Thiophene-Containing Pechmann Dye Derivatives
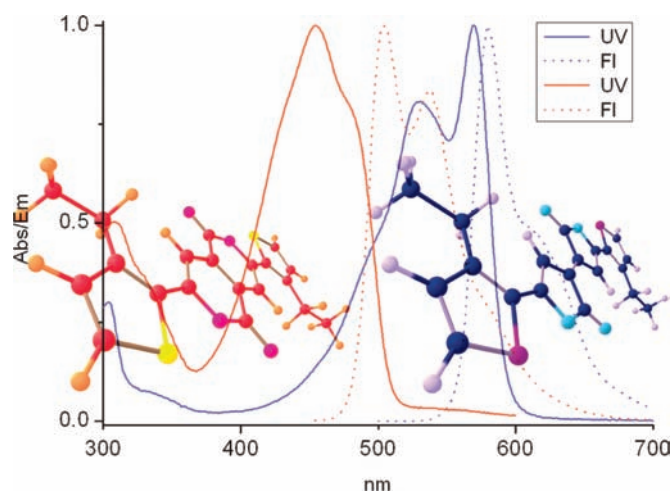
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ABSTRACT

Thiophene-containing Pechmann dyes (unsaturated *exo*-5,5-dilactones) were easily prepared by Cu-catalyzed dehydration of the corresponding *β*-aroylacrylic acids. Introduction of long alkyl chains greatly enhances solubility. Isomerization of an alkyl-substituted thiophene Pechmann dye (TPD) gave the corresponding *endo*-6,6-dilactone. The redox and electronic properties of these new dyes were investigated by CV, UV/vis, and fluorescence spectroscopy and DFT and TD-DFT computations. Strong absorption and emission in the visible region were recorded.

The first Pechmann dye was unwittingly synthesized in 1882 by Hans von Pechmann in an attempt to prepare 1,4-naphthoquinone from *β*-benzoyl acrylic acid.[1] von Pechmann did not ascribe a structure to the product, and in the first half of the 20th century, there was much debate over the structure and mechanism of formation of these compounds that came to be referred to as "Pechmann dyes".[2] The structure has since been demonstrated to be a 3-butenolide dimer centered about an alkene bridge and most often containing a benzene ring at the 5 and 5′ positions of the lactone rings (Figure 1). Due to their extreme
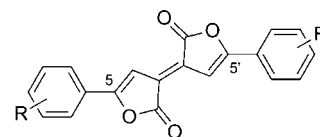

Figure 1. General structure of Pechmann dye.

insolubility in most organic solvents, likely due to aggregation known for such highly conjugated planar structures, there have been few reports of new Pechmann dyes since the mid 1950s.[3,4]

Coupling of oligo- and polythiophenes structures to electron-deficient moieties such as dihydropyrrolopyrrole-

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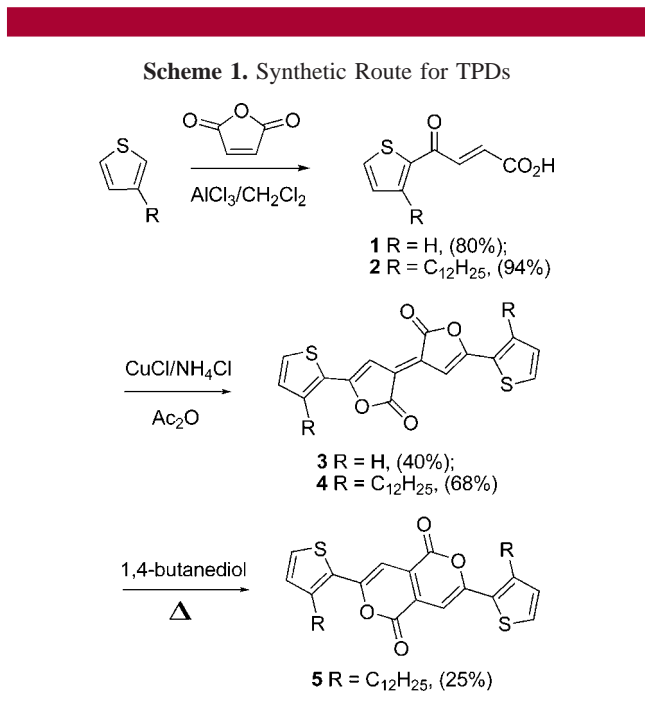‡ Institute of High Performance Computing.
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dione (DPP) and napthalenediimide (NDI) has proven to be a successful strategy in the preparation of high efficiency low band gap oligomers and polymers for n-channel organic thin film transistors (OTFT)[5] and organic photovolatics (OPV).[6] Both DPP and NDI are good building blocks for the above-mentioned organic electronic applications because they provide: (1) an electron-deficient core that is fully conjugated, planar, and allows for the direct attachment of conjugated bridging moieties such as thiophene and (2) carboxylate equivalents that can be amidated with various aryl- or alkylamines for control of solubility. This permits the preparation of solution processable, hydrid oligo- and polythiophene structures with intermolecular $\pi-\pi$ stacking ability and a high degree of intramolecular conjugation necessary for efficient charge transfer through the materials.

The ease of synthesis of Pechmann dyes through the dehydration of β-aroylacrylic acids[7] permits the direct incorporation of thiophene and substituted thiophene rings onto the core Pechmann chromophore. This, coupled with their planar and conjugated structures which are known attributes for promoting electron/hole transport in organic electronic frameworks, prompted us to explore the synthesis and materials properties of hitherto unknown thiophene Pechmann dyes (TPD) and their derivatives in search of new building blocks for organic electronics.

Friedel–Crafts acylation of thiophene and 3-dodecylthiophene with maleic anhydride afforded the corresponding (E)-4-oxo-4-(2-thienyl)-2-butenoic acids **1** and **2** in high yields (Scheme 1). TPDs **3** and **4** were then prepared by refluxing of **1** and **2** in acetic anhydride in the presence of CuCl and NH₄Cl in 40–68% yields.[8] Isolation of the sparingly soluble TPD **3** was accomplished by prolonged Soxhlet extraction into refluxing CHCl₃. The dodecyl side chain renders TPD **4** significantly more soluble than **3**; **4** can be isolated in much higher yields by simple fitration with CHCl₃ (Celite) to remove the insoluble Cu salts. Pechmann dyes are known to isomerize under basic conditions and/or at elevated temperatues in alcoholic solvents to yield their corresponding 6,6′-dilactone counterparts.[4] Alkaline isomerization of **3** and **4** failed to yield the corresponding 6,6-dilactone; however, thermal isomerization of TPD **4** in butanediol gave the 6,6′-dilactone **5** in moderate yield.

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Scheme 1. Synthetic Route for TPDs

In the solid state, **3**−**5** were thermally stable up to 250 °C by thermogravimetric analysis (TGA). No transitions were evident by differential scanning calorimetry (DSC) for **3**, while **4** and **5** showed sharp melting endotherms at 149 and 168 °C, respectively. The lack of transitions corresponding to an isomerization process in the DSC of **3** and **4** demonstrates that both an elevated temperature and an alcoholic matrix is necessary to promote the isomerization process. By cyclic voltammetry (CV) (Figure 2), TPD **4**
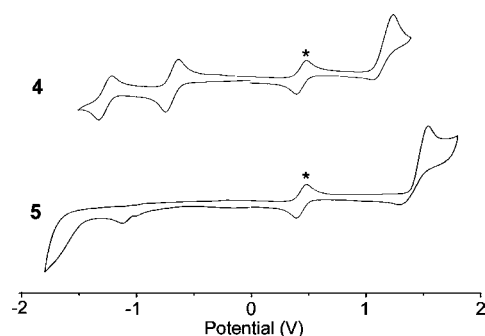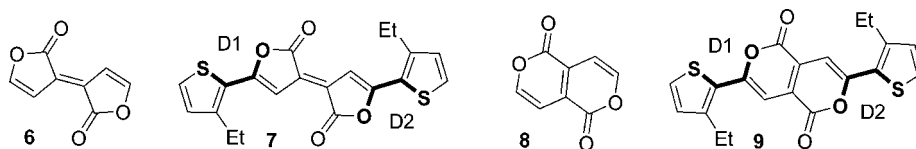

Figure 2. Cyclic voltammogram of **4** and **5** in CH₂Cl₂ (0.1 M n-Bu₄NPF₆ as the supporting electrolyte). Scan rate, 50 mV s⁻¹; working electrode, Pt foil; counter electrode, Au; reference electrode, Ag/AgCl with ferrocene/ferrocenium couple (*) used as an internal standard.

exhibits two reversible reduction potentials. The first onset of reduction is at −0.60 V with a reversible reduction wave at −0.75 V, and the second reversible reduction wave is at −1.33 V. The onset of oxidation is found to be at 1.05 V with a nonreversible oxidation event at 1.26 V. Dilactone **5** exhibits one nonreversible reduction

Table 1. Computational (DFT) Characterization of Thiophene Pechmann Dyes at B3LYP/DZVP Levels of Theory in the Gas Phase and in CH_2Cl_2 under the Polarized Continuum Implicit Solvation Model (IEF-PCM)

structure	D1 °	D2 °	ΔG kcal mol^{-1} [a]	$\Delta G(CH_2Cl_2)$ kcal mol^{-1} [a]	HOMO/LUMO eV	HOMO/ LUMO(CH_2Cl_2) eV	HOMO/ LUMO(exp) eV [b]
6	-	-	-	-	6.63/3.72	6.50/3.64	-
7	178.9	179.0	0.00	0.00	5.41/3.38	5.47/3.53	
7a	180.0	0.0	0.51	0.11	5.45/3.39	5.51/3.54	5.31/3.66
7b	1.6	1.6	−0.22	−0.77	5.49/3.40	5.55/3.55	
8	-	-	-	-	6.85/3.10	6.72/3.00	-
9	180.0	180.0	0.00	0.00	5.65/2.91	5.68/2.97	
9a	179.7	4.5	−0.79	−0.27	5.68/2.93	5.75/3.01	5.52/3.29
9b	0.0	0.0	−0.63	−0.20	5.71/2.96	5.74/3.05	

[a] Relative to the *anti,anti*-conformers (**7** and **9**, respectively). [b] Estimated from the E_{ox} and E_{red} onset potentials vs Fc/Fc$^+$ using $E_{HOMO} = E_{ox} + 4.8$ eV and $E_{LUMO} = E_{ox} + 4.8$ eV.

potential at −1.07 V with the onset of reduction at −0.94 V. The onset of oxidation is found to be at 1.29 V with a nonreversible oxidation event at 1.51 V. The energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated from the onset of oxidation and reduction vs Fc/Fc$^+$.[9] They were found to be 5.31 and 3.66 eV for **4** (E_g 1.65 eV) and 5.52 and 3.29 eV for **5** (E_g 2.23 eV), respectively (Table 1). With a band gap (E_g) of 1.65 eV, an appropriately functionalized TPD would be well suited to be coupled with other thiophene-containing monomers to create low band gap polymers for OPV applications.[6] For both **7** and **9** (models for **4** and **5**, respectively), a potential energy scan (PES) around the thiophene-core chromophore bond (D1 dihedral angle) at the B3LYP[10]/DZVP[11] level of theory found two minima, at ∼0 and ∼180°, with a maximum at ∼90°. Significantly, the three possible stable conformers (**7**, **7a**, **7b** and **9**, **9a**, **9b**; Table 1) were found to be very close in energy. Conformer HOMO/LUMO energies were within ≤0.09 eV from each other, implying low sensitivity of the electronic properties of TPDs on conformation. The Kohn−Sham frontier orbital energies were in good agreement with the experiment, provided solvent effects were included by an implicit solvation model (IEF-PCM).[12]

UV−vis spectroscopy of TPD **4** in hexane resulted in a pink−red solution with a λ_{max} of 552 nm (Table 2).

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Table 2. Absorption Maximum (λ_{max}) and Emission Maximum (Em$_{max}$) and Prediction of λ_{max} of TPD Derivatives by TD-DFT B3LYP/DZVP or PBE0/DZVP under the Polarized Continuum Implicit Solvation Model (IEF-PCM)

TPD	solvent	Em$_{max}$(exp) nm	λ_{max}(exp) nm	λ_{max}(calc), nm [a] B3LYP/DZVP	PBE0/DZVP
3	heptane	564	552[b]	615	601
3	CHCl$_3$	[c]	570	629	614
4/7b	heptane	582	568[b]	621	607
4/7b	CHCl$_3$	[c]	588	636	621
5/9b	heptane	505	455[b]	511	497
5/9b	CHCl$_3$	530	465	518	503

[a] Structures optimized at B3LYP/DZVP, IEFPCM, solvent as specified. [b] Spectra recorded in hexane. [c] No emission detected.

Dissolution in a more polar solvent such as CHCl$_3$ resulted in a large positive solvochromatic effect (∼18 nm red-shift), resulting in a λ_{max} of 570 nm and a violet colored solution. TPD **3** lacking the alkyl side chain showed a similar trend in both hexane and CHCl$_3$. However, both spectra were ∼18 nm blue-shifted relative to the alkyl containing TPD **4**. Both **3** and **4** exhibit a large shoulder that is blue-shifted by ∼30 nm with respect to the absorption maximum; this effect is most pronounced in hexane. In hexane, the λ_{max} of the 6,6-dilactone **5** is blue-shifted by ∼100 nm relative to its isomeric counterpart **4** (Table 2). Similar to the TPD, a positive solvochromatic shift is noticed for **5** in CHCl$_3$ albeit to a lesser degree (∼10 nm). The emission maximum and intensity of the TPD derivatives are strongly dependent on solvent. All TPD derivatives fluoresce more strongly in hexane than in CHCl$_3$, and in the case of TPDs **3** and **4** in CHCl$_3$ no emission was detected (Figure 3). Modeling of the electronic spectra[13] of substituted TPDs by
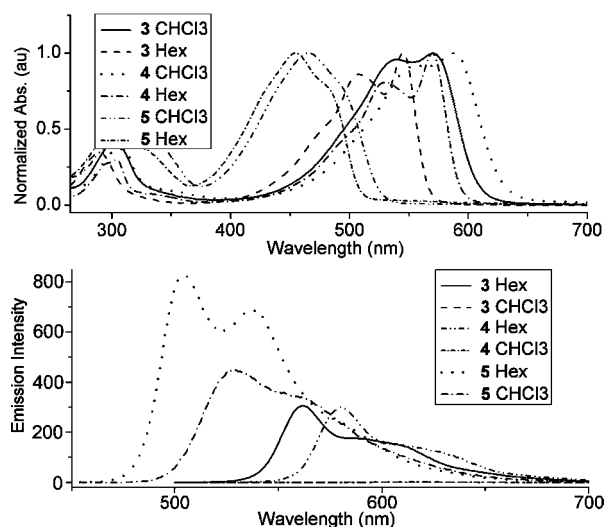
Figure 3. Top: Normalized absorption spectra of **3−5** in chloroform and hexane. Bottom: Emission spectra of **3−5** in chloroform and hexane ($c \sim 5 \times 10^{-7}$ M, $\lambda_{ex} = 450$ nm).

TD-DFT with implicit solvent treatment (IEF-PCM)[12] was conducted on the most stable *syn,syn*-conformation (D1, D2 $\sim$ 0°) (Table 2). TD-DFT B3LYP/DZVP computations found only one allowed transition (oscillator strength > 0) representing $\pi-\pi*$ electron excitation from the HOMO to the LUMO orbital (Figure 4). The λ_{max} values were overestimated by 55 ± 8 nm from the experimental values. The PBE0 functional,[14] which has shown better performance for TD-DFT of other organic dyes,[15] led to a closer match with the experiment, and the overestimation was 41 ± 8 nm (B3LYP/DZVP-optimized geometry). However, for each TPD, changing the implicit solvent from heptane to CHCl$_3$ led to a red-shift of λ_{max} by 15 ± 2 nm for B3LYP and 14 ± 1 nm for PBE0, in excellent agreement with the experiment (15 ± 5 nm). Likewise, the hypsochromic shift upon lactone rearrangement (114 ± 4 nm) was in excellent agreement with the experiment (118 ± 5 nm).

In conclusion, we have synthesized novel, purple-colored (**3, 4**), and orange-colored (**5**) thiophene-substituted Pechmann dye (TPD) derivatives carrying solubilizing side chains.

Figure 4. Contour plots of Kohn−Sham LUMO (top) and HOMO (bottom) of **7b** (a) and **9b** (b) at the B3LYP/DZVP level of theory.

Further investigations of TPDs and polymers thereof for optoelectronic applications are ongoing.

Supporting Information Available: Synthetic procedures and characterization data for all new compounds, TGA and DSC curves, and CV for compound **3**, computational methodology, results, and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Jacquemin, D.; Perpette, P. A.; Scuseria, G. E.; Ciofini, I.; Adamo, C. *J. Chem. Theory Comput.* **2008**, *4*, 123. (b) Jacquemin, D.; Preat, J.; Wathelet, V.; Fontaine, M.; Perpette, P. A. *J. Am. Ch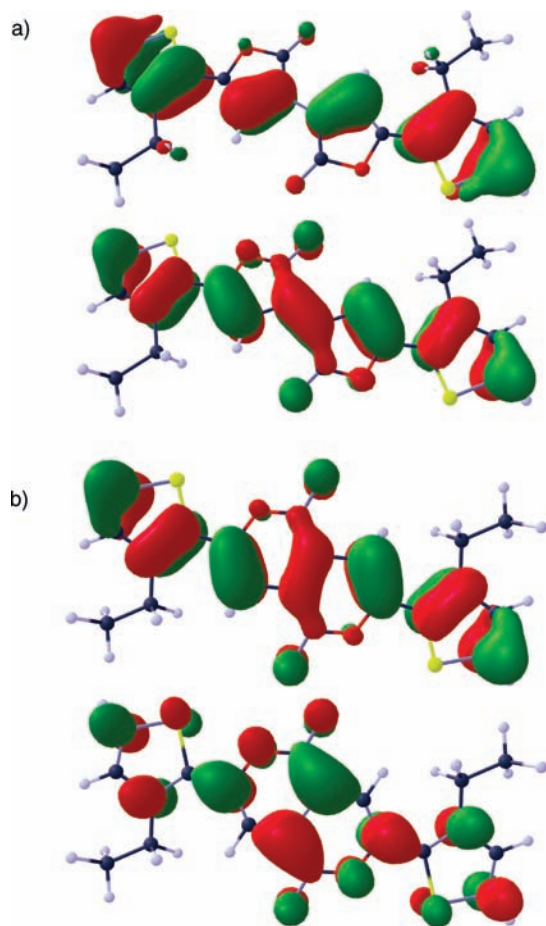em. Soc.* **2006**, *128*, 2072.