Efficient Emission from Charge Recombination during the Pulse Radiolysis of Electrochemical Luminescent Substituted Quinolines with Donor–Acceptor Character

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Efficient emission from various donor–acceptor quinolines with an ethynyl linkage (PnQ), which are known as efficient electrogenerated chemiluminescent molecules, was observed with time-resolved fluorescence measurement during the pulse radiolysis in benzene. On the basis of the transient absorption and emission measurements, and steady-state measurements, the formation of PnQ in the singlet excited state can be interpreted by charge recombination between the PnQ radical cation and the PnQ radical anion which are generated initially from the radiolytic reaction in benzene. The strong electronic coupling between the donor and acceptor through conjugation is responsible for the efficient emission during the pulse radiolysis of PnQ in benzene. It is suggested that the positive and negative charges are localized on the donor and acceptor moieties in the radical cation and anion, respectively. This mechanism is reasonably explained by the relationship between the annihilation enthalpy changes and singlet excitation energies of PnQ. The formation of the intramolecular charge transfer state is assumed for PnQ in the singlet excited state with a strong electron donating substituent. The emission from PnQ is suggested to originate from PnQ in the singlet excited state formed from the charge recombination between the PnQ radical cation and the PnQ radical anion during the pulse radiolysis. This is strong evidence for the efficient electrogenerated chemiluminescence of PnQ.

Introduction

In the pulse radiolysis of solutions, the solvent molecules are initially ionized to give hole and electron which react with the solvent molecules. Therefore, the hole or electron can be trapped selectively by the solvent molecules.1 For example, the electron is trapped by 1,2-dichloroethane (DCE) through the dissociative electron attachment, while the hole is trapped by solute molecule (M) with a lower oxidation potential to give M radical cation (M+).2 On the other hand, the hole is trapped by N,N-dimethylformamide (DMF), while the electron is trapped by M with a lower reduction potential to give M radical anion (M−).3

The hole and electron are initially formed in nonpolar solvents, and undergo mainly the fast geminate charge recombination to give the solvent molecules in the excited states. For example, initial products during the pulse radiolysis of benzene (Bz) are solvated electron (e−3), 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+ and M−, respectively) as shown in Scheme 1.4 Usually M* is the main product, while M+ and M− are produced in minor yields because only a small fraction of initially formed coulomb-correlated pairs (Bz*/e−3) is capable of undergoing diffusion escape resulting in the formation of relatively long-lived, homogeneously distributed M+ and M− in a radiolytic process. Therefore, the formation of M* from the charge recombination

SCHEME 1: Pulse Radiolysis of M in Bz

\[
\begin{align*}
\text{Bz} & \rightarrow e^{-3} + \text{Bz}^{*+} \\
\text{Bz}^{*+} + e^{-3} & \rightarrow \text{Bz}^{*} \\
\text{e}^{-3} + M & \rightarrow M^{*} \\
\text{Bz}^{*} & \rightarrow \text{Bz} + M^{*} \\
\text{Bz}^{*} + M & \rightarrow \text{Bz} + M^{*} \\
M^{*+} + M^{*} & \rightarrow M^{*+} + M
\end{align*}
\]

between M+ and M− is a minor process, and no M* and only a little M* exist at a few tens of nanoseconds after an electron pulse during the pulse radiolysis.

In electrogenerated chemiluminescence (ECL),5 M+ and M− are generated from the electrochemical reaction in solution, and the emission mainly results from M* and/or the singlet excimer of M* (*M2*), generated directly from the charge recombination between M+ and M− and/or from the triplet–triplet annihilation as shown in Scheme 2.6 However, the formation of M* and/or M2* as the emissive species has not been fully understood.

Recently, design, synthesis, and photophysical properties of the efficient ECL molecules have been developed by various groups.7 For example, donor–acceptor type molecules such as (4-phenylethynyl)quinolines and (4-phenylethynyl)isoquinolines, in which the donor and acceptor moieties are linked with an ethynyl group, showed efficient ECL.8 It is known that the ECL efficiency is sensitive to the properties of molecules.
SCHEME 2: Mechanism for the Electrogenerated Chemiluminescence (ECL)

\[
\begin{align*}
M + e^- & \rightarrow M^{+} \\
M - e^- & \rightarrow M^{-} \\
M^{+} + M^{-} & \rightarrow \cdot M + M, \cdot M^+ + M, \text{and/or } \cdot M_2^+ \\
\cdot M + M & \rightarrow \cdot M + M \text{ and/or } \cdot M_2^+ \\
\cdot M_2^+ & \rightarrow 2M + h\nu \\
\end{align*}
\]

According to the ECL mechanism, if \( M^{+} \) and \( M^{-} \) are produced at sufficient concentrations, \( M^{+} \) can be generated from the charge recombination between \( M^{+} \) and \( M^{-} \) during the pulse radiolysis of the ECL molecules in Bz. However, the formation of \( M^{+} \) and \( M^{-} \) is usually a minor process during the pulse radiolysis of various molecules in Bz. We report here, for the first time, observation of the efficient emission from the charge recombination between radical cation and anion of various donor–acceptor type ECL molecules, quinolines and isoquinolines isoquinoline substituted by the 4-(p-methoxyphenylethynyl) group (\( PnQ = 2- \) and \( 3-(p\text{-methoxyphenylethynyl}) \)) quinolines (\( P2Q \) and \( P3Q \), respectively), 4-(p-methoxyphenylethynyl)-isoquinolines (\( P4Q \)) and 6-(p-substituted phenylethynyl)quinolines (\( P6Q_{a-d} \)) during the pulse radiolysis of \( PnQ \) in Bz. In addition, as the parent unsubstituted molecules of \( PnQ \), quinoline (\( Q \)), isoquinoline (\( iQ \)), and several phenylacetylene derivatives (\( PAs = \text{phenylacetylene (PA), diphenylacetylene (DPA), and 4-methylphenylacetylene (DPA}_b) \)) were also examined for the emission measurement (Scheme 3).

For \( P2Q \), \( P3Q \), and \( P4Q \), some authors have previously reported the ECL in the electrochemical method.\(^5\)

Experimental Section

Materials. \( PnQ \) were prepared according to the procedure previously described in the literature.\(^6\) Quinoline (\( Q \)), isoquinoline (\( iQ \)), and phenylacetylene (\( PA \)) were purchased from Tokyo Kasei, Aldrich, and Nacalai Tesque, respectively, and used as received. Diphenylacetylene (\( DPA \)) was purchased from Wako and was recrystallized from ethanol before use. \( DPA_b \) was synthesized from reactions of phenylacetylenylcopper with the methyl-substituted iodobenzene in pyridine according to literature procedures,\(^7\) and recrystallized from ethanol before use. Spectral grade benzene (Bz) and 1,2-dichloroethane (DCE) were purchased from Tokyo Kasei and Nacalai Tesque, and \( N,N\)-dimethylformamide (DMF) was purchased from Wako. They were used as solvents without further purification.

Steady-State Measurements. UV absorption spectra were measured in Bz by a Shimadzu UV-3100PC UV/visible spectrometer with a transparent rectangular cell made from quartz (1.0 \( \times \) 1.0 \( \times \) 4.0 cm\(^2\), path length 1.0 cm). Fluorescence spectra were measured by a Hitachi 850 spectrophotometer.

Pulse Radiolysis. The solutions containing samples (5.0 mM) in Bz, DCE, and DMF were prepared in a rectangular quartz cell (0.5 \( \times \) 1.0 \( \times \) 4.0 cm\(^2\), path length 1.0 cm). These samples were saturated with Ar gas by bubbling 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.\(^10\) The monitor light was obtained from a 450-W Xe lamp (Osram, XBO-450), which was operated by a large current pulsed-power supply that was synchronized with the electron pulse. The monitor light was passed through an iris with a diameter of 0.2 cm and into the sample solution with a perpendicular intersection of the electron pulse. Time profiles of the emission and transient absorption were measured with a monochromator (CVI Laser, Digikrom-240) equipped with a PMT (Hamamatsu Photonics, R928) and the signal from the PMT was recorded on a transient digitizer (Tektronix, TDS 580D Digital Phosphor Oscilloscope) and transmitted to a personal computer with a GPIB interface. Time-resolved spectra were measured by a gated-multichannel spectrometer (Unisoku, TSP-601-02). To avoid heating of the sample solution by monitor light, a suitable cutoff filter was used.

Laser Flash Photolysis. To assign the transient species observed during the pulse radiolysis, laser flash photolysis experiments were also carried out by using the third harmonic oscillation (355 nm) of a nanosecond Nd\(^3+\):YAG laser (Quantel, Brilliant; 5-ns fwhm, 10 mJ pulse\(^{-1}\)) as an excitation source. The monitor light was obtained from a 450-W Xe lamp (Osram, XBO-450) synchronized with the laser flash. Transient absorption and emission spectra were measured by a streak camera (Hamamatsu Photonics C7700) equipped with a CCD camera (Hamamatsu Photonics C4742-98) or a silicon detector (Hamamatsu Photonics, SS343). Ar- and air-saturated Bz solutions were contained in a transparent rectangular quartz cell (1.0 \( \times \) 1.0 \( \times \) 4.0 cm\(^2\), path length 1.0 cm) at room temperature. The concentration of \( PnQ \) was 20–30 \( \mu \text{M} \).

Fluorescence Lifetime Measurements. Fluorescence lifetimes were measured by the single photon counting method, using a streakscope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Acton Research, SpectraPro150). Femtosecond laser pulse was generated with a Ti:sapphire laser (Spectra-Physics, Tsunami 3941-M1BB, fwhm 100 fs) pumped
TABLE 1: Photophysical and Electrochemical Properties of PnQ, Q, iQ, and PAs

<table>
<thead>
<tr>
<th>compd</th>
<th>λ\text{abs/nm}</th>
<th>(\tau\text{fl/nm} )</th>
<th>λ\text{ECL max/nm}</th>
<th>(\phi_\lambda (\times 10^{-2}) )</th>
<th>(\tau_d/\text{ns} )</th>
<th>(E_{31}/\text{eV} )</th>
<th>(E_{red}/\text{eV} )</th>
<th>(E_{ox}/\text{eV} )</th>
<th>(\Delta\text{H}/\text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2Q</td>
<td>346(^	ext{a})</td>
<td>405(^	ext{a})</td>
<td>479(^	ext{a})</td>
<td>350</td>
<td>375</td>
<td>15</td>
<td>0.23</td>
<td>3.31</td>
<td>\text{Not determined}</td>
</tr>
<tr>
<td>P3Q</td>
<td>342(^	ext{a})</td>
<td>406(^	ext{a})</td>
<td>(b)</td>
<td>336</td>
<td>373</td>
<td>50</td>
<td>1.0</td>
<td>3.32</td>
<td>(1.20^\text{b})</td>
</tr>
<tr>
<td>P4Q</td>
<td>334(^	ext{a})</td>
<td>414(^	ext{a})</td>
<td>(b)</td>
<td>338</td>
<td>394</td>
<td>62</td>
<td>1.1</td>
<td>3.15</td>
<td>(0.91^\text{a})</td>
</tr>
<tr>
<td>P6Q(\alpha)</td>
<td>338</td>
<td>364</td>
<td>460</td>
<td>313</td>
<td>369</td>
<td>0.55</td>
<td>0.050</td>
<td>3.36</td>
<td>(1.90^\text{a})</td>
</tr>
<tr>
<td>P6Q(\beta)</td>
<td>339</td>
<td>376</td>
<td>450(\beta)</td>
<td>315</td>
<td>371</td>
<td>2.8</td>
<td>0.11</td>
<td>3.34</td>
<td>(0.90^\text{a})</td>
</tr>
<tr>
<td>P6Qc</td>
<td>341</td>
<td>412</td>
<td>475</td>
<td>318</td>
<td>378</td>
<td>44</td>
<td>0.85</td>
<td>3.28</td>
<td>(0.88^\text{a})</td>
</tr>
<tr>
<td>P6QiQ</td>
<td>346</td>
<td>536</td>
<td>534</td>
<td>372</td>
<td>434</td>
<td>88</td>
<td>1.4</td>
<td>2.86</td>
<td>(0.90^\text{a})</td>
</tr>
<tr>
<td>Q</td>
<td>270</td>
<td>335</td>
<td>d</td>
<td>314</td>
<td>405</td>
<td>0.42</td>
<td>d</td>
<td>3.06</td>
<td>(1.00^\text{a})</td>
</tr>
<tr>
<td>Q</td>
<td>267</td>
<td>336</td>
<td>d</td>
<td>319</td>
<td>393</td>
<td>0.076</td>
<td>d</td>
<td>3.16</td>
<td>(1.20^\text{b})</td>
</tr>
<tr>
<td>PA</td>
<td>270</td>
<td>317</td>
<td>d</td>
<td>280</td>
<td>402</td>
<td>11</td>
<td>2.2</td>
<td>3.06</td>
<td>(1.55^\text{a})</td>
</tr>
<tr>
<td>DPA</td>
<td>279</td>
<td>331</td>
<td>520(\text{d})</td>
<td>300</td>
<td>372</td>
<td>3.8</td>
<td>d</td>
<td>3.33</td>
<td>(1.52^\text{a})</td>
</tr>
<tr>
<td>DPA(\text{b})</td>
<td>326</td>
<td>420</td>
<td>d</td>
<td>279</td>
<td>374</td>
<td>0.017</td>
<td>d</td>
<td>3.32</td>
<td>(1.52^\text{a})</td>
</tr>
</tbody>
</table>

\(E_{red}/\text{eV}\) and \(E_{ox}/\text{eV}\) are determined from the integration of the fluorescence, using an oscilloscope and a photomultiplier. The values were estimated vs Ag/Ag\(\text{+}\) (Supporting Information, Figure S1a, Table 1). The fluorescence peaks in Bz were observed at 369–434 nm (Figure 1a), while those in acetonitrile were at 364–536 nm with a large red shift due to the high polarity. With use of a setup consisting of a fluorescence spectrophotometer and a voltammmograph with a PC interface, the ECL emission of P2Q (1.0 mM) was observed at 479 nm in acetonitrile with 0.05 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. On the other hand, no ECL was observed in P3Q and P4Q under the same conditions. The different emission behavior results are reasonably explained by the annihilation enthalpy change (\(-\Delta H^\text{f}\)) for the charge recombination between \(\text{M}^+\) and \(\text{M}^-\). Therefore, the charge recombination gives 1P2Q, leading to the efficient ECL.

\(-\Delta H^\text{f} = E_{ox} - E_{red} - 0.16 \text{ eV}\) (1)

where \(E_{ox}\) and \(E_{red}\) are the oxidation and reduction potentials of M, respectively. The calculated \(-\Delta H^\text{f}\) values for PnQ are listed in Table 1. For P2Q, \(-\Delta H^\text{f}\) of the charge recombination between P2Q\(^+\) and P2Q\(^-\) is sufficiently larger than \(E_{31}\). Therefore, the charge recombination gives 1P2Q, leading to the efficient ECL.

For P6Q\(\alpha\)-d, the ground-state absorption peaks of P6Q\(\alpha\)-d in Bz and acetonitrile were observed at 313–372 nm with a little influence of the solvent polarity (Supporting Information, Figure S1b, Table 1). The fluorescence peaks in Bz were observed at 369–434 nm (Figure 1b), while those in acetonitrile were at 364–536 nm with a large red shift due to the high polarity. It was shown that both absorption and fluorescence peaks shifted to the longer wavelength with increasing electron donating character of the substituent. In addition, the \(E_{31}\) values decrease and \(\phi_\lambda\) values increase with increasing electron donor character of the substituent. The ECL emissions of P6Q\(\alpha\)-d (1.0 mM) were observed at 450–534 nm in acetonitrile. The \(-\Delta H^\text{f}\) values of the charge recombination between P6Q\(\alpha\)-d\(^+\) and P6Q\(\alpha\)-d\(^-\) are not sufficient to populate their \(E_{31}\). Thus, the charge recombination may produce 3P6Q\(\alpha\)-d\(^+\), which undergo the triplet–triplet annihilation to give 3P6Q\(\alpha\)-d\(^\ast\). The compounds bearing weak donors (P6Q\(\alpha\)-e) exhibit the ECL emission of the excimers because of the twisted angle between two planes of the donor and acceptor moieties. The ECL emission peak of P6Q\(\gamma\) (534 nm) was blue shifted as compared with the solution photoluminescence peak (536 nm), suggesting the formation of an H-type excimer in which two quinolyl moieties are stacked face-to-face with donor-bearing phenyl groups projecting perpendicularly away from each other. For Q and iQ, the fluorescence intensities were very weak.

Emission Spectra Observed during the Pulse Radiolysis of PnQ in Bz. The time-resolved emission spectra were recorded and they showed monotonically decay in the 40 ns time scale after the electron pulse during the pulse radiolysis of PnQ in Ar-saturated Bz (Figures 2 and 3). The emission peaks of iP4Q and P6Q\(\alpha\)-d were observed at almost the same wavelengths where the fluorescence peaks were observed by the steady-state
measurement. However, the emission peaks during the pulse radiolysis of P2Q and P3Q were observed at 10–20 nm longer wavelengths compared to the fluorescence peaks observed by the steady-state measurement. This is because of the self-absorption as a result of the high concentrations (5 mM) of P2Q and P3Q in the pulse radiolysis experiment. It is confirmed that at high concentrations, fluorescence peaks of P2Q and P3Q in Bz were also observed at a longer wavelength. For Q and iQ, no emission was observed during the pulse radiolysis. Contrary to PnQs, very weak emissions of PAs were observed during the pulse radiolysis. The emission spectral data of PnQ, Q, iQ, and PAs obtained during the pulse radiolysis are summarized in Table 2, together with the ECL emission data. The relative emission intensity was determined from the integration of emission observed at all wavelengths at 10 ns after an electron pulse in Figure 4.

It should be noted that all PnQ show emissions with peaks at 370–437 nm in the 40 ns time scale after the electron pulse during the pulse radiolysis. The donor moieties of PnQ are toluene and anisole auxochrome having the fluorescence peaks at 280–300 nm, while the acceptor moieties of PnQ is Q or iQ having the fluorescence peaks at 350–500 nm. Therefore, the emission from the pulse radiolysis originates from the acceptor moiety. According to the $-\Delta H^*$ values, no emission should be observed during the pulse radiolysis of P4iQ in Bz, because P4iQ$^+$ cannot be generated from the charge recombination between P4Q$^+$ and P4Q$^-$. However, P4Q showed the strongest fluorescence during the pulse radiolysis of PnQ. Therefore, the occurrence of the efficient emission during the pulse radiolysis of PnQ cannot be explained by the $-\Delta H^*$ value for the charge recombination between PnQ$^+$ and PnQ$^-$. The emission intensities of P6Qa–d observed during the pulse radiolysis were much higher than those of Q and the corresponding PAs. For example, the emission intensity of P6Qa was 14 times higher than that of DPAa. This result indicates that the strong emission is due to the strong electronic coupling between the donor and acceptor through conjugation of P6Qa–d. In addition, for P6Qa the long-lifetime emission was observed during the pulse radiolysis (Figure 3d, inset). It should be noted that the emission intensity, observed during the pulse radiolysis of P6Qa–d, increased with increasing electron donor character of the substituents. This tendency is different from that observed for the ECL of P6Qa–d.

\[
\text{ECL intensity} = \frac{\text{rel emission intensity}}{\text{intensity for } P3Q = 100}\]

### Table 2: Emission Peak ($\lambda_{\text{Em}}$) and Relative Emission Intensity of PnQ, Q, iQ, and PAs Observed at 10 ns after an Electron Pulse during the Pulse Radiolysis, Together with the ECL Intensity

<table>
<thead>
<tr>
<th>compd</th>
<th>$\lambda_{\text{Em}}$ (nm)</th>
<th>rel emission intensity (%)</th>
<th>$\lambda_{\text{ECL}}$ (nm)</th>
<th>ECL intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2Q</td>
<td>395</td>
<td>16.9</td>
<td>479</td>
<td>37.8</td>
</tr>
<tr>
<td>P3Q</td>
<td>383</td>
<td>100</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>P4Q</td>
<td>395</td>
<td>144</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>P6Qa</td>
<td>370</td>
<td>2.97</td>
<td>460</td>
<td>6.0</td>
</tr>
<tr>
<td>P6Qb</td>
<td>370</td>
<td>5.74</td>
<td>450</td>
<td>1.5</td>
</tr>
<tr>
<td>P6Qc</td>
<td>379</td>
<td>38.5</td>
<td>475</td>
<td>1.2</td>
</tr>
<tr>
<td>P6Qd</td>
<td>437</td>
<td>143</td>
<td>534</td>
<td>0.5</td>
</tr>
<tr>
<td>Q</td>
<td>b</td>
<td>0</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>iQ</td>
<td>b</td>
<td>0</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>PA</td>
<td>378</td>
<td>0.85</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>DPA</td>
<td>338, 467</td>
<td>2.06, 520</td>
<td>7.0</td>
<td>b</td>
</tr>
<tr>
<td>DPAa</td>
<td>422, 577</td>
<td>0.41</td>
<td>b</td>
<td>b</td>
</tr>
</tbody>
</table>

* Relative to the intensity for P3Q = 100%. Emission intensity was obtained by integration of emission observed at all wavelengths at 10 ns after an electron pulse irradiation. ** No or very weak emission was observed. * Relative to the intensity for tris(2,2-bipyridyl) ruthenium(II) oxalate complex = 100%. Reference 8b. * Observation of the ECL at this wavelength for DPA is quite unusual.

### Transient Absorption Spectra Observed during the Pulse Radiolysis of PnQ

To generate both $\text{e}^-$ and $\text{e}^+$, the pulse radiolysis of P2Q and P3Q was performed in the presence of Bz, which has been used as a solvent for the pulse radiolysis of M. Figure 4 shows the transient absorption spectra observed during the pulse radiolysis of P2Q, P3Q, and P4Q 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 very small molar absorption coefficients, $\epsilon_{400} = 1.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{235} = 1.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively. The transient absorption spectrum of $\text{e}^-_5$ in Bz has not been reported. It is assumed that $\text{e}^-_5$ is rapidly trapped by PnQ or undergoes the fast geminate charge recombination. Therefore, these species cannot be observed. The transient absorption spectra observed at $t = 50$ ns after an electron pulse in Figure 4 can be assigned to PnQ$^+$, PnQ$^-$, and/or PnQ$^*$.

To confirm the transient absorption spectra of PnQ$^+$ and PnQ$^-$, the pulse radiolysis of PnQ in DCE and DMF was examined. It is established that M$^+$ is generated during the pulse
Figure 4. Transient absorption spectra observed at time \( t = 50 \) (solid line) ns, 500 (broken line) ns, 1 (dotted line) \( \mu \)s, and 5 (broken and dotted line) \( \mu \)s after an electron pulse (8 ns) during the pulse radiolysis of \( \text{P}2\text{Q} \) (a), \( \text{P}3\text{Q} \) (b), and \( \text{P}4\text{Q} \) (c) (5.0 mM) in Ar-saturated Bz.

**SCHEME 4:** Pulse Radiolysis of M in DCE

\[
\text{DCE} \rightarrow \text{DCE}^* + e^- \\
\text{DCE}^* + \text{M} \rightarrow \text{M}^+ + \text{DCE} \\
e^- + \text{DCE} \rightarrow \text{ClCH}_2\text{CH}_2\text{Cl}^- + \text{Cl}^-
\]

**SCHEME 5:** Pulse Radiolysis of M in DMF

\[
\text{DMF} \rightarrow \text{DMF}^* + e^- \\
e^- + \text{M} \rightarrow \text{M}^* \\
\text{DMF}^* + \text{DMF} \rightarrow \text{DMF}(\text{H})^* + \text{DMF}(\text{H}^*)^*
\]

radiolysis of \( \text{M} \) in DCE,\(^2\) while \( \text{M}^- \) is in DMF,\(^3\) as shown in Schemes 4 and 5, respectively.

Figure 5a shows the transient absorption spectrum observed during the pulse radiolysis of \( \text{P}2\text{Q} \) in Ar-saturated DCE. Although a peak at 465 nm disappeared, that around 430 nm remained even at \( > 5 \) \( \mu \)s. Therefore, the absorption around 430–450 nm is assumed to be a stable product, while the peak observed at 465 nm (\( \tau_{1/2} = 0.25 \) \( \mu \)s) is assigned to \( \text{P}2\text{Q}^+ \). It seems that \( \text{Cl}^- \) reacts with \( \text{P}2\text{Q}^+ \) to give the product having an absorption peak around 430–450 nm. Figure 5b shows the transient absorption spectrum observed during the pulse radiolysis of \( \text{P}2\text{Q} \) in Ar-saturated DMF. The peak observed at 449 nm (\( \tau_{1/2} = 0.67 \) \( \mu \)s) is assigned to \( \text{P}2\text{Q}^- \). Similarity, the transient absorption spectra assigned to \( \text{PnQ}^- \) and \( \text{PnQ}^* \) were observed during the pulse radiolysis of other \( \text{PnQ} \) in DCE and DMF, respectively (Supporting Information, Figures S2 and S3). These results are summarized in Table 3. Since the transient absorption spectra of \( \text{PnQ}^- \) and \( \text{PnQ}^* \) have peaks around 430–500 nm in DCE and DMF, respectively, \( \text{PnQ}^- \) and \( \text{PnQ}^* \) seem to be involved in the transient absorption spectra, observed during the pulse radiolysis of \( \text{PnQ} \) in Bz. However, it is not clear whether \( \text{PnQ}^* \) is involved in the transient absorption spectra or not.

Emission and Absorption Spectra Observed during the Laser Flash Photolysis of \( \text{PnQ} \) in Bz. To assign the transient species in detail, the transient absorption spectra of \( \text{PnQ} \) in Bz were measured during the 355-nm 5-ns laser flash photolysis of \( \text{P}2\text{Q} \) (20 \( \mu \)M) in Ar-saturated Bz. A broad transient absorption band was observed.

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

<table>
<thead>
<tr>
<th>compd</th>
<th>( \lambda_{\text{max}} / \text{nm} )</th>
<th>( \tau_{1/2} / \mu \text{s} )</th>
<th>( \lambda_{\text{max}} / \text{nm} )</th>
<th>( \tau_{1/2} / \mu \text{s} )</th>
<th>( \lambda_{\text{max}} / \text{nm} )</th>
<th>( \tau_{1/2} / \mu \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P}2\text{Q} )</td>
<td>465</td>
<td>0.53</td>
<td>465</td>
<td>0.25</td>
<td>449</td>
<td>0.67</td>
</tr>
<tr>
<td>( \text{P}3\text{Q} )</td>
<td>427, 465</td>
<td>0.70</td>
<td>455, 483</td>
<td>0.35</td>
<td>456, 478</td>
<td>0.51</td>
</tr>
<tr>
<td>( \text{P}4\text{Q} )</td>
<td>489, 517</td>
<td>0.15</td>
<td>453, 475</td>
<td>0.30</td>
<td>452</td>
<td>0.36</td>
</tr>
<tr>
<td>( \text{P}6\text{Q}_6 )</td>
<td>603, 658</td>
<td>0.60</td>
<td>470</td>
<td>0.30</td>
<td>398</td>
<td>0.45</td>
</tr>
<tr>
<td>( \text{Q} )</td>
<td>400, 560</td>
<td>1.3</td>
<td>402</td>
<td>0.022</td>
<td>398</td>
<td>0.45</td>
</tr>
<tr>
<td>( \text{Q} )</td>
<td>420, 540</td>
<td>1.3</td>
<td>418, 546</td>
<td>0.019</td>
<td>416</td>
<td>0.34</td>
</tr>
</tbody>
</table>

\(^*\) A broad transient absorption band was observed.

Figure 6. Time-resolved transient absorption spectrum at time \( t = 3 \) (solid line), 5 (broken line), and 10 (dotted line) \( \mu \)s after a laser pulse during the laser flash photolysis of \( \text{P}2\text{Q} \) in Ar-saturated Bz.
Because the emission intensities of these compounds were significantly high, we did not measure the emission in the time scale of 0–3 µs after the 355-nm 5-ns laser pulse using the streak camera or the silicon detector. Under air-saturated conditions, the long-lived emissions were completely quenched by oxygen through the triplet energy transfer quenching mechanism (Figure 7, inset, and Figure 8), suggesting that the emission originated from P2Q. The time profile of ΔOD(t)−1 of P2Q* shows the decay of P2Q* obeys second-order kinetics (Figure 8, inset). These results suggest that the long lifetime emission corresponds to the “P-type” delayed fluorescence from P2Q* generated from the triplet−triplet annihilation.

For P6Q, the peaks assigned to the excimer emission were observed at t = 500 ns at around 500 nm (Supporting Information, Figure S5). This emission is assumed to be derived from the excimer generated from the triplet−triplet annihilation. For P6Q, the long-lifetime emission was observed during the laser flash photolysis. This emission is also assigned to be the “P-type” delayed fluorescence from P2Q* generated from the triplet−triplet annihilation.

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The emission mechanism during the pulse radiolysis of PnQ(A−D) in Bz seems to result from the donor−acceptor structure, the characteristic emission mechanism for the donor−acceptor molecules should be assumed. It is suggested that negative charge is localized on the electron acceptor moiety in the radical anion (A−D). On the other hand, 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 PnQ. For P2Q, the −ΔH° value of the donor moiety (corresponding to anisole) is 1.35 V, while that of the acceptor moiety (corresponding to Q) is −2.40 V. Therefore, the −ΔH° value for the charge recombination between P2Q+ and P2Q− with localized charges can be estimated to be 3.59 eV, which is sufficiently larger than the E51 value. Similarly, the −ΔH° values for P3Q, P4Q, and P6Q are larger than the E51 values of PnQ* (Table 4). Therefore, the charge recombination between A− and D+ occurs to give PnQ2 in the pulse radiolysis of PnQ in Bz (Scheme 6). The emission intensity seems to depend on the Q values of PnQ.

However, the −ΔH° value of P6Q is not sufficient to populate PnQ*. Therefore, it is suggested that the emission mechanism for P6Q is quite different from that for other PnQ. For P6Q, bearing a strong donor (NEt2), the emissive singlet intramolecular charge transfer (ICT) state (1(A−D)+) with the larger twisted angle is assumed.17 The ICT state for P6Q is also expected by the slightly longer τi than those of other PnQ (Table 1).

The emission mechanism during the pulse radiolysis of PnQ can be divided into two categories. For P2Q, P3Q, P4Q, and P6Q, with no or weak electron donating substituents and no or small twist angle between the donor and acceptor planes, it is less favorable to populate the emissive singlet ICT state. For P6Q with a strong electron donating substituent and large twist angle between the donor and acceptor planes, the emission mechanism is quite different from that for other PnQ. It is suggested that the radical cation and anion collide neck-to-neck.

**Table 4: Oxidation Potentials (E°) of Donor Moiety, Reduction Potentials (E°) of Acceptor Moiety, Estimated Annihilation Enthalpy Values (−ΔH°) for the Charge Recombination between P2Q+ and P2Q− with Localized Charges on the Donor and Acceptor Moieties, and E51 of PnQ**

<table>
<thead>
<tr>
<th>compd</th>
<th>donor E°/V</th>
<th>acceptor E°/V</th>
<th>−ΔH°/eV</th>
<th>E51/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2Q</td>
<td>anisole</td>
<td>Q</td>
<td>−2.40</td>
<td>3.59</td>
</tr>
<tr>
<td>P3Q</td>
<td>anisole</td>
<td>Q</td>
<td>−2.40</td>
<td>3.59</td>
</tr>
<tr>
<td>P4Q</td>
<td>anisole</td>
<td>Q</td>
<td>−2.51</td>
<td>3.70</td>
</tr>
<tr>
<td>P6Q</td>
<td>benzene</td>
<td>Q</td>
<td>−2.40</td>
<td>4.32</td>
</tr>
<tr>
<td>P6Q</td>
<td>toluene</td>
<td>Q</td>
<td>−2.40</td>
<td>4.22</td>
</tr>
<tr>
<td>P6Q</td>
<td>anisole</td>
<td>Q</td>
<td>−2.40</td>
<td>5.09</td>
</tr>
<tr>
<td>P6Q</td>
<td>N,N-diethyl-aniline</td>
<td>Q</td>
<td>−2.40</td>
<td>2.71</td>
</tr>
</tbody>
</table>

* Redox potentials were estimated vs Ag/Ag+. Reference 16a.

**SCHEME 6: Mechanism for the Emission during the Pulse Radiolysis of PnQ(A−D) in Bz**

\[
\begin{align*}
\text{c}^- + \text{A-D} & \rightarrow \text{A}^*-\text{D} \\
\text{Bz}^* + \text{A-D} & \rightarrow \text{Bz} + \text{A-D}^* \\
\text{A}^*-\text{D} + \text{A-D}^* & \rightarrow 1(\text{A-D})^+ + \text{A-D} \\
1(\text{A-D})^+ & \rightarrow \text{A-D} + h\nu_B
\end{align*}
\]

**Emission Mechanism.** Because the efficient emission of PnQ seems to result from the donor−acceptor structure, the characteristic emission mechanism for the donor−acceptor molecules should be assumed. It is suggested that negative charge is localized on the electron acceptor moiety in the radical anion (A−). On the other hand, 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 PnQ. For P2Q, the −ΔH° value of the donor moiety (corresponding to anisole) is 1.35 V, while that of the acceptor moiety (corresponding to Q) is −2.40 V. Therefore, the −ΔH° value for the charge recombination between P2Q+ and P2Q− with localized charges can be estimated to be 3.59 eV, which is sufficiently larger than the E51 value. Similarly, the −ΔH° values for P3Q, P4Q, and P6Q, are larger than the E51 values of PnQ*.
to produce the singlet ICT state \((1(A^+D^-))\) (Scheme 7).\(^8\) It is assumed that the \(-\Delta H^\circ\) value of \(P6Q_6\) is sufficient to populate the singlet ICT state \((1(A^-D^+))\), although it is deficient to populate the singlet state \((1(A-D))\), therefore the efficient emission derived from the directly formed ICT state can be observed during the pulse radiolysis. The emission is possibly derived from \(1P6Q_6^*\), which is generated from the triplet–triplet annihilation. However, this cannot explain the higher emission intensity obtained during the pulse radiolysis (Table 2), because the emission pathway through the triplet–triplet annihilation is assumed to be inefficient.

In the electroluminescence experiment, the emission peaks of \(P2Q\) and \(P6Q_6\) in acetonitrile were observed at 450–534 nm. For \(P2Q\), it has reported that the \(P2Q\) excimer \((1P2Q_2^*)\) is the emissive species in the electrochemical reaction in acetonitrile (Scheme 2).\(^8\) On the other hand, the emission peaks were observed at 370–437 nm during the pulse radiolysis of \(PnQ\) in Bz, almost same as those observed by the steady-state measurement at concentrations of 20 \(\mu\)M to 5 \(\mu\)M. Therefore, the emissive species is assigned to \(PnQ^*\) during the pulse radiolysis of \(PnQ\) in Bz. Because \(PnQ^+\) and \(PnQ^-\) are generated as the initial species during both pulse radiolysis and electrochemical reaction, the difference of the emissive species corresponds to other experimental conditions such as the solvent and concentrations of \(PnQ\), \(PnQ^+\), and \(PnQ^-\). It is suggested that the formation of \(1PnQ_2^*\) was enhanced by the stabilization in acetonitrile as a polar solvent, and with higher concentrations of \(PnQ\), \(PnQ^+\), and \(PnQ^-\) during the electrochemical reaction.

Conclusions

Various donor–acceptor quinolines \(PnQ\) with an ethynyl linkage, which are known as the efficient ECL molecules by the electrochemical reaction, showed the efficient emission as well during the pulse radiolysis in Bz. The emission is suggested to originate from \(1PnQ^*\) generated from the charge recombination between \(PnQ^+\) and \(PnQ^-\) which yield from the initial radiolytic reaction in Bz. The emission intensities of \(PnQ\) observed at 0 ns after an electron pulse, were 1.5–70 times higher than that of \(DPA\) during the pulse radiolysis. These results indicate that the efficient emission is due to the strong electronic coupling between the donor and acceptor through conjugation of \(PnQ\). It is suggested that the positive and negative charges in \(PnQ^+\) and \(PnQ^-\) are localized on the donor (substituted phenyl groups) and acceptor \((Q)\) moieties, respectively. For \(P2Q\), \(P3Q\), \(P4Q\), and \(P6Q_6\), the estimated \(-\Delta H^\circ\) values (3.6–4.3 eV) for the charge recombination between \(PnQ^+\) and \(PnQ^-\) with localized charges are estimated from \(E_{oa}\) of substituted phenyl groups and \(E_{red}\) of \(Q\) to be sufficiently larger than \(E_{si}\) of \(PnQ\) (2.8–3.3 eV). For \(P6Q_6\), the \(-\Delta H^\circ\) value (2.71 eV) is not sufficiently larger than \(E_{si}\) of \(P6Q_6\) (2.86 eV), suggesting the formation of the singlet ICT state, which emits light generated from the charge recombination due to the strong electron donating substituent. Therefore, it is confirmed that \(PnQ^+\) and \(PnQ^-\) are generated during the pulse radiolysis of \(PnQ\) in Bz and that the emission is responsible for \(1PnQ^*\) generated from the charge recombination between \(PnQ^+\) and \(PnQ^-\).

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Supporting Information Available: Ground-state absorption spectra of \(PnQ\) in Bz, transient absorption spectra observed during the pulse radiolysis of \(PnQ\) (5.0 mM) in Ar-saturated Bz, DCE, and DMF, and transient absorption and emission spectra observed during the laser flash photolysis of \(PnQ\) (20–30 \(\mu\)M) in Ar- and air-saturated Bz. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mozumder, A.; Hatano, Y. Charged Particle and Photon Interactions with Matter: Chemical, Physicochemical, and Biological Consequences with Applications; Marcel Dekker Inc.: New York, 2004.


