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Short Alkyl Chain Engineering Modulation on Naphthalene Flanked Diketopyrrolopyrrole Towards High-Performance Single Crystal Transistors and Organic Thin Film Displays

*Qian Liu, Sudam Chavhan, Hantang Zhang, Huabin Sun, Aidan Brock, Sergei Manzhos, Yingqian Chen, Krishna Feron, Steven E. Bottle, John McMurtrie, Jwo-Huei Jou, Ho-Shin Chen, Mangey Ram Nagar, Wenping Hu, Yong-Young Noh, Yonggang Zhen, and Prashant Sonar**

Q. Liu, Dr. A. Brock, Prof. S. E. Bottle, Prof. J. McMurtrie, Prof. P. Sonar
School of Chemistry and Physics
Science and Engineering Faculty
Queensland University of Technology
Brisbane, QLD 4000, Australia
E-mail: sonar.prashant@qut.edu.au

Prof. S. E. Bottle, Prof. J. McMurtrie, Prof. P. Sonar
Centre for Materials Science
Queensland University of Technology
Brisbane, QLD 4000, Australia

Dr. S. Chavhan, Prof. J.-H. Jou, Prof. H.-S. Chen, Prof. M. R. Nagar
Department of Materials Science and Engineering
National Tsing-Hua University
101 Sec-2, Kuang-Fu Road, Hsinchu, Taiwan 30013, P. R. China

Dr. H. Zhang
College of Chemistry and Material Science
Shandong Agricultural University
61 Daizong Street, Tai'an, Shandong 271018, P. R. China

Dr. H. Zhang, Prof. Y. Zhen
Institute of Chemistry
Chinese Academy of Sciences
2 North First Street, Zhongguancun, Beijing 100190, P. R. China

Dr. H. Sun, Prof. Y.-Y. Noh
Department of Chemical Engineering

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Pohang University of Science and Technology
77 Cheongam-Ro, Nam-Gu, Pohang 37673, Republic of Korea

Prof. S. Manzhos
Centre Énergie Matériaux Télécommunications
Institut National de la Recherche Scientifique
1650 boulevard Lionel-Boulet, Varennes, QC J3X1S2, Canada

Dr. Y. Chen
Department of Mechanical Engineering
Faculty of Engineering
National University of Singapore
Block EA #07-08, 9 Engineering Drive 1, 117576, Singapore

Dr. K. Feron
CSIRO Energy Centre
10 Murray Dwyer Circuit, Mayfield West, NSW 2304, Australia

Dr. K. Feron
Centre for Organic Electronics
University of Newcastle
Callaghan, NSW 2308, Australia

Prof. W. Hu
Tianjin Key Laboratory of Molecular Optoelectronic Sciences
Department of Chemistry, School of Science
Tianjin University
Tianjin 300072, P. R. China

Studying multi-purpose applications of a specific material is a challenging topic in organic electronics community. In this work, through molecular engineering and smart device structure design strategy, high performances in transistors and thin film display devices have been simultaneously achieved by applying a simple new dye molecule, naphthalene flanked diketopyrrolopyrrole (DPPN), as the active layer material. Short alkyl chains (hexyl or octyl side groups for H-DPPN and O-DPPN, respectively) are adapted to improve the hole mobility in organic thin film transistors (OTFTs) and single crystal transistors (SCTs). Specifically, H-DPPN shows a similar hole mobility in either OFETTs or SCTs, while O-DPPN exhibits a

dramatically enhanced mobility, reaching $0.125 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in SCTs. Additionally, a smart organic light emitting diode (OLED) device is designed by using DPPN molecule as the dopant with a host matrix. The promising external quantum efficiencies (EQEs) of 4.0% and 2.3% are achieved for H-DPPN and O-DPPN fabricated OLEDs. Overall, in this work, it is reported that DPP-based small molecules can simultaneously function well in both transistors and thin film displays with high device performances through molecular and smart device engineering.

Introduction

Diketopyrrolopyrrole (DPP) derivatives have proven to be an important class of high-performance organic semiconductors that can be used as active materials in various types of electronic devices.^[1-7] As representative examples, the power conversion efficiency (PCE) of organic photovoltaic (OPV) devices have reached more than 12% by using some DPP derivatives as the active layer materials.^[8, 9] In DPP semiconductors for organic thin film transistors (OTFTs), impressive hole mobilities exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been demonstrated.^[1] Recently, DPP materials are being exploited in more applications like OLEDs, sensors, photodetectors, and memory devices.^[2, 10-17] Flanking groups substituted at the 3- and 6-position of the DPP core play significant roles in the optoelectronic properties of resultant materials.^[18] Flanking moieties such as thiophene, furan, selenophene, thiazol, thienothiophene, phenyl and pyridyl groups have been reported.^[19, 20] Thiophene flanked DPP (DPPT) is one of the most promising building blocks to construct high-performance materials for both OTFTs and OPVs. We previously reported the polymer, PDPP-TNT, consisting of DPPT and naphthalene.^[21, 22] The introduction of conjugation-extended naphthalene promoted strong intermolecular interactions and resulted in favourable π stacking between polymer backbones. Thus, a high hole mobility of $\sim 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed in OTFTs

and a promising PCE of 4.7% was obtained in OPVs as donor mixing with PC₇₁BM. Simultaneously achieving high performance in both OPVs and OTFTs is feasible, because the good charge carrier transport for a molecule is also a beneficial factor for improving both the short-circuit current (J_{SC}) and fill factor (FF) when it is used in active layer of OPV devices.^[23] In addition to DPPT, other DPP derivatives based semiconductors also successfully demonstrated high performance in electronic devices.^[24-26]

It is worth mentioning that phenyl flanked DPP (DPPh) has been proven to be a great choice of luminescent material for OLEDs and related applications.^[10] One reason making DPPh a promising molecule is that the dihedral angles between the phenyl groups and the DPP core (estimated to be around 40°) to some extent weaken the π stacking which minimizes the fluorescence quenching in solid state.^[27] Recently, we reported novel naphthalene flanked DPP (DPPN) with different alkyl chains as a new member in the DPP family.^[28] Compared with five- or six-membered ring DPPs, the fused aromatic ring of naphthalene resulted in a more extended π -conjugation leading to a larger intermolecular orbital overlap and thus facilitated the charge transport. Our primary attempt has demonstrated that *n*-decyl substituted DPPN (D-DPPN) monomer showed the highest hole mobility of 0.019 cm² V⁻¹ s⁻¹ in OTFTs as the active semiconductor directly, without any further functionalization. It is believed that there is still room to further improve the mobility by decreasing the length of side chains. Moreover, shorter chains substituted DPPN monomers are more suitable for growing single crystals, which prompted us to study their intrinsic charge carrier transport behaviour by fabricating single crystal transistors (SCTs). Naphthalene, a common acene type of benzene derivative that has been proven to form J-aggregation in solid state, can be used as a building block in materials that can retain efficient emission and thus lead to high photo-luminescence quantum yield.^[29] Our DPPNs were

observed to show strong luminescence under a laboratory lamp thus could be also promising in related devices like OLEDs.

In this work, *n*-hexyl and *n*-octyl alkylated DPPN compounds, H-DPPN and O-DPPN, were synthesized and their thermal, optical, and electronic properties were studied. The hole mobility of OTFTs was further enhanced by decreasing the length of side chains to *n*-octyl (O-DPPN) but dropped then for shorter *n*-hexyl H-DPPN. Moreover, single crystals for both materials were successfully grown and the fabricated SCTs indicated their high intrinsic hole transporting property. Due to the strong luminescence feature under laboratory UV light, we also fabricated OLED devices by using H-DPPN and O-DPPN as the dopant mixed with tris(4-carbazoyl-9-ylphenyl)amine (TCTA) host and achieved promising performance with EQEs of 4.0% and 2.3% respectively. It is well known that compact packing of molecules can induce strong and plentiful intermolecular interactions that generally facilitate charge transport in OTFTs. However, the interactions will also quench the solid-state luminescence, which makes it difficult to achieve both high mobility in OTFTs and high EQE in OLEDs. Nevertheless, in our current scenario, we have achieved high performance in both OTFTs and OLEDs via smart device and molecular engineering approaches. This is the first report of novel flanking group naphthalene attached DPP based small molecules, which can simultaneously function well in several different electronic devices, and the afforded high performance is encouraging for the future advancement of organic electronics.

Results and Discussion

Our previous report on DPPNs has demonstrated that a linear and short side alkyl chain enhances charge carrier mobility; in particular, the obtained hole mobility was higher.^[28] We perform a systematic study to investigate this type of material further, in particular, to find

the most suitable side chains for this series of DPPN compounds. In this work, we continuously shorten the side chains to synthesize *n*-hexyl and *n*-octyl substituted DPPN based small molecular materials namely H-DPPN and O-DPPN. Besides, both materials are expected to show versatility for use in various electronic devices considering the structural advantages; i) higher hole mobility is expected according to our previous report; ii) monomers with short side chains are more feasible to grow single crystals, being beneficial for SCTs fabrication; iii) as an analogue of DPPh, H-DPPN and O-DPPN solutions were observed to be highly fluorescent under the laboratory UV lamp (**Figure S1**), demonstrating their potential in OLEDs. As per our previous report, the synthetic route to H-DPPN and O-DPPN is shown in **Figure 1a**.^[30] The alkylation of NH-DPPN was performed in the presence of *n*-hexyl or *n*-octyl bromide, respectively, at 120°C in dimethylformamide (DMF) with anhydrous potassium carbonate (K₂CO₃) as the base. The purity and structures of H-DPPN and O-DPPN were characterized with ¹H, ¹³C NMR spectra, and high-resolution mass spectrometry (HRMS).

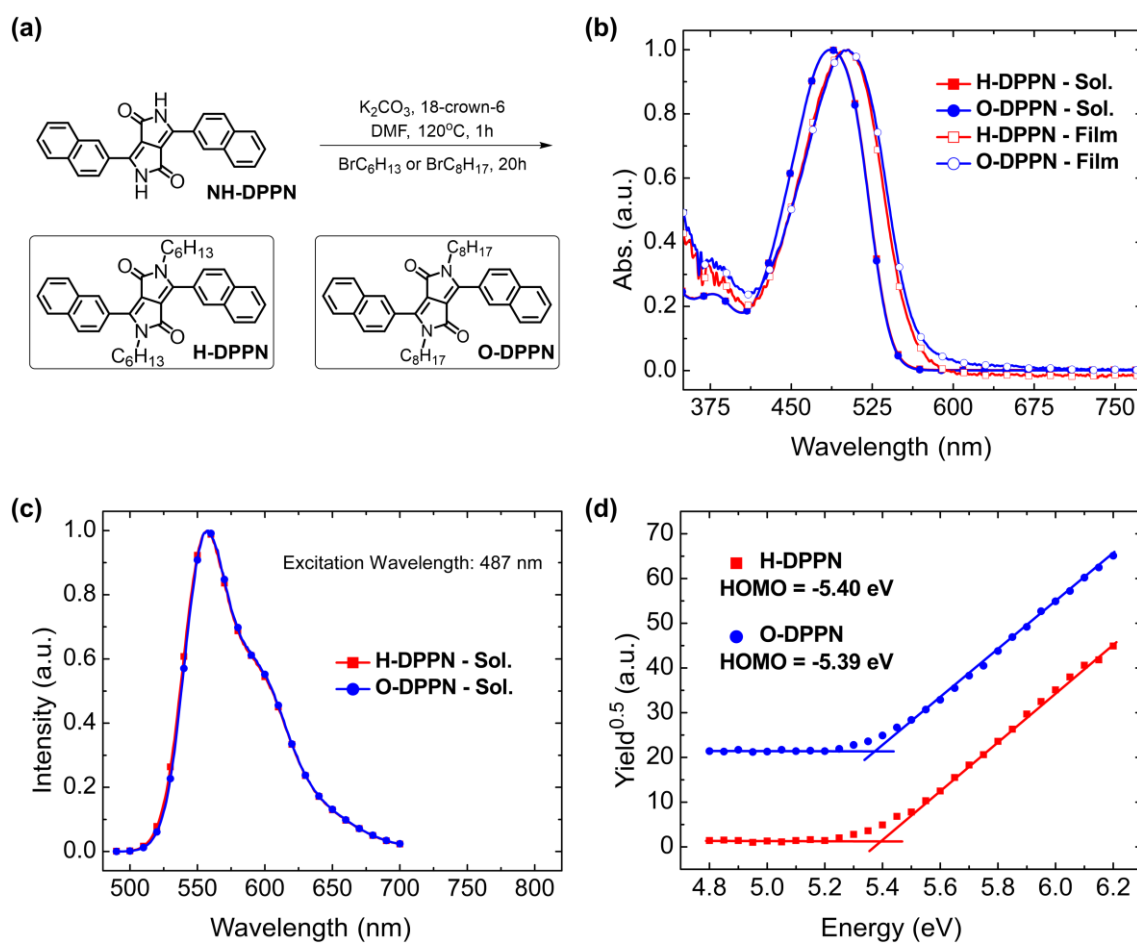


Figure 1. (a) The synthetic route to H-DPPN and O-DPPN. (b) UV-vis absorption spectra of H-DPPN and O-DPPN in both chloroform solutions and thin films. (c) Photoluminescence (PL) spectra of H-DPPN and O-DPPN in chloroform solutions. (d) Photoelectron spectroscopy in air (PESA) measurements of H-DPPN and O-DPPN films.

The thermogravimetric analysis (TGA, **Figure S2a**) indicated that both H-DPPN and O-DPPN appear to possess excellent thermal stability with the decomposition temperature (T_d , 5% weight loss) of 340°C and 348°C, respectively. These values are high enough to perform annealing or other thermal processing required for devices fabrication. The differential scanning calorimetry (DSC, **Figure S2b-d**) demonstrated that small variation in side chains on DPPN has dramatic influences on their crystallinity. H-DPPN undergoes a classic melting transition at 162 °C (91.22 J/g) and a crystalline transition at 102 °C (72.74 J/g). However, O-DPPN shows a different behaviour in that an endothermic peak at 119 °C followed by a cold crystallization at 125 °C (18.96 J/g) was observed before the material was completely melted

at 147 °C (79.80 J/g). This feature is an indication of the melting and secondary recrystallization of the amorphous area. The crystallinity peak is observed at about 84 °C during cooling process with the enthalpy of 29.59 J/g. The original DSC analysis labelled with enthalpy values are present in **Figure S3** in Supporting Information.

The UV-vis absorption spectra (**Figure 1b**) of both compounds in solutions are well overlapped due to the similar molecular backbone and the absence of interchain interactions. This observation has also been confirmed by density functional theory (DFT) modelling where both molecules exhibit the same visible peak position (503 nm, **Figure S4a**). The measured absorption maximum in solution is located around 487 nm, which is attributed to the intramolecular charge transfer (ICT) from naphthalene to the DPP core. This peak was red-shifted to 502 and 503 nm for H-DPPN and O-DPPN thin films, respectively, due to the molecular aggregation. In thin films, both materials only exhibit H-aggregation which follows a similar trend to that observed in our previous work, namely, that the shorter the side chains, the stronger the H-aggregation.^[28] After annealing the thin films at 100 °C and 130 °C for 10 mins (**Figure S5a-b**), the J-aggregation of H-DPPN has been enhanced, whereas for O-DPPN, not only the J-aggregation was enhanced after 100 °C annealing, an extra absorption peak and a red-shifted spectrum are observed. After annealing at 130 °C, the spectrum went back to the dominant H-aggregation, but the red shift remains the same. This phenomenon is consistent with the DSC analysis, since the secondary recrystallization of the amorphous area of O-DPPN promoted further aggregation and caused the change from J- to H-aggregation. The bandgaps of both compounds are calculated from the onset of thin film spectra (559 and 565 nm for H-DPPN and O-DPPN, respectively) to be 2.22 and 2.19 eV. In solutions, both materials show a strong PL emissive peak at 558 nm (**Figure 1c** and **Figure S5c**). In thin films, aggregation caused quenching was observed for both materials with a dominant emissive peak at 388 nm and 422 nm for H-DPPN and O-DPPN, respectively,

under excitation wavelength of 325 nm. Upon exciting at 502 or 503 nm, both compounds exhibited weak emission with a peak located at around 610 nm (**Figure S5d**).

The highest occupied molecular orbital (HOMO) energy levels are determined through photoelectron spectroscopy in air (PESA) measurements to be -5.40 and -5.39 eV respectively as shown in **Figure 1d**. In our previous publication,^[28] we observed that the side chains on DPPN can have a significant influence on the energy levels (despite of same conjugated backbone) due to the different solid state stacking, which is supported by the significant colour variation. However, for H-DPPN and O-DPPN, the HOMOs are only slightly changed. This can be further confirmed from the similar colour appearance of both compounds and the similarity of the absorption spectra in solutions and thin films. The lowest unoccupied molecular orbital (LUMO) energy levels are estimated from the difference between optical bandgaps and HOMOs to be -3.18 and -3.20 eV for H-DPPN and O-DPPN, respectively.

DFT calculations were employed to investigate the electronic structure and molecular geometry of H-DPPN and O-DPPN. As shown in **Figure S6**, both molecules have same HOMO and LUMO distributions, which are found to be localized at the completely molecular backbone that can be beneficial to facilitate the intramolecular charge carrier transport. The computed molecular HOMO levels are -5.35 eV for both molecules, which is in an excellent agreement with the experimental results. The calculated bandgaps (2.62 eV) and LUMO (-2.73 eV) values are higher than the experimental values which could be attributed to the fact that the measured onset of optical absorption is affected by vibrational broadening while the computed levels are at the equilibrium geometry, as well as errors due to approximations used. The optimized backbone conformation indicates the same dihedral angles of 37° and 31° for both molecules (**Figure S6**). Since both H-DPPN and O-DPPN solutions have shown strong fluorescence under a UV lamp, the relatively large dihedral

angles can, to some extent, restrain the emission quenching effect in solid state, demonstrating their promise for application in OLEDs.

Top gate bottom contact (TG/BC) OTFT devices were fabricated to evaluate the electrical properties of newly synthesized H-DPPN and O-DPPN semiconductors. The representative device schematic and transfer curves after annealing at 100 °C or 120 °C are shown in **Figure S7** and **Figure 2a-b**. The hole mobility values (μ_h), threshold voltage (V_{th}), subthreshold swing (SS) and on/off ratio (I_{on}/I_{off}) extracted from transfer curves at the saturation regime are summarized in **Table 1**.

Table 1. Summary of TG/BC structured OTFT device performance.

Material	T_{anneal} (°C)	$\mu_h^{ave.} \times 10^{-2}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_h^{max.} \times 10^{-2}$ (cm ² V ⁻¹ s ⁻¹)	SS (V/Dec)	V_{th} (V)	I_{on}/I_{off} ($\times 10^6$)
H-DPPN	100	0.66±0.27	1.02	0.95±0.20	20.1±4.1	0.43±0.49
	120	0.23±0.19	0.61	0.77±0.17	23.5±1.8	0.54±0.63
O-DPPN	100	4.29±1.38	5.03	-4.70±1.0	-8.9±2.6	0.63±0.13
	120	0.04±0.06	0.16	5.62±5.60	--	0.13±0.27

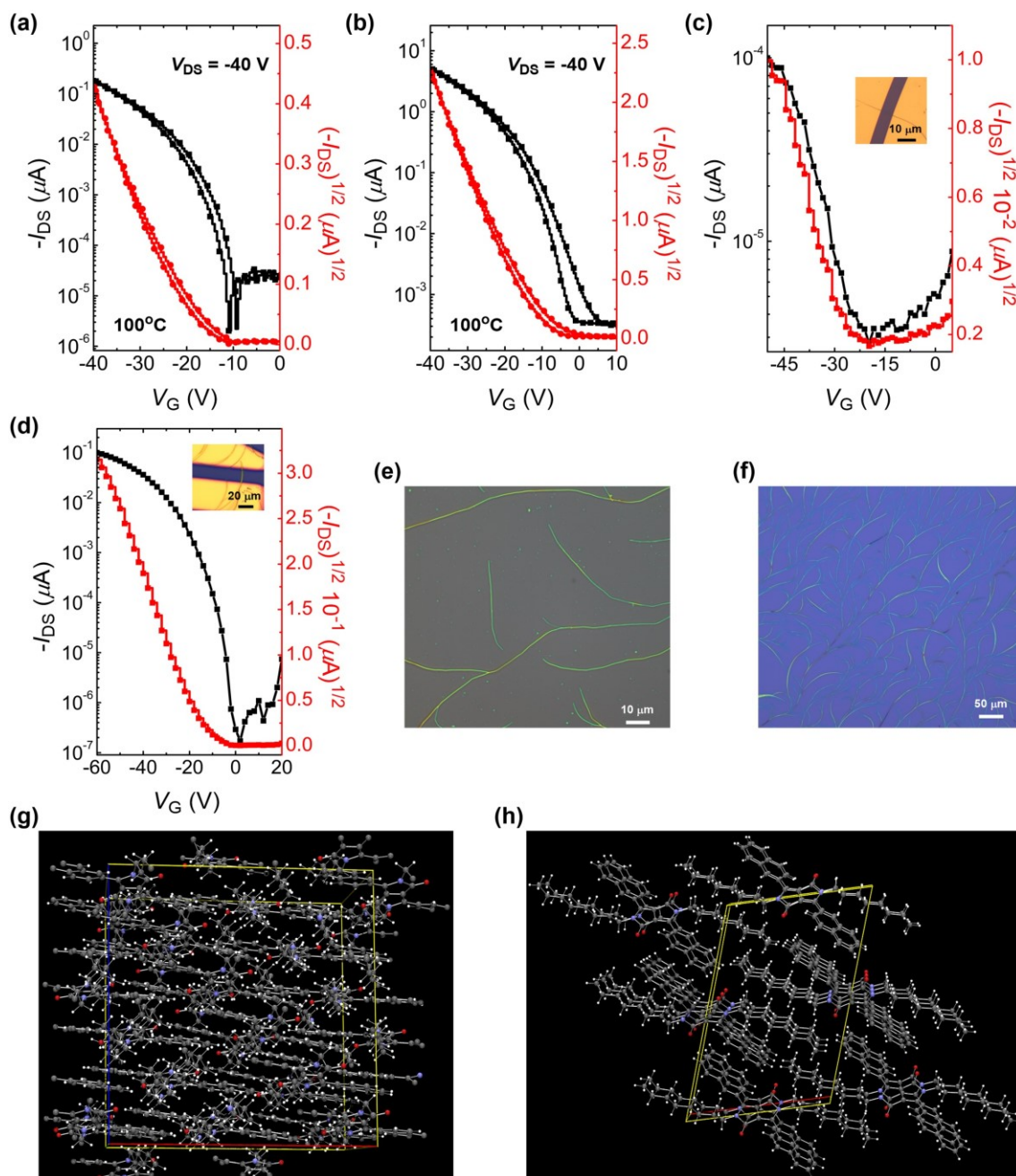


Figure 2. Transfer curves of OTFTs based on (a) H-DPPN and (b) O-DPPN thin films. Transfer curves of SCTs based on (c) H-DPPN and (d) O-DPPN crystals with the corresponding optical device structure images in the insets. Optical images of (e) H-DPPN and (f) O-DPPN single crystals. X-ray determined unit cells of (g) H-DPPN and (h) O-DPPN crystals.

It was found that the devices annealed at 100 °C exhibited better performance with a highest hole mobility of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for H-DPPN and $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for O-DPPN. This performance is better than some reported alkylated thiophene DPP monomers in solution

processed thin film transistors as compared in **Table S1**.^[31] When the thin films were annealed at 120 °C, the mobility decreased to 0.006 and 0.001 cm² V⁻¹ s⁻¹, respectively. By comparing with our reported compounds, O-DPPN was observed to show the best performance and H-DPPN shows an even worse mobility than D-DPPN (0.019 cm² V⁻¹ s⁻¹).^[28] From the polarized microscopic images shown in **Figure S8**, it is clear that the films of both materials easily form large crystalline domains, which is beneficial for charge carrier transport. However, the H-DPPN film has many defects while the O-DPPN film is smoother that contributed to the higher hole mobility. Upon annealing at 120 °C, the defects become more obvious in H-DPPN film which caused a decreased hole mobility, while the crystal domains did not change much, that is consistent with the high melting point >160 °C observed from the DSC curve. From the AFM (atomic force microscope) images of H-DPPN and O-DPPN films annealed at 120 °C, similar phenomenon is observed as shown in **Figure S9**. For the O-DPPN film, the crystal domains were broken, and a cullet-shaped film was observed. After 120 °C annealing, the amorphous area experienced melting process, which, we assume, caused the broken of crystalline regions of O-DPPN films. This phenomenon can easily cause disconnection along the conducting channel and thus result in a large decrease in mobility. Microstructure, defects, and domain walls are thus critical determinants of mobility in these materials. Computed estimates of charge transfer rates (see Supporting Information) also point the critical role of domains and microstructure: while the computed single crystal charge hopping rate is higher for H-DPPN than for O-DPPN, the packing of H-DPPN favours one-dimensional hopping pathways, while the packing of O-DPPN favours two-dimensional pathways (**Figure S10**). The low-dimensional hopping paths imply strong dependence of the measured bulk rate on crystal domain size, whereby domain boundaries are expected to be a significant bottleneck to transport in particular because ideal crystal transport is low-dimensional. The grain boundaries are expected to be a more significant bottleneck in H-

DPPN due to one-dimensional transport in the ideal crystal, explaining the better measured mobility with O-DPPN.

To investigate the intrinsic charge transport behaviour, transistor devices based on H-DPPN or O-DPPN single crystals were fabricated. By drop-casting a H-DPPN (0.1 mg/mL) solution in chlorobenzene on bare Si/SiO₂ wafer and after solvent evaporation, well-defined ribbon-shaped crystals were grown in three days (**Figure 2e**). Since ill-defined clusters of O-DPPN were grown in chlorobenzene, we screened the solvent species and used a mixed solvent (chloroform:ethyl acetate = 1:2) to grow ribbon-shaped crystals (**Figure 2f**) by drop-casting method (0.05 mg/mL). The optical images of H-DPPN and O-DPPN single crystals are also present in **Figure S11** with a same scale plate for better comparison. The single crystals were annealed in vacuum at 80°C to remove residual solvent before devices fabrication. Drain and source electrodes (40 nm) were deposited on H-DPPN and O-DPPN crystals by thermal evaporation of a gold film with the “Au stripe mask”.^[32] The transfer curves and optical images (insets) of fabricated devices are shown in **Figure 2c-d**. The electrical characteristics of all devices were measured under ambient conditions. From the saturation regime of the transfer characteristics, the mobility is calculated by linear fitting of the dependence of $(I_{DS})^{1/2}$ vs. V_G . The mobility of the best devices for O-DPPN crystals is up to 0.125 cm² V⁻¹ s⁻¹, over ten times higher than that of H-DPPN crystals. The I_{on}/I_{off} ratio of the best device for O-DPPN crystals was measured to be 10⁶, five orders of magnitude higher than that of H-DPPN crystals. These results further demonstrated that O-DPPN crystals exhibit much better charge transport behaviours compared with H-DPPN.

To better understand the difference between single crystals for H-DPPN and O-DPPN, we grew H-DPPN and O-DPPN single crystals as shown in **Figure S12**. Their structures and unit cells were determined through X-ray diffraction as shown in **Figure S13** and **Figure 2g-h**. H-DPPN and O-DPPN crystallise in the space groups $P2_1/c$ and $P2_1/n$,

respectively. In the crystal structure of H-DPPN, the molecules stack in one-dimensional chain, with the principal interaction being an offset face-to-face π - π interaction between adjacent naphthalene units (3.278 Å). In the O-DPPN crystal structure, chains of stacked O-DPPN molecules (vertical offset 2.760 Å) interact with adjacent chains via weak naphthalene CH- π interactions (3.808 Å) between neighbouring naphthalene units. CH- π interactions (2.695 Å) are also observed between naphthalene rings and adjacent alkyl chains. Obviously, the favourable backbone stacking in **Figure 2h** for O-DPPN crystals explained its higher mobility in SCTs. The comparison of single crystal data of H-DPPN and O-DPPN with thiophene, selenophene, and phenyl DPPs (with hexyl side chains) indicate that DPPN compounds exhibit a much closer π stacking than other DPP derivatives as compared in **Table S1**.^[33] That is a much favourable feature for intermolecular charge carrier transport. We also performed large-scale calculations on crystals and clusters of H-DPPN and O-DPPN to estimate the effect of solid-state packing on electronic properties. First, density functional tight binding (DFTB) and time-dependent DFTB (TD-DFTB) were benchmarked to DFT and TD-DFT in single-molecule calculations. The results are given in **Table S2** and **Figure S4**, showing that while (TD)-DFTB results in somewhat different values of the HOMO, LUMO energies, the gap, and the visible absorption peak (as is expected given that the DFTB parameterization is based on GGA calculations), it can be used for qualitative assessment and is reliable for comparison between the two molecules and between different molecular environments. We therefore compared properties computed in periodic crystals and clusters to those of the molecules.

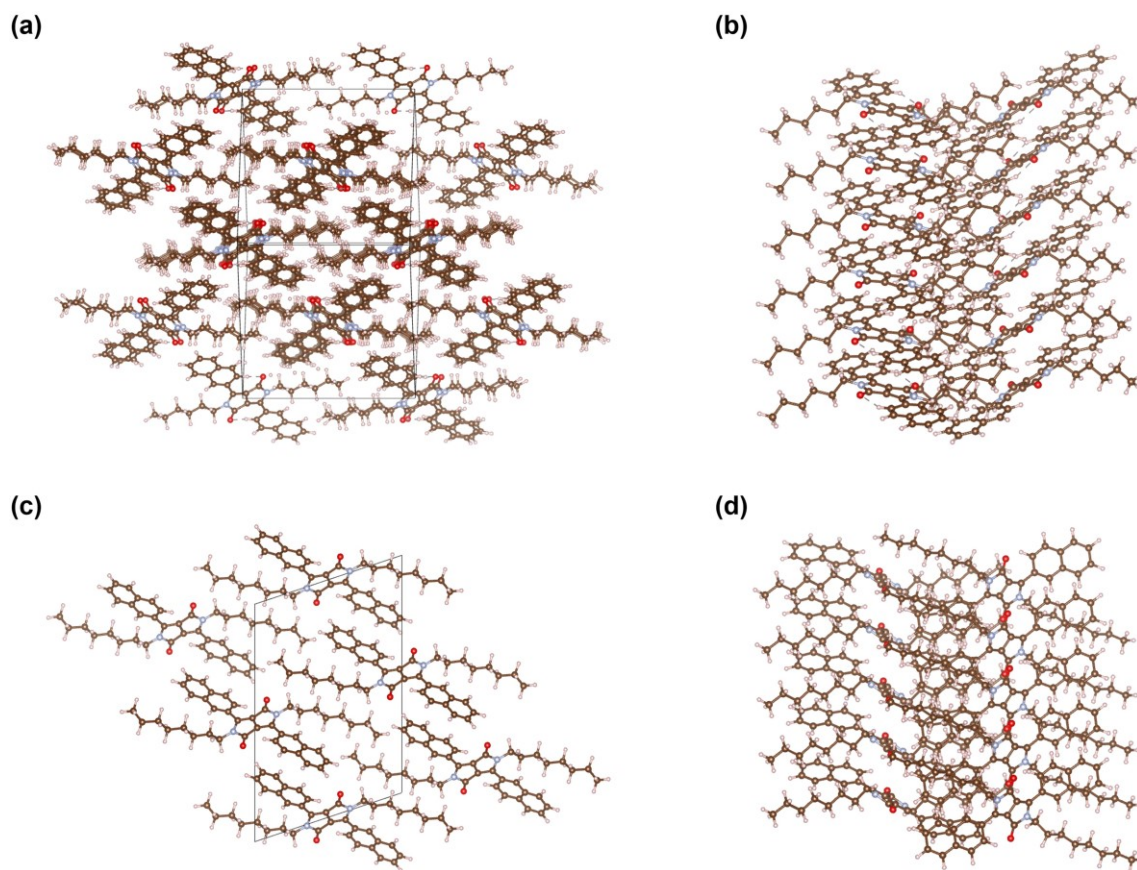


Figure 3. DFTB-computed unit cells (delimited by the box) of crystalline (a) H-DPPN and (c) O-DPPN. Molecular clusters of (b) H-DPPN and (d) O-DPPN.

The unit cells of H-DPPN and O-DPPN crystals are shown in **Figure 3a** and **3c**. Experimental structures were used as a starting point of optimizations. Clusters were cut preserving the optimized geometry of the periodic calculation (**Figure 3b** and **3d**). The DFTB-optimized cell parameters are given in **Table S3**. As TD-DFTB calculations had to be done with the Γ point, a supercell with 10 molecules was then optimized for O-DPPN to make Γ point calculations sufficiently accurate (for H-DPPN, the unit cell is big enough for a Γ point calculation). The calculated HOMO, LUMO values and the gap for crystals and clusters are also shown in **Table S2**. For crystals, they show stabilization of the HOMO about 0.3 eV for H-DPPN and approximately 0.4 eV for O-DPPN. The band gap becomes about 0.3 eV lower in H-DPPN vs. O-DPPN, while the HOMO-LUMO gap is practically the same at the single-molecule level. While the absolute values of HOMO and LUMO in periodic

systems are generally not directly comparable to molecular levels, changes in the gap are comparable and indicate stronger effects of aggregation on the gap with H-DPPN. The cluster calculations result in higher HOMO values vs. single molecules, by 0.2-0.3 eV. They confirm the decrease in the gap in H-DPPN vs. O-DPPN due to aggregate state effects, by 0.36 eV, similar to the results of the periodic calculations. Both periodic and cluster calculations indicate a slightly (approximately 0.1 eV) lower HOMO of O-DPPN in solid state vs. H-DPPN even though molecular HOMO are nearly identical. The calculations also clearly confirmed the π stacking between naphthalene for O-DPPN, while H-DPPN tends to stack parallel.

A family of DPP molecules is gaining significant importance in OLED technology because of its high fluorescent quantum yield, thermal and photostability.^[10, 27] In the present study, H-DPPN and O-DPPN were used to fabricate yellowish orange OLED by using cost-effective solution processing. Specifically, the device structure is shown in **Figure S14** where PEDOT:PSS is employed as a hole injecting and transporting layer (HIL/HTL), the emissive layer (EML) is composed of TCTA host doped with 2wt% H-DPPN or O-DPPN orange emitter, TPBi is used as an electron transporting layer (ETL), and LiF/Al acts as a cathode. The energy level diagram of all used materials is shown in **Figure 4a**. The J - V curve as shown in **Figure 4b** exhibits well-defined diode characteristics, revealing that the fabricated OLED behaves as a rectifying device. The forward bias current for both devices rises with the increase of applied bias voltage, however, the reverse bias current remained significantly low (not shown in J - V curve), suggesting both OLEDs act as rectifying diodes. The rapid increase in forward-bias current is observed for O-DPPN based OLED, implying a small sheet resistance of the device, whereas H-DPPN OLED has a high sheet resistance.

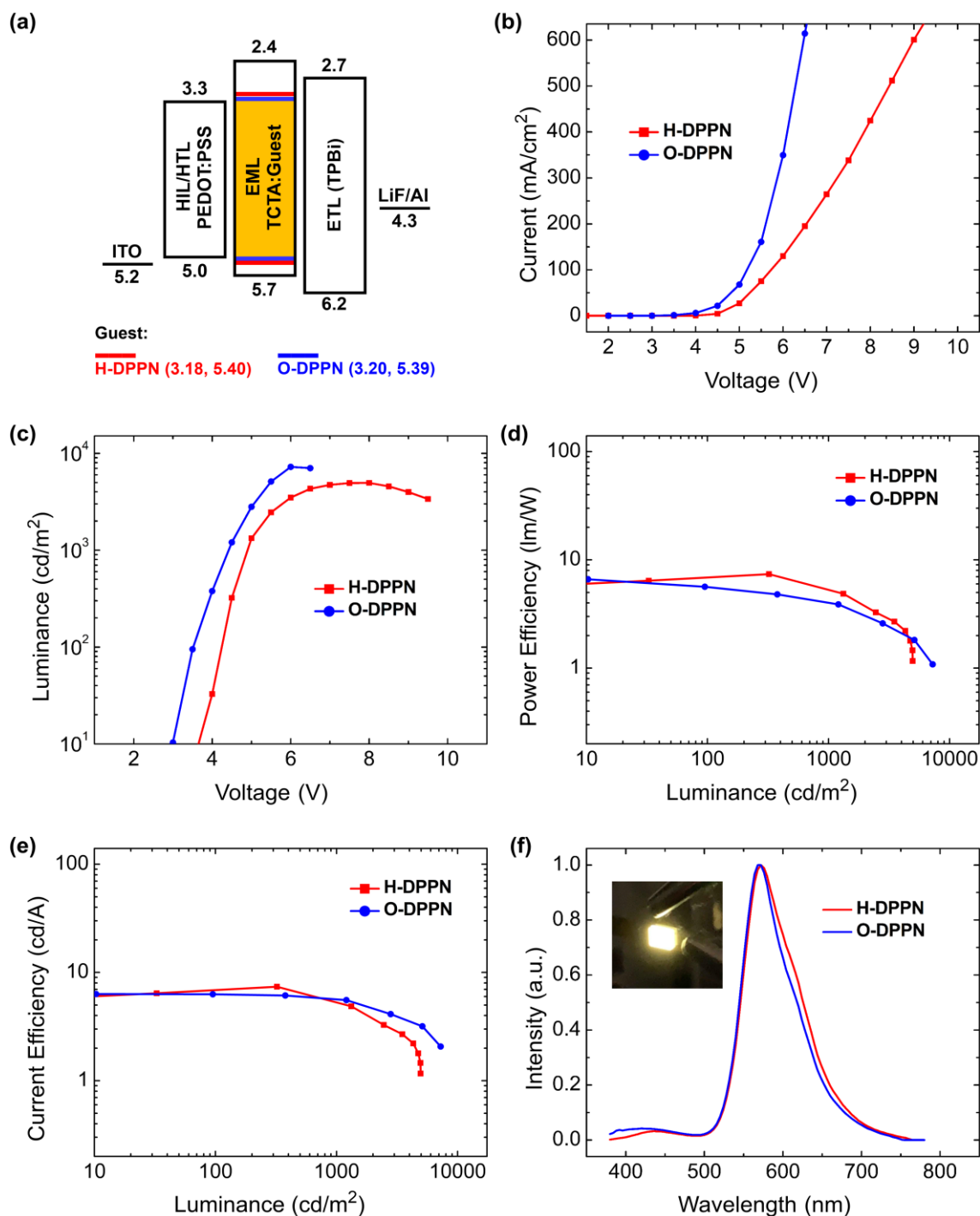


Figure 4. (a) Energy level diagram of studied OLED device. (b) Current-voltage ($J-V$), (c) luminance, (d) power efficiency, and (e) current efficiency of studied OLED devices based on TCTA host doped with 2wt% H-DPPN or O-DPPN molecules. (f) Electroluminescence (EL) spectra of the fabricated OLED devices at $100 \text{ cd}/\text{m}^2$. Inset picture is the photograph of the working O-DPPN based OLED device.

The difference in high forward bias current is attributed to differences in charge carrier mobility of the corresponding molecules.^[34] From the OTFTs and SCTs study, it is confirmed

that O-DPPN possesses a higher mobility compared to H-DPPN. The influence of hole mobility is vividly observed in OLED device turn-on voltage as shown in **Figure 4c** which is the plot of luminescence vs. applied voltage. The O-DPPN based OLED requires a 3.0 V to emit 10 cd/m^2 luminescence, whereas to get the same luminescence, 3.8 V is needed for H-DPPN emitter OLED (0.8 V more). However, the power efficiency obtained for H-DPPN OLED is 8.8 lm/W which is 27% higher than that of O-DPPN (6.5 lm/W) based device at 100 cd/m^2 (**Figure 4d**) and a similar trend is noticed for current efficiency (**Figure 4e**). **Table 2** details electroluminescent properties of the fabricated OLEDs. The maximum power efficiency, current efficiency, and EQE were found to be 8.3 lm/W , 11.8 cd/A , and 4.0%, respectively, at 100 nits, for the H-DPPN based OLED. The overall performance of the H-DPPN OLED is superior to the O-DPPN counterpart, except the maximum luminance. To emphasize the advantage of DPPN compound in OLEDs, we compared the EQE values with other DPP derivatives (**Table S1**). Also as the dopant for a host material, the device fabricated with TAPC (4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine]) host doped with 10wt% furan flanked DPP exhibited a much lower EQE value of 0.7%.^[27] Although this value is further enhanced to 12.1% by introducing a second dopant (9-[2,8]-9-carbazole-[dibenzothiophene-S,S-dioxide]-carbazole, initialled as 2d), it is not competitive since the 2d doped TAPC shows a EQE value of 15%.^[35]

Table 2. OLED device parameters with TCTA host doped with 2wt% DPPNs.

Dopant	OV/V	PE/lm/W	CE/cd/A	EQE/%	CIE/(x,y)	Max. L
@100/1000 cd/m ²						/cd/m ²
H-DPPN	4.5/5.2	8.3/4.7	11.8/7.8	4.0/2.7	(0.50,0.48)/(0.49,0.47)	5371
O-DPPN	3.5/4.5	6.5/4.5	7.3/6.5	2.3/2.0	(0.49,0.48)/(0.48,0.48)	6065

OV: Operating Voltage; PE: Power Efficiency; CE: Current Efficiency; EQE: External Quantum Efficiency; CIE 1931 Color Coordinates; Max. L: Maximum Luminance.

Figure 4f shows the normalized electroluminescent (EL)spectra of two OLED devices. Each one was made with 2wt% H-DPPN and O-DPPN molecules doped in the TCTA host, obtained at 100 nits. The main emission peak is obtained at 570 nm for both devices, which corresponds to the absorbance band of H-DPPN and O-DPPN molecules, confirming the direct excitation of DPP cores. The CIE (x,y) coordinate of EL spectra (0.50, 0.48) evidences that the fabricated OLED devices generate greenish-yellow light. However, emission noticed at 400-450 nm originates from the TCTA host molecules. The EL spectrum of O-DPPN OLED is narrower than that of the H-DPPN counterpart, suggesting the recombination zone of the injected charge carriers is narrower as compared to H-DPPN based OLED. To explain this behaviour, it is important to consider the charge carrier mobility of O-DPPN and H-DPPN. It is a well-known fact that the OLED device with a TCTA host with TPBi ETL is a hole charge carrier-dominated device and therefore the charge carrier recombination zone is mainly available at the interface of the emissive layer (EML) and the electron transporting layer (ETL).^[36] O-DPPN possesses a higher hole mobility allowing for more efficient hole injection and transport through the EML layer up to the ETL interface, resulting in a narrower

recombination zone. On the other hand, the H-DPPN molecule has a slightly lower hole-mobility that assists to widen the charge carrier recombination zone up to the interface of the HTL and EML.^[34, 37] As a result of this, we have obtained higher power and current efficacy and EQE for H-DPPN based OLED compared to the O-DPPN counterpart.

Conclusions

To summarize, we designed and synthesized two naphthalene flanked DPP dye based versatile materials, namely, H-DPPN and O-DPPN. It was found that, through molecular engineering and smart device structure design, high performance can be achieved in both transistors and thin film displays, which is encouraging for researchers working on organic electronics. DPPNs with different side chains were first reported by our group, and in this work, we demonstrated that the octyl side chain is most suitable for this series of molecules due to its highest hole mobility of $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OTFTs. The better performance was ascribed to the uniform morphology with a highly crystalline nature. Molecule with short side chains allows growing single crystals for SCTs. O-DPPN shows a largely enhanced performance with mobility of up to $0.125 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is 10 times higher than that of H-DPPN. This is attributed to the stacking mode suggested by X-ray determined unit cells and DFTB computations. H-DPPN crystals appear to stack in one dimensional chain with a face to face π - π interaction that lacks favourable backbone stacking for charge carrier transport. However, obvious backbone stacking from X-ray diffraction for O-DPPN crystals and naphthalene-naphthalene stacking from DFTB calculations are observed. This is a favourable feature for better charge carrier transport, explaining its higher hole mobility in SCTs. Additionally, as the analogue of phenyl DPP, H-DPPN and O-DPPN also exhibit potential in OLEDs. To avoid the emission quenching effect of pristine DPPN film in the active layer, we smartly modified the OLED device structure by using the DPPN molecule as a dopant for

TCTA. H-DPPN based OLED shows better performances with maximum power efficiency, current efficiency, and EQE of 8.3 lm/W, 11.8 cd/A, and 4.0%, respectively, at 100 nits. Overall, in this work, we have clearly disclosed the versatility of two DPPN molecules in various types of electronic devices. Especially, simultaneously achieving high performance in both transistors and thin film displays through molecular engineering and smart device structure design is a new scenario in organic electronics community which is expected to advance the future development of electronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Author Contributions

Qian Liu is responsible for the materials synthesis, properties characterization as well as managing the final manuscript preparation. Sudam Chavhan, Jwo-Huei Jou, Ho-Shin Chen, and Mangey Ram Nagar are responsible for the OLED device fabrication and characterization. Hantang Zhang, Yonggang Zhen and Wenping Hu are responsible for the single crystal transistors fabrication and characterization. Huabin Sun and Yong-Young Noh are responsible for the thin film transistors fabrication and characterization. Aidan Brock and John McMurtrie are responsible for the X-ray determined single crystal data. Sergei Manzhos and Yingqian Chen are responsible for the DFT and DFTB calculations. Krishna Feron is responsible for the PESA measurement. Steven E. Bottle reviewed and revised the manuscript. Prashant Sonar conceived and directed the project. All authors have reviewed or commented the final version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

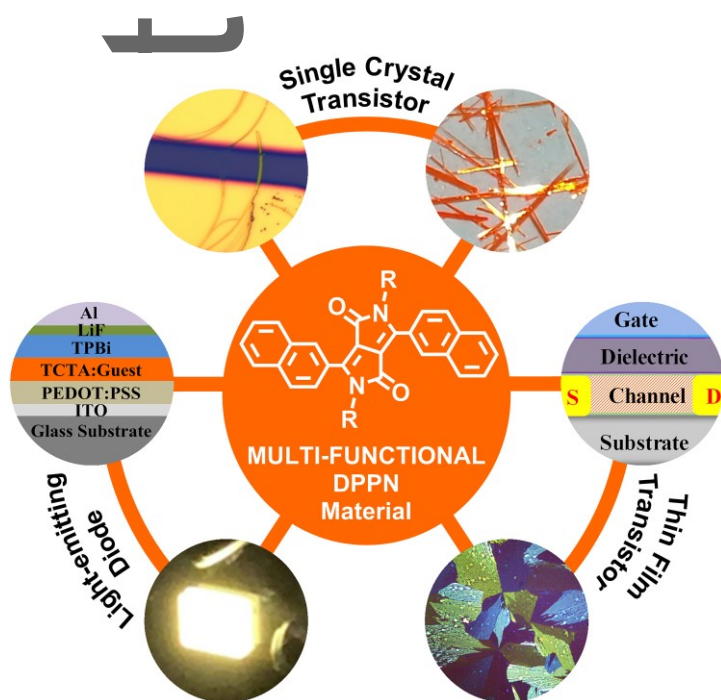
molecular engineering, smart device structure design, versatility, naphthalene flanked diketopyrrolopyrrole, transistors, thin film displays

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Studying the multi-functional applications of a specific material is a challenging topic in organic electronics community. In this work, through molecular engineering (short alkyl chain substituted naphthalene flanked diketopyrrolopyrrole) and smart device structure design, high device performance in transistors and thin film displays are simultaneously achieved.