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

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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. ^{1}H NMR spectroscopy revealed that all the new bipyridyl ligands were obtained exclusively in their fully *E* isomers.

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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′-bidpyridine (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 coefficient. 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

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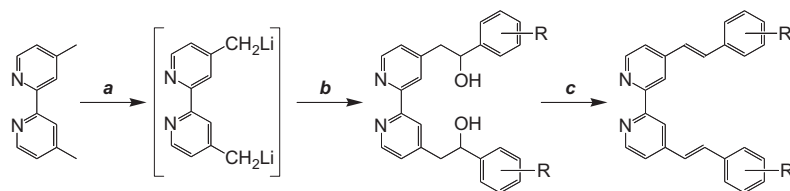
Scheme 1. Synthetic route to functionalized 4,4'-distyryl-2,2'-bipyridines. Reagents and conditions: (a) THF, −78 °C, LDA (2 equiv); (b) functionalized benzaldehydes; (c) toluene, PPTS.
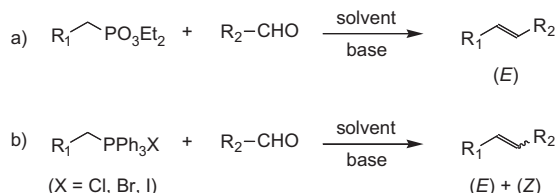
Scheme 2. Horner–Emmons–Wadsworth reaction (a) versus Wittig reaction (b).

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(diethylmethylphosphonate)-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).[11] Thus the oxidation of **1** with $K_2Cr_2O_7$ in concentrated H_2SO_4 afforded the well-known diacid derivative **2** which was directly esterified to diester **3** in a refluxing mixture of $EtOH/H_2SO_4$. The subsequent diester **3** was, respectively, reduced to diol **4** with $NaBH_4$ in refluxing EtOH, brominated into **5** with aqueous HBr, and finally phosphonated with $P(OEt)_3$ in $CHCl_3$ 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.[12,13] (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 Cl_3CCCl_3 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%.[14] ^{1}H, ^{31}P, and ^{13}C NMR spectra of compound **8** obtained following this methodology were similar with those observed when method A was employed. It is note-worthy 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-thiophenecarboxylate substituents in its 4 and 4' positions was attempted (Scheme 4). Thiophenes are becoming increasingly popular for the preparation of highly absorbing dyes. [15–17]

Thus, reaction of compound **8** with 2.5 equiv of ethyl 2-formyl-5-thiophenecarboxylate **9**[18] and 2.5 equiv of *t*-BuOK in anhydrous DMF gave the desired symmetrically disubstituted bipyridine **10** in reasonable yield (53%).[19] The stereoselectivity of the reaction leading to the only (*E,E'*) isomer was confirmed by ^{1}H NMR analysis. A large coupling constant, typically $J_{CH=CH} \approx 17$ Hz, was observed for each of the protons H_d and H_e 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,
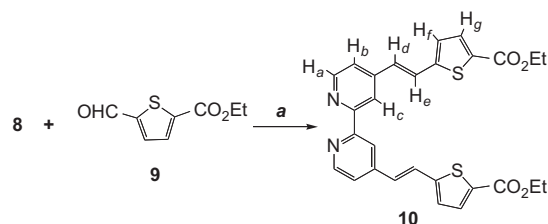
Scheme 4. Synthesis of compound **10**. Reagents and conditions: (a) *t*-BuOK, DMF, 25 °C.
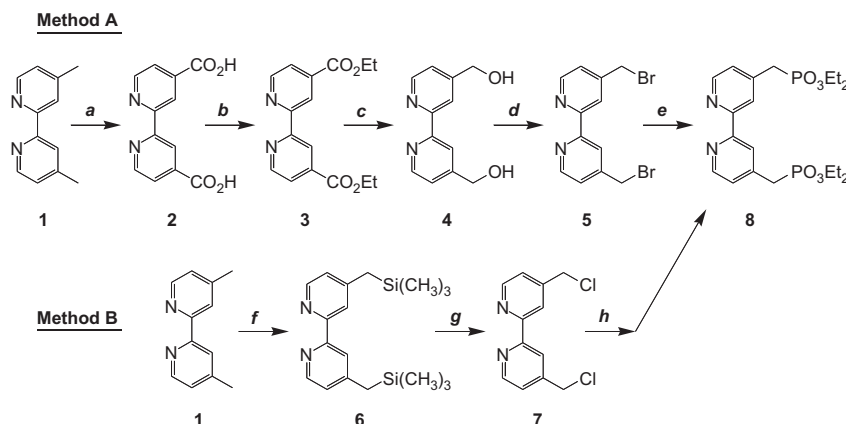
Scheme 3. Synthesis of compound **8** following two different strategies. Reagents and conditions: (a) H_2SO_4, $K_2Cr_2O_7$ (85%); (b) EtOH, H_2SO_4 (90%); (c) EtOH, $NaBH_4$ (81%); (d) HBr 48%, H_2SO_4 (85%); (e) $CHCl_3$, $P(OEt)_3$ (80%); (f) THF, −78 °C, LDA then TMSCl (89%); (g) DMF, KF, Cl_3CCCl_3 (91%); (h) $P(OEt)_3$ (85%).

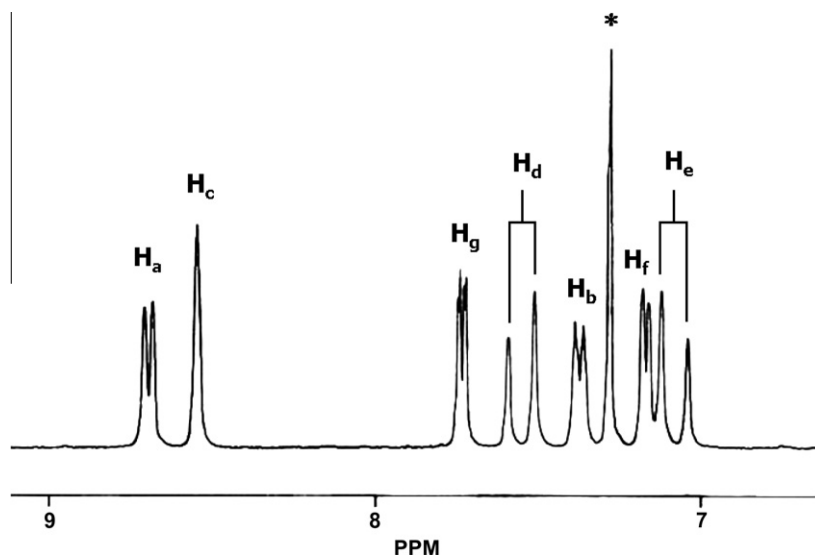**Figure 1.** Aromatic region of the 200 MHz ^{1}H NMR spectrum of compound **10**, recorded in CDCl$_3$ at 25 °C; * solvent peak.
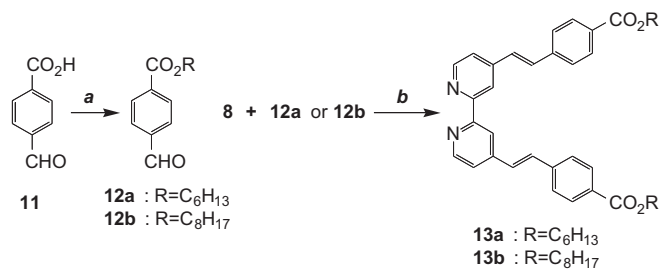
bipyridyls **13a** and **13b** being end-capped by *n*-alkyl carboxylic esters were both synthesized in 68% yield upon the reaction of **8** with benzaldehydes **12a** or **12b** by following the same procedure used for the synthesis of compound **10** (Scheme 5). The stereoselectivity of the Horner–Emmons–Wadsworth reaction leading to compounds **13a–b** was again demonstrated by ^{1}H 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 K$_2$CO$_3$ 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′-disty-

ryl-2,2′-bipyridine analogs showed to be again limited by some solubility problems[7] we introduced solubilizing *n*-alkyl chains at an early stage. According to compounds **13a** and **13b**, linear alkyl

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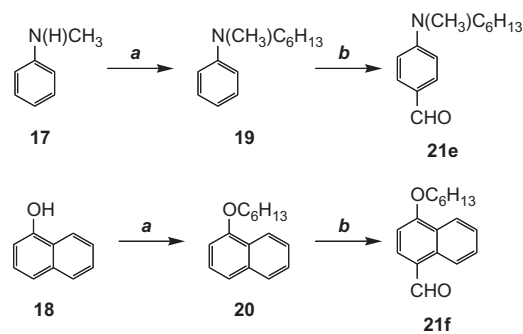Characteristics of compounds **21a–d**

Entry	Reactant	RX	Product	R$_1$	R$_2$	R$_3$	Yield (%)
1	**14**	IC$_6$H$_{13}$	**21a**	H	H	OC$_6$H$_{13}$	94
2	**14**	BrC$_9$H$_{19}$	**21b**	H	H	OC$_9$H$_{19}$	90
3	**15**	BrC$_6$H$_{13}$	**21c**	H	OC$_6$H$_{13}$	OC$_6$H$_{13}$	77
4	**16**	BrC$_9$H$_{19}$	**21d**	OCH$_3$	H	OC$_9$H$_{19}$	97

Scheme 7. Synthesis of compound **21e–f**. Reagents: (a) CH$_3$CN, C$_6$H$_{13}$X (X = Br or I), K$_2$CO$_3$; (b) DMF, POCl$_3$.

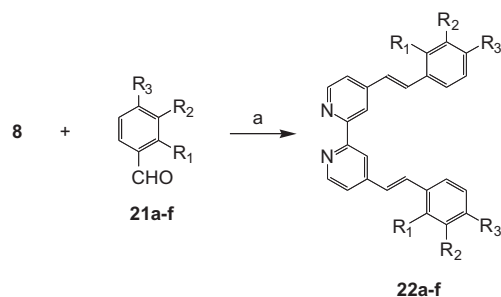**Scheme 5.** Synthesis of bipyridine compounds **13a** and **13b**. Reagents and conditions: (a) DMF, K$_2$CO$_3$, RI; (b) DMF, *t*-BuOK, 25 °C.
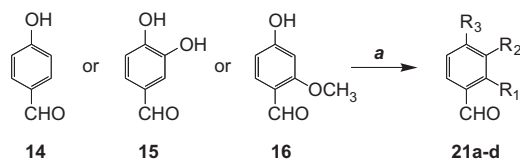
Scheme 6. Synthesis of compounds **21a–d**. Reagents: (a) CH$_3$CN, RX, K$_2$CO$_3$.

Scheme 8. Synthesis of disubstituted 4,4′-distyryl-2,2′-bipyridine derivatives **22a–f**. Reagents and conditions: (a) DMF, *t*-BuOK, 25 °C.

Table 2
Characteristics of functionalized bipyridine derivatives **22a–f**

Entry	Benzaldehyde	Product	R₁	R₂	R₃	Yield (%)
1	**21a**	**22a**	H	H	OC_6H_{13}	85
2	**21b**	**22b**	H	H	OC_9H_{19}	87
3	**21c**	**22c**	H	OC_6H_{13}	OC_6H_{13}	79
4	**21d**	**22d**	OCH_3	H	OC_9H_{19}	78
5	**21e**	**22e**	H	H	$N(CH_3)C_6H_{13}$	87
6	**21f**	**22f**	–(CH=CH)₂–	–(CH=CH)₂–	OC_6H_{13}	78

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 = C_6H_{13} or C_9H_{19}; X = Br or I) and K_2CO_3 in refluxing CH_3CN. 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 bipyridyl 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-halohexyl to afford **19** and **20** followed by a Vilsmeier formylation with an overall yield of 40% and 46%, respectively.

Benzaldehyde adducts **21a–f** were used for the synthesis of functionalized disubstituted bipyridines **22a–f** following the general procedure depicted in Scheme 8.

Bipyridines **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).[20]

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**, bipyridyl 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′-bipyridine 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-bipyridine 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

References and notes

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14. *4,4′-Bis(chloromethyl)-2,2′-bipyridine.* Compound **7** was synthesized according to published procedure[11] with the following modifications. A solution of **6**[12] (2 g, 6.1 mmol), hexachloroethane (5.8 g, 24.3 mmol), and KF (1.42 g, 24.3 mmol) in anhydrous DMF (30 ml) was stirred at room temperature under nitrogen. EtOAc (200 ml) and water (100 ml) were then added. The organic layer was separated and washed with water (5 × 100 ml), dried over MgSO₄ and evaporated to dryness. The resulting solid was dissolved in the minimum volume of hexane and let to stand in the freezer for few hours. The resulting white crystalline solid was filtered and washed with small portions of cold hexane to afford 1.4 g (91%) of **7** as a slightly yellow solid. ¹H NMR was in agreement with those reported in the literature.
4,4′-Bis(diethylmethylphosphonate)-2,2′-bipyridine **8**. A solution of **7** (2.6 g, 10.3 mmol) in triethylphosphite (50 ml) was heated to 160 °C overnight under nitrogen. Excess P(OEt)₃ was evaporated to afford a brown oil. The crude product was purified by column chromatography (SiO₂, EtOAc/MeOH, 80:20) to afford 4 g (85%) of **8** as a white solid. ¹H and ³¹P NMR were in agreement with those reported in literature.[11]
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19. *4,4′-Bis(ethyl 2-thienylvinyl-5-carboxylate)-2,2′-bipyridine* **10**. To a solution of **8** (1 g, mmol) and 924 (2.5 equiv) in anhydrous DMF (50 ml) was added *t*-BuOK (2.5 equiv). A copious precipitate formed after few minutes. The resulting slurry was stirred overnight at room temperature under nitrogen. DMF was evaporated and MeOH (150 ml) was added. The resulting mixture was let to stand in the fridge for 1 h before being filtered. The obtained solid was washed with small portions of cold MeOH (3 × 10 ml) and dried to afford compound **10** (53%) as a white solid. ¹H NMR (CDCl₃, 298 K, 200 MHz, δ ppm) 1.41 (t, *J* = 7 Hz, 6H), 4.39 (q, *J* = 7 Hz, 4H), 7.07 (d, *J* = 16 Hz, 2H), 7.16 (m, 2H), 7.37 (d, *J* = 5 Hz, 2H), 7.55 (d, *J* = 16 Hz, 2H), 7.73 (m, 2H), 8.54 (s, 2H), 8.69 (d, *J* = 5 Hz, 2H). ¹³C NMR (CDCl₃, 298 K, 50 MHz, δ ppm) 14.3, 61.3, 118.0, 121.2, 125.6, 127.8, 128.2, 133.3, 133.8, 144.6, 147.7, 149.7, 156.4, 161.9.
20. *General procedure for the synthesis of functionalized bipyridines* **22a–f**. To a solution of **8** (1 g, 2.2 mmol) and the corresponding benzaldehyde **21a–f** (2.5 equiv) in anhydrous DMF (50 ml) was added solid *t*-BuOK (4 equiv). A copious precipitate formed after few minutes. The resulting mixture was stirred overnight at room temperature under nitrogen. DMF was evaporated and MeOH (150 ml) was added. The resulting mixture was sonicated 2 min and let to stand in the fridge for 1 h before being filtered. The obtained solid was washed with small portions of cold MeOH (3 × 10 ml) and air-dried to afford pure compounds **22a–f**.
4,4′-Bis(p-hexyloxystyryl)-2,2′-bipyridine **22a**. This compound was obtained as a white solid in 85% yield starting from **8** and **21a**. ¹H NMR (CDCl₃, 298 K, 200 MHz, δ ppm) 0.93 (t, *J* = 6.3 Hz, 6H), 1.2–1.5 (m, 12H), 1.85 (m, 4H), 4.00 (t, *J* = 6.4 Hz, 4H), 6.93 (d, *J* = 8.7 Hz, 4H), 7.00 (d, *J* = 17 Hz, 2H), 7.38 (d, *J* = 5 Hz, 2H), 7.43 (d, *J* = 17 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 4H), 8.53 (s, 2H), 8.66 (d, *J* = 5 Hz, 2H). ¹³C NMR (CDCl₃, 298 K, 50 MHz, δ ppm) 14.0, 22.6, 25.7, 29.2, 31.6, 68.1, 114.8, 118.0, 120.8, 123.8, 128.4, 128.8, 133.0, 146.1, 149.4, 156.5, 159.7.
4,4′-Bis(p-nonyloxystyryl)-2,2′-bipyridine **22b**. This compound was obtained as a white solid in 87% yield starting from **8** and **21b**. 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), 4.00 (t, J = 6.4 Hz, 4H), 6.93 (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). ^{13}C NMR (CDCl$_3$, 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**. ^{1}H NMR (CDCl$_3$, 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). ^{13}C NMR (CDCl$_3$, 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, 120.9, 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**. ^{1}H NMR (CDCl$_3$, 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). ^{13}C NMR (CDCl$_3$, 298 K, 50 MHz, δ ppm) 14.1, 22.7, 26.0, 29.1, 29.2, 29.4, 29.5, 31.9, 55.5, 68.2, 98.9, 105.7, 118.2, 118.6, 120.6, 124.2, 128.3, 128.6, 147.1, 149.0, 156.1, 158.7, 161.0.

4,4′-Bis(p-N,N-methylhexylaminostyryl)-2,2′-bipyridine **22e**. This compound was obtained as a yellow solid in 87% yield starting from **8** and **21e**. ^{1}H NMR (CDCl$_3$, 298 K, 200 MHz, δ ppm) 0.92 (t, J = 6.3 Hz, 6H), 1.2–1.4 (m, 12H), 1.62 (m, 4H), 3.00 (s, 6H), 3.37 (t, J = 7 Hz, 4H), 6.69 (d, J = 8 Hz, 4H), 6.92 (d, J = 16 Hz, 2H), 7.32 (d, J = 16 Hz, 2H), 7.36 (d, J = 5 Hz, 2H), 7.46 (d, J = 8 Hz, 4H), 8.49 (s, 2H), 8.63 (d, J = 5 Hz, 2H). ^{13}C NMR (CDCl$_3$, 298 K, 50 MHz, δ ppm) 14.0, 22.6, 26.7, 26.8, 31.7, 38.3, 52.6, 111.8, 117.8, 120.4, 121.0, 123.8, 128.4, 133.5, 146.7, 149.3, 149.6, 156.5.

4,4′-Bis(p-hexyloxynaphthalene-1-vinyl)-2,2′-bipyridine **22f**. This compound was obtained as a white solid in 78% yield starting from **8** and **21f**. ^{1}H NMR (CDCl$_3$, 298 K, 200 MHz, δ ppm) 0.96 (t, J = 7 Hz, 6H), 1.3–1.7 (m, 12H), 1.98 (m, 4H), 4.21 (t, J = 6.4 Hz, 4H), 6.88 (d, J = 8 Hz, 2H), 7.13 (d, J = 16 Hz, 2H), 7.50–7.67 (m, 6H), 7.75 (d, J = 8 Hz, 2H), 8.20 (d, J = 16 Hz, 2H), 8.22–8.27 (m, 2H), 8.36–8.41 (m, 2H), 8.64 (s, 2H), 8.73 (d, J = 5 Hz, 2H). ^{13}C NMR (CDCl$_3$, 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.