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Coordination-induced broadband optical nonlinearity through axial bonding of pyridine anchored methine-bridged polypyrrole to metal-porphyrins

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ABSTRACT

A facile route to assemble pyridine anchored methine-bridged polypyrrole to metal-porphyrins through axial bonding has been demonstrated, and the as-prepared nanocomposites exhibit very distinctive broadband nonlinear optical performances compared to their precursors at both 532 and 1064 nm, due to an accumulation effect.

1. Introduction

The increased utilization of high intensity laser beams has rendered great challenges for designing efficient nonlinear optical (NLO) materials to protect human eyes and various delicate optical instruments, so it is of critical importance to explore and evaluate innovative NLO materials required for the practical applications [1]. It is now clear that organic-inorganic nanocomposites offer novel and improved performances for NLO and quantum optical applications. New variations of the conducting polymers or porphyrins have recently been generated for this purpose [2]. Among the conducting polymers, polypyrrole has emerged as a promising class of NLO materials [3]. Structural modifications of this polymer can lead to optimized properties for specific applications. Porphyrins as planar, electron-donor and aromatic materials have been widely used to design and prepare highly efficient optoelectronic materials, due to their remarkably high extinction coefficient in the visible-light region and prospective photochemical electron-transfer ability [4]. There is still a need to create superior self-assembled materials as building blocks for novel optical applications. Indeed, the well-organized self-assemblies have been demonstrated to exhibit a better performance than their individual constituent molecules [5]. The ability to prepare self-assemblies with defined optoelectronic properties is an essential premise for future applications.

Taking above into account, we wondered if the combination of polypyrrole and optoelectronic porphyrin molecules would afford species that possess not only the intrinsic properties of polypyrrole and porphyrins, but also novel functions originating from the mutual electronic interactions between polypyrrole and porphyrins; multifunctional nanometer-scale systems for optoelectronic applications may thereby be generated. However, to the best of our knowledge, there is no report in the literature of the fabrication of axially functionalized metalloporphyrin-polypyrrole nanocomposites. In this contribution, we designed and prepared three non-covalently functionalized polypyrrole with metalloporphyrins by assembling pyridine anchored methine-bridged polypyrrole (PPy) to metal-porphyrins (MTPPs, M = Zn, Co and Cu) through axial bonding. Special attention is paid to the effects of central metal ions on the photophysical and NLO properties of the PPy-MTPP nanocomposites. These nanomaterials exhibit very distinctive broadband NLO properties compared to their precursors at both 532 and 1064 nm, due to an accumulation effect.

2. Experimental

Synthesis of pyridine anchored methine-bridged polypyrrole (PPy): The PPy was obtained through the APS-catalyzed polymerization. The polymerization mixture was pyrrole (1.20 g, 17.88 mmol), pyridine-4-carbaldehyde (0.48 g, 4.47 mmol), ammonium persulfate (APS, 10 mg), tetrabutylammonium iodide (TBAI, 10 mg), 3 mL of THF, and 3 mL of deionized water. The reaction mixture was kept at room temperature for 24 h. After the reaction was finished, the resultant dark suspension was filtered through a nylon membrane, and the collected solid was washed with deionized water, THF and EtOH, until the filtrate was colorless. The desired PPy polymer was obtained as a black powder, and was dried under vacuum overnight. For the purpose of comparison, the

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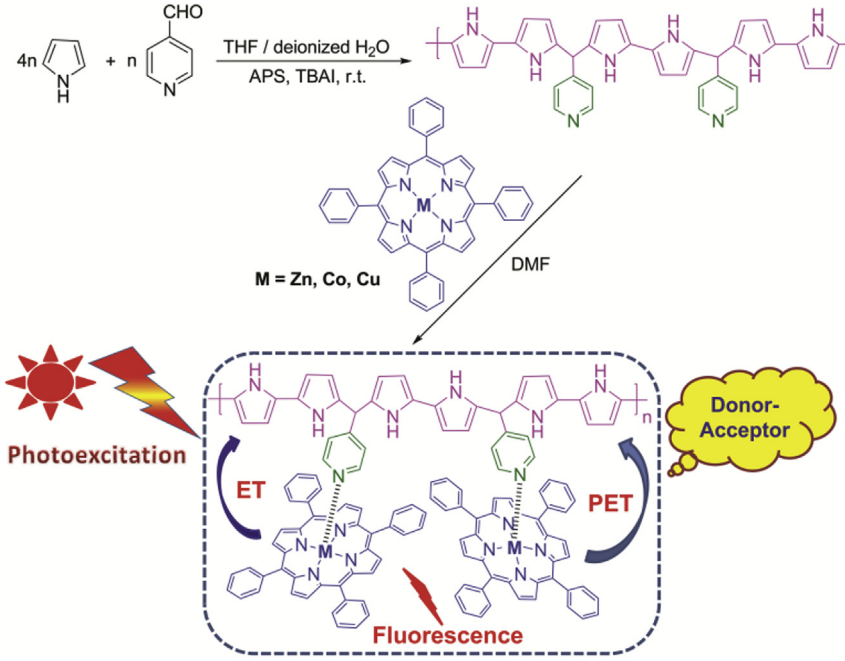

Scheme 1. Synthetic routes and schematic representation of part of the structure of PPy-MTPP nanocomposites.

benzene anchored methine-bridged polypyrrole (PPy-C_6H_5) were also prepared by the same method just using benzaldehyde instead of pyridine-4-carbaldehyde.

Assembly of PPy to metal-porphyrins: In a typical synthetic procedure (Scheme 1), 50 mg PPy was added to a solution of 10 mg MTPPs (M = Zn, Co and Cu) in 15 mL anhydrous DMF, and the resultant mixture was stirred at 145 °C under N_2 for 24 h. After the reaction was complete, the temperature was allowed to cool to room temperature while stirring was maintained. The resultant purple solution was poured into iced water (100 mL) and then filtered through a nylon membrane. To remove excess MTPPs and other contaminants, the filter cake was washed with deionized water, CH_2Cl_2 and EtOH, after which the filtrate was colorless. The product was dried overnight under vacuum at room temperature, affording the desired PPy-MTPP nanocomposites as a black powder. Control experiments, in which the reactant PPy bearing pyridine groups was replaced by PPy-C_6H_5 having benzene units, were also performed to confirm the formation of PPy-MTPP nanocomposites. The formation of these nanocomposites (PPy-ZnTPP, PPy-CoTPP and PPy-CuTPP) was further confirmed by FTIR, TEM, SEM, and TGA spectroscopic techniques (see Supporting information, Figs. S1–S4).

Nonlinear optical measurements: The NLO and optical limiting (OL) performances were investigated by using open-aperture Z-scan, which has been widely used to study the third-order NLO process. Since the sample experiences different incident laser energy at each position as it moving along the z direction, any nonlinearity in transmission can be revealed by this measurement. In the present work, the Z-scan experiments were performed by employing a mode-locked Nd:YAG laser of 4 ns pulses, operated at the fundamental 1064 nm and its second harmonic, 532 nm. DMSO solutions of the as-prepared samples were positioned at the focal point (z = 0) of a lens with a focal length of 30 cm, and the cells were then moved along the axis of the incident beam (z-direction) with respect to the focal point. A quartz cuvette with 1 mm length of optical path was used to hold the sample solutions, the linear transmittance of which was adjusted to be 75%. The OL curves, which can be plotted as normalized transmission versus input fluence, were extracted from the open-aperture Z-scan data of the samples. To avoid cumulative thermal effects interfering with experiments directed at identifying the major OL mechanisms, the laser pulses were delivered at a low frequency of 2 Hz; each pulse of light was therefore ensured to encounter a fresh sample.

3. Results and discussion

Porphyrins and metalloporphyrins can interact with graphene through π-stacking between their electron-abundant aromatic cores and the conjugated surfaces of graphene [6–8]. Similar interactions between metalloporphyrins and PPy are expected to occur, which can be identified from the ground-state absorption spectroscopy. Shown in Fig. 1 is the UV/Vis absorption spectra of the samples in N,N-dimethylformamide (DMF) solutions. The pure PPy displays a strong absorption band at 425 nm, corresponding to the polaron and bipolaron

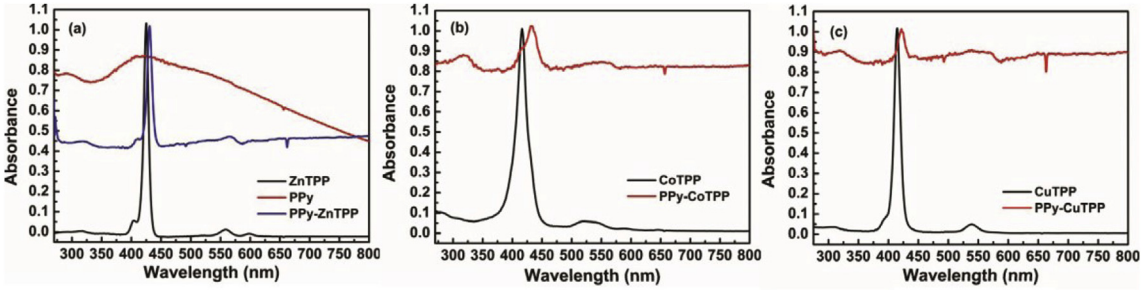

Fig. 1. UV/Vis absorption spectra of (a) ZnTPP, PPy and PPy-ZnTPP, (b) CoTPP and PPy-CoTPP, and (c) CuTPP and PPy-CuTPP, in DMF.