

Supporting Information

Designed Metal-organic π -clusters Combining Aromaticity of Metal Cluster and Ligands for Third-order Nonlinear Optical Response

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Computational details

All the calculations were implemented in Gaussian 16¹. The ground-state equilibrium geometries of these structures were fully optimized with density functional theory (DFT) using B3LYP functional and 6-31G(d,p) basis sets for C, H, and Lanl2DZ basis set for Os with D3 dispersion correction of Grimme²⁻¹⁰. The analysis of nucleus-independent chemical shift (NICS)^{11, 12} were also using B3LYP functional and 6-311++G(d,p) basis sets for C, H. Anisotropy of the Induced Current Density (AICD)^{13, 14} and iso chemical shielding surface (ICSS)^{15, 16} analysis used 6-31+G(d,p) basis sets for C, H. The static third-order nonlinear polarizability calculations and TDDFT were used cam-B3LYP functional¹⁷ and aug-cc-pVDZ basis set for C, H. The frequency-dependent second hyperpolarizabilities were calculated by the sum-over-states (SOS) method^{18, 19}. In order to get a deeper understanding of the wave function, Multiwfn 3.8(dev) code²⁰ and VMD software²¹ were used to analyze the electronic structures, hyperpolarizability, excitation characteristics, and aromaticity.

The electron-hole distributions are defined as follows:

$$\rho^{hole}(r) = \sum_{i \rightarrow a} (w_i^a)^2 \phi_i(r) \phi_i(r) + \sum_{i \rightarrow a} \sum_{j \rightarrow a} w_i^a w_j^a \phi_i(r) \phi_j(r)$$

$$\rho^{electron}(r) = \sum_{i \rightarrow a} (w_i^a)^2 \phi_a(r) \phi_a(r) + \sum_{i \rightarrow a} \sum_{i \rightarrow b} w_i^a w_i^b \phi_a(r) \phi_b(r)$$

where i and j are the occupied orbital labels, a and b are the virtual orbital labels, and Φ is the orbital wave function. w corresponds to the configuration coefficient of excitation.

The D index is used to measure the distance between the center of mass of holes and electrons.

$$D = \sqrt{(X_{ele} - X_{hole})^2 + (Y_{ele} - Y_{hole})^2 + (Z_{ele} - Z_{hole})^2}$$

The t index is used to measure the separation degree of holes and electrons.

$$t = D - H_{CT}$$

E_{coul} represents the electron-hole coulomb attractive energy.

$$E_{coul} = \iint \frac{\rho^{hole}(r_1)\rho^{ele}(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

The hole delocalization index (*HDI*) and the electron delocalization index (*EDI*) are

$$HDI = 100 \times \sqrt{\int [\rho^{hole}(r)]^2 dr}$$

$$EDI = 100 \times \sqrt{\int [\rho^{ele}(r)]^2 dr}$$

Table S1. Os-Os Bond Lengths of Different Os-organic π -clusters.

Cluster	Os-Os bond length/Å										Average/Å
Os₃	Os1-Os2	Os2-Os3	Os3-Os1								2.527
	2.479	2.386	2.716								
Os₄	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os1							2.462
	2.462	2.462	2.462	2.461							
Os₅	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os5	Os5-Os1						2.471
	2.567	2.408	2.481	2.457	2.440						
Os₆	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os5	Os5-Os6	Os6-Os1					2.428
	2.428	2.429	2.428	2.428	2.428	2.428					
Os₇	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os5	Os5-Os6	Os6-Os7	Os7-Os1				2.430
	2.433	2.429	2.439	2.437	2.426	2.418	2.425				
Os₈	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os5	Os5-Os6	Os6-Os7	Os7-Os8	Os8-Os1			2.420
	2.420	2.419	2.420	2.419	2.420	2.420	2.418	2.420			
Os₉	Os1-Os2	Os2-Os3	Os3-Os4	Os4-Os5	Os5-Os6	Os6-Os7	Os7-Os8	Os8-Os9	Os9-Os1		2.415
	2.420	2.411	2.413	2.399	2.394	2.445	2.413	2.428	2.416		

Table S2. Os-Os Bond Angle of Different Os-organic π -clusters.

Cluster	Os-Os bond angle/°									Average/Å
Os₃	Os1-Os2-Os3	Os1-Os3-Os2	Os2-Os1-Os3	-	-	-	-	-	-	60.0
	67.9	57.7	54.5							
Os₄	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os1	Os4-Os1-Os2	-	-	-	-	-	88.7
	88.7	88.7	88.7	88.7						
Os₅	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os5	Os4-Os5-Os1	Os5-Os1-Os2	-	-	-	-	103.0
	107.4	98.0	106.5	97.5	105.8					
Os₆	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os5	Os4-Os5-Os6	Os5-Os6-Os1	Os6-Os1-Os2	-	-	-	109.2
	109.2	109.2	109.3	109.2	109.2	109.3				
Os₇	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os5	Os4-Os5-Os6	Os5-Os6-Os7	Os6-Os7-Os1	Os7-Os1-Os2	-	-	115.1
	114.8	121.6	112.3	116.7	112.4	112.9	115.4			
Os₈	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os5	Os4-Os5-Os6	Os5-Os6-Os7	Os6-Os7-Os8	Os7-Os8-Os1	Os8-Os1-Os2	-	117.3
	117.7	117.4	117	117.4	117.6	117.3	117.1	117.3		
Os₉	Os1-Os2-Os3	Os2-Os3-Os4	Os3-Os4-Os5	Os4-Os5-Os6	Os5-Os6-Os7	Os6-Os7-Os8	Os7-Os8-Os9	Os8-Os9-Os1	Os9-Os1-Os2	120.8
	117.6	123.3	117.1	124.1	126.1	117.4	119.7	120.9	120.9	

Table S3. NPA Charge of Different Os-organic π -clusters.

Cluster	Os1	Os2	Os3	Os4	Os5	Os6	Os7	Os8	Os9	sum
Os ₃	0.241	-0.022	0.081	-	-	-	-	-	-	0.300
Os ₄	0.024	0.024	0.024	0.025	-	-	-	-	-	0.097
Os ₅	0.129	0.020	0.059	-0.014	0.126	-	-	-	-	0.320
Os ₆	0.063	0.063	0.063	0.063	0.064	0.063	-	-	-	0.379
Os ₇	0.077	0.019	0.059	0.068	0.051	-0.002	0.084	-	-	0.356
Os ₈	0.046	0.051	0.053	0.050	0.048	0.049	0.054	0.051	-	0.402
Os ₉	0.089	0.058	0.029	0.020	0.065	0.020	0.065	0.040	-0.009	0.377

Table S4. Calculated Formation Free Energy of Different Os-organic π -clusters.

Cluster	N×Os ₁ /Hartree	Zero-point correction /Hartree	Electronic and zero- point Energies /Hartree	Electronic /Hartree	Electronic and thermal Free Energies /Hartree	Thermal Free Energies /Hartree	G /Hartree	ΔG /Hartree	$\Delta G_{\text{average}}$ /Hartree
Os ₁	-361.099	0.101	-361.167	-361.269	-361.200	0.069	-361.099	0.000	0.000
Os ₃	-1083.297	0.311	-1083.780	-1084.091	-1083.835	0.256	-1083.524	-0.227	-0.076
Os ₄	-1444.396	0.416	-1445.111	-1445.526	-1445.175	0.351	-1444.759	-0.363	-0.091
Os ₅	-1805.495	0.520	-1806.395	-1806.914	-1806.469	0.445	-1805.949	-0.455	-0.091
Os ₆	-2166.594	0.627	-2167.731	-2168.359	-2167.810	0.548	-2167.183	-0.589	-0.098
Os ₇	-2527.693	0.734	-2529.016	-2529.750	-2529.106	0.644	-2528.372	-0.679	-0.097
Os ₈	-2888.792	0.840	-2890.334	-2891.174	-2890.433	0.741	-2889.593	-0.801	-0.100
Os ₉	-3249.891	0.947	-3251.623	-3252.570	-3251.731	0.839	-3250.784	-0.893	-0.099

Table S5. Nucleus-Independent Chemical Shift of Different Os-organic π -clusters.

Cluster	NICS(0) /ppm	NICS(1) /ppm	NICS(0) _{zz} /ppm	NICS(1) _{zz} /ppm	NICS(0) _{πzz} /ppm	NICS(1) _{πzz} /ppm
Os₃	-18.51	-17.22	-96.62	-35.29	-54.45	-27.05
Os₄	-21.11	-19.33	-87.78	-49.69	-59.40	-38.18
Os₅	-9.37	-4.20	-42.28	-20.78	-27.59	-13.04
Os₆	2.25	4.00	-6.11	-0.96	-10.01	-6.15
Os₇	2.54	4.48	-8.17	-6.34	-22.42	-17.39
Os₈	0.41	2.36	-8.02	-5.91	-22.30	-17.40
Os₉	5.30	4.92	-2.65	-3.92	-11.48	-10.28

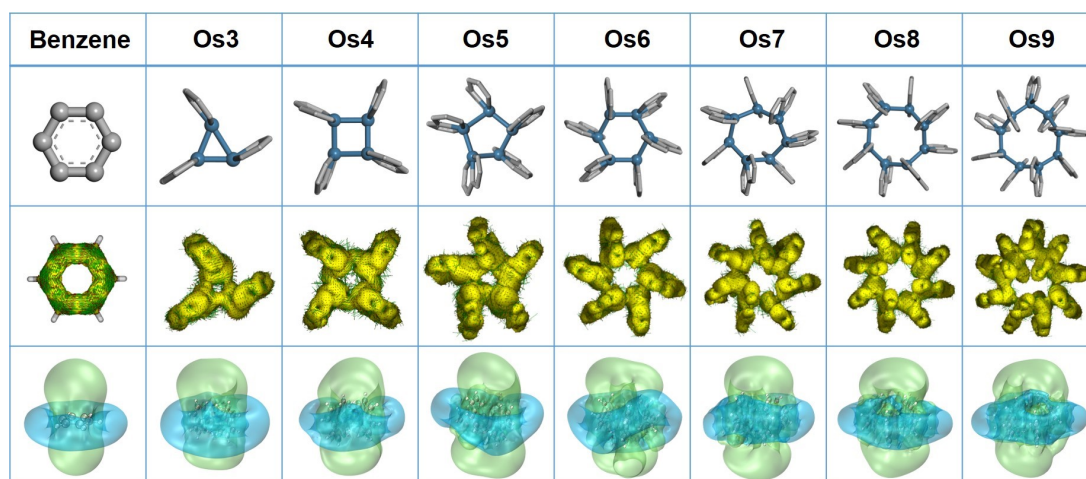
**Figure S1.** Analysis of the aromaticity of Os-organic π -clusters: Structures (line 2). The π contribution of anisotropy of the induced current density (AICD- π , iso=0.03 a.u.) (line 3). Iso-chemical shielding surfaces in the Z direction (ICSS_{zz}) (line 4).

Table S6. Third-order NLO Coefficients of Different Os-organic π -clusters.

Cluster	Magnitude of gamma/a.u.	Average of Magnitude of gamma/a.u.
Os ₃	7.610900E+04	2.536967E+04
Os ₄	1.001181E+05	2.502953E+04
Os ₅	1.640102E+05	3.280204E+04
Os ₆	1.398585E+05	2.330975E+04
Os ₇	1.708772E+05	2.441103E+04
Os ₈	1.997905E+05	2.497381E+04
Os ₉	2.443956E+05	2.715507E+04

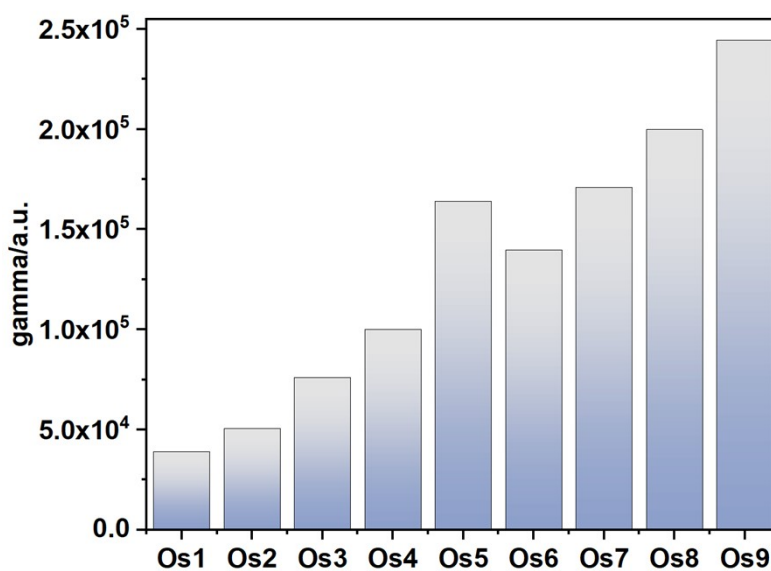


Figure S2. Third-order NLO coefficients of different Os-organic π -clusters.

Table S7. Molecular Orbitals Energy and HOMOs Components of Different Os-organic π -clusters.

Cluster	HOMO/eV	LUMO/eV	E _{gap} /eV	Os (5d)	C (2p)	Other
Os₁	-4.71	-2.03	2.68	68.64%	2.26%	29.10%
Os₃	-4.98	-2.86	2.13	74.39%	13.73%	11.88%
Os₄	-4.92	-2.58	2.34	53.86%	38.45%	7.69%
Os₅	-4.32	-2.86	1.47	41.86%	44.13%	14.01%
Os₆	-4.60	-2.40	2.20	39.80%	41.46%	18.74%
Os₇	-4.42	-2.53	1.88	48.04%	34.21%	17.75%
Os₈	-4.70	-2.27	2.43	45.84%	32.47%	21.69%
Os₉	-4.29	-2.60	1.69	44.05%	32.62%	23.33%

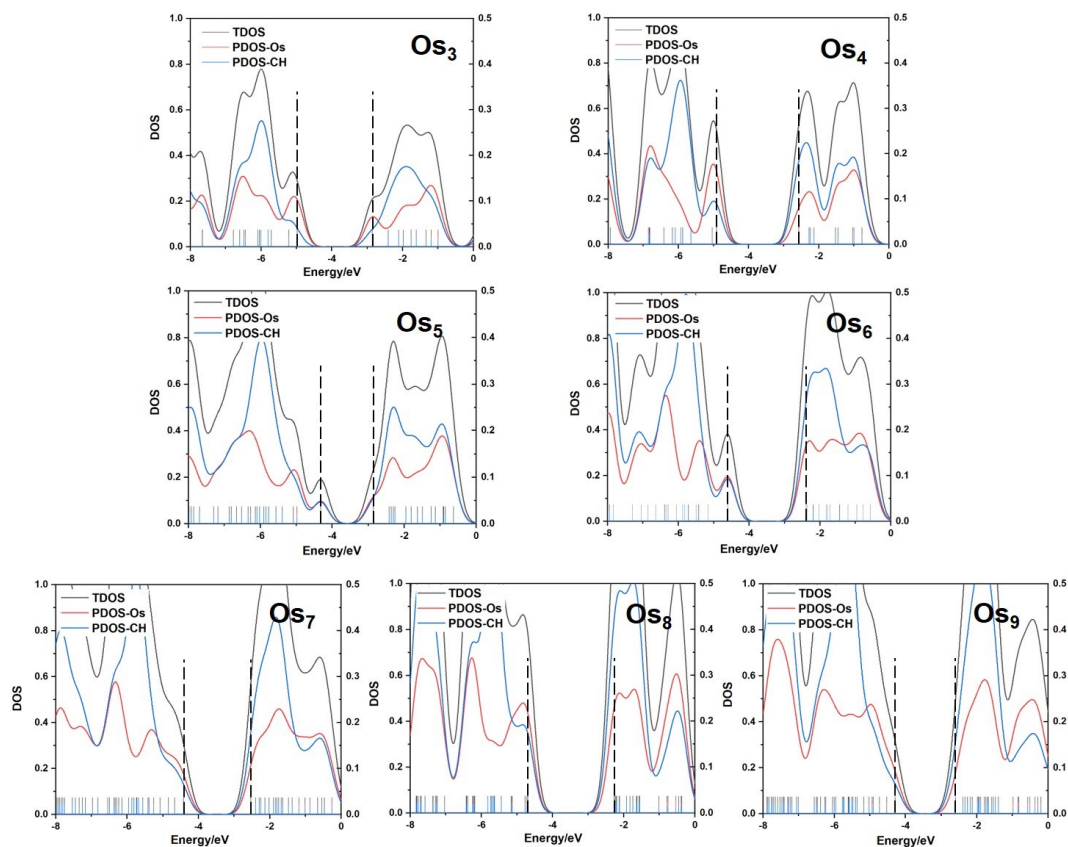


Figure S3. Density of states (DOS) of different Os-organic π -clusters.

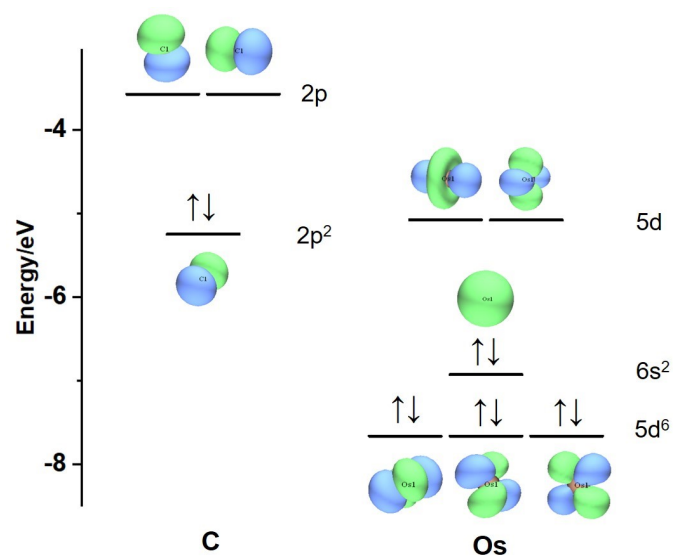


Figure S4. Atomic orbitals of C and Os.

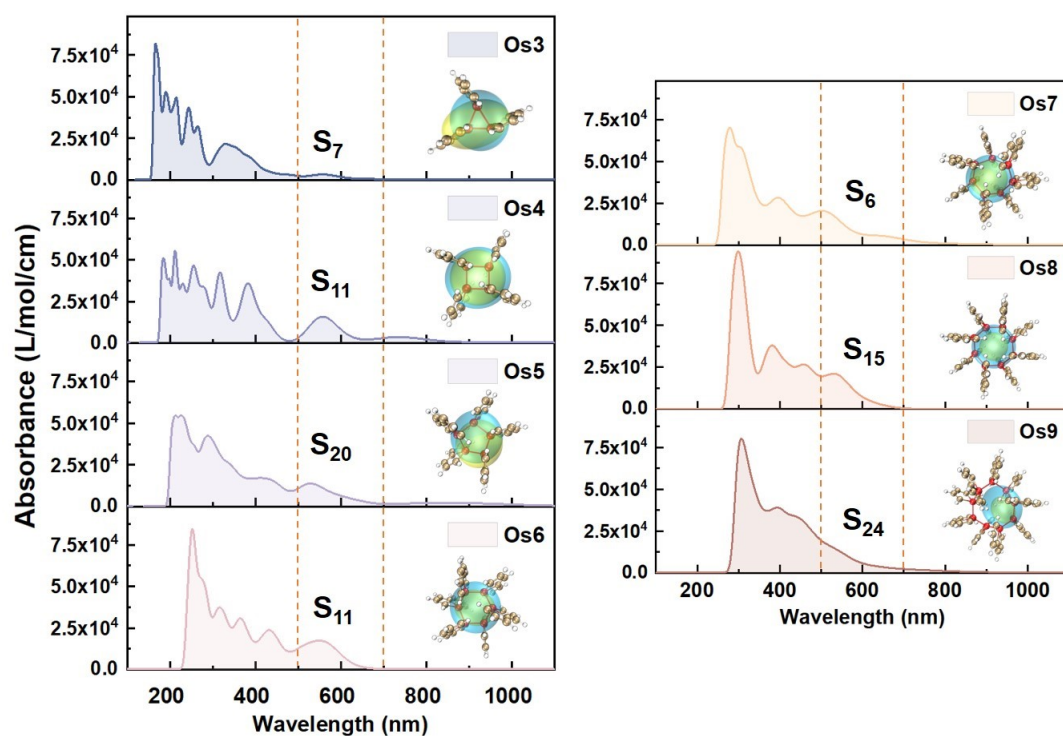


Figure S5. Normalized UV-vis absorption spectra and electron-hole distribution smoothing isosurface schematic of Os-organic clusters (in).

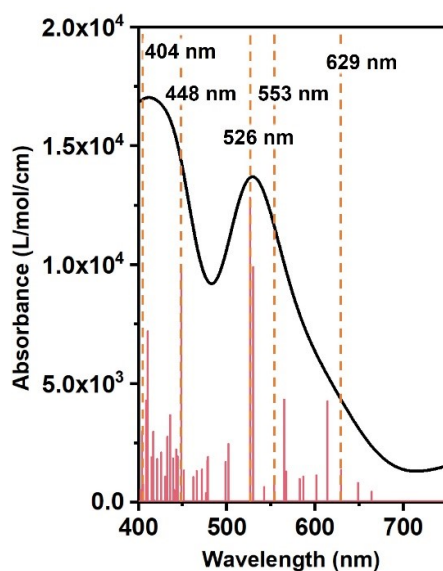


Figure S6. Normalized UV-vis absorption spectra in the visible-light range of the Os_5 cluster.

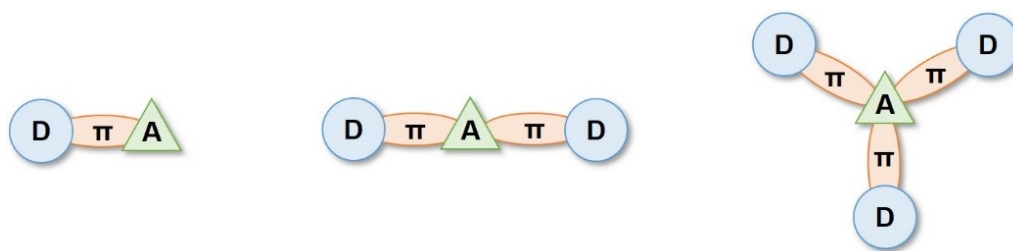


Figure S7. Schematic for dipolar (left), quadrupole (middle), and octupole (right) molecular unit.

Table S8. The Transition Nature of the Major Electron Excitations.

Cluster	Wavelength	f	Major MO transitions
Os ₃	S ₀ -S ₇ : 558.69 nm	0.02600	H-1 -> L+1 72.0%, H-1 -> L+6 7.6%, H-1 -> L+2 5.8%
Os ₄	S ₀ -S ₁₁ : 564.05 nm	0.06670	H-2 -> L+2 45.6%, H-2 -> L+3 31.7%
Os ₅	S ₀ -S ₂₀ : 526.05 nm	0.06410	H -> L+8 24.2%, H -> L+6 14.9%, H-2 -> L+1 7.6%, H-3 -> L+1 6.9%
Os ₆	S ₀ -S ₁₁ : 566.53 nm	0.07730	H-1 -> L+3 25.1%, H -> L+4 25.0%, H -> L+5 14.9%, H-4 -> L 9.0%, H-2 -> L+1 8.2%
Os ₇	S ₀ -S ₆ : 654.03 nm	0.02240	H-1 -> L+2 19.9%, H-2 -> L 12.7%, H-1 -> L+1 10.5%, H -> L+3 5.4%, H-3 -> L 5.3%, H-2 -> L+1 5.1%
Os ₈	S ₀ -S ₁₅ : 545.92 nm	0.07900	H -> L+7 10.6%, H-3 -> L+5 7.4%, H-2 -> L+6 6.4%, H-2 -> L+5 6.3%, H-3 -> L+6 5.7%
Os ₉	S ₀ -S ₂₄ : 544.94 nm	0.01000	H-1 -> L+15 14.7%, H -> L+10 7.6%, H -> L+15 5.6%

Table S9. Electron-hole Analysis of Main Excited States of Different Os-organic π -clusters.

Cluster	Wavelength	S_r (a.u.)	D (Å)	H (Å)	t (Å)	HDI	EDI	E_{coul} (eV)
Os ₃	S ₀ -S ₇ : 558.69 nm	0.75	0.548	2.87	-1.24	6.56	6.03	4.88
Os ₄	S ₀ -S ₁₁ : 564.05 nm	0.83	0.223	3.19	-1.10	6.37	4.01	4.46
Os ₅	S ₀ -S ₂₀ : 526.05 nm	0.85	0.868	3.44	-1.29	4.23	3.85	4.08
Os ₆	S ₀ -S ₁₁ : 566.53 nm	0.85	0.001	3.74	-2.46	3.63	3.15	3.81
Os ₇	S ₀ -S ₆ : 654.03 nm	0.82	0.209	3.86	-2.05	3.74	3.71	3.70
Os ₈	S ₀ -S ₁₅ : 545.92 nm	0.87	0.051	4.14	-1.90	3.17	2.82	3.47
Os ₉	S ₀ -S ₂₄ : 544.94 nm	0.80	0.492	4.20	-2.23	4.37	3.66	3.42

Table S10. Contribution Ratio of Cluster Cores and Ligands to Electron-hole Distribution.

Cluster	Wavelength	% <i>Ele</i> _M	% <i>Ele</i> _L	% <i>Hole</i> _M	% <i>Hole</i> _L	<i>Ele</i> _M -0.5	<i>Ele</i> _L -0.5	<i>Hole</i> _M -0.5	<i>Hole</i> _L -0.5	Σ
Os ₃	S ₀ -S ₇ : 558.69 nm	32.08%	67.92%	55.34%	44.66%	0.1792	0.1792	0.0534	0.0534	0.4652
Os ₄	S ₀ -S ₁₁ : 564.05 nm	37.73%	62.27%	71.79%	28.20%	0.1227	0.1227	0.2179	0.2180	0.6813
Os ₅	S ₀ -S ₂₀ : 526.05 nm	36.93%	63.07%	57.39%	42.61%	0.1307	0.1307	0.0739	0.0739	0.4092
Os ₆	S ₀ -S ₁₁ : 566.53 nm	34.85%	65.15%	68.34%	31.66%	0.1515	0.1515	0.1834	0.1834	0.6698
Os ₇	S ₀ -S ₆ : 654.03 nm	41.50%	58.50%	75.16%	24.84%	0.0850	0.0850	0.2516	0.2516	0.6732
Os ₈	S ₀ -S ₁₅ : 545.92 nm	49.05%	50.95%	71.27%	28.73%	0.0095	0.0095	0.2127	0.2127	0.4444
Os ₉	S ₀ -S ₂₄ : 544.94 nm	45.01%	54.99%	85.36%	14.64%	0.0499	0.0499	0.3536	0.3536	0.8070

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