Convenient synthesis of functionalized 4,4'-disubstituted-2,2'-bipyridine with extended π-system for dye-sensitized solar cell applications

Cédric Klein, Etienne Baranoff, Md. Khaja Nazeeruddin *, Michael Grätzel

Laboratory for Photonics & Interfaces, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

ABSTRACT

Exploration of new ruthenium-based sensitizers for dye-sensitized solar cell (DSC) applications requires an easy access to multifunctionalized ligands for efficient screening of sensitizers' properties. Based on the Horner–Emmons–Wadsworth reaction, a convenient synthetic route for the extension of the π-system on 4,4'-disubstituted-2,2'-bipyridines was used to develop a novel series of functionalized 2,2'-bipyridine ligands with either electron-withdrawing or donating end-capping group. 1H NMR spectroscopy revealed that all the new bipyridyl ligands were obtained exclusively in their fully E isomers.

Keywords:
Bipyridine
Horner–Emmons–Wadsworth reaction
Dye-sensitized solar cells
Extended π-systems

Heteroleptic ruthenium complexes have emerged as a promising class of sensitizers for dye-sensitized solar cell (DSC) applications.1–4 Those complexes contain a 4,4'-dicarboxy-2,2'-bipyridine (dcbp) ligand for anchoring on the titanium oxide (TiO$_2$) surface, two thiocyanate ligands that tune the photo- and electrochemical properties of the dyes to relevant levels, and a second bipyridine ligand used as an antenna for improving the light harvesting performances. This particular design leads to complexes with significantly improved extinction coefficients in the visible part of the absorption spectrum. With such properties in hand, it is possible to reduce the TiO$_2$ film thickness compared to less absorbing dyes, resulting in higher open circuit voltage ($V_{oc}$) values and fill factor ($ff$) for the device. Champion cells with power conversion efficiencies reaching 12% under one sun illumination (AM 1.5) are actually obtained with this promising design. To further increase the performances of dye-sensitized solar cell, it is of paramount importance to engineer ligands at a molecular level and thus to endow sensitizers with both panchromatic absorption and relatively high molar extinction coefficients. Therefore, to accelerate the discovery and improvement of better performing sensitizers, easily accessible strategies for the functionalization of bipyridyl derivatives are required. In this Letter, we report such an efficient synthetic route for the preparation of a series of symmetrically substituted 4,4'-π-conjugated-2,2'-bipyridines being end-capped by either electron-withdrawing or electron-donating groups. This end-capping diversity will allow us to tune the photophysical properties of the corresponding Ru-based sensitizers in a rational manner.

Synthesis and characterization of functionalized 4,4'-π-conjugated-2,2'-bipyridines have been described in the literature mainly for non-linear optical applications.5–7 Although, both symmetrically and asymmetrically substituted styryl-bipyridine-based ligands were easily obtained in multi-gram scales, the related synthetic procedure showed to be limited by means of the nature of the functional groups initially grafted on the required benzaldehyde reactants (Scheme 1).

One commonly used strategy involves the dilithiated form of 4,4'-dimethyl-2,2'-bipyridine 1 as an intermediate, which implicitly exclude the presence of sensitive functionality, such as carboxylic ester (Scheme 1).

A more general strategy is based on the Horner–Emmons–Wadsworth reaction (Scheme 2). This approach has been used for extending the π-conjugated system of bipyridine, however, using mainly alkoxy donor substituents on the π-system.8–10 To further enlarge the scope of the reaction with various substituents we present the synthesis of functionalized and symmetrically substituted 4,4'-π-conjugated-2,2'-bipyridines for DSC application. In all the cases, this new strategy based on the Horner–Emmons–Wadsworth reaction allowed us to synthesize π-conjugated-bipyridines in high yield and in multi-gram scale. In addition, it showed to be relatively tolerant toward the nature of the end-capped functionalities being present on the aldehyde reactant.

The Horner–Emmons–Wadsworth reaction was preferred to the conventional Wittig reaction because it showed better results both in yield and selectivity toward the E isomers (Scheme 2).

Our preference for E-conformation over Z-type is due to the effective electronic coupling in the former case. Thus, the properties of the resulting metal-complexes containing such ligands
should be conveniently tuned by the nature of the functionalities acting as end-capped groups.

Following these considerations and in the purpose of varying the nature of the end-capped group, the starting material for the synthesis of compounds 10, 13a–b, and 22a–f appeared to be 4,4'-bis(diethylphosphonate)-2,2'-bipyridine 8. At first, we attempt a four step sequence for the synthesis of building block 8, from the commercially available 4,4'-dimethyl-2,2'-bipyridine 1 (Scheme 3, method A). Thus the oxidation of 1 with K2Cr2O7 in concentrated H2SO4 afforded the well-known diacid derivative 2 which was directly esterified to diester 3 in a refluxing mixture of EtOH/H2SO4. The subsequent diester 3 was, respectively, reduced to diol 4 with NaBH4 in refluxing EtOH, brominated into 5 with aqueous HBr, and finally phosphonated with P(OEt)3 in CHCl3 to afford the desired compound 8. The 45% overall yield obtained using this methodology was consistent with the literature (42%).

A shorter synthetic route was also applied to get 8 based on the works of Fraser et al. (Scheme 3, method B). In this approach, commercially available compound 1 was converted into 4,4'-bis(trimethylsilyl)methyl)-2,2'-bipyridine derivative 6, which was directly reacted with Cl3CCl3 in the presence of KF to afford 4,4'-bis(chloromethyl)-2,2'-bipyridine 7. Compound 7 was finally converted into 8 upon reacting with neat refluxing P(OEt)3 with an overall yield of 68%. 1H, 31P, and 13C NMR spectra of compound 8 obtained following this methodology were similar with those observed when method A was employed. It is noteworthy that for a large-scale synthesis of 8, the longer but easier method A was preferred for its convenience and simplicity.

The ability of the Horner–Emmons–Wadsworth synthetic procedure to be tolerant toward various functional groups with the interest for DSC applications was tested. In this purpose, synthesis of bipyridyl compound 10 bearing ethyl 2-vinyl-5-thiophene-carboxylate substituents in its 4 and 4' positions was attempted (Scheme 4). Thiophenes are becoming increasingly popular for the preparation of highly absorbing dyes. Thus, reaction of compound 8 with 2.5 equiv of ethyl 2-formyl-5-thiophene-carboxylate 9 and 2.5 equiv of t-BuOK in anhydrous DMF gave the desired symmetrically disubstituted bipyridine 10 in reasonable yield (53%). The stereoselectivity of the reaction leading to the only (E,E) isomer was confirmed by 1H NMR analysis. A large coupling constant, typically J3CH–CH ≈ 17 Hz, was observed for each of the protons H3 and H6 of both double bond linkages (Fig. 1).

Replacement of thienyl spacers in compound 10 by phenyl moieties was also investigated in view of more classical designs. Thus,

---

**Scheme 1.** Synthetic route to functionalized 4,4'-distyryl-2,2'-bipyridines. Reagents and conditions: (a) THF, −78 °C, LDA (2 equiv); (b) functionalized benzaldehydes; (c) toluene, PPTS.

**Scheme 2.** Horner–Emmons–Wadsworth reaction (a) versus Wittig reaction (b).

**Scheme 3.** Synthesis of compound 8 following two different strategies. Reagents and conditions: (a) H2SO4, K2Cr2O7 (85%); (b) EtOH, H2SO4 (90%); (c) EtOH, NaBH4 (81%); (d) HBr 48%, H2SO4 (85%); (e) CHCl3, P(OEt)3 (80%); (f) THF, −78 °C, LDA then TMSCI (89%); (g) DMF, KF, Cl3CCl3 (91%); (h) P(OEt)3 (85%).

**Scheme 4.** Synthesis of compound 10. Reagents and conditions: (a) t-BuOK, DMF, 25 °C.
bipyridyls 13a and 13b being end-capped by n-alkyl carboxylic esters were both synthesized in 68% yield upon the reaction of 8 with benzaldehydes 12a or 12b by following the same procedure used for the synthesis of compound 10 (Scheme 5). The stereoselectivity of the Horner-Emmons-Wadsworth reaction leading to compounds 13a–b was again demonstrated by 1H NMR analysis with evidences for the only (E,E) isomer. This type of ligand can be used as an anchoring ligand thanks to the presence of carboxylic acid moiety and allows the extension of the antenna effect on the anchoring part of the complex as well.

Benzaldehyde reactants 12a and 12b were easily obtained by the reaction of commercially available 4-carboxybenzaldehyde 11 with 1-iodo-n-alkyl (n = 6 or 8) and K2CO3 in DMF in 94 and 83% yields, respectively (Scheme 5). In these cases, alkyl chains bearing six carbons or more were necessary to ensure a good solubility of the resulting bipyridines 13a and 13b. In fact, using compound 11 as such or under its methyl or ethylester form afforded only insoluble and uncharacterizable materials. Introduction of electron-donating functionalities, such as N,N-dialkylamino- or alkoxy-end-capped groups was also investigated. However, as the preparation of such symmetrically functionalized 4,4'-distyryl-2,2'-bipyridine analogs showed to be again limited by some solubility problems we introduced solubilizing n-alkyl chains at an early stage. According to compounds 13a and 13b, linear alkyl

**Figure 1.** Aromatic region of the 200 MHz 1H NMR spectrum of compound 10, recorded in CDCl3 at 25 °C; * solvent peak.

**Table 1** Characteristics of compounds 21a–d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant RX</th>
<th>Product</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14 IC6H13</td>
<td>21a</td>
<td>H</td>
<td>H</td>
<td>OC6H13</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>14 BrC9H19</td>
<td>21b</td>
<td>H</td>
<td>H</td>
<td>OC9H19</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>15 BrC6H13</td>
<td>21c</td>
<td>H</td>
<td>OC6H13</td>
<td>OC6H13</td>
<td>77</td>
</tr>
<tr>
<td>4</td>
<td>16 BrC9H19</td>
<td>21d</td>
<td>OCH3</td>
<td>H</td>
<td>OC9H19</td>
<td>97</td>
</tr>
</tbody>
</table>

**Scheme 5.** Synthesis of bipyridine compounds 13a and 13b. Reagents and conditions: (a) DMF, K2CO3, RI; (b) DMF, t-BuOK, 25 °C.

**Scheme 6.** Synthesis of compounds 21a–d. Reagents: (a) CH3CN, RX, K2CO3.

**Scheme 7.** Synthesis of compound 21e–f. Reagents: (a) CH3CN, C6H13X (X = Br or I), K2CO3; (b) DMF, POCl3.

**Scheme 8.** Synthesis of disubstituted 4,4’-distyryl-2,2’-bipyridine derivatives 22a–f. Reagents and conditions: (a) DMF, t-BuOK, 25 °C.
chains bearing six carbons seemed to be sufficient to ensure a good solubility of the resulting ligands. Taking into account this observation, substituted benzaldehyde adducts 21a–d bearing n-alkyl chains (n = 6 and 9) located in the para position regarding the required aldehyde functionality were then synthesized (Scheme 6).

Compounds 21a–d were obtained from the corresponding commercially available hydroxybenzaldehydes 14–16 upon reacting with 1-haloalkyls RX (R = C3H7 or C6H5; X = Br or I) and K2CO3 in refluxing CH2CN. Classical work-up, followed by flash column chromatography purification afforded the desired benzaldehydes 21a–d in good to excellent yields (Table 1).

In order to increase further the light harvesting ability of conjugated bipyrudyl ligands, the synthesis of benzaldehyde reactants 21e–f was also investigated (Scheme 7).

Compounds 21e–f were then both obtained by a two-step synthesis involving N or O-alkylation of commercially available compounds 17 and 18 with 1-haloethyl to afford 19 and 20 followed by a Vilsmeyer formylation with an overall yield of 40% and 46%, respectively. Benzaldehyde adducts 21a–f were used for the synthesis of functionalized disubstituted bipyrudines 22a–f following the general procedure depicted in Scheme 8.

Bipyrudines 22a–f were obtained upon reacting compound 8 with 2.5 equiv of the desired benzaldehyde 21a–f and 4 equiv of t-BuOK in anhydrous DMF. Evaporation of the solvent followed by trituration of the resulting solids with methanol and filtration afforded pure compounds 22a–f in yields up to 78% (Table 2).

This general and rather easy work-up procedure gives an additional advantage to the Horner–Emmons–Wadsworth route for the synthesis of styryl-functionalized bipyridines. As previously observed for compounds 10 and 13a–b, bipyrudine derivatives 22a–f were exclusively obtained in their (E,E)-conformations.

In summary, a series of new symmetrically functionalized 4,4′-π-conjugated,2,2′-bipyrudine bidentate ligands have been synthesized using the Horner–Emmons–Wadsworth reaction. This easy and convenient synthetic strategy allowed us to introduce either electron-withdrawing or electron-donating end-capped groups on the π-conjugated-bipyrudine core. This methodology was relatively tolerant toward most of the functionalities desired for dye-sensitized solar cell application. 1H NMR analysis revealed that all the new synthesized ligands were exclusively obtained in their fully E isomers. This simple synthetic approach is expected to expedite the development of antenna-type ligands for ruthenium sensitizers.

Acknowledgments

This work was supported by the Swiss Science Foundation, Swiss Federal Office for Energy and the European Office of U.S. Air Force under contract No. F61775-00-C0003. MKN thanks the World Class University (WCU) program funded by the Ministry of Education, Science and Technology (Grant No. R31-2009-000-10035-0).

References and notes

200 MHz, δ ppm) 0.90 (t, J = 6.3 Hz, 6H), 1.2–1.5 (m, 24H), 1.82 (m, 4H), 3.93 (d, J = 8.7 Hz, 4H), 7.00 (d, J = 17 Hz, 2H), 7.39 (d, J = 5 Hz, 2H), 7.43 (d, J = 17 Hz, 2H), 7.51 (d, J = 8.7 Hz, 4H), 8.56 (s, 2H), 8.66 (d, J = 5 Hz, 2H). 13C NMR (CDCl3, 298 K, 50 MHz, δ ppm) 14.1, 22.6, 26.0, 29.2, 29.3, 29.4, 29.5, 31.9, 68.1, 114.8, 118.1, 120.9, 123.6, 128.4, 128.8, 133.3, 146.4, 149.2, 156.0, 159.8.

4,4''-Bis(m,p-dihexyloxystyryl)-2,2''-bipyridine 22c. This compound was obtained as a white solid in 79% yield starting from 8 and 21c. 1H NMR (CDCl3, 298 K, 200 MHz, δ ppm) 0.93 (m, 12H), 1.2–1.6 (m, 24H), 1.85 (m, 8H), 4.06 (m, 8H), 6.88–7.46 (m, 12H), 8.54 (s, 2H), 8.66 (d, J = 5 Hz, 2H).

13C NMR (CDCl3, 298 K, 50 MHz, δ ppm) 14.00, 14.02, 22.60, 22.62, 25.67, 25.71, 29.17, 29.25, 31.57, 31.60, 69.18, 69.33, 111.7, 113.5, 118.0, 120.8, 123.9, 129.3, 133.2, 146.0, 149.3, 149.4, 150.0, 156.5.

4,4''-Bis(o-methoxy-p-nonyloxystyryl)-2,2''-bipyridine 22d. This compound was obtained as a white solid in 78% yield starting from 8 and 21d. 1H NMR (CDCl3, 298 K, 200 MHz, δ ppm) 0.90 (t, J = 6.3 Hz, 6H), 1.2–1.5 (m, 24H), 1.82 (m, 4H), 3.91 (s, 6H), 4.00 (t, J = 6.4 Hz, 4H), 6.50 (s, 2H), 6.53 (d, J = 8.7 Hz, 2H) 7.09 (d, J = 17 Hz, 2H), 7.44 (d, J = 5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 17 Hz, 2H), 8.51 (s, 2H), 8.64 (d, J = 5 Hz, 2H). 13C NMR (CDCl3, 298 K, 50 MHz, δ ppm) 14.4, 22.6, 25.9, 29.2, 31.6, 68.3, 104.6, 118.4, 120.9, 122.7, 123.3, 124.8, 125.2, 125.7, 126.1, 126.9, 127.0, 130.4, 132.3, 146.3, 149.5, 155.7, 156.6.