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Versatile 2,7-Substituted Pyrene Synthons for the Synthesis of Pyrene-Fused Azaacenes

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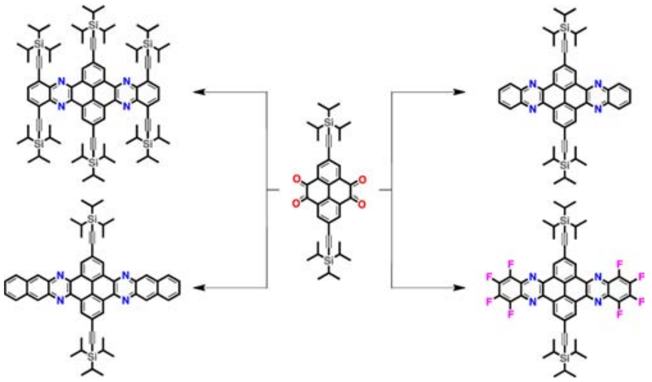
ABSTRACT



A new synthetic route to prepare a series of versatile 2,7-substituted pyrene synthons for the synthesis of pyrene-fused azaacenes is described. By using such synthons, a library of eight pyrene-fused azacenes with different electronic structures and in most cases with enhanced solubility has been synthesized and characterized.

In recent years, the development of straightforward and solid routes to access the synthesis of *N*-containing polycyclic aromatic hydrocarbons (*N*-PAH) has permitted study of their properties in great detail and demonstration that they are a unique platform for developing novel organic semiconductors.[1] For instance, by varying the number and position of N atoms and the substitution on the aromatic core along the π-framework it is possible to modulate the *N*-PAH's electronic structure, stability, solubility, and supramolecular organization.[2] Among *N*-PAH, pyrene-fused oligoazaacenes and other laterally extended azaacenes have recently attracted much attention since they are stable,[3] display low band gaps and NIR absorption bands,[3a] self-organize into discotic phases[4] and complex nanostructures,[5] disperse carbon nanotubes and

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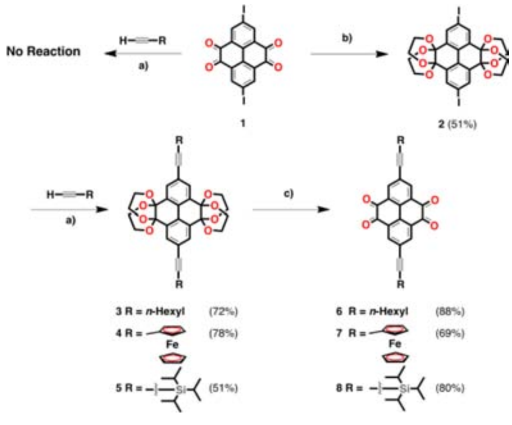
graphene,[6] and have proven useful for anion-sensing[7] and orientation measurements in nucleic acids.[8] In addition, pyrene-fused oligoazaacenes are relatively easy to synthesize and can be usually obtained by means of cyclocondensation of 4,5,9,10-tetraketopyrene[9] with 1,2-diamines. 4,5,9,10-Tetraketopyrene derivatives with symmetrical substitution patterns on the 1,3,6,8 or 2,7 positions[9,10] have been described and used to enhance the solubility and to avoid the formation of multiple isomers. Building blocks based on 1,3,6,8-substituted pyrenes are highly versatile since substituents are introduced through palladium-based C–C bond-forming reactions. Conversely, other substituents different from *t*-Bu groups on the 2,7 positions of pyrene are rarely found. One reason for the low number of examples is the limited availability of methods for the functionalization of the pyrene core on the 2,7 positions.[11]

Since the electronic properties and the morphologies of pyrene-fused azaacenes are frequently controlled by side-group manipulation, a reliable and a versatile synthetic methodology that allows the synthesis of 2,7-functionalized pyrene tetraketones with a wide variety of groups is highly desirable. Herein we report a versatile synthetic route to prepare a series of 2,7-substituted pyrene synthons for the synthesis of pyrene-fused azaacenes. In fact, we have used such methodology to prepare a library of eight pyrene fused-azacenes with different electronic structures and in most cases with enhanced solubility.

This methodology starts from 2,7-diodo-4,5,9,10-tetraketopyrene (**1**)[12] (Scheme 1) that is readily available in two steps from pyrene. First, we attempted to functionalize positions 2,7 of **1** by means of Sonogashira reactions.[13] Nevertheless, after screening several standard palladium sources, ligands, and bases for Sonogashira reactions, no evolution toward the desired products was observed. This is consistent with the lack of reactivity of **1** in other C–C forming reactions, such as Suzuki coupling.[12] In order to check if the ketone substituents are influencing the reactivity, all ketones were transformed into diketals. This is not only a way to protect ketones but also a way to inverse the polarity of the carbonyl group (umpolung). Compound **2** was easily obtained by refluxing **1** in *o*-dichlorobenzene (ODCB) in the presence of ethylene glycol and *p*-toluenesulfonic acid in a Dean–Stark apparatus. With the protected ketones, Sonogashira reactions performed on **2** proceeded successfully with good yields (up to 78%) with acetylenes displaying solubilizing alkyl chains, ferrocenyl electron-donating moieties, and bulky triisopropylsilyl (TIPS) groups to provide **3**–**5**. We have selected these among several acetylenes for their availability, their high solubilizing power, and in the case of ferrocene derivatives their electron-donating behavior that allow preparation of donor–acceptor systems.[14] The deprotections of the diketals **3**–**5** is straightforward, and the desired tetraketones **6**–**8** are obtained in good yields (up to 88%) in the presence of trifluoroacetic acid (TFA) and water.

Scheme 1. Synthesis of 2,7-Disubstituted Synthons[a]



[a] Key: (a) CuI, $[Pd(PPh_3)_2Cl_2]$, *i*-Pr_2NH, THF, reflux, N_2; (b) ethylene glycol, *p*-toluenesulfonic acid, ODCB, reflux, Dean–Stark apparatus; (c) TFA–H_2O 9:1, rt.

The reaction of hexyl-substituted tetraketone **6** with 1,2-phenylenediamine (**9**) provides "hexacene" **10** (Scheme 2). In the same way, the reaction of **6** with 2,3-diaminonaphthalene (**11**) provides "octacene" **12**. Remarkably, **10** and **12** were soluble in comparison with unsubstituted analogues in chlorinated solvents.[3a] In fact, well-resolved ^{1}H NMR and ^{13}C NMR spectra were easily obtained from $CDCl_3$ solutions with a drop of TFA-d_1.

The cyclocondensation reactions between tetraketone **7** bearing two ferrocenyl substituents with aromatic diamines **9** and **11** proceeded normally without being affected by the bulkier ferrocenyls. "Hexacene" **13** and "octacene" **14** were obtained from 1,2-phenylenediamine (**9**) and 2,3-diaminonaphthalene (**11**) in good yields (60%). Their solubility, however, was limited in comparison to hexyl-substituted hexacene **10** and octacene **12**, most probably

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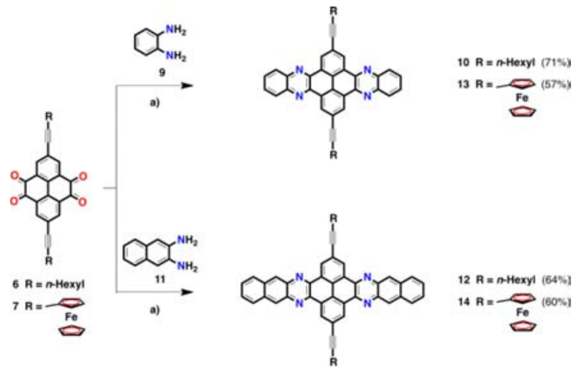
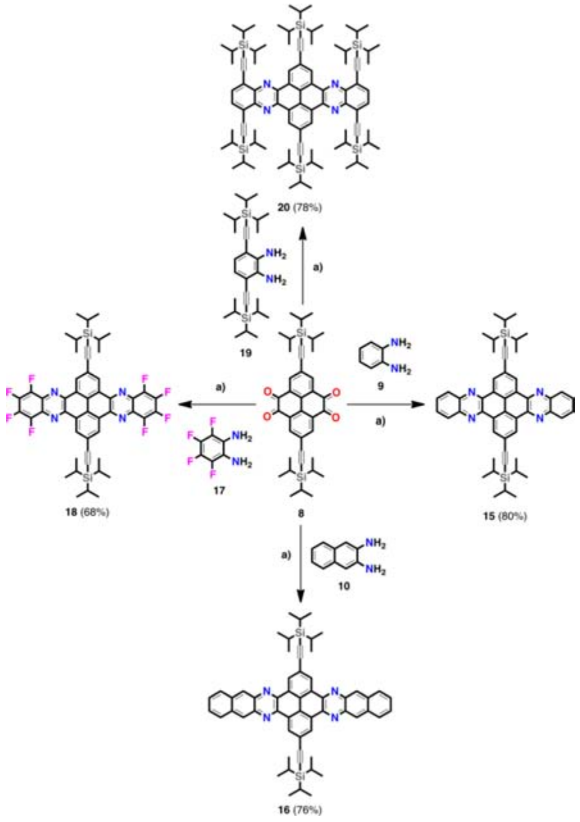
Scheme 2. Synthesis of "Hexacenes" **10** and **13** and "Octacenes" **12** and **14**[a]



[a] Key: (a) EtOH−AcOH, reflux.

Scheme 3. Synthesis of "Hexacenes" **15**, **18**, and **20** and "Octacene" **16**[a]



[a] Key: (a) EtOH−AcOH, reflux.

because of the rigidity of ferrocenylacetylene substituents and only ^{1}H NMR could be obtained for hexacene **13** in ODCB-d_4. The structure of hexacene **13** and octacene **14** is consistent with MS and optical and electrochemical characterization (see Figure 1 and the Supporting Information).

On the other hand, the reaction of TIPS-substituted tetraketone **8** with 1,2-phenylenediamine (**9**) and 2,3-diaminonaphthalene (**11**) provided "hexacene" **15** and "octacene" **16** with a very high solubility and both ^{1}H NMR and ^{13}C NMR spectra were obtained with no difficulties even for "octacene" **16** (Scheme 3). Synthon **8** is indeed superior in terms of solubilization power, which makes it an ideal platform to prepare a series of pyrene-fused azaacenes with different substituents in order to study their influence in the overall optoelectronic properties. The reaction of tetraketone **8** with perfluorinated 1,2-phenylenediamine **17** proceeded with good yields to provide perfluorinated hexacene **18** even if the nucleophilicity of **17** is compromised by the strong electron-withdrawing fluorine substituents. The cyclocondensation reaction also proceeds with diamine **19**[15] to yield hexasubstituted hexacene **20**.

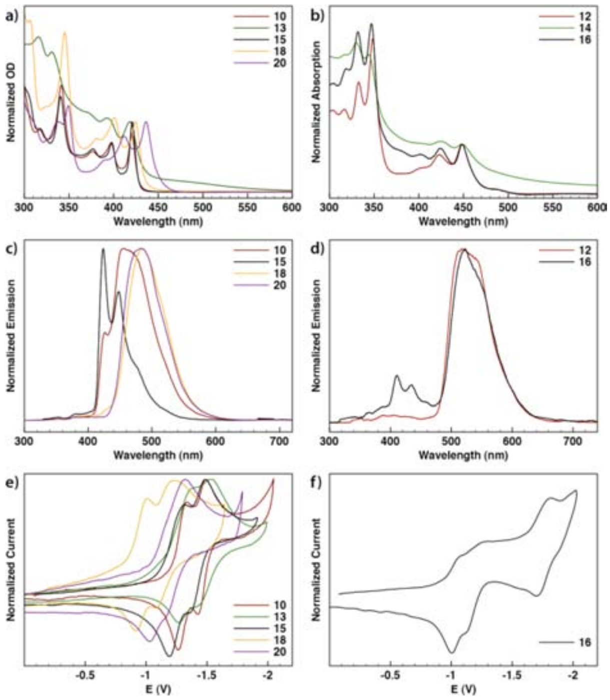


Figure 1. Absorption spectra (a, b), photoluminescence spectra (c, d), and cyclic voltammograms (e, f) of the "hexacene" (left) and "octacene" (right) series.

Photophysical characterization was carried out in ODCB. In the "hexacene" series, all spectra were well-resolved with clear vibronic features consistent with the molecular structure (Figure 1a). Almost identical absorption features were observed on disubstituted compounds **10** and **15** ($\lambda_{\max}$ = 420 and 421 nm, respectively), while in **13** a blue shift centered on the "hexacene" core (λ = 418 nm) and an additional broad band on the 440−600 nm range that evolves of the broad absorption of the ferrocene moieties ($\lambda_{\max}$ = 443 nm) is observed. Conversely, the absorption bands of **18** and **20** are red-shifted ($\lambda_{\max}$ = 425 and 436 nm, respectively). Such hipsochromic and bathochromic shifts centered on the "hexacene" core are attributed to the electron-donating (ferrocenylethylene) and electron-withdrawing (F atoms) nature of the substituents

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Table 1. Selected Photophysical and Electrochemical Data. Experimental and Calculated Energy Levels

	compd	λ_{max}[a]	λ_{onset}[a]	λ_{em}[a]	$E_{1/2}$[b]	E_{onset}[b]	$E_{gap(opt)}$[d]	$E_{LUMO(CV)}$[c]	$E_{gap(calc)}$[e]	$E_{LUMO(calc)}$[e]
"hexacene" series	**10**	420	435	420	−1.30	−1.19	2.85	−3.18		
	13	broad			−1.31	−1.11	1.42[f]	−3.21		
	15	421	430	450	−1.25	−1.06	2.88	−3.21	3.4	−2.9
	18	425	445	484	−0.96	−0.87	2.78	−3.43	3.3	−3.5
	20	436	460	482	−1.09	−1.02	2.69	−3.27	3.2	−3.1
"octacene" series	**12**	485	512	520			2.42			
	14	broad								
	16	485	512	522	−1.03	−0.97	2.42	−3.38	2.8	−3.2

[a] Measured in ODCB (nm). [b] Measured from 0.1 M ODCB/TBAP vs SCE (V). [c] Estimated from CV E_{ONSET} according to $E_{LUMO} = -4.8 - e(E_{ONSET} - E_{1/2}^{Fc})$ where $E_{1/2}^{Fc}$ was measured in situ (eV). [d] Estimated from absorption onset (eV). [e] Calculated B3LYP/6-31G*/6-311++G** using Spartan 10, sylanes have been removed to reduce computation time (eV). [f] Estimated from CV according to $E_{LUMO} = -(E_{ONSET}^{red} - E_{ONSET}^{ox})$ (eV).

in the case of **13** and **18**, respectively, and the longer effective conjugation in **20** because of the four aditional acetylenes. "Octacenes" **12**, **14**, and **16** display almost identical absorption features consistent with the structure (Figure 1b). In the case of **14**, the bands are (i) broadened, which reflects its limited solubility, and (ii) blue-shifted in the UV region (3 nm) as an effect of the electron-donating nature of ferrocenyl substituents, and (iii) a broad absorption that corresponds to the ferrocenyl moieties spans above 475 nm.

A similar trend was observed for the emission spectra. For example, **20** exhibits a bathocromic shift (λ_{em} = 482 nm) that is more substantial for **18** (λ_{em} = 484 nm) in comparison to **10** and **15** (Figure 1c). Compound **13** bearing ferrocene substituents shows no emission, which is frequent in donor−acceptor systems. In the case of the "octacenes", similar emission features were observed for **12** and **16** (Figure 1d) and no emission for **14**, which is also consistent with its donor−acceptor nature.

The electron-deficient nature of the pyrene-fused azaacene core is reflected by cyclic voltammetry. Electrochemically reversible reduction waves were observed for "hexacenes" **10**, **13**, **15**, **18**, and **20** (Figure 1e), and only a reversible oxidation wave centered on the ferrocene moieties was observed for **13**. While **10**, **13**, and **15** display similar half-wave potentials ($E_{1/2}$) around −1.3 V, the reduction waves of **20** are shifted toward less negative potentials due to the extended conjugation and even further for **18** due to the electron-withdrawing F atoms. The voltammograms of "octacenes" **12** and **14** revealed strong aggregation displaying multiple and very broad waves. On the contrary, due to the enhanced solubility **16** three reduction processes were observed (Figure 1f) with more anodically shifted half-wave potentials than for the analogous "hexacene" **15**.

The band gaps of the "hexacenes" were estimated from from the absorption onsets of **10**, **15**, **18**, and **20** in the range 2.7−2.9 eV (see Table 1). As expected, the band gap of **13** was as low as 1.42 eV (estimated electrochemically) because of the combination of ferrocene electron-rich moieties with the electron defficient pyrene-fused azaacene core. The band gaps of the "octacenes" **12** and **16** (2.42 eV) were smaller than those of the hexacenes because of their extended conjugation. The broad bands on the absoption measurementes and the strong signs of aggregation on the voltammograms did not allow an accurate stimation of the band gap of **14**.

The LUMO levels were estimated from the potential onsets of the first reduction waves.[16] The E_{LUMO} for **10**, **13**, and **15** are in the same range (−3.2 eV), which reflects the small influence of the substituents on the acetylene ends while the E_{LUMO} for **20** and **18** are substantially lowered because of the extended conjugation and the electron-withdrawing nature of the F atoms, respectively. Notably, the E_{LUMO} of "hexacene" **18** is lower than for "octacene" **16**, which reflects that the presence of electron-withdrawing groups directly attached to the π-core has a higher influence on the LUMO than the extension of the conjugation. A theoretical estimation of the HOMO and LUMO levels in vacuo (B3LYP/6-31G*/6-311++G**) follow the same trends of the measured optical band gaps and were particularly accurate for the electrochemical LUMO levels (Table 1). The overestimation by 0.4 eV of the calculated band gap is reasonable due to the lack of the solvent in the simulations.

In summary, we have developed a synthetic route based on the inversion of the polarity of the carbonyl group (umpolung) to prepare versatile 2,7-substituted pyrene synthons for the synthesis of pyrene-fused azaacenes. By using such synthons, we have synthesized a library of eight pyrene fused-azacenes with different electronic structures and in most cases enhanced solubility. Overall, this work makes available a versatile and reliable new methodology for the functionalization of pyrene compounds on positions 2,7 and opens the door for preparing and for modulating the electronic properties of new pyrene derivatives and pyrene-fused azaacenes.

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Supporting Information Available. Full experimental details and characterization; ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.