nevertheless, two-fold and four-fold numbers of strong absorptions are calculated for **1sss** and **1saa** in correspondence of the most intense peak, this phenomenon being an effect of the presence of the third ferrocenyl group.

Conclusions

We have synthesized two multi(ferrocenyl) compounds, the tris(ferrocenyl) **1** and bis(ferrocenyl) **2** of **BTT** and **BDT**, respectively, by manifold thioannulation of the corresponding bromo derivatives of the (ethynilferrocene)benzenes. In particular, to the best of our knowledge **1** represents the first examples of metallorganic complex of **BTT**. Furthermore, we prepared the parent **BTT** following an alternative and high-yield approach foreseeing the thioannulation of the fluorinated **5c**.

All these compounds were obtained via one-pot CuI/TMEDA catalyzed thioannulations of bromoethynyl (**1** and **2**) and of fluoroethynyl (**BTT**) benzene derivatives in good or quantitative yields and in appreciably short reaction times if compared with previously reported methods.[20] The structures of **1** and **2** were investigated through DFT calculations. Computed vertical excitations allowed to assign the bands recorded in the 500–400 nm range of the UV-vis spectra. In addition, the higher intensity of the whole spectrum experimentally found for **1** is ascribed to the much higher number of close transitions due to the presence of the third ferrocenyl pendant.

The features of these compounds make them promising candidates for the study of intramolecular electron transfer and for potentials applications as photoelectronic materials.

Experimental Section

General Methods: All reactions and complex manipulations were performed under oxygen and moisture-free atmosphere utilizing standard Schlenk techniques. Diisopropylamine (DIPA) was purified by distillation from calcium hydride and tetrahydrofuran (THF) was freshly distilled from sodium and benzophenone ketyl under nitrogen. Iodine, periodic acid, potassium iodide, 1,3,5-trichlorobenzene, 1,3,5-tribromobenzene, 1,3,5-trifluorobenzene, 1,4-dibromobenzene, triphenylphosphine, copper iodide, bis-(triphenylphosphine)-palladium(II)dichloride, ethynyltrimethyl-silane, ethynylferrocene, sodium sulfide nonahydrate, tetramethylethylenediamine (TMEDA), and anhydrous dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO) were purchased from commercial suppliers and used without further purification. 1,3,5-trifluoro-2,4,6-triiodio-benzene,[30] 1,3,5-trichloro-2,4,6-triiodio-benzene,[31] 1,3,5-tribromo-2,4,6-triiodio-benzene[26] and 1,4-dibromo-2,5-diiodio-benzene[32] were prepared following the reported procedures. Compound **6b** was prepared following the procedure previously reported.[31] Microanalyses were performed at the Dipartimento di Scienze Chimiche, Università di Padova. HRMS spectra were obtained using an ESI-TOF Mariner 5220 (Applied Biosystem) mass spectrometer with direct injection of the sample and collecting data in the positive mode. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance IIIHD spectrometer (T = 298 K) operating at 400.13 MHz and 100.61 MHz or on Bruker Avance DMX 599.90 MHz, respectively. The ^{13}C resonances for compound **2** were attributed through 2D-heterocorrelated COSY experiments (HMQC for the H-bonded carbon atoms, HMBC for the quaternary ones). Flash column chromatography was performed using a Biotage^{TM} Isolera One flash purification system with SNAP-ULTRA columns.

Computational details. Amsterdam Density Functional (ADF) program was used to carry out all the calculations.[33] Geometries were fully optimized with OPBE functional[34] combined and TZ2P basis sets (triple-ζ-Slater-type orbital (STO) basis, extended with two polarization functions) for all the atoms, frozen core up to 2p for Fe, up to 1s for C, and up to 2p for S. This level of theory is denoted OPBE/TZ2P. Frequency calculations were run to assess the stationary nature of the minima and no imaginary frequency was found. The scan (series of constrained geometry optimizations) to estimate the energy associated to the rotation of a ferrocenyl pendant about the C-C bond connecting the pendant to the π core, was run at a lower level of theory, i.e. OPBE/TZP using steps of 10º. TD-DFT calculations were carried out on the optimized geometries using all electron TZ2P basis sets for all of the atoms; the lowest 20 excitations were computed. The approximate xc potential obtained with the statistical averaging of (model) orbital potentials (SAOP) was employed.[35] This level of theory, denoted SAOP/TZ2P all electron, was recently adopted by some of us to study the excited states of ferrocenylindenes and of their radical cations.[36] Solvent effects were taken into account with the Conductor-like Screening Model (COSMO),[37] as implemented in the ADF program.[33] For dichloromethane we used a solvent-excluding surface with an effective radius and relative dielectric constant of 2.94 Å and 8.9, respectively. The empirical parameter in the scaling function in the COSMO equation was set to 0.0. The radii of the atoms were taken to be MM3 radii,[38] divided by 1.2, giving 1.350 Å for H, 1.700 Å for C, 1.792 for S and 1.858 Å for Fe.[39] For **1** conformers, the number of computed excitation energies was increased to 50 to reach the spectral region close to 300 nm and COSMO-SAOP/TZP level was employed. The use of a smaller basis set shifted the lowest absorptions only by few nm and so results are trustworthy.

Preparation of 1,3,5-tricloro-2,4,6-tris(trimethylsilyl)-ethynylbenzene (5a). In a dry three necked flask,10 mL of diisopropylamine, 10 mL of THF, 6.00 mol% of CuI (82.6 mg, 0,43 mmol) and 1 mol% of $[PdCl_2(PPh_3)_2]$ (52.0 mg, 0.072 mmol) were added and the solution was stirred for 5 min. The reaction mixture was treated with 1,3,5-trichloro-2,4,6-triiodiobenzene (1.00 g, 1.79 mmol), ethynyltrimethylsilane (703 mg, 7.16 mmol) and 6.00 mol% of PPh_3 (117.7 mg, 0.43 mmol). The resulting mixture was refluxed T = 85 °C for 24 h, diluted with water (10 mL) and extracted with chloroform (10 mL × 3). The extract was washed with brine (50 mL × 3) and dried over Na_2SO_4 (anhydrous). After removal of the solvent under vacuum, the product was purified by Biotage flash chromatography on silica gel eluted with hexane. Yield: 381.4 mg (0.814 mmol, 45%) as white solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$, ppm) δ: 0.29 (s, 27 H $Si(CH_3)_3$). ^{13}C-NMR (100.61 MHz, $CDCl_3$, ppm) δ: - 0.16 ($Si(\mathbf{C}H_3)_3$), 98.00 ($C\equiv\mathbf{C}Si$), 108.16 ($C_6\mathbf{C}\equiv C$), 122.07 ($\mathbf{C_6}C\equiv C$), 139.80 (**C**Cl) Anal. Calcd for $C_{21}H_{27}Cl_3Si_3$: C, 53.66; H, 5.79. Found: C, 53.51; H, 5.77.

Preparation of 1,3,5-tribromo-2,4,6-tris(trimethylsilyl)-ethynyl-benzene (5b). In a dry three necked flask 18 mL of diisopropylamine, 1,3,5-tribromo-2,4,6-triiodiobenzene (500 mg, 0.73 mmol), 3% of $[PdCl_2(PPh_3)_2]$ and 3% of CuI were added. Then a solution of trimethylsilylacetylene (245.5 mg, 2.5 mmol) in DIPA (9 mL) was added dropwise and lastly 3% of PPh_3 (19.6 mg, 0.075 mmol). At the end of the addition, the mixture was warmed up to 80 °C. After 1 h, THF (9 mL) was added, and the mixture was left stirring 16 h under argon. The mixture was filtered over Celite, diluted with water (35 mL) and extracted with chloroform (35 mL × 3). The extract was washed with brine (50 ml × 3) and dried over Na_2SO_4 (anhydrous). After removal of the solvent, the residue was purified by Biotage's flash chromatography on silica gel eluted with hexane. Yield: 131.4 mg (0.22 mmol, 30%) as white solid. ^{1}H-NMR (599.90 MHz, $CDCl_3$, ppm) δ: 0.26 (s, 27 H $Si(CH_3)_3$). ^{13}C-NMR (100.61 MHz, $CDCl_3$, ppm) δ: - 0.23 ($Si(\mathbf{C}H_3)_3$), 104.74 ($C\equiv\mathbf{C}Si$), 106.45 ($C_6\mathbf{C}\equiv C$), 126.14 ($\mathbf{C_6}C\equiv C$), 134.51 (**C**Br) Anal. Calcd for $C_{21}H_{27}Br_3Si_3$: C, 41.80; H, 4.51. Found: C, 41.71; H, 4.30.

Preparation of 1,3,5-trifluoro-2,4,6-tris(trimethylsilyl)-ethynyl-benzene (5c). In a dry three necked flask 18 mL of diisopropylamine, 1,3,5-trifluoro-2,4,6-triiodiobenzene (500 mg, 0.98 mmol), 3% of $[PdCl_2(PPh_3)_2]$ and 3% of CuI were added. Then a solution of ethynyltrimethylsilane (245.5 mg, 2.5 mmol) in DIPA (9 mL) was added dropwise and lastly 3% of PPh_3 (19.6 mg, 0.075 mmol). At the end of the addition, the mixture was warmed up to 80 °C. After 1 h, THF (9 mL) was added, and the mixture was left stirring 16 h under argon. The mixture was filtered over Celite, diluted with water (35 ml) and extracted with chloroform (35 ml × 3). The extract was washed with brine (50 ml × 3) and dried over Na_2SO_4 (anhydrous). After evaporated all the solvent, the residue was purified by Biotage's flash chromatography on silica gel eluted with hexane. Yield: 403.8 mg (0.96 mmol, 98%) as white solid. ^{1}H-NMR (400.13 MHz, $CDCl_3$, TMS, ppm) δ: 0.26 (s, 27 H $Si(CH_3)_3$). ^{13}C-NMR (100.61 MHz, $CDCl_3$, TMS, ppm) δ: 0.0 ($Si(\mathbf{C}H_3)_3$), 88.96 ($C\equiv\mathbf{C}Si$), 107.16 ($\mathbf{C_6}C\equiv C$), 162.05 ($C_6\mathbf{C}\equiv C$), 164.66 (**C**F). ^{19}F-NMR (376.50 MHz, $CDCl_3$, ppm) δ: -99.77 (s, 3F). Anal. Calcd for $C_{21}H_{27}F_3Si_3$: C, 59.95; H, 6.47. Found: C, 59.90; H, 6.40.

Preparation of Benzo(1,2-*b*;3,4-*b'*;5,6-*b''*)trithiophene (BTT). In a dry three necked flask containing 17 mL of dimethylformamide backfilled with argon (3 cycles), **5c** (100 mg, 0.23 mmol), 30 mol% of CuI (13.8 mg, 0.069 mmol), 60 mol% of TMEDA (16.3 mg, 0.14 mmol) and $Na_2S\cdot 9H_2O$ (497.17 mg, 2.07 mmol) were added and the reaction mixture was stirred at 110 ºC for two h. After the reaction was completed, the mixture was filtered through a glass filter and washed with ethyl acetate (100 mL). The mixture was washed with brine (3x200 mL), the organic layers were dried with anhydrous Na_2SO_4 and evaporated under vacuum. The brown residue was purified by silica gel column chromatography eluted with hexane. Yield: 45 mg (0.18 mmol, 78%) as pale white needles. ^{1}H-NMR (400.13 MHz, $CDCl_3$, ppm) δ: 7.63 (d, 3H $CH{=}C\mathbf{H}S$), 7.52 (d, 3H $C\mathbf{H}{=}CHS$). ^{13}C-NMR (100.61 MHz, $CDCl_3$, ppm) δ: 122.48 ($\mathbf{C}H{=}CHS$), 125.15 ($CH{=}\mathbf{C}HS$), 131.60 ($\mathbf{C_6}CH$), 131.99 ($\mathbf{C_6}S$), Anal. Calcd for $C_{12}H_6S_3$: C, 58.50; H, 2.45; S, 39.04. Found: C, 58.51; H, 2.50; S, 39.09. HRMS (ESI+): *m/z* calcd for $C_{12}H_6S_3$ (M+), 246.9704. Found: 246.9723.

Preparation of 1,3,5-tribromo-2,4,6-tris(ethynylferrocenyl)-benzene (6a). In a dry three necked flask 30 mL of diisopropylamine, 6.00 mol% of CuI (27 mg, 0.14 mmol) and 1.00 mol% of $[PdCl_2(PPh_3)_2]$ (16 mg, 0.023 mmol) were added and the solution was stirred for 5 min. The reaction mixture was treated with 1,3,5-tribromo-2,4,6-triiodio-benzene (413 mg, 0.6 mmol), ethynylferrocene (500 mg, 2.4 mmol) and 6.00 mol% of PPh_3 (37 mg, 0.14 mmol). The resulting mixture was refluxed for 24 h whereby the red solution turned into an orange suspension. After cooling it to room temperature and the evaporation of all volatiles, the orange residue was worked-up by Soxhelet extraction with diethyl ether (9 h) to remove the appropriate ammonium salt. After elimination of the solvent in vacuo, the product was purified by Biotage flash chromatography on silica gel eluted with hexane and increasingly dichloromethane from 2% to 25%. Yield: 365 mg (0.39 mmol, 65%) as orange solid. ^{1}H-NMR (400.13 MHz, CD_2Cl_2, ppm) δ: 4.31 (s, 15H C_5H_5), 4.35 (m, 6H C_5H_4), 4.62 (m, 6H C_5H_4). ^{13}C-NMR (100.61 MHz, CD_2Cl_2, ppm) δ: 64.13 (FcC≡**C**C$_6$) 70.27 (C_5H_4), 70.85 (C_5H_5), 72.35 (C_5H_4), 84.49 (Fc**C**≡CC$_6$), 100.49 (C_i-C_5H_4), 127.06 (FcC≡C**C$_6$**), 128.63 (**C**Br). Anal. Calcd for $C_{42}H_{27}Fe_3Br_3$: C, 53.73; H, 2.90. Found: C, 53.62; H, 2.97. HRMS (ESI+): *m/z* calcd for $C_{42}H_{27}Fe_3Br_3$ (M+), 937.7695. Found: 937.8595.

Preparation of 2,5,8-triferrocenylbenzo[1,2-*b*;3,4-*b'*;5,6-*b''*]-trithiophene (1). In a dry three necked flask containing 6 mL of dimethylformamide backfilled with argon (3 cycles), **6a** (80 mg, 0.08 mmol), 30 mol% of CuI (4.6 mg, 0.024 mmol), 60 mol% of TMEDA (5.6 mg 0.048 mmol) and $Na_2S{\cdot}9H_2O$ (172 mg, 0.72 mmol) were added, and the reaction mixture was stirred at 110–115 ºC for two h. After the reaction was completed, the mixture was filtered through a glass filter and washed with ethyl acetate (15 mL). The mixture was washed with brine (3x20 mL), the organic layers were dried with anhydrous Na_2SO_4 and evaporated under vacuum. Yield: 82.5 mg (0.098 mmol, 98%) as red solid. ^1H-NMR (400.13 MHz, CD_2Cl_2, ppm) δ: 4.17 (s, 15H C_5H_5), 4.42 (m, 6H C_5H_4), 4.78 (m, 6H C_5H_4), 7.47 (s, 3H CH=C-Fc). ^{13}C-NMR (100.61 MHz, CD_2Cl_2, ppm) δ: 67.86 (C_5H_4), 69.92 (C_5H_4), 70.77 (C_5H_5), 79.91 (C_i-C_5H_4), 116.61 (**C**H=C-Fc), 129.41 (**C$_6$**-CH), 132.56 (**C$_6$**-S), 143.82 (CH=**C**-C_i). Anal. Calcd for $C_{42}H_{30}Fe_3S_3$: C, 63.18; H, 3.79; S, 12.05. Found: C, 63.05; H, 3.89; S, 12.02. HRMS (ESI+): *m/z* calcd for $C_{42}H_{30}Fe_3S_3$ (M+), 797.9555. Found: 797.9672.

Preparation of 1,4-dibromo-2,5-bi(ethynylferrocenyl)-benzene (7). In a dry flask 5.1 ml of diisopropylamine, 25.6 ml of THF, 6 mol% of CuI (52 mg 0.28 mmol) and 1.00 mol% of $[PdCl_2(PPh_3)_2]$ (32 mg, 0.046 mmol) were added and the solution was stirred for 5 min. The reaction mixture was treated with 1,4-dibromo-2,5-diiodio-benzene (1.00 g 2.05 mmol), ethynylferrocene (882 mg, 4.1 mmol) and 6 mol% of PPh_3 (73 mg, 0.28 mmol). The resulting mixture was stirred overnight at room temperature under argon. After the evaporation of all volatiles, an orange residue was isolated. Yield: 1.08 g (1.66 mmol, 81%). ^1H-NMR (400.13 MHz, CD_2Cl_2, ppm) δ: 4.28 (s, 10H C_5H_5), 4.32 (m, 4H C_5H_4), 4.56 (m, 4H C_5H_4) 7.73 (s, 2H C_6H_2). ^{13}C-NMR (100.61 MHz, CD_2Cl_2, ppm) δ: 64.33 (FcC≡**C**C$_6$), 70,10 (C_5H_4), 70,75 (C_5H_5), 72,27 (C_5H_4), 83,61 (Fc**C**≡CC$_6$), 97.15 (C_i-C_5H_4), 123.66 (**C**Br), 126.93 (FcC≡C**C$_6$**), 136.28 (**C$_6$**H). Anal. Calcd for $C_{30}H_{20}Fe_2Br_2$: C, 55.27; H, 3.09. Found: C, 55.15; H, 3.12. HRMS (ESI+): *m/z* calcd for $C_{30}H_{20}Fe_2Br_2$ (M+), 651.8610. Found: 651.8716.

Preparation of 2,6-diferrocenylbenzo[1,2-4,5]dithiophene (2). In a dry three necked flask containing 5 mL of dimethylformamide backfilled with argon (3 cycles), **7** (130 mg, 0.20 mmol), 30 mol% of CuI (11 mg, 0.06 mmol), 40 mol% of TMEDA (9 mg, 0.08 mmol) and $Na_2S{\cdot}9H_2O$ (288 mg, 1.2 mmol) were added, and the reaction mixture was stirred at 110 ºC for 2 h. After the reaction was completed, the mixture was filtered through a glass filter and washed with ethyl acetate (15 mL). The mixture was washed with brine (3x30 mL), the organic layers were dried with anhydrous Na_2SO_4 and evaporated under vacuum. The product was purified by washing with hexane. Yield: 60 mg, (0.11 mmol, 55%) as brownish red solid. ^1H-NMR (400.13 MHz, CD_2Cl_2, ppm) δ: 4.14 (s, 10H C_5H_5), 4.39 (m, 4H C_5H_4), 4.71 (m, 4H C_5H_4) 7.24 (s, 2H CH=CC$_i$) 8.04 (s, 2H C_6H). ^{13}C-NMR (100.61 MHz, CD_2Cl_2, ppm) δ: 67.76 (C_5H_4), 69.72 (C_5H_4), 70.55 (C_5H_5), 79.75 (C_i-C_5H_4), 115.59 (**C$_6$**H), 117.34 (**C**H=C-Fc), 137.65 (**C$_6$**-CH), 138.52 (**C$_6$**-S), 144.25 (CH=**C**–C_i). Anal. Calcd for $C_{30}H_{22}Fe_2S_2$: C, 64.54; H, 3.97; S, 11.49. Found: C, 64.41; H, 3.90; S, 11.41. HRMS (ESI+): *m/z* calcd for $C_{30}H_{22}Fe_2S_2$ (M+), 557.9868. Found: 558.0051.

Acknowledgements

Financial supports by Italian MIUR (DOR 2016) and the University of Padova (CPDA142751/14) are acknowledged. We wish to gratefully acknowledge Dr. Daniele Dalzoppo and Dr. Marta De Zotti for ESI-MS analyses. Computational facilities at CINECA were available thanks to the ISCRA grant STREGA (PI: L.O.).

Keywords: benzotrithiophene • benzodithiophene • triferrocenyl • diferrocenyl • TD-DFT calculations

[1] L. Berrade, B. Aisa, M. J. Ramirez, S. Galiano, S. Guccione, L. R. Moltzau, F. O. Levy, F. Nicoletti, G. Battaglia, G. Molinaro, I. Aldana, A. Monge, S. Perez-Silanes *J. Med. Chem.* **2011**, *54*, 3086–3090.

[2] A. Venturelli, D. Tondi, L. Cancian, F. Morandi, G. Cannazza, B. Segatore, F. Prati, G. Amicosante, B. K. Shoichet, M. P. Costi *J. Med. Chem.* **2007**, *50*, 5644–5654.

[3] V. A. Bren, A. D. Dubonosov, V. I. Minkin, A. V. Tsukanov, T. N. Gribanova, E. N. Shepelenko, Y. V. Revinsky, V. P. Rybalkin *J. Phys. Org. Chem.* **2007**, *20*, 917–928.

[4] F. Wudl, R. C. Haddon, E. T. Zellers, F. B. Bramwell *J. Org. Chem.* **1979**, *44*, 2491–2493.

[5] M. Mazzeo, V. Vitale, F. Della Sala, D. Pisignano, M. Anni, G. Barbarella, L. Favaretto, A. Zanelli, R. Cingolani, G. Gigli *Adv. Mater.* **2003**, *15*, 2060–2063.

[6] R. De Bettignies, Y. Nicolas, P. Blanchard, E. Levillain, J. M. Nunzi, J. Roncali *Adv. Mater.* **2003**, *15*, 1939–1943

[7] (a) T. Yamamoto, K. Takimiya, *J. Am. Chem. Soc.* **2007**, *129*, 2224–2225. (b) K. Takimiya, Y. Kunugi, Y. Toyoshima, T. Otsubo *J. Am. Chem. Soc.* **2005**, *127*, 3605–3612.

[8] (a) X. Guo, S. Wang, V. Enkelmann, M. Baumgarten, K. Müllen *Org. Lett.* **2011**, *13*, 6062–6065. (b) A. Mishra, C.-Q. Ma, P. Bäuerle *Chem. Rev.* **2009**, *109*, 1141–1276. (c) H. E. Katz, A. J. Lovinger, J. G. Laquindanum *Chem. Mater.* **1998**, *10*, 457–459.

[9] (a) K. Takimiya, Y. Konda, H. Ebata, N. Niihara, T. Otsubo *J. Org. Chem.* **2005**, *70*, 10569–10571. (b) C. H. Wang, R. R. Hu, S. Liang, J. H. Chen, Z. Yang, J. Pei *Tetrahedron Lett.* **2005**, *46*, 8153–8157. (c) W. Graupner, G. Grem, F.Meghdadi, C. Paar, U. Scherf, K. Mullen, W. Fischer, F. Stelzer, M. C. Liq, B. J. G. Laquindanum, H. E. Katz, A. J. Lovinger, A. Dodabalapur *Adv. Mater.* **1997**, *9*, 36–39. (d) S. Yoshida, M. Fujii, Y. Aso, T. Otsubo, F. Ogura *J. Org. Chem.* **1994**, *59*, 3077–3081.

[10] (a) L. Ye, S. Zhang, W. Zhao, H. Yao, J.Hou *Chem. Mater.* **2014**, *26*, 3603–3605. (b) L. Zheng, Y.-H. Chung, Y. Ma, L. Zhang, L. Xiao, Z. Chen, S. Wang, B. Qu, Q. Gong *Chem. Commun.* **2014**, *50*, 11196–11199. (c) D. Patra, T.-Y. Huang, C.-C. Chiang, R. O. V. Maturana, C.-W. Pao, K.-C. Ho, K.-H. Wei, C.-W. Chu *ACS Appl. Mater. Interfaces* **2013**, *5*, 9494–9500. (d) J. Zhou, Y. Zuo, X. Wan, G. Long, Q. Zhang, W. Ni, Y. Liu, Z. Li, G. He, C. Li, B. Kan, M. Li, Y. Chen *J. Am. Chem. Soc.* **2013**, *135*, 8484-8487. (e) Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian, Y. Chen *Adv. Mater.* **2011**, *23*, 5387–5391.

[11] (a) X. Guo, S. Wang, V. Enkelmann, M. Baumgarten, K. Müllen *Org. Lett.* **2011**, *13*, 6062–6065. (b) C. B. Nielsen, J. M. Fraser, B. C. Schroeder, J. Du, A. J. P. White, W. Zhang, I. Mcculloch *Org. Lett.* **2011**, *13*, 2414–2417. (c) P. Rademacher, C. Heinemann, S. Jänsch, K. Kowski, M. E. Weiß *Spectrochim. Acta A* **2000**, *56*, 1179–1190.

[12] A. Riańo, I. Arrechea-Marcos, M. J. Mancheńo, M. P. Burrezo, A. De la Peńa, S. Loser, A. Timalsina, A. Facchetti, T. J. Marks, J. Casado, J. T. L. Navarrete, R. P. Ortiz, J. L. A. Segura *Chem. Eur. J.* **2016**, *22*, 6374–6381. (b) Y. Jiang, D. Yu, L. Lu, C. Zhan, D. Wu, W.You, Z. Xie, S. Xiao *J. Mater. Chem. A* **2013**, *1*, 8270–8279. (c) T. Kashiki, M. Kohara, I. Osaka, E. Miyazaki, K. *J.* Takimiya *Org. Chem.* **2011**, *76*, 4061–4070. (d) T. Taerum, O. Lukoyanova, R. G. Wylie, D. F. Perepichka *Org. Lett.* **2009**, *11*, 3230–3233. (e) Y. Nicolas, P. Blanchard, E. Levillain, M. Allain, N. Mercier, J. Roncali *Org. Lett.* **2004**, *6*, 273–276.

[13] X. Zhao, D.Yang, H. Lv, L.Yind, X.Yang *Polym. Chem.* **2013**, *4*, 57–60.

[14] H. Kuwabara, M. Ikeda, K. Takimiya **2010** *European Patent Application* EP 2 147 923 A1 H. Kuwabara, M. Ikeda, K. Takimiya **2011** *European Patent Application* EP 2 361 915 A1.

[15] (a) J. Weiss *Coord. Chem. Rev.* **2010**, *254*, 2247–2248. (b) H. Bayley *Nature* **2010**, *467*, 164. (c) F. Giacalone, N. Martin *Adv. Mater.* **2010**, *22*, 4220–4248. (d) T. Fukino, N. Fujita, T. Aida *Org. Lett.* **2010**, *12*, 3074–3077. (e) V. J. Chebny, D. Dhar, S. V. Lindeman, R. Rathore *Org. Lett.* **2006**, *8*, 5041–5044.

[16] (a) A. Donoli, A. Bisello, R. Cardena, M. Crisma, L. Orian, S. Santi *Organometallics* **2015**, *34*, 4451−4463. (b) S. Santi, A. Bisello, R.

Cardena, A. Donoli *Dalton Trans.* **2015**, *44*, 5234–5257. (c) A. Donoli, A. Bisello, R. Cardena, C. Prinzivalli, Santi S. *Organometallics* **2013**, *32*, 1029−1036. (d) O. Gidron, Y. Diskin-Posner, M. Bendikov *Chem. Eur. J.* **2013**, *19*, 13140–13150. (e) J. M. Speck, R. Claus, A. Hildebrandt, T. Ru, E. Erasmus, L. Van As, J. C. Swarts, H. Lang *Organometallics* **2012**, *31*, 6373−6380. (f) A. Hildebrandt, S. W. Lehrich, D. Schaarschmidt, R. Jaeschke, K. Schreiter, S. Spange, H. Lang *Eur. J. Org. Chem.* **2012**, *5*, 1114–1121. (g) K. Kaleta, A. Hildebrandt, F. Strehler, P. Arndt, H. Jiao, A. Spannenberg, H. Lang, U. Rosenthal *Angew. Chem. Int. Ed.* **2011**, *50*, 11248–11252. (h) M. Wagner *Angew. Chem. Int. Ed.* **2006**, *45*, 5916–5918. (i) S. Barlow, *Inorg. Chem.* **2001**, *40*, 7047–7053 (l) S. Barlow, D. O'Hare *Chem. Rev.* **1997**, *97*, 637–670.

[17] (a) A. Donoli, A. Bisello, R. Cardena, C. Prinzivalli, M. Crisma, S. Santi *Organometallics* **2014**, *33*, 1135–1143. (b) A. Donoli, A. Bisello, R. Cardena, F. Benetollo, A. Ceccon, S. Santi *Organometallics* **2011**, *30*, 1116–1121.

[18] (a) B. Jin, F. Tao, P. Liu *J. Electroanal. Chem.* **2008**, *624*, 179–185. (b) H. Yao, L. Ye, H. Zhang, S. Li, S. Zhang, J. Hou *Chem.Rev.* **2016**,*116*, 7397–7457. (c) A. Hildebrandt, H. Lang *Organometallics* **2013**, *32*, 5640–5653. (d) T. L. Stott, M. O. Wolf *Coord. Chem. Rev.* **2003**, *246*, 89–101.

[19] (a) Y.-P. Ou, F. Hu, S. Tang, J. Yu, J. Li, F. Zhang, D. Kuang *J. Organomet. Chem.* **2017**, *843*, 66–74. (b) Y.-P. Ou, J. Zhang, F. Zhang, D. Kuang, F. Hartl, L. Rao, S.H. Liu *Dalton Trans.* **2016**, *45*, 6503–6516.

[20] T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara *Org. Lett.* **2009**, *11*, 2473–2475.

[21] L. L. Sun, C. L. Deng, R. Y. Tang, X. G. Zhang *J. Org. Chem.* **2011**, *76*, 7546–7550.

[22] V. Gueilarte, M. A. Fernández-Rodríguez, P. García-García, E. Hernando, R. Sanz *Org. Lett.* **2011**, *13*, 5100–5103.

[23] B. Rungtaweevoranit, A. Butsuri, K. Wongma, K. Sadorn, K. Neranon, C. Nerungsi, T. Thongpanchang *Tetrahedron Lett.* **2012**, *53*, 1816–1818

[24] (a) I. P. Beletskaya, V. P. Ananikov *Chem. Rev*. **2011**, *111*, 1596–1636. (b) I. Nakamura, T. Sato, Y. Yamamoto *Angew. Chem. Int. Ed.* **2006**, *45*, 4473–4475.

[25] An alternative synthesis of **5b** was schematically reported but no yield and experimental details are available: Y. Rubin *Chimia* **1998**, *52*, 117–126

[26] K. Kobayashi, N. Kobayashi *J. Org. Chem.* **2004**, *69*, 2487–2497

[27] H. Tsuji, G. Cantagrel, Y. Ueda, T. Chen, L.-J. Wan, E. Nakamura *Chem. Asian J.* **2013**, *8*, 2377–2382.

[28] (a) Y. Li, L. Cheng, B. Li, S. Yiang, L. Chen, Y. Shao *ChemistrySelect* **2016**, *5*, 1092–1095. (b) Y. Li, L. Cheng, X. Liu, B. Li, N. Sun *Beilstein J. Org. Chem.* **2014**, *10*, 2886–2891.

[29] J. Lieffrig, O. Jeannin, M. Fourmigué *J. Am. Chem. Soc.* **2013**, *135*, 6200–6210.

[30] H. H. Wenk, W. Sander *Eur. J. Org. Chem.* **2002**, *2002*, 3927–3935.

[31] U. Pfaff, G. Filipczyk, A. Hildebrandt, M. Korb, H. Lang *Dalton Trans.* **2014**, *43*, 16310–16321.

[32] F. He, W. Wang, W. Chen, T. Xu, S. B. Darling, J. Strzalka, Y. Liu, L. Yu *J. Am. Chem. Soc.* **2011**, *133*, 3284–3287.

[33] (a) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler *J. Comput. Chem.,* **2001**, *22*, 931–967. (b) Computer code ADF2016.01: E. J. Baerends, et al., SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, **2016**.

[34] M. Swart, A. W. Ehlers, K. Lammertsma *Mol. Phys.* **2004**, *102*, 2467–2474

[35] (a) O. V. Gritsenko, P. R. T. Schipper, E. J. Baerends *Chem. Phys. Lett.* **1999**, *302*, 199–207. (b) P. R. T. Schipper, O. V. Gritsenko, S. J. A. van Gisbergen, E. J. Baerends *J. Chem. Phys.* **2000**, 112, 1344–1352.

[36] (a) S. Scuppa, L. Orian, A. Donoli, S. Santi, M. Meneghetti *J. Phys. Chem. A* **2011**, *115*, 8344–8349 (b) L. Orian, S. Scuppa, S. Santi, M. Meneghetti *Phys. Chem. Chem. Phys.* **2013**, *15*, 12971–12976.

[37] (a) A. Klamt, G. J Schürmann *Chem. Soc., Perkin Trans. 2* **1993**, *5*, 799–805. (b) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224–2235

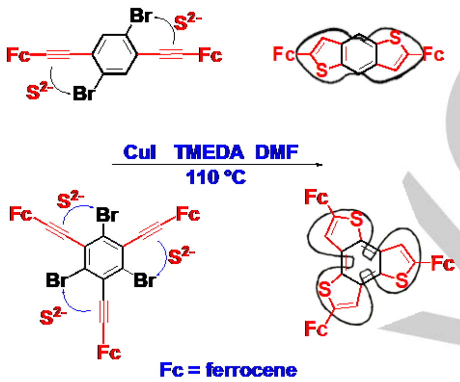
[38] C. C. Pye, T. Ziegler *Theor. Chem. Acc.* **1999**, *101*, 396–408.

[39] N. L. Allinger, X. Zhou, J. Bergsma, *J. Mol. Struct. (Theochem)* **1994**, *312*, 69–83.

Entry for the Table of Contents

FULL PAPER

The syntheses of two- and three-blade propeller-shaped bis and tris-(ferrocenyl) derivatives of benzodithiophene and benzotrithiophene are described via one-pot manyfold thioannulation of bromoethynilbenzene ferrocenyl derivatives with Na_2S. In addition, an approach to prepare in good yield and short reaction time the parent benzotrithiophene is achieved. The presence of the third ferrocenyl moiety drastically changes the intensity of the UV-vis absorptions, as rationalized through TD-DFT calculations.



Ferrocenyl Benzothiophenes

*Serena Rossi, Annalisa Bisello, Roberta Cardena, Laura Orian and Saverio Santi**

Page No. – Page No.

Benzodithiophene and Benzotrithiophene as π-Core for for Two- and Three-Blade Propeller-Shaped Ferrocenyl-Based Conjugated Systems

Supporting Information