X-ray Diffraction and Photophysical Studies of Pyromellitic Dianhydride-Anthracene Molecular Charge Transfer Complex at 298K

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ABSTRACT

A molecular charge transfer (CT) complex was characterized by crystal structure analysis, and photophysical studies, followed by theoretical calculations, utilizing anthracene as a donor and pyromellitic dianhydride (PMDA) as an acceptor. A (π-π) stacking interconnection is observed in the 1:1 PMDA-Anthracene charge transfer complex. The optimized geometry structures obtained from the density functional theory (DFT) calculation in the gas phase support the observed result. In pure and mixed solvents, an unusual decrease in wavelength was observed in steady state absorption and emission spectra with increasing solvent polarity. The binding constant for the PMDA-Anthracene charge transfer (CT) complex is determined to be in the order of 10^3.

Keywords: Charge Transfer Complex; Crystal Structure; Stacking Interconnection; Binding Constant

Introduction

Donor-acceptor charge transfer (CT) complexes possessing low-energy electronic states serve as valuable systems for studying the influence of molecular interactions on electron hole delocalization as well as transfer rates. Molecular donor-acceptor cocrystals indeed represent ideal systems for investigating charge transfer phenomena due to their chemical simplicity and well-defined structures.

Various chemical reactions like addition, substitution, and condensation are known to involve the participation of charge transfer complexes (Datta *et al.,* 2000). Non-linear optical materials and electrical conductivities have received significant attention due to their involvement in these complexes (Yakuphanoglu *et al.,* 2005). The electron donor-acceptor (EDA) interaction plays a crucial role not only in the drug-receptor binding mechanism but also in interface chemistry, solar energy storage, and various biological fields (Andrade *et al.,* 2000). In pharmaceutical analysis, the EDA interactions of specific π-acceptors have been utilized, highlighting their significance in this field (Hamed *et al.,* 2000).

Methodology

Pyromellitic dianhydride (PMDA) (Figure 1A), anthracene (Figure. 1B), acetonitrile (ACN), dichloromethane (DCM), and potassium bromide (KBr) used in the study were all reagent grade chemicals purchased from Sigma-Aldrich. Unless otherwise mentioned, these chemicals were used without purification. ACN and DCM were purified by distillation while anthracene was purified by sublimation.
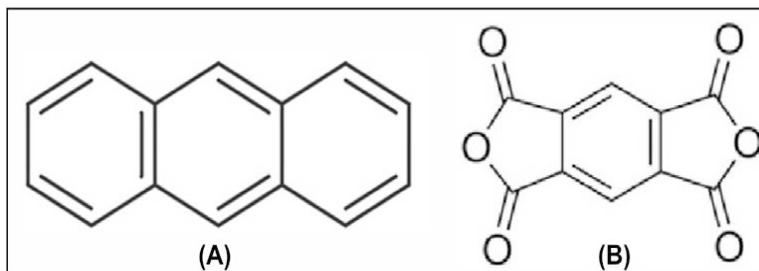
Figure 1: Structures of (A) PMDA (Pyromellitic dianhydride) and (B) Anthracene

Synthesis of the complex

The single crystal of the CT complex was grown by allowing a 1:1 solution of the donor and the acceptor in dichloromethane (DCM) to slowly evaporate at room temperature. The solution was transferred into a glass tube, which was then covered by parafilm with a tiny orifice. The tube was placed inside a desiccator and left undisturbed for a period of two months. PMDA-Anthracene CT complex was found in red color. To prepare a powder sample, a little quantity (5%) of the crystal was combined with potassium bromide (KBr). The mixture was then ground together and a transparent pellet of the CT complex was prepared for photophysical studies.

Instrumentations

Crystallography study

The convenient crystal of the PMDA-Anthracene CT complex (red block) was arranged on glass fiber. The intensity data of the crystal was determined at a temperature of 298 K. During the data collection no crystal decay was observed. Absorption corrections based on multi-scans were applied in all cases using the SADABS software. The structure was solved using the direct method (Sheldrick *et al.,* 1990), which involved all available data and aimed to minimize the residuals. For structural solutions and refinements, SHELXL-97 software (Sheldrick, 1996) was employed. In the study, Table 1 provides the crystallographic data and refinement details. Anisotropic refinement was performed for all non-hydrogen atoms in the study. In the final refinement, the hydrogen atoms were fixed isotropically with a C-H bond length in the order of 0.95 Å. Data collection was performed using the SMART software package, while data reduction was carried out using the SAINT software package.

Absorption, and steady state emission studies

The UV-Vis absorption spectra were recorded using a Hitachi U-4010 spectrophotometer Model at room temperature. The steady state emission measurements were conducted using a Hitachi F-7000 Spectrofluorimeter Model equipped with a Xenon lamp (150W). A quartz cell with a path length of 1 cm and solid-state accessories were employed for the measurements.

Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) calculations:

The results reported here were performed using the "Gaussian 03 program package" with the support of Gauss View. The geometry structures of the PMDA-anthracene charge transfer (CT) complex in the gas phase have been developed at 6-31 G and 6-31(d) G (Hehre *et al.,* 1972) levels. The optimizations were carried out using the BELYP functional for the ground state. Optimized geometry structures in the excited state were also obtained using the CIS method with the same basis sets.

Results and Discussion:

Descriptions of Crystal Structure:

A single crystal of PMDA-Anthracene CT complex, which is convenient for solid state structural investigation has been obtained and is depicted in Figure 2. Figure 2A displays a view of the subunit with a (1:1) stoichiometry, showcasing the atom labeling. In the triclinic P-1 space group, the donor and acceptor subunits of PMDA-Anthracene are crystallized, with one molecular mass unit accommodated per unit cell. A closer examination of the packing arrangement in the subunit reveals that the cocrystal is primarily composed of alternating π-acceptor/π-donor stacks (Figure 2B). The planes of the acceptor and donor components are nearly parallel to each other. Figure 2C illustrates the distance between the two planes in the stack, which measures 3.25Å.

Table 1: The Crystallographic Data for the PMDA-Anthracene Charge Transfer (CT) Complex

Parameters	PMDA-Anthracene
Composition	$C_{24}H_{12}O6$
Formula wt.	396.35
Crystal System	Triclinic
Space group	P-1
Stoichiometry	1:1
Data collection temperature	298 K
a, Å	7.2308(7)
b, Å	7.3652(6)
c, Å	9.5532(8)
α, deg	69.516(4)
β, deg	87.440(5)
γ, deg	68.744(5)
V, Å^3	442.202
ρ_{calc}, Mg.m^{-3}	1.462
λ(Mo K$_\alpha$), [Å]	0.71073
Z	9
F (000) / μ mm^{-1}	848 / 0.101
$2\theta_{max}$ [°]	55
Reflections Collected/Unique	4108 / 3882
R_{int}/ GOF on F^2	0.0212 / 0.837
No. of parameters	289
$R1^a(F_0)$, $wR2^b(F_0)$	0.0349, 0.1017
Largest difference peak, Deepest hole, eÅ^{-3}	0.228, -0.254
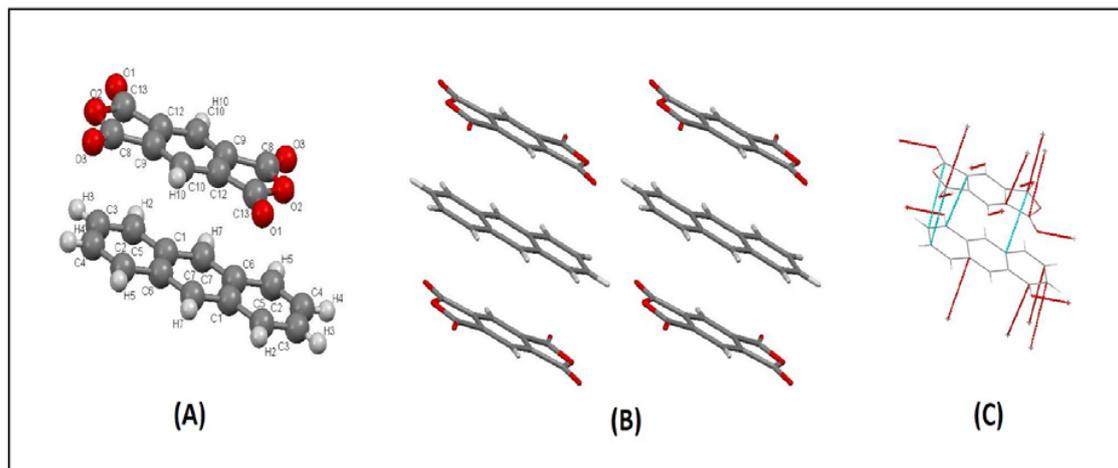
Source: Primary Source

Figure 2: The Single Crystal Structure of the PMDA-Anthracene Charge Transfer Complex Demonstrating (A) Repeating Donor and Acceptor Unit with Labeling, (B) The Packing Arrangement (Hydrogen Atoms Omitted) Showing the Extended Stacks of the Alternate Units, (C) Short Contacts Observed within the CT Complex.

Absorption Studies in Pure and Mixed Solvents at 298K:

Figure 3 and Table 2 display the absorption spectra of the CT complex recorded at 298K in various solvents, including acetonitrile (ACN), dichloromethane (DCM), and mixed solvents containing both ACN and DCM.

For the determination of the binding constant of the PMDA-Anthracene charge transfer (CT) complex, the increase of the charge transfer band in the absorption spectra was monitored by gradually adding the acceptor to a constant concentration of the donor. The binding constant was calculated using the Benesi Hilderbrand equation (Benesi *et al.,* 1949) represented by Equation 1.

$$\frac{1}{\Delta A} = \frac{1}{b\Delta\epsilon[C]_0[H]_0 K_a} + \frac{1}{b\Delta\epsilon[H]_0} \qquad ....(1)$$

Where:

ΔA represents the enhancement in the CT absorbance, H_0 is the total concentration of the donor, C_0 is the concentration of the acceptor, K_a is the binding constant, and ϵ is the molar absorptivity of the charge transfer complex.

Binding constant (K_a) of PMDA-Anthracene charge transfer (CT) complex was determined by plotting $1/\Delta A$ against $[C]_0^{-1}$ according to the Benesi-Hilderbrand equation. Figure 4 illustrates the Benesi Hilderbrand plot of the CT complex. Slope of this linear plot corresponds to the binding constant (Ka). In this case, the calculated binding constant is found to be 4.0×10^3.

Table 2: Absorption and Emission Spectral Data of PMDA-Anthracene Charge Transfer (CT) Complex in Pure Solvents and Mixed Solvents At 298K.

Solvent	$\lambda_{max}^{(A)}$ (nm)	$\bar{v}_A$ (cm^{-1})	$\lambda_{max}^{(F)}$ (nm)	$\bar{v}_F$ (cm^{-1})
Pure DCM	502	1.9920×10^4	605	1.6528×10^4
DCM:MeCN(4:1)	488	2.0491×10^4	590	1.6949×10^4
DCM:MeCN(3:2)	484	2.0661×10^4	585	1.7094×10^4
DCM:MeCN(1:1)	482	2.0746×10^4	582	1.7182×10^4
DCM:MeCN(2:3)	480	2.0833×10^4	580	1.7241×10^4
DCM:MeCN(1:4)	478	2.0920×10^4	578	1.7301×10^4
Pure MeCN	476	2.1008×10^4	576	1.7361×10^4
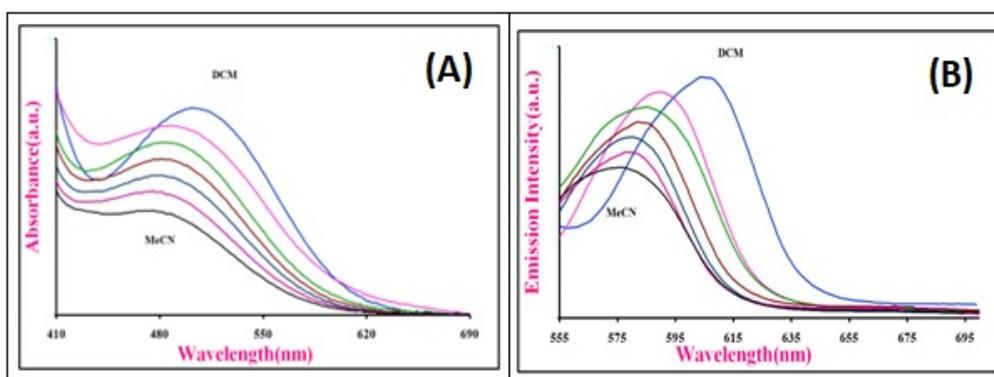
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Figure 3: The (A) Absorption and (B) Steady State Emission Spectra of PMDA-Anthracene Charge Transfer (CT) Complex at 298K in the Following Solvents: 1. Dichloromethane (DCM) 2. DCM : ACN (4:1) 3. DCM : ACN (3:2) 4. DCM : ACN (1:1) 5. DCM : ACN (2:3) 6. DCM : ACN (1:4) 7. Acetonitrile (ACN)
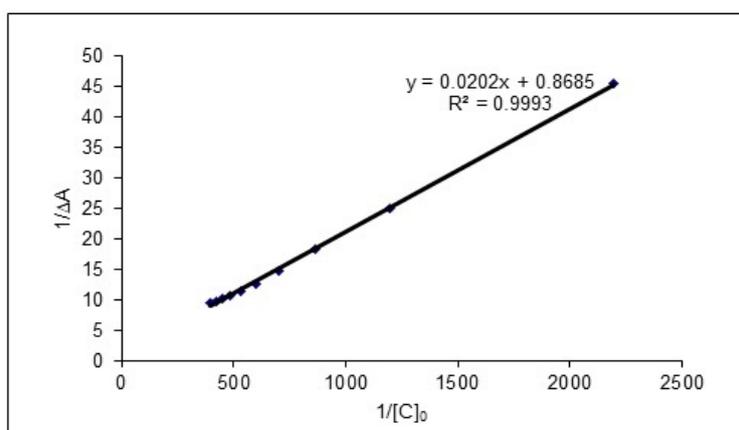
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Figure 4: The Benesi Hildebrand Plot for the PMDA-Anthracene CT Complex

Steady State Emission Spectra Studies at 298K:

Figure 3 (Table 2) displays the steady state emission spectra of the PMDA-Anthracene charge transfer (CT) complex in various solvents, including acetonitrile (ACN), dichloromethane (DCM), and mixed solvents. The stacking structure of the PMDA-Anthracene complex exhibits an interesting phenomenon of blue shift as the polarity of the solvent increases, in two pure solvents and mixed solvents. In acetonitrile (ACN), the PMDA-Anthracene complex shows a blue shift of 3647 cm^{-1}, while in dichloromethane (DCM), the blue shift is observed to be 3392 cm^{-1}. Figure 5 presents the steady state emission spectra of PMDA-Anthracene charge transfer (CT) complex in solid state. The emission peak of the charge transfer complex is observed at 618 nm. The PMDA-Anthracene charge transfer (CT) complex in the solid state demonstrates a red shift in the absorption and emission spectra compared to that observed in the solution (Table 2).
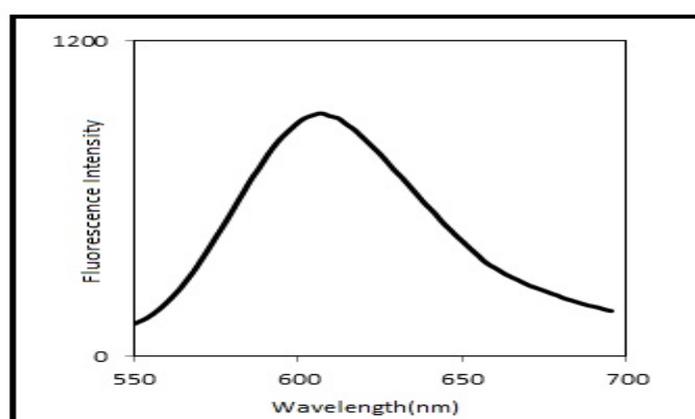
Source: Primary source

Figure 5: Emission Spectra of PMDA-Anthracene Charge Transfer (CT) Complex in Solid State at 298K

Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) calculations:

All the bond distances of the PMDA-Anthracene charge transfer (CT) complex in the gas phase, as obtained from the optimized structure, closely resemble those determined from the X-ray diffraction studies. Table 3 provides the ionization potential values and presents the dipole moment values for both the ground state and excited state of PMDA-Anthracene charge transfer (CT) complex. Additionally, it highlights the presence of a (π-π) stacking interconnection in the complex. Figure 6 illustrates the geometry-optimized structures of the PMDA-Anthracene CT complex in both ground and excited states. The distance between the acceptor and donor plane is determined to be 3.3Å. Figure 7 displays the distribution of formal charges on different atoms within the PMDA-Anthracene charge transfer (CT) complex. The calculated values obtained from the DFT-TDDFT studies exhibit a good agreement with the experimental data. This indicates that the theoretical calculations accurately capture the properties and behavior of the PMDA-Anthracene charge transfer (CT) complex, providing reliable insights and supporting the experimental findings.

Table 3: Excitation Properties of PMDA-Anthracene CT Complex from Theoretical Calculation

Complex	λ_{ab}(nm)	E_{CT}(theo) (eV)	ν_0(eV)	IP_1 (eV)	IP_2 (eV)	IP_{av} (eV)	μ_{ground}(D)	$\mu_{excited}$(D)
PMDA-Anthracene	502	2.4594	2.4701	6.5068	6.829	6.6679	0.1433	0.3841
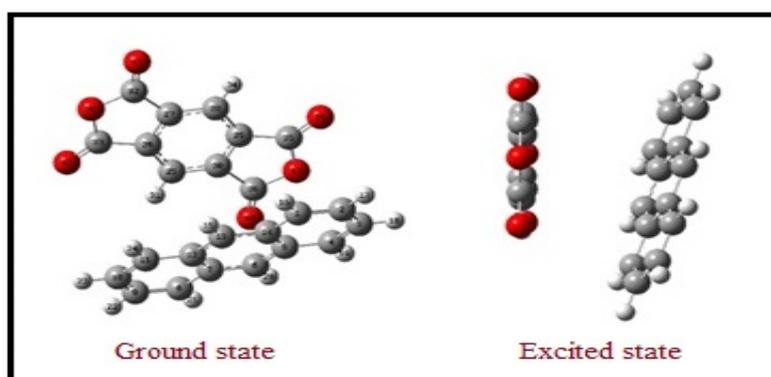
Source: Primary source

Figure 6: Geometry Optimized Structure of PMDA-Anthracene CT Complex
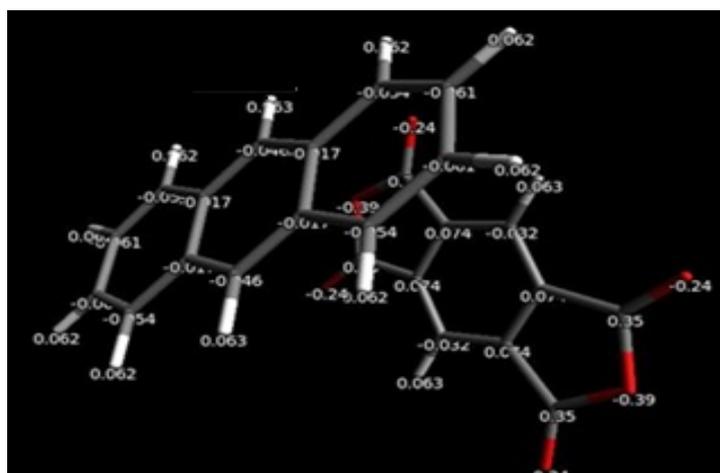
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Figure 7: Distribution of Formal Charges on Different Atoms of PMDA-Anthracene CT Complex

Conclusion:

The crystal structure of PMDA with anthracene demonstrates a (π-π) stacking interaction between the acceptor and donor molecules. The electronic spectra of the PMDA-Anthracene charge transfer (CT) complex have been extensively characterized in two pure solvents, various mixed solvents, and solid state. The observed unusual blue shift in the electronic spectra of the PMDA-Anthracene charge transfer (CT) complex with increasing solvent polarity can be attributed to the specific interactions of the acceptor molecule with the solvent. The stacking structure of the PMDA-Anthracene charge transfer (CT) complex, as determined by X-ray crystallography, exhibits a close

agreement with the structure obtained from theoretical calculations. The features of the stacked PMDA-Anthracene charge transfer (CT) complex described in this study have implications beyond the specific system investigated. The observed stacking interaction provides valuable insights into the intermolecular interactions in supramolecular assemblies, biomolecules, and their complexes with other molecules.

Acknowledgement:

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