Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplemental information for

Heteroleptic copper(I)-polypyridine complexes as efficient sensitizers for dye sensitized solar cells

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	$\lambda_{10\%}$	E_{00}	$E(S^+/S^*)$	ΔG_{inj}	ΔG_{reg} [I_3^-/ I^-]	ΔG_{reg} [$I_2^{\bullet-}$/ I^-]
C1	581	2.13	-1.19	-0.49	-0.84	-0.39
C2	603	2.06	-1.15	-0.45	-0.81	-0.36
C3	605	2.05	-0.97	-0.27	-0.70	-0.25
C4	599	2.07	-1.04	-0.34	-0.85	-0.40

Table S1. Estimated $E(S^+/S^*)$, ΔG_{inj} and ΔG_{reg} values for the complexes **C1-4**. $E_{CB,TiO2}$ = -0.7 V vs. SCE; $E^0(I_3^-/I^-)$ = 0.10 V vs. SCE; $E^0(I_2^{\bullet-}/I^-)$ = 0.55 V vs. SCE. E_{00} calculated from the wavelength (λ) at 10% of the MLCT absorption with the equation $E_{00} = 1240/\lambda$. $E(S^+/S^*) = E(S^+/S) - E_{00}$. $\Delta G_{inj} = E(S^+/S^*) - E_{CB,TiO2}$. ΔG_{reg} [I_3^-/ I^-] = $E(S^+/S) - E(I_3^-/I^-)$. ΔG_{reg} [$I_2^{\bullet-}$/ I^-] = $E(S^+/S) - E(I_2^{\bullet-}/I^-)$.

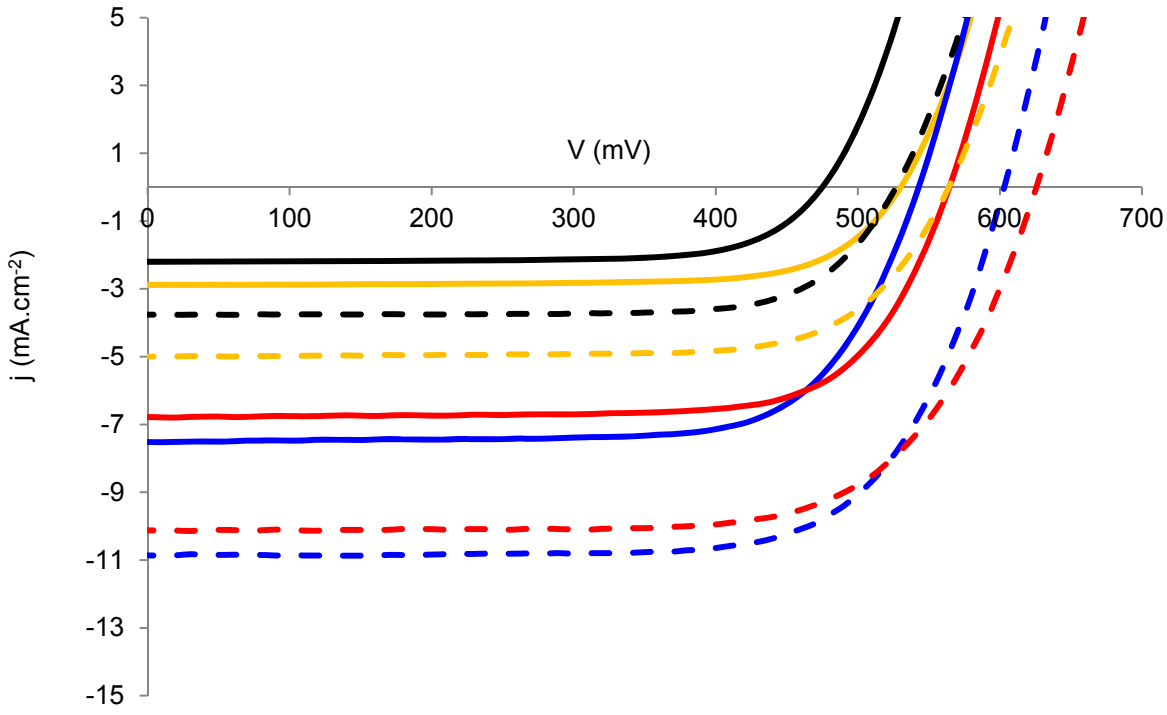


Figure S1. J vs. V characteristics of DSCs based upon the sensitization of TiO_2 by **C1** (black), **C2** (yellow), **C3** (blue), and **C4** (red) under AM 1.5 calibrated illumination, in absence (plain lines) or in presence (dashed lines) of chenodeoxycholic acid (**CDCA**).

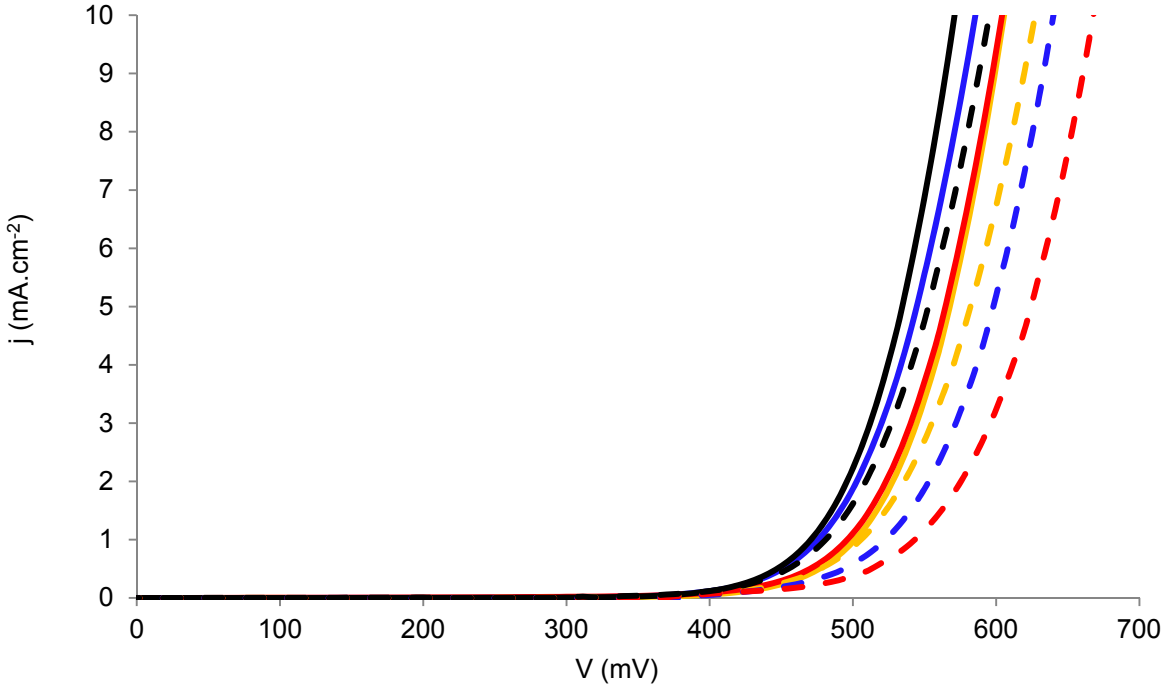


Figure S2. J vs. V characteristics of DSCs based upon the sensitization of TiO_2 by **C1** (black) **C2** (yellow), **C3** (blue), and **C4** (red) recorded in the dark, in absence (plain lines) or in presence (dashed lines) of chenodeoxycholic acid (**CDCA**).

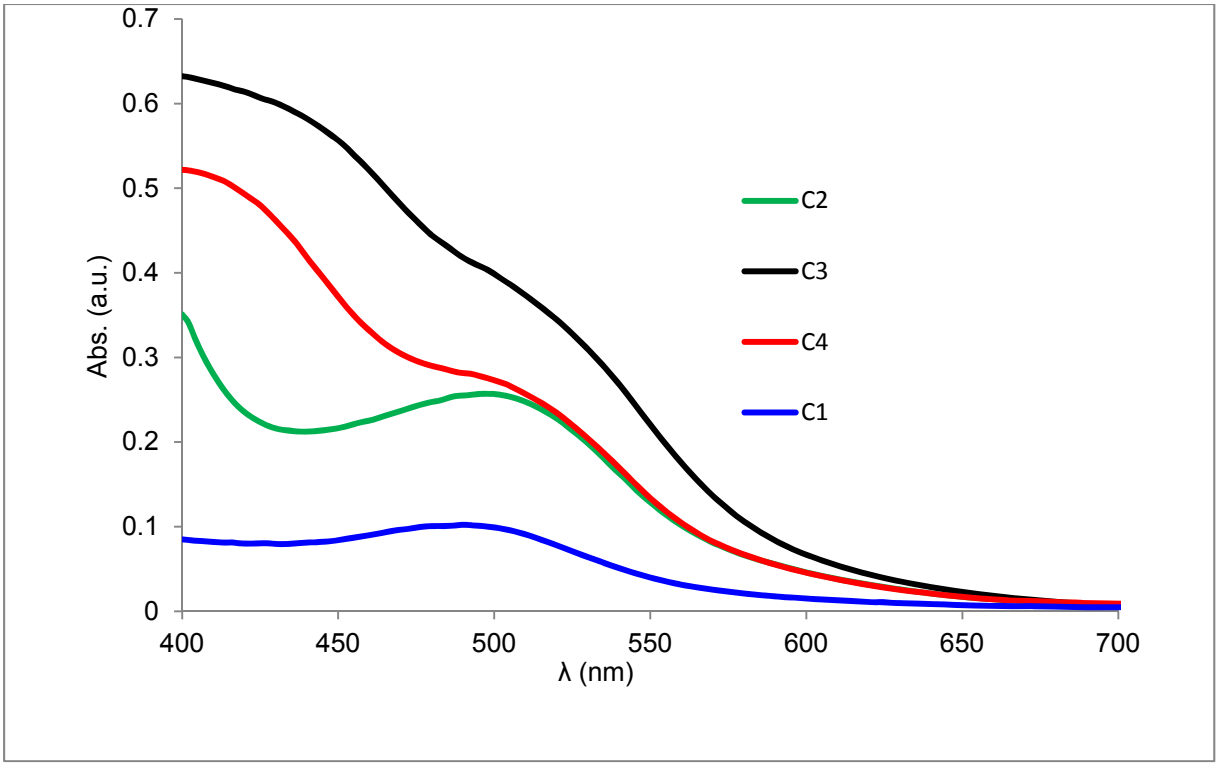


Figure S3. UV-Visible spectra of complexes **C1-C4** and chemisorbed on a 4 µm thick transparent TiO_2 film.

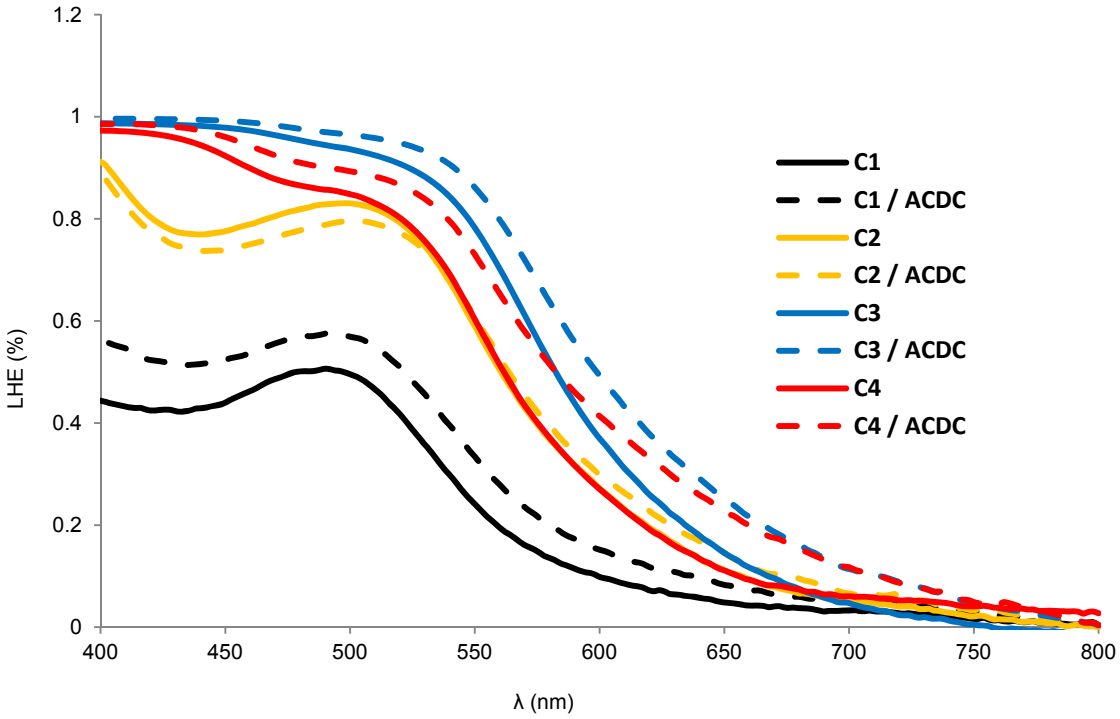


Figure S4. LHE for TiO_2 mesoporous electrodes dyed with **C1**, **C2**, **C3** and **C4** before and after **CDCA** treatment. Absorbances for 12µm thick electrodes were extrapolated from the measurements obtained for 4µm thick transparent TiO_2 electrodes.

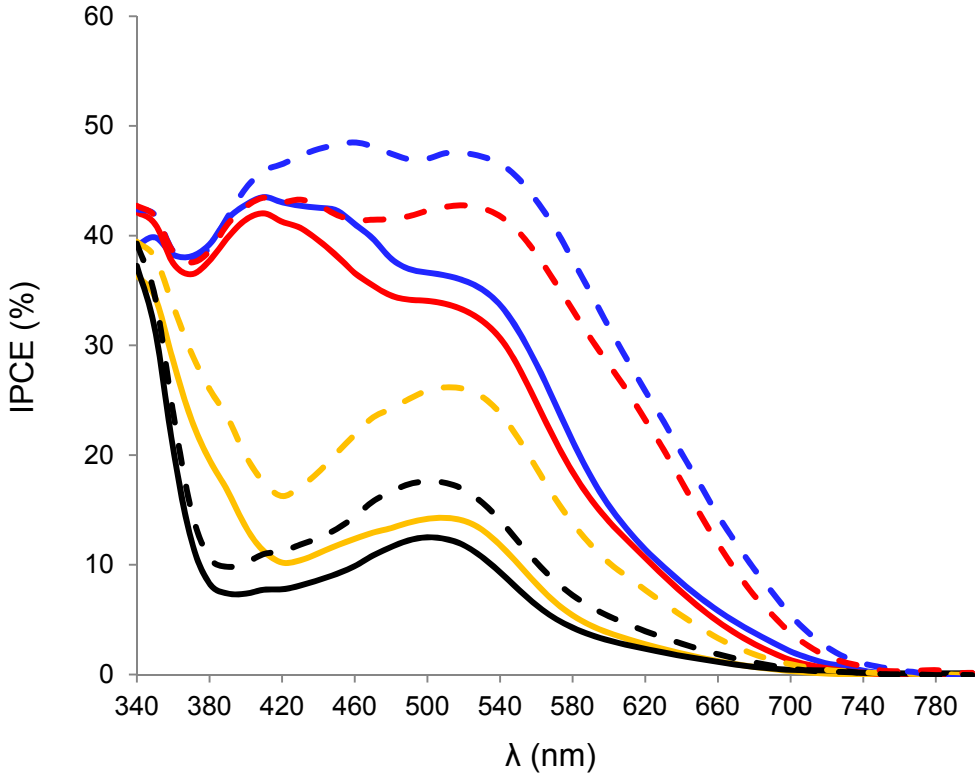


Figure S5. IPCE for DSCs based upon the sensitization of TiO_2 by **C1** (black), **C2** (yellow), **C3** (blue) and **C4** (red) in absence (plain line) or presence (dashed line) of **CDCA**.

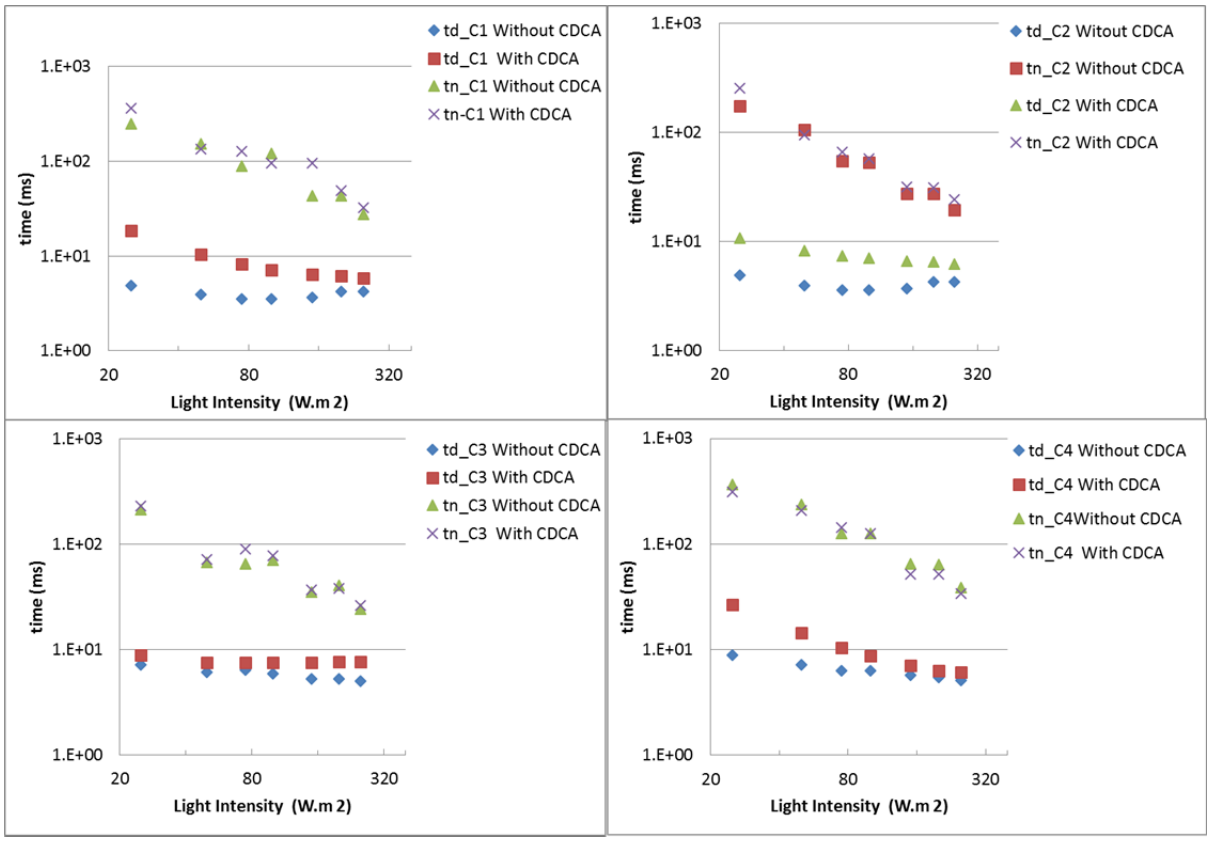
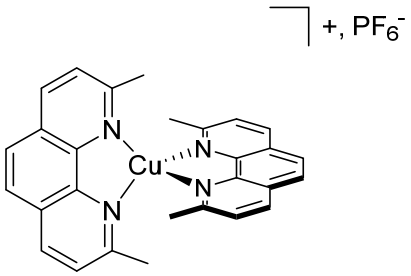


Figure S6. Evolution of mean transit times (t_d) and electron lifetimes (t_n) with light intensity for **C1**, **C2**, **C3** and **C4** in presence or in absence of **CDCA**.



complex **C5**

Figure S7. Structure of the bis-neocuproine Cu(I) complex **C5.**

Experimental section

General methods:

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker ARX 300 MHz or Bruker AMX 400 MHz or Bruker AVANCE III 500 spectrometers. Chemical shifts for ^{1}H-NMR spectra are referenced relative to residual protium in the deuterated solvent ($CDCl_3$, singlet δ = 7.26 ppm; MeOD, singlet δ = 4.84 ppm). Hydrogen nuclei numbering is given in SI. MALDI-TOF analyses were performed on a BRUKER Ultraflex III, micrOTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix. UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer, using optically matched quartz cuvettes with a 1 cm path length for the reference and the sample. Steady-state luminescence spectra were recorded using a FluoroMax3 (Jobin Yvon Horiba), and emission was corrected for the spectral sensitivity of the instrument. The electrochemical measurements were performed with an Autolab PGSTAT 302N potentiostat controlled by GPES software using a conventional single-compartment three-electrode cell. The working electrode was a Pt disc, the counter electrode was a Pt foil and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 M nBu$_4$NPF$_6$ in freshly distilled dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. The CV experiments were performed at a scan rate of 100 mV/s.

FTO conductive glass substrates (F-doped SnO_2) were purchased from Pilkington (TEC8). The plates were cleaned by successive sonication in soapy water, then an ethanolic solution of HCl (0.1 M) for 10 minutes, and finally dried in air. TiO_2 films were then prepared

in three steps. A first treatment is applied by immersion for 30 min in an aqueous $TiCl_4$ solution at 80°C. Layers of TiO_2 were then screen printed with transparent colloidal paste DSL 18NR-T and light scattering DSL 18NR-AO (Dyesol) as final layer, with 20-minute long drying steps at 150°C between each layer. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second $TiCl_4$ treatment was immediately conducted afterwards. Thicknesses were measured by a Sloan Dektak 3 profilometer. The prepared TiO_2 electrodes were soaked while still hot (80°C) in a 0.1 mM solution of **C1** (methanol) or **C2** (THF) for 48 hours. Solar cells were prepared using the dye-sensitized electrodes as the working electrodes and platinum-coated conducting glass electrodes as counter electrodes. The latter were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (2 mg per mL) and subsequent firing at 380°C for 20 minutes. The two electrodes were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 25 μm) as a spacer to form the electrolyte space. A drop of electrolyte was introduced by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with surlyn and a cover glass. The cell had an active area of *ca.* 0.25 cm^2. Photovoltaic measurements were performed with a calibrated AM 1.5 artificial solar light simulator (Oriel) and a Keithley 2400 source-meter; data were collected with a home-made software (labview).

Electrochemical impedance measurements (EIS) were carried out using a Zahner Electrochemical Station. Before proceeding to intensity-modulated photovoltage spectroscopy (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS) measurements, electrochemical impedance spectra (EIS) was conducted for checking the DSSC cells, a perturbation of 10mV was applied and impedance spectra were obtained from 100kHz to 50mHz. IMVS under open-circuit conditions and IMPS under short-circuit conditions were performed using the Zahner CIMPS-2 system. The electron transport time (τ_d) and the recombination time (τ_n) were estimated from the IMPS and the IMVS plots, respectively. A white-light-emitting diode (WLR02) from Zahner controlled by a PP211 (Zahner) frequency response analyzer was used and provided both the DC and AC components of the illumination. The AC component of the current to the LED generated a modulation (10%) superimposed on the DC light intensity in the range of [20 ; 300] $W.m^{-2}$ with the frequency range from 100 to 0.010 Hz for IMPS and IMVS.

Synthesis:

4,4',6,6'-tetramethyl-2,2'-bipyridine (**L^1**) and neocuproine were purchased from Sigma-Aldrich and used as received. 4,4'-methylphosphonateethyl ester-6,6'-dimethyl-2,2'-bipyridine,[1] **1**,[2] **L^3**,[3] **L^4**,[4] and **C5**[5] were synthesized according to previously published procedures.

***4,4'-dianisylaminostyryl-6,6'-dimethyl-2,2'-bipyridine* (L^2)**

In a Schlenk flask, 4,4'-methylphosphonateethyl ester-6,6'-dimethyl-2,2'-bipyridine (200 mg, $4.13.10^{-4}$ mol) and 4-octyloxybenzaldehyde (387 mg, 1.65 mmol, 4 equiv.) were dissolved in THF (10 mL) and tBuOK (185 mg, 1.65 mmol) was slowly added at room temperature. The solution, which immediately turned brown, was then stirred for 3 h. Addition of water led to the formation of a pale precipitate, which was filtered. The crude solid was purified by column chromatography on silica gel (eluent CH_2Cl_2: AcOEt = 90:10 → 85: 15) to afford pure **L^2** (170 mg, 64 %). **^{1}H-NMR** (400 MHz, $CDCl_3$, 25 ºC): δ = 8.30 (s, 2H, H^3), 7.50 (d, J = 8.5 Hz, 4H, H^9), 7.38 (d, J = 16.3 Hz, 2H, H^7), 7.24 (s, 2H, H^5), 6.98 (d, J = 16.3 Hz, 2H, H^8), 6.92 (d, J = 8.5 Hz, 4H, H^{10}), 3.99 (t, J = 6.5 Hz, 4H, OCH_2^{nOct}), 2.68 (s, 6H, CH_3), 1.81 (m, 4H, CH_2^{nOct}), 1.48 (m, 4H, CH_2^{nOct}), 1.31 (m, 16H, 4 CH_2^{nOct}), 0.90 (m, 6H, CH_3^{nOct}) ppm. **HR-MS** (MALDI): m/z = 645.4438, calculated for $[M-H]^+$= 645.4415.

***6,6'-dimesityl-2,2'-bipyridine-4,4'-dicarboxylate dimethyl ester* (L^{0}ester):**

6,6'-dichloro-2,2'-bipyridine-4,4'-dicarboxylate dimethyl ester **1** (253 mg, $7.4\ 10^{-1}$ mmol), mesitylboronic acid (264 mg, 1.6 mmol), $Pd_2(dba)_3$ (20 mg, 6%), SPhos (33 mg, $8.7\ 10^{-2}$ mmol) and potassium phosphate (782 mg, 3.7 mmol) were put in a dry schlenk tube under Ar, and dry toluene was added. The mixture was refluxed overnight then allowed to cool to room temperature. Water was added and the mixture was extracted 3 times with dichloromethane, the organic phase was then washed with brine and the solvent was removed under reduced pressure. The obtained solid was first washed with methanol, then purified by chromatography on silica gel (CH_2Cl_2) to afford **L^{0}ester** (0.33 mmol, 170 mg, 45%) as a white solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 8.93 (d, 2H, J = 1.4 Hz, H^3), 7.83 (d, 2H, J = 1.4 Hz, H^5), 7.02 (s, 4H, H^{Mes}), 3.96 (s, 6H, OCH_3), 2.39 (s, 6H, CH_3^{Mes}), 2.12 (s, 12H, CH_3^{Mes}) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 166.14, 160.54, 156.82, 138.99, 138.08, 137.37, 136.09, 128.67, 124.54, 118.69, 52.78, 21.29, 20.56 ppm. **HR-MS** (MALDI+): m/z = 509.2458, calculated for $(MH)^+$ m/z = 509.2434.

***6,6'-dimesityl-2,2'-bipyridine-4,4'-dicarboxylic acid* (L^0)**

L^0ester (100 mg, 0.20 mmol) was suspended in 7 mL of THF, and a solution of LiOH (49 mg, 2.1 mmol) in 1 mL of water was added. The mixture is heated to reflux (**L^0ester** dissolves completely upon heating) for 6 hours, then allowed to cool to room temperature. Water was added, and the THF was removed under reduced pressure. The mixture was acidified with HCl 1 M until a pH of 1-2 was reached, and the precipitate was collected by filtration (95 mg, quantitative). **^{1}H-NMR** (300 MHz, DMSO-d_6): δ = 8.72 (d, 2H, J = 1.4 Hz, H^3), 7.72 (d, 2H, J = 1.2 Hz, H^5), 7.02 (s, 4H, H^{Mes}), 2.32 (s, 6H. CH_3^{Mes}), 2.03 (s, 12H, CH_3^{Mes}) ppm. **HR-MS** (MALDI+): m/z = 481.2130, calculated for $(MH)^+$ m/z = 2122.

Complex C1ester

L^0ester (41 mg, $8.0\cdot10^{-2}$ mmol) and $[Cu(CH_3CN)_4]PF_6$ (28 mg, $7.5\cdot10^{-2}$ mmol) were dissolved in 4 mL of dry degassed dichloromethane and stirred under Ar at room temperature until complete dissolution. 4,4',6,6'-tetramethyl-2,2'-bipyridine (14 mg, $6.7\cdot10^{-2}$ mmol) was dissolved in 4 mL of dry dichloromethane, degassed for 5 minutes by Ar bubbling and injected dropwise into the orange-red solution while stirring. After 40 minutes the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent CH_2Cl_2: CH_3OH = 98: 2) to afford pure **C4'** (52 mg, 84%) as a violet solid. **^{1}H-NMR** (300 MHz, acetone-d_6): δ = 9.24 (d, 2H, J = 1.3 Hz, H^3), 8.17 (d, 2H, J = 1.3 Hz, H^5), 7.95 (s, 2H, $H^{3'}$), 7.20 (s, 2H, $H^{5'}$), 6.38 (s, 4H, H^{Mes}), 4.06 (s, 6H, OCH_3), 2.45 (s, 6H, 2 CH_3), 2.02 (s, 6H, 2 CH_3), 1.89 (s, 6H, 2 CH_3^{Mes}), 1.66 (s, 12H, 4 CH_3^{Mes}) ppm. **HR-MS** (MALDI+): m/z = 783.2951, calculated for $(M\text{-}PF_6)^+$ m/z = 783.2966.

Complex C2ester

The same protocol than the synthesis of **C1ester** was employed to isolate **C2ester**.

Violet solid, 88% yield. **^{1}H-NMR** (300 MHz, acetone-d_6): δ = 9.26 (d, 2H, J = 1.1 Hz, H^3), 8.32 (s, 2H, $H^{5'}$), 8.19 (d, 2H, J = 1.0 Hz, H^5), 7.73-7.64 (m, 6H, $H^{7'}$ and $H^{10'}$), 7.51 (s, 2H, $H^{3'}$), 7.18 (d, 2H, J = 16.4 Hz, $H^{8'}$), 7.03 (d, 4H, J = 8.6 Hz, $H^{9'}$), 6.41 (s, 4H, H^{Mes}), 4.09-4.05 (m, 10H, 2 OCH_3 and 2 OCH_2^{nOct}), 2.34 (s, 6H, 2 CH_3), 1.88 (s, 6H, 2 CH_3^{Mes}), 1.86-1.76 (m, 4H, 2 CH_2^{nOct}), 1.70 (s, 12H, 4 CH_3^{Mes}), 1.53-1.43 (m, 4H, 2 CH_2^{nOct}), 1.42-1.30 (m, 16H, 8 CH_2^{nOct}), 0.89 (t, 6H, J = 6.6 Hz, 2 CH_3^{nOct}) ppm. **HR-MS** (MALDI+): m/z = 1215.5959, calculated for $(M\text{-}PF_6)^+$ m/z = 1215.5994.

Complex C3ester

The same protocol than the synthesis of **C1ester** was employed to isolate **C3ester**.

Red solid, 77% yield. **^{1}H-NMR** (500 MHz, acetone-d_6): δ = 9.25 (d, 2H, J = 1.4 Hz, H^3), 8.24 (s, 2H, $H^{3'}$), 8.18 (d, 2H, J = 1.3 Hz, H^5), 7.62 (d, 2H, J = 16.3 Hz, $H^{7'}$), 7.53 (d, 4H, J = 8.8 Hz, $H^{9'}$), 7.42 (s, 2H, $H^{5'}$), 6.99 (d, 2H, J = 16.2 Hz, $H^{8'}$), 6.78 (d, 4H, J = 8.7 Hz, $H^{10'}$), 6.42 (s, 4H, H^{Mes}), 4.07 (s, 6H, OCH_3), 3.77 (s, 6H, CH_3^{bpy}), 3.48 (m, 8H, NCH_2^{Et}), 1.89 (s, 6H, CH_3^{Mes}), 1.71 (s, 12H, CH_3^{Mes}), 1.20 (t, 12H, J = 7.1 Hz, CH_3^{Et}) ppm. **HR-MS** (MALDI+): m/z = 1101.5062, calculated for $(M\text{-}PF_6)^+$ m/z = 1101.5062.

***Complex C4*ester**

The same protocol than the synthesis of **C1ester** was employed to isolate **C4ester**.

Red solid, 97% yield. **^{1}H-NMR** (300 MHz, acetone-d_6): δ = 9.27 (d, 2H, J = 1.3 Hz, H^3), 8.32 (s, 2H, $H^{3'}$), 8.19, (d, 2H, J = 1.5 Hz, H^5), 7.70 (d, 2H, J = 16.4 Hz, $H^{7'}$), 7.60 (d, 4H, J = 8.7 Hz, $H^{9'}$), 7.52 (s, 2H, $H^{5'}$), 7.36 (t broad, 8H, J = 7.9 Hz, $H^{12'}$), 7.20 (d, 2H, J = 16.4 Hz, $H^{8'}$), 7.15-7.10 (m, 12H, $H^{11'}$ and $H^{13'}$), 7.03 (d, 4H, J = 8.6 Hz, $H^{10'}$), 6.41 (s, 4H, H^{Mes}), 4.07 (s, 6H, OCH_3), 2.08 (s, 6H, 2 CH_3), 1.89 (s, 6H, 2 CH_3^{Mes}), 1.71 (s, 12H, 4 CH_3^{Mes}) ppm. **HR-MS** (MALDI+): m/z = 1293.5017, calculated for $(M\text{-}PF_6)^+$ m/z = 1293.5062.

Complex C2

L^0 (9.3 mg, 0.019 mmol) and $[Cu(CH_3CN)_4]PF_6$ (6.5 mg, 0.017 mmol) were dissolved in 4 mL of freshly distilled and degassed dimethylformamide, and stirred under Ar at room temperature until complete dissolution. Ligand **L^2** (10 mg, 0.015 mmol) was dissolved in 4 mL of dry, degassed dimethylfomarmide and subsequently syringed dropwise into the orange-red solution while stirring, at room temperature. After 40 minutes the solvent was removed under reduced pressure and the crude product was purified by Sephadex chromatography (LH20) (eluent CH_2Cl_2: CH_3OH = 50:50) to afford pure **C2** (12.5 mg, 56%) as an orange solid. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 10.14 (s, 2H, H^3), 8.22 (s, 2H, $H^{3'}$), 7.72 (s, 2H, H^5), 7.56 (d, 4H, J = 8.4 Hz, $H^{9'}$), 7.41 (d, 2H, J = 16.8 Hz, $H^{7'}$), 7.38 (s, 2H, $H^{5'}$), 6.96 (m, 6H, $H^{8'}$ and $H^{10'}$), 6.28 (s, 4H, H^{Mes}), 4.02 (t, 4H, J = 6.0 Hz, O-CH_2), 2.5-1.9 (m, 16H, CH_2^{nOct} and CH_3), 1.85 (s, 6H, H^{Mes}), 1.64 (s, 12H, H^{Mes}), 1.5-1.1 (m, 28H, CH_2^{nOct}), 1.0-0.8 (m, 8H, CH_2^{nOct}). **HR-MS** (ESI+): m/z = 1187.56982, calculated for $(M\text{-}PF_6)^+$ m/z = 1187.56814.

Complex C3

The same procedure used for **C2** was employed to synthesize **C3**. **^{1}H-NMR** (300 MHz, CD_3OD): δ = 9.11 (s, 2H, H^3), 8.17 (s, 2H, $H^{3'}$), 8.09 (s, 2H, H^5), 7.68 (m, 6H, $H^{7'}$ and $H^{9'}$), 7.36 (s, 2H, $H^{5'}$), 7.07 (m, 6H, $H^{8'}$ and $H^{10'}$), 6.35 (s, 4H, H^{Mes}), 3.52 (q, 2H, J = 6.9 Hz, N-CH_2), 1.98 (s, 6H, CH_3), 1.84 (s, 6H, H^{Mes}), 1.64 (s, 12H, H^{Mes}), 1.16 (t, 6H, J = 7.2 Hz, CH_3) **HR-MS** (ESI+): m/z = 1073.4789, calculated for $(M\text{-}PF_6)^+$ m/z = 1073.4749.

Complex C4

The same procedure used for **C2** was employed to synthesize **C4**. **^{1}H-NMR** (300 MHz, CD_3OD): δ = 9.00 (s, 2H, H^3), 8.12 (s, 2H, $H^{3'}$), 7.90 (s, 2H, H^5), 7.60 (d, 2H, J = 16.5 Hz, $H^{7'}$), 7.51 (d, 4H, J = 8.7 Hz, $H^{9'}$), 7.30-7.20 (m, 10H, H^{Arom}), 7.10-7.00 (m, 12H, H^{Arom} and $H^{8'}$), 6.96 (d, 4H, J = 8.7 Hz, $H^{10'}$), 6.31 (s, 4H, H^{Mes}), 1.99 (s, 6H, CH_3), 1.83 (s, 6H, H^{Mes}), 1.62 (s, 12H, H^{Mes}). **HR-MS** (ESI+): m/z = 1265.47546, calculated for $(M\text{-}PF_6)^+$ m/z = 1265.47491.

Complex C1

The same procedure used for **C2** was employed to synthesize **C1**. **^{1}H-NMR** (300 MHz, CD_3OD): δ = 9.04 (s, 2H, H^3), 8.03 (s, 2H, H^5), 7.76 (s, 2H, $H^{3'}$), 7.04 (s, 2H, $H^{5'}$), 6.27 (s, 6H, H^{Mes}), 2.36 (s, 6H, CH_3), 1.89 (s, 6H, CH_3), 1.81 (s, 6H, H^{Mes}), 1.55 (s, 12H, H^{Mes}). **HR-MS** (ESI+): m/z = 755.26654, calculated for $(M\text{-}PF_6)^+$ m/z = 755.26531.

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