Heteroheptacenes with Fused Thiophene and Pyrrole Rings

Peng Gao, Don Cho, Xiaoyin Yang, Volker Enkelmann, Martin Baumgarten, and Klaus Müllen^{*[a]}

Abstract: The preparation of conjugated heteroheptacenes using an electrophilic coupling reaction induced by a super acid is reported. The new molecules containing thiophene and/or pyrrole rings are bisbenzo[b,b']thienodithieno[3,2-b:2',3'-d]pyrrole, bisbenzo-[b,b']thienocyclopenta[2,1-b:3,4-b']dithiophene, and bisthieno[3,2b]thieno[2,3-f:5,4-f]carbazole. Dithieno[3,2-b:2',3'-d]pyrrole, cyclopenta[2,1b:3,4-b']dithiophene, and carbazole are used as the aromatic cores. This versatility provides access to molecules with systematically controllable physicochemical properties. Single-crystal X-

ray analyses demonstrate that the type and position of the alkyl substituents significantly changes the packing properties of the new molecules. The optical and optoelectronic properties of the heteroheptacenes vary considerably depending on the number and position of the sulfur or nitrogen linkages and reveal the improved environmental stability over their hydrocarbon counterparts. The analysis of the experimental

Keywords: conjugation • fused-ring systems • heteroacenes • semiconductors • solid-state structures

Introduction

Investigations in the field of organic electronics have spurred the advance of new molecular building blocks for applications in organic field-effect transistors (OFETs),^[1] organic light-emitting diodes (OLEDs),^[2] and photovoltaic cells.^[3] In this context, materials derived from linear organic π -conjugated oligomers are particularly appealing.^[4] These materials, when suitably modified, enable low-cost fabrication processes of stable, large-area, and lightweight electronic devices.^[5]

In the context of organic electronics, dithieno[3,2-b:2',3'-d]pyrrole (DTP) and cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) have emerged as popular building blocks for poly-

as a new functional unit in conjugated polymers due to its planarity and N–H bond, which can be easily substituted by functional groups.^[8] On the other hand, CPDT, which is regarded as a fused-ring analogue of 3-alkylthiophene and a structural analogue of fluorene (Scheme 1), shows an out-ofplane arrangement of the substituents due to the sp³-hybridized carbon atom in the bridge position. It has been reported that homopolymers based on CPDT can not self-assemble into ordered structures.^[9] However, much less research has been devoted to the structurally defined oligomeric molecules based on DTP^[10] and CPDT as models of their polymeric counterparts. In an effort to broaden the family of heteroheptacenes,^[11] we reported the synthesis of dibenzol*b.b*'lthieno[2,3-f;5,4-

meric semiconducting materials.^[6,7] DTP, a structural analogue of carbazole (Scheme 1), has received much interest

we reported the synthesis of dibenzo[b,b']thieno[2,3-f:5,4-f]carbazoles with the inclusion of both thiophene and pyrrole ring units (Scheme 2).^[12] In spite of the extended π system, the spectroscopic and electrochemical characterization of dibenzo[b,b']thieno[2,3-f:5,4-f]carbazoles indicates that it possesses lower HOMO energy levels and larger band gaps than pentacene.^[13] Meanwhile, subsequent single-crystal X-ray diffraction (SCXRD) studies of this heteroheptacene

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results from UV/Vis absorption/photoluminescence (PL) spectroscopy and cyclic voltammetry were combined with DFT quantum-chemical calculations and compared with other model heteroheptacenes. The results suggest that among the acenes with the same number of fused rings, the thiophene ring fusion inside the skeleton stabilizes both HOMO and LUMO levels more effectively than pyrrole and benzene rings. The present study also shows that the new heteroheptacenes are promising candidates for the construction of electronic materials.

[[]a] Dr. P. Gao, D. Cho, Dr. X. Yang, Dr. V. Enkelmann, Dr. M. Baumgarten, Prof. Dr. K. Müllen Max Planck Institute for Polymer Research Ackermannweg 10 55128, Mainz (Germany) Fax: (+49)6131-379-350 E-mail: muellen@mpip-mainz.mpg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903562.



Scheme 1. Carbazole versus dithienopyrrole versus cyclopentadithiophene versus fluorene as fused π systems.

DFT calculations provided valuable insight into the molecular electronic structure.

Results and Discussion

Synthesis and characterization of 1, 2, and 4: Oxidative cou-



Scheme 2. Structure of dibenzo[b,b']thieno[2,3-f:5,4-f]-carbazoles

have revealed the existence of π - π stacking between cofacially arranged molecules and a short interplanar separation of 3.33 Å, which is smaller than the layer separation of graphite (3.35 Å) and points toward the presence of π - π interactions in the crystal lattice. These results motivated us to study similar heteroheptacenes with DTP or CPDT as the core structure.

Herein, we present the facile synthesis and properties of new heteroheptacenes bisbenzo[b,b']thienodithieno[3,2b:2',3'-d]pyrrole (1) and bisbenzo[b,b']thienocyclopenta[2,1b:3,4-b']dithiophene (2) with five-membered subunits (e.g., thiophene, pyrrole, and cyclopenta-1,3-diene). The synthesis of **3** has been described previously.^[12] For comparison, another heteroheptacene, carbazole-based bisthieno[3,2-b] thieno[2,3-f:5,4-f]carbazole (4), which possesses four fused thiophene rings outside the carbazole skeleton, was also synthesized (Scheme 3). All the new compounds were characterized by a combination of FT-NMR and optical (UV/Vis and photoluminescence) spectroscopic, SCXRD, and electrochemical (cyclic voltammetry) techniques. In addition,



Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**10**) was prepared by following a reported method^[17] and was dialkylated with hexyl bromide in the presence of KOH as the base and KI as the catalyst in dimethyl sulfoxide (DMSO), thus affording **11** in excellent yield (Scheme 5). The distannylated com-



Scheme 3. Ladder-type π -conjugated heteroheptacenes.^[14]

pound 12 was made by dilithiation of 11 with tBuLi, followed by quenching with Me₃SnCl. The tin compound was an oil that could not be purified by column chromatography (due protiodestannylation).^[18] to However, the compound was sufficiently pure to be used in the next step. Precursor 13 was synthesized by a Stille coupling of 12 and 1-bromo-2-(methylsulfinyl)benzene (8) in an overall yield of 85 %. Finally, by following the same procedure as for precursor 9, product 2 was achieved as a light-yellow powder in 88% yield.

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Scheme 4. Synthesis of bisbenzo[b,b']thienodithieno[3,2-b:2',3'-d]pyrrole (1). dba=dibenzylideneacetone, BINAP=2,2'-bis(diphenylphosphino)-1,1'-binaphthyl.



Scheme 5. Synthesis of bisbenzo[b,b']thienocyclopenta[2,1-b:3,4-b']dithiophene (2). DMSO = dimethyl sulfoxide. NBS = N-bromosuccinimide.

The synthesis of **4** is outlined in Scheme 6. The Stille coupling reaction between 2,7-dibromo-9-methyl-9*H*-carbazole (**14**) and (5-hexylthiophen-2-yl)trimethylstannane (**15**) was carried out in DMF with $[Pd(PPh_3)_4]$ as the catalyst to give **16** in 80% yield. Afterwards, regioselective bromination at the 3- and 6-positions of the carbazole core of **16** was achieved by using two equivalents of *N*-bromosuccinimide (NBS) in a 1:1 mixture of CHCl₃ and acetic acid. Compound **17** was obtained after a flash column chromatography and further treated with two equivalents of *n*BuLi to form the

corresponding 3.6-dilithiated species. The latter was quenched with dimethyl disulfide to afford 18 in 50% yield of the isolated product. Oxidation of 18 with hydrogen peroxide in acetic acid gave precursor 19 in 72% yield. By following the same ring-closing procedure as for precursor 9, 4 was obtained in 95% yield as a lightyellow solid. The structures of

the products were verified by

their ¹H NMR spectra (see Fig-

ure S1 in the Supporting Infor-

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mation). Solid-state structures of the heteroheptacenes: Elucidation of the solid-state packing of conjugated materials in single crystals is essential to understand how the molecular assembly is influenced by substituents.[19] Single crystals of the heteroheptacenes suitable for SCXRD studies were obtained from CH_2Cl_2 /hexane (for 1 and 3) or CH₂Cl₂/MeOH (for 2) at room temperature. Crystals of 4 were too thin for structural determination.

The skeleton of **1** is planar and two molecules form a pair in a head-to-head structure. The pairs further stack into a column with the aromatic skeleton that forms a herringbone structure, in which the tilt angle between two mean planes of the framework of compound **1** is 45.6°, relative to 60 and 52° in DBTCz^[12] and pentacene,^[20] respectively. Two intermolecular S–C close contacts are observed between the two molecules in the pair (Figure 1a,

marked in dashed line); for example, the distances between the sulfur atoms in molecules of **1** (i.e., atoms S1 and S3; see the Supporting Information) and carbon atoms (i.e., atoms C14 and C2) from the adjacent molecules are 3.44 and 3.34 Å, which are shorter than the sum of their van der Waals radii (3.55 Å). The same distances could be observed between the two carbon atoms of each molecule and the sulfur atoms of one additional molecule as well. In addition, these columns form lamellae with aliphatic chains that lie between every two aromatic columns (Figure 1b, marked in



Scheme 6. Synthesis of bisthieno[3,2-b]thieno[2,3-f:5,4-f]-carbazole (4).



Figure 1. Packing diagram of 1. a) View down the stacking axis of headto-head column pairs (dashed rectangle illustrates the head-to-head pairs; dashed lines illustrate intermolecular close contacts within and between the columns). b) View along the long molecular axis that shows a "lamella herringbone" structure formed by antiparallel column pairs (dashed rectangle illustrates the antiparallel lamella structure; the hydrogen atoms are omitted for clarity).

a dashed rectangle). Interestingly, intermolecular close contacts were also found between the columns. The distance between S2 of one molecule and C8 of the molecule in another column was 3.48 Å (as marked in Figure 1 a), which suggests that a single crystal of **1** may have a two-dimensional electronic structure. A similar packing was seen in DBTCz, but with only a one-dimensional electronic structure.^[12]

By changing the *N*-alkyl substituent in 1 to a dialkylmethylene unit in 2, the single crystal of 2 exhibits dramatic differences from 1 (Figure 2). The fully ladderized skeleton is planar and with the 4,4'-substituted alkyl chains lying above and below the plane of the backbone, respectively, in an almost vertical geometry. In one unit cell, two adjacent molecules are packed so that they form a pair with a headto-head structure as in 1. However, due to the extended extra alkyl chains, the two molecules in the pair are separated and almost perpendicular from each other. To fill the space, one molecule from a second pair embeds in and has cofacial overlap, to a small extent, with one molecule in the first pair. The loose packing nature of the material could be seen from the interplanar distance (3.83 Å) of the cofacial part, and no short contact was detected in the solid. Obviously, the perpendicularly oriented alkyl chain causes a distinct bulge, which is essential to prevent the molecule of 2 from close packing.

Compound **3** crystallizes in the monoclinic $P2_1/c$ space group with four molecules in the unit cell. The conjugated



Figure 2. Packing diagram of 2. a) View down the *b* axis of the unit cell (dashed rectangle illustrates the head-to-head pairs). b) View along the long molecular axis that shows the perpendicularly oriented alkyl chain (dashed lines illustrate cofacial distance; the hydrogen atoms are omitted for clarity).

molecules have the same aromatic backbone as DBTCz,^[12] but with two *n*-butyl chains in the long molecular axis instead of the short molecular axis. As expected, the packing characteristics of **3** are dramatically changed by altering the position of the substituents (Figure 3). The crystal structure of **3** is based on a sandwiched herringbone structure in which its dimers are packed tightly in the crystal (Figure 3b, marked in the dashed rectangle). These dimers are formed by two inversely packed molecules in an antiparallel fashion to the direction of the short molecular axis. The plane-toplane distance is approximately 3.45 Å, thus suggesting π - π overlapping, and short C-S contacts (3.49 Å) also exist in a face-to-edge manner between the dimers, thus indicating the two-dimensional electronic structure of the crystal (marked in dashed line).

These different solid-state structures of the three heteroheptacenes nicely illustrate how the effect of the alkyl substituents and different heteroatoms could efficiently be utilized to tune the organization in the solid state of organic semiconductors. The more sulfur atoms that are present, the



Figure 3. Packing diagrams of **3**. The hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 50% probability. a) View down the stacking axis of dimers (dashed rectangle illustrates the dimers of the molecules). b) View along the long molecular axis that shows a sandwiched herringbone structure (dashed rectangle illustrates the dimers of the molecules; dashed lines illustrate intermolecular close contacts within and between the dimers).

more intermolecular short contacts exist, which can facilitate charge-carrier transport in devices. It is known that tight packing of the chromophores in the solid state will lead to self-quenching of fluorescence and excimer or exciplex formation.^[21] To prevent this phenomenon, bulky or branched substituents are always employed to intrinsically disperse the packing arrangement of the chromophores. In this study, a branched alkyl substitution in **2** instead of a linear one in **1** effectively loosens the solid packing, and therefore may prevent self-quenching and suppress the formation of aggregates/excimers. On the other hand, changing the alkyl substitution from the short molecular axis to the long molecular axis changed the packing motif of the compound from a highly slipped herringbone structure to a densely packed π - π stacking structure.

Optical properties of heteroheptacenes 1–4: UV/Vis absorption and photoluminescence (PL) spectra of **1–4** were measured in solution and as drop-cast thin films (Figure 4) to



Figure 4. a) Normalized UV/Vis absorption and PL spectra of 1–4 in THF (10^{-6} M). b) Normalized UV/Vis absorption and PL spectra of 1–4 as thin film.

Chem. Eur. J. 2010, 16, 5119-5128

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absorption/emission maxima of the heteroheptacenes and the optical energy gap. Table 1 collects the UV/Vis and PL

assess the effect of heteroatom and alkyl substitution on the

Table 1. UV/Vis absorption and PL data for 1-4.

Compound		Film (solid state)			
•	absorption ^[a,b] λ _{max} [nm]	$\mathrm{PL}^{[\mathrm{a}]} \ \lambda_{\mathrm{f}} \ [\mathrm{nm}]$	quantum yield $^{[\mathrm{a},\mathrm{c}]} arPsi_{\mathrm{f}}$	absorption λ_{\max} [nm]	PL $\lambda_{\rm f} [\rm nm]$
1	387	407	0.22	414	465
2	413	457	> 0.75	420	468
3	423	439	0.03	438	450
4	413	426	0.12	432	444

[a] Solvent: THF (10^{-6} M); $\eta = 1.4070$. [b] A $\pi - \pi^*$ HOMO–LUMO transition as λ_{max} . [c] Quantum yield relative to diphenylanthracene (10^{-7} M, cyclohexane solution); excitation at $\lambda = 365$ nm.

data for all the compounds in THF. The UV/Vis absorption spectra of 1 and 2 display structured absorption bands in the UV range that are attributed to the β (Platt ¹B_b) band and p band of the π - π * transitions. Although in the case of 3 and **4**, in addition to the β band, one can also see two weak α (Platt ¹L_b) bands and/or p bands in the visible region (Figure 4 a).^[22] Similar UV absorption bands have been observed in the case of diindolocarbazoles.^[11c] Relative to the DTPbased heteroheptacene 1, the absorption maximum of CPDT-based **2** is red-shifted by $\Delta \lambda = 26$ nm from $\lambda = 387$ nm when the central pyrrole ring is replaced by a 1,3-cyclopentadiene unit. This result for 1 is surprising because the introduction of electron-rich heterocycles into conjugated systems has been an established strategy for achieving lowband-gap chromophores.^[23] In fact, a similar case has been observed in the homopolymers of DTP and CPDT before.^[24] In a comprehensive study of poly(DTP)s, Ogawa and Rasmussen^[6b] attributed this phenomenon to the difference in the rigidity of the two monomers. With CPDT- and DTPbased oligomers, however, they claim that by changing the bridgehead from a CHR to NR group (R = alkyl groups) results in no change in the absorbance spectra.^[16] When two more sulfur atoms are incorporated into the skeleton, 4 shows less-resolved absorption spectra than 3 and the α band of **4** is also blue-shifted by $\Delta \lambda = 10$ nm relative to **3**.

Solution optical band gaps E_{g}^{op} of **1–4**, defined by the 0–0 transition energies, were estimated based on the λ_{max} absorption edge (Table 3). All the compounds have significantly larger band gaps than hydrocarbon heptacene,^[25,26] thus indicating that in planarized aromatic systems, the increased thiophene units widen the HOMO–LUMO gaps.^[27]

The PL spectra of 1–4 were measured in THF by exciting 10^{-6} M solutions at the corresponding λ_{max} values. Interestingly, **2** shows an unstructured strong emission maximum ($\lambda_f = 457$ nm), which is bathochromically shifted by $\Delta\lambda = 50$ nm relative to the emission wavelength of **1** and shows a Stokes shift of $\Delta\lambda = 44$ nm. In marked contrast, **1**, **3**, and **4** exhibit weak emissions with the maxima at $\lambda = 407$, 439, and 426 nm, respectively, and much smaller Stokes shifts due to their rigid coplanar structures. Relative PL quantum yields Φ_f of these heteroheptacenes were determined by using di-

phenylanthracene in cyclohexane as the standard,^[28] (see Table 1 for the PL data). The quantum yield Φ_f can be described by the relative rates of the radiative and nonradiative pathways, which deactivate the excited state. In this study, **2** (with the CPDT core) shows the highest Φ_f value ($\Phi_f > 0.75$), thus indicating that nonradiative decay pathways are nearly suppressed in such a structure. Obviously, the two alkyl chains on the central tetrahedral carbon atom of **2** effectively hinder the molecular association, as shown in the single-crystal packing (Figure 2).

The solid-state optical absorption/PL data for 1-4 are collected in Table 1. In general, the film absorption spectra exhibit characteristic transitions that are bathochromically shifted relative to their solution values, which is indicative of the presence of π - π stacking in the solid state. Compounds 1, 3, and 4 show a large red-shift of $\Delta \lambda = 9-27$ nm, whereas in contrast 2 possesses a red-shift of $\Delta \lambda = 5$ nm (Figure 4b). This behavior indicates a weaker intermolecular interaction of 2 relative to 1, 3, and 4. Thin-film PL spectra were obtained by excitation at λ_{max} (Table 1). The spectral shapes and maxima strongly depend on the molecular structure and the packing characteristics, with most of the plots exhibiting red-shifts relative to the emission maxima in solution. It can be seen that the intermolecular interactions dominate the optical properties in the solid state and surmount the effects of the heteroatom substitution on the photophysics of the compounds.

Electrochemical properties of new heteroheptacenes 1-4: As already indicated by the absorption and PL spectra of the heteroheptacenes, variation in the substitution has a significant impact on optical properties. These results led us to investigate the electrochemical behavior of heteroheptacenes 1-4 further. Cyclic voltammetry (CV) measurements were performed under N2 in 0.1 M CH2Cl2/tetrabutylammonium hexafluorophosphate ($TBAPF_6$) with a scanning rate of 50 mVs⁻¹. All the systems exhibited one or two reversible and/or quasireversible one-electron oxidation waves within the solvent/electrolyte window range. Figure S2 (see the Supporting Information) illustrates voltammograms of 1-4 (the electrochemical data are summarized in Table 2). It is possible to extract the formal halfwave potentials $E^{1/2}$ as the midpoints between the peak potentials for the forward and reverse scans when the voltammograms are (quasi)reversible. Single-electron oxidation processes (versus SCE) were obtained at E = 0.84/0.99, 0.99, and 1.04 V for 1-3, respec-

Table 2. Electrochemical data for 1-4 in dry CH_2Cl_2 under nitrogen.

Compound	Oxidation ^[a]						
	anodic			cathodic		half	
E^{onset}	$E_{\rm a1}$	E_{a2}	E_{c1}	E_{c2}	$E_1^{1/2}$	$E_2^{1/2}$	
[V]	[V]	[V]	[V]	[V]	[V]	[V]	
1 0.71	0.87	1.02	0.81	0.96	0.84	0.99	
2 0.90	1.04	-	0.94	-	0.99	-	
3 0.97	1.09	-	0.99	-	1.04	_	
4 0.82	1.04	-	0.91	-	0.98	-	

[a] Referenced to the Ag/Ag⁺ couple.

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tively, versus E=0.98 V for 4. The reduction potentials, however, were out of the range of our experimental setup (< -2 eV) and could not be determined. The oxidation of 1 (see Figure S2 in the Supporting Information) occurs in two reversible steps, the maxima of which appear at E_{a1} and E_{a2} (0.87 and 1.02 V, respectively), whereas 2 (with a CPDT core) shows only one quasireversible oxidation at E_{a1} = 1.04 V. According to $E_{\rm HOMO} = -(E^{\rm ox}_{\rm onset}+4.34) \, {\rm eV},^{[29]}$ the HOMO levels of 1-4 could be estimated (Table 3). By taking into account their optical band gaps, which were derived from the absorption onset in the UV/Vis spectrum, the LUMO values are calculated.

Table 3. Comparison of electrochemical, optical, and calculated HOMO–LUMO energy gaps E_g and absolute HOMO and LUMO energies for 1–4 and known heteroheptacenes.

Compound		E_{g} [eV]				
	experimental ^[a] theoretical ^[b]			etical ^[b]	0	
	HOMO	LUMO	HOMO	LUMO	$E_{\rm g}^{\rm op[c]}$	$E_{\rm g}^{\rm th[d]}$
1	-5.09	-1.99	-4.98	-1.42	3.10	3.56
2	-5.28	-2.38	-5.03	-1.72	2.90	3.31
3	-5.19	-2.36	-5.11	-1.51	2.83	3.60
4	-5.20	-2.30	-5.18	-1.54	2.90	3.64
DBTBT			-5.50	-1.71	2.83	3.79
DIoCz	-	_	-4.54	-1.15	2.59	3.39
DIeCz	-5.30	-2.10	-5.07	-1.22	3.20	3.85
LTP	-	-	-4.98	-1.43	-	3.55

[a] HOMO energy was estimated from the relationship: $E_{\text{HOMO}} = -(E^{\text{exo}}_{\text{onset}}+4.34) \text{ eV}$; tLUMO energy was estimated from the empirical relationship: LUMO (eV)=HOMO (eV)+ E_{g}^{op} . [b] Gaussian 03, B3LYP, 6-31G*. [c] From absorption onset of the UV/Vis absorption data. [d] From DFT calculations.

Molecular-orbital calculation: To gain deeper insight into the electronic structures of the new heteroheptacenes and related analogues, molecular-orbital (MO) calculations of the HOMO levels, LUMO levels, and band gaps were performed by using DFT methods (B3LYP, 6-31G*). Table 3 summarizes the electrochemical data, optical data, and calculated energy gaps for 1-4. Reported heptacenes (dibenzothienobisbenzothiophene (DBTBT),^[11a] diindolocarbazole (DIoCz),^[11c] diindenocarbazoles (DIeCz),^[11d] and laddertype tetraphenylene (LTP)^[30]) were also included and compared in terms of orbital levels from both experiment and calculation. An excellent agreement between the experimental HOMO energy and the theoretical results is seen, with differences of only approximately 0.1-0.2 eV for almost all molecules. However, the theoretical gaps predicated from vertical transitions are significantly larger than the optical band gaps E_{g}^{op} (Table 3). A systematic study of the accuracy of the DFT calculations has been previously shown by Zhang and Musgrave.^[31]

The HOMOs and LUMOs are delocalized practically along the entire π -conjugated backbones with generally two different types of HOMO delocalization states and identical LUMO states (Figure 5). The HOMOs of **1** and **2** have antibonding character (or intra-ring bonding) between the adja-



Figure 5. Schematic representation of the HOMOs and LUMOs of 1–4, DBTBT, DIoCz, DIeCz, and LTP for comparison (DFT//B3LYP/6-31G*).

cent hetero rings and are delocalized over the molecular backbone, whereas the LUMO represents inter-ring bonding interactions, thus exhibiting significant quinoid character. In contrast, the HOMO orbital plots of **3** and **4** are different from **1** and **2**, with obvious inter-ring bonding interactions, and are mainly localized around the central carbazole system. On the other side, the LUMOs of **3** and **4** represent the same fashion of delocalization as **1** and **2**.

It is surprising that the LUMO energy of **2** is lower by 0.3 eV than **1** when the carbon atom is replaced by a more electronegative nitrogen atom (Figure 5). Nguyen et al. found from a time-dependent DFT calculation that the LUMO energy of an organic molecule is dramatically influenced by its aromacity, and the LUMO level of nonaromatic cyclopentadiene is 1.7 eV lower than that of pyrrole. The HOMOs, however, are not significantly influenced by the aromaticity of the building blocks.^[32] Obviously, heteroheptacenes **1** and **2** in this study follow the same trend. From DFT calculations, the small difference between the HOMO and LUMO energy levels of **3** and **4** is in line with the CV experiments.

To compare the electronic effects of heteroatoms on the frontier orbitals of heteroheptacenes, we also carried out calculations for DBTBT, DIoCz, DIeCz, and LTP by using the same computational method. The HOMO and LUMO energies of DBTBT and DIoCz resemble those of **3** and **4** in shape (Figure 5), in which the orbital shows inter-ring bonding interactions and is mainly localized around the central π system. In contrast, the E_{HOMO} and E_{LUMO} values of DIoCz differ markedly from those of **3**, **4**, and DBTBT (i.e., $\Delta E_{\text{HOMO}} = 0.96 \text{ eV}$, $\Delta E_{\text{LUMO}} = 0.6 \text{ eV}$). It seems that more pyrrole ring fusion into the heteroacenes tends to destabilize both the HOMO and LUMO energy levels. The calculation of DIeCz and LTP indicates that their HOMOs resemble those of **1** and **2** in shape, in which the bridging (hetero)atoms are on the node of the orbitals. The E_{HOMO} value of

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DieCz and LTP lie close to the E_{HOMO} values of **1** and **2** (i.e., $\Delta E_{\rm HOMO} < 0.09 \text{ eV}$). The LUMOs of DleCz and LTP reveal similar inter-ring bonding interactions to 1 and 2 and move slightly upward. Among all the heteroheptacenes in this study, the thiophene-ring-containing heteroheptacenes 1-4 and DBTBT have average HOMO and LUMO energies of -5.20 and -1.60 eV, respectively, which are lower than the other three analogues (average $E_{\rm HOMO} = -4.86$ and $E_{\rm LUMO} =$ -1.27 eV). These findings suggest that the thienyl ring fusion inside the heteroacenes is an effective method to stabilize both the HOMO and LUMO levels.

Conclusion

Three new heteroheptacenes (1, 2, and 4) with the inclusion of both thiophene and/or pyrrole ring units have been synthesized by an intramolecular electrophilic coupling reaction induced with triflic acid. The NMR spectroscopic measurements disclosed the symmetric structure of the new heteroheptacenes. The SCXRD characterization demonstrated that the solid structure of the heteroheptacenes can be significantly influenced by the mode (position and type) of alkyl-chain substitution. The experimental results (absorption/emission spectroscopy and CV) confirmed DFT calculations that both hetero ring fusion and the substituents have significant impact on the optical and electrochemical properties of the heteroheptacenes. Visualization of the MOs showed that carbazole-based compounds 3 and 4 represent a unique inter-ring bonding character between the adjacent hetero rings and less delocalized HOMO relative to 1 and 2. The appropriate substitution of thiophene units inside the ladder-type heteroacenes can effectively stabilize their frontier orbitals. The present study suggests that the new heteroheptacenes are promising candidates for optoelectronic applications. Further studies on the structure/properties relationship of more complex heteroheptacenes and the potential of using these compounds as semiconductors in devices are currently underway.

Experimental Section

4-Hexyl-2,6-bis[2-(methylsulfinyl)phenyl]-4H-dithieno[3,2-b:2',3'-d]pyrrole (9): 2-Bromo(methylsulfinyl)benzene (**8**; 736 mg, 3.36 mmol) was added to a solution of **7** (0.9 g, 1.53 mmol) in anhydrous DMF (25 mL). The resulting mixture was purged with Ar for 30 min, and $[Pd(PPh_3)_4]$

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(87 mg, 0.075 mmol) was added. The reaction mixture was heated overnight to 80 °C. Excess DMF was removed under high vacuum, and the residue was dissolved in ethyl acetate and treated with 10% aqueous KF. The mixture was filtered through a pad of celite. The filtrate was dried over Mg₂SO₄, filtered, and the solvent removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: hexane/THF 3:1) to afford **9** as an off-white solid (0.95 g, 88% relative to **6**). ¹H NMR (250 MHz, CD₂Cl₂): δ =7.03 (s, 2H), 7.40 (ddd, *J*=14.20, 9.58, 4.15 Hz, 6H), 7.88 (d, *J*=7.53 Hz, 2H), 4.06 (t, *J*=6.88, 6.88 Hz, 2H), 2.30 (s, 6H), 1.77–1.61 (m, 2H), 1.18–0.99 (m, 6H), 0.66 ppm (t, *J*=6.68, 6.68 Hz, 3H); ¹³C NMR (62.5 MHz, CD₂Cl₂): δ =145.553, 145.009, 136.753, 133.024, 131.181, 131.045, 129.456, 124.098, 115.986, 112.256, 47.98, 42.34, 31.82, 30.69, 27.11, 22.94, 14.14 ppm; FDMS: *m/z* (%): 539.80 (100.0) [*M*⁺]; elemental analysis (%) calcd for C₂₈H₂₉NO₂S₄: C 62.30, H 5.42; found: C 62.35, H 5.39.

Bisbenzo[b,b']thienodithieno[3,2-b:2',3'-d]pyrrole (1): A 10-mL roundbottomed flask was filled with 9 (200 mg, 0.37 mmol), phosphorus pentoxide (28 mg, 0.2 mmol), and trifluoromethanesulfonic acid (6 mL). The mixture was stirred for 72 h at room temperature to give a dark-blue solution, which was then poured into ice-water (100 mL). The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in apolar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by heating to reflux in pyridine (30 mL) for 12 h. When the suspension was cooled to room temperature, a large volume of CH₂Cl₂ was added to extract the product. Compound 1 was thus obtained as light-yellow powder after chromatography on silica gel with CH2Cl2/ hexane (1:9) as the eluent (145 mg, 85%). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 7.91$ (d, J = 7.83 Hz, 2H), 7.86 (d, J = 7.87 Hz, 2H), 7.52–7.44 (m, 2H), 7.41-7.33 (m, 2H), 4.48 (t, J=7.13, 7.13 Hz, 2H), 2.13-2.00 (m, 2H), 1.32 (td, J = 13.44, 5.09, 5.09 Hz, 6H), 0.93–0.84 ppm (m, 3H); ¹³C NMR (62.5 MHz, CD_2Cl_2): $\delta = 141.14$, 136.53, 134.09, 133.65, 125.53, 124.41, 122.32, 120.42, 118.34, 32.36, 31.81, 30.07, 26.95, 22.84, 14.09 ppm; FDMS: m/z (%): 475.71 (100) [M⁺]; elemental analysis (%) calcd for C₂₆H₂₁NS₄: C 65.64, H 4.45; found: C 64.70, H 4.45.

4,4-Dihexyl-2,6-bis2-(methylsulfinyl)phenylcyclopenta[**2,1-***b***:3,4-***b*']**dithiophene (13)**: The same procedure was followed as for the synthesis of **9** starting from **12**. The crude product was purified by flash chromatography on silica gel (eluent: hexane/THF 3:1) to afford **13** (0.56 g, 88 % relative to**11**). ¹H NMR (250 MHz, CD₂Cl₂): δ =8.06 (dd, *J*=6.84, 1.20 Hz, 2H), 7.63–7.47 (m, 6H), 7.11 (s, 2H), 3.92–3.83 (m, 4H), 2.49 (s, 6H), 1.18 (td, *J*=10.06, 9.33, 9.33 Hz, 12H), 1.04–0.89 (m, 4H), 0.81 ppm (td, *J*=13.44, 6.74, 6.74 Hz, 6H); ¹³C NMR (62.5 MHz, CD₂Cl₂): δ =145.424, 139.72, 133.0, 131.54, 131.31, 129.81, 124.6, 123.27, 68.36, 38.57, 30.41, 29.94, 25.44, 23.36, 14.60 ppm; FDMS: *m/z* (%): 622.97 (100) [*M*⁺]; elemental analysis (%) calcd for C₃₅H₄₂O₂S₄: C 67.48, H 6.80; found: 67.40, H 6.75.

Bisbenzo[*b*,*b'*]**thienocyclopenta**[**2**,1-*b*:**3**,4-*b'*]**dithiophene (2**): The same procedure was followed as for the synthesis of **1** starting from **13**. The product was isolated by chromatography on silica gel (eluent: CH₂Cl₂/hexane 1:9) as a light-yellow oil, which solidified as yellow crystals on cooling (165 mg, 85 %). ¹H NMR (250 MHz, CD₂Cl₂): δ = 7.79 (t, *J* = 7.23, 7.23 Hz, 4H), 7.39–7.31 (m, 2H), 7.30–7.21 (m, 2H), 2.14–2.01 (m, 4H), 1.10–0.91 (m, 12H), 0.89–0.74 (m, 4H), 0.63 ppm (t, *J* = 6.73, 6.73 Hz, 6H); ¹³C NMR (62.5 MHz, CD₂Cl₂): δ = 148.84, 142.13, 139.97, 135.72, 133.69, 132.72, 125.37, 124.47, 124.31, 120.50, 37.04, 31.82, 29.83, 24.86, 22.86, 14.06 ppm; FDMS: *m/z* (%): 558.15 (100) [*M*⁺]; elemental analysis (%) calcd for C₃₃H₃₄S₄: C 70.92, H 6.13; found: 70.98, H 6.11.

2,7-Bis(5-hexylthiophen-2-yl)-9-methyl-3,6-bis(methylsulfinyl)-9H-carbazole (19): 2,7-Bis(5-hexylthiophen-2-yl)-9-methyl-3,6-bis(methylthio)-9Hcarbazole (**18**; 100 mg, 0.17 mmol) was dissolved in a 1:1 mixture of glacial acetic acid and CHCl₃ and cooled with an ice-bath until the solvent was about to freeze. Hydrogen peroxide (35%, 35 mg, 0.36 mmol) was added slowly. The cooling bath was removed and the mixture was stirred at room temperature for 12 h. Acetic acid was removed by vacuum evaporation and CH₂Cl₂ was added to the residue. The organic fraction was washed with a saturated solution of NaHCO₃ and dried over MgSO₄. The product was purified by column chromatography on silica gel (eluent: THF/hexane 1:1), thus affording the pure product as a white solid (101 mg, 95% yield). ¹H NMR (250 MHz, CD_2Cl_2): δ =8.93 (d, J=3.97 Hz, 2 H), 7.55 (d, J=1.76 Hz, 2 H), 7.13 (dd, J=3.51, 1.71 Hz, 2 H), 6.88 (d, J=3.51 Hz, 2 H), 3.95 (d, J=0.84 Hz, 3 H), 2.92 (t, J=7.59, 7.59 Hz, 4 H), 2.58 (d, J=4.99 Hz, 6 H), 1.85–1.71 (m, 4H), 1.48–1.33 (m, 12 H), 0.96 ppm (t, J=8.77, 5.17 Hz, 6 H); ¹³C NMR (62.5 MHz, CD_2Cl_2): δ =148.68, 143.20, 137.13, 136.88, 130.93, 128.19, 125.24, 122.72, 117.56, 111.43, 43.25, 32.12, 31.99, 30.51, 30.17, 29.20, 23.03, 14.29 ppm; FDMS: *m*/z (%): 637.22 (100) [*M*⁺]; elemental analysis (%) calcd for C₃₅H₄₃NO₂S₄: C 65.89, H 6.79; found: C 65.85, H 6.88.

Bisthieno[3,2-*b***]thieno[2,3-***f***:5,4-***f***']-carbazoles (4): The same procedure was followed as for the synthesis of 1 starting from 19. The product 4 was isolated by chromatography on silica gel with (eluent: CH₂Cl₂/hexane 1:9) as a light-yellow oil, which solidified as yellow crystals on cooling (55 mg, 80%). ¹H NMR (250 MHz, CD₂Cl₂): \delta=8.55 (s, 2H), 7.74 (s, 2H), 7.10 (s, 2H), 3.98 (s, 3H), 3.02 (t,** *J***=7.55, 7.55 Hz, 4H), 1.89–1.77 (m, 4H), 1.53–1.43 (m, 4H), 1.39 (ddd,** *J***=7.39, 4.59, 2.45 Hz, 8H), 0.95 ppm (t,** *J***=9.34, 4.82 Hz, 6H); ¹³C NMR (62.5 MHz, CD₂Cl₂): \delta=150.10, 141.65, 138.34, 133.65, 132.48, 132.12, 121.33, 118.02, 115.13, 99.18, 32.04, 31.68, 30.08, 29.86, 29.15, 23.00, 14.25 ppm; FDMS:** *m/z* **(%): 573.90 (100) [***M***⁺]; elemental analysis (%) calcd for C₃₃H₃₅NS₄: C 69.06, H 6.15; found: C 69.12, H 6.23.**

X-ray crystallographic analysis: Single crystals of 1-3 were grown from cold CH₂Cl₂ or a hexane/methanol mixture. Crystals were mounted on glass fibers and the data collected at 173(1) K on a diffractometer with graphite-monochromated Mo_{Ka} radiation. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10–30-s exposure and collected and integrated with the SAINT software package. The data were corrected for absorption effects by using the multiscan technique (SADABS) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods and refined by using the SHELXTL crystallographic software package. For each structure, all the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were included in calculated positions but were not refined. Compounds 1 and 3 crystallize with one-half molecule that resides on an inversion center. Unfortunately, the crystals of 4 were too thin for structural determination with a standard diffractometer. CCDC-769583 (1), CCDC-769584 (2), and CCDC-769585 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Optical spectroscopic measurements: UV/Vis absorption spectra were recorded at room temperature on a Perkin–Elmer Lambda 9 spectrophotometer. The PL spectra were recorded on a SPEX-Fluorolog II (212) spectrometer. The solutions were prepared with an absorbance between 0 and 0.1 at the wavelength region of experimental interest. The PL quantum yields were determined by comparison with 10^{-7} M diphenylan-thracenein cyclohexane as a reference and corrected for the refractive index of different solvents.

Electrochemical measurements: CV experiments were performed in 0.1 M TBAPF₆ solutions in dry, oxygen-free CH₂Cl₂. Glassy carbon was used as the working electrode, a platinum wire as the auxiliary electrode, and Ag/AgCl as the reference electrode, which was checked against the ferrocene/ferrocenium (Fc/Fc⁺) couple after each measurement. These measurements were carried out on a computer-controlled PGSTAT12 at room temperature.

Calculation methods: DFT calculations were carried with the Gaussian03 program package.^[33] The Becke three-parameter exchange functional combined with the LYP correlation functional (B3LYP) was used.^[34] Op-timized molecular geometries were determined on isolated entities. The 6–31G* basis was chosen for all molecules.

Acknowledgements

We thank Mr. Michael Steiert for XRD analysis. Financial support from the Max Planck Society through the program ENERCHEM, European

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Commission Project ONE-P, and the German Science Foundation (Korean–German IRTG) is gratefully acknowledged.

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Received: December 28, 2009 Published online: March 26, 2010