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Aggregation of cationic *p*-phenylene ethynylenes on Laponite clay in aqueous dispersions and solid films

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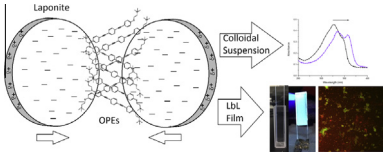
GRAPHICAL ABSTRACT



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ABSTRACT

Previous studies of cationic *p*-phenylene ethynylenes oligomers (OPEs) have revealed strong antimicrobial activity and strong photophysical changes upon their aggregation that can be utilized for sensing various chemicals and biomolecules. In this article, the adsorption of two types of OPEs with different placement of charged groups onto the synthetic clay Laponite is studied, and the changes to photophysical properties, photochemical degradation efficiency, and biocidal effectiveness are determined. In addition to solution-phase studies, the material and biocidal properties of solid films formed from the OPE-Laponite complex were assessed. The results of this study suggest that OPEs aggregate on Laponite and induce aggregation between Laponite discs, leading to drastic changes to their photophysical and material properties. Solid OPE-Laponite films were shown to have fair resistance to dissolution in aqueous solution compared with Laponite alone, and adhesion and minor killing of both Gram-negative and Gram-positive bacteria on the surface was observed. The results of this study give insight into controlling the colloidal phases of Laponite via molecular aggregation, may be useful for development of sensors and biocides involving Laponite as a scaffold, and lead to further control over slow-release and surface interactions of biocidal materials.

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1. Introduction

The formation of molecular aggregates and assemblies has been of great interest to researchers for decades, due to the changes in material and physical properties that can occur as individual molecules take on an aggregated state. This is a notable property of conjugated organic molecules such as dyes, as a result of coupling of the π molecular orbitals in conjugated molecules and the interactions of their strong dipoles. Davydov first described these interactions based on Frenkel's exciton theory, and this framework was applied to dimers by Kasha and coworkers [1–3]. The framework as constructed by Kasha et al. in 1965 gives a model by which the orientation of two molecular dipole moments dictates the change to the electronics of the system such as altered excitation energy, among other properties [4]. The typical intermolecular aggregates formed by conjugated organic chromophores are described by the alignment of transition dipoles between molecules. Systems where conjugated molecules are aligned with parallel transition dipoles, or in a "face-face" orientation, are known as H-aggregates [5].

Abbreviations: OPE, oligo *p*-phenylene ethynylene; Lap, Laponite RD; LbL, layer by layer.

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These aggregates generally result in a higher excitation energy and quenched fluorescence. Conjugated molecules which have transition dipoles perpendicular or in-line with one another have a lower energy of excitation and a small stokes shift, and are known as "J-aggregates" [6]. Compounds which can form J-aggregates, such as cyanine dyes, have been of particular interest due to their use in photographic materials and chemical sensors [7]. Cyanine dyes have been shown to aggregate in and on a diverse array of macromolecules, colloidal particles, and surfaces [8–15]. In one interesting study by Lu and coworkers, aggregates of cyanine dyes adsorbed onto Laponite clay particles were shown to exhibit fluorescence Stern–Volmer quenching constants of up to 10^8 [15].

Recent studies in the Whitten group have focused on the photophysical and biocidal properties of a series of cationic p-phenylene ethynylene oligomers (OPEs) [16,17]. These compounds consist of phenyl rings connected by triple-bonds, with quaternary ammonium charged groups attached via a propoxy linker off of the terminal groups at the ends of the molecules or branched off of the central phenyl ring. They tend to have high triplet yields, with some compounds having up to 70% [17]. Their high triplet yields lead to the generation of singlet oxygen, which is their primary mode of antimicrobial activity in the light [17,18]. In the dark their dominant mechanism is the disruption of bacterial cell membranes, and their mechanism of disruption has been shown experimentally and in all-atom molecular dynamics studies to be dictated by the placement of the charged groups on the phenylene ethynylene backbone [18,19]. There are a variety of properties which make these molecules interesting models for studying chromophore aggregation, such as the high sensitivity of OPE-2 to quenching molecules (K_{sv} = 2.05E^5 M^{-1}; 9,10-Anthraquinone-2,6-disulfonic acid), and the high light-activated biocidal activity of EO-OPE (3 logs or greater killing of both Gram-negative and Gram-positive bacteria). First, they have been shown to form molecular aggregates on biomolecules, surfactants, and anionic scaffolds such as carboxymethylcellulose, giving rise to spectral changes which can be utilized for sensing purposes [16,20,21]. Second, their aggregation can affect their tendency to undergo photochemical degradation [22]. Finally, the phenylene ethynylene backbone is highly rigid, so effects of changes in chemical substituents and their placement on the backbone can be monitored without large deflections in the backbone. For this study, two OPEs were chosen with unique properties despite their structural similarities. The structure of the OPEs used in this study are given in Fig. 1.

As can be observed in Fig. 1, one of the OPEs has cationic groups located on sidechains, and the other "end-only" OPE (EO-OPE) has them located at the ends of the molecule. OPE-2 has terminal carboxyester substituents, which give the molecule a very weak

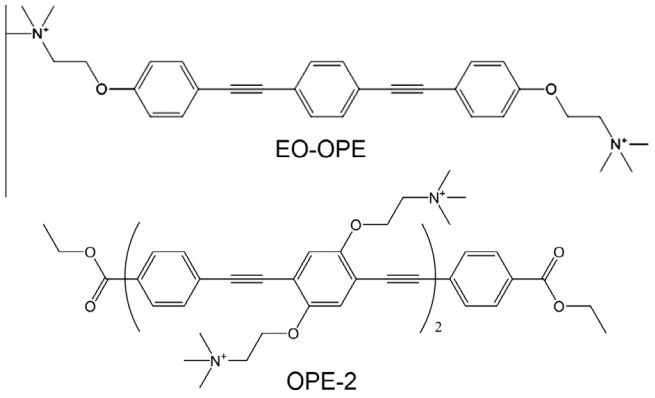

Fig. 1. Chemical structures of compounds used in this study.

fluorescence in water due to quenching of the excited state by interactions with the solvent [20]. The other molecule, EO-OPE, has no sidechains off of the central ring, but has the cationic groups located on the ends of the molecules. This molecule has been shown to be a highly effective biocide in both the light and in the dark, both alone and as a molecular aggregate formed with the surfactant sodium dodecyl sulfate [17,18,23]. It is also highly photolabile, with a photodegradation quantum yield of nearly 1%, where the primary photoproducts arise from the addition of water or O_2 across the triple-bond [22]. A study of the aggregation of these molecules with sodium dodecyl sulfate revealed that the EO-OPEs formed typical H-aggregates at a ratio of OPE to surfactant above 1:1, while the OPEs with sidechains led to formation of an aggregate with red-shifted absorbance [21]. In the case of OPE-2 discussed in this paper, it was shown to have a significant enhancement and red-shift of the fluorescence, in addition to the red-shifted absorbance [20]. These studies shed light on the state of aggregation that occurs when the molecules are not confined by any sort of structural constraint, but do not address the question of how these molecules aggregate when outside of a purely solvent environment. In order to confront the question of how confinement affects the resulting aggregates and their photophysical and biocidal properties, inspiration is drawn from previous studies of dyes on Laponite.

Clay minerals of natural origin (montmorillonite, kaolinite, hectorite) and the synthetic clay Laponite consist of particles made up of a layer of tetrahedral alumina or magnesium oxide connected to an octahedral silicate layer through the oxygen atoms [24]. The structure and a schematic of the delamination of Laponite is given below, in Fig. 2.

When in the stacked structure, the interlayer space between two Laponite disc layers is 0.9–1.3 nm and contains hydrated exchangeable cations such as $[Na(H_2O)_x]^+$. The exchangeable ions lend a high cation-exchange ability, with a charge-exchange capacity (CEC) of 0.6 mequiv/g [25]. This ion-exchange capacity and internal surface area allows smectite clays to undergo cation exchange reactions with cationic dyes such as methylene blue and Rhodamine 6G at the surfaces of the layers [26–32]. When diluted to below 0.01 g/mL concentration the individual particles are exfoliated, with the faces exhibiting an anionic character and a partial positive charge on the edges. The size of a single Laponite crystal is roughly 25 nm in diameter and 0.92 nm thick (excluding interfacial hydrated cations), as shown in Fig. 2 [33–35]. These single layers yield an interesting opportunity to study the formation of molecular aggregates, and for hybrid systems where the particles serve as a scaffold for polymerization reactions. Aqueous dispersions with a concentration of ~1% Laponite form a thixotropic gel, while a range of concentrations give a viscous liquid [36]. The structure of the Laponite gel has been shown to be a "house of cards" where the common motif is an edge of a layer intersecting with the face of another layer, and the large internal volume is responsible for the swelling that occurs upon gelation of Laponite [37,38].

The gel phase of Laponite allows for preparation of solid films for various purposes [39]. Studies have reported high-strength solid films made from Laponite for use as high-strength composites [40], optical waveguides [41], and loading of molecules such as dyes and drugs [28,42–44]. Since Laponite is cheap, inert, and safe for consumption, it is an ideal material to explore the preparation of solid, transparent films. In this study, the aggregation of two types of cationic OPEs with Laponite is studied, and the changes in photophysical and biocidal properties in solution are determined. Films of OPE-Laponite aggregates are formed by a layer-by-layer (LbL) process using a tensiometer as a dip-coater using either alternating layers of OPE solution and an aqueous dispersion of Laponite, or an OPE-Laponite mixture. The material properties of

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