Supporting Information

# Switching the Activity of a Photoredox Catalyst Through Reversible Encapsulation and Release

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## Synthesis of Ru(bpy)<sub>3</sub>•(OTf)<sub>2</sub> 2

In a round bottomed flask were placed 250 mg (0.334 mmol) of  $Ru(bpy)_3Cl_2 \cdot (H_2O)_6$  together with 10 mL of water. To this solution, 6.8 mL of a solution of AgOTf in acetone (0.098 M)were added. The white precipitate was filtered and the solution was evaporated. The residual orange solid was dried under vacuum providing 273 mg of the product (94 % yield). <sup>1</sup>H (CDCl<sub>3</sub>, 300.15 MHz) 8.45 (d, 2H, J=6.0 Hz), 8.04 (t, 2H, J=6.0 Hz), 7.86 (d, 2H, J=6.0 Hz), 7.53 (t, 2H, J=6.0 Hz). Elemental analysis: calc. C 39.55%, H 2.30%, N 10.64%, S 8.12%; found C 39.60%, H 2.33%, N 10.74%, S 8.06%.

### Synthesis of (NEt<sub>4</sub>)/(OTf) 3

In a round bottom flask equipped with magnetic stirring and protected from light were introduced 500 mg (3.02 mmol) of tetraethylammonium chloride, 775.3 mg (3.02 mmol) of silver trifluoromethanesulfonate and 15 ml dichloromethane. The reaction was left at room temperature for 3 hours, after which the solution was filtered and the precipitated silver chloride was washed three times with dichloromethane. The organic phase was concentrated under vacuum leading to 689 mg (2.47 mmol) of tetramethylammonium trifluoromethanesulfonate **3** as a fluffy white solid (yield 82%). <sup>1</sup>H (CD<sub>3</sub>OD, 300.15 MHz) 3.30 (q, J=7.31 Hz), 1.29 (tt, 12H, J=1.83 Hz, J=7.31 Hz); <sup>13</sup>C{<sup>1</sup>H} (CD<sub>3</sub>OD, 75,6 MHz), 53.27, 7.59. Elemental analysis: calc. C 38.60%, H 7.22%, N 5.01%, S 11.48%; found C 38.51%, H 7.18%, N 5.11%, S 11.52%

### Synthesis of (NPr<sub>4</sub>)/(OTf) 8

In a round bottom flask equipped with magnetic stirring protected from light were introduced 500 mg (1.59 mmol) of tetraethylammonium iodide, 410.1 mg (1.59 mmol) of silver trifluoromethanesulfonate and 15 ml dichloromethane. The reaction was left at room temperature for 3 hours, after which the solution was filtered and the precipitated silver chloride was washed three times with dichloromethane. The organic phase was concentrated under vacuum leading to 455.9 mg (1.35 mmol) of tetrapropylammonium trifluoromethanesulfonate **8** as a grey solid (yield 85%). <sup>1</sup>H (CD<sub>3</sub>OD, 300.15 MHz) 3.19 (m, 8H), 1.71 (m, 8H), 1.01 (t, J=7.31, 12H); <sup>13</sup>C{<sup>1</sup>H} (CD<sub>3</sub>OD, 75.6 MHz), 61.36, 16.37, 10.89. Elemental analysis: calc. C 46.55%, H 8.41%, N 4.18%, S 9.56%; found C 46.44%, H 8.37%, N 4.15%, S 9.61%.

#### Typical experimental procedure for the on-off catalytic oxidation experiment:

In a 3 mL vial equipped with a magnetic stirring were introduced 2mL of a solution of Ru(BPY)<sub>3</sub> **1** in water saturated CDCl<sub>3</sub> (2.3mM). The solution was purged three times with  $O_2$  and the vial thermostatted at 50°C under  $O_2$ . 40.3µL of dibutyl sulfide were added and the vial was exposed to a 120W visible lamp. The progression of the oxidation reaction was monitored by sampling the solution followed by GC analysis. After 100 min, 255.2 µL of a solution of resorcin[4]arene **2** (0.112 M) in water saturated CDCl<sub>3</sub> were added observing the stop of the catalytic activity. After 165 min, 120µL of a solution of tetraethylammonium triflate **3** (0.38 M) in water saturated CDCl<sub>3</sub> were added to the system observing the restoration of the catalytic activity. After 230 min, 1,4mL of a solution of resorcin[4]arene **2** (0.112M) in water saturated CDCl<sub>3</sub> were added observing a second stop of the catalytic activity.



Figure S1. <sup>1</sup>H NMR spectra in chloroform-d: A) 1 (2.3 mM); B) 1 (2.3 mM) and 2 (13.8 mM); C) 1 (2.3 mM), 2 (13.8 mM) and 3 (22.9 mM); D) 2 (13.8 mM).



**Figure S2.** UV-VIS spectra for chloroform-d solutions of  $[Ru(bpy)_3](OTf)_2$  **1** (2.3 mM, red);  $[Ru(bpy)_3]$  **1**(2.3 mM) and resorcin[4]arene **2** (13.8 mM, yellow);  $[Ru(bpy)_3]$  **1** (2.3 mM) and resorcin[4]arene **2** (13.8 mM) and N(Et)<sub>4</sub>(OTf) **3** (22.9 mM, green).