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A Stable, Highly Oxidizing Radical Cation

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Figure S1. Thermal ellipsoid plot of neutral EPT (a), 3,7-DMeEPT (b), 1,9-DMeEPT (c), 3,7-BCF₃EPT (d), and 1,9-DMe-3,7-BCF₃EPT (e). Radical cation forms of EPT-SbCl₆ (f), 3,7-DMeEPT-SbCl₆ (g), 1,9-DMeEPT-SbCl₆ (h), 3,7-BCF₃EPT-SbCl₆ (i), and 1,9-DMe-3,7-BCF₃EPT-SbCl₆. Obtained by single crystal X-ray diffraction. Note: The unit cell for BCF₃EPT contains two molecules and 3,7-DMeEPT-SbCl₆ contains two SbCl₆ anions; only one is displayed here.



Figure S2. Cyclic voltammograms of the first oxidation event of EPT, 3,7-DMeEPT, 1,9-DMeEPT, 3,7-BCF₃EPT, and 1,9-DMe-3,7-BCF₃EPT at 1 mM in 0.1 M nBu₄NPF₆ in DCM, recorded at a scan rate of 100 mV/s. Voltammograms were calibrated to $Cp_2Fe^{+/0}$ at 0 V, using ferrocene (Cp_2Fe) or decamethylferrocene (Cp^*_2Fe) as an internal reference.



Figure S3. Cyclic voltammograms of EPT, 3,7-DMeEPT, 1,9-DMeEPT, 3,7-BCF₃EPT, and 1,9-DMe-3,7-BCF₃EPT at 1 mM in 0.1 M nBu₄NPF₆ in DCM, containing ferrocene (Cp₂Fe) or decamethylferrocene (Cp*₂Fe) as an internal reference (the reference used is noted in the figure), recorded at a scan rate of 100 mV/s.



Figure S4. Cyclic voltammograms of EPT, 3,7-DMeEPT, 1,9-DMeEPT, 3,7-BCF₃EPT, and 1,9-DMe-3,7-BCF₃EPT at 1 mM in 0.1 M nBu_4NPF_6 in DCM, recorded at a scan rate of 100 mV/s. The potential is calibrated to $Cp_2Fe^{+/0}$ at 0 V.

Randles-Sevcik Plots



Figure S5. Cyclic voltammograms of 3,7-DMeEPT (a), EPT (c), 1,9-DMeEPT (e), and 3,7-BCF₃EPT (g) at 1 mM in 0.1 M nBu₄NPF₆/DCM at scan rates of 25, 50, 75, 100, 200, 300, 400 and 500 mV s⁻¹. Additionally, the corresponding Randles-Sevcik plots are shown for 3,7-DMeEPT (b), EPT (d), 1,9-DMeEPT (f), and 3,7-BCF₃EPT (h).

Table S1. Adiabatic ionization potentials (AIP) from density functional theory calculations performed with the B3LYP functional at the 6-311g(d,p) level of theory, half-wave first oxidation potentials ($E_{1/2}^{0/+}$) vs. Cp₂Fe^{0/+}, peak current ratios for $E_{1/2}^{0/+}$, and diffusion coefficients of neutral and radical cation forms of EPT, 3,7-DMeEPT, 1,9-DMeEPT, 3,7-BCF₃EPT, 1,9-DMe-3,7-BCF₃EPT, from electrochemical measurements performed at 1 mM in 0.1 M *n*Bu₄NPF₆ in DCM. Absorption maxima for the neutral and radical cation forms in DCM.

Compound	AIP (eV)	E _{1/2} 0/+	Peak	Diffusion		Absorption maxima (nm)*	
		(V)	Current	Coefficient (x10 ⁻⁵			
		VS.	Ratio	cm ² /s)			
		Cp ₂ Fe ^{0/+}	(lpa/lpc)	neutral	radical	neutral	radical cation
		at 0 V			cation		
EPT	6.48 ^[a]	0.27	0.99	1.12	1.05	312	516, 692, 774, 865
3,7-DMeEPT	6.24 ^[a]	0.13	1.00	0.86	0.75	316	552 , 695 760, 852
3,7-BCF₃EPT	7.06 ^[a]	0.61	1.02	0.81	0.83	319	446, 499, 695 760, 847
1,9-DMeEPT	6.68 ^[a]	0.53	1.02	0.98	0.91	298	394, 574, 965
1,9-DMe-3,7-	7.22	0.88	1.05	0.81	0.52	308	392, 545, 945
BCF₃EPT							

[a] Ref. 1, *The most intense peak is bolded.

Table S2. Comparing butterfly angles from DFT calculations and X-ray crystallography for all compounds in their neutral and radical cation forms. DFT calculations were done at the B3LYP/6-311G(d,p) level of theory. Radical cations salts had hexachloroantimonate ($SbCl_{6}$) as a counter ion.

Compound	Butterfly angles [°] (neutral)		Butterfly angles [°] (radical cation)	
	DFT	experimental	DFT	experimental
EPT	138.7 ^[a]	136.8 ^[a]	171.4 ^[a]	174.8 ^[a]
3,7-DMeEPT	138.8 ^[a]	149.3 ^[a]	171.1 ^[a]	174.9
1,9-DMeEPT	143.1 ^[a]	146.5 ^[a]	156.6 ^[a]	164.9
3,7-BCF₃EPT	139.7 ^[a]	144.5-152.1 ^[a,b]	171.1 ^[a]	164.5 ^[a]
1,9-DMe-3,7-BCF₃EPT	142.8	140.5	156.9	162.8

[a] Ref. 1, [b] Multiple molecules in asymmetric unit.



Figure S6. UV-vis absorption spectra of neutral phenothiazines at 0.2 mM in DCM. UV-vis absorption spectra were recorded using 10 mm path length quartz cuvettes.



Figure S7. UV-vis absorption spectra of EPT-SbCl₆ (a), 3,7-DMeEPT-SbCl₆ (b), 1,9-DMeEPT-SbCl₆ (c), 3,7-BCF₃EPT-SbCl₆ (d), and 1,9-DMe-3,7-BCF₃EPT-SbCl₆ (e), radical cations at 0.2 mM in DCM, and a plot of absorbance vs. time for radical cations in DCM (f), collected at 5,15, 30, 60, 120, 180, 240, and 300 min. The absorption intensity was monitored at absorption maxima of each radical cation (provided in Table S1). UV-vis absorption spectra were recorded using 10 mm path length quartz cuvettes.



Figure S8. Solid state stability of EPT-SbCl₆ on day 0, 7, 14, and 21 following storage in glass vials, placed in the glove box in the light and on a bench top in the light. Normalized absorbance intensity at 516 nm vs. time for EPT-SbCl₆ (a). UV-vis absorption spectra of EPT-SbCl₆, stored in the glove box (b), on bench top (c) at 0.2 mM in DCM. UV-vis absorption spectra were recorded using 10 mm path length quartz cuvettes.



Figure S10. ¹³C NMR spectrum of 1,9-DMe-3,7-DBrPT in CDCl₃.



Figure S11. ¹H NMR spectrum of 1,9-DMe-3,7-DBrEPT in DMSO-*d*₆.



Figure S12. ¹³C NMR spectrum of 1,9-DMe-3,7-DBrEPT in CDCI₃.



Figure S14. ¹³C NMR spectrum of 1,9-DMe-3,7-BCF3EPT in CDCl₃.



Figure S15. ¹⁹F NMR spectrum of 1,9-DMe-3,7-BCF3EPT in CDCl₃.



Figure S16. ¹⁹F NMR spectrum of 1,9-DMe-3,7-BCF3EPT in $CDCI_3$ using hexafluorobenzene as the internal standard (-164.9 ppm).

Computational Studies

1,9-DMe-3,7-BCF₃EPT

neutral state (0,1); total energy: -1747.35385504 a.u.; zero negative frequencies C -3.62570 -0.54072 -0.25720

C	-3.02370	-0.34072	-0.23720
С	-2.54207	-1.16661	0.34968
С	-1.35588	-0.45895	0.516008
С	-1.22243	0.864085	0.062785
С	-2.30645	1.471239	-0.60656
С	-3.50135	0.760579	-0.73368
С	1.222432	0.864084	0.062777
С	1.355884	-0.45895	0.516005
С	2.542081	-1.16661	0.349679
Н	2.616914	-2.19248	0.686649
С	3.625708	-0.54072	-0.25720
С	3.501345	0.760583	-0.73369
С	2.306446	1.471236	-0.60658
Н	-2.61690	-2.19249	0.686646
Н	-4.33827	1.221176	-1.24406
Н	4.33826	1.221181	-1.24407
S	0.000003	-1.24417	1.364737
Ν	0.000001	1.573602	0.239748
С	4.938372	-1.26296	-0.37443
С	-4.93837	-1.26297	-0.37444
С	-2.20512	2.852823	-1.20253
С	2.205097	2.852809	-1.20257
С	0.000004	2.679849	1.223236
Н	0.874247	3.301802	1.025356
Н	-0.87422	3.30182	1.025343
С	-1.2E-05	2.235375	2.688613
Н	-5.1E-05	3.113873	3.341206
Н	-0.88448	1.639191	2.922603
Н	0.884479	1.639241	2.922641
F	-5.64438	-0.86231	-1.45469
F	-5.72771	-1.04671	0.705268
F	-4.77713	-2.60033	-0.47319
F	5.644442	-0.86222	-1.45461
F	5.72766	-1.0468	0.705335
F	4.777128	-2.60032	-0.4733
Н	-2.47193	3.631674	-0.48016
Н	-2.88658	2.951544	-2.04933
Н	-1.19007	3.057441	-1.54497
Н	1.190048	3.057406	-1.54503
Н	2.47190	3.631678	-0.48022
Н	2.886561	2.951519	-2.04938

1,9-DMe-3,7-BCF₃EPT-SbCl₆ radical-cation state (+1,2); total energy: -1747.0885279 a.u.; zero negative frequencies

С	3.736669	-0.51776	-0.13670
С	2.635512	-1.23865	0.267241
С	1.387114	-0.60242	0.318898
С	1.250748	0.776228	0.012712
С	2.382556	1.487939	-0.47768
С	3.596438	0.821427	-0.53290
С	-1.19968	0.765647	-1.1E-05
С	-1.31404	-0.61816	0.296508
С	-2.54718	-1.28165	0.222147
Н	-2.61554	-2.33524	0.460596
С	-3.65991	-0.58078	-0.18346
С	-3.54489	0.76755	-0.55363
С	-2.34588	1.460225	-0.48067
Н	2.725159	-2.28740	0.519413
Н	4.459331	1.341633	-0.93170
Н	-4.41721	1.277465	-0.94471
S	0.038412	-1.56897	0.845334
Ν	0.021916	1.424831	0.204353
С	2.299481	2.892503	-1.02955
Н	1.319428	3.104579	-1.45778
Н	2.509629	3.652219	-0.27158
Н	3.040435	3.015954	-1.81984
С	0.035616	2.705587	0.991201
Н	1.078511	2.908945	1.21164
С	-2.30417	2.87735	-1.00028
Н	-2.39677	3.616596	-0.19958
Н	-1.38486	3.080012	-1.55221
Н	-3.13894	3.039511	-1.68194
С	5.106502	-1.15963	-0.19787
С	-5.01440	-1.25142	-0.26983
F	5.657187	-0.99101	-1.41266
F	5.929224	-0.59476	0.703487
F	5.050163	-2.47609	0.057414
F	-4.93221	-2.56946	-0.03051
F	-5.55388	-1.07909	-1.48905
F	-5.86020	-0.71615	0.628382
Н	-0.34105	3.525231	0.384141
С	-0.74049	2.582743	2.302420
Н	-0.35246	1.769532	2.919256
Н	-0.61829	3.514592	2.859083
Н	-1.80796	2.424639	2.144550

References

1. Casselman, M. D.; Elliott, C. F.; Modekrutti, S.; Zhang, P. L.; Parkin, S. R.; Risko, C.; Odom, S. A., Beyond the Hammett Effect: Using Strain to Alter the Landscape of Electrochemical Potentials. *Chemphyschem* **2017**, *18*, 2142-2146.