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Morphology directing synthesis of benzo[a]pyrene microstructures and their photo physical properties

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ABSTRACT

Morphologically interesting microstructures of benzo[a]pyrene (BaP) have been synthesized using sodium dodecyl sulfate (SDS) as morphology directing agent. Here we have presented a reprecipitation method to synthesize cube, rectangular bar, square rod and rectangular plate shaped microstructures of benzo[a]pyrene. Morphology of the materials has been characterized using optical microscopy and SEM measurements. UV–Vis absorption, fluorescence emission and computational study revealed that the neighboring BaP molecules are arranged in slipped head to head arrangement in its aggregated structures. Computation of second order Fukui parameter as local reactivity descriptor on each atomic center of the titled compound also substantiate that neighboring BaP molecules are arranged in parallel face to face slipped conformation in its aggregated structures and this is in conformity with the crystal structure of BaP.

1. Introduction

In comparison with the inorganic analogs, nanometer and micrometer-sized crystals of functional organic molecules offer large variability in their composition and physical properties. Their chemical and photo physical stability is better than that of the isolated molecules and they display their characteristic optical and optoelectronic properties. Therefore, they are of considerable interest for various potential applications in the field of photo switches [1], OLEDs [2,3], sensor [4–7], photo catalyst [8], phototransistors [9,10], memory devices [11], etc. Most of the organic chromospheres which are highly fluorescent in solution at low concentration show a drastic decrease of their emission efficiency in the solid state. This behavior is generally attributed to interactions that provide non-radiative decay routes, in particular, the frequently encountered plane to plane staking of fluorophore.

The size dependence of organic crystals has not been investigated as much as that of inorganic crystals. The strong effect of electron confinement on electron–hole pairs in all three directions result in the size-tunable optoelectronic properties of semiconducting quantum dots [12]. But this is not expected in organic molecular crystals (OMCs), because of the small radius of the Frenkel exciton [13]. The primary differences between inorganic and organic semi-conductors are in the band width, or the degree of orbital overlap. In the case of OMCs, the electronic and optical properties are fundamentally different from those of inorganic semi-conductors, because of weak van der Waals intermolecular forces [14,15]. The controlling of size, shape and hence the properties of OMCs is still a challenge and an important aspect in the development of material science.

Much effort has been devoted to synthesize organic nano/micro particles having various sizes and shapes. These include zero dimensional (0-D) spherical or tetrahedral quantum dots [16,17], one-dimensional (1-D) nano rods and wires from small organic compound [18–20] and two-dimensional (2-D) nanoplates [21], nanoribbons and nanotubes [22], microcapsule [23], organic nano flower [24], sub-microtube [25], etc. Various techniques were developed to prepare organic nano/micro particle, such as reprecipitation [26], physical vapor deposition [27], microemultion [28], ultra-sonication [29], template method [30], self-organization [31], postchemistry [32–35], etc. Molecular beam deposition method [36] and laser ablation method [37] are also available for the preparation of organic nanoparticles. Among the above methods, reprecipitation is one of the most favored routes toward the cost-effective large-scale production of nano/micro building blocks. Reprecipitation is rapidly injecting micro amounts of the solution in a good solvent, into macro amounts of poor solvent. In this process, sudden changes of environment for organic molecules induce precipitation.

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Like pyrene and its derivatives, benzo[a]pyrene also displays excimer emission at high concentration [38], and has been used widely as a fluorescence probe molecule due to the strong dependence of the monomer fluorescence on the solvent polarity [39]. Here we report the synthesis of cube, rectangular bar, square rod and rectangular plate shaped microstructures of benzo[a]pyrene using SDS as morphology directing agent of microstructures. The morphology and the structures of the as prepared microstructures are studied by optical microscope, scanning electron microscope (SEM). Photo physical properties of the aqueous dispersion of benzo[a]pyrene microstructures are investigated using UV–VIS absorption and steady state as well as time resolved fluorescence emission measurements. Computation of Fukui parameter as local reactivity descriptors (LRD) is carried out using DFT based method to understand the possible interaction and orientation of neighboring benzo[a]pyrene moieties in its aggregated structures. Our study suggests that benzo[a]pyrene molecules are not perfectly parallel in the microcrystal; rather the planes of two benzo[a]pyrene are slipped from each other. Our computation study is in agreement with the single crystal data of BaP [40], where the adjacent BaP molecules are present in slipped face to face conformation in its monoclinic unit cell geometry. To the best of our knowledge, this is for the first time that we have used the second order Fukui parameter $f^{(2)}(r)$ as local reactivity descriptor to understand the possible orientations of the neighboring BaP moieties in its aggregated structures.

2. Experimental

2.1. Materials

Benzo[a]pyrene and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich Chemical Corp. THF and ethanol were obtained from E-Mark India Ltd. All the chemicals were of analytical grade. SDS was recrystallized from 1:1 water methanol mixtures. THF was distilled from sodium/benzophenone under argon atmosphere to make it free from moisture, oxygen, and peroxide and ethanol was double distilled prior to use in the experiment. Triply distilled deionized water was used throughout the experiments.

2.2. Synthesis of benzo[a]pyrene microparticles

Benzo[a]pyrene microstructures were synthesized by reprecipitation method where SDS was used as soft template. In a typical preparation, small volume of benzo[a]pyrene (10 mM) in THF was injected into 5 mL of continuously stirred aqueous SDS (1 mM) at room temperature (25 °C). Volume of benzo[a]pyrene and concentration of SDS were varied to synthesize different shaped benzo[a]pyrene microstructures.

Sample-a (cube) was prepared by injecting 0.2 mL of 10 mM benzo[a]pyrene in THF into 5 mL of 1 mM SDS with vigorous stirring. Sample-b (rectangular bar), sample-c (square rod) and sample-d (rectangular plate) were prepared by injecting 0.3 mL, 0.5 mL, & 0.8 mL benzo[a]pyrene (10 mM) into 5 mL 1 mM SDS solution respectively. After 5 min of vigorous stirring, each solution was kept undisturbed for 30 min at room temperature before characterization and subsequent analysis.

2.3. Characterization

Optical microscopy images were taken using a NIKON ECLIPSE LV100POL upright microscope equipped with a 12 V–50 W halogen lamp. The samples for optical microscopic study were prepared by placing a drop of colloidal solution onto a clean glass slide. The morphologies of the synthesized nano/micro structures were studied using ZEISS EVO 18 scanning electron microscope (SEM) operated at an accelerating voltage of 5 kV. Samples were prepared by placing a small drop of aqueous hydrosol on a glass plate and then dried under vacuum. To minimize sample charging, thin layer of Au was deposited onto the samples for SEM study. The UV–Vis spectroscopy was used to characterize the optical properties and was measured in a 1 cm quartz cuvette with a Shimadzu UV-1800 spectrophotometer. The spectra were recorded at room temperature in the range between 200 and 500 nm. Steady state fluorescence spectra were recorded using Hitachi F-7000 Fluorescence Spectrophotometer. Fluorescence lifetime of samples was measured using TCSPC from PTI, U.S.A., equipped with sub-nanosecond pulsed LED source (370 nm) having pulse width of 600 ps FWHM operating at high repetition rate of 10 MHz driven by PDL 800-B driver, PicoQuant, Germany. Lamp profiles were measured with a band-pass of 3 nm using Ludox as the scatterer. The decay parameters were recovered using a non-linear iterative fitting procedure based on the Marquardt algorithm [41]. The quality of fit was assessed over the entire decay, and tested with a plot of weighted residuals and other statistical parameters e.g., the reduced χ^2 ratio [42]. X-ray diffraction was recorded on a Panalytical high resolution XRD-11, PW 3040/60 with CoKα ($\lambda = 0.1789$ nm) radiation in the angular range of 7–30° (2θ) with 40 kV operating voltage and 30 mA current.

2.4. Computational study

In the aggregated structures of molecules, where weak interaction between different atomic centers of similar kind of molecule take place, a second-order local reactivity descriptor (LRD) called Fukui function [43–47] may be used instead of electronic density. Fukui function is defined in terms of the derivative of $\rho(r)$, electronic charge density with respect to total number of electron, N.

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]_{v(r)} = \left[\frac{\partial \mu}{\partial v(r)}\right]_N. \tag{1}$$

The function $f(r)$ reflects the ability of a molecular site to accept or donate electrons. High values of $f(r)$ are related to a high reactivity at point 'r' [43]. Since the number of electrons 'N' is a discrete variable [48], right and left derivatives of $\rho(r)$ with respect to N are emerged. By applying a finite difference approximation to Eq. (1), two definitions of Fukui functions depending on total electronic densities are obtained:

$$f^{+}(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]^{+}_{V(r)} = \rho_{N+1}(r) - \rho_N(r) \tag{2}$$

$$f^{-}(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]^{-}_{V(r)} = \rho_N(r) - \rho_{N-1}(r) \tag{3}$$

where $\rho_{N+1}(r)$, $\rho_N(r)$, and $\rho_{N-1}(r)$ are the electronic densities at point 'r' for the system with N + 1, N and N − 1 electrons, respectively. The first one, $f^{+}(r)$, is associated to reactivity for a nucleophilic attack so that it measures the intermolecular reactivity at site 'r' toward a nucleophilic reagent. The second one, $f^{-}(r)$, is associated to reactivity for electrophilic attack and it measures the intermolecular reactivity at site 'r' toward an electrophilic reagent [44].

Morell et al. [49–55] have proposed a local reactivity descriptor (LRD) which is called the dual descriptor (DD) $f^{(2)}(r) \equiv \Delta f(r)$. Morell and co-workers used the notation $\Delta f(r)$, but currently it has been replaced by the modern notation $f^{(2)}(r)$ in order to highlight the fact that this is a Fukui function of second order. Its physical meaning is to reveal nucleophilic and electrophilic sites on a molecular system at the same time. Mathematically, it is defined in terms of the derivative of the Fukui function, $f(r)$ [43], with respect to the number of electrons, 'N'. Through a Maxwell relation, this LRD may be interpreted as the variation of 'η' (the molecular hardness which measures the resistance to charge transfer [56]) with respect to $v(r)$, the external