Supplementary Materials

Bis(3-methylthio-1-azulenyl)phenylmethyl Cations and Dications Connected by 1,4-Phenylene Spacer: Synthesis and their Electrochemical Properties

Taku Shoji*, Naoko Sakata, Ryuta Sekiguchi, and Shunji Ito

➢ *Contents*

1. **Copies of ^{1}H NMR, ^{13}C NMR, and COSY of 3a,b$^{+\cdot}$·PF$_6^-$ and 4a,b^{2+}·2PF$_6^-$ (Figures S1–S12).**

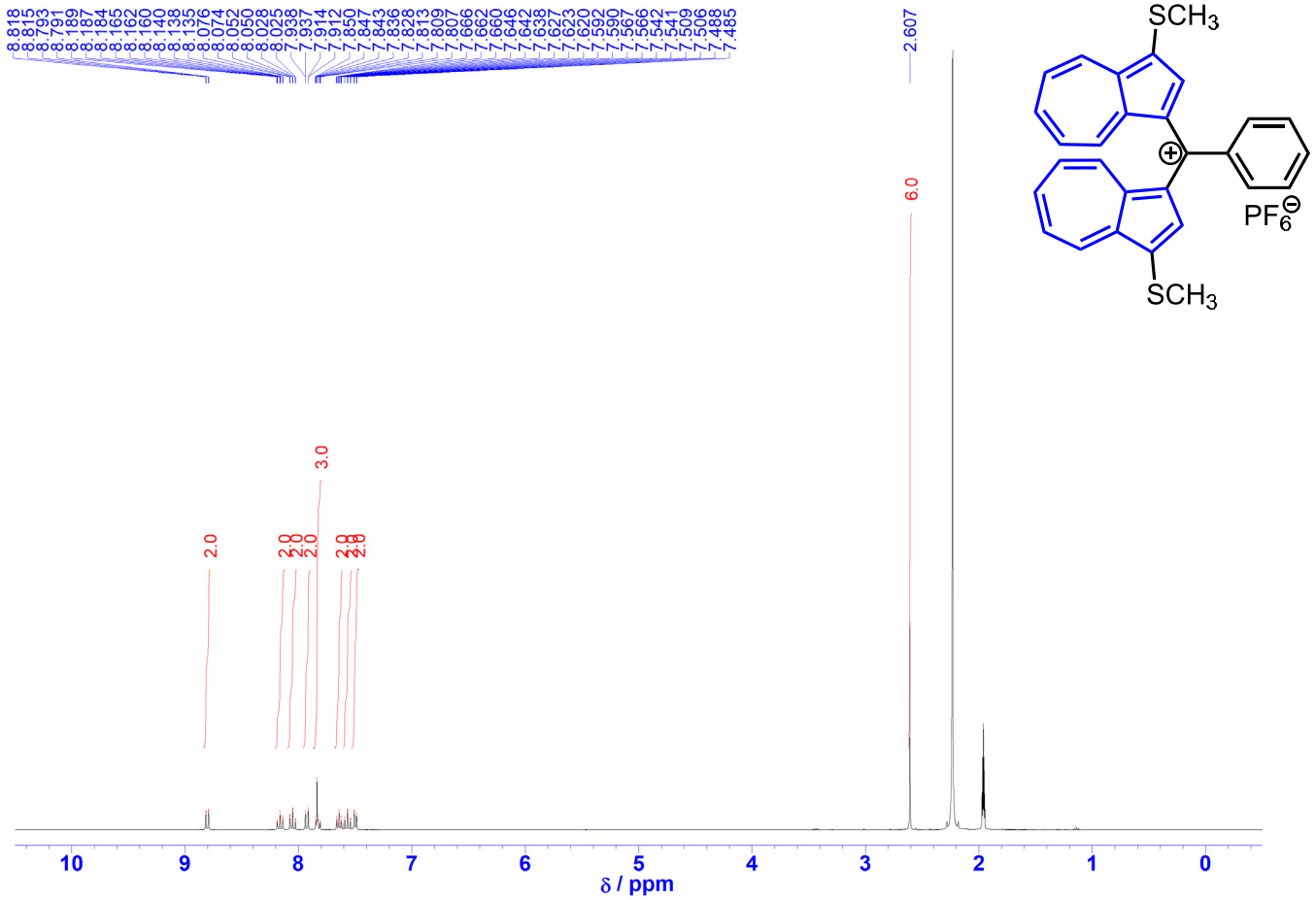

Figure S1. ^{1}H NMR spectrum of **3a$^{+\cdot}$·PF$_6^-$** in CD_3CN (400 MHz).

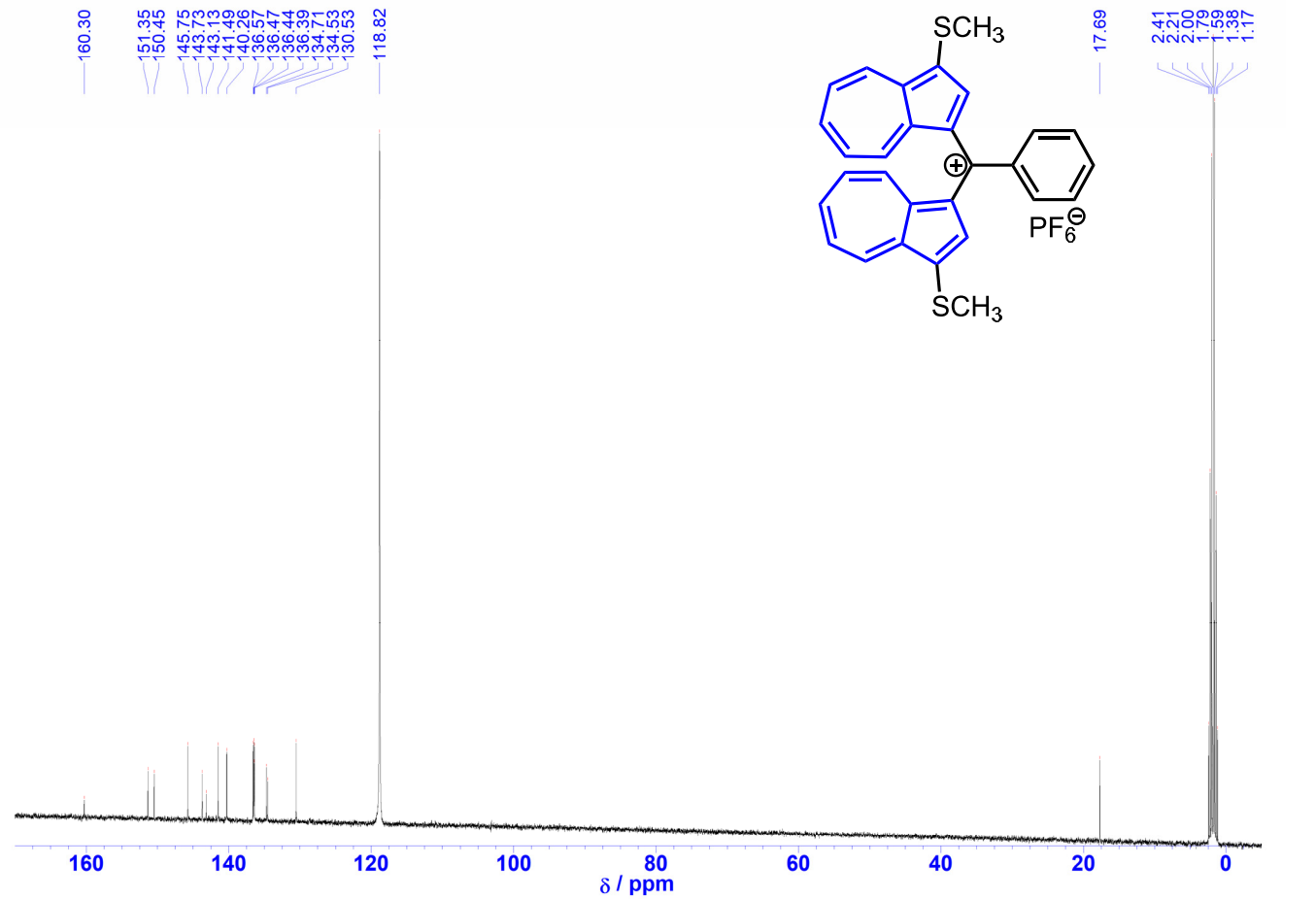

Figure S2. ^{13}C NMR spectrum of **3a$^{+\cdot}$·PF$_6^-$** in CD_3CN (100 MHz).

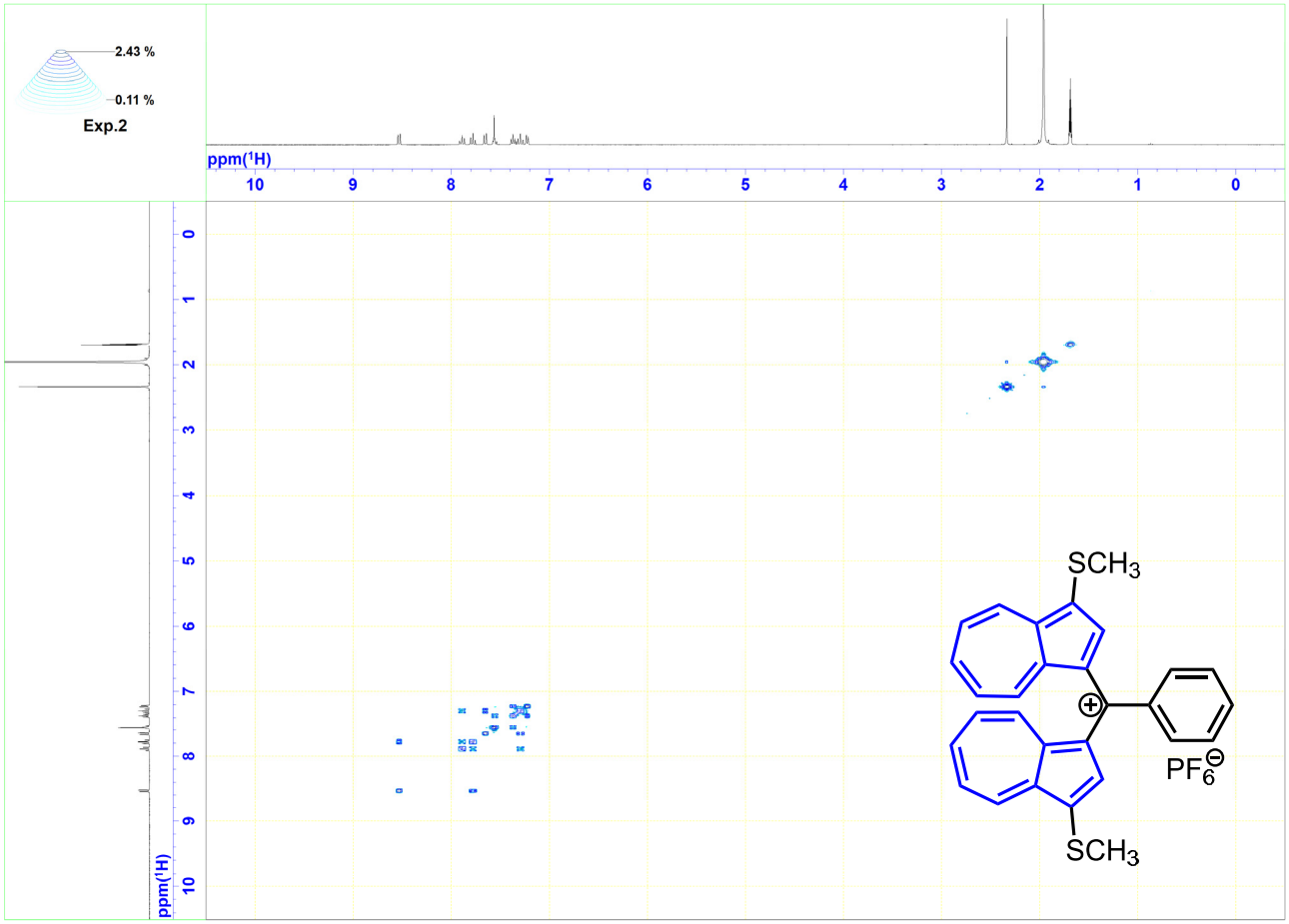

Figure S3. COSY spectrum of **3a**$^{+}$·**PF**$_6^-$ in CD_3CN (400 MHz).

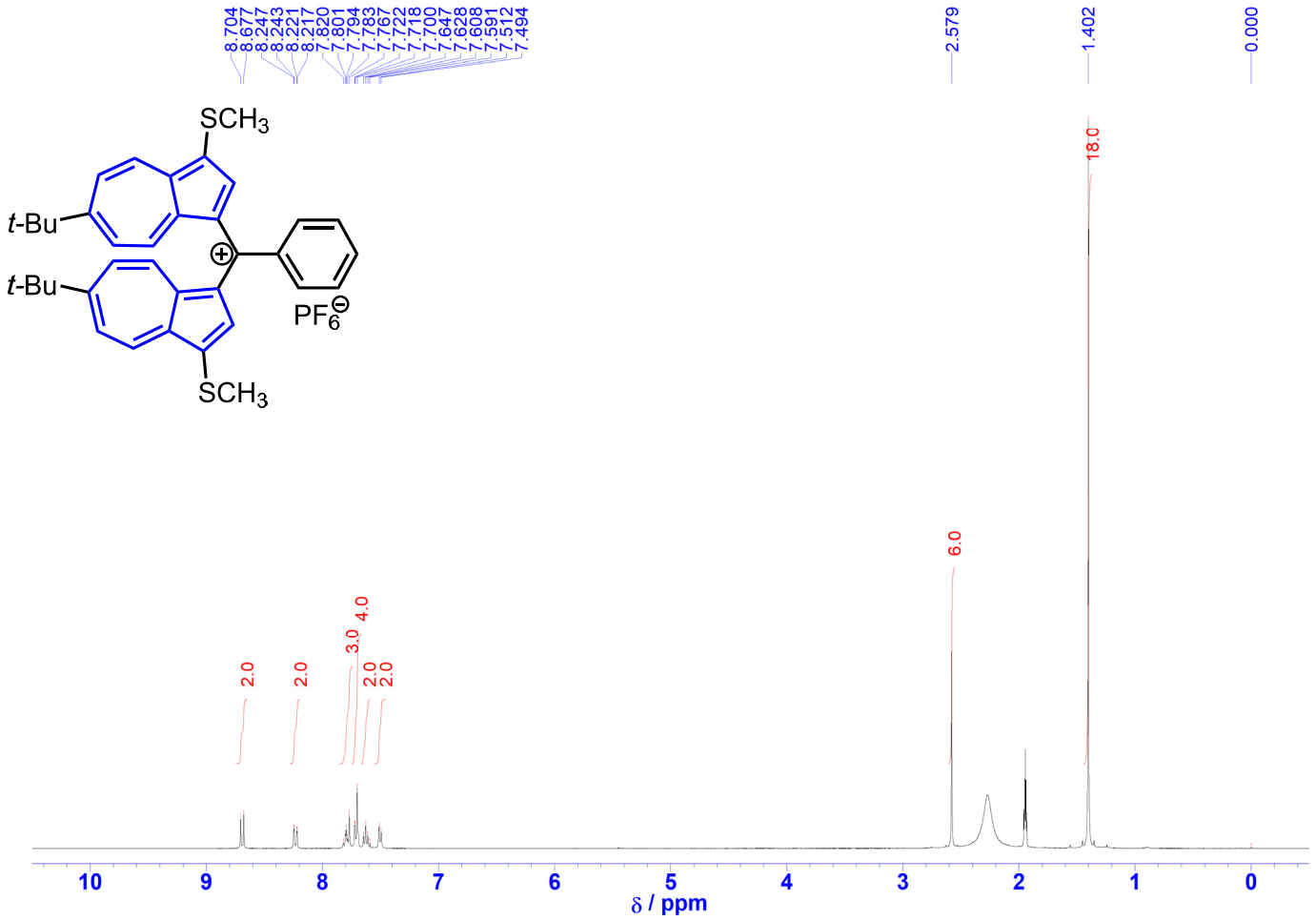

Figure S4. ^{1}H NMR spectrum of **3b**$^{+}$**·PF**$_6^-$ in CD_3CN (400 MHz).

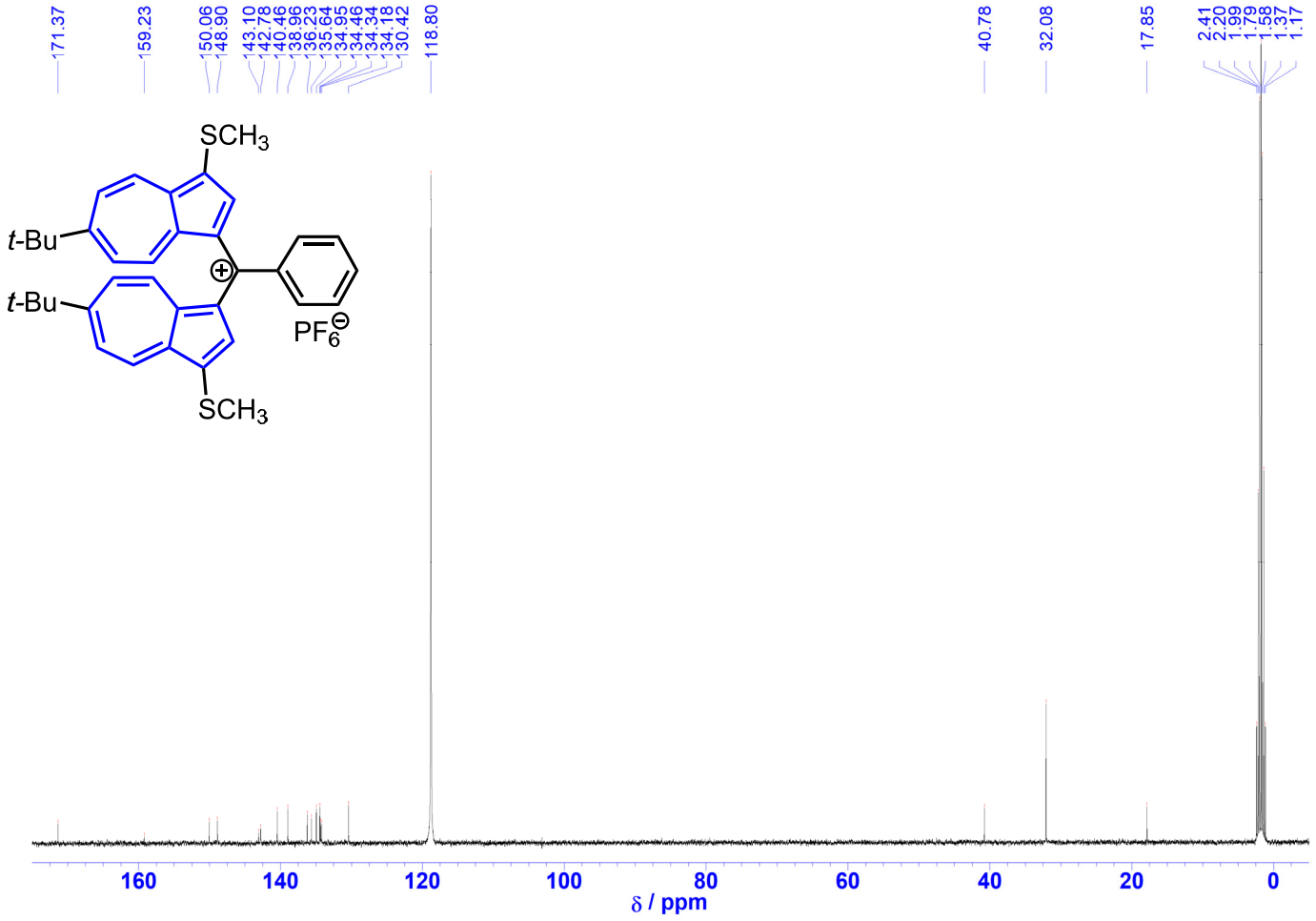

Figure S5. ^{13}C NMR spectrum of **3b**$^{+}$**·PF**$_6^-$ in CD_3CN (100 MHz).

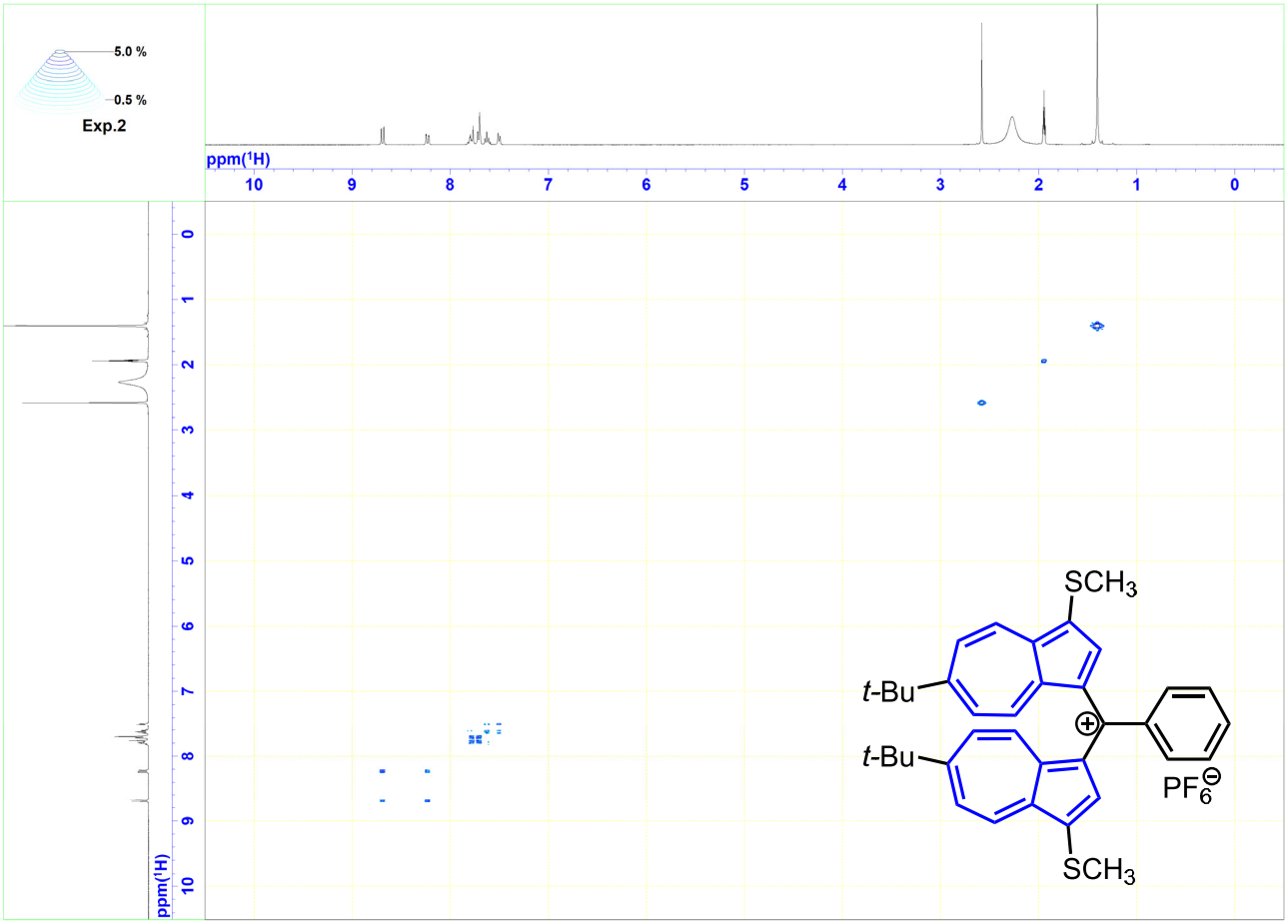

Figure S6. COSY spectrum of **3b**$^{+}$·**PF**$_6^-$ in CD_3CN (400 MHz).

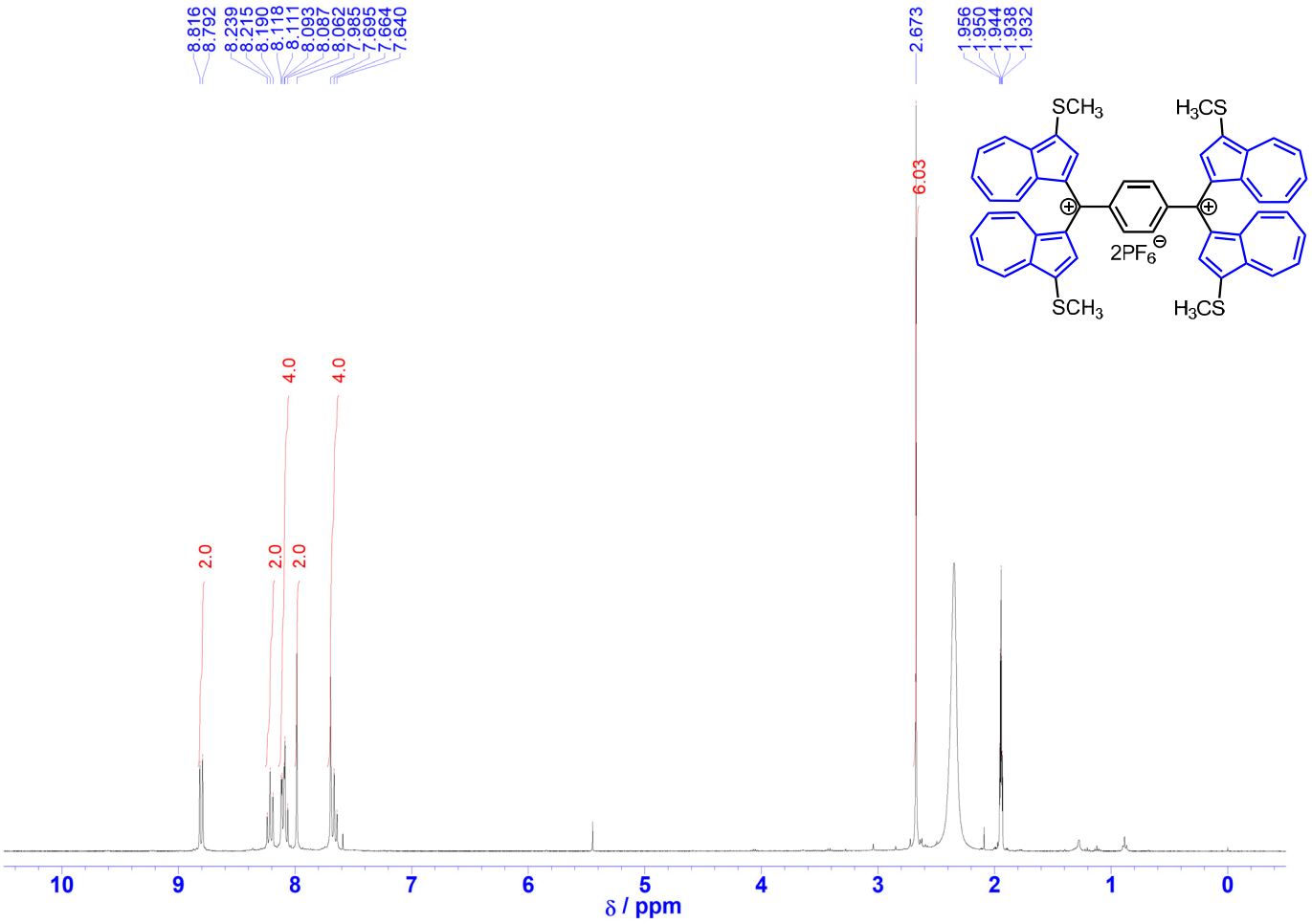

Figure S7. ^{1}H NMR spectrum of **4a**$^{2+}$·**2PF**$_6^-$ in CD_3CN (400 MHz).

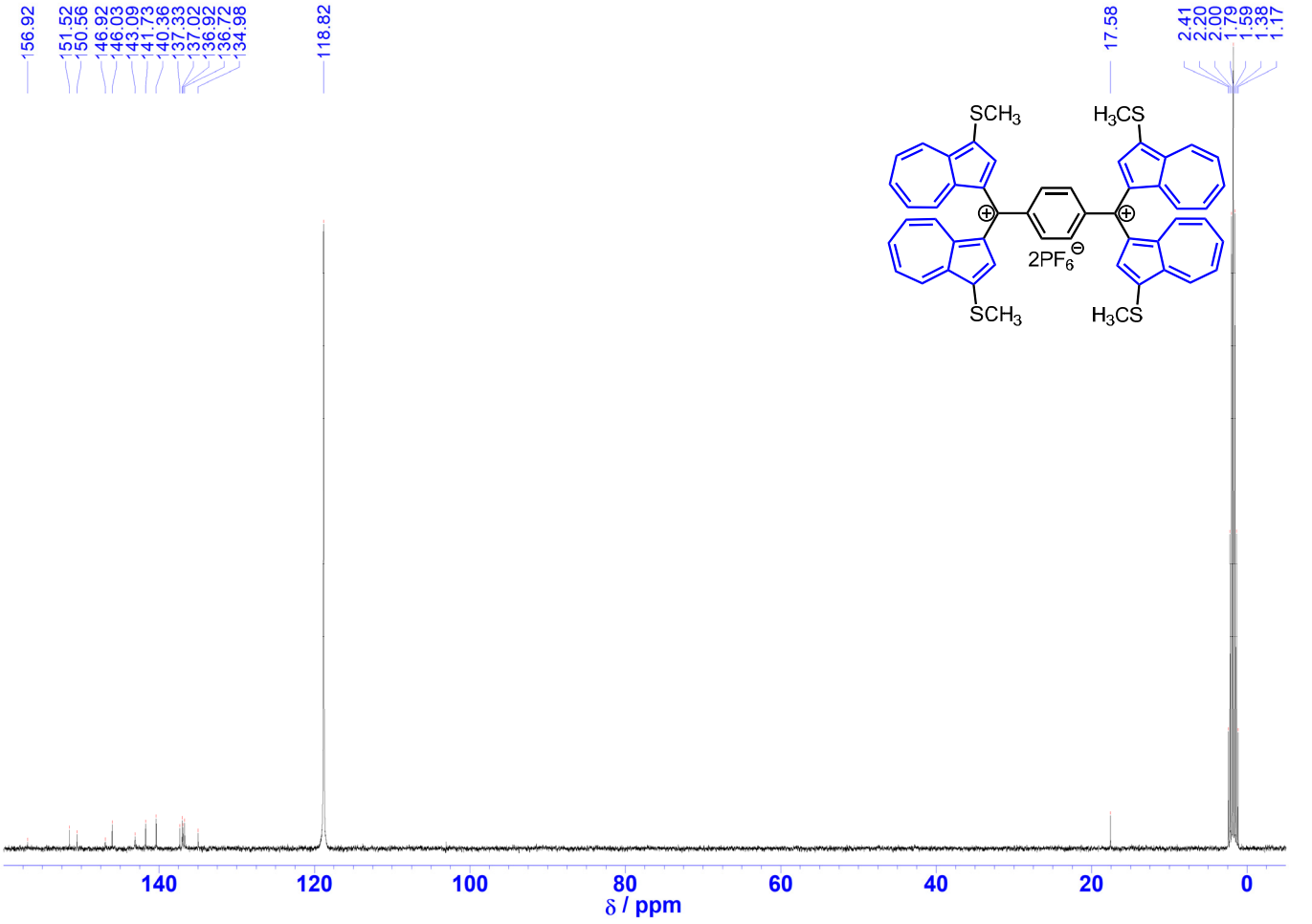

Figure S8. ^{13}C NMR spectrum of **4a**$^{2+}$·**2PF**$_6^-$ in CD_3CN (100 MHz).

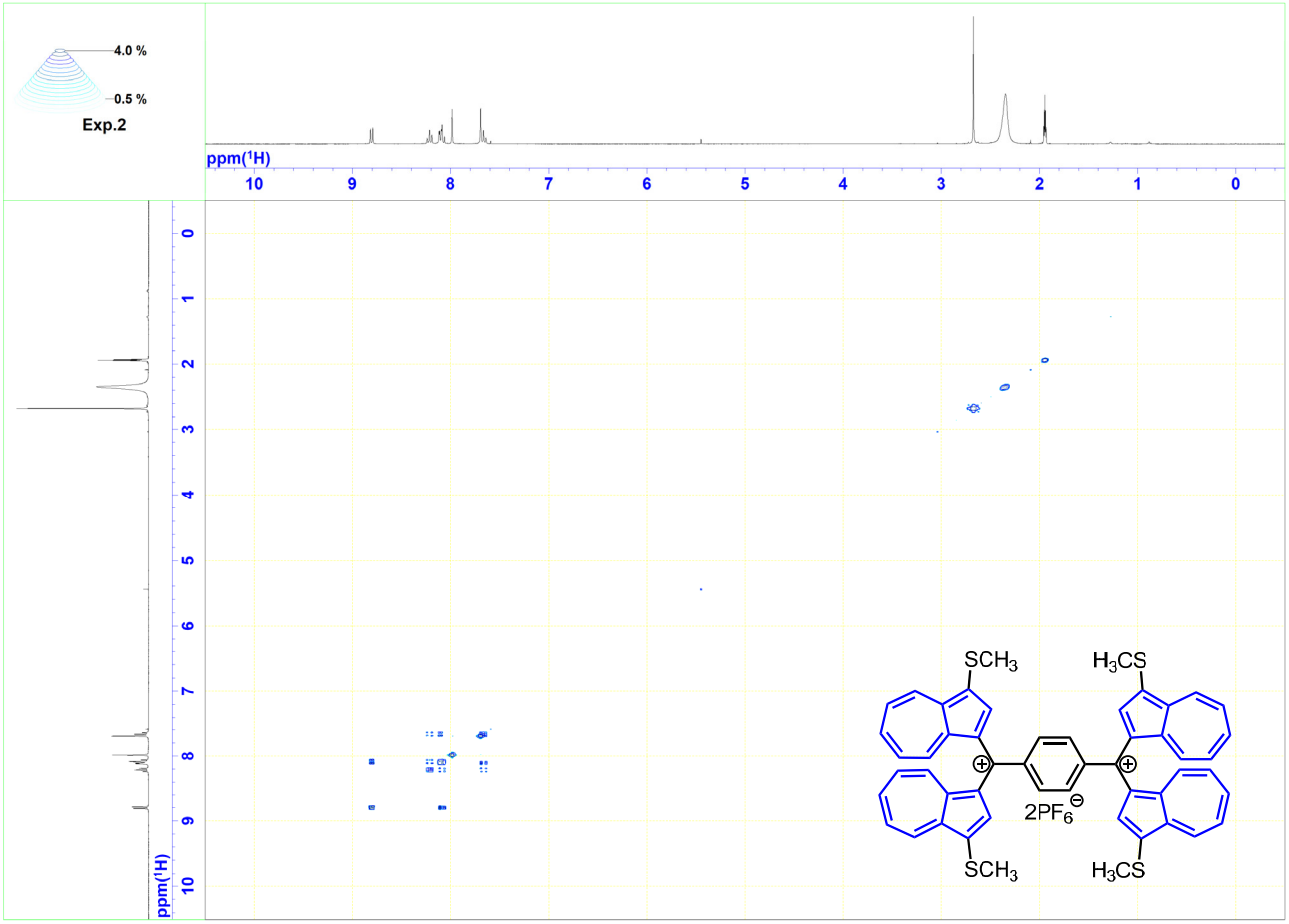

Figure S9. COSY spectrum of **4a**$^{2+}$·**2PF**$_6^-$ in CD_3CN (400 MHz).

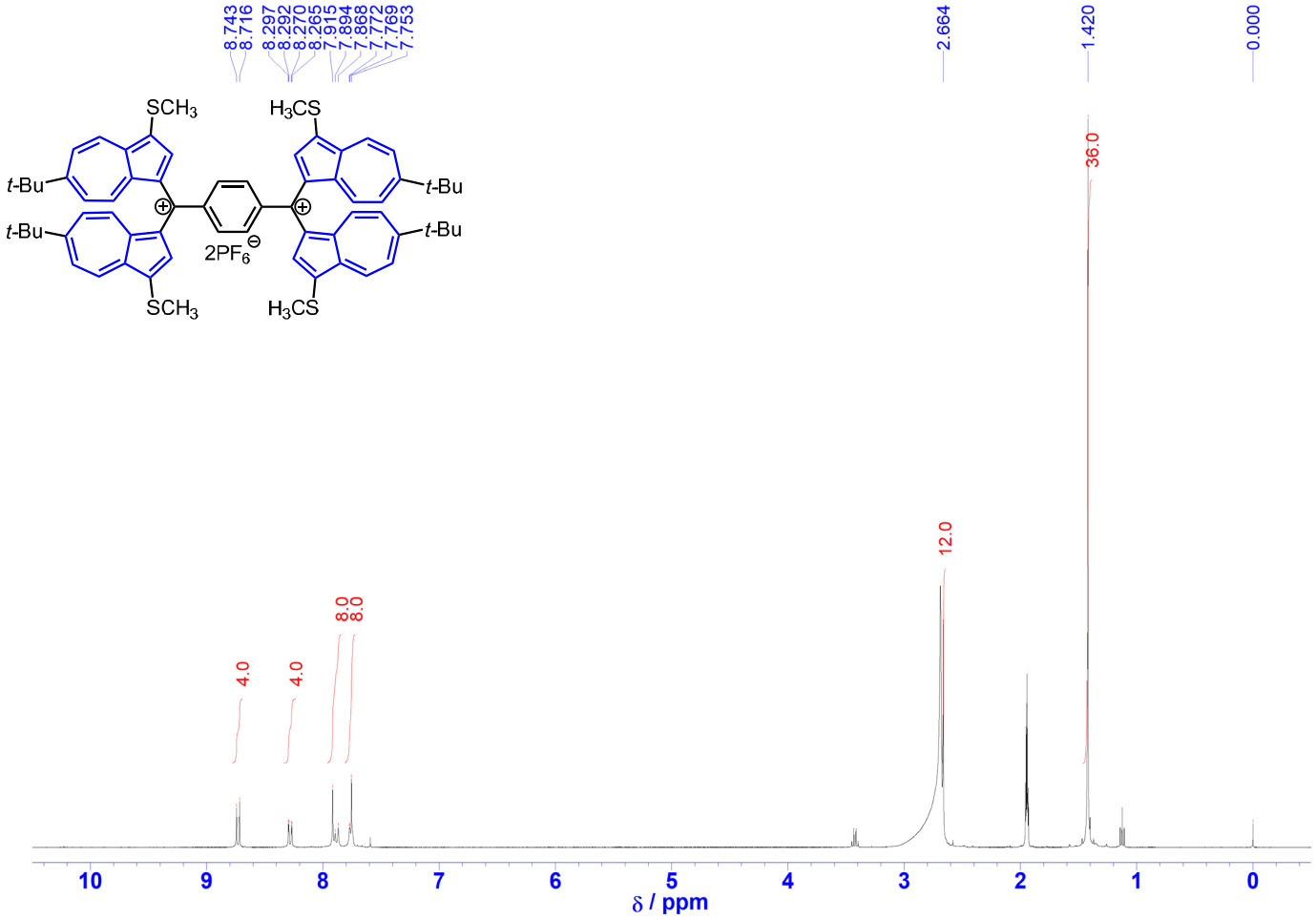

Figure S10. ^{1}H NMR spectrum of **4b**$^{2+}$·**2PF**$_6^-$ in CD_3CN (400 MHz).

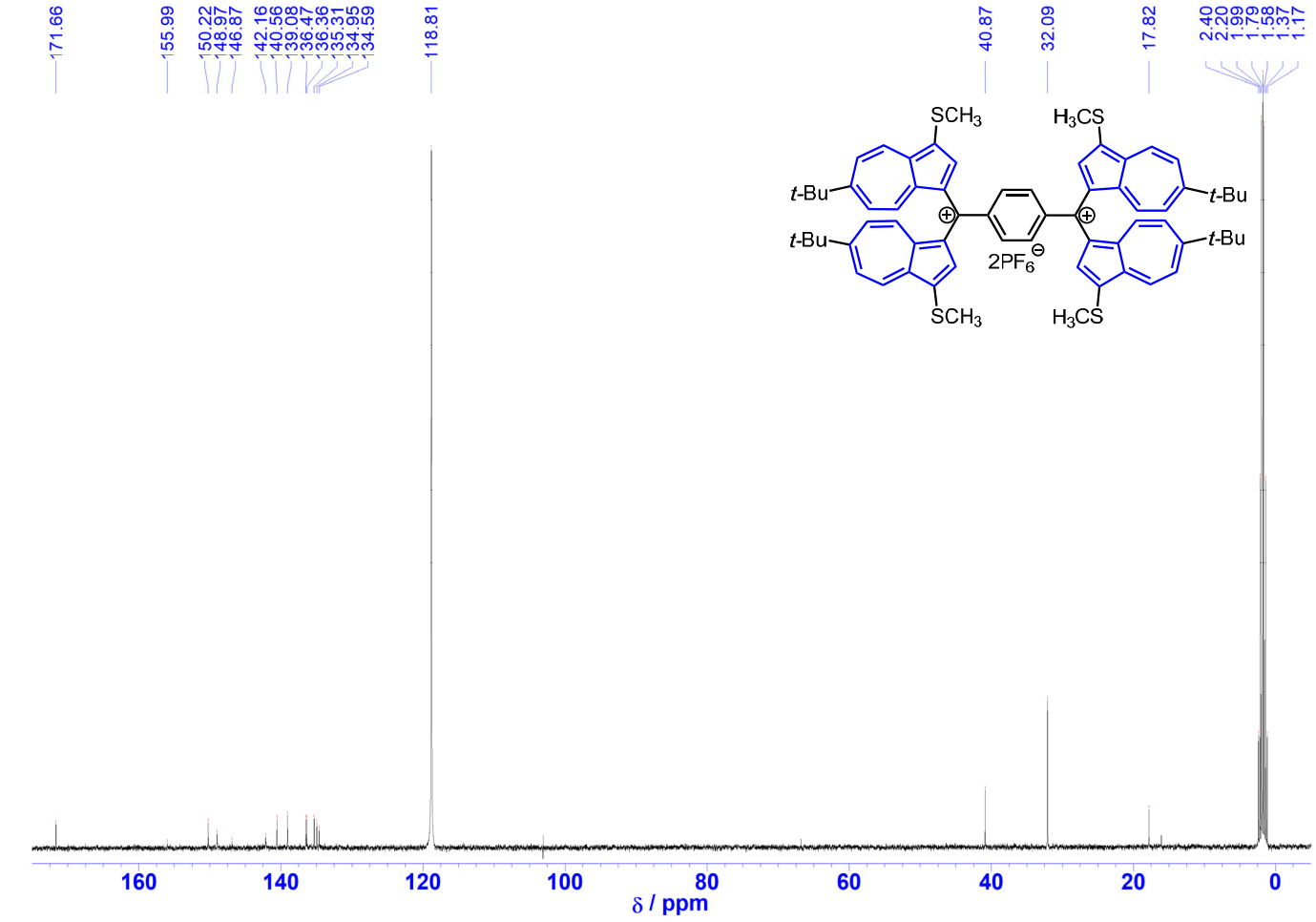

Figure S11. ^{13}C NMR spectrum of **4b**$^{2+}$·**2PF**$_6^-$ in CD_3CN (100 MHz).

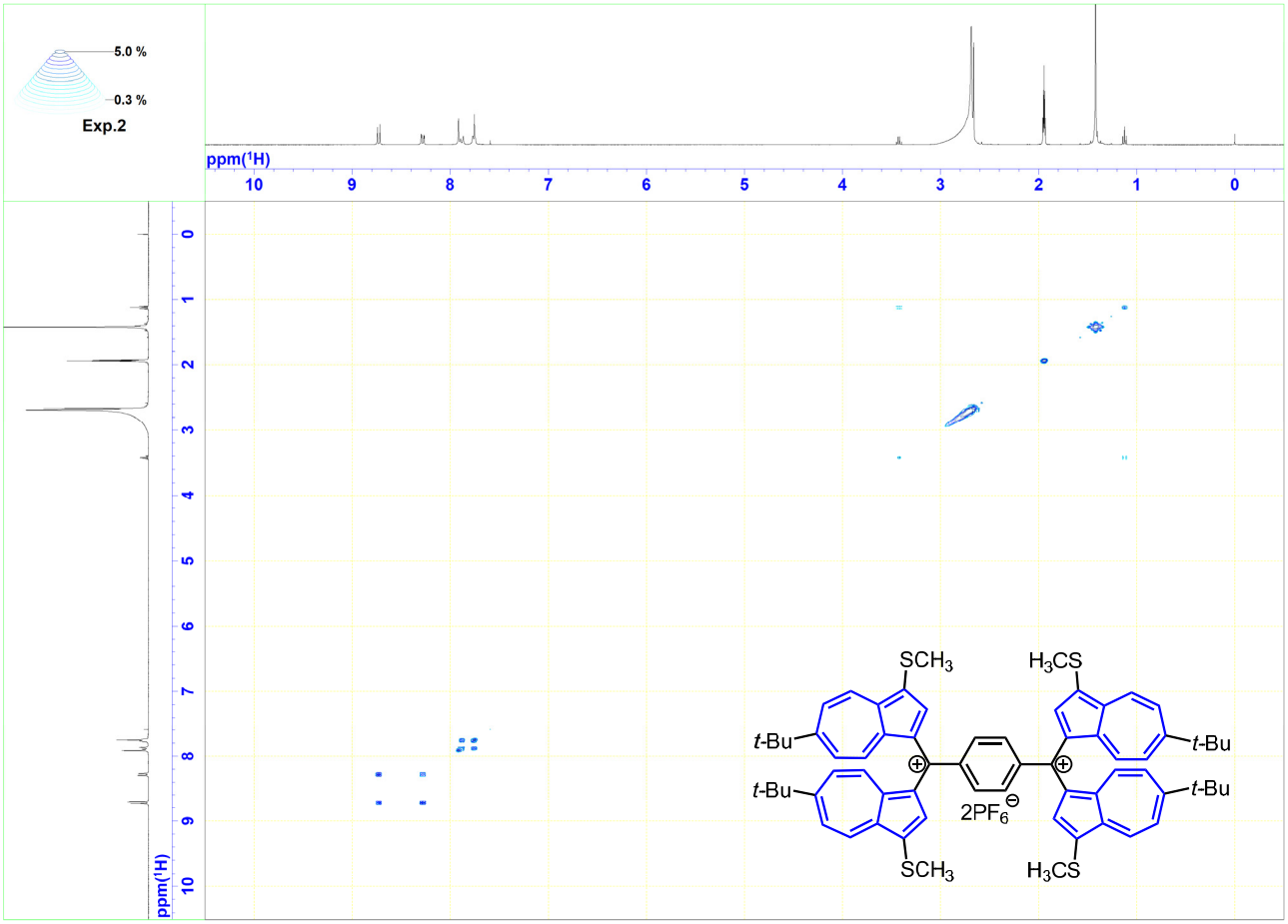

Figure S12. COSY spectrum of **4b**$^{2+}$·**2PF**$_6^-$ in CD_3CN (400 MHz).

2. UV/Vis spectra of 3a,b^{+}·PF$_6^-$ and 4a,b^{2+}·2PF$_6^-$ (Figures S13–S15).

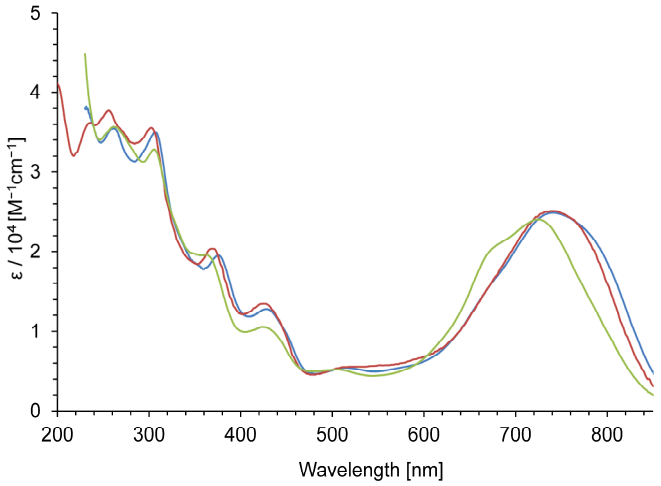

Figure S13. UV/Vis spectrum of **3b^{+}·PF$_6^-$** in dichloromethane (blue line), acetonitrile (red line), and hexane (light-green line).

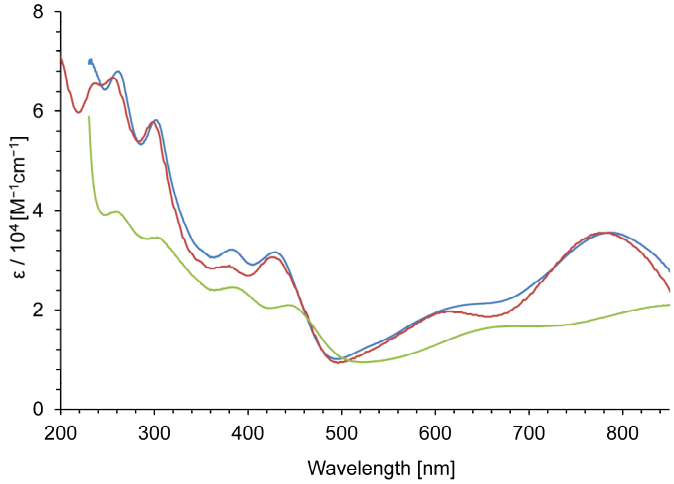

Figure S14. UV/Vis spectrum of **4a^{2+}·2PF$_6^-$** in dichloromethane (blue line), acetonitrile (red line), and hexane (light-green line).

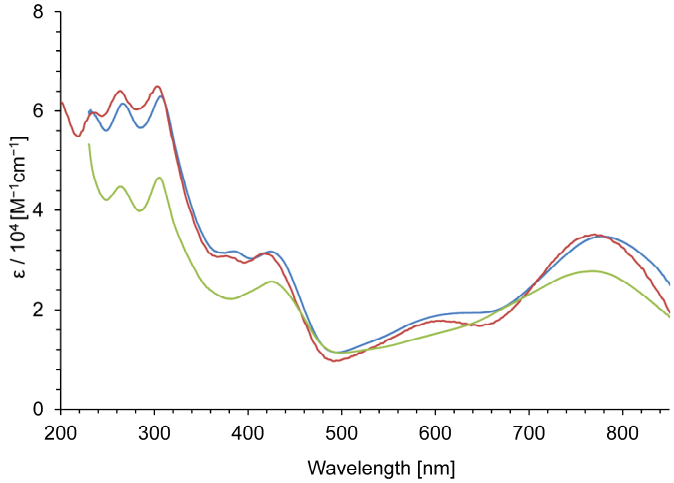

Figure S15. UV/Vis spectrum of **4a^{2+}·2PF$_6^-$** in dichloromethane (blue line), acetonitrile (red line), and hexane (light-green line).

3. **Continuous change in the visible spectra and their photos of 3a,b^{+}·PF$_6^-$ and 4a,b^{2+}·2PF$_6^-$ (Figures S16–S19).**

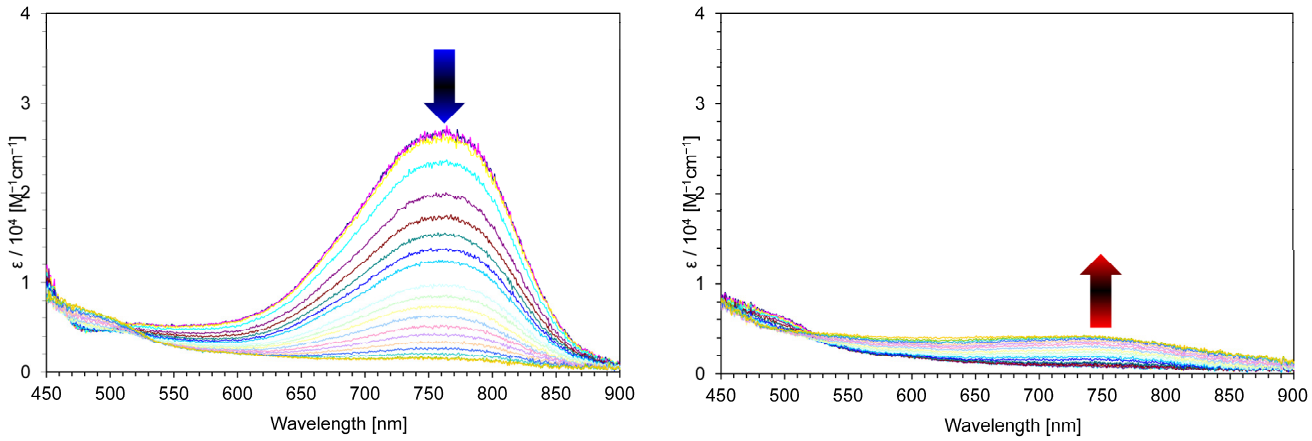

Figure S16. Continuous change in visible spectra of **3b^{+}·PF$_6^-$** in benzonitrile containing Et$_4$NClO$_4$ (0.1 M): constant-current electrochemical reduction (50 uA) at 30 sec intervals (left) and the reverse oxidation (right) of the reduced species (50 uA) at 30 sec intervals.

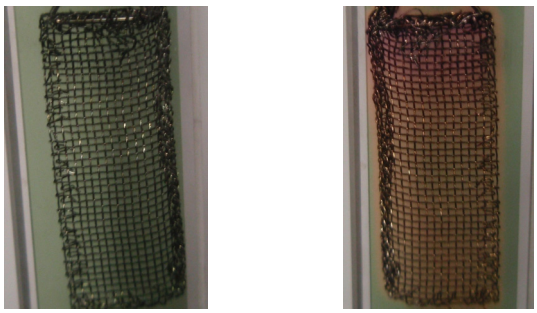

Figure S17. Color changes of **3b^{+}·PF$_6^-$** upon the electrochromic analysis in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) upon (50 uA): before electrochemical reduction (left) and after electrochemical reduction (right).

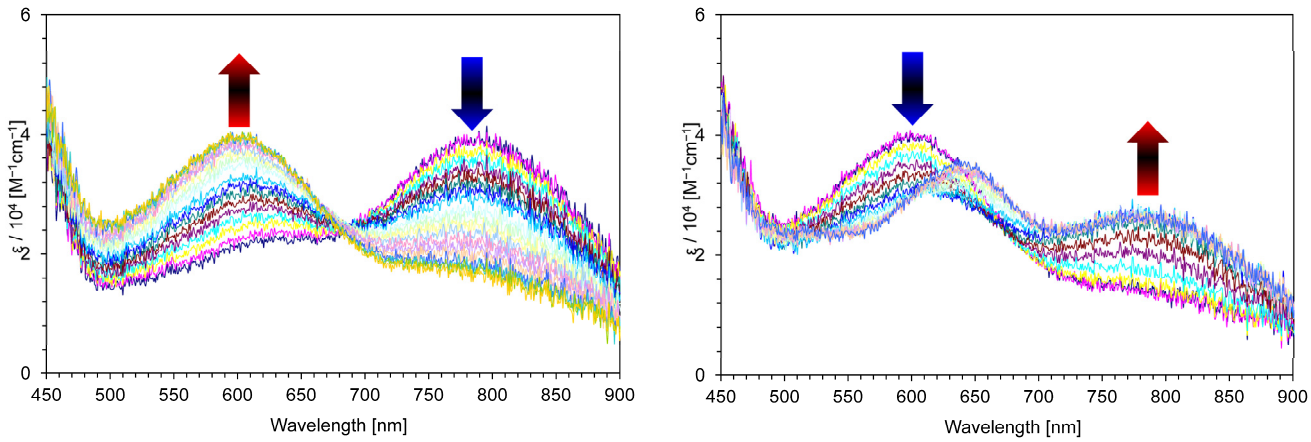

Figure S18. Continuous change in visible spectra of **4a**$^{2+}$**·2PF**$_6^-$ in benzonitrile containing Et_4NClO_4 (0.1 M): constant-current electrochemical reduction (50 uA) at 30 sec intervals (left) and the reverse oxidation (right) of the reduced species (50 uA) at 30 sec intervals.

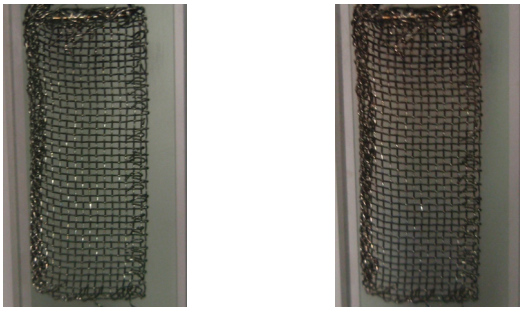

Figure S19. Color changes of **4a**$^{2+}$**·2PF**$_6^-$ upon the electrochromic analysis in benzonitrile containing Et_4NClO_4 (0.1 M) upon (50 uA): before electrochemical reduction (left) and after electrochemical reduction (right).

4. Cyclic voltammograms of 3a,b^{+}·PF_6^- and 4a,b^{2+}·2PF_6^- (Figures S20–S22).

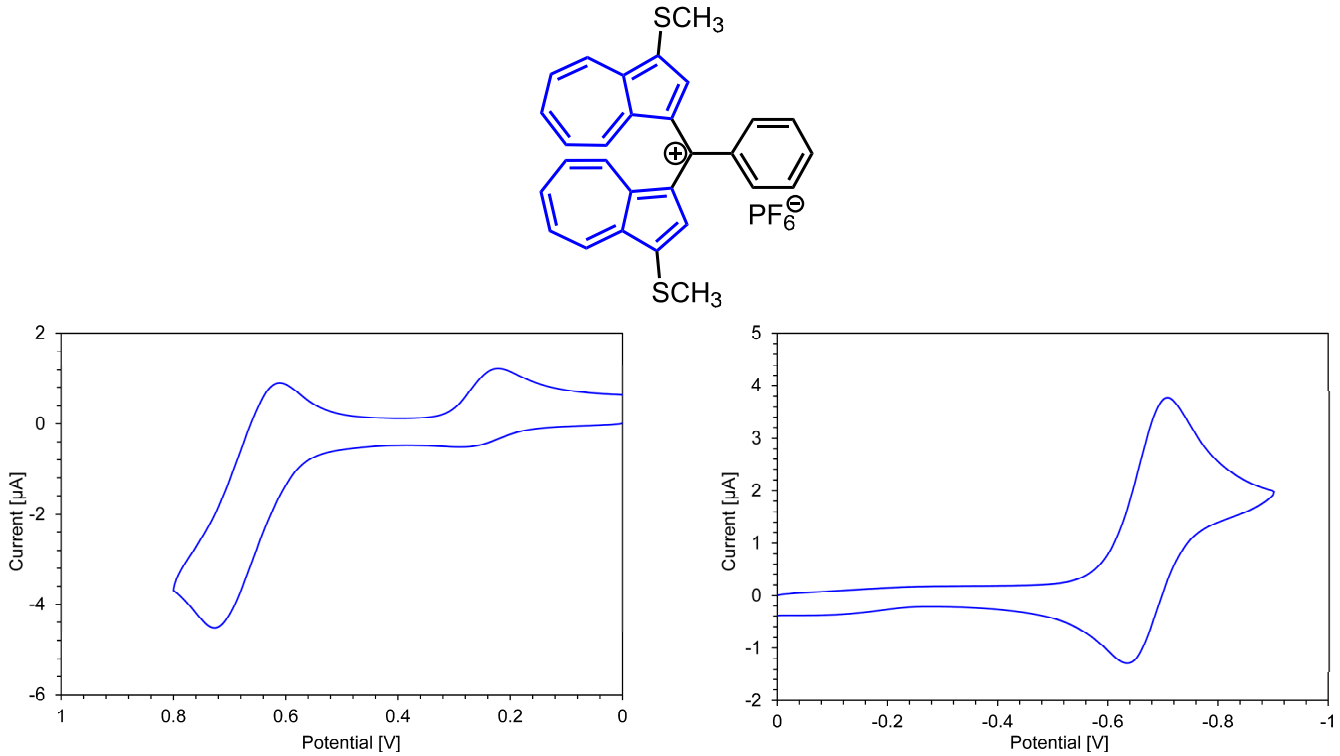

Figure S20. Cyclic voltammogram for oxidation (left) and reduction (right) of **3a**$^{2+}$·2PF_6^- (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mVs^{-1}.

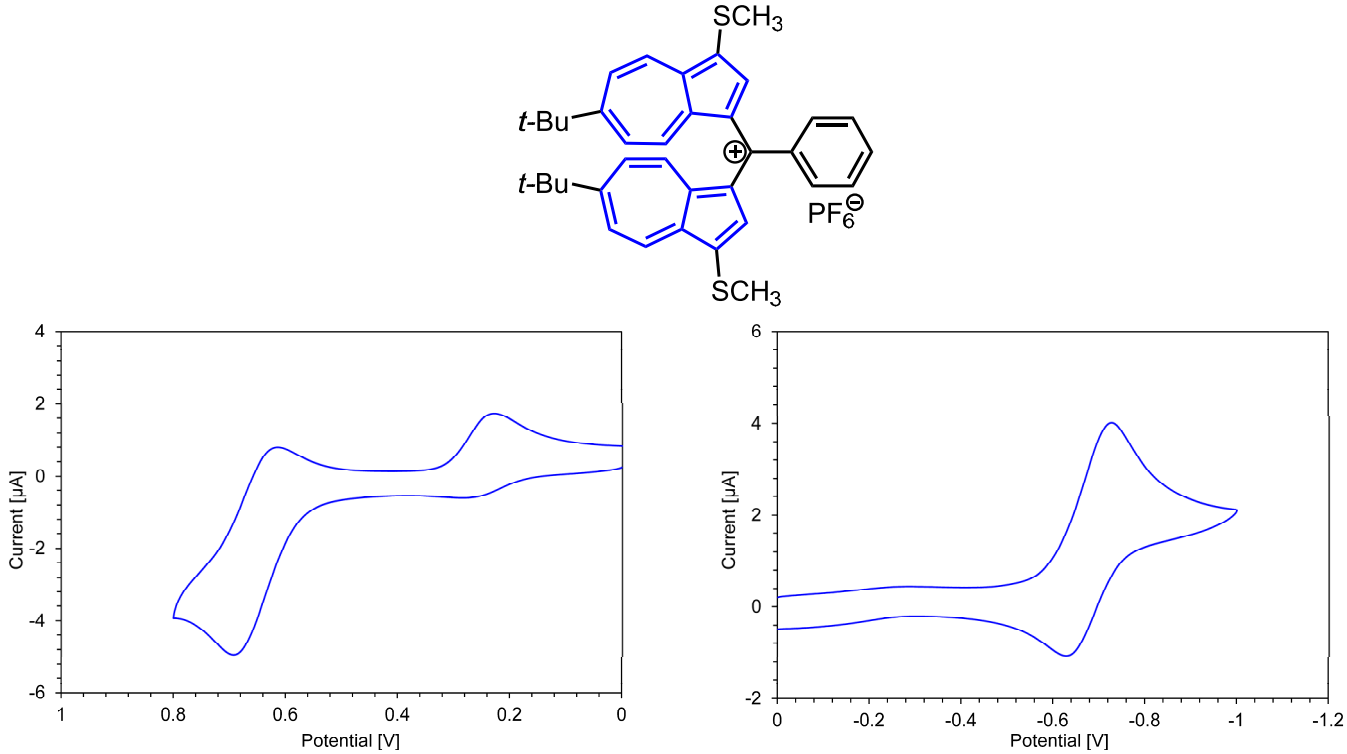

Figure S21. Cyclic voltammogram for oxidation (left) and reduction (right) of **3b**$^{2+}$·2PF_6^- (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mVs^{-1}.

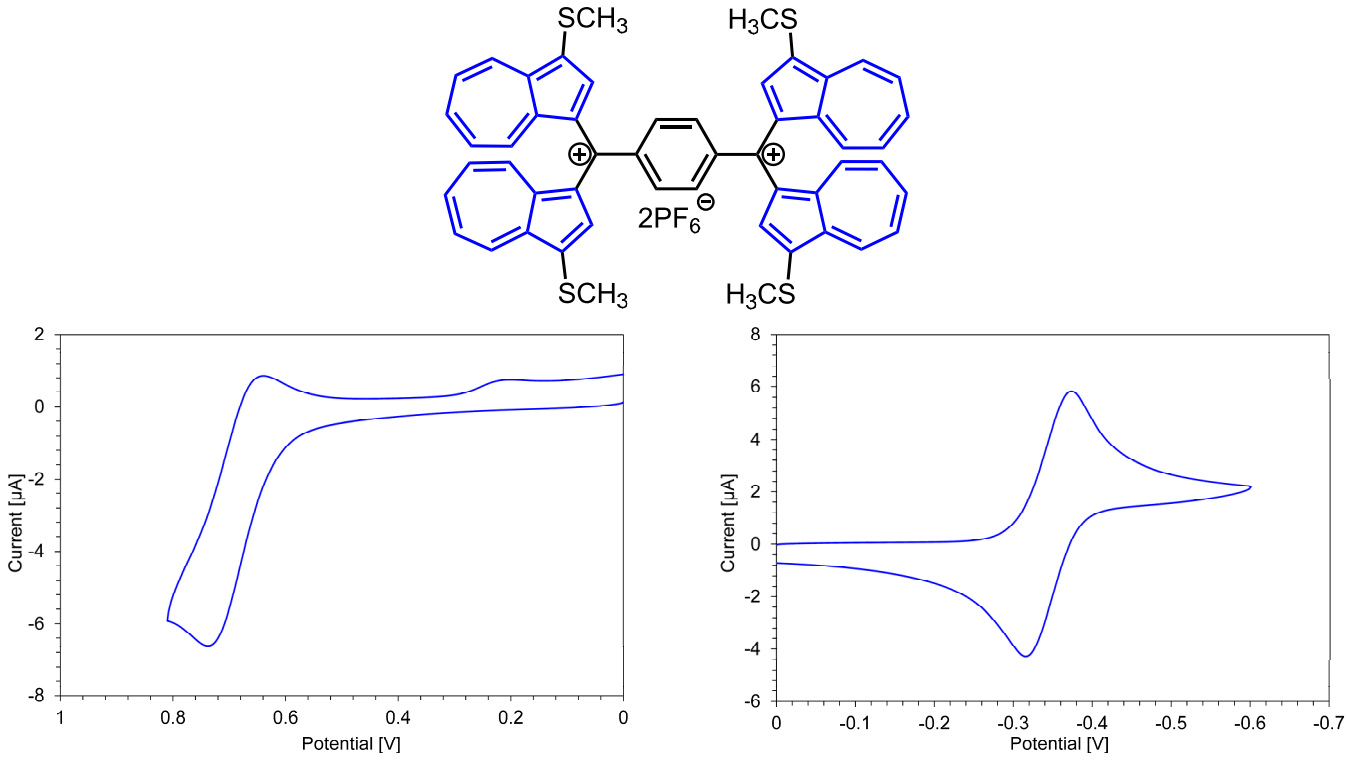

Figure S22. Cyclic voltammogram for oxidation (left) and reduction (right) of **4a**$^{+}$**·PF**$_6^-$ (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as the supporting electrolyte; scan rate = 100 mVs^{-1}.