Encapsulation of the [Ru(bpy)₃]²⁺ Luminophore in a Unique Hydrogen-Bonded Host Framework

Marcel Handke, Yang Wu, Yuantao Li, Chunhua T. Hu and Michael D. Ward *

Department of Chemistry and Molecular Design Institute, New York University, 100 Washington Square East, New York, New York 10003-6688, United States Email: <u>mdw3@nyu.edu</u>

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S1. Material and Methods

All chemicals were commercially available and used as received without further purification. Guanidine hydrochloride and sodium nitrate were purchased from Sigma-Aldrich. Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ($[Ru(bpy)_3]Cl_2$) was purchased from Acros Organics.

¹H NMR spectra were recorded in DMSO-d₆ solution using a BRUKER Advance 600 (600 MHz) spectrometer. Luminescence measurements were performed using a FluoroMax-4 spectrofluorometer (HORIBA Scientific).

S2. Synthesis and Crystal Image

The ligand hexa(4-sulfophenyl)benzene ($H_6(HSPB)$) was synthesized according to the published procedure [S1].

101.5 mg (0.1 mmol) $H_6(HSPB)$, 57.3 mg (0.6 mmol) guanidinium chloride and 74.9 mg (0.1 mmol) [Ru(bpy)_3]Cl_2·6H_2O were dissolved in 0.8 ml of a freshly prepared mixture of dimethylformamide (DMF):water:formic acid (2:1:1 by volume). The resulting solution was placed in a desiccator and the solvent was allowed to evaporate, affording brilliant red crystals (Figure S1) after approximately one week. NMR experiments for determining composition were performed after rinsing the crystal surfaces in DMF and CHCl₃ to remove any extraneous material.

¹H-NMR (600 MHz, DMSO-d₆): δ [ppm] = 8.84 (d, 6H, CH of [Ru(bpy)₃]), 8.24 (br, NH of dimethylammonium ions), 8.14 (m, 6H, CH of [Ru(bpy)₃]), 8.13 (s, 2H, HCO₂H), 7.95 (s, 2H, H-CO of DMF), 7.74 (d, 6H, CH of [Ru(bpy)₃]), 7.52 (m, 6H, CH of [Ru(bpy)₃]), 7.10 (d, 12H, CH of HSPB), 6.94 (s, 24H, NH₂ of guanidinium), 6.82 (d, 12H, CH of HSPB), 3.40 (br, H₂O), 2.89 (s, 6H, CH₃ of DMF), 2.73 (s, 6H, CH₃ of DMF), 2.47 (t, 3.6H, CH₃ of dimethylammonium ions). Formula: G₄(HSPB)[Ru(bpy)₃](DMF)₂(HCO₂H)₂(H₂O)(DMA)_{0.6} (the amount of water was deduced from single crystal structure data; charge balance is assumed to be realized through deprotonated formic acid or chloride ions).



Figure S1. Single crystals of compound 1.

S3. Unit Cells and Single Crystal Structure Data

A single crystal of compound 1 was selected and mounted on a Bruker D8 APEX-II CCD diffractometer for data collection. The X-ray generated from a sealed Mo tube was monochromated with a graphite crystal and collimated with a 0.5 mm MONOCAP, providing a focused spot beam (Mo-K α λ = 0.71073 Å). The temperature is controlled by an Oxford Cryosystems 700+ Cooler. The data were collected with the ω scan method at 100 K. The dataset was processed with the INTEGRATE program of the APEX2 software for reduction and cell refinement [S2]. Multi-scan absorption corrections were applied by the SCALE program for the area detector. The structure was solved by intrinsic phasing methods (SHELXT) [S3], and the structure models were completed and refined using the full-matrix least-square methods on F^2 (SHELXL) [S4]. Non-hydrogen atoms in the structure were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.95-1.00 Å) and included as riding with Uiso(H) = 1.2 or 1.5 Ueg(non-H). All of the phenyl rings, one of the guanidinium ions, formic acids, and DMF were disordered, so their geometry and displacements were constrained and restrained with theoretical values. Some residual peaks in the difference Fourier map did not form any meaningful chemically entities so their contributions were treated with the PLATON/SQUEEZE program [S5]. The selected crystallographic parameters for compound **1** are listed in Table S1. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. 1981967. Copies of available material can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

	G₄HSPB·[Ru(bpy)₃]
Formula based on X-ray	C _{80.21} H _{81.43} N ₁₉ O _{22.43} Ru S ₆
Formula weight (g/mol)	1963.90
Т (К)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group (no.)	<i>C</i> 2/ <i>m</i> (12)
a (Å)	16.8829(11)
b (Å)	35.023(2)
c (Å)	15.9550(10)
β (°)	91.0190(10)
V (Å ³)	9432.5(10)
Z	4
<i>D</i> (cal.) (g/cm ³)	1.386
μ (mm ⁻¹)	0.378
<i>F</i> (000)	4071
Crystal size (mm ³)	0.34 × 0.50 × 0.56
θ range (°)	1.276 - 28.269
Total reflections collected	74145
Independent reflections	11888
Observed reflections $(I > 2\sigma(I))$	9962
R _{int}	0.0226
No. of refined parameters	557
Data completeness (%)	100
GOF	1.738
$R_1 \left[l > 2\sigma(l) \right]$	0.0827
wR_2 (all data)	0.3128

 Table S1. Single crystal structure data for compound 1.

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \ w R_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]\}^{1/2}$

R(D)+F	R(A)+0.50,	d(HA)	< R(H)+R(A	A)-0.12	Ang., D-H	.A > 100.0 Deg
Donor	H	Acceptor	D - H	HA	DA	D - HA
N4	H4A	04	0.88	2.18	3.036(6)	166
N4	H4B	01	0.88	2.02	2.902(7)	176
N4	H4B	01'	0.88	2.16	2.929(19)	145
N5	H5A	02	0.88	2.18	3.042(8)	165
N5	H5A	01'	0.88	2.02	2.810(19)	149
N5	H5B	013_\$3	0.88	2.54	3.095(13)	122
N6	H6A	05	0.88	2.07	2.900(6)	157
N6	H6B	012	0.88	2.37	3.182(5)	154
N7	H7A	06	0.88	2.10	2.952(8)	161
N7	H7B	012	0.88	2.52	3.350(5)	157
N8	H8A	07	0.88	2.12	2.959(5)	158
N8	H8B	07_\$2	0.88	2.12	2.959(5)	160
N9	H9A	02	0.88	1.99	2.844(12)	162
N9	H9A	01'	0.88	2.46	3.15(2)	135
N9	H9B	010'_\$4	0.88	2.32	3.01(3)	135
N9	H9B	011_\$4	0.88	2.01	2.870(14)	166
N10	H10A	01	0.88	2.17	3.014(11)	160
N10	H10A	01'	0.88	2.26	3.00(2)	142
N10	H10B	010	0.88	2.02	2.884(14)	165
N10	H10B	011_\$1	0.88	2.20	2.975(14)	146
N11	H11A	09	0.88	2.07	2.874(14)	152
N11	H11A	011_\$1	0.88	1.97	2.782(14)	153
N11	H11B	019	0.88	2.42	3.208(19)	148
N11	H11B	09'_\$3	0.88	2.50	3.07(2)	123

Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) <

Table S2. Hydrogen bond distances about guanidinium ions

Symmetry operations

\$1 = 1-x,y,1-z
\$2 = x,1-y,z
\$3 = 1/2-x,1/2-y,1-z

4 = -1/2 + x, 1/2 - y, z



Fig. S2. Hydrogen bonding of guanidinium ion with C44. Bond geometry refers to Table S2.



Fig. S3. Hydrogen bonding of guanidinium ion with C45. Bond geometry refers to Table S2.



Fig. S4. Hydrogen bonding of guanidinium ion with C46. Bond geometry refers to Table S2.

S4. Luminescence measurements

Luminescence measurements were performed after rinsing the crystal surface with DMF and $CHCI_3$.



Figure S5. Luminescence measurements of compound **1**, acquired for two different single crystals (λ_{exc} = 450 nm; red, λ_{max} = 611 nm; black, λ_{max} = 611 nm).

S5. References

- [S1] Y. Liu, A. Comotti, C. Hu and M. D. Ward, Science, 2011, 333, 436.
- [S2] **APEX2**, version 2014.11.0, *Program for Bruker CCD X-ray Diffractometer Control and Data Analysis*, Madison, WI.
- [S3] SHELXT, G. M. Sheldrick, Acta Crystallogr. 2015, A71, 3.
- [S4] SHELXL, G. M. Sheldrick, Acta Crystallogr. 2015, C71, 3.
- [S5] PLATON, A. L. Spek, Acta Crystallogr. 2015, C71, 9.