Electronic Supplementary Information (ESI) for

Construction of covalent- and hydrogen-bonded assemblies from 1′,1‴-biferrocenediboronic acid as a new organobimetallic building block

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Contents

1. Electrochemical data

Table S1 Redox potentials $E_{1/2}$ for **2** and **C**.[a]

Compound	$E_{1/2}{}^{1}$	$E_{1/2}{}^{2}$	$E_{1/2}{}^{3}$	$E_{1/2}{}^{4}$
2	–90	–33	551	666
C	56	138	-	-

[a] Potentials in mV vs. Fc^{+}/Fc (Fc = ferrocene).

2. ESI-MS and NMR spectra of new compounds

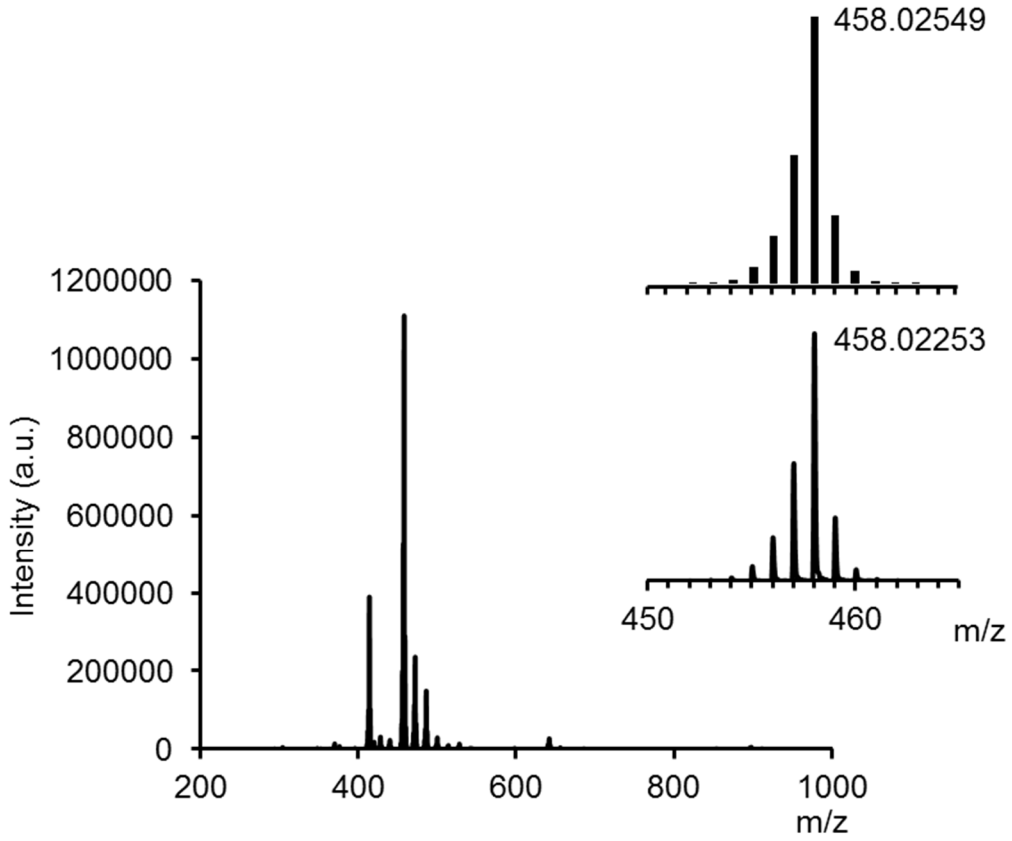


Fig. S1 HR-ESI-MS of a THF solution of **1**. Inset: experimental (bottom) and theoretical (top) isotopic distributions for $\mathbf{1}^{+}$.

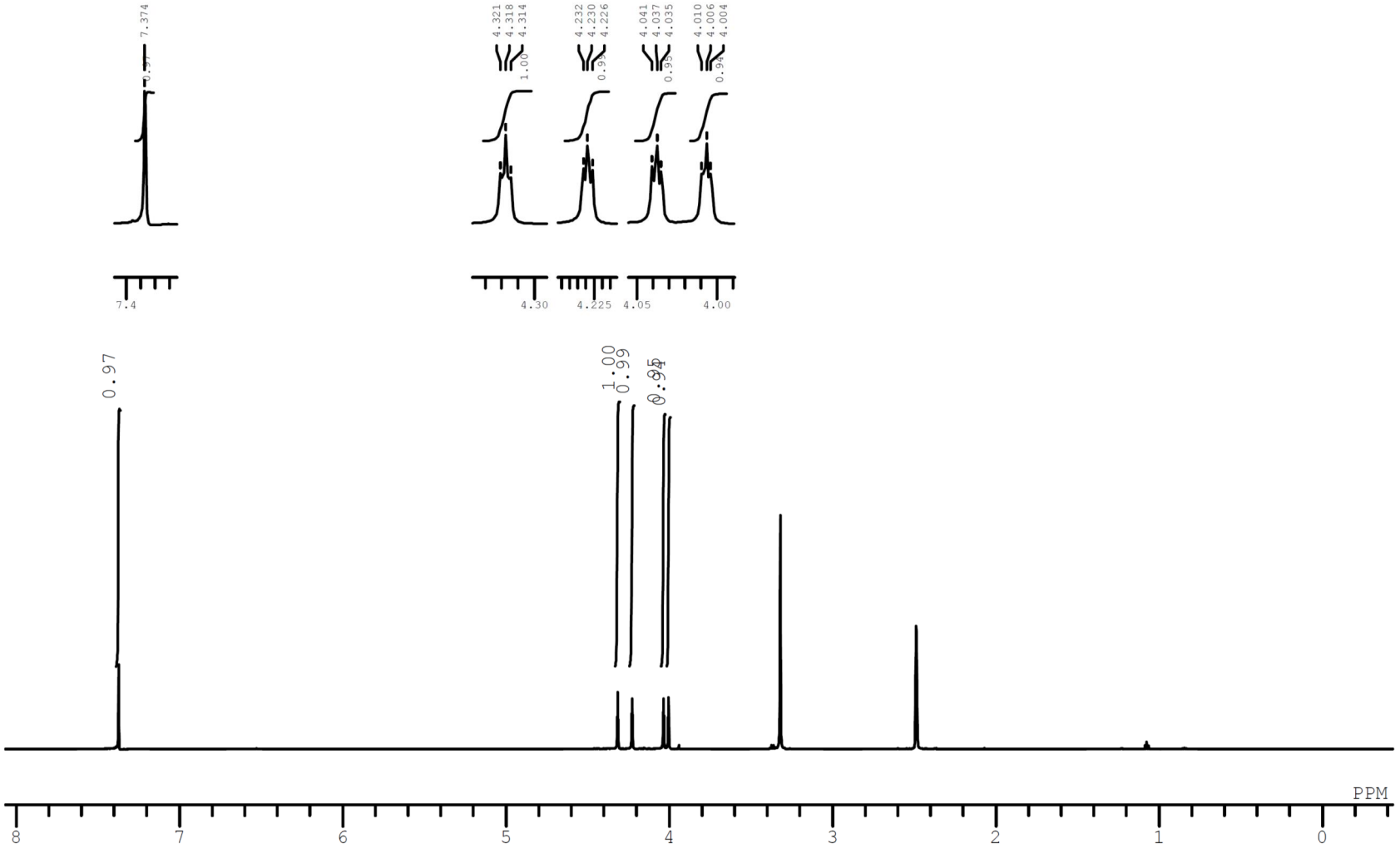


Fig. S2 ^{1}H-NMR spectrum of **1** in DMSO-d_6 (600 MHz).

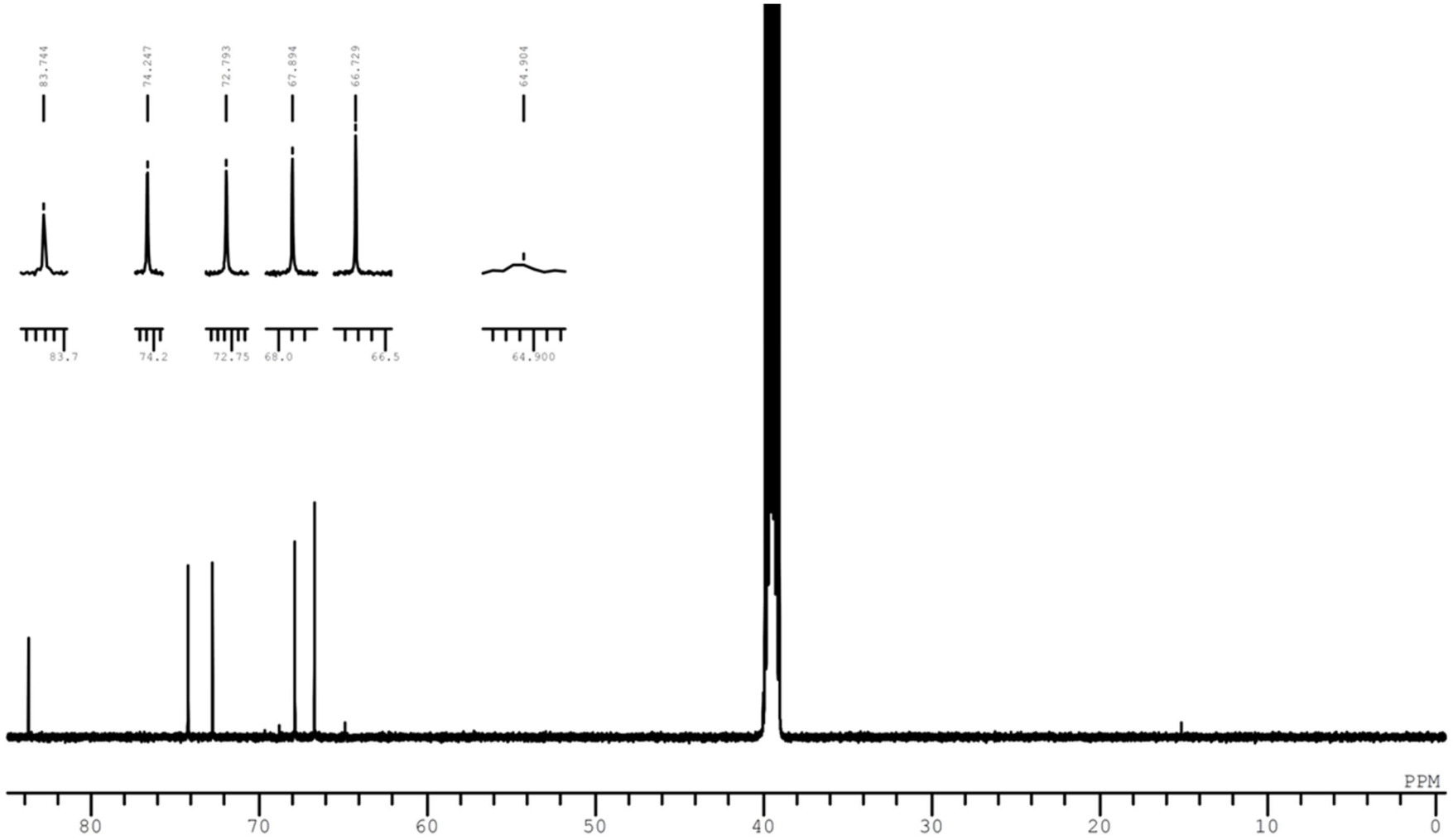


Fig. S3 ^{13}C-NMR spectrum of **1** in DMSO-d_6 (125 MHz).

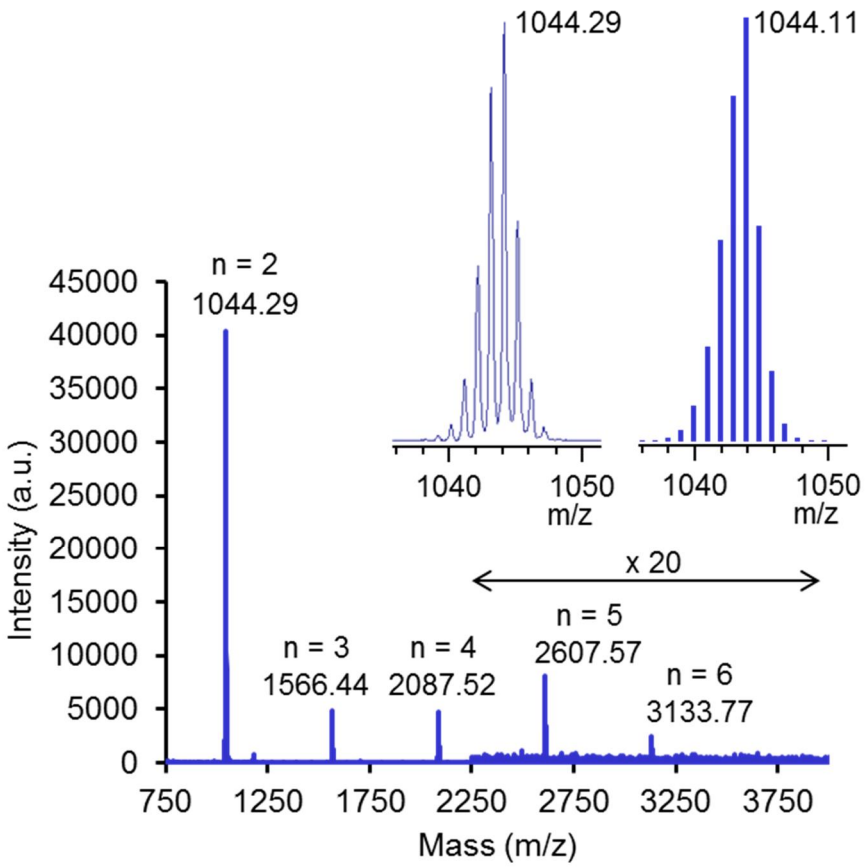


Fig. S4 MALDI-TOF-mass spectrum of oligomer $[BiFcBO_2C_5H_8O_2B]_n$ (positive mode, dithranol matrix). The intensities in the 2250-4000 m/z range were multiplied by a factor of 20. Inset: experimental (left) and theoretical (right) isotopic distributions for $[BiFcBO_2C_5H_8O_2B]_2$ (n = 2).

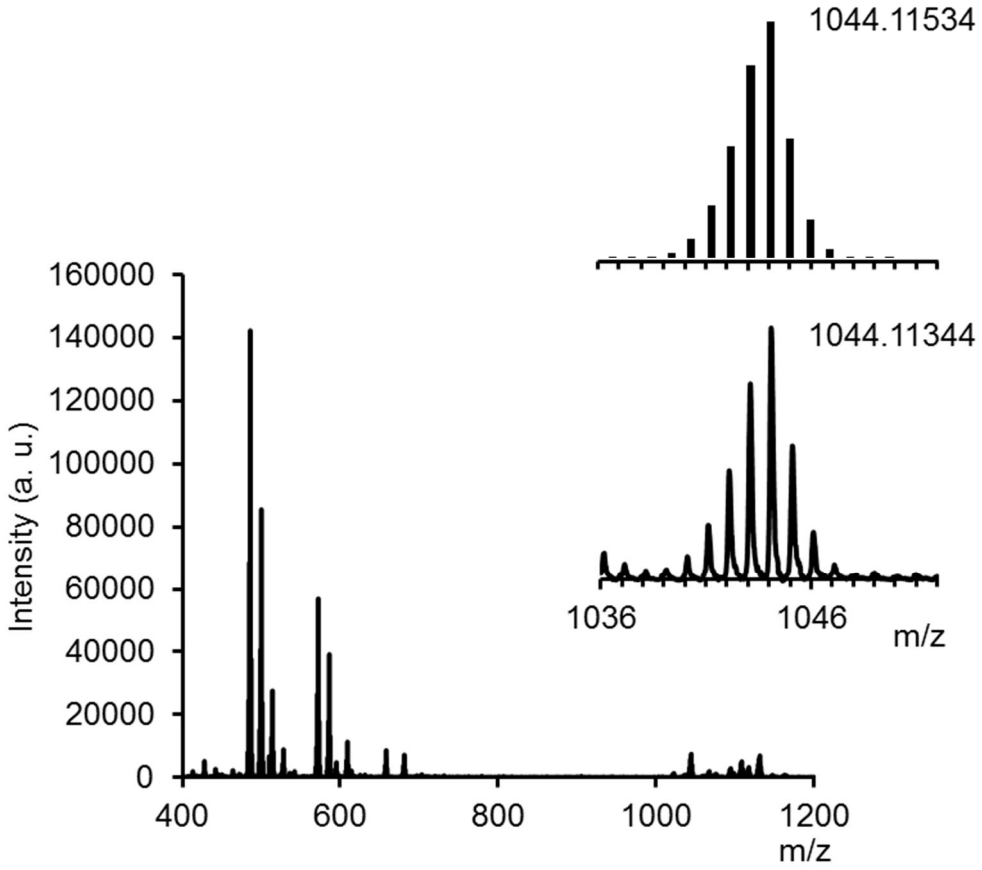


Fig. S5 HR-ESI-MS of a $CHCl_3$ solution of **2**. Inset: experimental (bottom) and theoretical (top) isotopic distributions for $\mathbf{2}^{+}$.

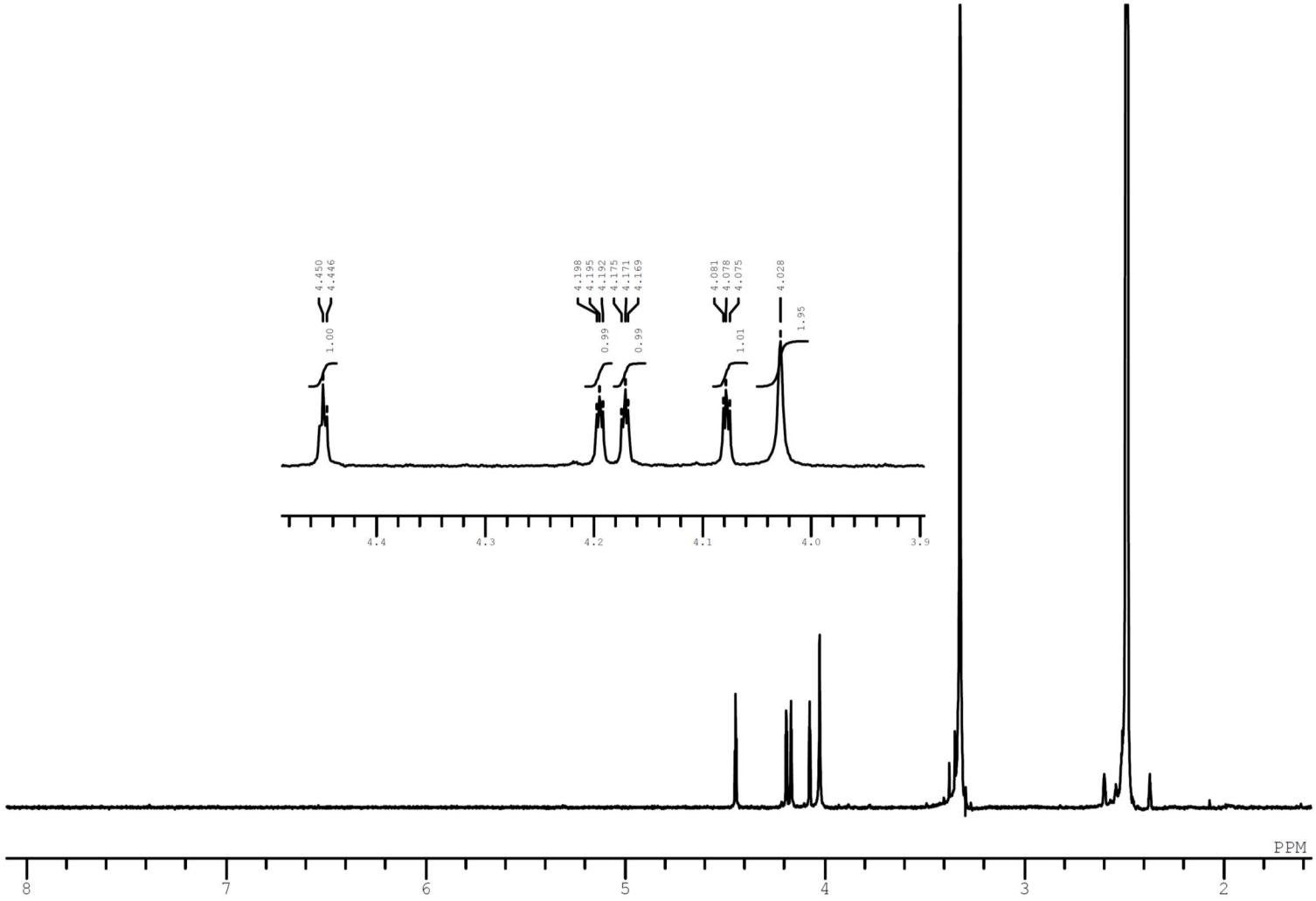


Fig. S6 ^{1}H-NMR spectrum of **2** in DMSO-d_6 (600 MHz).

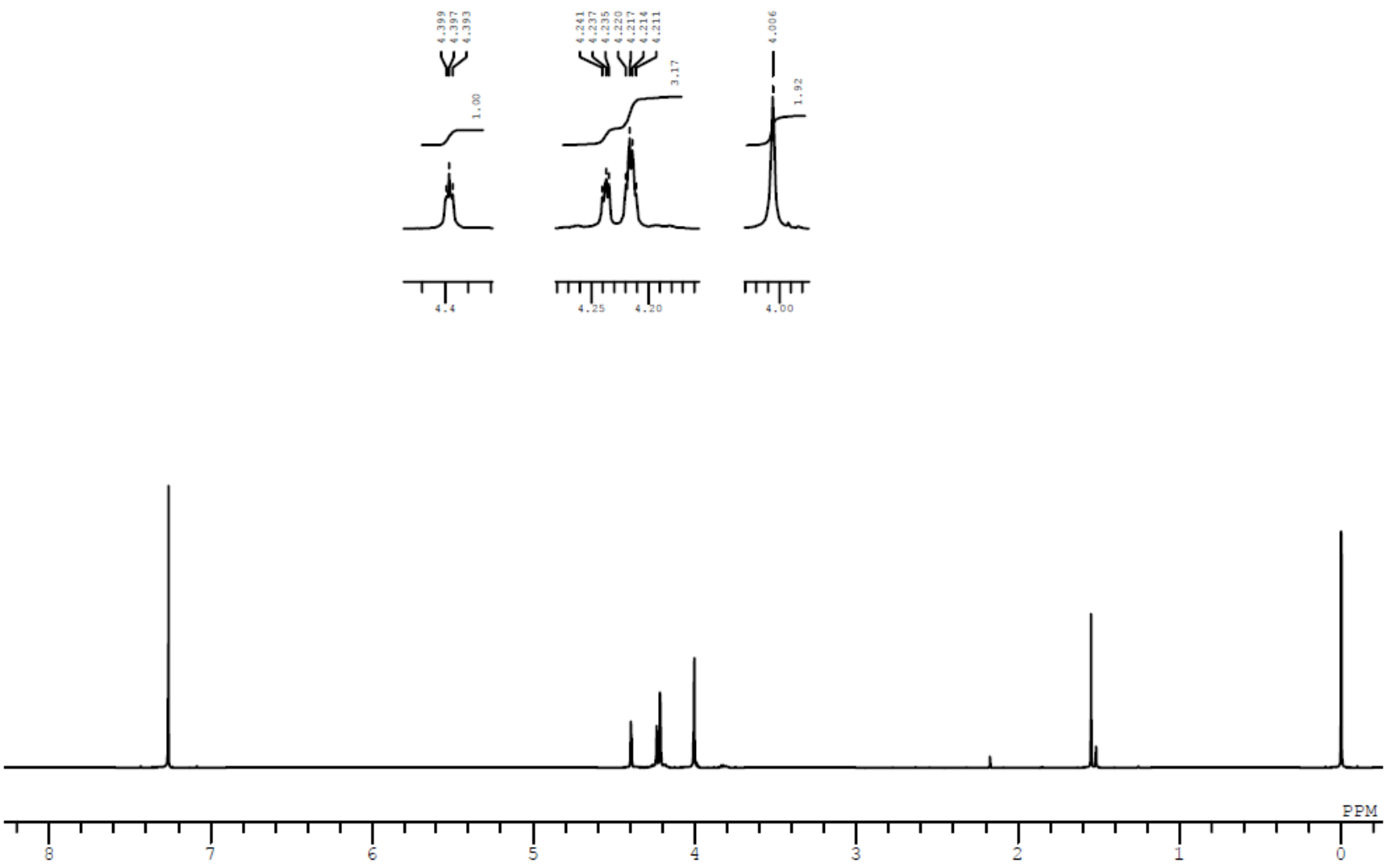


Fig. S7 ^{1}H-NMR spectrum of **2** in $CDCl_3$ (600 MHz).

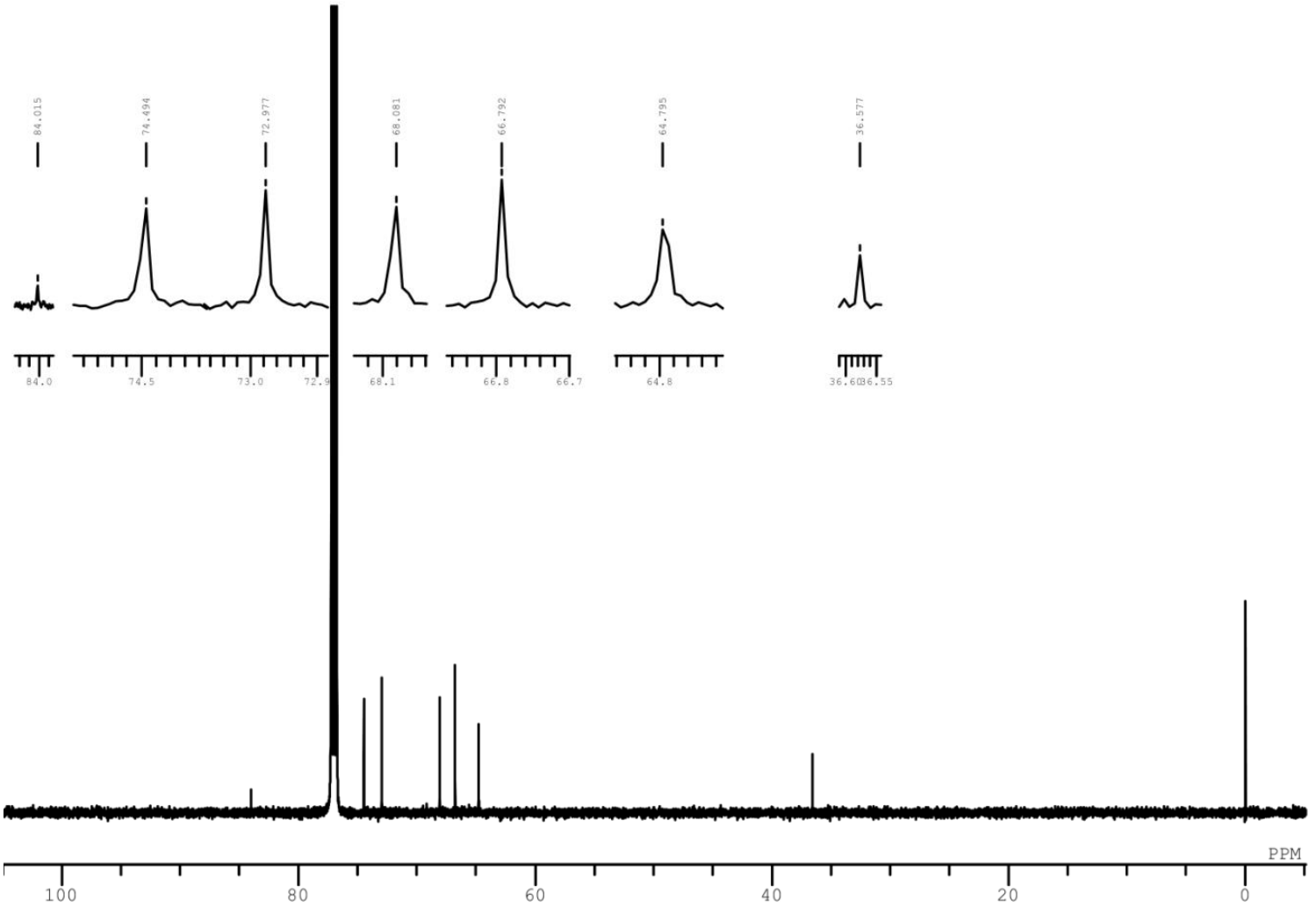


Fig. S8 ^{13}C-NMR spectrum of **2** in $CDCl_3$ (125 MHz).

3. X-ray Crystallographic Data and Structure Data

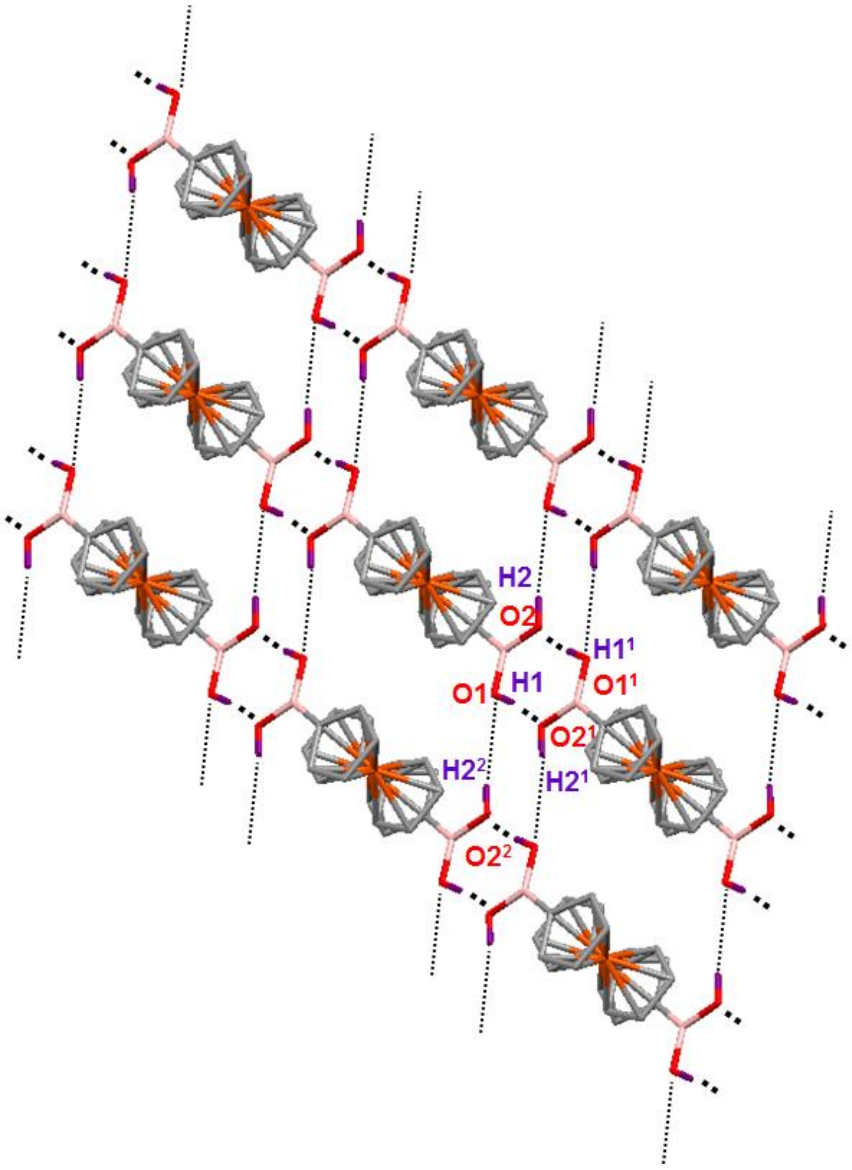


Fig. S9 Expanded structures of **1** in the crystal of Form I. Hydrogen atoms are omitted for clarity expect for the O-H hydrogen atoms (purple). Hydrogen bonds (bold dotted lines) and O-H short contacts (dotted lines) are indicated. O-O distances (Å): O^1-$O2^1$ 2.7936(16); O^1-$O2^2$ 3.491(2).

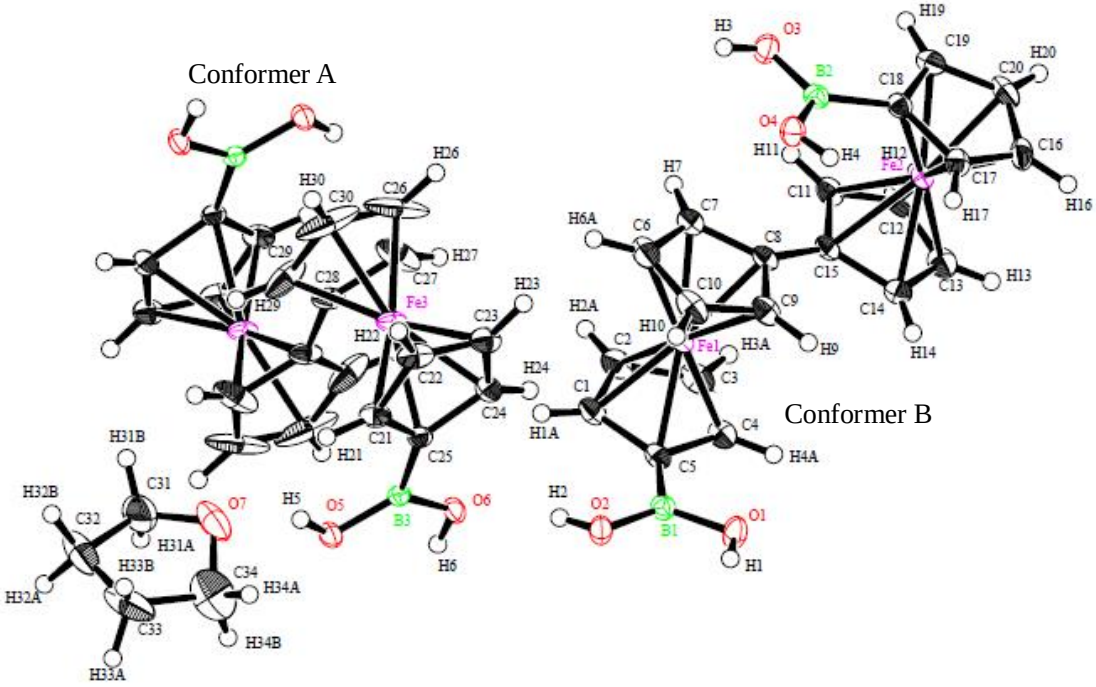


Fig. S10 ORTEP drawing of molecular structure in the crystal of $(\mathbf{1})_3(THF)_2$ (Form II) with thermal ellipsoids set at the 50% probability level. Selected bond lengths (Å) and angles (deg): O1-B1 1.374(3), O2-B1 1.362(2), C5-B1 1.548(3), C8-C15 1.463(2), O3-B2 1.358(3), O4-B2 1.366(3), C18-B2 1.556(3), O5-B3 1.368(3), O6-B3 1.3675(19), C25-B3 1.552(3), C28-C28^1 1.461(3), O1-B1-C5 118.36(14), O2-B1-C5 124.28(19), O1-B1-O2 117.36(18), O3-B2-C18 118.21(16), O4-B2-C18 124.41(18), O3-B2-O4 119.32(15), O5-B3-C25 124.37(14), O6-B3-C25 117.61(15), O5-B3-O6 118.00(17).

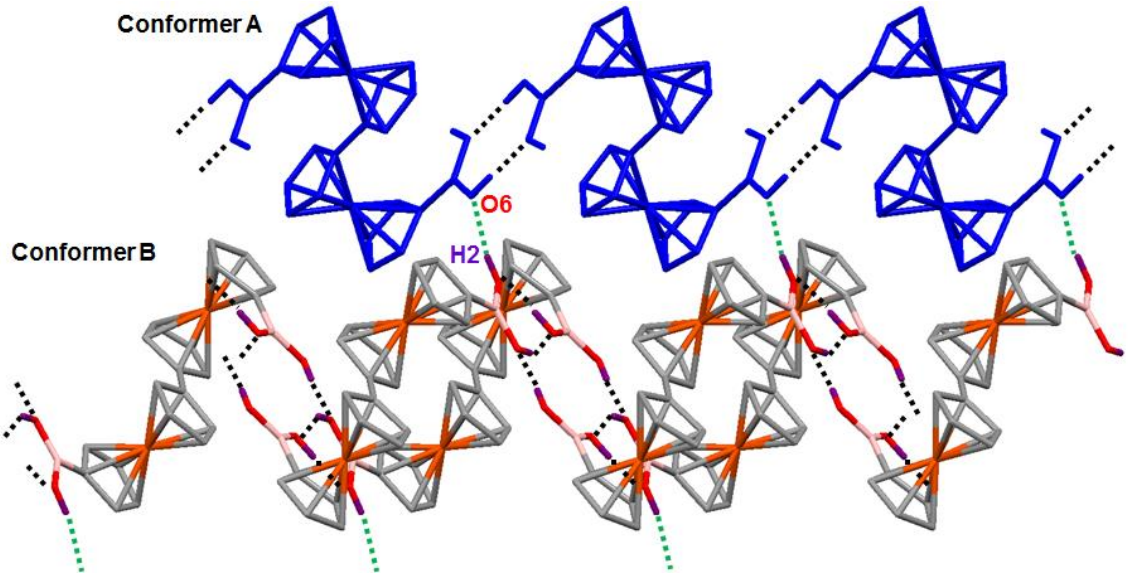
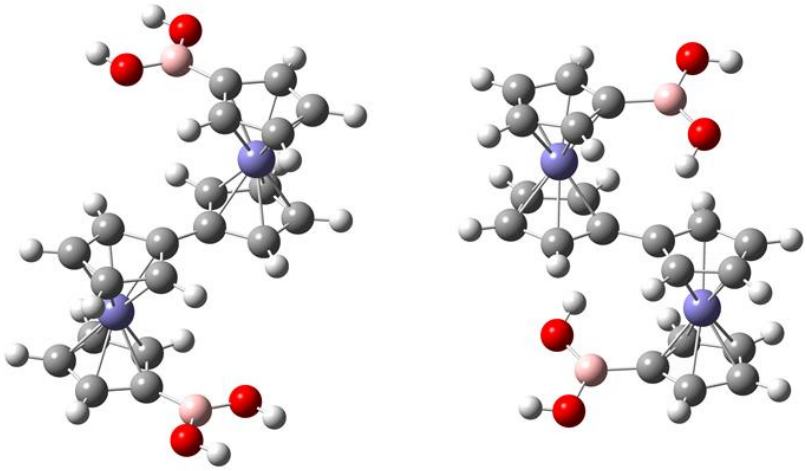


Fig. S11 Secondary structure composed of 1D (blue) and laminated stepwise hydrogen-bonded networks in the crystal of $(\mathbf{1})_3(THF)_2$ (Form II). O-H hydrogen atoms are purple except for those in the 1D network. C-H hydrogen atoms are omitted for clarity. Hydrogen bonds are indicated as black dotted lines inside the first network structure and green dotted lines between networks.

4. DFT Calculations



1 **1'**

Fig. S12 Optimised gas-phase structures of **1** (having a nearly eclipsed conformation) and **1'** (having a more staggered conformation) calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory).

Table S2 Coordinates of the optimised gas-phase geometries of **1** calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	2.446779	–0.916747	0.014398
2	8	3.416298	3.048487	1.1259
3	8	1.995404	2.933951	–0.738079
4	6	3.510192	0.152976	–1.405925
5	6	4.139832	–1.105491	–1.180821
6	6	4.512267	–1.165895	0.196544
7	6	4.12114	0.057687	0.808709
8	6	3.497162	0.897996	–0.174145
9	6	1.517383	–2.309551	1.242756
10	6	0.902695	–1.031332	1.407246
11	6	0.368359	–0.617515	0.137222
12	6	0.684885	–1.65037	–0.805711
13	6	1.382107	–2.690378	–0.124967
14	5	2.92998	2.328831	0.066534
15	1	2.966738	3.906784	1.175162

16	1	1.538676	2.315443	–1.325772
17	1	3.108508	0.489663	–2.354205
18	1	4.274653	–1.891282	–1.912875
19	1	4.973142	–2.010126	0.693168
20	1	4.242563	0.313725	1.853118
21	1	2.033492	–2.868458	2.012147
22	1	0.877981	–0.454435	2.322372
23	1	0.443876	–1.636358	–1.860137
24	1	1.769063	–3.594858	–0.575076
25	6	–1.518426	2.309218	–1.244668
26	6	–0.903703	1.031036	–1.409137
27	6	–0.368198	0.617873	–0.139431
28	6	–0.684061	1.65107	0.803364
29	6	–1.382057	2.690654	0.122777
30	1	–2.035353	2.867675	–2.013841
31	1	–0.87961	0.453792	–2.324062
32	1	–0.442028	1.637587	1.857563
33	1	–1.768838	3.595226	0.572853
34	26	–2.446511	0.916782	–0.014834
35	8	–3.420352	–3.050209	–1.121755
36	8	–1.993544	–2.933348	0.737557
37	6	–3.508504	–0.15236	1.406966
38	6	–4.138347	1.106035	1.181957
39	6	–4.512175	1.165861	–0.195052
40	6	–4.121764	–0.058033	–0.80706
41	6	–3.496798	–0.897923	0.175504
42	5	–2.930524	–2.329187	–0.064936
43	1	–2.971	–3.908601	–1.171322
44	1	–1.534369	–2.314046	1.32254
45	1	–3.105906	–0.488739	2.354962
46	1	–4.272416	1.892136	1.91382
47	1	–4.973463	2.009909	–0.691606
48	1	–4.244355	–0.314557	–1.851215

Table S3 DFT-calculated molecular orbital compositions of **1** in the gas phase.

MO	*E* /eV	Composition / %		
		Fe	Cp	$B(OH)_2$
115	0.71	83	10	7
114	0.58	73	3	24
113	0.5	92	7	1
112	0.25	55	44	0
111	0.18	77	3	20
110	-0.04	55	37	8
109	-0.09	55	33	12
108 (LUMO)	-0.21	58	38	4
107 (HOMO)	-4.99	81	19	0
106	-5.17	85	14	0
105	-5.18	87	13	0
104	-5.23	84	16	0
103	-5.79	22	78	0
102	-6.18	89	11	1
101	-6.2	91	8	1
100	-6.41	8	89	3

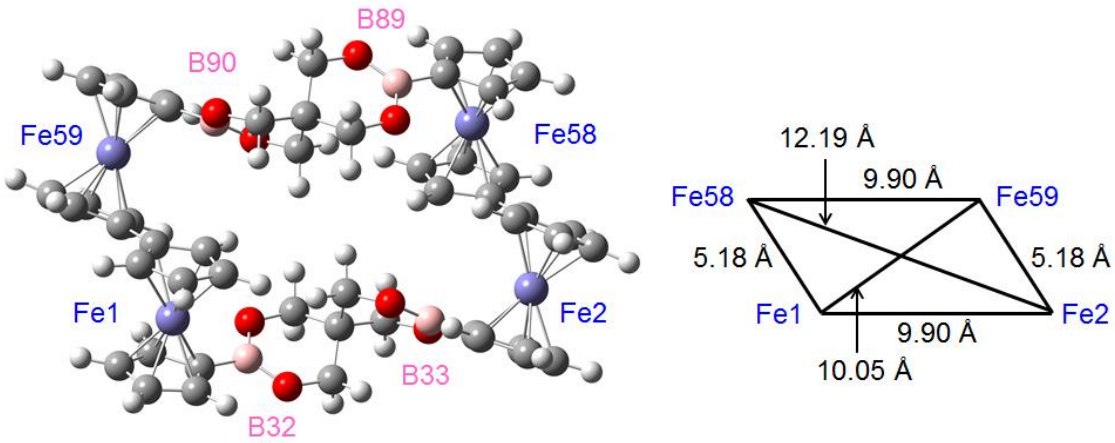


Fig. S13 Optimised gas-phase structure of **2** calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory). Selected distances are also shown.

Table S4 Coordinates of the optimised gas-phase geometries of **2** calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	–4.116582	–2.677082	1.075091
2	26	5.745445	–1.864547	0.796647
3	8	–0.964255	–4.548559	–0.80859
4	8	–1.999886	–2.771657	–2.050177
5	8	1.86504	–2.252744	–0.007241
6	8	2.916677	–2.964731	–2.048157
7	6	–5.589408	–3.974328	0.377197
8	6	–4.822273	–4.622632	1.393752
9	6	–3.468037	–4.663302	0.959374
10	6	–3.371576	–4.033332	–0.330123
11	6	–4.701789	–3.606405	–0.674002
12	6	–4.619993	–0.648898	0.94973
13	6	–5.00664	–1.186652	2.223004
14	6	–3.842361	–1.678298	2.883229
15	6	–2.724628	–1.460342	2.022395
16	6	–3.203052	–0.832145	0.830619
17	6	0.269631	–4.355145	–1.496019

18	6	–0.779684	–2.482263	–2.731084
19	6	0.462755	–2.888757	–1.923987
20	6	0.646154	–1.979928	–0.693486
21	6	1.722752	–2.731683	–2.789633
22	6	4.223043	–3.13189	0.098275
23	6	4.339983	–3.201529	1.530339
24	6	5.649553	–3.648359	1.864835
25	6	6.369095	–3.848689	0.646267
26	6	5.498032	–3.529955	–0.433702
27	6	–5.532879	–0.105839	–0.062027
28	6	–5.311294	–0.050745	–1.478913
29	6	–6.495124	0.44427	–2.100984
30	6	–7.45024	0.720408	–1.076451
31	6	–6.855304	0.390317	0.177741
32	5	–2.056387	–3.775445	–1.10983
33	5	2.954963	–2.73201	–0.695325
34	1	0.290644	–5.004719	–2.382236
35	1	1.064569	–4.686269	–0.823186
36	1	–0.773486	–1.405565	–2.938321
37	1	–0.78049	–3.004985	–3.698294
38	1	0.641054	–0.927895	–1.010974
39	1	–0.163849	–2.118524	0.02826
40	1	1.715369	–3.447124	–3.620803
41	1	1.759559	–1.720539	–3.218487
42	1	–6.648884	–3.757264	0.418841
43	1	–5.198943	–4.983592	2.342245
44	1	–2.632138	–5.063527	1.518239
45	1	–4.973485	–3.057997	–1.566225
46	1	–6.020274	–1.246127	2.59655
47	1	–3.818877	–2.169982	3.846814
48	1	–1.702581	–1.755923	2.222655
49	1	–2.612854	–0.564798	–0.034911
50	1	3.557529	–2.939476	2.230232
51	1	6.046125	–3.771737	2.86455
52	1	7.405953	–4.148257	0.563037
53	1	5.751441	–3.558545	–1.48535

54	1	–4.400831	–0.350341	–1.980756
55	1	–6.629567	0.618762	–3.1605
56	1	–8.435144	1.144879	–1.220449
57	1	–7.31149	0.518182	1.150527
58	26	4.116601	2.677113	–1.075052
59	26	–5.745452	1.864545	–0.796667
60	8	0.964253	4.548539	0.808614
61	8	1.999874	2.771618	2.050182
62	8	–1.86505	2.252742	0.00719
63	8	–2.916688	2.964712	2.048112
64	6	5.589423	3.974348	–0.377126
65	6	4.822295	4.622668	–1.393675
66	6	3.468057	4.663331	–0.959307
67	6	3.371586	4.033341	0.33018
68	6	4.701797	3.606406	0.674061
69	6	4.620008	0.648926	–0.949721
70	6	5.006666	1.186702	–2.222983
71	6	3.842393	1.67836	–2.883209
72	6	2.724653	1.460392	–2.022386
73	6	3.203067	0.832174	–0.830618
74	6	–0.269649	4.355095	1.496007
75	6	0.77966	2.48219	2.731054
76	6	–0.462772	2.8887	1.923953
77	6	–0.646177	1.979886	0.693442
78	6	–1.722774	2.73162	2.78959
79	6	–4.22305	3.131905	–0.098323
80	6	–4.340002	3.201524	–1.530386
81	6	–5.649577	3.648346	–1.864877
82	6	–6.369111	3.848686	–0.646305
83	6	–5.498038	3.529967	0.43366
84	6	5.532886	0.105848	0.062033
85	6	5.311292	0.050735	1.478916
86	6	6.495115	–0.444294	2.100988
87	6	7.450237	–0.720422	1.076456
88	6	6.85531	–0.390311	–0.177734
89	5	2.056393	3.775444	1.109876

90	5	–2.95496	2.732044	0.695271
91	1	–0.290687	5.004656	2.382232
92	1	–1.064578	4.686221	0.823163
93	1	0.773465	1.405486	2.93826
94	1	0.780448	3.004884	3.698279
95	1	–0.641102	0.927849	1.010919
96	1	0.163831	2.118471	–0.0283
97	1	–1.715386	3.44704	3.620778
98	1	–1.759596	1.720465	3.218418
99	1	6.648899	3.757285	–0.418765
100	1	5.198972	4.983644	–2.34216
101	1	2.632162	5.063566	–1.51817
102	1	4.973486	3.057984	1.566277
103	1	6.020303	1.246181	–2.59652
104	1	3.818917	2.170061	–3.846785
105	1	1.702608	1.755978	–2.22265
106	1	2.612862	0.564813	0.034903
107	1	–3.557553	2.939468	–2.230283
108	1	–6.046158	3.771711	–2.86459
109	1	–7.405969	4.14825	–0.563071
110	1	–5.751439	3.558567	1.48531
111	1	4.400827	0.350329	1.980758
112	1	6.629551	–0.618802	3.160502
113	1	8.435138	–1.1449	1.220454
114	1	7.311501	–0.518164	–1.150519

Table S5 DFT-calculated molecular orbital compositions of **2** in the gas phase.

MO	*E* /eV	Composition / %		
		Fe	Cp	$BO_2C_5H_8O_2B$
263	0.66	82	14	4
262	0.61	74	15	10
261	0.6	75	15	10
260	0.44	88	7	5
259	0.4	92	7	1
258	0.27	85	6	9
257	0.26	90	6	4
256	0.01	57	41	2
255	0.01	58	41	2
254	-0.1	54	40	6
253	-0.11	55	39	6
252	-0.26	54	34	12
251	-0.27	53	34	13
250	-0.51	53	36	11
249 (LUMO)	-0.51	52	36	12
248 (HOMO)	-5.16	82	17	1
247	-5.17	82	17	1
246	-5.31	86	14	0
245	-5.31	86	14	0
244	-5.35	87	13	0
243	-5.35	87	13	0
242	-5.36	84	15	1
241	-5.37	84	15	1
240	-5.97	22	77	1
239	-5.97	22	77	0
238	-6.34	86	13	1
237	-6.34	86	13	1
236	-6.37	91	9	1
235	-6.37	91	9	1
234	-6.55	8	90	2

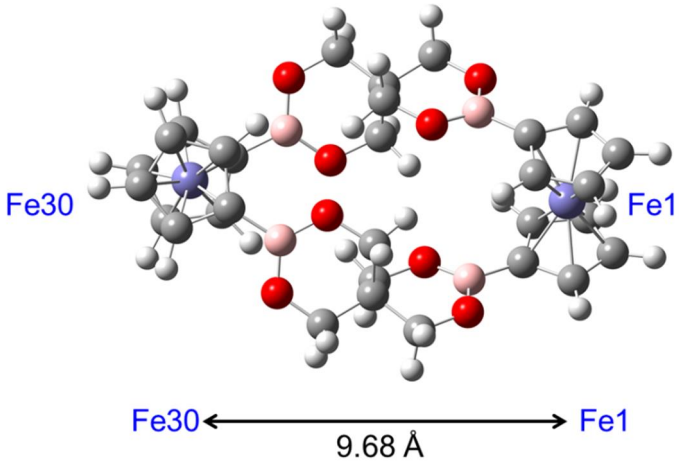


Fig. S14 Optimised gas-phase structure of **C** calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory). Selected distances are also shown.

Table S6 Coordinates of the optimised gas-phase geometries of **C** calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	26	4.839096	0.000428	-0.00162
2	6	3.792115	-1.224795	-1.335937
3	6	3.983187	0.08572	-1.898258
4	6	5.377137	0.354477	-1.985985
5	6	6.075242	-0.786192	-1.480661
6	6	5.107003	-1.749514	-1.078853
7	6	3.793749	1.224163	1.335613
8	6	5.108227	1.749408	1.077479
9	6	6.077158	0.785728	1.476648
10	6	5.379865	-0.355689	1.981521
11	6	3.985783	-0.087062	1.895984
12	5	2.443008	1.908335	1.009537
13	8	1.275432	1.326887	1.438296
14	6	0.022448	1.995634	1.267225
15	6	0.000287	2.873419	0.001721
16	6	-1.241041	3.781153	-0.026977

17	8	-2.450909	3.087631	-0.303875
18	6	1.241034	3.781987	0.03157
19	8	2.451298	3.088923	0.307582
20	6	-0.021126	1.997124	-1.2648
21	8	-1.273802	1.328119	-1.437303
22	8	1.274133	-1.330862	-1.440077
23	6	0.020661	-1.997691	-1.264935
24	6	-0.000417	-2.873601	0.001909
25	6	-0.022018	-1.995684	1.267354
26	8	-1.275503	-1.328232	1.44022
27	5	-2.442997	-1.908123	1.009421
28	6	-3.793533	-1.223431	1.335477
29	6	-3.985231	0.087843	1.895843
30	26	-4.83954	0.000077	-0.001228
31	6	-5.379267	0.356531	1.982183
32	6	-6.076877	-0.784876	1.477797
33	6	-5.108211	-1.748642	1.078177
34	6	-3.792061	1.224195	-1.336274
35	6	-5.107026	1.749226	-1.080159
36	6	-6.075142	0.785597	-1.481499
37	6	-5.376894	-0.355569	-1.98553
38	6	-3.982988	-0.086791	-1.897542
39	8	-2.451564	-3.087545	0.305407
40	6	-1.24134	-3.781825	0.032145
41	6	1.241003	-3.781146	-0.026774
42	8	2.450935	-3.086195	-0.29979
43	5	2.441824	-1.908968	-1.007578
44	5	-2.441749	1.908326	-1.008011
45	1	3.19025	0.767581	-2.175072
46	1	5.82851	1.274002	-2.335193
47	1	7.148908	-0.881623	-1.381935
48	1	5.314945	-2.709686	-0.625453
49	1	5.315368	2.710241	0.625092
50	1	7.150689	0.881615	1.376956
51	1	5.831917	-1.275573	2.328885
52	1	3.193315	-0.769587	2.172487

53	1	-0.743744	1.21794	1.230737
54	1	-0.164	2.617563	2.154035
55	1	-1.104545	4.563728	-0.788182
56	1	-1.368554	4.284494	0.939073
57	1	1.368162	4.2867	-0.933836
58	1	1.103994	4.563501	0.79377
59	1	0.165492	2.620079	-2.150833
60	1	0.745316	1.219635	-1.228829
61	1	-0.168439	-2.620563	-2.150507
62	1	-0.744418	-1.218882	-1.228022
63	1	0.743309	-1.217176	1.229864
64	1	0.166172	-2.617262	2.154019
65	1	-3.192667	0.77033	2.172173
66	1	-5.830995	1.27655	2.329621
67	1	-7.150472	-0.880794	1.37879
68	1	-5.315654	-2.709472	0.62592
69	1	-5.315057	2.709825	-0.627699
70	1	-7.148866	0.881147	-1.383558
71	1	-5.828246	-1.275286	-2.334264
72	1	-3.190001	-0.769105	-2.17306
73	1	-1.367693	-4.288318	-0.932402
74	1	-1.105384	-4.561887	0.796017
75	1	1.105948	-4.561915	-0.790114
76	1	1.367075	-4.286734	0.938263

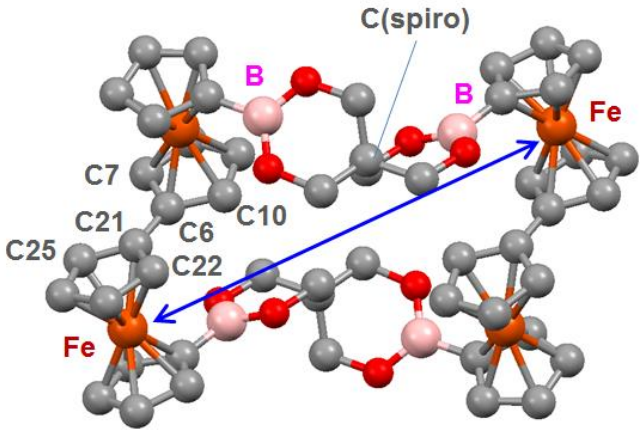
Table S7. DFT-calculated molecular orbital compositions of **C** in the gas phase.

MO	*E* /eV	Composition / %		
		Fe	Cp	$BO_2C_5H_8O_2B$
172	0.6	92	5	3
171	0.59	87	10	3
170	0.51	69	17	14
169	0.51	83	9	8
168	-0.1	53	38	9
167	-0.11	52	38	10
166	-0.33	50	32	19
165 (LUMO)	-0.34	49	31	20
164 (HOMO)	-5.3	85	13	1
163	-5.3	85	13	1
162	-5.33	86	13	1
161	-5.33	86	13	1
160	-6.29	86	11	3
159	-6.3	86	11	3
158	-6.53	7	90	3
172	0.6	92	5	3

Table S8. Selected Fe···Fe distances, B···C(spiro)···B angles, torsion angles in the fulvalenide moiety of **2** in the X-ray and DFT-optimized structures.

	Fe···Fe (Å) [a]	B···C(spiro)···B (deg)	C10-C6-C21-C22 (deg)	C7-C6-C21-C25 (deg)
X-ray	11.733	130.45	9.00	11.61
DFT	12.19	134.20	21.74	22.03

[a] Fe atoms located on the longer diagonal of the parallelogram.



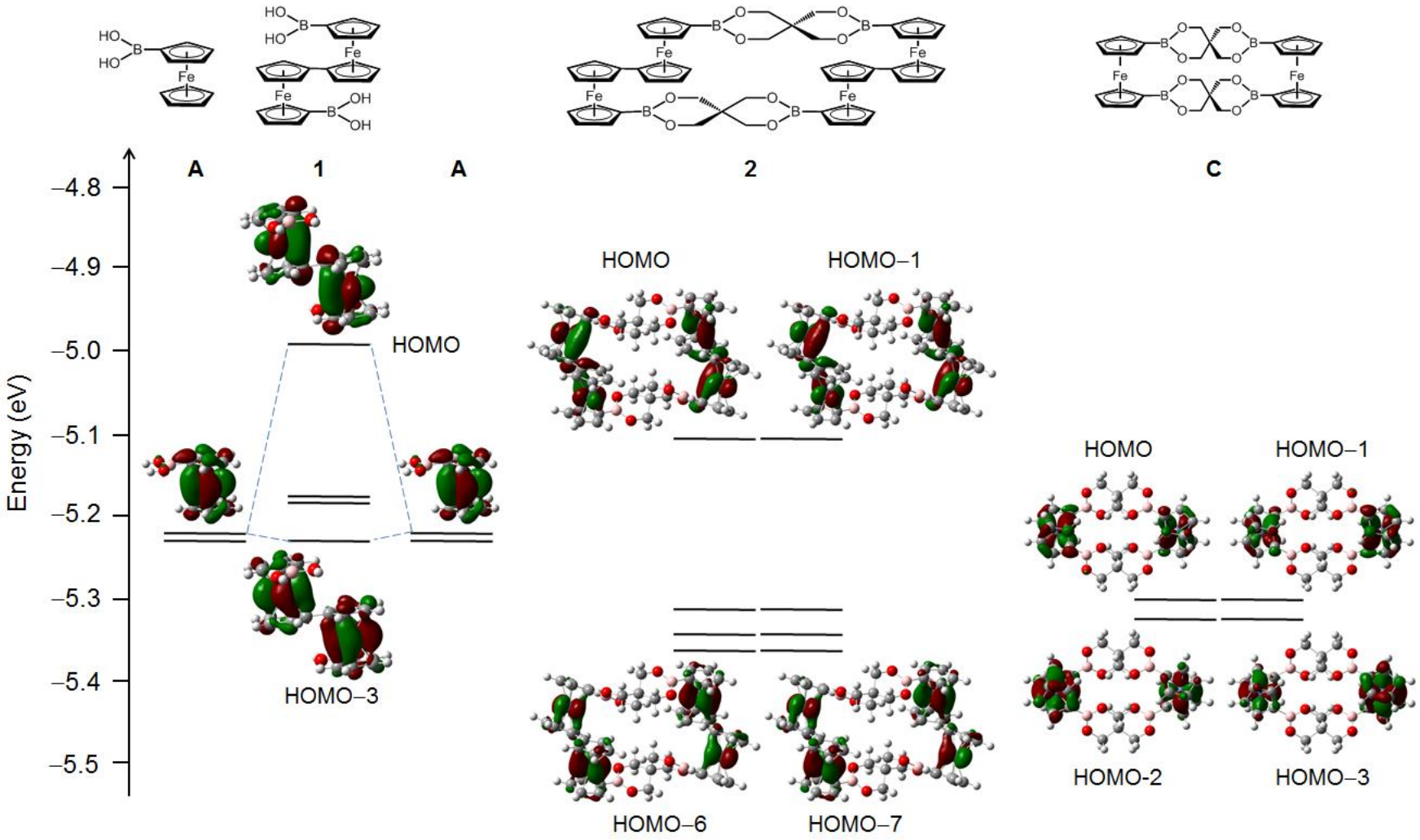


Fig. S15 Selected molecular orbital contributions and energy diagrams for ferroceneboronic acid (**A**), **1**, **2** and **C** in gas phase, calculated using a DFT method (B3LYP/LanL2DZ (Fe atom) and 6-31G(d) (all other atoms) levels of theory) (isosurface values 0.02 au).