Computational design of three Cu-induced triangular pyrimidines-based DNA motifs with improved conductivity

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Supporting Information

Part 1. Structural parameters (bond lengths, BO, MO contributions, IR frequencies) and optimized geometries of the natural and 3Cu-induced triangular pyrimidines.

Part 2. Electronic properties (HOMO-LUMO gaps, IPs, EAs, spin density distribution) of the natural and 3Cu-induced triangular pyrimidines.

Part 3. Indicators of transverse electronic communication (vertical transition energies, oscillator strengths, and state assignments, ELF- π isosurface, ESP maps) for natural and 3Cu-induced triangular pyrimidines.

Part 1. Structural parameters (bond lengths, BO, MO contributions, IR frequencies) and optimized geometries of the natural and 3Cu-induced triangular pyrimidines.

Table S1. The selected bond lengths (Å) and dihedral angles (deg) for the natural and 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

U3-1	HB(N3-H···O4)	H-N3-O4-H	U3Cu3-1	Cu-N3	Cu-O4	Cu···Cu	Cu-N3-O4-Cu
	2.891	0.0		1.926	1.897	3.577	58.6°
	2.890	0.0		1.930	1.902	3.061	-32.8°
	2.891	0.0		1.929	1.897	3.170	-34.5°
U3-2	HB(N3-H···O2)	H-N3-O2-H	U3Cu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	2.908	0.8		1.924	1.901	3.724	58.3°
	2.895	0.0		1.928	1.905	3.412	-30.4°
	2.897	-0.4		1.921	1.902	3.255	-34.7°
U3-3	HB(N1-H···O2)	H-N1-O2-H	U3Cu3-3	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
	2.801	0.1		1.918	1.890	3.529	60.6°
	2.801	0.0		1.918	1.888	3.092	-39.5°
	2.801	-0.1		1.919	1.887	3.193	-37.2°
C3-1	HB(N3-H···N4)	H-N3-N4-H	C3Cu3-1	Cu-N3	Cu-N4	Cu···Cu	Cu-N3-N4-Cu
	2.899	0.0		1.940	1.909	3.404	47.0
	2.900	0.0		1.937	1.908	3.096	-35.5°
	2.900	0.0		1.946	1.911	3.139	-32.9°
C3-2	HB(N3-H···O2)	H-N3-O2-H	C3Cu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	2.907	2.1		1.927	1.907	3.773	60.1°
	2.912	1.2		1.936	1.913	3.371	-34.2°
	2.883	1.1		1.933	1.908	3.246	-33.1°
C3-3	HB(N1-H···O2)	H-N1-O2-H	C3Cu3-3	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
	2.749	1.0		1.912	1.865	4.028	88.8°
	2.749	1.0		1.925	1.878	3.270	-76.0°
	2.750	0.9		1.933	1.884	4.014	-37.9°
U2C-1	HB(N3-H···O4/N4)	H-N3-O4/N4-H	U2CCu3-1	Cu-N3	Cu-O4/N4	Cu···Cu	Cu-N3-O4/N4-Cu
	2.812	-0.4		1.928	1.900	3.536	59.0°
	2.939	0.0		1.939	1.906	3.044	-37.8°
	2.914	-177.2		1.928	1.898	3.210	-28.8°
U2C-2	HB(N3-H···O2)	H-N3-O2-H	U2Ccu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	2.851	0.1		1.929	1.904	3.745	59.2°
	2.922	0.0		1.927	1.909	3.275	-32.5°
	2.933	-0.2		1.924	1.902	3.386	-33.5°
U2C-3	HB(N1-H···O2)	H-N1-O2-H	U2CCu3-3	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu

	2.731	0.0		1.916	1.896	3.548	61.2°
	2.835	0.4		1.921	1.871	3.085	-31.0°
	2.788	0.0		1.922	1.888	3.117	-46.6°
UC2-1	HB(N3-H...O4/N4)	H-N3-O4/N4-H	UC2Cu3-1	Cu-N3	Cu-O4/N4	Cu...Cu	Cu-N3-O4/N4-Cu
	2.947	0.1		1.926	1.898	3.580	57.5°
	2.906	-0.2		1.942	1.910	3.032	-36.6°
	2.863	-0.1		1.939	1.905	3.156	-30.4°
UC2-2	HB(N3-H...O2)	H-N3-O2-H	UC2Cu3-2	Cu-N3	Cu-O2	Cu...Cu	Cu-N3-O2-Cu
	3.017	-14.5		1.925	1.901	3.746	60.4°
	2.769	-75.7		1.937	1.911	3.421	-30.7°
	3.015	112.3		1.927	1.910	3.247	-36.1°
UC2-3	HB(N1-H...O2)	H-N1-O2-H	UC2Cu3-3	Cu-N1	Cu-O2	Cu...Cu	Cu-N1-O2-Cu
	2.756	0.4		1.919	1.897	3.483	55.8°
	2.825	0.3		1.920	1.874	3.025	-45.0°
	2.719	0.5		1.924	1.870	3.109	-40.5°

Table S2. The relative energy and binding energy [eV] of the natural and 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	Relative Energy	Binding Energy		Relative Energy	Binding Energy
U3-1	2.69	0.71	U3Cu3-1	0.02	5.41
U3-2	2.59	0.73	U3Cu3-2	1.23	5.09
U3-3	0.00	1.28	U3Cu3-3	0.00	5.84
C3-1	4.32	0.98	C3Cu3-1	0.00	6.61
C3-2	6.15	0.60	C3Cu3-2	7.66	4.97
C3-3	0.00	1.66	C3Cu3-3	1.43	6.24
U2C-1	3.36	0.82	U2CCu3-1	0.00	5.79
U2C-2	3.95	0.69	U2CCu3-2	3.31	5.05
U2C-3	0.00	1.45	U2CCu3-3	0.38	6.10
UC2-1	4.12	0.87	UC2Cu3-1	0.00	7.46
UC2-2	3.96	0.92	UC2Cu3-2	5.52	5.01
UC2-3	0.00	1.57	UC2Cu3-3	1.09	6.34

Table S3. The selected delocalization energy $\Delta E_{i-j}^{(2)}$ [kcal/mol] from NBO analysis for the 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].^a

	Charge Transfer	$\Delta E_{i-j}^{(2)}$		Charge Transfer	$\Delta E_{i-j}^{(2)}$
U3Cu3-1	nO4→n*Cu/σ*N3	38.67/18.02/22.02	C3Cu3-1	σN3-Cu→σ*Cu-N4	9.06/8.92/8.75
	-Cu				
	σC2-N3→n*Cu	53.99		σCu-N4→σ*N3-Cu	10.00/10.16/10.15
	n*Cu→/σ*N3-Cu'	39.29/16.21		nCu→n*Cu'	3.08/4.08

U3Cu3-2	nN3→n*Cu	61.74/65.93/64.91	C3Cu3-2	nN3→n*Cu	58.13/61.17/63.15
	nO2→n*Cu	36.52/37.13/23.64		nO2→n*Cu	34.32/35.86/23.37
	n*Cu→n*Cu'	11.57/7.69/6.32		n*Cu→n*Cu'	6.32/6.55
U3Cu3-3	nO2→σ*N1-Cu/n*Cu	21.65/22.02/17.28	C3Cu3-3	nN1→σ*O2-Cu/n*Cu	44.84/63.11/72.06
	nCu→n*Cu'	3.98/2.96		nO2→σ*O2-Cu/n*Cu	32.31/23.47/44.16
				σ*O2-Cu/n*Cu→n*Cu'	11.16/6.33
U2CCu3-1	nO4/σC4-N3→n*Cu	37.84/17.71/55.58	UC2Cu3-1	nO4/σC2-N3→n*Cu	17.58/29.28
	nCu→nN3	14.19		σCu-N4→σ*N3-Cu	10.97
	σCu-N4→σ*N3-Cu	10.31		n*Cu/σ*Cu-N4/σ*N3-Cu→σ*Cu'-N4'	23.27/10.42/32.60
	n*Cu/σ*N3-Cu→n*Cu'/σ*Cu'-N4	24.07/10.18			
U2CCu3-2	nN3→n*Cu	61.53/65.12/63.31	UC2Cu3-2	nN3→n*Cu	58.21/65.16/63.05
	nO2→n*Cu	36.97/21.92/36.63		nO2→n*Cu	36.54/35.72/22.62
	n*Cu→n*Cu'	7.16/6.59/6.18		n*Cu→n*Cu'	7.23/9.24/5.80
U2CCu3-3	nN1→n*Cu/σ*O2-Cu	63.80/45.44/48.42	UC2Cu3-3	nN1→n*Cu/σ*O2-Cu	63.21/46.33/44.36
	nO2→n*Cu/σ*O2-Cu	42.44/22.48/32.30		nO2→n*Cu/σ*O2-Cu	37.17/26.69/36.34
	σO2-Cu→σ*O2'-Cu'/n*Cu'	63.64/13.97/21.01		σO2-Cu→σ*N1-C2	62.79/64.33
	n*Cu→n*Cu'/σ*O2-Cu'	38.96/43.70		σ*O2-Cu/n*Cu→n*Cu'/σ*O2'-Cu'	28.10/29.06/47.44/41.21

^a Another Cu or atoms of another base are denoted with '.

Table S4. The major molecular orbital and contributions (absolute value larger than 0.1) to the typical Cu-N/O bonds for U3Cu3-3, C3Cu3-1, U2CCu3-3, and UC2Cu3-1 [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

U3Cu3-3					
Cu1-N1	MO78	0.64			
Cu2-N1	MO76	0.67			
Cu3-N1	MO77	0.63			
Cu1-O2	MO80	-0.19			
Cu2-O2	MO81	-0.14	MO67	-0.13	
Cu3-O2	MO68	-0.10	MO79	-0.20	
Cu1-Cu2	-				
Cu1-Cu3	MO107	-0.11			

Cu2-Cu3	MO76	-0.13	MO106	-0.14	MO107	-0.12				
C3Cu3-1										
Cu1-N3	MO81	0.59								
Cu2-N3	MO80	0.63								
Cu3-N3	MO79	0.60	MO99	-0.15						
Cu1-N4	MO77	0.67	MO85	-0.12	MO105	-0.11				
Cu2-N4	MO78	0.64	MO86	-0.10						
Cu3-N4	MO76	0.63	MO99	-0.14						
Cu1-Cu2	-									
Cu1-Cu3	MO77	-0.11	MO99	-0.15	MO105	-0.19	MO108	-0.15	MO110	-0.14
Cu2-Cu3	MO99	-0.13	MO102	-0.17	MO110	-0.14	MO109	-0.16		
U2CCu3-3										
Cu1-N1	MO79	-0.55								
Cu2-N1	MO81	-0.54	MO86	-0.10						
Cu3-N1	MO80	-0.53								
Cu1-O2	MO76	-0.29								
Cu2-O2	MO67	-0.11	MO78	-0.11	MO86	0.20				
Cu3-O2	MO71	-0.11	MO77	-0.19	MO89	0.15				
Cu1-Cu2	-									
Cu1-Cu3	MO110	-0.15								
Cu2-Cu3	MO109	-0.14	MO110	-0.13						
UC2Cu3-1										
Cu1-N3	MO80	0.56								
Cu2-N3	MO79	0.62	MO109	-0.11						
Cu3-N3	MO81	-0.28	MO101	-0.15						
Cu1-N4	MO77	0.70	MO84	-0.12	MO108	-0.11				
Cu2-O4	MO72	-0.17	MO78	-0.26	MO90	-0.22				
Cu3-N4	MO76	0.54	MO101	-0.13						
Cu1-Cu2	-									
Cu1-Cu3	MO77	-0.11	MO101	-0.13	MO105	-0.19	MO108	-0.17	MO110	-0.11
Cu2-Cu3	MO79	-0.11	MO101	-0.12	MO104	-0.12	MO109	-0.20	MO110	-0.15

Table S5. IR frequencies assigned to Cu-N/O stretching vibrations (symmetric, ν_s , and asymmetric, ν_{as}) and the Cu···Cu stretching vibrations of U3Cu3-3 and C3Cu3-1 [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

frequencies/cm ⁻¹	stretching vibration assignments	intensity
<hr/>		
U3Cu3-3		
162	ν_s (Cu1-Cu2-Cu3)	2.01
110	ν_{as} (Cu1-Cu2-Cu3)	0.12
338	ν_s (N1-Cu-O2)	27.23
253	ν_{as} (N1-Cu-O2)	3.83
C3Cu3-1		

109	ν_s (Cu1-Cu2-Cu3)	0.78
140	ν_{as} (Cu1-Cu2-Cu3)	4.25
206	ν_s (N1-Cu-N4)	2.59
321	ν_{as} (N1-Cu-N4)	8.44

Figure S1. The optimized geometries of the natural and the 3Cu-induced triangular pyrimidines [B3LYP/6-31+G*(C,H,O,N)/LANL2DZ(Cu)].

Figure S2. The major orbitals (absolute value larger than 0.1) contributed to the typical Cu-N/O bonds for U3Cu3-3 and C3Cu3-1 mentioned in Table S4 [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

Part 2. Electronic properties (HOMO-LUMO gaps, IPs, EAs, spin density distribution) of the natural and 3Cu-induced triangular pyrimidines.

Table S6. The HOMO, LUMO energy, HOMO-LUMO gaps, singlet-triplet gaps (ΔE_{ST}), the ionization potentials and the electron affinities [eV] of the natural and 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	HOMO	LUMO	Gap	Gap Decline(%)	$ \Delta E_{ST} $	VIP	AIP	VEA	AEA
U3-1	-6.96	-1.50	5.46		3.60	8.22	8.16	-1.46	-1.84
U3-2	-7.07	-1.49	5.58		3.62	8.33	8.28	-1.60	-1.95
U3-3	-7.37	-1.84	5.52		3.63	8.62	8.55	-3.50	-3.90
U3Cu3-1	-6.14	-1.61	4.53	16.95	3.54	7.63	7.39	-2.23	-2.62
U3Cu3-2	-6.24	-1.39	4.85	13.10	3.88	7.79	7.42	-1.27	-1.61
U3Cu3-3	-6.96	-1.84	5.12	7.22	3.54	8.18	7.98	-3.55	-11.11
U3H3-1	-6.57	-1.60	4.97						
U3H3-2	-6.60	-1.41	5.19						
U3H3-3	-7.18	-1.83	5.35						
C3-1	-6.31	-1.21	5.10		4.01	7.57	7.50	0.02	-0.35
C3-2	-6.30	-1.08	5.23		3.35	7.51	7.47	0.49	0.15
C3-3	-6.35	-1.03	5.32		4.33	7.61	7.50	0.23	0.05
C3Cu3-1	-5.78	-1.32	4.47	12.36	3.35	7.13	7.01	-0.82	-1.23
C3Cu3-2	-5.68	-1.01	4.66	10.77	3.31	7.10	6.65	0.71	0.31
C3Cu3-3	-5.68	-0.96	4.71	11.46	3.68	7.01	6.53	0.37	0.56
C3H3-1	-6.00	-1.26	4.74						
C3H3-2	-5.97	-1.05	4.92						
C3H3-3	-6.01	-0.99	5.02						
U2C-1	-6.34	-1.51	4.83		3.36	7.93	7.77	-1.01	-1.59
U2C-2	-6.48	-1.40	5.07		3.36	7.99	7.92	-0.91	-1.28
U2C-3	-6.96	-1.61	5.35		4.36	8.26	8.00	-1.51	-2.56
U2CCu3-1	-6.02	-1.52	4.50	6.87	3.77	7.55	7.43	-1.71	-2.14
U2CCu3-2	-6.04	-1.28	4.75	6.31	3.85	7.52	7.22	-0.87	-0.97
U2CCu3-3	-6.65	-1.57	5.08	5.08	3.76	7.92	7.47	-2.16	-9.04
U2CH3-1	-6.17	-1.52	4.65						
U2CH3-2	-6.20	-1.30	4.90						
U2CH3-3	-6.77	-1.58	5.19						
UC2-1	-6.22	-1.41	4.81		3.36	7.73	7.60	-0.59	-1.09
UC2-2	-6.26	-1.56	4.70		3.34	7.81	7.86	-0.57	-6.60
UC2-3	-6.62	-1.36	5.26		4.37	7.93	7.83	-0.76	-1.26
UC2Cu3-1	-5.87	-1.46	4.42	8.14	3.37	7.95	7.21	-1.27	-1.73
UC2Cu3-2	-5.83	-1.16	4.66	0.75	3.80	7.29	6.78	0.08	-0.34

UC2Cu3-3	-6.28	-1.31	4.97	5.58	3.75	7.56	6.94	-3.66	-7.07
UC2H3-1	-6.02	-1.44	4.58						
UC2H3-2	-5.88	-1.23	4.65						
UC2H3-3	-6.43	-1.33	5.10

Figure S3. Frontier molecular orbitals of the natural and the 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

U3-1⁺

U3Cu3-1⁺

U3-1⁻

U3Cu3-1⁻

U3-2⁺

U3Cu3-2⁺

U3-2⁻

U3Cu3-2⁻

U3-3⁺

U3Cu3-3⁺

U3-3⁻

U3Cu3-3⁻

C3-1⁺

C3Cu3-1⁺

C3-1⁻

C3Cu3-1⁻

C3-2⁺

C3Cu3-2⁺

C3-2⁻

C3Cu3-2⁻

C3-3⁺

C3Cu3-3⁺

C3-3⁻

C3Cu3-3⁻

U2C-1⁺

U2CCu3-1⁺

U2C-1⁻

U2CCu3-1⁻

U2C-2⁺

U2CCu3-2⁺

U2C-2⁻

U2CCu3-2⁻

U2C-3⁺

U2CCu3-3⁺

U2C-3⁻

U2CCu3-3⁻

UC2-1⁺

UC2Cu3-1⁺

UC2-1⁻

UC2Cu3-1⁻

UC2-2⁺

UC2Cu3-2⁺

UC2-2⁻

UC2Cu3-2⁻

UC2-3⁺

UC2Cu3-3⁺

UC2-3⁻

UC2Cu3-3⁻

Figure S4. Spin density distributions of the oxidized, reduced and triplet-excited states for natural and 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**_(C,H,O,N)/LANL2DZ(Cu)].

Part 3. Indicators of transverse electronic communication (vertical transition energies, oscillator strengths, and state assignments, ELF- π isosurface, ESP maps) for natural and 3Cu-induced triangular pyrimidines.

Table S7. The vertical transition energies, oscillator strengths, and state assignments^a to the low-lying singlet states of the natural and the 3Cu-induced triangular pyrimidines calculated at TD-B3LYP/6-311++G** Level (f>0.003).

State		E/eV	f	Assign.	State		E/eV	f	Assign.
U3-1	S ₄	5.00	0.134	$\pi_U\pi_U^*$	C3-1	S ₂	4.76	0.063	$n_C\pi_C^*$
	S ₅	5.00	0.134	$\pi_U\pi_U^*$		S ₃	4.76	0.063	$n_C\pi_C^*$
	S ₈	5.14	0.058	$\pi_U\pi_U^*$		S ₄	4.84	0.085	$n_C\pi_C^*$
	S ₉	5.14	0.057	$\pi_U\pi_U^*$		S ₅	4.84	0.085	$n_C\pi_C^*$
	S ₁₁	5.18	0.007	$\pi_U\pi_U^*$		S ₈	4.95	0.077	$n_C\pi_C^*$
	S ₁₂	5.18	0.007	$\pi_U\pi_U^*$		S ₉	4.95	0.077	$n_C\pi_C^*$
U3Cu3-1	S ₄	3.92	0.014	$n_U\pi_U^*$	C3Cu3-1	S ₄	3.89	0.006	$n_C\pi_C^*$
	S ₅	4.06	0.007	$n_U\pi_U^*$		S ₅	4.00	0.011	$n_C\pi_C^*$
	S ₇	4.24	0.025	$n_U\pi_U^*$		S ₆	4.03	0.024	$n_C\pi_C^*$
	S ₈	4.31	0.008	$n_U\pi_U^*$		S ₇	4.10	0.006	$n_C\pi_C^*$
	S ₉	4.40	0.019	$n_U\pi_U^*$		S ₈	4.13	0.011	$n_C\pi_C^*$
	S ₁₀	4.44	0.153	$n_U\pi_U^*$		S ₉	4.18	0.029	$n_C\pi_C^*$
	S ₁₂	4.53	0.033	$n_U\pi_U^*$		S ₁₀	4.20	0.036	$n_C\pi_C^*$
	S ₁₄	4.57	0.006	$n_{Cu}\pi_U^*$		S ₁₁	4.29	0.013	$n_C\pi_C^*$
	S ₁₅	4.59	0.104	$n_{Cu}\pi_U^*$		S ₁₂	4.37	0.144	$n_{Cu}\pi_C^*$
U3-2	S ₅	5.17	0.142	$\pi_U\pi_U^*$	C3-2	S ₁	4.79	0.015	$n_C\pi_C^*$
	S ₆	5.17	0.151	$\pi_U\pi_U^*$		S ₂	4.79	0.109	$n_C\pi_C^*$
	S ₇	5.22	0.015	$\pi_U\pi_U^*$		S ₃	4.80	0.116	$n_C\pi_C^*$
	S ₈	5.22	0.018	$\pi_U\pi_U^*$		S ₄	4.87	0.003	$n_C\pi_C^*$
	S ₉	5.22	0.031	$\pi_U\pi_U^*$		S ₅	4.88	0.022	$n_C\pi_C^*$
	S ₁₁	5.25	0.004	$\pi_U\pi_U^*$		S ₆	4.88	0.020	$n_C\pi_C^*$
	S ₁₂	5.25	0.006	$\pi_U\pi_U^*$		S ₈	4.92	0.024	$n_C\pi_C^*$
U3Cu3-2	S ₁	4.08	0.004	$n_U\pi_U^*$	C3Cu3-2	S ₁	3.93	0.004	$n_{Cu}\pi_U^*$
	S ₃	4.15	0.006	$n_U\pi_U^*$		S ₂	4.00	0.005	$n_{Cu}\pi_U^*$

	S ₄	4.31	0.006	$n_U\pi_U^*$		S ₄	4.15	0.005	$n_{Cu}\pi_U^*$
	S ₇	4.49	0.034	$n_U\pi_U^*$		S ₅	4.22	0.012	$n_{Cu}\pi_U^*$
	S ₈	4.50	0.006	$n_U\pi_U^*$		S ₆	4.26	0.017	$n_{Cu}\pi_U^*$
	S ₉	4.55	0.008	$n_{Cu}\pi_U^*$		S ₇	4.27	0.039	$n_{Cu}\pi_U^*$
	S ₁₂	4.62	0.027	$n_U\pi_U^*$		S ₈	4.33	0.004	$n_{Cu}\pi_U^*$
	S ₁₃	4.66	0.016	$n_U\pi_U^*$		S ₉	4.35	0.030	$n_{Cu}\pi_U^*$
	S ₁₄	4.67	0.008	$n_{Cu}\pi_U^*$		S ₁₀	4.42	0.024	$n_{Cu}\pi_U^*$
						S ₁₁	4.48	0.005	$n_{Cu}\pi_U^*$
U3-3	S ₅	5.11	0.235	$n_U\pi_U^*$	C3-3	S ₂	4.76	0.113	$\pi_C\pi_C^*$
	S ₆	5.11	0.235	$n_U\pi_U^*$		S ₃	4.76	0.113	$\pi_C\pi_C^*$
	S ₇	5.17	0.044	$n_U\pi_U^*$		S ₄	4.91	0.004	$\pi_C\pi_C^*$
	S ₈	5.18	0.043	$n_U\pi_U^*$		S ₅	4.91	0.004	$\pi_C\pi_C^*$
	S ₉	5.22	0.026	$n_U\pi_U^*$		S ₇	5.02	0.005	$\pi_C\pi_C^*$
	S ₁₀	5.22	0.024	$n_U\pi_U^*$		S ₈	5.02	0.004	$\pi_C\pi_C^*$
						S ₁₂	5.06	0.005	$n_C\pi_C^*$
U3Cu3-3	S ₁	4.26	0.005	$n_U\pi_U^*$	C3Cu3-3	S ₁	3.90	0.003	$n_C\pi_C^*$
	S ₂	4.35	0.006	$n_U\pi_U^*$		S ₂	4.18	0.008	$n_{Cu}\pi_C^*$
	S ₃	4.55	0.021	$n_U\pi_U^*$		S ₃	4.21	0.018	$n_C\pi_C^*$
	S ₄	4.58	0.058	$n_U\pi_U^*$		S ₅	4.28	0.035	$n_{Cu}\pi_C^*$
	S ₅	4.59	0.050	$n_U\pi_U^*$		S ₆	4.37	0.013	$n_C\pi_C^*$
	S ₆	4.62	0.036	$n_{Cu}\pi_U^*$		S ₇	4.42	0.024	$n_{Cu}\pi_C^*$
	S ₇	4.65	0.045	$n_{Cu}\pi_U^*$		S ₈	4.46	0.082	$n_{Cu}\pi_C^*$
	S ₈	4.67	0.022	$n_{Cu}\pi_U^*$		S ₉	4.46	0.006	$n_C\pi_C^*$
	S ₉	4.69	0.153	$n_U\pi_U^*$		S ₁₀	4.53	0.031	$n_{Cu}\pi_C^*$
	S ₁₀	4.72	0.056	$n_{Cu}\pi_U^*$		S ₁₁	4.56	0.041	$n_{Cu}\pi_C^*$
	S ₁₁	4.73	0.078	$n_{Cu}\pi_U^*$		S ₁₂	4.59	0.023	$n_{Cu}\pi_C^*$
	S ₁₂	4.77	0.020	$n_{Cu}\pi_U^*$		S ₁₄	4.64	0.022	$n_{Cu}\pi_C^*$
	S ₁₃	4.80	0.057	$n_{Cu}\pi_U^*$		S ₁₅	4.65	0.004	$n_{Cu}\pi_C^*$
	S ₁₄	4.83	0.004	$n_{Cu}\pi_U^*$					
U2C-1	S ₁	4.36	0.014	$n_C\pi_U^*$	UC2-1	S ₁	4.36	0.008	$n_C\pi_C^*$
	S ₅	4.87	0.141	$n_C\pi_U^*$		S ₂	4.50	0.008	$n_C\pi_U^*$
	S ₆	4.96	0.053	$n_C\pi_U^*$		S ₄	4.74	0.047	$n_C\pi_C^*$
	S ₇	5.07	0.154	$n_U\pi_U^*$		S ₅	4.87	0.102	$n_C\pi_U^*$
	S ₈	5.09	0.056	$n_C\pi_U^*$		S ₆	4.91	0.154	$n_C\pi_U^*$
	S ₁₃	5.29	0.005	$n_U\pi_U^*$		S ₇	5.06	0.108	$n_U\pi_C^*$
	S ₁₅	5.38	0.006	$n_U\pi_U^*$		S ₉	5.11	0.004	$n_U\pi_C^*$
						S ₁₁	5.24	0.022	$n_U\pi_U^*$
						S ₁₂	5.25	0.006	$n_C\pi_U^*$
U2CCu3-1	S ₁	3.77	0.004	$n_C\pi_U^*$	UC2Cu3-1	S ₁	3.72	0.010	$n_C\pi_U^*$
	S ₂	3.78	0.006	$n_U\pi_U^* \& n_C\pi_C^*$		S ₅	3.99	0.027	$n_C\pi_U^*$
	S ₃	3.85	0.004	$n_U\pi_U^* \& n_C\pi_C^*$		S ₇	4.12	0.073	$n_C\pi_C^* \& n_C\pi_U^*$
	S ₄	3.93	0.005	$n_C\pi_U^*$		S ₈	4.17	0.005	$n_C\pi_C^*$
	S ₅	3.96	0.010	$n_U\pi_C^*$		S ₉	4.22	0.018	$n_C\pi_C^*$
	S ₆	4.11	0.002	$n_C\pi_U^*$		S ₁₀	4.25	0.023	$n_C\pi_C^*$

	S ₇	4.18	0.008	$n_C\pi_C^* \& n_C\pi_U^*$		S ₁₁	4.32	0.007	$n_C\pi_C^* \& n_C\pi_U^*$
	S ₈	4.21	0.005	$n_U\pi_U^*$		S ₁₂	4.38	0.013	$n_C\pi_C^*$
	S ₉	4.28	0.048	$n_{Cu}\pi_U^*$		S ₁₃	4.41	0.040	$n_{Cu}\pi_U^*$
	S ₁₀	4.31	0.029	$n_C\pi_U^* \& n_{Cu}\pi_U^*$		S ₁₄	4.47	0.040	$n_{Cu}\pi_U^*$
	S ₁₂	4.47	0.103	$n_U\pi_U^* \& n_U\pi_C^*$		S ₁₅	4.52	0.060	$n_{Cu}\pi_U^*$
	S ₁₃	4.49	0.037	$n_{Cu}\pi_U^*$					
	S ₁₄	4.53	0.045	$n_U\pi_U^* \& n_U\pi_C^*$					
	S ₁₅	4.57	0.085	$n_{Cu}\pi_U^* \& n_{Cu}\pi_C^*$					
U2C-2	S ₃	4.69	0.011	$n_U\pi_U^*$	UC2-2	S ₁	4.24	0.004	$n_U\pi_C^*$
	S ₅	4.83	0.097	$n_U\pi_C^*$		S ₃	4.66	0.020	$n_U\pi_C^*$
	S ₆	5.15	0.049	$n_C\pi_U^*$		S ₄	4.73	0.121	$n_U\pi_C^*$
	S ₇	5.17	0.169	$n_C\pi_U^* \& n_U\pi_U^*$		S ₆	4.89	0.115	$n_U\pi_C^*$
	S ₉	5.22	0.016	$n_U\pi_U^*$		S ₈	5.15	0.104	$n_U\pi_C^*$
	S ₁₁	5.24	0.004	$n_C\pi_U^*$		S ₁₁	5.21	0.005	$n_C\pi_C^*$
	S ₁₂	5.37	0.005	$n_U\pi_C^*$					
	S ₁₅	5.50	0.024	$n_U\pi_C^*$					
U2CCu3-2	S ₁	4.02	0.005	$n_U\pi_U^*$	UC2Cu3-2	S ₁	3.96	0.005	$n_U\pi_C^*$
	S ₃	4.12	0.005	$n_U\pi_U^*$		S ₃	4.06	0.006	$n_{Cu}\pi_U^*$
	S ₄	4.49	0.006	$n_U\pi_U^*$		S ₄	4.13	0.006	$n_U\pi_U^* \& n_{Cu}\pi_U^*$
	S ₅	4.31	0.008	$n_U\pi_U^*$		S ₅	4.30	0.026	$n_{Cu}\pi_C^*$
	S ₆	4.36	0.035	$n_{Cu}\pi_U^*$		S ₆	4.33	0.021	$n_{Cu}\pi_C^*$
	S ₈	4.46	0.009	$n_U\pi_C^*$		S ₇	4.35	0.013	$n_{Cu}\pi_C^*$
	S ₉	4.46	0.005	$n_U\pi_C^*$		S ₈	4.38	0.021	$n_{Cu}\pi_U^* \& n_{Cu}\pi_C^*$
	S ₁₀	4.49	0.019	$n_{Cu}\pi_U^*$		S ₁₁	4.49	0.014	$n_{Cu}\pi_U^*$
	S ₁₂	4.55	0.009	$n_{Cu}\pi_U^*$		S ₁₄	4.58	0.005	$n_{Cu}\pi_U^*$
	S ₁₄	4.62	0.021	$n_{Cu}\pi_U^*$					
	S ₁₅	4.67	0.005	$n_U\pi_U^*$					
U2C-3	S ₃	4.78	0.070	$n_U\pi_U^*$	UC2-3	S ₁	4.74	0.039	$n_C\pi_U^*$
	S ₄	4.93	0.004	$n_U\pi_U^*$		S ₃	4.78	0.104	$n_U\pi_C^*$
	S ₅	5.02	0.050	$n_U\pi_C^*$		S ₄	4.87	0.018	$n_U\pi_U^* \& n_U\pi_C^*$
	S ₆	5.05	0.006	$n_U\pi_U^*$		S ₁₀	5.11	0.098	$n_C\pi_C^*$
	S ₈	5.09	0.007	$n_U\pi_U^*$		S ₁₁	5.14	0.115	$n_C\pi_C^*$
	S ₉	5.13	0.254	$n_C\pi_U^*$		S ₁₂	5.22	0.005	$n_C\pi_C^*$
	S ₁₀	5.16	0.109	$n_U\pi_C^*$					
	S ₁₂	5.34	0.003	$n_C\pi_C^*$					
	S ₁₄	5.49	0.080	$n_U\pi_U^* \& n_C\pi_U^*$					
	S ₁₅	5.54	0.013	$n_U\pi_C^*$					
U2CCu3-3	S ₁	4.33	0.017	$n_U\pi_C^*$	UC2Cu3-3	S ₁	4.25	0.019	$n_C\pi_C^*$
	S ₂	4.36	0.011	$n_U\pi_C^*$		S ₂	4.31	0.020	$n_U\pi_U^* \& n_U\pi_C^*$
	S ₃	4.44	0.016	$n_U\pi_C^*$		S ₃	4.33	0.013	$n_C\pi_U^*$
	S ₄	4.47	0.014	$n_U\pi_C^*$		S ₄	4.35	0.012	$n_C\pi_C^*$
	S ₅	4.50	0.003	$n_U\pi_U^* \& n_U\pi_U^*$		S ₅	4.38	0.007	$n_{Cu}\pi_C^*$
	S ₆	4.55	0.011	$n_{Cu}\pi_U^*$		S ₆	4.41	0.025	$n_C\pi_C^* \& n_{Cu}\pi_C^*$
	S ₇	4.56	0.090	$n_U\pi_U^*$		S ₇	4.47	0.108	$n_U\pi_U^*$

S ₈	4.63	0.042	$n_U\pi_C^*$	S ₉	4.55	0.004	$n_{Cu}\pi_U^* \& n_{Cu}\pi_C^*$
S ₉	4.63	0.084	$n_U\pi_U^* \& n_U\pi_U^*$	S ₁₀	4.59	0.035	$n_U\pi_C^*$
S ₁₀	4.67	0.128	$n_U\pi_U^*$	S ₁₁	4.61	0.058	$n_C\pi_C^*$
S ₁₁	4.69	0.091	$n_U\pi_U^*$	S ₁₂	4.65	0.005	$n_{Cu}\pi_C^*$
S ₁₃	4.76	0.008	$n_{Cu}\pi_C^* \& n_U\pi_C^*$	S ₁₃	4.68	0.031	$n_{Cu}\pi_C^*$
S ₁₄	4.77	0.010	$n_{Cu}\pi_U^*$	S ₁₄	4.68	0.045	$n_{Cu}\pi_C^*$

^aThe charge-transfer transitions are in bold.

Table S8. Difference values of Cu-N/O bond lengths, Cu···Cu distances (Å) and selected dihedral angles (deg) between ground state and electron transfer excited state of 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].

	Cu-N3	Cu-O4	Cu···Cu	Cu-N3-O4-Cu
U3Cu3-1	-0.011	-0.003	0.032	-3.25
	0.001	-0.002	-0.001	5.62
	0.00	-0.006	-0.019	-2.41
U3Cu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	0.038	0.044	-0.790	-29.05
	0.068	0.063	-0.933	-31.57
U3Cu3-3	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
	0.053	0.049	-0.692	-37.04
	0.071	0.057	-0.750	-39.08
C3Cu3-1	Cu-N3	Cu-N4	Cu···Cu	Cu-N3-N4-Cu
	-0.005	-0.023	-0.012	-0.69
	-0.004	-0.001	-0.019	-1.19
C3Cu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	-0.007	-0.003	-0.015	-1.9
	-0.006	-0.001	-0.017	0.73
C3Cu3-3	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
	-0.028	0.009	0.793	37.72
	0.005	-0.004	0.055	2.32
U2CCu3-1	Cu-N3	Cu-O4/N4	Cu···Cu	Cu-N3-O4/N4-Cu
	-0.012	-0.003	0.04	2.9
	-0.003	-0.006	0.017	-2.99
U2CCu3-2	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
	-0.003	-0.001	-0.021	-3.61
	-0.004	-0.002	-0.003	2.9

	0	0.001	-0.006	-0.01
	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
U2CCu3-3	-0.002	0.001	-0.057	6.09
	-0.004	0.003	-0.004	-2.98
	0	0	-0.007	-1.01
	Cu-N3	Cu-O4/N4	Cu···Cu	Cu-N3-O4/N4-Cu
UC2Cu3-1	-0.002	-0.017	-0.094	-12.28
	-0.07	-0.051	0.088	6.1
	0.002	0.001	-0.025	9.19
	Cu-N3	Cu-O2	Cu···Cu	Cu-N3-O2-Cu
UC2Cu3-2	-0.006	0	0.041	1.88
	0.003	-0.002	-0.049	-1.9
	-0.002	0	-0.055	-2.16
	Cu-N1	Cu-O2	Cu···Cu	Cu-N1-O2-Cu
UC2Cu3-3	-0.006	0	-0.002	-1.35
	0	-0.002	0.002	0.09
	-0.003	0.001	-0.05	0.01

Figure S5. Molecular orbitals involved in several electronic singlet transitions of U3Cu3-2, C3Cu3-2, U2CCu3-2 and UC2Cu3-2 mentioned in Table S5 calculated at TD-B3LYP/6-311++G** level.

U3Cu3-1

C3Cu3-1

U2CCu3-1

UC2Cu3-1

U3Cu3-2

C3Cu3-2

U2CCu3-2

UC2Cu3-2

U3Cu3-3

C3Cu3-3

U2CCu3-3

UC2Cu3-3

Figure S6. ELF- π isosurfaces above 1.5 bohr of the molecular plane and the electrostatic potential (ESP) maps with contour lines for 3Cu-induced triangular pyrimidines [B3LYP/6-311++G**(C,H,O,N)/LANL2DZ(Cu)].