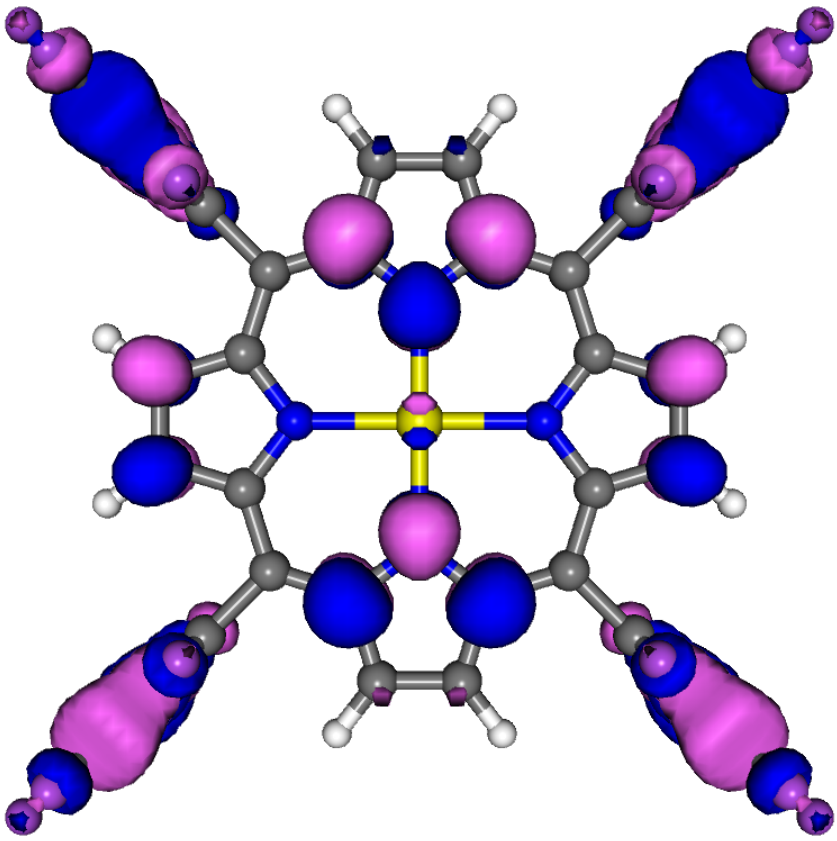
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.



$25e_g$

Table S1-ESI. Energy-ordered $1s^{C/N/F}$-based linear combinations of CuTPP and CuTPP(F) in D_{4h} symmetry. The atom numbering corresponds to the one recommended by the IUPAC and adopted in Fig. 1.

CuTPP	a_{1g}	a_{2g}	b_{1g}	b_{2g}	e_g	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
N	3		1							2
C^1 (C^{Py})	4	1	2	1						3/4
C^2 (C^{Py})	10	2	3	7						10/11
C^5 (C^m)	5			2						5
C^{25}($C_{\parallel}^{Ph}$)	6			3						6
C^{29}($C_{\perp}^{Ph}$)	8			5	2		3	2		8
C^{37}($C_{\perp}^{Ph}$)	7			4	1		2	1		7
C^{45}($C_{\parallel}^{Ph}$)	9			6						9

CuTPP(F)	a_{1g}	a_{2g}	b_{1g}	b_{2g}	e_g	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
F^{49}($F_{\perp}$)	5			3	2		3	2		4
F^{57}($F_{\perp}$)	4			2	1		2	1		3
F^{65} ($F_{\parallel}$)	3			1						2
N	6		1							5
C^1(C^{Py})	11	1	2	8						10/11
C^2(C^{Py})	13	2	3	10						13/14
C^5(C^m)	12			9						12
C^{25}($C_{\parallel}^{Ph}$)	10			7						9
C^{29}($C_{\perp}^{Ph}$)	9			6	4		5	4		8
C^{37}($C_{\perp}^{Ph}$)	8			5	3		4	3		7
C^{45}($C_{\parallel}^{Ph}$)	7			4						6

Table S2a-ESI. Γ_{XS} representation products corresponding to electric dipole allowed transitions in D_{4h} symmetry.

$\otimes(a_{2u}+e_u)\otimes$	a_{1g}	a_{2g}	b_{1g}	b_{2g}	e_g	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
a_{1g}							x			x
a_{2g}						x				x
b_{1g}									x	x
b_{2g}								x		x
e_g						x	x	x	x	x
a_{1u}		x			x					
a_{2u}	x				x					
b_{1u}				x	x					
b_{2u}			x		x					
e_u	x	x	x	x	x					

Table S2b-ESI. Localization and symmetry of heavy atom 1s → π* transitions

	Transition Symmetry	
	a_{2u}	e_u
C^{Py}-based	$1s(a_{1g}) \rightarrow \pi_{\perp}^*(a_{2u})$ $1s(a_{2g}) \rightarrow \pi_{\perp}^*(a_{1u})$ $1s(b_{1g}) \rightarrow \pi_{\perp}^*(b_{2u})$ $1s(b_{2g}) \rightarrow \pi_{\perp}^*(b_{1u})$ $1s(e_u) \rightarrow \pi_{\perp}^*(e_g)$	$1s(e_u) \rightarrow$ SOMO[a]
C^{m}-based	$1s(a_{1g}) \rightarrow \pi_{\perp}^*(a_{2u})$ $1s(b_{2g}) \rightarrow \pi_{\perp}^*(b_{1u})$ $1s(e_u) \rightarrow \pi_{\perp}^*(e_g)$	
$C^{Ph(\perp)}$-based $F^{\perp}$	$1s(e_g) \rightarrow \pi_{\parallel}^*(e_u)$ $1s(e_u) \rightarrow \pi_{\parallel}^*(e_g)$	$1s(a_{1g}) \rightarrow \pi_{\parallel}^*(e_u)$ $1s(b_{2g}) \rightarrow \pi_{\parallel}^*(e_u)$ $1s(e_g) \rightarrow \pi_{\parallel}^*(a_{1u})$ $1s(e_g) \rightarrow \pi_{\parallel}^*(b_{2u})$ $1s(a_{2u}) \rightarrow \pi_{\parallel}^*(e_g)$ $1s(b_{1u}) \rightarrow \pi_{\parallel}^*(e_g)$ $1s(e_u) \rightarrow \pi_{\parallel}^*(a_{2g})$ $1s(e_u) \rightarrow \pi_{\parallel}^*(b_{1g})$
$C^{Ph(\parallel)}$-based $F^{\parallel}$	$1s(e_u) \rightarrow \pi_{\parallel}^*(e_g)$	$1s(a_{1g}) \rightarrow \pi_{\parallel}^*(e_u)$ $1s(b_{2g}) \rightarrow \pi_{\parallel}^*(e_u)$ $1s(e_u) \rightarrow \pi_{\parallel}^*(b_{1g})$ $1s(e_u) \rightarrow \pi_{\parallel}^*(a_{2g})$
N-based	$1s(a_{1g}) \rightarrow \pi_{\perp}^*(a_{2u})$ $1s(b_{1g}) \rightarrow \pi_{\perp}^*(b_{2u})$ $1s(e_u) \rightarrow \pi_{\perp}^*(e_g)$	$1s(e_u) \rightarrow$ SOMO[a]

[a]Both the C-based and N-based 1s → SOMO transitions have a 1s → σ* character.

Table S3-ESI. *EE*s (eV) and oscillator strengths *f* for the $1s^C$ excitation spectrum of CuTPP from spin-unrestricted SR ZORA TD-DFT calculations. Only excitations lying at *EE* lower than 290 eV and contributions > 10% are reported.[a,b]

N	Atom	sym	*EE*	isos	fsos	f ($\times 10^3$)	Assignment
1	$C^{Py(\beta)}$	e_u	280.28	$10e_u^{\downarrow}$	$12b_{1g}^{(100)}$	1.07	
2	$C^{Py(\beta)}$	a_{2u}	281.41	$11e_u^{\downarrow}+11e_u^{\uparrow}+10e_u^{\downarrow}$	$13e_g^{(50)}+13e_g^{(31)}+13e_g^{(12)}$	34.2	**A** ($\pi_\perp$*)
3	C^{m}	a_{2u}	281.99	$5e_u^{\downarrow}+5e_u^{\uparrow}$	$13e_g^{(66)}+13e_g^{(34)}$	17.1	**A** ($\pi_\perp$*)
4	$C^{Py(\alpha)}$	a_{2u}	282.44	$4e_u^{\downarrow}+4e_u^{\uparrow}$	$13e_g^{(60)}+13e_g^{(36)}$	33.1	**A** ($\pi_\perp$*)
5	$C^{Py(\beta)}$	a_{2u}	282.66	$7b_{2g}^{\downarrow}+7b_{2g}^{\uparrow}$	$9b_{1u}^{(53)}+9b_{1u}^{(47)}$	40.5	**A** ($\pi_\perp$*)
6	C^{m}	a_{2u}	283.20	$2b_{2g}^{\downarrow}+2b_{2g}^{\uparrow}$	$9b_{1u}^{(59)}+9b_{1u}^{(41)}$	12.2	**B** ($\pi_\perp$*)
7	$C_{\parallel}^{Ph}$	e_u	283.42	$9e_u^{\downarrow}+9e_u^{\uparrow}+9a_{1g}^{\downarrow}+6b_{2g}^{\downarrow}+9a_{1g}^{\uparrow}+6b_{2g}^{\uparrow}$	$9a_{2g}^{(17)}+9a_{2g}^{(17)}+32e_u^{(12)}+32e_u^{(12)}+32e_u^{(12)}+32e_u^{(12)}$	52.2	**B** ($\pi_{\parallel}$*-$^2e_{2u}$)
8	$C_{\perp}^{Ph}$	e_u	283.44	$1b_{1u}^{\downarrow}+2a_{2u}^{\downarrow}+1b_{1u}^{\uparrow}+2a_{2u}^{\uparrow}$	$14e_g^{(11)}+14e_g^{(11)}+14e_g^{(11)}+14e_g^{(11)}$	46.5	**B** ($\pi_\perp$*-$^1e_{2u}$)
9	$C_{\perp}^{Ph}$	e_u	283.45	$2b_{1u}^{\downarrow}+3a_{2u}^{\downarrow}+2b_{1u}^{\uparrow}+3a_{2u}^{\uparrow}$	$14e_g^{(9)}+14e_g^{(9)}+14e_g^{(9)}+14e_g^{(9)}$	167.0[c]	**B** ($\pi_\perp$*-$^1e_{2u}$)
10	$C_{\parallel}^{Ph}$	e_u	283.77	$6e_u^{\downarrow}+6e_u^{\uparrow}+3b_{2g}^{\downarrow}+6a_{1g}^{\downarrow}+3b_{2g}^{\uparrow}+6a_{1g}^{\uparrow}+6e_u^{\downarrow}+6e_u^{\uparrow}$	$9a_{2g}^{(16)}+9a_{2g}^{(16)}+32e_u^{(12)}+32e_u^{(12)}+32e_u^{(12)}+32e_u^{(12)}+13b_{1g}^{(10)}+13b_{1g}^{(10)}$	49.9	**B** ($\pi_{\parallel}$*-$^2e_{2u}$)
11	$C^{Py(\beta)}$	a_{2u}	284.75	$11e_u^{\downarrow}+11e_u^{\uparrow}$	$15e_g^{(47)}+15e_g^{(37)}$	51.0	**C'** ($\pi_\perp$*)
12	$C^{Py(\beta)}$	a_{2u}	285.14	$2a_{2g}^{\downarrow}+2a_{2g}^{\uparrow}$	$4a_{1u}^{(48)}+4a_{1u}^{(44)}$	80.5	**C** ($\pi_\perp$*)
13	$C^{Py(\alpha)}$	a_{2u}	285.32	$2b_{1g}^{\downarrow}+2b_{1g}^{\uparrow}$	$5b_{2u}^{(69)}+5b_{2u}^{(28)}$	25.5	**C** ($\pi_\perp$*)
14	$C^{Py(\alpha)}$	a_{2u}	285.76	$4e_u^{\downarrow}+4e_u^{\uparrow}$	$15e_g^{(53)}+15e_g^{(39)}$	45.6	**C** ($\pi_\perp$*)
15	$C^{Py(\beta)}$	a_{2u}	285.91	$7b_{2g}^{\downarrow}+7b_{2g}^{\uparrow}$	$11b_{1u}^{(54)}+11b_{1u}^{(40)}$	18.6	**C** ($\pi_\perp$*)
16	$C^{Py(\alpha)}$	a_{2u}	286.09	$1a_{2g}^{\downarrow}+1a_{2g}^{\uparrow}$	$4a_{1u}^{(51)}+4a_{1u}^{(44)}$	24.7	**C** ($\pi_\perp$*)
17	$C_{\perp}^{Ph}$	a_{2u}	286.12	$4b_{2g}^{\downarrow}+7e_u^{\uparrow}+7e_u^{\downarrow}$	$10b_{1u}^{(15)}+16e_g^{(27)}+16e_g^{(25)}$	14.8	**C** (σ*)
18	$C_{\perp}^{Ph}$	a_{2u}	286.19	$4b_{2g}^{\downarrow}+4b_{2g}^{\uparrow}$	$11b_{1u}^{(43)}+11b_{1u}^{(40)}$	24.2	**C** ($\pi_\perp$*)
19	$C^{Py(\beta)}$	a_{2u}	286.20	$11e_u^{\downarrow}+10e_u^{\downarrow}+11e_u^{\uparrow}$	$17e_g^{(42)}+17e_g^{(34)}+17e_g^{(18)}$	19.5	**C** ($\pi_\perp$*)
20	$C^{Py(\alpha)}$	a_{2u}	286.38	$4a_{1g}^{\downarrow}+4a_{1g}^{\uparrow}$	$13a_{2u}^{(68)}+13a_{2u}^{(29)}$	26.9	**C** ($\pi_\perp$*)
21	C^{m}	a_{2u}	286.78	$5e_u^{\downarrow}+5e_u^{\uparrow}$	$17e_g^{(70)}+17e_g^{(29)}$	16.9	**D** ($\pi_\perp$*)
22	$C_{\parallel}^{Ph}$	e_u	286.85	$6b_{2g}^{\uparrow}+9a_{1g}^{\uparrow}+6b_{2g}^{\downarrow}+9a_{1g}^{\downarrow}$	$37e_u^{(17)}+37e_u^{(17)}+37e_u^{(16)}+37e_u^{(16)}$	11.6	**D** (σ*)
23	$C^{Py(\alpha)}$	a_{2u}	286.93	$1b_{2g}^{\downarrow}+1b_{2g}^{\uparrow}$	$11b_{1u}^{(47)}+11b_{1u}^{(42)}$	23.5	**D** ($\pi_\perp$*)
24	$C^{Py(\alpha)}$	a_{2u}	287.33	$3e_u^{\downarrow}+3e_u^{\uparrow}$	$17e_g^{(51)}+17e_g^{(42)}$	123.0	**D** ($\pi_\perp$*)
25	$C^{Py(\alpha)}$	a_{2u}	287.86	$3e_u^{\downarrow}+3e_u^{\uparrow}$	$18e_g^{(57)}+18e_g^{(40)}$	16.9	**D** ($\pi_\perp$*)
26	$C^{Py(\alpha)}$	a_{2u}	288.13	$4a_{1g}^{\downarrow}+4a_{1g}^{\uparrow}$	$16a_{2u}^{(89)}+16a_{2u}^{(10)}$	10.6	**D** ($\pi_\perp$*)

[a]The lowest lying transition herein reported has a $f^C = 1.1 \times 10^{-3}$; nevertheless, it has been included because it is the only transition having a $1s^C \rightarrow 3d^{Cu}$ character.
[b]The fso character is reported in parenthesis.
[c]All the contributions are < 10%; those reported are the largest ones.

Table S4-ESI. *EE*s (eV) and oscillator strengths *f* for the $1s^C$ excitation spectrum of CuTPP(F) from spin-unrestricted SR ZORA TD-DFT calculations. Only excitations lying at *EE* lower than 290 eV and contributions > 10% are reported.[a,b]

N	Atom	sym	*EE*	*iso*s	*fso*s	f ($\times 10^3$)	Assignment	
1	$C^{Py(\beta)}$	e_u	280.26	$13e_u^{\downarrow}$	$15b_{1g}^{(100)}$	1.05		
2	$C^{Py(\beta)}$	a_{2u}	281.33	$14e_u^{\downarrow}+14e_u^{\uparrow}+13e_u^{\downarrow}$	$22e_g^{(50)}+22e_g^{(31)}+22e_g^{(12)}$	34.3	**A**	($\pi_\perp$*)
3	C^{m}	a_{2u}	282.29	$12e_u^{\downarrow}+12e_u^{\uparrow}$	$22e_g^{(55)}+22e_g^{(44)}$	42.2	**A'+B'**	($\pi_\perp$*)
4	$C^{Py(\alpha)}$	a_{2u}	282.46	$11e_u^{\downarrow}+11e_u^{\uparrow}$	$22e_g^{(56)}+22e_g^{(36)}$	36.3	**A'+B'**	($\pi_\perp$*)
5	$C^{Py(\beta)}$	a_{2u}	282.58	$10b_{2g}^{\downarrow}+10b_{2g}^{\uparrow}+3b_{1g}^{\uparrow}+3b_{1g}^{\downarrow}$	$16b_{1u}^{(35)}+16b_{1u}^{(31)}+6b_{2u}^{(16)}+6b_{2u}^{(11)}$	22.4	**B'+B**	($\pi_\perp$* + $\pi_{\|\|}$*-$^1e_{2u}$)
6	C^{m}	a_{2u}	283.48	$9b_{2g}^{\downarrow}+9b_{2g}^{\uparrow}+12e_u^{\uparrow}+12e_u^{\downarrow}$	$16b_{1u}^{(41)}+16b_{1u}^{(37)}+23e_g^{(12)}+23e_g^{(10)}$	21.3	**B'+B**	($\pi_\perp$* + $\pi_{\|\|}$*-$^1e_{2u}$)
7	C^{m}	a_{2u}	283.51	$12e_u^{\downarrow}+12e_u^{\uparrow}+9b_{2g}^{\downarrow}+9b_{2g}^{\uparrow}$	$23e_g^{(46)}+23e_g^{(32)}+16b_{1u}^{(11)}+16b_{1u}^{(10)}$	11.0	**B'+B**	($\pi_{\|\|}$*-$^1e_{2u}$ + $\pi_\perp$*)
8	$C_{\|\|}^{Ph}$	e_u	284.16	$9e_u^{\downarrow}+9e_u^{\uparrow}+7b_{2g}^{\downarrow}+10a_{1g}^{\downarrow}+7b_{2g}^{\uparrow}+10a_{1g}^{\uparrow}+9e_u^{\downarrow}+9e_u^{\uparrow}$	$12a_{2g}^{(16)}+12a_{2g}^{(16)}+43e_u^{(12)}+43e_u^{(12)}+43e_u^{(12)}+43e_u^{(12)}+16b_{1g}^{(10)}+16b_{1g}^{(10)}$	50.6	**C'**	($\pi_{\|\|}$*-$^2e_{2u}$)
9	$C^{Py(\beta)}$	a_{2u}	284.72	$14e_u^{\downarrow}+14e_u^{\uparrow}+10b_{2g}^{\uparrow}$	$24e_g^{(38)}+24e_g^{(32)}+17b_{1u}^{(11)}$	29.6	**C'**	($\pi_\perp$* + σ*)
10	$C^{Py(\beta)}$	a_{2u}	284.76	$10b_{2g}^{\downarrow}+10b_{2g}^{\uparrow}$	$17b_{1u}^{(46)}+17b_{1u}^{(36)}$	14.4	**C'**	(σ* + $\pi_\perp$*)
11	$C^{Py(\beta)}$	a_{2u}	285.15	$2a_{2g}^{\downarrow}+2a_{2g}^{\uparrow}$	$6a_{1u}^{(48)}+6a_{1u}^{(44)}$	86.6	**C**	($\pi_\perp$*)
12	$C^{Py(\alpha)}$	a_{2u}	285.41	$2b_{1g}^{\downarrow}+2b_{1g}^{\uparrow}$	$7b_{2u}^{(69)}+7b_{2u}^{(28)}$	24.8	**C**	($\pi_\perp$*)
13	$C^{Py(\alpha)}$	a_{2u}	285.80	$11e_u^{\downarrow}+11e_u^{\uparrow}$	$24e_g^{(47)}+24e_g^{(37)}$	16.6	**C**	($\pi_\perp$*)
14	$C^{Py(\alpha)}$	a_{2u}	286.01	$11e_u^{\downarrow}+10e_u^{\downarrow}+10e_u^{\uparrow}+11e_u^{\uparrow}$	$25e_g^{(28)}+25e_g^{(22)}+25e_g^{(17)}+25e_g^{(17)}$	29.6	**C**	(σ* + $\pi_\perp$*)
15	$C_{\|\|}^{Ph}$	e_u	286.13	$6e_u^{\downarrow}+6e_u^{\uparrow}+4b_{2g}^{\downarrow}+7a_{1g}^{\downarrow}+4b_{2g}^{\uparrow}+7a_{1g}^{\uparrow}+6e_u^{\downarrow}+6e_u^{\uparrow}$	$12a_{2g}^{(16)}+12a_{2g}^{(16)}+43e_u^{(12)}+43e_u^{(12)}+43e_u^{(12)}+43e_u^{(12)}+16b_{1g}^{(10)}+16b_{1g}^{(10)}$	48.0	**C**	($\pi_{\|\|}$*-$^2e_{2u}$)
16	$C^{Py(\beta)}$	a_{2u}	286.15	$10b_{2g}^{\downarrow}+10b_{2g}^{\uparrow}$	$18b_{1u}^{(55)}+18b_{1u}^{(42)}$	19.3	**C**	($\pi_\perp$* + σ*)
17	$C_{\perp}^{Ph}$	e_u	286.16	$4b_{1u}^{\downarrow}+5a_{2u}^{\downarrow}+4b_{1u}^{\uparrow}+5a_{2u}^{\uparrow}+4e_g^{\uparrow}+4e_g^{\downarrow}+4e_g^{\uparrow}+4e_g^{\downarrow}$	$23e_g^{(12)}+23e_g^{(12)}+23e_g^{(12)}+23e_g^{(12)}+5a_{1u}^{(11)}+5a_{1u}^{(11)}+6b_{2u}^{(10)}+6b_{2u}^{(10)}$	119.0	**C**	($\pi_{\|\|}$*-$^1e_{2u}$)
18	$C_{\perp}^{Ph}$	e_u	286.17	$8a_{1g}^{\uparrow}+5b_{2g}^{\uparrow}+8a_{1g}^{\downarrow}+5b_{2g}^{\downarrow}$	$44e_u^{(17)}+44e_u^{(17)}+44e_u^{(14)}+44e_u^{(14)}$	26.7	**C**	(σ*)
19	$C_{\perp}^{Ph}$	e_u	286.18	$5b_{2g}^{\downarrow}+8a_{1g}^{\downarrow}$	$44e_u^{(10)}+44e_u^{(10)}$	49.3	**C**	(σ*)
20	$C^{Py(\alpha)}$	a_{2u}	286.21	$1a_{2g}^{\downarrow}+1a_{2g}^{\uparrow}$	$6a_{1u}^{(49)}+6a_{1u}^{(43)}$	44.5	**C**	($\pi_\perp$*)
21	$C_{\perp}^{Ph}$	a_{2u}	286.26	$3b_{1u}^{\downarrow}+3b_{1u}^{\uparrow}+3e_g^{\downarrow}+3e_g^{\uparrow}$	$28b_{2g}^{(21)}+28b_{2g}^{(21)}+44e_u^{(23)}+44e_u^{(23)}$	30.9	**C**	(σ*)
22	$C_{\|\|}^{Ph}$	e_u	286.38	$6e_u^{\downarrow}+6e_u^{\uparrow}+4b_{2g}^{\downarrow}+7a_{1g}^{\downarrow}+4b_{2g}^{\uparrow}+7a_{1g}^{\uparrow}$	$28b_{2g}^{(19)}+28b_{2g}^{(19)}+44e_u^{(12)}+44e_u^{(12)}+44e_u^{(12)}+44e_u^{(12)}$	13.7	**C**	(σ*)
23	$C^{Py(\beta)}$	a_{2u}	286.39	$14e_u^{\downarrow}+14e_u^{\uparrow}+13e_u^{\downarrow}$	$26e_g^{(43)}+26e_g^{(24)}+26e_g^{(22)}$	37.4	**C**	($\pi_\perp$*)
24	$C^{Py(\alpha)}$	a_{2u}	286.77	$11a_{1g}^{\downarrow}+11a_{1g}^{\uparrow}$	$21a_{2u}^{(70)}+21a_{2u}^{(28)}$	23.3	**D**	($\pi_\perp$* + σ*)
25	$C^{Py(\alpha)}$	a_{2u}	287.27	$8b_{2g}^{\downarrow}+8b_{2g}^{\uparrow}$	$18b_{1u}^{(49)}+18b_{1u}^{(44)}$	16.7	**D**	($\pi_\perp$* + σ*)
26	C^{m}	a_{2u}	287.35	$12e_u^{\downarrow}+12e_u^{\uparrow}$	$26e_g^{(52)}+26e_g^{(41)}$	53.9	**D**	($\pi_\perp$*)
27	$C^{Py(\alpha)}$	a_{2u}	287.61	$10e_u^{\downarrow}+10e_u^{\uparrow}$	$26e_g^{(50)}+26e_g^{(41)}$	134.0	**D**	($\pi_\perp$*)
28	C^{m}	a_{2u}	287.81	$12a_{1g}^{\downarrow}+12a_{1g}^{\uparrow}$	$22a_{2u}^{(69)}+22a_{2u}^{(29)}$	14.0	**D**	($\pi_\perp$* + σ*)
29	$C_{\|\|}^{Ph}$	e_u	287.83	$9e_u^{\downarrow}+9e_u^{\uparrow}+9e_u^{\uparrow}+9e_u^{\downarrow}$	$13a_{2g}^{(19)}+13a_{2g}^{(19)}+18b_{1g}^{(11)}+18b_{1g}^{(11)}$	28.9	**D**	(σ*)
30	$C_{\perp}^{Ph}$	a_{2u}	288.21	$8e_u^{\downarrow}+8e_u^{\uparrow}$	$25e_g^{(49)}+25e_g^{(40)}$	29.5	**D**	(σ* + $\pi_\perp$*)
31	$C_{\perp}^{Ph}$	a_{2u}	288.27	$7e_u^{\downarrow}+7e_u^{\uparrow}$	$25e_g^{(48)}+25e_g^{(40)}$	55.9	**D**	(σ*+$\pi_\perp$*)
32	$C_{\|\|}^{Ph}$	e_u	289.82	$6e_u^{\downarrow}+6e_u^{\uparrow}+6e_u^{\downarrow}+6e_u^{\uparrow}$	$13a_{2g}^{(15)}+13a_{2g}^{(15)}+18b_{1g}^{(13)}+18b_{1g}^{(13)}$	25.6	**D**	(σ*)

[a]The fso character is reported in parenthesis.
[b]The lowest lying transition has a $f^C = 1.05 \times 10^{-3}$; nevertheless, it has been herein included because it is the only transition having a $1s^C \rightarrow 3d^{Cu}$ character.

Table S5-ESI. *EE*s (eV) and oscillator strengths *f* for the $1s^N$ excitation spectrum of CuTPP from spin-unrestricted SR ZORA TD-DFT calculations. Only excitations up to *EE* 400 eV and contributions > 10% are reported.[a,b]

N	sym	*EE*	isos	fsos	$f(\times 10^3)$	Assignment
1	e_u	394.18	$2e_u^{\downarrow}$	$12b_{1g}^{(100)}$	9.0	**A** ($^{Cu}\sigma^*$)
2	a_{2u}	395.29	$2e_u^{\downarrow}+2e_u^{\uparrow}$	$13e_g^{(72)}+13e_g^{(28)}$	17.7	**A** ($^{pmc}\pi_{\perp}^*$)
3	a_{2u}	398.18	$1b_{1g}^{\downarrow}+1b_{1g}^{\uparrow}$	$5b_{2u}^{(71)}+5b_{2u}^{(26)}$	20.2	**C** ($^{pmc}\pi_{\perp}^*$)
4	a_{2u}	398.59	$2e_u^{\downarrow}+2e_u^{\uparrow}$	$15e_g^{(71)}+15e_g^{(26)}$	21.5	**C** ($^{pmc}\pi_{\perp}^*$)

[a]The fso character is reported in parenthesis.
[b]The lowest lying transition herein reported has a $f^N < 10 \times 10^{-3}$, nevertheless it has been included because it is the only one having a $1s^N \rightarrow \sigma^*$ character.

Table S6-ESI. *EE*s (eV) and oscillator strengths *f* for the $1s^N$ excitation spectrum of CuTPP(F) from spin-unrestricted SR ZORA TD-DFT calculations. Only excitations up to *EE* 400 eV and contributions > 10% are reported.[a,b]

N	sym	*EE*	isos	fsos	$f(\times 10^3)$	Assignment
1	e_u	394.20	$5e_u^{\downarrow}$	$15b_{1g}^{(100)}$	9.0	**A** ($^{Cu}\sigma^*$)
2	a_{2u}	395.22	$5e_u^{\uparrow}+5e_u^{\downarrow}$	$22e_g^{(73)}+22e_g^{(27)}$	16.6	**A** ($^{pmc}\pi_{\perp}^*$)
3	a_{2u}	398.19	$1b_{1g}^{\downarrow}+1b_{1g}^{\uparrow}$	$7b_{2u}^{(70)}+7b_{2u}^{(27)}$	20.1	**C** ($^{pmc}\pi_{\perp}^*$)
4	a_{2u}	398.82	$5e_u^{\downarrow}+5e_u^{\uparrow}$	$25e_g^{(73)}+25e_g^{(23)}$	16.2	**C** ($^{pmc}\pi_{\perp}^*+^{Ph}\sigma^*$)

[a]The fso character is reported in parenthesis.
[b]The lowest lying transition herein reported has a $f^N < 10 \times 10^{-3}$, nevertheless it has been included because it is the only one having a $1s^N \rightarrow \sigma^*$ character.

Table S7. *EE*s (eV) and oscillator strengths *f* for the $1s^F$ excitation spectrum of CuTPP(F) from spin-unrestricted SR ZORA TD-DFT calculations. Only excitations lying at *EE* lower than 685 eV and contributions > 10% are reported.[a,]

N	sym	*EE*	isos	fsos	f ($\times 10^3$)	Assignment
1	e_u	681.26	$2b_{1u}^{\downarrow}+3a_{2u}^{\downarrow}+2b_{1u}^{\uparrow}+3a_{2u}^{\uparrow}+2e_g^{\uparrow}+2e_g^{\downarrow}$	$23e_g^{(15)}+23e_g^{(15)}+23e_g^{(15)}+23e_g^{(15)}+5a_{1u}^{(11)}+5a_{1u}^{(11)}$	13.2	$(\pi_{\|\|}^*\text{-}^1e_{2u})$
2	e_u	681.35	$1b_{1u}^{\downarrow}+2a_{2u}^{\downarrow}+1b_{1u}^{\uparrow}+2a_{2u}^{\uparrow}+1e_g^{\uparrow}+1e_g^{\downarrow}$	$23e_g^{(15)}+23e_g^{(15)}+23e_g^{(15)}+23e_g^{(15)}+5a_{1u}^{(11)}+5a_{1u}^{(11)}$	12.8	$(\pi_{\|\|}^*\text{-}^1e_{2u})$
3	a_{2u}	681.53	$2b_{1u}^{\downarrow}+2b_{1u}^{\uparrow}+2e_g^{\downarrow}+2e_g^{\uparrow}$	$28b_{2g}^{(19)}+28b_{2g}^{(19)}+44e_u^{(23)}+44e_u^{(23)}$	14.4	(σ^*)
4	a_{2u}	681.68	$1b_{1u}^{\downarrow}+1b_{1u}^{\uparrow}+1e_g^{\downarrow}+1e_g^{\uparrow}$	$28b_{2g}^{(17)}+28b_{2g}^{(17)}+44e_u^{(24)}+44e_u^{(24)}$	29.6	(σ^*)
5	e_u	681.81	$2e_u^{\downarrow}+2e_u^{\uparrow}+1b_{2g}^{\downarrow}+3a_{1g}^{\downarrow}+1b_{2g}^{\uparrow}+3a_{1g}$	$28b_{2g}^{(16)}+28b_{2g}^{(16)}+44e_u^{(12)}+44e_u^{(12)}+44e_u^{(12)}+44e_u^{(12)}$	12.1	(σ^*)

[a]The fso character is reported in parenthesis.