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Synthesis and Characterization of Urethane Side Chain Substituted Diketopyrrolopyrrole

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Abstract

The synthesis of Diketopyrrolopyrrole (DPP) having secondary interaction in the side chain explores its possibility to use in electronic and sensing applications. Herein we report easy method to engineer side chains of DPP. The hydrogen bonding is introduced on the side chain by substitution of urethane side chains on Diketopyrrolopyrrole ($\text{DPP}_{\text{urethane}}$).The urethane side chain comprises a branched alkyl chain with good yields and purities. The $\text{DPP}_{\text{urethane}}$ characterized by NMR and IR, optical properties along with energy minimized structure were studied.

Keywords: Diketopyrrolopyrrole; Chromophore; Hydrogen bonding, Urethane.

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1. Introduction

Diketopyrrolopyrrole (DPPs) are known as high performance organic pigments used in paints, inks, lacquers, printings and plastics [1-3]. The different color shade can be achieved ranging from yellowish green to bluish red, depending on the aryl group attached to the chromophore unit [4-6]. The DPPs are resistant to chemicals have good thermal stability, light and weather fastness, indicating high quality of color retention. Apart from this, DPP has strong emission in the visible region with a high fluorescence quantum yield [7-9].

The DPP based soluble conjugated molecules (sCM) have been widely applied for fabrication of electronic devices such as organic field effect transistor (OFET) [10-13], organic photovoltaic devices (OPV) [14,15]. The DPP molecule is virtually planar, however degree of planarity soluble conjugated molecule (sCM) depends upon the type of

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heterocyclic ring attached [16,17].The heterocyclic ring not only alters the planarity but influences the solid state microstructure [18,19]. Thus, solid state structure and optical properties of DPPs depend upon molecular structure. These can also be influenced by supramolecular interaction such as π-π stacking and hydrogen bonding etc. Nevertheless, un-substituted DPPs are insoluble in most common organic solvents, except in polar aprotic solvents. To use DPPs in electronic devices, it is necessary to functionalize the DPP chromophore in order to prepare soluble and film forming compounds. To increase the solubility, the NH group of the DPP unit is substituted long and branched alkyl side chain [20,21]. Hydrophilic side chain substituted DPP polymers have showed excellent charge transport, but limits the solubility of these polymers [22,23]. Herein, we report the synthesis of $DPP_{urethane}$ comprising urethane functionality in the side chain. The urethane moiety in the side chain is substituted with branched alkyl chain. The $DPP_{urethane}$ chromophore is characterized using ^{1}HNMR, IR and UV. We believe that $DPP_{urethane}$ may be the choice of material for synthesis of high charge carrier mobility polymers.

2. Materials and Synthesis

1 bromoundecanoic acid and 2 octyldodecanol were purchased from TCI chemicals, and diketopyrrolopyrrole (DPP) was synthesized as reported procedure. K_2CO_3, NaN_3, iodine and ethyl chloroformate were bought from local supplier (Avra chemicals). The anhydrous DMF was prepared in the laboratory. All the compounds were purified by coloumn chromatography using silica gel; reprecipitation and recrystallization were performed in the purification of final products only. ^{1}HNMR and ^{13}C NMR spectra were measured on Brukerarx 400 MHz and 100 MHz AVANS spectrometer, respectively. UV-Vis spectra were recorded using a Perkin Elmer Lambda -35 UV-Vis spectrometer and band gap were calculated by onset of low energy peak using formula band gap=1245/λmax(onset).

2.1. *Synthesis of C10-urethane*

Compound 1 (5 g, 17 mmol) was dissolved in anhydrous toluene (50 mL) and heated the mixture at 70 °C for 1 h followed by addition of a solution of 2 octyldodecanol (5.1 g, 17 mmol) in toluene drop-wise over 15 min. The resulting solution was heated at same temperature for 12 h. The solution was poured into the water and extracted with diethyl ether; the organic layer was washed with brine and dried over Na_2SO_4. The product was purified using column chromatography eluting with ethyl acetate: pet ether (20:80) to get viscous oil (yield 90 %). Fig. 1 is ^{1}H NMR of C10-urethane (400 MHz, $CDCl_3$): δ 4.62 (s, 1H), 3.95 (d, J = 5.3 Hz, 2H), 3.41 (t, J = 6.9 Hz, 2H), 3.16 (d, J = 6.3 Hz, 2H), 1.87 (m, 2H), 1.46 (m, 1H), 1.28 (m, 44H), 0.89 (s, 3H). Fig. 2 is ^{13}C NMR of C10-urethane (50 MHz, $CDCl_3$): δ 157.09, 67.92, 41.41, 37.94, 34.31, 33.12, 32.22, 31.52, 30.30, 29.97, 29.95, 29.92, 29.88, 29.72, 29.66, 29.63, 29.03, 28.45, 27.04, 22.99, 14.42.

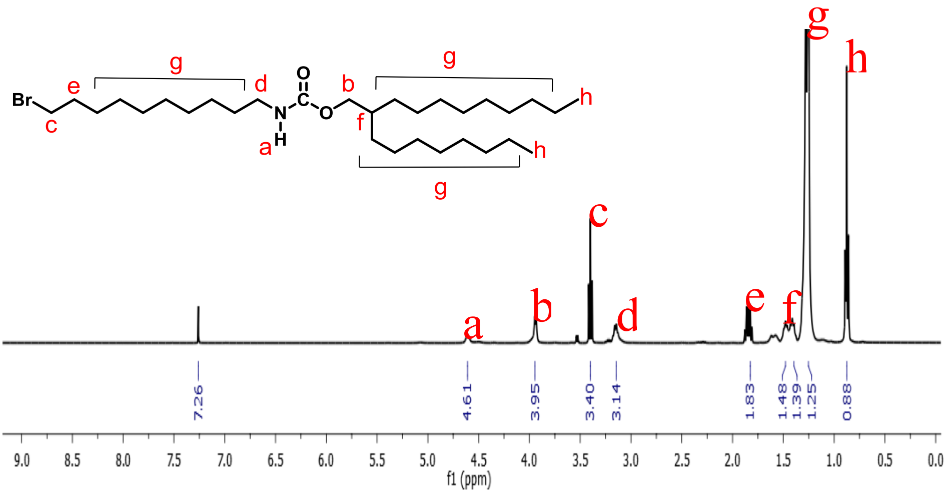


Fig. 1. ^{1}HNMR of C10-urethane.

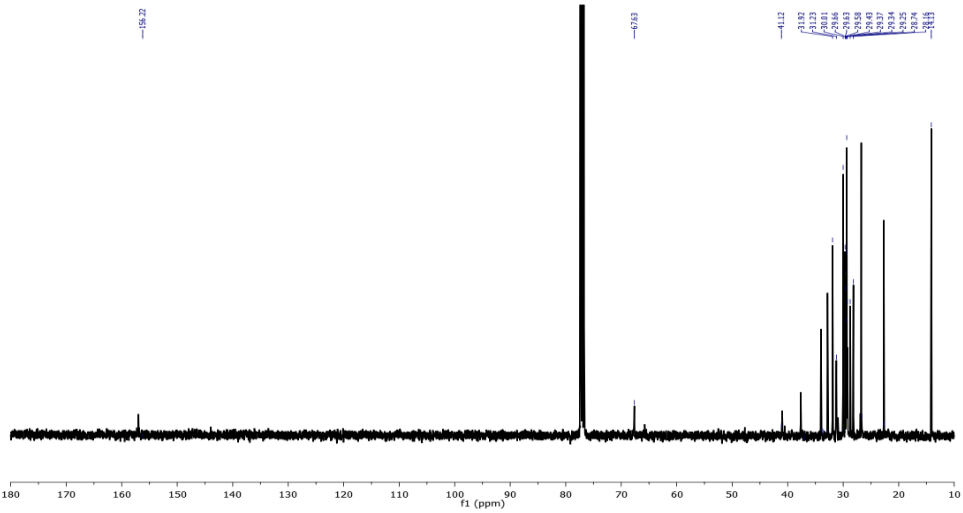


Fig. 2. ^{13}C NMR of C10-urethane.

2.2. *Synthesis of DPP$_{urethane}$*

DPP (1 g, 3 mmol) was added into the mixture of K_2CO_3 (0.15 g, 8.3 mmol) and anhydrous DMF then heated the solution at 100 °C for an hour under argon atmosphere. The solution of compound 2 (4.5 g, 8.3 mmol) in anhydrous DMF (30 mL) was added to the reaction mixture slowly. The resulting solution was heated at 100 °C for 24 h. The reaction mixture was allowed to become cool and then added in water, then extracted with dichloromethane. The organic layer was washed with brine for two-three times and dried over Na_2SO_4. The product was purified using silica gel chromatography eluting with dichloromethane: hexane (50:50) to get red solid (yield 65 %). Fig. 3 is ^{1}H NMR of $\text{DPP}_{\text{urethane}}$ (400 MHz, chloroform-*d*):δ 8.92 (d, *J* = 3.8 Hz, 2H), 7.64 (d, *J* = 5.0 Hz, 2H), 7.31 – 7.26 (m, 2H), 4.62 (s, 2H), 4.11 – 4.01 (m, 4H), 3.94 (d, *J* = 4.8 Hz, 4H), 3.23 – 3.02 (m, 4H), 1.83 – 1.67 (m, 4H), 1.61 – 1.53 (m, 2H), 1.52 – 1.37 (m, 10H),1.37 – 1.13 (m, 48H), 0.87 (t, *J* = 6.7 Hz, 12H). Fig. 4 is ^{13}C NMR of $\text{DPP}_{\text{urethane}}$ (101 MHz, $CDCl_3$): δ 161.36, 156.95, 140.01, 135.27, 130.69, 129.76, 128.61, 107.68, 77.03, 67.61, 42.21, 41.01, 37.65, 31.93, 31.22, 30.01, 29.95, 29.68, 29.66, 29.63, 29.58, 29.43, 29.36, 29.34, 29.26, 29.20, 26.74.

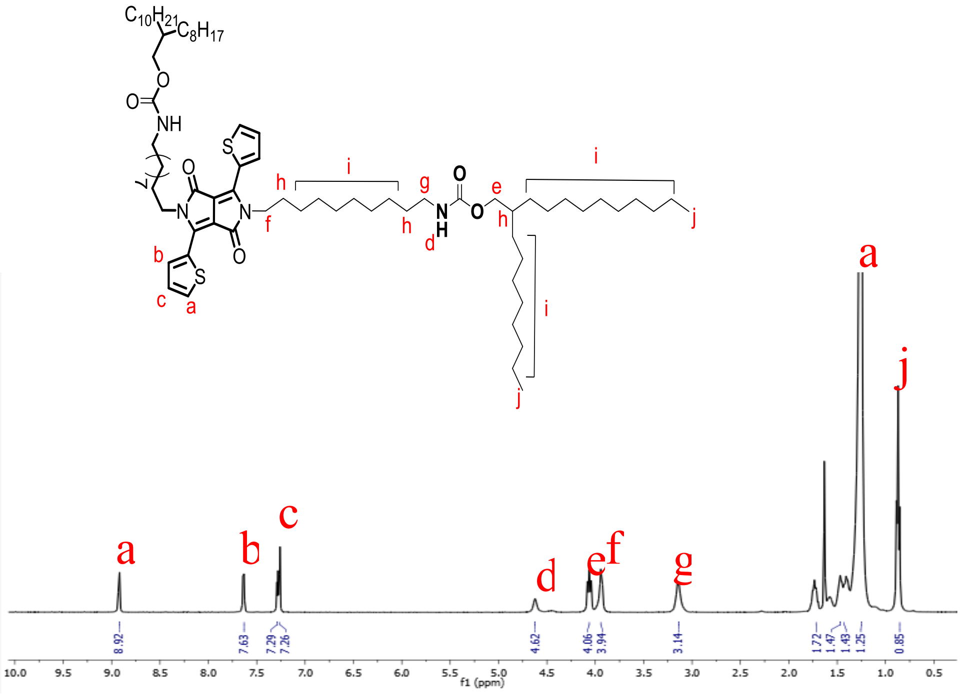


Fig. 3. ^{1}HNMR of $\text{DPP}_{\text{urethane}}$.

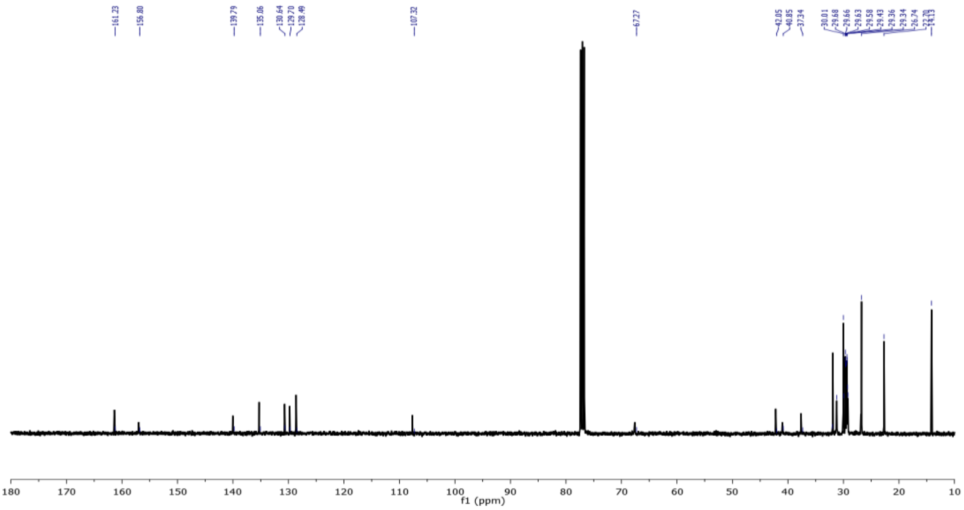
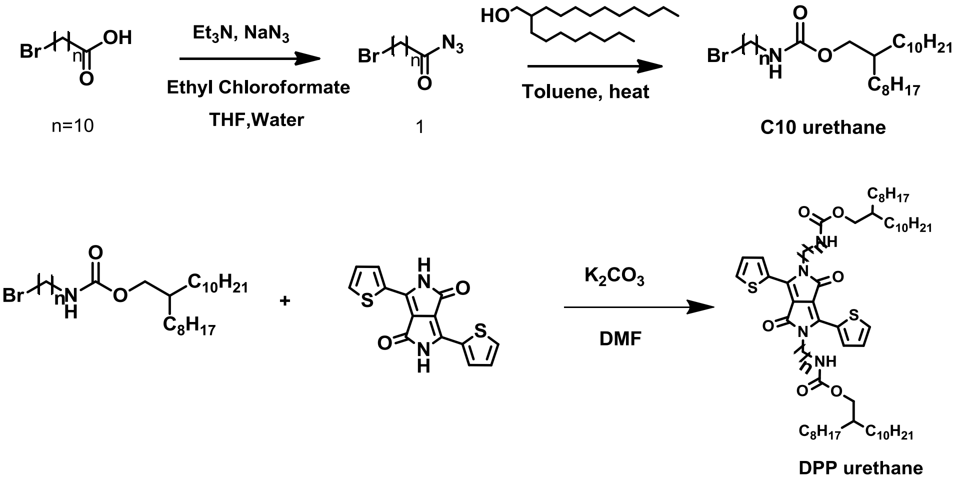


Fig. 4. ^{13}C NMR of $DPP_{urethane}$.

3. Result and Discussion



Scheme 1. Synthesis of side chains and $DPP_{urethane}$.

As shown in scheme, 1 bromoundecanoic acid was converted into acid azide by treating with sodium azide in presence of ethylchloroformate at low temperature to obtained compound **1**. The acid azide to urethane was achieved by Curtis reaction. First, the acid azide **1** was converted into reactive isocynate followed by addition of 2 octyldodecanol to obtained C10-urethane. Please note that the C10-urethane side chain may be difficult to purify due to presence of hydrogen bonding, nevertheless can be purified using silica gel chromatography. DPP was then treated with C10-urethane under basic condition to obtainDPP$_{\text{urethane}}$. TheDPP$_{\text{urethane}}$was purified, usingprocedure mentioned earlier. Final DPP$_{\text{urethane}}$ derivative were characterized using ^{1}H NMR and ^{13}C NMR.

Optical properties of DPP$_{\text{urethane}}$ were recorded in chloroform solvent shown in Fig. 5, The absorption of DPP$_{\text{urethane}}$consist of two peaks, high energy peak at 330 nm which is due to π to π^* transition while low energy peak at 550 nm corresponds to charge transfer between thiophene and DPP shown in Fig. 5 (a). Similarly, the photoluminounce spectra of DPP$_{\text{urethane}}$ was recorded and observed two emission peaks at 570 nm and 615 nm shown in Fig. 5 (b).

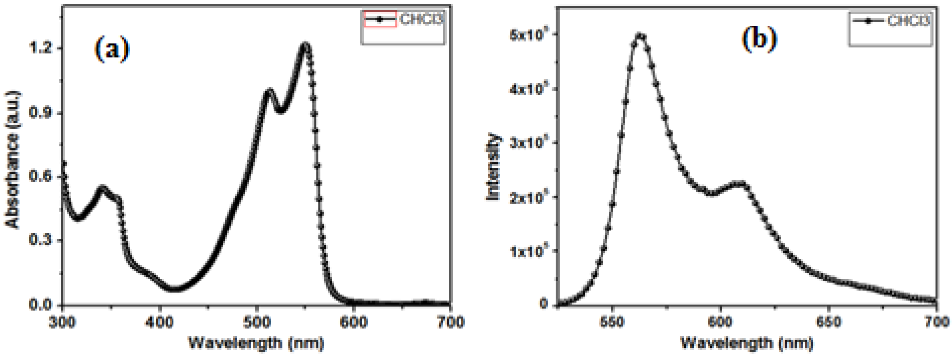


Fig. 5. (a) Absorption spectra of DPP$_{\text{urethane}}$ and (b) Emission spectra of DPP$_{\text{urethane}}$.

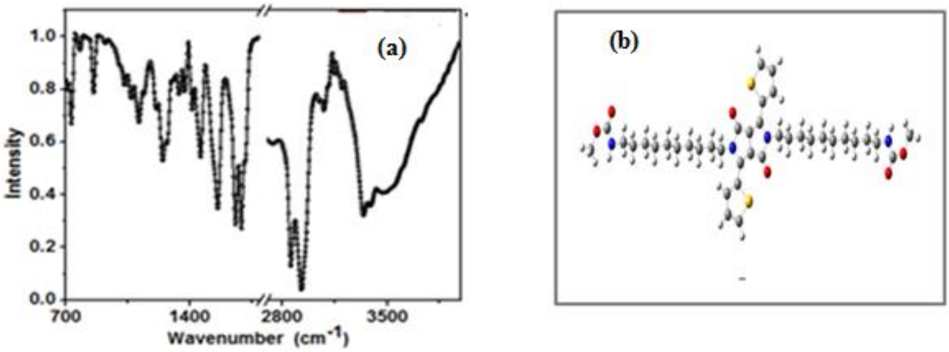


Fig. 6. (a) IR spectra of DPP$_{\text{urethane}}$ and (b) Energy minimized structure of DPP$_{\text{urethane}}$.

An IR spectrum of DPP$_{\text{urethane}}$ is as shown in Fig. 6(a). In the IR spectra, the peaks at1680 and 1710 cm^{-1} correspond to N-H stretching in DPP unit and side chain urethane group respectively. The results of the calculation reported in this work have been obtained using the Gaussian 09 ab initio/DFT quantum chemical simulation package. The geometry optimizations of $DPP_{urethane}$ with truncated terminal alkyl group have been carried out at B3LYP/6- 31G* level Fig. 6(b).

4. Conclusion

In the conclusion, we have synthesized a urethane side chain substituted $DPP_{urethane}$ chromophore. This structural feature may induce strong intermolecular interaction. We characterized $DPP_{urethane}$ using ^{1}HNMR, IR and UV spectroscopy. Since the side chains are substituted with branched alkyl chains, this would be useful monomer to synthesize DPP soluble polymers.

References

1. Z. Hao and A. Iqbal, Chem. Soc. Rev. **26**, 203 (1997). https://doi.org/10.1039/CS9972600203
2. W. W. Bao, R. Li, Z. C. Dai, J. Tang, X. Shi, J. T. Geng, Z. F. Deng, and J. Hua, Front. Chem. **8**, 679 (2020). https://doi:10.3389/fchem.2020.00679
3. J. David, M. Weiter, M. Vala, J. Vynuchal, and J. Kucerik, Dyes and Pigments **89**, 137143 (2011). https://doi.org/10.1016/j.dyepig.2010.10.001
4. T. H. Kim, B. J. Lee, S.O. An, J. H. Lee, and J. H.Choi, Dyes and Pigments **174**, ID 108053 (2020). https://doi.org/10.1016/j.dyepig.2019.108053
5. J. Dhar, N. Venkatramaiah, A. Anitha, and S. Patil, J. Mater. Chem. C **2**, 3457(2014). https://doi.org/10.1039/C3TC32251C
6. D. M. Grzybowski and D. T. Gryko, Adv. Optical Mater. **3**, 280 (2015). https://doi.org/10.1002/adom.201400559
7. G. Zhang, S. Bi, L. Song, F. Wang, J. Yu, and L. Wang, Dyes and Pigments **99**, 779786 (2013). https://doi.org/10.1016/j.dyepig.2013.06.027
8. S. türkçen, H. dinçalp, and G. M. Saltan, J. Molecul. Struct. **1195**, 485493 (2019). https://doi.org/10.1016/j.molstruc.2019.06.022
9. M. Kaur and D. H. Choi, Chem. Soc. Rev. **7**, 58 (2015). https://doi.org/10.1039/C4CS00248B
10. H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney, and I. McCulloch, J. Am. Chem. Soc. **133**, 3272 (2011). https://doi.org/10.1021/ja110619k
11. I. Kang, T. K. An, J. Hong, H. J. Yun, R. Kim, D. S. Chung, C. E. Park, Y. H. Kim, and S. K. Kwon, Adv. Mater. **25**, 524 ((2013).https://doi.org/10.1002/adma.201202867
12. M. S. Chen, O. P. Lee, J. R. Niskala, Alan T. Yiu, C. J. Tassone, K. Schmidt, P. M. Beaujuge, S. S. Onishi, M. F. Toney, A. Zettl, and J. M. J. Frechet, J. Am. Chem. Soc. **135**, 19229 (2013). https://doi.org/10.1021/ja4088665
13. A. Tang, C. Zhan, J. Yao, and E. Zhou, Adv. Mater. **29**, 1600013(2017). https://doi.org/10.1002/adma.201600013
14. W. Li, K. H. Hendriks, M. M. Wienk, and R. A. J. Janssen, Acc. Chem. Res. **49**, 78 (2016). https://doi.org/10.1021/acs.accounts.5b00334
15. W. Li, W. S. C. Roelofs, M. M. Wienk, and R. A. J. Janssen, J. Am. Chem. Soc. **134**, 13787 **(**2012). https://doi.org/10.1021/ja305358z
16. S. Dharmapurikar, S. Chithiravel, M. V Mane, G. Deshmukh, and K. Krishnamoorthy, Chem. Phy. Lett. **695**, 51 (2018). https://doi.org/10.1016/j.cplett.2018.01.052
17. C. Kanimozhi, M. Naik, N. Y. Gross, E. K. Burnett, A. L. Briseno, T. D. Anthopoulos, and S. Patil, J. Phys. Chem. C **118**, 11536 (2014). https://doi.org/10.1021/jp501526h

18. P. E. Hartnett, E. A. Margulies, C. M. Mauck, S. A. Miller, Y. Wu, Y. L. Wu, T. J. Marks, and M. R. J. Wasielewski, J. Phys. Chem. B **120**, 1357 (2016). https://doi.org/10.1021/acs.jpcb.5b10565
19. S. H. Yu, K. H. Park, Y.H. Kim, D. S. Chung, and S. K. Kwon, Macromolecules **50**, 11, 4227 (2017). https://doi.org/10.1021/acs.macromol.7b00624
20. C. K. Lo and J. R. Reynolds, Polymer **99**, 741 (2016). https://doi.org/10.1016/j.polymer.2016.07.066
21. Z. Wang, Z. Liu, L. Ning, M. Xiao, Y. Yi, Z. Cai, A. Sadhanala, G. Zhang, W. Chen, H. Sirringhaus, and D. Zhang, Chem. Mater. **30**, 3090 (2018). https://doi.org/10.1021/acs.chemmater.8b01007
22. J. Mei, K. R. Graham, R. Stalder, S. P. Tiwari, H. Cheun, J. Shim, M. Yoshio, C. Nuckolls, B.Kippelen, R. K. Castellano, and J. R. Reynolds, Chem. Mater. **23**, 2285 (2011). https://doi.org/10.1021/cm1036869
23. C. Kanimozhi, N. Y. Gross, K. W. Chou, A. Amassian, T. D. Anthopoulos, and S. Patil, J. Am. Chem. Soc. **134**, 16532 (2012). https://doi.org/10.1021/ja308211n