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# Perylene diimide dye/layered carbide charge transfer composite: Design, synthesis, and photophysical properties

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ABSTRACT

Brominated perylene diimide dye (BrPDI) was found to intercalate into a host layer of two-dimensional OH-$Ti_3C_2$ to produce BrPDI–O$Ti_3C_2$ nanocomposites that gave a stable dispersion in polar solvents. Compared to the parent BrPDI, BrPDI–O$Ti_3C_2$ exhibited a novel lower energy electronic transition (max. at ~700 nm) in addition to solvatochromism. Furthermore, molecular simulations (density functional theory) indicated that intramolecular charge transfer occurred from the perylene core units to the OH-$Ti_3C_2$ moiety in the HOMO–LUMO excitation process of BrPDI–O$Ti_3C_2$.



## 1. Introduction

Recently, the preparation of a large family of 2D transition metal carbide and/or nitride materials known as MXenes has been reported, with this preparation involving extraction of the A-element from layered ternary carbides such as $Ti_3AlC_2$ and other MAX phases (M=transition metal; A=an A group element; and X=either C or N) [1]. Note that 2D MXene surfaces are not M-terminated, but covered with oxygen-containing groups such as OH, in addition to fluorine. OH-$Ti_3C_2$, for example, has a layered structure with abundant activated Ti-OH sites, and has potential for application in environmental fields such as absorption and detection [2]. Furthermore, the hydroxyl group in 2D MXene surfaces may provide an opportunity to construct novel organic–inorganic functional nanocomposites *via* chemical methods.

Perylene diimide derivatives (PDIs) are promising and versatile candidates for use in organic photo-electronic applications [3–5]. Substitution at bay positions is an effective strategy for designing new functional PDIs [6]. Furthermore, the preparation of perylene diimide dye-inorganic nanocomposites has received increased attention due to their potential application in optoelectronic devices [7,8]. The LUMO and HOMO energy levels of perylene diimide derivatives make them particularly suitable for such applications, with values ranging from −3.8 to −4.2 eV and from −5.8 to −6.1 eV, respectively [9,10]. As the work function of many carbides is between −4.7 and −5.2 eV [11], novel charge transfer composites can be designed using OH-$Ti_3C_2$ as the electron acceptor and perylene diimide derivatives as the electron donors.

We herein report, for the first time, the intercalation reaction of OH-$Ti_3C_2$ with *N,N′*-diethylhexyl-1,7-dibromo perylene diimide (BrPDI) dissolved in DMF, using $K_2CO_3$ as the catalyst.

## 2. Results and discussion

A schematic representation of the MXene intercalation reaction is shown in Fig. 1c. X-ray diffraction (XRD) showed that the (0001) peaks were present following intercalation with BrPDI, but shifted to lower 2$\theta$ angles (Fig. 1a). The initial c-lattice parameters (c-LPs) of OH-$Ti_3C_2$ and F-$Ti_3C_2$ were 1.28 nm and 0.99 nm, respectively. Following exposure to a DMF solution of BrPDI in the presence of $K_2CO_3$ at 80 °C for 24 h, the c-LPs increased to 2.14 nm. The internal arrangement of this nanostructure was obtained from the molecular dimensions of the dye. The molecular breadth of BrPDI obtained from the energy-minimized structure using Chem 3D Pro 8.0 was 0.83 nm (Fig. 1d). This value is closer to the difference between the initial c-LPs of OH-$Ti_3C_2$ and the c-LPs of OH-$Ti_3C_2$ intercalated with BrPDI. This indicates that the perylene diimide adopts a confined perpendicular geometry within the 2D carbide layers (Fig. 1c).

The resulting BrPDI–O$Ti_3C_2$ nanocomposites were then characterized using Fourier transform infrared (FTIR) and $^1$H nuclear

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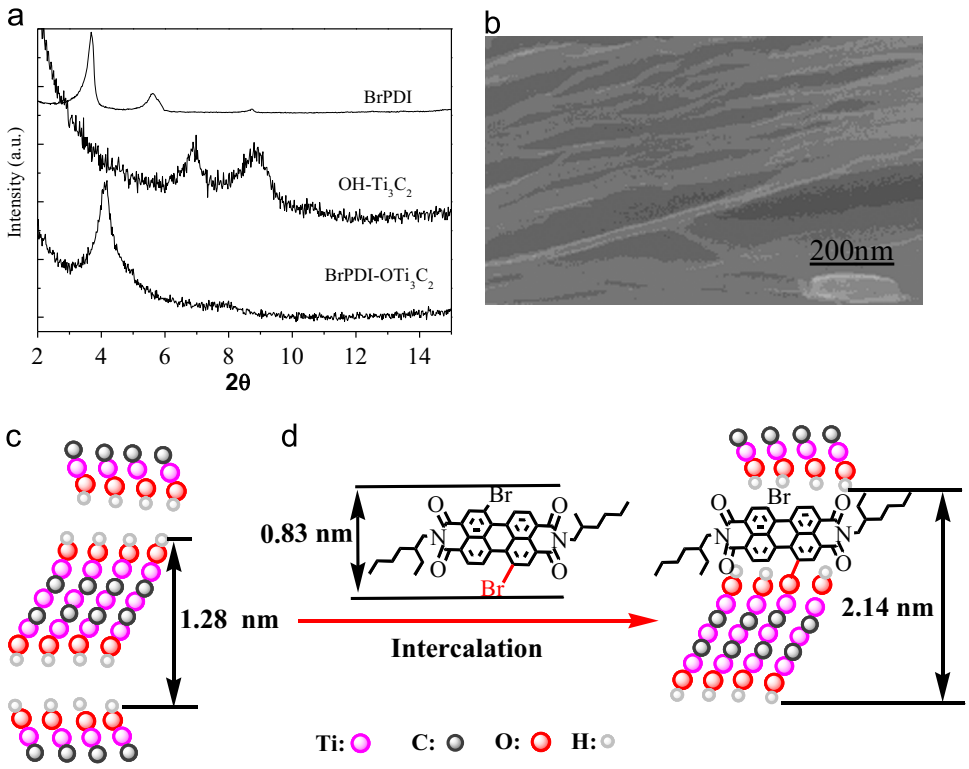


**Fig. 1.** (a) XRD spectra of BrPDI, OH-$Ti_3C_2$, and their resulting nanocomposites. (b) SEM of OH-$Ti_3C_2$. (c) A schematic representation of the OH-$Ti_3C_2$ structure before and after BrPDI intercalation. (d) Molecular dimensions of the dye.

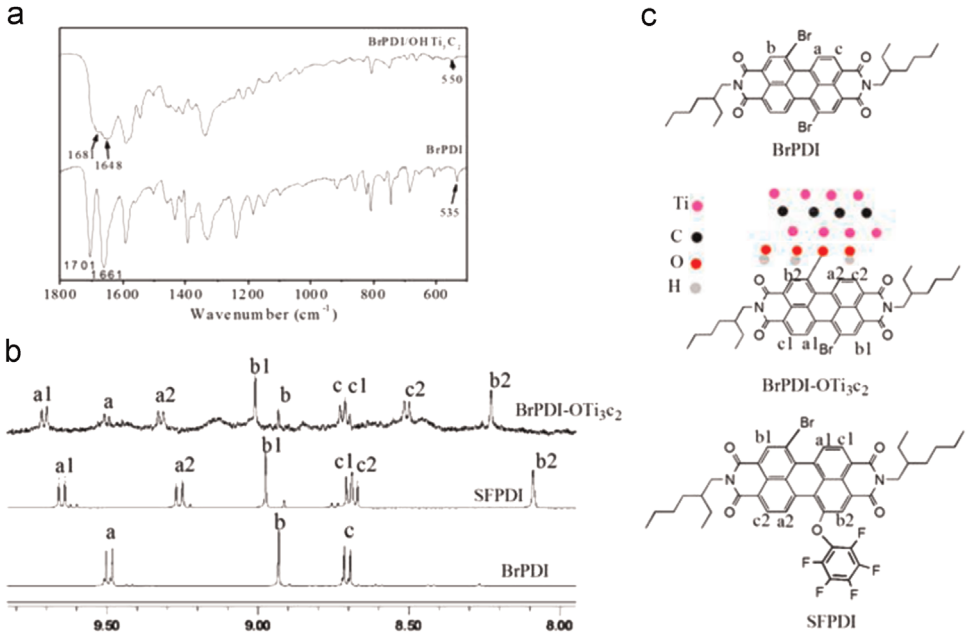


**Fig. 2.** a) FTIR spectra of BrPDI/OH$Ti_3C_2$ and BrPDI. b) $^1$H NMR spectra of BrPDI, SFPDI, and BrPDI–O$Ti_3C_2$ nanocomposites. c) Structures of BrPDI, BrPID–O$Ti_3C_2$, and SFPDI.

magnetic resonance spectroscopy (NMR) (Fig. 2). The FTIR spectrum of BrPDI exhibited characteristic absorption bands at 1701 $cm^{-1}$ (imide stretch), 1661 $cm^{-1}$ (C=O stretch), 1590 $cm^{-1}$ (C=C stretch), 1330 $cm^{-1}$ (C–N stretch), and 535 $cm^{-1}$ (aromatic C–Br stretch) [12]. In contrast to BrPDI, the FTIR spectra of BrPDI–O$Ti_3C_2$ nanocomposites displayed a clear shift in the characteristic absorption bands, with the imide and C=O stretching bands appearing at 1681 and 1648 $cm^{-1}$, respectively, and the C–Br stretch appearing at 550 $cm^{-1}$ suggesting that intercalation was successful. The intensity ratio of the aromatic C–Br band to the C=O band decreased significantly compared with the corresponding FTIR spectrum of BrPDI, indicating that at least one Br atom reacts during the treatment of OH-$Ti_3C_2$ with BrPDI. To aid interpretation of the BrPDI–O$Ti_3C_2$ chemical structure, an asymmetrical perylene diimide dye (SFPDI) was synthesized (see S1). The $^1$H NMR spectrum of the BrPDI–O$Ti_3C_2$ nanocomposite shows two groups of signals of different intensities in the aromatic region: one group of signals (a, b and c) was observed in the $^1$H NMR spectrum of BrPDI, while the other group ($a_1$, $a_2$; $b_1$, $b_2$; and $c_1$, $c_2$) was observed in the $^1$H NMR spectrum of SFPDI. This indicates the presence of both