Solubility of Iridium and Ruthenium Organometallic Photoredox Catalysts

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Abstract:

Despite the exponential growth of the field of photocatalysis, for reasons that are not entirely clear, these precious photocatalysts are often used in the literature at loadings that exceed their maximum solubility. On an industrial scale, the quantity of any precious metal catalyst can be a substantial financial burden or a sourcing issue, not to mention concerns as to the ecological and earth abundance of these catalysts. We believe that inattention to solubility has made these reactions appear less efficient than they actually are, because much of the photocatalyst remains undissolved. Therefore, the maximum solubilities of iridium and ruthenium centered photocatalysts have been systematically identified in industrially relevant solvents. Further, a literature photocatalytic reaction which our results suggested was beyond the maximum solubility has been revisited, with interesting results.

Keywords: Photocatalysis, photocatalyst, photoredox, iridium, ruthenium, heteroleptic, homoleptic, solubility, saturation, solvent

Introduction

Recently, the footprint of photocatalysis has grown exponentially. Given the generally mild reaction conditions, many photocatalytic reactions are remarkable tolerant of functional groups, and as such have been used as a means of synthesis of complex organic molecules,[1-8] such as the synthetic core building block for the hepatitis-C drug elbasvir developed by the groups of DiRocco and Knowles,[9] or the perfluoroalkylated (hetero)aryl building blocks developed by the Stephenson group.[10] To date, however, no published industrial process has implemented any of the recently developed photocatalytic methods. As more photocatalysts are developed and give rise to a multitude of new reactions, the need for physical data regarding these catalysts increases.[2] Unfortunately, these physical data are frequently absent from the literature, or reported in isolation, preventing logical comparisons between potential catalysts. In fact, we have often observed in the literature the excessive use photocatalysts beyond their solubility limits. Given the low natural abundance[2, 11] in the earth's crust and thus the exotic nature of iridium and ruthenium, any iridium or ruthenium-based photocatalyst used in a commercial process would need to be highly efficient. As such, awareness of the maximum photocatalyst concentration provides a clear starting point from which to initiate a reaction process. To help address this dearth of information, we provide herein solubility data for a wide

range of iridium-, and ruthenium-based photocatalysts in relevant solvents, and demonstrate how knowledge of this information can lead to improvements in catalyst efficiency within reactions from the literature.

The solubility of photocatalysts in various solvents is an important aspect of reactions. Too little catalyst will result in a suboptimal rate, as the low concentration cannot fully utilize the amount of light given it. On the other hand, at a high enough photocatalyst concentration, the penetration of light into the reaction vessel will become negligible, wherein almost all of the photons are absorbed by the photocatalysts very near the interface between the vessel and the reaction mixture, again retarding rates of reaction. To a large extent, this situation can be circumvented by use of a photo-flow setup, in which the path length of the light is kept very small by flowing the light absorbing reaction mixture through a small tube. At even higher concentrations, the photocatalysts precipitate. The precipitated photocatalysts almost certainly play no significant role in the reactions.[12-13] In addition to significant monetary waste, in reference to the high cost of iridium or ruthenium catalysts discussed in this study, misinterpretation of the data can occur that can affect the development of the reaction. For instance, the catalyst loading is often used to make inferences about its effect on the reaction rate. However, this interpretation is highly suspect if the solubility limit of the photocatalyst is exceeded, because while the loading went up, the concentration remained constant. Finally, understanding of the solubility of the photocatalysts can heavily influence the choice of solvent used for purification or recovery of the photocatalysts, which becomes more important with scale.

Experimental Section

We limited the purview of this study to only commercially available, commonly implemented photocatalysts that are analogs to *fac*-$Ir(ppy)_3$ and $Ru(bpy)_3PF_6$. The solvents used in this study were those determined to be generally useful or commonly used in the laboratory setting.[14]

General Procedure A

For each solvent which could support a concentration greater than 1 ppt (part per thousand) of photocatalyst, ~1.5±0.1 mg of each catalyst was weighed into an 8 mL test tube. Solvent was incrementally added and after each subsequent addition, the mixture was sonicated and centrifuged. An average time of sonication was 4 minutes. The necessary centrifugation time varied widely, depending on the solvent used, ranging from 2-4 minutes.[15] After centrifugation, the tube was inspected visually for particulate photocatalyst. If particulates were observed, additional solvent was added and the process repeated. Once a homogenous mixture was reached by visual examination, the mixture was centrifuged for a period of 60 minutes to ensure homogeneity. Due to the propensity for rapid evaporation of the more volatile solvents, it was necessary to measure the final volume of the solution in order to ensure an accurate result of the concentration at the end of the experiment.

General Procedure B

For measuring in relatively nonsolvating solvents, general procedure A would be followed to the point that additional solvent could not be safely transferred into the test tube. The solution would then be capped with a septum and centrifuged for between 30 and 60 minutes. A majority of the supernatant would be removed, leaving enough to prevent disturbance of the precipitant photocatalyst. This would be repeated until there was no visual evidence of photocatalyst suspended in solution after centrifugation.

General Procedure C

Into a clean 8 mL test tube was weighed ~1.0±0.1 mg of photocatalyst. A solvent experimentally determined to readily solvate the photacatalyst was used to create a serial dilution. The solvent was then removed from the diluted solutions by evaporation and high vacuum in order

to obtain an accurately weighed, small amount of photocatalyst. General Procedure A or B was then implemented.

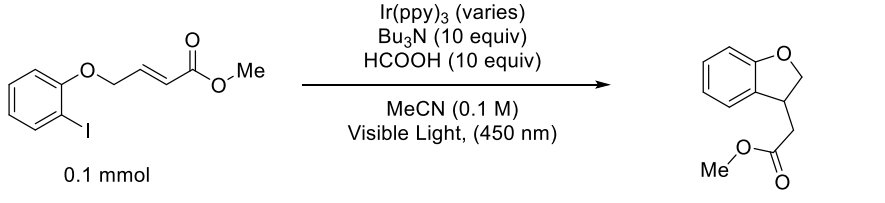
General Procedure D

For solvents in which less than 1 ppt photocatalyst was soluble, a different method was employed in order to avoid the use of copious amounts of solvent. To begin, each photocatalyst was dissolved in a clear, colorless, previously determined solvent in which it was highly soluble, and then serially diluted to 1000, 100, 10, and 1 ppm (part per million). To a new tube, an amount of solid photocatalyst (~1 mg) was added to each of the solvents. The heterogeneous mixture was then sonicated and centrifuged. Afterwards, the intensity of the color of the supernatant was then compared to the intensity of the solutions of known concentration, i.e. 1000, 100, 10, and 1 ppm (part per million). The solubility of each photocatalyst was then determined by comparison to the standard solutions, operating under the assumption that the color vibrancy, or intensity of emission, of each photocatalyst is constant across all solvents which appears reasonable based on our experience.

Photocatalytic Reaction Procedure

All reagents were either obtained from commercial suppliers or synthesized according to literature methods. The majority of the photocatalysts used in the study were obtained through commercial sources, while some were synthesized using literature methods.[16] Photocatalytic reactions were conducted in a light bath of blue LEDs (450 nm).

Scheme 1: Testing rates for the supersaturated literature reaction against variable concentrations of photocatalyst



A dry NMR tube was charged with reagents as indicated above (Scheme 1), varying the loading of photocatalyst. The reaction mixtures were sonicated to ensure homogeneity prior to introduction into the light bath. The reaction mixtures were monitored at the indicated timepoints by NMR spectroscopy and GCMS analysis of aliquots of the reaction mixture.[17]

Discussion

While the primary purpose of this study is to provide important physical data on these photocatalysts, it would be fruitful to reassess reactions found in the literature making use of these catalysts. For example, the Stephenson group's 2012 paper concerning the harnessing of iodides for radical cyclization was found to be supersaturated with respect to photocatalyst, according to the data recorded in this study.[18] One of these reactions was recreated on a reduced scale and in tandem, implementing a range of catalyst loadings bounded by the concentration given in the procedure and concentrations less than the maximum presented in this study. Indeed, neither the initial rate, nor overall conversion of each reaction was observed to have any significant dependence on the concentration of the photocatalyst in the range between 0.25 mol% and 2.5 mol% reported in the original work. This finding demonstrates that judicious application of the solubility data for the photocatalysts presented here could represent a significant economic advantage, in addition to the obvious prudence toward ecological and earth abundance concerns.

In order to render the data more applicable in an industrial setting, an additional study was conducted in order to determine the solubility of certain representative photocatalysts in binary solutions of acetonitrile and water of varying mole fraction. The resulting data is presented below and in the respective tables pertaining to each photocatalyst (Tables 1, 9, and 13). For charged species, the response to the use of a binary solvent system appears to correlate linearly with regard to the combination of the solubilities of those solvents (Figure 1). For the neutral *fac*-$Ir(ppy)_3$,

however, while the method of determination of solubility precludes the inclusion of explicit values, and requires reporting as a range, the intensity of the coloration qualitatively diminishes with increasing mole fraction of water.

Solubility of Specific Photocatalysts in Binary Solutions of Acetonitrile and Water (Molar)	1:1 Acetonitrile:Water (v:v)	2:1 Acetonitrile:Water (v:v)	4:1 Acetonitrile:Water (v:v)	Acetonitrile
Mole Fraction of Acetonitrile	0.257	0.409	0.580	1.00
$Ir[dF(CF_3)ppy]_2(dtbby)PF_6$	$3.6x10^{-3}$	$8.5x10^{-3}$	$6.1x10^{-2}$	$1.3x10^{-1}$
$Ru(bpy)_3(PF6)_2$	$1.3x10^{-2}$	$1.7x10^{-2}$	$4.4x10^{-2}$	$1.4x10^{-1}$

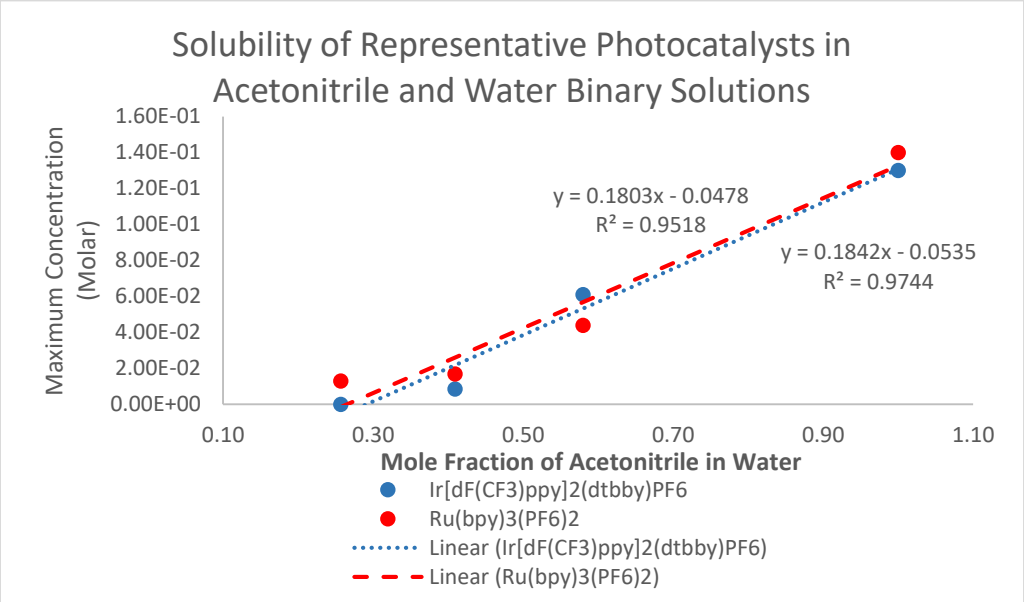


Figure 1. The solubility of photocatalysts in aqueous acetonitrile

Conclusion

We have determined and reported herein valuable physical data that was missing from the literature. The value of this data is evident when considering both the high cost of iridium and ruthenium and their relative terrestrial scarcity. It is our hope that disseminating these data will accelerate the adoption of photocatalysis not only as a routine laboratory procedure, but also in industry.

fac-Ir(ppy)$_3$		
CAS # 94928-86-6		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	6.0×10^{-4}	5.0×10^{2}
Acetonitrile[19]	4.1×10^{-4}	3.5×10^{2}
Dichloromethane[19]	7.3×10^{-3}	3.6×10^{3}
N,N-Dimethylformamide[19]	1.5×10^{-3}	1.0×10^{3}
Dimethysulfoxide[19]	3.7×10^{-3}	2.2×10^{3}
Ethyl Acetate[20]	3.4×10^{-4}	2.5×10^{2}
Methanol[20]	1.1×10^{-5}	9.4×10^{0}
Methyl-t-butyl ether[20]	6.2×10^{-5}	5.5×10^{1}
N-Methyl 2-pyrrolidinone[19]	5.2×10^{-2}	3.3×10^{4}
Tetrahydrofuran[19]	2.1×10^{-3}	1.6×10^{4}
Toluene[20]	5.9×10^{-4}	4.4×10^{2}
Water[19]	-	<1
4:1 Acetonitrile:Water[21]	-	10-100
1:1 Acetonitrile:Water[21]	-	10-100

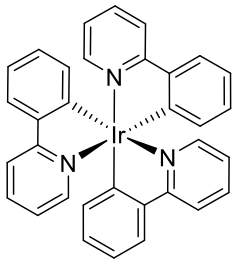


Table 1

fac-Ir(4'-Fppy)$_3$		
CAS # 370878-69-6		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	8.0×10^{-3}	7.2×10^{3}
Acetonitrile[19]	9.2×10^{-4}	8.3×10^{2}
Dichloromethane[19]	4.2×10^{-3}	2.3×10^{3}
N,N-Dimethylformamide[19]	5.6×10^{-2}	4.2×10^{4}
Dimethylsulfoxide[19]	1.4×10^{-2}	8.9×10^{3}
Ethyl Acetate[19]	1.1×10^{-3}	8.7×10^{2}
Methanol[20]	5.6×10^{-5}	5.0×10^{1}
Methyl-t-butyl ether[20]	7.3×10^{-5}	7.0×10^{1}
N-Methyl 2-pyrrolidinone[19]	2.0×10^{-1}	1.4×10^{5}
Tetrahydrofuran[19]	1.8×10^{-2}	1.4×10^{4}
Toluene[19]	2.8×10^{-4}	2.3×10^{2}
Water[19]	-	<1

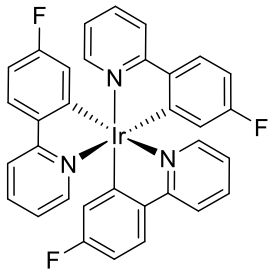


Table 2

Ir(4'-CF_3ppy)$_3$		
CAS # 500295-52-3		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$1.4x10^{-2}$	$1.5x10^{4}$
Acetonitrile[19]	$1.5x10^{-3}$	$1.6x10^{3}$
Dichloromethane[19]	$1.0x10^{-3}$	$6.4x10^{2}$
N,N-Dimethylformamide[19]	$3.0x10^{-2}$	$2.7x10^{4}$
Dimethylsulfoxide[19]	$4.6x10^{-3}$	$3.6x10^{3}$
Ethyl Acetate[19]	$2.3x10^{-3}$	$2.2x10^{3}$
Methanol[20]	$5.6x10^{-5}$	$6.1x10^{1}$
Methyl-t-butyl ether[20]	$7.3x10^{-5}$	$8.4x10^{1}$
N-Methyl 2-pyrrolidinone[19]	$5.4x10^{-2}$	$4.4x10^{4}$
Tetrahydrofuran[19]	$1.4x10^{-2}$	$1.4x10^{4}$
Toluene[20]	$1.4x10^{-4}$	$1.4x10^{2}$
Water[19]	-	<1

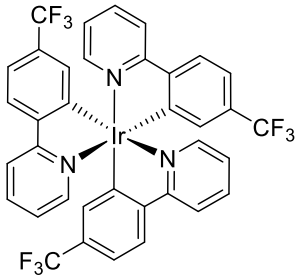


Table 3

Ir(ppy)$_2$(dtbbpy)PF_6		
CAS # 676525-77-2		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$1.7x10^{-1}$	$2.0x10^{5}$
Acetonitrile[19]	$2.7x10^{-1}$	$3.2x10^{5}$
Dichloromethane[19]	$1.9x10^{-1}$	$1.3x10^{5}$
N,N-Dimethylformamide[19]	$1.4x10^{-1}$	$1.4x10^{5}$
Dimethylsulfoxide[19]	$1.5x10^{-1}$	$1.2x10^{5}$
Ethyl Acetate[19]	$8.1x10^{-4}$	$8.3x10^{2}$
Methanol[19]	$5.8x10^{-3}$	$6.7x10^{3}$
Methyl-t-butyl ether[21]	-	10-100
N-Methyl 2-pyrrolidinone[19]	$2.2x10^{-1}$	$1.9x10^{5}$
Tetrahydrofuran[20]	$3.6x10^{-3}$	$3.8x10^{3}$
Toluene[21]	-	100-1000
Water[21]	-	1-10

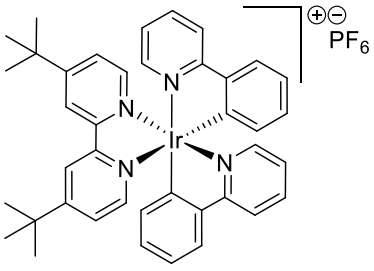


Table 4

$Ru(dmb)_3(PF_6)_2$		
CAS # 83605-44-1		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$2.2x10^{-2}$	$2.7x10^{4}$
Acetonitrile[19]	$6.4x10^{-2}$	$7.6x10^{4}$
Dichloromethane[19]	$9.9x10^{-3}$	$7.0x10^{3}$
N,N-Dimethylformamide[19]	$9.9x10^{-2}$	$9.9x10^{4}$
Dimethylsulfoxide[19]	$7.1x10^{-2}$	$6.1x10^{4}$
Ethyl Acetate[19]	$1.8x10^{-3}$	$1.9x10^{3}$
Methanol[19]	$3.9x10^{-3}$	$4.7x10^{3}$
Methyl-t-butyl ether[21]	-	1-10
N-Methyl 2-pyrrolidinone[19]	$1.2x10^{-1}$	$1.1x10^{5}$
Tetrahydrofuran[20]	$4.6x10^{-5}$	$4.9x10^{1}$
Toluene[21]	-	1-10
Water[20]	$4.0x10^{-5}$	$3.8x10^{1}$

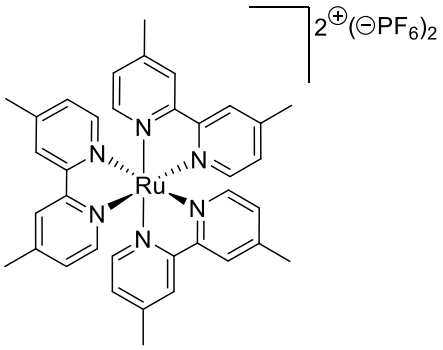


Table 5

$Ru(phen)_3(PF_6)_2$		
CAS # 60804-75-3		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$2.6x10^{-2}$	$3.6x10^{4}$
Acetonitrile[19]	$1.7x10^{-1}$	$2.3x10^{5}$
Dichloromethane[19]	$2.5x10^{-3}$	$2.0x10^{3}$
N,N-Dimethylformamide[19]	$2.5x10^{-1}$	$2.8x10^{5}$
Dimethylsulfoxide[19]	$2.8x10^{-1}$	$2.7x10^{5}$
Ethyl Acetate[21]	-	1-10
Methanol[19]	$5.5x10^{-4}$	$7.5x10^{2}$
Methyl-t-butyl ether[21]	-	1-10
N-Methyl 2-pyrrolidinone[19]	$1.9x10^{-1}$	$1.9x10^{5}$
Tetrahydrofuran[21]	-	10-100
Toluene[22]	$1.3x10^{-5}$	$1.6x10^{1}$
Water[21]	-	10-100

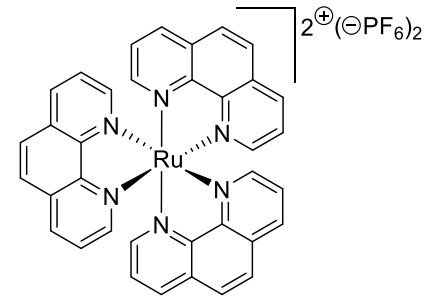


Table 6

$Ru(dtbbpy)_3(PF_6)_2$		
CAS # 75777-87-6		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$5.3x10^{-2}$	$8.0x10^4$
Acetonitrile[19]	$1.5x10^{-1}$	$2.3x10^5$
Dichloromethane[19]	$7.4x10^{-2}$	$6.6x10^4$
N,N-Dimethylformamide[19]	$1.5x10^{-1}$	$1.9x10^5$
Dimethylsulfoxide[19]	$6.1x10^{-2}$	$6.7x10^4$
Ethyl Acetate[21]	-	100-1000
Methanol[21]	-	100-1000
Methyl-t-butyl ether[21]	-	10-100
N-Methyl 2-pyrrolidinone[19]	7.7x10	$8.9x10^4$
Tetrahydrofuran[19]	$2.6x10^{-3}$	$3.5x10^3$
Toluene[21]	-	1-10
Water[21]	-	1-10

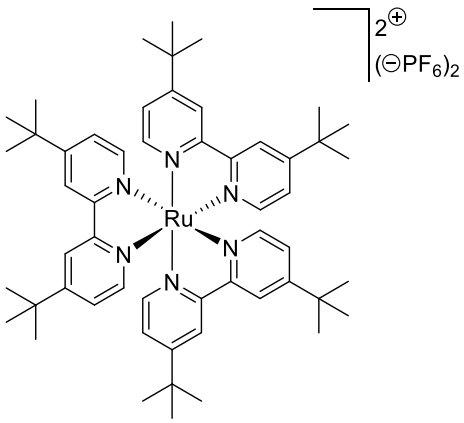


Table 7

$Ru(bpz)_3(PF_6)_2$		
CAS # 80907-56-8		
Solvents	**Molar Concentration**	**ppm**
Acetone[21]	-	100-1000
Acetonitrile[21]	-	100-1000
Dichloromethane[21]	-	10-100
N,N-Dimethylformamide[19]	$4.4x10^{-2}$	$4.1x10^4$
Dimethylsulfoxide[19]	$3.7x10^{-1}$	$2.9x10^5$
Ethyl Acetate[21]	-	10-100
Methanol[21]	-	100-1000
Methyl-t-butyl ether[21]	-	10-100
N-Methyl 2-pyrrolidinone[19]	$1.8x10^{-1}$	$1.5x10^5$
Tetrahydrofuran[21]	-	10-100
Toluene[21]	-	10-100
Water[21]	-	100-1000

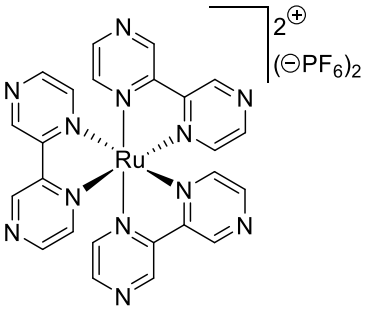


Table 8

$Ru(bpy)_3(PF_6)_2$		
CAS # 60804-74-2		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$3.3x10^{-2}$	$3.6x10^{4}$
Acetonitrile[19]	$1.4x10^{-1}$	$1.5x10^{5}$
Dichloromethane[21]	-	100-1000
N,N-Dimethylformamide[19]	$2.3x10^{-1}$	$2.1x10^{5}$
Dimethylsulfoxide[19]	$1.5x10^{-1}$	$1.2x10^{5}$
Ethyl Acetate[21]	-	1-10
Methanol[21]	-	100-1000
Methyl-t-butyl ether[21]	-	1-10
N-Methyl 2-pyrrolidinone[19]	$7.0x10^{-2}$	$5.8x10^{4}$
Tetrahydrofuran[21]	-	10-100
Toluene[21]	-	1-10
Water[21]	-	100-1000
4:1 Acetonitrile:Water[19]	$4.4x10^{-2}$	-
2:1 Acetonitrile:Water[19]	$1.7x10^{-2}$	-
1:1 Acetonitrile:Water[19]	$1.3x10^{-2}$	-

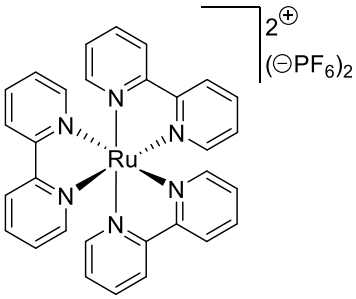


Table 9

***fac*-Ir(Fppy)$_3$**		
CAS # 387859-70-3		
Solvents	**Molar Concentration**	**ppm**
Acetone[21]	-	100-1000
Acetonitrile[21]	-	1000-100
Dichloromethane[19]	$2.1x10^{-3}$	$1.2x10^{3}$
N,N-Dimethylformamide[19]	$2.0x10^{-3}$	$1.7x10^{3}$
Dimethylsulfoxide[21]	-	100-1000
Ethyl Acetate[21]	-	100-1000
Methanol[21]	-	100-1000
Methyl-t-butyl ether[21]	-	100-1000
N-Methyl 2-pyrrolidinone[19]	$1.7x10^{-2}$	$1.3x10^{4}$
Tetrahydrofuran[19]	$5.8x10^{-3}$	$5.0x10^{3}$
Toluene[21]	-	100-1000
Water[21]	-	1-10

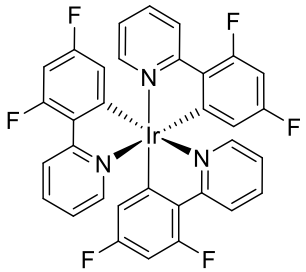


Table 10

$Ir(dtbppy)_2(dtbbpy)PF_6$		
CAS # 808142-80-5		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$2.3x10^{-2}$	$3.3x10^4$
Acetonitrile[19]	$3.8x10^{-2}$	$5.5x10^4$
Dichloromethane[19]	$1.8x10^{-1}$	$1.5x10^5$
N,N-Dimethylformamide[19]	$1.5x10^{-2}$	$1.8x10^4$
Dimethylsulfoxide[19]	$5.3x10^{-3}$	$5.6x10^3$
Ethyl Acetate[19]	$8.6x10^{-4}$	$1.1x10^3$
Methanol[19]	$3.8x10^{-3}$	$5.5x10^3$
Methyl-t-butyl ether[21]	-	100-1000
N-Methyl 2-pyrrolidinone[19]	$4.8x10^{-2}$	$5.3x10^4$
Tetrahydrofuran[19]	$6.6x10^{-3}$	$8.5x10^3$
Toluene[19]	$2.0x10^{-3}$	$2.6x10^3$
Water[21]	-	<1

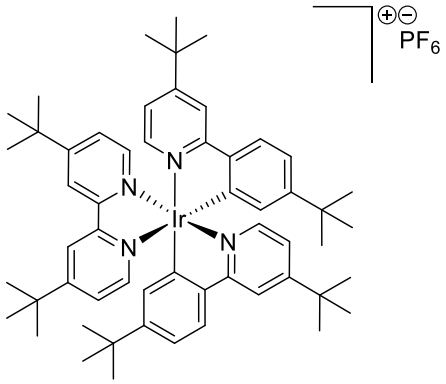


Table 11

***fac*-$Ir(tBuppy)_3$**		
CAS # 359014-76-9		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$9.0x10^{-3}$	$9.5x10^3$
Acetonitrile[19]	$1.1x10^{-3}$	$1.1x10^3$
Dichloromethane[19]	$9.1x10^{-3}$	$5.7x10^3$
N,N-Dimethylformamide[19]	$7.4x10^{-3}$	$6.4x10^3$
Dimethylsulfoxide[19]	$8.4x10^{-4}$	$6.3x10^2$
Ethyl Acetate[19]	$1.7x10^{-2}$	$1.5x10^4$
Methanol[21]	-	100-1000
Methyl-t-butyl ether[21]	-	100-1000
N-Methyl 2-pyrrolidinone[19]	$1.4x10^{-2}$	$1.1x10^4$
Tetrahydrofuran[19]	$2.1x10^{-2}$	$1.9x10^4$
Toluene[19]	$3.5x10^{-2}$	$3.3x10^4$
Water[21]	-	10-100

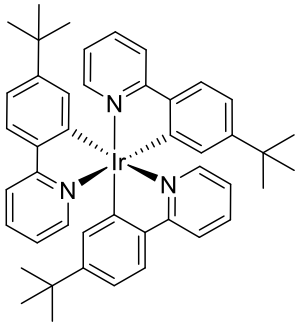


Table 12

Ir[dF(CF3)ppy]2(dtbbpy)PF6		
CAS # 870987-63-6		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$9.9x10^{-2}$	$1.4x10^{5}$
Acetonitrile[19]	$1.3x10^{-1}$	$1.8x10^{5}$
Dichloromethane[19]	$5.6x10^{-3}$	$4.7x10^{3}$
N,N-Dimethylformamide[19]	$2.2x10^{-1}$	$2.6x10^{5}$
Dimethylsulfoxide[19]	$1.6x10^{-1}$	$1.7x10^{5}$
Ethyl Acetate[19]	$8.6x10^{-3}$	$1.1x10^{4}$
Methanol[19]	$2.4x10^{-2}$	$3.4x10^{4}$
Methyl-t-butyl ether[21]	-	100-1000
N-Methyl 2-pyrrolidinone[19]	$1.7x10^{-2}$	$1.8x10^{-4}$
Tetrahydrofuran[19]	$6.9x10^{-3}$	$8.8x10^{3}$
Toluene[21]	-	100-1000
Water[21]	-	10-100
4:1 Acetonitrile:Water[19]	$6.1x10^{-2}$	-
2:1 Acetonitrile:Water[19]	$8.5x10^{-3}$	-
1:1 Acetonitrile:Water[19]	$3.6x10^{-3}$	-

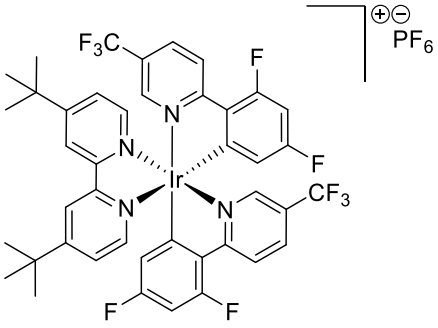


Table 13

Ir(dmppy)2(dtbbpy)PF6		
CAS # 1607469-49-7		
Solvents	**Molar Concentration**	**ppm**
Acetone[19]	$2.9x10^{-1}$	$3.6x10^{5}$
Acetonitrile[19]	$1.5x10^{-1}$	$1.8x10^{5}$
Dichloromethane[19]	$5.2x10^{-1}$	$3.8x10^{5}$
N,N-Dimethylformamide[19]	$5.8x10^{-1}$	$6.0x10^{5}$
Dimethylsulfoxide[19]	$1.0x10^{-1}$	$9.2x10^{4}$
Ethyl Acetate[19]	$9.5x10^{-3}$	$1.0x10^{4}$
Methanol[19]	$5.0x10^{-3}$	$6.2x10^{3}$
Methyl-t-butyl ether[21]	-	10-100
N-Methyl 2-pyrrolidinone[19]	$1.1x10^{-1}$	$1.0x10^{5}$
Tetrahydrofuran[19]	$1.1x10^{-2}$	$1.3x10^{4}$
Toluene[21]	-	100-1000
Water[21]	-	1-10

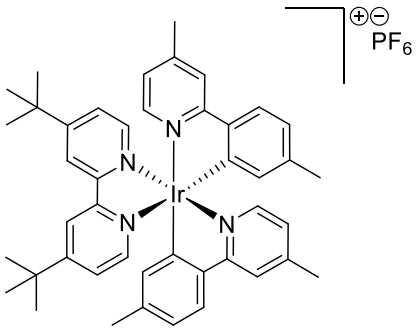


Table 14

Table 1 – Table 14. Maximum solubility of catalyst in various solvents, with some given as a range in ppm.[20]

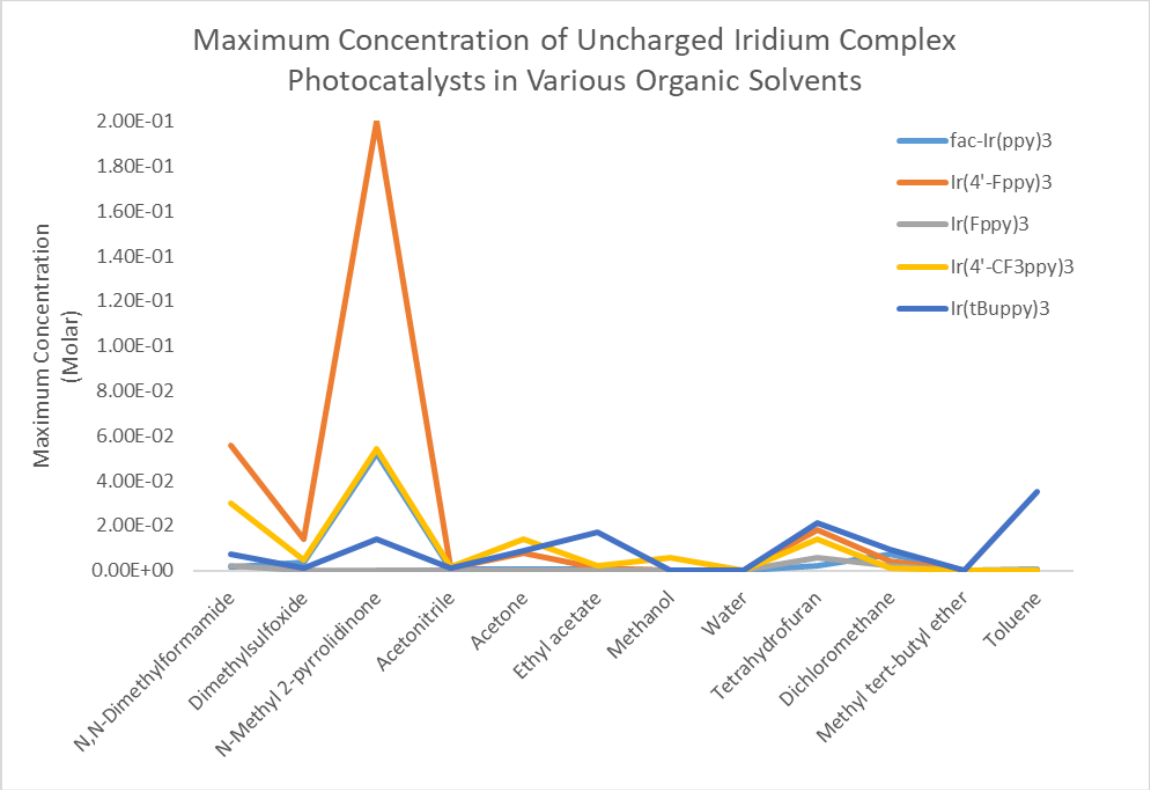


Figure 2

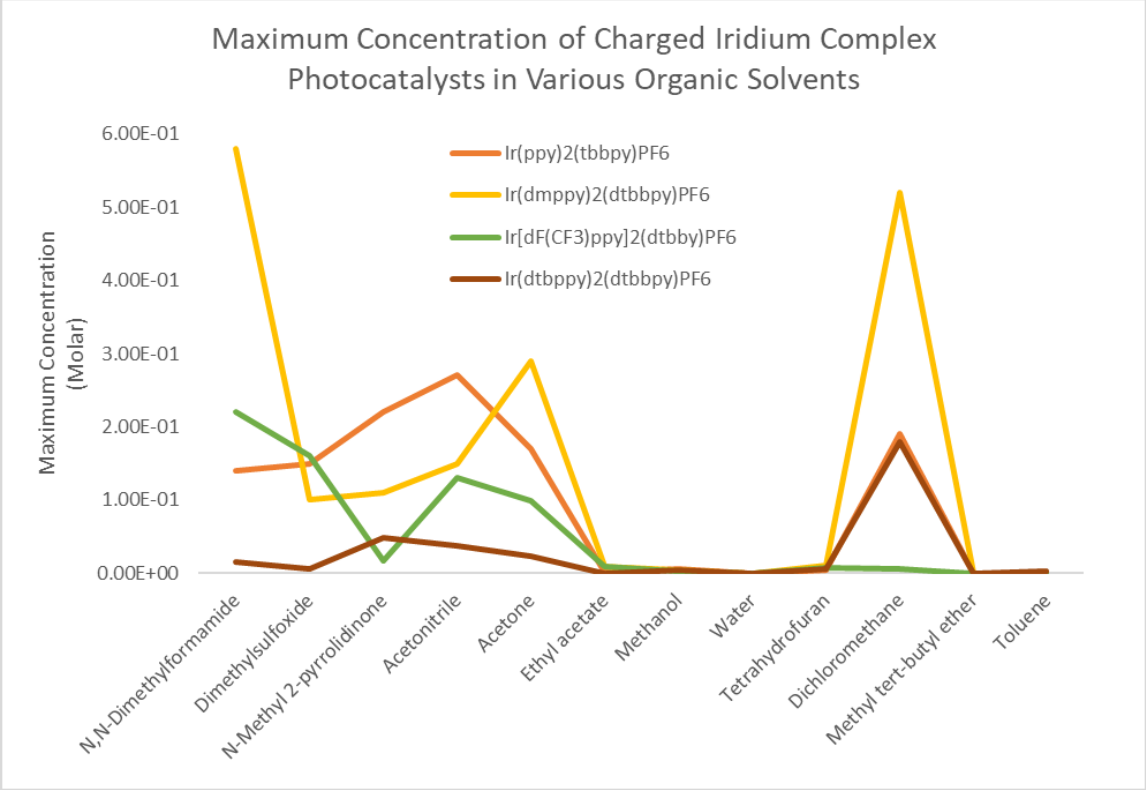


Figure 3

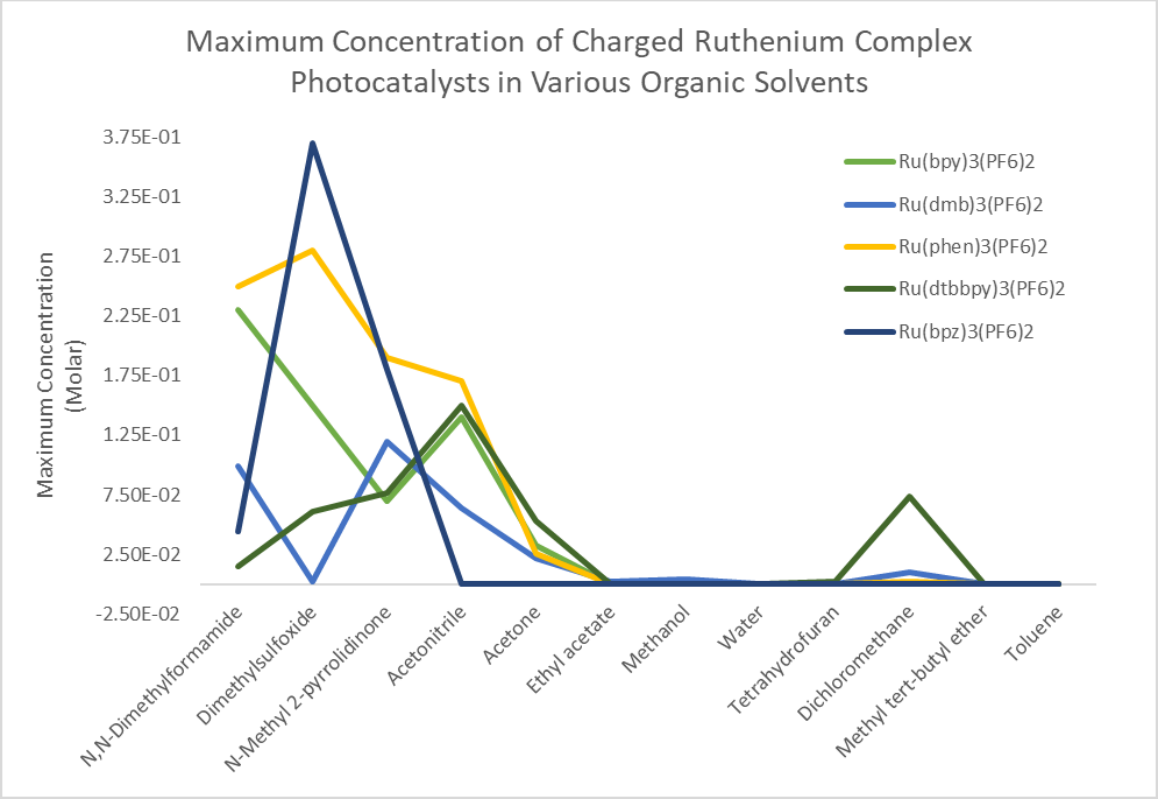


Figure 4

Figure 2 – Figure 4. Maximum concentration of iridium and ruthenium complex photocatalysts in common organic solvents[14]. Solvents are listed by decreasing Dipole Moment.[23]

Concentration of Iridium and Ruthenium Complex Photocatalysts in Various Organic Solvents (Molar)	Acetone	Acetonitrile	Dichloromethane	N,N-Dimethylformamide	Dimethylsulfoxide	Ethyl acetate	Methanol	Methyl tert-butyl ether	N-Methyl 2-pyrrolidinone	Tetrahydrofuran	Toluene	Water
Solvent Dipole Moment (D)	2.78	3.51	1.53	3.91	3.86	1.84	1.77	1.36	3.75	1.75	0.36	1.76
***fac*-Ir(ppy)$_3$**	6.0×10^{-4}	4.2×10^{-4}	7.3×10^{-3}	1.5×10^{-3}	3.7×10^{-3}	3.3×10^{-4}	1.1×10^{-5}	6.2×10^{-5}	5.2×10^{-2}	2.1×10^{-3}	5.9×10^{-4}	$<1.5\times10^{-6}$
Ir(4'-Fppy)$_3$	8.0×10^{-3}	9.2×10^{-4}	4.2×10^{-3}	5.6×10^{-2}	1.4×10^{-2}	1.1×10^{-3}	5.6×10^{-5}	7.4×10^{-5}	2.0×10^{-1}	1.8×10^{-2}	2.8×10^{-4}	$<1.4\times10^{-6}$
Ir(Fppy)$_3$	1.0×10^{-4}	1.0×10^{-4}	2.1×10^{-3}	2.0×10^{-3}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	1.7×10^{-4}	5.8×10^{-3}	1.0×10^{-4}	1.0×10^{-6}
Ir(4'-CF$_3$ppy)$_3$	1.4×10^{-2}	1.5×10^{-3}	1.0×10^{-3}	3.0×10^{-2}	4.6×10^{-3}	2.3×10^{-3}	5.6×10^{-3}	7.3×10^{-5}	5.4×10^{-2}	1.4×10^{-2}	1.4×10^{-4}	$<1.1\times10^{-6}$
Ir(tBuppy)$_3$	9.0×10^{-3}	1.1×10^{-3}	9.1×10^{-3}	7.4×10^{-3}	8.4×10^{-4}	1.7×10^{-2}	9.5×10^{-5}	9.5×10^{-5}	1.4×10^{-2}	2.1×10^{-2}	3.5×10^{-2}	9.5×10^{-6}
Ir(ppy)$_2$(tbbpy)PF$_6$	1.7×10^{-1}	2.7×10^{-1}	1.9×10^{-1}	1.4×10^{-1}	1.5×10^{-1}	8.1×10^{-4}	5.8×10^{-3}	8.6×10^{-6}	2.2×10^{-1}	3.6×10^{-3}	8.6×10^{-5}	8.6×10^{-7}
Ir(dmppy)$_2$(dtbbpy)PF$_6$	2.9×10^{-1}	1.5×10^{-1}	5.2×10^{-1}	5.8×10^{-1}	1.0×10^{-1}	9.5×10^{-3}	5.0×10^{-3}	8.1×10^{-6}	1.1×10^{-1}	1.1×10^{-2}	8.1×10^{-5}	8.1×10^{-7}
Ir[dF(CF$_3$)ppy]$_2$(dtbby)PF$_6$	9.9×10^{-2}	1.3×10^{-1}	5.6×10^{-3}	2.2×10^{-1}	1.6×10^{-1}	8.6×10^{-3}	2.4×10^{-3}	7.0×10^{-5}	1.7×10^{-2}	6.9×10^{-3}	7.0×10^{-5}	7.0×10^{-6}
Ir(dtbppy)$_2$(dtbbpy)PF$_6$	2.3×10^{-2}	3.8×10^{-2}	1.8×10^{-1}	1.5×10^{-2}	5.3×10^{-3}	8.6×10^{-5}	3.8×10^{-3}	6.9×10^{-5}	4.8×10^{-2}	6.6×10^{-3}	2.0×10^{-3}	$<6.9\times10^{-7}$
Ru(bpy)$_3$(PF$_6$)$_2$	3.3×10^{-2}	1.4×10^{-1}	9.1×10^{-5}	2.3×10^{-1}	1.5×10^{-1}	9.1×10^{-7}	9.1×10^{-5}	9.1×10^{-7}	7.0×10^{-2}	9.1×10^{-6}	9.1×10^{-7}	9.1×10^{-5}
Ru(dmb)$_3$(PF$_6$)$_2$	2.2×10^{-2}	6.4×10^{-2}	9.9×10^{-3}	9.9×10^{-2}	2.0×10^{-3}	1.8×10^{-3}	3.9×10^{-3}	8.3×10^{-7}	1.2×10^{-1}	4.6×10^{-5}	8.3×10^{-7}	4.0×10^{-5}
Ru(phen)$_3$(PF$_6$)$_2$	2.6×10^{-2}	1.7×10^{-1}	2.5×10^{-3}	2.5×10^{-1}	2.8×10^{-1}	7.3×10^{-7}	5.5×10^{-4}	7.3×10^{-7}	1.9×10^{-1}	7.3×10^{-6}	1.3×10^{-5}	7.3×10^{-6}
Ru(dtbbpy)$_3$(PF$_6$)$_2$	5.3×10^{-2}	1.5×10^{-1}	7.4×10^{-2}	1.5×10^{-2}	6.1×10^{-2}	6.6×10^{-5}	6.6×10^{-5}	6.6×10^{-6}	7.7×10^{-2}	2.6×10^{-3}	6.6×10^{-7}	6.6×10^{-7}
Ru(bpz)$_3$(PF$_6$)$_2$	9.1×10^{-5}	9.1×10^{-5}	9.1×10^{-6}	4.4×10^{-2}	3.7×10^{-1}	9.1×10^{-6}	9.1×10^{-5}	9.1×10^{-6}	1.8×10^{-1}	9.1×10^{-6}	9.1×10^{-6}	9.1×10^{-5}

Table 15. Maximum solubility of various iridium and ruthenium complex photocatalysts in common organic solvents.[14] Each value determined by General Procedure C indicates the concentration calculated from the lower limit of the range indicated in Table 1-Table 14. The dipole moment data is given in debyes.[23] For reference on the procedure used in each test, see Tables 1-14.

Associated Content:

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI. Spectral data and collected data tables included. (PDF)

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Notes

Drs. Anuradha Singh and Jimmie Weaver III are a senior scientist and co-founder of Weaver Labs LLC. (www.weaver-labs.com), respectively, which produces some of these photocatalysts commercially.

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