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Photoredox Catalysis using a new Iridium Complex As an Efficient Toolbox for Radical, Cationic and Controlled Polymerizations under Soft Blue to Green Lights.

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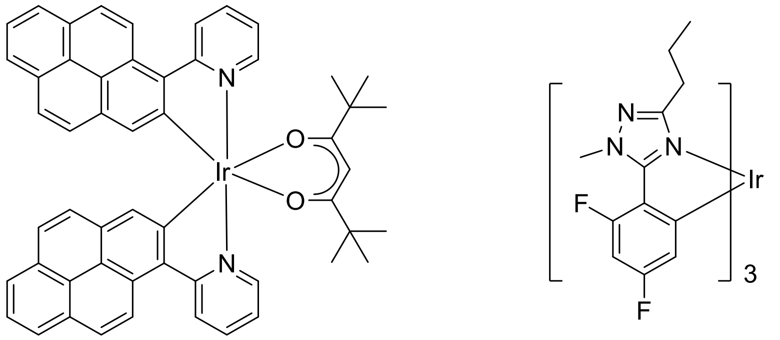
Scheme S1. Other Iridium complexes used for surface modifications.



nIr-a **nIr-b**

fac-*Tris*[5-(4,6-difluorophenyl)-1-methyl-3-propyl-[1,2,4]triazolyl]iridium (III) **nIr-b** was synthesized as previously reported.[Lo S.-C.; Shipley C.P.; Bera R.N.; Harding R.E.; Cowley A.R.; Burn P.L.; Samuel I.D.W. *Chem. Mater*. **2006**, 18, 5119-5129]

Synthesis of 2-(1-pyrenyl)pyridine (L)

Tetra*kis*(triphenylphosphine)palladium (0) (0.23 g, 0.2 mmol) was added to a mixture of pyrene-1-boronic acid (1 g, 4.06 mmol), 2-bromopyridine (0.64 g, 0.4 mL, 4.06 mmol), toluene (27 mL), ethanol (13 mL) and an aqueous potassium carbonate solution (2 M, 13 mL) under vigorous stirring. The mixture was stirred at 90 °C for 48 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water and extracted with DCM. The organic layers were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using a gradient of solvents, from pentane to CH_2Cl_2. The proligand was isolated as a light-yellow solid (1.04 g, 92% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.36 (m, 1H), 7.70 (td, 1H, J = 7.9 Hz, J = 0.9 Hz), 7.86 (td, 1H, J = 7.7 Hz, J = 1.9 Hz), 8.00 (t, 1H, J = 7.2 Hz), 8.05-8.09 (m, 3H), 8.14-8.20 (m, 3H), 8.24 (d, 1H, J = 8.0 Hz), 8.36 (d, 1H, J = 9.2 Hz), 8.85-8.88 (m, 1H); ^{1}H NMR (THF-d_8) δ (ppm): 7.39 (ddd, 1H, J = 1.2 Hz, J = 4.8 Hz, J = 7.5 Hz), 7.77 (td, 1H, J = 7.8 Hz, J = 1.0 Hz), 7.92 (td, 1H, J = 7.5 Hz, J = 2.0 Hz), 8.01 (t, 1H, J = 7.5 Hz), 8.14 (s, 2H), 8.17-8.23 (m, 3H), 8.28 (d, 1H, J = 8.0 Hz), 8.52 (d, 1H, J = 9.3 Hz), 8.82-8.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm): 122.0, 124.8, 124.9, 125.1, 125.4, 125.8, 126.0, 127.4, 127.6, 127.9, 128.0, 128.6, 131.4, 131.5, 135.6, 136.4, 149.7, 159.5; HRMS (ESI MS) m/z: theor: 280.1121 found: 280.1124 ($[M+H]^+$ detected). NMR characterizations were consistent with those previously reported [Wu W.; Wu W.; Ji S.; Guo H.; Zhao J.; *Eur. J. Inorg. Chem*. **2010**, 4470–4482].

Synthesis of $Ir(L)_2\mu\text{-}Cl_2Ir(L)_2$

$IrCl_3.3H_2O$ (0.38 g, 1.20 mmol) and water (2.5 mL) were added to a solution of 2-(1-pyrenyl)pyridine (L) (1.34 g, 4.80 mmol) in 2-ethoxyethanol (10 mL). The mixture was refluxed at 120°C for a night. After cooling, the brown red precipitated was filtered off, washed with water and dried in vacuum. 839 mg of iridium dimer (89 % yield) were obtained. It was used without any further purification. HRMS (ESI MS) m/z: theor: 809.1306 found: 809.1309 ($[M/2+Na]^+$ detected).

Synthesis of $Ir(L)_2(tmd)$ ***nIr-a***

In a 50 mL flask, the μ-chloride-bridged dimer Ir(III) complex (0.5 g, 0.318 mmol), 1,1,7,7-tetramethylheptan-3,5-trione (tmd) (176 mg, 3 eq.) and K_2CO_3 (308 mg, 7 eq.) were mixed with 2-ethoxyethanol (30 mL) and the mixture was stirred under reflux overnight. After cooling to room temperature, 2-ethoxyethanol was removed under reduced pressure. The crude product was dissolved in dichloromethane (20 mL) and the obtained solid was filtered off. The dichloromethane solution (20 mL) was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2) using a gradient of solvents from pentane to CH_2Cl_2. The complex was isolated under the form of an orange-red powder (130 mg, 88% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.91 (s, 18H), 5.59 (s, 1H), 7.12 (s, 2H), 7.22 (td, 2H, J = 1.0 Hz, J = 6.0 Hz), 7.50 (d, 2H, J = 9.0 Hz), 7.74 (d, 2H, J = 9.0 Hz), 7.81 (t, 2H, J = 7.6 Hz), 7.91-7.96 (m, 4H), 8.05-8.11 (m, 4H), 8.67 (d, 2H, J = 7.5 Hz), 8.73 (d, 2H, J = 9.4 Hz), 8.92 (d, 2H, J = 9.4 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 28.1, 41.2, 89.7, 120.7, 121.9, 122.4, 123.1, 124.1, 124.8, 125.4, 125.8, 127.1, 127.6, 127.7, 128.5, 129.3, 130.3, 130.7, 130.9; HRMS (ESI MS) m/z: theor: 932.2954 found: 932.2957 ($M^{+\cdot}$ detected).

Figure S1. Retention time for photoinitiating system: nIr (0.6 mg, 0.7 µmol), inititator ethyl α-bromophenylacetate (0.1 g, 0.5 mmol), DMF (5 g, 68.41 mmol) and the monomer MMA (5 g, 49.94 mmol) after irradiation with diode laser 405 nm. Under nitrogen.

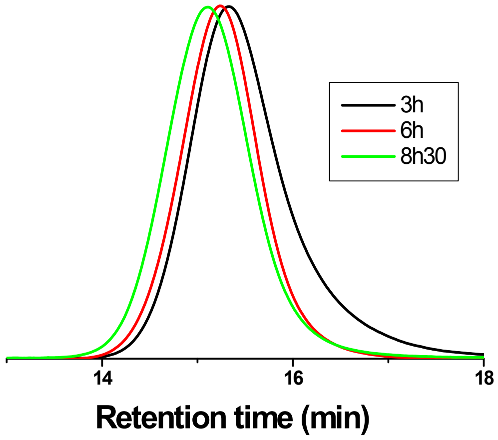


Figure S2. UV-vis absorption spectra of nIr-a and nIr-b in acetonitrile.

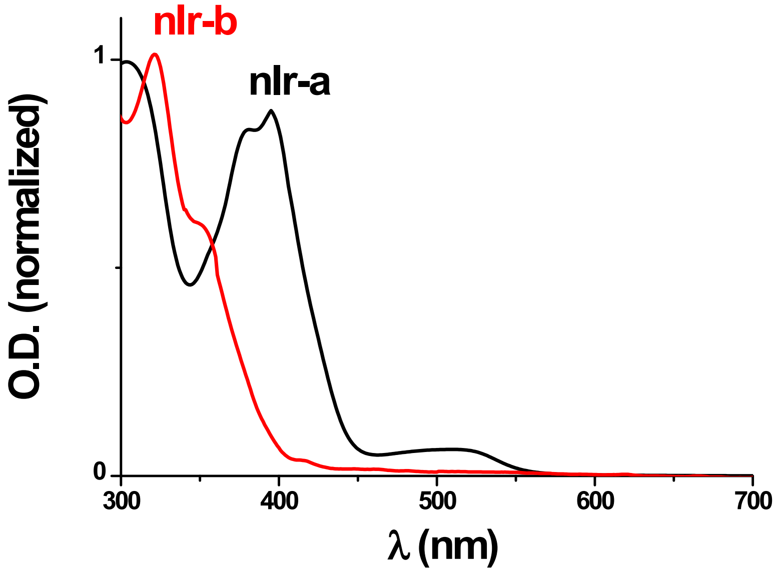


Figure S3. Contact angles of **(A)** the polymerized TMPTA first layer using nIr-a/PBr (0.5%/3% w/w) and **(B)** the polymerized fluoromonomer (PmA) second layer after re-initiation. Halogen lamp irradiation.