Widely Electronically Tunable 2,6-Disubstituted Dithieno[1,4]thiazines—Electron-Rich Fluorophores Up to Intense NIR Emission

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Supporting Information

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1 General Considerations

All reactions were carried out in flame-dried Schlenk tubes by using syringes under nitrogen atmosphere. Dry solvents for reactions and analytics were directly used from a MB-SPS 800 solvent drying system (MBraun) except of toluene, which was refluxed under nitrogen atmosphere over sodium, destilled and stored in a Schlenk flask over molecular sieve 4 Å under nitrogen atmosphere. 4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine (2a-aa), 8-phenyl-8H-dithieno[3,2-b:2',3'-e][1,4]thiazine (2b-ss) and 3,7-dibromo-10-phenyl-10H-phenothiazine (5) were synthesized according to the literature procedures as indicated. Commercial grade reagents were purchased from Sigma Aldrich, Alfa Aesar, ABCR, Fluorochem and ACROS and used as supplied without further purification. Crude mixtures were adsorbed on Celite® 545 (0.02–0.20 mm) from Carl Roth GmbH Co.KG. The purification of products was performed on silica gel 60 M (0.04–0.063 mm) from Macherey–Nagel by using the flash technique under a pressure of 2 bar. For TLC silica gel coated aluminium plates (60, F254) from Merck were employed and analyzed with UV light at 254 or 365 nm.

1H, 13C, and 135-DEPT NMR spectra were recorded at 293 K, 373 K or 393 K on 300 MHz (Bruker AVIII 300), 500 MHz (Bruker Avance DRX 500) or 600 MHz (Bruker Avance III 600) and the resonances of the residues of non-deuterated DMSO-d6 (1H δ = 2.50 ppm, 13C δ = 39.52 ppm) was locked as internal standard. The multiplicities of signals are abbreviated as follows: s = singlet, d = doublet and m = multiplet. The assignments of Cquat and CH nuclei are based on DEPT spectra.

IR spectra were recorded on a Shimadzu IR Affinity-1 with ATR technique. The intensities of IR signals are abbreviated as s (strong), m (medium) and w (weak).

EI mass spectra were recorded on Triple-Quadrupole mass spectrometer TSQ 7000 (Finnigan MAT). MALDI-TOF mass spectra were measured on an UltraflExtreme apparatus (Bruker Daltonics). High-resolution ESI mass spectra were recorded on a UHR-QTOF maXis 4G apparatus (Bruker Daltonics).

The elemental analyses were carried out on a Perkin Elmer Series II Analyser 2400 at the Institute for Pharmaceutical and Medicinal Chemistry at Heinrich-Heine-University Düsseldorf.

Melting points (uncorrected) were measured with a Büchi B545 apparatus.

Absorption spectra were recorded in dichloromethane high performance liquid chromatography (HPLC) grade at 293 K on Perkin Elmer UV/vis/NIR Lambda 19 spectrometer. For the determination of the extinction coefficients ε absorption measurements at five different concentrations were carried out. Emission spectra were recorded in dichloromethane HPLC grade at 293 K on a Perkin Elmer LS55 spectrometer. Emission spectra were recorded at
293 K on a LS55 spectrometer (Perkin Elmer). Phosphorescence spectra were recorded in toluene, degassed for at least 15 min with nitrogen, at 77 K (cooling with liquid nitrogen) using the phosphorescence mode of the LS55 spectrometer. Fluorescence quantum yields \( \Phi_F \) were determined relative to a fluorescence standard (measurements at five concentrations). Nile Blue A perchlorate in MeOH (\( \lambda_{\text{exc}} = 626 \text{ nm}, \ \Phi_F = 0.21^{[4]} \)) was used for compounds 3a-aa and 3b-ss, 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) in MeOH (\( \lambda_{\text{exc}} = 492 \text{ nm}, \ \Phi_F = 0.43^{[5]} \)) was used for compounds 3c-aa, 3d-ss and 6 and Coumarine 153 in ethanol (\( \lambda_{\text{exc}} = 422 \text{ nm}, \ \Phi_F = 0.38^{[6]} \)) was used for compounds 3e-aa and 3f-ss.

Quantum chemical calculations were carried out utilizing the HPC-Cluster Ivybridge of the Zentrum für Informations- und Medientechnologie (ZIM) at the Heinrich-Heine-University Düsseldorf.

Fluorescence lifetimes were measured on the FluoTime 300 (PicoQuant) using a picosecond white light laser (SuperK Extreme with SuperK Extend-UV, NKT Photonics).

Cyclic voltammetry experiments (EG&G Princeton Applied Research Model 263A potentiostat) were performed under argon atmosphere in dry and degassed dichloromethane at 293 K using n-Bu_4NPF_6 (0.1 M) as electrolyte and at scan rates \( v \) of 100, 250, 500 and 1000 mVs\(^{-1}\). The three-electrode array consists of a working electrode with a 2 mm platinum disk, a platinum wire counter electrode, and an Ag/AgCl (3.0 M NaCl) reference electrode. The potentials were corrected by adding the internal standard decamethylferrocene to each measurement. Decamethylferrocene was referenced to the internal redox standard ferrocene (\( E_0^{0+/1}(\text{ferrocene}) = 450 \text{ mV} \)).\(^{[7]}\) Therefore the outlined potentials are indirectly referenced to ferrocene.

2 Syntheses

2.1 General procedure 1 (GP1) for the synthesis of 3a-aa, 3b-ss and 6 via Lithiation-Formylation-Knoevenagel sequence (LiForK)\(^{[8]}\)

In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere \( N \)-phenyl dithieno[1,4]thiazine 2a-aa or 2b-ss or 3,7-dibromo-10-phenyl-10H-phenothiazine (6) (1.00 equiv) and tetramethylethylenediamine (2.50 equivs) were dissolved in dry THF (10 mL/mmol) and cooled to -78 °C (isopropanol/dry ice). Then, \( n \)-butyllithium (2.50 equivs, 1.6 M in hexane) was added dropwise slowly via syringe to the vigorously stirred solution. Stirring was continued at -78°C for 2 h. Then dry DMF (3.00 eq.) was added, stirring was continued at -78 °C for another 90 min and then at ambient temperature for 30 min. To the reaction mixture acetic acid (5.00 eq.) was added. After stirring for 15 min at ambient temperature,
malononitrile (4) (3.00 eq.) was added and the stirring was continued for 20 – 40 min at ambient temperature. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography and further suspension in ethanol. For Experimental details see Table S1.

| Entry | Thiazine [mg] (mmol) | DMF [µl] (mmol) | Malononitrile (4) [mg] (mmol) | tKnovenagel [min] | Yield [mg] (%) |
|-------|---------------------|-----------------|-----------------------------|-------------------|---------------|
| 1     | 146 (0.510)         | 118 (1.53)      | 101 (1.53)                  | 20                | 185 (84)      |
|       | of 2a-aa             |                 |                             |                   |               |
| 2     | 311 (1.08)          | 249 (3.24)      | 214 (3.24)                  | 40                | 191 (40)      |
|       | of 2b-ss             |                 |                             |                   |               |
| 3a    | 433 (1.50)          | 346 (4.50)      | 297 (4.50)                  | 30                | 315 (74)      |
|       | of 5                 |                 |                             |                   |               |

\[a\]: Stirring for 30 min for lithiation.

2.1.1 2,2’-((8-Phenyl-8H-dithieno[3,2-b:2’,3’-e][1,4]thiazine-2,6-diyl)bis(methanyleylene))dimalononitrile (3a-aa)

The crude product was synthesized according to GP1 and purified by flash column chromatography using gradient elution (n-hexane/ethyl acetate 2:1 → ethyl acetate) and suspension in ethanol to give product 3a-aa (185 mg, 88%) as a dark blue powder.

Mp.: 316–320 °C (decomposition). Rf (n-hexane/ethyl acetate 2:1) = 0.23. \( ^1\)H NMR (600 MHz, DMSO-d₆, 372K): \( \delta \) 7.51 (s, 2H), 7.69 – 7.75 (m, 3H), 7.77 - 7.81 (m, 2H), 8.10 (s, 2H). \( ^{13}\)C NMR (150 MHz, DMSO-d₆): \( \delta \) 69.2 (C_{quat}), 110.8 (C_{quat}), 114.5 (C_{quat}), 115.2 (C_{quat}), 124.8 (C_{quat}), 127.7 (CH), 131.6 (CH), 131.7 (CH), 132.0 (CH), 139.8 (C_{quat}), 150.1 (CH), 152.2 (C_{quat}). MS(MALDI-TOF) m/z: 438.980 ([M]+). IR: \( \tilde{\nu} \) [cm\(^{-1}\)] = 2212 (w), 1561 (s), 1555 (s), 1501
(w), 1489 (w), 1423 (w), 1368 (s), 1325 (s), 1314 (s), 1287 (s), 1273 (s), 1254 (s), 1209 (s), 1169 (s), 1148 (s), 1121 (s), 1074 (m), 1057 (m), 1026 (m), 930 (m), 887 (m), 866 (m), 851 (m), 810 (m), 797 (m), 691 (s), 648 (m), 604 (s).

**Anal. calcd. for C$_{22}$H$_9$N$_5$S$_3$ (439.5):**
C 60.12, H 2.06, N 15.93, S 21.88; **Found:** C 60.00, H 1.96, N 15.68, S 21.64.

2.1.2 2,2'-(4-Phenyl-4H-dithieno[2,3-b:3',2'-e][1,4]thiazine-2,6-diyl)bisis(methanylylidenene))dimalononitrile (3b-ss)

![Chemical Structure](image)

The crude product was synthesized according to **GP1** and purified by flash column chromatography using gradient elution ($n$-hexane/ethyl acetate 2:1 → ethyl acetate) and suspension in ethanol to give product **3b-ss** (191 mg, 40%) as a dark blue powder.

Mp.: 330–335 °C (decomposition). **R$_f$** ($n$-hexane/ethyl acetate 2:1) = 0.30. **$^1$H NMR** (600 MHz, DMSO-d$_6$, 372K): $\delta$ 6.78 (s, 2H), 7.47 – 7.50 (m, 2H), 7.52 – 7.56 (m, 1H), 7.62 – 7.66 (m, 2H), 8.23 (s, 2H). **$^{13}$C NMR** (150 MHz, DMSO-d$_6$, 372K): $\delta$ 73.7 ($C_{\text{quat}}$), 113.1 ($C_{\text{quat}}$), 113.8 ($C_{\text{quat}}$), 118.3 ($C_{\text{quat}}$), 125.8 (CH), 127.9 (CH), 128.6 (CH), 130.7 (CH), 132.4 ($C_{\text{quat}}$), 140.8 ($C_{\text{quat}}$), 142.8 ($C_{\text{quat}}$), 149.7 (CH). **MS**(MALDI-TOF) **m/z:** 439.073 ([M$^+$]). **IR:** $\tilde{\nu}$ [cm$^{-1}$] = 3088 (w), 2988 (w), 2901 (w), 1560 (s), 1549 (s), 1489 (m), 1420 (s), 1369 (s), 1342 (s), 1267 (s), 1209 (s), 1184 (m), 1155 (m), 1111 (m), 1084 (s), 1024 (m), 991 (m), 930 (m), 916 (s), 839 (s), 795 (s), 694 (s), 667 (m). **Anal. calcd. for C$_{22}$H$_9$N$_5$S$_3$ (439.5):** C 60.12, H 2.06, N 15.93, S 21.88; **Found:** C 60.00, H 1.96, N 15.68, S 21.64.
2.1.3 2,2’-((10-Phenyl-10H-phenothiazine-3,7-diyl)bis(methanylylidene))dimalononitrile (6)

![Chemical Structure]

The crude product was synthesized according to GP1 and purified by flash column chromatography using gradient elution (n-hexane/ethyl acetate 2:1 → ethyl acetate) and suspension in ethanol to give product 6 (315 mg, 74%) as a dark red powder.

Mp.: 322-326 °C. Rf (n-hexane/ethyl acetate 2:1) = 0.35. $^1$H NMR (500 MHz, DMSO-d$_6$): $\delta$ 6.16 (d, $^3$J$_{HH}$ = 8.83 Hz, 2H), 7.48 - 7.56 (m, 4H), 7.61 (d, $^4$J$_{HH}$ = 2.15 Hz, 2H), 7.62 - 7.70 (m, 1H), 7.72 - 7.78 (m, 2H), 8.21 (s, 2H). $^{13}$C NMR (125 MHz, DMSO-d$_6$): $\delta$ 77.8 (C$_{quat}$), 99.4 (C$_{quat}$), 113.5 (C$_{quat}$), 114.4 (C$_{quat}$), 116.4 (CH), 118.6 (C$_{quat}$), 126.8 (C$_{quat}$), 128.2 (CH), 129.7 (CH), 129.8 (CH), 131.2 (CH), 131.6 (CH), 146.1 (C$_{quat}$), 158.4 (CH). MS(El) m/z: 428 ([M + H]$^+$, 32), 427 ([M]$^+$, 100), 401 ([M – CN]$^+$, 13), 400 ([M – HCN]$^+$, 35), 350 ([M – C$_6$H$_5$]$^+$, 22), 349 (16), 77 (25), 51 (17). IR: $\tilde{\nu}$ [cm$^{-1}$] = 2218 (w), 1557 (m), 1518 (w), 1508 (w), 1474 (s), 1443 (w), 1383 (m), 1325 (m), 1298 (m), 1273 (m), 1248 (m), 1223 (s), 1200 (m), 1179 (s), 1148 (m), 1113 (m), 1065 (m), 1038 (m), 1020 (m), 970 (w), 939 (m), 916 (m), 883 (m), 804 (s), 773 (s), 716 (s), 692 (s), 646 (m), 611 (s). Anal. calcd. for C$_{26}$H$_{13}$N$_5$S (427.5): C 73.05, H 3.07, N 16.38, S 7.50; Found: C 72.83, H 3.08, N 16.26, S 7.26.
2.2 General procedure 2 (GP2) for the synthesis of 3c-aa – 3f-ss via dilithiation–lithium–zinc exchange–Negishi coupling

In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere N-phenyl dithieno[1,4]thiazine 2a-aa or 2b-ss (1.00 equiv) and tetramethylethylenediamine (2.50 equivs) were dissolved in dry THF (10 mL/mmol) and cooled to -78 °C (isopropanol/dry ice). Then, n-butyllithium (2.50 equivs, 1.6 M in hexane) was added dropwise slowly via syringe to the vigorously stirred solution. Stirring was continued at -78°C for 2 h, while zinc dibromide (3.00 equivs) was vacuum dried at 120 °C for 1.5 h. After cooling to ambient temperature dry THF (1.0 mL/mmol) was added to zinc dibromide. The resulting zinc dibromide solution (1.0 M in THF) was added dropwise to the reaction mixture, which was stirred at -78 °C for 30 min. After slowly warming to ambient temperature, tetrakis(triphenylphosphine)palladium(0) (5 mol%) and 4-bromobenzonitrile (7) or 4-iodoansole (8) (2.50 equivs) were added to the reaction mixture and the reaction solution was stirred at 70 °C for 1 – 2 h. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography and further suspension in acetone. For experimental details, see table 2.

Table 2. Experimental details GP2.

| Dithieno[1,4]thiazine 2 [mg] (mmol) | Aryl halide [mg] (mmol) | tNegishi [h] | Yield 3 [mg] (%) |
|-----------------------------------|------------------------|-------------|-----------------|
| 206 (0.720) of 2a-aa              | 328 (1.80) of 7         | 1           | 249 (71) of 3c-aa |
| 287 (1.00) of 2b-ss               | 455 (2.50) of 7         | 2           | 99 (20) of 3d-ss |
| 277 (0.960) of 2a-aa              | 562 (2.40) of 8         | 1           | 314 (65) of 3e-aa |
| 98.0 (0.340) of 2b-ss             | 199 (0.850) of 8        | 1           | 87.0 (51) of 3f-ss |
2.2.1 4,4’-(8-Phenyl-8H-dithieno[3,2-b:2’,3’-e][1,4]thiazine-2,6-diyl)dibenzonitrile (3c-aa)

The crude product was synthesized according to GP2 and purified by flash column chromatography using gradient elution (n-hexane/ethyl acetate 4:1 with 1% triethyl amine → n-hexane/ethyl acetate 1:1 with 1% triethyl amine) and suspension in acetone to give product 3c-aa (249 mg, 71%) as a violet powder.

Mp 274–276 °C. Rf (n-hexane/ethyl acetate 3:1) = 0.36. 1H NMR (600 MHz, DMSO-d6, 393K): δ 6.23 (s, 2H), 7.54 – 7.57 (m, 1H), 7.57 – 7.60 (m, 4H), 7.62 – 7.66 (m, 2H), 7.66 – 7.70 (m, 6H). 13C NMR (150 MHz, DMSO-d6, 393K): δ 108.3 (Cquat), 117.8 (Cquat), 122.9 (CH), 124.0 (CH), 126.7 (CH), 128.9 (CH), 130.1 (CH), 130.4 (Cquat), 132.1 (CH), 136.7 (Cquat), 142.2 (Cquat), 142.7 (Cquat). MS(MALDI-TOF) m/z: 489.115 ([M]+). IR: ¯ν [cm⁻¹] 3678 (w), 3057 (w), 2990 (w), 2886 (w), 2218 (w), 1559 (m), 1493 (m), 1435 (s), 1408 (s), 1362 (w), 1296 (w), 1283 (w), 1271 (w), 1227 (w), 1177 (m), 1165 (m), 1111 (w), 1045 (w), 1016 (w), 984 (w), 964 (w), 945 (w), 918 (w), 880 (w), 835 (w), 818 (s), 802 (m), 772 (w), 743 (w), 719 (w), 691 (m), 651 (w). Anal. calcd. for C28H15N3S3 (489.6): C 68.69, H 3.09, N 8.58, S 19.64; Found: C 68.67, H 3.00, N 8.40, S 19.93.

2.2.2 4,4’-(4-Phenyl-4H-dithieno[2,3-b:2’,3’-e][1,4]thiazine-2,6-diyl)dibenzonitrile (3d-ss)

The crude product was synthesized according to GP2 and purified by flash column chromatography (n-hexane/ethyl acetate 4:1 with 1% triethyl amine) and suspension in acetone to give product 3d-ss (99 mg, 20%) as an orange powder.

Mp 253–256 °C. Rf (n-hexane/ethyl acetate 4:1) = 0.38. 1H NMR (300 MHz, DMSO-d6): δ 6.83 (s, 2H), 7.39 – 7.46 (m, 1H), 7.46 – 7.51 (m, 2H), 7.52 – 7.60 (m, 2H), 7.61 – 7.68 (m, 4H), 7.74 – 7.82 (m, 4H). 13C NMR (75 MHz, DMSO-d6): δ 107.9 (Cquat), 109.8 (Cquat), 118.1 (CH), 122.7 (S7)
118.5 ($C_{quat}$), 125.0 (CH), 126.6 (CH), 127.2 (CH), 130.4 (CH), 132.9 (CH), 136.7 ($C_{quat}$), 139.2 ($C_{quat}$), 142.8 ($C_{quat}$), 143.7 ($C_{quat}$). MS(MALDI-TOF) $m/z$: 489.124 ([M$^+$]). IR: $\tilde{\nu}$ [cm$^{-1}$] 2220 (w), 1601 (s), 1497 (s), 1425 (m), 1371 (m), 1273 (m), 1180 (m), 943 (w), 826 (s), 806 (w), 789 (w), 739 (s), 681 (m).

Anal. calcd. for $C_{28}H_{15}N_3S_3$ (489.6): C 68.69, H 3.09, N 8.58, S 19.64; Found: C 68.43, H 3.06, N 8.47, S 19.39.

2.2.3 2,6-Bis(4-methoxyphenyl)-8-phenyl-8$H$-dithieno[3,2-\textbf{b}:2',3'-\textbf{e}][1,4]thiazine (3e-aa)

The crude product was synthesized according to GP2 and purified by flash column chromatography using gradient elution ($n$-hexane/ethyl acetate 3:1 with 1% triethyl amine → $n$-hexane/ethyl acetate 1:1 with 1% triethyl amine) and suspension in acetone to give product 3e-aa (314 mg, 65%) as an orange powder.

Mp 250–253 °C. $R_f$ ($n$-hexane/ethyl acetate 5:1) = 0.37. $^1$H NMR (600 MHz, DMSO-$d_6$, 373K): $\delta$ 3.77 (s, 6H), 6.90 (s, 2H), 6.90 –6.93 (m, 4H), 7.37 – 7.40 (m, 4H), 7.44 – 7.47 (m, 1H), 7.56 – 7.59 (m, 2H), 7.60 – 7.63 (m, 2H). $^{13}$C NMR (150 MHz, DMSO-$d_6$, 373K): $\delta$ 54.9 (CH$_3$), 99.0 ($C_{quat}$), 114.2 (CH), 118.9 (CH), 125.4 (CH), 125.5 (CH), 125.7 (CH), 127.6 ($C_{quat}$), 129.8 (CH), 133.9 ($C_{quat}$), 139.6 ($C_{quat}$), 143.7 ($C_{quat}$), 158.6 ($C_{quat}$). MS(ESI-HRMS) $m/z$: Calcd. for $C_{28}H_{21}NO_2S_3$: 499.0734, Found: 499.0735 ([M$^+$]). IR: $\tilde{\nu}$ [cm$^{-1}$] 3026 (w), 3005 (w), 2930 (w), 2905 (w), 2833 (w), 1603 (w), 1558 (w), 1501 (s), 1489 (s), 1472 (m), 1449 (s), 1337 (w), 1283 (m), 1244 (s), 1223 (m), 1179 (m), 1159 (m), 1125 (w), 1111 (m), 1072 (w), 1026 (s), 962 (w), 858 (w), 818 (s), 802 (m), 789 (m), 741 (w), 694 (w), 664 (s). Anal. calcd. for $C_{28}H_{21}NO_2S_3$ (499.7): C 67.31, H 4.24, N 2.80, S 19.25; Found: C 67.30, H 4.34, N 2.75, S 19.55.
2.2.4 2,6-Bis(4-methoxyphenyl)-4-phenyl-4H-dithieno[2,3-b:3′,2′-e][1,4]thiazine (3f-ss)

The crude product was synthesized according to GP2 and purified by flash column chromatography (n-hexane/ethyl acetate 3:1 with 1% triethyl) and suspension in acetone to give product 3f-ss (87 mg, 51%) as a yellow powder.

Mp 237–239 °C. R$_f$(n-hexane/ethyl acetate 3:1) = 0.61. $^1$H NMR (600 MHz, DMSO-d$_6$, 373K): δ 3.77 (s, 6H), 6.48 (s, 2H), 6.89 – 6.95 (m, 4H), 7.33 – 7.38 (m, 4H), 7.38 – 7.43 (m, 1H), 7.45 – 7.50 (m, 2H), 7.52 – 7.58 (m, 2H). $^{13}$C NMR (150 MHz, DMSO-d$_6$, 373K): δ 54.9 (CH$_3$), 103.7 (C$_{quat}$), 114.3 (CH), 115.0 (CH), 125.3 (C$_{quat}$), 125.8 (CH), 126.1 (CH), 126.4 (CH), 129.7 (CH), 141.3 (C$_{quat}$), 143.6 (C$_{quat}$), 143.2 (C$_{quat}$), 159.0 (C$_{quat}$). MS(MALDI-TOF) m/z: 499.090 ([M$^+$]). IR: $\tilde{\nu}$ [cm$^{-1}$] 2995 (w), 2907 (w), 2835 (w), 1603 (w), 1504 (m), 1489 (s), 1454 (m), 1441 (m), 1369 (m), 1292 (m), 1250 (m), 1233 (m), 1206 (w), 1177 (m), 1169 (m), 1157 (m), 1128 (w), 1113 (m), 1028 (s), 1001 (m), 980 (w), 908 (w), 826 (s), 806 (s), 783 (m), 729 (s), 696 (s), 675 (w), 667 (w). Anal. calcd. for C$_{28}$H$_{21}$N$_2$O$_2$S$_3$: C 67.31, H 4.24, N 2.80, S 19.25; Found: C 67.21, H 4.20, N 2.80, S 19.13.
3 $^1$H and $^{13}$C NMR spectra

3.1 2,2'-(8-Phenyl-8H-dithieno[3,2-b:2',3'-e][1,4]thiazine-2,6-diyl)bismethanlylidene)dimalononitrile (3a-aa)

Figure S1. $^1$H NMR spectrum of 3a-aa (DMSO-$d_6$, 372 K, 600 MHz).

Figure S2. $^{13}$C-NMR spectrum of 3a-aa (DMSO-$d_6$, 293 K, 150 MHz).
3.2 2,2’-((4-phenyl-4H-dithieno[2,3-b:3’,2’-e][1,4]thiazine-2,6-diyl)bis(methanlylidenene))dimalononitrile (3b-ss)

Figure S3. $^1$H NMR spectrum of 3b-ss (DMSO-d$_6$, 372 K, 600 MHz).

Figure S4. $^{13}$C NMR spectrum of 3b-ss (DMSO-d$_6$, 372 K, 150 MHz).
3.3 2,2’-((10-Phenyl-10H-phenothiazine-3,7-diyl)bis(methanylylidene))dimalononitrile (6)

Figure S5. $^1$H NMR spectrum of 6 (DMSO-$d_6$, 298 K, 500 MHz).

Figure S6. $^{13}$C-NMR spectrum of 6 (DMSO-$d_6$, 298 K, 125 MHz).
3.4 4,4’-(8-Phenyl-8H-dithieno[3,2-b:2’,3’-e][1,4]thiazine-2,6-diyl)dibenzonitrile (3c-aa)

Figure S7. $^1$H NMR spectrum of 3c-aa (DMSO-$d_6$, 393 K, 600 MHz).

Figure S8. $^{13}$C NMR spectrum of 3c-aa (DMSO-$d_6$, 393 K, 150 MHz).
3.5 4,4’-(4-Phenyl-4H-dithieno[2,3-b:3’,2’-e][1,4]thiazine-2,6-diyl)dibenzonitrile (3d-ss)

Figure S9. $^1$H NMR spectrum of 3d-ss (DMSO-d$_6$, 293 K, 300 MHz).

Figure S10. $^{13}$C NMR spectrum of 3d-ss (DMSO-d$_6$, 293 K, 75 MHz).
3.6 2,6-Bis(4-methoxyphenyl)-8-phenyl-8H-dithieno[3,2-b:2',3'-e][1,4]thiazine (3e-aa)

Figure S11. $^1$H NMR spectrum of 3e-aa (DMSO-$d_6$, 373 K, 600 MHz).

Figure S12. $^{13}$C NMR spectrum of 3e-aa (DMSO-$d_6$, 373 K, 150 MHz).
3.7 2,6-Bis(4-methoxyphenyl)-4-phenyl-4H-dithieno[2,3-b:3’,2’-e][1,4]thiazine (3f-ss)

Figure S13. $^1$H NMR spectrum of 3f-ss (DMSO-d$_6$, 373 K, 600 MHz).

Figure S14. $^{13}$C NMR spectrum of 3f-ss (DMSO-d$_6$, 373 K, 150 MHz).
4 Cyclovoltammetric Data

Figure S15. Cyclic voltammograms of 3a-aa (red), 3b-ss (black) and 6 (blue) (CH₂Cl₂, \( T = 298 \) K, 0.1 \( \text{m} \) [Bu₄N][PF₆], \( v = 100 \) mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me₁₀Fc]/[Me₁₀Fc]⁺ as an internal standard; Me₁₀Fc = decamethylferrocene, \( E_{0,1} = -95 \) mV vs. ferrocene with \( E_{0,1}(\text{Fc/Fc}^+) = 450 \) mV).

The cyclic voltammograms of 3a-aa and 3b-ss were processed by convolution and deconvolution (Figures S16 and S17) for the determination of the second oxidation potentials using the condecon program[^10].
Figure S16. Convolution-deconvolution of the cyclic voltammograms of 3a-aa (CH₂Cl₂, T = 298 K, 0.1 M [Bu₄N][PF₆], v = 100 mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me₁₀Fc]/[Me₁₀Fc]⁺ as an internal standard; Me₁₀Fc = decamethylferrocene, E₀⁺₁ = -95 mV vs. ferrocene with E₀⁺₁(Fc/Fc⁺) = 450 mV).

Figure S17. Convolution-deconvolution of the cyclic voltammograms of 3b-ss (CH₂Cl₂, T = 298 K, 0.1 M [Bu₄N][PF₆], v = 100 mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me₁₀Fc]/[Me₁₀Fc]⁺ as an internal standard; Me₁₀Fc = decamethylferrocene, E₀⁺₁ = -95 mV vs. ferrocene with E₀⁺₁(Fc/Fc⁺) = 450 mV).
5 Photophysical Properties of Compounds 3 and 6

5.1 Solvatochromism Studies

Compounds 3a-aa – 3d-ss and 6 showed positive solvatochromism since the emission bands are shifted more bathochromically with increasing solvent polarity (Figures S19 – S28). The change of the dipole moments from the electronic ground- to excited-states $\Delta \mu$ were obtained by Lippert-Mataga plots (Figures S19–S28; equations 1, 2).\(^\text{[11]}\)

$$\Delta \tilde{\nu} = \frac{\Delta \mu^2}{2 \pi \hbar c \varepsilon_0 \omega^3} \Delta f$$  
(eq. 1)

$\Delta f$ orientation polarization
$\Delta \tilde{\nu}$ stokes shift
a Onsager radius

$$\Delta f = \frac{\varepsilon - 1}{2 \varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$  
(eq. 2)

$\varepsilon$ solvent permittivity
n refractive index

The Onsager radii were estimated from the optimized ground-state geometries (Figure S18). Due to the $C_s$ symmetry of all compounds, the Onsager radii were measured between the dithienothiazines' centers and acceptor substituents respectively.

Figure S18. Exemplarily estimation of the Onsager radius of 3a-aa from the optimized ground-state geometry (mean of marked distances, PBE1PBE/6-31G**, PCM CH\(_2\)Cl\(_2\)).
Figure S19. Normalized absorption and emission spectra of 3a-aa recorded in different solvents (c(3a-aa) = 10^{-6} M, 298 K).

Figure S20. Lippert plot of compound 3a-aa.
Figure S21. Normalized absorption and emission spectra of 3b-ss recorded in different solvents (c(3b-ss) = 10^{-6} M, 298 K).

Figure S22. Lippert plot of compound 3b-ss.
Figure S23. Normalized absorption and emission spectra of 6 recorded in different solvents (c(6) = 10^{-6} M, 298 K).

Figure S24. Lippert plot of compound 6.
Figure S25. Normalized absorption and emission spectra of 3c-aa recorded in different solvents ([3c-aa] = 10^{-6} M, 298 K).

Figure S26. Lippert plot of compound 3c-aa.
Figure S27. Normalized absorption and emission spectra of 3d-ss recorded in different solvents (c(3d-ss) = 10^{-6} M, 298 K).

Figure S28. Lippert plot of compound 3d-ss.
5.2 Fluorescence Lifetimes of 3a-aa and 3b-ss and Phosphorescence Lifetime of 3f-ss

![Graph showing fluorescence decay for compound 3b-ss](image)

**Figure S29.** Exponential fit and fluorescence lifetime $\tau$ (red) of the fluorescence decay of compound **3b-ss** ($\text{CH}_2\text{Cl}_2$, $c(3b-ss) = 10^{-6}$ M, 298 K, $\lambda_{\text{exc}} = 623$ nm, $\lambda_{\text{em}} = 750$nm).

$r^2 = 0.92578$

$\tau = 0.21262$ ns

![Graph showing fluorescence decay for compound 3a-aa](image)

**Figure S30.** Exponential fit and fluorescence lifetime $\tau$ (red) of the fluorescence decay of compound **3a-aa** ($\text{CH}_2\text{Cl}_2$, $c(3a-aa) = 10^{-6}$ M, 298 K, $\lambda_{\text{exc}} = 641$ nm, $\lambda_{\text{em}} = 719$nm).

$r^2 = 0.99967$

$\tau = 2.47648$ ns
Figure S31. Exponential fit and phosphorescence lifetime $\tau_p$ (red) of the phosphorescence decay of compound 3f-ss (toluene, $c(3f-ss) = 10^{-6}$ M, 77 K, $\lambda_{\text{exc}} = 420$ nm, $\lambda_{\text{em}} = 620$ nm, degassed with N$_2$ for 15 min).

6 Data of Quantum Chemical Calculations

The ground state geometries of the compounds 3 and 6 were optimized using the Gaussian09 program package, the PBE1PBE hybrid-functional and the 6-31G** basis set. The Excitation energies of compounds 3 and 6 and the excited state geometries ($S_1$) of 3a-aa, 3b-ss, 3c-aa and 6 were calculated with TDDFT methods implemented in the Gaussian09 program package using the same PBE1PBE functional and either the 6-31G** or the 6-31+G** basis set as indicated. The polarizable continuum model (PCM) with dichloromethane or toluene as a solvent was applied for the calculations. For the calculation of redox potentials (see chapter 6.2) the ground state geometries of the radical cations and dications of compounds 3 and 6 were optimized using the Gaussian09 program package, the uB3LYP functional and the 6-311G* basis set in the gas-phase. Then, single point calculations on the gas phase geometries was applied to determine the solvation enthalpies using the SMD solvation model with dichloromethane as a solvent. All optimized geometries were confirmed as minima (NImag = 0) or as saddle points (transition states, NImag = 1) by analytical frequency analyses.
6.1 Computed xyz-Coordinates, excitations of compounds 3 and 6 and selected properties derived from the DFT-calculations

Table 3. S,N-folding angles of the S₀ and S₁-geometries \( \vartheta \) and the HOMO- and LUMO-energies \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) derived from the optimized geometries of compounds 3 and 6 (PBE1PBE/6-31G**, PCM CH₂Cl₂).

| Compound | \( E_{\text{HOMO}} \) [eV] | \( E_{\text{LUMO}} \) [eV] | \( \vartheta(S₀) \) [°] | \( \vartheta(S₁) \) [°] |
|----------|----------------|----------------|----------------|----------------|
| 3a-aa    | -5.594         | -3.042         | 174            | 180            |
| 3b-ss    | -5.622         | -3.028         | 160            | 180            |
| 6        | -5.923         | -2.959         | 155            | 180            |
| 3c-aa    | -5.133         | -1.975         | 152            | 180            |
| 3d-ss    | -5.232         | -1.942         | 146            | -             |
| 3e-aa    | -4.829         | -1.046         | 146            | -             |
| 3f-ss    | -4.914         | -1.105         | 146            | -             |

6.1.1 Compound 3a-aa

6.1.1.1 Computed xyz-Coordinates of compound 3a-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S32. Optimized ground state geometry of 3a-aa (PBE1PBE/6-31G** PCM CH₂Cl₂).

| C     | 1.33692 | -1.05961 | 0.17801 |
| C     | 1.18717 | 0.32165  | 0.11099 |
| N     | -0.00002| 1.01482  | 0.14157 |
| C     | -1.18724| 0.32168  | 0.11097 |
| C     | -1.33701| -1.05958 | 0.17799 |
| S     | -0.00006| -2.19102 | 0.41776 |
| Element | X         | Y         | Z         | Charge |
|---------|-----------|-----------|-----------|--------|
| C       | 2.67471   | -1.45366  | 0.09069   |        |
| C       | 3.56103   | -0.38627  | -0.02930  |        |
| S       | 2.69003   | 1.13386   | -0.05617  |        |
| S       | -2.69007  | 1.13391   | -0.05617  |        |
| C       | -3.56110  | -0.38620  | -0.02931  |        |
| C       | -2.67481  | -1.45360  | 0.09068   |        |
| C       | 0.00002   | 2.45249   | 0.09360   |        |
| C       | 4.97014   | -0.33853  | -0.12984  |        |
| C       | 5.87500   | -1.37746  | -0.14731  |        |
| C       | 7.26662   | -1.09855  | -0.25667  |        |
| C       | 5.51191   | -2.74879  | -0.06142  |        |
| C       | -4.97022  | -0.33845  | -0.12980  |        |
| C       | -5.87505  | -1.37739  | -0.14728  |        |
| C       | -7.26669  | -1.09852  | -0.25658  |        |
| C       | -5.51192  | -2.74872  | -0.06144  |        |
| N       | 8.40446   | -0.87258  | -0.34612  |        |
| N       | 5.21105   | -3.87087  | 0.00945   |        |
| N       | -8.40453  | -0.87257  | -0.34599  |        |
| N       | -5.21088  | -3.87075  | 0.00940   |        |
| C       | -0.00019  | 3.09339   | -1.14479  |        |
| C       | -0.00011  | 4.48436   | -1.18181  |        |
| C       | 0.00019   | 5.21447   | 0.00482   |        |
| C       | 0.00040   | 4.56129   | 1.23578   |        |
| C       | 0.00032   | 3.17109   | 1.28761   |        |
| H       | 2.99225   | -2.48851  | 0.12352   |        |
| H       | -2.99237  | -2.48845  | 0.12351   |        |
| H       | 5.41220   | 0.65202   | -0.20605  |        |
| H       | -5.41228  | 0.65211   | -0.20597  |        |
| H       | -0.00038  | 2.50687   | -2.05833  |        |
| H       | -0.00028  | 4.99598   | -2.13873  |        |
| H       | 0.00028   | 6.29946   | -0.02976  |        |
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|-------------|
| H    | 0.00062      | 5.13310      | 2.15802     |
| H    | 0.00047      | 2.64237      | 2.23550     |

SCF Done: $E_{\text{RPBE1PBE}} = -2310.24984389$ A.U. after 1 cycles

Zero-point correction = 0.255560 (Hartree/Particle)

Thermal correction to Energy = 0.281885

Thermal correction to Enthalpy = 0.282829

Thermal correction to Gibbs Free Energy = 0.194331

Sum of electronic and zero-point Energies = -2309.994284

Sum of electronic and thermal Energies = -2309.967959

Sum of electronic and thermal Enthalpies = -2309.967015

Sum of electronic and thermal Free Energies = -2310.055513

### 6.1.1.2 Computed Excitations of compound 3a-aa (PBE1PBE/6-31+G** PCM CH$_2$Cl$_2$)

| Excited State | Multiplicity | $\Delta E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ |
|---------------|--------------|-----------------|---------------|----|---------------------|
| 1             | Singlet-A    | 1.9850          | 624.61        | 0.9395 | 0.000 |
|               |              | 112 -> 113     | 0.70343       |    |                     |

This state for optimization and/or second-order correction.

Total Energy, $E_{\text{TD-HF/TD-KS}} = -2310.21026603$

Copying the excited state density for this state as the 1-particle RhoCl density.

| Excited State | Multiplicity | $\Delta E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ |
|---------------|--------------|-----------------|---------------|----|---------------------|
| 2             | Singlet-A    | 2.5981          | 477.20        | 0.0504 | 0.000 |
|               |              | 111 -> 113     | -0.11074      |    |                     |
|               |              | 112 -> 114     | 0.69524       |    |                     |

| Excited State | Multiplicity | $\Delta E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ |
|---------------|--------------|-----------------|---------------|----|---------------------|
| 3             | Singlet-A    | 3.4792          | 356.36        | 0.3642 | 0.000 |
|               |              | 110 -> 113     | 0.69580       |    |                     |

| Excited State | Multiplicity | $\Delta E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ |
|---------------|--------------|-----------------|---------------|----|---------------------|
| 4             | Singlet-A    | 3.6245          | 342.08        | 0.1856 | 0.000 |
|               |              | 111 -> 113     | 0.69607       |    |                     |
|               |              | 112 -> 114     | 0.11187       |    |                     |

| Excited State | Multiplicity | $\Delta E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ |
|---------------|--------------|-----------------|---------------|----|---------------------|
| 5             | Singlet-A    | 3.6568          | 339.05        | 0.0659 | 0.000 |

S29
112 ->115  0.63301
112 ->116  -0.27741

Excited State 6:  Singlet-A  3.7484 eV  330.77 nm  f=0.2728  <S**2>=0.000
112 ->115  0.29296
112 ->116  0.62814

6.1.1.3 Computed xyz-Coordinates of S1 of compound 3a-aa (PBE1PBE/6-31G** PCM CH2Cl2)

Figure S33. Optimized S1 geometry of 3a-aa (PBE1PBE/6-31G** PCM CH2Cl2).

C  -1.33248  -1.03199  -0.00001
C  -1.18407   0.36702   -0.00004
N   0.00000   1.03662   -0.00010
C   1.18407   0.36702   -0.00001
C   1.33248  -1.03199    0.00000
S    0.00000  -2.14871    0.00024
C  -2.66691  -1.44247   -0.00005
C  -3.56756  -0.37544  -0.00016
S  -2.71572   1.17835  -0.00015
S   2.71572   1.17835  -0.00014
C   3.56756  -0.37544  -0.00017
C   2.66691  -1.44247   -0.00005
C    0.00000   2.48082   0.00005
C  -4.97632  -0.35469  -0.00022
C  -5.86086  -1.42738  -0.00008
C  -7.25921  -1.18176  -0.00016
C  -5.46814  -2.78904  0.00016
C   4.97632  -0.35469  -0.00024
C   5.86086  -1.42738  -0.00010
C   7.25921  -1.18176  -0.00020
C   5.46814  -2.78904  0.00013
N  -8.40671  -0.97857  -0.00022
N  -5.14360  -3.90900  0.00038
N   8.40671  -0.97857  -0.00027
N   5.14360  -3.90900  0.00035
C  0.00016   3.15392  1.21909
C  0.00016   4.54512  1.20987
C  0.00000   5.23667  0.00031
C -0.00016   4.54536 -1.20938
C -0.00016   3.15415 -1.21884
H  -2.97272  -2.48061  -0.00007
H   2.97272  -2.48061  -0.00007
H  -5.44752   0.62458  -0.00038
H   5.44752   0.62458  -0.00040
H   0.00028   2.59520  2.14946
H   0.00029   5.08676  2.14997
H   0.00000   6.32206  0.00042
H  -0.00029   5.08716 -2.14938
H  -0.00028   2.59558 -2.14930

Excited State 1: Singlet-A  1.7443 eV  710.80 nm  f=1.0400  <S**2>=0.000

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2310.18282357

SCF Done: E(RPBE1PBE) = -2310.24692472  A.U. after 7 cycles

Zero-point correction = 0.253662 (Hartree/Particle)

Thermal correction to Energy = 0.280227
Thermal correction to Enthalpy = 0.281171
Thermal correction to Gibbs Free Energy = 0.192340
Sum of electronic and zero-point Energies = -2309.929161
Sum of electronic and thermal Energies = -2309.902596
Sum of electronic and thermal Enthalpies = -2309.901652
Sum of electronic and thermal Free Energies = -2309.990483

6.1.1.4 Computed Excitations of S₁ (Emission of S₁) of compound 3a-aa (PBE1PBE/6-31+G** PCM CH₂Cl₂)

Excited State 1: Singlet-A 1.8148 eV 683.18 nm f=0.8789 <S**2>=0.000
112 ->113 0.70340
This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2310.21382814
Copying the excited state density for this state as the 1-particle RhoCl density.

6.1.1.5 Computed xyz-Coordinates of radical cation of compound 3a-aa (uB3LYP/6-311G*)

Figure S34. Optimized ground state geometry of radical cation of 3a-aa (uB3LYP/6-311G* PCM CH₂Cl₂).

C 1.34035  -1.02030  0.33359
C 1.19413   0.34941  0.18266
N 0.00000  1.05432  0.23854
C -1.19412  0.34941  0.18266
C -1.34035 -1.02030  0.33359
S  0.00000 -2.10172  0.79512
C  2.66756 -1.44867  0.17370
C  3.56106 -0.41629 -0.07962
S  2.70366  1.12740 -0.16196
S -2.70366  1.12739 -0.16196
C -3.56106 -0.41629 -0.07962
C -2.66756 -1.44867  0.17370
C  0.00000  2.49773  0.17820
| Element | X  | Y   | Z    |
|---------|----|-----|------|
| C       | 4.96980 | -0.39354  | -0.27236  |
| C       | 5.86558 | -1.43406  | -0.27539  |
| C       | 7.25020 | -1.17203  | -0.49380  |
| C       | 5.48957 | -2.79059  | -0.06711  |
| C       | -4.96980 | -0.39354  | -0.27236  |
| C       | -5.86558 | -1.43406  | -0.27539  |
| C       | -7.25020 | -1.17203  | -0.49380  |
| N       | 8.37073  | -0.94955  | -0.67169  |
| N       | 5.15760  | -3.88478  | 0.10618   |
| N       | -8.37072 | -0.94955  | -0.67169  |
| N       | -5.15760 | -3.88478  | 0.10618   |
| C       | 0.00001  | 3.13850   | -1.06125  |
| C       | 0.00001  | 4.53063   | -1.10826  |
| C       | -0.00000 | 5.26919   | 0.07346   |
| C       | -0.00001 | 4.62050   | 1.30764   |
| C       | -0.00001 | 3.22962   | 1.36496   |
| H       | 2.96716  | -2.48430  | 0.25754   |
| H       | -2.96716 | -2.48430  | 0.25754   |
| H       | 5.40884  | 0.58514   | -0.44507  |
| H       | -5.40884 | 0.58513   | -0.44507  |
| H       | 0.00002  | 2.55137   | -1.97306  |
| H       | 0.00002  | 5.03589   | -2.06772  |
| H       | -0.00000 | 6.35306   | 0.03289   |
| H       | -0.00002 | 5.19637   | 2.22646   |
| H       | -0.00002 | 2.70887   | 2.31602   |

SCF Done: E(UB3LYP) = -2312.01711920 A.U. after 1 cycles
Zero-point correction= 0.251861 (Hartree/Particle)
Thermal correction to Energy= 0.278354
Thermal correction to Enthalpy= 0.279298
Thermal correction to Gibbs Free Energy= 0.190737
Sum of electronic and zero-point Energies= -2311.765258
Sum of electronic and thermal Energies= -2311.738766
Sum of electronic and thermal Enthalpies= -2311.737821
Sum of electronic and thermal Free Energies= -2311.826382
6.1.1.6 Computed xyz-Coordinates of dication (S\textsubscript{0}) of compound 3a-aa (uB3LYP/6-311G*)

Figure S35. Optimized ground state geometry of dication of 3a-aa (uB3LYP/6-311G* PCM CH\textsubscript{2}Cl\textsubscript{2}).

\[
\begin{array}{ccc}
C & -1.33538 & -1.07416 \\
C & -1.18366 & 0.34339 \\
N & 0.00000 & 0.99781 \\
C & 1.18366 & 0.34339 \\
C & 1.33538 & -1.07416 \\
S & 0.00000 & -2.17263 \\
C & -2.67356 & -1.47303 \\
C & -3.55648 & -0.39420 \\
S & -2.70919 & 1.16066 \\
S & 2.70919 & 1.16066 \\
C & 3.55648 & -0.39420 \\
C & 2.67356 & -1.47303 \\
C & 0.00000 & 2.47376 \\
C & -4.98620 & -0.33768 \\
C & -5.86719 & -1.39029 \\
C & -7.26689 & -1.13926 \\
C & -5.45817 & -2.75421 \\
C & 4.98620 & -0.33768 \\
C & 5.86719 & -1.39029 \\
C & 7.26689 & -1.13926 \\
C & 5.45817 & -2.75421 \\
N & -8.40421 & -0.92986 \\
N & -5.07703 & -3.84507 \\
N & 8.40421 & -0.92986 \\
N & 5.07703 & -3.84507 \\
C & 0.00004 & 3.13803 \\
C & 0.00004 & 4.53078 \\
C & -0.00004 & 4.53090 \\
\end{array}
\]
C  -0.00004  3.13815  -1.22602
H   -2.98817   -2.50745  -0.00011
H    2.98817   -2.50745  -0.00016
H    -5.43594   0.65031    0.00006
H     5.43594   0.65031   -0.00005
H     0.00007  2.59065   2.16274
H     0.00007  5.07280   2.15085
H     0.00000  6.30563   0.00029
H   -0.00007  5.07301  -2.15039
H   -0.00007  2.59086  -2.16251

SCF Done: E(UB3LYP) = -2311.62617605 A.U. after 3 cycles
Zero-point correction= 0.252140 (Hartree/Particle)
Thermal correction to Energy= 0.278626
Thermal correction to Enthalpy= 0.279570
Thermal correction to Gibbs Free Energy= 0.191478
Sum of electronic and zero-point Energies= -2311.374036
Sum of electronic and thermal Energies= -2311.347550
Sum of electronic and thermal Enthalpies= -2311.346606
Sum of electronic and thermal Free Energies= -2311.434698

6.1.1.7 Reoptimization of compound 3a-aa (uB3LYP/6-311G*)

Compound 3a-aa in the gas phase (uB3LYP/6-311G*):
SCF Done: E(UB3LYP) = -2312.27309502 A.U. after 1 cycles
Zero-point correction= 0.252016 (Hartree/Particle)
Thermal correction to Energy= 0.278543
Thermal correction to Enthalpy= 0.279487
Thermal correction to Gibbs Free Energy= 0.191034
Sum of electronic and zero-point Energies= -2312.021079
Sum of electronic and thermal Energies= -2311.994552
Sum of electronic and thermal Enthalpies= -2311.993608
Sum of electronic and thermal Free Energies= -2312.082061

Compound 3a-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2312.31485331 A.U. after 14 cycles

Radical cation of compound 3a-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

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Dication of compound 3a-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -2311.87979427 A.U. after 15 cycles

6.1.1.8 Computed xyz-Coordinates of transition state of the acceptor rotation of compound 3a-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S36. Optimized geometry of the transition state of the acceptor rotation of 3a-aa (PBE1PBE/6-31G** PCM CH₂Cl₂).

|    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|
|    |    |    |    |    |    |    |    |
|    |    |    |    |    |    |    |    |
C  -1.19557    -1.22448    -0.94076
C  -1.20283    0.10669    -0.61660
N  -0.08367    0.92431    -0.46540
C   1.14082    0.33005    -0.33887
C   1.43429    -1.00680    -0.61469
S    0.27349    -2.11445    -1.36520
C   -2.49843    -1.78973    -0.94115
C   -3.46986    -0.88099    -0.62290
S   -2.79954     0.69022    -0.29047
S    2.51135    1.18367    0.25179
C    3.51816    -0.24986    0.11744
C    2.76257    -1.32963    -0.34079
C   -0.24110    2.33369    -0.24017
C   -4.92102    -1.08801    -0.60076
C   -5.60123    -1.42842    0.51504
C   -7.02057    -1.62712    0.49008
C   -4.94891    -1.61457    1.77839
C    4.87821    -0.13613    0.46567

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| Element | x     | y     | z     | Coordinates |
|---------|-------|-------|-------|-------------|
| C       | 5.86067 | -1.10783 | 0.47815 |
| C       | 7.18430 | -0.76673 | 0.87074 |
| C       | 5.63953 | -2.46321 | 0.11749 |
| N       | -8.16940 | -1.78866 | 0.47390 |
| N       | -4.44322 | -1.76890 | 2.81119 |
| N       | 8.26814  | -0.48894 | 1.19206 |
| N       | 5.45420  | -3.57372 | -0.17985 |
| C       | -0.43283 | 2.80591  | 1.05843 |
| C       | -0.58825 | 4.17397  | 1.26366 |
| C       | -0.55155 | 5.05060  | 0.18185 |
| C       | -0.35904 | 4.56723  | -1.11122 |
| C       | -0.20244 | 3.2024   | -1.32924 |
| H       | -2.70800 | -2.82536 | -1.18153 |
| H       | 3.17644  | -2.31855 | -0.49480 |
| H       | -5.48550 | -0.96449 | -1.52375 |
| H       | 5.21346  | 0.85164  | 0.77362 |
| H       | -0.45882 | 2.10819  | 1.88995 |
| H       | -0.73826 | 4.55258  | 2.26957 |
| H       | -0.67354 | 6.11665  | 0.34688 |
| H       | -0.33076 | 5.25283  | -1.95204 |
| H       | -0.05189 | 2.80456  | -2.32778 |

SCF Done: $E_{\text{RPBE1PBE}} = -2310.23053850$ A.U. after 1 cycles

Zero-point correction= 0.254929 (Hartree/Particle)
Thermal correction to Energy= 0.280670
Thermal correction to Enthalpy= 0.281614
Thermal correction to Gibbs Free Energy= 0.194935

Sum of electronic and zero-point Energies= -2309.975609
Sum of electronic and thermal Energies= -2309.949869
Sum of electronic and thermal Enthalpies= -2309.948925
Sum of electronic and thermal Free Energies= -2310.035603
6.1.2 Compound 3b-ss

6.1.2.1 Computed xyz-Coordinates of compound 3b-ss (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S37. Optimized ground state geometry of 3b-ss (PBE1PBE/6-31G** PCM CH₂Cl₂).

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -1.30194  | -1.21188  | 0.41265   |
| C    | -1.20126  | 0.16696   | 0.29710   |
| N    | -0.00012  | 0.86287   | 0.43219   |
| C    | 1.20114   | 0.16674   | 0.29739   |
| C    | 1.30166   | -1.21207  | 0.41309   |
| S    | -0.00029  | -2.30292  | 0.84477   |
| S    | -2.89807  | -1.79507  | 0.16634   |
| C    | -3.48944  | -0.17056  | -0.05826  |
| C    | -2.45294  | 0.74984   | 0.03050   |
| C    | 2.45280   | 0.74956   | 0.03073   |
| C    | 3.48931   | -0.17084  | -0.05779  |
| S    | 2.89780   | -1.79540  | 0.16707   |
| C    | -4.83456  | 0.19617   | -0.31180  |
| C    | -5.95727  | -0.58327  | -0.43773  |
| C    | -7.21887  | 0.02526   | -0.69871  |
| C    | -5.94986  | -2.00143  | -0.32290  |
| C    | 0.00014   | 2.29042   | 0.30989   |
| C    | 4.83441   | 0.19579   | -0.31151  |
| C    | 5.95706   | -0.58371  | -0.43773  |
| C    | 7.21860   | 0.02475   | -0.69917  |
C          5.94960   -2.00186   -0.32292
C          0.00038    2.88755   -0.95159
C          0.00079    4.27588   -1.05230
C          0.00099    5.05953     0.10021
C          0.00078    4.45746     1.35645
C          0.00037    3.06928     1.46499
N          -5.94341   -3.16119   -0.22981
N          -8.24964    0.51956   -0.91188
N          5.94317   -3.16162   -0.22972
N          8.24920    0.51924   -0.91275
H          -2.60977    1.81523   -0.08796
H          2.60954    1.81493   -0.08805
H          -4.98817    1.26670   -0.42483
H          4.98805    1.26631   -0.42454
H          0.00024    2.26465   -1.84144
H          0.00097    4.74476   -2.03139
H          0.00132    6.14219     0.01842
H          0.00094    5.06781     2.25415
H          0.00021    2.58215     2.43511

SCF Done:  E(RPBE1PBE) = -2310.24468646     A.U. after 1 cycles
Zero-point correction= 0.255568 (Hartree/Particle)
Thermal correction to Energy= 0.281827
Thermal correction to Enthalpy= 0.282772
Thermal correction to Gibbs Free Energy= 0.194805
Sum of electronic and zero-point Energies= -2309.989118
Sum of electronic and thermal Energies= -2309.962859
Sum of electronic and thermal Enthalpies= -2309.961915
Sum of electronic and thermal Free Energies= -2310.049882
6.1.2.2 Computed Excitations of compound 3b-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$)

Excited State 1: Singlet-A 1.9490 eV 636.14 nm f=0.4468 <S**2>=0.000
   112 -> 113 0.70383

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2310.17306121

Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2: Singlet-A 2.3499 eV 527.60 nm f=0.0200 <S**2>=0.000
   112 -> 114 0.69862

Excited State 3: Singlet-A 3.5472 eV 349.53 nm f=0.5038 <S**2>=0.000
   110 -> 113 0.69321

Excited State 4: Singlet-A 3.6622 eV 338.55 nm f=0.0102 <S**2>=0.000
   110 -> 114 -0.26343
   111 -> 113 0.64776

Excited State 5: Singlet-A 3.7851 eV 327.56 nm f=0.9112 <S**2>=0.000
   111 -> 114 0.68041
   112 -> 115 -0.14553

Excited State 6: Singlet-A 3.8547 eV 321.65 nm f=0.0571 <S**2>=0.000
   110 -> 114 0.64470
   111 -> 113
6.1.2.3 Computed xyz-Coordinates of $S_1$ of compound 3b-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$)

Figure S38. Optimized $S_1$ geometry of 3b-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$).

|   |      |      |      |      |
|---|------|------|------|------|
| C | -1.30459 | -1.27774 | 0.00044 |
| C | -1.20478 | 0.12726 | 0.00020 |
| N | -0.00000 | 0.79976 | 0.00012 |
| C | 1.20478 | 0.12726 | 0.00021 |
| C | 1.30459 | -1.27774 | 0.00047 |
| C | 0.00000 | -2.38202 | 0.00073 |
| S | -2.95437 | -1.81226 | 0.00023 |
| C | -3.52295 | -0.14195 | 0.00004 |
| C | -2.45911 | 0.75349 | -0.00001 |
| C | 2.45911 | 0.75349 | -0.00002 |
| C | 3.52295 | -0.14195 | 0.00004 |
| S | 2.95437 | -1.81226 | 0.00026 |
| C | -4.87652 | 0.25291 | -0.00013 |
| C | -6.02458 | -0.52216 | -0.00034 |
| C | -7.29853 | 0.10764 | -0.00053 |
| C | -6.03353 | -1.94134 | -0.00043 |
| C | -0.00000 | 2.23805 | 0.00015 |
| C | 4.87652 | 0.25291 | -0.00014 |
| C | 6.02458 | -0.52216 | -0.00036 |
| C | 7.29853 | 0.10764 | -0.00057 |
| C | 6.03353 | -1.94134 | -0.00044 |
| C | -0.00009 | 2.91639 | -1.21566 |
| C | -0.00009 | 4.30841 | -1.20845 |
C  -0.0000  5.00154  0.00014
C   0.0009  4.30840  1.20874
C   0.0009  2.91639  1.21598
N   -6.0602  -3.10687 -0.00049
N   -8.3418  0.62545  -0.00070
N    6.0602  -3.10687 -0.00049
N    8.3418  0.62545  -0.00074
H   -2.5984  1.82690  -0.00004
H    2.5984  1.82690  -0.00006
H   -5.0306  1.32870  -0.00012
H    5.0306  1.32870  -0.00014
H   -0.0016  2.35842  -2.14666
H   -0.0016  4.84943  -2.14916
H    0.0000  6.08702   0.00017
H    0.0016  4.84945   2.14944
H    0.0016  2.35844   2.14699

Excited State 1:  Singlet-A  1.5546 eV  797.55 nm  f=0.5973  <S**2>=0.000
               112 ->113  -0.70526

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2310.18317739

SCF Done:  E(RPBE1PBE) = -2310.24030626  A.U. after 7 cycles

Zero-point correction= 0.253969 (Hartree/Particle)
Thermal correction to Energy= 0.280413
Thermal correction to Enthalpy= 0.281357
Thermal correction to Gibbs Free Energy= 0.193423
Sum of electronic and zero-point Energies= -2309.929208
Sum of electronic and thermal Energies= -2309.902765
Sum of electronic and thermal Enthalpies= -2309.901820
Sum of electronic and thermal Free Energies= -2309.989755
6.1.2.4 Computed Excitations of S₁ (Emission of S₁) of compound 3b-ss (PBE1PBE/6-31G** PCM CH₂Cl₂)

Excited State 1:  Singlet-A  1.6233 eV  763.79 nm  f=0.4802  <S**2>=0.000

112 ->113  0.70440

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2310.18065176

Copying the excited state density for this state as the 1-particle RhoCl density.

6.1.2.5 Computed xyz-Coordinates of radical cation of compound 3b-ss (uB3LYP/6-311G*)

Figure S39. Optimized ground state geometry of radical cation of 3b-ss (uB3LYP/6-311G* PCM CH₂Cl₂).

| Atom | X    | Y    | Z    | 1            |
|------|------|------|------|--------------|
| C    | -1.30911 | -1.22181 | 0.42190 |
| C    | -1.21046 | 0.15408 | 0.29478 |
| N    | 0.00000  | 0.85588 | 0.43328 |
| C    | 1.21047  | 0.15409 | 0.29478 |
| C    | 1.30911  | -1.22180 | 0.42189 |
| S    | 0.00000  | -2.30936 | 0.89106 |
| S    | -2.91212 | -1.81600 | 0.16641 |
| C    | -3.50547 | -0.17987 | -0.07541 |
| C    | -2.46446 | 0.73453  | 0.01195 |
| C    | 2.46446  | 0.73453  | 0.01195 |
| C    | 3.50547  | -0.17987 | -0.07541 |
| S    | 2.91213  | -1.81599 | 0.16640 |
| C    | -4.85495 | 0.18909  | -0.33774 |
| C    | -5.98361 | -0.57734 | -0.45824 |
| C    | -7.23738 | 0.04754  | -0.72919 |
| C    | -5.98480 | -1.99532 | -0.32638 |
| C    | -0.00000 | 2.29103  | 0.32266 |
| C    | 4.85496  | 0.18910  | -0.33774 |
C  5.98362  -0.57733  -0.45824
C  7.23738   0.04755  -0.72918
C  5.98481  -1.99531  -0.32637
C  0.00003  2.90513  -0.93200
C  0.00003  4.29543  -1.02145
C -0.00002  5.07003   0.13801
C -0.00006  4.45473   1.38836
C -0.00005  3.06421  1.48289
N -5.97382  -3.14665  -0.21797
N -8.24874   0.56218  -0.94891
N  5.97383  -3.14664  -0.21796
N  8.24875   0.56219  -0.94889
H -2.61793   1.79811  -0.11373
H  2.61794   1.79811  -0.11372
H -5.00149  1.25852  -0.46213
H  5.00150  1.25852  -0.46213
H  0.00007  2.93967  -1.82845
H  0.00005  4.77264  -1.99562
H -0.00003  6.15242   0.06620
H -0.00010  5.05575   2.29129
H -0.00008  2.57080   2.44859

SCF Done:  E(UB3LYP) =  -2312.0138740  A.U. after  1 cycles
Zero-point correction=  0.252247  (Hartree/Particle)
Thermal correction to Energy=   0.278640
Thermal correction to Enthalpy=   0.279584
Thermal correction to Gibbs Free Energy=   0.191603
Sum of electronic and zero-point Energies=  -2311.761627
Sum of electronic and thermal Energies=  -2311.735234
Sum of electronic and thermal Enthalpies=  -2311.734290
Sum of electronic and thermal Free Energies=  -2311.822271
6.1.2.6 Computed xyz-Coordinates of dication (S$_0$) of compound 3b-ss (uB3LYP/6-311G*)

![Optimized ground state geometry of dication of 3b-ss](image)

**Figure S40.** Optimized ground state geometry of dication of 3b-ss (uB3LYP/6-311G* PCM CH$_2$Cl$_2$).

|   |   |   |
|---|---|---|
| C | 1.31118 | -1.26659 | -0.00004 |
| C | 1.20540 | 0.16045 | 0.00002 |
| N | 0.00000 | 0.81110 | 0.00004 |
| C | -1.20540 | 0.16045 | 0.00002 |
| C | -1.31118 | -1.26659 | -0.00003 |
| S | -0.00000 | -2.34595 | -0.00008 |
| S | 2.94495 | -1.82085 | -0.00006 |
| C | 3.51814 | -0.13714 | -0.00000 |
| C | 2.47319 | 0.77014 | 0.00004 |
| C | -2.47319 | 0.77014 | 0.00004 |
| C | -3.51814 | -0.13714 | 0.00001 |
| S | -2.94495 | -1.82085 | -0.00005 |
| C | 4.89642 | 0.25084 | 0.00001 |
| C | 6.01234 | -0.54113 | -0.00003 |
| C | 7.30662 | 0.04927 | -0.00003 |
| C | 5.94635 | -1.96474 | -0.00011 |
| C | 0.00000 | 2.28039 | 0.00010 |
| C | -4.89642 | 0.25084 | 0.00002 |
| C | -6.01234 | -0.54113 | -0.00001 |
| C | -7.30662 | 0.04928 | -0.00001 |
| C | -5.94635 | -1.96474 | -0.00009 |
| C | 0.00000 | 2.94861 | 1.22265 |
| C | 0.00000 | 4.34261 | 1.21107 |
| C | 0.00000 | 5.03530 | 0.00019 |
C  -0.00000   4.34270   -1.21074
C  -0.00000   2.94870   -1.22241
N   5.84474  -3.11632   -0.00016
N   8.35558   0.53511   -0.00004
N  -5.84474  -3.11632   -0.00014
N  -8.35558   0.53511   -0.00001
H   2.62434   1.84040   0.00007
H  -2.62434   1.84040   0.00008
H   5.06342   1.32356   0.00005
H  -5.06342   1.32356   0.00006
H   0.00001   2.40191   2.15959
H   0.00001   4.88373   2.15021
H   0.00000   6.11918   0.00023
H  -0.00001   4.88388  -2.14983
H  -0.00001   2.40206  -2.15939
SCF Done:  E(UB3LYP) = -2311.61890387 A.U. after 1 cycles
Zero-point correction= 0.252047 (Hartree/Particle)
Thermal correction to Energy= 0.278433
Thermal correction to Enthalpy= 0.279377
Thermal correction to Gibbs Free Energy= 0.191772
Sum of electronic and zero-point Energies= -2311.366857
Sum of electronic and thermal Energies= -2311.340471
Sum of electronic and thermal Enthalpies= -2311.339527
Sum of electronic and thermal Free Energies= -2311.427131

6.1.2.7 Reoptimization of compound 3b-ss (uB3LYP/6-311G*)
Compound 3b-ss in the gas phase (uB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -2312.26932403 A.U. after 1 cycles
Zero-point correction= 0.251865 (Hartree/Particle)
Thermal correction to Energy= 0.278348
Thermal correction to Enthalpy= 0.279293
Thermal correction to Gibbs Free Energy= 0.190961
Sum of electronic and zero-point Energies= -2312.017459
Sum of electronic and thermal Energies= -2311.990976
Sum of electronic and thermal Enthalpies= -2311.990031
Sum of electronic and thermal Free Energies= -2312.078363

Compound 3b-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2312.30962381 A.U. after 15 cycles

Radical cation of compound 3b-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2312.11729747 A.U. after 22 cycles

Dication of compound 3b-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2311.87603765 A.U. after 16 cycles

6.1.2.8 Computed xyz-Coordinates of transition state of the acceptor rotation of compound 3b-ss (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S41. Optimized geometry of the transition state of the acceptor rotation of 3b-ss (PBE1PBE/6-31G** PCM CH₂Cl₂).

|   |    |     |    |
|---|----|-----|----|
| C | 1.34110 | -1.20093 | -0.73430 |
| C | 1.10657 | 0.15166 | -0.52093 |
| N | -0.12620 | 0.75778 | -0.77512 |
| C | -1.26880 | -0.05132 | -0.77027 |
| C | -1.22910 | -1.40403 | -1.00569 |
| S | 0.20726 | -2.31386 | -1.47048 |
| S | 2.93109 | -1.68348 | -0.30254 |
C 3.34679 -0.04521  0.12919
C 2.25396  0.79936 -0.03116
C -2.58877  0.40283 -0.48301
C -3.50806 -0.61026 -0.49207
S -2.77787 -2.14424 -0.83425
C 4.60907  0.39508  0.59432
C 5.76987 -0.30707  0.81178
C 6.92910  0.36775  1.29110
C 5.90140 -1.70512  0.58459
C -0.26228  2.16878 -0.56903
C -4.95696 -0.49830 -0.29710
C -5.5535  -0.63991  0.90491
C -6.97622 -0.51601  1.04683
C -4.81170 -0.91255  2.10025
C -0.43905  2.68199  0.71717
C -0.56979  4.05632  0.89588
C -0.52290  4.91119 -0.20382
C -0.34487  4.39397 -1.48491
C -0.21361  3.02015 -1.67064
N  6.01098 -2.84886  0.40009
N  7.87701  0.91651  1.68235
N -4.23079 -1.13148  3.08045
N -8.12595 -0.41568  1.16606
H  2.30042  1.85851  0.19241
H -2.84230  1.43591 -0.28128
H  4.65488  1.45926  0.81346
H -5.58773 -0.29041 -1.15976
H -0.47456  2.00475  1.56573
H -0.70861  4.45875  1.89459
H -0.62513  5.98270 -0.06123
H -0.30799  5.05938 -2.34189
H  -0.07426  2.59827  -2.66112

SCF Done:  \( E(\text{RPBE1PBE}) = -2310.22667657 \) A.U. after 1 cycles

Zero-point correction= 0.254974 (Hartree/Particle)

Thermal correction to Energy= 0.280641

Thermal correction to Enthalpy= 0.281585

Thermal correction to Gibbs Free Energy= 0.195012

Sum of electronic and zero-point Energies= -2309.971703

Sum of electronic and thermal Energies= -2309.946036

Sum of electronic and thermal Enthalpies= -2309.945092

Sum of electronic and thermal Free Energies= -2310.031664

6.1.3 Compound 6

6.1.3.1 Computed xyz-Coordinates of compound 6 (PBE1PBE/6-31G** PCM CH\(_2\)Cl\(_2\))

![Optimized ground state geometry of 6 (PBE1PBE/6-31G** PCM CH\(_2\)Cl\(_2\)).](image)

Figure S42. Optimized ground state geometry of 6 (PBE1PBE/6-31G** PCM CH\(_2\)Cl\(_2\)).

C  1.34435  -1.06771  0.58936
C  1.22712   0.30526  0.29163
N  0.00001   0.96701  0.37188
C  -1.22701   0.30515  0.29134
C  -1.34420  -1.06783  0.58904
S  0.00002  -1.95122  1.31473
C  2.55606  -1.71492  0.43546
C  3.71989  -1.02665  0.03847
C  3.60526   0.35282 -0.21075
C  2.38885  0.99607  -0.09531
C  -2.38870  0.99587  -0.09591
C  -3.60505  0.35253  -0.21157
C  -3.71964  -1.02695  0.03767
C  -2.55582  -1.71514  0.43484
C  4.92699  -1.79983  -0.07054
C  6.19444  -1.44187  -0.44315
C  7.22227  -2.43319  -0.46483
C  6.60753  -0.13297  -0.82857
C  -4.92665  -1.80022  -0.07161
C  -6.19433  -1.44208  -0.44327
C  -7.22196  -2.43360  -0.46562
C  -6.60788  -0.13281  -0.82691
C  -0.00007  2.40376  0.27530
C  -0.00034  3.15037  1.44985
C  -0.00046  4.54094  1.37569
C  -0.00032  5.17452  0.13551
C  -0.00005  4.41972  -1.03616
C  0.00007  3.02954  -0.97116
N  8.06133  -3.23757  -0.48339
N  6.97203  0.92415  -1.14768
N  -8.06087  -3.23813  -0.48475
N  -6.97285  0.92460  -1.14451
H  2.61219  -2.77815  0.65255
H  4.46655  0.93779  -0.50834
H  2.33291  2.05604  -0.30819
H  -2.33277  2.05581  -0.30888
H  -4.46629  0.93741  -0.50945
H  -2.61190  -2.77839  0.65185
H  4.81686  -2.85172  0.18279
H  -4.81624  -2.85233  0.18066

S50
6.1.3.2 Computed Excitations of compound 6 (PBE1PBE/6-31G** PCM CH2Cl2)

Excited State  1:  Singlet-A  2.3171 eV  535.09 nm  f=0.6349  <S**2>=0.000
110 ->111  0.70086

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1668.77535535

Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State  2:  Singlet-A  2.9458 eV  420.89 nm  f=0.0706  <S**2>=0.000
110 ->112  0.69417

Excited State  3:  Singlet-A  3.4187 eV  362.66 nm  f=0.7812  <S**2>=0.000
109 ->111  0.68747
110 ->113  -0.10821

Excited State  4:  Singlet-A  3.9214 eV  316.17 nm  f=0.0001  <S**2>=0.000
105 ->111  -0.14632
108 ->111  -0.33620
109 ->112  0.57254
110 ->114  -0.15126
Excited State 5: Singlet-A 3.9694 eV 312.35 nm f=0.1125 <S**2>=0.000
106 ->111 0.17976
108 ->111 0.59325
109 ->112 0.26083
110 ->112 -0.10455
110 ->114 -0.14412

Excited State 6: Singlet-A 4.0241 eV 308.11 nm f=0.7064 <S**2>=0.000
108 ->112 0.12274
110 ->113 0.65752
110 ->116 -0.13343

6.1.3.3 Computed xyz-Coordinates of \( S_1 \) of compound 6 (PBE1PBE/6-31G** PCM CH\(_2\)Cl\(_2\))

\[
\begin{array}{ccc}
C & 1.35341 & -1.18297 & 0.00008 \\
C & 1.22552 & 0.23836 & -0.00005 \\
N & 0.00000 & 0.86876 & -0.00007 \\
C & -1.22551 & 0.23836 & -0.00005 \\
C & -1.35341 & -1.18297 & 0.00008 \\
S & -0.00000 & -2.25870 & 0.00010 \\
C & 2.60542 & -1.78663 & 0.00015 \\
C & 3.79182 & -1.03831 & 0.00005 \\
C & 3.65634 & 0.38328 & -0.00009 \\
C & 2.42707 & 0.98748 & -0.00014 \\
C & -2.42706 & 0.98748 & -0.00013 \\
C & -3.65633 & 0.38328 & -0.00009 \\
C & -3.79182 & -1.03831 & 0.00005 \\
C & -2.60542 & -1.78663 & 0.00015 \\
\end{array}
\]

*Figure S43.* Optimized \( S_1 \) geometry of 6 (PBE1PBE/6-31G** PCM CH\(_2\)Cl\(_2\)).
|   |   |    |    |    |
|---|---|----|----|----|
| C | 5.02119 | -1.76167 | 0.00008 |
| C | 6.33102 | -1.30803 | -0.00004 |
| C | 7.39124 | -2.25654 | -0.00003 |
| C | 6.74426 | 0.05025 | -0.00017 |
| C | -5.02119 | -1.76166 | 0.00008 |
| C | -6.33102 | -1.30803 | -0.00004 |
| C | -7.39124 | -2.25654 | -0.00003 |
| C | -6.74426 | 0.05025 | -0.00017 |
| C | 0.00000 | 2.31424 | 0.00001 |
| C | 0.00000 | 2.99143 | 1.21527 |
| C | 0.00000 | 4.38343 | 1.20835 |
| C | -0.00000 | 5.07730 | 0.00023 |
| C | -0.00000 | 4.38361 | -1.20801 |
| C | -0.00000 | 2.99162 | -1.21514 |
| N | 8.25839 | -3.03462 | -0.00005 |
| N | 7.11530 | 1.15551 | -0.00028 |
| N | -8.25838 | -3.03462 | -0.00005 |
| N | -7.11532 | 1.15551 | -0.00028 |
| H | 2.66189 | -2.87210 | 0.00031 |
| H | 4.53600 | 1.01424 | -0.00016 |
| H | 2.37362 | 2.06866 | -0.00024 |
| H | -2.37361 | 2.06866 | -0.00023 |
| H | -4.53599 | 1.01424 | -0.00015 |
| H | -2.66189 | -2.87210 | 0.00030 |
| H | 4.92029 | -2.84354 | 0.00018 |
| H | -4.92029 | -2.84353 | 0.00018 |
| H | 0.00000 | 2.43371 | 2.14640 |
| H | 0.00000 | 4.92386 | 2.14940 |
| H | -0.00000 | 6.16272 | 0.00030 |
| H | -0.00000 | 4.92421 | -2.14896 |
| H | -0.00000 | 2.43402 | -2.14635 |

S53
Excited State 1: Singlet-A 1.8263 eV  678.88 nm f=0.6197  <S**2>=0.000
110 -> 111 -0.70375

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1668.78756592
SCF Done: E(RPBE1PBE) = -1668.85468164   A.U. after 7 cycles
Zero-point correction= 0.320970 (Hartree/Particle)
Thermal correction to Energy= 0.347895
Thermal correction to Enthalpy= 0.348839
Thermal correction to Gibbs Free Energy= 0.259869
Sum of electronic and zero-point Energies= -1668.466595
Sum of electronic and thermal Energies= -1668.439671
Sum of electronic and thermal Enthalpies= -1668.438727
Sum of electronic and thermal Free Energies= -1668.527697

6.1.3.4 Computed Excitations of S_1 (Emission of S_1) of compound 6 (PBE1PBE/6-31G**) PCM CH\textsubscript{2}Cl\textsubscript{2})

Excited State 1: Singlet-A 1.8815 eV  658.97 nm f=0.4870  <S**2>=0.000
110 -> 111  0.70200

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1668.78553875
Copying the excited state density for this state as the 1-particle RhoCl density.

6.1.3.5 Computed xyz-Coordinates of radical cation of compound 6 (uB3LYP/6-311G*)

Figure S44. Optimized ground state geometry of radical cation of 6 (uB3LYP/6-311G* PCM CH\textsubscript{2}Cl\textsubscript{2}).

- C 1.36277  -1.19406  -0.00008
- C 1.23436  0.22061  -0.00017
- N -0.00003  0.86200  -0.00016
C  -1.23439   0.22056  -0.00017
C  -1.36274   -1.19412  -0.00009
S    0.00004   -2.28487  -0.00016
C    2.62476   -1.78860  -0.00001
C    3.80022   -1.03199  -0.00006
C    3.66452    0.38062  -0.00021
C    2.42819    0.98005  -0.00026
C   -2.42826    0.97995  -0.00026
C   -3.66455    0.38048  -0.00022
C   -3.80019   -1.03214  -0.00006
C   -2.62471   -1.78871  -0.00002
C    5.05727   -1.76048  0.00005
C    6.34315   -1.31140  0.00011
C    7.41399   -2.25929  0.00018
C    6.73175    0.06287  0.00008
C   -5.05723   -1.76064  0.00004
C   -6.34308   -1.31148  0.00010
C   -7.41399   -2.25929  0.00018
C   -6.73155    0.06283  0.00009
C   -0.00007    2.32436  -0.00003
C   -0.00009    3.00159  1.21633
C   -0.00013    4.39510  1.20929
C   -0.00014    5.08951  0.00026
C   -0.00012    4.39536  -1.20892
C   -0.00009    3.00185  -1.21624
N    8.27334   -3.03054  0.00026
N    7.04193    1.17536  0.00005
N   -8.27340   -3.03047  0.00025
N   -7.04149    1.17539  0.00007
H    2.68882   -2.87200  0.00009
H    4.53625    1.01881  -0.00030
H          2.37233        2.05842        -0.00035
H          -2.37244       2.05833        -0.00036
H          -4.53633       1.01861        -0.00032
H          -2.68873       -2.87211       0.00009
H           4.95537       -2.84123        0.00010
H          -4.95537       -2.84139       0.00009
H          -0.00008       2.45119       2.15091
H          -0.00015       4.93518       2.14910
H          -0.00017       6.17353        0.00037
H          -0.00013       4.93563       -2.14862
H          -0.00007       2.45163       -2.15093

SCF Done:  E(UB3LYP) = -1670.48252963  A.U. after  1 cycles
Zero-point correction= 0.319252 (Hartree/Particle)
Thermal correction to Energy= 0.346172
Thermal correction to Enthalpy= 0.347117
Thermal correction to Gibbs Free Energy= 0.257395
Sum of electronic and zero-point Energies= -1670.163277
Sum of electronic and thermal Energies= -1670.136357
Sum of electronic and thermal Enthalpies= -1670.135413
Sum of electronic and thermal Free Energies= -1670.225134

6.1.3.6 Reoptimization of compound 6 (uB3LYP/6-311G*)

Compound 4 in the gas phase (uB3LYP/6-311G*):

SCF Done:  E(UB3LYP) = -1670.74815348  A.U. after  1 cycles
Zero-point correction= 0.319327 (Hartree/Particle)
Thermal correction to Energy= 0.346086
Thermal correction to Enthalpy= 0.347030
Thermal correction to Gibbs Free Energy= 0.258537
Sum of electronic and zero-point Energies= -1670.428826
Sum of electronic and thermal Energies= -1670.402068
Sum of electronic and thermal Enthalpies= -1670.401124
Sum of electronic and thermal Free Energies= -1670.489617
Compound 6 in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done:  E(UB3LYP) = -1670.79174203   A.U. after 14 cycles

Radical cation of compound 6 in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done:  E(UB3LYP) = -1670.59154871   A.U. after 20 cycles

6.1.4 Compound 3c-aa

6.1.4.1 Computed xyz-Coordinates of compound 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S45. Optimized ground state geometry of 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂).

|   | x            | y            | z            |
|---|--------------|--------------|--------------|
| C | 1.32379      | -1.16032     | 0.84709      |
| C | 1.18286      | 0.16631      | 0.51325      |
| N | -0.00007     | 0.89044      | 0.55092      |
| C | -1.18305     | 0.16636      | 0.51276      |
| C | -1.32398     | -1.16028     | 0.84662      |
| S | -0.00023     | -2.10214     | 1.55942      |
| S | -2.66339     | 0.83605      | -0.08458     |
| C | -3.50243     | -0.67874     | 0.15867      |
| C | -2.63770     | -1.63793     | 0.63223      |
| C | 2.63742      | -1.63808     | 0.63239      |
| C | 3.50210      | -0.67899     | 0.15852      |
| S | 2.66314      | 0.83585      | -0.08471     |
| C | -4.92619     | -0.79895     | -0.11799     |
| C | 4.92585      | -0.79929     | -0.11821     |
| C | 0.00028      | 2.30459      | 0.31856      |
C   5.75109  0.33269   -0.23949
C   7.10429  0.20849   -0.50128
C   7.67521 -1.06363   -0.64329
C   6.86608 -2.20358   -0.52525
C   5.51302 -2.06885   -0.27369
C   0.00413  3.17280    1.40887
C   0.00468  4.54606    1.18607
C   0.00128  4.16964   -1.20124
C   0.00292  2.79359   -0.98856
C  -5.51341 -2.06847   -0.27363
C  -6.86650 -2.20312   -0.52508
C  -7.67560 -1.06313   -0.64286
C  -7.10464  0.20895   -0.50070
C  -5.75141  0.33307   -0.23900
C   9.07062 -1.19833   -0.91024
C  -9.07104 -1.19775   -0.90970
N   10.20777 -1.30816   -1.12743
N  -10.20822 -1.30752   -1.12681
H  -2.94179 -2.65089    0.86959
H   2.94152 -2.65101    0.86983
H   5.33278  1.32679   -0.11062
H   7.72600  1.09314   -0.58837
H   7.30223 -3.18989   -0.64315
H   4.89847 -2.96065   -0.21389
H   0.00659  2.76531    2.41484
H   0.00766  5.22829    2.03035
H   0.00165  6.11535   -0.28553
H  -0.00504  4.55722   -2.21507
H  -0.00557  2.09958   -1.82381
H  -4.89887 -2.96030   -0.21404

S58
6.1.4.2 Computed Excitations of compound 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Excited State 1:  Singlet-A  2.4700 eV  501.97 nm  f=0.8492  <S**2>=0.000

Excited State 2:  Singlet-A  2.9356 eV  422.35 nm  f=0.0386  <S**2>=0.000

Excited State 3:  Singlet-A  3.5783 eV  346.49 nm  f=0.0108  <S**2>=0.000

Excited State 4:  Singlet-A  3.7554 eV  330.15 nm  f=0.1396  <S**2>=0.000

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2432.85187213

Copying the excited state density for this state as the 1-particle RhoCl density.
126 ->133  -0.43062
126 ->136  -0.18227

Excited State  5: Singlet-A  3.8315 eV  323.59 nm  f=0.0004  <S**2>=0.000
126 ->130  0.58277
126 ->132  0.36341
126 ->133  0.11394

Excited State  6: Singlet-A  3.9123 eV  316.91 nm  f=0.0020  <S**2>=0.000
126 ->131  0.66413
126 ->134  0.13740
126 ->135  0.14445

Excited State  7: Singlet-A  4.0019 eV  309.81 nm  f=0.0020  <S**2>=0.000
126 ->130  -0.30615
126 ->132  0.38578
126 ->133  0.47525
126 ->136  0.10268

Excited State  8: Singlet-A  4.0408 eV  306.83 nm  f=0.0626  <S**2>=0.000
125 ->127  0.69692

Excited State  9: Singlet-A  4.1488 eV  298.84 nm  f=0.9124  <S**2>=0.000
124 ->127  0.64158
125 ->128  0.26370

Excited State 10: Singlet-A  4.2850 eV  289.34 nm  f=0.2203  <S**2>=0.000
124 ->127  -0.26410
125 ->128  0.64170
6.1.4.3 Computed xyz-Coordinates of $S_1$ of compound 3c-aa (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$)

Figure S46. Optimized $S_1$ geometry of 3c-aa (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$).

|     |     |     |     |
|-----|-----|-----|-----|
| C   | 1.18487 | 0.03778 | -0.00013 |
| C   | 1.33244 | -1.35801 | -0.00014 |
| S   | 0.00000 | -2.47476 | -0.00035 |
| C   | -1.33244 | -1.35801 | -0.00013 |
| C   | -1.18487 | 0.03778 | -0.00011 |
| N   | -0.00000 | 0.71205 | -0.00009 |
| C   | -2.67413 | -1.76363 | -0.00008 |
| C   | -3.57464 | -0.70898 | -0.00001 |
| S   | -2.72752 | 0.84641 | -0.00002 |
| S   | 2.72752 | 0.84641 | -0.00002 |
| C   | 3.57464 | -0.70898 | -0.00002 |
| C   | 2.67413 | -1.76363 | -0.00009 |
| C   | 5.01064 | -0.75340 | 0.00002 |
| C   | -5.01064 | -0.75340 | 0.00002 |
| C   | -0.00000 | 2.15326 | -0.00003 |
| C   | 5.70148 | -1.99080 | 0.00019 |
| C   | 7.07807 | -2.04205 | 0.00023 |
| C   | 7.83647 | -0.85297 | 0.00011 |
| C   | 7.16728 | 0.38477 | -0.00005 |
| C   | 5.78857 | 0.42963 | -0.00010 |
| C   | -5.78857 | 0.42963 | -0.00011 |
| C   | -7.16728 | 0.38476 | -0.00007 |
| C   | -7.83647 | -0.85297 | 0.00010 |
|  |  |  |  |
|---|---|---|---|
| C  | -7.07807 | -2.04205 | 0.00023 |
| C  | -5.70148 | -1.99080 | 0.00020 |
| C  | 0.00006 | 2.82952 | -1.21735 |
| C  | 0.00006 | 4.22090 | -1.20908 |
| C  | -0.00000 | 4.91304 | 0.00100 |
| C  | -0.00006 | 4.22078 | 1.20922 |
| C  | -0.00006 | 2.82940 | 1.21735 |
| C  | 9.25614 | -0.90366 | 0.00016 |
| C  | -9.25614 | -0.90366 | 0.00015 |
| N  | 10.42099 | -0.94579 | 0.00022 |
| N  | -10.42099 | -0.94579 | 0.00020 |
| H  | -2.97390 | -2.80419 | -0.00008 |
| H  | 2.97390 | -2.80419 | -0.00008 |
| H  | 5.14712 | -2.92319 | 0.00033 |
| H  | 7.58471 | -3.00169 | 0.00037 |
| H  | 7.74037 | 1.30620 | -0.00015 |
| H  | 5.30262 | 1.40157 | -0.00025 |
| H  | -5.30262 | 1.40157 | -0.00028 |
| H  | -7.74037 | 1.30620 | -0.00018 |
| H  | -7.58471 | -3.00169 | 0.00038 |
| H  | -5.14712 | -2.92319 | 0.00035 |
| H  | 0.00010 | 2.27081 | -2.14774 |
| H  | 0.00010 | 4.76249 | -2.14938 |
| H  | -0.00000 | 5.99854 | 0.00015 |
| H  | -0.00010 | 4.76228 | 2.14957 |
| H  | -0.00010 | 2.27060 | 2.14768 |

**Excited State 1:** Singlet-A 1.8876 eV 656.82 nm f=1.0361 \(<S^{**2}>=0.000\)

126 ->127 0.70022

This state for optimization and/or second-order correction.

Total Energy, \(E(TD-HF/TD-KS) = -2432.86685164\)

SCF Done: \(E(RPBE1PBE) = -2432.93622076\) A.U. after 6 cycles
Zero-point correction= 0.350865 (Hartree/Particle)
Thermal correction to Energy= 0.379450
Thermal correction to Enthalpy= 0.380394
Thermal correction to Gibbs Free Energy= 0.285526
Sum of electronic and zero-point Energies= -2432.515986
Sum of electronic and thermal Energies= -2432.487402
Sum of electronic and thermal Enthalpies= -2432.486457
Sum of electronic and thermal Free Energies= -2432.581325

6.1.4.4 Computed Excitations of S₁ (Emission of S₁) of compound 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Excited State   1:      Singlet  A  1.9594 eV  632.75 nm  f=0.8906  <S**2>=0.000
                   126 ->127  0.69905

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2432.86421280
Copying the excited state density for this state as the 1-particle RhoCl density.

6.1.4.5 Computed xyz-Coordinates of radical cation of compound 3c-aa (uB3LYP/6-311G*)

![Figure S47. Optimized ground state geometry of radical cation of 3c-aa (uB3LYP/6-311G* PCM CH₂Cl₂).](image)

C    1.19022  0.03002  0.00398
C    1.33840 -1.35429 -0.06948
S   -0.00003 -2.48293 -0.14752
C   -1.33843 -1.35427 -0.06916
C   -1.19022  0.03004  0.00407
N    0.00001  0.71583  0.03557
C   -2.69358 -1.75468 -0.09299
C   -3.57788 -0.70249 -0.03558
S  -2.72961  0.83958  0.06256
S   2.72963  0.83949  0.06260
C   3.57786 -0.70253 -0.03586
C   2.69354 -1.75471 -0.09341
C   5.03739 -0.74389 -0.03556
C  -5.03743 -0.74383 -0.03532
C   0.00003  2.17039  0.10248
C   5.70808 -1.87871  0.45599
C   7.09143 -1.94108  0.45197
C   7.84288 -0.86325 -0.04052
C   7.18493  0.27520 -0.52799
C   5.80066  0.33060 -0.52496
C  -5.80064  0.33059 -0.52494
C  -7.18491  0.27517 -0.52812
C  -7.84291 -0.86321 -0.04057
C  -7.09151 -1.94095  0.45219
C  -5.70815 -1.87857  0.45634
C   0.00004  2.90178 -1.08392
C   0.00006  4.29235 -1.01273
C   0.00008  4.92948  0.22754
C   0.00007  4.18284  1.40490
C   0.00005  2.79131  1.35019
C   9.27075 -0.92376 -0.04241
C  -9.27078 -0.92376 -0.04265
N  10.42438 -0.97232 -0.04405
N -10.42440 -0.97238 -0.04442
H  -3.00722 -2.78636 -0.18489
H   3.00717 -2.78635 -0.18577
H   5.14496 -2.70610  0.87200
H   7.59875 -2.81656  0.83900
H   7.76320  1.10574 -0.91435
### Computed xyz-Coordinates of dication (S₀) of compound 3c-aa (uB3LYP/6-311G*)

| Atom | x    | y    | z    |
|------|------|------|------|
| C    | 1.18528 | 0.02714 | 0.00261 |
| C    | 1.34075 | -1.38292 | -0.02104 |
| S    | 0.00002 | -2.48759 | -0.04675 |
| C    | -1.34072 | -1.38294 | -0.02129 |

**Figure S48.** Optimized ground state geometry of dication of 3c-aa (uB3LYP/6-311G* PCM CH₂Cl₂).
|  |  |  |  |
|---|---|---|---|
| C | -1.18527 | 0.02713 | 0.00253 |
| N | -0.00000 | 0.68162 | 0.01118 |
| C | -2.67904 | -1.77202 | -0.02892 |
| C | -3.57119 | -0.69995 | -0.00972 |
| S | -2.71507 | 0.84793 | 0.02379 |
| S | 2.71508 | 0.84796 | 0.02394 |
| C | 3.57119 | -0.69989 | -0.00959 |
| C | 2.67909 | -1.77199 | -0.02865 |
| C | 5.01065 | -0.74033 | -0.01066 |
| C | -5.01063 | -0.74039 | -0.01071 |
| C | -0.00001 | 2.15443 | 0.03116 |
| C | 5.69018 | -1.97629 | 0.12735 |
| C | 7.06851 | -2.02840 | 0.12729 |
| C | 7.81765 | -0.84483 | -0.01351 |
| C | 7.15907 | 0.39186 | -0.15184 |
| C | 5.78074 | 0.43965 | -0.14868 |
| C | -5.78075 | 0.43987 | -0.14631 |
| C | -7.15907 | 0.39213 | -0.14942 |
| C | -7.81767 | -0.84483 | -0.01350 |
| C | -7.06853 | -2.02869 | 0.12486 |
| C | -5.69020 | -1.97661 | 0.12492 |
| C | 0.00010 | 2.83702 | -1.18386 |
| C | 0.00012 | 4.22951 | -1.15291 |
| C | -0.0001 | 4.90459 | 0.06789 |
| C | -0.00015 | 4.19723 | 1.27015 |
| C | -0.00013 | 2.80433 | 1.26395 |
| C | 9.24088 | -0.89744 | -0.01519 |
| C | -9.24089 | -0.89741 | -0.01516 |
| N | 10.39563 | -0.93932 | -0.01664 |
| N | -10.39565 | -0.93926 | -0.01653 |
| H | -2.99454 | -2.80572 | -0.06298 |
6.1.4.7 Reoptimization of compound 3c-aa (uB3LYP/6-311G*)

Compound 3c-aa in the gas phase (uB3LYP/6-311G*):

SCF Done:  E(UB3LYP) = -2435.11980901  A.U. after  1 cycles
Zero-point correction= 0.348525 (Hartree/Particle)
Thermal correction to Energy= 0.376847
Thermal correction to Enthalpy= 0.377791
Thermal correction to Gibbs Free Energy= 0.284413
Sum of electronic and zero-point Energies= -2434.771284
Sum of electronic and thermal Energies= -2434.742963
Sum of electronic and thermal Enthalpies= -2434.742018
Sum of electronic and thermal Free Energies= -2434.835396

Compound 3c-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2435.16524136  A.U. after 14 cycles

Radical cation of compound 3c-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2434.99326328  A.U. after 20 cycles

Dication of compound 3c-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2434.77599913  A.U. after 15 cycles

6.1.4.8 Computed xyz-Coordinates of transition state of the benzonitrile rotation of compound 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

![Figure S49. Optimized geometry of the transition state of the benzonitrile rotation of 3c-aa (PBE1PBE/6-31G** PCM CH₂Cl₂).](image)

|      | x       | y       | z       |
|------|---------|---------|---------|
| C    | 1.32479 | -1.08226| 1.00131 |
| C    | 1.18373 | 0.21698 | 0.59025 |
| N    | -0.00332| 0.94934 | 0.61206 |
| C    | -1.18087| 0.21883 | 0.57722 |
| C    | -1.32055| -1.09025| 0.97723 |
| S    | -0.00225| -1.96898| 1.77707 |
| S    | -2.65128| 0.84009 | -0.09517|
| C    | -3.48398| -0.66891| 0.20630 |
| C    | -2.62303| -1.59297| 0.75164 |
|   |        |        |        |
|---|--------|--------|--------|
| C | 2.63369 | -1.59280 | 0.77303 |
| C | 3.47664 | -0.67701 | 0.20997 |
| S | 2.65371 | 0.82912 | -0.09966 |
| C | -4.89883 | -0.81599 | -0.09925 |
| C | 4.91121 | -0.82369 | -0.11384 |
| C | -0.00011 | 2.34743 | 0.30097 |
| C | 5.88812 | -0.51671 | 0.84112 |
| C | 7.23598 | -0.66637 | 0.54806 |
| C | 7.62018 | -1.12651 | -0.71795 |
| C | 6.65279 | -1.43383 | -1.68297 |
| C | 5.30830 | -1.27882 | -1.37682 |
| C | 0.00756 | 3.27672 | 1.33981 |
| C | 0.01197 | 4.63557 | 1.04054 |
| C | 0.00871 | 5.05881 | -0.28739 |
| C | 0.00133 | 4.12576 | -1.32138 |
| C | -0.00268 | 2.76390 | -1.03139 |
| C | -5.47410 | -2.09662 | -0.20173 |
| C | -6.81897 | -2.25521 | -0.48145 |
| C | -7.63236 | -1.12976 | -0.68179 |
| C | -7.07334 | 0.15254 | -0.59293 |
| C | -5.72850 | 0.30113 | -0.30301 |
| C | 9.00814 | -1.28341 | -1.02715 |
| C | -9.01904 | -1.28951 | -0.97803 |
| N | 10.13538 | -1.41063 | -1.27861 |
| N | -10.14928 | -1.41962 | -1.21919 |
| H | -2.92385 | -2.59541 | 1.03394 |
| H | 2.94429 | -2.59633 | 1.04072 |
| H | 5.58390 | -0.16187 | 1.82058 |
| H | 7.99039 | -0.43092 | 1.29105 |
| H | 6.95724 | -1.79031 | -2.66115 |
| H | 4.55379 | -1.51601 | -2.11992 |
|     |         |         |         |
|-----|---------|---------|---------|
| H   | 0.00962 | 2.92614 | 2.36702 |
| H   | 0.01771 | 5.36404 | 1.84531 |
| H   | 0.01204 | 6.12009 | -0.51667|
| H   | -0.00088| 4.45584 | -2.35544|
| H   | -0.00784| 2.02485 | -1.82707|
| H   | -4.85572| -2.97907| -0.07753|
| H   | -7.24534| -3.24988| -0.55795|
| H   | -7.69801| 1.02654 | -0.74358|
| H   | -5.32033| 1.30404 | -0.21737|

SCF Done: E(RPBE1PBE) = -2432.93539748 A.U. after 1 cycles
Zero-point correction= 0.353210 (Hartree/Particle)
Thermal correction to Energy= 0.380485
Thermal correction to Enthalpy= 0.381429
Thermal correction to Gibbs Free Energy= 0.291012
Sum of electronic and zero-point Energies= -2432.582188
Sum of electronic and thermal Energies= -2432.554913
Sum of electronic and thermal Enthalpies= -2432.553969
Sum of electronic and thermal Free Energies= -2432.644386

6.1.5 Compound 3d-ss

6.1.5.1 Computed xyz-Coordinates of compound 3d-ss (PBE1PBE/6-31G** PCM CH₂Cl₂)

![Figure S50](image)

Figure S50. Optimized ground state geometry of 3d-ss (PBE1PBE/6-31G** PCM CH₂Cl₂).

|     |         |         |         |
|-----|---------|---------|---------|
| C   | 1.29144 | -1.63881| 0.88887 |
| C   | 1.19808 | -0.27477| 0.72448 |
| N   | 0.00009 | 0.42587 | 0.92421 |
C  -1.19792   -0.27482   0.72471
C  -1.29129   -1.63885   0.88918
S   0.00016   -2.65524   1.52093
C  -2.42415    0.29563   0.29013
C  -3.42729   -0.62982   0.12324
S  -2.85646   -2.23378   0.47722
S   2.85661   -2.23375   0.47691
C   3.42748   -0.62979   0.12314
C   2.42437    0.29569   0.29004
C  -0.00013   1.85367   0.82677
C   4.80451   -0.39309  -0.29730
C  -4.80430   -0.39318  -0.29731
C   5.38073    0.88007  -0.14544
C   6.67946   1.12687  -0.55419
C   7.44388    0.09446  -1.11648
C   6.88689   -1.18292  -1.26452
C   5.58260   -1.41614  -0.86371
C  -0.00197   2.61089   1.99644
C  -0.00240   4.00133   1.91966
C  -0.00093   4.63198   0.67762
C   0.00091   3.87287  -0.49118
C   0.00125   2.48252  -0.42009
C  -5.58269  -1.41657  -0.86271
C  -6.88694  -1.18340  -1.26367
C  -7.44363   0.09425  -1.11680
C  -6.67892   1.12699  -0.55553
C  -5.38022   0.88026  -0.14663
C   8.78641   0.34333  -1.53462
C  -8.78612   0.34306  -1.53509
N   9.87927   0.54628  -1.87539
N  -9.87897   0.54577  -1.87604
H  -2.54753  1.35163  0.08477
H   2.54787  1.35169  0.08476
H   4.81052  1.67947  0.31588
H   7.11232  2.11373 -0.42972
H   7.47476 -1.98236 -1.70244
H   5.15647 -2.40420 -1.01133
H  -0.00304  2.10205  2.95538
H  -0.00383  4.59134  2.83109
H  -0.00122  5.71628  0.61957
H   0.00201  4.36276 -1.46014
H   0.00255  1.88009 -1.32402
H  -5.15683 -2.40488 -1.00943
H  -7.47502 -1.98313 -1.70079
H  -7.11151  2.11408 -0.43198
H  -4.80982  1.67999  0.31387

SCF Done:  E(RPBE1PBE) = -2432.94087638  A.U. after 1 cycles
Zero-point correction= 0.353628 (Hartree/Particle)
Thermal correction to Energy= 0.381593
Thermal correction to Enthalpy= 0.382537
Thermal correction to Gibbs Free Energy= 0.290290
Sum of electronic and zero-point Energies= -2432.587249
Sum of electronic and thermal Energies= -2432.559284
Sum of electronic and thermal Enthalpies= -2432.558339
Sum of electronic and thermal Free Energies= -2432.650586

6.1.5.2 Computed Excitations of compound 3d-ss (PBE1PBE/6-31G** PCM CH2Cl2)
Excited State  1:  Singlet-A  2.5717 eV  482.11 nm  f=0.3337  <S**2>=0.000
               126 ->127  0.69512

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2432.84636815
Copying the excited state density for this state as the 1-particle RhoCI density.

S72
Excited State 2: Singlet-A 2.7733 eV 447.07 nm f=0.0641 $<S^2>=0.000$
126 -> 128 0.70188

Excited State 3: Singlet-A 3.7344 eV 332.00 nm f=0.1958 $<S^2>=0.000$
126 -> 127 0.11095
126 -> 129 0.59025
126 -> 131 0.27203
126 -> 133 -0.15229
126 -> 135 0.13626

Excited State 4: Singlet-A 3.8794 eV 319.60 nm f=0.0203 $<S^2>=0.000$
126 -> 131 -0.18579
126 -> 132 0.64948
126 -> 133 -0.14319

Excited State 5: Singlet-A 3.9905 eV 310.70 nm f=1.2624 $<S^2>=0.000$
124 -> 127 -0.22093
125 -> 128 0.65191

Excited State 6: Singlet-A 4.0077 eV 309.37 nm f=0.0056 $<S^2>=0.000$
125 -> 127 -0.14391
126 -> 130 0.66585
126 -> 136 0.13452

6.1.5.3 Computed xyz-Coordinates of radical cation of compound 3d-ss (uB3LYP/6-311G*)

Figure S51. Optimized ground state geometry of radical cation of 3d-ss (uB3LYP/6-311G* PCM CH₂Cl₂).
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | -1.30952 | -1.75996 | -0.09237 |
| C       | -1.20915 | -0.36726 | -0.01911 |
| N       | 0.00000  | 0.30769  | 0.02314  |
| C       | 1.20915  | -0.36727 | -0.01902 |
| C       | 1.30953  | -1.75997 | -0.09223 |
| S       | 0.00000  | -2.89556 | -0.14354 |
| C       | 2.48568  | 0.25723  | 0.01862  |
| C       | 3.53076  | -0.62967 | -0.02801 |
| S       | 2.95922  | -2.29013 | -0.13547 |
| S       | -2.95921 | -2.29012 | -0.13566 |
| C       | -3.53076 | -0.62968 | -0.02810 |
| C       | -2.48568 | 0.25723  | 0.01860  |
| C       | -4.96475 | -0.34363 | -0.01464 |
| C       | -0.00000 | 1.75902  | 0.09383  |
| C       | 4.96475  | -0.34363 | -0.01460 |
| C       | -5.44154 | 0.87340  | -0.53238 |
| C       | -6.79492 | 1.16741  | -0.51558 |
| C       | -7.70813 | 0.24498  | 0.01702  |
| C       | -7.24349 | -0.97424 | 0.53029  |
| C       | -5.88787 | -1.26168 | 0.51374  |
| C       | -0.00050 | 2.49750  | -1.08745 |
| C       | -0.00050 | 3.88904  | -1.01433 |
| C       | -0.00001 | 4.52453  | 0.22675  |
| C       | 0.00049  | 3.77289  | 1.40094  |
| C       | 0.00050  | 2.38062  | 1.34048  |
| C       | 5.88784  | -1.26149 | 0.51413  |
| C       | 7.24347  | -0.97405 | 0.53061  |
| C       | 7.70812  | 0.24498  | 0.01691  |
| C       | 6.79493  | 1.16723  | -0.51603 |
| C       | 5.44155  | 0.87322  | -0.53276 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -9.10527| 0.54673 | 0.03354 |
| C    | 9.10527 | 0.54672 | 0.03335 |
| N    | -10.23329| 0.79257 | 0.04722 |
| N    | 10.23329| 0.79256 | 0.04697 |
| H    | 2.61920 | 1.32492 | 0.11278 |
| H    | -2.61919| 1.32491 | 0.11285 |
| H    | -4.75244| 1.58168 | -0.97766|
| H    | -7.15491| 2.10437 | -0.92321|
| H    | -7.94672| -1.68545| 0.94631 |
| H    | -5.54612| -2.19748| 0.94304 |
| H    | -0.00085| 1.99130 | -2.04669|
| H    | -0.00088| 4.47429 | -1.92694|
| H    | -0.00001| 5.60749 | 0.27903 |
| H    | 0.00088 | 4.26767 | 2.36552 |
| H    | 0.00088 | 1.78511 | 2.24694 |
| H    | 5.54607 | -2.19713| 0.94375 |
| H    | 7.94669 | -1.68511| 0.94692 |
| H    | 7.15495 | 2.10404 | -0.92399|
| H    | 4.75246 | 1.58134 | -0.97830|

SCF Done:  $E(\text{UB3LYP}) = -2434.89020227$  A.U. after  1 cycles

Zero-point correction= 0.349606 (Hartree/Particle)
Thermal correction to Energy= 0.377689
Thermal correction to Enthalpy= 0.378633
Thermal correction to Gibbs Free Energy= 0.286154

Sum of electronic and zero-point Energies= -2434.540596
Sum of electronic and thermal Energies= -2434.512513
Sum of electronic and thermal Enthalpies= -2434.511569
Sum of electronic and thermal Free Energies= -2434.604048
6.1.5.4 Computed xyz-Coordinates of dication (S₀) of compound 3d-ss (uB3LYP/6-311G*)

![Diagram of dication](image)

**Figure S52.** Optimized ground state geometry of dication of 3d-ss (uB3LYP/6-311G* PCM CH₂Cl₂).

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.31137 | -1.74973 | -0.00017 |
| C    | -1.21089 | -0.32763 | 0.00011 |
| N    | 0.00000  | 0.32534  | 0.00001 |
| C    | 1.21089  | -0.32763 | -0.00034 |
| C    | 1.31137  | -1.74973 | -0.00054 |
| S    | 0.00000  | -2.82924 | -0.00050 |
| C    | 2.47445  | 0.28473  | -0.00017 |
| C    | 3.53008  | -0.61263 | -0.00039 |
| S    | 2.94917  | -2.29002 | -0.00110 |
| S    | -2.94917 | -2.29002 | 0.00004 |
| C    | -3.53007 | -0.61263 | 0.00015 |
| C    | -2.47445 | 0.28473  | 0.00022 |
| C    | -4.94758 | -0.34477 | 0.00024 |
| C    | 0.00000  | 1.78961  | 0.00017 |
| C    | 4.94758  | -0.34477 | -0.00029 |
| C    | -5.41952 | 0.99022  | 0.00462 |
| C    | -6.77199 | 1.26075  | 0.00463 |
| C    | -7.70222 | 0.20352  | 0.00024 |
| C    | -7.25052 | -1.12882 | -0.00409 |
| C    | -5.89624 | -1.39436 | -0.00405 |
| C    | -0.00001 | 2.46219  | -1.21982 |
| C    | -0.0003  | 3.85614  | -1.21003 |
| C    | -0.00000 | 4.54921  | 0.00043 |
| C    | 0.00002  | 3.85591  | 1.21076 |
|  |  |  |  |
|---|---|---|---|
| C | 0.00001 | 2.46195 | 1.22028 |
| C | 5.89624 | -1.39435 | 0.00676 |
| C | 7.25051 | -1.12881 | 0.00708 |
| C | 7.70222 | 0.20352 | 0.00022 |
| C | 6.77199 | 1.26074 | -0.00701 |
| C | 5.41952 | 0.99021 | -0.00723 |
| C | -9.09866 | 0.48420 | -0.00723 |
| C | 9.09866 | 0.48420 | 0.00050 |
| N | -10.23101 | 0.71424 | 0.00020 |
| N | 10.23100 | 0.71424 | 0.00075 |
| H | 2.60265 | 1.35613 | 0.00087 |
| H | -2.60265 | 1.35613 | -0.00009 |
| H | -4.72626 | 1.82193 | 0.00843 |
| H | -7.12534 | 2.28455 | 0.00812 |
| H | -7.96801 | -1.94001 | -0.00751 |
| H | -5.57982 | -2.43242 | -0.00782 |
| H | -0.00005 | 1.91428 | -2.15600 |
| H | -0.00007 | 4.39730 | -2.14919 |
| H | -0.00001 | 5.63319 | 0.00053 |
| H | 0.00006 | 4.39689 | 2.15002 |
| H | 0.00005 | 1.91386 | 2.15636 |
| H | 5.57981 | -2.43240 | 0.01279 |
| H | 7.96801 | -1.93998 | 0.01272 |
| H | 7.12534 | 2.28453 | -0.01257 |
| H | 4.72627 | 1.82190 | -0.01352 |

SCF Done: $E(\text{UB3LYP}) = -2434.52512875$ A.U. after 1 cycles

Zero-point correction= 0.349435 (Hartree/Particle)

Thermal correction to Energy= 0.377614

Thermal correction to Enthalpy= 0.378558

Thermal correction to Gibbs Free Energy= 0.285139

Sum of electronic and zero-point Energies= -2434.175693

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Sum of electronic and thermal Energies= -2434.147515
Sum of electronic and thermal Enthalpies= -2434.146571
Sum of electronic and thermal Free Energies= -2434.239989

6.1.5.5 Reoptimization of compound 3d-ss (uB3LYP/6-311G*)
Compound 3d-ss in the gas phase (uB3LYP/6-311G*):

SCF Done:  E(UB3LYP) = -2435.11888743 A.U. after 1 cycles
Zero-point correction= 0.348946 (Hartree/Particle)
Thermal correction to Energy= 0.377110
Thermal correction to Enthalpy= 0.378054
Thermal correction to Gibbs Free Energy= 0.285795
Sum of electronic and zero-point Energies= -2434.769941
Sum of electronic and thermal Energies= -2434.741777
Sum of electronic and thermal Enthalpies= -2434.740833
Sum of electronic and thermal Free Energies= -2434.833093

Compound 3d-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -2435.16302718 A.U. after 14 cycles

Radical cation of compound 3d-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -2434.99014177 A.U. after 20 cycles

Dication of compound 3d-ss in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):

SCF Done:  E(UB3LYP) = -2434.76722517 A.U. after 15 cycles
6.1.5.6 Computed xyz-Coordinates of transition state of the benzonitrile rotation of compound 3d-ss (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S53. Optimized geometry of the transition state of the benzonitrile rotation of 3d-ss (PBE1PBE/6-31G** PCM CH₂Cl₂).

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.29614| -1.63782| -0.88352|
| C    | -1.19911| -0.27628| -0.73027|
| N    | -0.00001| 0.42150  | -0.94570|
| C    | 1.19650 | -0.27828| -0.73440|
| C    | 1.28722 | -1.64489| -0.88178|
| S    | -0.00458| -2.66163| -1.51118|
| C    | 2.42302 | 0.29492 | -0.30415|
| C    | 3.42430 | -0.63021| -0.12342|
| S    | 2.85028 | -2.23745| -0.45785|
| S    | -2.86049| -2.22507| -0.44392|
| C    | -3.41770| -0.61805| -0.10192|
| C    | -2.42462| 0.30406 | -0.28433|
| C    | 0.00344 | 1.85002 | -0.86379|
| C    | -4.81121| -0.38066| 0.33047 |
| C    | 4.80110 | -0.39089| 0.29548 |
| C    | -5.81346| -0.14240| -0.61730|
| C    | -7.12153| 0.09188 | -0.21854|
| C    | -7.43896| 0.08601 | 1.14566 |
| C    | -6.44498| -0.15361| 2.10283 |
| C    | -5.14060| -0.38638| 1.69082 |
| C    | 0.01292 | 2.59465 | -2.04151|
| C    | 0.01740 | 3.98591 | -1.98040|
C  0.01240  4.63049  -0.74560
C  0.00318  3.88431   0.43145
C  -0.00103  2.49329   0.37572
C  5.57993  -1.41059   0.86723
C  6.88458  -1.17523  1.26546
C  7.44180   0.10117  1.10957
C  6.67673  1.13037   0.54217
C  5.37763   0.88137  0.13616
C  -8.78578   0.32637  1.56392
C  8.78478   0.35222  1.52464
N  -9.87952   0.52183  1.90397
N   9.87814   0.55684  1.86294
H   2.54818   1.35332  -0.11253
H  -2.56357   1.36379  -0.10932
H  -5.56092  -0.13893  -1.67270
H  -7.89607   0.27886  -0.95446
H  -6.69776  -0.15635  3.15762
H  -4.36573  -0.57280  2.42738
H   0.01638   2.07517  -2.99474
H   0.02445   4.56563  -2.89840
H   0.01557   5.71537  -0.69961
H  -0.00075   4.38500  1.39490
H  -0.00803   1.90104  1.28632
H   5.15415  -2.39793  1.02060
H   7.47279  -1.97231  1.70724
H   7.10950   2.11649  0.41158
H   4.80725   1.67838  -0.32904

SCF Done:  E(RPBE1PBE) = -2432.93445701  A.U. after  1 cycles
Zero-point correction= 0.353478 (Hartree/Particle)
Thermal correction to Energy= 0.380647
Thermal correction to Enthalpy= 0.381591

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Thermal correction to Gibbs Free Energy= 0.291626
Sum of electronic and zero-point Energies= -2432.580979
Sum of electronic and thermal Energies= -2432.553810
Sum of electronic and thermal Enthalpies= -2432.552866
Sum of electronic and thermal Free Energies= -2432.642831

6.1.6 Compound 3e-aa

6.1.6.1 Computed xyz-Coordinates of compound 3e-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

Figure S54. Optimized ground state geometry of 3e-aa (PBE1PBE/6-31G** PCM CH₂Cl₂).

\[
\begin{array}{cccc}
\text{C} & 1.36168 & -0.96108 & 1.06860 \\
\text{C} & 1.18283 & 0.33131 & 0.64697 \\
\text{N} & -0.01720 & 1.03656 & 0.69871 \\
\text{C} & -1.18166 & 0.27411 & 0.69057 \\
\text{C} & -1.28430 & -1.02479 & 1.11736 \\
\text{S} & 0.07394 & -1.85459 & 1.90286 \\
\text{S} & -2.67100 & 0.82775 & -0.01279 \\
\text{C} & -3.45053 & -0.70753 & 0.30243 \\
\text{C} & -2.56861 & -1.58371 & 0.88269 \\
\text{C} & 2.67526 & -1.44437 & 0.82762 \\
\text{C} & 3.50041 & -0.51867 & 0.24120 \\
\text{S} & 2.62703 & 0.96299 & -0.08091 \\
\text{C} & -0.06332 & 2.43437 & 0.39742 \\
\text{C} & -4.86181 & -0.90817 & -0.01700 \\
\text{C} & 4.91457 & -0.64274 & -0.10605 \\
\end{array}
\]
C 5.76332 0.47534 -0.17852
C 7.10211 0.34115 -0.50101
C 7.64565 -0.92393 -0.75445
C 6.81909 -2.04883 -0.68767
C 5.47181 -1.89868 -0.37621
C -5.62288 -1.86040 0.68547
C -6.95394 -2.07909 0.38229
C -7.58265 -1.33801 -0.62690
C -6.84890 -0.37849 -1.32796
C -5.50519 -0.18020 -1.02404
O 8.96539 -0.95402 -1.05611
O -8.88887 -1.62019 -0.84361
C -9.56355 -0.88873 -1.84904
C 9.55557 -2.21385 -1.31193
C -0.15174 3.35517 1.44046
C -0.20077 4.71536 1.15132
C -0.15958 5.15052 -0.17214
C -0.07229 4.22714 -1.21108
C -0.02641 2.86394 -0.93045
H -2.82760 -2.60468 1.13937
H 3.01023 -2.42995 1.13065
H 5.37246 1.46582 0.03983
H 7.75348 1.20795 -0.55129
H 7.20689 -3.04041 -0.89079
H 4.83833 -2.78068 -0.36042
H -5.16554 -2.42376 1.49332
H -7.53719 -2.81342 0.92901
H -7.30449 0.20830 -2.11728
H -4.94581 0.54978 -1.60382
H -10.58799 -1.26140 -1.85853
H -9.57192 0.18505 -1.62757
H  -9.11163  -1.05028  -2.83483  
H  10.60764  -2.01826  -1.52032  
H  9.47719  -2.87838  -0.44336  
H  9.10054  -2.70223  -2.18181  
H  -0.17952  2.99602  2.46438  
H  -0.26897  5.43580  1.96057  
H  -0.19624  6.21285  -0.39381  
H  -0.04241  4.56577  -2.24205  
H  0.03622  2.13257  -1.73078  

SCF Done:  \( E(\text{RPBE1PBE}) = -2477.46172030 \) A.U. after 1 cycles

Zero-point correction= 0.421820 (Hartree/Particle)
Thermal correction to Energy= 0.451420
Thermal correction to Enthalpy= 0.452364
Thermal correction to Gibbs Free Energy= 0.356801
Sum of electronic and zero-point Energies= -2477.039900
Sum of electronic and thermal Energies= -2477.010300
Sum of electronic and thermal Enthalpies= -2477.009356
Sum of electronic and thermal Free Energies= -2477.104920

6.1.6.2 Computed Excitations of compound 3e-aa (PBE1PBE/6-31+G** PCM CH₂Cl₂)

Excited State  1:  Singlet-A  2.8418 eV  436.28 nm  f=0.5106  \(<S^{*2}>=0.000\)
  130 \(\rightarrow\) 131  0.69361
This state for optimization and/or second-order correction.
Total Energy, \( E(\text{TD-HF/TD-KS}) = -2477.39224026 \)
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State  2:  Singlet-A  3.3008 eV  375.62 nm  f=0.0177  \(<S^{*2}>=0.000\)
  130 \(\rightarrow\) 132  0.55144
  130 \(\rightarrow\) 133  -0.43242

Excited State  3:  Singlet-A  3.4207 eV  362.46 nm  f=0.0216  \(<S^{*2}>=0.000\)
  130 \(\rightarrow\) 132  0.41868
  130 \(\rightarrow\) 133  0.54327
  130 \(\rightarrow\) 134  0.12471
| Excited State | Singlet-A | E (eV) | λ (nm) | f | <S^2> |
|---------------|-----------|--------|--------|---|-------|
| 4             | 3.5330    | 350.93 | 0.0050 | 0.000 |
| 5             | 3.7781    | 328.17 | 0.0056 | 0.000 |
| 6             | 3.8321    | 323.54 | 0.0764 | 0.000 |
| 7             | 3.9458    | 314.22 | 0.1393 | 0.000 |
| 8             | 4.1287    | 300.30 | 0.0694 | 0.000 |
| 9             | 4.2000    | 295.20 | 0.0038 | 0.000 |
| 10            | 4.2552    | 291.37 | 0.0096 | 0.000 |
6.1.6.3 Computed xyz-Coordinates of radical cation of compound 3e-aa (uB3LYP/6-311G*)

Figure S55. Optimized ground state geometry of radical cation of 3e-aa (uB3LYP/6-311G* PCM CH2Cl2).

|     | x    | y    | z    |
|-----|------|------|------|
| C   | -1.37982 | -1.28942 | -0.01034 |
| C   | -1.19173 |  0.08945 | -0.00869 |
| N   |  0.01832 |  0.74429 | -0.01373 |
| C   |  1.19057 |  0.02441 | -0.02944 |
| C   |  1.30240 | -1.36261 | -0.04378 |
| S   | -0.06964 | -2.46074 | -0.02996 |
| S   |  2.75495 |  0.79269 | -0.03788 |
| C   |  3.56517 | -0.77619 | -0.03380 |
| C   |  2.64363 | -1.80182 | -0.04386 |
| C   | -2.74318 | -1.65401 | -0.02248 |
| C   | -3.60655 | -0.57881 | -0.02501 |
| S   | -2.71095 |  0.94266 |  0.00008 |
| C   |  0.05735 |  2.19678 | -0.00543 |
| C   |  5.01507 | -0.85825 | -0.03862 |
| C   | -5.05890 | -0.57551 | -0.03057 |
| C   | -5.79841 |  0.53093 | -0.50111 |
| C   | -7.17667 |  0.51781 | -0.51002 |
| C   | -7.88045 | -0.60779 | -0.04705 |
| C   | -7.16364 | -1.71671 |  0.42740 |
| C   | -5.77698 | -1.69128 |  0.43338 |
| C   |  5.66289 | -2.02109 | -0.51231 |
| C   |  7.03689 | -2.12115 | -0.51253 |
| C   |  7.82984 | -1.05928 | -0.04061 |
| C   |  7.20567 |  0.10472 |  0.43016 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 5.82087   | 0.19342   | 0.42728   |
| O       | -9.22153  | -0.52091  | -0.09798  |
| O       | 9.15924   | -1.25768  | -0.08520  |
| C       | 10.03840  | -0.22733  | 0.36664   |
| C       | -10.01414 | -1.62233  | 0.34684   |
| C       | 0.10882   | 2.88174   | -1.21800  |
| C       | 0.14474   | 4.27367   | -1.20275  |
| C       | 0.12843   | 4.96052   | 0.01028   |
| C       | 0.07662   | 4.26164   | 1.21542   |
| C       | 0.04076   | 2.86963   | 1.21488   |
| H       | 2.92403   | -2.84654  | -0.01625  |
| H       | -3.08064  | -2.68124  | -0.06607  |
| H       | -5.28521  | 1.40369   | -0.89222  |
| H       | -7.74452  | 1.36291   | -0.88071  |
| H       | -7.67667  | -2.59244  | 0.80288   |
| H       | -5.24615  | -2.54711  | 0.83545   |
| H       | 5.07901   | -2.84288  | -0.91144  |
| H       | 7.53541   | -3.00817  | -0.88525  |
| H       | 7.78679   | 0.93581   | 0.80753   |
| H       | 5.36401   | 1.09434   | 0.82476   |
| H       | 11.04234  | -0.61918  | 0.22524   |
| H       | 9.91515   | 0.68348   | -0.22594  |
| H       | 9.87781   | -0.00928  | 1.42619   |
| H       | -11.04646 | -1.31515  | 0.20060   |
| H       | -9.81227  | -2.51827  | -0.24684  |
| H       | -9.84170  | -1.82896  | 1.40680   |
| H       | 0.11904   | 2.33347   | -2.15345  |
| H       | 0.18449   | 4.81932   | -2.13861  |
| H       | 0.15569   | 6.04447   | 0.01645   |
| H       | 0.06381   | 4.79800   | 2.15739   |
| H       | 0.00050   | 2.31210   | 2.14403   |
SCF Done:  $E(\text{UB3LYP}) = -2479.48804651$  A.U. after  1 cycles
Zero-point correction= 0.417346 (Hartree/Particle)
Thermal correction to Energy= 0.447134
Thermal correction to Enthalpy= 0.448079
Thermal correction to Gibbs Free Energy= 0.352290
Sum of electronic and zero-point Energies= -2479.070701
Sum of electronic and thermal Energies= -2479.040912
Sum of electronic and thermal Enthalpies= -2479.039968
Sum of electronic and thermal Free Energies= -2479.135757

6.1.6.4 Computed $xyz$-Coordinates of dication ($S_0$) of compound 3e-aa ($uB3LYP/6-311G^*$)

Figure S56. Optimized ground state geometry of dication of 3e-aa ($uB3LYP/6-311G^*$ PCM CH$_2$Cl$_2$).

|     |      |      |       |
|-----|------|------|-------|
| C   | -1.37982 | -1.28942 | -0.01034 |
| C   | -1.19173 | 0.08945  | -0.00869 |
| N   | 0.01832  | 0.74429  | -0.01373 |
| C   | 1.19057  | 0.02441  | -0.02944 |
| C   | 1.30240  | -1.36261 | -0.04378 |
| S   | -0.06964 | -2.46074 | -0.02996 |
| S   | 2.75495  | 0.79269  | -0.03788 |
| C   | 3.56517  | -0.77619 | -0.03380 |
| C   | 2.64363  | -1.80182 | -0.04386 |
| C   | -2.74318 | -1.65401 | -0.02248 |
| C   | -3.60655 | -0.57881 | -0.02501 |
| S   | -2.71095 | 0.94266  | 0.00008  |
| C   | 0.05735  | 2.19678  | -0.00543 |
C  5.01507  -0.85825  -0.03862
C  -5.05890  -0.57551  -0.03057
C  -5.79841   0.53093  -0.50111
C  -7.17667   0.51781  -0.51002
C  -7.88045  -0.60779  -0.04705
C  -7.16364  -1.71671   0.42740
C  -5.77698  -1.69128   0.43338
C   5.66289  -2.02109  -0.51231
C   7.03689  -2.12115  -0.51253
C   7.82984  -1.05928  -0.04061
C   7.20567   0.10472   0.43016
C   5.82087   0.19342   0.42728
O  -9.22153  -0.52091  -0.09798
O   9.15924  -1.25768  -0.08520
C  10.03840  -0.22733   0.36664
C -10.01414  -1.62233   0.34684
C   0.10882   2.88174  -1.21800
C   0.14474   4.27367  -1.20275
C   0.12843   4.96052   0.01028
C   0.07662   4.26164   1.21542
C   0.04076   2.86963   1.21488
H   2.92403  -2.84654  -0.01625
H  -3.08064  -2.68124  -0.06607
H  -5.28521   1.40369  -0.89222
H  -7.74452   1.36291  -0.88071
H  -7.67667  -2.59244   0.80288
H  -5.24615  -2.54711   0.83545
H   5.07901  -2.84288  -0.91144
H   7.53541  -3.00817  -0.88525
H   7.78679   0.93581   0.80753
H   5.36401   1.09434   0.82476
H 11.04234 -0.61918  0.22524
H  9.91515  0.68348 -0.22594
H  9.87781 -0.00928  1.42619
H -11.04646 -1.31515  0.20060
H  -9.81227  -2.51827  0.24684
H  -9.84170  -1.82896  1.40680
H  0.11904  2.33347  -2.15345
H  0.18449  4.81932  -2.13861
H  0.15569  6.04447  0.01645
H  0.06381  4.79800  2.15739
H  0.00050  2.31210  2.14403

SCF Done:  E(UB3LYP) = -2479.48804651 A.U. after 1 cycles
Zero-point correction= 0.417346 (Hartree/Particle)
Thermal correction to Energy= 0.447134
Thermal correction to Enthalpy= 0.448079
Thermal correction to Gibbs Free Energy= 0.352290
Sum of electronic and zero-point Energies= -2479.070701
Sum of electronic and thermal Energies= -2479.040912
Sum of electronic and thermal Enthalpies= -2479.039968
Sum of electronic and thermal Free Energies= -2479.135757

6.1.6.5 Reoptimization of compound 3e-aa (uB3LYP/6-311G*)
Compound 3e-aa in the gas phase (uB3LYP/6-311G*):

SCF Done:  E(UB3LYP) = -2479.68784172 A.U. after 1 cycles
Zero-point correction= 0.416387 (Hartree/Particle)
Thermal correction to Energy= 0.446206
Thermal correction to Enthalpy= 0.447150
Thermal correction to Gibbs Free Energy= 0.350665
Sum of electronic and zero-point Energies= -2479.271455
Sum of electronic and thermal Energies= -2479.241636
Sum of electronic and thermal Enthalpies= -2479.240691
Sum of electronic and thermal Free Energies= -2479.337177

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Compound 3e-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2479.72752041  A.U. after  13 cycles

Radical cation of compound 3e-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2479.56877858  A.U. after  19 cycles

Dication of compound 3e-aa in CH₂Cl₂ (uB3LYP/6-311G* SMD CH₂Cl₂):
SCF Done: E(UB3LYP) = -2479.37252684  A.U. after  15 cycles

6.1.6.6 Computed xyz-Coordinates of transition state of the anisyl rotation of compound 3e-aa (PBE1PBE/6-31G** PCM CH₂Cl₂)

![Optimized geometry of the transition state of the anisyl rotation of 3e-aa](Figure S57)

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -1.34083 | -0.91499 | -1.22429 |
| C    | -1.18479 | 0.34707  | -0.71399 |
| N    | 0.00860  | 1.06881  | -0.71219 |
| C    | 1.18108  | 0.31917  | -0.72416 |
| C    | 1.30615  | -0.94783 | -1.23289 |
| S    | -0.02949 | -1.72826 | -2.10328 |
| S    | 2.64775  | 0.83505  | 0.05286  |
| C    | 3.44826  | -0.67070 | -0.34344 |
| C    | 2.58886  | -1.51265 | -1.00258 |
| C    | -2.64497 | -1.44404 | -1.00543 |
| C    | -3.47874 | -0.58101 | -0.35233 |
| S    | -2.64048 | 0.89767  | 0.05721  |
| C    | 0.03260  | 2.45038  | -0.34266 |
C  4.85276  -0.88173  -0.00112
C  -4.90448  -0.74750  -0.00660
C  -5.91375  -0.34663  -0.89492
C  -7.25110  -0.51297  -0.57683
C  -7.61756  -1.08566  0.64787
C  -6.62600  -1.48810  1.54620
C  -5.28509  -1.31290  1.21209
C  5.64266  -1.77485  -0.74786
C  6.96716  -2.00331  -0.42353
C  7.55990  -1.33117  0.65348
C  6.79723  -0.43026  1.39992
C  5.46046  -0.22209  1.07294
O  -8.94730  -1.20622  0.86840
O  8.86239  -1.61769  0.88683
C  9.50102  -0.95643  1.96197
C  -9.36543  -1.77746  2.09360
C  0.11278  3.42196  -1.33937
C  0.14064  4.76725  -0.98543
C  0.08704  5.13769  0.35717
C  0.00762  4.16420  1.34995
C  -0.01789  2.81550  1.00405
H  2.86336  -2.51226  -1.32004
H  -2.96193  -2.42295  -1.34724
H  -5.63940  0.09724  -1.84758
H  -8.03403  -0.20680  -1.26350
H  -6.88268  -1.93423  2.50004
H  -4.51833  -1.62747  1.91433
H  5.21331  -2.28299  -1.60614
H  7.57296  -2.69160  -1.00457
H  7.22474  0.10254  2.24145
H  4.87725  0.45953  1.68708
| H      | 10.52792 | -1.32220 | 1.97502 |
|--------|----------|----------|---------|
| H      | 9.50683  | 0.13061  | 1.81898 |
| H      | 9.02200  | -1.19165 | 2.91975 |
| H      | -10.45527| -1.78213 | 2.06838 |
| H      | -9.00237 | -2.80622 | 2.20179 |
| H      | -9.02650 | -1.18304 | 2.95020 |
| H      | 0.15109  | 3.11270  | -2.37913|
| H      | 0.20246  | 5.52664  | -1.75880|
| H      | 0.10756  | 6.18850  | 0.63002 |
| H      | -0.03247 | 4.45251  | 2.39581 |
| H      | -0.07519 | 2.04602  | 1.76820 |

SCF Done: $E_{\text{RPBE1PBE}} = -2477.45693660$ a.u. after 1 cycles
Zero-point correction= 0.421725 (Hartree/Particle)
Thermal correction to Energy= 0.450468
Thermal correction to Enthalpy= 0.451413
Thermal correction to Gibbs Free Energy= 0.358457
Sum of electronic and zero-point Energies= -2477.035211
Sum of electronic and thermal Energies= -2477.006468
Sum of electronic and thermal Enthalpies= -2477.005524
Sum of electronic and thermal Free Energies= -2477.098479
6.1.7 Compound 3f-ss

6.1.7.1 Computed xyz-Coordinates of compound 3f-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$)

Figure S58. Optimized ground state geometry of 3f-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$).

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -1.20410 | -0.38322 | -0.76938 |
| C    | -1.25983 | -1.75588 | -0.81871 |
| S    | 0.05397  | -2.78680 | -1.38140 |
| C    | 1.32210  | -1.68712 | -0.84649 |
| C    | 1.19243  | -0.31973 | -0.79330 |
| N    | -0.02668 | 0.33184  | -1.04379 |
| C    | -2.44969 | 0.19283  | -0.38895 |
| C    | -3.43051 | -0.73685 | -0.14486 |
| S    | -2.81191 | -2.35127 | -0.34598 |
| S    | 2.90875  | -2.19836 | -0.38833 |
| C    | 3.43045  | -0.55440 | -0.15456 |
| C    | 2.40125  | 0.32133  | -0.39844 |
| C    | -4.81667 | -0.50556 | 0.25798  |
| C    | -0.06173 | 1.76180  | -1.02381 |
| C    | 4.80450  | -0.24703 | 0.23905  |
| C    | -5.83821 | -1.42193 | -0.04530 |
| C    | -7.14721 | -1.18856 | 0.33562  |
| C    | -7.48440 | -0.01931 | 1.02892  |
| C    | -6.48341 | 0.90535  | 1.33929  |
| C    | -5.16905 | 0.65236  | 0.96140  |
| C    | -0.10264 | 2.45809  | 0.18624  |
C  -0.13377  3.84979  0.18246  
C  -0.12257  4.54547  -1.02525 
C  -0.08070  3.84885  -2.23060 
C  -0.05057  2.45633  -2.23165 
C   5.38431  0.98604  -0.10867 
C   6.67798  1.29900  0.26545  
C   7.44720  0.38080  0.99239  
C   6.89254  -0.85325  1.34025  
C   5.58509  -1.15044  0.96813  
O   -8.79024  0.12145  1.35362  
C   -9.17762  1.29296  2.04628  
O    8.70237  0.77714  1.30543  
C    9.51803  -0.12209  2.03235  
H   -2.61990  1.26075  -0.33016  
H    2.49400  1.39316  -0.27424  
H   -5.60614  -2.32346  -0.60638  
H   -7.93358  -1.89681  0.09485  
H   -6.71081  1.81360  1.88525  
H   -4.39925  1.36666  1.23816  
H   -0.10870  1.90477  1.12100  
H   -0.16536  4.39073  1.12348  
H   -0.14631  5.63113  -1.02601 
H   -0.07209  4.38872  -3.17264 
H   -0.01880  1.89707  -3.16159 
H    4.81633  1.69972  -0.69793  
H    7.12369  2.25010  -0.00828  
H    7.45972  -1.58196  1.90757  
H    5.16272  -2.10471  1.27269  
H  -10.25331  1.20972  2.20231  
H   -8.67689  1.36909  3.01861  
H   -8.96662  2.19485  1.45968  

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SCF Done:  \( E(RPBE1PBE) = -2477.46208170 \) A.U. after 1 cycles

Zero-point correction= 0.422024 (Hartree/Particle)
Thermal correction to Energy= 0.451555
Thermal correction to Enthalpy= 0.452499
Thermal correction to Gibbs Free Energy= 0.357169

Sum of electronic and zero-point Energies= -2477.040058
Sum of electronic and thermal Energies= -2477.010527
Sum of electronic and thermal Enthalpies= -2477.009583
Sum of electronic and thermal Free Energies= -2477.104913

6.1.7.2 Computed Excitations of compound 3f-ss (PBE1PBE/6-31+G** PCM CH\(_2\)Cl\(_2\))

Excited State 1: Singlet-A  2.8611 eV  433.34 nm  \( f=0.1836 \)  \( <S^{**2}> = 0.000 \)

130 -> 131  0.69387

This state for optimization and/or second-order correction.

Total Energy, \( E(TD-HF/TD-KS) = -2477.39220185 \)

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A  3.2453 eV  382.05 nm  \( f=0.0793 \)  \( <S^{**2}> = 0.000 \)

130 -> 132  0.69921

Excited State 3: Singlet-A  3.5422 eV  350.02 nm  \( f=0.0036 \)  \( <S^{**2}> = 0.000 \)

130 -> 133  0.69737

Excited State 4: Singlet-A  3.7847 eV  327.59 nm  \( f=0.0095 \)  \( <S^{**2}> = 0.000 \)

130 -> 134  0.37801
130 -> 135  -0.34325
130 -> 136  0.42339
130 -> 137  0.18403
| Excited State | Singlet-A | $E$ (eV) | $\lambda$ (nm) | $f$ | $\langle S^2 \rangle$ | $|\langle \chi | S | \chi \rangle|^2$ |
|---------------|-----------|----------|----------------|-----|----------------------|----------------------------|
| 5             |           | 3.8607   | 321.14         | 0.0093 | 0.000                |
| 130 -> 134          | 0.55039       |          |                |     |                      |
| 130 -> 135          | 0.25241       | 0.24563  |                |     |                      |
| 130 -> 137          | 0.18212       | 0.11002  |                |     |                      |
| 130 -> 139          | 0.11002       |          |                |     |                      |
| 6             |           | 3.8972   | 318.14         | 0.0772 | 0.000                |
| 130 -> 135          | -0.18166      |          |                |     |                      |
| 130 -> 136          | -0.43305      |          |                |     |                      |
| 130 -> 137          | 0.46011       |          |                |     |                      |
| 130 -> 138          | -0.16726      |          |                |     |                      |
| 7             |           | 3.9486   | 314.00         | 0.0579 | 0.000                |
| 130 -> 135          | 0.51009       |          |                |     |                      |
| 130 -> 136          | 0.22482       |          |                |     |                      |
| 130 -> 137          | 0.38476       |          |                |     |                      |
| 8             |           | 4.0929   | 302.92         | 0.0962 | 0.000                |
| 128 -> 132          | 0.10276       |          |                |     |                      |
| 129 -> 131          | 0.68392       |          |                |     |                      |
| 9             |           | 4.1765   | 296.86         | 1.2881 | 0.000                |
| 128 -> 131          | 0.31609       |          |                |     |                      |
| 129 -> 132          | 0.60457       |          |                |     |                      |
| 130 -> 139          | -0.10562      |          |                |     |                      |
| 10            |           | 4.2531   | 291.51         | 0.0337 | 0.000                |
| 128 -> 131          | -0.12212      |          |                |     |                      |
| 130 -> 134          | 0.14769       |          |                |     |                      |
6.1.7.3 Computed xyz-Coordinates of $T_1$ of compound 3f-ss (uPBE1PBE/6-31G** PCM toluene)

Figure S59. Optimized $T_1$ geometry of 3f-ss (uB3LYP/6-311G* PCM CH₂Cl₂).

C  1.22689 -1.75279  0.17343
C  1.19922 -0.37591  0.00807
N  0.02895  0.36561  0.36561
C  1.20929 -0.23669 -0.18356
C  1.30103 -1.67363 -0.45796
S  0.16187 -2.78028  0.27063
C  2.43669  0.37650  0.04925
C  3.53997 -0.48342  0.20640
S  2.98454 -2.14207 -0.60729
S  2.85170 -2.35594  0.22012
C  3.50765 -0.74577  0.06628
C  2.50952  0.18332 -0.05293
C  4.95243 -0.52982  0.05496
C  0.09454  1.78986  0.03997
C  4.93058 -0.19477 -0.08907
C  5.50329  0.56574 -0.61945
C  6.87327  0.80241 -0.62797
C  7.73290 -0.07611  0.03731
C  7.19903 -1.18383  0.70678
C  5.83383 -1.40168  0.71653
| Element | x    | y    | z    |
|---------|------|------|------|
| C       | 0.46301 | 2.37302 | 1.25103 |
| C       | 0.52652 | 3.75990 | 1.35183 |
| C       | 0.21288 | 4.55655 | 0.25328 |
| C       | -0.16165 | 3.96619 | -0.95223 |
| C       | -0.21963 | 2.58061 | -1.06418 |
| C       | -5.91412 | -1.20336 | -0.19765 |
| C       | -7.27097 | -0.92494 | -0.09694 |
| C       | -7.70014 | 0.38690 | 0.11674 |
| C       | -6.74327 | 1.40946 | 0.22833 |
| C       | -5.39891 | 1.12850 | 0.12987 |
| O       | 9.07812 | 0.05471 | 0.08904 |
| O       | -8.99630 | 0.77308 | 0.22924 |
| C       | 9.66024 | 1.16237 | -0.56658 |
| C       | -9.98796 | -0.22475 | 0.12465 |
| H       | -2.54784 | 1.43315 | 0.15850 |
| H       | 2.69822 | 1.24524 | -0.14715 |
| H       | 4.85183 | 1.23915 | -1.16854 |
| H       | 7.25853 | 1.66085 | -1.16608 |
| H       | 7.87733 | -1.85536 | 1.22304 |
| H       | 5.43969 | -2.25297 | 1.26544 |
| H       | 0.69575 | 1.73896 | 2.10100 |
| H       | 0.81387 | 4.21709 | 2.29374 |
| H       | 0.25964 | 5.63818 | 0.33623 |
| H       | -0.40309 | 4.58490 | -1.81115 |
| H       | -0.50514 | 2.10424 | -1.99690 |
| H       | -5.61037 | -2.23488 | -0.35544 |
| H       | -7.98324 | -1.73756 | -0.18567 |
| H       | -7.08985 | 2.42490 | 0.39437 |
| H       | -4.68810 | 1.94392 | 0.21901 |
| H       | 10.73420 | 1.08472 | -0.39556 |
| H       | 9.29678 | 2.11116 | -0.15343 |

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|       |       |       |       |
|-------|-------|-------|-------|
| H     | 9.46482 | 1.14021 | -1.64559 |
| H     | -10.94550 | 0.28424 | 0.24091 |
| H     | -9.88488 | -0.98159 | 0.91245 |
| H     | -9.96064 | -0.72082 | -0.85373 |

SCF Done: E(UPBE1PBE) = -2477.39194507 A.U. after 1 cycles
Zero-point correction= 0.419881 (Hartree/Particle)
Thermal correction to Energy= 0.449732
Thermal correction to Enthalpy= 0.450676
Thermal correction to Gibbs Free Energy= 0.354422
Sum of electronic and zero-point Energies= -2476.972064
Sum of electronic and thermal Energies= -2476.942213
Sum of electronic and thermal Enthalpies= -2476.941269
Sum of electronic and thermal Free Energies= -2477.037523

6.1.7.4 Computed Excitations of T_1 (Emission of T_1) of compound 3f-ss (uPBE1PBE/6-31G** PCM toluene)

| Excited State |       |       |
|---------------|-------|-------|
| Excited State 1: Triplet-A | 0.7782 eV 1593.26 nm f=0.0000  <S**2>=2.000 |
| 129 ->131     | 0.20202 |
| 130 ->131     | 0.70266 |
| 129 <131      | 0.11126 |
| 130 <131      | 0.24156 |

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2477.40491166
Copying the excited state density for this state as the 1-particle RhoCl density.

| Excited State 2: Triplet-A | 2.0005 eV 619.78 nm f=0.0000  <S**2>=2.000 |
|---------------------------|---------------------------------------------|
| 129 ->131                | 0.28191 |
| 129 ->132                | -0.17267 |
| 130 ->132                | 0.57179 |
6.1.7.5 Computed xyz-Coordinates of radical cation of compound 3f-ss (uB3LYP/6-311G*)

![Optimized ground state geometry of radical cation of 3f-ss (uB3LYP/6-311G* PCM CH₂Cl₂).](image)

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 1.21492    | -0.41250   | 0.01692    |
| C       | 1.27599    | -1.80792   | 0.01022    |
| S       | -0.06417   | -2.90948   | 0.01366    |
| C       | -1.34338   | -1.73798   | 0.03064    |
| C       | -1.20748   | -0.34795   | 0.04302    |
| N       | 0.02173    | 0.29616    | 0.03508    |
| C       | 2.50512    | 0.17819    | 0.02655    |
| C       | 3.53412    | -0.73464   | 0.02103    |
| S       | 2.91278    | -2.38377   | -0.00960   |
| S       | -3.00910   | -2.22517   | 0.04338    |
| C       | -3.54083   | -0.54474   | 0.03322    |
| C       | -2.46417   | 0.31120    | 0.04150    |
| C       | 4.96770    | -0.49300   | 0.01829    |
| C       | 0.05994    | 1.74544    | 0.04552    |
| C       | -4.95819   | -0.22190   | 0.03605    |
| C       | 5.88393    | -1.45709   | 0.48941    |
| C       | 7.24065    | -1.21305   | 0.48885    |
| C       | 7.74267    | 0.01156    | 0.01500    |
| C       | 6.84739    | 0.98148    | -0.46059   |
| C       | 5.48435    | 0.72394    | -0.45652   |
| C       | 0.07799    | 2.43756    | -1.16348   |
| C       | 0.11297    | 3.83048    | -1.14800   |
| C       | 0.12976    | 4.51642    | 0.06557    |
| C       | 0.11211    | 3.81300    | 1.26908    |
C   0.07667   2.42001   1.26443
C  -5.40437   1.02961   0.51409
C  -6.74285   1.35695   0.51074
C  -7.69929   0.44397   0.03049
C  -7.27560  -0.80587  -0.44319
C  -5.92481  -1.12349  -0.43664
O   9.07957   0.15127   0.05713
C   9.67402  -1.36706  -0.39772
O  -8.97707   0.86099   0.06984
C -10.01304  -0.00731  -0.39114
H   2.66379   1.24530   0.07435
H  -2.56533   1.38589   0.00998
H   5.52625  -2.40119   0.88789
H   7.94422  -1.94913   0.85919
H   7.20410   1.92781  -0.84544
H   4.81394   1.47544  -0.85883
H   0.06269   1.89224  -2.10083
H   0.12543   4.37756  -2.08405
H   0.15618   5.60043   0.07346
H   0.12591   4.34640   2.21295
H   0.06285   1.86122   2.19384
H  -4.69246   1.74016   0.91887
H  -7.08872   2.31265   0.88663
H  -7.98506  -1.52804  -0.82511
H  -5.62238  -2.08644  -0.83614
H  10.74396   1.23794  -0.25637
H   9.46415   1.53610  -1.45763
H   9.32809   2.21988   0.19312
H  -10.93798   0.54789  -0.25834
H  -9.88149  -0.24970  -1.44935
H  -10.05003  -0.92557   0.20153
SCF Done: E(UB3LYP) = -2479.48581251  A.U. after 1 cycles
Zero-point correction= 0.417793 (Hartree/Particle)
Thermal correction to Energy= 0.447492
Thermal correction to Enthalpy= 0.448436
Thermal correction to Gibbs Free Energy= 0.353052
Sum of electronic and zero-point Energies= -2479.068019
Sum of electronic and thermal Energies= -2479.038320
Sum of electronic and thermal Enthalpies= -2479.037376
Sum of electronic and thermal Free Energies= -2479.132760

6.1.7.6 Computed xyz-Coordinates of dication (S₀) of compound 3f-sS (uB3LYP/6-311G*)

![Figure S61. Optimized ground state geometry of dication of 3f-sS (uB3LYP/6-311G* PCM CH₂Cl₂).](image)

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 1.21910 | -0.37505| 0.00003 |
| C       | 1.27559 | -1.79408| 0.00004 |
| S       | -0.06736| -2.83924| -0.00005|
| C       | -1.34850| -1.71917| -0.00012|
| C       | -1.21021| -0.30580| 0.00003 |
| N       | 0.02299 | 0.31744 | 0.00008 |
| C       | 2.49665 | 0.19834 | 0.00004 |
| C       | 3.53464 | -0.72963| 0.00006 |
| S       | 2.89891 | -2.38620| -0.00000|
| S       | -3.00364| -2.21658| -0.00027|
| C       | -3.54253| -0.52589| -0.00006|
| C       | -2.45283| 0.34012 | 0.00007 |
| C       | 4.94705 | -0.50828| 0.00009 |
| Element | X  | Y  | Z     |
|---------|----|----|-------|
| C       | 0.06371 | 1.77516 | 0.00015 |
| C       | -4.93779 | -0.21465 | -0.00011 |
| C       | 5.87548  | -1.58649 | 0.00051  |
| C       | 7.22615  | -1.36450 | 0.00047  |
| C       | 7.73212  | -0.04102 | -0.00000 |
| C       | 6.82870  | 1.04730  | -0.00038 |
| C       | 5.47326  | 0.80991  | -0.00034 |
| C       | 0.08156  | 2.45207  | -1.21743 |
| C       | 0.11810  | 3.84537  | -1.20954 |
| C       | 0.13591  | 4.53886  | 0.00028  |
| C       | 0.11816  | 3.84526  | 1.21003  |
| C       | 0.08161  | 2.45195  | 1.21779  |
| C       | -5.37863 | 1.13953  | -0.00045 |
| C       | -6.71152 | 1.45043  | -0.00045 |
| C       | -7.68876 | 0.42319  | -0.00010 |
| C       | -7.27434 | -0.92821 | 0.00022  |
| C       | -5.93088 | -1.22694 | 0.00020  |
| O       | 9.04863  | 0.06684  | -0.00005 |
| C       | 9.69176  | 1.35723  | -0.00043 |
| O       | -8.94527 | 0.83038  | -0.00010 |
| C       | -10.03454| -0.11520 | 0.00025  |
| H       | 2.65566  | 1.26566  | 0.00011  |
| H       | -2.55126 | 1.41463  | 0.00025  |
| H       | 5.52703  | -2.61433 | 0.00094  |
| H       | 7.93510  | -2.18336 | 0.00081  |
| H       | 7.19145  | 2.06645  | -0.00074 |
| H       | 4.80518  | 1.66262  | -0.00069 |
| H       | 0.06630  | 1.90289  | -2.15271 |
| H       | 0.13159  | 4.38619  | -2.14889 |
| H       | 0.16313  | 5.62261  | 0.00032  |
| H       | 0.13170  | 4.38599  | 2.14943  |

S103
H  0.06643  1.90270  2.15303
H -4.65962  1.94946  -0.00077
H -7.05307  2.47840  -0.00073
H -7.99953 -1.73079   0.00048
H -5.64651 -2.27453   0.00047
H  10.75561  1.14158  -0.00029
H  9.42541  1.91547  -0.89969
H  9.42530  1.91605   0.89845
H -10.93441  0.49182  -0.89861
H -10.00209 -0.73328  -0.89861
H -10.00188 -0.73286   0.89939

SCF Done:  E(UB3LYP) = -2479.15864278 A.U. after 3 cycles
Zero-point correction= 0.418284 (Hartree/Particle)
Thermal correction to Energy= 0.448010
Thermal correction to Enthalpy= 0.448954
Thermal correction to Gibbs Free Energy= 0.354457
Sum of electronic and zero-point Energies= -2478.740359
Sum of electronic and thermal Energies= -2478.710633
Sum of electronic and thermal Enthalpies= -2478.709689
Sum of electronic and thermal Free Energies= -2478.804186

6.1.7.7 Reoptimization of compound 3f-ss (uB3LYP/6-311G*)
Compound 3f-ss in the gas phase (uB3LYP/6-311G*):
SCF Done:  E(UB3LYP) = -2479.68816136 A.U. after 1 cycles
Zero-point correction= 0.416387 (Hartree/Particle)
Zero-point correction= 0.416890 (Hartree/Particle)
Thermal correction to Energy= 0.446626
Thermal correction to Enthalpy= 0.447570
Thermal correction to Gibbs Free Energy= 0.352366
Sum of electronic and zero-point Energies= -2479.271272
Sum of electronic and thermal Energies= -2479.241535
Sum of electronic and thermal Enthalpies= -2479.240591
Sum of electronic and thermal Free Energies= -2479.335795

S104
Compound 3f-ss in CH$_2$Cl$_2$ (uB3LYP/6-311G* SMD CH$_2$Cl$_2$):  
SCF Done:  $E$(UB3LYP) = -2479.72783635 A.U. after 14 cycles

Radical cation of compound 3f-ss in CH$_2$Cl$_2$ (uB3LYP/6-311G* SMD CH$_2$Cl$_2$):  
SCF Done:  $E$(UB3LYP) = -2479.56579036 A.U. after 20 cycles

Dication of compound 3f-ss in CH$_2$Cl$_2$ (uB3LYP/6-311G* SMD CH$_2$Cl$_2$):  
SCF Done:  $E$(UB3LYP) = -2479.36192183 A.U. after 16 cycles

6.1.7.8 Computed xyz-Coordinates of transition state of the anisyl rotation of compound 3f-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$)

Figure S62. Optimized geometry of the transition state of the anisyl rotation of 3f-ss (PBE1PBE/6-31G** PCM CH$_2$Cl$_2$).

\[
\begin{array}{ccc}
C & -1.20275 & -0.23500 & -0.76645 \\
C & -1.28035 & -1.59067 & -0.97585 \\
S & 0.00925 & -2.55614 & -1.69448 \\
C & 1.30335 & -1.55048 & -1.04921 \\
C & 1.19384 & -0.19766 & -0.83271 \\
N & -0.02021 & 0.49128 & -0.98814 \\
C & -2.42691 & 0.30323 & -0.26534 \\
C & -3.40373 & -0.63905 & -0.09434 \\
S & -2.82410 & -2.22107 & -0.52139 \\
S & 2.88467 & -2.13428 & -0.66419 \\
C & 3.43131 & -0.53618 & -0.24173 \\
C & 2.41343 & 0.37622 & -0.37278 \\
\end{array}
\]

S105
|   |       |       |       |
|---|-------|-------|-------|
| C | -4.78609 | -0.45042 | 0.39004 |
| C | -0.02934 | 1.91380 | -0.84140 |
| C | 4.81038 | -0.29814 | 0.18129 |
| C | -5.08446 | -0.52129 | 1.75865 |
| C | -6.37810 | -0.33442 | 2.21573 |
| C | -7.41428 | -0.07383 | 1.31012 |
| C | -7.13489 | -0.00220 | -0.05719 |
| C | -5.82873 | -0.19250 | -0.50187 |
| C | -0.09026 | 2.50310 | 0.42346 |
| C | -0.09358 | 3.89027 | 0.54058 |
| C | -0.03006 | 4.68799 | -0.60049 |
| C | 0.03580 | 4.09808 | -1.86063 |
| C | 0.03585 | 2.71088 | -1.98273 |
| C | 5.40659 | 0.96132 | -0.00872 |
| C | 6.70361 | 1.20783 | 0.40182 |
| C | 7.45997 | 0.19543 | 1.00714 |
| C | 6.88954 | -1.06590 | 1.19503 |
| C | 5.57891 | -1.29655 | 0.78926 |
| O | -8.64267 | 0.09273 | 1.85248 |
| C | -9.72358 | 0.35347 | 0.97734 |
| O | 8.71899 | 0.53317 | 1.36925 |
| C | 9.52220 | -0.46174 | 1.97544 |
| H | -2.57951 | 1.35197 | -0.04201 |
| H | 2.52120 | 1.42429 | -0.12187 |
| H | -4.28754 | -0.72333 | 2.46845 |
| H | -6.61242 | -0.38610 | 3.27430 |
| H | -7.91801 | 0.19962 | -0.77881 |
| H | -5.61722 | -0.13580 | -1.56580 |
| H | -0.13421 | 1.87120 | 1.30591 |
| H | -0.14289 | 4.34776 | 1.52412 |
| H | -0.03137 | 5.76985 | -0.50667 |
H 0.08558  4.71753  -2.75105
H 0.08253  2.23373  -2.95671
H 4.84821  1.75105  -0.50253
H 7.16180  2.18012   0.25053
H 7.44695  -1.86806  1.66445
H 5.14402  -2.27599   0.97163
H -10.60705  0.44869  1.60887
H -9.57482  1.28689   0.42196
H -9.87369  -0.46892   0.26812
H 10.48301  0.01008  2.18182
H 9.08341  -0.81387  2.91643
H 9.67585  -1.31653  1.30638

SCF Done:  E(RPBE1PBE) = -2477.45719525  A.U. after  1 cycles

Zero-point correction= 0.421950 (Hartree/Particle)
Thermal correction to Energy= 0.450633
Thermal correction to Enthalpy= 0.451577
Thermal correction to Gibbs Free Energy= 0.358402
Sum of electronic and zero-point Energies= -2477.035246
Sum of electronic and thermal Energies= -2477.006562
Sum of electronic and thermal Enthalpies= -2477.005618
Sum of electronic and thermal Free Energies= -2477.098793
6.2 DFT-Calculation of the redox potentials of compounds 3 and 6

In addition to the experimental determination via cyclic voltammetry the redox potentials were also calculated adapting a literature procedure (equation 3) based on DFT methods (Tables 4 and 5).\[^{19}\]

\[
E_{\text{redox}} = \frac{\Delta G_{\text{redox (solv)}}}{-F} = \frac{\Delta G_{\text{redox (gas)}} + \Delta G_{\text{solv (ox)}} - \Delta G_{\text{solv (red)}}}{-F}
\]

(eq. 3)

\(E_{\text{redox}}\)\hspace{1cm} redox potential vs. vacuum

\(\Delta G_{\text{redox (solv/gas)}}\)\hspace{1cm} free enthalpy of oxidation in solution/gas phase

\(\Delta G_{\text{solv (ox/red)}}\)\hspace{1cm} free enthalpy of solvation of the oxidized/reduced compound

\(F\)\hspace{1cm} Faraday constant (23.06 kcal mol\(^{-1}\) V\(^{-1}\))

\(\Delta G_{\text{solv (gas)}}, \Delta G_{\text{solv (solv)}}\) and \(\Delta G_{\text{redox (gas)}}\) were calculated from the values of the free enthalpies obtained from the geometry optimizations given in chapter 6.1 (uB3LYP/6-311G* SMD CH\(_2\)Cl\(_2\)). The SMD solvation model\[^{18}\] with dichloromethane as a solvent was applied to determine the solvation enthalpies, since all experimental determined oxidation potentials were measured in dichloromethane solutions.

### Table S4. Calculated \(\Delta G_{\text{solv}}, \Delta G_{\text{redox}}\) and \(E_{\text{redox}}^{0+/1}\) of compounds 3 and 6 (uB3LYP/6-311G* SMD CH\(_2\)Cl\(_2\)).

| Compound | \(\Delta G_{\text{redox (gas)}}\) [kcal/mol] | \(\Delta G_{\text{solv (red)}}\) [kcal/mol] | \(\Delta G_{\text{solv (ox)}}\) [kcal/mol] | \(\Delta G_{\text{redox (solv)}}\) [kcal/mol] | \(E_{\text{redox}}^{0+/1}\) vs. vacuum [V] |
|----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 3a-aa    | 160.1807                        | -26.1862                        | -64.3391                        | 122.1807                        | 5.3018                          |
| 3b-ss    | 160.5927                        | -25.2716                        | -64.8558                        | 121.0085                        | 5.2509                          |
| 6        | 165.8539                        | -27.3339                        | -68.3648                        | 124.8231                        | 5.4165                          |
| 3c-aa    | 143.2015                        | -28.4902                        | -63.0470                        | 108.6446                        | 4.7144                          |
| 3d-ss    | 143.6312                        | -27.6796                        | -62.6710                        | 108.6398                        | 4.7142                          |
| 3e-aa    | 126.3086                        | -24.8821                        | -50.6263                        | 100.5644                        | 4.3638                          |
| 3f-ss    | 127.0476                        | -24.8798                        | -50.1533                        | 102.0476                        | 4.4282                          |
Table S5. Calculated $\Delta G_{\text{solv}}$, $\Delta G_{\text{redox}}$ and $E_{\text{redox}}^{+1/+2}$ of compounds 3 and 6 (uB3LYP/6-311G* SMD CH$_2$Cl$_2$).

| Compound | $\Delta G_{\text{redox}}$ (gas) [kcal/mol] | $\Delta G_{\text{solv}}$ (red) [kcal/mol] | $\Delta G_{\text{solv}}$ (ox) [kcal/mol] | $\Delta G_{\text{redox}}$ (solv) [kcal/mol] | $E_{\text{redox}}^{+1/+2}$ vs. vacuum [V] |
|----------|-------------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|---------------------------------|
| 3a-aa    | 245.6212                                  | -64.3391                             | -159.041                             | 150.9188                            | 6.5488                          |
| 3b-ss    | 247.3976                                  | -64.8558                             | -161.2460                            | 151.3976                            | 6.5696                          |
| 6        | 249.6894                                  | -68.3648                             | -165.0930                            | 152.9261                            | 6.6375                          |
| 3c-aa    | 223.9806                                  | -63.0470                             | -151.1170                            | 135.9105                            | 5.8976                          |
| 3d-ss    | 228.1522                                  | -62.6710                             | -151.2974                            | 139.1522                            | 6.0382                          |
| 3e-aa    | 200.8855                                  | -50.6263                             | -127.5750                            | 123.9366                            | 5.3780                          |
| 3f-ss    | 206.0458                                  | -50.1533                             | -127.4740                            | 128.7249                            | 5.5858                          |

The calculated redox potentials reproduce the experimental data correctly as indicated by linear correlation (Figure S63).

Figure S63. Correlation of the experimental oxidation potentials (0.1 M [Bu$_4$N][PF$_6$], $\nu = 100$ mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, [Me$_{10}$Fc]/[Me$_{10}$Fc]$^+$ as an internal standard; Me$_{10}$Fc = decamethylferrocene, $E_{0,+1}$ = -95 mV vs. ferrocene with $E_{0,+1}(\text{Fc/Fc}^+)=450$ mV) of the monooxidation $E_{0,+1}$ (red) and the dioxidation $E_{+1/+2}$ (blue) with the calculated redox potentials $E^{\text{cal}}$ respectively (uB3LYP/6-311G* SMD CH$_2$Cl$_2$) of the compounds 3 and 6.
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