Design and Synthesis of Cyclometalated Iridium(III) Complex-Chromophore Hybrids that Exhibit Long-Emission Lifetimes Based on a REET (Reversible Electronic Energy Transfer) Mechanism

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Table of Contents

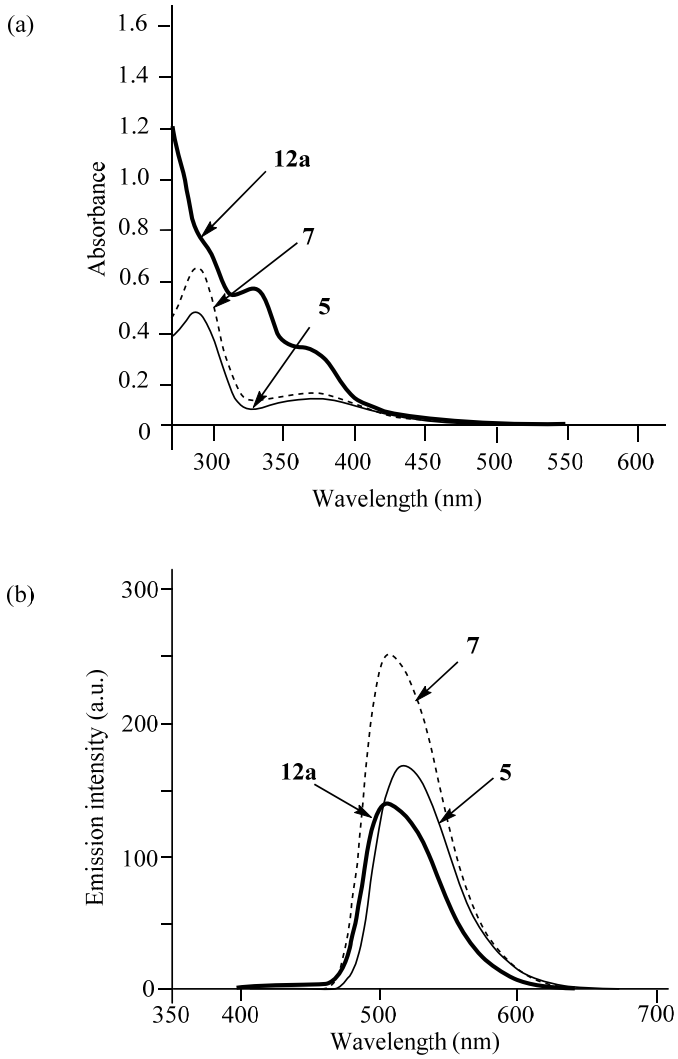


Figure S1. (a) UV/vis absorption spectra of **5**, **7**, and **12a** (10 μM) in degassed DMSO at 298 K. (b) Emission spectra of **5**, **7**, and **12a** (10 μM) in degassed DMSO at 298 K (excitation at 366 nm).

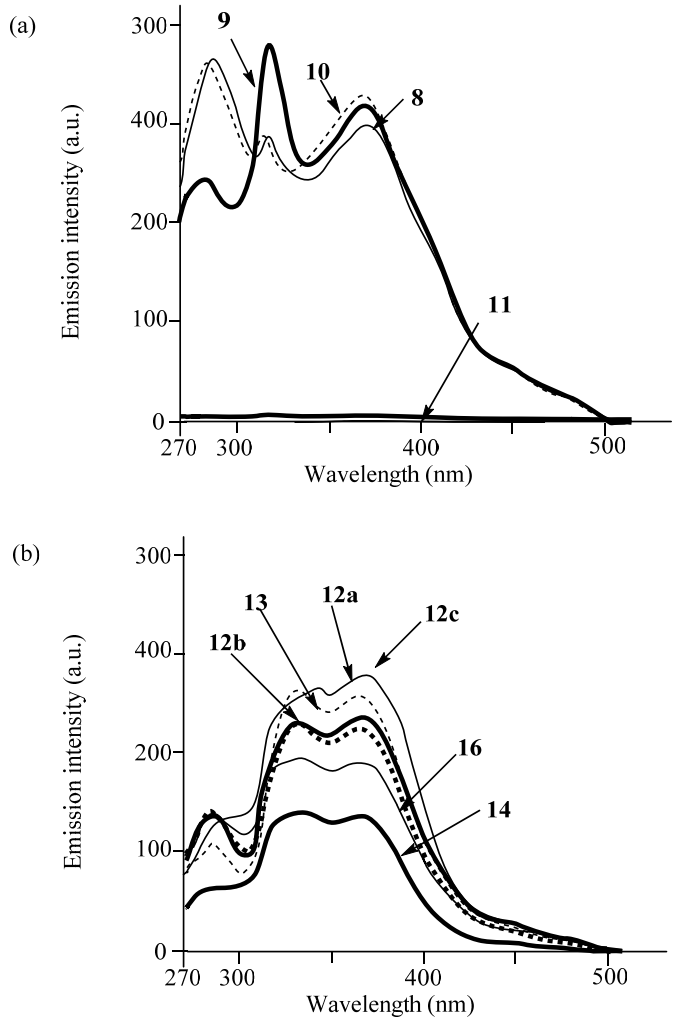


Figure S2. Excitation spectra of (a) **8-11** and (b) **12a-c**, **13-14**, and **16** (10 μM) in degassed DMSO at 298 K (emission at 500 nm).

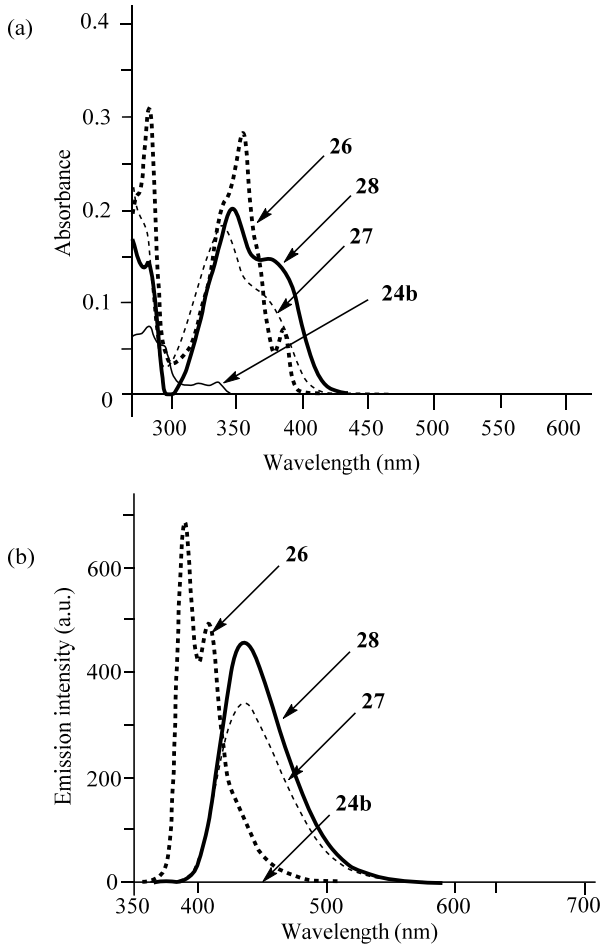


Figure S3. (a) UV/vis absorption spectra of **24b** (plain curve)**, 26** (bold dashed curve)**, 27** (dashed curve) and **28** (bold curve) (10 μM) in DMSO at 298 K. (b) Luminescence (fluorescence) emission spectra of **24b** (plain curve)**, 26** (bold dashed curve)**, 27** (dashed curve) and **28** (bold curve) (10 μM) in DMSO at 298 K. Excitation wavelength is 366 nm and a.u. denotes arbitrary units.

Table S1. Photophysical properties of **24b**, **26**, **27**, and **28** (10 μM) in degassed DMSO at 298 K.

Compounds	λ_{abs} (nm)	λ_{em} (nm)[a]	Φ^b
24b	281, 319, 334	-	-
26	282, 337, 352, 384	389, 410	0.73
27	277, 339, 373	436	0.57
28	282, 346, 374	436	0.84

[a]excitation at 366 nm. [b]Quinine sulfate in 0.1 M H_2SO_4 ($\Phi = 0.55$) was used as a reference.

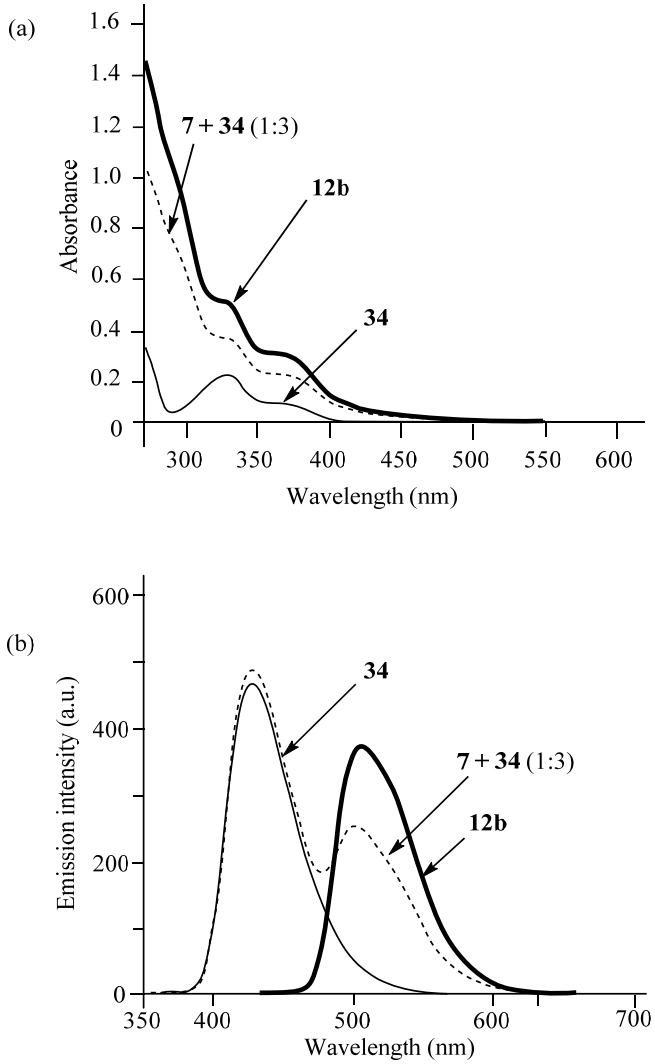


Figure S4. (a) UV/vis absorption spectra of **12b** (10 μM) (bold curve), **34** (30 μM) (solid curve) and a 1:3 mixture of **7** and **34** ([**7**] = 10 μM and [**34**] = 30 μM) (dashed curve) in DMSO at 298 K. (b) Emission spectra of **12b** (10 μM) (bold curve), **34** (30 μM) (solid curve) and a 1:3 mixture of **7** and **34** ([**7**] = 10 μM and [**34**] = 30 μM) (dashed curve) in degassed DMSO at 298 K (excitation at 366 nm).

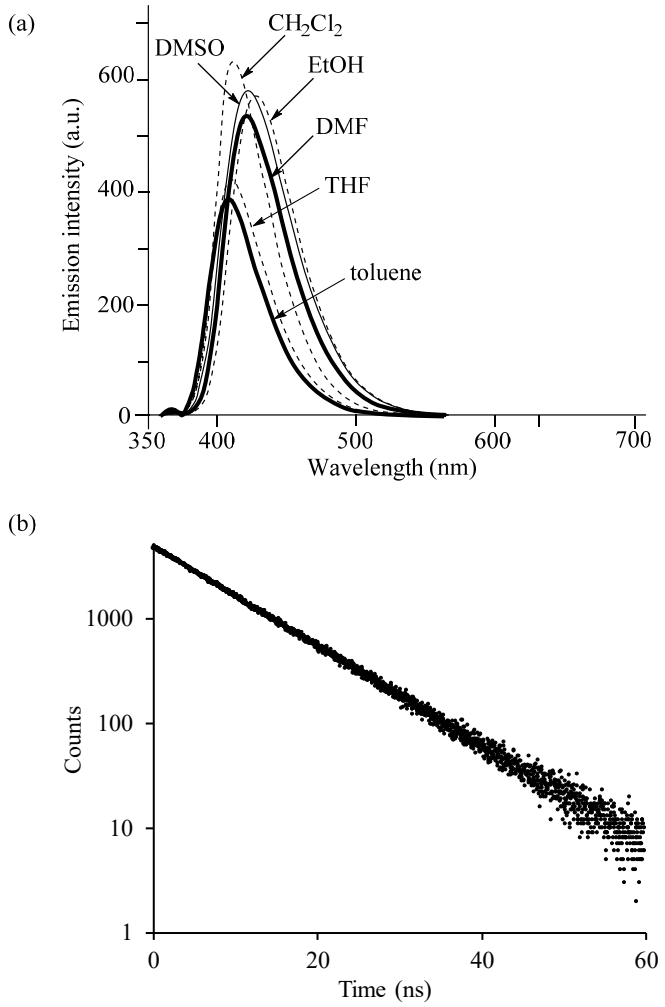


Figure S5. (a) Emission specta of **34** (10 μM) in different solvents at 298 K (excitation at 366 nm). (b) Emission decay curve of **34** (10 μM) at 430 nm in DMSO at 298 K (excitation at 371 nm).

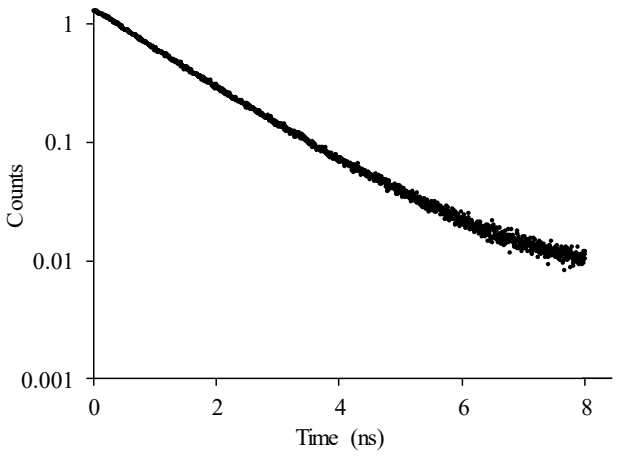


Figure S6. Emission decay curve of a 1:3 mixture of **7** and **34** ([**7**] = 10 μM and [**34**] = 30 μM) at > 475 nm in degassed DMSO at 298 K (excitation at 355 nm).

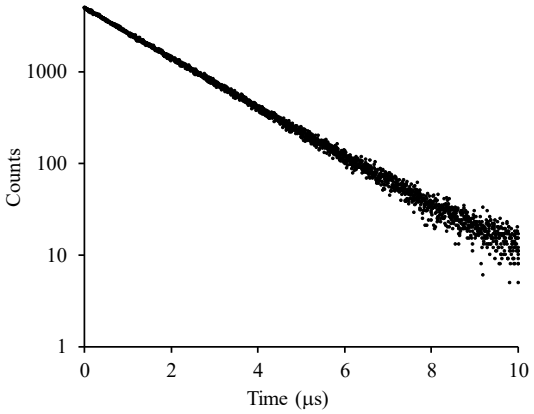
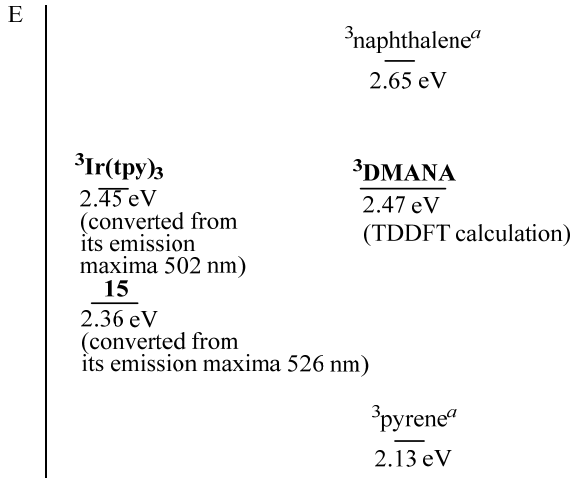


Figure S7. Emission decay curve of **10** (10 μM) at 512 nm in degassed DMSO at 298 K (excitation at 371 nm).



^{a}The values of triplet energy from the reference described in the legend

Figure S8. The triplet energy of Ir complexes and chromophores (Ref.: Murov, S. L.; Carmichael, L.; Hug, G. L. *Handbook of Photochemistry,* 2nd Ed.; Marcel Dekker, Inc.: New York, 1993).

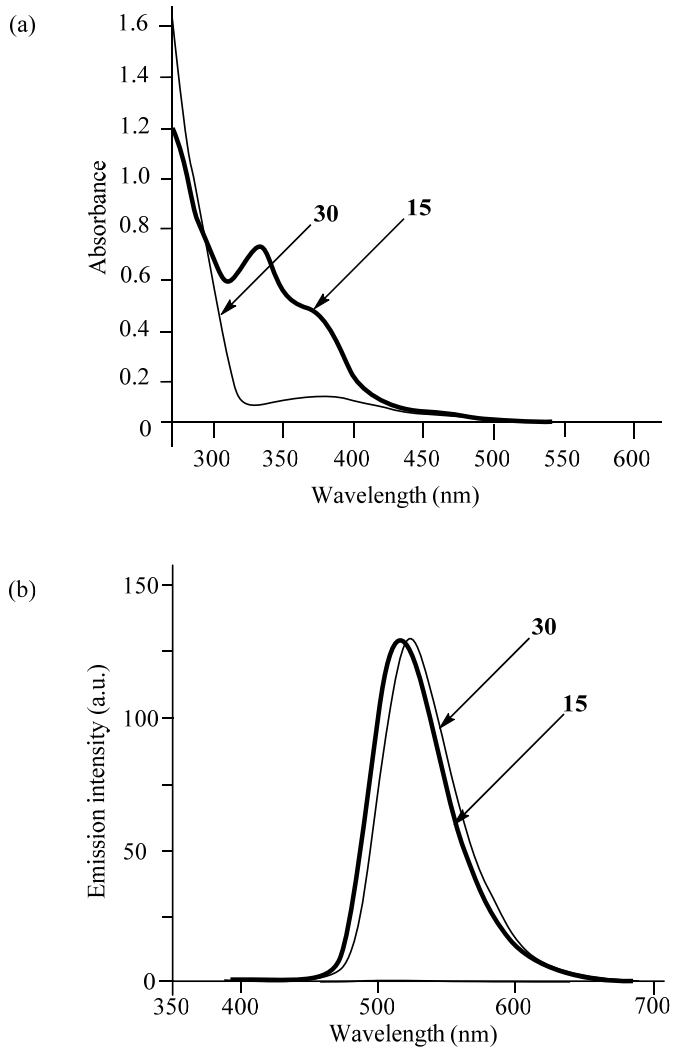


Figure S9. (a) UV/vis absorption spectra of **15** and **30** (10 μM) in degassed DMSO at 298 K. (b) Emission spectra of **15** and **30** (10 μM) in degassed DMSO at 298 K (excitation at 366 nm).

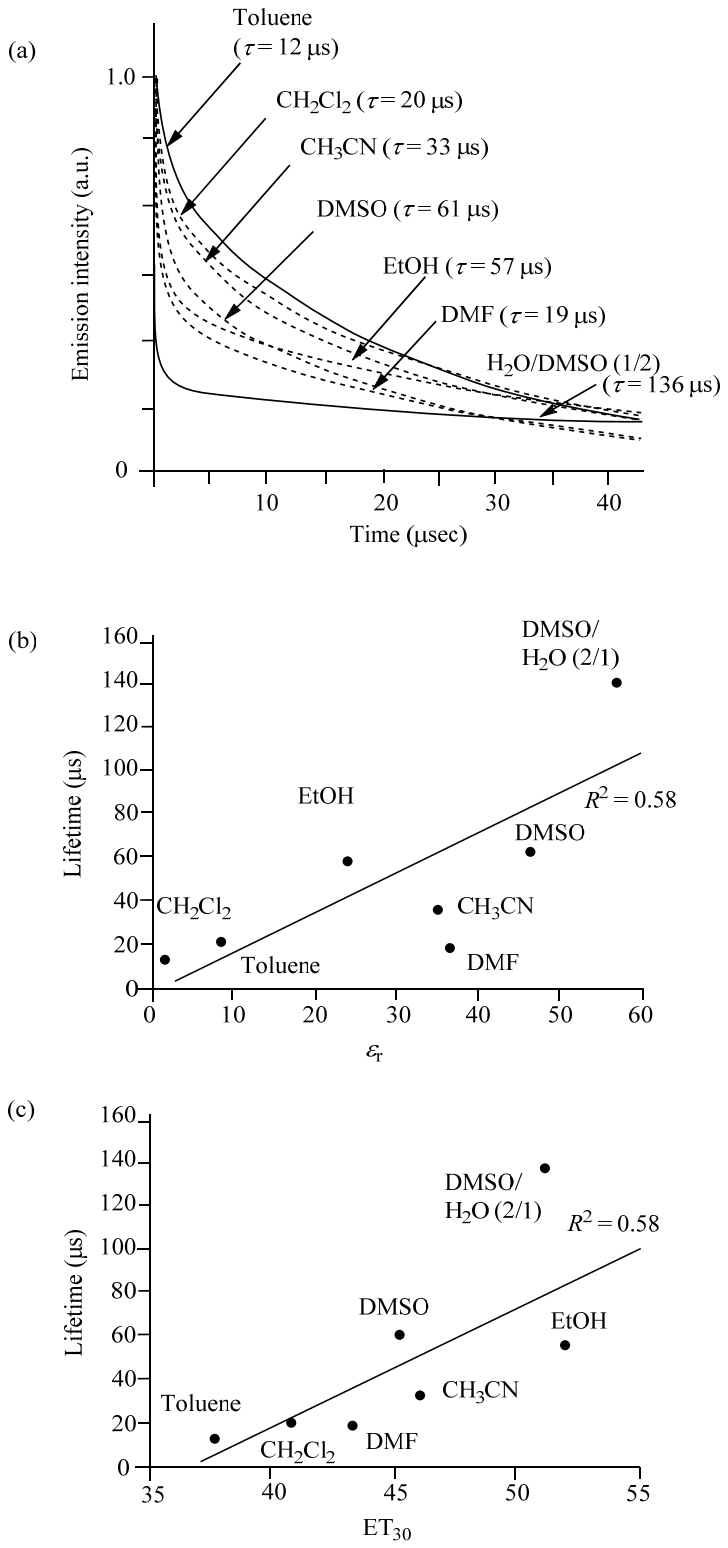


Figure S10. (a) Emission decay curves of **12a** (10 μM) at > 475 nm in degassed different solvents at 298 K (excitation at 366 nm). (b) Correlation between ε_T values of the solvents and the lifetime of **12a**. (c) Correlation between ET_{30} values of the solvents and the lifetime of **12a**.

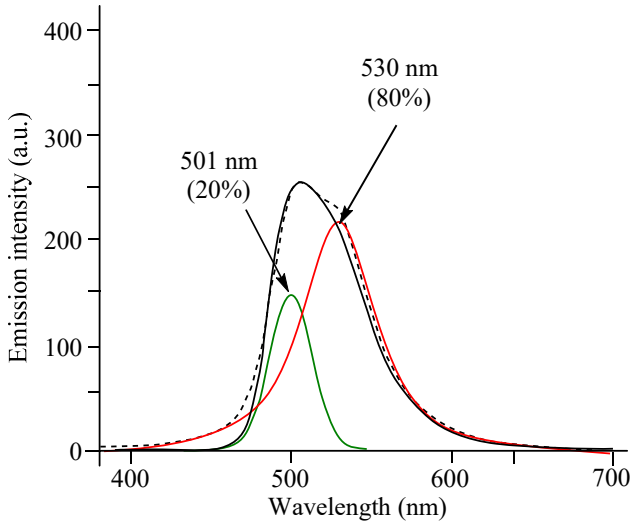


Figure S11. Observed emission spectrum of **7** (solid black curve) and its two deconvolution components having 501 nm (green curve) and 530 nm (red curve), respectively. The dashed curve is the reconstructed emission curve from the two component emission curves.

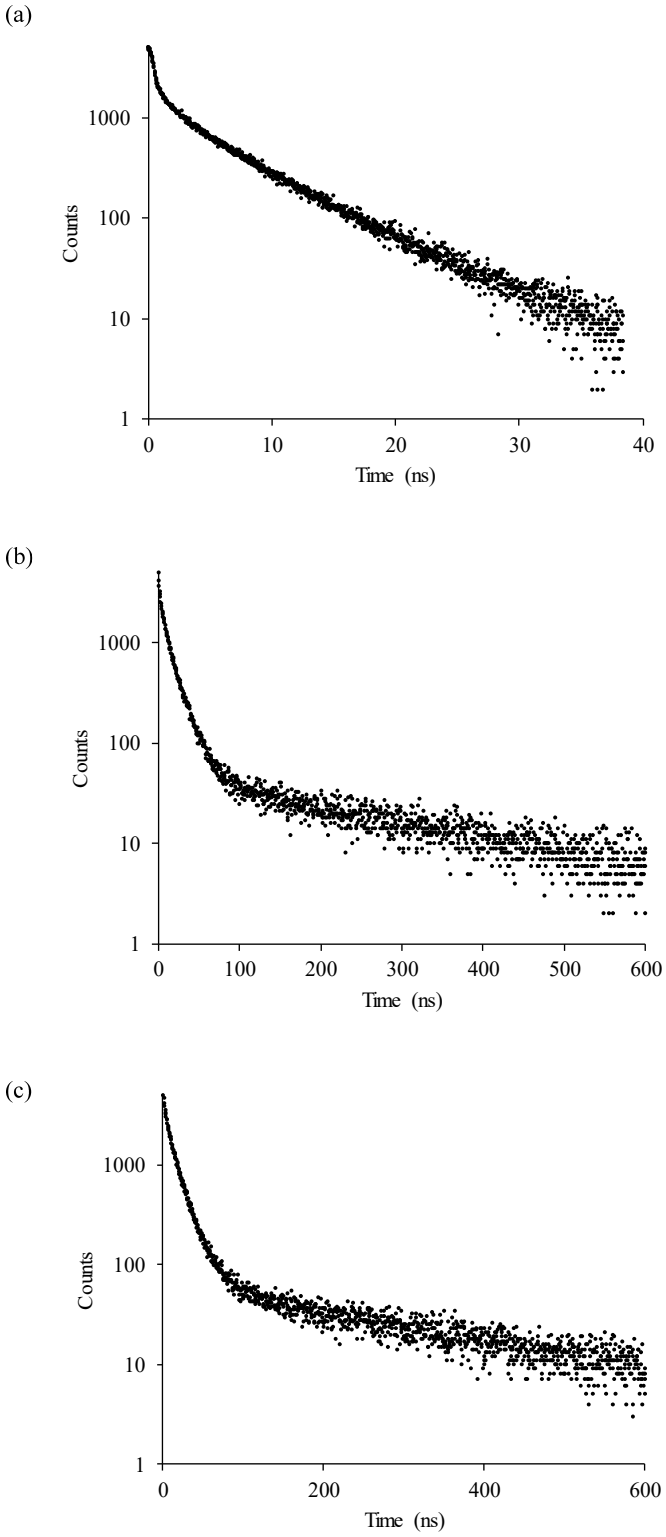


Figure S12. Emission decay curve of **12a** at 438 nm (a), at 495 nm (b), and at 507 nm (c) in DMSO at 298 K after bubbling air (excitation at 371 nm).

Table S2. Emission lifetime of **12a** (10 μM) in DMSO at 298 K after bubbling air (excitation at 371 nm).

Compond	$\tau_{1/2}$ at 438 nm (ns)		$\tau_{1/2}$ at 495 nm (ns)			$\tau_{1/2}$ at 507 nm (ns)			$\tau_{1/2}$ (μs)
	$\tau_{(ns)1}$	$\tau_{(ns)2}$	$\tau_{(ns)1}$	$\tau_{(ns)2}$	$\tau_{(ns)3}$	$\tau_{(ns)1}$	$\tau_{(ns)2}$	$\tau_{(ns)3}$	
12a	1.8	6.9	2.8	15	282	2.2	14	124	–

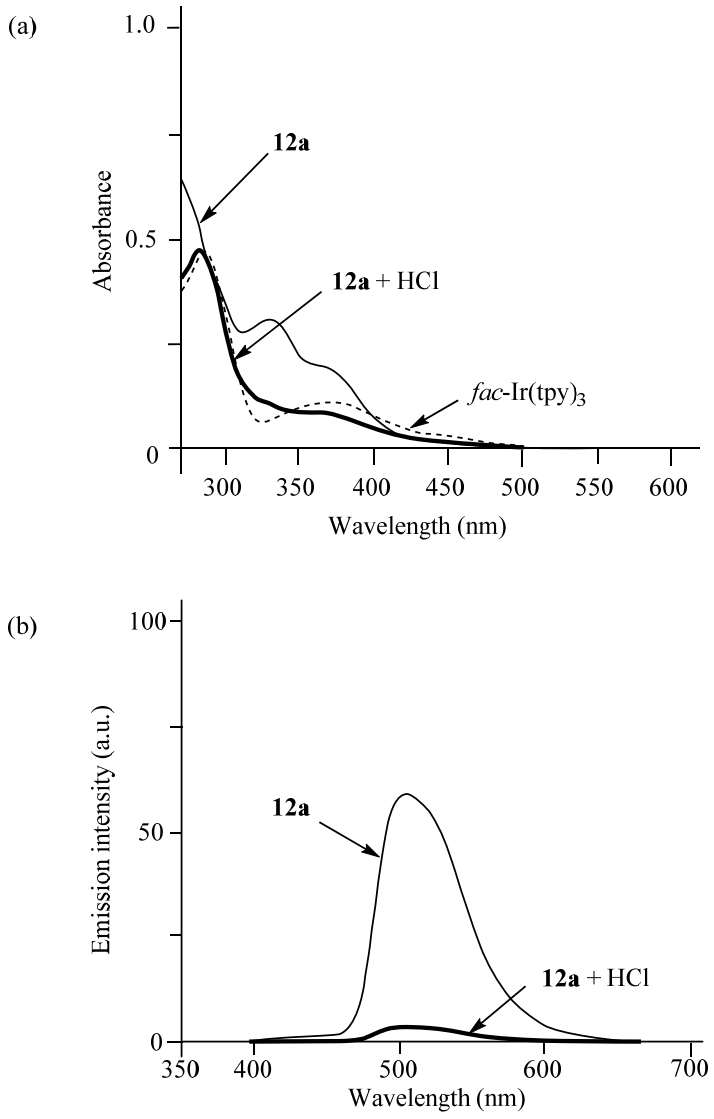


Figure S13. (a) UV/vis absorption spectra of *fac*-Ir(tpy)$_3$ (dashed curver) and **12a** (plain curve) (10 μM) in degassed DMSO/H_2O (2/1) solution and degassed DMSO/3 M aqueous HCl (2/1) solution (bold curve) at 298 K. (b) Emission spectra of **12a** (10 μM) in degassed DMSO/H_2O (2/1) solution (solid curve) and degassed DMSO/3 M aqueous HCl (2/1) solution (bold curve) at 298 K (excitation at 366 nm).

Table S3. Photophysical properties of **12a** (10 μM) upon the protonation of the dimethylamino groups of DMANA moieties.

Solvent	λ_{abs} (nm)	λ_{em} (nm)[a]	Emission lifetime[b] $\tau_{(\mu s)1}$
DMSO/H_2O (2/1)	270, 295, 327, 364	433, 505	136 μs
DMSO/3 M aqueous HCl (2/1)	287, 373	501	31 ns

[a]excitation at 366 nm. [b]excitation at 355 nm.

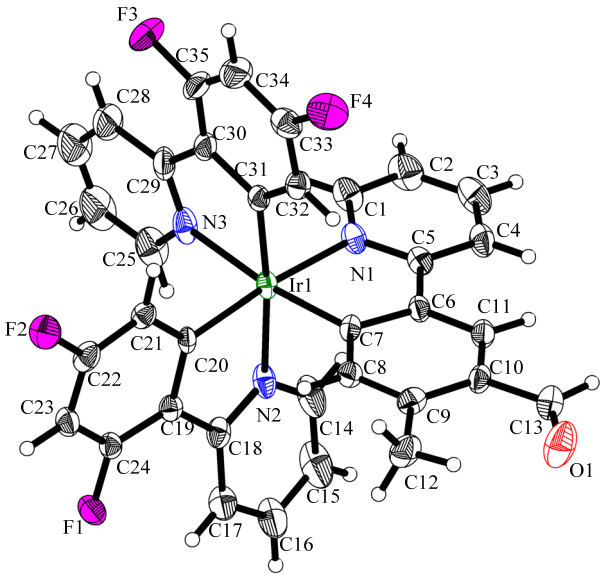


Figure S14. ORTEP drawing of single crystal structure of **37** with 50% probability ellipsoids.

Table S4. Crystal data and structure refinement for **37**.

CCDC Deposition Number	1978738
Empirical formula	$C_{35}H_{22}F_4IrN_3O$
Formula weight	768.79
Temperature	123 K
Wavelength	0.71075 Å
Crystal system	Triclinic
Space group	*P*–1
Unit cell dimensions	a = 10.343(3) Å
	b = 11.858(4) Å
	c = 12.720(4) Å
	α = 93.128(4)
	β = 93.388(4)
	γ = 104.051(5)
Volume	1506.9(8) $Å^3$
Z	2
Density (calcd.)	1.694 $g \cdot cm^{-3}$
Absorption coefficient	4.488 mm^{-1}
F(000)	748
Crystal size	0.12 x 0.08 x 0.06 mm^3
Theta range for data collection	3.3 to 27.5°
Index ranges	-13<=h<=13 -15<=k<=12, -14<=l<=16
Reflections collected	11955
□ndependent reflections	5217 [R(int) = 0.1247]
Completeness to theta = 27.480°	95.1 %
Absorption correction	multi-scan
Max. and min. transmission	0.851 and 1.000
Refinement method	Full-matrix least-square on F^2
Goodness-of-fit on F^2	0.718
Final R indices [I>2sigma(I)]	R_1 = 0.0279, wR_2 = 0.0835
R indices (all data)	R_1 = 0.0308, wR_2 = 0.0879

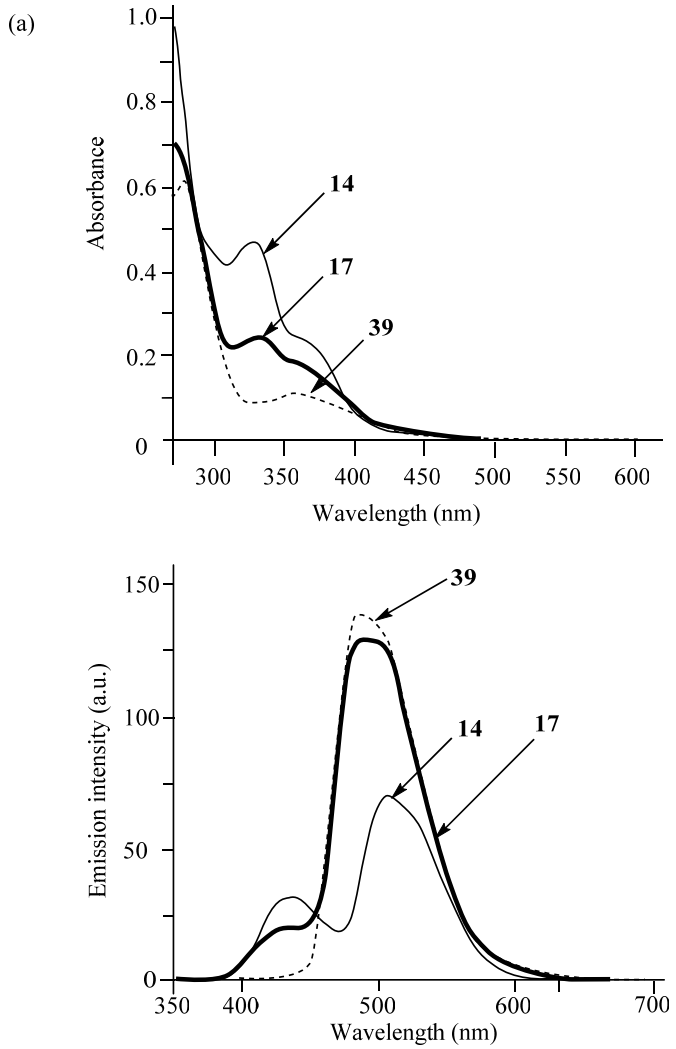


Figure S15. (a) UV/vis absorption spectra of **14** (plain curve), **17** (bold curve) and **39** (dashed curve) (10 μM) in DMSO at 298 K. (b) Emission spectra of **14** (plain curve), **17** (bold curve) and **39** (dashed curve) (10 μM) in degassed DMSO at 298 K (excitation at 366 nm).

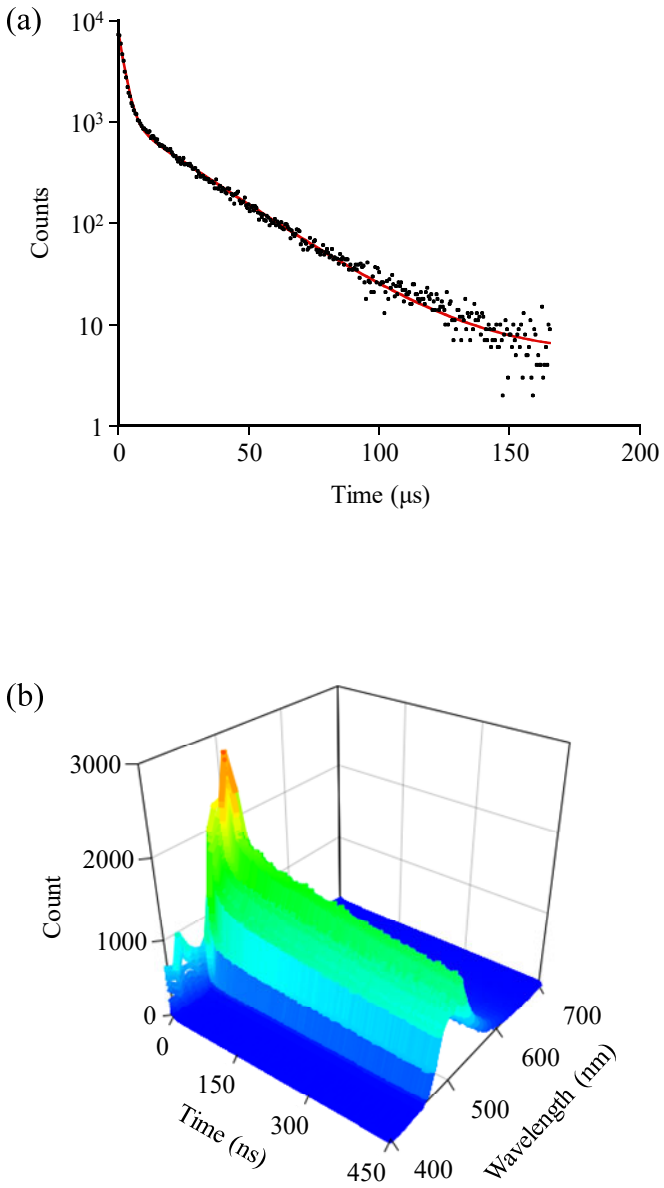
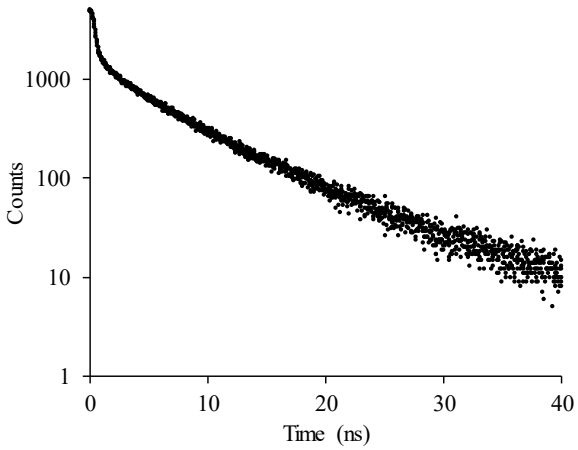


Figure S16. (a) An emission decay curve of **17** (10 μM) at 507 nm in degassed DMSO at 298 K (excitation at 371 nm). (b) Time-resolved emission spectra of **17** (10 μM). Excitation wavelength is 371 nm.

(a)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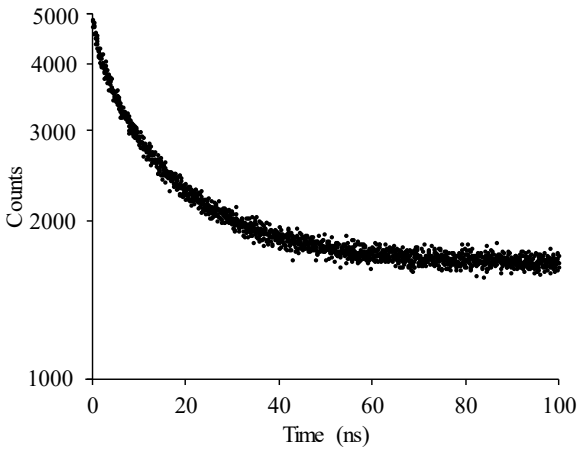
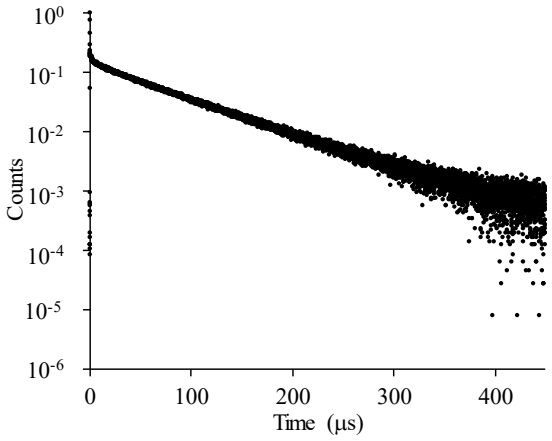
100
10
1
Counts
0
10
20
30
40
Time (ns)

(b)


5000
4000
3000
2000
1000
Counts
0
20
40
60
80
100
Time (ns)

(c)


10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
Counts
0
100
200
300
400
Time (μs)

(d)

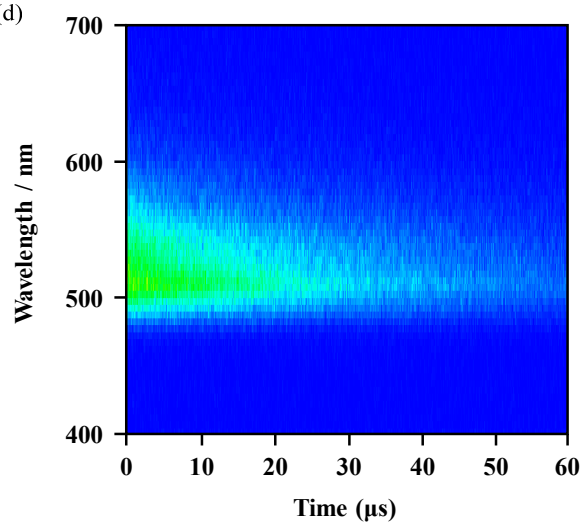

700
600
500
400
Wavelength / nm
0
10
20
30
40
50
60
Time (μs)

Figure S17. Emission decay curves of **12a** (10 μM) at 431 nm on a nanosecond scale (excitation at 371 nm) (a), at 512 nm on a nanosecond scale (excitation at 371 nm) (c) and at at > 475 nm on a microsecond scale (excitation at 355 nm) (b) and in degassed DMSO at 298 K. (d) Time-resolved emission spectra of **12a** (10 μM). Excitation wavelength is 371 nm.

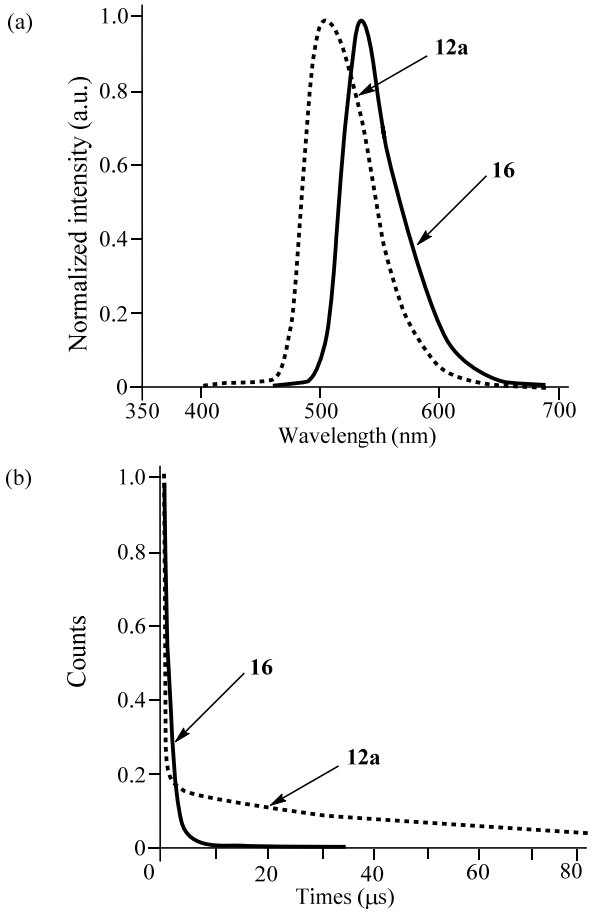


Figure S18. (a) Emission spectra of **12a** and **16** (10 μM) in DMSO at 298 K. (b) Emission decay curves of **12a** and **16** (10 μM) at at > 475 nm in degassed DMSO at 298 K.