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Synthesis, electrochemical and photophysical characterization of new 4,4'- π -conjugated 2,2'-bipyridines end-capped with an cyanoacrylic acid and its ester

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Abstract: Two new functionalized 4,4'-disubstituted 2,2'-bipyridines for the first time end-capped with cyanoacrylic acid and cyanoacrylic acid ester anchoring groups (promising an efficient functionalization of TiO₂ or other metal oxide semiconductor surfaces) have been synthesized and characterized by analytical, electrochemical and spectroscopic measurements. The electrochemical and photophysical characterisation of these new 4,4'-disubstituted 2,2'-bipyridines with extended π -system make them promising candidates for designing inorganic/organic hybrid photosensitizers which from their LUMO energies are well suitable for sensitization of metal oxide semiconductors (e.g. TiO₂ nanoparticles and/or nanotubes).

Introduction

Due to the finite nature of fossil fuels, and the negative impact of fossil fuel usage on the climate, it is foreseeable that harvesting solar light will become the ultimate source for clean and renewable energy. This in regards the energy obtained by the sun in form of light needs to be efficiently converted into storable forms, such as electric power or transformed to "solar fuel" such as hydrogen obtained from photocatalytic water splitting.^[1] Such light harvesting systems, which are commonly based on a photosensitizer dye and a metal oxide or organic electron acceptor molecular building blocks, which show strong absorption cross-sections in a wide range of the optical spectrum as well as sufficiently high LUMO energies for efficient

electron transfer reactions to the acceptor (metal oxide semiconductor conduction band or HOMO of the molecular electron acceptor). Strongly fluorescent dyes based on nitrogen containing heterocycles are commonly employed as such photosensitizer building blocks.^[2,3] They are good accessible from a synthetic point of view, moreover the derivatization of the pyridine ring by introduction of functionalities allows a fine-tuning of the optical and electronic properties of the building block, as well as attaching anchoring groups for the linkage to metal oxide surfaces.^[4]

Pure organic bipyridine based π -extended compounds can be applied as photo luminescent materials in e.g. non-linear optics (NLO). These systems absorb light due to intramolecular charge transfer (ICT) and emit from the corresponding photoexcited state.^[5] Besides bipyridine, terpyridine or phenanthroline based π -extended compounds are widely used as ligands in metal complexes (Figure 1)^[6] e.g. for electrochemical applications,^[7] in particular for light emitting diode devices^[8] or as dyes for Dye Sensitized Solar Cells (DSSC).^[4] They herein provide a fine tuning effect on photophysical and electrochemical properties of the complex by influencing the metal to ligand charge transfer (MLCT) process.^[9,10]

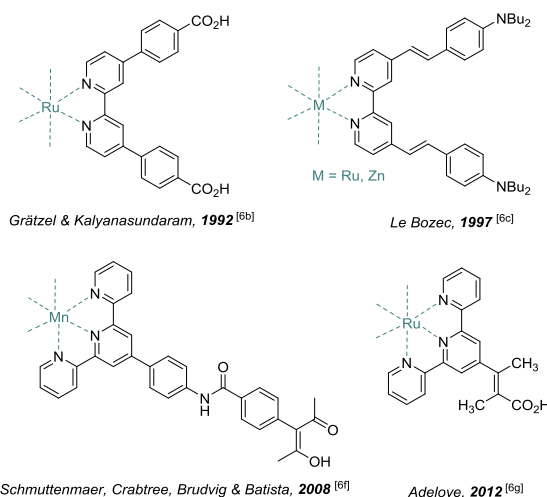


Figure 1. Multifunctional applicability of pyridine-based π -extended ligands in emissive materials^[6b-g]

This tuning properties can be performed by either a ligand with an electron withdrawing nature providing a low lying π^* molecular orbital or a strong donor ligand which destabilizes the metal t_{2g} orbitals.^[6g,11]

A further possibility to adapt the spectral and redox properties of the complex to its requirements is the extension of the coordinating pyridine-based moiety with a large π -extended system, so called antenna function, in order to suppress charge

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recombination by spatial separation.^[12] Focusing on π -conjugated-2,2'-bipyridines,^[6] the field of research is dominated by the donor end-capped antennas.

To the best of our knowledge examples of 2,2'-bipyridine 4,4'- π -extended systems end-capped with electron withdrawing groups (also applicable as anchoring acceptor moieties on metal oxide surface) remain rare,^[6b,13] and, therefore, the development of new derivatives is still highly demanded. Notably furthermore, only carboxylic acids (COOH) and esters (COOR), attached directly to a corresponding phenyl framework, were used in these known systems as anchoring groups so far. Commonly, however, cyanoacrylic acid groups are employed as organic photosensitizer's anchors in DSSCs,^[14] since excited electrons can effectively be injected into the conduction band of TiO₂ through the carboxyl anchoring group adjacent to the electron accepting cyano group of organic photosensitizer.^[15]

Interestingly, π -conjugated-2,2'-bipyridines with cyanoacrylic acids as anchoring acceptor moieties, have never been presented before. Herein, we report on the design and synthesis, electrochemical and photophysical characterization of new fluorescent 4,4'- π -conjugated 2,2'-bipyridines **5** and **6** compounds, which are for the first time end-capped with a cyanoacrylic acid and a cyanoacrylic acid ester moiety for its potential application in photocatalytic processes e.g. as ligands in inorganic/organic hybrid hole transport materials, as well as DSSC.

Results and Discussions

Synthesis

The design of new 4,4'- π -conjugated 2,2'-bipyridines **5** and **6** was inspired by known neutral organic dyes, containing cyanoacrylic acid as the acceptor moiety.^[16] We assumed that the introduction of an additional C=C double bond between the selected 2,5-dimethoxy-phenyl framework and cyanoacrylic-COOR anchoring groups might increase the π -conjugation and can result in a wider absorption in the visible region. In addition, such molecules are synthetically more easily accessible in comparison to literature known 4,4'- π -conjugated 2,2'-bipyridines.^[6b,13]

On the way to prepare new bipyridine dyads, a four step synthesis from literature towards 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**, Figure 2) was first carried out starting from commercially available 4,4'-dimethyl 2,2'-bipyridine.^[13]

In order to avoid side product formation in the following Horner-Wadsworth-Emmons (HWE) reaction (Figure 2) an aldehyde protection step of the dialdehyde was applied (see ESI). The monoprotected dibenzaldehyde 4-(1,3-dioxolan-2-yl)2,5-dimethoxybenzaldehyde (**2**) was synthesized under stoichiometric control using ethylene glycol and *p*-toluene sulfonic acid as catalyst. After purification via column chromatography the monoacetal **2** was obtained in moderate yield. 4-(1,3-Dioxolan-2-yl)2,5-dimethoxybenzaldehyde (**2**) and 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**) (2:1-ratio) were then applied in a *trans*-selective C=C bond forming HWE reaction (Figure 2). The π -conjugated two-armed bipyridine

compound **3** could be obtained with excellent yield without any further purification. After the successful HWE coupling acidic hydrolysis of the acetals could regain the free aldehyde functions of the bipyridine compound **4** in almost quantitative yield.

In order to obtain compound **5**, a typical Knoevenagel condensation with the aldehyde containing two-armed bipyridine **4** and an excess of CH-acidic cyanoacetic acid was carried out using piperidine as base.

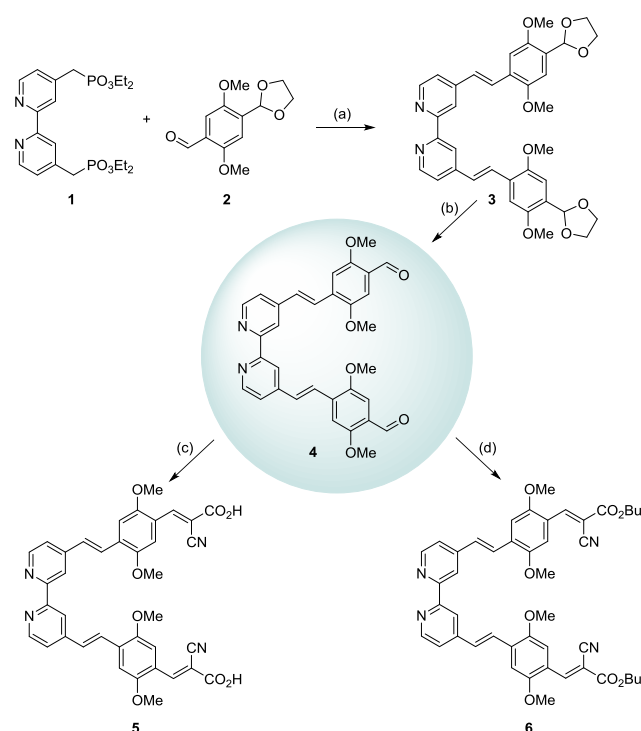


Figure 2. (a) K₂CO₃, THF, 70 °C, 24 h (97% yield); (b) 2 M HCl, chloroform, r.t., 10 h (98% yield); (c) cyanoacetic acid (40 eq.), piperidine, acetonitrile, 90 °C, 24 h (46% yield); (d) cyanoacetic acid butyl ester, (40 eq.), piperidine, acetonitrile, 90 °C, 24 h (63% yield).

The target compound **5** was obtained as orange hardly soluble solid after trituration with THF and acetone. Due to insolubility, the compound was not able to be characterized via carbon NMR. For inducing better solubility to the bipyridine dyads, a more unipolar ester function instead of the carboxylic acid function derived from cyanoacetic acid became desirable. Hereupon a Knoevenagel condensation was carried out with the aldehyde containing two-armed bipyridine **4** and using an excess of cyanoacetic acid butyl ester as CH-acidic compound, yielding target compound **6**, which provides good solubility in dichloromethane.

Adsorption behavior

The utilization of molecular dyes in dye-sensitized solar cells necessitates that the bipyridine ligands bind to the surface of TiO₂ colloids via an ester linkage. For this purpose, crystalline colloids are usually coated with a thin layer of amorphous TiO₂, which provides more reactive sites.^[17,18]

Both **5** and **6** adsorb on amorphous TiO₂ (Figure 3a), even from the polar DMSO solvent (**5**). The spectroscopic ellipsometry

curves display a marked shift upon soaking of planar substrates in the corresponding solutions, and do not revert to the initial state after extensive rinsing in pure solvent. The results are different on crystalline TiO_2 , which provides less reactive surface sites.^[17,18] Here, **5** (end-capped with cyanoacrylic acid) does not yield a stable chemisorbed layer, whereas **6** does (Figure 3b). The difference is not due to a solvent effect, since it is also observed when both compounds are dissolved in a 1:1 mixture of DCM and DMSO. It could be due to H-bonding between the carboxylic acid moieties and the bipyridine units, which might reduce the reactivity of the linker significantly.

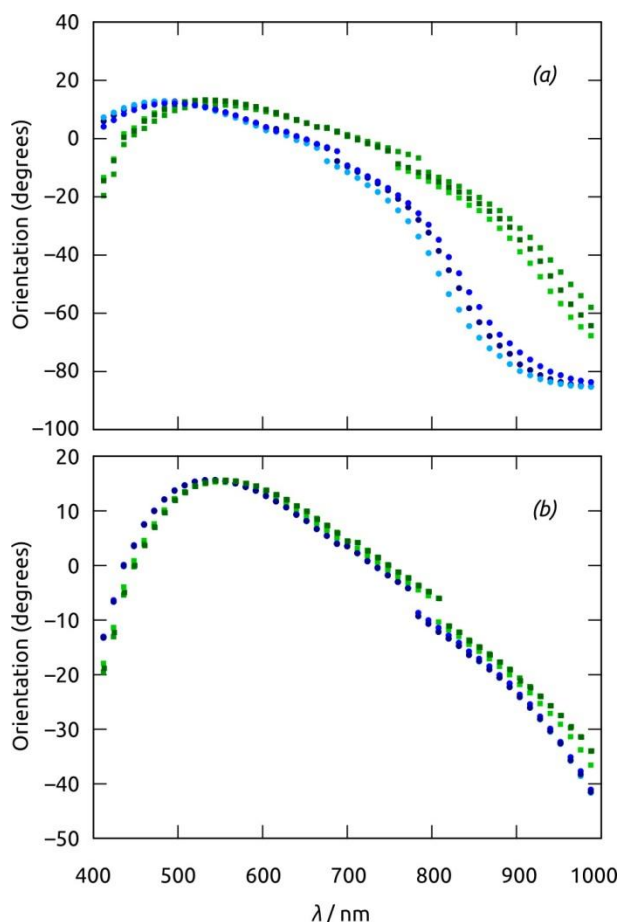


Figure 3. Adsorption behavior of **5** (blue) and **6** (green) on TiO_2 studied by spectroscopic ellipsometry (orientation traces $\theta(\lambda)$ of $\text{Si} / \text{SiO}_2 / \text{TiO}_2$ wafers (a) with amorphous TiO_2 layer and using pure DMSO (**5**) or DCM (**6**), and (b) with TiO_2 layer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

LUMO energy

The next requirement on the bipyridine ligand as far as it pertains to its use in dye-sensitized solar cells or other light harvesting devices is, that an electron photoexcited into the bipyridine LUMO must have sufficient energy to be injected into the TiO_2 conduction band.

A first approximation of the LUMO energy can be obtained by voltammetric methods. Figure 4 displays differential pulse

voltammetric (DPV) curves recorded on dilute solutions of **5** and **6**. The reductions are observed at -0.22 V and -0.06 V (vs. NHE) for **5** and **6**, respectively. The difference is most likely due to electrostatic (protonation) effects. Importantly, both reduction potentials are near the energy of the TiO_2 valence band (-4.21 eV on the absolute scale, corresponding to -0.31 V vs. NHE).^[19]

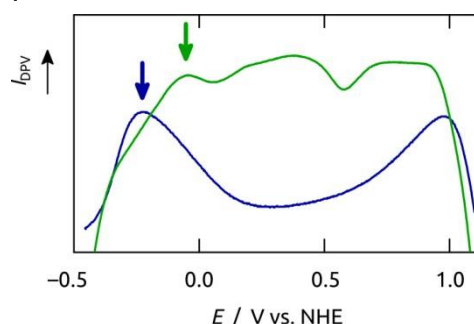


Figure 4. Differential pulse voltammetry of **5** (blue) and **6** (green) as dilute ($5 \mu\text{M}$) solutions in 1:1 DCM / DMSO. The arrows highlight the reduction peak of each compound.

Photophysical properties

The ground-state absorption spectra of **6** and **5** in THF exhibits nearly identical characteristic absorptions with bands in the UV and blue region of the optical spectrum maximizing at 350 and 436 nm (**6**) and 346 and 430 nm (**5**) respectively (see Figure 5 and Figure S14 in the ESI).

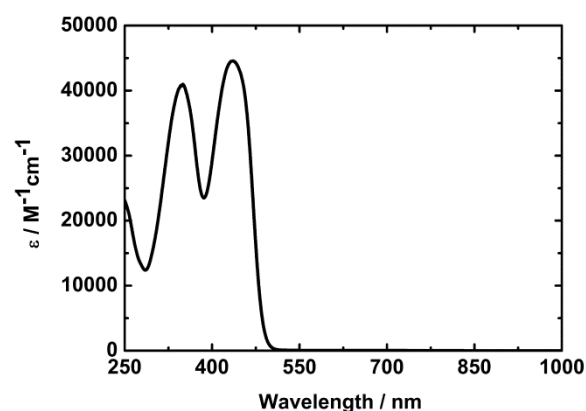


Figure 5. Absorption spectrum of **6** obtained in THF.

Fluorescence measurements of **6** and **5** in THF upon 420 nm photoexcitation exhibits a strong fluorescence between 450 and 750 nm maximizing at 513 nm (**6**) and 496 nm (**5**) (see Figure 6 and Figure S15 in the ESI). A fluorescence quantum yield of 0.075 (**6**) and 0.085 (**5**) in THF, were determined, using H_2TTP and ZnTTP as reference compounds with fluorescence quantum yields of 0.11 and 0.03 in toluene^[20]. Fluorescence lifetimes of 1.1 ns (**6**) and 1.3 ns (**5**) were obtained upon 403 nm photoexcitation (Figure 6 and ESI Figure S15).

Transient absorption measurements based on femtosecond laser photolysis provides insights into the formation and fate of excited states in particular into the S_1 - S_N transitions. Solutions of **6** and **5** in THF were photoexcited with femtosecond laser

pulses with a wavelength of 387 nm. Both samples show practically the same transient absorption spectra with two dominating maxima at 580 nm and 810 nm - dedicated to the S_1 - S_N transitions, accompanied by a minor minimum around 510 nm (originating from spontaneous emission – see fluorescence spectra) and a not fully resolved transient bleaching around 430 nm mirroring the ground state absorption (see Figure 7 and ESI Figure S16). For both samples the transient absorption decays with lifetimes of 1.0 ns (**6**) and 1.2 ns (**5**) – well in line with the measured fluorescence lifetimes – back into the ground state.

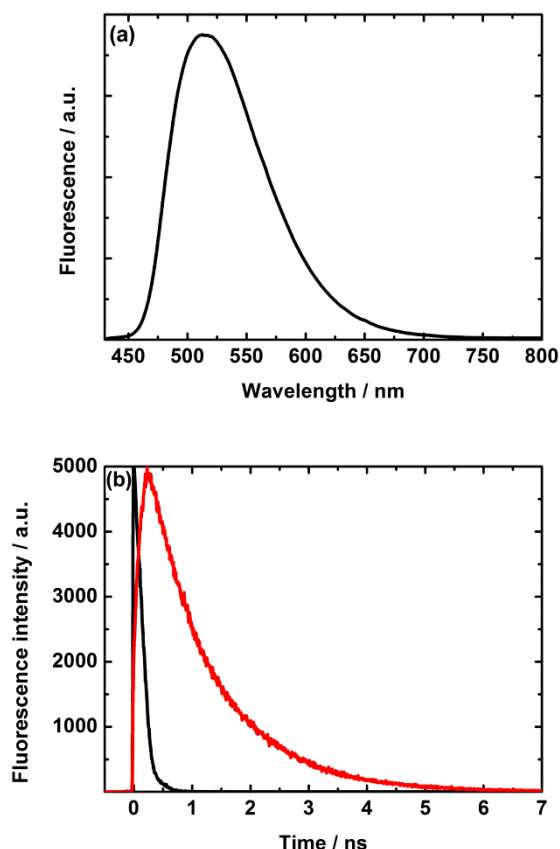


Figure 6. a) Fluorescence spectrum of **6** in THF upon photo excitation at 420 nm. b) Fluorescence time profile for **6**, obtained in THF at 500 nm, upon 403 nm photoexcitation (red), the IRF is shown in black.

Conclusion

We reported on the synthesis, electrochemical and photochemical properties of two new symmetrically disubstituted bipyridines **5** and **6**, for the first time end-capped with a cyanoacrylic acid or a cyanoacrylic acid ester moieties, suitable as ligands for generation of metal-based photosensitizers and for the chemical functionalization of TiO_2 . The adsorption behavior on TiO_2 was studied by spectroscopic ellipsometry and a first approximation of the LUMO energy was obtained by voltammetric methods. These measurements are providing solid evidence for an efficient anchoring of **6** on TiO_2 and showed a sufficient LUMO energy for an efficient electron transfer into the TiO_2 conduction band.

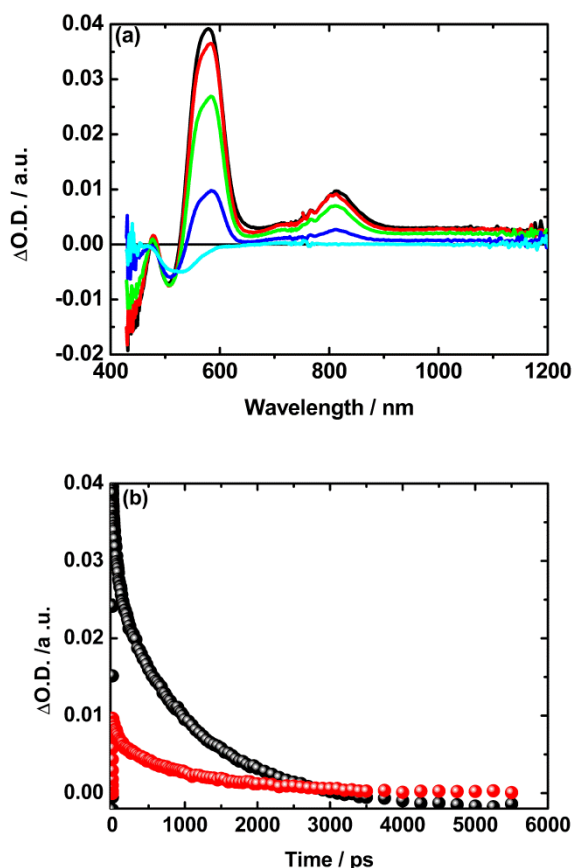


Figure 7. a) Femtosecond transient absorption spectra of **6** in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue) and 5500 ps (cyan) after excitation with femtosecond laser pulses (387 nm, 200 nJ /pulse, < 150 fs FWHM). b) Corresponding absorption time profiles at 580 (black) and 810 nm (red).

Photophysical studies demonstrated the feasibility of the investigated compounds as potential photo-sensitizer dyes. In particular appealing is the combination of matching LUMO energies relative to the TiO_2 conduction band accompanied with a sufficient long lived singlet first excited state (> 1 ns) giving rise to the expectation of an efficient electron transfer from the disubstituted bipyridines derivative into the TiO_2 conduction band, which is expected to be obtained in a subsequent follow up study. The synthesis of corresponding Ru-, Mn- and Fe-complexes (the promising results of a preliminary complexation experiment are given in Figure S17 of the SI) using our new organic photosensitizers (ligands **5** and **6**) and their subsequent covalent binding to the surface of TiO_2 nanoparticles and / or nanotubes for applications in visible-light photocatalytic water oxidation and/or DSSC is currently underway in our laboratory.

Experimental Section

Materials and general procedures

For synthesis, 4,4'-Bis(diethylphosphonomethyl)-2,2'-bipyridine (**1**)^[13] was prepared as starting material according to literature procedures. Chemicals purchased from commercial sources were used without further purification. All solvents were purified by distillation, dried according to standard procedures or were purchased in HPLC-quality. All 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 stationary phase. All products were dried in high vacuum (10⁻³ bar). Thin layer chromatography (TLC) chromatography was performed on precoated aluminium silica gel SIL G/UV254 plates (Macherey-Nagel & Co.). ¹H NMR (¹³C NMR) spectra were recorded at room temperature on a Bruker Avance 300 or JEOL JNM GX 400 spectrometer operating at 300 MHz or 400 MHz. All chemical shifts are given in the scale in ppm and refer to the non-deuterized proportion of the solvent. NMR raw data was processed with the program MestReNova. Maldi Mass spectra were recorded with Shimadzu Biotech AXIMA Confidence ESI Mass spectra were recorded with Bruker Daltonik maXis 4G or a Bruker Daltonik micrOTOF II focus.

IR spectra were recorded on a Varian IR-660 apparatus. The Absorption is indicated in wave numbers [cm⁻¹].

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 *p*-toluenesulfonic acid (9.80 mg, 2 mol%) are dissolved in dry toluene (10 mL) and stirred for 21 hours under reflux. After cooling to room temperature, the solution is washed with distilled water (3 x 20 mL), dried over MgSO₄ and the solvent is removed by rotary evaporation. Subsequently the crude product is purified via column chromatography (SiO₂) with petroleum ether/ethyl acetate = 4/1. The main product **2** is obtained in the second fraction after removal of the eluent as a white solid (307 mg, 1.29 mmol; 50%).

¹H NMR (300 MHz, CDCl₃): δ [ppm]: 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 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 189.5, 156.6, 151.9, 133.7, 125.3, 110.8, 109.3, 98.7, 65.4, 56.2, 56.2.

MALDI-MS: 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 65 mg potassium *tert*-butoxide in 6 ml anhydrous THF is added drop wise under nitrogen atmosphere to a solution containing 89 mg of compound **1** (0.195 mmol) and 102 mg 4-(1,3-dioxolan-2-yl)-2,5-dimethoxybenzaldehyde (**2**) (0.428 mmol) in 2 ml anhydrous THF. The yellow brownish reaction mixture is then heated to reflux for 39 h. After completion the reaction is quenched by the addition of 30 ml water (HPLC grade). After filtration the residue is taken up with dichloromethane. The filtered matter is extracted with dichloromethane. The combined organic phases are dried with MgSO₄. After removal of the solvent the product is dried in vacuum. The title compound **3** is obtained as yellowish solid (119 mg, 0.190 mmol; 97%).

¹H NMR (300 MHz, CDCl₃): δ [ppm]: 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 Hz, 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 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 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.

MALDI-MS: m/z = 625 [M+H]⁺.

4,4'-((1E,1'E)-[2,2'-bipyridine]-4,4'-diylbis(ethene-2,1-diyl))bis(2,5-dimethoxybenzaldehyde) (**4**):

6 ml 2 M HCl is gradually added to a solution of 119 mg of compound **3** (0.190 mmol) in 18 ml chloroform. The red reaction mixture is stirred for 14.5 h. Then the organic layer is separated, washed with saturated NaHCO₃ solution and brine and finally dried with MgSO₄. The solvent is evaporated. In order to complete the deprotection step the crude product is again treated gradually with 6 ml 2 M HCl in 18 ml chloroform. Then again the organic layer is separated, washed with saturated NaHCO₃ solution and brine and finally dried over MgSO₄. The solvent is evaporated and the title compound is obtained as yellow solid (100 mg, 0.186 mmol; 98%).

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 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 (s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 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. MALDI-MS: 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**):

970 mg Cyanoacetic acid (11.4 mmol) and 1.13 ml piperidine (11.4 mmol) are added to a suspension of 153 mg of compound **4** (0.285 mmol) in 12 ml dry acetonitrile. The yellow suspension is stirred for 24 h at 90°C. After the addition of dichloromethane and 2 M H₃PO₄ the mixture turned orange, is filtered and washed with THF and acetone. The filtrate is dried in vacuum. The title compound is obtained as orange hardly soluble solid (87.2 mg (0.13 mmol); 46%). 280°C (decomp.); (NMR-Characterization partially enabled by addition of small amounts of hot DMF);

¹H NMR (400 MHz, DMSO-d₆): δ [ppm] = 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, J_1 = 4.9 Hz, J_2 = 1.5 Hz, 2H), 7.66 (d, J = 16.3 Hz, 2H), 7.54 (s, 2H), 3.95 (s, 6H), 3.90 (s, 6H).

¹³C NMR could not be recorded due to superior long measurement

MALDI-MS: m/z = 671 [M+H]⁺.

HRMS (MALDI) m/z [M+H]⁺ calcd for C₃₈H₃₀N₄O₈: 671.21364; found: see ESI.

FT-IR (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 (s).

(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**):

1.24 ml Butyl cyanoacetate (14.5 mmol) and 862 μ l piperidine (14.5 mmol) are added to a suspension of 117 mg 4,4'-((1E,1'E)-[2,2'-bipyridine]-4,4'-diylbis(ethene-2,1-diyl))bis(2,5-dimethoxybenzaldehyde) (**4**) (0.218 mmol) in 9 ml dry acetonitrile. The yellow suspension is stirred for 24 h at 90°C. After cooling to room temperature the mixture is filtered and the residue is taken up with dichloromethane. After evaporation of the solvent the product is dried in vacuum. The title compound is obtained after recrystallization from dichloromethane and Et₂O (107 mg (0.137 mmol); 63%). M.p. 255 °C;

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 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, J_1 = 14.4 Hz, J_2 = 7.3 Hz, 4H), 0.97 (t, J = 7.4 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 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.

MALDI-MS: m/z = 783 [M+H]⁺

HRMS (ESI) m/z [M+H]⁺ calcd for C₄₆H₄₇N₄O₈: 783.33884; found: 783.33781.

FT-IR (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 (m).

Sodium tetrafluoroborate (NaBF_4) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) were used as supporting salts from Sigma Aldrich. Dichloromethane (DCM) and dimethyl sulfoxide (DMSO) were purchased from commercial suppliers and used as received. The ALD precursor $\text{Ti}(\text{O}^i\text{Pr})_4$ was 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 ordered from Silicon Materials. Pt wires (Alfa Aesar) were used as working and auxiliary electrodes. A Ag / AgCl (sat.) / NaCl (3 M) reference electrode (+0.209 V vs. NHE) from Bionalytical Systems, Inc. (BASi) was obtained as a reference electrode.

Instrumental methods. Spectroscopic ellipsometry data were collected from 400 to 1000 nm under a 70° incidence angle with an instrument model EL X-02 P Spec from DRE Dr Riss Ellipsometerbau GmbH. Fits were performed using the database of material files provided with the instrument. The electrochemistry data were collected with a Gamry interface 1000. Atomic layer deposition of TiO_2 was performed at 120°C from $\text{Ti}(\text{O}^i\text{Pr})_4$ and water in a home-made hot-wall reactor.

Adsorption tests. Si wafers were coated with several nanometers of TiO_2 by ALD. These substrates before annealing (amorphous TiO_2) or after annealing (crystalline TiO_2) were soaked in the solution of **5** or **6** (0.01 mM in DMSO, DCM or a 1:1 mixture of both solvents) for 20 min. The samples were then rinsed well with the pure solvent (or solvent mixture) before the ellipsometry measurements. As an additional check, they were subsequently soaked in the solvent overnight and rinsed before ellipsometry measurements.

Electrochemistry measurements. Differential pulse voltammetry (DPV) was measured in 5 mM NaBF_4 in a 1:1 mixture of DCM and DMSO. Compounds **5** and **6** were dissolved in 50 μM concentration. The parameters of the DPV experiments are: 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 measured on PerkinElmer Lambda 2 two-beam spectrophotometers. Fully corrected steady-state fluorescence spectra were taken with a FluoroMax3 spectrometer (Horiba Jobin Yvon).

Time-resolved fluorescence studies: Fluorescence lifetimes were determined through the time-correlated single photon counting (TCSPC) technique using 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 with output from a Ti/sapphire laser system (CPA2110, Clark-MXR Inc.): 775 nm, 1 kHz, and 150 fs FWHM pulses. The excitation wavelength was generated by second harmonic generation (387 nm), pulse widths of < 150 fs and energies of 200 nJ/pulse were selected. The transient absorption detection was performed with a transient absorption pump/probe system (TAPPS, Ultrafast Systems).

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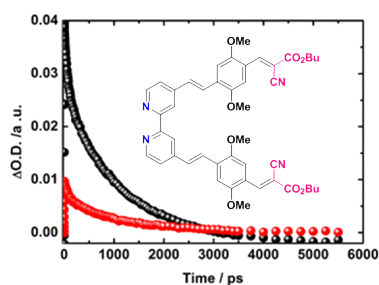
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Photosensitizers

A. Fingerhut, Y. Wu, A. Kahnt,*
J. Bachmann,* and S.B. Tsogoeva*

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Synthesis, electrochemical and photophysical characterization of new 4,4'- π -conjugated 2,2'-bipyridines end-capped with a cyanoacrylic acid and its ester



Text for Table of Contents

The electrochemical and photophysical characterisation of new 4,4'-disubstituted 2,2'-bipyridines with extended π -system (for the first time end-capped with cyanoacrylic acid and cyanoacrylic acid ester anchoring groups) make them promising candidates for designing inorganic/organic hybrid photosensitizers which from their LUMO energies are well suitable for sensitization of metal oxide semiconductors (e.g. TiO₂ nanoparticles and/or nanotubes).