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Fluorescence behaviour of supramolecular hybrids containing graphene quantum dots and pyrene-derivatized phthalocyanines and porphyrins

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ABSTRACT

Novel pyrene-derivatized zinc and cobalt phthalocyanines (Pcs) and porphyrins (Ps) were immobilized on graphene quantum dots (GQDs) to form GQDs-Pcs and GQDs-Ps supramolecular hybrids via the π–π stacking interaction method. Spectroscopic evidence shows that the resultant hybrids were stable owing to the strong π–π stacking interaction between the GQDs and the respective Pcs and Ps, thus leading to the fabrication of interesting and functional supramolecular hybrids by taking advantage of the delocalized π electron systems of GQDs and the macrocycles. The conjugates showed increased fluorescence quantum yields for the Pcs/Ps, but decreased values for the GQDs in the conjugates. These novel hybrid materials could potentially be deployed for studies in both fundamental and applied perspectives due to the synergistic contributions resulting from the combination of their excellent electronic and optical properties.

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1. Introduction

Graphene quantum dots (GQDs) possess excellent optical and electronic properties coupled with high photostability, aqueous solubility and bio-compatibility [1,2]. These properties have made GQDs attractive alternatives to semiconductor QDs for applications in fluorescence bio-imaging, sensing (biosensors and chemo-sensors), photocatalysis, drug delivery and as photosensitizers in photodynamic therapy (PDT) [3–6]. The presence of delocalized π electrons facilitates the interaction of GQDs with a wide array of aromatic molecules through non-covalent π–π stacking. The exploration of the potential of hybrid supramolecular assembles of GQDs and organic macrocycles such as phthalocyanines (Pcs) or porphyrins (Ps) is envisaged to considerably advance several areas of applications.

Phthalocyanines and porphyrins are structurally similar macrocyclic and aromatic compounds with unique electronic features such as high molar absorption coefficients, robust redox chemistry and ability to transfer and accept energy/electrons [7]. Over the years, Pcs and Ps have been deployed for various applications such as in organic photovoltaic devices, electrocatalysis, photocatalysis, photodynamic therapy (PDT), and non-linear optical (NLO) materials [8]. The versatility of these compounds is rooted in their excellent optical and electronic properties which make them appealing tools for the construction of supramolecular ensembles and functional hybrid materials [9].

Nanocomposites of Pcs or Ps with carbon-based nanomaterials such as carbon nanotubes (CNTs), fullerenes (C_{60}), graphene and graphene oxide have been widely explored in the literature with interesting applications in many areas [10–14]. However, not much is known about the characterization and photophysical behaviours of GQDs and Pcs or Ps nanocomposites. Recently, the fluorescence behaviour of GQDs in the presence of Pcs was reported [15]. Another study reported on the application of GQDs assembled with Ps as a probe for analyte sensing [16]. Fe (II) porphyrin loaded onto GQDs surface has been employed as a photocatalyst for the oxidation of alcohols [17]. GQDs and Pcs or Ps nanocomposites and their potentials are still relatively unexplored. Hence, it is highly imperative that more efforts be channelled in this direction.

In line with our interest and studies on nanocomposites of GQDs and Pcs or Ps and their potential applications, we characterized and explored the fluorescence behaviour of GQDs upon coordination to novel pyrene-derivatized Pcs/Ps (Zn and Co as central metals). Pyrene and its derivatives are known to have a

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strong affinity for carbon nanomaterials due to the presence of delocalized π electrons (sp^2 carbon) in their structures [18,19]. Pyrene-derivatized Pcs have been reported in the literature with phenoxy or oxo bridges, hence disrupted π conjugation [20,21]. There is only one report on a mono-pyrene substituted ZnPc where the π conjugation with pyrene was not disrupted [22]. Tetra-substituted pyrene-derivatized Pcs where the conjugation is not disrupted are presented in this work for the first time. It is also the first time where Co is used as a central metal for a pyrene-substituted Pc. CoPc/P complexes are known for their excellent electrocatalytic behaviour [23]. CoPc derivatives have been employed as components for molecular materials [24]. The presence of Co as a central metal in Ps/Pcs will result in reduced fluorescence behaviour due to the paramagnetic behaviour of Co metal. However, we show in this work that CoP/CoPcs have Förster resonance energy transfer (FRET) efficiency that is higher than those of the Zn derivatives. The synthesis of metal free tetrapyrene porphyrin (H_2TPyP) ligand used in this work has been reported [25]. Zn, Cu, Ni, Pt and Au derivatives of tetrapyrene porphyrin (TPyP) have also been reported [25–27]. The Co derivative is reported in this work for the first time. Also, studies on GQDs interactions with Pcs or Ps bearing pyrene units are non-existent in the literature.

In this study, GQDs were non-covalently coordinated to pyrene-derivatized Pcs or Ps via π–π stacking interaction. The pyrene moieties on the Pcs and Ps could assist in the immobilization of the complexes onto the GQDs due to the delocalized π electron structure of pyrene. GQDs-Pcs/Ps nanocomposites could expand and improve on areas of applications in which other carbon-based nanomaterials and their nanocomposites have achieved immense success [9,28].

2. Experimental

2.1. Materials

Cobalt (II) chloride, 1-pyrene- carboxyaldehyde, sodium acetate (CH_3COONa), anhydrous potassium carbonate, anhydrous sodium sulphate, quinine sulphate, Zn tetraphenyl porphyrin (ZnTPP), Zn phthalocyanine (ZnPc), and dialysis membrane tubing (MWCO 1.5 kDa) were obtained from Sigma Aldrich. Dimethyl formamide (DMF), dichloromethane (DCM), and deuterated DMF-d_7 were obtained from Merck. Absolute ethanol was obtained from SAARCHEM. Column chromatography was performed using silica gel. All other reagents and solvents were obtained from commercial suppliers and used as received. Graphene quantum dots (GQDs) were synthesized following procedures reported elsewhere [15]. Zinc tetraamino phthalocyanine (ZnTAPc) and cobalt tetraamino phthalocyanine (CoTAPc) were synthesized according to procedures described in the literature [29]. 5,10,15,20-Tetra(1-pyrenyl)porphyrin (H_2TPyP) and zinc 5,10,15,20-tetra(1-pyrenyl) porphyrin (ZnTPyP, **3**) were synthesized as previously reported [25].

2.2. Equipment

Excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Ground state electronic absorption was performed on a Shimadzu UV-2550 spectrophotometer in the range of 300–800 nm. Infra-red spectra were collected on a Bruker Alpha model FT-IR Spectrometer with platinum-ATR. ^{1}H NMR spectra were obtained using a Bruker AVANCE 600 MHz NMR spectrometer in DMF-d_7. Elemental analyses were done using a Vario-Elementar Microcube ELIII. Mass spectra data were collected on a Bruker Auto-FLEX III Smart-beam TOF/TOF mass spectrometer using dithranol as the matrix in the positive ion mode. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser. Details have been previously described [15].

X-ray powder diffraction patterns were recorded on a Bruker D8 Discover equipped with a Lynx Eye detector, using Cu-K_α radiation (l = 1.5405 Å, nickel filter). Data were collected in the scan range of 2θ = 10° to 60°, scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. A Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd:YAG laser and liquid nitrogen cooled germanium detector) was used to collect Raman data as reported previously [15]. Transmission electron microscope (TEM) micrographs were obtained using a Zeiss Libra 120 TEM operating at 80 kV. Dynamic light scattering (DLS) experiments were done on a Malvern Zetasizer nanoseries, Nano-ZS90.

2.3. Synthesis

2.3.1. Zinc phthalocyanine 1-pyrene-1-carboxaldehyde (ZnTPyPc, 1)

A mixture of zinc tetraamino phthalocyanine (ZnTAPc) (0.10 g, 0.092 mmol) and 1-pyrene-1-carboxaldehyde (0.094 g, 0.41 mmol) was refluxed in 5 mL dry ethanol (EtOH) at 80–85 °C under an inert atmosphere for 2 days. The crude product was cooled to room temperature and washed, respectively in ethanol, methanol, acetone and *n*-hexane by centrifugation and was allowed to dry in air. The product was thereafter purified over a silica gel column using a DMF/EtOH mixture (2:1). Complex **1** yield: (40.5%). UV–vis (DMF): λ_{max}/nm (log ε): 724 (5.02), 648 (2.74), 396 (2.81), 360 (5.19). Anal. Calc. for $C_{100}H_{52}N_{12}Zn$, C, 80.77; H, 3.52; N, 11.30. Found: C, 81.14; H, 3.97; N, 10.82. MALDI-TOF-MS (*m*/*z*): 1486 amu; Found: 1490 $[M-4H]^+$. FT-IR [ATR (ν_{max}/cm^{-1})]: 3102 (C—H aromatic), 1737–1635 (C—N imine), 1455 (C=C aromatic). ^{1}H NMR (600 MHz, DMF-d_7): *δ* ppm: 11.10 (s, 4H, imine-H), 9.72 (d, *J* = 9.3 Hz, 4H, Py-H), 8.86 (d, *J* = 7.9 Hz, 4H, Pc-H), 8.72–8.67 (m, 8H, Pc-H), 8.56 (m, 9H, Py-H), 8.41 (dd, *J* = 24.6, 17.0 Hz, 6H, Py-H), 8.55–8.54(m, 8H, Py-H), 8.43–8.37(m, 9H, Py-H) (Scheme 1).

2.3.2. Cobalt phthalocyanine 1-pyrene-1-carboxaldehyde (CoTPyPc, 2)

The synthesis and purification process of complex **2** was as outlined for complex **1**, except that cobalt tetraamino phthalocyanine (**CoTAPc**) (0.05 g, 0.98 mmol) was employed (Scheme 1).

Complex **2** yield: (42%). UV–vis (DMF): λ_{max}/nm (log ε): 706 (4.25), 641 (2.47), 395 (3.47) 360 (5.18). Anal. Calc'd for $C_{100}H_{52}N_{12}Co$, C, 81.13; H, 3.54; N, 11.35. Found: C, 81.90; H, 4.02; N, 11.05. MALDI-TOF-MS (*m*/*z*): 1482 amu; Found: 1486 $[M-4H]^+$. FT-IR [ATR (ν_{max}/cm^{-1})]: 1728–1626 (C—N imine), 1446 (C=C aromatic).

2.3.3. Cobalt 5,10,15,20-tetra(1-pyrenyl) porphyrin (CoTPyP, 4)

The synthesis of complex **4** (Scheme 2) was achieved by the metallation of H_2TPyP as follows: In a 25 mL reaction flask, the unmetallated porphyrin (H_2TPyP) (0.047 g, 0.042 mmol) was dissolved in 15 mL toluene followed by the addition of sodium acetate (0.31 g, 3.78 mmol), anhydrous K_2CO_3 (0.31 g, 2.23 mmol) and $CoCl_2$ (0.19 g, 1.07 mmol). The reaction mixture was refluxed under argon for 24 h, after which it was allowed to cool to room temperature, neutralized with acetic acid and washed thoroughly with water. The organic layer was separated and dried under anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified over a silica gel column using DCM as the eluent.

Yield: (61%). UV/Vis (DMF) λ_{max} nm (log ε): 440 (4.27), 563 (3.86), Anal. Calc. for $C_{84}H_{44}N_4Co$: C, 86.36; H, 3.80; N, 4.80, Found: C, 85.28; H, 3.39; N, 4.39. MALDI-TOF-MS (*m*/*z*): 1167 amu, Found: 1165 $[M+2H]^+$.

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