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Nonlinear optical properties of symmetrical and asymmetrical porphyrin derivatives with click chemistry modification

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ABSTRACT

The novel kind of charge-transfer porphyrin complexes with symmetrical and asymmetrical side groups were synthesized by the high-yielding [2 + 2] click chemistry reaction involved a two-step procedure. Both electrochemical and UV–vis studies were characterized and proved that the side groups of the porphyrin complexes played an important role on optical properties and energy gaps. The novel series did show the narrower band gap and broader absorption in the visible and near infrared region. As the side groups, the click moieties also affected the third-order nonlinear optical responses, and all the compounds exhibited the expected nonlinear optical properties which were affected by the chemical structures. The optical-limiting performance had also been studied, which was in agreement with the result of Z-scan experiments.

1. Introduction

Considerable attention has been concentrated dramatically on organic third-order nonlinear optical (NLO) materials in recent years for their promise in optical telecommunications, ultrahigh speed signal processing, real-time target recognition, and aberration-corrected imaging, where linear and nonlinear absorption must be minimized, and in optical power limiting (OPL), where nonlinear absorption must be maximized [1–3]. The organic materials with prominent π-electron delocalization include porphyrins, phthalocyanines, fullerenes, and organometallic compounds. Among them, porphyrins emerged as promising candidates are of interest since a significant enhancement of hyperpolarizability can be achieved through metal insertion at the ring center or by functionalization at the peripheral positions. Usually, large nonlinear optical properties are always accompanied with highly conjugated large π-system or extended aromatic core of the molecular structure [4,5]. From a more fundamental perspective, many studies have concerned porphyrins [6,7], which offer great scope for imaginative molecular engineering with the aim of realizing new, multifunctional NLO materials. However, comparing with the actually applications of inorganic materials, up to date, search for new organic materials and studying on the factors affecting the nonlinear optical properties of these organic compounds as nonlinear optical materials are still necessary.

In order to solve these problems, the most attractive characteristic of organic based materials derives from the versatility of modern organic synthetic methods, which enable the chemist to tune the photophysical properties of a material to enhance a particular NLO effect simply by altering flexible synthetic routes. While – theoretically – almost any desired β-substituted porphyrin can be prepared based on historical contributions from eminent chemists such as Willstätter, Fischer, Woodward, Eschenmoser and Smith [8–10] there were still limitations in the preparation of asymmetrical porphyrins [11,12]. Meanwhile, post-functionalization may be a good method for designing and preparing the asymmetric porphyrins. Recently, [2 + 2] click chemistry [13–19] became one of the most important techniques to attach various chromophores to porphyrins or other derivatives, affording

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a variety of new organics in a straightforward way. The strong polarizability and long conjugated system can be obtained at the same time by [2 + 2] click chemistry, and both the factors has been proven effective to improve the NLO properties [20–26]. The asymmetrical porphyrins were simply synthesized by the high-yielding [2 + 2] click reaction. It's kind of a necessity that, the field of nonlinear optics [20–26] has attracted substantial research interest, with most of the attention being focused on establishing the fundamental relationship between nonlinear optical response and chemical structures. Furthermore, the design and preparation of asymmetrical porphyrins would be more of a challenge.

In this paper, the high-yielding [2 + 2] click reaction was used to design and prepare asymmetrical porphyrins, and a series of porphrins with the different click moieties were obtained. The different conjugated π-systems and electron-withdrawing properties of the novel porphyrins may be discussed based on the series or amount of click moieties. Maybe, they had the potential applications as the nonlinear optical materials or optical-limiting materials.

2. Result and discussion

2.1. Synthesis

The synthesis scheme of porphyrins was shown in Fig. 1, and the highlight parts represented click structures of charge-transfer porphyrin complexes. After the porphyrin (**R**) that branched chain contained alkynyl needed to be synthesized, the synthesis of symmetrical and asymmetrical porphyrins with different click moieties involved a two-step procedure. First, by controlling the reactant molar ratio, the series of single substituted **R-X** (**R-1**, **R-2**, and **R-3**) was synthesized by the high-yielding [2 + 2] click reaction [27] using the first electron acceptors (**TCNE**, **TCNQ**, and **F_4-TCNQ**) as click reagents [13–26]. Then the second electron acceptors were appended by the similar way to obtain **R-XY** (**R-11**, **R-12**, **R-13**, **R-22**, **R-23**, **R-33**). As far as we know, it is very difficult to synthesize the asymmetrical porphyrin-system for enhancing the push-pull character with highly asymmetrical substitution [28–31]. In this paper, we try to synthesize the symmetrical porphyrins with two same reactable groups first, then try to make one of the reactable groups to react with click reagent by controlling the feed weight ratio. The symmetrical porphyrins with two same click moieties also can be synthesized by the one step method, and the excess of click reagents were added. The asymmetrical porphyrins were simply synthesized by the high-yielding [2 + 2] click reaction here, but the total yields still were limits in the yields of porphyrin (**R**) itself and reactant that branched chain contained alkynyl. It is significant to note that the mixtures of two products and one reactant are obtained for synthesizing the asymmetric click products. In the experimental section, we showed different yields for every chemical composition. Due to great difference in polarity from the click moieties, all the porphyrin derivatives could be very

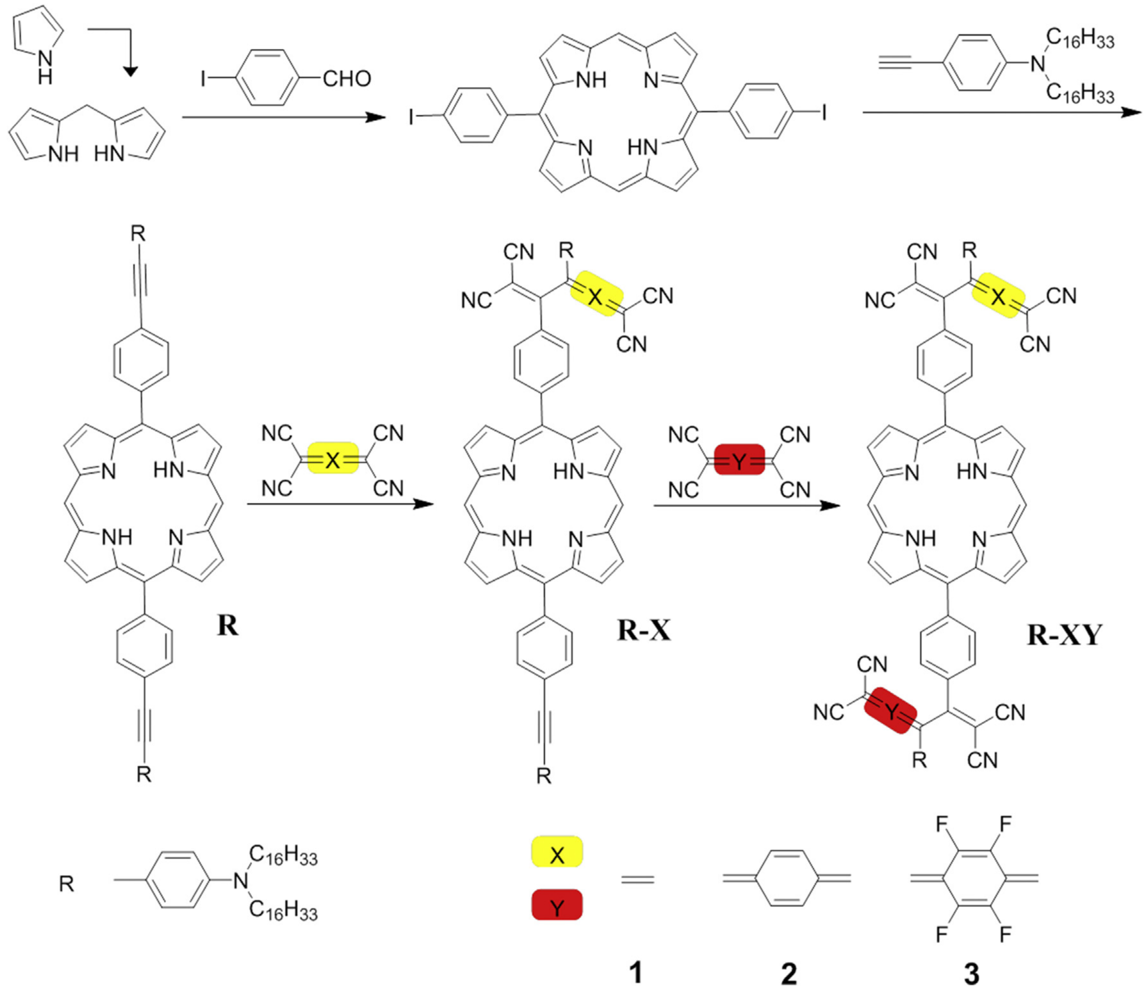

Fig. 1. General scheme for the synthesis of porphyrins.