CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Supplementary Material

Interfacial Behavior and Film Patterning of Redox-active Cationic Copper(II)-containing Surfactants

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Figure S1: ORTEP diagram for **2** as a loosely associated dimer in the solid state. Selected bond lengths and angles: Cu(1)–N(1) = 2.0115(8), Cu(1)–N(2) = 2.0302(8), Cu(1)–Cl(1) = 2.2496(3), Cu(1)–Cl(2) = 2.2961(3) Å; N(1)–Cu1–N(2) = 81.25(3), N(1)-Cu1-Cl(1) = 95.72(2), N(2)–Cu1–Cl(1) = 176.95(2), N(1)–Cu1–Cl(2) = 160.33(2), N(2)–Cu1–Cl(2) = 89.44(2), Cl(1)–Cu(1)–Cl(2) = 93.341(14) °.

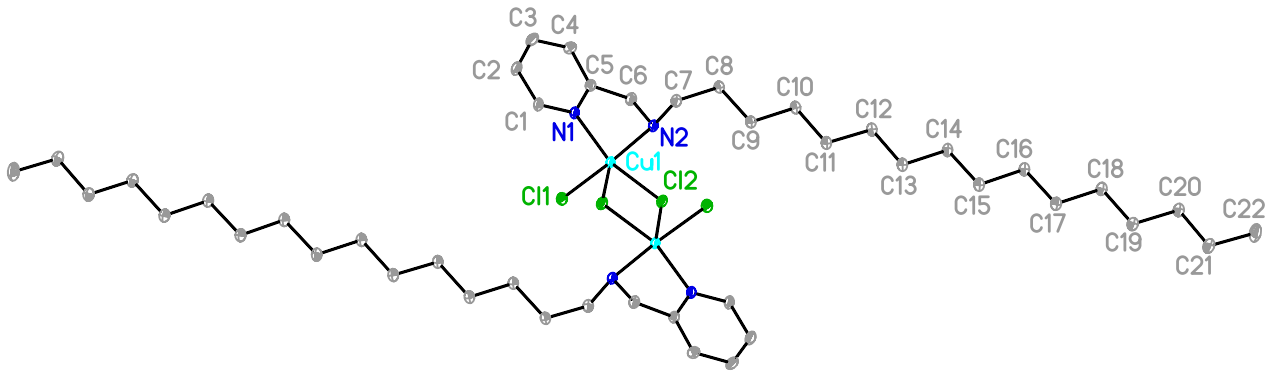


Figure S2: ORTEP diagram for **3**. Selected bond lengths and angles: Cu(1)–N(1) = 2.0074(11), Cu(1)–N(2) = 2.0325(11), Cu(1)–Cl(1) = 2.2524(3), Cu(1)–Cl(2) = 2.2911(4) Å; N(1)–Cu–N(2) = 81.20(4), N(1)-Cu-Cl(1) = 95.77(3), N(2)–Cu–Cl(1) = 176.96(4), N(1)–Cu–Cl(2) = 160.49(3), N(2)–Cu1–Cl(2) = 89.58(3), Cl(1)–Cu(1)–Cl(2) = 93.247(13) °.

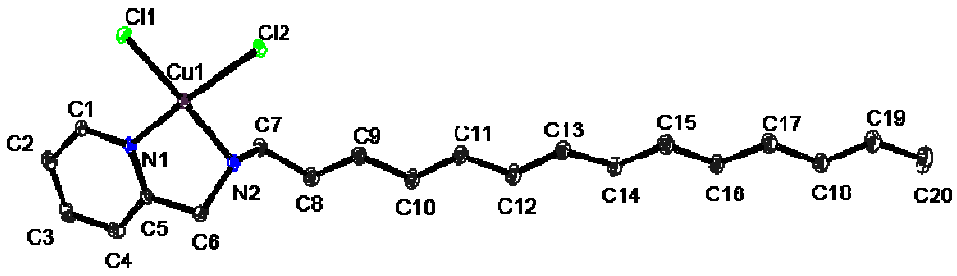


Figure S3: BAM data for $\mathbf{L^{PyC16}}$ and **2**.

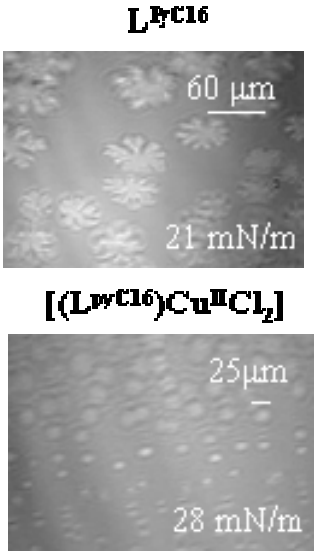
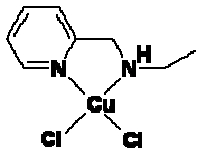


Table: Cartesian Coordinates and Energies of the Optimized Structures:
(B3LYP/6-311G(d) level of theory)

Model for 1 – 3:



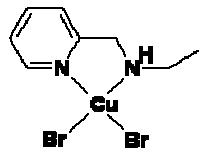
[$LCu^{II}Cl_2$]

E = -2982.548941 **a.u.**

H	0.96546600	4.04592700	1.98943900
H	-4.03239700	-2.07131000	0.71571400
H	1.66234500	1.73403200	1.44736900
H	-0.08475500	1.79558900	1.63925500
H	-1.53246800	-2.34326400	0.67841600
C	-3.39791200	-1.26444000	0.36942300
C	0.74513600	2.13600400	1.01383400
C	-2.01849400	-1.42917100	0.35806700
C	0.81213200	3.66086000	0.97830900
H	-5.00554400	0.10579600	-0.06325400
C	-3.93297300	-0.05640300	-0.06469000
Cl	0.95363800	-2.72160900	0.40832100
Cl	3.06680300	-0.16200900	-0.48625000
N	-1.19051100	-0.46056300	-0.06073700
H	-0.10263500	4.11905500	0.59332800

Cu	0.87706900	-0.55013800	-0.09601200
C	-3.07168200	0.94766200	-0.49770800
C	-1.70269500	0.70855100	-0.48658200
N	0.60096500	1.48564900	-0.31577500
H	-3.45428700	1.90278400	-0.84044500
H	1.38054300	1.76938800	-0.90283600
H	-1.05762700	2.73109600	-0.88071300
C	-0.68603400	1.70821300	-0.99305500
H	-0.53042800	1.53995000	-2.06372800
H	1.65123900	4.00321700	0.36657800

Model for 4 – 6:

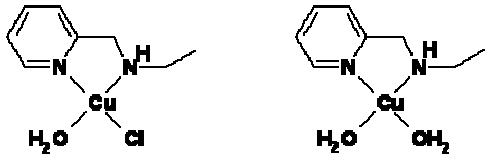


[LCu^{II}Br$_2$]

E = -7210.406013 **a.u.**

H	-0.48691200	4.17537800	2.37864500
H	-4.10196900	-2.63039000	0.35155800
H	0.69340000	2.10973900	1.69604600
H	-1.03503600	1.80239800	1.77849400
H	-1.59771500	-2.41687600	0.45293200
C	-3.62061900	-1.69343600	0.09841100
C	-0.26515100	2.35900900	1.23727200
C	-2.23649500	-1.59048100	0.16138100
C	-0.51061400	3.86303700	1.33165500
H	-5.44112900	-0.62491300	-0.34232400
C	-4.35864100	-0.57979100	-0.28770300
N	-1.59147200	-0.45443300	-0.14110600
H	-1.48113100	4.16142500	0.92738200
Cu	0.47128500	-0.13660900	-0.07569700
C	-3.68831000	0.59967800	-0.59847700
C	-2.30072700	0.62504600	-0.51813200
N	-0.20918200	1.81937300	-0.14642200
H	-4.23181000	1.48868500	-0.89926900
H	0.52506100	2.30242300	-0.65788000
H	-2.05160800	2.75847900	-0.73307200
C	-1.47808200	1.83966700	-0.88892500
H	-1.23628300	1.78993400	-1.95574900
H	0.26712300	4.42210200	0.80438200
Br	2.66963200	0.73891300	-0.48030400
Br	1.04085800	-2.38084700	0.40012900

Models for aqua-species:



$[LCu^{II}(H_2O)Cl]^{+}$

E = -2598.655497 **a.u.**

H	-1.39879500	3.99767500	-1.65388700
H	4.04183600	-1.91103600	-1.00835300
H	-1.86004900	1.59594300	-1.33095800
H	-0.12592100	1.83759300	-1.52549700
H	1.57983400	-2.33577400	-0.89411600
C	3.37787700	-1.17230900	-0.57707800
C	-0.97734700	2.04257500	-0.87182600
C	2.01522700	-1.41989200	-0.51295400
C	-1.18591300	3.54095800	-0.68512700
H	4.91896300	0.26638100	-0.12890100
C	3.85956000	0.03973500	-0.08881600
N	1.15444200	-0.53176600	0.01478700
H	-0.31034900	4.04961000	-0.27542500
Cu	-0.82510500	-0.69382200	0.09218000
C	2.96452300	0.96635500	0.43973200
C	1.61310700	0.65007600	0.47845400
N	-0.74794900	1.29399800	0.40869400
H	3.31046700	1.92282000	0.81423800
H	-1.51064900	1.52144100	1.04264300
H	0.84959100	2.60884100	0.97648700
C	0.55693800	1.56089100	1.06424900
H	0.44787100	1.34621400	2.13191200
H	-2.04112500	3.74502000	-0.03555000
O	-0.81621200	-2.71951200	-0.13002900
H	-1.70692800	-3.01712700	-0.36945600
H	-0.47033700	-3.32112800	0.54005100
Cl	-3.02682000	-0.76561800	0.09644900

$[LCu^{II}(H_2O)_2]^{2+}$

E = -2214.629124 **a.u.**

H	-2.06160400	3.74466000	-1.61894900
H	4.06217000	-1.39436200	-1.07088700
H	-2.17489700	1.30473000	-1.39119300
H	-0.48908700	1.79172600	-1.48724700
H	1.68823900	-2.14276700	-0.97369500
C	3.30938500	-0.76056600	-0.61864000
C	-1.38666600	1.85365600	-0.86899100
C	1.99253500	-1.18790200	-0.56437400
C	-1.82104500	3.29815700	-0.65200200
H	4.65328100	0.85058800	-0.12315600
C	3.63174900	0.48876800	-0.09224200
N	1.02563300	-0.43088400	-0.00769600
H	-1.04136700	3.91487800	-0.20242300
Cu	-0.88391500	-0.85971100	0.08815300
C	2.62527600	1.27792400	0.46229100

C	1.32697000	0.79185100	0.49049200
N	-1.09880400	1.10507700	0.41190000
H	2.84784000	2.25950700	0.86463400
H	-1.87943700	1.26731800	1.04674000
H	0.29478900	2.61378400	1.03007500
C	0.16175900	1.53336600	1.09542200
H	0.07223100	1.28386100	2.15715700
H	-2.71883900	3.36492100	-0.03185200
O	-2.85680300	-1.24485200	0.08120100
H	-3.26864800	-1.89442900	0.66513400
O	-0.65966600	-2.86236800	0.00870900
H	-1.12840200	-3.45005500	-0.59724100
H	-3.54730500	-0.82595600	-0.44723700
H	-0.07126500	-3.38991200	0.56325600