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Functionalized tetradentate ligands for Ru-sensitized solar cells

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Abstract—Syntheses of 6,6′-bis(1-*H*-benzimidazol-2-yl)-4,4′-bis(methoxycarbonyl)-2,2′-bipyridine and a series of new quaterpyridines as functionalized tetradentate ligands is described. A molecular engineering was developed allowing different solubilities, π-systems or grafting modes. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the last two decades, ruthenium polypyridyl complexes have been widely studied because of their photophysical and photochemical properties. Some important industrial applications are related to these properties, as for example energy transduction.[1,2] Recently in our laboratory, *cis*-X_2 bis(bipyridyl)ruthenium complexes ($X=Cl^-$, Br^-, I^-, CN^-, SCN^-) have shown remarkable efficiencies in the conversion of light to electricity.[3] In the course of improving the ability for light absorption of these sensitizers, a *trans*-X_2 bis-(bipyridyl) ruthenium complex ($X=SCN^-$) exhibited a 44 nm redshift of the lowest energy MLCT band.[4] This complex was stable for weeks, but it finally tended to convert to the *cis*-form. Thus, we investigated the preparation of functionalized tetradentate ligands that could lead to stable *trans*-complexes, preventing any *cis*-isomerization. The present study reports on the synthesis and characterization of such ligands.

2. Results and discussion

The target molecules had to meet two requirements: being tetradentate and bearing an anchoring group for the adsorption on TiO_2-films. The latter point had been widely studied in our laboratory and the carboxylate group was chosen because of its good compromise between strong attachment to the TiO_2 surface and efficient injection of electron into the semiconductor conduction band. The first type of tetradentate ligand we synthesized was the 6,6′-bis(1-*H*-benzimidazol-2-yl)-4,4′-bis(methoxycarbonyl)-2,2′-bipyridine **4**. In an initial strategy, the 6,6′-bis(1-*H*-benzimidazol-2-yl)-4,4′-dimethyl-2,2′-bipyridine was synthesized in three steps, starting from the 4,4′-dimethyl-2,2′-bipyridine and using Haga's procedure.[5] Unfortunately, the final oxidation of the methyls to the corresponding carboxylic acid groups always led to decomposition of the ligand. Thus, we decided to introduce the anchoring carboxylate groups in the very first step and to protect them as esters (Scheme 1).

The synthesis of the 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine **1** was realized in two steps from the 4,4′-dimethyl-2,2′-bipyridine by using the literature procedure.[6] The *N*-oxidation to compound **2** was performed by commercial peracetic acid in acetic acid at 40°C for 3 days with an almost quantitative yield.[7] The excess of peracetic acid was neutralized by slow addition of dimethyl sulfide before evaporation of the solvent. Fine needles of **2** were obtained by precipitation in cold methanol from a dichloromethane solution. The next reaction was assumed to proceed as follows: methylation of both *N*-oxides by dimethyl sulfate and nucleophilic substitution by cyanide ions on the α-positions, which induces the liberation of methanol. All attempts to synthesize compound **3** in a one-pot procedure failed. The use of different reagents (Me_2SO_4/KCN or PhCOCl/KCN,[8] Me_3SiCN in refluxing acetonitrile[9] or Me_2NCOCl/Me_3SiCN in dichloromethane[10]) as well as different reaction conditions of temperature, time, or solvent always led either to the starting material or to a mixture of two products that were assigned to be the monosubstituted and the disubstituted bipyridines (vide infra). Whereas repeating exactly the same conditions, the reaction was not reproducible and the average ratio of these two compounds varied respectively from 1:1 to 5:1. It's worth noting that this problem was never encountered with the first strategy when starting from the 4,4′-dimethyl-2,2′-bipyridine-*N*,*N*′-dioxide.

The ^1H NMR spectrum of the mixture allowed us to clearly establish the different compounds synthesized (Fig. 1). The integration of the 7.8–9.7 ppm region revealed two groups of peaks. The first two peaks (labelled 3″ and 5″) were attributed to the expected disubstituted bipyridine **3**. The last five peaks were assigned to a monosubstituted bipyridine. This was emphasized by the multiplicities and

Keywords: tetradentate; bipyridine; quaterpyridine; heterocycles.

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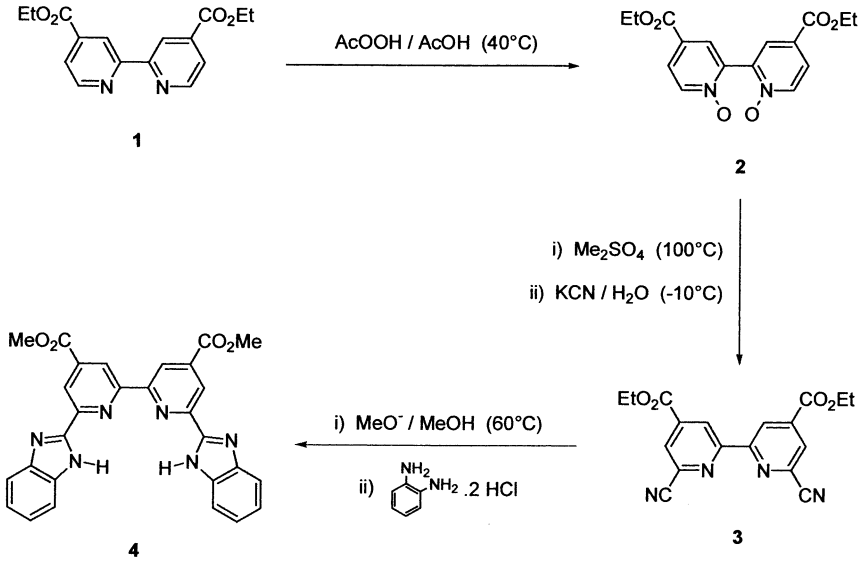


Scheme 1. Synthesis of the bipyridine-bis(benzimidazole).

the coupling constants. At this point, we had to determine which part of the reaction (methylation or cyanation) wasn't achieved quantitatively. Once more, evidence was obtained from the ^{1}H NMR spectrum. Whereas the chemical shift of H^6 suggests the presence of a N–O bond (when compared to compound **2**), there is no methyl peak in the alkyl region of the spectrum. We can conclude that the major fraction of compound **2** is only monomethylated in the first step of the reaction, which explains that a monosubstituted bipyridine is obtained most of the time.

One might guess that the presence of the electron withdrawing ester groups on the 4 and 4′ positions of the bipyridine can strongly destabilize the positively charged nitrogens in compound **2**. Thus, when the first methylation has occurred, the remaining negatively charged oxygen

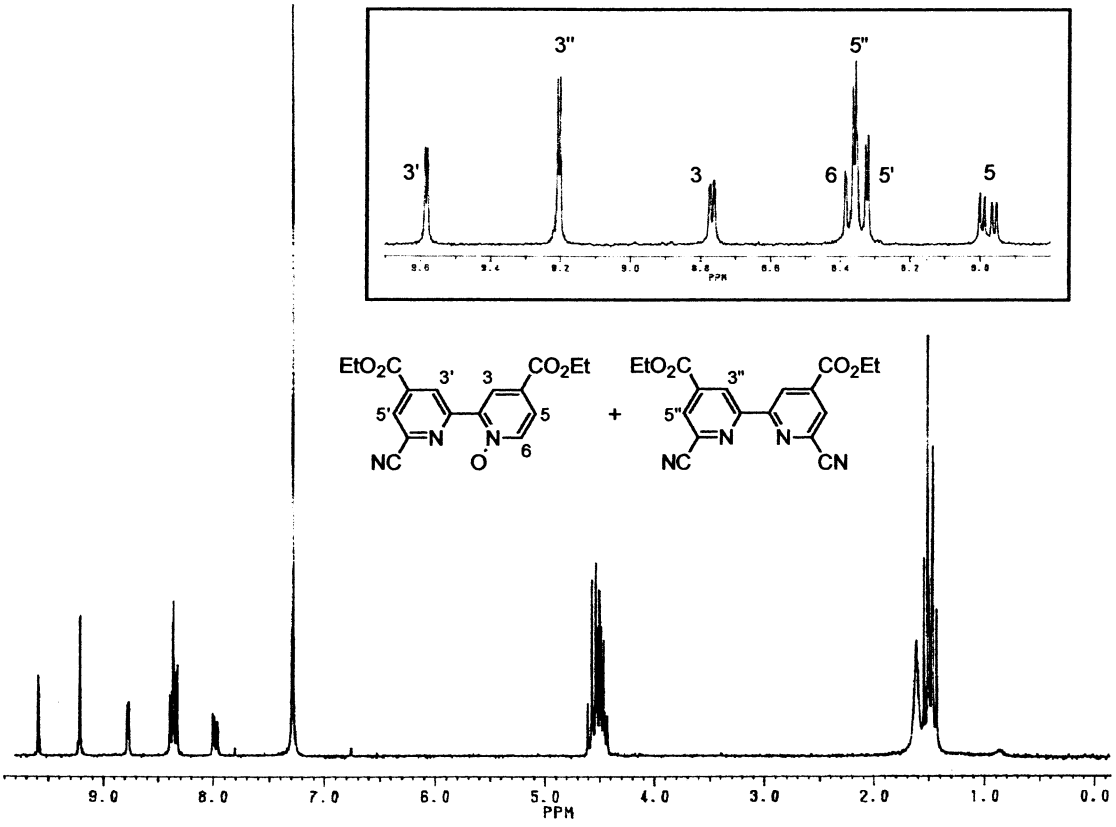


Figure 1. ^{1}H NMR spectrum of the solid obtained after the first 'Me_2SO_4/KCN' procedure.

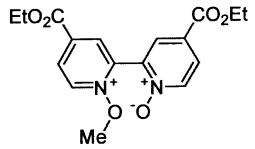


Figure 2. Proposed formula for the intermediate.

might be partially engaged to stabilize the methoxypyridinium, therefore becoming less accessible for the second methylation (Fig. 2). Then, only one substitution occurs and the second *N*-oxide is recovered as such.

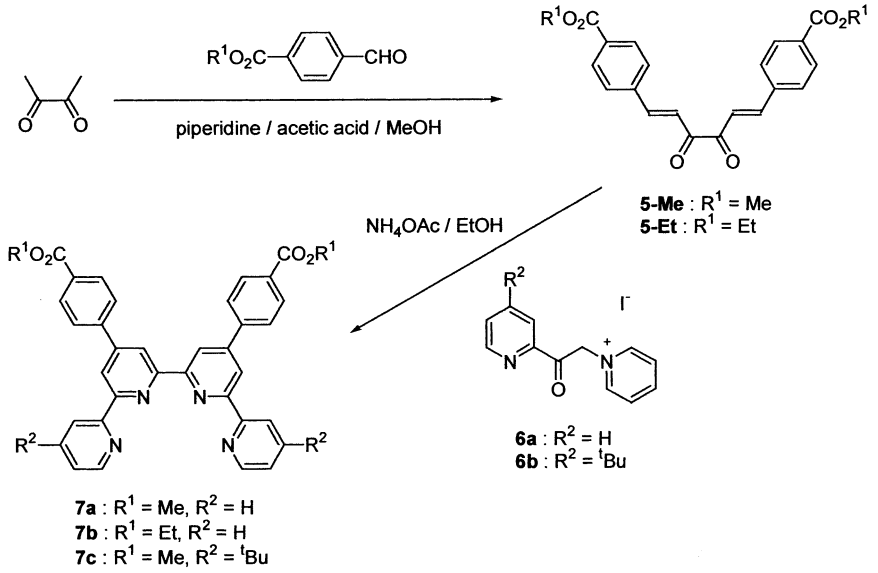
Nevertheless, after the first cyanation, the second *N*-oxide can react by repeating the 'Me_2SO_4/KCN' procedure. By this way, 6,6′-dicyano-4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine **3** was obtained as a white powder by precipitation in methanol from a dichloromethane solution in 55% overall yield. The presence of the ester groups prevents us from applying the usual 'polyphosphoric acid technique' to generate the imidazolyl rings. An alternative route has been proposed by Gandour et al. as follows[11]: the cyano group is first converted to methoxyketimine using sodium methylate in freshly distilled methanol and the benzimidazolyl moiety is then generated by addition of *o*-phenylenediamine dihydrochloride. Using these conditions, the final ligand **4** was obtained as a white powder in 67% yield. Due to the utilization of sodium methylate, all ethyl esters were recovered as methyl esters. Despite drying at 60°C under reduced pressure for 5 days, compound **4** stayed a little bit sticky, which was assumed to be due to the presence of water. However, the chemical shifts are consistent with those reported for the 6,6′-bis(1-*H*-benzimidazol-2-yl)-2,2′-bipyridine that was previously synthesized by Haga.

We also developed a new series of functionalized quaterpyridines. The strategy used for the synthesis of these ligands is based on the methodology of Kröhnke,[12] which has been recently applied by Constable et al. to prepare quaterpyridines bearing phenyl rings on the central pyridines (Scheme 2).[13]

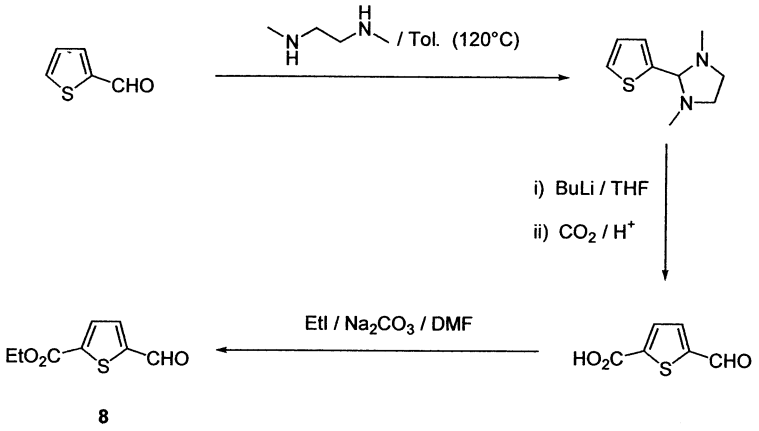
First, the reaction of 2,3-butanedione with methyl 4-formylbenzoate in methanol, catalyzed by piperidinium acetate, afforded the synthesis of the cinnamil **5-Me** as fine orange crystals in moderate yields (20–25%).[14] The reaction of this cinnamil with the so-called Kröhnke's reagent **6a** in the presence of ammonium acetate allowed the formation of the central pyridyl rings and yielded the expected quaterpyridine **7a** as a brownish powder in 34% yield. This ligand proved to be slightly soluble in chlorinated solvents, but its solubility was significantly increased either by using ethyl ester groups (ligand **7b**) or by introducing *tert*-butyl moieties on the external pyridyl rings. For this purpose, the analog **6b** to the Kröhnke's reagent was prepared by heating 2-acetyl-4-*tert*-butylpyridine[15] and one equivalent of iodine in pyridine with 66% yield. This compound is hygroscopic and its color can vary from yellow to green, depending on its exposition to air moisture. In the same conditions as mentioned above, the reaction of this compound with cinnamil **5-Me** led to the highly soluble quaterpyridine **7c**.

The main interest of this technique is to prepare functionalized ligands in a two-step procedure, starting from readily available and inexpensive materials. Moreover, for each step, the compounds are recovered by filtration of the reaction mixture and they do not need any further purification. Another advantage of the quaterpyridine type ligands is the possibility to modify the π-system or the grafting mode by the simple change of the starting aldehyde. Modification of the π-system is one of the tools we can monitor to increase the light absorption efficiency of the sensitizers. We chose to replace the phenyl ring by thiophene because of its lowest resonance energy. Thus, an analog to methyl 4-formylbenzoate was synthesized starting from thiophene-2-carbaldehyde (Scheme 3).

Synthesis of 5-formyl-2-thiophene carboxylic acid was



Scheme 2. Synthesis of substituted quaterpyridines.



Scheme 3. Synthesis of ethyl 5-formyl-2-thiophenecarboxylate.

previously reported by Chadwick.[16] The corresponding ethyl ester **8** can be easily prepared in DMF at room temperature using ethyl iodide and a large excess of sodium carbonate.[17] Concerning the grafting mode, the anchoring carboxylate groups can be substituted by the α-dimethoxy moieties that are the protected forms of the chelating α-diol. In that case, the starting aldehyde should be the commercially available 3,4-dimethoxybenzaldehyde. In the same conditions as mentioned above, the reaction of the aldehyde **8** or the 3,4-dimethoxybenzaldehyde with 2,3-butanedione led to the corresponding cinnamils **9** and **10** and finally to the respective quaterpyridines **11** and **12** (Fig. 3).

3. Conclusion

We present the syntheses of a series of tetradentate ligands for the preparation of stable *trans*-X_2 ruthenium complexes. For the bipyridine-bis(benzimidazole) ligand, the presence of the ester groups forced us to modify the procedure applied with non-substituted bipyridines. We also developed a molecular engineering, which allowed the synthesis of quaterpyridines exhibiting different solubilities, π-systems or grafting modes. The *trans*-$(NCS)_2$ Ru(L) complexes where L is one of the tetradentate ligands described above have already been synthesized. They showed a redshift of the lowest energy MLCT band up to 110 nm as compared to the previously reported *cis*-$(NCS)_2$ bis(bipyridyl)ruthenium. The synthesis of these complexes and their efficiency in dye-sensitized solar cells will be the subject of a forthcoming publication.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer. The reported chemical shifts are against TMS. Elemental analyses were performed by 'Ilse Beetz, Mikroanalytisches laboratorium'. Deuteriated solvents were obtained from Dr Glaser A. G. All chemicals were supplied from Fluka. The reagents were of puriss grade quality and used without further purification, unless specified.

4.1.1. 4,4′-Bis(ethoxycarbonyl)-2,2′-bipyridine-*N*,*N*′-dioxide (2). To a solution of 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine **1** (2.0 g, 6.6 mmol) in acetic acid (20 mL) was added peracetic acid (37% w/w in acetic acid) (4.0 mL, 24.0 mmol) dropwise. The reaction mixture was stirred at 40°C for 3 days. This solution was cooled to room temperature and the remaining peracetic acid was neutralized by slow addition of dimethyl sulfide (2.5 mL, excess). The solvents were evaporated to dryness. The resulting sluggish mixture was dissolved in the smallest amount of dichloromethane and dropped to cold methanol (50 mL). The white precipitate that formed was filtered and washed with cold methanol (2×10 mL) to yield the title compound as white needles (2.1 g; 95%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.36 (2H, dd, $H^{6,6'}$, *J*=6.8, 0.4 Hz); 8.18 (2H, dd, $H^{3,3'}$, *J*=2.5, 0.4 Hz); 7.99 (2H, dd, $H^{5,5'}$, *J*=6.8, 2.5 Hz); 4.42 (4H, q, CH_2, *J*=7.1 Hz); 1.41 (6H, t, CH_3, *J*=7.1 Hz). Anal. found: C, 57.87; H, 4.82; N, 8.39%. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.84; H, 4.85; N, 8.43%.

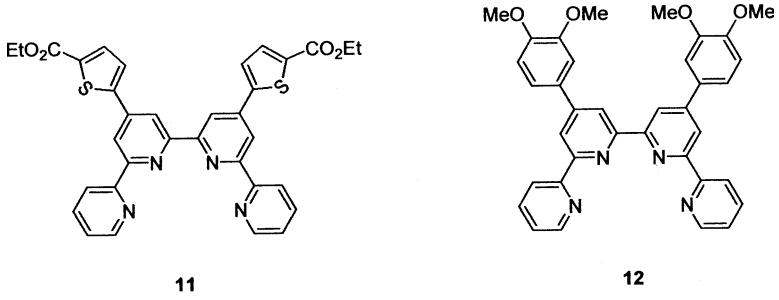


Figure 3. Modified quaterpyridines **11** and **12**.

4.1.2. 6,6′-Dicyano-4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine (3). A solution of freshly distilled dimethyl sulfate (5 mL) and 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine-*N*,*N*′-dioxide **2** (0.66 g, 2.0 mmol) was warmed at 100°C for 4 h. After cooling to room temperature, the viscous yellow mixture was added dropwise to a rapidly stirred, cooled (−10°C) and saturated aqueous potassium cyanide solution (25 mL). A fawn colored solid developed during the course of the addition. Stirring was continued at −10°C for 4 h and the reaction mixture was placed at −20°C overnight. Then, the brownish precipitate was filtered, washed with water (2×10 mL) and dried under vaccuum. Using this precipitate, the same reaction was repeated once more. The resulting solid was dissolved in the smallest amount of dichloromethane, filtered and made precipitate by slow addition to methanol (50 mL) to yield the title compound as a white powder (0.38 g, 55%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz): 9.20 (2H, d, $H^{3,3'}$, *J*=1.4 Hz); 8.36 (2H, d, $H^{5,5'}$, *J*=1.4 Hz); 4.55 (4H, q, CH_2, *J*=7.1 Hz); 1.50 (6H, t, CH_3, *J*=7.1 Hz). Anal. found: C, 61.79; H, 4.10; N, 15.85%. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.03; N, 15.99%.

4.1.3. 6,6′-Bis(1-*H*-benzimidazol-2-yl)-4,4′-bis(methoxycarbonyl)-2,2′-bipyridine (4). Sodium methylate (62 mg, 1.0 mmol) and 6,6′-dicyano-4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine **3** (175 mg, 0.5 mmol) were heated at 60°C in freshly distilled methanol (40 mL) for 6 h. To this solution was added *o*-phenylenediamine dihydrochloride (0.2 g, 1.0 mmol). The solution turned yellow followed by formation of a precipitate. This mixture was stirred at 60°C for 12 h. After cooling to room temperature, the solution was treated with aqueous sodium carbonate (20 mL). The precipitate was filtered and washed with methanol (2×10 mL) to yield the title compound as an hygroscopic pale yellow powder (170 mg, 67%). ^{1}H NMR (DMSO-d_6, δ ppm, *J* Hz): 9.28 (2H, d, $H^{3,3'}$, *J*=1.4 Hz); 8.86 (2H, d, $H^{5,5'}$, *J*=1.4 Hz); 7.75 (4H, m, Ar–H); 7.31 (4H, m, Ar–H); 4.07 (6H, s, CH_3). Anal. found: C, 60.28; H, 4.65; N, 15.36%. Calcd for $C_{28}H_{20}N_6O_4{\cdot}3H_2O$: C, 60.21; H, 4.69; N, 15.04%.

4.1.4. 1,6-Bis[*p*-(methoxycarbonyl)phenyl]hexa-1,5-diene-3,4-dione (5-Me). Piperidine (0.5 mL, 5.0 mmol) and acetic acid (0.3 mL, 5.0 mmol) were added to a stirred solution of methyl 4-formylbenzoate (1.55 g, 9.0 mmol) and 2,3-butanedione (0.4 mL, 4.5 mmol) in methanol (15 mL). The mixture was refluxed for 6 h, while bright orange crystals started to form. After cooling to room temperature, the crystals were filtered and washed with methanol (25 mL) to yield the title compound (0.42 g, 25%). ^{1}H NMR (DMSO-d_6, δ ppm, *J* Hz): 8.03 (4H, d, Ar–H, *J*=8.0 Hz); 7.95 (4H, d, Ar–H, *J*=8.0 Hz); 7.84 (2H, d, =CH, *J*=16.0 Hz); 7.50 (2H, d, =CH, *J*=16.0 Hz); 3.88 (6H, s, CH_3).

4.1.5. 1,6-Bis[*p*-(ethoxycarbonyl)phenyl]hexa-1,5-diene-3,4-dione (5-Et). Using the same conditions as for compound **5-Me**, starting from ethyl 4-formylbenzoate (5.9 g, 33 mmol) the title compound was obtained as orange crystals (1.13 g, 17%). ^{1}H NMR (DMSO-d_6, δ ppm, *J* Hz): 8.02 (4H, d, Ar–H, *J*=8.5 Hz); 7.95 (4H, d, Ar–H, *J*=8.5 Hz); 7.84 (2H, d, =CH, *J*=16.3 Hz); 7.50 (2H, d, =CH, *J*=16.3 Hz); 4.35 (4H, q, CH_2, *J*=6.8 Hz); 1.34 (6H, t, CH_3, *J*=6.8 Hz). Anal. found: C, 71.00; H, 5.42%. Calcd for $C_{24}H_{22}O_6$: C, 70.93; H, 5.45%.

4.1.6. *N*-{2-oxo-2-[2-(4-*tert*-butyl)pyridyl]ethyl}pyridinium iodide (6b). 2-Acetyl-4-*tert*-butylpyridine (1.6 g, 9.0 mmol) was added to a solution of iodine (5.0 g, 20 mmol) in anhydrous pyridine (20 mL) and the mixture was heated at 70°C for 1 h. The dark solution was cooled to room temperature and the solvent was evaporated. To the resulting mixture was added dichloromethane (20 mL). After filtration and evaporation, the title compound was collected as fine brownish crystals (0.94 g, 66%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz): 9.01 (2H, d, $H^{2',6'}$, *J*=6.6 Hz); 8.78 (1H, dd, H^6, *J*=5.1, 0.55 Hz); 8.28 (2H, d, $H^{3',5'}$, *J*=6.6 Hz); 8.15 (1H, d, $H^{4'}$, *J*=7.7 Hz); 8.02 (1H, dd, H^3, *J*=1.2, 0.55 Hz); 7.85 (1H, dd, H^5, *J*=5.1, 1.2 Hz); 1.34 (9H, s, ^{t}Bu). Anal. found: C, 48.14; H, 4.88; N, 7.02%. Calcd for $C_{16}H_{19}N_2OI.H_2O$: C, 48.01; H, 5.28; N, 6.99%.

4.1.7. 4′,4″-Bis[*p*-(methoxycarbonyl)phenyl]-2,2′:6′,2″:6″,2‴-quaterpyridine (7a). 1,6-bis[*p*-(methoxycarbonyl)-phenyl]hexa-1,5-diene-3,4-dione **5-Me** (0.19 g, 0.5 mmol), *N*-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide **6a** (0.33 g, 1.0 mmol) and ammonium acetate (1.0 g, 13 mmol) were refluxed in ethanol (25 mL) for 12 h. The mixture was cooled to room temperature and the precipitate that formed was filtered and washed with ethanol (2×5 mL) to yield the title compound as an off-white solid (0.1 g, 34%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.98 (2H, d, $H^{3',5''}$, *J*=1.6 Hz); 8.82 (2H, d, $H^{5',3''}$, *J*=1.6 Hz); 8.77 (2H, d, $H^{3,3'''}$, *J*=4.2 Hz); 8.73 (2H, d, $H^{6,6'''}$, *J*=9.1 Hz); 8.26 (4H, d, Ar–H, *J*=8.4 Hz); 8.02 (4H, d, Ar–H, *J*=8.4 Hz); 7.93 (2H, dd, $H^{4,4'''}$, *J*=7.7, 1.7 Hz); 7.41 (2H, dd, $H^{5,5'''}$, *J*=6.5, 4.9 Hz); 4.01 (6H, s, CH_3).

4.1.8. 4′,4″-Bis[*p*-(ethoxycarbonyl)phenyl]-2,2′:6′,2″:6″,2‴-quaterpyridine (7b). Using the same conditions as for compound **7a**, starting from 1,6-bis[*p*-(ethoxycarbonyl)-phenyl]hexa-1,5-diene-3,4-dione **5-Et** (1.1 g, 2.7 mmol) the title compound was obtained as a brownish powder (0.48 g, 30%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz): 8.97 (2H, d, $H^{3',5''}$, *J*=1.7 Hz); 8.82 (2H, d, $H^{5',3''}$, *J*=1.7 Hz); 8.77 (2H, ddd, $H^{3,3'''}$, *J*=4.7, 1.6, 0.8 Hz); 8.72 (2H, dt, $H^{6,6'''}$, *J*=7.9, 0.9 Hz); 8.26 (4H, d, Ar–H, *J*=8.6 Hz); 8.01 (4H, d, Ar–H, *J*=8.6 Hz); 7.93 (2H, dd, $H^{4,4'''}$, *J*=7.8, 1.8 Hz); 7.41 (2H, ddd, $H^{5,5'''}$, *J*=7.5, 4.8, 1.2 Hz); 4.48 (4H, q, CH_2, *J*=6.8 Hz); 1.48 (6H, t, CH_3, *J*=6.8 Hz). Anal. found: C, 75.19; H, 4.95; N, 9.30%. Calcd for $C_{38}H_{30}N_4O_4$: C, 75.23; H, 4.98; N, 9.26%.

4.1.9. 4,4‴-Bis(*tert*-butyl)-4′,4″-bis[*p*-(methoxycarbonyl)-phenyl]-2,2′:6′,2″:6″,2‴-quaterpyridine (7c). Using the same conditions as for compound **7a**, starting from 1,6-bis[*p*-(methoxycarbonyl)phenyl]hexa-1,5-diene-3,4-dione **5-Me** (1.65 g, 4.3 mmol) and *N*-{2-oxo-2-[2-(4-*tert*-butyl)-pyridyl]ethyl}pyridinium iodide **6b** (3.5 g, 9.2 mmol) the title compound was obtained as a brownish powder (0.68 g, 23%). ^{1}H NMR ($CDCl_3$, δ ppm, *J* Hz) 9.06 (2H, d, $H^{3',5''}$, *J*=1.6 Hz); 8.82 (2H, d, $H^{5',3''}$, *J*=1.6 Hz); 8.81 (2H, d, $H^{3,3'''}$, *J*=1.4 Hz); 8.68 (2H, d, $H^{6,6'''}$, *J*=5.3 Hz); 8.24 (4H, d, Ar–H, *J*=8.5 Hz); 8.05 (4H, d, Ar–H, *J*=8.5 Hz); 7.42 (2H, dd, $H^{5,5'''}$, *J*=5.3, 1.9 Hz); 4.00 (6H, s, CH_3); 1.49 (18H, s, ^{t}Bu). Anal. found: C, 76.53; H,

6.10; N, 8.05%. Calcd for $C_{44}H_{42}N_4O_4$: C, 76.49; H, 6.12; N, 8.11%.

4.1.10. Ethyl 5-formyl-2-thiophenecarboxylate (8). A solution of 5-formyl-2-thiophene carboxylic acid (3.0 g, 19 mmol), ethyl iodide (3 mL, 37 mmol) and sodium carbonate (10 g, 94 mmol) in DMF (45 mL) was stirred overnight at room temperature. The mixture was poured into water (100 mL) and extracted with ethyl acetate (3×25 mL). The combined extracts were dried and the solvent evaporated. The crude product was distilled (kugelrohr) to yield the title compound as a pale yellow oil which crystallizes (1.84 g, 53%). ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 9.97 (1H, s, CHO); 7.83 (1H, d, Ar–H, J=3.9 Hz); 7.73 (1H, d, Ar–H, J=3.9 Hz); 4.39 (2H, q, CH_2, J=7.0 Hz); 1.40 (2H, t, CH_3, J=7.0 Hz).

4.1.11. 1,6-Bis(5-ethoxycarbonyl-2-thienyl)hexa-1,5-diene-3,4-dione (9). Using the same conditions as for compounds **5**, starting from ethyl 5-formyl-2-thiophene-carboxylate (1.84 g, 10 mmol) the title compound was obtained as an orange powder (0.45 g, 13%). ^{1}H NMR (DMSO-d_6, δ ppm, J Hz): 7.95 (2H, d, =CH, J=16.1 Hz); 7.80 (4H, d, Ar–H, J=3.9 Hz); 7.74 (4H, d, Ar–H, J=3.9 Hz); 7.24 (2H, d, =CH, J=16.1 Hz); 4.33 (4H, q, CH_2, J=7.1 Hz); 1.32 (6H, t, CH_3, J=7.1 Hz). Anal. found: C, 56.48; H, 4.54%. Calcd for $C_{20}H_{18}O_6S_2$: C, 57.40; H, 4.34%.

4.1.12. 1,6-Bis[3,4-(dimethoxy)phenyl]hexa-1,5-diene-3,4-dione (10). Using the same conditions as for compounds **5**, starting from 3,4-dimethoxybenzaldehyde (16.6 g, 0.1 mol) the title compound was obtained as an orange powder (1.54 g, 8%). ^{1}H NMR (DMSO-d_6, δ ppm, J Hz): 7.68 (2H, d, =CH, J=16.2 Hz); 7.41 (1H, d, Ar–H, J=1.7 Hz); 7.37 (1H, dd, Ar–H, J=8.3, 1.7 Hz); 7.21 (2H, d, =CH, J=16.2 Hz); 7.04 (1H, d, Ar–H, J=8.3 Hz); 3.84 (6H, s, 2×CH_3). Anal. found: C, 69.04; H, 5.78; O, 25.14%. Calcd for $C_{22}H_{22}O_6$: C, 69.09; H, 5.79; O, 25.10%.

4.1.13. 4′,4″-Bis(5-ethoxycarbonyl-2-thienyl)-2,2′:6′,2″:6″,2‴-quaterpyridine (11). Using the same conditions as for compounds **7**, starting from 1,6-bis(5-ethoxycarbonyl-2-thienyl)hexa-1,5-diene-3,4-dione **9** (0.2 g, 0.5 mmol) the title compound was obtained as a greenish powder (63 mg, 21%). ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 8.98 (2H, broad, $H^{3',5''}$); 8.94 (2H, d, $H^{5',3'''}$, J=1.4 Hz); 8.85 (2H, m, $H^{3,3'''}$); 8.79 (2H, d, $H^{6,6'''}$, J=7.9 Hz); 8.13 (2H, m, $H^{4,4'''}$); 7.92–7.88 (4H, m, Ar–H); 7.55 (2H, m, $H^{5,5'''}$); 4.44 (4H, q, CH_2, J=7.0 Hz); 1.45 (6H, t, CH_3, J=7.0 Hz). Anal. found: C, 66.13; H, 4.06; N, 8.92%. Calcd for $C_{34}H_{26}N_4O_4S_2$: C, 66.00; H, 4.23; N, 9.05%.

4.1.14. 4′,4″-Bis[3,4-(dimethoxy)phenyl]-2,2′:6′,2″:6″,2‴-quaterpyridine (12). Using the same conditions as for compounds **7**, starting from 1,6-bis[3,4-(dimethoxy)-phenyl]hexa-1,5-diene-3,4-dione **10** (1.5 g, 4 mmol) the title compound was obtained as a pale yellow powder (475 mg, 21%). ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 8.91 (2H, d, $H^{3',5''}$, J=1.7 Hz); 8.78 (2H, m, $H^{3,3'''}$); 8.75 (2H, m, $H^{5',3''}$); 8.71 (2H, m, $H^{6,6'''}$); 7.94 (2H, dd, $H^{4,4'''}$, J=7.7, 1.6 Hz); 7.55 (2H, d, Ar–H, J=8.3, 2.0 Hz); 7.46 (2H, d, Ar–H, J=2.0 Hz); 7.41 (2H, dd, $H^{5,5'''}$, J=7.4, 1.5 Hz); 7.07 (2H, d, Ar–H, J=8.3 Hz); 4.06 (3H, s, CH_3); 4.00 (3H, s, CH_3). Anal. found: C, 72.30; H, 5.35; N, 9.46%. Calcd for $C_{36}H_{30}N_4O_4$: C, 74.21; H, 5.20; N, 9.61%.

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