# Supplementary information

## Preparation, characterization, and magnetic properties of poly(3-methoxythiophene)-$Fe_3O_4$ conducting nanocomposite

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**Elemental maps for P3MeOT-Cl**

The results of the elemental mapping analysis of P3MeOT-Cl are shown in Fig. S1. The images exhibited minimal contrast for Fe (attributed to iron chloride) and C, O, and S (attributed to P3MeOT), suggesting a nearly uniform distribution of these elements throughout the sample. This observation corroborates the minimal contrast observed in the TEM images of P3MeOT-Cl.

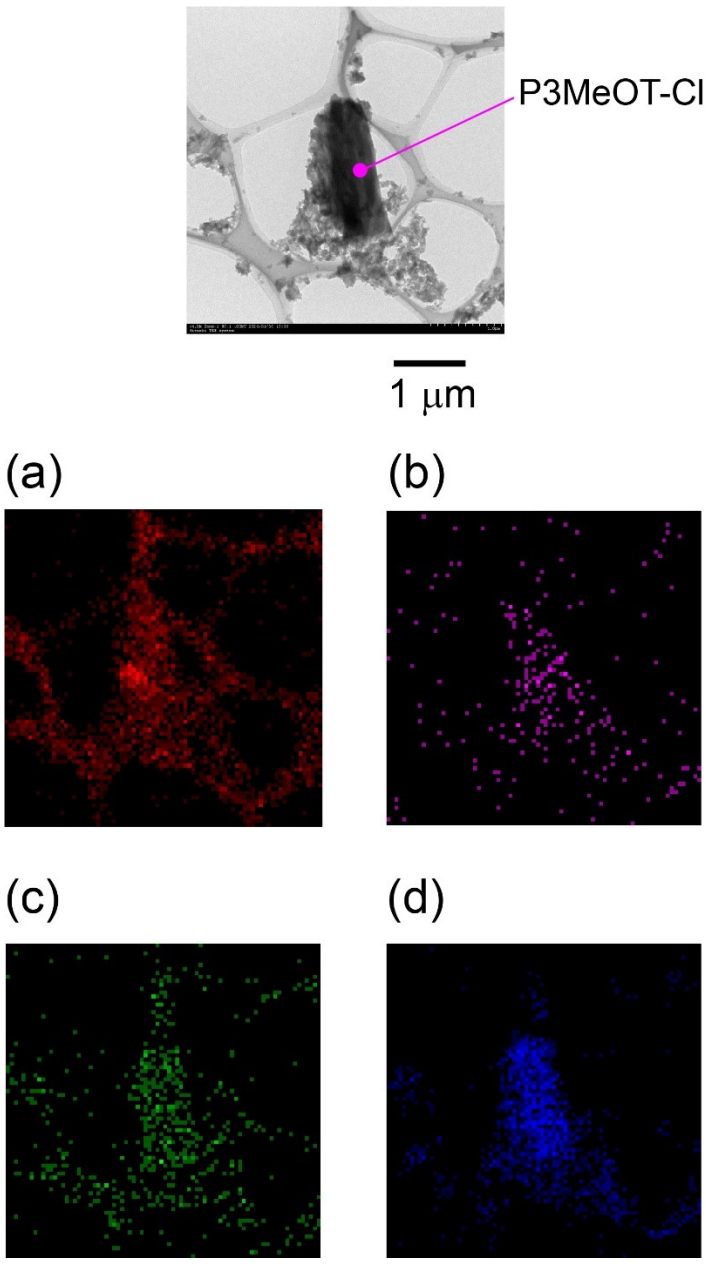


**Fig. S1** EDX elemental mapping images recorded for the (a) C, (b) Fe, (c) O, and (d) S components of P3MeOT-Cl. The mapping process was conducted using the TEM image presented at the top of each elemental map.

**EDX measurements of P3MeOT-$ClO_4$ and Red 2**

The EDX elemental analysis results obtained for P3MeOT-$ClO_4$ and Red 2 are listed in Table S1, wherein the atomic ratios of S, Cl, and Fe are given. The atomic ratios of Cl and Fe were normalized to an atomic concentration of 1 for S. The Fe/S ratios were determined to be zero for both samples, indicating that neither P3MeOT-$ClO_4$ nor Red 2 contains any detectable amounts of Fe. In addition, the difference in the degree of polymerization between P3MeOT-Cl (the precursor of Red 1) and P3MeOT-$ClO_4$ (the precursor of Red 2) is small,[1] and so Red 2 can be regarded as a model compound that would be obtained if the Fe-containing product could be removed from Red 1.

**Table S1. Atomic ratios of Cl and Fe relative to S in the P3MeOT-$ClO_4$ and Red 2 molecules[a]**

| Molecule | S | Cl | Fe |
|---|---|---|---|
| P3MeOT-$ClO_4$ | 1.00 | 0.27 | 0.00 |
| Red 2 | 1.00 | 0.018 | 0.00 |

[a] The atomic ratios were obtained by EDX measurements and normalized to S

**Magnetism demonstrations for P3MeOT-$ClO_4$ and Red 2.**

Fig. S2 shows photographic images of the P3MeOT-$ClO_4$ and Red 2 powders being brought close to a ferrite magnet through a glass vial. Since neither P3MeOT-$ClO_4$ nor Red 2 is attracted to the black circular magnet placed at the center of the blue plastic support, it can be concluded that they do not exhibit strong magnetism.

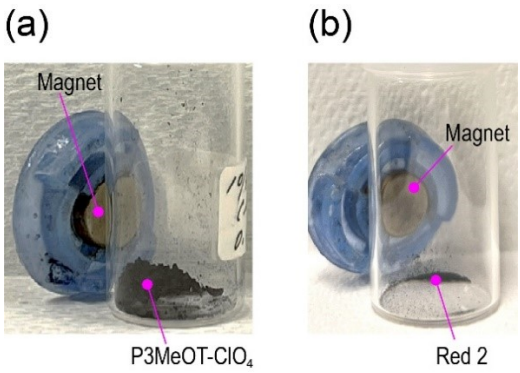


**Fig. S2** Photographic images showing the behaviors of the (a) P3MeOT-$ClO_4$ and (b) Red 2 powders when brought close to a magnet. The diameter of the glass vial is 20 mm.

**XPS measurements for P3MeOT-$ClO_4$**

Fig. S3 shows the XPS spectra recorded for the Fe $2p_{3/2}$, O 1s, and Cl 2p components of P3MeOT-$ClO_4$. In the Fe $2p_{3/2}$ spectrum, no signal is observed, indicating that Fe originating from the oxidizing agent, $Fe(ClO_4)_3$, is not present in the P3MeOT-$ClO_4$ structure. Additionally, the O 1s spectrum shows a peak centered at 531.7 eV, which was attributed to superposition of the signals originating from the methoxy oxygen moiety of P3MeOT and the $ClO_4^-$ dopant. In the Cl 2p spectrum, two peaks can be observed at 205.6 and 207.1 eV, which were attributed to the Cl $2p_{3/2}$ and Cl $2p_{1/2}$ components of Cl in $ClO_4^-$. Compared with the values observed for $Cl^-$ (see Fig. 6 in the main text), these values are shifted toward higher binding energies. This shift was caused by a partial displacement of the chlorine valence electrons in $ClO_4^-$ toward the oxygen atoms. Consequently, this displacement strengthens the interactions between the Cl 2p electrons and the chlorine nucleus.

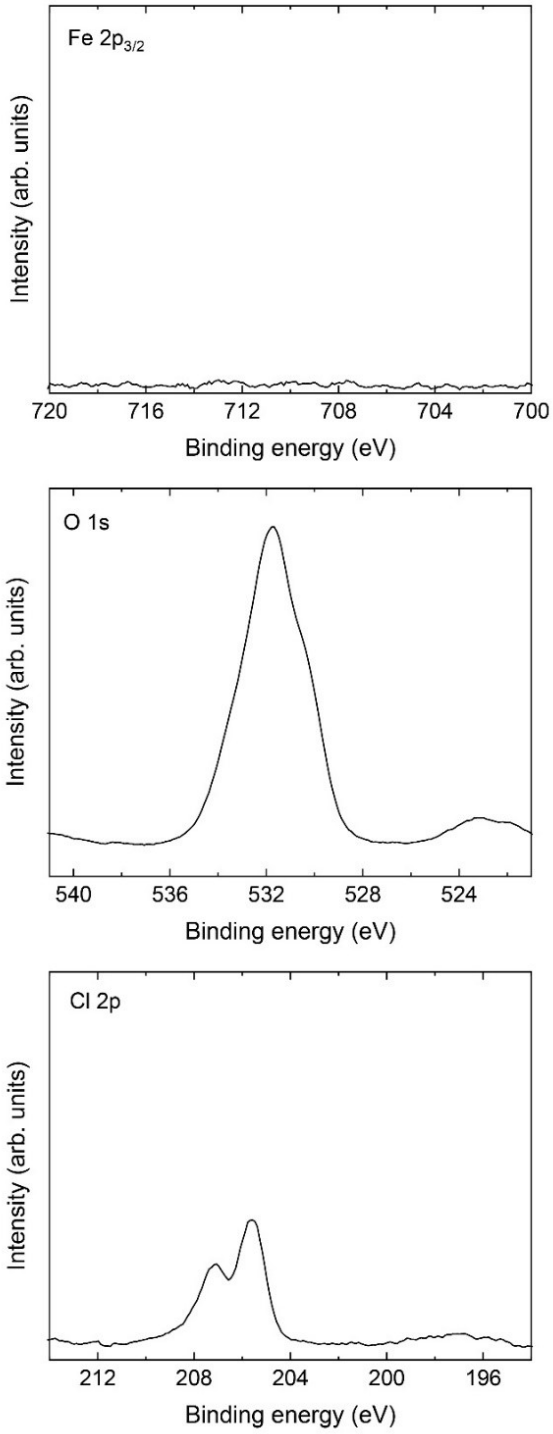


**Fig. S3** XPS spectra of the Fe $2p_{3/2}$ (top), O1s (middle), and Cl 2p (bottom) components of P3MeOT-$ClO_4$.

As a result, the binding energy of the Cl 2p electrons increases, leading to the observed shift in binding energy shown in Fig. S3.[2]

**XPS survey spectra of P3MeOT-Cl and Red 1**

Fig. S4 shows the XPS survey spectra recorded for P3MeOT-Cl and Red 1. As can be seen, no detectable amount of nitrogen was observed in the N 1s binding energy region around 400 eV, indicating that neither P3MeOT-Cl nor Red 1 contain nitrogen.

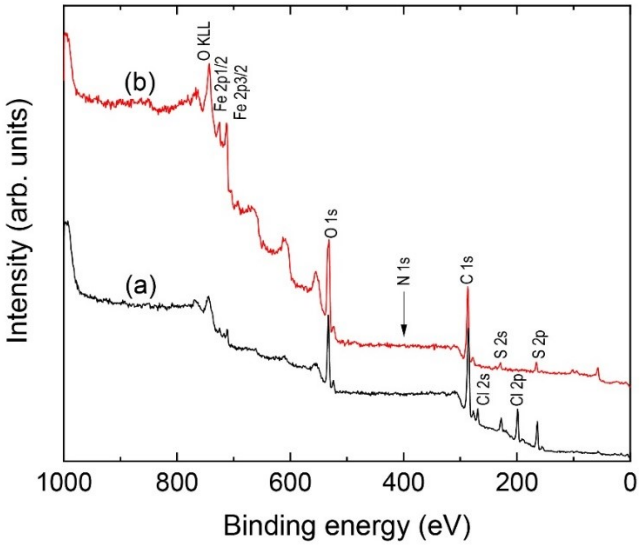


**Fig. S4** XPS survey spectra recorded for (a) P3MeOT-Cl and (b) Red 1.

**EDX spectra of P3MeOT-Cl and Red 1**

Fig. S5 shows the EDX spectra recorded for P3MeOT-Cl and Red 1, in addition to their corresponding SEM images. In the EDX spectra, if N were present, its N Kα signal would be expected to appear at 0.39 keV, namely between the carbon (C Kα: 0.28 keV) and oxygen (O Kα: 0.53 keV) peaks.[3,4] However, since no signal corresponding to N was detected in either of the spectra, it was deduced that neither P3MeOT-Cl nor Red 1 contains nitrogen. This finding supports the results shown in Fig. S4.

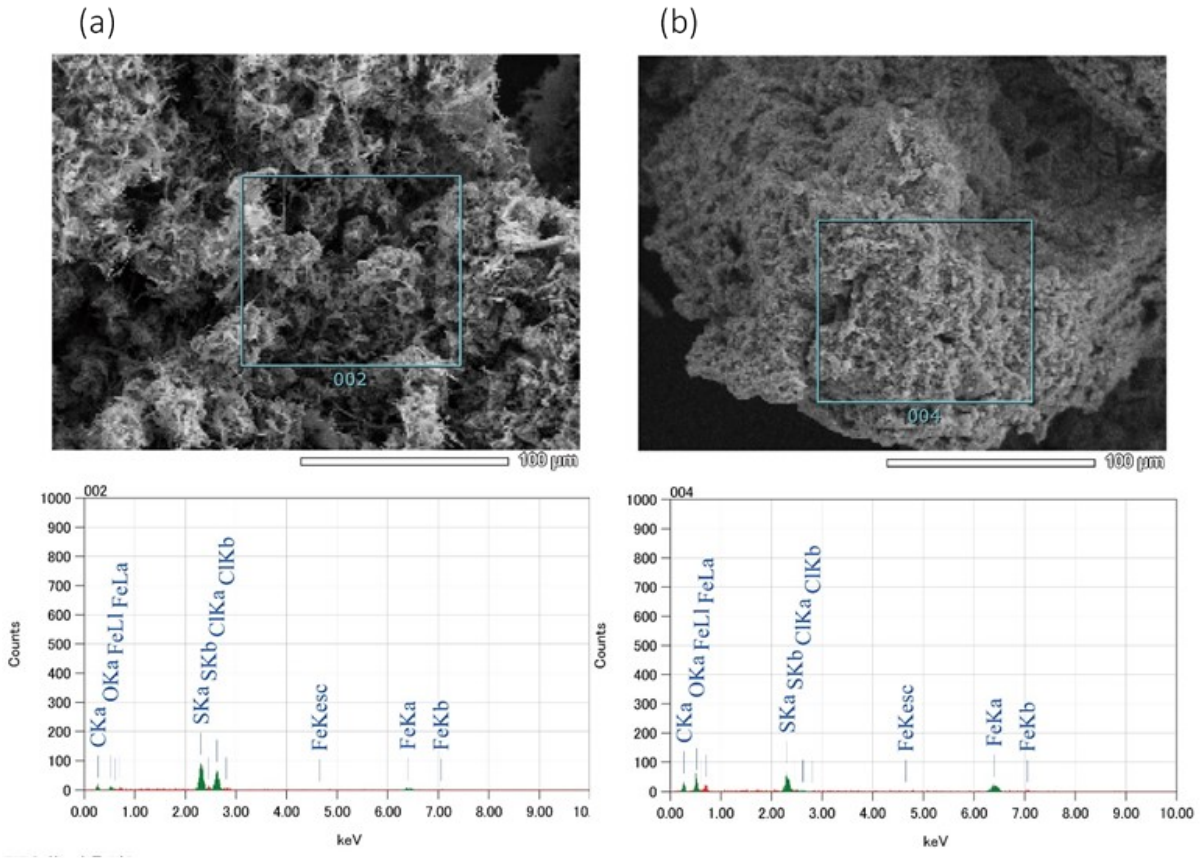


**Fig. S5** EDX spectra recorded for (a) P3MeOT-Cl and (b) Red 1. Above each spectrum, the corresponding SEM image is presented.

**Magnetic property measurements for Red 2**

Fig. S6 shows the magnetic hysteresis loop of Red 2 measured at 5 K and its magnified view along the y-axis. The magnified hysteresis loop exhibits a saturation magnetization of 0.1 emu/g under a 50 kOe magnetic field, which is negligibly small compared to that of Red 1 (i.e., 20.2 emu/g under a 50 kOe magnetic field; see subsection 3.8 of the main text). A similar trend was observed at 300 K. Consequently, it was apparent that the development of magnetization in Red 1 is not attributable to the P3MeOT backbone, but rather to $Fe_3O_4$.

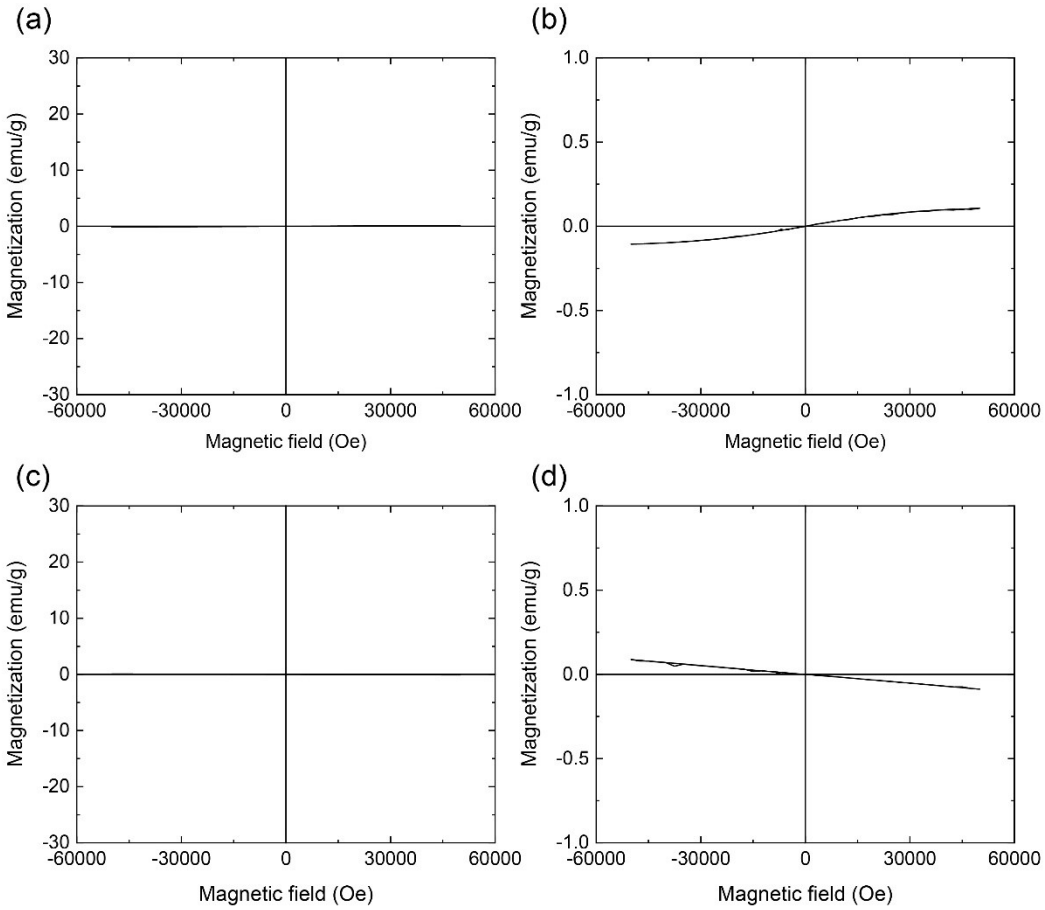


**Fig. S6** Magnetic hysteresis loops of Red 2 recorded at (a, b) 5 K and (c, d) 300 K. Panels (b) and (d) represent expanded views of the data presented in panels (a) and (c), respectively.

**Magnetic property measurements for P3MeOT-$ClO_4$**

Fig. S7 shows the magnetic hysteresis loop of P3MeOT-$ClO_4$ measured at 5 K and its magnified view along the y-axis. The magnified hysteresis loop exhibits a saturation magnetization of 0.2 emu/g under a 50 kOe magnetic field, which is negligibly small compared to that of Red 1 (i.e., 20.2 emu/g under a 50 kOe magnetic field; see subsection 3.8 of the main text). A similar trend was observed at 300 K.

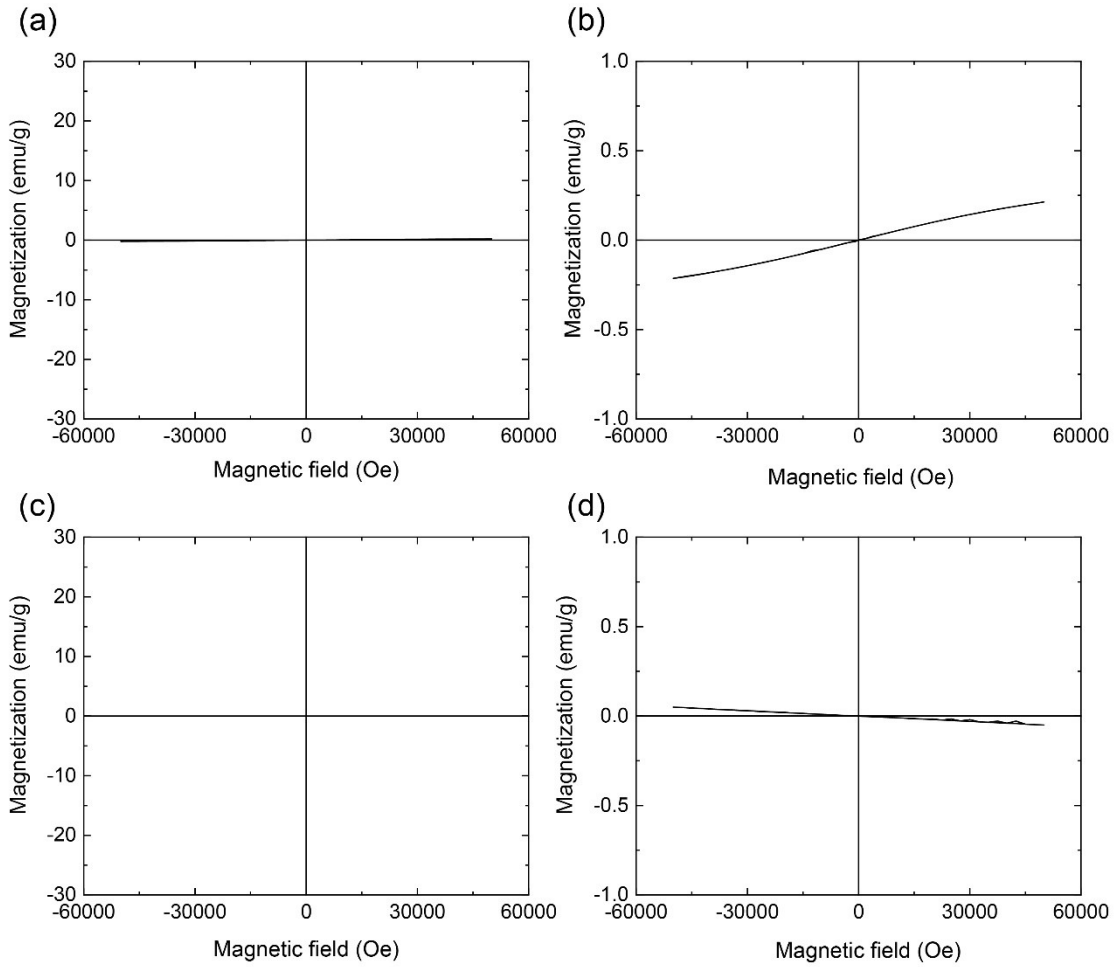


**Fig. S7** Magnetic hysteresis loops of P3MeOT-$ClO_4$ recorded at (a, b) 5 K and (c, d) 300 K. Panels (b) and (d) represent expanded views of the data presented in panels (a) and (c), respectively.

## Supplementary References


1 Supporting Information in: M. Tachiki, R. Tagawa and K. Hoshino, Oligo(3-methoxythiophene)s as Water-Soluble Dyes for Highly Lustrous Gold- and Bronze-Like Metal-Effect Coatings and Printings, *ACS Omega,* 2020, **5**, 24379−24388.

2 Y. Zhang, S. Mu, B. Deng, J. Zheng, Electrochemical Removal and Release of Perchlorate Using Poly(aniline-co-o-aminophenol), *J. Electroanal. Chem.*, 2010, **641**, 1–6.

3 Y. Ye, J. Chen, Q. Ding, D. Lin, R. Dong, L. Yang, J. Liu, Sea-Urchin-Like $Fe_3O_4$@C@Ag Particles: an Efficient SERS Substrate for Detection of Organic Pollutants, *Nanoscale*, 2013*,* **5**, 5887–5895.

4 D. Menga, F. Ruiz-Zepeda, L. Moriau, M. Šala, F. Wagner, B. Koyutürk, M. Bele, U. Petek, N. Hodnik, M. Gaberšček, T.-P. Fellinger, *Adv. Energy Mater.*, 2019, **9**, 1902412.