

Supplementary Information

Solution-cast self-assembled films of perchlorate-doped oligo(3-methoxythiophene) showing a gold-like luster

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Electric conductivity measurements. For the electric conductivity measurements, the apexes of the four point probes are brought into contact with a film surface (Fig. S1). The conductivity values measured with this probe arrangement might be significantly affected by the conductivity in the in-plane direction.^{S1}

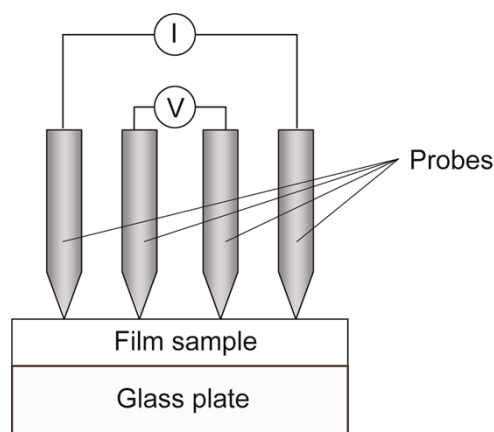


Fig. S1 Schematic illustration of the apparatus for the conductivity measurements of the films by a four-point probe method.

¹H-NMR spectroscopy. The product was dissolved in DMSO-*d*₆, and the ¹H NMR spectrum was recorded as a function of the elapsed time (Fig. S2).

Immediately after the dissolution, the spectrum exhibited broad signals in the vicinity of 4.0 and 7.1 ppm. This broadening may be due to the decrease in the resolution of the NMR caused by the presence of radical species. These signals gradually changed into multiple sharp peaks with time, *t*, and the change stopped after *t* = ca. 3 days. This can be explained by assuming that the radical species gradually

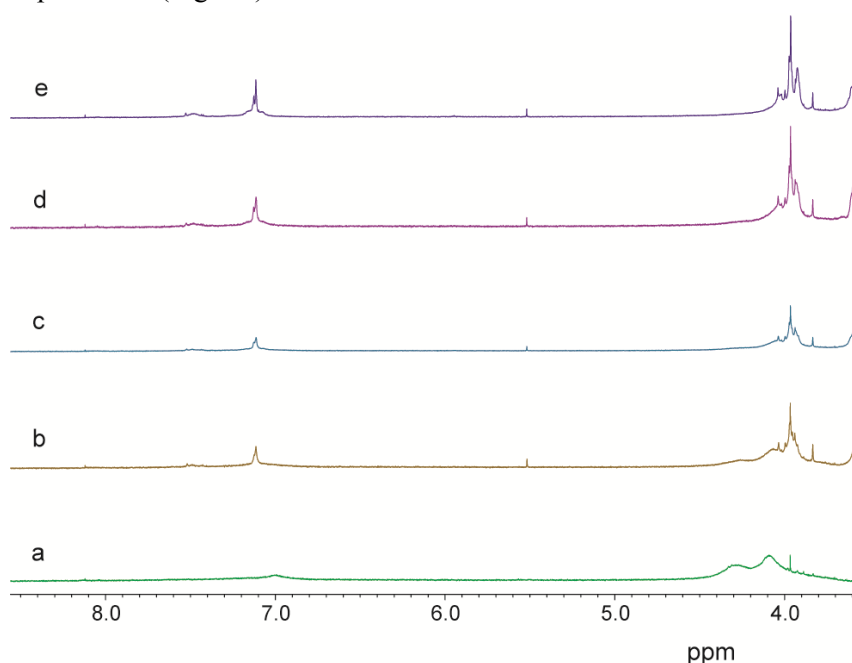


Fig. S2 The change in the shape of the ¹H NMR spectrum of the product with the elapsed time of 0 (a), 1 (b), 2 (c), 3 (d), and 7 days (e).

disappeared in DMSO (dedoping of ClO₄⁻) and converted completely to the neutral species in ca. 3 days.^{S2} Fig. S3 shows the steady-state ¹H NMR spectrum of the product, which exhibits a peak at ca. 4.0 ppm due to the methoxy proton and a peak (ca. 7.1 ppm) in the region of aromatic protons. Based on the comparison of the area of the proton peaks, three methoxy protons and one aromatic proton are involved in the sample. These peaks can be assigned to the protons of 3-methoxythiophene-2,5-diyl.^{S3,S4} The signals at 2.49 and 3.51 ppm are attributed to residual DMSO protons and water, respectively.^{S5} Close observation of the peaks at 4.0 and 7.1 ppm revealed that these peaks are

composed of multiple signals. In order to determine the reason for the slight peak splitting, ^1H NMR spectrum was measured at elevated temperature (Fig. S4). The shape of the spectrum was not altered by a change in temperature. This demonstrates that the peak splitting does not arise from a slow conformational change of the molecule in the solution, but the molecular weight distribution of the oligomers. In conclusion, it is strongly suggested that the product is oligo(3-methoxythiophene-2,5-diyl).

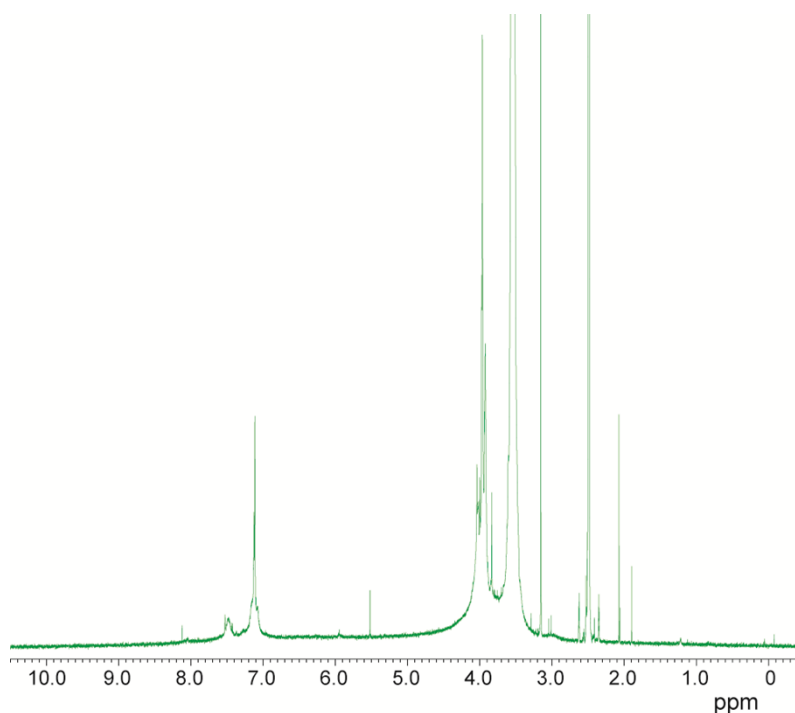


Fig. S3 The steady-state ^1H NMR spectrum of the product.

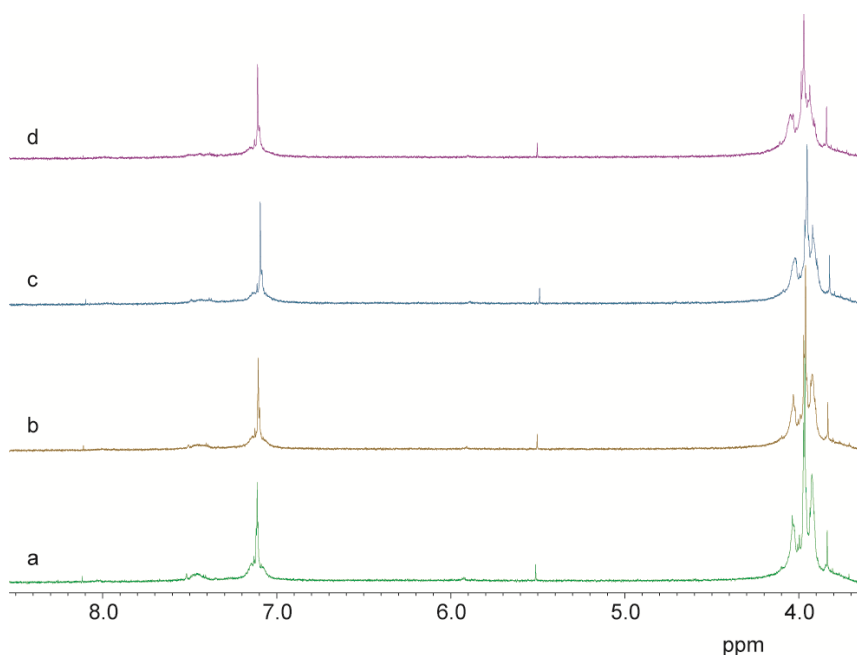


Fig. S4 The effect of the measuring temperature on the shape of the ^1H NMR spectrum of the product: **a**, 313; **b**, 323; **c**, 333; **d**, 343 K.

FT-IR spectroscopy. Fig. S5 shows the FT-IR transmission spectrum of the product (KBr method). The peak at 820 cm^{-1} is assigned to the C-H deformation vibration of the 2,3,5-trisubstituted thiophene ring.^{S6,S7} It was reported that the 3-methoxythiophene monomer shows two strong bands at 1238 and 1158 cm^{-1} which correspond to the C_{α} -H in-plane bending vibrations;^{S3} however, the bands nearly disappeared in Fig. S4, indicating that the oligomerization happened through α - α' coupling. The peak at 1259 cm^{-1} is assigned to the C-O-C stretching vibration of the methoxy group.^{S8} The signals caused by ClO_4^- were observed near 1060 and 616 cm^{-1} .^{S8,S9} The product was thus identified as oligo(3-methoxythiophene-2,5-diyl) partially doped with ClO_4^- .

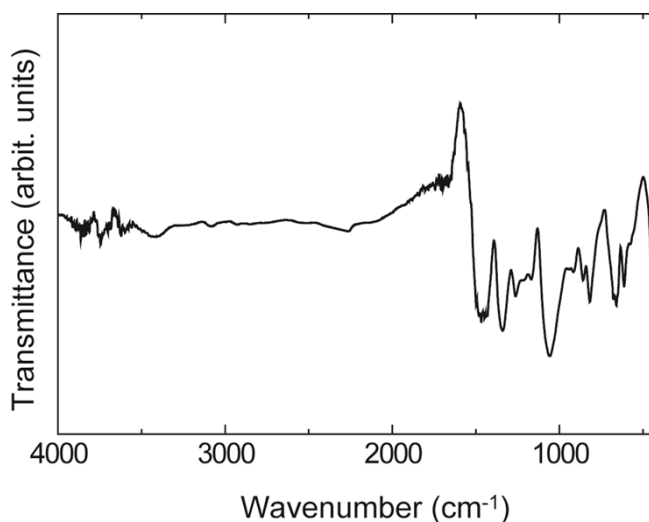


Fig. S5 FT-IR spectrum of the product in a KBr pellet.

Elemental analysis. The result and method of the elemental analysis of the product are described in the text. The result showed that the product involved molecular oxygen as a constituent. However, it is very likely to happen for conducting polymers.^{S10} Khomenko et al.^{S11} studied the reduction of oxygen at conducting polymer electrodes, such as polythiophene, poly(3-methylthiophene), polypyrrole, and polyaniline, and revealed that the chemisorptions of O_2 on the conducting polymers in the undoped state was induced to form complexes of the conducting polymers with O_2 . The complex formation leads to the activation of O_2 , and accordingly, the ready reduction of O_2 at the conducting polymer surfaces. Based on this report, it is not surprising that molecular oxygen forms a complex with the undoped 3-methoxythiophene unit in the oligo(3-methoxythiophene).

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