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Exploring Electronically Polarized Pentacenes

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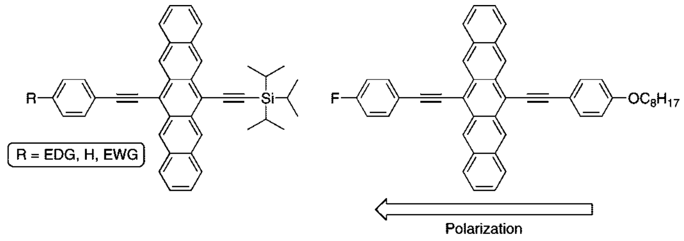
ABSTRACT



Unsymmetrically functionalized pentacenes with electron-rich and/or -poor substituents at the 6- and 13-positions were synthesized. The electronic influence was evaluated by solution-state UV−vis absorption and emission spectroscopies. These materials exhibit good solubility in common organic solvents and are stable in the presence of air and water.

To date, there has been a limited number of examples of unsymmetrically substituted pentacenes that give rise to a dipolar acene framework, and there are even fewer such derivatives that can be isolated or handled in the presence of air.[1−3] In some cases, unsymmetrical pentacenes have been prepared and characterized as a mixture of regioisomers,[2i] while in others, the acene is in equilibrium with its unconjugated, tautomeric counterpart at high temperatures.[2a,b] Other unsymmetrical pentacenes have been arrived at as part of a specific synthetic sequence that ultimately presents a rather limited scope.[2j,n] Desymmetrized pentacene building blocks have also been used for the construction of pentacene oligomers, as well as several polymers.[3] Thus, in the vast majority of pentacene systems studied to date as semiconductors, the functionalized pentacene molecules used as the active component have had a symmetric or nearly symmetric electronic make up.[4] To provide an opportunity to explore the effects of a pentacene chromophore electronically polarized due to the presence of electronically varied substituents, i.e., donors and acceptors, we targeted a synthetic pathway that would afford ready

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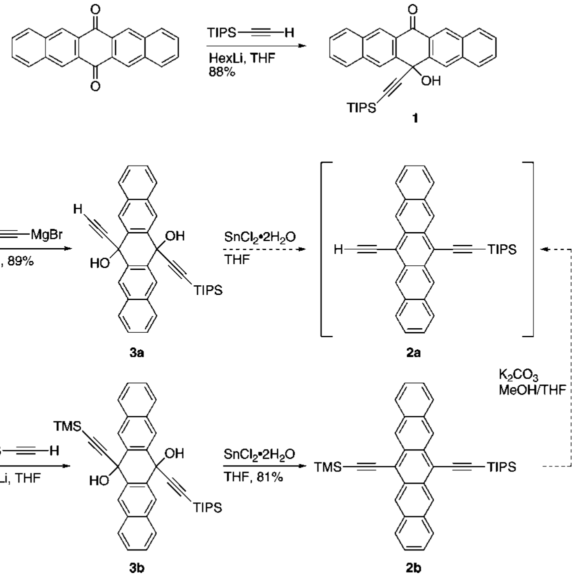
(4) (a) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926–952. (b) Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971–5003.

(5) A related approach has been used by Dehaen and co-workers to form an unsymmetrical, 6,13-diarylpentacene (ref 2f).

10.1021/ol801464k CCC: $40.75

access to such molecules.[5] The results of this study are presented here.

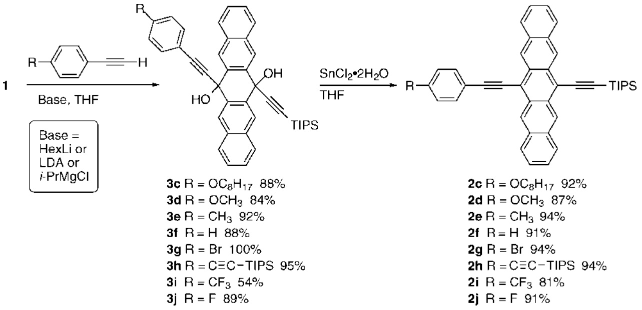
Scheme 1. Attempts toward a Divergent Unsymmetrical Pentacene Building Block



Unsymmetrically substituted pentacenes were synthesized from a common intermediate, ketone **1** (Scheme 1).[6] Briefly, the reaction of one equivalent of $\text{TIPS}-\text{C}\equiv\text{C}-\text{Li}$ with a slight excess of 6,13-pentacenequinone in THF gives **1** in 88% yield. This reaction can be performed easily on a multigram scale as a result of a facile purification procedure which employed orthogonal solubility between **1** and undesired materials.

Initially, derivative **2a** was envisioned as a general precursor to unsymmetrical pentacenes via the incorporation of the desired donor/acceptor moiety via the Sonogashira or related cross-coupling reactions.[7] To this end, the addition of excess ethynyl Grignard to **1** gave diol **3a** in 89% yield, following workup and purification by column chromatography. Aromatization through the addition of $SnCl_2 \cdot 2H_2O$ to **3a** in THF provided the deep-blue colored solution expected for pentacene **2a**, when the reaction was carried out under a nitrogen atmosphere. Unfortunately, when the reaction mixture was exposed to air, the characteristic blue color quickly disappeared, and none of the desired product, **2a**, could be isolated. Since **2a** proved to be elusive/unstable in the presence of oxygen, an alternative route based on the differentially protected 6,13-bis(silylethynyl)pentacene **2b** was explored. Unsymmetrical diol **3b** was obtained in 90% yield through the reaction of **1** with $\text{TMS}-\text{C}\equiv\text{C}-\text{Li}$, and subsequent aromatization gave pentacene **2b** as an air-stable product in excellent yield over the two steps. Unfortunately, however, all attempts to effect a process of selective in situ desilylation and Sonogashira coupling with substrate **2b** have been unsuccessful. Thus, a more direct method to access unsymmetrical pentacenes was developed in which the frustratingly unstable intermediate **2a** could be avoided entirely.

Scheme 2. Synthesis of Unsymmetrical Pentacenes **2c−j**



As outlined in Scheme 2, the formation of an acetylide nucleophile from the appropriate terminal alkyne was achieved with HexLi, LDA, or *i*-PrMgCl, dependent on the particular nature of the aryl substituent R. When an excess of this acetylide (typically ca. 3 equiv) was added to ketone **1**, unsymmetrical pentacene diols **3c−j** were obtained in excellent yields (84−100%), with the exception of diol **3i** that was isolated in only a moderate yield. Several of these transformations deserve particular comment. For the formation of diol **3j**, the use of HexLi was not a problem for the acetylide formation, despite the presence of the fluorine atom on the aromatic ring. On the other hand, synthesis of diol **3g** required formation of the acetylide with LDA rather than HexLi to circumvent competition from lithium−halogen exchange at the aromatic bromide in 1-bromo-4-ethynylbenzene. In the presence of the CF_3 group, the synthesis of diol **3i** required the use of *i*-PrMgCl solution to minimize formation of side products, as previously shown by Ong and co-workers.[8] Unfortunately, the electron-deficient nature of this substrate also rendered it less nucleophilic, and as a result, the formation of diol **3i** was sluggish. Even after 7 h, only 54% of **3i** was obtained, along with the recovery of unconsumed starting material **1**.

Diols **2c−j** were then reduced using excess $SnCl_2 \cdot 2H_2O$ in THF to obtain unsymmetrically substituted pentacenes **2c−j** in excellent yield (81−94%). Unlike the conditions typically reported for the tin(II)-mediated reduction of diethynylated pentacene diols,[9] the reductions here were carried out without the presence of an acid, such as 10% HCl. In our hands, these milder conditions have the

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(6) (a) Boudebous, A.; Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S. *Acta Crystallogr. Sect. C* **2006**, *62*, o243–o245. (b) See also: Ried, W.; Dankert, G. *Chem. Ber.* **1959**, *92*, 1223–1236.

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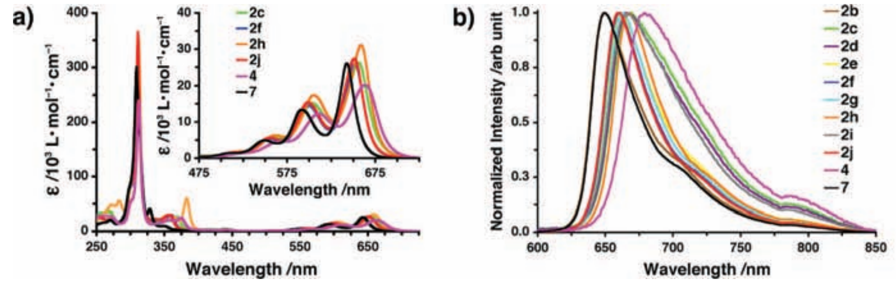
(9) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15–18.



c)

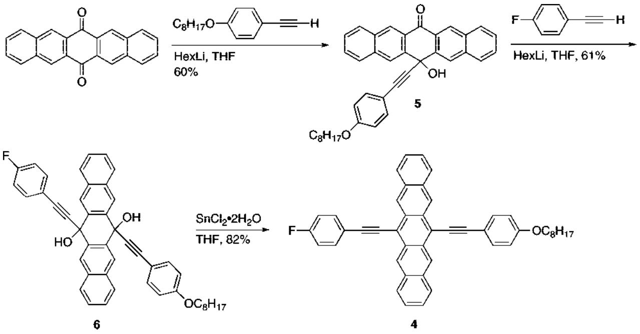
compound	$\lambda_{max,abs}$ /nm	$\lambda_{max,em}$ /nm	Stokes shift /nm	Φ_F
2b	642	649	7	0.13
2c	656	666	10	0.05
2d	655	666	11	0.05
2e	654	661	7	0.10
2f	652	661	9	0.12
2g	654	663	9	0.12
2h	659	668	9	0.12
2i	654	667	13	0.06
2j	651	660	9	0.13
4	664	679	15	0.03
7	643	649	6	0.15

Figure 1. (a) UV−vis absorption spectra for selected pentacenes (250−725 nm). Inset: expansion of the low-energy region of the UV−vis absorption spectra (475−725 nm). (b) Fluorescence of selected pentacenes (600−850 nm) using $\lambda_{exc} = 551$ nm. (c) Table of photophysical properties (all spectra and data as measured in CH_2Cl_2).

advantage of improved functional group tolerance while still providing excellent yields.

Given the success of the stepwise formation of pentacenes **2b**−**j**, the final synthetic target was one with donor−acceptor functionalization across the pentacene skeleton, compound **4** (Scheme 3).[10] As a donor, the *para*-octyloxy group was incorporated to ensure solubility of the product, given the formal removal of the TIPS group which provided solubility to **2b**−**j**. Thus, the reaction of the lithium acetylide formed from 1-*n*-octyloxy-4-ethynylbenzene with 6,13-pentacenequinone afforded ketone **5** in 60% yield. In the second step, the addition of excess lithiated 1-fluoro-4-ethynylbenzene afforded diol **6** in 61% yield. Finally, aromatization of **6** gave pentacene **4** in 82% yield.

Scheme 3. Synthesis of Polarized Pentacene **4**



UV−vis spectroscopy (in CH_2Cl_2) was used to explore the electronic outcome of varying the constitution of the pendent substituents on the pentacene framework. Figure 1a shows the absorption spectra for the range of 250−725 nm for selected pentacene derivatives, and the inset highlights the low-energy absorption region (475−725 nm). The spectrum of unsymmetrical **2b** ($\lambda_{max} = 642$ nm) is nearly identical to symmetrical analogue 6,13-bis(triisopropylsilylethynyl)pentacene **7** ($\lambda_{max} = 643$ nm) (Figure 2).[11] The effect of the various auxochromes at the para position of the benzene ring resulted mainly in a change of energy for λ_{max} values, with little or no change in the vibronic fine structure. The λ_{max} value of 652 nm for 6-triisopropylsilylethynyl-13-phenylethynyl pentacene **2f** represents a red shift of 10 nm compared to that of **2b**, a result of extending the conjugation length through the incorporation of the additional phenyl ring. Electron-donating substituents such as alkoxy groups in **2c** and **2d** produced slightly red-shifted λ_{max} values of 656 and 655 nm, respectively, in comparison to **2f**. A similar red shift was found for derivatives bearing a CH_3, CF_3, or Br group, with $\lambda_{max} = 654$ nm in all three cases. Meanwhile, the fluoro-substituted pentacene **2j** had a slightly blue-shifted λ_{max}, found at 651 nm. The effect of extending the π-system through the additional TIPS-ethynyl group on the aromatic ring of **2h** ($\lambda_{max} = 659$ nm) red-shifted λ_{max} by 7 nm in comparison to **2f**, in addition to a more intense high-energy band at 383 nm. Push−pull pentacene **4** had the lowest HOMO−LUMO gap with a λ_{max} of 664 nm. Compound **4** in toluene has a λ_{max} of 661 nm which is slightly red-shifted in comparison to that of **8a** ($\lambda_{max} = 655$ nm in benzene)[12] but similar to **8b** ($\lambda_{max} = 660$ nm in toluene),[8] **8c** ($\lambda_{max} = 662$ nm in toluene),[8] and bis-donor pentacene **8d** ($\lambda_{max} =$

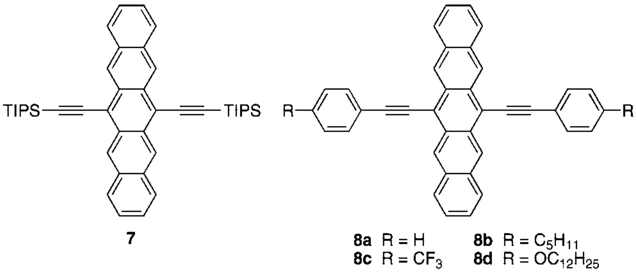


Figure 2. Related symmetrical pentacenes **7** and **8a**−**d**.

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(10) To date, attempts to incorporate an aryl moiety with a stronger acceptor group (e.g., $-NO_2$ or $-CN$) have not been successful.

(11) λ_{max} of ca. 643 nm is typical for 6,13-bis(trialkylsilylethynyl) pentacenes. See: (a) ref 9a and (b) Chen, J.; Subramanian, S.; Parkin, S. R.; Siegler, M.; Gallup, K.; Haughn, C.; Martin, D. C.; Anthony, J. E. *J. Mater. Chem.* **2008**, *18*, 1961–1969.

(12) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1969**, *34*, 1734–1736.

664 nm in toluene).[8] Thus, there seems to be little added affect on the optical HOMO−LUMO gap from the incorporation of the fluorine atom as a weak acceptor versus an additional alkoxy donor group. It is worth noting, however, that overall the effect of placing ethynyl and arylethynyl groups at the 6- and 13-positions of pentacene provides for a substantial red shift for λ_{max} compared to that of pristine pentacene ($\lambda_{max} = 576$ nm in benzene).[12]

Fluorescence spectra for **2b**−**j** were measured in CH_2Cl_2 ($\lambda_{exc} = 651$ nm), and quantum yields of fluorescence (Φ_F) were determined relative to cresyl violet perchlorate in methanol ($\Phi_F = 0.67$ at 5.9×10^{-7} M).[13] The spectrum of **2b** was analogous to symmetrical analogue **7**, while the spectra of **2c**−**j** varied slightly in terms of emission wavelength, Stokes shift, quantum yield, and the shape of the emission trace (Figure 1b). The table provided in Figure 1 summarizes the salient emission properties. Overall, λ_{max} of emission for **2c**−**j** occurred in a narrow range (660−668 nm) irrespective of the nature of the substituent. Stokes shifts were small, 7−13 nm, as expected for a rigid chromophore. The Φ_F values ranged from 0.05 to 0.13, and pentacenes bearing an electron-donating alkoxy group (**2c** and **2d**) or a CF_3 group (**2i**) showed the lowest Φ_F values, accompanied by a broader emission trace and the largest Stokes shifts. Donor−acceptor **4** has the largest Stokes shift of 15 nm which was accompanied by the lowest emission efficiency ($\Phi_F = 0.03$).

Thermal stability of **2b**−**j** and **4** was assessed by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). TGA showed no significant weight loss (<5%) below 410 °C for pentacenes **2c**−**j** and **4**, which is slightly higher than that for **2b** (385 °C) and **7** (375 °C). In the DSC traces, however, an exotherm peak was observed at much lower temperatures and assigned to decomposition, likely through a Diels−Alder reaction.[14] More specifically, DSC analysis showed melting points for compounds **2c** and **2d** at 134 and 65 °C, respectively, followed by decomposition at 136 and 149 °C, respectively. For pentacenes **2e**−**j** and **4**, no melting points were found by DSC, and decomposition occurred in the range of 175−215 °C.[15]

A crystal of unsymmetrical tolyl pentacene **2e** suitable for X-ray crystallography was grown from a CH_2Cl_2 solution which had been layered with acetone and allowed to slowly evaporate at 4 °C.[16] Pentacene **2e** crystallizes as a centrosymmetric dimeric pair (Figure 3) in which four aromatic rings of one pentacene molecule overlap with four aromatic rings of its dimeric neighbor. This packing motif places the phenyl moiety approximately on top of a TIPS group and results in a bowing of the conjugated backbone of the molecule. This is most noticeable in the pendent acetylene groups where bond angles range from 174−179°. Despite this fact, the two pentacene moieties are still able to achieve close contact in which the interplanar distance between the acene cores is on average only 3.45 Å.[17] This is comparable to, for example, that of **7** at 3.47 Å, which adopts a 2-D slipped-stacked arrangement in which the TIPS groups are staggered while still maintaining overlap of about 2.5 rings from each pentacene moiety.[9a]

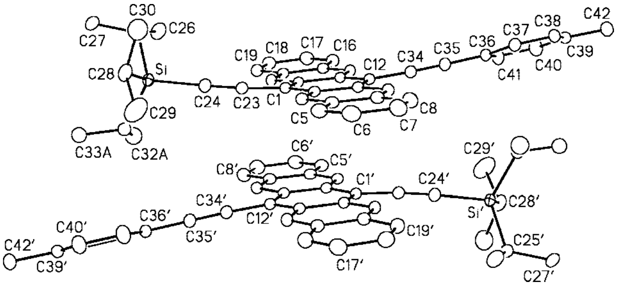

Figure 3. X-ray structure of **2e** illustrating its solid-state geometry (20% probability level). Selected bond angles (deg): C(1)−C(23)−C(24) 174.4(2), C(23)−C(24)−Si 174.03(18), C(12)−C(34)−C(35) 177.2(2), C(34)−C(35)−C(36) 179.2(2).

In conclusion, we have demonstrated that a variety of unsymmetrically substituted pentacenes can be synthesized in two steps from a common intermediate. This synthetic method should be broadly applicable as a gateway to new pentacene derivatives with both varied electronic structure and extended conjugated skeletons. Evaluation of charge-transport properties of these new materials is underway toward fostering a better understanding of the electronic effects that result from the electronic polarization of the pentacene core, and these results will be reported in due course.

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Supporting Information Available: Experimental procedures, spectroscopic data, ^1H and ^{13}C NMR spectra for compounds **1**−**6**, and CIF file (**2e**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Isak, S. J.; Eyring, E. M. *J. Phys. Chem.* **1992**, *96*, 1738–1742.

(14) This is analogous to the behavior of related pentacenes. See, for example, refs 8 and 11b.

(15) See Supporting Information for details.

(16) X-ray crystallographic data for **2e**: $C_{42}H_{40}Si$, $M = 572.83$; triclinic space group $P\bar{1}$ (No. 2); $\rho_{calcd} = 1.153$ g cm^{-3}; $a = 12.0801$ (14) Å, $b = 13.1806$ (15) Å, $c = 13.6258$ (16) Å; $\alpha = 95.3146$ (18)°, $\beta = 115.2970$ (16)°, $\gamma = 116.2079$ (16)°; $V = 1650.6$ (3) Å^3; $Z = 2$; $\mu = 0.099$ mm^{-1}. Final $R_1(F) = 0.0553$ (4807 observations $[F_o^2 \geq 2\sigma(F_o^2)]$); $wR_2(F^2) = 0.1529$ for 386 variables and 6264 data with $[F_o^2 \geq -3\sigma(F_o^2)]$; CCDC 692481. X-ray data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)-122−333−6033.

(17) The interplanar distance was measured by calculating the distance between the least-squares plane of each pentacene moiety as defined by the 22 carbon atoms of the acene framework.