A new functionalization strategy for pentacene†

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Functionalization of the pro-*cata* positions of pentacene with groups held perpendicular to the aromatic plane, in this case through a rigid 1,3-dioxole unit, yields pentacene derivatives that are stable and soluble, and still maintain edge-to-face interactions in the solid state.

Pentacene's (**1**, Fig. 1) excellent thin-film morphology and resulting high field-effect mobility have made it a benchmark in the field of organic electronics.[1] The performance of pentacene transistors is comparable to that of amorphous silicon transistors, and pentacene-based active matrix displays have been demonstrated.[2] These early successes led to a number of investigations into methods to overcome pentacene's low solubility and poor stability in solution. The majority of these functionalization strategies alter pentacene's solid-state order from an edge-to-face herringbone arrangement to a face-to-face π-stacking arrangement, and recent studies have explored the effect of changes in π-stacking order on the electronic properties of films and crystals.[3] These structure–property relationship studies have yielded new materials exhibiting improved stability and processing characteristics along with excellent performance in both field-effect transistors[4] and light emitting diodes.[5]

Investigation of more subtle changes to pentacene's native herringbone motif has received little attention, due to the paucity of pentacene derivatives that adopt this packing arrangement. Because substitution at the *peri*-positions disrupts edge-to-face interactions, herringbone arrangements are typically seen only in pentacene functionalized at the 2,3,9,10-positions—the "ends" of the acene. The lack of substituents on the central aromatic ring leaves the material vulnerable to endoperoxide formation and "butterfly" dimerization, both of which occur rapidly in solution.[6] Only two 2,3,9,10-substituted pentacene derivatives have been reported: tetramethyl pentacene, which adopts a packing almost identical to that of unsubstituted pentacene[7] and tetrakis(trimethylsilyl) pentacene, which is soluble but remarkably unstable.[8] A few 2,3-dialkoxy pentacenes have been reported, and are well-characterized, but none were subjected to X-ray crystallographic structure determination.[9]

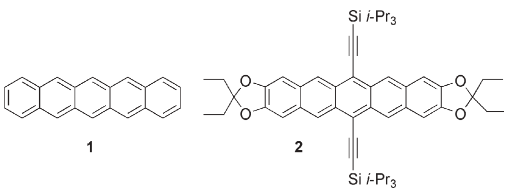
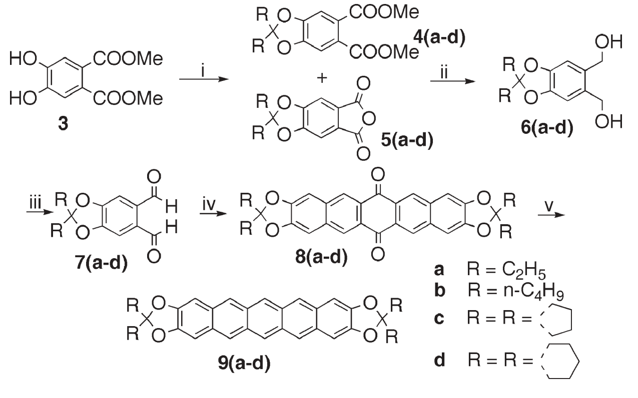


Fig. 1 Pentacene **1** and solubilized dioxolane pentacene **2**.

The study of crystal packing–property relationships in herringbone-arranged pentacene derivatives has the potential to be as fruitful as similar studies of π-stacked pentacene, but requires a functionalization strategy that yields stable, soluble, easily crystallized derivatives. During our investigation of new red-emitting materials for organic light emitting diodes,[5] we noticed that dioxolane-functionalized ethynyl pentacenes (**2**, Fig. 1) exhibited higher solution stability than the parent ethynyl pentacenes. The increased stability may arise from the steric bulk of dioxolane substituents held orthogonal to the pentacene plane, hindering close approach of the pentacene π-faces and retarding dimerization.[6] Such steric effects are commonly employed to stabilize reactive species, and have been found to retard the dimerization of acenes such as anthracene.[10] We reasoned that in pentacenes such as **9**, the size of the substituents on the dioxolane rings could be tuned to minimize face-to-face interactions, while avoiding interference with the edge-to-face interactions that lead to the electronically important herringbone arrangement. The substituents should also improve the solubility and processability of the materials. We report here the synthesis and characterization of dioxolane-functionalized pentacenes **9a–d** as a new class of materials that will allow the exploration of pentacene's edge-to-face interactions.

Dioxolane-functionalized pentacenes are easily synthesized by classical methods from known catechol **3** (Scheme 1).[11] Acetal formation yields a mixture of diester **4** and anhydride **5**, which is



Scheme 1 *Reagents and conditions*: i. ketone, *p*-toluenesulfonic acid, benzene, reflux, ∼100%; ii. LiAlH$_4$, THF, 60–90%; iii. Swern oxidation, 60–90%; iv. 1,4-cyclohexanedione, NaOH–EtOH, 50–60%; v. Al/Hg, cyclohexanol, 100 °C, 30–70%.

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reduced to provide dimethanol **6** in good yield. Oxidation followed by condensation with 1,4-cyclohexanedione[12] yields quinone **8**, which is reduced[13] to the corresponding pentacene. The deep red dioxolane pentacene solubility is strongly dependent on the substituents on the dioxolane ring, bracketed by butyl derivative **9b** (soluble up to 100 mg mL^{-1} in toluene), and cyclopentylidine derivative **9c** (only sparingly soluble in hot chlorobenzene). Solutions of pentacenes **9** stored in the dark or under diffuse laboratory lighting were stable for a period of several days. Under the same diffuse lighting conditions, solutions of pentacene bleached with a half-life of ~20 min (Fig. S2†). Crystals and crystalline films of **9a** and **9d** have persisted for more than a year without appreciable decomposition.

Electrochemical analysis of pentacenes **9a–d** in dichloromethane solution (0.1 M Bu_4NPF_6 electrolyte, ferrocene internal standard) showed a single reversible oxidation at approximately 570 mV (*vs.* SCE) for all four pentacene derivatives. This value compares well with that reported for unsubstituted pentacene,[7] indicating that the addition of the four oxygen substituents in the dioxolane rings did not drastically perturb the HOMO energy of the pentacene chromophore (see below). UV-Vis spectroscopy of these compounds in dichloromethane (Fig. 2) shows $\lambda_{max} = 557$ nm for all of these derivatives, corresponding to a blue shift of ~620 cm^{-1} *vs.* pentacene ($\lambda_{max} = 577$ nm).

The significant blue-shift in absorption observed for pentacenes **9** relative to unsubstituted pentacene is somewhat surprising, since the addition of alkoxy groups to an aromatic chromophore is generally expected to yield a red-shift in absorption. The red-shift is classically explained by the simple Hückel picture of alternate hydrocarbons, where LCAO coefficients in the HOMO and LUMO are symmetrical. Alkoxy substitution on such systems should always lead to a red-shift in absorption, since the inductive effect of the substituent will lead to the same stabilization of the HOMO and LUMO orbitals, while destabilization from mesomeric (resonance) effects will have a greater impact on the HOMO, due to the low-lying energetic position of the oxygen lone pair in relation to that orbital.[14] Such an effect is indeed observed in 1,4,8,11-tetramethoxy pentacene, which has $\lambda_{max} = 595$ nm, compared with 577 nm for pentacene.[15]

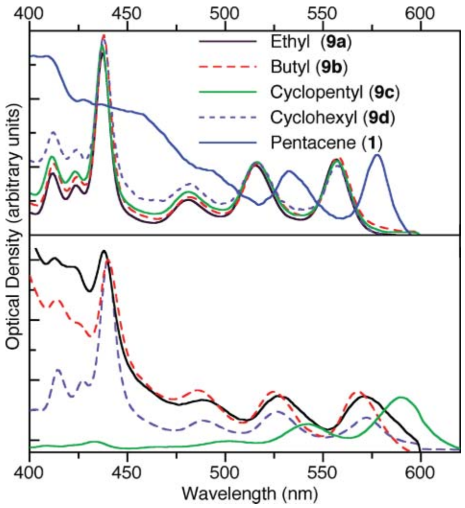

Fig. 2 UV-Visible spectra of pentacene derivatives in dichloromethane solution (top) and in thin (100 nm) films (bottom).

To further investigate the unusual substituent effects in **9a–d**, we performed a detailed study of their electronic structure using time-dependent DFT. Although on such large molecules this method cannot predict *absolute* values of HOMO–LUMO gaps, it will yield the *relative* effect of substitution on HOMO and LUMO energies.[16] The geometries and electronic structures for **1**, **10** and **11** (Fig. 3) were calculated at the DFT level using the B3LYP functional and the 6-311G* basis sets. To calculate the optical vertical transition energies, the time-dependent DFT approach was used. All calculations were performed using the Gaussian03 program package.[17] In general, the calculations reproduced the absorption shifts observed in these systems, mirroring the observed increase in HOMO–LUMO gap upon dioxolane substitution of pentacene (Fig. 3, left). Inspection of the calculated LCAO coefficients of the HOMO and LUMO for pentacene (Fig. 3, right) shows that the pro-*cata* positions (2,3,9,10 positions) are electronically unique, in that the coefficients are small, and the coefficients for the HOMO at these positions are larger than those for the LUMO. This disparity will lead to a stronger inductive stabilization of the HOMO, thus contributing to an *increase* in HOMO–LUMO gap upon substitution. In order to determine whether geometrical issues associated with the dioxolane substituent contribute to the blue-shifted absorption, the HOMO–LUMO gap for 2,3,9,10-tetramethoxy pentacene **11** was also calculated. In this case as well, a blue-shift in absorption *vs.* the unsubstituted compound was predicted. Our calculations show that it is strictly the unique electronic nature of the pro-*cata* positions of acenes that causes inductively electron-withdrawing substituents to induce blue-shifts in absorption. A brief survey of the literature has shown similar blue-shifts in solubilized pentacenes substituted at the pro-*cata* positions with fluorine[18] or ethers,[5] and has also been reported in solubilized 2,3,6,7-tetramethoxy anthracene.[19]

An indicator of the electronic interaction between molecules in the solid state is the degree of red-shift observed in the absorption spectra of the thin films of **9a–d**. The butyl derivative **9b**, with long bulky side groups, shows only a ~10 nm red shift, implying weak electronic coupling. In contrast, cyclopentyl derivative **9c** exhibits a 33 nm red shift, indicating strong intermolecular overlap.

Pentacenes **9b** and **9d** yielded crystals suitable for X-ray crystallographic analysis.‡ Derivative **9d** crystallized from chlorobenzene in space group *Pbca*, with one molecule per asymmetric unit. The packing of this derivative is dominated by edge-to-face

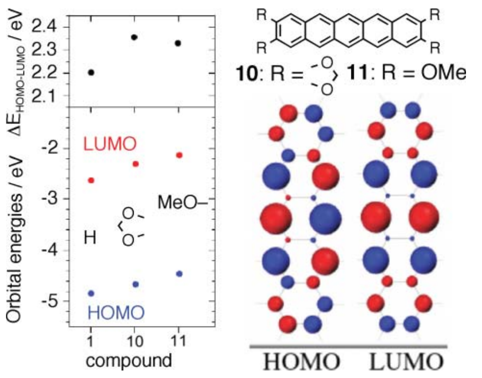

Fig. 3 Calculated HOMO, LUMO energies and optical gap for pentacene and pentacene ethers, and calculated HOMO and LUMO of pentacene.

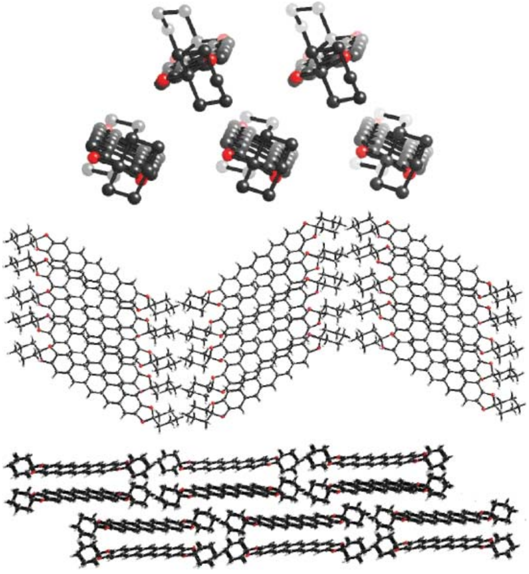

Fig. 4 Crystal packing of pentacene **9d**.

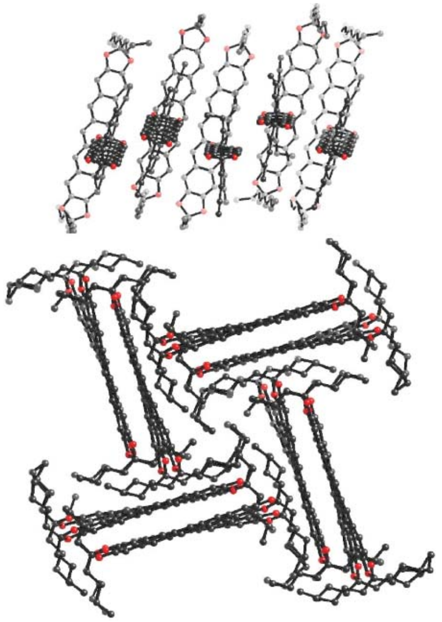

Fig. 5 Crystal packing of pentacene **9b**.

interactions, with a herringbone angle of 49° and a π-face separation of 5.95 Å (Fig. 4, top—compare with 53° and 6.27 Å for pentacene[20]). These edge-to-face dimers are angled at 114° to form a secondary chevron motif in the crystallographic *b*–*c* plane (Fig. 4, middle), which in turn are offset by half a molecule length (Fig. 4, bottom) to yield the three-dimensional crystal packing. Pentacene **9b** crystallized from anisole in space group $P2_1/n$, with two molecules per asymmetric unit. The prediction of minimal C_{Ar}–C_{Ar} contacts from thin-film UV-Vis spectra are confirmed by this structure (Fig. 5). The *n*-butyl chains induce the pentacene molecules to adopt a coplanar arrangement with minimal π-overlap. The overall arrangement is similar to a "rolled" π-stack, a motif intermediate between cofacial π-stacks and herringbone packing.[21] The pentacene π-faces in these "stacks" are almost completely covered by the alkyl chains of adjacent symmetry-related pentacene stacks. Studies of the effect of crystal packing on the charge transport properties of these materials are currently underway.

Notes and references

‡ CCDC 655471 and 655472. For crystallographic data in CIF format see DOI: 10.1039/b711296c

1 R. Ruiz, D. Choudhary, B. Nickel, T. Toccoli, K.-C. Chang, A. C. Mayer, P. Clancy, J. M. Blakely, R. L. Headrick, S. Iannotta and G. G. Malliaras, *Chem. Mater.*, 2004, **16**, 4497; A. R. Murphy and J. M. J. Frechet, *Chem. Rev.*, 2007, **107**, 1066.

2 L. Zhou, A. Wanga, S.-C. Wu, J. Sun, S. Park and T. N. Jackson, *Appl. Phys. Lett.*, 2006, **88**, 083502; G.-S. Ryu, K.-B. Choe and C.-K. Song, *Thin Solid Films*, 2006, **514**, 302.

3 Q. Miao, X. Chi, S. Xiao, R. Zeis, M. Lefenfeld, T. Siegrist, M. L. Steigerwald and C. Nuckolls, *J. Am. Chem. Soc.*, 2006, **128**, 1340; J. E. Anthony, D. L. Eaton and S. R. Parkin, *Org. Lett.*, 2002, **4**, 15.

4 S. K. Park, T. N. Jackson, J. E. Anthony and D. A. Mourey, *Appl. Phys. Lett.*, 2007, **91**, 063514.

5 M. A. Wolak, J. H. Delcamp, C. A. Landis, P. A. Lane, J. E. Anthony and Z. H. Kafafi, *Adv. Funct. Mater.*, 2006, **16**, 1943.

6 A. Maliakal, K. Raghavachari, H. Katz, E. Chandross and T. Siegrist, *Chem. Mater.*, 2004, **16**, 4980; P. Coppo and S. G. Yeates, *Adv. Mater.*, 2005, **17**, 3001.

7 H. Meng, M. Bendikov, G. Mitchell, R. Helgeson, F. Wudl, Z. Bao, T. Siegrist, C. Kloc and C.-H. Chen, *Adv. Mater.*, 2003, **15**, 1090.

8 S. H. Chan, H. K. Lee, Y. M. Wang, N. Y. Fu, X. M. Chen, Z. W. Cai and H. N. C. Wong, *Chem. Commun.*, 2005, 66.

9 J. Reichwagen, H. Hopf, J.-P. Desvergne, A. Del Guerzo and H. Bouas-Laurent, *Synthesis*, 2005, 3505.

10 H. Bouas-Laurent, A. Castellan, J.-P. Desvergne and R. Lapouyade, *Chem. Soc. Rev.*, 2000, **29**, 43.

11 D. R. Anderson and T. H. Koch, *J. Org. Chem.*, 1978, **43**, 2726.

12 W. Ried and F. Anthofer, *Angew. Chem.*, 1953, **65**, 601.

13 J. G. Laquindanum, H. E. Katz and A. J. Lovinger, *J. Am. Chem. Soc.*, 1998, **120**, 664.

14 For absorption spectra in aromatics, see: T. P. Troy and T. W. Schmidt, *Mon. Not. R. Astron. Soc.*, 2000, **371**, L41. For a Hückel treatment of substituent effects, see: B. M. Mamaev, G. V. Ponomarev and R. P. Evstigneeva, *Chem. Heterocycl. Compd. (Engl. Transl.)*, 1967, **3**, 681.

15 A. R. Wartini, H. A. Staab and F. A. Neugebauer, *Eur. J. Org. Chem.*, 1998, 1161.

16 J. Gierschner, J. Cornil and H.-J. Egelhaaf, *Adv. Mater.*, 2007, **19**, 173.

17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

18 C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.*, 2005, **7**, 3163.

19 C. A. Landis, S. R. Parkin and J. E. Anthony, *Jpn. J. Appl. Phys., Part 1*, 2005, **44**, 3921.

20 D. Holmes, S. Kumaraswamy, A. J. Matzger and K. P. C. Vollhardt, *Chem.–Eur. J.*, 1999, **5**, 3399.

21 M. D. Curtis, J. Cao and J. W. Kampf, *J. Am. Chem. Soc.*, 2004, **126**, 4318.