Electronic Supplementary Material (ESI) for Dalton Transactions.

Theoretical Insight into the Intermolecular Interactions of d^8 Organometallic Self-Aggregation

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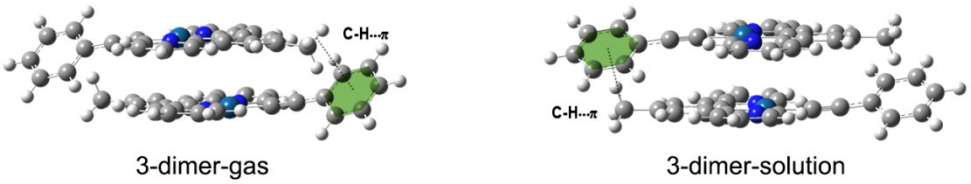
Table S1. The calculated structural parameters of 1-monomer in gas and solution phases under the B3LYP-D3/LanL2DZ, 6-31G(d) theoretical level. All distance data are in Å, all angle data are in degree.

parameter	1-mon-gas	1-mon-solution	Exp
Pt-N1	2.074	2.083	2.038
Pt-N2	2.073	2.082	2.040
Pt-C1	1.955	1.959	1.925
Pt-C2	2.054	2.062	2.072
C2-C3	1.229	1.231	1.204
C3-C4	1.426	1.428	1.442
Pt-C2-C3	179.95	179.70	169.74
C2-C3-C4	179.98	179.84	178.83
β	90.05	90.02	90.00

Table S2. The structural parameters of **1- 2-**and **3-** dimer (face-to-face style). The "–" in the table represent the dimer structure is non-existent in the simulations. All distance data are in Å, all angle data are in degree.

Dimer	Theory level	d_m	d_p	α	α'	β	β'	θ
1-dimer-gas	B3LYP	6.10	3.97	175.8	179.3	11.5	53.5	-81.5
1-dimer-gas	PBE	4.81	4.00	173.8	174.8	28.1	16.4	-68.0
1-dimer-gas	TPSS	6.10	3.99	178.6	176.0	30.8	10.8	-80.9
1-dimer-gas	B3LYP−D3	3.51	3.43	171.5	171.5	51.0	51.0	-44.2
1-dimer-gas	PBE−D3	3.47	3.44	171.8	171.8	49.5	50.2	-44.8
1-dimer-gas	TPSS−D3	3.42	3.29	178.5	173.2	15.6	23.0	-51.1
1-dimer-gas	M062X	3.88	3.39	173.6	171.8	79.4	27.2	-43.9
1-dimer-solution	B3LYP	—	—	—	—	—	—	—
1-dimer-solution	B3LYP−D3	3.67	3.48	169.5	173.4	51.1	59.6	-40.6
1-dimer-solution	ωb97x	3.57	3.55	173.0	176.2	45.0	60.6	-57.1
1-dimer-solution	ωb97xD	3.72	3.48	172.8	177.1	36.7	86.1	-43.1
1-dimer-solid	ωb97x	3.36	3.35	172.4	170.4	84.5	73.4	-58.7
1-dimer-solid	ωb97xD	3.28	3.26	172.2	169.4	89.8	68.0	-57.6
2-dimer-gas	B3LYP	—	—	—	—	—	—	—
2-dimer-gas	PBE	—	—	—	—	—	—	—
2-dimer-gas	TPSS	—	—	—	—	—	—	—
2-dimer-gas	B3LYP−D3	3.36	3.35	172.9	172.9	48.6	48.6	-52.8
2-dimer-gas	PBE−D3	3.34	3.34	173.5	173.5	48.4	48.4	-53.0
2-dimer-gas	TPSS−D3	3.16	3.15	173.6	173.7	49.9	50.0	-51.9
2-dimer-gas	M062X	3.81	3.34	173.1	172.7	74.5	19.9	-68.1
3-dimer-gas	B3LYP	—	—	—	—	—	—	—
3-dimer-gas	PBE	—	—	—	—	—	—	—
3-dimer-gas	TPSS	—	—	—	—	—	—	—
3-dimer-gas	B3LYP−D3	3.40	3.38	172.3	174.3	51.1	43.1	-53.9
3-dimer-gas	PBE−D3	3.37	3.37	173.7	174.1	48.8	42.3	-55.2
3-dimer-gas	TPSS−D3	3.19	3.19	173.8	173.8	48.1	51.3	-53.5
3-dimer-gas	M062X	3.33	3.31	172.6	172.6	50.3	51.4	-54.4

Figure S1. The optimized geometries 3-dimer in gas and solution phase employed head-to-head aggregation style. The C−H···π interaction found in 8-dimer was emphasized herein.



3-dimer-gas　　3-dimer-solution

Figure S2. Schematic diagram of interaction area of 2-dimer-gas possess face-to-face and head-to-head aggregation style.

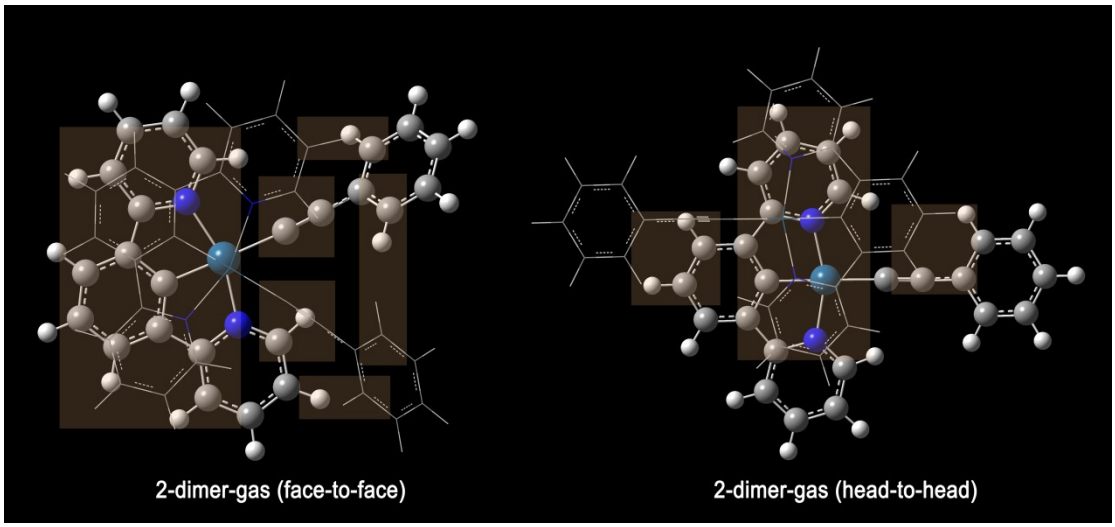


Table S3. Energy and composition of the frontier molecular orbitals of complex **1**.

structure	MO	Energy/eV	comp
1-mon	LUMO+4	-0.337	3%Pt-py, 3%Pt-dxy, 90% pπ + pπ*
	LUMO+3	-0.988	2%Pt-py, 94%pπ + pπ*
	LUMO+2	-1.244	2%Pt-dyz, 92% pπ + pπ*
	LUMO+1	-2.035	3%Pt-dxy, 95% pπ + pπ*
	LUMO	-2.081	2%Pt-dyz, 92% pπ + pπ*
	HOMO	-5.041	6%Pt-dxz, 2%Pt-dz^2, 88% pπ + pπ*
	HOMO-1	-5.430	21%Pt-dxy, 2%Pt-dyz, 70% pπ + pπ*
	HOMO-2	-6.333	98% pπ + pπ*
	HOMO-3	-6.339	54% Pt-dx^2-y^2, 21%Pt-dz^2, 22%Pt-s
	HOMO-4	-6.475	48% Pt-dyz, 4%Pt-dxy, 53% pπ + pπ*
1-dimer-gas	LUMO+4	-1.128	4% Pt-dyz, 90% pπ + pπ*
	LUMO+3	-1.770	2% Pt-dxz, 93% pπ + pπ*
	LUMO+2	-1.882	94% pπ + pπ*
	LUMO+1	-1.947	2% Pt-dyz, 92% pπ + pπ*
	LUMO	-2.120	2% Pt-dxz, 94% pπ + pπ*
	HOMO	-5.040	7% Pt-dxz, 84% pπ + pπ*
	HOMO-1	-5.043	8% Pt-dxz, 83% pπ + pπ*
	HOMO-2	-5.430	10% Pt-dxz, 4% Pt-dx^2-y^2, 76% pπ + pπ*
	HOMO-3	-5.598	72% Pt-dz^2, 16% Pt-s, 2% Pt-pz
	HOMO-4	-5.611	16% Pt-dxz, 4% Pt-dx^2-y^2, 71% pπ + pπ*
1-dimer-solution	LUMO+4	-1.067	2% Pt-dyz, 94% pπ + pπ*
	LUMO+3	-1.794	2% Pt-dxz, 92% pπ + pπ*
	LUMO+2	-1.865	95% pπ + pπ*
	LUMO+1	-1.916	2% Pt-dxz, 90% pπ + pπ*
	LUMO	-2.122	2% Pt-dxz, 93% pπ + pπ*
	HOMO	-5.321	10% Pt-dxz, 1% Pt-dxy, 1% Pt-dx^2-y^2, 81% pπ + pπ*
	HOMO-1	-5.369	8% Pt-dxz, 2%Pt-dxy, 2%Pt-dx^2-y^2, 79% pπ + pπ*
	HOMO-2	-5.710	15% Pt-dxz, 4% Pt-dxy, 65% pπ + pπ*
	HOMO-3	-5.806	10% Pt-dxz, 2% Pt-dx2-y2, 71% pπ + pπ*
	HOMO-4	-5.862	64% Pt- dz^2, 9% Pt-dyz, 18% Pt-s
1-dimer-solid	LUMO+4	-1.153	2% Pt-dyz, 89% pπ + pπ*
	LUMO+3	-1.591	2% Pt-dxz, 1% Pt-dyz, 90% pπ + pπ*
	LUMO+2	-1.955	2% Pt-dxz, 93% pπ + pπ*
	LUMO+1	-1.984	2% Pt-dxz, 91% pπ + pπ*
	LUMO	-2.081	2% Pt-dxz, 2% Pt-dyz, 93% pπ + pπ*
	HOMO	-4.968	6% Pt-dx^2-y^2, 1% Pt-dxy, 1% Pt-dxz, 81% pπ + pπ*
	HOMO-1	-5.075	6% Pt-dx^2-y^2, 5% Pt-dz2, 80% pπ + pπ*
	HOMO-2	-5.228	33% Pt-dz^2, 2% Pt-dx^2-y^2, 50% dpπ + pπ*
	HOMO-3	-5.437	26% Pt-dz^2, 2% Pt-dx^2-y^2, 49% dpπ + pπ*
	HOMO-4	-5.450	18% Pt-dz^2, 62% pπ + pπ*

Table S4. Calculated vertical excited energy (λ/nm), oscillator strength, corresponding

excitation transition and coeff of the main absorption for three complexes. F2F and H2H represent the face-to-face and head-to-head aggregation style, respectively.

	λ/nm	*f*	assignment	coeff
1-mon-gas	450.6	0.048	H-1-L	0.70
	442.9	0.052	H-1-L+1	0.70
1-dimer-gas	516.9	0.023	H-1-L	0.68
	493.7	0.015	H-1-L+1	0.70
	492.2	0.016	H-L+1	0.69
1-dimer-solution	463.5	0.039	H-L	0.68
			H-L+1	0.11
	456.6	0.012	H-1-L	0.68
	441.3	0.020	H-L+1	0.68
	432.8	0.022	H-1-L+1	0.68
1-dimer-solid	541.2	0.005	H-L	0.70
	516.2	0.004	H-1-L	0.68
	505.0	0.015	H-2-L	0.49
			H-L+1	0.44
			H-3-L	0.11
	501.8	0.010	H-L+1	0.48
			H-2-L	0.44
			H-3-L	0.12
2-mon-gas	447.2	0.042	H-1-L	0.70
	445.7	0.057	H-1-L+1	0.70
2-dimer-gas(H2H)	465.4	0.111	H-L	0.55
			H-1-L+1	0.40
2-dimer-gas(F2F)	481.1	0.041	H-1-L	0.69
	457.7	0.028	H-2-L	0.52
3-mon-gas	452.6	0.041	H-1-L	0.70
	451.2	0.061	H-1-L+1	0.68
3-dimer-gas(H2H)	453.5	0.122	H-1-L	0.50
			H-L+1	0.48
	440.7	0.060	H-L+1	0.50
			H-1-L	0.42
3-dimer-gas(F2F)	492.5	0.017	H-L	0.69
	485.3	0.039	H-1-L	0.67
			H-L+1	0.16

Details of the GKS-EDA scheme

The generalized Kohn-Sham energy decomposition analysis is a method used to calculate intermolecular interaction energy. The interaction energy is allowed to be decomposed into physical components. The theoretical kernel of this method can be briefly described as following.

The many-electron Hamiltonian H can be expressed as

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} \tag{1}$$

$\hat{T}$ is the kinetic operator, $\hat{V}_{ee}$ is the electron-electron interaction operator, and $\hat{V}_{ne}$ is the nuclear-electron interaction operator, regarded as external potential operator.

In GAMESS-US program, the total interaction energy can be divided into the following terms:

$$\Delta E^{\mathrm{TOT}} = \Delta E^{\mathrm{ele}} + \Delta E^{\mathrm{ex}} + \Delta E^{\mathrm{rep}} + \Delta E^{\mathrm{pol}} + \Delta E^{\mathrm{corr}} + \Delta E^{\mathrm{disp}} \tag{2}$$

Where the subscripts ele, ex, rep, pol, corr, and disp denote electrostatic, exchange, repulsion, polarization, correlation and dispersion. Notice that the GKS-EDA interaction terms are defined according to the generalized Kohn-Sham scheme. The exchange, repulsion and polarization terms are determined by DFT determinant; the correlation term is attributed by the GKS correlation energy; the dispersion term, which is optional for dispersion correction DFT, defined as the difference of the dispersion corrections from monomers to supermolecule without BSSE correction.

Table S5. GKS-EDA results based on the B3LYP-D3 dimer geometries. All energy data were in kcal/mol. Here, F2F and H2H represent the face-to-face and head-to-head aggregation style, respectively.

	style	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	ΔE^{pol}	ΔE^{disp}	ΔE^{corr}	ΔE^{tot}
1-dimer-gas	F2F	-29.25	-97.32	160.95	-10.15	-51.32	-8.55	-35.64
2-dimer-gas	F2F	-23.77	-91.31	149.07	-8.38	-46.52	-8.40	-29.32
2-dimer-gas	H2H	-24.01	-80.84	133.82	-8.23	-43.40	-5.31	-27.97
3-dimer-gas	F2F	-23.51	-92.24	150.59	-8.44	-48.43	-8.29	-30.33
3-dimer-gas	H2H	-24.60	-85.93	141.30	-8.13	-46.73	-6.42	-30.51

Table S6. GKS-EDA results of M062X functional, MP2 and SCS-MP2 method. All energy data were in kcal/mol and all test dimer-structures were face-to-face style.

Method	Dimer-structure	ΔE^{ele}	ΔE^{ex}	ΔE^{rep}	ΔE^{pol}	ΔE^{disp}	ΔE^{corr}	ΔE^{tot}
M062X	1-dimer-gas	-27.68	-91.21	151.23	-9.63	-45.29		-22.58
	2-dimer-gas	-21.56	-85.53	139.73	-9.06	-43.36		-19.78
	3-dimer-gas	-21.33	-86.65	141.51	-9.05	-44.77		-20.28
MP2	1-dimer-gas	-29.49	-91.74	150.74	-7.43		-33.16	-11.08
	2-dimer-gas	-25.15	-93.85	152.16	-6.99		-34.62	-8.44
	3-dimer-gas	-22.74	-88.84	143.32	-7.16		-35.74	-11.17
SCS−MP2	1-dimer-gas	-29.49	-91.74	150.74	-7.43		-24.99	-2.9
	2-dimer-gas	-25.15	-93.85	152.16	-6.99		-26.7	-0.52
	3-dimer-gas	-22.74	-88.84	143.32	-7.16		-27.46	-2.89

Figure S3. Dispersion contributions (B3LYP−D3) of the metal and ligand fragments of **2**-dimer-gas.

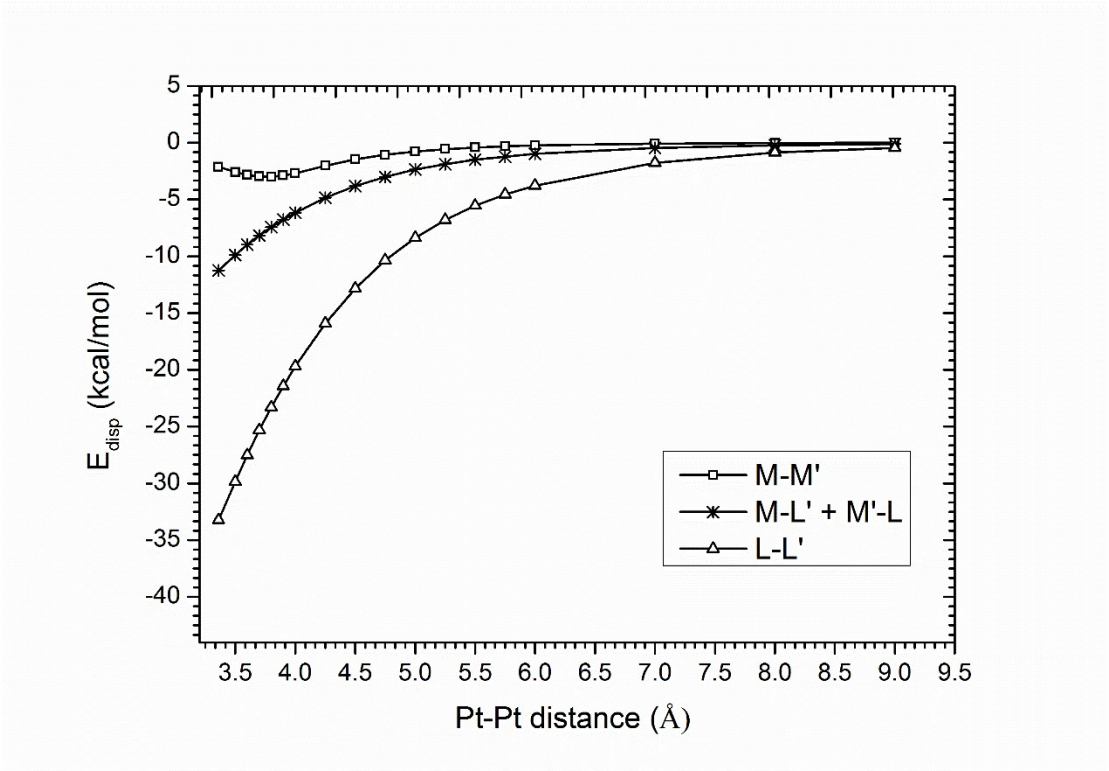


Figure S4. Dispersion contributions (B3LYP−D3) of the metal and ligand fragments of **3**-dimer-gas.

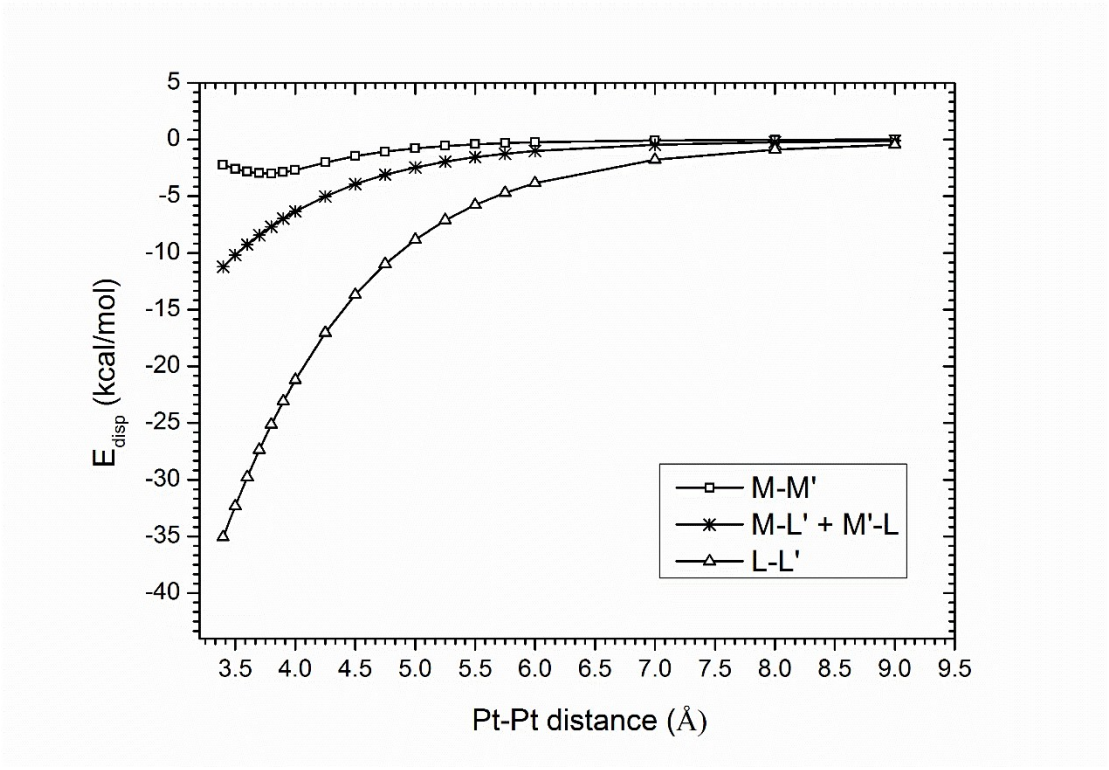


Table S7. Formation free energies in eV of 1-dimer-solution and 2-dimer-solution with different corrections.

	1-dimer-solution	2-dimer-solution
[a]Initial value	-1.03	-0.87
Trouton's rule[1, 2]	-1.30	-1.14
IGRRHO[3]	-0.82	-0.71
STSS[4-6]	-2.03	-1.85
TYCM[7]	-1.59	-1.42
PS[8, 9]	-1.36	-1.14
DL[10-12]	-2.03	-1.69
MHP[13]	-1.30	-1.13
ST[14]	-1.25	-1.05

[a]The initial values were calculated based on the optimized structure of monomers and dimers with B3LYP-D3/PCM theoretical model.

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