



Cite this: *Chem. Commun.*, 2016, 52, 8127

Received 18th April 2016,
Accepted 27th May 2016

DOI: 10.1039/c6cc03259a

www.rsc.org/chemcomm

Synthesis, electrochemical properties, and crystal packing of perfluororubrene†

Zhuoran Zhang, William A. Ogden,‡ Victor G. Young Jr. and Christopher J. Douglas*

A synthesis of perfluorinated rubrene is reported. Electrochemical analysis revealed the significantly increased electron affinity of perfluororubrene compared with non-modified rubrene. Crystallographic investigation revealed two polymorphs and a solvate, each displaying twisted backbone conformations of perfluororubrene. Taken together, these results suggest perfluororubrene will find applications as a new n-type semiconductor.

Understanding the nature of intermolecular interactions in solid states is crucial to the design of π -functional materials.¹ Chemical synthesis provides a way to make structural modifications at the molecular level and establish structure–property relationships. Acene-based organic molecules have been recognized as excellent targets for making next-generation organic electronic devices.^{2,3} Extensive efforts have been made towards the syntheses of molecules with novel structural features, as well as the optimization of electronic device configurations and fabricating techniques.^{2,4} Rubrene (**1**), as a benchmark semiconductor has been studied extensively in the field of organic electronic materials.⁵ The highest hole mobilities reported for non-substituted rubrene so far have reached $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁶ Studies have indicated that by altering the electron density of functional acene derivatives, the optoelectronic properties, such as frontier molecular orbital (FMO) energy levels, absorption and emission spectra and crystal packing can be fine-tuned, resulting in unique device performance.⁷ Specifically, lowering the electron density of π -system of an acene *via* fluorination is an effective method to convert a p-type semiconductor parent structure to n-type semiconductor.⁸ In order to elucidate

the relationship between the structure features, electrochemical properties and optoelectronic device performances, various structural modifications to rubrene have been made, including the introduction of electron donating/withdrawing substituents onto peripheral phenyls, perdeuteration, and inclusion of different functional groups on tetracene cores.^{5,9} Of all the possible structural analogues of rubrene, perfluororubrene ($\text{C}_{42}\text{F}_{28}$, **2**) is an interesting structure to explore because of the significant change in its electronic structure brought by the inherent electron-withdrawing nature of the twenty-eight fluorine substitutions. Unlike other fluorinated rubrene derivatives investigated to date, perfluorination maintains the molecular symmetry of the parent structure.¹⁰ Further, we expect that steric issues will be minimized since fluorine atoms are less bulky than the other functional groups examined in rubrene derivatives to date, such as alkyl, alkoxy, and fluoroalkyl.¹¹ Thus, perfluororubrene is a compelling target for chemical synthesis (Fig. 1).

Recently, the physical properties of perfluororubrene, including optical behavior and vibrational modes, have been reported for both solution and thin films.¹² Interface dipole and growth mode on Au and Ag substrates have also been explored.¹³ To our best knowledge, however, a synthesis of perfluororubrene has not been disclosed. We now report a complete synthesis of perfluororubrene. Our route is based on sequential addition of pentafluorophenyl lithium to perfluorotetracenequinone (**6**, Scheme 1). We also report on perfluororubrene's electrochemical properties through cyclic voltammetry to measure the FMO energies in

Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455, USA. E-mail: cdouglas@umn.edu

† Electronic supplementary information (ESI) available: Experimental procedures, tabulated characterization data for perfluororubrene and key synthetic intermediates, X-ray crystallographic data and figures, cyclic voltammetry plots, copies of ^1H NMR, ^{13}C NMR (^1H , ^{19}F), ^{19}F NMR, and IR spectra. CCDC 1473574–1473576. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc03259a

‡ Current address: Department of Chemistry, University of California, Irvine, 1102 Natural Sciences 2, Irvine, CA, 92697.

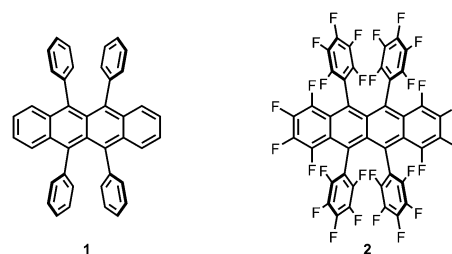
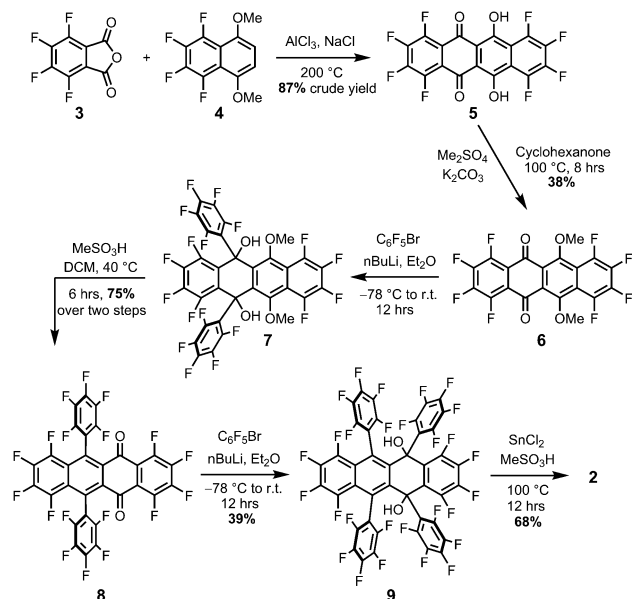


Fig. 1 Structure of rubrene (**1**) and perfluororubrene (**2**).



Scheme 1 Synthesis of perfluororubrene (2).

solution. Finally, single-crystal X-ray analysis revealed the packing motif of perfluororubrene in three crystalline states. Our results indicate that perfluororubrene is possibly a strong candidate for n-type semiconducting behavior.

Although the methodologies for rubrene synthesis have been well studied, the synthesis of perfluororubrene is not trivial. The original synthesis of rubrene involves the dimerization of a propargyl chloride or a one-pot transformation from a propargyl alcohol.¹⁴ Another synthetic route *via* cycloaddition of an isobenzofuran and 1,4-naphthoquinone followed by phenyl lithium addition and reduction provided an opportunity for derivatization on the tetracene backbone.⁹ A more convenient synthetic approach using 6,11-dichloro-5,12-tetracenedione as a key intermediate offered more feasibility for late-stage structural modifications with respect to substituted peripheral phenyl groups.^{5b} However, the synthesis of perfluororubrene requires complete halogen substitution on both the tetracene backbone and the peripheral phenyls, which appeared challenging since the perfluorinated congeners of the key intermediates described above were not easily accessible.

In order to obtain the perfluorinated tetracene core, we first adopted Ono's synthesis of 1,2,3,4,7,8,9,10-octafluoro-6,11-dihydroxy-5,12-naphthacenedione *via* a Friedel-Crafts acylation between 1,2,3,4-tetrafluoro-5,8-dimethoxy-naphthalene and tetrafluorophthalic anhydride (Scheme 1).¹⁵ The hydroxyl groups were then protected using dimethylsulfate under basic conditions to give the corresponding dimethoxytetracenedione (6). We noted that employing cyclohexanone instead of acetone as the reaction solvent was crucial to the transformation, probably because the reaction required a higher temperature to proceed. Nucleophilic addition of perfluorophenyl lithium to the dione (6) formed an inconsequential mixture of diol diastereomers (7), which was then converted into 6,11-diaryltetracene-5,12-dione (8) *via* an acid-promoted rearrangement. The second set of perfluorophenyl

substituents was installed using the same method. However, organolithium addition was less efficient this time, probably due to nucleophilic aromatic substitution between the *in situ* formed alkoxide and the nearby *peri*-perfluorophenyl group, which could lead to decomposition. Finally, reductive aromatization of diol using SnCl₂ in methanesulfonic acid afforded perfluororubrene (2) in moderate yield. Using the route described above, we have prepared significant quantities of perfluororubrene.

The electrochemical properties of perfluororubrene were investigated by cyclic voltammetry using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal reference. The cyclic voltammogram of 2 showed two reversible reduction waves in THF, which was unusual compared to all other rubrene derivatives of which we are aware.¹⁶ We did not, however, observe an oxidation event. The lack of an oxidation wave is probably due to the electron-deficient nature of this molecule's π -system. The low-lying LUMO energy (−4.05 eV) measured for perfluororubrene indicates it may have potential as an electron-transporting semiconducting material (Table 1).

Three different methods, including solvent evaporation, sublimation, and physical vapor transport (PVT) were employed to grow single crystals of perfluororubrene.¹⁷ Interestingly, each method gave a different crystal. The degree of twist in the tetracene backbone was different in each crystal. By slowly evaporating solvent from a chloroform solution, an orthorhombic crystal A (chloroform solvate) was obtained. In the crystal structure, the perfluororubrene molecule adopted a twisted backbone conformation with an end-to-end twist angle of 39.32° (Fig. 2a). Since solvent molecule was present, the solvate crystal A possessed the longest *c* lattice dimension in the unit cell compared to the other two polymorphic crystal structures (see ESI,† Table S1). As a result, the intermolecular packing was very loose. No face-to-face packing between tetracene backbones of nearby molecules was observed. Sublimation at 290 °C gave a monoclinic crystal B with the space group of *P*2₁/*n*, in which the tetracene backbone possessed a larger end-to-end twist angle of 45.37° (Fig. 2b). Compared to the solvate crystal structure, a tighter packing arrangement, including one-dimensional stack packing along the crystallographic *a*-axis was found in the monoclinic crystal B (Fig. 3a). A closer investigation of intermolecular interactions revealed that edge-face interactions between a *peri*-perfluorophenyl group and the tetracene backbone of a nearby molecule exist in the spatial ordering. Although there are many examples of orthorhombic crystals for rubrene derivatives that are grown from vapor transport, in our experiments, the crystal structure obtained from PVT (argon as

Table 1 Electrochemical properties of rubrene (1) and perfluororubrene (2)

Compound	E_{ox} (V)	E_{red1}^a (V)	E_{red2}^a (V)	HOMO ^b (eV)	LUMO ^b (eV)
1	0.38	−1.44	—	−5.18	−3.36
2	—	−0.83	−1.60	—	−4.05

^a The 1st and 2nd half-wave reduction potentials (vs. Fc⁺/Fc) was measured by cyclic voltammetry in THF. ^b The LUMO energy level was calculated from the onset of the first reduction wave, using the equation: LUMO = −(4.8 + $E_{\text{red}}^{\text{onset}}$) eV.

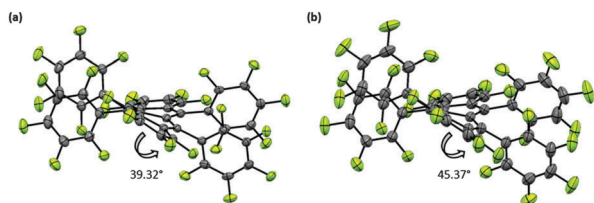


Fig. 2 End-to-end twist angle of tetracene backbone in (a) crystal A and (b) crystal B.

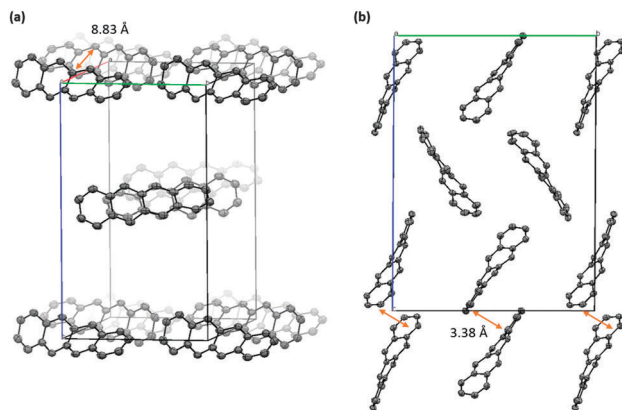


Fig. 3 Packing arrangements for (a) crystal B and (b) crystal C, only the tetracene backbone was shown for clarity.

the carrier gas, 220–230 °C) was found to be triclinic with the space group of $P1$.¹⁸ The triclinic crystal C featured an asymmetric unit containing three unique perfluororubrene molecules. The end-to-end twist angles for each molecule were different: 44.03°, 47.12° and 47.97°, respectively (see ESI,† Fig. S4). In the triclinic crystal C, a herringbone-type packing arrangement was observed. Both the C–F... π interaction and the π – π interaction may be responsible for the packing arrangement. The distance measured for C–F... π interaction was 3.04 Å with a bond-ring angle of 143.7°. A close π – π interaction was found between tetracene cores with a face-to-face distance of 3.38 Å (Fig. 3b). We note that even though the tetracene backbone is twisted, which usually results in poor packing arrangements for charge transport, close intermolecular interactions still existed, which may be attributed to the inherent electron deficiency of perfluororubrene.

In conclusion, we have established a complete synthetic route for the preparation of perfluorinated rubrene from known fluorinated precursors. Our synthesis of this molecule provides a new entry to further understanding the structure–property relationships in the growing family of rubrene derivatives. Through perfluorination, the electron density of perfluororubrene was significantly decreased compared to rubrene. The low-lying LUMO level suggested the potential for applications in n-type organic semiconductors and organic photovoltaics as electron acceptors. Single-crystal X-ray analysis afforded the structural conformation and packing arrangements of three unique crystals. Perfluorination of the *peri*-phenyl groups and the acene backbone seems to promote the rubrene core to adopt a twisted backbone conformation in the solid state. Close intermolecular

interactions, such as C–F... π interaction and π – π interaction, were observed within the crystal packing motifs. We have not yet identified a polymorph of perfluororubrene that adopts the slipped π -stack arrangement deemed beneficial for charge transport in orthorhombic rubrene. Future studies of this molecule will be focused on identifying additional polymorphs and developing applications in the fields of small molecule organic field effect transistors and organic photovoltaic devices.

Acknowledgements are made to Ms Xue Zhen (UMN) for assistance with cyclic voltammetry and Mr Nicholas Serratore (UMN) for assistance with ^{19}F decoupled ^{13}C NMR. WAO thanks the University of Minnesota for UROP support. WAO also thanks the Heisig/Gleysteen Chemistry Summer Research Program (UMN) for an undergraduate research fellowship. CJD thanks DuPont for a Young Investigator Award and the NSF (DMR-1006566) for support of this work. We thank Dr Kathryn McGarry and Ms Susan Krzmarzick for informative early work on the perfluororubrene synthesis at Minnesota.

Notes and references

- 1 C. Sutton, C. Risko and J.-L. Brédas, *Chem. Mater.*, 2016, **28**, 3.
- 2 (a) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028; (b) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Brédas, *Chem. Rev.*, 2007, **107**, 926.
- 3 (a) Q. Ye and C. Chi, *Chem. Mater.*, 2014, **26**, 4046; (b) J. Zhou, Q. Liu, W. Feng, Y. Sun and F. Li, *Chem. Rev.*, 2015, **115**, 395; (c) J. Mei, Y. Diao, A. L. Appleton, L. Fang and Z. Bao, *J. Am. Chem. Soc.*, 2013, **135**, 6724; (d) J. E. Anthony, A. Facchetti, M. Heeney, S. R. Marder and X. Zhan, *Adv. Mater.*, 2010, **22**, 3876.
- 4 A. Yassar, *Polym. Sci., Ser. C*, 2014, **56**, 4.
- 5 (a) V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J. A. Rogers and M. E. Gershenson, *Phys. Rev. Lett.*, 2004, **93**, 086602; (b) K. A. McGarry, W. Xie, C. Sutton, C. Risko, Y. Wu, V. G. Young Jr., J.-L. Brédas, C. D. Frisbie and C. J. Douglas, *Chem. Mater.*, 2013, **25**, 2254; (c) W. Xie, K. A. McGarry, F. Liu, Y. Wu, P. P. Ruden, C. J. Douglas and C. D. Frisbie, *J. Phys. Chem. C*, 2013, **117**, 11522; (d) W. Xie, P. L. Prabhumirashi, Y. Nakayama, K. A. McGarry, M. L. Geier, Y. Urugami, K. Mase, C. J. Douglas, H. Ishii, M. C. Hersam and C. D. Frisbie, *ACS Nano*, 2013, **7**, 10245; (e) T. K. Mullenbach, K. A. McGarry, W. A. Luhman, C. J. Douglas and R. J. Holmes, *Adv. Mater.*, 2013, **25**, 3689; (f) D. A. da Silva Filho, E. G. Kim and J.-L. Brédas, *Adv. Mater.*, 2005, **17**, 1072.
- 6 J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda and S. Ogawa, *Appl. Phys. Lett.*, 2007, **90**, 102120.
- 7 (a) J. F. Tannaci, M. Noji, J. L. McBee and T. D. Tilley, *J. Org. Chem.*, 2008, **73**, 7895; (b) M. J. Bruzek and J. E. Anthony, *Org. Lett.*, 2014, **16**, 3608; (c) B. Purushothaman, S. R. Parkin and J. E. Anthony, *Org. Lett.*, 2010, **12**, 2060; (d) C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.*, 2005, **7**, 3163; (e) J. E. Anthony, D. L. Eaton and S. R. Parkin, *Org. Lett.*, 2002, **4**, 15.
- 8 Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato and S. Tokito, *J. Am. Chem. Soc.*, 2004, **126**, 8138.
- 9 A. S. Paraskar, A. R. Reddy, A. Patra, Y. H. Wijsboom, O. Gidron, L. J. W. Shimon, G. Leitens and M. Bendikov, *Chem. – Eur. J.*, 2008, **14**, 10639.
- 10 A. R. Waterloo, A.-C. Sale, D. Lehnher, F. Hampel and R. R. Tykwinski, *Beilstein J. Org. Chem.*, 2014, **10**, 1692.
- 11 R. N. Baral and S. W. Thomas III, *J. Org. Chem.*, 2015, **80**, 11086.
- 12 (a) F. Anger, R. Scholz, E. Adamski, K. Broch, A. Gerlach, Y. Sakamoto, T. Suzuki and F. Schreiber, *Appl. Phys. Lett.*, 2013, **102**, 013308; (b) F. Anger, R. Scholz, A. Gerlach and F. Schreiber, *J. Chem. Phys.*, 2015, **142**, 224703.
- 13 F. Anger, H. Glowatzki, A. Franco-Cañellas, C. Bürker, A. Gerlach, R. Scholz, Y. Sakamoto, T. Suzuki, N. Koch and F. Schreiber, *J. Phys. Chem. C*, 2015, **119**, 6769.

- 14 D. Braga, A. Jaafari, L. Miozzo, M. Moret, S. Rizzato, A. Papagni and A. Yassar, *Eur. J. Org. Chem.*, 2011, 4160.
- 15 K. Ono, J. Hashizume, H. Yamaguchi, M. Tomura, J.-I. Nishida and Y. Yamashita, *Org. Lett.*, 2009, **11**, 4326.
- 16 While we were preparing this manuscript, a report on the electrochemistry of perfluororubrene appeared: F. Anger, T. Breuer, A. Ruff, M. Klues, A. Gerlach, R. Scholz, S. Ludwigs, G. Witte and F. Schreiber, *J. Phys. Chem. C*, 2016, **120**, 5515.
- 17 The coordinates for all crystallography in this work have been deposited with the Cambridge Structural Database (CSD).
- 18 L. Huang, Q. Liao, Q. Shi, H. Fu, J. Ma and J. Yao, *J. Mater. Chem.*, 2010, **20**, 159.