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Intramolecular Charge Resonance in Dimer Radical Anions of Di-, Tri-, Tetra-, and Pentaphenylalkanes

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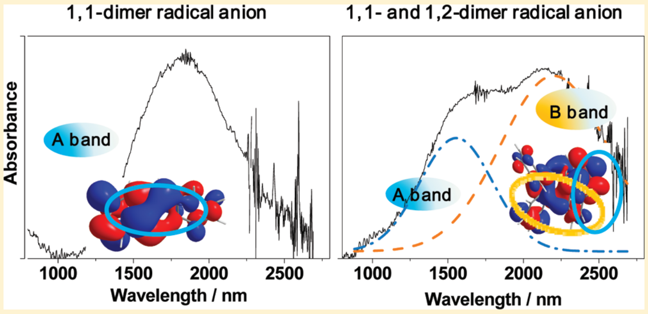
Ⓢ *Supporting Information*

ABSTRACT: Intramolecular dimer radical anions of di-, tri-, tetra-, and pentaphenylalkanes were investigated on the basis of absorption spectral measurements during γ-radiolysis in 2-methyltetrahydrofuran (MTHF) glassy matrix at 77 K and theoretical calculations. The absorption spectrum of 1,1,2,2-tetraphenylethane (1,1,2,2-Ph_4E) radical anion showed two bands in the near-infrared (NIR) region (900−2600 nm). One band observed at shorter wavelength than 2000 nm is assigned to the intramolecular charge resonance (CR) band between two phenyl groups of the 1,1-diphenylmethyl chromophore (1,1-dimer radical anion). The intramolecular CR band of the 1,1-dimer radical anion was observed for various alkanes having 1,1-diphenylmethyl chromophore such as 1,1,1-triphenylmethane (1,1,1-Ph_3M), 1,1,1,1-tetraphenylmethane (1,1,1,1-Ph_4M), and so on. The other intramolecular CR band observed at longer wavelength than 2200 nm is assigned to intramolecular dimer radical anion between two phenyl groups of the 1,2-diphenylethyl chromophore (1,2-dimer radical anion). The intramolecular CR band of the 1,2-dimer radical anion was observed for various alkanes having a 1,2-diphenylethyl chromophore, such as 1,1,2-triphenylethane (1,1,2-Ph_3E), 1,1,2,2-Ph_4E, and 1,1,1,2,2-pentaphenylethane (1,1,1,2,2-Ph_5E) and so on. No dimer radical anion was observed for 1,n-diphenylalkanes ($n > 2$) without 1,1-diphenylmethyl chromophore. The relationship between the structure and negative charge delocalization over two phenyl groups connected by an sp^3 carbon is discussed.



■ INTRODUCTION

Charge delocalization is important for understanding various radical ions in organic molecular materials and biological phenomena.[1−4] It was found in the 1960s that aromatic hydrocarbon radical cations interact with the parent neutral molecules in a $\pi-\pi$ face-to-face manner to generate the dimer radical cations having the absorption band in the NIR region of 800−2000 nm.[5−9] The band can be attributed the CR band of dimer radical cation, which is one of characteristic properties of stabilized charge between a neutral molecule and radical cation.[10] The CR band represents the charge delocalization over two chromophores.[11] The peak wavelength of the CR band corresponds to two times of the CR stabilization energy (E_{CR}) of the dimer radical cations and depends on various structural factors such as the distance, orientation, and overlapping of two chromophores.[12−14] In addition, the CR band was used as a powerful probe to monitor the dynamics of the photodissociation of the naphthalene dimer radical cation.[15]

Despite a number of the reports on dimer radical cations, little has been reported for the formation of the dimer radical anions.[16−22] Only a few intramolecular dimer radical anions of aromatic hydrocarbons have been reported even at low temperature.[16,20,22,23] In the previous paper,[22] we have reported intramolecular dimer radical anions of benzene cyclophanes. Similarly to the dimer radical cations, it was revealed that the E_{CR} of the dimer radical anions depends on the distance between two benzene rings of cyclophanes.[22] In the case of [2.2](4,7)-benzothiadiazolophane radical anions ($BTD^{\bullet-}$), the CR band is influenced by the geometry of two benzothiadiazole rings.[23] For further understanding of the negative charge delocalization over chromophores, investigating radical anions of various molecules with multiple chromophores is essential.

In the present study, we studied the intramolecular dimer radical anions of di-, tri-, tetra-, and pentaphenylalkanes (Figure 1) based on the absorption spectral measurement during γ-irradiation in low-temperature glassy matrix. Two kinds of the CR bands were observed for the intramolecular dimer radical anions of various 1,1-diphenyl- and 1,2-diphenylalkanes, suggesting two-type negative charge delocalization between two phenyl groups for 1,1-diphenylmethyl and 1,2-diphenylethyl chromophores, respectively. The relationship between structure and negative charge delocalization is discussed.

■ RESULTS AND DISCUSSION

Intramolecular Dimer Radical Anion of 1,1-Diphenylalkane. It is well established that the γ-ray irradiation of a substrate (S) in MTHF glassy matrix at 77 K generates S radical anion ($S^{\bullet-}$) as follows.[24] The counter MTHF radical cation ($MTHF^{\bullet+}$) concomitantly produced during radiolysis is transformed into a more

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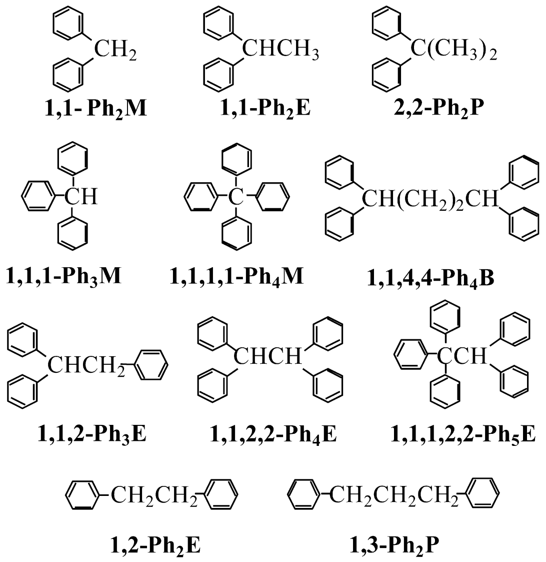


M: methane; E: ethane; P: propane; B: butane

Figure 1. Di-, tri-, tetra-, and pentaphenylalkanes used in this study.

stable free radical through the reaction with an intact MTHF molecule by reaction 2. The electrons migrate in the matrix to be

$$\mathrm{MTHF} \rightsquigarrow \mathrm{MTHF}^{\bullet +} + e_s^- \qquad (1)$$

$$\mathrm{MTHF} + \mathrm{MTHF}^{\bullet +} \rightarrow \mathrm{MTHF}^{+} + \mathrm{MTHF}^{\bullet} \qquad (2)$$

$$\mathrm{S} + e_s^- \rightarrow \mathrm{S}^{\bullet -} \qquad (3)$$

captured by S. Consequently, S$^{\bullet-}$ is selectively produced in MTHF matrices by reaction 3.

The absorption spectrum after the γ-irradiation of 1,1-diphenylmethane (1,1-Ph$_2$M) in MTHF glassy matrix showed absorption peaks at 1180, 1380, and 1830 nm. The absorption peaks at 1180 and 1380 nm are assigned to the trapped electron in MTHF,[22] which disappeared upon photobleaching. The absorption band with a peak at 1830 nm was observed as shown in Figure 2. This band is similar to that reported by Shida et al.[24] The absorption band and spectra shape were independent of the concentration of 1,1-Ph$_2$M, indicating that the absorption band at 1830 nm is due to radical anion of 1,1-Ph$_2$M (1,1-Ph$_2$M$^{\bullet-}$) (Figure S1, Supporting Information). No local excitation (LE) band similar to benzene radical anion (285 and 385 nm) was observed for 1,1-Ph$_2$M$^{\bullet-}$ in the visible region, suggesting that the negative charge delocalizes over two phenyl groups in 1,1-Ph$_2$M$^{\bullet-}$. Therefore, the band at 1830 nm can be assigned to the CR band of the intramolecular dimer radical anion of 1,1-Ph$_2$M (1,1-Ph$_2$M$^{\bullet-}$) (1,1-dimer radical anion). The energy-minimized structure of 1,1-Ph$_2$M$^{\bullet-}$ was estimated by dispersion-corrected density functional (DFT-D) theory at ωB97XD/6-31+G(d) level as shown in Figure 3, where two phenyl groups in 1,1-Ph$_2$M$^{\bullet-}$ do not take a face-to-face structure but are almost perpendicular each other with little overlap. The structure of 1,1-Ph$_2$M$^{\bullet-}$ is similar to that of neutral 1,1-Ph$_2$M (Figure 3). However, the distance (3.253 Å) between C1−C9 (C$_{ortho}$−C$_{ortho}$) atoms of the two phenyl groups in 1,1-Ph$_2$M$^{\bullet-}$ is significantly shorter by 0.368 Å than that (3.621 Å) in the corresponding neutral 1,1-Ph$_2$M, indicating an existence of an attractive interaction between two phenyl rings of 1,1-Ph$_2$M$^{\bullet-}$. There is no report for the intermolecular formation of dimer radical anion of two benzenes, while the CR band of cyclophane radical anions has been observed.[22] Thus, the alkyl chain connecting two benzene rings seems to be essential for the formation of the intramolecular dimer radical anion. The CR band at 1830 nm for 1,1-Ph$_2$M$^{\bullet-}$ is considerably red-shifted by 620 nm as compared with that at 1210 nm for [3$_2$](1,3)cyclophane$^{\bullet-}$ with the face-to-face overlap between two phenyl groups. The E_{CR} values for 1,1-Ph$_2$M$^{\bullet-}$ and [3$_2$](1,3)cyclophane$^{\bullet-}$ are calculated to be 32.7 and 49.4 kJ/mol, respectively, suggesting that the E_{CR} decreases with a decrease in the overlap between two phenyl groups in intramolecular dimer radical anions.

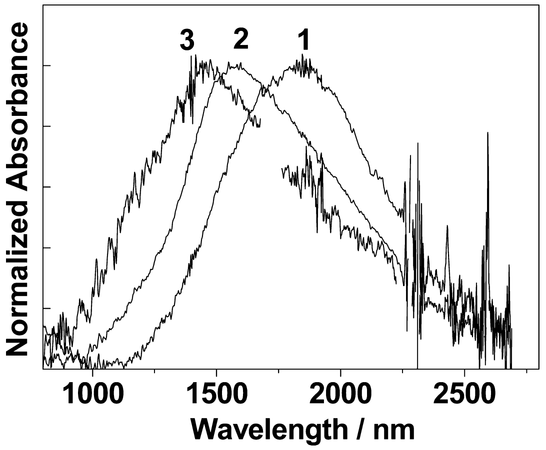
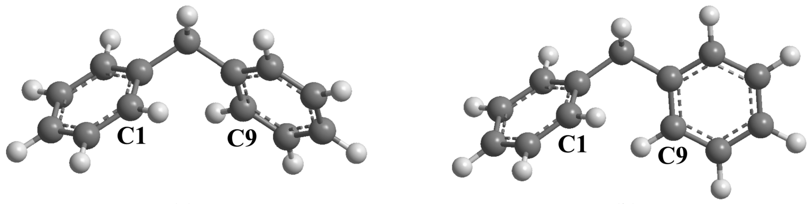


Figure 2. NIR absorption spectra of diphenylalkanes (1 × 10^{-2} M) in MTHF glassy matrix at 77 K observed after the γ-radiolysis: 1, 1,1-Ph$_2$M; 2, 1,1-Ph$_2$E; 3, 2,2-Ph$_2$P.

The CR bands of 1,1-dimer radical anions were also observed in radical anions of various 1,1-diphenylalkanes (Figure 2). The CR band of 1,1-diphenylethane radical anion (1,1-Ph$_2$E$^{\bullet-}$) was observed around 1580 nm, which is shorter wavelength than that of 1,1-Ph$_2$M$^{\bullet-}$. The E_{CR} of 1,1-Ph$_2$E$^{\bullet-}$ (37.8 kJ/mol) is slightly larger than that of 1,1-Ph$_2$M$^{\bullet-}$. In the case of 2,2-diphenylpropane radical anion (2,2-Ph$_2$P$^{\bullet-}$), the CR band showed a peak at 1470 nm (E_{CR} = 40.7 kJ/mol). The CR interaction and E_{CR} in the 1,1-dimer radical anion increases in the order of 1,1-Ph$_2$M$^{\bullet-}$ < 1,1-Ph$_2$E$^{\bullet-}$ < 2,2-Ph$_2$P$^{\bullet-}$. The peak of the CR band and other data are summarized in Table 1. The two phenyl groups in all 1,1-dimer radical anions take almost perpendicular structure as shown in the energy-minimized structures (Figure S3, Supporting Information).

Intramolecular Dimer Radical Anions of 1,1,2,2-Tetraphenylethane (1,1,2,2-Ph$_4$E$^{\bullet-}$). The absorption spectrum of 1,1,2,2-Ph$_4$E$^{\bullet-}$ in MTHF glassy matrix after γ-irradiation was observed as shown in Figure 4. The spectral shape was independent of the concentration of 1,1,2,2-Ph$_4$E. The LE band was not observed in the visible region, while the intramolecular CR band between phenyl groups of 1,1,2,2-Ph$_4$E$^{\bullet-}$ was observed in the NIR region. The spectrum was fitted to two Gaussian functions representing A and B bands with the peaks at 1550 and 2200 nm, respectively. The A band at 1550 nm was similar to that of 1,1-Ph$_2$E$^{\bullet-}$ and assigned to the CR band of the intramolecular 1,1-dimer radical anion of 1,1,2,2-Ph$_4$E$^{\bullet-}$. The energy-minimized structure of 1,1,2,2-Ph$_4$E$^{\bullet-}$ was estimated by the DFT-D as shown in Figure 5. The distance between C11−C16 (C$_{ortho}$−C$_{ortho}$) atoms of two phenyl groups at 1,1-position (3.238 Å) is slightly shorter by 0.015 Å than that of 1,1-Ph$_2$M$^{\bullet-}$ (3.253 Å). In addition, the distance between C11−C26 (C$_{ortho}$−C$_{ortho}$) atoms



(a) (b)

Figure 3. Energy-minimized structures of neutral 1,1-Ph_2M (a) and 1,1-$Ph_2M^{\bullet-}$ (1,1-dimer radical anion = intramolecular dimer radical anion between two phenyl groups) (b).

Table 1. Absorption Peak (λ) and Stabilization Energy (E_{CR}) of 1,1- and 1,2-Dimer Radical Anions, and Distance ($r_{Cortho-Cortho}$) between Two C_{ortho} of Two Phenyl Groups in 1,1-Dimer Radical Anions

	A band (1,1-dimer)			B band (1,2-dimer)	
di-, tri-, tetra-, and pentaphenylalkane radical anion	λ/nm	E_{CR} (kJ mol^{-1})	$r_{Cortho-Cortho}$[a] (Å)	λ (nm)	E_{CR} (kJ mol^{-1})
1,1-$Ph_2M^{\bullet-}$	1830	32.7	3.253		
1,1-$Ph_2E^{\bullet-}$	1580	37.8	3.191		
2,2-$Ph_2P^{\bullet-}$	1470	40.7	3.105		
1,1,2-$Ph_3E^{\bullet-}$	1450	41.2	3.421	1950	30.7
1,1,2,2-$Ph_4E^{\bullet-}$	1550	38.6	3.238	2200	27.2
1,1,1,2,2-$Ph_5E^{\bullet-}$	1210	49.4	3.006	2380	25.1
			3.064		
1,1,4,4-$Ph_4B^{\bullet-}$	1515	39.5	3.382		
1,1,1-$Ph_3M^{\bullet-}$	1505	39.7	3.142		
	1865	32.1	3.200		
1,1,1,1-$Ph_4M^{\bullet-}$	1075	55.9	3.086		
	1850	32.3	3.333		

[a] Estimated from DFT-D calculations at the ωB97XD/6-31+G(d) level.

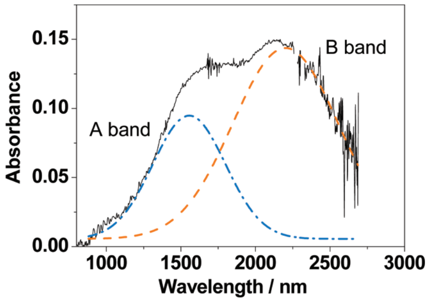


Figure 4. NIR absorption spectrum observed after the γ-radiolysis of 1,1,2,2-Ph_4E (1×10^{-2} M) in MTHF matrix at 77 K. The spectrum was composed of A and B bands.

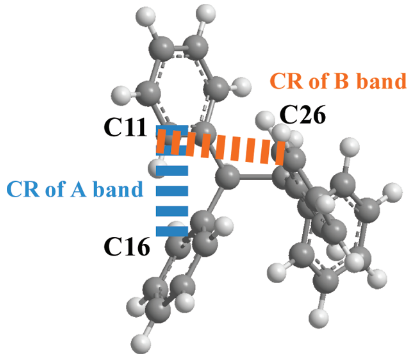


Figure 5. Energy-minimized structure of 1,1,2,2-$Ph_4E^{\bullet-}$ (1,1-dimer radical anion and 1,2-dimer radical anion = intramolecular dimer radical anion between two phenyl groups at 1- and 2-positions).

of two phenyl groups at 1,2-position of 1,1,2,2-$Ph_4E^{\bullet-}$ (3.454 Å) is shorter by 0.060 Å than that of 1,2-diphenylethane radical anion (1,2-$Ph_2E^{\bullet-}$) (3.514 Å). The two phenyl groups at not only 1,1-position but also 1,2-position are located closely in 1,1,2,2-$Ph_4E^{\bullet-}$. Thus, the B band is assigned to the CR band between two phenyl groups at 1,2-position (1,2-dimer radical anion) of 1,1,2,2-$Ph_4E^{\bullet-}$. The E_{CR} of B band (27.2 kJ/mol) is smaller than that of A band (38.5 kJ/mol). Consequently, two-type CR interactions between two phenyl groups at 1,1- and 1,2-positions are observed in 1,1,2,2-$Ph_4E^{\bullet-}$.

Intramolecular Dimer Radical Anions of 1,1,1,2,2-Pentaphenylethane (1,1,1,2,2-$Ph_5E^{\bullet-}$). The absorption spectrum of 1,1,1,2,2-$Ph_5E^{\bullet-}$ in MTHF glassy matrix after the γ-irradiation was observed as shown in Figure 6. 1,1,1,2,2-$Ph_5E^{\bullet-}$ showed a strong CR band at 2380 nm and a weak CR band at 1210 nm. The weak CR band at 1210 nm is considered to be the same as A band of 1,1,2,2-$Ph_4E^{\bullet-}$ and is assigned to the CR band of 1,1-dimer radical anion of 1,1,1,2,2-$Ph_5E^{\bullet-}$. The formation of intramolecular trimer radical anion among three phenyl groups is excluded because of no red-shift of the CR band. The E_{CR} of 1,1-dimer radical anion for 1,1,1,2,2-$Ph_5E^{\bullet-}$ (49.4 kJ/mol) is larger than that for 1,1-$Ph_2M^{\bullet-}$. This can be explained by larger overlap between two phenyl groups, while three phenyl groups at 1-position in 1,1,1,2,2-$Ph_5E^{\bullet-}$ cannot take a structure with overlapping each other because of the steric hindrance.

The absorption band at 2380 nm was similar to the B band at 2200 nm of 1,1,2,2-$Ph_4E^{\bullet-}$ and assigned to the CR band of 1,2-dimer radical anion of 1,1,1,2,2-$Ph_5E^{\bullet-}$. The two phenyl groups at 1,2-positions take a suitable structure for the interaction (Figure S3, Supporting Information). The two phenyl groups at not only 1,1-position but also 1,2-position are located closely in 1,1,1,2,2-$Ph_5E^{\bullet-}$ similar to 1,1,2,2-$Ph_4E^{\bullet-}$.

Intramolecular Dimer Radical Anions of 1,1,2-Triphenylethane (1,1,2-$Ph_3E^{\bullet-}$). The absorption spectrum of 1,1,2-

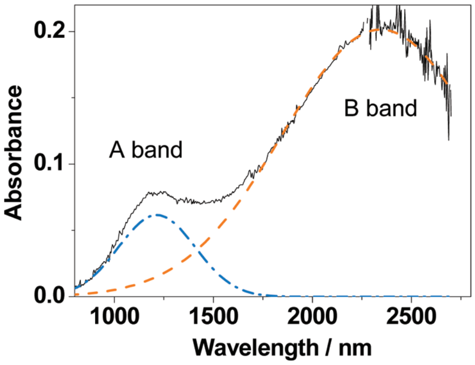


Figure 6. NIR absorption spectrum observed after the γ-radiolysis of 1,1,1,2,2-$\mathrm{Ph_5E}$ in MTHF matrix (1×10^{-2} M) at 77 K. The spectrum was composed with A and B bands.

triphenylethane radical anion (1,1,2-$\mathrm{Ph_3E^{\bullet-}}$) was observed as shown in Figure S2 (Supporting Information). 1,1,2-$\mathrm{Ph_3E^{\bullet-}}$ showed two characteristic absorption bands around 1500 nm and a shoulder at ~2200 nm. The absorption band at 1500 nm was the same as that of 1,1-$\mathrm{Ph_2E^{\bullet-}}$ and was assigned to the CR band of 1,1-dimer radical anion of 1,1,2-$\mathrm{Ph_3E^{\bullet-}}$. The shoulder at ~2200 nm was similar to that of B band of 1,1,2,2-$\mathrm{Ph_4E^{\bullet-}}$ and was assigned to the CR band of 1,2-dimer radical anion of 1,1,2-$\mathrm{Ph_3E^{\bullet-}}$.

Intramolecular Dimer Radical Anions of 1,1,4,4-Tetraphenylbutane (1,1,4,4-$\mathrm{Ph_4B^{\bullet-}}$). The absorption spectrum of 1,1,4,4-tetraphenylbutane radical anion (1,1,4,4-$\mathrm{Ph_4B^{\bullet-}}$) was observed as shown in Figure S2 (Supporting Information). 1,1,4,4-$\mathrm{Ph_4B^{\bullet-}}$ showed an absorption band at 1560 nm quite similar to that of 1,1-$\mathrm{Ph_2E^{\bullet-}}$. In addition, the optimized structure of 1,1-diphenylmethyl chromophore for 1,1,4,4-$\mathrm{Ph_4B^{\bullet-}}$ was similar to that of 1,1-$\mathrm{Ph_2E^{\bullet-}}$ (Figure S3, Supporting Information). This band was assigned to the CR band of 1,1-dimer radical anion of 1,1,4,4-$\mathrm{Ph_4B^{\bullet-}}$. On the other hand, the longer wavelength CR band corresponding to the B band of 1,1,2,2-$\mathrm{Ph_4E^{\bullet-}}$ was not observed, suggesting that two phenyl groups at the 1,4-position do not take a structure with enough overlap.

Intramolecular Dimer Radical Anions of 1,1,1-Triphenylmethane (1,1,1-$\mathrm{Ph_3M^{\bullet-}}$) and 1,1,1,1-Tetraphenylmethane (1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$). The absorption spectra of 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ and 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$ in MTHF glassy matrix after the γ-irradiation were observed as shown in Figure 7. The absorption spectra showed composite bands around 1000−2000 nm for both 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ and 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$. Those bands were independent of the concentration of 1,1,1-$\mathrm{Ph_3M}$ and 1,1,1,1-$\mathrm{Ph_4M}$, indicating that the absorption bands are due to monomeric radical anions. The longer wavelength CR band around 2000 nm corresponding to the B band was not observed for both 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ and 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$. No spectral shift was observed with increasing number (3 and 4) of phenyl groups. Formation of the intramolecular trimer or multimer radical anions is excluded, while the formations of trimer benzene radical cation or π-stacked multibenzene rings radical cation have been reported.[25,26] Those bands were fitted to two Gaussian functions representing $\mathrm{A_1}$ and $\mathrm{A_2}$ bands. The absorption of 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ showed a weak CR band at 1505 nm and a strong CR band at 1865 nm. The absorption of 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$ showed absorption bands at 1075 and a strong CR band at 1850 nm. The energy-minimized structures of 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ and 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$ were estimated by the DFT-D as shown in Figure S3 (Supporting Information), where the three or four phenyl groups at the 1-position are not coplanar and located closely. In particular, the distance (3.086 Å) between C14−C15 (C_{ortho}−C_{ortho}) atoms of two phenyl groups in 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$ is much shorter than that of 1,1-$\mathrm{Ph_2M^{\bullet-}}$ (3.253 Å). In addition, the dihedral angle of two phenyl groups including C14 and C15 was 37.46°. Consequently, the two phenyl groups can have the twisted orientations different from the orthogonal structure of 1,1-$\mathrm{Ph_2M^{\bullet-}}$, indicating that different conformers of 1,1-dimer radical anion can be formed in 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$. The $\mathrm{A_1}$ bands with the relatively larger E_{CR} (55.9 kJ/mol) may be induced by charge resonance of twisted 1,1-diphenylmethyl chromophore. The $\mathrm{A_2}$ bands of 1,1,1-$\mathrm{Ph_3M^{\bullet-}}$ and 1,1,1,1-$\mathrm{Ph_4M^{\bullet-}}$ were similar to that of 1,1-$\mathrm{Ph_2M^{\bullet-}}$, and the two phenyl groups are almost perpendicular each other. Those results suggests that the two types of CR interactions occur between two phenyl groups of the 1,1-diphenylmethyl chromophore.

Intramolecular Dimer Radical Anions of 1,*n*-Diphenylalkanes. Shida et al. reported the weak CR band at 1650 nm for the intramolecular dimer radical anion of 1,2-$\mathrm{Ph_2E}$ (1,2-$\mathrm{Ph_2E^{\bullet-}}$).[24] We examined formation of intramolecular dimer radical anion of 1,2-$\mathrm{Ph_2E}$ and 1,3-diphenylpropane (1,3-$\mathrm{Ph_2P}$) by the γ-radiolysis at 77 K. In both cases, no intramolecular CR bands of 1,2- or 1,3-dimer radical anion were observed in the NIR region (Figure S4, Supporting Information). The energy-minimized structure of 1,2-$\mathrm{Ph_2E^{\bullet-}}$ was estimated by DFT-D theory as shown in Figure S3 (Supporting Information). Discussion of the distance dependence is difficult, but the distance between C11−C26 (C_{ortho}−C_{ortho}) atoms of two phenyl groups at 1,2-position of 1,2-$\mathrm{Ph_2E^{\bullet-}}$ (3.514 Å) is much longer than those of 1,1,2-$\mathrm{Ph_3E^{\bullet-}}$ (3.364 Å), 1,1,2,2-$\mathrm{Ph_4E^{\bullet-}}$ (3.454 Å), and 1,1,1,2,2-$\mathrm{Ph_5E^{\bullet-}}$ (3.203 Å). Therefore, the CR band of 1,2-$\mathrm{Ph_2E^{\bullet-}}$ may be located at longer wavelength because of less overlap between two phenyl groups of 1,2-$\mathrm{Ph_2E^{\bullet-}}$. The energy-minimized structure of 1,3-$\mathrm{Ph_2P^{\bullet-}}$ was also estimated by DFT-D theory as shown in Figure S3 (Supporting Information).

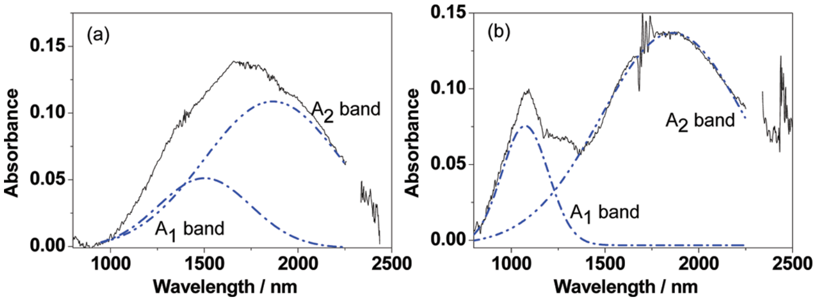


Figure 7. NIR absorption spectra observed after the γ-radiolysis of 1,1,1-$\mathrm{Ph_3M}$ (a) and 1,1,1,1-$\mathrm{Ph_4M}$ (b) in MTHF matrices (1×10^{-2} M) at 77 K.

Two phenyl groups at the 1,3-position do not take a structure with overlapping of two phenyl groups at all. It is well-known that two aromatic chromophores at 1,3-position of alkyl chain take a structure favorable for the formation of an intramolecular excimer ("$n = 3$ rule").[27] Takamuku et al. reported the formation of the intramolecular dimer radical cation of 1,3-diarylpropane.[28] Furthermore, Yamamoto et al. reported that the "$n = 3$ rule" is effective for the formation of the intramolecular dimer radical cations between two aromatic groups linked by a trimethylene chain.[29] On the other hand, the "$n = 3$ rule" was not observed for the intramolecular dimer radical anions between two aromatic groups. Although we examined the formation of the intramolecular dimer radical anions for 1,3-bis(4-cyanophenyl)propan-1-ol during the γ-radiolysis in MTHF glassy matrix at 77 K in the previous paper, no intramolecular CR band was observed.[20] Yamamoto et al. reported that radical anion of aromatic chromophores as the side group of polyalkanes was stabilized by the interaction with neighboring aromatic chromophores to form the intramolecular dimer radical anions, and that the intramolecular dimer radical anions of 1,2-methylterephthalate (1,2-MTP$^{\bullet-}$) is more stable than that of 1,3-MTP$^{\bullet-}$.[30] These results suggest that "$n = 3$ rule" does not exist for the formation of the intramolecular dimer radical anions.

Stabilization Energy of Intramolecular Dimer Radical Anions of Di-, Tri-, Tetra-, and Pentaphenylalkanes. As shown in above, two-type intramolecular CR bands of intramolecular dimer radical anions were observed. One is 1,1-dimer radical anion involving two phenyl groups at 1,1-position such as 1,1-$Ph_2M^{\bullet-}$ which was observed in all 1,1-diphenylalkanes radical anions (A band). The energy-minimized structures of 1,1-dimer radical anions are similar to those of neutral 1,1-diphenylalkanes (Figure S3, Supporting Information). The two phenyl groups in the 1,1-dimer radical anion take a twisted structure, where the planes of two phenyl groups are almost perpendicular each other. In 1,1-diphenylmethyl chromophore, the CH_2 linker between two phenyl groups does not make the effective through-space $\pi-\pi$ overlap between two phenyl groups. Thus, the intramolecular CR interaction of 1,1-dimer radical anion is different from that of benzene cyclophane radical anions with the face-to-face $\pi-\pi$ overlap. The SOMO electron of 1,1-$Ph_2M^{\bullet-}$ is delocalized mainly on two phenyl groups as shown in Figure 8 (ωB97XD/6-31+G(d)).

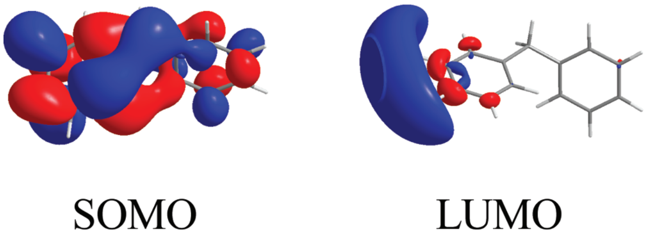


Figure 8. MO diagram of 1,1-$Ph_2M^{\bullet-}$ obtained from the DFT-D calculation.

The charge delocalization of 1,1-$Ph_2M^{\bullet-}$ is significantly different from that of face-to-face full overlapped intramolecular dimer radical anions such as benzene cyclophane radical anions and *syn*-BTD$^{\bullet-}$. As a result, the negative charge is effectively delocalized over two phenyl groups of 1,1-$Ph_2M^{\bullet-}$ through transannular interaction in the perpendicular twisted structure.

In addition, the CR bands of 1,1-dimer radical anions are expected to be influenced by the structural parameters such as the distance between *ortho* carbons of two phenyl groups. If only the distance between two chromophores (r) is changed, generally the E_{CR} value should be a function of r as $E_{CR} \propto \exp(-\beta r)$, where β is a constant.[12,22,31] As shown in Figure 9, although the E_{CR} tends to decrease with an increase in r, clear linearity was not observed for a plot of ln E_{CR} and $r_{Cortho-Cortho}$ (Figure 9), indicating that other structural parameters such as dihedral angle and so on are also important. Thus, it is indicated that the consequent CR interaction is very sensitive to the structural parameters such as distance of 1,1-dimer radical anions.

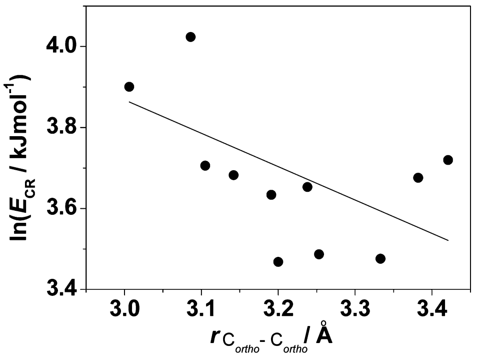


Figure 9. Dependence of E_{CR} for 1,1-dimer radical anion having a 1,1-diphenylmethyl chromophore on the distance between the *ortho* carbons of two phenyl groups ($r_{Cortho-Cortho}$).

The other CR band was observed at wavelength longer than 2000 nm and was assigned to the intramolecular 1,2-dimer radical anion involving two phenyl groups at the 1,2-position (B band). The two phenyl groups at the 1,2-position of 1,1,2,2-$Ph_4E^{\bullet-}$ are located closer than those of 1,2-$Ph_2E^{\bullet-}$ because of the steric hindrance of 1,1-diphenylmethyl chromophore (Figure S3, Supporting Information). The formation of 1,2-dimer radical anion is enhanced by the presence of 1,1-diphenylmethyl chromophore. The SOMO electron of 1,1,2,2-$Ph_4E^{\bullet-}$ is delocalized on four phenyl groups as shown in Figure 10 (ωB97XD/6-31+G(d)).

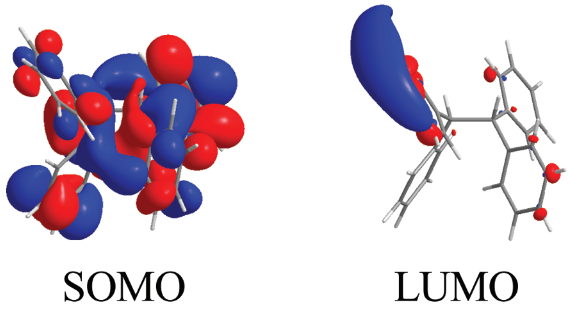


Figure 10. MO diagram of 1,1,2,2-$Ph_2E^{\bullet-}$ obtained from the DFT-D calculation.

The nodal pattern in SOMO of 1,1,2,2-$Ph_4E^{\bullet-}$ differs from that of 1,1-$Ph_2M^{\bullet-}$. This E_{CR} value (27.2 kJmol^{-1}) is much lower than that for the CR interaction of 1,1-dimer radical anions. The lower stabilization is caused by less overlap between two phenyl groups at 1,2-position.

It is concluded that the CR interaction between two phenyl groups in dimer radical anion increases in the order of 1,2-diphenylethyl <1,1-diphenylmethyl < cyclophane. It should be emphasized that the suitable structure of two phenyl groups plays a key role for the formation of the CR interaction between two phenyl groups of 1,1- and 1,2-dimer radical anions. As a result, the charge delocalization of radical anion does not necessarily require full face-to-face sandwich structure. It is suggested that the formation of the intramolecular dimer radical anions is considerably different from that of the intramolecular dimer radical cations and singlet excimer ("$n = 3$ rule"). Generally, the negative charge may be delocalized in two aromatic groups of various aromatic hydrocarbon radical anions to have very weak CR interaction and low stabilization energy. Therefore, the CR bands between two aromatic groups of various radical anions are located at longer wavelengths than 2500 nm and are not observed with the present absorption measurement.

■ CONCLUSIONS

Two kinds of CR band for the intramolecular 1,1- and 1,2-dimer radical anions of di-, tri-, tetra-, and pentaphenylalkanes were observed for the first time during the γ-radiolysis in low-temperature glassy matrix. One CR band was observed at shorter wavelength than 2000 nm for 1,1-diphenylalkane radical anions which is resulted from the CR interaction between two phenyl groups at 1,1-position and depends on the structural parameters such as distance between the *ortho*−*ortho* carbons between two phenyl groups. The other CR band was observed at longer wavelength than 2200 nm for the intramolecular dimer radical anions with 1,2-diphenylethane chromophore, in which two phenyl groups interact each other at 1,2-position with the structure induced by the steric effect of 1,1-diphenylmethyl chromophore. It should be emphasized that the twisted structure of 1,1-dimer radical anions is favorable for the CR interaction between two phenyl groups in 1,1-diphenylalkane radical anions, although the stabilization energy is smaller than in the face-to-face π−π interaction for intramolecular dimer radical anion of cyclophanes.

■ EXPERIMENTAL SECTION

Materials. 1,1-Diphenylmethane (1,1-Ph_2M), 2,2-diphenylpropane (2,2-Ph_2P), 1,1,1-triphenylmthane (1,1,1-Ph_3M), 1,1,1,1-tetraphenylmethane (1,1,1,1-Ph_4M), 1,2-diphenylethane (1,2-Ph_2E), and 1,3-diphenylpropane (1,3-Ph_2P) were used without further purification. 1,1-Diphenylethane (1,1-Ph_2E), 1,1,2,2-tetraphenylethane (1,1,2,2-Ph_4E), 1,1,4,4-tetraphenylbutane (1,1,4,4-Ph_4B), and 1,1,2-triphenylethane (1,1,2-Ph_3E) were synthesized by hydrogenation of the corresponding olefin by the use of Pd/C in ethanol. These phenylalkanes were purified by column chromatography (Silica gel). 1,1,1,2,2-Pentaphenylethane (1,1,1,2,2-Ph_5E) is known a compound and was prepared by a method similar to that reported by Smith.[32] 2-Methyltetrahydrofuran (MTHF) was distilled over CaH_2 before use.

γ-Radiolysis. The γ-radiolysis of rigid glass of MTHF solutions degassed by the freeze−pump−thaw method was carried out in 1 mm thick Suprasil cells in liquid nitrogen at 77 K by a ^{60}Co γ source (total dose, 1.65 kGy). The absorption spectra were measured in Dewar vessel at 77 K by a with Shimadzu UV-3100 UV−vis−NIR spectrometer. The absorption spectrum was noisy in the wavelength region longer than 2200 nm because of the overlap of the vibrational overtone absorptions of MTHF in this region.

Theoretical Calculations. Optimized structures of radical anion of phenylalkanes were estimated by DFT-D at the ωB97XD/6-31+G(d) level using the Gaussian09 package.[33]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NIR absorption spectrum observed after the γ-radiolysis of 1,1,2-Ph_3E, 1,1,4,4-Ph_4B, 1,2-Ph_2E, and 1,3-Ph_2P in MTHF. NIR absorption spectrum of the concentration independence of 1,1-$Ph_2M^{\bullet -}$. Optimized structures of radical anion of polyphenylalkane and neutral 1,1-Ph_2M. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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