Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Intensified Effects of Multi-Cu Modification on Electronic Properties of the Modified Base Pairs Containing Hetero-Ring-Expanded Pyrimidine Bases

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Supporting Information

Part 1. Structural parameters (bond lengths, DI, BO) and optimized geometries of the natural, the size-expanded and the M-x modified base pairs.

Part 2. Electronic properties (orbital composition, spin density distribution) of the natural, the size-expanded and the M-x modified base pairs.

Part 3. Indicators of transverse electronic communication (vertical transition energies, oscillator strengths, and state assignments; Differences of WC H-bond; Absorption spectra; ELF-π isosurface; DOS Plots) for natural and modified base pairs.

Part 1. Structural parameters (bond lengths, DI, BO) and optimized geometries of the natural, the size-expanded and the M-x modified base pairs.

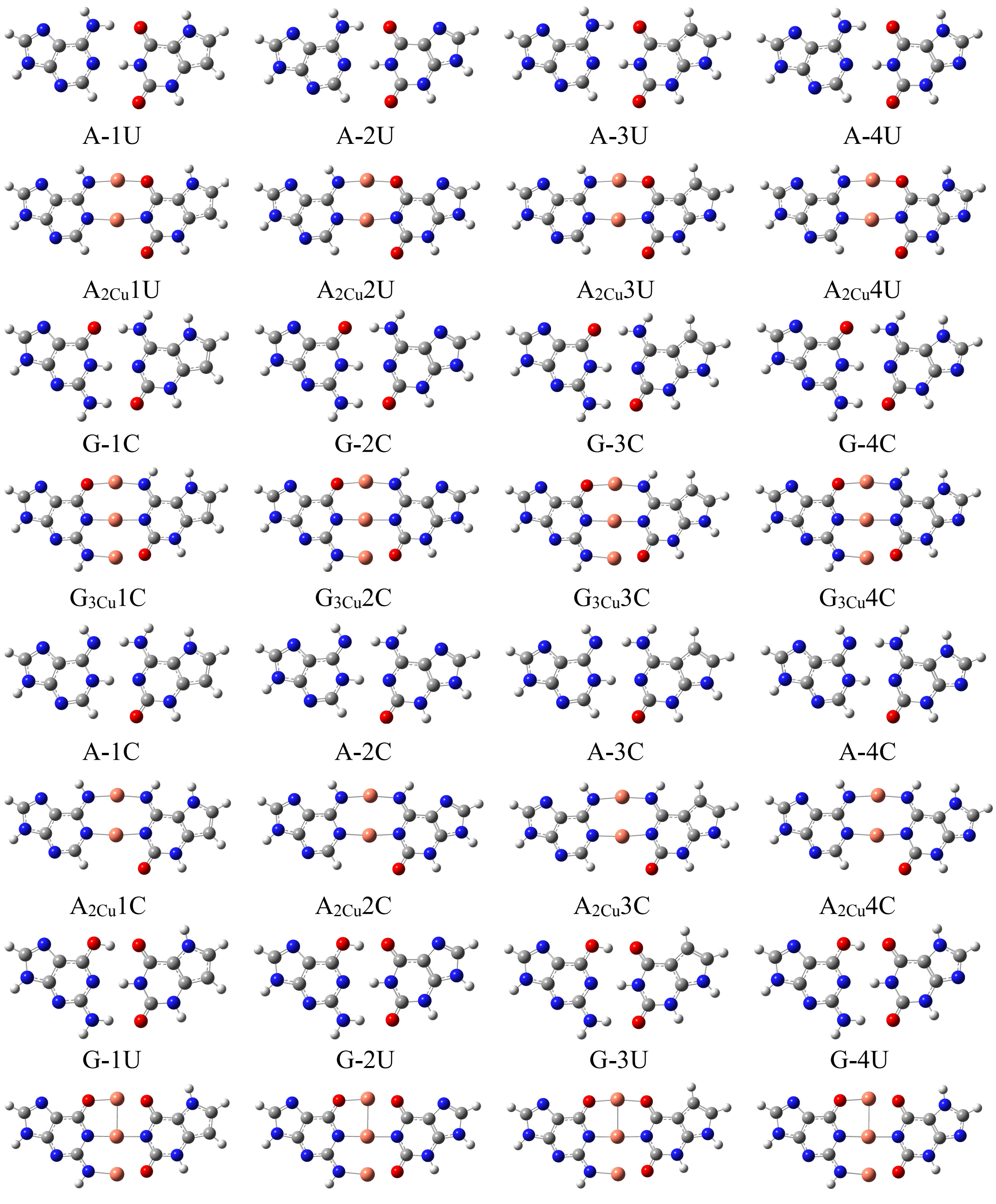
Table S1. The selected structural parameters of A-nU, G-nU and their M-x modified ones (bond lengths in Å) [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	A-nU			G-nU			
	N6-H···O4	N1···H-N3		O6-H···O4	N1···H-N3	N2-H···O2	
natural	2.950	2.908		2.749	2.908	3.038	
1	2.951	2.918		2.745	2.920	3.010	
2	2.943	2.916		2.742	2.931	3.020	
3	2.937	2.923		2.735	2.927	3.021	
4	2.964	2.908		2.752	2.923	3.007	
	A-nC			G-nC			
	N6···H-N4	N1-H···N3		O6···H-N4	N1-H···N3	N2-H···O2	
natural	2.928	2.902		2.824	2.967	2.943	
1	2.917	2.890		2.807	2.971	2.895	
2	2.926	2.903		2.825	2.977	2.933	
3	2.930	2.895		2.822	2.979	2.914	
4	2.901	2.900		2.797	2.979	2.906	
	$\mathrm{A_{2Cu}}$nU			$\mathrm{G_{3Cu}}$nU			
	N6-Cu-O4	N1-Cu-N3	Cu1-Cu2	O6-Cu-O4	N1-Cu-N3	N2-Cu-O2	Cu1-Cu2-Cu3
1	3.801	3.873	2.579	3.824	3.842	3.816	2.477/2.482
2	3.794	3.881	2.570	3.817	3.851	3.818	2.475/2.490
3	3.795	3.878	2.569	3.819	3.846	3.818	2.473/2.486
4	3.802	3.875	2.581	3.823	3.846	3.816	2.480/2.484
	$\mathrm{A_{2Cu}}$nC			$\mathrm{G_{3Cu}}$nC			
	N6-Cu-N4	N1-Cu-N3	Cu1-Cu2	O6-Cu-N4	N1-Cu-N3	N2-Cu-O2	Cu1-Cu2-Cu3
1	3.799	3.878	2.586	3.801	3.861	3.806	2.484/2.485
2	3.795	3.880	2.590	3.802	3.857	3.815	2.491/2.491
3	3.796	3.880	2.580	3.800	3.860	3.811	2.482/2.488
4	3.799	3.879	2.587	3.799	3.865	3.806	2.486/2.486

Table S2. DI and BO (>0.003) values for the natural and modified base pairs [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	DI(*10^{-3})		BO(*10^{-2})			
	C6···C4	C2···C2	C6···C4	C2···C2	N6-N1-N3-N4	
A-C	0.44	0.43	/	/	/	
A-1C	0.71	1.06	0.35	0.68	0.365	
A-2C	0.68	0.95	0.61	0.36	0.585	
A-3C	0.58	0.84	/	0.74	0.56	
A-4C	0.72	1.01	0.35	0.44	0.49	
A_{2Cu}1C	2.57	2.72	11.84	0.73	2.26	
A_{2Cu}2C	2.29	2.09	9.1	1.92	1.78	
A_{2Cu}3C	1.09	2.28	18.69	1.08	2.1	
A_{2Cu}4C	0.89	0.08	7.07	1.75	2.11	
	C6···C4	C2···C2	C6···C4	C2···C2	N6-N1-N3-O4	
A-U	0.5	0.75	/	/	/	
A-1U	0.49	0.74	2.88	0.41	/	
A-2U	0.49	0.79	/	/	/	
A-3U	0.49	0.75	2.89	/	/	
A-4U	0.49	0.8	/	0.44	/	
A_{2Cu}1U	0.53	0.13	17.72	0.49	2.525	
A_{2Cu}2U	1.56	2.34	9.5	1.16	2.615	
A_{2Cu}3U	0.79	0.41	19.57	0.39	2.585	
A_{2Cu}4U	2.5	1.36	8.33	0.82	2.44	
	C6···C4	C2···C2	C6···C4	C2···C2	O6-N1-N3-N4	N1-N2-O2-N3
G-C	0.73	1.52	/	/	/	/
G-1C	0.62	0.49	/	0.54	/	/
G-2C	0.59	0.47	/	0.67	/	/
G-3C	0.59	0.48	1.17	/	/	/
G-4C	0.63	0.47	/	0.67	/	/
G_{3Cu}1C	1.09	1.82	9.07	4.06	3.24	1.75
G_{3Cu}2C	1.48	1.11	10.65	3.58	2.68	1.84
G_{3Cu}3C	0.47	0.46	15.28	2.47	3.46	1.925
G_{3Cu}4C	1.57	0.25	9.58	4.24	3.04	1.905
	C6···C4	C2···C2	C6···C4	C2···C2	O6-N1-N3-O4	N1-N2-O2-N3
G-U	0.64	0.45	/	/	/	/
G-1U	0.64	0.45	/	/	0.52	0.36
G-2U	0.64	0.46	0.31	/	0.52	0.35
G-3U	0.64	0.45	4.93	0.53	/	0.34
G-4U	0.63	0.45	/	/	0.43	0.33
G_{3Cu}1U	0.4	0.14	29.85	3.04	2.945	1.525
G_{3Cu}2U	0.72	0.25	12.73	4.44	2.885	1.48
G_{3Cu}3U	0.51	2.37	13.7	3.23	2.95	1.675

G_{3Cu}4U	0.55	1.39	12.33	4.77	2.69	1.66



A-1U A-2U A-3U A-4U

A_{2Cu}1U A_{2Cu}2U A_{2Cu}3U A_{2Cu}4U

G-1C G-2C G-3C G-4C

G_{3Cu}1C G_{3Cu}2C G_{3Cu}3C G_{3Cu}4C

A-1C A-2C A-3C A-4C

A_{2Cu}1C A_{2Cu}2C A_{2Cu}3C A_{2Cu}4C

G-1U G-2U G-3U G-4U

G_{3Cu}1U G_{3Cu}2U G_{3Cu}3U G_{3Cu}4U

Figure S1. The optimized geometries of the natural, the size-expanded and the M-x modified base pairs [B3LYP/6-31+G*(C,H,O,N)/LANL2DZ(Cu)].

Part 2. **Electronic properties (orbital composition, spin density distribution) of the natural, the size-expanded and the M-x modified base pairs.**

Table S3. The HOMO, LUMO energy, HOMO-LUMO gaps, the ionization potentials and the electron affinities [eV] of the natural, the size-expanded and the M-x modified base pairs [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	HOMO	LUMO	Gaps	VIP	AIP	VEA
A-U	-6.2	-1.63	4.57	7.97	7.74	0.91
A-1U	-6.13	-1.33	4.80	7.62	7.52	1.11
A-2U	-6.13	-1.08	5.05	7.72	7.60	-4.04
A-3U	-6.09	-0.91	5.18	7.50	7.40	-1.42
A-4U	-6.22	-1.60	4.62	7.81	7.70	-0.83
A_{2Cu}1U	-5.71	-1.43	4.28	7.18		-0.94
A_{2Cu}2U	-5.71	-1.24	4.47	7.23		-4.21
A_{2Cu}3U	-5.67	-1.06	4.61	7.09		-2.27
A_{2Cu}4U	-5.80	-1.67	4.13	7.33		-4.99
G-C	-5.5	-1.74	3.76	7.29	6.92	-1.20
G-1C	-5.43	-1.58	3.85	7.11	6.81	-0.78
G-2C	-5.45	-1.36	4.09	7.18	6.85	-5.12
G-3C	-5.42	-1.17	4.25	7.06	6.80	-2.71
G-4C	-5.52	-1.83	3.69	7.24	6.91	-2.74
G_{3Cu}1C	-4.61	-1.96	2.64	6.17		-10.51
G_{3Cu}2C	-4.64	-1.72	2.92	6.21		-11.44
G_{3Cu}3C	-4.60	-1.55	3.04	6.16		-8.73
G_{3Cu}4C	-4.69	-2.21	2.47	6.26		-15.32
A-C	-5.69	-1.47	4.22	7.46	7.15	1.19
A-1C	-5.64	-1.36	4.27	7.23	7.04	1.27
A-2C	-5.65	-1.12	4.53	7.30	7.07	-3.33
A-3C	-5.60	-0.93	4.67	7.14	7.01	-1.17
A-4C	-5.73	-1.60	4.14	7.38	7.15	-2.11
A_{2Cu}1C	-5.54	-1.33	4.21	6.95		0.41
A_{2Cu}2C	-5.55	-1.08	4.47	6.98		-2.20
A_{2Cu}3C	-5.50	-0.95	4.55	6.88		-1.62
A_{2Cu}4C	-5.64	-1.57	4.07	7.09		-3.55
G-U	-5.73	-2.02	3.71	7.54	7.23	-5.63
G-1U	-5.62	-1.68	3.95	7.34	7.09	-2.20
G-2U	-5.66	-1.44	4.22	7.42	7.13	-7.29
G-3U	-5.61	-1.21	4.40	7.28	7.07	-4.18

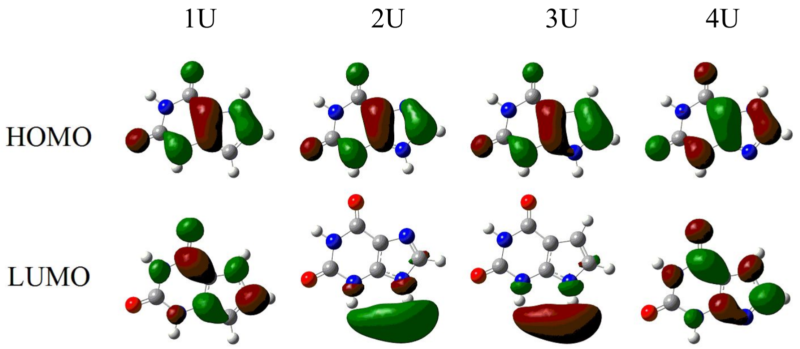
G-4U	-5.70	-1.95	3.75	7.46	7.19	-5.68
G$_{3Cu}$1U	-4.72	-2.10	2.62	6.29		-12.45
G$_{3Cu}$2U	-4.75	-1.95	2.81	6.33		-13.80
G$_{3Cu}$3U	-4.70	-1.74	2.97	6.28		-10.34
G$_{3Cu}$4U	-4.80	-2.36	2.44	6.37		-17.46

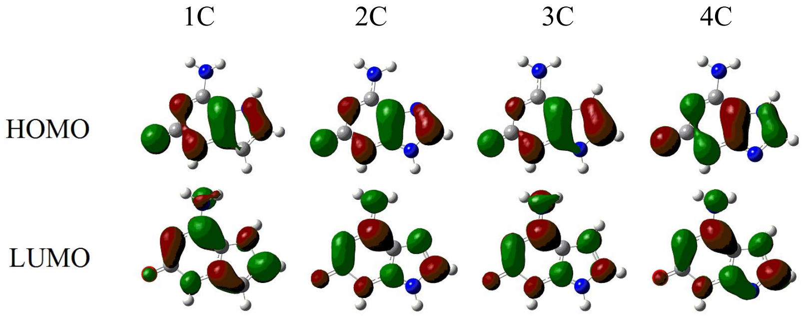
Table S4. Orbital composition (%) of atoms on the expanded ring for LUMOs of A-nU and A$_{2Cu}$nU analogs [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)]. (Σ is the sum value of listed compositions for each analog.)

	A-1U	A-2U	A-3U	A-4U	A$_{2Cu}$1U	A$_{2Cu}$2U	A$_{2Cu}$3U	A$_{2Cu}$4U
C5	7.23	-23.72	-130.46	7.71	3.98	2.28	1.67	4.48
C6	11.84	-45.29	81.86	10.00	11.72	11.06	11.38	10.37
C8	24.55	30.29	16.95	28.05	21.57	7.64	3.58	25.00
C7	1.30	/	/	/	1.03	/	/	/
N7	/	-47.16	-40.41	1.29	/	1.24	1.48	1.07
C9	/	/	-26.33	/	/	/	6.26	/
N9	6.68	-2.25	/	7.43	5.94	6.17	/	6.68
Σ	51.60	-88.13	-98.39	54.48	44.24	28.39	24.37	47.60

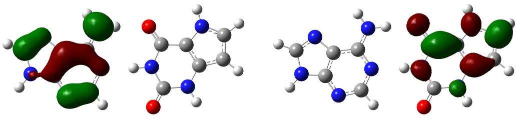
Table S5. Orbital composition (%) of atoms on imidazole rings for HOMOs and LUMOs of modified analogs (n=4) [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)]. (Σ is the sum value of listed compositions for each analog; Δ is the change value of Σ from expanded base pairs to M-x modified ones)

	A-4U	A$_{2Cu}$4U	A-4C	A$_{2Cu}$4C	G-4U	G$_{3Cu}$4U	G-4C	G$_{3Cu}$4C
				HOMO				
C4	6.09	5.48	9.17	4.72	5.95	4.08	7.96	3.97
C5	16.32	13.31	16.98	11.95	19.45	18.55	21.50	18.54
C8	12.07	8.83	12.24	7.75	14.36	12.3	15.88	12.20
N7	5.44	2.20	2.27	1.85	5.27	3.59	4.83	3.48
N9	1.09	0.33	0.20	0.31	1.26	1.35	0.88	1.36
Σ_H	41.01	30.15	40.86	26.58	46.29	39.87	51.05	39.55
Δ_H	-10.86		-14.28		-6.42		-11.5	
				LUMO				
C5	7.71	4.48	4.96	5.12	7.02	3.82	4.59	4.7
C6	10	10.37	9.34	9.41	10.89	11.16	9.74	10.3
C8	28.05	25	29.23	25.87	26.81	24.39	28.48	25.61
N7	1.29	1.07	2.17	1.53	1.05	0.9	1.98	1.33
N9	7.43	6.68	6.89	6.81	7.38	6.44	6.8	6.82
Σ_L	54.48	47.6	52.59	48.74	53.15	46.71	51.59	48.76
Δ_L	-6.88		-3.85		-6.44		-2.83	
$\lvert\Sigma(\Delta_H+\Delta_L)\rvert$	17.74		18.13		12.86		14.33	

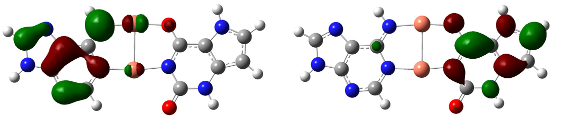




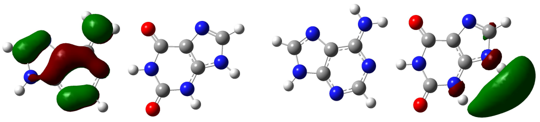
HOMO LUMO HOMO LUMO



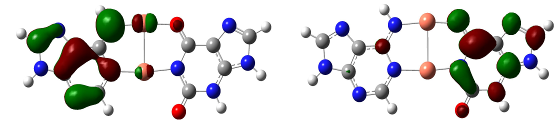
A-1U



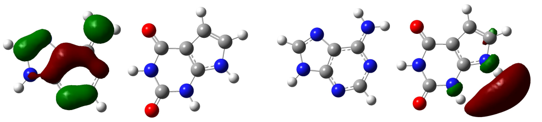
A$_{2\text{Cu}}$1U



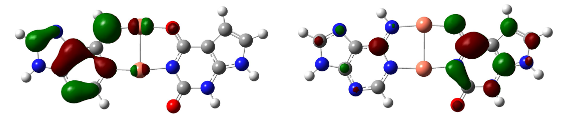
A-2U



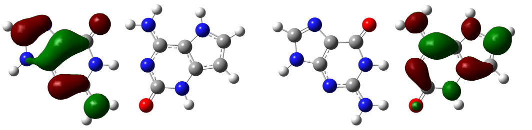
A$_{2\text{Cu}}$2U



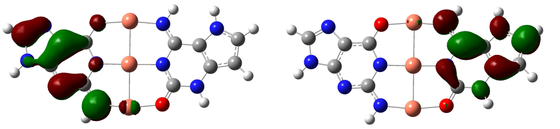
A-3U



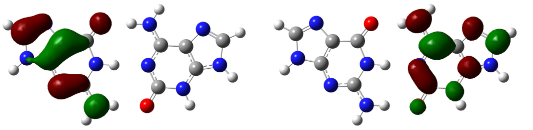
A$_{2\text{Cu}}$3U



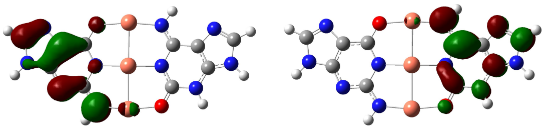
G-1C



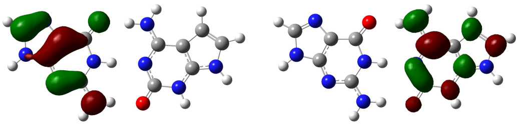
G$_{3\text{Cu}}$1C



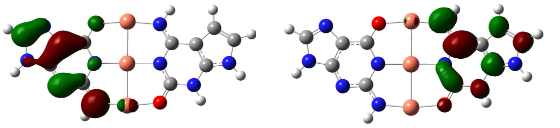
G-2C



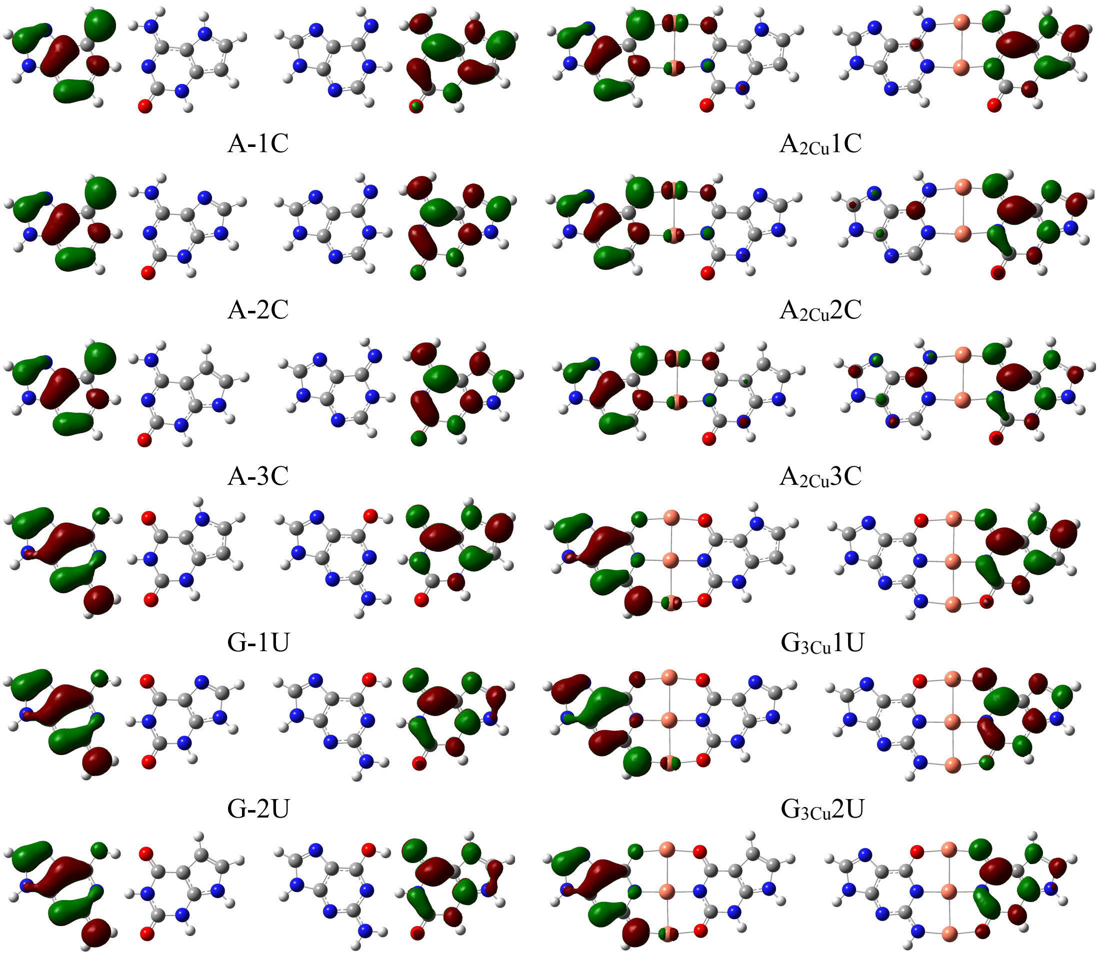
G$_{3\text{Cu}}$2C



G-3C



G$_{3\text{Cu}}$3C



A-1C A$_{2Cu}$1C

A-2C A$_{2Cu}$2C

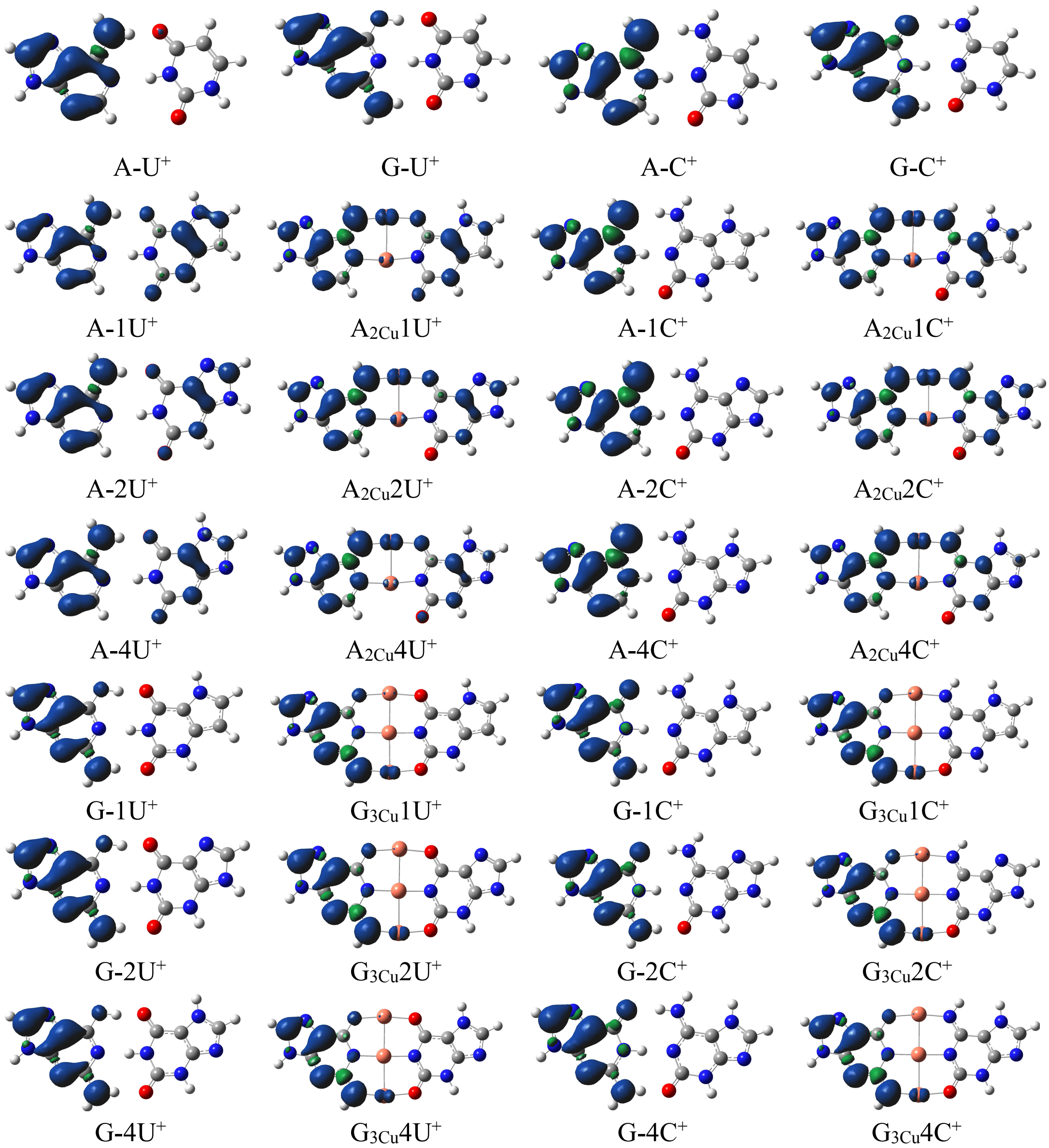
A-3C A$_{2Cu}$3C

G-1U G$_{3Cu}$1U

G-2U G$_{3Cu}$2U

G-3U G$_{3Cu}$3U

Figure S2. Frontier molecular orbitals of the natural, the size-expanded bases and the M-x modified base pairs (n=1, 2, 3) [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].



A-U$^+$ G-U$^+$ A-C$^+$ G-C$^+$

A-1U$^+$ A$_{2Cu}$1U$^+$ A-1C$^+$ A$_{2Cu}$1C$^+$

A-2U$^+$ A$_{2Cu}$2U$^+$ A-2C$^+$ A$_{2Cu}$2C$^+$

A-4U$^+$ A$_{2Cu}$4U$^+$ A-4C$^+$ A$_{2Cu}$4C$^+$

G-1U$^+$ G$_{3Cu}$1U$^+$ G-1C$^+$ G$_{3Cu}$1C$^+$

G-2U$^+$ G$_{3Cu}$2U$^+$ G-2C$^+$ G$_{3Cu}$2C$^+$

G-4U$^+$ G$_{3Cu}$4U$^+$ G-4C$^+$ G$_{3Cu}$4C$^+$

Figure S3. Spin density distributions of the oxidized natural, the size-expanded and the M-x modified base pairs (n=1, 2, 4) [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

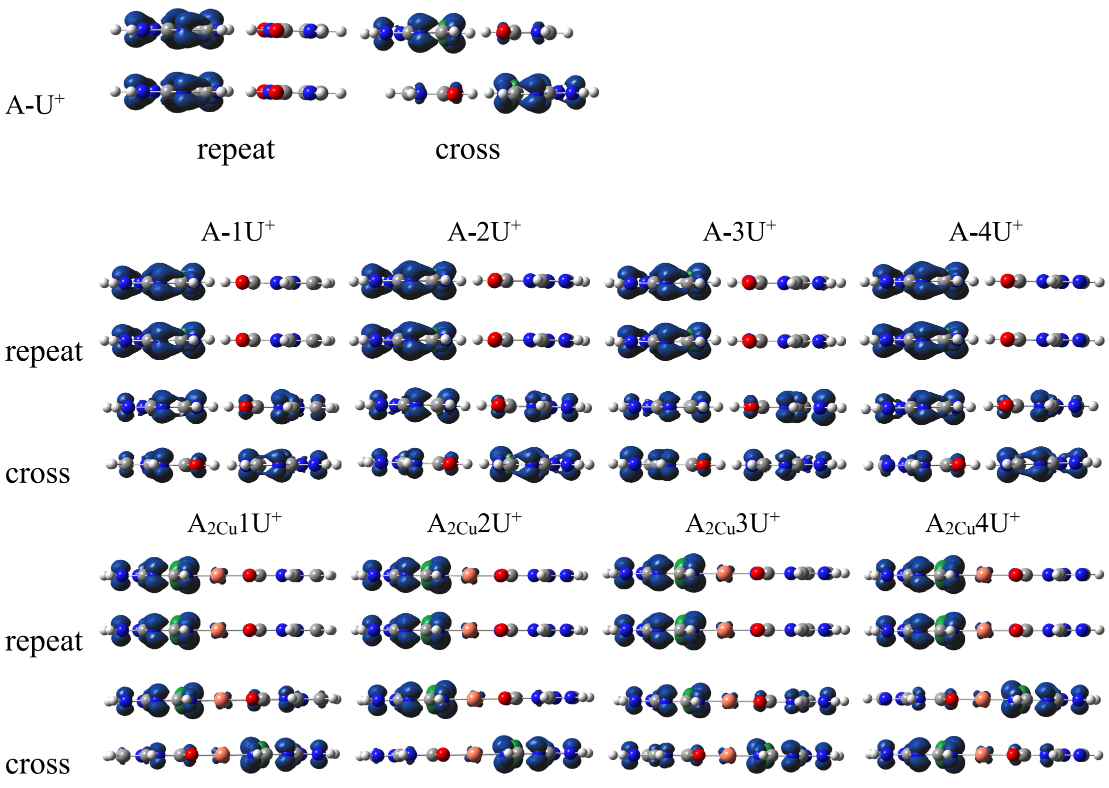


Figure S4. Spin density distributions of the oxidized natural and modified two-layer A-nU pairs [M06-2X/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

Part 3. Indicators of transverse electronic communication (vertical transition energies, oscillator strengths, and state assignments; Differences of WC H-bond; Absorption spectra; ELF-*π* isosurface; DOS Plots) for natural and modified base pairs.

Table S6. The vertical transition energies, oscillator strengths, and state assignments[a] to the low-lying singlet states of the natural, the size-expanded and the M-x modified A-nU, G-nU pairs. calculated at TD-B3LYP/6-311++G** Level.

State		E/eV	f	Assign.	State		E/eV	f	Assign.
A-U	S_1	4.09	0.003	$\boldsymbol{\pi_A\pi_U}$*	G-U	S_2	4.49	0.004	$\boldsymbol{\pi_G\pi_U}$*
	S_3	4.91	0.250	$\pi_A\pi_A$*		S_5	4.59	0.148	$\pi_G\pi_G$*
	S_4	5.05	0.070	$\pi_U\pi_U$*		S_9	5.10	0.072	$\pi_U\pi_U$*
	S_7	5.16	0.067	$\pi_A\pi_A$*		S_{10}	5.21	0.009	$\pi_G n_G$*
	S_{11}	5.45	0.011	$\boldsymbol{\pi_A\pi_U}$*		S_{11}	5.25	0.218	$\pi_G n_G$*
						S_{12}	5.29	0.003	$n_G\pi_G$*
						S_{14}	5.44	0.018	$\boldsymbol{\pi_G\pi_U}$*
A-1U	S_1	4.33	0.010	$\boldsymbol{\pi_A\pi_U}$*	G-1U	S_1	3.51	0.004	$\boldsymbol{\pi_G\pi_U}$*
	S_2	4.59	0.171	$\pi_U\pi_U$*		S_2	4.56	0.216	$\pi_G\pi_G$*
	S_3	4.91	0.226	$\pi_A\pi_A$*		S_3	4.66	0.071	$\pi_U\pi_U$*
	S_9	5.16	0.060	$\pi_A\pi_A$*		S_4	4.66	0.004	$\pi_G n_U$*
	S_{11}	5.31	0.135	$\pi_U\pi_U$*		S_7	4.88	0.041	$\boldsymbol{\pi_G\pi_U}$*
						S_8	4.89	0.004	$\pi_G n_U$*
						S_{11}	5.22	0.003	$\pi_G n_U$*
						S_{12}	5.26	0.259	$\pi_U\pi_U$*&$\boldsymbol{\pi_G\pi_{GU}}$*
						S_{13}	5.27	0.070	$\pi_U\pi_U$*&$\boldsymbol{\pi_G\pi_{GU}}$*
						S_{14}	5.29	0.002	$n_G\pi_G$*
						S_{15}	5.38	0.002	$\pi_U n_U$*
A_{2Cu}1U	S_2	0.028	3.74	$\boldsymbol{\pi_A\pi_U}$*	G_{3Cu}1U	S_1	2.21	0.011	$\boldsymbol{\pi_G\pi_U}$*
	S_3	0.302	4.29	$\pi_U\pi_U$*		S_3	3.26	0.015	$\boldsymbol{\pi_G\pi_U}$*
	S_5	0.099	4.40	$\pi_A\pi_A$*		S_5	3.48	0.002	$\boldsymbol{\pi_G\&n_{Cu}\pi_U}$*
	S_6	0.002	4.46	$\pi_A n_U$*		S_8	3.87	0.031	$\boldsymbol{\pi_G\pi_U^{G*}}$
	S_7	0.078	4.47	$\pi_A\pi_A$*					
	S_9	0.040	4.70	$\boldsymbol{\pi_A\pi_U}$*					
	S_{10}	0.007	4.74	$\boldsymbol{n_{Cu}\pi_U}$*					

	S_{11}	0.048	4.79	Ryd on U & **$\pi_A\pi_U^*$**					
	S_{14}	0.002	4.95	$\pi_An_U^*$					
A-2U	S_1	0.014	4.55	**$\pi_A\pi_U^*$**	G-2U	S_1	3.75	0.005	**$\pi_G\pi_U^*$**
	S_4	0.314	4.90	$\pi_A\pi_A^*$		S_4	4.60	0.170	$\pi_G\pi_G^*$
	S_5	0.068	5.02	$\pi_U\pi_U^*$		S_9	5.04	0.128	$\pi_U\pi_U^*$
	S_8	0.033	5.15	$\pi_A\pi_A^*$&**$\pi_A\pi_U^*$**		S_{10}	5.11	0.061	**$\pi_G\pi_U^*$**
	S_{10}	0.021	5.25	**$\pi_A\pi_U^*$**		S_{12}	5.24	0.009	$n_G\pi_G^*$&$n_G{}^U\pi_G^*$
	S_{11}	0.017	5.37	**$\pi_U\pi_A^*$**		S_{13}	5.26	0.074	**$\pi_G\pi_U^*$**&$\pi_G\pi_G^*$
	S_{14}	0.211	5.57	$\pi_U\pi_U^*$		S_{14}	5.30	0.069	**$\pi_G\pi_U^*$**&$\pi_G\pi_G^*$
						S_{15}	5.33	0.006	$n_G\pi_G^*$
A_{2Cu}2U	S_2	0.043	3.88	**$\pi_A\pi_U^*$**	G_{3Cu}2U	S_1	2.38	0.016	**$\pi_G\pi_U^*$**
	S_5	0.161	4.39	$\pi_A\pi_A^*$&**$\pi_A\pi_A^{U*}$**		S_3	2.98	0.010	**$\pi_G\pi_U^*$**
	S_6	0.038	4.44	Ryd on U		S_6	3.62	0.002	**π_G&$n_{Cu}\pi_U^*$**
	S_7	0.078	4.51	**$\pi_A\pi_A^{U*}$**		S_8	3.68	0.013	**$\pi_G\pi_U^*$**
	S_{10}	0.188	4.62	$\pi_U\pi_U^*$		S_{12}	4.04	0.027	**$\pi_G\pi_{UG}^*$**
	S_{13}	0.029	4.88	**$\pi_A\pi_U^{A*}$**					
	S_{14}	0.005	4.88	**$n_{Cu}\pi_U^*$**					
	S_{15}	0.002	4.92	**$n_{Cu}\pi_U^{A*}$**					
A-3U	S_2	0.066	4.71	**$\pi_A\pi_U^{A*}$**	G-3U	S_1	3.92	0.008	**$\pi_G\pi_U^*$**
	S_3	0.092	4.77	**$\pi_U\pi_U^{A*}$**		S_3	4.53	0.037	**$\pi_G\pi_U^*$**
	S_5	0.178	4.91	**$\pi_A\pi_A^{U*}$**		S_5	4.63	0.153	$\pi_G\pi_G^*$
	S_6	0.021	4.99	**$\pi_U\pi_A^{U*}$**		S_6	4.77	0.066	$\pi_U\pi_U^*$
	S_{10}	0.050	5.17	**$\pi_A\pi_A^{U*}$**		S_{11}	5.23	0.211	**$\pi_G\pi_{GU}^*$**
	S_{12}	0.156	5.43	**$\pi_U\pi_U^{A*}$**		S_{13}	5.40	0.140	$\pi_U\pi_U^*$
	S_{13}	0.025	5.48	**$\pi_A\pi_U^{A*}$**					
	S_{15}	0.007	5.59	**$\pi_U\pi_A^{U*}$**					
A_{2Cu}3U	S_2	0.056	4.00	**$\pi_A\pi_U^*$**	G_{3Cu}3U	S_1	2.53	0.016	**$\pi_G\pi_U^*$**
	S_4	0.225	4.38	$\pi_A\pi_A^*$		S_3	3.11	0.011	**$\pi_G\pi_U^*$**
	S_6	0.094	4.45	$\pi_U\pi_U^*$		S_8	3.77	0.002	**π_G&$n_{Cu}\pi_U^*$**
	S_9	0.029	4.51	$\pi_A\pi_A^*$		S_9	3.83	0.019	**$\pi_G\pi_U^*$**
	S_{10}	0.020	4.59	Ryd on U		S_{15}	4.26	0.117	**$\pi_G\pi_{UG}^*$**
	S_{13}	0.025	4.90	**$n_{Cu}\pi_U^*$**					
	S_{14}	0.010	4.96	**$\pi_U\pi_A^*$**					
	S_{15}	0.040	4.98	**$n_{Cu}\pi_U^*$**					
A-4U	S_1	0.005	4.16	**$\pi_A\pi_U^*$**	G-4U	S_1	3.32	0.003	**$\pi_G\pi_U^*$**
	S_2	0.210	4.63	$\pi_U\pi_U^*$		S_2	4.55	0.179	$\pi_G\pi_G^*$
	S_4	0.201	4.93	$\pi_A\pi_A^*$		S_5	4.70	0.130	$\pi_U\pi_U^*$
	S_6	0.050	5.16	$\pi_A\pi_A^*$		S_6	4.75	0.035	**$\pi_G\pi_U^*$**
	S_{11}	0.004	5.33	**$\pi_U\pi_A^*$**		S_{11}	5.17	0.038	**$\pi_G\pi_U^*$**
	S_{12}	0.009	5.51	**$\pi_A\pi_U^*$**		S_{12}	5.28	0.097	$\pi_G\pi_G^*$&$n_G\pi_G^*$
						S_{13}	5.29	0.055	$n_G\pi_G^*$&$\pi_G\pi_G^*$
A_{2Cu}4U	S_2	0.021	3.61	**$\pi_A\pi_U^*$**	G_{3Cu}4U	S_1	2.04	0.011	**$\pi_G\pi_U^*$**
	S_3	0.329	4.31	$\pi_U\pi_U^*$		S_3	3.16	0.014	**$\pi_G\pi_U^*$**

S_5	0.078	4.41	**$n_{Cu}\pi_A^*$**	S_4	3.34	0.002	**$\pi_G\&n_{Cu}\pi_U^*$**
S_6	0.100	4.45	$\pi_A\pi_A^*$	S_7	3.74	0.020	**$\pi_G\pi_U^*$**
S_9	0.006	4.64	**$n_{Cu}\pi_U^*$**	S_{14}	4.12	0.012	**$\pi_G\pi_U{}^{G*}$**
S_{10}	0.026	4.65	**$\pi_A\pi_U^*$**	S_{15}	4.13	0.003	**$\pi_G\pi_U^*$**
S_{11}	0.011	4.79	Ryd on U				

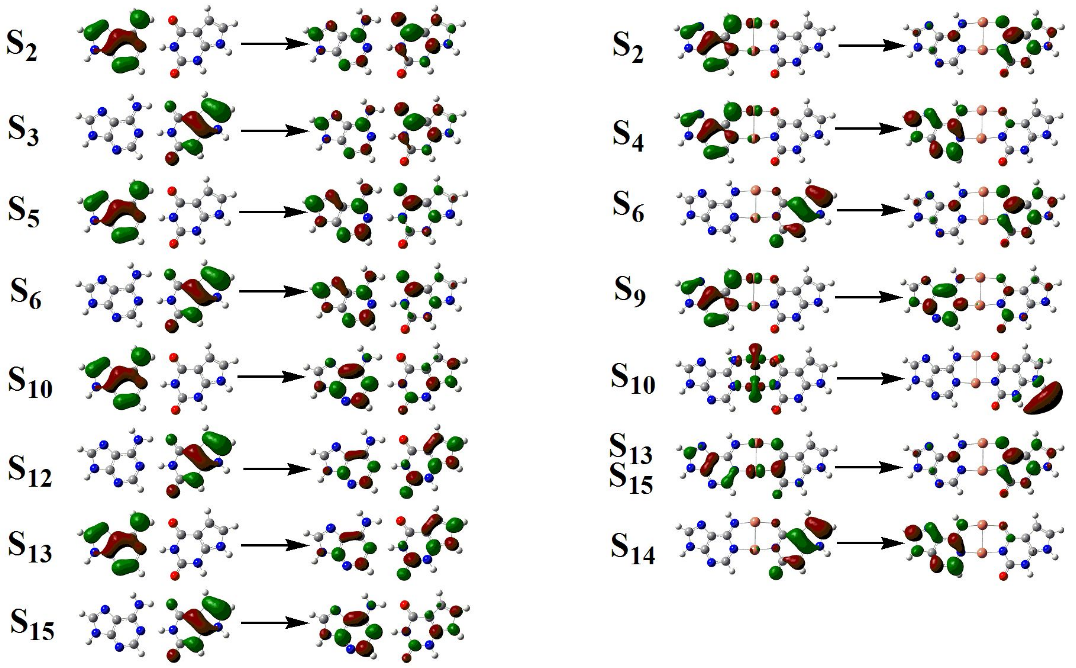
[a]The charge-transfer transitions are in bold.

Table S7. Difference value of WC H-bond and N/O-Cu-N/O lengths (Å) between ground states and electronic excited states for G-nU and $G_{3Cu}nU$ series.

	G-nU			$G_{3Cu}nU$		
	O6-H···O4	N1···H-N3	N2-H···O2	O6-Cu-O4	N1-Cu-N3	N2-Cu-O2
natural	0.002	-0.053	-0.061			
1	0.028	-0.027	-0.047	-0.032	-0.033	-0.024
2	0.027	-0.025	-0.049	-0.039	-0.029	0.002
3	0.028	-0.026	-0.048	-0.058	-0.048	-0.01
4	0.026	-0.028	-0.049	-0.031	-0.033	-0.027

A-3U

A$_{2Cu}$3U



G-4U

G$_{3Cu}$4U

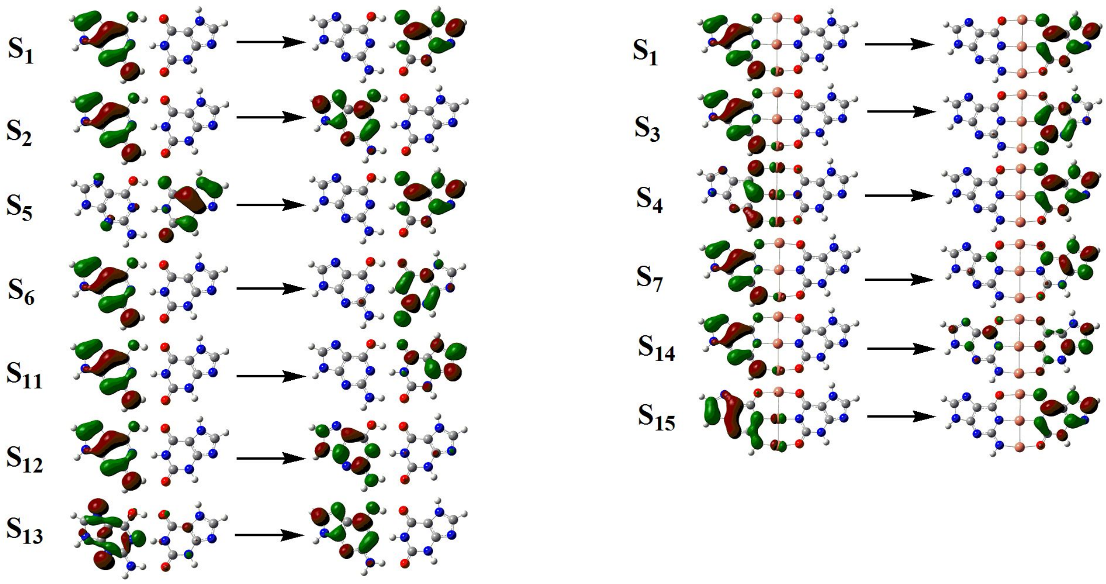


Figure S5. Molecular orbitals involved in several electronic singlet transitions of A-3U, A$_{2Cu}$3U and G-4U, G$_{3Cu}$4U mentioned in Table S6 calculated at TD-B3LYP/6-311++G** level.

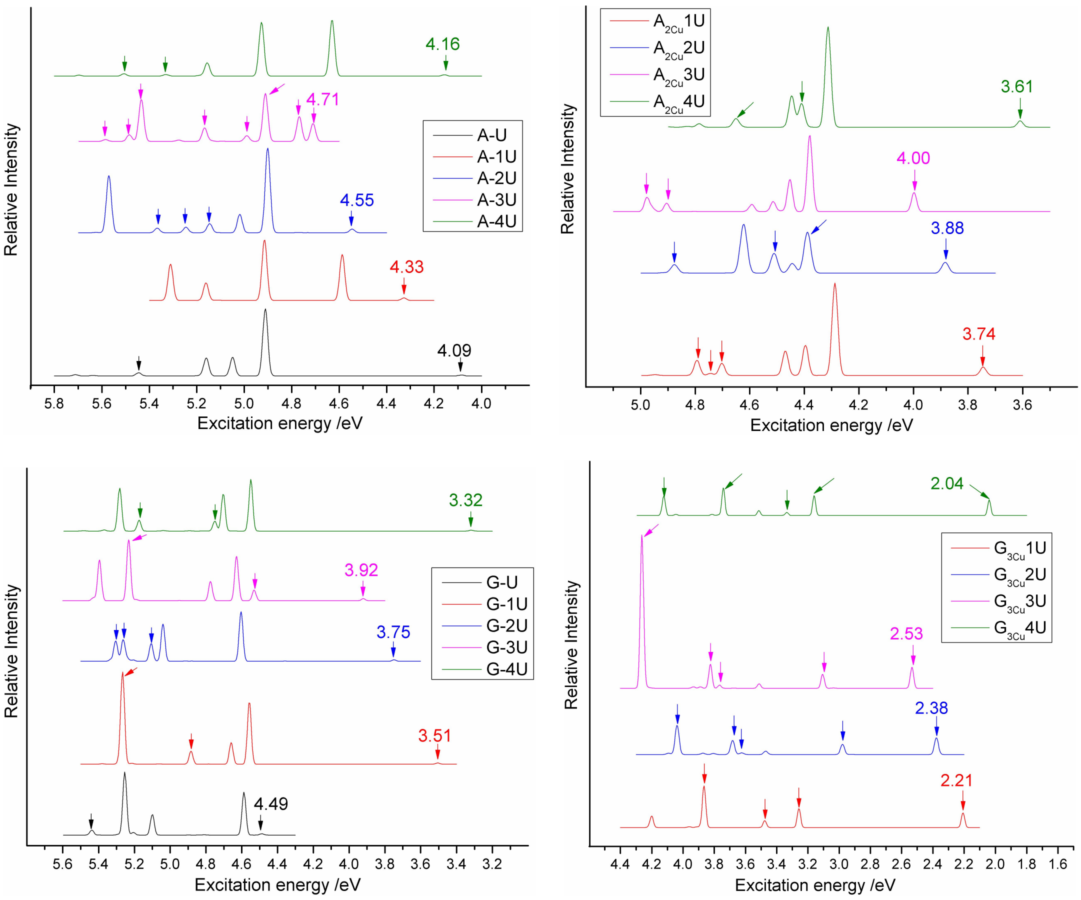
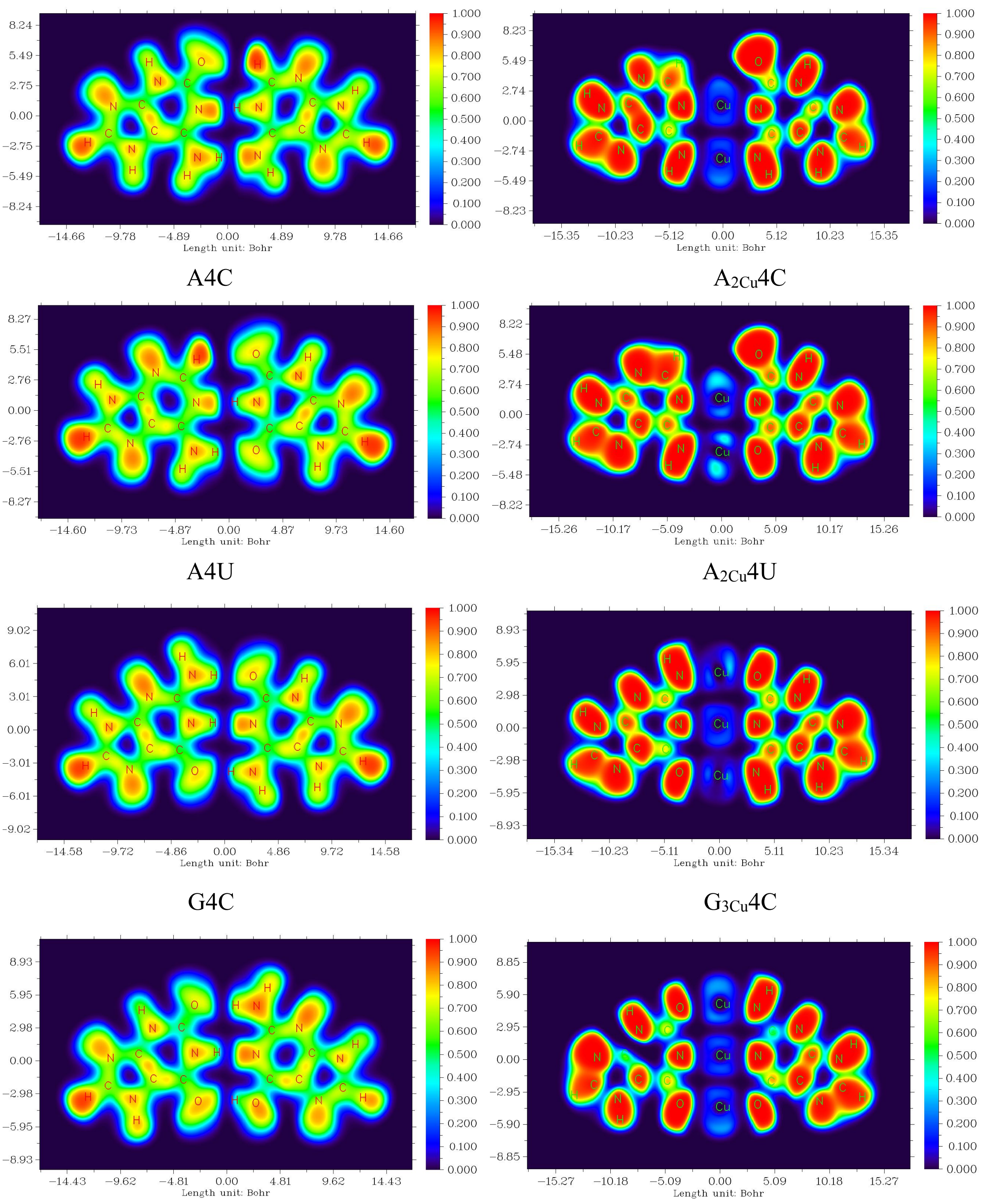


Figure S6. Absorption spectrum of the natural, the size-expanded and the M-x modified A-nU, G-nU pairs in the ultraviolet region obtained at TD-B3LYP/6-311++G** level. (half-bandwidths: 100 cm^{-1}). The charge transfer transitions are identified with arrows.



A4C

$A_{2Cu}4C$

A4U

$A_{2Cu}4U$

G4C

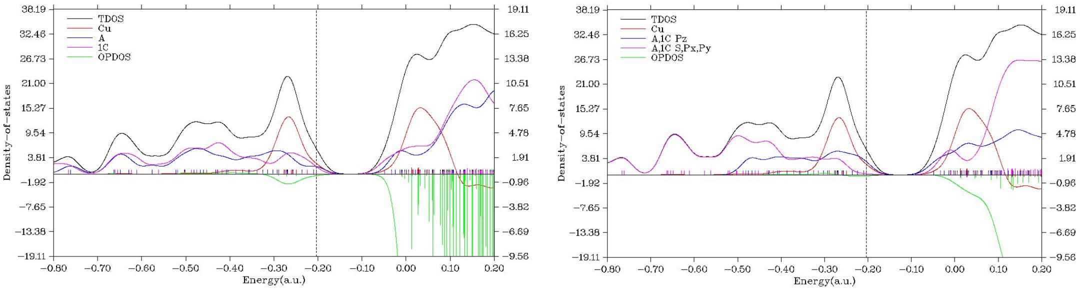
$G_{3Cu}4C$

G4U

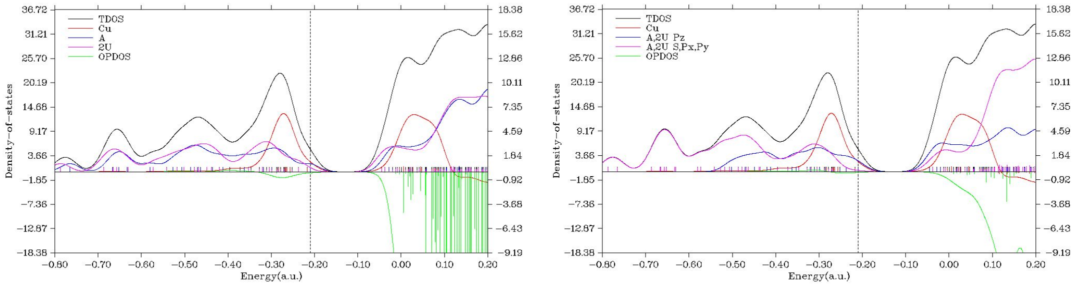
$G_{3Cu}4U$

Figure S7. ELF-π isosurfaces above 1.5 bohr of the molecular plane for modified analogs (n=4).

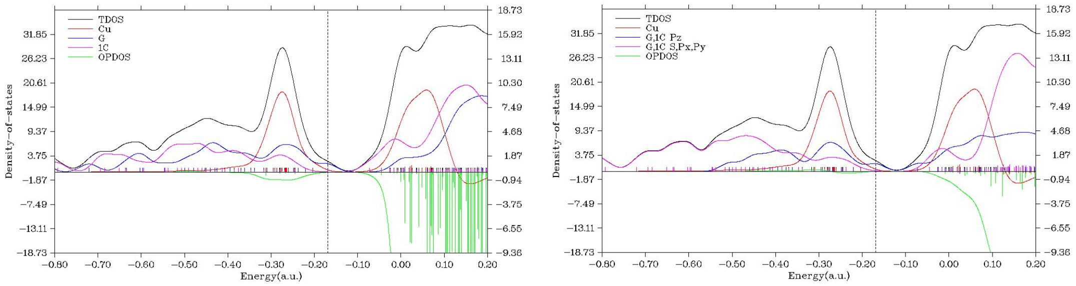
$A_{2Cu}1C$



$A_{2Cu}2U$



$G_{3Cu}1C$



$G_{3Cu}3U$

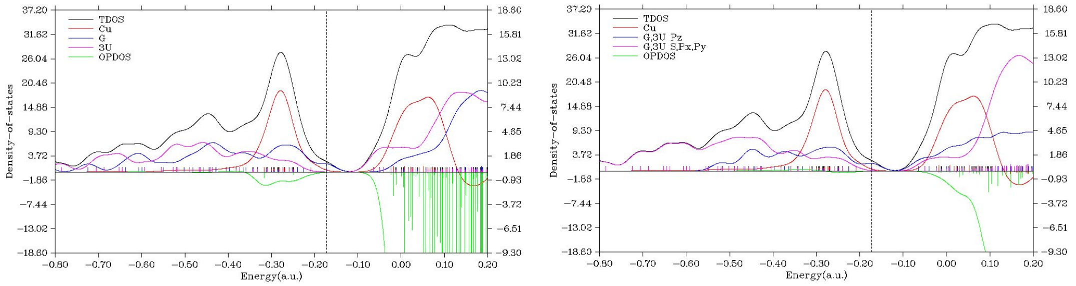


Figure S8. Plots of TDOS, PDOS and OPDOS for $A_{2Cu}1C$, $A_{2Cu}2U$, $G_{3Cu}1C$ and $G_{3Cu}3U$.