Synthesis of 2,5-dibutyl-3,6-dimethyl-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione: A diketopyrrolopyrrole scaffold for the formation of alkenyl-diketopyrrolopyrrole compounds
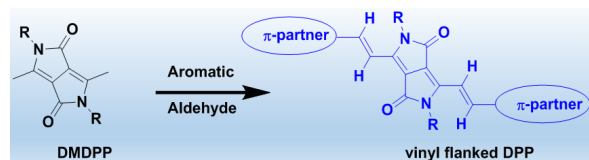
Daijun Feng,[a] George Barton[b] and Colleen N. Scott[a]*

AUTHOR ADDRESS

(a) Department of Chemistry, Mississippi State University, Mississippi State, MS 39762

(b) Department of Natural Sciences, Chemistry, Parkland College, Champaign, IL 61821
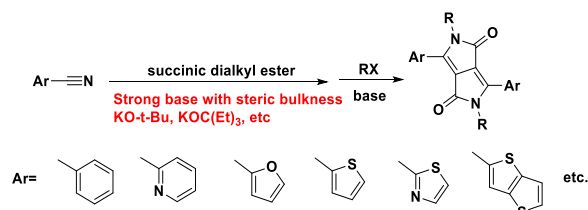
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ABSTRACT: This manuscript describes an unprecedented and efficient synthesis of a new DPP scaffold, 2,5-dibutyl-3,6-dimethyl-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione (**DMDPP**), containing methyl groups at the 3,6-positions as a precursor to prepare 3,6-divinyl substituted DPP compounds. Subsequently, following the synthesis of **DMDPP**, we performed an efficient and mild C-H functionalization of the methyl groups with a variety of aromatic aldehydes to synthesize the first examples of 3,6-divinyl substituted DPP compounds in moderate to good yields.

Since the discovery of diketopyrrolopyrrole (DPP) in 1974 by Farnum et al.,[1] it has become one of the most widely used prototypical π-core for organic electronic devices and high-performance pigments.[2-4] The unique optoelectrical properties and good thermo- and photostability of DPP-based compounds have resulted in their extensive utilization in organic semi-conductive materials[5-6] and fluorescent probes.[3,7-11] For example, several applications of DPP-containing compounds in the area of organic field effect transistors (OFETs),[12-19] organic photovoltaics (OPVs),[20-24] organic light-emitting diodes (OLEDs),[25-29] and dye-sensitized solar cells (DSSC)[30-36] have been reported. Our group is also interested in DPP-containing polymers as ambipolar materials for application in organic electronic devices.[37] Unfortunately, the current conventional synthesis of the DPP core limits the scope of its molecular structure design, since the synthesis is limited to aromatic groups at one or both of the 3,6-positions flanking the DPP core.[38-39] This synthetic limitation prevents other symmetrically, non-aromatic architecture at the 3,6-positions to be prepared and explored. Overcoming this weakness will significantly increase DPP's versatility and functionality.

The conventional synthesis of the DPP core involves heating a mixture of aromatic nitrile (Ar-CN) and succinic acid ester in the presence of a strong base such as potassium *tert*-butoxide (KO^{t}Bu) giving rise to a DPP unit bearing two aromatic rings at the 3,6-positions (Scheme 1).[40-41] The aromatic flanked DPP unit can undergo further functionalization such as transition-metal-catalyzed cross-coupling reactions to extend the π-conjugated backbone depending on the design re-

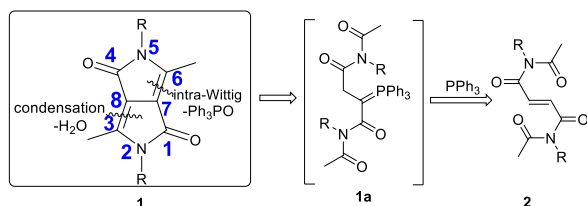**Scheme 1 Conventional synthesis of DPP scaffold**

quirements for the small molecules or polymeric materials. It is not difficult to see that both the tolerance of the aryl groups to the harsh reaction conditions, and the availability of the aromatic nitriles seriously limit the variety of π-conjugated flanked DPP units to only a very few aromatic rings.

To date, no DPP derivatives bearing vinyl groups at the 3,6-positions have been reported, although several symmetrically and unsymmetrically substituted alkyl and aryl derivatives are known.[38,39] Having a vinyl bridge between the DPP unit and the aryl substituent provides an attractive structure for the development of new π-conjugated semi-conductive materials

and pigments. The vinyl substituted DPP structure provides an alternative way to tailor the frontier orbitals of the DPP core due to the weak electron donating ability of the vinyl group, while maintaining the planar and rigid π-conjugated framework. For example, it was shown that the incorporation of double bonds with defined configuration in the backbone of polythiophene led to a lowering of the band gap (E_g) as a result of the extended π-electron delocalization from the decrease in the overall aromatic character of the system.[42-45] Unfortunately, vinyl substituted DPP cannot be reached through the typical methods of preparing vinyl compounds such as, Stille coupling, Suzuki coupling, Wittig reaction, etc., due to the unavailability of the corresponding DPP precursors. Therefore, to achieve this DPP framework, there is a need for a new DPP building block, one that can be easily functionalized to produce vinyl compounds.

Herein, we report an unprecedented and efficient synthesis of a new DPP scaffold, 2,5-dibutyl-3,6-dimethyl-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione (**DMDPP**), using readily available starting materials under fairly mild conditions. This dimethyl substituted DPP core cannot be accessed by the conventional synthesis due to the intolerance of acetonitrile toward the strongly basic condition. To our knowledge, this is the first reported synthesis of this compound. Moreover, the remarkably acidic nature of the methyl group allows us to perform C-H functionalization under transition metal free conditions to produce vinyl functionalities. Accordingly, we performed a variation of the Aldol condensation of **DMDPP** with aryl aldehydes, thereby constructing original vinyl substituted DPP substrates that could be of interest to the organic semiconducting, sensing, and pigment communities.

Scheme 2 Retrosynthesis analysis of DMDPP

In our synthetic approach to **DMDPP**, we envisioned generating it through a tandem bis-cyclization of fumaric acid derivative **2** triggered by triphenylphosphine (PPh$_3$). Thus, triphenyl phosphonium ylide **1a** was imagined as the intermediate of the tandem cyclization, which can be generated by the conjugate addition of PPh$_3$ onto the α,β-unsaturated double bond of compound **2** (Scheme 2).[46] The synthetic route to **DMDPP** is shown in Scheme 3. N, N'-dibutylfumaramide (**3**) was synthesized according to the known procedure,[47] and acylated with pTsOH-isopropenyl acetate to give compound **2** in 75% yield.[48] It was found that neither acetyl chloride, nor acetic anhydride was a good acylating agent for the reaction. Next, we examined the tandem cyclization of compound **2** promoted by PPh$_3$ to give **DMDPP**. We first performed the reaction in both toluene and acetonitrile without any additives (Table 1, entries 1 and 2); however, after 8 h refluxing, only trace amounts of the desired product was isolated with a majority of the starting material remaining. The addition of pTsOH did not improve the yield, while pyridine resulted in a 20% yield of the desired product (Table 1, entries 3 and 4). While pTsOH·Py complex in acetonitrile at 70 °C only gave a 25% yield, increasing the temperature to 100 °C supplied the product in 86% isolated yield after 5 h (Table 1, entries 5 and
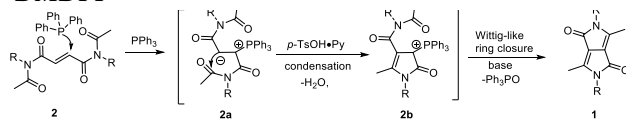
6 respectively). The sensitivity of the reaction towards the solvent and reaction temperature can be seen from the decrease in the yield to 10-25% when the reaction was carried out at 70 °C, or with THF and toluene as the solvents. To demonstrate the scalability and reproducibility of **DMDPP** synthesis, we carried out the reaction on a 5 gram-scale and isolated the product without any significant decrease in the yields. The scope of the substituents on the amide nitrogen is currently being explored.

Table 1 Optimization of the tandem bis-cyclization of compound 2 to form DMDPP

entry	additives	solvent	temp (ºC)	yields (%)
1	-	toluene	110	<5
2	-	CH$_3$CN	100	<5
3	pTsOH	CH$_3$CN	100	<5
4	Py	CH$_3$CN	100	20
5	pTsOH·Py	CH$_3$CN	70	25
6	pTsOH·Py	CH$_3$CN	100	86
7	pTsOH·Py	THF	70	15
8	pTsOH·Py	toluene	110	10

A plausible mechanism for this tandem bis-cyclization is outlined in Scheme 4. Addition of PPh$_3$ to the electron deficient double bond generates a zwitterion intermediate (**2a**) that undergoes an intramolecular condensation to produce intermediate **2b**. This process is similar to the initial step of the tertiary phosphine catalyzed Baylis-Hillman reaction.[49-50] The second five-membered ring closure is perceived to happen through an intramolecular Wittig "like" reaction, where deprotonation at C-7 forms an ylide that reacts with the nearby carbonyl to give the **DMDPP** skeleton (**1**) and triphenylphosphine oxide. The mechanism was probed by mass spectrometry (MS) and ^{1}H NMR. Due to the rapid cyclization of the transient species under the reaction conditions, we were unable to detect the mass peaks for **2a**; however, the mass peak for **2b** and other related species were detected (Support-

Scheme 4 Proposed mechanism for the formation of DMDPP

ing Information). To confirm the formation of the zwitterion intermediate, we performed the reaction with fumaric acid diester, which is unable to undergo the intramolecular cyclization. Expectedly, the phosphonium salt, which was protonated during the workup was isolated in 75% yield, and confirmed by ^{1}H NMR and MS (Supporting Information).

The strong electron withdrawing nature of the DPP core is expected to facilitate deprotonation at the methyl group of **DMDPP** under weakly basic conditions. A facile deprotonation of **DMDPP** will allow us to perform a variation of the Aldol condensation reaction (DMDPP aldol) with aldehydes to produce vinyl substituted DPP compounds. To explore the DMDPP aldol condensation, we first performed the reaction with benzaldehyde as a model. The condensation between **DMDPP** and benzaldehyde in DMF with KO^{t}Bu as the base at 0 ºC gave trace amounts of the (E)-monovinyl product (**4**) (Table 2, entry 1). Upon increasing the temperature to 40 °C, trace amounts of the (E), (E)'- divinyl product (**5**) was isolated (Table 2, entry 2). To determine if the instability of the starting **DMDPP** compound under strong basic condition was causing these low yields, we investigated this phenomena. Treatment of a THF solution of **DMDPP** with KO^{t}Bu in the absence of aldehyde turned the solution from colorless to a black complex in 1 h, confirming our spec-

Scheme 3 Synthesis of DMDPP

ulation. Switching the base to aqueous NaOH solution in toluene gave a 25% yield of a 1:1 mixture of mono- and divinyl products (**4** and **5**). Indeed, addition of a phase-transfer agent led to exclusive generation of **5**; albeit, in low yields (Table 2, entry 5). These results clearly demonstrate that strong inorganic bases are not suitable reagents for the DMDPP aldol condensation of **DMDPP** with aldehydes.

Inspired by the report on the synthesis of α,β-unsaturated ketones by L-proline-TEA-catalyzed Aldol condensation,[51] we investigated the feasibility of this method in our study. In the model reaction with benzaldehyde under the reported conditions, a dark solid precipitated from the reaction solution at room temperature, and after 12 h, product **5** was isolated in 63% yield; there was no observation of **4** (Table 2, entry 6). A mixture of methanol and toluene (1:5), resulted in a remarkable improvement of the desired product to 86% yield after 4 h (Table 2, entry 7). However, in the absence of Et$_3$N, L-proline or methanol in three separate reactions, only the **DMDPP** starting material was recovered (Table 2, entries 8, 9 and 10). Thus, the combination of Et$_3$N, L-proline in a mixture of toluene:methanol is necessary to achieve the highest yield in a relatively short reaction time.

Next we investigated the substrate scope for the condensation of **DMDPP** with a variety of aldehydes. We chose to investigate aromatic aldehydes that are of interest to the organic semiconducting material community. Consequently, we se-

lected aromatic aldehydes that are electron-rich, electron deficient, and those containing alkene, heteroatoms, and halogens (Figure 1). The electron-rich aldehydes, such as thiophene-2-carbaldehyde and furan-2-carbaldehyde gave the corresponding products **6** and **7** in 90 % and 88 % yield respectively. The reaction conditions are compatible with aryl halides as 4-bromobenzaldehyde, 5-bromothiophene-2-carbaldehyde, and 5-(4-chlorophenyl)furan-2-carbaldehyde also produced products **8, 9** and **10** respectively, in moderate to good yields. The yields for the halogenated compounds (62 % - 75 %) are slightly lower than those of **5, 6** and **7**, possibly due to the mild electron withdrawing effect of the halogen atoms. The reaction with cinnamaldehyde gave a low yield (20 %) of the desired product **11**. The results of the reaction with electron deficient aromatic aldehydes are interesting. In general, the yields are lower than those of the electron-rich aldehydes. However, the difference in the yields of these electron deficient aldehydes vary with the degree of electron deficiency at the position where the carbaldehyde group is connected. Aldehydes with the carbaldehyde group connected at the most electron deficient positions resulted in the lowest yields. For example, 2-pyridyl aldehyde furnished **12** in 65% yield in 5h, while 3-pyridyl aldehyde gave product **13** in 75% yield in a shorter reaction time. In contrast, 4-pyridyl aldehyde did not yield isolable product. Other examples of the reactivity differences in the electron withdrawing aldehydes are also seen with the thiazolyl and the fluorinated carbaldehydes. For instance, 2-thiazolyl carbaldehyde gave a 35% yield of **15**, which is significantly lower than the 65 % yield that is observed with the 5-thiazolyl carbaldehyde to give product **16**. Similarly, due to the extreme electron deficiency of the pentafluorobenzaldehyde, only a 45% yield of **18** was observed in the condensation reaction compared to the 82 % yield of **17** that resulted from the reaction with the lesser electron deficient 2,3-difluoro-4-bromobenzaldehyde. These results demonstrate that our synthetic approach to 3,6-divinyl DPP derivatives is viable and materials containing these architecture can now be prepared and explored.

The absorption and emission spectra were recorded for the DPP-alkenyl compounds (Figure 2). All the compounds displayed maximum absorption wavelength between 550 nm and 700 nm with two transition peaks in that region. Compound **10** had the longest absorption maximum wavelength due to the extended π-conjugation. In the emission spectrum, the electron deficient compounds **12, 17** and **18** had the highest emission intensity with a 20 – 35 nm Stokes shift, while the lesser electron deficient compounds **8** and **13** had moderate emission intensity with smaller Stoke shifts.

Table 2 Investigation of DMDPP aldol condensation conditions of DMDPP with benzaldehyde

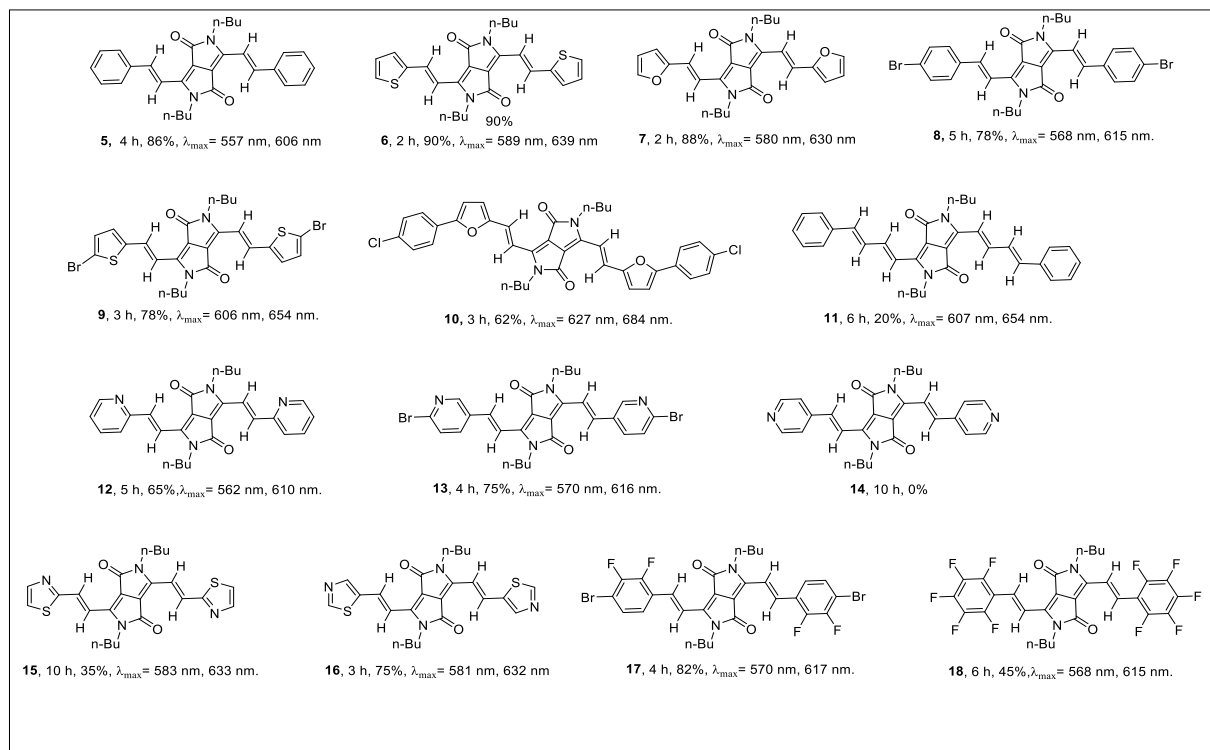| entry	additives	solvent	temp (°C)	time (h)	product 4:5	yields (%)
1	KO^{t}Bu (2.0 eq)	DMF	0	1	(100:0)	<5
2	KO^{t}Bu (2.0 eq)	THF	40	1	(0:100)	<5

3	KO^{t}Bu (2.0 eq)	THF	0	1	-	NPD
4	NaOH (1 N)	Tol	70	4	(1:1)	25
5	NaOH (1 N), TBAB (10 mol %)	Tol	70	4	(0:100)	15
6	L-proline (20 mol %), Et$_3$N (2.0 eq)	MeOH	rt	12	(0:100)	63
7	L-proline (20 mol %), Et$_3$N (2.0 eq)	Tol:MeOH (5:1)	rt	4	(0:100)	86
8	L-proline (20 mol %),	Tol:MeOH (5:1)	rt	4	-	NPD
9	L-proline (20 mol %), Et$_3$N (2.0 eq)	Tol	rt	4	-	NPD
10	Et$_3$N (2.0 eq)	Tol:MeOH (5:1)	rt	4	-	NPD

NPD: no product detected. Unless otherwise indicated, all reactions were carried out in 0.25 M under the indicated conditions. The reactions were monitored by TLC until completion. (*E*)-configuration was assigned by ^{1}H NMR.

They had a major emission peak around 630 nm with a shoulder around 700 nm, which is attributed to a single electronic

be converted to 3,6-divinyl DPP derivatives by a mild DMDPP aldol condensation. To our knowledge, this is also the first re-

5, 4 h, 86%, λ$_{max}$= 557 nm, 606 nm

6, 2 h, 90%, λ$_{max}$= 589 nm, 639 nm

7, 2 h, 88%, λ$_{max}$= 580 nm, 630 nm

8, 5 h, 78%, λ$_{max}$= 568 nm, 615 nm.

9, 3 h, 78%, λ$_{max}$= 606 nm, 654 nm.

10, 3 h, 62%, λ$_{max}$= 627 nm, 684 nm.

11, 6 h, 20%, λ$_{max}$= 607 nm, 654 nm.

12, 5 h, 65%, λ$_{max}$= 562 nm, 610 nm.

13, 4 h, 75%, λ$_{max}$= 570 nm, 616 nm.

14, 10 h, 0%

15, 10 h, 35%, λ$_{max}$= 583 nm, 633 nm.

16, 3 h, 75%, λ$_{max}$= 581 nm, 632 nm

17, 4 h, 82%, λ$_{max}$= 570 nm, 617 nm.

18, 6 h, 45%, λ$_{max}$= 568 nm, 615 nm.

transition with vibronic structure. Interestingly, compound **5** also showed moderate emission intensity, while all the other compounds have very low emission intensity; albeit, they are further red shifted compared to the others.

In conclusion, we report the first direct and efficient synthesis of a new DPP scaffold (**DMDPP**). The reaction is scalable and the **DMDPP** compound provides a precursor that can

ported synthesis of 3,6-divinyl flanked DPP derivatives. Our synthetic approach to this new **DMDPP** scaffold provides a way to prepare a variety of new DPP derivatives, which were inaccessible by the previous approaches.
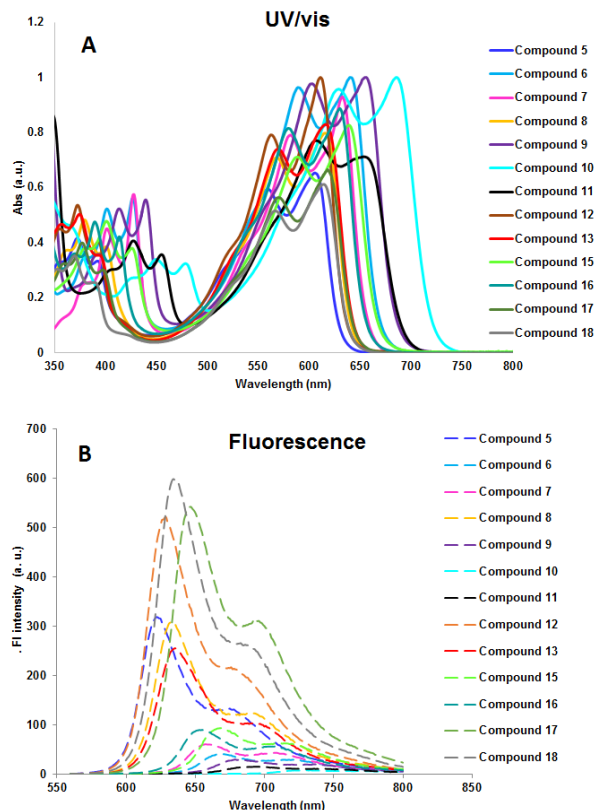
Experimental procedures and characterization data (^{1}H NMR, ^{13}C NMR, HRMS and mechanistic study. (PDF)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

UV/vis

A

Fluorescence

B

Corresponding Author

cscott@chemistry.msstate.edu

Notes

The authors declare no competing financial interest.

REFERENCES

1. Farnum, D. G.; Mehta, G.; Moore, G. G. I.; Siegal, F. P., Attempted reformatskii reaction of benzonitrile, 1,4-diketo-3,6-diphenylpyr-rolo[3,4-C]pyrrole. A lactam analogue of pentalene. *Tetrahedron Lett.* **1974,** *15,* 2549-2552.

2. Grzybowski, M.; Gryko, D. T., Diketopyrrolopyrroles: Synthesis, Reactivity, and Optical Properties. *Adv. Opt. Mater.* **2015,** *3,* 280-320.

3. Kaur, M.; Choi, D. H., Diketopyrrolopyrrole: brilliant red pigment dye-based fluorescent probes and their applications. *Chem. Soc. Rev.* **2015,** *44,* 58-77.

4. Patil, Y.; Misra, R., Diketopyrrolopyrrole-Based and Tetracyano-Bridged Small Molecules for Bulk Heterojunction Organic Solar Cells. *Chemistry – Asian J. Chem.* **2018,** *13,* 220-229.

5. Mauck, C. M.; Hartnett, P. E.; Margulies, E. A.; Ma, L.; Miller, C. E.; Schatz, G. C.; Marks, T. J.; Wasielewski, M. R., Singlet Fission via an Excimer-Like Intermediate in 3,6-Bis(thiophen-2-yl)diketopyrrolopyrrole Derivatives. *J. Am. Chem. Soc.* **2016,** *138,* 11749-11761.

6. Shen, L.; Tang, Z.; Wang, X.; Liu, H.; Chen, Y.; Li, X., Effects of aromatic substituents on the electronic structure and excited state energy levels of diketopyrrolopyrrole derivatives for singlet fission. *Phys. Chem. Chem. Phys.* **2018,** *20,* 22997-23006.

7. Shou, K.; Tang, Y.; Chen, H.; Chen, S.; Zhang, L.; Zhang, A.; Fan, Q.; Yu, A.; Cheng, Z., Diketopyrrolopyrrole-based semiconducting polymer nanoparticles for in vivo second near-infrared window imaging and image-guided tumor surgery. *Chem. Sci.* **2018,** *9,* 3105-3110.

8. Wang, Y.; Huang, X.; Tang, Y.; Zou, J.; Wang, P.; Zhang, Y.; Si, W.; Huang, W.; Dong, X., A light-induced nitric oxide controllable release nano-platform based on diketopyrrolopyrrole derivatives for pH-responsive photodynamic/photothermal synergistic cancer therapy. *Chem. Sci.* **2018,** *9,* 8103-8109.

9. Yang, X.; Zhang, Y.; Li, Y.; Liu, X.; Mao, J.; Yuan, Y.; Cui, Y.; Sun, G.; Zhang, G., A diketopyrrolopyrrole-based fluorescence turn-on probe for the detection of Pb2+ in aqueous solution and living cells. *RSC Adv.* **2016,** *6,* 52004-52008.

10. Ardizzone, A.; Blasi, D.; Vona, D.; Rosspeintner, A.; Punzi, A.; Altamura, E.; Grimaldi, N.; Sala, S.; Vauthey, E.; Farinola, G. M.; Ratera, I.; Ventosa, N.; Veciana, J., Highly Stable and Red-Emitting Nanovesicles Incorporating Lipophilic Diketopyrrolopyrroles for Cell Imaging. *Chem. Eur. J.* **2018,** *24,* 11386-11392.

11. Sassi, M.; Buccheri, N.; Rooney, M.; Botta, C.; Bruni, F.; Giovanella, U.; Brovelli, S.; Beverina, L., Near-infrared roll-off-free electroluminescence from highly stable diketopyrrolopyrrole light emitting diodes. *Sci. Rep.* **2016,** *6,* 34096.

12. Yi, Z.; Wang, S.; Liu, Y., Design of High-Mobility Diketopyrrolopyrrole-Based π-Conjugated Copolymers for Organic Thin-Film Transistors. *Adv. Mater.* **2015,** *27,* 3589-3606.

13. Naik, M. A.; Patil, S., Diketopyrrolopyrrole-based conjugated polymers and small molecules for organic ambipolar transistors and solar cells. *J. Polym. Sci., Part A: Polym. Chem.* **2013,** *51,* 4241-4260.

14. Nielsen, C. B.; Turbiez, M.; McCulloch, I., Recent Advances in the Development of Semiconducting DPP-Containing Polymers for Transistor Applications. *Adv. Mater.* **2013,** *25,* 1859-1880.

15. Li, Y.; Sonar, P.; Murphy, L.; Hong, W., High mobility diketopyrrolopyrrole (DPP)-based organic semiconductor materials for organic thin film transistors and photovoltaics. *Energy Environ Sci.* **2013,** *6,* 1684-1710.

16. Wang, B.; Huynh, T.-P.; Wu, W.; Hayek, N.; Do, T. T.; Cancilla, J. C.; Torrecilla, J. S.; Nahid, M. M.; Colwell, J. M.; Gazit, O. M.; Puniredd, S. R.; McNeill, C. R.; Sonar, P.; Haick, H., A Highly Sensitive Diketopyrrolopyrrole-Based Ambipolar Transistor for Selective Detection and Discrimination of Xylene Isomers. *Adv. Mater.* **2016,** *28,* 4012-4018.

17. Ashraf, R. S.; Meager, I.; Nikolka, M.; Kirkus, M.; Planells, M.; Schroeder, B. C.; Holliday, S.; Hurhangee, M.; Nielsen, C. B.; Sirringhaus, H.; McCulloch, I., Chalcogenophene Comonomer Comparison in Small Band Gap Diketopyrrolopyrrole-Based Conjugated Polymers for High-Performing Field-Effect Transistors and Organic Solar Cells. *J. Am. Chem. Soc.* **2015,** *137,* 1314-1321.

18. Fei, Z.; Chen, L.; Han, Y.; Gann, E.; Chesman, A. S. R.; McNeill, C. R.; Anthopoulos, T. D.; Heeney, M.; Pietrangelo, A., Alternating 5,5-

Dimethylcyclopentadiene and Diketopyrrolopyrrole Copolymer Prepared at Room Temperature for High Performance Organic Thin-Film Transistors. *J. Am. Chem. Soc.* **2017,** *139,* 8094-8097.

19.   Mueller, C. J.; Singh, C. R.; Fried, M.; Huettner, S.; Thelakkat, M., High Bulk Electron Mobility Diketopyrrolopyrrole Copolymers with Perfluorothiophene. *Adv. Funct. Mater.* **2015,** *25,* 2725-2736.

20.   Tang, A.; Zhan, C.; Yao, J.; Zhou, E., Design of Diketopyrrolopyrrole (DPP)-Based Small Molecules for Organic-Solar-Cell Applications. *Adv. Mater.* **2017,** *29,* 1600013.

21.   Li, W.; Hendriks, K. H.; Wienk, M. M.; Janssen, R. A. J., Diketopyrrolopyrrole Polymers for Organic Solar Cells. *Acc. Chem. Res.* **2016,** *49,* 78-85.

22.   Chandran, D.; Lee, K.-S., Diketopyrrolopyrrole: A versatile building block for organic photovoltaic materials. *Macromol. Res.* **2013,** *21,* 272-283.

23.   Qu, S.; Tian, H., Diketopyrrolopyrrole (DPP)-based materials for organic photovoltaics. *Chem. Commun.* **2012,** *48,* 3039-3051.

24.   Sun, P.; Li, X.; Wang, Y.; Shan, H.; Xu, J.; Liu, C.; Zhang, C.; Chen, F.; Xu, Z.; Chen, Z.-k.; Huang, W., Diketopyrrolopyrrole-based acceptors with multi-arms for organic solar cells. *RSC Adv.* **2018,** *8,* 25031-25039.

25.   Leventis, A.; Royakkers, J.; Rapidis, A. G.; Goodeal, N.; Corpinot, M. K.; Frost, J. M.; Bučar, D.-K.; Blunt, M. O.; Cacialli, F.; Bronstein, H., Highly Luminescent Encapsulated Narrow Bandgap Polymers Based on Diketopyrrolopyrrole. *J. Am. Chem. Soc.* **2018,** *140,* 1622-1626.

26.   Data, P.; Kurowska, A.; Pluczyk, S.; Zassowski, P.; Pander, P.; Jedrysiak, R.; Czwartosz, M.; Otulakowski, L.; Suwinski, J.; Lapkowski, M.; Monkman, A. P., Exciplex Enhancement as a Tool to Increase OLED Device Efficiency. *J. Phys. Chem. C* **2016,** *120,* 2070-2078.

27.   Cao, D.; Liu, Q.; Zeng, W.; Han, S.; Peng, J.; Liu, S., Diketopyrrolopyrrole-Containing Polyfluorenes: Facile Method To Tune Emission Color and Improve Electron Affinity. *Macromolecules* **2006,** *39,* 8347-8355.

28.   Jin, Y.; Xu, Y.; Qiao, Z.; Peng, J.; Wang, B.; Cao, D., Enhancement of electroluminescence properties of red diketopyrrolopyrrole-doped copolymers by oxadiazole and carbazole units as pendants. *Polym.* **2010,** *51,* 5726-5733.

29.   Cao, D.; Liu, Q.; Zeng, W.; Han, S.; Peng, J.; Liu, S., Synthesis and characterization of novel red-emitting alternating copolymers based on fluorene and diketopyrrolopyrrole derivatives. *J. Polym. Sci., Part A: Polym. Chem.* **2006,** *44,* 2395-2405.

30.   Yum, J.-H.; Holcombe, T. W.; Kim, Y.; Yoon, J.; Rakstys, K.; Nazeeruddin, M. K.; Grätzel, M., Towards high-performance DPP-based sensitizers for DSC applications. *Chem. Commun.* **2012,** *48,* 10727-10729.

31.   Holcombe, T. W.; Yum, J.-H.; Yoon, J.; Gao, P.; Marszalek, M.; Censo, D. D.; Rakstys, K.; Nazeeruddin, M. K.; Graetzel, M., A structural study of DPP-based sensitizers for DSC applications. *Chem. Commun.* **2012,** *48,* 10724-10726.

32.   Guo, F.; Liu, X.; Ding, Y.; Kong, F.; Chen, W.; Zhou, L.; Dai, S., Broad spectral-response organic D – A – π – A sensitizer with pyridine-diketopyrrolopyrrole unit for dye-sensitized solar cells. *RSC Adv.* **2016,** *6,* 13433-13441.

33.   Farré, Y.; Raissi, M.; Fihey, A.; Pellegrin, Y.; Blart, E.; Jacquemin, D.; Odobel, F., A Blue Diketopyrrolopyrrole Sensitizer with High Efficiency in Nickel-Oxide-based Dye-Sensitized Solar Cells. *ChemSusChem* **2017,** *10,* 2618-2625.

34.   Pham, T. T. T.; Saha, S. K.; Provost, D.; Farré, Y.; Raissi, M.; Pellegrin, Y.; Blart, E.; Vedraine, S.; Ratier, B.; Aldakov, D.; Odobel, F.; Bouclé, J., Toward Efficient Solid-State p-Type Dye-Sensitized Solar Cells: The Dye Matters. *J. Phys. Chem. C* **2017,** *121,* 129-139.

35.   Farré, Y.; Zhang, L.; Pellegrin, Y.; Planchat, A.; Blart, E.; Boujtita, M.; Hammarström, L.; Jacquemin, D.; Odobel, F., Second Generation of Diketopyrrolopyrrole Dyes for NiO-Based Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2016,** *120,* 7923-7940.

36.   Zhang, L.; Favereau, L.; Farré, Y.; Mijangos, E.; Pellegrin, Y.; Blart, E.; Odobel, F.; Hammarström, L., Ultrafast and slow charge recombination dynamics of diketopyrrolopyrrole – NiO dye sensitized solar cells. *Phys. Chem. Chem. Phys.* **2016,** *18,* 18515-18527.

37.   Bisen, M.; Scott, C. N., Synthesis and Optoelectronic Properties of a Reduced Band Gap Copolymer Derived from Silacyclopentadiene and Diketopyrrolopyrrole. *Macromolecules* **2014,** *47,* 8196-8202.

38.   Morton, C. J. H.; Gilmour, R.; Smith, D. M.; Lightfoot, P.; Slawin, A. M. Z.; MacLean, E. J., Synthetic studies related to diketopyrrolopyrrole (DPP) pigments. Part 1: The search for alkenyl-DPPs. Unsaturated nitriles in standard DPP syntheses: a novel cyclopenta[c]pyrrolone chromophore. *Tetrahedron* **2002,** *58,* 5547-5565.

39.   Pfenninger, J. I., A.; Rochat, A. C.; Wallquist, O., Process for the preparation of pyrrolo (3,4-c) pyrroles   patent.pdf. *US Patent 4,778,899* **1986.**

40.   Tieke, B.; Rabindranath, A. R.; Zhang, K.; Zhu, Y., Conjugated polymers containing diketopyrrolopyrrole units in the main chain. *Beilstein J Org Chem.* **2010,** *6,* 830-845.

41.   Abul Iqbal, L. C. Process for dyeing high-molecular organic material, and novel polycyclic pigments 1983.

42.   Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J., Effect of Chain Extension on the Electrochemical and Electronic Properties of π -Conjugated Soluble Thienylene-vinylene Oligomers. *J. Am. Chem. Soc.* **1997,** *119,* 10774-10784.

43.   Roncali, J., Synthetic Principles for Bandgap Control in Linear π -Conjugated Systems. *Chem. Rev.* **1997,** *97,* 173-206.

44.   Hernandez, V.; Castiglioni, C.; Del Zoppo, M.; Zerbi, G., Confinement potential and π-electron delocalization in polyconjugated organic materials. *Phys. Rev. B* **1994,** *50,* 9815-9823.

45.   Zhou, Z.; Parr, R. G., New measures of aromaticity: absolute hardness and relative hardness. *J. Am. Chem. Soc.* **1989,** *111,* 7371-7379.

46.   Hoffmann, H., Zur Reaktion von Triphenylphosphin mit Olefinen. *Chemische Berichte* **1961,** *94* (5), 1331-1336.

47.   Kelly, T. R.; Lebedev, R. L., Synthesis of Some Unsymmetrical Bridged Terpyridines. *J. Org. Chem.* **2002,** *67* (7), 2197-2205.

48.   Eyjolfsson, R., Stereoselective synthesis of triglochinic acid, (E)-2-butene-1,2,4-tricarboxylic acid, derived from the cyanogenic glucoside triglochinin. *Acta Chem. Scand.* **1970,** *24,* 3075-8.

49.   Zhao, L.; Chen, X. Y.; Ye, S.; Wang, Z.-X., Computational Mechanistic Study of PMe3 and N-Heterocyclic Carbene Catalyzed Intramolecular Morita–Baylis–Hillman-Like Cycloalkylations: The Origins of the Different Reactivity. *J. Org. Chem.* **2011,** *76,* 2733-2743.

50.   Shi, M.; Liu, Y.-H., Traditional Morita – Baylis – Hillman reaction of aldehydes with methyl vinyl ketone co-catalyzed by triphenylphosphine and nitrophenol. *Org. Biomol. Chem.* **2006,** *4,* 1468-1470.

51.   Wang, J.-f.; Lei, M.; Li, Q.; Ge, Z.-m.; Wang, X.; Li, R.-t., A novel and efficient direct aldol condensation from ketones and aromatic aldehydes catalyzed by proline – TEA through a new pathway. *Tetrahedron* **2009,** *65,* 4826-4833.