SUPPLEMENTARY MATERIAL

Deprotonation of benzoxazolium salt: trapping of a radical-cation intermediate

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Materials and methods

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk-line interfaced to a high-vacuum (10^{-3} mbar) line, or in an argon-filled MBraun glovebox. THF and diethyl ether were distilled under nitrogen from potassium benzophenone ketyl prior to use. Methanol was refluxed with freshly prepared sodium methylate and distilled under nitrogen prior to use. n-Hexane was refluxed over Na/K alloy and distilled off under nitrogen prior to use. All solvents for vacuum-line manipulations were stored in vacuo (C_6D_6 over Na/K alloy) in resealable flasks.

Triethyl orthoformate (EtO)_3CH, tetrafluoroboric acid diethyl ether complex HBF_4·OEt_2 and sodium hydride NaH 60 % dispersion in mineral oil were purchased from Aldrich GmbH and used as received. t-BuOK was freshly prepared by means of dissolving potassium in tert-butanol with the following evaporation of unreacted alcohol excess to dryness in vacuum. 2,4-di-tert-butyl-6-((2,6-diisopropylphenyl)amino)phenol was prepared according to the following procedure: a sample of 4,6-di-tert-butyl-N-(2,6-di-isopropylphenyl)-o-benzoquinone (1 g, 2.64 mmol) was dissolved in methanol (50 ml) and 0.3 ml of hydrazine hydrate was slowly added to this solution. After gas release was complete, bright-yellow solution was diluted with 10 ml of water and allowed to stay at -18°C for a night. White crystalline solid was collected by filtration and dried at reduced pressure. Yield is 0.85 g (85%).

NMR spectra were recorded with a Bruker Avance DPX-200 (for 1) and a Bruker Avance II 300 (for 2). Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (^{1}H and ^{13}C{^{1}H} NMR spectroscopy).

IR spectra were obtained with a Fourier-IR spectrometer FSM-1201 in Nujol (for 1 and 3) and a Bruker FTIR Tensor 37 instrument by the attenuated total reflection method (ATR) (for 2).

X-band EPR spectrum of radical cation 2^{+} was measured in THF solution at 297 K with X-band EPR spectrometer Bruker EMX-8/2,7.

Elemental analyses (CHN) were carried out with a Euro EA 3000 analyzer (Eurovector).

Voltammetric measurements and controlled-potential electrolysis were carried out with a BASi Epsilon potentiostat/galvanostat (USA) at room temperature in THF/0.2 M Bu_4NBF_4 solutions with 1.5 \times 10^{-3} M substrate concentration under dry nitrogen atmosphere. Voltammograms were carried out with a platinum working electrode (0.07 cm^2), a platinum auxiliary electrode, and an Ag/AgNO_3 reference electrode. Scan rate was 100 mV/s. All potentials were referred against the ferrocenium/ferrocene redox couple. Controlled-potential electrolysis was carried out in a divided cell with a Pt working electrode, a platinum auxiliary electrode, and an Ag/AgNO_3 reference electrode at vigorous stirring.

UV/Vis spectrum of 2^{+}·BF_4^{-} was recorded at room temperature in THF in sealed 0.5 cm quartz cuvette with a Perkin Elmer Lambda 25 spectrophotometer.
UV/Vis spectra of reaction mixtures for redox and protonation reactions were recorded at room temperature in 1 cm quartz cuvette with a PerkinElmer Lambda 365 spectrometer. Spectra were registered with a scan speed of 480 nm min⁻¹, using a spectral width of 1 nm. The reaction mixtures were diluted to the appropriate concentration in each case in order to record UV/Vis spectra.

**Synthesis**

1. **5,7-Di-tert-butyl-3-(2,6-diisopropylphenyl)benzoazol-3-ium tetrafluoroborate (1)**
   A solution of HBF₄·OEt₂ (1.40 ml, d 1.19g/ml, 10.3 mmol) in 10 ml of MeOH was added to a solution of 2,4-di-tert-butyl-6-((2,6-diisopropylphenyl)amino)phenol (3.82 g, 10.0 mmol) in 40 ml of MeOH. The mixture was stirred for 1 h at room temperature and then the solvent was removed in vacuum. (EtO)₂CH (30 ml) was added. The resulting solution was stirred for 24 h at ambient temperature and then volatiles were removed in vacuum. A crude product was dissolved in ca. 30 ml of diethyl ether and the solution was allowed to store at -18°C overnight to give 4.28 g of 1 (89% yield) as colorless crystals suitable for X-ray diffraction which were collected by filtration. Anal. Calc. for C$_{27}$H$_{35}$BF$_4$NO (479.40): C, 67.65; H, 7.99; N, 3.47. Found: C, 67.28; H, 8.03; N, 2.84%. IR (Fig. S4), cm⁻¹: 1638(w), 1598(w), 1540(w), 1483(m), 1368(m), 1349(w), 1313(w), 1269(w), 1220(m), 1138(m), 1092(s), 1058(s), 929(w), 890(w), 858(w), 830(w), 814(w), 764(w), 756(w), 670(w), 628(w), 600(w), 578(w), 520(w), 462(w). $^1$H NMR (Fig. S7) (CDCl₃, 200 MHz, δ, ppm): 1.05 (d, $^3$I$_{HH}$ = 6.7 Hz, 6H, CH₃ of iPr), 1.27 (d, $^3$I$_{HH}$ = 6.7 Hz, 6H, CH₃ of iPr), 1.33 (s, 9H, tBu), 1.63 (s, 9H, tBu), 2.23 (sept, $^3$I$_{HH}$ = 6.7 Hz, 2H, CH of iPr), 7.04 (d, $^4$I$_{HH}$ = 1.7 Hz, 1H, arom. C₆H₅), 7.45-7.49 (m, 2H, arom. C₆H₅), 7.68-7.72 (m, 1H, arom. C₆H₅), 7.77 (d, $^3$I$_{HH}$ = 1.7 Hz, 1H, arom. C₆H₅), 10.34 (s, 1H, CH). $^{13}$C{¹H} NMR (Fig. S8) (CDCl₃, 50 MHz, δ, ppm): 23.97 (CH₃ of iPr), 24.32 (CH₃ of iPr), 28.99 (CH of iPr), 30.01 (CH₃ of tBu), 31.39 (CH₃ of tBu), 35.21 (C of tBu), 35.91 (C of tBu), 107.73 (CH, arom. C₆H₅), 124.35 (CH, arom. C₆H₅), 125.61 (CH, arom. C₆H₅), 130.38 (α-C, arom. C₆H₅), 133.29 (CH, arom. C₆H₅), 138.78 (i-C, arom. C₆H₅), 145.60 (C(tBu), arom. C₆H₅), 145.69 (C(tBu), arom. C₆H₅), 154.41 (C-arom.-O), 157.19 (C-arom.-N), 193.23 (NCHO).

2. **(E)-5,5',7,7'-Tetra-tert-butyl-3,3'-bis(2,6-diisopropylphenyl)-3H,3'H-2,2'-bibenzo[d]-oxazolylidene (2)**
100 mg of 60% dispersion of sodium hydride in mineral oil was washed with n-hexane (5 ml) two times and dried in vacuum to afford ca. 60 mg (2.5 mmol) of oil-free NaH. A solution of benzoazolium salt 1 (0.96 g, 2 mmol) in 30 ml of THF was added to oil-free sodium hydride. The resulting solution turned fuchsia-pink immediately. The mixture was stirred for 2 h while an intensive evolution of gas and simultaneous precipitation of sodium tetrafluoroborate was observing. The gas evolution has been slowing down and the color has been changing over red-orange to yellow-greenish gradually during the stirring within next 5 h. NaBF₄ was filtered off. THF was slow evaporated to ca. 5 ml to obtain the compound 2 as pale-yellow crystals suitable for single crystal X-ray diffraction analysis which were collected by filtration, washed with cold THF and dried in vacuum (0.52 g, yield 67 %). Anal. Calc. for C$_{58}$H$_{74}$N$_2$O$_2$ (783.18): C, 82.81; H, 9.52; N, 3.58. Found: C, 82.63; H, 9.39; N, 3.47%. IR (Fig. S5), cm⁻¹: 1694(w), 1654(w), 1527(w), 1594(m), 1464(s), 1423(s), 1388(w), 1360(m), 1336(w), 1287(s), 1225(s), 1196(s), 1154(w), 1106(s), 1002(m), 932(w), 881(w), 841(m), 803(m), 766(m), 742(w), 657(w), 631(w), 600(w), 461(w), 429(w). $^1$H NMR (Fig. S10) (CD$_6$D$_6$, 300 MHz, δ, ppm): 1.04 (s, 9H, tBu), 1.15
(d, $^{3}J_{HH} = 6.9$ Hz, 6H, CH$_{3}$ of iPr), 1.17 (s, 9H, tBu), 1.41 (d, $^{3}J_{HH} = 6.9$ Hz, 6H, CH$_{3}$ of iPr), 1.41 (m, 4H, THF), 3.48 (sept, $^{3}J_{HH} = 6.9$ Hz, 2H, CH of iPr), 3.58 (m, 4H, THF), 6.11 (d, $^{4}J_{HH} = 1.9$ Hz, 1H, arom. C$_{6}$H$_{2}$), 6.77 (d, $^{4}J_{HH} = 1.9$ Hz, 1H, arom. C$_{6}$H$_{2}$), 7.18-7.26 (m, 3H, arom. C$_{6}$H$_{3}$). $^{13}$C($^{1}$H) NMR (Fig. S11) (C$_{6}$D$_{6}$, 75 MHz, $\delta$, ppm): 24.20 (CH$_{3}$ of iPr), 24.36 (CH$_{3}$ of iPr), 25.82 (THF), 29.01 (CH of iPr), 30.31 (CH$_{3}$ of tBu), 31.73 (CH$_{2}$ of tBu), 33.74 (C of tBu), 34.82 (C of tBu), 67.83 (THF), 100.81 (C=C), 124.77 (CH, arom. C$_{6}$H$_{2}$), 126.28 (CH, arom. C$_{6}$H$_{3}$), 129.35 (CH, arom. C$_{6}$H$_{2}$), 132.74 (o-C, arom. C$_{6}$H$_{3}$), 138.45 (CH, arom. C$_{6}$H$_{2}$), 141.32 (i-C, arom. C$_{6}$H$_{3}$), 143.85 (C$_{arom}$-N), 145.36 (C$_{arom}$-O), 148.88 (C(tBu), arom. C$_{6}$H$_{2}$).

3. Tetrafluoroborate salt of radical-cation $2^{+}$ (2$^{+}$·BF$_{4}$)

The suspension of benzoxazolium salt 1 (0.48 g, 1 mmol) in 20 ml of toluene was added to a mixture of oil-free sodium hydride (60 mg, 2.5 mmol) and t-BuOK (ca. 15 mg, 0.13 mmol). The mixture was shook for 10 days. The gas was evolved very slowly and the solvent remained nearly colorless while a small amount of fuchsia-pink rhomb shape crystals of 2$^{+}$·BF$_{4}$ were formed. The crystals of 2$^{+}$·BF$_{4}$ (45 mg, yield 10%) were separated by hand from the mixture of insoluble powdery starting materials and sodium tetrafluoroborate and used for single crystal X-ray diffraction as well as other analyses. Anal. Calc. for C$_{54}$H$_{74}$BF$_{5}$O$_{2}$ (870.00): C, 74.55; H, 8.57; N, 3.22. Found: C, 74.06; H, 8.4

X-ray crystallography

The diffraction data for 1 were collected on a Oxford Diffraction Gemini S diffractometer with MoKα radiation ($\lambda = 0.71073$, graphite monochromator) by doing $\omega$ scan of narrow (1.0°) frames at room temperature. The diffraction data for 2 were collected on a STOE IPDS 2 diffractometer with MoKα radiation ($\lambda = 0.71073$, graphite monochromator), STOE image plate (34 cm diameter), by rotation method at 150 K. Absorption correction was done numerically using multifaceted crystal model based [1] in CrysAlisPro software [2] and empirically using SADABS [3].

Structures were solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2017/1 [4] in ShelXle program [5]. Hydrogen atoms placed in calculated positions and refined in the “riding-model”.

The diffraction data for 2$^{+}$·BF$_{4}$ were collected on a Bruker X8 Apex diffractometer with MoKα radiation ($\lambda = 0.71073$) by doing $\varphi$ and $\omega$ scans of narrow (0.5°) frames at 150 K. Absorption correction was done empirically using SADABS [3]. Crystallographic data and refinement details for 2$^{+}$·BF$_{4}$ are given in Table S1, main bond distances are summarized in Table S2. Structure was solved with SHELXT [6] and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXL 2017/1 [7] in ShelXle program [5]. Hydrogen atoms were refined in geometrically calculated positions.

The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition codes CCDC 1851514 (for 1), 1852042 (for 2) and 1883398 (for 2$^{+}$·BF$_{4}$). Crystallographic data and refinement details for 1, 2 and 2$^{+}$·BF$_{4}$ are given in Table S1.
Table S1. Crystallographic data and refinement details

|                          | 1                      | 2                      | 2⁺·BF₄⁻ |
|--------------------------|------------------------|------------------------|---------|
| Chemical formula         | C₂₇H₄₈BF₄NO            | C₅₄H₇₂N₂O₂            | C₅₃H₇₃BF₅N₂O₂ |
| Mᵣ                      | 479.39                 | 783.15                 | 869.96  |
| Crystal system, space group | Triclinic, P ̅T       | Orthorhombic, P 2₁ 2₁ 2₁ | Monoclinic, C2/c |
| Temperature (K)          | 298(2)                 | 150(2)                 | 150     |
| a, b, c (Å)              | 10.0842(11), 11.2186(11), 14.1105(10) | 10.7071(7), 19.5593(8), 22.8987(11) | 11.5751 (8), 21.0035 (19), 20.5205 (18) |
| α, β, γ (°)              | 72.875(8), 83.039(7), 63.876(10) | 90, 90, 90 | 96.432 (3) |
| V (Å³)                   | 1369.6(3)              | 4795.5(4)              | 4957.5 (7) |
| Z                        | 2                      | 4                      | 4       |
| Radiation type           | MoKα (λ = 0.71073 Å), Graphite | MoKα (λ = 0.71073 Å), Graphite | Mo Kα |
| μ (mm⁻¹)                 | 0.087                  | 0.064                  | 0.08    |
| Crystal size (mm)        | 0.2557 × 0.0839 × 0.0694 | 0.2257 × 0.0939 × 0.0594 | 0.35 × 0.22 × 0.10 |
| Diffractometer           | Oxford Diffraction Gemini S | STOE IPDS 2 | Bruker X8Apex |
| Absorption correction    | CrysAlisPro [Clark, R. C. & Reid, J. S. (1995), Acta Cryst. A51, 887-897] | SADABS [ Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.] | Multi-scan SADABS (Bruker-AXS, 2004) |
| Tmin, Tmax               | 0.983, 0.995           | 0.985, 0.998           | 0.546, 0.592 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 8050, 4631, 1518 | 43317, 11900, 4918 | 19821, 5961, 4233 |
| Rint                     | 0.0522                 | 0.1428                 | 0.036   |
| θ values (°)             | 3.358 — 24.708         | 1.779 — 28.281         | θmax = 28.3, θmin = 1.9 |
| (sinθ/λ)max (Å⁻¹)        | 0.5881                 | 0.6666                 | 0.667   |
| Range of h, k, l         | -11 ≤ h ≤ 11           | -14 ≤ h ≤ 14           | -15 ≤ h ≤ 9 |
|                          | -9 ≤ k ≤ 13            | -23 ≤ k ≤ 26           | -28 ≤ k ≤ 28 |
|                          | -16 ≤ l ≤ 16           | -30 ≤ l ≤ 30           | -27 ≤ l ≤ 26 |
| R[F² > 2σ(F²)], wR(F²), S | 0.0622, 0.1261, 0.749 | 0.0711, 0.1016, 0.803 | 0.061, 0.168, 1.06 |
| No. of reflections, parameters, restraints | 4631, 312, 0 | 11900, 543, 0 | 5961, 303, 0 |
| H-atom treatment         | H atoms treated by a mixture of independent and constrained refinement | H-atom parameters constrained | H-atom parameters constrained |
| Weighting scheme         | w=1/[σ²(Fo)² + (0.0588 P)²], where P=(Fo² + 2 Fc²)/3 | w=1/[σ²(Fo)² + (0.0380 P)²], where P=(Fo² + 2 Fc²)/3 | w = 1/[σ²(Fo)² + (0.063P)² + 7.7915P] |
|                          | where P=(Fo² + 2 Fc²)/3 |                           | where P = (Fo² + 2 Fc²)/3 |
| Δρmax, Δρmin (e Å⁻³)    | -0.195 / 0.464         | -0.282 / 0.173          | 0.32, -0.29 |
| CCDC                     | 1851514                | 1852042                | 1883398 |

Computer programs: SHELXS2014 (Sheldrick, 2014), SHELXL2014 (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014), SADABS (Sheldrick, 1996), CrysAlisPro (Oxford Diffraction, 2010), APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004).
Table S2. Selected bond lengths (Å) and angles (°) of 1, 2 and $2^{+} \cdot \text{BF}_4^{-}$

|          | 1         | 2         | $2^{+} \cdot \text{BF}_4^{-}$ |
|----------|-----------|-----------|-------------------------------|
| N1–C2   | 1.290(4)  | 1.409(5)  | 1.414(5)                     |
| O1–C2   | 1.311(4)  | 1.403(5)  | 1.402(5)                     |
| N1–C3   | 1.418(4)  | 1.390(5)  | 1.406(6)                     |
| O1–C1   | 1.403(4)  | 1.400(5)  | 1.402(5)                     |
| C1–C3   | 1.376(4)  | 1.395(5)  | 1.394(6)                     |
| C2–C2'  |           |           | 1.312(6)                     |
| N1–C2–O1| 114.4(4)  | 107.5(3)  | 108.0(4)                     |

Figure S1. Molecular structure of 1 omitting hydrogen atoms except H1. The thermal ellipsoids are drawn at 50% probability.

Figure S2. Molecular structure of 2 omitting hydrogen atoms. The thermal ellipsoids are drawn at 50% probability.
Figure S3. Molecular structure of $2^+\cdot\text{BF}_4^-$ omitting hydrogen atoms. The thermal ellipsoids are drawn at 50% probability.
**Figure S4.** IR spectrum of 1.

**Figure S5.** IR spectrum of 2.
Figure S6. IR spectrum of $2^+\cdot$BF$_4^-$.
Figure S7. $^1$H NMR (CDCl$_3$) of 1.

Figure S8. $^{13}$C($^1$H) NMR (CDCl$_3$) of 1.
Figure S9. $^{13}$C DEPT NMR (CDCl$_3$) of 1.

Figure S10. $^1$H NMR ($C_6D_6$) of 2.
Figure S11. $^{13}$C{${}^1$H} NMR (C$_6$D$_6$) of 2.
Figure S12. UV/vis spectrum of 2 in THF at room temperature.

Figure S13. UV/vis spectrum of $2^+\cdot\text{BF}_4^-$ in THF at room temperature.

Figure S14. Fuchsia-pink colored solution of $2^+\cdot\text{BF}_4^-$ in THF.
Computational details

The density functional theory (DFT) calculations were performed applying the Gaussian 09 program package [8] with the use of the UB3LYP functional [9] and 6-31g(d,p) basis set. The stationary points on the potential energy surfaces were located by full geometry optimization and checked for the stabilities of the DFT wave function. The calculations were performed without symmetry constraints. Electronic spectrum of $2^+$ was calculated by TD-DFT with taking into account for non-specific solvation (CPCM, solvent – THF). Structural visualizations in Figs. S15, 16 were produced with the program suite ChemCraft [10].

1. Geometry and energy characteristics of the carbene 3 and compound 2 are presented in Figure S15. Optimization of the geometry of 3 on the triplet and singlet potential energy surfaces has shown that the structure with closed electronic shell corresponds to the most stable state. Comparison of total energies of the dimer 2 and two monomers 3 indicated preference of the first one by 33.0 kcal/mol. Such a significant stabilization of the compound 2 explains difficulties with the isolation of the carbene 3.

![Figure S15. Geometry and energy characteristics of the compounds 3 and 2, according to the DFT UB3LYP/6-31g(d,p) calculations.](image)

$E_{\text{mol}} = -1181.17192254 \text{ a.u.}$

$E_{\text{mol}} = -2362.39637386 \text{ a.u.}$

2. Spin density distribution

![Figure S16. The Mulliken population analysis (left) and spin density distribution (right) of radical cation $2^+$ according to the DFT UB3LYP/6-31g(d,p) calculations.](image)
3. The TD-DFT UB3LYP/6-31g(d,p) calculated electronic spectrum of $2^+$ (with taking into account for non-specific solvation (CPCM, solvent – THF)) presented in Figure S17 is in a good agreement with the experimental one (Figure S13). The greatest contribution to the long-wave absorption comes from the LUMO-SOMO transition (97%).

![Figure S17. Electronic spectrum of $2^+$, according to the TD-DFT UB3LYP/6-31g(d,p) calculations with taking into account for non-specific solvation (CPCM, solvent – THF).](image-url)
Protonation and redox experiments

1. Reaction of 2 with HBF₄

A weighted sample of HBF₄·OEt₂ (0.1 ml, d 1.19g/ml, 0.07 mmol) was added to a solution of 2 (78.3 mg, 0.1 mmol) in 20 ml of THF with a microsyringe at room temperature. The pale yellow solution turned fuchsia-pink immediately with the simultaneous gas evolution. The formation of radical cation salt 2⁺·BF₄⁻ in the process was confirmed by UV/vis spectroscopy. The observed UV/vis spectrum of the reaction mixture (Figure S18) is identical to the UV/vis spectrum of 2⁺·BF₄⁻ (Figure S13).

![Figure S18. UV/vis spectrum of reaction mixture by the addition of HBF₄ to 2 in THF at room temperature.](image1)

2. Electrolysis of 2

During the controlled-potential electrolysis dioxadiazafulvalene 2 was successively oxidized in one (at -0.05 V) and two-electron (at 0.60 V) processes and UV/vis spectra of the products were recorded (Figure S19). The initial dioxadiazafulvalene 2 is pale-yellow colored and exhibits a broad absorption band in the UV region with \( \lambda_{\text{max}} = 372 \text{ nm} \). The product of one-electron oxidation shows two broad absorption bands in UV/vis region typical for radical cation salt 2⁺·BF₄⁻. The product of two-electron oxidation seems to be dication salt 2²⁺·2BF₄⁻ and shows only short-wave absorption lower than 320 nm. The mixing of the solution of two-electron oxidized product with the initial dioxadiazafulvalene 2 led to the fuchsia-pink coloration.

![Figure S19. UV/vis spectra of the dioxadiazafulvalene 2 (red line), radical cation salt 2⁺·BF₄⁻ (blue line) and dication salt 2²⁺·2BF₄⁻ (violet line) in THF at room temperature.](image2)
3. Oxidation of 2 with AgBF$_4$

1:1 reaction

A weighted sample of AgBF$_4$ (19.5 mg, 0.1 mmol) was added to a solution of 2 (78.3 mg, 0.1 mmol) in 20 ml of THF at room temperature with stirring. The pale yellow solution turned fuchsia-pink immediately and was stirred for 30 min. After filtration of a black precipitate of metallic silver the solution was examined with UV/vis spectroscopy and the typical UV/vis spectrum of radical cation salt 2$^+$·BF$_4^-$ was observed (Figure S20).

1:2 reaction

A weighted sample of AgBF$_4$ (39.0 mg, 0.2 mmol) was added to a solution of 2 (78.3 mg, 0.1 mmol) in 20 ml of THF at room temperature with stirring. The pale yellow solution turned fuchsia-pink immediately and then discolored. The mixture was stirred for 30 min. After filtration of a black precipitate of metallic silver the solution was examined with UV/vis spectroscopy and the typical absorption of dication salt 2$^{2+}$·2BF$_4^-$ was observed (Figure S20). The mixing of the obtained colorless solution with the initial dioxadiazafulvalene 2 led to the fuchsia-pink coloration.

Figure S20. UV/vis spectra of radical cation salt 2$^+$·BF$_4^-$ (blue line) and dication salt 2$^{2+}$·2BF$_4^-$ (violet line) in THF at room temperature.
References

1. Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897.

2. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171.NET) (compiled Jan 5 2010,16:28:46).

3. Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.

4. G.M. Sheldrick, Acta Cryst. Sect. A. 71 (2015) 3–8.

5. C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 44 (2011) 1281–1284.

6. G.M. Sheldrick, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8.

7. G.M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 71 (2015) 3–8.

8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2013.

9. A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652.

10. Chemcraft: http://www.chemcraftprog.com