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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.

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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.

2.2. In-situ spectroelectrochemical and in-situ electrocolorimetric measurements

UV–Vis absorption spectra and chromaticity diagrams were measured by an Ocean Optics QE65000 diode array spectrophotometer. *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a semipermeable Pt sheet. Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. *In-situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an Ocean Optics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. Prior to each set of measurements, background color coordinates (*x*, *y* and *z* values) were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

2.3. Synthesis

2.3.1. 4-Pent-4-ynyloxy-phthalonitrile (2)

Phthalonitrile derivative were prepared by a similar method reported in the literature [27]. 4-nitrophthalonitrile (1 g, 5.77 mmol) and 4-pentyn-1-ol (0.364 g, 4.32 mmol) were added successively with stirring to DMSO (10 mL). After dissolution, anhydrous K_2CO_3 (1.08 g, 7.78 mmol) was added portion-wise during 2 h and stirred for 48 h under nitrogen. Then the reaction mass was poured into 200 ml of cold water and extracted with CH_2Cl_2. The organic phase was washed several times with water, dried with $MgSO_4$ and the solvent removed under reduced pressure. The recrystallization from hexane gives the desired compound as a yellow-white crystalline powder.

Yield 0.843 g (69.49%), melting point (mp) 50–54 °C. FT-IR γ (cm^{-1}): 3279.45 (≡C–H); 2230.50 (CN); 2115.46 (C≡C) 1597.21, 1494.39 (C=C phenyl); 1257.75 (Ar–O–C). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.698 (Ar–H, d, 1H), 7.273 (Ar–H, d, 1H), 7.214 (Ar–H, dd, 1H), 4.182 (CH_2–O-, t, 2H), 2.421 (CH_2, dt, 2H), 2.044 (CH_2, m, 2H), 1.993 (C≡CH, t, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ ppm 161.972 (Ar–C–O), 135.235 (Ar–C), 119.576 (Ar–C), 119.355 (Ar–C), 117.441 (Ar–C), 115.680 (C≡N), 115.253 (C≡N), 107.301 (Ar–C), 82.455 (C≡CH), 69.616 (CH_2–O), 67.344 (C≡CH), 27.486 (CH_2), 14.930 (CH_2). MS: *m*/*z* ($C_{13}H_{10}N_2O$) found = 256.21 (calcd. for $[M+2Na]^+$ 255.2814). Anal. Calcd. for $C_{13}H_{10}N_2O$: C 74.27, H 4.79, N 13.33%; found: C 73.65, H 4.84, N 13.67%.

2.3.2. 9,16,23-Tri-tert-butyl-2-(pent-4-ynoxy) phthalocyaninatozinc(II) (3)

A mixture of 0.028 g (0.133 mmol) of 4-pent-4-ynyloxyphthalonitrile and 0.074 g (0.402 mmol) of 4-tert-butylphthalonitrile, 0.024 g (0.133 mmol) of $Zn(CH_3COO)_2$ in 1 mL of 1-pentanol was refluxed with stirring for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was treated with MeOH and the precipitate filtered. The crude product was subjected to silica gel column chromatography and eluted with dioxane: petroleum ether = 1:5 (*v*/*v*), and the second greenish color band was the desired phthalocyanine. Yield: 25 mg (22.7%), m.p. >200 °C. It is soluble in acetone, THF, chloroform, dichloromethane, and DMSO. FT-IR γ (cm^{-1}): 3287 (≡C–H); 3072 (Ar–H); 2956–2861 (CH, aliphatic); 2112 (C≡C); 1391, 1362, 1331 ($C(CH_3)_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.44, 8.20, 7.86, 7.77, 7.66, 7.18 (Ar–H, m, 12H), 4.93 (CH_2–O-, m, 2H), 2.34 (CH_2, m, 2H), 2.20 (CH_2, m, 2H), 1.92 (C≡CH, m, 1H), 1.77–1.29 (C-$(CH_3)_3$, m, 27H). ^{13}C NMR (500 MHz, $CDCl_3$): δ ppm 174.04, 168.21, 158.99, 152.18, 135.75, 131.34, 129.84, 126.61, 125.50, 123.36, 121.46, 120.65, 118.08 (Ar–C), 83.76 (C≡CH), 69.06 (CH_2–O), 66.63 (C≡CH), 38.62–34.21 ($C(CH_3)_3$), 31.94–29.07 (($CH_3)_3$), 24.95–21.17 (CH_2), 15.23–10.96 (CH_2). MS: *m*/*z* ($C_{49}H_{46}N_8OZn$) found = 828.384 (calcd. for $[M]^+$ 828.33). Anal. Calcd. for $C_{49}H_{46}N_8OZn$: C 71.05, H 5.60, N 13.53%; found: C 70.43, H 5.65, N 13.87%. UV–Vis (THF) λ_{max}/nm: 673, 349.

2.3.3. PS-N_3 (4)

PS-N_3 was prepared in two steps with conditions modified from previously reported methods [55]. As a first step, bromo end-functionalized PS (PS-Br) was prepared by ATRP of St. To a 50 ml Schlenk tube, styrene (20 mL, 173 mmol), PMDETA (0.181 mL, 0.86 mmol), CuBr (0.125 g, 0.86 mmol), and EiBr (0.127 mL, 0.86 mmol) were added and the reaction mixture was degassed by three freze-pump-thaw (FPT) cycles and left under nitrogen. The tube was then placed in a thermostated oil bath at 110 °C for 40 min. The dark green polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in vacuum oven at 40 °C. $[M]_0/[I]_0$ = 200, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1. Conversion = 11%; $M_{n,GPC}$ = 2600; M_w/M_n = 1.13 (relative to PS standards); $M_{n,theo}$ = 2290. ^{1}H NMR ($CDCl_3$, δ): 7.5–6.2 (br, ArH of PS), 4.4 (br, 1H, CH(Ph)-Br end group of PS), 3.7–3.4 (br, 2H, CH_3CH_2O), 2.2–0.8 (m, aliphatic protons of PS and CH_3).

Then, previously obtained PS-Br (2 g, 0.76 mmol, $M_{n,GPC}$ = 2600 g/mol) dissolved in DMF (15 mL) and NaN_3 (0.49 g, 7.6 mmol) was added to the flask. After stirring overnight at room temperature it was filtered and evaporated to remove DMF. CH_2Cl_2 (100 mL) was added, and the reaction mixture was washed three times with distilled water. The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed in vacuo. The polymerization mixture was diluted with THF and precipitated in methanol. The recovered polymer PS-N_3 was dried in vacuum oven at 40 °C for 24 h. Yield = 1.9 g (95%); $M_{n,GPC}$ = 2950 g/mol; M_w/M_n = 1.11 relative to PS standards. ^{1}H NMR ($CDCl_3$, δ): 7.5–6.2 (br, ArH of PS), 3.9 (br, 1H, CH(Ph)-N_3 end group of PS), 3.7–3.4 (br, 2H, CH_3CH_2O), 2.2–0.8 (m, aliphatic protons of PS and CH_3). FT-IR γ (cm^{-1}): 3083–3026 (Ar–H), 2848–2923 (CH, aliphatic), 2092 (–N_3), 1724 (C=O), 1492 (C=C phenyl).

2.3.4. PtBA-N_3 (5)

PtBA-N_3 was prepared in two steps with conditions modified from previously reported methods [55]. As a first step, bromo end-functionalized P*t*BA (P*t*BA-Br) was prepared by ATRP of *t*BA. To a 50 mL Schlenk tube, *t*BA (20 mL, 136 mmol), PMDETA (226 μL, 1.08 mmol), CuBr (0.1553 g, 1.08 mmol), ethyl 2-bromoisobutyrate (EiBr) (0.158 mL, 1.08 mmol), and acetone (*v*/*v* = 1/1) were added. The reaction mixture was degassed by three FPT cycles and left under nitrogen. The tube was then placed in a thermostated oil bath at 60 °C for 130 min. The polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated into water/methanol mixture (*v*/*v* = 1/4). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and the water phase was again extracted with CH_2Cl_2 and combined organic phase was dried over Na_2SO_4 and evaporated. The polymer was dried in a vacuum oven at 40 °C. $[M]_0/[I]_0$ = 126; $[I]_0/[CuBr]_0/[PMDETA]_0$ = 1/1/1. Conversion = 19%; $M_{n,GPC}$ = 3860; M_w/M_n = 1.15, relative to PS standards; $M_{n,theo}$ = 3150. ^{1}H NMR ($CDCl_3$, δ): 4.1 (m, C=OOCH$_2$ and CHBr end group of P*t*BA), 2.2 (br, CH of P*t*BA), 2.0–1.0 (br, aliphatic protons of P*t*BA).

Then, previously obtained P*t*BA-Br (3 g, 0.77 mmol, $M_{n,GPC}$ = 3860 g/mol) was dissolved in 40 mL of DMF and NaN_3

(0.5 g, 7.70 mmol) was added. The reaction mixture was stirred at 50 °C for overnight, after which time it was cooled to room temperature and diluted with CH_2Cl_2, and extracted 2 times with water. The organics were dried over Na_2SO_4 and evaporated. The polymer was dried in a vacuum oven at 40 °C. Yield = 2.4 g (80%); ^{1}H NMR ($CDCl_3$, δ): 4.1 (m, C═$OOCH_2$), 3.7 (br, CHN_3 end group of P*t*BA), 2.2 (br, CH of P*t*BA), 2.0–1.0 (br, aliphatic protons of P*t*BA). FT-IR γ (cm^{-1}) : 2977–2931 (CH, aliphatic), 2110 (-N_3), 1723 (C═O).

2.3.5. 9,16,23-tri-tert-butyl-2-(pent-4-ynoxy) zinc phthalocyanine-polystyrene (ZnPc-PS) (6)

PS-N_3 (0.065 g, 0.022 mmol, based on $M_{n,GPC}$), ZnPc (0.005 g, 0.005 mmol), PMDETA (2.3 μL, 0.011 mmol), CuBr (1.6 mg, 0.011 mmol) and DMF (5 mL) were added to a 10 mL of Schlenk tube. Reaction mixture was degassed by three FPT cycles, left under nitrogen and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in methanol. The dissolution-precipitation procedure was repeated two times. The recovered Pc-terminated polymer was dried in a vacuum oven at 40 °C for 24 h. $M_{n,GPC}$ = 11650; M_w/M_n = 1.03, relative to PS standards. ^{1}H NMR ($CDCl_3$, δ): 9.9–9.1 (br, ArH of Pc), 7.5–6.2 (br, ArH of PS), 5.2 (br, 1H, CH(Ph)-triazole-Pc), 3.7–3.4 (br, 2H, CH_3CH_2O), 2.2–0.8 (m, aliphatic protons of PS and Pc). FT-IR γ (cm^{-1}): 3083–3026 (Ar–H), 2848–2923 (CH, aliphatic), 1722 (C═O), 1492 (C═C phenyl), 1391, 1362, 1331 (C(CH_3)$_3$).

2.3.6. 9,16,23-Tri-tert-butyl-2-(pent-4-ynoxy) zinc phthalocyanine-poly(tert-butyl acrylate) (ZnPc-PtBA) (7)

P*t*BA-N_3 (0.1483 g, 0.0362 mmol, based on $M_{n,GPC}$), ZnPc (0.03 g, 0.0362 mmol), PMDETA 0.023 mL, 0.1086 mmol), CuBr (0.0156 g, 0.1086 mmol) and DMF (2.5 mL) were added to a 10 mL of Schlenk tube. Reaction mixture was degassed by three FPT cycles, left under nitrogen and stirred for 24 h at room temperature. After the specified time, solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and precipitated in cold methanol/water (4:1) mixture. After the precipitation, it was decanted and extracted with CH_2Cl_2. The organic layer was dried with anhydrous Na_2SO_4 and filtered, and the solvent was removed in vacuo. The recovered Pc-terminated polymer was dried in a vacuum oven at 40 °C for 24 h. $M_{n,GPC}$ = 8500; M_w/M_n = 1.05, relative to PS standards. ^{1}H NMR ($CDCl_3$, δ): 9.6-8.7 (br, ArH of Pc), 7.7 (br, CH, triazole), 4.0 (m, C═$OOCH_2$), 2.2 (br, CH of P*t*BA), 2.0-1.0 (br, aliphatic protons of P*t*BA and Pc). FT-IR γ (cm^{-1}): 2977–2931 (CH, aliphatic), 1723 (C═O), 1392, 1362, 1334 (C(CH_3)$_3$).

3. Results and discussion

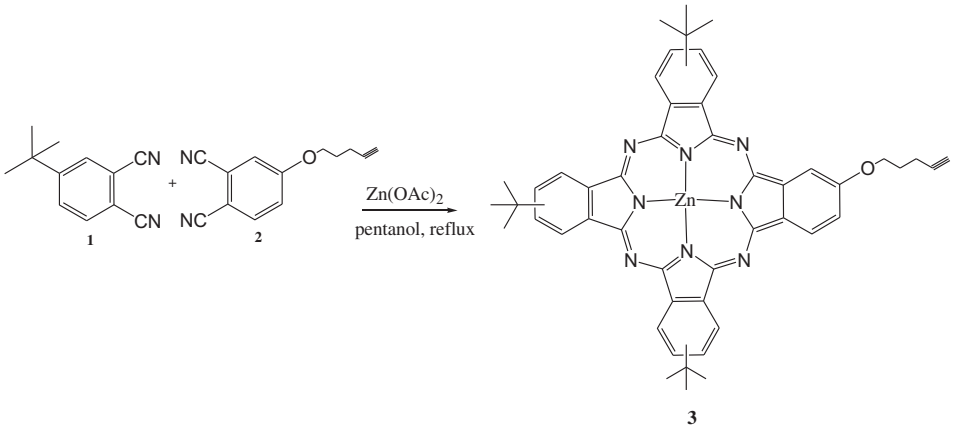
3.1. Synthesis

In recent years unsymmetrical Pcs have been attracted increasing interest with the aim of fine-tuning the properties of these complexes since symmetrically substituted Pcs do not always answer the requirements for many of the more recent high technology applications [56]. The most common strategy for the formation of unsymmetrical Pcs based on condensation reactions between two different precursors to form compounds with AAAA, AAAB, AABB, ABAB, ABBB, and BBBB structures [10]. AAAB type structure can be obtained through statistical condensation by adjusting the ratio of the precursors, and its chromatographic separation from the other products is usually relatively straightforward [57–59].

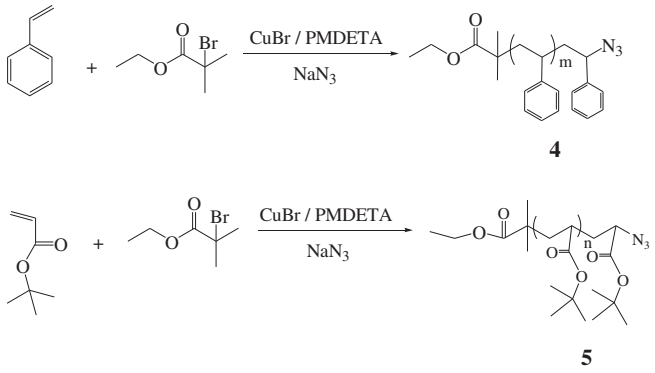
In the present paper, we describe the synthesis and characterization of unsymmetrically substituted zinc phthalocyanine and its polystyrene and poly(*tert*butylacrylate) functionalized derivatives. We first synthesized unsymmetrical zinc Pc having four "arms" with one terminalalkynyl group on each through the statistical condensation of 4-*tert*-butylphthalonitrile (**1**) and 4-pent-4-ynyloxyphthalonitrile (**2**) in the presence of template zinc acetate (Scheme 1). The direct statistical reaction of **1** (A) and unprotected **2** (B) in a ratio of approximately 3:1 gave six products, the desired AAAB could be easily separated by column chromatography as a second fraction. The yield of ZnPc is 22.7% which is quite comparable to values reported in the literature [60–62]. This novel unsymmetrical zinc phthalocyanine bearing one terminal –C≡C–H group was conjugated with azide end functional polystyrene and poly(*tert*butyl acrylate) via click reactions based on the reaction of an alkyne and an azide catalyzed by copper(I) ions.

Taking into account that utilization of Pcs in click chemistry requires terminal alkyne functionality and good solubility, we note that the 4-pentynyloxy and tert-butyl groups provide these for that purpose. This unsymmetrical Pc compound was readily soluble in CH_2Cl_2, $CHCl_3$, acetone, DMSO, and THF.

On the other hand, well-defined bromo-end functional polymers polystyrene (PS–Br) and poly(*tert*-butyl acrylate) (P*t*BA-Br) were prepared by ATRP and then subjected to a reaction with sodium azide to provide the corresponding azide derivatives **4** and **5** (Scheme 2). PS-N_3 and P*t*BA-N_3 chains were then reacted with the ZnPc in DMF with CuBr/PMDETA as catalyst to produce zinc phthalocyanine-terminated polymers, as illustrated in Scheme 3. Indeed, it was found that this copper ion-catalyzed reaction led to high yields of highly soluble phthalocyanine-terminated polymers.



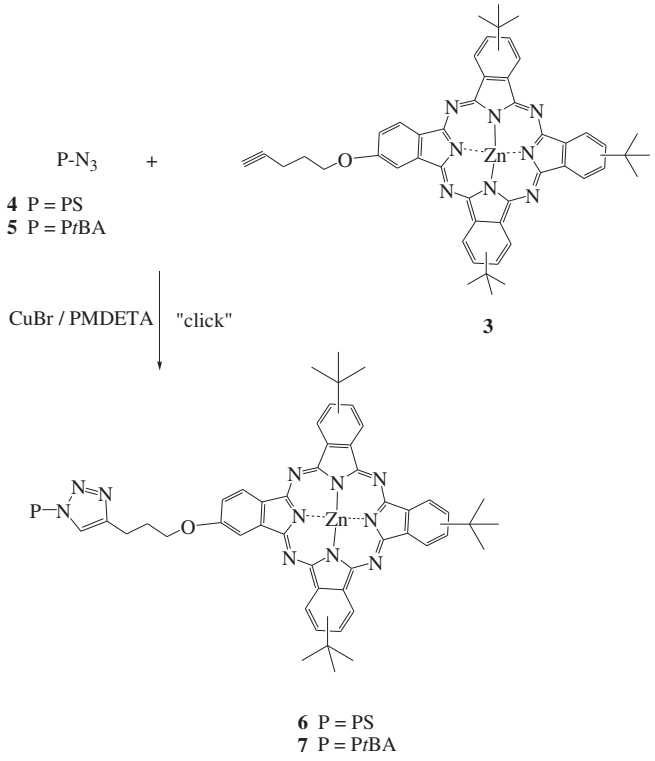
Scheme 1. The synthesis of unsymmetrical zinc (II) phthalocyanine.



Scheme 2. The syntheses of azido-terminated polystyrene (PS–N_3) and poly(*tert*-butyl acrylate) (P*t*BA-N_3).

3.2. Characterization of unsymmetrical ZnPc and azido-polymers

Characterization of the novel unsymmetrical ZnPc, PS-N_3 and P*t*BA-N_3 were achieved using elemental analysis, IR, ^{1}H and ^{13}C NMR, UV–Vis, GPC and mass spectra. Phthalonitrile cyclization was proved by the absence of the sharp CN vibration peak (~2230 cm^{-1}) in the IR spectrum of ZnPc. Infra-red spectrum further showed the presence of terminalalkynyl group bands around 3287 cm^{-1}, 2112 cm^{-1} and *tert*butyl groups bands around 1391 cm^{-1}, 1362 cm^{-1}, 1331 cm^{-1}. The ^{1}H NMR spectrum of ZnPc showed characteristic signals for the aromatic Pc ring protons between 7.18 and 8.44 ppm corresponding to the required number of Pc protons. Moreover the ^{1}H NMR spectrum showed the signals at 4.93 ppm specific to CH_2–O protons, 2.34 and 2.20 for CH_2–CH_2 protons, 1.92 for C≡CH proton and 1.77–1.29 for C-(CH_3)$_3$ protons. The ^{13}C NMR spectrum of ZnPc showed all carbons in their respective regions and results were given in experimental section.



Scheme 3. The syntheses of ZnPc-Terminated Polymers.

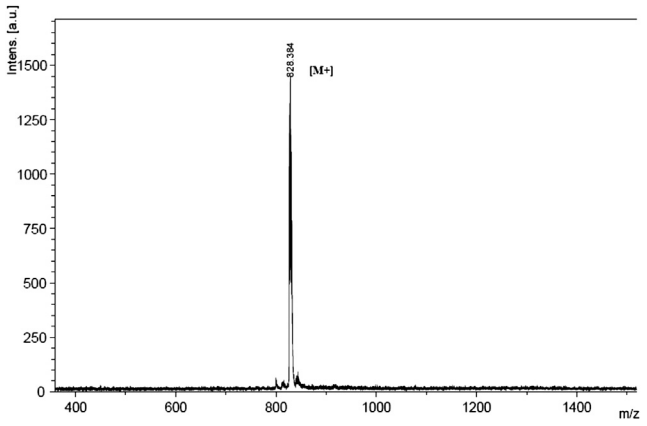


Fig. 1. MALDI-TOF MS spectrum of ZnPc.

MALDI-TOF MS further confirmed the formation of the unsymmetrical zinc phthalocyanine with the molecular ion peak observed at 828.38 as expected (Fig. 1).

Bromo-end functional polymers poly(styrene) (PS–Br) and poly(*tert*-butyl acrylate) (P*t*BA-Br) were prepared by ATRP. The polymerizations were stopped at a relatively lower monomer conversion (<30%) to keep a high degree of bromo-end functionality for the following nucleophilic substitution reaction with NaN_3. The obtained polymers had predicted molecular weights and narrow molecular weight distributions ($M_w/M_n \leq 1.15$). Molecular weights obtained by GPC ($M_{n,GPC}$) and theoretical molecular weights ($M_{n,theo}$) were found to be close to each other indicating high initiation efficiencies. $M_{n,theo}$ values were calculated using the following equation

$$M_{n,thero} = [M]_0/[I]_0 * \%\ \text{Conversion} * M_{W,monomer}$$

where $[M]_0$ and $[I]_0$ are initial monomer and initiator concentration respectively, $M_{w,monomer}$ is molecular weight of the monomer used. Bromo-end groups of polymers were quantitatively converted to the azide form with a well-known procedure [63]. The ω-azide end functionality of both PS and P*t*BA was confirmed with FT-IR and ^{1}H NMR. The FT-IR spectra of azido-terminated polystyrene (PS–N_3) and poly(*tert*-butyl acrylate) (P*t*BA-N_3) exhibit the expected characteristic signal at 2092 cm^{-1} and 2110 cm^{-1} respectively, due to the N_3 stretching vibration, hence confirming the presence of azido groups. In the ^{1}H NMR spectra, for PS–N_3, a signal at 4.4 ppm, assigned to *CH*–Br,

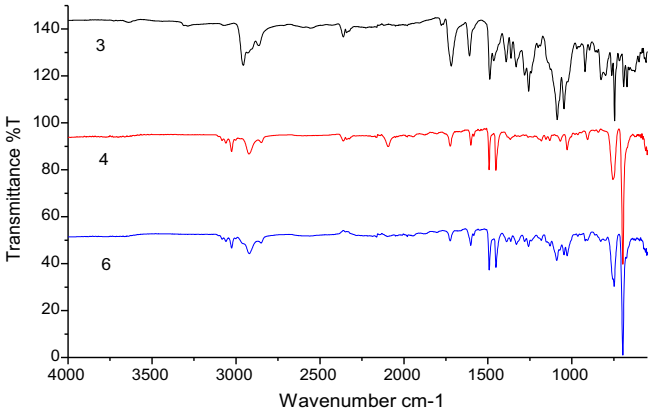


Fig. 2. FT-IR spectra of 3, 4, and 6.

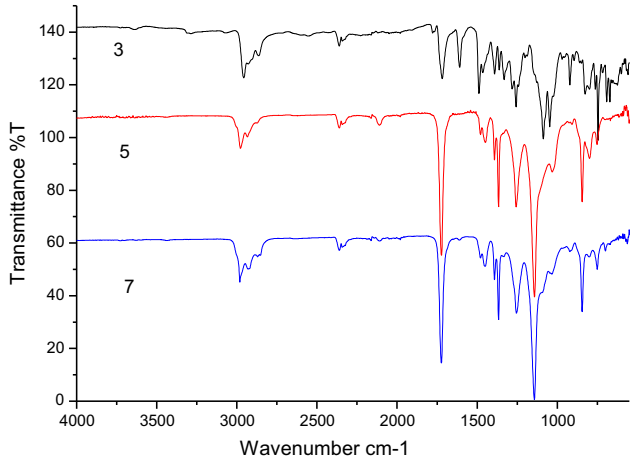


Fig. 3. FT-IR spectra of 3, 5, and 7.

disappeared, and a new peak appeared at 3.9 ppm, indicating *CH* linked to the azide end group. For P*t*BA–N_3, the *CH*–N_3 end-functional group was detected at 3.7 ppm, whereas *CH*–Br was detected at 4.1 ppm.

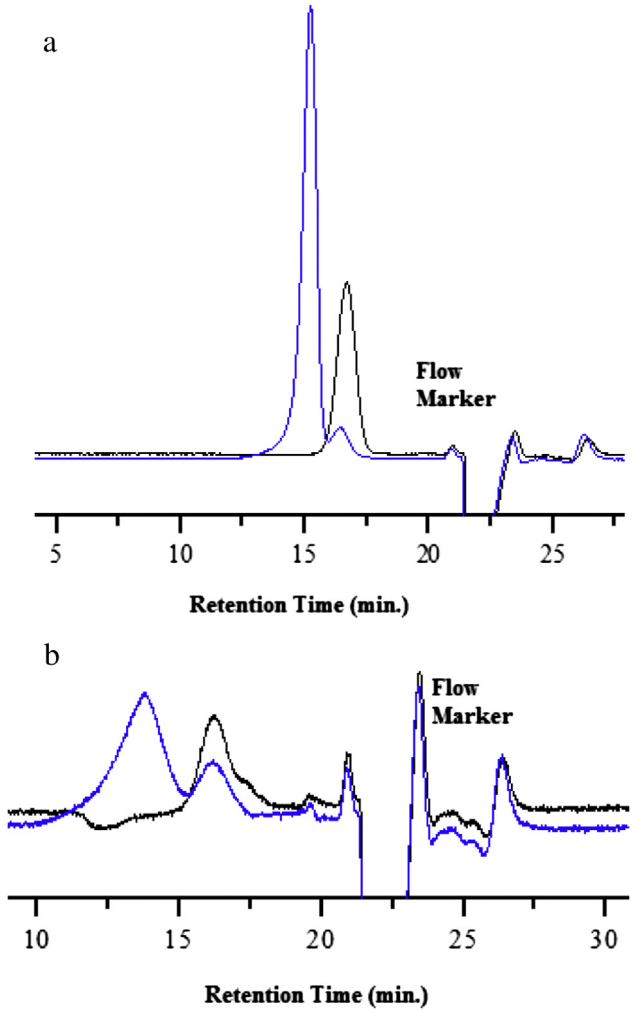


Fig. 4. (a) GPC curves of PS-N_3 (black) and its coupling product (blue) with ZnPc. (b) GPC curves of P*t*BA-N_3 (black) and its coupling product (blue) with ZnPc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

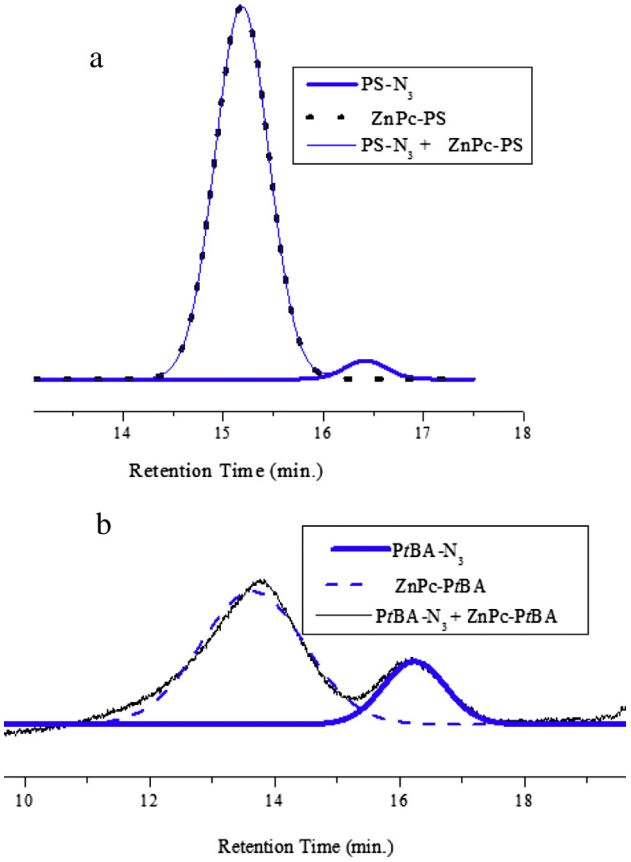


Fig. 5. (a)Peak splitting of the GPC curve of the PS-N_3 + ZnPc-PS using Gaussian function. (b) Peak splitting of the GPC curve of the P*t*BA-N_3+ZnPc-P*t*BA using Gaussian function.

3.3. Characterization of ZnPc-terminated polymers

Newly synthesized unsymmetrically substituted zinc phthalocyanine was used as precursor for Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) with azido-terminated polystyrene (PS–N_3) and poly(*tert*-butyl acrylate) (P*t*BA-N_3). Owing to the polystyrene (PS), poly(*tert*-butyl acrylate) (P*t*BA) present on the

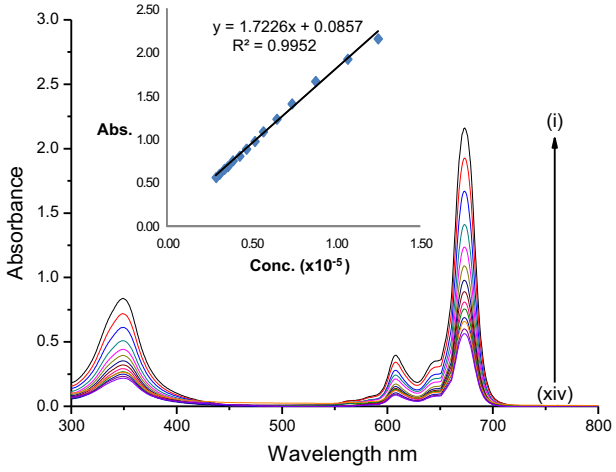


Fig. 6. Electronic absorption spectra of 3 at various concentrations:(i) 1.25×10^{-5}, (ii) 1.07×10^{-5}, (iii) 0.88×10^{-5}, (iv) 0.74×10^{-5}, (v) 0.65×10^{-5}, (vi) 0.57×10^{-5} (vii) 0.52×10^{-5}, (viii) 0.47×10^{-5}, (ix) 0.43×10^{-5}, (×) 0.39×10^{-5}, (xi) 0.36×10^{-5}, (xii) 0.34×10^{-5}, (xiii) 0.31×10^{-5}, (xiv) 0.29×10^{-5} mol dm^{-3} in THF.

Table 1
Voltammetric data of the complexes recorded on a Pt working electrode in different electrolyte systems. All voltammetric data were given versus SCE.

		[a]$E_{1/2}$	[b]ΔE_p (mV)	[c]$I_{p,a}/I_{p,c}$	[d]$\Delta E_{1/2}$
ZnPc	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-1}]^{+1}$	0.62	62	0.83	1.55
(in DMSO)	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$	−0.93	60	0.96	
	$[Zn^{II}Pc^{-3}]^{-1}/[Zn^{II}Pc^{-4}]^{-2}$	−1.35	–	–	
	$[Zn^{II}Pc^{-4}]^{-2}/[Zn^{II}Pc^{-5}]^{-3}$	−1.64	64	0.81	
ZnPc-PS	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-1}]^{+1}$	0.56	100	0.64	1.56
(in DMSO)	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$	−1.00	87	0.93	
	$[Zn^{II}Pc^{-3}]^{-1}/[Zn^{II}Pc^{-4}]^{-2}$	−1.44	70	0.37	
ZnPc	$[Zn^{II}Pc^{-1}]^{+1}/[Zn^{II}Pc^{0}]^{+2}$	1.30	120	0.32	1.51
(in DCM)	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-1}]^{+1}$	0.55	90	0.97	
	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$	−0.96 (−1.18)[e]	60	0.82	
	$[Zn^{II}Pc^{-3}]^{-1}/[Zn^{II}Pc^{-4}]^{-2}$	−1.26	92	0.75	
	$[Zn^{II}Pc^{-1}]^{+1}$ $[Zn^{II}Pc^{0}]^{+2}$	1.26	125	0.28	
ZnPc-PS	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-1}]^{+1}$	0.48	90	0.93	1.55
(in DCM)	$[Zn^{II}Pc^{-2}]/[Zn^{II}Pc^{-3}]^{-1}$	−0.97	350	0.75	
	$[Zn^{II}Pc^{-3}]^{-1}/[Zn^{II}Pc^{-4}]^{-2}$	−1.28	167	0.81	

All voltammetric data were derived from the CVs recorded at 0.100 V s^{-1} scan rate.
[a] $E_{1/2} = (E_{pa} + E_{pc})/2$.
[b] $\Delta E_p = |E_{pa}\text{-}E_{pc}|$.
[c] $I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation processes.
[d] $\Delta E_{1/2} = E_{1/2}$ (first oxidation) − $E_{1/2}$ (first reduction).
[e] Redox reaction of the aggregated species.

peripheral position of phthalocyanine structures, products showed good solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$ or THF, thus facilitating spectroscopic characterization. The structures of products were characterized by ^1H NMR, FT-IR, UV–Vis spectroscopy, and gel permeation chromatography (GPC).

The FT-IR spectra of azido-terminated polystyrene (**4**) and poly(*tert*-butyl acrylate) (**5**) exhibit a signal at ≈ 2100 cm^{-1}, due to the N_3 stretching vibration (Figs. 2 and 3). The spectrum of unsymmetrically terminalalkynyl substituted zinc phthalocyanine (**3**) shows peaks at 3287 cm^{-1} and 2112 cm^{-1}, associated with the terminal alkyne group (Figs. 2 and 3). After the performing of the copper-catalyzed click reaction, the signal at ≈ 2100 cm^{-1} assigned to the azido frequency decreases drastically (Figs. 2 and 3). On the other hand, the peaks at 3287 cm^{-1} and 2112 cm^{-1} have totally disappeared, thus suggesting the absence of unreacted Pc in the phthalocyanine-terminated polymers (**6 and 7**) (Figs. 2 and 3).

Click reactions for ZnPc-PS, and ZnPc-P*t*BA were also confirmed with ^1H NMR for PS–N_3, signal at 3.9 ppm assigned to C*H*–N_3, disappeared, and a new peak appeared at 5.2 ppm, for P*t*BA–N_3, signal at 3.7 ppm assigned to C*H*–N_3, disappeared, and a new peak appeared at 4.1 ppm, indicating triazol formation.

Zinc phthalocyanine-terminated polymers were also characterized with GPC measurements. $M_{n,GPC}$ values for ZnPc-PS and ZnPc-P*t*BA were found to be 11650 and 8500 respectively which were higher than expected values. This result can be attributed to the changing chain chemistry due to the presence of rigid phthalocyanine structure. However, from GPC traces, it was clearly observed that the reaction mixture contained mainly zinc phthalocyanine-terminated polymers (Fig. 4a and b). Click reaction efficiencies which is calculated using deconvolution method (Gaussian area) were 96, 78% for ZnPc-PS, ZnPc-P*t*BA, respectively. Moreover, the splitting of GPC traces with the deconvolution method is displayed in Fig. 5a and b.

UV–Vis absorption spectra of **3, 6** and **7** were measured in THF and the spectra showed a shape typical for Pc and related compounds with a high energy B-band in the region around 349 nm

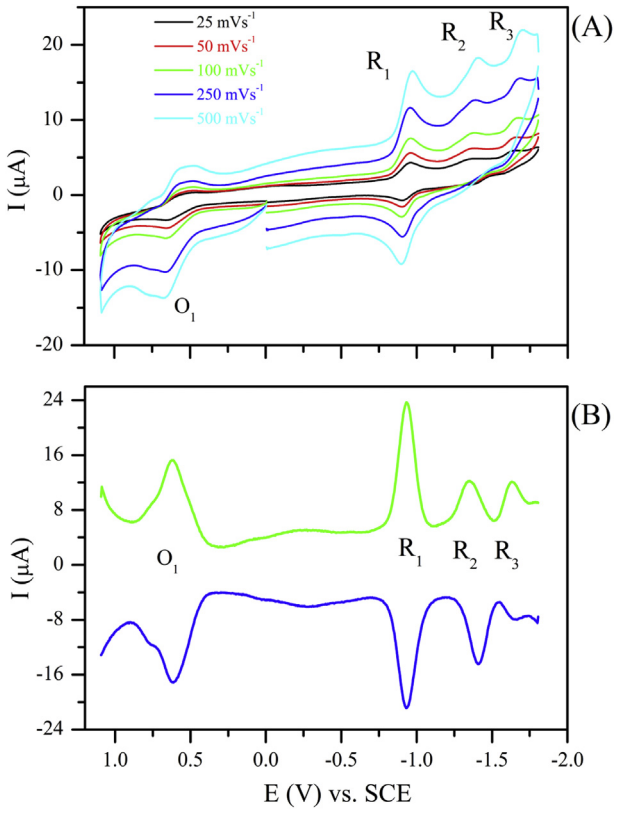


Fig. 7. a) CVs and b) SWV of ZnPc at various scan rates on a Pt working electrode in DMSO/TBAP.

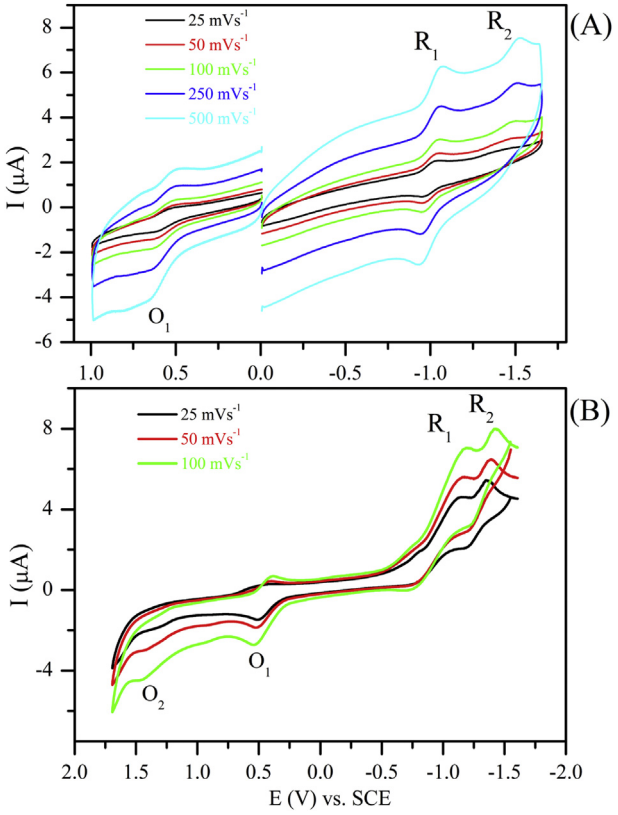


Fig. 8. CVs of ZnPc-PS at various scan rates on a Pt working electrode in a) DMSO/TBAP and b) DCM/TBAP electrolyte system.

and a low energy Q-band in the region around 673 nm. As shown in Fig. 6 (using ZnPc as an example), Beer Lambert law was obeyed at concentrations below 1.25×10^{-5} mol dm^{-3}. Phthalocyanine-terminated polymers **6** and **7** also show the same trend.

3.4. Voltammetric measurements

ZnPc has a redox inactive Zn(II) metal center and redox inactive 4-pentynyloxy and *tert*butyl substituents. Thus all redox reactions should be resulted from the 18 π electrons system of the Pc ring. Altering the metal center with redox inactive metal ions and substituents just affect the character of Pc ring electron transfer reactions and stabilities of the electrogenerated anionic and cationic forms of MPcs. ZnPc complex synthesized here has inactive metal center and substituents, thus should give Pc based electron transfer reactions. To support the proposed structure, electrochemical characterization of ZnPc and Pc-end functional PS were performed in solution. Analyses of the voltammograms were performed and the basic electrochemical parameters derived from the voltammograms of ZnPc and Pc-end functional PS are tabulated in Table 1. As shown in Table 1, basic electrochemical parameters of the complexes are in harmony with the similar complexes in the literature [64–66].

Fig. 7a and b shows the CV and SWV responses of ZnPc in DMSO/TBAP electrolyte system. ZnPc gives three reduction processes. The first reduction reaction (R_1 at −0.93 V) has an electrochemically reversible character when the potential was switched just after the reduction reaction (Fig. 8). After R_1 process, a quasi-reversible second reduction and an irreversible third reduction reactions are also recorded (R_2 at −1.34 V and R_3 at −1.63 V). While R_1 and R_2 have unity $I_{p,a}/I_{p,c}$ ratios at all scan rates, these values decrease up to 0.28 due to the chemical irreversibility of R_3 process. Changing ΔE_p values from 57 mV to 85 mV with increasing scan rate from 0.025 V s^{-1} to 0.50 V s^{-1} scan rates indicates that electrochemical reversibility of the R_1 process at all scan rate. The R_2 and R_3 processes are electrochemically quasi-reversible processes with respect to ΔE_p values. These redox characters are well illustrated with the SWV measurements (Fig. 7b). In addition to the reduction processes, ZnPc gives a well resolved reversible oxidation couple at 0.61 V when anodic potentials were scanned in DMSO/TBAP electrolyte system. CV and SWVs of ZnPc were also recorded in DCM, a noncoordinating nonpolar solvent to investigate the solvent effect to the electrochemical behavior of the complex. It was clearly distinguished that the reduction reactions of ZnPc were more reversible chemically and electrochemically in DMSO than those recorded in DCM. ZnPc aggregated in DCM and the first reduction process split to two waves due to the aggregation. The reduction processes shifted to negative sides in DCM due to the less polarizing effect of DCM with respect to DMSO.

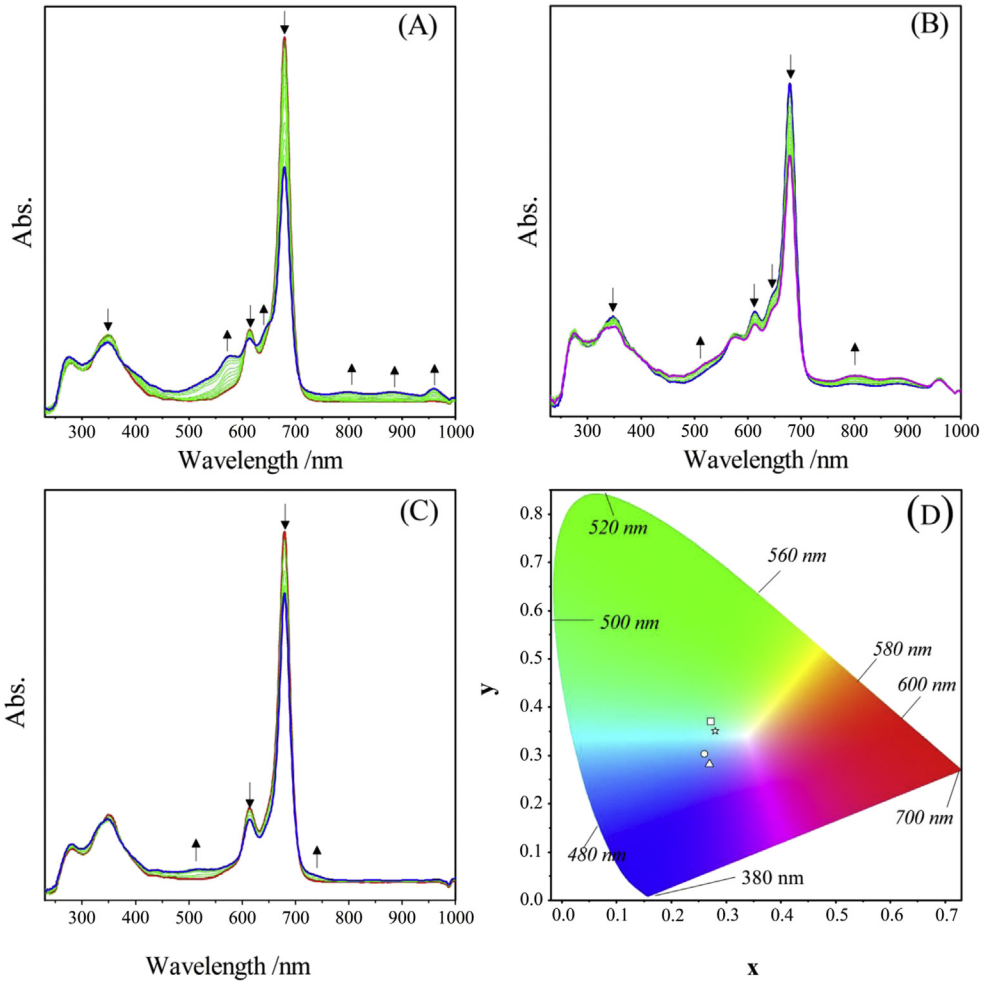


Fig. 9. *In-situ* UV–Vis spectral changes of ZnPc in DMSO. a) $E_{app} = -1.00$ V b) $E_{app} = -1.30$ V c) $E_{app} = 0.70$ V d) Chromaticity diagram (each symbol represents the color of electrogenerated species; □: $Zn^{II}Pc^{-2}$, ○: $Zn^{II}Pc^{-3}$, △: $Zn^{II}Pc^{-4}$, ☆: $Zn^{II}Pc^{-1}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To understand the effects of polystyrene conjugation to the electrochemical behaviors of ZnPc, redox responses of ZnPc-PS were recorded in both DMSO (Fig. 8a) and DCM (Fig. 8b). The main electrochemical differences between ZnPc and ZnPc-PS recorded in DMSO are; i) reduction reactions of ZnPc-PS shifts to the negative sides and oxidations to the positive sides with respect to those of ZnPc. ii) While ZnPc gives three reduction reactions, two reduction processes are recorded with ZnPc-PS. iii) While the electrochemical reversibilities of the electron transfer reactions of ZnPc-PS decrease, chemical reversibilities increase with respect to those of ZnPc. Similar electrochemical differences were also recorded between ZnPc and ZnPc-PS in DCM solvents.

3.5. Spectroelectrochemical measurements

To perform the assignments for the redox processes recorded with the CVs and SWVs of the complexes and to investigate the effects of the polystyrene group to the spectral changes of ZnPc, spectroelectrochemical studies were employed.

ZnPc and ZnPc-PS illustrate very similar in situ spectroelectrochemical responses in both of DCM and DMSO solvents, which indicated that the conjugation of PS on ZnPc had not got pronounced effects to the spectroscopic behaviors of Pc ring. Fig. 9a–d illustrates *in-situ* UV–Vis spectral changes of ZnPc in DMSO/TBAP electrolyte system. Under open circuit, ZnPc gives a sharp Q band at 680 nm and a B band at 350 nm. During the reduction at −1.00 V, the Q band decreases and new bands are observed at 573, 802, 882, and 960 nm. At the same time, the B band decreases slightly in intensity. Clear isosbestic points are recorded at 370, 604, 624, 655 and 709 nm (Fig. 9a). The green color ($x = 0.272$ and $y = 0.371$) of the neutral ZnPc turns to light blue color ($x = 0.26$ and $y = 0.303$) after the first reduction reaction (Fig. 9d). These spectral changes are characteristic changes for the ring based reduction of MPcs having redox inactive metal center [67–70].

During the second reduction reaction, the Q band continues to decreases while a new small band starts to increase at 520 nm. At the same time the bands at 573 and 960 nm remains as stable, while the bands at 802 and 882 nm continue to increases (Fig. 9b). These spectral changes are in harmony with the reduction of monoanionic ZnPc to dianionic ZnPc. The color of the light blue monoanionic ZnPc ($x = 0.26$ and $y = 0.303$) turns to deep blue color ($x = 0.27$ and $y = 0.282$) after the second reduction reaction (Fig. 9d). Fig. 9c illustrates the spectral changes recorded during the first oxidation reaction of ZnPc, which are in consistent with the spectral changes of common MPc complexes having redox inactive metal centers.

4. Conclusion

New ZnPc-end functional polymers have been successfully prepared and characterized through CuAAC “click” reaction between unsymmetrically terminalalkynyl substituted zinc phthalocyanine and azide -end functional polystyrene and poly(*tert*-butyl acrylate). For this purpose, the successful synthesis and separation of unsymmetrical terminalalkynyl substituted zinc pc was achieved. Classical statistical condensation reaction with unprotected phthalonitrile **2** was applied for the first time. The presence of terminalalkynyl function makes this compound suitable precursor for the click chemistry. Well-defined bromo-end functional poly(-styrene) (PS–Br) and poly(*tert*-butyl acrylate) (P*t*BA-Br) were synthesized with controlled molecular weights and narrow molecular weight distributions by ATRP. Bromo-end groups of polymers were easily converted to azide group through nucleophilic substitution reaction in DMF in the presence of excess NaN_3. Electrochemical and spectroelectrochemical measurements support the proposed structures of the complexes. ZnPc gives common phthalocyanine ring based reduction and oxidation reactions. Solvent of the electrolyte system only affects the potentials of the electron transfer processes and reversibility of the redox couples. Functionalization of ZnPc with PS increases chemical stability of the complex during redox reactions, but decreases the electrochemical reversibility of the redox processes. As expected, the presence of polystyrene has no obvious effect on the spectroelectrochemical and electrocolorimetric responses of ZnPc. The syntheses of water soluble derivatives and investigations of photodynamic activities of these symmetrically and unsymmetrically terminalalkynyl substituted phthalocyanines after click reaction with appropriate substituents modified with azido group such as PEG (Poly(ethylene glycol)) and PCL (Poly(ε-caprolacton) are in progress in our laboratory.

Acknowledgments

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