Electronic supplementary information (ESI)

Synthesis and structural characterization of the racemic and meso forms of 2,2''-dibromo-1,1''-biferrocenes and their mixed-valence salts

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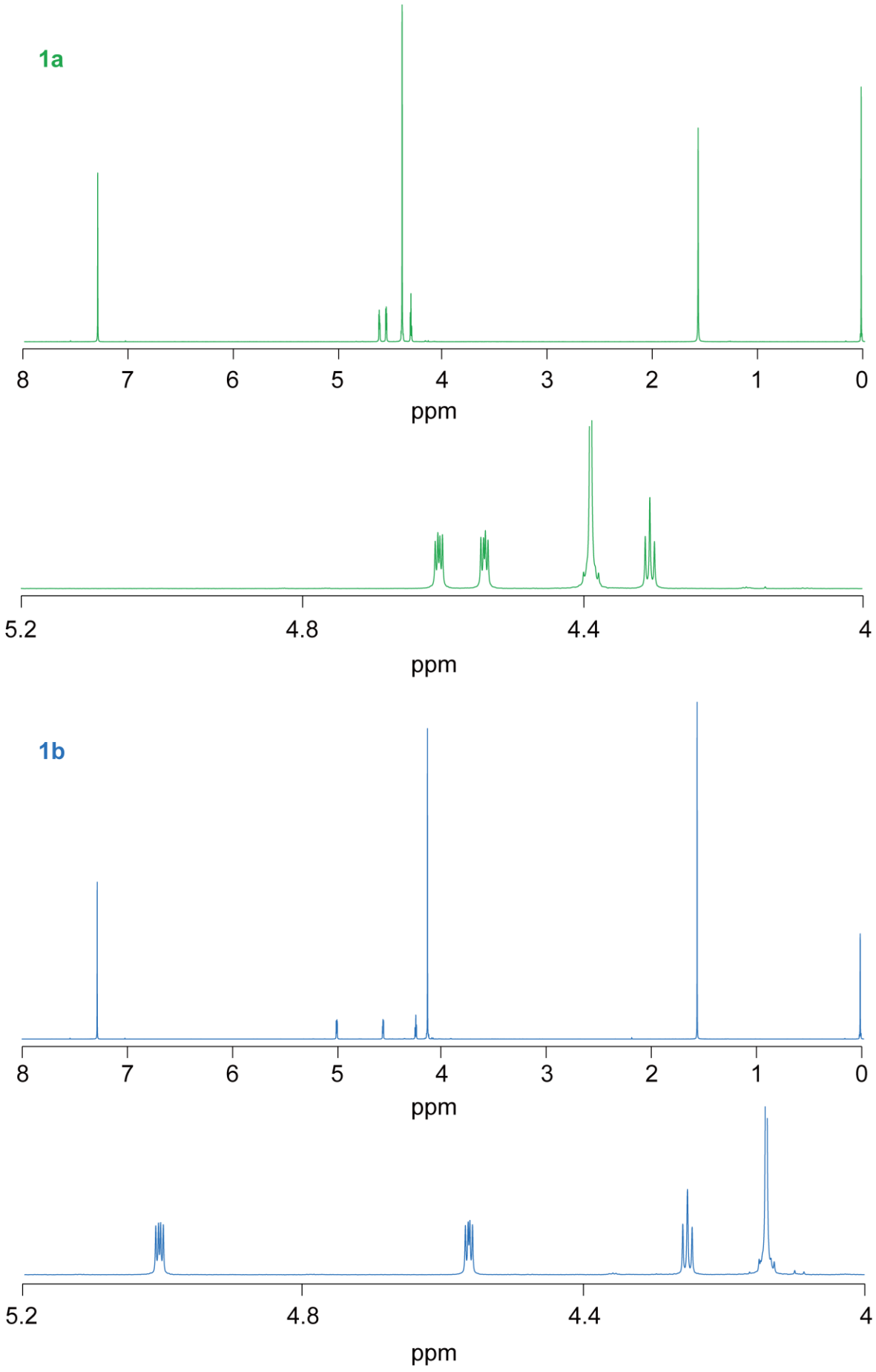


Fig. S1 ^{1}H NMR spectra of **1a** and **1b** in deuterated chloroform.

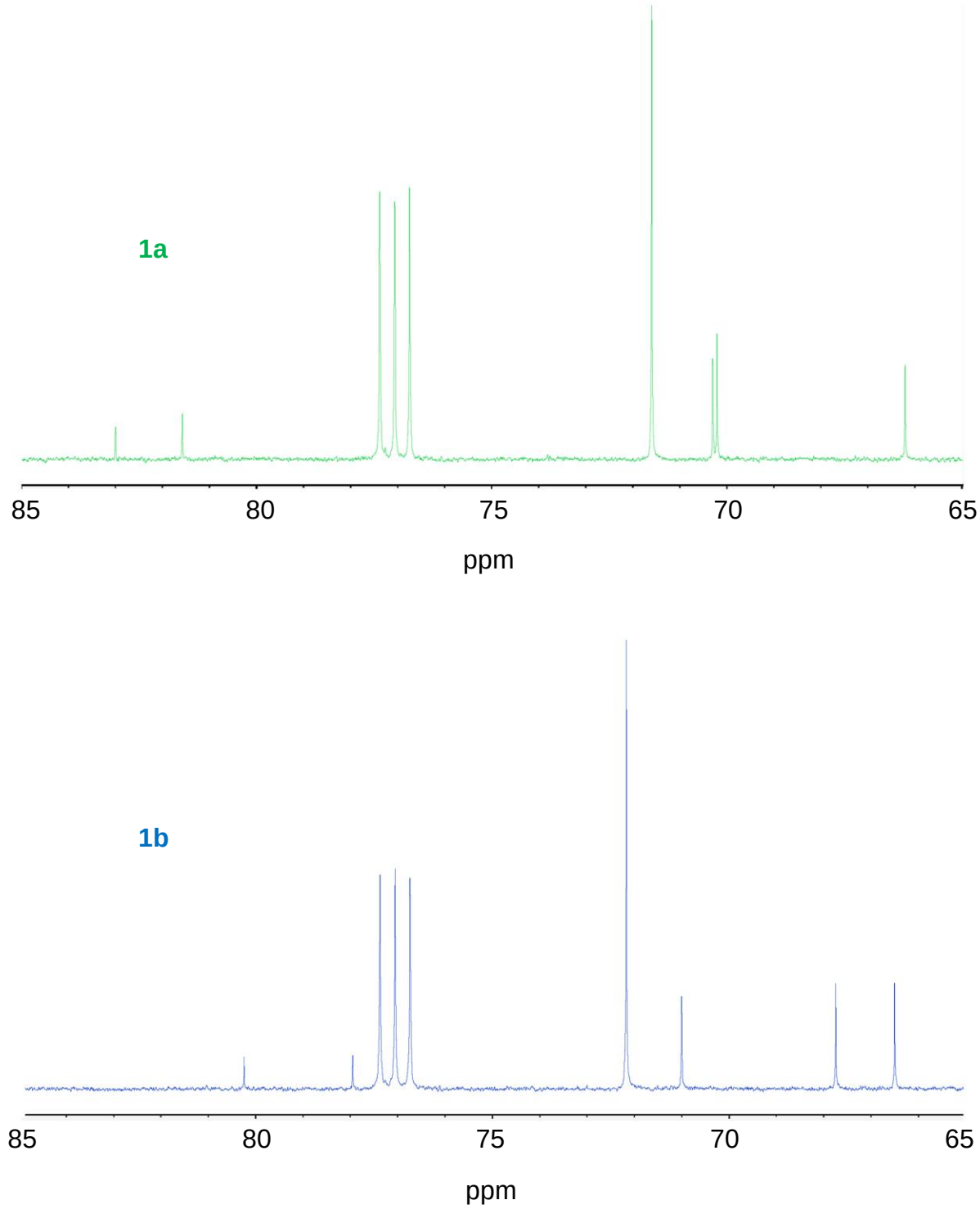
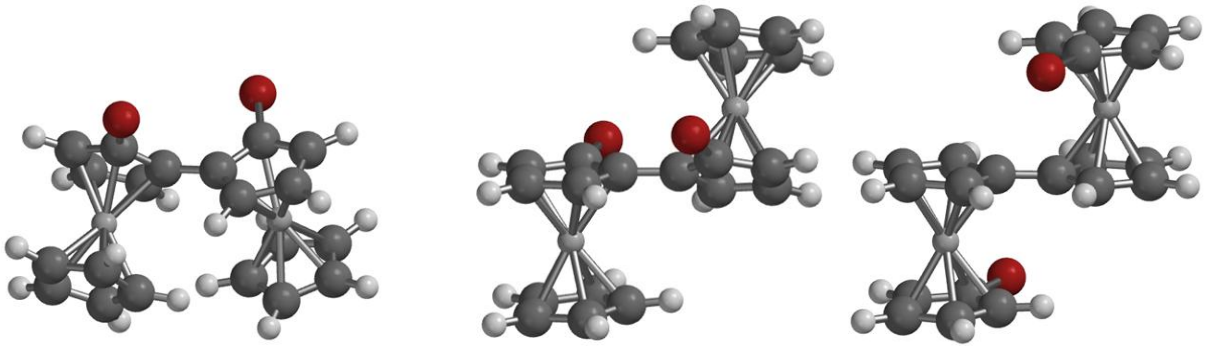


Fig. S2 ^{13}C NMR spectra of **1a** and **1b** in deuterated chloroform.



	1a	**1b**	**1c**
E / au	−8447.5874	−8447.5841	−8447.5867
G^0 / au	−8447.3281	−8447.3252	−8447.3278
HOMO / ev	−8.01	−7.84	−7.81
LUMO / ev	1.35	1.28	1.33

Fig. S3 Optimized molecular structures of **1a**–**1c** obtained from DFT calculations (ωB97X-D/6-311+G(d,p) level). The corresponding energies and MO levels are shown below.

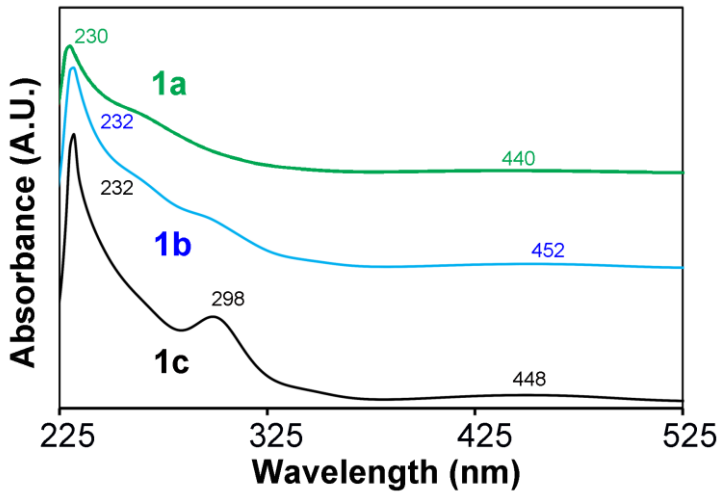


Fig. S4 UV–vis absorption spectra of **1a**–**1c** in 0.1 M dichloromethane solution.

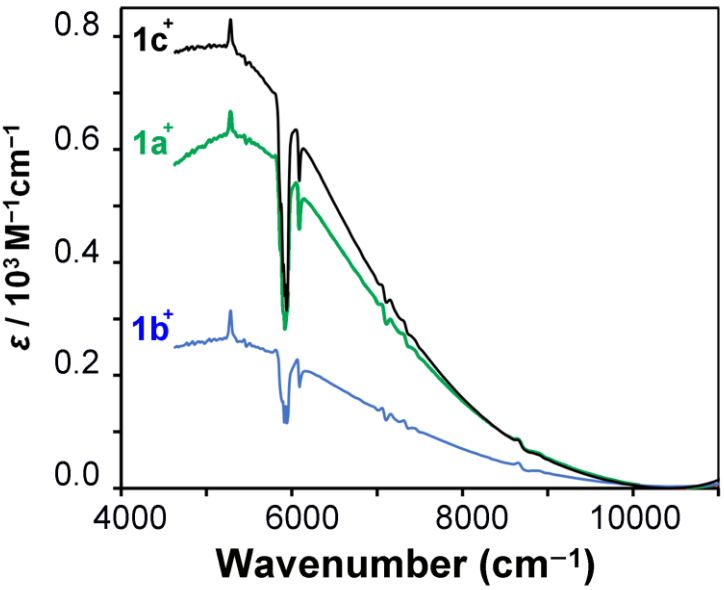


Fig. S5 NIR absorption spectra of **1a**$^{+}$–**1c**$^{+}$ in 1 mM dichloromethane solution.

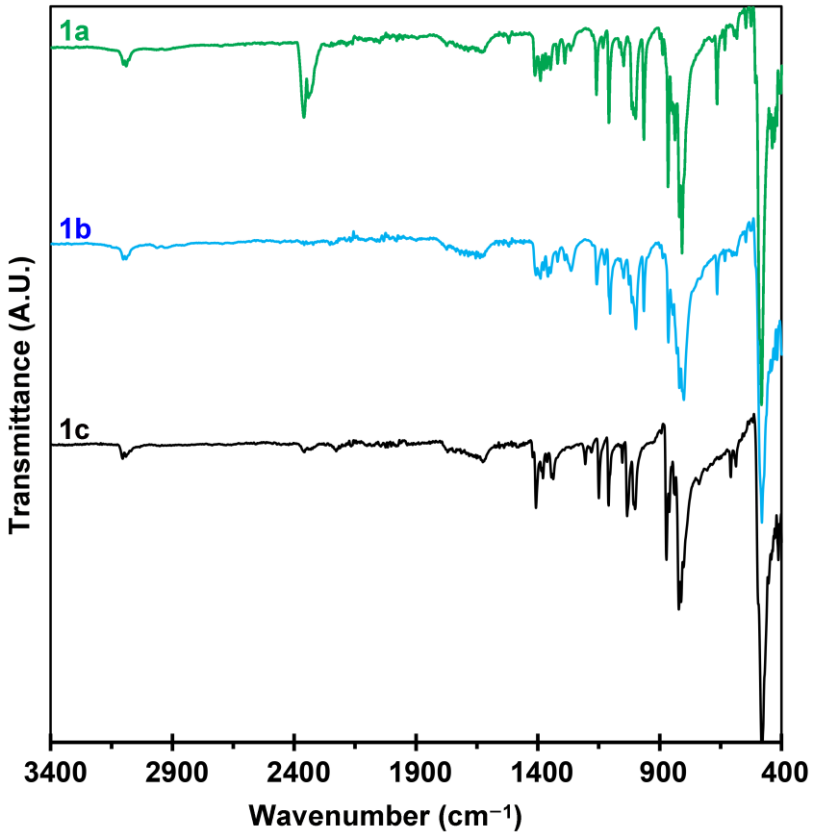


Fig. S6 FTIR spectra of **1a**–**1c**.

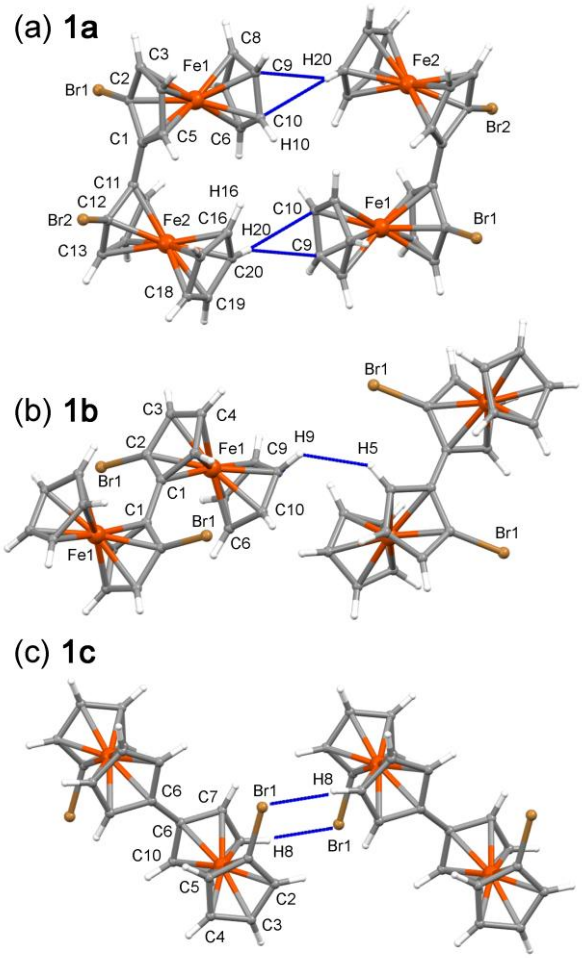


Fig. S7 Two adjacent molecules with atomic numbering schemes: (a) **1a**, (b) **1b**, and (c) **1c**. Dashed blue lines represent intermolecular interactions.

Selected bond distances (Å)

	1a	**1b**	[**1a**]I_7
C1–C1#		1.46	
C1–C2	1.43	1.45	1.43
C1–C5	1.42	1.44	1.45
C1–C11	1.48		1.47
C1–Fe1	2.05	2.05	2.06
C2–Br1	1.89	1.89	1.88
C2–Fe1	2.01	2.02	2.02
C3–Fe1	2.04	2.05	2.05
C4–Fe1	2.04	2.05	2.04
C5–Fe1	2.05	2.05	2.04
C6–Fe1	2.05	2.04	2.07
C7–Fe1	2.04	2.04	2.04
C8–Fe1	2.04	2.05	2.04
C9–Fe1	2.04	2.04	2.05
C10–Fe1	2.05	2.04	2.04
C11–Fe2	2.05		2.16
C12–Br2	1.89		1.85
C12–Fe2	2.00		2.12
C13–Fe2	2.04		2.05
C14–Fe2	2.06		2.04
C15–Fe2	2.07		2.07
C16–Fe2	2.05		2.11
C17–Fe2	2.05		2.07
C18–Fe2	2.05		2.05
C19–Fe2	2.05		2.06
C20–Fe2	2.05		2.09

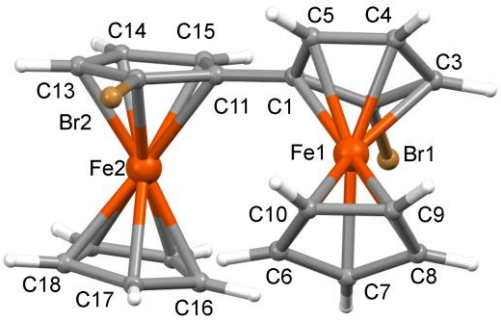


Fig. S8 Atomic numbering schemes of [**1a**]I_7.

Selected torsion angles (°)

	1a	**1b**	[**1a**]I_7
C2–C1–C11–C12	−117.3		−152.3
C2–C1–C1#–C2#		180	

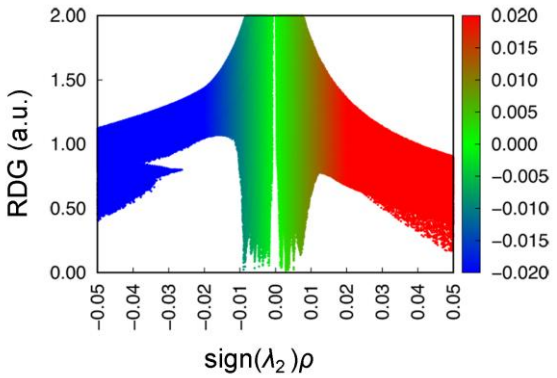


Fig. S9 Scatter plot of reduced density gradient (RDG) *vs*. sign(λ_2)ρ (grid size 0.1 Bohr) for a Br···HC hydrogen bond dimer of **1a**.

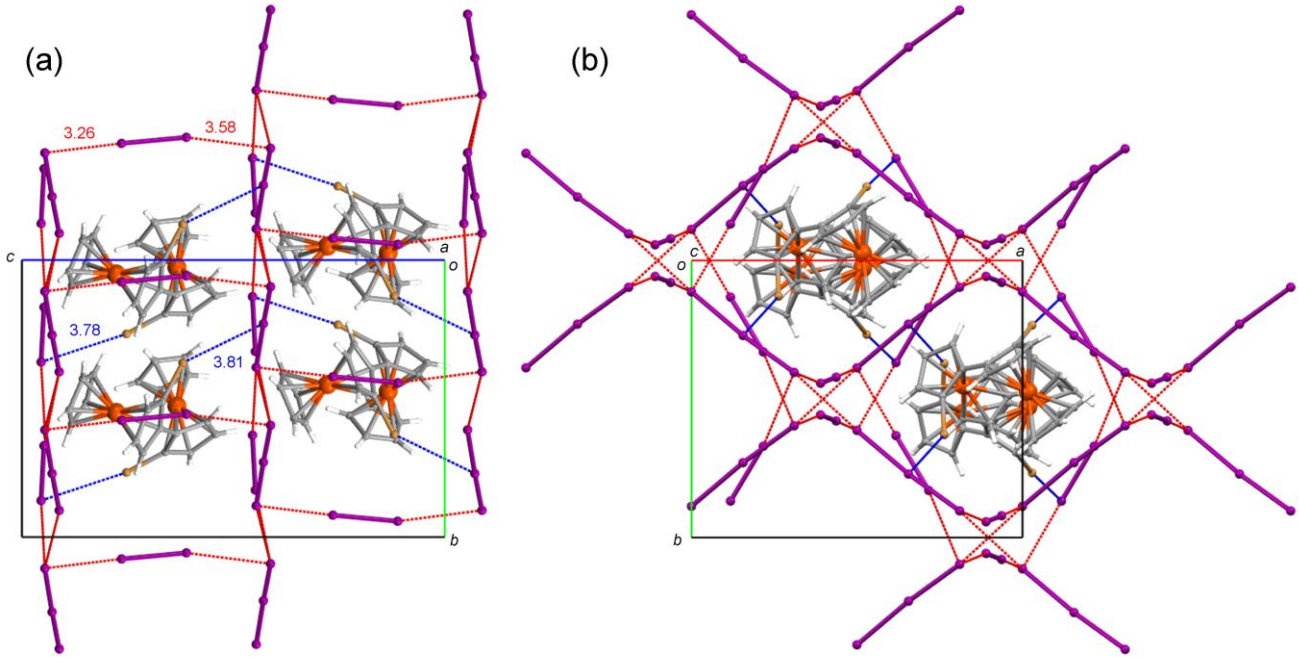


Fig. S10 Packing diagram of [**1a**]I_7, viewed along the (a) *a*- and (b) *c*-axis. Dashed blue and red lines indicate Br···I and I···I interactions, respectively.

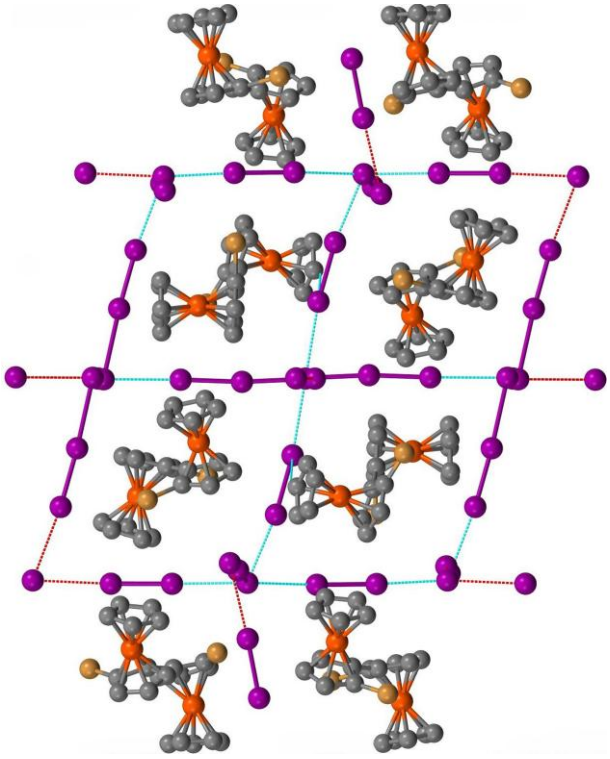


Fig. S11 Packing diagram of [**1b**]I_7. Dashed light blue and red lines indicate interactions between I_3^- and I_2.

Table S1 UV–vis–NIR absorption data of **1a**–**1c** and **1a**$^{+}$–**1c**$^{+}$

	λ [nm] (ε [$M^{-1}cm^{-1}$])
1a	230 (19970), 440 (378)
1b	232 (31530), 452 (695)
1c	232 (42050), 298 (13380), 448 (1072)
1a^{+}	598 (757), 1920 (270)
1b^{+}	584 (1816), 1890 (640)
1c^{+}	570 (2053), 1940 (780)

Table S2 Individual contributions (%) of intermolecular atom–atom contacts present in the crystal structure of [**1a**]I_7

Contact	**1a**
Br···I	6.3
Br···Br	0
Br···C	0
Br···H	7.7
C···I	5.6
C···Br	0
C···C	1.9
C···H	7.4
H···I	38.5
H···Br	5.0
H···C	6.6
H···H	21.1

Table S3 Calculated interaction energies [kcal / mol] between biferrocene cation and four I_3^- anions (**A**–**D**) in [**1a**]I_7

Anion	E_{ele}	E_{pol}	E_{disp}	E_{rep}	E_{tot}
A	−195.9	−28.0	−26.5	37.5	−227.8
B	−213.8	−33.1	−29.2	33.2	−255.5
C	−228.4	−29.9	−21.5	38.8	−258.4
D	−198.3	−22.8	−17.1	26.5	−225.1

E_{ele}, E_{pol}, E_{disp}, E_{rep}, and E_{tot} indicate electrostatic, polarization, dispersion, repulsion, and total energies, respectively.

Table S4 Crystallographic parameters of **1a**, **1b**, and **2** and [**1a**]I_7

	1a	**1b**	**2**	[**1a**]I_7
Empirical formula	$C_{20}H_{16}Br_2Fe_2$	$C_{20}H_{16}Br_2Fe_2$	$C_{11}H_8BrFeN$	$C_{20}H_{16}Br_2Fe_2I_7$
M (g mol^{-1})	527.85	527.85	289.94	1416.15
T (K)	90	90	90	90
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*bca	$P2_1/n$	$P2_12_12_1$	*C*c
a (Å)	13.194(3)	9.487(1)	9.018(8)	14.684(2)
b (Å)	14.160(3)	7.496(1)	10.319(9)	11.657(2)
c (Å)	18.352(4)	12.276(2)	10.748(1)	18.755(3)
β (°)		104.888(2)		108.410(2)
V (Å^3)	3428(1)	843.6(2)	1000(2)	3046.2(9)
Z	8	2	4	4
$\rho_{calc.}$ (g cm^{-3})	2.045	2.078	1.925	3.088
μ (mm^{-1})	6.351	6.453	5.455	10.680
Reflections collected	18960	4714	5561	8741
Independent reflections	3937	1922	2209	4903
R(int)	0.0619	0.0169	0.0271	0.0298
Observed reflections	2916	1759	2102	4493
Goodness-of-fit on F^2	1.003	1.052	1.086	0.964
Final R_1/wR_2 [$I > 2\sigma(I)$]	0.0339/0.0671	0.0260/0.0692	0.0196/0.0485	0.0293/0.0464
R_1/wR_2 (all data)	0.0596/0.0740	0.0289/0.0704	0.0209/0.0488	0.0358/0.0480
Largest diff. peak/hole (e Å^{-3})	0.981/−0.459	1.073/−0.642	0.438/−0.440	1.118/−1.022
Flack parameter			0.045(7)	

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^bR_w = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2}$.

Table S5 Cell parameters of [**1b**]I_7

Empirical formula	$C_{20}H_{16}Br_2Fe_2I_7$
M (g mol^{-1})	1416.15
T (K)	90
Crystal system	Triclinic
Space group	$P-1$
a (Å)	9.277(6)
b (Å)	18.57(1)
c (Å)	52.95(4)
α (°)	85.368(9)
β (°)	85.50(1)
γ (°)	81.932(9)
V (Å^3)	8989.(11)