The Growth and Fluorescence of Phthalocyanine Monolayers, Thin Films and Multilayers on Hexagonal Boron Nitride

Manal Alkhamisi[a], Vladimir V. Korolkov[a], Anton S. Nizovtsev[b,c], James Kerfoot[a], Takashi Taniguchi[d], Kenji Watanabe[d], Nicholas A. Besley[b], Elena Besley[b] and Peter H.Beton[a]

[a]School of Physics & Astronomy, University of Nottingham, Nottingham NG7 2RD, U.K.

[b]School of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.

[c]Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Academician Lavrentiev Avenue 3, 630090, Novosibirsk, Russian Federation.

[d]National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

ELECTRONIC SUPPLEMENTARY INFORMATION

1. Computational details

The geometric parameters of the species under study were optimized using the range-separated hybrid ωB97X-D functional with empirical dispersion correction[1] in combination with the correlation-consistent cc-pVDZ basis set[2] employing the (75,302) integration grid. The maximum overlap method (MOM)[3] was used for the structural optimization of compounds in the S_1 excited state. The *h*BN surface was modelled by a flake consisting of 65 boron atoms and 65 nitrogen atoms, the flake's edges were capped with hydrogen atoms. The B–N bond lengths were calculated to be of 1.44 Å in average. Atomic positions of the surface were optimized and kept fixed in the subsequent calculations. The adsorption energy of H_2Pc molecule was calculated using the ωB97X-D/cc-pVTZ method with the structure optimized with the smaller cc-pVDZ basis set. The most energetically preferred adsorption site was used for calculating excited state properties. Excitation energies corresponding to absorption ($S_1 \leftarrow S_0$ transition) and fluorescence ($S_0 \leftarrow S_1$ transition) were determined with time-dependent density functional theory (TD-DFT) at the same level of theory using the (MOM-)ωB97X-D/cc-pVDZ optimized structures of the S_0 and S_1 states, respectively.

0–0 energies were estimated using zero-point vibrational energies computed at the (MOM-)ωB97X-D/cc-pVDZ level of theory within harmonic approximation. To save computational time, vibrational frequencies of adsorbed molecules were calculated without taking into account *h*BN surface. Atomic partial charges were calculated within ChelpG formalism.[4] All calculations were performed with the Q-Chem software package.[5]

Results and discussion

The equilibrium structures of the H_2Pc molecule adsorbed on the *h*BN surface are shown in Figure S1. The molecule-surface separation was calculated to be *ca.* 3.3 Å. The adsorption energy computed at the ωB97X-D/cc-pVTZ level is 3.35 eV (Table S1). To calculate fluorescence energies, structural optimization of the first singlet excited state, which is the first dipole-allowed excited state for all systems under study, was performed using MOM. It is worth noting that MOM provides structural parameters which are comparable to those calculated by TD-DFT but at lower computational cost.[6]

Figure S2 shows that the difference between the S_0 and S_1 relaxed structures is rather small (Δr = 0.00–0.02 Å). Upon interaction with the surface bond lengths of H_2Pc are only slightly changed and absorbed molecule maintains its planarity. The most intense band in the fluorescence spectra of isolated and adsorbed H_2Pc arises from the electronic transition between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals which have π and π* character, respectively (Figure S3). The corresponding transition density is presented in Figure S4 (see Krueger et al.[7] for a discussion of transition density).

Calculated absorption ($S_1 \leftarrow S_0$) and fluorescence ($S_0 \leftarrow S_1$) energies with the corresponding transition dipole moments and oscillator strengths for compounds under study are collated in Table S2. Computed vertical transition energies agree well with the available experimental data ($\Delta\Delta E$ = 0.01–0.08 eV; Table S3). 0–0 energies that include relaxation of the final electronic state and zero-point energy correction were also calculated (Table S3).

When going from the gas phase to absorbed on the *h*BN surface the calculated position of maximum in the fluorescence spectrum is red-shifted by 0.11 eV. This corresponds to the non-resonant shift discussed in the main text. In order to explain the origin of this contribution to the observed red shift in fluorescence spectra after adsorption of H_2Pc molecule, an energy decomposition of the shift into the contributions from molecular distortion, electrostatic and orbital interactions was performed according to methodology suggested by Hochheim and Bredow.[8] The orbital interactions between the molecule and the surface atoms were found to be responsible for the red shift (ΔE_{chem} = 0.11 eV; Table S4).

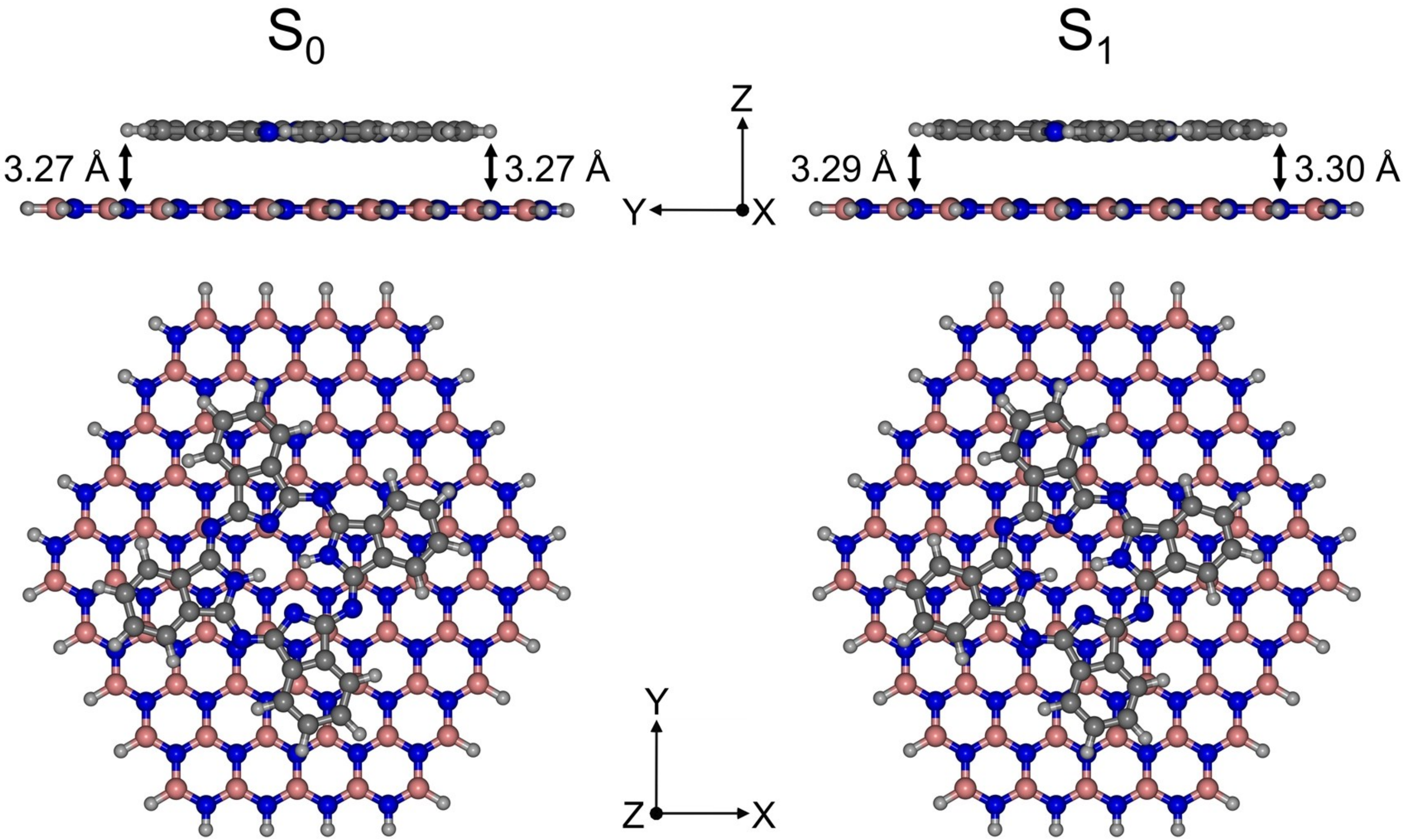

Figure S1. Structure of the H_2Pc/*h*BN system in S_0 and S_1 electronic states calculated at the (MOM-)ωB97X-D/cc-pVDZ level of theory.

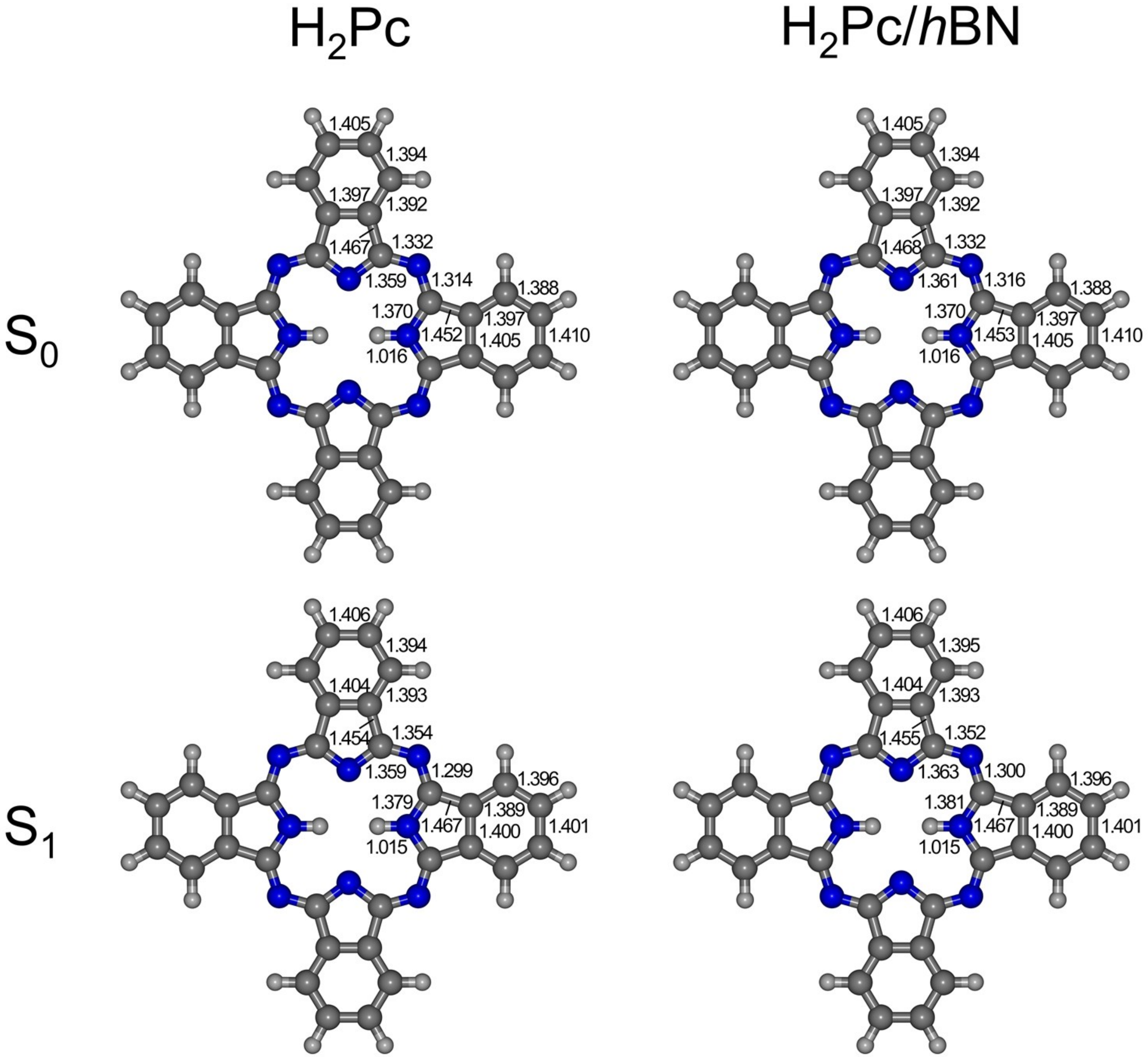
H2Pc
H2Pc/hBN
S0
S1
1.405
1.394
1.397
1.392
1.467
1.332
1.359
1.314
1.388
1.370
1.397
1.452
1.410
1.405
1.016
1.405
1.394
1.397
1.392
1.468
1.332
1.361
1.316
1.388
1.370
1.397
1.453
1.410
1.405
1.016
1.406
1.394
1.404
1.393
1.454
1.354
1.359
1.299
1.396
1.379
1.389
1.467
1.401
1.400
1.015
1.406
1.395
1.404
1.393
1.455
1.352
1.363
1.300
1.396
1.381
1.389
1.467
1.401
1.400
1.015

Figure S2. Selected bond lengths (Å) of H_2Pc in the gas phase and adsorbed on *h*BN in S_0 and S_1 electronic states calculated at the (MOM-)ωB97X-D/cc-pVDZ level of theory.

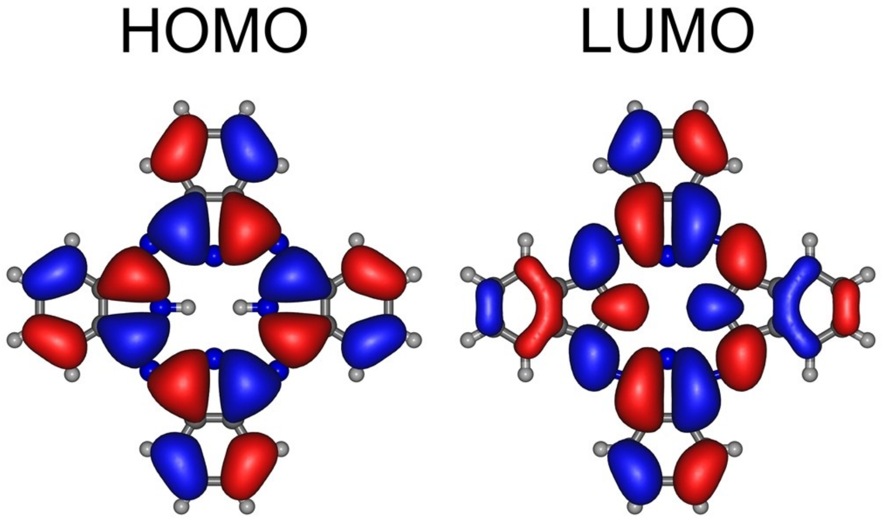

Figure S3. Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of H_2Pc in its equilibrium S_1 geometry on the *h*BN surface calculated at the *ω*B97X-D/cc-pVDZ level of theory. Isosurfaces with ±0.01 a.u. isovalues are shown.

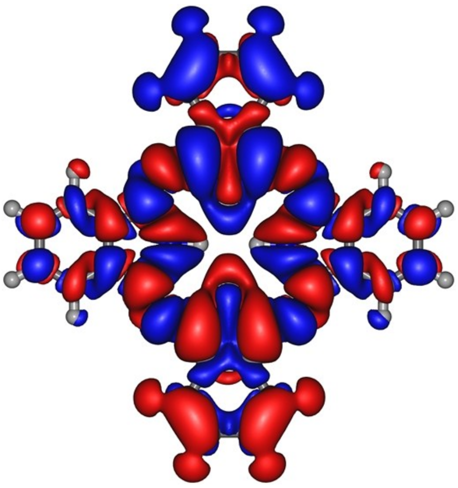

Figure S4. Transition density ($S_0 \leftarrow S_1$ fluorescence process) calculated for H_2Pc molecule in its equilibrium S_1 geometry on the *h*BN surface at the TD-*ω*B97X-D/cc-pVDZ level of theory. An isosurface with ±0.0003 a.u. isovalues is shown.

Table S1. Energy of adsorption of H_2Pc molecule on the *h*BN surface (ΔE_{ads}) calculated at the *ω*B97X-D/cc-pVTZ//*ω*B97X-D/cc-pVDZ and *ω*B97X-D/cc-pVDZ//*ω*B97X-D/cc-pVDZ (in parentheses) theoretical levels.

System	**ΔE_{ads}, eV**
H_2Pc/*h*BN	3.35 (3.68)

Table S2. Details of absorption ($S_1 \leftarrow S_0$) and fluorescence ($S_0 \leftarrow S_1$) processes for H_2Pc, H_2Pc/*h*BN (in parentheses) and H_2Pc at H_2Pc/*h*BN geometry (in brackets) calculated at the TD-*ω*B97X-D/cc-pVDZ//(MOM)*ω*B97X-D/cc-pVDZ level of theory. Energies of frontier molecular orbitals are also given.

	Absorption	**Fluorescence**
Transition energy, eV / nm	1.96 / 632 (1.88) / (660) [1.96] / [632]	1.87 / 663 (1.76) / (703) [1.87] / [662]
Transition dipole moment, D	(-7.89, 0.00, 0.00) ((-6.34, -3.07, 0.06)) [(-7.62, -2.02, 0.04)]	(0.00, -8.93, 0.00) ((-1.18, 7.92, 0.02)) [(-1.60, 8.77, -0.01)]
Oscillator strength, au	0.46 (0.35) [0.46]	0.57 (0.43) [0.56]
E_{HOMO} / E_{LUMO}, eV	-6.31 {-6.41} [a] / -1.66 (-6.31 / -1.71) [-6.31 / -1.66]	-6.26 / -1.88 (-6.26 / -1.93) [-6.26 / -1.88]
$\Delta E_{\mathrm{HOMO\text{-}LUMO}}$, eV	4.65{4.03} [b] (4.60) [4.65]	4.38 (4.33) [4.38]

[a] -IP (ionization potential) experimental value. [9]

[b] Value calculated by GW-BSE method. [9]

Table S3. Absorption ($S_1 \leftarrow S_0$), fluorescence ($S_0 \leftarrow S_1$), and 0–0 energies of H_2Pc and H_2Pc/*h*BN calculated at the TD-*ω*B97X-D/cc-pVDZ//(MOM)*ω*B97X-D/cc-pVDZ level of theory.

System	**Absorption, eV / nm**	**Fluorescence, eV / nm**	**$\Delta E^{0\text{–}0}$, eV / nm**
H_2Pc	1.96 / 632 [a] [1.88 / 661] [d] [1.83 / 677] [e]	1.87 / 663 [b] [1.83 / 677] [e]	1.88 / 661 [c]
H_2Pc/*h*BN	1.88 / 660 [a]	1.76 / 703 [b] [1.75 / 708] [f]	1.75 / 706 [c]

[a] Vertical absorption energy.

[b] Vertical fluorescence energy.

[c] Zero-point vibrational energy corrected 0–0 transition energy.

[d] Experimental value (free jet). [10]

[e] Experimental value (Ar matrix). [10]

[f] Experimental value. This work.

Table S4. Energy decomposition of fluorescence shift for H_2Pc/*h*BN calculated at the TD-*ω*B97X-D/cc-pVDZ//(MOM)*ω*B97X-D/cc-pVDZ level of theory. All values are given in eV.

System	E_{gas}	E_{dist}	E_{pc}	E_{ads}	ΔE_{dist}	ΔE_{elec}	ΔE_{chem}	ΔE_{tot}
H_2Pc/*h*BN	1.87	1.87	1.87	1.76	0.00	0.00	0.11	0.11

2. Experimental Methods

Substrates are prepared by mechanically exfoliating hBN flakes from mm-scale crystals using the scotch tape method; the flakes are transferred to thermally oxidised silicon wafers, with an oxide thickness of 300 nm. The flakes are then immersed in toluene for approximately 12 hours, annealed in H_2:Ar (5% : 95%) at 400 °C for 8 hours, subjected to brief flame annealing prior to the introduction to the vacuum system.

Fluorescence spectroscopy is carried out using a Horiba LabRAM HR spectrometer, equipped with a 660 nm excitation laser. Laser powers in the range of 1-50 µW are used to reduce photo-bleaching and damage to the sample. The sample morphology is determined using AFM, carried out under ambient conditions in tapping mode using the Asylum Research Cypher S with Mulit75Al-G silicon cantilevers from Budget Sensors.

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