ELECTRONIC SUPPORTING INFORMATION

Tunability of triplet excited states and photophysical behaviour of bis-cyclometalated iridium(III) complexes with imidazo[4,5-f][1,10]phenanthroline

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EXPERIMENTAL DETAILS

NMR spectra were taken with use of Bruker Avance 500 NMR spectrometer in 298 K. DMSOd₆ was used as solvent. For ¹H NMR (registered in 500 MHz) and ¹³C{¹H} NMR (registered in 125 MHz) chemical shifts (in ppm) were referenced to residual signal of the solvent. Chemical shifts of ³¹P{¹H} NMR (registered in 202 MHz) were referenced to 85% phosphoric acid solution as external standard. In addition, multidimensional correlation NMR was taken: homonuclear ¹H–¹H 2D COSY and heteronuclear ¹H–¹³C{¹H} HMQC and HMBC (long-range) correlation spectra.

HRMS analyses were performed with use of Xevo G2 Q-TOF mass spectrometer (Waters) with an ESI ion source in positive and negative ion modes. The collection of data was performed from 100 to 1000 Da, scan time 0.5 s, in centroid mode, with the mass corrected using external reference (Lock-SprayTM leucine enkephalin solution, reference ion $[M+H]^+$ at m/z 556.2771 Da). Data analysis was performed with the MassLynx software (Waters) incorporated with the instrument.

FT-IR spectra were recorded with use of Nicolet iS5 FTIR spectrophotometer in the range $4000-400 \text{ cm}^{-1}$. The samples were prepared in the form of KBr pellets.

Elemental analyses were performed with use of Elementar Vario EL Cube for C, H and N content.

The X-ray structural data of compound **2** were collected using four-circle diffractometer Gemini A Ultra (Oxford Diffraction) with CCD Atlas detector using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). CrysAlis^{Pro} software¹ was used to perform the data collection and reduction, while solving and refinement using direct methods and least square minimization was performed using SHELXS and SHELXL-2014 programs²⁻⁴. The non-hydrogen atoms were refined with anisotropic thermal parameters, while the hydrogen atoms were defined geometrically and refined with riding constrains: d(C-H) = 0.93 Å, $U_{iso}(H) = 1.2$ $U_{eq}(C)$. Crystallographic data in CIF format was deposited in the Cambridge Crystallographic Data Center, CCDC 2369644.

UV-Vis spectra were measured using ThermoScientific Evolution 220 spectrometer in dichloromethane and acetonitrile solutions. The kinetic stability studies were performed in dichloromethane, acetonitrile, and DMSO, and the UV-Vis spectra were monitored for 12 h, with spectra measured every two hours. The photostability studies were performed in dichloromethane, acetonitrile, and DMSO. The solutions of complexes were irradiated with

xenon light source at their respective low-energy excitation wavelengths for 120 min, and their UV-Vis spectra were measured every 20 min. Singlet oxygen generation (${}^{1}O_{2}$) efficiency was measured with use of the Evolution 220 UV–vis spectrometer in DMSO. 1,3-Diphenylisobenzofuran (DPBF) was used as a probe and $[Ru(bipy)_{3}](PF_{6})_{2}$ was used as a standard reference sensitizer ($\Phi_{\Delta} = 0.656$)⁵. Concentrations of DPBF and sensitizers were adjusted so that the absorbances in the 420 nm irradiation wavelength were approximately 1.0 for DPBF and 0.2 for the sensitizers. The 1 cm path length cuvettes containing mixtures of DPBF and selected sensitizer were irradiated with 420 nm wavelength using xenon light source in 15 s intervals, and the UV-Vis absorbance spectra were measured.

The DFT and TD-DFT calculations were employed with no symmetry constraints to investigate optimized geometries of complexes 1-4. The X-ray structural parameters of complex 2 were used as a starting point for the singlet ground-state optimization of all compounds, with modifications of the cyclometalating ligands performed in Chemcraft 1.8⁶. Vibrational frequency calculations were used to verify that the singlet ground state was in the minimum on the potential energy surface. All the further calculations were obtained based on the optimized geometries. PBE0 functional^{7,8} with Stuttgart/Dresden Relativistic Small Core ECP basis set with the corresponding pseudopotentials^{9,10} was used to treat the Ir atom (basis set input obtained from Basis Set Exchange Database^{11,12}), whereas the def2-TZVP basis set was used for other elements^{13–15}. Solvent effects for acetonitrile were taken into consideration using the polarized continuum model (PCM)^{16–18} within the SCRF theory. All computations were performed with GAUSSIAN-16 rev. C.01¹⁹ software package using resources provided by Wroclaw Centre for Networking and Supercomputing (<u>http://wcss.pl</u>). Measurements of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out using an Autolab PGSTAT 128N (Eco Chemie). A classic one-compartment, threeelectrode cell system with GC working electrode (2 mm diam.), Ag/Ag⁺ reference electrode and Pt wire counter electrode was used. All experiments were carried out in deoxygenated 1 mM solutions of the studied compound in the supporting electrolyte (0.1 M Bu₄NPF₆ in MeCN). Scan rate was equal to 0.1 V \vee s⁻¹, while the potential was calibrated against ferrocene.

The steady-state emission and excitation spectra were measured using FLS-980 fluorescence spectrophotometer (Edinburgh Instruments), with a 450 W Xe lamp as a light source and high-gain photomultiplier with 500 nm diffraction grating (Hamamatsu, R928P) as a detector. Measurements were carried out for the deaerated and aerated dichloromethane and acetonitrile solutions, and the deaeration was performed through argon purging of freshly prepared samples for 1 h. The 77 K emission spectra were recorded in an ethanol:methanol (4:1 v/v) matrix using liquid nitrogen to freeze the samples. The quantum yields of luminescence were measured on FLS-980 using an absolute method with integrating sphere. As a reference, respective solvents or Spectralon[®] standard were used. Calculations of the quantum yield were performed using FLS-980 software. The emission lifetime measurements were carried out on FLS-980 with TCSPC (using EPLED 405 nm diode as excitation source) or MCS (using 60 W microsecond Xe flash lamp as excitation source) methods. If needed, IRF was measured on the Ludox[®] solution. Calculations of the lifetimes were performed via FLS-980 software and the obtained decay curves were fitted using deconvolution or tail fit analysis.

The femtosecond transient absorption spectra were measured using a pump–probe transient absorption system (Ultrafast Systems, Helios) described in previous works^{20–22}. The samples dissolved in MeCN were placed in 2 mm path length quartz cells equipped with

magnetic stirring and deaerated using 30 min argon-bubbling method. The concentration of the samples was chosen so that the ground state absorption in 355 nm excitation wavelength was about 0.5 (which corresponded to concentrations 2.5×10^{-4} M for **2** and **4** and 5×10^{-4} M for **1** and **3**). The obtained fs-TA data were prepared using Surface Xplorer (Ultrafast Systems) software: the background and scattered light were subtracted, and the coherent artifact analysis was performed for the corrections of the probe chirp. The global analysis of the TA maps was carried out using the linear unidirectional sequential model implemented in the OptimusTM software²³. This analysis allowed us to perform the deconvolution of the transient spectra into evolution-associated spectra (EAS), providing the decay-associated spectra (DAS) as a linear combination of the EAS.

The triplet state lifetimes of the compounds were performed using a LKS 60 laser flash photolysis spectrometer (Applied Photophysics). A third harmonic nanosecond Nd-YAG laser with a wavelength of 355 nm (Brilliant) was used for sample excitation. Each laser pulse had a maximum power of 100 mJ, with an instantaneous power of 20 MW. Detection was achieved using a 150 W xenon lamp flash (OSRM XBO CR-OFR) coupled with a monochromator featuring a 1/1200 mm diffraction grating. Signal detection was performed using a photomultiplier. Compounds were dissolved acetonitrile, exhibiting an absorbance of 0.2 at the 355 nm excitation wavelength. Triplet state kinetic decay curves were monitored at wavelengths corresponding to the maximum absorption determined from the triplet-triplet transition absorption spectrum specific to each compound. Measurements were carried out in a quartz cuvette with a 1 cm optical path length, maintaining room temperature equilibrium and near anaerobic conditions achieved by nitrogen purging for 30 minutes to eliminate oxygen. The kinetic decay curves were measured ten times for each sample. All decay profiles were analyzed using monoexponential fitting via LKS Pro-Data software.



Scheme S1. Schematic of synthesis of complexes 1-4.

NMR SPECTRA









Figure S1. ¹H (a), ¹³C{¹H} (b), ¹H–¹H COSY (c), ¹H–¹³C{¹H} HMQC (d), ¹H–¹³C{¹H} HMBC (e) and ³¹P{¹H} NMR (f) spectra of compound **1** in DMSO-d₆.









Figure S2. ¹H (a), ¹³C{¹H} (b), ¹H–¹H COSY (c), ¹H–¹³C{¹H} HMQC (d), ¹H–¹³C{¹H} HMBC (e) and ³¹P{¹H} NMR (f) spectra of compound **2** in DMSO-d₆.









Figure S3. ¹H (a), ¹³C{¹H} (b), ¹H–¹H COSY (c), ¹H–¹³C{¹H} HMQC (d), ¹H–¹³C{¹H} HMBC (e) and ³¹P{¹H} NMR (f) spectra of compound **3** in DMSO-d₆.







Figure S4. ¹H (a), ¹³C{¹H} (b), ¹H–¹H COSY (c), ¹H–¹³C{¹H} HMQC (d), ¹H–¹³C{¹H} HMBC (e) and ³¹P{¹H} NMR (f) spectra of compound **4** in DMSO-d₆.

HRMS SPECTRA

Mult Tolers Elem Numi Mono 63 for Elem	Subject Mass Analysis: 4 mass(es) processed - Jenneer 1960 DPL 7 UPE: mm = 1.5, max = 50.0 - Jenneer 1960 DPL 2004 DPL Fm = 1.5, max = 50.0 - Jenneer 1960 DPL 2004 DPL Fm = 3 - Jonoids Holes Alss, Odd and Even Electron Ions - Stemulately evaluated with 1 results within limits (up to 2 best isotopic matches for each mass) -																	
Mass	RA	Calc. Mass	mDa PPM E	DBE Formula	i-FIT i-FIT N	Iorm Fit Cont	f% C H N.	Ir										
720.16 721.16 722.17	00 58.30 90 21.95 93 100.00 14 38.26	 721.1692 	0.1 0.1 2	8.0 C35	5 n/a	n/a	35 24 6	1										
Ir-Ph-p 1: TOF	y-imphen 883 (MS ES+	1.824)																
100-									721	1693								1.79e+006
							7	19.1666										
%-																		
										722.	1714							
									00.4600									
									20.1090									
											722 1740							
	740 444	712 1404	744 4407	746 4647	746 4000	747 4000	710 4147 719.079	719.44	721.0635	721.4515	722.9429	724.1757	705 4770	708 1540	707 4464	700 107 :	700 4000	700 4564
0-4	712.144	713.0	714.1437	715.0	716.0	717.1328	718.0 71	9.0 72	20.0 721.	ارب اربار ارب ار 0 722.0	723.0	724.0	725.0	726.0	727.0	728.0	729.0	730.001 m/z 730.0

1 HRMS (ESI, positive mode): calcd for $C_{35}H_{24}IrN_6^+$ 721.1692 found 721.1693

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of ratopp parks used for FTT = 3 Monoids ofper Maas, Even Echtorh Inor, Even Echtorh Inor 1 formulate) evaluates with 1 results within limits (up to 2 best isotopic matches for each mass) Elements Used:	
Mass RA Cate. Mass mDa PPM DE Formula +FTI +FTI Norm FtC orf % C + F P r 4443648 0000 14436457 0.6 41 - 1.5 F6 P - 1.5 n/a - n/a - 6 1	
Ir-Ph-or-implen neg 975 (2, 110) Cm (972, 983)	
1: TOF INS E3. 144 9648	9.49e+005
100.9641 112.9678 122.0287 127.0388 139.0382 148.9528 153.0522 168.0129.168.0459.180.044 198.0732 197.8089 265.0255 212.0673 218.1738 223.0253 233.1521 243.0019 255.2305	269.2171 279.9146 283.2595 297.0454 m/z

1 HRMS (ESI, negative mode): calcd for PF_6^- 144.9642 found 144.9648



 $\boldsymbol{2}$ HRMS (ESI, positive mode): calcd for $C_{43}H_{28}IrN_{6}^{+}$ 821.2005 found 821.2012

2 HRMS (ESI, negative mode): calcd for PF_6^- 144.9642 found 144.9641

(b)



3 HRMS (ESI, positive mode): calcd for $C_{39}H_{24}IrN_6S_2^+$ 833.1133 found 833.1138

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Image: 1.5, max = 50.0 Image: 1.5, max = 50.0 Element yeolicitor: Off Number of isotope packs used for I-FT = 3 Image: 1.5, max = 50.0 Image: 1.5, max = 50.0 Monosolopic Maxas. Even Electron ions Image: 1.5, max = 50.0 Image: 1.5, max = 1.5								
Ir-Ph-bztz-imphen neg 114 (0.273) 1: TOF MS ES-		_						
100 144.5	273#+0	,05						
56- 101.0616 110 0000 110 0/64 120 0/64 143.1066	156 6975 155 0101 178 0213 198 0603 193.0028 335 025 219.1719 220 2775 324 4448241 3173 255 2307 355 4405 270 1189 323 353 203 1754 303 1088 ^{312.9160}							
100 105 110 115 120 125 130 135 140 14	5 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315	n/z						

3 HRMS (ESI, negative mode): calcd for PF₆⁻ 144.9642 found 144.9642

(c)



4 HRMS (ESI, positive mode): calcd for $C_{39}H_{24}IrN_6S_2^+$ 833.1133 found 833.1147

Tolerance = 5.0 mDa / DBE: min = 1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for I-FIT = 3 Monotadory Max Serve Electron lone 1 formulaey invaluated with 1 results within limits (up to 2 best isotopic matches for each mass) Elements Used.								
E RA Calc. Mass mDa PPM DBE Formula I-FIT I-FIT Norm Fit Conf % C H, Iz F P								
644 100.00 1443642 0.2 1.4 -1.5 Ho V -1.5 m/s o 1								
لملاية المراجع المراجع المراجع المراجع								
	3.490+004							
312950								
	552,328.0561 m/z							

4 HRMS (ESI, negative mode): calcd for PF_6^- 144.9642 found 144.9644

(d)

Figure S5. HRMS spectra of the complexes 1-4 (a-d).











Figure S6. FT-IR spectrum of compound 1 (a); FT-IR spectra of compounds 2–4 (lower, red) in comparison with their respective $H(N^{C})$ ligands (upper, green) (b–d); FT-IR spectrum of ligand imphen (e).

,					
Complex	2				
Empirical formula	C ₄₃ H ₂₈ F ₆ IrN ₆ P				
Formula weight	965.88				
Temperature [K]	293.0(2)				
Wavelength [Å]	0.71073				
Crystal system	Orthorhombic				
Space group	P2 ₁ 2 ₁ 2 ₁				
	<i>a</i> = 15.2609(5)				
Unit cell dimensions [Å,°]	<i>b</i> = 15.7886(5)				
	<i>c</i> = 15.9948(6)				
Volume [Å ³]	3853.9(2)				
Z	4				
Density (calculated) [Mg/m ³]	1.665				
Absorption coefficient [mm ⁻¹]	3.575				
F(000)	1896				
Crystal size [mm]	$0.06 \times 0.06 \times 0.25$				
heta range for data collection [°]	3.73 to 27.75				
	-14 ≤ h ≤ 20				
Index ranges	$-21 \le k \le 16$				
	-17 ≤ I ≤ 20				
Reflections collected	21048				
Independent reflections	9075 (R _{int} = 0.0389)				
Completeness to 20	99.6%				
Min. and max. transm.	0.632 and 1.000				
Data / restraints / parameters	9075 / 0 / 514				
Goodness-of-fit on F2	1.049				
Final R indices [1>2a(1)]	$R_1 = 0.0422$				
	wR ₂ = 0.0868				
R indices (all data)	R ₁ = 0.0587				
	wR ₂ = 0.0962				
Largest diff. peak and hole [e Å ⁻³]	1.99 and -0.75				
CCDC deposit no.	2369644				

X-RAY STRUCTURAL ANALYSIS

Table S2. Short intra- and intermolecular hydrogen bonds of complex 2.

D–H∙∙∙A	D–H [Å]	H●●●A [Å]	D–A [Å]	D−H●●●A [°]
N(4)−H(4)●●●F(1) ^a	0.86	2.40	3.19(2)	155.00
N(4)−H(4) ●●●F(4) ^a	0.86	2.37	3.111(18)	144.00
C(2)−H(2) ●●●F(1)	0.93	2.42	3.269(15)	152.00
C(1)5−H(15)•••N(1)	0.93	2.22	3.070(12)	151.00
C(16)−H(16)●●F(4) ^b	0.93	2.54	3.19(2)	127.00
C(30)−H(30)•••N(2)	0.93	2.43	3.108(12)	130.00

Symmetry codes: (a) = -2-x,-1/2+y,-1/2-z; (b) = -1/2+x,-1/2-y,-z

X–H●●●Cg(J)	H(I)●●●Cg(J)	X-Perp [Å]	γ [°]	X-H(I)●●●Cg(J)					
	[Å]			[°]					
C(10)−H(10)•••Cg(13) ^c	2.67	-2.58	14.93	147					
C(20)–H(20)•••Cg(12) ^c	2.82	2.65	20.02	136					
C(26)−H(26)•••Cg(10) ^d	2.81	-2.73	13.27	148					
C(35)–H(35)•••Cg(10) ^e	2.77	2.67	15.46	168					
C(40)−H(40)•••Cg(9) ^e	2.94	-2.87	12.28	148					
C(41)−H(41)•••Cg(5) ^e	2.96	-2.96	4.14	142					

Table S3. X–H•••Cg(J)(π -ring) interactions of complex 2.

symmetry codes: (c) = -1/2+x, -3/2-y, -z; (d) = 1/2+x, -3/2-y, -z; (e) = -3/2-x, -1-y, -1/2+z. γ = angle X(I) \rightarrow Cg(J) vector and normal to plane J. Cg(13) is the centroid of atoms = C38/C39/C40/C41/C42/C43; Cg(12) is the centroid of atoms = C29/C30/C31/C32/C33/C34; Cg(10) is the centroid of atoms = C14/C15/C16/C17/C18/C19; Cg(9) is the centroid of atoms = C4/C5/C7/C8/C12/C13; Cg(5) is the centroid of atoms = N1/C1/C2/C3/C4/C13;

DFT CALCULATIONS

Table S4. Comparison of theoretical (DFT/PBE1PBE/SDD/def2-TZVP) and experimental (X-Ray) bond lengths and angles for complex **2**. The theoretical structures were fully optimized with use of spin-restricted (S₀) or unrestricted (T₁) DFT approach.

	X-ray	S ₀	T ₁							
	bond	lenghts								
lr(1)–N(1)	Ir(1)–N(1) 2.195(7) 2.20572 2.2254									
lr(1)–N(2)	2.166(7)	2.20580	2.21001							
lr(1)–N(5)	2.081(7)	2.10699	2.1299							
lr(1)–N(6)	2.078(7)	2.10717	2.0357							
lr(1)–C(28)	1.998(7)	1.99808	1.9984							
lr(1)–C(43)	1.996(8)	1.99790	1.9812							
	bond	l angles								
N(2)–Ir(1)–N(1)	75.7(3)	74.797	74.62							
N(5)–Ir(1)–N(1)	104.9(3)	104.225	104.57							
N(5)–Ir(1)–N(2)	84.1(3)	82.306	83.20							
N(6)–Ir(1)–N(1)	80.6(3)	82.239	81.78							
N(6)–Ir(1)–N(2)	102.8(3)	104.162	100.62							
N(6)–Ir(1)–N(5)	172.2(3)	172.007	173.34							
C(28)–Ir(1)–N(1)	170.4(3)	170.738	171.38							
C(28)–Ir(1)–N(2)	96.7(3)	97.610	98.59							
C(28)–Ir(1)–N(5)	79.8(3)	79.580	79.48							
C(28)–Ir(1)–N(6)	95.7(3)	94.743	94.49							
C(43)–Ir(1)–N(1)	97.0(3)	97.577	96.18							
C(43)–Ir(1)–N(2)	171.6(3)	170.740	170.16							
C(43)–Ir(1)–N(5)	93.8(3)	94.743	96.02							
C(43)–Ir(1)–N(6)	79.8(3)	79.579	81.15							
C(43)–Ir(1)–C(28)	91.0(3)	90.447	90.89							

•	1	1	,	3	4								
	S ₀	T ₁	S ₀	T ₁	S ₀	T ₁							
	bond lengths												
lr(1)–N(1)	2.1701	2.1677	2.1710	2.1640	2.1529	2.1476							
lr(1)–N(2)	2.1716	2.1662	2.1728	2.1634	2.1543	2.1465							
lr(1)–N(5)	2.0602	2.0604	2.0789	2.0754	2.0718	2.0681							
lr(1)–N(6)	2.0599	2.0604	2.0789	2.0754	2.0718	2.0681							
lr(1)–C(28)	2.0111	1.9879	2.0160	1.9954	2.0240	1.9924							
lr(1)–C(43)	2.0106	1.9883	2.0155	1.9956	2.0235	1.9922							
		bon	d angles										
N(2)–Ir(1)–N(1)	76.21	76.10	76.07	76.17	76.80	77.14							
N(5)–Ir(1)–N(1)	96.64	95.45	86.03	85.09	86.43	85.68							
N(5)–Ir(1)–N(2)	88.30	87.40	101.24	100.26	95.28	93.55							
N(6)–Ir(1)–N(1)	88.43	87.43	101.13	100.20	95.22	93.53							
N(6)–Ir(1)–N(2)	96.77	95.47	85.95	85.08	86.41	85.66							
N(6)–Ir(1)–N(5)	173.58	176.36	170.97	173.30	177.88	178.99							
C(28)–Ir(1)–N(1)	172.99	169.43	173.04	170.04	172.22	170.58							
C(28)–Ir(1)–N(2)	97.42	93.76	97.15	94.06	96.84	94.92							
C(28)–Ir(1)–N(5)	80.06	80.91	93.90	94.94	98.74	100.01							
C(28)–Ir(1)–N(6)	95.32	96.63	79.67	80.56	79.76	80.69							
C(43)–Ir(1)–N(1)	97.52	93.72	97.38	94.41	96.96	95.06							
C(43)–Ir(1)–N(2)	173.13	169.39	173.24	170.38	172.34	170.71							
C(43)–Ir(1)–N(5)	95.31	96.65	79.67	80.53	79.76	80.69							
C(43)–Ir(1)–N(6)	80.07	80.91	93.84	94.88	98.70	100.00							
C(43)–Ir(1)–C(28)	88.98	96.56	89.45	95.42	89.72	93.27							

Table S5. Comparison of theoretical singlet and triplet-optimized bond lengths and angles for complexes **1**, **3** and **4** (DFT/PBE1PBE/SDD/def2-TZVP). The structures were fully optimized with use of spin-restricted (S₀) or unrestricted (T₁) DFT approach.



Figure S7. Selected molecular orbitals of **1**, calculated with the Gaussian-16 software at TD-DFT/PBE1PBE/SDD/def2-TZVP level with the use of the PCM model at polarities corresponding to acetonitrile.



Figure S8. Selected molecular orbitals of **2**, calculated with the Gaussian-16 software at TD-DFT/PBE1PBE/SDD/def2-TZVP level with the use of the PCM model at polarities corresponding to acetonitrile.



Figure S9. Selected molecular orbitals of **3**, calculated with the Gaussian-16 software at TD-DFT/PBE1PBE/SDD/def2-TZVP level with the use of the PCM model at polarities corresponding to acetonitrile.



Figure S10. Selected molecular orbitals of **4**, calculated with the Gaussian-16 software at TD-DFT/PBE1PBE/SDD/def2-TZVP level with the use of the PCM model at polarities corresponding to acetonitrile.



Figure S11. Percentage contribution of selected molecular fragments to the frontier molecular orbitals for complexes **1–4** according to DFT/PBE1PBE/SDD/def2-TZVP calculations with the use of the PCM model at polarities corresponding to acetonitrile.



Table S6. Calculated electron transitions of complex 1, assigned to its experimental UV-Vis spectrum in acetonitrile.



Table S7. Calculated electron transitions of complex **2**, assigned to its experimental UV-Visspectrum in acetonitrile.

	12 1 1 0.8 0.6 0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.4 0.5 0 0.6 0.4 0.5 0 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0	-1+3 (0%) UKO (2%) H-3-LUMO (6%) H-3-LUMO (6%)	D (81%) 0 (11%) L+2 (92%) HOMOL+1 (83%) HOMOL-UMO (1 450	0.6 0.5 0.4 0.3 ts 0.2 0.2 0.2			
Exp. absorption		Calcul	, ated transi	tions			
2. nm		Calcul			Oscillator	transition	
(10 ⁴ ε; M ⁻¹ cm ⁻¹)	Major contribution (%)	Character	E [eV]	λ [nm]	strength	No.	
	HOMO→LUMO (98%)	MLLCT	2.85	435.11	0.0003	S1	
427 (0.72)	HOMO→L+2 (92%)	MLLCT	3.12	397.60	0.142	S2	
	HOMO→L+1 (83%)	MLLCT	3.17	391.40	0.0009	S3	
	H-1→LUMO (81%)	MLLCT/LC	2.24	274.24	0.0545	6.4	
	H-3→LUMO (11%)	LC	3.34	371.34	0.0646	54	
368 (1.1)	H-2→LUMO (69%)	MLLCT	2.44	200.20	0.0000	65	
	HOMO→L+3 (19%)	MLLCT	3.44	360.20	0.0022	55	
	HOMO→L+3 (60%)	MLLCT	2.44		0.0100	66	
	H-2→LUMO (21%)	MLLCT	3.44	360.00	0.0109	S6	
	H-3→LUMO (76%)	LC	3.53	350.86	0.0472	S7	
344 (1.7)	H-1→L+2 (47%)	MLLCT/LC	2.65	220.40	0.0501	60	
	H-1→L+1 (37%)	MLLCT/LC	3.65	339.49	0.0501	58	
	H-1→L+1 (43%)	MLLCT/LC	2.00	220 72	0.0027	60	
	H-1→L+2 (39%)	MLLCT/LC	3.66	338.72	0.0627	59	
	H-2→L+2 (79%)	MLLCT	3.80	326.35	0.0774	S10	
	H-5→LUMO (72%)	LC/MLLCT	3.82	324.78	0.0195	S11	
	H-2→L+1 (69%)	MLLCT	3.86	321.53	0.0127	S12	
216 (4 5)	H-1→L+3 (74%)	MLLCT/LC	3.88	319.08	0.0192	S14	
310 (4.5)	H-3→L+1 (60%)	LC	3.92	315.88	0.0426	S15	
	H-5→L+1 (41%)	LC/MLLCT					
	H-3→L+3 (21%)	LC	4.07	304.56	0.3505	S18	
	H-4→L+2 (10%)	LC/MLLCT					
	H-4→L+2 (31%)	LC/MLLCT					
	HOMO→L+4 (26%)	MLLCT	4.16	298.10	0.0887	S20	
	H-4→L+1 (11%)	LC/MLLCT					
	H-4→L+1 (43%)	LC/MLLCT					
282 (5 2)	H-4→L+2 (11%)	LC/MLLCT	4.17	297.26	0.0788	S21	
203 (3.2)	H-5→L+1 (10%)	LC/MLLCT					
	HOMO→L+4 (60%)	MLLCT	1 20	295 54	0.0415	\$22	
	H-4→L+2 (26%)	LC/MLLCT	4.20	255.54	0.0415	522	
	H-8→LUMO (70%)	LC	4 35	284 92	0.0279	\$27	
	H-9→LUMO (18%)	LC	1.55	237.32	0.0275	52,	
	H-9→LUMO (48%)	LC					
	H-3→L+3 (16%)	LC	4.50	275.26	0.3767	S31	
	H-8→LUMO (10%)	LC			ļ	ļ	
268 (5.9)	H-7→L+1 (57%)	MLLCT/LC	4.54	273.24	0.1177	S32	
	H-3→L+4 (15%)	LC					
	H-7→L+2 (46%)	MLLCT/LC	4.57	271.26	0.063	S33	
	H-9→L+1 (11%)	LC					

Table S8. Calculated electron transitions of complex **3**, assigned to its experimental UV-Vis spectrum in acetonitrile.



Table S9. Calculated electron transitions of complex 4, assigned to its experimental UV-Visspectrum in acetonitrile.

	H-1→L+5 (42%)	ILCT/LC					
	H-5→L+2 (25%)	MLLCT	4.10	302.06	0.0338	S24	
	H-4→L+3 (10%)	LC/MLLCT					
	H-5→L+1 (37%)	MLLCT					
	H-2→L+3 (16%)	ILCT/LC	4 17	297.34	0.046	526	
	H-3→L+2 (13%)	ILCT/LC	4.17			320	
	H-4→L+2 (9%)	LC/MLLCT					
	H-1→L+5 (46%)	ILCT/LC		291.55	0.3138	S29	
200 (11)	H-4→L+3 (17%)	LC/MLLCT	4.25				
288 (11)	H-5→L+2 (16%)	MLLCT					
	H-8→LUMO (59%)	LC	A AC	270.05	0 2714	624	
	H-4→L+1 (20%)	LC/MLLCT	4.40	278.05	0.3714	534	
	H-7→L+2 (38%)	MLLCT					
	H-2→L+4 (28%)	ILCT/LC	4.65	266.41	0.2125	S42	
	HOMO→L+7 (9%)	ILCT /MLLCT					

Table S10. Comparison of the experimental luminescence and theoretical DFT properties for complexes **1-4**. The theoretical phosphorescence energies were calculated as the vertical energy difference between the ground singlet and triplet excited states $\Delta E_{T_1-S_0}$.using Gaussian-16 software with PBE0/SDD/def2-TZVP level. The solvent environment (acetonitrile) was taken into account by PCM equilibrium solvation within the linear response approach.

complex	$\Delta E_{T_1-S_0}$ (eV) / (nm)	λ _{exp} (nm)								
1	2.13 eV / 583 nm	601								
2	2.04 eV / 608 nm	562, 588								
3	2.26 eV / 548 nm	525, 563, 605								
4	1.87 eV / 662 nm	591, 640, 692								



Figure S12. Spin density maps of complexes **1–4**, calculated with the Gaussian-16 software at TD-DFT/PBE1PBE/SDD/def2-TZVP level with the use of the PCM equilibrium solvation within the linear response approach at polarities corresponding to acetonitrile. The wavefunctions used for computing the spin densities refer to the optimized geometries at the T₁ minima.

ELECTROCHEMISTRY

Ligand	E _{pa} ^{ox1} [V]	E _{pa} ^{ox2} [V]	E _{pa} ^{red1} [V]	E _{pc} ^{red1} [V]	ΔΕ ^{red1} [V]	E _{1/2} red1 [V]	E _{pa} ^{red2} [V]	E _{pc} ^{red2} [V]	ΔE ^{red2} [V]	E _{1/2} [V]	E _{onset} ox1 [V]	E _{onset} red1 [V]	IP [eV]	EA [eV]
Нрру	1.64	-	-2.82	-	-	-	-	-	-	-	1.51	-2.61	6.61	2.49
Hpquin	1.44	-	-2.41	-	-	-	-	-	-	-	1.37	-2.29	6.47	2.81
Hpbztz	1.46	1.69	-2.44	-2.36	0.81	-2.40	-2.82	-	-	-	1.36	-2.34	6.46	2.76
pybzthH	1.13	1.46	-2.53	-2.42	0.12	-2.47	-2.76	-2.60	0.16	2.68	1.04	-2.41	6.14	2.69
imphen		electrochemical peaks were not registered due to poor solubility of the compound												

Table S11. Electrochemical properties of ligands.

 E_{pa} and E_{pc} – anodic and cathodic potentials vs Fc/Fc⁺; ΔE - peak potential difference estimated from equation $\Delta E = E_{pa} - E_{pc}$; $E_{1/2}$ – redox potentials estimated from equation $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{onset}^{ox1} - oxidation onset potential; E_{onset}^{red1} - reduction onset potential; IP - Ionization Potential estimated from equation IP=|e⁻|(5.1+E_{onset}^{ox1}); EA - Electron Affinity estimated from equation EA=|e⁻|(5.1+E_{onset}^{red1}); CG working electrode, electrolyte: MeCN/Bu₄NPF₆; scan rate 0.1 V s⁻¹





Figure S13. Cyclic voltammetry and differential pulse voltammetry of the complexes **1–4** and their respective cyclometalating ligands in the solution MeCN/Bu₄NPF₆; scan rate 0.1 V s⁻¹

SPECTROSCOPY



Figure S14. UV-Vis spectra in dichloromethane ($c = 10^{-5}$ M, Inset: $c = 5 \times 10^{-4}$ M).

Table S12. The a	bsorption maxima a	and molar extinction	coefficients of com	pounds 1–4.

compound	medium	$\lambda_{abs} (\epsilon \times 10^4)$
1	MeCN	462 (0.08), 387 (1.1), 333 (1.5), 314 (2.5), 288 (5.5), 252 (11)
	CH_2CI_2	504 (0.02), 473 (0.10), 390 (1.0), 288 (4.6), 268 (5.7), 252 (9.2)
2	MeCN	514 (0.07), 434 (0.83), 390 (1.1), 348 (3.0), 330 (3.5), 281 (7.8), 255 (11), 233 (15)
	CH_2CI_2	467 (0.06), 437 (1.1), 392 (1.4), 333 (3.8), 283 (8.4), 257 (11)
3	MeCN	503 (0.02), 427 (0.72), 368 (1.1), 344 (1.7), 316 (4.5), 283 (5.2), 268 (5.9), 253 (7.9), 234 (14)
	CH_2CI_2	519 (0.05), 438 (0.47), 397 (1.8), 372 (2.1), 316 (6.4), 288 (9.4), 254 (13)
4	MeCN	491 (0.05), 428 (1.7), 386 (2.0), 341 (4.7), 316 (6.0), 288 (11), 252 (11)
	CH ₂ Cl ₂	506 (0.04), 442 (2.2), 391 (2.2), 323 (6.9), 291 (13), 253 (14)









Figure S18. UV-Vis photostability of Ir(III) complexes upon 420 nm light irradiation in MeCN. $c = 10^{-5}$ M.



Figure S19. UV-Vis photostability of Ir(III) complexes upon 420 nm light irradiation in CH₂Cl₂. $c = 10^{-5}$ M.



3 4 Figure S20. UV-Vis photostability of Ir(III) complexes upon 420 nm light irradiation in DMSO. $c = 10^{-5}$ M.

compound	medium	λ _{exc}	λ_{em}	PL lifetime (ns)	X²	ns-TA lifetime (μs)	QY (%)	$k_r (10^5 \mathrm{s}^{-1})^b$	$k_{nr} (10^5 \mathrm{s}^{-1})^b$
1	MeCN	387, 371, 292, 250	601	Ar : 743	1.049	Ar: 0.612 ± 0.029	Ar : 21.23	2.86	10.6
				Air: 151	0.989	Air: 0.069 ± 0.005	Air: 6.85		
	CH_2CI_2	392, 372, 292, 254	591	Ar : 1296	1.026	-	Ar : 36.42	2.81	4.91
				Air: 418	1.067		Air: 7.08		
	77 K ^a	433, 407, 388, 368, 291	534	4898 (67.8%), 9995 (32.2%) /τ _{av} : 6539	1.015	_	_	_	_
	solid	466, 364	560	206 (24.6%), 778 (61.2%), 3129 (14.2%) /τ _{av} : 971	1.002	-	8.05	0.83	9.5
2	MeCN	433, 387, 330, 237	562, 588sh	Ar : 1853	1.044	Ar: 2.191 ± 0.206	Ar : 53.18	2.87	2.53
				Air: 446	0.928	Air: 0.198 ± 0.004	Air: 7.94		
	CH_2CI_2	438, 389, 333, 280, 258	556 <i>,</i> 586sh	Ar : 3029	1.088	-	Ar : 56.40	1.86	1.44
				Air: 253 (2.0%), 1183 (98.0%) /τ _{av} : 1164	1.037		Air: 30.25		
	77 K ^a	440, 408, 389, 369, 350, 332, 291	540, 584, 632	4524 (96.4%), 11 331 (3.6%) /τ _{av} : 4769	0.911	_	_	_	_
	solid	526, 473, 440, 370	588, 671	232 (24.6%), 1716 (75.4%) /τ _{av} : 1351	1.054	-	1.51	0.11	7.3
3	MeCN	389, 310, 292, 251	525, 563, 605	Ar : 3840	1.042	Ar: 3.148 ± 0.130	Ar : 33.62	0.88	1.73
				Air: 618	1.150	Air: 0.269 ± 0.006	Air: 5.35		
	CH_2CI_2	430, 396, 312, 293, 254	522, 562, 602	Ar : 3467	1.047	-	Ar : 36.64	1.06	1.83
				Air: 1243	1.062		Air: 19.85		
	77 K ^a	434, 409, 392, 372, 317, 295	514, 526, 554,	11 663	1.003	-	_	_	-
			570, 603, 658						
	solid	512, 488, 368, 311	576, 619	178 (23.1%), 558 (56.7%), 1955 (20.2%) /τ _{av} : 752	1.031	_	3.36	0.45	12.8
4	MeCN	426, 324, 296, 260	591, 640, 692	Ar : 1365 (93.0%), 4779 (7.0%) /τ _{av} : 1604	1.032	Ar: 0.799 ± 0.037	Ar : 2.08	0.13	6.10
				Air: 247 (21.7%), 386 (78.3%) /τ _{av} : 356	1.084	Air: 0.157 ± 0.005	Air: 5.83		
	CH_2CI_2	441, 324, 296, 255	597, 644, 692	Ar : 943 (64.1%), 1941 (35.9%) /τ _{av} : 1301	1.044	-	Ar : 7.69	0.59	7.10
				Air: 297 (14.6%), 679 (85.4%) /τ _{av} : 623	0.975		Air: 5.53		
	77 K ^a	444, 422, 389, 320, 290, 254	580, 633, 697	13 378	0.952	-	_	_	_
	solid	565, 500, 417, 368, 303	649, 673, 694	220 (44.0%), 1243 (26.3%), 5934 (29.8%) /τ _{av} : 2192	1.082	-	0.72	0.03	4.5

Table S13. Summary of the absorption and luminescence properties of 1–4.

^a 77 K – measurement in EtOH:MeOH (4:1 v/v) rigid matrix. ^b Correlation between emission lifetimes (τ), quantum yields (QY) and their radiative and non-radiative constants

$$(k_r \text{ and } k_{nr})$$
 were calculated according to the equations: $\tau = \frac{1}{k_r + k_{nr}}$ and $QY = \frac{k_r}{k_r + k_{nr}}$. k_r and k_{nr} were calculated: $k_r = \frac{QY}{\tau}$ and $k_{nr} = \frac{1-QY}{\tau}$



Figure S21. Summary of photoluminescence properties of complex 1.



Figure S22. Summary of photoluminescence properties of complex 2.



Figure S23. Summary of photoluminescence properties of complex 3.



em

exc 1.75 1.5

1.25 () 1 approvement (

0.25

- 0 800

700





500

wavelength (nm)

600

normalized intensity

0.5

0.25

0 -

300

400



77 K (EtOH:MeOH 4:1 v/v)





Fit = A + B1.exp(-t/T1) + B2.exp(-t/T2) + B3.exp(-t/T3)

	Value	Std Dev		Value	Std Dev	Rel %
T1	2.206E-7	8.308E-9	B1	4.569E-1	5.072E-2	43.99
T2	1.243E-6	7.264E-8	B2	4.843E-2	3.408E-3	26.27
T3	5.934E-6	1.774E-7	B3	1.149E-2	6.497E-4	29.75
Chisq	1.082E+0		Α	1.749E+0		
Shift	-2.724E-9					

solid

Figure S24. Summary of photoluminescence properties of complex 4.



Figure S25. Emission spectra of Ir(III) complexes in argon-saturated and air-equilibrated dichloromethane and acetonitrile solutions upon excitation at 405 nm.



Figure S26. 77 K EtOH:MeOH (4:1 v/v) rigid matrix emission of complexes **1–4** (a), respective H(N^C) ligands (b), and comparison of the phosphorescence of the complex in RT and in 77 K vs 77 K phosphorescence of their respective ligands (c-f). In panels (d-f) ligands Ph-quin, Ph-bztz and Py-bzth were additionally sensibilized towards phosphorescence with addition of 10% (v:v) of ethylene iodide.



(b)

Figure S27. Phosphorescence emission of compounds **1–4 (a)** and their respective H(N^C) ligands (b) in MeOH:EtOH (1:4 v:v) in 77 K, along with tangent lines computed by the linear fit of the high-energy side of the phosphorescence bands. Ligands Ph-quin, Ph-bztz and Py-bzth were additionally sensibilized towards phosphorescence with addition of 10% (v:v) of ethylene iodide.

FEMTO- and NANOSECOND TRANSIENT ABSORPTION



Figure S28. UV-Vis spectra of the acetonitrile solutions of **1–4** before and after their measurements of femtosecond transient absorption – photodamage test.



Figure S29. Summary of the global lifetime analysis of **1** (pump wavelength 355 nm; pump power 0.25 μJ per pulse, solvent: acetonitrile) containing evolution associated spectra (a), residual map (b), time traces at several wavelengths (c), and transient spectra (d).



Figure S30. Summary of the global lifetime analysis of 2 (pump wavelength 355 nm; pump power 0.25 μJ per pulse, solvent: acetonitrile) containing evolution associated spectra (a), residual map (b), time traces at several wavelengths (c), and transient spectra (d).



Figure S31. Summary of the global lifetime analysis of 3 (pump wavelength 355 nm; pump power 0.25 μJ per pulse, solvent: acetonitrile) containing evolution associated spectra (a), residual map (b), time traces at several wavelengths (c), and transient spectra (d).



Figure S32. Summary of the global lifetime analysis of 4 (pump wavelength 355 nm; pump power 0.25 μJ per pulse, solvent: acetonitrile) containing evolution associated spectra (a), residual map (b), time traces at several wavelengths (c), and transient spectra (d).



Figure S33. Transient triplet-triplet absorption spectrum (a) recorded at different times after excitation with a laser pulse at a wavelength of 355 nm and kinetic decay curve of triplet states with fitting recorded in aerated (b) and in de-aerated (c) conditions for compound 1. The decay curves were recorded at a wavelength of 510 nm which corresponding to the maximum of the transient absorption spectrum. Solvent: acetonitrile.



Figure S34. Transient triplet-triplet absorption spectra (a,d) recorded at different times after excitation with a laser pulse at a wavelength of 355 nm and kinetic decay curve of triplet states with fitting recorded in aerated (b,e) and in de-aerated (c,f) conditions for compound **2** (upper) and ligand Ph-quin (lower). The decay curves were recorded at a wavelength of 415 nm which corresponding to the maximum of the transient absorption spectrum. Solvent: acetonitrile.



Figure S35. Transient triplet-triplet absorption spectra (a,d) recorded at different times after excitation with a laser pulse at a wavelength of 355 nm and kinetic decay curve of triplet states with fitting recorded in aerated (b,e) and in de-aerated (c,f) conditions for compound **3** (upper) and ligand Phbztz (lower). The decay curves were recorded at a wavelength of 390 nm which corresponding to the maximum of the transient absorption spectrum. Solvent: acetonitrile.



Figure S36. Transient triplet-triplet absorption spectra (a,d) recorded at different times after excitation with a laser pulse at a wavelength of 355 nm and kinetic decay curve of triplet states with fitting recorded in aerated (b,e) and in de-aerated (c,f) conditions for compound **4** (upper) and ligand Pybzth (lower). The decay curves were recorded at a wavelength of 395 nm which corresponding to the maximum of the transient absorption spectrum. Solvent: acetonitrile.



Figure S37. Comparison of decay associated spectra of **1–4** in 100 ps delay time and UV-Vis spectra in acetonitrile.

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