

# Synthesis of a Series of Pd(II) Complexes of the Type [Pd(1,10-phen)(SR<sub>F</sub>)<sub>2</sub>]·Solvent. An Interesting Case of Solvatomorphism.

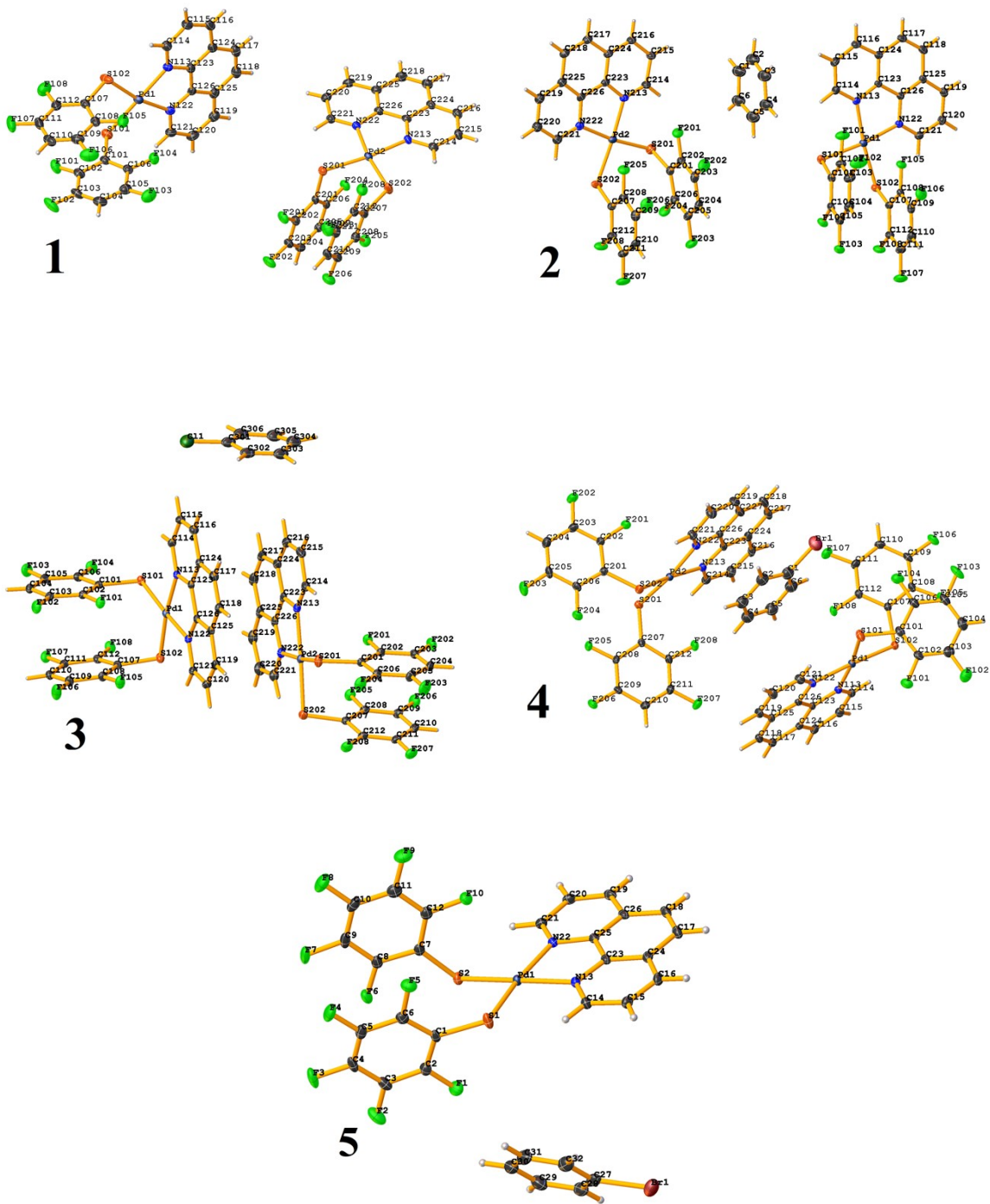
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- Figure S1            Molecular structures **1-5** with numbering
- Table S1            Relevant metal-ligand bonds lengths and angles in the structures **1-5**
- Figure S2           Visualization of the  $\pi_F$ - $\pi_F$ ,  $\pi$ - $\pi$  and  $\pi_F$ - $\pi$  interactions (intra- and intermolecular) in **1**. Colored in red are the crystallographic independent molecules Pd1.
- Figure S3           Schematization of the *phen*···*phen* intermolecular interactions (*head-to-tail*) forming the parallel infinite column (molecule Pd1).
- Figure S4           Visualization of the *phen*···*phen*  $\pi$ - $\pi$  intermolecular interactions (intra- and intermolecular) in **2**. C<sub>6</sub>H<sub>6</sub> solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.
- Figure S5           *phen*···*phen* interactions in **2**. Colored in red is the crystallographic independent molecule Pd1.
- Figure S6           Projections presenting *phen*···*phen* interactions distorted from a perfect *head-to-tail* orientation in **2**. Colored in red is the crystallographic independent molecules Pd1.
- Figure S7           Visualization of the  $\pi_F$ - $\pi_F$  interactions (intra- and intermolecular) in **2**. Colored in red are the Pd1 molecules.
- Figure S8.           Visualization of the  $\pi_F$ - $\pi_F$  and *phen*···*phen*  $\pi$ - $\pi$  interactions (intra- and intermolecular) in **3**. C<sub>6</sub>H<sub>6</sub>Cl solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.

- Figure S9                      Projections presenting *phen*···*phen* interactions distorted from a perfect *head-to-tail* orientation in **3**. Colored in red is the crystallographic independent molecules Pd1.
- Figure S10                     Visualization of the  $\pi$ - $\pi$  interactions (intermolecular) in **4**. C<sub>6</sub>H<sub>6</sub>Br solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.
- Figure S11                     Projections presenting *phen*···*phen* interactions displaced from a perfect *headto-tail* and *head-to-head* orientation in **4**. Colored in red is the crystallographic independent molecules Pd1.
- Figure S12                     Visualization of the  $\pi$ - $\pi$  interactions (intermolecular) in **5**. C<sub>6</sub>H<sub>6</sub>Br solvate is drawing in ball and stick style.
- Figure S13                     Relevant non-covalent interactions involved around the Pd1 (colored in red) and Pd2 in the structures **1-5**.
- Figure S14                     HOMO – LUMO plots for structures **1-5** and the interaction *phen*···C<sub>6</sub>H<sub>5</sub>Br.



**Figure S1.** Molecular structures 1-5 with numbering. Ellipsoids were drawn at 30% of probability.

1	2	3	4	5
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### Bond lengths [Å]

Pd1-N113 2.087(4)	Pd1-S101 2.289(1)	Pd1-S101 2.296(1)	Pd1-S101 2.280(2)	Pd1-S1 2.2678(8)
Pd1-N122 2.093(4)	Pd1-S102 2.287(1)	Pd1-S102 2.290(1)	Pd1-S102 2.282(2)	Pd1-S2 2.2861(9)
Pd1-S101 2.302(1)	Pd1-N113 2.101(3)	Pd1-N113 2.100(3)	Pd1-N113 2.080(4)	Pd1-N13 2.086(2)
Pd1-S102 2.267(1)	Pd1-N122 2.097(4)	Pd1-N122 2.104(3)	Pd1-N122 2.086(4)	Pd1-N22 2.094(2)
Pd2-N213 2.081(4)	S201-Pd2 2.293(2)	Pd2-S201 2.289(1)	Pd2-S201 2.285(2)	
Pd2-N222 2.077(4)	S202-Pd2 2.279(1)	Pd2-S202 2.298(1)	Pd2-S202 2.288(2)	
Pd2-S201 2.287(1)	Pd2-N213 2.05(1)	Pd2-N213 2.088(4)	Pd2-N213 2.081(5)	
Pd2-S202 2.265(1)	Pd2-N222 2.08(2)	Pd2-N222 2.083(3)	Pd2-N222 2.084(5)	

### Angles [°]

S1-Pd1-S2 95.16(3)	S101-Pd1-S102 92.74(6)	S101-Pd1-S102 90.66(4)	S101-Pd1-S102 90.83(5)	S101-Pd1-S102 93.65(5)
S1-Pd1-N13 90.53(7)	S101-Pd1-N113 172.4(1)	S101-Pd1-N113 94.21(8)	S101-Pd1-N113 95.6(1)	S101-Pd1-N113 172.3(1)
S1-Pd1-N22 170.49(8)	S101-Pd1-N122 93.1(1)	S101-Pd1-N122 173.72(8)	S101-Pd1-N122 173.0(1)	S101-Pd1-N122 94.8(1)
S2-Pd1-N13 172.97(8)	S102-Pd1-N113 94.6(1)	S102-Pd1-N113 173.46(8)	S102-Pd1-N113 173.4(1)	S102-Pd1-N113 91.3(1)
S2-Pd1-N22 94.32(7)	S102-Pd1-N122 174.1(1)	S102-Pd1-N122 95.51(8)	S102-Pd1-N122 94.3(1)	S102-Pd1-N122 169.4(1)
N13-Pd1-N22 80.1(1)	N113-Pd1-N122 79.6(2)	N113-Pd1-N122 79.7(1)	N113-Pd1-N122 79.4(1)	N113-Pd1-N122 79.6(1)
Pd1-S1-C1 114.6(1)	Pd1-S101-C101 110.2(2)	Pd1-S101-C101 108.0(1)	Pd1-S101-C101 102.5(2)	Pd1-S101-C101 107.9(2)
Pd1-S2-C7 108.2(1)	Pd1-S102-C107 107.0(2)	Pd1-S102-C107 102.7(1)	Pd1-S102-C107 107.9(2)	Pd1-S102-C107 113.2(2)
Pd1-N13-C14 129.1(2)	Pd1-N113-C114 129.2(4)	Pd1-N113-C114 128.9(2)	Pd1-N113-C114 129.1(3)	Pd1-N113-C114 129.2(3)
Pd1-N13-C23 112.6(2)	Pd1-N113-C123 113.4(3)	Pd1-N113-C123 112.6(2)	Pd1-N113-C123 112.3(3)	Pd1-N113-C123 112.7(3)
Pd1-N22-C21 129.2(2)	Pd1-N122-C121 128.6(4)	Pd1-N122-C121 129.3(3)	Pd1-N122-C121 128.5(3)	Pd1-N122-C121 129.2(3)
Pd1-N22-C25 112.4(2)	Pd1-N122-C126 112.9(3)	Pd1-N122-C126 112.1(2)	Pd1-N122-C126 112.8(3)	Pd1-N122-C126 112.4(3)
	S201-Pd2-S202 90.21(6)	S201-Pd2-S202 90.02(4)	C201-S201-Pd2 99.7(2)	S201-Pd2-S202 94.74(5)
	S201-Pd2-N213 96.1(1)	S201-Pd2-N213 95.0(1)	C207-S202-Pd2 108.4(2)	S201-Pd2-N213 173.9(1)
	S201-Pd2-N222 170.5(1)	S201-Pd2-N222 173.6(1)	S201-Pd2-S202 89.92(5)	S201-Pd2-N222 94.2(1)
	S202-Pd2-N213 171.1(1)	S202-Pd2-N213 174.9(1)	S201-Pd2-N213 91.8(4)	S202-Pd2-N213 90.9(1)
	S202-Pd2-N222 95.1(1)	S202-Pd2-N222 94.9(1)	S201-Pd2-N222 172.7(6)	S202-Pd2-N222 171.0(1)
	N213-Pd2-N222 79.5(2)	N213-Pd2-N222 80.1(1)	S202-Pd2-N213 175.4(4)	N213-Pd2-N222 80.2(1)
	Pd2-S201-C207 106.7(2)	Pd2-S201-C201 108.3(1)	S202-Pd2-N222 97.4(6)	Pd2-S201-C201 107.4(1)
	Pd2-S202-C201 107.2(2)	Pd2-S202-C207 100.2(1)	N213-Pd2-N222 80.9(7)	Pd2-S202-C207 113.4(2)

Pd2-N213-C214 128.2(4)	Pd2-N213-C214 129.2(3)	Pd2-N213-C214 129(1)	Pd2-N213-C214 129.7(3)
Pd2-N213-C223 113.2(4)	Pd2-N213-C223 112.0(2)	Pd2-N213-C223 112.9(9)	Pd2-N213-C223 112.5(3)
Pd2-N222-C221 128.7(4)	Pd2-N222-C221 128.7(3)	Pd2-N222-C221 132(1)	Pd2-N222-C221 129.9(3)
Pd2-N222-C226 112.6(4)	Pd2-N222-C226 112.9(2)	Pd2-N222-C226 113(1)	Pd2-N222-C226 112.9(3)

Table S1 Relevant metal-ligand bonds lengths and angles in the structures 1-5

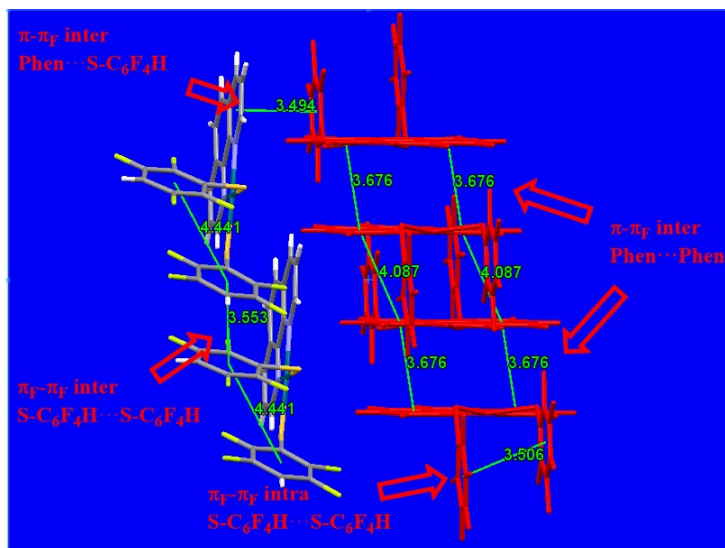


Figure S2. Visualization of the  $\pi_F$ - $\pi_F$ ,  $\pi$ - $\pi$  and  $\pi_F$ - $\pi$  interactions (intra- and intermolecular) in 1. Colored in red are the crystallographic independent molecules Pd1.

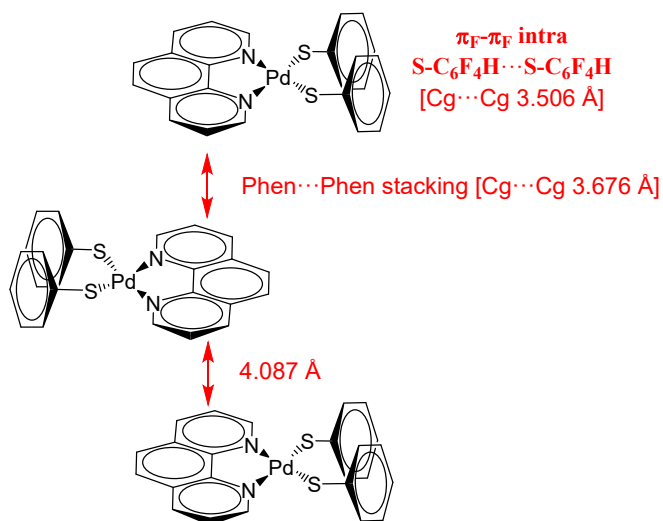
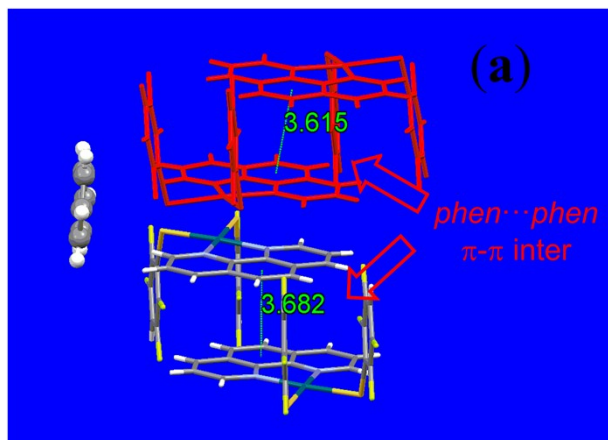
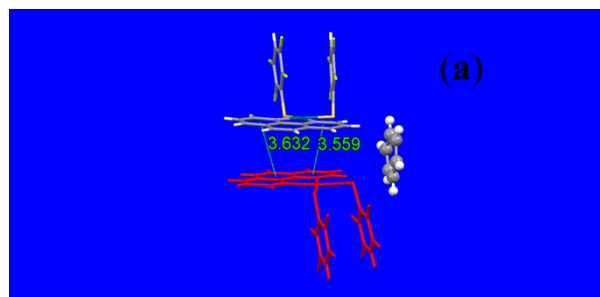


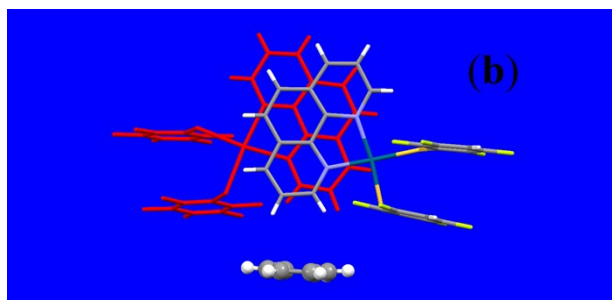
Figure S3. Schematization of the *phen*...*phen* intermolecular interactions (*head-to-tail*) forming the parallel infinite column (molecule Pd1).



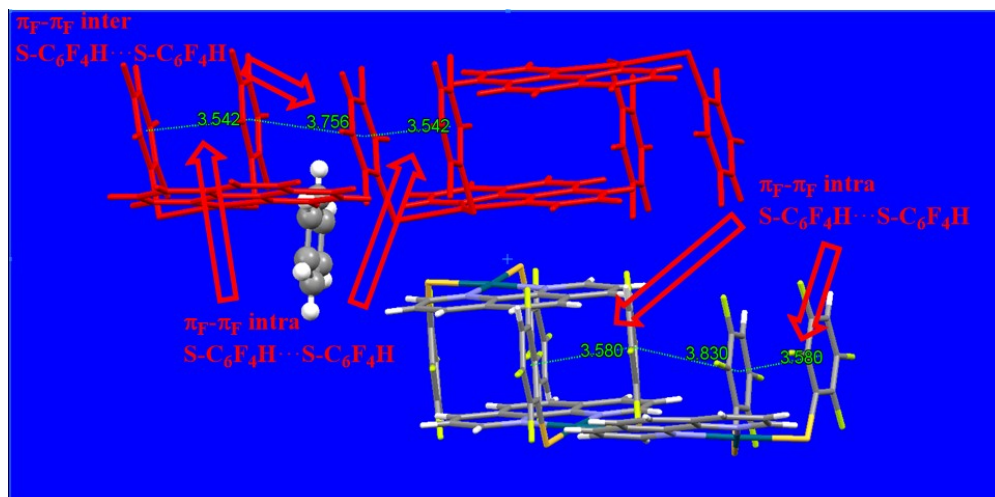
**Figure S4.** Visualization of the *phen*...*phen*  $\pi$ - $\pi$  intermolecular interactions (intra- and intermolecular) in **2**.  $C_6H_6$  solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.



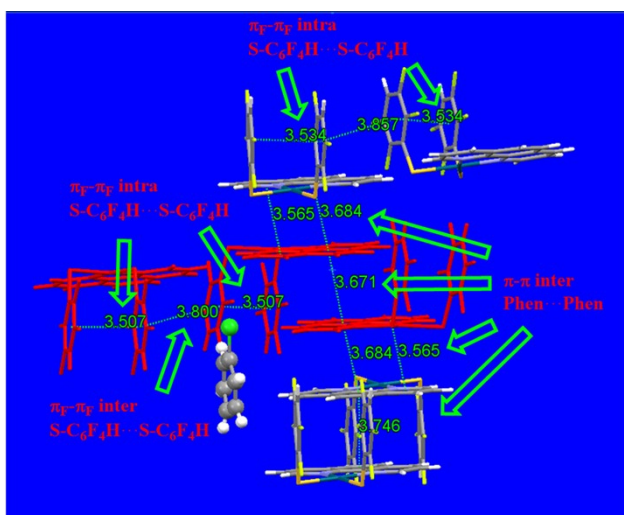
**Figure S5.** *Phen*...*phen* interactions in **2**. Colored in red is the crystallographic independent molecule Pd1.



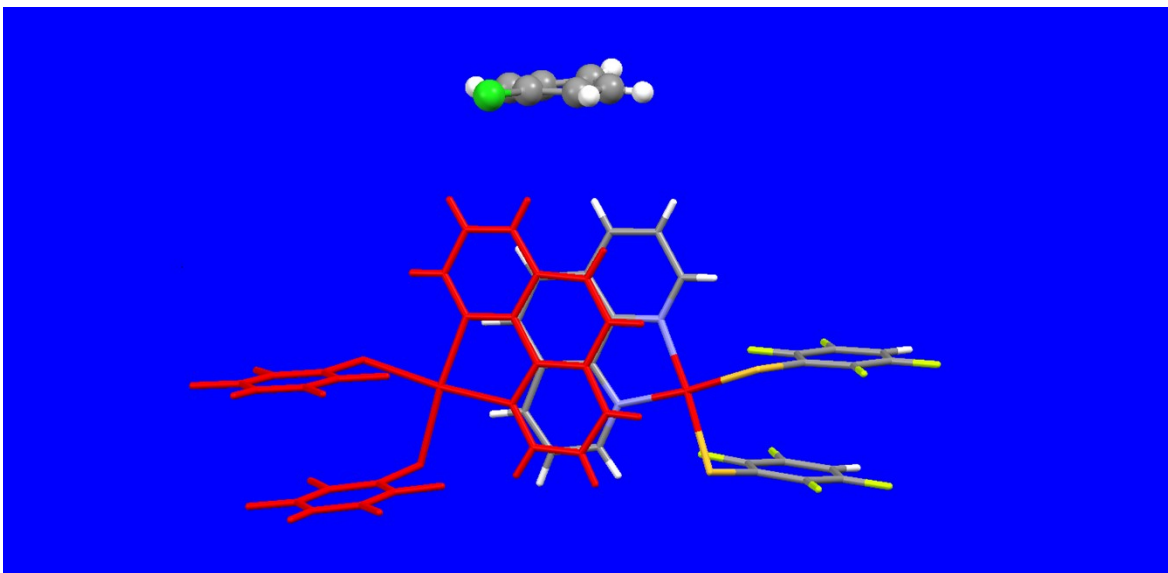
**Figure S6.** Projections presenting *phen*...*phen* interactions distorted from a perfect *head-to-tail* orientation in **2**. Colored in red is the crystallographic independent molecule Pd1.



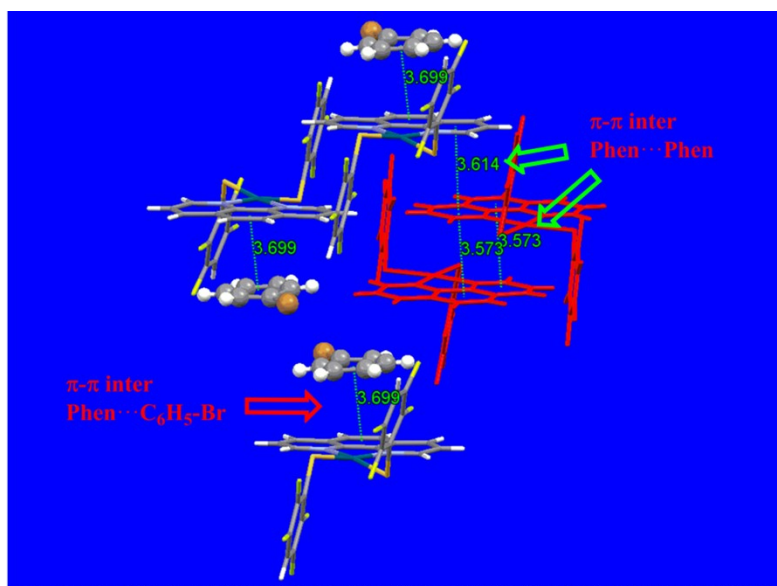
**Figure S7.** Visualization of the  $\pi_F$ - $\pi_F$  interactions (intra- and intermolecular) in **2**. Colored in red are the Pd1 molecules.



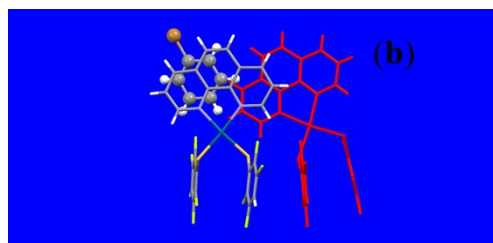
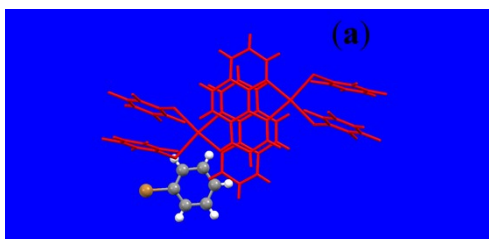
**Figure S8.** Visualization of the  $\pi_F$ - $\pi_F$  and *phen...phen*  $\pi$ - $\pi$  interactions (intra- and intermolecular) in **3**.  $C_6H_6Cl$  solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.



**Figure S9.** Projections presenting *phen*⋯*phen* interactions distorted from a perfect *head-to-tail* orientation in **3**. Colored in red is the crystallographic independent molecules Pd1.



**Figure S10.** Visualization of the  $\pi$ - $\pi$  interactions (intermolecular) in **4**.  $C_6H_6Br$  solvate is drawing in ball and stick style. Colored in red are the crystallographic independent molecules Pd1.





**Figure S11.** Projections presenting *phen*⋯*phen* interactions displaced from a perfect *head to-tail* and *head-to-head* orientation in **4**. Colored in red is the crystallographic independent molecules Pd1.

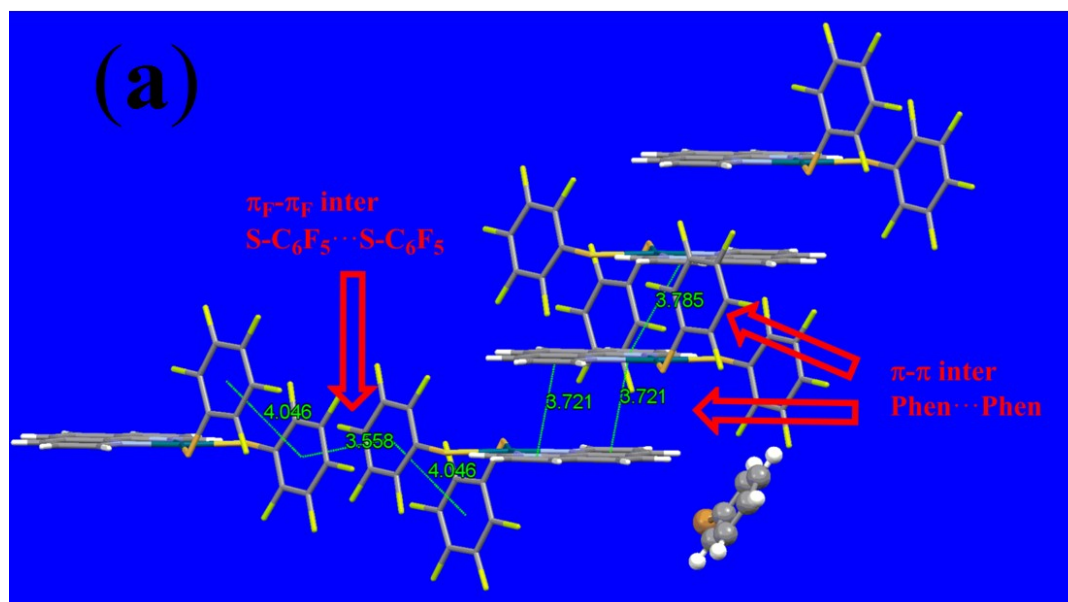
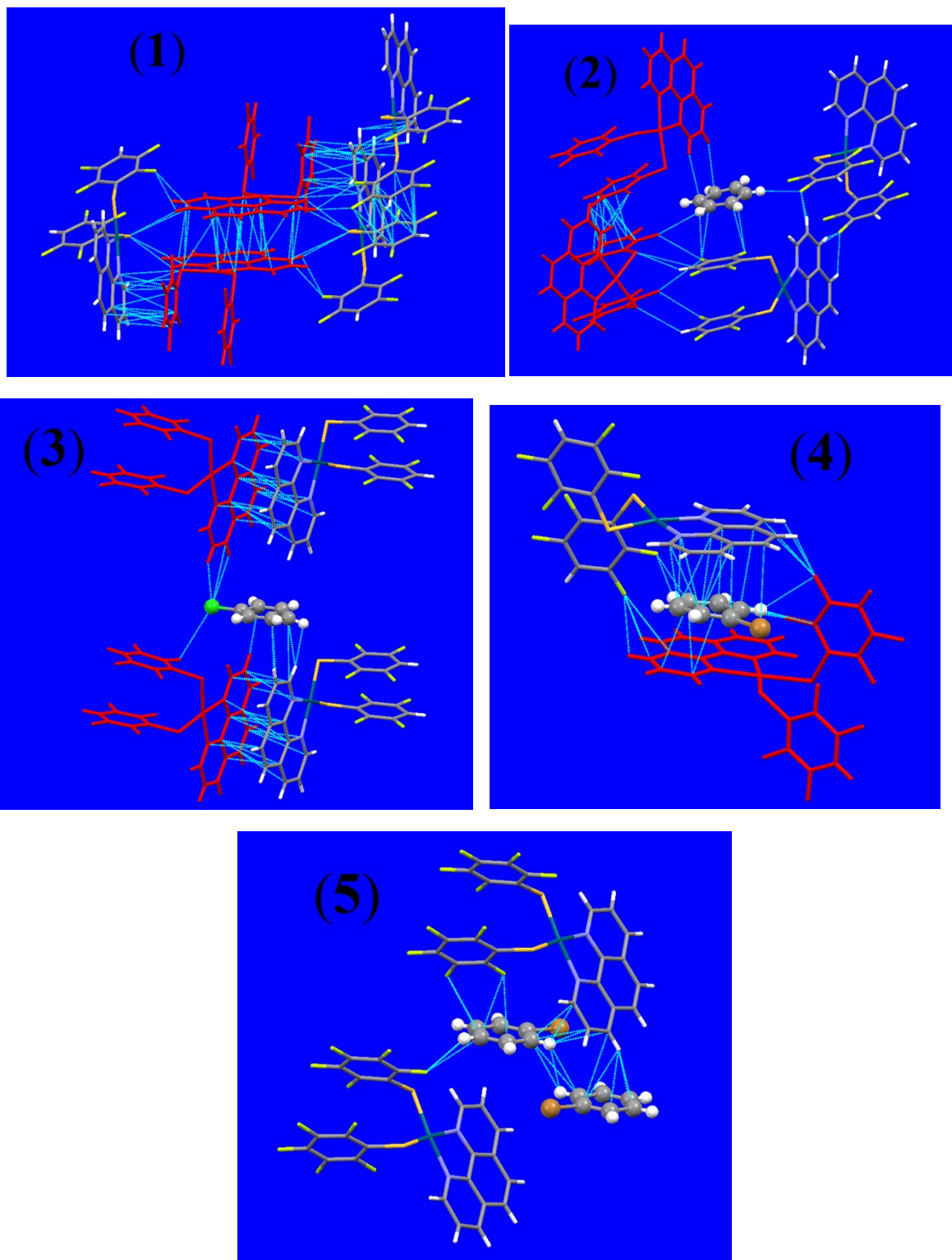


Figure S12. Visualization of the  $\pi$ - $\pi$  interactions (intermolecular) in **5**. C<sub>6</sub>H<sub>6</sub>Br solvate is drawing in ball and stick style.



**Figure S5.** Relevant non-covalent interactions involved around the Pd1 (colored in red) and Pd2 in the structures 1-5.

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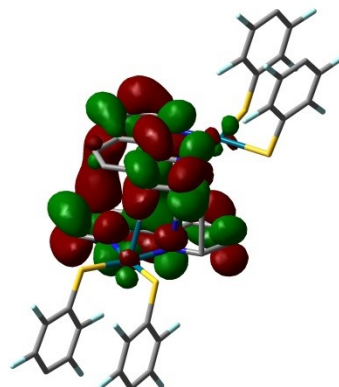
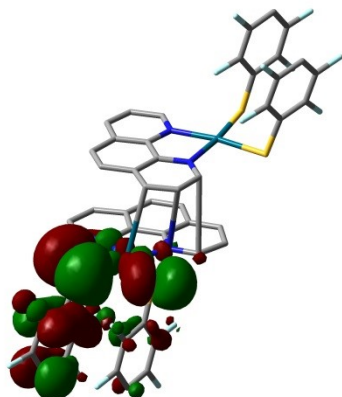
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**HOMO**

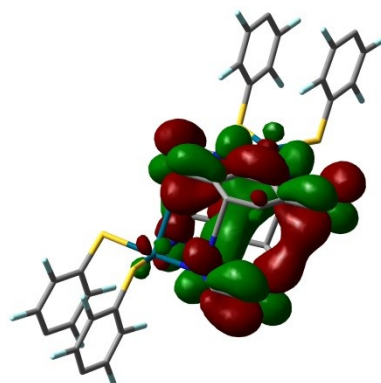
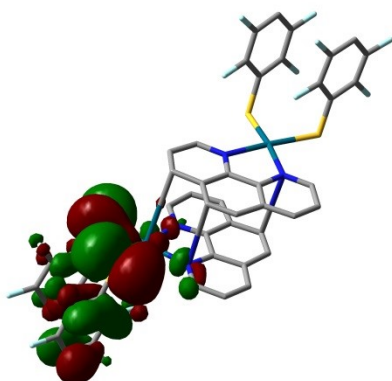
**LUMO**

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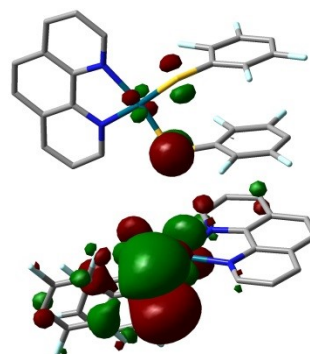
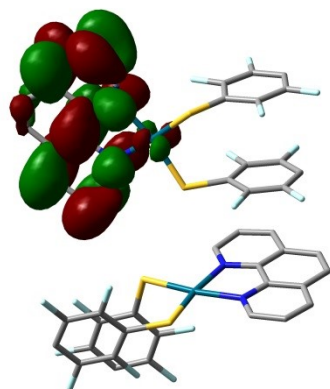
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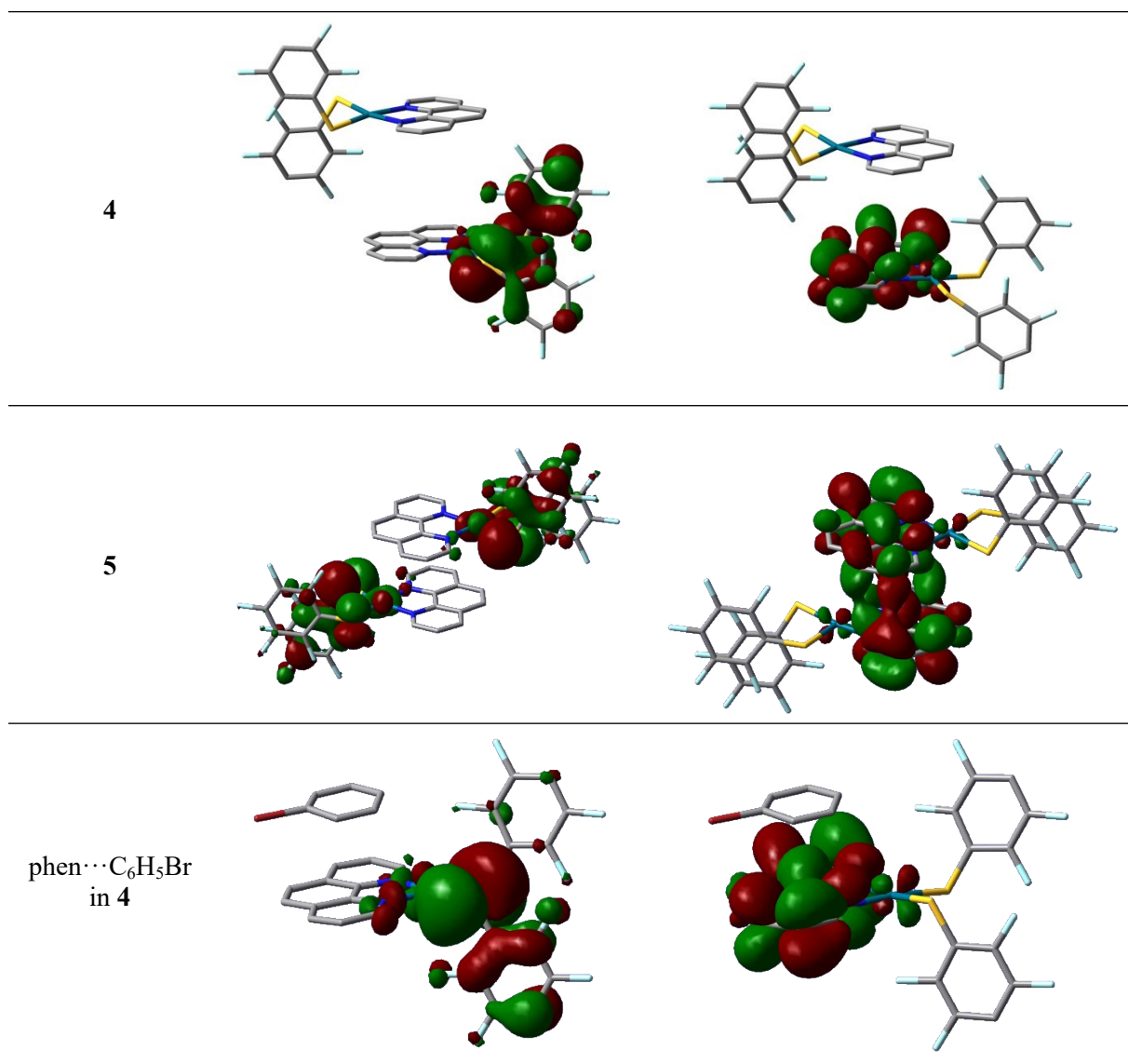


3



1





**Figure S14.** HOMO – LUMO plots for structures **1-5** and the interaction *phen*...C<sub>6</sub>H<sub>5</sub>Br.