CHEMISTRY
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Supporting Information

Synthesis and Electrochemical and Photophysical Characterization of New 4,4′-π-Conjugated 2,2′-Bipyridines that are End-Capped with Cyanoacrylic Acid/Ester Groups

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General Information

Synthesis:
4,4'-Bis(diethylphosphonatomethyl)-2,2'-bipyridine (**1**)[1] 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.). ^{1}H NMR (^{13}C 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. HRMS (MALDI) spectra was recorded using a reflectron time-of-flight instrument(reflex IV, Bruker Daltonics). maXis-HRMS (ESI) was acquired using ultra-high resolution time-of-flight electrospray ionization UHR-TOF-ESI-MS Bruker Daltonik maXis capable of resolution of at least 40,000 FWHM. Detection was in negative-ion mode and the source voltage was 4 kV. The flow rates were 500 µL/hour. The drying gas (N_2) was held at 180 °C. The machine was calibrated prior to the experiment via direct infusion of the Agilent ESI-TOF low concentration tuning mixture. IR spectra were recorded on a Varian IR-660 apparatus. The Absorption is indicated in wave numbers [cm^{-1}].

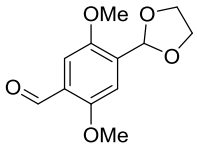
Absorption behavior:
Sodium tetrafluoroborate ($NaBF_4$) and tetrabutylammonium tetrafluoroborate ($^{t}Bu_4NBF_4$) were used as supporting salts from Sigma Aldrich. Dichloromethane (DCM) and dimethyl sulfoxide (DMSO) were purchased from commercial suppliers and used as received. The ALD precursor $Ti(O^{i}Pr)_4$ 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 auxillary 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 $Ti(O^{i}Pr)_4$ 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).

[1] M. Myahkostupov, F. N. Castellano, *Inorg. Chem.* **2011**, *50*, 9714-9727.

1 Synthesis

1.1 4-(1,3-Dioxalan-2-yl)2,5-dimethyloxybenzaldehyde (2)



2,5-Bis-methyloxy-1,4dibenzaldehyd (500 mg, 2.58 mmol), ethylene glycol (187 µL, 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 $MgSO_4$ and the solvent is removed by rotary evaporation. Subsequently the crude product is purified via column chromatography (SiO_2) 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%).
^{1}H NMR (300 MHz, $CDCl_3$): 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).
^{13}C NMR (100 MHz, $CDCl_3$): 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 $[M+H]^+$.

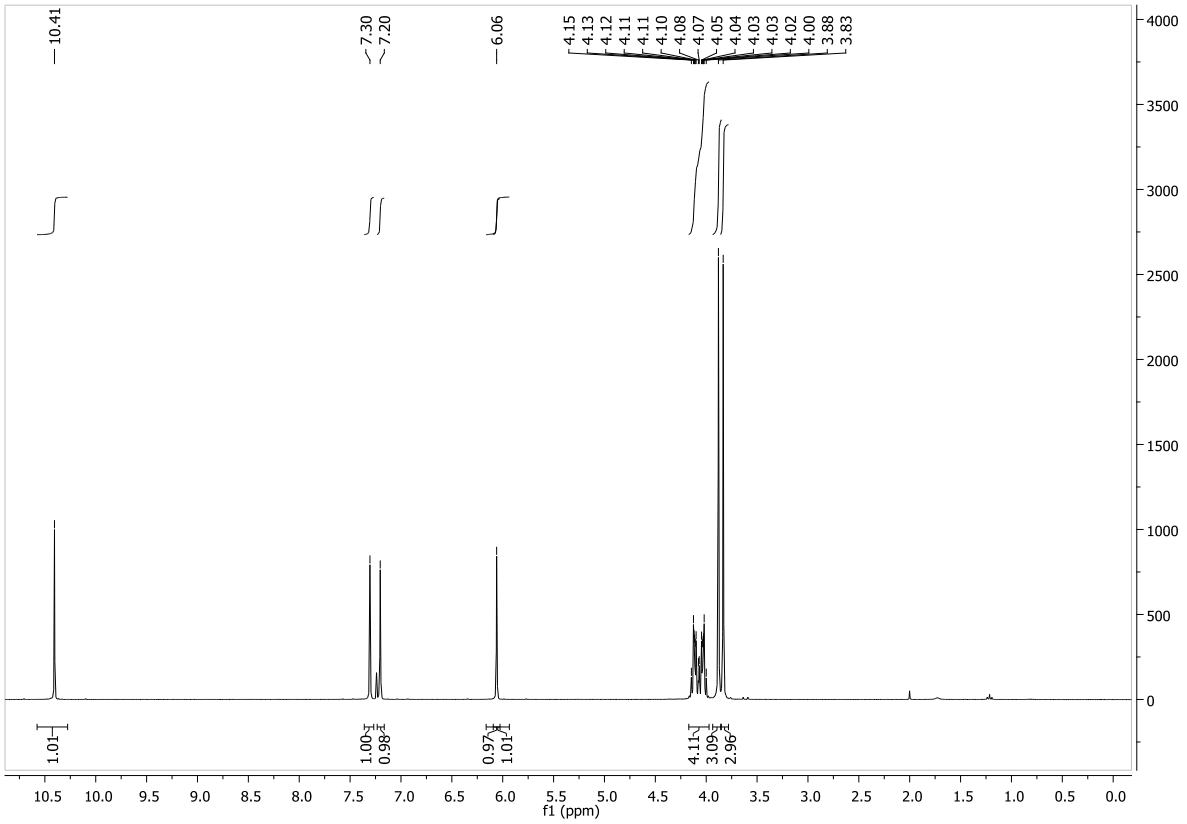


Figure S1: ^{1}H NMR (300 MHz) of compound **2** in $CDCl_3$.

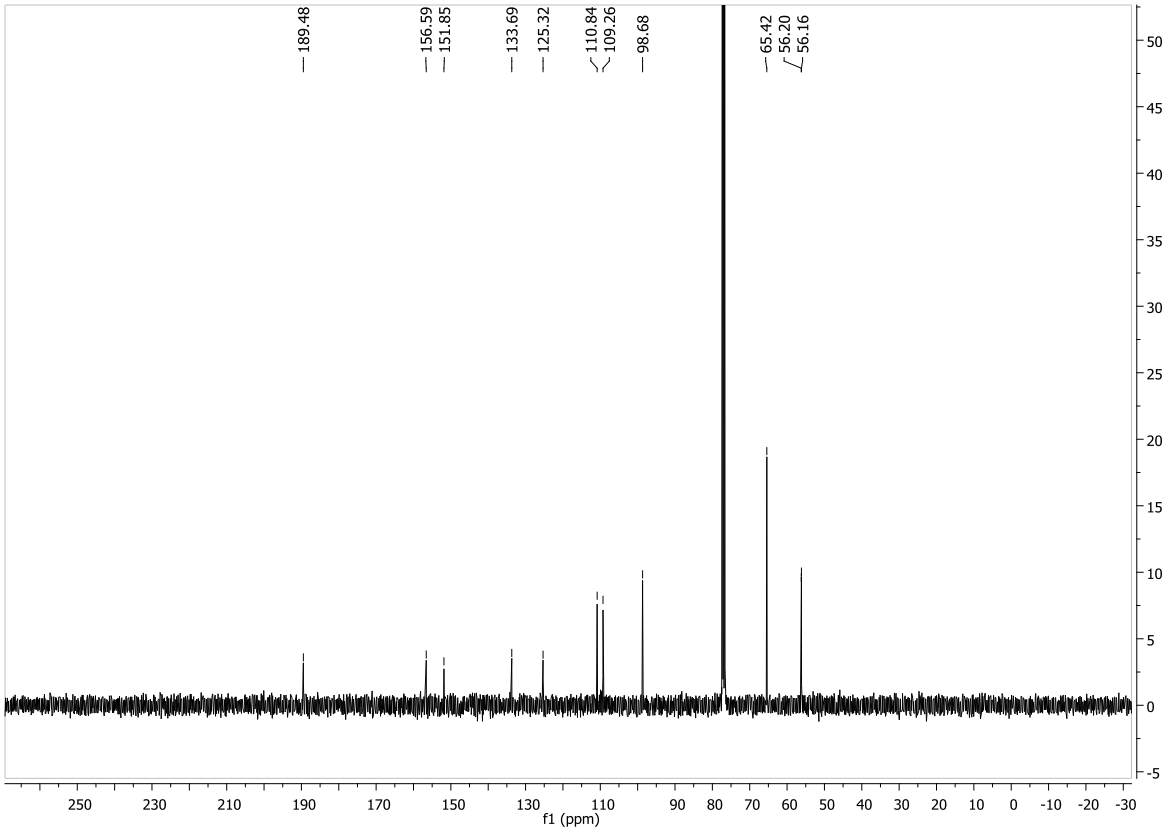
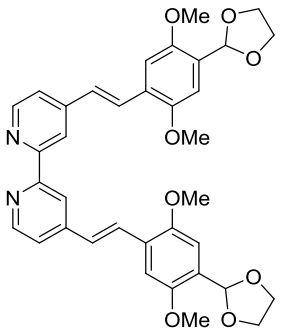


Figure S2: ^{13}C NMR (100 MHz) of compound **2** in $CDCl_3$.

1.2 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 $MgSO_4$. 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%).

^{1}H NMR (300 MHz, $CDCl_3$): 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, 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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 $[M+H]^+$.

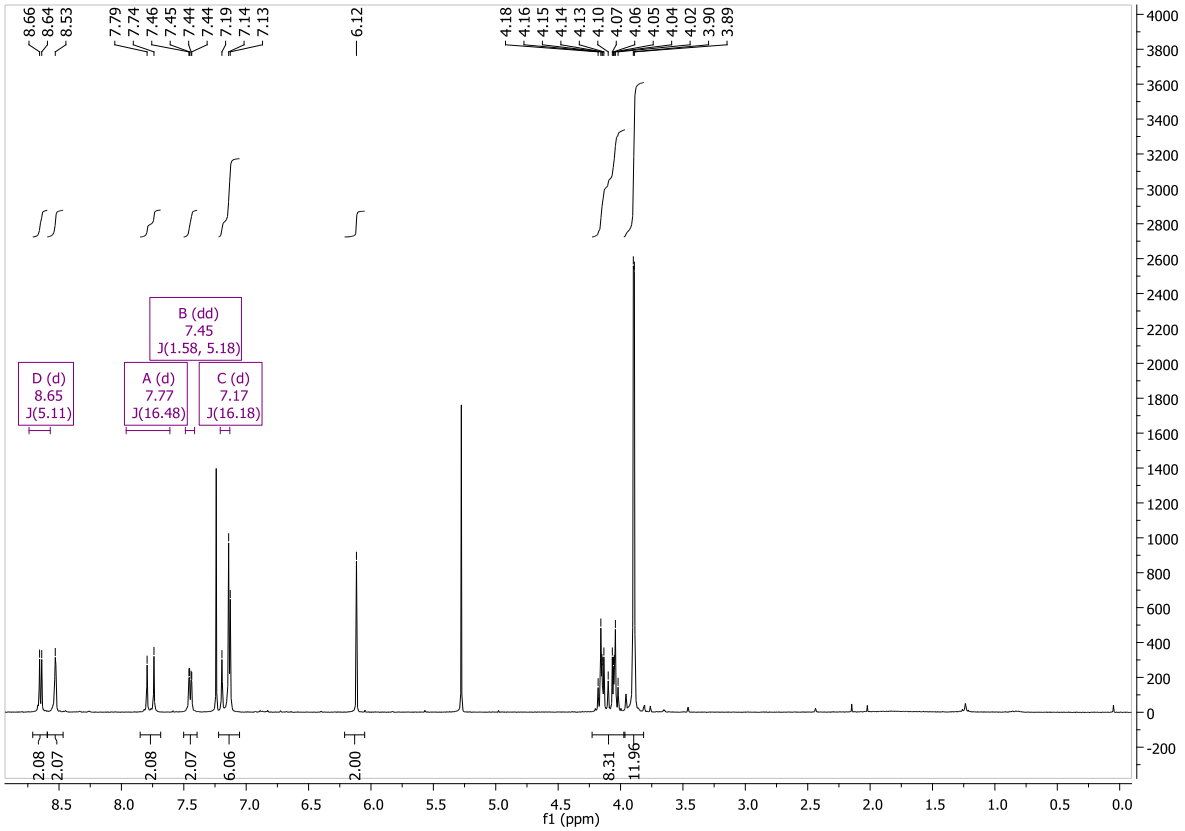


Figure S3: ^{1}H NMR (300 MHz) of compound **3** in $CDCl_3$.

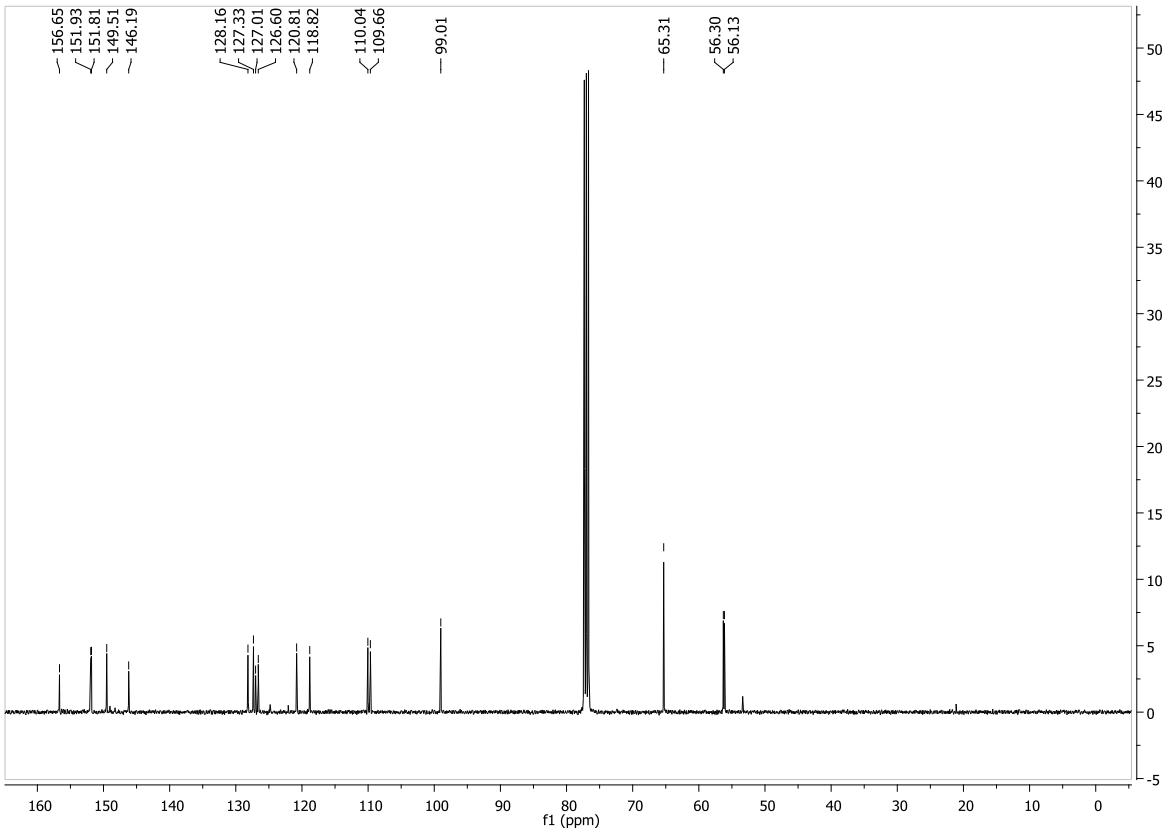
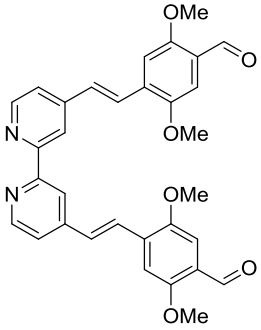


Figure S4: ^{13}C NMR (100 MHz) of compound **3** in $CDCl_3$.

1.3 4,4'-((1*E*,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 $NaHCO_3$ solution and brine and finally dried with $MgSO_4$. 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 $NaHCO_3$ solution and brine and finally dried over $MgSO_4$. The solvent is evaporated and the title compound is obtained as yellow solid (100 mg, 0.186 mmol; 98%).
^{1}H NMR (300 MHz, $CDCl_3$): 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).
^{13}C NMR (75 MHz, $CDCl_3$): 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 $[M+H]^+$.

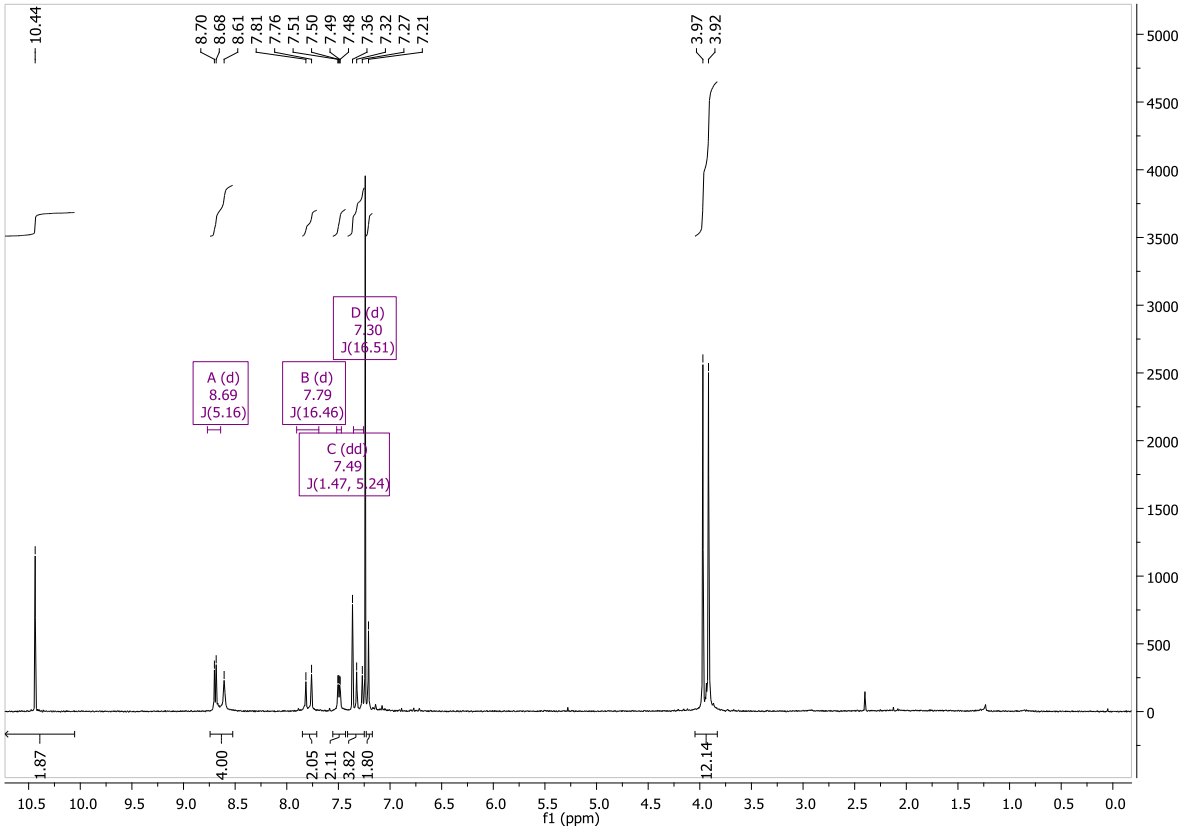


Figure S5: ^{1}H NMR (300 MHz) of compound **4** in $CDCl_3$.

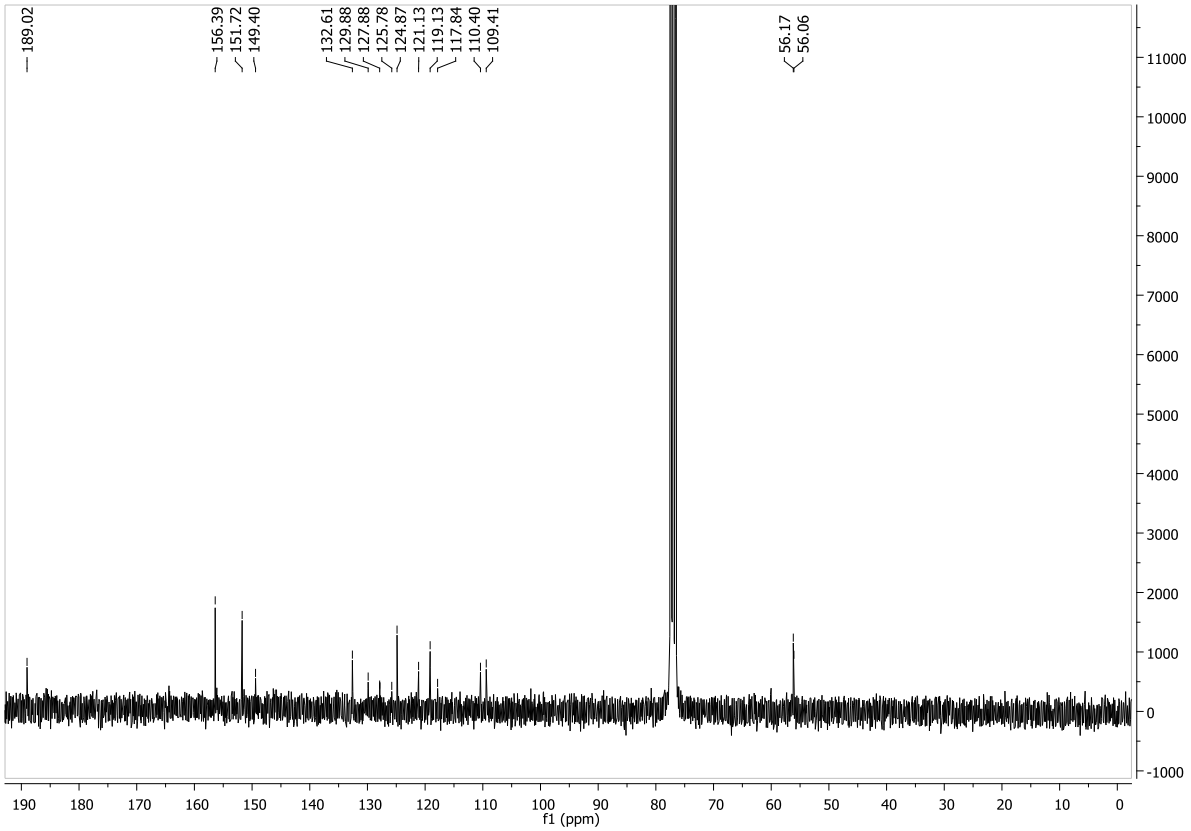
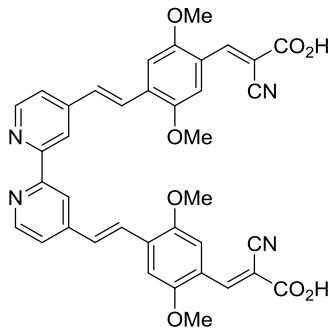


Figure S6: ^{13}C NMR (75 MHz) of compound **4** in $CDCl_3$.

1.4 (2*E*,2'*E*)-3,3'-(((1*E*,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 H_3PO_4 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);

^{1}H NMR (400 MHz, DMSO-d_6): 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).

^{13}C 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 $C_{38}H_{30}N_4O_8$: 671.21364; found: see **Figure** S9.

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).

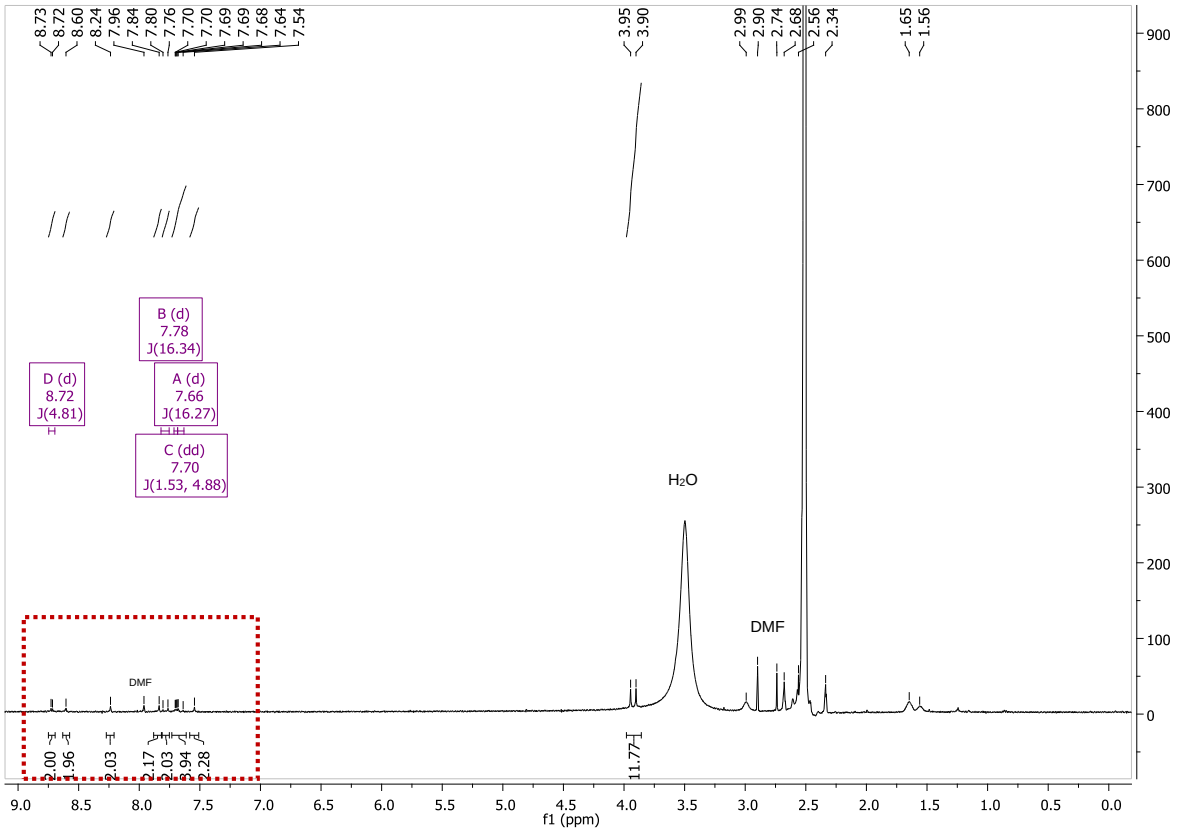


Figure S7: ^{1}H NMR (400 MHz) of compound **5** in DMSO-d_6.

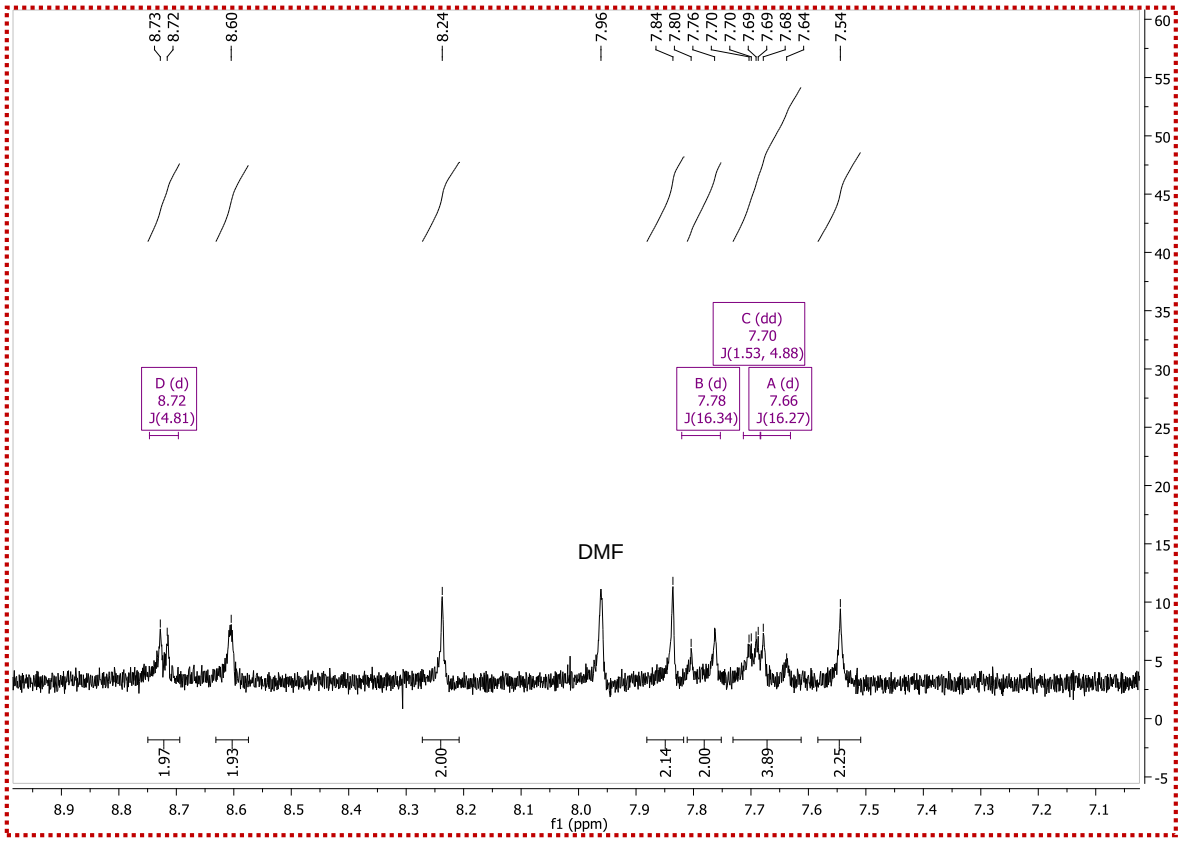


Figure S8: low field area of ^{1}H NMR (400 MHz) of compound **5** in DMSO-d_6.

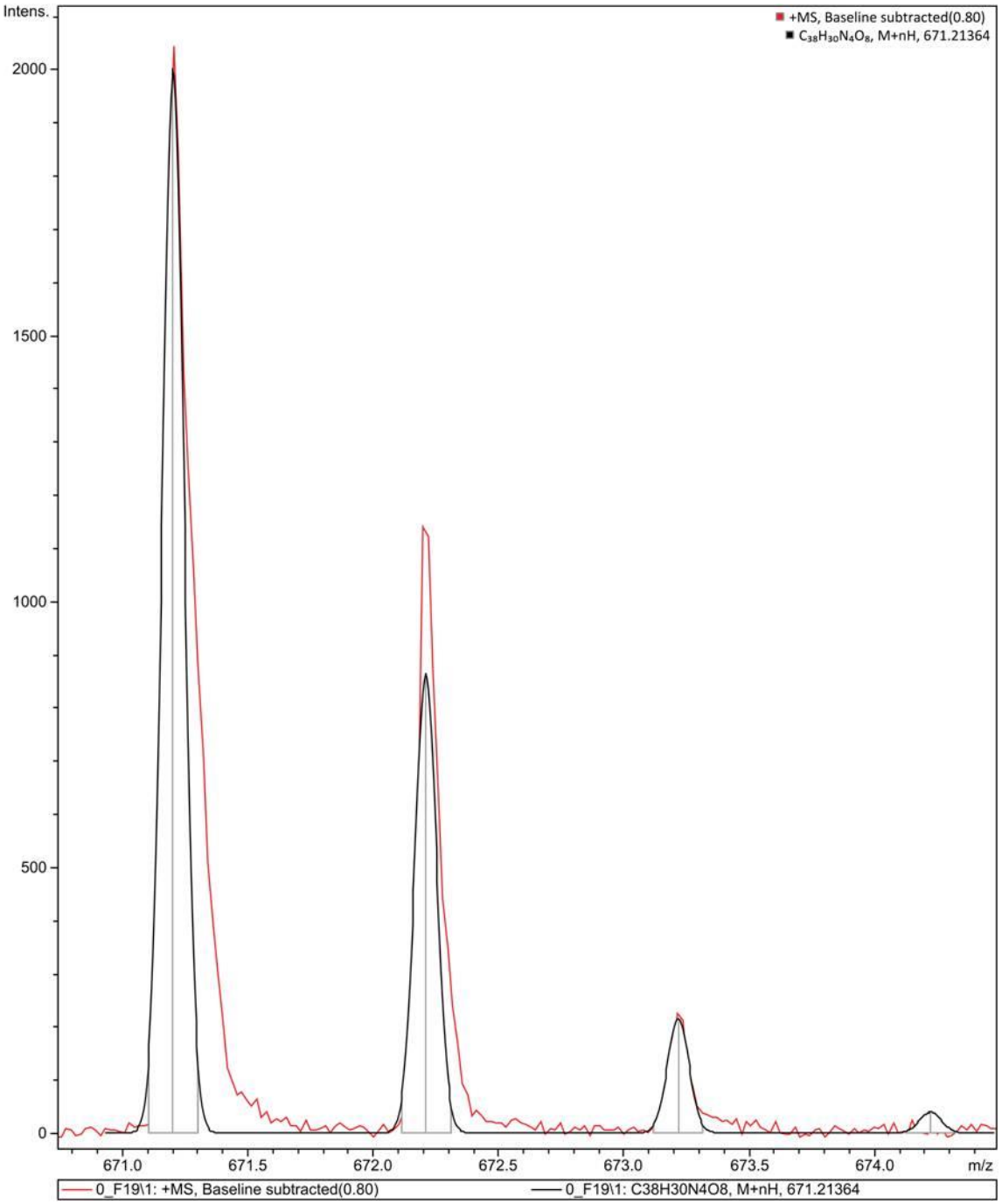


Figure S9: HRMS (MALDI) measurement of compound **5**.

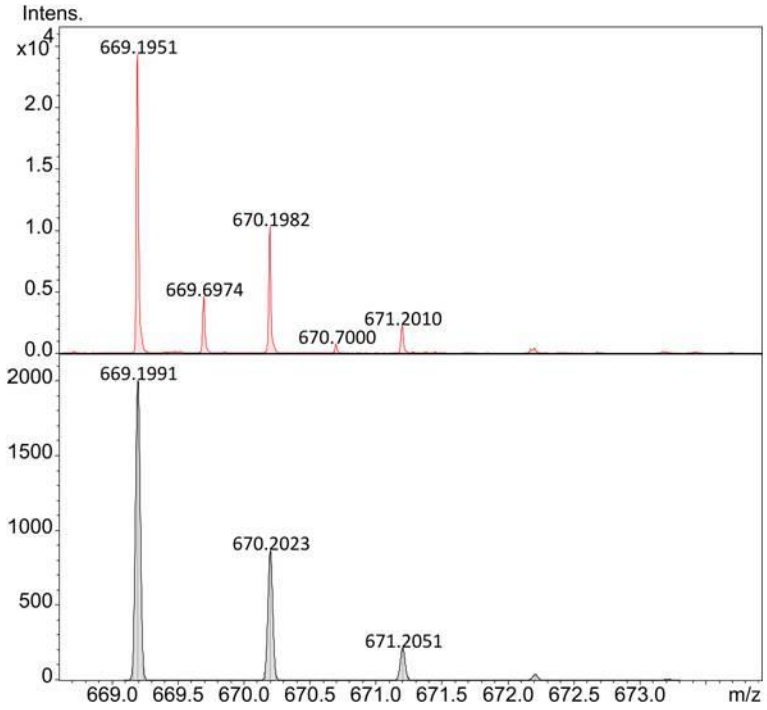
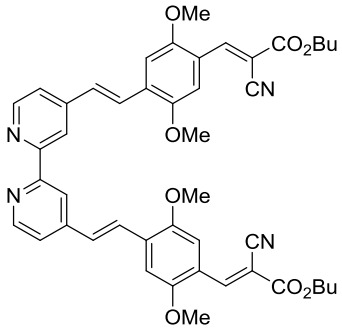


Figure S10: maXis-HRMS (ESI) measurement of compound **5** (detected in negative-ion mode).

1.5 (2*E*,2'*E*)-dibutyl-3,3'-(((1*E*,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 µl piperidine (14.5 mmol) are added to a suspension of 117 mg 4,4'-((1E,1'E)-[2,2'-bipyridine]-4,4'-diylbis (ethane-2,1-diyl))bis(2,5-di-methoxybenzalde-hyde) (**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 Et_2O (107 mg (0.137 mmol); 63%). M.p. 255 °C;
^{1}H NMR (300 MHz, $CDCl_3$): 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).
^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{46}H_{47}N_4O_8$: 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).

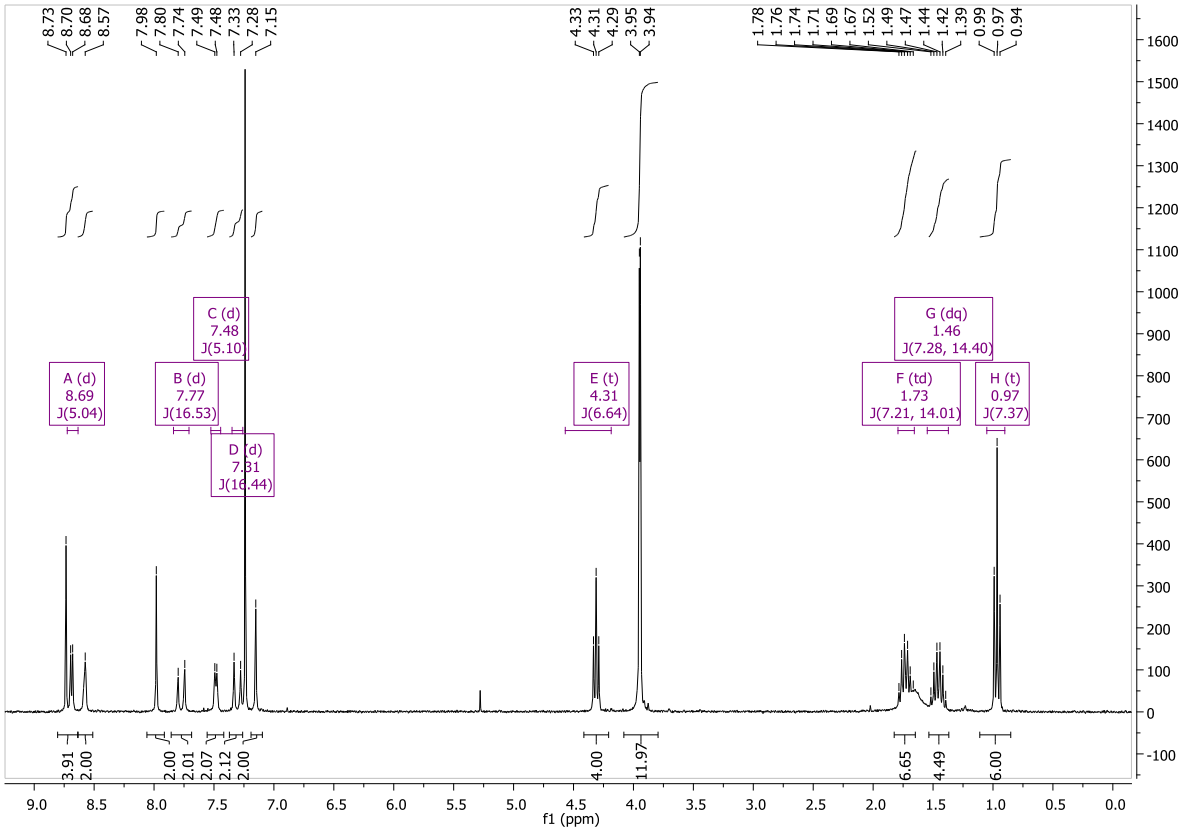


Figure S11: ^{1}H NMR (300 MHz) of compound **6** in $CDCl_3$.

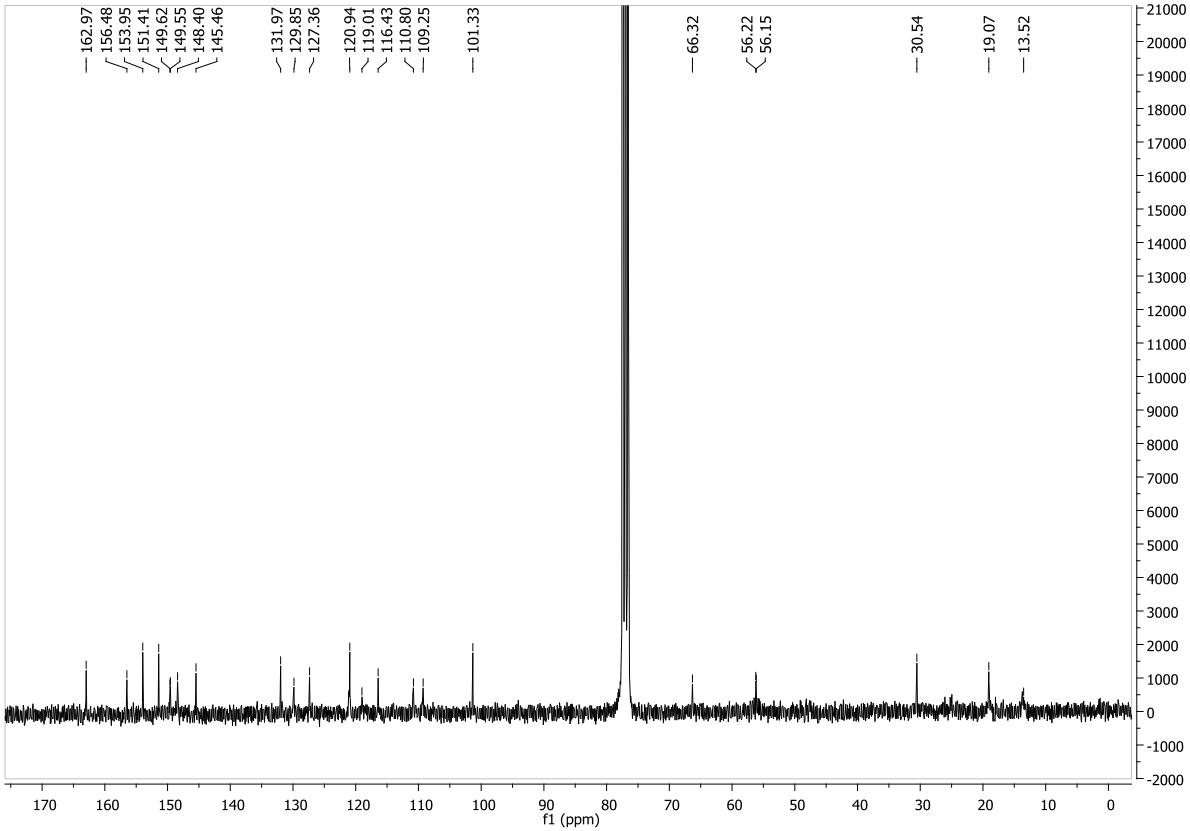


Figure S12: ^{13}C NMR (75 MHz) of compound **6** in $CDCl_3$.

Figure S13: HRMS (ESI) measurement of compound **6**.

2 Photophysical Properties of 5

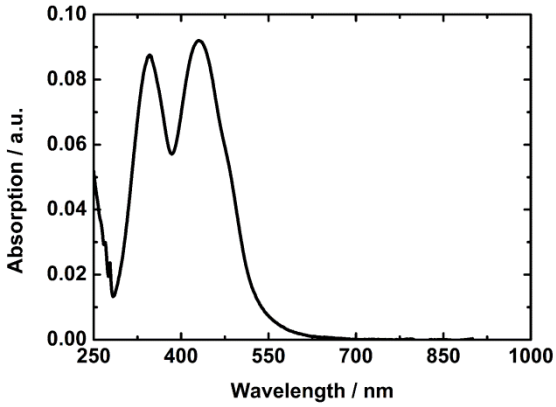


Figure S14: Absorption spectrum of **5** obtained in THF.

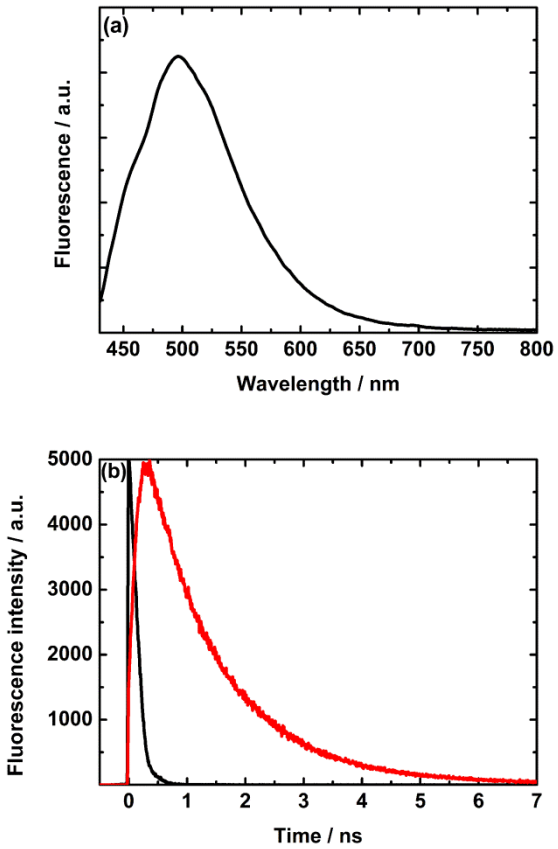


Figure S15: a) Fluorescence spectrum of **5** in THF upon photo excitation at 420 nm. B) Fluorescence time profile for **5**, obtained in THF at 500 nm, upon 403 nm photoexcitation (red), the IRF is shown in black.

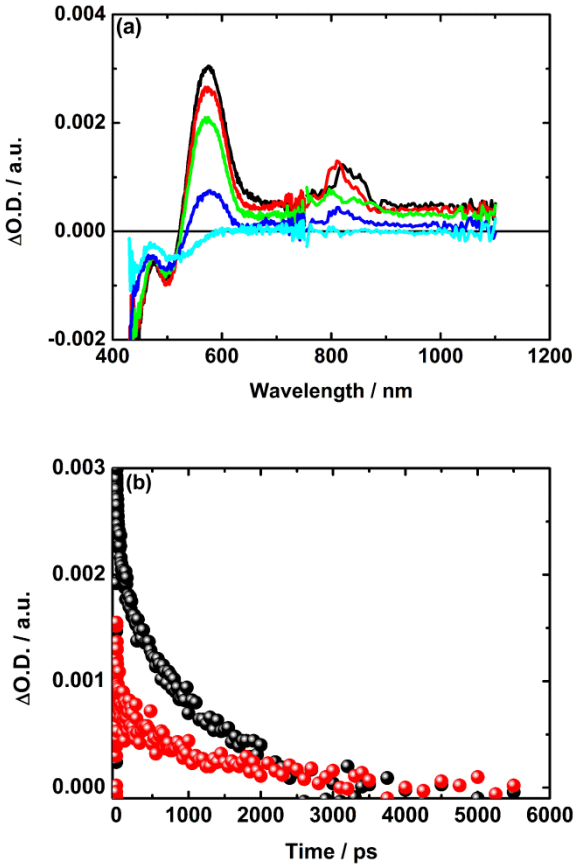
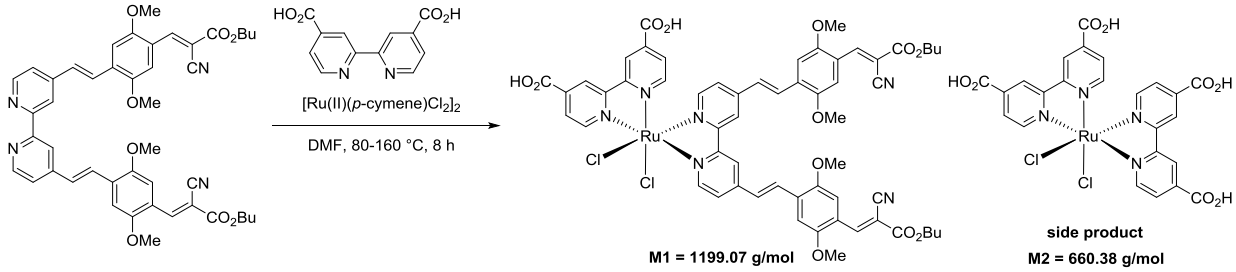


Figure S16: a) Femtosecond transient absorption spectra of **5** in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue) and 5500 ps (cyan) after excitation with femtosecond laser pulses (387 nm, 200 nJ /pulse, < 150 fs FWHM). b) Corresponding absorption time profiles at 580 (black) and 810 nm (red).

3 Preliminary complexation experiment



Test reaction: To a solution of 10 mg $[RuCl_2(p\text{-cymene})]_2$ (0.016 mmol) in 2 ml of dry DMF, 26 mg of **6** was added (0.033 mmol) under stirring. After reaction at 80 °C under nitrogen for 4 h in the dark, 8 mg dcbpy (0.033 mmol) was added. After refluxing at 160 °C for another 4 h, the solvent was removed under vacuum. The raw material was analyzed *via* MALDI-MS.

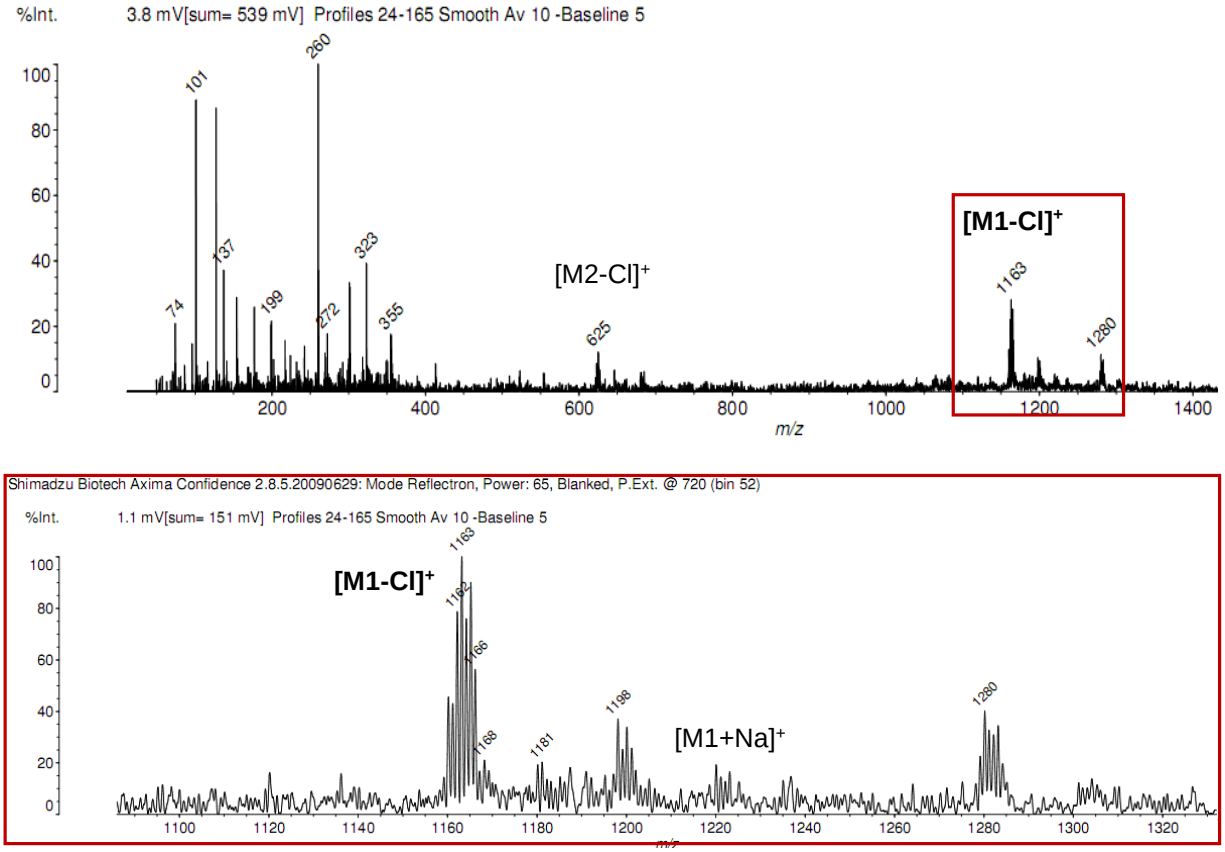


Figure S17: MALDI-MS measurement of raw material, depicting product signals with characteristic isotopic pattern of the Ru-complex.