Electronic Supporting Information for

## Ruthenium(II)-polypyridyl doped zirconium(IV) metal-organic frameworks as solid-state electrochemiluminescence detectors

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Supporting figures & analysis



Fig. S1 N<sub>2</sub> adsorption-desorption isotherm of UiO-67-Ru powders at 77 K, 1 atm.



Fig. S2 UV-Visible spectrum of UiO-67-Ru@FTO in MeCN



Fig. S3 Steady-state emission spectra of UiO-67-Ru@FTO and RuDCBPY in MeCN



Fig. S4 Amperometry of UiO-67-Ru@FTO in MeCN with a controlled potential at 1.38 V vs.  $Fc/Fc^+$  for 30 min

To calculate electroactive  $Ru^{2+}$  coverage, the charge Q can be obtained by integration. Based on the assumption that the charge that passed during electrolysis (0-1800 s) was only due to the oneelectron transfer process of  $Ru^{2+}/Ru^{3+}$  redox couple, and all electroactive Ru contribute to the

charge, the amount of Ru can be calculated using equation  $n = \frac{Q}{F}$ , where n is the number of moles of Ru<sup>2+</sup>, Q is the charge, and F is Faraday constant. The coverage of electroactive Ru<sup>2+</sup> is thereby obtained by n over the film area (2.75 cm<sup>2</sup>). The total amount of Ru<sup>2+</sup> can be obtained from ICP-MS of digested films. Finally, the ratio of electroactive coverage calculated from potential-step electrolysis to the total Ru content determined by ICP-MS.



Fig. S5 ECL of solution-based  $Ru(bpy)_3^{2+}/TPA$  system in the presence of 20 mM TPA in MeCN containing 0.1 M LiClO<sub>4</sub>



Fig. S6 SEM of UiO-67-Ru@FTO after ECL measurement

## Associated with Fig. 4C

The linear relationship between ECL intensity and TPA concentration ranging from 0.04 mM to 20 Mm can be represented by equation  $I_{ECL}$  (a.u.) = 129.08857 + 413.62138C<sub>TPA</sub> (mM), with a correlation coefficient of 0.99747.

## Associated with Fig. 5

The curve can be fitted to the equation  $I_{ECL}/I_0=1.87112-0.74028 \log(C_{DA}) (\mu M)$  with a correlation coefficient of 0.96036.