Electronic Supplementary Information
For

Photophysical properties and OLED performance of light-emitting platinum(II) complexes

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Contents

Synthetic procedures and characterization of all compounds for complexes 2-7:

Synthesis of *N,N,N',N'*-tetramethylmethanediamine.[1] Dimethylamine (40%, 45 mL, 0.4 mol) was added drop-wise to a stirred ice cooled solution of formaldehyde (37%, 15 mL, 0.2 mol). Yield: 16.7 g (81%), bp.: 82 °C (Lit.[2] Yield: 85%, bp.: 81.5-83°C). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.23 (s, 12 H, $N(CH_3)_2$), 2.72 (s, 2 H, CH_2).

Synthesis of *N,N*-dimethyliminiumchloride.[1] Acetylchloride (8.5 ml, 0.12 mol) in diethylether (50 mL) was added drop-wise to a ice cooled suspension of *N,N,N',N'*-tetramethylmethanediamine (10.2 g, 0.10 mol). The mixture was stirred overnight at room temperature. The iminium salt was collected by filtration, washed with diethyl ether and then dried under vacuum. Yield: 8.4 g (90%) (Lit.[3] Yield: 92%). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 3.79 (s, 6 H, $N(CH_3)_2$), 8.49 (s, 2 H, CH_2=N).

General procedure for the Mannich-bases.[1,4] The ketone (10 mmol) and *N,N*-dimethyliminiumchloride (10 mmol) were refluxed in abs. acetonitrile (25 mL) for 3 – 4 h under argon atmosphere. After cooling down to 0 °C the Mannich-base was collected by filtration and dried in vacuum.

Synthesis of dimethyl-(3-oxo-3-phenyl)-propylammonium-chloride. Acetophenone (12.96 g, 0.11 mol) and 10 g (0.11 mol) *N,N*-dimethyliminiumchloride. Yield: 12.56 g (54%) colourless solid. Bp.: 150.6 °C (Lit[5] 146–148 °C). ν_{max} (cm^{-1}) = 3456, 3053, 3006, 2954, 2933, 2907, 2645, 2572, 2510, 2462, 2441, 1681, 1594, 1580, 1465, 1378, 1332, 1318, 1222, 1135, 1070, 1029, 1002, 955, 749, 694, 652, 570, 446; ^{1}H-NMR (500 MHz, $CDCl_3$; Me_4Si): δ = 2.80–2.88 (d, 6H), 3.47–3.56 (m, 2H), 3.70–3.79 (t, 2H), 7.44–7.49 (m, 2H), 7.56–7.62 (m, 1H), 7.96–8.00 (m, 2H), 12.53–12.86 (bs, 1H) ppm; ^{13}C-NMR (125 MHz; $CDCl_3$; Me_4Si): δ = 33.8 (t), 43.4 (q), 52.8 (t), 128.3 (d), 128.9 (d), 134.2 (d), 135.5 (s), 195.8 (s) ppm; MS (70 eV): *m/z* (%) = 178 (19), 177 (74), 176 (13), 105 (78), 77 (79), 72 (67), 59 (59), 58 (100), 42 (71), 36 (73), 30 (34).

Synthesis of dimethyl-(3-oxo-3-(4-trifluoromethylphenyl))-propylammoniumchloride.[1] 4-(Trifluoromethyl)-acetophenone 5.0 g (26.5 mmol) and *N,N*-dimethyliminiumchloride (2.5 g, 26.5 mmol). Yield: 4.32 g (58%) colourless solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ.= 2.87 (s, 6H), 3.50–3.57 (t, 2H), 3.80–3.84 (t, 2H), 7.85–7.90 (m, ^3J = 8.0 Hz, 2H), 8.11–8.16 (m, ^3J = 8.0 Hz, 2H), 12.54–12.72 (bs, 1H).

Synthesis of dimethyl-(3-oxo-3-(4-fluorophenyl))-propylammoniumchloride.[1] 4-Fluoroacetophenone (500 mg, 3.6 mmol) and 339 mg (3.6 mmol) *N,N*-dimethyliminiumchloride. Yield: 740 mg (89%) colourless solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.85 (s, 6H), 3.48–3.53 (t, 2H), 3.72–3.76 (t, 2H), 7.12–7.18 (m, $^3J_{H,F}$ = 9.0 Hz, 2H), 8.01–8.06 (m, $^4J_{H,F}$ = 5.5 Hz, 2H), 12.62–12.88 (bs, 1H).

Synthesis of dimethyl-(3-oxo-3-(4-bromophenyl))-propylammoniumchloride.[1] 4'-Bromoacetophenone (9.96 g, 50 mmol) and *N,N*-dimethyliminiumchloride (4.69 g, 50 mmol). Yield: 8.38 g (57%) colourless crystals. Bp.: 194.6 °C (Lit.[5]: 200.5–201.5°C). ^{1}H-NMR (500 MHz, $CDCl_3$/MeOD): δ = 2.80 (s, 6H), 3.41–3.46 (t, 2H), 3.56–3.61 (t, 2H), 7.54–7.58 (d, ^3J = 8.5 Hz, 2H), 7.79–7.83 (d, ^3J = 8.5 Hz, 2H).

General procedure for the diketones.[1] The enamine (0.1 mol) and the Mannich-base (0.1 mol) were stirred in abs. dioxane (100 mL) for 16 h under reflux. After the addition of distilled water (30 mL) the mixture was heated for 1 h. The mixture was cooled down to room temperature and after the addition of water (30 mL), the product was extracted with dichloromethane (4 × 40 mL). The organic phases were combined and washed with diluted hydrochloric acid (20 mL) and water.

Synthesis of 2-(3-oxo-3-(phenyl)-propyl)-cyclohexanone.[1] Dimethyl-(3-oxo-3-phenyl)-propylammoniumchloride (5.0 g, 23.4 mmol) and (3.9 mg, 23.4 mmol) enamine 1-morpholinocyclohexene. Yield: 2.1 g (40%) yellow oil after purification by column chromatography on silica gel (petrolether/EtOAc 9/1 as eluent). ^{1}H-NMR (500 MHz, $CDCl_3$; Me_4Si): δ = 1.33–1.49 (m, 1H), 1.59–1.72 (m, 3H), 1.80–1.89 (m, 2H), 1.99–2.16 (m, 3H), 2.22–2.46 (m, 2H), 2.87–

3.14 (m, 2H), 7.38–7.45 (m, 2H), 7.49–7.54 (m, 1H), 7.93–7.97 (m, 2H) ppm; ^{13}C-NMR (125 MHz; $CDCl_3$; Me_4Si): δ = 24.6 (t), 25.1 (t), 28.1 (t), 34.6 (t), 36.3 (t), 42.2 (t), 50.0 (d), 128.1 (d), 128.5 (d), 132.9 (d), 136.9 (s), 200.2 (s), 213.1 (s).

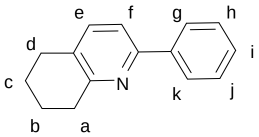
Synthesis of 2-(3-oxo-3-(4-trifluoromethylphenyl)-propyl)-cyclohexanone.[1] Dimethyl-(3-oxo-3-(4-trifluoromethylphenyl))-propylammoniumchloride (4.1 g, 22 mmol) and 1-morpholinocyclohexene (3.6 g, 22 mmol). Yield: 2.0 g (30%) pale yellow solid after purification by column chromatography on silica gel (CH_2Cl_2/Et_2O 1/1 as eluent). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.34–1.44 (m, 1H), 1.55–1.68 (m, 3H), 1.74–1.84 (m, 1H), 1.95–2.10 (m, 3H), 2.20–2.28 (m, 1H), 2.28–2.43 (m, 2H), 2.87–2.95 (m, 1H), 3.04–3.12 (m, 1H), 7.61-7.65 (d, ^{3}J = 8.0 Hz, 2H), 7.98-8.03 (d, ^{3}J = 8.0 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.4 (t), 25.0 (t), 28.0 (t), 34.5 (t), 36.7 (t), 42.2 (t), 49.8 (d), 123.6 (q, $^{1}J_{C,F}$ = 272 Hz), 125.5 (q, $^{3}J_{C,F}$ = 4 Hz), 128.4 ($^{4}J_{C,F}$ = 1 Hz), 134.1 (q, $^{2}J_{C,F}$ = 32 Hz), 139.5 (s), 199.1 (s), 212.8 (s).

Synthesis of 2-(3-oxo-3-(4-fluorophenyl)-propyl)-cyclohexanone.[1] Dimethyl-(3-oxo-3-(4-fluorophenyl))-propylammoniumchloride (740 mg, 3.2 mmol) and (530 mg, 3.2 mmol) enamine 1-morpholinocyclohexene. Yield: 128 mg (16%) yellow oil after purification by column chromatography on silica gel (CH_2Cl_2/Et_2O 1/1 as eluent). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.39–1.50 (m, 1H), 1.61–1.73 (m, 3H), 1.83–1.89 (m, 1H), 2.02–2.17 (m, 3H), 2.26–2.34 (m, 1H), 2.36–2.46 (m, 2H), 2.87–2.96 (m, 1H), 3.04–3.14 (m, 1H), 7.07-7.13 (t, 2H), 7.97-8.03 (m, $^{3}J_{H,F}$ = 9.0 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.7 (t), 25.1 (t), 28.1 (t), 34.6 (t), 36.3 (t), 42.3 (t), 50.0 (d), 115.6 (d, $^{2}J_{C,F}$ = 20 Hz), 130.8 (d, $^{3}J_{C,F}$ = 8 Hz), 133.3 (d, $^{4}J_{C,F}$ = 3 Hz), 165.7 (d, $^{1}J_{C,F}$ = 245 Hz), 198.7 (s), 213.1 (s).

Synthesis of 2-(3-oxo-3-(4-bromophenyl)-propyl)-cyclo-hexanone.[1] Dimethyl-(3-oxo-3-(4-bromophenyl))-propylammoniumchloride (6.04 g, 20.7 mmol) and 1-morpholinocyclohexene (3.5 g, 20.7 mmol). Yield: 4.17 g (65%) brown oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.32–1.48 (m, 1H), 1.58–1.71 (m, 3H), 1.79–1.88 (m, 2H), 1.99–2.14 (m, 3H), 2.21–2.44 (m, 2H), 2.82–3.10 (m, 2H), 7.53–7.57 (d, ^{3}J = 8.5 Hz, 2H), 7.79–7.82 (d, ^{3}J = 8.5 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.6 (t), 25.1 (t), 28.1 (t), 34.6 (t), 36.4 (t), 42.2 (t), 49.9 (d), 128.1 (s), 129.7 (d), 131.8 (d), 135.6 (s), 199.2 (s), 213.0 (s).

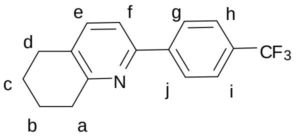
General procedure for the functionalized C^N ligands L4-L7.[1] The diketone (10 mmol) and the hydroxylamine hydrochloride (10 mmol) were stirred overnight under reflux in ethanol (10 mL). The reaction mixture was subsequently cooled down to room temperature, neutralized with Na_2CO_3, mixed with water (50 mL) and the product was extracted with dichloromethane (4 × 30 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

Synthesis of 2-phenyl-5,6,7,8-tetrahydroquinoline.



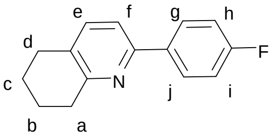
2-(3-Oxo-3-(phenyl)-propyl)-cyclohexanone (5.5 g, 23.8 mmol) and $NH_2OH \cdot HCl$ (1.65 g, 23.8 mmol). Yield: 4.9 g (98%) brown oil after purification by column chromatography on silica gel (CH_2Cl_2 as eluent). ν_{max}/cm^{-1} 3060, 3029, 2933, 2857, 2659, 2319, 1953, 1895, 1808, 1680, 1587, 1567, 1494, 1454, 1433, 1399, 1355, 1297, 1248, 1214, 1155, 1128, 1073, 1026, 987, 944, 901, 835, 823, 768, 737, 721, 694, 600, 581, 514; ^{1}H-NMR (500 MHz; $CDCl_3$; Me_4Si): δ = 1.81–1.87^{c} (m, 2H), 1.91–1.97^{b} (m, 2H), 2.77–2.81^{d} (t, 2H), 3.02–3.07^{a} (t, 2H), 7.37–7.41^{e,f} (m, 2H), 7.44–7.49^{h,i,j} (m, 3H), 7.98–8.01^{g,k} (m, 2H) ppm; ^{13}C-NMR (125 MHz; $CDCl_3$; Me_4Si): δ = 22.9 (t), 23.3 (t), 28.6 (t), 32.9 (t), 117.9 (d), 126.9 (d), 128.4 (d), 128.7 (d), 130.8 (s), 137.5 (d), 139.9 (s), 154.6 (s), 157.2 (s) ppm; MS (70eV): *m/z* (%) = 211 (3), 210 (37), 209 (100), 208 (88), 181 (35), 105 (16), 77 (16).

Synthesis of 2-(4-trifluoromethylphenyl)-5,6,7,8-tetrahydroquinoline.[1]



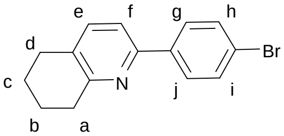
2-(3-Oxo-3-(4-trifluoromethylphenyl)-propyl)-cyclohexanone (2.68 g, 9 mmol) and $NH_2OH·HCl$ (626 mg, 9 mmol). Yield: 1.35 g (54%) yellow oil after purification by column chromatography on silica gel (petrolether/Et_2O 6/1 as eluent). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.81–1.89^{c} (m, 2H), 1.90–1.98^{b} (m, 2H), 2.79–2.84^{d} (t, 2H), 2.97–3.03^{a} (t, 2H), 7.42–7.50^{e,f} (q, ^3J = 8.0 Hz, 2H), 7.67–7.70^{h,i} (d, ^3J = 8.0 Hz, 2H), 8.05–8.09^{g,j} (d, ^3J = 8.0 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 22.7 (t), 23.1 (t), 28.6 (t), 32.8 (t), 118.1 (d), 124.3 (q, $^1J_{C,F}$ = 272 Hz), 125.5 (q, $_3J_{C,F}$ = 4 Hz), 127.0 (d), 130.2 (q, $^2J_{C,F}$ = 32 Hz), 131.8 (s), 137.5 (d, $^4J_{C,F}$ = 1 Hz), 143.2 (s), 153.0 (s), 157.7 (s). IR (KBr): ν (cm^{-1}) = 2942, 2867, 2361, 1688, 1620, 1569, 1460, 1329, 1255, 1164, 1124, 1067, 1015, 856, 833, 810, 599. MS (70 eV): *m/z* (%) = 279 (1), 278 (15), 277 (100), 249 (17), 180 (3). $C_{16}H_{14}F_3N$ (277.11): calcd. C 69.30, H 5.09, N 5.05; found C 69.13, H 4.41, N 5.00.

Synthesis of 2-(4-fluorophenyl)-5,6,7,8-tetrahydroquinoline.[1]



2-(3-Oxo-3-(4-fluorophenyl)-propyl)-cyclohexanone (2.4 g, 4.8 mmol) and $NH_2OH·HCl$ (672 mg, 4.8 mmol). Yield: 1.1 g (50%) yellow oil after purification by column chromatography on silica gel (petrolether/Et_2O 6/1 as eluent). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.81–1.86^{c} (m, 2H), 1.90–1.95^{b} (m, 2H), 2.77–2.81^{d} (t, 2H), 2.96–3.00^{a} (t, 2H), 7.09–7.14^{h,i} (m, $^3J_{H,F}$ = 9.0 Hz, 2H), 7.39–7.40^{e,f} (s, 2H), 7.91–7.95^{g,j} (m, $^4J_{H,F}$ = 5.5 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 22.8 (t), 23.2 (t), 28.5 (t), 32.8 (t), 115.4 (d), 115.5 (d), 117.5 (d), 128.5 (d), 128.6 (d), 130.7 (s), 136.1 (s), 137.5 (d), 153.6 (s), 157.3 (s), 163.2 (d, $^1J_{C,F}$ = 255 Hz). IR (KBr): ν (cm^{-1}) = 3068, 3048, 3018, 2934, 2880, 2860, 2835, 1684, 1600, 1589, 1570, 1511, 1458, 1433, 1419, 1388, 1355, 1293, 1230, 1185, 1159, 1126, 1096, 1048, 1015, 989, 938, 849, 834, 812, 749, 668, 557, 520, 483. MS (70 eV): *m/z* (%) = 228 (67), 229 (6), 227 (100), 226 (92), 199 (70), 133 (19), 77 (10). $C_{15}H_{14}FN$ (227.11): calcd. C 79.27, H 6.21, N 6.16; found C 79.35, H 7.31, N 6.54.

Synthesis of 2-(4-bromophenyl)-5,6,7,8-tetrahydroquinoline.[1,6]



2-(3-Oxo-3-(4-bromophenyl)-propyl)-cyclohexanone (3.0 g, 4.4 mmol) and $NH_2OH·HCl$ (674 mg, 9.7 mmol). Yield: 1.27 g (46%) yellow solid after purification by column chromatography on silica gel (CH_2Cl_2 as eluent). Bp.: 114.5 °C (Lit.[7]:109°C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.79–1.85^{c} (m, 2H), 1.88–1.94^{b} (m, 2H), 2.74–2.79^{d} (t, 2H), 2.96–3.00^{a} (t, 2H), 7.34–7.39^{e,f} (m, 2H), 7.52–7.55h,i (m, 2H), 7.81–7.84^{g,j} (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 22.8 (t), 23.2 (t), 28.6 (t), 32.9 (t), 117.5 (d), 122.8 (s), 128.4 (d), 131.2 (s), 131.7 (d), 137.5 (d), 138.7 (s), 153.2 (s), 157.4 (s). IR (KBr): ν (cm^{-1}) = 2929, 2859, 2360, 2343, 1683, 1653, 1575, 1560, 1541, 1510, 1487, 1456, 1256, 1131, 1068, 1005, 806, 743. MS (70 eV): *m/z* (%) = 289 (97), 288 (54), 287 (100), 261 (13), 208 (5), 180 (10), 77 (6). $C_{15}H_{14}BrN$ (287.03): calcd. C 62.52, H 4.90, N 4.86; found C 62.29, H 4.40, N 4.87.

Dimer D2.[1,8] 2-Phenylpyridine (400 mg, 2.577 mmol) and K_2PtCl_4 (486 mg, 1.171 mmol). Yield: 325 mg (72%) yellow green powder.

Dimer D3.[1,9] 2,4-Difluorophenylpyridine (442 mg, 2.312 mmol) and K_2PtCl_4 (441 mg, 1.051 mmol). Yield: 356 mg (80%) yellow green powder

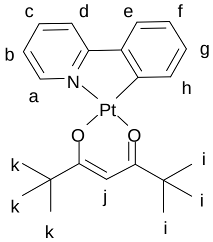
Dimer D4.[1] 2-Phenyl-5,6,7,8-tetrahydroquinoline (350 mg, 1.674 mmol) and K_2PtCl_4 (316 mg, 0.761 mmol). Yield: 232 mg (70 %) dark green powder.

Dimer D5.[1] 2-(4-Trifluoromethylphenyl)-5,6,7,8-tetrahydroquinoline (212 mg, 0.765 mmol) and K_2PtCl_4 (144 mg, 0.347 mmol). Yield: 120 mg (68%) yellow-green powder.

Dimer D6.[1] 2-(4-Fluorophenyl)-5,6,7,8-tetrahydroquinoline (214 mg, 0.942 mmol) and K_2PtCl_4 (178 mg, 0.428 mmol). Yield: 137 mg (70%) dark green powder.

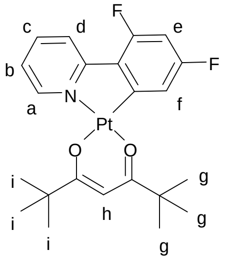
Dimer D7.[1] 2-(4-Bromophenyl)-5,6,7,8-tetrahydroquinoline (697 mg, 2.420 mmol) and K_2PtCl_4 (457 mg, 1.100 mmol). Yield: 480 mg (84%) dark green powder.

Complex 2.[1]



Dimer **D2** (311 mg, 0.405 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (166 mg, 0.903 mmol) and Na_2CO_3 (319 mg, 3.01 mmol). Purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) yielded yellow crystals (252 mg, 58%). (Found: C 50.06, H 5.37, N 2.52. $C_{22}H_{27}NO_2Pt$ requires C 49.62, H 5.11, N 2.63); ν_{max}/cm^{-1} 3106, 3045, 2952, 2919, 2855, 2352, 1731, 1605, 1583, 1523, 1487, 1458, 1308, 1272, 1243, 1218, 1181, 1139, 1066, 1023, 1010, 952, 930, 873, 822, 787, 740, 722, 658 and 629; ^{1}H-NMR (600 MHz; $CDCl_3$; Me_4Si): δ = 1.30^{k} (s, 9 H, CH_3), 1.31^{i} (s, 9 H, CH_3), 5.83^{j} (s, 1H, CH), 7.06–8.18^{b,g} (m, 2H, ArH), 7.23^{f} (td, *J* = 7.4, 1.3 Hz, 1 H, ArH), 7.43–7.52^{h} (m, 1H, ArH), 7.63^{d} (d, *J* = 8.0 Hz, ArH), 7.69^{e} (dd, *J* = 7.6, 1.1 Hz, 1H, ArH), 7.81^{c} (td, *J* = 7.8, 1.5 Hz, 1H, ArH) and 9.03^{a} (d, *J* = 5.2 Hz, 1H, ArH); ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 28.4, 28.6, 41.1, 41.5, 93.2, 118.3, 121.2, 122.9, 123.4, 129.3, 131.0, 138.0, 140.1, 144.7, 147.1, 168.6, 193.8, 195.1; *m/z* (ESI): 533.2 (M^+-$C_{22}H_{27}NO_2Pt$ requires 532.17); $\lambda_{max\text{-}absorption}$($CH_2Cl_2$)/nm 253 ($\varepsilon$/dm^3 mol^{-1} cm^{-1} 52600), 280 (37300), 315 (17700), 367 (11000); $\lambda_{max\text{-}emission}$($CH_2Cl_2$)/nm 486, 518.

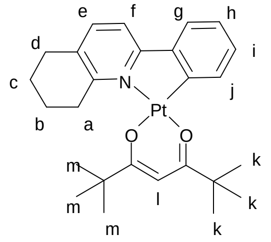
Complex 3.[1]



Dimer **D3** (151 mg, 0.180 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (100 mg, 0.540 mmol) and Na_2CO_3 (191 mg, 1.800 mmol). Purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) yielded yellow crystals (74 mg, 36%). (Found: C 47.08, H 4.23, N 2.49. $C_{22}H_{25}F_2NO_2Pt$ requires C 46.48, H 4.43, N 2.46); ν_{max}/cm^{-1}

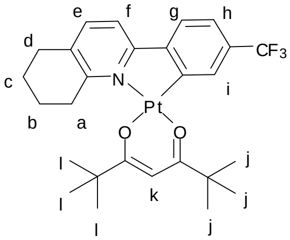
2977, 2948, 2923, 2901, 2858, 2362, 1605, 1545, 1530, 1497, 1437, 1397, 1362, 1297, 1243, 1225, 1189, 1160, 1143, 1114, 1095, 1066, 984, 956, 876, 848, 801, 768, 751, 737, 701, 658 and 633; ^{1}H-NMR (600 MHz; $CDCl_3$; Me_4Si): $\delta = 1.31^{i}$ (s, 9H, CH_3), 1.31^{g} (s, 9H, CH_3), 5.87^{h} (s, 1H, CH), 6.60^{e} (m, 1H, ArH), $7.15–7.19^{b,f}$ (m, 2H, ArH), 7.86^{c} (m, 1H, ArH), 8.00^{d} (d, J = 8.1 Hz, 1H, ArH), 9.05^{a} (d, J = 6.1 Hz, 1H, ArH). ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 28.3, 28.4, 28.6, 28.9, 41.1, 41.5, 93.5, 99.2, 112.9, 121.1, 122.1, 138.6, 147.1, 194.3, 195.5 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -112.75, -106.94 ppm; *m/z* (ESI): 569.2 (M^{+}-$C_{22}H_{25}F_2NO_2Pt$ requires 568.15); $\lambda_{\text{max-absorption}}$($CH_2Cl_2$)/nm 249 ($\varepsilon$/dm^{3} mol^{-1} cm^{-1} 46900), 309 (15900), 323 (16600), 364 (10600); $\lambda_{\text{max-emission}}$($CH_2Cl_2$)/nm 468, 498.

Complex 4.



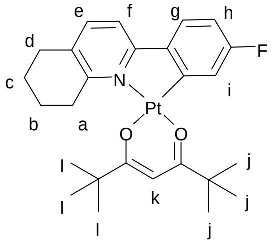
Dimer **D4** (150 mg, 0.171 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (95 mg, 0.513 mmol) and Na_2CO_3 (181 mg, 1.710 mmol). After purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) yellow crystals (0.140 g, 70%) were obtained. (Found C 53.26, H 6.268, N 2.486; $C_{26}H_{33}NO_2Pt$ requires C 53.23, H 5.67, N 2.39); ν_{max}/cm^{-1} 3049, 2963, 2938, 2861, 2826, 2377, 2349, 2314, 1601, 1585, 1563, 1522 1493, 1477, 1474, 1458, 1445, 1417, 1398, 1388, 1356, 1331, 1312, 1290, 1270, 1245, 1213, 1185, 1140, 1124, 1067, 1045, 1029, 1019; ^{1}H-NMR (600 MHz, $CDCl_3$; Me_4Si): $\delta = 1.24^{m}$ (s, 9H, CH_3), 1.30^{k} (s, 9H, CH_3), $1.77–1.93^{b,c}$ (m, 4H, CH_2), 2.82^{d} (t, J = 6.3 Hz, 2H, CH_2), 3.60^{a} (t, J = 6.3 Hz, 2H, CH_2), 5.86^{l} (s, 1H, CH), 7.09^{h} (t, J = 7.4 Hz, 1H, ArH), 7.15^{i} (t, J = 7.4 Hz, 1H, ArH), 7.37^{j} (d, 7.6 Hz, 1H, ArH), $7.44^{e,f}$ (q, J = 8.1 Hz, 2H, ArH), 7.72^{g} (d, 7.7 Hz, 1H, ArH) ppm; ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 21.9, 23.0, 28.5, 28.7, 29.1, 32.2, 40.8, 42.2, 53.4, 92.3, 115.1, 122.4, 123.6, 127.7, 130.0, 131.0, 136.0, 138.8, 146.4, 162.5, 166.8 193.3, 195.3 ppm; *m/z* (ESI): 587.2 (M^{+}-$C_{26}H_{33}NO_2Pt$ requires 586.22); $\lambda_{\text{max-absorption}}$($CH_2Cl_2$)/nm 250 ($\varepsilon$/dm^{3} mol^{-1} cm^{-1} 27600), 278 (25100), 317 (11700), 367 (6500); $\lambda_{\text{max-emission}}$($CH_2Cl_2$)/nm 498, 528.

Complex 5.[1]



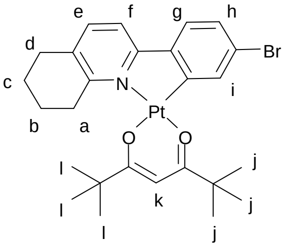
Dimer **D5** (103 mg, 0.099 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (55 mg, 0.296 mmol) and Na_2CO_3 (105 mg, 0.990 mmol). After purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) a yellow solid (66 mg, 50%) was obtained. (Found C 49.57, H 4.31, N 2.29. $C_{27}H_{32}F_3NO_2Pt$ requires C 49.54, H 4.93, N 2.14); ν_{max}/cm^{-1} 2966, 2930, 2866, 2362, 1591, 1562, 1530, 1497, 1480, 1454, 1412, 1389, 1362, 1311, 1243, 1164, 1120, 1074, 959, 902, 873, 808, 791, 747, 712, 650 and 610; ^{1}H-NMR (600 MHz; $CDCl_3$; Me_4Si): $\delta = 1.25^{l}$ (s, 9H, CH_3), 1.31^{j} (s, 9H, CH_3), $1.79–1.94^{b,c}$ (m, 4H, CH_2), $2.81–2.83^{d}$ (t, J = 6.3 Hz, 2H, CH_2), $3.56–3.63^{a}$ (t, J = 6.4 Hz, 2H, CH_2), 5.90^{k} (s, 1H, CH), 7.32^{h} (dd, J = 8.0, 1.3 Hz, 1H, ArH), 7.43^{g} (d, J = 8.1 Hz, 1H, ArH), 7.46^{f} (d, J = 8.1 Hz, 1H, ArH), 7.50^{e} (d, J = 8.1 Hz, 1H, ArH), 8.05^{i} (d, J = 1.3 Hz, 1H, ArH) ppm. ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 21.8, 22.9, 28.5, 28.6, 29.2, 32.3, 40.8, 42.2, 53.4, 92.6, 115.8, 120.3, 122.0, 126.3, 132.5, 136.2, 139.0, 149.6, 163.1, 165.2, 193.7, 195.6 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -63.21 ppm; *m/z* (ESI): 655.2 (M^+-$C_{27}H_{32}F_3NO_2Pt$ requires 654.20); $\lambda_{max\text{-}absorption}$($CH_2Cl_2$)/nm 251 (ε/dm^3 mol^{-1} cm^{-1} 36600), 280 (34700), 317 (15800), 332 (15500), 381 (8800); $\lambda_{max\text{-}emission}$($CH_2Cl_2$)/nm 501, 537.

Complex 6.[1]



Dimer **D6** (105 mg, 0.115 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (71 mg, 0.385 mmol) and Na_2CO_3 (136 mg, 1.280 mmol). Purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) yielded yellow crystals (110 mg, 79%). (Found C 51.70, H 5.46, N 1.71. $C_{26}H_{32}FNO_2Pt$ requires C 51.65, H 5.33, N 2.32); ν_{max}/cm^{-1} 2995, 2934, 2858, 1587, 1545, 1530, 1494, 1451, 1412, 1389, 1358, 1308, 1268, 1243, 1221, 1185, 1142, 873, 848 and 791; ^{1}H-NMR (600 MHz; $CDCl_3$; Me_4Si): δ = 1.23^l (s, 9H, CH_3), 1.30^j (s, 9H, CH_3), 1.77–1.94^{b,c} (m, 4H, CH_2), 2.81^d (t, *J* = 6.2 Hz, 2H, CH_2), 3.56^a (t, *J* = 6.2 Hz, 2H, CH_2), 5.88^k (s, 1H, CH), 6.79^h (td, *J* = 8.6, 2.6 Hz, 1H, ArH), 7.30–7.40^{f,g,i} (m, 3H, ArH), 7.44^e (d, *J* = 8.1 Hz, 1H, ArH) ppm. ^{13}C-NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 21.9, 22.9, 28.5, 28.7, 29.0, 32.2, 40.8, 42.7, 92.5, 110.5, 110.7, 115.1, 115.8, 116.0, 124.0, 124.1, 130.9, 139.0, 142.5, 162.4, 165.8, 193.5, 195.5 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -75.21 ppm; *m/z* (ESI): 605.2 (M^+-$C_{26}H_{32}FNO_2Pt$ requires 604.21); $\lambda_{max\text{-}absorption}$($CH_2Cl_2$)/nm 251 (ε/dm^3 mol^{-1} cm^{-1} 26000), 274 (25900), 330 (9500), 361 (7400); $\lambda_{max\text{-}emission}$($CH_2Cl_2$)/nm 489, 523.

Complex 7.[1]



Dimer **D7** (178 mg, 0.173 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (95 mg, 0.518 mmol) and Na_2CO_3 (183 mg, 1.725 mmol). Purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane 1/3 as eluent) yielded yellow crystals (150 mg, 65%). (Found C 47.28, H 4.99, N 2.16. $C_{26}H_{32}BrNO_2Pt$ requires C 46.92, H 4.85, N 2.10); ν_{max}/cm^{-1} 2955, 2934, 2905, 2866, 2366, 2334, 1591, 1587, 1548, 1526, 1497, 1443, 1412, 1389, 1358, 1243, 1221, 1185, 1143, 1070, 1038, 873, 822, 794, 751, 708, 654 and 614; ^{1}H-NMR (600 MHz; $CDCl_3$; Me_4Si): 1.24^l (s, 9H, CH_3), 1.31^j (s, 9H, CH_3), 1.79–1.92^{b,c} (m, 4H, CH_2), 2.82^d (t, *J* = 6.3 Hz, 2H, CH_2), 3.57^a (t, *J* = 6.4 Hz, 2H, CH_2), 5.88^k (s, 1H, CH), 7.19–7.24^{g,h} (m, 2H, ArH), 7.37^f (d, *J* = 8.1 Hz, 1H, ArH), 7.46^e (d, *J* = 8.1 Hz, 1H, ArH), 7.86^i (d, *J* = 1.7 Hz, 1H, ArH) ppm. δ_C (100 MHz; $CDCl_3$; Me_4Si) 21.8, 22.9, 28.5, 28.7, 29.1, 30.9, 32.3, 40.7, 42.2, 92.5, 115.3, 122.0, 123.7, 126.4, 131.6, 132.4, 138.2, 139.0, 145.2, 162.7, 165.8, 193.6, 195.5, 206.8 ppm; *m/z* (ESI): 666.1 (M^+-$C_{26}H_{32}BrNO_2Pt$ requires 664.13); $\lambda_{max\text{-}absorption}$($CH_2Cl_2$)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 38900), 280 (40600), 335 (16100), 372 (10200); $\lambda_{max\text{-}emission}$($CH_2Cl_2$)/nm 501, 535.

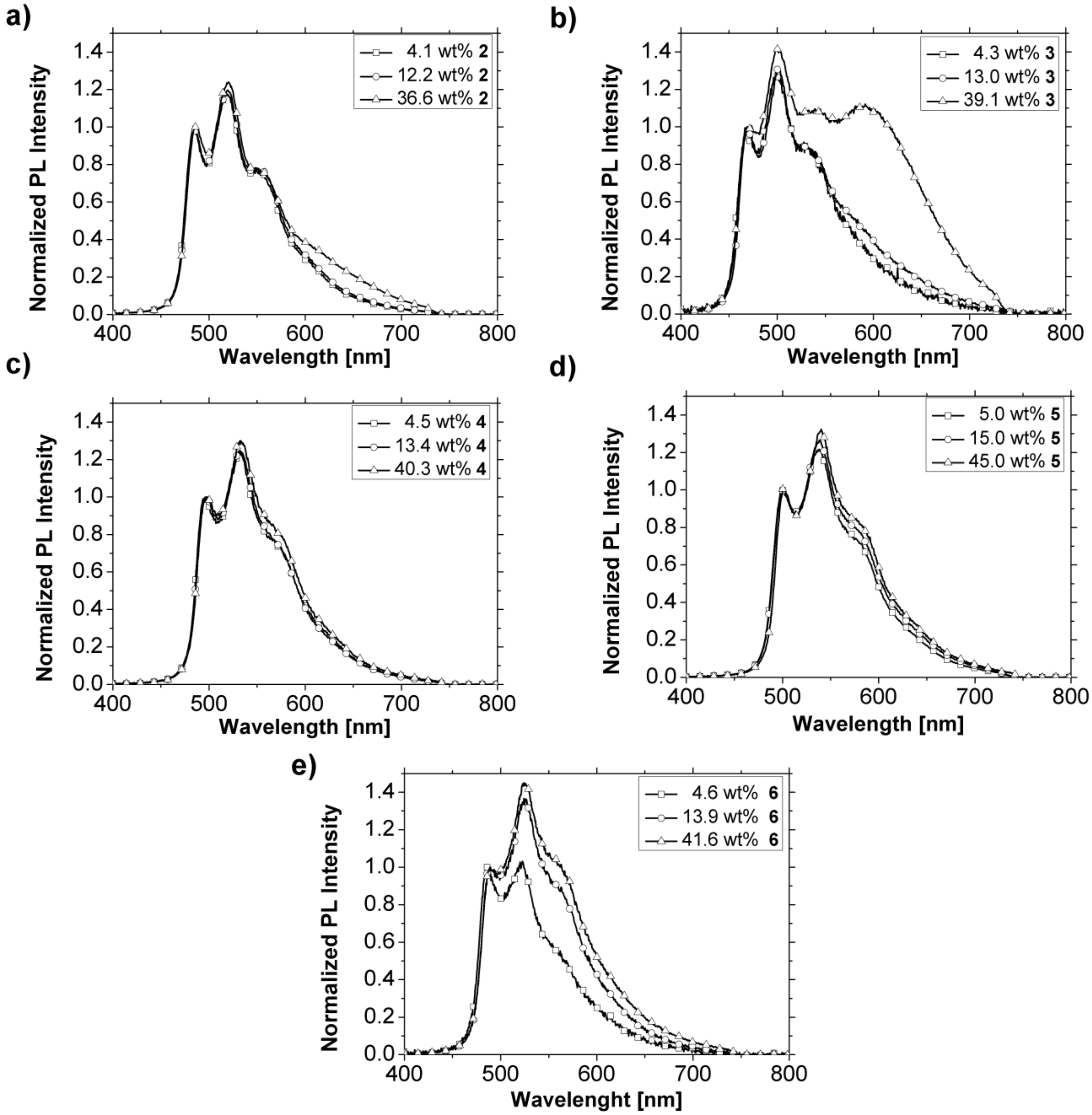


Fig. S1 Photoluminescence spectra of films consisting of various equimolar amounts of the complexes a) **2**, b) **3**, c) **4**, d) **5** and e) **6** in a PVK/OXD-7-matrix recorded at 295 K, 720 ns after excitation with a laser pulse. The spectra were normalized to the highest energy emission peak.

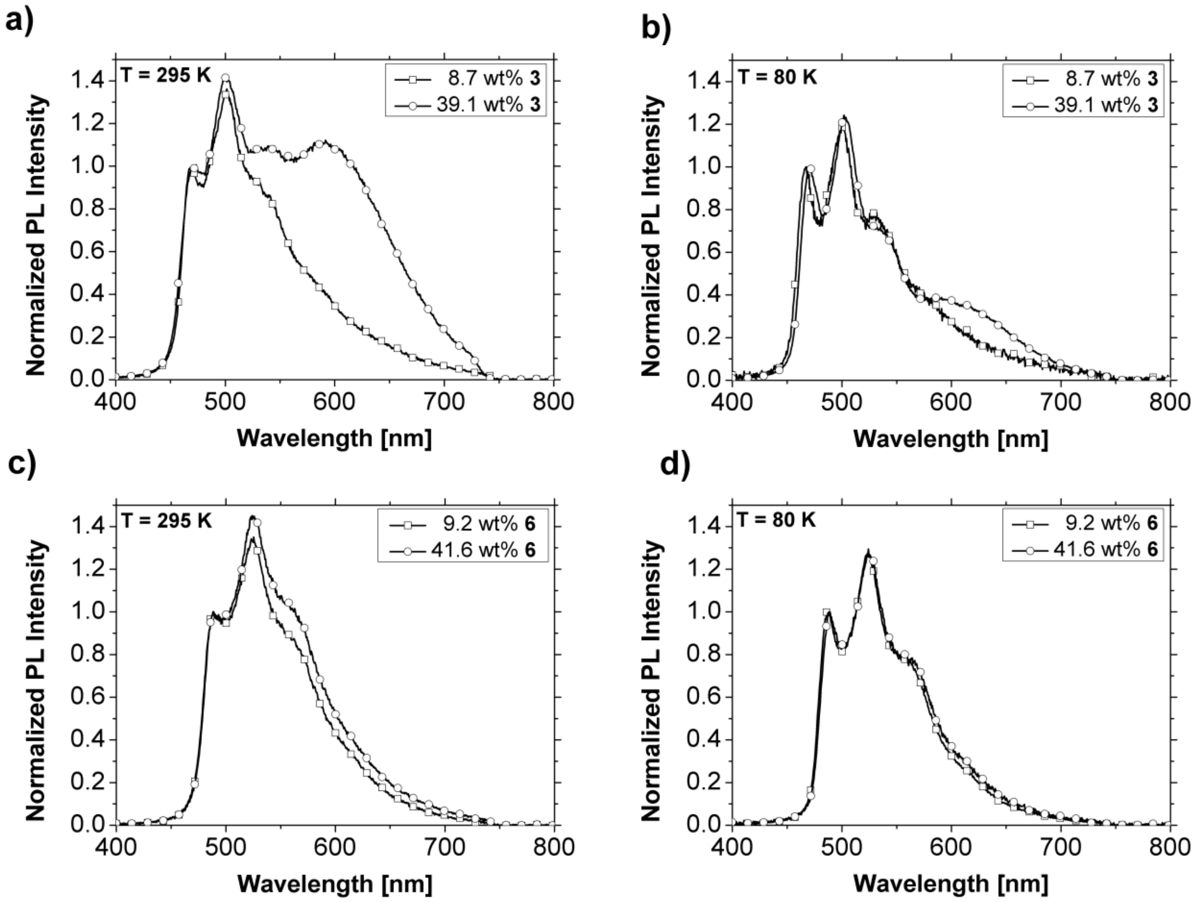


Fig. S2 Temperature depended photoluminescence spectra of films consisting of PVK/OXD-7 doped with various amounts of a.) **3** (recorded at 295 K), b) **6** (recorded at 80 K), c) **6** at (recorded at 295 K) and d) **3** (recorded at 80 K). The spectra were recorded 720 ns after excitation with a laser pulse and normalized to the highest energy emission peak.

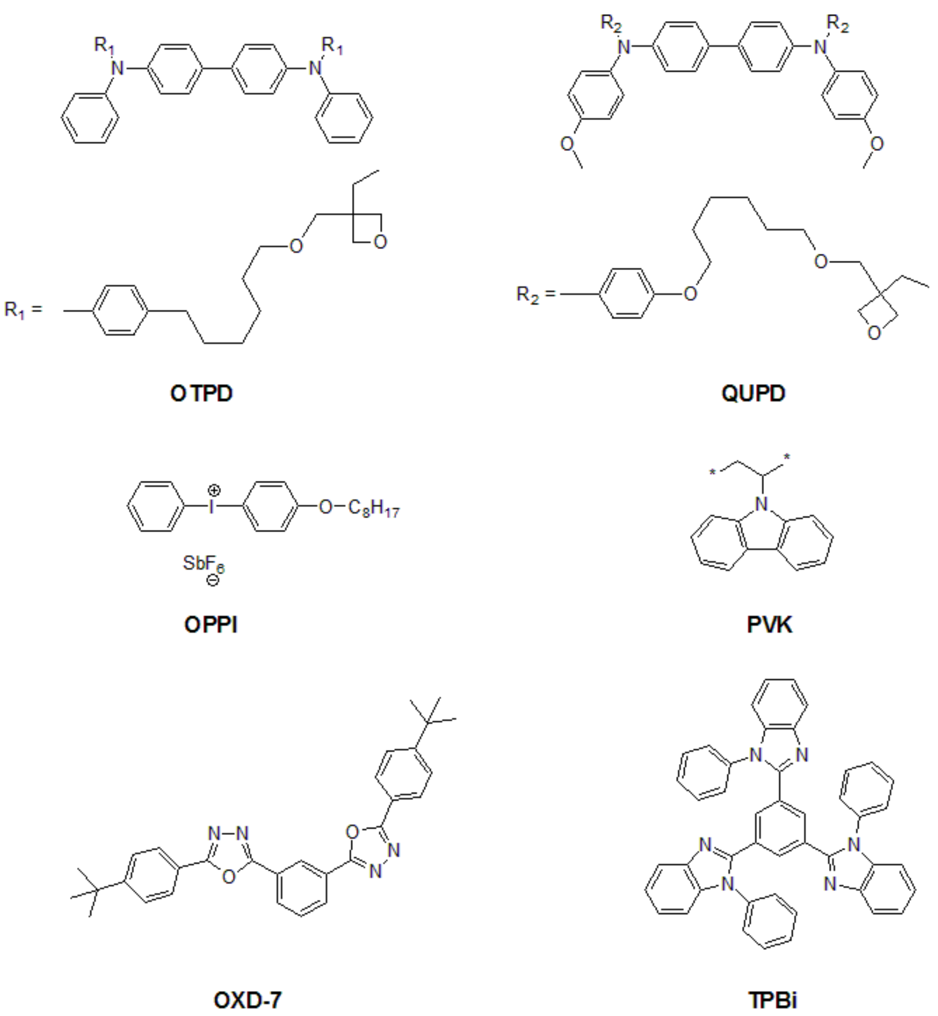


Fig. S3 Chemical structures of **OTPD** (*N,N'-bis*(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexylphenyl]-*N,N'*-diphenyl-4,4'-diamine)), **QUPD** (*N,N'-bis*(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexyloxy)phenyl]-*N,N'-bis*(4-methoxyphenyl)biphenyl-4,4'-diamine)), **OPPI** (4-octyloxydiphenyl-iodonium-hexafluoroantimonate), **PVK** (Poly(vinyl)carbazole), **OXD-7** (1,3-*bis*(*N,N*-t-butyl-phenyl)-1,3,4-oxadiazole) and **TPBi** (1,3,5-*tris*(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene), which were used for the fabrication of solution-processed OLEDs.

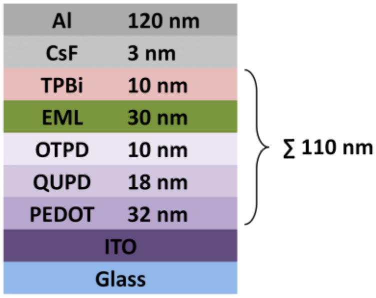
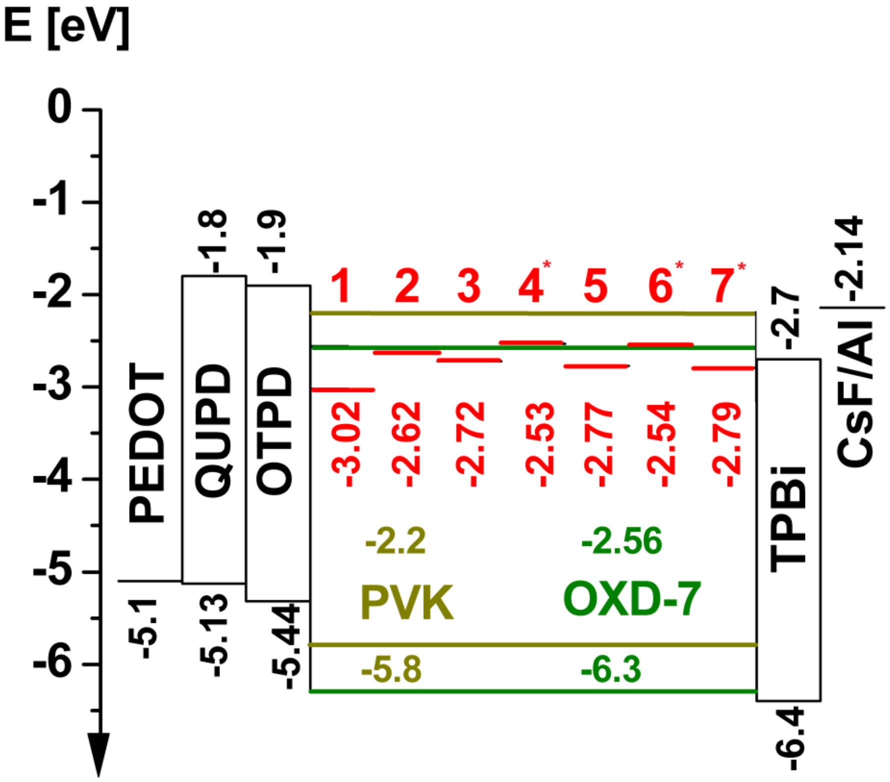


Fig. S4 Device architecture of the OLEDs using **1** – **7** as emitter.



*LUMOs were estimated based on CV-measurements with irreversible reductions

Fig. S5 Schematic representation of the energy levels in fabricated OLEDs. The LUMOs of **1** – **7** and OXD-7 were estimated based on CV-measurements with a scan rate of 100 mV/s.

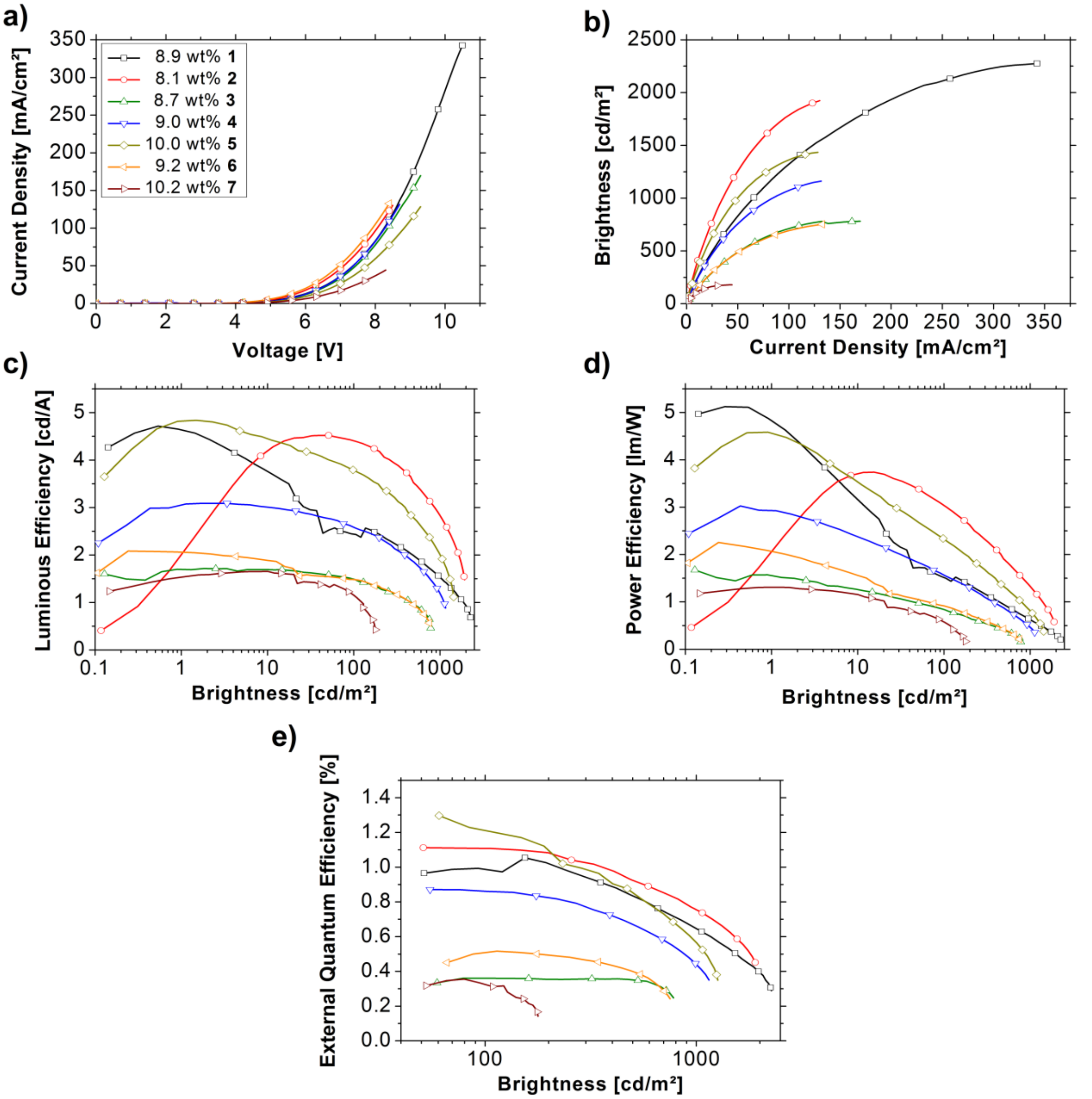


Fig. S6 Performance of the investigated OLEDs containing equimolar amounts of **1** – **7**. a) current density *vs.* voltage, b) brightness *vs.* current density and c) power efficiency, d) luminous efficiency and e)external quantum efficiency (EQE) *vs.* brightness plots. The EQE were calculated according to literature.[10]

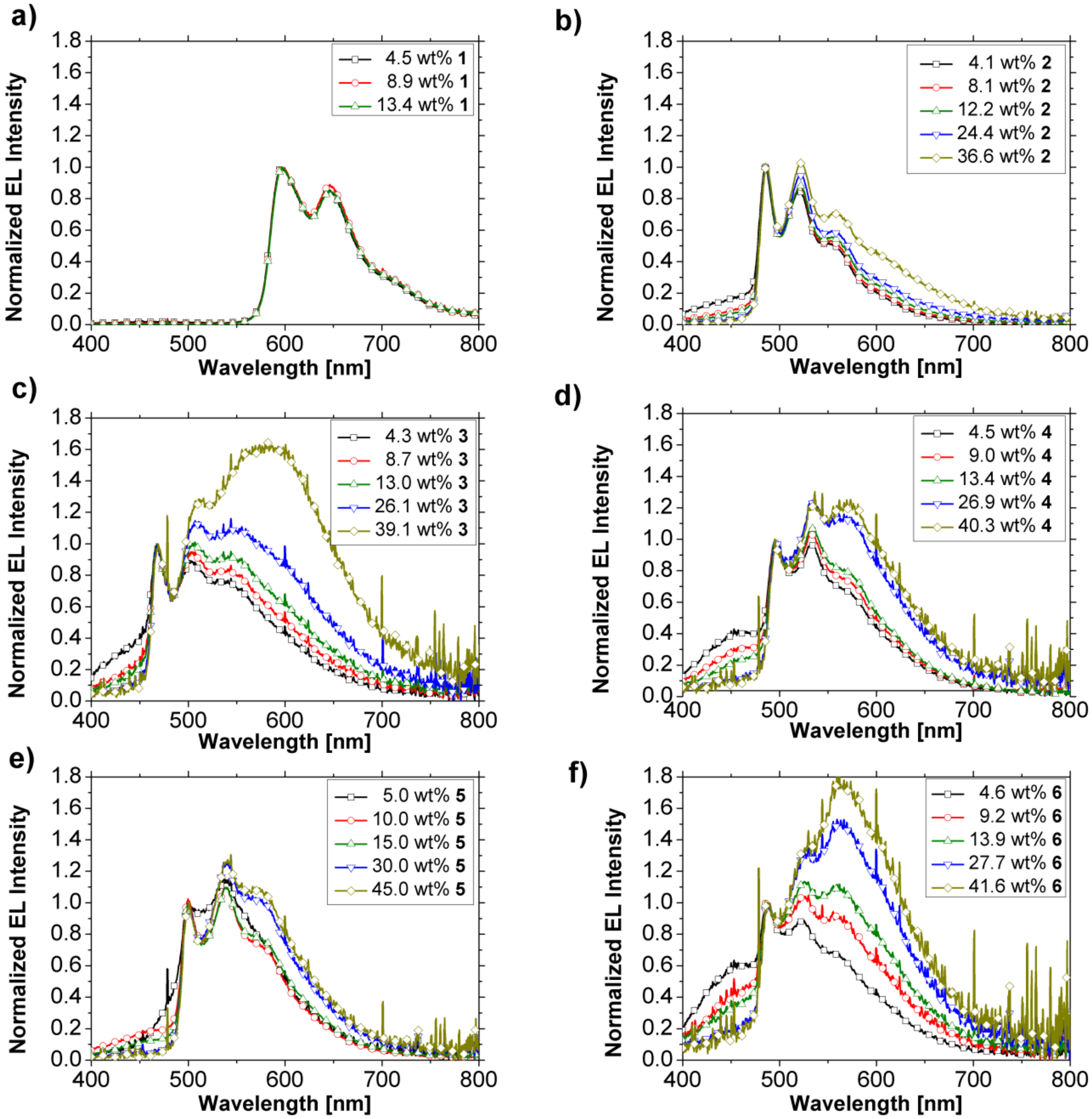


Fig. S7 Electroluminescence spectra of OLEDs with various equimolar concentrations of a) **1**, b) **2**, c) **3**, d) **4**, e) **5** and f) **6** recorded at a current density of 20 mA/cm².

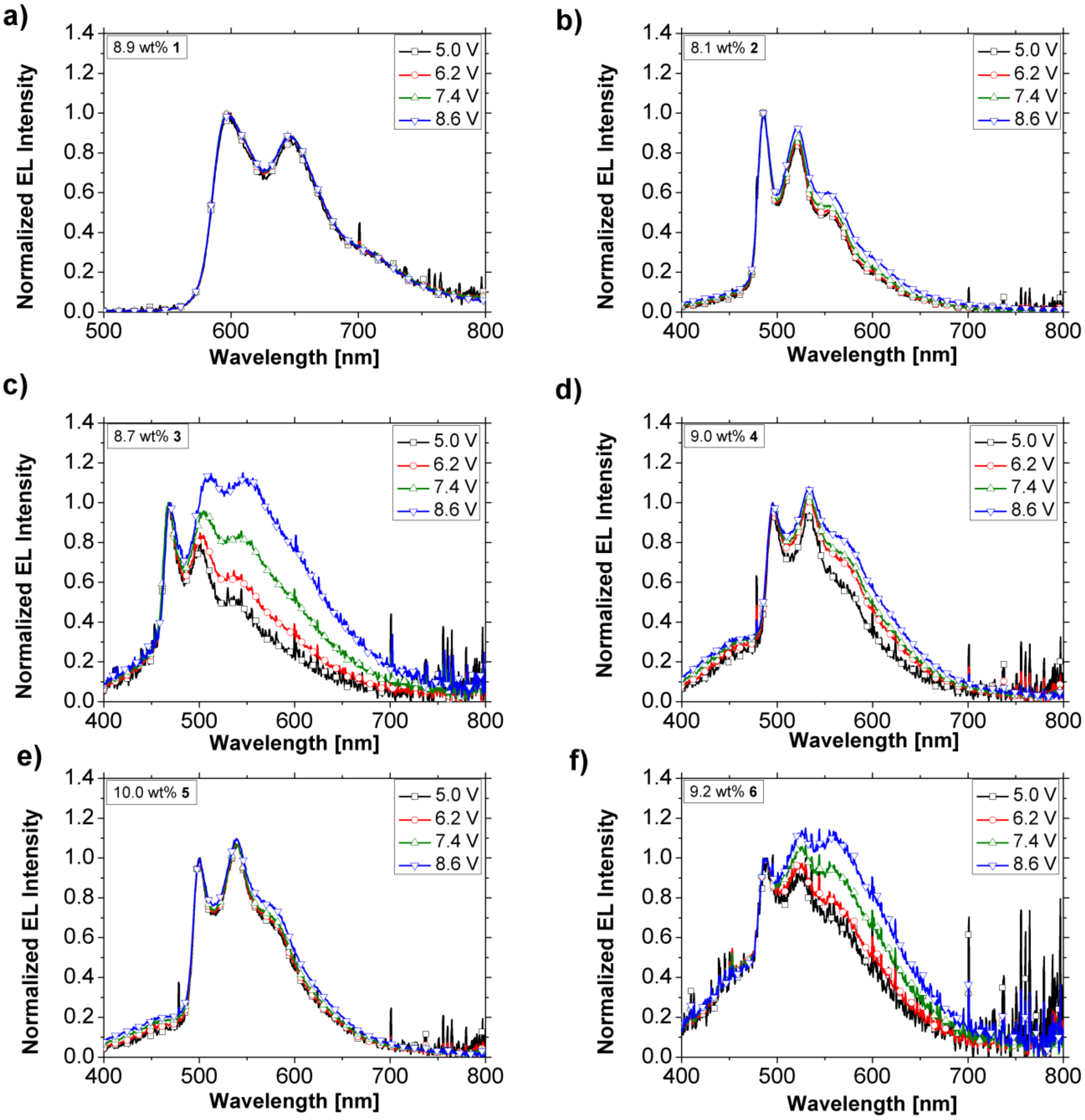


Fig. S8 Electroluminescence spectra of OLEDs with equimolar concentrations of a) 8.9 wt% **1**, b) 8.1 wt% **2**, c) 8.7 wt% **3**, d) 8.9 wt% **4**, e) 10.0 wt% **5** and f) 9.2 wt% **6** driving at various voltages.

Table S1 Electrochemical properties of **1 -7** and estimated LUMOs based in CV-measurements, that were carried out with different scan rate (100 V/s and 100 mV/s).

compound	redox [V] $E_{1/2}^{Red}$ (ν = 100 V/s)	LUMO based on the CV-measurements with ν = 100 V/s	redox [V] $E_{1/2}^{Red}$ (ν = 100 mV/s)	LUMO based on the CV-measurements with ν = 100 mV/s
1	-2.18[a]	-2,92	-2,08[c]	-3,02
2	-2.52[b]	-2,58	-2,48[c]	-2,62
3	-2.42[b]	-2,68	-2,38[c]	-2,72
4	-2.75[c]	-2,35	-2,57[c]	-2,53
5	-2.37[a]	-2,73	-2,33[c]	-2,77
6	-2.58[c]	-2,52	-2,56[c]	-2,54
7	-2.46[c]	-2,64	-2,31[c]	-2,79
OXD-7	---	---	-2,54[c]	-2,56

[a] roughly reversible [b] partially reversible [c] irreversible

Table S2 Phosphorescence lifetimes (τ_i), average phosphorescence lifetimes (τ_{av}), emission maxima ($\lambda_{max\text{-}em.}$) and photoluminescence quantum yield (φ) for various **1 – 7** concentrations in a PVK/OXD-7-matrix with at room temperature.

complex [wt%]		τ_1 [µs]	τ_2 [µs]	τ_{av}[a] [µs]	$\lambda_{max\text{-}em.}$ [nm]	φ
1	4.5	4.49	---	---	599, 647	0.26
1	8.9	4.13	---	---	599, 647	0.24
1	13.4	3.94	---	---	599, 647	0.22
2	4.1	(45%) 2.71	(55%) 6.82	4.97	485, 519	0.63
2	8.1	(18%) 2.04	(82%) 5.41	4.80	485, 519	0.69
2	12.2	(21%) 1.53	(79%) 5.34	4.45	485, 519	0.60
2	24.4	(59%) 2.27	(41%) 5.03	3.40	488, 520	0.60
2	36.6	(61%) 2.45	(39%) 4.82	3.37	488, 520	0.52
3	4.3	(70%) 1.89	(30%) 8.00	3.72	469, 500	0.36
3	8.7	(55%) 1.73	(45%) 6.10	3.70	469, 501	0.45
3	13.0	(58%) 1.40	(42%) 5.67	3.19	469, 501	0.39
3	26.1	(45%) 1.13	(55%) 4.33	2.89	469, 502, 538	0.31
3	39.1	(59%) 1.60	(41%) 4.09	2.62	470, 502, 538, 592	0.33
4	4.5	(41%) 1.02	(59%) 6.41	4.20	495, 533	0.28
4	9.0	(53%) 1.86	(47%) 6.39	3.99	496, 533	0.23
4	13.4	(48%) 1.00	(52%) 4.97	3.06	496, 533	0.19
4	26.9	(64%) 0.99	(36%) 3.85	2.02	496, 533	0.11
4	40.3	(70%) 0.62	(30%) 3.63	1.52	496, 533	0.08
5	5.0	(65%) 4.15	(35%) 8.19	5.56	499, 537	0.30
5	10.0	(47%) 2.94	(53%) 7.14	5.17	500, 538	0.31
5	15.0	(55%) 3.27	(45%) 7.25	5.06	500, 538	0.26
5	30.0	(72%) 2.52	(28%) 5.88	3.46	501, 539	0.20
5	45.0	(80%) 2.47	(20%) 6.98	3.37	501, 539	0.19
6	4.6	(43%) 0.84	(57%) 6.57	4.11	486, 522	0.19
6	9.2	(50%) 1.31	(50%) 6.44	3.88	489, 524	0.22
6	13.9	(47%) 1.84	(53%) 5.68	3.88	489, 524	0.17
6	27.7	(73%) 1.02	(27%) 5.02	2.10	489, 524	0.10
6	41.6	(78%) 0.77	(22%) 4.05	1.49	489, 524	0.07

a) average lifetime

Table S3 Detailed performance data of the investigated OLEDs based on **1** – **7**.

complex [wt%]		max. luminous efficiency [cd/A]	max. luminous efficiency [lmW]	luminous efficiency [cd/A] @ 100 cd/m²	luminous efficiency [cd/A] @ 500 cd/m²	luminous efficiency [cd/A] @ 1000 cd/m²	max. brightness [cd/m²]
1	4.5	3.31	3.26	2.28	1.73	1.33	1865
1	8.9	4.71	5.12	2.43	1.98	1.52	2276
1	13.4	2.15	1.32	2.11	1.88	1.46	2289
2	4.1	3.89	3.14	3.69	2.84	2.23	1646
2	8.1	4.52	3.73	4.39	3.52	2.82	1924
2	12.2	4.03	2.88	3.93	3.31	2.61	1859
2	24.4	4.18	3.36	3.73	2.62	1.82	1385
2	36.6	3.39	2.31	3.16	2.47	1.69	1317
3	4.3	1.64	1.68	1.40	0.87	---	760
3	8.7	1.71	1.57	1.48	0.95	---	781
3	13.0	1.57	1.17	1.37	0.84	---	715
3	26.1	1.56	1.00	1.49	0.98	---	783
3	39.1	1.33	0.83	1.18	0.89	---	724
4	4.5	2.68	2.43	2.29	1.67	1.00	1071
4	9.0	3.09	3.02	2.62	1.86	1.20	1161
4	13.4	0.83	0.47	0.76	0.43	---	647
4	26.9	1.98	1.93	1.51	0.87	---	732
4	40.3	2.64	1.93	2.39	1.56	---	973
5	5.0	1.52	0.97	1.33	1.03	---	907
5	10.0	4.88	4.65	3.63	2.39	1.58	1264
5	15.0	3.60	2.41	3.40	2.41	1.55	1204
5	30.0	3.19	2.02	3.17	2.44	1.63	1256
5	45.0	2.49	1.65	2.31	1.64	---	872
6	4.6	1.47	0.90	1.43	0.97	---	788
6	9.2	2.08	2.25	1.48	0.95	---	751
6	13.9	1.59	1.16	1.48	0.94	---	745
6	27.7	1.43	1.06	1.28	0.64	---	578
6	41.6	1.14	0.83	0.93	---	---	404
7	5.1	1.93	1.44	1.54	---	---	246
7	10.2	1.66	1.31	1.14	---	---	178
7	15.2	0.80	0.50	0.61	---	---	130

Table S4 External quantum efficiency (EQE) of the most efficient OLEDs based on **1** – **7**. The EQEs were calculated according to literature.[10]

complex [wt%]		max. EQE [%]	EQE [%] @ 100 cd/m²	EQE [%] @ 500 cd/m²	EQE [%] @ 1000 cd/m²
1	8.9	1.05	0.99	0.83	0.62
2	8.1	1.11	1.11	0.92	0.73
3	8.7	0.36	0.36	0.35	---
4	9.0	0.87	0.86	0.65	0.45
5	10.0	1.30	1.22	0.87	0.56
6	9.2	0.51	0.50	0.40	---
7	10.2	0.35	0.31	---	---

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[1] C. Karakus, L. H. Fischer, S. Schmeding, J. Hummel, N. Risch, M. Schäferling, E. Holder, *Dalton Trans.* 2012, **41**, 9623.

[2] M. Gaudry, Y. Jasor, T. B. Khac, *Org. Synth.* 1979, **59**, 153.

[3] L. F. Tietze, T. Eicher Reaktionen und Synthesen im organisch-chemischen Praktikum, 1. Aufl., Thieme-Verlag Stuttgart 1981.

[4] J. Hummel, Untersuchungen zur effizienten Synthese verbrückter und funktionalisierter U- und S-förmiger Terpyridine, Dissertation, Universität Paderborn, 2007.

[5] A. F. Casy, J. L. Myers, *J. Chem. Soc.* 1965, 4092.

[6] W. B. Connick, D. Geiger, R. Eisenberg, *Inorg. Chem.* 1999, **38**, 3264; A. Díez, J. Forniés, C. Larraz, E. Lalinde, J. López, A. Martín, M. T. Moreno, V. Sicilia, *Inorg. Chem.* 2010, **49**, 3239.

[7] D. Sielemann, Synthese polycyclischer Pyridinderivate - Mannich-Basen und Iminiumsalze als Schlüsselbausteine für den Aufbau neuartiger Ligandsysteme, Dissertation, Universität Paderborn, 2000.

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[8] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, J. Lewis *J. Chem. Soc., Dalton Trans.* 1973, 404.

[9] V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest, M. E. Thompson, *New J. Chem.* 2002, **26**, 1171.

[10] S. Okamoto, K. Tanaka, Y. Izumi, H. Adachi, T. Yamaji, T. Suzuki, *Jpn. J. Appl. Phys.*, **2001**, *40*, L783.