

# Organic & Biomolecular Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

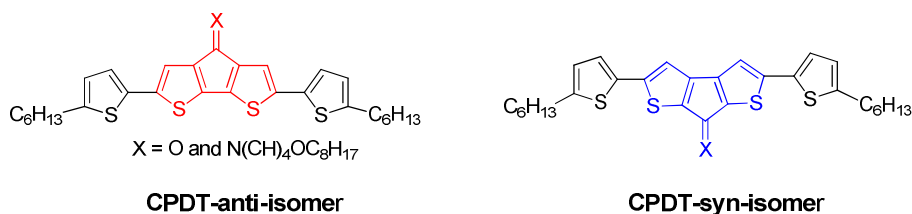
Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Effect of Heteroatom and Conformation on Optoelectronic Properties of Cyclopentadithiophenes Derivatives

Sompit Wanwong, Ambata Poe, Ganapathy Balaji, and S. Thayumanavan\*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

## Abstract

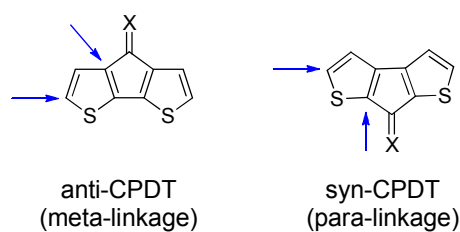


Cyclopentadithiophene (CPDT) derivatives with different heteroatom conformations have been synthesized. The optical, electrochemical and charge transport properties of these molecules are reported. The CPDT-anti-ketone not only exhibits the lowest optical and electronic bandgaps, but also exhibits reasonable hole mobility,  $3 \times 10^{-3} \text{ cm}^2/(\text{V s})$ . Changing the carbonyl conformation to the syn position or incorporating with the imine functionality results in a blue-shift in the lower energy band of the absorption spectrum indicative of the increased bandgaps.

Cyclopentadithiophene (CPDT) derivatives have attracted research interest owing to their potential to serve as a building block for the construction of organic semiconductors.<sup>1</sup> The fused ring system and planar geometry lead to enhanced conjugation, lower bandgap and increase in

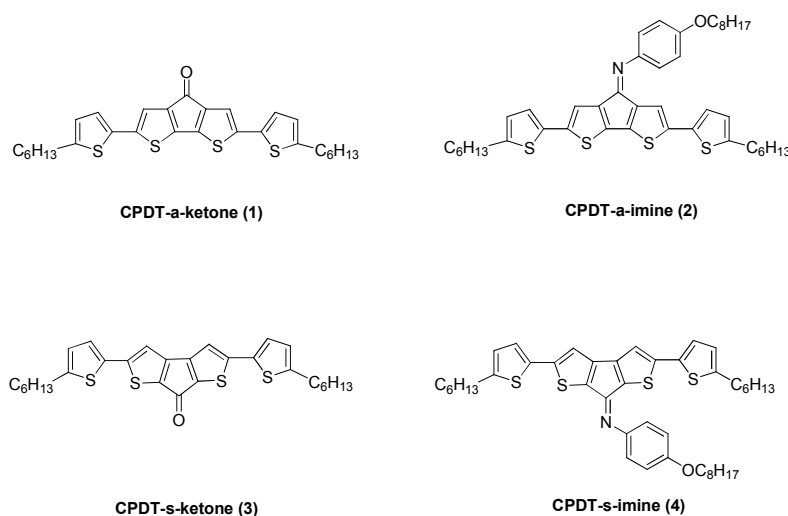
intermolecular interaction.<sup>1a, 2</sup> The CPDT unit has two locations where substituents can be incorporated: (a) the  $\alpha$ -positions of thiophenes, and (b) the bridgehead position.<sup>3</sup> Varying the substituents at either of these positions provides the opportunity to tune the electronic properties of the system. For example, it has been shown that incorporation of electron-withdrawing functionalities, such as carbonyl and dicyanomethylene, at the bridgehead position of CPDT renders the system more electron deficient, and often results in reduced bandgap.<sup>3c, 4</sup> In addition to exploring CPDT based molecules for photovoltaics through optical tuning, these molecules also have potential as semiconductors in thin film field effect transistors.<sup>1a, 5</sup>

Although many CPDT-based molecules have low electrochemical bandgaps, the optical absorption in the longer wavelength region (red edge) is typically low. This may be related to the meta-linkage of the ketone or dicyanomethylene group with the thiophene unit, in which the pi-conjugation may not extend to the heteroatom of the bridgehead.<sup>3c, 4a, 6</sup> We hypothesized that the para-conjugated isomer, where sulfur atoms and the bridgehead are located on the same side, may provide a pathway to increased red-edge absorption. The reason for this expectation stems from the possibility that the keto-group in the para-isomer affords the opportunity to provide a keto-cyanine type conjugation.<sup>7</sup> Therefore, we targeted the anti (meta-linkage) and syn (para-linkage) isomer of CPDT compounds (Chart 1) to understand the effect of heteroatom conformation on the optical and electrical properties.



**Chart 1.** Model of anti-CPDT and syn-CPDT

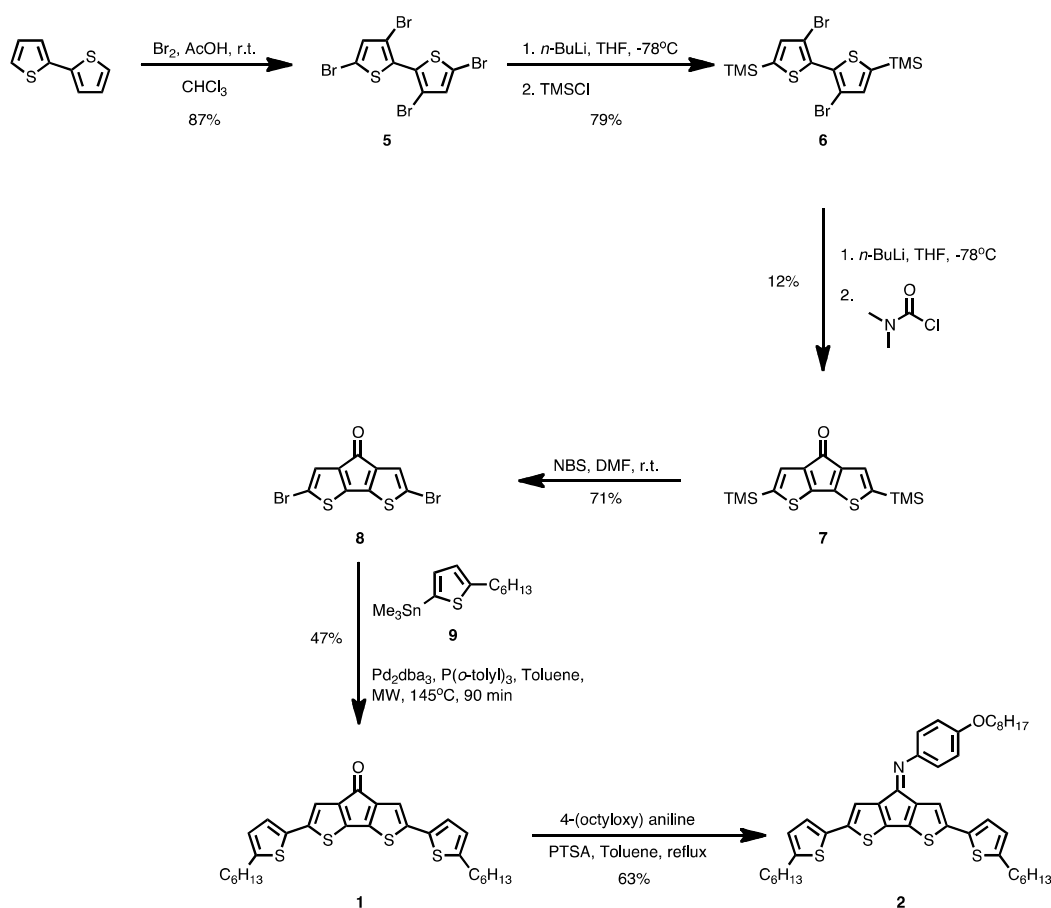
In our work here, ketone and imine will serve as the bridgehead functionalities. Incorporation of imine group will provide extended conjugation at the bridgehead along with *n*-octyl solubilizing group. The bridgehead and the sulfur atoms of anti-CPDT molecules are located on the opposite side, while the bridgehead and the sulfur atoms of syn-CPDT molecules are located on the same side. The structures of the CPDT derivatives are shown in Figure 1 and the synthetic routes of the target molecules are described in Schemes 1 and 2.



**Figure 1.** Chemical structure of CPDT derivatives 1-4.

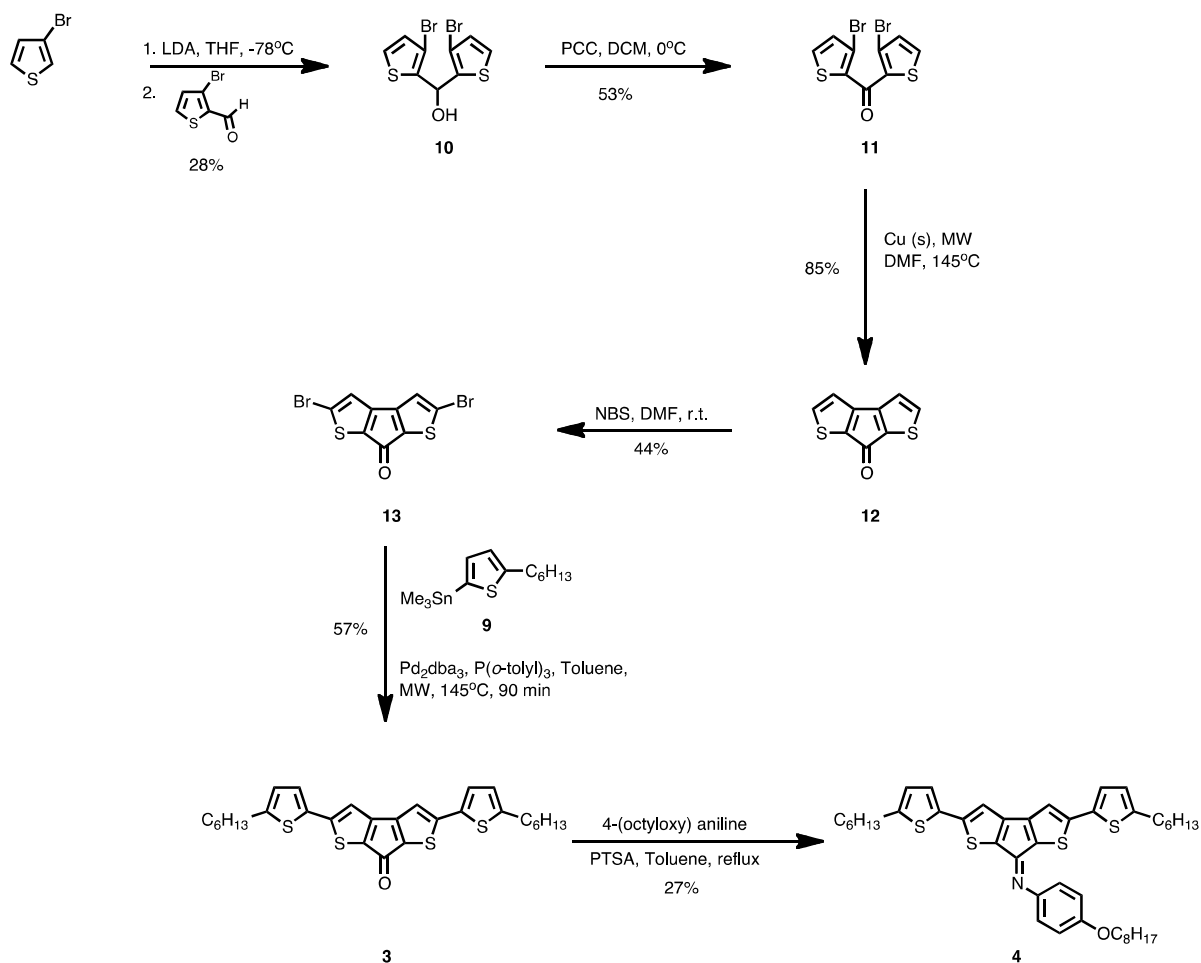
The anti-CPDT derivatives were synthesized according to the procedures shown in Scheme 1.<sup>8</sup> Treatment of bithiophene using bromine/acetic acid yielded the tetrabromobithiophene derivative **5** in 91 % yield. The bromine moieties at the  $\alpha$ -position of **5** were first protected as trimethylsilyl groups. This was achieved through bromine-lithium exchange with only two equivalents of *n*-BuLi, which selectively converts the  $\alpha$ -bromo functionalities to the

corresponding lithio derivative. The dilithio intermediate was treated with trimethylsilyl chloride to obtain **6** in 46% yield. Compound **6** was then treated with two more equivalents of *n*-BuLi to generate the corresponding  $\beta$ -dilithio intermediate, which was treated with *N,N*-dimethylcarbamoyl chloride to obtain the ketone **7** in only 15% yield. The TMS groups were then converted to bromo moieties to afford the dibromide derivative **8** using *N*-bromosuccinimide (NBS). Compound **8** was then coupled with 2-hexyl-5-trimethylstannyl thiophene **9** using Pd(II)-catalyzed Stille coupling reactions in microwave to obtain targeted CPDT- $\alpha$ -ketone molecule **1** in 47% yield. Condensation of **1** with 4-(octyloxy)aniline gave CPDT- $\alpha$ -imine molecule **2** in 63% yield.



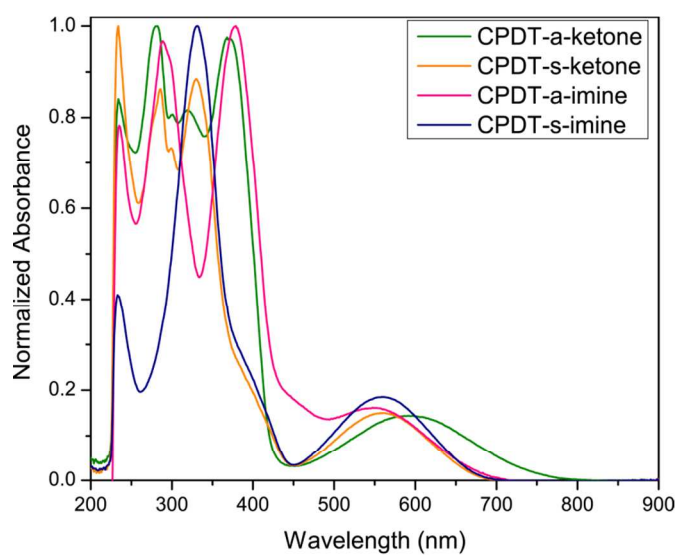
**Scheme 1.** Synthesis of CPDT- $\alpha$ -ketone and CPDT- $\alpha$ -imine

The syn-CPDT derivatives were synthesized starting from lithiation of 3-bromothiophene and subsequent treatment with 3-bromothiophene-2-carboxaldehyde to obtain **10** in 28 % yield. The alcohol **10** was then oxidized by PCC to obtain **11** in 82 % yield. Microwave assisted-Ullman coupling reaction of **11** using Cu powder as a catalyst provided syn-CPDT **12** in good yield. The bromination of **12** using NBS afforded **13** in 65 % yield. Compound **13** was coupled with 2-hexyl-5-trimethyl thiophene **9** using Pd (II) catalyzed Stille coupling reactions via microwave irradiation to obtain **3** with 57 % yield. Condensation of **3** with 4-(octyloxy)aniline gave compound **4** in 30% yield.



**Scheme 2.** Synthesis of CPDT-s-ketone and CPDT-s-imine

To determine the effect of the position and functionality of the bridgehead on the optical absorption and the optical energy gaps ( $E_{g,opt}$ ), linear absorption spectra of the CPDT derivatives were measured in  $\text{CH}_2\text{Cl}_2$  solution (Figure 2). The optical band gap is determined from the onset of the long-wavelength absorption edge ( $E_{g,opt} = 1240/\lambda_{onset}$ ).



**Figure 2.** UV-vis spectra of CPDT derivatives in  $\text{CH}_2\text{Cl}_2$  solution

**Table 1.** Summary of optical absorption maxima, absorption coefficient and the optical bandgaps of CPDT derivatives

Compounds	$\lambda_{max}$ (nm)	$\epsilon_{max}$ ( $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{onset}$ (nm)	$E_{g,opt}$ (eV)
<b>CPDT-a-ketone</b>	234, 281, 320, 368, 592	4.1, 4.9, 4.0, 4.7, 0.7	780	1.59
<b>CPDT-s-ketone</b>	234, 286, 330, 559	4.8, 4.1, 4.2, 0.7	699	1.77
<b>CPDT-a-imine</b>	235, 289, 379, 547	6.7, 8.2, 8.5, 1.3	711	1.74
<b>CPDT-s-imine</b>	238, 332, 559	0.4, 1, 0.2	700	1.77

All molecules exhibited a relatively broad low energy absorption band and several higher energy bands. **CPDT-a-ketone** exhibits absorption bands that are most red-shifted; the low energy band of this molecule had the onset around 780 nm with the  $\lambda_{\text{max}}$  of this band centering around 592 nm. Changing the carbonyl bridgehead from the anti- to the syn-position results in a significant blue shift ( $\Delta\lambda_{\text{max}} = 33$  nm), as discerned from comparing **CPDT-a-ketone** with **CPDT-s-ketone**. The low energy absorption band of the latter molecule centers around 599 nm with the onset at 699 nm. The change in absorption wavelength maxima can be attributed to the less conjugated quinoid form of **CPDT-s-ketone**, as compared to **CPDT-a-ketone**. Nonetheless, the fact that the interruption of the CPDT conjugation results in only a 33 nm blue shift in the absorption also suggests that the keto-cyanine type contribution to the optical properties exists. It is noteworthy however that this positional variation had no effect on the absorption coefficients of the low energy bands (Table 1).

Next, we investigated the effect of the imine substitution upon the optical properties of the molecules. Incorporation of the imine group, especially an aromatic imine, offers another opportunity to evaluate the possibility of the keto-cyanine contribution to the optical properties of the molecule. Here, the charge distribution possibility into the aromatic ring of the aniline moiety could provide an enhanced contribution from the cyanine type structure. Upon analyzing the absorption spectra of these molecules, we found that the bridgehead in the anti-isomer, **CPDT-a-imine**, results in a large blue-shift ( $\Delta\lambda_{\text{max}} = 45$  nm) with a higher absorption coefficient compared to **CPDT-a-ketone**. Interestingly however, in the case of the syn-isomer, the imine substitution had very little effect on the absorption spectrum of the molecule, compared to the corresponding ketone (Table 1). This supports the possibility that the cyanine-type contribution allows for the syn-isomers to exhibit low energy absorption bands.



Next, the electrochemical properties of the compounds were analyzed using cyclic voltammetry. The estimated HOMO and LUMO energy levels are summarized in Table 2. The electrochemical band gaps of all the CPDT molecules were found to be similar to their optical band gaps (Table 1). Indeed, **CPDT-a-ketone** exhibited the lowest band gap of 1.53 eV and the effect of incorporating imines was also consistent with the photophysical measurements shown above.

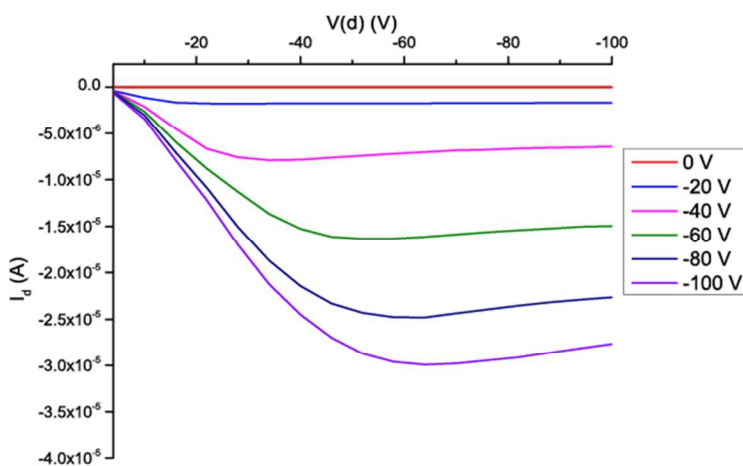
**Table 2.** Summary of electrochemical data for **CPDT** derivatives

Compounds	HOMO (eV)	LUMO (eV)	$E_{g, \text{elec}}$ (eV)
<b>CPDT-a-ketone</b>	-5.08	-3.55	1.53
<b>CPDT-s-ketone</b>	-5.27	-3.46	1.81
<b>CPDT-a-imine</b>	-5.22	-3.44	1.78
<b>CPDT-s-imine</b>	-5.23	-3.43	1.80

The cyclic voltammograms were recorded in anhydrous  $\text{CH}_2\text{Cl}_2$  with 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) at a scan rate of 50 mV/s. The electrochemical potentials were estimated from the onset of the oxidation and reduction peaks. All voltammograms were normalized to  $E_{1/2}(\text{Fc}/\text{Fc}^+)$ . The HOMO and LUMO energy levels were calculated using the following relationship;  $\text{HOMO} = -(E_{\text{ox, onset}} + 4.8) \text{ eV}$  and  $\text{LUMO} = -(E_{\text{red, onset}} + 4.8) \text{ eV}$ .

Finally, we were interested in investigating the charge carrier mobility of these CPDT derivatives using bottom-contact field-effect transistors.<sup>1b, 9</sup> An example of the output characteristics of CPDT and a summary of the mobilities of all the semiconductors are shown in Figure 3 and Table 3, respectively. All molecules were tested for both hole and electron conductivity and the thin film was prepared by spin-cast the molecules on the substrate. All CPDT molecules exhibited only hole mobility. The mobility of **CPDT-a-ketone** was found to be  $0.003 \text{ cm}^2/(\text{V s})$ . Changing the position of the carbonyl group from the anti to the syn-position

results in dramatically decreased mobility to  $6.9 \times 10^{-6} \text{ cm}^2/(\text{V s})$  as observed for **CPDT-s-ketone**. We do not fully understand the reason for such a large change in mobility, but these are usually attributed to the differences in molecular packing.<sup>10</sup> The mobilities of **CPDT-a-imine** and **CPDT-s-imine** were found to be  $1.4 \times 10^{-5} \text{ cm}^2/(\text{V s})$  and  $2.2 \times 10^{-9} \text{ cm}^2/(\text{V s})$ , respectively. Overall, the syn-isomers show significantly lower mobilities compared to the corresponding anti-isomers. In addition, replacing the ketone group with the imine group lowered the mobility. Thus, the syn-imine exhibited the lowest mobility, since it has the unfavorable conformation and functionality. The significant decrease in mobility in imines may be attributed to the insulation from the long alkyl chain of the imine units that prevent efficient intermolecular packing in the solid-state. Moreover, the effect of annealing was studied for all compounds. **CPDT-s-ketone** exhibited the highest enhancement in mobility from  $6.9 \times 10^{-6} \text{ cm}^2/(\text{V s})$  to  $6.4 \times 10^{-4} \text{ cm}^2/(\text{V s})$ . However, this mobility was still lower than that of corresponding anti-isomer, **CPDT-a-ketone**. Also, the thermal annealing effect is not significant for other CPDT derivatives. Our attempts to grow single-crystals of these semiconductor molecules were not successful. When analyzed by differential scanning calorimetry (DSC), **CPDT-a-ketone** is the only molecule that clearly exhibited a crystalline phase (see supporting information).



**Figure 3.** Output characteristics of **CPDT-a-ketone** at  $W/L = 500$ **Table 3.** Charge mobility of CPDT derivatives

Compounds	$\mu_h$ [ $\text{cm}^2/(\text{V s})$ ], As cast	$\mu_h$ [ $\text{cm}^2/(\text{V s})$ ], annealed 80 °C
<b>CPDT-a-ketone</b>	$(3.0 \pm 0.8) \times 10^{-3}$	$(8.2 \pm 0.7) \times 10^{-3}$
<b>CPDT-s-ketone</b>	$(6.9 \pm 3.0) \times 10^{-6}$	$(6.4 \pm 2.3) \times 10^{-4}$
<b>CPDT-a-imine</b>	$(1.4 \pm 0.9) \times 10^{-5}$	$(1.3 \pm 0.9) \times 10^{-5}$
<b>CPDT-s-imine</b>	$(2.2 \pm 0.6) \times 10^{-9}$	no mobility

In summary, four CPDT cores were designed and synthesized to study the effect of heteroatom conformation on optoelectronic properties of CPDT derivatives. We found that **CPDT-a-ketone** exhibits the lowest optical and electrical band gaps and highest hole mobility,  $0.003 \text{ cm}^2/(\text{V s})$ . On the other hand, changing the carbonyl conformation to the syn-position or replacing it with the imine group results in no significant change of the absorption coefficient in the lower energy region. However, these changes do result in increased optical and electrochemical bandgaps, as well as reduced charge carrier mobilities.

**Acknowledgement.** The authors thank the U.S. Department of Energy, Basis Energy Science for funding through the PHaSE- Energy Frontier Research Center at UMass Amherst. The authors also thank Army Research Office for financial support.

**Supporting Information Available:** Experimental procedures, cyclic voltammograms, thermal analyses are available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (a) P. T. Coppo, M. L., *J. Mater. Chem.*, 2005, **15**, 1123-1133; (b) A. R. F. c. Murphy, J. M. J., *Chem. Rev.*, 2007, **107**, 1066-1096; (c) T. L. F. Lambert, J. P., *J. Chem. Soc., chem. commun*, 1991, 752-754; (d) J. P. L. Ferraris, T. L., *J. Chem. Soc., Chem. Commun*, 1991, 1268-1270; (e) M. H. D. Yoon, S. A.; Russell, M. T.; Facchetti, A.; Marks, T. J., *Chem. Mater.*, 2007, **19**, 4864-4881; (f) J. Y. L. Kim, K.; Coates, N. E.; Moses, D. Nguyen, T. Q.; Dante, M.; Heeger, A. J., *Science*, 2007 **317**, 222-225; (g) D. L. Niedzialek, V.; Dudenko, D.; Shu, J.; Hansen, M. R.; Andreasen, J. W.; Pisula, W.; Müllen, K.; Cornil, J.; Belijonne, D., *Adv. Mater.*, 2013, **25**, 1939-1947.
- (a) C. H. H. Chen, C. H.; Dubosc, M.; Cheng, Y. J.; Hsu, C. S., *Macromolecules*, 2010, **43**, 697-708; (b) H. N. C. Tsao, D. M.; Park, I.; Hansen, M. R.; Mavrinskiy, A.; Yoon, D. Y.; Graf, R.; Pisula, W.; Spiess, H. W.; Müllen, K., *J. Am. Chem. Soc.*, 2011, **133**, 2605-2612; (c) H. Y. Zhou, L.; You, W., *Macromolecules*, 2012, **45**, 607-632; (d) P. C. Coppo, C. D.; Yeates, S. G.; Turner, M. L., *Macromolecules*, 2003, **36**, 2705-2711; (e) G. K. Balaji, T. S.; Keerthi, A.; Pelle, A. M. D.; Thayumanavan, S.; Valiyaveetil, S., *Org. Lett.*, 2011, **13**, 18-21; (f) M. H. R. Nurmawati, R.; Ajikumar, P. K.; Sindhu, S.; Cheong, F. C.; Sow, C. H.; Valiyaveetil, S., *Adv. Funct. Mater.*, 2006, **16** 2340-2345.
- (a) J. Rocali, *Chem. Rev.*, 2007, **97**, 173-205; (b) S. O. Barlow, S. A.; Lancaster, K.; Getmanenko, Y. A.; Mason, R.; Coropceanu, V.; Bre'das, J. L.; Marder, S. R., *J. Phys. Chem. B*, 2010, **114**, 14397-14407; (c) J. R. K. Reddy, T.; Balaji, G.; Chandrasekaran, A.; Thayumanavan, S., *J. Phys. Chem. Lett.*, 2011, **2**, 648-654; (d) J. D. K. Azoulay, Z. A.; Wong, B. M.; Bazan, G. C., *Macromolecules*, 2013, **46**, 1337-1342.
- (a) H. Y. Zhou, L.; You, W., *Macromol. Rapid. Commun*, 2012, **33**, 1162-1177; (b) P. C. Willot, L. D.; Koeckelberghs, G., *Macromol. Chem. Phys*, 2012, **213**, 1216-1224; (c) Z. W. Zhu, D.; Gaudiana, R.; Morana, M.; Mühlbacher, D.; Scharber, M.; Brabec, C., *Macromolecules*, 2007, **40**, 1981-1986.
- (a) M. H. D. Yoon, S. A.; Russell, M. T.; Facchetti, A.; Marks, T. J., 2007, **19**, 4864-4881; (b) M. K. Horie, J.; Yu, C. Y.; Majewski, L. A.; Chang, S. W.; Kirkpatrick, J.; Tuladhar, S. M.; Nelson, J.; Saundersh, B. R.; Turner, M. L., *J. Mater. Chem.*, 2012, **22**, 381-389.
- (a) B. Y. Pal, W. C.; Yang, J. S.; Chao, C. Y.; Hung, Y. C.; Lin, S. T.; Chuang, C. H.; Chen, C. W.; Su, W. F., *Macromolecules*, 2008, **41**, 6664-6671; (b) J. S. L. Yang, K. L.; Tu, C. W.; Hwang, C. Y., *J. Phys. Chem. A*, 2005, **109**, 6450-6456.
- (a) R. D. Jansen-van Vuuren, A. Pivrikas, A. K. Pandey and P. L. Burn, *J. Mater. Chem. C*, 2013, **1**, 3532; (b) U. Mayerhoffer, M. Gsanger, M. Stolte, B. Fimmel and F. Wurthner,

*Chem. Eur. J.*, 2013, **19**, 218-232; (c) N. Kedia, A. Sarkar, M. Shannigrahi and S. Bagchi, *Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy*, 2011, **81**, 79-84.

8. (a) B. C. P. Popere, A. D. M.; Poe, A.; Balaji, G.; Thayumanavan, S., *Chem. Sci*, 2012, 3093-3102; (b) K.-C. H. Li, Y., -C.; Lin, J., -T.; Yang, C.,-C.; Wei, K. -H.; Lin, H., -C., *J. Polym. Sci. A Polym. Chem.*, 2009, **43**, 2073; (c) K. S. Masatoshi, T.; Yoshiro, Y., *Chemistry Letters* 1993, **3**, 533.

9. (a) Y. K. Shirota, H., *Chem. Rev.*, 2007, **107**, 953-1010; (b) Y. Y. Guo, G.; Liu, Y., *Adv. Mater.*, 2010, **22**, 4427-4447.

10. (a) H. Z. Moon, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z., *J. Am. Chem. Soc.*, 2004, **126**, 15322-15323; (b) C. D. Wang, H.; Hu, W.; Liu, Y.; Zhu, D., *Chem. Rev.*, 2012, **112**, 2208-2267; (c) J. E. E. Anthony, D. L.; Parkin, S. R., *Org. Lett.*, 2002, **4**, 15-18; (d) G. R. R. Hutchison, M. A.; Marks, T. J., *J. Am. Chem. Soc.*, 2005, **127**, 16866-16881; (e) H. W. Dong, C.; Hu, W., *Chem. Commun.*, 2010, **46**, 5211-5222; (f) M. M. P. Pyne, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N., *J. Am. Chem. Soc.*, 2005, **127**, 4986-4987