# Novel Heteroleptic Ru(II) Complexes: Synthesis, Characterization and Application in Dye-Sensitized Solar Cells.

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## Electronic Supplementary Information

**1. Synthesis of MC118, MC120-123 ruthenium complexes**

**1.1. 2-bromo-1,3-bis(octyloxy)benzene (1)** (80%)**.** To an ice-cooled suspension of KOH (0.118 g, 2.116 mmol) in DMF (10 mL) was added 2-bromobenzene-1,3-diol (0.200 g, 1.058 mmol) and 1-iodooctane (0.401 mL, 2.222 mmol). The suspension was stirred at room temperature for 16 h under $N_2$. The mixture was cooled at room temperature and brine was added. The organic layer was collected with ethylacetate and dried over $Na_2SO_4$. After evaporation of solvent, the crude compound was purified over silica gel column and desired compound was eluted using ethylacetate:hexane (1:9).

$^1$H NMR (300 MHz, $CDCl_3$, δ): 7.12 (t, 1H), 6.52 (d, 2H), 3.92 (t, 4H), 1.68-1.80 (m, 4H), 1.24-1.48 (m, 20H), 0.9 (t, 6H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.08, 22.63, 25.96, 29.20, 29.29, 29.34, 31.78, 63.33, 106.06, 118.84, 135.45, 146.66. ESI-MS:m/z $[M]^+$: 413.

**1.2. 2,6-bis(octyloxy)phenylboronic acid (2)** (79%)**.** To a solution of 2-bromo-1,3-bis(octyloxy)benzene (0.200 g, 0.484 mmol) and trimethylborate (0.112 mL, 1.016 mmol) in anhydrous THF (15 mL) cooled to -70 ºC under an inert atmosphere was slowly added n-BuLi (0.907 mL, 1.452 mmol). The reaction mix was stirred at -70 ºC for 1h then warmed up slowly to -10 to 0 ºC, poured into 1N HCl (20 mL) and allowed to stir 16 h under nitrogen. Then resulting suspension was neutralized to pH 7 with 5 N aq LiOH. The precipitate of boronic acid was filtered washed with minimal amount of cold water and dried to give desired product.

$^1$H NMR (300 MHz, $CDCl_3$, δ): 7.10 (t, 1H), 6.50 (d, 2H), 4.00 (t, 4H), 1.44-1.56 (m, 4H), 1.24-1.36 (m, 20H), 0.9 (t, 6H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.08, 22.63, 25.93, 29.18, 29.29, 29.34, 31.76, 63.40, 105.86, 118.78, 135.45, 146.66. ESI-MS:m/z $[M+78]^+$: 457.

**1.3. 4-(2,6-bis(octyloxy)phenyl)-2-(4-(2,6-bis(octyloxy)phenyl)pyridin-2-yl)pyridine (L1)** (74%). A 50 mL of Schlenk tube was charged with aryl 4,4'-dibromobipyridine (0.500 g, 1.592

mmol) 2,6-bis(octyloxy)phenylboronic acid (1.264 g, 3.343 mmol), $Pd(PPh_3)_4$ (0.115g, 0.1 mmol). Dimethoxy ethane(8 mL) and 2 M aqueous sodium carbonate (2 mL) were added, and the tube was purged with argon gas with 5 evacuate /refill cycles. The tube was sealed and heated at 90 $^0$C vigorously for 18 h. Upon cooling to ambient temperature, the organics were extracted into dichloromethane (3 X 30 mL) from 30 mL water. The combined organics were washed with water (1 X 30 mL) and brine (1 X 30 mL), dried over $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. The crude compound was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) to give desired product.

$^1$H NMR (300 MHz, $CDCl_3$, δ): 8.63 (d, 2H), 8.44 (s, 2H), 7.30-7.32 (m, 2H), 7.25-7.27 (m, 2H), 6.67 (d, 4H), 3.89 (t, 8H), 1.60 (qt, 8H), 1.20-1.32 (m, 40H), 0.9 (t, 12H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.08, 22.58, 25.94, 29.04, 29.17, 29.68, 31.75, 68.59, 105.00, 117.63, 123.88, 126.01, 129.43, 143.64, 148.04, 155.63, 157.01. ESI-MS:m/z $[M+78]^+$: 822.

**1.4 1-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (3)** (80%). The sameprocedure as for **1** but with 1-bromohexane (0.097 mL, 0.699 mmol) instead of 1-iodooctane. **3** purified over silica gel column and desired compound was eluted using ethylacetate:hexane (1:9).

$^1$H NMR (300 MHz, $CDCl_3$, δ): 8.16 (s, 1H), 7.64 (d, 1H), 7.32 (d, 1H), 7.04 (d, 1H), 6.48 (d, 1H), 4.08 (t, 2H), 1.76-1.84 (m, 2H), 1.36 (s, 12H), 1.24-1.32 (m, 6H), 0.9 (t 3H);$^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.11, 22.50, 24.86, 26.61, 29.68, 30.20, 46.37, 83.35, 101.58, 108.76, 114.04, 127.34, 127.91, 128.88, 137.88, 139.26.ESI-MS:m/z $[M+H]^+$: 328.

**1.5. 1-hexyl-5-(2-(4-(1-hexyl-1H-indol-5-yl)pyridin-2-yl)pyridin-4-yl)-1H-indole (L2)** (78%). The sameprocedure as for **L1** but with 3 (1.093 g, 3.343 mmol) instead of **2**. **L2** purified over silica gel column and desired compound was eluted using ethylacetate:hexane (1:9).

$^1$H NMR (300 MHz, $CDCl_3$, δ): 8.80 (s,2H), 8.68 (d, 2H), 8.04 (s,2H), 7.56-7.68 ((m, 4H), 7.40 (d, 2H), 7.08 (d, 2H), 6.52 (d, 2H), 4.12 (t, 4H), 1.84-1.92 (m, 4H), 1.32 (s, 12H), 0.9 (t, 6H);$^{13}$C NMR

(300MHz, $CDCl_3$, δ): 13.96, 22.50, 26.64, 30.24, 31.39, 46.57, 101.71, 109.86, 119.23, 119.33, 120.77, 121.57, 128.80, 129.09, 129.45, 136.48, 149.39, 150.60, 156.71. ESI-MS:m/z $[M+H]^+$: 555.

**1.6. 7-bromo-4-hexyl-1,2,3,4-tetrahydrocyclopenta[b]indole (4)** (82%). The same procedure as for **1** but with 1-bromohexane (0.142 mL, 1.016 mmol) instead of 1-iodooctane. **4** purified over silica gel column and desired compound was eluted using ethylacetate:hexane (1:9).

$^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.54 (d, 1H), 7.14-7.16 (m, 1H), 7.02-7.11 (m, 1H), 3.97 (t, 2H), 2.78-2.86 (m, 4H), 2.48-2.56 (m, 2H), 1.70-1.76 (m, 2H), 1.26-1.28 (m, 6H), 0.9 (t, 3H);$^{13}C$ NMR (300MHz, $CDCl_3$, δ): 13.99, 22.52, 24.39, 25.17, 26.62, 28.32, 29.69, 30.26, 31.44, 44.97, 83.37, 112.05, 114.04, 117.14, 121.06, 122.31, 125.85, 139.32, 147.45.ESI-MS:m/z $[M+18]^+$: 338.

**1.7. 4-hexyl-1,2,3,4-tetrahydro-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) cyclopenta [b]indole (5)** (78%). A solution of compound **4** (0.500 g, 1.567 mmol), bis(pinacolato)diboron (0.437 g, 1.723 mmol), were dissolved in dry dimethoxy ethane (8 mL) and KOAc (0.374 g, 4.701 mmol) was added. The mixture was stirred for 15 min under an argon atmosphere at room temperature. Then the $Pd(dppf)_2Cl_2$ (0.068 g, 0.094 mmol) catalyst was added and the reaction mixture was stirred overnight at 80 $^0C$. After being cooled to room temperature, the mixture was poured into water (20 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 X 20 mL) and the combined organic layers were dried over anhydrous $Na_2SO_4$. The organic solvent was evaporated under reduced pressure and the crude product was pre-adsorbed onto silica gel and chromatographed (8:2 n-hexane/ethyl acetate) to give viscous liquid **5**

$^1H$ NMR (300 MHz, $CDCl_3$, δ): 7.38-742 (m, 1H), 7.26-7.38 (m, 1H), 7.24-7.28 (m, 1H),4.00 (t, 2H), 2.80-2.86 (m, 4H), 2.48-2.56 (m, 2H), 1.74-1.78 (m, 2H), 1.36 (m, 12H), 1.32-1.34 (m, 6H), 0.9 (t, 3H); $^{13}C$ NMR (300MHz, $CDCl_3$, δ): 14.11, 22.69, 24.89, 28.96, 29.36, 29.70, 30.19, 31.93, 33.82, 83.28, 108.97, 114.04, 115.90, 123.96, 124.45, 126.04, 133.84, 139.26. ESI-MS:m/z $[M+H]^+$: 368.

**1.8 4-hexyl-7-(2-(4-(4-hexyl-1,2,3,4-tetrahydrocyclopenta[b]indol-7-yl)pyridin-2-yl) pyridin-4-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole (L3)** (76%). The synthesis method resembles that of compound **L1**, but with **5** (1.226 g, 3.343 mmol) instead of **2**. Light yellow viscous liquid of **L3** was obtained.$^{1}$H NMR (300 MHz, $CDCl_3$, δ): 8.76-8.70 (m, 2H), 7.88-7.92 (m, 2H), 7.64-7.68 (m, 2H), 7.54-7.60 (m, 2H), 7.32-7.36 (m, 2H), 4.04 (t, 4H), 2.84-2.96 (m, 8H), 2.52-2.64 (m, 4H), 1.72-1.84 (m, 4H), 1.28-1.36 (m, 12H), 0.9 (t, 6H););$^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.01, 22.54, 24.66, 26.68, 28.42, 29.68, 30.37, 31.48, 45.03, 109.95, 117.62, 118.36, 119.10, 119.67, 121.57, 124.79, 128.85, 141.24, 147.28, 149.30, 150.91, 156.63. ESI-MS:m/z $[M+H]^+$: 635.

**1.9. 2-bromo-9,9-didecyl-9H-fluorene (6)** (83%). The same procedure as for **1** but with 1-bromodecane (0.260 mL, 1.714 mmol) instead of 1-iodooctane in DMSO solvent. **6** purified over silica gel column and desired thick oily compound was eluted using ethylacetate:hexane (1:9).$^{1}$H NMR (300 MHz, $CDCl_3$, δ ): 7.64-7.68 (m, 1H), 7.53-7.56 (m, 1H), 7.42-7.46 (m, 2H), 7.30-7.34 (m, 3H), 1.86-1.94 (m, 4H), 1.22-1.28 (m, 4H), 1.16-1.20 (m, 10H) 1.12-1.15 (m, 4H), 1.00-1.10 (m, 14H), 0.9 (t, 6H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.11, 22.65, 23.65, 29.22, 29.52, 29.93, 31.85, 40.24, 55.34, 119.70, 120.92, 120.98, 122.83, 126.08, 128.87, 127.41, 129.82, 130.98, 140.09, 150.26, 152.92. ESI-MS:m/z $[M]^+$: 526.

**1.10 2-(9,9-didecyl-9H-fluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)** (82%). The synthesis method resembles that of compound **5**. Yellow thick oily liquid of **7** was obtained.$^{1}$H NMR (300 MHz, $CDCl_3$, δ ): 7.78-7.82 (m, 1H), 7.74-7.76 (m, 1H), 7.68-7.73 (m, 2H), 7.30-7.36 (m, 3H), 1.92-2.02 (m, 4H), 1.39 (s, 12H), 1.20-1.32 (m, 8H), 1.10-1.20 (m, 12H) 0.98-1.08 (m, 12H), 0.88 (t, 6H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.13, 22.69, 23.71, 24.96, 29.29, 29.57, 30.05, 31.88, 40.25, 55.07, 83.69, 118.95, 120.09, 122.94, 126.66, 127.48, 128.82, 133.70, 140.92, 144.12, 149.88, 151.30. ESI-MS:m/z $[M]^+$: 572.

**1.11. 4-(9,9-didecyl-9H-fluoren-2-yl)-2-(4-(9,9-didecyl-9H-fluoren-7-yl)pyridin-2-yl)pyridine (L4)** (76 %). The synthesis method resembles that of compound **L1**. Light yellow powder of **L4** was obtained. $^{1}$H NMR (300 MHz, $CDCl_3$, δ): 8.80-8.04 (m, 4H), 7.74-7.88 (m, 8H), 7.64-7.68 (m, 2H), 7.32-7.40 (m, 6H), 2.00-2.32 (m, 8H), 1.24-1.28 (m, 8H), 1.12-1.20 (m, 4H), 0.9 (t, 12H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 14.08, 22.63, 23.77, 29.69, 30.43, 31.49, 31.62, 31.92, 33.82, 40.35, 55.34, 114.05, 121.33, 121.82, 122.92, 123.45, 126.18, 126.85, 127.52, 136.88, 139.23, 140.33, 142.29, 149.53, 149.98, 151.13, 151.66, 156.73.ESI-MS:m/z $[M+H]^+$:1046

**1.12. 3-bromo-9-hexyl-9H-carbazole (8)** (82%). The synthesis method resembles that of compound **1** but with 1-bromohexane (0.093 mL, 0.666 mmol) instead of 1-iodooctane. Viscous liquid of **8** was obtained. $^{1}$H NMR (300 MHz, $CDCl_3$, δ): 8.18 (d, 1H), 8.00-8.04 (d, 1H), 7.49-7.54 (m, 1H), 7.44-7.47 (m, 1H), 7.36-7.40 (m, 1H), 7.20-7.25 (m, 1H), 4.21-4.26 (t, 3H), 1.77-1.87 (m, 2H), 1.23-1.36 (m, 6H), 0.9 (t, 3H); $^{13}$C NMR (300MHz, $CDCl_3$, δ):13.97, 22.48, 26.85, 28.79, 31.48, 43.05, 108.83, 110.01, 119.06, 120.4, 121.68, 122.93, 124.93, 124.42, 126.22, 128.08, 128.85, 138.92. ESI-MS:m/z $[M]^+$:330.

**1.13 9-hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (9)** (80%). The synthesis method resembles that of compound **5**. Color less liquid of **9** was obtained. $^{1}$H NMR (300 MHz, $CDCl_3$, δ): 8.60 (s, 1H), 8.06 (d, 1H), 7.86 (d, 1H), 7.42-7.44 (m, 1H), 7.38-7.40 (m, 2H), 7.20-7.23 (m, 1H), 4.22-4.36 (t, 2H), 1.82-1.86 (qt, 2H), 1.40 (s, 12H), 1.22-1.38 (m, 6H), 0.9 (t, 3H); $^{13}$C NMR (300MHz, $CDCl_3$, δ):13.93, 22.45, 24.88, 26.86, 28.82, 31.50, 43.00, 83.47, 108.01, 108.65, 119.11, 120.47, 122.54, 123.06, 125.51, 127.69, 132.09, 140.54, 142.54. ESI-MS:m/z $[M+H]^+$:338.

**1.14 9-hexyl-3-(2-(4-(9-hexyl-9H-carbazol-6-yl)pyridin-2-yl)pyridin-4-yl)-9H-carbazole (L5)** (73%). The synthesis method resembles that of compound **L1**. White powder of **L5** was obtained. $^{1}$H NMR (300 MHz, $CDCl_3$, δ): 8.84-8.86 (m, 2H), 8.78-8.82 (m, 2H), 8.58-8.60 (m, 2H), 8.20-8.22 (m, 2H), 7.96-7.98 (m, 2H), 7.72-7.76 (m, 2H), 7.50-7.56 (m, 4H), 7.44-7.48 (m, 2H), 7.28-7.32 (m, 2H), 4.36-4.40 (t, 4H), 1.88-1.96 (qt, 4H), 1.56-1.64 (m, 4H), 1.40-1.48 (m, 4H), 1.28-1.36 (m,

4H),0.9 (t, 6H); $^{13}$C NMR (300MHz, $CDCl_3$, δ): 13.99, 22.51, 26.94, 28.92, 31.54, 43.21, 108.92, 109.08, 119.05, 119.18, 119.22, 120.59, 121.54, 122.80, 123.41, 124.87, 126.03, 128.80, 140.89, 140.94, 149.50, 150.17, 156.71. ESI-MS:m/z $[M+H]^+$:656.

**1.15 General procedure for the synthesis of ruthenium complexes.** A solution of ligand **L1** – L5(0.121mmol) and dichloro(p-cymene)-ruthenium dimer (0.037 g, 0.060mmol) dissolved in dry DMF (100 mL) was heated at 60 °C for 4 h under a nitrogen atmosphere in the dark. Subsequently, 4,4′-dicarboxylic acid-2,2′-bipyridine (0.029 g, 0.121mmol) was added and the reaction mixture was heated to 140 °C for another 4 h. To the resulting dark green solution was added solid $NH_4NCS$ (0.276 g, 3.630mmol) and the reaction mixture was further heated for4 h at 140 °C. After completion of the reaction (monitored by absorption) the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure and water (200 mL) was added to get the precipitate. The purple solid was filtered off and washed with distilled water, ether and dried under vacuum. The crude compound was dissolved in methanol and further purified on sephadex LH-20 methanol as an eluent. The main band was collected and concentrated to give

**MC118** (65%). $^1$H NMR (300 MHz, $CDCl_3$+$CD_3OD$, δ):9.40-9.48 (m, 2H), 8.88-9.00 (m, 2H), 8.20-8.40 (m, 4H), 7.70-7.80 (m, 4H), 7.55-7.65 (m, 2H), 7.20-7.40 (m, 2H), 6.40-6.80 (m, 4H), 3.80-4.10 (m, 8H), 3.23-3.43 (m, 2H), 2.60-2.80 (m, 2H), 2.00-2.46 (m, 2H), 1.40-1.80 (m, 40H), 0.9 (t, 12H). FT-IR (KBr) ($cm^{-1}$): 3403, 2925, 2853, 2100, 1974, 1717, 1593, 1537, 1458, 1408, 1377, 1248, 1097, 1020. Anal. cal.: $C_{68}H_{88}N_6O_8RuS_2$. C: 66.37, H: 6.92, N: 6.55, S: 5.00 found: C: 66.30, H: 6.89, N: 6.50, S: 4.90%.

**MC120** (64%). $^1$H NMR (300 MHz, $CDCl_3$+$CD_3OD$, δ): 9.40-9.56 (m, 2H), 8.84-9.00 (m, 2H), 8.42-8.60 (m, 2H), 8.16-8.24 (m, 2H) 7.82-8.00 (m, 2H), 7.68-7.76 (m, 2H), 7.56-7.64 (m, 2H), 7.44-7.52 (m, 2H), 7.32-7.36 (m, 2H), 7.16-7.28 (m, 2H), 6.60-6.72 (m, 2H), 3.40 (t, 4H), 1.80-1.96 (m, 4H), 1.32-1.48 (m, 12H), 0.9 (t, 6H). FT-IR (KBr) ($cm^{-1}$): 3403, 2958, 2929, 2872, 2103, 1969, 1603, 1466, 1357, 1235, 1020. Anal. cal.: $C_{52}H_{50}N_8O_4RuS_2$. C: 63.54, H: 5.33, N: 11.03, S: 6.31 found: C: 63.50, H: 5.30, N: 11.00, S: 6.28 %.

**MC121** (63%). $^1$H NMR (300 MHz, $CDCl_3$+$CD_3OD$, δ): 9.40-9.52 (m, 2H), 8.84-9.00 (m, 2H), 8.52-8.60 (m, 2H), 8.36-8.44 (m, 2H) 8.16-8.24 (m, 2H), 7.88-7.96 (m, 2H), 7.64-7.72 (m, 2H), 7.54-7.60 (m, 2H), 7.44-7.52 (m, 2H), 4.00-4.16 (m,4H), 2.48-2.64 (m, 8H), 1.72-1.88 (m, 8H), 1.54-1.68 (m, 12H), 0.9 (t, 6H). FT-IR (KBr) ($cm^{-1}$): 3401, 2957, 2928, 2871, 2102, 1972, 1604, 1465, 1365. Anal. cal.: $C_{58}H_{58}N_8O_4RuS_2$. C: 63.54, H: 5.33, N: 10.22, S: 5.85 found: C: 63.50, H: 5.31, N: 10.20, S: 5.81%.

**MC122** (68%). $^1$H NMR (300 MHz, $CDCl_3$+$CD_3OD$, δ): 9.52-9.72 (m, 2H), 8.80-8.96 (m,2H), 8.48-8.64 (m, 2H), 8.20-8.28 (m, 1H), 8.04-8.08 (m, 2H), 7.92-8.00 (m, 2H), 7.80-7.88 (m, 4H), 7.72-7.79 (m, 2H), 7.62-7.68 (m, 3H), 7.56-7.60 (m, 2H), 7.44-7.52 (m, 4H), 1.96-2.16 (m, 8H), 1.04-1.16 (m,64H), 0.9 (t, 12H). FT-IR (KBr) ($cm^{-1}$): 3422, 2924, 2852, 2101, 1607, 1465, 1374, 1233, 1021. Anal. cal.: $C_{90}H_{112}N_6O_4RuS_2$. C: 71.73, H: 7.49, N: 5.58, S: 4.26 found: C: 71.70, H: 7.46, N: 5.56, S: 4.23%.

**MC123** (70%). $^1$H NMR (300 MHz, $CDCl_3$+$CD_3OD$, δ): 9.18-9.42 (m, 2H), 8.40-8.80 (m, 8H), 7.80-8.20 (m, 6H), 7.40-7.60 (m, 10H), 3.30-3.42 (m, 4H), 1.90-2.00 (m, 4H), 1.30-1.40 (m, 12H), 0.9 (t, 6H). FT-IR (KBr) ($cm^{-1}$): 3413, 2926, 2853, 2100, 1976, 1717, 1593, 1465, 1376, 1240, 1159, 1020. Anal. cal.: $C_{60}H_{54}N_8O_4RuS_2$. C: 64.56, H: 4.88, N: 10.04, S: 5.74 found: C: 64.52, H: 4.85, N: 10.01, S: 5.72%.

## 2. Synthesis of MC126 ruthenium complex

The synthetic procedure for the ruthenium complex is summarized in Scheme 3.

**2.1. Synthesis of 4-substituted-4'-bromobipyridine (1)** (55%)**.** To a degassed solution of 4,4'-dibromobipyridine (500 mg, 1.592 mmol) in DMF (10 mL) were added the corresponding hexylthiopheneboronic acid pinacol ester (1.592 mmol) dissolved in DMF (5 mL), $Pd(dppf)_2Cl_2$ (35 mg, 0.047 mmol), KOAc (1.56g, 15.92 mmol), KF (923 mg, 15.92 mmol) under argon atmosphere. The reaction mixture was heated at 85 °C for 7 h. The reaction mixture was filtered off and solvent

was removed under reduced pressure. The crude compound was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) to give 4-substituted-,4'-bromobipyridine.

$^{1}$H NMR (300 MHz, $CDCl_3$, δ ): 8.65 (s, 1H), 8.55-8.56 (m, 2H), 8.45-8.47 (d, 1H), 7.38-7.46 (m, 3H), 6.76-6.78 (d, 1H), 2.83 (t, 2H), 1.66-1.76 (m, 2H), 1.29-1.37 (m, 6h), 0.9 (t, 3H); $^{13}$CNMR (300MHz, $CDCl_3$, δ) 157.54, 155.11, 149.73, 149.58, 148.80, 142.87, 133.91, 126.92, 125.61, 125.55, 124.60, 119.79, 116.94, 31.49, 30.34, 29.67, 28.7122.51, 14.05, ESI-MS (m/z) calcd for 401, found 401$(M)^+$.

**2.2 Synthesis of 4-(4'-(5-hexylthiophen-2-yl)-[2,2'-bipyridin]-4-yl)benzaldehyde (2)** (73%)**.** A 50 mL of Schlenk tube was charged with aryl boronic acid (200mg, 1.33mmol), $Pd(PPh_3)_4$ (154 mg, 0.1 mmol). Dimethoxy ethane (8 mL) and 2 M aqueous sodium carbonate (2 mL)were added, and the tube was purged with argon gas with 5 evacuate /refill cycles. 4-bromo-4'-(5-hexylthiophen-2-yl)-2,2'-bipyridine (0.533 mg, 1.33 mmol) was subsequently added as a neat liquid. The tube was sealed and heated at 90 °C for 18 h. Upon cooling to ambient temperature, the organics were extracted into dichloromethane (3 × 30 mL) from 30 mL water. The combined organics were washed with water (1 × 30 mL) and brine (1 × 30 mL), dried over $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. The crude product was pre-adsorbed onto silica gel and chromatographed (9:1 hexane/ethyl acetate) to give unsymmetrically substituted bipyridine **2.**

$^{1}$H-NMR (300 MHz, $CDCl_3$, δ in ppm): 10.104 (s, 1H), 8.813(d, 1H), 8.727(s,1H), 8.646 (d, 2H), 8.033(dd, 2H), 7.948 (dd, 2H), 7.589 (d, 1H), 7.582 (d 1H), 7.492 (m, 2H), 7.263 (s, 1H), 2.863(t,2H), 1.406 (t,2H),1.334 (m, 6H), 0.904(t 3H).$^{13}$C NMR (300MHz, CDCl3 δ) 191.2, 155.9, 155.6, 149.4, 147.9, 144.8, 144.8, 143.2, 137.2, 135.7, 130,3, 128.1, 126.7, 125.7, 121.8, 121.3, 120.3, 113.1, 38.7, 32.3, 31.7, 28.6, 22.6, 14.3. ESI-MS (m/z) calcd for 426, found, 427 $(M+H)^+$. FT-IR (KBr) ($cm^{-1}$):472.99, 732.96, 803.21, 847.21, 895.81, 1103.73,1166.90,1262.15, 1362.61, 1458.14, 1540.95,1587.40,1687.87,2852.99, 2925.75.4

**2.3 Synthesis of 2-cyano-3-(4-(4'-(5-hexylthiophen-2-yl)-[2,2'-bipyridin]-4-yl)phenyl)acrylic acid (3).** Compound **2** (250 mg, 1mmol) and 2-cyanoacetic acid (128 mg, 1.5 mmol) were added to 15 mL of glacial acetic acid and refluxed for 3 h in the presence of 150 mg of ammonium acetate. After cooling to room temperature, the mixture was poured into ice water. The precipitate was filtered, washed by distilled water, dried under vacuum, and purified by column chromatography (acetate/ethanol), resulting in white ash colour of **3** (42.3%). FT-IR (KBr) ($cm^{-1}$):725.28, 824.11, 1195.46, 1374.23, 1468.81, 1592.08, 2219.73, 2854.54, 2926.87, 3394.12. ESI-MS (m/z) calcd for 494, found, 495 $(M+H)^+$. Anal Calcd for $C_{30}H_{27}N_3O_2S$, C, 70.17; H, 5.56; N, 8.64; S, 6.37 found C, 69.87; H, 5.39; N, 8.47; S, 6.26.

**2.4 General procedure for the synthesis of ruthenium complex.** A solution of ligand **3** (200 mg, 0.454 mmol) and dichloro(p-cymene)-ruthenium dimer (139 mg, 0.227 mmol) dissolved in dry DMF (200 mL) was heated at 60 °C for 4 h under nitrogen atmosphere in the dark. Subsequently, 4, 4'-dicarboxylic acid-2,2'-bipyridine (111 mg, 0.454 mmol) was added and the reaction mixture was heated to 140 °C for another 4 h. To the resulting dark green solution was added solid $NH_4NCS$ (1.038 g, 13.635 mmol) and the 3reaction mixture was further heated for 4 h at 140 °C. After completion of the reaction (monitored by absorption) the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure and water (200 mL) was added to get precipitate. The purple solid was filtered off and washed with distilled water, ether and dried under vacuum. The crude compound was dissolved in methanol and further purified on sephadex LH-20 methanol as eluent. The main band was collected and concentrated to give **MC**126.

**MC126** (65%). $^1$H-NMR (300 MHz, $CDCl_3$, δ in ppm): 9.43-9.37(m,1H), 9.30-9.28(d,1H), 9.13-9.28 (d, 1H), 8.8 (s,1H), 8.72-8.44 (m,3H), 8.18-8.08 (m, 2H), 7.99-7.96 (d, 2H),7.89-7.86 (m,1H), 7.75-7.70 (m, 2H), 7.63-7.58(m, 1H), 7.45-7.42(m, 1H), 7.35-7.16 (m, 2H), 7.01-6.83 (m, 2H), 2.92-2.75 (dt, 2H), 1.76-1.56 (dq, 2H), 1.38-117(m,6H),0.86-0.77(m,3H). ESI-MS (m/z) calcd for 955, found, 957 $(M+2H)^+$. Anal Calcd for $C_{44}H_{35}N_7O_6RuS_3$, C, 55.17; H, 3.74; N, 10.27; S,

10.57.found C, 54.92; H, 4.09; N, 9.98; S, 10.01.FT-IR (KBr) ($cm^{-1}$): 721.08, 808.56, 902.47, 1020.05, 1232.76, 1257.47, 1371.75, 1403.85, 1460.66, 1480.69, 1542.74, 1609.97, 1751.79, 1975.50, 2103.79, 2216.76, 2852.84, 2925.02, 3422.57.

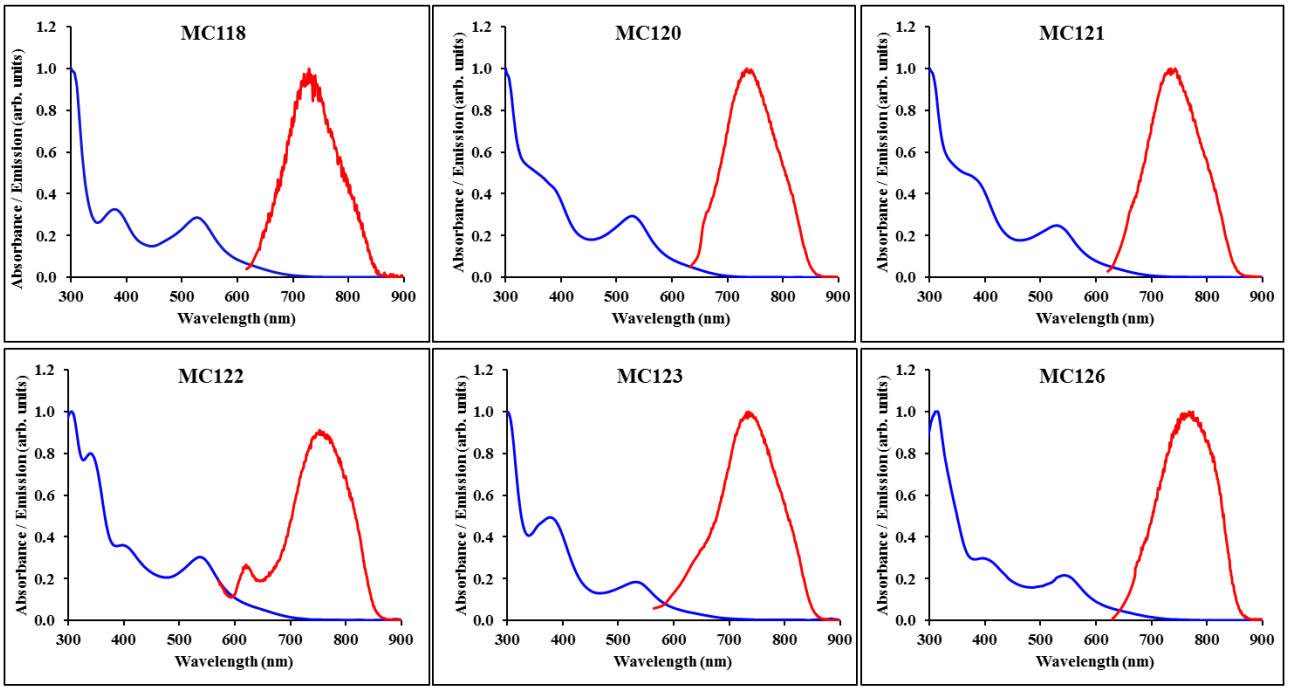


**Figure S1.** Absorption (blue line) and emission (red line) spectra for MC dyes in DMF solution.

**Table S1.** Calculated excitation energies for MC118 in DMF solution.

| N_state | E (eV) | WL (nm) | f | Composition (%) | |
|---|---|---|---|---|---|
| 1 | 2.12 | 585 | 0.04 | H → L | 91 |
| 2 | 2.25 | 550 | 0.02 | H → L+1 | 91 |
| 4 | 2.47 | 502 | 0.14 | H-2 → L | 74 |
| 6 | 2.66 | 466 | 0.06 | H-1 → L+1<br>H-2 → L+1 | 44<br>34 |
| 7 | 3.00 | 413 | 0.01 | H → L+3 | 81 |
| 8 | 3.02 | 411 | 0.10 | H→ L+2 | 87 |
| 9 | 3.17 | 391 | 0.03 | H-3 → L | 93 |
| 10 | 3.21 | 386 | 0.02 | H-1 → L+2 | 85 |
| 11 | 3.24 | 382 | 0.02 | H→ L+4 | 55 |
| 12 | 3.25 | 382 | 0.02 | H-1→ L+3<br>H→ L+4 | 60<br>32 |
| 13 | 3.27 | 379 | 0.03 | H-2→ L+2 | 69 |
| 14 | 3.29 | 376 | 0.06 | H→ L+5 | 47 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | H-2 → L+3 | 30 |
| 15 | 3.32 | 373 | 0.01 | H-2→ L+3 | 59 |
| 16 | 3.38 | 367 | 0.12 | H-4→ L | 62 |

**Table S2.** Calculated excitation energies for MC120 in DMF solution.

| **N_state** | **E (eV)** | **WL (nm)** | **f** | **Composition (%)** | |
|---|---|---|---|---|---|
| 1 | 2.08 | 595 | 0.04 | H → L | 92 |
| 2 | 2.25 | 550 | 0.02 | H → L+1 | 82 |
| 4 | 2.42 | 512 | 0.17 | H-2 → L | 80 |
| 5 | 2.48 | 499 | 0.01 | H-2 → L+1<br>H-3 → L+1 | 60<br>34 |
| 6 | 2.65 | 468 | 0.07 | H-2 → L+1<br>H-1 → L+1 | 54<br>27 |
| 7 | 2.97 | 417 | 0.03 | H→ L+2 | 94 |
| 8 | 3.04 | 407 | 0.04 | H-3 → L | 97 |
| 9 | 3.07 | 404 | 0.04 | H-4 → L | 97 |
| 10 | 3.11 | 398 | 0.09 | H→ L+3 | 82 |
| 11 | 3.17 | 391 | 0.03 | H-5→ L | 90 |

**Table S3.** Calculated excitation energies for MC121 in DMF solution.

| **N_state** | **E (eV)** | **WL (nm)** | **f** | **Composition (%)** | |
|---|---|---|---|---|---|
| 1 | 2.09 | 592 | 0.05 | H → L | 92 |
| 2 | 2.25 | 551 | 0.02 | H → L+1 | 89 |
| 4 | 2.43 | 510 | 0.18 | H-2 → L<br>H-1 → L | 45<br>25 |
| 5 | 2.48 | 501 | 0.01 | H-1 → L+1 | 76 |
| 6 | 2.65 | 468 | 0.06 | H-2 → L+1 | 69 |
| 7 | 2.73 | 454 | 0.01 | H-3 → L | 97 |
| 9 | 2.97 | 417 | 0.04 | H → L+2 | 94 |
| 12 | 3.12 | 397 | 0.10 | H → L+3 | 83 |
| 13 | 3.18 | 390 | 0.06 | H-5→ L | 92 |

**Table S4.** Calculated excitation energies for MC122 in DMF solution.

| **N_state** | **E (eV)** | **WL (nm)** | **f** | **Composition (%)** | |
|---|---|---|---|---|---|
| 1 | 2.01 | 618 | 0.06 | H → L | 92 |
| 3 | 2.26 | 548 | 0.03 | H → L+1 | 89 |
| 4 | 2.37 | 523 | 0.16 | H-2 → L | 85 |
| 6 | 2.65 | 467 | 0.09 | H-1 → L+1<br>H-2 → L+1 | 44<br>39 |
| 7 | 2.85 | 435 | 0.18 | H → L+2 | 79 |
| 8 | 2.91 | 426 | 0.04 | H → L+4 | 77 |
| 9 | 3.06 | 406 | 0.02 | H-1 → L+3 | 72 |

| | | | | | |
|---|---|---|---|---|---|
| 10 | 3.07 | 404 | 0.06 | H-3 → L+1 | 83 |
| 11 | 3.09 | 401 | 0.03 | H-2→ L+2 | 81 |
| 13 | 3.20 | 388 | 0.23 | H-2→ L+3 | 90 |

**Table S5.** Calculated excitation energies for MC123 in DMF solution.

| **N_state** | **E (eV)** | **WL (nm)** | **f** | **Composition (%)** | |
|---|---|---|---|---|---|
| 1 | 2.06 | 601 | 0.05 | H → L | 91 |
| 2 | 2.25 | 550 | 0.02 | H → L+1 | 87 |
| 4 | 2.41 | 515 | 0.19 | H-2 → L<br>H-1 → L | 63<br>20 |
| 6 | 2.65 | 467 | 0.07 | H-1 → L+1<br>H-2 → L+1 | 44<br>39 |
| 7 | 2.94 | 421 | 0.02 | H → L+2<br>H-3 → L | 55<br>35 |
| 8 | 2.95 | 420 | 0.16 | H-3 → L<br>H → L+2 | 61<br>35 |
| 9 | 2.99 | 415 | 0.12 | H-4 → L | 96 |
| 10 | 3.07 | 404 | 0.12 | H → L+3 | 82 |

**Table S6.** Calculated excitation energies for MC126A in DMF solution.

| **N_state** | **E (eV)** | **WL (nm)** | **f** | **Composition (%)** | |
|---|---|---|---|---|---|
| 1 | 1.95 | 637 | 0.06 | H → L | 82 |
| 3 | 2.26 | 549 | 0.18 | H-1 → L<br>H-2→ L<br>H→ L+1 | 38<br>33<br>16 |
| 4 | 2.33 | 531 | 0.03 | H → L+2 | 75 |
| 5 | 2.51 | 494 | 0.02 | H-1→ L+2 | 86 |
| 6 | 2.54 | 489 | 0.12 | H → L+1 | 75 |
| 7 | 2.68 | 463 | 0.13 | H-2→ L+2 | 77 |
| 8 | 2.75 | 451 | 0.02 | H-1 → L+1 | 78 |
| 9 | 2.79 | 444 | 0.01 | H-2 → L+1 | 88 |
| 10 | 2.85 | 435 | 0.01 | H→ L+3 | 92 |
| 11 | 2.96 | 419 | 0.03 | H-3→ L | 94 |
| 12 | 3.06 | 405 | 0.05 | H-1→ L+3 | 87 |
| 14 | 3.13 | 385 | 0.18 | H-4→ L | 77 |

**Table S7.**Calculated HOMOs and LUMOs energies (eV) of the MC sensitizers in DMF solution.

| | MC118 | MC120 | MC121 | MC122 | MC123 | MC126 |
|---|---|---|---|---|---|---|
| **L+2** | -1.60 | -1.58 | -1.57 | -1.86 | -1.61 | -2.18 |
| **L+1** | -2.19 | -2.19 | -2.18 | -2.20 | -2.19 | -2.23 |
| **L** | -2.34 | -2.38 | -2.36 | -2.50 | -2.40 | -2.64 |
| **H** | -5.19 | -5.19 | -5.18 | -5.21 | -5.19 | -5.23 |
| **H-1** | -5.44 | -5.43 | -5.42 | -5.47 | -5.43 | -5.44 |
| **H-2** | -5.51 | -5.47 | -5.47 | -5.51 | -5.46 | -5.49 |
| **H-L Gap** | 2.85 | 2.81 | 2.82 | 2.71 | 2.79 | 2.59 |

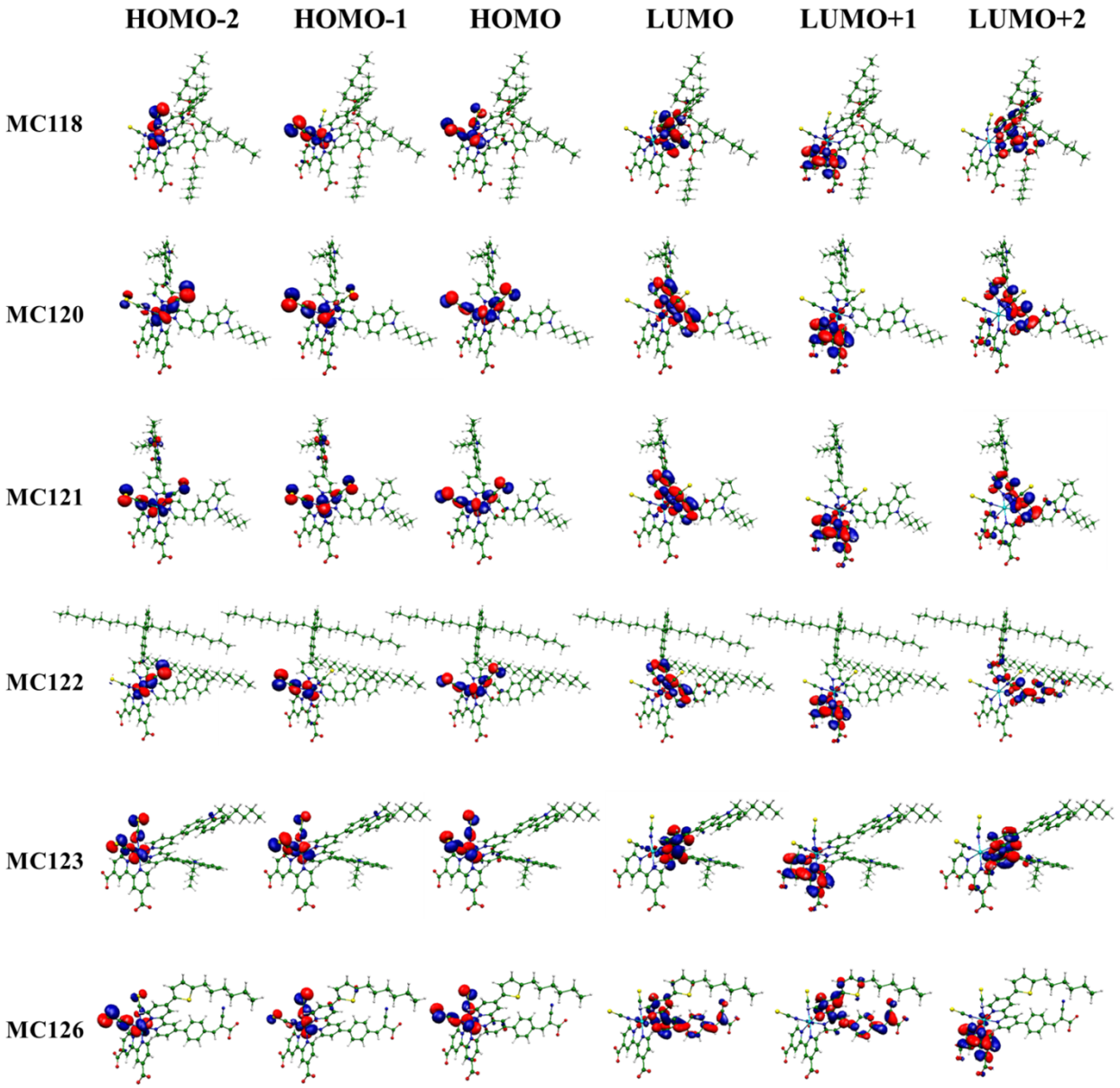


**Figure S2.** Isodensity surface plots (isodensity contour: 0.035) of the most relevant molecular orbitals for the investigated MC dyes.

**Table S8.** Dye loading measurement for the new heteroleptic dyes. The evaluation was made without using the chenodeoxycholic acid coadsorbent.

| | **Dye Loading ($*10^{-7}$ mol/cm$^2$)** |
|---|---|
| **MC118** | 0.86 |
| **MC120** | 1.43 |
| **MC121** | 1.28 |
| **MC122** | 1.32 |
| **MC123** | 1.51 |
| **MC126** | 1.36 |