Electronic Supplementary Information for

Structural Change Dynamics of Heteroleptic Cu(I) complexes Observed by Ultrafast Emission Spectroscopy

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Contents

1. Absorption spectrum of Cu-dimer

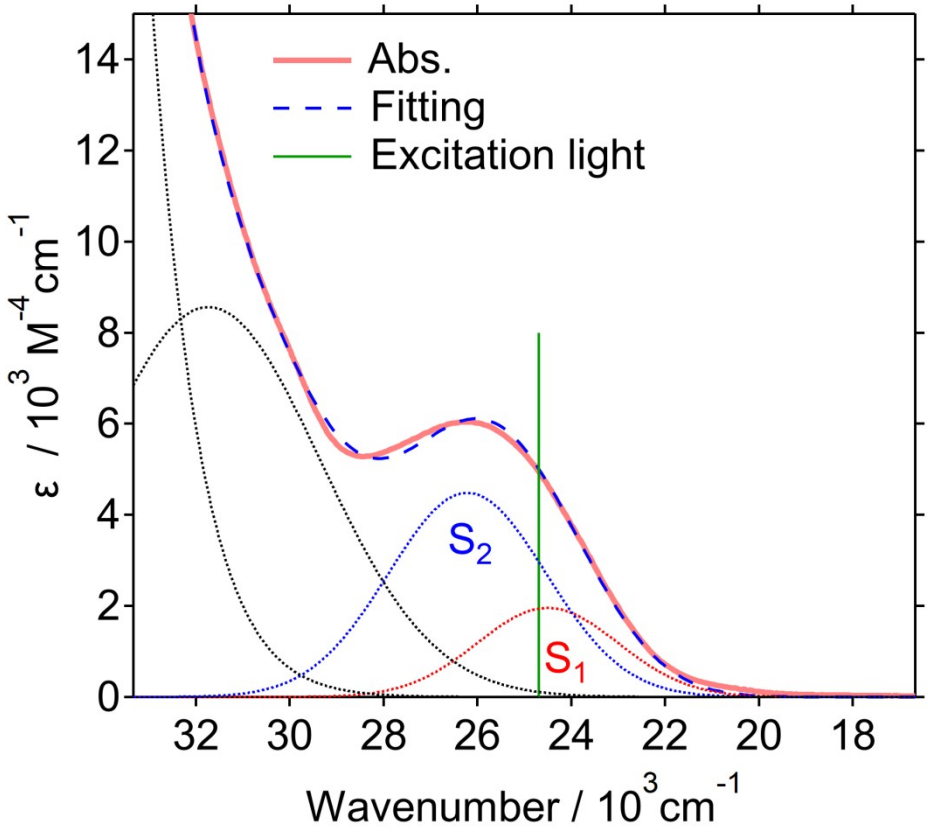

Figure S1. Absorption spectrum of Cu-dimer in acetonitrile. Fitting was performed with a multi-peak Gaussian line-shape function of wavenumber. Red solid line is the absorption spectrum, where dotted lines are Gaussian line components represented in wavenumber estimated by the Gaussian multi peak fitting to the absorption spectrum.

2. Temporal profiles of femtosecond fluorescence data Cu-dimer

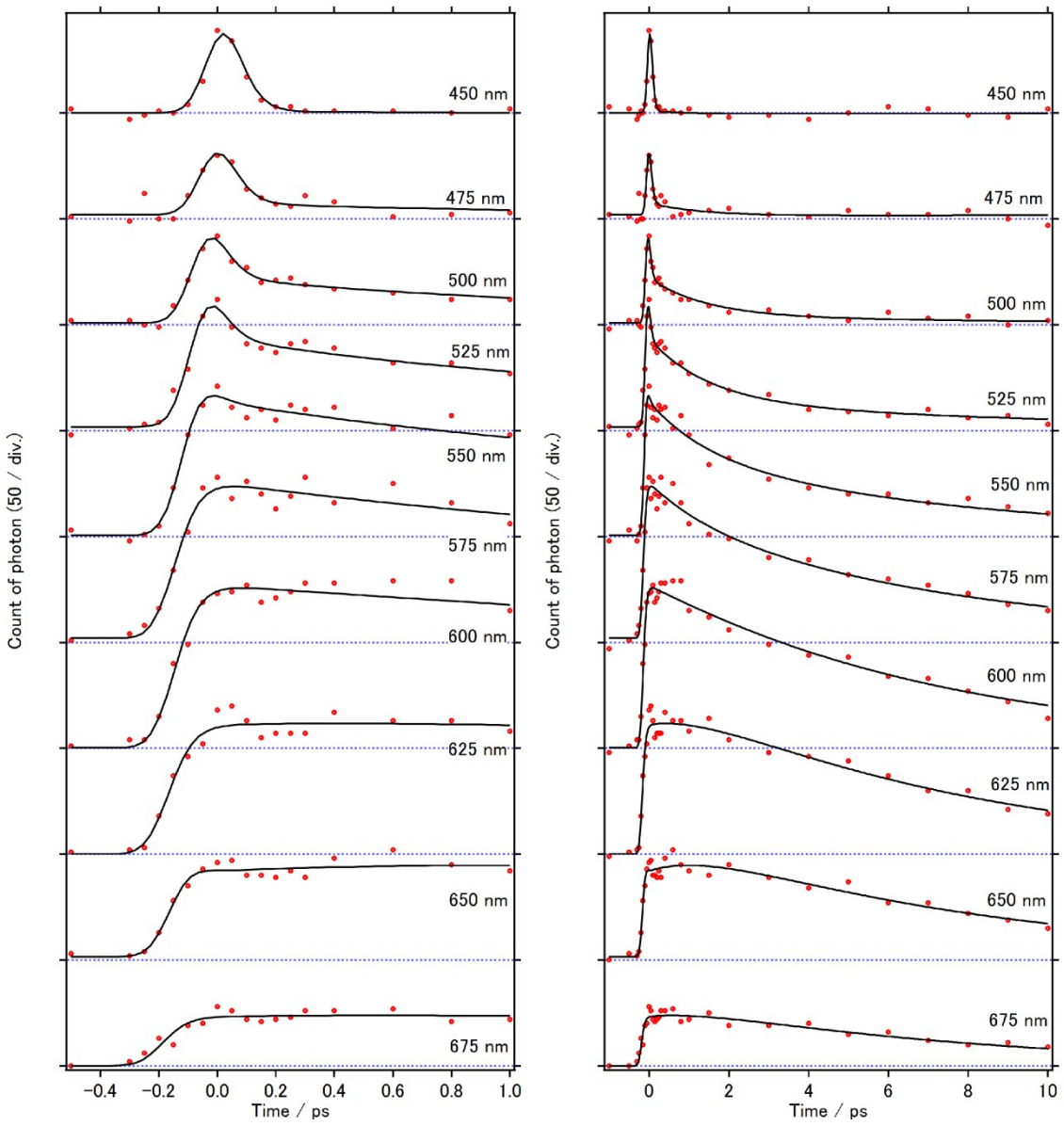

Figure S2. Temporal profiles of emission intensity in the time region within 1 ps (a) and 10 ps (b) for Cu-dimer in butyronitrile. (λ_{ex} = 405 nm, 2.5×10^{-4} mol/dm^3) Fitting curves (solid lines) were represented by a tri-exponential function using three time constants of 0.043 ± 0.01 ps, 1.4 ± 0.3 ps and 7.2 ± 0.5 ps.

3. Temporal profiles of femtosecond fluorescence data Cu-monomer

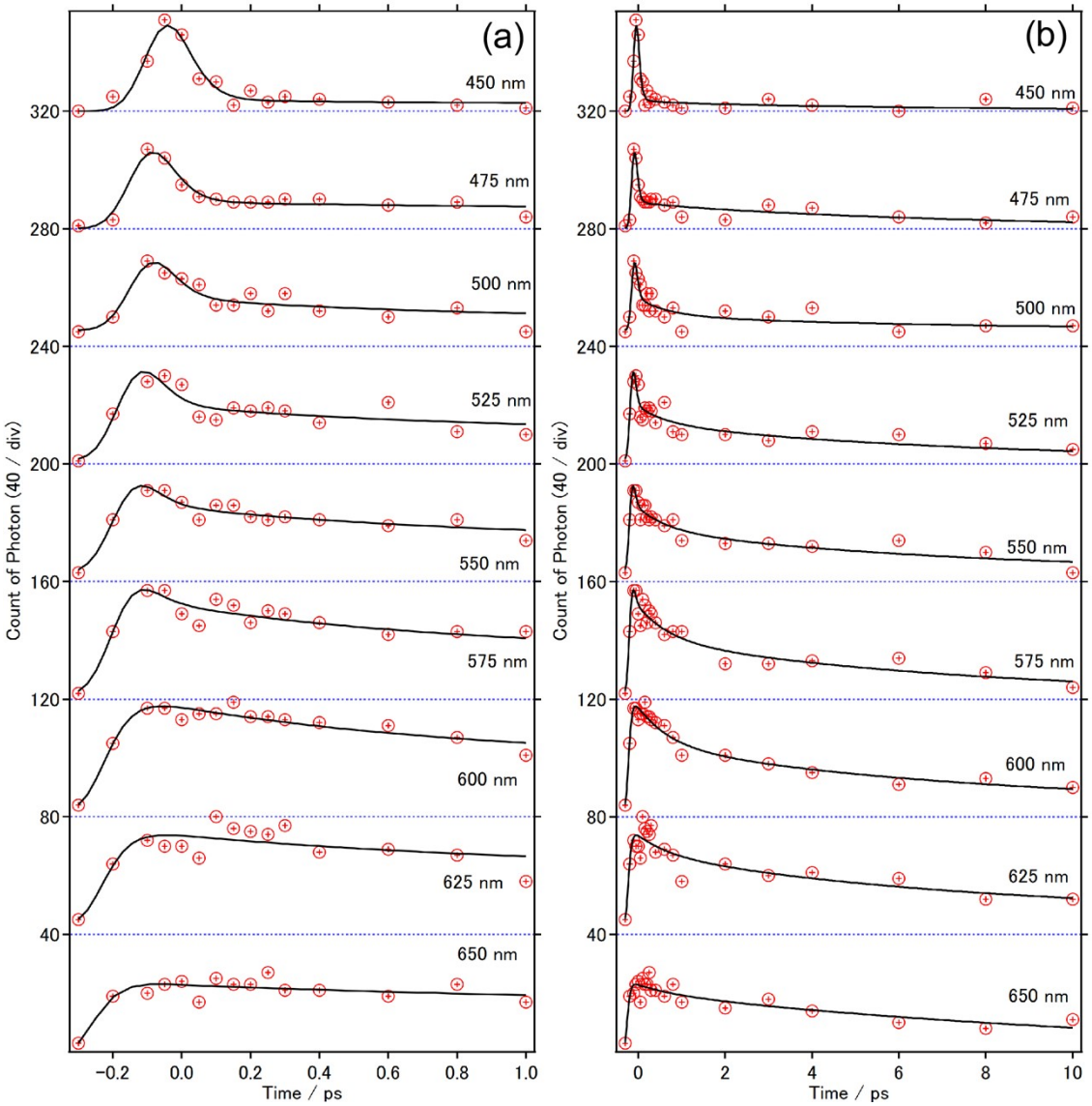

Figure S3. Temporal profiles of emission intensity in the time region within 1 ps (a) and 10 ps (b) for Cu-monomer in acetonitrile. (λ_{ex} = 405 nm, 4.9×10^{-4} mol/dm^3) Fitting curves (solid lines) were represented by tri-exponential function using three time constants of 0.040 ± 0.01 ps, 0.77 ± 0.31 ps and 8.0 ± 2.7 ps.

4. Femtosecond time-resolved emission spectra of Cu-monomer

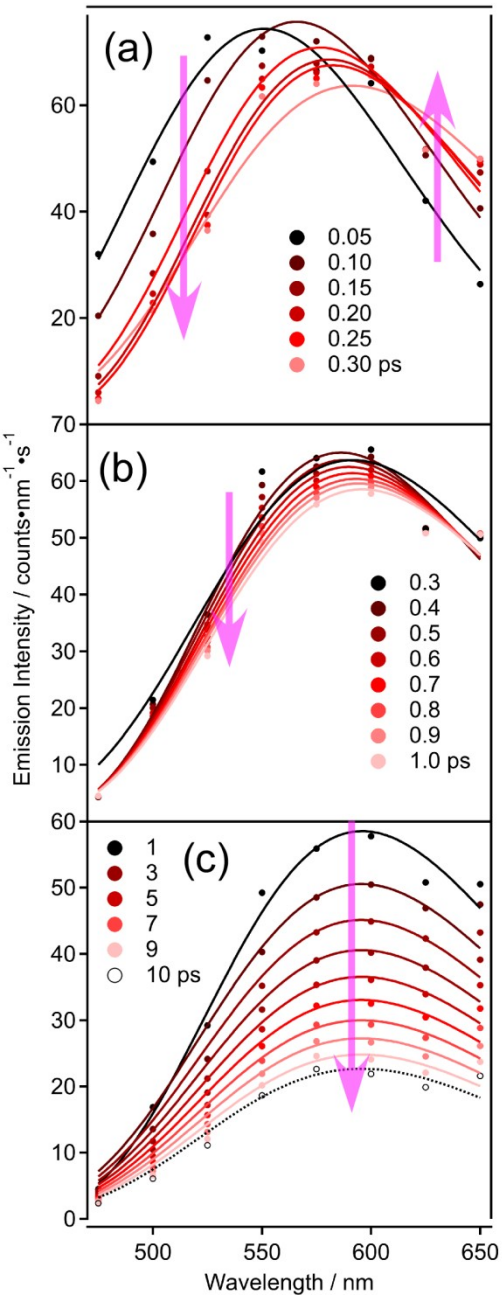

Figure S4. Femtosecond time-resolved emission spectra of Cu-monomer in acetonitrile. (a) 0.05 - 0.30 ps (b) 0.3 - 1.0 ps (c) 1 - 10 ps (λ_{ex} = 405 nm, 4.9×10^{-4} mol/dm^3). Solid lines are fittig curves.

5. Absorption spectrum and Species associated spectra of Cu-monomer

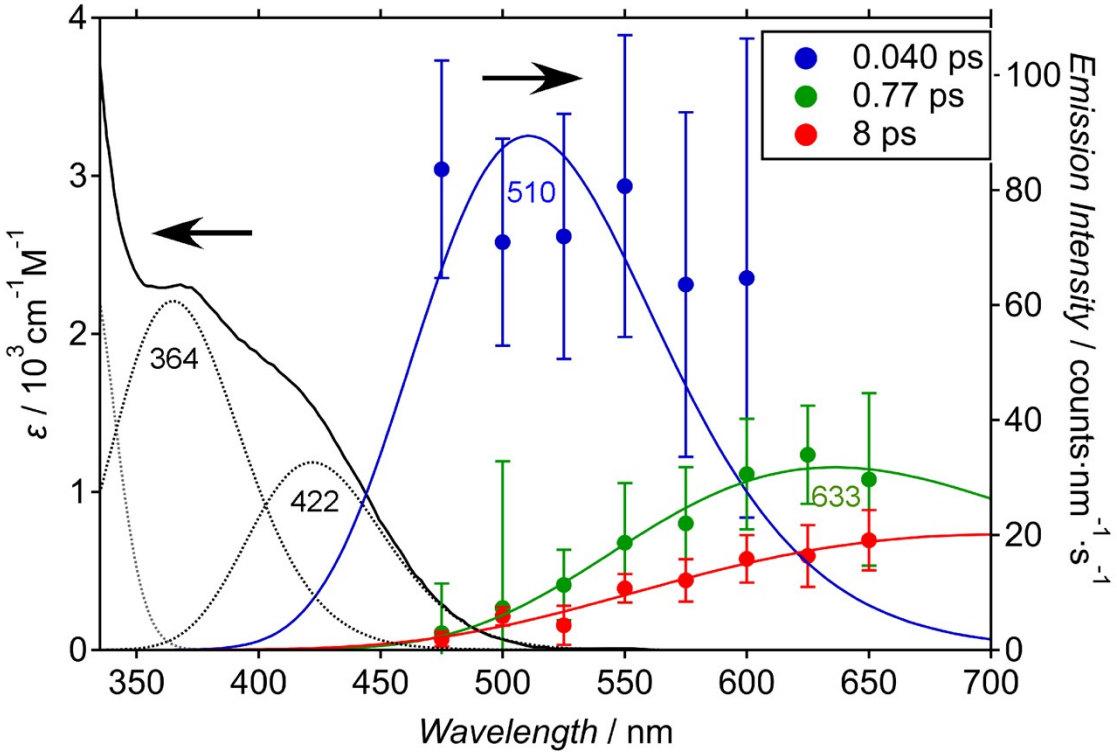

Figure S5. Absorption spectrum and species associated spectra of Cu-monomer in acetonitrile. Blue: 0.045-ps, Green: 0.72-ps, Red: 7.6-ps components. Fitting was performed with a multi-peak Gaussian line-shape function of wavenumber. Solid lines are fitting curves for the species-associated spectra made from the Gaussian line shape function represented in wavenumber. (λ_{ex} = 405 nm, 4.9 × 10^{-4} mol/dm^3) Black solid line is the absorption spectrum, where dotted lines are Gaussian line components represented in wavenumber estimated by the Gaussian multi peak fitting to the absorption spectrum. Numbers on the spectra are peak wavelengths (nm) of the absorption or emission bands.

6. TD-DFT calculations of Cu-monomer

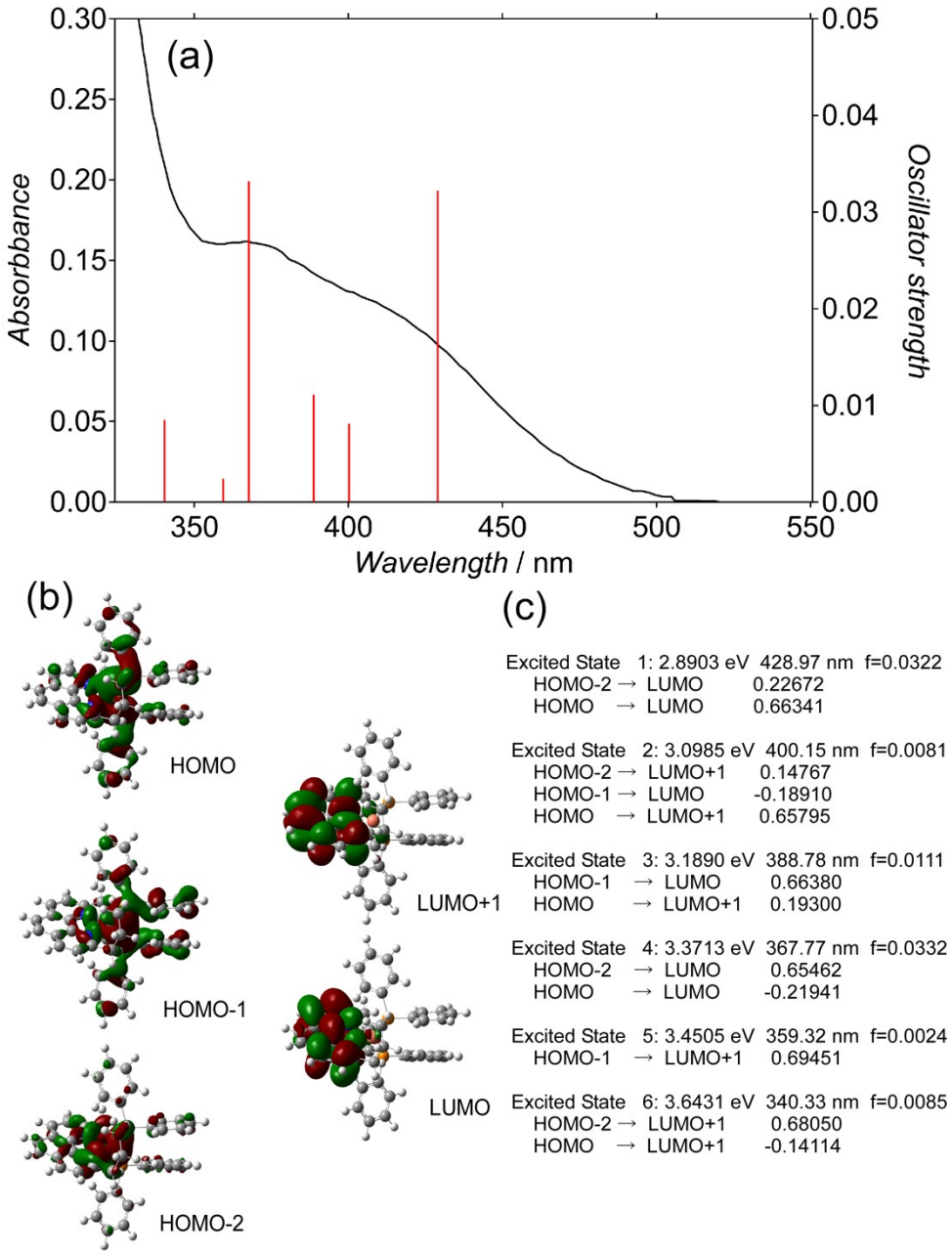

Figure S6. Absorption spectrum and results of TD-DFT Calculations of Cu-monomer. (a) Absorption spectrum and calculated oscillator strength in the electronic transitions of Cu-monomer. (b) Frontier orbitals of Cu-monomer. (c) Calculated electronic transitions in the visible region.

7. Optimized structures of Cu-monomer and Cu-dimer

Table S1. Optimized structure of Cu-monomer in the S_0 state in acetonitrile.

Atom	Coordinates (Angstroms)		
	X	Y	Z
Cu	0.311749	-0.023548	0.008517
P	-0.612595	2.088479	-0.609069
P	-0.802788	-2.047062	0.590478
N	1.925041	-0.194172	1.365609
N	1.939276	-0.017064	-1.330435
C	1.853581	-0.366038	2.696795
C	3.035881	-0.527375	3.468089
H	2.953616	-0.655158	4.542388
C	4.277986	-0.505209	2.848705
H	5.187771	-0.610830	3.433011
C	4.361035	-0.346249	1.440257
C	5.598950	-0.310405	0.708503
H	6.532097	-0.407865	1.256274
C	5.608281	-0.151251	-0.654497
H	6.549021	-0.118333	-1.196918
C	4.379551	-0.034475	-1.393280
C	4.313642	0.114749	-2.803782
H	5.231171	0.153659	-3.384230
C	3.078679	0.208196	-3.430894
H	3.010870	0.323458	-4.507633
C	1.884555	0.136317	-2.664388
C	3.138569	-0.209788	0.737431
C	3.147288	-0.079979	-0.695898
C	0.477320	-0.424447	3.299655
H	-0.197759	0.167974	2.669885
H	0.479448	0.028871	4.297570
C	-0.058339	-1.873589	3.421147
H	-1.098808	-1.814815	3.763740
H	0.499441	-2.395138	4.211499

C	0.036670	-2.733424	2.149752
H	-0.363451	-3.735629	2.344966
H	1.084580	-2.874963	1.858752
C	-2.631642	-2.161047	0.950653
C	-3.158863	-2.938075	1.998431
H	-2.503761	-3.497463	2.659853
C	-4.545273	-3.014750	2.196255
H	-4.940987	-3.617009	3.008798
C	-5.418235	-2.325669	1.341487
H	-6.491909	-2.391729	1.490850
C	-4.898741	-1.552952	0.292126
H	-5.566734	-1.017200	-0.375872
C	-3.512739	-1.466490	0.102102
H	-3.119254	-0.858406	-0.708488
C	-0.503688	-3.476645	-0.589947
C	-1.436583	-4.511142	-0.773026
H	-2.387792	-4.490798	-0.248984
C	-1.147912	-5.570884	-1.645825
H	-1.875067	-6.365377	-1.786149
C	0.073261	-5.607626	-2.334836
H	0.294476	-6.431300	-3.007234
C	1.004974	-4.573692	-2.156940
H	1.950028	-4.594621	-2.692316
C	0.714211	-3.507913	-1.293892
H	1.430185	-2.698033	-1.173322
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C	-3.335394	1.991852	0.098563
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C	-4.707106	2.243668	-0.036681
H	-5.390709	1.930996	0.747183
C	-5.193942	2.895840	-1.179938
H	-6.257055	3.090469	-1.286389
C	-4.301017	3.298759	-2.183198
H	-4.670615	3.806056	-3.069542
C	-2.925926	3.058801	-2.041548
H	-2.252291	3.398857	-2.822262

C	-0.122184	3.517496	0.505369
C	-0.829204	4.732171	0.515562
H	-1.715997	4.855616	-0.100257
C	-0.401820	5.786821	1.335039
H	-0.954731	6.721615	1.342101
C	0.734221	5.636907	2.144806
H	1.062918	6.456020	2.777685
C	1.439386	4.424298	2.139487
H	2.316116	4.302126	2.769226
C	1.009089	3.365519	1.326607
H	1.545893	2.419696	1.335628
C	0.235647	2.641674	-2.216567
H	-0.104943	3.658531	-2.447594
H	1.294488	2.731208	-1.944622
C	0.074489	1.739690	-3.451279
H	0.659359	2.193409	-4.263636
H	-0.969025	1.732442	-3.788843
C	0.516278	0.265773	-3.274549
H	-0.195912	-0.258626	-2.625451
H	0.489701	-0.224663	-4.254514

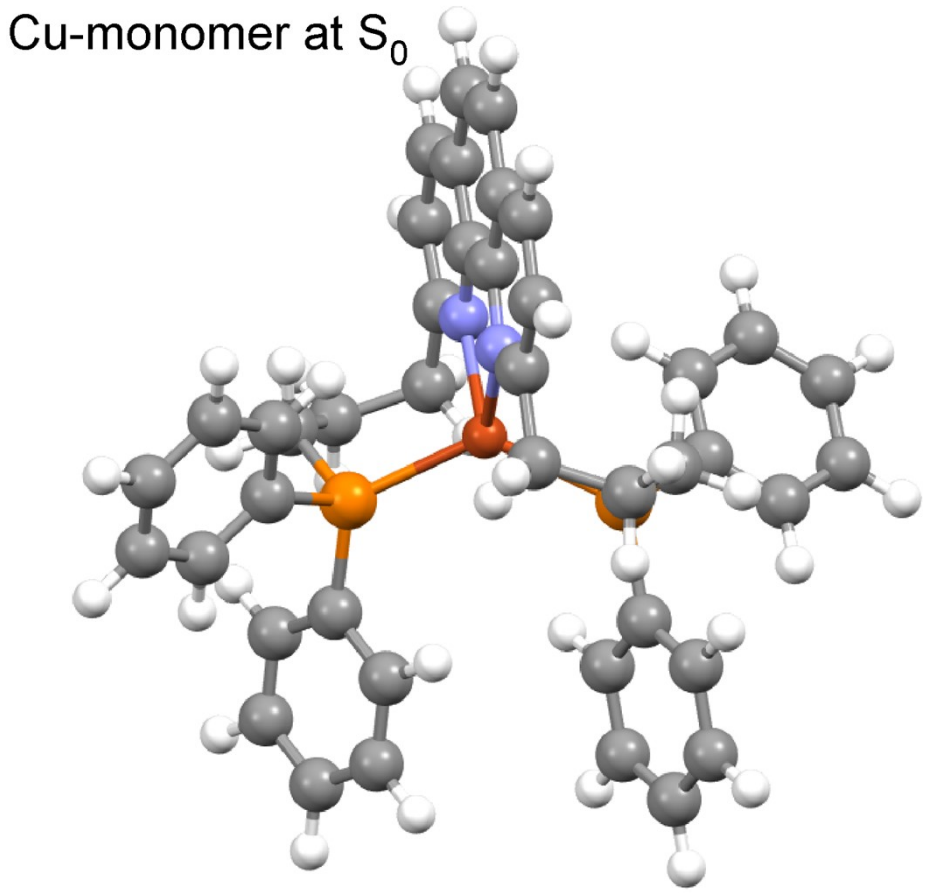

Figure S7. Optimized structure of Cu-monomer at S_0

Table S2. Optimized structure of Cu-monomer in the T_1 state in acetonitrile.

Atom	Coordinates (Angstroms)		
	X	Y	Z
Cu	0.492220	-0.000276	-0.000444
P	-0.793052	1.904059	-0.804095
P	-0.792213	-1.904485	0.804344
N	1.953653	-0.165595	1.325572
N	1.953773	0.166225	-1.326029
C	1.895649	-0.216213	2.691435
C	3.067146	-0.251428	3.452648
H	2.988569	-0.284509	4.534188
C	4.337839	-0.234823	2.827810

H	5.242972	-0.280163	3.425790
C	4.418349	-0.131941	1.432613
C	5.650022	-0.058361	0.682945
H	6.588939	-0.100707	1.228532
C	5.650084	0.060459	-0.682992
H	6.589051	0.103166	-1.228465
C	4.418466	0.133651	-1.432777
C	4.338052	0.236877	-2.827955
H	5.243246	0.282691	-3.425812
C	3.067448	0.253336	-3.452934
H	2.988966	0.286856	-4.534465
C	1.895883	0.217428	-2.691824
C	3.196886	-0.080890	0.695519
C	3.196945	0.081973	-0.695814
C	0.531076	-0.222070	3.332420
H	-0.161264	0.345061	2.695396
H	0.582489	0.311542	4.288012
C	-0.038083	-1.632964	3.597441
H	-1.060344	-1.522293	3.981290
H	0.545054	-2.110579	4.395612
C	-0.007560	-2.572380	2.385214
H	-0.478009	-3.535508	2.617554
H	1.029062	-2.788232	2.102801
C	-2.634803	-2.072430	0.992267
C	-3.219169	-2.605793	2.155050
H	-2.605591	-2.922467	2.992487
C	-4.611357	-2.751901	2.240649
H	-5.053807	-3.167123	3.141018
C	-5.427811	-2.374674	1.164483
H	-6.504680	-2.497508	1.229370
C	-4.848157	-1.841958	0.002870
H	-5.472957	-1.545448	-0.833953
C	-3.458823	-1.684341	-0.080799
H	-3.022342	-1.264056	-0.983273
C	-0.309840	-3.222171	-0.438599
C	-1.226544	-4.168800	-0.926154

H	-2.261993	-4.153118	-0.599796
C	-0.800813	-5.148605	-1.835296
H	-1.511239	-5.881929	-2.205040
C	0.535561	-5.188894	-2.259070
H	0.860978	-5.951035	-2.960619
C	1.451343	-4.243787	-1.772039
H	2.487587	-4.269690	-2.095233
C	1.031385	-3.259344	-0.868157
H	1.752138	-2.531176	-0.503076
C	-2.635656	2.071550	-0.992569
C	-3.459941	1.682905	0.080087
H	-3.023669	1.262476	0.982588
C	-4.849294	1.840139	-0.004019
H	-5.474289	1.543214	0.832510
C	-5.428707	2.373025	-1.165672
H	-6.505590	2.495558	-1.230894
C	-4.611982	2.750818	-2.241434
H	-5.054229	3.166179	-3.141839
C	-3.219780	2.605096	-2.155391
H	-2.606015	2.922225	-2.992512
C	-0.311519	3.221546	0.439387
C	-1.228675	4.167757	0.926896
H	-2.264011	4.151842	0.600201
C	-0.803542	5.147465	1.836425
H	-1.514324	5.880461	2.206137
C	0.532686	5.188081	2.260622
H	0.857641	5.950147	2.962466
C	1.448926	4.243399	1.773623
H	2.485067	4.269563	2.097128
C	1.029562	3.259051	0.869361
H	1.750658	2.531195	0.504331
C	-0.008183	2.572918	-2.384491
H	-0.478841	3.536030	-2.616477
H	1.028299	2.788947	-2.101687
C	-0.038094	1.634161	-3.597251
H	0.545124	2.112402	-4.394990

H	-1.060212	1.523414	-3.981455
C	0.531368	0.223258	-3.332929
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H	0.582988	-0.309847	-4.288793

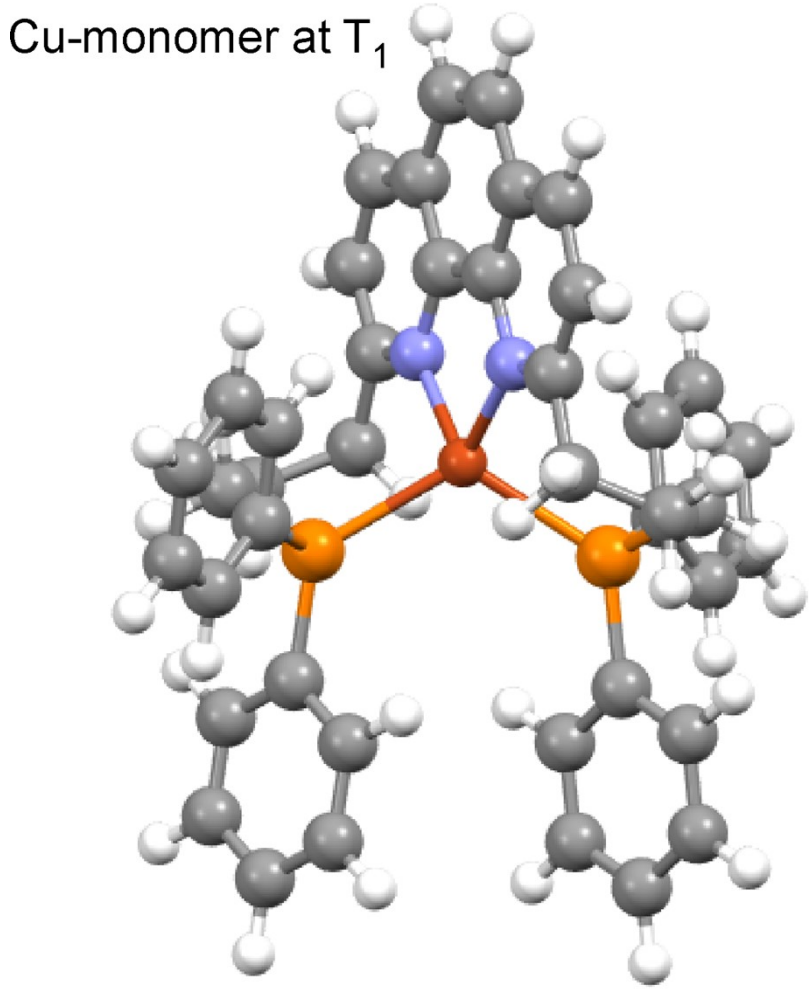


Figure S8. Optimized structure of Cu-monomer at T_1

Table S3. Optimized structure of Cu-dimer in the S_0 state in acetonitrile.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-2.913776	-0.353154	2.684036
C	-2.856537	-0.414216	4.093439
H	-1.902779	-0.588165	4.591137
C	-4.006553	-0.255436	4.835114
H	-3.976590	-0.302064	5.926820
C	-5.234845	-0.032572	4.181324
C	-6.472392	0.139516	4.879526
H	-6.467589	0.102089	5.971338
C	-7.633087	0.343169	4.197235
H	-8.576892	0.473012	4.731956
C	-7.643624	0.388550	2.766604
C	-8.820312	0.590019	2.012420
H	-9.775437	0.726868	2.525919
C	-8.748237	0.611711	0.639799
H	-9.645376	0.766561	0.036751
C	-7.501294	0.438307	-0.006595
C	-6.438473	0.227727	2.044579
C	-5.206938	0.011847	2.766070
C	-1.691521	-0.487725	1.820668
H	-1.515063	0.499952	1.357548
H	-1.959185	-1.154348	0.982673
C	-0.418335	-0.966971	2.500853
H	-0.605559	-1.928934	3.009833
H	-0.121615	-0.248642	3.283994
C	0.748015	-1.128642	1.529916
H	0.927252	-0.170582	1.015295
H	0.480138	-1.860980	0.748302
C	2.020969	-1.566268	2.240719
H	2.308694	-0.793727	2.971792
H	1.856603	-2.493747	2.813909
C	3.035010	-3.238538	0.089960

C	3.475024	-3.251847	-1.238992
H	4.044016	-2.400297	-1.619250
C	3.205582	-4.344134	-2.065501
H	3.567758	-4.349215	-3.096461
C	2.483248	-5.428795	-1.572197
H	2.273348	-6.286587	-2.215633
C	2.034745	-5.422104	-0.249475
H	1.476077	-6.275454	0.142417
C	2.312741	-4.337404	0.578901
H	1.977908	-4.362298	1.619181
C	4.690307	-2.566254	2.327547
C	5.528247	-3.613884	1.923491
H	5.421822	-4.048035	0.926268
C	6.495174	-4.119855	2.791430
H	7.134459	-4.944036	2.465656
C	6.640960	-3.587222	4.071532
H	7.394605	-3.990050	4.752131
C	5.811821	-2.543774	4.482156
H	5.913142	-2.127134	5.487321
C	4.846138	-2.033923	3.616028
H	4.208863	-1.214852	3.959579
C	-2.870748	-2.300351	-2.289847
C	-1.717392	-2.794198	-1.660114
H	-1.745859	-3.050824	-0.597051
C	-0.543013	-2.999779	-2.379897
H	0.339167	-3.406385	-1.878320
C	-0.499804	-2.710726	-3.745219
H	0.417043	-2.885982	-4.313292
C	-1.637070	-2.218983	-4.382375
H	-1.618337	-2.007585	-5.454470
C	-2.814795	-2.014055	-3.660762
H	-3.697456	-1.646165	-4.188896
C	-4.567331	-3.548098	-0.343301
C	-4.950131	-3.484113	1.001169
H	-5.077435	-2.507702	1.473888
C	-5.169747	-4.654001	1.729444

H	-5.472842	-4.594666	2.777495
C	-5.003911	-5.894586	1.118618
H	-5.176728	-6.811903	1.686582
C	-4.617927	-5.966990	-0.221652
H	-4.489026	-6.940165	-0.701466
C	-4.400429	-4.801292	-0.950782
H	-4.093612	-4.868437	-1.998509
C	-5.749839	-2.092212	-2.511026
H	-5.651459	-1.229389	-3.190979
H	-5.578772	-2.994555	-3.118962
C	-7.150803	-2.111772	-1.872063
H	-7.702162	-2.976967	-2.269742
H	-7.084274	-2.295070	-0.785372
C	-7.976552	-0.856184	-2.136445
H	-9.008582	-1.024178	-1.785287
H	-8.054473	-0.694481	-3.224752
C	-7.423416	0.425612	-1.503095
H	-6.373453	0.576778	-1.792335
H	-7.983580	1.289721	-1.895139
N	-4.068153	-0.148980	2.053770
N	-6.386234	0.260322	0.693082
P	-4.370496	-1.984809	-1.279362
P	3.496504	-1.812633	1.149139
Cu	-4.401294	-0.025394	-0.056105
C	2.913351	0.352356	-2.684013
C	2.855921	0.413031	-4.093427
H	1.902096	0.586822	-4.591049
C	4.005845	0.254054	-4.835209
H	3.975748	0.300416	-5.926921
C	5.234229	0.031384	-4.181515
C	6.471712	-0.140779	-4.879817
H	6.466788	-0.103536	-5.971636
C	7.632499	-0.344235	-4.197619
H	8.576255	-0.474093	-4.732423
C	7.643198	-0.389357	-2.766979
C	8.819973	-0.590604	-2.012872

H	9.775063	-0.727441	-2.526436
C	8.748038	-0.612029	-0.640235
H	9.645260	-0.766630	-0.037244
C	7.501148	-0.438605	0.006250
C	6.438109	-0.228494	-2.044865
C	5.206486	-0.012755	-2.766254
C	1.691250	0.487438	-1.820483
H	1.514469	-0.500160	-1.357335
H	1.959248	1.153965	-0.982510
C	0.418156	0.967244	-2.500481
H	0.605488	1.929525	-3.008817
H	0.121474	0.249439	-3.284124
C	-0.748257	1.128448	-1.529540
H	-0.927717	0.170074	-1.015580
H	-0.480294	1.860214	-0.747413
C	-2.021092	1.566797	-2.240122
H	-2.308989	0.794786	-2.971696
H	-1.856405	2.494587	-2.812727
C	-3.034883	3.238446	-0.088781
C	-3.476008	3.252020	1.239813
H	-4.045957	2.400881	1.619573
C	-3.206370	4.344047	2.066604
H	-3.569394	4.349378	3.097266
C	-2.482617	5.428079	1.573992
H	-2.272569	6.285672	2.217645
C	-2.032920	5.421054	0.251679
H	-1.473081	6.273894	-0.139649
C	-2.311182	4.336673	-0.577022
H	-1.975223	4.361206	-1.616951
C	-4.690423	2.567098	-2.326377
C	-5.528744	3.614175	-1.921713
H	-5.422640	4.047630	-0.924150
C	-6.495640	4.120501	-2.789477
H	-7.135227	4.944259	-2.463224
C	-6.641012	3.588786	-4.070006
H	-7.394642	3.991910	-4.750447

C	-5.811468	2.545903	-4.481255
H	-5.912438	2.130003	-5.486762
C	-4.845812	2.035695	-3.615302
H	-4.208170	1.217125	-3.959355
C	2.870922	2.301002	2.289202
C	1.717353	2.793950	1.659141
H	1.745546	3.049440	0.595795
C	0.543027	3.000001	2.378869
H	-0.339304	3.405954	1.877017
C	0.500049	2.712252	3.744476
H	-0.416764	2.887869	4.312494
C	1.637462	2.221239	4.381934
H	1.618880	2.010730	5.454206
C	2.815138	2.015854	3.660359
H	3.697883	1.648474	4.188702
C	4.567522	3.548044	0.342274
C	4.949740	3.483549	-1.002343
H	5.076359	2.506954	-1.474892
C	5.169600	4.653161	-1.730986
H	5.472227	4.593445	-2.779150
C	5.004568	5.893970	-1.120389
H	5.177577	6.811067	-1.688650
C	4.619189	5.966880	0.220021
H	4.490974	6.940235	0.699656
C	4.401496	4.801456	0.949540
H	4.095249	4.868970	1.997405
C	5.750090	2.092635	2.510316
H	5.651758	1.229984	3.190494
H	5.579158	2.995159	3.118023
C	7.150969	2.111954	1.871147
H	7.702424	2.977242	2.268488
H	7.084264	2.294918	0.784410
C	7.976711	0.856395	2.135697
H	9.008689	1.024264	1.784325
H	8.054818	0.694953	3.224027
C	7.423411	-0.425536	1.502755

H	6.373468	-0.576545	1.792150
H	7.983547	-1.289591	1.894963
N	4.067791	0.148225	-2.053855
N	6.386002	-0.260877	-0.693362
P	4.370647	1.985028	1.278797
P	-3.496558	1.812949	-1.148365
Cu	4.401321	0.025354	0.056058

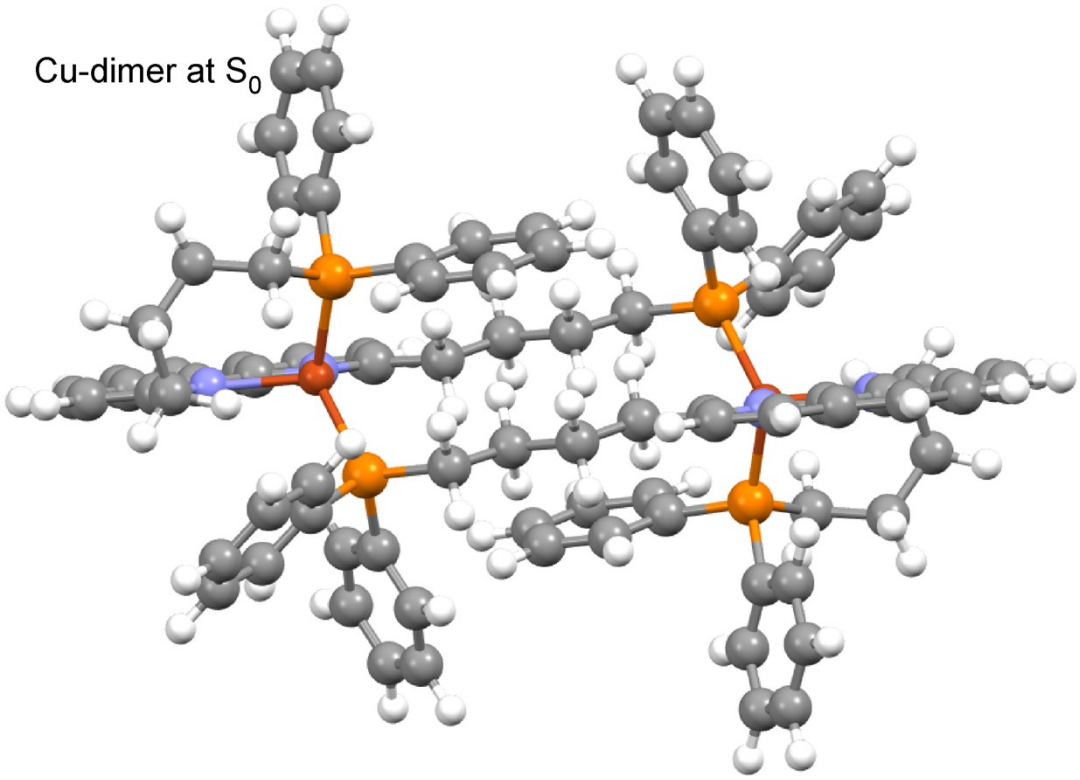


Figure S9. Optimized structure of Cu-dimer at S_0

Table S4. Optimized structure of Cu-dimer in the T_1 state in acetonitrile.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.137595	0.166199	2.751706
C	3.127547	0.142630	4.162183
H	2.202356	0.340649	4.703398
C	4.290615	-0.129787	4.850685
H	4.299074	-0.149792	5.943540
C	5.481231	-0.384755	4.141113
C	6.727816	-0.678276	4.780816
H	6.762580	-0.709914	5.872213
C	7.849167	-0.911023	4.043887
H	8.799798	-1.133358	4.534162
C	7.810054	-0.865789	2.613422
C	8.945338	-1.092021	1.804670
H	9.906133	-1.322095	2.272139
C	8.826178	-1.019116	0.436973
H	9.690755	-1.190788	-0.207585
C	7.572608	-0.724638	-0.150625
C	6.595335	-0.583081	1.947965
C	5.405693	-0.337615	2.727503
C	1.910779	0.432791	1.927639
H	1.802433	-0.424214	1.240431
H	2.138327	1.292218	1.272267
C	0.601460	0.666644	2.663963
H	0.696477	1.528871	3.347052
H	0.362586	-0.208051	3.293389
C	-0.552572	0.914904	1.696295
H	-0.625292	0.070128	0.994616
H	-0.330083	1.807543	1.086803
C	-1.882980	1.091066	2.414210
H	-2.166358	0.151997	2.915937
H	-1.809018	1.859761	3.201972
C	-2.829121	3.150167	0.557367

C	-3.207296	3.410312	-0.765472
H	-3.738285	2.646447	-1.338844
C	-2.911108	4.642834	-1.350540
H	-3.221310	4.839774	-2.379329
C	-2.230138	5.616541	-0.623371
H	-2.001503	6.582313	-1.080342
C	-1.847302	5.361552	0.695753
H	-1.322395	6.127549	1.271372
C	-2.149312	4.138274	1.287321
H	-1.868261	3.966721	2.329615
C	-4.573926	2.077056	2.570233
C	-5.418420	3.163190	2.298963
H	-5.291999	3.742280	1.380989
C	-6.413292	3.523169	3.205736
H	-7.056480	4.379319	2.989178
C	-6.582450	2.802401	4.387338
H	-7.358174	3.091517	5.100116
C	-5.751058	1.716277	4.660987
H	-5.872147	1.155807	5.591184
C	-4.754518	1.350455	3.757459
H	-4.107717	0.502350	3.995627
C	3.071573	2.474928	-2.071786
C	1.979450	3.007620	-1.368875
H	2.059447	3.183217	-0.291954
C	0.804488	3.354298	-2.030889
H	-0.029755	3.784369	-1.470616
C	0.697962	3.170664	-3.410965
H	-0.221338	3.448007	-3.932129
C	1.774973	2.643906	-4.120596
H	1.707046	2.512521	-5.203347
C	2.953646	2.297163	-3.457018
H	3.788123	1.901197	-4.040185
C	4.910931	3.465061	-0.116297
C	5.297512	3.296387	1.217929
H	5.351002	2.288132	1.634773
C	5.613442	4.402791	2.007603

H	5.918059	4.260845	3.047195
C	5.542602	5.684998	1.468540
H	5.791293	6.552607	2.084355
C	5.155153	5.862226	0.138442
H	5.100647	6.867613	-0.285847
C	4.840862	4.760049	-0.651178
H	4.533303	4.911722	-1.689822
C	5.915247	2.074593	-2.413738
H	5.732387	1.265464	-3.140623
H	5.784373	3.022097	-2.959691
C	7.336429	1.963019	-1.832302
H	7.929480	2.814228	-2.198976
H	7.322040	2.082243	-0.734762
C	8.065633	0.676450	-2.207203
H	9.117532	0.752485	-1.884306
H	8.097238	0.583601	-3.305780
C	7.447222	-0.606162	-1.639313
H	6.380489	-0.668903	-1.900242
H	7.935735	-1.476310	-2.106339
N	4.256848	-0.064992	2.069379
N	6.495418	-0.523381	0.600154
P	4.574565	1.981211	-1.138801
P	-3.310293	1.571927	1.343096
Cu	4.508173	-0.062599	-0.050763
C	-2.854680	0.271376	-2.621774
C	-2.741403	0.384348	-3.996108
H	-1.760674	0.300130	-4.461770
C	-3.876206	0.608941	-4.803014
H	-3.778326	0.714510	-5.885194
C	-5.132199	0.670773	-4.203158
C	-6.356982	0.854166	-4.932124
H	-6.298301	0.961998	-6.017920
C	-7.562739	0.896045	-4.301068
H	-8.482877	1.048051	-4.870302
C	-7.654982	0.742961	-2.880215
C	-8.850691	0.793312	-2.166465

H	-9.794260	0.944844	-2.696198
C	-8.829085	0.672967	-0.775011
H	-9.751131	0.750494	-0.196512
C	-7.621619	0.459016	-0.103330
C	-6.448277	0.542670	-2.143539
C	-5.202992	0.532760	-2.787008
C	-1.657305	0.042783	-1.739474
H	-1.428687	0.983982	-1.205919
H	-1.952136	-0.678408	-0.955193
C	-0.404677	-0.453153	-2.451522
H	-0.655271	-1.353009	-3.039354
H	-0.069377	0.307220	-3.175312
C	0.760387	-0.769208	-1.519484
H	1.032633	0.132551	-0.947239
H	0.452679	-1.534476	-0.784726
C	1.980927	-1.255045	-2.291464
H	2.332958	-0.446845	-2.952718
H	1.722245	-2.106537	-2.942836
C	2.822092	-3.180027	-0.291333
C	3.173244	-3.295680	1.058695
H	3.777020	-2.511204	1.520891
C	2.773486	-4.406732	1.804077
H	3.069832	-4.493975	2.852320
C	2.010256	-5.407634	1.206509
H	1.701466	-6.281672	1.785034
C	1.650632	-5.298639	-0.139086
H	1.062212	-6.087803	-0.613273
C	2.057795	-4.195786	-0.885447
H	1.793243	-4.140386	-1.944673
C	4.543508	-2.524259	-2.478104
C	5.346869	-3.609140	-2.100302
H	5.253577	-4.037500	-1.099007
C	6.259682	-4.159082	-2.998312
H	6.870198	-5.012546	-2.693516
C	6.387999	-3.631774	-4.283104
H	7.099406	-4.068240	-4.987931

C	5.595210	-2.551112	-4.666687
H	5.682256	-2.138918	-5.674931
C	4.680687	-1.998428	-3.770744
H	4.068831	-1.153647	-4.096636
C	-3.308337	-2.365278	2.150841
C	-2.129841	-2.698033	1.463709
H	-2.130783	-2.747564	0.371266
C	-0.966743	-3.012583	2.162166
H	-0.062522	-3.294451	1.616267
C	-0.962608	-2.993542	3.558264
H	-0.053855	-3.254851	4.105767
C	-2.126327	-2.662962	4.250671
H	-2.135065	-2.664119	5.343242
C	-3.293998	-2.350756	3.552897
H	-4.198500	-2.117380	4.118206
C	-4.919169	-3.276407	-0.050666
C	-5.282358	-2.987701	-1.371752
H	-5.449464	-1.955628	-1.685938
C	-5.436671	-4.020867	-2.296599
H	-5.722546	-3.785803	-3.324190
C	-5.229808	-5.342181	-1.908928
H	-5.354008	-6.150657	-2.633263
C	-4.865485	-5.635754	-0.592965
H	-4.705446	-6.672228	-0.286892
C	-4.709268	-4.610195	0.334092
H	-4.418222	-4.851966	1.360161
C	-6.203312	-2.269133	2.328078
H	-6.128373	-1.567970	3.176040
H	-6.009497	-3.277328	2.728335
C	-7.597581	-2.188912	1.690928
H	-8.205550	-3.009203	2.101683
H	-7.544889	-2.384315	0.605843
C	-8.316041	-0.873587	1.960952
H	-9.340757	-0.934149	1.560737
H	-8.426186	-0.741406	3.050878
C	-7.616008	0.361951	1.396402

H	-6.579281	0.419710	1.760553
H	-8.116929	1.261321	1.789110
N	-4.068870	0.372989	-2.005034
N	-6.461898	0.365458	-0.774302
P	-4.797894	-1.931218	1.181547
P	3.432065	-1.734525	-1.246091
Cu	-4.591068	0.109592	-0.094420

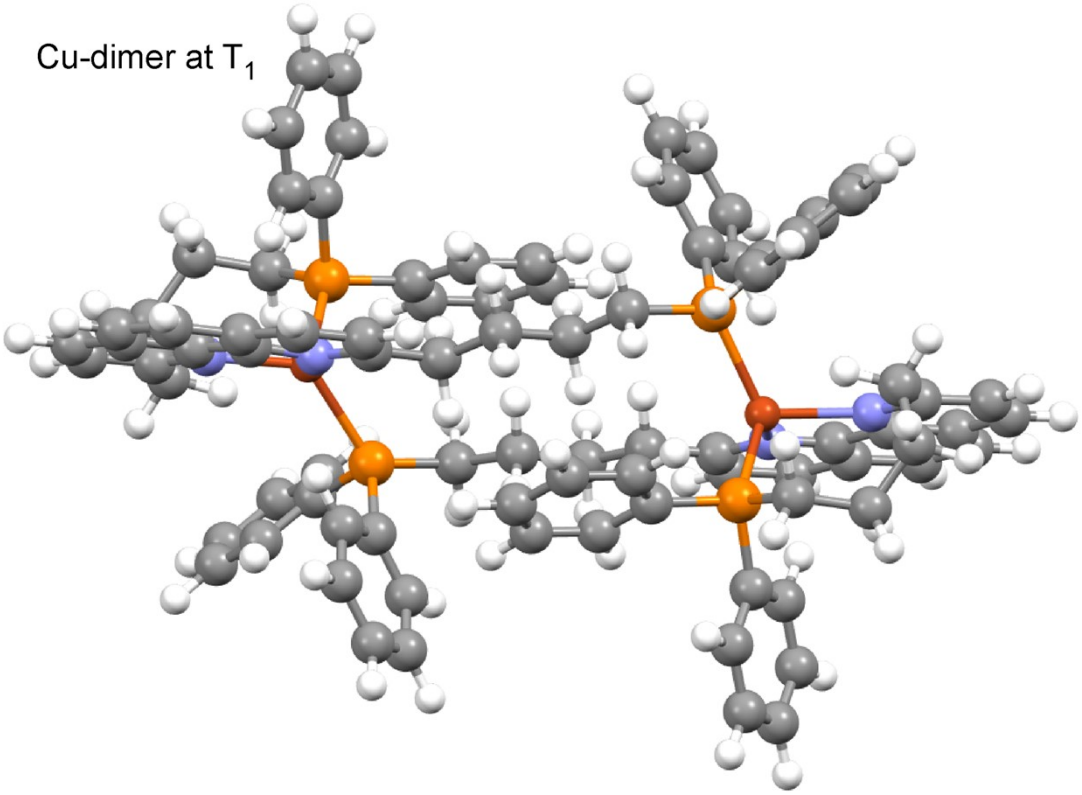
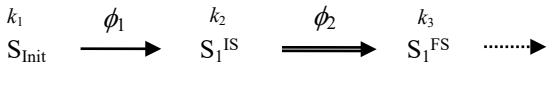


Figure S10. Optimized structure of Cu-monomer at T_1

8. Procedure for obtaining species-associated spectra

We evaluate species-associated spectra from the fitting analysis of the time-resolved fluorescence data with the multi-exponential function. In the analysis, we assume that the sequential relaxation process occurs after the $S_{Init} \leftarrow S_0$ excitation in Scheme S1,



(Scheme S1)

Here, k_1, k_2 and k_3 are decay rate constants from the S_{Init}, S_1^{IS} and S_1^{FS}, respectively and ϕ_1 and ϕ_2 are yields of the $S_{Init} \rightarrow S_1^{IS}$ and the $S_1^{FS} \rightarrow S_1^{IS}$ transitions, respectively. By solving the rate equations corresponding to this scheme with an initial condition that only the S_{Init} state is populated at $t = 0$, we obtain the following expressions for the time-dependent population of each excited state:

$$[S_{Init}(t)] = [S_{Init}]_0 \exp(-k_1 t) \quad \text{(S1)}$$

$$[S_1^{IS}(t)] = \phi_2 [S_{Init}]_0 \frac{k_1}{k_1 + k_2} (\exp(-k_2 t) - \exp(-k_1 t)) \quad \text{(S2)}$$

$$[S_1^{FS}(t)] = \phi_1 \phi_2 [S_{Init}]_0 k_1 k_2 \left\{ \frac{exp(-k_1 t)}{(k_2 - k_1)(k_3 - k_1)} + \frac{exp(-k_2 t)}{(k_1 - k_2)(k_3 - k_1)} + \frac{exp(-k_3 t)}{(k_1 - k_3)(k_2 - k_3)} \right\}. \quad \text{(S3)}$$

The time-resolved emission intensity observed at each wavelength is the sum of these three contributions, and it can be written as:

$$\begin{aligned} I(t,\lambda) &= a_1(\lambda)[S_{Init}(t)] + a_2(\lambda)[S_1^{IS}(t)] + a_3(\lambda)[S_1^{FS}(t)] \\ &= A_1(\lambda)\exp(-k_1 t) + A_2(\lambda)\exp(-k_2 t) + A_3(\lambda)\exp(-k_3 t) \end{aligned} \quad \text{(S4)}$$

The coefficient $a_1(\lambda)$, $a_2(\lambda)$ and $a_3(\lambda)$ denote the intrinsic radiative transition probability of S_{Init}, S_1^{IS} and S_1^{FS} at wavelength λ, respectively and it is related to the amplitudes of the three exponential components (A_i's) that can be obtained by the fitting analysis of the observed time-resolved emission signals:

$$a_1(\lambda) \cdot C_0 \propto A_1(\lambda) + A_2(\lambda) + A_3(\lambda), \quad \text{(S5)}$$

$$a_2(\lambda) \cdot \phi_2 \cdot C_0 \propto \frac{1}{k_1}[(k_1 - k_2)A_2(\lambda) + (k_2 - k_3)A_3(\lambda)] \quad \text{(S6)}$$

$$a_3(\lambda) \cdot \phi_1 \cdot \phi_2 \cdot C_0 \propto \left\{ \frac{(k_1 - k_2)(k_2 - k_3)}{k_1 k_2} \right\} A_3(\lambda). \quad \text{(S7)}$$

Here, C_0 is the population (concentration) of the excited state species at $t = 0$ (*i.e.*, C_0

= $[S_{Init}]_0$ in the case of $S_{Init} \leftarrow S_0$ excitation). The relative values of a_1, $a_2 \cdot \phi_1$ and $a_3 \cdot \phi_1 \cdot \phi_2$ are evaluated at each wavelength with equations (5) – (7), and the species-associated spectra (a_1, $a_2 \cdot \phi_1$ and $a_3 \cdot \phi_1 \cdot \phi_2$ at various wavelength) are shown in Figure 6 for Cu-dimer and Figure S5 for Cu-monomer. The spectra are denoted with their time constants such as 0.040-ps, 0.72-ps and 8.0 ps components in Figure 6 and 0.045-ps, 0.72 ps and 7.6-ps components in Figure S5, respectively. Because ϕ_1 and ϕ_2 are evaluated as unity as described in the main text, the radiative rate constants of a_1-a_3 were directly estimated from the area intensity of the species-associated fluorescence spectra (Table 1).

9. Synthesis of Cu-monomer

A THF solution (200 ml) containing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bcp: 909 mg, 2.52 mmol) and CuI (528 mg, 55.4 mmol) was degassed by bubbling using cooled N_2 gas, followed by cooling to –45ºC. A LDA solution (6.09 ml, 6.09 mmol, 1.0 M in THF/*n*-hexane) was added dropwise to the solution, turning color to red-purple, and the mixture was stirred for 15 min at r.t. under a N_2 atmosphere. The solution was transferred to deoxygenized 1-chloro-2-bromoethane (10 g) under a N_2 atmosphere at r.t. The resulting solution was stirred for one night. The reaction was quenched by addition of CH_3OH and dried using a rotary evaporator. The residue was dissolved in CH_2Cl_2 and washed with water three times. The CH_2Cl_2 phase was recovered and the solvent was removed by a rotary evaporator. The residue was dissolved in CH_2Cl_2 again and re-precipitated with *n*-hexane. This re-precipitation was repeated three times in order to remove excess amount of 1-chloro-2-bromoethane and the red precipitate was recovered by decantation and dried in vacuo. This was dissolved in THF (25 ml) and degassed by bubbling using N_2 gas. Another THF solution (50 ml) containing diphenylphosphine (716 mg, 3.85 mmol) was degassed by bubbling using cooled N_2 gas and cooled to 0ºC. A ^{n}BuLi (2.4 ml, 3.85 mmol, 1.6 M in *n*-hexane) was added dropwise to this solution and stirred at r.t. for 15 min. This THF solution was added to the prepared THF solution at r.t. and stirred for 2 h at r.t. This reaction was quenched by the addition of KPF_6 aqueous solution and extracted with CH_2Cl_2. The recovered CH_2Cl_2 solution was washed with water three times and dried using a rotary evaporator. This phosphination was repeated one more time. The obtained solid was purified by sequential column chromatography on alumina (3 cm × 8 cm; aluminum oxide 90 standard (Merck)) with CH_2Cl_2 and on silica gel (3 cm × 15 cm; silica gel 60 (Kanto)) with CH_2Cl_2/Et_2O/*n*-hexane (1:1:1 v/v/v). The recovered sample was purified by the preparative size-exclusion chromatography[S1] two times. Because the sample still contained impurity, it was further purified by column chromatography on alumina (2.5 cm × 9 cm; aluminum oxide 90 standard (Merck)) with CH_2Cl_2 and CH_2Cl_2/CH_3CN (10%), on silica gel (2.5 cm × 6 cm; silica gel 60 (Kanto)) with CH_2Cl_2/Et_2O/*n*-hexane (1:1:1 v/v/v), and on alumina (2.5 cm × 8 cm; aluminum oxide 90 standard (Merck)) with CH_2Cl_2/Et_2O (1:1 v/v), CH_2Cl_2, and CH_2Cl_2/CH_3CN (10%). The recovered sample was further purified by the preparative size-exclusion chromatography and column chromatography on alumina (2 cm × 8 cm; aluminum oxide 90 standard (Merck)) with CH_2Cl_2/Et_2O (1:1 v/v), CH_2Cl_2, and CH_2Cl_2/CH_3CN (4%). The purified sample was finally obtained by further

purification through a re-precipitation using CH_2Cl_2/*n*-hexane. The sample was dried in vacuo at 80ºC. Yield: 29.3 mg (1.2%). ^{1}H NMR (400 MHz, JEOL ECA-400II spectrometer, CD_3CN): δ /ppm, 7.98 (2H, s, 5,6-phen), 7.77 (2H, s, 3,8-phen), 7.63–7.57 (10H, m, *Ph*-bcp), 7.57-7.48 (4H, br, $o_{3,4}$-P*Ph*$_2$-), 7.48-7.37 (2H, $p_{3,4}$-P*Ph*$_2$-), 7.37-7.27 (4H, br, $m_{3,4}$-P*Ph*$_2$-), 7.27-7.19 (2H, br, $p_{1,2}$-PPh$_2$-), 7.19-7.09 (8H, br, *o,* $m_{1,2}$-P*Ph*$_2$-), 3.66-3.37 (4H, m, -C*H*$_2$phen), 2.55-2.40 (2H, br, -C*H*$_2$PPh$_2$), 2.16-2.05 (4H, br, -C*H*$_2$PPh$_2$, -CH$_2$C*H*$_2$CH$_2$PPh$_2$), 2.04-1.96 (2H, br, -CH$_2$C*H*$_2$CH$_2$PPh$_2$). ESI-MS: m/z, 847 [M –PF$_6$]$^+$. Anal. Calcd (%) for $C_{54}H_{46}CuF_6N_2P_2$: C, 65.29; H, 4.67; N, 2.82. Found: C, 65.55; H, 4.86; N, 2.89.

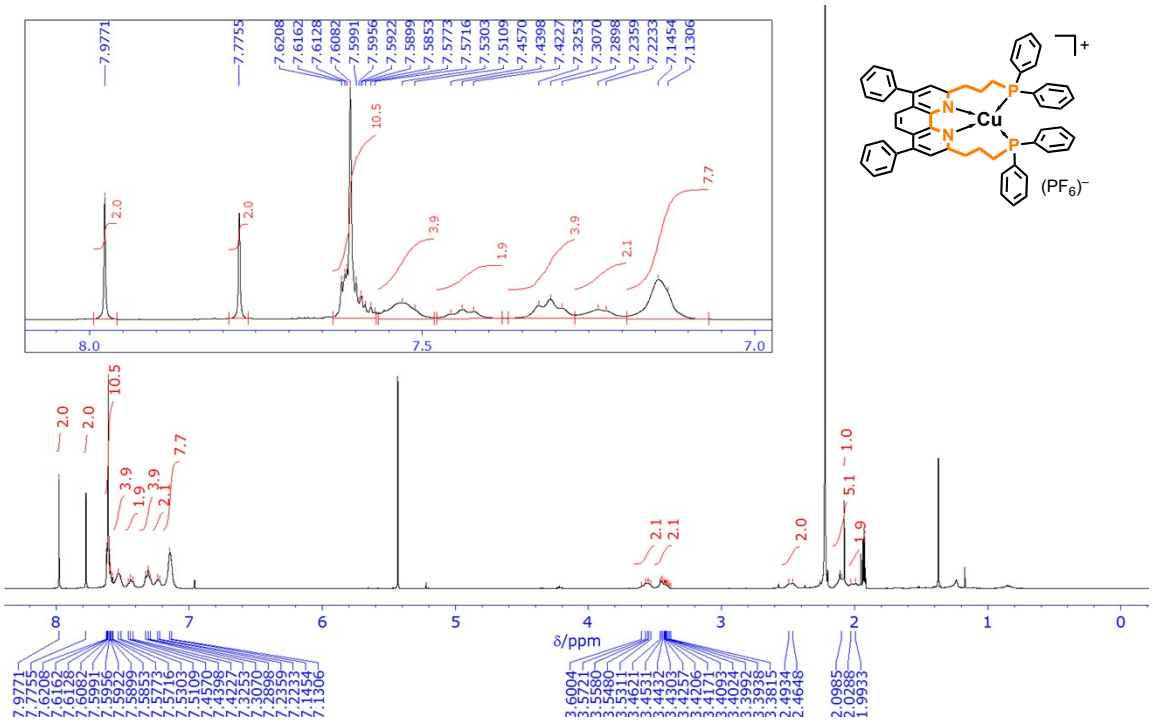


Figure S11. ^{1}H NMR spectrum (400 MHz, CD_3CN at r.t.) of Cu-monomer

10. Crystal structure of Cu-monomer

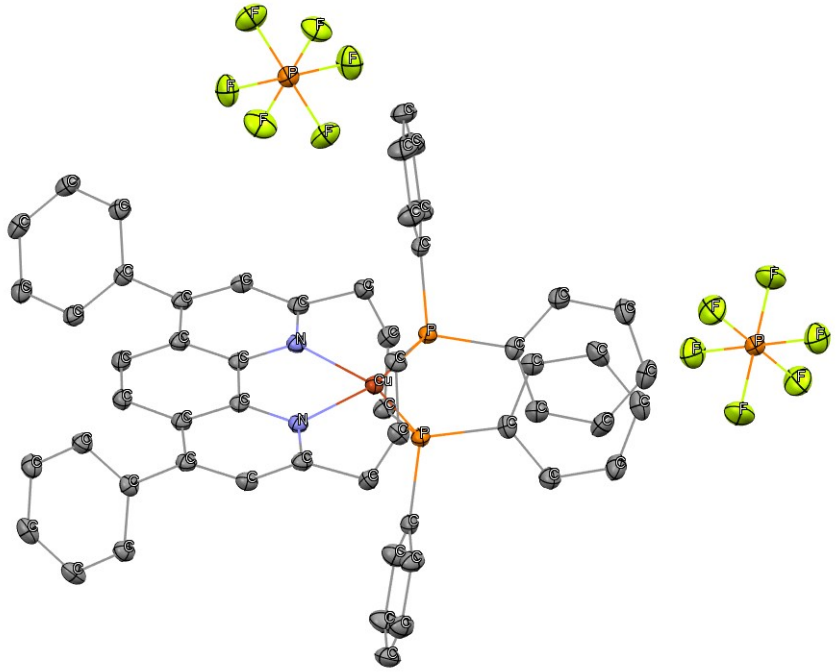


Figure S12. Ortep drawing of Cu-monomer

Table S5 Crystallograhic data for Cu-monomer

empirical formula	C_{54} H_{46} Cu N_2 P_2 P F_6
formula weight	466.69
crystal system triclinic monoclinic	
space group	*P–3 C1/*
a / Å	19.7560(4)
b / Å	19.7560(4)
c / Å	20.2456(4)
α / deg	90
β / deg	90
γ / deg	120
V / Å^3	6843.2(3)
Z	12
T / K	93(2)
Number of total reflections	70220
R1	0.0377

Table S6. Selected bond lengths (Å) and angles (º) for Cu-monomer

Bond Lengths					
Cu(1)–P(1)	2.2502(5)	Cu(1)–N(1)	2.0782(16)	P(1)–C(9)	1.8563(19)
P(1)–C(10)	1.8290(19)	P(1)–C(16)	1.8352(19)	C(1)–C(7)	1.499(3)
Bond Angles					
P(1)–Cu(1)–P(1)^{i}	125.32(3)	P(1)–Cu(1)–N(1)	122.27(4)	P(1)^{i}–Cu(1)–N(1)	100.05(4)
N(1)–Cu(1)–N(1)^{i}	79.09(8)	Cu(1)–P(1)–C(10)	116.11(6)	Cu(1)–P(1)–C(16)	119.02(6)
Cu(1)–P(1)–C(9)	109.07(6)	C(10)–P(1)–C(16)	103.74(9)	C(9)–P(1)–C(10)	105.65(9)
C(9)–P(1)–C(16)	101.60(9)				
Symmetry code: (i) x-y, -y, -z+1/2.					

Suitable crystals (Yellow platelet crystal, 0.18 × 0.10 × 0.07 mm^3) for X-ray diffraction analysis were obtained by slow cooling of CH_3OH solution from 40ºC to r.t.

Diffraction data were collected on a Rigaku R-AXIS RAPID II (SPIDER) imaging-plate diffractometer using a Rigaku VariMaxCu confocal optical system with monochromated Cu-Kα radiation (λ = 1.54184 Å) at 93 K with a Rigaku low-temperature apparatus. The structure was solved by the direct methods using the SIR2014[S2] program and was refined on F^2 by means of full-matrix least-squares procedures, using the SHELXL-2014/6 program.[S3] Details of the crystallographic data are given in Tables S1 and S2.

In the least-squares refinements, all non-hydrogen atoms were refined with anisotropic displacement parameters. For each methylene group and each aromatic C-H bond, the H atoms were calculated using a riding-model with isotropic thermal parameters 1.2 times those of the attached C atoms. Crystallographic data for the structure of Cu-monomer have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2248070).

References

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S3. G. M. Sheldrick, *Acta Cryst.* 2008, ***A64***, 112-122.