

Advanced Photonics Materials with AIE Feature

Ben Zhong Tang

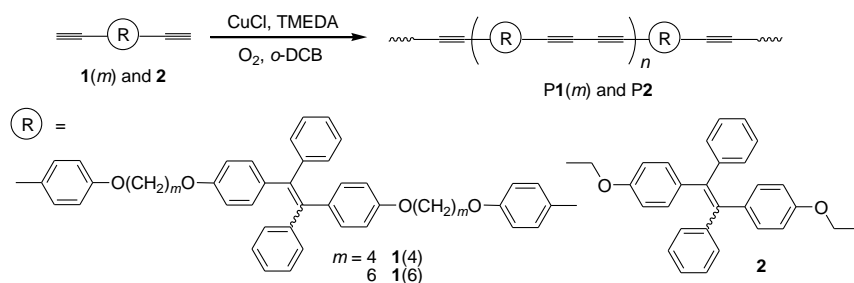
Department of Chemistry, Institute for Advanced Study, State Key Laboratory of Molecular Neuroscience, Institute of Molecular Functional Materials and Division of Biomedical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Email: tangbenz@ust.hk

Abstract: Tetraphenylethene-containing polyynes with aggregation-induced emission characteristics are synthesized. The polymers are highly transparent in the entire visible spectral region and show high refractive indices ($n = 1.7787\text{--}1.6543$) in a wide wavelength region of 400–1700 nm.

1. Introduction

Conjugated polymers are highly emissive in solution but become nonluminescent or weakly emissive in the solid state due to the aggregate formation. This notorious “aggregation-caused quenching” (ACQ) effect has greatly hampered their practical applications in optics and electronics. We discovered a phenomenon of aggregation-induced emission (AIE) [1,2] that is exact opposite to the ACQ effect observed in conventional luminophores: a series of nonemissive molecules, such as tetraphenylethene (TPE), hexaphenylsilole, diphenyldibenzofulvene and their derivatives were induced to emit efficiently by aggregate formation. The AIE effect greatly boosts the fluorescence quantum yields (Φ_F) of the molecules by up to three orders of magnitude, turning them from faint luminophores into strong emitters. This novel AIE effect enables the molecules to find high-tech applications as chemical sensors, biological probes, stimuli-responsive nanomaterials, and active layers for the fabrication of organic light-emitting diodes. Among the AIE luminogens, TPE has been intensively studied because of its facile synthesis, easy functionalization, and high Φ_F value [3,4]. In this work, we explored the utility Glaser-Hay coupling [5–8] into a useful tool for the preparation of AIE-active polyynes (Scheme 1). The resulting polymers **P1**(m) and **P2** are optically transparent and show high refractive indices. They undergo crosslinking reaction readily under UV irradiation, generating fluorescent negative photoresist pattern with good resolution.



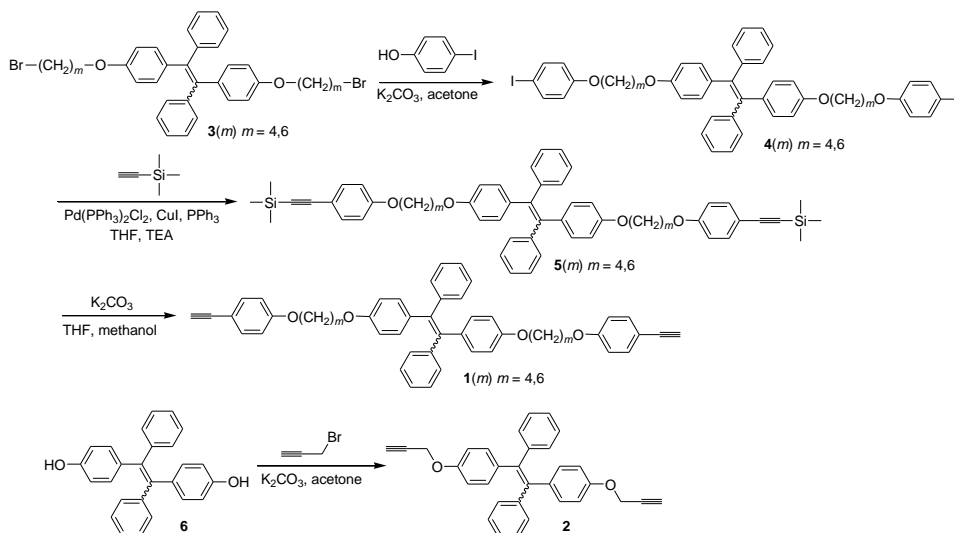
Scheme 1. Polymerizations of **1**(m) and **2** mediated by CuCl and TMEDA.

2. Results and Discussion

TPE-containing diynes **1**(m) and **2** were synthesized according to the synthetic procedures shown in Scheme 2. Etherization of **3**(m) with 4-iodophenol furnished **4**(m), which underwent coupling reaction with trimethylsilylacetylene in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI to give **5**(m). Desilylation of **5**(m) was carried out in THF/methanol mixture of K_2CO_3 , generating **1**(m) in high isolated yields. Diyne **2** was prepared by nucleophilic substitution of **6** with propargyl bromide. Exploration of new polymerization reactions for the synthesis of new polymers is a fundamentally important area in macromolecular science. In our previous investigation, we found that Hay-Glaser polycoupling of triynes could generate processable hyperbranched polyynes [9–11]. We thus tried to polymerize **1**(4) using the procedures we developed previously. Reaction of **1**(4) in *o*-DCB at 60 °C in the presence of CuCl and TMEDA (Scheme 1) for 3 h gives **P1**(4) with an M_w of 18 300 in a high yield. Under the same conditions, **1**(6) and **2** are converted into polymers **P1**(4) and **P2** with similar molecular weights ($M_w = 14,800$ for **P1**(4) and 17,600 for **P2**) in satisfactory yields. All the obtained polyynes are completely soluble in common organic solvents such as THF, toluene and chloroform, thus enabling us to characterize their molecular structures by “wet” spectroscopic methods.

Fig. 1A shows the UV spectra of **1**(6) and **2** along with their polymers **P1**(m) and **P2** in THF solutions. Both monomers exhibit an absorption peak centered at ~320 nm associated with the $\pi\text{--}\pi^*$ transition of the TPE moiety. It is noteworthy that all the polymers show no absorption peaks at wavelengths larger than 400 nm, demonstrating that

they possess high optical transparency and are promising for advanced optical applications. The photoluminescence (PL) spectrum of the diluted THF solution of **P1(6)** gives almost a flat line parallel to the abscissa, manifesting that the polymer is a weak emitter in the solution state (Inset in Fig. 1B). In contrast, when a large amount of water is added into the solution, an intense PL peak centered at ~480 nm is recorded under the same measurement conditions. As water is a non-solvent for **P1(6)**, the polymer chains must have aggregated in THF/water mixtures with high water contents. **P1(6)** is thus induced to emit by aggregate formation; in other words, it is AIE-active. Similar PL behaviors are observed in **P1(4)** and **P2**. We compared the emission intensities of solutions of the polymers and their aggregates at 90% aqueous mixtures at the maximum emission wavelength from which their AIE factors ($\alpha_{\text{AIE}} = I_{90}/I_0$) are determined (Fig. 1B). The quantum yields of the polymeric thin films are determined by an integrating sphere and equal to 26.0, 39.2 and 34.2% for **P1(4)**, **P1(6)** and **P2** respectively.



Scheme 2. Synthetic routes for monomers **1(m)** and **2**.

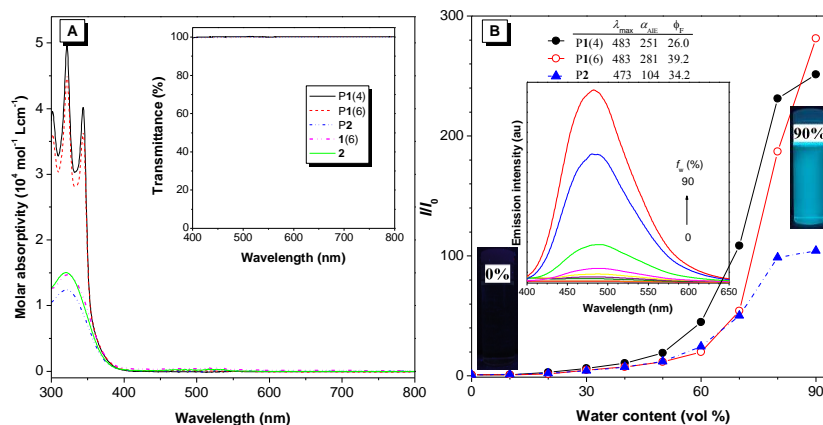


Fig. 1. (A) Absorption spectra of THF solutions (10 μM) of **1(6)** and **2** and their polymers **P1(m)** and **P2**. Inset: transmittance spectra of the monomers and polymers in THF solutions. (B) Plot of I/I_0 values at the maximum emission wavelength (λ_{max}) versus the compositions of the aqueous mixtures of **P1(m)** and **P2**. Inset: emission spectra of **P1(6)** in THF/water mixtures. Concentration: 10 μM ; excitation 345 nm. $\alpha_{\text{AIE}} = \text{AIE factor} = I_{90}/I_0$, where I_{90} and I_0 are the emission intensities at the λ_{max} in THF/water mixtures with 90 and 0% water contents, respectively. Φ_{F} = fluorescence quantum yield of the polymer thin films determined by an integrating sphere.

All the polymers possess high thermal stability, showing 5% weight loss or degradation temperature (T_d) higher than 370 $^{\circ}\text{C}$ under nitrogen. Among them, **P2** shows the highest weight residue (> 50%) after pyrolyzed at 800 $^{\circ}\text{C}$, presumably due to its higher aromatic content. Previous studies show that hyperbranched polyyne shows high refractive index (RI) due to the presence of numerous polarizable aromatic rings and diacetylene units [9–11]. This is also the case for the newly synthesized linear polyyne. **P1(6)** displays high refractive indices (RI = 1.7787–1.6543) in a wide spectroscopic region (400–1700 nm). The refractive index (n) of **P1(6)** is much higher than those of commercially important optical plastics such as poly(methyl methacrylate) ($n \sim 1.49$), poly(ethylene

terephthalate) ($n \sim 1.59$), etc. The refractive index of the polymer film is tunable. Upon UV exposure, the RI value decreases in the whole spectral region. No or little birefringence is detected, indicative of the amorphous nature of the solid film.

The polyynes contain a large number of photosensitive diacetylene groups, which enable them to crosslink readily upon UV irradiation and use as negative photoresist materials for pattern generation. Indeed, when a thin solid film of P1(6) spin-coated on a silicon wafer is irradiated in air through a copper photomask, the PL of the exposed region is quenched, whereas the unexposed area remains emissive. A two-dimensional fluorescent pattern is thus readily generated without going through the development process (Fig. 2A). After development in 1,2-dichloroethane, a three-dimensional photopattern with clear-cut edges is generated (Fig. 2B).

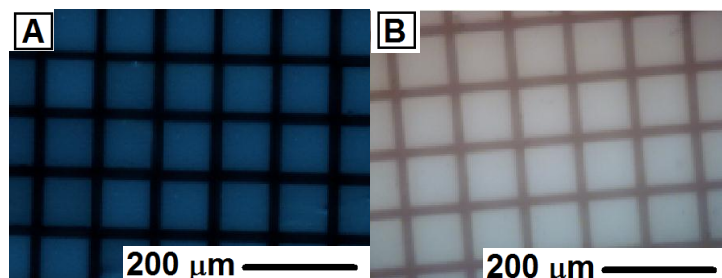


Fig. 2. (A) Two-dimensional fluorescent image and (B) three-dimensional negative photopattern generated by UV irradiation of P1(6) for 5 min. The photographs were taken under (A) UV illumination and (B) normal room lighting.

3. Conclusion

In this work, TPE-containing diacetylenes are synthesized and their polycoupling reactions proceed smoothly in *o*-dichlorobenzene in the presence of CuCl, producing linear polyynes in high yields. All the polymers are soluble film-forming, and thermally stable. They enjoy high optical transparency and their films exhibit high refractive indices. Their refractive index can be readily tuned by UV irradiation. The polyynes are photoresponsive and UV irradiation of their films crosslinks the polymers, generating well-resolved fluorescent patterns. These unique features make the polymers promising candidates as advanced materials for high-tech applications.

4. Acknowledgement

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