

Synthesis and photophysical properties of porphyrin-containing polymers

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Abstract A series of porphyrin-containing polymers with triazole rings as linkers have been successfully synthesized by click polymerization. The polycycloadditions of porphyrin-containing dialkyne **1** and 1,4-diazidobenzene **2** were initiated either by simple heating or by Cu(I)-catalyst, affording polymers **P1-P8** with relatively high molecular weight. The polymerization process was monitored by gel permeation chromatography analysis. The polymer prepared by thermally initiated click polymerization has unimodal molecular weight distribution and moderate polydispersity index after prolonging reaction time to 170 h. Compared with the metal-free click polymerization, the rate of molecular weight growth in Cu(I)-catalyzed click polymerization declined, leading to relatively low molecular weight of the

resulting polymer. The as-synthesized polymers are soluble in common organic solvents and stable at a temperature up to 350 °C. The photophysical properties of the porphyrin monomer and the polymer were investigated by UV-vis and fluorescence spectroscopy. This approach offers practical advantages over other synthetic methods used to prepare main-chain porphyrin-containing polymers with regard to the absence of byproducts generated during the polymerization reaction.

Keywords Porphyrin-containing polymer · Click polymerization · Photophysical properties

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Introduction

Porphyrins and their derivatives have attracted considerable attention for many years because of their outstanding physicochemical properties and applications in diverse fields such as oxygen binding, electron transfer, catalysis, light harvesting, optoelectronic devices, and photodynamic therapy [1–3]. Additionally, there are multitudes of synthetic porphyrinoid molecules that have been prepared and studied for purposes ranging from basic research to functional applications [4]. Although the porphyrin ring is a macromolecule, it is highly flexible and a number of structural changes involving different central metal ions and peripheral substituents can be introduced without compromising its excellent chemical and thermal stability [5]. Moreover, the extensively conjugated π -conjugated systems of porphyrins increase their electron-donating ability and make them suitable for donors in artificial photosynthetic systems [6].

Recently, much effort has been devoted to the design and synthesis of porphyrin-containing polymers. As a matter of fact, porphyrins have been incorporated into polymers as

pendant groups [7], in the backbone of networks [8], and in linear polymers [9]. Porphyrin polymers have better properties in electron transfer, energy conversion, and nonlinear optical materials than their monomers [10]. For example, copolymers based on porphyrin and fullerene with distinct donor and acceptor properties have been reported [11]. In previous articles dealing with the preparation of porphyrin-containing polymers, experimental observations were interpreted as two aspects. One involves polycondensation-like polymerizations based on well-known coupling reactions between two different functional groups that have been incorporated into porphyrins and other monomers [12]. On the other hand, porphyrin-containing polymers can also be achieved by chain polymerization of vinylated porphyrin monomers [13]. Traditionally, porphyrin based polymers have been mainly prepared by polycondensation-like polymerizations. Although effective in affording the desired polymers, almost all of the coupling reactions must be performed using rigorously anhydrous solvents under inert atmospheres, limiting their scalability and practicality. Additionally, the presence of byproducts makes the purification of polymer challenging. Thus, alternative synthetic routes that afford polymers containing porphyrins in their main chains in a straightforward and practical manner are of value. Fortunately, the recently introduced 1,3-dipolar Huisgen's cycloaddition as a prototypic click reaction presented a promising opportunity to prepare porphyrin-containing polymers [14]. This cycloaddition reaction is remarkably efficient and reliable, which can theoretically afford polymeric products with high molecular weights.

Attracted by the prospect, chemists tried to utilize click reaction to prepare polytriazoles (PTAs) since 2004 [15–17]. The Cu(I)-catalyzed click polymerizations of ethynylene diazides (AB_2) monomer [18] and diazide and triyne (A_2+B_3) monomers [19] have been used to prepare dendritic oligomers and hyperbranched PTAs, respectively. Additionally, linear PTAs have also been synthesized through the click polymerizations of diazide and diyne (A_2+B_2) monomers [20] or azidoacetylene (AB) monomer [21]. Although the Cu(I)-catalyzed click reaction is fast for the synthesis of small molecules, the metallic catalysts used in the click polymerizations can form complexes with the triazole ring or monomer, which leads to a very poor solubility in common organic solvent. In addition, the metallic residues can not be completely removed from the polymeric products and detrimental to the electronic and optical properties of the resulting polymers. With the deepening of the research, some other methods were developed. For example, Tang and coworkers demonstrated the utility of thermally initiated click reaction to synthesize PTAs [22]. In comparison to the Cu(I)-catalyzed system, the thermal click reaction is more environmentally friendly, economically sounder and free of the problems discussed above.

In this work, we used an A_2+B_2 monomers, i.e., porphyrin-containing dialkyne **1** and 1,4-diazidobenzene **2**, for clickable synthesis of linear polymers. We made our choice based on the fact that azidoacetylene AB monomer tends to undergo undesired self-oligomerization or autopolymerization during its preparation and storage due to the existence of two mutually reactive functional groups in a single molecular species. Additionally, the photophysical properties of the as-prepared porphyrin-containing polymers were also investigated.

Experimental

General

All solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Pyrrole was dried by distillation from CaH_2 . DMF was obtained by distillation from CaH_2 under reduced pressure. NMR spectra were recorded with a Bruker AV-400 NMR spectrometer. FTIR spectra in KBr pellets were recorded on a PE Spectrum One FTIR spectrometer. The molecular weight and polydispersity index of polymer were determined by a PL-GPC120 setup equipped with a PL HTRI RI detector, and a column set consisting of two PL gel 5 μm mixed-D columns (7.5×300 mm, effective molecular weight range of $0.2\text{--}400.0$ kg mol⁻¹) using DMF that contained 1.0 g L⁻¹ LiBr as an eluent at 80 °C at a flow rate of 1.0 mL min⁻¹. Narrowly distributed polystyrene standards over the molecular weight range of $0.5\text{--}7500$ kg mol⁻¹ (PS, Mainz, Germany) were utilized for calibration. Thermogravimetric analysis (TGA) measurement was performed on a Netzsch TG 209 analyzer under nitrogen at a scan rate of 20 °C min⁻¹. MALDI-TOF mass spectrum was recorded on a Bruker BIFLEXeIII mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. UV–vis spectra of the polymer solution and film were recorded with a Perkin-Elmer Lambda-25 UV–vis spectrometer. Photoluminescence emission spectra of the polymer solution and film were recorded with a Perkin-Elmer LS-50b luminescence spectrometer. The thin-film samples were prepared by spin-coating polymer or monomer solutions onto clear quartz slide at 2500 rpm. After being completely dried under vacuum, a film with average thickness approximately 100 nm was obtained. The thickness of the film was measured using a F20-UV thin-film measurement system.

Synthesis of meso-phenyldipyrromethane

Pyrrole (26.8 g, 400 mmol) and benzaldehyde (2.12 g, 20.0 mmol) were added to a 50 mL flask containing a

magnetic stir bar. The solution was degassed with a stream of argon for 30 min. Then trifluoroacetic acid (150 μ L, 2.00 mmol) was added via syringe. After complete addition, the reaction mixture was allowed to stir for 0.5 h at room temperature, slowly becoming yellow in color. The reaction was quenched by the addition of NaOH (2.40 g, 60.0 mmol) and stirring continued for 0.5 h. The solvent was removed under reduced pressure to afford an orange crude product and purified by silica gel chromatography (petroleum ether/dichloromethane, v/v, 7/3) to give a pale yellow solid in 78 % yield. ^1H NMR (CDCl_3 , δ , ppm): 5.49 (s, H, CH), 5.92 (s, 2 H, Py-H), 6.16 (m, 2 H, Py-H), 6.7 (m, 2 H, Py-H), 7.19–7.35 (m, 5 H, Ar-H), 7.94 (br s, 2 H, NH).

Synthesis of 4-propargyloxybenzaldehyde

A solution of propargyl bromide (5.95 g, 50.0 mmol) in DMF (60 mL) was added dropwise to a mixture of 4-hydroxybenzaldehyde (4.88 g, 50.0 mmol) and anhydrous potassium carbonate (28.0 g, 200 mmol) in DMF (60 mL) at 90 °C. After complete addition, the reaction mixture was allowed to stir for 12 h at 90 °C. The resulting mixture was cooled to room temperature and was diluted with 300 mL of water. After extraction with EtOAc (4 \times 60 mL), the combined organic phase was washed with brine (4 \times 60 mL) and dried with anhydrous MgSO_4 . After removing the solvent, the resulting solid was recrystallized from ethanol to give a white solid (5.8 g, 91 %). ^1H NMR (CDCl_3 , δ , ppm): 2.57 (t, 1 H, CH), 4.79 (d, 2 H, CH_2), 7.09 (d, 2 H, Ar-H), 7.87 (d, 2 H, Ar-H), 9.91 (s, 1 H, CHO).

Synthesis of 5,15-bis(phenyl)-10,20-bis(4-propargyloxyphenyl) porphyrin (**1**)

A dichloromethane solution (400 mL) of 4-propargyloxybenzaldehyde (650 mg, 4.00 mmol) and *meso*-phenyldipyromethane (900 mg, 4.00 mmol) was stirred at room temperature for 2 h, under argon, in the presence of trifluoroacetic acid (40 μ L). The reaction was quenched by the addition of DDQ (1.97 g, 8.00 mmol) and stirring continued for 2 h. The mixture was basified with Et_3N and filtered through silica. After removing the solvent, the crude product was purified by flash column chromatography on silica gel using dichloromethane as the eluent to give a purple solid (71.3 mg, 4.6 %). ^1H NMR (CDCl_3 , δ , ppm): 8.86 (q, 8 H, Py-H), 8.22 (d, 4 H, Ar-H), 8.14 (d, 4 H, Ar-H), 7.76 (m, 6 H, Ar-H), 7.36 (d, 4 H, Ar-H), 4.98 (d, 4 H, CH_2), 2.69 (s, 2 H, CH). ^{13}C ^1H NMR (CDCl_3 , δ , ppm): 157.49, 142.24, 135.57, 135.49, 134.58, 127.71, 126.69, 120.10, 120.03, 119.71, 119.64, 113.17, 78.70, 76.70, 75.86, 56.20. $[\text{M}]^+$: 722.2682; found: 722.2671.

Synthesis of 1,4-diazidobenzene (**2**)

The synthesis of **2** was performed by two successive processes. Firstly, a solution of benzene-1,4-diamine (3.30 g, 30.0 mmol) and sodium nitrite (4.50 g, 60.0 mmol) in water (100 mL) was added dropwise to a stirred solution of sodium borofluoride (8.80 g, 80.0 mmol) in hydrochloric acid (3.87 M, 120 mL) at -10 °C under argon. After 1 h, the precipitate was filtered and washed with water (2 \times 50 mL), ethanol (1 \times 50 mL), and ethyl ether (1 \times 30 mL) to give powdery $\text{F}_4\text{BN}_2\text{-C}_6\text{H}_4\text{-N}_2\text{BF}_4$ (4.9 g, 53 %).

The as-produced $\text{F}_4\text{BN}_2\text{-C}_6\text{H}_4\text{-N}_2\text{BF}_4$ (2.50 g, 8.00 mmol) was added to an aqueous solution (150 mL) of sodium azide (1.30 g, 20.0 mmol) in three increments (833 mg, each) at regular intervals of 20 min at room temperature. The precipitate was filtered and recrystallized from ether to give crystalline product (0.8 g, 59 %). ^1H NMR (CDCl_3 , δ , ppm): 7.06 (s, 4 H, Ar-H). ^{13}C NMR (CDCl_3 , δ , ppm): 136.70, 120.43.

Click polymerization

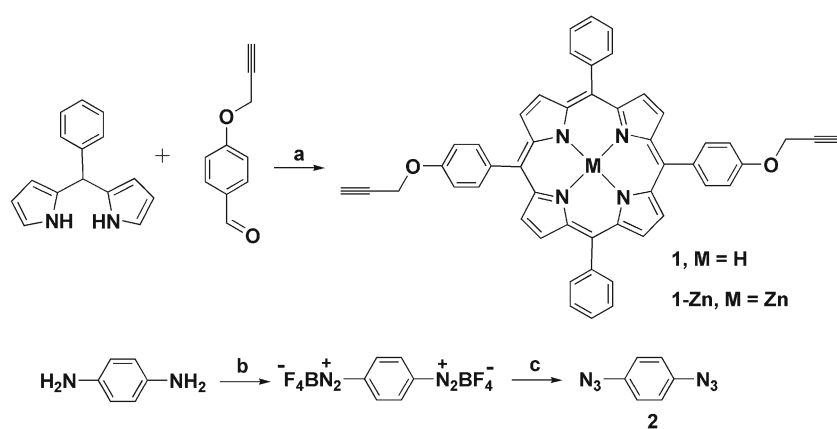
The polymerization reactions were carried out under argon in Schlenk tubes. Typical thermal click reactions are given below. In a Schlenk tube was added **1** (0.0200 mmol) and **2** (0.0200 mmol). Then 1.5 mL of DMF was injected. After stirring at 100 °C for 72 h, the mixture was diluted with chloroform and added dropwise into 60 mL of ethyl ether through a cotton filter under stirring. The precipitate was collected by filtration, and dried under vacuum at room temperature to a constant weight.

Typical Cu(I)-catalyzed click reactions are given below. CuBr (17.3 mg, 0.120 mmol), **1** (29.2 mg, 0.0400 mmol), **2** (6.4 mg, 0.0400 mmol), and DMF (1.5 mL) were added into a Schlenk. After three freeze-vacuum-thaw cycles, pentamethyldiethylenetriamine (26.0 μ L, 0.120 mmol) was injected. The reaction was allowed to stir at room temperature for 72 h. The mixture was diluted with chloroform and passed through an alumina column to remove copper salt. After precipitating into 50 mL of ethyl ether, the precipitates were collected by filtration, and dried under vacuum at room temperature to a constant weight.

Results and discussion

Synthesis of monomers

As mentioned previously, although Cu(I)-catalyzed click reaction is fast for the synthesis of small organic compounds, early attempts to synthesize polymer had met with great difficulties. The general restrictions of this method are limited efficiency, slow reaction rate, and low solubility of

Scheme 1 Synthesis of monomers **1**, and **2**

the resulting polymer. Recently, great efforts have been made to overcome these obstacles through design of monomer structures, exploration of catalyst systems, and control of reaction conditions.

In this work, we used an A_2+B_2 monomers, i.e., porphyrin-containing dialkyne **1** and 1,4-diazidobenzene **2**, for the synthesis of linear polymers. The monomers were prepared according to the synthetic routes shown in Scheme 1. In order to avoid the formation of insoluble by-products, we first mixed pyrrole with excess benzaldehyde in the presence of trifluoroacetic acid to afford *meso*-phenyldipyrromethane. Alkynyl groups were introduced by the etherization reaction of 4-hydroxybenzaldehyde with propargyl bromide. Monomer **1** was then synthesized by the reaction between *meso*-phenyldipyrromethane and 4-propargyloxybenzaldehyde in a degassed dichloromethane in the presence of trifluoroacetic acid [23]. Porphyrin **1** was easily metallated by heating with $Zn(OAc)_2$ in DMF. Diazide **2** was prepared from *p*-phenylenediamine via the Sandmeyer reaction [24]. The substitution of aromatic amino groups in *p*-phenylenediamine was carried out via preparation of its diazonium salt and subsequent nucleophilic displacement with sodium azide in water. All the monomers were carefully purified and characterized, from which

satisfactory analysis data corresponding to their molecular structures were obtained (Supporting Information).

Click polymerization

Recently, Tang and coworkers reported the synthesis of PTAs in high yields via a metal-free click polymerization of diazides and bis(aryolacetylene)s in polar solvent at 100 °C [22]. The obtained polymers exhibit high solubility in common organic solvents. This polymerization can propagate smoothly in an open atmosphere without protection from air and moisture, which broadens the types of alkyne monomers, simplifies the process of click polymerization. Following the procedure, the metal-free click polymerization of porphyrin-containing dialkyne **1** and diazide **2** was performed in DMF at a temperature of 100 °C (Scheme 2). For comparison, Cu(I)-catalyzed click polymerization of these monomers in DMF at room temperature was also investigated. The polymerization process was monitored by GPC analysis of samples withdrawn at predetermined time intervals. The influence of polymerization time on molecular weight of the resulting polymer was thus systematically studied.

GPC traces as a function of time for the meta-free and Cu (I)-catalyzed click polymerization of the A_2+B_2 monomers

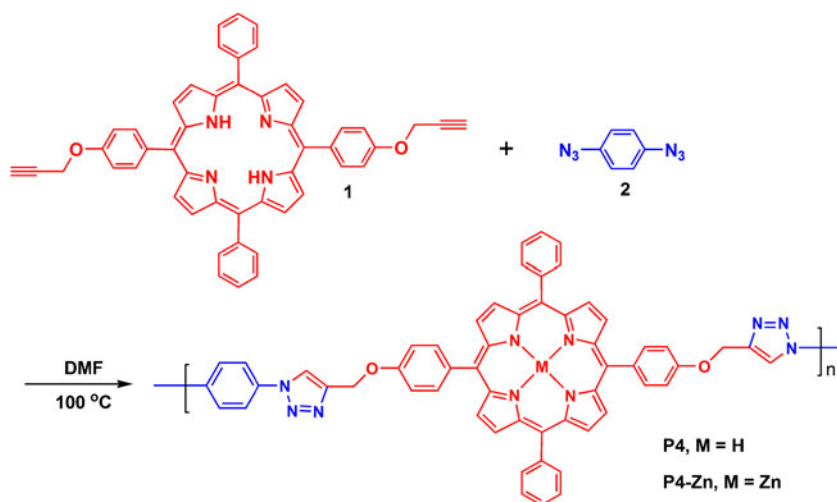
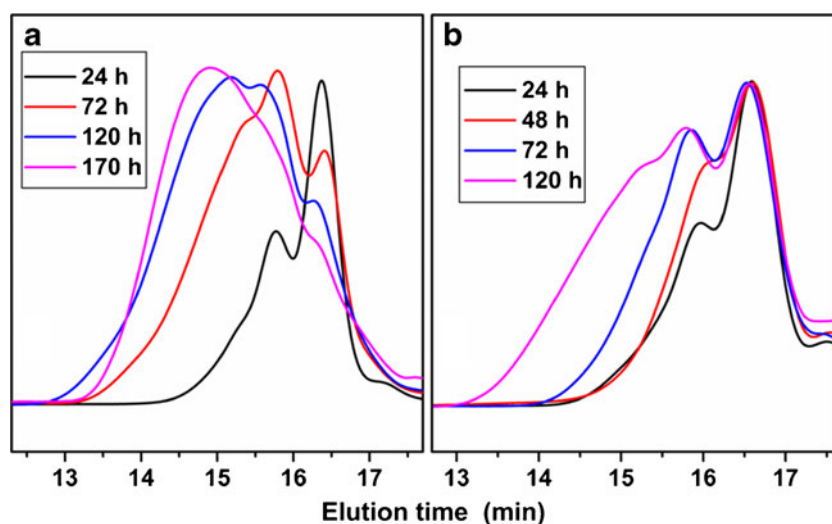
Scheme 2 Synthesis of porphyrin-containing polymer by click polymerization

Fig. 1 GPC traces for porphyrin-containing polymers prepared by thermal initiated (a), and Cu(I)-catalyzed (b) click polymerizations in DMF



are shown in Figs. 1a and b, respectively. Table 1 lists the number-average molecular weights (M_n) and polydispersity index ($PDI = M_w/M_n$) data for each of the samples shown in Fig. 1. The data in Table 1 exhibit a systematic trend of M_n increase with prolonging click polymerization time. For the thermal click system, polycondensation between **1** and **2** proceeded smoothly in DMF at a moderate temperature of 100 °C. After 24 h of polymerization, product **P1** (Table 1) shows two separate M_n values of 6.5 and 3.1 kDa, respectively, as evidenced by the corresponding GPC trace in Fig. 1a, which is found to have a bimodal character with much high content of oligomers containing fewer than 3 repeating units. After 72 h, bimodal peaks are still observed in the GPC trace, while the content of oligomers is sharply decreased. Further prolonging the polymerization time to 170 h, a unimodal and almost symmetrical peak is observed in the GPC trace with the M_n and PDI of 11.1 kDa and 1.75, respectively.

Table 1 Synthesis and characterization of porphyrin-containing polymers^a

Polymers	Time (h)	Temperature (°C)	M_n (KDa)	PDI	Yield (%)
P1	24	100	6.5, 3.1	1.04, 1.02	60
P2	72	100	8.5, 1.8	1.10, 1.21	72
P3	120	100	7.2	1.87	82
P4	170	100	11.1	1.75	82
P5	24	30	6.6, 3.3	1.00, 1.05	70
P6	48	30	7.6, 3.1	1.07, 1.04	70
P7	72	30	8.3, 2.8	1.03, 1.12	72
P8	120	30	9.4, 2.5	1.27, 1.12	72

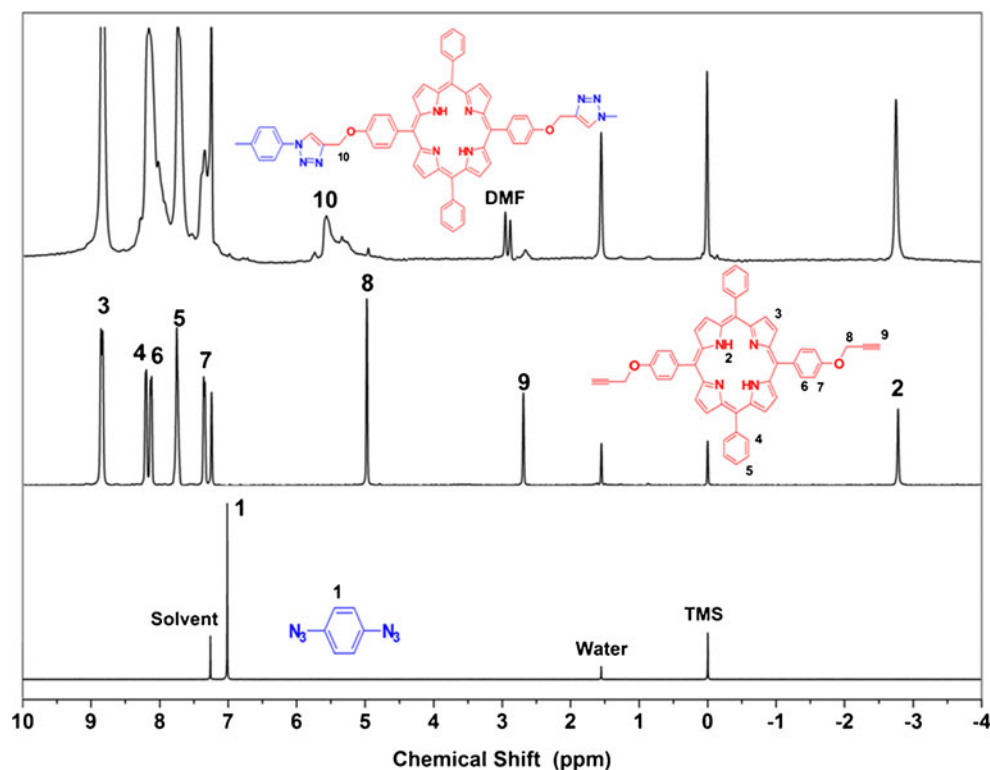
^a **P1–P4** for thermal click polymerizations, and **P5–P8** for Cu(I)-catalyzed click polymerizations

The Cu(I)-catalyzed click polymerization was also monitored by GPC analysis. As shown in Fig. 1b, the elution time shifts to lower values as a function of polymerization time, which is a qualitative indication of increasing M_n with prolonging click reaction time. Compared with the thermal click polymerization, the rate of M_n increase in Cu(I)-catalyzed click polymerization is relatively low as evidenced by the presence of oligomeric products even after long reaction time. For example, the GPC trace for polymer after 120 h of polymerization is found to have bimodal character with two separate M_n of 11.4 and 2.8 kDa, respectively.

Structural characterization

The characterization data for **P4** (Table 1) are discussed here as an example. The good solubility of **P4** in chloroform enabled characterization of its molecular structure by NMR technique. The ¹H NMR spectra of **P4**, monomers **1** and **2** are shown in Fig. 2. The polymer shows the presence of the expected repeating unit in the proper molar ratio. By comparing the ¹H NMR spectra of **P4** (spectrum c) with its monomers **1** (spectrum b) and **2** (spectrum a), click polymerization between the alkyne and azide groups of the monomers was confirmed. The azidophenyl proton of monomer **2** resonates at δ 7.01 ppm, which almost disappears in **P4** after the click polymerization. The resonance of the alkyne protons of monomer **1** at δ 2.69 ppm as well as the methylene protons adjacent to the alkyne group at δ 4.98 ppm also becomes much weaker, further substantiating the click polymerization [25]. The new peaks at δ 5.58 and 5.74 ppm are associated with the resonances of the methylene protons adjacent to 1,4-isomeric and 1,5-isomeric triazole ring [22], respectively. But the peak associated with the proton in triazole ring is overlapped by porphyrin protons.

Fig. 2 ^1H NMR spectra of dialkyne **1**, diazide **2**, and their polymer **P4** measured in CDCl_3 at room temperature



FTIR spectra of **P4** and its monomers **1** and **2** are given in Fig. 3. As shown in Fig. 3, signal at 2105 cm^{-1} corresponding to the azide stretching frequency of monomer **2** is present (spectrum a). Additionally, signals corresponding to the C–C and C–H stretches of the alkyne groups in the monomer **1** can be seen at 2121 and 3301 cm^{-1} (spectrum b), respectively. Upon polymerization, **P4** shows weak stretching vibration bands of $\equiv\text{C–H}$ at 3301 cm^{-1} and $\text{C}\equiv\text{C}$ at 2121 cm^{-1} (spectrum c), indicating that most of the alkyne and azide groups of

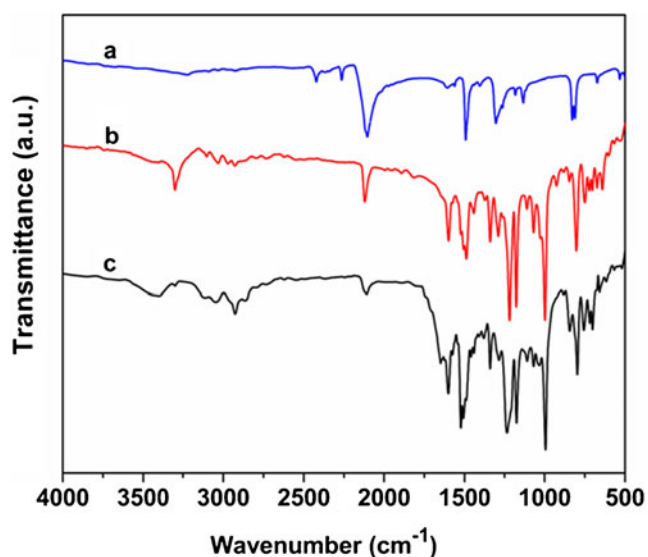


Fig. 3 FTIR spectra of diazide **2** (a), dialkyne **1** (b), and their polymer **P4** (c)

the monomers have been consumed and transformed into triazole rings in polymer. Moreover, small, but clearly discernible, shoulder band at 3410 cm^{-1} due to the characteristic peak of 1,2,3-triazole can be easily observed [26].

Thermal stability of the polymer was measured by TGA. As can be seen from Fig. 4, the polymer **P4** is thermally stable, lose about 5 % of its weight at a temperature about $350\text{ }^\circ\text{C}$.

Photophysical properties

The photophysical properties of the polymer and its porphyrin monomer were investigated by UV–vis and fluorescence

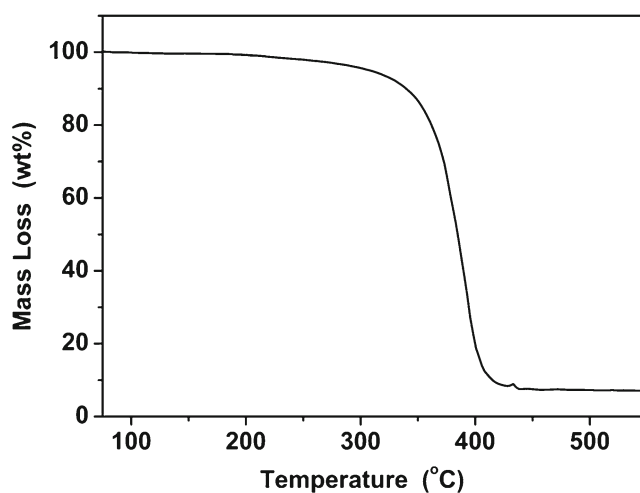


Fig. 4 TGA curve of porphyrin-containing polymer **P4**

spectroscopies. For comparison, metalated porphyrin monomer **1** and polymer **P4** samples were also studied. It is well-known that the photophysical properties of porphyrins can be tuned by metal insertion into the core. Since the electrons of metal ion can be donated to the porphyrin molecule, forming delocalized π bonds, which permit the easy flow of electrons within the delocalized π system [27, 28]. In an attempt to metalate **1** and **P4** in chloroform, their solutions were treated with a solution of zinc(II) acetate in methanol under reflux, affording zinc porphyrin complexes, **1-Zn** and **P4-Zn**. Evidence for complete metalation by Zn^{2+} is provided by the complete disappearance of the pyrrole protons in porphyrin at $\delta -2.78$ ppm in the ^1H NMR spectra (Supporting Information).

Figure 5 shows the UV–vis absorption spectra of original monomer **1** and polymer **P4** as well as their metalated samples, **1-Zn** and **P4-Zn**, in DMF. Generally, porphyrin absorption include an intense near-UV band (Soret) and two visible bands (Q), in which one represents excitation from the lowest vibrational level of the ground state singlet to the lowest vibrational level of the first excited singlet electronic state, and the other has one quantum of vibration in the first excited singlet electronic state [29]. As shown in Fig. 5, the absorption spectra are characterized by the intense Soret band centered at 419 nm (λ_{max}) and four weaker Q-bands with maxima at 515, 551, 592, and 648 nm for both **1** and **P4**. Similarly, the electronic absorption spectra of zinc porphyrins (**1-Zn** and **P4-Zn**) in DMF show a characteristic Soret band at 426 nm and two Q-bands at 560 and 600 nm, respectively. Upon metalation, the delocalized π bands of zinc porphyrins increase the average electron density of the porphyrin, which lower the energy for electron transition, leading to a red shift in the Soret band [28]. For example, the Soret band of metalated porphyrins (**1-Zn** and **P4-Zn**) is red

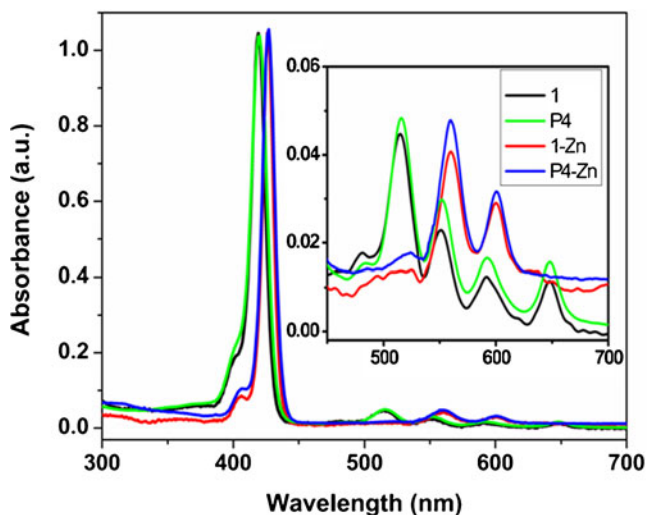


Fig. 5 UV–vis absorption spectra of **1**, **1-Zn**, **P4**, and **P4-Zn** in DMF solution with a concentration of 3.2×10^{-7} M based on porphyrin

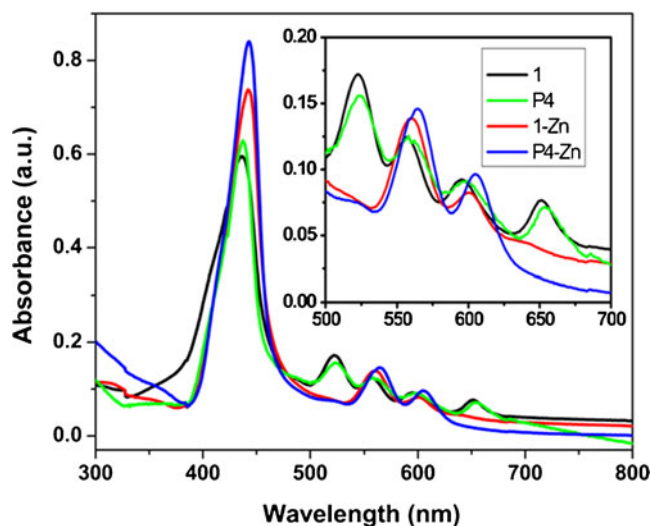


Fig. 6 UV–vis absorption spectra of **1**, **1-Zn**, **P4**, and **P4-Zn** thin films

shifted of 7 nm compared to those of metal-free porphyrins. Although almost no change in the λ_{max} values is noted for **1** and **P4**, the Q-bands of polymer exhibit slightly hyperchromicity (see inset Fig. 5, for sake of clarity). This effect is more pronounced in the case of the metalated porphyrins.

Figure 6 shows the UV–vis absorption spectra of **1** and **P4** as well as metalated **1-Zn** and **P4-Zn** thin films. Again, the absorption spectra are characterized by the intense Soret band centered at 436 nm and four weaker Q-bands with maxima at 522, 558, 595, and 651 nm for **1** and **P4**, and Soret band at 442 nm and Q-bands at 560 and 600 nm for metalated porphyrins **1-Zn** and **P4-Zn**, respectively. Similarly, the Soret band of zinc porphyrins including the monomer and polymer is red shifted of 6 nm compared to those of metal-free porphyrins. Obviously, the spectroscopic behavior observed for film are considerably different from those observed in DMF solution. Compared to the solution spectra (419 nm for **1** and **P4**, 426 nm for **1-Zn** and **P4-Zn**), the Soret band for film (436 nm for **1** and **P4**, 442 nm for **1-Zn** and **P4-Zn**) is red shifted of ca. 16 nm. These results can be attributed to the restricted vibrational and rotational motion of porphyrin molecule in solid phase, and such red-shifting has also been observed in Langmuir-Blodgett monolayer film of porphyrins [30].

The fluorescence spectra of porphyrins **1** and **P4** as well as metalloporphyrins, **1-Zn** and **P4-Zn**, in DMF solution and in film are given in Figs. 7 and 8. As shown in Fig. 7, the fluorescence spectrum in solution consists of two emission bands with maxima at 654 and 719 nm for **1** and **P4**, and 609 and 661 nm for **1-Zn** and **P4-Zn**, respectively, which can be attributed to Q transitions [28]. On the other hand, the sample in solid state leads to a suppression of the fluorescence intensity (Fig. 8). For example, the fluorescence spectra for **1** and **P4** film samples consist of two declined bands with maxima at 665 and 722 nm, but complete suppression for **1-Zn** and **P4-Zn** film samples. The fluorescence intensities of **1-Zn** and **P4-Zn**

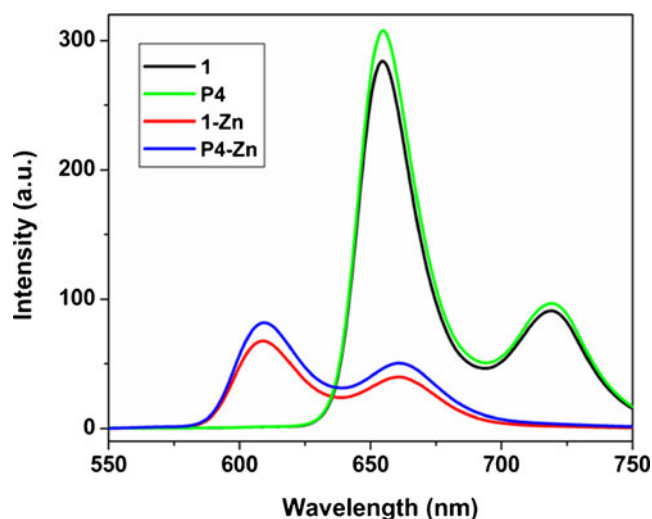


Fig. 7 Fluorescence spectra of **1**, **1-Zn**, **P4**, and **P4-Zn** in DMF solution with a concentration of 3.2×10^{-7} M based on porphyrin, $\lambda_{\text{ex}}=420$ nm

Zn are much weaker than those of the corresponding metal-free porphyrins **1** and **P4** because zinc weakens the fluorescence radiation [28].

The excitation and emission related data: excitation and emission wavelengths (λ , nm), Stokes shift values ($\Delta\lambda$, nm), and fluorescence quantum yields (Φ_f) of all samples are summarized in Table 2. The excitation wavelength was chosen at 420 nm and the emission spectra were recorded. Fluorescence quantum yield (Φ_{exp}) was calculated from [31]

$$\Phi_{\text{exp}} = \Phi_{\text{ref}} \frac{F(1 - \exp(-A_{\text{ref}} \ln 10))n^2}{F_{\text{ref}}(1 - \exp(-A \ln 10))n_{\text{ref}}^2}$$

where F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength,

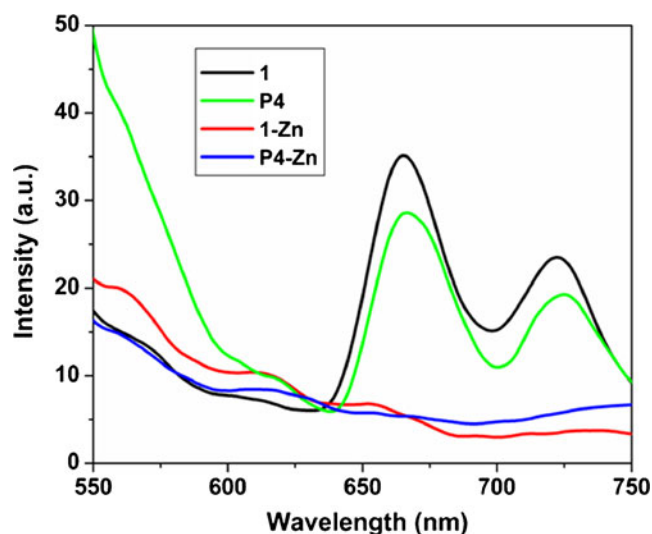


Fig. 8 Fluorescence spectra of **1**, **1-Zn**, **P4**, and **P4-Zn** thin films, $\lambda_{\text{ex}}=420$ nm

Table 2 Fluorescence properties of porphyrin monomer and porphyrin-containing polymer in solution and film^b

Samples	Medium	λ_{max} (ex) (nm)	λ_{max} (em) (nm)	$\Delta\lambda$ (nm)	Φ_{exp}
1	film	420	665	245	0.014
1	DMF	420	654	234	0.068
P4	film	420	666	246	0.011
P4	DMF	420	654	234	0.074
1-Zn	DMF	420	609	189	0.018
P4-Zn	DMF	420	609	189	0.022

^bExcitation (ex), and emission (em) wavelengths, λ_{max} (nm), Stokes shift values, $\Delta\lambda$ (nm), and fluorescence quantum yields, Φ_{exp} , for all porphyrin samples

and n is the refractive index of the medium. The reference system used were tetraphenylporphyrin ($\lambda_{\text{ex}}=560$ nm, $\Phi_f=0.13$ in benzene [31]).

As shown in Table 2, the unmetallated porphyrins exhibit Stokes shift ranging from 234 to 245 nm in solution and solid, respectively. For metalloporphyrins, **1-Zn** and **P4-Zn**, the Stokes shift as well as the quantum yield decreased significantly. The quantum yield values in film are much lower than those in solution media for all porphyrins. The low quantum yield of porphyrin polymer indicates that the radiative decay from the first excited singlet state is of minor importance among the competitive relaxation processes, which can be attributed to the intersystem crossing and/or internal conversion in the decay of their excited singlet states [32]. These results are in agreement with those obtained for similar porphyrins. For example, Durantini et al. showed that zinc insertion into *meso*-tetrakis-(4-methoxyphenyl)porphyrin and halogenated tetraarylporphyrins results in reduced fluorescence quantum yield [33].

Conclusions

In conclusion, porphyrin-containing polymers with triazole rings as linkers have been successfully synthesized by metal-free click polymerization of 1,4-diazidobenzene and porphyrin-containing dialkyne. The polymerization process was monitored by gel permeation chromatography analysis. Compared with the metal-free click polymerization, the rate of molecular weight growth in Cu(I)-catalyzed click polymerization declined, leading to relatively low molecular weight of the resulting polymer. The as-synthesized polymers are soluble in common organic solvents and stable at a temperature up to 350 °C. The photophysical properties of the porphyrin monomer and the polymer were investigated by UV-vis and fluorescence spectroscopy. The low quantum yield of the porphyrin polymers can be attributed to the

intersystem crossing and/or internal conversion in the decay of their excited singlet states.

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