Electronic Supplementary Information

The role of bridging ligand in hydrogen generation by photocatalytic Ru/Pd assemblies

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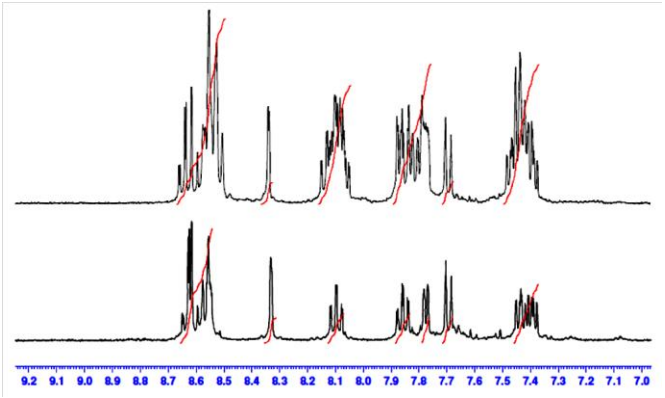


Fig. S1a *^{1}H NMR spectra for non-deuteriated (top) and deuteriated(bottom) complex of $[Ru(bpy)_2(2,5\text{-}bpp)]^{2+}$ (**1**) in in CD_3CN.*

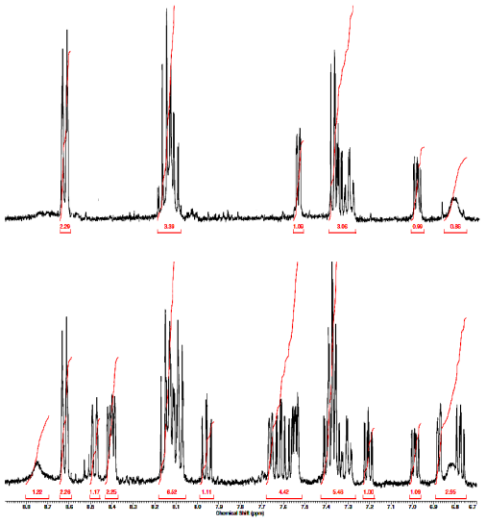


Fig. S1b *^{1}H NMR spectra for non-deuteriated (bottom) and deuteriated (top) complex of $[Ru(bpy)_2(2,6\text{-}bpp)]^{2+}$ (**2**) in CD_3CN.*

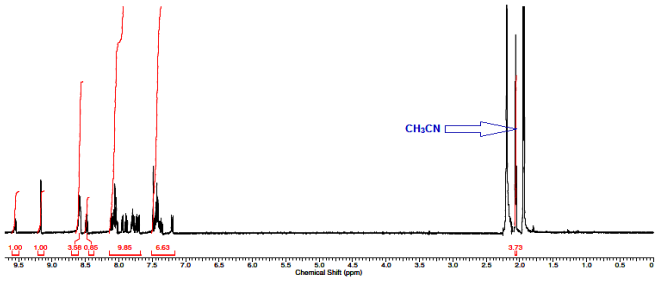


Fig. S2a. ^{1}H-NMR of $[Ru(bipy)_2(2,5\text{-bpp})PdCl(CH_3CN)]^{2+}$ (**1a**) in CD_3CN**.**

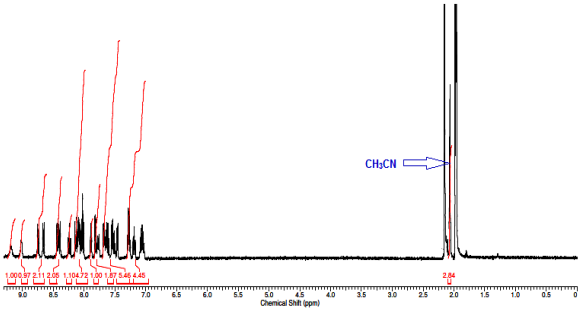


Fig. S2b: *^{1}H-NMR of $[Ru(bpy)_2(2,6\text{-bpp})PdCl(CH_3CN)]^{2+}$ (**2a**) in CD_3CN*

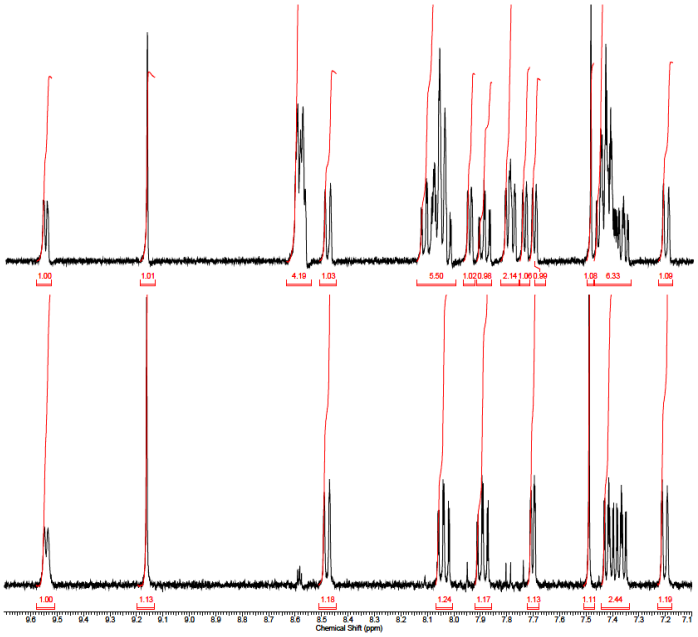


*Fig. S2c. ^{1}H NMR spectra for non-deuteriated (top) and deuteriated (bottom) complexes of **1a.***

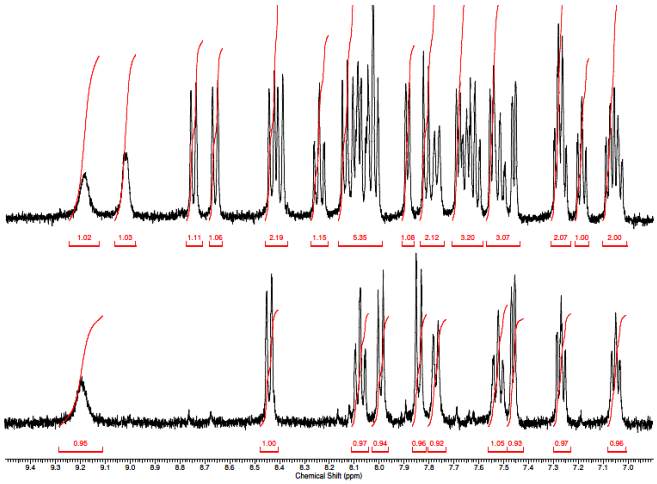
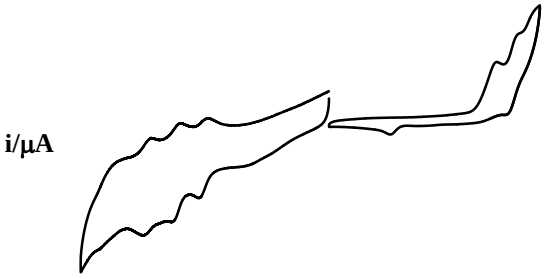
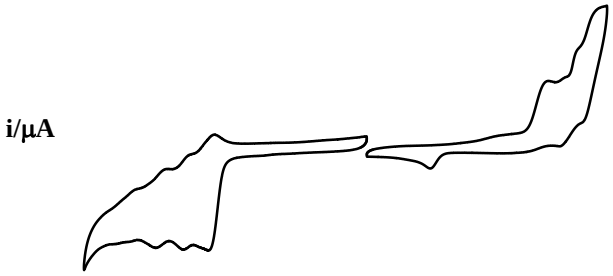


Fig. S2d. ^{1}*H NMR spectra for non-deuteriated (top) and deuteriated (bottom) complexes of* ***2a***



1a in DMF/0.1 M Bu_4NPF_6. ν = 20 mV/sec. E vs. Fc/Fc^+.



2a in DMF/0.1 M Bu_4NPF_6. ν = 20 mV/sec. E vs. Fc/Fc^+

Fig. S3 Cyclic Voltammograms for **1a** and **2a**

Table S1 Presentation of percent contributions (M06 functional) of selected parts of **1a** in the singlet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions β molecular orbitals									
No.	Sym	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
184	A	L+5	-1,54	1	1	22	8	64	4	1	0	L+5	-1,54	1	1	22	8	64	4	1	0
183	A	L+4	-1,73	43	4	19	25	7	1	0	0	L+4	-1,73	43	4	19	25	7	1	0	0
182	A	L+3	-1,98	0	0	0	23	11	51	3	12	L+3	-1,98	0	0	0	23	11	51	3	12
181	A	L+2	-2,35	93	7	0	0	0	0	0	0	L+2	-2,35	93	7	0	0	0	0	0	0
180	A	L+1	-2,42	91	4	1	2	2	0	0	0	L+1	-2,42	91	4	1	2	2	0	0	0
179	A	LUMO	-2,71	5	2	28	39	23	3	0	0	LUMO	-2,71	5	2	28	39	23	3	0	0
178	A	HOMO	-6,12	10	84	2	4	0	1	0	0	HOMO	-6,12	10	84	2	4	0	1	0	0
177	A	H-1	-6,28	12	75	5	6	0	1	0	0	H-1	-6,28	12	75	5	6	0	1	0	0
176	A	H-2	-6,31	18	77	3	1	0	0	0	0	H-2	-6,31	18	77	3	1	0	0	0	0
175	A	H-3	-7,18	0	0	6	11	12	38	0	33	H-3	-7,18	0	0	6	11	12	38	0	33
174	A	H-4	-7,31	0	0	0	8	3	64	0	25	H-4	-7,31	0	0	0	8	3	64	0	25
173	A	H-5	-7,34	1	2	15	29	28	13	0	12	H-5	-7,34	1	2	15	29	28	13	0	12

Table S2 Presentation of percent contributions (M06 functional) of selected parts **2a** in the singlet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions β molecular orbitals									
No.	Sym	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
184	A	L+5	-1,63	68	4	13	4	5	5	0	1	L+5	-1,63	68	4	13	4	5	5	0	1
183	A	L+4	-1,93	12	1	2	19	16	38	2	9	L+4	-1,93	12	1	2	19	16	38	2	9
182	A	L+3	-2,2	9	3	30	36	13	7	1	1	L+3	-2,2	9	3	30	36	13	7	1	1
181	A	L+2	-2,46	74	3	7	9	6	2	0	0	L+2	-2,46	74	3	7	9	6	2	0	0
180	A	L+1	-2,48	89	6	2	2	0	0	0	0	L+1	-2,48	89	6	2	2	0	0	0	0
179	A	LUMO	-2,67	20	6	3	36	28	5	1	1	LUMO	-2,67	20	6	3	36	28	5	1	1
178	A	HOMO	-6,17	12	81	5	2	0	0	0	0	HOMO	-6,17	12	81	5	2	0	0	0	0
177	A	H-1	-6,43	11	79	2	6	2	0	0	0	H-1	-6,43	11	79	2	6	2	0	0	0
176	A	H-2	-6,52	16	80	3	1	0	0	0	0	H-2	-6,52	16	80	3	1	0	0	0	0
175	A	H-3	-7,03	1	2	16	43	15	21	1	1	H-3	-7,03	1	2	16	43	15	21	1	1
174	A	H-4	-7,22	2	0	0	0	6	47	0	44	H-4	-7,22	2	0	0	0	6	47	0	44
173	A	H-5	-7,3	4	1	1	8	4	58	0	25	H-5	-7,3	4	1	1	8	4	58	0	25

Table S3 Presentation of percent contributions (M06 functional) of selected parts of **1a** in the triplet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions β molecular orbitals									
No.	Sym	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
185	A	L+5	-1,66	25	22	15	11	21	4	0	1	L+7	-1,58	94	4	0	0	0	0	0	0
184	A	L+4	-1,72	2	4	2	23	12	46	2	10	L+6	-1,65	67	3	0	7	4	16	1	3
183	A	L+3	-1,78	49	44	2	4	0	0	0	0	L+5	-1,68	29	2	0	16	8	36	2	7
182	A	L+2	-1,9	86	5	4	3	1	0	0	0	L+4	-1,88	91	4	2	2	0	0	0	0
181	A	L+1	-2,77	97	3	0	0	0	0	0	0	L+3	-2,45	1	2	34	38	21	3	0	0
180	A	LUMO	-2,79	97	3	0	0	0	0	0	0	L+2	-2,76	97	3	0	0	0	0	0	0
179	A	SOMO	-4,16	1	2	36	45	13	3	0	0	L+1	-2,78	97	3	0	0	0	0	0	0
178	A	SOMO-1	-6,92	0	1	12	22	21	28	0	16	LUMO	-4,36	9	82	3	5	1	0	0	0
177	A	HDOMO	-7,08	0	0	2	10	7	63	0	18	HDOMO	-6,68	1	4	20	41	27	6	0	2
176	A	H-3	-7,09	0	1	6	15	17	37	0	24	H-1	-7,02	0	2	0	4	9	46	0	38
175	A	H-4	-7,25	0	0	0	3	1	46	1	50	H-2	-7,06	0	0	0	9	4	72	0	14
174	A	H-5	-7,42	1	8	14	31	0	43	2	0	H-3	-7,18	2	16	15	31	1	32	2	1

Table S4 Presentation of percent contributions (M06 functional) of selected parts of **2a** in the triplet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions β molecular orbitals									
No.	Sym	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl	MO	eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
185	A	L+5	-1,66	73	4	13	4	1	4	0	0	L+7	-1,47	29	8	20	2	38	2	0	0
184	A	L+4	-1,9	5	1	2	22	12	45	3	11	L+6	-1,67	64	6	18	4	1	6	0	1
183	A	L+3	-2,03	4	2	49	35	4	5	1	0	L+5	-1,91	6	1	3	20	13	44	3	10
182	A	L+2	-2,24	10	2	1	33	48	4	0	1	L+4	-2,04	11	5	29	31	17	6	1	0
181	A	L+1	-2,35	94	3	0	1	2	0	0	0	L+3	-2,31	50	3	3	19	23	2	0	0
180	A	LUMO	-2,61	88	4	1	3	3	1	0	0	L+2	-2,4	60	9	8	14	8	1	0	0
179	A	SOMO	-5,71	26	58	3	12	1	1	0	0	L+1	-2,62	74	7	0	9	7	1	0	0
178	A	SOMO-1	-6,96	3	7	12	43	16	18	1	0	LUMO	-3,16	11	84	3	1	1	0	0	0
177	A	HDOMO	-7,16	0	0	0	1	6	49	0	44	HDOMO	-6,42	14	81	2	3	1	0	0	0
176	A	H-3	-7,22	3	9	0	9	3	61	0	15	H-1	-6,71	11	84	5	1	0	0	0	0
175	A	H-4	-7,31	7	45	5	6	1	14	0	21	H-2	-6,99	2	3	12	45	15	22	1	0
174	A	H-5	-7,35	14	59	3	1	0	9	0	13	H-3	-7,16	0	0	0	1	6	49	0	44

Table S5 Presentation of percent contributions (M06 functional) of selected parts of **1a** in the doublet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions of β molecular orbitals									
No.	Sym		eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl		eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
185	A	L+5	-1,17	92	7	0	0	1	0	0	0	L+6	-1,1	90	8	1	1	0	0	0	0
184	A	L+4	-1,2	9	3	26	12	46	3	1	0	L+5	-1,17	93	7	0	0	0	0	0	0
183	A	L+3	-1,43	85	4	5	4	1	0	0	0	L+4	-1,42	80	4	3	5	2	6	0	1
182	A	L+2	-1,47	1	0	0	22	11	53	2	10	L+3	-1,43	10	1	0	20	10	48	2	9
181	A	L+1	-2,16	92	7	0	0	0	0	0	0	L+2	-1,99	8	4	26	33	25	3	1	0
180	A	LUMO	-2,23	94	5	0	1	1	0	0	0	L+1	-2,15	92	7	0	0	0	0	0	0
179	A	SOMO	-3,62	2	3	28	43	21	3	0	0	LUMO	-2,25	88	3	3	4	2	0	0	0
178	A	HDOMO	-5,7	9	82	3	4	1	1	0	0	HDOMO	-5,65	8	75	4	10	3	1	0	0
177	A	H-2	-5,89	16	74	2	6	0	1	0	0	H-1	-5,82	13	74	6	6	0	1	0	0
176	A	H-3	-5,91	15	76	6	2	0	0	0	0	H-2	-5,88	18	74	4	3	1	0	0	0
175	A	H-4	-6,6	1	4	19	32	26	12	0	6	H-3	-6,33	3	13	19	38	23	3	0	1
174	A	H-5	-6,86	0	0	0	10	4	75	0	11	H-4	-6,83	0	0	1	2	10	51	0	35

Table S6 Presentation of percent contributions (M06 functional) of selected parts of **2a** in the doublet state to the frontier orbitals along with the respective eigenvalue in eV and symmetry.

		Percent contributions of α molecular orbitals										Percent contributions β molecular orbitals									
No.	Sym		eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl		eV	Bipy	Ru	A-py	B-py	C-py	Pd	ACN	Cl
185	A	L+5	-1,2	79	6	4	4	2	5	0	0	L+6	-1,13	80	3	1	4	5	6	0	1
184	A	L+4	-1,3	58	3	7	7	7	15	0	2	L+5	-1,24	62	3	0	6	7	17	1	3
183	A	L+3	-1,5	35	2	7	13	10	26	1	5	L+4	-1,41	50	4	20	6	4	13	1	3
182	A	L+2	-1,7	8	4	42	31	7	7	1	0	L+3	-1,56	19	4	35	27	8	6	1	0
181	A	L+1	-2,1	87	4	3	2	3	1	0	0	L+2	-1,91	12	6	11	33	27	9	1	2
180	A	LUMO	-2,2	94	6	0	0	0	0	0	0	L+1	-2,14	84	6	1	5	3	2	0	0
179	A	SOMO	-3,6	5	6	3	47	30	7	1	1	LUMO	-2,21	94	6	0	0	0	0	0	0
178	A	HDOMO	-5,7	11	81	4	3	0	1	0	0	HDOMO	-5,59	10	82	3	4	0	1	0	0
177	A	H-2	-5,9	13	73	1	9	4	0	0	0	H-1	-5,69	12	65	2	14	6	1	0	0
176	A	H-3	-6	15	80	4	1	0	0	0	0	H-2	-5,96	16	79	4	1	0	0	0	0
175	A	H-4	-6,4	2	5	12	42	19	19	1	0	H-3	-6,19	3	11	10	43	16	15	1	0
174	A	H-5	-6,7	1	1	0	6	6	68	0	17	H-4	-6,65	2	0	0	1	10	55	0	32