Electronic Supplementary Information for Dalton Transactions

Supporting Information

Self-assembly of a Pd(II) neutral molecular rectangle *via* a new organometallic Pd^{II}_2 clip and oxygen donor linker

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X-ray crystallographic data collection and refinement. The crystal data of the "clip" **1a** were collected on a Bruker SMART APEX CCD diffractometer using the MART/SAINT software.[2] X-ray-quality crystals were mounted on a glass fiber with traces of viscous oil. Intensity data were collected using graphite-monochromatized Mo K radiation (0.71073 Å) at 150 K. The structure was solved by direct methods using the SHELX-97[2] program incorporated into WinGX.[2] Empirical absorption corrections were applied with SADABS.[2] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, *U*(H)) 1.2*U*(C) or 1.5*U*(C-methyl), and their coordinates were allowed to ride on their respective carbons.

The structure of this clip belongs to monoclinic crystal system with C2/c space group. The asymmetric unit contains half of the clip and total clip structure is generated by C_2-symmetry. In solid state of this clip $\mathbf{M_{Cl}}$, the two Pd-containing arms are not parallel rather diverging with an angle 61º. Moreover, the two palladium centers are not coplanar with anthracene plane. The dihedral angle is 7.1°. Such divergence and deviation from coplanarity can be atributed to the steric repulsion among the phosphenyl ethyl groups. Severe steric crowding is also reflected from the deviation from the ideal square planar geometry around the palladium coordinations. All the coordinating atoms in each palladium center are pushed back from each other. The angles of the *trans* ligands w.r.t. palladium centres range from 172° - 173º.

Table S1 Crystal Data and Structure Refinement Parameters for Clip $\mathbf{M_{Cl}}$

Empirical formula	$C_{42}H_{68}Cl_2P_4Pd_2$	
Formula weight	980.54	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	monoclinic, C2/c	
Unit cell dimensions	a = 26.723(3) Å	α = 90º
	b=12.9521(16) Å	β = 100.178(3)º
	c = 53.97(2) Å	γ = 90°
Volume	4793.0(10) $Å^3$	
Z, Calculated density	4, 1.359 g/cm^3	
Absorption coefficient	1.022 mm^{-1}	
F(000)	2024	
Theta range for data collection	1.75 to 26.37°	
Reflections collected / unique	18892 / 4916 [R(int) = 0.0485]	
Completeness to θ = 25.05°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4916 / 0 / 233	
Goodness-of-fit* on F^2	1.007	
Final R indices† [I>2□(I)]	R1 = 0.0562, wR2 = 0.1179	
R indices† (all data)	R1 = 0.1155, wR2 = 0.1433	
Largest diff. peak and hole	0.515 and -0.340 $e.Å^{-3}$	

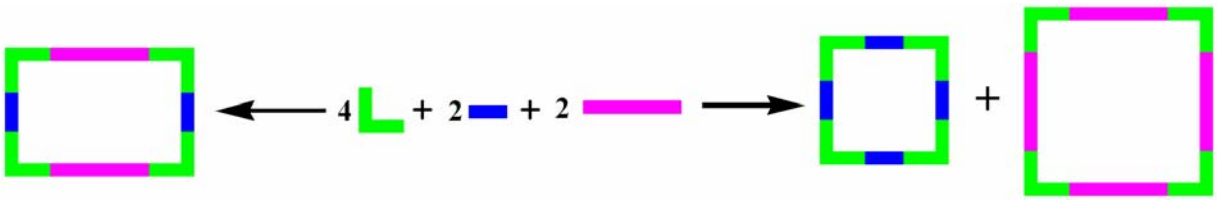
†$wR2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$; $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o$

·$GooF = S = \{\Sigma[w(F_o^2-F_c^2)^2] / (n-p)\}^{½}$

Table S2 Selected bond lengths [Å] and bond angles (deg.) for Clip $\mathbf{M_{Cl}}$

Pd(1)-C(1)	1.953(5)	Pd(1)-P(2)	2.3091(15)
Pd(1)-P(1)	2.3169(16)	Pd(1)-Cl(1)	2.3517(15)
P(1)-C(15)	1.821(6)	P(1)-C(13)	1.823(8)
P(1)-C(11)	1.825(7)	P(2)-C(19)	1.785(9)
P(2)-C(21)	1.807(7)	P(2)-C(17)	1.809(8)
C(1)-C(2)	1.199(6)	C(2)-C(3)	1.433(7)
C(3)-C(4)	1.378(7)	C(3)-C(8)	1.434(7)
C(4)-C(5)	1.412(8)	C(5)-C(6)	1.339(9)
C(6)-C(7)	1.427(8)	C(7)-C(9)	1.379(6)
C(7)-C(8)	1.439(6)	C(8)-C(10)	1.387(5)
C(11)-C(12)	1.494(10)	C(13)-C(14)	1.487(10)
C(15)-C(16)	1.533(8)	C(17)-C(18)	1.484(15)
C(19)-C(20)	1.183(10)	C(21)-C(22)	1.513(8)

C(1)-Pd(1)-P(2)	85.58(14)	C(1)-Pd(1)-P(1)	90.74(14)
P(2)-Pd(1)-P(1)	172.09(6)	C(1)-Pd(1)-Cl(1)	173.96(16)
P(2)-Pd(1)-Cl(1)	93.57(6)	P(1)-Pd(1)-Cl(1)	89.35(6)



Scheme S1: Possible cyclic products in the [4 + 2 + 2] self-assembly of a 90° acceptor and two linear linkers of different lengths.

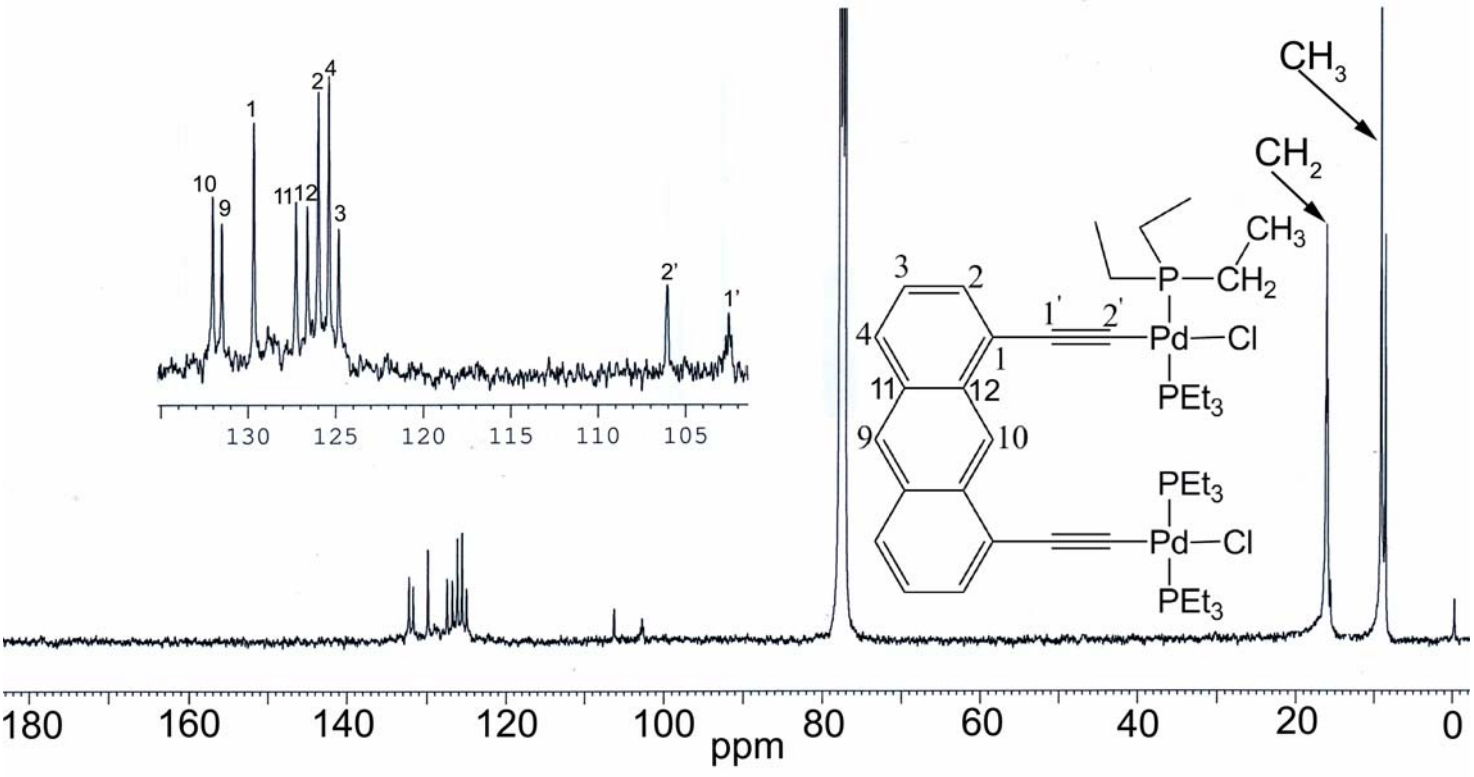


Fig. S1: ^{13}C NMR spectrum of $\mathbf{M_{Cl}}$ in $CDCl_3$.

UV-Vis studies:

The absorption spectra of $\mathbf{M_{Cl}}$ and **1** were recorded in commercially available $CHCl_3$ solvent 5×10^{-5} (M) concentration nsolutions (Fig. S2). For the absorption spectral study of the compound **1** along with trinitrotoluene (TNT), 5×10^{-5} (M) solution of **1** in $CHCl_3$ was mixed with $CHCl_3$ solution of TNT of 1×10^{-5} (M) concentration and kept for 5 min after uniform mixing.

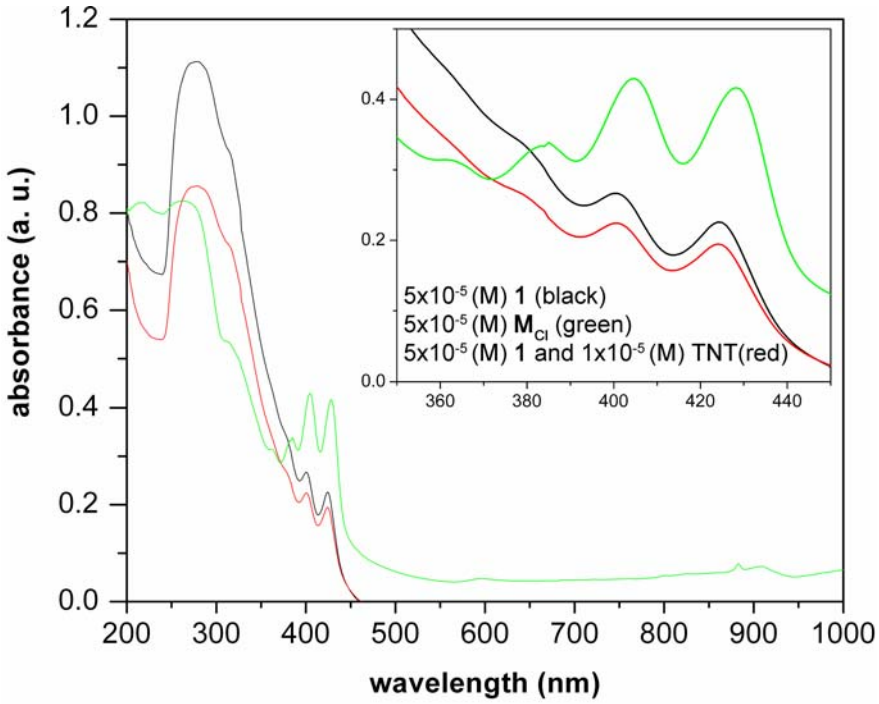


Fig. S2: Electronic absorption spectra of 5×10^{-5} (M) $\mathbf{M_{Cl}}$ (black), 5×10^{-5} (M) **1** (green) and (5×10^{-5} (M) **1** + 1×10^{-5} (M) TNT) (red). All were recorded in commercially available $CHCl_3$.

Fluorescence study:

Fluorescence enhancement or quenching phenomenon can be the signature for the host-guest interactions and/or collisional interactions among the fluorophore and the quencher in the molecular level in solution phase. Functionalized transition-metal containing supramolecules show selectivity towards the small guest molecules. Ethynyl functionalized transion-metallacyclophanes are emerging as efficient fluorophores. Exploring new functionalized metalasupramolecular fluorophores and their electronic emission spectral change on interactions with quencher(guest) can lead to specific

detection of chemicals. Both the molecular organometallic "clip" and rectangle reported here are fluorescence active. On excitation at 400 nm, compound **1** in $CHCl_3$ medium showed a strong emission band near the emission maximum 440 nm and two weak bands near the emission maxima 820 nm and 870 nm. On titration with TNT in $CHCl_3$, the band near 440 gradually died down (Fig. S3). The binding constant for the interaction of **1** with TNT was measured by Stern Volmer plot (Fig. S4) and it (K_{SV}) is 1.32×10^4 M^{-1}. So, the Stern-Volmer plot analysis implies that the molecular rectangle sensitive to TNT detection and this is presumably due to the fact that quencher molecule gets encapsulated into the molecular cavity by charge transfer interaction.

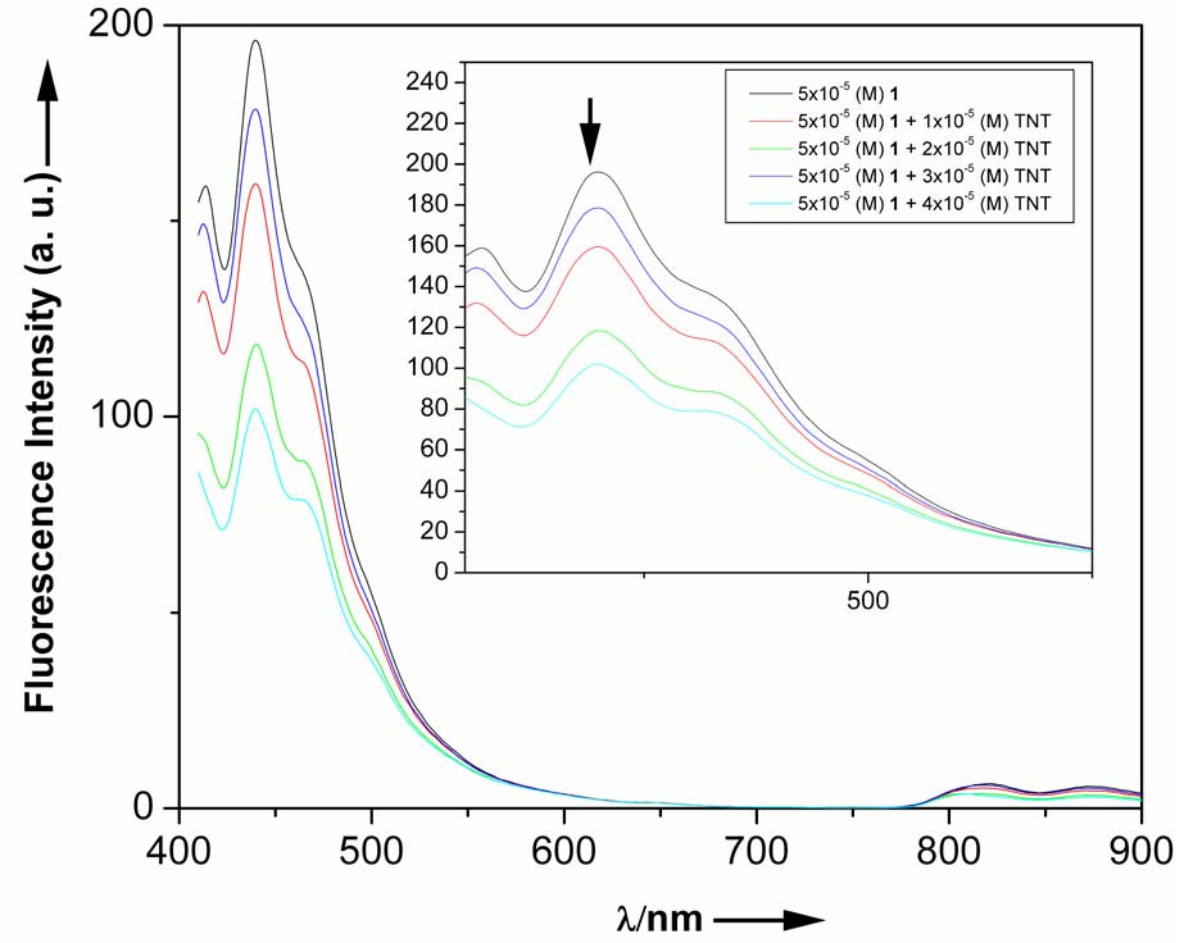


Fig. S3: Quenching of emission intensity of **1** (5×10^{-5} (M) in $CHCl_3$) on gradual increase of quencher TNT (in $CHCl_3$) concentration.

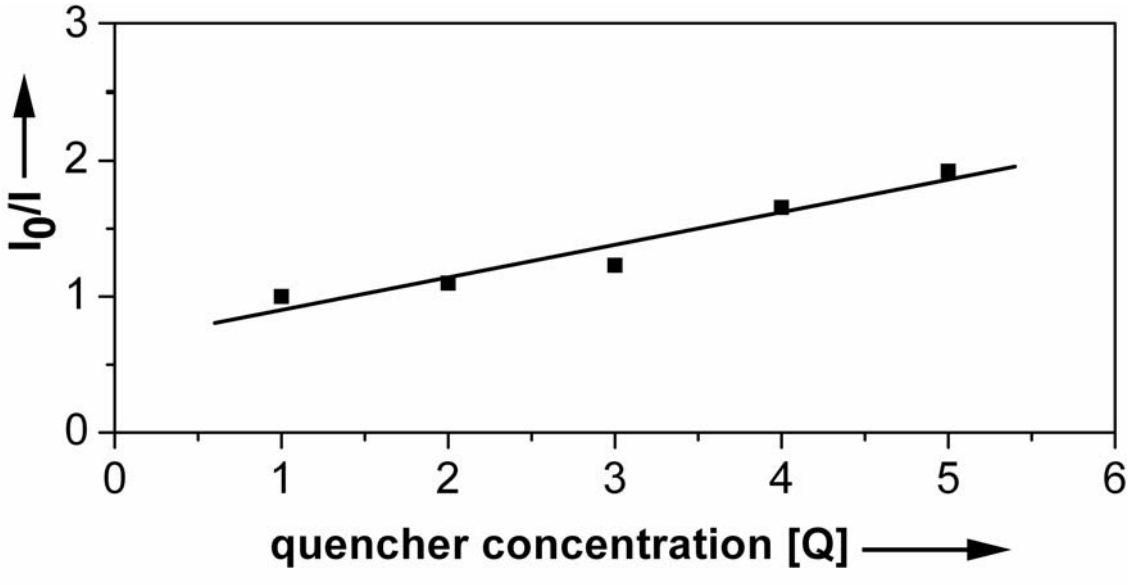


Fig. S4: Stern-Volmer plot for the titration of **1** with TNT (right) both taking in $CHCl_3$.