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Synthesis and characterization of terminalalkynyl-substituted unsymmetrical zinc phthalocyanine conjugated with well-defined polymers

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ABSTRACT

Synthesis of unsymmetrically terminalalkynyl substituted zinc (II) phthalocyanine (ZnPc) through an efficient statistical condensation reaction with the unprotected phthalonitrile (**2**) is reported for the first time. Isolated ZnPc bearing one terminalalkynyl group is a good precursor for Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) reaction which is classified under the term “click chemistry”. This was approved by the successful click reaction between ZnPc and azide end-functional well-defined polymers obtained by atom transfer radical polymerization (ATRP), and consecutive azidation of corresponding bromo end-functional polymers. The click-reaction efficiencies for the formation of Pc-end functional poly(*tert*-butyl acrylate) (P*t*BA), and polystyrene (PS) have been found to be 75, 93% respectively. Functionalization of ZnPc with PS increased the chemical stability of the complex but decreased the electrochemical reversibility during redox reactions. *In-situ* electrocolorimetric measurements of the complexes allowed the quantification of color coordinates of the each electrogenerated anionic and cationic redox species.

1. Introduction

Phthalocyanines (Pcs) are well-known 18-π-electron aromatic molecules with unique physicochemical properties that make them interesting building blocks to be used in different fields of science and technology [1,2]. Phthalocyanines have recently received an increasing interest for construction of new molecular materials, such as electronics and optoelectronics [3,4].

The chemical flexibility of phthalocyanines allows the preparation of a large variety of related structures and tailoring of the optical, electronic, and physical properties [5]. The substitution of phthalocyanines with bulky groups or hydrocarbon chains, e.g. alkyl, alkoxy or alkylthio groups [6–8] enhances their solubility and makes these compounds valuable in different application fields [9]. However, the inherent symmetry of phthalocyanines sometimes represents a limitation for many purposes. Thus, the synthesis of unsymmetrically substituted phthalocyanines has become the focus of intense interest amongst many researchers [10–13]. The presence of different functional groups in the same molecule may provide coexistent features, such as enhanced solubility and reactivity in one or two edges of the molecule, thus allowing better control over the molecule [14]. Monosubstituted type low symmetrical Pc derivatives have been prepared either by mixed condensation reaction [15], polymer support method [16], or ring-expansion reaction of subphthalocyanines [17].

The preparation of phthalocyanines using click reaction is a powerful tool for the new materials with outstanding properties under mild conditions. The best known click reaction is the copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and alkynes has been recently applied to phthalocyanines. The synthetic challenge lies in the introduction of the terminalalkynyl groups on the phthalocyanine derivatives and few examples of terminalalkynyl substituted Pcs have been reported [18–27]. Asymmetric Pcs bearing terminalalkynyl group are quite uncommon. To our knowledge, the group of van Lier reported mono acetylene substituted zinc phthalocyanines using a palladium catalyzed coupling reaction method between corresponding iodophthalocyanines and protected or unprotected acetylenes

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[28–30]. Torres and co-workers described a method that includes mixed condensation of 4-tertbutyl-phthalonitrile and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile and then protecting group of the ethynyl function was removed for the synthesis of Pcs that bear a terminal ethynyl group [31]. To the best of our knowledge, herein, we report an efficient method for the preparation of terminalalkynyl substituted unsymmetrical zinc pc by the use of the classical statistical condensation method with unprotected terminalalkynyl substituted phthalonitrile and *tert*butyl substituted phthalonitrile for the first time.

Recently, Pc conjugated polymers is gaining much interest due to their unique electronic and optical properties that stem from Pc macrocycle [32–35]. Conjugation of the macrocycles with polymer chains enhances their processability, provides a means to control the molecular arrangement of the phthalocyanine rings, improves their solubility in common organic solvents [34]. Pc derivatives can be incorporated into polymeric structures as pendant group [36–42], the core of a star polymer [27,43–45], and end group. Synthetic methodology utilized for the preparation of Pc conjugated polymers is an important aspect. Kimura et al. reported the synthesis of amphiphilic polymers which self-assembled in solution into fibrous aggregates by using a phthalocyanine functionalized ATRP initiator [46]. Similarly, Nolte and co-workers have synthesized amphiphilic Pc-terminated polymers through ATRP polymerization of styrene from a Pc-functionalized initiator and studied the self-organizing properties in solution [47]. However the synthesis of ATRP initiator was tedious due to purification steps. Mandal and Hay synthesized low molecular weight poly(aryl ether sulfone)s with metallophthalocyanine end groups by reacting *o*-phthalonitrile end-capped poly(aryl ether sulfone)s with excess phthalonitrile and metal salts/metals in high boiling solvents [48]. In a similar manner Jiang and co-workers synthesized a series of poly(aryl ether ketone) oligomers terminated with metallophthalocyanine from dicyanobenzene-terminated poly(aryl ether ketone) oligomers with different metal chloride and phthalonitrile [49]. However this method used for the synthesis of Pc-end functional polymers suffers from time consuming and multistage synthesis procedures.

Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction which was initially postulated as a powerful tool for organic synthesis, has been extensively applied as a successful polymer functionalization technique. In recent years we have witnessed the rapid development in the available range of polymer architectures and functional materials offered the by the combination of click chemistry and various polymerization techniques. However, so far Controlled/'Living' Radical Polymerization (CRP) has involved the CuAAC click reaction more often than any of the others. CRP techniques allows for the preparation of polymers with predetermined molecular weight, narrow molecular weight distribution, chain end functionality, and complex architecture [50]. Among CRP techniques ATRP [51–53] is best suited with CuI click chemistry since the halogen end groups of polymers prepared by ATRP are easily converted to azido moieties by simple nucleophilic substitution [54].

In continuation of our studies of the synthesis of new Pcs with teminalalkynyl substituents and their click reaction with azide-end functional polymers [27], we concern here for the first time the synthesis of unsymmetrical zinc phthalocyanine in which terminalalkynyl group to be able to afford click reaction was attached to the periphery together with *tert*butyl groups to enhance solubility in the organic solvents through a new method that include statistical reaction of unprotected terminalalkynylphthalonitrile (**2**) with *tert*butylphthalonitrile (**1**). The terminalalkynyl function on ZnPc allows facile incorporation of azido-terminated polystyrene (PS–N_3) and poly(*tert*-butyl acrylate) (P*t*BA-N_3) through Cu(I)-catalyzed azide-alkyne click reaction. Thus, the formation of the desired two new phthalocyanine-terminated polymers, 9,16,23-tri-tert-butyl-2-(pent-4-ynoxy) zinc phthalocyanine-polystyrene (ZnPc-PS) and 9,16,23-tri-tert-butyl-2-(pent-4-ynoxy) zinc phthalocyanine-poly(*tert*-butyl acrylate) (ZnPc-P*t*BA) has also been described. Furthermore, we have investigated the electrochemical and spectroelectrochemical properties of terminalalkynyl substituted unsymmetrical zinc phthalocyanine and Pc-end functional PS.

2. Experimental

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent VNMRS at 500 MHz using $CDCl_3$ or DMSO-d_6 as solvent. IR spectra were recorded on Perkin–Elmer One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 UV–Vis spectrophotometer. Elemental analyses were performed on a Thermo Flash EA 1112. Mass spectra were measured on a Bruker Daltonics MALDI-TOF mass spectrometer. Gel-permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX, USA), a combined light-scattering (Model 270 Dual Detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Viscotek Corp.). The light scattering detector ($\lambda_0 = 670$ nm) included two scattering angles: 7° and 90°. The RI detector was calibrated with polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns 7.8 × 300 mm, (LT5000L, Mixed, Medium Org and LT3000L, Mixed, Ultra-Low Org) with a guard column 4.6 × 10 mm (Viscotek, TGuard) were used for the chloroform eluent at 35 °C (flow rate: 1 mL. min^{-1}). Data were analyzed using Viscotek OmniSEC Omni-01 software. Styrene (St; 99%; Merck) and *tert*-butyl acrylate (*t*BA; 99%; Aldrich) were passed through a basic alumina column to remove the inhibitor and then distilled over CaH_2 in vacuo before use. *N,N,N',N",N"*-Pentamethyldiethylenetriamine (PMDETA; Aldrich) was distilled over NaOH before use. All other reagents were purchased from Aldrich and used as received. 4-Pent-4-ynyloxy-phthalonitrile was synthesized according to the literature [27]. 4-Nitro-phthalonitrile, 4-tert-butyl-phthalonitrile (**1**), 4-pentyne-1-ol, 1-pentanol, anhydrous K_2CO_3, Dimethyl sulfoxide (DMSO) were purchased commercially. All other solvents and chemicals used in this work were analytical grade and used without further purification. Column chromatography was performed on silica gel [60]. The homogeneity of the products was tested in each step by TLC (SiO_2).

2.1. Electrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode cell configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) and dimethyl sulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. For each measurement, the reference electrode tip was moved as close as possible to the working electrode so that uncompensated resistance of the solution was a smaller fraction of the total resistance, and therefore the potential control error was low. Moreover, IR compensation was also applied to the voltammetric measurements to minimize the potential control error.