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# EFFECT OF END GROUPS ON THE BAND GAP OF DONOR-ACCEPTOR BASED SMALL MOLECULES CONTAINING DIKETOPYRROLOPYRROLE

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**Abstract** – (Acceptor-donor-acceptor type compounds 5,5'-(4,4'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4,1-phenylene))dithiophene-2-carbonitrile **(DPPTCN)**, 4',4''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)dibiphenyl-4-carbonitrile **(DPPPhCN)**, 2,2'-(5,5'-(4,4'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(thiophene-5,2-diyl))-bis(methan-1-yl-1-ylidene)dimalononitrile **(DPPT2CN)**, 2,2'-(4',4''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)dimalononitrile **(DPPPh2CN)** were designed and synthesized. All the compounds have central diketopyrrolopyrrole common acceptor unit, the donor groups differ either thiophene or phenyl group and the terminal end groups are differ either nitrile or dicyanovinylene groups. In order to study the relationship between chemical structure and properties, their optical, thermal and electrochemical properties were investigated. Thermal properties indicate that all the compounds have high thermal stability. Among **DPPT2CN** with thiophene groups as donor and dicyanovinylene as acceptor has shown lowest LUMO energy level of -3.77 eV and low HOMO-LUMO band gap 1.86 eV.

## INTRODUCTION

Donor-acceptor type compounds have been extensively researched for organic semiconductors. Organic semiconductors have applications in solar cells,[1,2] radio frequency identification (RFID) tags[3,4] and organic thin film transistors (OTFTs).[5,6] Donor-acceptor type combinations results in lowering of energy band gap between the HOMO and LUMO energy levels.[7] These low band gap compounds are highly desirable for solar cells and OTFTs. The donor groups are thienothiophene,[8,9] (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT),[10,11] benzodithiophene,[12,13] and dithienothiophene.[14,15] The common acceptors are isoindigo (Ii),[16,17] diketopyrrolopyrrole (DPP),[18,19] benzobisthiadiazole (BBT),[20,21] benzothiadiazole (BTD),[22,23] arylene diimides,[24,25] nitrile[26,27] and dicyanovinylene groups.[28,29]

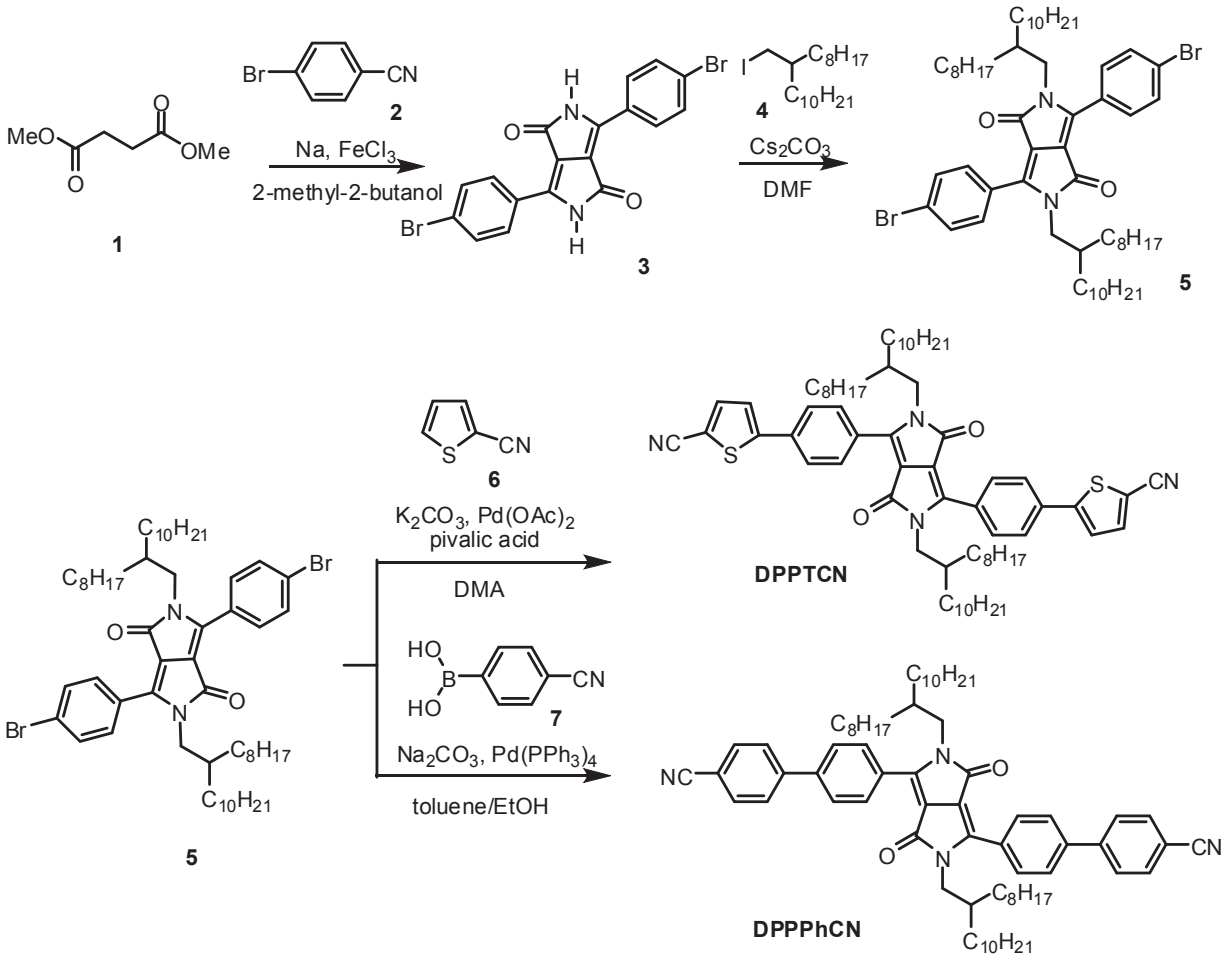
Donor-acceptor based compounds containing the Ii, DPP, BBT, BTD and arylene diimides as acceptors are extensively synthesized and studied compared to nitrile and dicyanovinylene groups. The polymers consist of donor-acceptor type molecules have shown better device performances in terms of good mobility and higher power conversion efficiencies. But the consistency of device performance is less that leads to variation in performances with different batch polymers. Small molecules have advantages like consistency in device performance and their performances can be easily correlated with the structure.

For high-performance in solar cells and OTFTs compounds with strong absorption in the visible spectral region are required. DPP based compounds can show strong absorption in the visible spectral region. Acceptor-donor-acceptor based small molecules composed of diketopyrrolopyrrole and nitrile or dicyanovinylene groups as acceptor and thiophene or phenyl groups as donor synthesized. All the compounds have central diketopyrrolopyrrole as common acceptor unit, the donor groups differ either thiophene or phenyl group and the terminal end groups acceptor are differ either nitrile or dicyanovinylene groups. The nitrile and dicyanovinylene groups lower the LUMO energy level as well as the energy band gap between HOMO and LUMO levels. In order to study the relationship between chemical structure and properties, their optical, thermal and electrochemical properties were investigated. The molecules are synthesized by using reactions such as Suzuki coupling and direct arylation methods. All the compounds are soluble in solvents like chloroform, methylene chloride, chlorobenzene and dichlorobenzene. The optical properties were investigated by UV-visible absorption spectroscopy, the thermal properties were analyzed by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The electrochemical properties were analyzed by cyclic voltametry (CV).

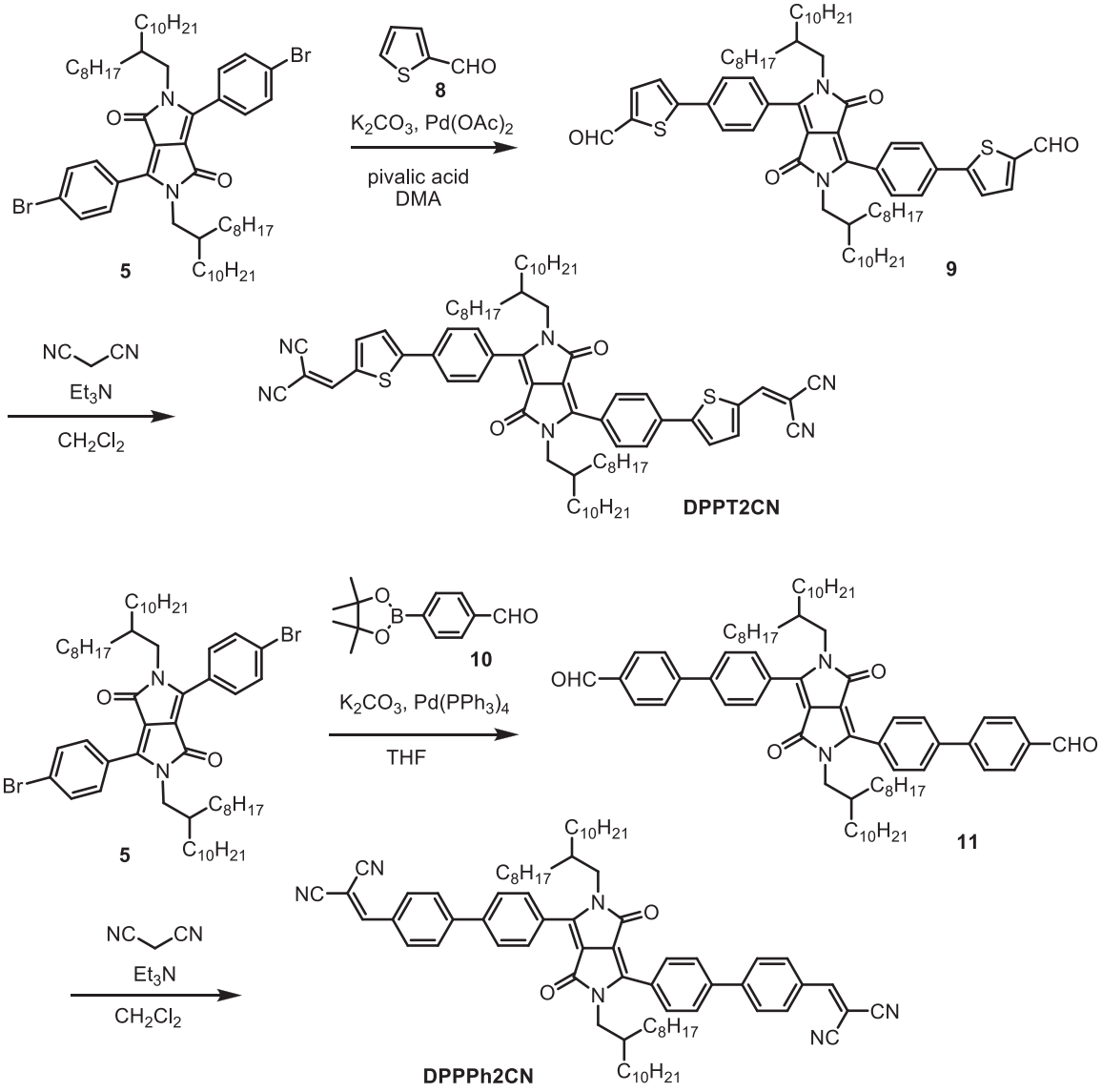
## RESULTS AND DISCUSSION

The synthesis of the compounds is shown in **Schemes 1** and **2**. Compounds **4**, **7** and **10** were synthesized by following the literature procedures.[30-32] Compound **3** was obtained by reaction of dimethyl succinate with 4-bromobenzonitrile in the presence of Na and $FeCl_3$. Alkylation of compound **3** produced compound **5**. **DPPTCN** was obtained by direct arylation of compound **5** with **6**. Even though the yield was less in direct arylation reaction, due to no need of using stanylated or borynylation reactants, this method was used. **DPPPhCN** was synthesized by Suzuki coupling reaction of compounds **5** and **7**.

Compound **9** was obtained by direct arylation of compound **5** with **8**. **DPPT2CN** was synthesized by Knoevenagel condensation reaction of compound **9**. Compound **11** was obtained by Suzuki coupling reaction of compounds **5** and **10**. Finally **DPPPh2CN** was synthesized by Knoevenagel condensation reaction of compound **11**. The synthesized compounds are characterized by $^1$H NMR, $^{13}$C NMR, and mass spectroscopic analysis.




**Scheme 1.** Synthesis of **DPPTCN** and **DPPPhCN**




**Scheme 2.** Synthesis of **DPPT2CN** and **DPPPh2CN**

## OPTICAL PROPERTIES

The optical properties of the synthesized compounds were investigated by using UV-visible absorption spectra in a $CHCl_3$ solution as well as in thin films. **Figure 1** represents the UV-visible absorption spectra of the **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**. The absorption values are listed in **Table 1**. In the solution state the absorption values are, 334 and 501 nm for **DPPTCN**, 314 and 489 nm for **DPPPhCN**, 407 and 528 nm for **DPPT2CN**, 353 and 496 nm for **DPPPh2CN**. Where as in the film state the absorption values are, 342 and 519 nm for **DPPTCN**, 320 and 499 nm for **DPPPhCN**, 412 and 548 nm for **DPPT2CN**, 363 and 515 nm for **DPPPh2CN**. The low wavelength band corresponds to π-π* transitions, while the high wavelength band corresponds to intramolecular charge transfer (ICT).[33,34] The

appearance of two bands is the characteristic of donor-acceptor type compounds. In all the four compounds, the film state absorption values are red-shift than the solution state due to more intermolecular interactions in the film state. When compared to **DPPPhCN**, the **DPPTCN** has shown more red-shift of absorption values both in solution and film state due to well intermolecular interactions originated by the more polarizable thiophene group. In the similar way when compared to **DPPPh2CN**, the **DPPT2CN** has shown more red-shift of absorption values both in solution and film state. The absorption values of dicyanovinylene compounds, **DPPT2CN** and **DPPPh2CN** are more red-shifted than the compounds containing nitrile groups, because of the increase of conjugation length in the dicyanovinylene compounds. The optical band gap energy calculated for **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** were 2.08, 2.18, 1.86 and 2.07 eV, respectively. Among four compounds the **DPPT2CN** has lower energy band gap due to increase in conjugation and well intermolecular interactions originated by the more polarizable thiophene group. **Figure 2** represents the PL emission spectra of the **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**. The PL emissions of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** in $CHCl_3$ solution were observed at 591, 576, 648, and 604 nm, respectively. The PL emissions of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** in film state are red-shifted compared to the solution state and observed at 654, 627, 712, and 661 nm, respectively. Similar to the UV-visible absorption values, the PL emission values of dicyanovinylene compounds, **DPPT2CN** and **DPPPh2CN** are more red-shifted than the compounds containing nitrile groups.

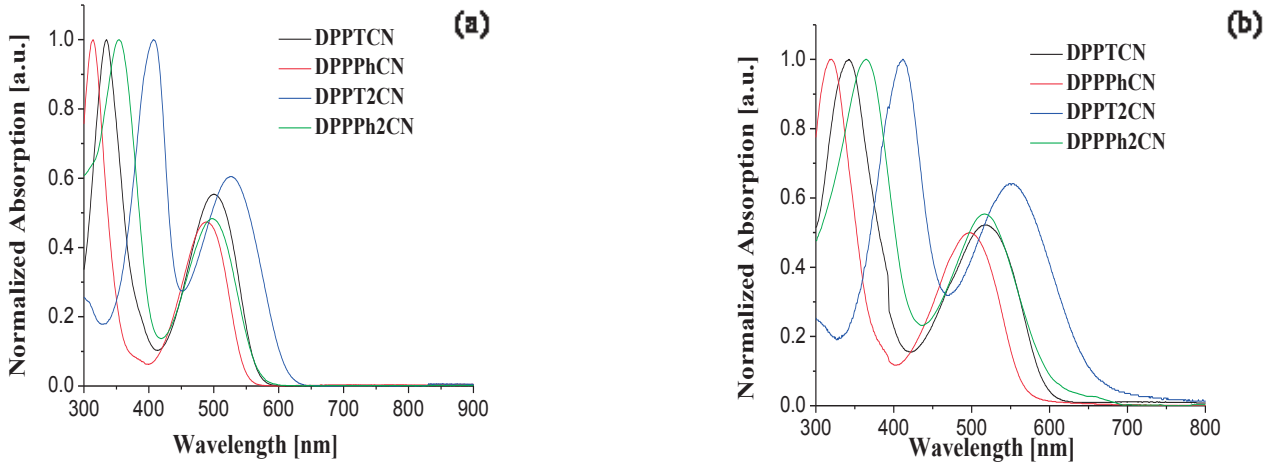



**Figure 1.** UV-vis absorption spectra of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** (a) in $CHCl_3$ solution and (b) in film state

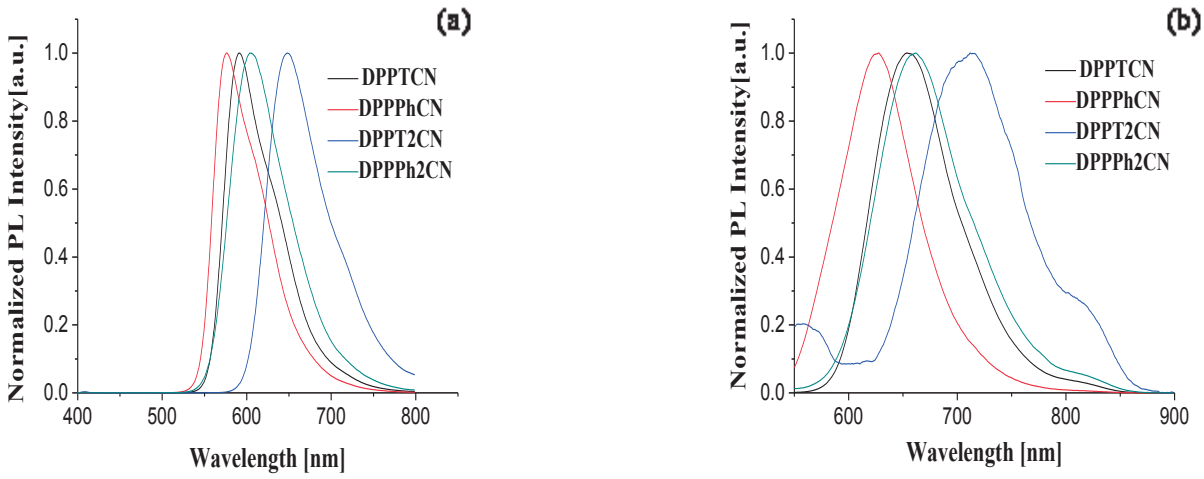



**Figure 2.** Photoluminescence spectra of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** (a) in $CHCl_3$ solution and (b) in film state

## ELECTROCHEMICAL PROPERTIES

Oxidation potentials of the compounds were determined by performing CV measurements. From the oxidation potentials, the HOMO and LUMO energy levels were estimated [HOMO = -(4.4+$E_{ox,\ onset}$), LUMO = (HOMO +$E_g$opt)]. CV graphs of the compounds are shown in **Figure 3**. The HOMO energy levels of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** were calculated from onset oxidation potential, which were -5.64, -5.62, -5.63, and -5.60 eV, respectively. The LUMO energy levels of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** were calculated from the HOMO and optical energy band gap were -3.56, -3.44, -3.77, and -3.53 eV, respectively. The HOMO and LUMO values are listed in **Table 1**. All the compounds have similar HOMO energy level but variation in the LUMO energy levels. By the introduction of electron withdrawing groups, the LUMO energy level of all the compounds decreased. The **DPPT2CN** has lower LUMO energy level than the other compounds due to presence of stronger electron withdrawing dicyanovinylene groups.

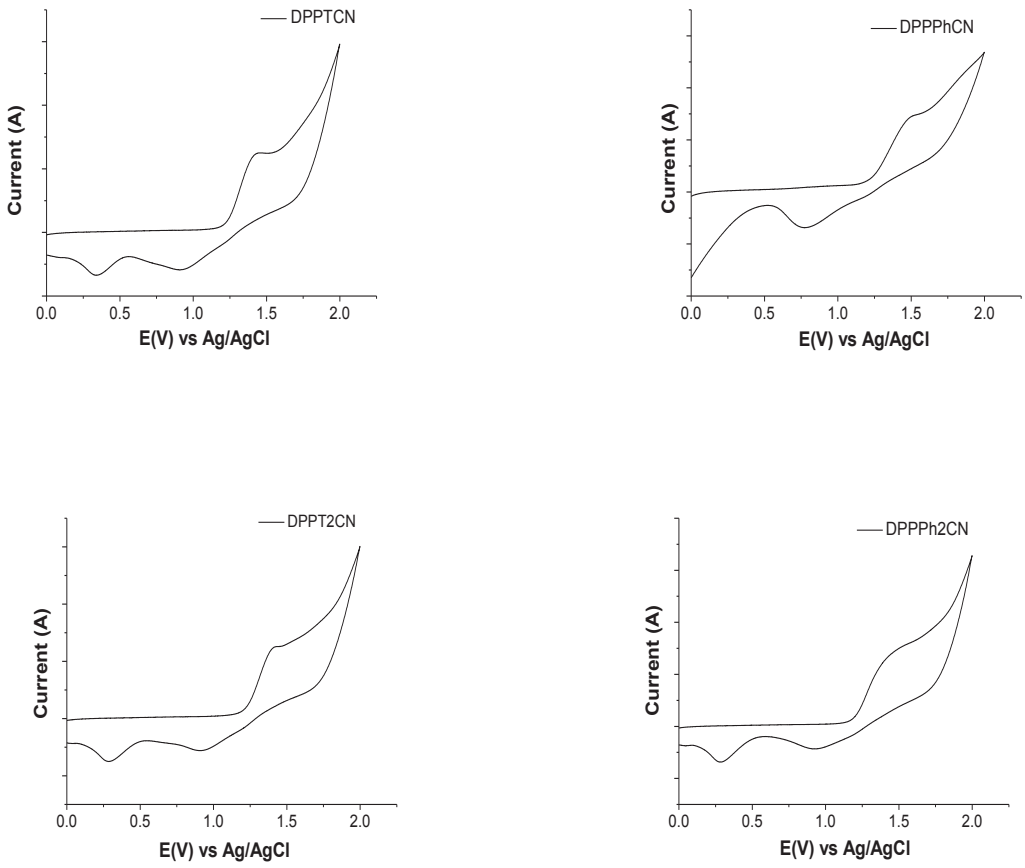



**Figure 3.** Cyclic voltammograms of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**

## THERMAL PROPERTIES

The thermal properties of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis. **Figure 4** represents the TGA graphs. The decomposition temperature (5% weight loss) for compounds **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN** were observed at 426, 433, 360 and 404 °C, respectively, indicated all the compounds were thermally stable. **Figure 5** represents the DSC graphs. The endothermic melting temperatures for **DPPTCN** and **DPPPhCN** were observed at 98 and 142 °C, respectively. The **DPPT2CN** has shown two endothermic peaks at 70 and 126 °C, respectively. The first peak represents the liquid-crystalline mesophase and the second peak represents the melting temperature. The **DPPPh2CN** has shown liquid-crystalline mesophase and melting temperature at 124 and 149 °C, respectively. The absence of crystallization temperature indicated the less crystalline nature of these compounds. The TGA and DSC properties are listed in **Table 1**.

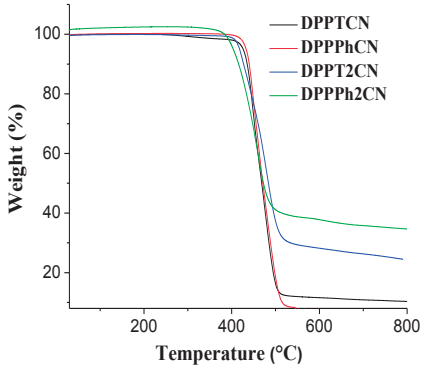



**Figure 4.** TGA curves of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**

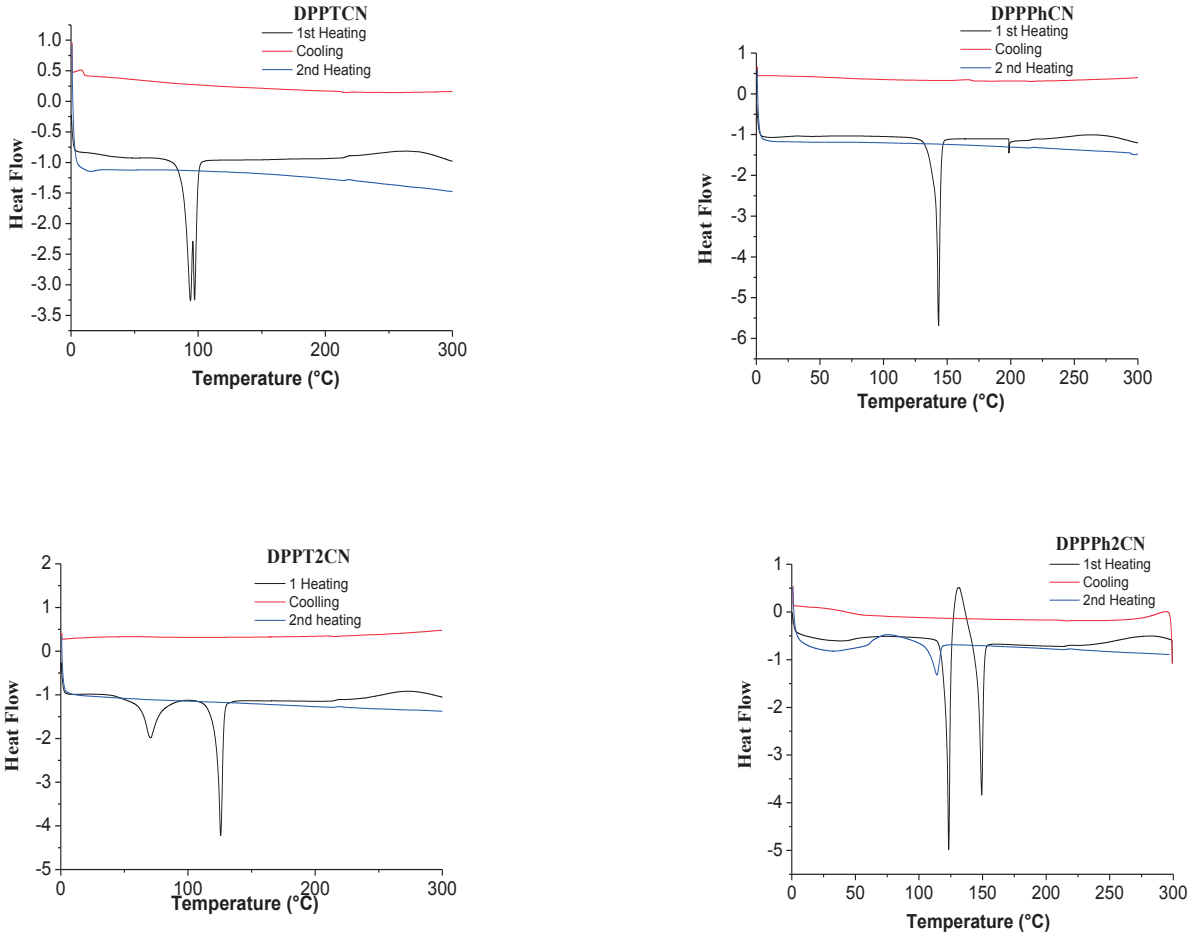



**Figure 5.** DSC curves of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**

**Table 1.** Optical, electrochemical and thermal properties of **DPPTCN**, **DPPPhCN**, **DPPT2CN** and **DPPPh2CN**

| Compound | $\lambda_{abs}$ Sol (nm) | $\lambda_{abs}$ Film (nm) | $\lambda_{em}$ Sol (nm) | $\lambda_{em}$ Film (nm) | HOMO (eV)[a] | LUMO (eV)[b] | $E_g$ (eV)[c] | $T_d$(5%) (°C)[d] | $T_m$ (°C)[e] |
|---|---|---|---|---|---|---|---|---|---|
| **DPPTCN** | 334, 501 | 342, 519 | 591 | 591 | -5.64 | -3.56 | 2.08 | 426 | 98 |
| **DPPPhCN** | 314, 489 | 320, 499 | 576 | 576 | -5.62 | -3.44 | 2.18 | 433 | 142 |
| **DPPT2CN** | 407, 528 | 412, 548 | 648 | 648 | -5.63 | -3.77 | 1.86 | 360 | 126 |
| **DPPPh2CN** | 353, 496 | 363, 515 | 604 | 604 | -5.60 | -3.53 | 2.07 | 404 | 149 |

[a] Estimated from the onset of oxidation potential, HOMO = -(4.4+$E_{ox,\ onset}$).
[b] Calculated from (LUMO = HOMO +$E_g$opt).
[c] Calculated from the absorption edge wavelength.
[d] Decomposition temperature at 5% weight loss.
[e] $T_m$ represent, endothermic melting temperature.

## CONCLUSIONS

Acceptor-donor-acceptor based small molecules composed of diketopyrrolopyrrole, nitrile and dicyanovinylene groups as acceptor and thiophene and phenyl groups as donor synthesized. All the compounds have exhibited good thermal stability. The strong electron withdrawing dicyanovinylene groups containing compounds **DPPT2CN** and **DPPPh2CN** have shown absorptions in the longer wavelength region than the nitrile groups containing compounds **DPPTCN** and **DPPPhCN**. In the similar way, the **DPPT2CN** and **DPPPh2CN** have low energy band gap. The extension of conjugation leads to lowering of energy gap between the HOMO and LUMO levels. The **DPPT2CN** has shown band gap energy of 1.86 eV. This molecular design strategy clearly indicates that the dicyanovinylene groups introduction leads to lowering of energy band gap. These optical and electrochemical properties suggesting, these materials can be utilized for optoelectronics.

## EXPERIMENTAL

All the reagents and chemicals were purchased from Sigma Aldrich co., TCI, or Alfa Aesar co. The solvents such as THF, $Et_2O$, toluene, and $CH_2Cl_2$ were used after distillation in the presence of sodium/benzophenone or calcium hydride under nitrogen gas. $^1H$ and $^{13}C$ NMR spectra were recorded on 300 MHz and 75 MHz spectrometers respectively. The chemical shift values were reported in δ units (ppm). Mass spectra analysis was carried on a JMS-700, JEOL. UV-visible absorption was obtained by using a Shimadzu UV-1065PC UV–vis spectrophotometer. Cyclic voltammogram measurements were carried out on an epsilon $E_3$ at room temperature in a tetrabutylammonium perchlorite (0.1 M solution) in

$CHCl_3$ under nitrogen atmosphere at a scan rate of 50 mV/s. A Pt wire and Ag/AgCl electrodes were served as the counter and reference electrodes, respectively. Thermogravimetric analysis (TGA) was obtained under nitrogen by using a TA instruments 2050 thermogravimetric analyzer, by heating at a 10 °C/min heating rate from 30 °C to 800 °C. Differential scanning calorimeter (DSC) measurements were carried out under nitrogen by using a TA instruments 2100 differential scanning calorimeter, heating from 0 °C to 300 °C at a rate of 10 ºC/min.

**Synthesis of 3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3).**

Sodium (1.26 g, 54.74 mmol) and anhydrous $FeCl_3$ (0.06 g) was added to dry 2-methyl-2-butanol (27.2 mL) under nitrogen atmosphere and the mixture was stirred at 90 °C until all the sodium was dissolved. The reaction mixture was cooled to 90 °C, then 4-bromobenzonitrile (4.98 g, 27.37 mmol) was added and again heated to 90 °C. A solution of dimethyl succinate (1.26 g, 10.95 mmol) in dry 2-methyl-2-butanol (8.2 mL) was added dropwise for 1 h. The reaction mixture was heated under nitrogen atmosphere at 90 °C for 24 h. Acetic acid (11.5 mL) was added to the mixture and stirred at 120 °C for 1 h. The reaction mixture was cooled down to room temperature and filtered. The filtered dark red solid was washed with hot water and hot MeOH several times and used for next reaction without further purification. Yield: 5.31 g, (60%).

**Synthesis of 3,6-bis(4-bromophenyl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (5).**

Compound **3** (0.5 g, 1.12 mmol) and cesium carbonate (1.46 g, 4.48 mmol) were added to DMF (15 mL), and stirred at 120 °C for 1 h. Compound **4** (1.83 g, 4.48 mmol) was added slowly dropwise to the reaction mixture. After the complete addition the reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was cooled to room temperature and poured into water. The aqueous layer was extracted with $CH_2Cl_2$. The combined organic layers were washed with water, brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel with *n*-hexane/ $CH_2Cl_2$ (1:1, v/v). The compound was recrystallized by using $CH_2Cl_2$ and MeOH to give compound **5** as orange solid. Yield: 0.35 g, (31%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 7.64 (s, 8H), 3.71 (d. $J$ = 7.5 Hz, 4H), 1.51 (m, 2H), 1.07-1.27 (m, 64H), 0.87-0.91 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 162.5, 147.7, 132.1, 130.1, 127.2, 125.6, 109.8, 37.0, 32.0, 31.2, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 19.4, 14.7; IR (KBr) ν: 2975, 2925, 2850, 1660, 1490, 1470, 1610, 1330 $cm^{-1}$; HRMS (FAB+$H^+$) calcd for $C_{58}H_{90}N_2Br_2O_2$ 1005.5369, found 1005.5420.

**Synthesis of 5,5'-(4,4'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-**

**1,4-diyl)bis(4,1-phenylene))dithiophene-2-carbonitrile (DPPTCN).**

Compound **5** (0.2 g, 0.20 mmol), compound **6** (0.054g, 0.496 mmol), anhydrous $K_2CO_3$ (0.069 g, 0.496 mmol), pivalic acid (0.006 g, 0.060 mmol) and $Pd(OAc)_2$ (0.0022 g, 0.010 mmol) were stirred in anhydrous DMA (2 mL) for 4 h at 100 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of NaCl. The precipitate was extracted with EtOAc. The combined organic layer was washed with distilled water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel with *n*-hexane/ $CH_2Cl_2$ (1:6, v/v) to give the **DPPTCN** as red solid. Yield: 0.065 g, (31%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 7.86 (d, *J* = 8.4 Hz, 4H), 7.71 (d, *J* = 8.1 Hz, 4H), 7.63 (d, *J* = 3.9 Hz, 2H), 7.36 (d, *J* = 3.9 Hz, 2H), 3.77 (d, *J* = 7.2 Hz, 4H), 1.54 (m, 2H), 1.09-1.22 (m, 64H), 0.84-0.91 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 162.4, 150.2, 147.7, 138.4, 134.1, 129.7, 129.1, 126.1, 123.1, 114.0, 110.0, 109.3, 45.1, 37.0, 31.9, 31.9, 31.2, 29.9, 29.7, 29.6, 29.6, 29.4, 29.4, 26.0, 22.7, 22.7, 14.2; IR (KBr) ν: 2950, 2920, 2850, 2220, 1675, 1610, 1460, 1100 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{68}H_{94}N_4O_2S_2$ 1063.6818, found 1063.6899.

**Synthesis of 4',4''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)dibiphenyl-4-carbonitrile (DPPPhCN).**

Compound **5** (0.60 g, 0.60 mmol), compound **7** (0.22 g, 1.49 mmol) and sodium carbonate (1.26 g, 11.92 mmol) were dissolved in toluene (24 mL)/EtOH (3 mL)/distilled water (5.97 mL). $N_2$ was bubbled for 10 min. Then $Pd(PPh_3)_4$ (0.049 g, 0.042 mmol) was added and degassed the flask, and the resulting mixture was heated at 110 °C for 24 h. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel with *n*-hexane/ EtOAc (7:1, v/v) to give the **DPPPhCN** as red solid. Yield: 0.45 g, (72%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 7.94 (d. *J* = 8.1 Hz, 4H), 7.74 - 7.81 (m, 12H), 3.81 (d. *J* = 6.9 Hz, 4H), 1.60 (m, 2H), 1.11-1.18 (m, 64H), 0.83-0.90 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 162.7, 148.0, 144.3, 141.4, 132.8, 129.5, 128.7, 127.7, 127.6, 118.7, 111.7, 110.2, 45.4, 37.1, 31.9, 31.9, 31.2, 29.9, 29.7, 29.6, 29.4, 26.3, 26.1, 22.7, 22.7, 14.2; IR (KBr) ν: 2955, 2925, 2855, 2230, 1660, 1615, 1455, 1100 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{72}H_{98}N_4O_2$ 1051.7690, found 1051.7762.

**Synthesis of 5,5'-(4,4'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4,1-phenylene))dithiophene-2-carbaldehyde (9).**

Compound **5** (0.2 g, 0.20 mmol), compound **8** (0.056 g, 0.496 mmol), anhydrous $K_2CO_3$ (0.069 g, 0.496 mmol), pivalic acid (0.0061 g, 0.060 mmol) and $Pd(OAc)_2$ (0.0022 g, 0.0099 mmol) were stirred in

anhydrous DMA (2 mL) for 4 h at 100 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of NaCl. The precipitate was extracted with EtOAc. The combined organic layer was washed with distilled water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography on silica gel first with *n*-hexane/ $CH_2Cl_2$ (4:1, v/v) and then with *n*-hexane/EtOAc (5:1, v/v) to give the compound **9** as red solid. Yield: 0.068 g, (32%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 9.91 (s 2H), 7.84 (d, *J* = 8.4 Hz, 4H), 7.73 - 7.75 (dd, 6H), 7.46 (d, *J* = 3.9 Hz, 2H), 3.77 (d, *J* = 7.2 Hz, 4H), 1.53-1.54 (m, 2H), 1.09-1.27 (m, 64H), 0.83-0.90 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 182.7, 162.4, 152.5, 147.9, 143.1, 137.3, 134.8, 129.7, 129.0, 126.0, 124.8, 109.8, 55.0, 45.0, 36.9, 31.9, 31.9, 31.2, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 26.0, 22.0, 22.7, 14.2; IR (KBr) ν: 2930, 2830, 2780, 2110, 1665, 1540, 1475, 1130, 1100 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{68}H_{96}N_2O_4S_2$ 1069.6812, found 1069.6930.

**Synthesis of 2,2'-(5,5'-(4,4'-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(thiophene-5,2-diyl))bis(methan-1-yl-1-ylidene)-dimalononitrile (DPPT2CN).**

To the solution of malononitrile (0.18 g, 2.75 mmol) in $CH_2Cl_2$ (135 mL), $Et_3N$ (0.39 mL) was added and stirred for 15 min. The compound **9** (0.49 g, 0.46 mmol) was added to the reaction mixture and stirred at room temperature for 6 h. The reaction was quenched by the addition of water and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with brine and dried over $MgSO_4$. The crude product was recrystallized by using $CH_2Cl_2$ and MeOH to give **DPPT2CN** as dark red solid. Yield: 0.39 g, (57%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 7.84-7.89 (m 6H), 7.80 (s, 2H), 7.75-7.77 (m, 4H), 7.51-7.52 (d, *J* = 3.9 Hz, 2H), 3.78 (d, *J* = 7.2 Hz, 4H), 1.53 (m, 2H), 1.09-1.27 (m, 64), 0.83-0.90 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 162.5, 154.5, 150.3, 147.7, 139.7, 135.1, 134.1, 129.8, 126.5, 125.5, 113.9, 113.2, 110.3, 77.9, 45.4, 37.1, 31.9, 31.2, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1; IR (KBr) ν: 2950, 2925, 2850, 2225, 1670, 1575, 1435, 1130, 1085 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{74}H_{96}N_6O_2S_2$ 1165.7036, found 1165.7128.

**Synthesis of 4',4''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)dibiphenyl-4-carbaldehyde (11).**

Compound **5** (1.0 g, 0.99 mmol) and compound **10** (0.58 g, 2.48 mmol) were dissolved in THF (75 mL), then 2 M $K_2CO_3$ solution (9.9 mL) was added and $N_2$ bubbled for 15 min. Then $Pd(PPh_3)_4$ (0.114 g, 0.099 mmol) was added to the reaction mixture and degassed the flask, the resulting mixture was heated at 90 °C for 24 h. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue

was purified by column chromatography on silica gel with *n*-hexane/EtOAc (5:1, v/v) to give the **11** as red solid. Yield: 0.65 g, (62%); $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 10.10 (s 2H), 8.01 (d, *J* = 8.4 Hz, 4H), 7.94 (d, *J* = 8.4 Hz, 4H), 7.79-7.84 (dd, 8H), 3.82 (d, *J* = 7.2 Hz, 4H), 1.60 (m, 2H), 1.11-1.27 (m, 64H), 0.83-0.90 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 191.8, 162.7, 148.1, 145.7, 141.9, 135.7, 130.4, 129.4, 128.5, 127.6, 127.6, 110.1, 45.3, 37.1, 31.9, 31.9, 31.2, 29.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 26.1, 22.7, 22.7, 14.1; IR (KBr) ν: 2950, 2930, 2885, 2700, 2650, 1700, 1540, 1460, 1100 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{72}H_{100}N_2O_4$ 1057.7683, found 1057.7760.

**Synthesis of 2,2'-(4',4''-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(biphenyl-4',4-diyl))bis(methan-1-yl-1-ylidene)dimalononitrile (DPPPh2CN).**

To the solution of malononitrile (0.16 g, 2.38 mmol) in $CH_2Cl_2$ (115 mL), $Et_3N$ (0.34 mL) was added and stirred for 15 min. The compound **11** was added to the reaction mixture and stirred at room temperature for 6 h. The reaction was quenched by the addition of water and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with brine and dried over $MgSO_4$. The crude product was recrystallized by using $CH_2Cl_2$ and MeOH to give **DPPPh2CN** as dark red solid. Yield: 0.27 g, (60%). $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ 8.01 (d, *J* = 8.7 Hz, 4H), 7.94 (d, *J* = 8.7 Hz, 4H), 7.84 (s, Hz, 2H), 7.75-7.81 (m, 8H), 3.82 (d, *J* = 7.2 Hz, 4H), 1.59 (m, 2H), 1.12-1.27 (m, 64H), 0.83-0.90 (m, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ; 161.7, 157.9, 147.0, 144.7, 140.0, 130.5, 129.4, 128.5, 128.0, 127.0, 126.5, 112.7, 111.7, 109.3, 81.6, 44.4, 36.1, 30.9, 28.9, 28.6, 28.5, 28.3, 25.1, 21.7, 21.6, 13.1; IR (KBr) ν: 2950, 2925, 2850, 2230, 1675, 1585, 1460, 1100 cm$^{-1}$; HRMS (FAB+H$^+$) calcd for $C_{78}H_{100}N_6O_2$ 1153.7908, found 1153.7999.

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