

Colloidal Clusters of Silica or Polymer Microspheres**

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The packing and aggregation of colloidal particles is important for a wide variety of applications, including biological assays, sensors, paints, ceramics, and photonic crystals.^[1-4] Over the years, different methods have been developed for controlling the structure and aggregation of large numbers of colloidal particles, thereby enabling the fabrication of coatings, artificial opals, and complex ceramic bodies. By contrast, relatively few methods exist for controlling the aggregation and structure of small numbers of colloidal particles. Motivated by recent interest in colloidal self-assembly for optical applications, a few groups have started developing schemes for making aggregates consisting of a small number of monodisperse colloidal microspheres.^[5-7] These small colloidal aggregates, which include dimers, tetrahedra, and more complex polyhedra, possess lower symmetry than the spheres from which they are made and offer the possibility of forming more complex colloidal phases and structures than can be realized using simple spheres, just as molecules form more complex phases and structures than do atoms. It has been suggested, for example, that tetrahedral colloidal clusters might be useful in developing schemes for assembling colloidal crystals in the diamond structure.^[5,6] Colloidal crystals with the diamond structure are predicted to exhibit a full photonic bandgap with many desirable properties.^[8]

We recently demonstrated a process that is capable of making a large number of identical clusters, approximately 10^8 – 10^{10} in the original experiments,^[6] where the number of spheres (n) in each cluster can be varied between approximately 2 and 15. The process is based on emulsifying a suspension of lightly crosslinked polystyrene microspheres in toluene with an aqueous surfactant solution. This yields a toluene-in-water emulsion with the polystyrene microspheres bound by surface tension to the droplet interfaces. When the toluene is

removed by evaporation, the particles form stable clusters of colloidal particles suspended in water. The particles within clusters are strongly bound together by the van der Waals' force, while cluster-cluster aggregation is prevented by the surface charge the clusters acquire when the sulfate groups covalently bonded to the particle surfaces dissociate in water. Clusters of different aggregation number are readily fractionated using density gradient centrifugation to produce monodisperse suspensions of clusters. The shapes of the different aggregates for $2 \leq n \leq 11$ correspond to compact packings that minimize the second moment of the mass distribution, defined as

$$M = \sum_{i=1}^n (r_i - r_{\text{cm}})^2 \quad (1)$$

where r_i is the position of the center of the a sphere and r_{cm} is the center of mass of a given cluster configuration.^[9] The packings of larger clusters do not minimize the second moment of the mass distribution, but yield unique clusters with values of the second moment that are close to the minimal values.

The process as originally demonstrated exploits certain unique properties of the polystyrene microspheres that are used to make the clusters.^[10] First, the polystyrene microspheres are lightly crosslinked. Thus, when placed in a good solvent such as toluene, they swell but do not lose their spherical shape. In toluene, they are stabilized against aggregation by steric (entropic) repulsion between chain ends and loops at the surfaces of different particles. Second, the microspheres are made with ionizable surface groups, which dissociate in water thereby charging the particles and rendering them stable against aggregation. These two critical properties of the polystyrene spheres render them stable in two immiscible liquids, an organic non-polar solvent (oil) and water.

To realize the full potential of these new clusters as "colloidal molecules",^[10] it is important that they can be formed using the wide variety of materials from which colloidal particles are made. Many colloidal particles (or nanoparticles) are made from inorganic materials such as silica or titania, which can be charged in water but not swollen in a water-immiscible solvent.^[11,12] Other colloidal particles are made from polymers such as poly(methyl methacrylate) (PMMA), which are sterically stabilized, usually in oil, and generally are not stable in water.^[13] Clearly, it would be useful to have procedures for making colloidal aggregates that could be applied to these other types of particles.

In this communication we describe a generalized approach that allows us to make colloidal clusters from a much wider range of colloidal materials. We show that different types of particles produce clusters that are identical or very similar at each n .

We demonstrate the cluster formation process using two different kinds of sterically stabilized colloidal particles. The first consists of silica microspheres with octadecyl (C_{18}) chains grafted to their surfaces. These spheres can be suspended in various organic media such as hexane, toluene, tetrahydrofu-

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ran (THF), and chloroform. The second type of colloidal particles consists of non-crosslinked PMMA microspheres stabilized by poly(dimethylsiloxane) (PDMS) chains with a molecular weight of approximately 55 kg mol^{-1} grafted to the particle surfaces. These PDMS-stabilized PMMA particles can be suspended in a variety of alkanes ranging from hexane to dodecane.

To form the colloidal clusters, we suspend either type of particles in the same solvent, hexanes, in order to better compare the resulting cluster configurations. The hexane suspension is mixed with an aqueous surfactant solution and sheared using a homogenizer. The surfactant is a triblock copolymer of poly(ethylene oxide) and poly(propylene oxide) (Pluronic P123, BASF, consisting of $\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$, where EO is ethylene oxide and PO is propylene oxide). The resulting emulsion consists of a polydisperse suspension of hexane droplets with either sterically stabilized silica or PMMA spheres attached to the droplet interfaces, as shown in Figure 1a. The hexane–water interfaces of the droplets are stabilized by the P123 triblock copolymer. Clusters of colloidal particles form when the hexane is removed by slow evaporation. The clusters are stable in water because the P123 triblock copolymer surfactant that stabilized the hexane–water interfaces adsorbs onto the colloidal clusters and thus prevents cluster–cluster aggregation. Removal of the P123 surfactant leads to rapid aggregation of the clusters.

While this process yields clusters of PMMA and silica microspheres that are stable in water, the PMMA clusters do not maintain their integrity when dried on a substrate. The large capillary forces between the wet clusters and substrate during drying deforms them. Moreover, stabilization of clusters with adsorbed surfactant is fragile and the system can easily be rendered unstable, simply by dilution, for example. To avoid these problems, we add a thin layer of silica to permanently encapsulate the clusters, following a procedure developed by van Blaaderen and Vrij.^[14] The resulting silica-coated clusters are charged and stable in water without surfactant. We can also modify the surface with a suitable silane coupling agent and redisperse our clusters in organic media.

Figure 2 shows scanning electron microscope (SEM) images of our silica and PMMA clusters, as well as the polystyrene clusters prepared in the original experiments. The silica and PMMA particles are coated with hydrophilic silica. To investigate the thickness of the silica shell, we burned out the organic cores of the clusters by heating to $450 \text{ }^\circ\text{C}$ for 2 h in an electric furnace, increasing from room temperature at a rate of $1 \text{ }^\circ\text{C min}^{-1}$. The rapid combustion of organic latex causes the silica shells to burst during calcination, as shown in Figure 3. From the electron micrographs, we estimate the thickness of the shell to be less than 10 nm.

For $n \leq 12$, we find that the silica clusters adopt the same configurations that we observed previously for clusters of

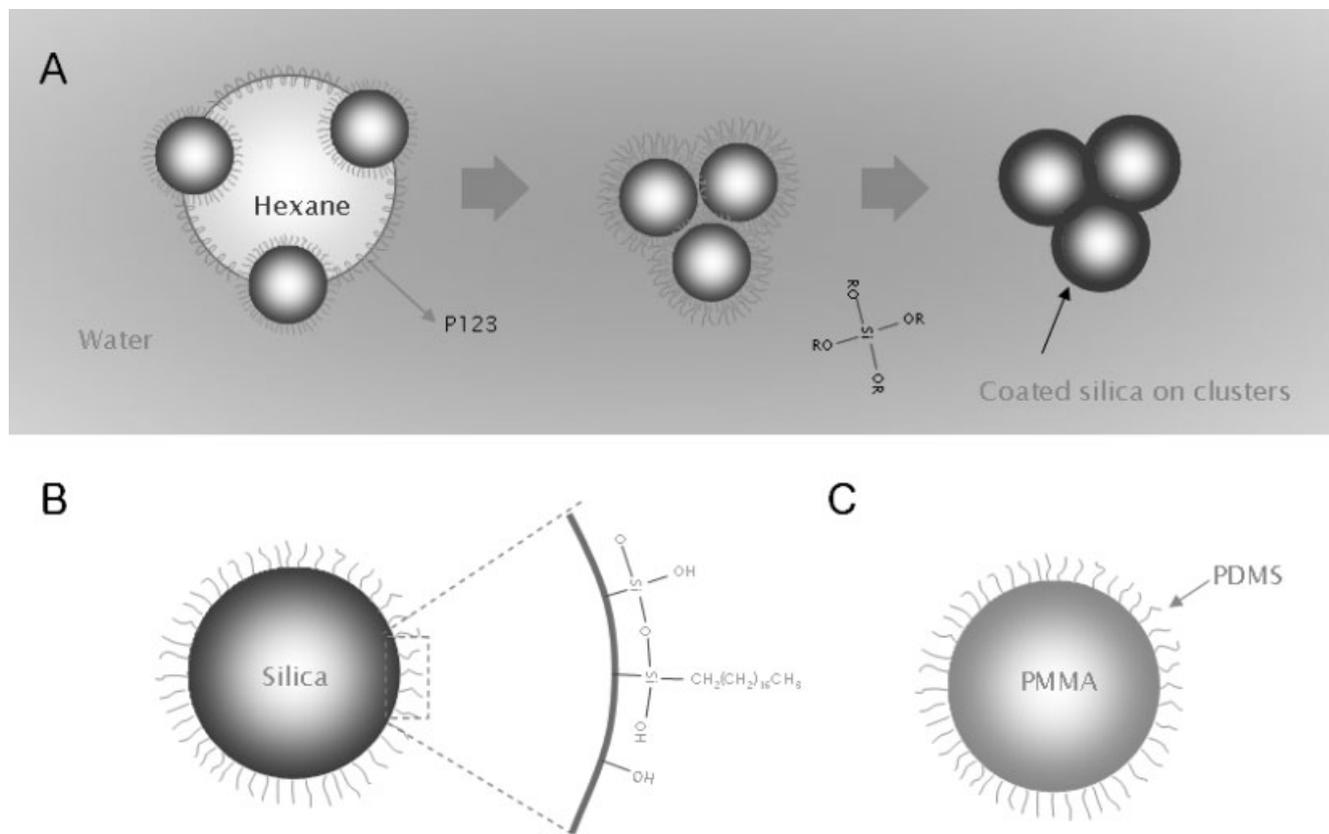


Figure 1. a) Experimental procedures for preparation of silica-coated colloidal clusters of silica and PMMA. b) Schematics of structures of silica, and surface modification with the silane coupling agent (octadecyltrimethoxysilane) c) PMMA with steric barrier of poly(dimethylsiloxane).

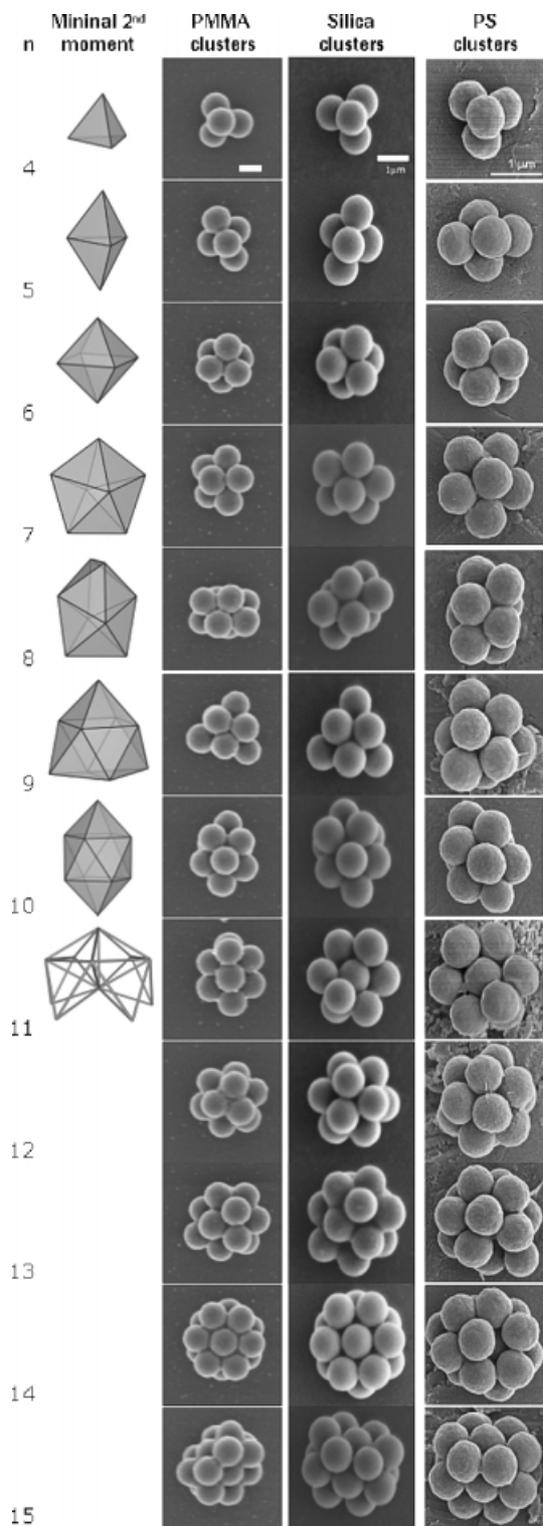


Figure 2. Minimal moment models and scanning electron micrographs of polystyrene, silica, and PMMA colloidal clusters. Scale bars are one micrometer.

polystyrene spheres.^[6] The polyhedra that correspond to these clusters are also shown in Figure 2. The $n=13$ and $n=14$ silica clusters differ slightly from those observed previously for the

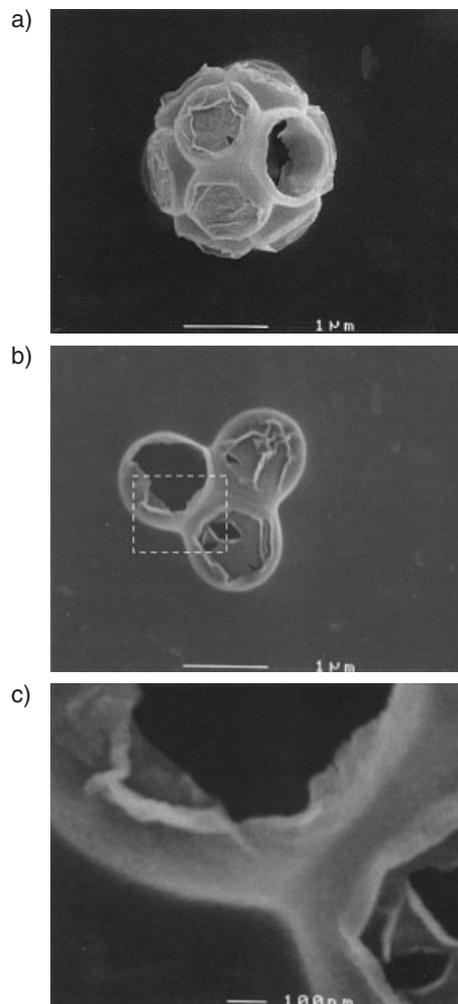


Figure 3. Scanning electron micrographs of icosahedron structure ($n=12$) (a) and triangle structure ($n=3$) at low magnification (b) and at higher magnification (c) after burning out PMMA.

polystyrene system while the $n=15$ cluster is the same. The PMMA clusters for $n=2-15$ are identical to those observed for the silica spheres, with the exception of the $n=11$ cluster.

The types of colloidal particles we use differ widely in their interactions and surface properties. For example, the polystyrene particles used in the original experiments are swollen with oil and must deswell in the final stages of oil evaporation, while the silica particles do not swell and the PMMA particles have a hard core with a thin swollen PDMS shell. The various types of particles also differ in their size, their Hamaker constants (and hence magnitude of their van der Waals' attractions) and their interactions with the oil–water interface of the emulsion droplet.

Given all these differences, it is remarkable that the ultimate cluster configurations are nearly identical for the various systems. This suggests that at least for $n < 11$ the configurations are insensitive to the precise nature of the forces controlling cluster formation, namely the capillary forces of the shrinking oil droplets that push the particles together, the

short-range repulsive interactions that keep them apart, and the van der Waals' interactions that ultimately cement them together. For larger numbers of spheres, there are more ways to pack clusters so that the structures that do form may be more sensitive to small differences in these forces. The $n = 11$ cluster, for example, has a non-convex configuration for polystyrene and silica spheres and a convex structure for PMMA spheres. The difference may arise because PMMA spheres are somewhat more difficult to detach from the hexane-water interface in the final stages of shrinkage. Another possible explanation for the small differences among the larger clusters is that interparticle van der Waals' attractions, which vary between systems, cement the structure at different points in the consolidation process before all the oil evaporates. On the other hand, we expect that the direct attractive potential between different spheres is very weak. Since even the larger ($n > 12$) silica, PMMA, and polystyrene clusters are similar, and the $n = 15$ clusters are in fact identical, the most important feature of the interparticle interactions is probably the hard-core repulsion common to all the systems. Thus the probable explanation for the shape of these clusters is that the packing constraints imposed by the hard-core repulsion between spheres and the inward pressure of the shrinking oil droplets, rather than the minimization of some potential energy, determine the final configurations. The shape of the clusters may therefore have broader implications and apply to any system of similarly sized hard spheres subject to a confining pressure. Such systems might include the local structure of granular media, glasses, and simple liquids.

We have shown that the emulsion encapsulation and shrinkage technique is a general method for preparing colloidal clusters of $n = 2-15$ hydrophobic, monodisperse microspheres. This generalized emulsion-based sphere packing method can be extended to colloidal particles made of virtually any material, and could even be used to assemble heterogeneous clusters made from spheres of different materials. The clusters can be stabilized in either water or oil, so the method is a flexible and easy way to produce large quantities of sphere doublets, tetrahedra, octahedra, and other specific kinds of colloidal aggregates for assembling materials.

Experimental

Synthesis of Non-Aqueous Monodisperse Silica Spheres: Hydrophilic silica microspheres with mean diameters ranging from 300 to 900 nm were synthesized by hydrolysis of tetraethylorthosilicate (TEOS, Acros, 98%) in an alcohol medium in the presence of water and ammonia using a modified seeded-growth procedure originally described by Zhang et al. [11]. The base-catalyzed hydrolysis and condensation of TEOS monomers provided particles with negative surface charges in water due to the ionization of surface hydroxyl groups. In a typical synthesis, 0.5 mL of TEOS were mixed rapidly with 2 mL of ethanol. Then the TEOS/ethanol solution was added to 100 mL of ethanol with 20 mL of NH_4OH (28–30%, Merck) and stirred for 2 h at room temperature. The resulting suspension contained particles approximately 300 nm in diameter. To make 600 nm particles, we added 8 mL of TEOS diluted with 32 mL of ethanol to this seed suspension of 300 nm spheres, stirred for another 2 h, and then stopped the reac-

tion (leaving some unreacted precursors). To make 900 nm silica particles, we added 8 mL of TEOS diluted with 32 mL of ethanol to the seed suspension of 300 nm spheres, and then we added the same amount of diluted TEOS 2 h later. Unreacted precursors were removed via solvent exchange: samples were centrifuged at 3000 rpm and redispersed in fresh ethanol by ultrasonication in a bath for 30 min. To prepare hydrophobic spheres, 10 mL of diluted octadecyltrimethoxysilane (OTMOS, Aldrich) in chloroform (10 vol.-%) and 7 mL of NH_4OH were added to a silica suspension in ethanol, and the mixture was stirred for 2 h [15]. The organically modified silica suspensions were cleaned by centrifugation and redispersion in ethanol (twice) and hexanes (mixture of isomers, 98%, twice) to remove chloroform and unreacted precursor. These organosilica spheres could be dispersed in other organic media such as chloroform and toluene.

Synthesis of Non-Aqueous Monodisperse Poly(methyl methacrylate) (PMMA) Spheres: PMMA spheres in hexane were synthesized by dispersion polymerization as reported in previous work [16]. Methacryloxypropyl-terminated poly(dimethylsiloxane), with a molecular weight of 55 kg mol^{-1} , was used as stabilizer. Particles were $1.17 \mu\text{m}$ in diameter.

Production of Silica-Coated Colloidal Clusters: In a typical procedure, 2 mL of a suspension of 900 nm hydrophobic silica spheres in hexane (~10 wt.-%) were added to 16 mL of aqueous Pluronic P123 surfactant (BASF) solution (0.3 wt.-%). This two-phase mixture was sheared in a homogenizer (IKA model T25) for 60 s at 8000 rpm. The resulting emulsion was diluted with 15 mL of water and heated gradually to 100°C over the course of 40 min, during which time the mixture was stirred slowly to prevent sedimentation. This process removed all the hexane from the system. We coated the resulting clusters with hydrophilic silica by adding 0.5 mL NH_4OH and 0.25 mL TEOS and stirring for 2 h [14]. The same procedure was used to prepare silica-coated PMMA clusters from $1.17 \mu\text{m}$ PMMA in hexane (8.95 wt.-%).

Characterization: To ascertain the configurations of clusters, we examined samples in the dispersed state with an optical microscope (Nikon) equipped with an oil-immersion objective and Nomarski differential interference contrast. Clusters in the dried state were imaged with a field-emission scanning electron microscope (JEOL 6300F) after sputter coating with gold and platinum. Electron micrographs were digitally post-processed to optimize brightness and contrast for print.

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Solvent-Induced Self-Assembly of a *Meta*-Linked Conjugated Polyelectrolyte. Helix Formation, Guest Intercalation, and Amplified Quenching**

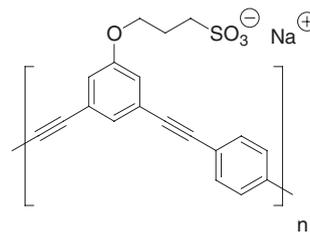
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It is well established that amphiphilic polymers self-assemble into a variety of supramolecular architectures, including micelles, vesicles, and liquid-crystalline phases.^[1,2] Recent interest in the self-assembly of functional materials has motivated a number of research groups to investigate the properties of amphiphilic π -conjugated oligomers and polymers.^[3–5] These studies reveal that self-assembly can give rise to unique materials properties such as changes in light absorption (color), fluorescence wavelength and fluorescence anisotropy, and induction of large amplitude circular dichroism signals.^[3,4,6] It has also been demonstrated that there is a direct relationship between architecture at the molecular and supramolecular levels. For example, molecular systems featuring large planar aromatic cores with protruding flexible alkyl chains self-assemble into discotic liquid-crystalline phases;^[7–9] linear π -conjugated systems consisting of poly(phenylene vinylene) (PPV) or poly(phenylene ethynylene) (PPE) backbones with flexible alkyl or alkyloxy side chains form lamellar aggregates;^[10–13] conjugated oligomers and polymers with kinked or bent, but otherwise rigid, backbones may self-assemble into helical structures.^[6,14–20]

We have an ongoing interest in the optical and self-assembly properties of water-soluble conjugated polyelectrolytes (CPEs).^[21–23] The CPE systems that have been of particular interest in our work are *para*-linked (linear-chain) PPE-type polymers, which feature ionic side groups that are tethered to the conjugated backbone by relatively short alkoxy

chains.^[21,23] These linear PPEs absorb and fluoresce strongly in the visible region, and on the basis of the study of solvent effects on the spectroscopic properties we conclude that the materials exist as “molecularly dissolved” chains in MeOH (a “good” solvent) and they self-assemble into π -stacked aggregates in water (a “poor” solvent). Aggregation of the *para*-PPEs in water is believed to arise due to the hydrophobic effect and favorable π - π interactions between phenylene units in the aggregated chains.^[21,23] Our interest in the PPE-type CPEs is motivated in part due to the fact that they exhibit a remarkable property of having their fluorescence quenched by ultra-low concentrations of oppositely charged quencher ions.^[21,24–28] This effect, which has been termed “amplified quenching”,^[29] is believed to arise due to ion-pair formation between the charged quencher and the CPE chain and the ability of the exciton to diffuse rapidly along a CPE chain.^[21,24–30] The amplified quenching effect has attracted considerable interest, since it allows CPEs to be used as a platform for highly sensitive detection of biologically relevant targets such as proteins, nucleic acids, and enzymes.^[24,28,31–36]

In a series of clever studies, Moore and co-workers demonstrated that *meta*-linked oligo(*m*-phenylene ethynylene)s (OPEs) that are substituted with oligo(ethyleneoxy) side chains self-assemble into a helical conformation in a poor solvent (acetonitrile).^[37–39] Their work demonstrates that formation of the helical conformation is a cooperative effect, requiring a minimum number of repeat units in the OPE chain before the process becomes thermodynamically favored. On the basis of this work, combined with our previous work on PPE-type CPEs,^[21,23] we speculated that *meta*-linked PPE-type CPEs would self-assemble into a helical conformation in aqueous solution. Thus, in the present communication we present the results of a spectroscopic investigation of *meta*-linked polymer, *m*PPE-SO₃ (Scheme 1). This work demonstrates that *m*PPE-SO₃ self-assembles into a helical conformation in water. In addition, the polymer exhibits



Scheme 1. Structure of *m*PPE-SO₃.

amplified quenching, and interestingly, the quenching is amplified more strongly in the helical conformation, suggesting that delocalization of the singlet exciton is facilitated in the helix.

The conjugated polyelectrolyte *m*PPE-SO₃ was synthesized by Pd-catalyzed coupling between 1-(3-sulfonatopropoxy)-3,5-diiodobenzene and 1,4-diethynylbenzene. The molecular weight of the polymer was analyzed by viscometry, ultrafiltration, and pulsed-gradient spin-echo NMR and these experi-

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