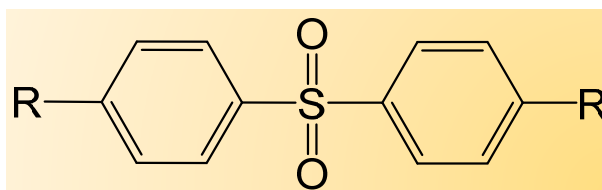




ジフェニルスルホン化合物の ダイマーラジカルイオン形成

Formation of dimer radical ions of diphenyl sulfones



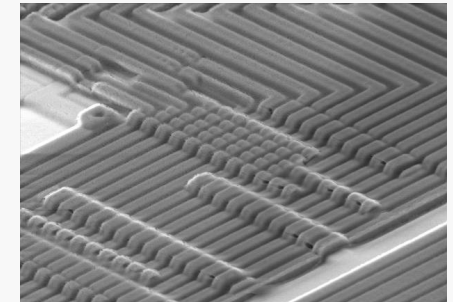
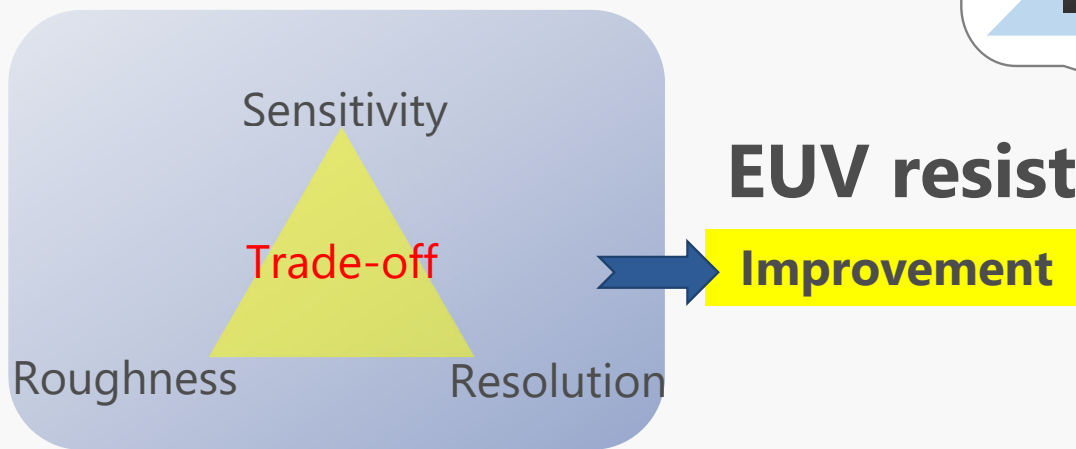
○岡本一将¹, 河合俊平², 古澤 孝弘¹

¹ 大阪大学 産業科学研究所 量子ビーム物質科学研究分野

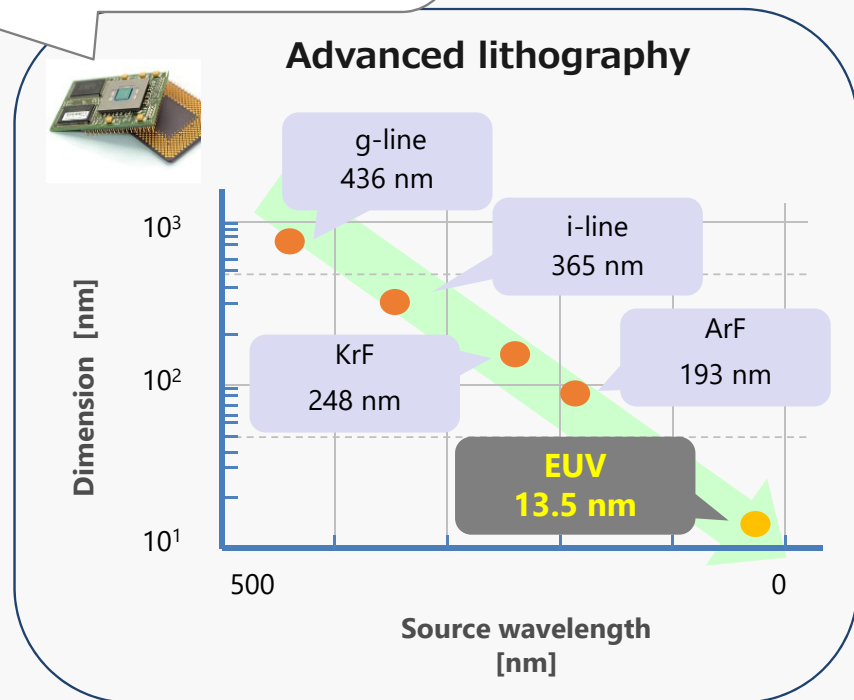
² 北海道大学大学院工学院

Next generation EUV resist materials

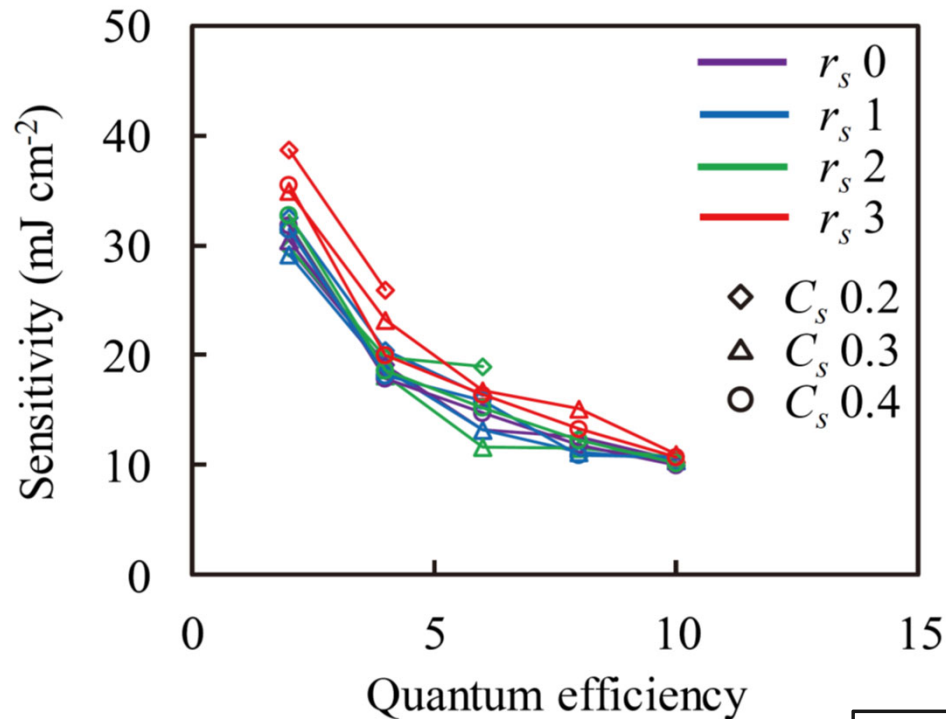
For HVM semiconductor devices



To break through the trade-off,
increase in number of absorbed photons and
efficiency of conversion from injected photon
image to latent image is important.



11 nm half pitch LWR to 20%CD



r_s : sensitization distance / nm
 C_s : total sensitizer conc. / nm⁻³

Methods of quantum efficiency increase

- PAG improvement
- Acid amplifier
- PS-CAR(TM)
- Proton yield (deprotonation)

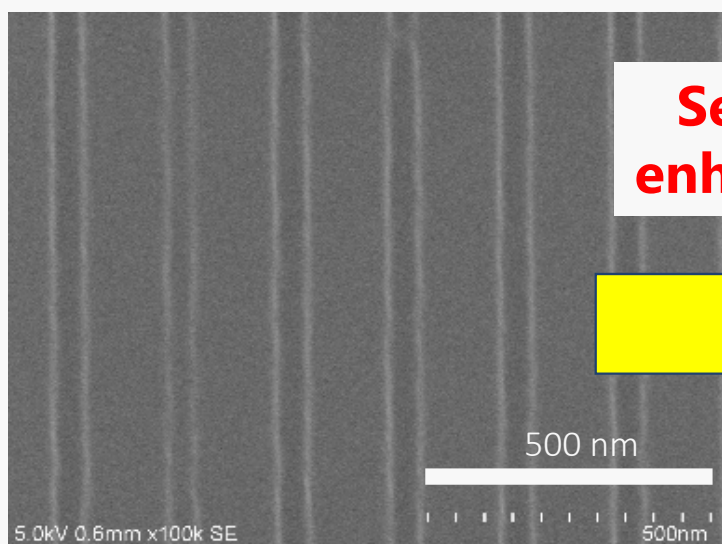
Quantum efficiency increase is effective to increase of sensitivity maintaining LWR

Kozawa et al., J. Photopolym. Sci. Technol. (2018)

Kozawa et al., J. Photopolym. Sci. Technol. (2019)

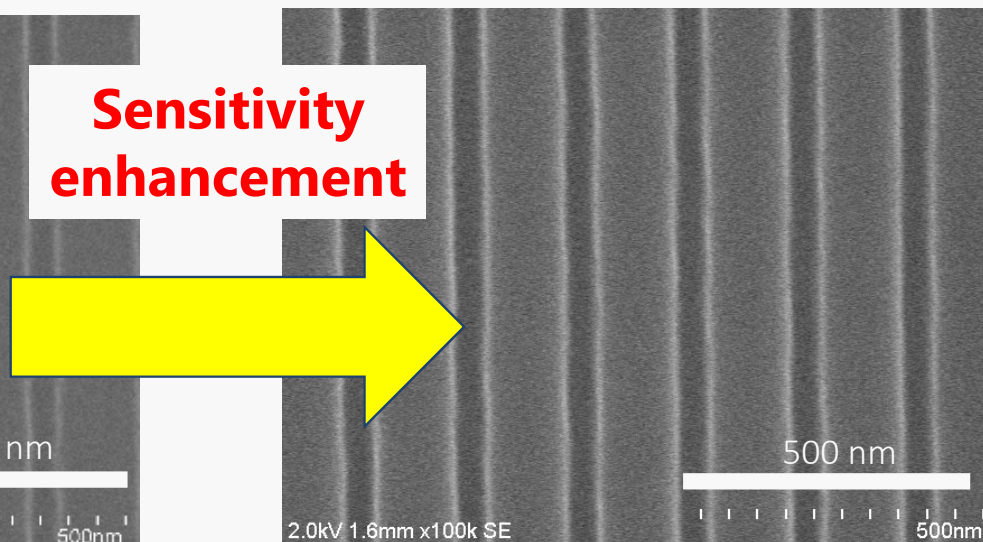
Chemically amplified resist (CAR)

Without additives



Dose : 1 6 0 ($\mu\text{C}/\text{cm}^2$)
CD: 45.0 nm
LWR: 5.8 nm

With DTS

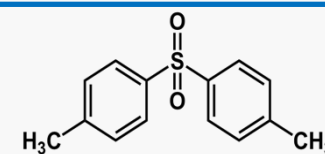


Dose : 6 4 ($\mu\text{C}/\text{cm}^2$)
CD: 44.5 nm
LWR: 4.1 nm

**Sensitivity
enhancement**



additive



DTS (di-*p*-tolyl sulfone)

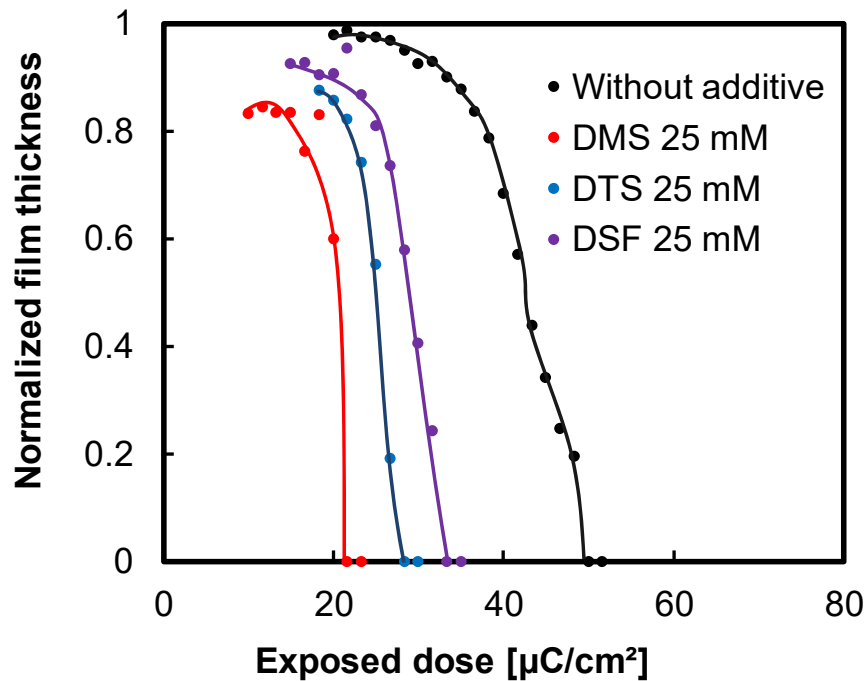
Acid generating
promoter(AGP)

Catalyst for
deprotonation

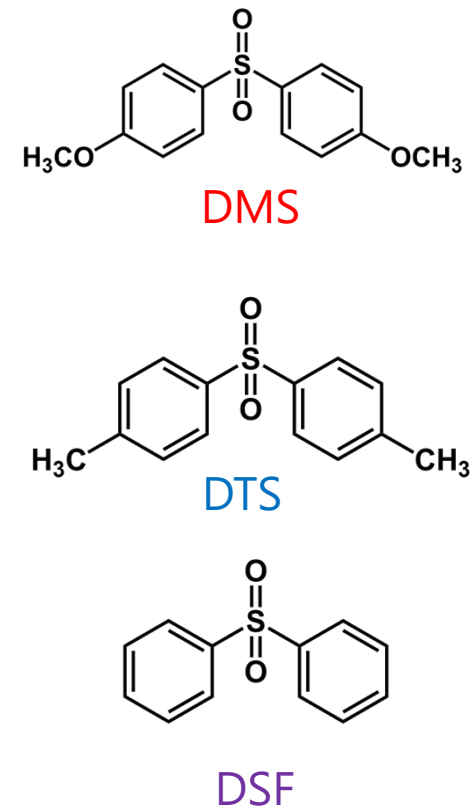
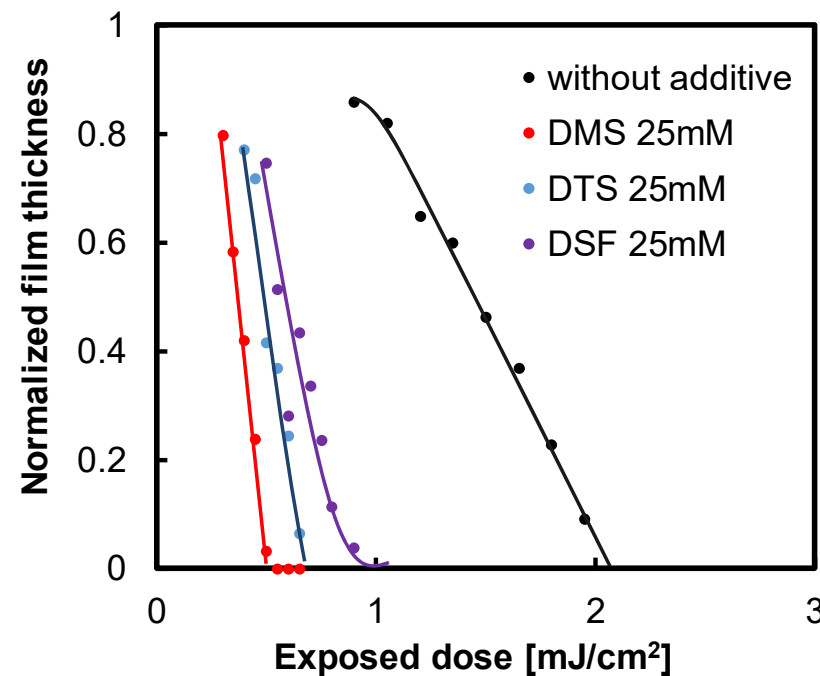
NOT

Decomposable acid
generator or acid amplifier

125 kV electron beam



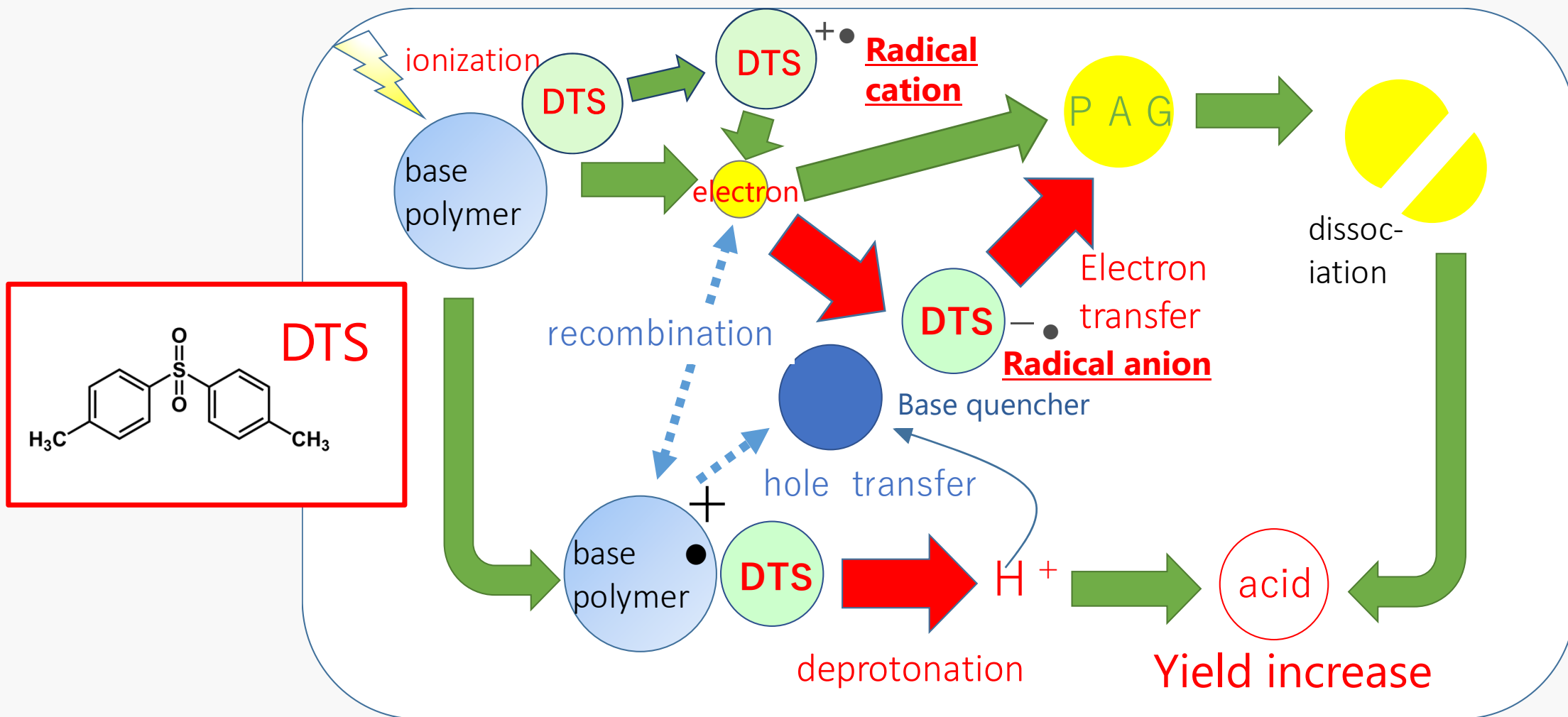
EUV



- CAR with sulfones shows **sensitivity enhancement**
- **DMS** shows more significant sensitivity improvement than DTS

K. Okamoto, S. Kawai, and T. Kozawa, Proc. SPIE 11326, 113260D (2020).

Sensitization mechanism



Pulse radiolysis method

Transient absorption measurement

Irradiation source :

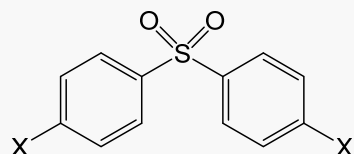
L-band electron beam Linac

(26 MeV, 8ns, 270Gy/pulse)

Analyzing source : Xe flash lamp

Scan wavelength : 300-1600 nm

Solutes



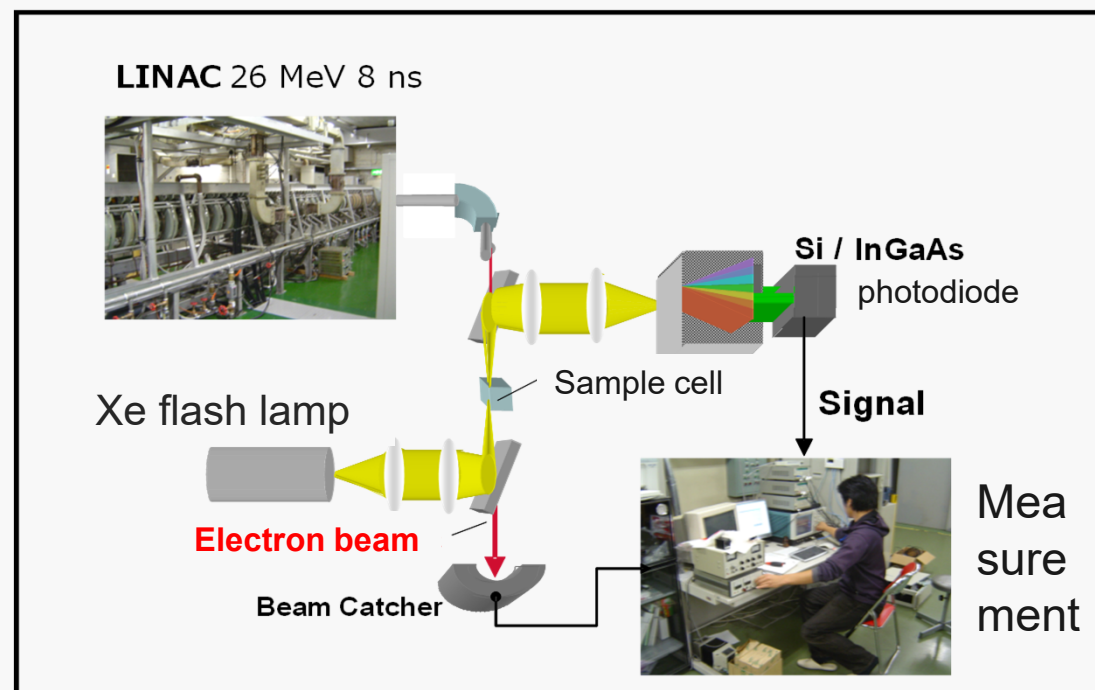
Diphenylsulfones (DPs)
X = (H, CH₃, OCH₃)

Solvent

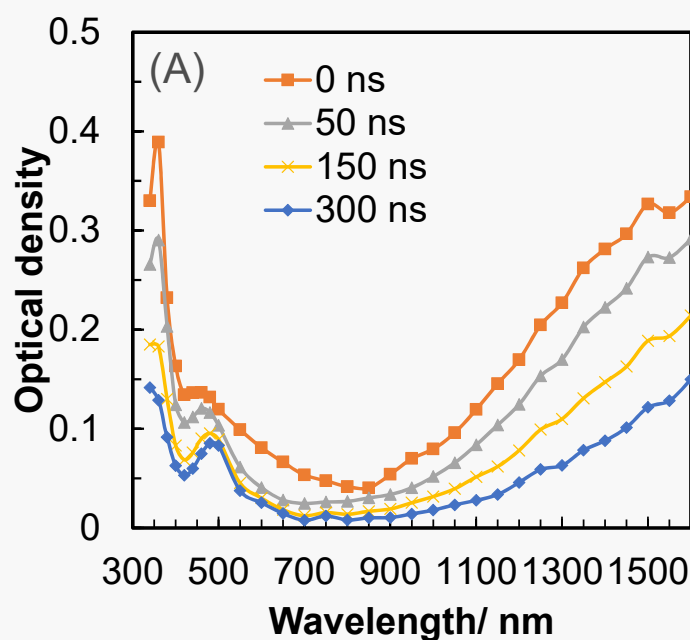
1,2-Dichloroethane (DCE)



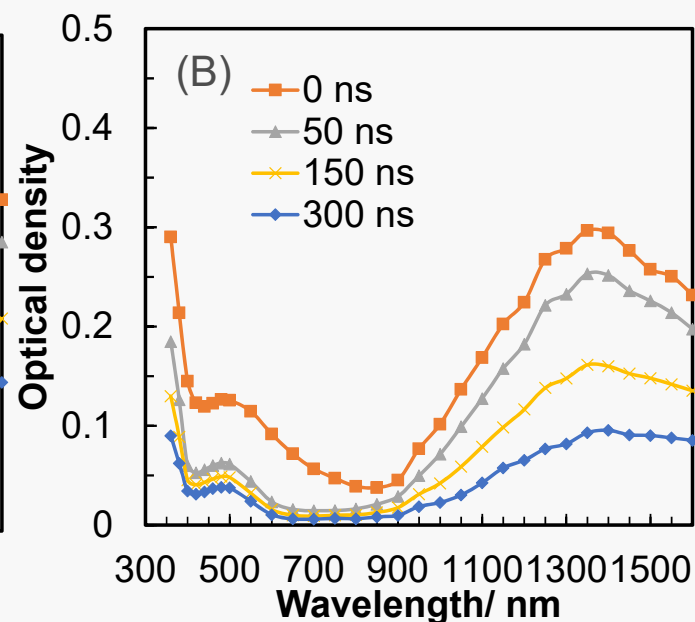
Tetrahydrofuran (THF)



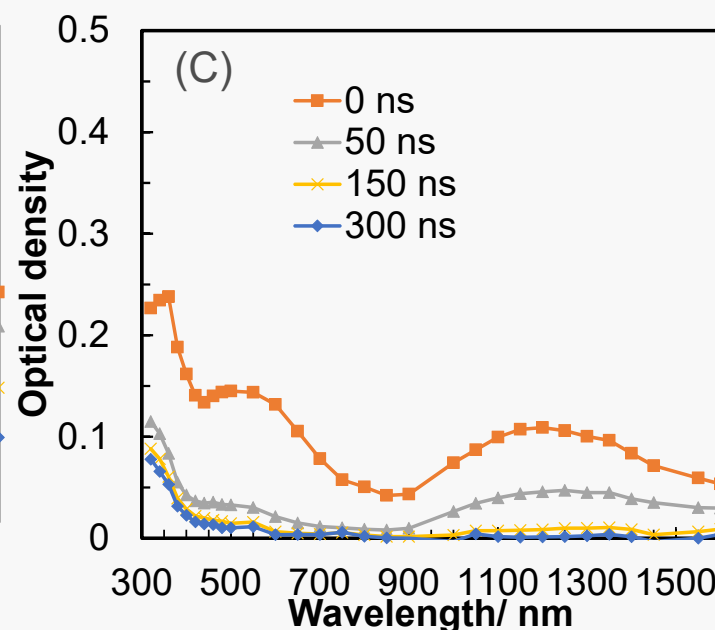
DMS/ DCE



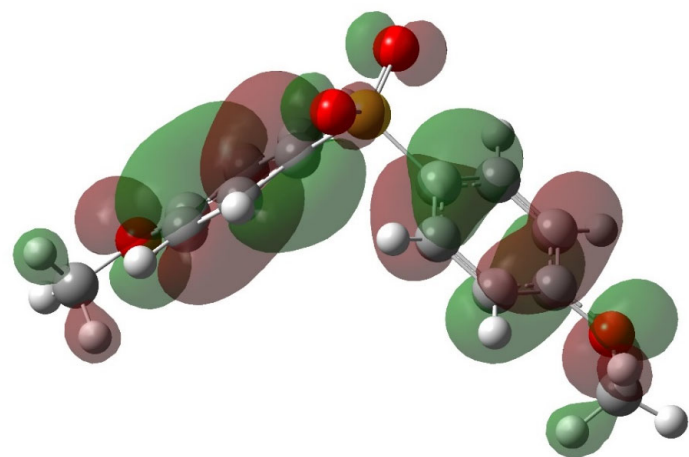
DTS/ DCE



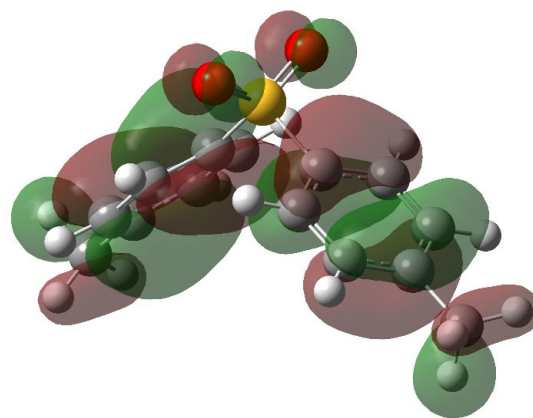
DPS/ DCE



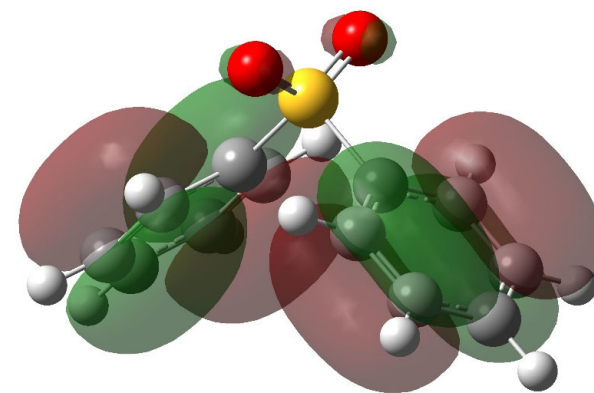
Transient absorption spectra of diphenyl sulfone derivative (DP) solutions (20 mM) in Ar-saturated 1,2-dichloroethane (DCE) obtained by the nanosecond-pulse radiolysis method. The DPs were (A) DMS, (B) DTS, and (C) DPS.



DMS(+)



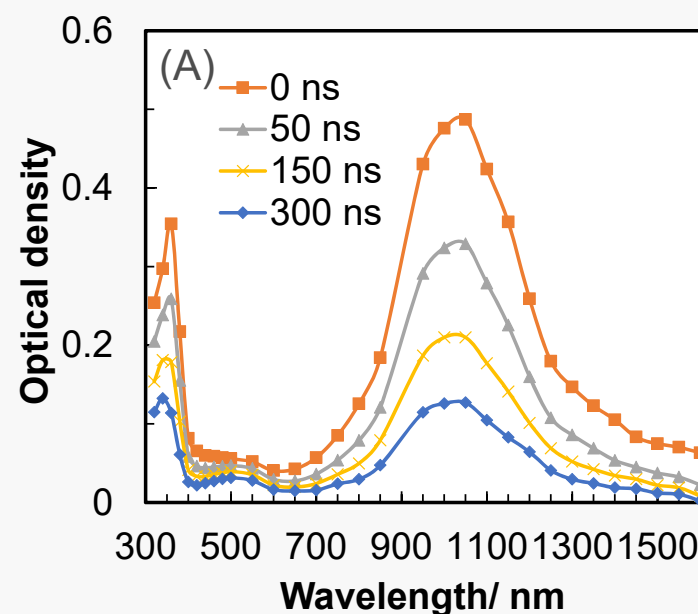
DTS(+)



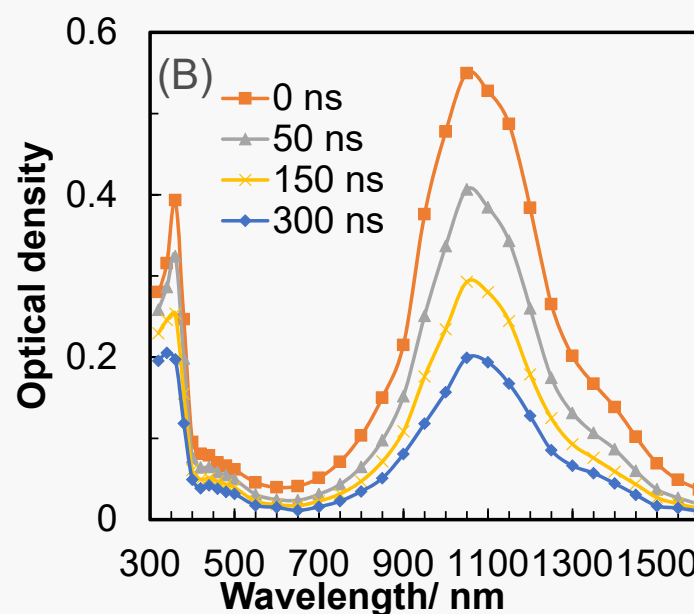
DPS(+)

Optimized structures with the SOMO alpha orbitals (isovalue = 0.02) for the radical cations of DMS [DMS(+)], DTS [DTS(+)], and DPS [DPS(+)] calculated by the DFT method [B3LYP/6-31g + (d,p)].

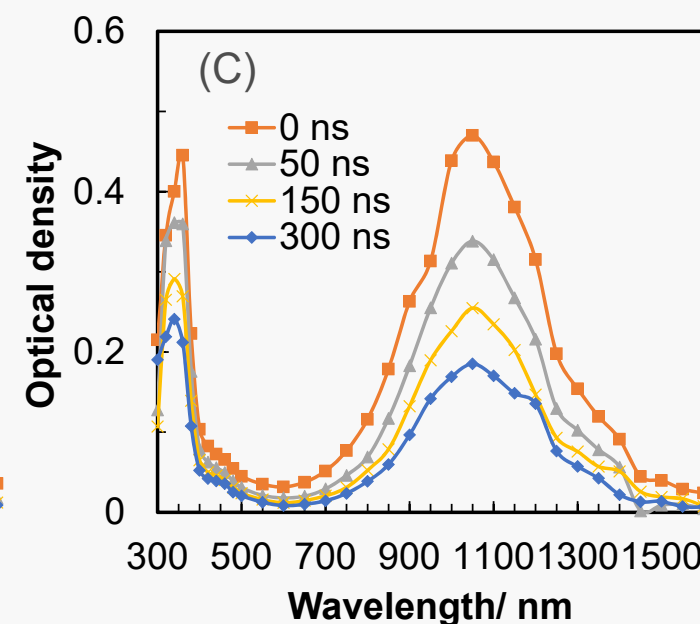
DMS/ THF



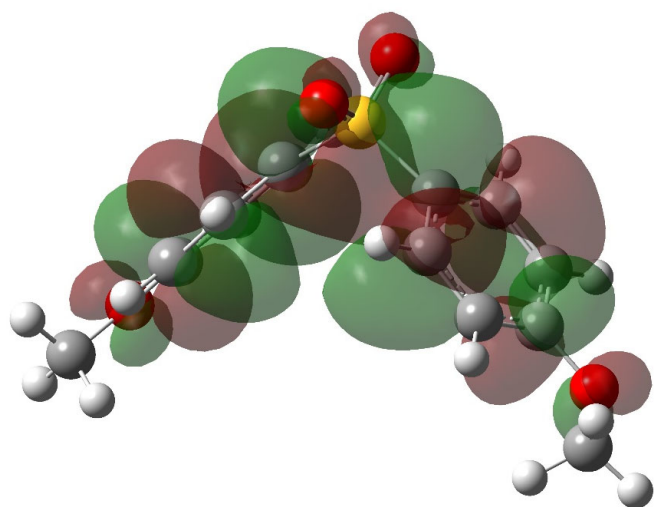
DTS/ THF



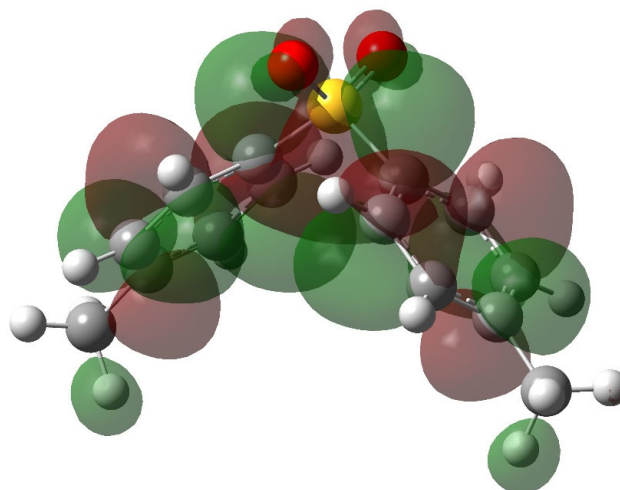
DPS/ THF



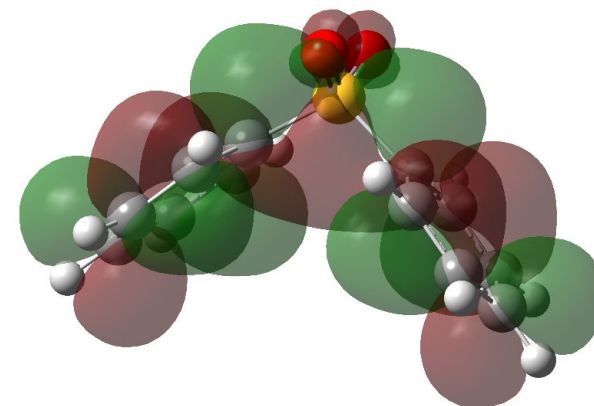
Transient absorption spectra of diphenyl sulfone derivative (DP) solutions (20 mM) in Ar-saturated tetrahydrofuran (THF) obtained by the nanosecond-pulse radiolysis method. The DPs were (A) DMS, (B) DTS, and (C) DPS.



DMS(-)



DTS(-)



DPS(-)

Optimized structures with the SOMO alpha orbitals (isovalue = 0.02) for the radical anions of DMS [DMS(-)], DTS [DTS(-)], and DPS [DPS(-)], calculated by the DFT method [B3LYP/6-31g + (d,p)].

Calculated parameters of diphenyl sulfones

12

Table

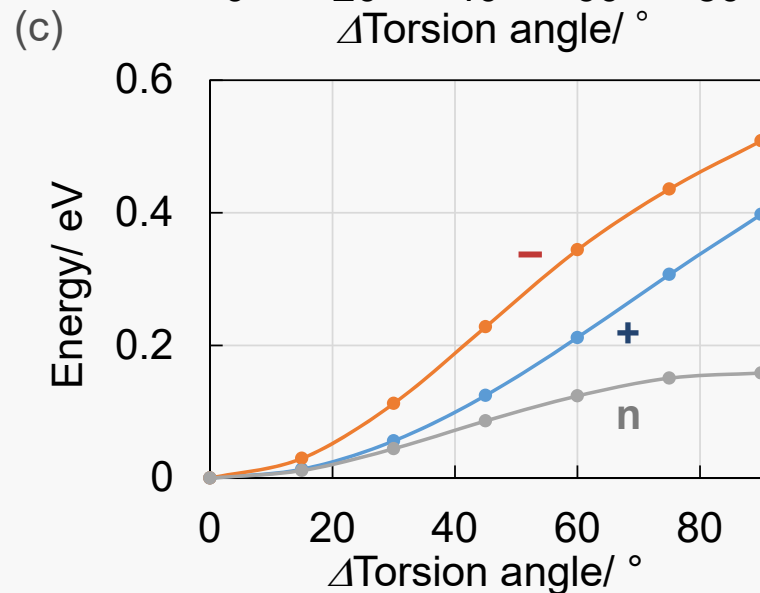
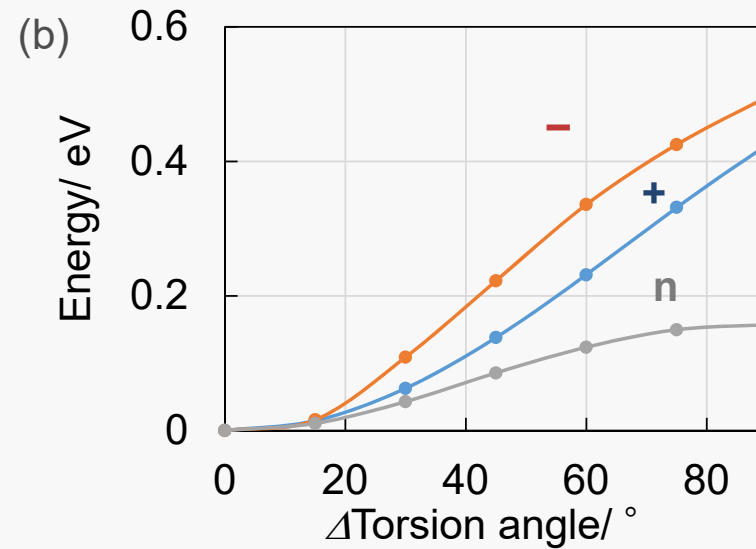
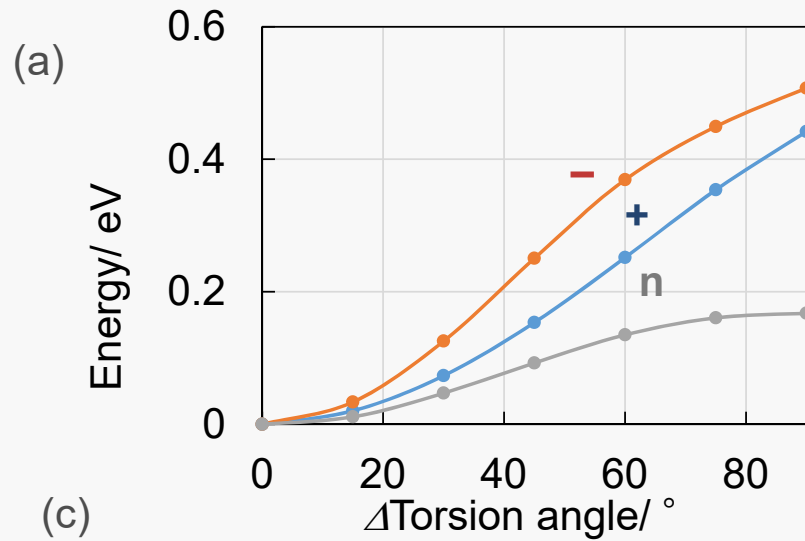
Calculated parameters (phenyl ring distances, C-S distances, dipole moments, and C-S-C angle) of DPs [neutral, radical cations (+), and radical anions(–)] calculated by DFT methods (B3LYP/6-31+g(d,p)).

Calculated parameters	DPS			DTS			DMS		
	neutral	+	–	neutral	+	–	neutral	+	–
phenyl rings distances* (nm)	0.506	0.499	0.486	0.508	0.500	0.487	0.509	0.504	0.485
C-S distances (nm)	0.181	0.180	0.177	0.180	0.180	0.177	0.180	0.179	0.177
dipole moment (debye)	5.61	7.72	4.22	6.28	8.19	5.81	7.09	8.95	7.95
C-S-C angle (deg)	104.9	102.4	108.5	105.2	101.9	108.6	105.8	102.9	109.6

*Distances between centers of phenyl rings.

Torsion barriers (S-C bond)

13

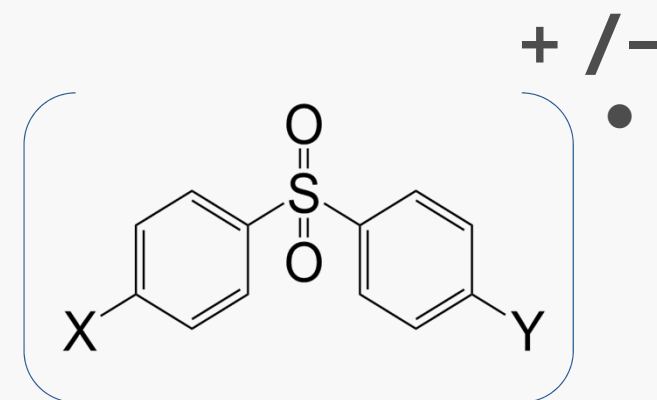


Torsion barriers of one phenyl ring in DPs from the optimized conformations of neutral states (n), radical cations (+), and radical anions (-) calculated by DFT methods [B3LYP/6-31 + g(d,p)] [(a) DMS, (b) DTS, and (c) DPS]. All geometric parameters except for the torsion angle was relaxed.

The dimer radical ions displayed CR interactions without the face-to-face overlapping of phenyl rings of sulfone.

The dimer radical cations experienced charge delocalization between the phenyl rings. In addition, we revealed that the dimer radical anion also showed excess charge delocalization on the phenyl rings and d-orbitals of the S atom. Not only the inductive effect of the sulfonyl group of DPs, but this conjugation induced the formation of the dimer radical anion and inhibited the rotation of the phenyl ring, enabling the formation of dimer radical anions even at RT.

This radical ion intermediate could play an important role in applications such as organic conductive materials, as well as EUV and EB resists. Additionally, we conclude that the properties contribute important insights for the development of materials containing diphenyl sulfones.



Publication

K. Okamoto, S. Kawai, and T. Kozawa, Sci. Rep. 10, 19823 (2020).

- We wish to express their thanks to members of the Research Laboratory for Quantum Beam Science, ISIR Osaka University, for the pulse radiolysis measurements.
- This work has been partly supported by the Grant-in-Aid for Scientific Research(project nos. 19K05330 and 18H03895) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.
- This work was partly performed under the Cooperative Research Program of Network Joint Research Center for Materials and Devices : Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials.