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Thin Film Field-effect Transistors of 2,6-diphenyl Anthracene (DPA)

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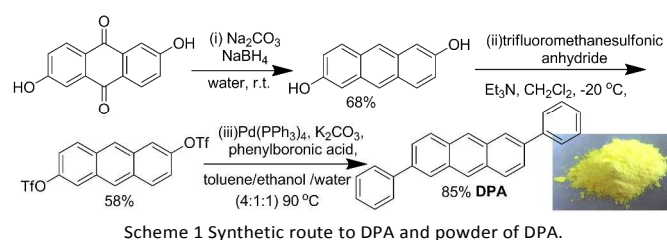
An anthracene derivative, 2,6-diphenyl anthracene (DPA), was successfully synthesized with three simple steps and high yields. The compound was determined as a durable high performing semiconductor with thin film device mobility over $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The efficient synthesis 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 $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ attributing to the new materials designed and device optimization.² Among the diverse organic semiconductors, polyacenes is one of the best performing systems, with the extension of π -conjugation system, higher charge carrier mobility could be expected owing to 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 from possible reactions by attaching bulky substituents at the active sites, such as at 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 are demonstrated for both of these two classes of organic semiconductors.^{2a,7} On the other hand, decrease of π -conjugation system in 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). One of the best performing anthracene derivatives is diphenylvinyl-anthracene (DPVAnt), which was firstly synthesized by Meng *et al.*,^{8c,8d} and exhibited mobility as high as $1.28 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and excellent ambient stability. Later, carrier mobility of $4.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ 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 are i) further improving the stability through reduction of the π -conjugation,^{8e} ii) achieving more dense molecular packing through reasonably reducing molecular size.¹⁰ Further characterizations proved that DPA has high thermal and environmental stability. In addition, over 80% vacuum deposited thin film field-effect transistors based on DPA exhibited mobility over $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with current on/off ratio up to 10^8 and 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 quantity 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 was shown in Fig. 1A with the absorption onset of 413 nm and the estimated energy band gap of 3.0 eV. UV-*vis*

absorption of its thin film was also studied and 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 its thin film.¹¹ Cyclic-voltammetry of DPA was performed and the calculated HOMO level is around -5.6 eV (Fig. 1B), 0.2 eV more negative than that of DPVAnt (-5.4 eV)⁹ and at the same level of that BTBT derivatives (Fig. 1B),^{10a} which indicates its high stability. And the decomposition temperature was determined as over 300 °C (Fig. S1), which further guaranteed its thermal stability.

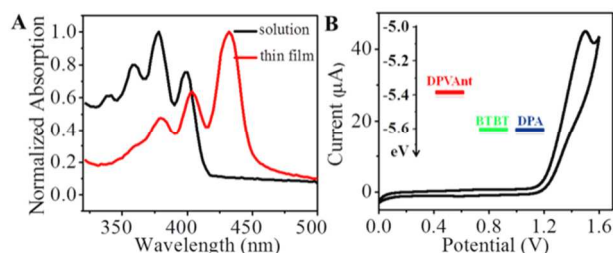


Fig. 1 (A) UV-vis spectra of DPA in solution (black) and thin film state (red), (B) CV curve of DPA and HOMO levels of typical p-type semiconductor (inlet).

To investigate the molecular packing, single crystals of DPA with sufficient quality for X-ray structural analysis were grown by slowly evaporation from chloroform (CCDC NO. 1044209). X-ray crystallographic results demonstrated that 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, $\beta = 90.646(9)^\circ$. 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 typical herringbone structure similar to that of DPVAnt (Fig. 2B), however, 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 to afford high charge carrier mobility.

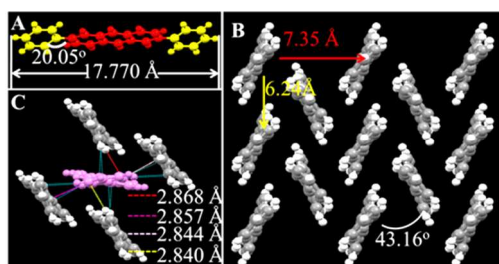


Fig. 2 (A) DPA molecular length, (B) herringbone packing and (C) short contacts in DPA.

Thin films of DPA deposited on OTS (octadecyltrichlorosilane) treated Si/SiO₂(300 nm) at substrate temperature of 50 °C and a deposition speed of 0.05 Å/s was studied. AFM image of 50 nm and 5 nm were shown in Fig. 3A and 3B, large and quite uniform grains were obtained. X-ray

diffraction measurement 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 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), the step heights of the crystalline terrace layers at around 1.7 nm were the same as shown in Fig. 3D, indicating the layer-by-layer growth mode of DPA films, which agreed well with the results of Fig. 3C.

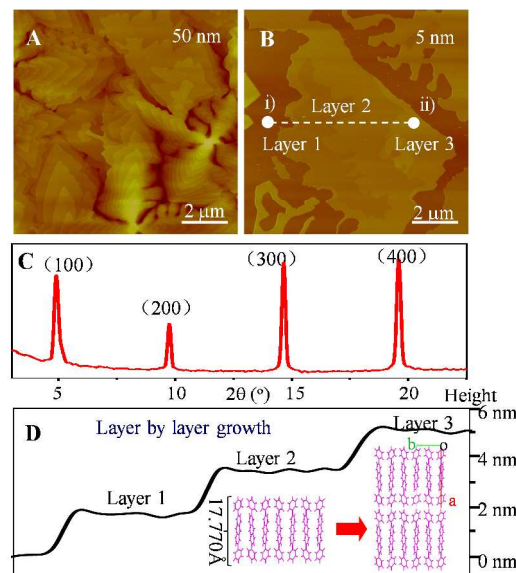


Fig. 3 AFM images of 50 nm (A) and 5 nm (B) thin films of DPA (C) out of plane XRD results of DPA 50 nm films, (D) the step heights of crystalline terrace layers as measured by a section analysis along the line marked in i) and ii) points, and DPA layer-by-layer packing mode in the films.

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 were shown in Fig. 4B and 4C. The saturation mobility distribution for 30 devices was shown in Fig. 4D. Over 80% devices exhibited mobility >10 cm²V⁻¹s⁻¹, with the highest mobility of 14.8 cm²V⁻¹s⁻¹ (corresponding device characteristics are shown in Fig. S2). Additionally, all the devices exhibited current on/off ratio $>10^7$. Despite the high 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), which also resulted in the relatively large threshold voltage from -34 V to -50 V. Additionally, some deviation for (I_{DS})^{1/2}-V_G plot from linearity at high V_G was observed, which might be assigned to the carrier supersaturation in the conducting channel at high source-drain current or factors such as charge traps at interface and/or contact resistance.¹² Nevertheless, much higher charge transport property could be expected for 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 cycle, and negligible decrease can be observed for the devices even stored in air for 5 months (Fig. 4F and Fig. S4).

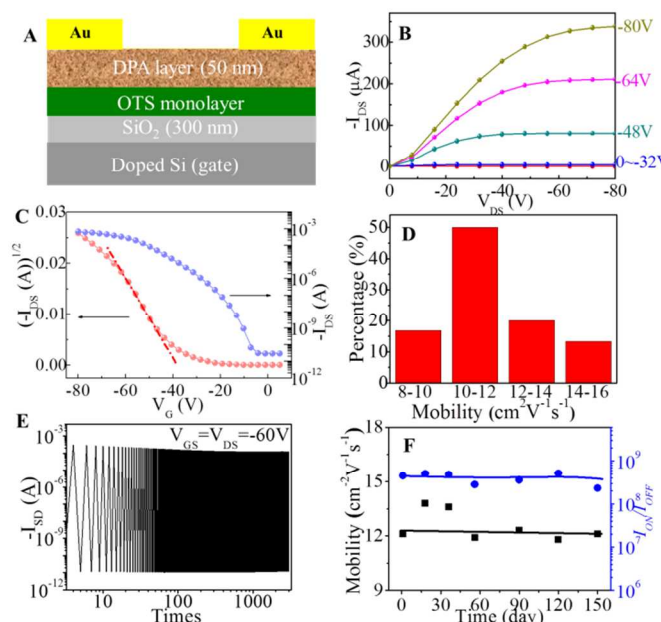


Fig. 4 (A) Device schematic of DPA thin film OFETs, (B) typical output and (C) transfer characteristics of the representative device. (D) The mobility distribution of DPA thin film OFETs, (E) Continuous electrical test, V_{DS} was -60 V, with V_{GS} switching from 0 V to -60 V. (F) Mobility and on/off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

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% device mobilities over $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the highest mobility up to $14.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved for DPA-based thin film devices. All these results indicate the great potential of DPA for applications in organic electronics.

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† Electronic Supplementary Information (ESI) available: [Summary of anthracene derivatives, synthesis procedures and characterization details, transfer and typical output curves of the devices, contact resistance, stability test and CIF of DPA.]. See DOI: 10.1039/c000000x/

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