

High Rates of Fluorescence Quenching Between Perylene Dodecyldiimide and Certain π -Electron Donors

S. İÇLİ

*Department of Chemistry, Faculty of Science,
Ege University, Bornova, İzmir-TURKEY*

H. İCİL

*Department of Chemistry, Faculty of Arts and Sciences,
Eastern Mediterranean University,
Famagusta, N. Cyprus, Mersin-TURKEY*

İ. GÜROL

*TÜBİTAK-Marmara Research Center, Research Institute for
Basic Sciences, Department of Chemistry,
P.O. Box 21, Gebze, Kocaeli-TURKEY*

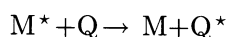
Received 2.5.1997

Perylene bis-n-dodecyl diimide is found to quench fluorescence emissions of naphthalene, phenanthrene and dihydrocarbazolocarbazole molecules at rates of 4.4×10^{11} , 2.8×10^{12} and $2.5 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$, in respective order of aromaticity. These unusually high rates of fluorescence quenchings are attributed to Perrin model static quenching and presence of electron transfer through singlet excited state of perylene diimide. Calculated free energy of electron transfer, $\Delta G_{ET} = -120.5 \text{ kJ/mol}$, between perylene diimide and dihydrocarbazolocarbazole is taken as evidence for observation of high fluorescence quenching rate for carbazolocarbazole molecule.

Keywords: Fluorescence quenching, Photoenergy transfer, Perylene diimide and Carbazolocarbazole

Introduction

If a molecule Q has an excited state Q^* lower than excited state of molecule M^* , the excitation energy can be transferred according to



Radiative or non-radiative deactivation of Q^* to Q then completes the quenching process. Major energy transfer processes that takes place are either by electron exchange (Dexter) or by dipole-dipole (Förster) mechanisms. Electron exchange occurs between an excited molecule M^* and a ground state molecule Q. The first requirement for energy transfer in electron change is $E(M-M^*) \geq E(Q-Q^*)$, and the

second requirement is that the orbitals should allow electron transfer from M^* to M and from Q to M . The molecules M^* and Q must be in close contact (van der Waals or hard sphere) for the overlap of orbitals to cause electron transfer. In dipole-dipole interaction the mechanism is via the transition moments of the excitation $Q \rightarrow Q^*$ and deactivation of $M^* \rightarrow M$. This interaction is a rather shallow distance dependence ($< 100 \text{ \AA}$) compared to orbital overlap interaction of electron exchange¹⁻³.

Energy transfer quenching can also either be dynamic or static. The molecules M^* and Q can come into contact through their random diffusional motion in dynamic quenching. The rate constant is then diffusion controlled and has an upper limit of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for any bimolecular reaction. Luminescence quantum yield follows the Stern-Volmer equation in dynamic quenching: $I_0/I = 1 + k_q \tau [Q]$. M and Q molecules should be in close proximity to each other in static quenching. Each excited molecule is then surrounded by one or several quencher so that quenching occurs instantaneously in Perrin model. Static quenching is given in logarithmic form as: $\ln(I_0/I) = c[Q]$. The quenching rates are independent of diffusion control in static quenching and may reach values above $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. Electron donor-acceptor molecules, due to favorable charge transfer attractions, are expected to quench by electron exchange and by static quenching. Electron acceptors are oriented as quenchers (Q) towards donors¹⁻³.

Perylene diimides are electron acceptors and also known to be excellent thermal and photo-stable sensitizers⁴. Absorption in the visible region (450-530 nm) enables them for use in solar applications. Energy and electron transfer processes proceed through singlet states. Fluorescence quantum yields of unity and high energy difference between singlet-triplet states, 54-27 kcal/mol, respectively, are taken as evidence of a singlet state photo processes^{5,6}. Recent study on electron transfer photoreaction of bis-dipneeylimide derivative with cyclic conjugated dienes, have proven that perylene diimide anion radical formed by singlet electron transfer initiates the reaction in presence of oxygen⁷. Neutral perylene diimide reforms in reaction conditions, act as an excellent solar photocatalyst. The fluorescence quenching rate between perylene diimide and cyclic conjugated diene abietic acid was measured to be $k_q = 2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in acetonitrile solutions⁷. This rate is close to diffusion controlled rates.

The fluorescence quenching rate between strong π -electron donor of dihydrocarbazolocarbazole and acceptor of tetranitrofluorenone is shown to give a high quenching rate⁸ at about $10^{13} \text{ M}^{-1} \text{ sec}^{-1}$. This rate is above diffusion rate limits. The causes are pointed as the presence of efficient electron exchange and static quenching from ground state charge-transfer complexation⁸. In this study we have taken perylene diimide as electron acceptor molecule instead of tetranitrofluorenone. Perylene diimides are not as strong electron acceptors as tetranitrofluorenone, but known to be moderate electron acceptors. The formation of stable perylene diimide anion radical in photoprocesses is proven. Additional quenching may rise for perylene diimide-donor bimolecular systems, by electron transfer and back electron transfer from radical ions, if donor cation radical is stable enough. In order to contribute to the mechanism of photochemical processes of perylene diimides, which are powerful solar photocatalysts, we have measured the fluorescence quenching rates between perylene bis(*n*-dodecyl) diimide-carbazolocarbazole molecules and with π -electron donors of naphthalene and phenanthrene.

Experimental

[MP]-5, 10-Dihydrocarbazolo[3,4-*c*]carbazole was synthesized by the method of Zander⁹. Bis-*n*-dodecyl perylene diimide (**Perim**) was synthesized as described⁶. Phenanthrene and naphthalene were supplied from Fluka at purum grade and used as supplied. The solvent chloroform was purchased from Solvay and fractionally distilled on a Normschliff Wertheim NGW-Shott path distillation column before use.

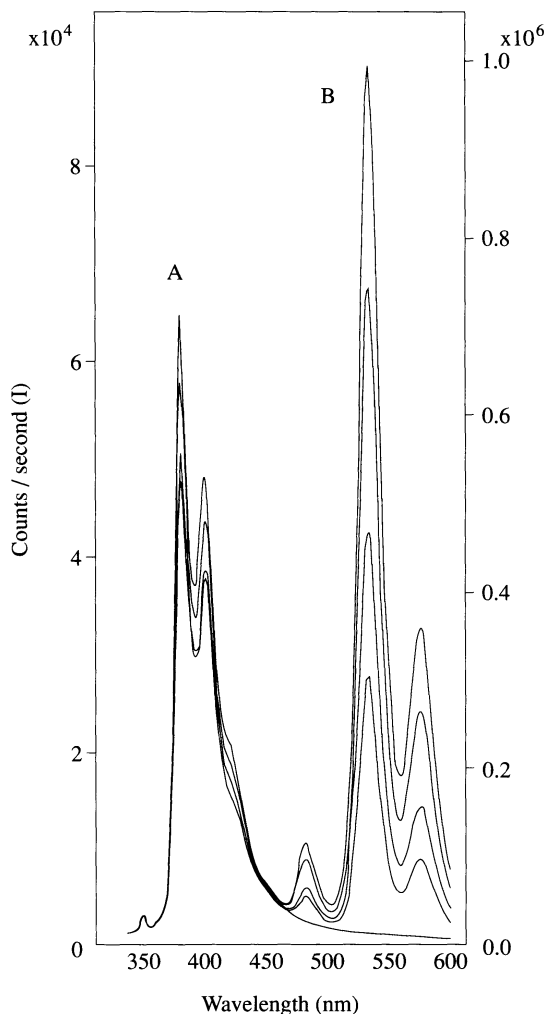
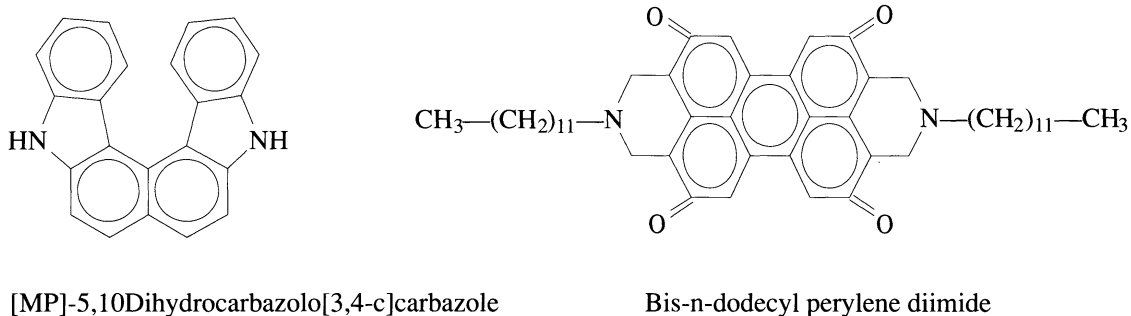


Figure 1. Quenching of fluorescence emission of dihydrocarbazolocarbazole(**A**) at excitation wavelength of 314 nm by addition of perylene bis-(n-dodecyl) diimide(**B**).

The UV-visible absorption spectra were recorded on a Varian DMS-90 spectrophotometer. Emission spectra were measured on a Shimadzu RF-540 fluorescence spectrophotometer. The fluorescence quantum yield measurements were done in reference to perylene bis-dodecyl diimide emission spectra in chloroform⁶. Quenching emission experiments were carried out by addition of bis-dodecyl perylene diimide (1×10^{-4} M) into phenanthrene, naphthalene, and carbazolocarbazole solutions in chloroform. The addition of perylene bis-dodecyl diimide caused the decline of donor molecule fluorescence emission (Figure 1). The concentration of perylene diimide quencher was calculated in mixed solution and plotted against the intensity difference of naphthalene, phenanthrene and carbazolocarbazole fluorescence emissions (Figure 2). The concentrations

of all the solutions were selected to be less than 10^{-5} M at UV absorptions of lower than 0.2, in order to avoid the misleading concentration effects on emission measurements.

Results and Discussion

The fluorescence quenching rates, calculated from Stern-Volmer plots (Figure 2), measured singlet energies and fluorescence quantum yields and literature values on fluorescence lifetimes are listed in Table 1.

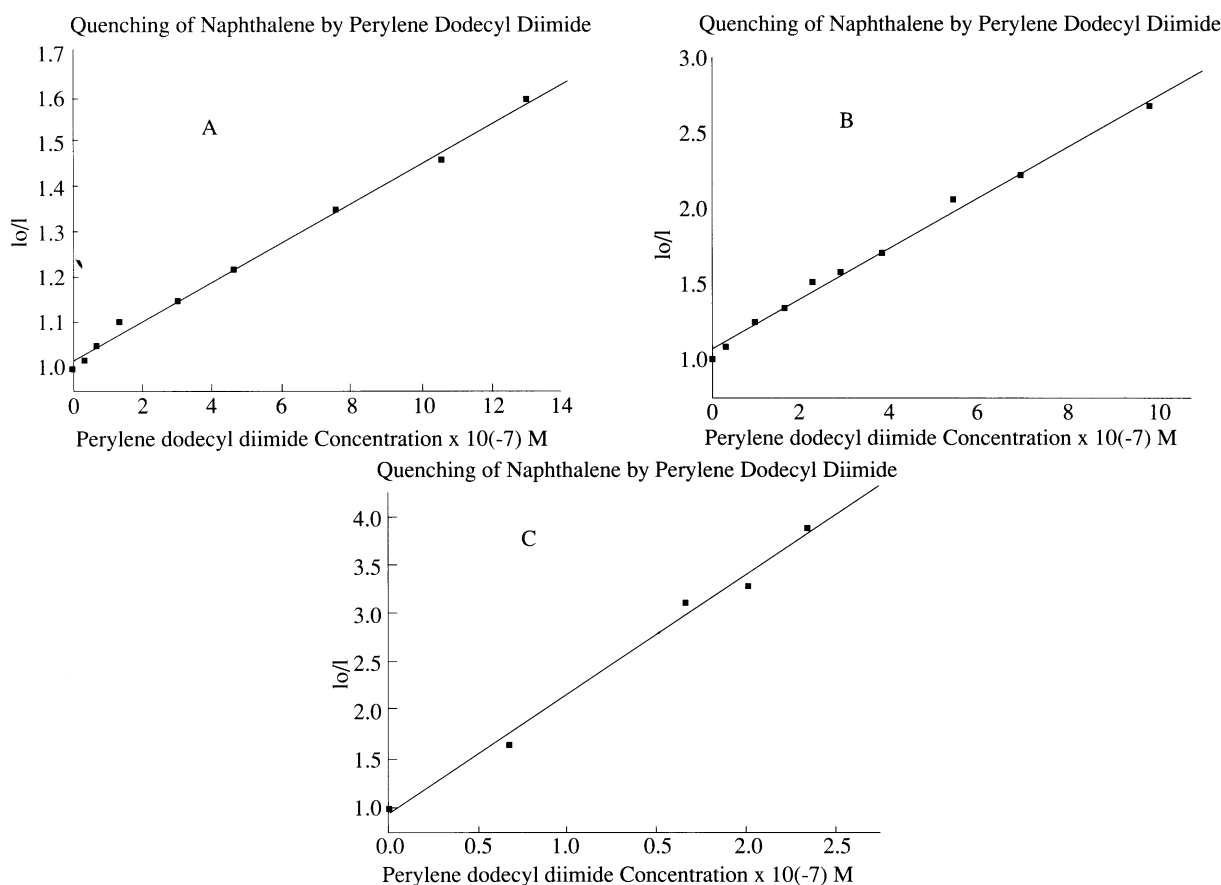


Figure 2. Stern-Volmer plots on fluorescence quenching of naphthalene (A), phenanthrene (B) and dihydrocarbazolocarbazole (C) on addition of perylene bis-(n-dodecyl) diimide.

A striking appearance of Table 1 is that fluorescence quenching rates increase in the order of increasing π -electron donor capacities of naphthalene, phenanthrene and carbazolocarbazole molecules. Carbazolocarbazole molecular structure, condensed hexahelicene ring type, is known to be one of the strongest aromatic π -electron systems, which is proven on anisotropy chemical shift effect on proton nmr¹¹. In accordance with this, it is seen that phenanthrene is quenched 50 times faster than naphthalene and dihydrocarbazolocarbazole is quenched about 5000 times faster than naphthalene (Table 1).

Another unusual result of Table 1 is that fluorescence quenching rates of 10^{11} - 10^{14} $\text{M}^{-1}\text{sec}^{-1}$ are above the limit of diffusion controlled quenching rates of 10^{10} $\text{M}^{-1}\text{sec}^{-1}$. A static quenching of Perrin model appears to be present rather than dynamic quenching of Stern Volmer equation. The first supporting evidence can be seen by the reported high quenching rate of dihydrocarbazolocarbazole by strong π -electron acceptor of tetranitrofluorenone⁸, $k_q = 7.4 \times 10^{12}$ $\text{M}^{-1}\text{sec}^{-1}$. A second piece of evidence is that the quenching between perylene bis-phenyldiimide and a weak π -electron donor abietic acid ($k_q = 2 \times 10^9$ $\text{M}^{-1}\text{sec}^{-1}$)

is proven to be completely due electron transfer of Dexter type⁷. The presence of electron transfer is shown on laser flash photolysis and spin trap ESR experiments, and the formation of perylene diimide anion radical is detected on transient absorption spectra at 705 nm⁷. Förster dipole-dipole interactions for quenching is unlikely to occur because donor-acceptor molecules are already in contact to each other prior to excitation in charge-transfer (C-T) type ground state complexations. These flat condensed aromatic donor acceptor couples are known to be in close proximity to each other at critical transfer distances of less than 10Å¹¹. Electron exchange and/or electron transfer processes are expected to proceed dominantly at these distances. The electron transfer should occur from singlet excited state of perylene diimide to donor aromatic molecule, leading to formation of stable radical anion and cations (1):

Table 1. Fluorescence quenching rates of naphthalene, phenanthrene, and dihydrocarbazolocarbazole with perylene bis-dodecyl diimide quencher. Fluorescence lifetimes, singlet energies and fluorescence quantum yields of naphthalene, phenanthrene, dihydrocarbazolocarbazole and perylene bis-N,N'-dodecyl diimide in chloroform.

	$k_g(\text{M}^{-1}\text{s}^{-1})$	$\tau_f(\text{ns})$	$E_s^\spadesuit(\lambda \text{ nm})$	Θ_f
Naphthalene	4.4×10^{11}	105*	384.9(311)*	0.20*
Phenanthrene	2.8×10^{12}	61*	346.9(345)*	0.12*
Dihydrocarbazolocarbazole	2.5×10^{14}	5♣	320.1(374)♣	0.07♣
Perylene bis-dodecyl diimide	–	4.3‘	227.6(526)‘	1.00‘

*Reference 10. ♣Reference 8. ♠kJ/mol. ‘Reference 7.



The transfer of electron from radical anion-cation couple to a third substrate is unlikely to occur. As proven, electron transfer from donor olefin molecule to perylene diimide occurs in less than 40 psec and in a cage. Dominant back electron transfer (2) is expected to decay the radical species, preventing the electron escape from the cage.



One may calculate the free energy for the electron transfer reaction, ΔG_{ET} , as shown in the scheme below by the use of redox potential values¹². Redox potential of perylene diimide is -1.050 volt¹³ to anion radical.

It is evident from Table 2 that electron transfer is most favored between perylene diimide and carbazolocarbazole molecules compared to naphthalene and phenanthrene molecules, in agreement with measured unusually high fluorescence quenching rate of $2 \times 10^{14} \text{ M}^{-1}\text{sec}^{-1}$. Strong π -electron donors evidently transfers electron(s) to perylene diimides easily. Favored back electron transfer from perylene diimide anion radical outputs an overall electron exchange interaction as in Dexter process, and additional static quenching causes the observation of high fluorescence quenching rates between perylene diimides and aromatic π -electron donors.

Table 2. Free energies for electron transfer between perylene diimide and π -electron donors, calculated from redox potentials and singlet energies.

$$\Delta G_{ET} = 23.06[E(D^{\cdot+}/D) - E(A/A^{\cdot-})] - E_s^D \quad (3)$$

$E(D^{\cdot+}/D)$: Redox potential of donor.

$E(A/A^{\cdot-})$: Redox potential of acceptor perylene diimide.

E_s^D : Singlet energy of donor.

	E_p (volt)	E_s (kJ/mol)	ΔG_{ET} (kJ/mol)
Napththalene	2.60 ¹⁰	384.9 ¹⁰	-32.6
Phenathrene	2.44 ¹⁰	346.9 ¹⁰	-10.0
Carbazolocarbazole	1.016 ⁸	320.1 ⁸	-120.5

Acknowledgements

Authors thank to TUBITAK for supports.

References

1. N.J. Turro, "Modern Molecular Photochemistry", pp. 296-361, The Benjamin/Cummings Publishing, Menlo Park-California, 1979.
2. P. Suppan, "Chemistry and Light", pp. 87-105, The Royal Society of Chemistry, Cambridge, 1994.
3. J.A. Baltrop and J.D. Coyle, "Excited States in Organic Chemistry", pp. 101-132, John Wiley & Sons, London, 1975.
4. H. Langhals, *Heterocycles* **40**(1), 477-500 (1995).
5. H. İcil and S. İçli, *Spectrosc. Lett.* **28**(4), 595-601 (1995).
6. S. İcli and H. İcil, *Spectroscopy Lett.*, **29**(7), 1253-1257 (1996).
7. L. Chen, L.A. Lucia, E.R. Gaillard, H. İcil, S. İçli and D.G. Whitten, submitted to *Jour. Am. Chem. Soc.*
8. S. İçli, H. İcil, D.G. Whitten, Ç. Sayıl and İ. Dityapak, submitted to *Journal of Luminescence*.
9. M. Zander, and W.H. Franke, *Chem. Ber.* **102**, 2728-2738 (1969).
10. S.L. Murov, in: *Handbook of Photochemistry*, pp. 4-5, Marcel Dekker, Inc., New York, 1973.
11. S. İçli, T. Burgemeister and A. Mannschreck, *Org. Magn. Resonance* **20**(3), 145-150 (1982).
12. G.J. Kavarnos and N.J. Turro, *Chem. Rev.* **86**, 401-449 (1986).
13. J. Salbeck, H. Kunkley, H. Langhals R.W. Saalfrank and J. Daub, *Forschung Chimia* **43**, 6-9 (1989).