Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary info for “Frenkel excitons in a copper azadipyrrin complex”

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For computational output below the Gaussian log file is available upon request (M.Waterland@massey.ac.nz).

A. Output from UB3LYP/6-31G(d) C-PCM optimised geometry

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.000000	0.000000	0.000000
2	7	0	-0.770362	1.233752	1.376214
3	6	0	-1.418496	2.411252	1.242753
4	6	0	-1.564701	3.046933	2.507873
5	1	0	-2.051650	3.995427	2.674991
6	6	0	-1.007962	2.217591	3.463592
7	6	0	-0.513432	1.065154	2.737434
8	7	0	0.000000	0.000000	3.324314
9	6	0	0.513432	-1.065154	2.737434
10	6	0	1.007962	-2.217591	3.463592
11	6	0	1.564701	-3.046933	2.507873
12	1	0	2.051650	-3.995427	2.674991
13	6	0	1.418496	-2.411252	1.242753
14	7	0	0.770362	-1.233752	1.376214
15	7	0	-0.770362	-1.233752	-1.376214
16	6	0	-1.418496	-2.411252	-1.242753
17	6	0	-1.564701	-3.046933	-2.507873
18	1	0	-2.051650	-3.995427	-2.674991
19	6	0	-1.007962	-2.217591	-3.463592
20	6	0	-0.513432	-1.065154	-2.737434
21	7	0	0.000000	0.000000	-3.324314
22	6	0	0.513432	1.065154	-2.737434
23	6	0	1.007962	2.217591	-3.463592
24	6	0	1.564701	3.046933	-2.507873
25	1	0	2.051650	3.995427	-2.674991
26	6	0	1.418496	2.411252	-1.242753
27	7	0	0.770362	1.233752	-1.376214
28	6	0	1.968296	2.926313	0.015339
29	6	0	2.503332	2.066573	0.993418
30	1	0	2.494666	0.993822	0.831062
31	6	0	3.072214	2.580957	2.158598
32	1	0	3.491213	1.901343	2.895609
33	6	0	3.113187	3.962278	2.373604
34	1	0	3.556596	4.360836	3.281541
35	6	0	2.586765	4.827640	1.409171
36	1	0	2.611527	5.901912	1.568557
37	1	0	-2.611527	5.901912	-1.568557
38	1	0	1.610831	4.995867	-0.500148
39	6	0	2.026963	4.316609	0.238284
40	6	0	-2.586765	4.827640	-1.409171
41	6	0	-2.026963	4.316609	-0.238284
42	1	0	-1.610831	4.995867	0.500148
43	6	0	-1.968296	2.926313	-0.015339
44	6	0	-2.503332	2.066573	-0.993418
45	1	0	-2.494666	0.993822	-0.831062

46	6	0	-3.072214	2.580957	-2.158598
47	1	0	-3.491213	1.901343	-2.895609
48	6	0	-3.113187	3.962278	-2.373604
49	1	0	-3.556596	4.360836	-3.281541
50	6	0	0.954492	2.456853	-4.908655
51	6	0	2.016818	3.125518	-5.551308
52	1	0	2.891216	3.415057	-4.974543
53	6	0	1.970724	3.392195	-6.919482
54	1	0	2.804568	3.899556	-7.396952
55	6	0	0.859743	3.003198	-7.674711
56	1	0	0.822882	3.213280	-8.739972
57	6	0	-0.202452	2.343864	-7.050417
58	1	0	-1.072694	2.044681	-7.628264
59	6	0	-0.157585	2.070168	-5.682647
60	1	0	-0.989590	1.568202	-5.201582
61	6	0	-0.954492	-2.456853	-4.908655
62	6	0	0.157585	-2.070168	-5.682647
63	1	0	0.989590	-1.568202	-5.201582
64	6	0	0.202452	-2.343864	-7.050417
65	1	0	1.072694	-2.044681	-7.628264
66	6	0	-0.859743	-3.003198	-7.674711
67	1	0	-0.822882	-3.213280	-8.739972
68	6	0	-1.970724	-3.392195	-6.919482
69	1	0	-2.804568	-3.899556	-7.396952
70	6	0	-2.016818	-3.125518	-5.551308
71	1	0	-2.891216	-3.415057	-4.974543
72	6	0	-1.968296	-2.926313	0.015339
73	6	0	-2.503332	-2.066573	0.993418
74	1	0	-2.494666	-0.993822	0.831062
75	6	0	-3.072214	-2.580957	2.158598
76	1	0	-3.491213	-1.901343	2.895609
77	6	0	-3.113187	-3.962278	2.373604
78	1	0	-3.556596	-4.360836	3.281541
79	6	0	-2.586765	-4.827640	1.409171
80	1	0	-2.611527	-5.901912	1.568557
81	6	0	-2.026963	-4.316609	0.238284
82	1	0	-1.610831	-4.995867	-0.500148
83	6	0	1.968296	-2.926313	-0.015339
84	6	0	2.503332	-2.066573	-0.993418
85	1	0	2.494666	-0.993822	-0.831062
86	6	0	3.072214	-2.580957	-2.158598
87	1	0	3.491213	-1.901343	-2.895609
88	6	0	3.113187	-3.962278	-2.373604
89	1	0	3.556596	-4.360836	-3.281541
90	6	0	2.586765	-4.827640	-1.409171
91	1	0	2.611527	-5.901912	-1.568557
92	6	0	2.026963	-4.316609	-0.238284
93	1	0	1.610831	-4.995867	0.500148
94	6	0	0.954492	-2.456853	4.908655
95	6	0	2.016818	-3.125518	5.551308
96	1	0	2.891216	-3.415057	4.974543
97	6	0	1.970724	-3.392195	6.919482
98	1	0	2.804568	-3.899556	7.396952
99	6	0	0.859743	-3.003198	7.674711
100	1	0	0.822882	-3.213280	8.739972
101	6	0	-0.202452	-2.343864	7.050417
102	1	0	-1.072694	-2.044681	7.628264
103	6	0	-0.157585	-2.070168	5.682647
104	1	0	-0.989590	-1.568202	5.201582
105	6	0	-0.954492	2.456853	4.908655
106	6	0	0.157585	2.070168	5.682647

107	1	0	0.989590	1.568202	5.201582
108	6	0	0.202452	2.343864	7.050417
109	1	0	1.072694	2.044681	7.628264
110	6	0	-0.859743	3.003198	7.674711
111	1	0	-0.822882	3.213280	8.739972
112	6	0	-1.970724	3.392195	6.919482
113	1	0	-2.804568	3.899556	7.396952
114	6	0	-2.016818	3.125518	5.551308
115	1	0	-2.891216	3.415057	4.974543

B. Transition Dipoles

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	0.3193	0.0000	0.0000	0.1020	0.0020
2	0.0000	0.4702	0.0000	0.2211	0.0044
3	0.0000	0.0000	0.1685	0.0284	0.0007
4	0.2645	0.0000	0.0000	0.0699	0.0020
5	0.0000	0.4098	0.0000	0.1680	0.0048
6	0.0000	-0.0091	0.0000	0.0001	0.0000
7	-0.0847	0.0000	0.0000	0.0072	0.0002
8	0.0000	-0.6953	0.0000	0.4834	0.0216
9	-0.2712	0.0000	0.0000	0.0735	0.0033
10	0.0000	0.3817	0.0000	0.1457	0.0066
11	-0.6201	0.0000	0.0000	0.3845	0.0178
12	0.0000	-0.6968	0.0000	0.4856	0.0226
13	0.1736	0.0000	0.0000	0.0301	0.0014
14	0.0000	0.0000	0.0000	0.0000	0.0000
15	**0.0000**	**0.0000**	**1.4325**	**2.0519**	**0.1041**
16	**2.4886**	**0.0000**	**0.0000**	**6.1930**	**0.3234**
17	0.0730	0.0000	0.0000	0.0053	0.0003
18	**0.0000**	**-2.9827**	**0.0000**	**8.8966**	**0.4868**
19	**0.0000**	**0.0000**	**1.3621**	**1.8553**	**0.1043**
20	**-0.0001**	**3.3766**	**0.0000**	**11.4017**	**0.6429**
21	0.0000	0.0000	0.0000	0.0000	0.0000
22	0.2705	0.0000	0.0000	0.0732	0.0043
23	0.0000	0.0000	-0.6878	0.4731	0.0290
24	-0.3769	-0.0001	0.0000	0.1420	0.0093

C. Output from TD-UB3LYP/6-31G(d) C-PCM excited transition energies and configurations

```
 Excited State  15:  2.455-B1     2.0709 eV  598.69 nm  f=0.1041
<S**2>=1.257
    245A -> 252A       0.15008
    248A -> 251A      -0.21273
    225B -> 250B       0.26488
    230B -> 250B      -0.24587
    235B -> 250B       0.17710
    244B -> 251B       0.17431
    245B -> 250B       0.80861
    245B -> 252B       0.14610

 Excited State  16:  2.033-B3     2.1316 eV  581.66 nm  f=0.3234
<S**2>=0.783
```

```
    249A -> 251A      -0.39850
    250A -> 252A      -0.51396
    248B -> 251B      -0.33423
    249B -> 250B       0.11830
    249B -> 252B       0.65595


 Excited State  18:  2.878-B2     2.2333 eV  555.17 nm  f=0.4868
<S**2>=1.821
    246A -> 251A      -0.32797
    247A -> 252A       0.30416
    249A -> 252A       0.36565
    250A -> 251A       0.28519
    246B -> 251B       0.42267
    247B -> 252B       0.33326
    248B -> 252B      -0.42765
    249B -> 251B       0.24493

 Excited State  19:  2.985-B1     2.2953 eV  540.16 nm  f=0.1043
<S**2>=1.978
    245A -> 252A      -0.42110
    248A -> 251A       0.67331
    225B -> 250B       0.11803
    230B -> 250B      -0.15332
    235B -> 250B       0.12396
    244B -> 251B      -0.29925
    245B -> 250B       0.27445
    245B -> 252B      -0.30307

 Excited State  20:  2.666-B2     2.3017 eV  538.67 nm  f=0.6429
<S**2>=1.526
    246A -> 251A      -0.41051
    247A -> 252A       0.37388
    249A -> 252A      -0.36437
    250A -> 251A      -0.28009
    246B -> 251B       0.29213
    247B -> 250B      -0.26727
    247B -> 252B       0.22087
    248B -> 250B       0.12174
    248B -> 252B       0.39165
    249B -> 251B      -0.27563
```

D. Optimised (dimensionless) Mode Displacements (Δ) and Reorganisation Energies (λ) from Wavepacket Modelling

Exciton State 1

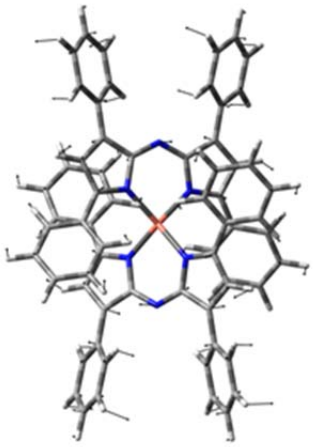
ν / cm^{-1}	Δ	λ / cm^{-1}
1601	0.35	98.0
1509	0.4	120.7
1486	0.22	35.9
1475	0.175	22.5
1413	0.55	213.7
1376	0.25	43
1322	0.85	477.5
1305	0.35	79.9
1275	0.35	78.0
1223	0.25	38.2
1130	0.04	0.9

1059	0.12	7.6
1031	0.275	38.9
1009	0.4	80.72
998	0.375	70.1
984	0	0
936	0.5	117
833	0.75	234.2
772	0.3	34.7
763	0.35	46.7
587	0.99	287.6
531	0.75	149.3
511	0.2	10.2
460	0.6	82.8
412	0.2	8.3

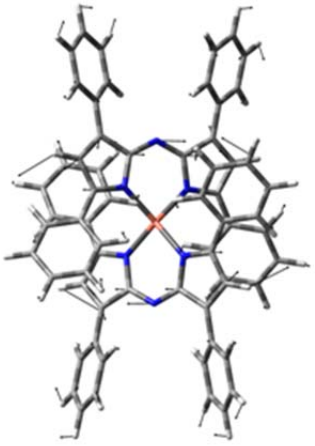
Exciton State 2 (X_2)

ν / cm^{-1}	Δ	λ / cm^{-1}
1601	0.6	288.2
1509	0.38	108.9
1486	0.27	54.1
1475	0.225	37.3
1413	0.45	143.0
1376	0.35	84.2
1322	0.75	371.8
1305	0.25	40.7
1275	0.37	87.2
1223	0.35	74.9
1130	0.425	102.0
1059	0.25	33.0
1031	0.25	32.2
1009	0.35	61.8
998	0.4	79.84
984	0.5	123
936	0.5	117
833	0.55	125
772	0	0
763	0	0
587	0.375	41.2
531	0.075	1.49
511	0	0
460	0	0
412	0	0

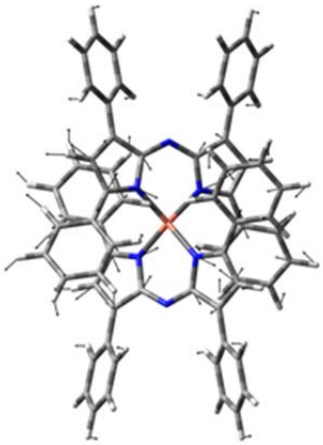
E. Selected Normal Modes(Gaussian log file is available upon request).



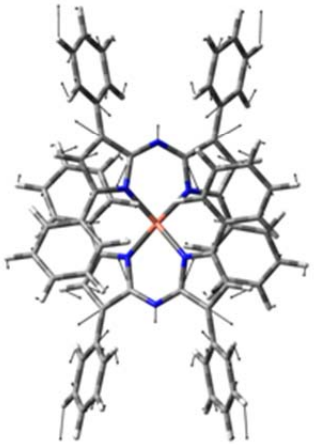
587 cm^{-1}



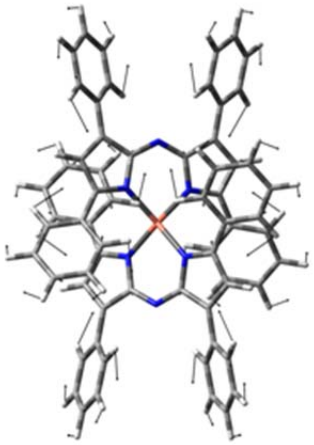
833 cm^{-1}



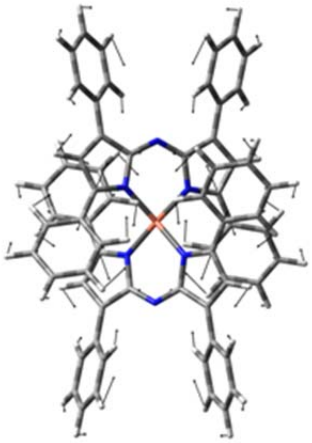
936 cm^{-1}



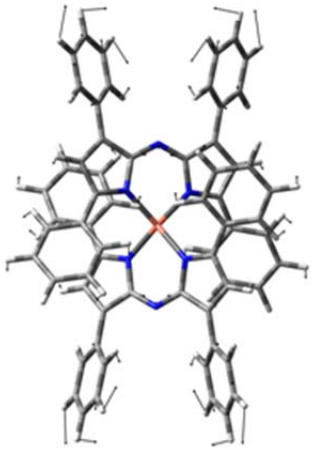
1305 cm^{-1}



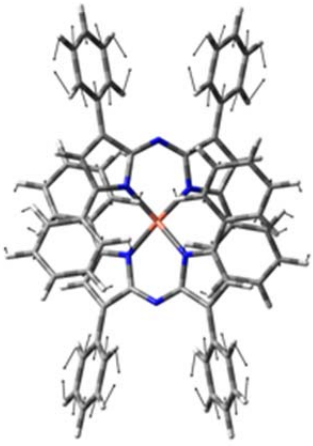
1322 cm^{-1}



1376 cm^{-1}

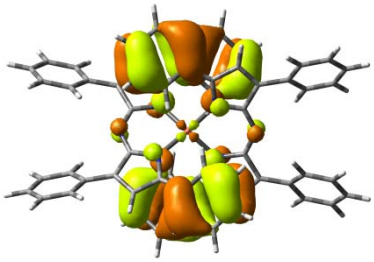


1413 cm^{-1}

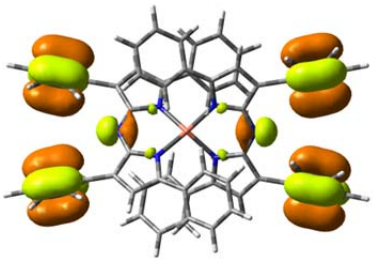


1601 cm^{-1}

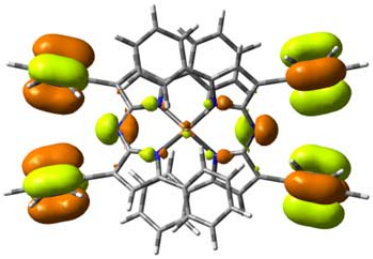
E. Selected Kohn-Sham Orbitals



HOMO-5(α)



HOMO-5(β)



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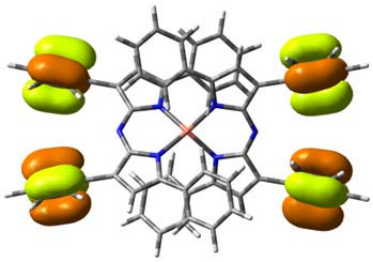

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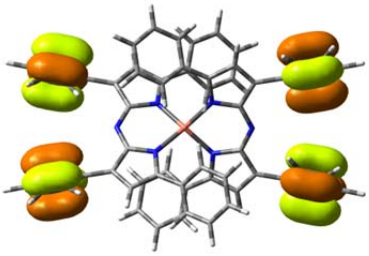

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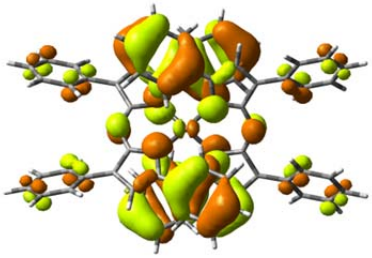
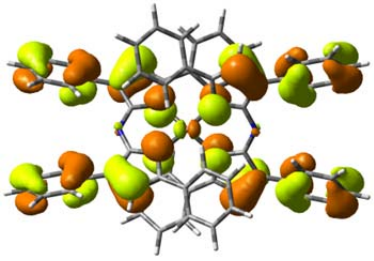


HOMO-3(β)



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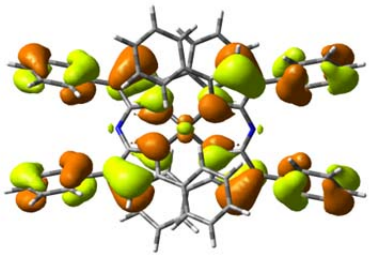

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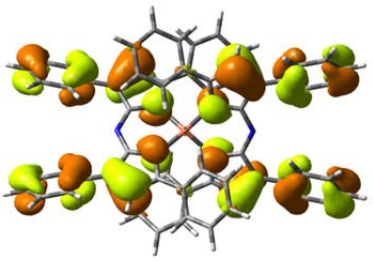
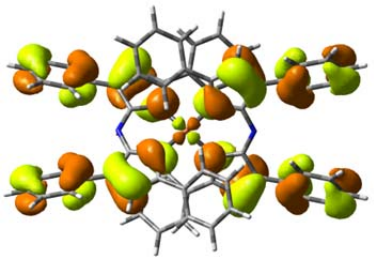


HOMO-1(α)



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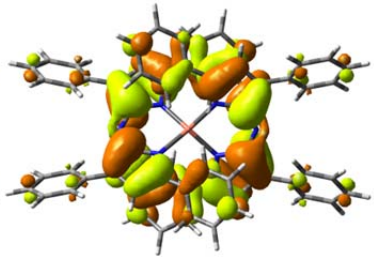

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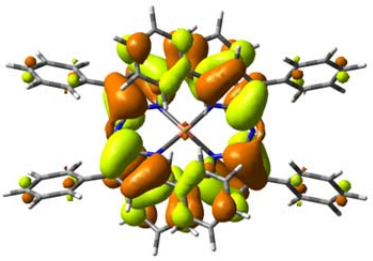
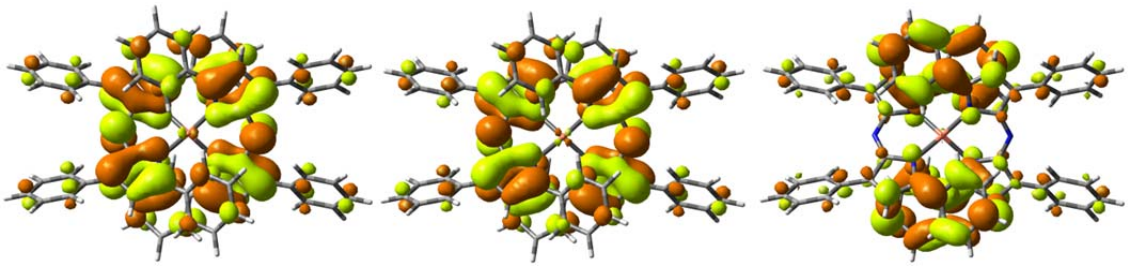
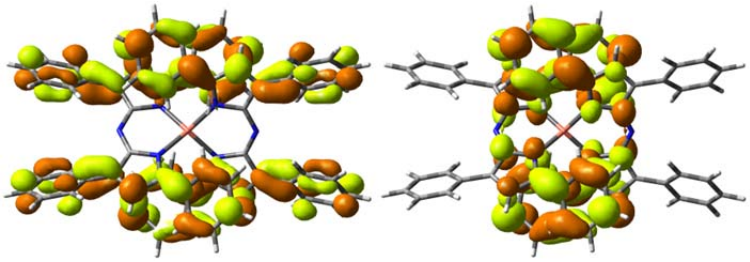


HOMO(β)



LUMO(α) **LUMO(β)** **LUMO+1(α)**



LUMO+1(β) **LUMO+2(β)**