Supporting Information

Singlet and Triplet Energy Transfer Rate Acceleration by Additions of Clusters in Supramolecular Pigment-Organometallic Cluster Assemblies†

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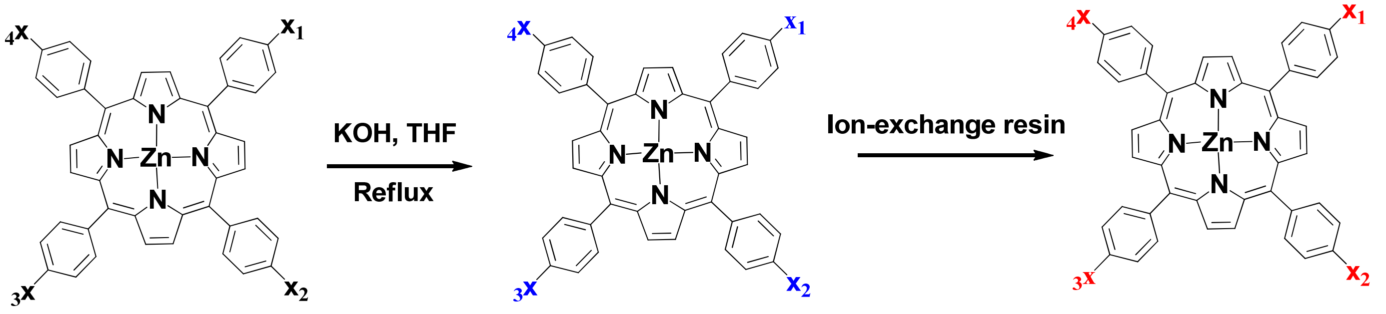
Materials.

The $[Pd_3(dppm)_3(CO)]^{2+}$ PF_6 cluster[1], 5-(4-carboxyphenyl)-10,15,20-tritolyporphyrinatozinc (**4**), 5,15-2-(4-carboxyphenyl)-10,20-ditolyporphyrinatozinc (**5**) and 5,10,15, 20-4-(4-carboxyphenyl)-tetratolyporphyrinatozinc (**6**) were synthesized according to the previous literature[3]. Carboylate salts MCO_2ZnP (**I**), DCO_2ZnP (**II**) and TCO_2ZnP (**III**) were synthesized by ion-exchange resin[4].



1 x_1= COOMe, x_2=x_3=x_4=Methyl
2 x_1=x_3= COOMe, x_2=x_4=Methyl
3 x_1=x_2=x_3=x_4=COOMe

4 x_1= COOH, x_2=x_3=x_4=Methyl
5 x_1=x_3= COOH, x_2=x_4=Methyl
6 x_1=x_2=x_3=x_4=COOH

I x_1= COONa, x_2=x_3=x_4=Methyl
II x_1=x_3= COONa, x_2=x_4=Methyl
III x_1=x_2=x_3=x_4=COONa

Figure S1. The synthetic routes of carboxylate-porphyrin salts

General Procedure for the Synthesis of Porphyrin Salts, with the synthesis of DCO_2ZnP (II) as an example. The porphyrin dicarboxylic acid (5, 0.05 mmol) was dissolved in methanol (20 mL). The solution was passed through DOWEX HCRW2 (Na form) ion-exchange resin. As the methanol and water were removed, the porphyrin salt was obtained as purple solid. Yield: 60 %. ^{1}H NMR (DMSO, δ, ppm): 8.19 (m, 8H), 8.25-8.22 (m, 4H), 8.08-8.03 (m, 8H), 87.62-7.59 (m, 4H), 2.68 (s, 6H). Elemental analysis (%) calcd for $C_{48}H_{30}N_4Na_2O_4Zn+4H_2O$: C, 63.34; H, 4.21; N, 6.16; Found: C, 63.87; H, 4.53; N, 5.78.

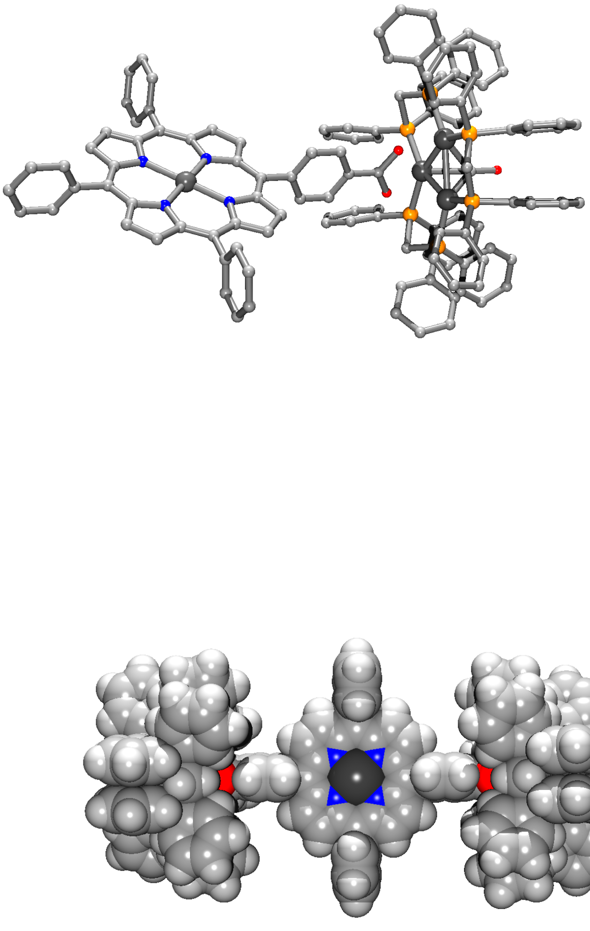


Figure S2. Models of $[Pd_3(dppm)_3(CO)]^{2+}$ with carboxylate-porphyrins showing the cavity above the unsaturated face of the Pd_3 center. Up, ball-and-stick model for *MCO_2ZnP*-($\mathbf{Pd_3^{2+}}$); bottom, space filling model for *DCO_2ZnP*-($\mathbf{Pd_3^{2+}}$)$_2$.

Spectroscopic Measurements.

The spectroscopic and photophysical measurements were carried out in methanol and the mixture of methanol and 2-MeTHF, which was distilled with calcium hydride under argon. The absorption measurements of the $[Pd_3(dppm)_3(CO)]^{2+}$ cluster, associated with the binding constant calculation, were carried out in methanol because the largest difference can be shown in λ_{max} between the free cluster and host-guest assembly.

Methodology.

The binding constants (K_{1n} : K_{11}, K_{12}, and K_{14}) were measured according to the typical method as follows: Two different solutions (A and B) were prepared in methanol. Solution A contained the “free cavity” cluster $[Pd_3(dppm)_3(CO)]^{2+}$ $(PF_6^-)_2$. Solution B was the mixture of the cluster, which contains exactly the same concentration as that used in solution A, with the porphyrin carboxylate salt. The spectroscopic changes induced by solution A as a result of additions of constant volume (0.1 mL) of solution B were monitored by measuring the absorption spectra after each addition. The competitive binding constants (K_{11}, K_{12}, and K_{14}) were measured by plotting 1/ΔA vs 1/[substrate] (Benesi-Hildebrand), where ΔA is the absorbance change upon an increase in the substrate concentration. The substrate concentration was corrected based on the change of the total volume at each addition, and these adjusted values were used for the plots. The ratio of intercept/slope in this plot gives K_{11}, K_{12}, and K_{14}. The binding constant values were more accurately evaluated by using the Scatchard and Scott plots ΔA/[substrate] vs -ΔA with K_{1n}= -slope (Scatchard) and -[substrate]/ΔA vs [substrate] with K_{1n}= slope/intercept (Scott) with the experimental uncertainties 10%. The uncertainties are based on multiple measurements. The Scott and Scatchard’s plots are presented in this ESI.

The measurement to identify the formation of 1:2 and 1:4 assembiles was carried out in the following way. Two different solutions (C and D) were prepared in methanol. Solution C contained the free carboxylate-porphyrins. Solution D was the mixture of the porphyrin, which contains exactly the same concentration as that used in solution C, with the cluster. The uncertainties (10%) are based on multiple measurements.

Instruments

UV-visible spectra were recorded on a Varian Cary 300 spectrophotometer. The emission spectra were obtained using a double-monochromator Fluorolog 2 instrument from Spex. The emission lifetimes were measured on a TimeMaster model TM-3/2003 apparatus from PTI. The source was a nitrogen laser with a high-resolution dye laser (fwhm ~ 1400 ps), and the fluorescence lifetimes were obtained from deconvolution or distribution lifetime analysis. The uncertainties were about 50-100 ps. The phosphorescence lifetimes were performed on a PTI LS-100 using a 1 μs tungsten flash lamp (fwhm ~1 μs). The flash photolysis spectra and the transient lifetimes were measured with a Luzchem spectrometer using the 355 nm line of a YAG laser from Continuum (Serulite) and the 530 nm line from a OPO module pump by the same laser (fwhm =3 ns).

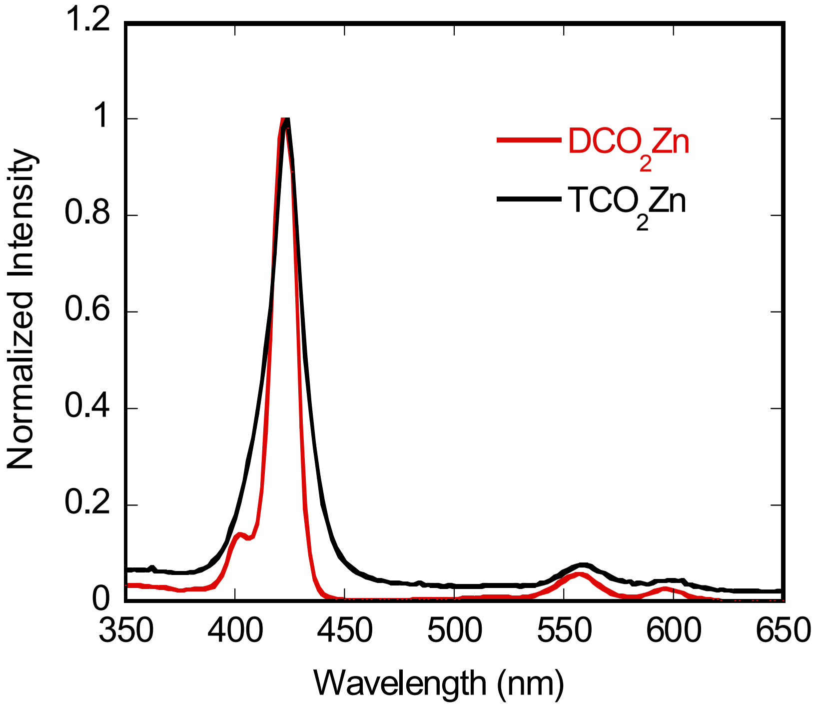


Figure S3. Absorption spectrum of *DCO_2ZnP* and *TCO_2ZnP* in MeOH at 298K.

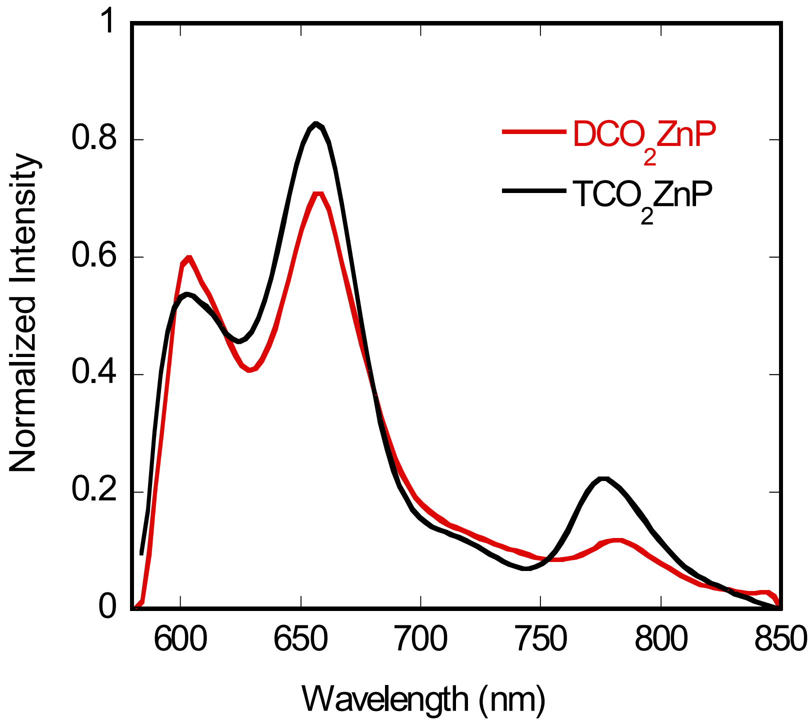


Figure S4. The corrected emission of *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$ and *TCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_4$ at 298 K in 2MeTHF:MeOH (20:1) mixture . λ_{exc} = 560nm.

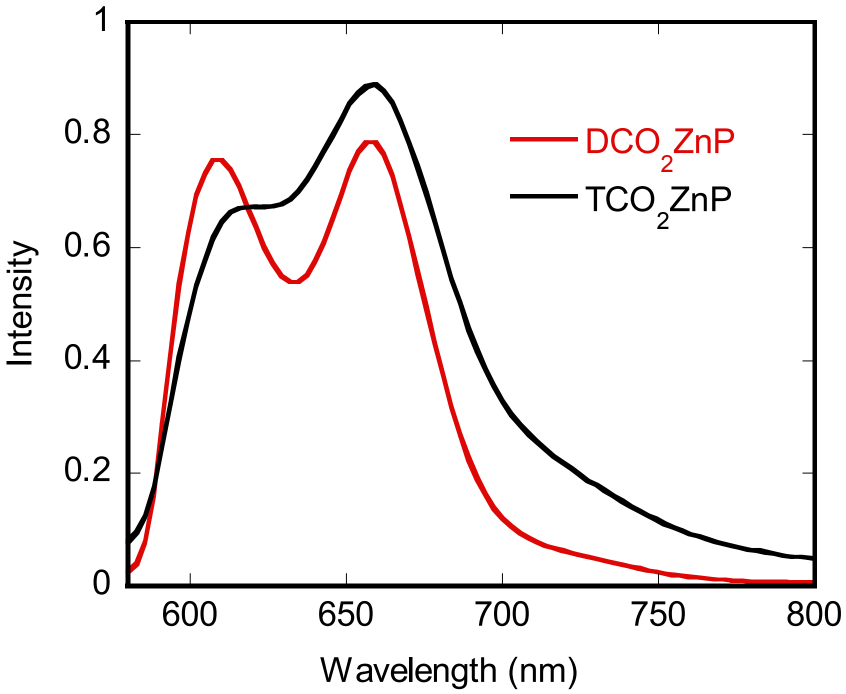


Figure S5. The corrected emission of *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$ and *TCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_4$ at 298 K in 2MeTHF:MeOH (20:1) mixture . λ_{exc} = 560nm.

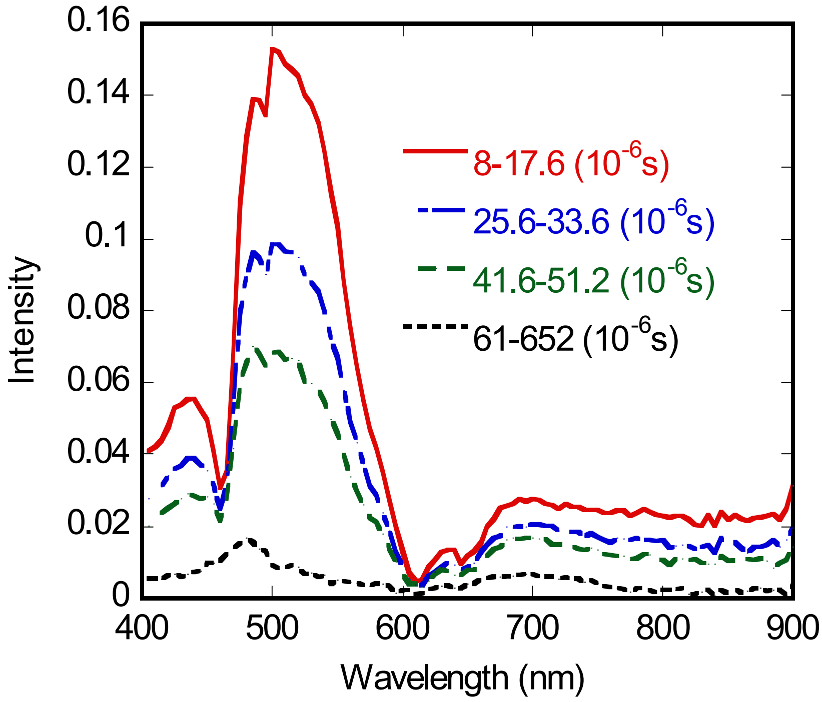


Figure S6. Transient absorption spectrum of *MCO_2ZnP* in MeOH at 298K. λ_{exc} = 355 nm. The delay times between the pump and probe pulses are placed in the figure.

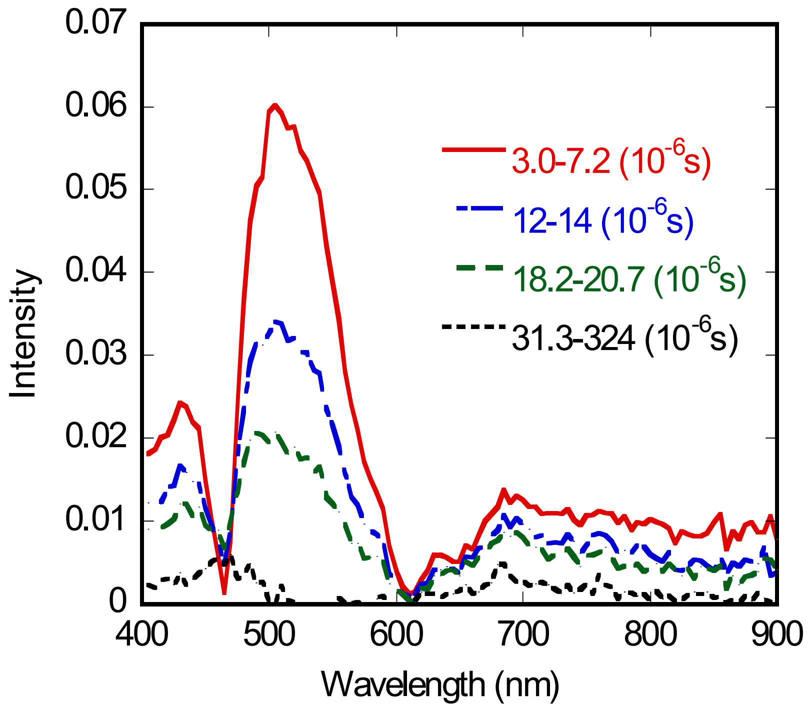


Figure S7. Transient absorption spectrum of *MCO_2ZnP*-(**Pd_3^{2+}**) in MeOH at 298K. λ_{exc} = 355 nm. The delay times between the pump and probe pulses are placed in the figure.

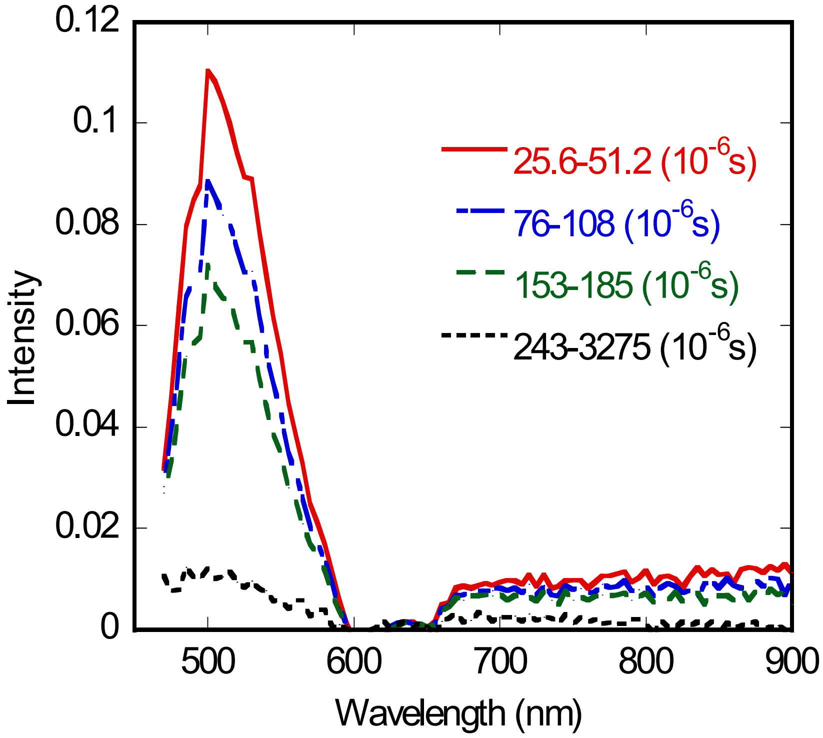


Figure S8.Transient spectrum of *DCO₂ZnP* in MeOH at 298K. λ_{exc} = 355 nm. The delay times between the pump and probe pulses are placed in the figure.

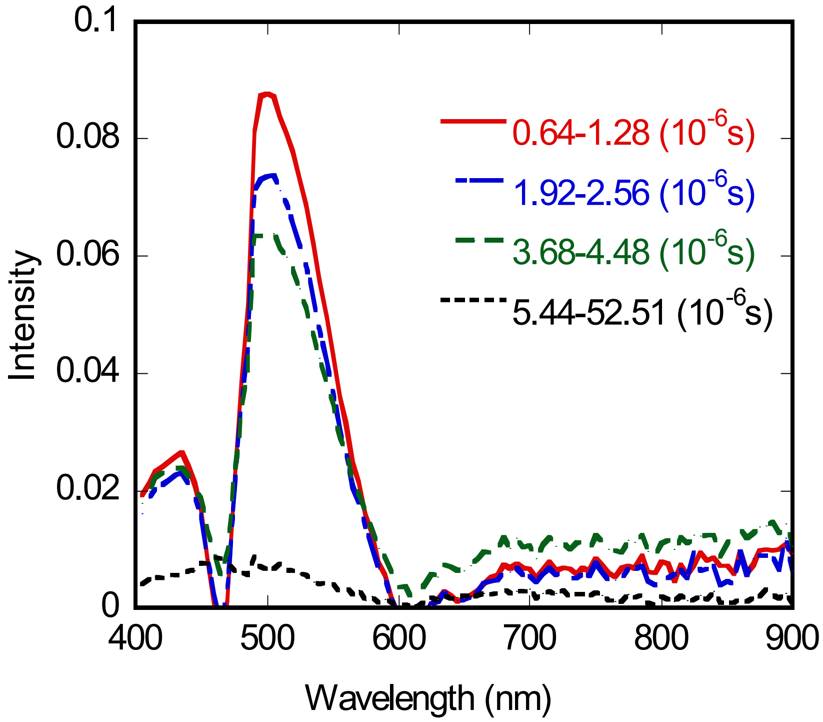


Figure S9. Transient absorption spectrum of *DCO₂ZnP*-(**Pd₃**$^{2+}$)$_2$ in MeOH at 298K. λ_{exc} = 355 nm. The delay times between the pump and probe pulses are placed in the figure.

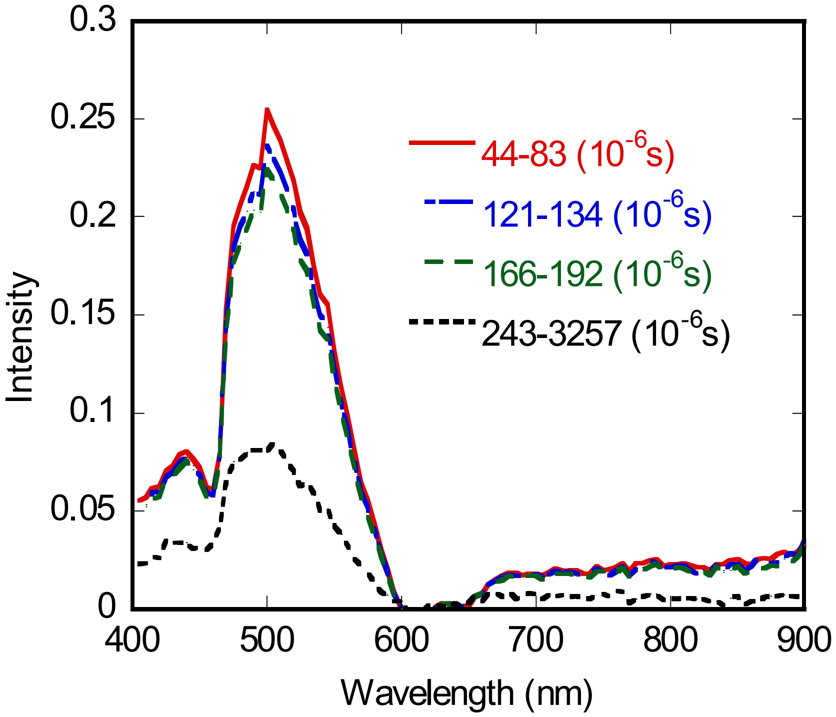


Figure S10. Transient absorption spectrum of *TCO_2ZnP* (alone) in MeOH at 298K. λ_{exc} = 355 nm. The delay times between the pump and probe pulses are placed in the figure.

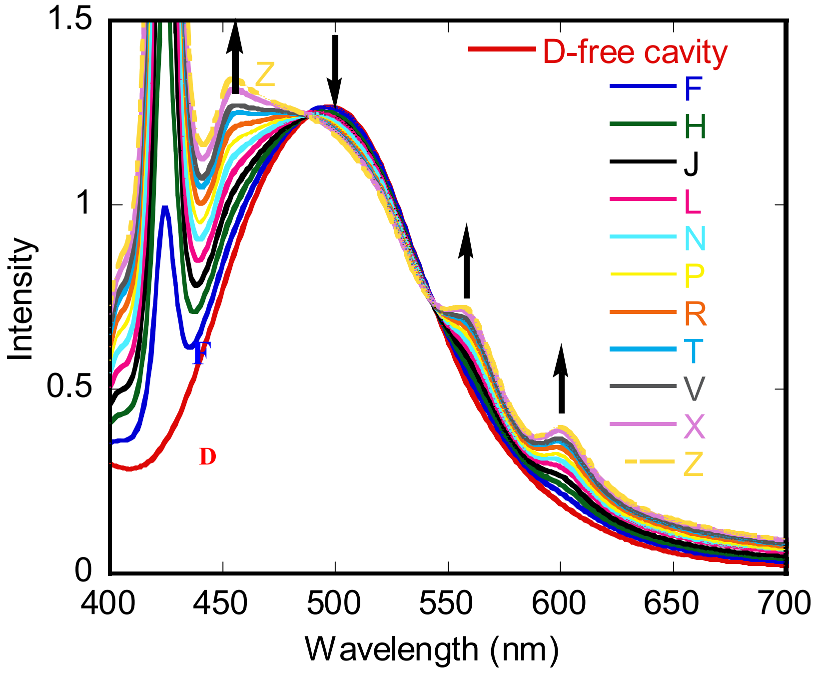


Figure S11. UV-vis spectra for the addition of *MCO_2ZnP* into a MeOH solution of $[Pd_3(dppm)_3(CO)_3](PF_6)_2 = 6.7 \times 10^{-5}$ M. Curve **F-Z** obtained with successive addition of 6.7×10^{-9} M of *MCO_2ZnP* with 0.1ml for every addition. (The arrows indicate the direction of absorption change with change in concentration).

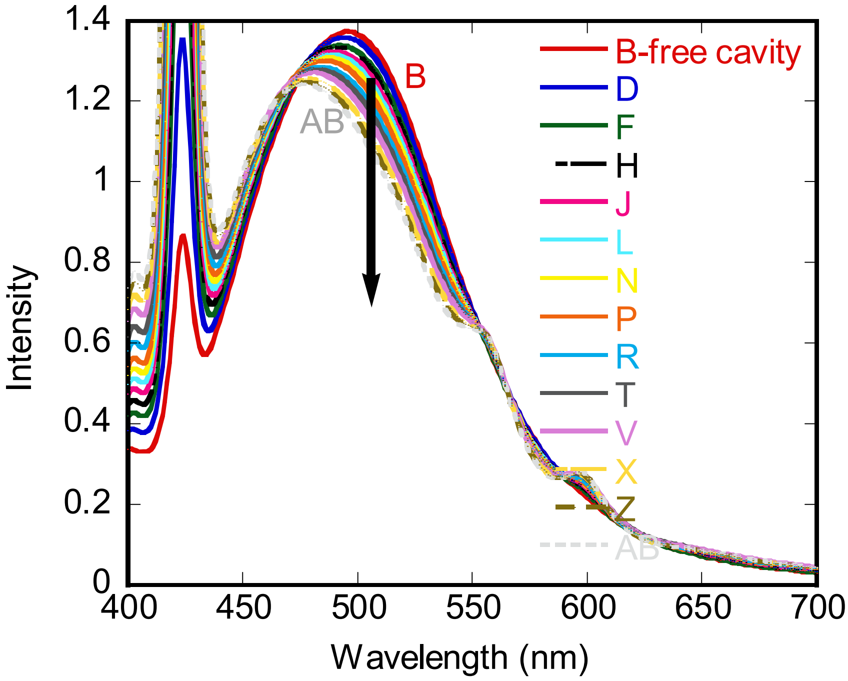
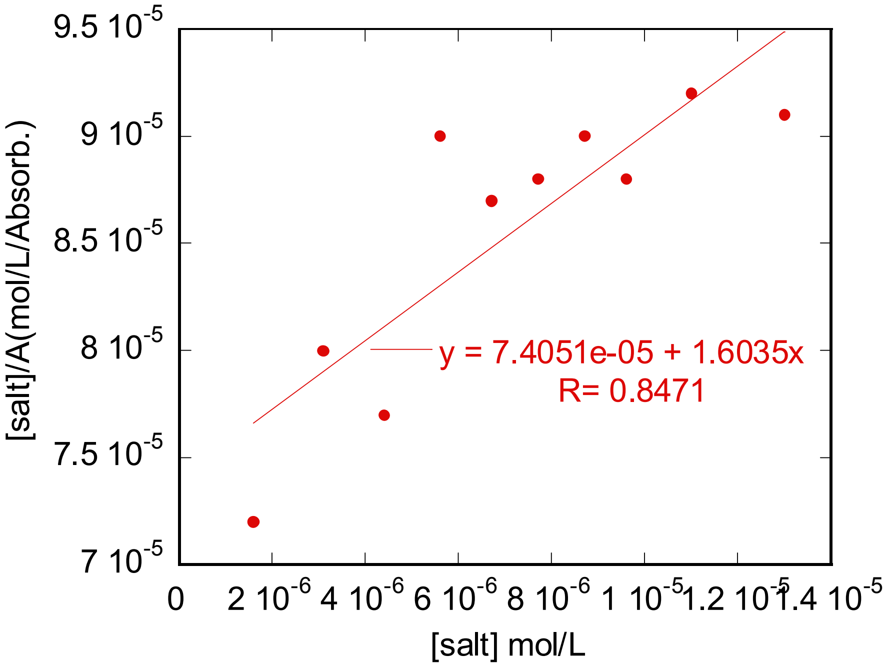
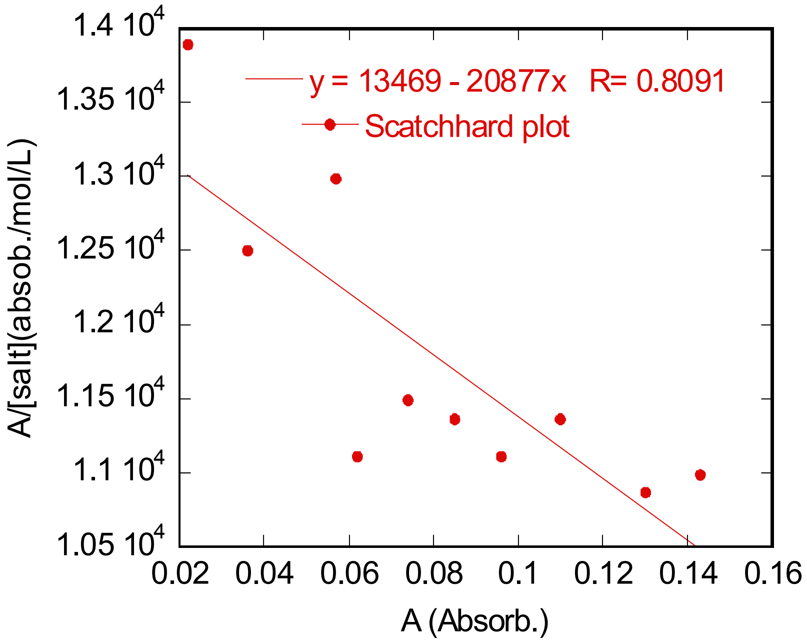


Figure S12. UV-vis spectra for the addition of *DCO_2ZnP* (3.35×10^{-5}M) into a MeOH solution of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$ (6.7×10^{-5}M) with 0.1ml for every addition. Curves **D-AB** obtained with successive additions of 3.35×10^{-9} M of *DCO_2ZnP*.



K_{12} 21654 M^{-1}



K_{12} 20877 M^{-1}

Figure S13. Scott plots and Scatchard for the 2:1 formation of *DCO_2ZnP*-(**Pd_3^{2+}**)$_2$ assembly at 298 K in MeOH (20:1) mixture.

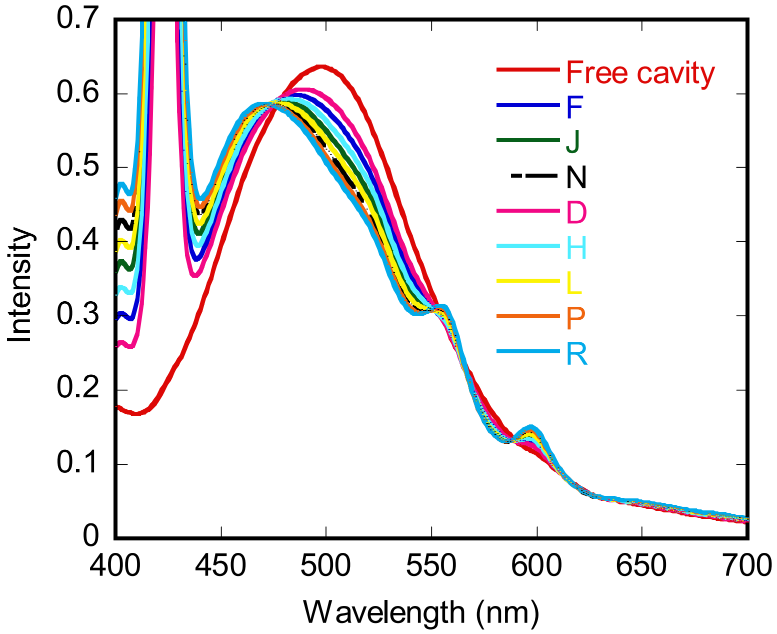


Figure S14. UV-vis spectra for the addition of *DCO_2ZnP* into a MeOH solution of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$ (3.35×10^{-5} M). Curves **D-R** obtained with successive additions of 3.35×10^{-5} M of *DCO_2ZnP* with 0.1ml for every addition. (The arrows indicate the direction of absorption change with change in concentration).

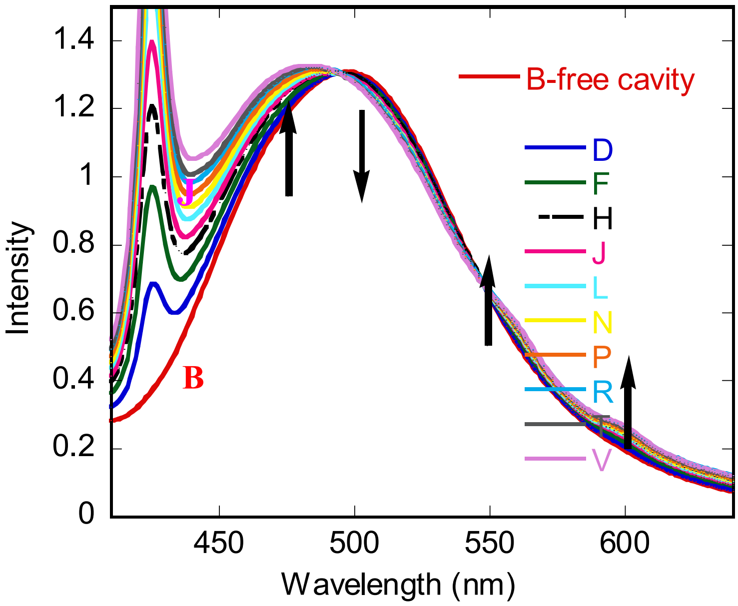
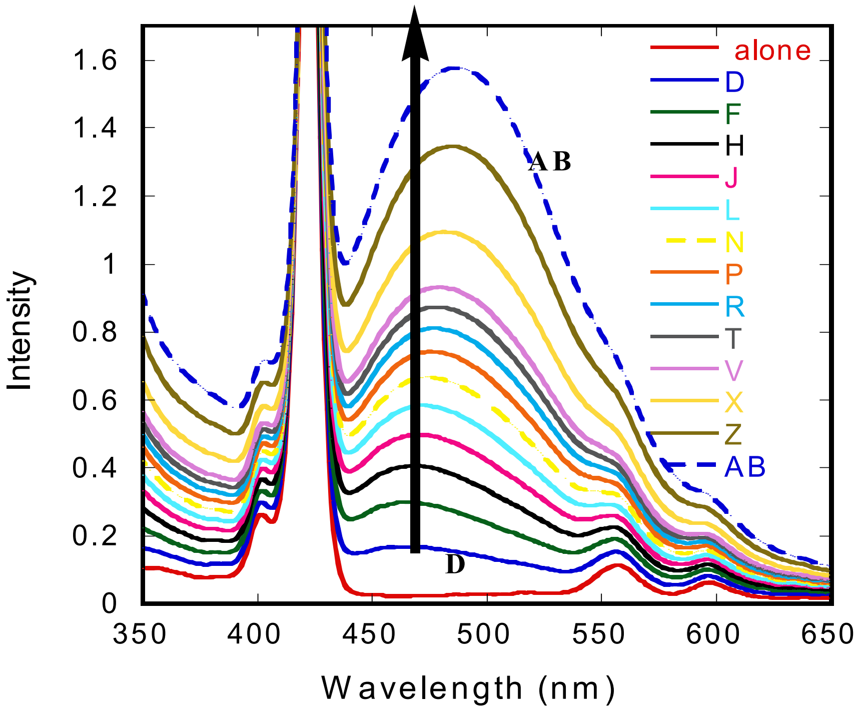


Figure S15. Uv-visible spectra for the addition of *TCO₂ZnP* into a MeOH solution of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$ (6.7×10^{-5} M). Curves **D-V** obtained with successive addition of 1.68×10^{-5} M of *TCO₂ZnP* with 0.1 ml for every addition. (The arrows indicate the direction of absorption change with change in concentration).



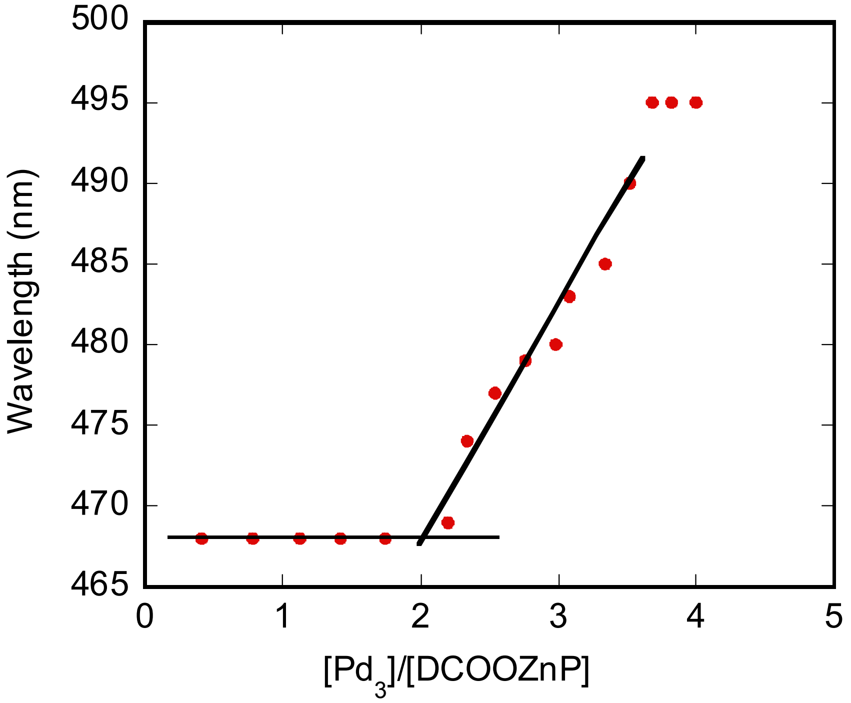
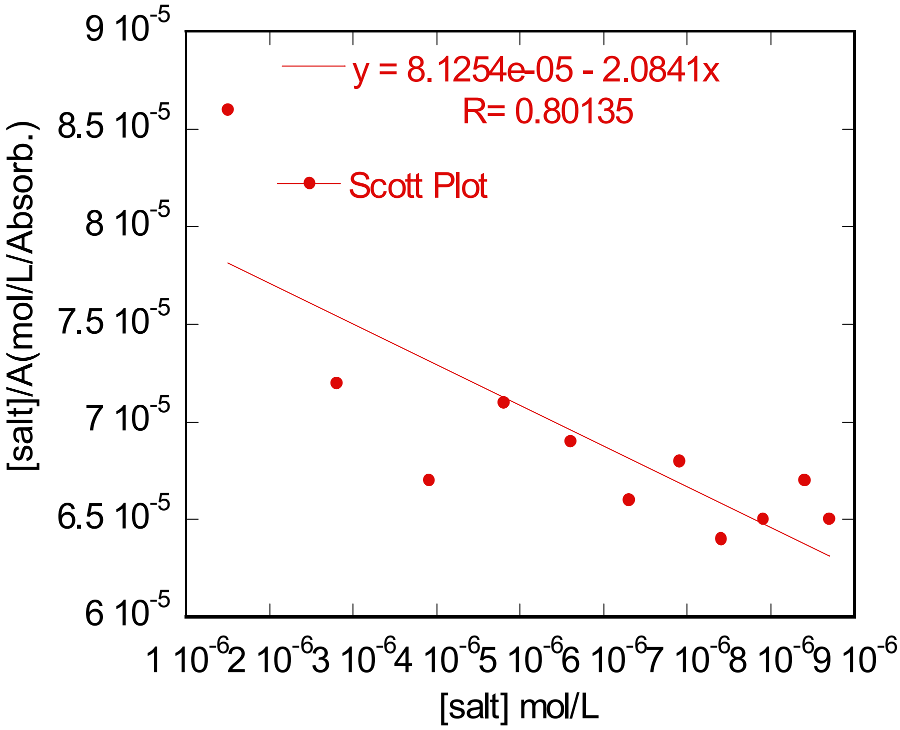
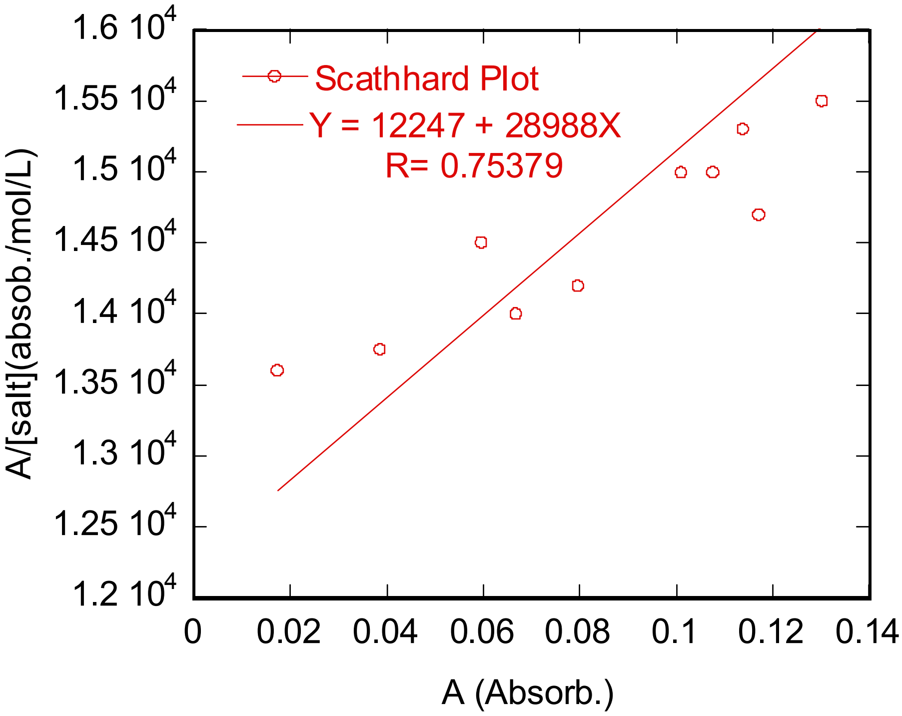


Figure S16. Top: UV-vis spectra for the addition of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$ into a MeOH solution of *DCO_2ZnP* (0.75 × 10^{-5} M). Curves **D-AB** obtained with successive additions of 6.7×10^{-5} M of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$. Bottom: Absorption shifts of $[Pd_3(dppm)_3(CO)_3](PF_6)_2$ in MeOH as a function of the ratio of added cluster to the *DCO_2ZnP* –containing solution.



K_{14} 25729 M^{-1}



K_{14} 28998 M^{-1}

Figure S17. Scott plots and Scatchard, for the formation of *TCO_2ZnP*-(**Pd_3^{2+}**)$_4$.

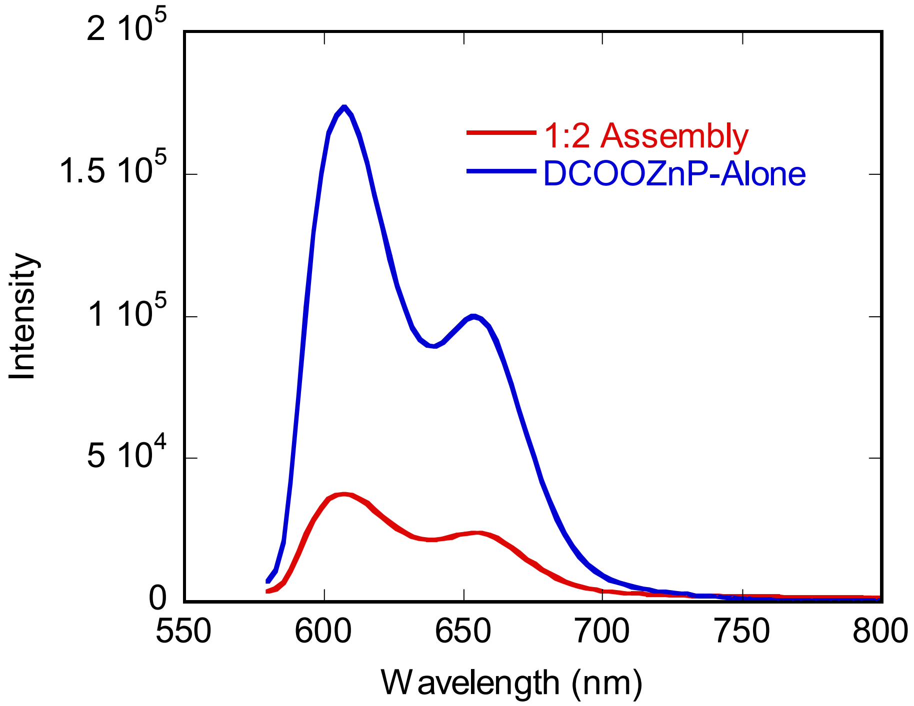


Figure S18. The emission of *DCO$_2$ZnP* and *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$ at 298 K in MeOH. λ_{exc} = 560nm (the concentration of *DCO$_2$ZnP* is the same with the concentration of *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$).

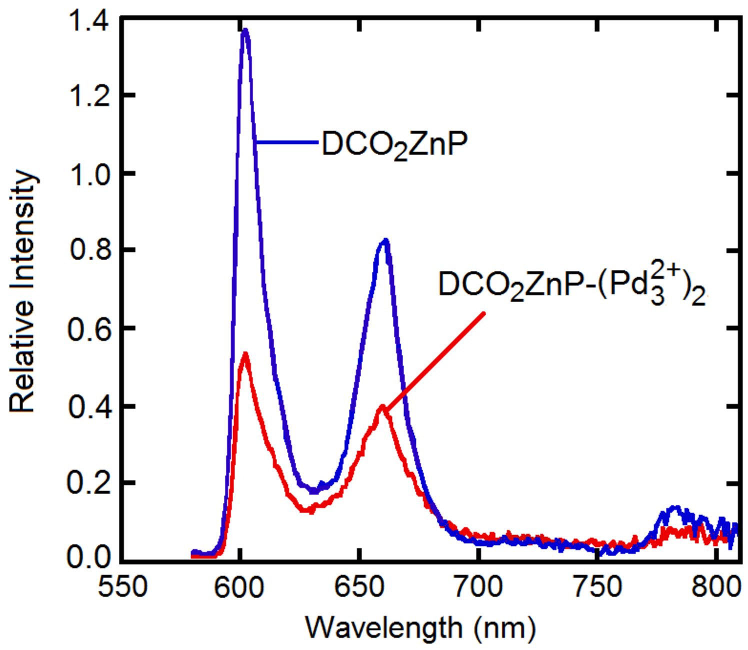


Figure S19. The emission of *DCO$_2$ZnP* and *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$ at 77 K in MeOH. λ_{exc} = 560nm (the concentration of *DCO$_2$ZnP* is the same with the concentration of *DCO$_2$ZnP*-(**Pd$_3$**$^{2+}$)$_2$).

Table S1. K_{1n} Values for MCO_2ZnP , DCO_2ZnP, and TCO_2ZnP with $[Pd_3(dppm)_3(CO)]^{2+}$ in MeOH at 298 K.[a]

Substrate	K_{1n}(M^{-1})	Scott	Scatchard
MCO_2ZnP-($\mathbf{Pd_3}^{2+}$) [b]	K_{11}	19300	19000
DCO_2ZnP-($\mathbf{Pd_3}^{2+}$)$_2$	K_{12}	21700	20900
TCO_2ZnP-($\mathbf{Pd_3}^{2+}$)$_4$	K_{14}	25700	29000

[a] The uncertainties are ~10% based on multiple measurements. [b] Ref. 2.

References:

1 (a) G. Ferguson, B. R. Lloyd, and R. Puddephatt, *Organometallics*, *1986*, 344. (b) L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1336.

2 S. M. Aly, C. Ayed, C. Stern, R. Guilard, Alaa S. Abd-El-Aziz, and P.D. Harvey, *Inorg. Chem.*, 2008, **47**, 21.

3 (a) E. Galoppini, J. Rochford, H. Chen, G. Saraf, Y. Lu, A. Hagfeldt, and G. Boschloo, *J. Phys. Chem. B.*, 2006, **110**, 16159; (b) J. Rochford, D. Chu, A. Hagfeldt, and E. Galoppini, *J. Am. Chem. Soc.*, 2007, **129**, 4655; (c) J. Rochford, and E. Galoppini, *Langmuir*, 2008, **24**, 5366.

4 J. Rochford, D. Chu, A. Hagfeldt, and E. Galoppini, *J. Am. Chem. Soc.*, 2007, **129**, 4655.

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