Supporting Information for:

**Isolable Zwitterionic Pyridinio-semiquinone π-Radicals. Mild and Efficient Single-Step Access to Stable Radicals**

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Experimental section

Materials
All chemicals and solvents were purchased from commercial sources and were used without further purification.

Physical measurements
FT-IR data were collected on a Perkin-Elmer Spectrum One spectrometer. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. Mass spectra were recorded on an Applied Biosystems/Sciex Qstar Pulsar for ESI.
Typical procedure for the synthesis of compound 1.

In a vial covered with aluminum foil, DDQ (227 mg, 1 mmol) was dissolved in 5 ml alcohol, and then pyridine (0.6 ml, 7.5 mmol) was dropwise added. The mixture was kept at room temperature for 2 h. The resulting precipitate was separated by centrifugation, washed successively with MeOH (3×10 ml) and dichloromethane (3×10 ml). A dark-red crystalline product was obtained.

Compound 1a: 120 mg, yield 45%; Selected IR data (cm⁻¹, KBr pellet): 3435, 2208, 1627, 1567, 1485, 1302, 1197, 761, 681. UV-vis in CH₃CN, λmax (nm): 255, 340, 420, 445, 550, 590. ESI-MS (positive) calcd for C₁₄H₈N₃O₃ 266.06 ([M]+), 268.07 ([M+2H]+), found 266.04 and 268.06, respectively.

Compound 1b: 82 mg, yield 28%; Selected IR data (cm⁻¹, KBr pellet): 3435, 2205, 1628, 1581, 1472, 1301, 1193, 760, 680. UV-vis in CH₃CN, λmax (nm): 250, 340, 410, 445, 540, 590. ESI-MS (positive) calcd for C₁₆H₁₂N₃O₃ 294.09 ([M]+), 296.10 ([M+2H]+), found 294.10 and 296.12, respectively.

Compound 1c: 135 mg, yield 44%; Selected IR data (cm⁻¹, KBr pellet): 3434, 2215, 1625, 1550, 1473, 1304, 1188, 1124, 1019, 761, 675. UV-vis in CH₃CN, λmax (nm): 244, 340, 410, 444, 545, 590. ESI-MS (positive) calcd for C₁₆H₁₂N₃O₄ 310.08 ([M]+), 312.10 ([M+2H]+), found 310.09 and 312.11, respectively.
Figure S1. Packing diagram of 1a, showing the hydrogen bonds CH (pyridinium ring)⋅⋅⋅O. Solvent molecules are omitted for clarity.
Figure S2. X-ray crystal structure of 1b (ORTEP, thermal ellipsoids set at the 50% probability level).

Figure S3. The $bc$-projection of the crystal structure of 1b, showing the hydrogen bonds CH(pyridium ring)···O.
Figure S4. X-ray crystal structure of 1c (ORTEP, thermal ellipsoids set at the 50% probability level).

Figure S5. Crystal packing of 1c, showing the hydrogen bonds CH(pyridium ring)···NC and CH(pyridium ring)···O as well as CH(CH$_3$)···O.
Figure S6. Cyclic voltammograms of 1b (5×10⁻⁴ M) in CH₃CN, supporting electrolyte 0.1 M (Bu₄N)PF₆, scan rate 100 mV s⁻¹.

Figure S7. Cyclic voltammograms of 1c (5×10⁻⁴ M) in CH₃CN, supporting electrolyte 0.1 M (Bu₄N)PF₆, scan rate 100 mV s⁻¹.
**Figure S8.** Electronic absorption spectrum of 1a (black line), 1b (red line), and 1c (blue line) in CH$_3$CN solution at room temperature.

**Figure S9.** UV-vis spectrum of 1a in the solid state (KBr pellet).
Figure S10. EPR spectrum of 1a in DMF.

Figure S11. EPR spectrum of 1b in DMF.
Figure S12. EPR spectrum of 1c in DMF.

Figure S13. Spin density distribution of 1a.