Electronic Supplementary Information for Dalton Transactions


# Tuning the Electronic Properties of dppz-Ligands and their Palladium(II) Complexes

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## Supplementary Information

**Supplementary Figures**

**Figure S1.** Calculated (B3-LYP, TZVP) electron density for the LUMOs of tfmdppz (left), cdppz (middle) and dcdppz (right).

**Figures S2-S7.** Selected optical spectra (absorption, emission and excitation).

**Supplementary Tables**

**Table S1.** Complete data of absorption and luminescence measurements.

**Table S2.** Complete electrochemical data of free ligands and $Pd^{II}$ complexes. Potentials in V vs. ferrocene/ferrocinium from cyclic voltammetry or square wave voltammetry in 0.1 M DMF/$n$Bu$_4$NPF$_6$ solutions at 298 K; Half wave potentials $E_{1/2}$ given for reversible processes, cathodic peak potentials $E_{pc}$ for irreversible processes.

**Table S3.** Short H···F contacts in the crystal structure of [(dppz)PdMe(Py)][SbF$_6$]

*In Situ* measurement of [(tfmdppz)Pd(Me)(Acetone)]$^+$: [(tfmdppz)Pd(Me)Cl] was suspended in 1 mL of $(CD_3)_2CO$ and an excess of $AgSbF_6$ was added as a solid. After 5 min reaction time at room temperature the mixture was filtered and the solution was analysed with NMR spectroscopy. $\delta_H$(300 MHz; $(CD_3)_2CO$): 9.79 (1 H, m, $H_{dppz8}$), 9.69 (1 H, m, $H_{dppz1}$), 9.04 (1 H, m, $H_{dppz6}$), 8.74 (1 H, s, $H_{dppz10}$), 8.69 (1 H, m, $H_{dppz3}$), 8.61 (1 H, m, $H_{dppz13}$), 8.34 (1 H, m, $H_{dppz12}$), 8.24 (2 H, m, $H_{dppz2,7}$), 1.04 (3 H, s, $H_{Pd-CH3}$). $\delta_C$(300 MHz; $(CD_3)_2CO$): 153.4 (1 C, d, $C_{dppz6}$), 153.2 (1 C, d, $C_{dppz6'}$), 150.9 (1 C, d, $C_{dppz3}$), 150.6 (1 C, d, $C_{dppz3'}$), 137.3 (1 C, d, $C_{dppz8}$), 137.2 (1 C, d, $C_{dppz8'}$), 136.5 (1 C, d, $C_{dppz1}$), 136.3 (1 C, d, $C_{dppz1'}$), 132.2 (1 C, d, $C_{dppz2}$), 132.0 (1 C, d, $C_{dppz2}$), 132.0 (1 C, d, $C_{dppz13}$), 128.4 (1 C, d, $C_{dppz7}$), 128.2 (1 C, d, $C_{dppz7'}$), 128.0 (1 C, d, $C_{dppz10}$), 127.8 (1 C, d, $C_{dppz12}$), 3.3 (1 C, q, $C_{Pd-CH3}$).

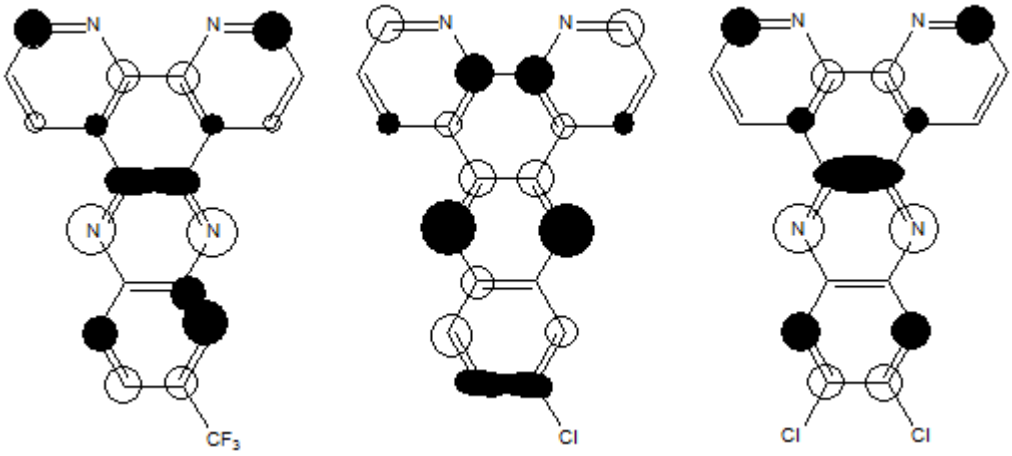
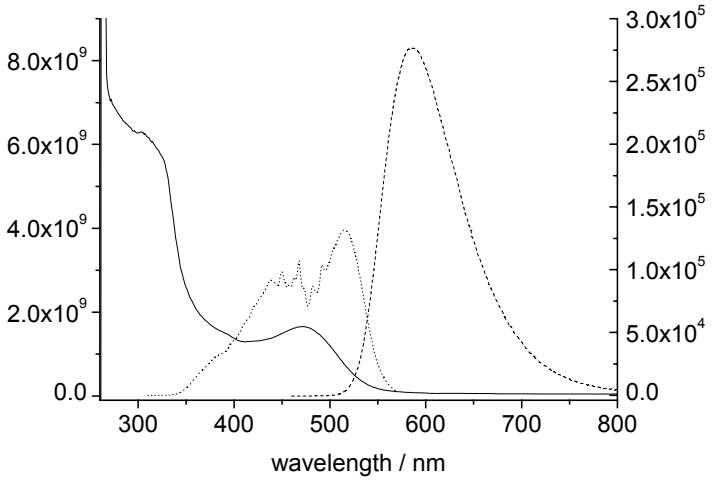



**Figure S1.** Calculated (B3-LYP, TZVP) electron density for the LUMOs of tfmdppz (left), cdppz (middle) and dcdppz (right).




**Figures S2**. Absorption (solid), emission (dashed) and excitation (dotted) spectra of [(adppz)Pd(Me)(Caf)][$SbF_6$] measured in DMF solution at room temperature.

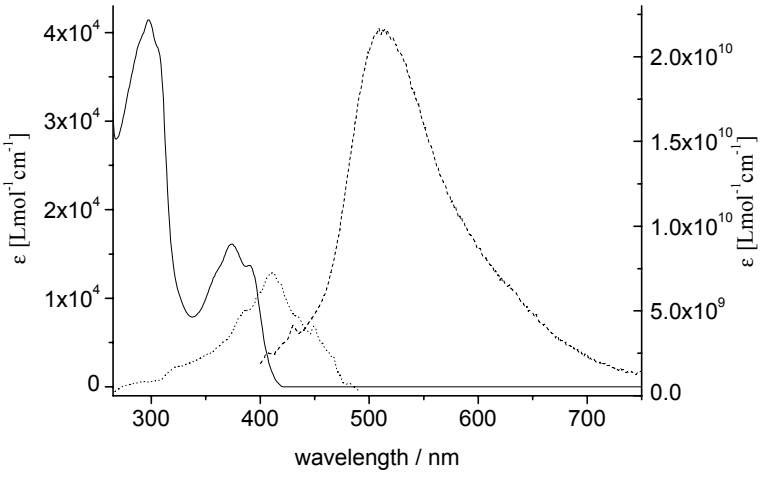



**Figure S3.** Absorption (solid), emission (dashed) and excitation (dotted) spectra of ndppz measured in DMF solution at room temperature

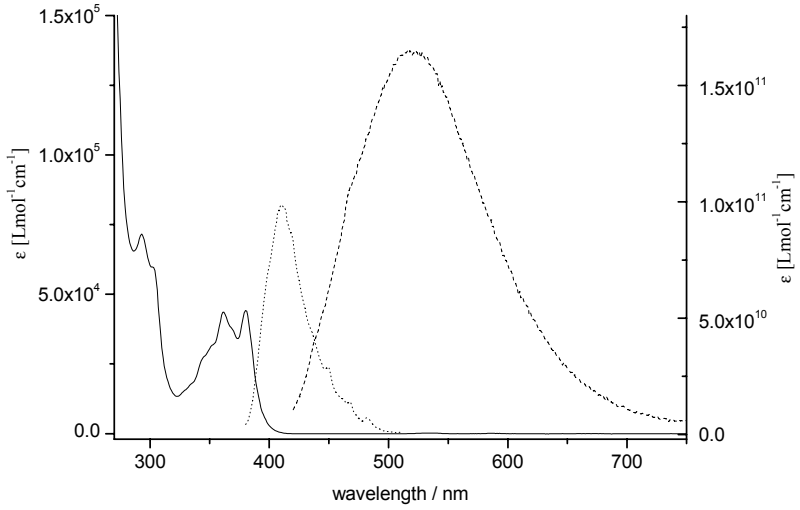



**Figure S4**. Absorption (solid), emission (dashed) and excitation (dotted) spectra of tfmdppz measured in DMF solution at room temperature

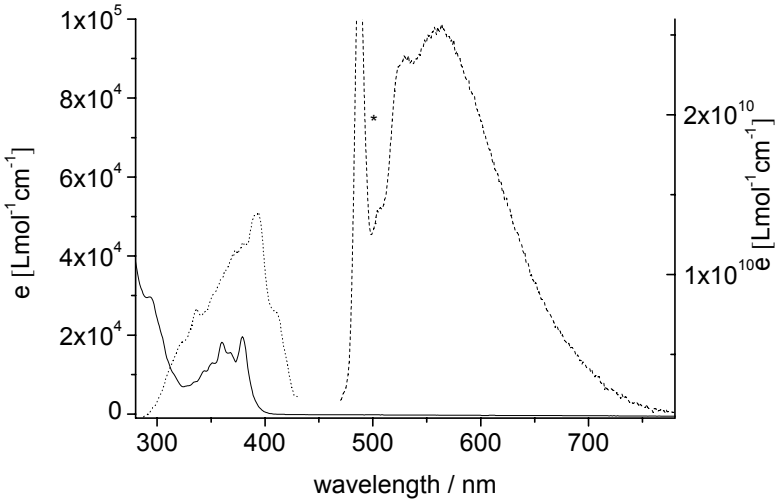



**Figure S5.** Absorption (solid), emission (dashed) and excitation (dotted) spectra of [(dppz)Pd(Me)(Caf)][$SbF_6$] measured in DMF solution at room temperature.

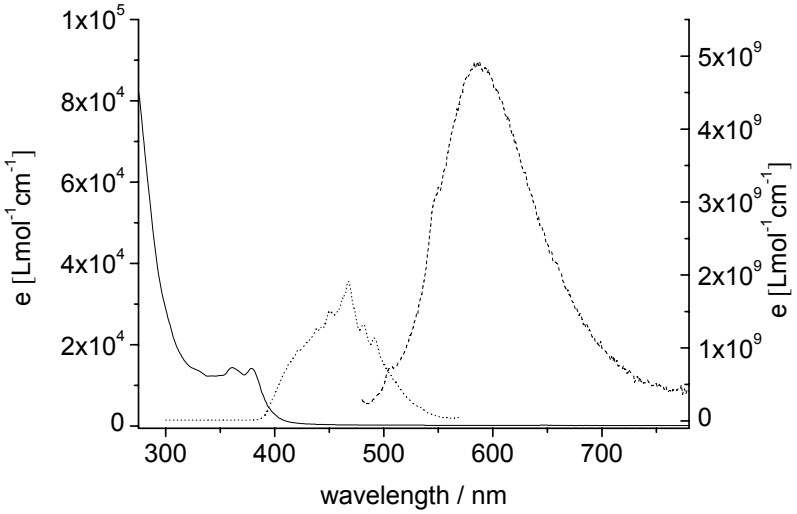



**Figure S6.** Absorption (solid), emission (dashed) and excitation (dotted) spectra of [(tfmdppz)Pd(Me)(Caf)][$SbF_6$] measured in DMF solution at room temperature.

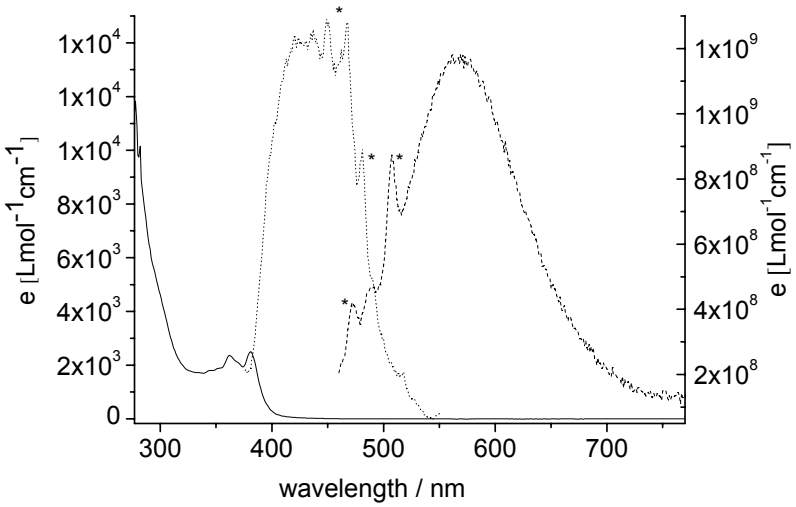



**Figure S7.** Absorption (solid), emission (dashed) and excitation (dotted) spectra of [(dppz)Pd(Me)(1MeUra)] measured in DMF solution at room temperature.

**Table S1.** Complete data of absorption and luminescence measurements

| compound | $\tilde{\nu}_{Abs.max}$ [a] | $\tilde{\nu}_{Exc.max}$ [a] | $\tilde{\nu}_{Em.max}$ [a] | Stokes-shift (1) [b] | Stokes-shift (2) [b] |
|---|---|---|---|---|---|
| adppz | 34130 / 32468 / 22371 | 21277 | 17900 | 4471 | 3377 |
| [(adppz)Pd(Me)(Caf)]$^+$ | 32895 / 21186 | 22222 | 17065 | 4121 | 5157 |
| dppz | 34130 / 27855 / 26385 | 25000 | 22222 | 4163 | 2778 |
| [(dppz)Pd(Me)(Caf)]$^+$ | 34247 / 27778 / 26385 | 22222 | 17700 | 8685 | 4522 |
| tfmdppz | 34130 / 27778 / 26385 | 24390 | 19200 | 7185 | 5190 |
| [(tfmdppz)Pd(Me)(Caf)]$^+$ | 36765 / 27778 / 26455 | 21277 | 17100 | 9355 | 4177 |
| cdppz | 34247 / 27322 / 25907 | 23810 | 19400 | 6507 | 4410 |
| [(cdppz)Pd(Me)(Caf)]$^+$ | 36363 / 27100 / 25707 | 22222 | 16000 | 9707 | 6222 |
| dcdppz | 33900 / 26954 / 25510 | 20000 | 18400 | 7110 | 1600 |
| [(dcdppz)Pd(Me)(Caf)]$^+$ | 35971 / 26882 / 25445 | 21739 | 17300 | 8145 | 4439 |
| ndppz | 33557 / 26810 / 25575 | 24390 | 19500 | 6075 | 4890 |
| [(ndppz)Pd(Me)(Caf)]$^+$ | 34965 / 26954 / 28169 / 25575 | 22222 | 17400 | 8175 | 4822 |

[a] Absorption (Abs.max), Excitation (Exc.max) and Emission maxima (Em.max) / $cm^{-1}$.

[b] Stokes-shift (1) = $\tilde{\nu}_{(Abs.max)} - \tilde{\nu}_{(Em.max)}$ / $cm^{-1}$; Stokes-shift (2) = $\tilde{\nu}_{(Exc.max)} - \tilde{\nu}_{(Em.max)}$ / $cm^{-1}$.

**Table S2.** Complete electrochemical data of free ligands and $Pd^{II}$ complexes Potentials in V vs. ferrocene/ferrocinium from cyclic voltammetry or square wave voltammetry in 0.1 M DMF/$n$Bu$_4$NPF$_6$ solutions at 298 K; Half wave potentials $E_{1/2}$ given for reversible processes, cathodic peak potentials $E_{pc}$ given for irreversible processes.

| **Compound** | $E_{½1}$ | $E_{½2}$ **or** $E_{pc2}$ | $\Delta E_{Red1} - E_{Red2}$ | $E_{pc3}$ | $E_{pc4}$ | **solvent** |
|---|---|---|---|---|---|---|
| ndppz | –1.08 | –1.53 | 0.44 | –2.73 | –2.80 | $CH_3CN$ |
| tfmdppz | –1.45 | –2.29 | 0.78 | –2.55 | –2.94 | $CH_3CN$ |
| dcdppz | –1.45 | –2.20 | 0.73 | –2.34 | –2.87 | $CH_3CN$ |
| cdppz | –1.61 | –2.42 | 0.79 | –2.48 | –2.93 | $CH_3CN$ |
| dppz | –1.64 | –2.46 | 0.78 | –2.94 | / | $CH_3CN$ |
| | | | | | | |
| ndppz | –1.18 | –1.73 | 0.53 | –2.91 | / | DMF |
| tfmdppz | –1.47 | –2.31 | 0.78 | –2.87 | / | DMF |
| dcdppz | –1.35 | –2.16 | 0.76 | –2.77 | / | DMF |
| cdppz | –1.53 | –2.33 | 0.76 | –2.33 | –2.85 | DMF |
| dppz | –1.66 | –2.46 | 0.73 | –2.89 | / | DMF |
| adppz | –1.84 | –1.88 | 0.51 | –2.84 | / | DMF |
| | | | | | | |
| $[(ndppz)Pd(Me)(Caf)]^+$ | −1.03 | −1.56 | 0.57 | −2.39 | / | DMF |
| $[(tfmdppz)Pd(Me)(Caf)]^+$ | −1.20 | −2.02 | 0.72 | −2.38 | / | DMF |
| $[(dcdppz)Pd(Me)(Caf)]^+$ | −1.23 | −2.06 | 0.79 | −2.33 | / | DMF |
| $[(cdppz)Pd(Me)(Caf)]^+$ | −1.27 | −2.01 | 0.73 | −2.30 | / | DMF |
| $[(dppz)Pd(Me)(Caf)]^+$ | −1.44 | −2.21 | 0.86 | −2.89 | / | DMF |
| $[(adppz)Pd(Me)(Caf)]^+$ | −1.38 | −2.14 | 0.78 | −3.18 | / | DMF |
| | | | | | | |
| [(ndppz)Pd(Me)Cl] | –1.05 | –1.54 (irr) | 0.49 | –2.38 | –2.91 | DMF |
| [(tfmdppz)Pd(Me)Cl] | –1.25 | –2.08 (irr) | 0.73 | –2.33 | –2.92 | DMF |
| [(dcdppz)Pd(Me)Cl] | –1.33 | –2.12 (irr) | 0.79 | –2.33 | –2.51 | DMF |
| [(cdppz)Pd(Me)Cl] | –1.33 | –2.07 (irr) | 0.64 | –2.30 | –2.81 | DMF |
| [(dppz)Pd(Me)Cl] | −1.35 | −2.06 (irr) | 0.71 | / | / | DMF |

**Table S3.** Short H···F contacts in the crystal structure of $[(dppz)PdMe(Py)][SbF_6]$

| | | | |
|---|---|---|---|
| F1···H8 | 2.586(7) | F4···H4 | 2.591(4) |
| F1···H9 | 2.610(8) | F4···H15 | 2.621(6) |
| F2···H5 | 2.695(5) | F5···H2 | 2.420(5) |
| F2···H6 | 2.629(5) | F5···H6 | 2.845(5) |
| F3···H3 | 2.665(5) | F5···H9 | 2.691(6) |
| F3···H14 | 2.538(6) | F6···H5 | 2.573(5) |
| F3···H23 | 2.439(5) | F6···H22 | 2.662(6) |
| F4···H3 | 2.594(4) | | |