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Supplemental Information

Distance Dependent Energy Transfer Dynamics from Molecular Donor to Zeolitic Imidazolate Framework Acceptor

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Experimental Methods.

Chemicals and Materials. Cobalt (II) nitrate hexahydrate was purchased from Alfa Aesar. 2-methylimidazole (2mIm，99%) was purchased from Acros Orvanics. Ruthenizer 535 (RuN3) was purchased from Solaronix. Methanol (MeOH), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2, 30%) and microscope slides were purchased from Fisher Scientific. Ethanol (EtOH 200 proof, anhydrous) was purchased from Decon Laboratories. Trimethylaluminum (98%) was purchased from Strem Chemicals. All chemicals were used as received without further purification.

Treatment of glass slides. Typically, the microscoped slides were first cut into 1.2 cm ×2.5 cm pieces. The glass slides were then washed with acetone, ethanol and water under sonication for 10 mins and rinsed with water. After the first step cleaning, the glass slides were immersed into 40 mL of Piranha solution (30 mL H_2SO_4 and 10 mL H_2O_2) and set it for 30 mins. The etched slides were washed sufficiently with deionized (DI) water and kept in DI water for later use.

Growth of ZIF-67 film. The synthesis of ZIF-67 was followed by previously reported method.[1, 2] Typically, 0.73 g $Co(NO_3)_2 \cdot 6H_2O$ and 1.65 g 2mIm were dissolved in 50 mL MeOH, respectively. 4 mL of $Co(NO_3)_2$ solution was added into 4 mL of 2mIm solution in 20 mL glass vial, where the mixture shows purple color. Two pieces of etched glass slides were immersed into the purple solution and sit for 1 h, during which ZIF-67 crystals form continuous and transparent thin film on the glass slides. The obtained ZIF-67 film was rinsed with MeOH and dried with N_2 flow. Because ZIF-67 films form on both sides of the glass, we scratched ZIF-67 off from one side of the film to make single-side ZIF-67 film.

Atomic Layer Deposition of Al_2O_3. A GEMStar™ XT Atomic Layer Deposition System was used for the Al_2O_3 deposition. The ZIF-67 films on glass slide were put at the center of the reactor. The gas lines of the system were held at 110°C to avoid precursor condensations.

Trimethylalumnimum (TMA) and H_2O were used as Al and O sources, respectively, and were reacted at 120°C. The deposition process was performed in the following sequence: 0.05 s TMA pulse, 60 s exposure, 60 s N_2 purge, 0.05 s H_2O pulse, 60 s exposure, 60 s N_2 purge. 10-40 cycles deposition cycles were applied to create 3-8.5 nm Al_2O_3 layers. The morphology and thickness of the Al_2O_3 were characterized by a HITACHI H-7700 TEM with an accelerating voltage of 100 kV. Due to the instability of ZIF-67 and ZIF-67 with 10 cycles of Al_2O_3 under electron beam, a 100-cycle Al_2O_3 deposited on ZIF-67 is measured by TEM (Figure S1d). A linear relationship between cycles of Al_2O_3 and their thicknesses on ZIF-67 was derived (Figure S1e) from the 20, 30, 40 and 100 cycle thickness. From the linear relationship, the 10-cycle thickness was estimated to be 3 nm.

Standard Characterization. Steady-state UV−visible absorption spectra were taken using an HP Agilent 8453 spectrophotometer (UV-Visible) and a Cary 5000 spectrometer (UV-Visible-NIR). A Rigaku MiniFlex II diffractometer with Cu Kα radiation was used to collect X-ray diffraction (XRD) patterns.

Time-resolved Optical Absorption Spectroscopy (TA). The femtosecond TA setup is based on a regenerative amplified Ti-Sapphire laser system (Solstice, 800 nm, <100 fs FWHM, 3.5 mJ/pulse 1 kHz repetition rate). The tunable pump (235-1100 nm), chopped at 500 Hz, is generated in TOPAS (Light Conversion) from 75% of the split output from the Ti-Sapphire laser. The tunable UV-visible probe pulses are generated from the other 25% of the Ti-Sapphire output through white light generation in a sapphire (430-750 nm) window on a translation stage. The femtosecond TA measurements were performed in a Helios ultrafast spectrometer (Ultrafast Systems LLC). The film samples were placed on a translation stage, and all samples were under translation during measurements to avoid sample damage.

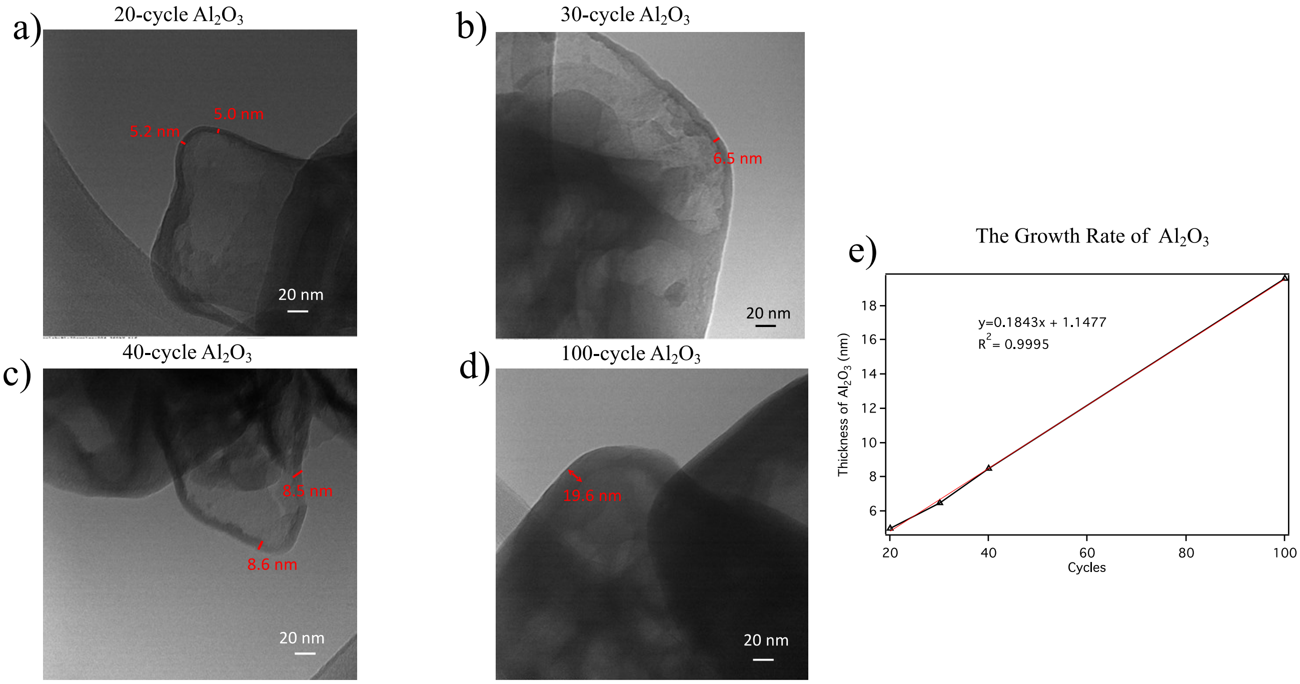

Figure S1. TEM images of various cycles of Al_2O_3 deposited on ZIF 67. (a) 20-cycle (b) 30-cycle (c) 40-cycle (d)100-cycle (e) cycles and thickness relationship of deposited Al_2O_3. It is worth to note that ZIF-67 with 10-cycle Al_2O_3 are unstable under electron beam of TEM so its thickness is not included.

Table S1 Al_2O_3 film thickness at different ALD cycles.

ALD Cycles	**Thickness of Al_2O_3 films (nm)**

10	3
20	5
30	6.5
40	8.5

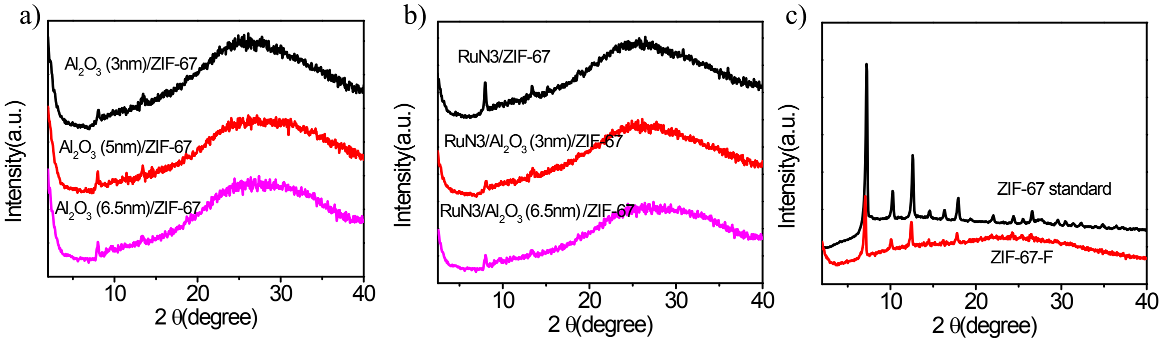

Figure S2. XRD pattens of Al$_2$O$_3$ on ZIF-67 films (a), RuN3 sensitized films (b), ZIF-67 crystals synthesized from standard growth (denoted ZIF-67 standard) and ZIF-67 powder scratched from ZIF-67 film (denoted ZIF-67-F) (c).

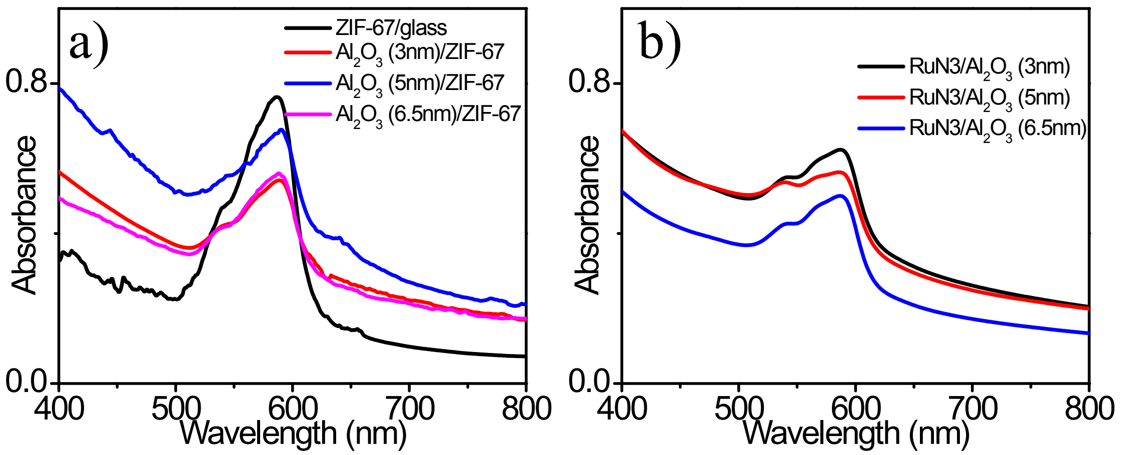

Figure S3. UV-visible absorption spectra of Al$_2$O$_3$ on ZIF-67 film (a) and RuN3 sensitized films (b) with different thickness of Al$_2$O$_3$.

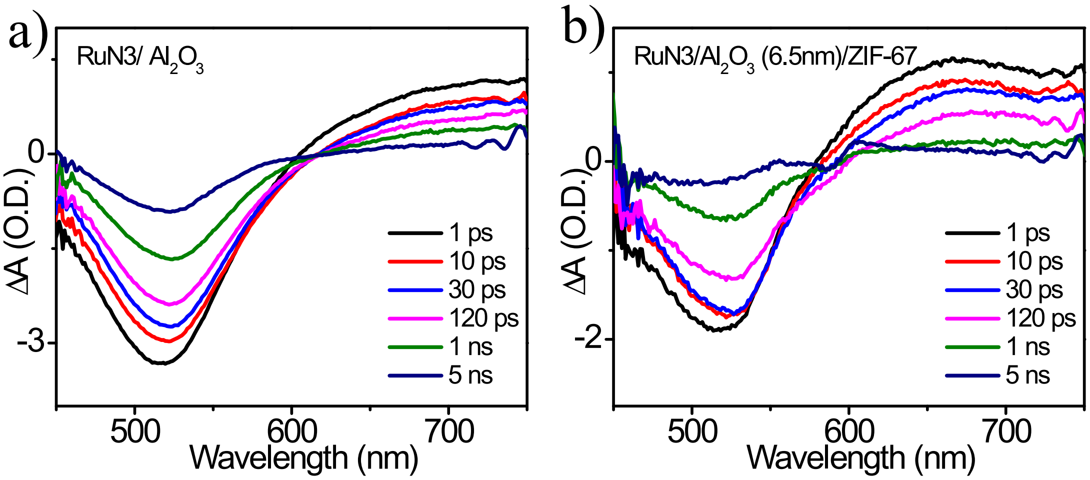

Figure S4. Transient absorption spectra of RuN3/Al_2O_3 (a) and RuN3/Al_2O_3(6.5nm)/ZIF-67 (b).

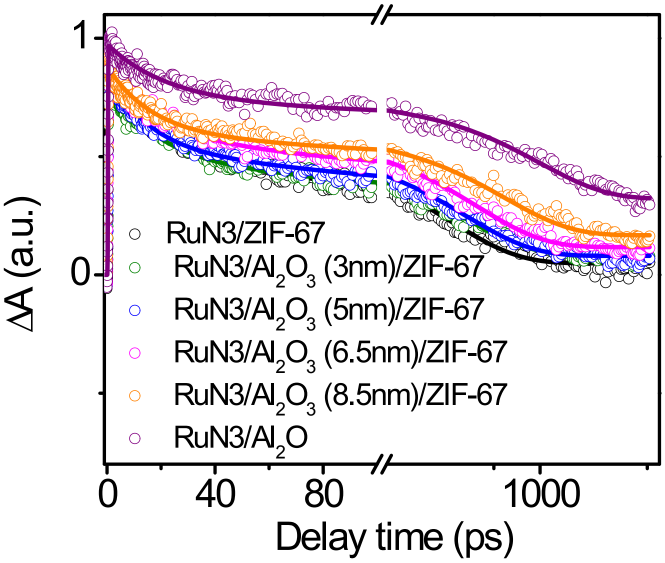

Figure S5. The comparison of excited state decay kinetics of RuN3 on different substrate.

Table S2 Fitting parameters of ESA decay traces of RuN3 on different substrates

	τ_1 (A_1) (ps)	τ_2 (A_2) (ps)	τ_3 (A_3)
RuN3/ZIF67	15.1 (43.2)	268 (51.4)	> 5 ns (5.3)
RuN3/Al_2O_3 (3nm)/ZIF67	16.5 (40.7)	336 (49.7)	> 5 ns (9.6)
RuN3/Al_2O_3 (5nm)/ZIF67	15.6 (38.4)	350 (52.5)	> 5 ns (9.1)
RuN3/Al_2O_3 (6.5nm)/ZIF67	17.1 (34.6)	390 (52.3)	> 5 ns (13.1)
RuN3/Al_2O_3 (8.5nm)/ZIF67	16.8 (32.1)	592 (48.9)	> 5 ns (19.1)
RuN3/Al_2O_3	22.8 (24.7)	1000 (42.2)	> 5 ns (33.1)

Reference

1. B. Pattengale, S. Z. Yang, J. Ludwig, Z. Q. Huang, X. Y. Zhang and J. Huang, J. Am. Chem. Soc **138** (26), 8072-8075 (2016).
2. S. Z. Yang, B. Pattengale, E. L. Kovrigin and J. Huang, ACS Energy Lett. **2** (1), 75-80 (2017).