Electronic Supplementary Information

The degree of π electron delocalization and the formation of 3D-extensible sandwich structure

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Table S1. Comparison between ωB97X-D/6-31G(d) and B3LYP/6-31G(d) results, including the point groups (PG), the lowest vibrational frequencies (ν_{min}, in cm^{-1}), the HOMO-LUMO gap (Gap, in eV), the total binding energies (BE_{total}) relative to the free starbenzenes, benzenes, and chromium atoms, the binding energies for extending a decker in sandwich chains ($BE_{1D\text{-}ext}$, in kcal/mol), and the average binding energies for the formation of a hydrogen bridge bond (BE_{HBB}).

	B3LYP/6-31G(d)						ωB97X-D/6-31G(d)				
	PG	ν_{min}	Gap	BE_{total}	$BE_{1D\text{-}ext}$		PG	ν_{min}	Gap	BE_{total}	$BE_{1D\text{-}ext}$
(Bz)2Cr	D_{6h}	39	4.06	-79.3		**(Bz)2Cr**	D_{6h}	57	8.11	-101.7	
1	D_{6d}	37	3.24	-84.1		**1**	D_{6d}	41*i*	7.28	-118.6	
2'	C_{6v}	16	3.75	-97.9		**2**	C_{6v}	37	7.94	-127.1	
3”	D_6	8	3.59	-172.0	-74.1	**3”**	D_6	23	7.44	-228.9	-101.8
4”	C_6	5	3.12	-238.2	-66.3	**4”**	C_6	29	6.67	-318.5	-89.6
5	D_{6h}	8	2.74	-298.1	-59.9	**5**	D_{6h}	7	6.23	-399.5	-81.0
	PG	ν_{min}	Gap	BE_{total}	BE_{HBB}		PG	ν_{min}	Gap	BE_{total}	BE_{HBB}
2PP2	C_{2v}	11	3.68	-224.8	-29.0	**2PP2**	C_{2v}	3	7.85	-287.8	-33.7
2PP3	C_{3v}	16	3.64	-380.9	-29.1	**2PP3**	C_{3v}	18	7.80	-482.1	-33.6
2EE2	C_{2v}	16	3.62	-243.9	-24.0	**2EE2**	C_{2v}	23	7.75	-309.9	-27.9
2PE4	C_{2v}	10	3.57	-543.8	-25.3	**2PE4**	C_{2v}	9	7.72	-686.2	-29.7
3PP2	D_{2h}	4	3.56	-405.7	-30.9	**3PP2**	D_{2h}	15	7.30	-528.2	-35.3
3PP3	D_{3h}	16	3.53	-700.5	-30.8	**3PP3**	D_{3h}	20	7.25	-898.3	-35.3
3EE2	D_{2h}	21	3.51	-446.5	-25.6	**3EE2**	D_{2h}	24	7.22	-576.6	-29.7

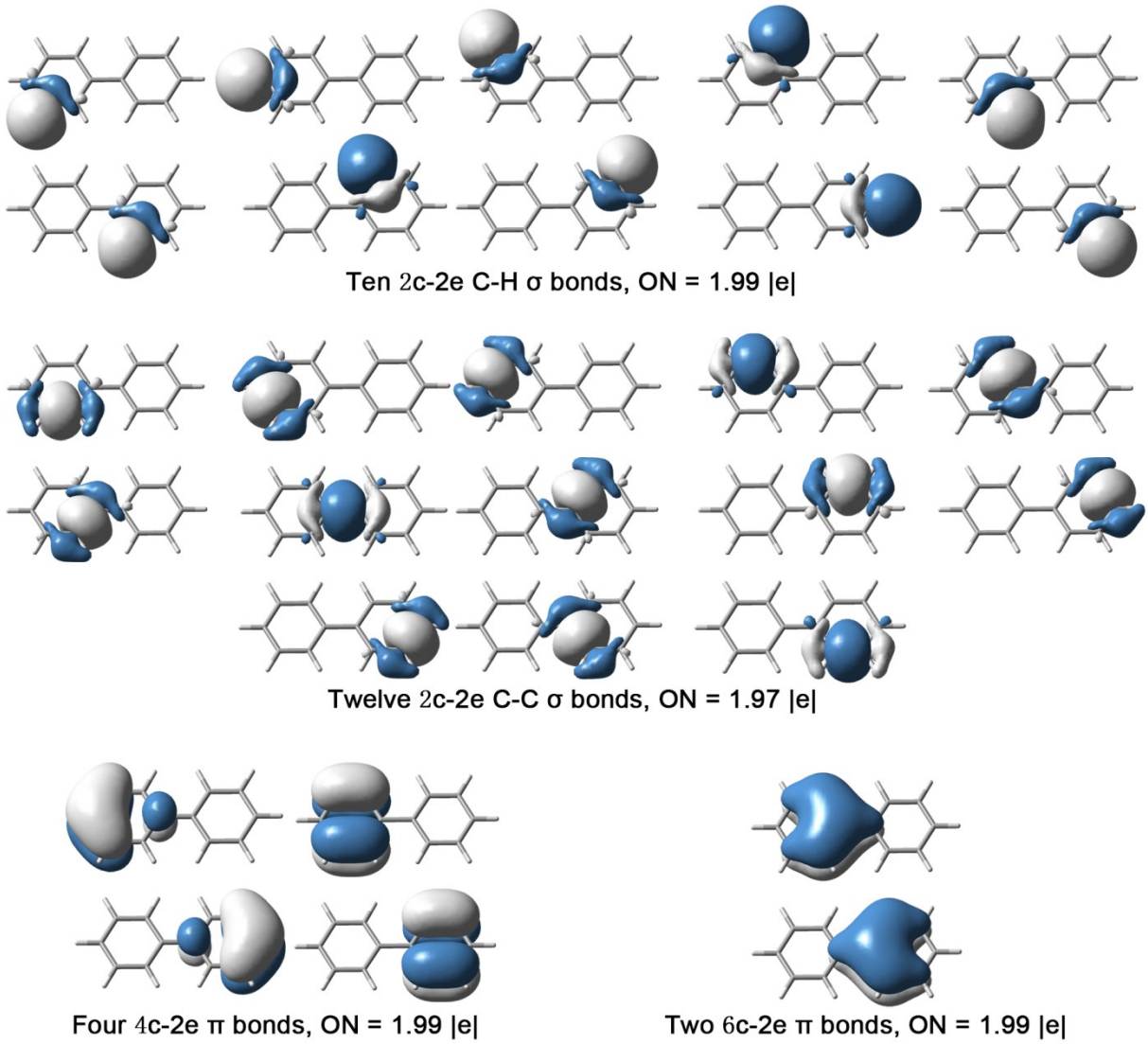


Figure S1. Full set of AdNDP orbitals of planarized biphenyl.

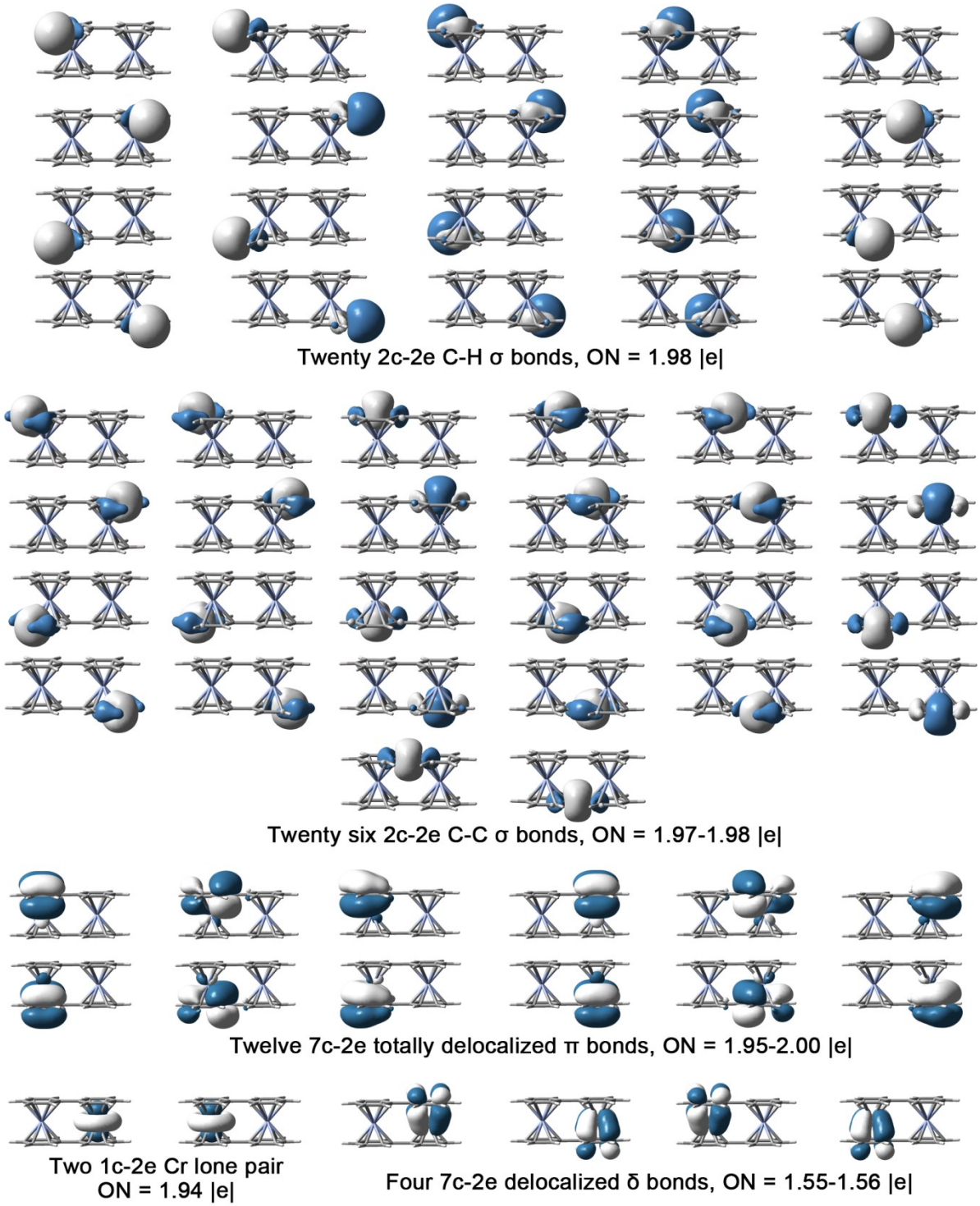
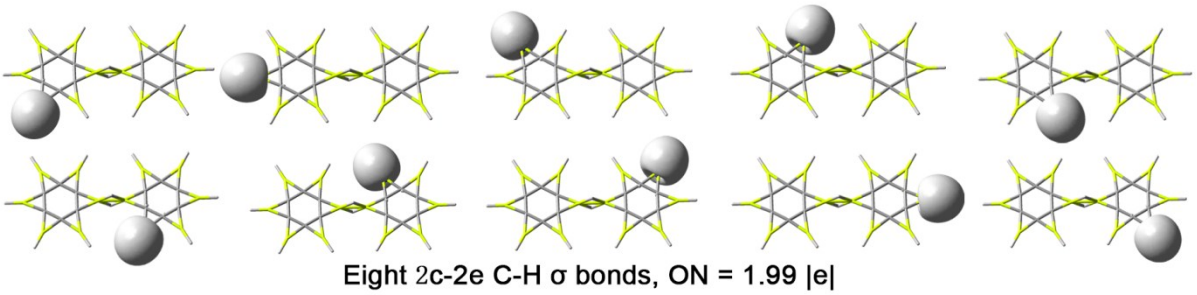
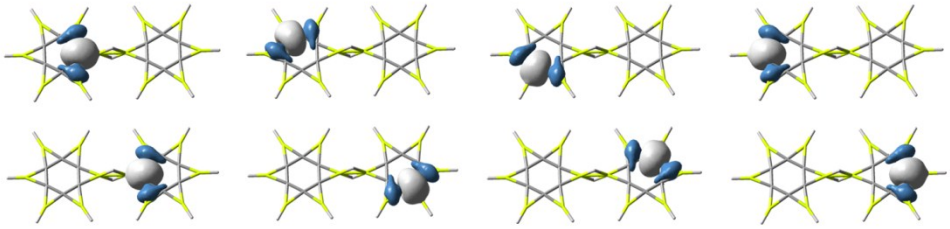


Figure S2. Full set of AdNDP orbitals of sandwich complex with two biphenyl ligands.

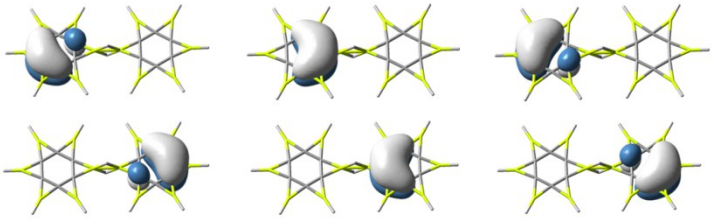


Eight 2c-2e C-H σ bonds, ON = 1.99 |e|



Eight 2c-2e C-C σ bonds, ON = 1.98 |e|

Two 3c-2e σ bonds, ON = 1.98 |e|



Six 4c-2e π bonds, ON = 1.97 |e|

Figure S3. Full set of AdNDP orbitals of starbenzene dimer.

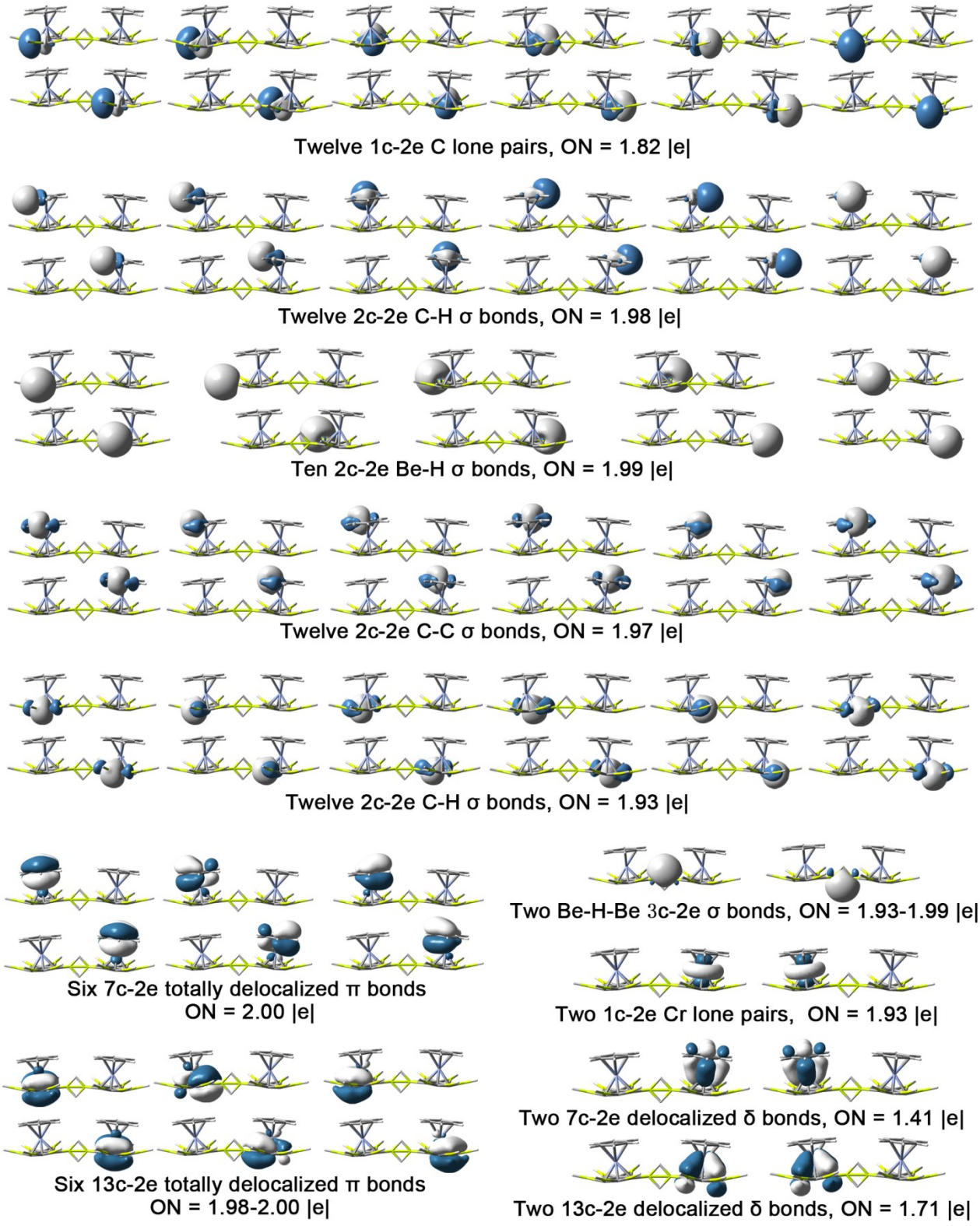


Figure S4. Full set of AdNDP orbitals of sandwich complex with mixed starbenzene dimer-benzene ligands.