

Bipyridines

SPECIAL
ISSUESynthesis and Electrochemical and Photophysical Characterization of New 4,4'- π -Conjugated 2,2'-Bipyridines that are End-Capped with Cyanoacrylic Acid/Ester GroupsAnja Fingerhut,^[a] Yanlin Wu,^[b] Axel Kahnt,^{*[c]} Julien Bachmann,^{*[b]} and Svetlana B. Tsogoeva^{*[a]}

Abstract: Two new functionalized 4,4'-disubstituted 2,2'-bipyridines that were end-capped with cyanoacrylic acid or cyanoacrylic acid ester anchoring groups, which might allow their efficient functionalization on TiO₂ or other metal-oxide semiconductor surfaces, have been synthesized and characterized by electrochemical, photophysical, and spectroscopic

measurements. The electrochemical and photophysical properties of these 4,4'-disubstituted 2,2'-bipyridines with extended π systems, in particular their LUMO energies, make them promising candidates to build up inorganic-organic hybrid photosensitizers for the sensitization of metal-oxide semiconductors (e.g., TiO₂ nanoparticles and/or nanotubes).

Introduction

Owing to the finite supply of fossil fuels and the negative impact of fossil-fuel usage on the climate, it is foreseeable that harvesting solar energy will obviously become the main source of clean and renewable energy. For this to be the case, solar

energy in the form of light needs to be efficiently converted into storable forms, such as electrical power, or transformed into "solar fuel", such as hydrogen, through photocatalytic water splitting.^[1]

Such light-harvesting systems typically comprise a photosensitizer dye and a metal-oxide or electron acceptor molecule, which show strong absorption cross-sections in a wide range of the visible spectrum, as well as sufficiently high LUMO energies to allow efficient electron-transfer reactions to the acceptor (the metal-oxide semiconductor conduction band or the HOMO of the molecular electron acceptor). Strongly fluorescent dyes based on nitrogen-containing heterocycles (e.g., bipyridines) are commonly employed as photosensitizer building blocks,^[2,3] because of their ease of synthesis; moreover, derivatization of the pyridine ring allows fine-tuning of the optical and electronic properties of the building blocks, as well as attaching anchoring groups for linking to metal-oxide surfaces.^[2b,4]

Organic bipyridine-based π -extended compounds have been employed as photoluminescent materials in, for example, nonlinear optics (NLO). These systems absorb light through intramolecular charge transfer (ICT) and emit from the corresponding photoexcited state.^[5] Moreover, bipyridine-, terpyridine-, or phenanthroline-based π -extended compounds are widely used as ligands in metal complexes (Figure 1),^[6] which are used in electrochemical applications,^[7] in particular in light-emitting diodes^[8] or as dyes for dye-sensitized solar cells (DSSCs).^[2b,4] These ligands enable the fine-tuning of the photophysical and electrochemical properties of the complexes by influencing the metal-to-ligand charge transfer (MLCT) process.^[9,10]

Such fine-tuning can either be performed by an π -acceptor ligand, which has a low-lying π^* molecular orbital, or a strong donor ligand, which destabilizes the metal t_{2g} orbitals.^[6g,11]

[a] A. Fingerhut, Prof. Dr. S. B. Tsogoeva
Department of Chemistry and Pharmacy
Organic Chemistry Chair I and Interdisciplinary Center for Molecular Materials (ICMM)
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Henkestrasse 42
91054 Erlangen (Germany)
E-mail: svetlana.tsogoeva@fau.de

[b] Y. Wu, Prof. Dr. J. Bachmann
Department of Chemistry and Pharmacy
Inorganic Chemistry Chair II
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Egerlandstrasse 1
91058 Erlangen (Germany)
E-mail: julien.bachmann@fau.de

[c] Dr. A. Kahnt
Department of Chemistry and Pharmacy
Physical Chemistry Chair I
Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)
Egerlandstrasse 3
91058 Erlangen (Germany)
E-mail: axel.kahnt@fau.de

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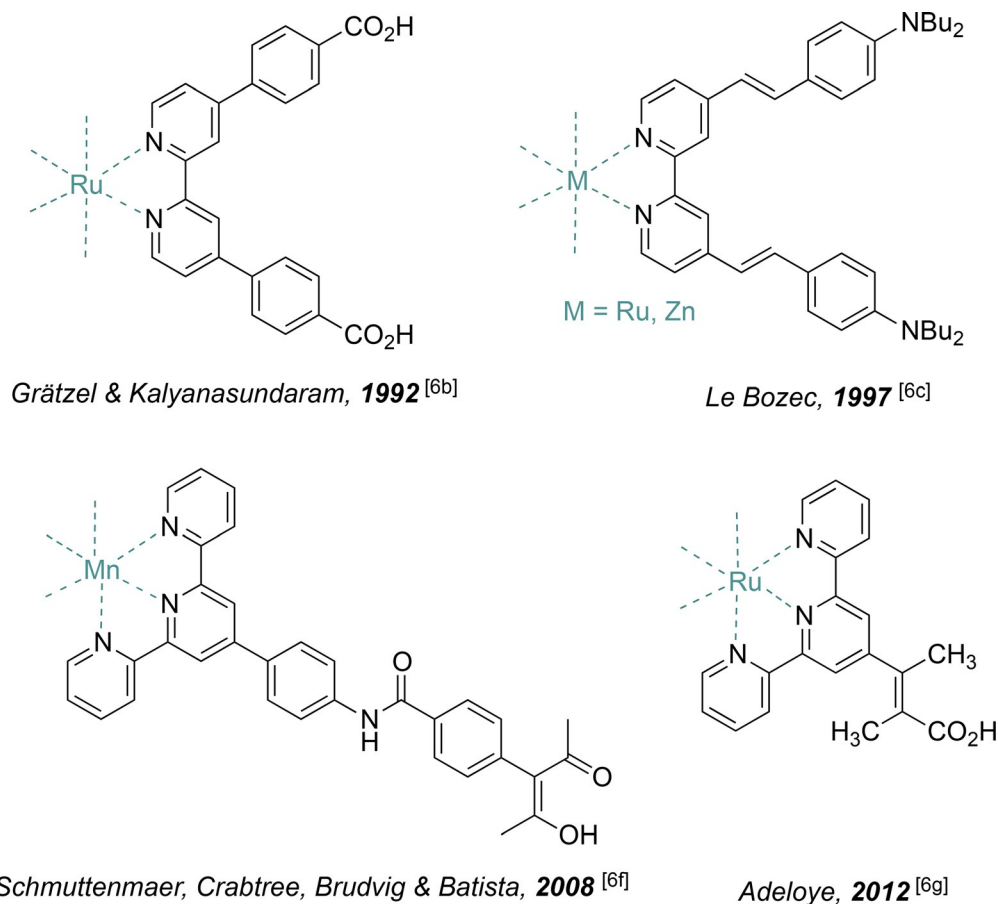


Figure 1. Known pyridine-based π -extended ligands and their metal complexes.^[6b,c,f,g]

A further possible method for modifying the spectroscopic and redox properties of the complexes is through extension of the coordinating pyridine-based moiety with a large π -extended system, the so-called “antenna function”, to suppress charge recombination by spatial separation.^[12] Application of this method to π -conjugated 2,2'-bipyridines^[6] has been dominated by using donor end-capped antennae.

To the best of our knowledge, examples of 2,2'-bipyridine 4,4'-based π -extended systems that are end-capped with electron-withdrawing groups (which can also be used as anchoring acceptor moieties on metal-oxide surfaces) are scarce;^[6b,13] therefore, the development of new derivatives is in high demand. Notably, only carboxylic acid (COOH) and ester (COOR) groups that were directly attached to the corresponding phenyl framework have been used as anchoring groups in these systems so far. However, cyanoacrylic acid groups are commonly employed as anchoring moieties of photosensitizers in DSSCs,^[14] because excited electrons can be effectively injected into the conduction band of TiO₂ through the carboxy anchoring group adjacent to the electron-accepting cyano group of the organic photosensitizer.^[15]

Interestingly, π -conjugated 2,2'-bipyridines with cyanoacrylic acids as anchoring acceptor moieties have never been reported before. Herein, we report the synthesis and electrochemical and photophysical properties of new fluorescent 4,4'- π -conju-

gated 2,2'-bipyridines (**5** and **6**) that are end-capped with cyanoacrylic acid or cyanoacrylic acid ester moieties, and investigate their potential applications in photocatalytic processes, for example, as ligands in inorganic–organic hybrid hole-transport materials and DSSCs.

Results and Discussion

Synthesis

Our design of new 4,4'- π -conjugated 2,2'-bipyridines **5** and **6** was inspired by known neutral organic dyes, which contain cyanoacrylic acid as an acceptor moiety.^[16] We assumed that the introduction of an additional C=C double bond between the 2,5-dimethoxyphenyl framework and the cyanoacrylic acid/ester anchoring groups might increase the π conjugation and can result in a broader absorption in the visible-light region of the electromagnetic spectrum. In addition, such molecules are synthetically more accessible in comparison to known literature compounds 4,4'- π -conjugated 2,2'-bipyridines.^[6b,13]

For the preparation of new bipyridine dyads, initially, a four-step literature procedure of 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**; Figure 2) was performed, starting from commercially available 4,4'-dimethyl-2,2'-bipyridine.^[13]

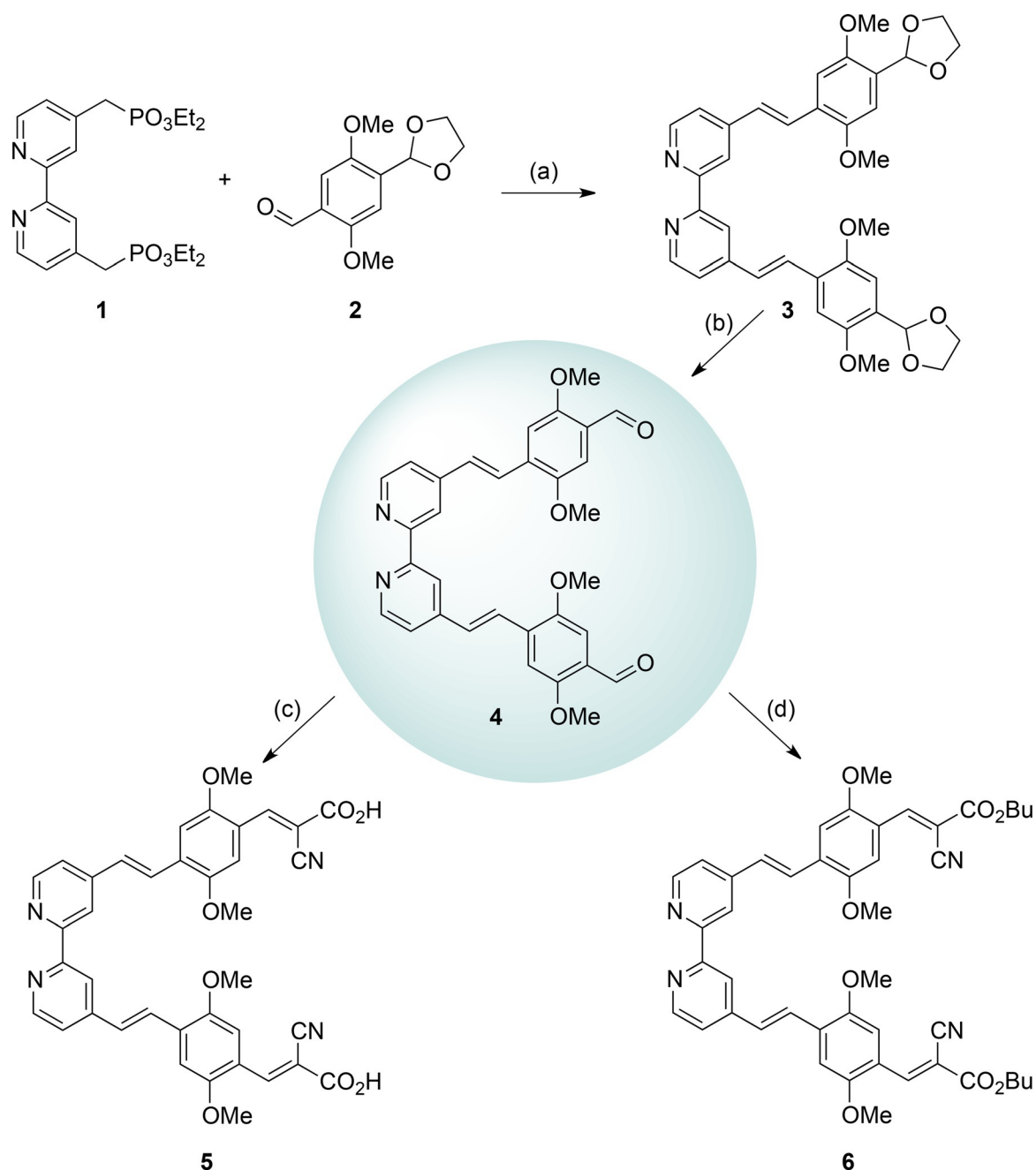


Figure 2. Reaction conditions: a) *t*BuOK, THF, 70 °C, 24 h (97% yield); b) 2 M HCl, CHCl₃, RT, 10 h (98% yield); c) cyanoacetic acid (40 equiv), piperidine, MeCN, 90 °C, 24 h (46% yield); d) cyanoacetic acid butyl ester, (40 equiv), piperidine, MeCN, 90 °C, 24 h (63% yield).

To avoid the formation of side products in the subsequent Horner–Wadsworth–Emmons (HWE) reaction (Figure 2), an additional dialdehyde-protection step was performed (see the Supporting Information). Thus, monoprotected dibenzaldehyde 4-(1,3-dioxolan-2-yl)-2,5-dimethoxybenzaldehyde (**2**) was synthesized under stoichiometric control by using ethylene glycol and *para*-toluenesulfonic acid as a catalyst. After purification by column chromatography on silica gel, monoacetal **2** was obtained in moderate yield. Then, 4-(1,3-dioxolan-2-yl)-2,5-dimethoxybenzaldehyde (**2**) and 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**) in a 2:1 molar ratio were applied in a *trans*-selective C=C bond-forming HWE reaction (Figure 2). π -

Conjugated two-armed bipyridine compound **3** was obtained in excellent yield without further purification. After the successful HWE coupling reaction, acid hydrolysis of the acetals regenerated the free aldehyde moieties in bipyridine compound **4** in almost quantitative yield.

A typical Knoevenagel condensation reaction between free-aldehyde-containing bipyridine **4** and an excess of cyanoacetic acid (as a CH-acidic compound) was performed with piperidine as a base to obtain compound **5** as an orange, sparingly soluble solid after trituration with THF and acetone. Owing to its insolubility, we could not characterize this compound by ¹³C NMR spectroscopy.

To improve the solubility of the bipyridine dyads, a less-polar ester function, rather than the carboxylic acid function derived from cyanoacetic acid, was desirable. Thus, a Knoevenagel condensation reaction was performed between aldehyde-containing two-armed bipyridine **4** and an excess of cyanoacetic acid butyl ester (as a CH-acidic compound), which yielded target compound **6** with good solubility in CH_2Cl_2 .

Adsorption Behavior

The utilization of molecular dyes in dye-sensitized solar cells necessitates that the bipyridine ligands bind to the surface of TiO_2 colloids through an ester linkage. For this purpose, crystalline colloids are typically coated with a thin layer of amorphous TiO_2 , which provides a high number of reactive sites.^[17,18]

Both compounds **5** and **6** adsorbed onto amorphous TiO_2 (Figure 3 a), even from the polar solvent DMSO (**5**). The spectroscopic ellipsometry curves displayed marked shifts upon soaking the planar substrates in the corresponding solutions,

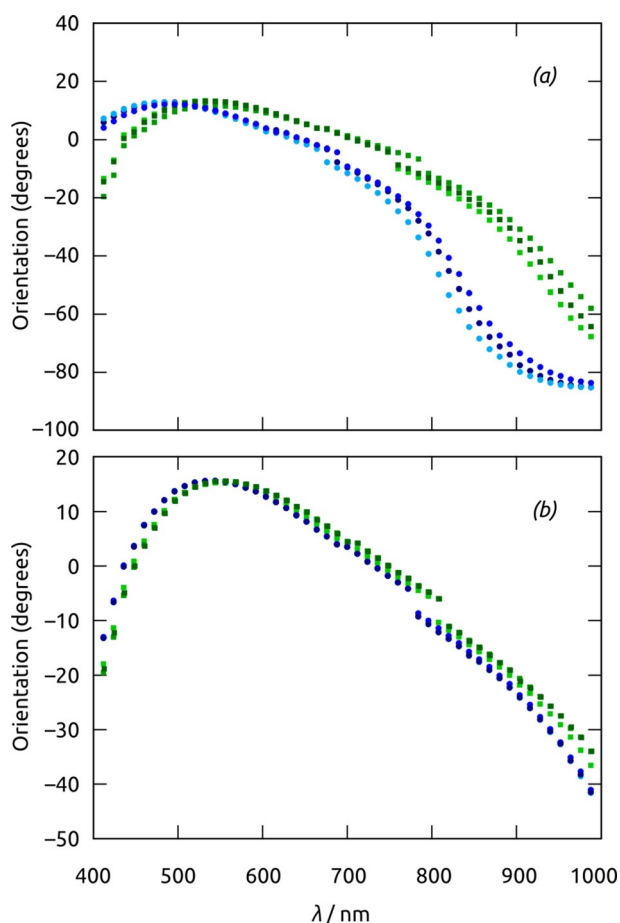


Figure 3. Adsorption behavior of compounds **5** (blue) and **6** (green) on TiO_2 studied by spectroscopic ellipsometry of $\text{Si}/\text{SiO}_2/\text{TiO}_2$ wafers: a) with an amorphous TiO_2 layer (before annealing) and pure DMSO (**5**) or CH_2Cl_2 (**6**); b) with a crystalline TiO_2 layer (after annealing) and DMSO/ CH_2Cl_2 (1:1, v/v) mixtures for both compounds. In each case, three curves are shown: before soaking (light blue/green), after soaking (blue/green), and after an additional overnight rinse in pure solvent (dark blue/green).

and the curves did not revert to their initial states, even after extensive rinsing in pure solvent. The results were different on crystalline TiO_2 , which provided fewer reactive surface sites.^[17,18] Compound **5** (end-capped with cyanoacrylic acid groups) did not yield a stable chemisorbed layer, whereas compound **6** did (Figure 3 b). This difference was not owing to solvent effects, because it was also observed if both compounds were dissolved in a mixture of CH_2Cl_2 and DMSO (1:1 v/v). The difference could be owing to hydrogen-bonding interactions between the carboxylic acid moieties and the bipyridine units, which might significantly decrease the reactivity of the linker.

LUMO Energies

The next requirement of bipyridine ligands for use in dye-sensitized solar cells or other light-harvesting devices is that an electron that is photoexcited into the LUMO of the bipyridine must have sufficient energy to be injected into the TiO_2 conduction band.

A first approximation of the LUMO energy was obtained by using voltammetric methods. Figure 4 shows differential pulse

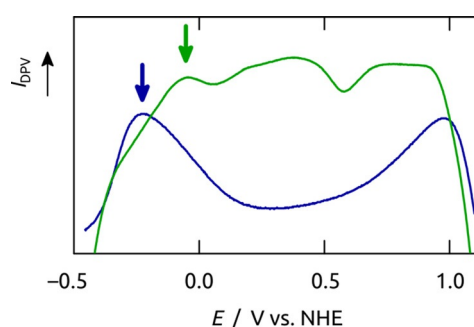


Figure 4. Differential pulse voltammetry of compounds **5** (blue) and **6** (green) as dilute ($5 \mu\text{M}$) solutions in $\text{CH}_2\text{Cl}_2/\text{DMSO}$ (1:1 v/v). Arrows denote the reduction peak for each compound.

voltammetry (DPV) curves for dilute solutions of compounds **5** and **6**. Reduction was observed at -0.22 V and -0.06 V (vs. NHE) for compounds **5** and **6**, respectively. The difference between these values was most likely owing to electrostatic (protonation) effects. Importantly, both reduction potentials were close to the energy of the TiO_2 valence band (-4.21 eV on the absolute scale, -0.31 V vs. NHE).^[19]

Photophysical Properties

The ground-state absorption spectra of compounds **6** and **5** in THF exhibited almost-identical characteristic absorptions, with bands in the UV and blue-light regions of the optical spectrum and maxima at 350 and 436 nm (**6**) and 346 and 430 nm (**5**); see Figure 5 and the Supporting Information, Figure S14).

Upon photoexcitation at 420 nm, solutions of compounds **6** and **5** in THF exhibited strong fluorescence between 450 and 750 nm, with maxima at 513 nm (**6**) and 496 nm (**5**)— see

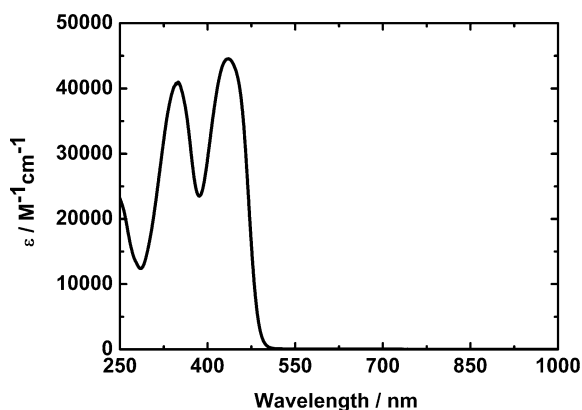


Figure 5. Absorption spectrum of compound 6 in THF.

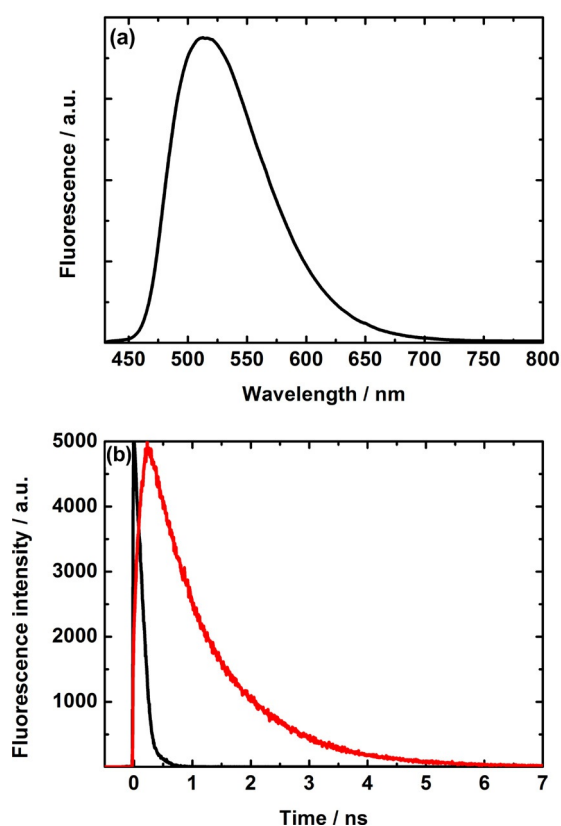


Figure 6. a) Fluorescence spectrum of compound 6 in THF upon photoexcitation at 420 nm. b) Fluorescence–time profile for compound 6 in THF at 500 nm, upon photoexcitation at 403 nm (red); the Instrument Response Function (IRF) is shown in black.

Figure 6 and the Supporting Information, Figure S15. Fluorescence quantum yields of 0.075 (6) and 0.085 (5) in THF were calculated by using tetraphenylporphyrin (H_2TPP) and zinc tetraphenylporphyrin ($ZnTPP$) as reference compounds, which have fluorescence quantum yields of 0.11 and 0.03 in toluene, respectively.^[20] Fluorescence lifetimes of 1.1 ns (6) and 1.3 ns (5) were obtained upon photoexcitation at 403 nm (Figure 6 and the Supporting Information, Figure S15).

Transient absorption measurements based on femtosecond laser photolysis provided insight into the formation and fate of the excited states, in particular the $S_1 \rightarrow S_N$ transitions. Solutions of compounds 6 and 5 in THF were photoexcited with femtosecond laser pulses with a wavelength of 387 nm. Both samples showed essentially identical transient absorption spectra, with two dominating maxima at 580 and 810 nm, which were owing to $S_1 \rightarrow S_N$ transitions, accompanied by a minor minimum around 510 nm, which originated from spontaneous emission (see the fluorescence spectra), and poorly resolved transient bleaching about 430 nm, which mirrored the ground-state absorption (see Figure 7 and the Supporting Information, Figure S16). For both samples, transient absorption decays to the ground state were recorded, with lifetimes of 1.0 ns (6) and 1.2 ns (5), in line with the measured fluorescence lifetimes.

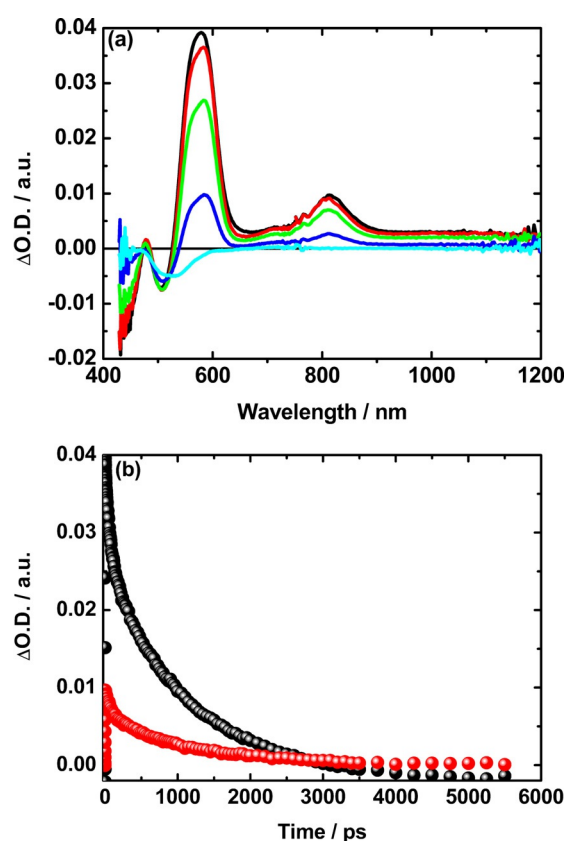


Figure 7. a) Femtosecond transient absorption spectra of compound 6 in Ar-saturated THF at different times after excitation with a femtosecond laser pulse (387 nm, 200 nJ pulse⁻¹, < 150 fs FWHM): 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 5500 ps (cyan). b) Corresponding absorption–time profiles at 580 nm (black) and 810 nm (red).

Conclusion

Herein, we have reported the synthesis and electrochemical and photochemical properties of two new symmetrically disubstituted bipyridines (5 and 6) that were end-capped with cyanoacrylic acid or cyanoacrylic acid ester moieties; these compounds are suitable as ligands for the generation of metal-

based photosensitizers and for the chemical functionalization of TiO₂. Their adsorption behavior on TiO₂ was studied by using spectroscopic ellipsometry and a first approximation of their LUMO energies was obtained by using voltammetric methods. These measurements provided solid evidence for the efficient anchoring of compound **6** on TiO₂ and showed a sufficient LUMO energy for efficient electron transfer into the TiO₂ conduction band.

Photophysical studies demonstrated the feasibility of these compounds as potential photosensitizer dyes. Particularly appealing was the combination of matching the LUMO energies relative to the TiO₂ conduction band with a sufficient long-lived singlet first excited state (> 1 ns), which we anticipate would give rise to efficient electron transfer from the disubstituted bipyridine derivative into the TiO₂ conduction band; this property is expected to be confirmed in a subsequent study. The synthesis of the corresponding Ru, Mn, and Fe complexes of our new organic photosensitizers (**5** and **6**; for promising results from a preliminary complexation experiment, see the Supporting Information, Figure S17) and their covalent binding to the surface of TiO₂ nanoparticles and/or nanotubes for applications in visible-light photocatalytic water oxidation and/or DSSCs is currently underway in our laboratory.

Experimental Section

Materials and General Procedures

4,4'-Bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**)^[15] was prepared according to a literature procedure. Chemicals were purchased from commercial sources and used without further purification. All solvents were purified by distillation, dried according to standard procedures, or of HPLC grade. All of the reactions were performed in flame-dried glassware under a nitrogen atmosphere by using standard Schlenk techniques. Preparative (flash) column chromatography was performed on Acros Silica gel 60 (0.035–0.070) as the stationary phase. All products were dried under high vacuum ($\times 10^{-3}$ bar). Thin-layer chromatography (TLC) was performed on precoated aluminum silica gel SIL G/UV254 plates (Macherey–Nagel & Co.). ¹H and ¹³C NMR spectra were recorded at RT on Bruker Avance 300 and JEOL JNM GX 400 spectrometers at 300 MHz and 400 MHz, respectively. All chemical shifts (ppm) are related to undeuterated solvent. NMR data were processed by using the MestReNova program. MS (MALDI) analysis was performed on a Shimadzu Biotech AXIMA Confidence; MS (ESI) analysis was performed on Bruker Daltonik maXis 4G or Bruker Daltonik micrOTOF II focus spectrometers. IR spectra were recorded on a Varian IR-660 apparatus; absorptions are reported in wavenumbers (cm⁻¹).

Sodium tetrafluoroborate (NaBF₄) and tetrabutylammonium tetrafluoroborate (tBu₄NBF₄) were purchased from Sigma–Aldrich and used as supporting salts. CH₂Cl₂ and DMSO were purchased from commercial suppliers and used as received. The atomic layer deposition (ALD) precursor Ti(OiPr)₄ was purchased from Alfa Aesar, and water was purified immediately before use in a Millipore Direct-Q system. Boron-doped [100] CZ silicon wafers with 200 nm thermal oxide were purchased from Silicon Materials. Pt wire (Alfa Aesar) was used as the working and auxiliary electrodes; Ag/AgCl (sat.)/NaCl (3 M) was purchased from Bionalytical Systems, Inc. (BASi) and used as a reference electrode (+0.209 V vs. NHE).

4-(1,3-Dioxolan-2-yl)2,5-dimethoxybenzaldehyde (**2**)

2,5-Bis-methoxy-1,4-dibenzaldehyd (500 mg, 2.58 mmol), ethylene glycol (187 μ L, 3.35 mmol), and *para*-toluenesulfonic acid (9.80 mg, 2 mol%) were dissolved in dry toluene (10 mL) and stirred for 21 h at reflux. After cooling to RT, the solution was washed with distilled water (3 \times 20 mL), dried over MgSO₄, and the solvent was removed by rotary evaporation. Subsequently, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc, 4:1 v/v), and compound **2** was obtained as the main product in the second fraction after removal of the eluent as a white solid (307 mg, 1.29 mmol, 50% yield). ¹H NMR (300 MHz, CDCl₃): δ = 10.41 (s, 1H), 7.30 (s, 1H), 7.20 (s, 1H), 6.06 (s, 1H), 4.15–4.00 (m, 4H), 3.88 (s, 3H), 3.83 ppm (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 189.5, 156.6, 151.9, 133.7, 125.3, 110.8, 109.3, 98.7, 65.4, 56.2, 56.2 ppm; MS (MALDI): *m/z*: 238 [M+H]⁺.

4,4'-Bis((E)-4-(1,3-dioxolan-2-yl)-2,5-dimethoxystyryl)-2,2'-bipyridine (**3**)

A suspension of potassium *tert*-butoxide (65 mg) in anhydrous THF (6 mL) was added dropwise under a nitrogen atmosphere to a solution of compound **1** (89 mg, 0.195 mmol) and 4-(1,3-dioxolan-2-yl)-2,5-dimethoxybenzaldehyde (**2**; 102 mg, 0.428 mmol) in anhydrous THF (2 mL) and the yellow-brownish reaction mixture was heated at reflux for 39 h. The reaction was quenched by the addition of water (HPLC grade, 30 mL) and, after filtration, the residue was taken up in CH₂Cl₂. The filtered matter was extracted with CH₂Cl₂ and the combined organic phases were dried with MgSO₄. After removal of the solvent, the product was dried under vacuum. The title compound (**3**) was obtained as a yellowish solid (119 mg, 0.190 mmol, 97% yield). ¹H NMR (300 MHz, CDCl₃): δ = 8.65 (d, *J* = 5.1 Hz, 2H), 8.53 (s, 2H), 7.77 (d, *J* = 16.5 Hz, 2H), 7.45 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.6 Hz, 2H), 7.17 (d, *J* = 16.2, 2H), 7.14 (s, 2H), 7.13 (s, 2H), 6.12 (s, 2H), 4.18–4.02 (m, 8H), 3.90 (s, 6H), 3.89 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 156.7, 151.9, 151.8, 149.5, 146.2, 128.2, 127.3, 127.0, 126.6, 120.8, 118.8, 110.0, 109.7, 99.0, 65.3, 56.3, 56.1 ppm; MS (MALDI): *m/z*: 625 [M+H]⁺.

4,4'-((1E,1'E)-[2,2'-Bipyridine]-4,4'-diylbis(ethene-2,1-diyl))-bis(2,5-di-methoxybenzaldehyde) (**4**)

2 M HCl (6 mL) was gradually added to a solution of compound **3** (119 mg, 0.190 mmol) in CHCl₃ (18 mL) and the red mixture was stirred for 14.5 h. Then, the organic layer was separated, washed with a saturated aqueous solution of NaHCO₃ and brine, and finally dried with MgSO₄. The solvent was evaporated and, to complete the deprotection step, the crude product was treated gradually with 2 M HCl (6 mL) in CHCl₃ (18 mL). The organic layer was separated, washed with a saturated aqueous solution of NaHCO₃ and brine, and finally dried over MgSO₄. The solvent was evaporated and the title compound was obtained as a yellow solid (100 mg, 0.186 mmol, 98% yield). ¹H NMR (300 MHz, CDCl₃): δ = 10.44 (s, 2H), 8.69 (d, *J* = 5.2 Hz, 2H), 8.61 (s, 2H), 7.79 (d, *J* = 16.5 Hz, 2H), 7.49 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.5 Hz, 2H), 7.36 (s, 2H), 7.30 (d, *J* = 16.5 Hz, 2H), 7.21 (s, 2H), 3.97 (s, 6H), 3.91 ppm (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 189.0, 156.4, 156.1, 151.7, 149.4, 132.6, 129.9, 127.9, 124.9, 121.1, 119.1, 117.8, 110.4, 109.4, 56.2, 56.1 ppm; MS (MALDI): *m/z*: 537 [M+H]⁺.

(2E,2'E)-3,3'-(((1E,1'E)-[2,2'-Bipyridine]-4,4'-diylbis(ethene-2,1-diyl))bis(2,5-dimethoxy-4,1-phenylene))bis(2-cyanoacrylic acid) (5)

Cyanoacetic acid (970 mg, 11.4 mmol) and piperidine (1.13 mL, 11.4 mmol) were added to a suspension of compound **4** (153 mg, 0.285 mmol) in dry MeCN (12 mL). The yellow suspension was stirred for 24 h at 90 °C. Then, CH₂Cl₂ and a 2 M aqueous solution of H₃PO₄ were added and the mixture turned orange. The mixture was filtered and washed with THF and acetone. The filtrate was dried under vacuum and the title compound was obtained as an orange, sparingly soluble solid (87.2 mg, 0.13 mmol, 46% yield). M.p. 280 °C (dec.); ¹H NMR (400 MHz, [D₆]DMSO; NMR analysis was facilitated by the addition of a small amount of hot DMF): δ = 8.72 (d, J = 4.8 Hz, 2H), 8.60 (s, 2H), 8.24 (s, 2H), 7.84 (s, 2H), 7.78 (d, J = 16.3 Hz, 2H), 7.70 (dd, J₁ = 4.9 Hz, J₂ = 1.5 Hz, 2H), 7.66 (d, J = 16.3 Hz, 2H), 7.54 (s, 2H), 3.95 (s, 6H), 3.90 ppm (s, 6H); FTIR (ATR): $\tilde{\nu}$ = 3599 (w), 2948 (w), 2836 (w), 2363 (m), 2215 (w), 2115 (w), 1921 (w), 1711 (m), 1588 (s), 1498 (m), 1464 (m), 1415 (m), 1352 (m), 1251 (s), 1215 (s), 1031 (s), 960 (s), 864 (m), 810 (m), 731 (m), 660 (m), 567 (s), 484 (m), 430 cm⁻¹ (s); MS (MALDI): m/z: 671 [M+H]⁺; HRMS (MALDI): m/z calcd for C₃₈H₃₀N₄O₈: 671.2136 [M+H]⁺; found: see the Supporting Information, Figure S9.

(2E,2'E)-Dibutyl-3,3'-(((1E,1'E)-[2,2'-bipyridine]-4,4'-diylbis(ethene-2,1-diyl))bis(2,5-dimethoxy-4,1-phenylene))bis(2-cyanoacrylate) (6)

Butyl cyanoacetate (1.24 mL, 14.5 mmol) and piperidine (862 μL, 14.5 mmol) were added to a suspension of 4,4'-((1E,1'E)-[2,2'-bipyridine]-4,4'-diylbis(ethane-2,1-diyl))bis(2,5-dimethoxybenzaldehyde) (**4**; 117 mg, 0.218 mmol) in dry MeCN (9 mL). The yellow suspension was stirred for 24 h at 90 °C. After cooling to RT, the mixture was filtered and the residue was taken up with CH₂Cl₂. After evaporation of the solvent, the product was dried under vacuum. The title compound was obtained by recrystallization from CH₂Cl₂/Et₂O (107 mg, 0.137 mmol, 63% yield). M.p. 255 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.73 (s, 2H), 8.69 (d, J = 5.0 Hz, 2H), 8.57 (s, 2H), 7.98 (s, 2H), 7.77 (d, J = 16.5 Hz, 2H), 7.48 (d, J = 5.1 Hz, 2H), 7.31 (d, J = 16.4 Hz, 2H), 7.15 (s, 2H), 4.31 (t, J = 6.6 Hz, 4H), 3.95 (s, 6H), 3.94 (s, 6H), 1.73 (m, 4H), 1.46 (dq, J₁ = 14.4 Hz, J₂ = 7.3 Hz, 4H), 0.97 ppm (t, J = 7.4 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 162.9, 156.5, 154.0, 151.4, 149.6, 149.6, 148.4, 145.5, 132.0, 129.9, 127.4, 120.9, 116.4, 110.8, 109.3, 109.2, 101.3, 66.3, 56.2, 56.2, 30.5, 19.1, 13.5 ppm; MS (MALDI): m/z: 783 [M+H]⁺; HRMS (ESI): m/z calcd for C₄₆H₄₇N₄O₈: 783.3388 [M+H]⁺; found: 783.3378; FTIR (ATR): $\tilde{\nu}$ = 3604 (w), 3057 (w), 2963 (m), 2362 (m), 2213 (m), 2017 (w), 1913 (w), 1804 (w), 1717 (s), 1635 (w), 1576 (s), 1497 (s), 1457 (s), 1404 (s), 1357 (m), 1296 (m), 1209 (s), 1150 (m), 1084 (m), 1024 (s), 951 (s), 906 (m), 849 (m), 737 (m), 677 (m), 641 (m), 602 (m), 550 cm⁻¹ (m).

Instrumental Methods

Spectroscopic ellipsometry data were collected from 400–1000 nm at a 70° incidence angle on an EL X-02 P Spec apparatus (DRE Dr Riss Ellipsometerbau GmbH). Fits were performed by using the database of material files provided with the instrument. Electrochemistry data were collected on a Gamry interface 1000. ALD of TiO₂ was performed at 120 °C from Ti(OiPr)₄ and water in a homemade hot-walled reactor.

Adsorption Tests

Si wafers were coated with TiO₂ to a thickness of several nanometers by using. The substrates before annealing (amorphous TiO₂) or after annealing (crystalline TiO₂) were soaked in solutions of compound **5** or **6** (0.01 mM in DMSO, CH₂Cl₂, or a 1:1 v/v mixture) for 20 min. The samples were well-rinsed with pure solvent (or the solvent mixture) before performing the ellipsometry measurements. As an additional check, the samples were subsequently soaked in the solvent overnight and rinsed before the ellipsometry measurements.

Electrochemical Measurements

Differential pulse voltammetry (DPV) was performed in 5 mM NaBF₄ solution in a mixture of CH₂Cl₂ and DMSO (1:1 v/v). Compounds **5** and **6** were added to a concentration of 50 μM. The parameters for the DPV experiments were as follows: voltage range: -0.791 V to +1.209 V (vs. NHE), step size: 2 mV, sample period: 0.25 s, pulse duration: 0.05 s, pulse size: 15 mV.

Photochemical Measurements

Steady-state UV/Vis absorption spectra were recorded on PerkinElmer Lambda 2 two-beam spectrophotometers. Fully corrected steady-state fluorescence spectra were recorded on a FluoroMax3 spectrometer (Horiba Jobin Yvon).

Fluorescence lifetimes were determined by using the time-correlated single-photon-counting (TCSPC) technique on a Fluorolog 3 (Horiba Jobin Yvon). The samples were excited with a NanoLED-405 (403 nm), and the signal was detected by a Hamamatsu MCP photomultiplier (type R3809U-50). The time profiles were recorded at 500 nm.

Transient absorption measurements based on femtosecond laser photolysis were performed by using the output of a Ti/sapphire laser system (CPA2110, Clark-MXR Inc.): 775 nm, 1 kHz, and 150 fs full width at half maximum (FWHM) pulses. The excitation wavelength was generated by second harmonic generation (387 nm), with pulse widths of < 150 fs and energies of 200 nJ pulse⁻¹. Transient absorption detection was performed by using a transient absorption pump/probe system (TAPPS, Ultrafast Systems).

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