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Thin film field-effect transistors of 2,6-diphenyl anthracene (DPA)†

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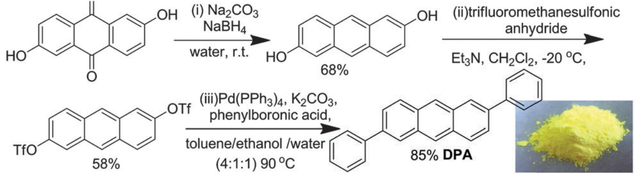
Jie Liu,[ab] Huanli Dong,*[ac] Zongrui Wang,[ab] Deyang Ji,[ab] Changli Cheng,[d] Hua Geng,[a] Hantang Zhang,[ab] Yonggang Zhen,[a] Lang Jiang,[e] Hongbing Fu,[a] Zhishan Bo,[f] Wei Chen,[g] Zhigang Shuai*[d] and Wenping Hu*[ah]

An anthracene derivative, 2,6-diphenyl anthracene (DPA), was successfully synthesized with three simple steps and a high yield. The compound was determined to be a durable high performing semiconductor with thin film device mobility over 10 cm^2 V^{-1} s^{-1}. The efficient synthesis and high performance indicates its great potential in organic electronics.

Organic field-effect transistors (OFETs) have gained great interest in the last decades, motivated by their potential applications in low-cost and flexible electronics such as transparent circuits and flexible displays.[1] A remarkable burst has been recently witnessed with charge mobility surpassing 10 cm^2 V^{-1} s^{-1} which has been attributed to the new materials designed and device optimization.[2] Among the diverse organic semiconductors, polyacenes are one of the best performing systems, with the extension of the π-conjugation system, higher charge carrier mobility can be expected because of their smaller reorganization energy and larger intermolecular transfer integrals.[3] However, the poor air/chemical stability of highly extended polyacenes, such as pentacene and hexacene, which usually undergo an easily photo-induced oxidation or Diels–Alder addition reaction, has severely hindered their commercial application.[4] To circumvent this issue of instability, a number of approaches have been developed: (i) kinetically preventing possible reactions by attaching bulky substituents at the active sites, such as at the 6,13-positions of pentacene;[5] (ii) lowering the highest occupied molecular orbital (HOMO) level by replacing the benzene rings with thiophene rings.[6] Materials with improved stability and comparable or even higher performance than pentacene have been demonstrated for both of these two classes of organic semiconductors.[2a,7] On the other hand, a decrease in the π-conjugation system in the parent acenes provides another approach to improve the stability,[8] such as anthracene derivatives, which also generally render practical applications for the efficient synthesis. Based on these considerations, various anthracene derivatives have been developed and investigated in organic electronic devices (Table S1, ESI†). One of the best performing anthracene derivatives is diphenylvinyl-anthracene (DPVAnt), which was first synthesized by Meng *et al.*,[8c,d] and exhibited mobility as high as 1.28 cm^2 V^{-1} s^{-1} and excellent ambient stability. Later, carrier mobility of 4.3 cm^2 V^{-1} s^{-1} was found for DPVAnt single crystals.[9]

Stimulated by the progress of anthracene derivatives, in this manuscript, 2,6-diphenyl anthracene (DPA, Scheme 1) was designed. The molecular design principles were (i) further improving the stability through a reduction in the π-conjugation,[8e] (ii) achieving denser molecular packing through reasonably reducing molecular size.[10] Further characterizations proved that DPA has high thermal and environmental stability. In addition, over 80% of the vacuum deposited thin film field-effect transistors based on DPA exhibited mobility over 10 cm^2 V^{-1} s^{-1} with a current on/off



Scheme 1 Synthetic route to DPA and powder of DPA.

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[a] *Beijing National laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: dhl522@iccas.ac.cn, huwp@iccas.ac.cn*

[b] *University of the Chinese Academy of Sciences, Beijing 100039, China*

[c] *Department of Chemistry, Capital Normal University, Beijing, 100037, China*

[d] *Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: zgshuai@tsinghua.edu.cn*

[e] *Cavendish Laboratory, Cambridge University, JJ Thomson Avenue, Cambridge CB3 0HE, UK*

[f] *Department of Chemistry, Beijing Normal University, Beijing 100875, China*

[g] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore*

[h] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin) & School of Science, Tianjin University, Tianjin 300072, China*

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ratio up to 10^8 and had long term stability. All these results were telling that DPA was a promising candidate for commercial research.

The synthetic route of DPA is depicted in Scheme 1, the final product can be easily synthesized through three simple steps and pure DPA was obtained in large quantities by sublimation (see full synthetic details in ESI†).

Physicochemical properties measurements were conducted on DPA to verify its stability. Its UV-vis absorption spectrum in solution is shown in Fig. 1A with an absorption onset of 413 nm and an estimated energy band gap of 3.0 eV. UV-vis absorption of the thin film was also studied, a redshift of 30 nm (red line in Fig. 1A) and an increased ratio of the first vibration peak intensity compared with the second one were observed, suggesting J-aggregation formation in the thin film.[11] Cyclic-voltammetry of DPA was performed and the calculated HOMO level was around −5.6 eV (Fig. 1B), 0.2 eV more negative than DPVAnt (−5.4 eV)[9] and at the same level as the BTBT derivatives (Fig. 1B),[10a] which indicates its high stability. And the decomposition temperature was determined as over 300 °C (Fig. S1, ESI†), which further guaranteed its thermal stability.

To investigate the molecular packing, single crystals of DPA with sufficient quality for X-ray structural analysis were grown by slow evaporation from chloroform (CCDC 1044209). X-ray crystallographic results demonstrated that the DPA crystal belongs to the $P2(1)/c$ space group with crystal parameters of a = 17.973(8) Å, b = 7.352(3) Å, c = 6.245(3) Å and β = 90.646(9)°. And a torsion angle of 20.05° out of the central anthracene ring was determined for the phenyl groups (Fig. 2A). The packing of DPA represents a typical herringbone structure similar to that of DPVAnt (Fig. 2B), however, a 10° smaller herringbone angle was demonstrated for DPA compared to that of DPVAnt (52.2°).[9] Moreover, multi C–H–π interactions (distance: ∼2.85 Å) are observed between every DPA molecule and its nearest four neighbor molecules (Fig. 2C). Such a dense packing structure is partially due to the small molecular size as well as strong intermolecular interactions, and thus hopefully affording high charge carrier mobility.

Thin films of DPA deposited on OTS (octadecyltrichlorosilane) treated Si/SiO_2 (300 nm) at a substrate temperature of 50 °C and a deposition speed of 0.05 Å s^{-1} were studied. AFM images of 50 nm and 5 nm are shown in Fig. 3A and B, large and quite uniform grains were obtained. X-ray diffraction measurements of the 50 nm film showed a series of peaks assignable to (h00) reflections (Fig. 3C). Moreover, the obtained d-spacing (1.80 nm) was very close to the length of DPA (1.777 nm), indicating that DPA were grown perpendicularly on the substrate. This conclusion was further confirmed by the AFM results of the 5 nm film of DPA as shown in Fig. 3B, it was obvious that the 3-layer domain was grown layer by layer. If the domain was crossed from point (i) to point (ii), then the step heights of the crystalline terrace layers would be around 1.7 nm which is the same as what is shown in Fig. 3D, indicating the layer-by-layer growth mode of the DPA films, which agreed well with the results of Fig. 3C.

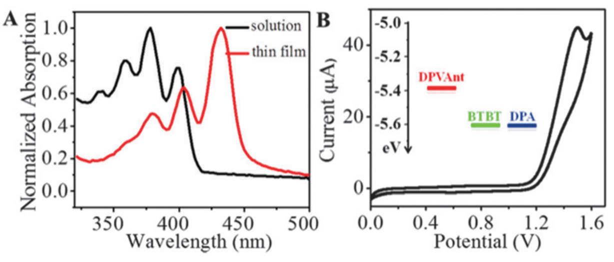

Fig. 1 (A) UV-vis spectra of DPA in solution (black) and thin film state (red), (B) CV curve of DPA and HOMO levels of typical p-type semiconductors (inset).

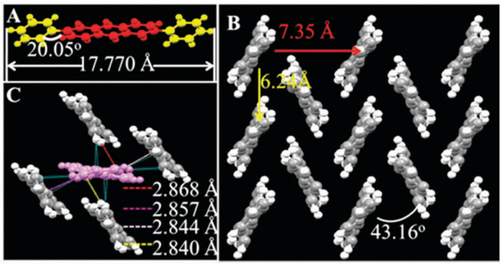

Fig. 2 (A) DPA molecular length, (B) herringbone packing and (C) short contacts in DPA.

To evaluate the charge transport properties of DPA, organic thin film transistors were fabricated based on the 50 nm films mentioned above with ''top-contact'' geometry (Fig. 4A). Typical output and transfer characteristics obtained in air for the thin film devices are shown in Fig. 4B and C. The saturation mobility distribution for 30 devices is shown in Fig. 4D. Over 80% of the devices exhibited mobility >10 $cm^2\ V^{-1}\ s^{-1}$, with a highest mobility of 14.8 $cm^2\ V^{-1}\ s^{-1}$ (corresponding device characteristics are shown in Fig. S2, ESI†). Additionally, all the devices exhibited a current on/off ratio $>10^7$. Despite the high

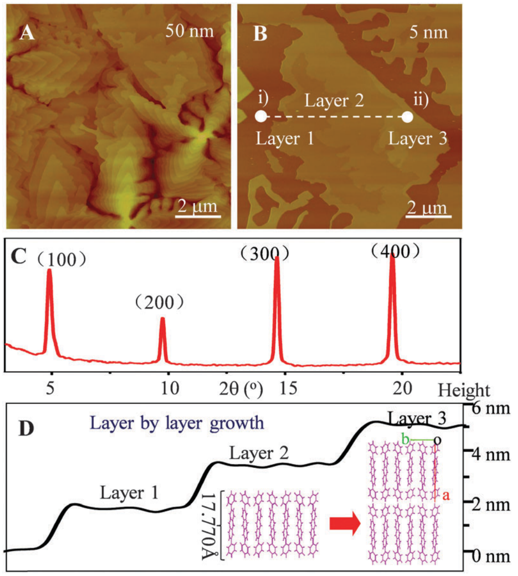

Fig. 3 AFM images of 50 nm (A) and 5 nm (B) thin films of DPA, (C) out of plane XRD results of DPA 50 nm films, (D) the step heights of crystalline terrace layers as measured by a section analysis along the line marked between the (i) and (ii) points, and DPA layer-by-layer packing mode in the films.

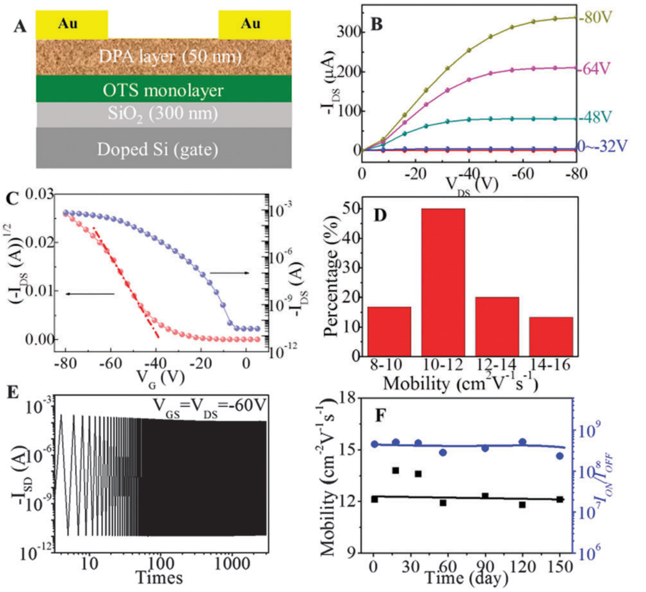

Fig. 4 (A) Device schematic of the DPA thin film OFETs, (B) typical output and (C) transfer characteristics of the representative device. (D) The mobility distribution of the DPA thin film OFETs, (E) continuous electrical test, V_{DS} was −60 V, with V_{GS} switching from 0 V to −60 V. (F) Mobility and on/off ratio dependence on time.

FET performance, nonlinear behavior of the output curve at low V_{DS} was observed, indicating the existence of contact resistance (∼0.1 MΩ, Fig. S3, ESI†), which also resulted in a relatively large threshold voltage from −34 V to −50 V. Additionally, some deviation from linearity for the $(I_{DS})^{1/2}$–V_G plot at high V_G was observed, which might be assigned to carrier supersaturation in the conducting channel at a high source–drain current or to factors such as charge traps at the interface and/or contact resistance.[12] Nevertheless, much higher charge transport properties can be expected for the DPA material under further device optimization. Besides, the stability of DPA-based thin film transistors was also characterized. As shown in Fig. 4E, the devices showed high stability over 3000 cycles, and a negligible decrease can be observed for the devices even stored in air for 5 months (Fig. 4F and Fig. S4, ESI†).

In summary, we have synthesized DPA in three simple and controlled steps with a high yield, which demonstrates high stability and dense molecule packing. Moreover, excellent performance with 80% of the devices having mobilities over 10 $cm^2\ V^{-1}\ s^{-1}$ and the highest mobility up to 14.8 $cm^2\ V^{-1}\ s^{-1}$ was achieved for the DPA-based thin film devices. All these results indicate the great potential of DPA for applications in organic electronics.

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