Near-infrared light-emitting electrochemical cells based on excimer emission of a cationic iridium complex

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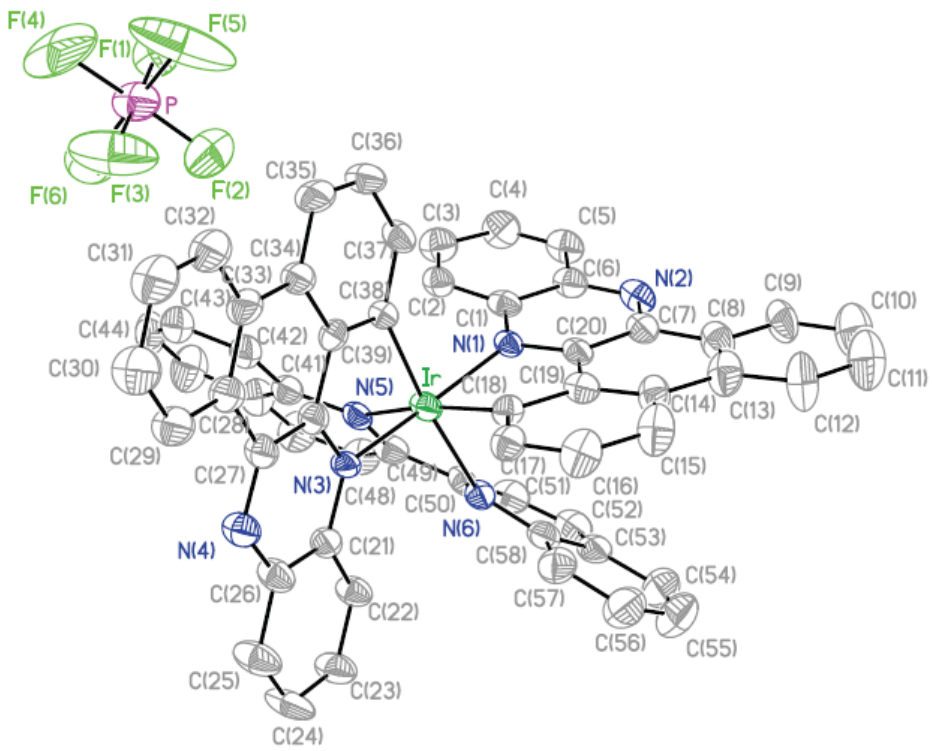


Figure S1. Crystal of complex **NIRex**. The hydrogen atoms are omitted for clarity.

Table S1. Crystal data of complex **NIRex**.

Complex	**NIRex (CCDC 1986267)**
Empirical formula	C_{58} H_{34} F_6 Ir N_6 P
Formula weight	1152.08
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 11.6607(18) Å a = 75.403(5)°. b = 15.168(2) Å b = 85.538(5)°.

	c = 16.304(3) Å
	g = 79.408(5)°.
Volume	2741.5(7) Å^3
Z	2
Density (calculated)	1.396 Mg/m^3
Absorption coefficient	2.526 mm^{-1}
F(000)	1140
Crystal size	0.420 x 0.230 x 0.010 mm^3
Theta range for data collection	2.817 to 28.080°.
Index ranges	-15<=h<=15, -20<=k<=19, -20<=l<=21
Reflections collected	51672
Independent reflections	13138 [R(int) = 0.1339]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9281 and 0.5590
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13138 / 0 / 649
Goodness-of-fit on F^2	0.991
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1453
R indices (all data)	R1 = 0.1200, wR2 = 0.1797
Extinction coefficient	n/a
Largest diff. peak and hole	2.844 and -3.396 e.Å^{-3}

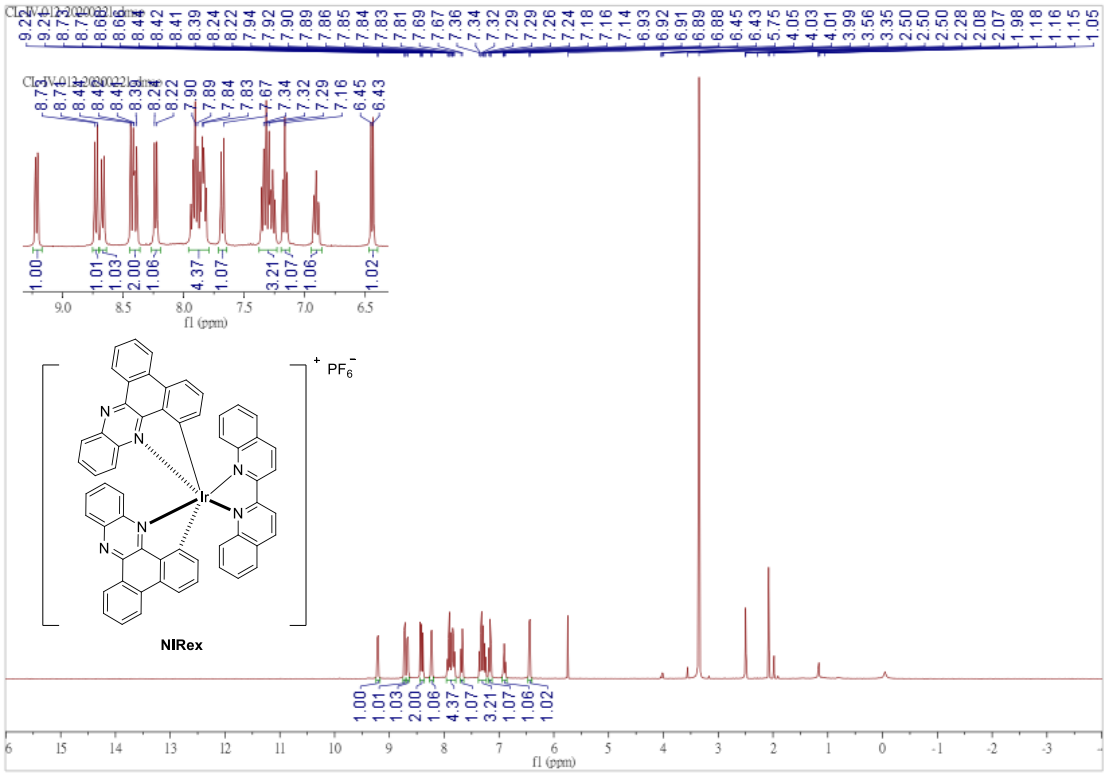


Figure S2. ^{1}H NMR spectrum for complex **NIRex** (400 MHz, DMSO-d_6, 298 K).

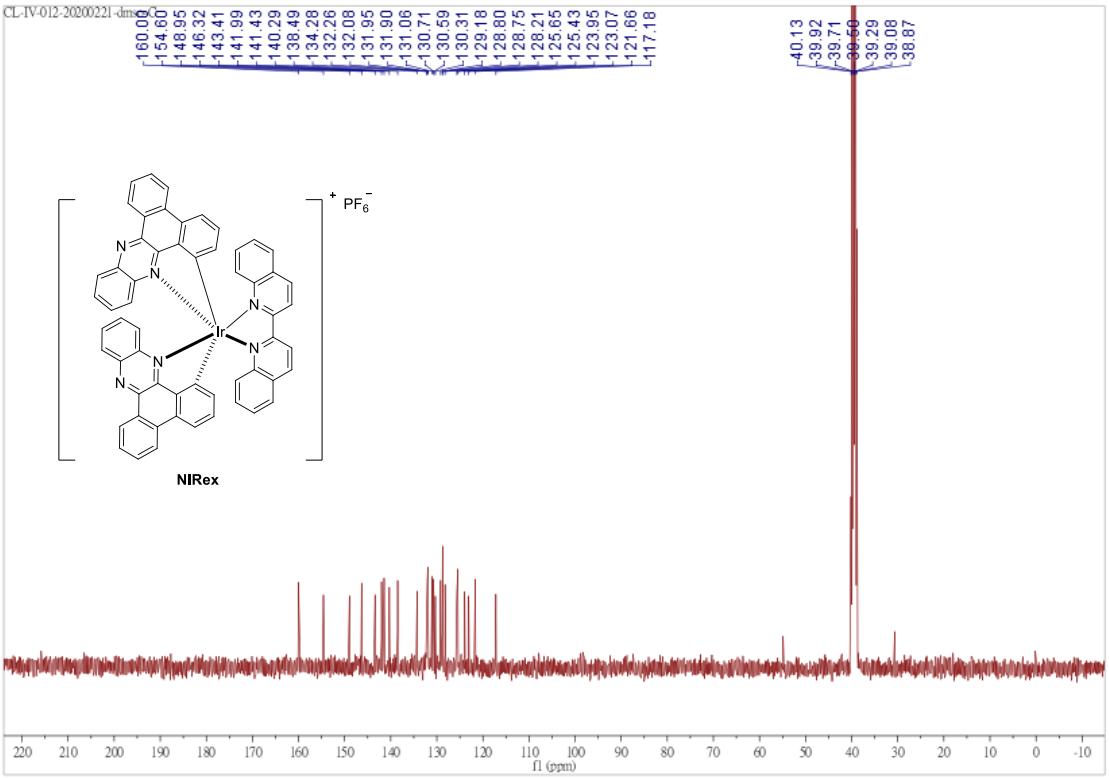


Figure S3. ^{13}C NMR spectrum for complex **NIRex** (100 MHz, DMSO-d_6, 298 K).

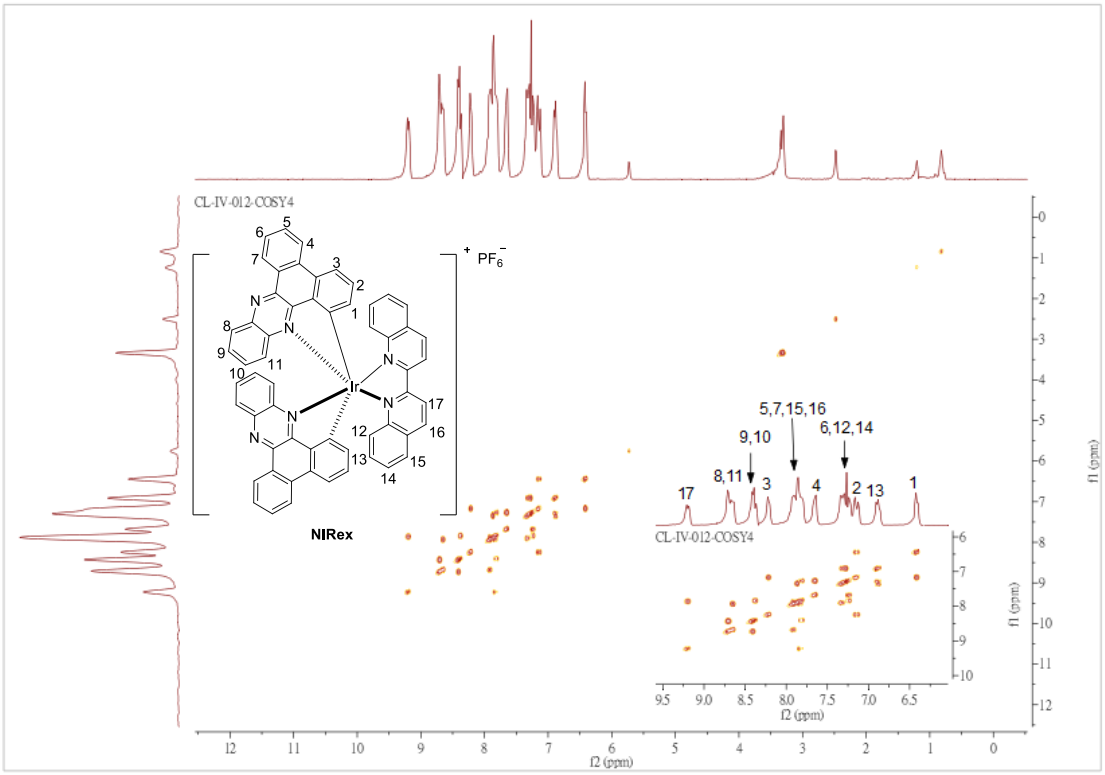


Figure S4. ^{1}H-^{1}H COSY spectrum (400 MHz, pulse width of 14.0) of complex **NIRex** in $CDCl_3$ at 298 K, the inset is the expansion of the aromatic region.

Data:CL-IV-012
Comment:
Description:
Ionization Mode:ESI+
History:Average(MS[1] 0.37..0.40)

Acquired:3/5/2020 11:53:57 AM
Operator:AccuTOF
m/z Calibration File:20200218-TFANa_...
Created:3/5/2020 4:08:56 PM
Created by:AccuTOF

Charge number:1 Tolerance:200.00[ppm], 200.00 .. 200.... Unsaturation Number:-150.0 .. 200.0 (...
Element:^{12}C:58 .. 58, ^{1}H:33 .. 35, ^{19}F:6 .. 6, ^{191}Ir:0 .. 1, ^{193}Ir:0 .. 1, ^{14}N:6 .. 6, ^{23}Na:0 .. 2, ^{31}P:0 .. 10, ^{32}S:1 .. 1

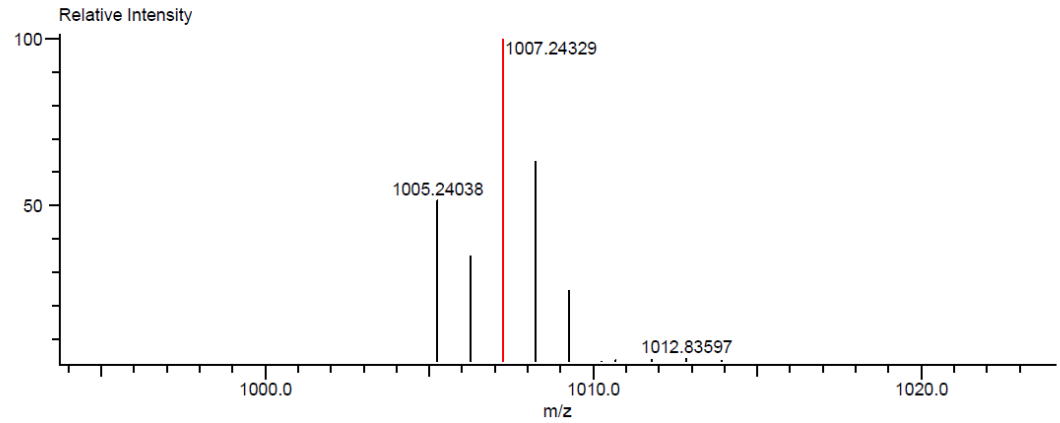
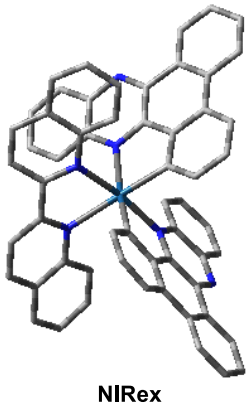


Figure S5. HRMS-ESI^{+} spectrum of **NIRex**.

Table S2. Calculated singlet and triplet states for cationic iridium complex **NIRex** by TD-DFT approach.

Complex	States	eV[(a)] (nm)	f[(b)]	Monoexcitations[(c)]	Ground state dipole moment [D]
NIRex	S_1	2.06 (601)	0.0066	H - 4 → L (1.3%) H - 2 → L (1.2%) H - 1 → L (6.6%) H → L (40%)	5.9337
	T_1	1.50 (826)	0.0000	H - 4 → L (8.0%) H - 4 → L + 1 (4.2%) H - 2 → L (3.3%) H - 2 → L + 1 (1.5%) H - 1 → L (4.4%) H - 1 → L + 1 (1.8%) H → L (17%) H → L + 1 (6.7%)	

(a) Calculated vertical excitation energies. (b) f = oscillator strength. (c) H and L denote the HOMO and LUMO, respectively; data in parentheses are the contributions of the excitation.



NIRex

Figure S6. Ground state geometries of complex **NIRex** obtain at B3LYB/6-31G(d)/LanL2DZ level of theory. Hydrogen atoms are omitted for clarity.

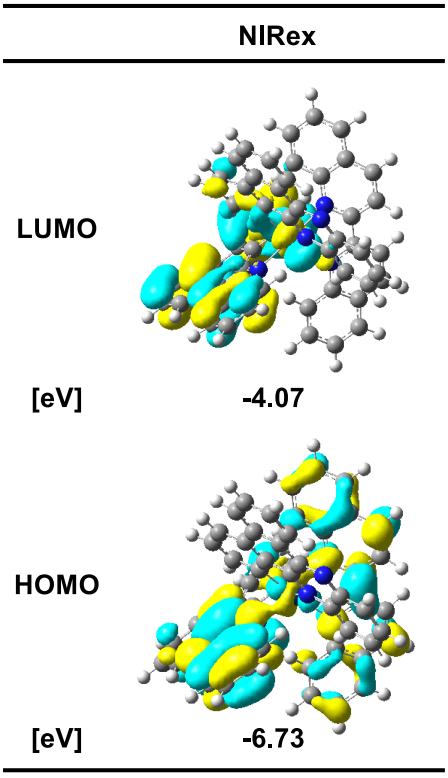


Figure S7. Electron density distribution pattern of the frontier molecular orbitals for complex **NIRex**, obtained at B3LYP/6-31G(d,p)/LanL2DZ level of theory.

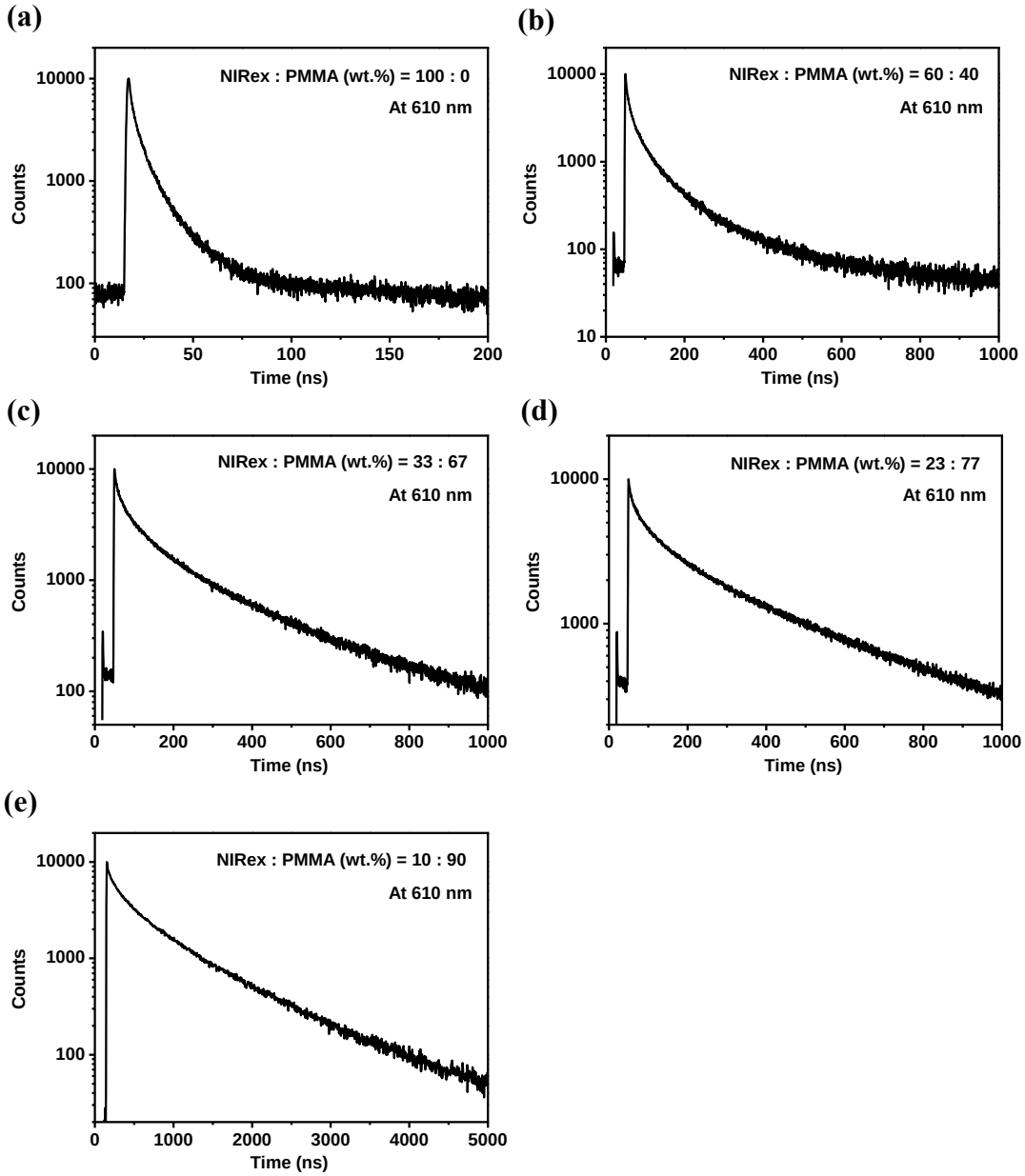


Figure S8. Excited-state lifetimes at 610 nm of thin films with weight ratios of complex **NIRex** and PMMA of (a) 100 : 0, (b) 60 : 40, (c) 33 : 67, (d) 23 : 77 and (e) 10 : 90.

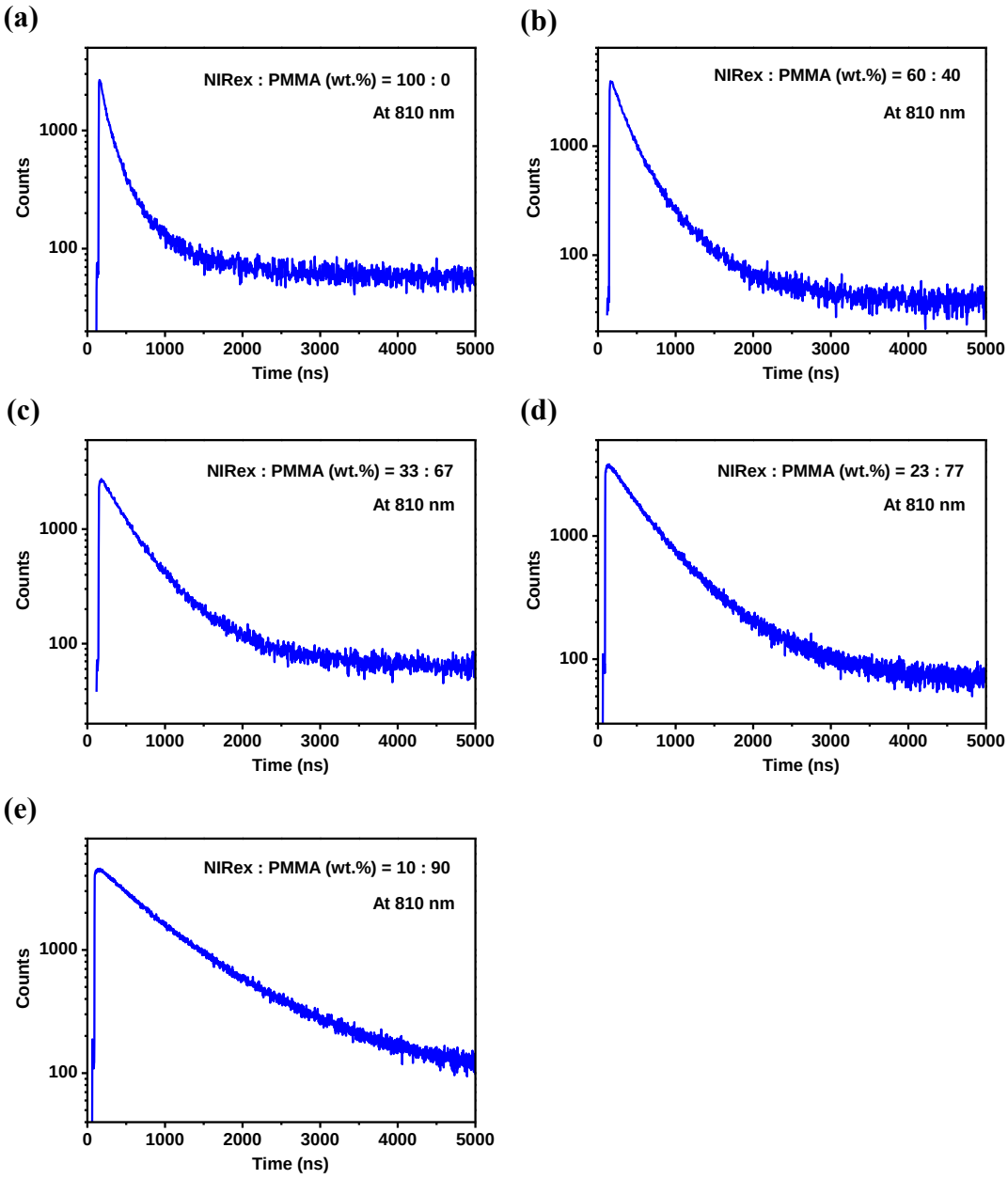


Figure S9. Excited-state lifetimes at 810 nm of thin films with weight ratios of complex **NIRex** and PMMA of (a) 100 : 0, (b) 60 : 40, (c) 33 : 67, (d) 23 : 77 and (e) 10 : 90.

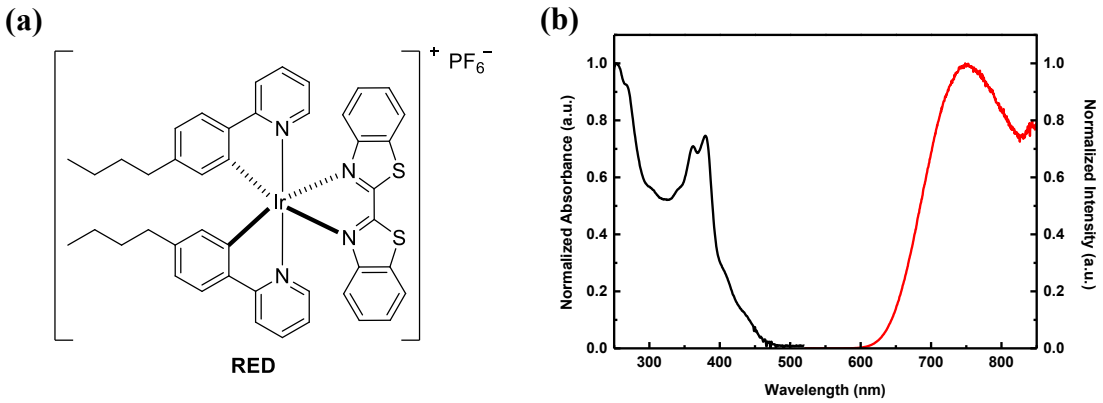


Figure S10. (a) Structure of complex **RED** for comparison. (b) Absorption (left axis) and PL spectra (right axis) of complex **RED** in MeCN solution (1.0×10^{-5} M, λ_{ex} = 385 nm).

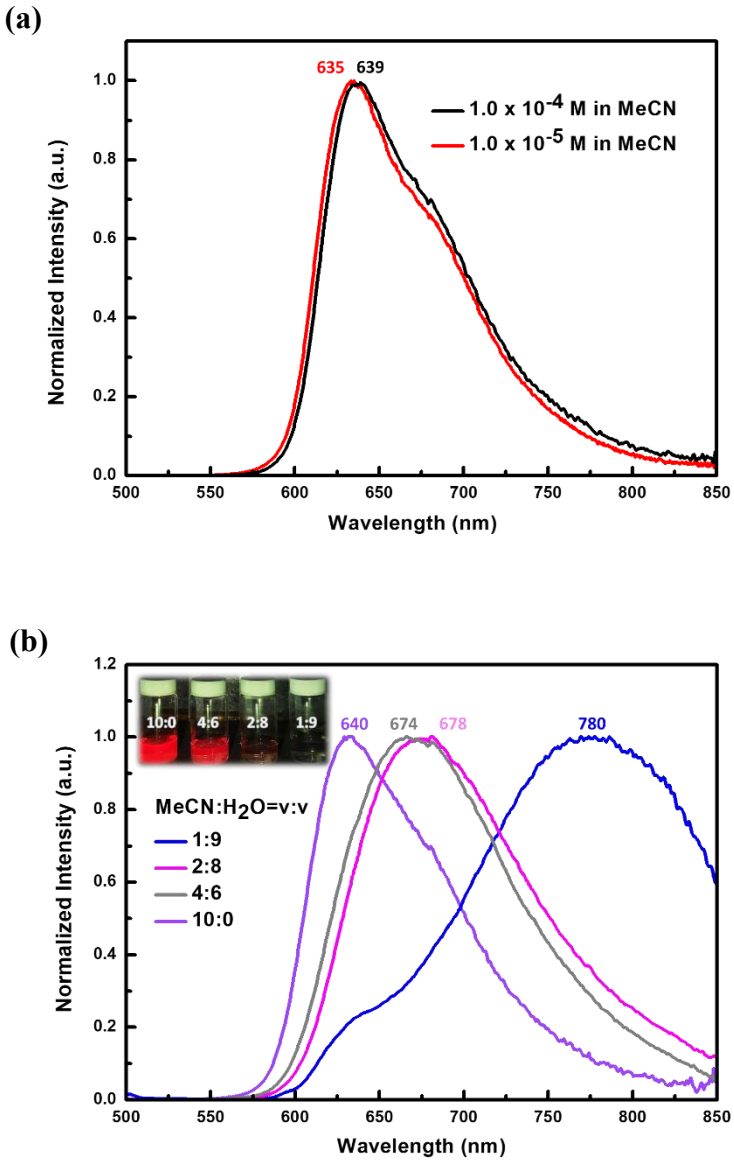


Figure S11. (a) Concentration-dependent PL spectra; (b) PL spectra of complex **NIRex** in MeCN with the increasing of water content (*ca.* 1.0 x 10^{-4} M, water fraction from 0 to 90% by volume).

Table S3. Summary of the characteristics of NIR LECs reported in literatures

Emissive material	$\lambda_{max, EL}$ [nm][a]	L_{max} [μW cm^{-2}][b]	$\eta_{ext, max}$ [%][c]	$\eta_{P, max}$ [mW W^{-1}][d]	Ref.
[Ir(ppy)$_2$(dasb)][PF$_6$]:DOTCI (1.0 wt.%)	729	2.42	0.93	6.43	1
[Ir(ppy)$_2$(dasb)][PF$_6$]:DTTCI (1.0 wt.%)	805	8.19	1.49	10.16	1
dye H: dye G (0.1 wt.%)	706	170	0.44	-	2
polymers with dinuclear Ru complexes	790	0.016[e]	5.4 x 10^{-6}[e]	-	3
PIDTT-TQ	705	129	0.1	0.48	4
PBDTTBTzT	723	169	0.135	-	5
PIDTT-SBS	725	263	0.214	-	6
PBDTSi-BDD:ZnP(TDPP)$_4$ (5 wt.%)	900	36	0.028	-	7
[Os(phen)$_3$][PF$_6$]$_2$	710	-	0.08[e]	-	8
[Ru(tpy)(tpy-O$_2$Et)][PF$_6$]$_2$	706	-	-	-	9
Ru complex (**3**)	780	30.8[e]	0.013	-	10
Ru complex (**4**)	880	5.7[e]	0.075	-	10
Ru complex (**5**)	900	2.5[e]	0.006	-	10
Ru complex (**6**)	945	3.1[e]	0.030	-	10
Ru complex (**7**)	1040	-	-	-	10
[Ru(tpy-CO$_2$Et)(trz)][PF$_6$]$_2$	725	-	0.005	-	11
heteroleptic bis(tridentate) Ru complexes	722	-	0.028	-	12
Ru(dtb-bpy)$_3$(PF$_6$)$_2$: DOTCI (1	739	14.9	2.75	9.37	13

wt.%)					
phenanthroimidazole Ru complex (**NE04**)	700	-	1.367	-	14
$[Ir(ppy)_2(2,2'$-bibenzo[d]thiazole)][PF_6]	705	260[e]	0.37	-	15
$Ru(dtb\text{-}bpy)_3(PF_6)_2$	718	33.6	0.64	3.76	16
Ir complex (**NIR3**)	882	44.1	0.036	0.122	17
Ir complex (**NIR6**)	790	56.9	0.05	0.181	17
complex **RED** : complex **NIR3** (20 wt.%)	778	12.6	0.116	0.747	17
complex **RED** : complex **NIR6** (20 wt.%)	778	13.6	0.093	0.631	17
Ru complex (**Bn2**)	706	-	0.93	-	18
complex **NIRex**	860	143	0.26	0.93	this work
complex **RED** : complex **NIRex** (60 wt.%)	824	164	0.39	1.46	this work
complex **RED** : complex **NIRex** (40 wt.%)	809	303	0.57	2.20	this work
complex **RED** : complex **NIRex** (20 wt.%)	744	637	0.82	3.29	this work

[a] EL peak wavelength. [b] Maximal light output power. [c] Maximal external quantum efficiency. [d] Maximal power efficiency. [e] Estimated from the reported data.

Abbreviations

1. ppy: 2-phenylpyridine
2. dasb: 4,5-diaza-9,9′-spirobifluorene
3. DOTCI: 3,3′-diethyl-2,2′-oxathiacarbocyanine iodide
4. DTTCI: 3,3′-diethylthiatricarbocyanine iodide
5. dye H: 1-ethyl-2-[3-(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)-propenyl]-3,3-dimethyl-3H-indolium hexafluorophosphate
6. dye G: 1-butyl-2-[5-(1-butyl-1,3-dihydro-3,3-dimethyl-2Hindol-2-ylidene)-penta-1,3-dienyl]-3,3-dimethyl-3H-indolium hexafluorophosphate
7. PIDTT-TQ: poly[indacenodithieno[3,2-b]thiophene-2,8-diyl-alt-2,3-bis(3-(octyloxy)phenyl)-5,8-di(thiophen-2-yl)quinoxaline-5,5′-diyl]
8. PBDTTBTzT: polybenzodithiophene 4,7-bis(5-bromothiophen-2-yl)-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole
9. PIDTT-SBS: poly(indacenodithieno[3,2-b]thiophene) 4,7-Bis(4,4-bis(2-ethylhexyl)-4Hsilolo[3,2-b:4,5-b′]dithiophen-2-yl)benzo[c][1,2,5]-thiadiazole
10. PBDTSi-BDD: poly[1,3-bis(2-ethylhexyl)-5-(5-(6-methyl-4,8-bis(5-(tributylsilyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophen-2-yl)thiophen-2-yl)-7-(5-methylthiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c′]dithiophene-4,8-dione]
11. TDPP: 2,5-thienyl diketopyrrolopyrrole
12. phen: 1,10-phenanthroline
13. tpy: terpyridine
14. trz: 2-phenyl-4,6-dipyridin-2-yl-1,3,5-triazine
15. dtb-bpy is 4,4′-ditertbutyl-2,2′-bipyridine

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