Electronic Supplementary Information

Frontier orbital engineering of photo-hydrogen-evolving molecular devices: a clear relationship between the H$_2$-evolving activity and the energy level of the LUMO

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Figure S1. Absorption spectra of [1](PF₆)₂·H₂O, [2](PF₆)₂·1.5H₂O, [3](PF₆)₂·5H₂O, [4](PF₆)₂·H₂O, [5](PF₆)₂·3H₂O and [6](PF₆)₂·3H₂O in acetonitrile at 20 °C in air.
Emission spectra

**Figure S2.** Normalized emission spectra of [4](PF$_6$)$_2$·H$_2$O (red), [5](PF$_6$)$_2$·3H$_2$O (blue) and [6](PF$_6$)$_2$·3H$_2$O (green) in acetonitrile at 25 °C under degassed condition. The spectra were not corrected for the overall sensitivity of the detector.
Electrochemistry

Figure S3a. Left: Cyclic voltammograms of [1](PF₆)₂·H₂O (red), [2](PF₆)₂·1.5H₂O (blue) and [3](PF₆)₂·5H₂O (green) in 0.1 M TBAP/dry acetonitrile, recorded at a scan rate of 50 mVs⁻¹. Right: Cyclic voltammograms of [4](PF₆)₂·H₂O (red), [5](PF₆)₂·3H₂O (blue) and [6](PF₆)₂·3H₂O (green) in 0.1 M TBAP/dry acetonitrile, recorded at a scan rate of 50 mVs⁻¹.

Figure S3b. Left: Square-wave voltammograms of [1](PF₆)₂·H₂O (red), [2](PF₆)₂·1.5H₂O (blue) and [3](PF₆)₂·5H₂O (green) in 0.1 M TBAP/dry acetonitrile, recorded at a step potential of 4 mV, an amplitude of 25 mV, and a frequency of 15 Hz. Right: Square-wave voltammograms of [4](PF₆)₂·H₂O (red), [5](PF₆)₂·3H₂O (blue) and [6](PF₆)₂·3H₂O (green) in 0.1 M TBAP/dry acetonitrile, recorded at a step potential of 4 mV, an amplitude of 25 mV, and a frequency of 15 Hz.
DFT calculation

Figure S4a. Frontier molecular orbitals of a fully optimized structure of $[5]^{2+}$ in water (polarizable continuum model), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.
Figure S4b. Frontier molecular orbitals of a fully optimized structure of $[5]^{2+}$ in water (polarizable continuum model), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.
Figure S5a. Frontier molecular orbitals of a fully optimized structure of [6]^{2+} in water (polarizable continuum model), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.
Figure S5b. Frontier molecular orbitals of a fully optimized structure of $[6]^{2+}$ in water (polarizable continuum model), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.
Figure S6. MO energy diagrams for the Ru(II)Pt(II) dimers, 4-6, obtained by the DFT calculations.
Photochemical hydrogen production from water

Figure S7. Photochemical H₂ production from an aqueous acetate buffer solution (0.03 M CH₃CO₂H and 0.07 M CH₃CO₂Na; pH 5.0, 10 mL) containing 30 mM EDTA, and 0.1 mM [6](NO₃)₂·2H₂O in the absence (green) and presence of 2.0 mM MV(NO₃)₂ (red).
Emission decay profiles

Figure S8. Emission decay profiles of [2](PF₆)₂·1.5H₂O (top) and [3](PF₆)₂·5H₂O (bottom) in acetonitrile at 25 °C under degassed condition. Colored dots correspond to the observed data and solid lines denote calculated lines according to a monoexponential functions (τ = 957 and 901 ns for 2 and 3, respectively).
Nanosecond transient absorption spectra

Figure S9. Transient absorption spectra of \([4](\text{PF}_6)_2\cdot\text{H}_2\text{O}\) (red), \([5](\text{PF}_6)_2\cdot3\text{H}_2\text{O}\) (blue) and \([6](\text{PF}_6)_2\cdot3\text{H}_2\text{O}\) (green) at 10 ns after laser pulse excitation at \(\lambda = 266\ \text{nm}\) in water at 20 °C under degassed condition.