Synthesis and properties of pyrimidine-containing linear molecules

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Abstract—Palladium-catalyzed Stille and Sonogashira coupling reactions were sequentially applied for constructing novel pyrimidine-containing linear molecules. The chemoselectivity of 5-bromo-2-iodopyrimidine (1) towards Pd-catalyzed coupling reaction serves as a tool for the successful control of the arrangement of dipolar pyrimidine moieties inside the conjugated backbone. The influence of the arrangement of dipolar pyrimidine in the linear backbone on their absorption and photoluminescence are not stupendous. Thermogravimetric analysis (TGA) indicate that all linear molecules in this study exhibit high thermal stability. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: pyrimidine; molecular wire; Sonogashira coupling.

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Rigid and rod-like molecules with extended π-conjugation are of interest due to their potential use in nanoscale electronics, e.g. molecular wires.1 Modifications of the primary properties of these well-defined linear systems have been achieved by introducing a functional moiety as a conjugated subunit or as a terminal group. For example, better electron delocalization along the molecular axis can be achieved by introducing a redox-active transition metal as the central linkage.2 The introduction of a photoactive moiety into the π-conjugated skeleton has also been found to perform a switch function.3 Heteroaromatics with potential coordinating ability have also been introduced as a part of the conjugated backbone4 or as terminal groups.5 In this paper, we report the synthesis of linear molecules containing pyrimidine subunits in the conjugated backbone of the molecule. Due to the high electron affinity,6 the presence of the pyrimidine moiety in a π-conjugated system could create a new class of compounds with high electron accessibility. Alternatively, control on the arrangement of the dipolar pyrimidine moiety in a defined π-conjugated system could serve as an additional tool for tuning the physical properties.

Under mild conditions, Pd-catalyzed coupling reactions of 5-bromo-2-iodopyrimidine (1) with arylboronic acids7 (Suzuki coupling) or terminal alkynes7,8 (Sonogashira reaction) have been found to proceed chemoselectively at the C2 position. The bromo substituent at the C5 position remains intact, allowing a consecutive coupling reaction with either arylboronic acids or terminal alkynes, using the same Pd-catalyst.8 Therefore, the dipolar orientation of the pyrimidine group in a linear conjugated system can be controlled by taking advantage of the difference in reactivity at C2 and C5 positions of 1. In our previous report,8 we have shown that the photophysical properties of a π-conjugated system with alternating triple bonds and aromatic rings were found to be irrespective of the difference in arrangement of the dipolar pyrimidine moiety. And, the molecules prefer to have a coplanar conformation in the ground state due to the lack of ortho–ortho steric interactions between the two aromatic rings, which are separated by a triple bond. However, in the case of a conjugated molecule containing a pyrimidine group attached to the phenyl ring, the physical properties could depend on the different arrangement of the pyrimidine unit in the backbone.

Compound 3 was obtained by the Pd-catalyzed coupling of the pyrimidine derivative 1 with metallo-compounds of the type 2, in which the trimethylsilylethynyl group serves as a masked reaction site for the further extension of π-conjugation. Compounds of the type 2 with different metallo substituents were tested for their coupling efficiency with 1 in the presence of various Pd-catalysts (cf. Table 1). Reaction of compound 1 with 2 (M = ZnCl) in the presence of PdCl2(dppf) or PdCl2(PPh3)2 as catalyst (entries 1 and 2, Table 1) resulted in the recovery of 1. Treating 1 with 2 (M = MgBr) in the presence of a catalytic amount of...
PdCl₂(PPh₃)₂ in refluxing THF led to the formation of 3, but in a very low yield (3%, entry 3, Table 1). In DMF, Sn-derivative 2 (M=SnBu₃) coupled with 1 more efficiently in the presence of PdCl₂(PPh₃)₂ to afford 3 in 48% yield. However, by changing the catalyst system from PdCl₂(PPh₃)₂ to Pd(PPh₃)₄ or by carrying out the reaction in the presence of Ag₂O, the yields of 3 were found to be further reduced (entries 5 and 6, Table 1). Finally, it was found that by changing the reaction solvent from DMF to toluene, the yield of 3 could be increased to 63%. The lack of ortho–ortho interactions between the pyrimidine ring and the phenyl ring could be beneficial for increasing the conjugation length of 3 in the ground state.

The conjugation length of 3 was extended by a Sonogashira coupling reaction by treating 3 with the dialkyne 4a or 4b in the presence of Pr₂NH and catalytic amounts of Pd(PPh₃)₄ and CuI in refluxing THF¹⁰ to yield the linear compounds 5a and 5b in 71 and 68%, respectively (Scheme 1). Changing the orientation of the pyrimidine group in 5 could be achieved by treating the dialkyne 4 with 1 to afford 6, followed by a Stille coupling reaction with 2 (M=SnBu₃) in the presence of PdCl₂(PPh₃)₂. Accordingly, the linear molecules 7a and 7b, which have the same π-conjugated backbone as that of 5a and 5b but with a different arrangement of the dipolar pyrimidine moieties were isolated in 48 and 45% yield, respectively. However, due to the ortho–ortho interaction between the pyrimidine ring and the phenyl ring in 7a and 7b could result in a noncoplanar conformation in the ground state. The terminal trimethylsilylthelynyl groups in 5a and 5b, as well as in 7a and 7b can be removed by standard desilylation procedures, resulting in the formation of new reaction sites, which provide the possibility for further modifying the end groups of the linear molecules 5a, 5b, 7a, and 7b.

Another approach towards increasing the conjugation length was achieved by treating 3 with alkyne 8 using a Sonogashira coupling reaction to obtain 9 in 65% yield. The trimethylsilyl group in 9 was cleaved in the presence of 2N NaOH in MeOH/THF (3:1) at room temperature to afford compound 10 in 77% yield. The Sonogashira coupling procedure used for the synthesis of 10 resulted in complex products, hence the procedure was slightly modified to obtain 10. Thus, three equal portions of 10 in THF was added every 4 h to the refluxing THF solution of the diiodo compound 11 in the presence of Pd(PPh₃)₄, CuI and Pr₂NH to yield 12 (45%).¹¹ From the above facts, it is evident that the conjugation length as well as the arrangement of the dipolar pyrimidine moieties in the conjugated backbone could be manipulated by employing different reaction sequences.

Optical absorption and photoluminescence studies were carried out on the pyrimidine-containing molecules 5a, 5b, 7a, 7b, and 12 (cf. Table 2). Due to the electron-donating property, the introduction of the dioctyloxy side chains leads to a significant red-shift in the electronic absorption and the emission maxima compared to that of the linear molecules with diol side chains (5a versus 5b and 7a versus 7b). The compounds 5a, 5b, 7a, 7b, and 12 show very intense blue fluorescence with high quantum yields upon irradiation at their absorption maxima. Dilute solutions of 5b and 7b in EtOAc and CHCl₃, exhibit similar absorption and emission spectra irrespective of the difference in the dipolar orientation of the pyrimidine moiety in the backbone. However, 5a and 7a show different emission maxima in EtOAc. Especially, dilute solution of 7a in EtOAc shows solvatochromic behavior with an emission maximum at 389 nm and a shoulder at 409 nm. In CHCl₃, the emission maximum of 7a is red shifted to 402 nm with a shoulder at 423 nm. But, in CHCl₃, the difference in the emission maxima of 5a and 7a is less than that in EtOAc. Interestingly, 5b, 7b, and 12 show a similar behavior in their absorption and emission maxima. Based on the structure, one would expect 12 to have a longer conjugation length compared with those of 5b and 7b; however, the photophysical studies indicate that the π-conjugation of 12 along the molecular axis is ‘saturated’ and not longer than that of 5b and 7b.

### Table 1. Pd-catalyzed coupling reactions of 1 with metallo compound 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>2 (M=)</th>
<th>Pd-catalyst</th>
<th>Solvent (temperature, °C)</th>
<th>3 Yield (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnCl</td>
<td>PdCl₂(dppe)</td>
<td>THF (80)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>ZnCl</td>
<td>PdCl₂(PPh₃)₂</td>
<td>THF (80)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>MgBr</td>
<td>PdCl₂(PPh₃)₂</td>
<td>THF (80)</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>SnBu₃</td>
<td>PdCl₂(PPh₃)₂</td>
<td>DMF (160)</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>SnBu₃</td>
<td>PdCl₂(PPh₃)₂</td>
<td>DMF (160)</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>SnBu₃</td>
<td>Pd(PPh₃)₄</td>
<td>DMF (160)</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>SnBu₃</td>
<td>PdCl₂(PPh₃)₂</td>
<td>PhCH₃ (120)</td>
<td>63</td>
</tr>
</tbody>
</table>

a Temperature of oil bath.

b Isolated yield.
Scheme 1.

Table 2. Physical properties of pyrimidine-containing linear molecules 5a, 5b, 7a, 7b, and 12

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (nm) in EtOAc</th>
<th>$\lambda_{\text{em}}$ (nm) in EtOAc</th>
<th>$\lambda_{\text{em}}$ (nm) in CHCl$_3$</th>
<th>Quantum yield (%)$^a$</th>
<th>$T_d$ (°C)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>362</td>
<td>398, 421</td>
<td>407, 427</td>
<td>87</td>
<td>359, 459</td>
</tr>
<tr>
<td>5b</td>
<td>332, 394</td>
<td>449$^c$</td>
<td>449</td>
<td>62</td>
<td>348, 434</td>
</tr>
<tr>
<td>7a</td>
<td>357</td>
<td>389, 409</td>
<td>402, 423</td>
<td>67</td>
<td>467</td>
</tr>
<tr>
<td>7b</td>
<td>331, 396</td>
<td>454$^c$</td>
<td>454</td>
<td>66</td>
<td>308, 423</td>
</tr>
<tr>
<td>12</td>
<td>387</td>
<td>450</td>
<td>455</td>
<td>35</td>
<td>372, 426</td>
</tr>
</tbody>
</table>

$^a$ In EtOAc, Coumarin I was employed as standard.

$^b$ Detected by TGA.

$^c$ The excitation spectra of 5b and 7b are similar to their absorption spectra, the emission spectra were recorded upon excitation at 394 nm for 5b and 396 nm for 7b.
Thermal stability of 5a, 5b, 7a, 7b and 12 was investigated by TGA. No decomposition was observed below 300°C, and the decomposition temperatures (T_d) are summarized in Table 2. The TG thermograms reveal that complete weight loss occurs before 500°C, which corresponds to the removal of the alkyl or alkoxy side chains. The residue is stable without any further decomposition up to 800°C. The high thermal stability of the residue could be attributed to the thermal cross-linking of the conjugated backbone.

In summary, we have established an efficient pathway for introducing the highly electronegative pyrimidine moiety into a π-conjugated backbone affording a new class of linear molecules. Control on the dipolar orientation of pyrimidine in the conjugated backbone was accomplished by taking advantage of the different reactivities at the C2 and C5 position of 1. However, the photophysical studies indicate that the difference in the arrangement of the pyrimidine moiety in the π-conjugated system has a slight influence on their properties.

Acknowledgements

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References

11. New compounds were characterized by spectroscopic techniques. Selected data: Compound 3: 1H NMR (CDCl3, 400 MHz) δ 8.83 (s, 2H), 8.35 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 0.27 (s, 9H). Anal. calcd for C13H12BrN3Si: C, 54.38; H, 4.56; N, 8.46, found: C, 54.23; H, 4.65; N, 8.41. Compound 5a: 1H NMR (CDCl3, 400 MHz) δ 8.90 (s, 4H), 8.42 (d, J = 7.4 Hz, 4H), 7.60 (d, J = 7.4 Hz, 4H), 7.43 (s, 2H), 2.83 (t, J = 7.6 Hz, 4H), 1.52–1.55 (m, 4H), 1.29–1.33 (m, 20H), 0.87–0.89 (m, 6H), 0.28 (s, 9H); Anal. calcd for C16H16N4Si2: C, 79.01; H, 7.81; N, 6.58, found: C, 78.90; H, 7.68; N, 6.63. Compound 5b: 1H NMR (CDCl3, 400 MHz) δ 8.90 (s, 4H), 8.42 (d, J = 8 Hz, 4H), 7.60 (d, J = 8 Hz, 4H), 7.06 (s, 2H), 4.06 (t, J = 6.6 Hz, 4H), 1.92–1.95 (m, 4H), 1.29–1.33 (m, 20H), 0.87–0.90 (m, 6H), 0.28 (s, 9H); Anal. calcd for C16H16N4O2Si2: C, 76.03; H, 7.65; N, 6.48. Compound 7a: 1H NMR (CDCl3, 400 MHz) δ 8.97 (s, 4H), 7.62 (d, J = 8.6 Hz, 4H), 7.57 (d, J = 8.6 Hz, 4H), 7.57 (s, 2H), 2.91 (t, J = 7.5 Hz, 4H), 1.73 (m, 4H), 1.25–1.41 (m, 20H), 0.84–0.87 (m, 6H), 0.28 (s, 9H); Anal. calcd for C36H36N6Si2: C, 76.14; H, 7.53; N, 6.34, found: C, 75.93; H, 7.55; N, 6.38. Compound 7b: 1H NMR (CDCl3, 400 MHz) δ 8.95 (s, 4H), 7.61 (d, J = 6.5 Hz, 4H), 7.17 (s, 2H), 4.04 (t, J = 6.7 Hz, 4H), 1.84–1.88 (m, 4H), 1.26–1.35 (m, 20H), 0.87–0.87 (m, 6H), 0.27 (s, 9H); Anal. calcd for C36H36N6O2Si2: C, 76.14; H, 7.53; N, 6.34, found: C, 76.03; H, 7.65; N, 6.48. Compound 12: 1H NMR (CDCl3, 400 MHz) δ 8.90 (s, 4H), 8.46 (d, J = 8.0 Hz, 4H), 7.67 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.05 (s, 2H), 4.07 (t, J = 6.2 Hz, 4H), 1.92–1.95 (m, 4H), 1.29–1.33 (m, 20H), 0.87–0.90 (m, 6H); Anal. calcd for C36H36N6O2: C, 83.79; H, 7.43; N, 5.58, found: C, 83.67; H, 7.25; N, 5.33.