Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information for:

Slow Excited State Injection and Charge Recombination at Star-Shaped Ruthenium Polypyridyl Compounds - TiO_2 Interfaces

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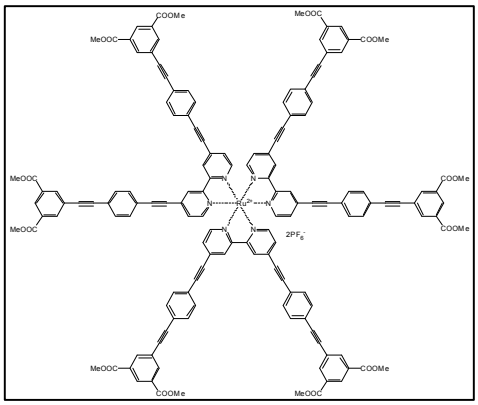
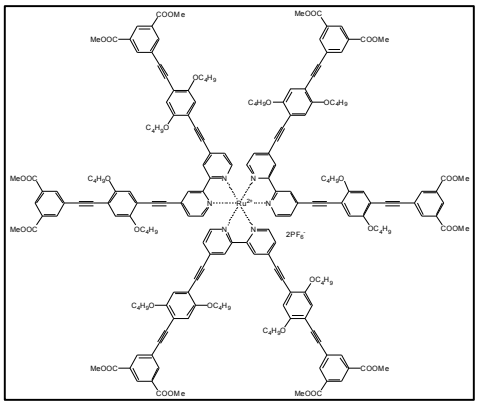
Synthesis and Characterization of Star Compounds



Homoleptic ruthenium compound Star (1). A flame-dried round bottom flask was charged with ruthenium tris(4,4'-dibromo-2,2'-bipyridine) (50 mg, MW 1333, 0.038 mmol), benzene (2.5 mL), diisopropylamine (2 mL), THF (4 mL), dimethyl 5-((4-ethynylphenyl) ethynyl) isophthalate (**17**, 180 mg, MW 390, 0.460 mmol), and $Pd(PPh_3)_4$ (5 mg, MW 1156, 0.004 mmol). The reaction mixture was stirred at 80°C under nitrogen atmosphere for 4 days and monitored with TLC. After it cooled to room temperature, the reaction mixture was filtered, and the solvent was removed *in vacuum*. The crude product was purified by silica gel column chromatography (acetonitrile:H_2O = 85:15) to remove any unreacted starting material. The last band of silica gel was isolated, concentrated, and triturated with THF and acetone to give an orange-red powder (**Star** 30 mg, Mw 2757). Yield: 30%. ^{1}H NMR (THF)-d_8: δ 8.92(s, 6H), δ 8.60 (broad, 6H), δ 8.36 (s, 12H), δ 8.04-8.06 (m, 6H), δ 7.67 (broad, 30H), δ 3.93 (s, 36H) ppm. MS (ESI) calcd for $C_{150}H_{96}N_6O_{24}Ru^{2+}$: 2466.55. Found: 2466.58. The ^{13}C is not available due to the low solubility. IR-ATR (cm^{-1}):

2956 (*C-H*$_{Ar}$), 2858 (*C-H*$_{CH3}$), 2216 (*C*≡*C*), 1724 (*C*=*O*), 1600 (*C*=*C*$_{Ar}$), 1508, 1459, 1438, 1378, 1351, 1247 (*C-O*), 1120, 1070, 1039, 993, 912, 837 (*C-H*$_{Ar}$).

Homoleptic ruthenium compound Star n—BuO (2). $Ru(DMSO)_4(PF_6)_2$ (12 mg, MW 703, 0.017 mmol), Tetramethyl 5,5'-((([2,2'-bipyridine]-4,4'-diylbis(ethyne-2,1-diyl))bis(2,5-dibutoxy-4,1-phenylene))bis (ethyne-2,1-diyl))diisophthalate (63 mg, Mw 1077, 0.058 mmol), THF (4 mL), and nitrogen-purged 1-butanol (4 mL) were



added into a round bottom flask, and the reaction mixture was heated to reflux under nitrogen atmosphere. Every 24 hours, the reaction mixture was monitored by UV-Vis spectroscopy until the reaction completed. The reaction mixture was cooled to room temperature and filtered. The crude product, a brown powder, was rinsed with acetone and filtered. The filtrate was condensed by in vacuum and an orange-red powder (**Star nBuO (2)**, 20 mg, MW 3597) was precipitated by addition of hexane. Yield: 34%. ^{1}H NMR (acetone)-d_6: δ 8.98-9.02 (broad, 6H), δ 8.56(s, 6H), δ 8.30(broad, 18H), δ 7.65-7.66 (broad, 6H), δ 7.35 (broad, 6H), δ 7.24-7.25 (broad, 6H), δ 4.14-4.18 (broad, 24H), δ 3.97 (s, 36H), δ 1.85-1.86 (m, 24H), δ 1.59-1.66 (m, 24H), δ 1.01-1.07 (m, 36H) ppm. ^{13}C NMR (acetone)-d_6: δ 164.84, 157.02, 154.43, 153.91, 152.13, 135.67, 133.26, 131.57, 129.68, 129.10, 126.19, 124.26, 117.14, 117.02, 115.49, 112.09, 95.45, 93.33, 90.78, 87.61, 69.28, 69.07, 52.09, 31.31, 31.14, 19.19, 19.05, 13.32, 13.28. MS (ESI) calcd for $C_{198}H_{192}N_6O_{36}Ru^{2+}$: 3331.24. Found: 3331.27. IR-ATR (cm^{-1}): 2956 (*C-H*$_{Ar}$), 2873 (*C-H*$_{CH3}$), 2208 (*C*≡*C*), 1728 (*C*=*O*), 1605 (*C*=*C*$_{Ar}$), 1502, 1438, 1411, 1382, 1355, 1326, 1245 (*C-O*), 1138, 1120, 1105, 1064, 1024, 1002, 9912, 839 (*C-H*$_{Ar}$).