Efficient Emission from Charge Recombination during the Pulse Radiolysis of Electrochemical Luminescent Donor–Acceptor Molecules with an Ethynyl Linkage

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An extensive number of studies have been devoted to radical cations (M¥+) and anions (M¥−) generated from detachment and attachment of an electron from and to a neutral solute molecule (M), respectively. Organic radical ions are important intermediates in photoinduced electron-transfer reactions and radiation chemical reactions, with attention being focused on their reactivities.1 The formation and reaction of radical ions in solution have been investigated by various methods such as pulse radiolysis, laser flash photolysis, and electrochemical reaction.

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In the pulse radiolysis of solutions, the solvent molecules are initially ionized to give holes and electrons which react with the solute molecules. In nonpolar
solvents, hole and electron are initially formed and undergo partly the fast geminate charge recombination to give the solvent molecules in the singlet and triplet excited states. For example, initial products during the pulse radiolysis of benzene (Bz) are solvated electron (e−), Bz radical cation (Bz+), and Bz in the excited state (Bz*), which react with M to give M−, M+, and M* in the singlet and triplet excited states (M* = M*s and M*), respectively, as shown in Scheme 1.2 Usually M* is the main product, while M+ and M− are produced in minor yields. Therefore, the formation of M* from the charge recombination between M+ and M− is a minor process, and no M*s and only a little M* exist at a few tens of nanoseconds after an electron pulse during the pulse radiolysis.

Radical ions are also formed by the electrochemical reaction in solution. Recently, various studies on the electrogenerated chemiluminescence (ECL) have been reported to confirm the emissive species through the charge recombination between M* and M− in solution. ECL mainly results from M* and/or the singlet excimer of M* (1M*), as shown in Scheme 2. For pyrene, perylene, poly(9,9-diocetylfluorene), donor-substituted phenylquinolinylethenes, donor-substituted phenyl(9-acridiny1)ethylenes, and phenyl(9-cyano-10-anthracenyl)ethylene, excimer type ECL was observed. However, the selective formation of 1M* as the emissive species has not been fully understood.

SCHEME 1. Pulse Radiolysis of M in Bz

Bz → e− + Bz+
Bz+ + e− → Bz (major process)
e− + M → M−
M+ + M → M
Bz* + M → Bz + M*
Bz* + M* → Bz + M

SCHEME 2. Mechanism for the Electrogenerated Chemiluminescence (ECL)

M + e− → M−
M− + M → M*
M* + M* → M + M, M + M, and/or M;
M* + M* → M + M
M* + M* + hν
M2* → 2M + hν

According to the ECL mechanism, when M+ and M− are produced at sufficient concentrations, 1M* and 1M*, and/or 1M* can be generated from the charge recombination between M* and M* during the pulse radiolysis of the ECL molecules in Bz. We have previously reported that the efficient emissions during the pulse radiolysis of electrochemical luminescent substitute quinoline with donor–acceptor character (PnQ). The emission was suggested to originated from the PnQ* generated from the charge recombination between PnQ+ and PnQ− which are yielded from the initial radiolytic reaction in Bz.

In this paper, we report the observation of the efficient emission from the charge recombination between radical cations and radical anions of various donor–acceptor substituted phenylethenes (PE) such as donor-substituted phenyl(9-acridiny1)ethylenes (1PE* and phenyl(9-cyano-10-anthracenyl)ethylene (2PE*), the pulse radiolysis of PE in Bz. In addition, the parent unsubstituted molecules of PE, acridine (3), and several phenylacetylene derivatives (PA = phenylacetylene (4), diphenylacetylene (5), 4-methyl diphenylacetylene (5), and 4,4′-dimethoxy diphenylacetylene (5)) were also examined for the emission measurement (Scheme 3). PE is known as the ECL molecule because PE in the singlet state (1PE*) and the emissive 1PE* excimer (1PE*) is generated from the triplet–triplet annihilation (T-route) of PE in the triplet excited state (1PE*). Using the pulse radiolysis technique, both PE* and PE− can be generated at the same time in Bz. It is expected that 1PE*, 3PE*, and/or 1PE* can be generated from the charge recombination between PE− and PE− during the pulse radiolysis of PE in Bz, when PE* and PE− are produced at sufficient concentrations. Therefore, the emission mechanism of ECL molecules can be investigated in detail with the time-resolved transient absorption and emission measurement during the pulse radiolysis.

Results and Discussion

Emission Properties and Photophysical and Electrochemical Properties

The photophysical properties of PE (1 and 2), 3, and PA (4 and 5) in acetonitrile and in Bz are listed in Table 1, together with the electrochemical properties in acetonitrile. Except for amino-
were determined from the integration of the fluorescence spectra of PE in CH$_3$CN in Bz in CH$_3$CN.

The fluorescence quantum yields ($\phi_f$) in acetonitrile solution were at 431 nm for 1a and 433 nm for 1b. The broad and very weak emission of PE$_2$* was observed at 417 nm in Ar-saturated Bz (Figure 1a and Table 1). The excitation energies of the lowest absorption peaks of PE were estimated from the peak wavelengths of the fluorescence spectra. The ground-state absorption peaks of PE in Bz and acetonitrile were observed at 417–490 nm with a little influence of the solvent polarity. The fluorescence peaks in Bz were observed at 433–554 nm (Figure 1), while those in acetonitrile were at 431–569 nm with a red-shift due to the high solvent polarity. PE$_2$ did not fluoresce in acetonitrile but showed emission with a peak at 604 nm in dichloromethane. Using a setup consisting of a fluorescence spectrophotometer and a voltammetric instrument with a PC interface, we observed ECL emission of PE$_2*$ generated through the T-route. The absorption and fluorescence peaks of 1 in Bz were observed at 398–450 and 433–515 nm, respectively (Figure 1a and Table 1). It was shown that both absorption and fluorescence peaks shifted to longer wavelength with an increase of the electron-donating character of the substituent. This tendency is also observed for PE$_2$ except for 2d increased with a higher potential, as in the ECL emission. Thus, the standard potentials for the half reactions can be estimated from cyclic voltammetric peak potentials in acetonitrile solution. The additional term (−0.16 eV) in eq 1 is due to the difference between their voltammetric peak potentials and their standard potentials (0.06 eV) and the TAS$^*$ term (0.1 eV).

The calculated $\Delta H^*$ values for PE are listed in Table 1. The change recombination between M$^+$ and M$^-$ occurs when $\Delta H^*$ values (eq 1) are higher than their $E_{S1}$ (Table 1). However, this relation can be applied only when the singlet excited state was directly formed through the charge recombination between M$^+$ and M$^-$. In the case of PE, it is assumed that PE$_2*$ is generated and followed by the triplet–triplet annihilation giving PE$_2$*, leading to the ECL (T-route), as shown in Figure 1b and Table 1. In the emissions generated through the T-route, the energy from the triplet–triplet annihilation must be pooled to be sufficient for the formation of the singlet excited state. Some monomer and excimer emissions cannot be explained by eq 1 because PE$_2$* is generated through the T-route. The absorption and fluorescence peaks of 1 in Bz were observed at 398–450 and 433–515 nm, respectively (Figure 1a and Table 1). It was shown that both absorption and fluorescence peaks shifted to longer wavelength with an increase of the electron-donating character of the substituent. This tendency is also observed for PE$_2$ except for 2d increased with a higher potential, as in the ECL emission. The $\phi_f$ values of PE except for 2d increased with an increase of the fluorescence lifetime ($\tau_f$), suggesting the lifetime of the S$_1$ state governs $\phi_f$. It is assumed that the longer $\tau_f$ value for PE$_2*$ bearing strong donors (1e, 2c, and 2d) results from the formation of the singlet intramolecular charge transfer (ICT) state with the larger twisted angle between the donor and acceptor moieties.

Emission Spectra Observed during the Pulse Radiolysis of PE in Bz. The time-resolved emission spectra were observed to show monotonic decay in the 40-ns time scale after an electron pulse during the pulse radiolysis of PE in Ar-saturated Bz (Figures 2 and 3). It should be noted that all PE show emissions with peaks at 457–618 nm in the 40-ns time scale after an electron pulse.
emission. For example, the emission intensity of 1c was 23 times higher than that of 5c. Similarly, that of 1e was 23 times higher than that of 5e. These results indicate that strong electronic coupling between the donor and acceptor is responsible for the efficient emission during the pulse radiolysis of PE in Bz. In addition, it is noteworthy that, although the φn value of 2e (0.73) is higher than that of 1e (0.65), the emission intensity of 2e during the pulse radiolysis is 18% lower than that of 1e (92%). Compared with 2e, although the φn value of 2f is low (0.44), the emission intensity of 2f during the pulse radiolysis is shown to be high (62). For 2f, the emission was observed with an extremely long lifetime because of the delayed fluorescence. However, the intensity of this delayed fluorescence observed during the pulse radiolysis was too weak. The same delayed fluorescence was also observed during the laser flash photolysis, as described later.

The emission behavior was investigated by changing the concentration of 1a (1, 5, and 10 mM) in Bz during the pulse radiolysis. In the steady-state measurement, the fluorescence spectra showed no excimer emissions at these concentrations. Figure 4 shows the emission spectra of 1a in Bz during the pulse radiolysis. The intensities were normalized to the emission peak intensity at 457 nm for three spectra. The emission intensity observed at 527 nm increased with an increase in the concentration, suggesting that the emission is assigned to the excimer. At 5 mM, the emission lifetimes at 457 and 550 nm were approximately 10 ns (Figure 4, inset). It is

Table 2. Emission Peak (λ\textsubscript{Em} \textsuperscript{max}) and Relative Emission Intensity of PE (1 and 2), 3, and PA (4 and 5) Observed at 10 ns after an Electron Pulse during the Pulse Radiolysis in Bz, Together with the ECL Emission Peak and Intensity in Acetonitrile

<table>
<thead>
<tr>
<th>PE</th>
<th>λ\textsubscript{Em} \textsuperscript{max}/nm</th>
<th>rel emission intensity\textsuperscript{a} (%)</th>
<th>λ\textsubscript{ECL} \textsuperscript{max}/nm</th>
<th>ECL intensity\textsuperscript{a} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>457, 527</td>
<td>21</td>
<td>473</td>
<td>4.4</td>
</tr>
<tr>
<td>1b</td>
<td>461, 534</td>
<td>27</td>
<td>482</td>
<td>2.2</td>
</tr>
<tr>
<td>1c</td>
<td>467, 550\textsuperscript{b}</td>
<td>92</td>
<td>480</td>
<td>9.0</td>
</tr>
<tr>
<td>1d</td>
<td>468, 570\textsuperscript{b}</td>
<td>140</td>
<td>487</td>
<td>1.2</td>
</tr>
<tr>
<td>1e</td>
<td>525, 618</td>
<td>54</td>
<td>534</td>
<td>2.1</td>
</tr>
<tr>
<td>2c</td>
<td>500, 545\textsuperscript{b}</td>
<td>18</td>
<td>536</td>
<td>20</td>
</tr>
<tr>
<td>2f</td>
<td>574, 680\textsuperscript{b}</td>
<td>62</td>
<td>550</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>410, 460</td>
<td>0.3</td>
<td>c</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>378</td>
<td>0.9</td>
<td>c</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>338, 467</td>
<td>2.1</td>
<td>520</td>
<td>7.0</td>
</tr>
<tr>
<td>5b</td>
<td>422, 577</td>
<td>0.4</td>
<td>c</td>
<td>0</td>
</tr>
<tr>
<td>5c</td>
<td>335, 507</td>
<td>4.0</td>
<td>c</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Relative to the intensity for 2-(p-methoxyphenylethynyl)quinoline = 100%.

\textsuperscript{b} Broad peak.

\textsuperscript{c} No or very weak emission was observed.

\textsuperscript{d} Reference 6. Relative to the ECL intensity of tris(2,2'-bipyridyl)ruthenium(II)oxalate complex = 100%.

Electrochemical reactions.\textsuperscript{6} However, compared to the ECL intensity, PE showed strong fluorescence during the pulse radiolysis in Bz (Table 2). In particular, 1a showed the highest fluorescence intensity (140) during the pulse radiolysis, in contrast to the lowest ECL intensity (1.2) among PE. Therefore, the occurrence of the efficient emission during the pulse radiolysis of PE corresponds to a mechanism different from the T-route mechanism.

The emission intensities of PE observed during the pulse radiolysis were much higher than those of 3 and the corresponding PA. For example, the emission intensity of 1b was 66 times higher than that of 5b. Similarly, that of 1e was 23 times higher than that of 5e. These results indicate that strong electronic coupling between the donor and acceptor is responsible for the efficient emission during the pulse radiolysis of PE in Bz. In addition, it is noteworthy that, although the φn value of 2e (0.73) is higher than that of 1e (0.65), the emission intensity of 2e during the pulse radiolysis is 18% lower than that of 1e (92%). Compared with 2e, although the φn value of 2f is low (0.44), the emission intensity of 2f during the pulse radiolysis is shown to be high (62). For 2f, the emission was observed with an extremely long lifetime because of the delayed fluorescence. However, the intensity of this delayed fluorescence observed during the pulse radiolysis was too weak. The same delayed fluorescence was also observed during the laser flash photolysis, as described later.

According to the −ΔH\textsuperscript{f} values (Table 2), PE emits light because PE is generated via the T-route in the
suggested that the monomer and excimer lifetimes are governed by the same precursor, which converts the monomer and excimer through the same reaction process.

**Transient Absorption Spectra Observed during the Pulse Radiolysis of PE.** To generate both PE$^+$ and PE$^-$ and to observe the annihilation of PE$^+$ and PE$^-$ through the charge recombination, Bz was used as solvent for the pulse radiolysis of PE. Figure 5a shows the transient absorption spectra observed during the pulse radiolysis of 1a in Ar-saturated Bz. The transient absorption spectra of Bz$^+$ and Bz$^-$ have been reported to have a peak at 400 and 235 nm with a very low molar absorption coefficient.$^{7,11}$ It is assumed that e$_{-}$ is rapidly trapped by 1a or undergoes fast geminate charge recombination. Therefore, e$_{-}$ cannot be observed under the present experimental conditions. The transient absorption spectrum observed at $t = 50$ ns after an electron pulse in Figure 5a can be assigned to 1a$^-$, 1a$^+$, and/or 3a$^\pm$.

**TABLE 3. Transient Absorption Peaks ($\lambda_{\text{max}}$) and Half Lifetimes ($\tau_{1/2}$) Observed during the Pulse Radiolysis of PE in Ar-Saturated Bz, DCE, and DMF**

<table>
<thead>
<tr>
<th>PE</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\tau_{1/2}$/ms</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\tau_{1/2}$/ms</th>
<th>$\lambda_{\text{max}}$/nm</th>
<th>$\tau_{1/2}$/ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>505 2.9</td>
<td>642 0.21</td>
<td>553, 604, 656 3.4</td>
<td>1b</td>
<td>512 2.1</td>
<td>658 0.17</td>
</tr>
</tbody>
</table>

* Not determined.

To confirm the transient absorption spectra of 1a$^+$ and 1a$^-$, the pulse radiolysis of 1a in Ar-saturated DCE and DMF was also examined. It is established that M$^+$ is generated during the pulse radiolysis of M in DCE,$^{12}$ while M$^-$ is in DMF.$^{13}$ Figure 5b shows the transient absorption spectra observed during the pulse radiolysis of 1a in Ar-saturated DCE. Although a broad peak at 642 nm disappeared, that around 450 nm remained even in the time scale longer than 10 ms. Therefore, the absorption peak around 450–500 nm is assumed to be that of a stable product, while the peak observed at 642 nm ($\tau_{1/2} = 210$ ns) is assigned to the radical cation of 1a (1a$^+$). It seems that Cl$^-$ reacts with 1a$^+$ to give the product having an absorption peak around 450–500 nm.$^7$ For AD in Ar-saturated DCE, two transient absorption peaks observed around 400–430 nm remained even in the time scale longer than 10 ms, and at 464 nm with $\tau_{1/2} = 86$ ns. The long-lived one observed around 400–430 nm is also assigned to a stable product. The peak at 464 nm is reasonably assigned to AD$^+$.$^{14}$

Figure 5c shows the transient absorption observed during the pulse radiolysis of 1a in Ar-saturated DMF. The peak observed at 553, 604, and 656 nm ($\tau_{1/2} = 3.4$ ms) is assigned to the radical anion of 1a (1a$^-$). At 10 ms, the new emission peak was observed at 528 nm. It seems that 1a$^-$ reacts to give a product having an absorption peak at 528 nm. Similarly, the transient absorption spectra assigned to 1a$^+$ and 1a$^-$ were observed during the pulse radiolysis of other PE in DCE and DMF, respectively. These results are summarized in Table 3. In Bz solution, the transient absorptions of PE$^+$ and PE$^-$ were not observed. Therefore, it is assumed that PE$^+$ and PE$^-$ immediately recombine to give 1PE$^+$, 1PE$^-$, and PE$^\pm$ within a pulse duration.$^7$

**Emission and Absorption Spectra Observed during the Laser Flash Photolysis of PE in Bz.** To assign the transient species in detail, the transient absorption spectra of PE in Bz were measured during the 355-nm
fluorescence of $1_{a^*}$ generated from the triplet–triplet annihilation. $^{15}$ Similarly, the “P-type” delayed fluorescence was observed during the laser flash photolysis of other PE in Bz (Figure S5, Supporting Information). On the other hand, very weak “P-type” delayed fluorescence was observed during the pulse radiolysis of PE in Bz. Therefore, it is expected that $\text{PE}^+$ and $\text{PE}^-$ are mainly generated from the charge recombination between $\text{PE}^+$ and $\text{PE}^-$ during the pulse radiolysis.

Emission Mechanism. Because the efficient emission of PE during the pulse radiolysis seems to result from the donor–acceptor structure of PE, the characteristic emission mechanism for the donor–acceptor molecules should be involved. We have previously reported that the efficient emission was observed during the pulse radiolysis of PnQ with strong electric coupling between donor and acceptor through conjugation. $^7$

It is suggested that the positive charge and negative charges in PnQ$^+$ and PnQ$^-$ are localized on the donor and acceptor moieties, respectively. It is also suggested for PE that negative charge is localized on the electron acceptor moiety in the radical anion ($A^−−D$), while positive charge is localized on the electron donor moiety in the radical cation ($A^+−D^+$). This scheme reasonably explains the emission mechanism during the pulse radiolysis of 1 in Bz. For 1a, the $E_{\text{od}}$ value of the donor moiety (corresponding to benzene) is 2.08 V, while the $E_{\text{od}}$ value of the acceptor moiety (corresponding to AD) is $−2.1$ V. Therefore, the $−\Delta H^o$ value for the charge recombination between $1_{a^+}$ and $1_{a^-}$ with localized charges can be estimated to be 4.02 eV, which is sufficiently larger than the $E_{\text{od}}$ value. Similarly, the $−\Delta H^o$ values for $1_b$, $1_c$, and $1_s$ are sufficiently larger than the $E_{\text{od}}$ values (Table 4). Therefore, it is suggested that the charge recombination between $A^+−D$ and $A^−−D^+$ occurs to give $1_{a^–e}$ and $1_{a^–e}$ during the pulse radiolysis of 1a in Bz (Scheme 4). The formation of $1_{a^–e}$ can be explained by the planar structure of $1_{a^–e}$ and $1_{a^–e}$ in which the $\pi$-donor and $\pi$-acceptor moieties exist in the same plane because of the weak donor moiety. The compounds bearing weak donors (1a–d) show excimer emission due to a very small twist angle between the donor and acceptor moieties.

For 2 their $−\Delta H^o$ values are not sufficient to populate $2^*$. This results in the lower emission intensity of 2 during the pulse radiolysis, although it shows strong fluorescence in the steady-state measurement. For PE bearing strong donors (1a, 2a, and 2f), the emissive singlet intramolecular charge transfer (ICT) state ($l(A^+−D^+)¥$) with the larger twisted angle is assumed. $^{15}$ The ICT states for 1a, 2e, and 2f are also expected by their slightly longer $\tau_0$ than those of other PE (Table 1).

The emission mechanism during the pulse radiolysis of PE can be divided into two categories. For 1a–d with

TABLE 4. Oxidation Potentials (E_{ox}) of Donor Moiety, Reduction Potentials (E_{red}) of Acceptor Moiety, Estimated Annihilation Enthalpy Values (−ΔH°), and E_{St} of PE

<table>
<thead>
<tr>
<th>PE</th>
<th>doner</th>
<th>E_{ox}/V in CH_{2}CN</th>
<th>acceptor</th>
<th>E_{red}/V in CH_{2}CN</th>
<th>−ΔH°/eV</th>
<th>E_{St}/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>benzene</td>
<td>2.08b</td>
<td>acridine</td>
<td>−2.1°</td>
<td>4.02</td>
<td>2.71</td>
</tr>
<tr>
<td>1b</td>
<td>toluene</td>
<td>1.98b,c</td>
<td>acridine</td>
<td>−2.1</td>
<td>3.92</td>
<td>2.70</td>
</tr>
<tr>
<td>1c</td>
<td>anisole</td>
<td>1.35c</td>
<td>acridine</td>
<td>−2.1</td>
<td>3.29</td>
<td>2.67</td>
</tr>
<tr>
<td>1d</td>
<td>isopropybenzene</td>
<td>d</td>
<td>acridine</td>
<td>−2.1</td>
<td>-</td>
<td>2.66</td>
</tr>
<tr>
<td>1e</td>
<td>N,N-dimethanoline</td>
<td>0.55e</td>
<td>acridine</td>
<td>−2.1</td>
<td>2.49</td>
<td>2.41</td>
</tr>
<tr>
<td>2f</td>
<td>anisole</td>
<td>1.35c</td>
<td>9-cyanoanthracene</td>
<td>−0.98b</td>
<td>2.17</td>
<td>2.48</td>
</tr>
<tr>
<td>2g</td>
<td>N,N-dimethanoline</td>
<td>0.47f</td>
<td>9-cyanoanthracene</td>
<td>−0.98</td>
<td>1.29</td>
<td>2.24</td>
</tr>
</tbody>
</table>

a Potential is estimated vs Ag/Ag°. b Reference 16a. c Reference 16b. d Not determined. e Reference 16c. f Reference 16d. g Reference 8.

SCHEME 4. Mechanism of the Emission during the Pulse Radiolysis of 1a-d in Bz$^{a}$

1. The emission is suggested to originate from PE$^{-}\text{ox}$ generated from the charge recombination between PE$^{+}$ and PE$^{-}$ which yield the initial radiolytic reaction in Bz.

2. The emission intensities of PE observed at 10 ns after an electron pulse were 8.8–91 times higher than that of 5 during the pulse radiolysis. These results indicate that the efficient emission is due to the donor–acceptor character of PE. It is suggested that the positive and negative charges in PE$^{+}$ and PE$^{-}$ are localized on the donor (substituted benzenes) and acceptor (3) moieties, respectively. For 1, the −ΔH° values (2.49–4.02 eV) estimated for the charge recombination between PE$^{+}$ and PE$^{-}$ with localized charges are estimated from E_{ox} of substituted benzenes and E_{red} of 3 to be sufficiently larger than E_{St} of PE (2.41–2.71 eV). While the electron donating substituents (1a-d) show the excimer emission due to a very small twist angle between the donor and acceptor moieties. For 2 (2e and 2f), although they also show monomer and excimer emissions, it cannot be explained by the −ΔH° (2.17 and 1.29 eV, respectively) and their singlet excitation energies (2.48 and 2.24 eV, respectively), suggesting the monomer emission is derived from the ICT state that is generated directly from the charge recombination or through the triplet–triplet annihilation. The excimer emission is assumed to be derived from the H-type excimer. The formation of the H-type excimer is suggested to be derived from the charge recombination for 1e or triplet–triplet annihilation for 2.

Conclusions

Various donor–acceptor PE with an ethynyl linkage, which are known as very efficient ECL molecules by the electrochemical reaction, showed the efficient monomer and excimer emission during the pulse radiolysis in Bz. The emission is suggested to originate from PE$^{-}\text{ox}$ generated from the charge recombination between PE$^{+}$ and PE$^{-}$ which yield the initial radiolytic reaction in Bz. The emission intensities of PE observed at 10 ns after an electron pulse were 8.8–91 times higher than that of 5 during the pulse radiolysis. These results indicate that the efficient emission is due to the donor–acceptor character of PE. It is suggested that the positive and negative charges in PE$^{+}$ and PE$^{-}$ are localized on the donor (substituted benzenes) and acceptor (3) moieties, respectively. For 1, the −ΔH° values (2.49–4.02 eV) estimated for the charge recombination between PE$^{+}$ and PE$^{-}$ with localized charges are estimated from E_{ox} of substituted benzenes and E_{red} of 3 to be sufficiently larger than E_{St} of PE (2.41–2.71 eV). While the electron donating substituents (1a-d) show the excimer emission due to a very small twist angle between the donor and acceptor moieties. For 2 (2e and 2f), although they also show monomer and excimer emissions, it cannot be explained by the −ΔH° (2.17 and 1.29 eV, respectively) and their singlet excitation energies (2.48 and 2.24 eV, respectively), suggesting the monomer emission is derived from the ICT state that is generated directly from the charge recombination or through the triplet–triplet annihilation. The excimer emission is assumed to be derived from the H-type excimer. The formation of the H-type excimer is suggested to be derived from the charge recombination for 1e or triplet–triplet annihilation for 2.

formation of the ICT state and the H-type excimer efficiently through the triplet–triplet annihilation.

**Experimental Section**

**Materials.** $1a$–$e$ and $2c,f$ were synthesized respectively by cross-coupling of 9-chloroacridine and 9-bromo-10-cyanoanthracene with corresponding donor-substituted phenylethyynes under modified Sonogashira reactions, respectively. $5b$ and $5cc$ were synthesized from reactions of phenylacetylcopper and 4-methoxyphenylenylcopper, respectively, with the corresponding substituted iodobenzene in pyridine according to literature procedures, and recrystallized from ethanol before use. Spectral grade benzene (Bz), 1,2-dichloroethane (DCE), and $N,N$-dimethylformamide (DMF) were used without further purification.

**Steady-State Measurements.** UV spectra were recorded in Bz with a UV/visible spectrometer, using a transparent rectangular cell made from quartz ($1.0 \times 1.0 \times 4.0$ cm$^3$, path length of 1.0 cm). Fluorescence spectra were measured with a spectrofluorometer.

**Pulse Radiolysis.** Except for $1e$ and $2\epsilon$, all the sample solutions were prepared in a 5 mM concentration in Bz, DCE, and DMF in a rectangular quartz cell ($0.5 \times 1.0 \times 4.0$ cm$^3$, path length of 1.0 cm). The solutions of 5 mM $1a$ and $2\epsilon$ were not prepared in Bz and DCE due to their poor solubility. Therefore, they were prepared in saturated concentrations ($0.01$–$0.1$ mM) in these solvents. These solutions were saturated with Ar gas by bubbling with it for 10 min at room temperature before irradiation. Pulse radiolysis was performed, as described previously, using an electron pulse (28 MeV, 8 ns, 0.7 kGy) from an L-band linear accelerator at SANKEN, Osaka University.

**Laser Flash Photolysis.** Laser flash photolysis experiments were also carried out, as described previously, using the third harmonic oscillation (355 nm) of a nanosecond Nd$^{3+}$: YAG laser (3-ns fwhm, 10 mJ pulse$^{-1}$) as an excitation source. Ar- and air-saturated Bz solutions were contained in a transparent rectangular quartz cell ($1.0 \times 1.0 \times 4.0$ cm$^3$, path length of 1.0 cm) at room temperature. The concentration of PE was adjusted to have an absorbance of 1.0 at excitation wavelength (355 nm).

**Fluorescence Lifetime Measurements.** Fluorescence lifetimes were measured by the single photon counting method, as described previously, using a streakscope equipped with a polychromator. In the presence of oxygen, PE showed the long lifetime emission corresponds to the “P-type” delayed fluorescence. In this measurement, therefore, PE were prepared in O$_2$-saturated Bz.

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**Supporting Information Available:** Ground-state absorption spectra of PE in Ar-saturated Bz, transient absorption spectra observed during the pulse radiolyses of 3 and PE (5.0 mM) in Ar-saturated Bz, DCE, and DMF, transient absorption and emission spectra observed during the laser flash photolyses of PE (30–300 μM) in Ar-saturated Bz. This material is available free of charge via the Internet at http://pubs.acs.org.