Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Theoretical Investigation on Electronic Structure and Second-Order Nonlinear Optical Properties of Novel Hexamolybdate-Organoimido-(Car)borane Hybrid

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General Comments

§ **Table S1** Transition energy (λ, nm; *E*, eV), oscillator strength (*f*), and the corresponding dominant MO transition for system **III** containing *B*-carboranyl by SAOP potential

§ **Table S2** Calculated energies of HOMO and LUMO for all systems at BP86/TZP level

§ **Table S3** Calculated frequency-dependent first hyperpolarizabilities β_{vec} ($\times 10^{-30}$ esu) for all systems

§ **Fig. S1** Molecular orbitals of systems **III**-2***p*, 4*m*, 9*o*** and **9*m*** involved in the dominant electron transitions. The black arrow represents the maximum absorption peak, red arrow for the absorption about 360 nm, and blue arrow for the absorption about 350 nm (the short line across the black arrow means the repetitive transition).

§ **Fig. S2** Molecular orbitals of systems **III**-2***m*, 3*o*** and **4*o*** involved in the dominant electron transitions. The black arrow represents the maximum absorption peak, red arrow for the absorption about 360 nm, and blue arrow for the absorption about 350 nm (the short line across the black arrow means the repetitive transition).

§ **Fig. S3** Total and partial density of states (TDOS and PDOS) around the HOMO-LUMO gap for all systems

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Table S1 Transition energy (λ, nm; *E*, eV), oscillator strength (*f*), and the corresponding dominant MO transition for systems III containing B-carboranyl by SAOP potential

	λ/nm	*E*/eV	*f*	MO transition
III-9*m*	419.9	2.95	0.2024	170a′→177a′ (46.24%) 170a′→176a′ (37.18%) 96a″→100a″ (10.47%)
	369.5	3.36	0.2084	170a′→177a′ (24.20%) 170a′→176a′ (20.43%) 168a′→171a′ (11.87%) 94a″→98a″ (11.21%)
	355.8	3.48	0.1961	96a″→103a″(73.93%)
III-9*o*	418.9	2.96	0.2154	90a″→100a″(50.08%) 90a″→98a″ (40.12%)
	369.1	3.36	0.2226	90a″→100a″(26.63%) 90a″→98a″ (22.45%) 86a″→91a″(11.54%)
	356.3	3.48	0.2137	177a′→179a′ (74.31%)
III-4*o*	409.1	3.03	0.2293	267a→283a (48.49%) 267a→279a (40.31%)
	364.8	3.40	0.1622	267a→283a (25.64%) 267a→279a (17.46%) 258a→279a (16.04%) 265a→275a (11.64%)
	354.4	3.50	0.2666	265a→275a (59.44%)
III-4*m*	414.0	3.00	0.2384	267a→283a (49.46%) 267a→280a (41.20%)
	367.5	3.37	0.2182	267a→283a (27.09%) 267a→280a (20.68%)
	354.7	3.50	0.2036	265a→275a (65.58%)
III-2*p*	416.3	2.98	0.2424	90a″→100a″ (47.77%) 90a″→98a″ (41.03%)
	368.4	3.37	0.1979	90a″→100a″ (23.69%) 90a″→98a″ (18.15%) 84a″→92a″(12.12%)
	354.8	3.49	0.1804	177a′→179a′ (69.15%)
III-2*m*	403.1	3.08	0.1396	89a″→98a″ (35.87%) 90a″→100a″(22.98%)
	402.0	3.08	0.1231	90a″→98a″(18.90%)
	362.3	3.42	0.1562	90a″→100a″(33.47%) 177a′→179a′ (22.32%) 90a″→98a″ (15.21%)
	352.9	3.51	0.1802	177a′→179a′ (25.52%) 88a″→94a″ (18.36%)
III-3*o*	406.1	3.05	0.2526	90a″→100a″ (43.68%) 90a″→98a″ (35.47%)
	364.8	3.40	0.2090	90a″→100a″ (32.16%) 90a″→98a″ (18.12%) 177a′→179a′ (10.12%)
	354.0	3.50	0.2244	177a′→179a′ (56.82%)

Table S2 Calculated energies of HOMO and LUMO for all systems at BP86/TZP level

systems	HOMO (eV)	LUMO (eV)
I	-5.582	-4.125
II	-5.179	-4.032
III-1*o*	-5.699	-4.147
III-1*m*	-5.662	-4.138
III-1*p*	-5.652	-4.138
III-9*m*	-5.507	-4.121
III-9*o*	-5.503	-4.119
III-4*o*	-5.590	-4.128
III-4*m*	-5.558	-4.126
III-3*o*	-5.626	-4.137
III-2*m*	-5.648	-4.135
III-2*p*	-5.547	-4.123

Table S3 Calculated frequency-dependent first hyperpolarizabilities β_{vec} ($\times 10^{-30}$ esu) for all systems

systems	1064 nm			1340 nm			1910 nm		
	β_{SHG}	β_{EOPE}	β_{OR}	β_{SHG}	β_{EOPE}	β_{OR}	β_{SHG}	β_{EOPE}	β_{OR}
I	-369.5	35.2	35.2	62.6	28.5	28.5	34.1	24.5	24.5
II	-215.5	-368.2	-368.2	4270.6	-335.3	-335.3	-301.3	-201.7	-201.7
III-1*o*	-953.8	55.6	55.6	96.8	45.5	45.5	53.8	39.2	39.2
III-1*m*	-713.2	63.1	63.1	113.2	51.5	51.5	61.1	44.3	44.3
III-1*p*	-671.5	66.5	66.5	121.1	54.1	54.1	64.5	46.5	46.5
III-9*m*	-221.0	101.7	101.7	222.9	79.6	79.6	74.8	72.9	72.9
III-9*o*	-227.7	93.4	93.4	204.0	73.0	73.0	86.6	61.7	61.7
III-4*o*	-328.3	62.8	62.8	124.9	50.3	50.3	61.1	42.8	42.8
III-4*m*	-282.0	85.7	85.7	171.9	68.4	68.4	126.0	58.3	58.3
III-3*o*	-469.1	65.0	65.0	63.0	44.8	44.8	63.0	44.8	44.8
III-2*m*	-755.9	59.3	59.3	108.8	47.8	47.8	57.4	40.7	40.7
III-2*p*	-275.2	100.1	100.1	203.1	79.3	79.3	92.5	67.4	67.4

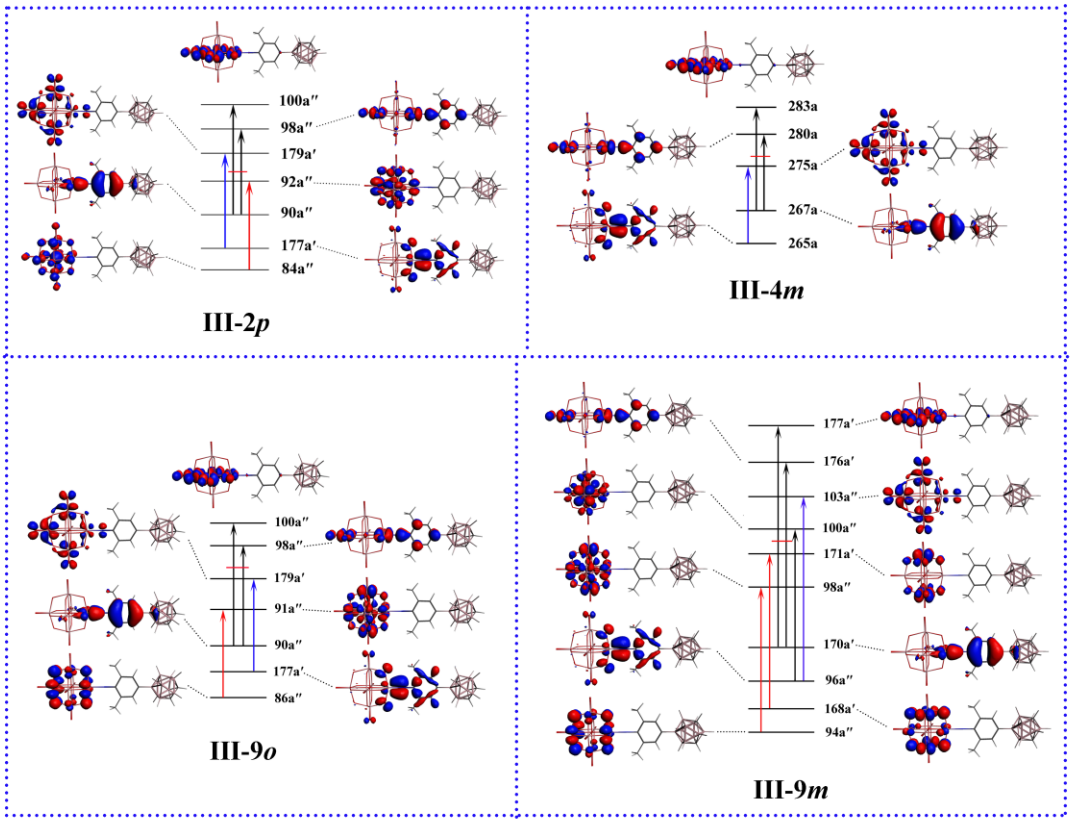


Fig. S1 Molecular orbitals of systems **III-2*p*, 4*m*, 9*o*** and **9*m*** involved in the dominant electron transitions. The black arrow represents the maximum absorption peak, red arrow for the absorption about 360 nm, and blue arrow for the absorption about 350 nm (the short line across the black arrow means the repetitive transition).

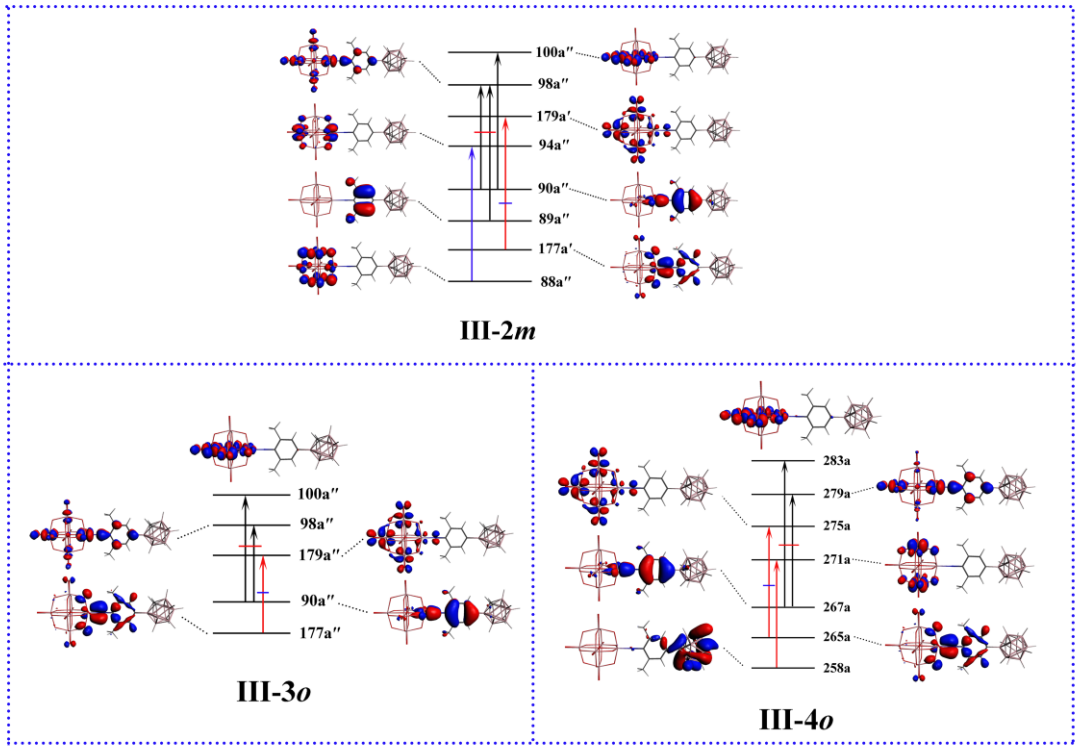
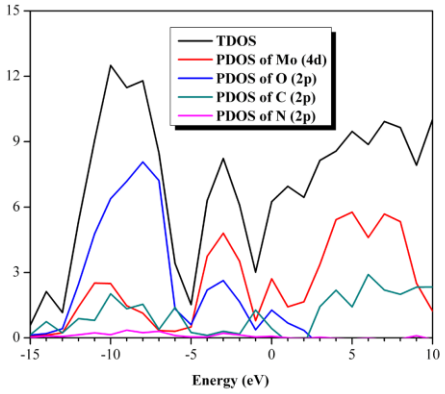
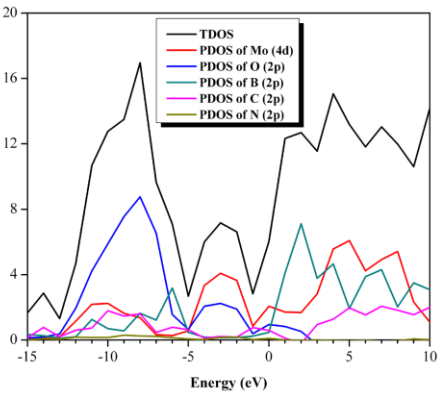


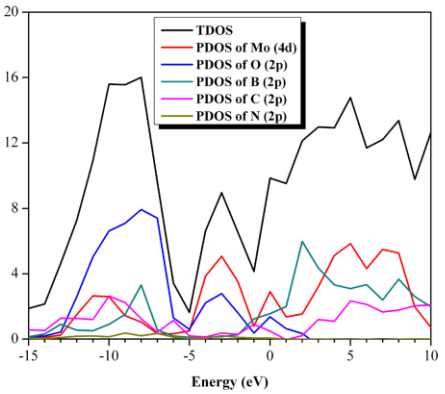
Fig. S2 Molecular orbitals of systems **III-2*m*, 3*o*** and **4*o*** involved in the dominant electron transitions. The black arrow represents the maximum absorption peak, red arrow for the absorption about 360 nm, and blue arrow for the absorption about 350 nm (the short line across the black arrow means the repetitive transition).



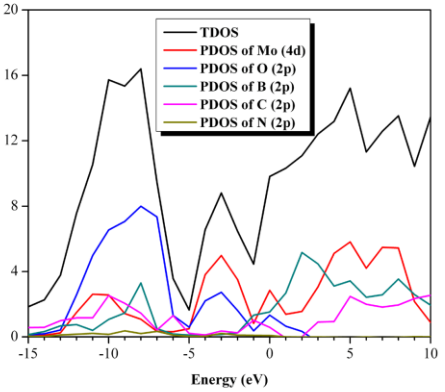
1 (system I)



2 (system II)



3 (system III-1*o*)



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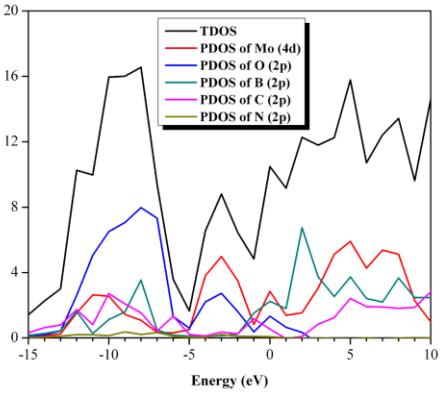

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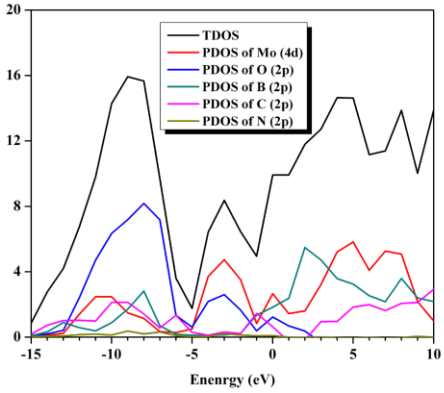

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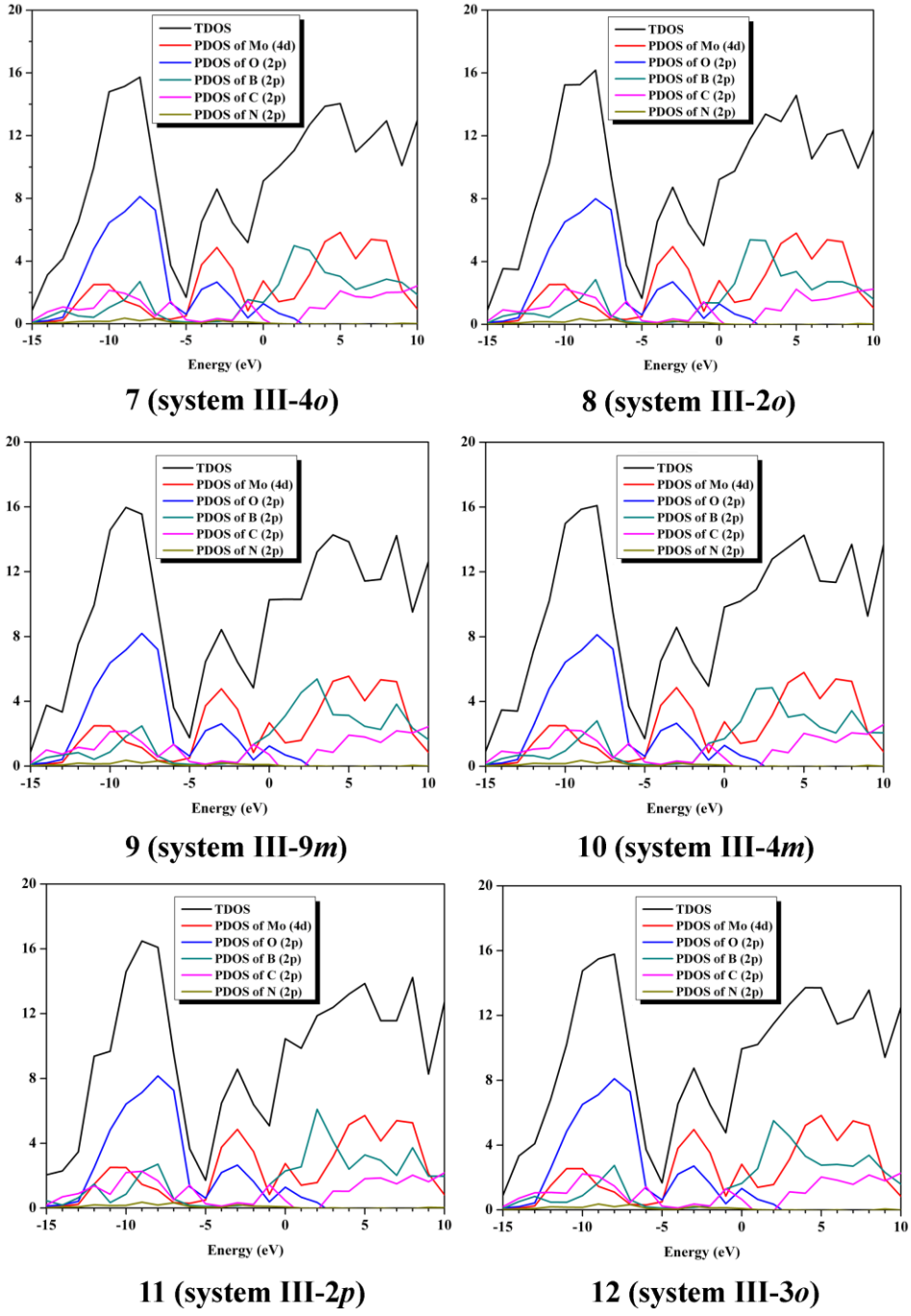

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