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Supplementary Information

Synthesis of Colorless and High-Refractive-Index Sulfoxide-Containing Polymers via the Oxidation of Poly(phenylene sulfide) Derivatives

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1. General Information

1.1 Estimation of S=O bonds

The amount of sulfoxide and sulfone of **Ox-PAS** was determined by IR absorbance spectroscopy, by estimating the relative amount of sulfoxide or sulfone per sulfide moieties through assigning the corresponding ratio of the integral values in the calibration curve formula (vide infra).

The preparation process of calibration curve was described as follows: In the case of **PMPS** and **Ox-PMPS**, the integral of the bands at 870 - 1140 cm^{-1} (C-S and S=O) and those at 770 - 870 cm^{-1} (Ar-H) mode were compared for the quantification of sulfoxide bonds of the polymer; the integral of the bands at 1140 - 1180 cm^{-1} (SO_2) and those at 770 - 870 cm^{-1} (Ar-H) were compared for sulfone. The calibration curves used for the estimation were shown in Figure S1 below.

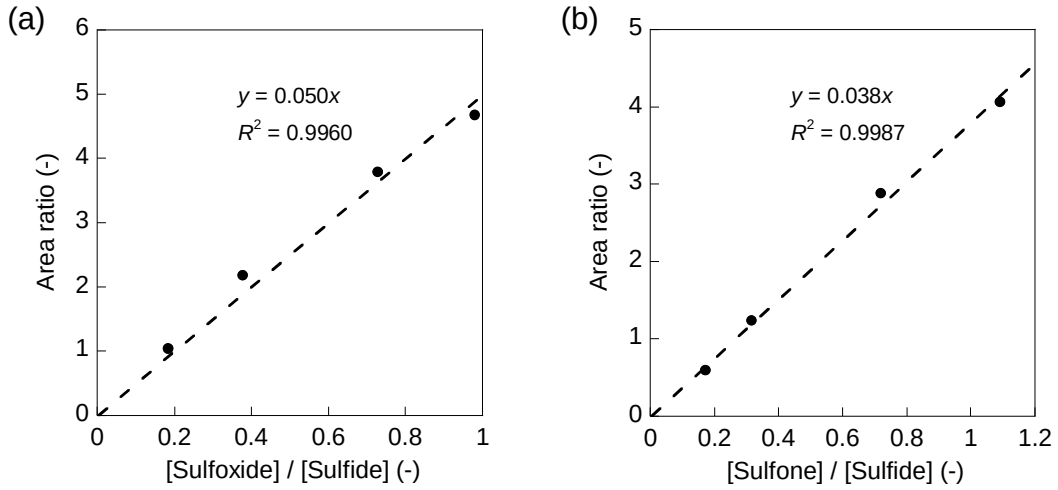

Figure S1. Relationship between the integral ratio and the amount of (a) sulfoxide and (b) sulfone per sulfide bonds for **PMPS**.

In the case of **OMePPS** and **Ox-OMePPS**, the integral of the bands at 780 - 920 cm^{-1} (C(Ar)-O-C(Me) and S=O) and those at 950 - 1110 cm^{-1} (Ar-H) mode were compared for the quantification of sulfoxide bonds of the polymer; the integral of the bands at 780 – 950 cm^{-1} (SO_2) and those at 1090 - 1200cm^{-1} (Ar-H) were compared for sulfone. The calibration curves used for the estimation were shown in Figure S2 below.

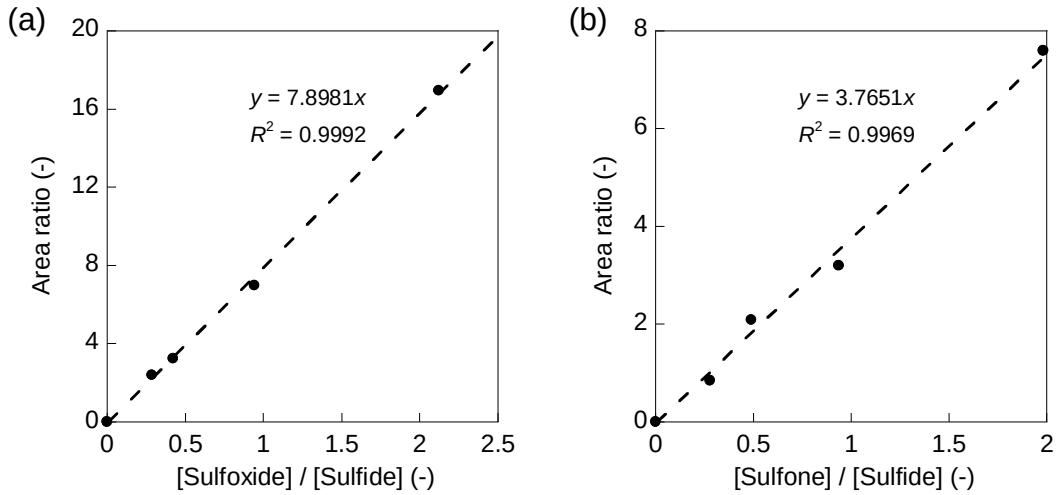

Figure S2. Relationship between the integral ratio and the amount of (a) sulfoxide and (b) sulfone per sulfide bonds for **OMePPS**.

2. Supplementary figures and tables

Table S1. Molecular weights of **PMPS** and **Ox-PMPS**

Run	Polymer	M_n[a] ($\times10^3$)	M_w[a] ($\times10^3$)	M_w / M_n[a] (-)
Initial	**PMPS**	5.7	10.0	1.8
1	**Ox-PMPS**	4.7	10.0	2.1
2		7.7	15.8	2.1
3		5.1	10.5	2.1
4		5.3	10.1	1.9

[a] Determined by GPC in chloroform.

Table S2. Molecular weights of **OMePPS** and **Ox-OMePPS**

Run	Polymer	M_n[a] ($\times10^3$)	M_w[a] ($\times10^3$)	M_w / M_n[a] (-)	M_n[b] ($\times10^3$)	M_w[b] ($\times10^3$)	M_w / M_n[b] (-)
Initial	**OMePPS**	2.5	4.9	2.0	4.3	5.9	1.4
1	**Ox-OMePPS**	1.3	2.3	1.8	3.8	4.5	1.2
2		0.5	0.9	1.8	3.8	4.6	1.2

[a] Determined by GPC in chloroform. [b] Determined by GPC in DMF containing 0.1 M LiCl.

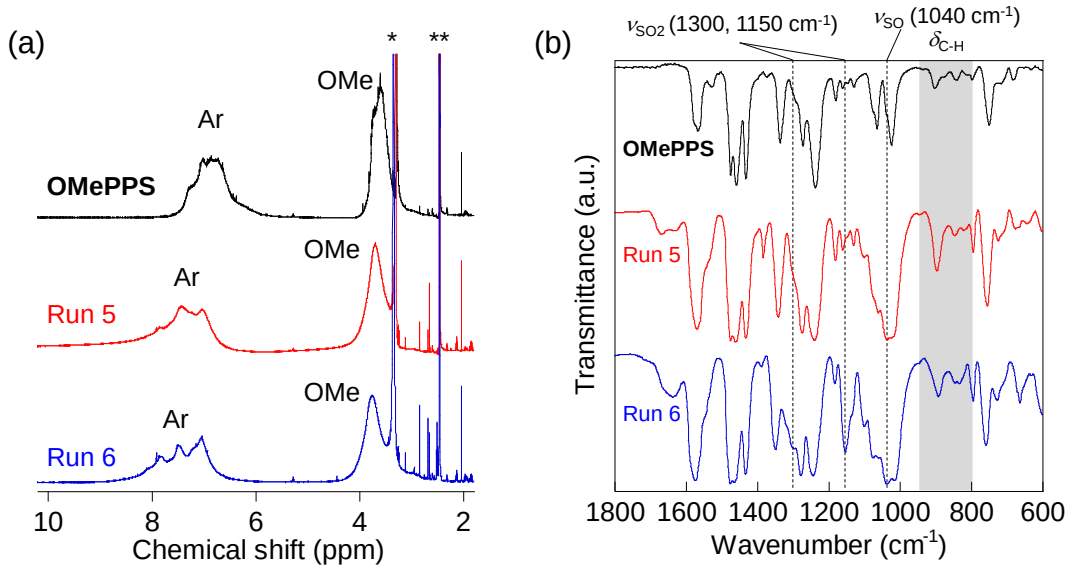

Figure S3. (a) ^{1}H NMR spectra of **OMePPS** and **Ox-OMePPS** in DMSO-d_6 (Peaks of *: water, **: DMSO). (b) IR spectra of **OMePPS** and **Ox-OMePPS**.

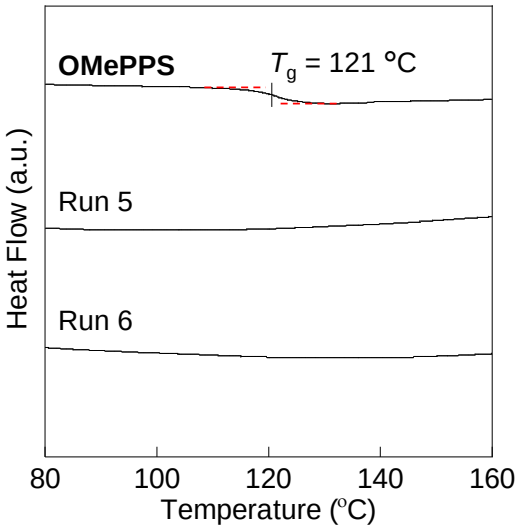

Figure S4. DSC curves of **OMePPS** and **Ox-OMePPS** (Scanning rate: 20 °C min^{-1}).

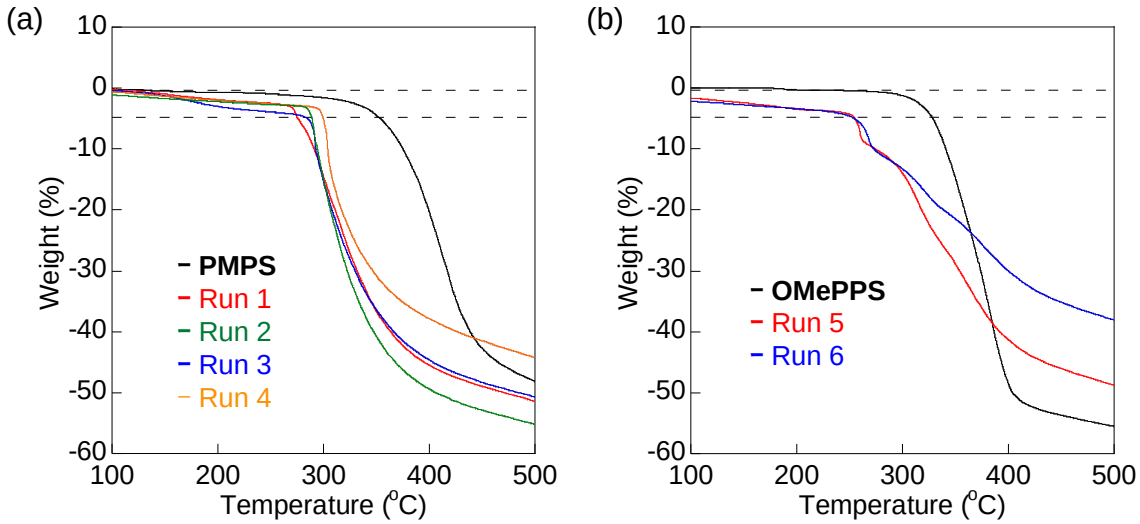

Figure S5. TGA traces of (a) **PMPS** and (b) **OMePPS** before and after the oxidation.

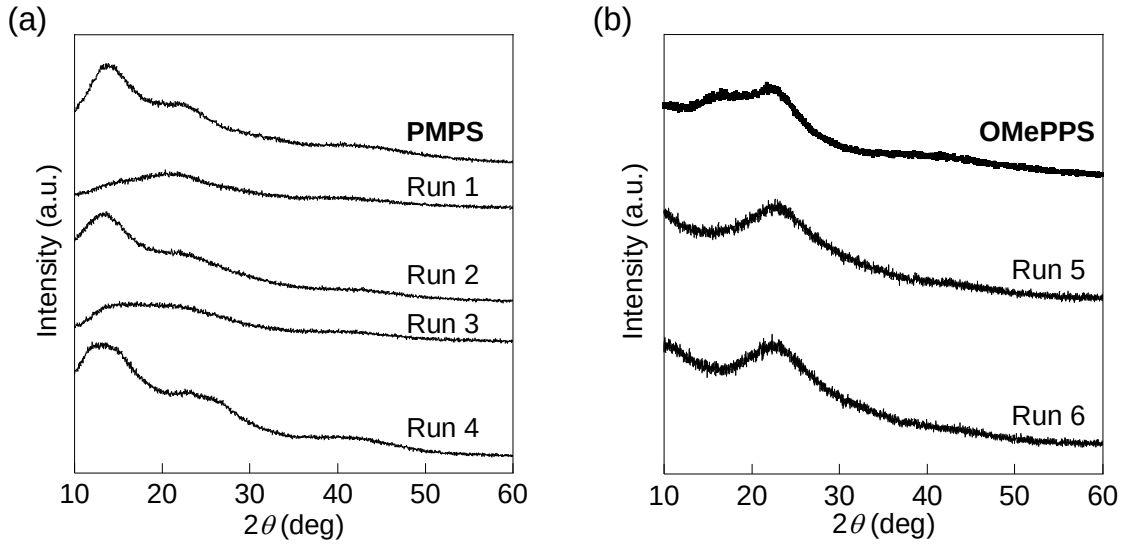

Figure S6. X-ray diffraction profiles of **PAS** before and after the oxidation: (a) **PMPS** and **Ox-PMPS**. (b) **OMePPS** and **Ox-OMePPS**.

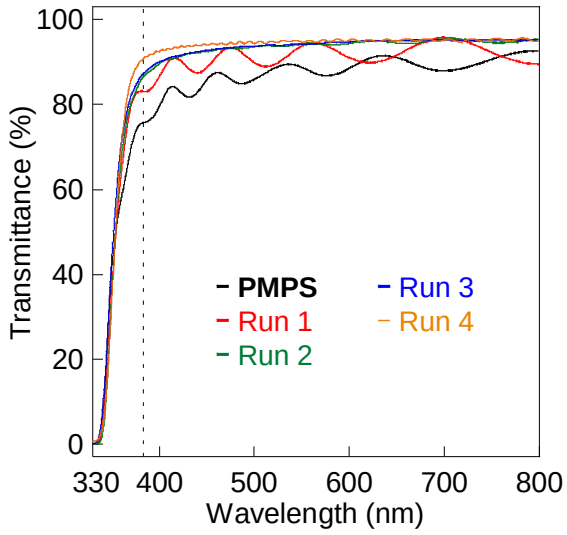

Figure S7. Normalized UV-vis transmittance spectra of the films of **PMPS** and **Ox-PMPS** on glass substrates (Thickness: 10 μm). The transmittance values were normalized according to the previously reported procedure.[1]

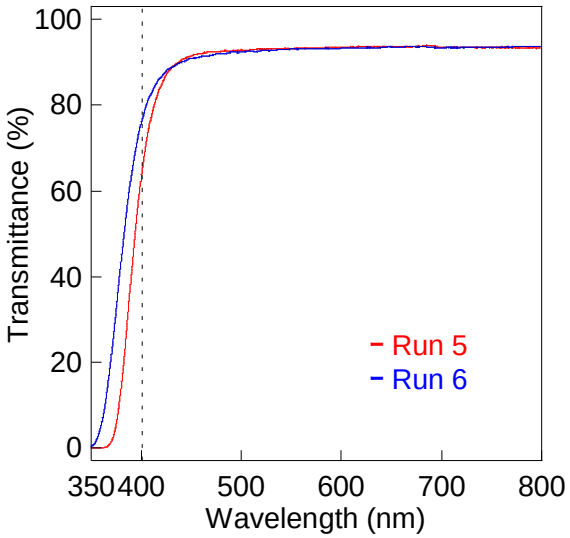

Figure S8. Normalized UV-vis transmittance spectra of the films of **Ox-OMePPS** on glass substrates (Thickness: 10 μm). The normalization process was the same as that of Figure S7. The normalized spectrum of the **OMePPS** film has already been reported in the previous report.[1]

3. DFT calculations

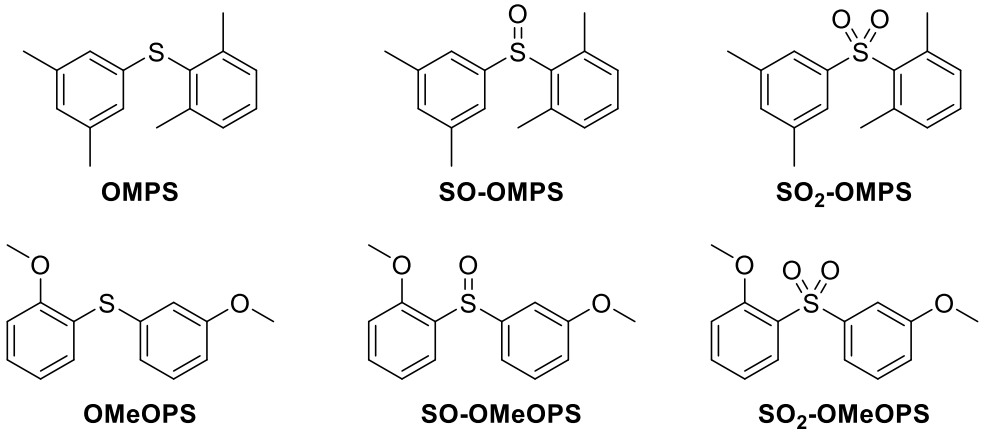

Figure S9. Structures of the model compounds used in DFT calculations**.**

Table S3. Calculated HOMO-1, HOMO, LUMO, LUMO+1 levels of model compounds

Model compound	HOMO-1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)
OMPS	-8.40	-7.53	1.35	1.88
SO-OMPS	-8.59	-7.96	1.08	1.42
SO_2-OMPS	-8.84	-8.74	0.73	1.30
OMeOPS	-7.93	-7.40	1.45	1.94
SO-OMeOPS	-8.25	-7.95	1.01	1.45
SO_2-OMeOPS	-8.93	-8.29	0.60	1.39

[a] Determined by DFT Calculation, at ωB97XD/6-31G(d,p) level of theory.

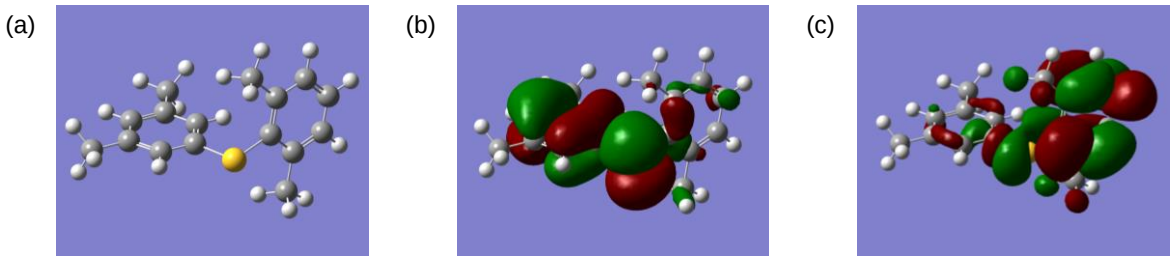

Figure S10. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **OMPS.**

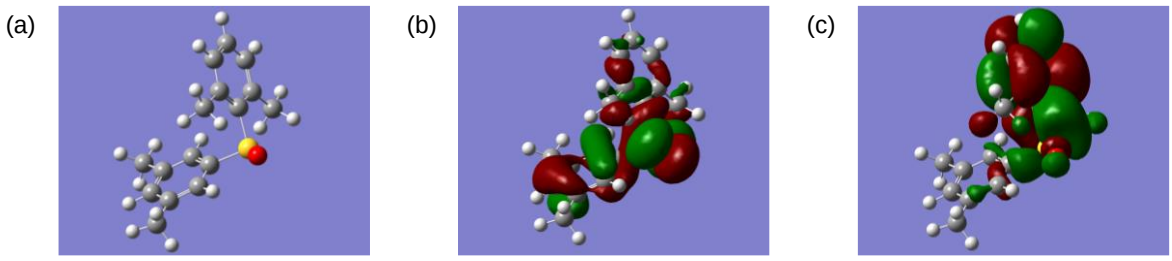

Figure S11. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **SO-OMPS**.

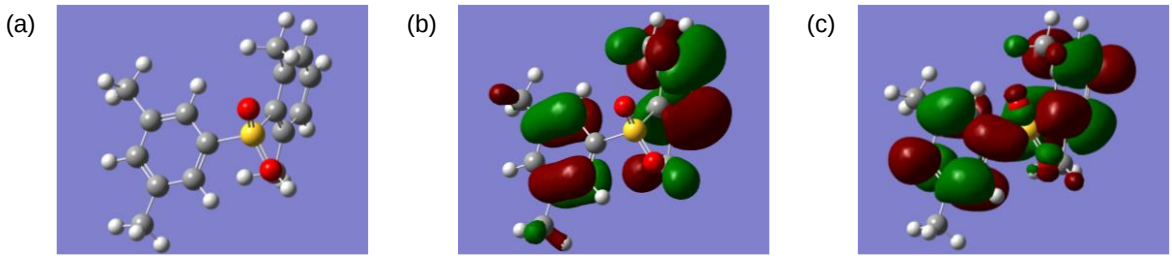

Figure S12. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **SO_2-OMPS**.

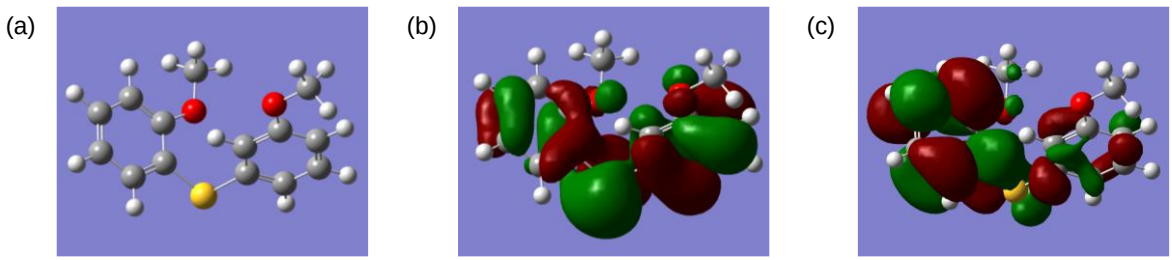

Figure S13. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **OMeOPS.**

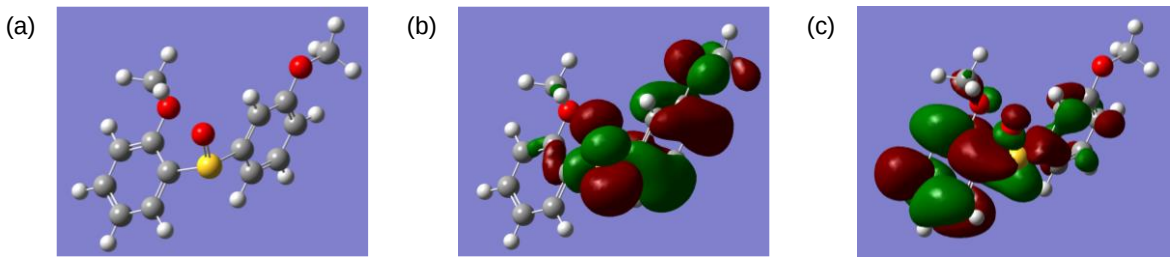

Figure S14. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **SO-OMeOPS**.

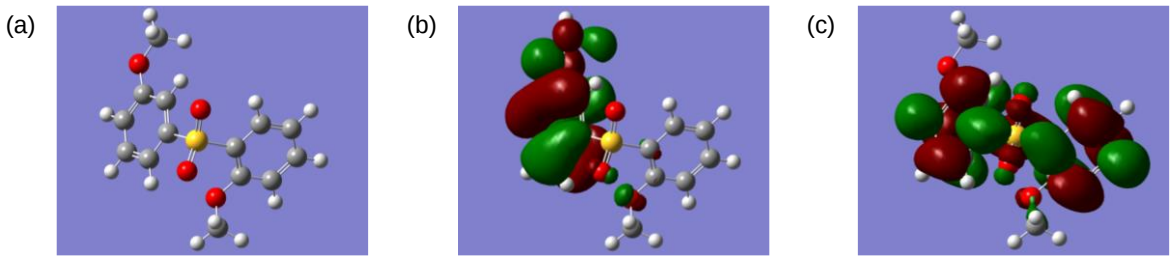

Figure S15. (a) Optimized structure, (b) HOMO shape, and (c) LUMO shape of **SO_2-OMeOPS**.

Reference

1 S. Watanabe and K. Oyaizu, *Bull. Chem. Soc. Jpn.*, 2020, **93**, 1287–1292.