Electronic Supplementary Information (ESI)

A tricolor-switchable stimuli-responsive luminescent binuclear Cu(I) complex with switchable NH···O interactions

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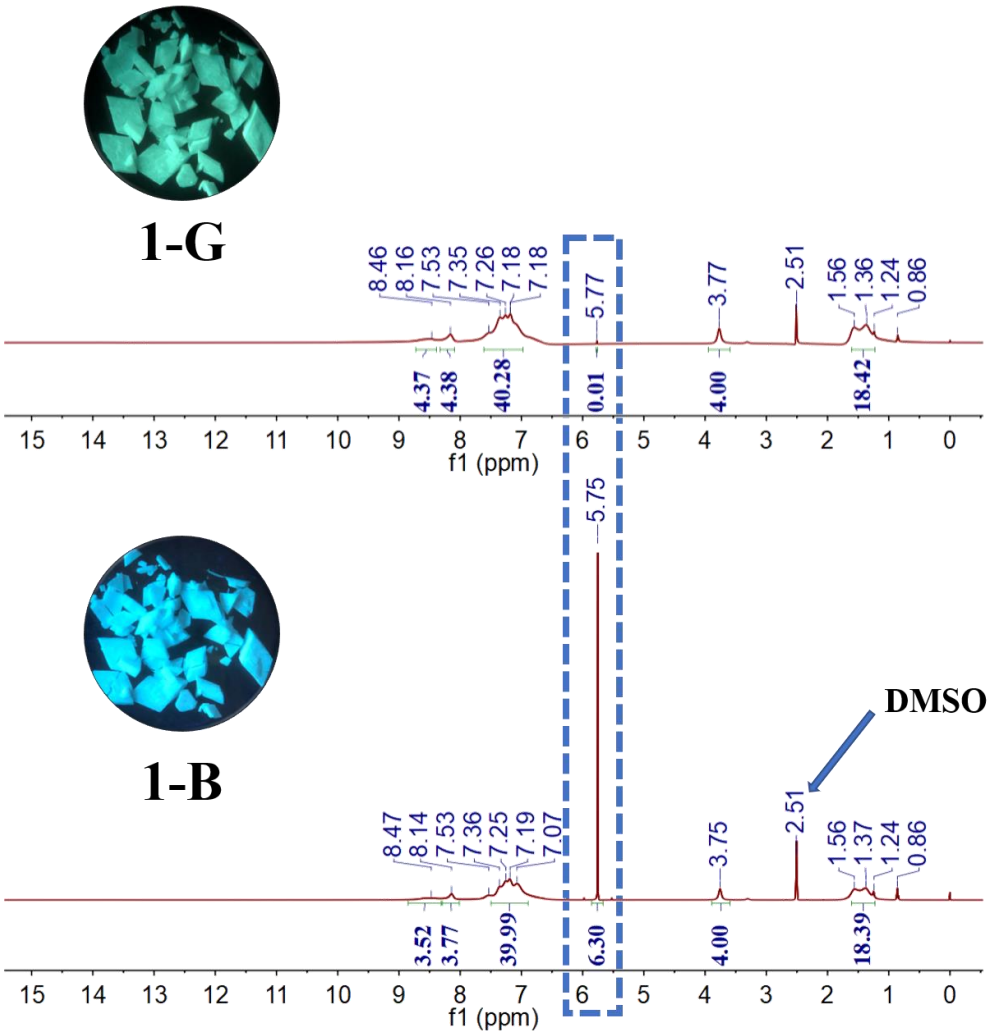

Fig. S1 ^{1}H NMR spectra of **1-B** and **1-G** in DMSO-d_6.

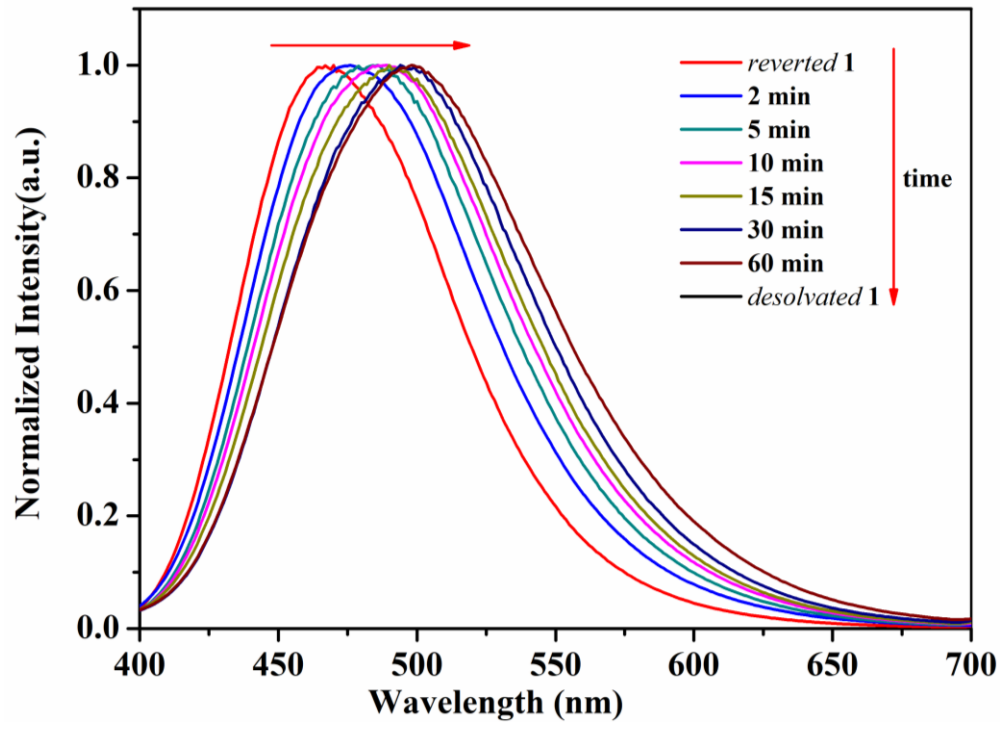

Fig. S2 Solid-state emission spectra of *reverted* **1** upon exposure to air.

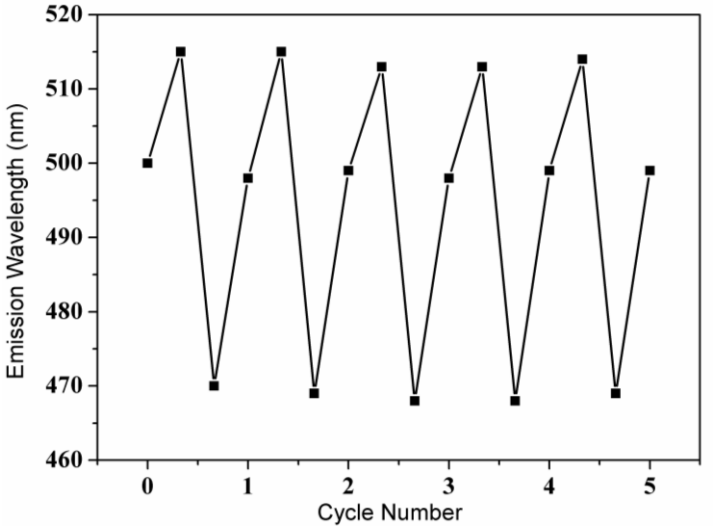

Fig. S3 Emission maximum variation of **1-B** under alternate treatment of grinding, CH_2Cl_2 vapor fuming, and exposure to air.

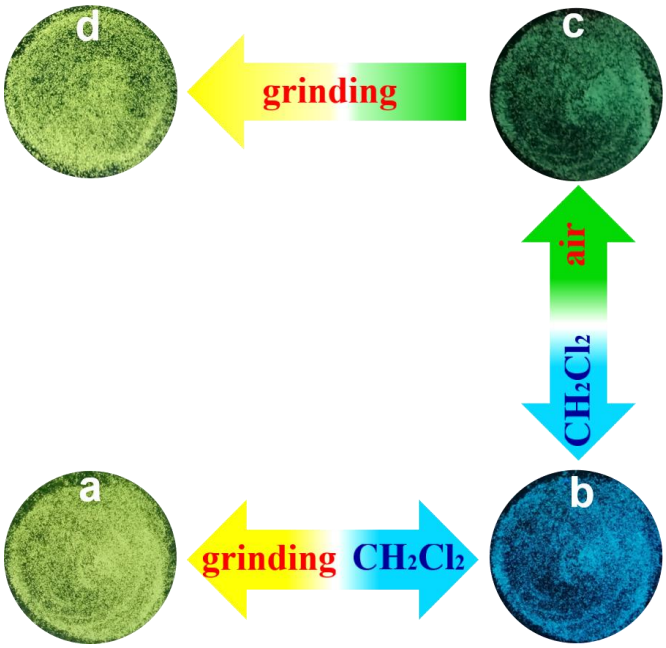

Fig. S4 Photographic images of **1-G** (5 wt %) doped in PMMA in various solid states.

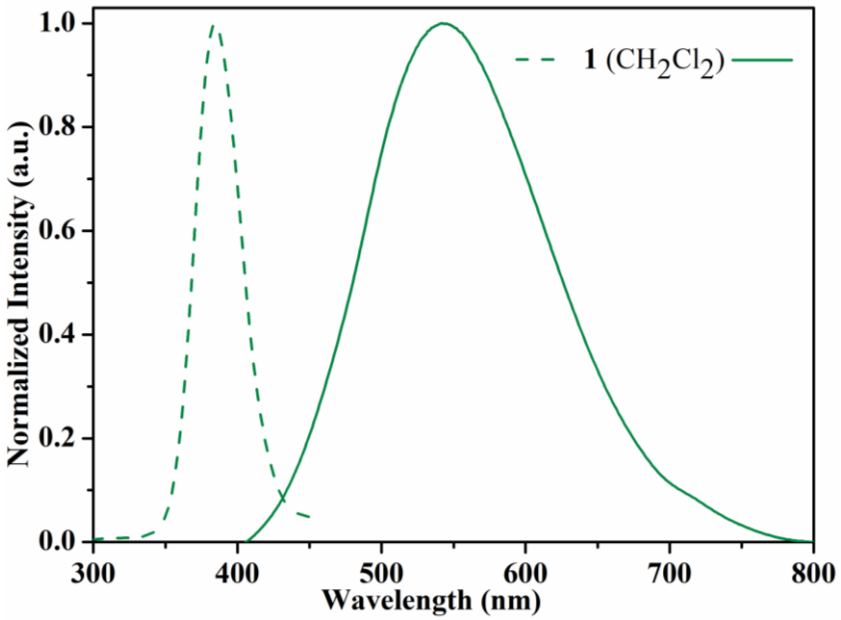

Fig. S5 Excitation (dotted line) and emission (solid line) spectra of **1** in degassed CH_2Cl_2.

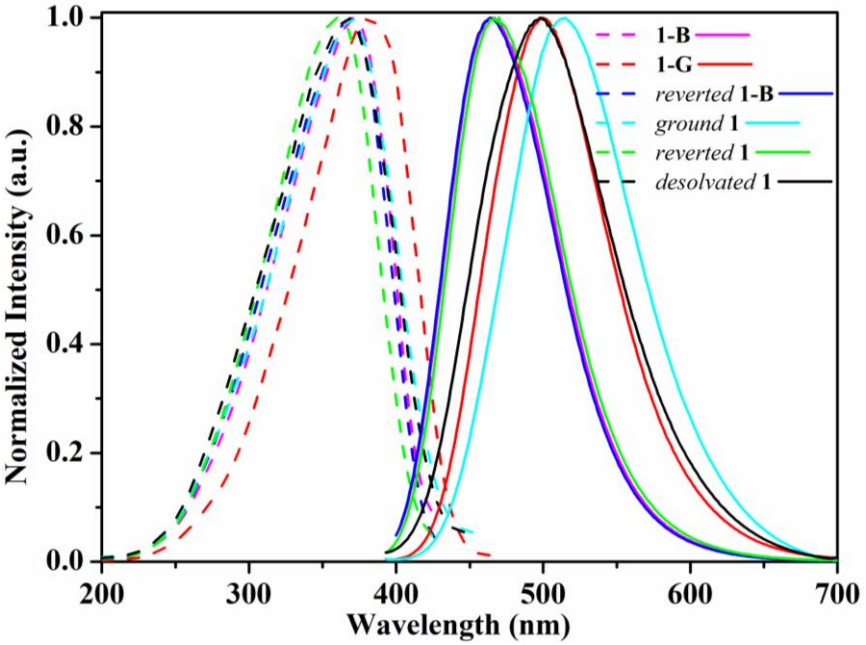

Fig. S6 Excitation (dotted lines) and emission (solid lines) spectra of **1-B** in various solid states.

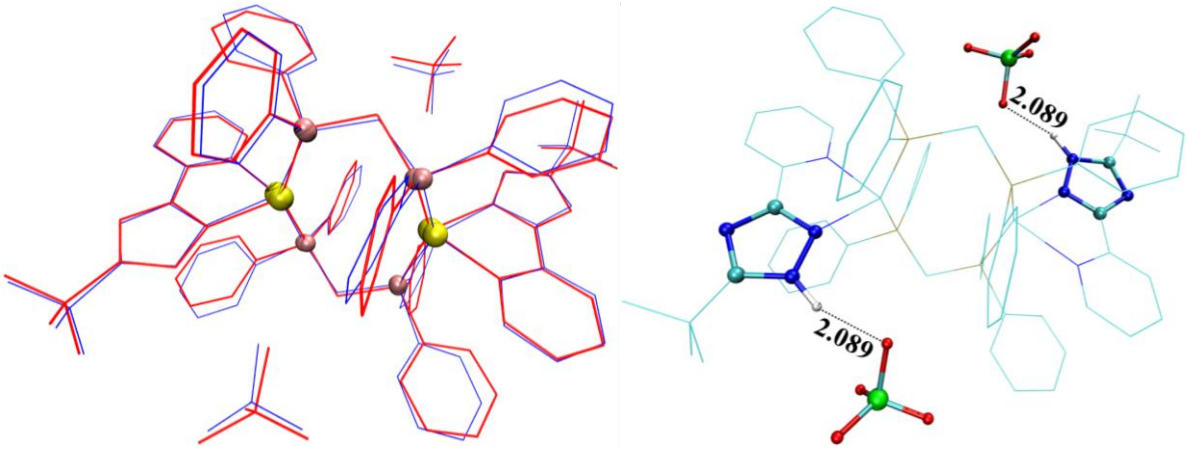

Fig. S7 Superimposition (left) of the calculated (red) and experimental (blue) structures for **1-G**. NH···O hydrogen bonds (right) in the calculated structure.

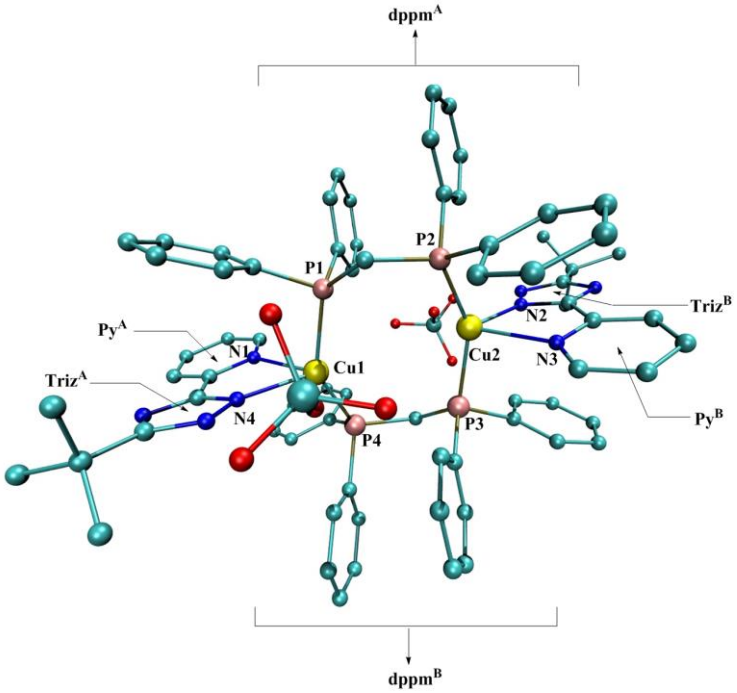

Fig. S8 Molecular fragments and atom numbering of **1-G**.

Table S1. Crystal data and structure refinement parameters of **1-B**

formula	$C_{75}H_{78}Cl_8Cu_2N_8O_8P_4$
fw	1754.03
T (K)	300.0
crystal system	Monoclinic
space group	*C2/c*
a (Å)	31.7882(16)
b (Å)	13.2770(7)
c (Å)	20.3615(10)
α (deg)	90
β (deg)	102.142(2)
γ (deg)	90
V (Å^3)	8401.4(7)
Z	4
ρ_{calcd} (g cm^{-3})	1.387
μ (mm^{-1})	0.893
no. reflections collected	62745
no. unique reflections	9659
R_{int}	0.0493
no. observed reflections	9659
no. parameters	472
GOF on F^2	1.077
$R1$ [$I > 2\sigma(I)$]	0.0789
$wR2$	0.2601

Table S2. Selected bond lengths (Å) and angles (deg) of **1-B**

Cu1−N1	2.171(4)	Cu1−N2	2.125(4)
Cu1−P1	2.2355(12)	Cu1−P2	2.2566(12)
N1−Cu1−N2	77.18(15)	N1−Cu1−P1	103.01(11)
N1−Cu1−P2	98.81(11)	N2−Cu1−P1	114.69(11)
N2−Cu1−P2	102.64(11)	P1−Cu1−P2	139.93(5)

Table S3. Cartesian coordinates of the optimized S_0 geometries of **1-G** with B3LYP-D3/6-31G*/ SDD level in the gas phase

Cu	4.02953300	4.42201500	9.39869400
P	5.21567000	4.68107700	7.46839900
P	4.31074600	4.12245300	11.64647000
N	1.74169400	4.10616800	9.26874000
N	3.05053700	6.51998100	9.56561500
C	7.00894600	4.15673900	7.36526600
C	5.25522700	6.48065200	7.07512000
C	4.50585000	3.95937700	5.93427000
C	4.66031200	2.47089000	12.44466700
C	5.43110800	5.30077700	12.49685400
C	2.67083400	4.55122400	12.36946200
N	0.74787300	3.18549700	9.25423800
C	1.06916800	5.25380600	9.16583700
C	1.73580800	6.55017900	9.27335900
C	3.67213700	7.68198800	9.78945000
Cl	1.60823400	-0.48181300	10.63664300
O	2.27714400	0.66202800	9.91494600
O	2.61812700	-1.48920500	10.44406100
O	1.36418200	0.00162900	12.01763400
O	0.31865800	-0.86855500	10.00306800
C	-0.45728500	3.79270600	9.14113400
C	1.01552100	7.74379300	9.15786600
C	5.38094300	5.43289200	13.89589800
C	6.28409900	6.13321500	11.75798100
C	2.34355500	5.88563500	12.65843800
C	1.67890900	3.56781100	12.48078600
N	-0.27812200	5.10728000	9.07022600
C	1.04832600	6.22368900	13.05100800
C	3.03579500	8.91864400	9.70674800
C	4.11559500	7.08229900	6.51245600
C	6.32346300	7.29394500	7.46366200
C	6.16563900	6.38141000	14.54289200
C	7.04165700	7.11625700	12.40668300
C	3.52518100	2.97149600	6.04454900
C	2.96548100	2.38382900	4.91193800
C	4.92917600	4.36052100	4.65674600
C	1.68160100	8.94684700	9.37249800
C	4.06333900	8.46547000	6.34803300
C	4.37193300	3.77385700	3.52058700
C	0.38892300	3.90624600	12.89061500
C	6.26804600	8.68038500	7.31346300
C	5.13511500	9.27023400	6.75324200
C	6.98409000	7.23452100	13.79490200
C	0.06725600	5.23585300	13.16970400
C	-1.77432600	3.05291900	9.11650400
C	3.38702100	2.78653900	3.64476700

C	-2.90298200	4.04576600	8.78856900
C	-2.02299900	2.42629400	10.50880900
C	-1.72046200	1.94696200	8.03883300
H	0.94703900	2.20914000	9.46587200
H	4.02769100	1.73354500	11.94136400
H	4.35445800	2.49468700	13.49532200
H	3.09693000	6.66173400	12.57296300
H	4.71502500	7.60922600	10.05629500
H	4.72086900	4.79681300	14.47783400
H	6.36539800	6.01925700	10.67990400
H	3.22892900	2.62784700	7.02042000
H	3.59716900	9.82780900	9.89273900
H	3.27001400	6.47151500	6.20868800
H	5.67953100	5.13972800	4.54993300
H	1.89780100	2.53892300	12.23128100
H	7.12198500	9.26416800	7.64735100
H	7.21777700	6.86939400	7.88330100
H	6.13325800	6.46117100	15.62569900
H	0.80738000	7.26163600	13.26516400
H	-0.35867800	3.12451600	12.98276300
H	3.17645700	8.91823100	5.91279900
H	7.66205800	7.79449100	11.83267900
H	-0.94020600	5.50165500	13.47838700
H	2.95756600	2.33439600	2.75475000
H	7.57933100	7.99286000	14.29663800
H	2.21985100	1.60511800	5.04626500
H	-0.04202800	7.69961100	8.92450200
H	4.70281600	4.09017400	2.53493000
H	5.08170100	10.34869000	6.63004000
H	1.15000200	9.89061600	9.28956500
H	-2.95234500	4.84787600	9.53076400
H	-3.86206400	3.51607900	8.77955600
H	-2.75129700	4.50786800	7.80777600
H	-1.22770400	1.73243500	10.79664900
H	-2.96601800	1.86854700	10.49900800
H	-2.09170700	3.20729200	11.27338800
H	-1.53493500	2.37712300	7.04779400
H	-2.67854200	1.41662700	8.00785700
H	-0.94171800	1.20835900	8.24689600
P	7.33287500	2.48907000	8.14157500
H	7.64343700	4.87677100	7.89548900
H	7.31715800	4.15410500	6.31438300
P	6.44578200	1.94709500	12.31944800
Cu	7.57438600	2.23915800	10.38548900
C	6.22190900	1.32290200	7.26810200
C	8.99349900	2.04487200	7.47805900
C	6.41412900	0.14567900	12.70651300
C	7.19750400	2.66741100	13.83322100
N	9.75640300	2.53065800	10.64004100

N	8.52141400	0.10853000	10.18962500
C	6.35640600	1.11811000	5.88350000
C	5.26339900	0.59043200	7.98337900
C	9.32786600	0.72581700	7.13390000
C	10.00501700	3.01202300	7.50978700
C	7.53631400	-0.45815500	13.29893700
C	5.36627700	-0.66864200	12.26892700
C	8.33410800	3.47382200	13.71518700
C	6.65583400	2.42379900	15.10577500
N	10.70957400	3.48063500	10.80409400
C	10.44950000	1.39523100	10.73818900
C	9.82269900	0.08963800	10.53351600
C	7.92312400	-1.05226400	9.90839600
H	7.09499600	1.68235900	5.32156300
C	5.55739200	0.18656000	5.22883000
H	5.12823900	0.75476300	9.04966300
C	4.46893000	-0.35530700	7.32469200
H	8.56503500	-0.04520300	7.11519900
C	10.64851800	0.39432600	6.82616700
H	9.77013400	4.01936600	7.81163400
C	11.32155500	2.68460400	7.19104300
H	8.36703800	0.15161400	13.64335500
C	7.58950400	-1.84471100	13.44169100
C	5.41727700	-2.05550000	12.40466700
H	4.49050800	-0.24386200	11.81582600
H	8.76333300	3.64242800	12.73696200
C	8.90824500	4.05767600	14.84626400
H	5.79220900	1.77279700	15.21646800
C	7.22972500	3.00463000	16.23480600
H	10.47285700	4.46491800	10.65179200
C	11.91910100	2.89449200	10.99363700
N	11.77441800	1.57397100	10.96555900
C	10.55940100	-1.09430300	10.63619700
H	6.88840800	-0.98456600	9.60330800
C	8.57623200	-2.28165900	9.98103700
H	5.66227000	0.04290400	4.15719600
C	4.61999200	-0.55743700	5.95289300
H	3.74305200	-0.93449300	7.88119300
H	10.89490300	-0.63220100	6.56765500
C	11.64901600	1.36975300	6.85321900
H	12.07849800	3.46301100	7.21941800
H	8.46348700	-2.30035900	13.89962200
C	6.53461100	-2.64871900	12.99293000
H	4.57153900	-2.63156500	12.03616100
C	8.35351700	3.82839400	16.10538400
H	9.78186000	4.69412200	14.73727300
H	6.80347000	2.81401600	17.21608600
C	13.21879500	3.64040800	11.17923600
H	11.60605100	-1.04338600	10.91348600

C	9.91887200	-2.29931800	10.36043400
H	8.03744000	-3.19449600	9.75083300
H	4.00217000	-1.29326500	5.44493300
H	12.67544000	1.10463600	6.61447000
H	6.58920100	-3.72836200	13.10471100
H	8.79588500	4.28450400	16.98701000
C	14.30378700	2.65276400	11.64607900
C	13.63358500	4.24990700	9.81867000
C	13.03570700	4.74282600	12.24460500
H	10.46141100	-3.23761700	10.43375800
H	14.44785700	1.84894300	10.91881200
H	15.25136200	3.18871900	11.77013800
H	14.03643500	2.19338300	12.60330500
H	12.86705400	4.91327800	9.41147200
H	14.55538300	4.83003100	9.93722100
H	13.81783100	3.45458100	9.08788400
H	12.76339200	4.30298800	13.21146700
H	13.97425500	5.29285100	12.37196500
H	12.26566900	5.46587900	11.96846700
Cl	9.98661000	7.10747200	9.29916400
O	9.21508200	6.01292500	10.03043800
O	9.00396400	8.14547900	9.33917700
O	10.34291700	6.55209300	7.97122800
O	11.22013800	7.49991000	10.03046700

Table S4. Selected bond lengths (Å) of **1-G** with (a) and without (b) NH···O interactions (Numbering of atoms as in Fig. S8).

	a	b
Cu1–N1	2.321	2.438
Cu1–P1	2.284	2.291
Cu1–N4	2.313	2.079
Cu1–P4	2.281	2.251
Cu2–N2	2.216	2.164
Cu2–P2	2.258	2.243
Cu2–N3	2.340	2.236
Cu2–P3	2.270	2.246

Table S5. Molecular orbital compositions (%) of **1-G** with NH···O interactions at B3LYP/6-31G(d) /SDD level (Numbering of fragments as in Fig. S8).

Orbital	Contribution (%)							
	Cu1	Cu2	$Triz^A$	Py^A	$dppm^A$	$Triz^B$	Py^B	$dppm^B$
LUMO	0.22	1.64	0.51	1.35	4.45	25.3	62.0	2.78
HOMO	24.2	27.3	0.82	3.72	17.5	4.59	1.28	20.3

Table S6. Molecular orbital compositions (%) of **1-G** without NH···O interactions at B3LYP/ 6-31G(d)/SDD level (Numbering of fragments as in Fig. S8).

Orbital	Contribution (%)							
	Cu1	Cu2	$Triz^A$	Py^A	$dppm^A$	$Triz^B$	Py^B	$dppm^B$
LUMO	2.42	0.50	28.4	58.4	3.57	0.02	0.03	5.46
HOMO	12.7	39.1	0.81	1.60	8.84	3.53	4.41	25.8