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Impact of substituent effects on the Raman spectra of structurally related N-substituted diketopyrrolopyrroles

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Abstract

Control over vibrational frequency modes is important in optimising the performance and behaviour of conjugated organic materials employed as charge transfer mediators and optical components in optoelectronic devices. Raman spectroscopy represents a powerful technique that can be employed to determine the structural implications of molecular substitution on photophysical properties in such conjugated organic systems. Herein, we report for the first time, the optimised geometries for a series of eight systematically varied N-substituted diketopyrrolopyrroles as well as their experimental and computed Raman spectra, with special emphasis placed upon their spectral band assignment. Clear out-of-plane structural re-arrangements, including pyramidalisation of the lactam nitrogens arising from intramolecular H-bonding interactions were observed upon N-substitution in the reported systems, leading to significant vibrational frequency shifts for ν(N-C) and ν(C=O) modes. In addition, mode scaling factors were determined and found to be comparable with those reported previously, employed using the same density functional. The following study addresses the implications of structural variation on the progression of those intense Raman modes which play a key role in tuning the photophysical properties of N-substituted diketopyrrolopyrrole systems and as such should be of broad interest to those developing functional materials based upon this molecular motif.

Keywords: Diketopyrrolopyrroles, Density Functional Theory, Raman, M06-2X, scaling factors.

1. Introduction

Over the previous 30 years, diketopyrrolopyrrole (DPP) derivatives have been widely used in the pigment industry as high performance colorants owing to their excellent properties such as brightness, low solubility and light and weather fastness.[1-5] More recently there has been an increasingly large surge of interest in DPP-based materials employed as charge transfer mediators in optoelectronic devices, either in the form of small molecules or polymers.[6-18] Currently, we are engaged in the in-depth investigation and rational design of DPP-based small molecules with special interest in their structure-property relationships, aimed to develop crystalline thin film devices for detection purposes and charge transport.[19] Control over the photophysical properties via systematic substitutions performed on a common moiety plays a crucial role in achieving optimum performance in various types of optoelectronic devices.[20, 21] Along these lines, in centrosymmetric systems such as those investigated herein, the most intense Raman active modes are known to exert control over the vibronic progression in absorption and emission spectra, where the quantum spacing $\hbar\omega$ determines the spacing between the maxima of the different Gaussian peaks forming the progression, as well as determining the intramolecular reorganisational energies, allowing a mode-by-mode analysis where the total reorganisation energy is computed as the sum of the products of the frequency of the different vibrational modes weighted by the associated electron vibrational coupling or Huang-Rhys factors.[22, 23] These denote the one dimensional displacement of the potential energy surfaces of the initial and final states involved in the transition with respect to the reaction coordinate.[22, 24, 25] As a consequence, rationalisation of the substitution effects on shifting the frequency of the most intense Raman active modes represents a very powerful tool in engineering future materials to match with desirable molecular properties. In light of the nature of the intermolecular interactions exhibited by conjugated organic materials, many of these systems can crystallise in a variety of polymorphic forms with associated optoelectronic properties than can differ dramatically.[20, 26] In this regard, Raman spectroscopy also serves as a useful technique to investigate the presence of polymorphism.[27]

Despite the increasing interest in DPP-based conjugated systems, there is a clear lack of Raman studies on DPP-based materials.[28, 29] Reported studies thus far, tend to focus on non N-substituted chromophores which are inherently less soluble owing to intermolecular H-bonding interactions between monomers. Substitution on the lactam nitrogens lead to an enhancement of the molecular solubility by disrupting these intermolecular interactions, making N-substituted DPP based systems more suitable candidates for optoelectronic purposes than their insoluble pigmentary analogues. In the following, we report for the first time, optimised geometries that are computed for a series of systematically varied N-butyloxycarbonyl (BOC) and N-benzyl diketopyrrolopyrrole derivatives as well as their experimental and computed Raman spectra with special emphasis placed upon band assignment of experimental frequencies by means of the computed harmonic modes. The different systems investigated are illustrated in Figure 1. These were given names with a form of **XYDPP** arising from their topology where **X** and **Y** represent the substitution on the R_1 and R_2 positions respectively.

FIGURE 1 HERE

The paper is laid out as follows: firstly, the experimental and computational methods employed are briefly described. We then describe the conformational searches performed on these systems, followed by a structural analysis of the most stable conformers obtained for **HBOCDPP** and **HBDPP** as representatives of the two investigated series. The C_i optimised geometries of N-benzyl systems are compared to the optimised geometries from their respective crystal structures, including an analysis of the different relative orientation of the benzyl groups with respect to the DPP core. The remainder of the paper focuses on the C_i and C_i^{xray} (optimised employing single crystal structures as starting points) optimised geometries of N-BOC and N-benzyl systems respectively. An in-depth analysis of these structural analogues and associated differences on progression from non-substituted DPP to phenyl and N-substituted systems is performed, highlighting the observed pyramidalisation of the lactam nitrogen atoms upon substitution. This is then followed by an examination of the computed and experimental Raman spectra focusing on spectral shifts observed upon substitution, with special emphasis placed upon the band assignments. The effects of intramolecular H-bonding interactions as well as polymorphism in **ClBDPP** are also investigated. We dedicate the final part of this section to a comparison of the experimental and computed harmonic vibrational frequencies for the most intense Raman active modes and discuss the averaged uniform scaling factor.

2. Experimental

Raman analyses were performed utilising a Thermo-Scientific DXR Raman microscope operated with the associated OMNIS array automations and OMNIC Atlus software supplied by the manufacturer. All measurements were performed by means of the 780 nm excitation wavelength in order to minimise fluorescence emission. All of the measurements were performed employing a 1mW power laser at sample. The powder samples were presented employing a microscope slide. Each measurement was taken as an average of 40 scans. In addition, each powder sample was interrogated 4 times, focusing on different sample areas to further discard possible anisotropic phenomenon occuring in these materials.

Powder X-ray diffraction (PXRD) data was collected using a Siemens D500 X-ray diffractometer at room temperature over the range 5-50° 2θ (Cu K-alpha 1.5406 Å, step size 0.020°, 1s per step). The instrument was operated by means of the software DIFFRAC plus XRD commander, supplied by the manufacturer.

2. 1 Synthesis

All of the N-benzyl DPP derivatives studied herein were prepared and characterised according to our previously reported methods.[26] The N-BOC derivatives **HBOCDPP**, **ClBOCDPP** and **BrBOCDPP** were prepared according to those methods reported previously and were spectroscopically identical in each case.[30-32] The solid state structure of **HBOCDPP** was confirmed to be the reported β-phase by pXRD analysis.[33] For the synthesis of **TbBOCDPP**, Pigment Orange 73 was obtained from BASF and used as received. Unless otherwise stated, all other starting materials and reagents were obtained from Sigma Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were determined using a JEOL ECS400 400 MHz spectrometer (in $CDCl_3$). Elemental analyses were carried out using the service provided at Jagiellonian University in Krakow, Poland. FTIR analyses were carried out on the neat samples by attenuated total reflectance using a Perkin Elmer, Spectrum One FTIR Spectrometer, with Universal ATR Sampling Accessory.

Di-tert-butyl-3,6-bis(4-tertbutylphenyl)-1,4-dioxopyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (TbBOCDPP)[34]

In a two-necked, oven-dried round bottom flask, Pigment Orange 73 (1.00 g, 2.49 mmol) was dissolved in 70 ml anhydrous THF and the resulting solution was purged with nitrogen for 10 minutes. To this mixture was added DMAP (0.80 g, 6.54 mmol) dissolved in 20 ml anhydrous THF and the resulting mixture was stirred for 15 minutes under nitrogen atmosphere at room temperature. Di-tert-butyl dicarbonate (2.72 g, 12.50 mmol) was then added and the mixture was stirred for 24 hours at room temperature. The resulting solution was concentrated under vacuum and the residue recrystallized from hexane/DCM (1:1) to give the title product (1.00 g, 67 %). ^{1}H NMR ($CDCl_3$): 1.36 (18H, s, ^{t}butyl), 1.44 (18H, s, ^{t}butyl), 7.49 (4H, d, ArH); 7.70 (4H, d, ArH); ^{13}C NMR ($CDCl_3$): 27.49 (CH_3), 31.08 (CH_3), 35.14 (^{t}butyl-C), 85.02 (^{t}butyl-C), 111.72 (C=C), 125.33 (C=C), 125.39 (C=C), 128.37 (C=C), 146.02 (C=C), 148.31 (C=C), 155.26 (C=O), 159.61 (C=O)**.** IR (ATR) cm^{-1}: 3010 (ArH), 2965 (CH_3), 1743 (C=O), 1710 (C=O), 1621 (C=C), 1589 (C=C), 1486 (C=C), 1285 (C-O), 1259 (C-O), 827 (ArH). Anal. Calcd. for $C_{36}H_{44}N_2O_6$: C, 71.97; H, 7.38; N, 4.66. Found: C, 71.07; H, 7.24; N, 4.46.

3. Computational methods

Geometries of the investigated derivatives were optimised by means of M06-2X density functional[35] at 6-31G(d) level without applying any constraints. A triple zeta basis set, 6-311G(d) was employed for the iodo containing system, **IBDPP** in order to account for the larger number of core electrons.[26, 36-38] Negligible differences were observed between optimised geometries obtained by means of double and triple zeta basis sets of **HBDPP**. Optimised geometries were subject to infrared analyses returning non negative frequencies in all cases, consistent with a true equilibrium minimum.[39-41] Harmonic frequencies and Raman intensities were computed at the same level of theory. All of the density functionals and basis sets employed were as implemented in Spartan ’10 v.1.1.0 software.[42]

4. Results and discussion

4.1 Structural analysis

In light of the different conformations that DPP based derivatives can exhibit,[43] systematic conformational searches were performed on N-BOC and N-benzyl substituted DPPs at MMFF level (Merck Molecular Force Field, MMFF94[44]). It was observed that in all cases an array of 8 different conformers were yielded; 2 of these being significantly energetically favoured with a Boltzmann’s population of ca. 47%.

FIGURE 2 HERE

Figure 2 illustrates the optimised geometries of the two most stable conformers for **HBOCDPP** and **HBDPP**. Detailed structural examination of the optimised geometries of the different C_2 and C_i geometries of the N-BOC and N-benzyl substituted systems (SI 1), revealed negligible differences in bond lengths and angles throughout each series other than the different relative torsion of the phenyl rings with respect to the DPP core (SI 1).

FIGURE 3 HERE

The geometries of the N-benzyl investigated derivatives were optimised further utilising their crystal structures (C_i^{xray}) as starting points, displaying a lower twist of the phenyl rings with respect to the DPP core (SI 1) in addition to a more perpendicular orientation of the benzylic phenyl rings with respect to the core of the DPP (see Figure 3). In light of the exhibited polymorphism of **ClBDPP**,[26] its geometry was optimised from the two different polymorphs. Despite the substantial variation in the dihedral angles of these crystal structures (44.03 and 20.07° for the α and β polymorphs respectively), optimised geometries obtained from each of the polymorph structures were observed to exhibit negligible differences in their computed twist angles (27.96 and 28.08° for $C_i^{xray\alpha}$ and $C_i^{xray\beta}$ respectively) and bond lengths ($\Delta_{BL} < 0.002$ Å).

FIGURE 4 HERE

We furthermore observed a clear out-of-plane structural re-arrangement of the central DPP core in these systems upon N-substitution, which we attribute to intramolecular H-bonding interactions (SI 2) as illustrated in Figure 4. These associated interactions are illustrated in Figure 4 (top) for **HBOCDPP** and **HBDPP**. Figure 4 (bottom) illustrates the out-of-plane re-arrangement of the BOC/benzyl groups with respect to the plane of the DPP core in **HBOCDPP** and **HBDPP**. We attribute the greater effect observed for N-BOC substituted systems than for their N-benzyl analogues (η = 27.45 and 16.40° for **HBOCDPP** and **HBDPP** respectively), to the involvement of different carbonyl groups in these intramolecular interactions in N-BOC systems. Lastly, it was observed that the variation in bond lengths clearly reflects the described structural re-arrangements upon N-substitution (SI 1).

The computed energy differences between the different C_2 optimised geometries and their associated C_i (and C_i^{xray} for N-benzyl DPPs) conformers were found to be lower than twice the thermal energy, K_BT in all cases. Therefore the rest of the paper will focus on the C_i optimised geometries for N-BOC DPPs and C_i^{xray} for N-benzyl DPPs since we propose that these are more representative geometries for these systems, in line with recent reports on crystalline DPP-based systems.[19, 26] Table 1 summarises all of the bond lengths and dihedral angles computed for the systems investigated herein.

TABLE 1 HERE

4.2 Raman spectroscopic analysis

The Raman spectrum for the non-phenyl substituted diketopyrrolopyrrole system, **DPP,** was initially computed for comparison, given its higher symmetry compared to the N-substituted derivatives. In such symmetrical planar systems, in-plane (a) and out-of-plane (b) vibrational frequencies were observed and identified. The computed fundamental harmonic frequencies, Γ^{vib} of **DPP** are as follows where the symmetrical and unsymmetrical frequencies are denoted by g and u respectively.

$$\Gamma^{\mathrm{vib}}(\mathbf{DPP}) = 14\mathrm{a_g} + 5\mathrm{b_g} + 5\mathrm{a_u} + 12\mathrm{b_u} \qquad (1)$$

FIGURE 5 HERE

Figure 5 illustrates the computed Raman spectra of **DPP**, where all of the most intense harmonic vibrational frequencies were observed to be associated with in-plane, a_g modes. In conjugated organic systems, such as those studied herein, the most intense Raman active modes are often attributed to vibrational modes involving C-C stretches throughout the conjugated backbone.[28, 29, 45] It was observed that the most intense Raman active modes in the case of **DPP** were due to the symmetrical stretching motion of the C-C (a_g9) and C=C (a_g11) bonds within the butadiene moiety, computed at 1382 and 1681 cm^{-1} respectively. Of note, was the high intensity exhibited by the vibrational mode associated to the symmetric stretching of the carbonyls (a_g12) computed at 1898 cm^{-1}. Variations in the computed frequencies for this mode are anticipated upon substitution in relation to the described intramolecular H-bonding interactions between electropositive phenylic and methylene hydrogens and electronegative carbonyl oxygen atoms. In addition, three other intense vibrational frequencies were observed at 850 (a_g5), 1030 (a_g6) and 1446 (a_g10) cm^{-1}. These are associated to C-N, C(=O)-N and C-C (coupled to C-N) vibrational motions.

The C_{2h} symmetry exhibited by **DPP** was observed to be degraded to C_i (or C_2 depending on the relative orientation of the phenyl rings) upon phenyl substitution of the DPP core, hence distorting the planarity of the system. In fact, we have recently reported that the optimised geometries of **H_2DPP** are strictly non-planar for a series of hybrid density functionals, with the dihedral angle between the phenyl rings and the core found to increase with increasing amount of Hartree-Fock exchange in the functional.[23] In relation to the Raman spectrum, this results in degeneracy of the in-plane and out-of-plane modes to a_g. Similarly, the asymmetrical in-plane and out-of-plane modes are degenerated to a_u. The following fundamental harmonic frequencies were computed for the different N-BOC and N-benzyl substituted systems as follows.

$$\Gamma^{\mathrm{vib}}(\mathbf{HBOCDPP}) = \Gamma^{\mathrm{vib}}(\mathbf{ClBOCDPP}) = \Gamma^{\mathrm{vib}}(\mathbf{BrBOCDPP}) = 93\mathrm{a_g} + 93\mathrm{a_u} \qquad (2)$$

$$\Gamma^{\mathrm{vib}}(\mathbf{TbBOCDPP}) = 129\mathrm{a_g} + 129\mathrm{a_u} \qquad (3)$$

$$\Gamma^{\mathrm{vib}}(\mathbf{HBDPP}) = \Gamma^{\mathrm{vib}}(\mathbf{ClBDPP}) = \Gamma^{\mathrm{vib}}(\mathbf{BrBDPP}) = \Gamma^{\mathrm{vib}}(\mathbf{IBDPP}) = 87\mathrm{a_g} + 87\mathrm{a_u} \qquad (4)$$

FIGURE 6 HERE

Figure 6 illustrates the experimental (solid line) and computed (vertical lines) Raman spectra of N-BOC (A-top) and N-benzyl (B-bottom) substituted diketopyrrolopyrroles from 1000-2000 cm^{-1}, where all of the most intense computed vibrational frequencies were observed to be analogous to those denoted as a_g in **DPP**. The Raman intensities were calculated from the Raman activities (S_i) obtained with the Spartan '10 software, using the following relationship (Equation 1) derived from the intensity theory of Raman scattering.[46]

$$I_i = \frac{f \cdot (v_0 - v_i)^4 \cdot S_i}{v_i \cdot \left[1 - exp\left(\frac{-hcv_i}{k_B T}\right)\right]} \qquad (1)$$

where v_0 and v_i denote the excitation energy and vibrational frequency in cm^{-1}, whereas h c and k_B represent the Planck's constant, speed of light in vacuum and Boltzmann constant respectively.

FIGURE 7 HERE

As summarised in Table 2 (vide infra), the computed frequencies consistently overestimate those observed experimentally. This is in agreement with previous reports[29, 45, 47, 48] and is associated to electron correlation effects and the use of relatively small basis sets[47] (we report negligible differences between 6-31G(d) and the wider triple zeta basis set, 6-311G(d)). The latter has resulted in the ubiquitous application of scaling factors in aiding the interpretation of experimental bands by computed frequencies. In this regard, Figure 7 illustrates a comparison between the experimental and computed frequencies for all the investigated Raman active modes, denoting a linear relationship (r^2 =

0.99) with a scaling factor of 0.95 for the vibrations in the region of 1000-2000 cm^{-1}. The scaling factor yielded for these systems was observed to agree well with previously reported values utilising the same density functional.[47, 48] The small fluctuations of the data points with respect to the regression line in Figure 7 are consistent with the application of a uniform scaling factor. In more complex systems like the ones studied herein, where a larger number of intramolecular interactions can occur, the use of non-uniform scaling factors for different vibrational frequencies would result in better linearity. In this regard, we find that on average, lower scaling factors would be required for single C-C compared with double C=C symmetrical stretching vibrations in these systems (0.959 ± 0.006 and 0.944 ± 0.005 for ν(C-C) and ν(C=C) respectively).

Via detailed investigation of the computed Raman spectra of these systems, it was observed that the most intense Raman active modes always fall into three regions for N-BOC and N-benzyl DPPs: 1104-1128 cm^{-1} ν(N-C), 1342-1474 cm^{-1} ν(C-C) and 1618-1695 cm^{-1} ν(C=C). The ν(N-C) modes were observed to shift to higher frequency upon substitution on the lactam nitrogens (1030, 1128 and 1108 cm^{-1} for **DPP**, **HBOCDPP** and **HBDPP** respectively. In turn, the computed vibrational frequencies for ν(C-C) and ν(C=C) of **DPP** (1382 and 1681 cm^{-1} respectively) were observed to fall within the limits of the two spectral regions identified for N-substituted systems. The computed harmonic vibrational frequency associated to the stretching motion of the transanular bond was observed to shift to higher frequencies on progression from DPP to N-BOC and N-benzyl substituted DPPs (1382, 1427 and 1423 cm^{-1} for **DPP**, **HBOCDPP** and **HBDPP** respectively). The latter ought to be caused by the shortening of this bond in N-substituted systems, hence increasing the force constant of the associated vibrational motion. The differences in computed vibrational frequencies for the stretching motion of the carbonyl bond within the core of these systems upon substitution is worthy of note (1898, 1882 and 1853 cm^{-1} for **DPP**, **HBOCDPP** and **HBDPP** respectively). We relate this effect to the described intramolecular H-bonding interactions in these systems upon phenyl and N-substitution. The larger computed differences for N-benzyl systems are consistent with the observed findings described before: in N-benzyl systems both intramolecular H-bonding interactions involve the electronegative carbonyl oxygen within the DPP core. In contrast, in N-BOC derivatives the additional H-bonding intramolecular interactions observed upon N-substitution involve the electronegative carbonyl oxygen within the BOC group. Consequently, the greater shift of the associated harmonic vibrational frequency in N-benzyl systems is in line with the stronger nature of the H-bonding intramolecular interactions in these systems.

Variation in substitution of the para positions of the core phenyl rings was observed to lead to only small differences in the computed frequencies for the C-C vibrational motion (1427, 1425, 1424 and 1426 cm^{-1} for **HBOCDPP**, **ClBOCDPP**, **BrBOCDPP** and **TbBOCDPP** and 1423, 1420, 1425 and 1427 cm^{-1} for **HBDPP**, **ClBDPP**, **BrBDPP** and **IBDPP** respectively). A similar influence was observed on the computed C=C vibrational frequencies (1681, 1676, 1680 and 1680 cm^{-1} for **HBOCDPP**, **ClBOCDPP**, **BrBOCDPP** and **TbBOCDPP** and 1644, 1638, 1640 and 1647 cm-1 for **HBDPP**, **ClBDPP**, **BrBDPP** and **IBDPP** respectively).

The experimental Raman spectrum of **HBOCDPP** illustrated in Figure 6A1 exhibits strong bands in the three regions previously described for the computed harmonic frequencies (ν(N-C), ν(C-C) and ν(C=C)). Two strong modes were observed at 1598 and 1573 cm^{-1} which are consistent with C=C stretching motions, analogous to a_g11 in **DPP**. The broadening of the band centred at 1598 cm^{-1} is proposed to be related to the presence of a second Raman active mode centred at 1605 cm^{-1}, assigned to C=C stretching motions within the phenyl rings. Another strong mode is identified at 1384 cm^{-1} associated to C-C stretching of the transanular bond in the DPP core (a_g9 in **DPP**), which in the case of N-BOC systems is observed to be coupled to stretching vibrations within the phenyl rings. Bands associated to C-C stretching motions are centred at 1310 cm^{-1} and 1384 cm^{-1} in **HBOCDPP**. The former assigned to the bonds linking the phenyl rings to the core (+2/-2) and the latter to the transanular bond (0 in Figure 1) within the core of these systems. Furthermore, an additional intense Raman mode is identified at 1068 cm^{-1} in **HBOCDPP** for N-C stretching (bond +3/-3). Subtle variations in the experimental vibrational frequencies were observed on progression from **HBOCDPP** to its R_1 substituted counterparts as anticipated theoretically. Nonetheless, the vibrational frequencies associated to C-C/C=C vibrational stretches within the core of these systems were identified to be lower for R_1 substituted systems (1384/1597, 1361/1586, 1365/1586 and 1362/1586 cm^{-1} for **HBOCDPP**, **ClBOCDPP**, **BrBOCDPP** and **TbBOCDPP** respectively).

The experimental Raman spectrum of **HBDPP** illustrated in Figure 6B1, exhibits a larger number of high intensity modes in the regions of C-C/C=C stretches related to the additional phenyl rings upon benzyl substitution. Three high intensity peaks associated to C=C vibrational stretches are identified at 1594, 1577 and 1543 cm^{-1} respectively. The relative intensity of these three modes closely matches those anticipated by the computed spectra as illustrated in Figure 6B1. The experimentally observed bands at 1295 and 1369 cm^{-1} were assigned to symmetrical single C-C bond stretches. As in the case of **HBOCDPP**, these frequencies are associated to the stretching motion of the +2/-2 and transanular (0) bonds respectively. Additionally, comparison of the experimentally determined vibrational frequencies for ν(C-C) and ν(C=C) of **HBOCDPP** and **HBDPP** reveals a clear shift to lower frequency for the latter, in agreement with theoretical predictions. The vibrational frequency for the N-C (bond +3/-3) stretching motion was assigned to the experimental mode centred at 1031 cm^{-1}, again found at lower frequency than the analogous vibration in **HBOCDPP** (1068 cm^{-1}). This shift is in agreement with the computed values and the lower frequency experimentally obtained for **HBDPP** can be accounted for on the basis of the different computed force constants for these Raman active vibrations (0.968 and 0.820 mdyn/Å for **HBOCDPP** and **HBDPP** respectively). We also find that the experimental frequencies (1751 and 1687 cm^{-1} for **HBOCDPP** and **HBDPP**) are consistent with the theoretically predicted shift to lower values for ν(C=O) on going from **HBOCDPP** (1882 cm^{-1}) to **HBDPP** (1853 cm^{-1}). To summarise, we find that N-substitution in DPP-based systems, over and above exerting a solubilising effect and playing a crucial role in determining packing motifs in the solid state,[26] is also associated with significant shifts in the vibrational frequencies for some of the most intense Raman active modes, which we propose can be systematically engineered, leading to optimised photophysical behaviour and performance in optical and optoelectronic devices. Table 2 summarises the experimental and computed Raman frequencies for the different derivatives investigated.

TABLE 2 HERE

FIGURE 8 HERE

A comparison between experimental and computed spectra for the derivatives in Figure 1 is shown in Figure 6. With the exception of **ClBDPP** (Figure 6B2 and Figure 8), we find that the relative intensity pattern observed for the experimental peaks assigned to C=C stretching vibrations for N-benzyl systems closely matches the computed intensities. **ClBDPP** exhibits two polymorphic forms in the solid state which significantly differ in the twist of the phenyl rings with respect to the DPP core (θ_1 = θ_2 = 44.03 and 20.07° for ***ClBDPPα*** and ***ClBDPPβ*** respectively).[26] The α form was found to be the sole phase in the powder from which the experimental Raman spectrum was obtained (Figure 8). This structure differs significantly from the optimised geometry employed to obtain the computed Raman spectrum (θ_1 = θ_2 = 28.03°). In turn, the β form exhibits dihedral twists which are more in line with the rest of the crystal structures of these systems.[26] We therefore conclude that the differences illustrated in Figure 8 for **ClBDPP** are related to the significant structural variation between the crystal structure and the optimised geometries which were not observed to such an extent for any of the other derivatives investigated.

5. Conclusions

In conclusion, we report the optimised geometries from a series of structurally related N-substituted diketopyrrolopyrroles by means of M06-2X DFT analysis. On progression from **DPP** to **H_2DPP** and N-substituted **DPP** a clear out-of-plane re-arrangement of the central core was observed (θ_3 = 0.00, 0.94 and 1.32° for **DPP**, **H_2DPP** and **HBOCDPP** respectively), with substitution on the lactam nitrogen leading to a pyramidalisation around the N atoms (η = 27.45 and 16.40° for **HBOCDPP** and **HBDPP** respectively, which is attributed a number of intramolecular H-bonding interactions.. As a result of these interactions, significant bond lengths variations were identified with larger variations computed for N-BOC systems arising from their greater re-arrangements. Experimental and computed

Raman spectra and associated band assignments for each of the studied systems are also reported. The most intense experimental Raman modes associated with ν(N-C), ν(C-C) and ν(C=C) were unequivocally assigned to symmetric vibrational modes by means of the computed Raman spectra. Significant vibrational frequency shifts were observed for ν(N-C) and ν(C=O) on progression from **HBOCDPP** (1068 and 1751 cm^{-1}) to **HBDPP** (1031 and 1687 cm^{-1}) consistent with the larger computed force constant and the greater structural changes observed in N-BOC systems. Accordingly, N-substitutions on DPP-based systems are responsible for significant shifts in the vibrational frequencies associated to some of the most intense Raman active modes. The impact of polymorphism, which is exhibited by **ClBDPP** in the solid state was identified by the different relative intensity pattern of the ν(C=C) mode. In addition, the calculated uniform scaling factor of 0.95 for vibrations in the region of 1000-2000 cm^{-1} was determined and found to be in agreement with values previously reported employing the same density functional. As a result, we hope that this study should be of broad interest to those engaged in the rationale design and optimisation of N-substituted DPP-based systems in optical and optoelectronic devices, especially given the importance of intense Raman active modes in controlling the photophysical properties of these systems.

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Captions

Figure 1. Structure of non-phenyl substituted (**DPP**), phenyl substituted DPP (**H_2DPP**) where R1 & R2 = H and the nomenclature for the various N-substituted systems investigated. Bond numbers are indicated on the **DPP** structure. Dihedral angles, θ_1/θ_2, θ_3 and η are denoted by blue, red and green stars respectively.

Figure 2. Optimised geometries of the two most stable conformers, C_2 (A and C) and C_i (B and D) for **HBOCDPP** and **HBDPP** respectively. M06-2X/6-31G(d).

Figure 3. Illustration of the structural differences between C_i (highlighted) and C_i^{xray} optimised geometries of **HBDPP**. M06-2X/6-31G(d).

Figure 4. Top: Illustration of the different intramolecular H-bonding interactions observed in these DPP-based systems and bottom: differences in pyramidalisation of the lactam nitrogens on progression from DPP (highlighted for comparison). **HBOCDPP** (left) and **HBDPP** (right). M06-2X/6-31G(d).

Figure 5. Computed Raman spectrum of **DPP** and illustration of the most intense vibrational modes. M06-2X/6-31G(d).

Figure 6. Experimental Raman spectra (grey solid line) and computed harmonic vibrational frequencies (blue vertical lines) of **HBOCDPP** (A1), **ClBOCDPP** (A2), **BrBOCDPP** (A3), **TbBOCDPP** (A4), **HBDPP** (B1), **ClBDPP** (B2), **BrBDPP** (B3) and **IBDPP** (B4). M06-2X/6-31G(d). Scaling factor, s = 0.95 (vide infra).

Figure 7. Top: Experimental (grey solid line) and scaled (s = 0.95) computed (blue vertical lines) Raman spectra of **HBDPP**. Bottom: Experimental (ν_{exp}) vs computed (ν_{comp}) vibrational frequencies for the most intense Raman active modes of the different DPP systems investigated. M06-2X/6-31G(d).

Figure 8. **A** Experimental Raman spectra (grey solid line) and computed harmonic vibrational frequencies (blue vertical lines, scaling factor, s = 0.95) of **ClBDPP**. M06-2X/6-31G(d). **B** PXRD pattern from **ClBDPP** bulk powder (bottom, black) and predicted XRD pattern determined in Mercury from single crystal X-ray structure of ***ClBDPPα*** (middle, blue) and ***ClBDPPβ*** (top, red) respectively.