

Supplementary Information

A perspective from frontier molecular orbit on contact-electro-catalysis

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Supplementary Fig. 5 | Energy diagram for illustrating the electron transfer during CE when the HOMO of polymer is not fully occupied.

Methods:

Chemicals:

Materials were obtained from commercial suppliers and were not further modified unless otherwise stated. The methyl orange ($C_{14}H_{14}N_3NaO_3S$, 98%), p-benzoquinone ($C_6H_4O_2$, 99.5%), p-phthalic acid ($C_8H_6O_4$, 99%), nitrotetrazolium blue chloride ($C_{40}H_{30}N_{10}O_6 \cdot 2Cl$, 98%) were purchased from Macklin. The tert-butanol was from Sinopharm Chemical Reagent Co., Ltd. Polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene (PE) were acquired from Dupont, polyvinylidene fluoride (PVDF) from ZHIMK TECHNOLOGY (Shenzhen) Co. The aqueous solution was prepared with deionized water having a resistivity of 18.2 M Ω cm.

Sample preparation:

A 5-ppm aqueous solution of methyl orange (MO) was prepared by adding 5 mg of $C_{14}H_{14}N_3NaO_3S$ to 1 liter of deionized water, followed by magnetic stirring for 1 hours.

The nitrotetrazolium blue chloride solution (NBT, $C_{40}H_{30}N_{10}O_6 \cdot 2Cl$) was prepared by adding 10 mg to 1 liter of deionized water, followed by magnetic stirring for 1 hours.

The terephthalic acid solution (THA, p- $C_6H_4(COOH)_2$) was prepared by adding 332.4 mg of p-phthalic acid and 760 mg of sodium phosphate tribasic dodecahydrate, followed by magnetic stirring for 1 hours.

Approximately 1.5 ml of aliquot was extracted after 0, 5, 10, 15, 30, and 60 min of ultrasonication (40 kHz, 200 W) for subsequent spectroscopic characterization. The temperature in the ultrasonic bath was regulated.

Sample characterization:

The absorbance of MO and NBT was recorded using a Cary 3500 UV-Vis multispectrometer scanning the wavelength range of 190-650 nm. The sample was placed in a Hellma Analytics QS High Precision cuvette with an optical range of 10 mm.

The fluorescence emission spectra of the aliquot were measured on an Edinburgh Instruments FLS 980 with an excitation wavelength of 312 nm and the characteristic THA-OH peak appearing at 426 nm.

The LC-MS measurements were conducted on a Thermo Scientific Q Exactive Orbitrap Quadrupole-Electrostatic Field Orbitrap High Resolution Tandem Mass Spectrometer. The HESI ion source of the mass spectrometer was set at -3.0 kV, positive ion mode. The scanning range of the mass spectrometer was 100-1000 m/z. The resolution of the instrument was 70,000 FMHM, and the column was Hypersil Gold C18 (2.1 \times 100 mm, 1.9 μ m) at 40 $^{\circ}$ C. The injection volume was 5 μ L, the mobile phase A was 0.1% formic acid aqueous solution, and the mobile phase B was acetonitrile solution.

Measurement of the transferred charge between the polymer membrane and deionized water was based on an electrostatic meter (KEITHLEY 6514) with a linear motor.

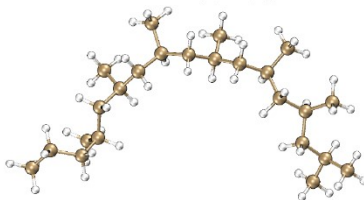
Supplementary Note 1:

All computations were conducted utilizing the Gaussian 16 software.¹ The polymer models for PE, PVDF, PVC, PP, and PTFE consisted of nine individual monomers respectively. Geometry optimizations and electronic structure calculations were carried out on the neutral molecules employing the B3LYP density functional method with the standard 6-311G(2d,2p) basis set.² The polarizable continuum model (PCM)³⁻⁵ with dielectric constant of 78.54 was used to simulate a solvent environment for the calculation. Vertical attachment energies (VAEs) were determined as the discrepancy between the total energy of the lowest anion and that of the neutral state, both within the optimized geometry of the neutral state, which are obtained by single-point energy calculation at the wB97XD/aug-cc-pVTZ level. Analysis of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) orbitals was performed using Multiwfn⁶ and VMD software⁷.

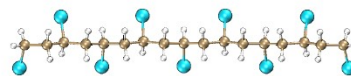
PE: Polyethylene



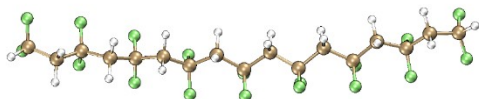
PP: Polypropylene



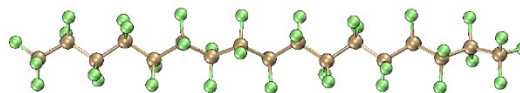
PVC: Polyvinyl chloride



PVDF: Polyvinylidene difluoride



PTFE: Polytetrafluoroethylene



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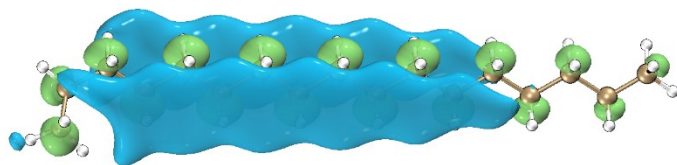
● : C

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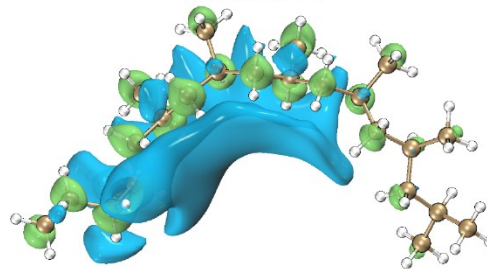
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Supplementary Fig. 1 | The optimized structures for different polymers.

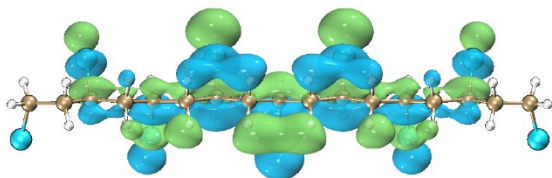
LUMO of PE



LUMO of PP



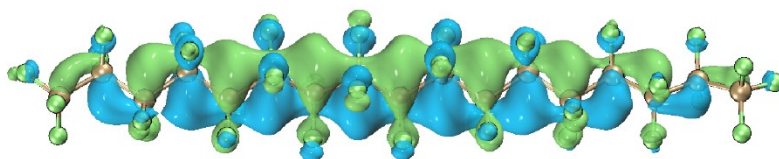
LUMO of PVC



LUMO of PVDF



LUMO of PTFE



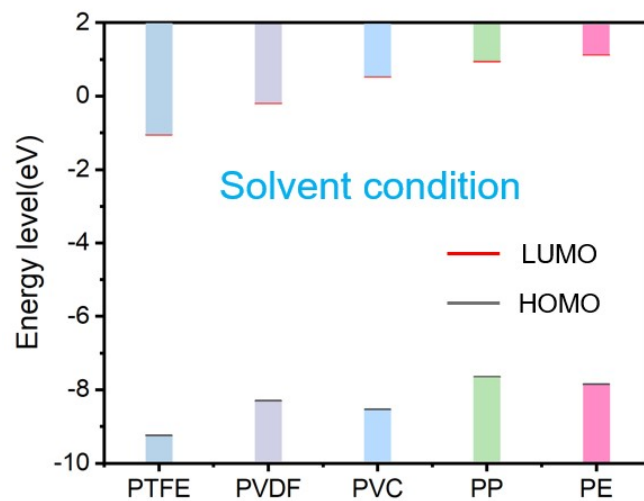
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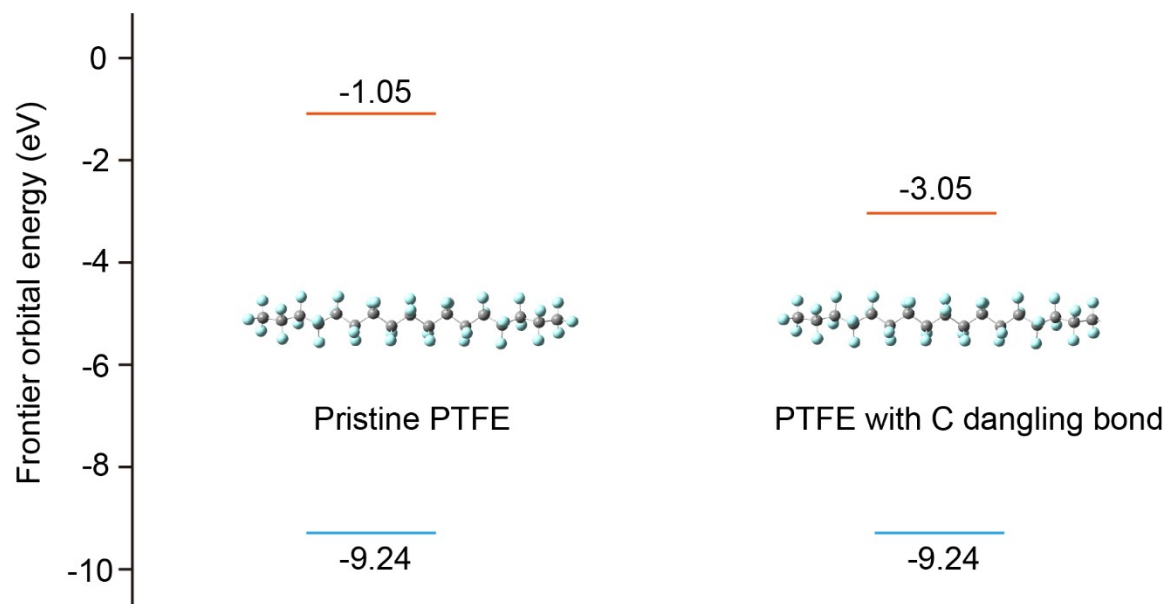
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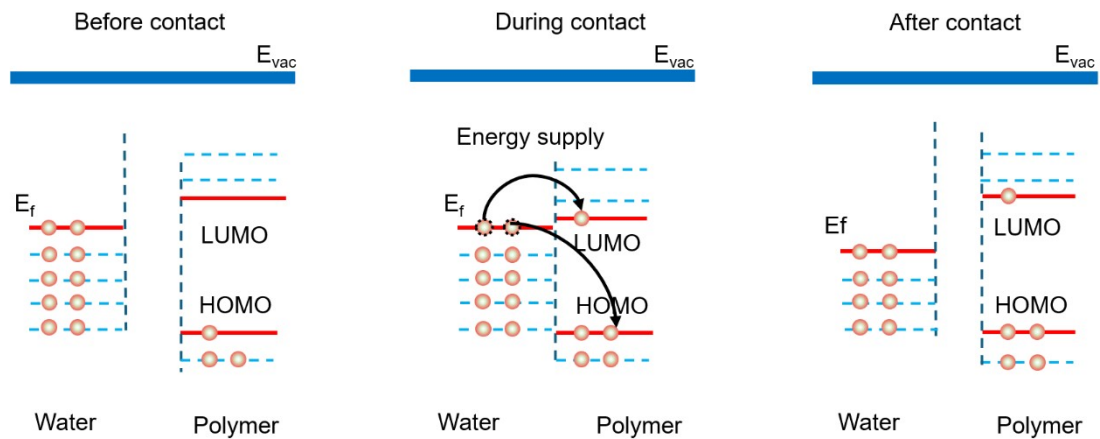
Supplementary Fig. 2 | The spatial distribution of LUMO for different polymers.



Supplementary Fig. 3 | Calculated values of FMO for different polymers under a solvent condition.



Supplementary Fig. 4 | Calculated values of FMO for PTFE with C dangling bonds.



Supplementary Fig. 5 | Energy diagram for illustrating the electron transfer during CE when the HOMO of polymer is not fully occupied.

Supplementary References

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