Electronic supporting information

Micropatterning of Electrochemiluminescent Polymers based on Multipolar Ru-Complexes Two-Photon Initiators.

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1. Figures and Schemes.



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Figure S2. A. CV of RuT (0.46 mM) in ACN on platinum electrode (0.1 M TBAPF₆, 100 mV s⁻¹). B. CV and ECL signal of RuT in ACN in presence of TPrA (50 mM) on screen-printed gold electrode (0.1 M TBAPF₆, 50 mV s⁻¹). Insets: ECL spectrum of RuT in presence of TPrA at 0.61 V vs. Fc/Fc⁺.



Figure S3. CVs of RuF (0.9 mM), $Ru(bpy)_3^{2+}$ (1 mM) and the free ligand L (0.1 mM) in ACN on a platinum working electrode (0.1 M TBAPF₆, 100 mV s⁻¹). Note: The ligand F is weakly soluble in ACN and leads to aggregation for concentration higher that 0.15 mM.



Figure S4. CVs of **RuT** (0.46 mM), **Ru(bpy)₃²⁺** (0.5 mM) and the free ligand L (0.07 mM) in ACN on a platinum working electrode (0.1 M TBAPF₆, 100 mV s⁻¹). Note: The ligand **T** is also weakly soluble in ACN.



Figure S5. Evolution of the absorption spectrum of **RuF** (0.3 wt %) in triacrylate resin upon irradiation at 485 nm.



Figure S6 Evolution of the luminescence spectrum of RuT (0.3 wt %) in triacrylate resin irradiated under microscope at 485 nm (P = 95 μ W). Inset: Corresponding changes of the absorption spectrum of RuT during the photopolymerization reaction.



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Figure S8. A. SEM micrograph of a periodic microstructure which was two-photon fabricated at 800 nm using the triacrylate resin with RuT (scale bar: 20 μ m). B. Epiluminescence image of the microstructure. C. Luminescence spectrum recorded from the μ -object.



Figure S9. A. Transmitted optical images of a photopolymerized PEGDA/PETIA dot in air and in ACN solution (scale bar: 40 μ m). B. Evolution of the luminescence signal recorded from the excited polymer dot during its incubation in ACN ($\lambda_{exc.} = 485$ nm). C. Luminescence images of the polymer dot recorded in ACN at the initial and final incubation time. Formulation: PEGDA/PETIA (70 / 30 wt %) with RuF (0.3 % wt)



Figure S10. A. Luminescence images of a polymer dot recorded in ACN at the initial and final incubation time. B. Evolution of the luminescence signal recorded from the excited polymer dot during its incubation in ACN ($\lambda_{exc.} = 485$ nm). Formulation: PEGDA/PETIA (70 / 30 wt %) with RuT (0.3 % wt).



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Figure S12. A. CV and ECL signal of μ-grids in ACN in presence of TPrA (50 mM) (0.1 M TBAPF₆, 30 mV s⁻¹). The μ-strutures were two-photon fabricated using the formulation with RuT. B. ECL-spectrum recorded at an applied potential of 0.90 V. C. AFM image of a two-photon polymerized μ-grid fabricated on a screen-printed gold electrode.

	λ_{abs} / nm	ε _{abs} / 10 ³ M ⁻¹ cm ⁻¹	λ _{em.} / nm	Φ_L	${\mathop{E_{{\rm{T1}}}}^{{\it{b}}}}{{\it{/}{\rm{eV}}}}$
RuT	450	39.8	696	0.0009 (0.011) ^a	1.78
RuF	451	66.1	698	0.0015 (0.014) ^{<i>a</i>}	1.78

 $\overline{^{a} \text{N}_{2}\text{-saturated ACN}, ^{b} \text{E}_{\text{T1}} \approx \text{hcv}_{phos}}$

Table S1.Photophysical data of the Ru-complexes in ACN.





PEGDA

Scheme S1. Molecular structures of the acrylate-based monomers.

2. Materials and General Characterization Methods.

2.1 Materials. The synthesis and the characterization of **RuT** and **RuF** are described elsewhere¹. Tri-n-propylamine (**TPrA**), n-tetrabutylammonium hexafluorophosphate (**TBAPF**₆), Tris(2,2'-bipyridine)ruthenium(II) hexafluorophosphate (**Ru(bpy)**₃²⁺), N-methyl diethanolamine (**MDEA**), polyethylene glycol diacrylate monomer (**PEGDA**, M_n 575) and pentaerythritol triacrylate (**PETIA**) were purchased from Aldrich. All the solvents which are spectroscopic grade were also purchased from Aldrich.

2.2 Steady-state absorption and luminescence spectra in solution. The absorption and fluorescence spectra were recorded using a Perkin Elmer Lambda 2 spectrometer and a FluoroMax-4 spectrofluorometer. Emission spectra are spectrally corrected, and luminescence quantum yields include the correction due to solvent refractive index and were determined relative to Ru(bpy)₃²⁺, 2PF6⁻ in aerated ACN ($\Phi_L = 0.018$)².

2.3 Two-photon excited luminescence measurements. The two-photon absorption (2PA) measurements were performed with femtosecond mode-locked laser pulse using a Ti: Sapphire laser (Coherent, Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz; wavelength range: 680-1040 nm). A relative two-photon excited luminescence (2PEL) method³ was employed to measure the two-photon absorption cross-sections, δ . The measurements of 2PA cross-sections were performed relative to a set of three reference molecules (*r*) : fluorescein^{3, 4} in water at pH = 11, Rhodamine 6G⁵ in methanol and Coumarin 153⁵ in DMSO. The value of δ for a sample (*s*) is given by:

$$\delta_{S} = \frac{S_{S} \Phi_{r} \eta_{r} c_{r}}{S_{r} \Phi_{S} \eta_{S} c_{S}} . \delta_{r}$$

Where S is the detected two-photon excited fluorescence integral area, c the concentration of the chromophores, and Φ is the fluorescence quantum yield of the chromophores. η is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were conducted in a regime where the luminescence signal showed a quadratic dependence on the intensity of the excitation beam. **2.4 Cyclic voltammetry.** The redox potentials of the compounds were measured by cyclic voltammetry using a Radiometer Voltalab 6 potentiostat. All measurements were performed at 300 K in N₂-saturated acetonitrile with 0.1 M of **TBAPF**₆ used as supporting electrolyte. The cyclic voltammograms (CVs) were recorded using a three-electrode cell with a platinum disk as working electrode. A platinum wire was used as auxiliary electrode. A saturated calomel electrode (SCE) used as a reference was placed in a separate compartment with a salt bridge containing the supporting electrolyte. Ferrocene (Fc) was used as an internal reference.

2.5 Electrochemiluminescence (ECL) measurements. All ECL measurements were performed on screen-printed gold electrodes (SPGE) purchased from Dropsens (C223AT type). The SPGEs which integrate a miniaturized three-electrode configuration on a ceramic substrate consist in a disk-shaped gold working electrode (1.6 mm diameter), a gold counterelectrode and a pseudo reference silver electrode which are both organized in an annular geometry. The ECL signal and the corresponding CV were recorded using a spectroelectrochemical module (SpectroECL type from Dropsens) which comprises a bipotentiostat/Galvanostat (\pm 4 V potential range, \pm 40 mA maximum measurable current) and a CMOS sensor coupled with a microspectrometer (spectral response range 340-850 nm). All ECL/CV measurements which were performed in ACN (0.1 M of TBAPF₆) were calibrated using Fc/Fc⁺ as an internal reference.

2.6 Epiluminescence Microscopy. The *in situ* luminescence signal of irradiated formulations was recorded using an Olympus IX73 inverted microscope equipped with a 75 W Xe lamp housing. The excitation of the sample at 485 nm occurred through a 40X, 0.65-NA objective using a fluorescence mirror unit (U-FBN from Olympus) associating a band pass filter centered at 485 nm (BP470-495), dichroic mirror (DM505) and long pass filter (BA510IF). The epi-luminescence signal from the sample is collected by the same objective, passes through the same fluorescence mirror unit and is either collected by a spectrometer (USB4000-UV-Vis Ocean Optics) or by a CMOS camera (ORCA-Flash4.0 from Hamamatsu). Neutral filters were placed on the excitation optical path of the microscope to attenuate the irradiation power which was adjusted to a value of about 100 μ W.

2.7 Two-Photon Microfabrication. The 3D lithographic microfabrication was carried out using a Zeiss Axio Observer D1 inverted microscope. The two-photon excitation was performed at 800 nm using respectively a mode-locked Ti: Sapphire oscillator (Coherent,

Chameleon Ultra II: pulse duration: ~140 fs; repetition rate: 80 MHz). The incident beam was focused through a 0.65 NA objective (40 X) which leads to a radial spot size 600 nm at $\lambda_{exc} =$ 800 nm (1/e² Gaussian). A drop of the resin is deposited on a glass cover slip or on a gold screen-printed electrode which are then mounted on a 3D piezoelectric stage allowing the translation relative to the laser focal point. The intensity of the entering laser is controlled with the use of an acousto optic modulator. The displacement of the sample and all photonic parameters (i.e. excitation power and irradiation times) are computer-controlled. The 3D microstructure is finally obtained by washing away the unexposed monomer resin using ethanol.

3. References.

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