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

Electronic Supplementary Information

for

Highly efficient blue and deep-blue emitting zwitterionic iridium(III) complexes: synthesis, photophysics and electroluminescence

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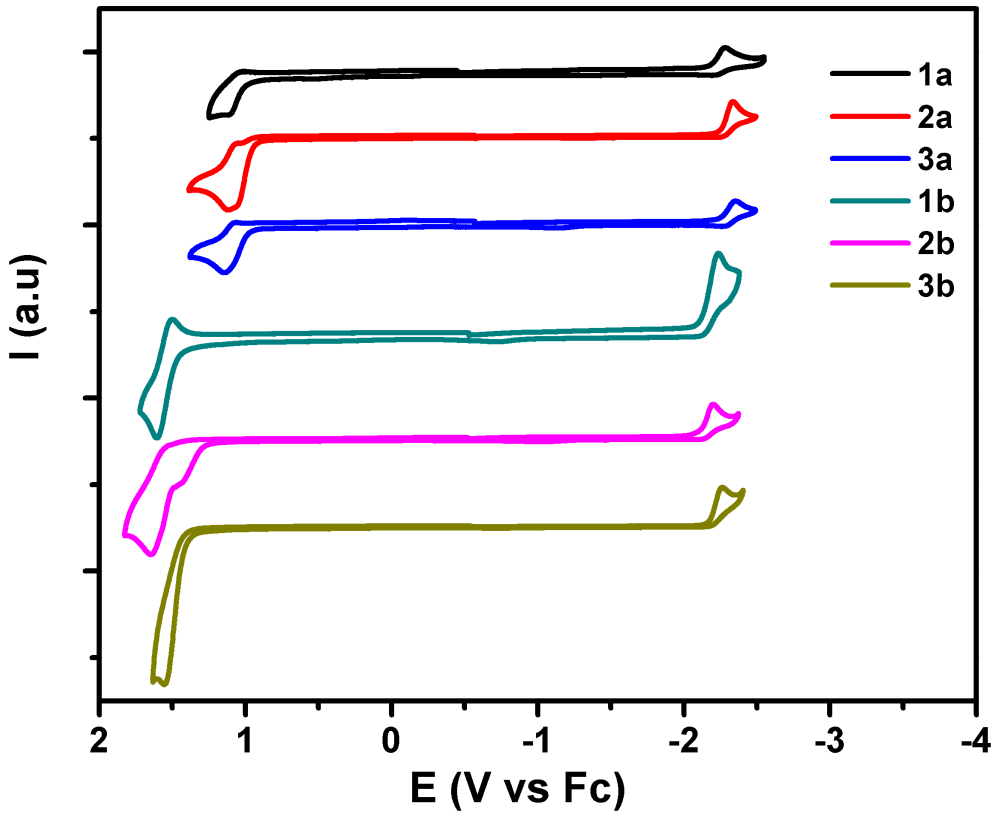

Fig. S1. Cyclic voltamograms of **1a**–**3b** (V vs Ferocene) were collected in deaerated CH_3CN with scan rate of 0.1 V s^{-1}.

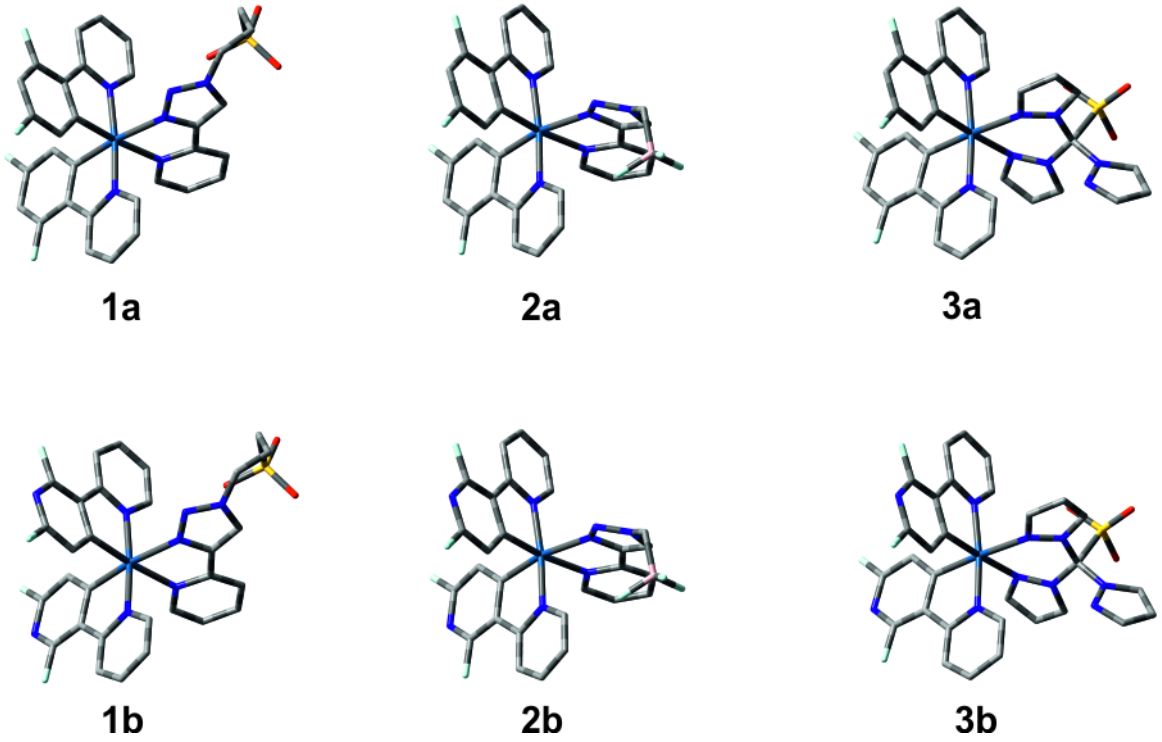

Fig. S2. DFT-optimized S_0 geometry for complexes **1a**–**3b** in gas phase.

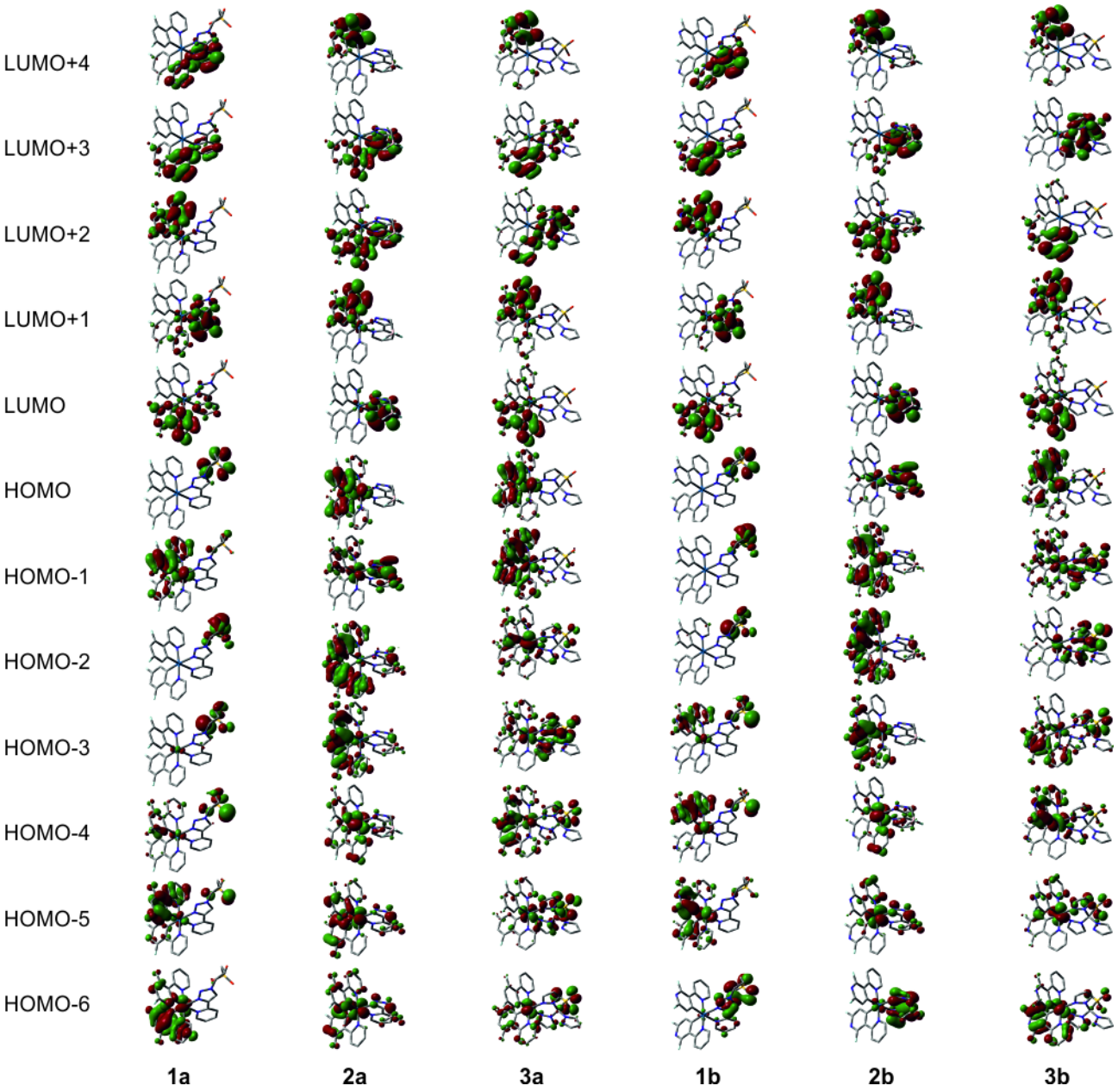

Fig. S3. Isodensity surface plots of some selected frontier molecular orbitals for complexes **1a**–**3b**, at their optimized S_0 geometry in gas phase. Isodensity value 0.035 *e* $Bohr^{-3}$.

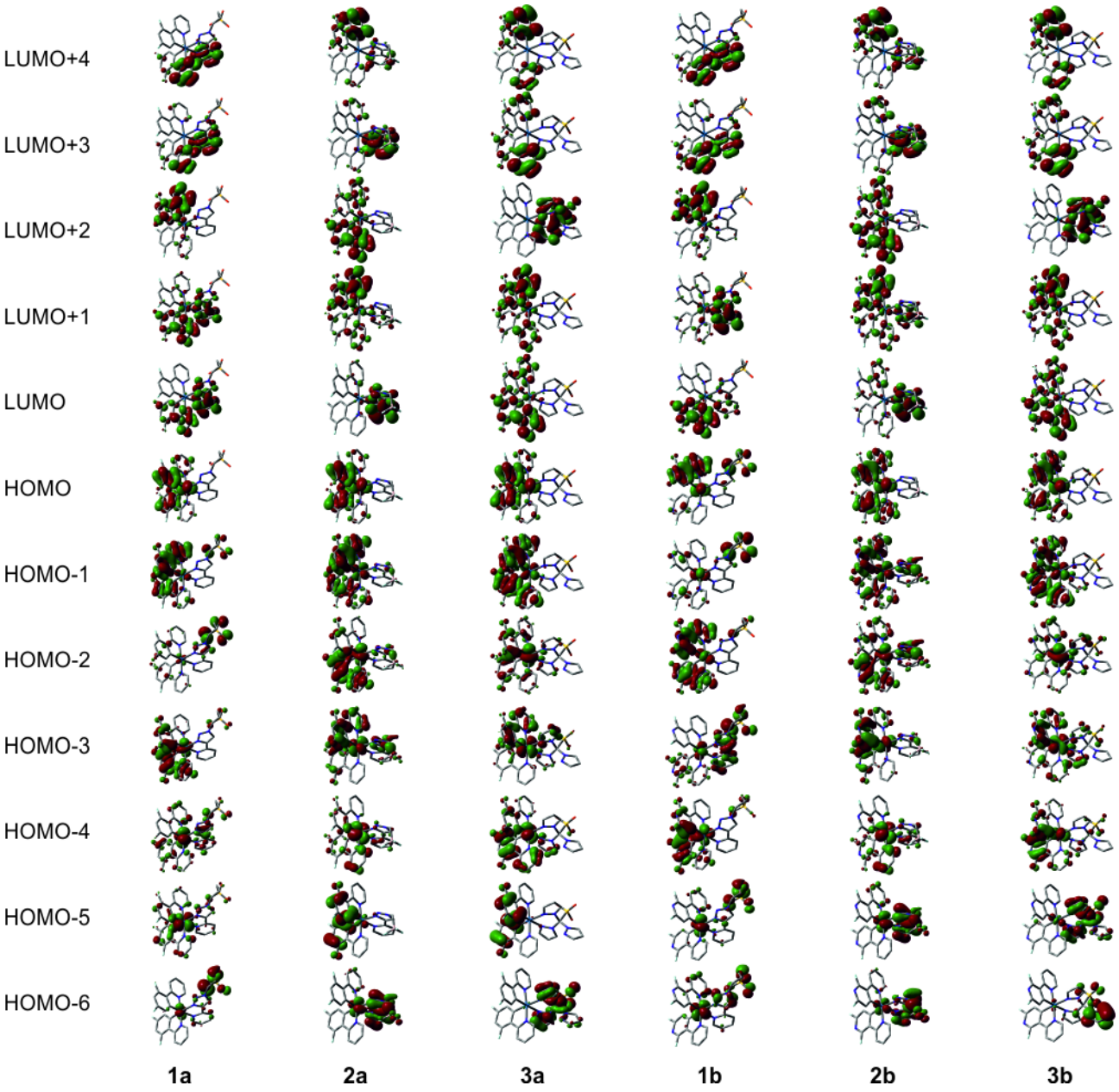

Fig. S4. Isodensity surface plots of some selected frontier molecular orbitals for complexes **1a**–**3b**, obtained as single point calculations in dichloromethane, at their optimized S_0 geometry in gas phase. Isodensity value 0.035 *e* $Bohr^{-3}$.

Table S1. Crystallographic data and structure refinements for **1a**, **2a** and **2b**.

	1a	**2a**	**2b**
Empirical formula	C_{34} H_{26} F_4 Ir N_7 O_3 S	C_{30} H_{19} B F_7 Ir N_6	C_{28} H_{23} B F_7 Ir N_{10}
Formula weight	880.88	799.52	807.52
Temperature	223(2) K	223(2) K	223(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å
Crystal system, space group	monoclinic,P_{21}/c No.14)	monoclinic,P_{21}/c No.14)	triclinic, P-1 (No.2)
Unit cell dimensions	a = 22.5873(5) Å b = 16.4337(4) Å c = 8.5110(2) Å β = 97.541(1)°	a = 9.6660(3) Å b = 23.6037(8)Å c = 12.8285(4) Å β = 101.336(2)°	a = 8.6423(1) Å b = 13.1265(2) Å c = 14.9287(2) Å α = 75.465(1)° β = 79.891(1)° γ = 88.149(1)°
Volume	3131.90(13) $Å^3$	2869.77(16) $Å^3$	1613.78(4) $Å^3$
Z, Calculated density	4, 1.868 Mg/m^3	4, 1.851 Mg/m^3	2, 1.818 Mg/m^3
Absorption coefficient	4.404 mm^{-1}	9.712 mm^{-1}	4.219 mm^{-1}
F(000)	1728	1544	860
Crystal size	0.30 x 0.20 x 0.07 mm	0.30 x 0.15 x 0.10 mm	0.40 x 0.12 x 0.10 mm
Theta range for data collection	4.14 to 27.78°	3.98 to 68.00°	4.10 to 27.90°
Limiting indices	-29<=h<=29, -21<=k<=16, -11<=l<=11	-11<=h<=11, -27<=k<=28, -15<=l<=14	-11<=h<=11, -13<=k<=17, -16<=l<=19
Reflections collected / unique	28704 / 7307 [R(int) = 0.045]	20569 / 5092 [R(int) = 0.047]	13509 / 7432 [R(int) = 0.043]
Completeness to theta = 29.99	98.8 %	97.3 %	96.2 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7480 and 0.3517	0.4434 and 0.1587	0.6777 and 0.2831
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7307 / 0 / 452	5092 / 0 / 406	7432 / 0 / 462
Goodness-of-fit on F^2	1.094	1.077	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR^2 = 0.0836	R1 = 0.0318, wR^2 = 0.0807	R1 = 0.0320, wR^2 = 0.0842
R indices (all data)	R1 = 0.0393, wR^2 = 0. 0916	R1 = 0.0330, wR^2 = 0.0816	R1 = 0.0334, wR^2 = 0.0864
Largest diff. peak and hole	1.098 and -2.232 e.$Å^{-3}$	0.980 and -0.990 e.$Å^{-3}$	1.135 and -2.355 e.$Å^{-3}$

Table S2. Selected geometrical parameters [pm, °] and energy [E_h][a] of the ground state optimized geometry for the complexes **1a**–**3b**. A partial atom labeling scheme is reported in Table 1 of the main text.

parameter	1a	2a	3a
R(Ir–C^1)	202.3	202.6	202.7
R(Ir–C^2)	202.7	202.1	202.8
R(Ir–N^1)	209.1	208.6	208.2
R(Ir–N^2)	208.2	208.9	208.7
R(Ir–N^3)	224.6	225.0	221.0
R(Ir–N^4)	218.6	217.3	220.1
Energy	–2689.246700	–2311.529444	–2797.477081

parameter	1b	2b	3b
R(Ir–C^1)	201.7	202.0	202.0
R(Ir–C^2)	202.0	201.5	202.1
R(Ir–N^1)	209.4	209.1	208.6
R(Ir–N^2)	208.6	209.2	209.1
R(Ir–N^3)	224.3	224.7	220.5
R(Ir–N^4)	217.8	216.6	219.6
Energy	–2721.350529	–2343.633012	–2829.580538

parameter	1a	2a	3a
<(C^1–Ir–N^3)	95.8	95.7	95.2
<(C^1–Ir–N^4)	171.1	168.0	176.8
<(C^2–Ir–N^4)	100.6	98.9	94.8
<(C^1–Ir–C^2)	88.4	90.8	86.9
<(N^1–Ir–N^2)	174.5	174.1	173.7
<(N^3–Ir–N^4)	75.3	74.9	83.1

parameter	1b	2b	3b
<(C^1–Ir–N^3)	95.9	95.9	95.2
<(C^1–Ir–N^4)	171.3	168.2	176.7
<(C^2–Ir–N^4)	100.3	98.8	96.8
<(C^1–Ir–C^2)	88.5	90.8	86.8
<(N^1–Ir–N^2)	174.4	173.9	173.6
<(N^3–Ir–N^4)	75.4	74.99	83.3

[a] 1 E_h = 2625.500 kJ mol^{-1}

Table S3. List of selected molecular orbital energies [eV] for the complexes **1a**–**3b**, and HOMO–LUMO energy gap in vacuum.

orbital	1a	2a	3a
LUMO + 6	–0.786	–0.586	–0.328
LUMO + 5	–0.941	–1.082	–0.739
LUMO + 4	–1.325	–1.367	–1.035
LUMO + 3	–1.534	–1.725	–1.270
LUMO + 2	–1.568	–1.804	–1.290
LUMO + 1	–1.971	–1.932	–1.710
LUMO	–2.088	–2.266	–1.915
HOMO	–5.506	–5.933	–5.988
HOMO – 1	–5.894	–6.274	–6.358
HOMO – 2	–5.950	–6.419	–6.430
HOMO – 3	–6.067	–6.510	–6.504
HOMO – 4	–6.228	–6.766	–6.574
HOMO – 5	–6.329	–6.843	–6.601
HOMO – 6	–6.556	–6.923	–6.690
HOMO – 7	–6.655	–7.294	–6.859
HOMO – 8	–6.698	–7.723	–7.048
HOMO – 9	–6.780	–8.063	–7.172
HOMO – 10	–6.812	–8.103	–7.354
HOMO–LUMO gap	3.418	3.667	4.074

orbital	1b	2b	3b
LUMO + 6	–1.017	–0.849	–0.773
LUMO + 5	–1.185	–1.343	–0.986
LUMO + 4	–1.556	–1.638	–1.297
LUMO + 3	–1.784	–1.970	–1.501
LUMO + 2	–1.845	–2.079	–1.543
LUMO + 1	–2.207	–2.226	–2.003
LUMO	–2.367	–2.508	–2.207
HOMO	–5.674	–6.500	–6.558
HOMO – 1	–6.114	–6.584	–6.705
HOMO – 2	–6.238	–6.768	–6.730
HOMO – 3	–6.369	–6.894	–6.812
HOMO – 4	–6.498	–7.134	–6.894
HOMO – 5	–6.732	–7.220	–6.910
HOMO – 6	–6.858	–7.525	–6.991
HOMO – 7	–6.921	–7.713	–7.226
HOMO – 8	–6.953	–7.898	–7.385
HOMO – 9	–7.049	–8.126	–7.560
HOMO – 10	–7.207	–8.241	–7.692
HOMO–LUMO gap	3.307	3.992	4.351

Table S4. List of selected molecular orbital energies [eV] for the complexes **1a**–**3b**, and HOMO–LUMO energy gap in dichloromethane by continuum solvatation model IEFPCM.

orbital	1a	2a	3a
LUMO + 6	–0.761	–0.672	–0.440
LUMO + 5	–0.935	–1.007	–0.799
LUMO + 4	–1.080	–1.098	–0.976
LUMO + 3	–1.274	–1.340	–1.117
LUMO + 2	–1.580	–1.686	–1.525
LUMO + 1	–1.777	–1.731	–1.650
LUMO	–1.853	–1.939	–1.791
HOMO	–5.859	–5.859	–5.946
HOMO – 1	–6.270	–6.299	–6.310
HOMO – 2	–6.393	–6.415	–6.407
HOMO – 3	–6.442	–6.522	–6.528
HOMO – 4	–6.568	–6.654	–6.569
HOMO – 5	–6.694	–6.825	–6.818
HOMO – 6	–6.732	–7.003	–6.894
HOMO – 7	–6.809	–7.319	–7.095
HOMO – 8	–6.860	–7.988	–7.281
HOMO – 9	–7.012	–8.033	–7.480
HOMO – 10	–7.119	–8.121	–7.636
HOMO–LUMO gap	4.006	3.920	4.155

orbital	1b	2b	3b
LUMO + 6	–0.866	–0.792	–0.696
LUMO + 5	–1.071	–1.158	–0.915
LUMO + 4	–1.199	–1.243	–1.128
LUMO + 3	–1.393	–1.439	–1.275
LUMO + 2	–1.770	–1.880	–1.607
LUMO + 1	–1.910	–1.921	–1.852
LUMO	–2.020	–2.054	–1.995
HOMO	–6.329	–6.410	–6.441
HOMO – 1	–6.439	–6.560	–6.604
HOMO – 2	–6.601	–6.689	–6.742
HOMO – 3	–6.732	–6.795	–6.778
HOMO – 4	–6.784	–6.915	–6.843
HOMO – 5	–6.830	–7.138	–6.978
HOMO – 6	–6.932	–7.403	–7.149
HOMO – 7	–6.976	–7.602	–7.347
HOMO – 8	–7.062	–8.127	–7.554
HOMO – 9	–7.174	–8.207	–7.609
HOMO – 10	–7.567	–8.214	–7.732
HOMO–LUMO gap	4.309	4.356	4.446

Table S5 Computed excitation energies and oscillator strengths for the $S_0 \rightarrow S_n$ (n = 1–40) transitions of the complexes **1a**–**3b** in vacuum. Except for S_1 transitions, only calculated excitations with $f \geq 0.02$ are listed. Also, only single excitation configurations with the two highest contributions are reported, together with the corresponding nature of the involved orbitals.

	1a	**2a**	**3a**
λ [nm, eV] (*f*) expansion coefficient	427, 2.902 (0.001) (S_1) –0.413 HOMO → LUMO 0.569 HOMO → LUMO+1	415, 2.990 (0.002) (S_1) 0.702 HOMO → LUMO	374, 3.317 (0.02) (S_1) 0.688 HOMO → LUMO
	344, 3.603 (0.024) 0.667 HOMO–1 → LUMO+2	379, 3.269 (0.030) 0.686 HOMO → LUMO+1	326, 3.804 (0.043) 0.547 HOMO–2 → LUMO 0.332 HOMO–1 → LUMO
	319, 3.884 (0.028) 0.323 HOMO–5 → LUMO 0.295 HOMO–8 → LUMO	329, 3.765 (0.051) 0.611 HOMO–1 → LUMO+1 –0.185 HOMO–4 → LUMO	309, 4.011 (0.032) 0.485 HOMO–2 → LUMO+1 –0.276 HOMO → LUMO+3
	308, 4.022 (0.028) –0.299 HOMO–2 → LUMO+3 –0.299 HOMO–8 → LUMO+1	318, 3.901 (0.021) 0.555 HOMO → LUMO+4 0.286 HOMO–3 → LUMO+1	300, 4.135 (0.036) 0.476 HOMO–4 → LUMO 0.326 HOMO–3 → LUMO
	306, 4.056 (0.047) 0.341 HOMO–6 → LUMO+1 –0.319 HOMO–7 → LUMO+1	308, 4.030 (0.078) –0.426 HOMO–2 → LUMO+1 0.351 HOMO–3 → LUMO+1	298, 4.159 (0.020) 0.447 HOMO–5 →LUMO –0.248 HOMO–3 → LUMO
	304, 4.083 (0.022) 0.336 HOMO–7 → LUMO+1 0.332 HOMO–10 → LUMO	305, 4.067 (0.027) 0.454 HOMO–2 → LUMO+2 0.275 HOMO–6 → LUMO	296, 4.196 (0.077) 0.327 HOMO–3 → LUMO+1 0.309 HOMO → LUMO+4
	299, 4.147 (0.029) –0.512 HOMO–11 → LUMO 0.227 HOMO–10 → LUMO	289, 4.295 (0.033) 0.394 HOMO–4 → LUMO+2 0.358 HOMO–3 → LUMO+3	285, 4.346 (0.052) 0.459 HOMO → LUMO+4 0.345 HOMO–4 → LUMO+1
	298, 4.161 (0.073) –0.533 HOMO–4 → LUMO+2 0.285 HOMO–5 → LUMO+2	286, 4.330 (0.041) 0.449 HOMO–6 → LUMO+1 0.233 HOMO–1 → LUMO+4	279, 4.445 (0.032) 0.369 HOMO → LUMO+5 0.273 HOMO–1 →LUMO+3
	296, 4.186 (0.020) –0.350 HOMO–10 → LUMO+1 –0.229 HOMO–7 → LUMO+1	280, 4.431 (0.034) –0.365 HOMO–6 → LUMO+2 0.319 HOMO–1 → LUMO+4	272, 4.550 (0.135) 0.338 HOMO–1 → LUMO+3 0.336 HOMO–2 → LUMO+3
		279, 4.448 (0.043)	266, 4.654 (0.028)

0.436 HOMO–6 → LUMO+2	0.493 HOMO–3 → LUMO+2
0.338 HOMO–1 → LUMO+4	–0.343 HOMO–1 → LUMO+2
273, 4.536 (0.021)	265, 4.680 (0.020)
0.395 HOMO–2 → LUMO+4	0.312 HOMO–8 → LUMO
0.373 HOMO–3 → LUMO+4	–0.291 HOMO–1 → LUMO+4
271, 4.572 (0.059)	262, 4.734 (0.021)
–0.326 HOMO–7 → LUMO	0.374 HOMO–2 → LUMO+4
–0.318 HOMO → LUMO+6	–0.329 HOMO–4 → LUMO+2
270, 4.586 (0.032)	259, 4.783 (0.066)
0.435 HOMO–1 → LUMO+5	0.421 HOMO–4 → LUMO+2
–0.274 HOMO → LUMO+6	0.257 HOMO–4 → LUMO+3
267, 4.638 (0.066)	256, 4.825 (0.155)
0.499 HOMO–6 → LUMO+3	0.361 HOMO–5 → LUMO+2
–0.277 HOMO–7 → LUMO	0.343 HOMO–6 → LUMO+2
266, 4.662 (0.158)	256, 4.836 (0.025)
0.434 HOMO–3 → LUMO+4	0.382 HOMO–5 → LUMO+3
–0.326 HOMO–2 → LUMO+4	–0.309 HOMO–9 → LUMO
261, 4.752 (0.049)	250, 4.950 (0.070)
0.420 HOMO → LUMO+7	0.323 HOMO–3 → LUMO+4
0.308 HOMO → LUMO+10	0.273 HOMO → LUMO+7
257, 4.816 (0.053)	
–0.346 HOMO–1 → LUMO+6	
0.284 HOMO–2 → LUMO+5	

to be continued

	1b	2b	3b
λ [nm, eV] (*f*) expansion coefficient	437, 2.835 (0.001) (S_1) 0.591 HOMO → LUMO+1 –0.382 HOMO → LUMO	368, 3.374 (0.008) (S_1) 0.515 HOMO–1 → LUMO 0.460 HOMO → LUMO	347, 3.577 (0.009) (S_1) 0.657 HOMO → LUMO 0.137 HOMO–6 → LUMO
	314, 3.945 (0.063) –0.501 HOMO–8 → LUMO –0.315 HOMO–10 → LUMO	345, 3.593 (0.021) 0.657 HOMO–1 → LUMO+1 0.174 HOMO–3 → LUMO+1	318, 3.901 (0.038) 0.383 HOMO–2 → LUMO –0.352 HOMO–5 → LUMO
	302, 4.107 (0.025) –0.393 HOMO–6 → LUMO+1 –0.373 HOMO–6 → LUMO	333, 3.725 (0.025) 0.601 HOMO–2 → LUMO 0.267 HOMO–3 → LUMO	312, 3.974 (0.026) 0.514 HOMO–1 → LUMO+1 0.282 HOMO–4 → LUMO+1
	298, 4.164 (0.025) –0.329 HOMO–8 → LUMO+1 0.298 HOMO–9 → LUMO+1	331, 3.748 (0.033) 0.447 HOMO–1 → LUMO+2 –0.393 HOMO → LUMO+1	298, 4.167 (0.054) 0.360 HOMO–3 → LUMO 0.322 HOMO–5 → LUMO
	294, 4.212 (0.032) 0.372 HOMO–4 → LUMO+3 0.316 HOMO–10 → LUMO	317, 3.910 (0.022) 0.596 HOMO–4 → LUMO 0.278 HOMO–3 → LUMO	295, 4.198 (0.024) 0.452 HOMO–6 → LUMO 0.257 HOMO–2 → LUMO+3
	289, 4.284 (0.090) 0.557 HOMO–5 → LUMO+2 –0.250 HOMO–4 → LUMO+2	308, 4.031 (0.022) –0.568 HOMO–5 → LUMO 0.236 HOMO–2 → LUMO+1	291, 4.266 (0.056) 0.473 HOMO–4 → LUMO+1 –0.247 HOMO–1 → LUMO+1
	286, 4.331 (0.040) –0.493 HOMO–10 → LUMO+1 0.235 HOMO–8 → LUMO+1	305, 4.061 (0.087) 0.415 HOMO–3 → LUMO+1 –0.390 HOMO–2 → LUMO +1	281, 4.410 (0.067) 0.560 HOMO → LUMO+2 –0.201 HOMO–4 → LUMO+2
		293, 4.226 (0.049) 0.588 HOMO–3 → LUMO+2 –0.252 HOMO–4 → LUMO+2	272, 4.550 (0.036) 0.391 HOMO–1 → LUMO+3 0.377 HOMO–1 → LUMO+2
		287, 4.322 (0.064) 0.475 HOMO–4 → LUMO+2 0.222 HOMO–3 → LUMO+2	271, 4.575 (0.051) 0.341 HOMO–1 → LUMO+2 –0.278 HOMO–5 → LUMO+2
		284, 4.371 (0.023) 0.418 HOMO–2 → LUMO+3 0.376 HOMO–4 → LUMO+3	269, 4.615 (0.059) –0.369 HOMO–2 → LUMO+2 0.314 HOMO–5 → LUMO+2

278, 4.456 (0.082)
–0.338 HOMO → LUMO+4
–0.323 HOMO–5 → LUMO+1

272, 4.559 (0.033)
0.418 HOMO–5 →LUMO+3
0.378 HOMO–4 → LUMO+3

268, 4.631 (0.037)
–0.364 HOMO–5 → LUMO+3
–0.278 HOMO–2 → LUMO+4

266, 4.657 (0.084)
–0.410 HOMO–3 → LUMO+4
–0.278 HOMO–6 → LUMO

263, 4.711 (0.176)
–0.441 HOMO–2 → LUMO+4
0.360 HOMO–3 → LUMO+4

257, 4.826 (0.026)
–0.225 HOMO–5 → LUMO+10
–0.213 HOMO–1 → LUMO+6

255, 4.863 (0.023)
0.343 HOMO–6 → LUMO+2
0.327 HOMO–7 → LUMO+2

253, 4.909 (0.046)
0.270 HOMO–8 → LUMO
–0.239 HOMO–4 → LUMO+10

267, 4.642 (0.043)
0.573 HOMO → LUMO+4
0.169 HOMO–1 → LUMO+4

260, 4.769 (0.024)
–0.394 HOMO–3 → LUMO+3
0.311 HOMO–4 → LUMO+2

259, 4.792 (0.080)
0.387 HOMO–1 → LUMO+4
0.300 HOMO–10 → LUMO

258, 4.808 (0.029)
0.470 HOMO–4 → LUMO+3
–0.252 HOMO–1 → LUMO+3

256, 4.845 (0.055)
0.252 HOMO–2 → LUMO+4
–0.252 HOMO–5 → LUMO+4

255, 4.857 (0.021)
0.275 HOMO–2 → LUMO+4
0.270 HOMO–3 → LUMO+2

Table S6. Computed excitation energies and oscillator strengths for the $S_0 \rightarrow S_n$ (n = 1–40) transitions of the complexes **1a**–**3b** in dichloromethane. Except for S_1 transitions, only calculated excitations with $f \geq 0.04$ are listed. Also, only single excitation configurations with the two highest contributions are reported, together with the corresponding nature of the involved orbitals.

	1a	**2a**	**3a**
λ [nm, eV] (f) expansion coefficient	377, 3.287 (0.028) (S_1) 0.631 HOMO → LUMO –0.288 HOMO → LUMO+1	384, 3.227 (0.009) (S_1) 0.699 HOMO → LUMO	366, 3.388 (0.039) (S_1) 0.690 HOMO → LUMO
	320, 3.874 (0.045) 0.399 HOMO–3 → LUMO 0.308 HOMO–4 → LUMO	367, 3.377 (0.057) 0.681 HOMO → LUMO+1 –0.122 HOMO → LUMO+2	321, 3.859 (0.043) 0.463 HOMO–2 → LUMO 0.369 HOMO–1 → LUMO
	315, 3.942 (0.041) 0.374 HOMO–2 → LUMO –0.372 HOMO–3 → LUMO+1	325, 3.816 (0.047) 0.470 HOMO–2 → LUMO –0.407 HOMO–1 → LUMO	314, 3.948 (0.058) 0.523 HOMO–1 → LUMO+1 0.308 HOMO–3 → LUMO+1
	303, 4.089 (0.047) –0.323 HOMO–5 → LUMO+1 0.250 HOMO–4 → LUMO+1	313, 3.955 (0.060) 0.445 HOMO–1 → LUMO+1 –0.246 HOMO–4 → LUMO	307, 4.038 (0.044) 0.574 HOMO–2 → LUMO+1 0.226 HOMO–1 → LUMO
	301, 4.115 (0.095) 0.428 HOMO–1 → LUMO+2 0.418 HOMO → LUMO+4	304, 4.075 (0.042) 0.385 HOMO–2 → LUMO+2 0.355 HOMO → LUMO+4	296, 4.192 (0.044) 0.595 HOMO–1 → LUMO+2 0.284 HOMO–3 → LUMO+2
	298, 4.159 (0.064) 0.391 HOMO–5 → LUMO 0.353 HOMO → LUMO+4	296, 4.192 (0.076) 0.390 HOMO–3 → LUMO+2 –0.278 HOMO-4 → LUMO+2	291, 4.255 (0.201) 0.384 HOMO → LUMO+3 –0.346 HOMO–4 → LUMO
	291, 4.254 (0.057) 0.426 HOMO–5 → LUMO+1 0.260 HOMO–2 → LUMO+2	294, 4.213 (0.060) 0.512 HOMO–3 → LUMO+1 –0.259 HOMO → LUMO+5	290, 4.272 (0.055) 0.522 HOMO–4 → LUMO+1 –0.260 HOMO → LUMO+4
	286, 4.334 (0.069) 0.317 HOMO–4 → LUMO+2 –0.316 HOMO → LUMO+5	289, 4.288 (0.128) 0.450 HOMO–4 → LUMO+2 –0.306 HOMO → LUMO+5	285, 4.343 (0.050) 0.519 HOMO → LUMO+4 0.283 HOMO–4 → LUMO+1
	277, 4.476 (0.045) 0.401 HOMO–6 → LUMO+1 –0.312 HOMO–8 → LUMO+1	274, 4.517 (0.090) 0.436 HOMO–6 → LUMO –0.400 HOMO–2 → LUMO+3	268, 4.625 (0.119) 0.421 HOMO–2 → LUMO+3 0.351 HOMO–1 → LUMO+3
	270, 4.597 (0.085)	269, 4.606 (0.077)	263, 4.712 (0.107)

0.406 HOMO–9 → LUMO 0.288 HOMO–2 → LUMO+3	0.458 HOMO–1 → LUMO+4 –0.227 HOMO–4 → LUMO+3	0.466 HOMO–1 → LUMO+4 0.329 HOMO–6 → LUMO+1
263, 4.713 (0.083) 0.462 HOMO–10 → LUMO 0.275 HOMO–10 → LUMO+1	264, 4.679 (0.050) 0.329 HOMO–4 → LUMO+3 0.274 HOMO–3 → LUMO+3	262, 4.727 (0.047) 0.591 HOMO–6 → LUMO+1 –0.227 HOMO–2 → LUMO+4
261, 4.752 (0.106) –0.396 HOMO–3 → LUMO+4 0.235 HOMO–5 → LUMO+3	262, 4.738 (0.076) 0.459 HOMO–6 → LUMO+2 0.286 HOMO–6 → LUMO+1	257, 4.816 (0.070) –0.369 HOMO–6 → LUMO+2 0.327 HOMO–7 → LUMO
	259, 4.793 (0.141) 0.372 HOMO–7 → LUMO 0.272 HOMO–1 → LUMO+4	254, 4.886 (0.071) 0.506 HOMO–7 → LUMO 0.307 HOMO–6 → LUMO+2
	257, 4.826 (0.116) 0.347 HOMO–2 → LUMO+5 0.272 HOMO–7 → LUMO	253, 4.908 (0.080) 0.445 HOMO–4 → LUMO+3 –0.346 HOMO → LUMO+7
	254, 4.885 (0.210) –0.253 HOMO–1 → LUMO+5 0.222 HOMO–2 → LUMO+5	251, 4.933 (0.168) 0.418 HOMO–6 → LUMO+2 0.380 HOMO–7 → LUMO+2
	251, 4.938 (0.129) 0.269 HOMO → LUMO+7 –0.249 HOMO–4 → LUMO+5	251, 4.945 (0.055) 0.537 HOMO–3 → LUMO+4 –0.332 HOMO–1 → LUMO+4

to be continued

	1b	**2b**	**3b**
λ [nm, eV] (*f*) expansion coefficient	346, 3.585 (0.022) (S_1) 0.551 HOMO → LUMO HOMO–1 → LUMO	341, 3.635 (0.025) (S_1) 0.653 HOMO → LUMO –0.188 HOMO → LUMO+1	339, 3.657 (0.020) (S_1) 0.665 HOMO → LUMO 0.164 HOMO–4 → LUMO
	309, 4.010 (0.043) 0.366 HOMO–5 → LUMO –0.238 HOMO → LUMO	326, 3.806 (0.055) 0.590 HOMO–1 → LUMO 0.336 HOMO–2 → LUMO	308, 4.027 (0.099) 0.470 HOMO–2 → LUMO –0.412 HOMO–1 → LUMO+1
	294, 4.212 (0.060) 0.357 HOMO–7 → LUMO –0.280 HOMO–3 → LUMO	313, 3.966 (0.052) 0.456 HOMO–2 → LUMO 0.358 HOMO–4 → LUMO	297, 4.176 (0.056) 0.493 HOMO–3 → LUMO –0.349 HOMO–1 → LUMO
	293, 4.224 (0.059) 0.401 HOMO–2 → LUMO+2 –0.297 HOMO–5 → LUMO+1	307, 4.035 (0.053) 0.450 HOMO–1 → LUMO+1 –0.383 HOMO–1 → LUMO+2	292, 4.248 (0.112) 0.617 HOMO–4 → LUMO –0.195 HOMO → LUMO+3
	291, 4.256 (0.099) 0.400 HOMO–4 → LUMO+1 –0.259 HOMO–2 → LUMO+2	292, 4.253 (0.088) 0.384 HOMO–3 → LUMO+1 0.250 HOMO–2 → LUMO+1	289, 4.294 (0.073) 0.531 HOMO–3 → LUMO+1 –0.350 HOMO–1 → LUMO+1
	283, 4.374 (0.119) –0.341 HOMO–6 → LUMO+1 0.287 HOMO–7 → LUMO+1	288, 4.302 (0.065) 0.373 HOMO–4 → LUMO+1 –0.258 HOMO → LUMO+3	284, 4.361 (0.104) 0.542 HOMO–1 → LUMO+2 0.295 HOMO–3 → LUMO+2
	283, 4.388 (0.054) -0.362 HOMO-7 → LUMO+1 0.307 HOMO → LUMO+3	284, 4.368 (0.070) 0.558 HOMO → LUMO+3 0.219 HOMO–4 → LUMO+2	273, 4.539 (0.158) 0.603 HOMO → LUMO+3 –0.181 HOMO–3 → LUMO+1
	280, 4.422 (0.050) –0.303 HOMO–6 → LUMO –0.291 HOMO–3 → LUMO+2	277, 4.476 (0.093) 0.610 HOMO–5 → LUMO 0.189 HOMO–2 → LUMO+3	266, 4.667 (0.047) 0.593 HOMO → LUMO+4 0.140 HOMO → LUMO+5
	279, 4.452 (0.057) 0.375 HOMO–3 → LUMO+2 0.320 HOMO–6 → LUMO+1	274, 4.524 (0.124) 0.463 HOMO → LUMO+4 0.394 HOMO–1 → LUMO+3	263, 4.707 (0.044) 0.495 HOMO–1 → LUMO+3 0.262 HOMO–3 → LUMO+3
	261, 4.743 (0.056) 0.471 HOMO–1 → LUMO+1 –0.233 HOMO–3 → LUMO+3	262, 4.738 (0.052) 0.473 HOMO–6 → LUMO 0.355 HOMO–2 → LUMO+3	258, 4.808 (0.055) 0.487 HOMO–1 → LUMO+4 0.257 HOMO–3 → LUMO+4

259, 4.792 (0.052) –0.266 HOMO–1 → LUMO+4 0.234 HOMO–10 → LUMO	260, 4.774 (0.153) 0.540 HOMO–1 → LUMO+5 0.202 HOMO–2 → LUMO+5	258, 4.811 (0.071) –0.402 HOMO–6 → LUMO+2 –0.372 HOMO–5 → LUMO+2
	254, 4.888 (0.140) 0.310 HOMO–4 → LUMO+3 0.237 HOMO–6 → LUMO	256, 4.848 (0.043) –0.485 HOMO–9 → LUMO 0.257 HOMO–2 → LUMO+4
	251, 4.937 (0.051) –0.251 HOMO → LUMO+6 0.248 HOMO–4 → LUMO+10	253, 4.898 (0.083) –0.319 HOMO–5 → LUMO+2 –0.258 HOMO–7 → LUMO
	247, 5.026 (0.080) –0.274 HOMO–7 → LUMO+2 –0.243 HOMO–6 → LUMO+1	251, 4.937 (0.052) –0.323 HOMO → LUMO+6 0.275 HOMO–3 → LUMO+3
		250, 4.961 (0.061) 0.366 HOMO–2 → LUMO+4 –0.251 HOMO–7 → LUMO

Table S7. Computed excitation energies of the three lowest $S_0 \rightarrow T_n$ transitions (where n = 1–3) for the complexes **1a**–**3b** in vacuum. Also, only single excitation configurations with the highest contributions are reported, together with the nature of the involved orbitals.

	1a	**2a**	**3a**
λ [nm, eV] (f) [a]	442, 2.803 (0.000) (T_1)	438, 2.829 (0.000) (T_1)	433, 2.864 (0.000) (T_1)
expansion coefficient	0.449 HOMO–1 → LUMO	0.458 HOMO → LUMO+1	0.472 HOMO → LUMO
	0.334 HOMO–6 → LUMO	0.262 HOMO–2 → LUMO+1	0.297 HOMO–1 → LUMO
	432, 2.872 (0.000) (T_2)	426, 2.908 (0.000) (T_2)	426, 2.913 (0.000) (T_2)
	0.568 HOMO → LUMO+1	0.353 HOMO → LUMO+2	0.453 HOMO → LUMO+1
	–0.382 HOMO → LUMO	–0.289 HOMO–2 → LUMO+2	–0.312 HOMO–1 → LUMO+1
	426, 2.908 (0.000) (T_3)	417, 2.974 (0.000) (T_3)	374, 3.311 (0.000) (T_3)
	0.491 HOMO–1 → LUMO+2	0.649 HOMO → LUMO	0.458 HOMO → LUMO
	–0.309 HOMO–5 → LUMO+2	–0.136 HOMO → LUMO+1	–0.313 HOMO–2 → LUMO

	1b	**2b**	**3b**
λ [nm, eV] (f) [a]	441, 2.809 (0.000) (T_1)	418, 2.969 (0.000) (T_1)	415, 2.984 (0.000) (T_1)
expansion coefficient	0.597 HOMO → LUMO+1	0.420 HOMO–1 → LUMO+1	0.388 HOMO → LUMO
	–0.350 HOMO → LUMO	0.419 HOMO–2 → LUMO+1	0.306 HOMO–3 → LUMO
	419, 2.958 (0.000) (T_2)	410, 3.021 (0.000) (T_2)	411, 3.013 (0.000) (T_2)
	–0.370 HOMO–8 → LUMO	0.387 HOMO–1 → LUMO+2	0.490 HOMO → LUMO+1
	0.319 HOMO–5 → LUMO	–0.319 HOMO–2 → LUMO+2	–0.237 HOMO–1 → LUMO+1
	417, 2.974 (0.000) (T_3)	400, 3.101 (0.000) (T_3)	350, 3.542 (0.000) (T_3)
	0.507 HOMO → LUMO	0.517 HOMO → LUMO	0.363 HOMO–4 → LUMO
	0.287 HOMO → LUMO+1	–0.277 HOMO–6 → LUMO	–0.244 HOMO → LUMO

[a] TD-DFT calculations performed with Gaussian09 neglect intersystem crossing processes, which mix states of the singlet and triplet manifolds. For this reason, the computed oscillator strengths for triplet excitation transitions are equal to zero.

Table S8. Computed excitation energies of the three lowest $S_0 \rightarrow T_n$ transitions (where n = 1–3) for the complexes **1a**–**3b** in dichloromethane. Also, only single excitation configurations with the highest contributions are reported, together with the nature of the involved orbitals.

	1a	**2a**	**3a**
λ [nm, eV]	432, 2.867 (0.000) (T_1)	430, 2.881 (0.000) (T_1)	429, 2.891 (0.000) (T_1)
(f) [a]	0.351 HOMO → LUMO+1	0.443 HOMO → LUMO+1	0.478 HOMO → LUMO
expansion coefficient	–0.331 HOMO → LUMO	0.292 HOMO–1 → LUMO+1	0.280 HOMO–1 → LUMO+1
	424, 2.922 (0.000) (T_2)	425, 2.918 (0.000) (T_2)	424, 2.924 (0.000) (T_2)
	0.459 HOMO → LUMO+2	0.438 HOMO → LUMO+2	0.431 HOMO → LUMO+1
	0.324 HOMO–1 → LUMO+2	0.294 HOMO–2 → LUMO+2	0.349 HOMO–1 → LUMO
	389, 3.191 (0.000) (T_3)	386, 3.209 (0.000) (T_3)	366, 3.391 (0.000) (T_3)
	0.332 HOMO → LUMO	0.630 HOMO → LUMO	0.443 HOMO → LUMO
	0.256 HOMO → LUMO+1	0.116 HOMO–6 → LUMO	–0.331 HOMO–2 → LUMO

	1b	**2b**	**3b**
λ [nm, eV]	413, 2.999 (0.000) (T_1)	412, 3.009 (0.000) (T_1)	412, 3.006 (0.000) (T_1)
(f) [a]	0.339 HOMO–2 → LUMO	0.358 HOMO → LUMO+1	0.440 HOMO → LUMO
expansion coefficient	–0.270 HOMO → LUMO	0.293 HOMO–1 → LUMO+1	0.299 HOMO–1 → LUMO
	410, 3.022 (0.000) (T_2)	409, 3.033 (0.000) (T_2)	410, 3.024 (0.000) (T_2)
	0.447 HOMO → LUMO+2	0.380 HOMO → LUMO+2	0.442 HOMO → LUMO+1
	0.265 HOMO–2 → LUMO+2	0.265 HOMO–2 LUMO+2	–0.335 HOMO–1 → LUMO
	384, 3.229 (0.000) (T_3)	380, 3.263 (0.000) (T_3)	345, 3.593 (0.000) (T_3)
	–0.326 HOMO–3 → LUMO+1	0.312 HOMO–2 → LUMO	0.344 HOMO–3 → LUMO
	0.238 HOMO → LUMO+1	–0.304 HOMO–5 → LUMO	0.293 HOMO–2 → LUMO

[a] TD-DFT calculations performed with Gaussian09 neglect intersystem crossing processes, which mix states of the singlet and triplet manifolds. For this reason, the computed oscillator strengths for triplet excitation transitions are equal to zero.

Table S9. Computed excitation energies and oscillator strengths for the $S_0 \rightarrow S_n$ (n = 1–40) transitions of the complexes **1a** in ethanol and *N*,*N*'-dimethylformamide. Except for S_1 transitions, only calculated excitations with $f \geq 0.04$ are listed.

	ethanol	*N,N'-dimethylformamide*
λ [nm, eV] (*f*)	374, 3.315 (0.027) (S_1)	373, 3.319 (0.029) (S_1)
expansion coefficient	318, 3.893 (0.046)	318, 3.897 (0.051)
	301, 4.113 (0.122)	301, 4.113 (0.113)
	296, 4.185 (0.078)	296, 4.187 (0.085)
	294, 4.216 (0.041)	294, 4.215 (0.043)
	290, 4.288 (0.045)	290, 4.277 (0.062)
	289, 4.288 (0.049)	288, 4.299 (0.064)
	287, 4.321 (0.055)	283, 4.379 (0.056)
	284, 4.365 (0.048)	280, 4.435 (0.058)
	280, 4.433 (0.051)	269, 4.602 (0.111)
	270, 4.597 (0.099)	260, 4.772 (0.208)
	260, 4.770 (0.207)	257, 4.817 (0.047)
	258, 4.812 (0.044)	

Table S10. Computed excitation energies of the three lowest $S_0 \rightarrow T_n$ transitions (where n = 1–3) for the complexes **1a** in ethanol and *N*,*N*'-dimethylformamide.

	ethanol	*N,N'-dimethylformamide*
λ [nm, eV] (*f*) [a]	431, 2.874 (0.000) (T_1)	431, 2.876 (0.000) (T_1)
expansion coefficient	424, 2.923 (0.000) (T_2)	424, 2.924 (0.000) (T_2)
	388, 3.199 (0.000) (T_3)	387, 3.201 (0.000) (T_3)

[a] TD-DFT calculations performed with Gaussian09 neglect intersystem crossing processes, which mix states of the singlet and triplet manifolds. For this reason, the computed oscillator strengths for triplet excitation transitions are equal to zero.

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