Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Design and Synthesis of New Ruthenium Complex for Dye-Sensitized Solar Cells

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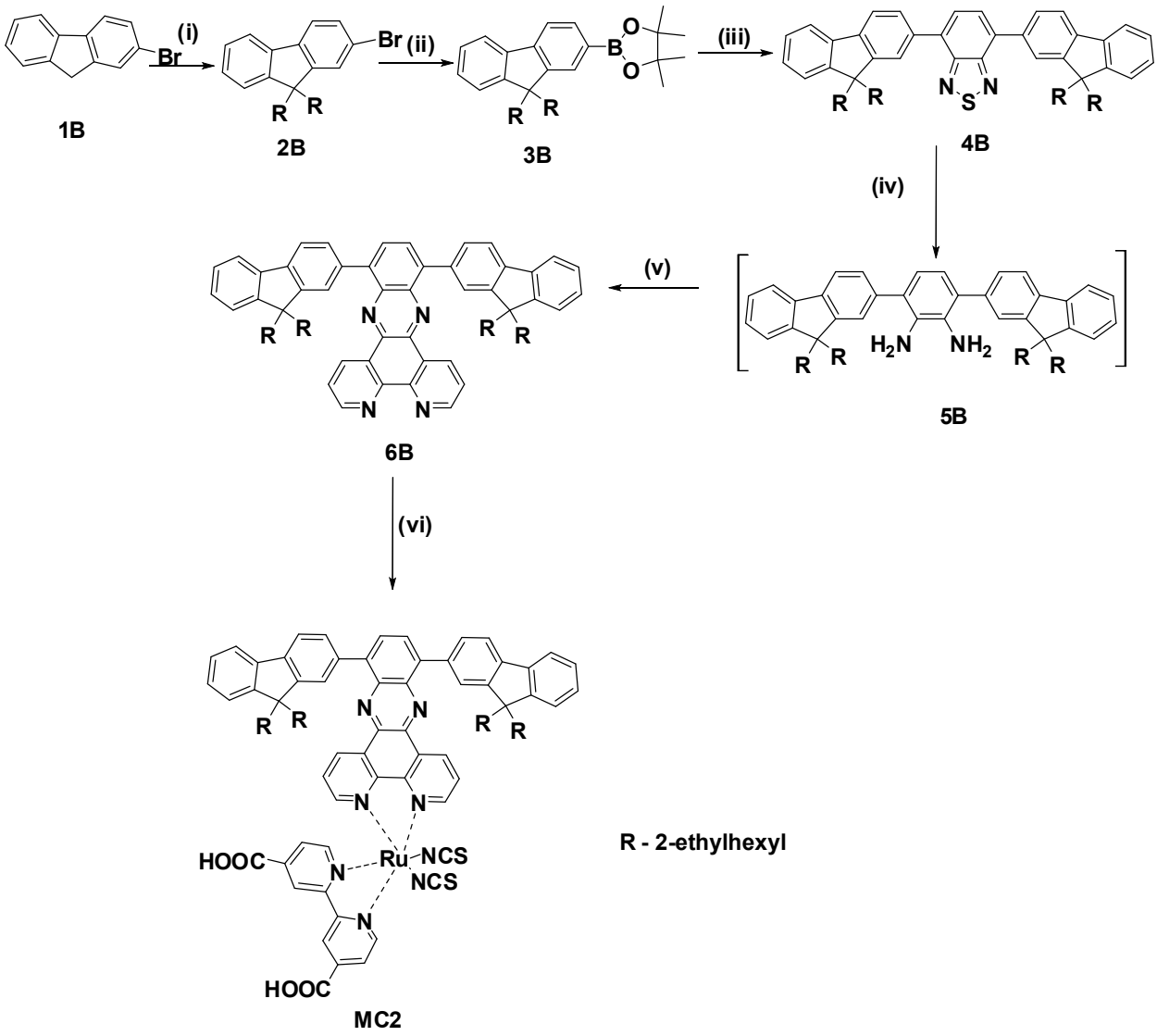
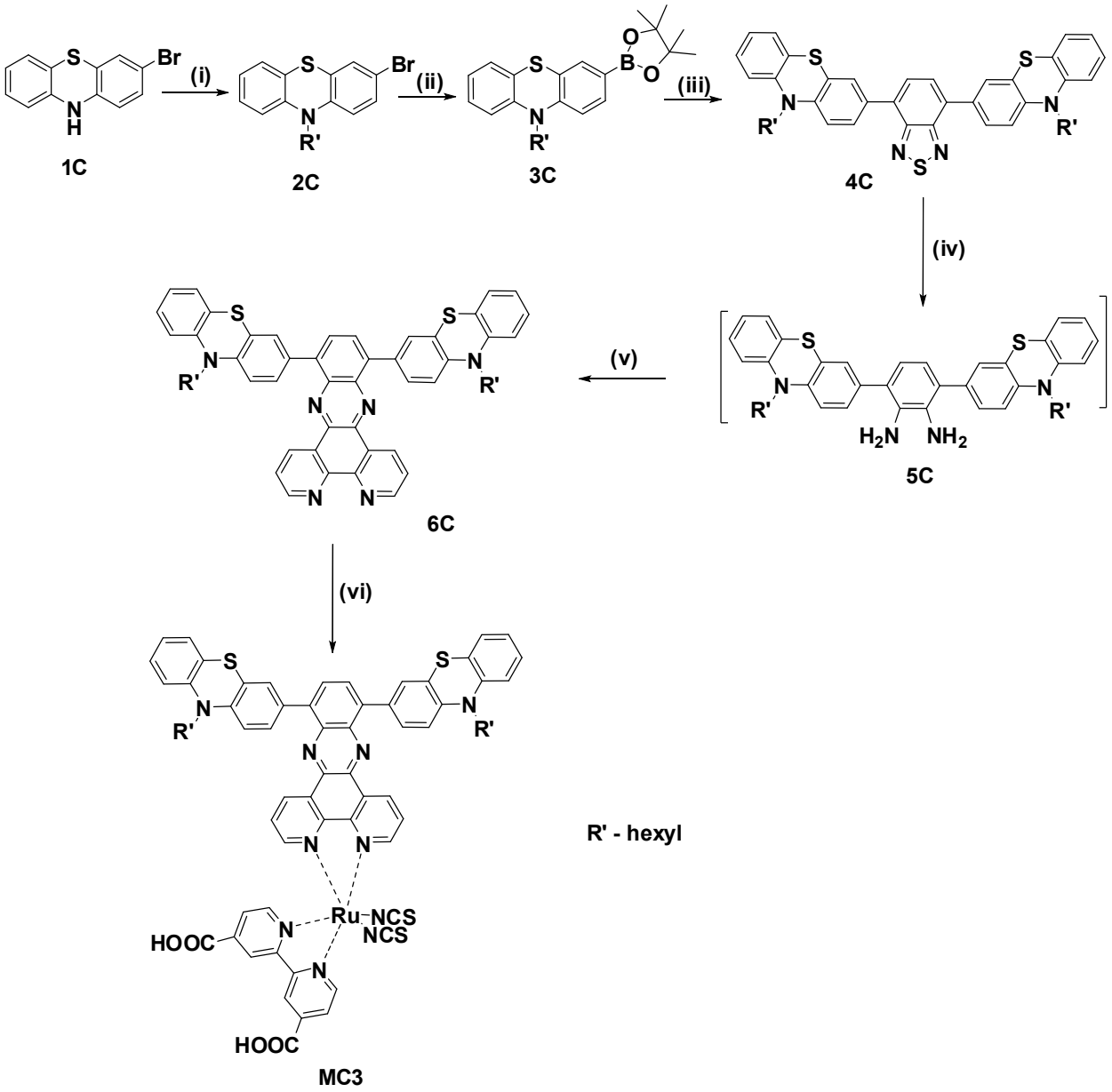
Scheme 2 and Scheme 3



Scheme 2. Synthetic route for MC2; (I) KOH, RBr, DMF, room temperature, 12h; (ii) Bis(pinacolato)diboron, CH_3COOK, $Pd(dppf)Cl_2.CH_2Cl_2$, 1,4-dioxane, 80 ^oC, 18h, (iii) 4,7-dibromo-2,1,3-benzothiadiazole, K_2CO_3, $Pd(PPh_3)_4$, $THF:H_2O$, reflux, 24 h; (iv) Zn, acetic acid, 70 ^oC, 6h; (v) 1,10-phenanthroline-5,6-dione, acetic acid, 70 ^oC, 12 h, (vi) Dichloro(p-cymene)ruthenium(II) dimer, 2,2'-bipyridine-4,4'-dicarboxylic acid, NH_4NCS, DMF, reflux.



Scheme 3. Synthetic route for MC3; (I) KOH, RBr, DMF, room temperature, 12h; (ii) Bis(pinacolato)diboron, CH_3COOK, $Pd(dppf)Cl_2.CH_2Cl_2$, 1,4-dioxane, 80 ^oC, 18h, (iii) 4,7-dibromo-2,1,3-benzothiadiazole, K_2CO_3, $Pd(PPh_3)_4$, THF:H_2O, reflux, 24 h; (iv) Zn, acetic acid, 70 ^oC, 6h; (v) 1,10-phenanthroline-5,6-dione, acetic acid, 70 ^oC, 12 h, (vi) Dichloro(p-cymene)ruthenium(II) dimer, 2,2'-bipyridine-4,4'-dicarboxylic acid, NH_4NCS, DMF, reflux.

1.1 Synthetic procedures and characterization data

Synthesis of compound 2A[26]

To a stirred solution of 3-bromocarbazole 1A (1 g, 4.06 mmol) in N,N-dimethylformamide (10 mL), anhydrous potassium hydroxide (0.34 g, 6.1 mmol) was added at 0 ºC under inert atmosphere and stirred for 15 min. Further, 2-ethylhexyl bromide (0.87 ml, 4.87 mmol) was added to the reaction mixture and stirred at room temperature for about 12 h, poured into ice water and extracted with ethyl acetate. The organic layer was washed with water three times, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified using silica gel column chromatography with hexane as eluent (1.2 g, yield 82 %).

Compound 2A: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): ^{1}H NMR ($CDCl_3$, 300 MHz): 8.25 (d, 1H), 7.58 (d, 1H), 7.52 (d, 1H), 7.44 (d, 1H), 7.32 (d, 2H) 7.27 (d, 1H), 4.32 (d, 2H), 2.0 (m, 1H), 1.35–1.28 (m, 8H), 0.86 (t, 6H).

Compound 2B: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.64 (d, 1H), 7.54 (d, 1H), 7.50 (t, 1H), 7.43 (d, 1H), 7.34 (t, 1H), 7.29 (t, 2H), 1.96 (t, 4H), 0.93–0.66 (m, 16H), 0.7 (t, 2H), 0.49 (t, 12H).

Compound 2C: ^{1}H NMR (DMSO-d_6, 300 MHz): 7.30 (d, 2H), 7.24–7.12 (m, 2H), 7.01–6.9 (m, 3H), 3.81 (t, 2H), 1.69 (q, 2H), 1.39–1.21 (m, 6H), 0.8 (t, 3H).

Synthesis of compound 3A[26]

Compound 2A (1.2 g, 3.33 mmol), potassium acetate (0.81 g, 8.33 mmol) and bis(pinacolato)diboron (1.26 g, 5 mmol) were dissolved in 1,4-dioxane (15 ml), purged with nitrogen gas for 20 min and catalyst Pd(dppf)Cl_2.CH_2Cl_2 (73 mg, 3 mol%) was added under inert atmosphere. The reaction mixture was stirred at 80 ºC for 18 h, cooled to room temperature, poured into ice water and extracted with dichloromethane. Organic layer was washed with water (3 x 25 ml), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography using hexane : ethyl acetate (95 : 5) as eluent to obtain pure compound 3A, a colorless liquid (0.97 g, yield 72 %).

Compound 3A: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.67 (s, 1H), 8.13 (d, 1H), 7.91 (d, 1H), 7.42 (d, 1H), 7.37 (s, 2H) 7.22 (d, 2H), 4.22 (d, 2H), 2.01 (m, 1H), 1.40 (s, 12 H), 1.37–1.26 (m, 8H), 0.88 (t, 6H). MS (EI): (M_w = 405.3) found m/z = 405.5 [M+]

Compound 3B: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.81 (d, 1H), 7.75 (d, 1H), 7.67 (t, 2H), 7.33 (d, 1H), 7.23 (t, 2H), 2.01 (t, 4H), 1.33 (s, 12H), 0.84–0.69 (m, 16H), 0.65 (t, 2H), 0.47 (t, 12H). MS (ESI): (M_w = 516.5) found m/z= 516.5 [M+]

Compound 3C: ^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 7.58 (d, 2H), 7.05 (d, 2H), 6.86–6.77 (m, 3H), 3.72 (t, 2H), 1.73 (q, 2H), 1.45–1.22 (m, 6H), 1.23 (s, 12H), 0.84 (t, 3H). MS (ESI): (M_w = 409.3) found m/z = 409.3 [M+]

Synthesis of compound 4A[27]

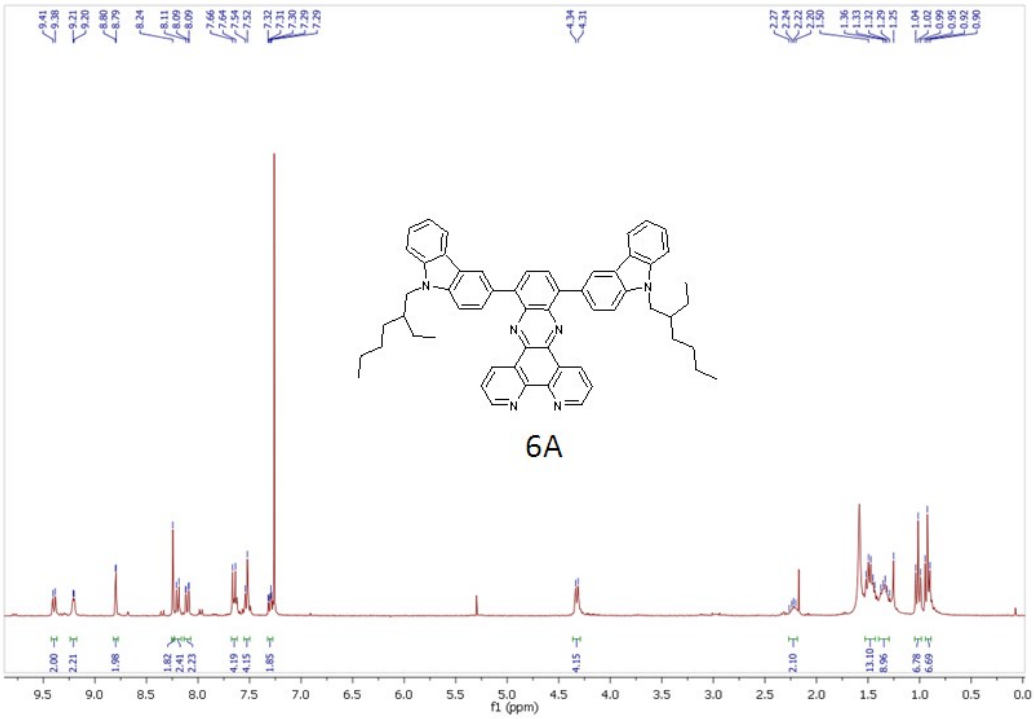
To a solution of compound 3A (0.8 g, 1.97 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.29 g, 0.98 mmol) in dry THF (10 ml), potassium carbonate (0.54 g, 3.92 mmol) dissolved in water (3 ml) was added, purged with nitrogen gas for 20 min, followed by the addition of catalyst $Pd(PPh_3)_4$ (80 mg, 7 mol%). The reaction mixture was refluxed for 24 h under nitrogen atmosphere, cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with water (3 x 25 ml), dried over anhydrous $Na_2SO_4$and concentrated. The crude product was purified by silica gel column chromatography using hexane : ethyl acetate(98 : 2) as eluent to obtain compound 4A as a red solid (0.89 g, yield 65 %).

Compound 4A: ^{1}H NMR ($CDCl_3$, 300 MHz): 8.71 (d, 2H), 8.21 (d, 2H), 8.14 (d, 2H), 7.94 (s, 2H), 7.57 (d, 2H), 7.5–7.43 (m, 6H), 4.25 (d, 4H), 2.1 (m, 2H), 1.44–1.25 (m, 16H), 0.9 (t, 12H). MS (ESI): (M_w = 690.9) found m/z = 690.5 [M+].

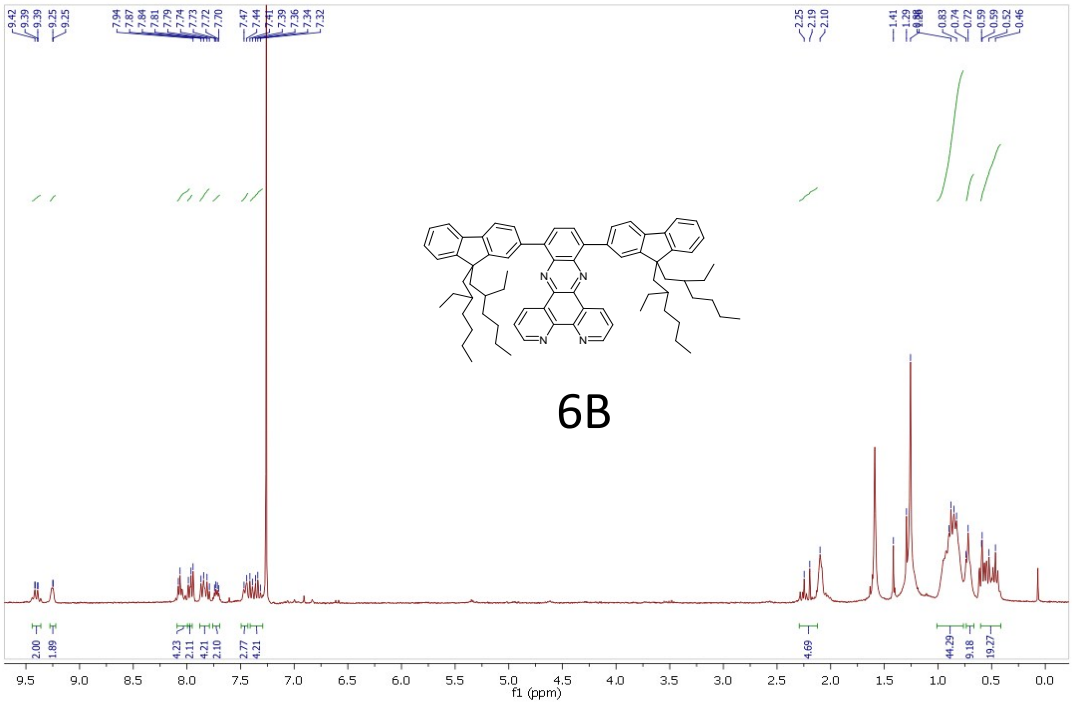
Compound 4B: ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.03 (d, 4H), 7.86 (d, 4H), 7.77 (d, 2H), 7.44 (d, 2H), 7.39–7.26 (m, 4H), 2.15 (t, 8H), 0.91–0.78 (m, 32H), 0.7 (t, 4H), 0.57 (t, 24H). MS (EI): (M_w = 913.4) found m/z = 913.7 [M+].

Compound 4C: ^{1}H NMR (DMSO-d_6, 300 MHz, δ ppm): 7.86–7.83 (m, 6H), 7.24 (t, 2H), 7.16 (q, 4H), 7.05 (d, 2H), 6.96 (t, 2H), 3.92 (t, 4H), 1.72 (q, 4H), 1.4 (q, 4H), 1.26–1.22 (m, 8H), 0.82 (t, 6H). MS (EI): (M_w = 699) found m/z = 698.4.

1.2 Appendix: NMR and Mass spectra of compounds



6A



6B

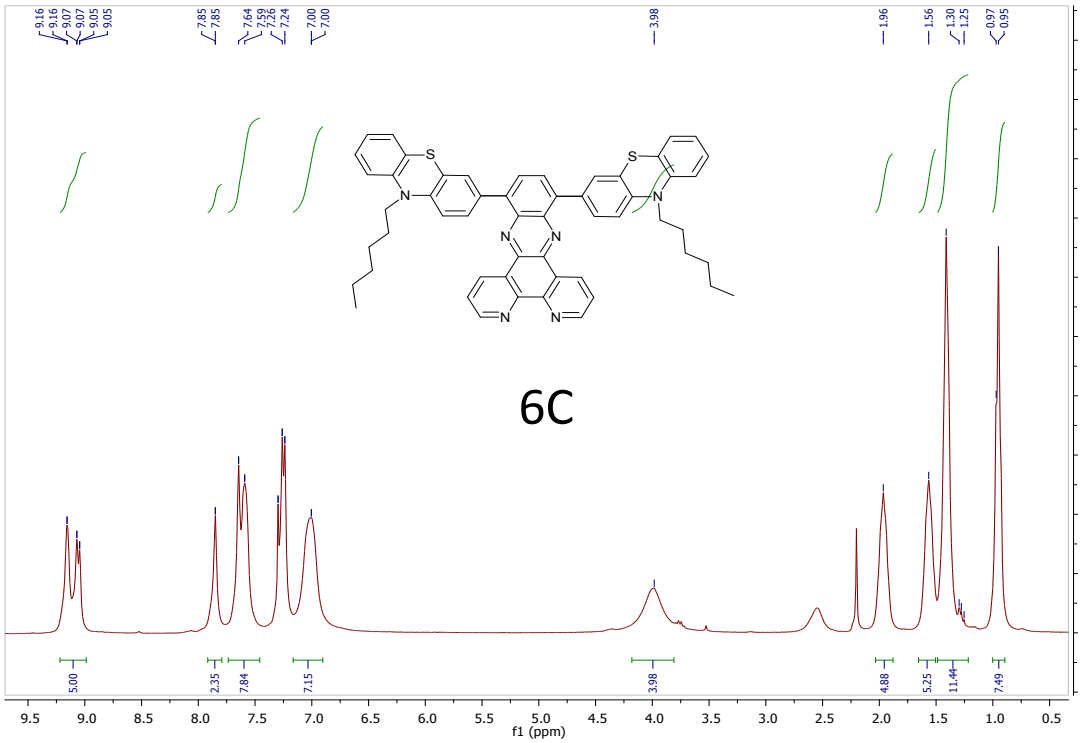
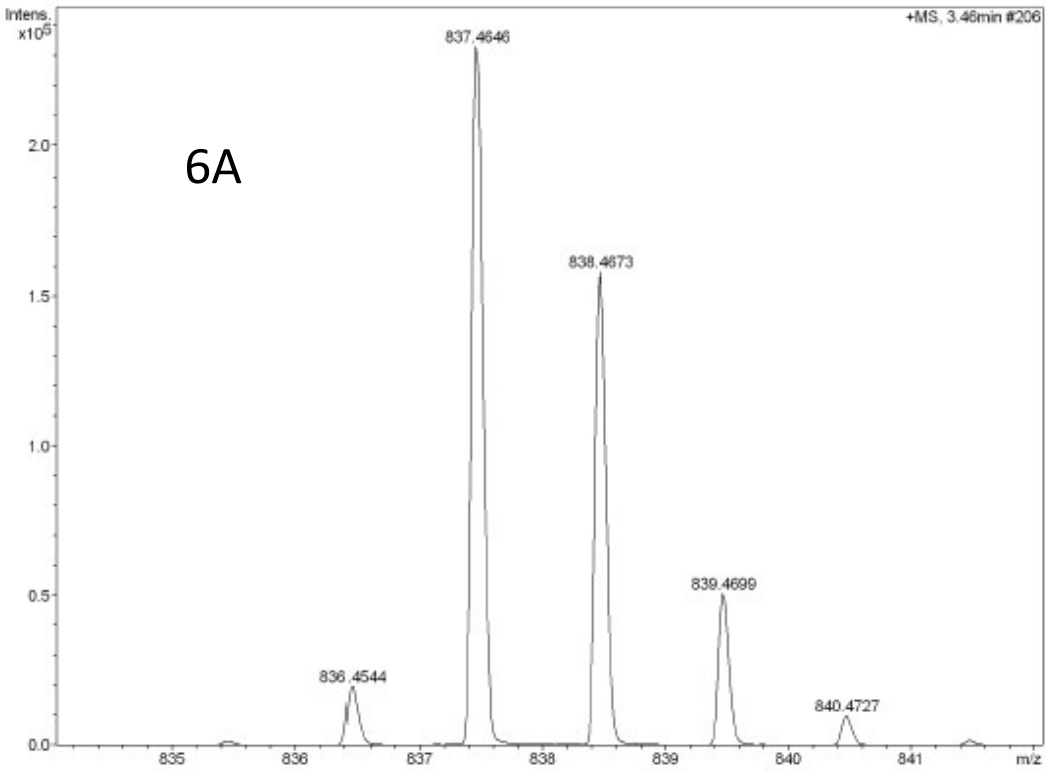


Figure S1 ^{1}H NMR spectra of ligands, 6A – 6C



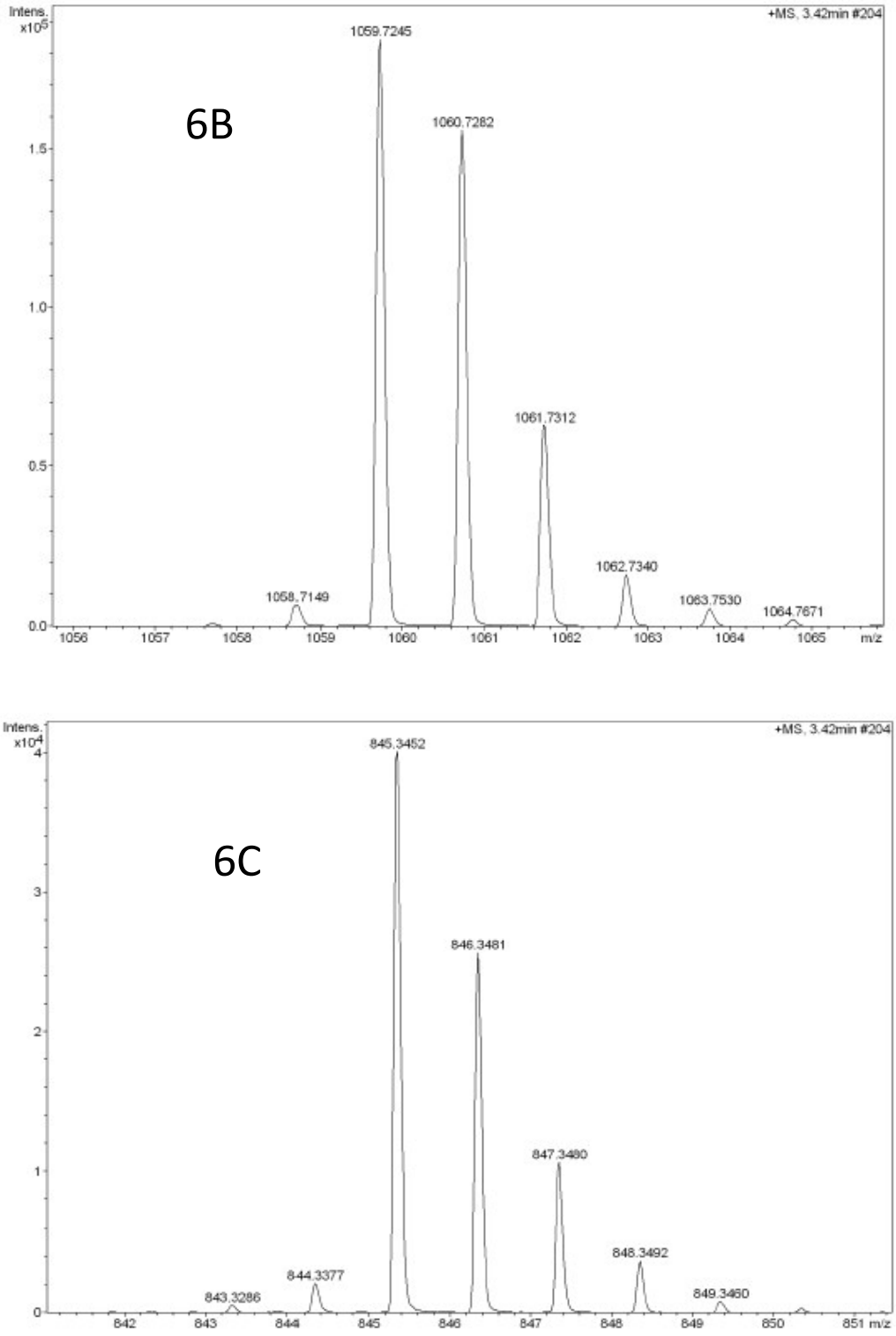
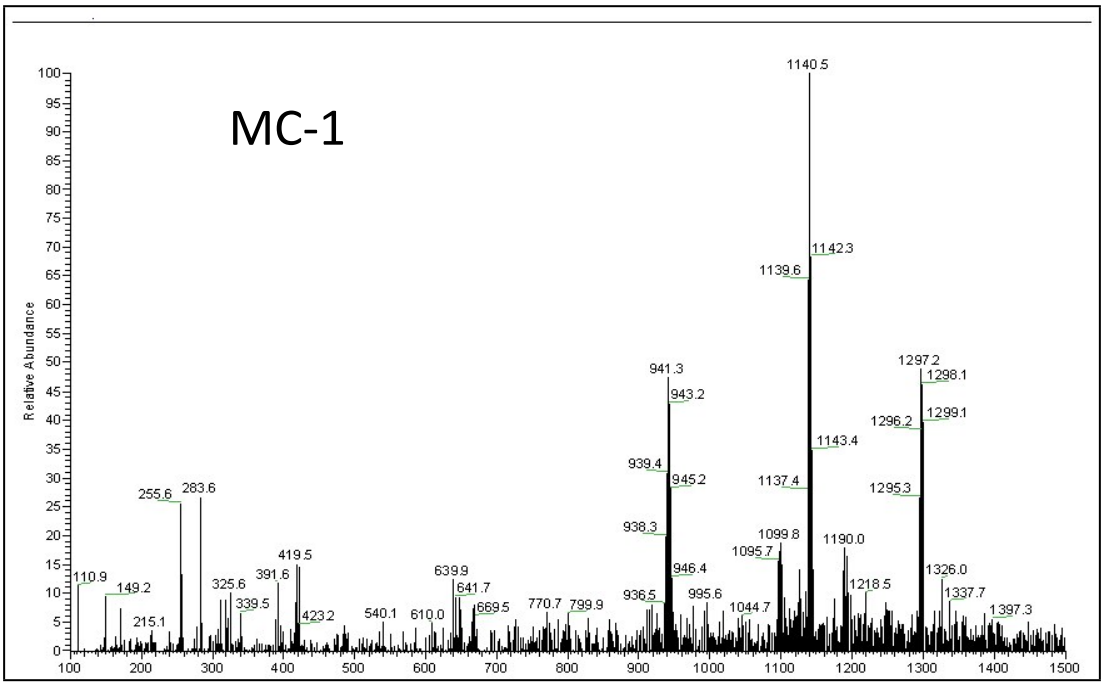
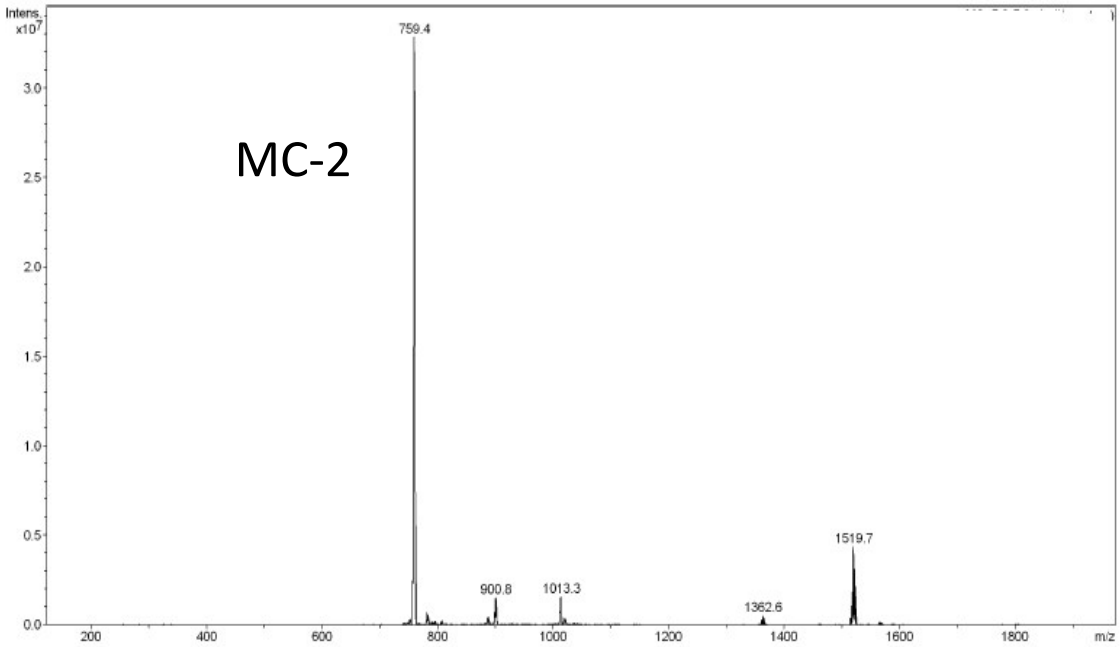


Figure S2 HR mass spectra of ligands, 6A – 6C


MC-1
Relative Abundance
1140.5
1142.3
1139.6
941.3
943.2
1297.2
1298.1
1296.2
1299.1
1143.4
939.4
945.2
1137.4
1295.3
938.3
1099.8
1095.7
1190.0
946.4
1326.0
1218.5
255.6
283.6
419.5
391.6
325.6
339.5
110.9
149.2
215.1
423.2
639.9
641.7
669.5
540.1
610.0
770.7
799.9
936.5
995.6
1044.7
1337.7
1397.3


MC-2
759.4
1519.7
900.8
1013.3
1362.6
m/z

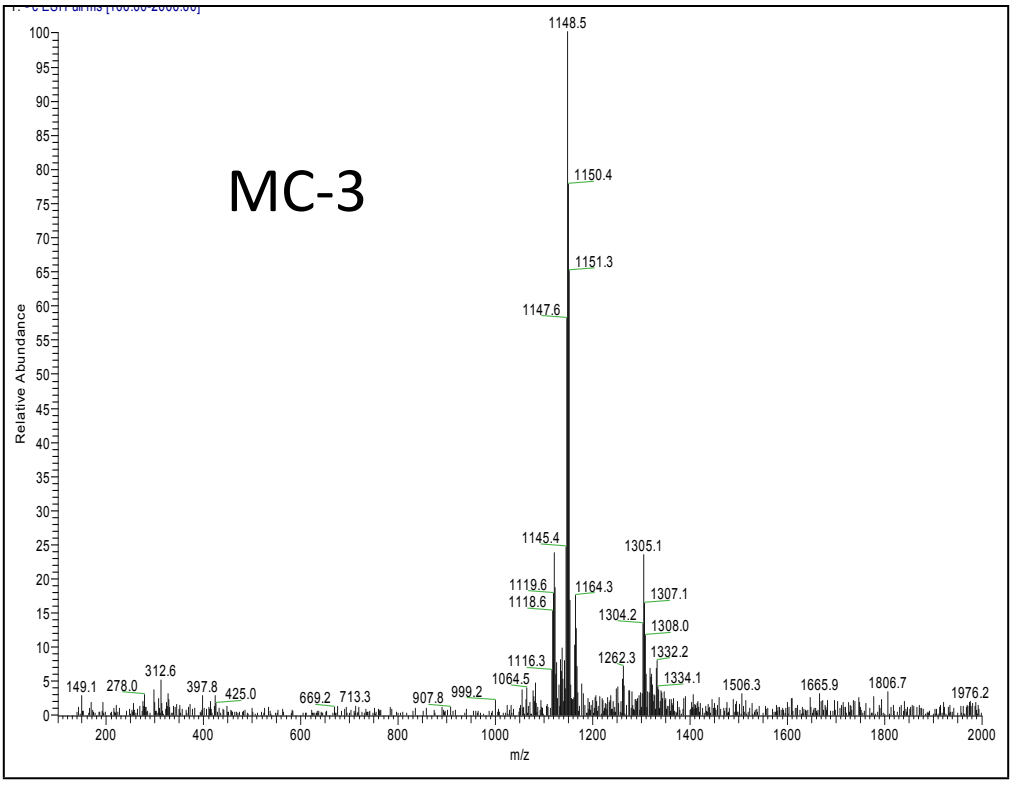


Figure S3 Mass spectra of MC1 – MC3

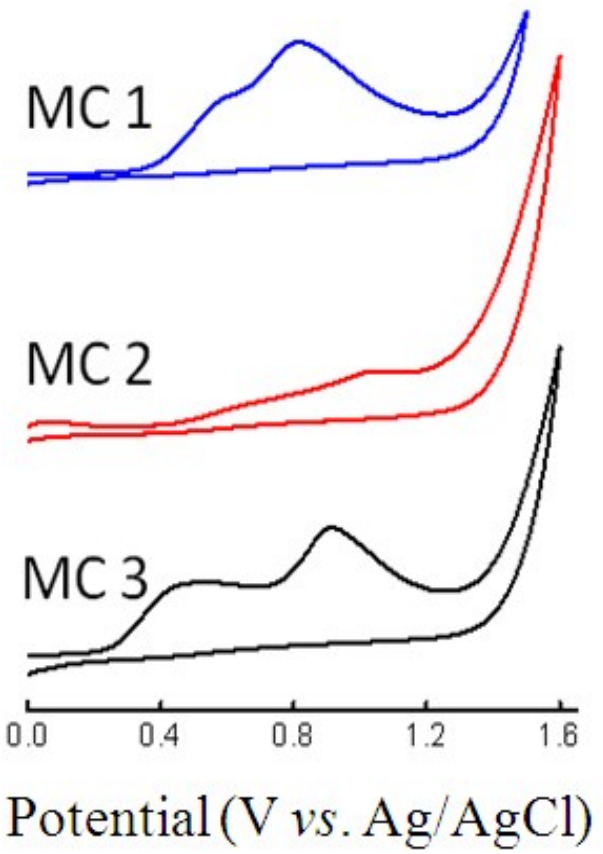


Figure S4 Cyclic voltammogram of MC1 – MC3 on TiO_2 film

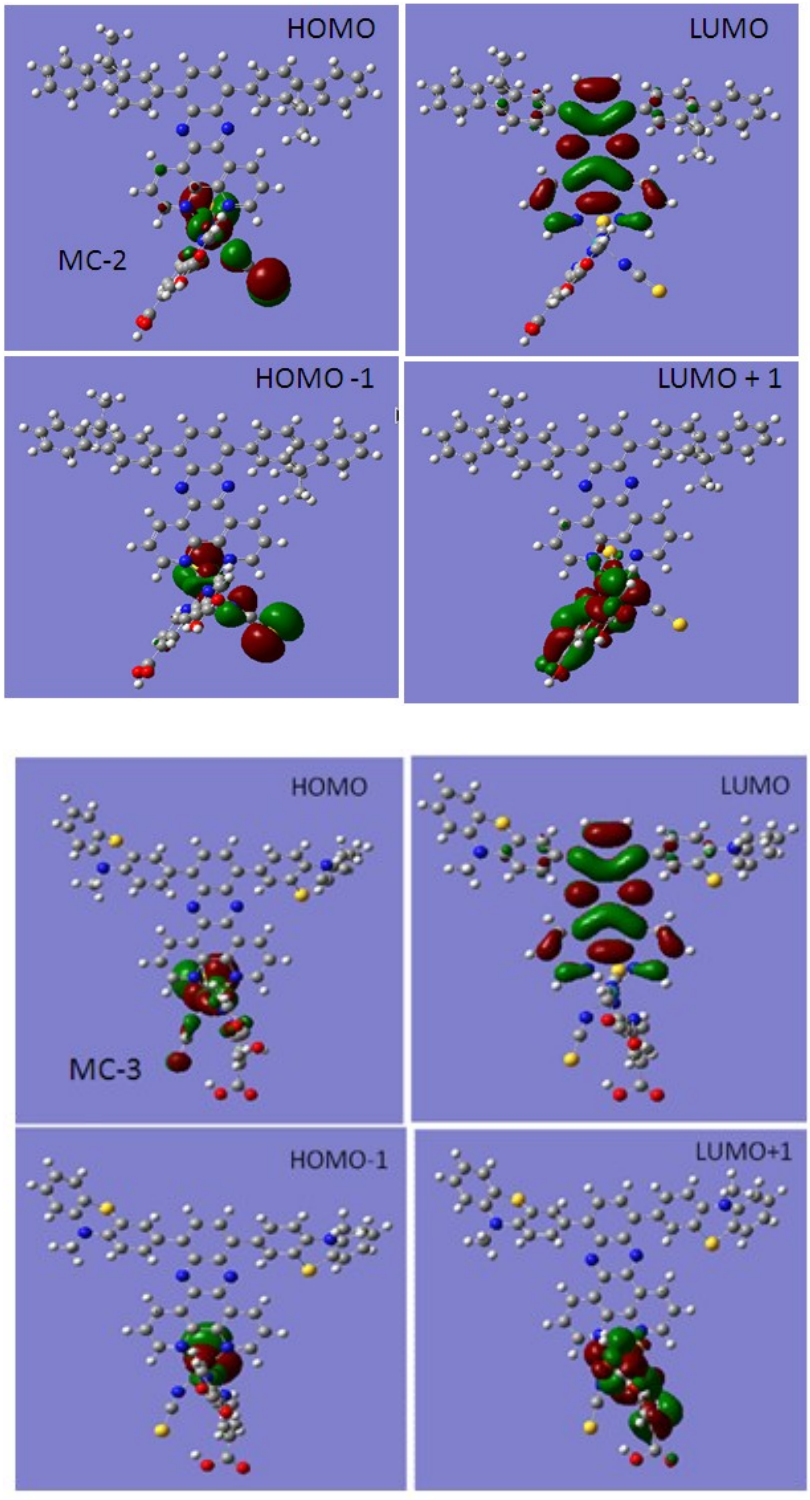


Figure S5 Graphical representation of the frontier orbitals of MC–2 and MC–3 calculated at the B3LYP/6-31G (d,p) level of theory. Atoms in red, yellow, brown, blue, and gray correspond to oxygen, sulfur, carbon, nitrogen, and ruthenium, respectively