



# Covalent functionalized black phosphorus quantum dots



Francesco Scotognella <sup>a, b, \*</sup>, Ilka Kriegel <sup>c, d</sup>, Simone Sassolini <sup>d</sup>

<sup>a</sup> Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

<sup>b</sup> Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Giovanni Pascoli, 70/3, 20133, Milan, Italy

<sup>c</sup> Department of Nanochemistry, Istituto Italiano di Tecnologia (IIT), Via Morego, 30, 16163, Genova, Italy

<sup>d</sup> Molecular Foundry, Lawrence Berkeley National Lab, One Cyclotron Rd, Berkeley, CA 94720, USA

## ARTICLE INFO

### Article history:

Received 5 October 2017

Received in revised form

5 November 2017

Accepted 8 November 2017

### Keywords:

Quantum dots

Black phosphorus

Nanomaterial functionalization

## ABSTRACT

Black phosphorus (BP) nanostructures enable a new strategy to tune the electronic and optical properties of this atomically thin material. In this paper we show, via density functional theory calculations, the possibility to modify the optical properties of BP quantum dots via covalent functionalization. The quantum dot selected in this study has chemical formula P<sub>24</sub>H<sub>12</sub> and has been covalently functionalized with one or more benzene rings or anthracene. The effect of functionalization is highlighted in the absorption spectra, where a red shift of the absorption is noticeable. The shift can be ascribed to an electron delocalization in the black phosphorus/organic molecule nanostructure.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The elemental two-dimensional analogues of graphene, i.e. germanene, phosphorene, silicene, and stanene, have emerged as a class of fascinating nanomaterials useful for optics and electronics [1–4]. Black phosphorus (BP) is particularly interesting because of its electronic band gap, which is 0.3 eV in the bulk, but that shows a layer-dependent tunability up to 2 eV [5–12]. From an optical point of view, a strong photoluminescence [8,13] and in-plane anisotropy [14] have been observed in BP. The integration of black phosphorus in one-dimensional photonic crystals and microcavities has been also presented [15].

An interesting treatment to BP is the covalent functionalization. Li et al. studied extensively with a first-principle approach the covalent functionalization of BP [16]. Ryder et al. experimentally demonstrated the covalent functionalization and passivation of exfoliated BP [17]. BP nanostructures enable a new strategy to tune the properties of the material. The first appearance of BP quantum dots is reported in 2015 [18,19]. The size dependence of absorption and emission of BP quantum dots has been studied [20] and show a peculiar behaviour, with the absorption gap following an inversely proportional law to the dot diameter, while the emission wavelength follows a mixed behaviour: proportional to the size up to

1.8 nm and inversely proportional above 1.8 nm. Moreover, the suitability of phosphorene quantum dots for photocatalysis has been discussed [21], while phosphorene quantum dot – fullerene composites have been suggested for solar energy conversion [22].

In this paper we study the possibility to tune the optical properties of BP quantum dots via covalent functionalization. The chosen quantum dot has chemical formula P<sub>24</sub>H<sub>12</sub> and has been covalently functionalized with one or more benzene rings or anthracene. The effect of such functionalization with aromatic hydrocarbons is highlighted in the absorption spectra, where a red shift of the absorption is noticeable. The shift can be ascribed to electron delocalization in the nanostructure.

## 2. Methods

The functionalized BP quantum dots have been designed with the Avogadro package [23]. The optimization of the ground state geometry and the calculation of the electronic transitions have been performed with the package ORCA 3.0.3 [24], using the B3LYP functional [25] in the framework of the density functional theory. The Ahlrichs split valence basis set [26] and the all-electron nonrelativistic basis set SVPalls1 [27,28] have been employed. Moreover, the calculation utilizes the Libint library [29].

## 3. Results and discussion

In Fig. 1 we show the optimized geometry of the P<sub>24</sub>H<sub>12</sub> BP

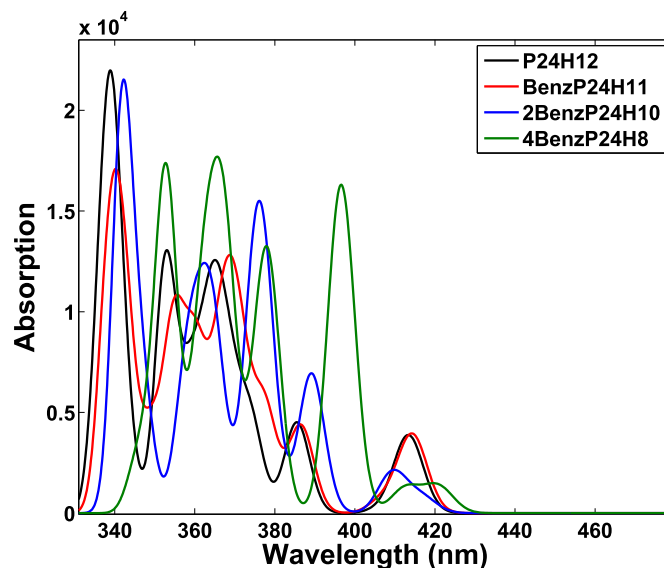
\* Corresponding author. Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy.

E-mail address: [francesco.scotognella@polimi.it](mailto:francesco.scotognella@polimi.it) (F. Scotognella).

quantum dot and three different functionalized quantum dots, with one, two, and four benzene rings. We report the coordinates of such geometries in the [Supporting Information](#).

We studied the electronic transitions of the four different BP quantum dots with density functional theory calculations and we report the absorption spectra in [Fig. 2](#). The transitions with the corresponding oscillator strengths are reported in the [Supporting Information](#). In the simulated absorption spectra we have considered a spectral linewidth of  $500\text{ cm}^{-1}$ . The bare quantum dots P24H12 are given in black ([Fig. 2](#)) and show several resonances dominating the spectrum with an absorption onset around 420 nm. We remark here that we observe a slightly different energy position than in [Ref. \[20\]](#) which is most probably due to a different optimization of the geometry. The functionalization of P24H12 with a benzene ring (we refer to this structure as BenzP24H11, red curve in [Fig. 2](#)) leads to a mild red shift of 1 nm of the first transition, while the higher energy transitions seem more influenced. Instead, the spectra of the BP quantum dot with two and four benzene rings (2BenzP24H10 and 4BenzP24H8, respectively) are significantly affected by the presence of the benzene rings, with a red shift of the first transition of 4BenzP24H8 by 7 nm (green curve in [Fig. 2](#)) with a remarkable strong peak at 397 nm appearing for 4BenzP24H8. This can be ascribed to a wavefunction delocalization in the black phosphorus/organic molecule hybrid system. In [Fig. 3](#) we report the LUMO orbitals for P24H12 and 4BenzP24H8 and the spreading of the wavefunction over the benzene rings in 4BenzP24H8 is clearly visible. In the [Supporting Information](#) we reported the orbitals involved in the lowest transition.

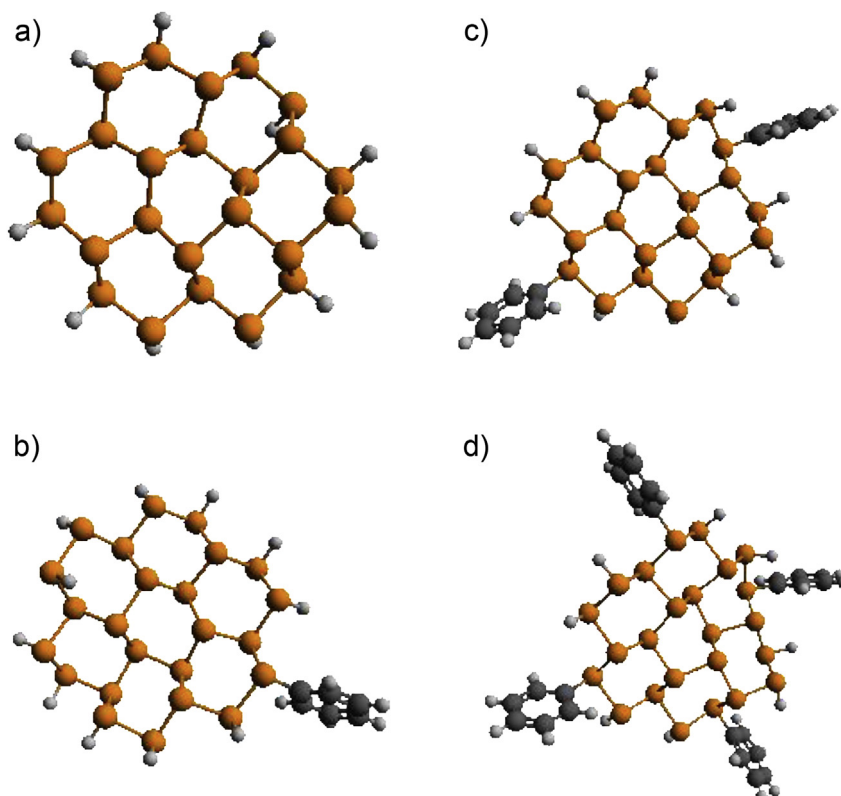
To study further the role of wavefunction delocalization we further studied the covalent functionalization of P24H12 with anthracene, an aromatic molecule composed of three benzene rings. The optimized geometry is shown in [Fig. 4](#) and highlights the



**Fig. 2.** Absorption spectra of P24H12 (black curve), BenzP24H11 (red curve), 2BenzP24H10 (blue curve), and 4BenzP24H8 (green curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

planar structure of this molecule due to the aromatic nature. The coordinates are reported in the [Supporting Information](#).

We report in [Fig. 5](#) the absorption spectra of P24H12 (black curve) and the BP quantum dot functionalized with anthracene (AnthP24H11, red curve). A mild red shift of 1.6 nm is noticeable for the first transition. To underline that this shift is not to a



**Fig. 1.** Optimized ground state geometry of (a) the P24H12 dot and of the benzene functionalized dots: (b) BenzP24H11; (c) 2BenzP24H10; (d) 4BenzP24H8.

Download English Version:

<https://daneshyari.com/en/article/7908076>

Download Persian Version:

<https://daneshyari.com/article/7908076>

[Daneshyari.com](https://daneshyari.com)