



## CHAPTER I INTRODUCTION

Self-assembly is defined as the spontaneous association of molecular components to form an ordered-structured molecules by ways of non-covalent forces i.e., hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces,  $\pi$ - $\pi$  interactions, and/or electrostatic effects (Atwood and Steed 2003). The self-assembly molecules were varied from the oligomolecular species to the polymeric entities. Self-assembly is often called upon to explain a variety of molecular process such as the spontaneous assembly of biological structures (Pallavicini *et al.* 2008), through complex organic syntheses (Klein *et al.* 2001), to the design of new materials.

Fluorescence is a phenomenon in which an absorption of light of a given wavelength by a fluorescent molecule is followed by an emission of light at longer wavelengths. Organic compounds showing fluorescence property are usually aromatic with conjugated bonds. Fluorescence detection has three major advantages over other optical-based investigation methods: high sensitivity, high speed, and no hazardous by products (Williams and Bridges 1964). Functionalizations with fluorescence are, for example, the conjugation with small molecules (Weiss 1999), the grafting with polymer backbone (Li *et al.* 2002), and adding in amphiphilic block copolymer to form micelle (Li *et al.* 2007). Micelle is a good structure to contain different hydrophobic molecules including fluorescence in the core volume (Pallavicini *et al.* 2008). Chen *et al.* showed the uniformity of fluorescent conjugated micelle via reversible addition fragmentation chain transfer (RAFT) polymerization (Chen *et al.* 2008).

Reversible addition fragmentation chain transfer (RAFT) polymerization, a versatile living radical polymerization technique, offers benefits of synthesizing polymers with predetermined molecular weight and narrow molecular weight distributions. It is practical for over a wide range of monomers with reactive terminal groups, including further polymerization with complicated architecture. RAFT can be used in simple condition such as solution, emulsion and suspension

polymerizations.(Chiefari *et al.* 1998; Barner-Kowollik *et al.* 2003). Recently, RAFT has been applied as a polymerization technique to prepare molecular assembly in terms of micelle, vesicles and nanoparticles (Stenzel 2008).

In the past, Chirachanchai *et al.* succeeded in unique reactions of benzoxazine to prepare *N,N*-bis(2-hydroxybenzyl) alkylamine derivatives and the macrocyclization (Laobuthee *et al.* 2001). The derivatives including their macrocycles perform host-guest inclusion based on molecular assembly. The complexation with metal ion is attractive as it is practical for catalysts, sensors including conductive materials (Phongtamrug *et al.* 2004).

It is important to note that as self-assembly is a key structure to induce molecular recognition, molecular designs and syntheses exploring certainly give us various types of molecular assembly as well as the function based on the external stimuli. In the past, various self-assembly structures were reported. For example, Schilli *et al.* reported how pH and temperature allow the swap between shell and core structure. It comes to our question that is it possible to obtain a specific self-assembly which either the structure is simple or the multi-responsive functions are possible. Therefore, the present work focuses on the molecular designs and syntheses to obtain a simple self assembly system which functions in chemiluminescence and fluorescence simple self assembly. In the first part (Chapter III), the introduction of the fluorescent substance, luminol, onto phenol based compounds and benzoxazine derivatives by diazotization reaction are considered. The work shows the molecular design and synthesis including characterization the complexation with Cu(II) ion which is important for enhancing chemiluminescence in basic solution of flow injection analysis (FIA) application. In the second part, we synthesized diblock copolymers of *N*-isopropylacrylamide (NIPAAm), a fluorescent tag, based on *N*-vinylcarbazole (NVC) and 2-(dimethylamino)ethyl acrylate (DMAEA) via RAFT polymerization. PNIPAAm undergoes a coil-globular transition at temperature above the lower critical solution temperature (LCST) and is thus tunable to be hydrophilic or hydrophobic whereas PDMAEA remains hydrophilic at all temperature but can be reversibly changed depending on pH. In Chapter IV, (PNIPAAm-*co*-PNVC)-*b*-PDMAEA block copolymers form micelle in aqueous solution. By varying pH and temperature, the changing in aggregation size was obtained. Crosslinking of the

PDMAEA shell layer leads to the formation of structurally stable shell cross-linked micelles, which possess pH-responsive PDMAEA coronas and thermoresponsive PNIPAAm cores. Chapter V proposed the new approaches to control the aggregation morphology of (PNIPAAm-*b*-PDMAEA) by pH and heating profile. The fluorescent nanoparticles obtained from (PNIPAAm-*co*-PNVC)-*b*-PDMAEA were reported in Chapter VI. The aggregation size and morphology depend on pH, temperature and polymer composition resulting in the as-designed self assembly structure for a particular application. In Chapter VII, mixed micellization behaviour of two amphiphilic copolymers: chitosan grafting with phthalic anhydride and polyethylene glycol and (PNIPAAm-*co*-PNVC)-*b*-PDMAEA diblock copolymer was studied.