Electronic Supporting Information

Wavelength dependent photocatalytic H_2 generation using Iridium-Pt/Pd complexes

Suraj Soman,[a] Gurmeet Singh Bindra,[a] Avishek Paul,[a] Robert Groarke,[a] Jennifer C. Manton,[a] Finn M. Connaughton,[a] Martin Schulz[a,b] Danilo Dini,[a,c] Conor Long,[a] Mary T. Pryce[a] and Johannes G. Vos[a],*

[a] *SRC for Solar Energy Conversion, School of Chemical Sciences, Dublin City University, Dublin 9, Dublin, Ireland, email: han.vos@dcu.ie*

[b] *Lehrstuhl für Pharmazeutische Radiochemie, Technische Universität München,Walther-Meißner-Str. 3, 85748 Garching, Germany*

[c] *Department. of Chemistry, University of Rome La Sapienza, Rome, Italy*

Experimental details

The reagents employed during the course of all experiments were purchased from Sigma-Aldrich and used without further purification. $[Ir(ppy)_2Cl]_2$ was prepared using the previously reported procedures[1]. The ^1H NMR, and COSY were recorded on a Bruker AC400 (400 MHz) NMR spectrometer and Bruker Avance:3 (600 MHz) instrument using deuteriated DMSO. The chemical shifts were recorded relative to TMS and spectra were converted from their free induction decay (FID) profiles using XWIN-NMR software. Carbon, hydrogen and nitrogen (CHN) elemental analyses were carried out on an Exador Analytical CE440 by the Microanalytical Department, University College Dublin. The CHN analyzer used is an Exador analytical CE440. The UV/Vis spectra were carried out on a Gilent 8453 UV-Vis Spectrophotometer, the spectra were obtained in the ultraviolet region in the wavelength range 200 to 800 nm.

Synthesis of $[Ir(ppy)_2Cl]_2$

Iridium trichloride hydrate (1 g, 2.8 mmol) was combined with 2-phenylpyridine (1.76 g, 11.3 mmol), dissolved in a mixture of 2- methoxyethanol (75 ml) and water (25 ml), and refluxed for 24 h. The solution was cooled to room temperature, and the yellow precipitate was collected on a glass frit. The precipitate was washed with ethanol (60 ml) and acetone (60 ml) and then dissolved in dichloromethane (75 ml) and filtered. Toluene (25 ml) and hexane (10 ml) were added to the filtrate which was then reduced in volume, and cooled to give crystals of $[Ir(ppy)_2Cl]_2$. (Yield 1.12 g, 74 %). ^1H NMR (400 MHz, DMSO), δ (ppm): 5.64 (d, 1H), 6.23 (d, 1H), 6.67 (t, 1H), 6.74 (t, 1H), 6.82 (t, 1H), 6.88 (t, 1H), 7.43 (t, 1H), 7.55 (t, 1H), 7.71 (d, 1H), 7.77 (d, 1H), 7.99 (t, 1H), 8.07 (t, 1H), 8.16 (d, 1H), 8.24 (d, 1H), 9.51 (d, 1H), 9.78 (d, 1H). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 5.89 (d, 1H), 6.53 (t, 1H), 6.74 (m, 2H), 7.45 (d, 1H), 7.70 (t, 1H), 7.84 (d, 1H), 9.20 (d, 1H). Elemental analysis for complex $[Ir(ppy)_2Cl]_2$, $C_{44}H_{32}Cl_2Ir_2N_4$; (calculated) : C : 49.29, H : 3.01, N : 5.23; (found) : C : 49.38, H : 3.00, N : 5.22.

Synthesis of Bridging Ligand BPP (2-(6-(pyridin-2-yl)pyridin-3-yl)pyridine)

In a dried two neck round bottom flask 0.299 g (0.258 mmol) of $Pd(PPh_3)_4$ and 2 g (8.44 mmol) of 2,5-dibromobipyridine were added under a nitrogen atmosphere. During the addition of 38.7 ml (16.8 mmol) of 2-pyridylzinc bromide to the reaction mixture, the temperature was kept at 0 ^{0}C. The reaction mixture was then stirred overnight at room temperature under a nitrogen atmosphere. A white precipitate formed. The reaction mixture was poured in a saturated aqueous solution of EDTA/Na_2CO_3 until the precipitate dissolves and yellow flakes come. The aqueous solution was then extracted with dichloromethane and dried over $MgSO_4$. The dichloromethane was allowed to evaporate at room temperature and the crude product was purified by alumina column using hexane/ethyl acetate (9:1). The second spot in TLC is the desired product. Yield (1.57 g, 6.75 mmol, 80 %). ^{1}H NMR (400 MHz, DMSO), δ (ppm): 7.2 (t, 1H), 7.3 (t, 1H), 7.78 (m, 2H), 7.8 (t, 1H), 8.44-8.37 (m, 2H), 8.5 (d, 1H), 8.7-8.65 (m, 2H), 9.3 (s, 1H). Elemental analysis for ligand BPP, $C_{15}H_{11}N_3$; (calculated) : C : 77.23, H : 4.75, N : 18.01; (found) : C : 77.25, H : 4.71, N : 17.98.

Synthesis of $[Ir(ppy)_2(BPP)]PF_6$ (a)

The ligand BPP (0.050 g, 0.2146 mmol) was weighed and transferred to a 100 ml round bottom flask (R.B) to which 10ml of solvent, DCM: EtOH (2:1) was added and stirred at 60 ^{0}C for 20 minutes to which the dichlorobridged dimer, $[Ir(ppy)_2Cl]_2$ (0.115 g, 0.1072 mmol) dissolved in 20 ml of solvent was added slowly over an hour. The reaction was heated at reflux (90 ^{0}C) for 7 hours. The reaction mixture was cooled and solvents were removed under vacuum, 10 ml of deionised water was added and saturated aqueous NH_4PF_6 (1 g in 10 ml of deionised water) was added resulting in the precipitation of the product as $[Ir(ppy)_2(BPP)].PF_6$ which was recrystalised from Acetone:H_2O (2:1), vacuum filtered and dried. Yield (0.149 g, 79 %). ^{1}H NMR (600 MHz, DMSO), δ (ppm): 6.21 (1H, d, (ppy)), 6.26 (1H, d, (ppy)), 6.94 (2H, m, (ppy)), 7.06 (2H, m, (ppy)), 7.17 (2H, m, (ppy)), 7.43 (1H, m, 10(BPP)), 7.67 (1H, d, (ppy)), 7.72 (1H, t, (BPP)), 7.78 (1H, d, (ppy)), 7.86 (1H, d, (BPP)), 7.91 (1H, d, (ppy)), 7.94 (4H, m, dd, (ppy),(BPP)), 8.28 (3H, m, (BPP),(ppy)), 8.56 (1H, d, (BPP)), 8.63 (1H, s, (BPP)), 8.852 (1H, d, (BPP)), 8.98 (1H, d, (BPP)), 8.99 (1H, d, (BPP)). Elemental analysis for complex **(a)**, ($C_{37}H_{27}F_6IrN_5P$); (calculated) : C : 50.57, H : 3.10, N : 7.97; (found) : C : 50.92, H : 3.10, N : 7.98.

Synthesis of $[(ppy)_2Ir(BPP)PtCl]_2(PF_6)_2$ (b)

Equimolar amounts of $[Ir(ppy)_2(BPP)]PF_6$ (0.05 g, 0.000055 mmol) and K_2PtCl_4 (0.023 g, 0.000055 mmol) were added together in an RB containing methanol (10 ml) and refluxed for 24 hours, the dimer complex get precipitated out itself in solution which was filtered, washed with diethyl ether, hexane and vacuum dried. The product was recrystalised from Acetone: Diethylether (2:1), vacuum filtered and dried. Yield (0.040 g, 82 %). ^1H NMR (600 MHz, DMSO), δ (ppm): 6.23 (1H, d, (ppy)), 6.30 (1H, d,(ppy)), 6.91 (1H, t, (ppy)), 7.03 (2H, dd, (ppy)), 7.11 (2H, dd, (ppy)), 7.18 (2H, t, (ppy)), 7.66 (1H, d, (ppy)), 7.73 (2H, m, (BPP)), 7.82 (1H, s, (BPP)), 7.88 (1H, d, (BPP)), 7.90 (1H, d, (BPP)), 7.94 (5H, m, (ppy), (BPP)), 8.25 (5H, m), 8.24 (3H, m, (ppy), (BPP)), 8.25 (1H, m, (BPP)), 8.34 (1H, d, (ppy)), 9.51 (1H, d, (BPP)), 9.55 (1H, s, (BPP)). Elemental analysis for complex **(b)**, $(C_{74}H_{52}Cl_2F_{12}Ir_2N_{10}P_2Pt_{24})H_2O$; (calculated) : C : 39.77, H : 2.44, N : 6.27; (found) : C : 39.47, H : 2.38, N : 6.09.

Synthesis of $[(ppy)_2Ir(BPP)PdCl]_2(PF_6)_2$ (c)

Equimolar amounts of $[Ir(ppy)_2(BPP)]PF_6$ (0.05 g, 0.000055 mmol) and $(NH_4)_2PdCl_2$ (0.015 g, 0.000055 mmol) were added together in a round bottom flask containing methanol (10 ml) and the solution was refluxed for 24 hours. The dimer complex precipitated out, and the solution was filtered, washed with diethyl ether, hexane and vacuum dried. The product was recrystalised from acetone:diethylether (2:1), vacuum filtered and dried. Yield (0.048 g, 86 %). ^1H NMR (600 MHz, DMSO), δ (ppm): 6.22 (1H, d, (ppy)), 6.26 (1H, d, (ppy)), 6.88 (1H, t, (ppy)), 6.94 (2H, m, (ppy), (BPP)), 7.02 (1H, t, (ppy)), 7.06 (1H, t, (ppy)), 7.15 (2H, m, (ppy)), 7.53 (1H, t, (BPP)), 7.63 (2H, t, (ppy), 7.64 (1H, s, (BPP)), 7.80 (1H, d, (ppy)), 7.85 (1H, d, (ppy)), 7.90 (5H, m, (ppy), (BPP)), 8.07 (1H, t, (BPP)), 8.23 (3H, m, (BPP)), 8.46 (1H, d, (BPP)), 9.09 (1H, s, (BPP)). Elemental analysis for complex **(c)**, $(C_{74}H_{52}Cl_2F_{12}Ir_2N_{10}P_2Pd_2)3H_2O$; (calculated) : C : 42.82, H : 2.72, N : 6.75; (found) : C : 42.31, H : 2.78, N : 6.45.

Photocatalytic experiments

Photocatalytic hydrogen production experiments were carried out using a home-built air-cooling apparatus for maintaining the solutions at room temperature (in this case 22 ^{0}C), during irradiation using LEDs (fig. S1). Acetonitrile used was dried over calcium hydride and the triethylamine dried over sodium before being freshly distilled under nitrogen. The samples for the irradiation experiments were prepared in GC vials (diameter = 13 mm, VWR) with a known headspace of 3 ml and a headspace-solution ratio of 3/2. Furthermore the GC vials were charged in the dark and under nitrogen stream. After adding of 2.15 M of dry triethylamine (V = 0.6 ml) and 10 % volume of degassed water the final concentration of Ir-Pd/Pt in acetonitrile was 6.0×10^{-5} M. Subsequently, the GC vials were irradiated with 470 nm wavelength LED's for 18 hours. After irradiation, 20 µl samples were drawn from the headspace and injected immediately into the GC apparatus. The hydrogen evolved was measured by headspace GC on a Varian CP3800 chromatograph, with a thermal conductivity detector and a CP7536 Plot Fused Silica 25 MX 0.32 MMID column (length 25 m, layer thickness 30 µm) with nitrogen as the carrier gas (purity 99.999 %). Irradiation experiments and hydrogen measurements were repeated several times.

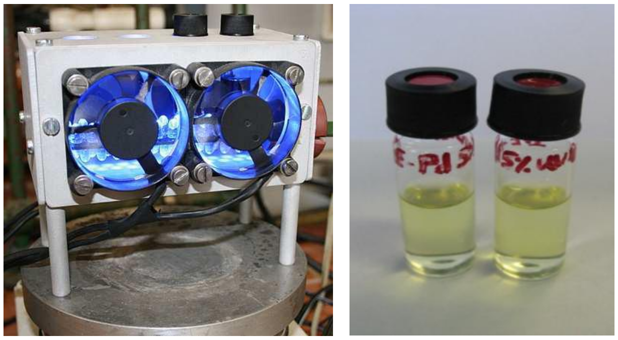

Fig. S1 On the left side there is the photo microreactor and on the right side a commercial available GC vial with septum and filled with reaction mixture.

Blue light (470 nm) experiment for the dinuclear Ir-Pt complex (ACN, TEA, 18h irradiation)

Complex(Conc.6x10^{-5}M)	H_2O %	Area (mV/sec)	TON (average)
	10%	1) 1253	308
		2) 1143	
		3) 1117	

Blue light (470 nm) experiment for the dinuclear Ir-Pd complex (ACN, TEA, 18h irradiation)

Complex(Conc.6x10^{-5}M)	H_2O %	Area (mV/sec)	TON (average)
	10%	1) 1037	254
		2) 929	
		3) 927	

UV light (350 nm) experiment for dinuclear Ir-Pt/Pd complexes (ACN, TEA, 18h irradiation)

Complexes (6x10^{-5} M)	Water %	Area (mV/sec)	TON (average)
$[Ir(ppy)_2(bpp)PtCl]_2(PF_6)_2$	10%	1) 261	65
		2) 234	
$[Ir(ppy)_2(bpp)PdCl]_2(PF_6)_2$	10%	1) 50	16
		2) 70	

Blue light (470 nm) experiment the mononuclear complexes (intermolecular reaction with [Pt(ACN)$_2$Cl$_2$] and [Pd(ACN)$_2$Cl$_2$]) (ACN, TEA, 18h irradiation)

Complexes	H_2O %	Area (mV/sec)	TON (average)
[Ir(ppy)$_2$(bpp)]PF$_6$ (6x10^{-5} M) + [Pt(ACN)$_2$Cl$_2$] (6x10^{-5} M)	10%	1) 715 2) 717 3) 661	166
[Ir(ppy)$_2$(bpp)]PF$_6$ (6x10^{-5} M) + [Pd(ACN)$_2$Cl$_2$] (6x10^{-5} M)	10%	1) 950 2) 978 3) 982	245

UV light (350 nm) experiment for mononuclear complexes (intermolecular reaction with [Pt(ACN)$_2$Cl$_2$] and [Pd(ACN)$_2$Cl$_2$]) (ACN, TEA, 18h irradiation)

Complexes	Water %	Area (in mV/sec)	TON (average)
[Ir(ppy)$_2$(bpp)](PF$_6$) (6x10^{-5} M) + [Pt(ACN)$_2$Cl$_2$] (6x10^{-5} M)	10%	1) 480 2) 511 3) 432	124
[Ir(ppy)$_2$(bpp)](PF$_6$) (6x10^{-5} M) + [Pd(ACN)$_2$Cl$_2$] (6x10^{-5} M)	10%	1) 420 2) 400 3) 425	117

UV-vis data and extinction coefficients

Complex	**Absorption λ_{abs} (nm) ε(LM^{-1}cm^{-1})**
(a)	256(56197), 291(45699), 318(37498), 350(6848), 420(563), 470(445)
(b)	262(77403), 303(66615), 350(22290), 420(8289), 470(1350)
(c)	256(86545), 287(72456), 350(36312), 420(7207), 470(1760)

Table S1. UV-vis data for the complexes $[Ir(ppy)_2(bpp)]PF_6$ **(a)**, $[Ir(ppy)_2(bpp)PtCl]_2(PF_6)_2$ **(b)** and $[Ir(ppy)_2(bpp)PdCl]_2(PF_6)_2$ **(c)**

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[1] (a) S. Sprouse, K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1984, **106**, 6647–6653; (b) M. S. Lowry, W. R. Hudson, J. Robert A. Pascal and S. Bernhard, *J. Am. Chem. Soc.*, 2004, **126**, 14129–14135.