Femtosecond to nanosecond excited states dynamics of novel Corroles

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Abstract: We report a comprehensive photphysical investigation of some corrole molecules employing fs/nanosecond (ns) transient-absorption and time-resolved photoluminescence spectroscopy with support from the time-dependent density-functional theory calculations to understand their intramolecular charge transfer and polaron-absorption character.
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1. Introduction

Corroles are molecules very similar to porphyrins. They have same tetrapyrrolic construction and their spectra consist of the characteristic B, Q bands [1]. Corroles have recently been subjected to intense research activity due to their attractive properties finding numerous applications, spanning from antitumor therapeutic properties to catalytic and important sensor applications, for light energy conversion and singlet oxygen generation. Corroles possess stronger fluorescence properties than their porphyrin counterparts opening up the potential for their utility in diverse areas such as cancer diagnosis. The spectral, electro-chemical, and photo-physical properties make these compounds promising building blocks to be used in dye sensitized solar cells (DSSC) with superior conversion efficiency [1,2]. Recently, we had synthesized a four novel Corroles and examined their (a) applicability for solar cell applications and (b) third order nonlinear optical properties using picosecond (ps) and femtosecond (fs) pulses for photonics applications [3,4]. The investigation of photo-physical properties of Corroles (and similar molecules) is imperative for their potential use. Herein, we present a comprehensive study of photo-physics in four Corroles: (a) Tetraphenyl Corrole (TPC) (b) Tetratolyl Corrole) (TTC) (c) Germanium substituted TTC (Ge-Corr) and (d) Phosphorous substituted TTC (P-Corr) using fs/nanosecond (ns) transient absorption techniques and time-resolved photoluminescence studies to understand the generation and lifetimes of the triplet states. The transient absorption peaks are interpreted by using natural transition orbitals (NTOs), which provides a simple orbital picture of time-dependent density functional theory (TDDFT) results.

2. Results and discussion

The details of synthesis of the corrole molecules understudy can be found elsewhere [3]. Figure 1 shows the absorption and photoluminescencspectra of the corroles. The details of the transient absorption experiment with fs laser pulses can be found elsewhere [5]. Considering the absorption maxima for the four corroles is around 400 nm, the pump wavelength for the transient studies is chosen to be 400 nm. All the measurements were performed in inert atmosphere to avoid interference of oxygen.

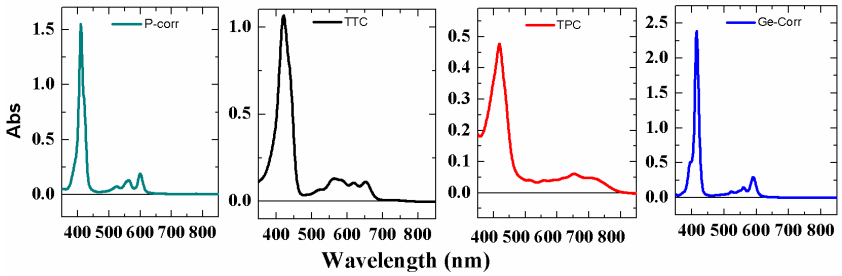

Fig.1. Absorption spectra of the four corroles

Figure 2 shows the representative plots of transient absorption data obtained with both fs and ns laser pulse excitation for GeTTC. From the figure 2(a) represents the differential transmission spectra of GeTTC molecule excited at 400 nm at different pulse delay times, while figure 2(b) shows the ns-triplet dynamics of GeTTC at probe wavelength of 450 nm where we obtained the triplet lifetime of ~3.5μs. Complete details of fs and ns transient absorption data and analysis of the obtained data will be presented.

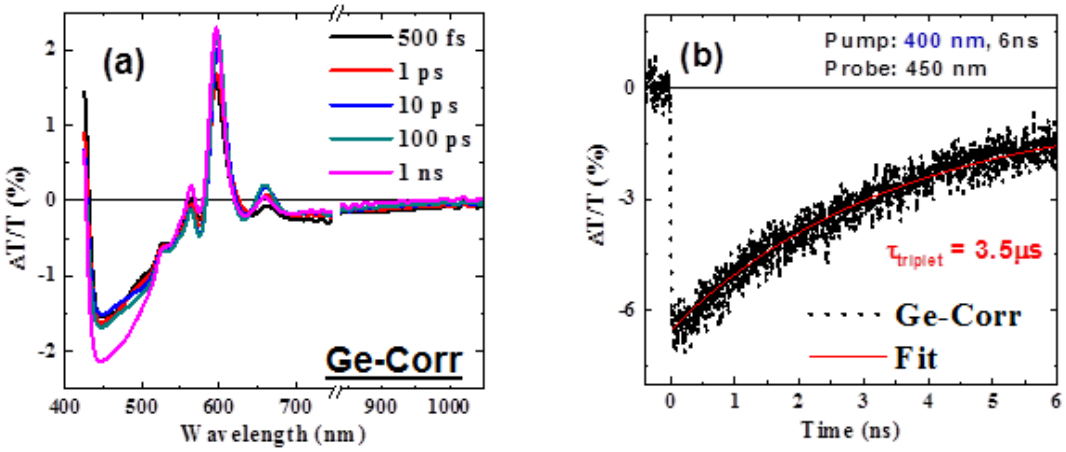

Fig. 2 (a) fs transient absorption data of Ge-Corr displaying complicated dynamics; (b) ns-triplet dynamics of Ge-Corr at probe wavelength of 450 nm

Evidently from figure 2(a) we observe complicated spectral dynamics for the Ge-Corr and this is true for all the four corroles considered. In order to understand the effect of molecular structure on the observed photophysical properties we computed the orbital picture of time-dependent density functional theory (TD-DFT). Figure 3 shows the complete analysis of the TD-DFT simulations for Ge-Corr. We obtained a close agreement between the calculated and experimentally observed absorption spectra with a small variation in the shape of the calculated spectra as well as the small spectral blue-shift of its maxima with respect to the experiment as expected.

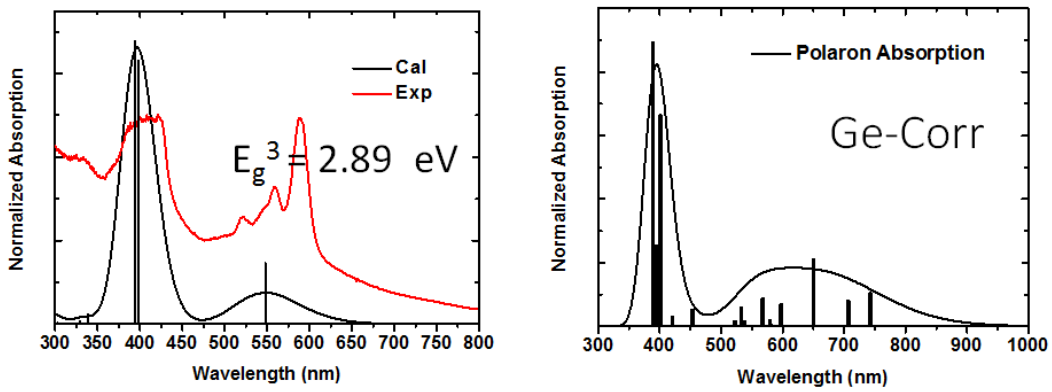

Fig. 3 TD-DFT simulation results for Ge-Corr showing the polaron absorption spectra and simulated absorption spectra

The transient absorption peaks are interpreted by using natural transition orbitals (NTOs). The corresponding dominant NTOs clearly show its significant intramolecular charge transfer and polaron absorption character of corrole molecules. Specifically, the central Ge atom in GeTTC or P atom in PTTC molecules can act as an electron donor for given optical transitions from the ground to excited states. Further, the HOMO and LUMO levels of these moecules are estimated and found to be slightly above the conduction band of various electron acceptors like metal-

oxides (TiO_2, SnO_2, ZnO) making these molecules useful candidates for application in dye-sensitized solar cells as shown recently in similar class of molecules [1].

3. Conclusions

Herein we present a comprehensive experimental and theoretical investigation of some corrole molecules that found myriads of applications from antitumor therapeutic properties to catalytic and important sensor applications, for light energy conversion and singlet oxygen generation. We empolyed fs/nanosecond (ns) transient absorption techniques and time-resolved photoluminescence studies in solution under inert atomosphere to understand the generation and lifetimes of the triplet states. The time dependent density functional theory (TDDFT) results show its significant intramolecular charge transfer and polaron absorption character of the studied corrole molecules demonstrating their application as a suitable candidates for light to energy conversion applications.

4. References

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