Molecular Engineering towards Tunable Morphology of Metal-Organic Complex Microcrystals for Efficient and Multicolor Electrochemiluminescence

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1. General Experimental and Equipment Information

a. Synthesis and Characterization

Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were recorded in CD₃CN on a Bruker Avance III 400 MHz spectrometer.

b. Photophysical Measurements

The fluorescence and UV-vis absorption spectra were measured with the Hitachi F-7000 spectrofluorometer and TU-1810DSP spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.), respectively. Solid state absorption spectra were recorded by Hitachi UH4150 spectrophotometer. Photoluminescence quantum yields were determined by a Hamamatsu absolute PL Quantum Yield Spectrometer C11347 with an integrating sphere. Emission lifetimes were measured by a Hamamatsu C11367-11 instrument using single photo counting measurement.

c. X-ray Diffraction Measurements

Powder X-ray diffraction was performed on the Rigaku D/max2500 instrument (Cu K α , 0.154 nm). Single crystal X-ray analysis was performed on the Rigaku Saturn 724 diffractometer on a rotating anode at 170 K with Mo K α radiation (0.71073 Å) or Cu K α radiation (1.54184 Å). The structure was solved by the direct method using SHELXS-97 and refined with Olex2.

d. Microscopic Images

Fluorescence microscopy characterization was conducted using Olympus IX83 Inverted fluorescence microscope equipped with a spot-enhanced charge couple device (CCD, Diagnostic Instrument, Inc.). TEM images and SAED patterns were obtained on a JEOL-1011 transmission electron microscope with an accelerating voltage of 100 kV.

e. Electrochemical and ECL Measurements

All cyclic voltammograms, differential pulse voltammograms and electrochemical impedance spectroscopy were carried out on a CHI 660D electrochemical analyzer. Before measurement, the glassy carbon working electrode was polished using 0.05 µm alumina polishing slurry. Then it was rinsed with water, sonicated in water and then acetone for several minutes and dried in air. ECL signals were recorded by an ultra-weak chemiluminescence analyzer (Bio-Equip Technology Co., Ltd., China) with 0.01 s of sample interval. A customized cuboid quartz cell was used as the electrochemical reaction cell. While collecting signals, the cell was placed directly above the photomultiplier. ECL spectra were recorded by the combination of F-380 spectrofluorometer and CHI 660D electrochemical analyzer. In all measurements, the reference electrode is Ag/AgCl electrode and the counter electrode is a platinum coil.

2. Synthesis and Characterization



General procedure for the preparation of intermediate a, b and c: a mixture of $RuCl_3 \cdot 3H_2O$ (0.40 mmol), corresponding ligand (2.02 equiv) and LiCl (6.83 equiv) in dry DMF (3 mL) were stirred under N₂ atmosphere at 143 °C for 8 h. Then the solution was cooled to rt, followed by the

addition of 10 mL of acetone. After storing in the refrigerator overnight, the mixture was filtered. The obtained precipitate was washed by water and ethyl ether to get the intermediate for the following reaction without further purification. **a**: black powder, 61.7 mg, 33%. **b**: dark purple powder, 112.6 mg, 51%. **c**: brown yellow powder, 122.3 mg, 56%.

General procedure for the synthesis of complexes 1, 2, 4 and 5: a mixture of the corresponding precursor (50.0 mg) and ligand (1.02 equiv) in ethylene glycol (4.5 mL) was irradiated by microwave (400 W) under N_2 atmosphere for 10 min. Then the solution was cooled to rt, followed by the addition of 0.5 mL of water and adequate aqueous KPF₆. The mixture was filtered and the obtained solid was washed with water and ethyl ether to afford the desired product.

1: orange powder, 67.8 mg, 74%. ¹H NMR (400 MHz, CD₃CN) δ 8.48 (d, *J* = 8.0 Hz, 4H), 8.34 (s, 2H), 8.03 (t, *J* = 7.7 Hz, 4H), 7.72 (s, 4H), 7.52 (d, *J* = 5.7 Hz, 2H), 7.38 (q, *J* = 7.4 Hz, 4H), 7.22 (d, *J* = 5.3 Hz, 2H), 2.52 (s, 6H). MALDI-TOF (m/z): calcd for C₃₂H₂₈N₆F₆PRu 743.11. Found: 742.8; calcd for C₃₂H₂₈N₆Ru: 598.15. Found: 596.7.

2: red powder, 58.6 mg, 69%. ¹H NMR (400 MHz, CD₃CN) δ 8.47 (d, J = 8.1 Hz, 2H), 8.33 (s, 4H), 8.02 (t, J = 7.7 Hz, 2H), 7.72 (d, J = 5.6 Hz, 2H), 7.54 – 7.48 (m, 4H), 7.39 – 7.34 (m, 2H), 7.21 (t, J = 6.9 Hz, 4H), 2.52 (s, 12H). MALDI-TOF (m/z): calcd for C₃₄H₃₂N₆F₆PRu, 771.14. Found: 770.8; calcd for C₃₄H₃₂N₆Ru: 626.18. Found: 624.7.

4: orange powder, 70.8 mg, 78%. ¹H NMR (400 MHz, CD₃CN) δ 8.52 – 8.45 (m, 4H), 8.31 (d, *J* = 8.3 Hz, 2H), 8.04 (q, *J* = 7.6 Hz, 4H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.73 – 7.66 (m, 4H), 7.47 (s, 2H), 7.38 (q, *J* = 6.0 Hz, 4H), 2.18 (s, 6H). MALDI-TOF (m/z): calcd for C₃₂H₂₈N₆F₆PRu, 743.11. Found: 742.8; calcd for C₃₂H₂₈N₆Ru: 598.15. Found: 596.8.

5: orange powder, 72.3 mg, 85%. ¹H NMR (400 MHz, CD₃CN) δ 8.48 (d, J = 8.2 Hz, 2H), 8.30 (dd, J = 8.0, 4.0 Hz, 4H), 8.03 (t, J = 7.8 Hz, 2H), 7.84 (t, J = 7.4 Hz, 4H), 7.69 (d, J = 5.2 Hz, 2H), 7.45 (d, J = 14.3 Hz, 4H), 7.37 (t, J = 6.5 Hz, 2H), 2.18 (d, J = 4.8 Hz, 12H). MALDI-TOF (m/z): calcd for C₃₄H₃₂N₆F₆PRu, 771.14. Found: 770.8; calcd for C₃₄H₃₂N₆Ru: 626.18, Found: 624.7.

General procedure for the synthesis of complexes 3 and 6: A mixture of $RuCl_3 \cdot 3H_2O$ (0.20 mmol), and corresponding ligand (3.06 equiv) in ethylene glycol (6 mL) was irradiated by microwave (400 W) under N₂ atmosphere for 30 min. Then the solution was cooled to rt, followed by the addition of 0.5 mL of water and adequate aqueous KPF₆. The mixture was filtered and the obtained solid was washed with water and ethyl ether to afford the desired product.

During the synthesis of **3**, the crude product was further purified by column chromatography using acetonitrile/aqueous KNO_3 as the eluent. The eluate was distilled under reduced pressure, followed by the addition of 7 mL of methanol and 3 mL of saturated aqueous KPF_6 . Then the mixture was filtered and the precipitate was washed with water and ethyl ether to afford the desired product **3**.

3: red powder, 68.3 mg, 35%. ¹H NMR (400 MHz, CD₃CN) δ 8.32 (s, 6H), 7.51 (d, J = 5.8 Hz, 6H), 7.20 (d, J = 4.9 Hz, 6H), 2.52 (s, 18H). MALDI-TOF (m/z): calcd for C₃₆H₃₆N₆F₆PRu, 799.17. Found: 798.8; calcd for C₃₆H₃₆N₆Ru: 654.21. Found: 652.8.

6: orange powder, 180.2 mg, 87%. ¹H NMR (400 MHz, CD₃CN) δ 8.30 (d, J = 8.3 Hz, 6H), 7.83 (d, J = 8.3 Hz, 6H), 7.43 (s, 6H), 2.19 (s, 18H). MALDI-TOF (m/z): calcd for C₃₆H₃₆N₆F₆PRu, 799.17. Found: 798.8; calcd for C₃₆H₃₆N₆Ru: 654.21. Found: 652.8.

3. DFT and TDDFT Calculations

The calculations were performed with Gaussian 09 program¹ by Density Functional Theory (DFT) or TDDFT method at the same calculation level of B3LYP/LANL2DZ for Ru/6-31g* for other atoms/CPCM (acetonitrile solvent included). The geometry optimizations were first carried out at the ground state. In addition, the geometries of the lowest triplet excited state (T₁) were optimized. Then, the emission energies were estimated by the difference value of the energies of T₁ state and S₀ state at optimized T₁ geometries.² The energy of the S₀ state at T₁ geometries was obtained through the single point energy calculation with spin multiplicity of 1.

4. Supplementary Figures and Tables



Figure S1. (a) Optical microscope image in bright field, (b) fluorescence microscope image, and (c) SEM image of microcrystals of $[Ru(bpy)_3](PF_6)_2$.



Figure S2. Cyclic voltammogram (CV) curves and differential pulse voltammogram (DPV) curves of complexes (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6** in 0.1 M CH₃CN. The electrolyte is ${}^{n}Bu_{4}NClO_{4}$. The scan speed is 100 mV/s.



Figure S3. Computational results of (a) 4, (b) 5 and (c) 6 molecules at T₁ geometries in CH₃CN.



Figure S4. The optical microscopic images in bright field of microcrystal (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5** and (f) **6**. The scale bar is 20 μm.



Figure S5. (a) Emission spectrum of compound 2 doped in PMMA film. (b) Lifetime decay of 2 doped in PMMA films. (c) Emission spectra of 2 in CH₃CN with different concentrations (from 0.01 mM to 10 mM). (d) Emission spectra of 2 in mixed solvent of CH₃CN/H₂O (from 10/0 to 0/10) with fixed concentration of 0.01 mM.

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compound	1	2	3	4	5	6
CCDC No.	2090226	2090227	2090228	2090229	2090230	2090231
empirical	$C_{32}H_{28}F_{12}N_6P_2Ru$	$C_{34}H_{32}F_{12}N_6P_2Ru$	$C_{36}H_{36}F_{12}N_6P_2Ru$	$C_{32}H_{28}F_{12}N_6P_2Ru$	$C_{34}H_{32}F_{12}N_6P_2Ru$	$C_{36}H_{36}F_{12}N_6P_2Ru$
formula	·CH₃CN		·CH₃CN			$\cdot 2(CH_3CN)$
formula weight	928.67	915.66	984.77	887.61	915.66	1025.82
crystal system	orthorhombic	triclinic	triclinic	triclinic	monoclinic	triclinic
Space group	P 2 ₁ 2 ₁ 2 ₁	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	P 1 2/c 1	$P\overline{1}$
a (Å)	13.3663(2)	8.59920(10)	8.4468(3)	11.42990(10)	8.0588(2)	11.5706(2)
b (Å)	13.4566(2)	14.2094(2)	14.7471(5)	13.03860(10)	12.1201(3)	14.2041(2)
c (Å)	20.3937(3)	17.6301(2)	17.4886(7)	13.85530(10)	18.7011(5)	14.5719(2)
V (Å ³)	3668.11(9)	2114.82(5)	2140.73(14)	1946.68(3)	1809.61(8)	2119.70(7)
α([°])	90	82.6650(10)	82.842(3)	104.4980(10)	90	62.387(2)
β(°)	90	85.9820(10)	85.689(3)	95.7590(10)	97.822(3)	88.313(2)
γ([°])	90	82.4220(10)	82.845(3)	99.9360(10)	90	87.318(2)
Z value	4	2	2	2	2	2
Density (g/cm ³)	1.682	1.438	1.528	1.514	1.680	1.607
R1 (final)	0.0316	0.0848	0.1007	0.0464	0.0604	0.0314
wR2 (final)	0.0872	0.2416	0.2824	0.1244	0.1565	0.0793
R1 (all)	0.0333	0.0874	0.1181	0.0483	0.0651	0.0351
wR2 (all)	0.0883	0.2436	0.2909	0.1259	0.1585	0.0813

Table S1. Crystallographic data of single crystals.



C-H/F: ① 2.374/② 2.663 Å

Figure S6. Molecular packing of the single crystal X-ray structure of 2 showing the C-H/F interactions.



C-H/F: ① 2.660/② 2.633 /③2.644Å

Figure S7. Molecular packing of the single crystal X-ray structure of 3 showing the C-H/F interactions.



Figure S8. Molecular packing of the single crystal X-ray structure of 5 showing the C-H/F interactions.



C-H/F: ① 2.465/② 2.415 /③2.322/④2.420 Å

Figure S9. Molecular packing of the single crystal X-ray structure of 6 showing the C-H/F interactions.

b) View from b axis



Figure S10. Molecular packing of 1 in crystal viewing from (a) a axis, (b) b axis and (c) c axis.



Figure S11. Powder XRD patterns (red curves) of microcrystals of (a) 2, (b) 3, (c) 5 and (d) 6 and calculated patterns (black curves) from corresponding single crystal data using Mercury software.

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Miller index { <i>hkl</i> }	$E_{\rm att}$ (kJ/mol)	Total facet area (a.u.)	%Total facet area			
{101}s	-84.7	7.53×10^{4}	45.68			
$\{002\}s$	-96.9	2.13×10^4	12.94			
{011}s	-112.3	4.48×10^4	27.19			
{110}s	-114.6	2.34×10^4	14.19			

Table S2. Attachment energies of various crystal facets of microcrystal 1 calculated using the Materials Studio package.

Table S3. Attachment energies of various crystal facets of microcrystal 4 calculated using the Materials Studio package.

Miller index { <i>hkl</i> }	$E_{\rm att}$ (kJ/mol)	Total facet area (a.u.)	%Total facet area	
{001}s	-27.2	7.16×10^{3}	31.08	
{010}s	-32.1	5.83×10^{3}	25.29	
{01-1}s	-37.6	2.48×10^{3}	10.75	
{100}s	-39.6	4.38×10^{3}	19.00	
{10-1}s	-41.1	2.10×10^{3}	9.14	
{1-10}s	-48.4	1.09×10^{3}	4.75	



Figure S12. TEM images and corresponding SAED patterns of microcrystals (a) **2**, (b) **3**, (c) **5** and (d) **6**. The scale bars are 4 μ m, 5 μ m, 500 nm and 2 μ m, respectively. No SAED patterns were obtained for **2** due to the high thickness of the crystal.



Figure S13. Molecular packing of the single crystal X-ray structure of **3** showing the intermolecular π/π interactions.



Figure S14. (a-c,g-i,m) CVs and (d-f,j-l,n) ECL intensity profiles of the solution of (a,d) **1**, (b,e) **2**, (c,f) **3**, (g,j) **4**, (h,k) **5**, (i,l) **6**, and (m,n) $Ru(bpy)_3(PF_6)_2$ (0.4 mM) in 0.1 M TBAP/CH₃CN containing 50 mM of TPrA. The working electrode was a glassy carbon disk (d = 3 mm).



Figure S15. CV and DPV curves of the microcrystals of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6 in 0.2 M PBS aq. solution (pH = 8.0). The microcrystals were deposited on the glassy carbon working electrode.



Figure S16. (a) CV and DPV of microcrystal of $Ru(bpy)_3(PF_6)_2$ immobilized on a glassy carbon electrode surface. Electrolyte solution: 0.2 M PBS aq. solution (pH = 8.0). (b) CV (black curve) and ECL intensity profile (red curve) of the immobilized microcrystal of $Ru(bpy)_3(PF_6)_2$ in 0.2 M PBS (pH = 8.0) containing 50 mM TPrA. (c) ECL stability tests upon continuous CV scans.



Figure S17. A comparison of the ECL (red curve) of microcrystals, photoluminescence (PL, black curve) of microcrystals, and PL in CH₃CN solution (blue) of (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.



Figure S18. Time-dependent ECL intensity profile of the microcrystal of **6** upon applying a constant potential at +1.3 V for 350 s.



Figure S19. (a) ECL intensity profile of microcrystal of **6** before and after the addition of Hyp (0.1 mM). (b) Variation of the ECL intensity upon five cycles of recyclable sensing of Hyp (1 mM).

5. NMR Spectra



Figure S20. ¹H NMR spectrum of 1 in CD₃CN.



Figure S21. ¹H NMR spectrum of 2 in CD₃CN.



Figure S22. ¹H NMR spectrum of 3 in CD₃CN.



Figure S23. ¹H NMR spectrum of 4 in CD₃CN.



Figure S25. ¹H NMR spectrum of 6 in CD₃CN.

6. References

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