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Stretching Toward the Near Infrared in Small Molecule Photovoltaics

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Final Report

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14. ABSTRACT The PI was successful in the proposed research objectives for this three year grant. The PI was able to generate a family of molecules that, when used in organic photovoltaic (OPV) cells, provide sensitivity into the near infrared spectrum. The PI accomplished the basic characterizations of all desired targets as well as the basic characterizations of D-Q-A donor TBTh-2CN and Q-Q-A donor DBTh-2CN. The PI briefed at AFOSR's Organic Chemistry Program Review. The PI has 2 peer reviewed journal articles as a direct result of the grant.						
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Technical Report

Specific Aims:

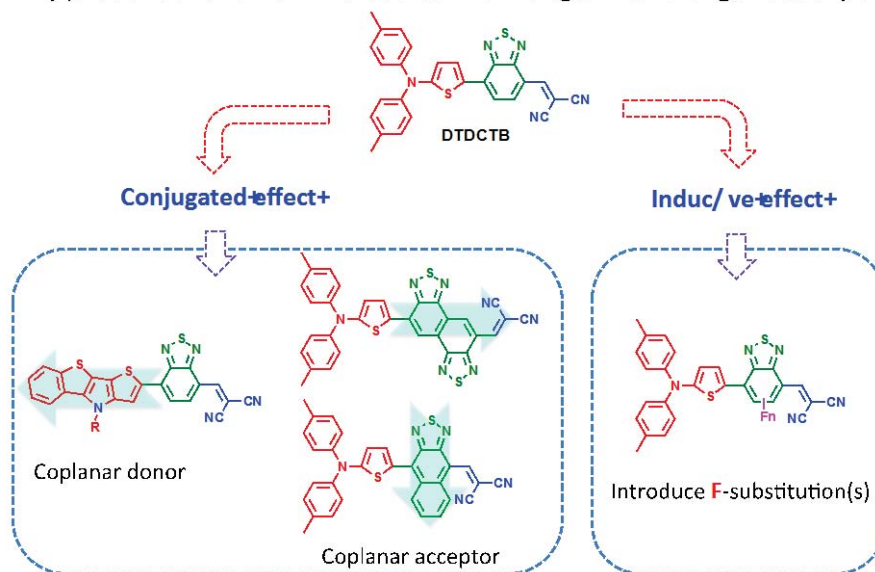
The objective of this collaborative program is to generate a family of molecules that, when used in organic photovoltaic (OPV) cells, provide sensitivity into the near infrared ($<1.1\ \mu\text{m}$ wavelength). A further objective is to develop a fundamental understanding the role that high dipole moments have on crystal morphology, charge mobility, and exciton transport. The collaboration combines the unique capabilities of the two groups: Synthesis and characterization of a class of dipolar small molecules that have demonstrated long wavelength response at NTU, and deposition and incorporation of these molecules in high performance OPV architectures at UM. This program builds on an on-going and successful collaboration between these groups, providing resources for personnel exchange and materials needed to make breakthroughs that will enable multijunction OPV cell power conversion efficiencies (PCEs) to exceed 15%.

Approaches:

The UM team had successfully achieved a triple junction cell with $\text{PCE} = 11.1\%$ [1] and a single cell with $\text{PCE} \sim 10\%$ [2] employing dipolar small molecules configured as donor-acceptor-acceptor' (D-A-A') developed by NTU team (Scheme 1). According to the optical model of a quad-junction cell with projected $\text{PCE} = 16\%$ proposed by the UM team, the NTU team needs to develop donor molecules that can absorb more deeply in the NIR (to wavelengths $\geq 900\ \text{nm}$). The NTU team will continue to make efforts on the design and synthesis of dipolar donors with a donor-acceptor-acceptor (D-A-A') structural configurations. To extend the spectral response of D-A-A' donors covering the near IR region together with suitable LUMO energy level for giving efficient electron-transfer to C_{70} , three levels of molecular design strategies based on DTDCTB will be explored (Scheme 1). DTDCTB is a good starting point for further structural modifications since its LUMO level has room for fine tuning. The electron-donating diarylthienyl group results in a strong intramolecular charge transfer character as it attaches to 2,1,3-benzothiadiazoole (BTD) in DTDCTB. The molecular design strategy level 1 will impose “**conjugation effect**” on the D part of D-A-A' with coplanar electron-donating systems to increase the molecular π -conjugation thus higher HOMO for reducing the optical gap. Nevertheless, the most effective strategy to impart a small optical gap is to increase the molecular π -conjugation, in this regard, the molecular design strategy will adopt expanded ring systems with BTD character as the new central A units in new D-A-A' donors. The central BTD subunit plays a crucial role for governing its physical properties, therefore, the molecular design strategy level 2 will utilize an “**inductive effect**” imposing onto the BTD ring to lower the LUMO level for reducing the optical gap.



Approaches for small molecules with longer wavelength absorption



Scheme 1. Molecular design strategies for reducing the optical gap of new D-A-A' donors.

Results and Discussions

a. Molecular design strategy based on “Conjugated Effect” using coplanar donor subunit:

Based on the molecular design strategy shown in Scheme 1, in order to improve the charge carrier transport in the solid state through the strong intermolecular π -interactions owing to the fully coplanar structural features, we introduced rigid and coplanar heterotetracene as an electron-donating subunit (D) to couple with benzothiadiazole-dicyanovinylene (A-A'), giving molecule **antiBTDC** (structure shown in Fig. 1), which can perform nicely to serve as electron donor to fabricate OPV device in the presence of C_{70} as electron acceptor, giving a power conversion efficiency (PCE) up to 7.5%, which is superior to its isomeric counterpart **synBTDC** showing a PCE of 6.4% (Fig. 1). This work results an excellent paper entitled as “Regioisomeric Effects of Donor–Acceptor–Acceptor2 Small-Molecule Donors on the Open Circuit Voltage of Organic Photovoltaics” have been successfully in *Advanced Materials*, 2016, 28, 8248.

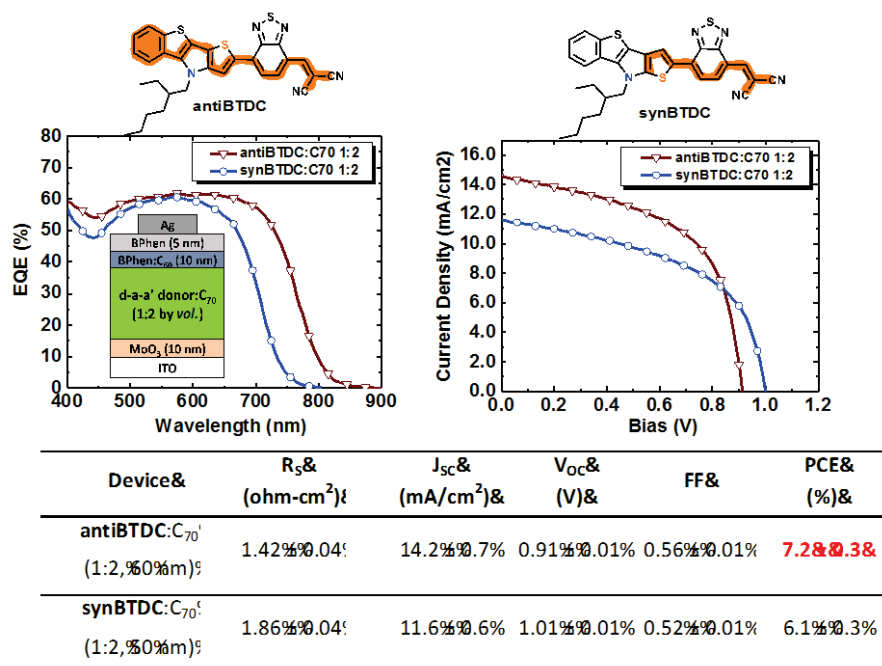


Figure 1. Molecular structures of **antiBTDC** and **synBTDC**, and their device performance.

The UM team have made efforts on physical characterizations on these new donors. The results indicated that inefficient exciton dissociation at the donor-acceptor interface in blends and possible back transfer; which are account for the relatively resulting low *FFs*. These observations imply that short the alkyl chains on the rigid coplanar donor subunit, or raising the LUMO energy for more complete exciton dissociation may lead to further improvements in *FF*, and ultimately the device performance.

To verify our assumption that the *FFs* might be improved with the short alkyl substitutions on the coplanar unit, Dr. Chin-Lung Chung accomplished two new analogous donors, namely, **iBuBTDC** and **nBuBTDC** (Fig. 2). The photophysical and electrochemical characters of these new analogues are very similar to its parent **antiBTDC**, which is very reasonable since the side chains should not have big impact on the electronic structures of the main chromophore. However, the obtained crystal densities based on the X-ray structures indicate the stronger intermolecular interactions between these new analogues (Fig. 3).

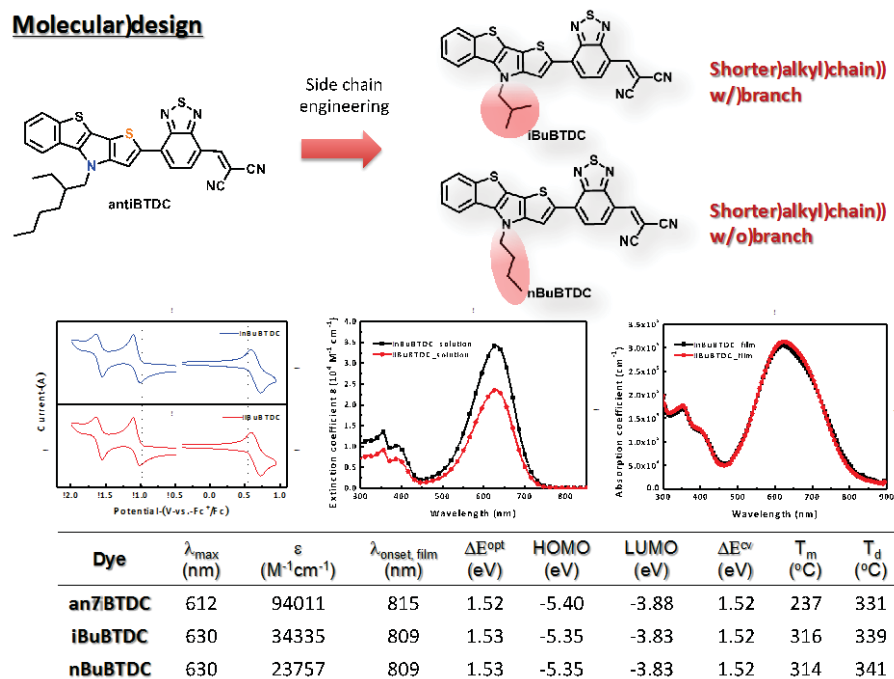


Figure 2. Structures of **iBuBTDC** and **nBuBTDC** and their physical characteristics.

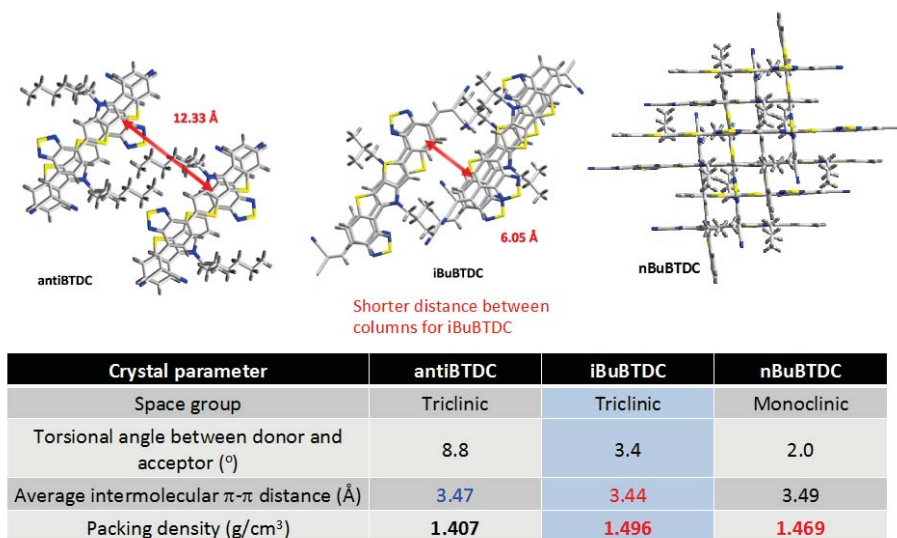
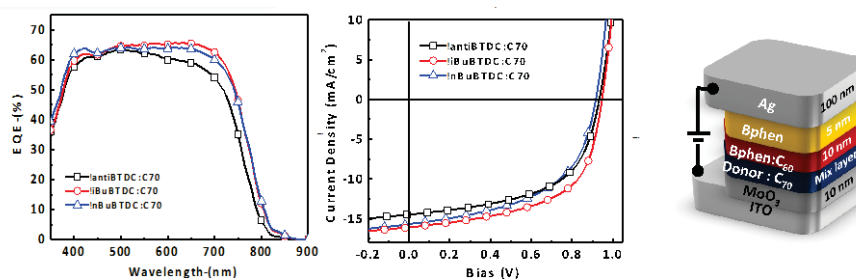


Figure 3. The X-ray structures of **antiBTDC**, **iBuBTDC** and **iBuBTDC** and selected data.

The UM team had accomplished the fabrication of OPV devices employing these modified donor materials. The obtained OPV results have verified our assumption that the active chromophore with short alkyl side groups can lead to stronger intermolecular interactions, benefiting to the exciton separation and charge transport, and result in higher OPV performance. The OPV device based on **iBuBTDC** has achieved a PCE of 9.8%; which is far beyond the parent donor **antiBTDC** (Fig. 4).



Device (ratio, thickness)	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	PCE [%]
iBuBTDC:C ₇₀ (1:3, 70 nm)	16.5 ± 0.8	0.94 ± 0.01	0.60 ± 0.01	9.3 ± 0.5
nBuBTDC:C ₇₀ (1:3, 70 nm)	15.7 ± 0.7	0.92 ± 0.01	0.52 ± 0.01	7.5 ± 0.4
antiBTDC:C ₇₀ (1:3, 70 nm)	14.4 ± 0.7	0.93 ± 0.01	0.56 ± 0.01	7.5 ± 0.4

Figure 4. The device structure and characteristics of OPVs based on the donors **iBuBTDC**, **nBuBTDC**, and **antiBTDC**.

The UM team also conducted the X-ray analysis of vacuum deposited pure films as well as donor-acceptor blended films using “Grazing Incident Wide Angle X-ray Scattering” (GIWAX). Although these three donor:C₇₀ blends were dominated by the highly crystalline feature of C₇₀, nevertheless, the pristine films were slightly distinguished by their preference of molecular alignments on top of substrate. Among them, **iBuBTDC** shows pronounced (010) signal in out-of-plane direction, which may benefit to charge transport, leading to better device performance (Fig. 5). The combined results had been published an excellent paper entitled “Donor-Acceptor-Acceptor's Molecules for Vacuum-Deposited Organic Photovoltaics with Efficiency Exceeding 9%” Che, Xiaozhou; Chung, Chin-Lung; Hsu, Chou-Chun; Liu, Feng; Wong, Ken-Tsung; Forrest, Stephen R. in *Advanced Energy Materials*, 2018,1703603.

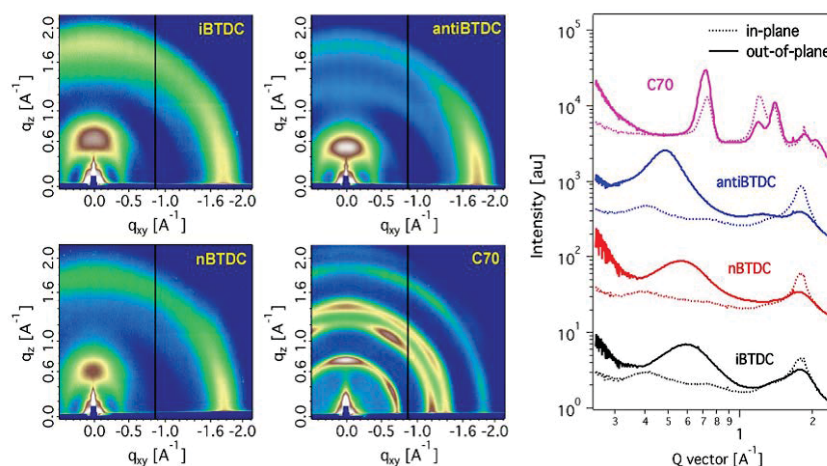


Figure 5. GIWAX analysis of pristine films of C₇₀, **iBuBTDC**, **nBuBTDC**, and **antiBTDC**

b. Molecular design strategy based on “Conjugated Effect” using coplanar acceptor subunit:

We devised a new two-step synthetic approach to de-symmetrize a symmetric di-bromo compound with extended π -system. Based on this strategy, we have successfully applied to accomplish two new D-A-A' donors **TNT** and **PNT**. These molecules verify the idea of using new central A block with extended π -system to reduce the optical energy gap of the resulting D-A-A' donor. Positively, the new donor **TNT** and **PNT** demonstrates evident red-shifted absorption as compared to that of **DTDCTB** due to the lower LUMO level (Figure 6).

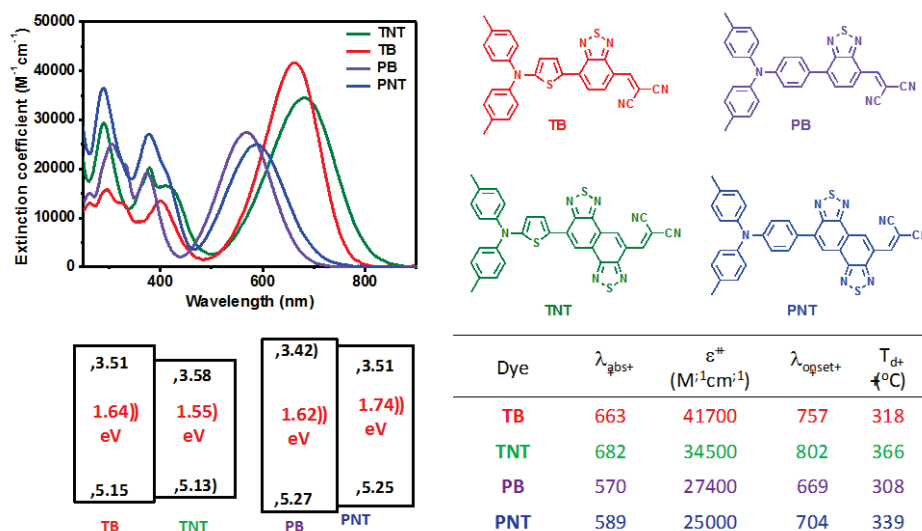


Figure 6. A comparison of the absorption spectra and energy levels of D-A-A' donors **DTDCTB** and **TNT**, **PNT**.

We have accomplished the characterizations of physical properties and the X-ray structures of new donors (**TNT**, **PNT**). The UM team has accomplished the examinations of these new donors for OPVs, in which the donor **PNT** can deliver a PCE of 8.3% with device optimization, whereas the donor **TNT** with longer absorption wavelength delivered inferior performance (Fig. 7). The superior performance of **PNT**-based device could be possibly attributed to the formation of central symmetric dimeric pair and very order crystal packing as shown in Fig. 8.

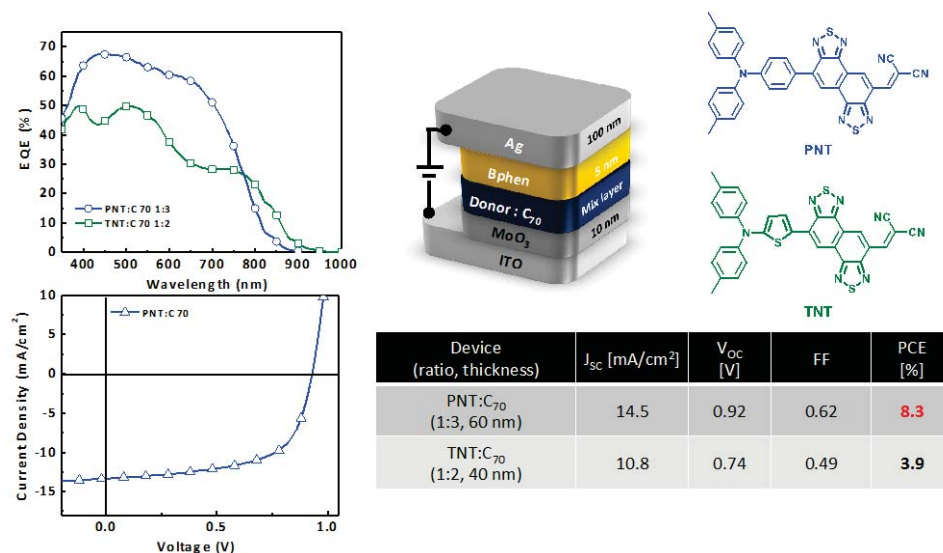


Figure 7. The device structure and characteristics of OPVs based on the donors **PNT** and **TNT**.

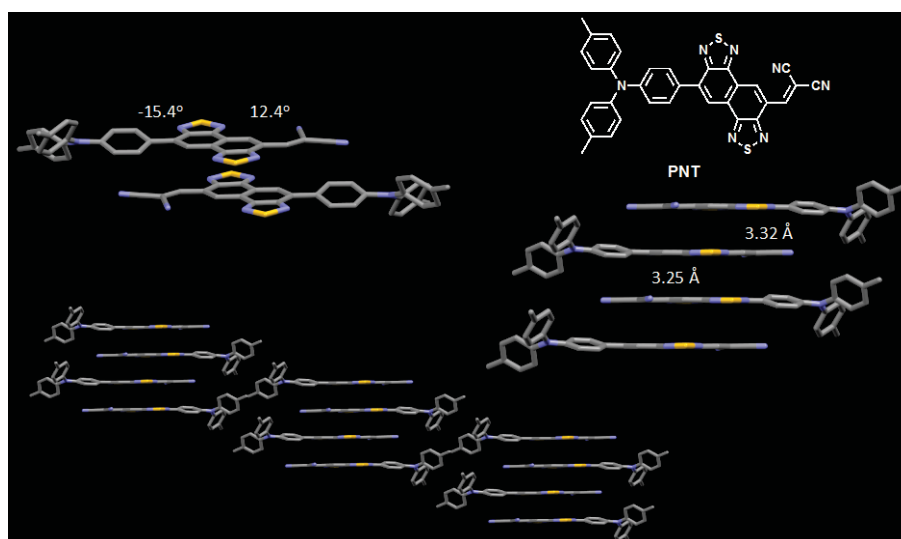


Figure 8. Crystal structure of the donor **PNT** and ordered crystal-packing manner.

The two-step synthetic strategy was further utilized to explore the feasibility of extending the central A unit with different structural features. In this regard, we have accomplished the synthesis of a pair of donors (**TNBT**, **PNBT**) with the central A unit BTD replaced by naphtha[2,3-c][1,2,5]thiadiazole (NBT). Very importantly, due to the high propensity to form quinoidal structure of the NBT unit, the absorption edge of the new donor **TNBT** is extended over 900 nm (Fig. 9), which is very close to our desired target range. However, the NBT exhibits large steric hindrance towards the phenylene bridge to strongly twist the molecular conformation and then create large space for accommodating solvent like hexane (Fig. 10). In addition, the highly twisted configurations also lead to reduced thermal stability, rendering the fabrication of OPV device with vacuum process unfeasible.

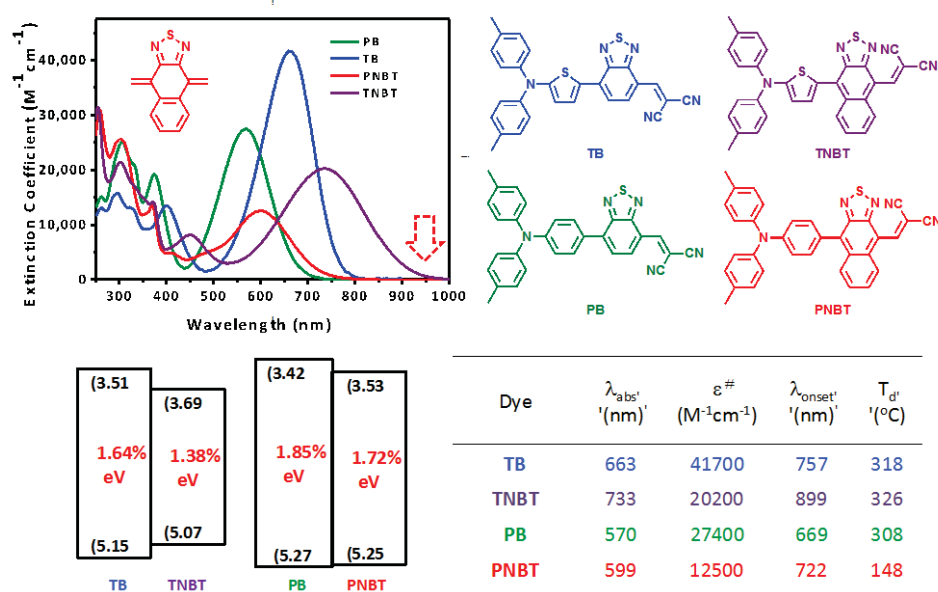


Figure 9. The new donors (**TNBT**, **PNBT**) based on NBT as central A unit and their physical properties.

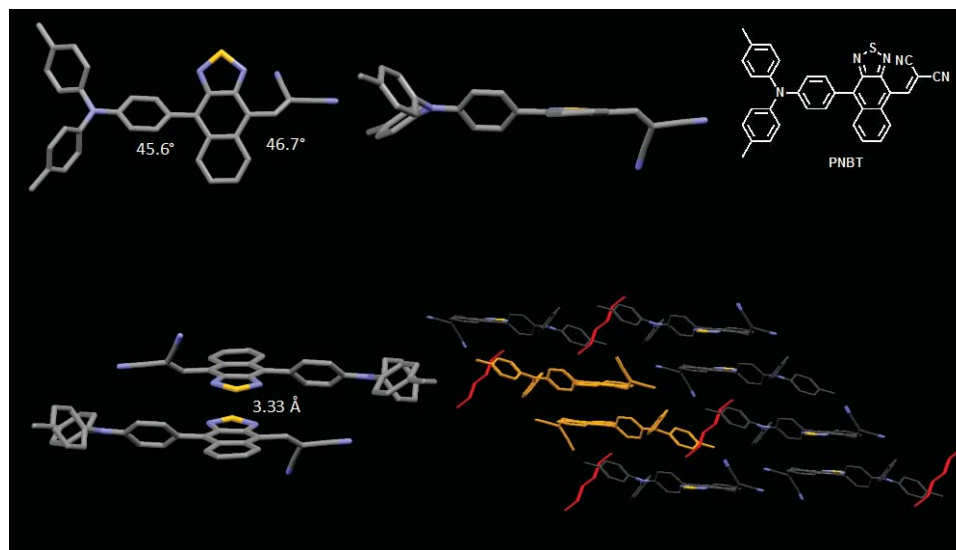


Figure 10. Crystal structure of the donor **PNBT** showing the contained hexane (red) inside the crystals.

c. Molecular design strategy based on “Inductive Effect”:

We utilized “Inductive Effect” as an alternative strategy to engineer the optical energy gap of small molecular donors. Ideally, the introduction of high electronegativity atom such as F onto the BTB ring should lower down the molecular LUMO level and lead to a reduced optical energy gap. Based on this simple idea and thank to the two-step

synthetic approach, we have accomplished a series of F-substituted **DTDCTB** and **DTDCPB** derivatives for a systematic study of structure-property relationship (Figures 11). The number and relative position of F-substitution(s) should play crucial factors governing the energy level shifting. Therefore, we have implemented one F onto the central BTB ring at different positions (in vs. out) relative to the donor unit as well as two F groups onto the BTB ring. Unfortunately, there are no significant changes of the absorption spectra of these new molecules as compared to those of their parent counterparts. Surprisingly, blue-shifted absorption peaks were observed for the cases with out-directed F-substitution and two F-substitutions. Only new donors with in-directed F-substitution show slightly red-shifted absorption peaks. All these molecules have been well characterized even with X-ray structure to indicate the effects of F-substitution(s) on the crystal packing manners.

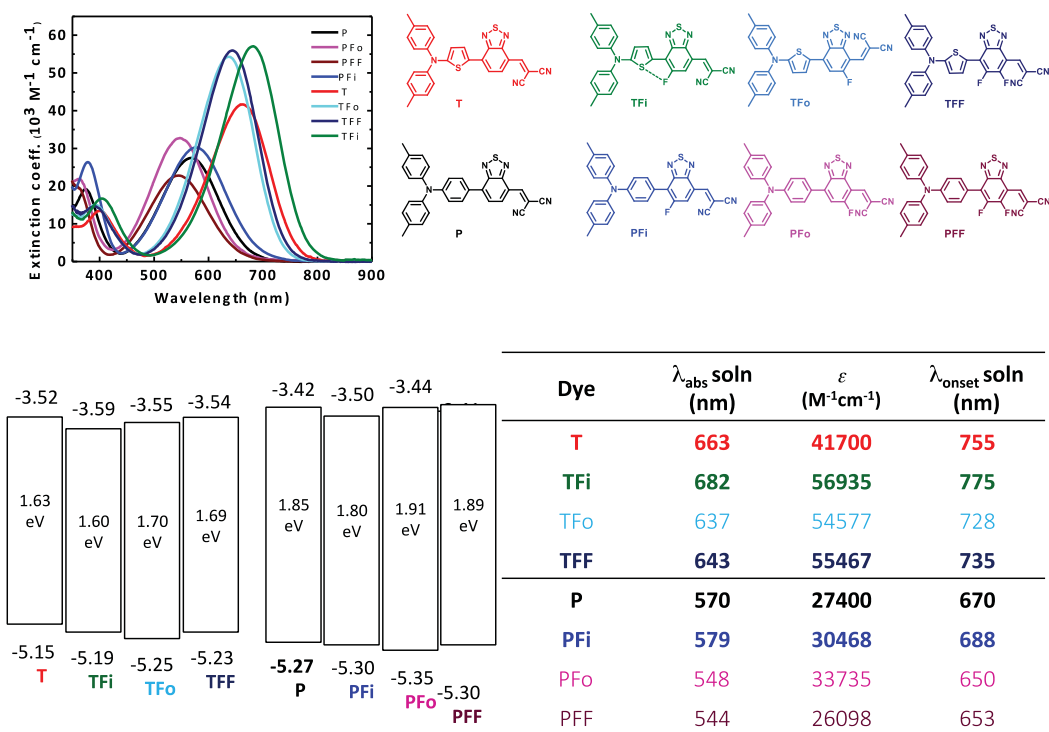


Figure 11. F-substituted **DTDCTB** (T) and **DTDCPB** (P) derivatives and their physical characteristics.

These new D-A-A' donors have been examined by UM team for their utilization as donors for OPVs. Their performances are comparable to those of devices based on parent counterparts (Fig. 12). For the P-series, UM team is now conducting the GIWAX study to figure out the correlation between crystal structure and device performance.

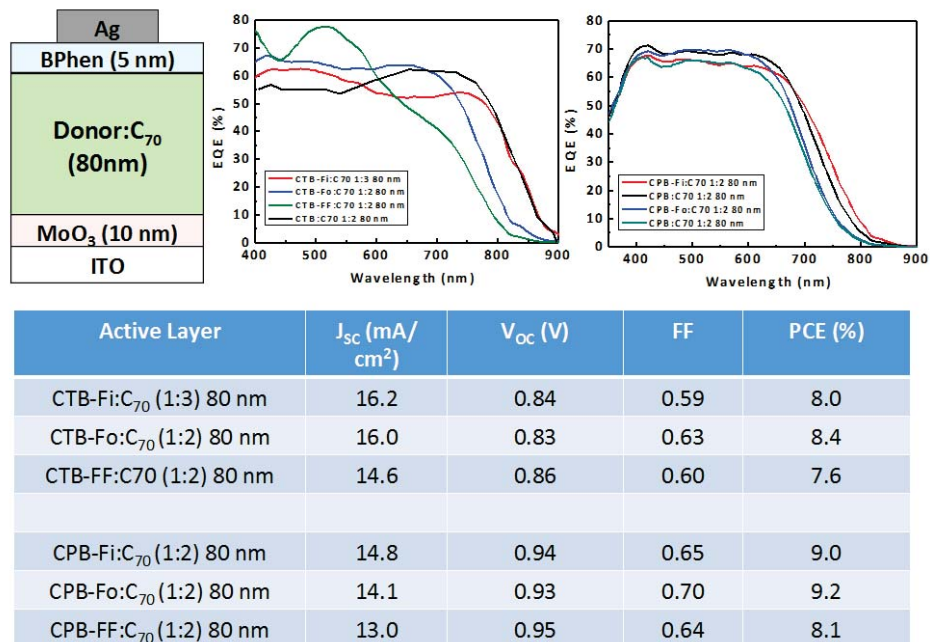


Figure 12. The device structure and characteristics of OPVs based on the donors with various F-substitution(s) on the BT ring.

d. Miscellaneous

The molecular design strategy based on D-A-A configuration for shifting the absorption wavelength to N-IR range gives only limited success. New molecular configuration is necessary to achieve the goal of new materials with absorption stretching to N-IR. We consider the quinoidal feature of benzothiophene will benefit to enhance π -conjugation and reduce the optical energy gap for realizing long wavelength absorption. Thus, a new π -conjugated system dubbed as “D-Q-A” configuration was developed. However, these new donors exhibit relatively high LUMO energy levels, leading to unnecessary energy lost. For lowering down the energy levels in D-Q-A systems, we introduced “inductive effect” onto the Q unit by incorporation of two CN groups (Fig. 13). As indicated, the energy levels are significantly lowered down, particularly, the LUMO levels, leading to reduced optical energy gaps. The thiophene-bridged one, **TBTh-2CN**, exhibit an onset absorption at 825 nm, which is significant red-shifted, even compared to that of the parent D-A-A-configured **TB** (**DTDCTB**). We stepped one step forward toward the N-IR absorption. Unfortunately, we are not able to have the single crystals of these two donors to probe the intermolecular interactions.

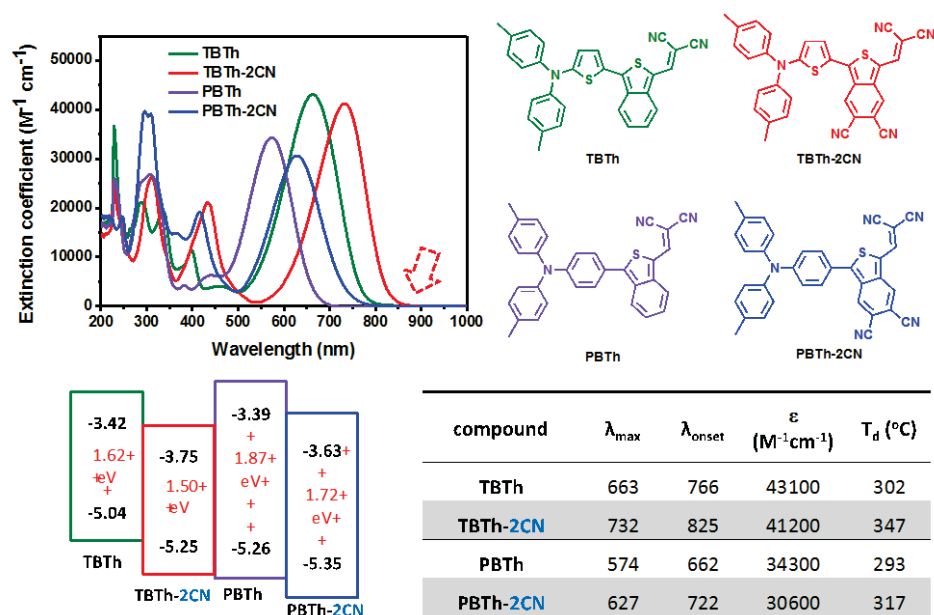


Figure 13. The structures of new donors **TBTh-2CN** and **PBTh-2CN**, and their physical properties.

Both of new D-Q-A configured donors implemented with CN-substitutions are OPV active donors, which were examined by the UM team. The phenylene-bridged one delivered higher efficiency (5.0%) as compared to the thiophene-bridged counterpart (Fig. 14). As indicated, the IPCE spectra did show the response extends to the N-IR range, which is much longer wavelength as compared to any previous cases in this project. However, these devices are suffering from the low FF, further device engineering and or introduce new acceptors may have the chance to improve the device efficiency.

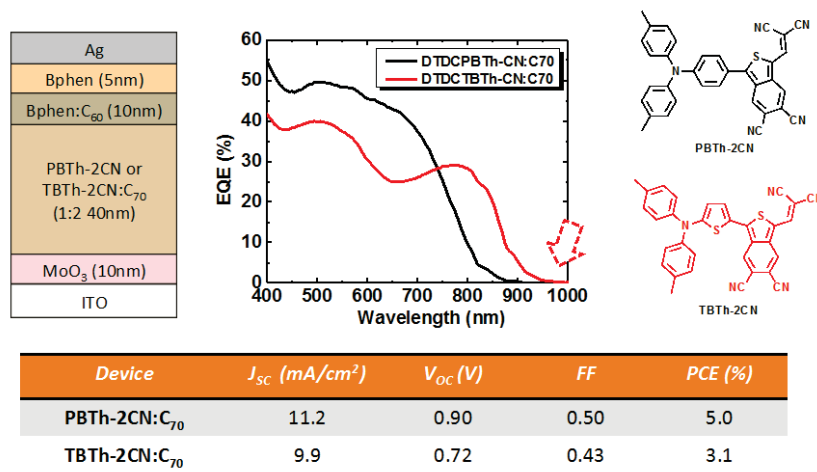


Figure 14. The device structure and characteristics of OPVs based on the donors **PBTh-2CN** and **TBTh-2CN**.

The ultimate approach to have small molecular donor with absorption edge reaching to 1000 nm is to bring the quinoidal D and CN-substituted benzothiophene as the central A.

The resulting molecule (**DBTh-2CN**) did exhibit on-set absorption > 900 nm due to the higher HOMO level. The film of this type donor typically shows red-shifted behavior, which may lead this material to have the absorption edge beyond 1000 nm (Fig. 15).

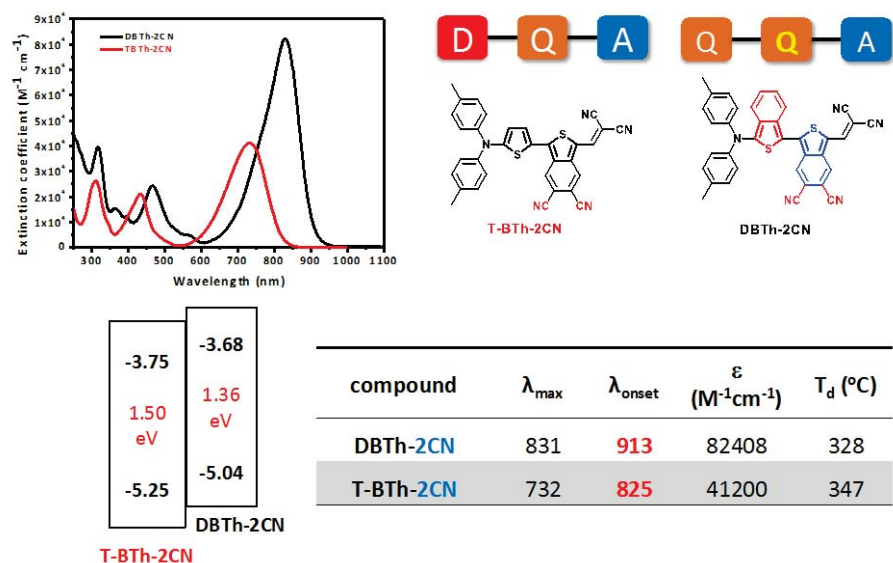


Figure 15. The structures of new donors **TBTh-2CN** and **DBTh-2CN**, and their physical properties.

Our preliminary examination of using **DBTh-2CN** as donor and C_{60} as acceptor for OPV device gave an inferior efficiency (Fig. 16). However, the IPCE indicates the donor did harvest photons extending to 1000 nm. The device optimization and/or find of suitable acceptor to combine with this interesting donor will be further conducted in the near future with scale-up synthesis of **DBTh-2CN** achieved. The molecular design strategy did reveal the feasibility of effectively extending the absorption of small molecules by modulating the electron donating and accepting features of conjugated constituents.

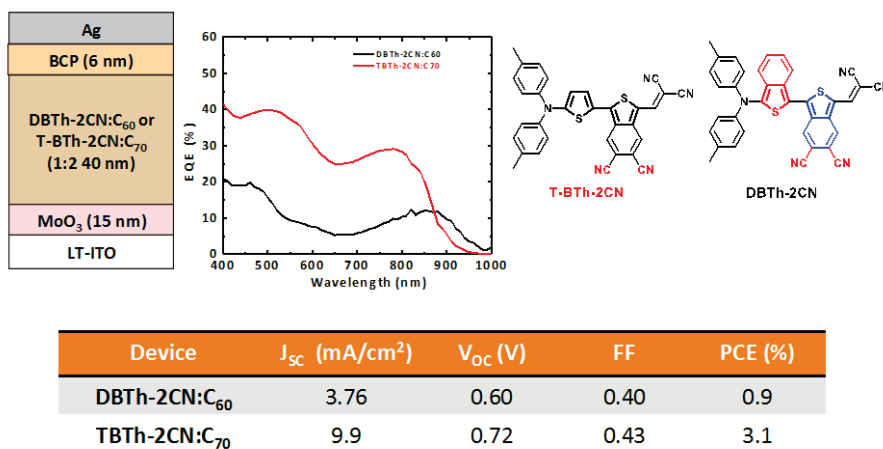


Figure 16. The device structure and characteristics of OPVs based on the donors **TBTh-2CN** and **DBTh-2CN**.

In summary, in order to develop D-A-A' type dipolar donors with absorption edge closing to the near infrared ($< 1.1 \mu\text{m}$ wavelength), different molecular design strategy has been tried based on modifying the model compound **BTDCtB**. The introduction of rigid and coplanar D blocks cannot effectively shift the absorption to the desired range, but lead to interesting results. With short alkyl side chains, the new donors can deliver comparably good PCEs as the parent donors achieved. The “conjugated effect” was then implemented onto the central acceptor unit, where the BT was replaced with NT or NBT unit with extended π -conjugation. The results have indicated that the absorption edge can be red-shifted, particularly for the NBT-cored cases. However, the low thermal stability impedes our further study for the examination of their OPV performances. For imposing “inductive effect” onto the central BT block, we have accomplished the syntheses and characterizations of six new F-substituted donors. The results have concluded that the inductive effect of F-substitution cannot significantly shift the absorption edge to longer wavelength. This systematic study on the effects of F-substitution(s) is almost completed if the GIWAX studies can provide useful information to figure out the correlation between the X-ray structure and device characteristics. In addition to the conjugation and inductive effects, we introduced highly quinoidal benzothiophene BTh as building block to design new molecular donors with D-Q-A configuration. We have found that new donors with 2CN-substituted BTh can significantly red-shifted the absorption edge, indicating a new molecular design direction for accessing new donors with absorption edge closing to the near infrared. Among these new molecules, the dipolar molecules with benzothiophene as the D combining with electron deficient BT or CN-substituted benzothiophene as the central A unit are more successful for shifting the absorption to the desired N-IR region.

Continuation plans:

1. NTU team has accomplished the basic characterizations of all desired targets. A Ph.D. student Mr. Chung-Kai Wang will join the UM team in the winter of 2018 for conducting device experiments with new donors.
2. NTU team has accomplished the basic characterizations of D-Q-A donor **TBTh-2CN** and Q-Q-A donor **DBTh-2CN**. These two donors exhibit most red-shifted absorption ranges. The preliminary studies on device performance indicated they are active donors for OPVs. NTU team will scale up the synthesis of these new donors and deliver them to UM team for further device studies.

Publications and Presentations:

The project has resulted two paper published as:

1. “Regioisomeric Effects of Donor-Acceptor-Acceptor' Small-Molecule Donors on the Open Circuit Voltage of Organic Photovoltaics” Che, X.; Chung, C.-L.; Liu, X.;

Chou, S.-H.; Liu, Y.-H.; Wong, K.-T.; Forrest, S. R. *Advanced Materials* **2016**, *28*, 8248.

2. "Donor-Acceptor-Acceptor's Molecules for Vacuum-Deposited Organic Photovoltaics with Efficiency Exceeding 9%" Che, Xiaozhou; Chung, Chin-Lung; Hsu, Chou-Chun; Liu, Feng; Wong, Ken-Tsung; Forrest, Stephen R. *Advanced Energy Materials*, 2018, 170360.

Some of the results based on this project have been (will be) presented in:

1. The 5th Hsinchu Workshop: Single Molecule/Nanoparticle Spectroscopy and Imaging, June 23, 2016. Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Taiwan.
2. The PIERS (Progress in Electromagnetics Research Symposium) 2016 in Shanghai, 8-11 August, 2016 China.
3. International Conference of Electroluminescence and Optoelectronic Devices, October 2~5, 2016, Raleigh, North Carolina, USA.
4. 13th International Symposium on Functional π -Electron Systems, June 4~9, 2017, Hong Kong University of Science and Technology, Hong Kong, China
5. Institut des Sciences Moléculaires CNRS UMR 5255, University of Bordeaux, July 12, 2017.
6. Asian Conference on Organic Electronics 2017 (A-COE-2017), Oct. 25~27, 2017, Daejeon, Korea.
7. International Conference of Electroluminescence and Optoelectronic Devices, October 14~17, 2018, Jeju Island, Korea.
8. Asian Conference on Organic Electronics 2018 (A-COE-2018), Dec. 5~7, 2018, City University of Hong Kong, China.

Reference

- [1] X. Xiao, K. J. Bergemann, J. D. Zimmerman, K. Lee, and S. R. Forrest, "Small molecule planar-mixed heterojunction photovoltaic cell with a fullerene-based electron filtering buffer," *Adv. Energy Mater.*, DOI: 10.1002/aenm.201301557, 2014.
- [2] O. L. Griffith, X. Liu, J. A. Amonoo, P. I. Djurovich, M. E. Thompson, P. F. Green, S. R. Forrest, " Charge transport and exciton dissociation in organic solar cells consisting of dipolar donors mixed with C₇₀" *Phys. Rev. B* 2015, 92.