

An electrically conducting crystal composed of an octahedrally ligated porphyrin complex with high-spin iron(III)

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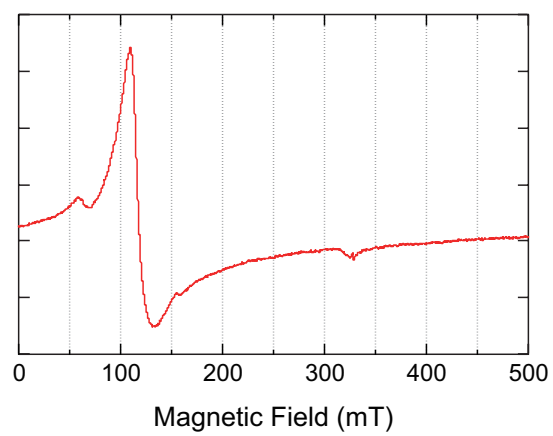


Fig. S1. ESR spectrum of $\text{TPP}[\text{Fe}^{\text{III}}(\text{tbp})\text{Br}_2]_2$ at 20 K.

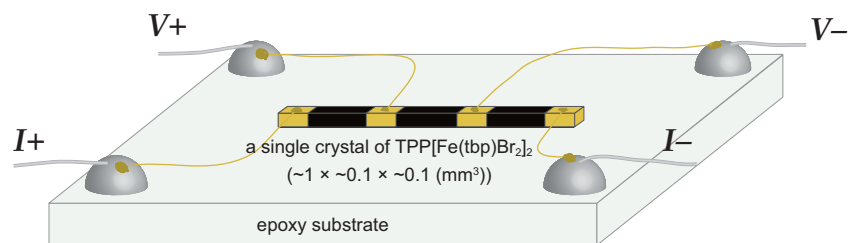


Fig. S2. Schematic of a single crystal on an epoxy substrate. Gold electrodes were fabricated by the vacuum deposition, and gold wires were attached to four terminals for the electrical measurement using gold paste.

Table S1-1. Cartesian coordinates of optimized geometries for Fe(Pc)(CN)₂ (Triplet).

Fe	0	0	0
N	0	1.949898	0
N	-1.963695	0	0
N	0	-1.949898	0
N	1.963695	0	0
C	-1.112545	2.744716	0
C	-2.75805	1.107097	0
C	-2.75805	-1.107097	0
C	-1.112545	-2.744716	0
C	1.112545	-2.744716	0
C	2.75805	-1.107097	0
C	2.75805	1.107097	0
C	1.112545	2.744716	0
C	0.700372	4.148593	0
C	-0.700372	4.148593	0
C	-4.167015	0.699949	0
C	-4.167015	-0.699949	0
C	-0.700372	-4.148593	0
C	0.700372	-4.148593	0
C	4.167015	-0.699949	0
C	4.167015	0.699949	0
N	-2.382162	2.376159	0
N	-2.382162	-2.376159	0
N	2.382162	-2.376159	0
N	2.382162	2.376159	0
C	1.423482	5.333105	0
C	-1.423482	5.333105	0
C	0.700167	6.528589	0
C	-0.700167	6.528589	0
H	1.230882	7.474723	0
H	-1.230882	7.474723	0
H	2.50711	5.32432	0
H	-2.50711	5.32432	0

C	-5.349555	1.422712	0
C	-5.349555	-1.422712	0
C	-6.547477	0.699059	0
C	-6.547477	-0.699059	0
H	-7.493068	1.230741	0
H	-7.493068	-1.230741	0
H	-5.341431	2.506437	0
H	-5.341431	-2.506437	0
C	-1.423482	-5.333105	0
C	1.423482	-5.333105	0
C	-0.700167	-6.528589	0
C	0.700167	-6.528589	0
H	-1.230882	-7.474723	0
H	1.230882	-7.474723	0
H	-2.50711	-5.32432	0
H	2.50711	-5.32432	0
C	5.349555	-1.422712	0
C	5.349555	1.422712	0
C	6.547477	-0.699059	0
C	6.547477	0.699059	0
H	7.493068	-1.230741	0
H	7.493068	1.230741	0
H	5.341431	-2.506437	0
H	5.341431	2.506437	0
C	0	0	1.980393
C	0	0	-1.980393
N	0	0	-3.140951
N	0	0	3.140951

Table S1-2. Cartesian coordinates of optimized geometries for Fe(Pc)(CN)₂ (Septet).

Fe	0	0	0
N	2.027632	0	0
N	0	2.027582	0
N	-2.027632	0	0
N	0	-2.027582	0
C	2.796576	1.123118	0
C	1.123131	2.796546	0
C	-1.123131	2.796546	0
C	-2.796576	1.123118	0
C	-2.796576	-1.123118	0
C	-1.123131	-2.796546	0
C	1.123131	-2.796546	0
C	2.796576	-1.123118	0
C	4.206258	-0.704369	0
C	4.206258	0.704369	0
C	0.704364	4.206219	0
C	-0.704364	4.206219	0
C	-4.206258	0.704369	0
C	-4.206258	-0.704369	0
C	-0.704364	-4.206219	0
C	0.704364	-4.206219	0
N	2.392622	2.392628	0
N	-2.392622	2.392628	0
N	-2.392622	-2.392628	0
N	2.392622	-2.392628	0
C	5.392065	-1.422304	0
C	5.392065	1.422304	0
C	6.589811	-0.698988	0
C	6.589811	0.698988	0
H	7.535268	-1.230837	0
H	7.535268	1.230837	0
H	5.385198	-2.506101	0
H	5.385198	2.506101	0

C	1.4223	5.392025	0
C	-1.4223	5.392025	0
C	0.698988	6.589769	0
C	-0.698988	6.589769	0
H	1.230831	7.53523	0
H	-1.230831	7.53523	0
H	2.506098	5.385153	0
H	-2.506098	5.385153	0
C	-5.392065	1.422304	0
C	-5.392065	-1.422304	0
C	-6.589811	0.698988	0
C	-6.589811	-0.698988	0
H	-7.535268	1.230837	0
H	-7.535268	-1.230837	0
H	-5.385198	2.506101	0
H	-5.385198	-2.506101	0
C	-1.4223	-5.392025	0
C	1.4223	-5.392025	0
C	-0.698988	-6.589769	0
C	0.698988	-6.589769	0
H	-1.230831	-7.53523	0
H	1.230831	-7.53523	0
H	-2.506098	-5.385153	0
H	2.506098	-5.385153	0
C	0	0	2.165984
C	0	0	-2.165984
N	0	0	-3.328551
N	0	0	3.328551

Table S2-1. Cartesian coordinates of optimized geometries for Fe(Pc)Br₂ (Triplet).

Fe	0	0	0
N	1.954277	0	0
N	0	1.947847	0
N	-1.954277	0	0
N	0	-1.947847	0
C	2.751865	1.106752	0
C	1.111434	2.744676	0
C	-1.111434	2.744676	0
C	-2.751865	1.106752	0
C	-2.751865	-1.106752	0
C	-1.111434	-2.744676	0
C	1.111434	-2.744676	0
C	2.751865	-1.106752	0
C	4.160357	-0.699618	0
C	4.160357	0.699618	0
C	0.69998	4.149331	0
C	-0.69998	4.149331	0
C	-4.160357	0.699618	0
C	-4.160357	-0.699618	0
C	-0.69998	-4.149331	0
C	0.69998	-4.149331	0
N	2.379745	2.37613	0
N	-2.379745	2.37613	0
N	-2.379745	-2.37613	0
N	2.379745	-2.37613	0
C	5.34316	-1.422512	0
C	5.34316	1.422512	0
C	6.540911	-0.699233	0
C	6.540911	0.699233	0
H	7.486591	-1.230918	0
H	7.486591	1.230918	0
H	5.334635	-2.506274	0
H	5.334635	2.506274	0

C	1.423059	5.333654	0
C	-1.423059	5.333654	0
C	0.700041	6.5296	0
C	-0.700041	6.5296	0
H	1.231021	7.475671	0
H	-1.231021	7.475671	0
H	2.506751	5.324637	0
H	-2.506751	5.324637	0
C	-5.34316	1.422512	0
C	-5.34316	-1.422512	0
C	-6.540911	0.699233	0
C	-6.540911	-0.699233	0
H	-7.486591	1.230918	0
H	-7.486591	-1.230918	0
H	-5.334635	2.506274	0
H	-5.334635	-2.506274	0
C	-1.423059	-5.333654	0
C	1.423059	-5.333654	0
C	-0.700041	-6.5296	0
C	0.700041	-6.5296	0
H	-1.231021	-7.475671	0
H	1.231021	-7.475671	0
H	-2.506751	-5.324637	0
H	2.506751	-5.324637	0
Br	0	0	2.456171
Br	0	0	-2.456171

Table S2-2. Cartesian coordinates of optimized geometries for Fe(Pc)Br₂ (Septet).

Fe	0	0	0
N	0	2.016702	0
N	-2.016492	0	0
N	0	-2.016702	0
N	2.016492	0	0
C	-1.121901	2.790531	0
C	-2.790375	1.122008	0
C	-2.790375	-1.122008	0
C	-1.121901	-2.790531	0
C	1.121901	-2.790531	0
C	2.790375	-1.122008	0
C	2.790375	1.122008	0
C	1.121901	2.790531	0
C	0.703679	4.199289	0
C	-0.703679	4.199289	0
C	-4.19938	0.703573	0
C	-4.19938	-0.703573	0
C	-0.703679	-4.199289	0
C	0.703679	-4.199289	0
C	4.19938	-0.703573	0
C	4.19938	0.703573	0
N	-2.390584	2.390323	0
N	-2.390584	-2.390323	0
N	2.390584	-2.390323	0
N	2.390584	2.390323	0
C	1.422056	5.385017	0
C	-1.422056	5.385017	0
C	0.699067	6.582781	0
C	-0.699067	6.582781	0
H	1.231005	7.528257	0
H	-1.231005	7.528257	0
H	2.50588	5.377754	0
H	-2.50588	5.377754	0

C	-5.385016	1.422035	0
C	-5.385016	-1.422035	0
C	-6.58282	0.699048	0
C	-6.58282	-0.699048	0
H	-7.528306	1.230971	0
H	-7.528306	-1.230971	0
H	-5.377676	2.505852	0
H	-5.377676	-2.505852	0
C	-1.422056	-5.385017	0
C	1.422056	-5.385017	0
C	-0.699067	-6.582781	0
C	0.699067	-6.582781	0
H	-1.231005	-7.528257	0
H	1.231005	-7.528257	0
H	-2.50588	-5.377754	0
H	2.50588	-5.377754	0
C	5.385016	-1.422035	0
C	5.385016	1.422035	0
C	6.58282	-0.699048	0
C	6.58282	0.699048	0
H	7.528306	-1.230971	0
H	7.528306	1.230971	0
H	5.377676	-2.505852	0
H	5.377676	2.505852	0
Br	0	0	2.586681
Br	0	0	-2.586681

Table S3-1. Cartesian coordinates of optimized geometries for Fe(tbp)(CN)₂ (Triplet).

Fe	0	0	0
N	0	2.02737	0
N	-2.044976	0	0
N	0	-2.02737	0
N	2.044976	0	0
C	-1.105004	2.833239	0
C	-2.850334	1.100306	0
C	-2.850334	-1.100306	0
C	-1.105004	-2.833239	0
C	1.105004	-2.833239	0
C	2.850334	-1.100306	0
C	2.850334	1.100306	0
C	1.105004	2.833239	0
C	0.700199	4.235289	0
C	-0.700199	4.235289	0
C	-4.256811	0.699958	0
C	-4.256811	-0.699958	0
C	-0.700199	-4.235289	0
C	0.700199	-4.235289	0
C	4.256811	-0.699958	0
C	4.256811	0.699958	0
C	1.417216	5.429628	0
C	-1.417216	5.429628	0
C	0.700609	6.624118	0
C	-0.700609	6.624118	0
H	1.23332	7.56913	0
H	-1.23332	7.56913	0
H	2.501891	5.443631	0
H	-2.501891	5.443631	0
C	-5.449341	1.416827	0
C	-5.449341	-1.416827	0
C	-6.645672	0.699769	0
C	-6.645672	-0.699769	0
H	-7.590368	1.233068	0
H	-7.590368	-1.233068	0
H	-5.463355	2.501611	0

H	-5.463355	-2.501611	0
C	-1.417216	-5.429628	0
C	1.417216	-5.429628	0
C	-0.700609	-6.624118	0
C	0.700609	-6.624118	0
H	-1.23332	-7.56913	0
H	1.23332	-7.56913	0
H	-2.501891	-5.443631	0
H	2.501891	-5.443631	0
C	5.449341	-1.416827	0
C	5.449341	1.416827	0
C	6.645672	-0.699769	0
C	6.645672	0.699769	0
H	7.590368	-1.233068	0
H	7.590368	1.233068	0
H	5.463355	-2.501611	0
H	5.463355	2.501611	0
C	0	0	1.974002
C	0	0	-1.974002
N	0	0	-3.134528
N	0	0	3.134528
C	-2.422598	2.415379	0
H	-3.184441	3.184582	0
C	2.422598	2.415379	0
H	3.184441	3.184582	0
C	2.422598	-2.415379	0
H	3.184441	-3.184582	0
C	-2.422598	-2.415379	0
H	-3.184441	-3.184582	0

Table S3-2. Cartesian coordinates of optimized geometries for Fe(tbp)(CN)₂ (Septet).

Fe	0	0	0
N	2.113041	0	0
N	0	2.112814	0
N	-2.113041	0	0
N	0	-2.112814	0
C	2.901546	1.112976	0
C	1.112989	2.901355	0
C	-1.112989	2.901355	0
C	-2.901546	1.112976	0
C	-2.901546	-1.112976	0
C	-1.112989	-2.901355	0
C	1.112989	-2.901355	0
C	2.901546	-1.112976	0
C	4.297701	-0.705991	0
C	4.297701	0.705991	0
C	0.705992	4.297467	0
C	-0.705992	4.297467	0
C	-4.297701	0.705991	0
C	-4.297701	-0.705991	0
C	-0.705992	-4.297467	0
C	0.705992	-4.297467	0
C	5.500206	-1.418182	0
C	5.500206	1.418182	0
C	6.689794	-0.702949	0
C	6.689794	0.702949	0
H	7.635663	-1.234288	0
H	7.635663	1.234288	0
H	5.516136	-2.503276	0
H	5.516136	2.503276	0
C	1.418198	5.50001	0
C	-1.418198	5.50001	0
C	0.702978	6.689553	0
C	-0.702978	6.689553	0
H	1.234271	7.635447	0
H	-1.234271	7.635447	0
H	2.503292	5.515934	0

H	-2.503292	5.515934	0
C	-5.500206	1.418182	0
C	-5.500206	-1.418182	0
C	-6.689794	0.702949	0
C	-6.689794	-0.702949	0
H	-7.635663	1.234288	0
H	-7.635663	-1.234288	0
H	-5.516136	2.503276	0
H	-5.516136	-2.503276	0
C	-1.418198	-5.50001	0
C	1.418198	-5.50001	0
C	-0.702978	-6.689553	0
C	0.702978	-6.689553	0
H	-1.234271	-7.635447	0
H	1.234271	-7.635447	0
H	-2.503292	-5.515934	0
H	2.503292	-5.515934	0
C	0	0	2.129377
C	0	0	-2.129377
N	0	0	-3.291086
N	0	0	3.291086
C	2.429534	2.429459	0
H	3.196636	3.19669	0
C	2.429534	-2.429459	0
H	3.196636	-3.19669	0
C	-2.429534	-2.429459	0
H	-3.196636	-3.19669	0
C	-2.429534	2.429459	0
H	-3.196636	3.19669	0

Table S4-1. Cartesian coordinates of optimized geometries for Fe(tbp)Br₂ (Triplet).

Fe	0	0	0
N	0	2.026789	0
N	-2.035962	0	0
N	0	-2.026789	0
N	2.035962	0	0
C	-1.103885	2.833975	0
C	-2.843727	1.099928	0
C	-2.843727	-1.099928	0
C	-1.103885	-2.833975	0
C	1.103885	-2.833975	0
C	2.843727	-1.099928	0
C	2.843727	1.099928	0
C	1.103885	2.833975	0
C	0.699956	4.237134	0
C	-0.699956	4.237134	0
C	-4.250253	0.699745	0
C	-4.250253	-0.699745	0
C	-0.699956	-4.237134	0
C	0.699956	-4.237134	0
C	4.250253	-0.699745	0
C	4.250253	0.699745	0
C	1.416756	5.431212	0
C	-1.416756	5.431212	0
C	0.700464	6.626478	0
C	-0.700464	6.626478	0
H	1.2336	7.571346	0
H	-1.2336	7.571346	0
H	2.501571	5.445169	0
H	-2.501571	5.445169	0
C	-5.443008	1.416478	0
C	-5.443008	-1.416478	0
C	-6.639585	0.699874	0
C	-6.639585	-0.699874	0

H	-7.584229	1.233431	0
H	-7.584229	-1.233431	0
H	-5.457048	2.501374	0
H	-5.457048	-2.501374	0
C	-1.416756	-5.431212	0
C	1.416756	-5.431212	0
C	-0.700464	-6.626478	0
C	0.700464	-6.626478	0
H	-1.2336	-7.571346	0
H	1.2336	-7.571346	0
H	-2.501571	-5.445169	0
H	2.501571	-5.445169	0
C	5.443008	-1.416478	0
C	5.443008	1.416478	0
C	6.639585	-0.699874	0
C	6.639585	0.699874	0
H	7.584229	-1.233431	0
H	7.584229	1.233431	0
H	5.457048	-2.501374	0
H	5.457048	2.501374	0
C	-2.419975	2.415496	0
H	-3.183559	3.183151	0
C	2.419975	2.415496	0
H	3.183559	3.183151	0
C	2.419975	-2.415496	0
H	3.183559	-3.183151	0
C	-2.419975	-2.415496	0
H	-3.183559	-3.183151	0
Br	0	0	2.440548
Br	0	0	-2.440548

Table S4-2. Cartesian coordinates of optimized geometries for Fe(tbp)Br₂ (Septet).

Fe	0	0	0
N	0	2.098901	0
N	-2.098904	0	0
N	0	-2.098901	0
N	2.098904	0	0
C	-1.113373	2.8838	0
C	-2.883803	1.113373	0
C	-2.883803	-1.113373	0
C	-1.113373	-2.8838	0
C	1.113373	-2.8838	0
C	2.883803	-1.113373	0
C	2.883803	1.113373	0
C	1.113373	2.8838	0
C	0.703223	4.290893	0
C	-0.703223	4.290893	0
C	-4.290896	0.703223	0
C	-4.290896	-0.703223	0
C	-0.703223	-4.290893	0
C	0.703223	-4.290893	0
C	4.290896	-0.703223	0
C	4.290896	0.703223	0
C	1.416154	5.485806	0
C	-1.416154	5.485806	0
C	0.699673	6.682528	0
C	-0.699673	6.682528	0
H	1.233436	7.627018	0
H	-1.233436	7.627018	0
H	2.501052	5.499949	0
H	-2.501052	5.499949	0
C	-5.485809	1.416154	0
C	-5.485809	-1.416154	0
C	-6.68253	0.699673	0
C	-6.68253	-0.699673	0

H	-7.627021	1.233437	0
H	-7.627021	-1.233437	0
H	-5.499952	2.501052	0
H	-5.499952	-2.501052	0
C	-1.416154	-5.485806	0
C	1.416154	-5.485806	0
C	-0.699673	-6.682528	0
C	0.699673	-6.682528	0
H	-1.233436	-7.627018	0
H	1.233436	-7.627018	0
H	-2.501052	-5.499949	0
H	2.501052	-5.499949	0
C	5.485809	-1.416154	0
C	5.485809	1.416154	0
C	6.68253	-0.699673	0
C	6.68253	0.699673	0
H	7.627021	-1.233437	0
H	7.627021	1.233437	0
H	5.499952	-2.501052	0
H	5.499952	2.501052	0
C	-2.432017	2.432016	0
H	-3.198297	3.198298	0
C	2.432017	2.432016	0
H	3.198297	3.198298	0
C	2.432017	-2.432016	0
H	3.198297	-3.198298	0
C	-2.432017	-2.432016	0
H	-3.198297	-3.198298	0
Br	0	0	2.546283
Br	0	0	-2.546283

Table S5-1. Cartesian coordinates of optimized geometries for [Fe(Pc)(CN)₂][−] (Doublet).

Fe	0	0	0
N	0	1.936597	0
N	-1.960403	0	0
N	0	-1.936597	0
N	1.960403	0	0
C	-1.112882	2.739565	0
C	-2.755782	1.10604	0
C	-2.755782	-1.10604	0
C	-1.112882	-2.739565	0
C	1.112882	-2.739565	0
C	2.755782	-1.10604	0
C	2.755782	1.10604	0
C	1.112882	2.739565	0
C	0.698794	4.151624	0
C	-0.698794	4.151624	0
C	-4.159574	0.701833	0
C	-4.159574	-0.701833	0
C	-0.698794	-4.151624	0
C	0.698794	-4.151624	0
C	4.159574	-0.701833	0
C	4.159574	0.701833	0
N	-2.378071	2.384976	0
N	-2.378071	-2.384976	0
N	2.378071	-2.384976	0
N	2.378071	2.384976	0
C	1.419475	5.335704	0
C	-1.419475	5.335704	0
C	0.699176	6.535537	0
C	-0.699176	6.535537	0
H	1.232811	7.481331	0
H	-1.232811	7.481331	0
H	2.503717	5.322817	0
H	-2.503717	5.322817	0

C	-5.348361	1.420791	0
C	-5.348361	-1.420791	0
C	-6.545104	0.700959	0
C	-6.545104	-0.700959	0
H	-7.491654	1.233386	0
H	-7.491654	-1.233386	0
H	-5.337737	2.5052	0
H	-5.337737	-2.5052	0
C	-1.419475	-5.335704	0
C	1.419475	-5.335704	0
C	-0.699176	-6.535537	0
C	0.699176	-6.535537	0
H	-1.232811	-7.481331	0
H	1.232811	-7.481331	0
H	-2.503717	-5.322817	0
H	2.503717	-5.322817	0
C	5.348361	-1.420791	0
C	5.348361	1.420791	0
C	6.545104	-0.700959	0
C	6.545104	0.700959	0
H	7.493068	-1.230741	0
H	7.493068	1.230741	0
H	5.341431	-2.506437	0
H	5.341431	2.506437	0
C	0	0	1.99597
C	0	0	-1.99597
N	0	0	-3.158012
N	0	0	3.158012

Table S5-2. Cartesian coordinates of optimized geometries for [Fe(Pc)(CN)₂]⁻ (Sextet).

Fe	0	0	0
N	2.000828	0	0
N	0	1.951606	0
N	-2.000828	0	0
N	0	-1.951606	0
C	2.786883	1.112055	0
C	1.125259	2.74458	0
C	-1.125259	2.74458	0
C	-2.786883	1.112055	0
C	-2.786883	-1.112055	0
C	-1.125259	-2.74458	0
C	1.125259	-2.74458	0
C	2.786883	-1.112055	0
C	4.177698	-0.706707	0
C	4.177698	0.706707	0
C	0.698637	4.155572	0
C	-0.698637	4.155572	0
C	-4.177698	0.706707	0
C	-4.177698	-0.706707	0
C	-0.698637	-4.155572	0
C	0.698637	-4.155572	0
N	2.386102	2.401265	0
N	-2.386102	2.401265	0
N	-2.386102	-2.401265	0
N	2.386102	-2.401265	0
C	5.373248	-1.422641	0
C	5.373248	1.422641	0
C	6.565711	-0.703461	0
C	6.565711	0.703461	0
H	7.513101	-1.234337	0
H	7.513101	1.234337	0
H	5.364825	-2.507139	0
H	5.364825	2.507139	0

C	1.419737	5.340061	0
C	-1.419737	5.340061	0
C	0.6997	6.538389	0
C	-0.6997	6.538389	0
H	1.23259	7.484493	0
H	-1.23259	7.484493	0
H	2.503797	5.325426	0
H	-2.503797	5.325426	0
C	-5.373248	1.422641	0
C	-5.373248	-1.422641	0
C	-6.565711	0.703461	0
C	-6.565711	-0.703461	0
H	-7.513101	1.234337	0
H	-7.513101	-1.234337	0
H	-5.364825	2.507139	0
H	-5.364825	-2.507139	0
C	-1.419737	-5.340061	0
C	1.419737	-5.340061	0
C	-0.6997	-6.538389	0
C	0.6997	-6.538389	0
H	-1.23259	-7.484493	0
H	1.23259	-7.484493	0
H	-2.503797	-5.325426	0
H	2.503797	-5.325426	0
C	0	0	2.225311
C	0	0	-2.225311
N	0	0	-3.389049
N	0	0	3.389049

Table S6-1. Cartesian coordinates of optimized geometries for [Fe(Pc)Br₂][−] (Doublet).

Fe	0	0	0
N	1.960801	0	0
N	0	1.954618	0
N	-1.960801	0	0
N	0	-1.954618	0
C	2.756169	1.109559	0
C	1.114047	2.748944	0
C	-1.114047	2.748944	0
C	-2.756169	1.109559	0
C	-2.756169	-1.109559	0
C	-1.114047	-2.748944	0
C	1.114047	-2.748944	0
C	2.756169	-1.109559	0
C	4.158008	-0.701326	0
C	4.158008	0.701326	0
C	0.701896	4.146086	0
C	-0.701896	4.146086	0
C	-4.158008	0.701326	0
C	-4.158008	-0.701326	0
C	-0.701896	-4.146086	0
C	0.701896	-4.146086	0
N	2.382221	2.377855	0
N	-2.382221	2.377855	0
N	-2.382221	-2.377855	0
N	2.382221	-2.377855	0
C	5.349522	-1.420869	0
C	5.349522	1.420869	0
C	6.543128	-0.702424	0
C	6.543128	0.702424	0
H	7.490365	-1.234004	0
H	7.490365	1.234004	0
H	5.338168	-2.505357	0
H	5.338168	2.505357	0

C	1.421551	5.339526	0
C	-1.421551	5.339526	0
C	0.703375	6.531151	0
C	-0.703375	6.531151	0
H	1.234175	7.478801	0
H	-1.234175	7.478801	0
H	2.505958	5.327757	0
H	-2.505958	5.327757	0
C	-5.349522	1.420869	0
C	-5.349522	-1.420869	0
C	-6.543128	0.702424	0
C	-6.543128	-0.702424	0
H	-7.490365	1.234004	0
H	-7.490365	-1.234004	0
H	-5.338168	2.505357	0
H	-5.338168	-2.505357	0
C	-1.421551	-5.339526	0
C	1.421551	-5.339526	0
C	-0.703375	-6.531151	0
C	0.703375	-6.531151	0
H	-1.234175	-7.478801	0
H	1.234175	-7.478801	0
H	-2.505958	-5.327757	0
H	2.505958	-5.327757	0
Br	0	0	2.476884
Br	0	0	-2.476884

Table S6-2. Cartesian coordinates of optimized geometries for [Fe(Pc)Br₂][−] (Sextet).

Fe	0	0	0
N	0	2.020619	0
N	-2.020577	0	0
N	0	-2.020619	0
N	2.020577	0	0
C	-1.124152	2.792977	0
C	-2.792929	1.124188	0
C	-2.792929	-1.124188	0
C	-1.124152	-2.792977	0
C	1.124152	-2.792977	0
C	2.792929	-1.124188	0
C	2.792929	1.124188	0
C	1.124152	2.792977	0
C	0.70519	4.195004	0
C	-0.70519	4.195004	0
C	-4.195096	0.705143	0
C	-4.195096	-0.705143	0
C	-0.70519	-4.195004	0
C	0.70519	-4.195004	0
C	4.195096	-0.705143	0
C	4.195096	0.705143	0
N	-2.392035	2.391889	0
N	-2.392035	-2.391889	0
N	2.392035	-2.391889	0
N	2.392035	2.391889	0
C	1.420611	5.389309	0
C	-1.420611	5.389309	0
C	0.702352	6.582506	0
C	-0.702352	6.582506	0
H	1.233899	7.529647	0
H	-1.233899	7.529647	0
H	2.505111	5.379131	0
H	-2.505111	5.379131	0

C	-5.389335	1.420594	0
C	-5.389335	-1.420594	0
C	-6.582572	0.702325	0
C	-6.582572	-0.702325	0
H	-7.529703	1.233891	0
H	-7.529703	-1.233891	0
H	-5.379142	2.50509	0
H	-5.379142	-2.50509	0
C	-1.420611	-5.389309	0
C	1.420611	-5.389309	0
C	-0.702352	-6.582506	0
C	0.702352	-6.582506	0
H	-1.233899	-7.529647	0
H	1.233899	-7.529647	0
H	-2.505111	-5.379131	0
H	2.505111	-5.379131	0
C	5.389335	-1.420594	0
C	5.389335	1.420594	0
C	6.582572	-0.702325	0
C	6.582572	0. 0.702325	0
H	7.529703	-1.233891	0
H	7.529703	1.233891	0
H	5.379142	-2.50509	0
H	5.379142	2.50509	0
Br	0	0	2.626438
Br	0	0	-2.626438

Table S7-1. Cartesian coordinates of optimized geometries for [Fe(tbp)(CN)₂][−] (Doublet).

Fe	0	0	0
N	1.436955	1.436955	0
N	-1.436955	1.436955	0
N	-1.436955	-1.436955	0
N	1.436955	-1.436955	0
C	1.230965	2.773371	0.192708
C	-1.230965	2.773371	0.192708
C	-2.773371	1.230965	-0.192708
C	-2.773371	-1.230965	-0.192708
C	-1.230965	-2.773371	0.192708
C	1.230965	-2.773371	0.192708
C	2.773371	-1.230965	-0.192708
C	2.773371	1.230965	-0.192708
C	3.476597	2.500576	-0.13413
C	2.500576	3.476597	0.13413
C	-2.500576	3.476597	0.13413
C	-3.476597	2.500576	-0.13413
C	-3.476597	-2.500576	-0.13413
C	-2.500576	-3.476597	0.13413
C	2.500576	-3.476597	0.13413
C	3.476597	-2.500576	-0.13413
C	4.821523	2.85606	-0.270763
C	2.85606	4.821523	0.270763
C	5.169619	4.193859	-0.135676
C	4.193859	5.169619	0.135676
H	6.208394	4.493186	-0.239928
H	4.493186	6.208394	0.239928
H	5.583049	2.111178	-0.481045
H	2.111178	5.583049	0.481045
C	-2.85606	4.821523	0.270763
C	-4.821523	2.85606	-0.270763
C	-4.193859	5.169619	0.135676
C	-5.169619	4.193859	-0.135676
H	-4.493186	6.208394	0.239928
H	-6.208394	4.493186	-0.239928
H	-2.111178	5.583049	0.481045

H	-5.583049	2.111178	-0.481045
C	-4.821523	-2.85606	-0.270763
C	-2.85606	-4.821523	0.270763
C	-5.169619	-4.193859	-0.135676
C	-4.193859	-5.169619	0.135676
H	-6.208394	-4.493186	-0.239928
H	-4.493186	-6.208394	0.239928
H	-5.583049	-2.111178	-0.481045
H	-2.111178	-5.583049	0.481045
C	2.85606	-4.821523	0.270763
C	4.821523	-2.85606	-0.270763
C	4.193859	-5.169619	0.135676
C	-5.169619	4.193859	-0.135676
H	4.493186	-6.208394	0.239928
H	6.208394	-4.493186	-0.239928
H	2.111178	-5.583049	0.481045
H	5.583049	-2.111178	-0.481045
C	0	0	1.983963
C	0	0	-1.983963
N	0	0	-3.144984
N	0	0	3.144984
C	0	3.390151	0.323838
H	0	4.465186	0.461308
C	3.390151	0	-0.323838
H	4.465186	0	-0.461308
C	0	-3.390151	0.323838
H	0	-4.465186	0.461308
C	-3.390151	0	-0.323838
H	-4.465186	0	-0.461308

Table S7-2. Cartesian coordinates of optimized geometries for [Fe(tbp)(CN)₂][−] (Sextet).

Fe	0	0	0
N	2.140473	0.000385	0
N	0	2.070743	0
N	-2.140473	-0.000385	0
N	0	-2.070743	0
C	2.922185	1.090802	0
C	1.140579	2.867655	0
C	-1.102676	2.860041	0
C	-2.92779	1.134886	0
C	-2.922185	-1.090802	0
C	-1.140579	-2.867655	0
C	1.102676	-2.860041	0
C	2.92779	-1.134886	0
C	4.314202	-0.729773	0
C	4.312269	0.691782	0
C	0.71701	4.274191	0
C	-0.688303	4.268985	0
C	-4.314202	0.729773	0
C	-4.312269	-0.691782	0
C	-0.71701	-4.274191	0
C	0.688303	-4.268985	0
C	5.525716	-1.430825	0
C	5.516977	1.403689	0
C	6.714278	-0.713566	0
C	6.711368	0.696004	0
H	7.662304	-1.24381	0
H	7.656222	1.231537	0
H	5.544482	-2.516958	0
H	5.526491	2.489887	0
C	1.421921	5.474208	0
C	-1.402953	5.464646	0
C	0.704983	6.670964	0
C	-0.694452	6.665892	0
H	1.237991	7.617132	0
H	-1.234036	7.608373	0
H	2.507587	5.489055	0

H	-2.48853	5.472127	0
C	-5.525716	1.430825	0
C	-5.516977	-1.403689	0
C	-6.714278	0.713566	0
C	-6.711368	-0.696004	0
H	-7.662304	1.24381	0
H	-7.656222	-1.231537	0
H	-5.544482	2.516958	0
H	-5.526491	-2.489887	0
C	-1.421921	-5.474208	0
C	1.402953	-5.464646	0
C	-0.704983	-6.670964	0
C	0.694452	-6.665892	0
H	-1.237991	-7.617132	0
H	1.234036	-7.608373	0
H	-2.507587	-5.489055	0
H	2.48853	-5.472127	0
C	0	0	1.984841
C	0	0	-1.984841
N	0	0	-3.145361
N	0	0	3.145361
C	2.437126	2.442247	0
H	3.199191	3.213938	0
C	2.435344	-2.439829	0
H	3.179792	-3.228817	0
C	-2.437126	-2.442247	0
H	-3.199191	-3.213938	0
C	-2.435344	2.439829	0
H	-3.179792	3.228817	0

Table S8-1. Cartesian coordinates of optimized geometries for [Fe(tbp)Br₂][−] (Doublet).

Fe	0	0	0
N	0	0	2.035884
N	0.003985	2.044185	0
N	0	0	-2.035884
N	-0.003985	-2.044185	0
C	0.000303	1.106779	2.841055
C	0.003849	2.850226	1.102998
C	0.003849	2.850226	-1.102998
C	0.000303	1.106779	-2.841055
C	-0.000303	-1.106779	-2.841055
C	-0.003849	-2.850226	-1.102998
C	-0.003849	-2.850226	1.102998
C	-0.000303	-1.106779	2.841055
C	-0.000503	-0.702932	4.234391
C	0.000503	0.702932	4.234391
C	0.004678	4.247373	0.702554
C	0.004678	4.247373	-0.702554
C	0.000503	0.702932	-4.234391
C	-0.000503	-0.702932	-4.234391
C	-0.004678	-4.247373	-0.702554
C	-0.004678	-4.247373	0.702554
C	-0.000885	-1.415673	5.438035
C	0.000885	1.415673	5.438035
C	-0.000417	-0.703666	6.62975
C	0.000417	0.703666	6.62975
H	-0.000689	-1.236865	7.576056
H	0.000689	1.236865	7.576056
H	-0.001465	-2.501482	5.449961
H	0.001465	2.501482	5.449961
C	0.005457	5.449494	1.415272
C	0.005457	5.449494	-1.415272
C	0.006226	6.642612	0.702991
C	0.006226	6.642612	-0.702991

H	0.006857	7.588682	1.23666
H	0.006857	7.588682	-1.23666
H	0.005417	5.461431	2.50117
H	0.005417	5.461431	-2.50117
C	0.000885	1.415673	-5.438035
C	-0.000885	-1.415673	-5.438035
C	0.000417	0.703666	-6.62975
C	-0.000417	-0.703666	-6.62975
H	0.000689	1.236865	-7.576056
H	-0.000689	-1.236865	-7.576056
H	0.001465	2.501482	-5.449961
H	-0.001465	-2.501482	-5.449961
C	-0.005457	-5.449494	-1.415272
C	-0.005457	-5.449494	1.415272
C	-0.006226	-6.642612	-0.702991
C	-0.006226	-6.642612	0.702991
H	-0.006857	-7.588682	-1.23666
H	-0.006857	-7.588682	1.23666
H	-0.005417	-5.461431	-2.50117
H	-0.005417	-5.461431	2.50117
C	0.002142	2.421539	2.416604
H	0.0022	3.186135	3.185087
C	-0.002142	-2.421539	2.416604
H	-0.0022	-3.186135	3.185087
C	-0.002142	-2.421539	-2.416604
H	-0.0022	-3.186135	-3.185087
C	0.002142	2.421539	-2.416604
H	0.0022	3.186135	-3.185087
Br	-2.460636	0.018063	0
Br	2.460636	-0.018063	0

Table S8-2. Cartesian coordinates of optimized geometries for [Fe(tbp)Br₂][−] (Sextet).

Fe	0	0	0
N	0	2.104059	0
N	-2.104092	0.000056	0
N	0	-2.104059	0
N	2.104092	-0.000056	0
C	-1.115734	2.888272	0
C	-2.888304	1.116042	0
C	-2.888265	-1.115681	0
C	-1.11603	-2.888289	0
C	1.115734	-2.888272	0
C	2.888304	-1.116042	0
C	2.888265	1.115681	0
C	1.11603	2.888289	0
C	0.706006	4.28581	0
C	-0.705743	4.285811	0
C	-4.285844	0.706036	0
C	-4.285817	-0.705703	0
C	-0.706006	-4.28581	0
C	0.705743	-4.285811	0
C	4.285844	-0.706036	0
C	4.285817	0.705703	0
C	1.415164	5.490101	0
C	-1.415064	5.489994	0
C	0.702867	6.682941	0
C	-0.70291	6.682912	0
H	1.236497	7.628961	0
H	-1.236584	7.628901	0
H	2.50102	5.502262	0
H	-2.500921	5.501936	0
C	-5.490128	1.41519	0
C	-5.48999	-1.415038	0
C	-6.682966	0.702881	0
C	-6.682919	-0.702891	0

H	-7.628989	1.236504	0
H	-7.628899	-1.236581	0
H	-5.502303	2.501043	0
H	-5.501923	-2.500896	0
C	-1.415164	-5.490101	0
C	1.415064	-5.489994	0
C	-0.702867	-6.682941	0
C	0.70291	-6.682912	0
H	-1.236497	-7.628961	0
H	1.236584	-7.628901	0
H	-2.50102	-5.502262	0
H	2.500921	-5.501936	0
C	5.490128	-1.41519	0
C	5.48999	1.415038	0
C	6.682966	-0.702881	0
C	6.682919	0.702891	0
H	7.628989	-1.236504	0
H	7.628899	1.236581	0
H	5.502303	-2.501043	0
H	5.501923	2.500896	0
C	-2.432712	2.432737	0
H	-3.199792	3.199993	0
C	2.432722	2.43266	0
H	3.199992	3.19973	0
C	2.432712	-2.432737	0
H	3.199792	-3.199993	0
C	-2.432722	-2.43266	0
H	-3.199992	-3.19973	0
Br	0	0	2.582492
Br	0	0	-2.582492
