Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Benzannulation of the Ditopic Ligand to Afford Mononuclear and Dinuclear Ir(III) complexes with intense phosphorescence. Application in Singlet Oxygen Generation and Bioimaging.

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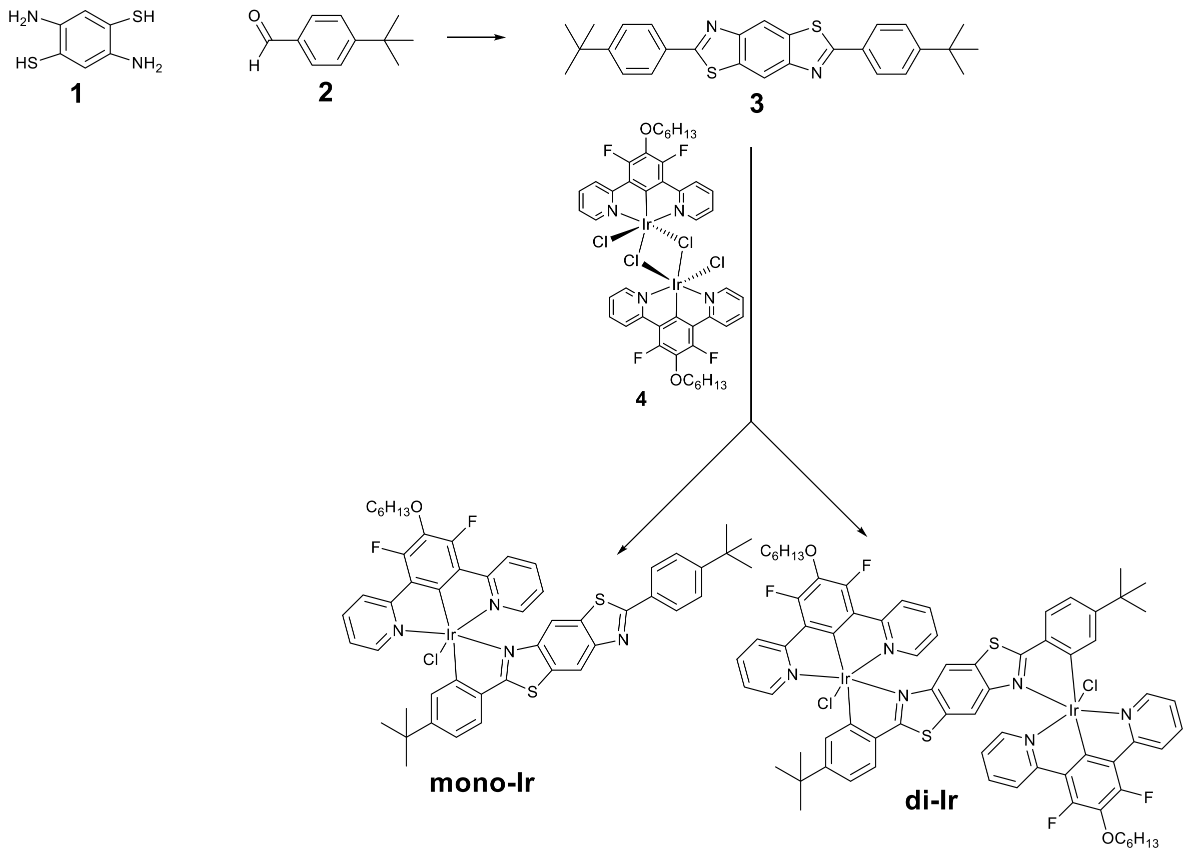
Synthesis and chemical characterization.

General

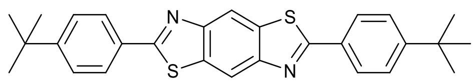
NMR spectra were recorded on a JEOL ECS400FT Delta spectrometer (399.78 MHz for 1H NMR, 100.53 MHz for 13C NMR). Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane as an internal standard. Coupling constants (J) are measured in hertz. Elemental analysis was carried out on ELEMENTAR vario MICRO CUBE instrument at central analytical services of the University of Regensburg. Mass-spectroscopy (FD-MS) was performed on a JEOL AccuTOF GCX instrument at the central analytical services of the University of Regensburg. The synthesis of dichlorobridged Ir(III) complex was reported earlier.[1]

Synthetic procedures and characterizations



Scheme S1. The synthesis of the ditopic ligand **3** and its mono- and dinuclear Ir(III) complexes **mono-Ir** and **di-Ir**

*Synthesis of the bis-bidentate bridging ligand **3***



2,5-Diaminobenzene-1,4-dithiol dihydrochloride **1** (200 mg, 0.82 mmol) and 4-*tert*-butylbenzaldehyde (266 mg, 1.64 mmol, 2eq) were dissolved in DMF (20 mL) and heated to reflux for 14 hours. The reaction was cooled to ambient temperature. Ethanol (20 mL) was added. The solid was filtered off, washed with ethanol (20 mL) and air dried to give **3** (140 mg, 37%).

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.52 (s, 2H), 8.04 (d, J = 8.4 Hz, 4H), 7.53 (d, J = 8.4 Hz, 4H), 1.37 (s, 18H).

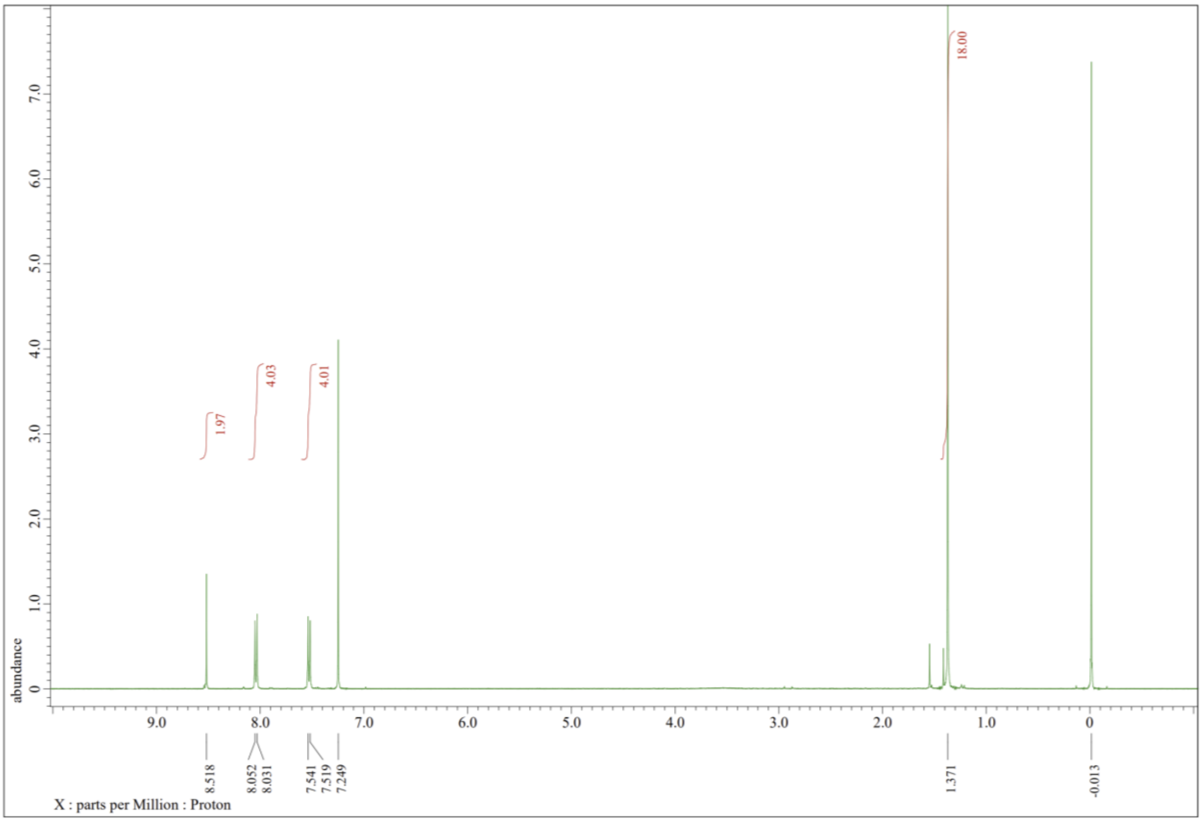
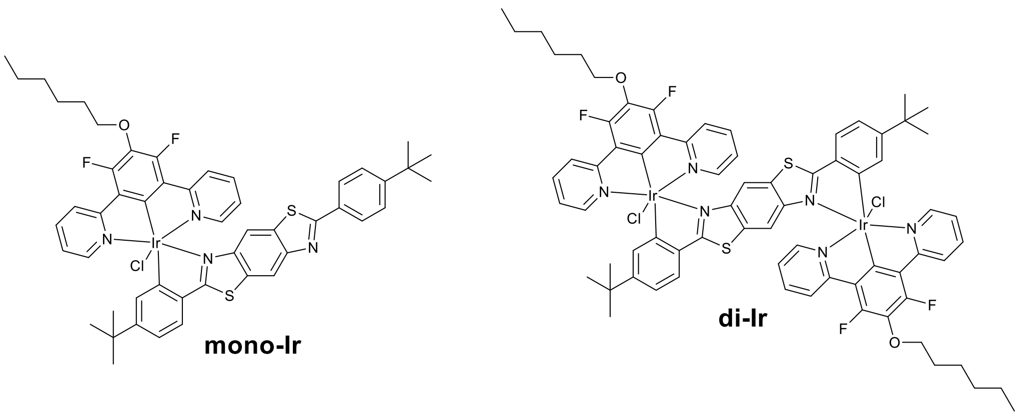


Figure S1. ^{1}H NMR spectrum of the bis-bidentate bridging ligand **3** in $CDCl_3$.

Synthesis of the mono and dimetallic complexes



A mixture of di-chlorobridged complex **4**[1] (387 mg, 0.3 mmol), ditopic ligand **3** (140 mg, 0.3 mmol) and silver triflate (231 mg, 0.9 mmol) in toluene (40 mL) was deoxygenated by bubbling argon through the mixture for 15 minutes. The mixture was then heated under reflux under argon for 4 days. The reaction was cooled to 60°C, HCl (2M, 20 mL) was added and the reaction stirred for 20 minutes. The reaction mixture was separated and the organic layer was rotary evaporated. The residue was triturated with methanol (40 mL). The formed solid was filtered off and washed with MeOH (5 mL) to give a mixture of the target complexes and some unreacted ditopic ligand **3**. Once dry, the solid was dissolved in DCM (20 mL) and filtered through celite. The products were separated by column chromatography (Al_2O_3, DCM/Tol, 2:1). The first fraction collected (Rf 0.9) with blue luminescence was unreacted bis-bidentate bridging ligand **3**, the second fraction collected at Rf 0.5 with yellow luminescence was **mono-Ir** complex and finally the third fraction collected at Rf 0.4 with yellow/orange luminescence was the **di-Ir** complex.

mono-Ir

Yield 36 mg, 7%

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.59 (s, 1H), 8.63 (s, 1H), 8.08 (d, *J* = 4.0 Hz, 2H), 8.07 (d, *J* = 4.0 Hz, 2H), 7.88 (d, *J* = 5.6 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 6.8, 2H), 6.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.06 (s, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 1.91 (quin, *J* = 7.6 Hz, 2H), 1.56-1.63 (m, 2H), 1.44-1.39 (m, 4H), 1.37 (s, 9H), 0.95 (s, 12H).

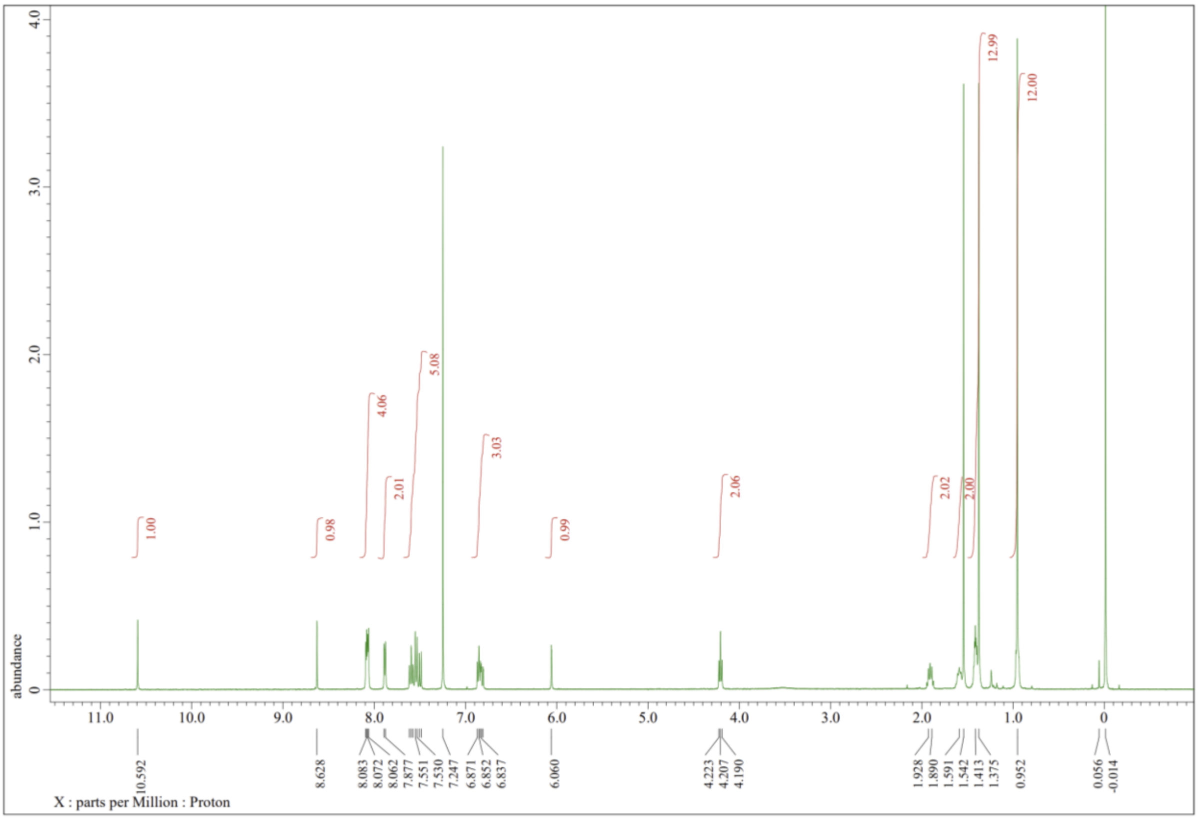


Figure S2. ^{1}H NMR spectrum of the mononuclear complex **mono-Ir** in $CDCl_3$.

Field desorption mass-spectrometry (FD-MS): calculated for $[M]^+$ ($C_{50}H_{48}ClF_2IrN_4OS_2$) 1050.2543, found 1050.3098.

Elemental analysis. Calculated for $C_{50}H_{48}ClF_2IrN_4OS_2$: C 57.15, H 4.60, N 5.33 %; found C 56.72, H 4.11, N 5.16 %.

di-Ir

Yield 88 mg, 18%

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.71 (s, 2H), 8.12 (d, *J* = 8 Hz, 4H), 7.94 (d, *J* = 5.6 Hz, 4H), 7.64 (t, *J* = 8 Hz, 4H), 7.52 (d, *J* = 8 Hz, 2H), 6.91 (t, *J* = 6.4 Hz, 4H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 2H), 4.22 (t, *J* = 6.4 Hz, 4H), 1.92 (quin, *J* = 7.2 Hz, 4H), 1.65-1.55 (m, 4H), 1.46-1.35 (m, 8H), 1.23 (s, 4H), 0.95 (s, 24H)

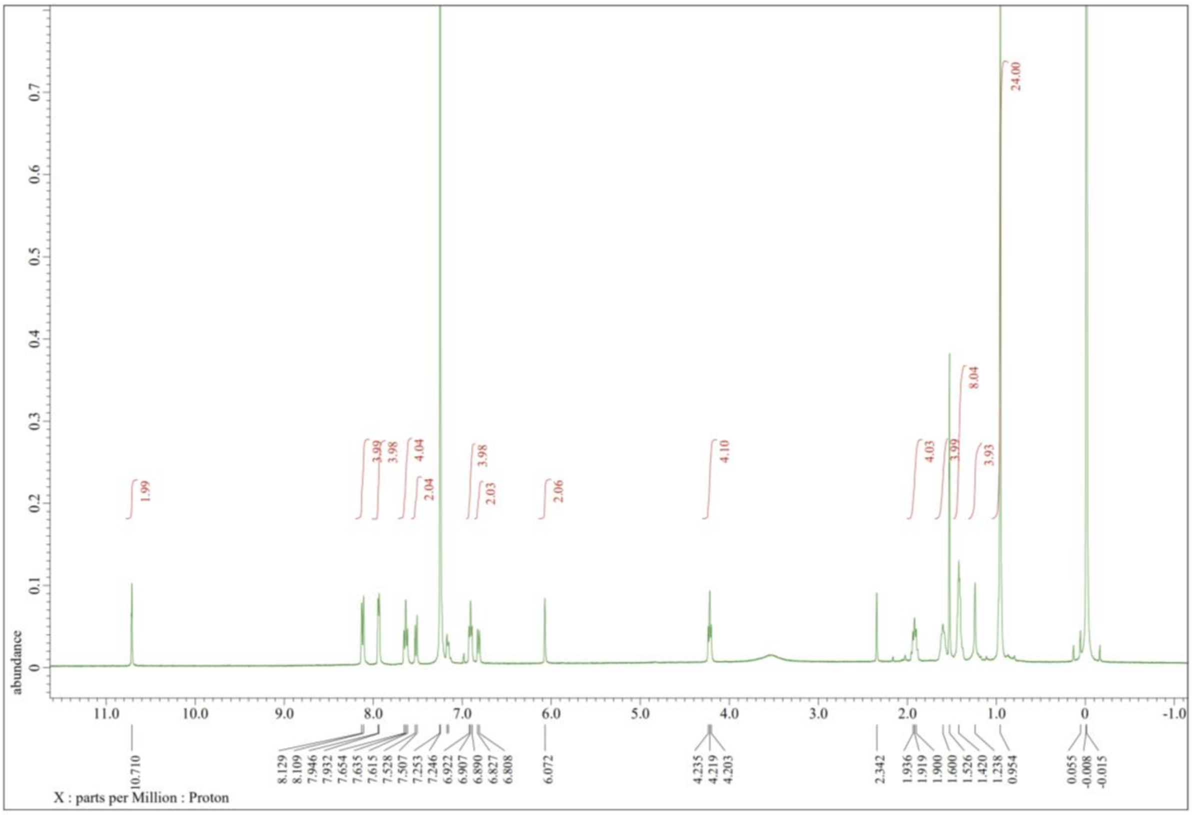


Figure S3. ^{1}H NMR spectrum of the dinuclear complex **di-Ir** in $CDCl_3$.

Field desorption mass-spectrometry (FD-MS): calculated for $[M]^+$ ($C_{72}H_{68}Cl_2F_4Ir_2N_6O_2S_2$) 1644.3395, found 1644.4146.

Elemental analysis. Calculated for $C_{72}H_{68}Cl_2F_4Ir_2N_6O_2S_2$: C 52.58, H 4.17, N 5.11 %; found C 53.06, H 3.59, N 4.83 %.

Optical spectroscopy. The steady state photophysical measurements were performed on solutions of complexes **mono-Ir** and **di-Ir** in dichloromethane. The UV-Vis absorption spectra were measured with a Varian Cary 300 double beam spectrometer. The emission and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog-3 steady-state fluorescence spectrometer. The emission decay times were measured with a PicoBright PB-375 pulsed diode laser (λ_{exc} = 378 nm, pulse width 100 ps) used as the excitation source, and the PL signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. The PL quantum yield was determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere

Singlet Oxygen Generation Studies.

Emission of photogenerated singlet oxygen ($^1O_2$ ($^1\Delta_g$) emission at λ_{max} = 1275 nm) was recorded with a custom-built experimental setup based on BENTHAM DTMc300 Double Monochromator and equipped with a TE Cooled PMT (Hamamatsu H10330C-75, 950–1700 nm registration range). A 405 nm continuous laser was used as photoexcitation source. The singlet oxygen quantum yield was determined by the relative method[2]. The efficiencies of $^1O_2(^1\Delta_g)$ generation, ϕ_Δ, were determined with respect to the well-known standard phenalenone (ϕ_Δ = 0.96 in dichloromethane at ambient temperature).[3] The accuracy in the estimation of singlet oxygen emission quantum yield was +/-10 %.

Material and methods of confocal microscopy studies.

For confocal microscopy analysis, HeLa cells (ATCC Catalog No. CCL-2™, human epithelial cells) were cultivated in RPMI 1640 medium free of fluorescent markers, supplemented with 10% fetal bovine serum (FBS) at 37 °C in a humidified atmosphere with 5 % CO_2. Twenty-four hours before the experiment, HeLa cells at density 1×10^5/mL were plated in 8 chamber culture slide with a glass bottom and cultured at the same conditions. After overnight incubation, the cells were treated with 10 µM of **mono-Ir** for 2 hours, then rinsed with phosphate buffered saline (PBS) (3 times) and subjected towards imaging with confocal luminescent microscopy. The 1 mM stock solution of **mono-Ir** was prepared in DMSO.

Imaging was performed using DMI 6000 CS inverted microscope with TCS SP8 confocal system operated by LAS 2.0.215022 software (Leica Microsystem, Wetzlar, Germany). The observations were made using HC PLAPO CS2 63x/1.40 oil immersion objective. The parameters of the excitation and the emission were unified for the control material and that stained with tested compound. The UV diode laser (405 nm, 5 mW nominal power, set to 5 % of maximum intensity) was used and the emission was collected at the range of 500-700 nm by a photomultiplier tube

PMT (gain 900, offset 0 %). Additionally, transmitted light was also collected by the PMT detector. Confocal scans were performed bidirectionally at 400 Hz speed and line average set at 3. Luminescence was registered from the single confocal section (pinhole 1.0 Airy unit). In order to check intercellular localization of **mono-Ir**, Z-stack scans were also performed (step 0.5 µm) and 3D cells reconstruction were analyzed.

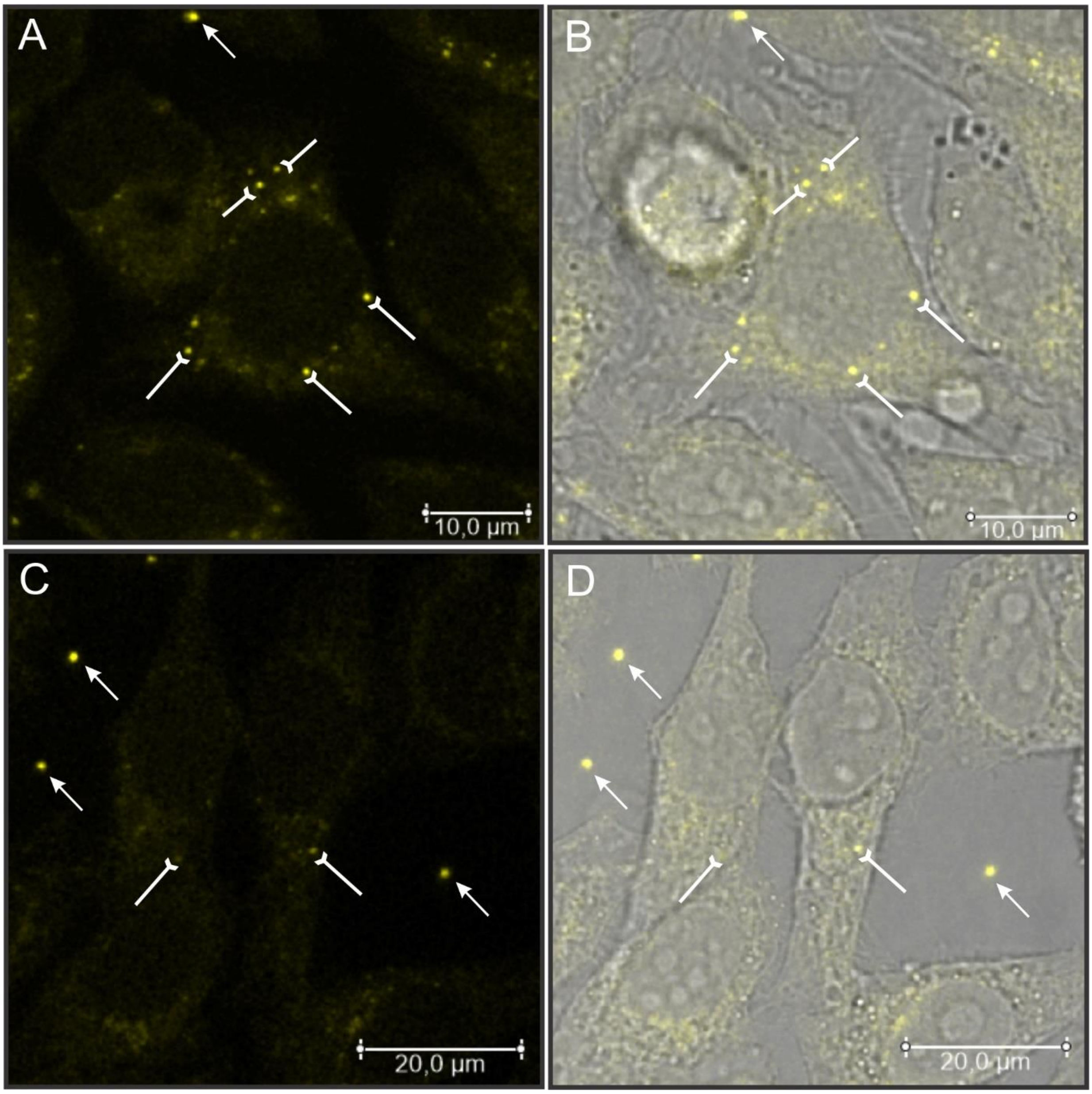


Figure S4. Cellular distribution of **mono-Ir** in HeLa cells. (A) Phosphorescence of **mono-Ir**. (B) Merged image of transmitted light and image (A). Precipitated **mono-Ir** outside the cells is indicated with arrows. Vesicles containing **mono-Ir** cargo in the cytoplasm area are indicated with inverted arrows.

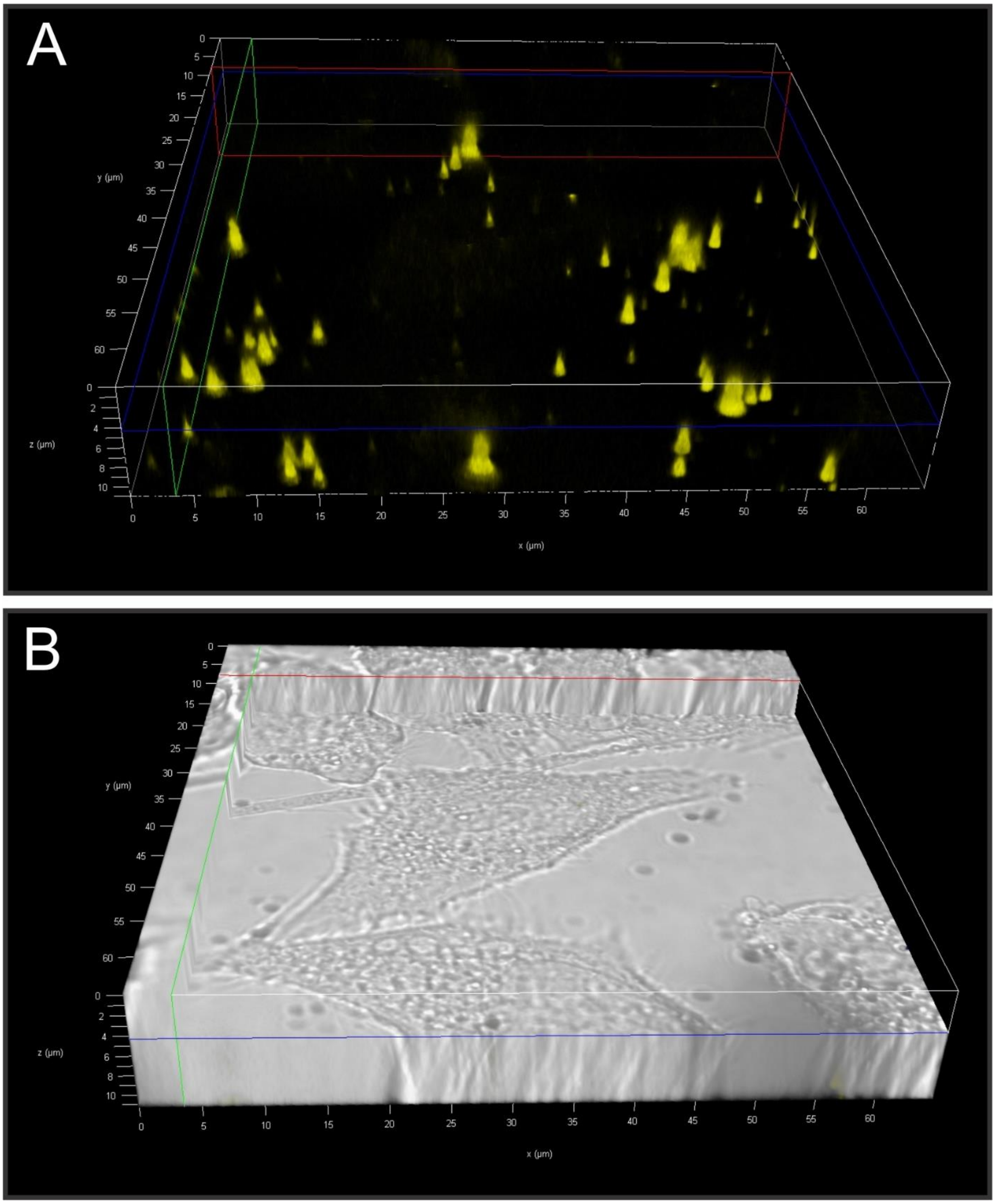


Figure S5. 3D reconstruction of Z-scan HeLa cells treated with **mono-Ir** (middle section). (A) Phosphorescence of **mono-Ir**. (B) Merged image of transmitted light and image (A).

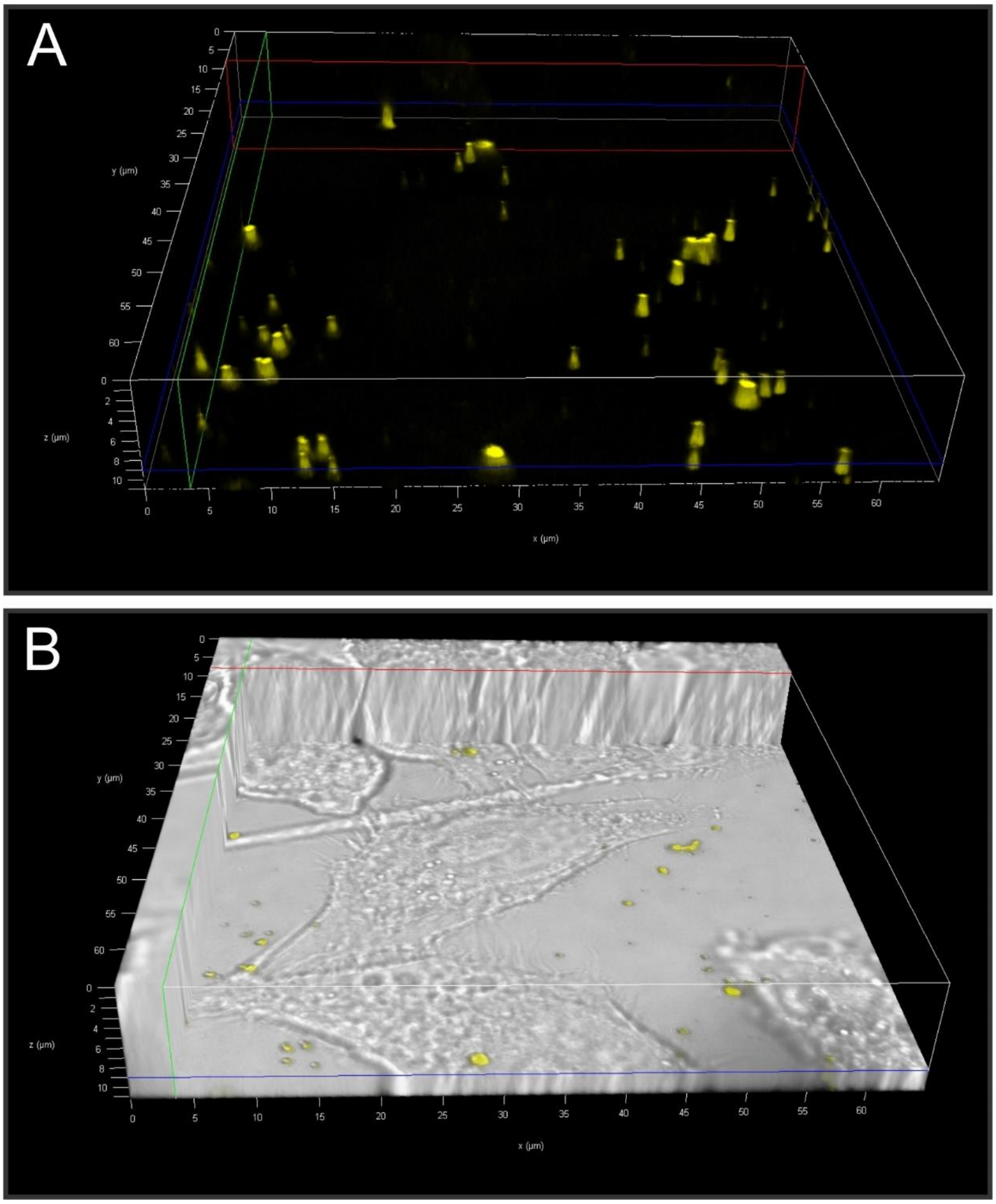


Figure S6. 3D reconstruction of Z-scan HeLa cells treated with **mono-Ir** (lower section). (A) Phosphorescence of **mono-Ir**. (B) Merged image of transmitted light and image (A).

To check the potential of **mono-Ir** as dioxygen photosensitizer in live cells, HeLa cells incubated with **mono-Ir** for two hours were irradiated with the 405 nm laser of the confocal microscope for 15 minutes and incubated for another 1 hour longer. After this time, the cell morphology was examined visually and compared with the morphology of non-illuminated cells incubated in parallel at the same conditions. For the irradiated batch, distinct changes in cell morphology (round cell shape) indicating increased apoptosis or necrosis rate was observed. However, similar changes were observed also for control cells irradiated with the 405 nm laser for the same time but incubated in a medium not containing **mono-Ir**. In a complementary experiment with the irradiation time reduced to 5 minutes, no distinct morphology change was observed neither for cells treated with **mono-Ir** and control cells incubated in pristine medium. Thus, no distinct phototoxic effect of **mono-Ir** was detected.

Computations.

All calculations were carried out with the Gaussian 09 package[4] utilizing the DFT approach with the M11L functional[5] and the def2-SVP basis set[6] including ECPs for the Ir(III) ion. Geometry optimizations were conducted with "tight" criteria. The C-PCM solvation model[7] was applied with solvent parameters for dichloromethane.

Table S1. DFT calculated frontier orbital energies and atomic contributions of complex **mono-Ir'** in the state T_1 geometry resulting from the Mulliken population analysis.

Orbital	Energy, eV	Contribution, % (Mulliken)			
		Ir	Cl	N^C^N	C^N-N^C
LUMO+4	−2.199	3	0	2	95
LUMO+3	−2.506	2	0	2	96
LUMO+2	−2.753	5	1	94	0
LUMO+1	−2.822	2	0	95	3
LUMO	−3.300	1	0	1	98
HOMO	−5.428	21	8	4	67
HOMO-1	−5.622	42	15	40	3
HOMO-2	−5.701	15	26	9	50
HOMO-3	−6.076	3	26	5	67
HOMO-4	−6.232	3	59	34	5

C^N−N^C – The ditopic (bis-bidentate) bridging ligand
N^C^N – The tridentate ligand.

Table S2. DFT calculated frontier orbital energies and atomic contributions of complex **di-Ir'** in the state T_1 geometry resulting from the Mulliken population analysis.

Orbital	**Energy, eV**	**Contribution, % (Mulliken)**						
		Ir1	**Cl1**	**N^C^N1**	**C^N-N^C**	**N^C^N2**	**Cl2**	**Ir2**
LUMO+4	−2.757	2	1	47	0	47	1	2
LUMO+3	−2.759	2	1	47	0	47	1	2
LUMO+2	−2.819	1	0	48	2	48	0	1
LUMO+1	−2.837	1	0	47	4	47	0	1
LUMO	−3.299	1	0	1	96	1	0	1
HOMO	−5.389	12	4	2	64	2	4	12
HOMO−1	−5.616	20	8	20	4	20	8	20
HOMO−2	−5.632	20	7	21	4	21	7	20
HOMO−3	−5.638	22	11	5	23	5	11	22
HOMO−4	−5.852	15	6	5	48	5	6	15

C^N−N^C – The ditopic (bis-bidentate) bridging ligand
N^C^N1 – The tridentate ligand coordinated to Ir1
N^C^N2 – The tridentate ligand coordinated to Ir2
Cl1 – The chloride coordinated to Ir1
Cl2 – The chloride coordinated to Ir2

Table S3. TD-DFT calculated lowest triplet and singlet states of **mono-Ir'** in the T_1 state geometry

State, energy (eV)	f (oscillator strength)	Contributing transition coefficients*	Character**
triplets			
T_1, 1.912	(triplet)	HOMO→LUMO (0.67) HOMO–2→LUMO (0.20)	$LC^{CN\text{-}NC}/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
T_2, 2.314	(triplet)	HOMO–1→LUMO (0.70)	$ML^{CN\text{-}NC}CT/L^{CNC}L^{CN\text{-}NC}CT/\ XL^{CN\text{-}NC}CT$
T_3, 2.376	(triplet)	HOMO–2→LUMO (0.67) HOMO→LUMO (-0.20)	$L^{CN\text{-}NC}C\ /XL^{CN\text{-}NC}CT\ /ML^{CN\text{-}NC}CT$
T_4, 2.558	(triplet)	HOMO→LUMO+1 (0.69)	$L^{CN\text{-}NC}L^{CNC}CT/ML^{CNC}CT/XL^{CNC}CT$
T_5, 3.635	(triplet)	HOMO→LUMO+2 (0.70)	$L^{CN\text{-}NC}L^{CNC}CT/ML^{CNC}CT/XL^{CNC}CT$
singlets			
S_1, 2.290	0.4529	HOMO→LUMO (0.65) HOMO–2→LUMO (-0.25)	$LC^{CN\text{-}NC}/ML^{CN\text{-}NC}CT/\ XL^{CN\text{-}NC}CT$
S_2, 2.3227	0.0006	HOMO–1→LUMO (0.70)	$ML^{CN\text{-}NC}CT/L^{CNC}L^{CN\text{-}NC}CT/\ XL^{CN\text{-}NC}CT$
S_3, 2.623	0.0431	HOMO→LUMO+1 (0.69) HOMO–2→LUMO (0.19)	$L^{CN\text{-}NC}L^{CNC}CT/ML^{CNC}CT/XL^{CNC}CT$

S_4, 2.686	0.0087	HOMO→LUMO+2 (0.70)	$L^{CN\text{-}NC}L^{CNC}CT/ML^{CNC}CT/XL^{CNC}CT$
S_5, 2.718	0.9219	HOMO–2→LUMO (0.62) HOMO→LUMO (0.25)	$L^{CN\text{-}NC}C$ /$XL^{CN\text{-}NC}CT$ /$ML^{CN\text{-}NC}CT$

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. XLCT – Halide (X) to Ligand (L) Charge Transfer. LC-Ligand Centered. LLCT – Ligand to Ligand Charge Transfer.

Table S4. TD-DFT calculated lowest triplet and singlet states of **di-Ir'** in the T_1 state geometry

State, energy (eV)	f (oscillator strength)	Contributing transition coefficients*	Character**
		triplets	
T_1, 1.912	(triplet)	HOMO→LUMO (0.68) HOMO–4→LUMO (-0.16)	$LC^{CN\text{-}NC}/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
T_2, 2.307	(triplet)	HOMO–3→LUMO (0.69) HOMO–1→LUMO (0.12)	$ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT/L^{NC\text{-}CN}C$
T_3, 2.310	(triplet)	HOMO–1→LUMO (0.70) HOMO–3→LUMO (0.11)	$L^{CNC}L^{CN\text{-}NC}CT/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
T_4, 2.326	(triplet)	HOMO–2→LUMO (0.71)	$L^{CNC}L^{CN\text{-}NC}CT/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
T_5, 2.4347	(triplet)	HOMO–4→LUMO (0.68) HOMO→LUMO (0.16)	$L^{CN\text{-}NC}C$ /$ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
		singlets	
S_1, 2.234	0.5926	HOMO→LUMO (0.69)	$LC^{CN\text{-}NC}/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
S_2, 2.318	0.0009	HOMO–1→LUMO (0.70)	$L^{CNC}L^{CN\text{-}NC}CT/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
S_3, 2.333	0.0001	HOMO–2→LUMO (0.70)	$L^{CNC}L^{CN\text{-}NC}CT/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
S_4, 2.380	0.0000	HOMO–3→LUMO (0.70)	$LC^{CN\text{-}NC}/ML^{CN\text{-}NC}CT/XL^{CN\text{-}NC}CT$
S_5, 2.567	0.0000	HOMO→LUMO+1 (0.70)	$L^{CN\text{-}NC}L^{CNC}CT/ML^{CNC}CT/XL^{CNC}CT$

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. XLCT – Halide (X) to Ligand (L) Charge Transfer. LC-Ligand Centered. LLCT – Ligand to Ligand Charge Transfer.

Table S5. DFT optimized ground state (S_0) and T_1 state geometry of **mono-Ir'** in cartesian (XYZ) coordinates

State S_0				State T_1			
C	-2.024181000	2.462744000	-0.000013000	C	2.018718154	2.468713188	-0.000039000
C	-1.423692000	1.176669000	-0.000003000	C	1.397030107	1.166758087	-0.000015000
C	-3.390787000	2.651939000	-0.000014000	C	3.371893258	2.646084200	-0.000041000
C	-4.191033000	1.510966000	-0.000006000	C	4.190437322	1.486253111	-0.000018000
C	-3.584543000	0.224722000	0.000004000	C	3.565795274	0.187995014	0.000006000
C	-2.216146000	0.032051000	0.000006000	C	2.210598169	0.003459000	0.000009000
N	-5.541802000	1.507361000	-0.000006000	N	5.508818402	1.487920115	-0.000018000
C	-6.016619000	0.309857000	0.000003000	C	6.009536445	0.267889020	0.000006000
S	-4.818441000	-0.972694000	0.000014000	S	4.800584368	-1.012890076	0.000030000
S	-0.796171000	3.674414000	-0.000021000	S	0.798295059	3.691856281	-0.000064000
C	0.403576000	2.431788000	-0.000011000	C	-0.421820032	2.453856188	-0.000042000
N	-0.060828000	1.208812000	-0.000003000	N	0.071862005	1.192216090	-0.000018000
C	-7.435138000	-0.003576000	0.000005000	C	7.403360585	-0.023993002	0.000011000
C	-7.908216000	-1.314355000	0.000010000	C	7.900432597	-1.338960101	0.000033000
C	-8.371527000	1.035456000	0.000002000	C	8.343127626	1.027607077	-0.000008000
C	-9.722438000	0.759218000	0.000004000	C	9.691579737	0.761905059	-0.000003000
C	-10.208844000	-0.553019000	0.000009000	C	10.194262775	-0.548926043	0.000019000
C	-9.266802000	-1.580422000	0.000012000	C	9.257472727	-1.587033119	0.000037000
C	-11.710416000	-0.806220000	0.000011000	C	11.696277891	-0.786262061	0.000022000
C	-12.037730000	-2.287029000	0.000016000	C	12.039755942	-2.263481174	0.000047000
C	-12.321799000	-0.174835000	1.244668000	C	12.302821965	-0.148243011	-1.244353094
C	-12.321801000	-0.174843000	-1.244649000	C	12.302822917	-0.148200011	1.244373097
C	1.819289000	2.664738000	-0.000012000	C	-1.803500137	2.671915204	-0.000049000
C	2.398863000	3.932837000	-0.000018000	C	-2.409247186	3.946084303	-0.000073000
C	3.773301000	4.070803000	-0.000018000	C	-3.778802288	4.061811308	-0.000076000
C	4.599912000	2.943504000	-0.000012000	C	-4.610387354	2.927035223	-0.000055000
C	3.996541000	1.682510000	-0.000006000	C	-3.995939303	1.667618125	-0.000032000
C	2.617589000	1.497527000	-0.000006000	C	-2.621927200	1.492460112	-0.000028000
C	6.121538000	3.039696000	-0.000010000	C	-6.129272482	3.017248228	-0.000058000
C	6.603723000	4.477867000	-0.000008000	C	-6.617959522	4.453378342	-0.000081000
C	6.665092000	2.347780000	1.244087000	C	-6.672135525	2.322385180	-1.243771094
C	6.665096000	2.347784000	-1.244108000	C	-6.672137535	2.322426175	1.243677096
H	-3.850194000	3.648168000	-0.000022000	H	3.839934294	3.637989275	-0.000060000
H	-1.746886000	-0.960973000	0.000014000	H	1.736222135	-0.985739076	0.000028000
H	-7.202980000	-2.159582000	0.000012000	H	7.203993533	-2.191317167	0.000047000
H	-8.012488000	2.073367000	-0.000001000	H	7.976467589	2.062598156	-0.000025000
H	-10.426869000	1.604265000	0.000002000	H	10.388889775	1.613113122	-0.000018000
H	-9.589658000	-2.629209000	0.000016000	H	9.592168711	-2.632399200	0.000054000
H	-13.133711000	-2.429520000	0.000017000	H	13.137222989	-2.394499185	0.000049000
H	-11.644778000	-2.805875000	-0.894050000	H	11.652118896	-2.786441215	0.894059070
H	-11.644777000	-2.805870000	0.894085000	H	11.652117891	-2.786472214	-0.893946070
H	-13.415055000	-0.343789000	1.268160000	H	13.398311000	-0.303629023	-1.265773099
H	-11.897362000	-0.609070000	2.169174000	H	11.885061927	-0.588277045	-2.169165167
H	-12.160533000	0.917707000	1.287055000	H	12.128098909	0.942212072	-1.287812098
H	-13.415057000	-0.343798000	-1.268139000	H	13.398313011	-0.303584023	1.265796097
H	-12.160535000	0.917699000	-1.287042000	H	12.128099914	0.942256074	1.287796101
H	-11.897365000	-0.609083000	-2.169153000	H	11.885065896	-0.588203045	2.169201167
H	1.764164000	4.833726000	-0.000022000	H	-1.785216137	4.853350372	-0.000090000
H	4.201897000	5.080617000	-0.000022000	H	-4.217843321	5.067942388	-0.000096000
H	4.647879000	0.793882000	-0.000001000	H	-4.640615355	0.774425059	-0.000016000
H	7.708773000	4.504971000	-0.000007000	H	-7.723106571	4.475826343	-0.000081000
H	6.266990000	5.035150000	-0.893932000	H	-6.283699474	5.012164381	0.893893067
H	6.266989000	5.035147000	0.893918000	H	-6.283700479	5.012135382	-0.894074067
H	7.769974000	2.404644000	1.269576000	H	-7.777659612	2.370784181	-1.266170098
H	6.285158000	2.820613000	2.169180000	H	-6.297844487	2.798767214	-2.169327164
H	6.392917000	1.276767000	1.283581000	H	-6.391962471	1.253409094	-1.284748098
H	7.769977000	2.404648000	-1.269594000	H	-7.777661570	2.370826182	1.266073094
H	6.392922000	1.276771000	-1.283605000	H	-6.391965488	1.253451095	1.284691101
H	6.285163000	2.820619000	-2.169201000	H	-6.297848456	2.798838214	2.169219164
C	1.385642000	-0.072497000	4.313583000	C	-1.389377109	-0.042109003	-4.312786329
C	2.502829000	-0.799976000	4.691200000	C	-2.497603191	-0.783386062	-4.689994356

C	3.319549000	-1.339235000	3.716095000	C	-3.307328252	-1.334629102	-3.715764281
C	3.012551000	-1.146330000	2.371042000	C	-3.002331229	-1.139492087	-2.370827182
N	1.908883000	-0.431409000	2.022243000	N	-1.906595148	-0.412328032	-2.023384154
C	1.133140000	0.084740000	2.965028000	C	-1.136986088	0.115903009	-2.964505227
C	3.774238000	-1.648437000	1.237781000	C	-3.758161285	-1.650658127	-1.237373092
C	3.223447000	-1.306560000	0.000002000	C	-3.212417243	-1.305287097	0.000018000
C	3.774234000	-1.648444000	-1.237777000	C	-3.758166286	-1.650617126	1.237418093
C	4.960260000	-2.373865000	-1.205549000	C	-4.937496376	-2.387944182	1.205709094
C	5.560999000	-2.732228000	0.000002000	C	-5.534131437	-2.752551212	0.000036000
C	4.960264000	-2.373859000	1.205553000	C	-4.937491375	-2.387983182	-1.205645090
C	3.012544000	-1.146343000	-2.371039000	C	-3.002341231	-1.139415086	2.370858181
N	1.908876000	-0.431421000	-2.022241000	N	-1.906605144	-0.412260032	2.023397156
C	3.319538000	-1.339254000	-3.716091000	C	-3.307342254	-1.334510101	3.715800281
C	2.502815000	-0.800002000	-4.691198000	C	-2.497622189	-0.783235061	4.690016359
C	1.385628000	-0.072522000	-4.313581000	C	-1.389397106	-0.041967003	4.312789330
C	1.133130000	0.084722000	-2.965026000	C	-1.137001085	0.116003009	2.964504226
H	0.708495000	0.374580000	5.050684000	H	-0.719020053	0.414821032	-5.049916383
H	2.740894000	-0.949515000	5.752917000	H	-2.734454207	-0.934300073	-5.751751453
H	4.207902000	-1.918242000	3.989330000	H	-4.188386320	-1.924229149	-3.989665304
H	0.259613000	0.652481000	2.610235000	H	-0.270139021	0.692955052	-2.608663198
Ir	1.629062000	-0.252533000	0.000001000	Ir	-1.620853123	-0.237168018	0.000004000
F	5.573082000	-2.747858000	-2.299343000	F	-5.547164437	-2.764985210	2.299269178
O	6.727968000	-3.387046000	0.000002000	O	-6.694920521	-3.416870260	0.000045000
F	5.573089000	-2.747846000	2.299347000	F	-5.547154436	-2.765059210	-2.299196178
H	4.207891000	-1.918262000	-3.989327000	H	-4.188399322	-1.924104146	3.989716306
H	2.740877000	-0.949546000	-5.752914000	H	-2.734476210	-0.934117073	5.751777435
H	0.708478000	0.374550000	-5.050683000	H	-0.719044056	0.414989032	5.049907387
H	0.259603000	0.652463000	-2.610234000	H	-0.270155020	0.693047054	2.608646200
C	6.605877000	-4.775466000	0.000004000	C	-6.561864511	-4.804691365	0.000063000
Cl	0.300977000	-2.387811000	0.000011000	Cl	-0.305628024	-2.370893181	0.000045000
H	6.072432000	-5.142092000	-0.899882000	H	-6.025646453	-5.166792397	0.900023067
H	6.072433000	-5.142089000	0.899892000	H	-6.025647458	-5.166816395	-0.899887068
H	7.624113000	-5.195346000	0.000004000	H	-7.576850552	-5.232104400	0.000069000

Table S6. DFT optimized ground state (S_0) and T_1 state geometry of **di-Ir’** in cartesian (XYZ) coordinates.

State S_0				**State T_1**			
C	4.414148000	-0.306885000	-4.314112000	C	-4.365653333	0.310851024	-4.301915330
C	5.680488000	-0.724088000	-4.691322000	C	-5.624541423	0.744785058	-4.685222357
C	6.607208000	-1.037442000	-3.715936000	C	-6.555358488	1.062744081	-3.715232284
C	6.260348000	-0.930591000	-2.371009000	C	-6.219896467	0.943594072	-2.368593181
N	5.010589000	-0.521217000	-2.022470000	N	-4.976774383	0.519323040	-2.014805153
C	4.129116000	-0.220258000	-2.965637000	C	-4.090845311	0.213499016	-2.952175227
C	7.124546000	-1.222874000	-1.237718000	C	-7.089445550	1.237134095	-1.239465094
C	6.504128000	-1.034716000	0.000003000	C	-6.481428511	1.035599077	0.001128000
C	7.124545000	-1.222865000	1.237726000	C	-7.107687560	1.219442091	1.235367092
C	8.457631000	-1.617681000	1.205494000	C	-8.437334670	1.626389127	1.196625089
C	9.130335000	-1.809640000	0.000007000	C	-9.098994671	1.833551140	-0.012453001
C	8.457632000	-1.617690000	-1.205482000	C	-8.419448638	1.644036124	-1.214479091
C	6.260347000	-0.930574000	2.371015000	C	-6.254870479	0.909268069	2.372780179
N	5.010589000	-0.521202000	2.022473000	N	-5.006772382	0.489650037	2.031228153
C	6.607207000	-1.037415000	3.715943000	C	-6.610312487	1.008562078	3.715875282
C	5.680486000	-0.724054000	4.691327000	C	-5.694320428	0.675236054	4.694762359
C	4.414147000	-0.306854000	4.314113000	C	-4.430118340	0.246031019	4.323814330
C	4.129116000	-0.220236000	2.965637000	C	-4.135181316	0.168970013	2.977004229
H	3.645488000	-0.047253000	-5.051314000	H	-3.594997275	0.046659004	-5.035314383
H	5.949479000	-0.806934000	-5.752951000	H	-5.884716444	0.837081063	-5.748251421
H	7.613984000	-1.370330000	-3.989122000	H	-7.556231584	1.408361110	-3.994069307
H	3.139398000	0.105728000	-2.611402000	H	-3.107677238	-0.125037009	-2.591663199
F	9.146614000	-1.819562000	2.299205000	F	-9.132684688	1.823995140	2.286515175
O	10.426744000	-2.140839000	0.000008000	O	-10.392275768	2.175023165	-0.019827001

F	9.146614000	-1.819579000	-2.299192000
H	7.613983000	-1.370301000	3.989132000
H	5.949477000	-0.806892000	5.752956000
H	3.645487000	-0.047216000	5.051313000
H	3.139398000	0.105747000	2.611400000
C	10.668111000	-3.513505000	0.000016000
Ir	4.693614000	-0.421369000	0.000001000
C	-0.471431000	-1.275245000	0.000002000
C	-1.380031000	-0.186594000	-0.000001000
C	0.900482000	-1.120196000	0.000002000
C	1.380031000	0.186594000	-0.000001000
C	0.471431000	1.275245000	-0.000005000
C	-0.900482000	1.120196000	-0.000004000
N	2.689639000	0.562775000	-0.000002000
C	2.826960000	1.864270000	-0.000006000
S	1.350698000	2.759782000	-0.000009000
S	-1.350698000	-2.759782000	0.000005000
C	-2.826960000	-1.864270000	0.000002000
N	-2.689639000	-0.562775000	-0.000001000
C	4.137453000	2.448552000	-0.000008000
C	4.377200000	3.822114000	-0.000012000
C	5.205578000	1.521866000	-0.000006000
C	6.492738000	2.049840000	-0.000007000
C	6.757063000	3.422456000	-0.000012000
C	5.671903000	4.303496000	-0.000013000
C	8.204539000	3.900988000	-0.000013000
C	8.306579000	5.414472000	-0.000013000
C	8.905763000	3.369640000	1.244124000
C	8.905761000	3.369641000	-1.244152000
C	-4.137453000	-2.448552000	0.000002000
C	-4.377200000	-3.822114000	0.000004000
C	-5.671903000	-4.303496000	0.000003000
C	-6.757063000	-3.422456000	0.000000000
C	-6.492738000	-2.049840000	-0.000001000
C	-5.205578000	-1.521866000	0.000000000
C	-8.204539000	-3.900988000	-0.000001000
C	-8.306579000	-5.414472000	0.000003000
C	-8.905764000	-3.369637000	1.244134000
C	-8.905760000	-3.369644000	-1.244142000
H	1.600897000	-1.966436000	0.000005000
H	-1.600897000	1.966436000	-0.000007000
H	3.535062000	4.532825000	-0.000013000
H	7.347694000	1.354977000	-0.000005000
H	5.830860000	5.388871000	-0.000016000
H	9.368751000	5.720469000	-0.000014000
H	7.839714000	5.868320000	-0.893973000
H	7.839717000	5.868320000	0.893950000
H	9.960326000	3.704208000	1.268815000
H	8.419003000	3.731839000	2.169108000
H	8.913437000	2.264628000	1.284472000
H	9.960324000	3.704210000	-1.268844000
H	8.913437000	2.264630000	-1.284500000
H	8.418999000	3.731840000	-2.169135000
H	-3.535062000	-4.532825000	0.000005000
H	-5.830860000	-5.388871000	0.000004000
H	-7.347694000	-1.354977000	-0.000002000
H	-9.368751000	-5.720469000	0.000002000
H	-7.839714000	-5.868323000	-0.893956000
H	-7.839717000	-5.868318000	0.893967000
H	-9.960327000	-3.704205000	1.268825000
H	-8.419005000	-3.731834000	2.169119000
H	-8.913439000	-2.264625000	1.284479000
H	-9.960323000	-3.704213000	-1.268834000
H	-8.913435000	-2.264633000	-1.284493000
H	-8.418998000	-3.731846000	-2.169123000

F	-9.098328702	1.858174143	-2.311572178
H	-7.615029579	1.350810104	3.984844303
H	-5.970372460	0.751568057	5.755047433
H	-3.670698282	-0.029831002	5.064616388
H	-3.146828242	-0.164653013	2.626228199
C	-10.623364827	3.549649272	-0.007562001
Ir	-4.671597355	0.408109031	0.009833001
C	0.464167035	1.290227099	0.019934002
C	1.391819108	0.193283015	0.019703002
C	-0.894657067	1.131711086	0.020589002
C	-1.391819108	-0.193284015	0.019706002
C	-0.464167035	-1.290228099	0.019932002
C	0.894657067	-1.131712086	0.020584002
N	-2.672351204	-0.554616043	0.016393001
C	-2.828506219	-1.891300147	0.013006001
S	-1.338169102	-2.780463211	0.016936001
S	1.338169102	2.780462211	0.016940001
C	2.828505218	1.891299147	0.013003001
N	2.672351204	0.554615043	0.016388001
C	-4.116375314	-2.455073189	0.002285000
C	-4.378286334	-3.837787295	-0.003662000
C	-5.200514397	-1.521511117	-0.004958000
C	-6.486916502	-2.038146156	-0.019027001
C	-6.763288528	-3.411333262	-0.026243002
C	-5.675012444	-4.298792327	-0.017628001
C	-8.211047630	-3.881140295	-0.043581003
C	-8.322087644	-5.394082402	-0.050032004
C	-8.925178678	-3.350227254	1.194137094
C	-8.897555678	-3.341534253	-1.293131097
C	4.116374314	2.455073189	0.002279000
C	4.378285333	3.837787295	-0.003666000
C	5.675012444	4.298792327	-0.017636001
C	6.763287523	3.411333262	-0.026257002
C	6.486916502	2.038146156	-0.019041001
C	5.200514397	1.521511117	-0.004969000
C	8.211046625	3.881141295	-0.043599003
C	8.322086639	5.394082402	-0.050048004
C	8.925182699	3.350225254	1.194115091
C	8.897550704	3.341537254	-1.293153100
H	-1.595905120	1.975792153	0.020678002
H	1.595905120	-1.975793153	0.020670002
H	-3.544529271	-4.557356348	0.002500000
H	-7.336156556	-1.336550101	-0.025071002
H	-5.844578456	-5.383208392	-0.022341002
H	-9.385893726	-5.694220413	-0.062373005
H	-7.848182588	-5.847563439	-0.940533072
H	-7.867273610	-5.853657444	0.847266064
H	-9.983402786	-3.674476280	1.202686090
H	-8.454351634	-3.722052283	2.123542161
H	-8.922589678	-2.245340174	1.240469097
H	-9.954797740	-3.667163278	-1.328372100
H	-8.895576661	-2.236314172	-1.330721102
H	-8.404880653	-3.705298283	-2.214367170
H	3.544528270	4.557355348	0.002501000
H	5.844577450	5.383208392	-0.022347002
H	7.336156556	1.336551101	-0.025089002
H	9.385893726	5.694220413	-0.062392005
H	7.848177614	5.847565450	-0.940546074
H	7.867276626	5.853656438	0.847254062
H	9.983406755	3.674474279	1.202661091
H	8.454358619	3.722049283	2.123523164
H	8.922593700	2.245338174	1.240446093
H	9.954791760	3.667166278	-1.328397104
H	8.895571687	2.236318173	-1.330744100
H	8.404871657	3.705302283	-2.214386168

C	-4.414146000	0.306869000	4.314112000	C	4.430131337	-0.246032019	4.323804329
C	-5.680485000	0.724069000	4.691325000	C	5.694333446	-0.675237049	4.694748357
C	-6.607206000	1.037428000	3.715940000	C	6.610322489	-1.008563078	3.715859285
C	-6.260346000	0.930581000	2.371012000	C	6.254876459	-0.909268069	2.372765182
N	-5.010588000	0.521209000	2.022471000	N	5.006778383	-0.489651038	2.031217157
C	-4.129115000	0.220246000	2.965636000	C	4.135189317	-0.168971013	2.976995228
C	-7.124545000	1.222869000	1.237723000	C	7.107691528	-1.219442091	1.235350095
C	-6.504128000	1.034716000	0.000000000	C	6.481428511	-1.035599077	0.001112000
C	-7.124546000	1.222870000	-1.237721000	C	7.089442533	-1.237133094	-1.239482096
C	-8.457632000	1.617686000	-1.205487000	C	8.419445621	-1.644035124	-1.214500094
C	-9.130335000	1.809640000	0.000002000	C	9.098994671	-1.833551140	-0.012476001
C	-8.457631000	1.617685000	1.205489000	C	8.437337633	-1.626389127	1.196604092
C	-6.260348000	0.930583000	-2.371012000	C	6.219889482	-0.943593072	-2.368608183
N	-5.010590000	0.521210000	-2.022471000	N	4.976769382	-0.519323040	-2.014816155
C	-6.607209000	1.037430000	-3.715939000	C	6.555348487	-1.062744081	-3.715248286
C	-5.680489000	0.724072000	-4.691325000	C	5.624528405	-0.744784058	-4.685235359
C	-4.414149000	0.306871000	-4.314113000	C	4.365641331	-0.310850024	-4.301925326
C	-4.129117000	0.220247000	-2.965638000	C	4.090837310	-0.213499016	-2.952184223
H	-3.645486000	0.047233000	5.051312000	H	3.670712279	0.029830002	5.064609387
H	-5.949476000	0.806911000	5.752954000	H	5.970388442	-0.751569057	5.755033463
H	-7.613982000	1.370314000	3.989128000	H	7.615041592	-1.350811105	3.984825306
H	-3.139397000	-0.105738000	2.611400000	H	3.146835243	0.164652012	2.626222198
Ir	-4.693614000	0.421369000	-0.000001000	Ir	4.671597355	-0.408109031	0.009822001
F	-9.146615000	1.819572000	-2.299197000	F	9.098322669	-1.858173143	-2.311596177
O	-10.426744000	2.140839000	0.000002000	O	10.392276774	-2.175023165	-0.019854001
F	-9.146613000	1.819569000	2.299200000	F	9.132691673	-1.823995140	2.286492177
H	-7.613985000	1.370317000	-3.989126000	H	7.556220577	-1.408360109	-3.994087305
H	-5.949480000	0.806915000	-5.752954000	H	5.884700463	-0.837080063	-5.748265445
H	-3.645490000	0.047236000	-5.051314000	H	3.594983273	-0.046658004	-5.035322384
H	-3.139399000	-0.105738000	-2.611402000	H	3.107670237	0.125037009	-2.591670200
C	-10.668111000	3.513505000	0.000006000	C	10.623364827	-3.549648272	-0.007588001
Cl	-3.946815000	2.824545000	-0.000001000	Cl	3.932020301	-2.807380214	0.033935003
H	-10.247871000	4.005744000	-0.899942000	H	10.190568800	-4.047973307	-0.898125067
H	-10.247873000	4.005739000	0.899959000	H	10.208444778	-4.028951306	0.901689070
H	-11.760337000	3.655376000	0.000006000	H	11.714418881	-3.699513285	-0.016798001
Cl	3.946815000	-2.824545000	0.000010000	Cl	-3.932020301	2.807380214	0.033944003
H	10.247871000	-4.005747000	-0.899931000	H	-10.190571764	4.047973307	-0.898100069
H	10.247873000	-4.005736000	0.899970000	H	-10.208440756	4.028952306	0.901713069
H	11.760336000	-3.655376000	0.000016000	H	-11.714417875	3.699514280	-0.016768001

References.

1. M. Z. Shafikov, R. Martinscroft, C. Hodgson, A. Hayer, A. Auch and V. N. Kozhevnikov, *Inorg. Chem.*, 2021, **60**, 1780-1789.
2. A. A. Gorman, I. Hamblett, C. Lambert, A. L. Prescott, M. A. J. Rodgers and H. M. Spence, *J. Am. Chem. Soc.*, 1987, **109**, 3091-3097.
3. C. Martí, O. Jürgens, O. Cuenca, M. Casals and S. Nonell, *J. Photochem. Photobiol. A*, 1996, **97**, 11-18.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., *Gaussian 09*, Gaussian, Inc., Wallingford, CT, USA, 2009.
5. R. Peverati and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11363-11370.
6. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
7. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669-681.