Supporting Information

Triplet Energy *vs* Electron Transfers in Porphyrin- and Tetrabenzoporphyrin-carboxylates/Pd$_3$(dppm)$_3$(CO)$^{2+}$ Cluster Assemblies; A Question of Negative Charge

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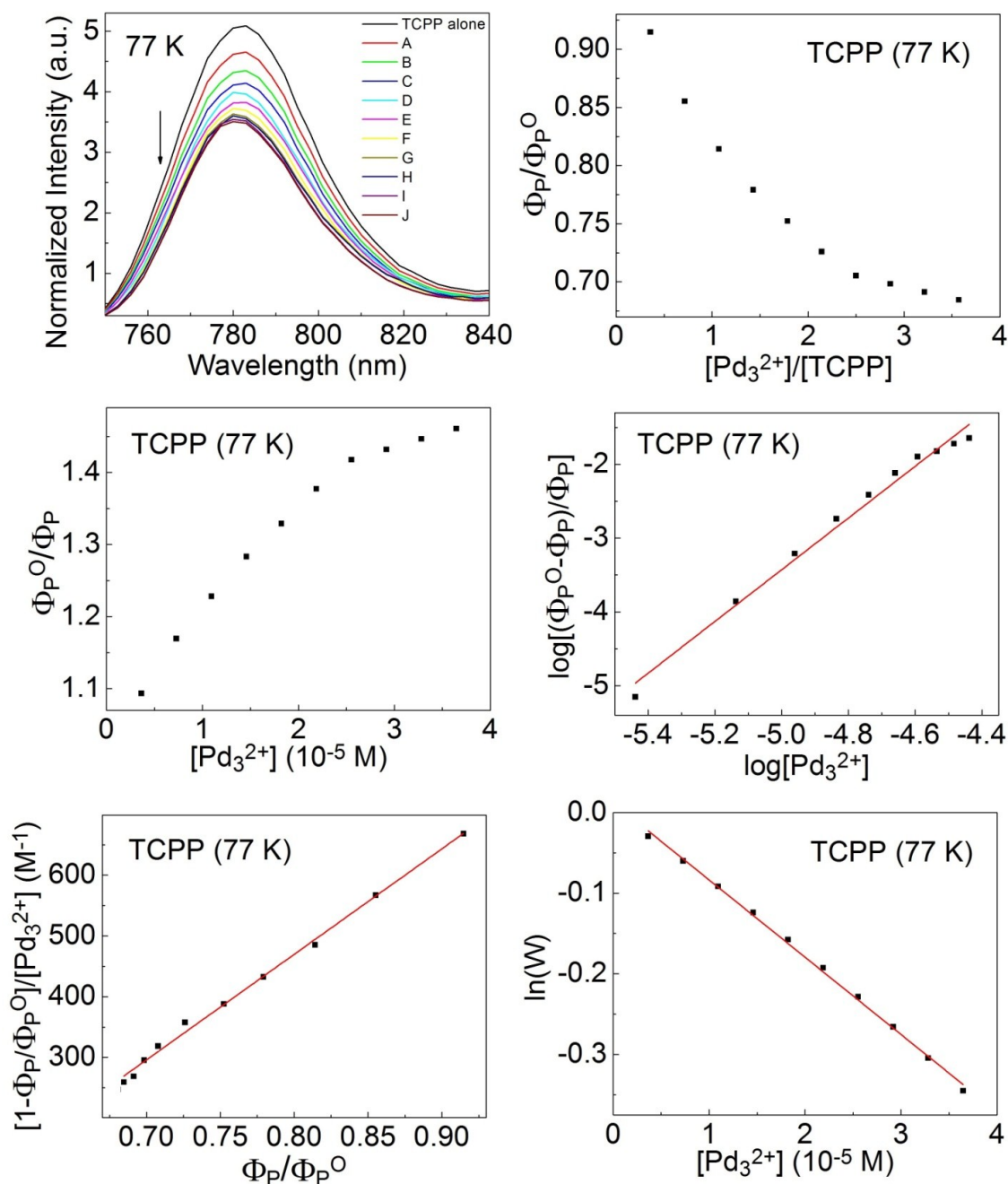bDépartement de chimie, Université du Québec à Montréal, Montréal, QC, H2X 2J6, Canada.

Table of Content

Table S1. Phosphorescence lifetimes for **TCPP** and **TCPBP** in 1:1 MeOH:2MeTHF mixture with increasing amount of **[Pd$_3^{2+}$]** at 77 K.

Porphyrins *vs* **[Pd$_3^{2+}$]**	**TCPP** (ms)	**TCPBP** (ms)
1:0	25.18±0.47	24.20±0.44
1:0.25	25.14±0.42	24.17±0.49
1:0.5	25.10±0.37	24.12±0.48
1:0.75	25.06±0.38	24.07±0.55
1:1	25.01±0.44	24.03±0.50

Figure S1. Top left: variation of phosphorescence spectra of **TCPP** (1.02×10^{-5} M) upon adding **[Pd$_3^{2+}$]** in 1:1 MeOH:2MeTHF at 77 K. Curves A-J were obtained with successive addition of **[Pd$_3^{2+}$]**. Each curve represents an increase in **[Pd$_3^{2+}$]** concentration by 3.65×10^{-6} for **TCPP**. Top right: relative decrease of intensity with respect to the starting intensity. Middle left: plot of $(\Phi_P°/\Phi_P)$ *vs* **[Pd$_3^{2+}$]** (*i.e.* Stern-Volmer plot). Middle right: graph of $\log[(\Phi_P°-\Phi_P)/\Phi_P]$ *vs* $\log[\textbf{Pd}_3^{2+}]$. Bottom left: graph of $[1-(\Phi_P/\Phi_P°)]/[\textbf{Pd}_3^{2+}]$ *vs* $(\Phi_P/\Phi_P°)$. Bottom right: graph of $\ln(W)$ *vs* [**Pd$_3^{2+}$**] for **TCPP•••[Pd$_3^{2+}$]$_x$** assembly in 1:1 MeOH:2MeTHF at 77 K.
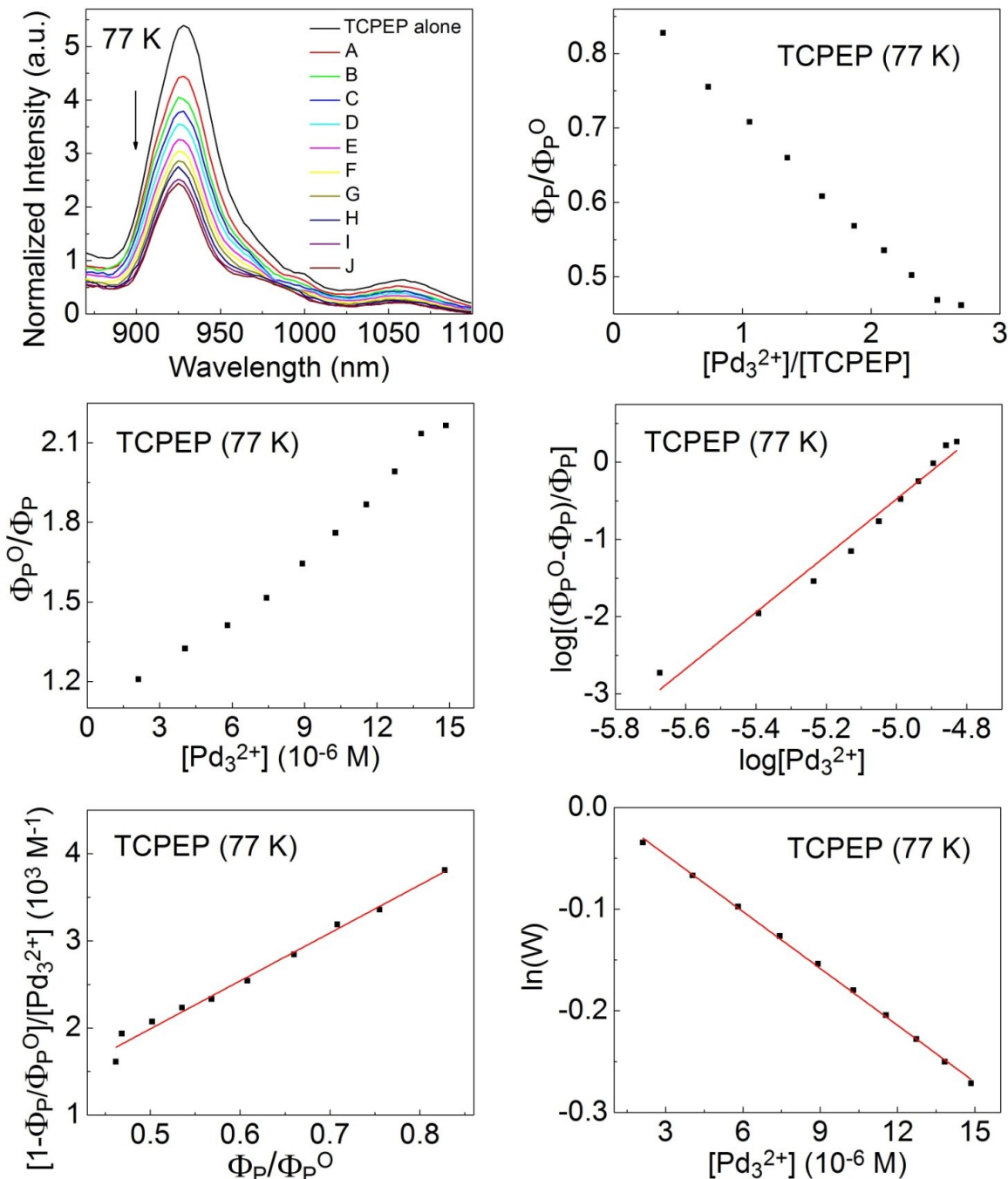
Figure S2. Top left: variation of phosphorescence spectra of **TCPEP** (5.50×10^{-6} M) upon adding **[Pd$_3^{2+}$]** in 1:1 MeOH:2MeTHF at 77 K. Curves A-J were obtained with successive addition of **[Pd$_3^{2+}$]**. Each curve represents an increase in **[Pd$_3^{2+}$]** concentration by 2.11×10^{-6} for **TCPEP**. Top right: relative decrease of intensity with respect to the starting intensity. Middle left: plot of ($\Phi_P°/\Phi_P$) *vs* **[Pd$_3^{2+}$]** (*i.e.* Stern-Volmer plot). Middle right: graph of $\log[(\Phi_P°-\Phi_P)/\Phi_P]$ *vs* $\log[\textbf{Pd}_3^{2+}]$. Bottom left: graph of $[1-(\Phi_P/\Phi_P°)]/[\textbf{Pd}_3^{2+}]$ *vs* ($\Phi_P/\Phi_P°$). Bottom right: graph of $\ln(W)$ *vs* **[Pd$_3^{2+}$]** for **TCPEP•••[Pd$_3^{2+}$]$_x$** assembly in 1:1 MeOH:2MeTHF at 77 K.
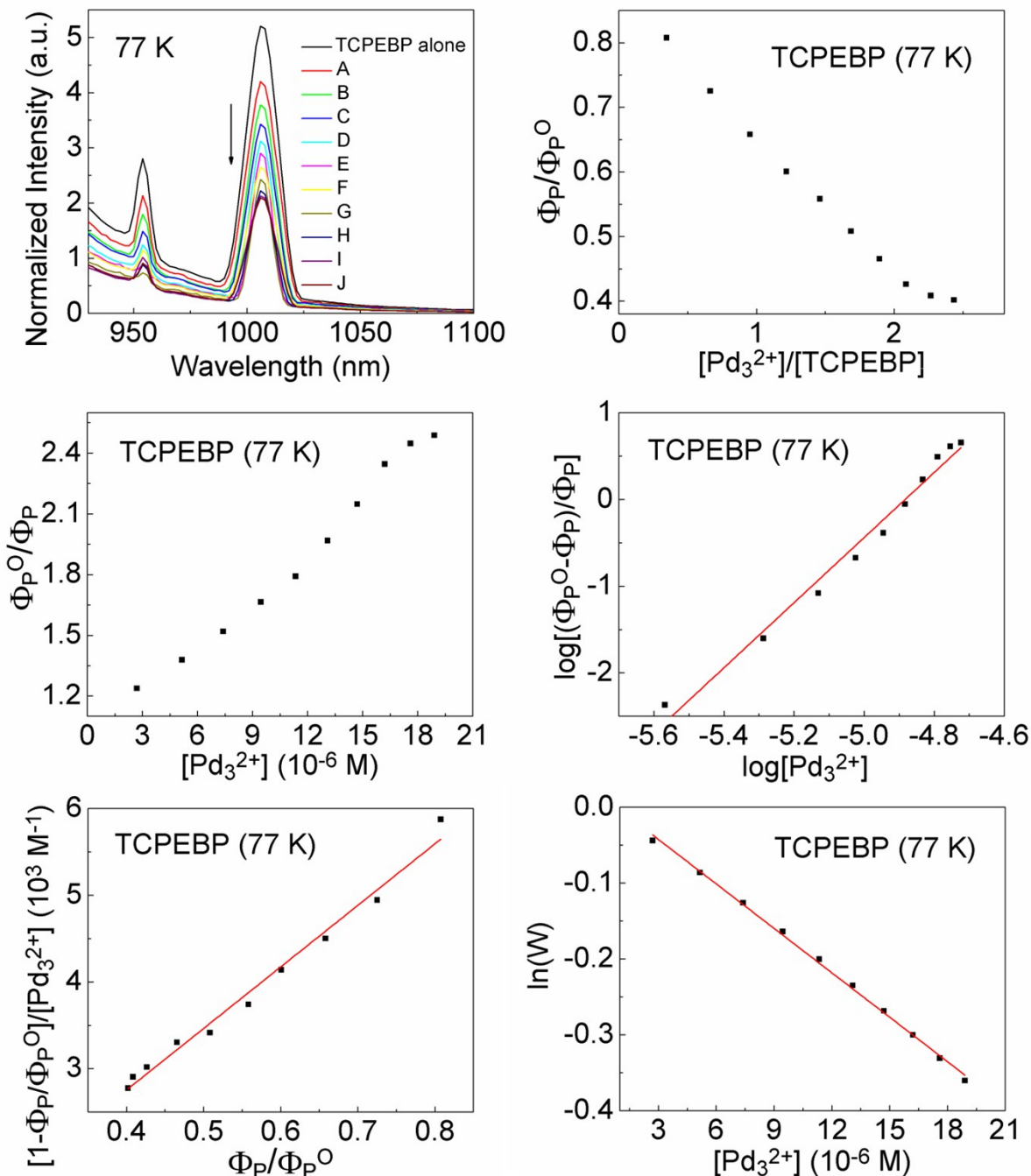
Figure S3. Top left: variation of phosphorescence spectra of **TCPEBP** (7.78×10^{-6} M) upon adding **[Pd$_3$$^{2+}$]** in 1:1 MeOH:2MeTHF at 77 K. Note that the phosphorescence peaks do not move upon changing the excitation wavelength. Curves A-J were obtained with successive addition of **[Pd$_3$$^{2+}$]**. Each curve represents an increase in **[Pd$_3$$^{2+}$]** concentration by 5.67×10^{-5} for **TCPEBP**. Top right: relative decrease of intensity with respect to the starting intensity. Middle left: plot of $(\Phi_P°/\Phi_P)$ *vs* **[Pd$_3$$^{2+}$]** (*i.e.* Stern-Volmer plot). Middle right: graph of $\log[(\Phi_P°-\Phi_P)/\Phi_P]$ *vs* $\log$**[Pd$_3$$^{2+}$]**. Bottom left: graph of $[1-(\Phi_P/\Phi_P°)]/$**[Pd$_3$$^{2+}$]** *vs* $(\Phi_P/\Phi_P°)$. Bottom right: graph of $\ln(W)$ *vs* **[Pd$_3$$^{2+}$]** for **TCPEBP•••[Pd$_3$$^{2+}$]$_x$** assembly in 1:1 MeOH:2MeTHF at 77 K.
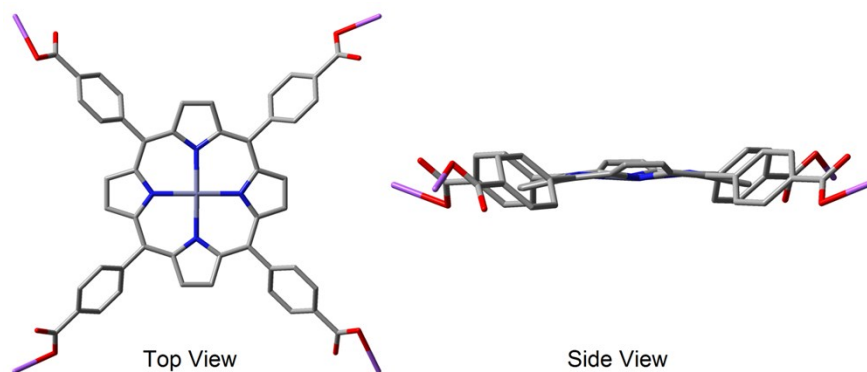
Figure S4. Optimized triplet geometry of **TCPP** (as Na$^+$ salt) in a MeOH solvent field.

| LSOMO-1 | LSOMO | HSOMO | HSOMO+1 |
| (-5.47942) | (-5.42418) | (-3.54038) | (-2.40624) |
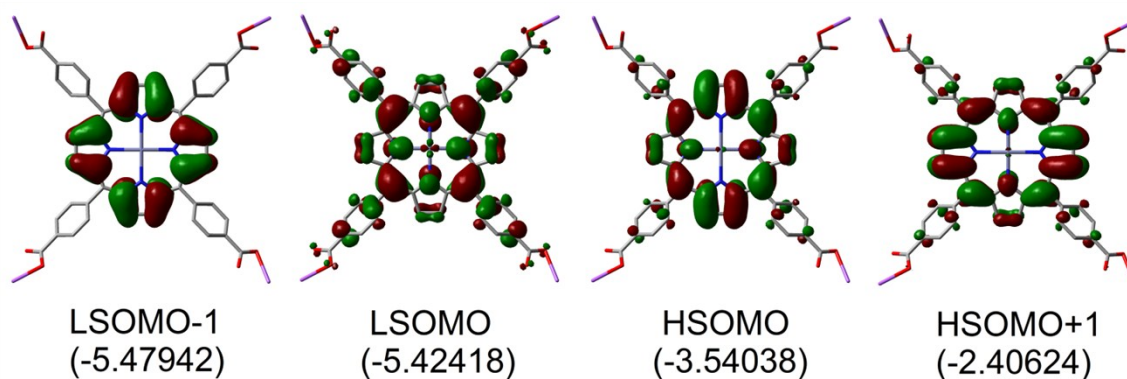
Figure S5. Representations of the semi-occupied frontier MOs of **TCPP** (Na$^+$ salt) in MeOH solvent field (energies in eV).

Table S2. Evaluation of the (S$_0$-T$_1$) energy gap for **TCPP**.

	Singlet S$_0$ (a.u.)	Triplet T$_1$ (a.u.)	(S$_0$-T$_1$) (a.u.)	(S$_0$-T$_1$) (eV)	Computed position of phosphorescence (nm)
TCPP	-3540.21912	-3540.16192	0.05720	1.55653	797
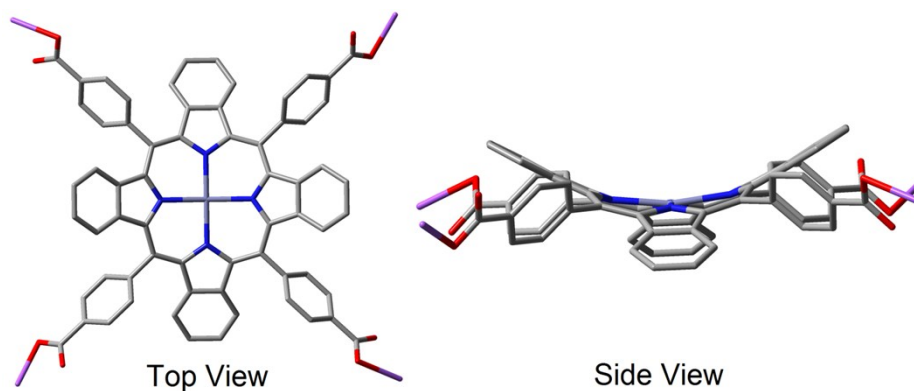
Figure S6. Optimized triplet geometry of **TCPBP** (Na$^+$ salt) in MeOH solvent field.

LSOMO-1
(-5.20513)

LSOMO
(-5.11126)

HSOMO
(-3.33821)

HSOMO+1
(-2.14502)

Figure S7. Representations of the semi-occupied frontier MOs of **TCPBP** (Na$^+$ salt) in MeOH solvent field (energies in eV).

Table S3. Evaluation of the (S$_0$-T$_1$) energy gap for **TCPBP**.

	Singlet S$_0$ (a.u.)	Triplet T$_1$ (a.u.)	(S$_0$-T$_1$) (a.u.)	(S$_0$-T$_1$) (eV)	Computed position of phosphorescence (nm)
TCPBP	-4154.76960	-4154.71623	0.05337	1.45227	855

Top View   Side View

Figure S8. Optimized triplet geometry of **TCPEP** (Na$^+$ salt) in MeOH solvent field.

LSOMO-1
(-5.63207)

LSOMO
(-5.25303)

HSOMO
(-3.76161)

HSOMO+1
(-2.85413)

Figure S9. Representations of the semi-occupied frontier MOs of **TCPEP** (as Na$^+$ salt) in a MeOH solvent field (energies in eV).

Table S4. Evaluation of the (S$_0$-T$_1$) energy gap for **TCPEP** in a MeOH solvent field.

	Singlet S$_0$ (a.u.)	Triplet T$_1$ (a.u.)	(S$_0$-T$_1$) (a.u.)	(S$_0$-T$_1$) (eV)	Computed position of phosphorescence (nm)
TCPEP	-3844.86559	-3844.81791	0.04768	1.29750	957
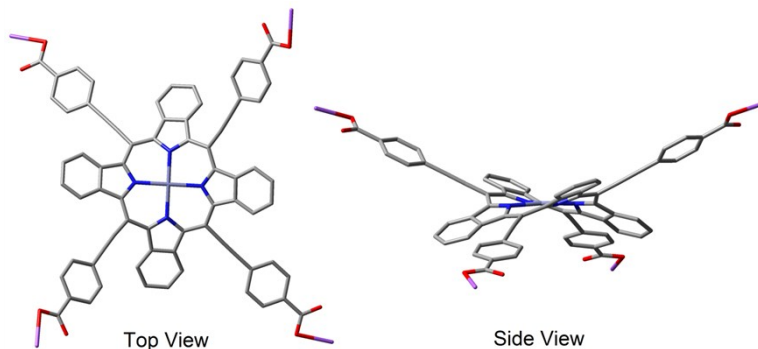
Figure S10. Optimized triplet geometry of **TCPEBP** (as Na$^+$ salt) in a MeOH solvent field.

LSOMO-1 (-5.32132)   LSOMO (-4.92378)   HSOMO (-3.75099)   HSOMO+1 (-2.71944)
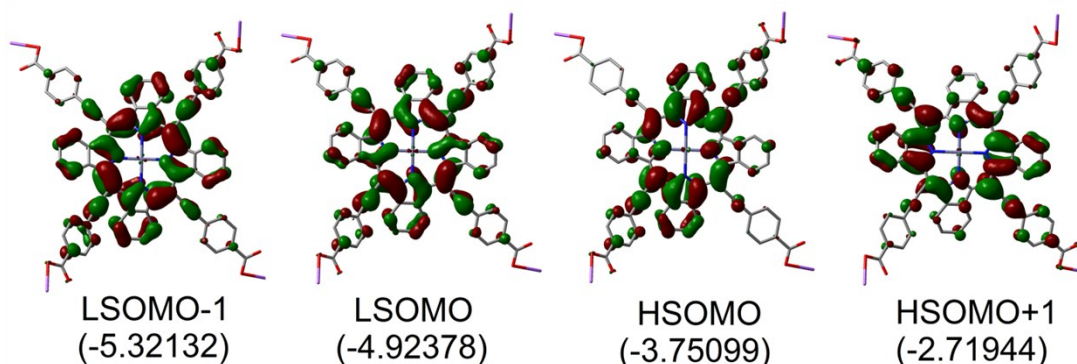
Figure S11. Representations of the semi-occupied frontier MOs of **TCPEBP** (as Na$^+$ salt) in a MeOH solvent field (energies in eV).
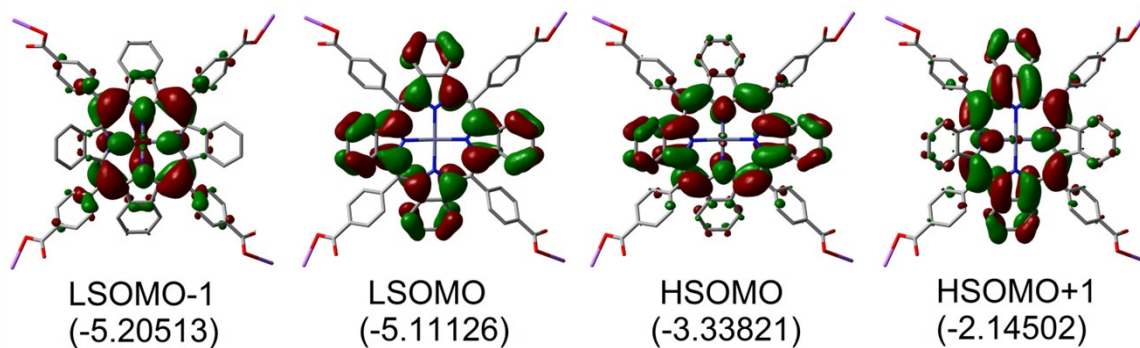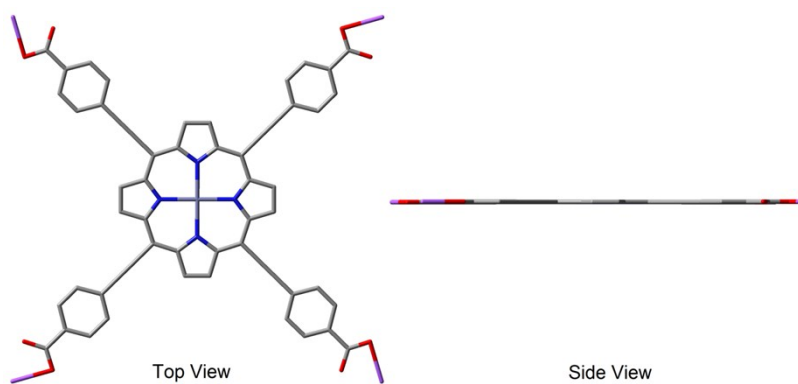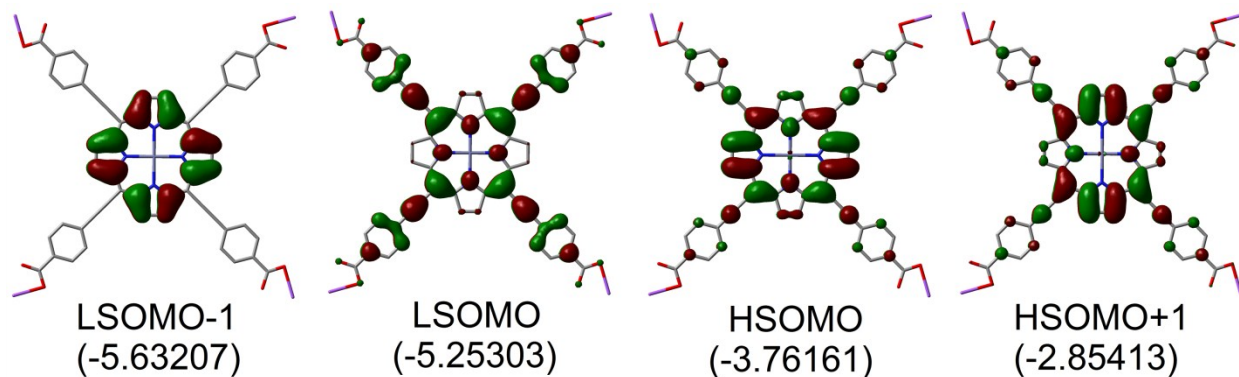
Table S5. Evaluation of the (S$_0$-T$_1$) energy gap for **TCPEBP**.

	Singlet S$_0$ (a.u.)	Triplet T$_1$ (a.u.)	(S$_0$-T$_1$) (a.u.)	(S$_0$-T$_1$) (eV)	Computed position of phosphorescence (nm)
TCPEBP	-4459.41685	-4459.37301	0.04384	1.19282	1041

Side View   Top View
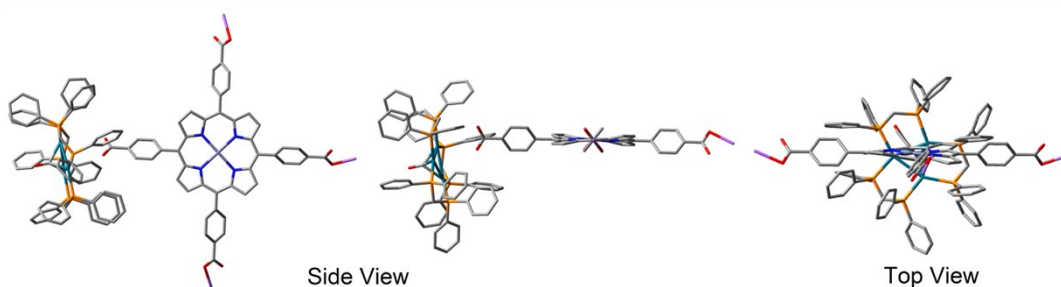
Figure S12. Optimized triplet geometry of the **TCPP•••[Pd$_3$$^{2+}$]** assembly in a MeOH solvent field.

LSOMO-1
(-5.74363)

LSOMO
(-5.44323)

HSOMO
(-4.16242)

HSOMO+1
(-3.04950)
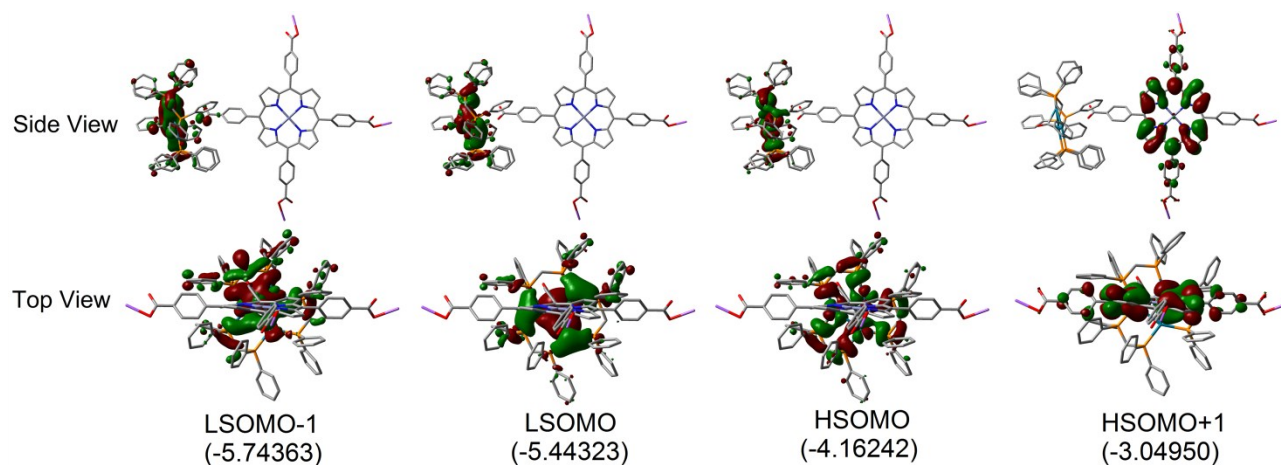
Figure S13. Representations of the semi-occupied frontier MOs of the **TCPP•••[Pd$_3^{2+}$]** assembly in MeOH solvent field (energies in eV).

Table S6. Comparison of selected calculated distances in the **TCPP•••[Pd$_3^{2+}$]** assembly.

	Singlet S$_0$ (Å)[a]	Triplet T$_1$(Å)
Pd-Pd	2.706, 2.696, 2.690 (av.=2.697)	2.829, 2.819, 2.802 (av.=2.817)
Pd-P	2.415, 2.408, 2.405, 2.401, 2.398, 2.394 (av.=2.404)	2.446, 2.430, 2.428, 2.426, 2.425, 2.422 (av.=2.430)
Pd•••O	1st O: 3.861, 3.754, 3.608 (av.=3.741) 2nd O: 5.605, 4.447, 4.444 (av.=4.832)	1st O: 4.002, 3.711, 3.031 (av.=3.581) 2nd O: 5.842, 4.747, 3.711 (av.=4.767)
Pd•••Zn	13.580, 13.339, 13.326 (av.=13.415)	13.472, 13.361, 13.165 (av.=13.333)

[a]From reference 22b of the text.

LSOMO-1
(-5.15942)

LSOMO
(-4.75398)

HSOMO
(-4.74119)

HSOMO+1
(-2.30012)

Figure S14. Representations of the semi-occupied frontier MOs of the **TCPBP•••[Pd$_3^{2+}$]** assembly in MeOH solvent field (energies in eV).
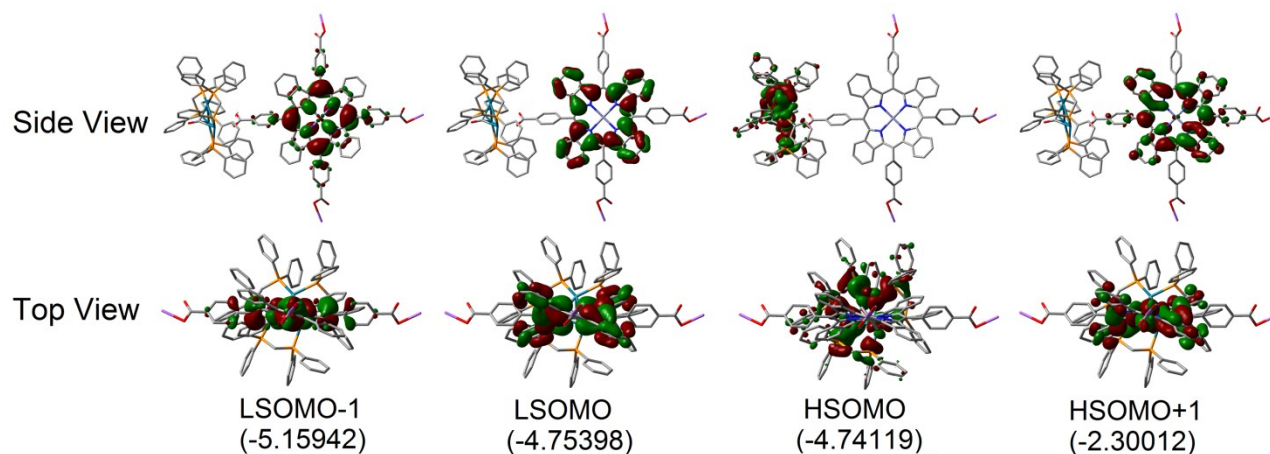
Table S7. Comparison of selected calculated distances in the **TCPBP•••[Pd₃²⁺]** assembly.

|	Singlet S_0 (Å)[a]	Triplet T_1 (Å)
Pd-Pd	2.702, 2.691, 2.675 (av.=2.689)	2.934, 2.885, 2.795 (av.=2.871)
Pd-P	2.449, 2.438, 2.403, 2.397, 2.392, 2.389 (av.=2.411)	2.501, 2.469, 2.459, 2.456, 2.413, 2.399 (av.=2.450)
Pd•••O	1st O: 3.645, 3.631, 3.485 (av.=3.587) 2nd O: 4.055, 3.745, 3.443 (av.=3.748)	1st O: 3.648, 3.545, 3.204 (av.=3.466) 2nd O: 4.209, 3.401, 3.303 (av.=3.638)
Pd•••Zn	13.340, 13.025, 12.354 (av.=12.906)	13.195, 13.083, 12.209 (av.=12.829)

[a]From reference 22b.of the text.
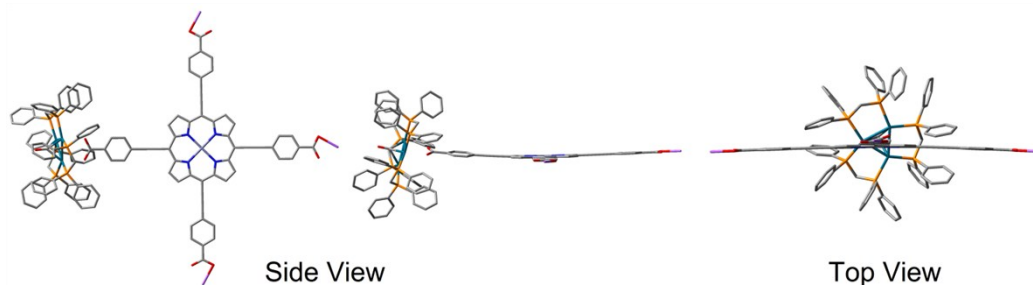
Figure S15. Optimized triplet geometry of the **TCPEP•••[Pd₃²⁺]** assembly in MeOH solvent field.

Side View

Top View

LSOMO-1	LSOMO	HSOMO	HSOMO+1
(-5.58146)	(-5.28541)	(-3.79181)	(-3.04243)
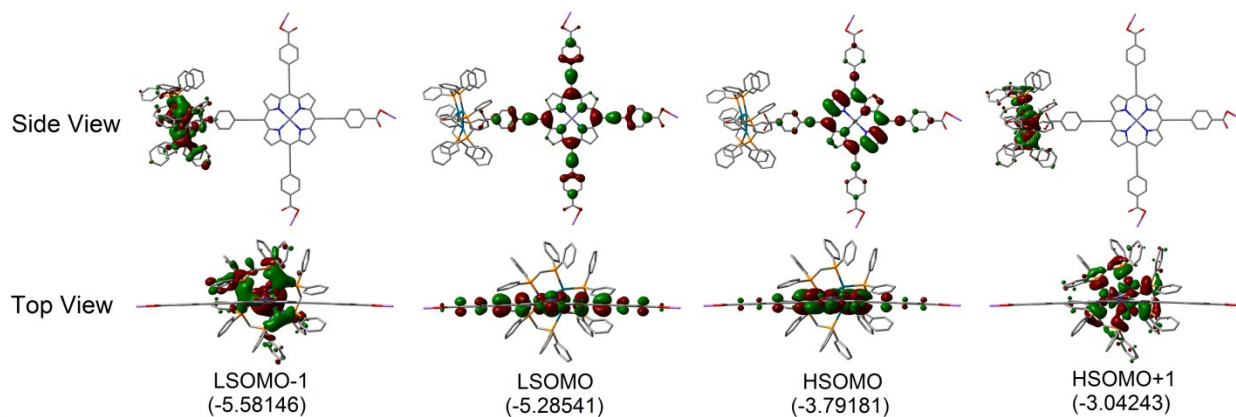
Figure S16. Representations of the semi-occupied frontier MOs of the **TCPEP•••[Pd₃²⁺]** assembly in MeOH solvent field (energies in eV).

Table S8. Comparison of selected calculated distances in the **TCPEP•••[Pd₃²⁺]** assembly.

	Singlet S_0 (Å)[a]	Triplet T_1 (Å)
Pd-Pd	2.682, 2.675, 2.670 (av.=2.676)	2.829, 2.819, 2.802 (av.=2.817)
Pd-P	2.443, 2.413, 2.409, 2.408, 2.399, 2.380 (av.=2.409)	2.446, 2.430, 2.428, 2.426, 2.425, 2.422 (av.=2.430)
Pd•••O	1st O: 3.617, 3.438, 3.079 (av.=3.378) 2nd O: 3.868, 3.573, 3.056 (av.=3.499)	1st O: 3.602, 3.211, 3.031 (av.=3.281) 2nd O: 3.642, 3.447, 3.011 (av.=3.367)
Pd•••Zn	15,582, 14.998, 14.956 (av.=15.179)	15,478, 14.893, 14.855 (av.=15.075)

[a]From reference 22c of the text.

Table S9. Comparison of selected calculated distances in the **TCPEBP•••[Pd$_3^{2+}$]** assembly.

	Singlet S$_0$ (Å)[a]	Triplet T$_1$ (Å)
Pd-Pd	2.707, 2.695, 2.678 (av.=2.693)	2.841, 2.807, 2.804 (av.=2.817)
Pd-P	2.433, 2.411, 2.407, 2.396, 2.395, 2.392 (av.=2.406)	2.453, 2.439, 2.431, 2.431, 2.429, 2.417 (av.=2.433)
Pd•••O	1st O: 3.543, 3.213, 2.896 (av.=3.217) 2nd O: 3.696, 3.184, 3.023 (av.=3.301)	1st O: 3.296, 3.153, 3.041 (av.=3.163) 2nd O: 3.530, 3.372, 2.803 (av.=3.235)
Pd•••Zn	15.181, 14.887, 14.642 (av.=14.903)	15.508, 14.417, 14.008 (av.=14.644)

[a]From reference 22c of the text.
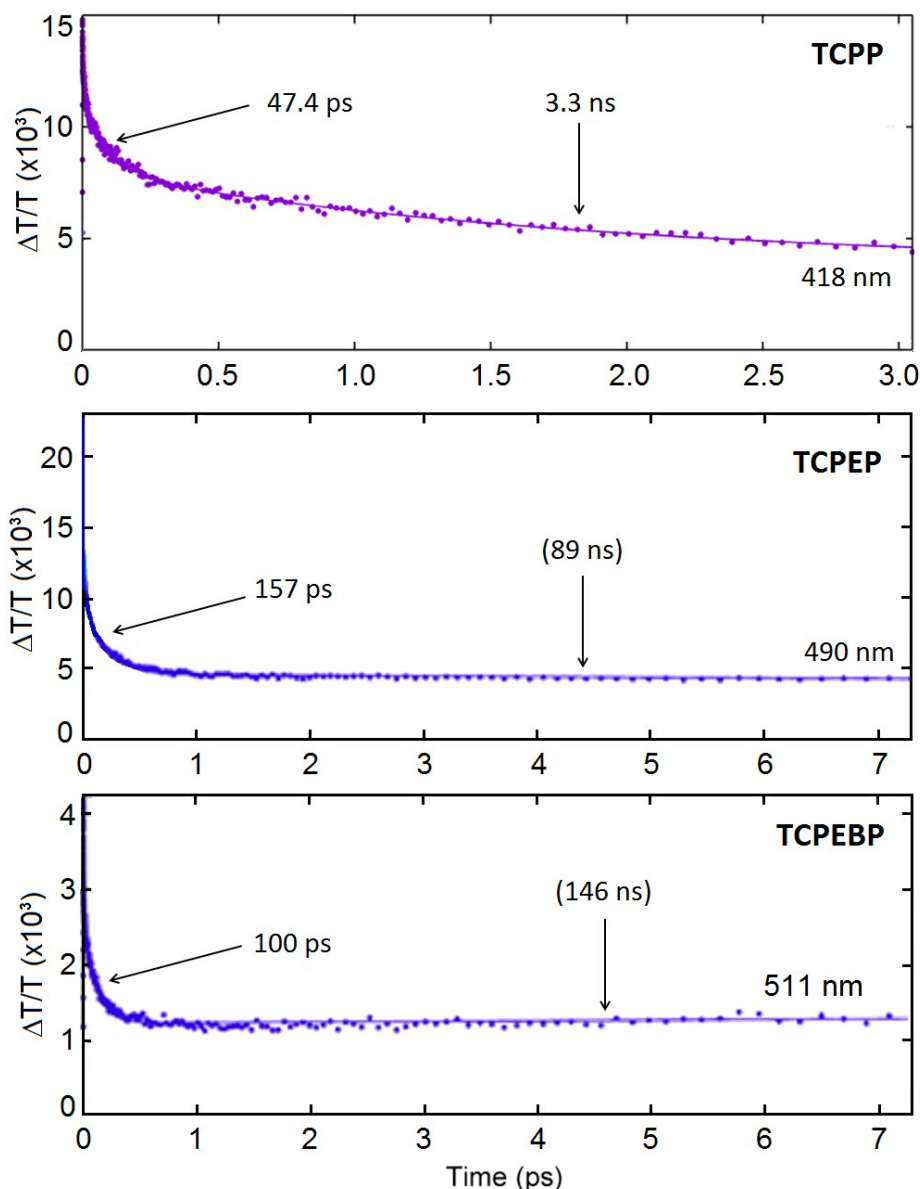
Figure S17. Monitoring of the transient signals of **TCPP**, **TCPEP** and **PCPEBP** in 2MeTHF in the presence of 2 equiv. of **[Pd$_3^{2+}$]** at 298 K. The monitoring wavelengths are indicated on the graphs. The ps and ns time constants are associated with the charge separation and charge recombination, respectively.