Halide Effect in Electron Rich and Deficient Discotic Phthalocyanines

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Content

1. ^{19}F-NMR of **6**

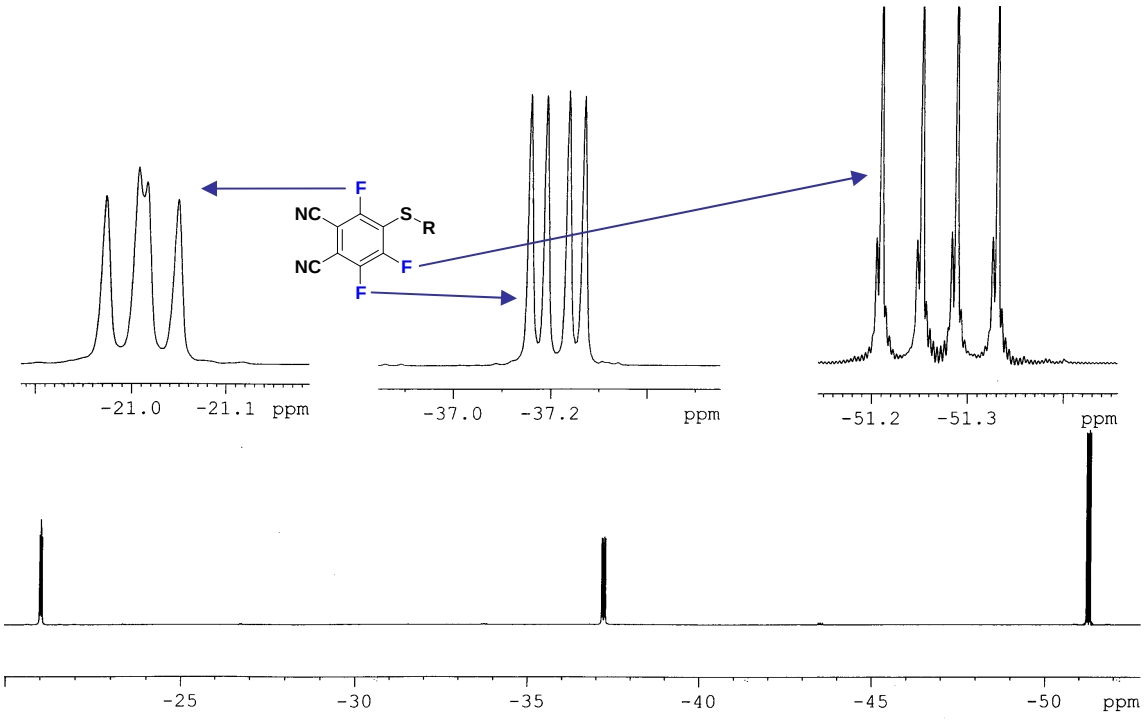


Figure SI-1. ^{19}F-NMR of **6** in $DCCl_3$

2. POM image

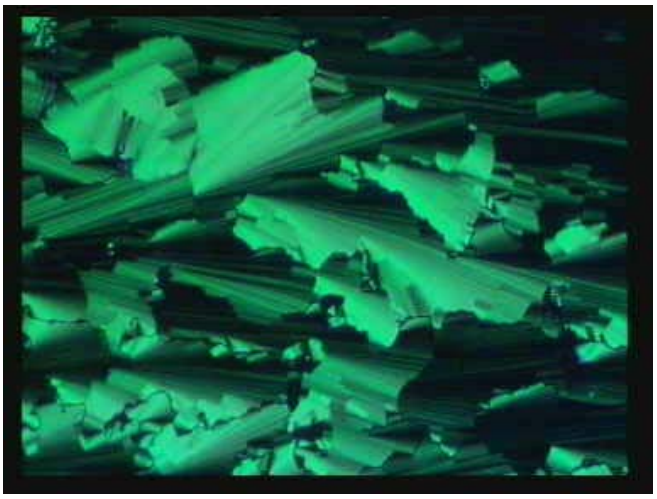


Figure SI-2. Fan-shaped texture of Pc **18** at 125 ºC (x 184, crossed polarizers)

3. TGA

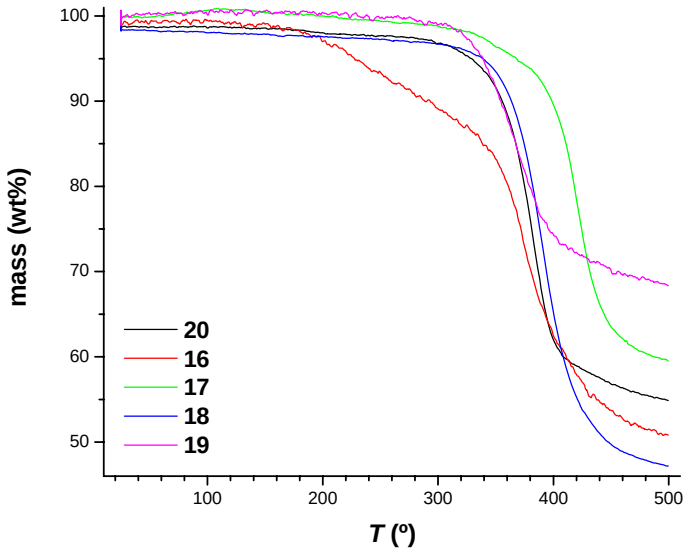


Figure SI-3. TGA of Pcs **17-21**

4. XRD tables

Table SI-1. XRD data for Pcs **17-20** at 25 ºC

Pc	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
17	21.99	VS	10		Col_H
	12.58	M	11		
	10.89	M	20		
	4.6	M			
	3.30	S			
18	21.15	VS	10		Col_H
	7.1	br			
	4.6	br			
	3..35	S			
19	19.10	VS	10		Col_H
	7.3	br			
	4.0	br			
	3.37	S			
20	21.99	VS	10		Col_H
	7.5	br			
	4.1	br			
	3.41	S			

Table SI-2. XRD data for Pc **21**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
50	21.28	VS	10		Col_H
	8.08	S	21		
	4.3	br			
	3.41	M			
100	21.70	VS	10		Col_H
	8.17	S	21		
	4.6	br			
	3.43	M			
150	21.76	VS	10		Col_H
	8.24	S	21		
	4.6	br			
	3.43	M			
200	21.95	VS	10		Col_H
	8.29	S	21		
	7.18	M	30		
	6.35	M	22		
	4.6	br			
	3.44	M			

Table SI-3. XRD data for Pc **22**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
25	17.68	VS	10		Col_H
	10.20	M	11		
	8.90	M	20		
	8.15	M			
	6.72	M			
	4.5	br			
	3.34	S			
100	17.98	VS	10		Col_H
	10.38	M	11		
	9.02	M	20		
	7.88	M			
	6.86	M			
	4.5	br			
	3.35	S			

Table SI-3. XRD data for Pc **23**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
25	18.01	VS	10		Col_H
	10.39	M	11		
	8.97	M	20		
	4.2	br			
	3.35	S			

Table SI-4. XRD data for Pc **24**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
130	21.70	VS	20	21.7	a = 43.4 Å, b = 21.63Å
	19.36	VS	11	19.36	
	10.82	M	40	10.85	
	9.61	M	22	9.68	
	8.04	S	51	8.06	
	7.13	S	13	7.11	
	6.42	M	33	6.45	
	6.00	M	43	6.00	
	4.5	br			
	3.5	M			
200	21.7	VS	20	21.7	a = 43.4 Å, b = 21.5 Å
	19.26	VS	11	19.26	
	8.03	M	51	8.05	
	7.67	M	42	7.63	
	7.06	M	13	7.06	
	4.5	br			
	3.6	M			
250	21.65	VS	20	21.65	a = 43.3 Å, b = 21.5Å
	19.26	VS	11	19.26	
	4.6	br			
	3.6	M			

Table SI-5. XRD data for Pc **25**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
25	22.74	VS	20	22.7	a = 45.48 Å, b = 23.28 Å
	20.72	VS	11	20.72	
	12.72	M	31	12.70	
	11.46	M	40	11.37	
	10.25	M	22	10.36	
	8.54	S	51	8.47	
	7.62	S	13	7.65	
	6.91	S	33	6.91	
	4.5	br			
	3.5	br			
100	22.39	VS	20		
	20.82	VS	11		
	12.74	S	31		
	11.41	S	40		
	10.29	S	22		
	8.45	M	51		
	7.66	M	13		
	6.94	M	33		
	4.6	br			
	3.5	br			

Table SI-6. XRD data for Pc **26**

T/°C	$d_{meas.}$/Å	I	*hk*	$d_{calc.}$/Å	Mesophase and parameters
100	23.85	VS	20		a = 47.7 Å, b = 25.5 Å
	22.46	VS	11		
	4.5	br			
	3.6	M			
150	23.7	VS	20	23.7	a = 47.4 Å, b = 25.0 Å
	22.13	VS	11	22.13	
	13.39	M	31	13.36	
	12.48	M	02	12.51	
	11.07	S	22	11.06	
	8.87	S	51	8.86	
	8.21	M	13	8.21	
	7.34	M	33	7.38	
	4.5	br			
	3.6	M			
200	23.7	VS	20		a = 47.4 Å, b = 25 Å
	22.07	VS	11		
	4.5	br			
	3.6	M			
250	23.6	VS	20		a = 47.2 Å, b = 24.9 Å
	22.0	VS	11		
	4.5	br			
	3.6	M			

5. UV-VIS Spectrsocopy

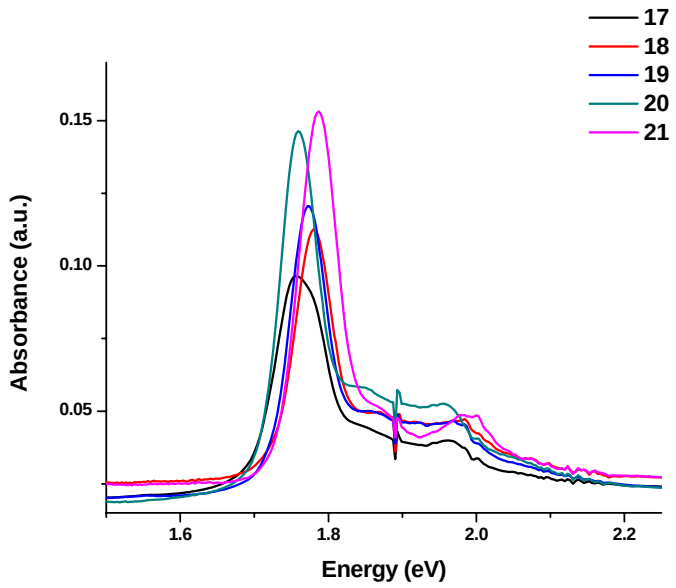


Figure SI-4. UV-VIS spectra of CuPc derivatives in pyridine solution (~10^{-6} M) plotted versus energy (eV).

6. Electrochemistry

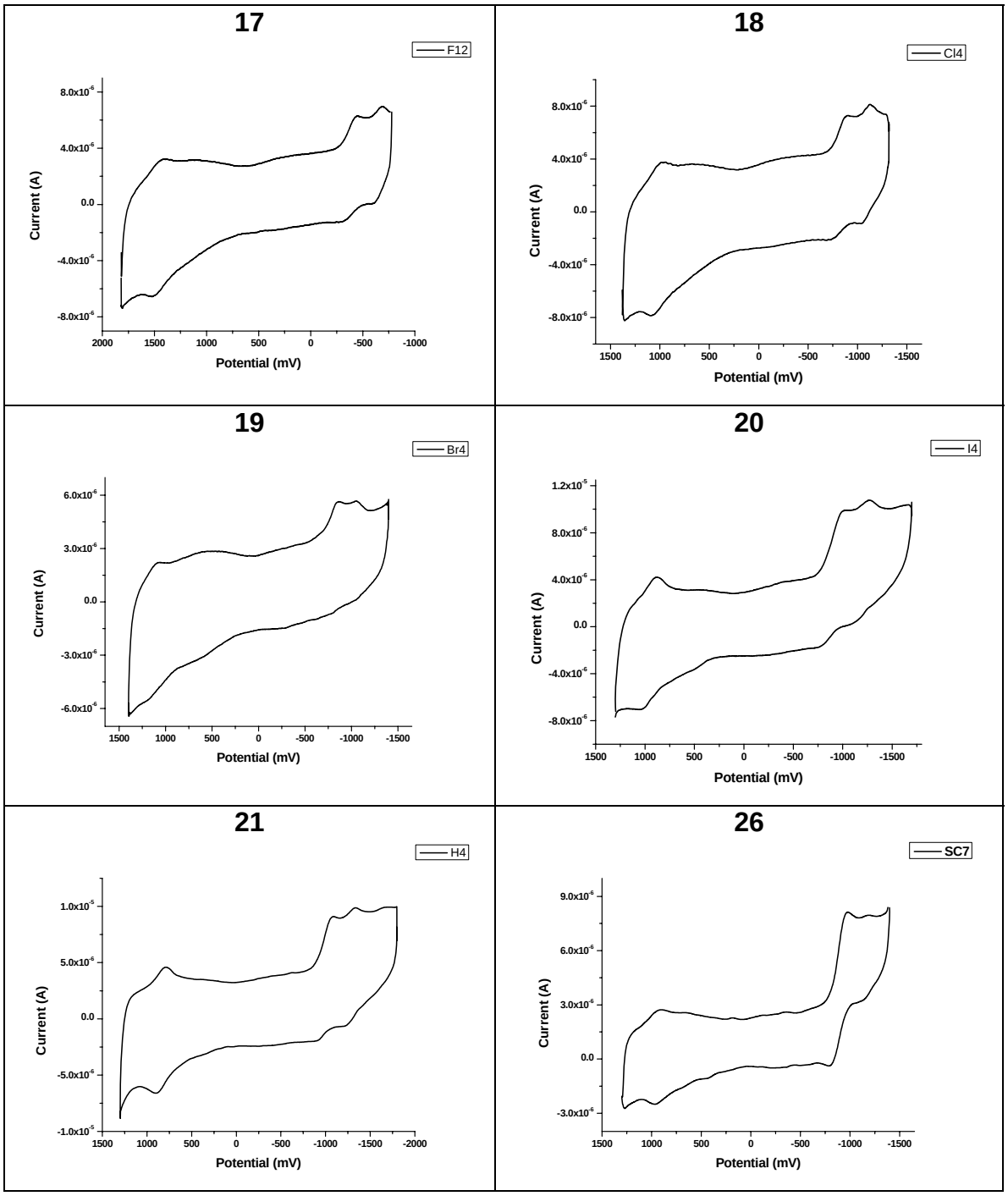


Figure SI-5. Cyclic voltammograms of compounds **17**-**21** and **26** in CH_2Cl_2

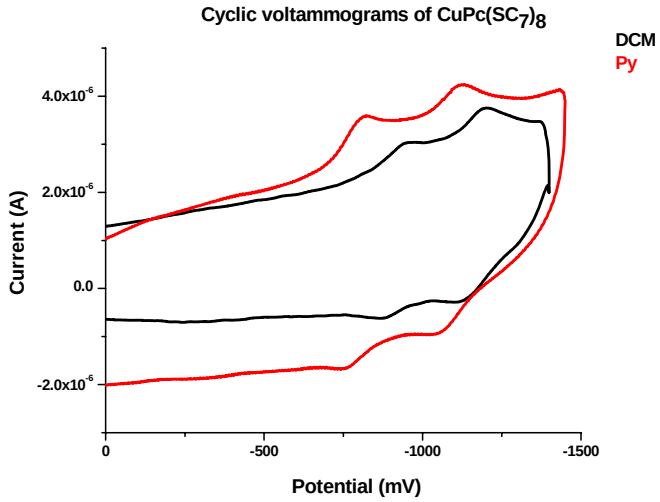
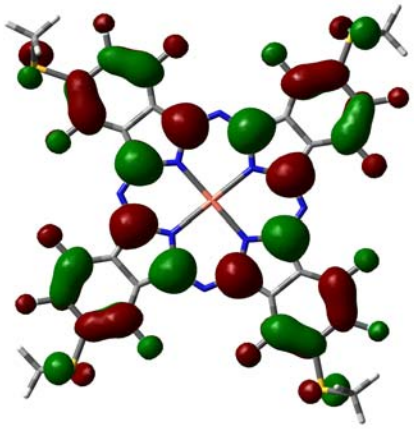
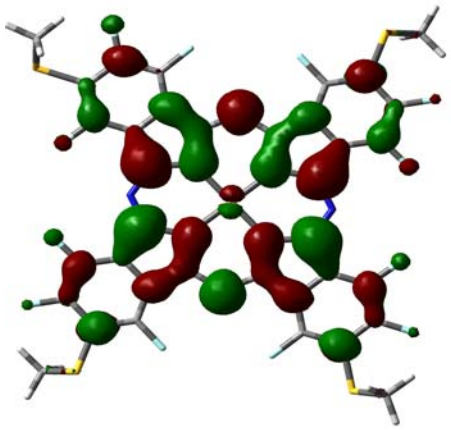
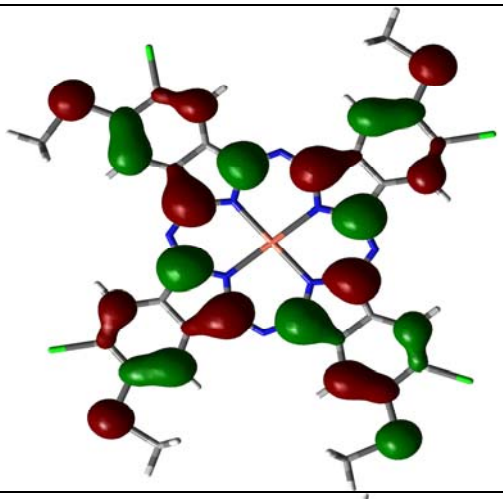
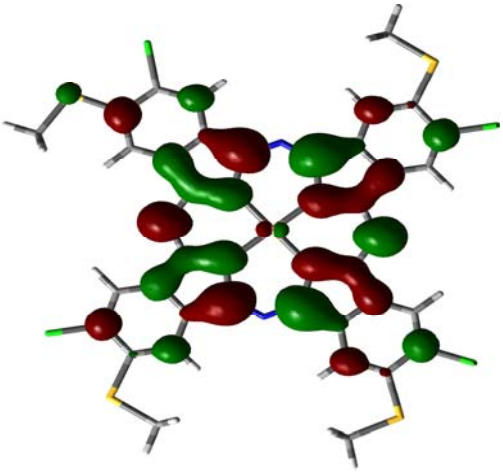
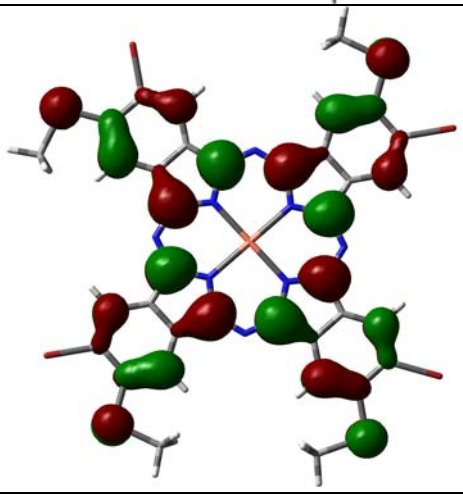
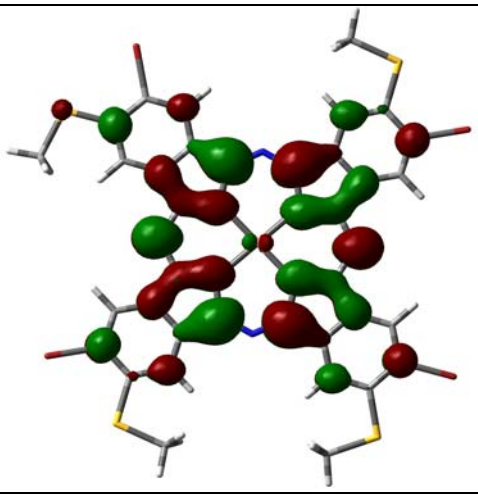


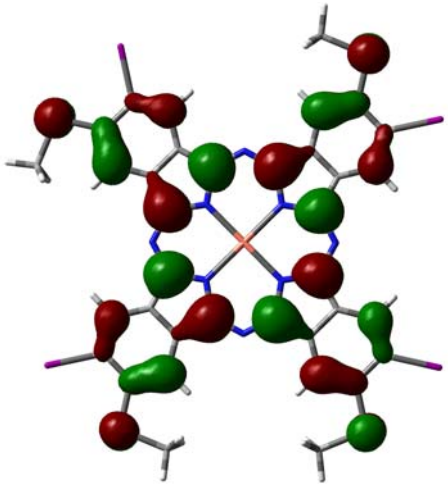
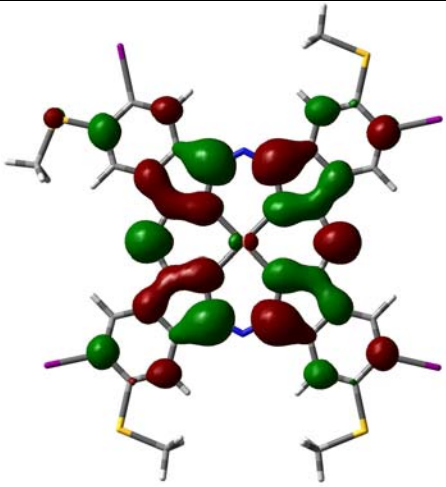
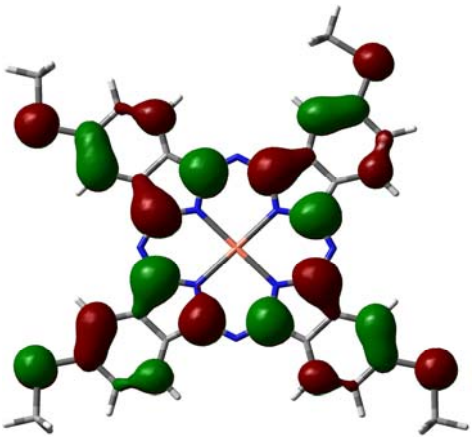
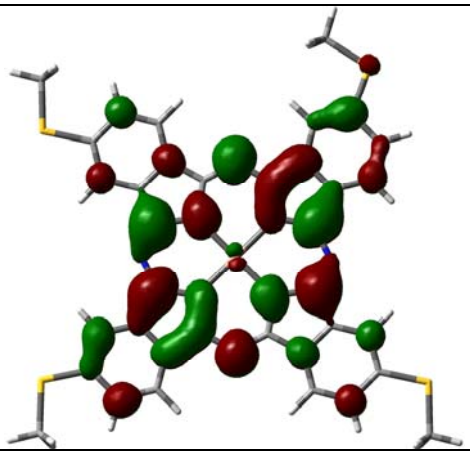
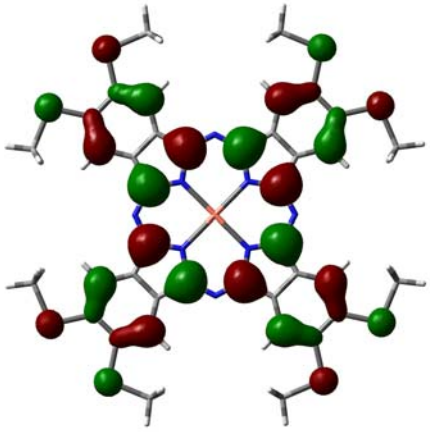
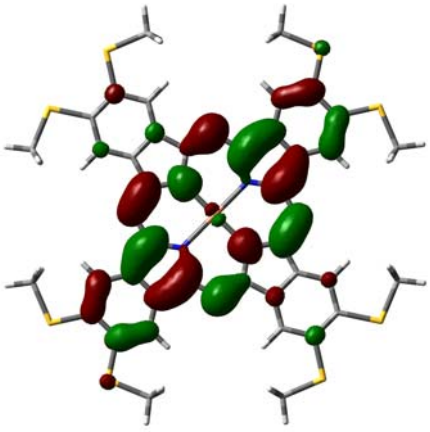
Figure SI-6. Cyclic voltammograms of compound **26** in CH_2Cl_2 (DCM) and pyridine (Py) for comparison.

7. DFT calculations in Gaussian 03 (DFT-UB3LYP-LANL2DZ)

Table SI-7. Calculated frontier orbital energies of Pcs **17**-**21**, **26**, **28**, **31**, and **32** in eV; Given are α (upper) and β (lower) values of the open shell calculations**.**

Pc	**17**	**18**	**19**	**20**	**21**	**26**	**28**	**31**	**32**
LUMO-2	-2.49 -3.83	-2.09 -3.41	-2.06 -3.38	-2.02 -3.34	-1.34 -2.77	-1.88 -3.15	-2.99 -4.46	-1.82 -2.90	-1.41 -2.83
LUMO-1	-4.07 -4.04	-3.72 -3.70	-3.68 -3.66	-3.64 -3.62	-3.04 -3.02	-3.47 -3.45	-4.65 -4.63	-3.49 -3.46	-3.12 -3.10
LUMO	-4.09 -4.07	-3.73 -3.71	-3.69 -3.67	-3.65 -3.63	-3.06 -3.04	-3.47 -3.45	-4.65 -4.63	-3.54 -3.50	-3.12 -3.10
E_{Gap}	2.06 2.10	2.15 2.19	2.15 2.19	2.14 2.17	2.07 2.11	2.16 2.20	2.16 2.19	2.20 2.21	2.21 2.24
HOMO	-6.15 -6.17	-5.88 -5.90	-5.84 -5.86	-5.79 -5.80	-5.13 -5.15	-5.63 -5.65	-6.81 -6.82	-5.74 -5.71	-5.33 -5.34
HOMO+1	-6.87 -6.88	-6.59 -6.59	-6.55 -6.55	-6.48 -6.48	-6.012 -6.00	-6.25 -6.25	-8.35 -8.33	-6.45 -6.45	-6.86 -6.97
HOMO+2	-6.88 -6.89	-6.59 -6.59	-6.55 -6.55	-6.48 -6.48	-6.02 -6.02	-6.25 -6.26	-8.35 -8.37	-6.45 -6.45	-7.02 -6.97

CuPc	HOMO	LUMO
17		
18		
19		

20		
21		
26		

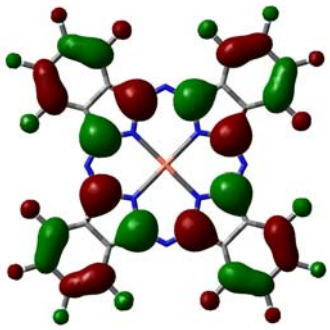
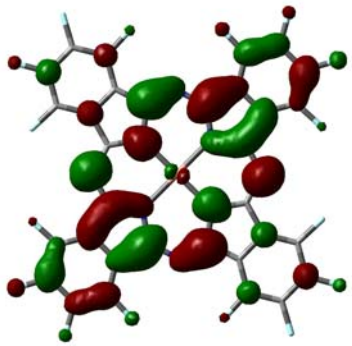
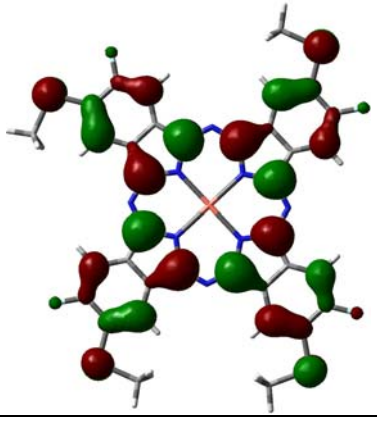
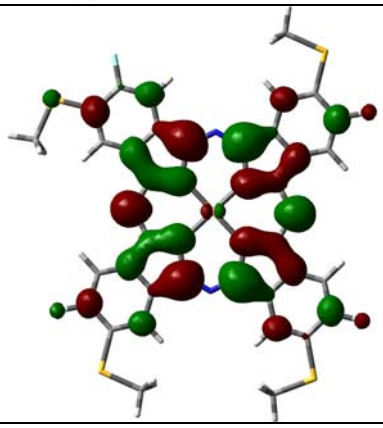
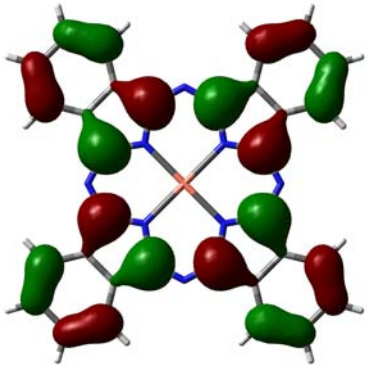
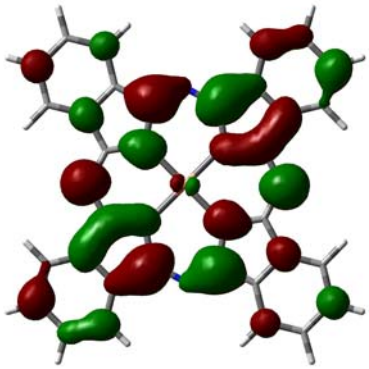
28		
31		
32		

Figure SI-7. Contributions to HOMO and LUMO orbitals when calculated by DFT-UB3LYP- LANL2DZ (alkyl groups were replaced by methyl groups).

Table SI-8. Calculated frontier orbital energies of Pcs **29** and **30** in eV

$CuPcF_8$	E_{HOMO} (eV)	E_{gap} (eV)	E_{LUMO} (eV)
29 (2,3-substitution)	-6.18/-6.15	2.23	-3.95/-3.92
30 (1,4-substitution)	-5.80/-5.77	2.15	-3.65/-3.62
Δ 29/30	0.38	0.08	0.30

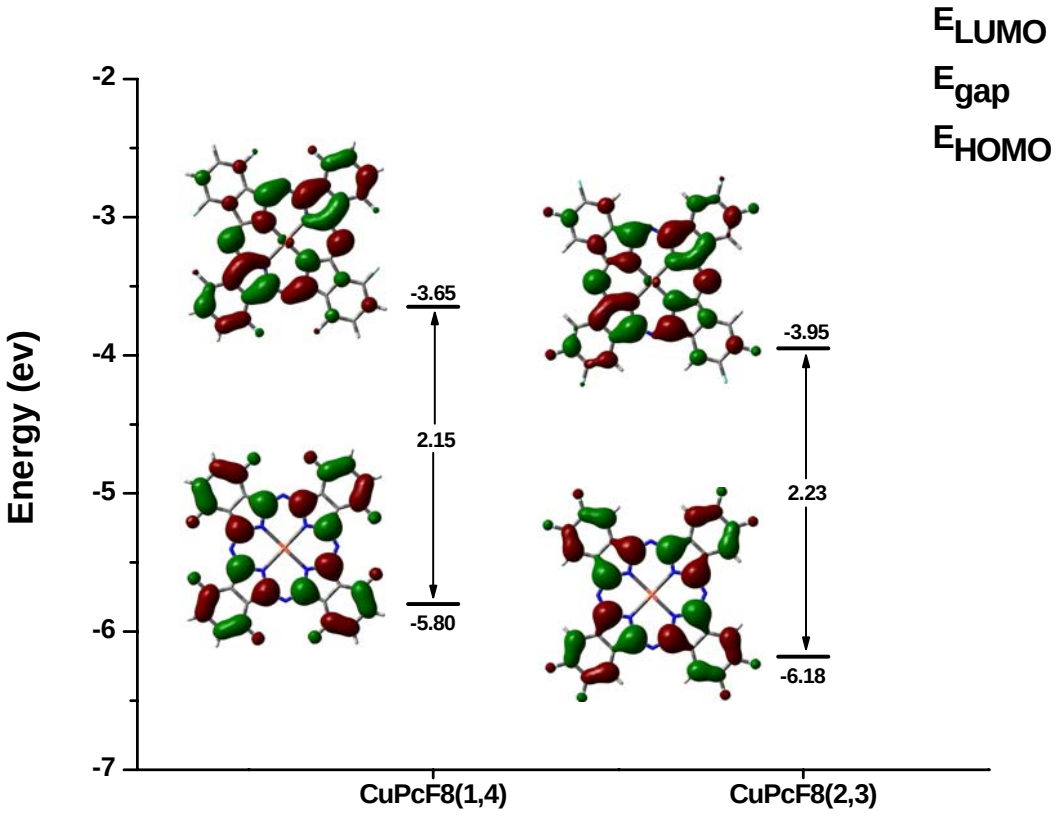
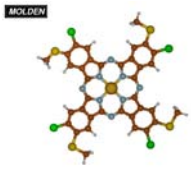
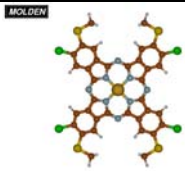
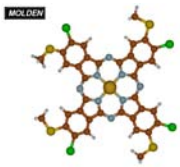


Figure SI-8. Contributions to HOMO and LUMO orbitals for **30** (left) and **29** (right).

Table SI-9. Calculated frontier orbital energies of four regio-isomers of Pc **18** (methyl for octyl groups).

$CuPc(SMe)_4Cl_4$	 **isomer-1**	 **isomer-2**	 **isomer-3**	 **isomer-4**
LUMO-2	-2.09/-3.41	-1.74/-2.83	-1.82/-2.88	-1.71/-2.83
LUMO-1	-3.72/-3.70	-3.37/-3.35	-3.54/-3.51	-3.35/-3.35
LUMO	-3.73/-3.71	-3.43/-3.40	-3.54/-3.52	-3.40/-3.37
Energy Gap	2.15/2.19	2.07/2.07	2.17/2.19	2.04/2.03
HOMO	-5.88-5.90	-5.50/-5.47	-5.71/-5.71	-5.44/-5.44
HOMO+1	-6.59/-6.59	-5.50/-5.50	-6.45/-6.45	-6.04/-6.04
HOMO+2	-6.59/-6.59	-6.37/-6.37	-6.45/-6.45	-6.17/-6.15
optimized HF energy (Hartree)	-2117.991	-2117.863	-2117.995	-2117.8321

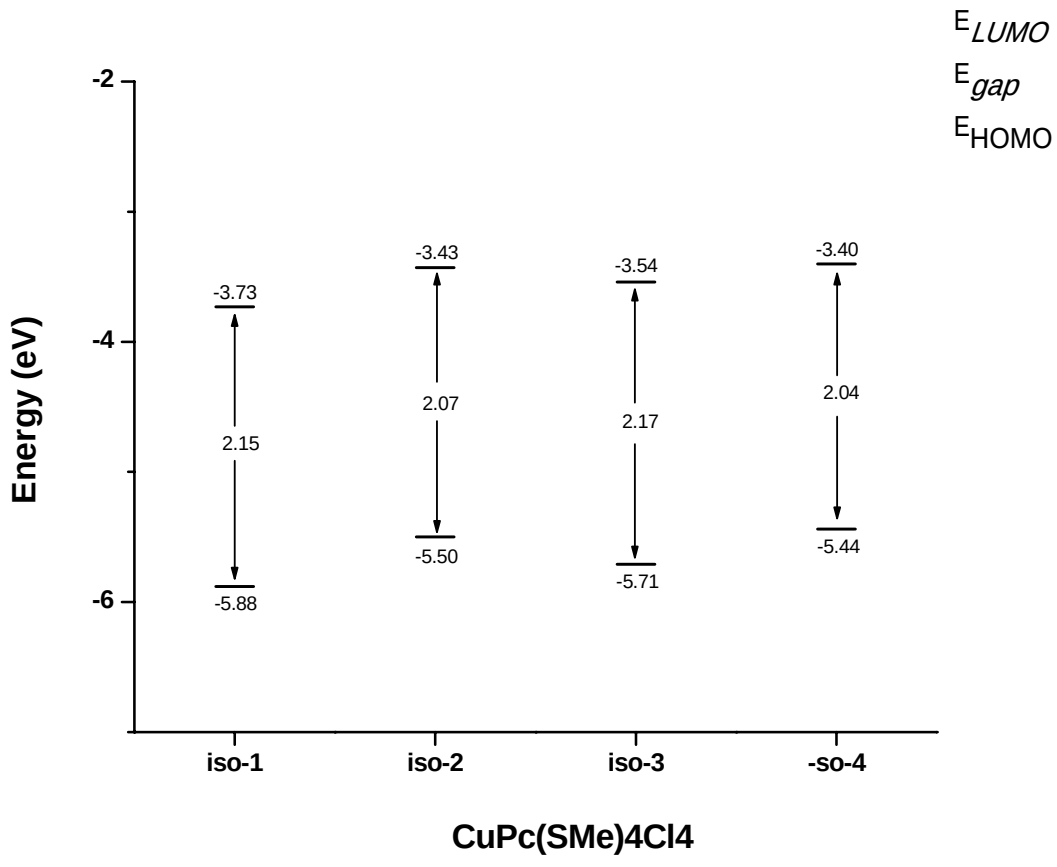


Figure SI-9. HOMO and LUMO gaps for the four different regio-isomers of Pc **18** (methyl for octyl groups).

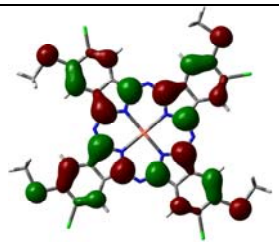
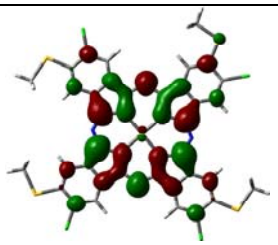
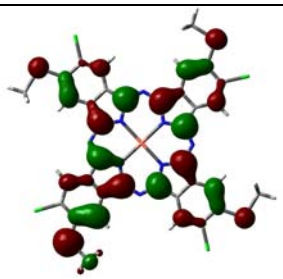
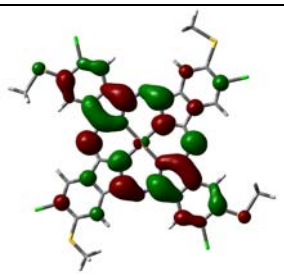
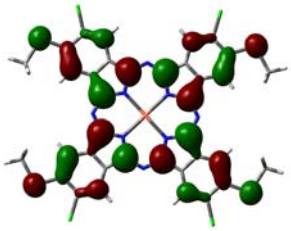
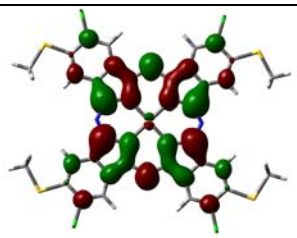
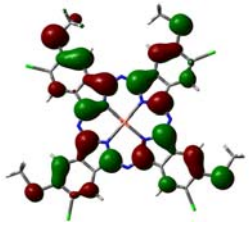
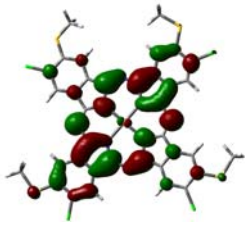
$CuPc(SMe)_4Cl_4$	HOMO	E_{gap}	LUMO
isomer-1	 -5.88	2.15	 -3.73
isomer-2	 -5.50	2.07	 -3.43
isomer-3	 -5.71	2.17	 -3.54
isomer-4	 -5.44	2.04	 -3.40

Figure SI-10. Contributions to HOMO and LUMO orbitals for the four different regio-isomers of Pc **18** (methyl for octyl groups).