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Synthesis, characterisation and optical studies of new tetraethyl-rubyrin-graphene oxide covalent adducts

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ABSTRACT

Tetrathia-rubyrin and graphene oxide (GO) covalent adduct was synthesized, characterised and optical properties were studied. GO-Rubyrin adducts showed fluorescence quenching of rubyrin due to electron or energy transfer from rubyrin to graphene oxide, which also reflected in UV–vis absorbance spectroscopy. The non-linear optical responses were measured through Z scan technique in nano-second regime. The enhanced optical non-linearity was observed after attachment of GO with rubyrin, can be ascribed to the photo-induced electron or energy transfer from the electron rich rubyrin moiety to the electron deficient GO.

1. Introduction

Graphene is an emerging star in the field of non-linear optics (NLO) [1–3]. Graphene oxide (GO) and graphene were demonstrated as NLO materials with second harmonic generations by various groups in nanosecond and picosecond regimes [1–3]. However, its insolubility in all solvents, limits its use in real optical devices. To improve its dispersing ability, a plenty of efforts has been made in derivatization of graphene sheets with other organic molecules with pronounced optical properties and solubility. There are only two plausible ways for making these adducts one by using van der Waal interactions and other by covalent-coupling [4,5]. Since, adducts formed by absorption of functional moieties on the surface are not stable and qualitatively irreproducible [5], covalent bonding strategy is gaining more attention due to the formation of strongly bonded adducts and reproducibility [6]. Formation of these covalent adducts not only will improve the dispersibility but also perturbs the chemical, optical and physical properties. Porphyrins are known to make these adducts because of their stability (structural and thermal) and optical properties. Till date, there are plenty of reports on NLO materials based on porphyrins, metalloporphyrins and phthalocyanins [7–9]. Since, by increasing π-conjugation in porphyrins we can induce or improve non-linear optical responses, expanded porphyrins are of prime interest in Non-Linear optics. Expanded porphyrins (EPs) have more than four meso-linked pyrroles or thiophenes or selenophenes and they can cover the entire optical absorption spectra, depending on the number of meso carbons and/or number of pyrroles in the system [10,11]. Recently it has been reported that absorption cross-section (σ) in porphyrin increases with in conjugation length [11,12]. Especially expanded porphyrins (rubyrins, sapphyrins etc.) with thiophenes are gaining special interest due to their two photon absorption and high absorption cross-section induced by more planarity in its structure compared to their aza-derivatives [13]. Till date there are very few examples of porphyrin-graphene covalent and non-covalent conjugates and all of them are based on basic tetra pyrrolic porphyrin (Tetra phenyl porphyrin (TPP)) [14–20]. Till date, the adducts of graphene with rubyrin modified with thiophenes are unexplored.

Here, we are demonstrating the synthesis, characterisation and optical properties of covalently bonded graphene oxide adducts with 5-(4-hydroxyphenyl), 10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (Fig. 1). The 5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin is synthesized by reported method [21]. Which on esterification with acid chloride derivative of graphene oxide gives graphene oxide-rubyrine adduct. The adducts are characterised by various spectroscopic, thermal and microscopic techniques.

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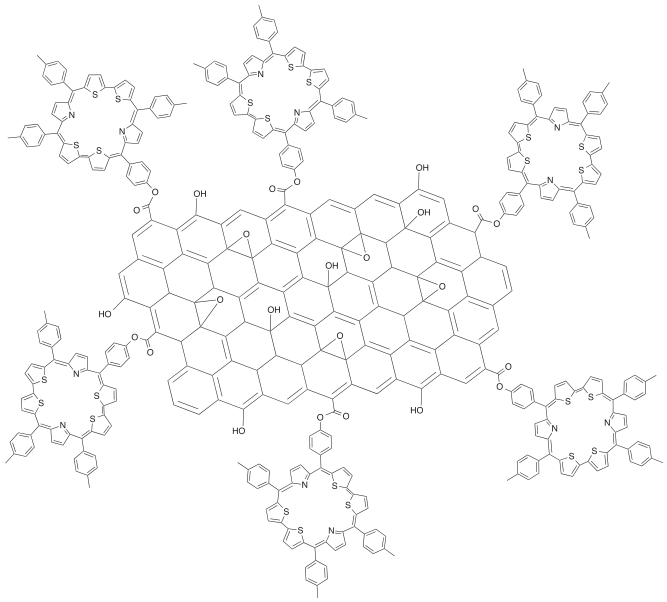


Fig. 1. Structure of GO-Rub adduct.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were procured from spectrochem, India, Fluka, Aldrich etc. Silica gel and basic alumina for Column chromatography was obtained from Sisco Research Laboratories, India. The graphite flakes (40 μm) was purchased from Sigma Aldrich and potassium permanganate, hydrogen peroxide (30%) from fluka. All the solvents like N, N-dimethyl formamide (DMF), chloroform ($CHCl_3$), thionyl chloride ($SOCl_2$) and dry tetrahydrofuran (THF) were distillated by using standard procedures.

2.2. Synthesis of 5-(4-Hydroxyphenyl),10,19,24-triphenyl-29,30,32,33-tetrathiarubyrin (Rub)

2.2.1. 5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (Rub)

The 5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin was synthesized by reported method (see Scheme 1) [21]. M. P. > 300 °C, ^{1}H NMR (Fig/ S1: 500 MHz, $CDCl_3$, δ) 11.47 (d, J = 21.5 Hz, 4H), 10.42 (d, J = 4.4 Hz, 4H), 9.01 (t, J = 4.9 Hz, 4H), 8.39 (dd, J = 16.7, 7.5 Hz, 8H), 7.76 (t, J = 8.6 Hz, 8H), 7.48 (d, J = 8.0 Hz, 3H), 2.85 (s, 9H)). LRMS (Figure S2): Calcd for $C_{55}H_{38}N_2OS_4$: m/z: 870.19; Found: 871.1 (M+H) Elemental analysis: Calcd (%) for $C_{55}H_{38}N_2OS_4$: C, 75.83; H, 4.40; N, 3.22; S, 14.72; Found: C 75.75, H 4.44, N 3.19, S 14.75.

2.3. Synthesis of acyl chloride - graphene oxide (GOCl)

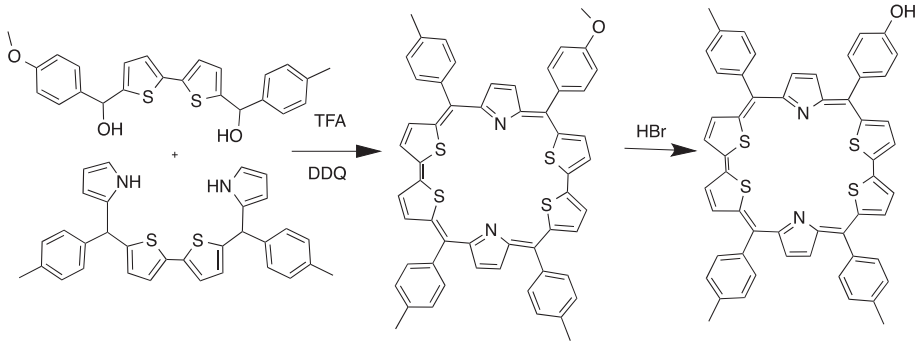
The graphene oxide was synthesized from graphite using modified hummers method [22]. GO powder (60 mg) was refluxed with freshly distilled $SOCl_2$ (40 mL) in the presence of DMF (1 mL) at 65 °C for ~18 h under anhydrous conditions. Excess solvent and $SOCl_2$ were removed by vacuum distillation. The product (GOCl) was dried under vacuum for 2 h and used for the next step without purification.

2.4. Synthesis of graphene oxide functionalized with rubyrin

GOCl (50 mg) and Rubyrin **1** (10 mg) were dissolved in DMF (20 mL) in presence of 0.5 mL of triethylamine (Et_3N) at 0 °C for 30 min under inert atmosphere. After completion of reaction, the reaction mixture was brought to room temperature and then kept undisturbed for 24 h. The resulting reaction mixture was ultracentrifuged and precipitate was successively washed to remove excess rubyrin with DCM, Acetone and water by ultracentrifugation and sonication, until no unreacted rubyrin remains in centrifuge. TLC ensured the absence of unreacted rubyrin in the final product. The final product of graphene oxide - rubyrin was dried in vacuum.

2.5. Characterisation

Absorption spectra were recorded with a Perkin Elmer (Lambda 35), UV−visible spectrophotometer in the range of 200–800 nm. Fourier transform infrared spectra were recorded in the transmission mode on a Perkin Elmer FTIR Spectrometer Spectrum 1000 spectrometer using the ATR method. Raman spectra were measured on a LabRAM HR from HORIBA Jobin−Yvon (532 nm laser source). Photoluminescence (PL) spectroscopy was done using a F-7000 FL Spectrophotometer. X-ray diffraction (XRD) measurements were performed at room temperature (25 °C) using Rigaku SmartLab X-ray diffractometer. Transmission electron microscope (TEM) analysis was carried out using the FEI Tecnai F30 S-TWIN TEM and using copper grid. The prepared samples were coated over silicon wafer. The sample was gold sputtering with 5 nm and subsequent imaging of the samples at 5 kV with SE2 detector using Carl Zeiss Ultra 55, field emission scanning electron microscope (FESEM). X-ray photoelectron spectroscopy (XPS) carried out using Kratos Axis Ultra X-ray Photoelectron Spectrometer(XPS). Thermogravimetric analyses (TGA) were carried out using a TA Instruments SDT Q600 V20.9 Build 20 under a 100 mL/min N_2 flow and a heating rate of 10 °C/min. ^{1}H NMR spectra were recorded with



Scheme 1. 5-(4-hydroxyphenyl), 10, 19, 24-tritolyl-29,30,32,33-tetrathiarubyrin.