Supporting Information

Title： Construction of Eight Mixed-Valence Pentanuclear $Cu^{I}_{4}Cu^{II}$ Clusters by Using the Ligands with Inhomogeneous Electron Density Distribution: Synthesis, Characterization and Photothermal Properties

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Characterization

Figures：

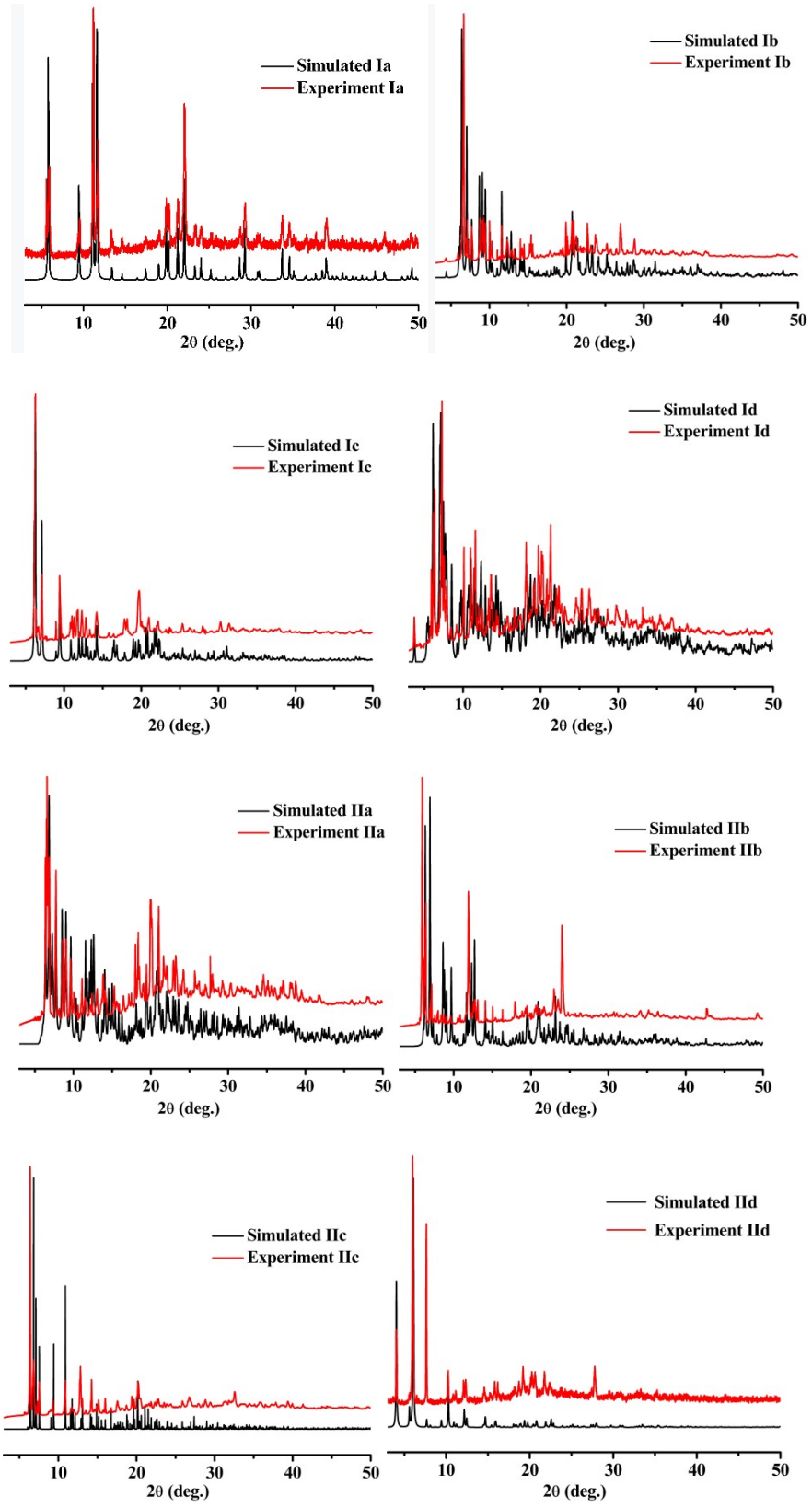


Figure S1. The powder XRD patterns of all clusters.

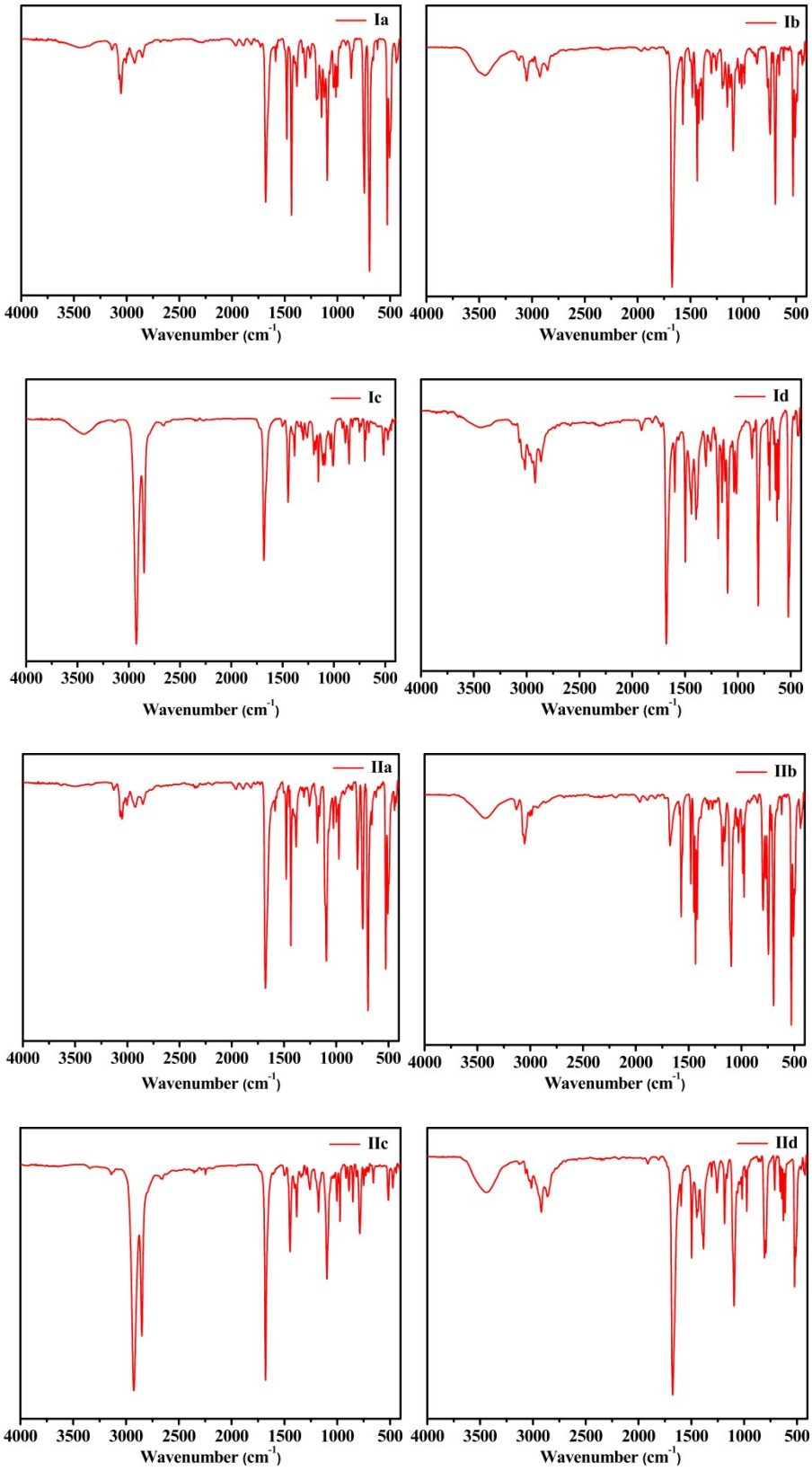


Figure S2. The IR spectra of all clusters.

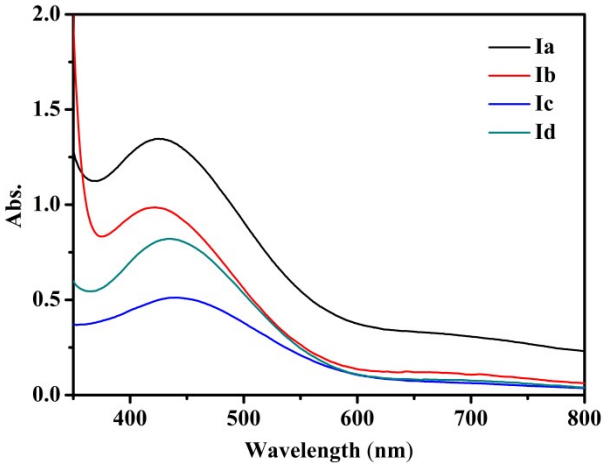


Figure S3. The UV spectra of clusters **Ia~d**.

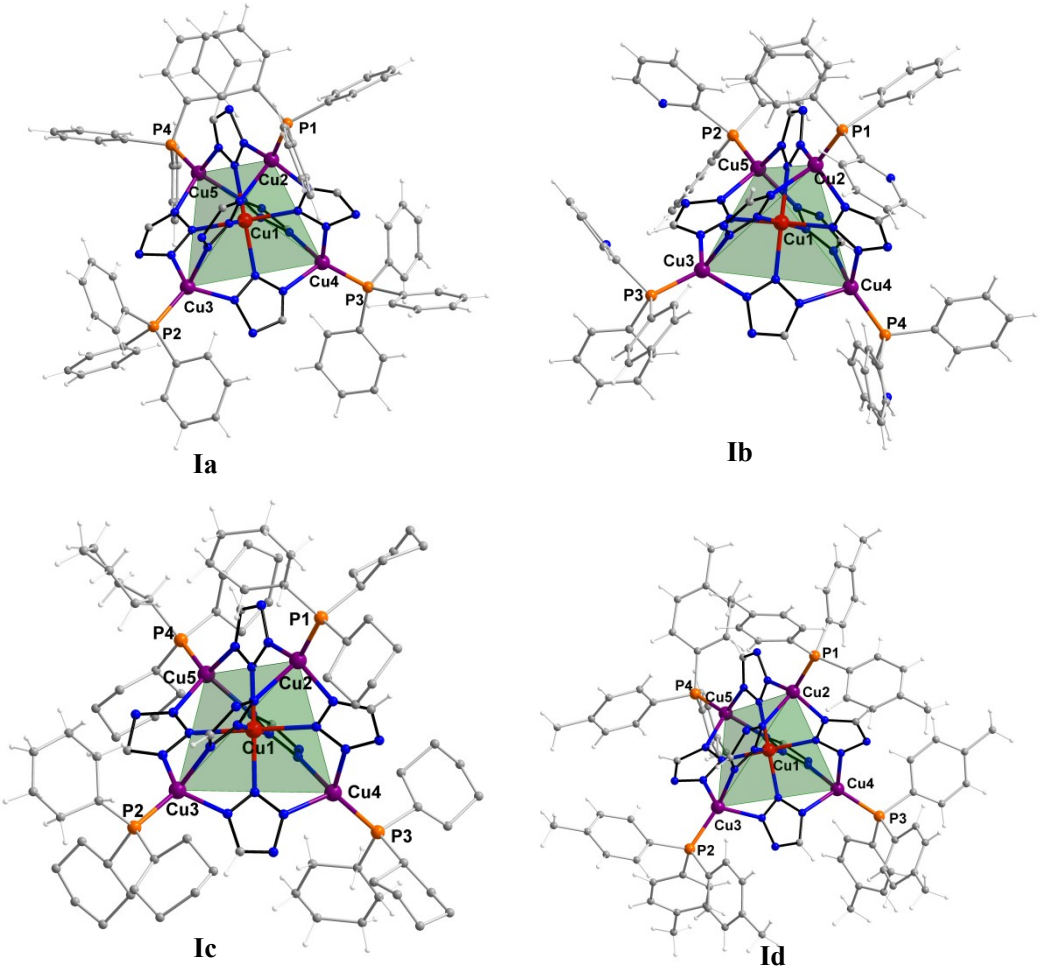


Figure S4. Crystal structures of **Ia~Id**. Color code: Cu^{II}, red; Cu^{I}, purple; Phosphines, golden; C, grey; N, blue; Pentanuclear $Cu^{I}_{4}Cu^{II}$ unit, cyan tetrahedron; five-membered rings are highlighted in black. The disorder parts and the solvent molecules are omitted for clearity.

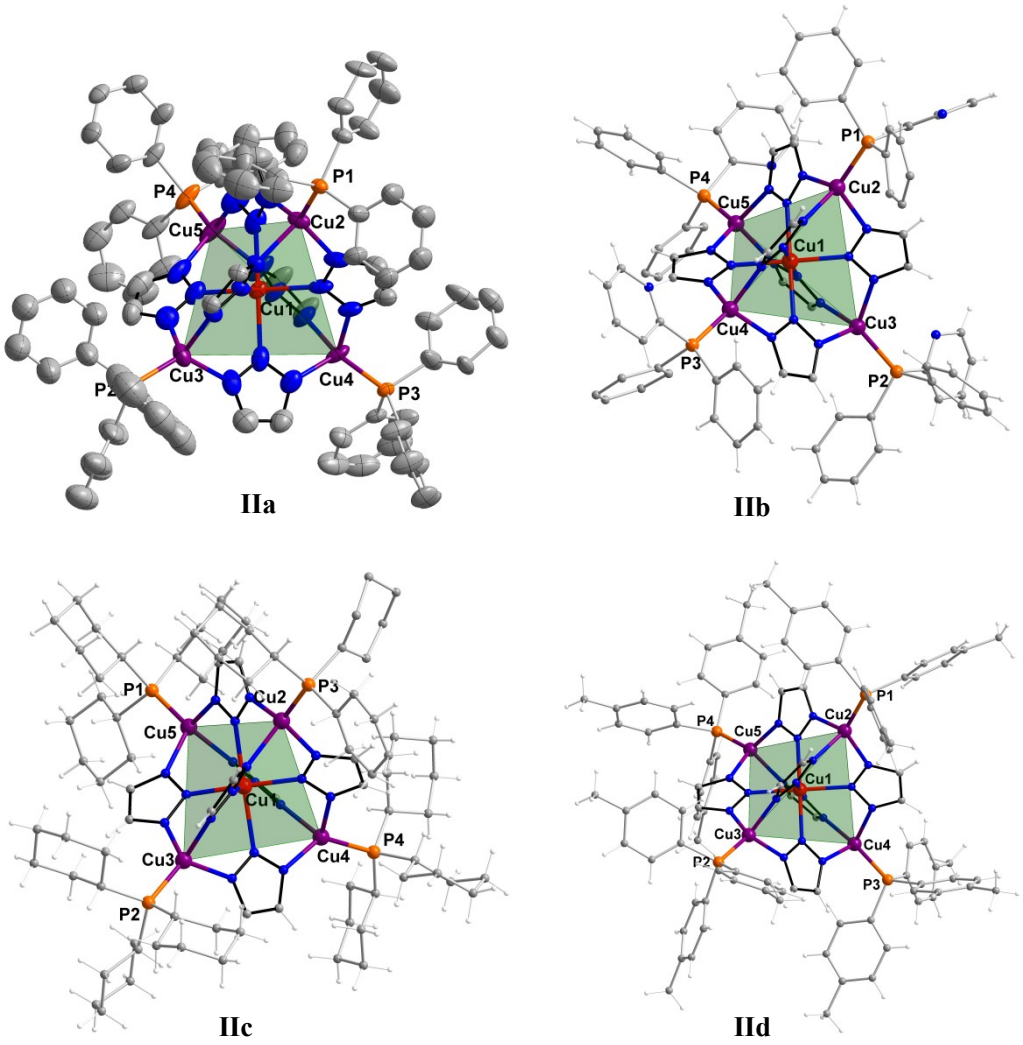


Figure S5. Crystal structures of **IIa~IId**. Color code: Cu^{II}, red; Cu^{I}, purple; Phosphines, golden; C, grey; N, blue; Pentanuclear $Cu^{I}_{4}Cu^{II}$ unit, cyan tetrahedron; five-membered rings are highlighted in black. The disorder parts and the solvent molecules are omitted for clearity.

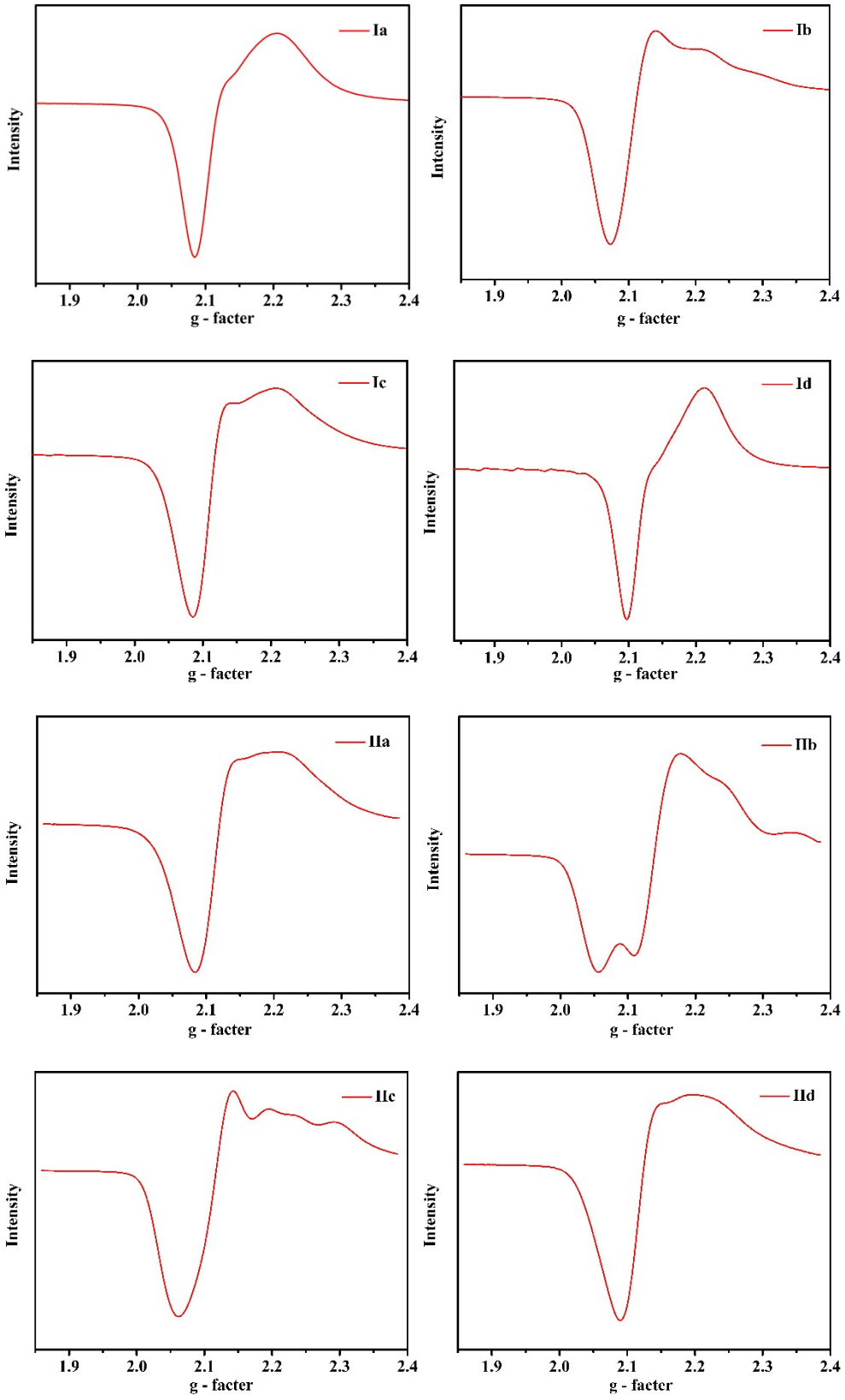


Figure S6. The EPR spectra of all clusters.

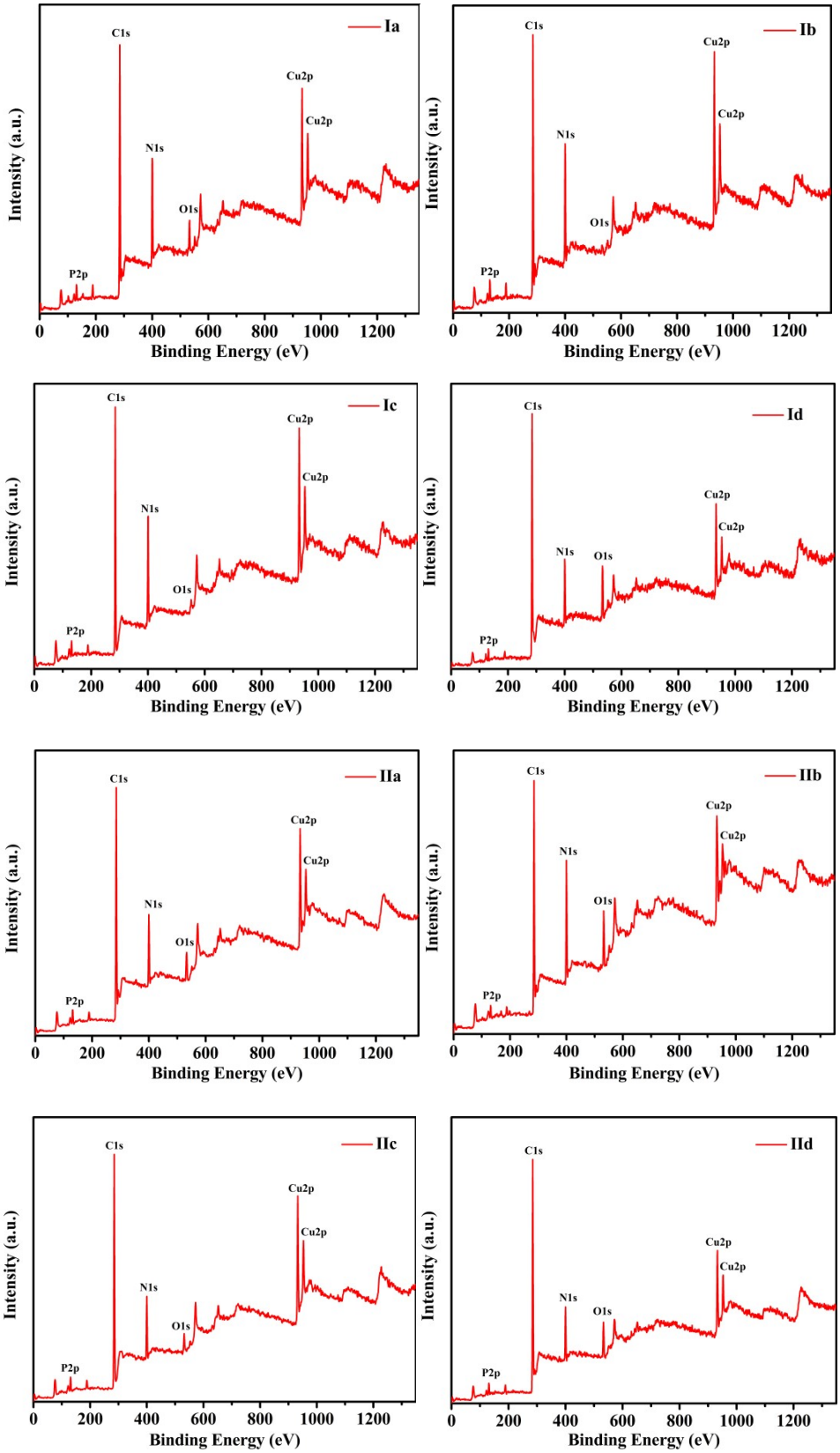


Figure S7. The XPS spectra of all clusters.

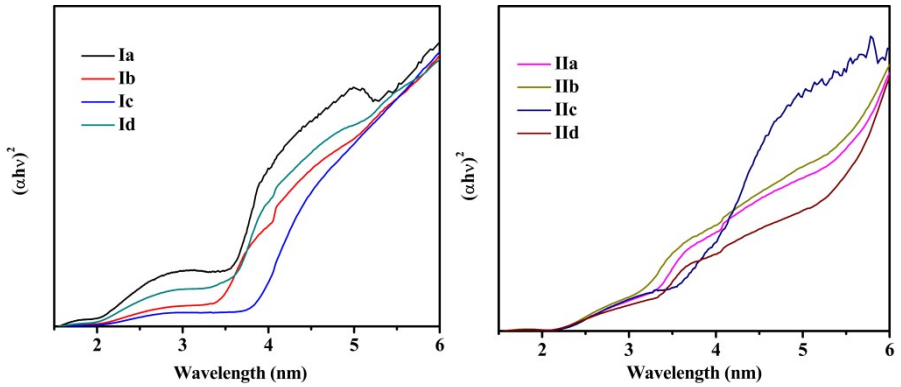
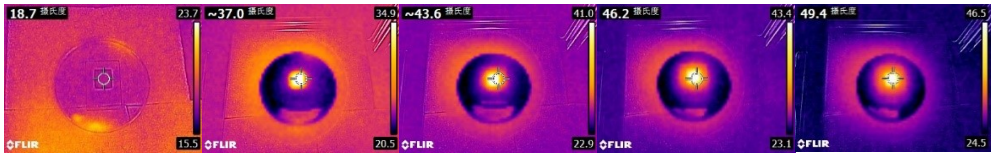
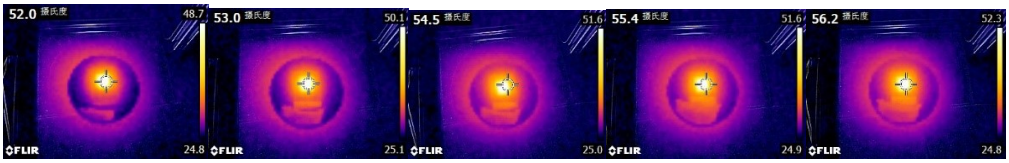


Figure S8. The solid UV–vis diffuse reflectance spectra of **Ia~d** and **IIa~d**.

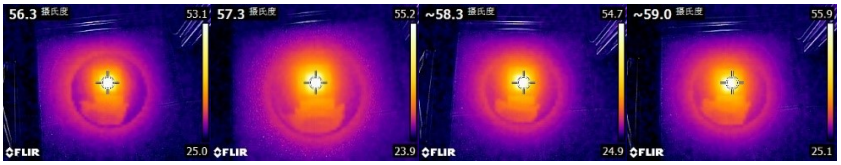
Compound Ia



0 min (i) **1 min (ii)** **2 min (iii)** **3 min (iv)** **4 min (v)**

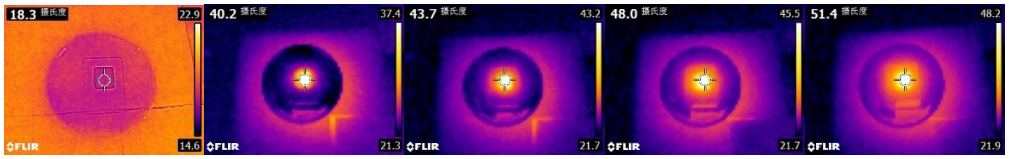


5 min (vi) **6 min (vii)** **7 min (viii)** **8 min (ix)** **9 min (x)**

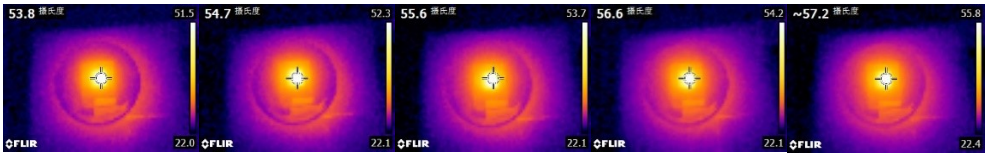


10 min (xi) **20 min (xii)** **30 min (xiii)** **60 min (xiv)**

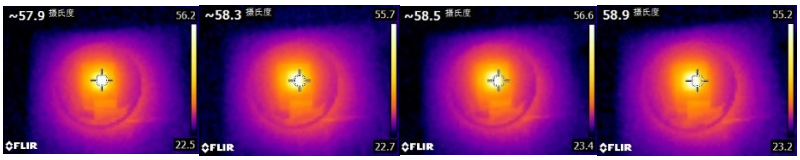
Compound Ib



0 min (i) **1 min (ii)** **2 min (iii)** **3 min (iv)** **4 min (v)**

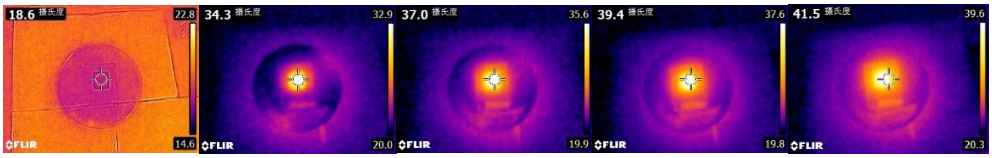


5 min (vi) **6 min (vii)** **7 min (viii)** **8 min (ix)** **9 min (x)**

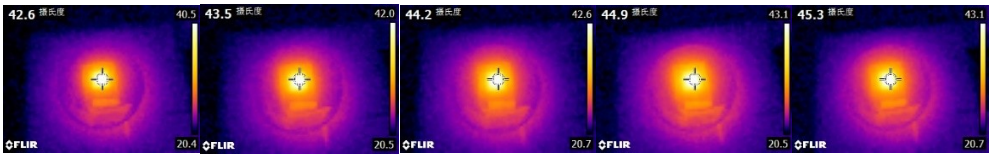


10 min (xi) 20 min (xii) 30 min (xiii) 60 min (xiv)

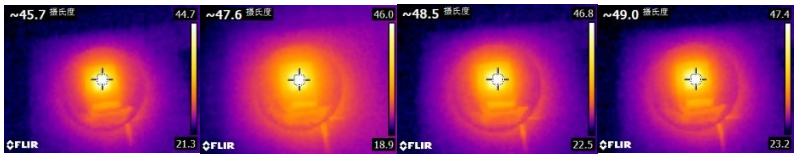
Compound Ic



0 min (i) 1 min (ii) 2 min (iii) 3 min (iv) 4 min (v)

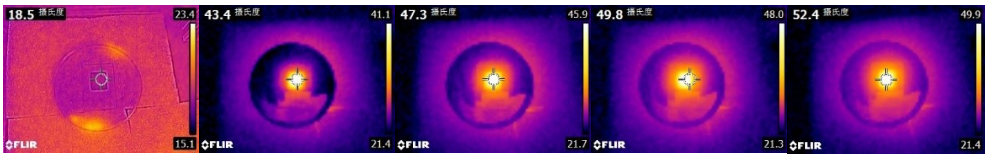


5 min (vi) 6 min (vii) 7 min (viii) 8 min (ix) 9 min (x)

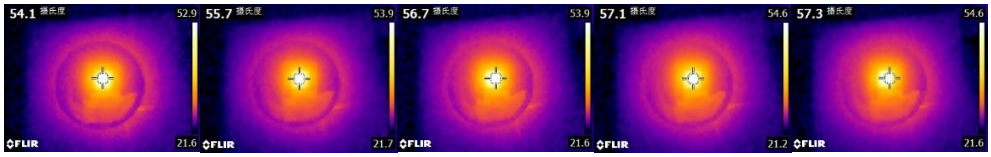


10 min (xi) 20 min (xii) 30 min (xiii) 60 min (xiv)

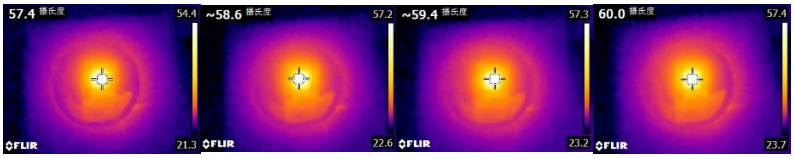
Compound Id



0 min (i) 1 min (ii) 2 min (iii) 3 min (iv) 4 min (v)

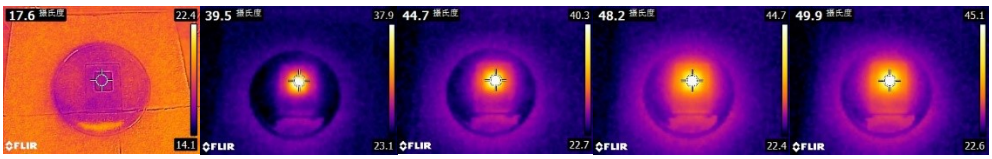


5 min (vi) 6 min (vii) 7 min (viii) 8 min (ix) 9 min (x)

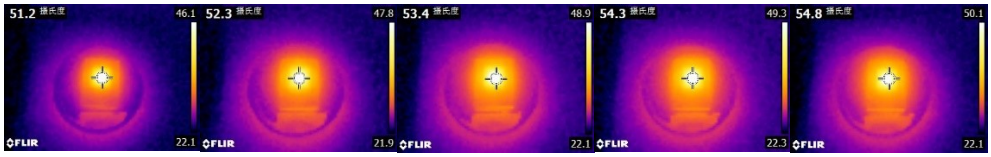


10 min (xi) 20 min (xii) 30 min (xiii) 60 min (xiv)

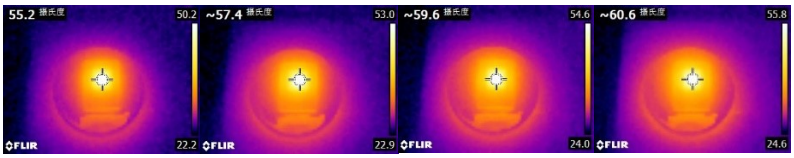
Compound IIa



0 min (i) 1 min (ii) 2 min (iii) 3 min (iv) 4 min (v)

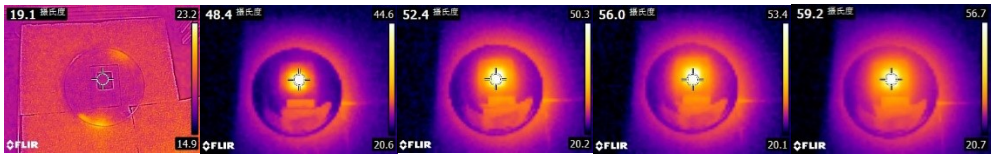


5 min (vi) **6 min (vii)** **7 min (viii)** **8 min (ix)** **9 min (x)**

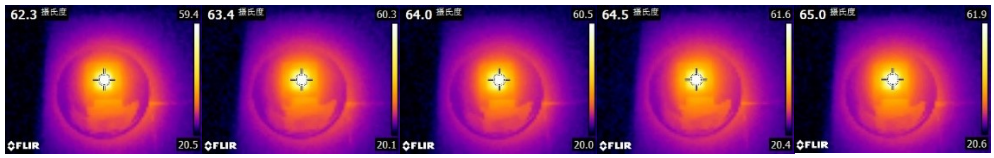


10 min (xi) **20 min (xii)** **30 min (xiii)** **60 min (xiv)**

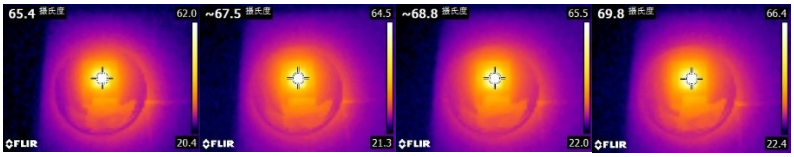
Compound IIb



0 min (i) **1 min (ii)** **2 min (iii)** **3 min (iv)** **4 min (v)**

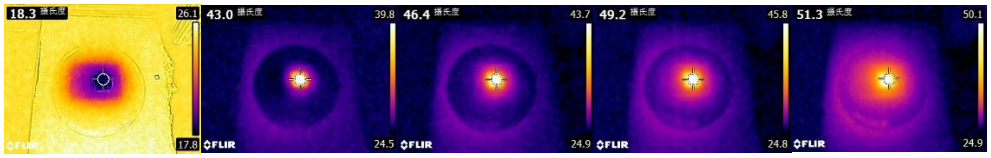


5 min (vi) **6 min (vii)** **7 min (viii)** **8 min (ix)** **9 min (x)**

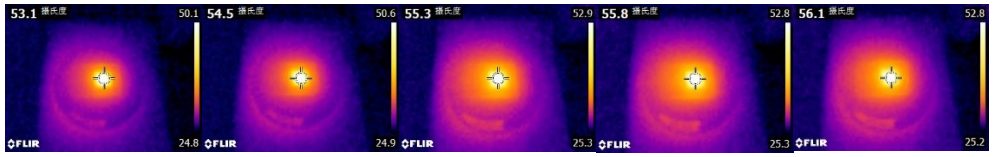


10 min (xi) **20 min (xii)** **30 min (xiii)** **60 min (xiv)**

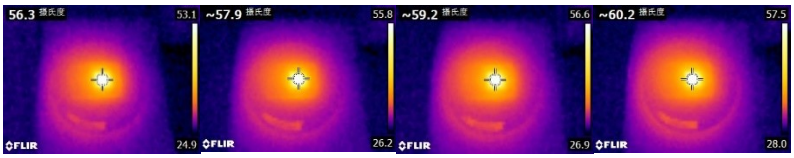
Compound IIc



0 min (i) **1 min (ii)** **2 min (iii)** **3 min (iv)** **4 min (v)**



5 min (vi) **6 min (vii)** **7 min (viii)** **8 min (ix)** **9 min (x)**



10 min (xi) **20 min (xii)** **30 min (xiii)** **60 min (xiv)**

Compound IId

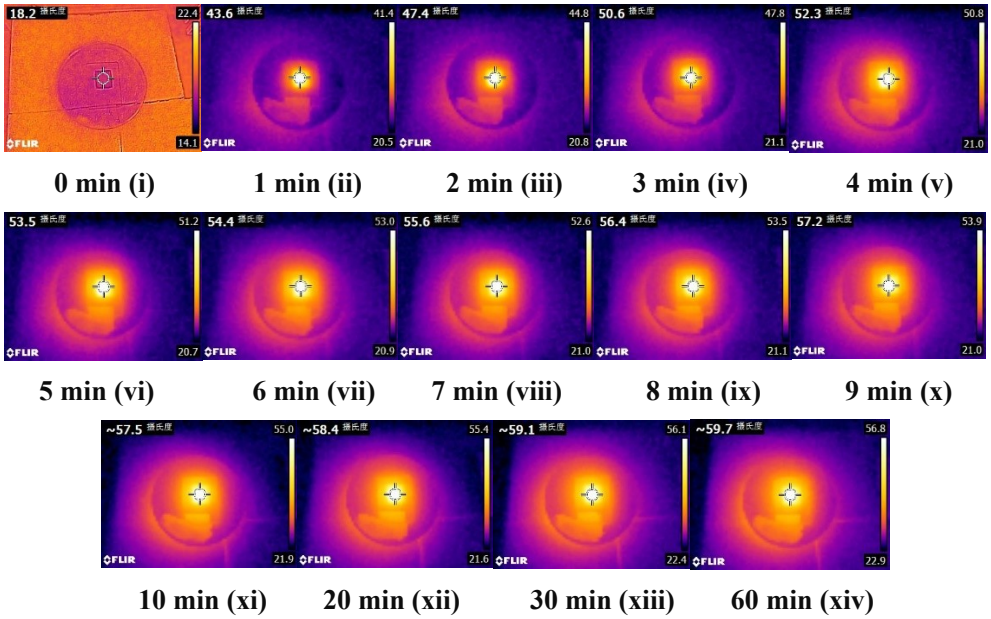


Figure S9. The tracking thermal pictures of samples **Ia~d** and **IIa~d**.

Tables：

Table S1. The XPS value of the assignments of the Cu 2P in clusters **Ia** ~ **d** and **IIa** ~ **d**.

Sample	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId
$Cu^{I}2p^{3/2}$	932.8	932.8	932.9	932.8	932.6	932.5	932.8	932.5
$Cu^{I}2p^{1/2}$	952.7	952.7	952.6	952.7	952.5	952.4	952.6	952.5
$Cu^{II}2p^{3/2}$	935.1	935.0	935.2	935.3	935.0	935.3	935.0	934.9
$Cu^{II}2p^{1/2}$	955.0	954.6	955.2	955.4	955.2	955.2	954.7	955.2

Table S2. The surface temperature of samples **Ia** ~ **d** and **IIa** ~ **d** changes with time.

Sample		Ia	Ib	Ic	Id	IIa	IIb	IIc	IId
	0 min	18.7	18.3	18.6	18.5	17.6	19.1	18.3	18.2
	1 min	37.0	40.2	34.3	43.4	39.5	48.4	43.0	43.6
	2 min	43.6	43.7	37.0	47.3	44.7	52.4	46.4	47.4
	3 min	46.2	48.0	39.4	49.8	48.2	56.0	49.2	50.6
	4 min	49.4	51.4	41.5	52.4	51.2	59.2	51.3	52.3
	5 min	52.0	53.8	42.6	54.1	52.3	62.3	53.1	53.5
	6 min	53.0	54.7	43.5	55.7	53.4	63.4	54.5	54.4
Temperture (℃)	**7 min**	54.5	55.6	44.2	56.7	54.3	64.0	55.3	55.6
	8 min	55.4	56.6	44.9	57.1	54.8	64.5	55.8	56.4
	9 min	56.2	57.2	45.3	57.3	55.2	65.0	56.1	57.2

10 min	56.3	57.9	45.7	57.4	57.4	65.4	56.3	57.5
20 min	57.3	58.3	47.6	58.6	59.0	67.5	57.9	58.4
30 min	58.3	58.5	48.5	59.4	59.6	68.8	59.2	59.1
60 min	59.0	58.9	49.0	60.0	60.6	69.8	60.2	59.7

Table S3. Crystal data and structure refinement for **Ia ~ d**.

Compound	**Ia**	**Ib**	**Ic**	**Id**
Chemical formula	$C_{80}H_{74}N_{24}O_2P_4Cu_5$	$C_{87}H_{93}N_{31}O_5P_4Cu_5$	$C_{81}H_{144}N_{24}P_4Cl_6Cu_5$	$C_{99}H_{113}N_{27}P_4O_4Cu_5$
Formula weight	1845.23	2094.50	2108.54	2186.80
Crystal system	Cubic	Triclinic	Orthorhombic	Monoclinic
Space group	*Fd-3*	*P-1*	*Pnma*	*P2(1)/n*
a, Å	26.4256(5)	15.7812(12)	28.4886(10)	15.5368(5)
b, Å	26.4256(5)	15.9961(11)	24.7344(10)	27.8343(8)
c, Å	26.4256(5)	21.4010(15)	16.0647(6)	23.8490(6)
α, deg	90	69.208(2)	90	90
β, deg	90	79.237(3)	90	91.8870(10)
γ, deg	90	67.621(3)	90	90
V, Å^3	18453.3(10)	4661.9(6)	11320.0(7)	10308.0(6)
Z	8	2	4	4
ρ_{calc}, g/cm^3	1.282	1.492	1.088	1.256
μ, mm^{-1}	1.255	1.260	1.025	1.129
Reflections collected	4469	79856	183255	93547
Independent reflections	1782	18119	10456	20295
R_{int}	0.0248	0.0680	0.0517	0.0471
Reflections I > 2σ(I)	1782	18119	10456	20295
Parameters	125	1293	861	1170
GOF on F^2	1.193	1.013	1.081	1.004
$R_1{}^a$ /$wR_2{}^b$ (I > 2σ(I))	0.0394/0.1108	0.0422/0.0848	0.0714/0.1765	0.0406/0.0969
$R_1{}^a$ /$wR_2{}^b$ (*all*)	0.0504/0.1172	0.0686/0.0951	0.0797/0.1823	0.0613/0.1076

Table S4. Crystal data and structure refinement for **IIa** ~ **d**.

Compound	**IIa**	**IIb**	**IIc**	**IId**
Chemical formula	$C_{89}H_{82}N_{20}P_4OCu_5$	$C_{85}H_{68}N_{23}P_4O_3Cu_5$	$C_{96}H_{172}N_{22}O_4P_4Cu_5$	$C_{101}H_{116}N_{18}P_4O_5Cu_5$
Formula weight	1889.40	1915.33	2140.13	2103.79
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Trigonal
Space group	*P2(1)/n*	*P2(1)/n*	*Pca2(1)*	*R-3*
a, Å	18.2935(5)	18.2696(5)	27.5353(6)	18.7274(4)
b, Å	24.4208(8)	24.0802(6)	14.4558(3)	18.7274(4)
c, Å	19.6271(5)	19.5200(6)	26.8451(7)	65.400(4)
α, deg	90	90	90	90
β, deg	94.0270(10)	95.2510(10)	90	90
γ, deg	90	90	90	120
V, Å^3	8746.6(4)	8551.5(4)	10685.6(4)	19863.9(14)
Z	4	4	4	6
ρ_{calc}, g/cm^3	1.348	1.381	1.330	0.975
μ, mm^{-1}	1.322	1.353	1.097	0.878
Reflections collected	17874	97384	121130	49453
Independent reflections	14834	17502	19573	6159
R_{int}	0.0500	0.0406	0.0909	0.0757
Reflections I > 2σ(I)	17874	17502	19573	6159
Parameters	1154	1196	1189	350
GOF on F^2	1.110	1.030	1.021	0.998
R_1[a] /wR_2[b] (I > 2σ(I))	0.0874/0.1898	0.0525/0.1393	0.0430/ 0.0969	0.0611/0.1746
R_1[a] /wR_2[b] (*all*)	0.1024/0.1978	0.0653/0.1481	0.0539/ 0.1037	0.0822/0.1877

[a] $R_1 = [\Sigma\ abs(abs(Fo) - abs(Fc))]/ [\Sigma\ abs(Fo)]$.

[b] $wR2 = [\Sigma(w(Fo^2 - Fc^2)^2)/ \Sigma[w(Fo^2)^2]^{0.5}$.