Heteroleptic Platinum(II) Complexes of 8-Quinolinolates Bearing Electron Withdrawing Groups in 5 Position

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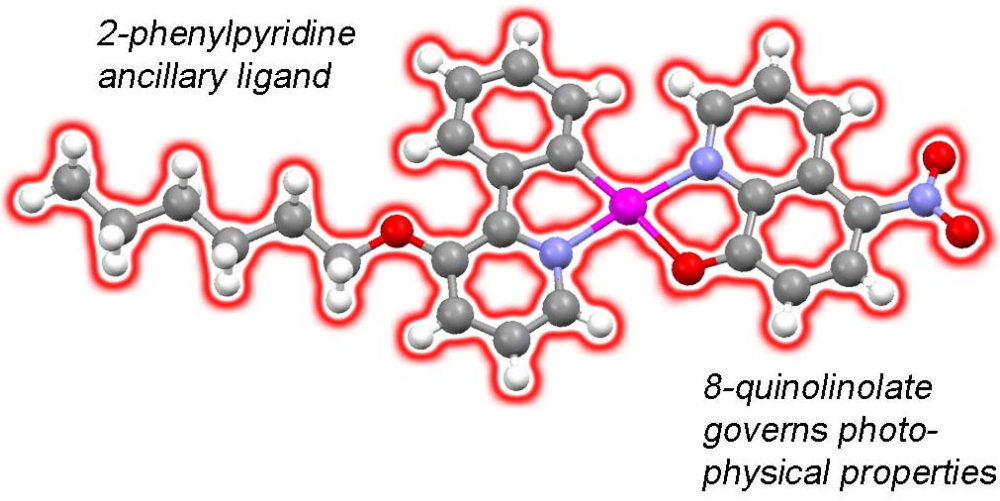
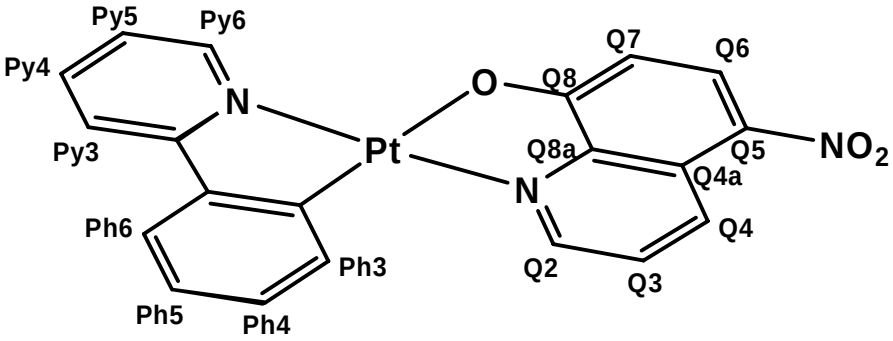
Electronic Supplementary Information



Labelling Mode – Example

κ^2(N,C^2)-(2-phenylpyridine)-κ^2(N,O)-(5-nitro-8-quinolinolato)platinum(II) (4a)



Synthesis

Synthesis of κ^2(N,C^2)-(2-phenylpyridine)-κ^2(N,O)-(5-formyl-8-quinolinolato) platinum(II) (4b) was prepared similarly to **4a**, using **1** (102.4 mg, 0.190 mmol), **3b** (48.3 mg, 0.279 mmol) and K_2CO_3 (160.9 mg, 1.164 mmol) as the starting materials. Purification was accomplished by washing the orange residue with MeOH. The precipitate was filtered off, dried, suspended in $CHCl_3$ and filtered over Na_2SO_4/Celite. The orange residue was recrystallized from $CHCl_3$/EtOH. Yield: 42.3 mg (43 %) orange crystals, $R_f \approx 0.3$ in CH_2Cl_2. Anal. Calcd for $C_{21}H_{14}N_2O_2Pt$: C, 48.37; H, 2.71; N, 5.37. Found: C, 48.54; H, 2.66; N, 5.24. ^{1}H-NMR (δ, 20°C, DMSO-d_6, 500 MHz): 10.00 (s, 1H, CHO), 9.76 (d, 1H, $^3J_{HH}$ = *8.5 Hz,* Q^4), 9.28 (d, 1H, $^3J_{HH}$ = *3.7 Hz*, Q^2), 9.08 (d, 1H, $^3J_{HH}$ = *4.9 Hz,* Py^6), 8.07-7.98 (m, 3H, Q^6, Ph^6, Py^4), 7.85 (m, 1H, Q^3), 7.68 (d, 1H, $^3J_{HH}$ = *7.3 Hz,* Py^3), 7.52 (d, 1H, $^3J_{HH}$ = *7.1 Hz*, Ph^3), 7.40 (t, 1H, $^3J_{HH}$ = *6.1 Hz*, Py^5), 7.22 (t, 1H, $^3J_{HH}$ = *7.3 Hz*, Ph^4), 7.13 (t, 1H, $^3J_{HH}$ = *7.3 Hz*, Ph^5), 6.94 (d, 1H, $^3J_{HH}$ = *8.3 Hz*, Q^7). $^{13}C\{^1H\}$-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 190.6 (1C, CHO), 174.1 (1C, Q^8), 167.1 (1C, Ph^2), 149.5 (1C, Py^6), 148.3 (1C, Py^2), 147.0 (1C, Q^{8a}), 146.3 (1C, Q^2), 143.4 (1C, Ph^3), 139.2 (1C, Ph^6), 137.9, 137.8 (2C, Py^4, Ph^1), 131.9 (1C, Q^4), 130.5 (1C, Q^{4a}), 129.8 (1C, Q^6), 124.3, 124.2, 124.1 (3C, Q^3, Py^3, Ph^5), 122.0 (1C, Ph^4), 118.5 (1C, Py^5), 117.6 (1C, Q^5), 115.2 (1C, Q^7). IR (film on KBr-window cast from CH_2Cl_2-solution, cm^{-1}): 2921 (w), 2850 (w), 2714 (w), 2322 (w), 1661 (s), 1609 (m), 1588 (m), 1562 (s), 1505 (s), 1472 (s), 1426 (m), 1365 (m), 1341 (s), 1243 (s), 1209 (m), 1150 (m), 1109 (w), 1062 (w), 841 (w), 751 (m).

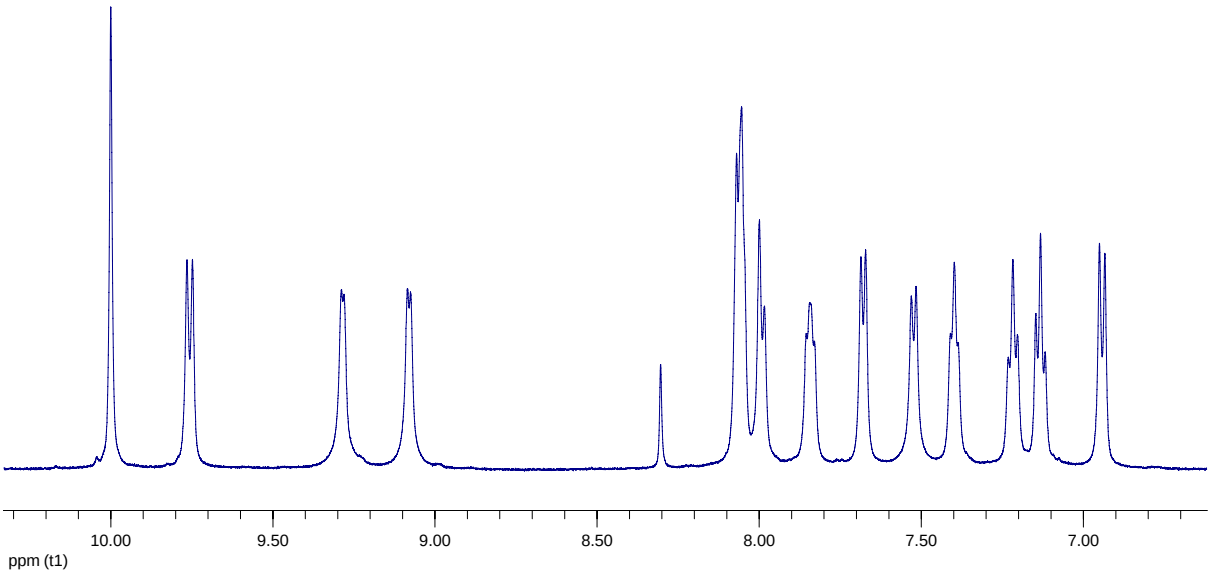


Figure S1. ^{1}H-NMR spectrum of **4b** in DMSO-d_6.

Synthesis of κ^2(N,C^2)-(3-hexyloxy-2-phenylpyridine)-κ^2(N,O)-(5-formyl-8-quinolinolato) platinum(II) (5b) was prepared similarly to **4a**, using **2** (100.0 mg, 0.135 mmol), **3b** (35.4 mg, 0.204 mmol) and K_2CO_3 (120.0 mg, 0.868 mmol) as the starting materials. Purification was accomplished by washing the orange residue with EtOH. The precipitate was filtered off, dried, suspended in $CHCl_3$ and filtered over Na_2SO_4/Celite. The orange residue was recrystallized from $CHCl_3$/MeOH. Yield: 27.0 mg (32 %) orange crystals, $R_f \approx 0.3$ in CH_2Cl_2. Anal. Calcd for $C_{27}H_{36}N_2O_3Pt$: C, 52.17; H, 4.22; N, 4.51. Found: C, 51.96; H, 4.34; N, 4.66. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 500 MHz): 10.00 (s, 1H, CHO), 9.97 (d, 1H, $^{3}J_{HH}$ = *8.5 Hz,* Q^4), 9.22 (d, 1H, $^{3}J_{HH}$ = *4.9 Hz,* Q^2), 9.04 (d, 1H, $^{3}J_{HH}$ = *5.6 Hz,* Py^6), 8.36 (d, 1H, $^{3}J_{HH}$ = *8.1 Hz*, Ph^6), 7.93 (d, 1H, $^{3}J_{HH}$ = *8.3 Hz*, Q^6), 7.65-7.62 (m, 1H, Q^3), 7.47 (d, 1H, $^{3}J_{HH}$ = *7.8 Hz,* Py^4), 7.38 (d, 1H, $^{3}J_{HH}$ = *8.3 Hz*, Ph^3), 7.26-7.23 (m, 1H, Py^5), 7.17-7.09 (m, 2H, Ph^4, Ph^5), 7.03 (d, 1H, $^{3}J_{HH}$ = *8.3 Hz*, Q^7), 4.16 (t, 2H, $^{3}J_{HH}$ = *6.3 Hz,* OHex^1), 1.99 (p, 2H, OHex^2), 1.60-1.56 (m, 4H, OHex^{3,4}), 1.40 (m, 2H, OHex^5), 0.94 (t, 3H, $^{3}J_{HH}$ = *6.8 Hz,* OHex^6). ^{13}C{^{1}H}-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 190.5 (1C, CHO), 174.0 (1C, Q^8), 156.3 (1C, Py^3), 153.2 (1C, Ph^2), 148.3 (1C, Py^6), 147.1, 146.9 (2C, Py^2, Q^{8a}), 143.3 (1C, Q^2), 141.5 (1C, Ph^3), 138.3 (1C, Ph^1), 137.4 (1C, Py^4), 131.4 (1C, Q^4), 130.4 (1C,

Q^{4a}), 128.70, 128.69 (2C, Ph^6, Q^6), 124.2, 123.8 (2C, Q^3, Ph^5), 121.62, 121.60 (2C, Ph^4, Py^5), 117.4 (1C, Q^5), 115.1 (1C, Q^7), 69.5 (1C, $OHex^1$), 31.6 (1C, $OHex^4$), 29.1 (1C, $OHex^2$), 26.0 (1C, $OHex^3$), 22.7 (1C, $OHex^5$), 14.2 (1C, $OHex^6$). IR (film on KBr-window cast from CH_2Cl_2-solution, cm^{-1}): 3094 (w), 3054 (w), 2924 (m), 2853 (m), 2712 (w), 1653 (s), 1590 (s), 1557 (s), 1506 (s), 1472 (m), 1425 (m), 1399 (w), 1366 (m), 1344 (s), 1308 (w), 1275 (m), 1245 (s), 1208 (s), 1148 (m), 1113 (w), 1081 (w), 1062 (m), 1024 (w), 837 (m), 781 (m), 726 (m).

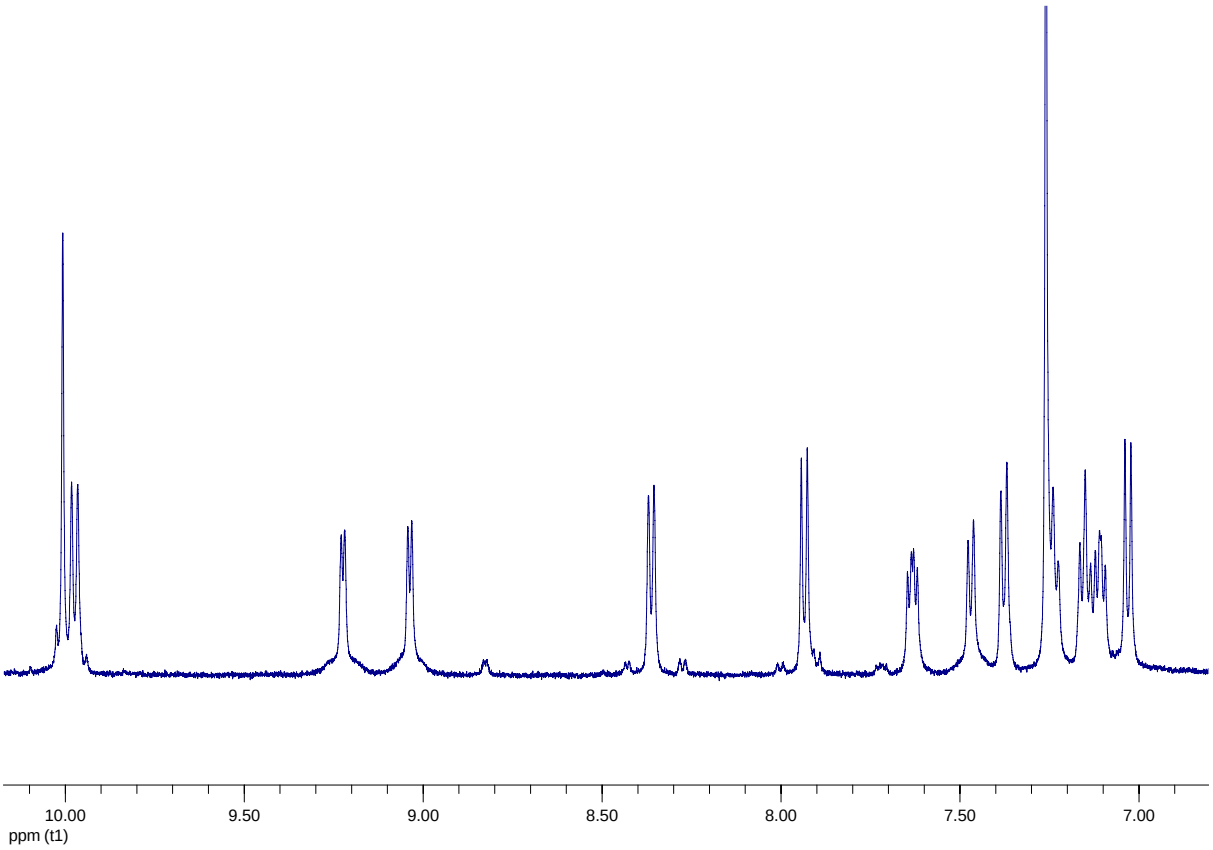


Figure S2. ^{1}H-NMR spectrum of **5b** in $CDCl_3$.

Synthesis of κ^2(N,C^2)-(2-phenylpyridine)-κ^2(N,O)-(5,7-dichloro-8-quinolinolato) platinum(II) (4c) was prepared similarly to **4a**, using **1** (100.9 mg, 0.187 mmol), **3c** (59.9 mg, 0.280 mmol) and K_2CO_3 (152.9 mg, 1.106 mmol) as the starting materials. Purification was accomplished by washing the orange residue with MeOH. The precipitate was filtered off and dried in vacuum. The dark red solid was then purified by column chromatography (silica, CH_2Cl_2 or acetone/ CH_2Cl_2) to give main orange or red fraction. The solvent was evaporated and Et_2O was added. Sonication precipitated the product which was filtered, washed with *n*-pentane and dried in vacuum. Yield: 20.55 mg (20 %) orange crystals, $R_f \approx 0.4$ in CH_2Cl_2. Anal. Calcd for

$C_{20}H_{12}Cl_2N_2OPt$: C, 42.72; H, 2.15; N, 4.98. Found: C, 42.76; H, 2.32; N, 5.11. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 500 MHz): 9.39 (d, 1H, $^3J_{HH}$ = *6.1 Hz,* Py^6), 9.29 (d, 1H, $^3J_{HH}$ = *5.1 Hz,* Q^2), 8.65 (d, 1H, $^3J_{HH}$ = *8.5 Hz,* Q^4), 7.86 (t, 1H, $^3J_{HH}$ = *7.8 Hz*, Q^3), 7.69 (s, 1H, Q^6), 7.66 (d, 1H, $^3J_{HH}$ = *7.8 Hz*, Ph^6), 7.56-7.51 (m, 3H, Py^4, Ph^{3,5}), 7.29 (m, 1H, Py^3), 7.22 (t, 1H, $^3J_{HH}$ = *7.0 Hz*, Ph^4), 7.17 (t, 1H, $^3J_{HH}$ = *7.0 Hz*, Py^5).

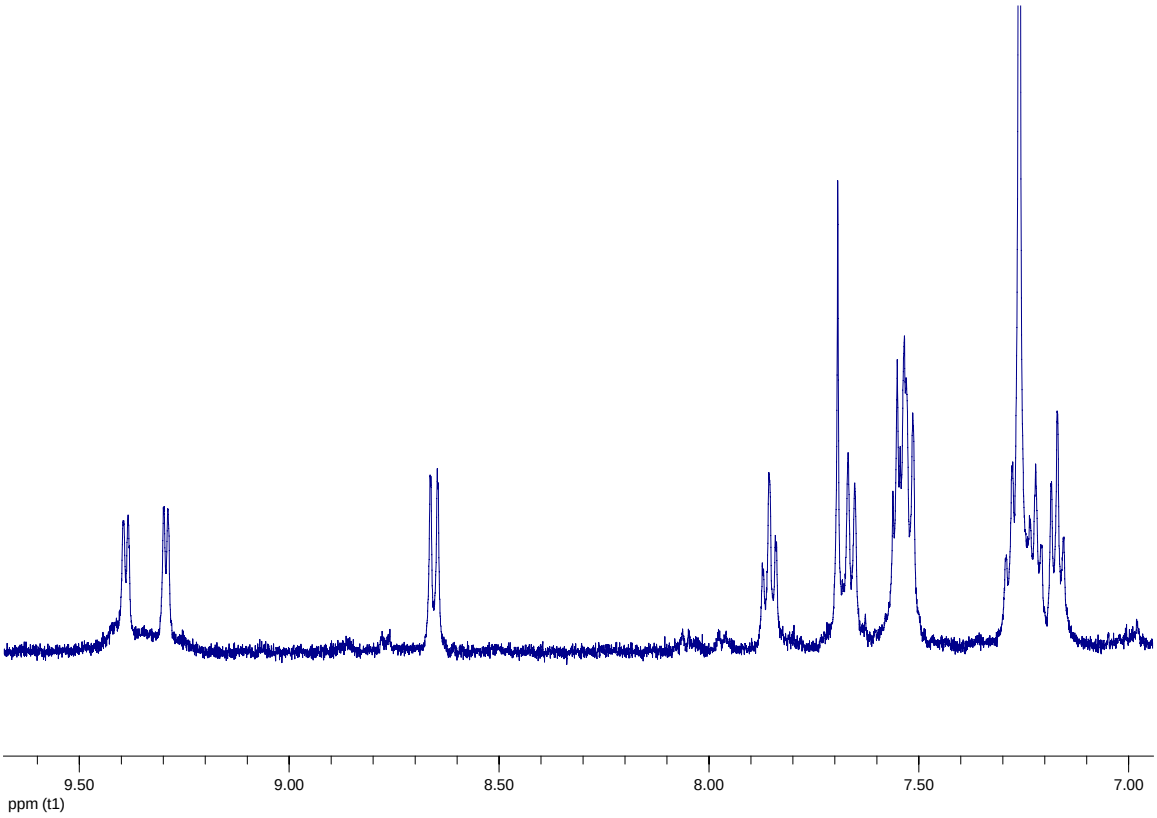


Figure S3. ^{1}H-NMR spectrum of **4c** in $CDCl_3$.

Table S1. Absorption and emission properties of **4c** at room temperature.

Complex	Abs, λ_{max}[a] λ [nm] (ε [10^{-3} cm^{-1} M^{-1}])	Emission λ_{max} [nm]	τ_{Air} [μs]	τ_{N_2} [μs]	Φ [%]
4c	261 (23.9), 363 (6.2), 477 (4.7)	-[b]	-[b]	-[b]	-[b]

[a] $CHCl_3$ solutions
[b] no emission observed in CH_2Cl_2 and in $CHCl_3$ solution

Synthesis of κ^2(N,C^2)-(2-phenylpyridine)-κ^2(N,O)-(8-quinolinolato) platinum(II) (4d) was prepared similarly to **4a**, using **1** (101.5 mg, 0.188 mmol), **3d** (42.6 mg, 0.293 mmol) and K_2CO_3 (130.3 mg, 1.106 mmol) as the starting materials.

Purification was accomplished by washing the orange-red residue with MeOH and acetone. The precipitate was filtered off and dried in vacuum. Yield: 52.2 mg (56 %) red crystals, $R_f \approx 0.8$ in acetone. Anal. Calcd for $C_{20}H_{14}N_2OPt$: C, 48.68; H, 2.86; N, 5.68. Found: C, 48.72; H, 3.01; N, 5.72. ^{1}H-NMR (δ, 20°C, $CDCl_3$, 500 MHz): 9.32 (d, 1H, $^3J_{HH}$ = *4.1 Hz,* Q^2), 9.29 (d, 1H, $^3J_{HH}$ = *5.6 Hz,* Py^6), 8.62 (d, 1H, $^3J_{HH}$ = *8.3 Hz,* Q^4), 8.10 (m, 2H, Q^{3,6}), 7.78 (d, 1H, $^3J_{HH}$ = *7.3 Hz*, Ph^6), 7.71 (t, 1H, Py^4), 7.67 (d, 1H, $^3J_{HH}$ = *7.6 Hz*, Py^3), 7.52-7.46 (m, 2H, Ph^{3,5}), 7.27 (t, 1H, $^3J_{HH}$ = *7.6 Hz*, Ph^4), 7.17 (t, 1H, $^3J_{HH}$ = *7.6 Hz*, Py^5), 7.04 (d, 1H, $^3J_{HH}$ = *8.1 Hz*, Q^5), 6.97 (d, 1H, $^3J_{HH}$ = *7.6 Hz*, Q^7). ^{13}C{^{1}H}-NMR (δ, 20°C, $CDCl_3$, 125 MHz): 166.6, 166.4 (2C, Q^8, Ph^2), 148.7, 148.4 (2C, Py^6, Py^2), 146.1 (1C, Q^{8a}), 145.8 (1C, Q^2), 140.1 (1C, Ph^3), 139.3, 139.1 (2C, Ph^6, Ph^1), 131.6, 131.2 (2C, Q^4, Py^4), 130.3 (1C, Q^{4a}), 129.4 (1C, Q^6), 124.4 (1C, Q^3), 123.3 (1C, Py^3), 122.6, 122.1 (2C, Ph^4, Ph^5), 119.1 (1C, Py^5), 115.1 (1C, Q^5), 111.5 (1C, Q^7). IR (film on KBr-window cast from CH_2Cl_2-solution, cm^{-1}): 3044 (w), 2917 (w), 2848 (w), 1608 (m), 1575 (s), 1500 (s), 1487 (m), 1465 (s), 1440 (w), 1423 (w), 1383 (s), 1323 (s), 1288 (m), 1237 (w), 1222 (w), 1173 (w), 1160 (w), 1113 (m).

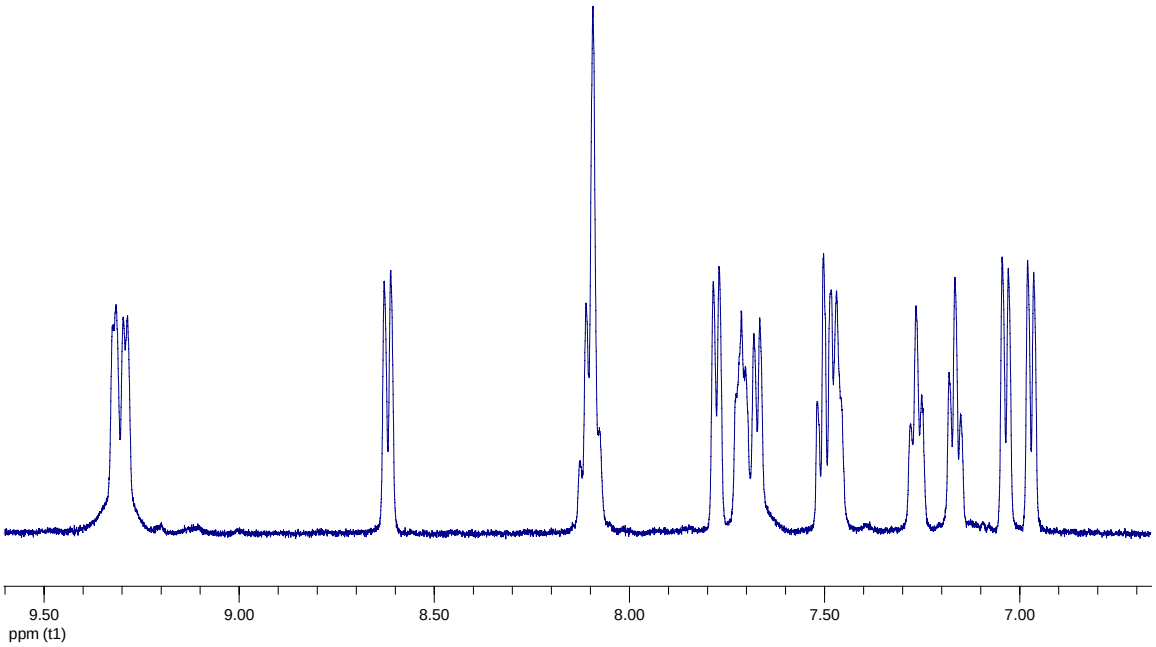


Figure S4. ^{1}H-NMR spectrum of **4d** in $CDCl_3$.

Table S2. Absorption and emission properties of **4d** at room temperature.

Complex	Abs, λ_{max}[a] λ [nm] (ε [10^{-3} cm^{-1} M^{-1}])	Emission λ_{max} [nm]	τ_{Air} [µs]	τ_{N_2} [µs]
4d	321 (10.2), 346 (7.7), 370 (7.1), 412 (4.7), 459 (7.6)	656[a] 628[b]	3.7[c] 4.7[d]	7[c] 10[d]

[a] $CHCl_3$ solutions; [b] film; 2 w.t. % complex in polystyrene; [c] apparent lifetimes measured at a modulation frequency of 5.5 kHz in $CHCl_3$ at a concentration of 2-3 · 10^{-5} M; [d] apparent lifetimes measured at a modulation frequency of 5 kHz for the embedded complex (2 w.t. %) in polystyrene.

^{1}H-NMR-Spectra

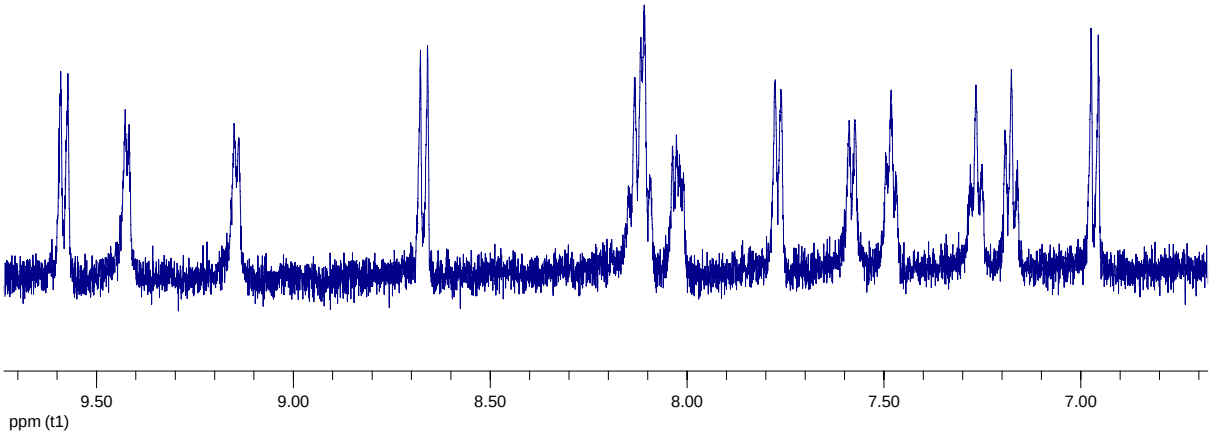


Figure S5. ^{1}H-NMR spectrum of **4a** in DMSO-d_6.

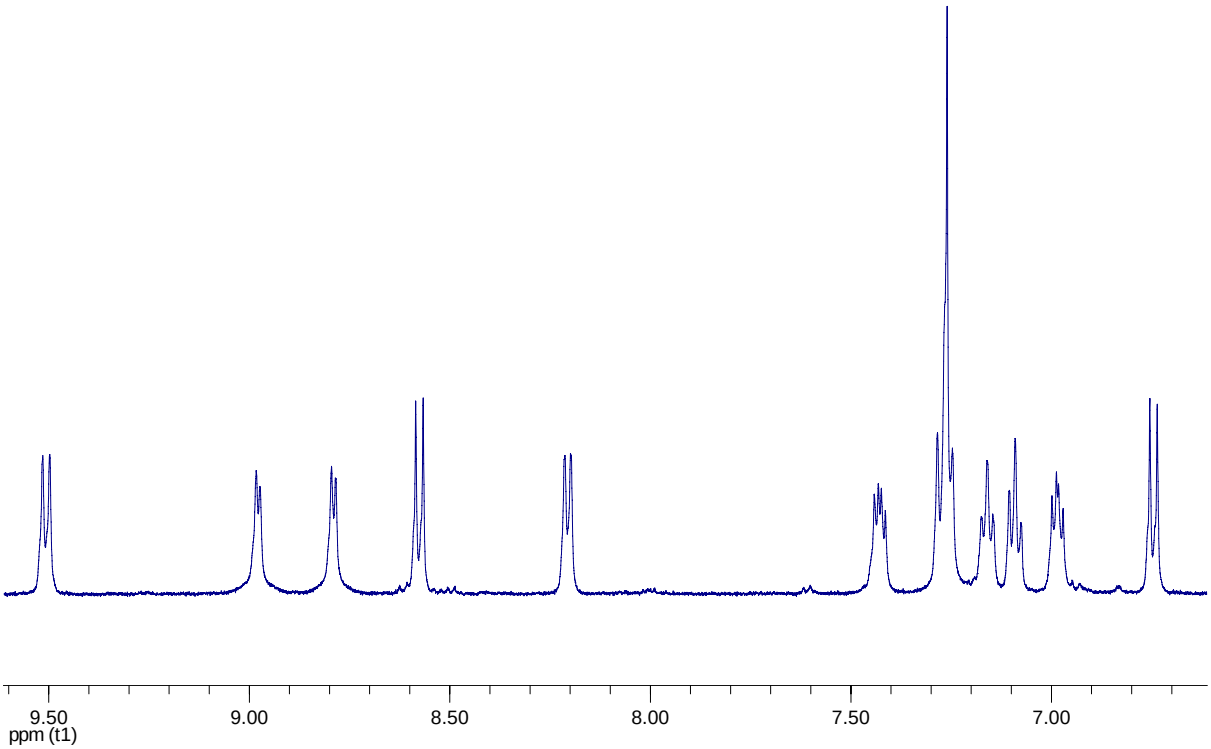


Figure S6. ^{1}H-NMR spectrum of **5a** in $CDCl_3$.

UV-VIS and Fluorescence Spectra

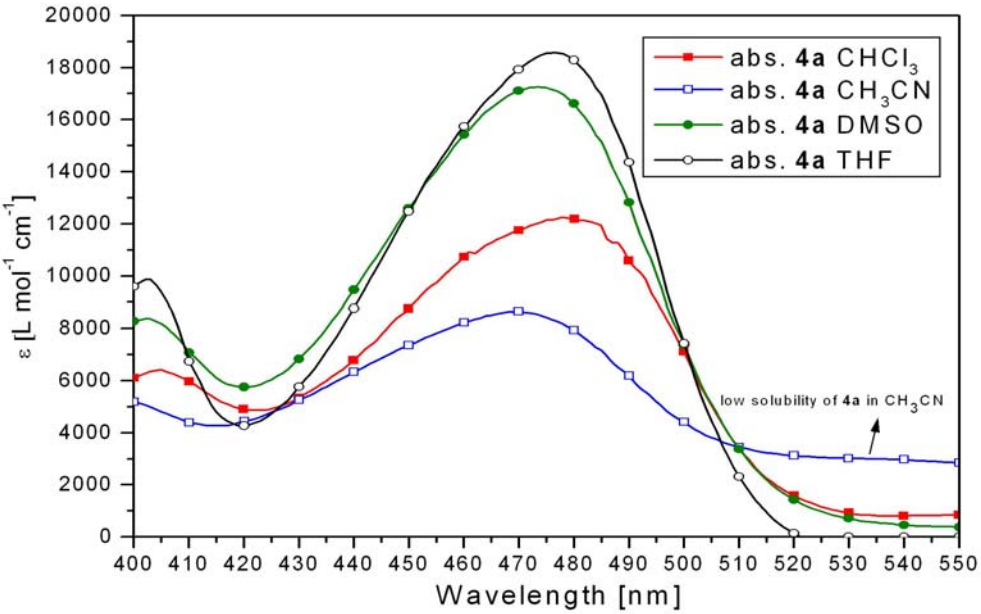


Figure S7. Absorption spectra of **4a** measured in $CHCl_3$, CH_3CN, DMSO and THF solution at room temperature: [**4a**] in $CHCl_3$ = 2.96 · 10^{-5} M; [**4a**] in CH_3CN = 1.84 · 10^{-5} M; [**4a**] in DMSO = 1.11 ·10^{-5} M; [**4a**] in THF = 1.24 · 10^{-5} M.

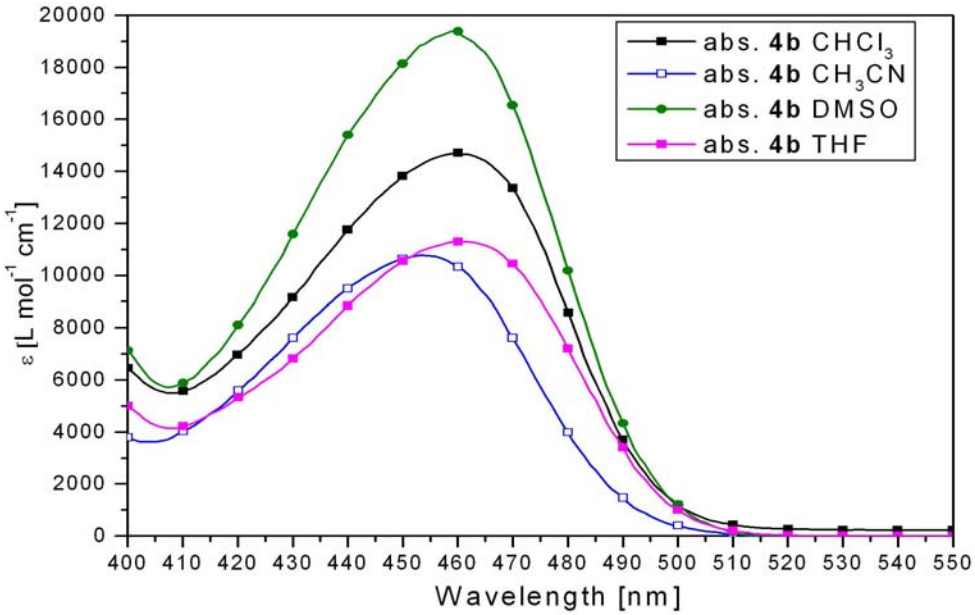


Figure S8. Absorption spectra of **4b** measured in $CHCl_3$, CH_3CN, DMSO and THF solution at room temperature: [**4b**] in $CHCl_3$ = 2.87 · 10^{-5} M; [**4b**] in CH_3CN = 1.49 · 10^{-5} M; [**4b**] in DMSO = 1.20 ·10^{-5} M; [**4b**] in THF = 1.33 · 10^{-5} M.

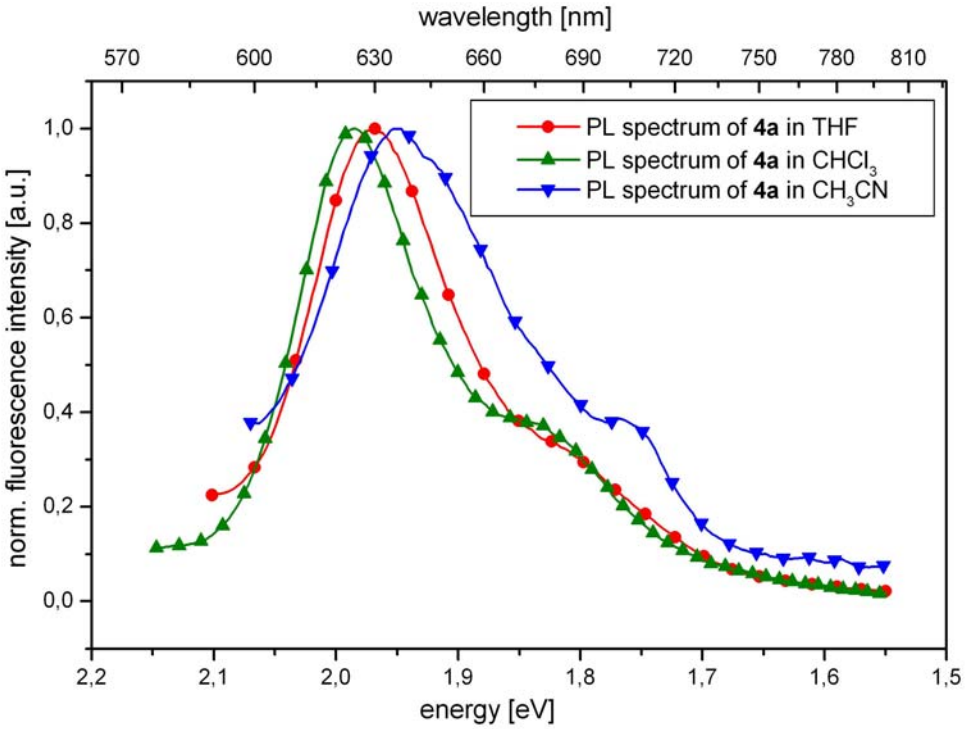


Figure S9. Emission spectra of **4a** measured in $CHCl_3$, CH_3CN and THF solution at room temperature: [**4a**] in $CHCl_3$ = 2.56 · 10^{-5} M; [**4a**] in CH_3CN = 6.23 · 10^{-6} M; [**4a**] in THF = 7.97 · 10^{-6} M.

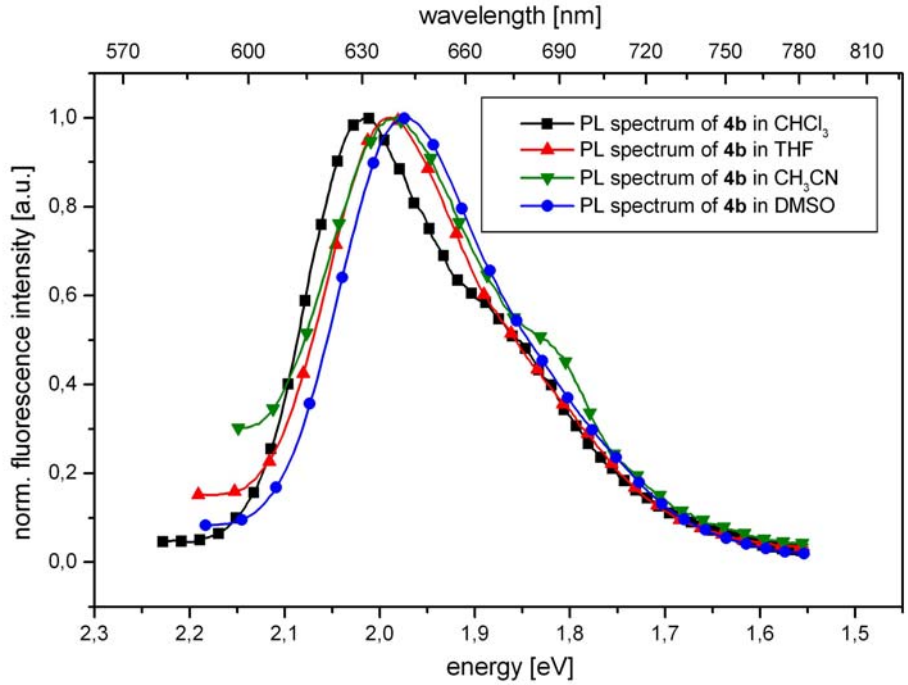


Figure S10. Emission spectra of **4b** measured in $CHCl_3$, CH_3CN, DMSO and THF solution at room temperature: [**4b**] in $CHCl_3$ = 1.88 · 10^{-5} M; [**4b**] in CH_3CN = 9.59 · 10^{-6} M; [**4b**] in DMSO = 7.73 ·10^{-6} M; [**4b**] in THF = 8.60 · 10^{-6} M.

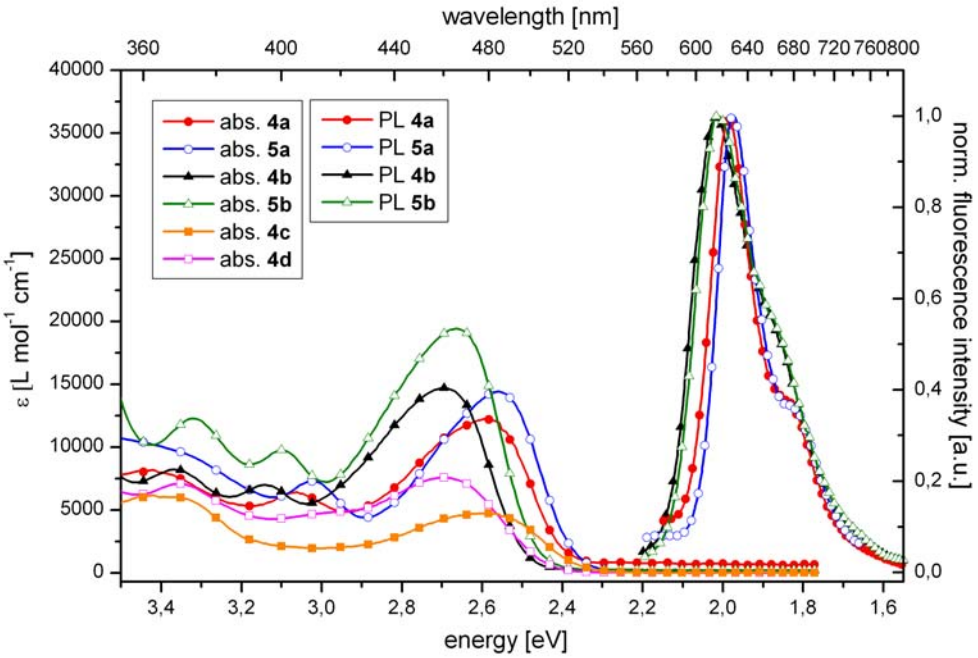


Figure S11. Low energy absorption features and emission spectra of **4a**, **4b, 5a** and **5b** measured in $CHCl_3$ at room temperature. For emission measurements: [**4a**] = $2.56 \cdot 10^{-5}$ M, λ_{ex} = 478 nm; [**5a**] = $2.62 \cdot 10^{-5}$ M, λ_{ex} = 484 nm: [**4b**] = $1.88 \cdot 10^{-5}$ M, λ_{ex} = 460 nm; [**5b**] = $1.22 \cdot 10^{-5}$ M, λ_{ex} = 465 nm.

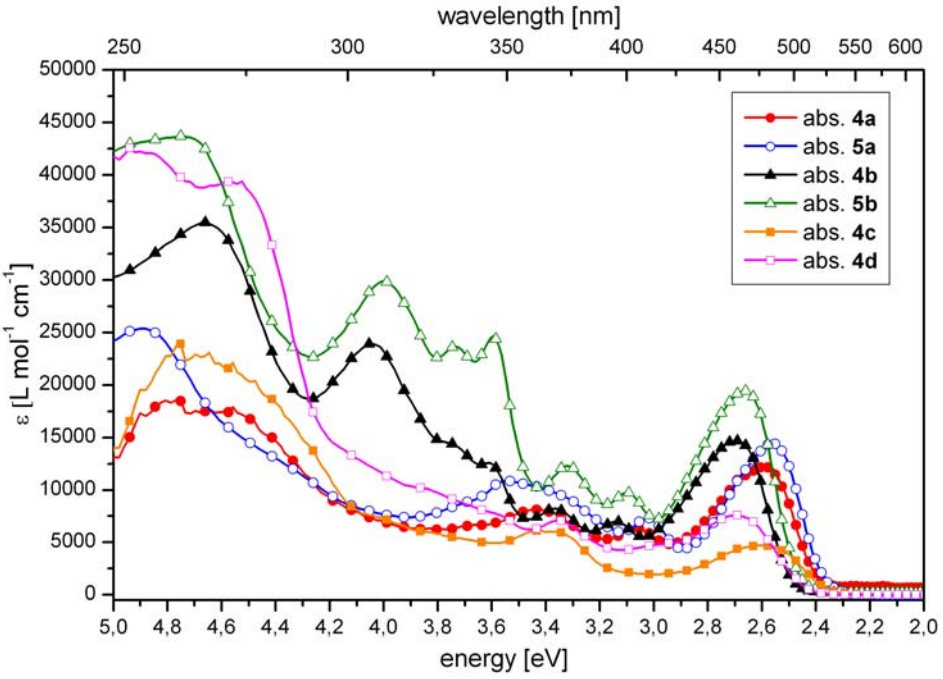


Figure S12. Absorption spectra measured in $CHCl_3$ solution at room temperature: [**4a**] = $2.96 \cdot 10^{-5}$ M; [**5a**] = $2.74 \cdot 10^{-5}$ M; [**4b**] = $2.87 \cdot 10^{-5}$ M; [**5b**] = $1.85 \cdot 10^{-5}$ M; [**4c**] = $3.42 \cdot 10^{-5}$ M, [**4d**] = $3.98 \cdot 10^{-5}$ M.

Lifetime Measurements and Thin Film Spectra

Table S3. Lifetime measurements of coated capillaries (2 w.t. % complex in polystyrene)

Compound	Conditions	Lifetime at 5 kHz / µs[a]	Lifetime at 10 kHz / µs[a]	Lifetime at 20 kHz / µs[a]
4a	air nitrogen	12 34	11 28	7 15
5a	air nitrogen	10 25	8 18	6 10
4b	air nitrogen	10 29	8 20	6 12
5b	air nitrogen	8 24	7 17	6 10
4d	air nitrogen	5 10	4 8	4 6

[a] Estimated experimental error: ± 2µs

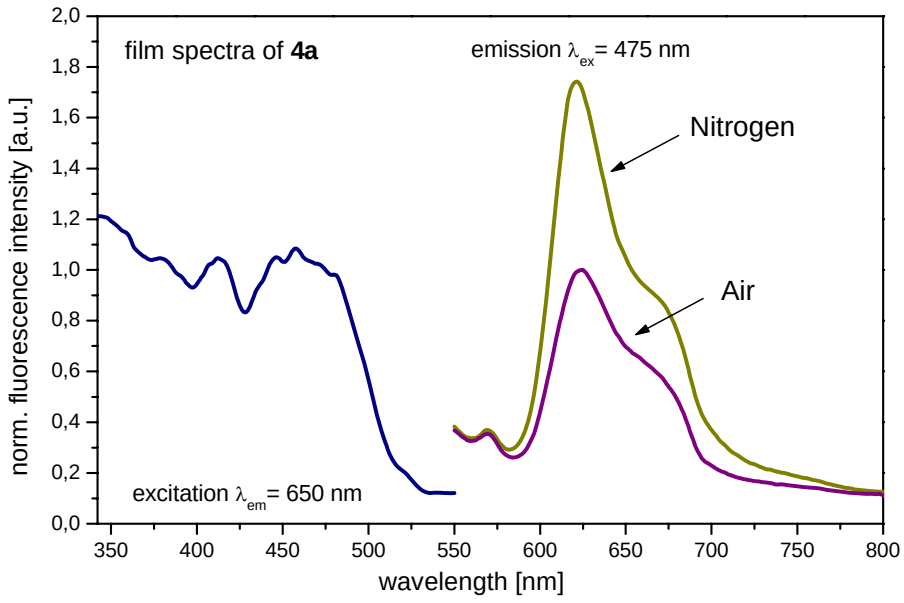


Figure S13. Thin film spectra of coated capillaries (2 w.t. % complex in polystyrene) of **4a** (λ_{ex} = 475 nm)

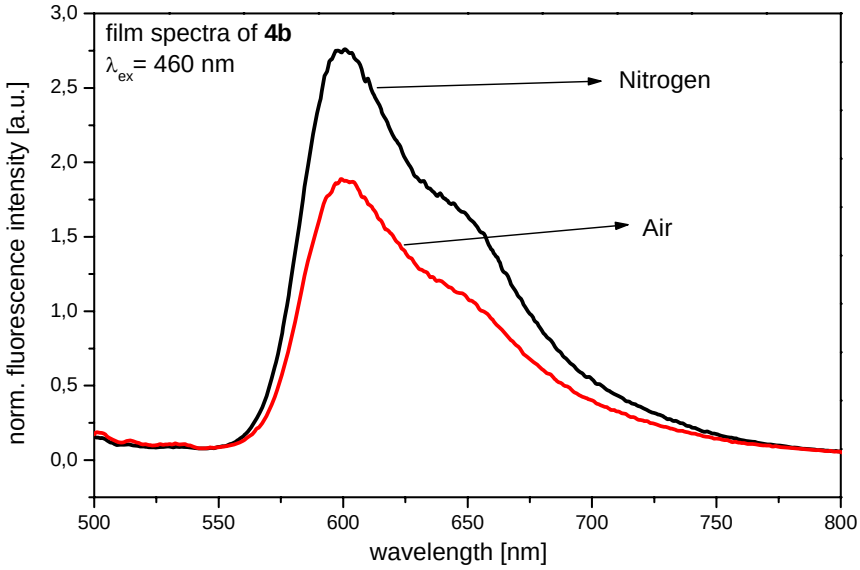


Figure S14. Thin film spectra of coated capillaries (2 w.t. % complex in polystyrene) of **4b** (λ_{ex} = 460 nm)

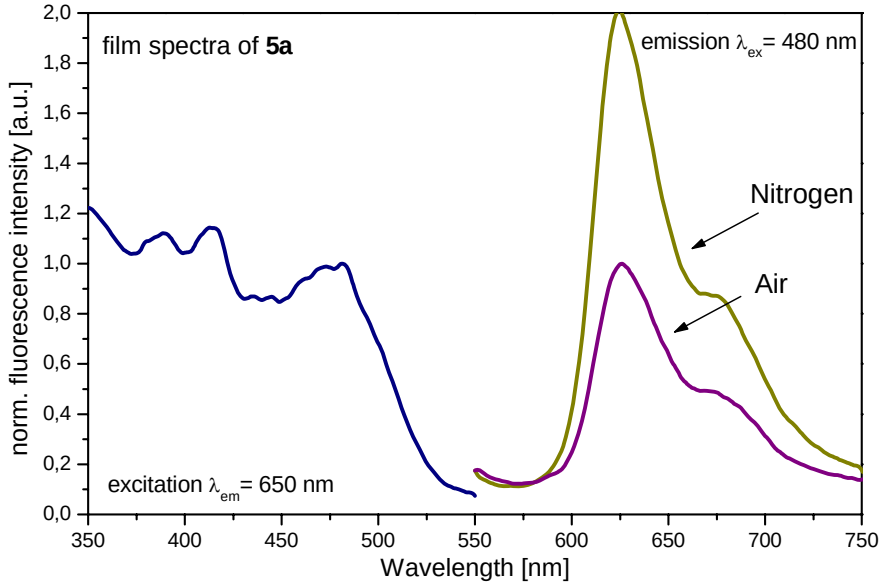


Figure S15. Thin film spectra of coated capillaries (2 w.t. % complex in polystyrene) of **5a** (λ_{ex} = 480 nm)

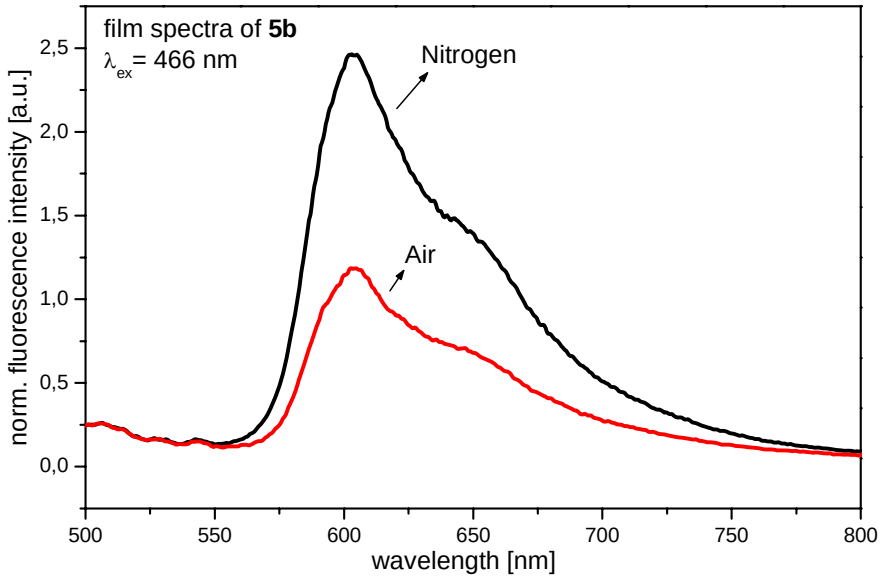


Figure S16. Thin film spectra of coated capillaries (2 w.t. % complex in polystyrene) of **5b** (λ_{ex} = 466 nm)

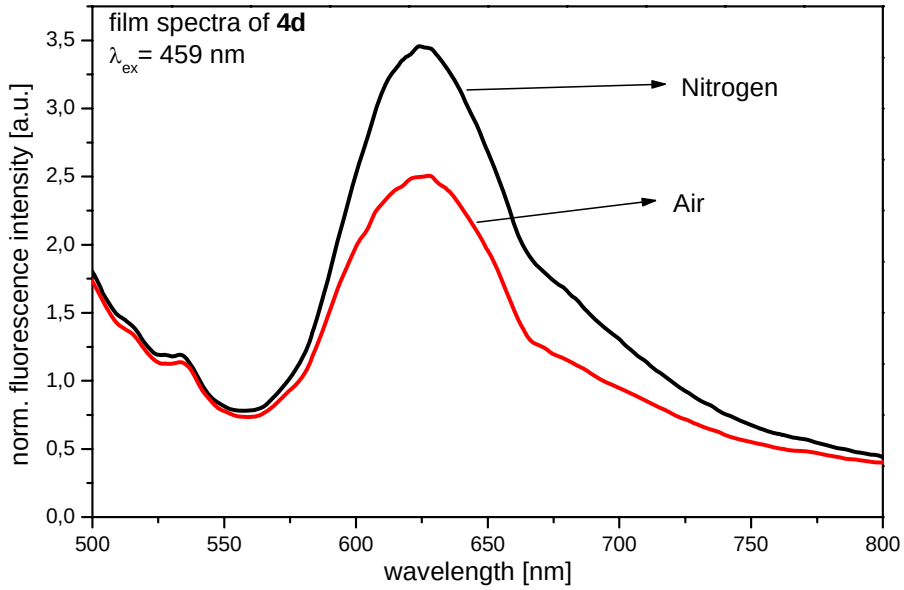


Figure S17. Thin film spectra of coated capillaries (2 w.t. % complex in polystyrene) of **4d** (λ_{ex} = 459 nm)

Table S4. Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillation Strengths from TDDFT Calculations for Pt Complex, **4a**

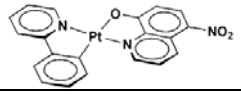
	E (eV)	nm	f	description
S_1	2.623	473	0.144	H – L
S_2	3.152	393	0.011	H – L+1
S_3	3.189	389	0.055	H-1 – L
S_4	3.235	383	0.012	H-2 – L
S_5	3.632	341	0.180	H – L+2
S_6	3.665	338	0.010	H-2 – L+1
S_7	3.669	338	0.058	H-2 – L+1, H – L+3, H-4 – L, H-3 – L
S_8	3.692	336	0.008	H-1 – L+1, H-5 – L
S_9	3.696	335	0.004	H-1 – L+1, H-5 – L
S_{10}	3.777	328	0.046	H – L+3, H-3 – L
T_1	1.955	634		H – L
T_2	2.564	484		H-1 – L, H – L+1, H-1 – L+1
T_3	2.922	424		H – L+1
T_4	3.008	412		H-1 – L+1, H-1 – L
T_5	3.070	404		H-11 – L, H-11 – L+2
T_6	3.108	399		H-2 – L
T_7	3.146	394		H – L+2, H – L+1, H-3 – L+1
T_8	3.233	384		H-5 – L, H-5 – L+2

Table S5. Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillation Strengths from TDDFT Calculations for Pt Complex, **4b**

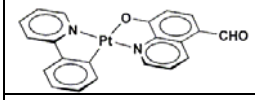
	E (eV)	nm	f	description
S_1	2.632	471	0.126	H – L
S_2	3.115	398	0.011	H – L+1
S_3	3.225	384	0.027	H-1 – L
S_4	3.315	374	0.005	H-2 – L
S_5	3.442	360	0.000	H-3 – L
S_6	3.569	347	0.016	H – L+2
S_7	3.680	337	0.010	H-1 – L+1
S_8	3.687	336	0.001	H-2 – L+1
S_9	3.763	329	0.180	H-4 – L
S_{10}	3.937	315	0.048	H – L+3
T_1	1.990	623		H – L
T_2	2.562	484		H-1 – L, H – L+1
T_3	2.948	421		H – L+1
T_4	3.114	398		H-1 – L+1, H-1 – L
T_5	3.121	397		H-3 – L, H-2 – L
T_6	3.186	389		H-2 – L, H-3 – L
T_7	3.217	385		H – L+3
T_8	3.385	366		H – L+2

Table S6. Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillation Strengths from TDDFT Calculations for Pt Complex, **4c**

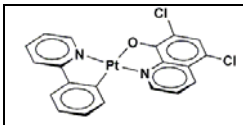
	E (eV)	nm	f	description
S_1	2.400	517	0.090	H – L
S_2	2.955	420	0.004	H – L+1
S_3	3.117	398	0.013	H-1 – L
S_4	3.276	379	0.003	H-2 – L
S_5	3.465	358	0.006	H – L+2
S_6	3.598	345	0.013	H-1 – L+1
S_7	3.675	337	0.080	H – L+3
S_8	3.681	337	0.002	H-2 – L+1
S_9	3.761	330	0.097	H-3 – L
S_{10}	3.912	317	0.050	H-4 – L
T_1	1.813	684		H – L
T_2	2.542	488		H-1 – L, H – L+1
T_3	2.887	429		H – L+1
T_4	3.008	412		H – L+3
T_5	3.067	404		H-1 – L+1, H-1 – L
T_6	3.147	394		H-2 – L
T_7	3.314	374		H – L+2, H-4 – L
T_8	3.354	370		H-3 – L, H – L+2, H-4 – L

Table S7. Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillation Strengths from TDDFT Calculations for Pt Complex, **4d**

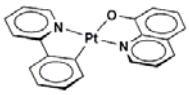
	E (eV)	nm	f	description
S_1	2.436	509	0.080	H – L
S_2	2.908	426	0.002	H – L+1
S_3	3.191	389	0.012	H-1 – L
S_4	3.323	373	0.004	H-2 – L
S_5	3.338	371	0.007	H – L+2
S_6	3.641	341	0.010	H-1 – L+1
S_7	3.688	336	0.000	H-2 – L+1
S_8	3.793	327	0.162	H-3 – L
S_9	3.882	319	0.019	H – L+3
S_{10}	3.967	313	0.019	H-4 – L, H-1 – L+2
T_1	1.872	662		H – L
T_2	2.503	495		H – L+1, H-1 – L
T_3	2.831	438		H – L+1, H-1 – L
T_4	3.131	396		H-1 – L+1, H-1 – L, H – L+2
T_5	3.168	391		H – L+3, H-2 – L+1
T_6	3.181	390		H-2 – L, H – L+3
T_7	3.252	381		H – L+2
T_8	3.398	365		H-3 – L

Table S8. Calculated triplet State Energies of Pt Complexes at the Various Levels of Theory

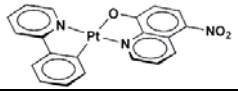
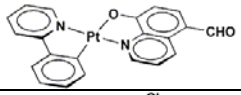
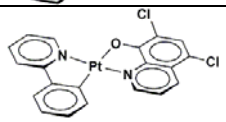
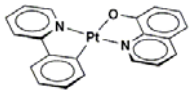
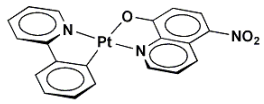
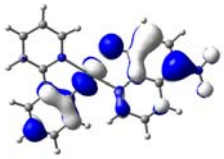
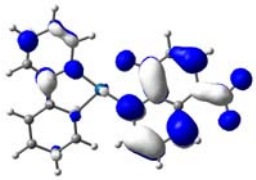
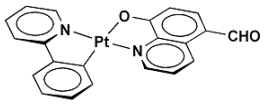
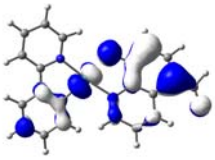
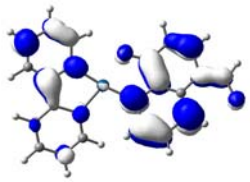
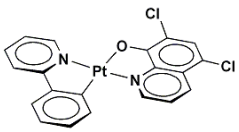
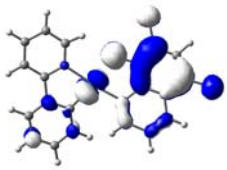
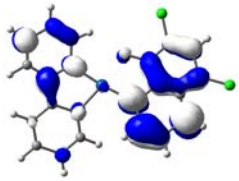
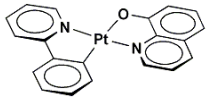
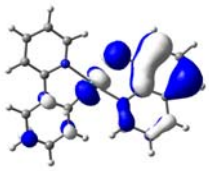
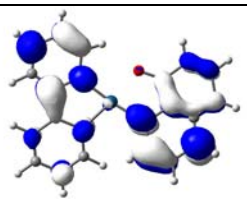
	triplet state energy (eV)	E (T_1-S_0)	TD-B3PW91// S_0 geometry	TD-B3PW91// T_1 geometry
4a		1.927	1.955	1.608
4b		1.961	1.990	1.586
4c		1.744	1.813	1.251
4d		1.802	1.872	1.304

Table S9. Calculated Kohn-Sham HOMO and LUMO and the corresponding orbital energies for complexes **4a**-**4d**

	Structure	HOMO	LUMO
4a			
		-5.699 eV	-2.533 eV
4b			
		-5.461 eV	-2.257 eV
4c			
		-5.273 eV	-2.261 eV
4d			
		-4.997 eV	-1.945 eV

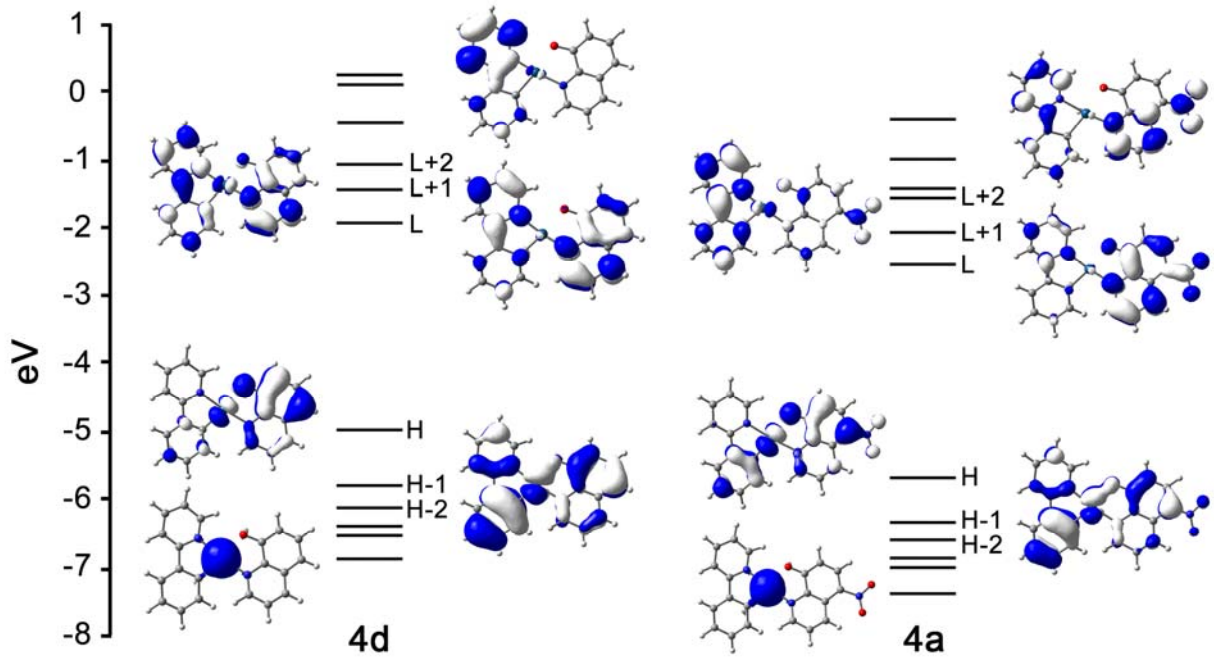


Figure S18. Kohn-Sham orbitals for HOMO, HOMO+1, HOMO+2, LUMO, LUMO+1 and LUMO+2 as well as orbital energies calculated for **4a** and **4d**.