Electronic Supporting Information

Engineering of efficient phosphorescent iridium cationic complex for developing oxygen-sensitive polymeric and nanostructured films

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Table 1 Photophysical data for the most relevant Ir-complexes immobilized or solved in [a]polystyrene, [b]polymerized poly(ethyleneglycol) ethyl ether methacrylate, [c]2-methyltetrahydrofuran, [d]toluene, [e]acetonitrile, [f]dichloromethane or [g] poly(9,9-dioctlfluorene).

Complexe	λ_{em} (nm)	Luminescence quantum yield	Reference
$Ir(ppy)_3$[a]	512	0.4	16
Ir(L)(L1)[b]	612	-	17
$Ir(L1)_2$[b]	620	-	17
(ppy)Ir(dpt-cy-dpt)Ir(ppy)[b]	520	-	17
$Ir(bo)_2(acac)$[c]	525	0.25	18
$Ir(bon)_2(acac)$[c]	586	0.11	19
$Ir(bzq)_2(acac)$[c]	548	0.27	19
$Ir(\alpha\text{-}bsn)_2(acac)$[c]	606	0.22	18
$Ir(\beta\text{-}bsn)_2(acac)$[c]	594	0.16	18
$Ir(btth)_2(acac)$[c]	593	0.21	18
$Ir(bt)_2(acac)$[c]	557	0.26	19
$Ir(btp)_2(acac)$[c]	612	0.21	18
$Ir(C6)_2(acac)$[c]	585	0.60	18
$Ir(op)_2(acac)$[c]	520	0.14	18
$Ir(dpo)_2(acac)$[c]	550	0.10	18
$Ir(ppy)_2(acac)$[c]	516	034	19
$Ir(pq)_2(acac)$[c]	597	0.10	19
$Ir(thp)_2(acac)$[c]	562	0.12	18
$Ir(tpy)_2(acac)$[c]	512	0.31	18
$Ir(ppy)_2(vpy)$[d]	506	0.06	20
$Ir(ppy)_2(DMPSEpy)$[d]	509	0.07	20
$Ir(ppy)_2(fppy)$[f]	612	0.60	21
$Ir(dbq)_2(acac)$[f]	614	0.53	22
$Ir(mdq)_2(acac)$[f]	600	0.48	22
$Ir(phq)_2(acac)$[g]	624	-	23
$Ir(C6)_2(vacac)$[d]	568	0.22	24
$Ir((ppy)_2(vacac)$[e]	520	0.02	24
fac-$Ir(ppy)_2(vppy)$[d]	514, 542	0.20	24
mer-$Ir(ppy)_2(vppy)$[f]	535,572	0.03	24
$Ir(ppy)_2(CN)_2$[f]	470	-	25

Complexe	λ_{em} (nm)	Luminescence quantum yield	Reference
fac-Ir(ppy)$_3$[d]	510	-	25
Ir(dpq)$_2$(acac)[d]	677	0.14	26
Ir(dpqx)$_2$(fppz)[f]	642	0.40	27
Ir(dfqx)$_2$(fppz)[f]	630	0.83	27
Ir(dfqx)$_2$(fptz)[f]	622	0.85	27
Ir(dfqx)$_2$(bppz)[f]	649	0.62	27
Ir(dbq)$_2$(cbdk)[f]	621	0.45	28
Ir(dbq)$_2$(fbdk)[f]	624	0.43	28
Ir(ppy)$_2$(pbpy-OBut)[f]	612	0.08	29
Ir(ppy)$_2$(tpy-COOH)[f]	626	0.02	29
Ir(ppz)$_2$(bpy)[e]	563	0.17	30
Ir(ppz)$_2$(bpy-*t*-butyl)[e]	555	0.08	30
Ir(ppz)$_2$(bpy-OCH_3)[e]	554	0.03	30
Ir(ppz)$_2$(bpy-CO_2Et)[e]	628	0.00	30
Ir(ppz)$_2$(biq)[e]	616	0.02	30
Ir(ppz-*t*-butyl)$_2$(biq)[e]	627	0.01	30
Ir(ppz-methoxy)$_2$(bpy-*t*-butyl)[e]	618	0.00	30
Ir(ppz-phenyl)$_2$(bpy-*t*-butyl)[e]	570	0.01	30
Ir(ppz-difluoro)$_2$(bpy-*t*-butyl)[e]	495	0.40	30
Ir(ppy)$_2$(L2)[e]	622	0.06	31
Ir(ppy)$_2$(L3)[e]	632	0.04	31
Ir(ppy)$_2$(L4)[e]	651	0.06	31
Ir(ppy)$_2$(hcbpy)[e]	688	0.02	31
Ir(ppy)$_2$(nbpy)[e]	589	0.20	31
N-926[a]	526	0.80	10
N-833[a]	529	0.60	10
N-837[a]	528	0.38	10
N-948[a]	665	0.58	This work

Abbreviations

ppy = 2-phenylpyridine; L = 2,6-bis(7'-methyl-4'-phenyl-2'-quinolyl)pyridine; L1 is a monoanion of L; dpt = dialkyldithiophosphate; cy ; cyclo phosphamide ; acac = acetylacetonate; bon = 2-(1-naphthyl)benzooxazolato; bzq = 7,8-benzoquinilinato; bsn =

2-(1-naphthyl)benzothiazolato; bt = 2-phenylquinolyl; btp = 2-(2'-benzothienyl)pyridinato; C6 = 3-(2-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-onato; op = 2-phenyl oxazolinato; dpo = 2,4-diphenyloxazolato; pq = 2-phenylquinolyl; thp = 2-(2'-thienyl)pyridinato; tpy = 2-(4-talyl)pyridinato; vpy= 4-vinylpyridine; fppy= 2-(4'-formylphenyl)-pyridyl ; dbq= dibenzo[f,h]quinoxaline ; mdq= 2-methyl-dibenzo[f,h]quinoxaline ; vacac = allylacetoacetate; vppy = 2-(4-vinyl)-phenylpyridine; dpq= 2,3-diphenylquinoxaline ; dpqx= 2,3-diphenylquinoxaline ; fppz= 3-tert-butyl-5-(2-pyridyl)pyrazole ; dfqx= 2,3-bis(4-fluorophenyl)quinoxaline ; fptz= 3-(trifluoromethyl)-5-(2-pyridyl)-triazole ; bppz= 3-tert-butyl-5-(2-pyridyl)pyrazole ; cbdk= 1-(carbazol-9-yl)-5,5-dimethylhexane-2,4-diketonate) ; fbdk= 1-(9-methyl-fluoren-9-yl)-6,6-dimethylheptane-3,5-diketonate) ; pbpy-OBut= 4-{4'-(4-phenyloxy)-6'-phenyl-2,2'-bipyridyl}butene; tpy-COOH= 4'-(4-carboxyphenyl)-2,2' :6'-2''-terpyridine; ppz= 1'-phenylpyrazolato-N,$C^{2'}$; bpy= 2,2'-bypiridine; bpy-*t*-butyl=4,4'-di-*tert*-butyl-2-2'bipyridine ; bpy-OCH_3= 4,4'-dinethoxy-2,2'-bipyridine; bpy-CO_2Et= 4,4'-(dicarboxylic acic diethyl ester)- 2,2'-bipyridine; biq= 2-2'-biquinoline; ppz-*t*-butyl= 1'-(4'-*tert*-butylphenyl)pyrazolato ; ppz-methoxy= 1'-(5'-methoxyphenyl)pyrazolato; ppz-phenyl= 1'-(3'-biphenyl)pyrazolato; ppz-difluoro= 1'-(4',6'-difluorophenyl)pyrazolato; L2= ($OC_{12}H_{25}$)-6'-phenyl-2,2'-bipyridine; L3= ($OCOC_6H_4OCO$)-6'-phenyl-2,2'-bipyridine ; L4= (COOCholestrol)-6'-phenyl-2,2'-bipyridine; hcbpy= 4,4'-dihexadecyloxycarbonyl-2,2'-bipyridine; nbpy=4,4'-di-*n*-nonyl-2,2'-bipyridine ; N-926 = bis(2-phenylpyridinyl)-N,N,N,N-tetramethyl-(4,4'-diamine-2,2'-bipyridinyl) iridium (III) chloride; N-833 = tetrabutylammonium bis(isothiocyanato) bis(2-phenylpyridinyl)- iridium (III) ; N-837 = tetrabutylammonium bis(cyanide) bis(2-phenylpyridinyl)- iridium (III) ; N-948 = Ir(2-phenylpyridine)$_2$(4,4'-bis(2-(4-N,N-methylhexylaminophenyl)ethyl)-2-2'-bypiridine)Cl.

Effect of the rigidity of the dye into the solid support on the luminescence quantum yield and the Stern-Volmer constant: Theoretical deduction.

Equations 1 and 2 show the fluorescence and phosphorescence quantum yields, respectively.

$$\phi_F = \frac{k_F}{k_F + \sum k_d + k_Q[Q]} \qquad \text{Equation 1}$$

$$\phi_P = \phi_{ISC} \cdot \frac{k_P}{k_P + \sum k_d + k_Q[Q]} \qquad \text{Equation 2}$$

where ϕ_F and ϕ_P are the fluorescence and phosphorescence quantum yields, k_F and k_P are the rate of spontaneous fluorescence and phosphorescence emissions, ϕ_{ISC} is the inter-system crossing efficiency, Σk_d denotes all the non-radiative process constants, k_Q is the quenching constants and *[Q]* is the concentration of the quencher.

For dynamic quenching, the quenching constant may be expresses as follow:

$$k_Q \propto \frac{T}{\eta} \qquad \text{Equation 3}$$

where T is the temperature and η is the viscosity of the media. Therefore, η is related with the conformational freedom or the rigidity of the molecule into the solid support.

Attending to these equations and applying them to N-948 dye supported in PS and AP200/19, the difference in luminescence quantum yield (0.57 for N948-PS and 0.20 for N948-AP200/19 films) at constant temperature may be due to the rigidity of the dye within the support. The rigidity of N-948 is higher in PS than in AP200/19 because the high lipophilicity of the dye:

$$\eta_{PS} > \eta_{AP200/19} \Rightarrow k_{Q,PS} < k_{Q,AP200/19} \Rightarrow \phi_{P,PS} > \phi_{P,AP200/19}$$

In addition, having in mind that k_Q is the K_{SV}, the Stern-Volmer constants of the dye incorporate in AP200/19 should be higher than in PS. Table 2 shows the experimental results and they confirm this approach: $K_{SV,PS} = 18.2$ bar^{-1} and $K_{SV,AP200/19} = 33.5$ bar^{-1}.

On the other hand, we can also use this dissertation to compare the experimental results of N948 with other Ir(III) dyes previously described in the literature such as N926, N833 and N837 (references 10 and 11). These dyes are less lipophilicity than N948 and therefore less soluble in PS than it. In this case, the rigidity of these dyes (N926, N833 and N837) in PS is similar than in AP200/19. Therefore, the luminescence quantum yields and the Stern-Volmer constants in PS and in AP200/19 should be very similar. Reference 11 shows these data and confirm this dissertation: for example for N926 the ϕ_{PS} is 0.85 the $\phi_{AP200/19}$ is 0.80, the $k_{SV,PS}$ is 1.6 and $k_{SV,2,AP200/19}$ is 1.8[§].

[§] N926 incorporated in AP200/19 has two Stern-Volmer constants $k_{SV,1}$ and $k_{SV,2}$. The first one is refereed to the dye within nanopores and the second one to the dye located in macropores. In order to compare PS and AP200/19 we must determine a similar microenvironment that is macropores. For this reason $k_{SV,PS}$ and $k_{SV,2,AP200/19}$ have been compared in this study.