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Optical materials: Studying the role of hetropolyacid to enhance the nonlinear optical responses of porphyrin in their hybrids system

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ABSTRACT

Nonlinear optical responses are measured to investigate the role of hetropolyacid (**HPA**) in porphyrin-Lindqvist type {$\sim$**P$_M$@HPA**} hybrid systems, {where **P$_M$@HPA** = [$(TBA)_8\{(MTPPN_4)(Mo_6O_{18})_4\}$]; M = 2H (**1**) and Mn (**2**)}. The well-known Z-scan technique with wavelength (λ) = 532 nm and pulse duration of $\tau = 6$ ns is used. The results clearly show the significant enhancement in nonlinear self-defocusing effect and reverse saturable absorption under closed and open-aperture configuration for **P$_M$@HPA** hybrids. It is also observed that the second hyperpolarizability γ values, {**1** (4.639×10^{-29} esu) < **2** (5.214×10^{-29} esu)}, are directly proportional to the discrepancy of LUMO level (ΔE) values {**1** (2.214 eV) < **2** (2.339 eV)} while they are inversely proportional to the HOMO − LUMO energy gap E_g values {**1** (2.003 eV) > **2** (1.862 eV)} in the **P$_M$@HPA** hybrid system where the porphyrin moiety acts as electron donor whilst **HPA** acts as electron acceptor. Therefore, the emergence of a facile electron transformation from the porphyrin moieties to the low-lying LUMO levels of **HPA** is mainly responsible for the enhancement in nonlinear optical responses of **P$_M$@HPA** hybrids system. As a consequence the hybrid compounds can be fascinating for optical limiting applications.

1. Introduction

Porphyrin-based nonlinear optical (NLO) materials have attracted significant research interests in the recent years owing to their fast response speed, flexibility, and facile modification with potential applications in the technology of optronics including all-optical switching, signal processing, and ultrafast optical communications etc. [1–4]. In such kind of NLO materials, porphyrin plays a key role to tune or enhance the optical nonlinearities because of their highly delocalized aromatic π-electron system, and small HOMO- LUMO energy gap [5]. NLO responses can also be tuned by mainly controlling two factors; 1) real part that is marked as nonlinear refraction (n_2) which has further scope in ultra-fast optical signal processing and 2) imaginary component ($\mathrm{Im}\chi^{(3)}$) that is useful for optical limiting [3]. In this context, highly conjugated materials normally possess strong third-order optical nonlinearity [2]. Recently, many approaches (such as asymmetric-, symmetric-, expanded-porphyrins, oligomers and porphyrin-based hybrids) are used to tune the NLO responses [6–10]. However, some limitations are associated with such kind of systems, especially the large π-conjugated porphyrin systems show saturation effect with respect to optical nonlinearity, which are still common obstacle towards getting awesome porphyrin-based NLO materials [11].

On the other hand, hetropolyacids (**HPAs**) are considered as potential candidates in the field of catalysis, biology, pharmacy, and material science because of their distinctive property in which they can exchange multiple electrons without any significant structural changes [12–14]. Consequently, **HPAs** are also considered as fascinating building blocks which can play an important role in hybrid system and are thought to be potential candidates in the optical fields [13]. Recently, we have developed and synthesized numbers of hybrid systems based on porphyrins and polyoxometalates (i.e., Dawson, Keggin and Anderson) which are either formed by electrostatic interactions or interconnected by covalent bonding [15–19]. The results imply that the hybrids composed of one Dawson anion moiety and one porphyrin

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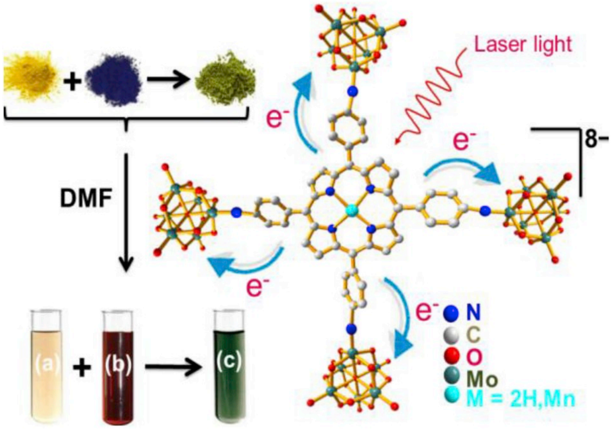

Scheme 1. The schematic diagram represents the role of **HPA** in the **P_M@HPA**, $[(MTPPN_4)(Mo_6O_{18})_4]^{8-}$ {M = 2H (**1**) and Mn (**2**)}, hybrid systems under light. The yellow, purple and green powders represent the $[(C_4H_9)_4N]_2[Mo_6O_{19}]$, $(NH_2)_4$TPP and a hybrid compound whereas their corresponding solutions in DMF are shown in (a), (b) and (c) respectively.

moiety bonded by covalent interaction through aromatic ring substituents exhibit remarkable enhancement in NLO response and the hybrid wherein Anderson type **HPA** is coupled covalently to porphyrin through shorter bridge has NLO response superior to the hybrid, wherein Anderson type HPA is bonded via longer bridge to porphyrin, and the hybrid having two porphyrins connected to Anderson type **HPA** shows more enhancement than the hybrid having single porphyrin fused to Anderson type HPA [15,16]. The HPA having lower LUMO level (versus LUMO of porphyrin moiety) can act as electron acceptor making easy the transfer of electrons from porphyrin moieties (acting as electron donor to HPAs), and the resulting hybrids exhibit better optical nonlinearities [19]. It is found that Hetropolyacids-porphyrin hybrid systems are one of the areas which are fruitful for exploitation of their nonlinear optical (NLO) responses [20]. Therefore, such systems are thought to be promising candidates for device applications in photonics and optoelectronics and high potential as lower power optical limiting (OL) materials.

In the present work, NLO responses are measured to investigate the role of **HPA** in the third- order NLO properties of **P_M@HPA** hybrids system (Scheme 1). For the sake of investigation, previously reported **P_M@HPA** hybrids system has been selected [21], {where $(TBA)_8[(MTPPN_4)(Mo_6O_{18})_4]$ {M = 2H (**1**) and Mn (**2**)} and measured their NLO responses for the first time by using well know Z-scan technique. The results clearly indicate that the hybrid compounds **1** and **2** show remarkable enhancements in nonlinear self-defocusing effect and reverse saturable absorption under closed and open-aperture configuration for **P_M@HPA** system. Additionally, optical-limiting thresholds are obtained being 0.473 J/cm^2 for **1** and 0.513 J/cm^2 for **2**, implying their high potential as low-power optical-limiting materials. The results open a new avenue for future exploration of **P_M@HPA** systems with remarkable NLO response because of increasing the acceptor strength more electron density will be transferred from the core of porphyrin to **HPAs**.

2. Materials and apparatus

P_M@HPA hybrids, {M = 2H (**1**) and Mn (**2**)} were synthesized and characterized according to reported method [21]. UV–vis. spectra were recorded with a UV-2550 spectrophotometer (Shimadzu). Cyclic voltammograms (CV) was obtained on a CHI660B electrochemical analyzer in dry DMF at room temperature at the rate of 10 mV/s in the presence of 0.1 M $[(n\text{-butyl})_4N]PF_6(TBAPF_6)$ as a supporting electrolyte. A glassy carbon electrode was used as a working electrode, Ag/AgCl as a reference electrode and a Pt wire as an auxiliary electrode. The scan range of the CV was selected carefully from the wide range to small range to ensure the peak used for calculating the HOMO or LUMO levels. Measurements of the third-order nonlinear optical properties of all the compounds were done using an EKSPLA NL303 Q-switched Nd:YAG laser. Photo-luminescence measurements were recorded by using a Hitachi F-7000 FL fluorescence spectrophotometer with both excitation and emission slits of 5 nm, using a xenon arc lamp as the light source (150 w), the photomultiplier tube voltage was 400 V, the scan speed was 1200 nm min^{-1}.

3. Results and discussion

3.1. Third-order nonlinear optical and optical limiting (OL) studies

The third-order nonlinear optical properties of all the compounds: **HPA** = $[(C_4H_9)_4N]_2[Mo_6O_{19}]$, $(NH_2)_4$TPPM (M = 2H and Mn), hybrids **1** and **2** were investigated by using the single beam Z-scan technology [22,23]. It is a well-known and efficient technique for the determination of the nonlinear optical parameters of materials, providing simultaneously the third-order nonlinear susceptibilities, the magnitude of nonlinear absorption as well as a sign of the nonlinear refraction. An EKSPLA NL303 Q-switched Nd:YAG laser with a wavelength of $\lambda = 532$ nm, a pulse duration of $\tau = 6$ ns, and a repetition rate of 10 Hz with intensity of light at the focus $E_0 = 20\,\mu J$ was employed as the light source.

The linear transmittance of the far-field aperture S (defined as the ratio of the pulse energy passing through the aperture to the total pulse energy) was measured to be 0.25. The laser beam (i.e., GAUSSIAN light beam), after being focused by a 20 cm focal length lens into the sample placed in an $L = 1$ mm path-length quartz cell, was passed through a large-area beam splitter. Before the measurements, the system was calibrated using CS_2 in a quartz cell as reference. The Z-scan curves under open aperture and closed aperture configuration along with the corresponding fits [23] are measured for all compounds: **HPA**, $(NH_2)_4$TPPM (M = 2H and Mn), hybrids **1** and **2**.

In the experimental setup of Z-scan technique, a portion of the input beam is divided by a beam splitter and measured by a photo detector to determine the incident energy on the entrance face of the sample. The other beam propagated in the *z*-direction and passed through the sample. The sample is translated along the *z*-direction and with nonlinear refractive index causes an additional (depending on *z*) focusing (at positive n_2) or defocusing (at negative n_2) of the light beam. It changes the transmitted intensity of the beam passing through a finite aperture placed in the far-field when moving the sample along *z* (closed aperture Z-scan). For an open aperture Z-scan, the aperture was removed to collect the entire laser beam transmitted through the sample. The intensity of the transmitted beam through the sample was measured with a closed- and open-aperture scheme using the photo detector fed to the digital power meter (Scheme 2).

The following formulas are used to calculate the third-order nonlinear refractive index n_2 (esu), the nonlinear absorption coefficient β (esu) and the third-order optical nonlinear susceptibility $\chi^{(3)}$ (esu).[22]

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}|\Delta\phi_0|, \tag{1}$$

$$\Delta\phi_0 = kL_{eff}\gamma I_0, \tag{2}$$

$$L_{eff} = \left(1-e^{\alpha_0 L}\right)/\alpha_0, \tag{3}$$

$$n_2(esu) = \frac{cn_0}{40\pi}\gamma(\mathrm{m^2/W}), \tag{4}$$

where, $\Delta T_{P\text{-}V}$ is the normalized peak-valley difference, $\Delta_{\varphi 0}$ is the phase shift of the beam at the focus, $K = 2\pi/\lambda$ is the wave vector, I_o (unit: W/m^2) is the intensity of the light at focus, L_{eff} is the effective length of the sample defined in terms of the linear-absorption coefficient α_0 and the true optical path length through the sample, n_0 is the linear refractive index, and γ is optical Kerr constant. The conversion can be realized