

curate to ± 0.2 eV.¹² Samples were run at source pressures of $1-3 \times 10^{-6}$ Torr, and at source temperatures ranging from 200 to 230 °C with an accelerating voltage of 3 kV.

Note Added in Proof. Christophorou has found that a large number of molecules,^{13a} including some mono- and disubstituted halogenated benzene derivatives,^{13b} form parent negative ions in the gas phase by capturing thermal or near thermal electrons. He has also obtained "threshold-electron-excitation spectra" of some mono-substituted benzene derivatives.^{13c} One could postulate some type of electron excitation of hexachlorobenzene, prior to formation of the molecular anion radical, perhaps by elastic and inelastic electron collisions with the molecule. This would provide a partial explanation for the relatively high 11-eV maximum observed in the IE curves for the formation of the molecular anion radical of hexachlorobenzene.

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References and Notes

- (1) (a) Portions of this work were presented at the ASMS 23rd Annual Conference on Mass Spectrometry and Allied Topics, May 1975, Houston, Texas. (b) NIH Career Development Awardee, 1975-1980.
- (2) G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, **94**, 6069 (1972), and references cited therein.
- (3) R. West, *Acc. Chem. Res.*, **3**, 130 (1970).
- (4) C. E. Melton, "Principles of Mass Spectrometry and Negative Ions", Marcel Dekker, New York, N.Y., 1970.
- (5) The formation of Cl_2^- is not well understood, and it may indeed be much more complex than shown in eq 2. We cannot completely rule out some type of ion molecule reaction to produce Cl_2^- , however, even at low source pressure (1×10^{-6} Torr) the ion is still observed. Furthermore, no Cl_2^- was observed even at high source pressure when pure Cl_2 was run in the mass spectrometer under similar conditions.
- (6) (a) T. L. Cottrell in "The Strength of Chemical Bonds", Butterworths London, 1956; (b) J. Roberts and M. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, p 86.
- (7) It is possible that these ions are being formed at abundance levels below the minimum detection capabilities of the instrument.
- (8) Trace amounts of molecular anion peaks for C_7Cl_8 were observed (see Table I).
- (9) The molecular ion is really a cluster of ions due to the isotopes chlorine. The most intense peak in the cluster (m/e 284 in this compound) was used to obtain the IE curve, which for reasons of brevity is not shown.
- (10) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960).
- (11) E. T. McBee and D. K. Smith, *J. Am. Chem. Soc.*, **77**, 389 (1955).
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- (13) (a) J. P. Johnson, D. L. McCorkle, L. G. Christophorou, and J. G. Carter, *J. Chem. Soc., Faraday 2*, **71**, 1742 (1975), and references cited therein; (b) R. N. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.*, **23**, 656 (1966); (c) L. G. Christophorou, D. L. McCorkle, and J. G. Carter, *J. Chem. Phys.*, **60**, 3779 (1974).

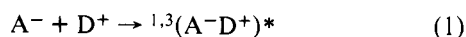
Energy Transfer from Exciplexes to Hydrocarbon Quenchers in Polar Solvents

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Abstract: Electrochemical techniques were used to generate the radical cation of tri-*p*-tolylamine (TPTA) and the radical anions of benzophenone (BP) and 1,4-dicyanobenzene (DCB). Redox processes involving these ions are chemiluminescent. The systems TPTA(+)/DCB(-) in benzonitrile and TPTA(+)/BP(-) in acetonitrile emit in bands assigned to the exciplexes $^1(\text{DCB-TPTA}^+)^*$ and $^1(\text{BP-TPTA}^+)^*$, respectively. Aromatic hydrocarbons (R) can be added without interference in the radical-ion chemistry. When anthracene or one of its phenyl or methyl derivatives is added to the TPTA(+)/DCB(-) system, a blue emission from the singlet $^1\text{R}^*$ appears and the exciplex band is slightly quenched. Fluoranthene, pyrene, and *trans*-stilbene exert no such effects. These results are consistent with energy transfer, in energetically favorable cases, from an exciplex state to R with the resulting formation of the triplet $^3\text{R}^*$. The blue bands may arise from triplet-triplet annihilation. Similar results are seen in the TPTA(+)/BP(-) system. The chemiluminescence efficiency (Φ_{cl}) for the TPTA(+)/DCB(-) system is 1.4×10^{-5} . The fluorescence efficiency (Φ_f') of the exciplex $^1(\text{DCB-TPTA}^+)^*$ is placed in the range $10^{-5} \leq \Phi_f' \leq 1$ and the exciplex yield of radical-ion annihilation (Φ_e) is between the limits $10^{-5} \leq \Phi_e \leq 1$.

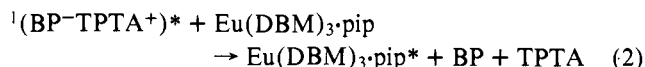
Theories of excited-state production in electron-transfer processes usually do not take into account the possible participation of intermediate complexes.¹⁻⁷ For example, the reaction between the radical ions A^- and D^+ is regarded as proceeding directly to the ground states A and D or to locally excited states A^* and D^* . An intervening complex state, such as the singlet or triplet exciplex $^1,^3(\text{A-D}^+)^*$, is not considered. As Weller and Zachariasse have demonstrated, this assumption does not hold for radical-ion annihilations in media of low polarity, where processes such as



can proceed with fairly high yields.^{5,8-10} Even so, it has been widely held that direct exciplex formation is not important for polar media, which strongly solvate the ions and destabilize the exciplex. Comparisons between experimental product-state

distributions and theoretical predictions have accordingly had an emphasis on data obtained in polar solvents.^{6,7}

Recently, Bard and Park have shown that exciplexes actually do arise from radical-ion reactions in polar solvents^{11,12} and their work raises doubt about the assumed unimportance of the exciplex pathway in such media. In addition, they and Hemingway have indicated that the benzophenone/tri-*p*-tolylamine exciplex $^1(\text{BP-TPTA}^+)^*$ can engage in energy transfer to the metal complex $\text{Eu}(\text{DBM})_3 \cdot \text{pip}$ with high apparent efficiency; that is,



where DBM is dibenzoylmethide and pip is piperidine.¹³

Their work stimulated our experiments in this area. We have used aromatic hydrocarbon interceptors to explore further the

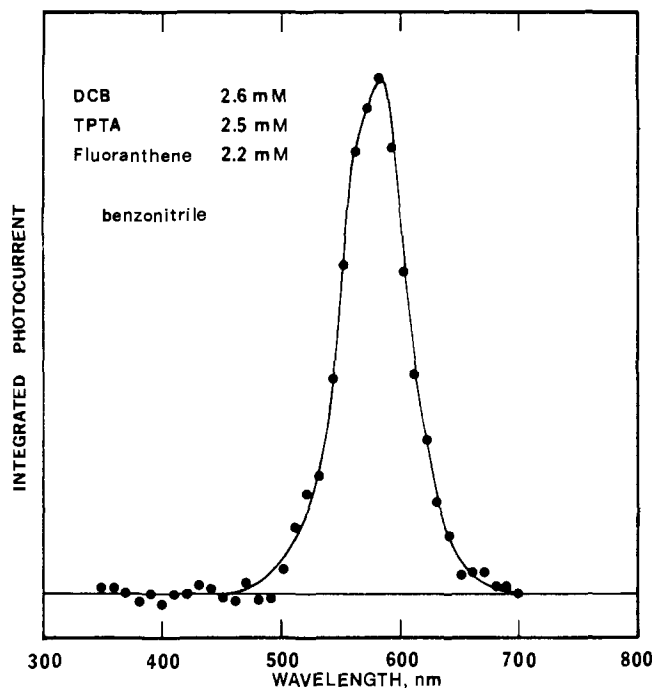


Figure 1. Ecl from the TPTA(+)/DCB(-) system with fluoranthene serving as an interceptor. An uncorrected curve obtained with a 1P21 phototube.

nature of energy transfer from exciplexes, and we have employed absolute luminescence measurements to obtain the exciplex chemiluminescence efficiency for the reaction between the TPTA cation radical and the anion of 1,4-dicyanobenzene (DCB). Electrochemical techniques were used to generate and react the ions in benzonitrile solutions. The results are useful in permitting an initial comment on the efficiency of exciplex formation in radical-ion annihilations occurring in polar media.

Experimental Section

Benzophenone (BP) and 1,4-dicyanobenzene (DCB) were usually used as received from Aldrich. Recrystallizing DCB twice from absolute ethanol produced no significant differences in the results. Tri-*p*-tolylamine (TPTA) was synthesized by Freed¹⁴ according to Walter's method¹⁵ and purified by sublimation. Pyrene supplied by Eastman was used without further purification, as were the *trans*-stilbene and fluoranthene from Aldrich (both 99.94%, zone refined). Anthracene from Eastman (blue-violet fluorescence) and Princeton Organics (99.999+%, zone refined) behaved identically and no changes followed recrystallization of the anthracene samples. Aldrich's Gold Label 9,10-diphenylanthracene (DPA, 99+%) was thrice recrystallized from xylene, then sublimed three times in vacuo. A sample of 9,10-dimethylanthracene (DMA) from Aldrich was recrystallized identically, then sublimed once. Aldrich's 9-methylanthracene and 9-phenylanthracene (both 99%) were recrystallized twice from absolute ethanol and xylene, respectively.

Tetra-*n*-butylammonium fluoborate (TBABF₄) produced by Southwestern Analytical Chemicals (electrometric grade) served as supporting electrolyte. It was dried at 90 °C under vacuum for 72 h and stored over P₂O₅.

Spectroquality benzonitrile was used as received from Matheson, Coleman, and Bell or Aldrich.

The electrochemical cell employed for spectral recording was essentially the same as one described previously.¹⁶ Techniques for preparing solutions are outlined in the same reference. The solutions contained about 2 mM concentrations of each solute except TBABF₄, which was present at 0.1 M.

For precise measurement of chemiluminescence intensities, a cell similar to that of Bezman was used.^{17,18} The working electrode was a Pt disk of 0.053 cm² geometric area. Wound coaxially with it was a helical counter electrode made from a 25-cm length of 24-gauge Pt wire. An Ag/AgCl, KCl (satd) electrode identical with the Freed

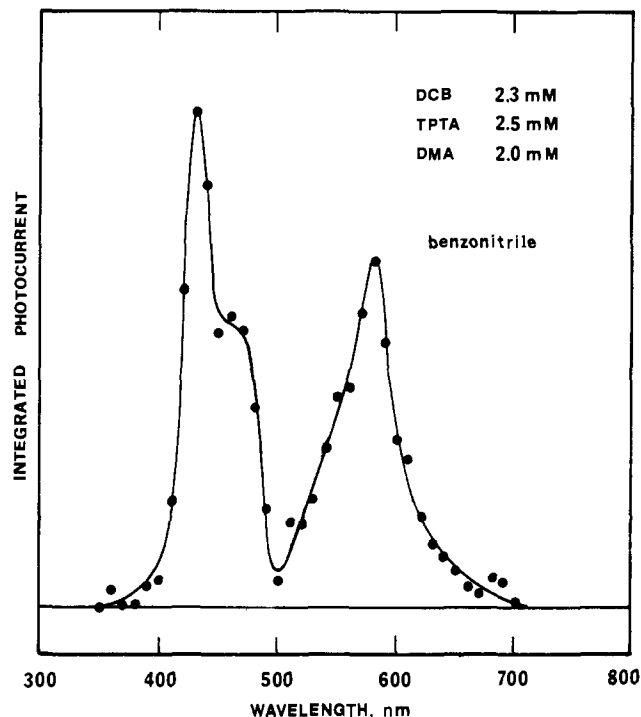


Figure 2. Ecl from the TPTA(+)/DCB(-) system with DMA serving as an interceptor. An uncorrected curve obtained with a 1P21 phototube.

design¹⁶ was used as reference. The outer body fit into Bezman's photometric apparatus¹⁹ and was shaped very much like that of the earlier cell. However, the part extending into the integrating sphere was shorter than in the Bezman design and had a total solution capacity of only 10 ml. The working solution (~6 ml) was initially loaded into a bulb on the upper cell body, where it could be degassed by the freeze-pump-thaw method and then poured into the section containing the electrodes. The working and counter electrodes remained in place during the degassing operation, but the reference was added afterward under a positive pressure of high-purity helium. Also on the upper cell body was a rotatable sidearm in which a second solution could be degassed simultaneously with the working solution.¹⁸ It could then be added to the working solution at a later time without exposing either solution to the atmosphere or to sealing grease.

Electrode potentials were controlled by a Princeton Applied Research Model 173 potentiostat and the desired potential program was imposed by either a function generator or a Nova 820 minicomputer acting through a 12-bit D/A converter. Potential overshoot in step experiments was expressly eliminated by connecting the counter electrode to the potentiostat's summing point via a 820 pF capacitance in series with a 4.7 MΩ resistance.

Spectra were obtained with an Aminco-Bowman spectrofluorometer fitted with a Hamamatsu 1P21 or R446S photomultiplier. The band-pass of the emission monochromator was 18 nm. For the 1P21, corrections for instrumental response could be made for wavelengths between 300 and 600 nm. The R446S, which has a much better red response, made corrected spectra possible over the 290–720 nm range.²⁰ Because the light levels were low, spectra were taken point-by-point. With the monochromator held at fixed wavelength, a triple-step experiment^{18,21} was performed and the light transient was acquired in digital form (750 points for $0 < t_r/t_f < 1.5$) by the computer. It was integrated numerically and the integral was preserved as the representative intensity for the wavelength in question. Figures 1–3 were obtained in this way.

Precise total-intensity measurements were made with the integrating sphere photometer described previously.¹⁹ To enhance sensitivity and restrict detection to the exciplex band, the usual quantum counter cell was replaced by an Oriel G-772-5400 filter. For these experiments, the computer directed the working electrode through ten cycles of alternate anion and cation generation, then returned the electrode to the initial intermediate potential. The photocurrent arising from this sequence was integrated electronically and the integral was read, corrected for baseline shift, and reported by the computer.

Absolute measurements were made in the triple-step mode as de-

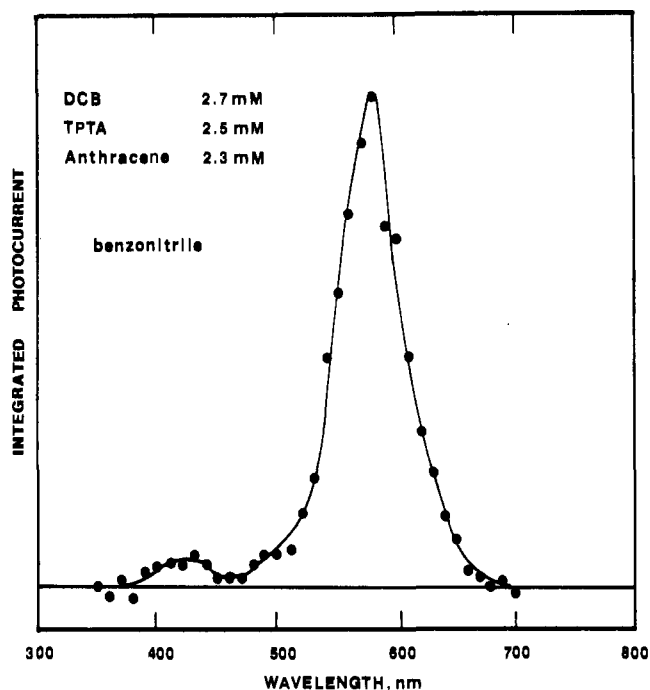


Figure 3. Ecl from the TPTA(+)/DCB(-) system with anthracene serving as an interceptor. An uncorrected curve obtained with a 1P21 phototube.

described elsewhere.^{18,21} Calibration of the integrating sphere photometer was carried out by two independent means, which gave good agreement.²⁰

Results and Discussion

Spectral Aspects. Electrogenerated chemiluminescence (ecl) spectra of TPTA/DCB systems (e.g., Figures 1–3) were obtained using potential limits of 1.06 and -1.61 V vs. Ag/AgCl. These limits are adequate to produce TPTA⁺ and DCB⁻, but they are not sufficiently extreme to implicate electrochemically any of the added quenching agents discussed here.

The spectrum of Figure 1 is essentially the same as that recorded from a solution containing only DCB and TPTA. The single broad maximum is identified as emission from the singlet exciplex ¹(DCB⁻TPTA⁺)*, since that state and its corresponding triplet ³(DCB⁻TPTA⁺)* are the only excited product states accessible to the radical-ion annihilation ($\Delta H^\circ \approx -2.5$ eV)⁷ (see Table I). The spectrum is severely distorted here by the photomultiplier response. Its maximum appears in Figure 1 at 575 nm; but with an R446S photomultiplier it is recorded

at 630 nm; and with correction of the R446S curve, it lies near 700 nm (1.8 eV). Beyond 700 nm, correction is uncertain, so it is difficult to locate the true maximum precisely. The width at half height in the corrected spectrum is about 80 nm. Figures 1–3 display uncorrected spectra in order to emphasize emission in the blue region.

A study of fluorescence from TPTA in benzonitrile solutions indirectly supports our assignment of the chemiluminescence. TPTA's ultraviolet (λ_{\max} 365 nm) fluorescence is accompanied by a broad luminescence having a maximum near 480 nm. The energy and the spectral shape of this second component are consistent with its assignment to the exciplex ¹(PhCN⁻TPTA⁺)*, which has been reported previously.⁹ Its energy is much higher than that of the observed emitter in chemiluminescence.

The addition of 0.1 M DCB to 10 mM TPTA solutions (excited frontally at 334 nm) did not produce additional long-wavelength emission. This result was not unexpected. We anticipate that TPTA will resemble triphenylamine in displaying a short (<5 ns) singlet lifetime,²² even in an inert solvent. In benzonitrile, a quenching medium, its fluorescence lifetime may fall into the picosecond range. Achieving a high enough DCB concentration to strongly quench TPTA and yield appreciable exciplex emission is impractical, if only because the absorption spectra of the two substances overlap significantly. Interestingly, we seem to have a situation here of being able to populate electrochemically a state that is extremely difficult, if not impossible, to reach by spectroscopic means.

The simple chemiluminescence of the TPTA(+)/DCB(-) system is complicated by the appearance of a second emission, in the blue, whenever anthracene, DPA, DMA, 9-MA, or 9-PA is added to the system. Figures 2 and 3 depict two examples. The new emission clearly arises from the first excited-singlet state of the added hydrocarbon. In contrast, no short-wavelength emission was observed with fluoranthene, pyrene, or *trans*-stilbene.²³ For example, Figure 1 discloses no trace of fluoranthene's characteristic emission, which maximizes near 450 nm.

The appearance of the blue band accompanies a slight quenching of the exciplex emission, as shown in the second column of Table II. The entire set there were obtained from the ten-cycle experiments described above. Again, the potential limits were +1.06 and -1.61 V vs. Ag/AgCl. First, the integrated intensity from the exciplex band was measured in the absence of the interceptor, then the rotatable sidearm was used to add an aliquot containing the interceptor to the working solution. Since the DCB, TPTA, and TBABF₄ concentrations in the initial working solution and the aliquot were the same,

Table I. Electrochemical and Spectroscopic Data

Substance (R)	$-E^\circ(\text{R/R}^-)$, V vs. Ag/AgCl ^a	$E^\circ(\text{R}^+/\text{R})$, V vs. Ag/AgCl ^a	First excited singlet, eV	Lowest triplet, eV
Tri- <i>p</i> -tolylamine	NR ^b	0.96	3.5 ^c	3.0 ^c
<i>trans</i> -Stilbene	2.09 ^d	NO ^b	3.8 ^e	2.0 ^e
Pyrene	2.07 ^d	1.41 ^f	3.3 ^e	2.1 ^e
9,10-Dimethylantracene	1.92 ^g	1.25	3.1 ^c	1.8 ^c
9-Methylantracene	1.90 ^g	1.33 ^h	3.2 ^c	1.8 ^c
Anthracene	1.88 ^g	1.41 ^h	3.3 ^e	1.8 ^e
9-Phenylantracene	1.85	1.42 ^f	3.1 ^c	1.8 ^c
9,10-Diphenylantracene	1.79	1.37	3.2 ^e	1.8 ^e
Fluoranthene	1.69	NO ^b	3.0 ^e	2.3 ^e
Benzophenone	1.69	NO ^b	3.2 ^c	3.0 ^c
1,4-Dicyanobenzene	1.49	NO ^b	4.3 ^c	3.2 ^c

^a Average of forward and reverse cyclic voltametric peaks for benzonitrile solutions containing 0.1 M TBABF₄. Exceptions are noted specifically. Ag/AgCl, KCl (satd) is -45 mV vs. SCE. ^b NR = not reduced, NO = not oxidized. Electrochemical activity was examined only in the range $-2.5 < E < 1.5$ V vs. Ag/AgCl. ^c See ref 9. ^d In *N,N*-dimethylformamide. ^e See ref 16. ^f R⁺ is slightly unstable. ^g In CH₃CN. ^h R⁺ is totally unstable. $E^\circ(\text{R}^+/\text{R})$ is taken as $E_p(\text{R}/\text{R}^+)$.

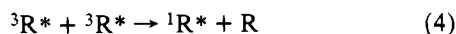
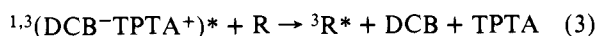
Table II. Effects of Interceptors

Interceptor	$\Delta I_e/I_e, \%^a$	$I_b/I_e, \%^b$
Anthracene	-6.2	0.09
9,10-Diphenylanthracene	-3.8	0.4
9,10-Dimethylanthracene	-2.2	2.0
9-Phenylanthracene	-1.8	0.3
Pyrene	0.6	<i>c</i>
<i>trans</i> -Stilbene	0.7	<i>c</i>

^a Change in integrated photocurrent upon addition of interceptor at ca. 2 mM. ^b Relative integrated area of interceptor emission. ^c Interceptor emission not detected.

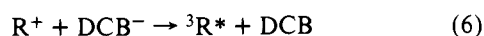
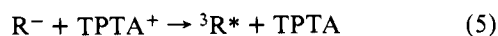
the addition changed only the interceptor concentration. Table II shows the percentage change of integrated exciplex intensity ($\Delta I_e/I_e$) upon the addition of a given interceptor. The anthracenes had a small quenching effect, whereas pyrene and *trans*-stilbene gave a slight, but probably insignificant, enhancement.

These results suggest that energy transfer from exciplex states to an interceptor may occur under favorable conditions. In no case, however, could the observed blue emission (~ 3.0 eV) have been sensitized directly. The lowest triplet-interceptor states are the only possible locally excited products, thus the blue emission would have to arise via triplet-triplet annihilation.

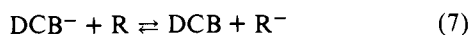


The data of Table I are consistent with this view. The triplet energies of the anthracenes are very close to the energies of ${}^{1,3}(\text{DCB-TPTA}^+)^*$, hence a transfer process like eq 3 seems thermodynamically possible. In contrast, the fluoranthene, pyrene, and *trans*-stilbene triplets lie well above the exciplex levels.

Another explanation for the blue bands is that they arise from ion annihilations other than the TPTA(+)/DCB(-) process. The reactions



generally lead to light with 10-100 times greater efficiency than the TPTA(+)/DCB(-) reaction does (see Table III). Moreover, residual concentrations of R^- and R^+ exist in our systems as consequences of the mobile equilibria.



If both eq 7 and 8 are established in the reaction zone, where under our conditions $[\text{R}] \approx [\text{DCB}] \approx [\text{TPTA}]$, then

$$[\text{DCB}^-]/[\text{R}^-] \approx \exp\{nF[E^\circ(\text{DCB}/\text{DCB}^-) - E^\circ(\text{R}/\text{R}^-)]/RT\} \quad (9)$$

$$[\text{TPTA}^+]/[\text{R}^+] \approx \exp\{nF[E^\circ(\text{R}^+/\text{R}) - E^\circ(\text{TPTA}^+/\text{TPTA})]/RT\} \quad (10)$$

These ratios exceed 10^3 for differences in standard potentials (ΔE°) greater than 180 mV. The smallest ΔE° in our experimental systems is 200 mV (for DCB and fluoranthene) and in that case no blue emission is noted at all. For every other case, the ion concentration ratios should exceed 10^5 . Table III shows that the efficiencies of the 9-PA(+)/DCB(-), DMA(+)/DCB(-), and TPTA(+)/fluoranthene(-) reactions are all about the same, so one cannot explain the great differences between the effects of DMA and fluoranthene in terms of a large disparity in side-reaction ecl

Table III. Chemiluminescence Efficiencies

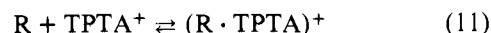
System	Applied potentials, V vs. Ag/AgCl ^a	Φ_{ecl}^b
9-PA(+)/DCB(-)	-1.61/1.54	9×10^{-4}
DMA(+)/DCB(-)	-1.61/1.36	6×10^{-4}
TPTA(+)/fluoranthene(-)	-1.79/1.06	6×10^{-4}
TPTA(+)/DCB(-)	-1.61/1.06	1.4×10^{-5}

^a Negative forward step. ^b Emission probability per homogeneous redox event.

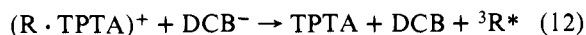
efficiencies. These considerations strongly indicate that side reactions involving the interceptor ions do not contribute to the apparent energy-transfer effect.

Further support comes from similar studies of the TPTA(+)/BP(-) system in acetonitrile, which also yields light solely from an exciplex.^{11,12} Addition of the anthracenes as interceptors gives results essentially equivalent with those detailed above for the TPTA(+)/DCB(-) system. Even the proportions of emission in the blue bands are about the same for a given interceptor operating in the two systems. Note, however, that the anion ratios (eq 9) are smaller for the TPTA(+)/BP(-) system by a factor exceeding 10^3 .

A reviewer has suggested a third possible explanation for our observations, i.e., that TPTA⁺ and the anthracenes could form cation complexes



which might react with the counterions to yield ${}^3\text{R}^*$ directly, without the need for an energy-transfer step.



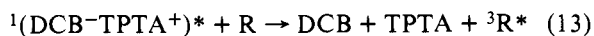
This possibility could account for both the appearance of the blue bands and the quenching of singlet exciplex emission. Only a few percent of the TPTA⁺ would have to be tied up in the complex.

Since the position of the cyclic voltametric peak potential for TPTA oxidation should be sensitive to the presence of an equilibrium like eq 11, we have examined it carefully.²⁴ It remains constant within ± 3 mV, regardless whether a hydrocarbon additive is present at the 2-mM level. We would regard a -6 mV shift as the minimum significant alteration. Such an effect would correspond to an equilibrium constant such that about 25% of the TPTA⁺ was complexed; thus the extent of complexation is certainly lower than 25%, but we cannot rule out directly the lower level of complexation necessary to explain our results.

Even so, two obstacles confront this hypothesis. (a) The electrochemical data show that the free energy of stabilization associated with eq 11 is certainly less than 0.15 eV, thus the free energy available from a reaction between DCB⁻ and (R·TPTA)⁺ would be smaller by less than 0.15 eV than that available from the reaction between DCB⁻ and TPTA⁺. The process in eq 12 should therefore be exoergic for all species R employed in our study; consequently, one has difficulty in explaining the inactivity of fluoranthene, pyrene, and *trans*-stilbene. (b) The efficacy of complexation depends, in principle, upon the energy match of the highest occupied orbitals in TPTA⁺ and R. Accordingly, one should expect a sensitivity to the value of $E^\circ(\text{R}^+/\text{R})$. Even though the standard potentials for effective quenchers vary over a 0.2 V range, only small differences in the quenching effects are seen.

These considerations lead us to favor an energy-transfer mechanism like eq 3 as the basis for our observations. Further characterization of the process requires an examination of the donor state's multiplicity, which is an interesting issue in itself.

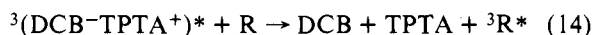
One might explain the results in terms of direct quenching of the emitting singlet exciplex by the hydrocarbon R,



However, exchange interactions leading to such a result are inhibited by the lack of spin conservation, so it is difficult to imagine eq 13 as being very efficient unless a true intermediate (e.g., a triple exciplex²⁵) were involved. The issue of quenching efficiency is important because a direct quenching step would have to be virtually diffusion controlled in order to account for even the weak quenching seen here, if ${}^1(\text{DCB-TPTA}^+)^*$ has a lifetime in the 1–10-ns range, which seems typical of singlet exciplexes in polar media.^{26–29}

It is interesting in this regard that Hemingway et al. observed total quenching of ${}^1(\text{BP-TPTA}^+)^*$ upon the addition of 1.6 mM Eu(DBM)₃·pip.¹³ If their quenching result is solely attributed to energy transfer, then the exciplexes would have to survive for several hundred nanoseconds, which seems exceptionally long on the basis of available direct evidence. The difference in degree of exciplex quenching between their study and ours might be due to some implication of Eu(DBM)₃·pip in the ion-radical chemistry. If, alternatively, the exciplex lifetime is indeed long, a high efficiency in a process like eq 13 is not essential to an explanation of our results.

Perhaps a more attractive hypothesis is to invoke energy transfer from triplet exciplexes,



This fully allowed energy transfer, if exoergic, could occur efficiently and straightforwardly account for the sensitization of blue emission. However, a more subtle point concerns the means by which eq 14 could influence the rate of singlet-exciplex emission, because one would require an interdependence between the singlet- and triplet-exciplex populations. Weller has suggested that such a linkage might arise from thermally activated intersystem crossing.²⁹ This exciplex analogue to E-type delayed fluorescence is easily conceived, since the singlet- and triplet-exciplex states are presumably separated by a very small energy gap.

Efficiencies. Absolute luminescence measurements place the emission efficiency Φ_{ecl} of the TPTA(+)/DCB(–) reaction at 1.4×10^{-5} , which is a good deal smaller than values shown by typical T-route systems (Table III). This efficiency is easily seen to be $\Phi_{\text{e}}\Phi_{\text{f}}'$, where Φ_{e} is the exciplex yield of radical-ion annihilation and Φ_{f}' is the exciplex fluorescence efficiency. Thus Φ_{e} could be obtained if Φ_{f}' were known.

Apparent Φ_{f}' data have been reported for the pyrene-*N,N*-dialkylaniline exciplexes in a variety of solvents.^{26,28,30,31} These measurements have typically involved optical excitation of pyrene to its S₁ state, ${}^1\text{Py}^*$, in the presence of a large concentration of the *N,N*-dialkylaniline (DAA). Thus ${}^1\text{Py}^*$ is quenched quantitatively, and Φ_{f}' can be evaluated in the usual ways. These apparent Φ_{f}' values decline very sharply with increasing solvent polarity and become a good deal smaller than 0.01 for dielectric constants greater than 20. However, a debate continues over the true emission efficiency of the exciplex itself^{26–28,30–32} because the quenching mechanism of DAA seems to involve the competitive formation of ion pairs and exciplexes.^{26,32} Since the ion-pair pathway becomes increasingly important as solvent polarity increases, the apparent Φ_{f}' falls sharply, but the true Φ_{f}' is less affected. Unfortunately, the difference between the two is unknown.

Similar considerations should also apply to ${}^1(\text{DCB-TPTA}^+)^*$, but two other factors need examination

in this particular case: (a) the energy of ${}^1(\text{DCB-TPTA}^+)^*$ is much smaller than that of ${}^1(\text{Py-DAA}^+)^*$, hence internal radiationless transition rates may be larger for the former species; (b) exciplex quenching by supporting electrolyte ions³³ may be operative even for short lifetimes and if longer lifetimes apply, DCB or TPTA may also enhance exciplex decay. It is therefore conceivable that Φ_{f}' for ${}^1(\text{DCB-TPTA}^+)^*$ is as low as 10^{-5} in our ecl systems. Obviously this figure is the lowest value consistent with our Φ_{ecl} result if Φ_{e} does not exceed unity.

For reasons outlined above, even an apparent Φ_{f}' could not be measured directly for ${}^1(\text{DCB-TPTA}^+)^*$ in benzonitrile. We can therefore say only that $10^{-5} \leq \Phi_{\text{f}}' \leq 1$ and that $10^{-5} \leq \Phi_{\text{e}} \leq 1$. The importance of exciplexes as intermediates in the redox processes considered here must remain an open issue. A more conclusive position will require better data for Φ_{f}' .

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References and Notes

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