Supporting Information 1. Cyclic voltammograms of a CH₃CN solution containing the mixture of Py (0.1 M) and TNF (2 mM) in the presence of 0.1 M of TEAP at 20 °C. Scan rate: a, 10; b, 20; c, 50; d, 100; e, 200 mV s⁻¹. Working electrode: Pt disk (0.021 cm²).
Supporting Information 2. Figure A shows the calculated spectra for (a) 3-(1-pyrrolyl)-9-oxo-2,4,7-trinitroindanyl-[5, 6-b]cyclohexadienate (3-Py-TNIC) and (b) 1-(1-pyrrolyl)-9-oxo-2,4,7-trinitroindanyl-[5, 6-b]cyclohexadienate (1-Py-TNIC). Curve c is the spectrum of 4a measured in CH₂CN, the 9:2 isomeric mixture of 3-Py-TNIC and 1-Py-TNIC. The spectra of a and b were calculated with the CAnhe system (Sony/Tektronix Co.). Optimization of molecular structure and geometry was conducted using the Block-Diagonal Newton Raphson method and the MNDO-PM3 method, respectively. Then the UV-vis spectra were calculated using the ZINDO method. The shape of the spectrum c may be regarded as the superposition of those of the spectra a and b. The absorption spectra of 4b and 4c shown in Figure B were nearly the same in shape and positions of peaks as that of 4a, suggesting that 4b and 4c are also the isomeric mixtures.
Supporting information 3. Penetration of O₂ into the main compartment of our electrolysis cell was confirmed by the cyclic voltammetry (CV) of O₂ in a CH₃CN solution containing (C₂H₅)₃N⁺ClO₄⁻ (0.1 M): The solution was degassed with N₂ for 1 h, then the CV reduction current at -1.2 V vs. SCE for the reduction of O₂, i_p(N₂), under a flow of N₂ was recorded at the same time intervals as those in Fig. 5. The ordinate is the ratio of i_p(N₂) to the reduction current of O₂ equilibrated with air at 20 °C, i_p(air), i.e., the current measured without N₂ bubbling. Charging-current corrections were made on all the measurements. The solution was stirred as in the case of controlled-potential preparation of 4 except when the CV measurements were conducted. Working electrode: Pt disk (0.021 cm²). Sweep rate: 20 mV/s. The result shows a gradual penetration of O₂ into the main compartment of the cell through the sintered glass frit, and an inflection point at 60 min may account for the variation in the shape of the UV-vis absorption spectra recorded under a flow of N₂ (condition 1) in Fig. 5. Note that the current ratio dropped abruptly to zero by N₂ bubbling (15 min) at elapsed times of 180 and 720 min, being the support for the absence of O₂ in the solution under continuous bubbling of N₂ (condition 2).